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CONTENTS

ii

Chapter 1. General Introduction

Crosslinking reaction is extremely important from the commercial standpoint. The term "curing" is used to denote crosslinking. Crosslinked polymers are increasingly used as engineering materials because of their excellent stability at elevated temperatures and for physical stress. Crosslinked polymers are formed when linear or branched polymer chains are joined together by covalent bonds. The polymers are also formed from polyfunctional monomers. "Network polymer" is synonymous with "crosslinked polymer". Because of crosslinking, the polymer chains lose their ability to flow past one another. As a result the polymer will not melt or flow and cannot, therefore, be molded. Such polymers are said to be thermosetting or thermoset. Vulcanization of rubber is an example of crosslinking. Crosslinkable polymer is very important with various field, such as synthetic rubbers, paint, coatings, sealant, and adhesives.[1,2]

There are several ways that crosslinking can be brought about, but basically they fall into two categories:[3]

    I. Crosslinking during polymerization by use of polyfunctional instead of difunctional monomers.

    II. Crosslinking in a separate processing step, after the formation of the linear (or branched) polymer.

This thesis describes the chemistry of crosslinking by type (II) which is advantageous to control crosslink points.

Crosslinking of type (II) can be brought about by the methods as follows:

(1) Vulcanization, using peroxides, sulfur, or sulfur-containing compounds.

(2) Free radical reactions caused by ionizing radiation.

(3) Photolysis involving photosensitive functional groups.

(4) Chemical reactions of labile functional groups.

It is difficult to control the number and location of crosslink during radical reaction. When the polymer having the controlled number and location of functional groups is used, a well-defined crosslinking polymer can be prepared. Therefore, it is a very challenging theme to establish the synthesis method of functional polymer to induce chemical crosslink.

Functional polymers are macromolecules that have unique properties and uses.[4,5] The properties of such materials are often determined by the presence of functional groups chemically different from the backbone chains. Examples are polar and ionic functional groups on hydrocarbon backbones and hydrophobic groups on polar polymer chains. These polymers often show unusual or improved properties in reactivity, phase separation, and associations.[6]

Functional polymers will continue to be in demand because the use of polymeric materials is spreading steadily. Today most functional polymers are tailored for the desired properties applications. The requirement, however, is more and more exacting. The synthesis of functional polymers becomes increasingly difficult because of incompatibility in a mixture of two different polymers. The solution to the problem is important in bringing the project to a successful conclusion.

The synthetic procedures of functional polymers mainly consist of three methods as follows:[7]

(1) Monomer having functional group is synthesized and then polymerized to form the functional polymer.

(2) The first process is the polymerization of reactive monomer and the second process is the introduction of functional group to the precursory polymer.

(3) Functional group is introduced to commodity polymers by the use of polymer reaction.

Structural factors of the polymer as molecular weight, molecular weight distribution, copolymer composition, microstructure, stereochemistry, chain-end functionality, and molecular architecture affect its property directly. A new development in the methodology to control these factors, therefore, is important for the polymer syntheses. This purpose is desired also in the preparation of functional polymers.[8]

Vinyl, ethynyl, epoxy, methylol, isocyanate groups are utilized as the crosslinkable functional group up to now.[9] In the crosslinkable polymer, it is profitable that the functional group reacts at a moderate heat. Moreover, the crosslink reaction must not be accompanied by volatile component from the point of physical property for the materials. Vinyl and ethynyl groups are advantageous to the problems under consideration. Vinyl group, however, has a difficulty in thermal stability during conservation. Because of its high polymerizability, the vinyl group is relatively difficult to be introduced into the polymer. On the other hand,

the ethynyl group has higher stability in room temperature than the vinyl group.

Until recently, a variety of imidazole and imide oligomers and polymers containing ethynyl group at chain end have been published.[3,10] These oligomers and polymers are characterized as a high-temperature material by crosslinking reaction. The control of crosslinking points, however, is given no attention. Polystyrene having pendant ethynyl groups is not clearly showed its fundamental problem concerning the synthesis and characterization.

The dual-functional monomers having vinyl and ethynyl groups in a molecule gives promise of a success to prepare the crosslinkable polymer with the ethynyl group through the selective polymerization of the vinyl group. Varying content of the ethynyl group controls the crosslinking points. The polymer containing the ethynyl groups is an interesting functional polymer to concern not only with thermal crosslinking reaction, also with transformation of the functional group. The ethynyl group can be converted to a variety of functional groups by nucleophilic and electrophilic addition reactions.[7] The syntheses of the dual-functional monomer and its selective polymerization, however, have many difficulties to be resolved. [11-13]

In this thesis the author focuses on the ethynyl group as crosslinkable group. The syntheses of new styrene derivatives containing the ethynyl groups, their polymerization with various methods, and the characterization of the obtained crosslinkable polymer are reported.

The outline of this thesis is as follows:

Chapter 1 presents an introductory overview in order to clarify the object of the thesis.

Chapter 2 offers two kinds of synthetic methods of monomers. The sixteen styrene derivatives containing ethynyl groups, such as trimethylsilylethynyl-, 4-trimethylsilyl-3-butynyl-, 3,3-dimethyl-1-butynyl-, 1-hexynyl-, and phenylethynyl- groups, are newly synthesized.

Chapter 3 deals with the radical homo- and copolymerization of styrene derivatives. Monomer reactivity ratios and Q-e values are estimated. Furthermore, the thermal properties of the obtained homo- and copolymers at elevated temperatures are characterized.

Chapter 4 shows the cationic polymerization of the styrene monomers having ethynyl groups. The content of ethynyl groups in the polymers are different from that in the polymers from the radical polymerization. The structure and thermal behavior for the

polymers are shown.

Chapter 5 describes the anionic living polymerization of the styrene monomers. The predicted molecular weights and the narrow molecular weight distributions are found in the resulting polymers. The novel block copolymers with well-defined chain structures are synthesized.

Chapter 6 clarifies quantitatively the chain crosslinking formation of ethynyl groups in the random copolymer of ethynylstyrene and styrene and the viscoelasticity of the crosslinked copolymer.

The concluding chapter 7 summarizes the results in this study.

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Chapter 2.   Syntheses of Ethynylstyrenes as Monomer

2-1. Introduction

Alkynes are usually prepared from either of the two most important synthetic methods: (1) elimination reactions of hydrogen halides from dihalides and vinylhalides and (2) coupling reactions of alkyl halides and carbonyl compounds with organometallic derivatives of acetylenes.[1,2]   In the former method, the preparation of ethynyl group depends on the property of halides and isomerization sometimes accompanies elimination, thereby resulting in the formation of such by-product as allene.   In the latter methods, metallo acetylenes, such as sodium acetylide, lithium acetylide, copper acetylide, and acetylenic Grignard reagent, react with alkyl halides or with carbonyl compounds to give excellent yields of ethynyl compounds.   A catalytic amount of Pd^0 or Pd^{II} compounds assists the reaction under mild conditions.

2-2. Materials

2-, 3-, and 4-Bromostyrenens were synthesized according to the reported procedure.[3] Commercially available (trimethylsilyl)acetylene, *tert*-butylacetylene, 3-methyl-1-hexyne, 1-hexyne, phenylacetylene, 1-(trimethylsilyl)-1-propyne, 4-chloromethylstyrene, triphenylphosphine, bis(triphenylphosphine)palladium(II) dichloride, copper(I) iodide, and *n*-butyllithium were used without further purification.   Triethylamine and diethynlamine were distilled over CaH_2.   Tetrahydrofurane (THF) was distilled over $LiAlH_4$ under a nitrogen atmosphere.

2-3. Syntheses of Ethynylstyrnes by Pd^{II}-Cu^{I} Catalyzed Coupling Reaction

Ethynylstyrenes contain two polymerizable functional groups of vinyl group and acetylene moiety in a molecule. Both functional groups are expected to be readily polymerizable under the various reaction conditions. Thus it is limited in method to synthesize the highly purified ethynylstyrenes in large quantities. Most ethynylstyrenes is prepared according to the convenient method reported by Sonogashira et al.[4] In this reaction, an acetylenic hydrogene of mono substituted alkynes is easily substituted by styryl halides in the presence of copper(I) iodide with bis(triphenylphosphin)palladium(II) dichloride catalyst in the amine solution. As shown in Scheme 2-1. The method is facile to synthesize aromatic acetylenes, which is difficult to be prepared by other methods.

Scheme 2-1.

R = -Si(CH$_3$)$_3$ (**1a-c**) ; -C(CH$_3$)$_3$ (**3a-c**) ; -CH(CH$_3$)CH$_2$CH$_2$CH$_3$ (**4a-c**)
 -CH$_2$CH$_2$CH$_2$CH$_3$ (**5a-c**); -Ph (**6a-c**)
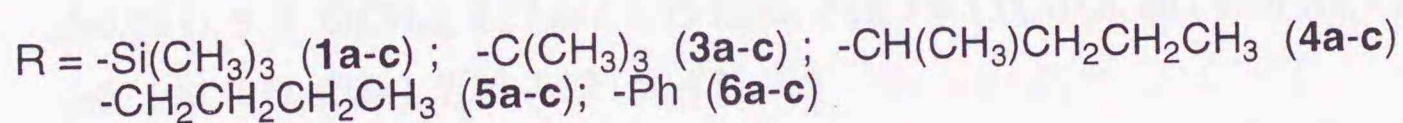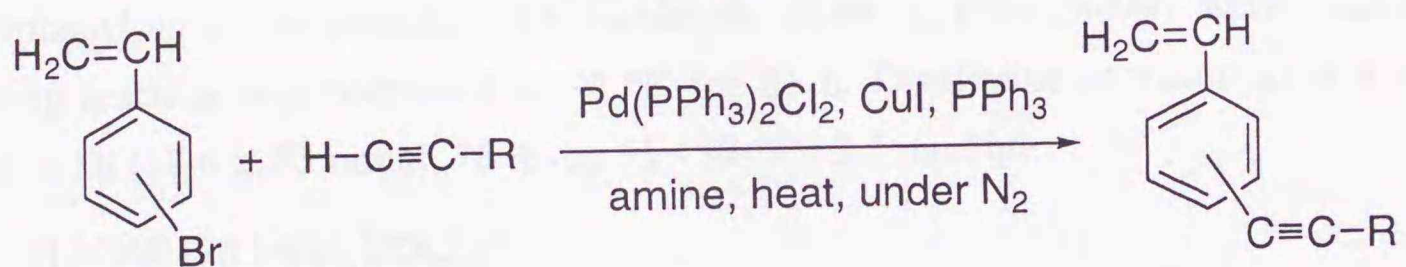
a) Preparation of 4-(2-Trimethylsilylethynyl)styrene (1a). The procedure employed improves the method previously reported.[4] Nitrogen was bubbled into a mixture of 4-bromostyrene (36.0 g, 197 mmol), (trimethylsilyl)acetylene (28.3 g, 288 mmol), copper(I) iodide (0.39 g, 2.0 mmol), triphenylphosphine (0.83 g, 3.2 mmol), and dry triethylamine (290 mL) at room temperature for 1 h. Bis(triphenylphosphine)palladium(II) dichloride (0.85 g, 1.2 mmol) was added and the mixture was stirred at 70 °C for 12 h under nitrogen. The reaction mixture was filtered and concentrated under vacuum. The residue was diluted with hexane (300 mL) and washed with 2N HCl and with water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated by use of a rotary evaporator. The residue was purified by column chromatography (silica gel, hexane) and vacuum distillation gave a colorless liquid of **1a** (38.2 g, 191 mmol, 97 %, bp 94 - 95 °C / 0.7 mmHg).

^{1}H NMR (270 MHz, CDCl$_3$)

δ 0.25 (s, 9 H, SiCH$_3$), 5.26 and 5.73 (2dd, 2 H, J = 0.7, 10.9, and 17.5 Hz, =CH$_2$),

6.66 (dd, 1 H, =CH), 7.29-7.43 (m, 4 H, Ar)

^{13}C NMR (67.5 MHz, CDCl$_3$)

δ 0.07 (SiCH$_3$), 94.9 (≡CSi), 105.2 (ArC≡), 114.9 (=CH$_2$), 122.5 (Ar, C4),

126.1 (Ar, C2), 132.2 (Ar, C3), 136.3 (=CH), 137.7 (Ar, C1)

IR (neat, cm^{-1})

760, 866, 1250 (CSi), 912 (CH=CH$_2$), 2156 (C≡C)

Elemental Analysis

Anal. Calcd for C$_{13}$H$_{16}$Si : C, 77.93; H, 8.05.   Found: C, 77.74 ; H, 8.10.

b) Preparation of 3-(2-Trimethylsilylethynyl)styrene (1b).   The procedure was the same as that described above for **1a**, except that 3-bromostyrene (20.0 g, 109 mmol), (trimethylsilyl)acetylene (14.8 g, 150 mmol), copper(I) iodide (0.21 g, 1.1 mmol), triphenylphosphine (0.19 g, 1.8 mmol), dry triethylamine (160 mL), and bis(triphenylphosphine)palladium(II) dichloride (0.69 g, 0.99 mmol) were mixed.   The coupling reaction was continued at 70 °C for 21 h. Distillation in vacuo gave a colorless liquid of **1b** (16.6 g, 83 mmol, 76 %, bp 91 - 92 °C / 3.5 mmHg).

^{1}H NMR (90 MHz, CDCl$_3$)

δ 0.26 (s, 9 H, SiCH$_3$), 5.27 and 5.75 (2dd, 2 H, J = 1.0, 10.8, and 17.6 Hz, CH$_2$=),

6.67 (dd, 1 H, CH=), 7.30-7.52 (m, 4 H, Ar)

^{13}C NMR (22.5 MHz, CDCl$_3$)

δ 0.10 (SiCH$_3$), 94.3 (≡CSi), 105.1 (ArC≡), 114.7 (CH$_2$=), 113.5 (Ar, C3),

128.5 (Ar, C6), 129.9 (Ar, C2) 131.3 (Ar, C4), 136.2 (=CH), 137.8 (Ar, C1)

IR (neat, cm^{-1})

759, 842, 1250 (CSi), 920 (CH=CH$_2$), 2150 (C≡C).

Elemental Analysis

Anal. Calcd for C$_{13}$H$_{16}$Si : C, 77.93; H, 8.05.   Found: C, 76.67 ; H, 8.04.

(The reason why content of carbon is lower than a calculated value may be that Si-C is formed.)

c) Preparation of 2-(2-Trimethylsilylethynyl)styrene (1c).   The same procedure as described above for **1a** was followed, except of using 2-bromostyrene (38.6 g, 211 mmol), (trimethylsilyl)acetylene (24.9 g, 253 mmol), copper(I) iodide (0.41 g, 2.2 mmol), triphenylphosphine (0.89 g, 3.4 mmol), dry triethylamine (310 mL), and bis(triphenylphosphine)palladium(II) dichloride (0.91 g, 1.28 mmol).   The coupling reaction was continued at 50 °C for 52 h and then at 70 °C for 40 h.   Distillation in vacuo gave a

colorless liquid of **1c** (36.9 g, 185 mmol, 88 %, bp 94 - 95 °C / 0.7 mmHg).

^{1}H NMR (400 MHz, CDCl$_3$)

δ 0.25 (s, 9 H, SiCH$_3$), 5.33 and 5.80 (2dd, 2 H, J = 1.2, 11.0, and 17.6 Hz, =CH$_2$),

7.19 (dd, 1H, =CH), 7.13-7.55 (m, 4 H, Ar)

^{13}C NMR (100 MHz, CDCl$_3$)

δ 0.1 (SiCH$_3$), 99.2 ($\equiv$CSi), 103.4 (ArC$\equiv$), 115.6 (CH$_2$=), 121.9 (Ar, C2),

124.6 (Ar, C6), 127.4 (Ar, C4), 128.7 (Ar, C5), 132.9 (Ar, C3), 134.9 (=CH),

139.4 (Ar, C1)

IR (neat, cm^{-1})

843, 868, 1250 (CSi), 914 (CH=CH$_2$), 2156 (C$\equiv$C).

Elemental Analysis

Anal. Calcd for C$_{13}$H$_{16}$Si : C, 77.93; H, 8.05.   Found: C, 77.40 ; H, 8.12.

(The reason why content of carbon is lower than a calculated value may be that Si-C

is formed.)

d) Preparation of 4-(3,3-Dimethyl-1-butynyl)styrene (3a).   The same procedure as that
described above for **1a** was followed using 4-bromostyrene (18.31 g, 100 mmol), *tert*-
butylacetylene (11.1 g, 135 mmol), copper(I) iodide (0.19 g, 1.00 mmol), triphenylphosphine
(0.42 g, 1.61 mmol), and dry diethylamine (160 mL), and bis(triphenylphosphine)palladium
(II) dichloride (0.43 g, 0.61 mmol).   The coupling reaction was continued at 38 °C for 100 h.
Distillation in vacuo gave a colorless liquid of **3a** (13.25 g, 72.0 mmol, 72 %, bp 72 - 74 °C /
0.3 mmHg).

^{1}H-NMR (270 MHz, CDCl$_3$)

δ 1.31 (s, 9H, CH$_3$), 5.25 and 5.73 (2d, 2H, J = 10.9 and 17.8 Hz, CH$_2$=),

6.67 (dd, 1H, -CH=), 7.27 - 7.37 (m, 4H, Ar)

^{13}C-NMR (67.5 MHz, CDCl$_3$)

δ 28.1 (CCH$_3$), 31.1 (CH$_3$), 79.1 (Ar-C$\equiv$), 99.3 (Ar-C$\equiv$$\underline{C}$), 114.2 (CH$_2$=),

123.5 (Ar, C4), 126.0 (Ar, C2), 131.8 (Ar, C3), 136.5 (-CH=), 136.7 (Ar, C1)

IR (neat, cm^{-1})

908 (CH=CH$_2$), 987, 1111, 1205, 1290, 1362, 1404, 1458, 1475, 1508, 1628,

2235 (C$\equiv$C), 2968.

Elemental Analysis

Anal. Calcd for C$_{14}$H$_{16}$: C, 91.25; H, 8.75.   Found: C, 91.06; H, 8.89.

9

e) Preparation of 3-(3,3-Dimethyl-1-butynyl)styrene (3b). The same procedure as that described above for **1a** was followed using 3-bromostyrene (25.20 g, 138 mmol), *tert*-butylacetylene (15.1 g, 184 mmol), copper(I) iodide (0.26 g, 1.8 mmol), triphenylphosphine (0.59 g, 2.2 mmol), dry diethylamine (220 mL), and bis(triphenylphosphine)palladium(II) chloride (0.58 g, 0.83 mmol). The coupling reaction was continued at 55 °C for 44 h. Distillation in vacuo gave a colorless liquid of **3b** (18.31 g, 99.5 mmol, 72 %, bp 79 - 82 °C / 0.7 mmHg).

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 1.32 (s, 9H, CH$_3$), 5.24 and 5.74 (2dd, 2H, J = 0.9, 10.9, and 17.7 Hz, CH$_2$=), 6.65 (dd, 1H, -CH=), 7.26 - 7.43 (m, 4H, Ar)

^{13}C-NMR (100 MHz, CDCl$_3$)

δ 28.0 (CCH$_3$), 31.1 (CH$_3$), 79.0 (Ar-C≡), 98.6 (Ar-C≡$\underline{C}$), 114.4 (CH$_2$=), 124.4 (Ar, C3), 125.4 (Ar, C6), 128.4 (Ar, C5), 129.5 (Ar, C4), 131.0 (Ar, C2), 136.4 (-CH=), 137.6 (Ar, C1)

IR (neat, cm^{-1})

798, 849, 894, 910 (CH=CH$_2$), 1201, 1294, 1362, 1458, 1473, 1576, 1595, 1631, 2216 (C≡C), 2966.

Elemental Analysis

Anal. Calcd for C$_{14}$H$_{16}$: C, 91.25; H, 8.75. Found: C, 91.25; H, 8.61.

f) Preparation of 2-(3,3-Dimethyl-1-butynyl)styrene (3c). The same procedure as that described above for **1a** was followed using 2-bromostyrene (25.38 g, 139 mmol), *tert*-butylacetylene (15.28 g, 186 mmol), copper(I) iodide (0.28 g, 1.5 mmol), triphenylphosphine (0.60 g, 2.3 mmol), dry diethylamine (220 mL), and bis(triphenylphosphine)palladium(II) chloride (0.58 g, 0.83 mmol). The coupling reaction was continued at 55 °C for 122 h. Distillation in vacuo gave a colorless liquid of **3c** (7.71 g, 41.9 mmol, 30 %, bp 71 - 73 °C / 0.6 mmHg).

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 1.36 (s, 9H, CH$_3$), 5.33 and 5.81 (2dd, 2H, J = 1.2, 11.0 and 17.8 Hz, CH$_2$=), 7.20 (dd, 1H, -CH=), 7.14 - 7.57 (m, 4H, Ar)

^{13}C-NMR (100 MHz, CDC$_3$)

δ 28.3 (CCH$_3$), 31.2 (CH$_3$), 77.4 (Ar-C≡C), 103.5 (Ar-C≡$\underline{C}$), 115.0 (CH$_2$=), 122.8 (Ar, C2), 124.5 (Ar, C6), 127.4 (Ar, C4), 127.7 (Ar, C5), 132.5 (Ar, C3), 135.2 (-CH=), 138.7 (Ar, C1)

IR (neat, cm^{-1})

912 (CH=CH$_2$), 991, 1205, 1273, 1291, 1362, 1448, 1458, 1473, 1628, 2237 (C≡C),

2966.

Elemental Analysis

Anal. Calcd for C$_{14}$H$_{16}$: C, 91.25; H, 8.75.   Found: C, 88.47; H, 8.82.

g) Preparation of 4-(3-Methyl-1-hexynyl)styrene (4a).   The same procedure as that described above for **1a** was followed using 4-bromostyrene (28.8 g, 157 mmol), 3-methyl-1-hexyne (15.5 g, 161 mmol), copper(I) iodide (0.32 g, 1.7 mmol), triphenylphosphine (0.67 g, 2.6 mmol) in dry triethylamine (225 mL), and bis(triphenylphosphine)palladium (II) dichloride (0.67 g, 0.95 mmol).   The coupling reaction was continued at 70 °C for 37 h. Distillation in vacuo gave a light yellow liquid of **4a** (18.1g, 91.4 mmol, 58 %, bp103 - 106 °C / 0.7 mmHg).

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 0.95 (t, 3H, CH$_2$C$\underline{H}_3$, J = 7.2 Hz), 1.24 (d, 3H, CHC$\underline{H}_3$, J = 6.8 Hz), 1.42 - 1.60 (m, 4H, CH$_2$CH$_2$), 2.61 - 2.70 (m,1H, CH), 5.24 and 5.72 (dd, 2H, =CH$_2$, J = 0.7, 10.9, and 17.6 Hz), 6.67 (dd, 1H, =CH) , 7.29 - 7.35   (m, 4H, Ar-H)

^{13}C-NMR (100 MHz, CDCl$_3$)

δ 14.0 (CH$_2$$\underline{C}H_3$), 20.7 (CH$\underline{C}H_3$), 21.2 ($\underline{C}H_2CH_3$), 26.4 (≡C-$\underline{C}$H), 39.3 (CH$\underline{C}H_2$) , 80.7 (Ar-C≡), 95.6 (Ar-C≡$\underline{C}$), 114.2 (=CH$_2$), 123.6 (ArC4), 126.1 (ArC2), 131.8 (ArC3), 136.5 (-CH=), 136.7 (ArC1)

IR (neat, cm^{-1})

908 (CH=CH$_2$), 2229 (C≡C).

Elemental Analysis

Anal. Calcd for C$_{15}$H$_{18}$: C, 90.91; H, 9.09.   Found: C, 90.79 ; H, 8.87.

h) Preparation of 3-(3-Methyl-1-hexynyl)styrene (4b).   The same procedure as that described above for **1a** was followed using 3-bromostyrene (31.6 g, 173 mmol), 3-methyl-1-hexyne (15.7 g, 164 mmol), copper(I) iodide (0.31 g, 1.6 mmol), triphenylphosphine (0.66 g, 2.5 mmol) in dry triethylamine (230 mL), and bis(triphenylphosphine)palladium (II) dichloride (0.67 g, 0.95 mmol).   The coupling reaction was continued at 65 °C for 20.5 h. Distillation in vacuo gave a light yellow liquid of **4b** (21.1g, 107 mmol, 65.2 %, bp101 - 103 °C / 0.8 mmHg).

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 0.95 (t, 3H, CH$_2$C$\underline{H}_3$, J = 7.1 Hz), 1.25 (d, 3H, CHC$\underline{H}_3$, J = 6.8 Hz), 1.41 - 1.60

11

(m, 4H, CH$_2$CH$_2$), 2.61 - 2.69 (m,1H, CH), 5.24 and 5.74 (2dd, 2H, =CH$_2$,

 J = 0.7, 10.8, and 17.6 Hz), 6.66 (dd, 1H, =CH), 7.20 - 7.44 (m, 4H, Ar-H)

^{13}C-NMR (100 MHz, CDCl$_3$)

δ 14.0 (CH$_2$C$\underline{\text{H}}_3$), 20.7 (CHC$\underline{\text{H}}_3$), 21.2 (C$\underline{\text{H}}_2$CH$_3$), 26.4 (≡C-C$\underline{\text{H}}$), 39.3 (CHC$\underline{\text{H}}_2$),

80.6 (Ar-C≡), 95.0 (Ar-C≡C̲), 114.4 (=CH$_2$), 124.4 (ArC3), 125.4 (ArC6),

128.4 (ArC5), 129.4 (ArC2), 131.0 (ArC4), 136.4 (-CH=), 137.6 (ArC1)

IR (neat, cm^{-1})

910 (CH=CH$_2$), 2222(C≡C).

Elemental Analysis

Anal. Calcd for C$_{15}$H$_{18}$: C, 90.91; H, 9.09.   Found: C, 90.90 ; H, 8.96.

i) Preparation of 2-(3-Methyl-1-hexynyl)styrene (4c).   The same procedure as that described above for **1a** was followed using 2-bromostyrene (31.8 g, 174 mmol), 3-methyl-1-hexyne (20.4 g, 213 mmol), copper(I) iodide (0.30 g, 1.6 mmol), and triphenylphosphine (0.68 g, 2.6 mmol) in dry triethylamine (260 mL), and bis(triphenylphosphine)palladium (II) dichloride (0.68 g, 0.97 mmol).   The coupling reaction was continued at 65 °C for 395 h. Distillation in vacuo gave a light yellow liquid of **4c** (18.2g, 91.9 mmol, 53 %, bp 96 - 98 °C / 0.7 mmHg).

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 0.95 (t, CH$_2$C$\underline{\text{H}}_3$, 3H, J = 7.1 Hz), 1.27 (d, 3H, CHC$\underline{\text{H}}_3$, J = 6.8 Hz), 1.44 - 1.63

(m, 4H, CH$_2$CH$_2$), 2.66 - 2.75 (m,1H, CH), 5.32 and 5.78 (dd, 2H, =CH$_2$,

 J = 1.1, 11.1, and 17.7 Hz), 7.21 (dd, 1H, CH=), 7.14 - 7.55 (m, 4H, Ar-H)

^{13}C-NMR (100 MHz, CDCl$_3$)

δ 14.0 (CH$_2$C$\underline{\text{H}}_3$), 20.7 (CHC$\underline{\text{H}}_3$), 21.2 (C$\underline{\text{H}}_2$CH$_3$), 26.6 (≡C-C$\underline{\text{H}}$), 39.3 (CHC$\underline{\text{H}}_2$),

79.0 (Ar-C≡), 99.8 (Ar-C≡C̲), 115.0 (=CH$_2$), 122.9 (ArC2), 124.5 (ArC6),

127.4 (ArC4), 127.7 (ArC5), 132.6 (ArC3), 135.3 (-CH=), 138.8 (ArC1)

IR (neat, cm^{-1})

910 (CH=CH$_2$), 2224 (C≡C).

Elemental Analysis

Anal. Calcd for C$_{15}$H$_{18}$: C, 90.91; H, 9.09.   Found: C, 90.88 ; H, 9.21.

j) Preparation of 4-(1-Hexynyl)styrene (5a).   The same procedure as that described above for **1a** was followed using 4-bromostyrene (9.29 g, 50.8 mmol), 1-hexyne (5.00 g, 60.9 mmol), copper(I) iodide (0.10 g, 0.53 mmol), triphenylphosphine (0.21 g, 0.80 mmol), dry triethylamine (75 mL), and bis(triphenylphosphine)palladium(II) dichloride (0.22 g, 0.31

12

mmol).   The coupling reaction was continued at 70 °C for 8.5 h. Distillation in vacuo gave a colorless liquid of **5a** (6.89 g, 37.4 mmol, 74 %, bp 115 - 120 °C / 2 mmHg).

^{1}H NMR (CDCl$_3$, 270 MHz)

δ 0.94 (t, 3H, J = 7.1 Hz, CH$_3$), 1.41 - 1.64 (m, 4H, CH$_2$CH$_2$CH$_3$), 2.41 (t, 2H, J = 6.9 Hz, ≡CCH$_2$), 5.24 and 5.72 (2d, 2H, J = 10.9 and 17.5 Hz, CH$_2$=), 6.67 (dd, 1H, -CH=), 7.27 - 7.38 (m, 4H, Ar)

^{13}C NMR (CDCl$_3$, 67.5 MHz)

δ 13.7 (CH$_3$), 19.3 (≡CCH$_2$), 22.0 (CH$_2$CH$_3$), 30.9 (≡CCH$_2$CH$_2$), 80.6 (Ar-C≡), 91.2 (Ar-C≡C), 114.3 (CH$_2$=), 123.6 (Ar, C4), 126.1 (Ar, C2), 131.8 (Ar, C3), 136.4 (-CH=), 136.7 (Ar, C1)

IR (neat, cm^{-1})

908 (CH=CH$_2$), 989, 1111, 1329, 1402, 1458, 1506, 1628, 2229 (C≡C), 2956.

Elemental Analysis

Anal. Calcd for C$_{14}$H$_{16}$: C, 91.25; H, 8.75.   Found: C, 91.27; H, 8.77.

k) Preparation of 3-(1-Hexynyl)styrene (5b).   The same procedure as that described above for **1a** was followed using 3-bromostyrene (15.0 g, 82.0 mmol), 1-hexyne (10.0 g, 122 mmol), copper(I) iodide (0.16 g, 0.88 mmol), triphenylphosphine (0.34 g, 1.39 mmol), dry triethylamine (121 mL), and bis(triphenylphosphine)palladium(II) dichloride (0.53 g, 0.76 mmol).   The coupling reaction was continued at 70 °C for 7 h. Distillation in vacuo gave a colorless liquid of **5b** (11.55 g, 62.8 mmol, 77 %, bp 105 - 106 °C / 3 mmHg).

^{1}H NMR (CDCl$_3$, 400 MHz)

δ 0.95 (t, 3H, J = 7.2 Hz, CH$_3$), 1.45 - 1.62 (m, 4H, CH$_2$CH$_2$CH$_3$), 2.41 (t, 2H, J = 7.1 Hz, ≡CCH$_2$), 5.24 and 5.74 (2d, 2H, J = 10.9 and 17.6 Hz, CH$_2$=), 6.65 (dd, 1H, -CH=), 7.20 - 7.44 (m, 4H, Ar)

^{13}C NMR (CDCl$_3$, 100 MHz)

δ 13.7 (CH$_3$), 19.2 (≡CCH$_2$), 22.1 (CH$_2$CH$_3$), 30.9 (≡CCH$_2$CH$_2$), 80.5 (Ar-C≡), 90.5 (Ar-C≡C), 114.4 (CH$_2$=), 124.4 (Ar, C3), 125.4 (Ar, C6), 128.4 (Ar, C5), 129.4 (Ar, C2), 130.9 (Ar, C4), 136.3 (-CH=), 137.6 (Ar, C1)

IR (neat, cm^{-1})

894, 910 (CH=CH$_2$), 988, 1328, 1429, 1466, 1478, 1572, 1596, 2227 (C≡C), 2872, 2958.

Elemental Analysis

Anal. Calcd for C$_{14}$H$_{16}$: C, 91.25; H, 8.75.   Found: C, 90.95; H, 8.86.

l) Preparation of 2-(1-Hexynyl)styrene (5c). The same procedure as that described above for **1a** was followed using 2-bromostyrene (15.0 g, 82.0 mmol), 1-hexyne (10.0 g, 122 mmol), copper(I) iodide (0.16 g, 0.88 mmol), triphenylphosphine (0.34 g, 1.39 mmol), dry triethylamine (121 mL), and bis(triphenylphosphine)palladium(II) dichloride (0.53 g, 0.75 mmol). The coupling reaction was continued at 70 °C for 46 h. Distillation in vacuo gave a colorless liquid of **5c** (7.40 g, 40.2 mmol, 49 %, bp 98 - 99 °C / 0.8 mmHg).

^{1}H NMR (CDCl$_3$, 400 MHz)

δ 0.96 (t, 3H, J = 7.2 Hz, CH$_3$), 1.47 - 1.65 (m, 4H, CH$_2$CH$_2$CH$_3$), 2.46 (t, 2H, J = 7.1 Hz, ≡CCH$_2$), 5.32 and 5.78 (2dd, 2H, J = 1.0, 11.0 and 17.8 Hz, CH$_2$=), 7.14 - 7.55 (m, 5H, -CH= and Ar)

^{13}C NMR (CDCl$_3$, 22.5 MHz)

δ 13.7 (CH$_3$), 19.4 (≡CCH$_2$), 22.1 (CH$_2$CH$_3$), 31.0 (≡CCH$_2$CH$_2$), 78.9 (Ar-C≡), 95.3 (Ar-C≡C), 115.1 (CH$_2$=), 122.9 (Ar, C2), 124.5 (Ar, C6), 127.4 (Ar, C4), 127.7 (Ar, C5), 132.6 (Ar, C3), 135.3 (-CH=), 138.9 (Ar, C1)

IR (neat, cm^{-1})

912 (CH=CH$_2$), 993, 1100, 1328, 1429, 1448, 1478, 1626, 2225 (C≡C), 2931.

Elemental Analysis

Anal. Calcd for C$_{14}$H$_{16}$: C, 91.25; H, 8.75. Found: C, 91.29; H, 8.87.

m) Preparation of 4-(2-Phenylethynyl)styrene (6a). The same procedure as that described above for **1a** was followed using 4-bromostyrene (25.0 g, 137 mmol), phenylacetylene (16.8 g, 164 mmol), copper(I) iodide (0.256 g, 1.36 mmol), triphenylphosphine (0.578 g, 2.21 mmol), dry triethylamine (200 mL), and bis(triphenylphosphine)palladium(II) dichloride (0.872 g, 1.24 mmol). The coupling reaction was continued at 70 °C for 21 h. Recrystallizations from methanol and hexane gave a white solid of **6a** (20.0 g, 98.0 mmol, 72 %, mp 81.3 - 82.0 °C (82-83.5 °C)[5]).

^{1}H-NMR (270 MHz, CDCl$_3$)

δ 5.29 and 5.77 (2d, 2H, =CH$_2$, J =10.9 and 17.5 Hz), 6.70 (dd, 1H, =CH), 7.55 - 7.32 (m, 9H, Ar)

^{13}C-NMR (67.9 MHz, CDCl$_3$)

δ 89.5 (ArC4-C≡), 90.1 (ArC4-C≡C), 114.8 (=CH$_2$), 122.6 (ArC4), 123.4 (ArC1'), 126.2 (ArC2), 128.3 (ArC4'), 128.4 (ArC3'), 131.7 (ArC3), 131.9 (ArC2'), 136.3 (CH=), 137.5 (ArC1)

IR (KBr, cm^{-1})

904 (CH=CH$_2$), 2218 (C≡C)

14

Elemental Analysis

Anal. calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92.   Found: C, 93.85; H, 5.89.

n) Preparation of 3-(2-Phenylethynyl)styrene (6b).   The same procedure as that described above for **1a** was followed using 3-bromostyrene (47.09 g, 257 mmol), phenylacetylene (31.50 g, 309 mmol), copper(I) iodide (0.490 g, 2.57mmol), triphenylphosphine (1.08 g, 4.13 mmol), dry triethylamine (380 mL), and bis(triphenylphosphine)palladium(II) dichloride (1.64 g, 2.34 mmol).   The coupling reaction was continued at 70 °C for 22 h. Recrystallizations from hexane at -30 °C and then distilled at 115 - 124 °C (0.2 mmHg) to give 30.4 g (58 %) of **6b** as white crystals (mp 36.0 - 37.5 °C).

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 5.29 and 5.78 (2d, 2H, =CH$_2$, J = 11.0 and 17.6 Hz), 6.70 (dd, 1H, =CH),

7.60 - 7.27 (m, 9H, Ar-H)

^{13}C-NMR (100MHz, CDCl$_3$)

δ 89.3 (ArC3-C≡), 89.5 (ArC3-C≡C̲), 114.8 (=CH$_2$), 123.3 (ArC3), 123.6 (ArC1'),

126.2 (ArC6), 128.4 (ArC5), 128.4 (ArC3'), 128.6 (ArC4'), 129.5 (ArC2),

130.9 (ArC4), 131.7 (ArC2'), 136.2 (CH=), 137.8 (ArC1)

IR   (KBr, cm^{-1})

920 (CH=CH$_2$), 2206 (C≡C)

Elemental Analysis

Anal. calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92.   Found: C, 94.11; H, 5.95.

o) Preparation of 2-(2-Phenylethynyl)styrene (6c).   The same procedure as that described above for **1a** was followed using 2-bromostyrene (35.0 g, 191 mmol), phenylacetylene (28.5 g, 279 mmol), copper(I) iodide (0.442 g, 2.32 mmol), and triphenylphosphine (0.570 g, 2.18 mmol) in dry triethylamine (285 mL), and bis(triphenylphosphine)palladium(II) dichloride (1.39 g, 1.98 mmol).   The coupling reaction was continued at 70 °C for 76 h.   Distillation in vacuo gave a yellow liquid of **6c** (29.1 g, 143 mmol, 86 %, bp 138 - 141 °C / 0.65 mmHg).

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 5.33 and 5.80 (2dd, 2H, =CH$_2$, J = 1.1, 11.1 and 17.7 Hz), 7.27 (dd, 1H, -CH=),

7.16 - 7.56 (m, 9H, Ar-H)

^{13}C-NMR (100MHz, CDCl$_3$)

δ 87.8 (ArC2-C≡), 94.1 (ArC2-C≡C̲), 115.7 (=CH$_2$), 122.0 (ArC2), 123.4 (ArC1'),

124.7 (ArC6), 127.6 (ArC4), 128.4 (ArC4'), 128.4 (ArC3'), 128.4 (ArC5),

131.6 (ArC2'), 132.6 (ArC3), 135.0 (CH=), 139.0 (ArC1)

IR (neat, cm^{-1})

    914 (CH=CH$_2$), 2213 (C≡C)

Elemental Analysis

    Anal. calcd. for C$_{16}$H$_{12}$: C, 94.08; H, 5.92. Found: C, 94.26; H, 5.87.

2-4. Synthesis of Ethynylstyrnes by Coupling Reaction of Metallated Alkyne with Halide.

3-Lithiated 1-(trimethylsilyl)propyne is a useful reagent for the preparation of terminal silylacetylenes. The reaction used the benzyl halide which showed the same behavior as the primary alkyl halide for nucleophilic reagent, as shown in Scheme 2-2. The coupling reaction that introduced an ethynyl group into 4-chloromethylstyrene gave a relatively good yield.

Scheme 2-2.
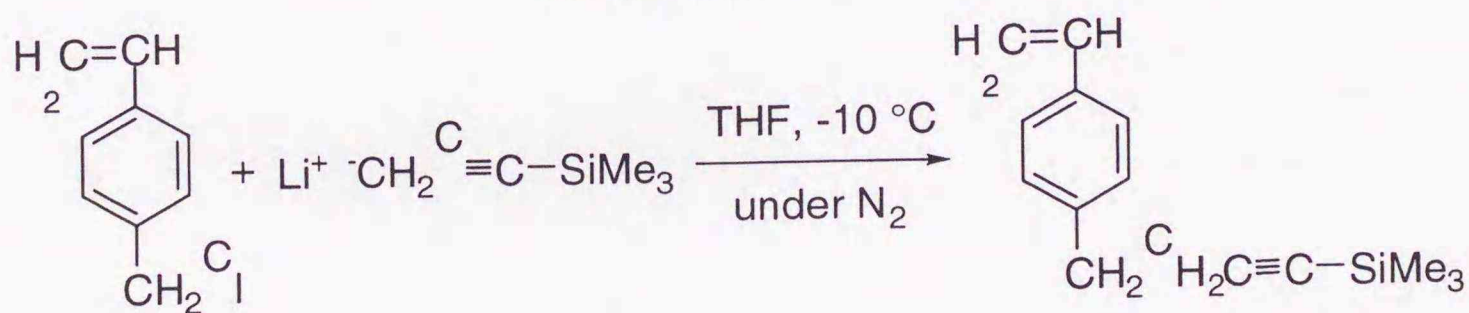
Preparation of 4-(4-Trimethylsilyl-3-butynyl)styrene (2). To a stirred solution of 1-(trimethylsilyl)-1-propyne (72.1 g, 642 mmol) in dry THF (600 mL), n-BuLi (770 mmol, 1.54 M solution in hexane) was added dropwise at -10 °C under nitrogen.[6] The reaction mixture was then heated at 35 °C for 0.5 h to complete the reaction. To the reaction mixture, 4-(chloromethyl)styrene (88.2 g, 578 mmol) was added dropwise at -10 °C and then stirred at 0 °C for 3 h.[7] The whole was poured into water (1 L) and extracted with Et$_2$O (300 mL x 3). The combined organic phase was washed with water and dried over anhydrous Na$_2$SO$_4$. After evaporation of the ether, the residue was purified by column chromatography (silica gel,

16

hexane) and the vacuum distillation gave a colorless liquid of **2** (60.9 g, 267 mmol, 46%, bp 96 - 101 °C / 0.4 mmHg).

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 0.13 (s, 9H, Si(CH$_3$)$_3$), 2.37-2.55 (m, 2H, CH$_2$C≡), 2.89-2.73 (m, 2H, ArCH$_2$), 5.20 and 5.71 (2d, 2H, J = 0.80, 10.9 and 17.6 Hz, =CH$_2$), 6.70 (dd, 1H, -CH=), 7.11-7.38 (m, 4H, Ar).

^{13}C-NMR (100MHz, CDCl$_3$)

δ 0.2 (Si(CH$_3$)$_3$), 22.2 (CH$_2$C≡), 34.9 (ArCH$_2$), 85.4 (SiC≡), 106.7 (CH$_2$C≡), 113.3 (=CH$_2$), 126.3 (Ar, C3), 128.8 (Ar, C2), 135.9 (Ar, C1), 136.7 (-CH=), 140.4 (Ar, C4).

IR (neat, cm^{-1}):

759, 841, and 1250 (≡CSi), 906 (CH=CH$_2$), 2175 (C≡C).

Elemental Analysis

Anal. calcd. for C$_{15}$H$_{20}$Si : C, 78.87; H, 8.83.   Found: C, 78.70; H, 9.03

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Chapter 3. Radical Polymerization of Styrene Derivatives Containing an Ethynyl Group

3-1. Introduction

Styrene derivatives **1a-c**, **2**, **3a-c**, **5a-c**, and **6a-c** are suitable monomers for producing polymers with pendent ethynyl groups and these polymers increase interest in the crosslinking property. The radical polymerization of styrenes with ethynyl groups, however, gives the insoluble polymeric product, because of sensitivity to crosslinking.[1,2,3] Not only vinyl group but also ethynyl group participates in the polymerization to form the crosslinking polymer.

In this chapter, the first interest is whether or not gel-free polystyrenes are produced during the radical polymerizations of **1a-c** and **2**, and the copolymerization with styrene. When the polymerization is to be carried out selectively at the vinyl group site in a bifunctional monomer, the ethynyl group must be temporarily blocked. The introduction of the trimethylsilyl group onto the ethynyl group is useful for this purpose. The polymers with internal $C\equiv C$ groups, which do not need to be blocked, therefore, are important for practice.
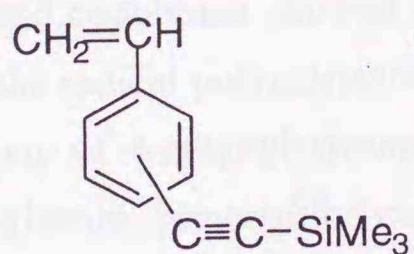
1a : *para*
1b : *meta*
1c : *ortho*
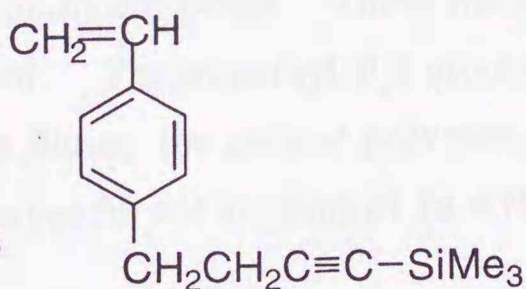
2
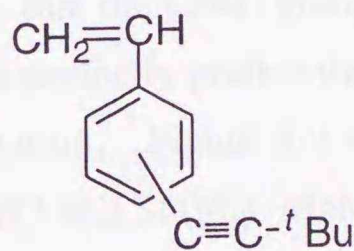
3a : *para*
3b : *meta*
3c : *ortho*
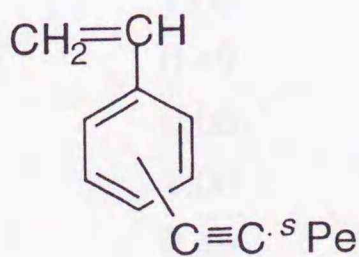
4a : *para*
4b : *meta*
4c : *ortho*
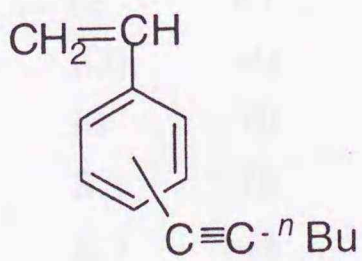
5a : *para*
5b : *meta*
5c : *ortho*
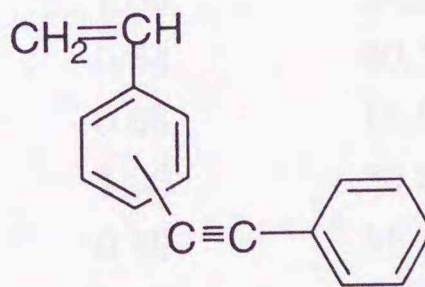
6a : *para*
6b : *meta*
6c : *ortho*

19

The second interest is the substituent effect of the 2-position of C≡C group on their polymerizability during the radical polymerizations of **1a-c**, **2**, **3a-c**, **5a-c**, and **6a-c**. The copolymerization parameter, such as monomer reactivity ratios and the Q and e values, are determined from the copolymerizations of **1a-c**, **2**, **5a**, and **6a-c** with styrene.

The third interest is the thermal crosslinking property of the obtained polymers and copolymers at elevated temperature. These polymers are characterized as a thermally curable material.

3-2. Results and Discussion

3-2-1. Radical Polymerizations of 1a-c.

