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Instructions for use

Cationic Polymerization of Dibenzofulvene Leading to a π-Stacked Polymer

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Abstract: Cationic polymerization of dibenzofulvene is conducted using BF_3-OEt_2, CH_3SO_3H, CF_3CO_2H, and CH_3CO_2H as catalyst or initiator in CH_2Cl_2 under various conditions. The cationic polymerization led to controlled stereochemistry and results in a π-stacked polymer through the polymerization. The polymers synthesized using BF_3-OEt_2 and CH_3SO_3H appears to possess different π-stacked structures. The polymer made using CH_3SO_3H has an all trans main-chain C-C bond conformation while the one prepared BF_3-OEt_2 may at least partially have a trans-gauche main-chain C-C bond conformation. π-Stacked conformations are confirmed on the basis of

remarkable anisotropy effects on aromatic signals in ^{1}H NMR spectra, hypochromic effects in electronic absorbance spectra, and dimer (excimer) emission in fluorescence spectra. π-Stacked conformation is found even for oligomer samples with Mn of as low as about 700, indicating that the conformation created by the cationic polymerization is rather stable.

1. Introduction

Polymer chain conformation often affects the properties and function of polymeric materials; conformational control through polymerization is thus important. Representative macromolecules with controlled chain conformation include helical and π-stacked polymers. [1-5] π-Stacked conformations can be found in polymers including poly(dibenzofulvene) (poly(DBF)) and derivatives,[6-9] polyether,[10] polyurethane,[11] polyphanathroline,[12] polyketone,[13] poly(benzofulvene) and derivatives,[14-15] and those based on cyclophanes.[16-19] Poly(DBF) is the first vinyl polymer having a π-stacked conformation in which the main-chain C-C bonds are nearly all trans and the side-chain fluorene moieties are stacked on top of each other (Scheme 1).[6,7] Such a conformation was fully elucidated by spectroscopic and x-ray crystallographic analyses of isolated oligomers having defined chain lengths. Poly(DBF) exhibits intriguing photo

electronic properties including a high charge mobility for a vinyl polymer ($\mu = 2.7$ x 10^{-4} cm^2 V^{-1}s^{-1} at 299 K at F = 7 x 10^5 V/cm) which is higher than those of some main-chain conjugating polymers such as poly(p-phenylenevinylene) (1 x 10^{-5} cm^2 V^{-1} s^{-1}) and poly(methylphenylsilane) (1 x 10^{-4} cm^2 V^{-1}s^{-1}) due to its strictly controlled π-stacked chain conformation.[20]

This polymer can be prepared by ionic or radical polymerization of DBF and full details of anionic and radical polymerization have been explored[6,21] while cationic polymerization has not yet been extensively studied. Herein we report the detailed results of cationic polymerization of DBF with an emphasis on the stereochemistry of polymerization (Scheme 1). In general, among various addition polymerization techniques, anionic polymerization and coordination polymerization have been mostly applied for the synthesis of stereo-controlled polymers of a wide variety of chemical structure, and there also have been examples of successful stereo regulation by radical polymerization of monomers leading polymers with a rigid conformation and polar monomers in the presence of Lewis acids. In a sharp contrast, achievements in stereo regulation by cationic polymerization have been much less significant compared with those by the other techniques. In this context, stereochemical studies on cationic

polymerization of DBF which is expected to lead to a rigid, π-stacked conformation of resulting polymer may open a new phase of cationic polymerization chemistry.
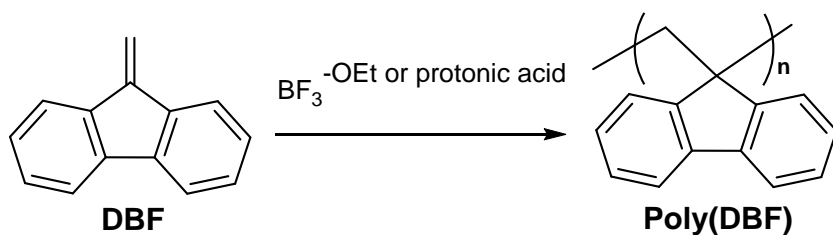
Scheme 1. Cationic polymerization of DBF.

2.   Experimental Section

2.1 Materials

DBF was prepared according to the literature.[6,7] BF$_3$-OEt$_2$ (95%, Kanto), CH$_3$CO$_2$H (TCI), CF$_3$CO$_2$H (TCI), were CH$_3$SO$_3$H (TCI) were used as obtained.   Styrene (TCI) and CH$_2$Cl$_2$ were dried and distilled over CaH$_2$.

