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Free-Radical Polymerization of Dibenzofulvene Leading to a π-Stacked Polymer: Structure and Properties of the Polymer and Proposed Reaction Mechanism

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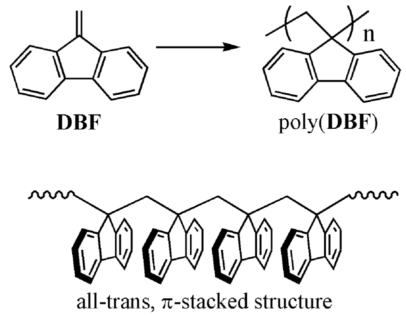
ABSTRACT: Free-radical polymerization of dibenzofulvene (DBF) was carried out under various conditions. The radical polymerization proceeded exclusively in vinyl fashion without isomerization of the growing radical or aromatic substitution by the initiator fragment. The polymerization was highly conformation-specific (stereospecific), giving a polymer with 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. The conformation specificity (stereospecificity) of the DBF radical polymerization was almost similar to that in the anionic polymerization although the radical polymerization products appeared to have a small amount of irregular, defective conformation incorporated into the mostly π-stacked chain. The conformation specificity was affected by the initial monomer concentration and reaction temperature. This observation was explained by a proposed mechanism where two types of the growing radicals having different conformations mediate the polymerization. The poly(DBF) obtained by the radical polymerization showed lower fluorescent intensity and higher solubility possibly due to a small amount of conformational defects.

Introduction

Stereoregulation in polymerization is an important goal in macromolecular science because the stereostructure of a polymer molecule often significantly affects properties and functions of materials derived therefrom. Aiming at novel functional polymeric materials, various polymers with regulated configuration and conformation have been synthesized. Regarding the polymers with a regulated conformation, we recently reported the anionic synthesis of poly(dibenzofulvene) (poly(DBF)) and its derivatives 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),[1−4] while most of the publications about polymers having a specific conformation deal with helical structures.[5]

The π-stacked DBF polymer has a potential for an novel electronic material because it indicates a high hole mobility for a vinyl polymer ($\mu = 2.7 \times 10^{-4}$ cm^2 V^{-1} s^{-1} at 299 K at $F = 7 \times 10^5$ V/cm).[6] The mobility is higher than that of main-chain π-conjugating poly(*p*-phenylenevinylene) ($\mu = 1 \times 10^{-5}$ cm^2 V^{-1} s^{-1}),[7] is comparable to that of main-chain σ-conjugating poly(methylphenylsilane) ($\mu = 1 \times 10^{-4}$ cm^2 V^{-1} s^{-1}),[8] and is slightly lower than that of Se ($\mu = 10^{-4}$ cm^2 V^{-1} s^{-1} order),[9] an inorganic semiconductor. Although polymers with a long main-chain conjugation such as polyfluorenes ($\mu = 4 \times 10^{-4}$, 8.5×10^{-3} cm^2 V^{-1} s^{-1})[10] and polythiophenes ($\mu = 10^{-2}$ cm^2 V^{-1} s^{-1} order)[11] have been exclusively studied for electronic applications, polymers with relatively short conjugations systems such as poly(DBF) having a relatively high charge mobility may also be usable for the same purposes. With the shorter conjugation, π-stacked polymers may have an advantage that they are generally less colored and probably less prone to degradation through oxidation by the air than the polymers with long main-chain conjugation.

Scheme 1. Polymerization of DBF Leading to a π-Stacked Polymer



The charge mobility of poly(DBF) is considered to be based on its strictly controlled π-stacked stereostructure constructed through anionic polymerization. Precise stereoregulation has been achieved for various monomers mainly by anionic or coordination polymerization so far. Although radical polymerization is more versatile and convenient than anionic or coordination polymerization, it is generally less effective in stereoregulation except for limited examples.[12] As an exceptional example, it has been reported that radical polymerizations of bulky acrylic monomers such as 1-phenyldibenzosubery methacrylate and triphenylmethyl methacrylate proceeds in a highly configuration- and conformation-specific manner, giving a highly isotactic, helical polymer.[13−15] As shown by these examples, it is of significant benefit if a polymer with a regulated conformation can be obtained by facile radical polymerization rather than the anionic polymerization which requires a strict control of reaction conditions.

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Table 1. Radical Polymerization of DBF[a]

							$CHCl_3$-insoluble part	$CHCl_3$-soluble part		
run	initiator	solvent	temp (°C)	[monomer]$_0$ (M)	[initiator]$_0$ (M)	conv[b] (%)	yield (%)	yield (%)	M_n[d] (vs St)	M_n[e] (vs DBF)
1	AIBN	benzene	60	0.40	0.020	54	40	14	1000[f]	1730[f]
2	$(i\mathrm{PrOCOO})_2$	toluene	40	0.40	0.020	73	40	33	1070[f]	1560[f]
3	none	benzene	60	0.40	0	45	42	17	2190[g]	n.d.
4	AIBN	toluene	60	0.40	0.020	39	26	13	950	1370
5	AIBN	THF	60	0.40	0.020	24	8	16	770	1080
6	AIBN	$CHCl_3$	60	0.42	0.020	27	8	19	780	1090
7	AIBN	MeOH	60	0.20	0.020	40	28	12	1100	1620
8	AIBN	hexane	60	0.40	0.020	45	22	23	1550	2340
9	AIBN	benzene	60	0.16	0.008	23	9	18	670	820
10	AIBN	benzene	60	0.08	0.004	22	4	18	510	690
11	AIBN	toluene	80	0.40	0.020	36	8	28	250	320
12	BPO−DMA[h]	toluene	0	0.40	0.020	n.d.	34	n.d.	870	n.d.