Table 3-1 lists the results of the polymerizations of **1a-c** and the copolymerizations with styrene (St). For all the polymerization, the organic solvent-soluble, powdery polymers were obtained. Furthermore, the size-exclusion chromatography curves of the resulting polymer and copolymer showed unimodal peaks. These mean that the C≡C groups did not interfere the radical polymerization. The trimethylsilyl groups perfectly protect the terminal C≡C group of 4-ethynylstyrene during the radical polymerization. Figure 3-1 shows the copolymerization composition curves for the systems of **1a-c** (M_1) and St (M_2). Mole fraction

Table 3-1. Radical Copolymerizations of **1a-c** (M_1) with Styrene (M_2)[a]

1 (M_1)	mole fraction of M_1 in monomer feed (F_1)	Time h	Yield %	mole fraction of M_1 in copolymer (f_1)[b]	M_n (M_w/M_n)[c]
1a	1.00	12	47	1.00	54,200 (2.09)
1a	0.49	6.0	40	0.54	40,500 (1.85)
1a	0.06	30	70	0.08	18,500 (1.79)
1b	1.00	8.3	78	1.00	50,800 (1.95)
1b	0.49	6.5	44	0.49	55,400 (1.74)
1b	0.05	29	71	0.05	18,500 (1.78)
1c	1.00	22	47	1.00	7,800 (1.77)
1c	0.50	22	74	0.59	7,300 (1.81)
1c	0.05	22	66	0.07	13,100 (1.80)

[a] Initiator, AIBN; [**1**] or [**1**+St] = 5.0 mol·L⁻¹; [AIBN] = 50 mmol·L⁻¹; temp. 60 °C; solvent, toluene.

[b] Determined by ¹H NMR spectra.

[c] Determined by SEC using polystyrene standard.

20
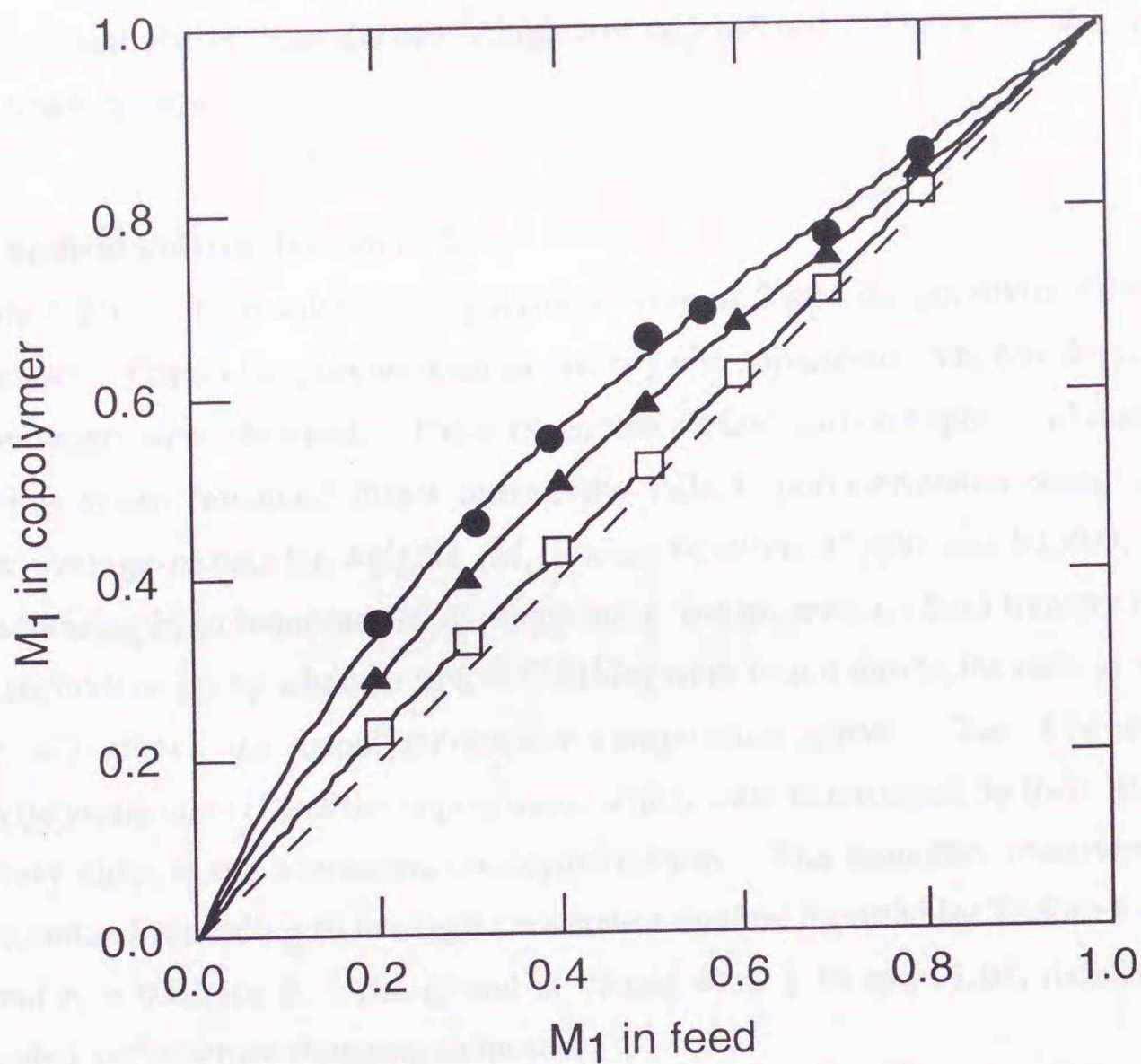
Figure 3-1. Composition curves for the copolymerization of 4-(2-(trimethylsilyl)-ethynyl)styrene (**1a**) with styrene (●), 3-(2-(trimethylsilyl)ethynyl)styrene (**1b**) with styrene (□), and 2-(2-(trimethylsilyl)ethynyl)styrene (**1c**) with styrene (▲).

M_1 in copolymer (f_1), which was determined by the ^{1}H-NMR spectra, was higher than mole fraction M_1 in monomer feed (F_1) for **1a** and **1c**. The curve for **1b** was very close to an azeotropic line. The monomer reactivity ratios, which were determined by the Kelen-Tüdõs method,[4] were $r_1 = 1.39$ and $r_2 = 0.36$ for **1a**, $r_1 = 1.05$ and $r_2 = 0.83$ for **1b**, and $r_1 = 1.22$ and $r_2 = 0.54$ for **1c**. The Q and e_1 values were 1.43 and 0.04 for **1a**, 0.95 and -0.43 for **1b**, and 1.11 and -0.15 for **1c**, respectively, indicating that they are conjugative and electron-withdrawing monomers. As for **1b** with *meta*-trimethylsilylethynyl group a slight resonance effect was exhibited.

The deprotection of the silyl groups in polymer **1a-c** and copolymers **1a-c**/St was carried out using $(C_4H_9)_4$NF in THF at 0 °C for 2 h. For the conversion of copolymer **1a**/St into poly(4-ethynylstyrene-*co*-St), the absorptions at 3293 and 2104 cm^{-1} due to the ≡C-H and -C≡C- strech vibrations were observed together with the disappearance of the absorption at

2158 cm^{-1} due to the C≡C-Si(CH$_3$)$_3$ group in the IR spectrum. The final spectrum indicated that the trimethylsilyl groups were completely deprotected. The result was also confirmed by the NMR spectra.

3-2-2. Radical Polymerization of 2.

Table 3-2 lists the results of the polymerization of 2 and the copolymerizations of 2 with styrene (St). For all the polymerization, the organic solvent-soluble, powdery, and unimodal peak polymers were obtained. These mean that carbon-carbon triple bond and trimethylsilyl protecting group remained intact during the radical polymerization same as 1a-c. The number-average molecular weights (M_ns) were between 22,400 and 91,400, and increased with increasing F$_1$ in monomer feeds, suggesting that no serious chain transfer reactions at the active methylene group adjacent to C≡C-SiMe$_3$ were found during the radical polymerization. Figure 3-2 shows the copolymerization composition curve. The 4-(4-trimethylsilyl-3-butynyl)styrene units (f$_1$) in the copolymers, which were determined by their ^{1}H-NMR spectra, were very close to the azeotropic copolymerization. The monomer reactivity ratios, which are determined according to the high conversion method reported by Tüdõs et al.,[5] were r_1 = 1.13 and r_2 = 0.82 for 2. The Q and e_1 values were 1.54 and –1.07, indicating that 2 is a conjugated and electron-donating monomer.

The deprotections of the silyl groups from the polymers were carried out using (C$_4$H$_9$)$_4$NF in THF at 0 °C for 2 h. For the conversion of copolymer 2/St into poly[(4-(3-butynyl)styrene)-co-St], the respective absorptions at 3298 and 2117 cm^{-1} due to the ≡C-H and -C≡C- strech vibrations of the C≡C-H group were observed together with the disappearance of the absorption at 2173 cm^{-1} due to the C≡C-Si(CH$_3$)$_3$ group in the IR spec-

Table 3-2. Radical Copolymerizations of 2 (M$_1$) with Styrene (M$_2$)^a

mole fraction of M$_1$ in monomer feed (F$_1$)	Time h	Yield %	mole fraction of M$_1$ in copolymer (f$_1$)^b	M_n (M_w/M_n)^c
1.00	1	9.4	1.00	91,400 (1.68)
0.50	2	11.4	0.53	41,300 (1.53)
0.10	3	11.5	0.12	22,400 (1.56)

^{a} Initiator, AIBN; [2] or [2+St] = 2.5 mol·L^{-1}; [AIBN] = 25 mmol·L^{-1}; temp. 60 °C; solvent, toluene.

^{b} Determined by ^{1}H NMR spectra.

^{c} Determined by SEC using polystyrene standard.

tra.   The trimethylsilyl groups were completely deprotected to form poly[(4-(3-butynyl)styrene)-*co*-St].   This was also confirmed by the NMR spectra.
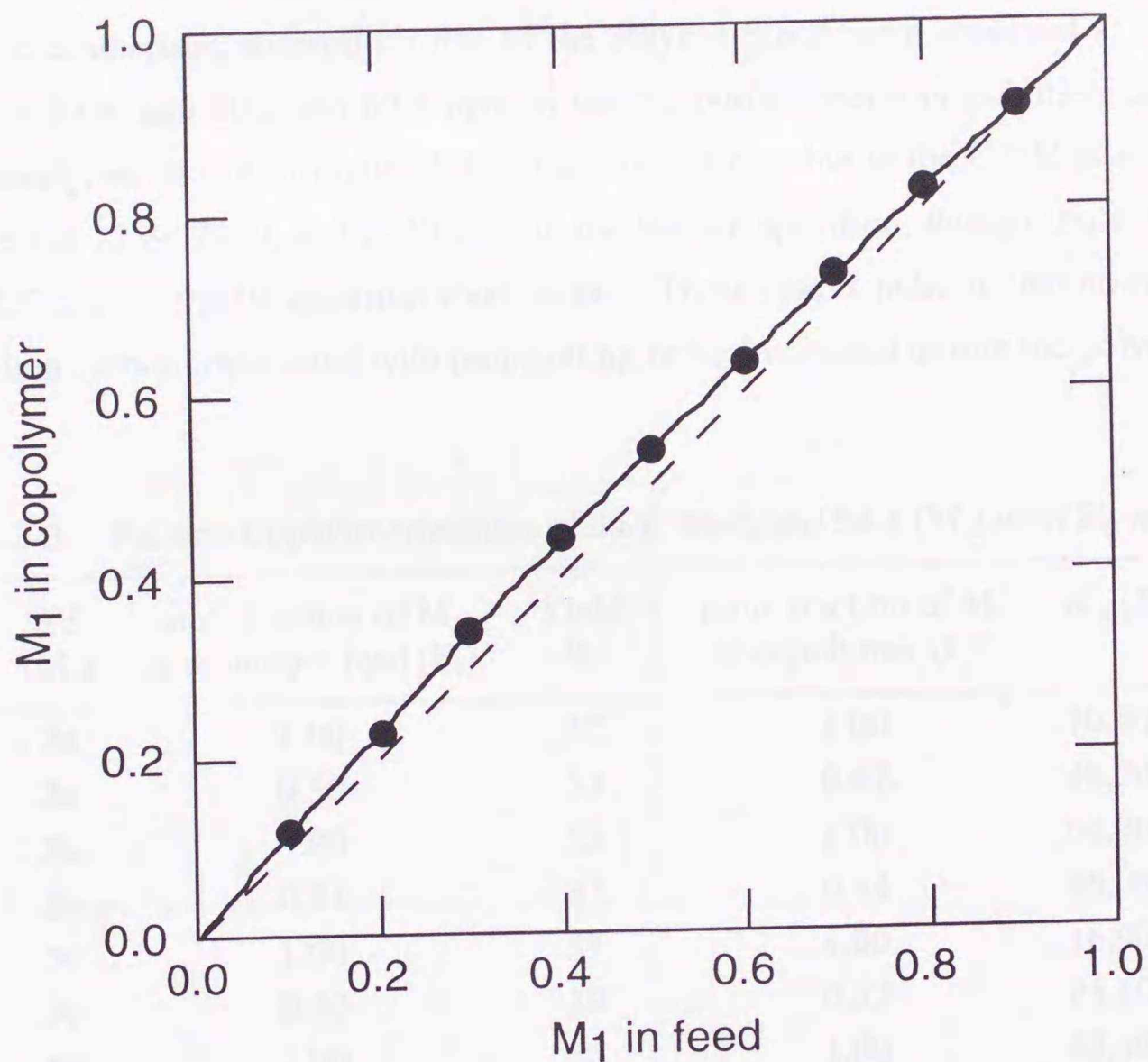
Figure 3-2. Composition curves for the copolymerization of 4-(4-trimethylsilyl-3-butynyl)styrene (**2**) with styrene (●).

3-2-3. Radical Polymerizations of 3a-c, 4a-c, and 5a-c.

Table 3-3 lists the results of the polymerizations of **3a-c**, **4a-c**, and **5a-c**, and the copolymerizations with styrene (St).   For all the polymerization, the organic solvent-soluble, powdery polymers were obtained.   This means that the C≡C groups did not interfere with the radical polymerization.   The SEC chromatograms for all the polymer samples showed a unimodal peak.   In spite of their substituted position, the M_ns of 3,3-dimethyl-1-butynyl substituted polystyrenes were higher than those of 3-methyl-1-hexynyl and 1-hexynyl substituted polystyrenes.   This tendency resembles the order of chain transfer to *t*-butylbenzene, isopropylbenzene, and ethylbenzne.[6]   In both of the polymers and copolymers, the increasing order of M_ns is as follows: *ortho*- < *meta*- ≤ *para*-substituted polystyrenes.   A

23

lowering of M_ns for *ortho*-ethynyl substituted styrenes could be caused by chain transfer to monomer during the radical polymerization. Therefoe, the lowest M_n of polymer **4c** could be influenced by *ortho*-substituted 3-methyl-1-hexynyl group.

The characteristic absorptions due to the ethynyl group were observed at 79.3 and 97.7, 80.9 and 93.9, and 80.8 and 89.5 ppm in the ^{13}C-NMR spectra of polymers **3a**, **4a**, and **5a**, respectively, as shown in Figure 3-3. The absorptions due to the C≡C group were clearly observed at 2239, 2230, and 2230 cm^{-1} in the Raman spectrum, though those at 2237, 2231, and 2229 cm^{-1} in the IR spectrum were weak. These results indicate that no side reaction of the carbon-carbon triple bond with propagating radical occurred during the polymerization.

Table 3-3. Radical Copolymerizations of **3a-c**, **4a-c**, and **5a-c** (M_1) with Styrene (M_2)[a]

3-5 (M_1)	mole fraction of M_1 in monomer feed (F_1)	Yield %	mole fraction of M_1 in copolymer (f_1)[b]	M_n (M_w/M_n)[c]
3a	1.00	37	1.00	70,900 (1.60)
3a	0.50	33	0.67	48,200 (1.52)
3b	1.00	55	1.00	64,700 (1.61)
3b	0.51	37	0.54	48,000 (1.57)
3c	1.00	53	1.00	16,900 (1.75)
3c	0.50	39	0.53	25,100 (1.69)
4a	1.00	36	1.00	42,400 (1.77)
4a	0.51	35	0.65	37,200 (1.66)
4b	1.00	37	1.00	35,000 (1.65)
4b	0.51	30	0.53	36,500 (1.63)
4c	1.00	8	1.00	7,820 (1.61)
4c	0.50	24	0.51	15,200 (1.78)
5a	1.00	22	1.00	35,100 (1.88)
5a	0.51	24	0.65	37,400 (1.81)
5b	1.00	28	1.00	29,300 (1.78)
5b	0.50	25	0.54	38,000 (1.72)
5c	1.00	18	1.00	10,200 (1.67)
5c	0.50	24	0.58	18,400 (1.66)

[a] Initiator, AIBN; [M_1] or [M_1+St] = 5.0 mol·L^{-1}; [AIBN] = 50 mmol·L^{-1}; temp. 60 °C; solvent, toluene; time, 6h.
[b] Determined by ^{1}H NMR spectra.
[c] Determined by SEC using polystyrene standard.
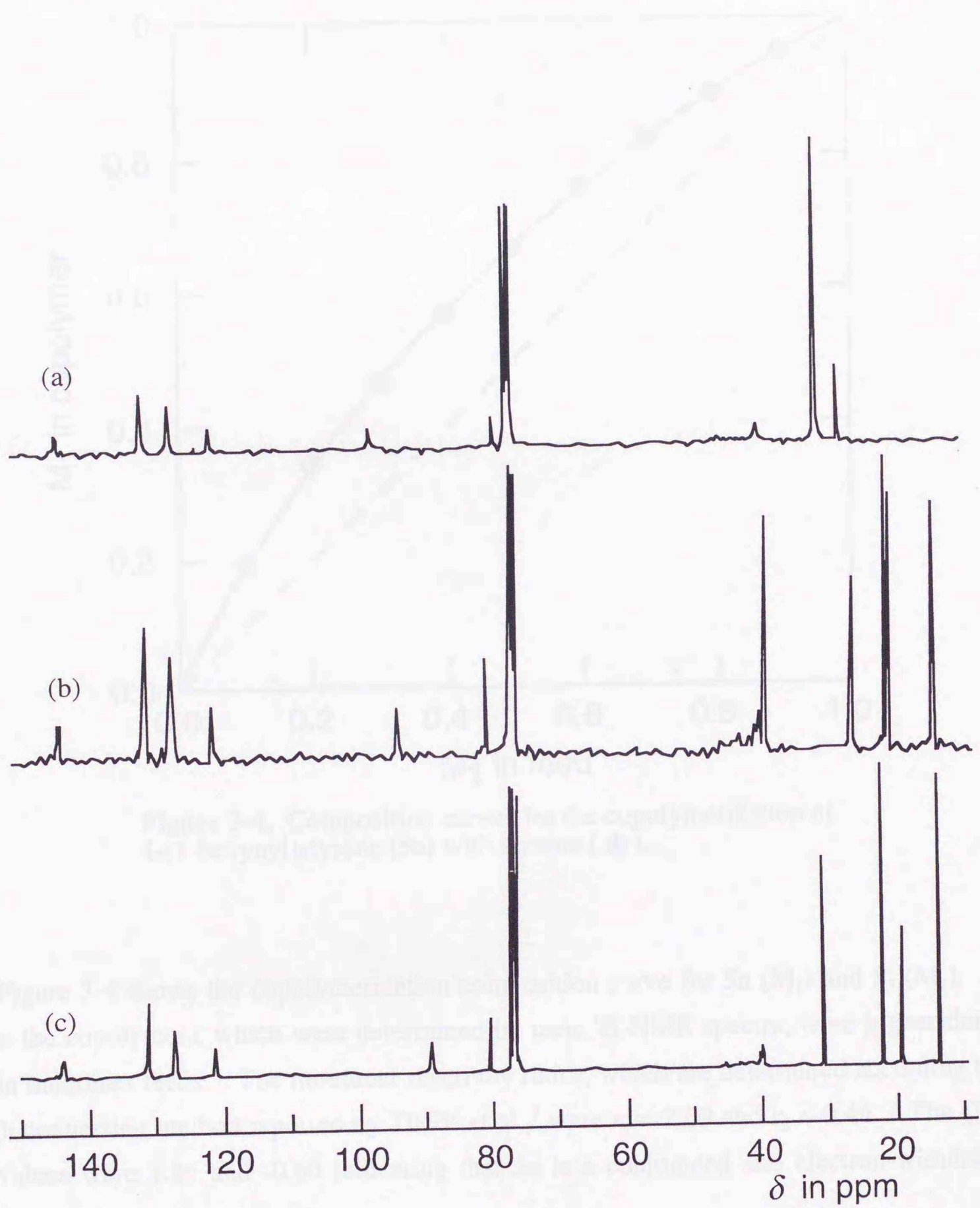
Figure 3-3. ^{13}C NMR spectra of poly[4-(3,3-dimethyl-1-butynyl)styrene] (**3a**) (a), poly[4-(3-methyl-1-hexynyl)styrene] (**4a**) (b), and poly[4-(1-hexynyl)styrene] (**5a**) (c).
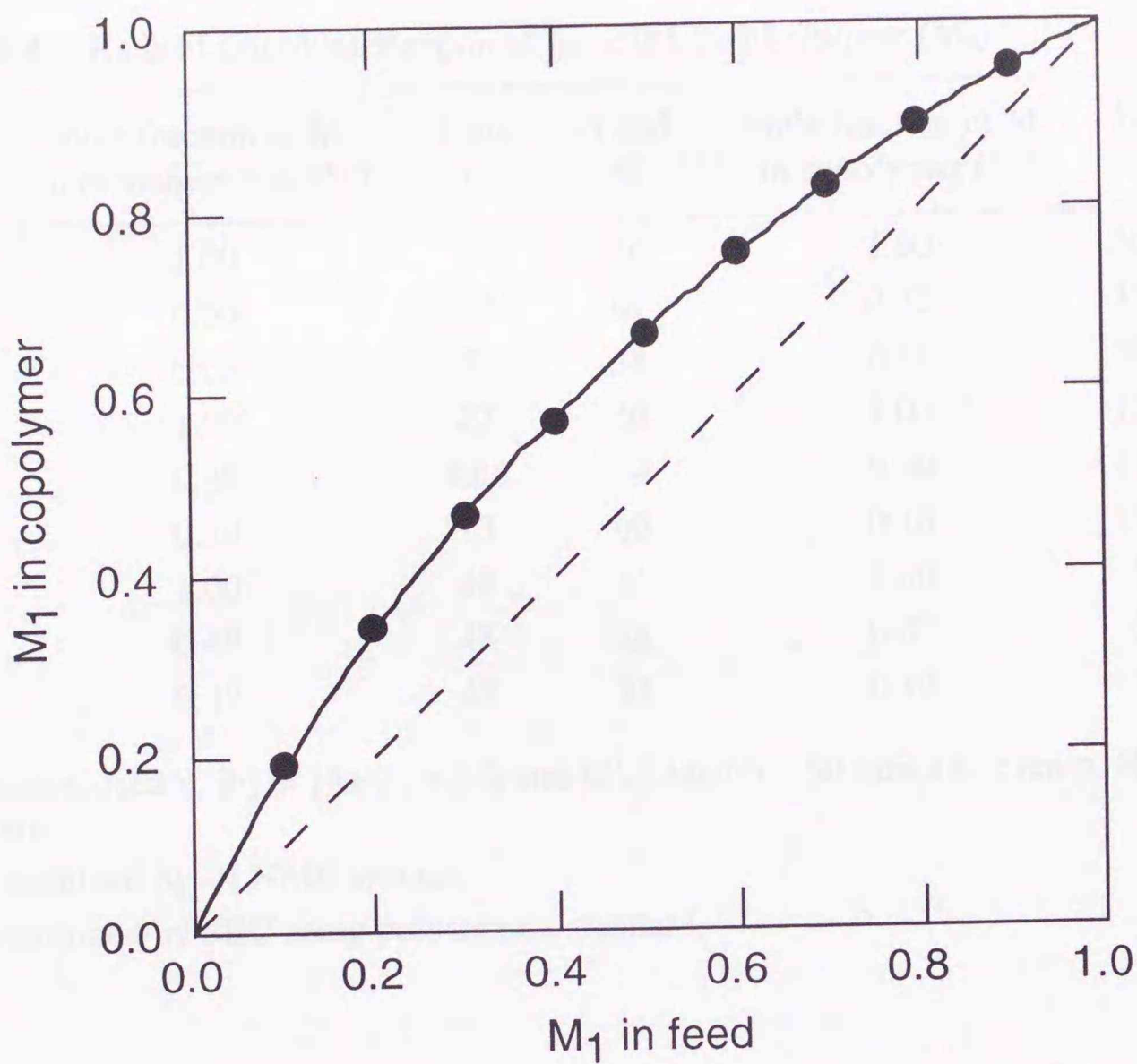
Figure 3-4. Composition curves for the copolymerization of
4-(1-hexynyl)styrene (**5a**) with styrene (●).

Figure 3-4 shows the copolymerization composition curve for **5a** (M_1) and St (M_2). The f_1 in the copolymers, which were determined by their ^{1}H-NMR spectra, were higher than the F_1 in monomer feeds. The monomer reactivity ratios, which are determined according to the high conversion method reported by Tüdõs et al.,[5] were $r_1 = 2.09$ and $r_2 = 0.46$. The Q_1 and e_1 values were 1.86 and -0.60 indicating that **5a** is a conjugated and electron-withdrawing monomer.

3-2-4. Radical Polymerizations of 6a-c.

The polymerization and copolymerizations with AIBN were carried out at 60 °C in toluene. Table 3-4 summarizes the results of the polymerizations and the copolymerizations with styrene. All the polymerizations proceeded homogeneously and the obtained polymers were soluble in common organic solvents such as benzene, THF, and chloroform and insoluble in methanol. The SEC chromatograms for these polymers showed a unimodal peak. The in-

26

Table 3-4.   Radical Copolymerization of **6a–c** (M_1) with Styrene (M_2) [a]

6 (M_1)	mole fraction of M_1 in monomer feed (F_1)	Time h	Yield %	mole fraction of M_1 in copolymer (f_1) [b]	M_n (M_w/M_n) [c]
6a	1.00	3.5	36	1.00	70,200 (1.61)
6a	0.50	13	61	0.78	35,600 (1.98)
6a	0.05	13.5	58	0.11	20,000 (1.67)
6b	1.00	22	40	1.00	13,300 (1.97)
6b	0.49	49.5	34	0.49	11,000 (1.92)
6b	0.10	23	60	0.10	14,600 (1.72)
6c	1.00	48	31	1.00	1,470 (1.13)
6c	0.49	48	28	0.57	1,690 (1.20)
6c	0.10	48	32	0.10	3,360 (1.33)

[a] Initiator, AIBN; [**6**] or [**6**+St] = 5.0 mol·L^{-1}; [AIBN] = 50 mmol·L^{-1}; temp. 60 °C; solvent, toluene.

[b] Determined by ^{1}H NMR spectra.

[c] Determined by SEC using polystyrene standard.

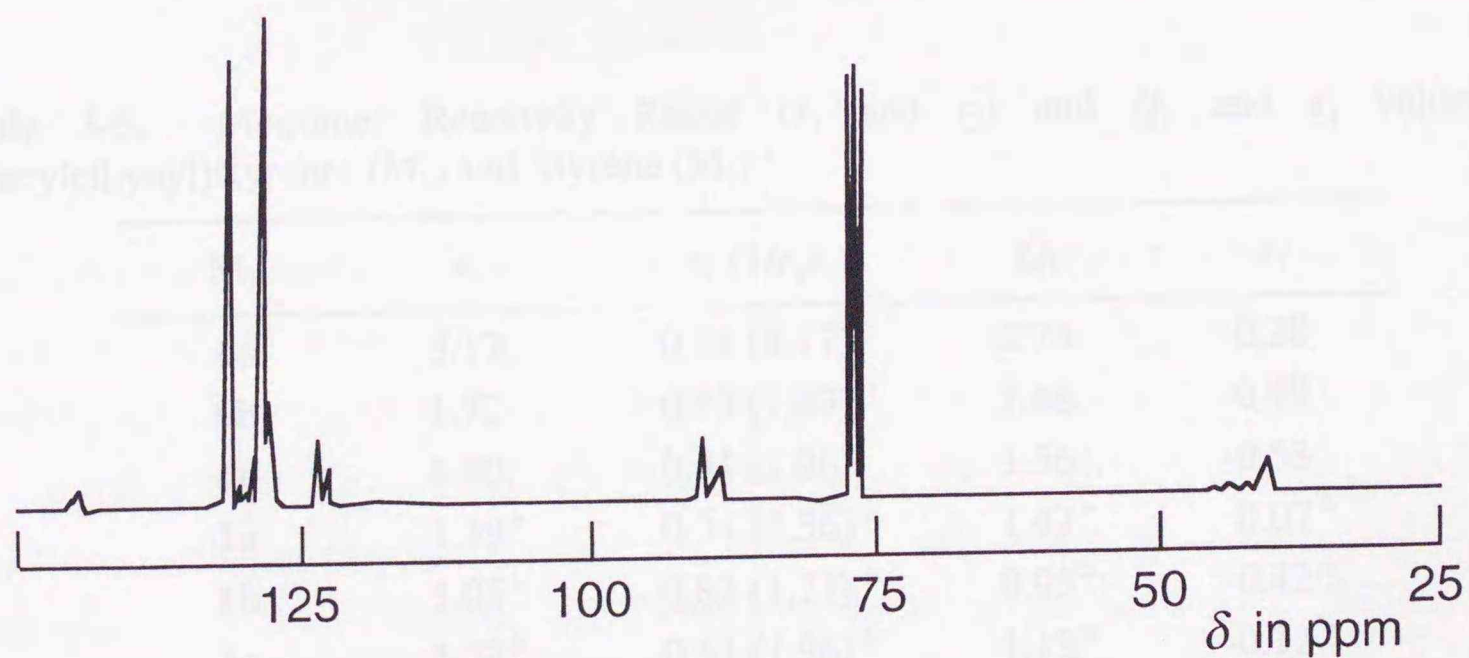**Figure 3-5.** ^{13}C-NMR spectrum of poly[(3-phenylethynyl)styrene] (**6b**) .

27

creasing order of the M_ns is as follows: polymer **6c** < polymer **6b** < polymer **6a**. The M_ns were extremely low for polymer **6c**. The lowest and highest M_n was 1,470 for polymer **6c** and 70,200 for polymer **6a**. The introduction of a styrene unit in polymer **6c** caused an increase in the M_ns, though they were still low, whereas the M_ns of polymer **6a**/St were lower than that of polymer **6a**. A similar tendency for the M_ns was observed for the polymers and copolymers obtained by the radical polymerization of **1a-c**,[7] **3a-c**, **4a-c**, and **5a-c**. These low M_ns of the *ortho*-ethynyl substituted polymers could be caused by dipole interactions between the ethynylene group and propagating radical.[8,9]

The characteristic absorptions due to the C≡C group were observed at 89.2 and 90.0 ppm in the ^{13}C-NMR spectrum of polymer **6b**, as shown in Figure 3-5. The absorption due to the C≡C group was observed at 2216 cm^{-1} in the Raman spectrum, though that at 2214 cm^{-1} in the IR spectrum was very weak. These results indicate that no polymerization of the carbon-carbon triple bond with radical species occured.

Figure 3-6 shows the copolymerization composition curves for **6a-c** (M_1) and styrene (M_2). The copolymer compositions were determined by the ratio of the adsorptions at 1-3 ppm and 6-8 ppm due to the methine and methylene protons and the aromatic protons, respectively, in the ^{1}H-NMR spectra. Monomer reactivity ratios, which are determined according to the high conversion method reported by Tüdõs et al.,[5] are $r_1 = 3.17$ and $r_2 = 0.24$ for **6a**, $r_1 = 1.72$ and $r_2 = 0.53$ for **6b**, and $r_1 = 1.80$ and $r_2 = 0.51$ for **6c**. The reactivity of **6a** toward the polystyryl radical, which can be estimated using the $1/r_2$ value, is higher than those of **6b** and **6c**, which is similar to the result for **1a-c**. In Table 3-5, the Q_1 and e_1 values are compared with those of **1a-c**. **6a-c** were found to be conjugative and electron withdrawing monomers,

Table 3-5. Monomer Reactivity Ratios (r_1 and r_2) and Q_1 and e_1 values for (Phenylethynyl)styrenes (M_1) and Styrene (M_2) [a]

M_1	r_1	r_2 ($1/r_2$)	Q_1	e_1
6a	3.17	0.24 (4.17)	2.74	-0.28
6b	1.72	0.53 (1.89)	1.48	-0.49
6c	1.80	0.51 (1.96)	1.56	-0.53
1a	1.39[b]	0.34 (2.56)[b]	1.47[b]	0.07[b]
1b	1.05[b]	0.82 (1.21)[b]	0.95[b]	-0.42[b]
1c	1.22[b]	0.51 (1.96)[b]	1.13[b]	-0.12[b]
5a	2.09	0.46 (2.17)	1.86	-0.60

[a] Calculated according to the high conversion method reported by Tüdõs et al..[5]

[b] See ref. 7, recalculated by the high conversion method.[5]
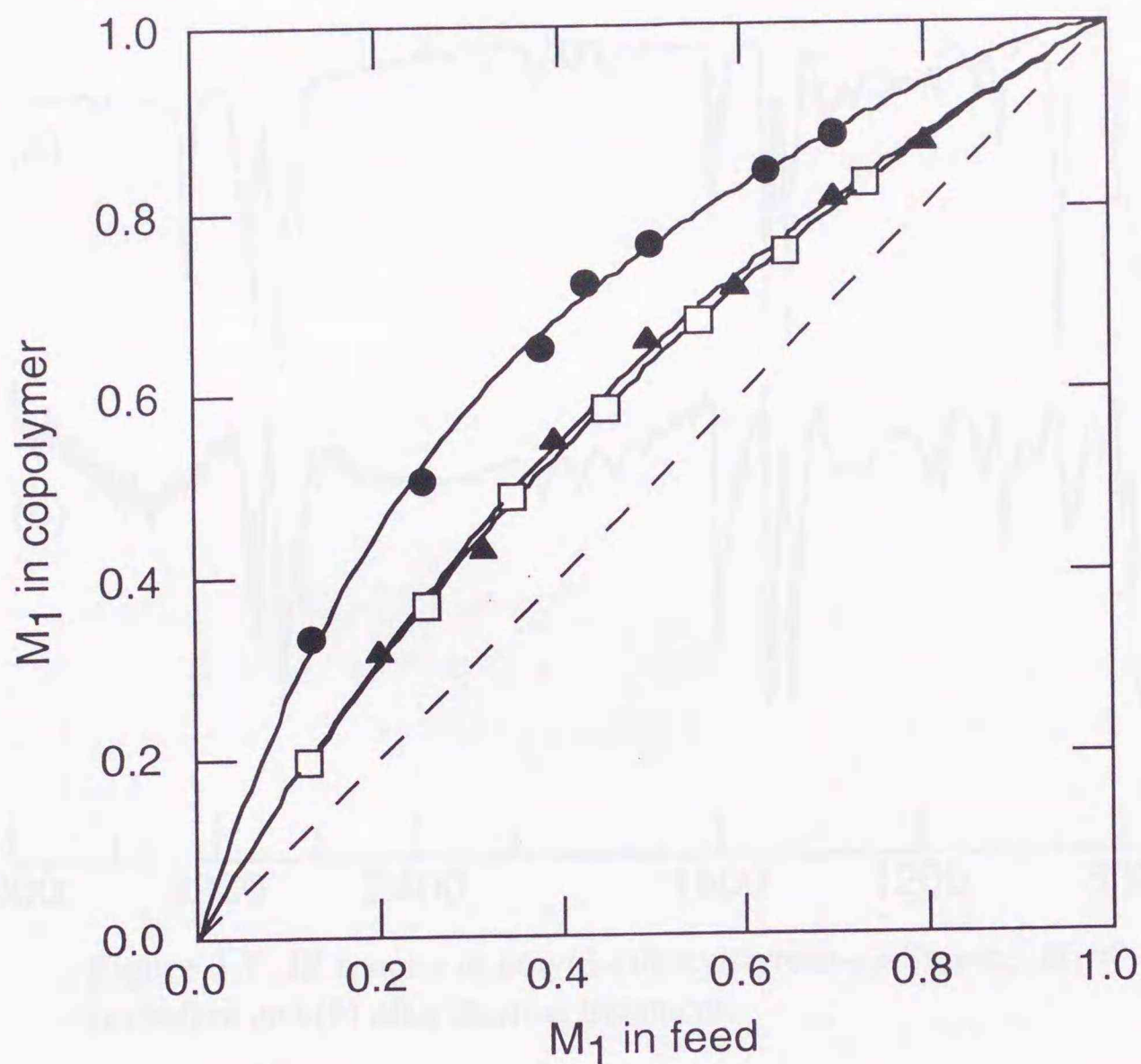
Figure 3-6. Composition curves for the copolymerization of 4-(phenylethynyl)-styrene (**6a**) with styrene (●), 3-(phenylethynyl)styrene (**6b**) with styrene (☐), and 2-(phenylethynyl)styrene (**6c**) with styrene (▲).

as well as **1a-c** and **5a**. The electron withdrawing character of phenylethynyl group is clarified by the Hammett values, i.e., $\sigma_m = 0.14$ and $\sigma_p = 0.16$.[10]

3-2-5. Thermal Properties of Poly(ethynylstyrene) and Poly(ethynylstyrene-*co*-St)

The thermal reactions of poly(ethynylstyrene) and poly(ethynylstyrene-*co*-St) were examined by heating at 350 °C for 1 h under nitrogen. After the thermal treatment, the absorptions at 2108 and 3300 cm^{-1} due to the ethynyl group completely disappeared in the IR spectra of poly[(3-ethynylstyrene)-*co*-St] (f_1=0.12) as shown in Figure 3-7. This disappearance of the C≡C bond was found also by the Raman spectrum. All the cured polymers were insoluble in common organic solvents, such as benzene, chloroform, and THF.

The thermal properties of poly(ethynylstyrene) and poly(ethynylstyrene-*co*-St) were characterized by the TG and DSC measurements. Figure 3-8 shows the TG and DSC curves

Figure 3-7. IR spectra of poly(3-ethynylstyrene-*co*-Styrene) (f$_1$=0.12) (a) before and (b) after thermal treatment.

Figure 3-8. TG and DSC thermograms of poly(4-ethynylstyrene-*co*-styrene) (f$_1$=0.54).

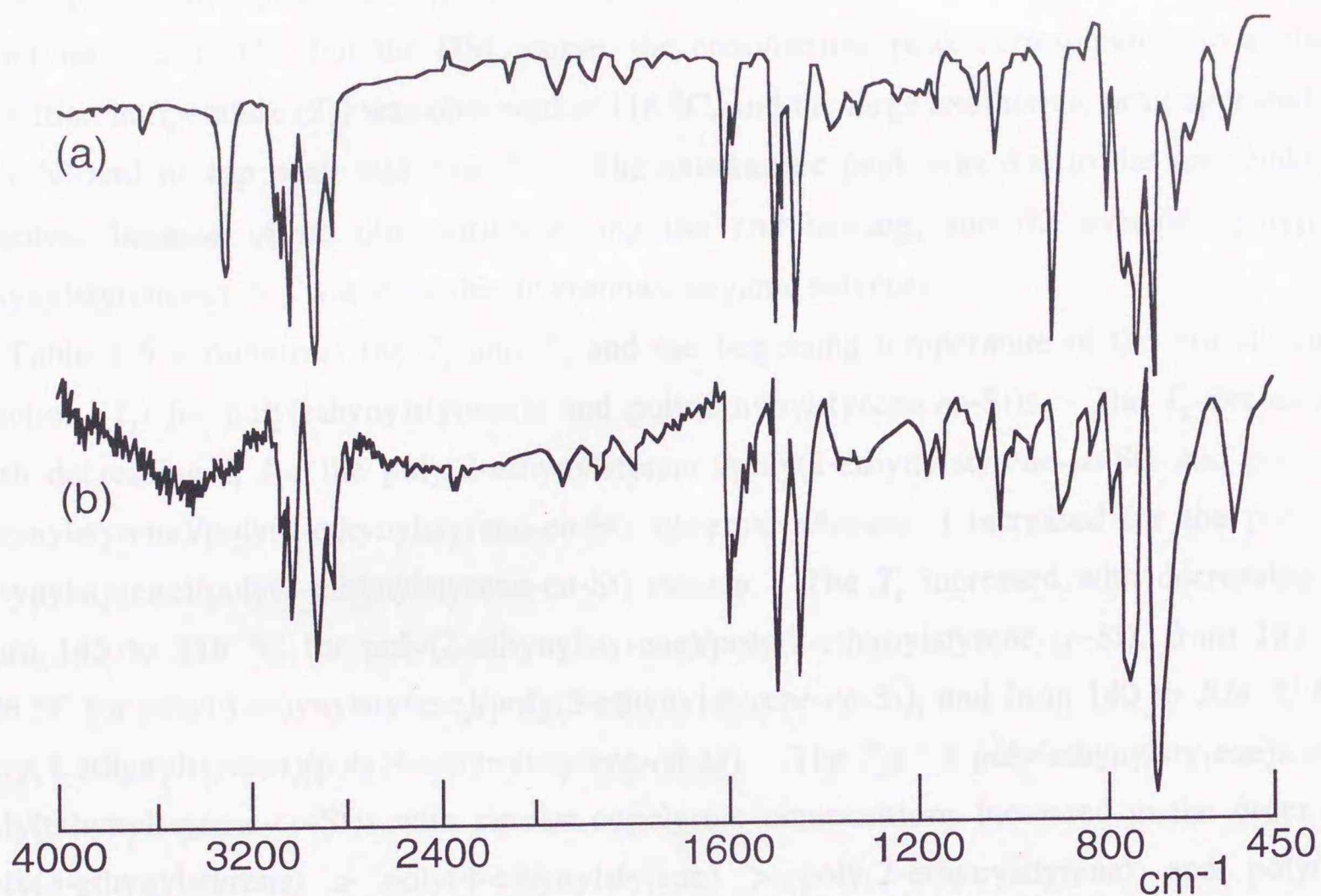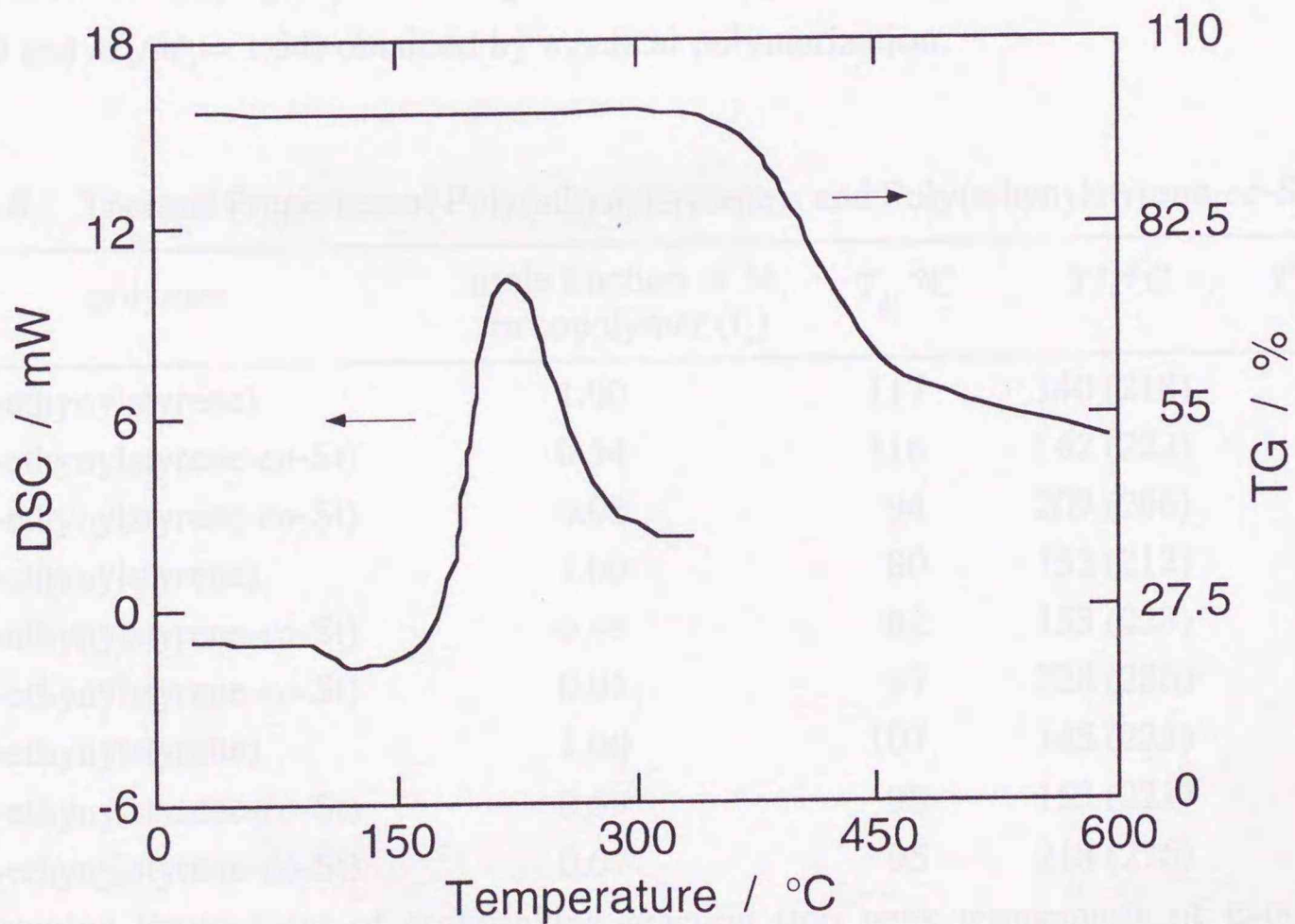of poly[(4-ethynylstyrene)-*co*-St] ($f_1 = 0.54$).   For the TG curve, a 10 % weight loss (T_d) was observed at 391 °C.   For the DSC curve, the endothermic peak corresponding to a glass transition temperature (T_g) was observed at 116 °C, and the large exothermic peak appeared at 203 °C and its top peak was 222 °C.   The exothermic peak was due to the crosslinking reaction, because of no observation during the 2nd heating, and the annealed poly[(4-ethynylstyrene)-*co*-St] was insoluble in common organic solvents.

Table 3-6 summarizes the T_g and T_d and the beginning temperature of the crosslinking reaction (T_r) for poly(ethynylstyrene)s and poly(ethynylstyrene-*co*-St)s.   The T_g decreased with decreasing f_1 for the poly(2-ethynylstyrene)/poly(2-ethynylstyrene-*co*-St) and poly(4-ethynylstyrene)/poly(4-ethynylstyrene-*co*-St) systems, whereas it increased for the poly(3-ethynylstyrene)/poly(3-ethynylstyrene-*co*-St) system.   The T_r increased with decreasing f_1 from 145 to 218 °C for poly(2-ethynylstyrene)/poly(2-ethynylstyrene-*co*-St), from 152 to 228 °C for poly(3-ethynylstyrene)/poly(3-ethynylstyrene-*co*-St), and from 140 to 209 °C for poly(4-ethynylstyrene)/poly(4-ethynylstyrene-*co*-St).   The T_ds for poly(ethynylstyrene)s and poly(ethynylstyrene-*co*-St)s with similar copolymer compositions increased in the order of poly(3-ethynylstyrene) > poly(4-ethynylstyrene) > poly(2-ethynylstyrene) and poly(3-ethynylstyrene-*co*-St) > poly(4-ethynylstyrene-*co*-St) > poly(2-ethynylstyrene-*co*-St), respectively.   Except for poly(2-ethynylstyrene-*co*-St) ($f_1 = 0.07$), the T_ds of polystyrenes having pendant ethynyl groups were higher than a temperature of 362 °C of poly(styrene) ($M_n = 19{,}500$ and $M_w/M_n = 1.54$) obtained by a radical polymerization.