2.2 Instrumentation

NMR spectra were recorded on a JEOL JMN-ECX400 spectrometer. Size-exclusion chromatography (SEC) measurements were carried out using a chromatographic system consisting of a JASCO DG-980-50 degasser, a HITACHI L-7100 pump, a HITACHI L-7420 UV-Vis detector and a HITACHI L-7490 RI detector, equipped with TOSOH TSKgel G3000H HR and G6000H HR columns (30×0.72 (i.d.) cm) connected in series (eluent: THF, flow rate: 1.0 mL/min). Preparative recycling SEC was performed with a JAI LC-9201 chromatograph consisting of a JAI PI-50 pump and a Soma S-3740 UV/Vis detector equipped with JAIGEL 1H and 2H columns (60×2 (i.d.) cm) connected in series (eluent: CHCl$_3$, rate: 3.5 mL/min). UV-Vis spectra were taken using quartz cells on JASCO V-550 and V-570 spectrophotometers, and fluorescence spectra were measured using quartz cells on a JASCO PF-8500 fluorescence spectrophotometer. IR spectra were recorded on a JASCO FT/IR-6100 spectrometer using KBr pellet samples. MALDI-TOF mass spectra were collected on a Bruker UltraFlex III and autoflex machine using dithranol (DIT) as matrix. 10.0 mg DIT dissolved in 1.0 mL THF.

2.3 Polymerization

Typical procedure of polymerization (entry 3 in Table 1): DBF (178 mg, 1.00 mmol) was dissolved in 5 ml of CH_2Cl_2 under N_2 atmosphere in a 10-ml round bottomed flask sealed with a three-way stop cock. A BF_3-OEt_2 solution in CH_2Cl_2 (0.775 M) (261 μl, 0.202 mmol) was added with a hypodermic syringe to the monomer solution cooled at 0 ^{o}C, and the reaction was run for 24 h. After confirming the monomer conversion ratio by NMR analysis of an aliquot of the mixture, the reaction mixture was poured into a large excess of MeOH, and the MeOH-insoluble part was collected with a centrifuge. The MeOH-insoluble part was further separated into THF-soluble and –insoluble parts through reprecipitation and collection with a centrifuge.

3. Results and Discussion

3.1. Polymerization behavior

Cationic polymerization of DBF was conducted in CH_2Cl_2 using BF_3-OEt_2 as catalyst at -40°C, 0°C, and 40°C or using CH_3CO_2H, CF_3CO_2H, or CH_3SO_3H as initiator at 0°C at various monomer and catalyst concentrations. The conditions and results are summarized in **Table 1**. In the polymerization using BF_3-OEt_2 under all conditions at $[DBF]_o$ = 0.2 M and 0.1 M at 0°C, the monomer was almost completely consumed

while the monomer conversion ratio was lower at $[DBF]_o$ = 0.05 and 0.025 M. As we

previously reported, the anionic and radical polymerization products of DBF contained

significant amounts of insoluble polymers. The insolubility of the polymer is considered

to arise from close packing of chains with the controlled conformation. In addition, the

yield of insoluble polymer is known to be higher at a condition where the production of

a longer chain is expected. The cationic polymerization products were also mostly

insoluble in solvents, suggesting that the cationic polymerization products possess a

controlled conformation.

In more detail, the yield of THF-insoluble polymer tended to be higher at a higher

$[DBF]_o$ at a constant $[DBF]/[BF_3]$ ratio ($[C/I]_o$ in Table 1) of 5 (runs 3, 6, 7, and 8 in

Table 1). On the other hand, $[DBF]/[BF_3]$ ratio seemed not to clearly affect the yield

of THF-insoluble polymer at a constant $[DBF]_o$ of 0.2 M. These results indicate that

DBF concentration is an important controlling factor of chain length in the cationic

polymerization while [monomer]/[initiator] ratio is not.

Temperature effects can be read from runs 3, 9, and 10 in Table 1 at $[DBF]_o$ = 0.2 M

and $[BF_3]_o$ = 0.04 M. While the monomer was almost completely consumed under

these three conditions, the yield of THF-insoluble product at 40°C was obviously lower

than those at -40°C and 0°C.   These result might suggest that chain transfer may have more significant role at 40°C than at 0°C and -40°C.

