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Unexpected Structural Defects in a Main-chain Conjugated Polymer Synthesized through Suzuki-Miyaura Cross Coupling Polymerization

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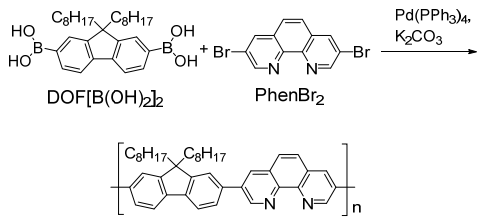
Abstract: Suzuki-Miyaura cross coupling (SMC) copolymerization of 3,8-dibromo-1,10-phenanthroline ($PhenBr_2$) and 9,9-dioctylfluorene-2,7-diboronic acid ($DOF[B(OH)_2]_2$ was conducted aiming to synthesized an alternating copolymer composed of 1,10-phenanthroline-3,8-diyl and 9,9-dioctylfluorene-2,7-diyl units in a mixture of 1,2-dimethoxyethane and water using $Pd(PPh_3)_4$ and K_2CO_3 as catalysts at different temperatures. Side reactions were unexpectedly found to take place in the reactions at 100°C where hydroxy and carbonyl groups appeared to be introduced probably to 1,10-phenanthroline units. Such reactions were more remarkable in the polymerization than in a model reaction leading to a triad molecule consisting of central 1,10-phenanthroline-3,8-diyl unit connected to two 9,9-dioctylfluorene-2-yl units, suggesting that a longer growing species has a role in such reactions. The extent of side reactions was higher with H_2O than with D_2O and was negligible with $H_2{}^{18}O$. The polymer with structural defects showed photo absorbance and emission profiles and thermal properties which were remarkably different from those of the alternating copolymer without structural defects.

Introduction

Cross-coupling reactions have been widely used for the synthesis of various functional molecules. One of the most efficient methods is Suzuki-Miyaura cross coupling (SMC) (the Suzuki reaction) involving Pd catalyst and base which efficiently creates C-C bonding between various aromatic compounds including small molecules to macromolecules having ordered structures.[1,2] Various macromolecules have been constructed by SMC including poly(*para*-phenylene), poly(*meta*-phenylene), polypyrroles, polyphenanthroline, and polyfluorene derivatives.[3-12] SMC has also been extended to controlled polymerization which makes regulation of molar mass and block sequence possible.[6-9] SMC is generally recognized to be versatile and robust, and serious side reactions in SMC polymerization have not been known so far reported to the best of our knowledge. However, we unexpectedly found that significant structural defects occurred in the synthesis of poly(9,9-dioctylfluorene-2,7-diyl-*alt*-1,10-phenathroline-5,6-diyl) [poly(DOF-*alt*-Phen)] as a potential polymer ligand for catalysis by SMC from 3,8-dibromo-1,10-phenanthroline ($PhenBr_2$) and 9,9-dioctylfluorene-2,7-diboronic acid ($DOF[B(OH)_2]_2$) (Scheme 1).



Scheme 1. Synthesis of poly(DOF-*alt*-Phen) through SMC.

While poly(DOF-*alt*-Phen) was once made by SMC from the same monomers, and no such structural alterations were reported,[12] spectral analyses suggested that hydroxyl and carbonyl groups were present in the polymer samples to a significant extent. In addition, the presence of 5,6-dihydroxy-5,6-dihydro-1,10-phenanthroline-3,8-diyl unit was suggested in a model reaction to synthesize a trimeric model compound.

Results and Discussion

The conditions and results of the copolymerization are summarized in Table 1. The polymerization was conducted in a mixture of 1,2-dimethoxyethane (DME) and water (H_2O or D_2O) under N_2 atmosphere. The products were purified by reprecipitation in MeOH, and MeOH-insoluble polymers were further fractionated into tetrahydrofuran (THF)-insoluble and -soluble parts. The insoluble polymers are considered to have higher molar masses, and the MeOH-insoluble, THF-soluble polymers were mainly subjected to analyses. The polymerization at 30 °C led to only 58% monomer conversion while the polymerizations at 60 °C or higher temperatures led to almost quantitative consumption of the monomers.