Table 3-6.   Thermal Properties of Poly(ethynylstyrene)s and Poly(ethynylstyrene-*co*-St)s

polymer	mole fraction of M_1 in copolymer (f_1)	T_g, °C	T_r^a, °C	T_d^b, °C
poly(4-ethynylstyrene)	1.00	117	140 (218)	428
poly(4-ethynylstyrene-*co*-St)	0.54	116	162 (222)	391
poly(4-ethynylstyrene-*co*-St)	0.08	94	209 (266)	393
poly(3-ethynylstyrene)	1.00	80	152 (212)	452
poly(3-ethynylstyrene-*co*-St)	0.49	82	153 (223)	410
poly(3-ethynylstyrene-*co*-St)	0.05	87	228 (286)	385
poly(2-ethynylstyrene)	1.00	107	145 (221)	393
poly(2-ethynylstyrene-*co*-St)	0.59	98	153 (221)	368
poly(2-ethynylstyrene-*co*-St)	0.07	95	218 (276)	330

[a] Beginning temperature of crosslinking reaction (top peak temperature of exothermic peak).

[b] Temperature of 10 % weight loss.

When heated, poly(2-ethynylstyrene-*co*-St) ($f_1 = 0.07$), poly(3-ethynylstyrene-*co*-St) ($f_1 = 0.05$), and poly(4-ethynylstyrene-*co*-St) ($f_1 = 0.08$) melted, flowed, and then cured. In addition, their cured sheet samples could be obtained using an injection molding apparatus, thus indicating that the polystyrene having the pendant ethynyl group is a new thermosetting material. Further investigations on the curing mechanism and the mechanical properties of the cured polystyrenes will be discussed in Chapter 6.

3-2-6. Thermal Properties of Poly[4-(3-butynyl)styrene] and Poly[4-(3-butynyl)styrene-*co*-St]

The thermal reactions of poly[4-(3-butynyl)styrene] and poly[(4-(3-butynyl)styrene)-*co*-St] were examined by heating at 350 °C for 20 min under nitrogen. After the thermal treatment, the absorptions at 2117 and 3298 cm^{-1} and 2116 cm^{-1} due to the ethynyl group completely disappeared in the IR and Raman spectrum, respectively. All the cured polymers were insoluble in common organic solvents, such as benzene, chloroform, and THF.

The thermal properties of poly[4-(3-butynyl)styrene] and poly[(4-(3-butynyl)styrene)-*co*-St] were characterized by the TG and DSC measurements. Figure 3-9 shows the TG and DSC curves of poly[4-(3-butynyl)styrene]. For the TG curve, a 10 % weight loss (T_d) was observed at 445 °C. For the DSC curve, the endothermic peak corresponding to a glass tran-
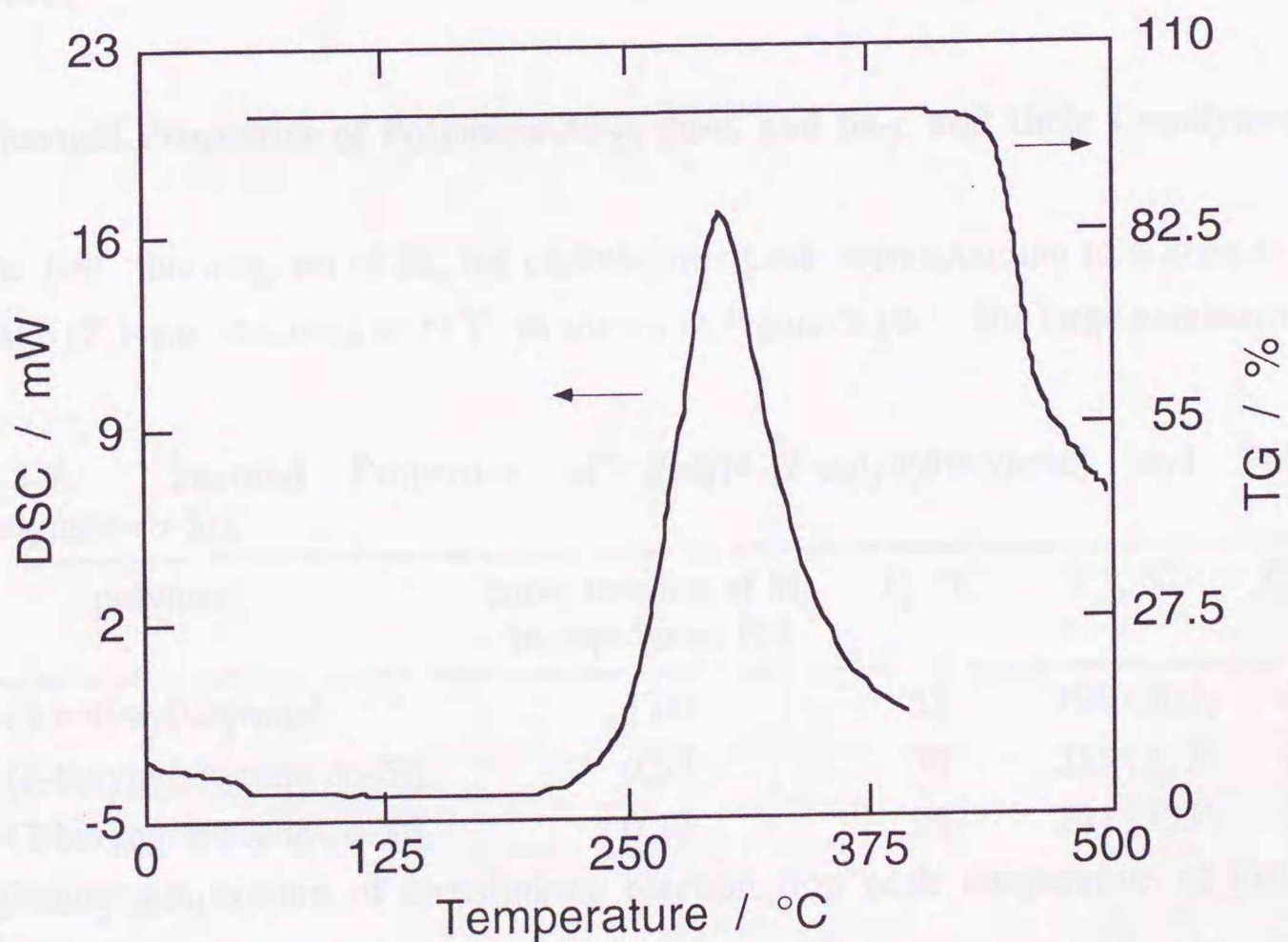

Figure 3-9. TG and DSC thermograms of poly[4-(3-butynyl)styrene] (**2**).

32

sition temperature (T_g) was observed at 52 °C, and the large exothermic peak appeared at 194 °C and its top peak was 302 °C. The exothermic peak was due to the crosslinking reaction, because of no observation during the 2nd heating, and the annealed poly[4-(3-butynyl)styrene] was insoluble in common organic solvents.

Table 3-7 summarizes the T_g and T_d and the beginning temperature of the crosslinking reaction (T_r) for poly[4-(3-butynyl)styrene] and poly[4-(3-butynyl)styrene-co-St]. The T_g increased with decreasing f_1. As expected, the T_g values was decreased by introducing two methylene units between phenyl ring and ethynyl group. The T_r increased with decreasing f_1 from 194 to 241 °C. The T_rs and T_ds of poly[4-(3-butynyl)styrene] and poly[4-(3-butynyl)styrene-co-St]s were higher than those of poly(4-ethynylstyrene) and poly(4-ethynylstyrene-co-St) with similar copolymer compositions. The T_ds of polystyrenes having pendant ethynyl groups were higher than a temperature of 362 °C of polystyrene (M_n = 19,500 and M_w/M_n = 1.54) obtained by radical polymerization.

When heated, poly[4-(3-butynyl)styrene] and poly[4-(3-butynyl)styrene-co-St] (f_1 = 0.53 and 0.12) melted, flowed, and then cured. The decrease in T_g values due to the insertion of two methylene units might be improved on the thermal workability. In addition, the T_ds of poly[4-(3-butynyl)styrene] and poly[4-(3-butynyl)styrene-co-St] were approximately the same temperature as those for the poly(3-ethynylystyrene) and poly(3-ethynylstyrene-co-St). The polystyrene having the pendant butynyl group becomes a new candidate for thermosetting.

3-2-7. Thermal Properties of Polymers 3a-c, 4a-c, and 5a-c and their Copolymers with Styrene

For the DSC thermogram of **5a**, the endothermic peak corresponding to a glass transition temperature (T_g) was observed at 72°C, as shown in Figure 3-10. The large exothermic peak

Table 3-7. Thermal Properties of Poly[4-(3-butynyl)styrene] and Poly[4-(3-butynyl)styrene-co-St].

polymer[a]	mole fraction of M_1 in copolymer (f_1)	T_g, °C	T_r [a], °C	T_d [b], °C
Poly[4-(3-butynyl)styrene]	1.00	52	194 (302)	445
Poly[4-(3-butynyl)styrene-co-St]	0.53	76	215 (313)	412
Poly[4-(3-butynyl)styrene-co-St]	0.12	98	241 (355)	393

[a] Beginning temperature of crosslinking reaction (top peak temperature of exothermic peak).
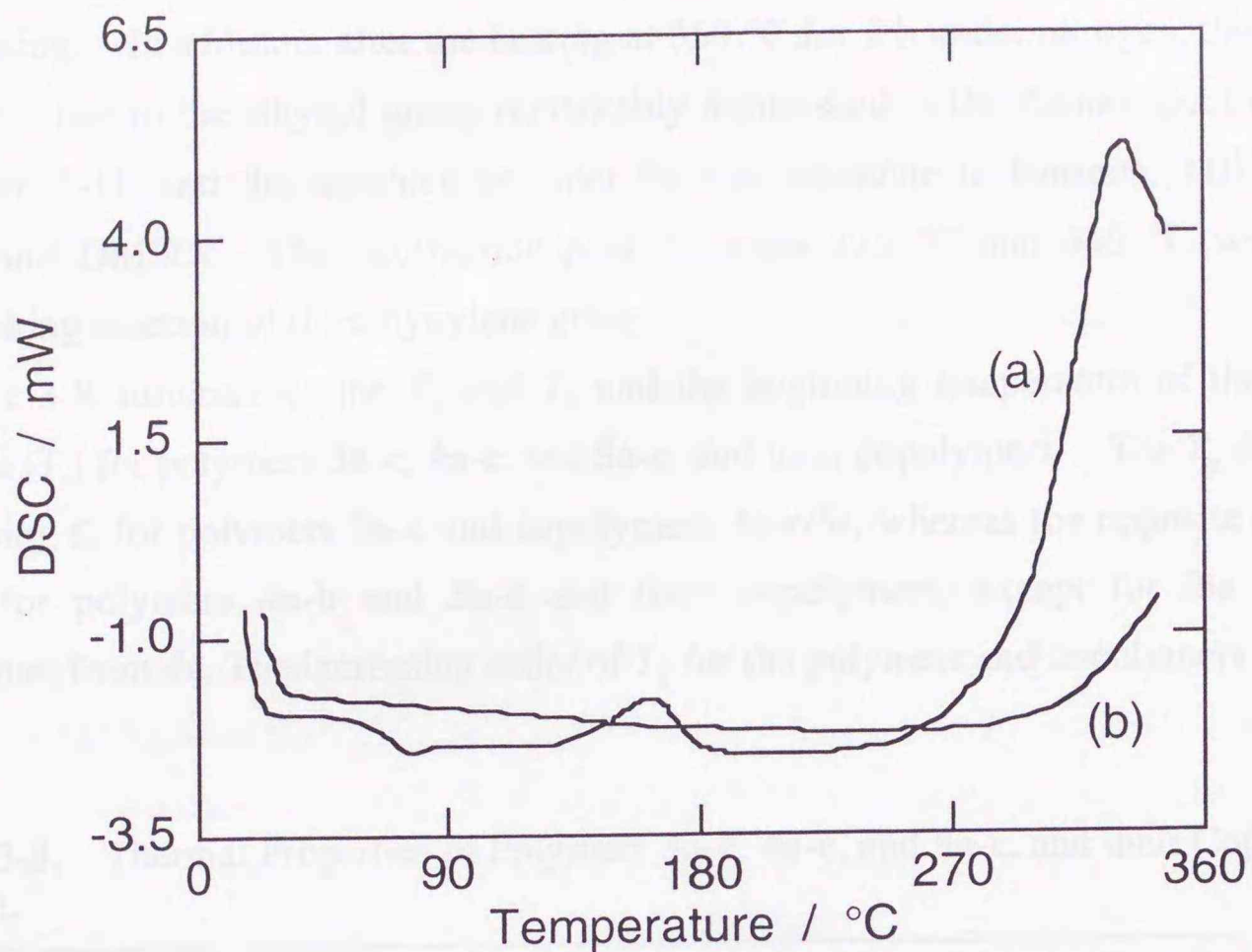[b] Temperature of 10 % weight loss.

33

Figure 3-10. The 1st heating (a) and 2nd heating (b) of poly[4-(1-hexynyl)styrene] (5a).
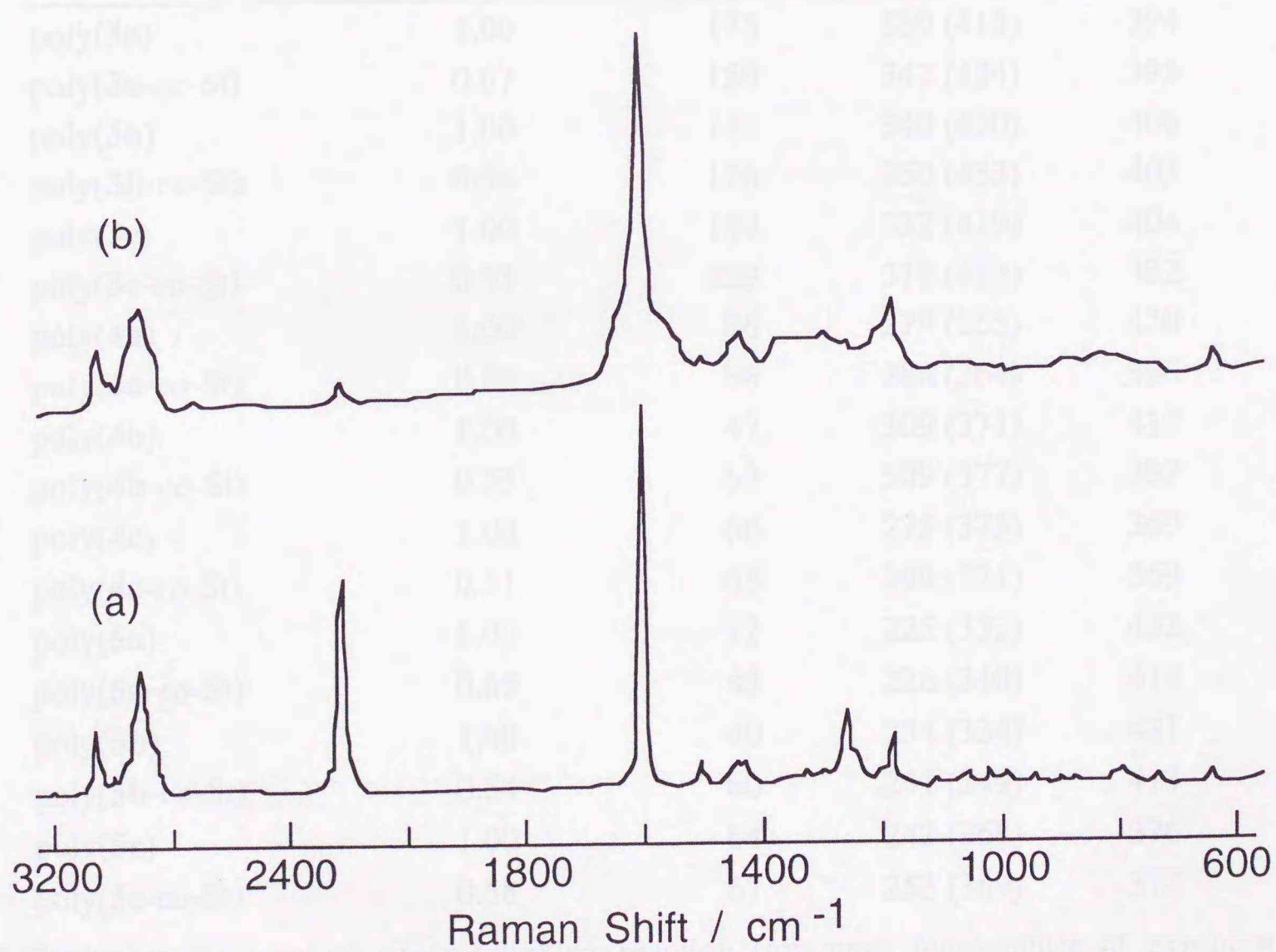

Figure 3-11. Raman spectra of poly[4-(1-hexynyl)styrene] (5a)
(a) before and (b) after thermal treatment.

appeared at 225 °C with a top peak temperature of 332 °C which was not observed during the 2nd heating.   In addition, after the heating at 350 °C for 2 h under nitrogen, the absorption at 2230 cm^{-1} due to the ethynyl group remarkably diminished in the Raman spectrum, as shown in Figure 3-11, and the annealed polymer **5a** was insoluble in benzene, THF, chloroform, DMF, and DMSO.   The exothermic peak between 225 °C and 440 °C was due to the crosslinking reaction of the ethynylene group.

Table 3-8 summarizes the T_g and T_d and the beginning temperature of the crosslinking reaction (T_r) for polymers **3a-c**, **4a-c**, and **5a-c**, and their copolymers.   The T_g decreased with decreasing f_1 for polymers **3a-c** and copolymers **3a-c**/St, whereas the opposite tendency was found for polymers **4a-b** and **5a-c** and their copolymers, except for the polymer and copolymer from **4c**. The increasing order of T_g for the polymers and copolymers is as follows:

Table 3-8.   Thermal Properties of Polymers **3a-c**, **4a-c**, and **5a-c**, and their Copolymers with Styrene.

polymer[a]	mole fraction of M_1 in copolymer (f_1)	T_g, °C	T_r[a], °C	T_d[b], °C
poly(**3a**)	1.00	175	339 (415)	394
poly(**3a**-*co*-St)	0.67	159	342 (424)	395
poly(**3b**)	1.00	132	340 (420)	406
poly(**3b**-*co*-St)	0.54	126	350 (433)	403
poly(**3c**)	1.00	139	332 (419)	404
poly(**3c**-*co*-St)	0.53	129	318 (432)	382
poly(**4a**)	1.00	86	279 (355)	420
poly(**4a**-*co*-St)	0.65	88	286 (364)	396
poly(**4b**)	1.00	47	309 (371)	414
poly(**4b**-*co*-St)	0.53	62	309 (377)	397
poly(**4c**)	1.00	66	275 (373)	369
poly(**4c**-*co*-St)	0.51	65	299 (371)	369
poly(**5a**)	1.00	72	225 (332)	432
poly(**5a**-*co*-St)	0.65	83	226 (340)	414
poly(**5b**)	1.00	40	234 (334)	431
poly(**5b**-*co*-St)	0.54	60	241 (349)	413
poly(**5c**)	1.00	64	242 (368)	376
poly(**5c**-*co*-St)	0.58	67	253 (369)	372

[a] Beginning temperature of crosslinking reaction (top peak temperature of exothermic peak).

[b] Temperature of 10 % weight loss.

$5a < 4a \ll 3a$ and $5b < 4b \ll 3b$.   The T_gs for the polymer and copolymer from 3a-c were strongly influenced by the introduction of a *t*-butyl group into the β-position of the ethynylene function.   The *t*-butyl group in the alkyl substituents, such as *n*-butyl, *t*-butyl, and *s*-pentyl group, brought the greatest influence on the T_gs.   The T_rs of polystyrenes having alkyl substituted ethynylene groups were higher than those of poly(ethynylstyrene)s and their copolymers and poly[4-(3-butynyl)styrene] and its copolymers.   This result should be caused by the steric hindrance of alkynyl group.   In particular, for the polymers and copolymers from 3a-c, the T_ds were lower than their top peak T_rs, and thus, the thermal decomposition of these polymers occurred prior to the crosslinking reaction.   The T_ds of polystyrenes having pendant 1-alkynyl groups were higher than that of polystyrene (M_n = 19,500 and M_w/M_n = 1.54) obtained by radical polymerization, T_d = 362 °C.   Figure 3-12 shows the TG curves of polymers 3a, 4a, and 5a.   The thermal decomposition gradually began at about 340 °C in polymers 4a and 5a, but rapidly proceeded from 370 °C in polymer 3a.   This result showed that the terminal ethynyl group (-C≡CH) is more sensitive in thermal crosslinking than the internal ethynyl group, i.e., the ethynylene group (-C≡C-).
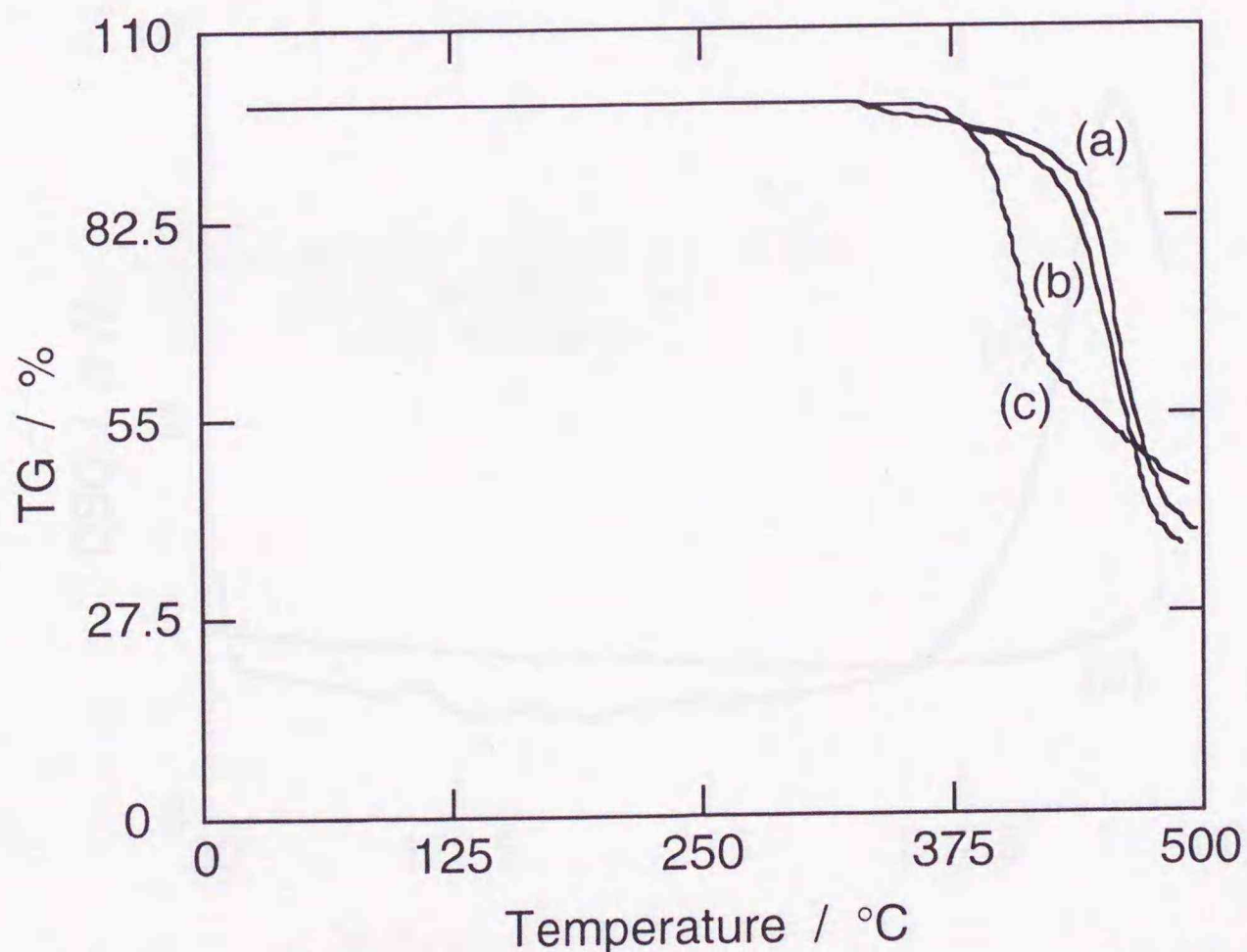

Figure 3-12 TG thermograms of poly[4-(1-hexynyl)styrene] (5a) (a), poly[4-(3-methyl-1-hexynyl)styrene] (4a) (b), and poly[4-(3,3-dimethyl-1-butynyl)styrene] (3a) (c).

36

3-2-8. Thermal Properties of Polymers 6a-c and their Copolymers with Styrene

For the DSC thermogram of polymer **6b**, the endothermic peak corresponding to a glass transition temperature (T_g) was observed at 118 °C, as shown in Figure 3-13. The large exothermic peak appeared at 294 °C with a top peak temperature of 366 °C which was not observed during the 2nd heating. After the heating at 400 °C for 1 h under nitrogen, the absorption at 2216 cm^{-1} due to the ethynyl group completely disappeared in the Raman spectrum, as shown in Figure 3-14, and the annealed polymer **6b** was insoluble in benzene, THF, chloroform, DMF, and DMSO. The exothermic peak between 294 °C and 440 °C was due to the crosslinking reaction of the ethynyl groups.

Table 3-9 summarizes the T_g, the temperature of 10 % weight loss (T_d), and the beginning temperature of the crosslinking reaction (T_r) and its top peak temperature in parenthesis for the polymers and copolymers from **6a-c**. The T_g decreased with increasing St units in these polymers. For the polymer and copolymer from **6c**, the T_ds were lower than the temperature of their top peak T_rs. The thermal decomposition of polymers occurred before crosslinking, because of lower molecular weights of the polymer and copolymer from **6c**. The T_r increased with increasing St units from 294 to 313 °C for **6b** and from 276 to 319 °C for **6a**.
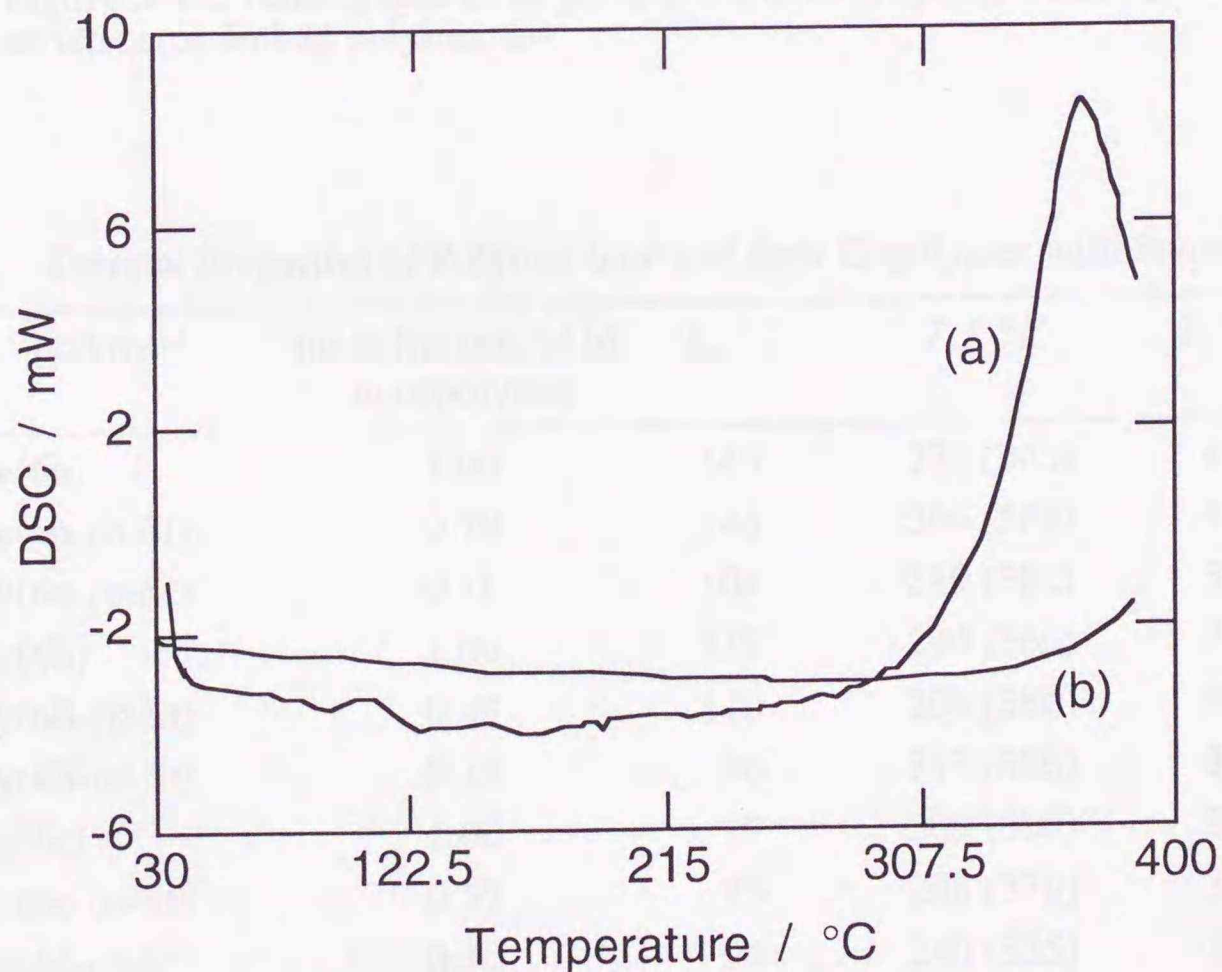
Figure 3-13 DSC thermograms of poly[(3-phenylethynyl)styrene](**6b**) (1st heating) (a) and crosslinked (**6b**) (2nd heating) (b).
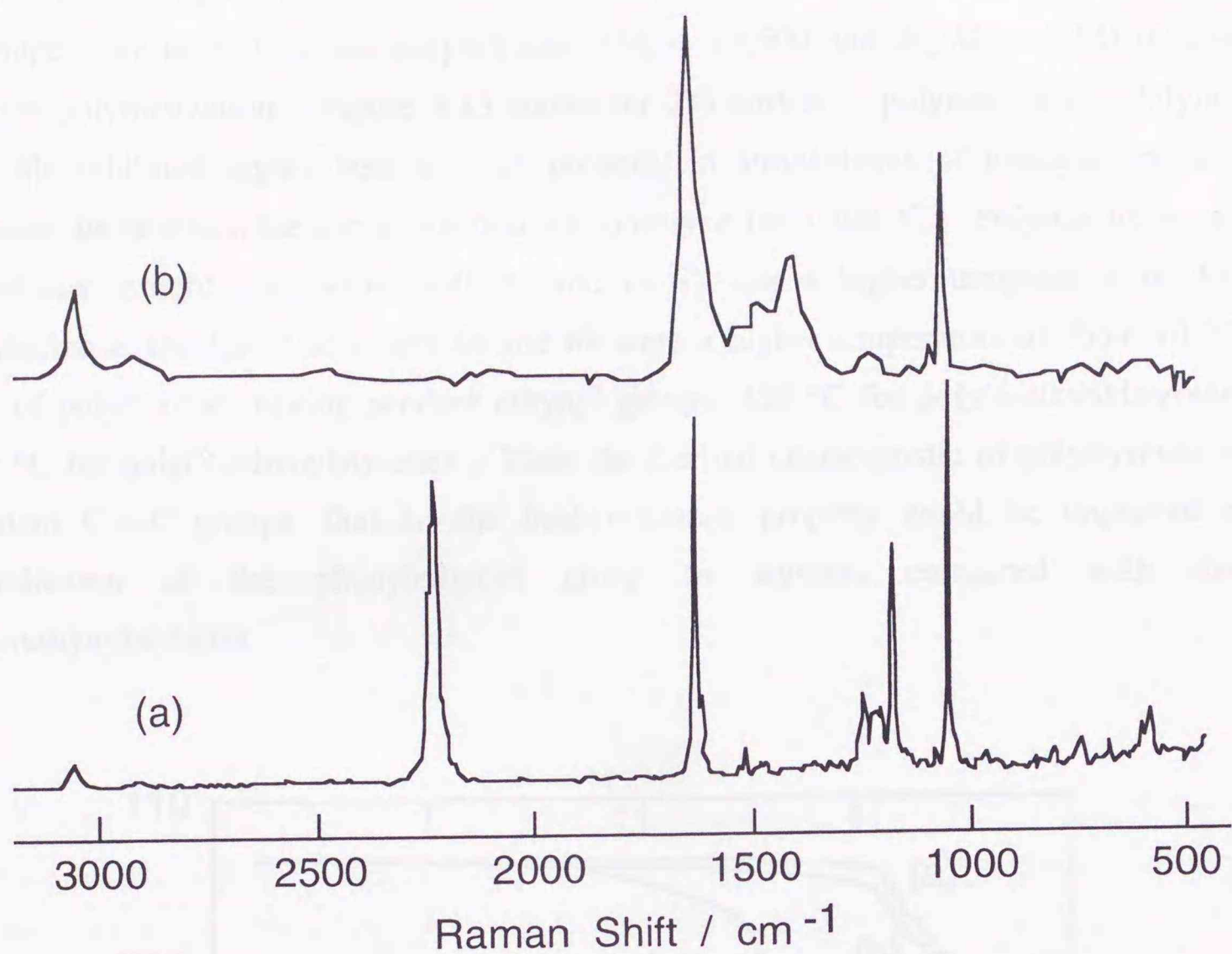
Figure 3-14. Raman spectra of poly[(3-phenylethynyl)styrene](**6b**) (a) and the crosslinked polymer (b).

Table 3-9. Thermal Properties of Polymer **6a-c** and their Copolymer with Styrene

polymer[a]	mole fraction of M_1 in copolymer	T_g, °C	$T_r{}^a$, °C	$T_d{}^b$, °C
poly(**6a**)	1.00	148	276 (363)	476
poly(**6a**-*co*-St)	0.78	146	296 (369)	433
poly(**6a**-*co*-St)	0.11	104	319 (382)	388
poly(**6b**)	1.00	118	294 (366)	491
poly(**6b**-*co*-St)	0.49	110	298 (380)	421
poly(**6b**-*co*-St)	0.10	96	313 (386)	383
poly(**6c**)	1.00	99	309 (389)	365
poly(**6c**-*co*-St)	0.57	95	298 (370)	343
poly(**6c**-*co*-St)	0.10	94	240 (335)	331

[a] Beginning temperature of crosslinking reaction (top peak temperature of exothermic peak).

[b] Temperature of 10 % weight loss.

38

In addition, the T_ds from 383 to 491 °C for **6b** and from 388 to 476 °C for **6a** were higher than a temperature of 362 °C for poly(styrene) (M_n = 19,500 and M_w/M_n = 1.54) obtained by radical polymerization. Figure 3-15 shows the TG curves of polymer **6a-c**. Polymers **6a** and **6b** exhibited higher heat-resistant property in atmospheres of nitrogen and air than polymer **6c** of which the decomposition was observed from 200 °C. Polymer **6b** showed no significant weight loss below 450 °C and its T_d was a higher temperature of 491 °C. Furthermore, the T_ds of polymers **6a** and **6b** were a higher temperature of about 40 °C than that of polystyrenes having pendent ethynyl groups: 428 °C for poly(4-ethynylstyrene) and 452 °C for poly(3-ethynylstyrene). Thus the thermal characteristic of polystyrenes having pendent C≡C groups, that is, the heat-resistance property could be improved by an introduction of the phenylethynyl group to styrene, compared with that of poly(ethynylstyrene).
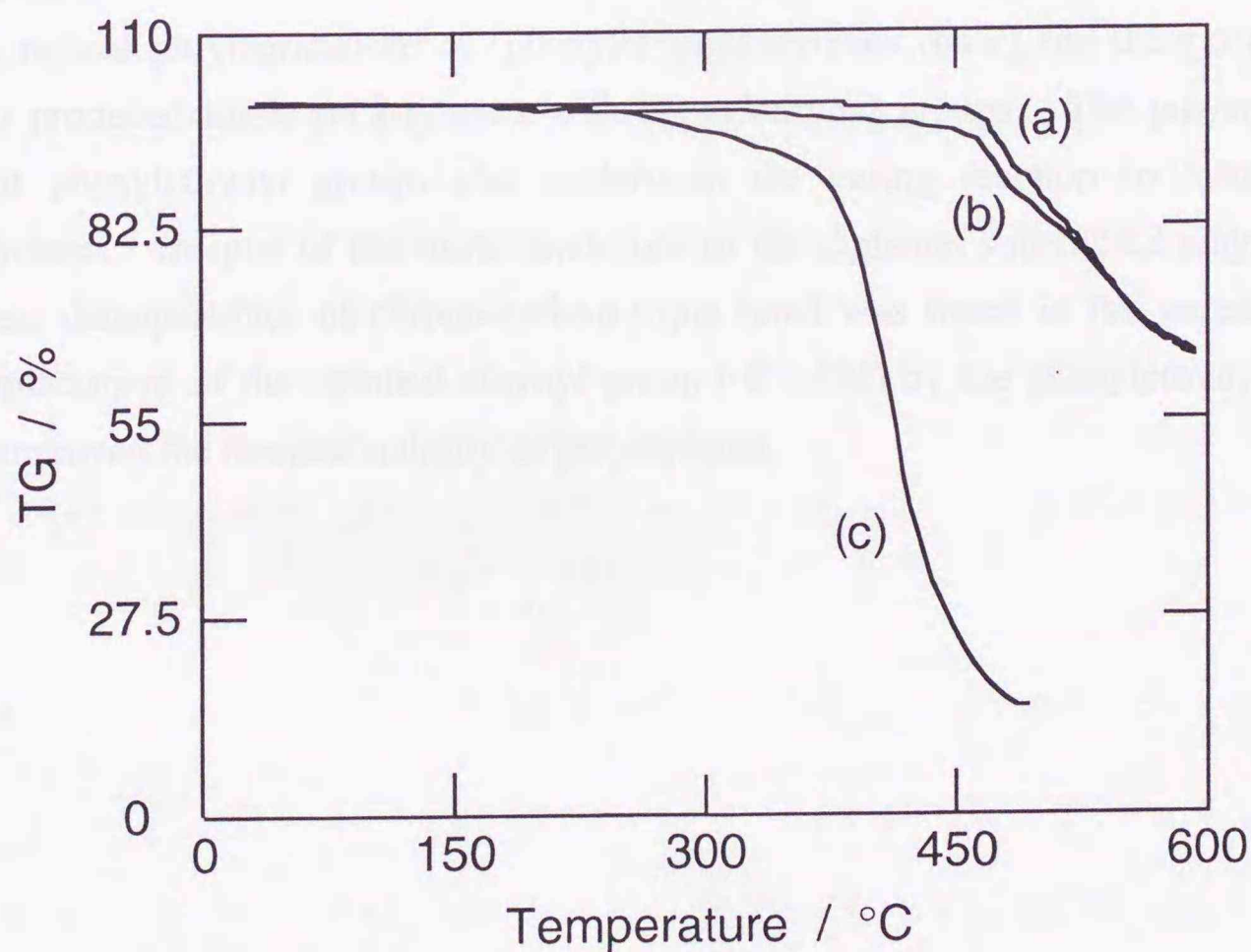

Figure 3-15 TG thermograms of poly[(4-phenylethynyl)styrene](**6a**) (a), poly[(3-phenylethynyl)styrene](**6b**) (b), and poly[(2-phenylethynyl)styrene](**6c**) (c).

3-3. Conclusion

The radical polymerizations of 2-(trimethylsilyl)ethynylstyrenes (**1a-c**) and 4-(4-trimethylsilyl-3-butynyl)styrene (**2**) and their copolymers with styrene produced gel-free polystyrenes with trimethylsilylethynyl groups. The deprotection of the silyl group from these polymers smoothly proceeded to convert into polystyrenes having pendent terminal ethynyl and butynyl groups, and subsequently underwent a curing reaction at the elevated temperature to form crosslinking polystyrenes.

The radical polymerizations of (3,3-dimethyl-1-butynyl)styrenes (**3a-c**), (3-methyl-1-hexynyl)styrenes (**4a-c**) and (1-hexynyl)styrenes (**5a-c**) and their use with styrene produced linear polystyrenes with alkylethynyl groups. The polystyrenes having pendent alkylethynyl groups form cured crosslinking polystyrenes at the elevated temperature. The crosslinking reaction of the C≡C groups was incomplete due to the steric hindrance in the polymers with alkyl substituted ethynyl group. However, the thermal stability was improved on that of polystyrene.

The radical polymerizations of (phenylethynyl)styrenes (**6a-c**) and their copolymers with styrene produced linear polystyrenes with phenylethynyl groups. The polystyrenes having pendent phenylethynyl groups also underwent the curing reaction to form crosslinking polystyrenes. In spite of the steric hindrance of the diphenyl substituted ethynyl group, the complete disappearance of carbon-carbon triple bond was found in the annealed polymers. The replacement of the terminal ethynyl group (-C≡CH) by the phenylethynyl group (-C≡CPh) improved the thermal stability of polystyrenes.

3-4. Experimental Section

Measurements. IR spectra were measured using a Perkin Elmer Paragon 1000 and a JEOL JIR RFX-4002F FT-IR spectrophotometer. Raman spectra were recorded using a Perkin Elmer Spectrum 2000 NIR FT-Raman and a JASCO NR-1800 Raman spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded using a Hitachi R-24B, JEOL JNM-EX270, and JEOL JNM-EX400 instruments. Size exclusion chromatograms (SEC) were obtained using a Showa Denko System-11 instrument equipped with three polystyrene gel columns (Shodex K-805L x 3) with a refractive index detection at 40 °C. Chloroform was used for the carrier solvent at a flow rate of 1.0 mL·min^{-1}. Differential scanning calorimetry (DSC) and thermal gravimetry (TG) measurements were carried out under N$_2$ gas using a Seiko DSC220 and a TG/DTA22 instrument, respectively. The heating scan rate was 10 °C·min^{-1} for all experiments.

Materials. Tetrabutylammonium fluoride ((C_4H_9)$_4$NF) solution in THF was purchased from Aldrich. Styrene and toluene were purified by the usual methods. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

Polymerization. Radical polymerization and copolymerization were carried out using AIBN as the initiator in toluene at 60 °C in sealed tubes under nitrogen. After polymerization, the solution was poured into a large amount of methanol. The precipitated polymers were purified by two reprecipitations from a THF/methanol system and freeze-dried from a benzene solution. The polymers thus obtained were characterized by ^{1}H and ^{13}C NMR, IR, and Raman spectroscopies. The following is the full list.

a) Polymer **1a** :

   Raman shift (cm^{-1}): 2157 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **1a** obtained by anionic polymerization.

b) Polymer **1b** :

   Raman shift (cm^{-1}): 2157 cm^{-1} (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **1b** obtained by anionic polymerization.

c) Polymer **1c** :

   Raman shift (cm^{-1}): 2155 cm^{-1} (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **1c** obtained by anionic polymerization.

d) Polymer **2** :

   Raman shift (cm^{-1}): 2176 cm^{-1} (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **2** obtained by anionic polymerization.

e) Polymer **3a** :

Raman shift (cm^{-1}): 2239 cm^{-1} (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **3a** obtained by anionic polymerization.

f) Polymer **3b** :

Raman shift (cm^{-1}): 2218 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **3b** obtained by anionic polymerization.

g) Polymer **3c** :

Raman shift (cm^{-1}): 2236 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **3c** obtained by anionic polymerization.

h) Polymer **4a** :

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 0.6 – 2.7 (br m, 14H, CHCH$_2$ and CH$_3$CHCH$_2$CH$_2$CH$_3$), 5.9 - 7.3 (br m, 4H, Ar-H)

^{13}C-NMR (100 MHz, CDCl$_3$)

δ 14.2 (CH$_2$CH$_3$), 20.9 (CHCH$_3$), 21.4 (CH$_2$CH$_3$), 26.5 (≡C-CH), 39.4 (CHCH$_2$) , 40 - 43 (CH$_2$CH), 80.9 (Ar-C≡C), 93.9 (Ar-C≡C), 121.5 (Ar, C4), 127.5 (Ar, C2), 131.4 (Ar, C3), 144.2 (Ar, C1).

IR (KBr, cm^{-1})

2229 (C≡C).

Raman shift (cm^{-1})

2231 cm^{-1} (C≡C)

i) Polymer **4b** :

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 0.5 – 2.7 (br m, 14H, CHCH$_2$ and CH$_3$CHCH$_2$CH$_2$CH$_3$), 5.9 - 7.6 (br m, 4H, Ar-H)

^{13}C-NMR (100 MHz, CDCl$_3$)

δ 14.2 (CH$_2$CH$_3$), 20.8 (CHCH$_3$), 21.3 (CH$_2$CH$_3$), 26.4 (≡C-CH), 39.4 (CHCH$_2$), 40 - 43 (CH$_2$CH), 81.1 (Ar-C≡C), 94.1 (Ar-C≡C), 123.7 (Ar, C3), 127.9 (Ar, C6), 129.3 (Ar, C4 and C5), 131.2 (Ar, C2), 145.0 (Ar, C1).

IR (KBr, cm^{-1})

2225 (C≡C).

Raman shift (cm^{-1})

2223 (C≡C)

j) Polymer **4c** :

^{1}H-NMR (400 MHz, CDCl$_3$)

δ 0.1 – 3.6 (br m, 14H, CHCH$_2$ and CH$_3$CHCH$_2$CH$_2$CH$_3$), 6.0 - 7.8 (br s, 4H, Ar-H)

^{13}C-NMR (100 MHz, CDCl$_3$)

δ 14.3 (CH$_2$CH$_3$), 20.7 (CHCH$_3$), 20.7 (CH$_2$CH$_3$), 26.1 (≡C-CH), 39.1 (CHCH$_2$), 35 - 42 (CH$_2$CH), 79.1 (Ar-C≡C), 97.6 (Ar-C≡C), 124.6 (Ar, C2), 125.4 (Ar, C6), 126.9 (Ar, C4 and C5), 132.2 (Ar, C3), 147.1 (Ar, C1).

IR (KBr, cm^{-1})

2229 (C≡C).