[a] Time = 24 h (runs 1−11), 48 h (run 12). [b] Determined by ^1H NMR analysis of the reaction mixture. [c] $CHCl_3$-soluble part was a mixture of oligomers and unreacted monomer. The yield of this part was calculated excluding the weight of the unreacted monomer. [d] Determined by SEC using two OligoPore columns connected in series with oligostyrenes as the standard samples (eluent: THF). [e] Determined by SEC using two OligoPore columns connected in series with oligo(DBF)s as the standard samples (eluent: THF). [f] Two TSKgel G1000H$_{HR}$ columns connected in series were used for SEC analysis. [g] Determined by SEC using TSKgel G6000H$_{HR}$ and G3000H$_{HR}$ columns connected in series with polystyrene as the standard sample (eluent: THF). [h] DMA = *N*,*N*-dimethylaniline, $[BPO]_0/[DMA]_0 = 1$.

As for the polymerization of DBF, we have shown the details of the anionic polymerization leading to a perfectly π-stacked conformation.[2] However, no details of the radical polymerization including the stereochemical aspect have been known. This paper describes the polymerization of DBF using radical initiators under various conditions and the structure and photophysical and solubility properties of the obtained polymers.

Experimental Section

Materials. DBF monomer was synthesized according to the published method.[2,16,17] Anionic polymerization products were available form our recent work.[2] α,α′-Azobis(isobutyronitrile) (AIBN) was recrystallized from an ethanol solution. Benzoyl peroxide (BPO) (Wako) was used as obtained. *N,N*-Dimethylaniline (DMA) was distilled and dried on KOH. $(i\mathrm{PrOCOO})_2$ was kindly provided by NOF Co. (Taketoyo-cho, Chita-gun, Aichi 470-23, Japan). Tetrahydrofuran (THF) (Wako) was refluxed over sodium benzophenone ketyl, distilled and stored on $LiAlH_4$ under a N_2 atmosphere, and distilled under vacuum immediately before use. The other solvents were purified by the usual methods, degassed under vacuum and flashed with N_2, and stored under a N_2 atmosphere.

Polymerization. The reactions were carried out in a glass ampule sealed with a glass-made three-way stopcock attached to the ampule via a ground joint. The joint was sealed with high-vacuum grease. The ampule was flame-dried under high vacuum and flashed with N_2 immediately before use. A typical procedure is described for run 1 in Table 1. DBF (534 mg, 3.00 mmol) and AIBN (24.6 mg, 0.15 mmol) were placed in a flame-dried ampule, and the ampule was evacuated for 5 min at room temperature and flashed with dry N_2 gas. Benzene (6.9 mL) was added using a syringe, and the monomer and the initiator were completely dissolved. The polymerization was initiated by heating the solution at 60 °C, and the reaction mixture was cooled at 0 °C after 24 h of heating. An aliquot (about 0.1 mL) of the solution part of the reaction mixture was transferred to an NMR sample tube (5 mm diameter), 0.6 mL of $CDCl_3$ was added, and the resulting diluted solution was subjected to ^1H NMR analysis. Comparison of the intensity of the vinyl proton signals of remaining DBF (s, 6.0 ppm) with that of the benzene signal (s, 7.4 ppm) as an internal standard gave a monomer consumption ratio of 54%. After removing the solvents from the rest of the reaction mixture, the residue was separated into $CHCl_3$-soluble and -insoluble parts using a Teflon-made membrane filter (pore size, 0.45 μm). The $CHCl_3$-soluble part was fractionated into the reaction products (polymers and oligomers) and the remaining monomer with a preparative SEC system. The chromatographically obtained fractions were further purified by reprecipitating in hexane seven times.