Table 1. Copolymerization of $DOF[B(OH)_2]_2$ with $PhenBr_2$ through Suzuki-Miyaura cross coupling using $Pd(PPh_3)_4$ and K_2CO_3 in DME/H_2O[a]

Entry	Temp. (°C)	Monomer Conv. (%)[b]	MeOH-insoluble product			
			THF-insol.	THF-sol.		
			Yield (%)	Yield (%)	M_n[c]	M_w/M_n[c]
1	30	58	0	10	2070	1.60
2	60	>99	25	67	3000	1.85
3	80	>99	13	68	1760	1.59
4	100	>99	28	72	1460	12.8
5[d]	100	>99	26	69	1490	6.23

[a][Monomer] = 0.005 M, $DOF[B(OH)_2]_2$ = 95.7 mg (0.2 mmol), $PhenBr_2$ = 67.6 mg (0.2 mmol), $Pd(PPh_3)_4$ = 23.1 mg (0.02 mmol) (10 mol%), K_2CO_3 = 276 mg (2 mmol), solvent = 4 mL, DME/H_2O(D_2O) = 3/1 (v/v), reaction time 24 h. [b]Determined by NMR analysis of crude material assuming $[DOF[B(OH)_2]_2]_t$ = $[PhenBr_2]_t$. [c]Estimated by SEC using poly(2-vinylpyridine) standard samples. [d]D_2O was used in place of H_2O.

Figure 1 shows the ^1H NMR spectra of the polymers. The spectrum of

the polymer obtained at 60 °C (entry 2 in Table 1) was similar to the one reported in literature 12 for the same polymer obtained at 60°C in a THF-water mixture and appeared consistent with the alternating copolymer structure consisting of 1,10-phenanthroline-3,8-diyl (Phen) unit and 9,9-dioctylfluorene-2,7-diyl (DOF) unit (Figure 1 a). On the other hand, the spectrum of the polymer obtained at 100 °C in DME/H_2O mixture (entry 4 in Table 1) showed a spectral pattern that is partially different from that in literature 12 with the signals in the ranges of 1.5-2.8 ppm, 3.2-4.5 ppm, 5-5.7 ppm, and 7.3-7.7 ppm suggestive of the presence of methylene and methine groups, methylene and methine groups having a heteroatom directly attached to them, olefinic groups, and aromatic signals, respectively, in addition to the signals which can be assigned to poly(DOF-*alt*-Phen) structure (Figure 1 c). The spectrum of the polymer obtained at 80 °C also such signals (Figure 1 b) while their relative intensities were much lower than those for the polymer prepared at 100 °C. Further, the polymer prepared in a DME/D_2O mixture at 100 °C also showed such additional signals while their relative intensities appear somewhat lower than those for the polymer prepared in DME/H_2O at 100 °C. These results may mean that the polymers prepared at 80 °C and 100 °C involve defective structures due to side reactions whose extent was higher at 100 °C.

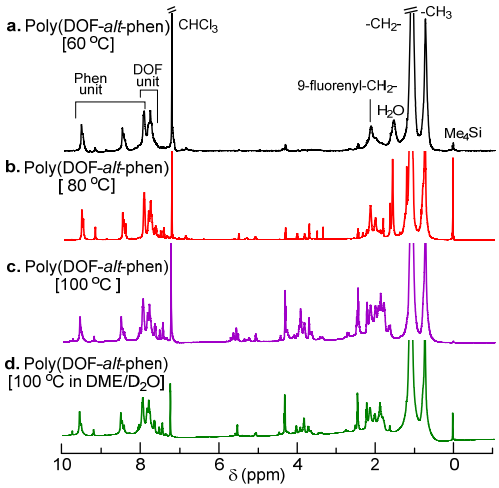


Figure 1. ^{1}H NMR spectra of polymers from entries 2 (a), 3 (b), 4 (c), and 5 (d) in Table 1 [400 MHz, r.t, $CDCl_3$].

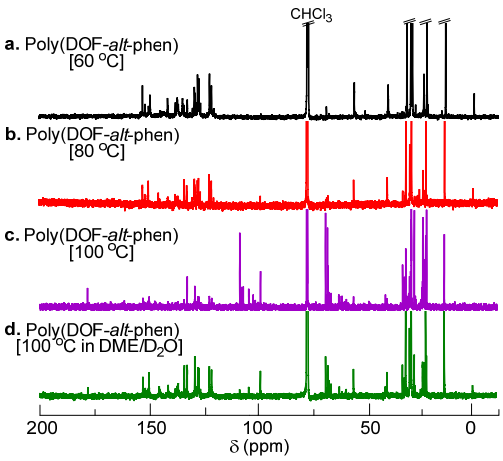


Figure 2. ^{13}C NMR spectra of polymers from entries 2 (a), 3 (b), 4 (c), and 5 (d) in Table 1 [100 MHz, r.t, $CDCl_3$].