Raman shift (cm^{-1})

2225 (C≡C)

k) Polymer **5a** :

Raman shift (cm^{-1}): 2230 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **5a** obtained by anionic polymerization.

l) Polymer **5b** :

Raman shift (cm^{-1}): 2228 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **5b** obtained by anionic polymerization.

m) Polymer **5c** :

Raman shift (cm^{-1}): 2228 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **5c** obtained by anionic polymerization.

n) Polymer **6a** :

Raman shift (cm^{-1}): 2223 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of polymer **6a** obtained by anionic polymerization.

o) Polymer **6b** :

^{1}H-NMR (400 MHz, CDCl$_3$):

δ 0.7 - 2.4 (br m, 3H, CH$_2$CH), 6.1 - 7.7 (br s, 9H, Ar-H)

^{13}C-NMR (100 MHz, CDCl$_3$):

δ 40.5 (CH$_2$), 43.3 (CH), 89.2 and 90.0 (C≡C), 123.0 (ArC3), 123.5 (ArC1'), 128.0 (ArC6), 128.4 (ArC5, C3' and C4'), 129.5 (ArC4), 130.9 (ArC2), 131.7 (ArC2'), 144.9 (ArC1)

IR (KBr, cm^{-1})

2214 (C≡C)

Raman Shift (cm^{-1})

2216 (C≡C)

p) Polymer **6c** :

^{1}H-NMR (400 MHz, CDCl$_3$):

δ 0.7 - 4.0 (br m, 3H, CH$_2$CH), 5.8 - 8.2 (br s, 9H, Ar-H)

43

^{13}C-NMR (100 MHz, CDCl$_3$)

 δ 37.0 (CHCH$_2$), 88.4 and 92.8 (C≡C), 123.5 (ArC2 and 1'), 125.5 (ArC4 and 6),

 128.1 (ArC5, 3', and 4'), 131.7 (ArC3 and 2'), 146.6 (ArC1)

IR (KBr, cm^{-1})

 2214 cm^{-1} (C≡C)

Raman Shift (cm^{-1})

 2216 (C≡C)

Deprotection. The deprotection of the trimethylsilyl groups from the copolymers was carried out as previously described.[11] The analytical results are as follows.

a) poly(4-ethynylstyrene) :

 Raman shift (cm^{-1}): 2108 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of poly(4-ethynylstyrene) obtained by anionic polymerization.

b) Poly(3-ethynylstyrene) :

 Raman shift (cm^{-1}): 2109 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of poly(3-ethynylstyrene) obtained by anionic polymerization.

c) Poly(2-ethynylstyrene) :

 Raman shift (cm^{-1}): 2105 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of poly(2-ethynylstyrene) obtained by anionic polymerization.

d) poly[4-(3-butynyl)styrene] :

 Raman shift (cm^{-1}): 2116 (C≡C), ^{1}H and ^{13}C NMR and IR spectral data were similar to those of poly[4-(3-butynyl)styrene] obtained by anionic polymerization.

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Chapter 4.   Cationic Polymerization of Styrene Monomers Containing an Ethynyl Group

4-1. Introduction

   In order to produce matrix resins for advanced composites, a great deal of effort has been expended to design polymers with reactive functional groups which can be crosslinked by heating.   The evolution of the volatile and low molecular weight compounds must be avoided during crosslinking and thus the limited functional groups are able to be available for this purpose.   The polymer with ethynyl group is one of the candidates for thermal curing materials.

   In previous chapter, the syntheses of gel-free polymers containing ethynyl groups by the radical polymerization were performed.[1]   However, D'Alelio et al. has reported that the cationic polymerization of styrenes having an ethynyl group give crosslinking polymers.[2] The polymerization was accompanied by the addition of Lewis acid to the ethynyl moiety. The condition of cationic polymerization, therefore, is examined to synthesize the gel-free polystyrene having pendent ethynyl groups.

   The influence of substituents and their sites on the cationic polymerizability for **1a-c, 2, 3a-c, 4a-c, 5a-c**, and **6a-c** are discussed.   Furthermore, the thermal crosslinking properties of the obtained polymers as a thermally curable material are shown.

4-2. Results and Discussion

4-2-1. Cationic Polymerization of 1a-c and 2.

Ttrimethylsilyl group was effective for the protection of the acetylenic proton of ethynylstyrenes and 4-(3-butynyl)styrene under the condition of radical polymerizations.[1,3] The effect of $C \equiv C\text{-SiMe}_3$ group for the condition of cationic polymerizations was evaluated in this chapter.

The cationic polymerizations of 1a-c and 2 were carried out in dichloromethane at 0 °C. These polymerizations proceeded homogeneously. The addition of $SnCl_4$ as an initiator produced a color such as yellow, orange, and purple in the solution. This coloration was kept throughout the polymerization, but it was independent of cationic polymerizability. (Ttrimethylsilylethynyl)styrenes (1a-c) produced no polymers through the cationic polymerization. (4-Trimethylsilyl-3-butynyl)styrene (2) showed high polymerizability and the polymer yield was 58 % only for 2.5 h. The presence of trimethylsilyl group did not disturb the cationic polymerization when the $C \equiv C\text{-SiMe}_3$ group and the aromatic ring were separated by the CH_2CH_2 chain.

The obtained polymer 2 was soluble in common organic solvents and insoluble in methanol, and was a white powder. The SEC curve was unimodal and possessed M_n value of 6,080. The structure was identified as poly[4-(4-trimethylsilyl-3-butynyl) styrene] by IR, Raman, ^{1}H- and ^{13}C-NMR spectra. The signal characteristic was due to methyl proton of the trimethylsilyl group appeared at 0.15 ppm with reasonable integral ratios to other signals, indicating no cleavage of the silicon-carbon bond. Also, the carbon-carbon triple bond remained intact during the cationic polymerization, and thus no occurrence of electrophilic addition to the $C \equiv C$ bond was found.

4-2-2. Cationic Polymerization of 3a-c, 4a-c, and 5a-c.

The cationic polymerizability of (3,3-dimethyl-1-butynyl)styrenes (3a-c) was compared with that of 1a-c. The tertiary carbon atom in the former monomers is replaced by the silicon atom to result in the latter monomers with trimethylsilyl group. The cationic polymerizability of 4a-c was compared with that of 5a-c. *Sec*-pentyl group binding to ethynylene (-$C \equiv C$-) in the former monomers is replaced by *n*-butyl group in latter monomers.

The cationic polymerizations of 3a-c, 4a-c, and 5a-c were carried out under the conditions similar to those for the polymerizations of 1a-c and 2. The coloration of solutions was inde-

Table 4-1. Cationic Polymerizations of Ethynylstyrene Derivatives (M₁) and Their Copolymerizations with Styrene (M₂)[a].

monomer M₁	mole fraction of M₁ in monomer feed	yield %	mole fraction of M₁ in copolymer[b]	M_n (M_w/M_n)[c]	T_g °C	T_r (top peak)[d] °C	T_d[e] °C
2[f]	1.00	58	1.00	6,080 (1.68)	49	242 (325)	395
2[f]	0.50	78	0.53	7,640 (1.93)	67	253 (333)	385
3a	1.00	92	1.00	6,340 (2.24)	169	246 (376)	371
3a	0.50	95	0.46	8,270 (2.75)	147	283 (372)	369
3b	1.00	19	1.00	2,740 (1.20)	123	241 (407)	359
3b	0.50	71	0.45	3,060 (1.63)	113	246 (nd)[i]	358
3c	0.50	24	0.41	2,020 (1.76)	112	196 (289)	335
4a	1.00	77	1.00	3,390 (2.32)	88	267 (369)	400
4a	0.50	88	0.48	4,560 (2.90)	98	275 (359)	388
4b	1.00	11	1.00	1,800 (1.23)	47	202 (371)	400
4b	0.50	55	0.42	2,070 (1.43)	60	205 (373)	378
4c	0.50	15	0.39	1,040 (1.31)	82	240 (308)	352
5a	1.00	37	1.00	3,380 (2.10)	90	222 (361)	418
5a	0.51	57	0.45	5,160 (5.25)	109	223 (332)	384
5b	0.50	49	0.44	2,150 (1.39)	62	219 (365)	381
5c	0.50	10	0.45	1,710 (1.16)	97	210 (310)	339
6a[j]	1.00	56	1.00	3,790 (1.79)	158	232 (337)	481
6a[j]	0.49	62	0.24	2,830 (1.93)	135	241 (349)	418
6b	0.50	32	0.35	1,610 (1.42)	101	223 (359)	400
dep(poly**2**)[g]	1.00	-	-		51	199 (297)	444
dep(copoly**2**)[h]	0.53	-	-		78	224 (310)	409

a) Initiator, SnCl₄ ; [M₁] or [M₁+M₂]=1.0 M ; [SnCl₄] = 0.1 M ; temp. 0 °C ; solvent, CH₂Cl₂; time, 22 h. b) Determined by ¹H NMR spectra. c) Determined by SEC using polystyrene standard. d) Beginning temperature of crosslinking reaction (top peak temperature of exothermic peak). e) Temperature of 10 % weight loss. f) Time, 2.5 h. g) poly[4-(3-butynyl)styrene]. h) poly[4-(3-butynyl)styrene/St]. i) Top peak was not observed under 450 °C. j) Time, 14 h.

pendent of the polymerizability also in these monomers.   Table 4-1 shows the results of polymerization. o -Substituted monomers **3c**, **4c**, and **5c** produced no polymers in the same conditions that p-substituted monomers **3a**, **4a**, and **5a** polymerized to form the polymers. For m-substituted monomers, **3b** and **4b** produced the poymers, but **5b** showed no polymerizability.   The obtained polymers were soluble in common organic solvents and insoluble in methanol, and produced a light beige color.   The increasing order of polymer yield was as follows: m-substituted monomers $< p$ -substituted monomers; monomers with n -butyl group (**5**) $\approx$ monomers with s-pentyl group (**4**) $<$ monomers with t-butyl (**3**).   The results indicate that the polymerizability is dependent on the bulkiness of substituent and the distance between the propagating carbocation and the substituent.

The SEC curves of polymers **3a**, **4a**, and **5a** showed a shoulder in the higher molecular weight region and a slightly broad molecular weight distributions (M_w/M_n = 2.10-2.32), suggesting some participation in chain transfer to polymer.   On the other hand, the SEC curves were unimodal for polymers **3b** and **4b**.   The increasing order of M_ns corresponded to that of polymer yield.   The lowest and highest M_ns were 1,800 for **4b** and 6,340 for **3a**.   The alkyl groups should participate in chain transfer to lower the molecular weight of polymers.

The side reaction of **3a**, **4a**, and **5a** was observed by the ^{1}H- and ^{13}C-NMR analyses of the resulting polymers.   In the ^{1}H-NMR spectrum of polymer **4a**, the resonances due to the residual vinyl proton (=CH$_2$) appeared at 5.2 and 5.8 ppm, although that due to CH= overlapped with aromatic protons, as shown in Figure 4-1.   Figure 4-2 shows the ^{13}C-NMR spectrum of polymer **4a**.   The characteristic absorptions due to the ethynyl carbon and the re-
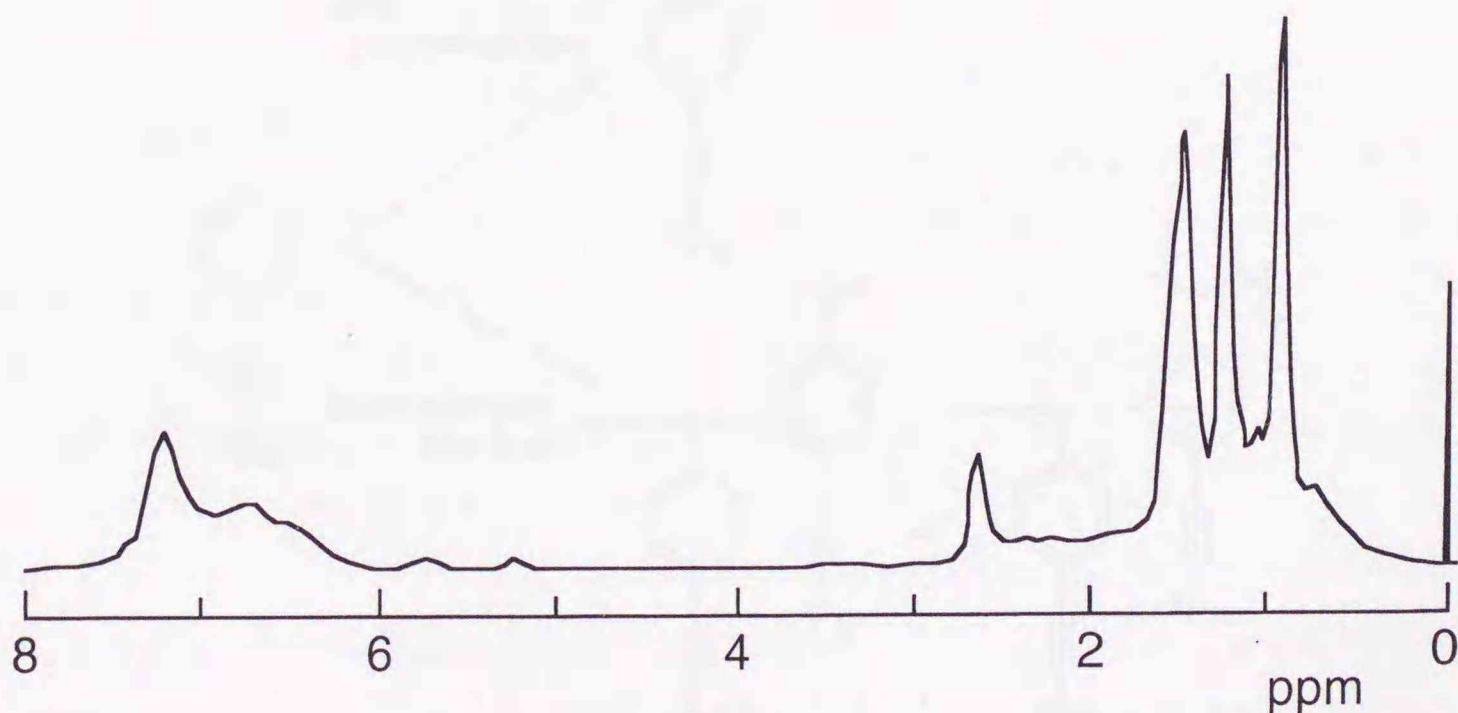
Figure 4-1. ^{1}H-NMR spectrum of poly[4-(3-methyl-1-hexynyl)styrene] (**4a**).

49
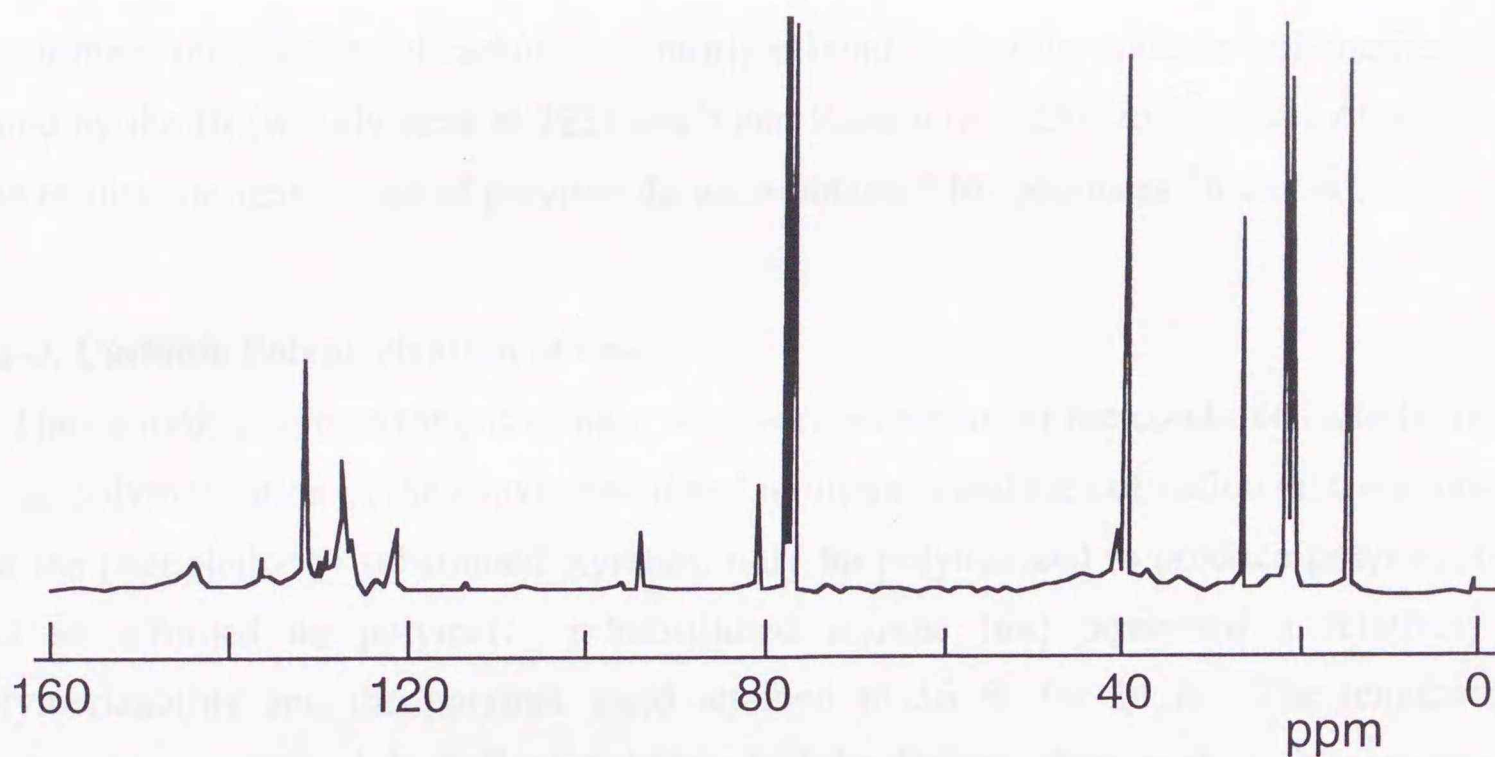
Figure 4-2. ^{13}C-NMR spectra of poly[4-(3-methyl-1-hexynyl)styrene] (**4a**) .

sidual vinyl carbon were observed clearly at 80.8 and 94.0 ppm and weakly at 113.6 and 135.8 ppm, respectively. Some small peaks were found in the regions of the chemical shifts for aromatic carbon. These small peaks should be derived from the chain transfer to monomer and polymer. Such side reactions are commonly found in cationic polymerization (Scheme 1).[7] The residual vinyl group was also observed by IR spectra at 904 and 989 cm^{-1}.

Scheme 1

50
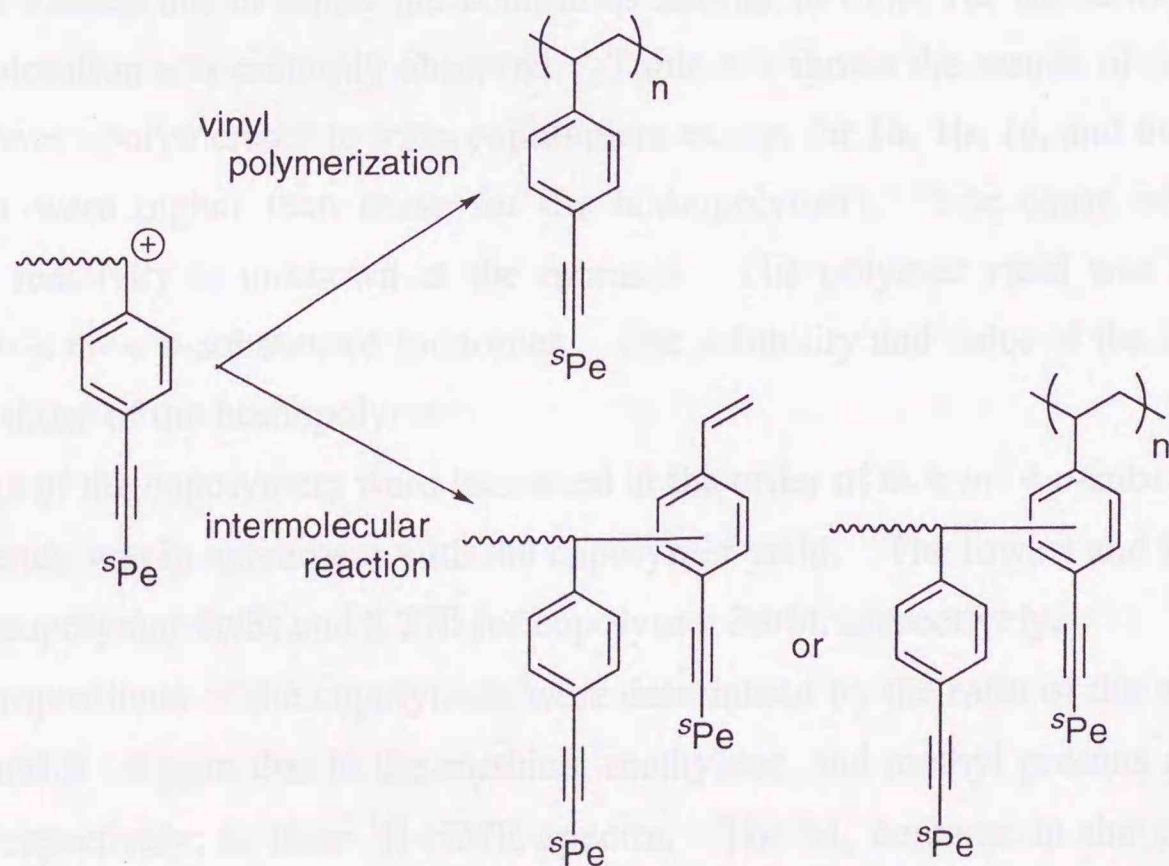
In addition, the unchanged carbon-carbon triple bond during the cationic polymerization was found by the IR (weakly peak at 2231 cm^{-1}) and Raman (at 2230 cm^{-1}) spectra of polymer **4a**. The results similar to those of polymer **4a** were obtained for polymers **3b** and **4b**.

4-2-3. Cationic Polymerization of 6a-c.

The cationic polymerizations of **6a-c** were carried out under the conditions similar to those of the polymerization of the above mentioned monomers and the coloration also was observed. For the phenylethynyl substituted styrenes, only **6a** polymerized to produce polymer, but **6b** and **6c** afforded no polymer. *p*-Substituted styrene (**6a**) possessed a relatively high polymerizability and the polymer yield attained to 56 % for 14 h. The lengthened π-conjugation system and the bulky substituent had the desired effect on the polymerization of *p*-substituted monomer.

The SEC curve of polymer **6a** was unimodal, but somewhat broad and the M_n was 3,790. The main structure of the polymer **6a** was identified to be poly[4-(phenylethynyl)styrene] by IR, Raman, ^{1}H- and ^{13}C-NMR spectra. Some small peaks were observed by ^{1}H- and ^{13}C-NMR spectra, which is interpreted as being caused by some participation similar to that described for polymer **4a**.

4-2-4. Cationic Copolymerizations of 1a-c, 2, 3a-c, 4a-c, 5a-c, and 6a-c with Styrene.

The cationic copolymerizations of **1a-c**, **2**, **3a-c**, **4a-c**, **5a-c**, and **6a-c** (M_1) with styrene (M_2) were carried out in under the conditions similar to those for the homopolymerizations and the coloration was certainly observed. Table 4-1 shows the results of copolymerization. The monomers polymerized to form copolymers except for **1a**, **1b**, **1c**, and **6c**. The yields of copolymer were higher than those for the homopolymers. The cause of changes of the monomer reactivity is unknown at the moment. The polymer yield was increased in the order of *o*- < *m*- < *p*-substituted monomer. The solubility and color of the copolymers were similar to those of the homopolymers.

The M_ns of the copolymers were increased in the order of *o*- < *m*- < *p*-substituted monomer. This tendency was in agreement with the copolymer yield. The lowest and highest M_ns were 1,040 for copolymer **4c**/St and 8,270 for copolymer **3a**/St, respectively.

The compositions of the copolymers were determined by the ratio of the adsorptions at 1 - 3.5 ppm and 6 - 8 ppm due to the methine, methylene, and methyl protons and the aromatic protons, respectively, in their ^{1}H-NMR spectra. The M_1 contents in the copolymers were less than those in the monomer feeds except for copolymer **2**/St. The larger the ^{13}C-chemical

shifts of vinyl β-carbon, the smaller the relative reactivity for the substituted styrenes became. The result is the same as those reported by Higashimura[5] and Hatada.[6]

A trifling amount of residual vinyl proton also was detected by the ^{1}H-NMR spectra of the copolymers. The presence of carbon-carbon triple bond was ascertained by the IR, Raman, and ^{13}C-NMR spectra. The structure was the same with the M_1 units in the copolymers as with the homopolymers.

4-2-5. Deprotection Reaction of Polymer 2 and Copolymer 2/St.

The deprotections of the silyl group in polymer **2** and copolymer **2**/St were carried out using $(C_4H_9)_4$NF in THF at 0 °C for 2h.[3] During the conversion of polymer **2** into poly[4-(3-butynyl)styrene], the absorptions at 2117 and 3298 cm^{-1} due to the $\equiv$C-H and C$\equiv$C stretch vibrations of the C$\equiv$C-H group appeared and the absorption at 2956 cm^{-1} due to the C$\equiv$C-SiMe$_3$ group disappeared in the IR spectrum. The trimethylsilyl groups were completely deprotected. The conversion was confirmed also by the NMR and Raman spectra. A poly[4-(3-butynyl)styrene/St] was successfully obtained by the procedure similar to that for the formation of poly[4-(3-butynyl)styrene].

4-2-6. Thermal Properties of Homopolymers and Copolymers.

For the DSC thermogram of polymer **5a**, the endothermic peak corresponding to a glass transition temperature (T_g) was observed at 90 °C, as shown in Figure 4-3. The large exothermic peak appeared at 222 °C with two top peaks at 328 and 361 °C which were not observed during the 2nd heating. The former top peak would be explained by the crosslinking reactions of ethynyl groups, as mentioned in poly[4-(1-hexynyl)styrene] obtained by radical polymerization, T_r(top peak) = 332 °C.[7] The latter top peak could be mainly due to the crosslinking reactions of the residual vinyl groups. After the heating at 350 °C for 2 h under nitrogen, the absorptions at 1629 cm^{-1} and 2230 cm^{-1} due to the residual vinyl group and the ethynyl group completely disappeared in the Raman spectrum, as shown in Figure 4-4. The annealed polymer **5a** was a black graphite-like material and insoluble in benzene, THF, chloroform, DMF, and DMSO. These results indicated that the exothermic peaks in the region of 222 °C and 380 °C were due to the crosslinking reaction of the residual vinyl group and the ethynyl group.

The T_g, the temperature of 10 % weight loss (T_d), and the beginning temperature of the crosslinking reaction (T_r) and its top peak temperature are summarized in Table 4-1. The T_gs
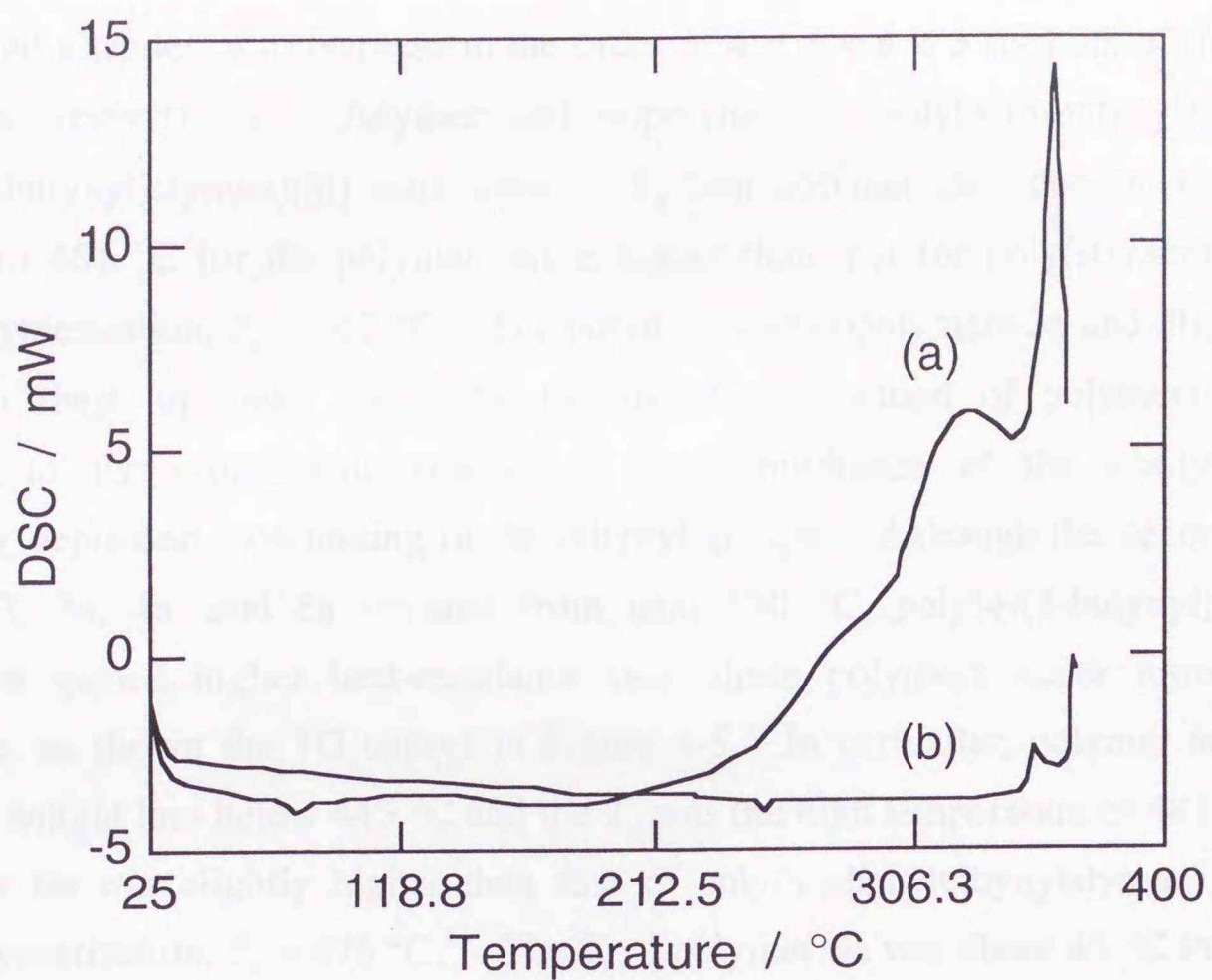
52

Figure 4-3. 1st heating (a) and 2nd heating (b) of poly[4-(1-hexynyl)styrene] (**5a**).
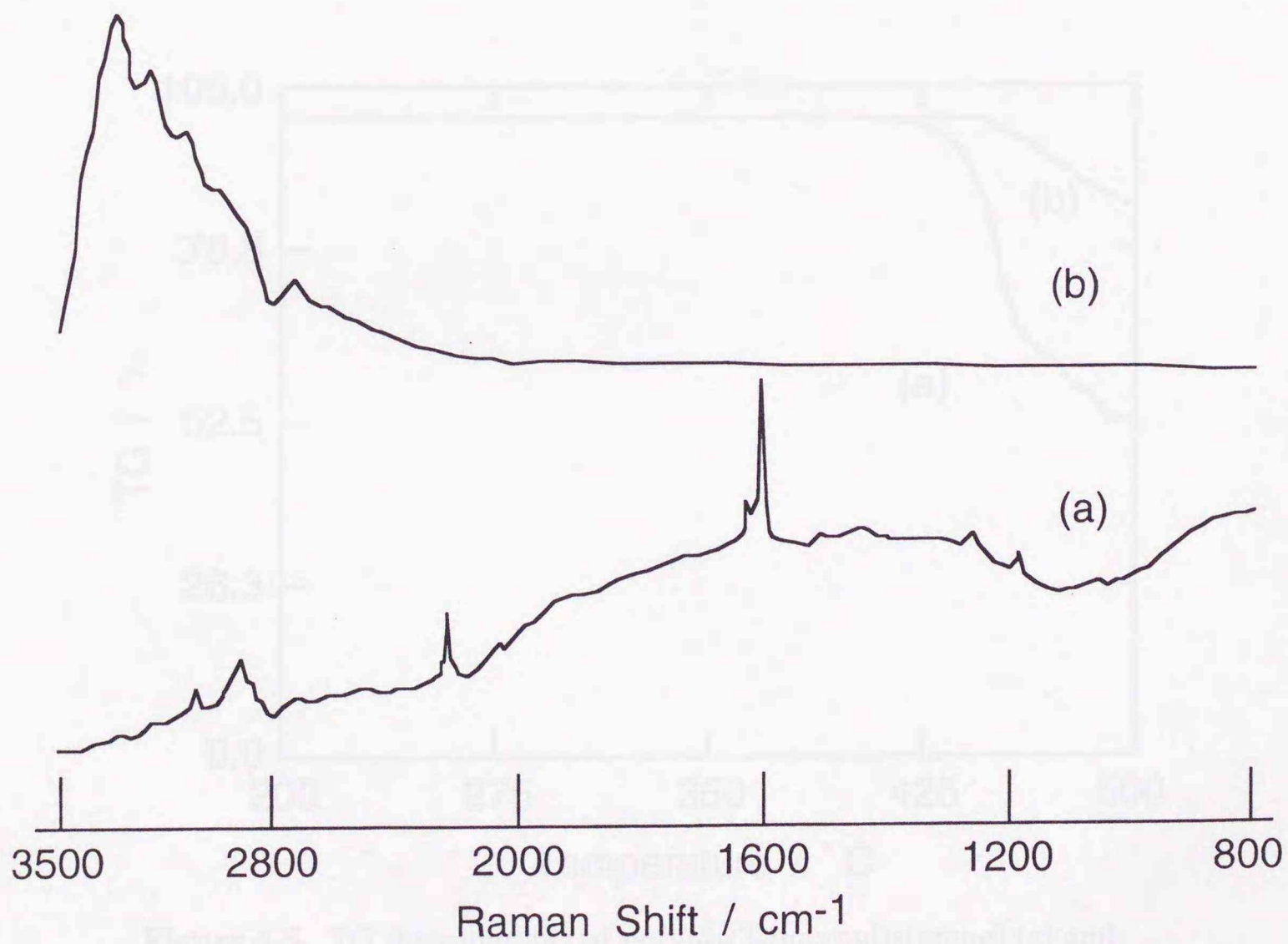

Figure 4-4. Raman spectra of poly[4-(1-hexynyl)styrene] (**5a**) (a) and its crosslinked polymer (b).

53

were showed a tendency to increase in the order of **4** < **5** < **6** < **3** for both of the homo- and copolymers, respectively. Polymer and copolymer **2**, poly[4-(3-butynyl)styrene], and poly[(4-(3-butynyl)styrene)/St] were lower in T_g than polymer and copolymer **4a**. The T_ds from 335 to 481 °C for the polymers were higher than that for poly(styrene) obtained by radical polymerization, T_d = 362 °C. For polymers and copolymers **3a** and **3b**, the T_ds were lower than their top peak T_rs. The thermal decomposition of polymers occurred in preference to the crosslinking reaction. Steric hindrance of the *t*-butyl substituent presumably depressed crosslinking of the ethynyl groups. Although the decompositions of polymers **2**, **3a**, **4a**, and **5a** occured from near 350 °C, poly[4-(3-butynyl)styrene] and polymer **6a** gained higher heat-resistance than these polymers under nitrogen and air atmosphere, as shown the TG curves in Figure 4-5. In particular, polymer **6a** showed no significant weight loss below 445 °C and the T_d was the high temperature of 481 °C. The T_d of polymer **6a** was slightly higher than that of poly(4-phenylethynylstyrene) obtained by radical polymerization, T_d = 476 °C.[1] The T_r of polymer **6a** was about 45 °C lower than that of radical polymer, T_r = 276 °C, and, therefore, the crosslinking reaction of polymer **6a** satisfactorily occurred in preference to decomposition of the polymers.
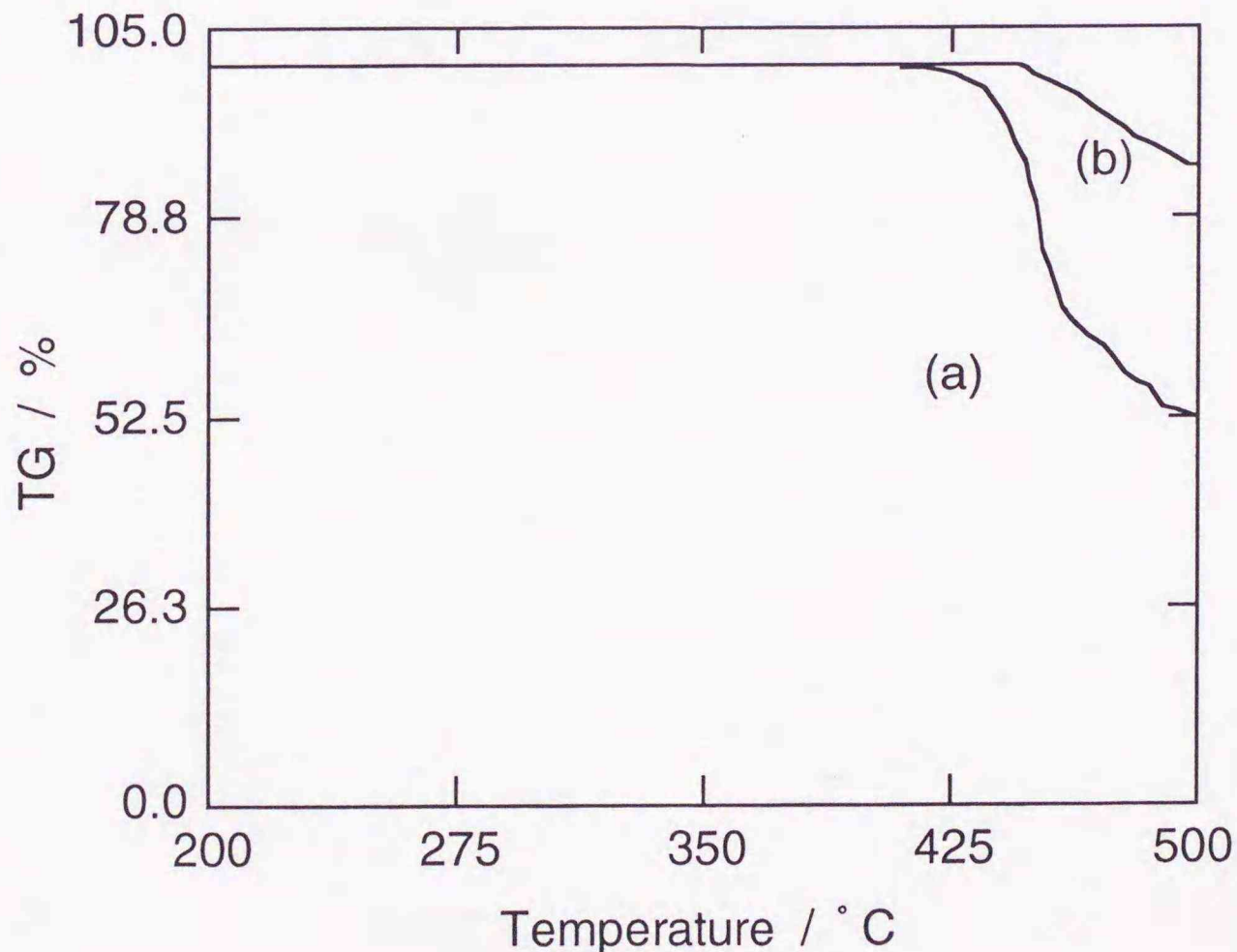
Figure 4-5. TG thermograms of poly[4-(3-butynyl)styrene] (a) and poly[4-(phenylethynyl)styrene] (**6a**) (b).

54

4-3. Conclusion

The cationic polymerization of styrene derivatives containing an ethynyl group and their copolymerization with styrene afforded gel-free polymers with ethynyl groups. However, the homo- and copolymers of the (2-trimethylsilylethynyl)styrenes (**1a-c**) and the homopolymer of *o*-substituted monomers (**3c**, **4c**, **5c**, and **6c**) were not quite obtained. Reactivity of monomers was depend on the steric hindrance and the substituted position of substituents. The structure of polymers was mainly constituted by linear chains with some intermolecular adducts. The polystyrenes having various pendent ethynyl groups were cured at elevated temperature to form crosslinking polystyrenes. The heat-resistance property was improved by the introduction of various ethynyl groups compared with polystyrene. In particular, in spite of the low M_n of poly[4-(phenylethynyl)styrene] by cationic polymerization, the T_d was higher than that of the polymer by radical polymerization.

4-4. Experimental Section

Measurements.　Infrared and Raman spectra were recorded using a JEOL JIR RFX-4002F FT-IR spectrophotometer and a Perkin Elmer Spectrum 2000 NIR FT-Raman spectrophotometer, respectively.　^{1}H and ^{13}C-NMR spectra were recorded using a Varian Mercury-300BB instruments.　Size exclusion chromatograms (SEC) were obtained using a Showa Denko System-11 instrument equipped with three polystyrene gel columns (Shodex K-805L x 3) with a refractive index detection at 40 °C.　Chloroform was used as carrier solvent at a flow rate of 1.0 mL·min^{-1}.　Differential scanning calorimetry (DSC) and thermal gravimetry (TG) measurements were carried out under N_2 using a Seiko DSC220 and a TG/DTA22 instrument, respectively.　The heating scan rate was 10 °C·min^{-1} for all experiments.

Materials.　Styrene and dichloromethane were purified by the usual methods. Tetrabutylammonium fluoride ((C_4H_9)$_4$NF) solution in THF was purchased from Aldrich.

Polymerization.　Cationic homo- and copolymerizations were carried out using SnCl$_4$ as an initiator in dichloromethane at 0 °C under nitrogen.　After polymerization, the solution was poured into a large amount of methanol.　The precipitated polymers were purified by two reprecipitation from a THF/methanol system and dried at 50 °C under reduced pressure.

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(7) In previous chapter

Chapter 5. Anionic Living Polymerization of Styrene Monomers Containing an Ethynyl Group.

5-1. Introduction

In order to synthesize well-defined functional polymers with precisely regulated polymer chain lengths, a new strategy has been recently developing, which combines both the methods of protection and anionic living polymerization of functional monomers.[1] The reason to protect the functional groups is that conventional anionic living polymers from styrene and 1,3-dienes do not tolerate most functional groups. This strategy involves protection of the functional group of a monomer and the anionic living polymerization of the protected monomer, followed by deprotection to regenerate the original functional group. If this route could successfully be executed, the resulting polymer would have a functional group in each monomer unit and desirable characteristics of the parent living polymer with respect to the main-chain structure.

Through the pioneering work, Nakahama and Hirao have successfully synthesized a variety of polystyrene derivatives mainly *para*-substituted with functional groups such as OH,[2,3] CH_2CH_2OH,[4,5] NH_2,[6,7] CH_2NH_2 and $CH_2CH_2NH_2$,[8] CHO,[9-11] $COCH_3$,[12] COOH,[13,14] and poly(2-hydroxyethyl methacrylate).[15] Similarly, other research groups also have synthesized poly(4-vinylphenol)[16,17] and poly(methacrylic acid).[18,19] Clearly, this protection - anionic living polymerization - deprotection strategy becomes generally and versatilely used for synthesizing such functional polymers.

As a part of this program to investigate the more general applicability of the above - mentioned strategy, this chapter have focused here on styrene monomers with an ethynyl group. They are a typical class of attractive dual-functional monomers that contain two polymerizable functions of vinyl group and acetylene moiety in the skeleton. Both functions are expected to be readily polymerizable under the various reaction conditions. If the chemoselective polymerization of each function proceeds well, the ideal linear polymer bearing another polymerizable function in each monomer unit can be obtained. However, it has been reported that the free-radical polymerization of 4-ethynylstyrene gives the insoluble polymeric product only in low yield, probably due to the serious cross-linking of the polymer.[20] The polymerization proceeds in a nonselective way and the radical addition toward the acetylene moiety might also take place along with the expected vinyl polymerization. Similar to the radical pathway, the anionic process will also meet the same problem in the selectivity of the polymerizable functions.[21] More seriously, the presence of the acidic acetylene protons on styrene monomers with an ethynyl group are particularly problematic when one attempts to anionically polymerize styrene monomers with an ethynyl

group. It is easy to imagine that the proton abstraction from C≡CH group (pKa = 25)[22] readily occurs with the strongly basic anionic initiators and/or the propagating benzylic carbanions at the initiation step or during the propagation. Moreover, the C≡C bond is believed to be susceptible to addition reactions as well as polymerization.[23]

This chapter have newly synthesized various ethynylstyrene derivatives to extend the range of functional monomers capable of the living anionic polymerization and to design the novel macromolecules that have well-defined chain structures as well as the C≡C bond in each monomer unit. The employed monomers are 4-, 3-, and 2-(2-(trimethylsilyl)ethynyl)styrenes (**1a**, **1b**, and **1c**), 4-(4-trimethylsilyl-3-butynyl)styrene (**2**), 4-, 3-, and 2-(3,3-dimethyl-1-butynyl)styrenes (**3a**, **3b**, and **3c**), 4-, 3-, and 2-(1-hexynyl)styrenes (**5a**, **5b**, and **5c**), and 4-(phenylethynyl)styrene (**6a**). In these monomers, the acidic acetylene proton of styrene monomer with an ethynyl group is purposefully substituted with trimethylsilyl, *tert*-butyl, *n*-butyl, or phenyl group. In addition, the introduction of a trimethylsilyl group into the β-position of the ethynyl function may become more resistant to undesirable nucleophilic addition reaction and anionic polymerization.

The first interest is whether or not a trimethylsilyl group protects efficiently the ethynyl function during the anionic living polymerization of **1a** and whether the silyl-protecting group can be completely and selectively removed from the resulting polymer **1a** or not. Among a number of known protecting groups,[24] the trimethylsilyl group would be the most suitable one, since it was reported that the SiC≡C bonds were stable toward carbanionic species[25] but readily cleaved with F[- 26] or OH^{-}. In addition, the anionic polymerization of corresponding *meta* and *ortho* isomers (**1b** and **1c**) are attempted for the ultimate goal of examining the general effectiveness of silyl protection under the anionic polymerization conditions.

The second interest is influence by substituent during the anionic polymerization of **2**. The reactivity of the carbanion derived from **2**, if produced, should be higher than from **1a**, because the benzylic anion and C≡C-SiMe$_3$ group are separated by two methylene groups to interrupt the extended π-conjugation existing in **1a**. Furthermore, the electron-donating character of CH$_2$CH$_2$C≡CSi-Me$_3$ substituent of **2** may enhance the nucleophilicity of the benzylic anion derived from **2**.[27] This is an opposite electronic effect to that observed in **1a** where C≡C-SiMe$_3$ group has electron-withdrawing character. This strongly suggests that the living polymer of **2** is much more reactive than that of **1a** and probably even more reactive than living polystyrene. More seriously, the deprotonation from the methylene group adjacent to the C≡C bond, since those protons are known to be considerably acidic,[28] may occur during the anionic polymerization. Thus, the C≡CCH$_2$ moiety in the styrene monomer also contains a serious problem to realize the anionic living polymerization besides
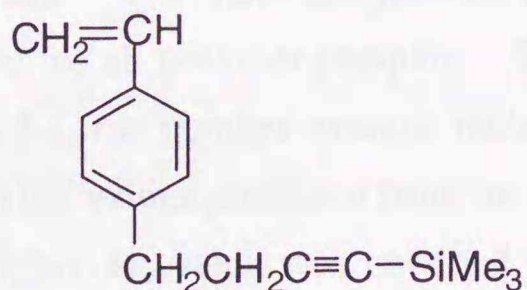
the $C\equiv CH$ function.

The third interest is the additional substituent effect on the β-position of ethynyl group on the anionic polymerizability of β-substituted *para*-ethynylstyrenes (**3a** and **5a**), which will be clarified by the comparison of polymerization behaviors. It is also attempted that *meta* (**3b** and **5b**) and *ortho* isomers (**3c** and **5c**) polymerize to evaluate the effect of substituent position. On the polymerization of **5a-c**, the presence of the acidic methylene protons adjacent to the C$\equiv$C linkage can be particularly problematic as is expected in the case of **2**.[29]

In the case of **6a**, the phenylethynyl substituent will provide the widely extended π-conjugation system and induce the enhanced anionic polymerizability of the monomer and the stabilization of propagating species.[30] However, it is reported that diphenylacetylene suffers from the nucleophilic addition of the carbanionic species due to the high electrophilicity of the extended conjugation system.[31] Therefore, the polymerization behavior of **6a** is a considerable interest in terms of the stability of the ArC$\equiv$CPh moiety toward the carbanionic species compared with the normal disubstituted C$\equiv$C linkage.