Measurements. The ^1H NMR spectra were recorded on a JEOL JNM-ECP600NK or a JEOL ECP500 spectrometer (600 and 500 MHz, respectively, for ^1H measurement). Analytical scale SEC was carried out using a chromatographic system consisting of a JASCO PU-980 chromatographic pump, a JASCO UV-975 UV detector (254 nm), and a JASCO RI-930 RI detector equipped with two PL-Oligopore columns (30 × 0.72 (i.d.) cm) (Polymer Laboratories) connected in series or on a system consisting of a Hitachi L-7100 pump, an L-7420 UV detector (254 nm), and an L-7490 RI detector equipped with TOSOH TSK gel G3000H$_{HR}$ and G6000H$_{HR}$ columns connected in series (eluent, THF; flow rate, 1.0 mL/min). Preparative SEC separation of oligomers was performed using a JAI LC-908 preparative recycle chromatograph equipped with JAIGEL-1H and JAIGEL-2H columns connected in series. IR spectra were measured with a JASCO FT/IR-420 spectrophotometer using KBr pellet samples. MALDI-mass spectra were taken on a Voyager DE-STR spectrometer equipped with a N_2 laser (337 nm, 3 ns pulse duration, frequency up to 20 Hz) under vacuum (sample chamber pressure 5.5×10^{-7} Torr) using the reflector mode (acceleration voltage 20 000 V). The excitation laser power was set to 2000−3000. Samples were prepared by mixing a $CHCl_3$ solution of polymer (concentration 10 mg/mL, 1 μL), a $CHCl_3$ solution of dithranol (concentration 10 mg/mL, 20 μL), and a methanol solution of silver trifluoroacetate (TFA-Ag) (concentration 0.1 mg/mL, 1 μL) and by drying the mixed solution in a sample well on a gold-plated sample slide under air flow. Absorption and emission spectra were measured at room temperature in a 1 cm quartz cell with a JASCO V-550 spectrophotometer and a JASCO FP-777W fluorescence spectrophotometer, respectively. The fluorescence spectrophotometer was calibrated using an aqueous solution of Rhodamine B. Fluorescent quantum yields were determined with reference to 9,10-diphenylanthracene ($\Phi_F = 0.90$).[18] Samples (THF solutions) were degassed by bubbling N_2 gas through for 10 min.

Simulation. Semiempirical calculations with the PM5[19] wave function were performed using the Cache ver. 5.02 software package (Fujitsu Ltd.). Molecular dynamic simulations were effected using the COMPASS[20] force field implemented in the Discover module of the Material Studio 3.2 (Accelrys) software package under a constant NVT conditions in which the numbers of atoms, volume, and thermodynamic temperature were held constant. Berendsen's thermocouple[21] was used for coupling to a thermal bath. The step time was 1 fs, and the decay constant was 0.1 ps.

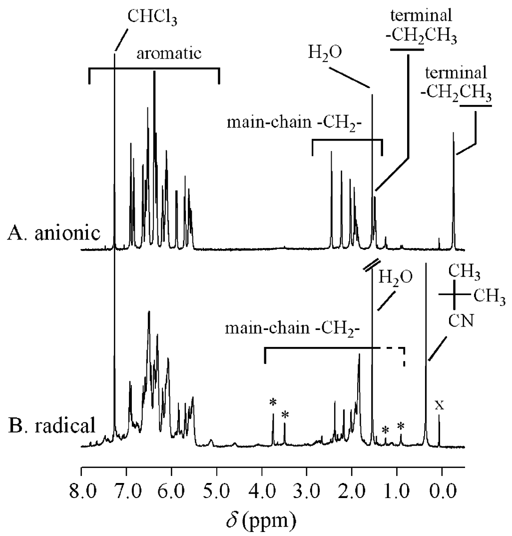


Figure 1. ^{1}H NMR spectra of poly(DBF)s prepared by anionic polymerization using MeLi as initiator and EtI as terminator (M_n = 1890 (vs oligo(DBF)s))[2] (A) and by radical polymerization using AIBN (run 1 in Table 1) (B). The signals marked by an asterisk in (B) may be based on conformational defects [500 MHz, CDCl$_3$, rt].

Results and Discussion

Chemical Structure of Radical Polymerization Products. Radical polymerization was carried out with and without initiator in several solvents (Table 1). Despite the bulky structure resembling 1,1-diphenylethylene (DPE), which does not homopolymerize,[22] DBF afforded polymers by polymerization using the radical initiators. The relatively low monomer conversions may suggest a relatively low ceiling temperature due to the bulkiness of the monomer. In all cases, the products consisted of CHCl$_3$-insoluble and -soluble parts. The CHCl$_3$-soluble and -insoluble parts of the polymer from run 1 in Table 1 indicated virtually the same IR spectral pattern, suggesting that they have the same chemical structure. The insoluble part is assumed to be produced by molecular aggregation of rigid polymer molecules and not by cross-linking. It is known that higher-molecular-weight fractions tend to form insoluble aggregates for helical polymethacrylates having a rigid, regulated chain structure.[23]

Interestingly, the reaction without an initiator also led to a polymer (run 3 in Table 1). A trace amount of oxygen in the reaction system might be responsible for the formation of an initiating radical[4] although generation of a Diels−Alder dimer similar to that reported for the thermal polymerization of styrene[24] cannot be ruled out. No more details have been investigated about this aspect.

To establish that the polymerization took place in vinyl fashion, the structure of the CHCl$_3$-soluble polymer obtained in run 1 was investigated by NMR and IR spectra. Figure 1 compares the ^{1}H NMR spectrum of the polymer from run 1 with that of the poly(DBF) obtained by anionic polymerization with MeLi as initiator and EtI as terminator[2] (M_n 1890). The two spectra had a very similar shape with the only clear difference in the signals of the terminal groups. These results suggest that the radical polymerization took place in vinyl fashion.