This conclusion was supported by ^{13}C NMR spectra (Figure 2). The polymers obtained at 100 °C showed signals in the ranges of 30-35 ppm, 60-70 ppm, and 90-115 ppm and those at around 178 ppm (Figure 2 c d) in addition to the signals observed for the polymer prepared at 60 °C (Figure 2 a). The signals at around 178 ppm indicate the presence of C=O group. The relative intensities of the defect-based signals were higher for the polymer obtained in DME/H_2O at 100 °C than the one obtained in DME/D_2O at 100 °C (Figure 2 c d) similarly to the results of ^{1}H NMR analysis, and the polymer obtained at 80 °C did not clearly show defects-based signals due to the limited signal-to-noise ratio (Figure 2 b).

IR spectra also supported the presence of defective structures in the polymers prepared at 80 °C and 100 °C (Figure 3). The spectra of the polymers obtained at 100 °C in DME/H_2O and in DME/D_2O indicated intense signals at around 1740 cm^{-1} and 1720 cm^{-1} based on C=O group and a broad signal in the range of 2200-3700 cm^{-1} which may be due to -OH group (Figure 3 b d) which were absent in the spectrum of the polymer obtained at 60 °C (Figure 3 a). The relative intensities of such signals appeared to be lower for the product obtained in DME/D_2O. Also, the polymers prepared at 100 °C showed spectral patterns remarkably different from that of the polymer prepared at 60°C in the range of 500-1500 cm^{-1}. The spectrum of the polymer prepared at 80 °C was also slightly different from that of the polymer prepared at 60 °C in this wavenumber range. However, it appears that all four polymers have the typical signals based on Phen and DOF units (1465 cm^{-1}, 1425 cm^{-1}, 12050 cm^{-1}, 912 cm^{-1}, 891 cm^{-1}, 805 cm^{-1} and 753 cm^{-1}).

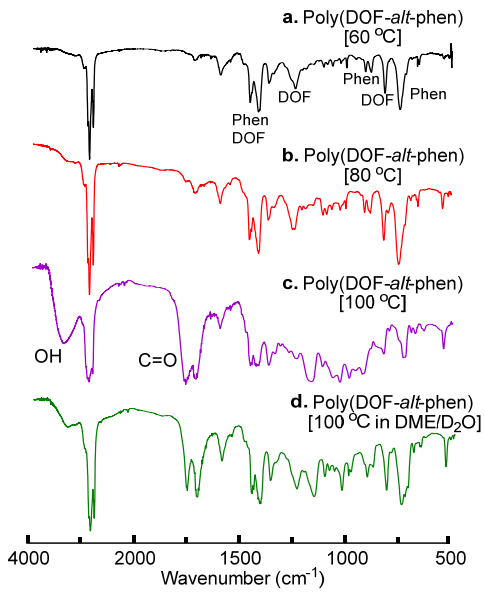


Figure 3. IR spectra of MeOH-insoluble, THF-soluble polymers from entry 2 (a), entry 3 (b), entry 4 (c) and entry 5 (d)[KBr].

These results along with the NMR spectra showing the signals based on both poly(DOF-*alt*-Phen) and defective structures suggest that the polymer samples are composed of poly(DOF-*alt*-Phen) sequence and defective sequences.

The NMR and IR spectral analyses thus suggested that the polymers obtained at 100 °C in DME/H_2O and DME/D_2O (entries 3 and 5 in

Table 1) have C=O group, -OH group, olefinic group, and alkyl groups attached to a hetero atom which should not exist in the chemical structure of poly(DOF-*alt*-Phen). Because the C_8H_{17} groups attached to the 9-position of fluorene units, which is the most vulnerable toward oxidation, appeared intact in ^{1}H and ^{13}C NMR spectra, the introduction of -OH and C=O groups may occur mainly to aromatic groups in DOF and/or Phen units, between which Phen unit may be more prone to side reactions especially at the 5- and 6-positions.

It should be pointed out that the products obtained in DME/D_2O at 100 °C showed lower relative intensities of the defect-based signals than those obtained in DME/H_2O at the same temperature as observed in the ^{1}H and ^{13}C NMR and IR spectra. This suggests that water is involved in the mechanism generating the irregular structures, and D_2O is less reactive than H_2O in the side reactions.