In addition, it is noteworthy that CH_3SO_3H effectively polymerized DBF (runs 11 and 12 in Table 1).   The monomer was almost completely consumed in the systems with CH_3SO_3H at 0°C while this initiator leads to much lower monomer conversions (3-4 %) in the polymerization of styrene under the same conditions. DBF was also polymerized using CF_3CO_2H and CH_3CO_2H (runs 13 and 14 in Table 1) while these initiators were not effective for styrene polymerization under the same conditions. These results clearly indicate that DBF is a highly reactive monomer in cationic polymerization as well as in anionic and radical polymerizations.

The monomer conversion in the polymerizations using the protonic acids at 0°C (runs 11, 13, 14 in Table 1) at $[DBF]_o = 0.2$ M and $[acid]_o = 0.04$ M seems to increase with a decrease in pKa of the acids, i.e., 1.6 for CH_3SO_3H, 3.4 for CF_3CO_2H, and 12.3 for CH_3CO_2H (in DMSO),[22,23] supporting that proton is the initiating species.   It is interesing that CF_3CO_2H and CH_3CO_2H having largely different pKa's led to rather similar monomer conversions.   Some interaction between DBF molecules and the acid molecules or the corresponding counter anions may have a role in the polymerization behaviors with the three acids.

Table 1. Cationic polymerization of DBF in CH_2Cl_2 for 24 h[a]

Run	C/I[b]	Temp. [°C]	[DBF]$_o$ [M]	[C/I[b]]$_o$ [M]	Conv.[c] [%]	THF-Insol. Yield [%]	THF-sol. Yield [%]	Mn[d] (vs PSt)	Mn[e] (vs DBF)
								MeOH-insoluble product	
1	BF$_3$-OEt$_2$	0	0.2	0.2	>99	90	9[f]	340	490
2	BF$_3$-OEt$_2$	0	0.2	0.1	>99	96	3[f]	370	520
3	BF$_3$-OEt$_2$	0	0.2	0.04	>99	95	4[f]	320	460
4	BF$_3$-OEt$_2$	0	0.2	0.02	>99	98	1[f]	320	460
5	BF$_3$-OEt$_2$	0	0.2	0.01	>99	96	3[f]	300	430
6	BF$_3$-OEt$_2$	0	0.1	0.02	>99	78	9	640	920
7	BF$_3$-OEt$_2$	0	0.05	0.01	89	68	8	690	990
8	BF$_3$-OEt$_2$	0	0.025	0.005	63	56	7[f]	680	970
9	BF$_3$-OEt$_2$	40	0.2	0.04	>99	13	29	1010	1440
10	BF$_3$-OEt$_2$	-40	0.2	0.04	>99	74	11[f]	500	720
11	CH$_3$SO$_3$H	0	0.2	0.04	>99	80	4	590	840
12	CH$_3$SO$_3$H	0	0.05	0.01	>99	49	9	640	920
13	CF$_3$CO$_2$H	0	0.2	0.04	17	8	6	1640	2350
14	CH$_3$CO$_2$H	0	0.2	0.04	10	2	6	2250	3220

[a]DBF (178 g, 1.00 mmol); [b]C/I denotes "catalyst or initiator"; [c]Determined on the basis of ^{1}H NMR analysis of crude products and the ratio of MeOH-insoluble, THF-insoluble part, MeOH-insoluble, THF-soluble part, and MeOH-soluble part; [d]Determined by SEC using polystyrene standards; [e]Mn value relative to poly(dibenzofulvene). Calculated by multiplying the Mn values relative to standard polystyrenes by a factor of 1.43 which was obtained through a comparison of ten experimental Mn values relative to standard polystyrene and those relative to standard poly(dibenzofulvene) reported in ref. 21. [f]Calculated on the basis of theoretical total polymer yields and experimental yields of THF-insoluble products.

Fig. 1 indicates the IR spectra of insoluble poly(DBF)s prepared by cationic, anionic and radical polymerizations. If any isomerization of the growing species occurs through the cationic polymerization, it may lead to a change in aromatic substitution which can be detected by IR spectra; aromatic substitution patterns are known to be sensitively reflected in IR spectra for overtone/combination vibration bands. The three spectra in the range of 2000-1750 cm^{-1} showing the overtone/combination vibration bands in Figure 1 have very similar spectral patterns, indicating that the cationic polymerization does not involve isomerization of growing species as well as anionic and radical polymerization.