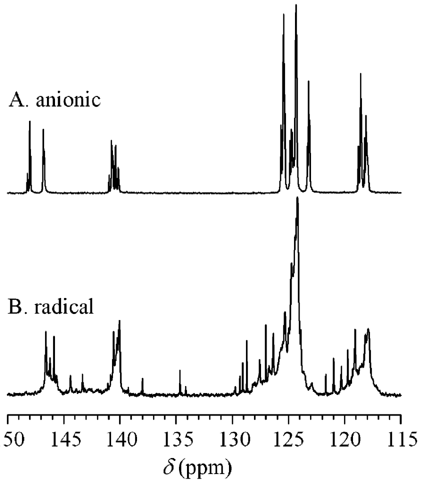


Figure 2. ^{13}C NMR spectra of poly(DBF)s prepared by anionic polymerization using MeLi as initiator and EtI as terminator (M_n 770, DP = 2−8 mixture)[2] (A) and by radical polymerization using AIBN (run 1 in Table 1) (B) [150 MHz, CDCl$_3$, rt].

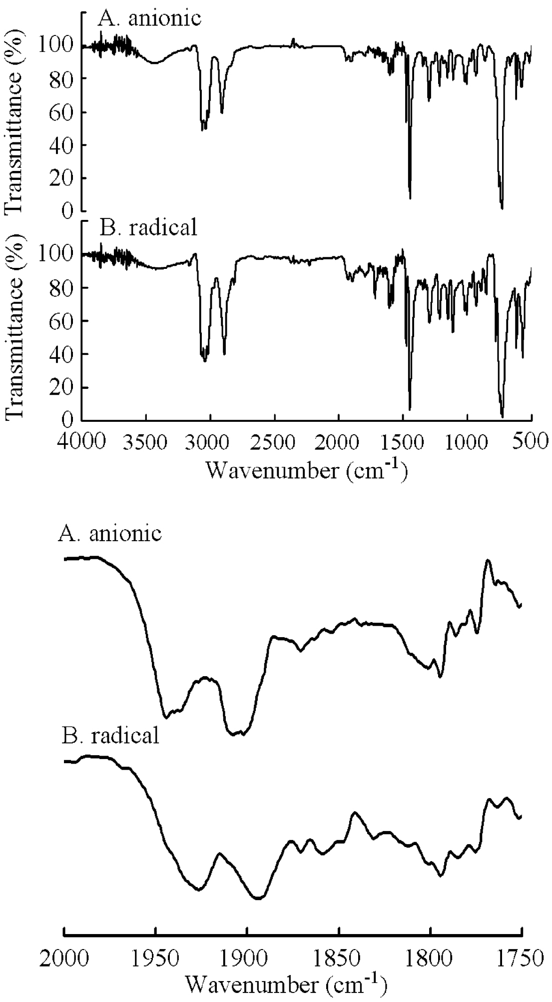
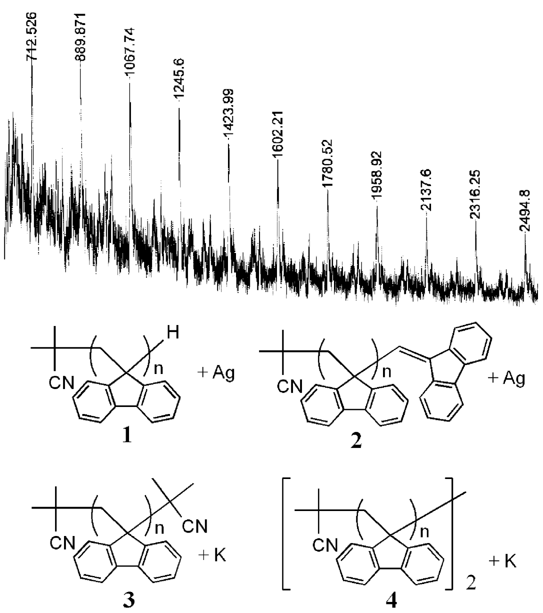


Figure 3. IR spectra of polymers prepared by anionic polymerization using MeLi as initiator and EtI as terminator (M_n = 1890 (vs oligo(DBF)s))[2] (A) and by radical polymerization using AIBN (run 1 in Table 1) (B): full (top) and overtone/combination band region (bottom) spectra.

The ^{13}C NMR and IR spectra of the poly(DBF) obtained by radical polymerization (run 1 in Table 1) were compared with those of the anionically synthesized poly(DBF)s[2] in Figures 2 and 3, respectively. The aromatic ^{13}C NMR spectrum in Figure 2 and the overtone/combination IR bands in Figure 3 are sensitive to the aromatic ring substitution pattern. The fact that

A. initiator = AIBN



B. initiator = (iPrOCOO)$_2$

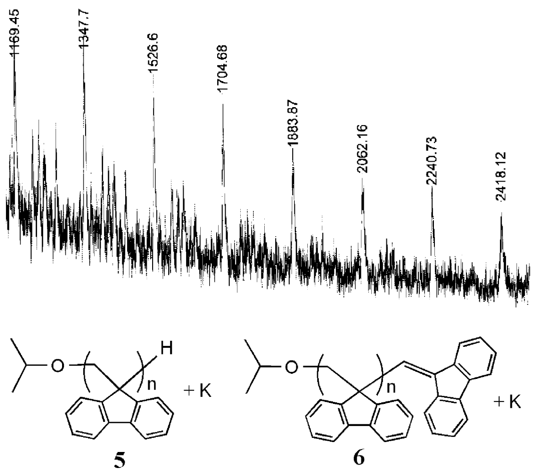


Figure 4. MALDI-TOF mass spectra of poly(DBF)s prepared by radical polymerization using AIBN (run 1 in Table 1) (A) and (^{i}PrOCOO)$_2$ (run 2 in Table 1) (B) (matrix: dithranol and TFA-Ag).