Thus, this chapter reports the results of homopolymerization and sequential block copolymerization of **1a–c**, **2**, **3a-c**, **5a-c**, and **6a** to elucidate the general polymerization behaviors and the anionic polymerizabilities of these dual-functional styrenes with C$\equiv$C groups.

CH$_2$=CH
C$\equiv$C–SiMe$_3$

1a : *para*
1b : *meta*
1c : *ortho*

CH$_2$=CH
CH$_2$CH$_2$C$\equiv$C–SiMe$_3$

2

CH$_2$=CH
C$\equiv$C-^{t}Bu

3a : *para*
3b : *meta*
3c : *ortho*

CH$_2$=CH
C$\equiv$C-^{n}Bu

5a : *para*
5b : *meta*
5c : *ortho*

CH$_2$=CH
C$\equiv$C

6a

60
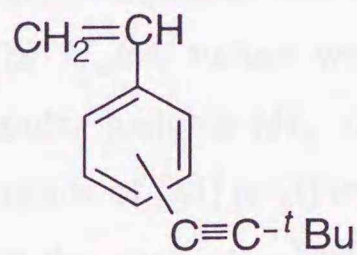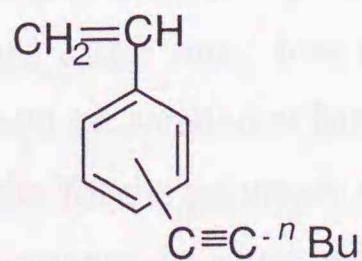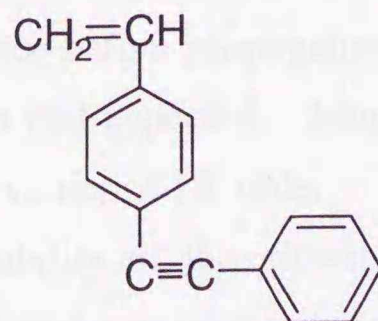
5-2. Results and Discussion

5-2-1. Anionic Polymerization of 1a.

The polymerization of **1a** was carried out with a variety of anionic initiators, including oligo(α-methylstyryl)lithium, n- and s-butyllithium (n-BuLi and s-BuLi), and potassium naphthalenide.

The reaction mixtures always exhibit a brownish red in the case of lithium salt or a dark red in the case of potassium salt, which indicate production of polystyryl anions from **1a**. The characteristic colors remained at -78 °C even after 24 h but immediately disappeared by quenching with a few drops of degassed methanol. The polymers were obtained quantitatively in all runs under the conditions. From the analytical results of ^{1}H and ^{13}C NMR and IR, it is obvious that the anionic polymerization of **1a** proceeds exclusively in a vinyl polymerization mode to afford the expected poly[4-(2-(trimethylsilyl)ethynyl)styrene]. Furthermore, no cleavage of the Si-C bond was observed after purification of the polymer by reprecipitation thrice using a THF-methanol system. The purified polymers, therefore, were directly characterized by SEC and VPO in the form of poly[4-(2-(trimethylsilyl)ethynyl)styrene].

Table 5-1 summarizes the molecular weights and molecular weight distributions, M_w/M_n values, of the resulting polymers. The SEC analyses revealed unimodal and symmetrical peaks with narrow distributions for all polymer samples. The M_w/M_n values were less than 1.1. As can be seen in Table 5-1, the number-average molecular weights (M_n) measured by VPO are in fair agreement with the values predicted from the ratios of [M] to [I] in most cases. However, a polymer with a higher M_n value was obtained in the case of n-BuLi initiation. This may be explained by the insufficient dissociation of n-BuLi.

The higher molecular weights tend to have more deviation from the calculated values. For example, a M_n was obtained to be 99,000 by VPO in the polymer with M_n calculated as 77,000. Since it still possessed a narrow molecular weight distribution, a trace of impurities in the monomer would cause some loss of initiator before propagation reaction, so that the molecular weight would be somewhat higher than that expected. More rigid purification of **1a** may possibly require for the polymers with M_n values of 10^5 order.

It is of great importance to elucidate the stability of the growing chain for proof of livingness of the polymerization. For this purpose, postpolymerization is one of the most suitable methods. After the first polymerization of **1a** with oligo(α-methylstyryl)dipotassium at -78 °C for 30 min, the second feed of **1a** was then added to the

Table 5-1. Anionic Polymerization of **1a** in THF at -78 °C for 0.5 - 1 h[a]

1a	initiator		α-methylstyrene	$10^{-3}M_n$		
(mmol)	type	mmol	(mmol)	calcd[b]	obsd[c]	M_w/M_n[d]
3.08	K-Naph[e]	0.105	0.322	12	10	1.04
3.14	K-Naph	0.0998		13	14	1.09
3.72	K-Naph	0.0633	0.319	25	25	1.04
3.17	s-BuLi[f]	0.0572		11	12	1.10
3.09	n-BuLi[g]	0.0497		12	17	1.09
3.69	n-BuLi	0.0456	0.304	17	15	1.04
5.04	Li-Naph[h]	0.0915	0.327	23	21	1.13
2.85	s-BuLi	0.0241	0.356	25	28	1.03
2.91	s-BuLi	0.0196	0.246	31	39	1.04
4.93	s-BuLi	0.0245	0.317	42	40 (39)[i]	1.08
3.38	s-BuLi	0.00921	0.257	77	99 (98)[i]	1.07

[a] Yields of polymers were quantitative in all runs.
[b] M_n(calcd) was calculated from the [M] to [I] ratio.
[c] M_n(obsd) was obtained by VPO.
[d] M_w/M_n was determined by SEC using polystyrene calibration.
[e] Potassium naphthalenide.
[f] s-Butyllithium.
[g] n-Butyllithium.
[h] Lithium naphthalenide.
[i] Values in parentheses were M_ws obtained by light scattering in benzene at 25 °C.

reaction mixture. It was allowed to stand an additional 30 min to complete further polymerization. Both pre- and postpolymers were obtained quantitatively. As shown in Figure 5-1, the peak of the postpolymer shifts completely to a higher molecular weight side and no peak is observed at all in the molecular weight region of the prepolymer. Both pre- and postpolymers possess the desirable M_n values and narrow molecular weight distributions. Evidently, the propagating polymer chain end is stable at -78 °C at least for 30 min and is capable of initiating further polymerization quantitatively. These results clarify the living character of the anionic polymerization of **1a**. Accordingly, the trimethylsilyl group perfectly protects the terminal ethynyl function of 4-ethynylstyrene during the anionic living polymerization. Furthermore, narrow distributions of molecular weight offer a convincing evidence that the initiation reaction must be sufficiently rapid under these conditions.
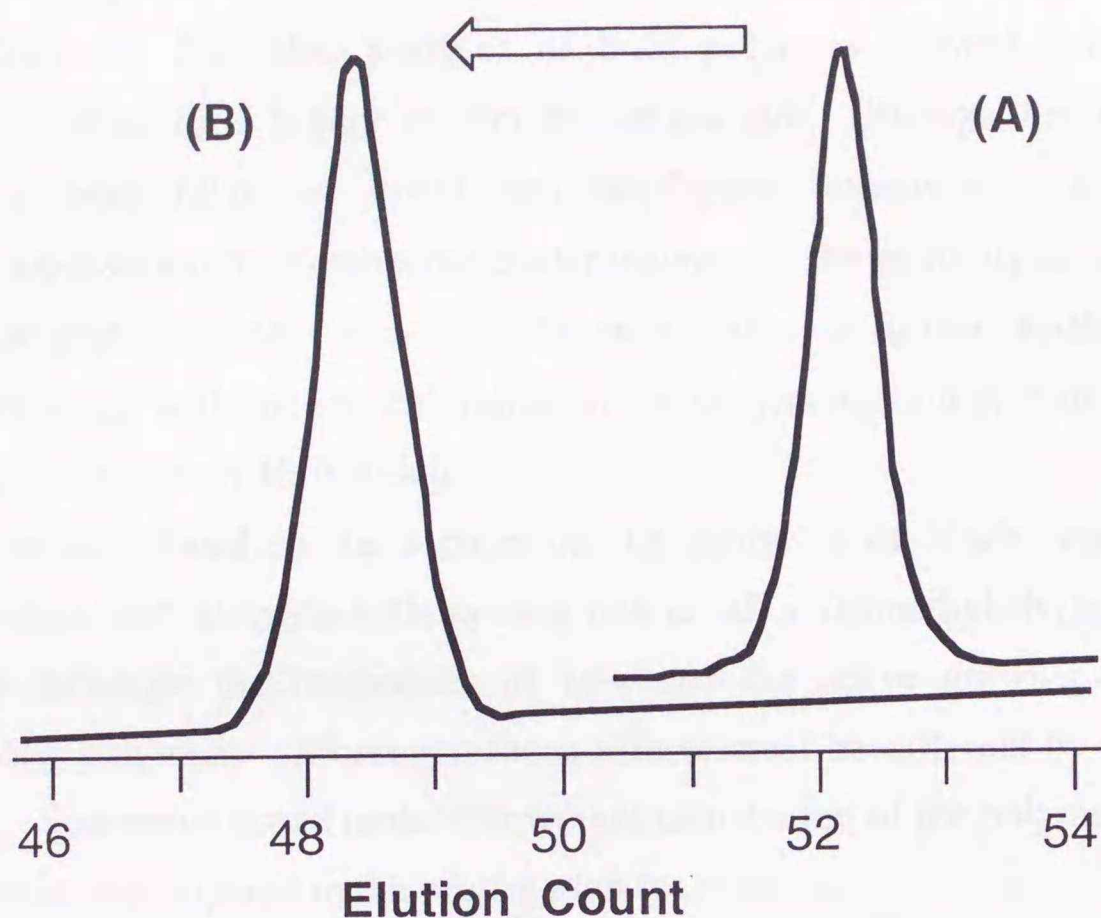
Figure 5-1. SEC charts of prepolymer with M_n(obsd) of 7,000 (A)
and postpolymers with M_n(obsd) of 17,000 (B).

5-2-2. Anionic Polymerizations of 1b and 1c.

In order to examine the effectiveness of the trimethylsilyl protecting group for other ethynylstyrenes, the corresponding *meta*- and *ortho*-substituted monomers, **1b** and **1c**, were synthesized and polymerized with anionic initiators under the same conditions that **1a** was used.

The anionic polymerization of the *meta* isomeric monomer, **1b**, was carried out in THF at -78 °C with either oligo(α-methylstyryl)dilithium or the dipotassium salt. A characteristic brownish-red color was observed in each of the polymerization mixtures. Yields of polymers were quantitative after 30 min. Occurrence of the vinyl polymerization of **1b** was ascertained by the IR and ^{1}H and ^{13}C NMR analyses. The Me$_3$Si-C bond was observed to be intact after a purification workup.

The results are summarized in Table 5-2. A comparison for the M_n value of each polymer shows that the values observed are in good agreement with those calculated within experimental error. The SEC traces of polymers show unimodal and symmetrical peaks, although the molecular weight distributions are observed to be somewhat broad in the M_w/M_n values ranging from 1.22 to 1.39. The living character of the polymerization of **1b** was

63

found by the postpolymerization similar to the case of **1a**. Yields of pre- and postpolymers were quantitative. The SEC analyses of both polymers showed that the peak of the postpolymer shifted to a higher molecular weight side, although the peaks of pre- and postpolymers were relatively broad and overlapped somewhat. Both the pre- and postpolymers possessed predictable molecular weights. The postpolymerization showed that the active propagating chain end from **1b** was stable to initiate further polymerization. These results along with the red coloration in the polymerization systems indicated that the anionic polymerization of **1b** is living.

As will be mentioned in the section on the synthesis of block copolymerization, the resonance effect and electron-withdrawing nature of a (trimethylsilyl)ethynyl group may significantly influence the reactivities of **1a-c** and the active growing chain ends of the resulting living polymers. Moreover, those effects must be different by the position of the substituent. Somewhat broad molecular weight distribution of the polymer **1b** is attributable to a slow initiation compared to the propagation reaction.

Similarly, the anionic polymerization of the *ortho*-substituted monomer, **1c**, was carried out at -78 °C in THF with oligo(α-methylstyryl)lithium, -dilithium, or -dipotassium. Upon addition of **1c** to the initiator solutions, a characteristic color change from dark red to dark violet immediately occurred in all the cases. Yields of polymers were quantitative after 30 min. Occurrence of vinyl polymerization and no cleavage of the Si-C bond are clearly dem-

Table 5-2. Anionic Polymerization of **1b** and **1c** in THF at -78 °C for 0.5 h[a]

monomer	initiator		α-methylstyrene	$10^{-3}M_n$		
(mmol)	type	(mmol)	(mmol)	calcd[b]	obsd[c]	M_w/M_n[d]
1b (2.86)	K-Naph	0.111	0.310	11	13	1.22
1b (3.80)	Li-Naph	0.161	0.358	10	11	1.28
1b (3.32)	Li-Naph	0.0635	0.351	22	21	1.39
1c (2.73)	K-Naph	0.113	0.332	10	10	1.08
1c (3.88)	K-Naph	0.101	0.270	16	15	1.10
1c (3.03)	K-Naph	0.0568	0.295	23	19	1.10
1c (2.35)	*s*-BuLi	0.0458	0.314	11	13	1.10
1c (2.86)	Li-Naph	0.0969	0.255	12	10	1.14

[a] Yields of polymers were quantitative in all runs.
[b] M_n(calcd) was calculated from the [M] to [I] ratio.
[c] M_n(obsd) was obtained by VPO.
[d] M_w/M_n was determined by SEC using polystyrene calibration.

onstrated by the IR and ^{1}H and ^{13}C NMR analyses.   The results of **1c** are summarized in Table 5-2 along with those of **1b**.

As can be seen, there is a fair agreement between the M_n values calculated and observed by VPO.   Narrow molecular weight distributions for all samples are found by the SEC measurement.   The M_w/M_n values gave the range 1.08 - 1.14.   These results indicate the living polymerization of **1c** under the conditions.   The postpolymerization of **1c** also introduces evidence for the living polymerization.   Trimethylsilyl protection for *p*-, *m*-, and *o*-ethynylstyrenes, thus, is effective against their anionic living polymerizations.

Anionic living polymerization of the *ortho*-substituted monomer is of particular interest for forming the stereoregulated polymers with well-regulated chain lengths.   In fact, the splitting of C1 carbon of the aromatic ring of the 2-ethynylstyrene unit appears different from those of the *meta* and *para* derivatives.

5-2-3. Anionic Polymerization of 2.

The anionic polymerization of **2** was carried out in tetrahydrofurane (THF) at -78 °C for 10 min with oligo(α-methylstyryl)lithium, -potassium and -dipotassium, and *s*-butyllithium. The polymerization was examined also in benzene with *s*-butyllithium at 40 °C.

In THF at −78 °C, the reaction mixture showed brownish red in the case of lithium salt and dark red in the case of potassium salt during the polymerization.   The red color remained unchanged at −78 °C for 2h, but immediately disappeared by the addition of a small amount of methanol for quenching the polymerization.   In each case, the polymer was quantitatively obtained.   After purification of the polymer, its chemical structure was analyzed by IR, ^{1}H and ^{13}C NMR spectroscopies.   The analytical results show that the vinyl polymerization of **2** selectively proceeded to afford the polymer.   The carbon-carbon triple bond and trimethylsilyl protecting group remained intact during the anionic polymerization and the following treatment.   No appreciable polymerization took place with *s*-butyllithium in benzene at 40 °C.   In this case, abstraction of the active methylene proton might occur with the strongly basic *s*-butyllithium at the initial stage.

Table 5-3 summarizes the polymerization results of **2** in THF.   All number-average molecular weights measured by means of vapor pressure osmometry agreed with the calculated values based on the molar ratio of monomer to initiator.   This strongly suggests the quantitative initiator efficiency and the absence of chain transfer reactions.   The size-exclusion chromatography (SEC) curves of the polymers showed unimodal peaks with narrow molecular weight distributions.   The M_w/M_n values were smaller than 1.11.   Even after allowing the reaction mixture to stand at -78 °C for 2h, the molecular weight distribution kept

Table 5-3. Anionic Polymerization of **2** in THF at -78 °C for 10 min[a]

run	amt of 2, mmol	amt of initiator, mmol	amt of α-MeSt[b], mmol	$10^{-3}M_n$ calcd[c]	$10^{-3}M_n$ obsd[d]	M_w/M_n[e]
1	1.84	s-BuLi, 0.0503	-	8.4	11	1.08
2	2.13	s-BuLi, 0.0464	0.353	12	13	1.06
3	3.06	s-BuLi, 0.0353	0.335	21	20	1.07
4	3.84	s-BuLi, 0.0369	0.305	25	21	1.05
5	2.06	Cumyl-K[f], 0.0629	0.225	7.9	9.5	1.11
6	1.89	K-Naph[g], 0.133	0.310	7.0	8.0	1.12
7	2.31	K-Naph, 0.0888	0.337	12	11	1.09

[a] Yields of polymers were almost quantitative in each case.

[b] α-Methylstyrene.

[c] M_n(calcd) = [monomer] x (MW of monomer) x f /[initiator] + (MW of initiator); f = 1 or 2, corresponding to the functionality of the initiators.

[d] M_n(obsd) was obtained by VPO in benzene.

[e] M_w/M_n was estimated from SEC calibration by using standard polystyrenes in THF solution.

[f] Cumylpotassium.

[g] Potassium naphthalenide.

a unimodal shape without broadening, thus suggesting that no termination and no nucleophilic attack toward the $C \equiv C$ bond occur during the process of the polymerization. The polymerization of **2** showed a living natures under the employed conditions. The carbanion of the propagating chain is expected to be more reactive than that derived from **1a**. The resulting polymer is also interesting with respect to the reactivity of the aliphatic ethynyl function, which is different from that of the ethynyl group directly attached to the phenyl ring in the polymer of **1a**.

5-2-4. Anionic Polymerizations of 3a–c, 5a-c, and 6a.

The anionic polymerization of *para*-substituted monomers, **3a**, **5a**, and **6a**, were carried out in THF at -78 °C for 0.5 h with cumyl potassium, potassium naphthalenide, (diphenylmethyl)potassium (Ph$_2$CHK), oligo(α-methylstyryl)dipotassium and -lithium, *n*-BuLi, and *s*-BuLi. On the addition of monomers, the reaction mixtures showed a typical red color similar to that in anionic living polystyrene. The red coloration instantaneously disappeared by quenching with degassed methanol. After termination, a polymer was obtained in 100% yield in each case. The analyses of the resulting polymers by the ^1H, ^{13}C

66

NMR and IR spectroscopies showed that the vinyl polymerization exclusively proceeds to afford the polymer having the expected repeating units.

Table 5-4 shows the results of polymerization. The polymerizations of **3a**, **5a**, and **6a** were completed in THF at -78 °C within 0.5 h, and the polymers were produced in quantitative yields. The size exclusion chromatograms (SEC) of the polymers showed unimodal and symmetrical peaks, suggesting the absence of the intermolecular side reaction to the polymers. The polydispersity indexes, M_w/M_n values were around 1.1, indicating the narrow MWDs. The number-average molecular weights of the polymer samples were determined by the vapor pressure osmometry (VPO) in benzene solution. The M_n values thus obtained agreed well with the calculated values based on the molar ratios of monomers to the employed initiators. The agreement in the M_n values supports the quantitative initiator efficiency and the rapid initiation reaction. Hence, the fine control of M_n and MWD for the polymers is attained. However, there were some exceptions as follows. Polymer **3a** produced with Ph_2CHK (Table 5-4, run 4) possessed the M_n value being higher than the calculated one, and the SEC curve showed a significant tailing toward a low molecular weight region. This can be explained by the low initiator efficiency of Ph_2CHK for **3a**, because of the steric hindrance and the low nucleophilicity of the resulting anion. The SEC curve of the polymer **5a** formed at 0 °C (Table 5-4, run 12) apparently possessed a higher molecular weight shoulder, resulting in a relatively broad MWD (M_w/M_n = 1.21). The intermolecular side reaction between the propagating chain end and the pendant C≡CBu moiety might occur to some extent at the elevated temperature of 0 °C in THF, as seriously observed during the polymerization in benzene. This will be discussed later. It is also noteworthy that polymer **6a** maintained a unimodal and narrow MWD at -78 °C at least for 4 h, as shown in Figure 5-2A. Conjugated ArC≡CPh moiety in the presence of the polystyryl anion from **6a** was satisfactorily stable over the course of polymerization.

The *meta* and *ortho* isomers, **3b**, **3c**, **5b**, and **5c**, also underwent the anionic polymerization quantitatively in THF at -78 °C for 0.5 h. The resultant polymers had the predicted molecular weights and fairly narrow MWDs. In particular, polydispersities of the *meta*-substituted polymers, **3b** and **5b**, were always within 1.15 and were narrower than the reported values of polymers **1b** which possessed relatively broad MWDs (M_w/M_n = 1.22-1.39).[32]

Table 5-4. Anionic Polymerizations of **3a-c**, **5a-c**, and **6a** in THF at -78 °C for 0.5 h[a]

run	amt of monomer, mmol	amt of initiator, mmol	amt of α-MeSt,[b] mmol	$10^{-3}M_n$ calcd[c]	obsd[d]	M_w/M_n[e]
1	**3a**, 2.66	Cumyl-K,[f] 0.102		4.9	4.9	1.06
2	**3a**, 2.11	K-Naph,[g] 0.0557		13	14	1.08
3	**3a**, 3.92	K-Naph, 0.0604	0.233	25	24	1.05
4	**3a**, 2.69	Ph$_2$CHK,[h] 0.0385		13	18	1.15
5	**3a**, 2.48	s-BuLi, 0.0414		11	11	1.15
6	**3a**, 3.16	s-BuLi, 0.0504	0.211	12	16	1.11
7	**3b**, 1.72	K-Naph, 0.0456	0.267	15	14	1.14
8	**3c**, 1.68	K-Naph, 0.0529	0.232	13	9.7	1.14
9	**5a**, 2.26	Cumyl-K, 0.0622		6.8	7.2	1.07
10	**5a**, 2.11	K-Naph, 0.0616	0.207	13	10	1.07
11	**5a**, 4.44	K-Naph, 0.0783	0.342	22	20	1.10
12[i]	**5a**, 2.90	K-Naph, 0.0956	0.342	13	13	1.21
13	**5a**, 2.71	s-BuLi, 0.0504		10	11	1.15
14	**5a**, 3.42	s-BuLi, 0.0493	0.236	13	16	1.06
15	**5b**, 3.32	Cumyl-K, 0.0853		7.3	6	1.10
16	**5b**, 3.19	K-Naph, 0.126	0.436	10	9.5	1.11
17	**5b**, 4.55	K-Naph, 0.0806	0.343	22	21	1.14
18	**5b**, 2.75	s-BuLi, 0.0460		11	12	1.09
19	**5b**, 3.19	s-BuLi, 0.0604	0.244	11	13	1.15
20	**5c**, 3.01	Cumyl-K, 0.0969		5.4	5.2	1.09
21	**5c**, 4.46	Cumyl-K, 0.0424		19	17	1.13
22	**5c**, 3.29	K-Naph, 0.112	0.382	12	12	1.12
23	**5c**, 2.97	s-BuLi, 0.0486		11	11	1.10
24	**6a**, 2.25	Cumyl-K, 0.0566		8.2	7.7	1.07
25	**6a**, 2.06	K-Naph, 0.0837	0.346	11	10	1.08
26	**6a**, 2.31	n-BuLi, 0.0678		7	7.6	1.11
27	**6a**, 1.48	s-BuLi, 0.0636		4.8	6	1.08
28[j]	**6a**, 1.53	s-BuLi, 0.0440	0.327	8	9	1.09
29	**6a**, 4.54	s-BuLi, 0.0345	0.264	28	27	1.09

[a] Yields of polymers were quantitative in all cases.
[b] α-Methylstyrene.
[c] M_n(calcd) = [monomer] x (MW of monomer) x f/[initiator] + MW of initiator residue ;
f = 1 or 2, corresponding to the functionality of the initiators.
[d] M_n(obsd) was obtained by VPO measurement in benzene.
[e] M_w/M_n was obtained by SEC calibration using polystyrene standards in THF solution.
[f] Cumyl potassium.   [g] Potassium naphthalenide.
[h] (Diphenylmethyl)potassium.   [i] At 0 °C.   [j] For 4 h.

The results indicate the living character of the polymerizations of monomers **3a-c**, **5a-c**, and **6a** in THF solution at -78 °C. The postpolymerization further confirmed the living character. For example, after a first-stage polymerization of **5a** with cumyl potassium in THF at -78 °C for 0.5 h, a second feed of **5a** was performed. The second-stage polymerization was continued for an additional 0.5 h. After the termination with methanol, both prepolymer and postpolymer were obtained in quantitative yields. The SEC curve of the postpolymer shifted toward a higher molecular weight side with keeping the sharp shape of the chromatogram. Pre- and postpolymer **5a** possessed the M_n values of 7,200 (M_w/M_n = 1.07) and 17,000 (M_w/M_n = 1.08), which were very close to the calculated ones of 6,800 and 16,000. These indicate that the propagating carbanion of prepolymer, thus, is stable at -78 °C at least for 0.5 h to initiate further polymerization with a quantitative efficiency. The persistencies of the active chain ends derived from **3a**, **5c**, and **6a** in THF at -78 °C were also substantiated using 2-vinylpyridine (2VP) as a second feed monomer.

The terminal carbanion of polymer **5b**, however, was not sufficiently stable even at -78 °C. About 12 % of chain ends of polymer **5b** were found to deactivate at -78 °C after 0.5 h. After 12 h, the deactivated terminals increased to up to 30 % , although the prepolymer maintained a unimodal and a very narrow MWD (M_w/M_n = 1.10). This suggests that the same deactivation occured after the complete consumption of the monomer. The deactivation
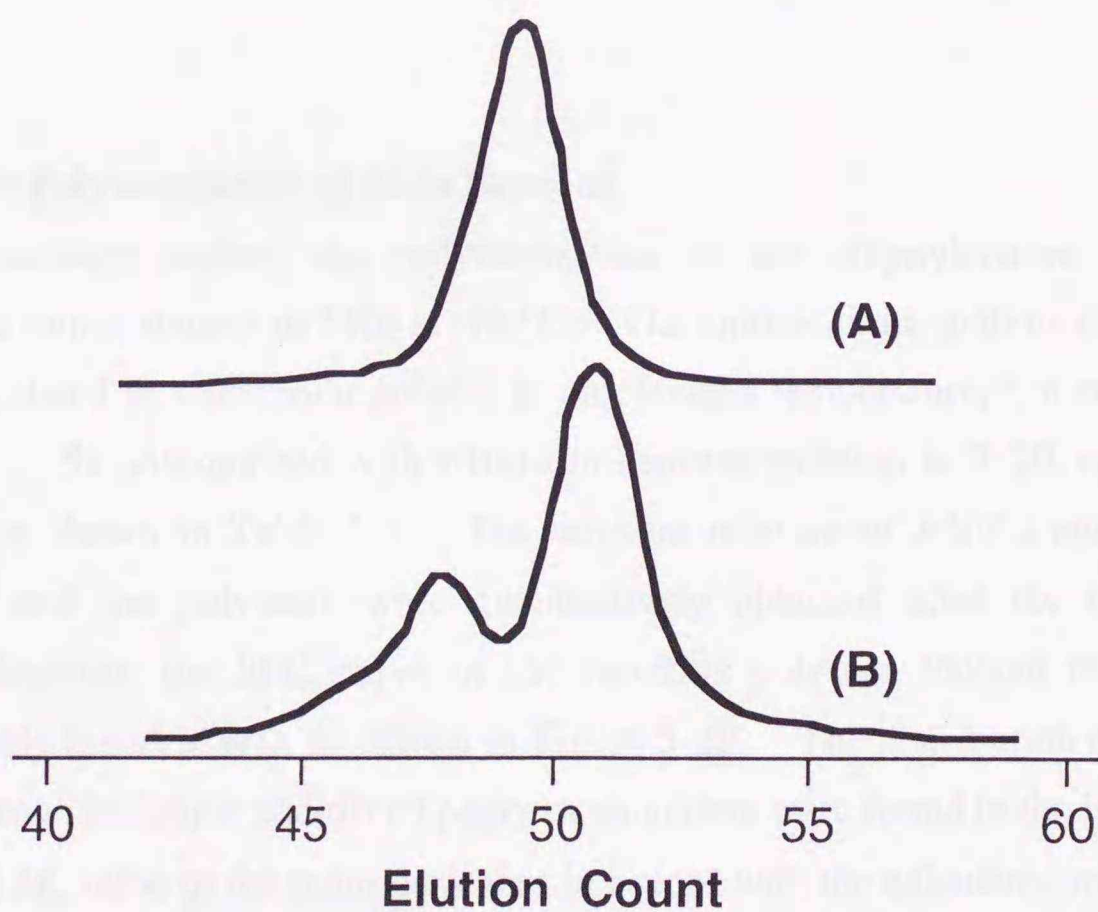

Figure 5-2. SEC curves of polymer **6a** produced at -78 °C for 4 h in THF (A) (Table 5-4, run 28) and polymer **5a** (B) (Table 5-5, run 30) at 40 °C for 1 h in benzene.

69

reaction during the polymerization of **5b** might not be an intermolecular nucleophilic addition toward the C≡C bond, but a proton abstraction from the methylene group adjacent to the C≡C group (Scheme 5-1), as observed in the case of **2**. Such deactivations were not observed in the corresponding *para* and *ortho* isomers, **5a** and **5c**. In addition, the propagating carbanion derived from *tert*-butylethynyl counterpart **3b** was also found to be stable, since it contained no acidic C≡CCH$_2$ type proton. Resonance stabilization[30] by the *meta*-substituted C≡CBu group might not be enough for the terminal benzylic carbanion of polymer **5b** to suppress the acidic proton abstraction in contrast to the sufficient stabilization effects of *para* and *ortho* isomers, **5a** and **5c**. Thus, the position of the substituent is also important to realize the anionic living polymerization of styrenes containing the C≡CBu groups.

Scheme 5-1.
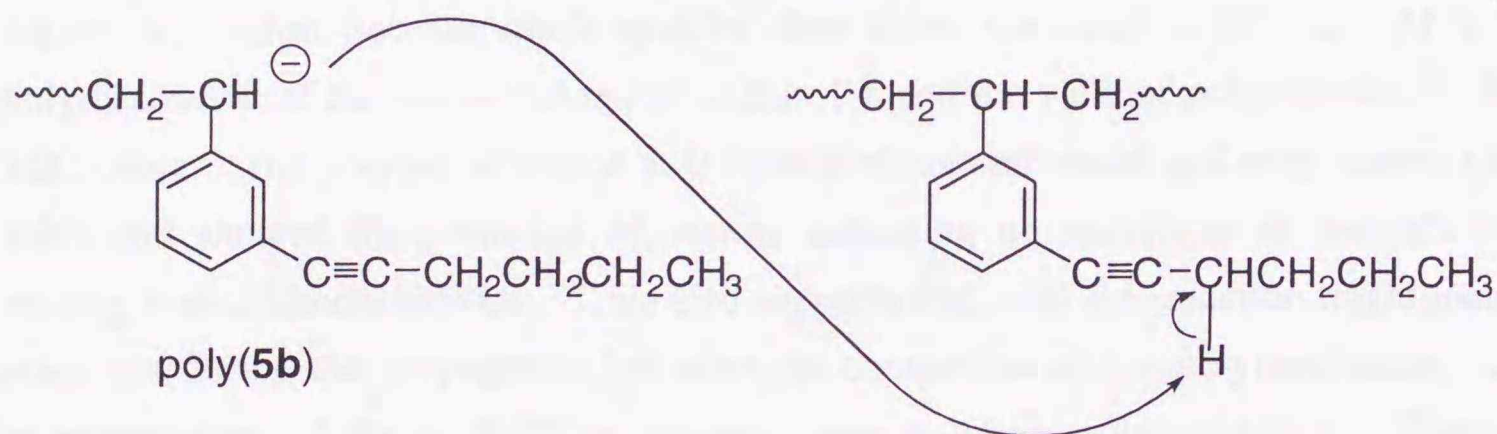
5-2-5. Anionic Polymerization of 5a in Benzene.

In the preceding section, the polymerization of the ethynylstyrene derivatives has succeeded in a living manner in THF at -78 °C. The anionic living polymerization of styrene can be also realized in a nonpolar solvent at an elevated temperature,[33] in contrast to that in polar solvent. **5a** polymerized with *s*-BuLi in benzene solution at 0, 20, and 40 °C for 1h. The results are shown in Table 5-5. The reaction mixture of *s*-BuLi and **5a** showed an orange color and the polymers were quantitatively obtained after the termination with methanol. However, the SEC curve of the resulting polymer showed multimodal peaks having relatively broad MWD, as shown in Figure 5-2B. The distribution of the main peak was fairly narrow, but some additional peaks or shoulders were found in the higher M_n region. The estimated M_n value of the main peak was in accord with the calculated molecular weight, and the peaks in the higher M_n region correspond to the double and triple M_ns of the main peak. The polymerization of **5a** at first proceeded well to afford a polymer having a controlled M_n and a narrow MWD, and then the propagating carbanion reacted with inter and

70

**Table 5-5.** Anionic Polymerization of **5a** with *s*-BuLi in Benzene for 1 h

run	amt of 5a, mmol	amt of s-BuLi, mmol	temp, °C	yield, %	$10^{-3}M_n$ calcd	obsd[a]	M_w/M_n
30	3.15	0.055	40	100	11	14	b
31	3.55	0.059	20	100	11	14	b
32	3.33	0.046	0	61	8.1	10	1.09

[a] M_n(obsd) was obtained by VPO in benzene.

[b] The MWD was multimodal.

intramolecularly pendant C≡CBu moiety to result in the multimodal MWD (Scheme 5-2). This side reaction could not be completely suppressed at 20 °C, although the shoulders in the higher M_n region became much smaller than those observed at 40 °C. At 0 °C, the polymerization of **5a** was not complete within 1 h and the yield of polymer was 61 %. The SEC curve of the polymer obtained at 0 °C was almost unimodal and very narrow (M_w/M_n = 1.09) and showed the predicted M_n value, indicating no occurence of the side reactions leading to multimodal MWDs. This also supports that the side reaction might mainly take place not during the propagation but after the completion of the polymerization. Anionic polymerization of **5a** at 0 °C in benzene was a living polymerization. There was a possibility that the polymerization in nonpolar solvent becomes a living nature only under the desirable condition.

Scheme 5-2.

poly(**5a**)

71
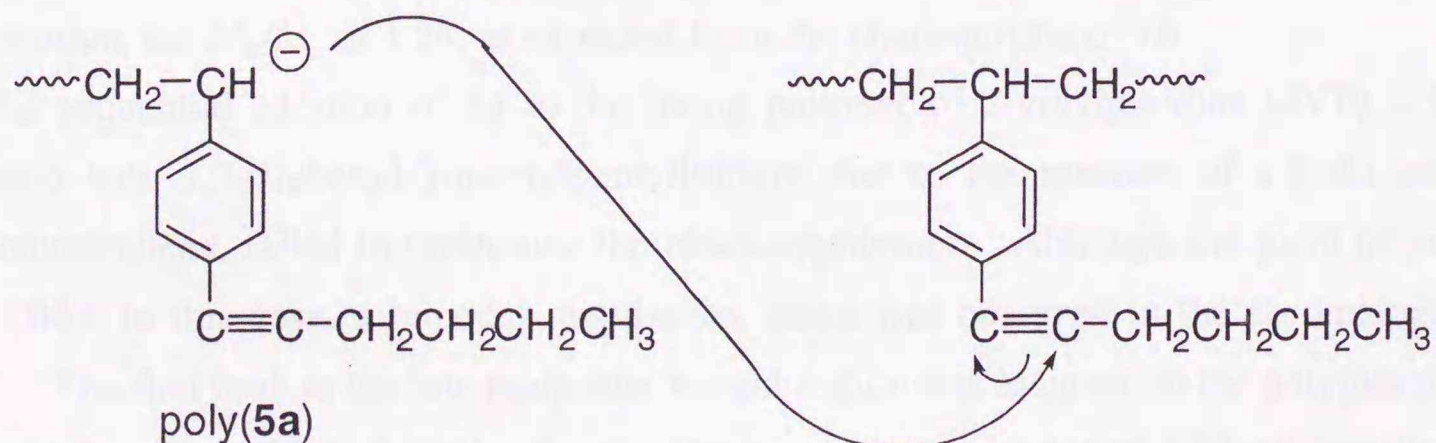
5-2-6. Block Copolymerizations of 1a-c with Isoprene, Styrene, 2-Vinylpyridine, and Methyl Methacrylate.

One of the most characteristic advantages of living polymerization is to provide the best method for creating block copolymers with precisely controlled chain structures and compositions. In addition to such a synthetic utility, the block copolymerization using living polymers can elucidate relative reactivities of monomers and the living growing chain ends from the effectiveness of copolymerization. The result gives direct information on the stability of the living polymer at the first stage. In this section, the block copolymerizations of 1a-c with isoprene (Isp), styrene (St), 2-vinylpyridine (2VP), and methyl methacrylate (MMA) are performed to produce novel block copolymers with poly(ethynylstyrene) block segments.

At first, an ABA triblock copolymer of 1a (A monomer) with St (B monomer) was synthesized by the addition of 1a to the difunctional living polystyrene initiated with potassium naphthalenide in THF at -78 °C. The polymerization proceeded quantitatively to yield the expected block copolymer having a predictable molecular weight and composition, and a narrow molecular weight distribution as shown in Table 5-6. The SEC trace also demonstrated the successful block copolymerization, resulting from the observation that the peak of the block copolymer shifted completely to the higher molecular weight side and converted to a symmetrical unimodal peak with a narrow distribution. Difunctional living polyisoprene was used for the synthesis of a well-defined ABA block copolymer, poly(1a-b-Isp-b-1a). Novel ABA triblock copolymers in which the A block consists of 1b or 1c were also successfully synthesized by the addition of 1b and 1c to the difunctional living polystyrene. Their well-defined and regulated structures are demonstrated by VPO, SEC, and ^{1}H NMR analyses. Poly(1b-b-St-b-1b) possessed a somewhat broad molecular weight distribution, the M_w/M_n of 1.24, as expected from the characteristic of 1b.

The sequential addition of 1a to the living polymer of 2-vinylpyridine (2VP), which is initiated with 1,1-diphenyl-3-methylpentyllithium due to the reaction of s-BuLi and 1,1-diphenylethylene, failed to synthesize the block copolymer. Although the yield of polymer was 100% in this case, a bimodal distribution curve was observed in the chromatogram of SEC. The first peak at the low molecular weight region was assigned to the polymer of 2VP. A second peak at the high molecular weight region corresponded to a block copolymer of 2VP and 1a. The carbanion produced from 2VP is not nucleophilic enough to polymerize 1a quantitatively. The cross propagation from 2VP to 1a, thereby, was very slow, but the polymerization of 1a was fast. The residue of unreacted living poly(2VP) after the second-stage polymerization of 1a showed a slow reactivity of the living poly(2VP) to 1a.

72

Table 5-6. Block Copolymerization of **1a-c** with Isoprene (Isp), Styrene (St), 2-Vinylpyridine (2VP), and Methyl Methacrylate (MMA) in THF at -78 °C [a]

		monomer		block copolymer (homopolymer[b])		
initiator	block type	A	B	$10^{-3}M_n$(calcd)[c]	$10^{-3}M_n$(obsd)[d]	M_w/M_n[e]
K-Naph	A-B-A	**1a**	Isp	23 (14)	26 (15)	1.05 (1.05)
K-Naph	A-B-A	**1a**	St	21 (12)	22 (10)	1.06 (1.03)
s-BuLi/DPE[f]	B-A	**1a**	2VP	22 (8.4)	h (7.8)	h (1.04)
Li-Naph	B-A-B	**1a**	2VP	21 (9.7)	19 (6.7)	1.09 (1.10)
K-Naph	A-B-A	**1b**	St	30 (9.3)	28 (8.2)	1.24 (1.09)
K-Naph	A-B-A	**1c**	St	19 (9.6)	18 (9.8)	1.06 (1.10)
Li-Naph/α-MeSt[g]	B-A-B	**1c**	MMA	20 (7.5)	24 (9.0)	1.18 (1.12)

[a] Yields of polymers were quantitative in all runs.

[b] Homopolymers were obtained by the first-stage polymerization.

[c] M_n(calcd) was calculated from the [M] to [I] ratio.

[d] M_n(obsd) was obtained by VPO.

[e] M_w/M_n was determined by SEC using polystyrene calibration.

[f] 1,1-Diphenylethylene.   [g] α-Methylstyrene.   [h] Bimodal distribution.

Next, the synthesis of the block copolymer with reversed sequence was attempted by addition of Isp, St, or 2VP to the difunctional living polymer of **1a**.   The living poly(**1a**) could not initiate the polymerization of Isp, and the homopolymer of **1a** was quantitatively recovered.   The cross propagation of **1a** to St was low efficiency, resulting in a mixture of the homopolymer of **1a** and the block copolymer consisting of a polystyrene segment with very high molecular weight.   The sequential addition of Isp and St to the living poly(**1a**), therefore, failed to form BAB block copolymer.   The living polymer from **1a** is not sufficiently nucleophilic enough to initiate the polymerization of Isp and St, although the latter appears to react slowly with the living polymer.   On the other hand, the polymerization of a more anionically reactive 2VP occurred quantitatively to produce the poly(2VP-*b*-**1a**-*b*-2VP) with a predictable molecular weight and a narrow molecular weight distribution.   The SEC analysis showed that the peak of the starting polymer **1a** shifted completely to a higher molecular weight side.   No peak corresponding to the homopolymer was observed.

The syntheses of a BAB triblock copolymer were also attempted by the cross propagating of the living poly(**1c**) with St or MMA as a second monomer.   The polymerization of St with the living poly(**1c**), however, encounted difficulties.   The cross propagation of the living polymer toward St was low efficiency.   This is very similar to the cross propagation of the

living polymer **1a** to St as mentioned before. On the other hand, MMA was quantitatively polymerized with the difunctional living polymer of **1c**. The VPO and ^{1}H NMR analyses showed a formation of poly(MMA-*b*-**1c**-*b*-MMA) with desirable segment lengths. The resulting polymer possessed a symmetrical unimodal peak and no peak corresponding to the homopolymer in the SEC curve.

Some block copolymers with poly(ethynylstyrene) segments were successfully synthesized. However, the sequential addition with certain combinations of **1a**, **1b**, or **1c** and conventional monomers restricts in the available initiating block. For example, the living polymer of **1a** has little or less ability to initiate the polymerization of Isp or St but not vice versa. **1a** is an anionically more reactive monomer than Isp and St, while the living poly(**1a**) is less reactive than those living polymers from Isp and St. The anionic reactivities of **1a** and its living polymer are nearly identical to that of 2VP, although a low reactivity of living poly(2VP) toward **1a** has been demonstrated. The electron-withdrawing nature of the (trimethylsilyl)ethynyl group[32] enhances the reactivity of the monomer to reduce the electron density of the vinyl bond, but lowers the nucleophilicity of the resulting living polymer. The resonance effect may also play an important role in determining their reactivities. Monomers **1a-c** are practically identical in reactivity.

5-2-7. Block Copolymerization of 2 with Styrene.

A diblock copolymer of **2** and styrene (St) synthesized through the sequential addition of **2** to the living polystyrene initiatated with *s*-butyllithium in THF at -78 °C. The yield of polymer was quantitative. In the ^{1}H NMR analysis, the composition in the polymer agreed well with the feed ratio of St and **2**. The SEC curve showed a sharp and unimodal chromatogram and a shift to the higher molecular weight side. The resulting copolymer possessed a narrow molecular weight distribution ($M_w/M_n = 1.03$) and a controlled molecular weight based on the molar ratios of monomers and initiator (Table 5-7). Thus, the further polymerization of **2** is possible with the anionic living polystyrene in quantitative efficiency to give a tailored diblock copolymer, poly(St-*b*-**2**).

A block copolymer with reversed sequence synthesized through the addition of St to the polymerization system of **2** in THF at −78 °C. Firstly, the polymerization of **2** was initiated with oligo(α-methylstyryl)lithium. After polymerization of **2** at -78 °C for 10 min, St was added to the reaction mixture. The complete conversion of St was attained within 10 min and the polymeric product was obtained in quantitative yield. The ^{1}H NMR analysis of the product revealed that the segment ratio between polymer **2** and polystyrene was nearly equal to the molar ratio of feed monomers. The SEC curve, however, was not unimodal, and

74

consisted of two sharp peaks, as shown in Figure 5-3. In curve B, the small peak eluted at lower molecular weight is completely identical to that of the starting polymer. The peak in the higher molecular weight region is considered to be that of the expected block copolymer. The presence of homopolymer is apparently due to deactivation of living poly(**2**) prior to the addition of St. The amount of deactivated homopolymer was estimated from these SEC peaks to be 30 mol-%. It was observed, as expected, that the degree of deactivation increased to 60 mol-% by allowing the polymerization system of **2** to react for a longer reaction time, i.e., 2 h at -78 °C. A similar result in view of the deactivation was also observed in the block copolymerization of **2** with methyl methacrylate. A living polymer of **2** initiated with oligo(α-methylstyryl)dipotassium also was found to be unstable, as one can infer from the result of block copolymerization with St. In this case, 60 mol-% of the original living polymer was already deactivated after 10 min at -78 °C in the copolymerization with St.

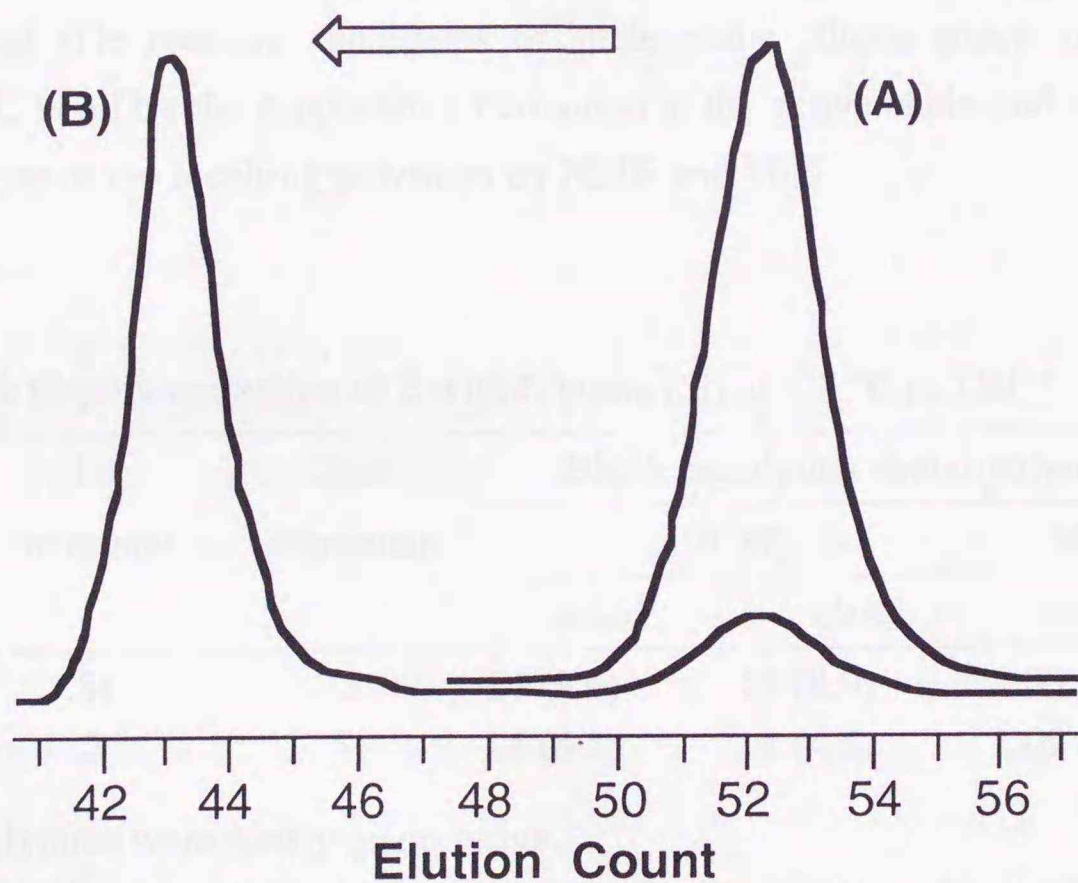**Figure 5-3.** SEC curves of polymer **2** at the first stage of polymerization (A) and of the copolymerization product obtained at –78 °C (B): peak A, M_n (obsd) = 6,800, M_w/M_n = 1.08 (styrene was added 2 h after the first stage of polymerization).