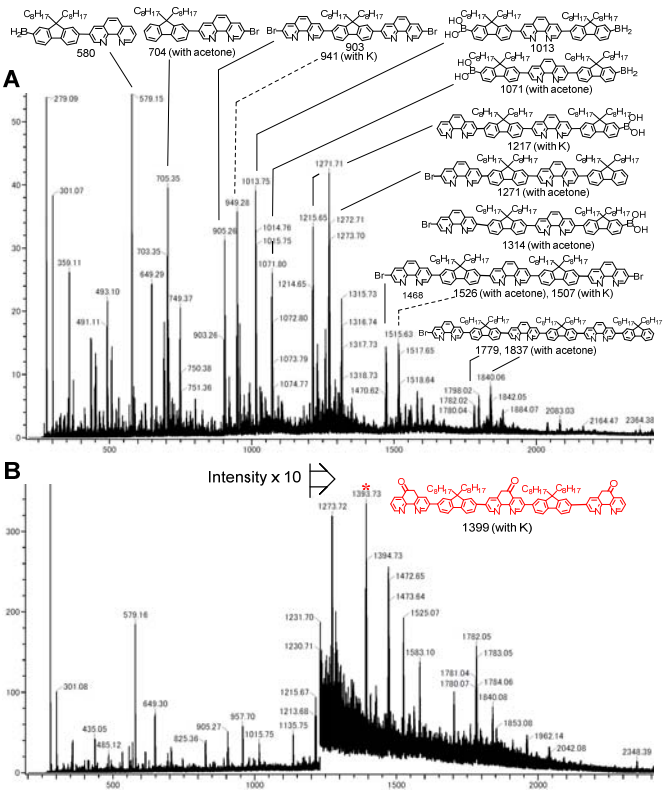
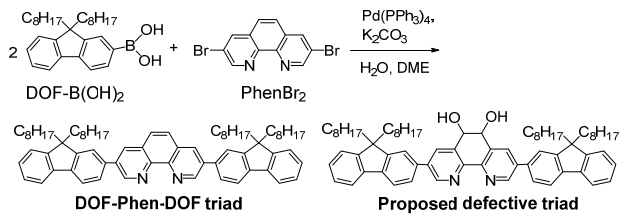


Figure 4. ESI-mass spectra of THF-soluble **poly(DOF-*alt*-Phen)**s prepared at 60 °C (A) and at 100 °C (B) in DME/H_2O from entries 2 and 4, respectively, with plausible.

Further structural information was obtained by ESI-mass spectrometry (Figure 4). Most of the major mass signals in the spectrum of the polymer prepared at 60 °C DME/H_2O (entry 2 in Table 1) were able to be assigned to DOF-*alt*-Phen 2-mers to 6-mers having different terminal structures (Figure 4 A), which is consistent with the production of poly(DOF-*alt*-Phen) without any structural defects. On the other hand, the polymer obtained at 100 °C in DME/H_2O (entry 3 in Table 1) showed overall only much weaker signals under the same spectrometry conditions, which may have connection with the presence of defective sequences, and the spectrum exhibited the signals mostly overlapping those of the polymer prepared at 60 °C (Figure 4 B). The only signal that did not obviously match DOF-*alt*-Phen oligomers was the one marked by * whose mass number was close to that of a defective 5-mer having the oxidized structure which are shown in red within Figure 3 B. Thus, the presence of an oxidized structure was indicated by the mass analysis. However, it seems that defective sequences were not effectively ionized and observed under the present spectrometry conditions.

In order to obtain about how structural defects were generated, the following experiments were conducted. **(1)** $PhenBr_2$ was treated with $Pd(PPh_3)_4$ in the presence of K_2CO_3 and in the absence of $DOF[B(OH)_2]_2$ in DME/H_2O at 100 °C for 24 h, leading to no changes in the structure of $PhenBr_2$ as confirmed by ^{1}H NMR spectra (Figure S1 in SI). **(2)** $DOF[B(OH)_2]_2$ was treated with $Pd(PPh_3)_4$ in the presence of K_2CO_3 and in the absence of $PhenBr_2$ in DME/H_2O at 100 °C for 24 h, leading to no changes the structure of $DOF[B(OH)_2]_2$ as confirmed by ^{1}H NMR spectra (Figure S2 in SI). **(3)** A reaction mimicking the polymerization was attempted between $PhenBr_2$ and $DOF[B(OH)_2]_2$ using only $Pd(PPh_3)_4$ without K_2CO_3 or using neither of $Pd(PPh_3)_4$ or K_2CO_3, leaving the monomers intact (Figure S3 in SI). **(4)** The polymer prepared at 60 °C in DME/H_2O (entry 2 in Table 1) was treated with $Pd(PPh_3)_4$ in the presence of K_2CO_3 in DME/H_2O at 100 °C for 24 h, leading to no obvious changes in structure as confirmed by ^{1}H NMR spectra (Figure S4 in SI). These results rule out the possibility that the monomers are damaged by the catalysts and the possibility that a polymer formed by SMC is damaged by the catalysts. The proposed side reactions thus are considered to occur through SMC.