the radical and the anionic polymerization products showed very similar patterns in both the ^{13}C NMR and the IR spectra indicates that isomerization of the growing radical[25] or aromatic substitution did not significantly contribute to the polymerization although such reactions are not completely ruled out because there still are minor differences between the two ^{13}C spectra which cannot be immediately explained.

Figure 4 shows the MALDI-TOF mass spectra of the CHCl$_3$-soluble polymer obtained using AIBN and (^{i}PrOCOO)$_2$ (runs 1 and 2 in Table 1). The spectra indicated the periodic mass peaks separated from each other by a mass number of ca. 178, corresponding to the molecular mass of DBF monomeric unit. In the spectrum of the polymer synthesized using AIBN (run 1 in Table 1), the mass numbers of the major peaks were close to those of molecular ions associated with Ag corresponding to structures **1** and **2** which may be produced by disproportionation or hydrogen abstraction from solvent. The mass numbers were also close to those of molecular ions associated with K corresponding to structures **3** and **4** having two (CH$_3$)$_2$C(CN)− groups at the chain terminals which may be obtained through primary radical termination and recombination termination, respectively; however, these structures are less plausible because the DP of the products from run 1 in Table 1 calculated from the ^{1}H NMR spectra in Figure 1B assuming structures **1** and **2** (DP = 15) was much closer than that calculated assuming structures **3** and **4** (DP = 30) to the DP of ca. 10 derived from the M_n estimated by SEC (M_n 1730 by SEC with oligo(DBF)s as reference samples).

On the other hand, the spectrum of the polymer obtained using (iPrOCOO)$_2$ (run 2) showed the mass numbers close to those of the molecular ions associated with K corresponding to structures **5** and **6** and no signals matching to the mass numbers of primary radical termination or recombination termination products. Hence, in the radical polymerization of DBF with AIBN or (iPrOCOO)$_2$ examined here, the termination reaction may occur mainly through disproportionation or hydrogen abstraction from solvent.

Stereochemistry of Radical Polymerization. Because poly(DBF) with a vinyl polymer structure has no asymmetric centers, conformation is the only aspect of the stereochemistry to be discussed. The ^{1}H NMR spectra shown in Figure 1 provide important information on the stereostructure (conformation) of the polymer obtained by the radical polymerization. The detailed studies on the completely π-stacked poly- and oligo(DBF)s have indicated that the aromatic proton signals are in the range 5.5−6.9 ppm due to the shielding effect and the main-chain −CH$_2$− signals are in the range 1.8−2.6 ppm.[2] It has also been predicted by density functional theory (DFT) calculations that the main-chain −CH$_2$− chemical shifts are sensitive to polymer conformation, and defective conformations (not-π-stacked parts) will shift the main-chain −CH$_2$− signals to a higher or a lower magnetic field from the 1.8−2.6 ppm range.[2]

The spectrum of the polymer obtained by the radical polymerization in benzene using AIBN (Figure 1B) indicated the most main-chain −CH$_2$− peaks in the range 1.8−2.8 ppm and the aromatic peaks in the range 5.5−7 ppm. This indicates that the polymer prepared by radical polymerization has a π-stacked conformation similar to that of the polymer by anionic polymerization. Hence, the radical polymerization of DBF was shown to be almost as conformation-specific as well as the anionic polymerization. However, the radically synthesized polymer may contain a small amount of some defective conformation because the peaks marked by an asterisk in Figure 1B of low intensities probably due to −CH$_2$− protons are observed in the 0.8−1.5 and 3−4 ppm regions where the peaks due to π-stacked conformation should not show. It is important to note that these peaks are considered not to arise from some low-molecular-weight impurities because the shapes and intensities of the peaks were unchanged through purification by reprecipitating in hexane seven times to remove silicon grease residue and also because no signals of such impurities were found by SEC analyses.

Effects of Solvent, Temperature, and Monomer Concentration on the Reaction Stereochemistry. Although solvent, monomer concentration, and temperature generally do not have a significant effect on radical polymerization stereochemistry, such factors have