In addition, the polymers prepared using BF_3-OEt_2 and CH_3SO_3H exhibited signals of mass numbers of 875.4, 1055.6, 1233.6, 1411.8, 1589.8 and those of 875.5, 1055.6, 1233.708, 1410.8, 1589.9, respectively (Fig. S2 in supporting information). The spacing of the peaks is ca. 178-180 which is close the DBF unit molar mass. These results support that the polymers prepared by cationic polymerization have no chemical structural defects as well as those made by radical and cationic polymerization.
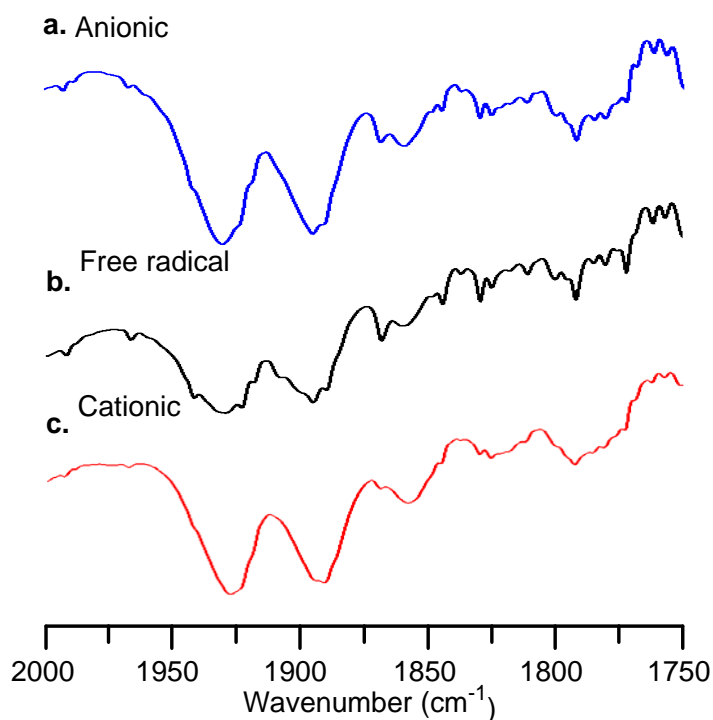
a. Anionic

b. Free radical

c. Cationic

Wavenumber (cm^{-1})

Fig. 1. IR spectra of poly(DBF)s prepared by anionic (a), radical (b), and cationic (c) polymerizations.   [THF-insoluble polymers, KBr pellet]

3.2. Chain conformation and polymer properties

Because poly(DBF) does not have any centers of chirality, chain conformation is the focus of stereochemical studies. Chain conformation of poly(DBF) prepared by cationic polymerization was assessed by ^{1}H NMR, UV absorbance, and fluorescence spectroscopic analyses of the THF-soluble part.   **Fig. 2** shows the ^{1}H NMR spectrum of THF-soluble poly(DBF)s prepared using BF_3-OEt_2 (run 10 in Table 1) and using CH_3SO_3H (run 11 in Table 1) along with that of fluorene as a unit model compound. In the spectra of the polymers, the aromatic proton signals appeared in the range of

4.8-7.8 ppm which are remarkably up-field shifted compared with those of fluorene (7.3

– 7.8 ppm).   This remarkable magnetic anisotropy effect strongly suggests that the

side-chain fluorene moieties are stacked on top of each other, i.e., the polymers have a

well-controlled π-stacked conformation.   It is interesting that the NMR spectrum of the

polymer prepared using BF_3-OEt_2 indicates –CH_2- signals in a much broader chemical

shift range of 0.2-3.8 ppm than the polymer prepared using CH_3SO_3H with –CH_2-

signals within the range of 1.6-2.8 ppm, suggesting that the two polymers have different

π-stacked structures. The spectral pattern of the polymer prepared using CH_3SO_3H is

very similar to those of poly(DBF)s prepared by anionic and radical polymerizations.

It has been predicted by DFT calculations that the positions of –CH_2- signals are very

sensitive to main-chain conformation of poly(DBF) and that they may largely up-field

shifted in a defective part in an all-trans π-stacked conformation and also in a π-stacked

conformation based on alternating trans-gauche main-chain structure[7] which had never

been reported for the anionic and radical polymerization products.   These results

suggest that cationic polymerization leads to two, different types of π-stacked

conformations depending on initiator or catalyst between which one is similar to those

of anionic and radical polymerization products with all-trans main-chain conformation

(**Fig. 3. a**) and the other may be a mixture of conformations including π-stacked one based on trans-gauche main-chain structure (**Fig. 3. b**).