Lowering the polymerization temperature to -95 °C gave a very satisfactory result in the block copolymerization (Table 5-7, run 9). Quantitative polymerizations proceeded at -95 °C in the first step for **2** (10 min) and the second step for St (20 min). The SEC trace demonstrates a unimodal peak with a narrow distribution of molecular weight, although a trace amount of less than 5 mol-% of the homopolymer was still present. Apparently, the deactivation was almost suppressed at -95 °C. The living polymer of **2** is able to initiate the polymerization of St quantitatively, which is in sharp contrast to the previous results that the living polymer of **1a** could initiate the polymerization of St only with a very low initiator efficiency (<5%). The living polymer of **2** has higher reactivity than that of **1a**, and therefore the former is superior to the latter in the preparation of block copolymer.

Proton abstraction at the active methylene group adjacent to $C\equiv C$-$SiMe_3$ (Scheme 5-3) is a plausible candidate for the side reaction causing the deactivation of the living polymer of **2**, although there is no direct evidence for this process. Because of the predicted molecular weights and narrow molecular weight distributions, the side reaction was not competitive with the propagation step. Accordingly, the proton abstraction from methylene in the polymer side chain should take place after the polymerization of **2**, i.e., when no more monomer is present. Another side reaction candidates of nucleophilic silicon attack and nucleophilic addition of $C\equiv C$ bond by the propagating carbanion at the active chain end can be ruled out by careful analyses of the resulting polymers by NMR and SEC.

Table 5-7. Block Copolymerization of **2** with Styrene (St) at -78 °C in THF [a]

run	1st monomer	2nd monomer	Block copolymer (homopolymer[b])		M_w/M_n [e]
			$10^{-3}M_n$		
			calcd[c]	obsd[d]	
8	St	2	14 (9.0)	15 (8.9)	1.03 (1.06)
9[f]	**2**	St	14 (4.5)	14 (4.5)	1.09 (1.09)

[a] Yields of polymers were nearly quantitative.

[b] Obtained at the first stage of polymerization.

[c] M_n(calcd) = [monomer] x (MW of monomer)/[initiator] + (MW of initiator).

[d] Determined by using the molecular weights of the homopolymers and the molar ratios of monomer units in the block copolymer analyzed by ^{1}H NMR.

[e] M_w/M_n was obtained by SEC calibration using standard polystyrenes in THF solution.

[f] Carried out at -95 °C. Efficiency of block copolymerization was estimated to be over 95 % from the analysis of the SEC.

Scheme 5-3.

poly(**2**)
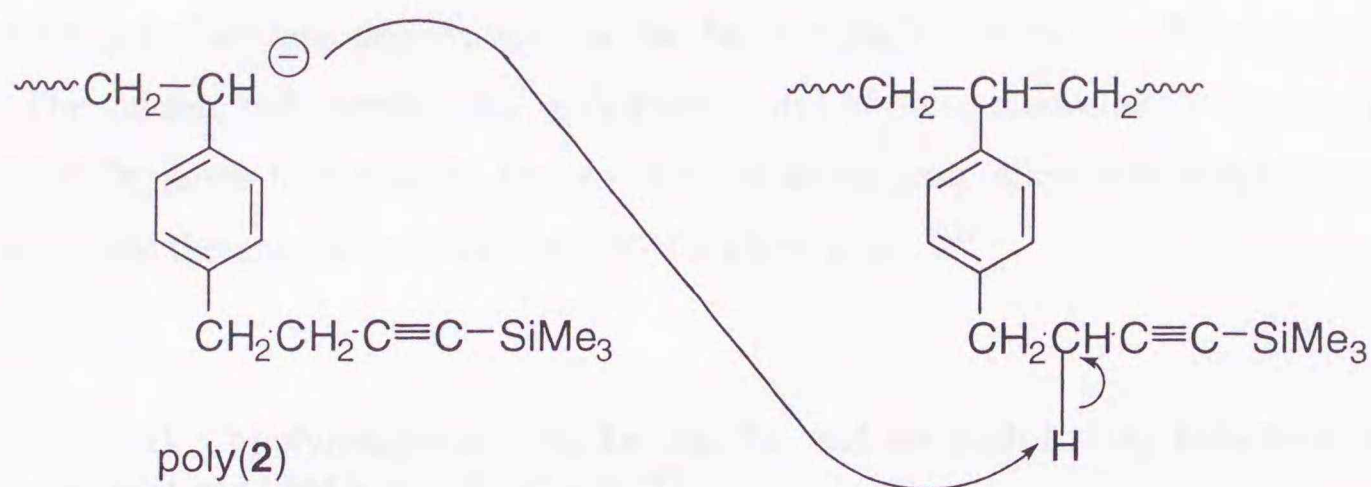
5-2-8. Block Copolymerizations between A(1a, 3a, 5a, and 6a) and B(Isoprene, Styrene, 2-Vinylpyridine, and *tert*-Butyl Methacrylate).

Herein, four conventional comonomers, isoprene (Isp), styrene (St), 2-vinylpyridine (2VP), and *tert*-butyl methacrylate (tBMA), were employed as a reference to evaluate the anionic polymerizabilities of **1a**, **3a**, **5a**, and **6a**.[27] The sequential copolymerizations were performed in THF at -78 °C with organopotassium initiators such as cumyl potassium and potassium naphthalenide except for some cases.

The results are summarized in Table 5-8. Yield refers to the polymer yield at the second-stage polymerization, and initiation efficiency presents the efficiency of the crossover reaction between the first living polymer and the second monomer. Living polyisoprene and polystyrene could initiate the polymerizations of **1a**, **3a**, **5a**, and **6a** quantitatively to afford the block copolymers having narrow MWDs and the predicted M_n's. The compositions of the block copolymers, which were determined from the ^{1}H NMR, were well regulated by the feed molar ratio. All SEC curves of the block copolymers showed narrow unimodal peaks and shifted completely toward the higher molecular weight side. The efficiency of the crossover reaction is quantitative to give the well-defined block copolymers in any combination.

With the first living polymer derived from 2VP or tBMA, the second polymerizations of **1a**, **3a**, **5a**, and **6a** also proceeded to consume all the monomers. However, the initiation efficiency of the second-stage polymerization was not necessarily quantitative. The combination of living poly(2VP) with **6a** gave a well-defined block copolymer in quantitative efficiency. Other combinations obtained the SEC curves of the polymeric products which showed the bimodal peaks consisting of the homopolymers of 2VP or tBMA and the block copolymers having the M_n's much higher than the expected values. The efficiency was

77

estimated to be 5 - 80 % from the SEC analyses, as shown in Table 5-8 (runs 41-48). It is noteworthy that even the low nucleophilic enolate anion of poly(tBMA) can initiate the polymerizations of styrene derivatives, **1a**, **3a**, **5a**, and **6a**, although the efficiency is only 5 - 40 %. The anionic polymerizability (electrophilicity) of these monomers is evidently higher than that of St, since it is already known that the living poly(alkyl methacrylate)s have no ability to initiate the anionic polymerization of styrene at all.[27,28]

Table 5-8. Block Copolymerizations of **1a**, **3a**, **5a**, and **6a** with Living Polymers Derived from Isp, St, 2VP and tBMA in THF at -78 °C

| | | | | | block copolymer (homopolymer [a]) | | | |
| | | 1st | 2nd | yield,[b] | $10^{-3}M_n$ | | | initiation |
run	countercation	monomer	monomer	%	calcd	obsd[c]	M_w/M_n	efficiency, %[d]
33	K+	Isp	**3a**	100	22 (9.4)	26 (11)	1.11 (1.11)	100
34	K+	Isp	**5a**	100	22 (6.4)	24 (8.0)	1.13 (1.13)	100
35	K+	Isp	**1a**	100	23 (14)	26 (15)	1.05 (1.05)	100
36	K+	Isp	**6a**	100	18 (6.0)	21 (7.3)	1.16 (1.14)	100
37	K+	St	**3a**	100	26 (7.6)	16 (8.0)	1.03 (1.06)	100
38	K+	St	**5a**	100	18 (6.1)	19 (6.7)	1.07 (1.06)	100
39	K+	St	**1a**	100	21 (12)	22 (10)	1.06 (1.03)	100
40	Li+	St	**6a**	100	18 (5.1)	18 (5.3)	1.10 (1.05)	100
41	K+	2VP	**3a**	100	16 (6.8)	e (7.1)	e (1.13)	~60
42	K+	2VP	**5a**	100	15 (6.8)	e (6.9)	e (1.10)	~60
43	Li+	2VP	**1a**	100	22 (8.4)	e (11)	e (1.04)	~80
44	K+	2VP	**6a**	100	16 (6.5)	17 (6.4)	1.08 (1.09)	100
45	K+	tBMA	**3a**	100	15 (5.3)	e (4.9)	e (1.05)	~5
46	K+	tBMA	**5a**	100	14 (5.4)	e (4.7)	e (1.06)	~5
47	K+	tBMA	**1a**	100	16 (5.4)	e (4.9)	e (1.05)	~20
48	K+	tBMA	**6a**	100	16 (6.3)	e (7.3)	e (1.06)	~40

[a] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases.

[b] Yield of the second-stage polymerization.

[c] M_n(obsd) values of the block copolymers were determined by the using the molecular weight of the homopolymer and the molar ratios of the monomer units in the block copolymer analyzed by ^{1}H NMR.

[d] Initiation efficiency in the second-stage polymerization.

[e] The initiation efficiency was not quantitative, forming a mixture of homopolymer and block copolymer.

78

Table 5-9. Block Copolymerizations of Isp, St, 2VP and tBMA with Living Polymers Derived from **1a**, **3a**, **5a**, and **6a** in THF at −78 °C

				block copolymer (homopolymer [a])				
	1st	2nd	yield,[b]	$10^{-3}M_n$			initiation	
run	countercation	monomer	monomer	%	calcd	obsd[c]	M_w/M_n	efficiency, %[d]
49	K⁺	**3a**	Isp	100	19 (4.6)	e (4.5)	e (1.08)	~50
50	K⁺	**5a**	Isp	~0	20 (5.9)	f (6.1)	f (1.06)	0[f]
51	K⁺	**1a**	Isp	0	25 (8.9)	g (7.6)	g (1.07)	0
52	K⁺	**6a**	Isp	0	35 (7.0)	g (5.5)	g (1.07)	0
53	K⁺	**3a**	St	100	50 (13)	51 (14)	1.15 (1.08)	100
54	K⁺	**5a**	St	100	16 (6.5)	e (5.7)	e (1.06)	~70
55	K⁺	**1a**	St	100	25 (11)	e (11)	e (1.12)	~5
56	K⁺	**6a**	St	100	16 (5.9)	e (4.8)	e (1.06)	~10
57	K⁺	**3a**	2VP	100	14 (5.1)	13 (4.3)	1.08 (1.07)	100
58	K⁺	**5a**	2VP	100	17 (6.4)	15 (5.8)	1.07 (1.06)	100
59	Li⁺	**1a**	2VP	100	21 (9.6)	19 (7.1)	1.09 (1.10)	100
60	K⁺	**6a**	2VP	100	26 (8.2)	24 (7.7)	1.04 (1.05)	100
61	K⁺	**3a**	tBMA	100	14 (4.9)	14 (4.9)	1.07 (1.06)	100
62	K⁺	**5a**	tBMA	100	15 (5.8)	15 (6.0)	1.08 (1.06)	100
63	K⁺	**1a**	tBMA	100	18 (6.2)	16 (5.2)	1.09 (1.06)	100
64	K⁺	**6a**	tBMA	100	16 (7.3)	16 (7.3)	1.07 (1.08)	100

[a] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases.

[b] Yield of the second-stage polymerization.

[c] M_n(obsd) values of the block copolymers were determined by the using the molecular weight of the homopolymer and the molar ratios of the monomer units in the block copolymer analyzed by ^{1}H NMR.

[d] Initiation efficiency in the second-stage polymerization.

[e] The initiation efficiency was not quantitative, forming a mixture of homopolymer and block copolymer.

[f] A side reaction occurs during the course of the second-stage polymerization, and the initiation efficiency was quite low.

[g] No polymerization proceeded at the second-stage, resulting in a quantitative recovery of the homopolymer of the first monomer.

Next, by changing the sequential addition order of the comonomers, Isp, St, 2VP, and tBMA polymerized with the living polymers derived from **1a**, **3a**, **5a**, and **6a**. As shown in Table 5-9, the well-defined block copolymers of 2VP and tBMA were obtained by the initiation of the anionic living polymers formed from **1a**, **3a**, **5a**, and **6a**. For example, the SEC curve of the block copolymer shifted from that of homopolymer **5a** toward the higher molecular weight side with keeping the narrow MWD after the addition of 2VP, as shown in Figure 5-4. Other block copolymers also possessed narrow MWDs ($M_w/M_n < 1.1$) and controlled M_n's along with the tailored compositions. Accordingly, the crossover polymerizations of 2VP or tBMA readily proceeded with the living polymers of ethynylstyrene derivatives in the quantitative efficiencies.

On the other hand, the results using St and Isp as second monomers were complicated. With the use of St, the initiation efficiencies were largely varied from 100 to 5 % (runs 53-56), although St was completely polymerized. Only the living poly(**3a**) initiated the second-stage polymerization with the initiation efficiency of 100 %. The low initiation efficiencies (5 - 10 %) of living poly(**1a**) and poly(**6a**) clearly suggest these propagating carbanions are lower nucleophilic than polymer **3a** (100 %) and polymer **5a** (70 %). Figure 5-5B shows a SEC
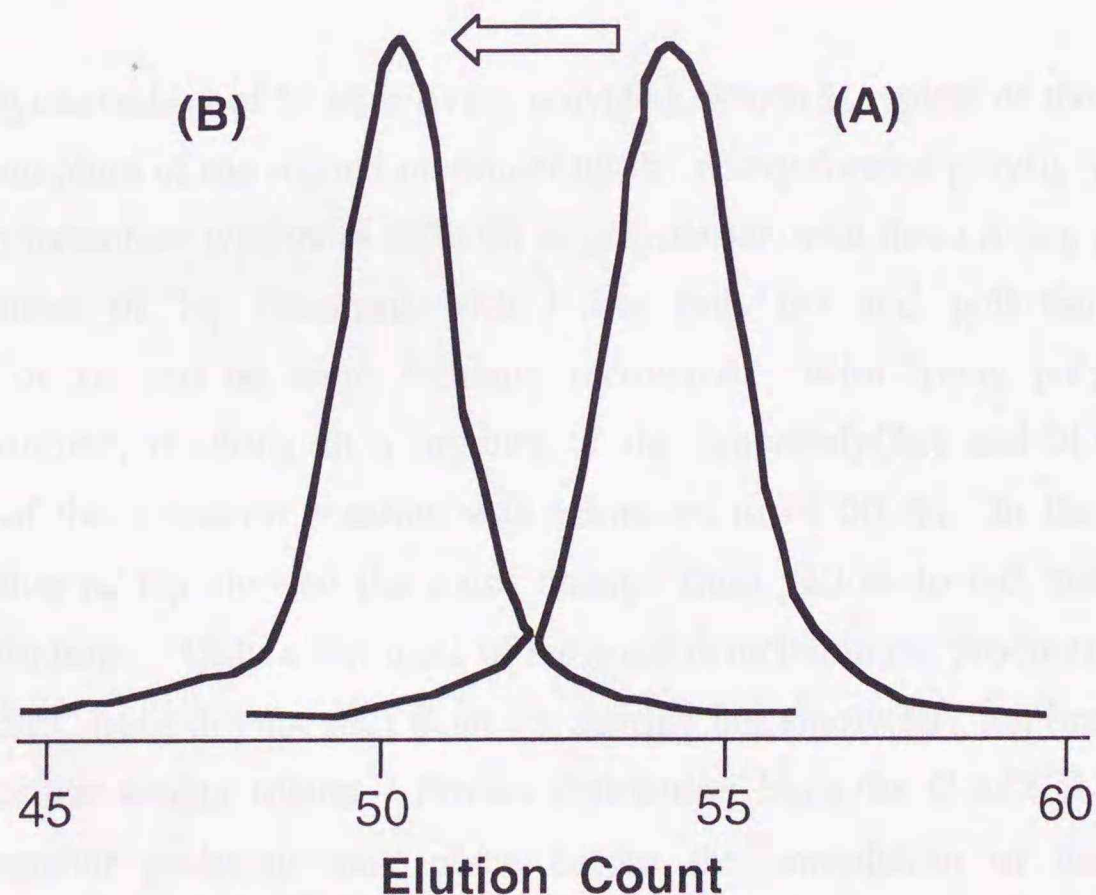

Figure 5-4. SEC curves of polymer **5a** at the first-stage polymerization (A) and of poly(2VP-*b*-**5a**-*b*-2VP) obtained at -78 °C (B) (Table 5-9, run 58): peak A, M_n(obsd) = 5,800, M_w/M_n = 1.06; peak B, M_n(obsd) = 15,000, M_w/M_n = 1.07 (the second monomer was added 0.5 h after the first-stage polymerization).
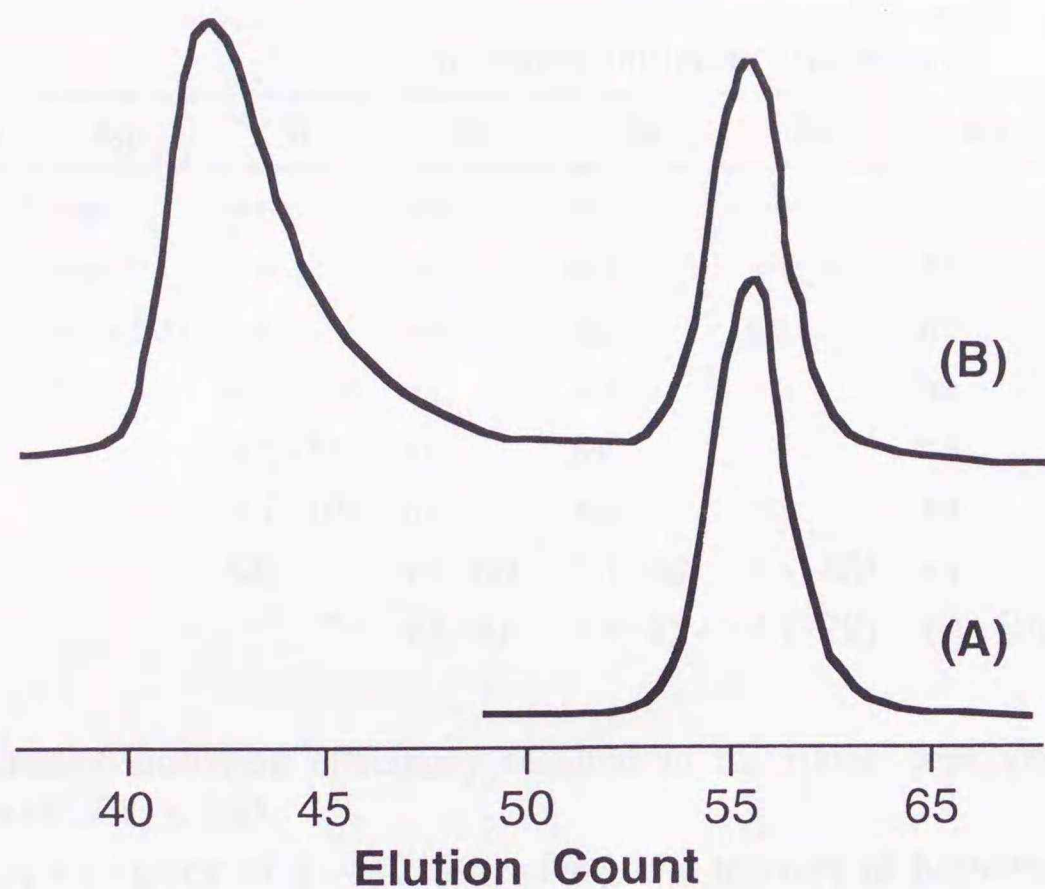
Figure 5-5. SEC curves of polymer **6a** at the first-stage polymerization (A) and of the copolymerization product after the second-stage polymerization of St in THF at −78 °C for 0.5 h (B) (Table 5-9, run 56): peak A, M_n(obsd) = 4,800, M_w/M_n = 1.06.

curve in the polymerization of St with living poly(**6a**), which is typical of the slow initiation with rapid consumption of the second monomer by the newly formed polystyryl anion. Less electrophilic Isp monomer was more difficult to polymerize with these living polymers. No crossover reactions of Isp occurred with living poly(**1a**) and poly(**6a**), and thereby homopolymers of **1a** and **6a** were virtually recovered. With living poly(**3a**), Isp was completely consumed, resulting in a mixture of the homopoly(**3a**) and block copolymer. The efficiency of the crossover reaction was estimated to be 50 %. In the case of living poly(**5a**), initiation of Isp showed the color change from yellow to red, but the red color slowly faded with time. Only a few units of Isp were detected in the products from ^{1}H NMR analysis. The SEC trace did not shift from the starting homopoly(**5a**), but broadened toward the higher molecular weight region. Proton abstraction from the C≡CCH$_2$ moiety in the polymer **5a** segment probably took place before the completion of the second-stage propagation of Isp. The presence of the C≡CCH$_2$ type pendant group is also a serious problem if one wishes to prepare the block copolymer of **5a** and diene monomers in this sequence. The low nucleophilicity of polystyryl anions derived from **1a**, **3a**, **5a**, and **6a** is clearly demonstrated from the initiation efficiencies of the crossover reaction.

81

Table 5-10. Summary of Block Copolymerization (Crossover Reaction) [a]

living polymer	monomer(initiation efficiency)							
	Isp	St	**3a**	**5a**	**1a**	**6a**	2VP	tBMA
poly(Isp)⁻	++	++	++	++	++	++	++	++
poly(St)⁻	++	++	++	++	++	++	++	++
poly(3a)⁻	+ (~50)	++	++	na	na	na	++	++
poly(5a)⁻	SR	+ (~70)	na	++	na	na	++	++
poly(1a)⁻	-	+ (~5)	na	na	++	na	++	++
poly(6a)⁻	-	+ (~10)	na	na	na	++	++	++
poly(2VP)⁻	-	SR	+ (~60)	+ (~60)	+ (~80)	++	++	++
poly(tBMA)⁻	-	-	+ (~5)	+ (~5)	+ (~20)	+ (~40)	-	++

[a] Key:

(++) quantitative initiation efficiency resulted in the block copolymers with narrow MWDs ($M_w/M_n < 1.2$)

(+) initiation efficiency of 5 – 80 % resulted in a mixture of homopolymer and block copolymer showing a bimodal and broad MWD

(SR) these polymeric products had multimodal and broad MWDs, probably due to the serious side reaction

(-) no reaction between the living polymer and the second monomer resulted in a quantitative recovery of the homopolymer of the first monomer

(na) not attempted.

The results of the sequential block copolymerization are then classified into four categories as summarized in Table 5-10 partly containing the result by Ishizone et al..[27]   The symbol (++) shows that a tailored block copolymer having a narrow MWD ($M_w/M_n = 1.03 - 1.15$), a predicted M_n, and a controlled composition is formed in quantitative yield.   The second one (+) indicates that a second-stage polymerization proceeds with a low initiation efficiency (5 - 80 %), generally resulting in a mixture of virtual homopolymer and block copolymer with ill-controlled structure.   The symbol SR indicates that some side reaction occurs after the addition of a second monomer, resulting in the formation of complicated products with multimodal and broad MWDs.   The last one (-) shows no crossover reaction at the second-stage.   From Table 5-10, one can easily choose the suitable additional order of the comonomers to synthesize a well-defined block copolymer.   Living polymers of St and Isp are useful macroinitiators for the polymerization of **1a**, **3a**, **5a**, and **6a** but neither living polymer of 2VP nor tBMA are effective.   On the other hand, tBMA and 2VP can be added to the living polymer of **1a**, **3a**, **5a**, and **6a** to prepare the block copolymers with well-regulated chain structures.   Only two combinations of **3a**/St and **6a**/2VP gave tailored block

copolymers regardless of a sequential additional order, indicating that the reactivity of **3a** and **6a** is comparable to that of St and 2VP, respectively.

The relative reactivities of monomers and the living polymers are clearly evaluated from Table 5-10. The monomer reactivity order increases as follows: Isp = St < **3a** ≅ **5a** < **1a** < **6a** = 2VP < tBMA. On the other hand, the relative nucleophilicity of the propagating carbanions is expressed in the following order: living poly(Isp) ≅ living polystyrene > living poly(**3a**) > living poly(**5a**) > living poly(**1a**) ≅ living poly(**6a**) ≅ living poly(2VP) > living poly(tBMA). As expected, the less reactive monomers produce the more reactive living polymers and vice versa.

Nakahama and Hirao have recently reported the block copolymerization of *para*-substituted styrenes containing electron-withdrawing groups.[34] The results of the sequential block copolymerization[27] showed the enhanced anionic polymerizability of these monomers and the lowered nucleophilicity of the propagating carbanions due to the strong electron-withdrawing effects of the substituents. The resonance stabilization of the terminal benzylic carbanion is also attained by the contribution of the extended π-conjugation system, including the C=O, C=N, S=O, and C≡N linkages.[30] The observed reactivity of **3a**, **5a**, **1a**, and **6a** also suggests the effect of the electron-withdrawing C≡C substituents, resulting in the enhanced anionic polymerizability of monomers and in the reduced nucleophilicity of the living polymers. The electron-withdrawing natures of the carbon-carbon triple bond such as C≡CH, C≡CMe, and C≡CPh moieties are supported from the reported Hammett σ_p values as 0.23, 0.03, and 0.16, respectively.[35] The C≡C bond attached to the styrene frameworks in **3a**, **5a**, **1a**, and **6a** also provides an π-resonance stabilization for the resultant active chain ends.[30]

As another useful parameter, the correlation between the reactivities of the *para*-substituted styrene containing the electron-withdrawing groups and their living polymers was previously clarified with the ^{13}C NMR chemical shifts of the β-carbon of the vinyl groups.[27] The β-carbon chemical shifts for **3a**, **5a**, **1a**, and **6a** appeared at downfields resonances of 114.2, 114.3, 114.8, and 114.8 ppm, respectively, while that of styrene itself is at 113.8 ppm. The order of these ^{13}C NMR chemical shifts is consistent with the relative reactivity of β-substituted ethynylstyrenes and the nucleophilicity of the living polymers. The downshifted chemical shifts also indicate the electron-withdrawing characters of the β-substituted ethynyl substituents such as C≡CBu^t, C≡CBu, C≡CSiMe$_3$, and C≡CPh. Small difference in the β-carbon chemical shifts ($\Delta\delta$ = 0.4 - 1.0) reflected the apparent relative reactivity of the employed monomers, supporting the effectiveness of this method. Thus, the availability of ^{13}C NMR chemical shifts of styrene derivatives to evaluate the reactivities of the monomers

and the resulting living polymers were successfully reconfirmed.

5-2-9. Deprotection of the Trimethylsilyl Group from Polymers of 1a-c.

As mentioned in the preceding section, the (trimethylsilyl)ethynyl functions in polymers **1a-c** were unchanged during the purification step of polymers. On the other hand, the Si-C bonds of the polymers were readily and completely cleaved.[36] For example, polymer **1a** was treated with $(C_4H_9)_4NF$ in THF at 0 °C for 1 h and the mixture was poured into methanol to precipitate the polymer. The yield was quantitative to poly(4-ethynylstyrene).

The IR spectrum of the resulting polymer showed new bands at 2109 and 3294 cm⁻¹ characteristic of $\nu_{C \equiv C}$ and ν_{C-H} along with complete disappearance of the absorptions at 759, 868, 1250, and 2159 cm⁻¹ due to δ_{Si-Me} and $\nu_{C \equiv CSiMe}$, respectively. The ^1H NMR spectrum of the polymer showed resonances assigned to poly(4-ethynylstyrene). A resonance due to the trimethylsilyl group at 0.24 ppm was no longer present, whereas the terminal ethynyl proton appeared instead at 3.04 ppm. The integral ratio of ethynyl to aromatic protons was exactly 1:4 as expected. The ^{13}C NMR also supported the result. Complete deprotection is achieved to afford poly(4-ethynylstyrene) under the conditions employed.

The SEC profile of the resulting poly(4-ethynylstyrene) demonstrated that the shapes of the peaks before and after deprotection were indeed identical. The sample after deprotection still possessed a narrow molecular weight distribution ($M_w/M_n = 1.04$) and eluted in a slightly lower molecular weight side than that of the parent polymer. This indicates no detectable side reactions leading to main-chain degradation and/or chain branching during the deprotection step. Similarly, polymers **1b** and **1c** were completely converted into poly(3-ethynylstyrene) and poly(2-ethnylstyrene). Their molecular weight distributions remained unchanged after deprotection, thus indicating no side reactions during the deprotection process.

5-2-10. Deprotection of the Trimethylsilyl Group from Polymer of 2.

The trimethylsilyl group was quantitatively deprotected from the polymer by treating it with $(C_4H_9)_4NF$ in THF at 0 °C for 1 h.[36] In the ^1H NMR spectrum, the signal of trimethylsilyl group at 0.15 ppm completely disappeared and a new signal due to the aliphatic acetylene proton clearly appeared at 2.0 ppm. The integral ratio of the proton signals clarified that the complete removal of the trimethylsilyl proton and the quantitative appearance of acetylene functionality were attained. Figure 5-6 shows the ^{13}C NMR spectra
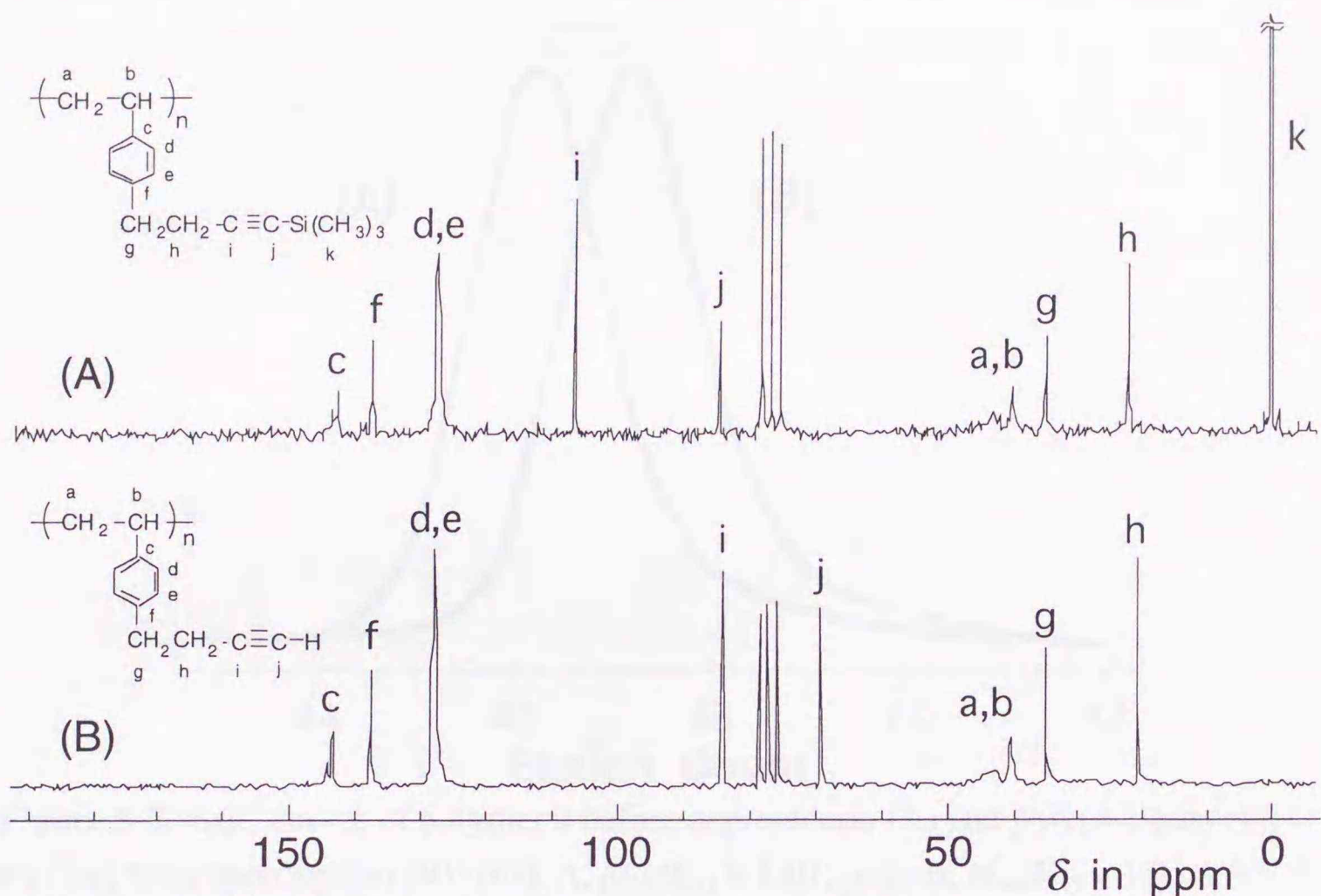
Figure 5-6. ^{13}C NMR spectra of poly[4-(4-trimethylsilyl-3-butynyl)styrene] (**2**) (A) and poly[4-(3-butynyl)styrene] (B) in CDCl$_3$.

of the polymers before deprotection (A) and after deprotection (B). The signal corresponding to the Me$_3$Si-C≡C moiety at 0.2 ppm completely disappears after deprotection. The two signals due to the protected acetylene carbons (C≡C-Si) at 85.0 and 107.0 ppm are no more observed, and alternatively new terminal acetylene signals at 69.0 and 84.1 ppm appear. In the IR spectrum, the characteristic absorptions at 1294 cm^{-1} (≡C-Si) and 2176 cm^{-1} (C≡C) were no longer present and new absorptions corresponding to $v_{C≡C}$ (2117 cm^{-1}) and $v_{≡C-H}$ (3298 cm^{-1}) appeared. These spectroscopic analyses strongly indicate that the deprotection of trimethylsilyl groups in polymer **2** proceeds quantitatively to give for poly[4-(3-butynyl)styrene] under the reaction conditions similar to those for polymer **1a**.

Figure 5-7 shows the SEC curves of the polymers before deprotection (A) and after deprotection (B). The SEC trace of the deprotected polymer eluted in a reasonable molecular weight region and shifted from that of polymer **2** toward the low molecular weight region, maintaining the narrow molecular weight distribution. No chain degradation and crosslinking occur during the course of the deprotection and polymer isolation to produce a well-defined poly[St-*b*-(4-(3-butynyl)styrene)].
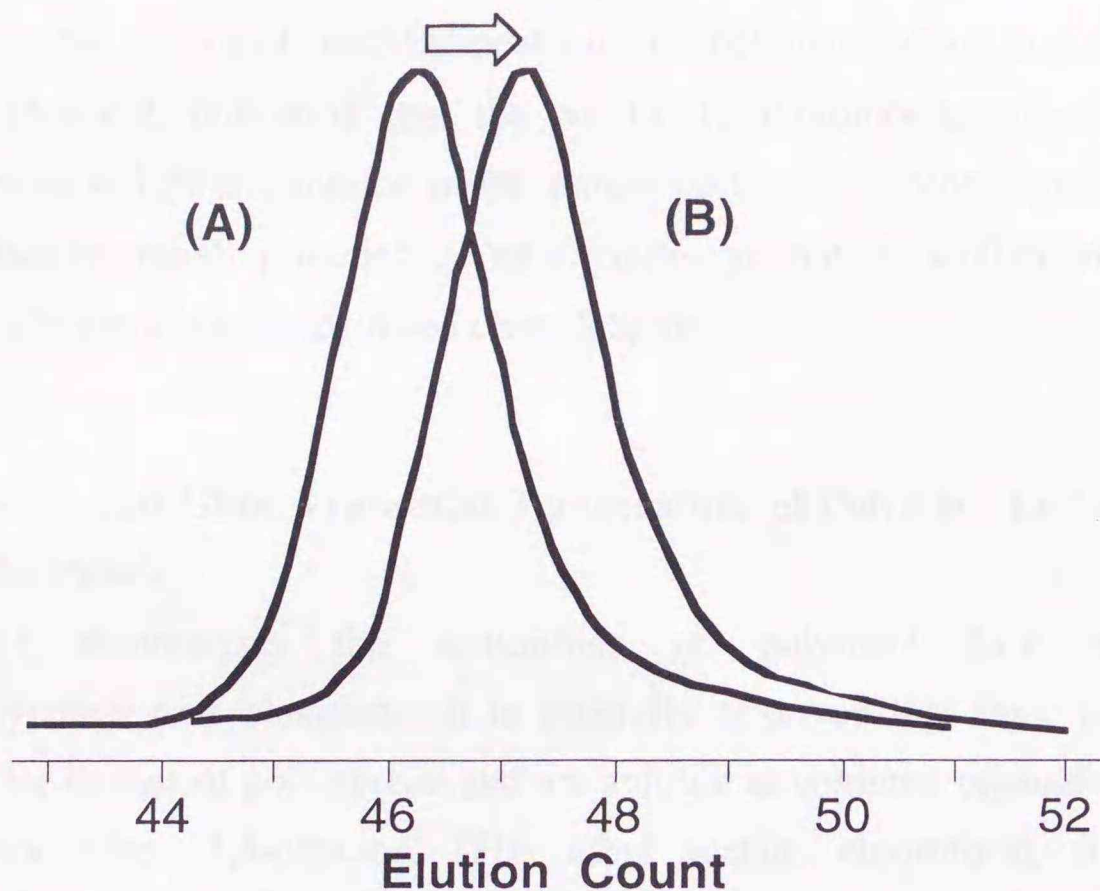
85

Figure 5-7. SEC curves of polymer **2** before deprotection (A) and poly(4-(3butynyl)-styrene) after deprotection (B): peak A, M_w/M_n = 1.07; peak B, M_w/M_n = 1.05.

5-2-11. Bromination of Poly(4-ethynylstyrene).

Since many reactions of the ethynyl group are known in organic synthesis, further chemical modifications of the poly(ethynylstyrene)s by means of these reactions are expected to derive other new functional polymers. Poly(4-ethynylstyrene) was allowed to react with a slight excess of bromine in chloroform at room temperature. The yield was almost quantitative on the formation of dibromo adduct. The IR spectrum of the polymer obtained showed that the two sharp bands at 3294 and 2109 cm^{-1} characteristic of $v_{\equiv C-H}$ and $v_{C\equiv C}$ disappeared completely, while new absorptions at 1654 cm^{-1} for $v_{C=CH}$, 1582 cm^{-1} for $v_{=CBr}$, and 689 cm^{-1} for v_{C-Br} appeared. In the ^{1}H NMR spectrum, a resonance for the ethenyl proton appeared at 7.80-5.80 ppm, though overlapped by aromatic protons. The signal at 3.04 ppm corresponding to the terminal ethynyl proton completely disappeared. The integral ratio of ethenyl and aromatic protons to methylene and methine protons of the main chain was exactly 5:3. ^{13}C NMR spectral analysis show no signals due to ethynyl carbons at 83.8 and 77.1 ppm at all but the resonances responsible for the dibromoethenyl group at 131.1 and 108.5 ppm and for *cis* and *trans* ArCBr=CHBr at 121.7 and 102.7 ppm, respectively. All signals in the spectrum are consistent with poly[4-(1,2-dibromoethenyl)styrene]. The C, H,

86

and Br percentages found by elemental analysis agreed well with those calculated.

Interestingly, the shapes of the SEC peaks of the polymers before and after bromination were almost identical, indicating that the poly[4-(1,2-dibromoethenyl)styrene] retained a narrow molecular weight distribution of the parent polymer. Accordingly, the bromination of poly(4-ethynylstyrene) provides a new route to obtain well-defined poly[4-(1,2-dibromoethenyl)styrene]s with regulated chain lengths.

5-2-12. Solubility and Glass Transition Temperature of Polymers 1a-c and Poly(4-, 3-, and 2-ethynylstyrene).

Table 5-11 summarizes the solubilities of polymers **1a-c** and the three poly(ethynylstyrene)s thus obtained. It is generally observed that these polymers show a solubility similar to that of polystyrene and are soluble in common organic solvents such as benzene, diethyl ether, 1,4-dioxane, THF, ethyl acetate, chloroform, and acetone, but insoluble in ethanol, methanol, and water. Interestingly, the solubility changed from the protected polymers to deprotected ones. For example, the polymers from **1a-c** are soluble in hexane but insoluble in DMSO. By contrast, the deprotected polymers showed the opposite

Table 5-11. Solubilities of Polymers **1a-c**, and Poly(4-, 3-, or 2-ethynylstyrene)[a]

solvent	poly(**1a**)	poly(**1b**)	poly(**1c**)	poly(4ESt)[b]	poly(3ESt)[c]	poly(2ESt)[d]
hexane	S	S	S	I	I	I
benzene	S	S	S	S	S	S
diethyl ether	S	S	S	S	S	S
ethyl acetate	S	S	S	S	S	S
chloroform	S	S	S	S	S	S
acetone	S	S	S	S	S	S
1,4-dioxane	S	S	S	S	S	S
THF	S	S	S	S	S	S
DMF	S	S	I	S	S	S
DMSO	I	I	I	S	S	S
ethanol	I	I	I	I	I	I
methanol	I	I	I	I	I	I
water	I	I	I	I	I	I

[a] S, soluble; I, insoluble.
[b] Poly(4-ethynylstyrene); $M_n = 12{,}000$.
[c] Poly(3-ethynylstyrene); $M_n = 13{,}000$.
[d] Poly(2-ethynylstyrene); $M_n = 13{,}000$.

87

Solubility to be soluble in DMSO but insoluble in hexane. Little difference in the solubility was observed among the polymers with different substituent positions.

The glass transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry. The results are summarized in Table 5-12. The T_g of polymer **1a** was higher than those of polymers **1b** and **1c**. The T_g increases with an increase of the molecular weight of the polymer. With poly(ethynylstyrene)s, their T_gs decrease to a large extent in comparison with their parent polymers.

Table 5-12. Glass Transition Temperatures (T_g) of Polymers **1a-c** and Poly(4-, 3-, or 2-ethynylstyrene)

polymer	$10^{-3}M_n$(obsd)	M_w/M_n	T_g (°C)
1a	10	1.04	156.6
1a	14	1.09	159.2
1a	21	1.13	165.0
1b	13	1.22	115.1
1b	21	1.39	118.9
1c	10	1.08	111.7
1c	19	1.10	118.4
4-ethymylstyrene	14	1.13	89.5
3-ethymylstyrene	14	1.39	69.2
2-ethymylstyrene	13	1.10	81.9

5-2-13. Solubility and Glass Transition Temperature of Polymer 2 and Poly[4-(3-butynyl) styrene].

Polymer **2** and poly[4-(3-butynyl)styrene] were white powders and could be cast into transparent films from solution. Table 5-13 summarizes the solubilities of polymer **2** and poly[4-(3-butynyl)styrene]. The polymers were soluble in a wide variety of organic solvents. Their solubility slightly changes after deprotection. The deprotected polymer was insoluble in hexane and soluble in DMSO.

The glass transition temperature (T_g) were 48 and 50 °C for polymer **2** and the deprotected poly[4-(3-butynyl)styrene], respectively. These T_gs are considerably lower than those of the corresponding *para*-substituted polymer **1a** ($T_g = 165$ °C) and the poly(4-ethynylstyrene) after deprotection ($T_g = 90$ °C). The introduction of two methylenes as spacer between the phenylene ring and the acetylene moiety apparently reduces the T_g of the polymers.

88

Table 5-13. Solubilities of Polymer **2** and Poly[4-(3-butynyl)styrene] [a]

solvent	polymer **2**	poly(4-(3-butynyl)styrene)
hexane	S	I
benzene	S	S
diethyl ether	S	S
ethyl acetate	S	S
chloroform	S	S
acetone	S	S
1,4-dioxane	S	S
THF	S	S
DMF	S	S
DMSO	I	S
ethanol	I	I
methanol	I	I
water	I	I

[a] I, insoluble;   S, soluble.

5-2-14. Solubility and Glass Transition Temperature of Polymers 3a-c, Polymers 5a-c and Polymer 6a.

All the polymers obtained were off-white powders and were stable in air for several months.   Table 5-14 summarizes the solubility of the polymers.   In particular, the polymers **3a-c** and polymers **5a-c** were readily soluble in various organic solvents and similar in solubility.   A small difference in the solubility was observed in terms of the substituent position.   DMF as a polar solvent was effective for *para-* and *meta*-substituted polymers, but ineffective for the polymers having *ortho* substituents.   The solubility of polymer **6a** having the phenylethynyl substituent was slightly different from that of polymers **3** and polymers **5**.

Table 5-15 shows the glass transition temperatures (T_g's) of the polymers measured by differential scanning calorimetry (DSC).   In general, the *para*-substituted polymers presented much higher T_g compared with those of the *meta* and *ortho* isomers.   Apparently, polymers **5** were lower in T_g than the corresponding polymer **3** analogues, which fact was caused by the high flexibility of the *n*-butylethynyl side chain, compared with the *tert*-butylethynyl moiety.   Polymer **6a** showed a high T_g that was comparable to those of polymer **1a** and polymer **3a**.   Thus, one can easily vary the T_g's of polystyrenes bearing the C≡CR functionalities from 30 to 170 °C by changing the C≡CR substituents and/or the substituent position.

89

Table 5-14. Solubility of Polymers **3-6a** and Related Polymers[a]

solvent	poly(3a)	poly(3b)	poly(3c)	poly(5a)	poly(5b)	poly(5c)	poly(6)	poly(1a)	poly(2)	polySt
hexane	S	S	S	S	S	S	I	S	S	I
benzene	S	S	S	S	S	S	S	S	S	S
Et$_2$O	S	S	S	S	S	S	I	S	S	S
AcOEt	S	S	S	S	S	S	S	S	S	S
CHCl$_3$	S	S	S	S	S	S	S	S	S	S
acetone	S	S	S	S	S	S	S	S	S	S
DOX[b]	S	S	S	S	S	S	S	S	S	S
THF	S	S	S	S	S	S	S	S	S	S
DMF	S	S	I	S	S	I	S	S	S	S
DMSO	I	I	I	I	I	I	I	I	I	I
EtOH	I	I	I	I	I	I	I	I	I	I
MeOH	I	I	I	I	I	I	I	I	I	I
water	I	I	I	I	I	I	I	I	I	I

[a] Key:
   S, soluble;   I, insoluble
[b] 1,4-dioxane

Table 5-15. Glass Transition Temperatures (T_g) of Polymers **3-6a** and Related Polymers[a]

polymer	$10^{-3}M_n$(obsd)	M_w/M_n	T_g, °C
3a	9.7	1.07	169
3a	24	1.05	174
3b	14	1.14	113
3c	9.7	1.14	109
5a	10	1.07	75
5a	20	1.10	75
5b	12	1.09	35
5b	21	1.14	40
5c	11	1.10	33
5c	17	1.13	37
6a	17	1.09	163
1a	21	1.13	165
2	11	1.09	48

[a] T_g was measured in the second heating scan at a rate of 20 °C·min^{-1}.