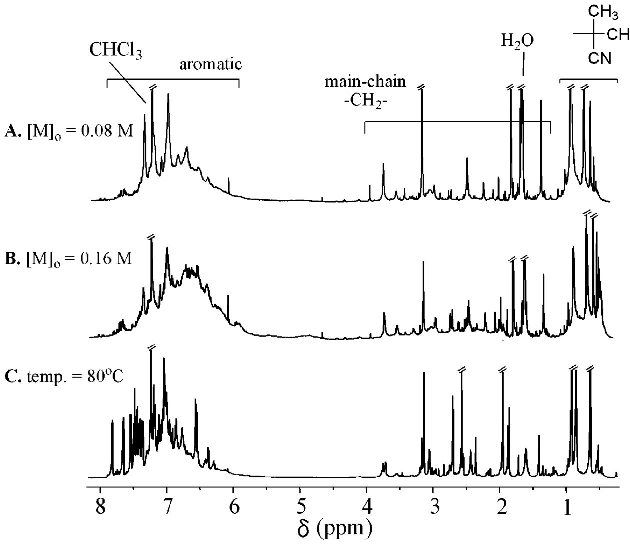


Figure 5. ^{1}H NMR spectrum of the radical polymerization products obtained in benzene at 60 °C at 0.08 M (run 10 in Table 1) (A) and $[M]_0 = 0.16$ M (run 9 in Table 1) (B) and in toluene at 80 °C at $[M]_0 = 0.40$ M (run 11 in Table 1) (C) [500 MHz, $CDCl_3$].

been reported to significantly affect the stereochemistry of triphenylmethyl methacrylate (TrMA) polymerization which leads to a polymer with a rigid, helical conformation.[26] These effects have been interpreted in terms of the proposed two growing species whose conformations differ in the vicinity of the active radical end, and the following have been proposed for the species: (1) one of the two adds monomer in a highly isotactic-specific manner while the other leads to lower stereospecificity in monomer addition, (2) the latter is formed on monomer addition and mutates to the former at a rate comparable to that of monomer addition, and (3) the mutation takes more obvious effects on the polymerization stereochemistry in a proper solvent, at a lower monomer concentration, and at a higher temperature. A similar situation might be possible for the radical polymerization of DBF because both poly(DBF) and poly(TrMA) have a rigid structure with a specific conformation.

To test this possibility, the polymerization of DBF was carried out in different solvents, at different monomer concentrations, and at different temperatures. First, solvent effects were examined by polymerization at 60 °C using benzene, toluene, tetrahydrofuran (THF), $CHCl_3$, methanol, and hexane as solvents (runs 1 and 4−8 in Table 1). Polymers were obtained in all solvents. Although polymer yields and molecular weights varied depending on solvents, all $CHCl_3$-soluble polymers obtained here showed very similar ^{1}H NMR spectral patterns which resemble the spectrum of a π-stacked polymer obtained by anionic polymerization (Figure 1A). This means that the stereochemistry was little affected by solvents in the DBF polymerization unlike in the TrMA polymerization.

Monomer concentration effects were next examined by polymerizations in benzene using AIBN at 60 °C (runs 1, 9, and 10 in Table 1). Polymerization reaction took place at all concentrations. The ^{1}H NMR spectra of the products obtained at $[M]_0 = 0.08$ and 0.16 M are shown in Figure 5A,B. The spectra were clearly different in pattern from that of the polymer obtained at $[M]_0 = 0.40$ M (Figure 1B): the aromatic signals are significantly less upfield shifted, and signals probably due to $-CH_2-$ were observed in a much wider chemical shift range.

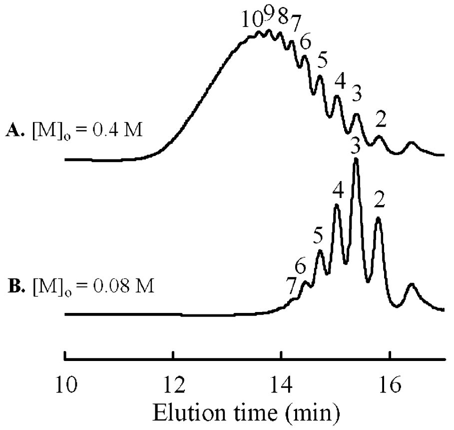


Figure 6. SEC curves of the radical polymerization products obtained at different initial monomer concentrations: $[M]_0 = 0.40$ M (run 1 in Table 1) (A) and 0.08 M (run 10 in Table 1) (B) [UV detection at 254 nm].

Although the products obtained at $[M]_0 = 0.08$ M had a much lower average molecular weight than that obtained at $[M]_0 = 0.4$ M and were oligomers with dimer, trimer, and tetramer as the major components (Figure 6A,B), the NMR profiles noted above are not due to the low DPs of the products because π-stacked oligomers (DP = 2−8) obtained by anionic polymerization did not show $-CH_2-$ signals in such a wide range. Some of the $-CH_2-$ signals in Figure 5A,B may be due to some defective, not-π-stacked, conformation.

Next, to investigate temperature effects on the polymerization stereochemistry, polymerization was carried out in toluene using AIBN at 80, 60, and 40 °C and using benzoyl peroxide−*N,N*-dimethylaniline (BPO−DMA) at 0 °C (runs 2, 4, 11, and 12 in Table 1). While the products at 0−60 °C showed similar ^{1}H NMR spectra resembling that of the anionic polymerization products, the reaction products obtained at 80 °C indicated a spectral pattern similar to those of the products obtained at $[M]_0 = 0.08$ and 0.16 M at 60 °C (Figure 5C). Again, this is considered not to arise from the low molecular weight of the products as discussed above.