Furthermore, a model reaction between $PhenBr_2$ and 9,9-di-*n*-octylfluorene-2-boronic acid ($DOF\text{-}B(OH)_2$) leading to the model triad compound (DOF-Phen-DOF) was conducted at 80 °C and 100 °C (Scheme 2). The structure of the crude products was assessed by ^{1}H NMR (Figure 5) and IR (Figure S8 in SI) spectral analyses.



Scheme 2. Synthesis of DOF-Phen-DOF triad compound through SMC leading to the authentic triad and a defective triad.

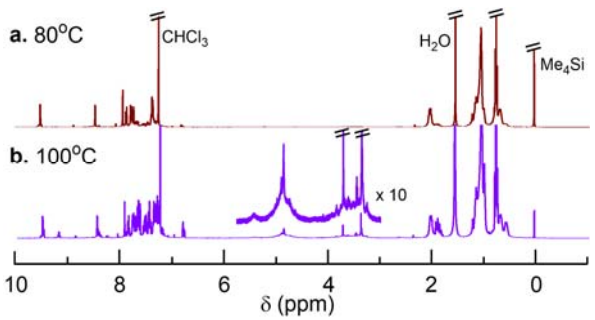


Figure 5. ^{1}H NMR spectra of the crude products of the reaction between $DOF\text{-}B(OH)_2$ and $PhenBr_2$ using $Pd(PPh_3)_4$ and K_2CO_3 in DME/H_2O (3/1, v/v) at 80 °C (a) and 100 °C (b) for 24 h. Reaction conditions: [$DOF\text{-}B(OH)_2$] 0.05 M, [Phen-Br_2] 0.025 M, [$Pd(PPh_3)_4$] 0.005 M, (10 mol%), [K_2CO_3] 0.5 M.

The spectral data of the product prepared at 80 °C were very similar to those of the polymer prepared at 60 °C having no defects (entry 2 in Table 1). On the other hand, the product obtained at 100 °C indicated signals that can be assigned to structural defects including those in 3-4 ppm, and those at around 1.8 ppm, 5 ppm, and 7.3-7.7 ppm, in the ^{1}H NMR spectrum (Figure 5). However, the signals had lower intensities than the corresponding ones for the polymers prepared at 100 °C in DME/H_2O or DME/D_2O mixture, indicating that the model triad compound made at 100 °C involves a lower amount of defective structures. In addition, the product prepared at 100 °C did not clearly show the signal due to C=O vibration in IR spectra (Figure S8 in SI).

In addition, mass spectrometry analysis indicated the major mass signal at m/z = 957 for the product obtained at 80 °C which well coincides with the molar mass of the targeted triad model compound whereas the product obtained at 100 °C showed a stronger signal at m/z = 956 as well as a weaker but clear signal at m/z = 990 corresponding to the defective triad compound having two -OH groups introduced to the Phen moiety (5,6-dihydro-1,10-phenanthroline-5,6-diol unit) shown in Scheme 2 (Figure S9 in SI). This unit may also be present in the polymers chain prepared at 80 100 °C. 5,6-Dihydro-1,10-phenanthroline-5,6-diol has been prepared by reduction of 1,10-phenanthroline-5,6-dione and also by epoxidation of 1,10-phenanthroline followed by hydroxylation.[13,14]

The generation of the structural defects was thus confirmed also for the model reaction. However, the extent of defects appeared to be much less in the model reaction than in the polymerization, suggesting that a growing species bearing a rather long pre-formed chain enhances the side reactions.