Polymer conformation thus varies depending on initiator/catalyst in cationic polymerization of DBF. The difference in stereochemistry in DBF cationic polymerizations using BF_3-OEt_2 and using CH_3SO_3H may be ascribed to effects of counter anions which are considered to be $[BF_3$-$OH]^-$ for the system with BF_3-OEt_2 and $CH_3SO_3^-$ for the system with CH_3SO_3H. Though the detailed structures of growing species including counter anions are not yet clear, structure and properties of counter anion seem to paly crucial roles in stereochemistry of cationic polymerization of DBF. Counter ion effects on stereochemistry of cationic vinyl polymerization have been suggested in only very limited cases.[24,25]

It is also noteworthy that the polymer prepared using BF_3-OEt_2 has much broader peak shapes in the entire chemical shift range (**Fig. 2 b**) while the one synthesized using CH_3SO_3H has rather sharp signals (**Fig. 2 c**) which are very similar to those of soluble poly(DBF)s prepared by anionic and radical polymerizations [7,21] in spite of the fact that the two polymers have similar Mn's as revealed by SEC. masses may be largely different leading to different spin relaxation times in NMR experiments. The

conformation of the polymer prepared with CH_3SO_3H may be much more rigid leading to a much shorter spin relaxation time compared with the all-trans, π-stacked polymer prepared with $BF_3\text{-}OEt_2$.

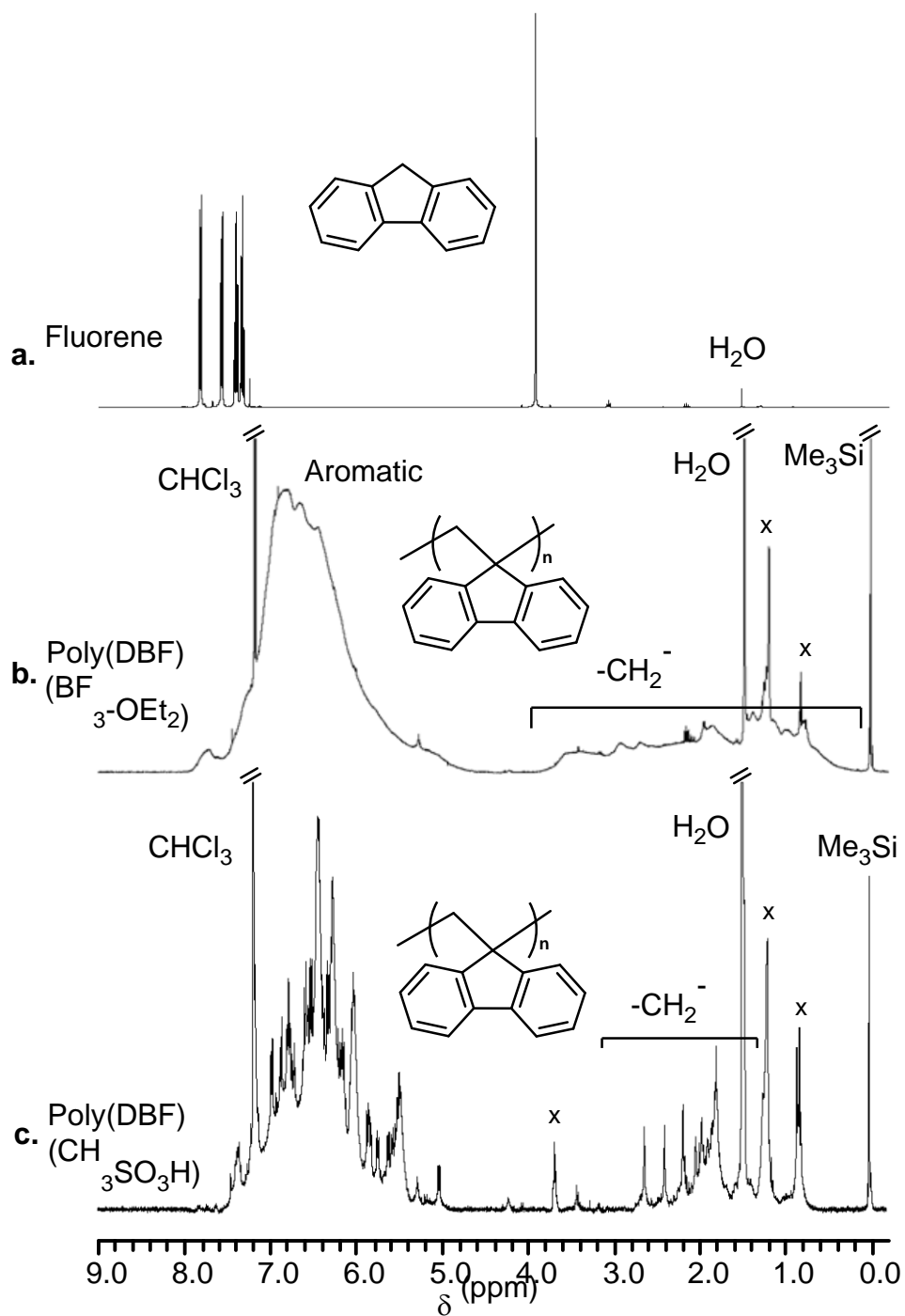**Fig. 2.** ^{1}H-NMR spectra of THF-soluble poly(DBF) prepared by cationic polymerization using BF_3-OEt_2 in CH_2Cl_2 at -40°C under the conditions same as those in run 10 in Table 1 using 851 mg (4.78 mmol) of DBF (a) and that of fluorene as a unit model compound (b). X denotes impurity. [400 MHz, $CDCl_3$, room temperature]
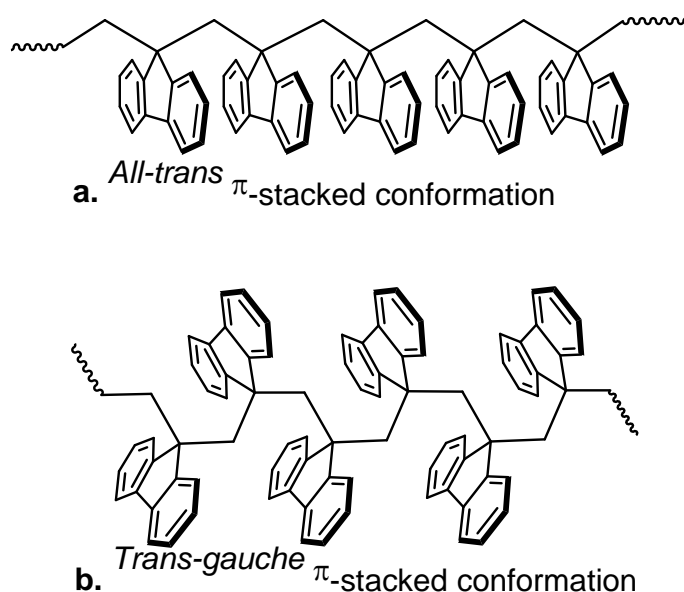