5-3. Conclusions

The well-defined poly(ethynylstyrene)s were synthesized by the anionic living polymerization of ethynylstyrenes through the trimethylsilyl protection for terminal ethynyl functions, followed by complete deprotection. As a result, poly(4-ethynylstyrene), poly(3-ethynylstyrene), and poly(2-ethynylstyrene) were obtained by this method. Some novel block copolymers with these poly(ethynylstyrene) segments are also synthesized. In addition, the bromination of poly(4-ethynylstyrene) proceeded quantitatively to provide a well-defined poly[4-(1,2-dibromoethenyl)styrene] with a narrow molecular weight distribution.

The well-defined poly[4-(3-butynyl)styrene] was obtained by the anionic living polymerization in a manner similar to the synthesis of poly(ethynylstyrene). Novel block copolymer with this poly[4-(3-butynyl)styrene] segment was also synthesized. In particular, the polymerization temperature was important in various kinds of the living anionic polymerization condition for realizing the controlled block copolymerization of **2**.

The living anionic polymerizations of novel functional monomers, (*tert*-butylethynyl)styrenes (**3a-c**), (butylethynyl)styrenes (**5a-c**), and 4-(phenylethynyl)styrene (**6a**), succeeded to give well-defined polymers with narrow MWDs and tailored M_n's. The polymerization conditions such as temperature and solvent were important for realizing the controlled anionic polymerization of these monomers. The enhanced anionic polymerizability of **3-6a** as styrene derivatives which were stimulated with the electron-withdrawing $C \equiv CR$ groups was clarified from the results of the sequential block copolymerization. The difference in the polymerizability of **3-6a** could be well accounted for by the ^{13}C NMR chemical shifts of the vinyl β-carbons of the monomers.

5-4. Experimental Section

Materials. Styrene, α-methylstyrene, methyl methacrylate, and isoprene were washed with 10% NaOH and water and were dried over $MgSO_4$ overnight. After filtration, they were dried over CaH_2 and distilled under a nitrogen atmosphere. Styrene and α-methylstyrene were distilled on a high-vacuum line after addition of appropriate amounts of benzylmagnesium chloride. Methyl methacrylate was distilled over trihexylaluminum on a high-vacuum line. Isoprene was distilled from its n-butyllithium solution on a high-vacuum line. 2-Vinylpyridine was distilled twice over KOH and then over CaH_2 under a nitrogen atmosphere. It was distilled on a high-vacuum line after addition of a small amount of n-butyllithium. These monomers were diluted with tetrahydrofuran and divided into several ampules with break-seals on the vacuum line. Tetrahydrofuran (THF) was refluxed over a sodium wire and distilled from its $LiAlH_4$ solution under a nitrogen atmosphere. Just before use, THF was distilled from its sodium naphthalenide solution on the vacuum line.

Initiators. Commercially available s-BuLi (1.0 M cyclohexane solution) and n-BuLi (1.6 M hexane solution) were diluted with n-heptane. Potassium naphthalenide was prepared from naphthalene and potassium metal in dry THF at room temperature. Cumyl potassium was prepared by the reaction of cumyl methyl ether and sodium-potassium alloy in THF at room temperature. (Diphenylmethyl)potassium was prepared by the reaction of potassium naphthalenide and a 1.5 molar excess of diphenylmethane in THF at room temperature for 3 days. Oligo(α-methylstyryl)lithium and -dipotassium were freshly prepared just prior to the polymerization from s-BuLi or potassium naphthalenide and a 2-4 M quantity of α-methylstyrene at 20 °C for 1min and then at -78 °C for 10 min. These initiators were stored at -30 °C in ampules equipped with breakseals. The concentration of initiators was determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.[3]

Monomer Purification. The liquid monomers, **1a–c**, **2**, **3a-c** and **5a-c**, were purified by fractional distillations over CaH_2 in vacuo and sealed off under a degassed condition (10^{-6} mmHg) in an apparatus equipped with a breakseal. After adding 3-5 mol% of benzylmagnesium chloride or phenylmagnesium chloride in THF into the monomer through the break-seal, the mixture was stirred for 0.5 h at room temperature and then distilled on a vacuum line into the break-seal-attached round-bottomed flask prewashed with sodium naphthalenide in THF. The monomer was diluted to 0.2-0.5 M solutions with THF and stored at -30 °C until ready for polymerization. For anionic polymerization in benzene, **2**

was distilled over calcium hydride and diluted with dry benzene. For the polymerization in benzene, **5a** was distilled from Bu$_2$Mg solution in heptane and diluted with dry benzene. The solid monomer, **6a**, was purified by the recrystallizations from methanol and hexane and finally distilled from CaH$_2$ under high vacuum condition. The monomer solutions (ca. 0.5 M) were stored at -30 °C until ready to use for the polymerization.

Homopolymerization. The polymerizations in THF were carried out at -78 °C for 0.5 - 1 h with shaking under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with break-seals in the usual manner. The desired charge of monomer in THF was added to the THF solution of the initiator with strong shaking. Both the solutions must be kept at -78 °C. Polymerization of **5a** and **2** in benzene was similarly attempted with s-BuLi at 0 - 40 °C. All polymerizations were terminated with a few drops of degassed methanol after an appropriate time. The polymer was then precipitated by pouring the mixture into a large amount of methanol, and purified by reprecipitation twice from THF solution to methanol and freeze-dried from the benzene solution.

a) Polymer **1a** :

^{1}H NMR (90 MHz, CDCl$_3$)

δ 7.35-7.00 (br s, 2 H, Ar), 6.60-6.10 (br s, 2 H, Ar), 2.10-0.90 (m, 3 H, CH$_2$CH), 0.24 (s, 9 H, SiCH$_3$).

^{13}C NMR (22.5 MHz, CDCl$_3$)

δ 145.3 (Ar, C1), 132.1 (Ar, C3), 127.6 (Ar, C2), 120.8 (Ar, C4), 105.5 (ArC≡), 93.7 (≡CSi), 43.6 (CH), 40.6 (CH$_2$), 0.2 (SiCH$_3$).

IR (KBr, cm^{-1})

759, 868, 1250 (CSi), 2159 (C≡C).

b) Polymer **1b** :

^{1}H NMR (90 MHz, CDCl$_3$)

δ 7.55-6.05 (m, 4 H, Ar), 2.30-0.80 (m, 3 H, CH$_2$CH), 0.21 (s, 9 H, SiCH$_3$).

^{13}C NMR (22.5 MHz, CDCl$_3$)

δ 144.8 (Ar, C1), 130.9 (Ar, C2), 130.0 (Ar, C4 and C5), 128.2 (Ar, C6), 123.0 (Ar, C3), 105.7 (ArC≡), 93.6 (≡CSi), 43.0 (CH), 40.4 (CH$_2$), 0.3 (SiCH$_3$).

IR (KBr, cm^{-1})

759, 842, 1250 (CSi), 2156 (C≡C).

c) Polymer **1c** :

^{1}H NMR (90 MHz, CDCl$_3$)

δ 7.65-6.25 (br s, 4 H, Ar), 3.25-2.10 (m, 1 H, CH), 1.90-0.80 (m, 2 H, CH$_2$),

-0.03 (br s, 9 H, SiCH$_3$).

^{13}C NMR (22.5 MHz, CDCl$_3$)

δ 147.5 (Ar, C1), 133.3 (Ar, C3), 128.5 (Ar, C5), 126.9 (Ar, C6), 125.1 (Ar, C4),

122.5 (Ar, C2), 104.7 (ArC≡), 97.2 (≡CSi), 47.0 (CH), 40.8 (CH$_2$), 0.3 (SiCH$_3$).

IR (KBr, cm^{-1})

841, 868, 1250 (CSi), 2154 (C≡C).

d) Polymer **2** :

^{1}H NMR (90 MHz, CDCl$_3$):

δ 0.15 (s, 9H, Si(CH$_3$)$_3$), 0.8-1.9 (m, 3H, CH$_2$CH),

2.1-3.0 (broad, 4H, ArCH$_2$CH$_2$C≡), 5.8-7.3 (m, 4H, Ar).

^{13}C NMR (23 MHz, CDCl$_3$):

δ 0.3 (Si(CH$_3$)$_3$), 22.3 (CH$_2$C≡), 35.0 (ArCH$_2$), 40-43 (CH$_2$CH), 85.0 (SiC≡),

107.0 (CH2C≡), 127.9 (Ar, C2 and C3), 137.9 (Ar, C4), 143.3 (Ar, C1).

IR (neat, cm^{-1}): 759, 841, and 1250 (≡CSi), 2176 (C≡C).

e) Polymer **3a** :

^{1}H NMR (CDCl$_3$, 300 MHz)

δ 1.33 (s, 9H, CH$_3$), 0.9 - 1.9 (m, 3H, CH$_2$CH), 6.2 - 7.3 (m, 4H, Ar).

^{13}C NMR (CDCl$_3$, 75 MHz)

δ 28.4 (CCH$_3$), 31.6 (CH$_3$), 40 - 43 (CH$_2$CH), 79.6 (Ar-C≡), 98.1 (Ar-C≡C),

121.8 (Ar, C4), 127.8 (Ar, C2), 131.9 (Ar, C3), 144.6 (Ar, C1).

IR (KBr, cm^{-1})

833, 1203, 1292, 1362, 1451, 1475, 1501, 2237 (C≡C), 2968.

f) Polymer **3b** :

^{1}H NMR (CDCl$_3$, 400 MHz)

δ 1.32 (s, 9H, CH$_3$), 0.6 - 2.2 (m, 3H, CH$_2$CH), 5.9 - 7.5 (m, 4H, Ar).

^{13}C NMR (CDCl$_3$, 100 MHz)

δ 28.0 (CCH$_3$), 31.3 (CH$_3$), 39 - 45 (CH$_2$CH), 79.6 (Ar-C≡), 97.8 (Ar-C≡C),

123.9 (Ar, C3), 128.0 (Ar, C6), 129.5 (Ar, C4 and C5), 130.6 (Ar, C2),

145.1 (Ar, C1).

IR (KBr, cm^{-1})

793, 893, 1219, 1294, 1362, 1456, 1473, 1597, 2220 (C≡C), 2970.

g) Polymer **3c** :

    ^{1}H NMR (CDCl$_3$, 400 MHz)

        δ 1.34 (s, 9H, CH$_3$), 0.6 - 3.2 (m, 3H, CH$_2$CH), 6.2 - 7.4 (m, 4H, Ar).

    ^{13}C NMR (CDCl$_3$, 100 MHz)

        δ 27.9 (C̲CH$_3$), 31.1 (CH$_3$), 35 - 37 (CH$_2$CH), 78.0 (Ar-C≡), 100.8 (Ar-C≡C̲),

        123.4 (Ar, C2), 124.6 (Ar, C6), 126.8 (Ar, C4 and C5), 132.8 (Ar, C3),

        147.6 (Ar, C1).

    IR (KBr, cm^{-1})

        1203, 1297, 1362, 1444, 1475, 2235 (C≡C), 2968.

h) Polymer **5a** :

    ^{1}H NMR (CDCl$_3$, 300 MHz)

        δ 0.95 (t, 3H, CH$_3$), 1.1 - 1.9 (m, 7H,   CH$_2$CH and CH̲$_2$CH̲$_2$CH$_3$),

        2.40 (s, 2H, ≡CCH$_2$), 6.2 - 7.3 (m, 4H, Ar).

    ^{13}C NMR (CDCl$_3$, 75 MHz)

        δ 13.7 (CH$_3$), 19.3 (≡CC̲H$_2$), 22.2 (C̲H$_2$CH$_3$), 31.2 (≡CCH$_2$C̲H$_2$), 81.0 (Ar-C≡),

        89.5 (Ar-C≡C̲), 121.7 (Ar, C4), 127.6 (Ar, C2), 131.5 (Ar, C3), 144.4 (Ar, C1).

    IR (KBr, cm^{-1})

        758, 833, 1107, 1217, 1329, 1454, 1504, 2229 (C≡C), 2956.

i) Polymer **5b** :

    ^{1}H NMR (CDCl$_3$, 300 MHz)

        δ 0.93 (s, 3H, CH$_3$), 1.1 - 2.2 (m, 7H, CH$_2$CH and CH̲$_2$CH̲$_2$CH$_3$),

        2.37 (s, 2H, ≡CCH$_2$), 6.2 - 7.3 (m, 4H, Ar).

    ^{13}C NMR (CDCl$_3$, 75 MHz)

        δ 13.8 (CH$_3$), 19.2 (≡CC̲H$_2$), 22.2 (C̲H$_2$CH$_3$), 31.0 (≡CCH$_2$C̲H$_2$), 81.0 (Ar-C≡),

        89.7 (Ar-C≡C̲), 123.8 (Ar, C3), 126 - 131 (Ar, C6, C5, C2, and C4), 145.0 (Ar, C1).

    IR (KBr, cm^{-1})

        792, 893, 1429, 1481, 1599, 2228 (C≡C), 2931.

j) Polymer **5c** :

    ^{1}H NMR (CDCl$_3$, 90 MHz)

        δ 0.82 (s, 3H, CH$_3$), 0.9 (m, 7H, CH$_2$CH and CH̲$_2$CH̲$_2$CH$_3$),

        2.66 (s, 2H, ≡CCH$_2$), 6.5 - 7.3 (m, 4H, Ar).

    ^{13}C NMR (CDCl$_3$, 22.5 MHz)

        δ 13.7 (CH$_3$), 19.2 (≡CC̲H$_2$), 22.1 (C̲H$_2$CH$_3$), 30.9 (≡CCH$_2$C̲H$_2$), 79.1 (Ar-C≡),

        92.8 (Ar-C≡C̲), 123.4 (Ar, C2), 124.5 (Ar, C6), 126.7 (Ar, C4 and C5),

131.7 (Ar, C3), 148.4 (Ar, C1);

IR (KBr, cm^{-1})

751, 942, 1029, 1104, 1192, 1378, 1445, 1484, 2228 (C≡C), 2933.

k) Polymer **6a** :

^{1}H NMR (CDCl$_3$, 90 MHz)

δ 1.0 - 2.2 (CH$_2$CH), 6.3 - 7.6 (m, 9H, Ar);

^{13}C NMR (CDCl$_3$, 22.5 MHz)

δ 40 - 44 (CH$_2$CH), 89.7 (Ph-C≡), 91.6 (Ph-C≡C̲), 120.9 (Ar, C4),

123.6 (Ar', C1), 128.3 (Ar, C2, Ar', C3 and C4), 131.7 (Ar, C3 and   Ar', C2),

145.8 (Ar, C1);

IR (KBr, cm^{-1})

753, 831, 1443, 1509, 1596, 2214 (C≡C), 2921.

Block Copolymerization. Block copolymerizations were carried out by the sequential addition of two different monomers. The first-stage polymerization was carried out in THF at -78 °C and somewhat sampled to determine the characteristics. The second block was prepared by adding an appropriate amount of second monomer to the living polymer produced in the first-stage polymerization. After quenching with degassed methanol, the polymer was precipitated in methanol, purified by reprecipitation twice, and then freeze-dried.

Deprotection of Trimethylsilyl-protected Polymers. Polymer **1a** (0.320 g, 1.6 mmol based on a monomer unit) was dissolved in dry THF (10 mL), and the solution was cooled at 0 °C. (C$_4$H$_9$)$_4$NF in THF (1 M, 3.3 mL) was added to the solution, and the mixture was stirred at 0 °C for 1 h. The polymer was precipitated in methanol and purified twice by reprecipitation using a THF-methanol system. The yield of polymer was quantitative. The polymer was identified as poly(4-ethynylstyrene).

The deprotection of trimethylsilyl groups from polymers **1b**, **1c**, and **2** was carried out by the procedure similar to that for polymer **1a**.

a) Poly(4-ethynylstyrene) :

^{1}H NMR (90 MHz, CDCl$_3$)

δ 7.40-6.20 (m, 4 H, Ar), 3.04 (s, 1 H, C≡CH), 2.30 - 0.70 (m, 3 H, CH$_2$CH).

^{13}C NMR (22.5 MHz, CDCl$_3$)

δ 145.8 (Ar, C1), 132.1 (Ar, C3), 127.6 (Ar, C2), 119.9 (Ar, C4), 83.8 (ArC≡),

77.1 (≡CH), 43.0 (CH), 40.8 (CH$_2$).

IR (KBr, cm^{-1})

2109 (C≡C), 3294 (≡CH).

b) Poly(3-ethynylstyrene) :

^{1}H NMR (90 MHz, CDCl$_3$)

δ 7.55-5.95 (m, 4 H, Ar), 3.01 (s, 1 H, C≡CH), 2.30 - 0.60 (m, 3 H, CH$_2$CH).

^{13}C NMR (22.5 MHz, CDCl$_3$)

δ 144.7 (Ar, C1), 131.2 (Ar, C2), 130.1 (Ar, C4 and C5), 128.3 (Ar, C6),

122.0 (Ar, C3), 84.0 (ArC≡), 77.1 (≡CH), 43.0 (CH), 40.5 (CH$_2$).

IR (KBr, cm^{-1})

2108 (C≡C), 3293 (≡CH).

c) Poly(2-ethynylstyrene) :

^{1}H NMR (90 MHz, CDCl$_3$)

δ 7.10-6.20 (m, 4 H, Ar), 3.35 - 2.00 (m, 1 H, CH), 2.54 (s, 1 H, C≡CH),

2.00 - 0.80 (br s, 2 H, CH$_2$);

^{13}C NMR (22.5 MHz, CDCl$_3$)

δ 148.8 (Ar, C1), 132.4 (Ar, C3), 128.6 (Ar, C5), 127.2 (Ar, C6), 125.2 (Ar, C4),

121.6 (Ar, C2), 82.6 (ArC≡), 80.5 (≡CH), 41.6 (CH), 37.7 (CH$_2$);

IR (KBr, cm^{-1})

2104 (C≡C), 3296 (≡CH).

d) Poly[4-(3-butynyl)styrene] :

^{1}H NMR (90 MHz, CDCl$_3$):

δ 0.5 - 3.2 (overlapping, 7H, CH$_2$CH and ArCH$_2$CH$_2$C≡), 2.0 (s, 1H, ≡CH),

5.8 - 7.1 (m, 4H, Ar).

^{13}C NMR (23 MHz, CDCl$_3$)

δ 20.7 (CH$_2$C≡), 34.6 (ArCH$_2$), 40-43 (CH$_2$CH), 69.0 (≡CH), 84.1 (CH$_2$C≡),

127.9 (Ar, C2 and C3), 137.7 (Ar, C4), 143.4 (Ar, C1).

IR (KBr, cm^{-1})

2117 (C≡C), 3298 (≡C-H).

Bromination of Poly(4-ethynylstyrene).[37]   To a stirred solution of poly(4-ethynylstyrene) (0.120 g, 0.94 mmol based on the ethynylstyrene unit) in CHCl$_3$ (12 mL) was added dropwise bromine in CHCl$_3$ (0.09 M, 12 mL) at 25 °C.   The mixture was stirred for an additional 30 min at room temperature.   The polymer was precipitated in methanol and purified by thrice reprecipitation using THF-methanol system.

97

^{1}H NMR (90 MHz, CDCl$_3$)

    δ 7.80-5.80 (overlapping m, 5 H, Ar and =CHBr), 2.70-0.80 (m, 3 H, CH$_2$CH);

^{13}C NMR (22.5 MHz, CDCl$_3$)

    δ 146.1 (Ar, C1), 136.0 (Ar, cis C4), 134.8 (Ar, *trans* C4), 131.1 (*cis* ArCBr=),

    129.5 (Ar, C3), 127.8 (Ar, C2), 121.7 (*trans* ArCBr=), 108.5 (*cis* =CHBr),

    102.7 (*trans* =CHBr), 43.2 (CH), 40.7 (CH$_2$);

IR (KBr, cm^{-1})

    689 (CBr), 1582 (=CBr), 1654 (C=CH).

Elemental analysis

    Anal. Calcd for (C$_{10}$H$_8$Br$_2$)$_{3.08}$(C$_9$H$_{10}$)$_{0.322}$: C, 43.75; H, 3.04; Br, 53.22.

    Found: C, 43.71; H, 3.10; Br, 53.21.

    The C$_9$H$_{10}$ shown here was the residue of the initiator.

Measurements.   Infrared (IR) spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (90 MHz ^{1}H and 22.5 MHz ^{13}C), a JNM-EX400 (400 MHz ^{1}H and 100 MHz ^{13}C), and a Bruker DPX300S (300 MHz ^{1}H and 75 MHz ^{13}C) in CDCl$_3$. Size-exclusion chromatograms (SEC) were obtained at 40 °C with a Toyo Soda HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, G300H$_{XL}$) with ultraviolet (254 nm) and refractive index detection.   THF was used for the carrier solvent at a flow rate of 1.0 mL·min^{-1}.   Vapor pressure osmometry (VPO) measurement was made with a Corona 117 instrument in benzene solution with a highly sensitive thermoelectric couple and equipment of very exact control of temperature.   The number-average molecular weights (M_n) up to 10^5 were obtained within an analytical error of ±5%.   Laser light scattering measurements for weight-average molecular weight (M_w) determination were performed at 25 °C with an Ootsuka Electronics SLS-600R instrument in a benzene solution.   The glass transition temperature (T_g) was measured by differential scanning calorimetry using a Seiko Instruments SSC/5200.   The samples were first heated to 200 °C, cooled rapidly to room temperature, and then scanned again at a rate of 20 °C·min^{-1}.

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Chapter 6. Fixed Crosslink Formation and Viscoelasticity of Polystyrene Networks

6-1. Introduction

Viscoelastic properties of amorphous polymers above the glass transition temperature (T_g) have been investigated by many authors over a wide range of frequency and temperature to clarify the underlying relaxation mechanism from molecular motion and molecular structure viewpoints. According to Tobolsky and coworkers,[1] the relaxation spectrum ($H(\tau)$) vs. relaxation time (τ) for the stress relaxation data of dispersed polyisobutylene consists of two relaxation parts of a wedge spectrum in the range of 10^{-8} to 10^{-2} sec, and a box spectrum from 10^0 to 10^5 sec. The wedge spectrum is characterized by a slope -1/2 of $\log H(\tau)$ *vs.* $\log\tau$ in the Rouse spectrum, and a box spectrum with a constant value of $\log H(\tau)$ vs. $\log\tau$, depending on M. The former is attributed to the intrachain relaxation of the configurational change in segmental chains between junctions, and the latter to the interchain relaxation of the relative displacement of many chains closely related to the annihilation and creation of junctions and the viscous flow of polymers. Doi built up the reptation theory of deGennes and predicted that the spectrum would scale as $\tau^{1/2}$ for a monodisperse polymer in a long τ region, in contrast to the box spectrum.[2,3] The $\tau^{-1/2}$ wedge - box spectrum and the $\tau^{-1/2}$ wedge - $\tau^{1/2}$ wedge spectrum are observed with most amorphous polymers, but they are not in quantitative agreement with the respective experimental data on dynamic moduli. Each relaxation spectrum seems to depend strongly on the chemical structure of the chain and the network structure of the junctions. Therefore, it is important to quantitatively determine the crosslink structure and the number of junctions in amorphous polymers. In this Chapter, the chain crosslinking formation of ethynyl groups in the 8/92 mol% random copolymer of 4-ethynylstyrene and styrene was quantitatively clarified and investigated the effect of its fixed crosslinking junctions on the wedge-box relaxation spectrum and the rubber elasticity from the experimental data on the dynamic Young moduli.

6-2. Results and Discussions

6-2-1. Ethynyl Crosslinking Formation in the 8/92 mol-% Random Copolymer of 4-Ethynylstyrene and Styrene.
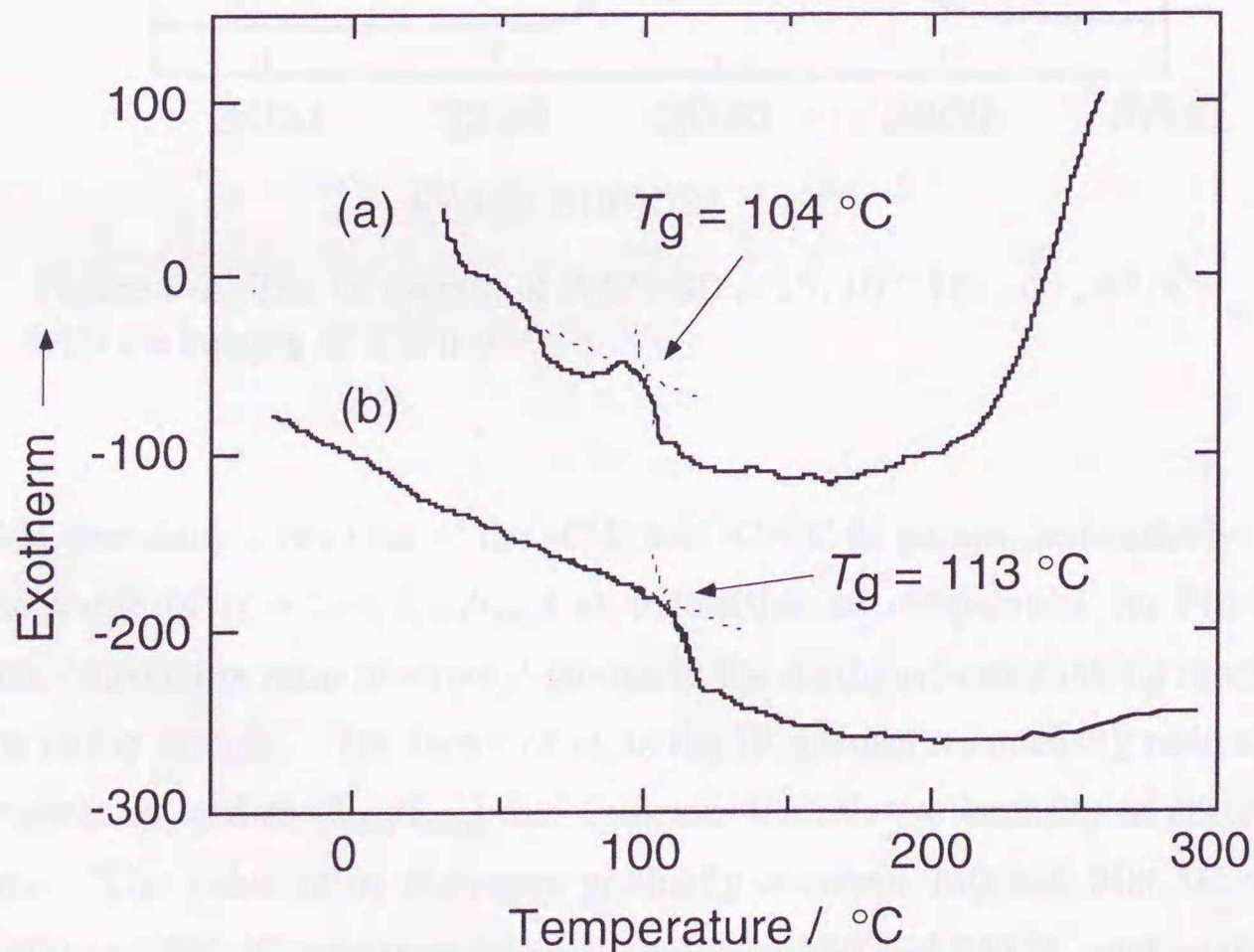
The DSC thermogram of the 8/92 mol% random copolymer of 4-ethynylstyrene and styrene, P(ESt/St), for the first heating process and the second heating one are shown in Figure 6-1. At the first heating, a variation of the DSC baseline and its slope in the temperature region from 25 to about 100 °C in trace (a) for P(ESt/St) occurs due to experimental error in the several DSC measurements, but the weight loss of the sample was not significant below 260 °C under N_2 gas. A glass transition behavior is observed at 104 °C, referred to as the glass transition temperature T_g = 104 °C, and a large exothermic reaction takes place above 200 °C. At the second heating, there is only the glass transition temperature at a higher T_g = 113 °C by 9 °C, and an exotherm slightly takes place above 260 °C. Figure 6-2 shows the IR spectra of P(ESt/St) at 25, 107, 167 and 347 °C on heating at 3 °C·min⁻¹. When the temperature increases, the IR absorption intensity I_{2890} at 2890 cm⁻¹ does not change, and the I_{3340} at 3340 cm⁻¹ eventually disappears. The two peaks are caused

Figure 6-1. The DSC thermograms of the 8/92 mol% random copolymer of 4-ethynylstyrene and styrene, P(ESt/St) in the first heating process (a) and the second heating one (b).
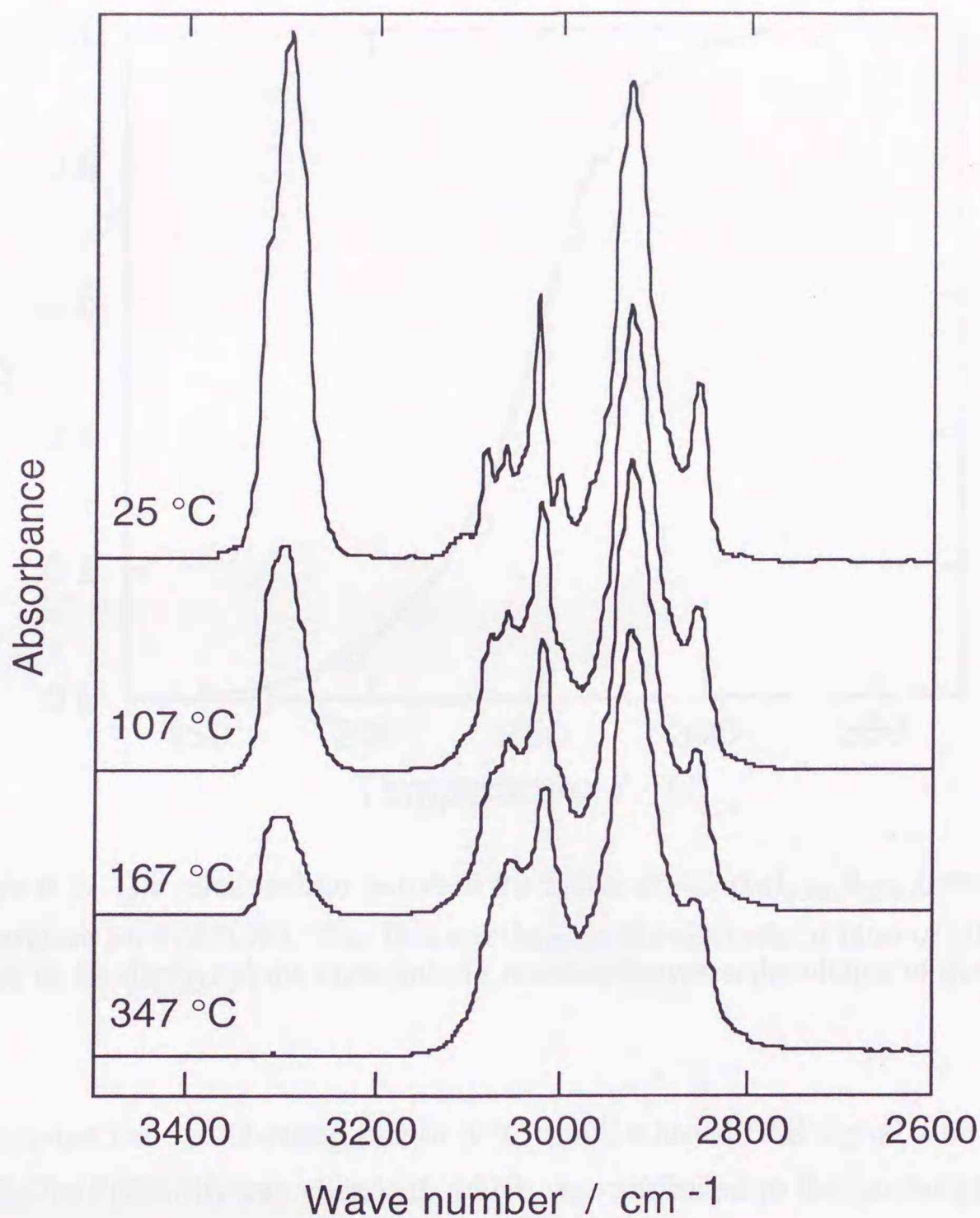
Figure 6-2. The IR spectra of P(ESt/St) at 25, 107, 167 and 347 °C with the heating of 3 K·min⁻¹.

by the C-H stretching vibrations of the $-CH_2$ and $-C{\equiv}C-H$ groups, respectively. Figure 6-3 shows the value of $\alpha = 1-\alpha_0(I_{3340}/I_{2890})$ as a function of temperature for P(ESt/St), which denotes the conversion ratio of ethynyl groups in the diethynyl crosslinking reaction between the chains in the sample. The factor of α_0 is the IR absorption intensity ratio of I_{3340}/I_{2890} at room temperature, and α_0 (I_{3340}/I_{2890}) then indicates the relative intensity of ethynyl groups in the sample. The value of α increases gradually between 150 and 200 °C, very rapidly between 200 and 250 °C, and then gradually between 250 and 340 °C, and attains a constant $\alpha = 1$ above 340 °C. Hereafter, the three temperature regions for the increase in α are referred to as the early, intermediate and final stages, respectively. No significant weight loss of the sample was observed between 150 and 347 °C under N_2. On the other hand, in
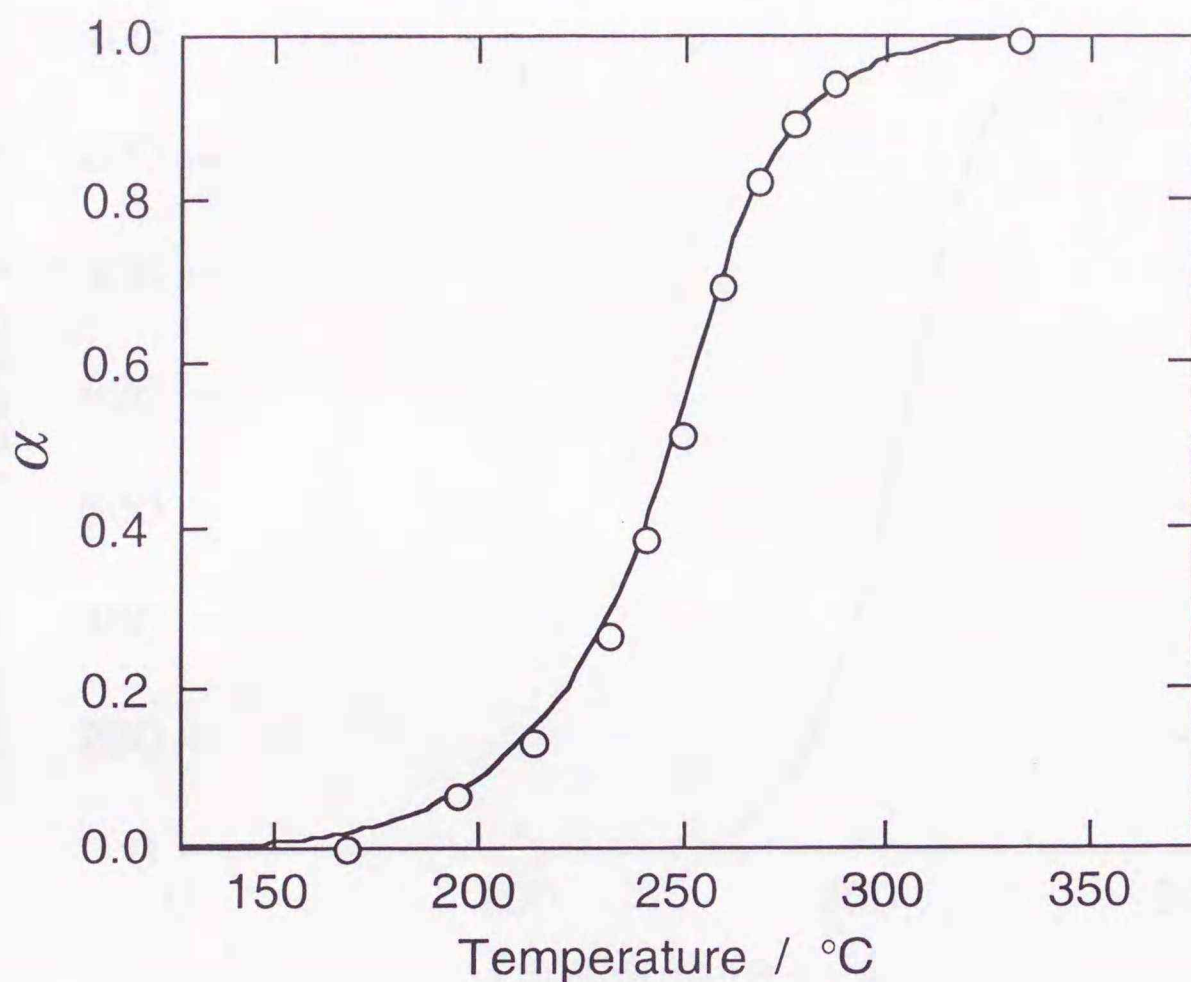
Figure 6-3. The relationships between the factor $\alpha\,(=1-\alpha_0(I_{3340}/I_{2890}))$ and the temperature for P(ESt/St). The factor α denotes the conversion ratio of ethynyl groups in the diethynyl the crosslinking reaction between the chains in the sample.

the ESR measurement at a heating rate of 5 °C·min^{-1}, a broad ESR signal with a line width of about 20 Gs for P(ESt/St) was observed, which was attributed to the exchange broadening of free radicals on the conjugated junctures formed chemically. The spin concentration ($S_{\text{free radical}}$) began to increase at 170 °C, and became maximal at 260 °C. The maximal value of $S_{\text{free radical}}$ increased by 1.3 x 10^3 times that at room temperature as shown in Figure 6-4. The experimental findings lead to the conclusion that the large DSC exotherm of P(ESt/St) above 200 °C at the first heating is due to the radically chemical reaction of each ethynyl group between the chains to give the completely crosslinked sample of P(ESt/St) abbreviated as CL-P(ESt/St) whose glass transition temperature of T_g = 113 °C is higher than that of T_g = 104 °C for P(ESt/St).

The crosslinking structure in the copolymer is formed homogeneously by a collision radical reaction of two ethynyl groups between the chains in P(ESt/St) due to the macro-Brownian motion of the segments and the chains above T_g. The reaction rate of two ethynyl groups in a homogeneous radical reaction at a constant temperature is given by

$$-d\alpha/dt = k\alpha^n, \quad (1)$$

where n denotes the order of reaction. The coefficient k denotes the rate constant, displaying
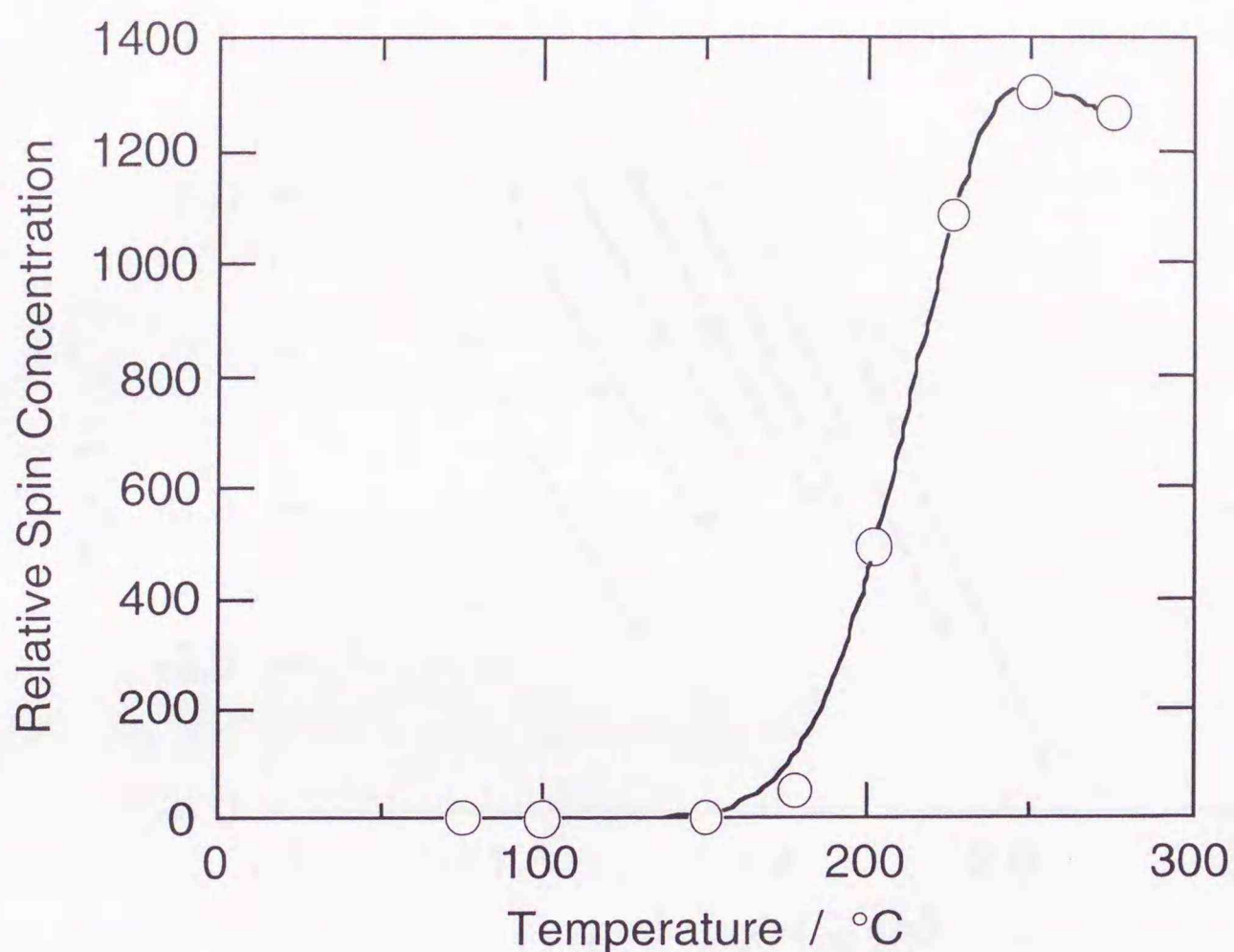
Figure 6-4. The relationships between the relative spin concentration and the temperature for P(ESt/St).

Arrehnius type temperature dependence:

$$k = A \exp(-\Delta E / RT), \qquad (2)$$

where A is the highest frequency factor, ΔE is an apparent activation energy, and R is a gas constant. In the IR measurement at a heating rate of $\beta = dT/dt$ (=3, 5, and 10 $°C \cdot min^{-1}$), using eq.(2), eq.(1) is expressed as

$$-\beta (d\alpha/dT) = A\exp(-\Delta E/RT)\alpha^n. \quad (3)$$

Figure 6-5 shows the semilogarithmic plot of $\beta (d\alpha/dT)$ against the inverse of temperature in the early, intermediate, and final stages. The symbols of ($\bigcirc$,$\blacktriangle$), ($\square$,$\bullet$,$\triangle$) and ($\blacklozenge$,$\triangledown$) denote respectively the slopes at temperatures in the early, intermediate and last stages. The value of ΔE, which was calculated from the slope of $\ln\beta (d\alpha/dT)$ against T^{-1} using eq.(3), increases from 25.2 $kcal \cdot mol^{-1}$ in the early stage to 33 $kcal \cdot mol^{-1}$ in the final stage. The slight increment of ΔH indicates that the collision reaction of ethynyl radials is slightly restricted by the increase of the permanent crosslinked junction density in the sample with the increase of temperature. However, because the value of α becomes a unit above 340 °C, the crosslinking reaction of the residue ethynyl groups between the chains is not entirely affected by the formation of the crosslinked junctions at each stage. The residue ethynyl groups between the chains collide and react with each other with great frequency. It is considered

106
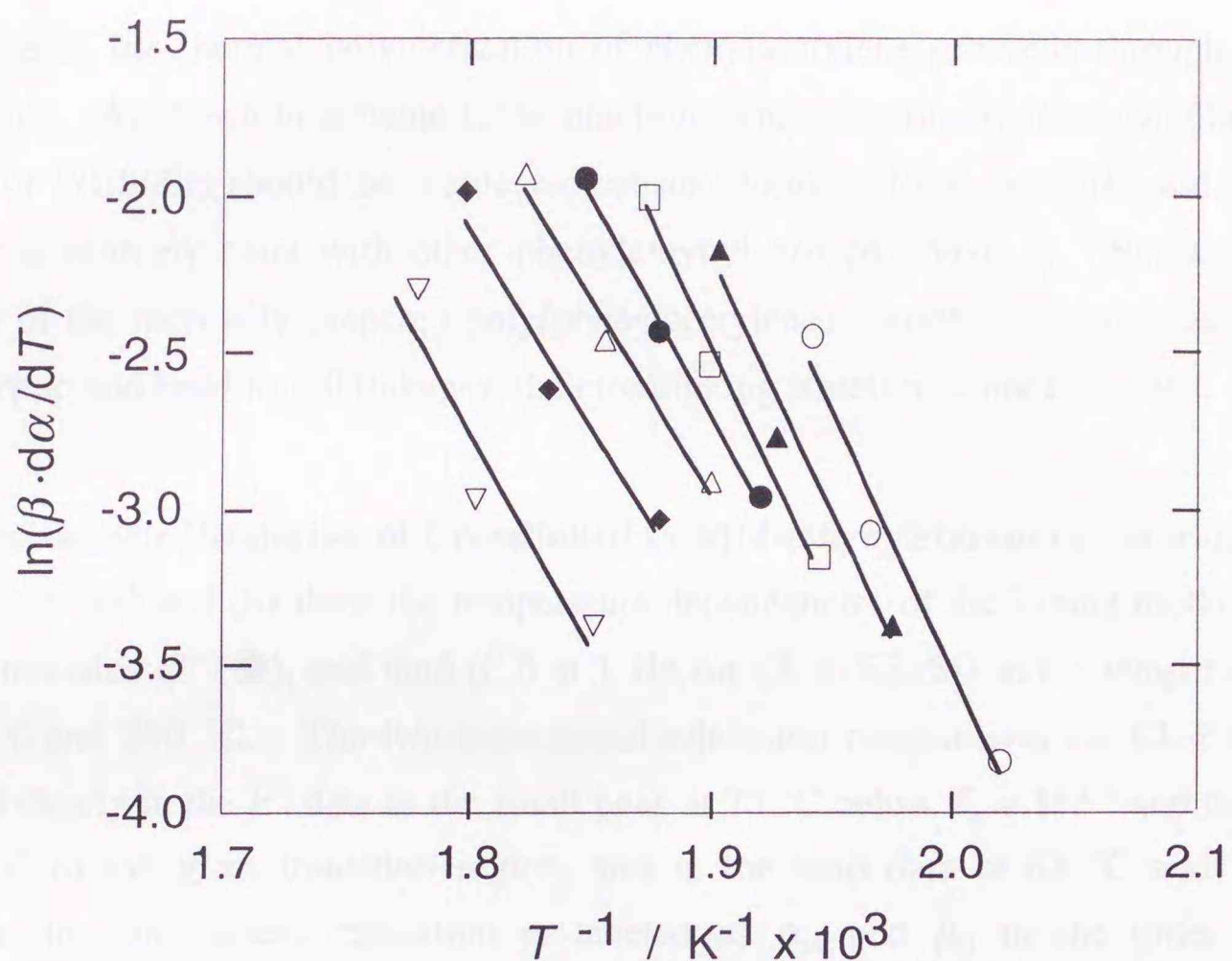
Figure 6-5. The semi-logarithmic plot of $\beta\,(d\alpha/dT)$ against the inverse of temperature T^{-1} in the IR measurement at heating rate of $\beta = dT/dt\ (= 3, 5,$ and $10\ ^\circ\text{C}\cdot\text{min}^{-1})$. The symbols of $(\bigcirc, \blacktriangle)$, $(\square, \bullet, \triangle)$ and $(\blacklozenge, \triangledown)$ denote respectively the slopes at temperatures in the early, intermediate and last stages.

that the macro-Brownian motions of the long strand between crosslinking junctions and the long dangling end chains with ethynyl groups play an important role to the collision and the crosslink formation. The average value of ΔE for the ethynyl crosslinking of the chains is estimated to be 29.2 ± 4 kcal·mol^{-1}.