Because all reactions were conducted under N_2 atmosphere, the source of -OH and =O groups may be H_2O (D_2O). This point was assessed through a reaction of the model triad compound synthesis at 100 °C using $H_2{}^{18}O$ (Figure S9 in SI). However, the extent of the side reaction was much lower compared with the case with H_2O and was too low to confirm the incorporation of ^{18}O atom in the irregular triad compound. Nevertheless, these results again suggest that water is involved in the side reactions, and $H_2{}^{18}O$ is much less reactive than H_2O.

Furthermore, the effects of the defective structures on polymer properties were investigated. Figure 6 shows the absorbance and fluorescent spectra of the polymers obtained at 60 and 100 °C in DME/H_2O mixture (entries 2 and 4 in Table 1). The absorbance spectrum of the polymer obtained at 60 °C has an intense peak at 390 nm similarly to the spectrum reported in the literature 12 (Figure 6 A-a) while that of the polymer obtained at 100 °C only has a shoulder signal at 390 nm and the bands in the shorter-wavelength range had greater intensities. The latter spectral character is suggestive of a shorter conjugating length which is consistent with the proposed, partially oxidized structures shown in Figure 4 and Scheme 2.

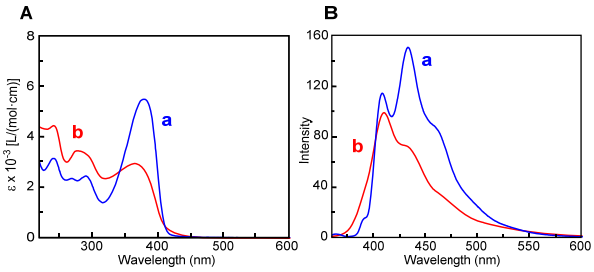


Figure 6. UV spectra (A) and fluorescence spectra (B) of **poly(DOF-*alt*-Phen)**s prepared at 60 °C (a) and 100 °C (b) from entries 2 and 4, respectively, in Table 1. [THF, rt, 10-mm cell; λ_{ex} = 350 nm for fluorescence]

The fluorescent spectrum of the polymer obtained at 60 °C showed emission bands with vibrational structure in the range of 400-550 nm with the main peak at around 440 nm where were over all similar to that of poly(dioctylfluorene-2,7-diyl).[15] This may mean that emission is contributed mainly from the conjugated fluorene units in the copolymer chain. The spectrum of the polymer obtained at 100 °C also showed emission bands with vibrational structure also in the range of 400-550 nm with the main peak at around 410 nm, suggestive of shorter conjugation involving fluorene units compared with the polymer obtained at 60 °C. These observations are consistent with the conclusion that proposed defective structures.

The defective structures also affected thermal properties. In the thermal gravimetric analysis (TGA) curves of the two polymers, the polymer obtained at 60 °C had a T_d of 375 °C which is rather close to the literature value of 417 °C while the polymer obtained at 100 °C had a much lower T_d of 210 °C (Figure S10 in supporting information). In addition, as a reference reaction, copolymerization between DOF[B(OH)$_2$]$_2$ and 1,4-dibromobenzene was conducted at 80 °C and 130 °C where no clear structural defects were found (Table S1, Figures S11-S13).[16] These results suggest that PhenBr$_2$ monomer or Phen unit have a role in producing defective structures at higher temperature.

Conclusions

The synthesis of poly(DOF-*alt*-phen)s at 100 °C in DME/H_2O or DME/D_2O by SMC led to defective structures which may include oxidized aromatic units possibly including 5,6-dihydro-1,10-phenanthroline-5,6-diol and 1,10-phenanthrolin-5(6H)-one units. Although the mechanism of the side reactions is not yet clear, it may involve H_2O (D_2O) and requires a growing species bearing a rather long pre-formed chain. The extent of the side reactions was higher with H_2O than D_2O was negligible with $H_2{}^{18}O$.

SMC is widely used and trusted because the reaction is generally more versatile, robust, and flawless than other reactions while dehalogenation side reactions have been pointed out.[17-19] There have been examples of SMC in small molecular synthesis using halogenated 1,10-phenthroline under reflux conditions;[20,21] however, production of structural defects has not been explicitly reported to the best of our knowledge. In the case of syntheses of small molecules, even if defective side products are formed, they might be removed in the process of purification and missed in identification. However, in polymer syntheses, structural alternations of monomers or units cannot be overlooked because they remain in the chain as

defective units.

The findings of the present work may give a suggestion that careful optimization of reaction conditions of SMC has to be conducted in order to obtain macromolecules having controlled chemical structure and also may mean that some unclarified aspects are involved in the mechanisms of SMC polymerization.

Acknowledgment

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