a. *All-trans* π-stacked conformation

b. *Trans-gauche* π-stacked conformation

Fig. 3. Proposed π-stacked conformations based on all trans main chain structure (a) and trans-gauche main chain structure (b).

Stability of the new conformation of the polymer prepared using BF_3-OEt_2 was assessed by heating the polymer in solution (Fig. S3 in supporting information). ^{1}H NMR spectral pattern did not change through heating a polymer solution in $CDCl_3$ at 60°C for 6 h, indicating that the conformation was stable under these conditions. This finding is interesting in connection to stability test of a trans-gauche, π-stacked conformation by force-field based molecular dynamics simulations which indicate that a trans-gauche

conformation swiftly transforms into an all-trans conformation; reliable force-field

parameters for π-stacked polymers might still need to be sought.

Absorbance and fluorescent spectra of the THF-soluble poly(DBF) prepared with

BF_3-OEt_2 are shown in **Fig. 4 A** and **B** along with those of fluorene as a unit model

compound.   The polymer indicated a remarkable red shifts and hypochromism with

respect to fluorene in the absorbance spectrum (**Fig. 4A**), and it exhibited an almost

exclusive dimer (excimer) emission centered at around 400 nm in the emission

spectrum (**Fig. 4B**).   These results are consistent with the conclusion that the polymer

has a π-stacked conformation.   The spectral shapes are similar to those reported for