Thus, a lower monomer concentration and a higher reaction temperature seem to lead to a defective conformation. To obtain information on the conformation produced under such conditions, the trimer fraction (the peak marked by “3” in Figure 6B) was isolated using a preparative SEC system and subjected to structural analyses. The MALDI-mass spectra of this isolated fraction indicated major molecular ion peaks at $m/z = 692.883$ and 708.905 which correspond to the mass numbers of a DBF trimer having two $(CH_3)_2C(CN)-$ groups (structure **3** in Figure 4A with $n = 3$) associated with Na and K, respectively. This structure is produced through primary radical termination of a trimer radical. In the low-molecular-weight range, primary radical termination appears to contribute to the polymerization, which is in contrast to the production of structures **1** and **2** in Figure 4A in the higher-molecular-weight range as discussed earlier.

Figure 7A shows the ^{1}H NMR spectrum of the isolated trimer. The two peaks in the 0.5−0.8 ppm range are assigned to the two $(CH_3)_2C(CN)-$ groups on the basis

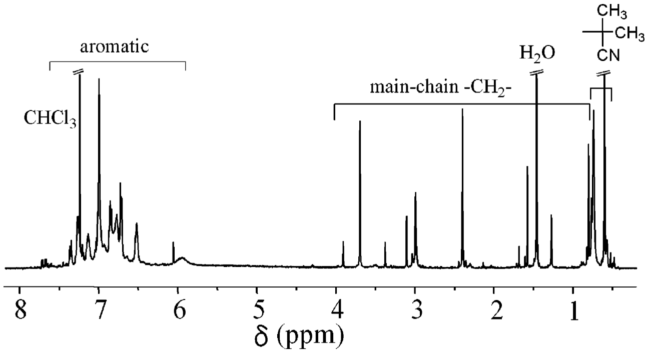
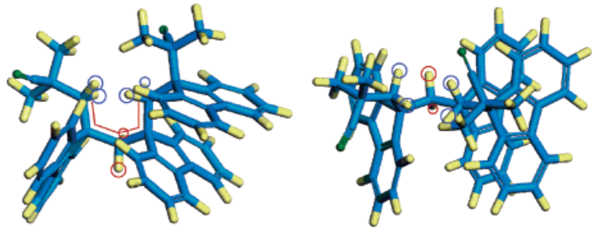


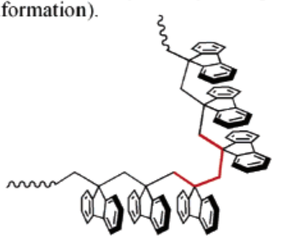
Figure 7. ^{1}H NMR spectrum of the trimer fraction isolated by SEC. See Figure 6B for the analytical SEC curve.

Scheme 2. A Defective, Not-π-Stacked, Conformation of a DBF Trimer Having $(CH_3)_2C(CN)-$ Groups at Chain Terminals: Side (Left) and Top (Right) Views[a]

A. Trimer structure with a defective conformation



B. A π-stacked chain with a gauche-gauche part (defective conformation).



[a] The red bars indicate the gauche−gauche part of the main chain (conformational defect), and the red and blue circles indicate protons expected to be upfield and downfield shifted, respectively, compared with the $-CH_2-$ protons in a completely π-stacked chain, by DFT calculations.[2]

of their intensities relative to that of aromatic signals. Several peaks probably due to $-CH_2-$ groups were in the 0.8−4 ppm range whereas $-CH_2-$ protons of a completely π-stacked trimer appear only at 2.8 ppm. To explain these chemical shift characteristics, a trimer structure with a gauche−gauche part in the main chain is proposed, as shown in Scheme 2A. From the published DFT calculation on the DBF oligomers,[2] the $-CH_2-$ protons marked by red and blue circles are expected to be downfield- and upfield-shifted, respectively, compared with those in a completely π-stacked conformation with the all-trans main chain on the basis of the published DFT calculations. Therefore, the proposed oligomer structure explains that the $-CH_2-$ signals were observed in a wide range though precise peak assignments have not been achieved. Because the total number of signals in the $-CH_2-$ region was greater than the number of $-CH_2-$ groups of a trimer, three, the fractionated sample may contain several conformational variations.

The proposed conformer was found to be stable in molecular dynamics (MD) simulations at 298 K in the duration periods of 9.99 ns. Although three other possible, defective conformers were examined under the same simulation conditions, they turned to a completely π-stacked structure within the duration time of ca. 500 ps. This supports the plausibility of the proposed conformation in Scheme 2A.

On the basis of the discussions here, poly(DBF) obtained by radical polymerization may possibly have gauche−gauche parts as a conformational defect in the mostly π-stacked, all-trans chain, as shown in Scheme 2B. Such a part may result in the $-CH_2-$ signals out of the 1.8−2.8 ppm range in ^{1}H NMR spectra (the signals marked by an asterisk in Figure 1B).