Scheme 1

107
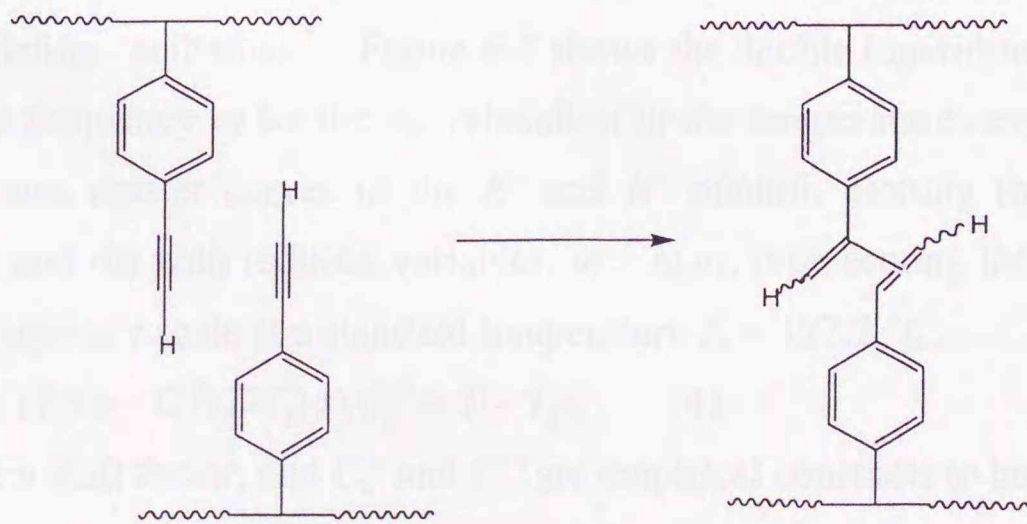
In general, the thermal polymerization of phenylacetylene proceeds through the radical mechanism. As shown in Scheme 1, the junction forming thermally from two phenylethynyl groups for P(ESt/St) should be stable radical and forms a local network, and thereby the radical can scarcely react with other phenylethynyl groups above T_g. Because the chain structure of the thermally prepared poly(phenylacetylene) involves *cis* and *trans*-forms, and head-to-head and head-to-tail linkages, the crosslinking structure is not estimated.

6-2-2. Viscoelastic Properties of Crosslinked Poly[(4-ethynylstyrene)-*co*-styrene]

Figures 6-6(a) and (b) show the temperature dependencies of the Young modulus E' ($\bigcirc$), the loss modulus E'' ($\bullet$), and $\tan\delta$ ($\bigcirc$) at 1 Hz for CL-P(ESt/St) in the temperature region between 0 and 290 °C. The two mechanical relaxation mechanisms for CL-P(ESt/St) are observed clearly in the E'' data as the small peak at 75 °C below $T_g = 113$ ° and the large one at 120 °C of the glass transition region, and in the $\tan\delta$ data at 83 °C and at 130 °C. Hereafter, the mechanical relaxation is labeled as α_M and β_M in the order which are encountered as the temperature is lowered. The E' decreases slightly in the β_M relaxation temperature region and greatly in the α_M temperature region. Above 210 °C, the respective values of E', E'' and $\tan\delta$ are constant. On the other hand, Iller and Jenkel[5] and Takayanagi[6] showed two kinds of mechanical relaxation mechanisms for atactic (amorphous) polystyrene (*at*-PSt) and lightly crosslinked (1% triacryl formal) polystyrene (1%-CL-PSt), corresponding to the α_M and β_M relaxations. Assuming the Arrhenius type for the measurement frequencies of 0.1, 1 and 10 Hz and the inverse of each E'' peak temperature in the relaxation map, the apparent activation energies of ΔE_α and ΔE_β for the α_M and β_M relaxations were determined to be 128.0 and 50.6 kcal·mol^{-1} for CL-P(ESt/St), respectively, and 86 - 91 and 35 - 40 kcal·mol^{-1} for *at*-PSt and 1%-CL-PSt. By comparison of the mechanical data for CL-P(ESt/St) with those for *at*-PSt and 1 %-CL-PSt, the α_M and β_M relaxations may be due to the micro-Brownian motion of the chain segments in the glass transition region and the local relaxation mode of its twisting oscillation.[7] Figure 6-7 shows the double logarithmic plots of E' and E'' vs. the angular frequency ω for the α_M relaxation in the temperature range of 110 to 157 °C. Figure 6-8 shows master curves of the E' and E'' moduli, plotting the respective data in Figures 6-7(a) and (b) with reduced variables, $\omega = \omega_0 a_T$, representing the WLF behavior over an extended frequency scale at a standard temperature $T_s = 127.2$ °C:

$$\log a_T (T_s) = - C_1^0 (T\text{-}T_s) / (C_2^0 + T - T_s), \qquad (4)$$

where $a_T(T_s)$ is a shift factor, and C_1^0 and C_2^0 are empirical constants to be obtained by fitting
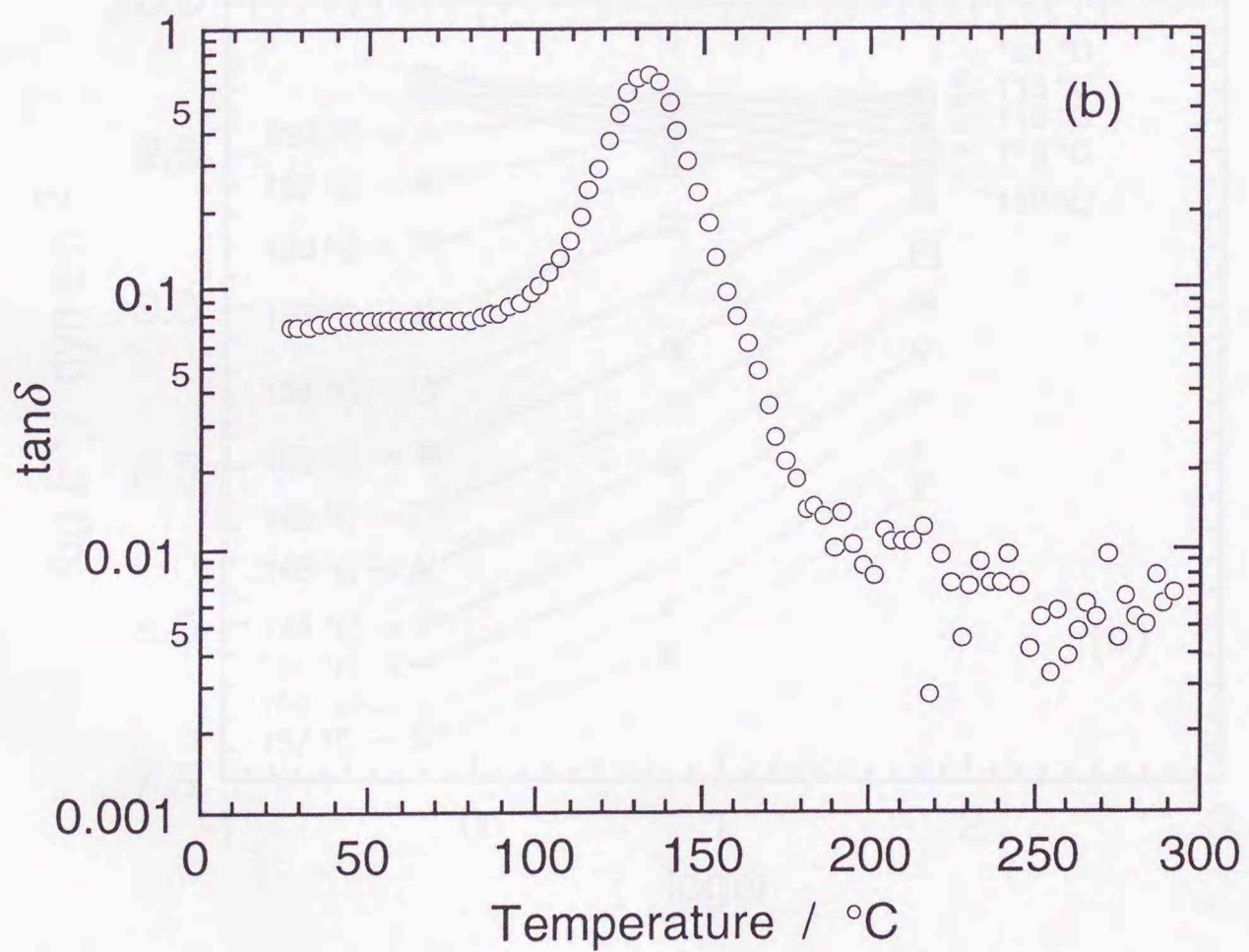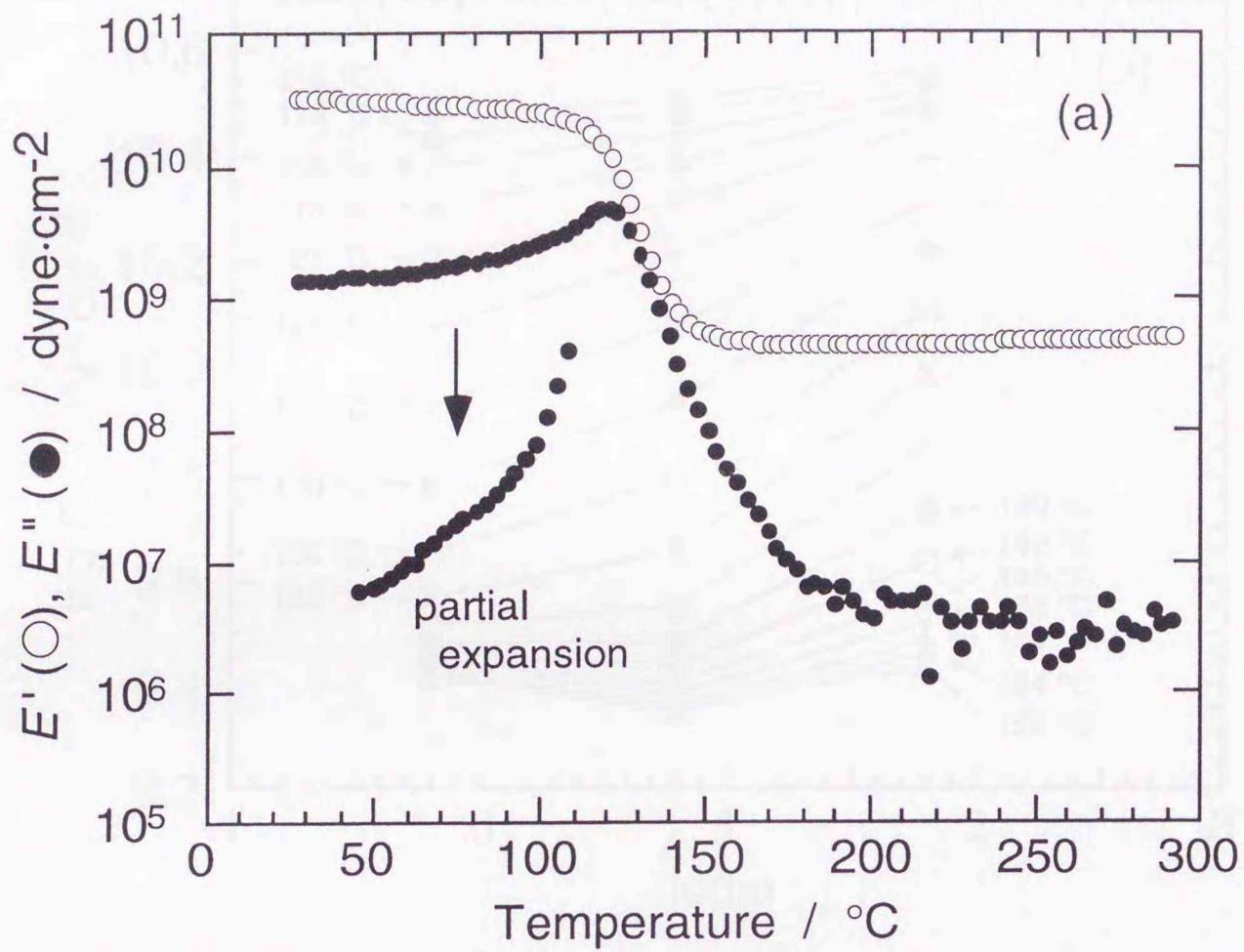
Figure 6-6. The temperature dependencies of the Young modulus E' ($\bigcirc$) and the loss modulus E'' ($\bullet$) (a), and $\tan\delta$ (b) at 1 Hz for CL-P(ESt/St) in the temperature region between 0 and 290 °C.
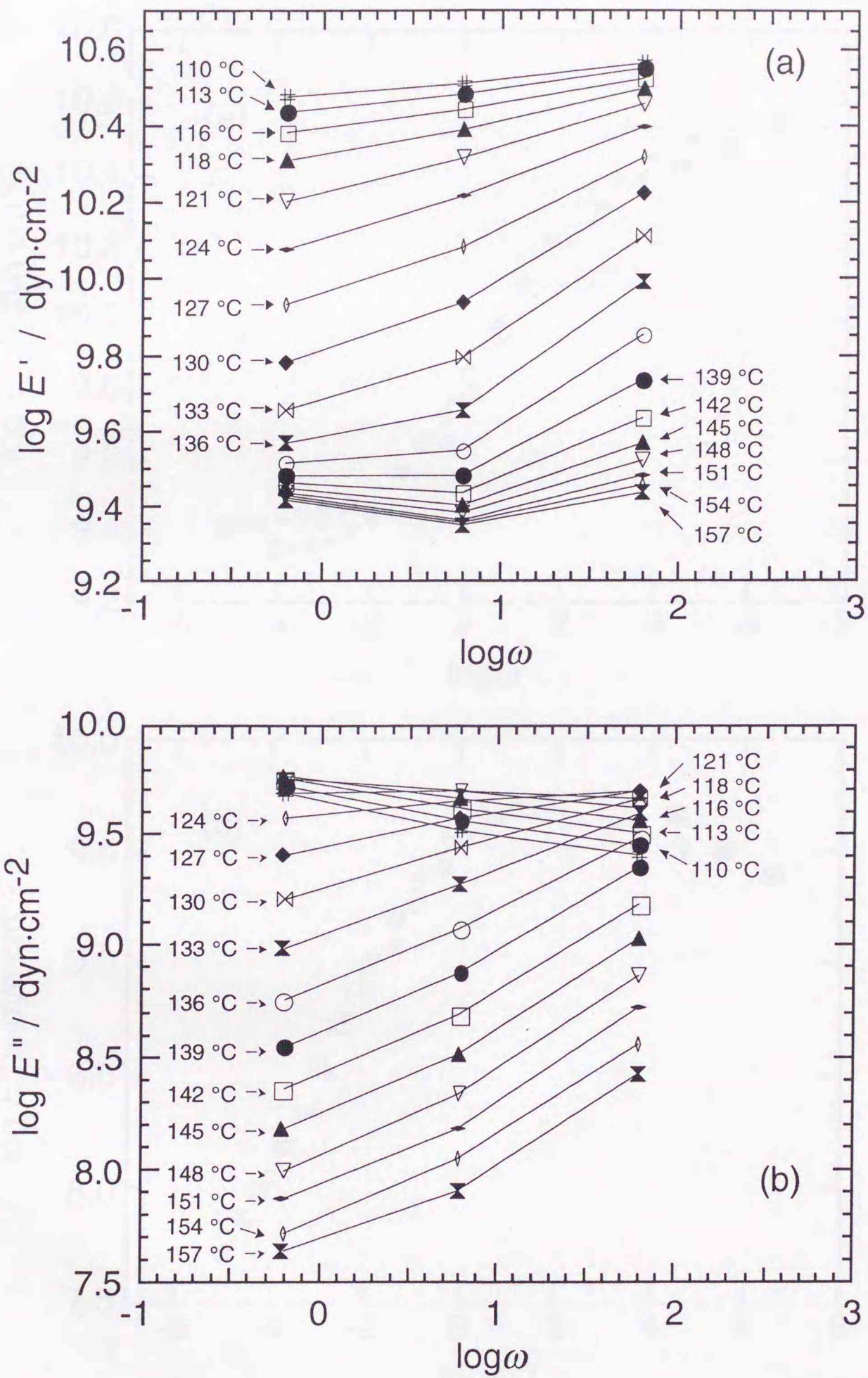
Figure 6-7. The double logarithmic plots of the Young modulus E' (a) and the loss modulus E'' (b) against the angular frequency ω for CL-P(ESt/St) in the temperature range 110 and 157 °C.
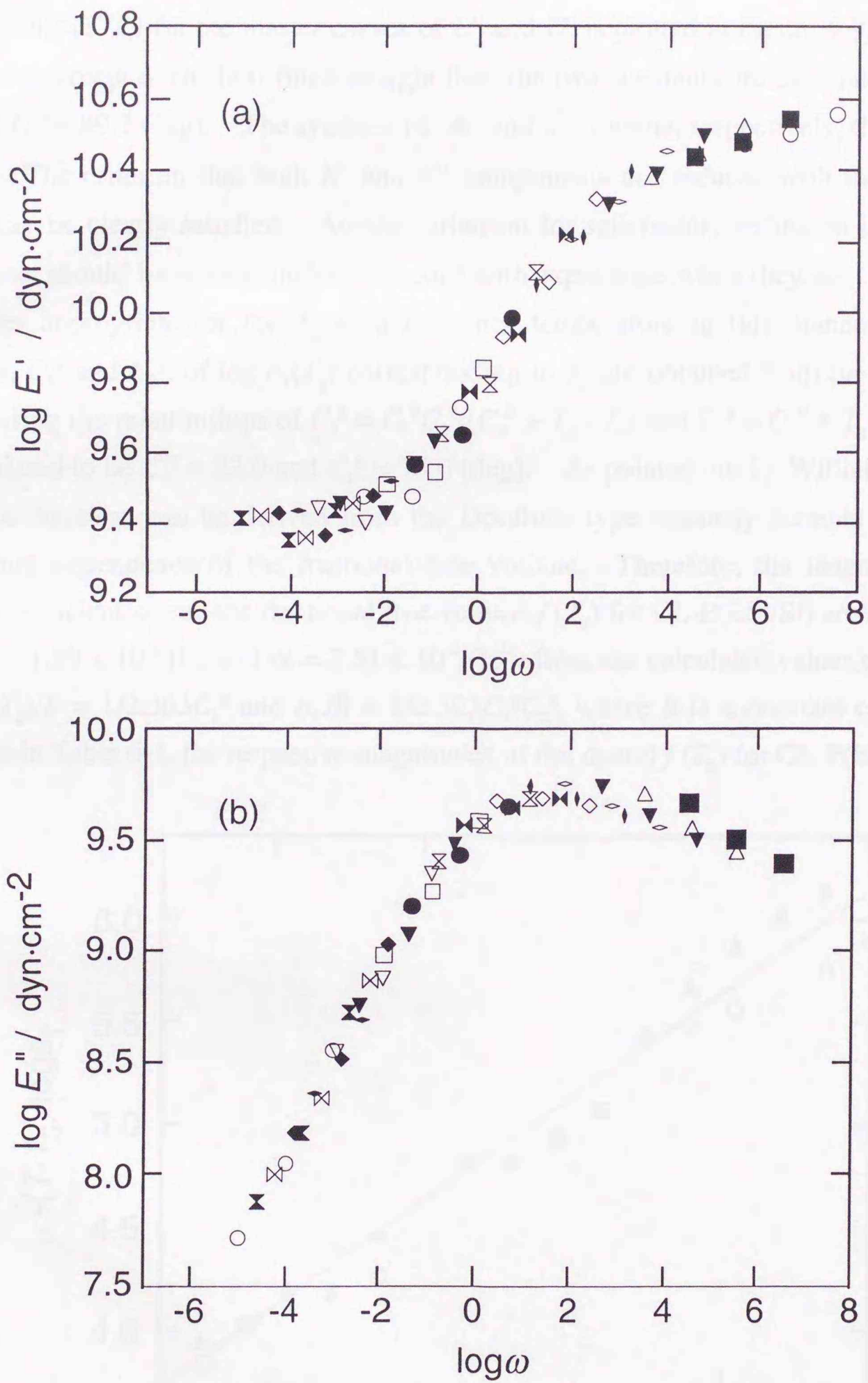
110

Figure 6-8. The master curve of the E' (a) and E'' (b) for CL-P(ESt/St) against the reduced angular frequency, $\omega = \omega_0 a_T (T_S)$.

the experimental results to eq.(4) using the least-squares method.[8]   The quantity of $(T-T_s)/\log$ $a_T(T_s)$ against $(T-T_s)$ for the master curves of E' and E'' is plotted in Figure 6-9, and from the slope and intercept of the best fitted straight line, the two constants are calculated to be $C_1^0 =$ 19.4 and $C_2^0 = 89.2$ (deg).   The symbols of ▲ and ◯ denote, respectively, the plots for E' and E''.   The criterion that both E' and E'' components are reduced with the same $a_T(T_s)$ values may be clearly satisfied.   Another criterion for satisfactory reduction is that the two coefficients should have magnitudes in accord with experience when they are transformed to the values appropriate for the T_g as a reference temperature in this manner.   The WLF constants, C_1^g and C_2^g, of $\log a_T(T_g)$ corresponding to T_g are obtained from the values of C_1^0 and C_2^0 using the relationships of $C_1^g = C_1^0 C_2^0/(C_2^0 + T_g - T_s)$ and $C_2^g = C_2^0 + T_g - T_s$ and then are calculated to be $C_1^g = 23.0$ and $C_2^g = 75.0$ (deg).   As pointed out by Williams et al.,[8] the WLF-type equation can be derived from the Doollittle-type viscosity formula with a linear temperature dependence of the fractional free volume.   Therefore, the magnitudes of the thermal coefficient α_f and the fractional free volume $f(T_g)$ for CL-P(ESt/St) are determined to be $f(T_g) = 1.89 \times 10^{-2}$ (K) and $\alpha_f = 2.51 \times 10^{-4}$ (K^{-1}) from the calculated values of C_1^g and C_2^g using $f(T_g)/B = 1/2.303C_1^g$ and $\alpha_f/B = 1/2.303C_1^g C_2^g$, where B is a constant close to unity. As shown in Table 6-1, the respective magnitudes of the α_f and $f(T_g)$ for CL-P(ESt/St) are
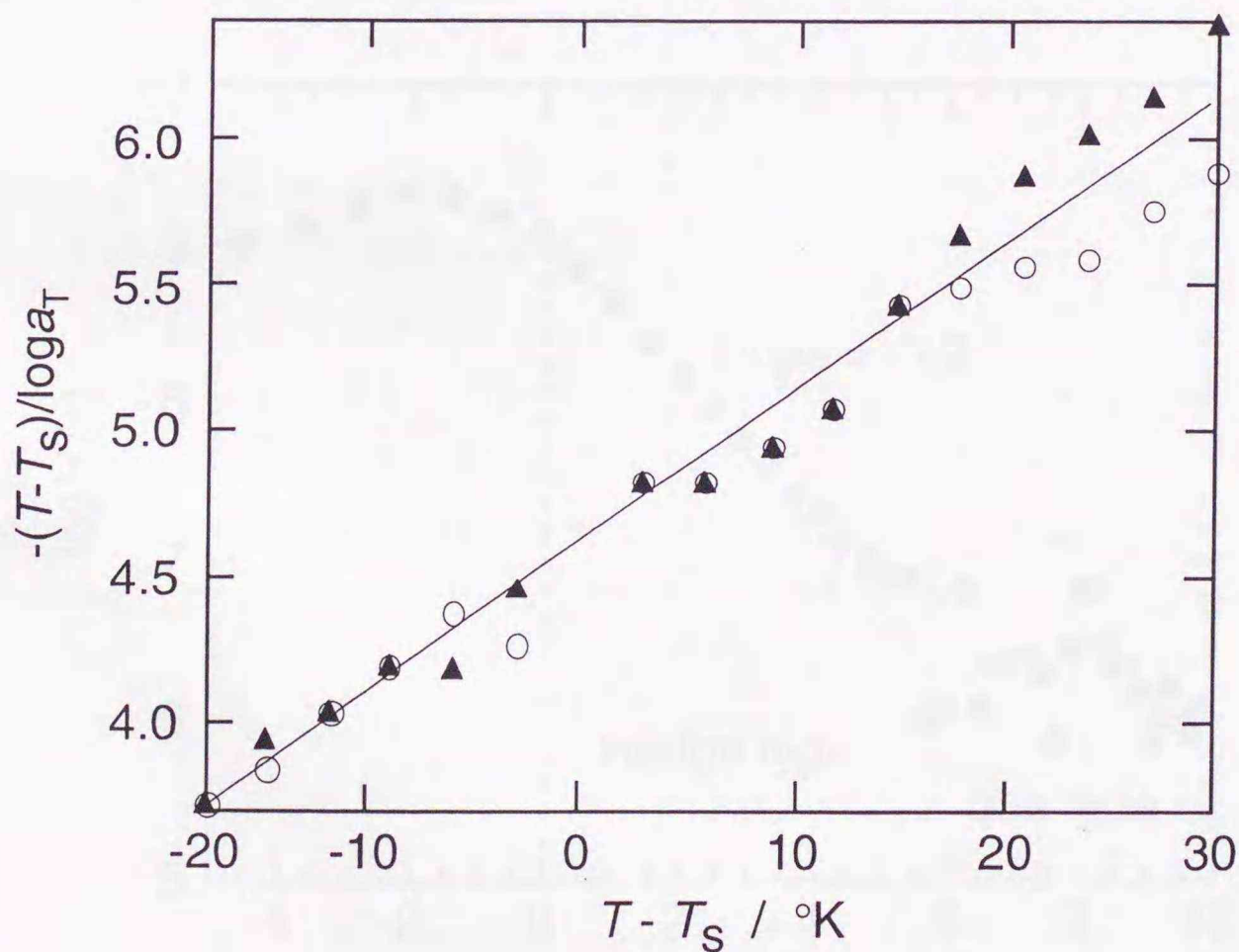

Figure 6-9. The $(T-T_s)/\log a_T(T_s)$ against $(T-T_s)$ plots for the master curves of E' and E'' in CL-P(ESt/St).   The symbols of ▲ and ◯ denote respectively the values of E' and E''.

112

Table 6-1. The WLF parameters of C_1 and C_2, $f(T_g)$ and α_f for polystyrene and crosslinked polystyrene

Polymer	T_0 (T_s, T_g)	C_1	C_2	$f(T_g) \times 10^2$	$\alpha_f \times 10^4$
	°C			K	K⁻¹
CL-P(ESt/St)	127.2 (T_s)	19.4	89.2		
	113.0 (T_g)	23.0	75.0	1.89	2.51
polystyrene [a]	105.5 (T_g)	13.4	55.0	3.24	6.42
amorphous polymer [b]	T_s	17.44	51.6	2.5	4.8

[a] References 3 and 4.

[b] Reference 6.

smaller than those for polystyrene and the universal parameters for amorphous polymers. This means that the mobility of the segments in the chains is slightly restricted due to the chemical crosslinking between the chains.

Figure 6-10 shows the corresponding relaxation time spectrum $H(\tau)$ for the α_M and the platea urelaxations that were calculated from the experimental curve of E' in Figure 6-6 using $H(\tau) \cong -| \, dE'(\omega)/d\ln\omega \, |_{\omega\tau=1}$. The log $H(\tau)$ vs. log τ consists of a wedge-type relaxation spectrum with a slope of -0.48 between 1 and 10^5 sec and a plateau spectrum like the box-type
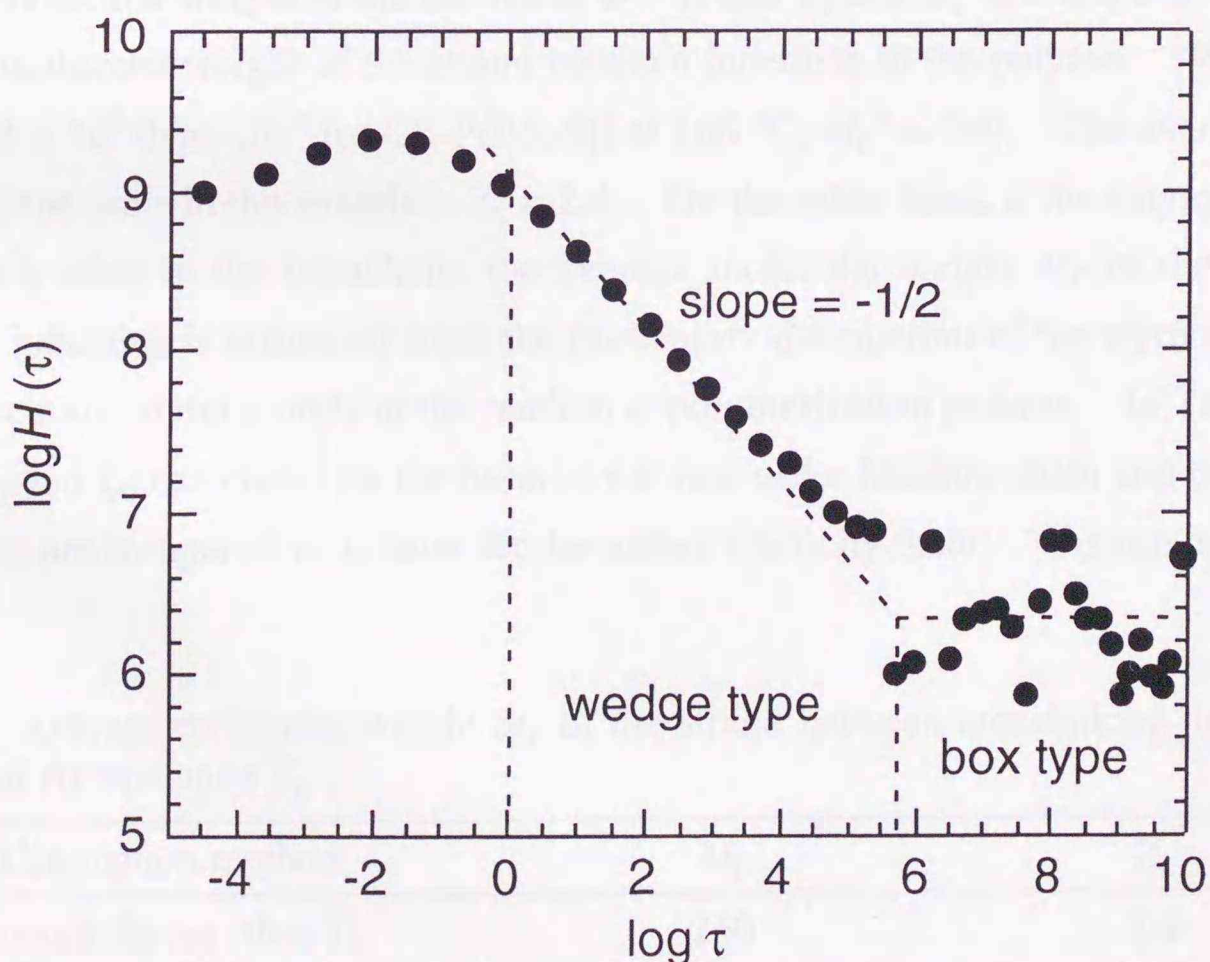
Figure 6-10. The corresponding relaxation time Spectrum $H_E(\tau)$ for the α_M and plateau relaxations.

113

above $\tau = 10^6$ sec. The former coincides with the well-known wedge-type spectrum with the characteristic slope of -1/2 for the intrachain relaxation in the Rouse chain model.[8] The agreement between experiment and model confirms that the α_M relaxation is attributed to the micro-Brownian motion of the segments. The latter is constant (or a plateau), although scattering of the data occurs around log $H(\tau) \cong 6.3$, which may be attributed to the equilibrium Young modulus in the rubber region, because the macro-Brownian motion of the strands never occurs in the fixed network.

6-2-3. Influence of the Fixed Crosslinks on the Equilibrium Young Modulus E_e in the Plateau Region

As shown in Figure 6-6, the magnitude of the equilibrium Young modulus E_e for CL-P(ESt/St) at 166 °C in the rubber region is 5.4 x 10^8 dyne·cm^{-2}, which is larger than that of rubber materials. It is well known that the E_e of a fixed crosslinked ideal polymer network is expressed as[8]

$$E_e = 3\Phi v_0 RT = 3\Phi (\rho /M_C)RT, \qquad (5)$$

and

$$\Phi = v_0/v_S = M_C{}^S/M_C{}^0, \qquad (6)$$

where Φ is the front factor, ρ is the density of the polymer, v_0 and $M_C{}^0$ are, respectively, the density and molecular weight of the strands at $\Phi = 1$, and v_S and $M_C{}^s$ are, respectively, the real density and molecular weight of the strand between junctions in the polymer. When $\Phi = 1$, with $E_e = 5.4$ x 10^8 dyne·cm^{-2} for CL-P(ESt/St) at 166 °C, $M_C{}^0 = 260$. The average number Z_C of the styrene units in the strands is $Z_C = 2.4$. On the other hand, if the ethynyl groups do not react each other in the intrachain, the average molecular weight M_C of the real strand between the junctions is estimated from the probability distribution of the styrene sequences between the ethynylstyrene units in the random copolymerization process. In Table 6-2, the values of M_C and Z_C calculated on the basis of the first order Markov chain and the Bernoulli trial processes are compared with those for the rubber elasticity theory. Assuming that the

Table 6-2. Average molecular weight M_C of the strand between crosslinking junctions and the number of styrene units Z_C

Calculation method	M_C	Z_C
network theory ($\Phi = 1$)	260	2.4
Bernoulli trial	1350	12.5
first order Markov chain	886	8.2

114

$M_C{}^S$ in eq.(6) equals M_c for each process, the front factor Φ is estimated to be 3.4 and 5.2 for the Markov and Bernoilli processes using $M_C{}^0$, respectively. According to Kats and Tobolsky,[9] the mean square end-to-end distance $<r^2>$ of the strand is given by $<r^2> = \Phi<r_0{}^2>$, where $<r_0{}^2>$ is the mean square end-to-end distance of the Gaussian chain for $\Phi = 1$: $<r_0{}^2> = n_C b_0{}^2$, where n_C is the average number of styrene monomer in the strand. With $b_0 = 1.54$ Å for the C-C single bond in the monomer unit, $n_C = 8.2$ and $\Phi = 3.4$ for the Markov process, $<r_0{}^2> = 1.94$ x 10^{-15} (cm^2) and then $<r_E{}^2> = 6.61$ x 10^{-15} (cm^2). With $n_c = 12.5$ and $\Phi = 5.2$ for Bernoulli processes, $<r_0{}^2> = 2.96$ x 10^{-15} (cm^2) and then $<r_E{}^2> = 1.54$ x 10^{-14} (cm^2). These results of $<r^2>$ and Φ mean that the network strands in CL-P(ESt) are subjected to a tensile force due to the crosslinks, and are expanded along the chain in the rubbery plateau region. As shown in Figure 6-6, the Young moduli E' against the temperature does not change between 170 °C and 250 °C, in contrast to the temperature dependence of E_e in the rubbery elasticity theory. This value of $E'(= E_e) = 5.4$ x 10^8 dyne·cm^{-2} scarcely increase at temperature above 260 °C, where an exotherm took place in the DSC measurement.

The viscoelastic properties of copolymer networks of ethyl acrylate with ethylene glycol dimethacrylate 20 mol%, and tetraethylene glycol dimethacrylate 68 mol%,[10,11] and epoxy resins[12] cured with various esters show the same plateau tempearture dependence of E_e in the rubbery elasticity region as the results for CL-P(ESt/St) described above. The value of equilibrium modulus for each polymer is the same order of 10^8 to 10^9 dyne·cm^{-2}. However, the viscoelastic relaxation in the glass transition region for each copolymer network is not explained by Rouse model, in contrary to the α_M relaxation of CL-P(ESt/St), because the relaxation spectrum becomes broader.

These findings indicate that the micro-Brownian motion of the segments in the strands for CL-P(ESt/St) is suppressed in the rubbery region in the wide temperature regions between 170 and 290 °C. It is considered that because the fixed crosslink density for CL-P(ESt/St) is low, an interaction between strands and the thermal fluctuation of the fixed junctions also play an important role on the anomalous temperature behavior of the rubber elasticity in the rubbery plateau region.

As a problem yet to be solved in the future, the effects of fixed crosslink junctions on the Rouse mode and the rubber elasticity of segments in the strand for CL-P(Est/St) must be clarified theoretically and experimentally as a function of the crosslinked density.

6-3. Conclusions

The formation mechanism of the ethynyl crosslinked junctions between the chains for the 8/92 mol% random copolymer of 4-ethynylstyrene and styrene and the effects of the fixed junctions on the mechanical relaxation processes in the glass transition and rubbery plateau region for the fixed crosslinked polystyrene, network polystyrene, were investigated.

On annealing, the fixed crosslinks in the network polystyrene were formed completely by the homogeneous chemical reaction of the ethynyl groups between the chains. The activation energy of the ethynyl crosslinking formation was 29.2 ± 4 kcal·mol^{-1}.

The dynamic Young moduli of E' and E'' vs. frequency at various temperatures for the network polystyrene were superposed onto their master curves by the time-temperature superposition principle obeying the WLF equation. The mechanical relaxation processes in the glass transition and rubbery plateau regions showed the wedge-type spectrum with the slope of $-1/2$ and a plateau spectrum without a terminal zone, respectively. The former was attributed to the micro-Brownian motion of the segments in the strands. The latter equilibrium Young modulus did not change with the increase of temperature, in contrast to predictions of ideal elasticity. The micro-Brownian motion in the rubbery elasticity region may be suppressed between the strands.

6-4. Experimental Section

The 8/92 mol-% random copolymer of ethynylstyrene and styrene and its fixed cross-linked sample. The random copolymerization of 4-(2-trimethylsilylethynyl)styrene (TMSESt) and styrene and the deprotection of the trimethylsilylated copolymer were described in Chapter 3.[4] The calibration of the M_n was done using standard polystyrene: M_n = 24200, M_w/M_n = 1.8.

A fixed crosslinked sample of the 8/92 mol% random copolymer, CL-P(ESt/St), was prepared in the following way: The sample of CL-P(ESt/St) was compression molded into plaques at 170 °C and 100 Kg·cm^{-2}. After the temperature was varied at a rate of 30 °C·min^{-1} from 170 to 260 °C, the plaque was annealed at 260 °C for 1 h under pressure in order to ensure an ethynyl cross-linking reaction between the chains in the sample and then cooled under 150 Kg·cm^{-2} to room temperature over 8 h.

Ethynyl Crosslinking Reaction and DSC Measurements. The ethynyl crosslinking reaction of the chains in P(ESt/St) was confirmed from the IR absorption intensities of 2890 cm^{-1} and 3340 cm^{-1}, I_{3340}/I_{2890}, for the CH$_2$ and ethynyl groups in the IR spectrum, which was measured under Ar gas using a JEOL JIR-WINSPEC 50 spectrometer with a heat-controller. DSC and TG thermograms were measured under N$_2$ gas using the SEIKO, Inc., DSC 220 and TG/DTA 220, respectively.

Viscoelastic Measurement. The real component, E', and the imaginary component, E'', of the complex Young modulus E^* (= E' + iE'') for CL-P(ESt/St) were measured using a Rheometric RMS machine from Rheometric Scientific F. E. Co., Ltd., operating with a 0.1 % strain at 0.1, 1 and 10 Hz. The measurement temperature was varied at a rate of 0.03 °C·min^{-1} between -100 and 290 °C.

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118

Chapter 7.   Conclusions

In chapter 2, the new functional monomers used in this thesis were readily synthesized by the palladium-mediated coupling reaction between 2-, 3-, and 4-bromostyrenes and the corresponding monosubstituted acetylenes and by the nucleophilic substitution reaction between 4-(chloromethyl)styrene and the lithiated ethynyl compound.   The yields of monomers were satisfactory results, which showed the versatility of these reactions to synthesize styrene derivatives containing an ethynyl group.

In chapter 3, the radical polymerization of the styrene monomers having an ethynyl group and the copolymerization with styrene produced the gel-free polystyrenes with various substituents, such as (trimethylsilyl)ethynyl, *para*-(4-trimethylsilyl-3-butynyl), 3,3-dimethyl-1-butynyl, 3-methyl-1-hexynyl, 1-hexynyl, and phenylethynyl groups.   From the *Q-e* values, it was shown that (2-(trimethylsilyl)ethynyl)styrenes, 4-(3,3-dimethyl-1-butynyl)styrene, 4-(3-methyl-1-hexynyl)styrene, 4-(1-hexynyl)styrene, and (phenylethynyl)styrenes which had ethynylstyrene flamework were conjugated and electron-withdrawing monomers.   On the other hand, 4-(4-trimethylsilyl-3-butynyl)styrene was a conjugated and electron-donating monomer.

The deprotection of the silyl protected group in polystyrenes with (2-trimethylsilyl)ethynyl and 4-trimethylsilyl-3-butynyl groups smoothly proceeded for conversion into polystyrenes having pendent terminal ethynyl and butynyl groups, and subsequently underwent curing reactions at elevated temperature to form crosslinking polystyrenes.

The polystyrenes having pendent alkylethynyl and phenylethynyl groups underwent curing reactions at elevated temperature to form crosslinking polystyrenes.   The crosslinking reaction of the C≡C groups was incompleted due to the steric hindrance of alkyl substituted ethynyl group.   However, the thermal stability was improved on polystyrene.   On the other hand, in spite of the steric hindrance of the diphenyl substituted ethynyl group, complete disappearance of the carbon-carbon triple bond was ascertained in the annealed polymers. The thermal stability was improved by replacement of the terminal ethynyl group to the phenylethynyl group.

In chapter 4, the cationic polymerization of styrene derivatives containing an ethynyl group and the copolymerization with styrene afforded the polymers with ethynyl groups.   For the (2-trimethylsilylethynyl)styrenes, however, its homo- and copolymers were not quite obtained. Reactivity of monomers for cationic initiator was under the influence of the steric hindrance

119

and substituted position of the substituent. The ethynylstyrene monomer contents in the copolymers were less than the composition of the monomer feeds. The composition ratio of the copolymer in the radical polymerization showed a reverse tendency. The structure of polymers obtained by the cationic polymerization was mainly linear. The polystyrenes having various pendent ethynyl groups underwent curing reactions at elevated temperature to form crosslinking polystyrenes. The heat-resistance property was mostly improved by the introduction of the various ethynyl group to the styrene compared with polystyrene. In particular, in spite of the low M_n of poly[4-(phenylethynyl)styrene] by the cationic polymerization, the T_d was risen by radical polymerization.

In chapter 5, the well-defined linear poly(ethynylstyrene)s and poly[4-(3-butynyl)styrene] were synthesized by the anionic living polymerization of ethynylstyrenes and 4-(3-butynyl)styrene through the trimethylsilyl protection for terminal ethynyl functions, followed by complete deprotection. As a result, poly(4-ethynylstyrene), poly(3-ethynylstyrene), poly(2-ethynylstyrene), and poly[4-(3-butynyl)styrene] were obtained by this method. Some novel block copolymers with these poly(ethynylstyrene) and poly[4-(3-butynyl)styrene] segments are also synthesized. In particular, the polymerization temperature was the important problem for realizing the controlled block copolymerization of 4-(4-trimethylsilyl-3-butynyl)styrene. At –95 °C, the anionic polymerization of 4-(4-trimethylsilyl-3-butynyl)styrene constructed almost a stable living polymer inhibiting the undesirable side reactions. In addition, the bromination of poly(4-ethynylstyrene) proceeded quantitatively to provide a well-defined poly[4-(1,2-dibromoethenyl)styrene] with a narrow molecular weight distribution.

The living anionic polymerizations of novel functional monomers, (3,3-dimethyl-1-butynyl)styrenes, (1-hexynyl)styrenes, and 4-(phenylethynyl)styrene, succeed to give well-defined polymers with narrow MWDs and tailored M_n's. The polymerization conditions such as temperature and solvent were important for realizing the controlled anionic polymerization of these monomers. The enhanced anionic polymerizability of (3,3-dimethyl-1-butynyl)styrenes, (1-hexynyl)styrenes, and 4-(phenylethynyl)styrene as styrene derivatives, which was stimulated with the electron-withdrawing C≡CR groups, was clarified from the results of the sequential block copolymerization and was actually ranked between those of styrene and 2-vinylpyridine. The difference in the polymerizability of (3,3-dimethyl-1-butynyl)styrenes, (1-hexynyl)styrenes, and 4-(phenylethynyl)styrene could be well accounted for by the ^{13}C NMR chemical shifts of the vinyl β-carbons of the monomers.

In chapter 6, the formation mechanism of the ethynyl crosslinked junctions between the chains for the 8/92 mol-% random copolymer of 4-ethynylstyrene and styrene and the effects of the fixed junctions on the mechanical relaxation processes in the glass transition and rubbery plateau region for the fixed crosslinked polystyrene, network polystyrene, were investigated.

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The dynamic Young moduli of E' and E" $vs.$ frequency at various temperatures for the network polystyrene were superposed onto their master curves by the time-temperature superposition principle obeying the WLF equation. The mechanical relaxation processes in the glass transition and rubbery plateau regions showed the wedge-type spectrum with the slope of $-1/2$ and a plateau spectrum without a terminal zone, respectively. The former was attributed to the micro-Brownian motion of the segments in the strands. The latter equilibrium Young modulus did not change with the temperature increase, in contrast to the rubbery elasticity. The micro-Brownian motion in the rubbery elasticity region was suppressed by the expansion of the strands.

In summary, functional polymer of the styrene framework having the carbon-carbon triple bond, which was polymerizable functional group, was newly synthesized. These polymers could be synthesized from radical, anionic, and cationic polymerization. Syntheses of precise polymers, the homo- and block copolymer of which primary structures is definite were successfully achieved by anionic living polymerization. Random copolymer of new monomers with styrene was synthesized from radical polymerization. In addition, radical reactivity of monomers containing an acetylenic moiety became clear. Side reaction occurred inconsiderably in cationic polymerization, but gel-free polymers were obtained. These successful synthesized functional polymers have heat resistance, and the contribution to the field of material science is expected.

121

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Chapter 3

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