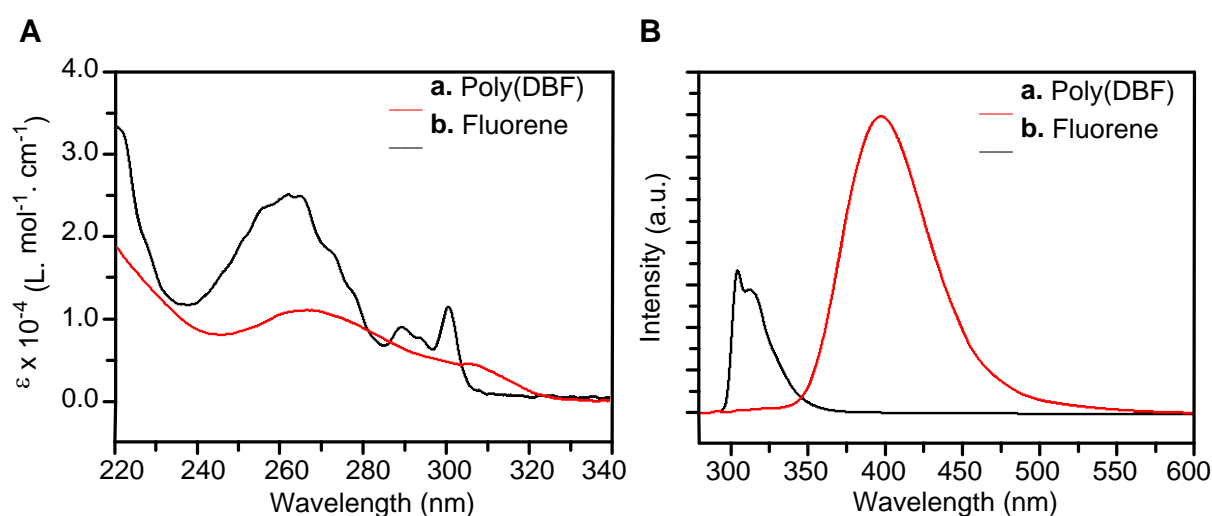poly(DBF)s prepared by anionic and radical polymerizations.

Fig. 4. Absorbance (A) and fluorescence (B) spectra of THF-soluble poly(DBF)
prepared by cationic polymerization under the conditions same as those in run 10 in

Table 1 using 851 mg (4.78 mmol) of DBF (a) and fluorene as a unit model (b) measured in THF. [Conditions for A; room temperature, cell path 10 mm, [fluorene] 1.00 x 10^{-5} M, [poly(DBF) (per residue)] 2.70 x 10^{-5} M: conditions for B; room temperature, cell path 10 mm, [fluorene] 1.00 x 10^{-6} M, [poly(DBF) (per residue)] 2.70 x 10^{-5} M]

Further, effects of chain length on the new π-stacked conformational were investigated using five different polymer samples obtained by preparative SEC fractionation of the THF-soluble poly(DBF) prepared using BF$_3$-OEt$_2$ at 0°C. Preparative SEC fractionation led to the samples having Mn's of 1430, 1000, 920, 820 and 740 whose Mw/Mn's were in the range of 1.0~1.1. UV and fluorescence spectra of these samples are shown in **Fig. 5 A** and **B**. All samples indicated red shifts and hypochromism in absorbance spectra, and the extent of hypochromism was greater for a sample having higher Mn (**Fig. 5A**); this tendency is similar to that reported for poly(DBF)s prepared by anionic polymerization.[6,7] A longer chain may lead to stronger electronic interactions between neighboring, stacked fluorene moieties in the poly(DBF) chain obtained using BF$_3$-OEt$_2$ whose conformation involves trans-gauche π-stacked structure as well as those in all-trans π-stacked poly(DBF) chain.

In the fluorescence spectra (**Fig. 5B**), all samples indicated spectra consisting of dimer (excimer) emission centered at around 400 nm and monomer emission centered at

around 310-320 nm between which the former had much higher intensity.   As for the

intensity ratios between monomer and excimer emissions, no clear tendency of decrease

or increase depending on Mn was found.   It is noteworthy that even the oligomer

sample having an Mn of 740 exhibited clear characters of π-stacked conformation in the

UV and emission spectra.   This may mean that the polymer prepared using BF_3-OEt_2

has a stable π-stacked conformation even when the chain is rather short.

In addition, the sample having the highest Mn of 1430 prepared at 0^oC indicated the

clear monomer emission (**Fig. 5 B a**) while no clear monomer emission was observed

for the poly(DBF) (Mn 500) prepared at -40°C using BF_3-OEt_2 (**Fig. 4B**).   This result

indicates that the extent of π-stacked conformational control is higher at -40°C.
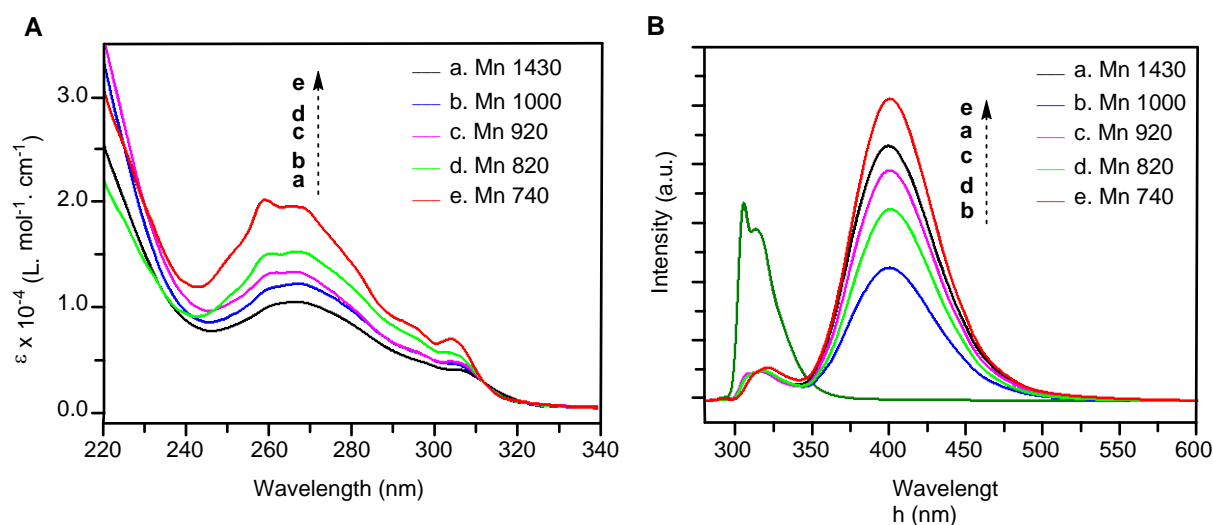
Fig. 5. Absorbance (A) and fluorescence (B) spectra of SEC-fractionated poly(DBF)s obtained from the polymer prepared by cationic polymerization using BF_3-OEt_2 at 0^oC under the conditions same as those in run 3 in Table 1 using 1.26 g (7.09 mmol) of DBF: Mn 1430 (a), 1000 (b), 920 (c), 820 (d), and 740 (e). The spectra in A were normalized at 312 nm according to the spectra in ref. 7. The spectra in B were normalized at 315 nm. [room temperature, cell path 10 mm, in THF]

4. Conclusions

Cationic polymerization of DBF was studied under various conditions. In the polymerization using BF_3-OEt_2, both [DBF]/[BF_3] ratio and DBF concentration appeared to affect chain length of the products. In addition to BF_3-OEt_2, CH_3SO_3H, CF_3CO_2H, and CH_3CO_2H led to polymers. The fact that the three protonic acids can lead to poly(DBF) indicates that DBF is a highly reactive monomer in cationic polymerization. The cationic polymerization products were found to have well controlled π-stacked conformations which may vary depending on initiator or catalyst.

The polymer obtained using BF$_3$-OEt$_2$ is proposed to possess a π-stacked conformation based on trans-gauche main chain at least in part while the one prepared using CH$_3$SO$_3$H has a π-stacked conformation based on all-trans main chain. There results may arise from stereochemical effects of counter anion through cationic polymerization. These features are in a sharp contrast to the facts that counter anion effects have been noticed in only in limited cases of cationic vinyl polymerization and that the extent of stereo control in cationic polymerization of vinyl monomers is generally rather moderate. In addition, even rather short chains prepared with BF$_3$-OEt$_2$ were confirmed to have a stable π-stacked conformation. This work hence clearly demonstrated that cationic polymerization is not just an alternative, effective method to prepare all-trans π-stacked poly(DBF) but also is a method to lead to a novel π-stacked conformation contributed by trans-gauche main chain.

Appendix A. Supplementary material

IR spectra, MALDI-TOF mass spectra, and ^{1}H-NMR spectra. Supplementary data related to this

article can be found at http://dx.doi.org/xxxx

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