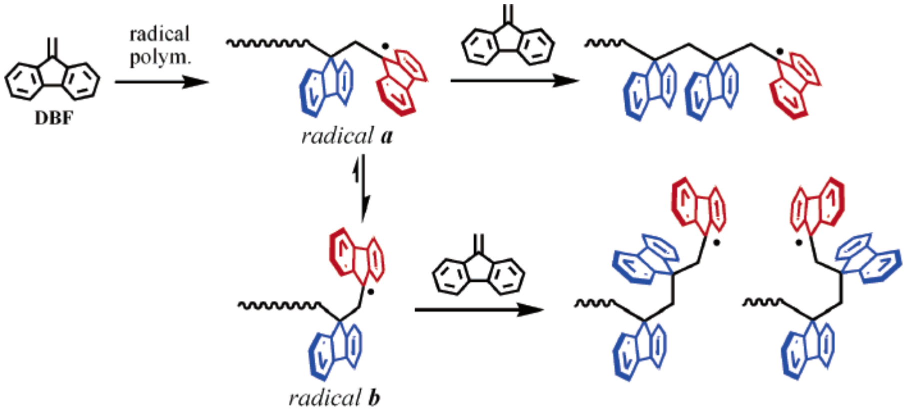
Proposed Stereochemical Mechanism of Polymerization. To explain the fact that the defective structures are produced at a lower monomer concentration and at a higher reaction temperature, we propose a reaction mechanism involving different conformations of the growing radical which lead to different conformations of the terminal diad on the reaction with a monomer (radicals **a** and **b** in Scheme 3). Radical **a** has a loosely π-stacked conformation at the growing terminal and gives a π-stacked diad on monomer addition while radical **b** has a flipped fluorene moiety at the growing terminal and gives a flipped diad with a gauche main-chain conformation on monomer addition. Radical **a** is less stable than radical **b** and can mutate to radical **b**. This mechanism explains the generation of defective structures at a lower monomer concentration where radical **a** has a larger chance to mutate to **b** before it attacks to a monomer and at a higher temperature where the mutation is faster. While the more stable growing species was the more stereospecific species in the proposed mechanism of TrMA polymerization,[26] the species giving a defective conformation is more stable in this case.

The validity of the proposed radicals **a** and **b** was checked by the semiempirical PM5[19] calculations of two model trimer radicals bearing an ethyl group at the initiation terminal (Scheme 4). The optimized trimer radical structures, **A** and **B** in Scheme 4, have similar shapes to those of the growing end of the proposed radicals, **a** and **b** in Scheme 3, respectively, and are likely to give a stacked and a flipped diads, respectively, on monomer addition. The heat of formation (H_f) for **A** was 168.75 kcal/mol, and that for **B** was 165.77 kcal/mol, indicating that the latter is slightly more stable. In addition, the rotation barrier between **A** and **B** was estimated to be ca. 10 kcal/mol by calculating the energies of 20 conformers generated by changing the dihedral angle marked by the curved arrows shown in Scheme 4 at the angle interval of 10°. Thus, the proposed mechanism that radical **a** mutates to radical **b** (Scheme 3), the more stable conformer, may be reasonable. Because the main-chain C−C bonds are the only rotatable bonds in poly(DBF), the molecular simulations presented here are expected to be reasonably accurate.

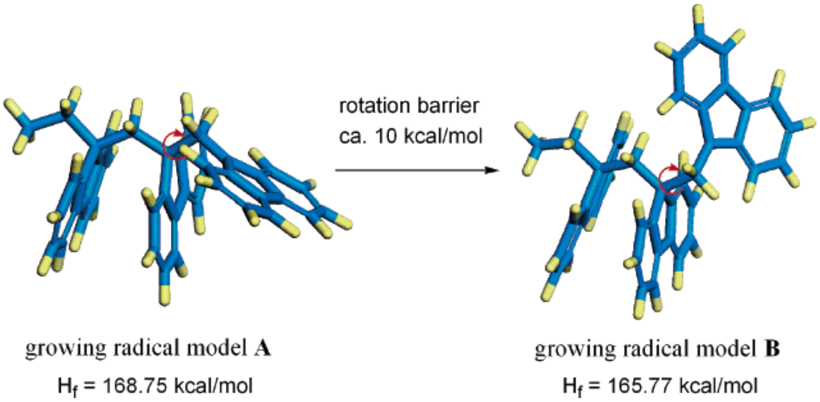
On the basis of these discussions, defective structures may occur in the mostly π-stacked poly(DBF) prepared by radical polymerization. At the later stages of polymerization where the monomer concentration is lower than at the earlier stages of polymerization, polymer chains with a higher content of conformational defect may be produced at a higher chance.

Photophysical Properties. Properties of the polymers and the oligomers were investigated. Absorption and emission spectra are shown along with those of the

Scheme 3. Proposed Reaction Mechanism Involving Two Conformers of the Growing Radical



Scheme 4. Structures and Heat of Formation (H_f) Values of Loosely π-Stacked (A) and Flipped (B) Trimer Growing Radical Models Optimized by PM5 Calculation



polymer synthesized by anionic polymerization[2] in Figures 8 and 9. The quantum yields of the emissions shown in Figure 9 are summarized in Table 2.

In the absorption spectra (Figure 8), the radical polymerization products obtained using AIBN in benzene at 60 °C (runs 1 and 10 in Table 1) showed a remarkable hypochromic effect which is characteristic of a π-stacked structure. However, the magnitude of hypochromicity of the products obtained at $[M]_0 = 0.08$ M was slightly lower compared with that for the anionic polymerization products while that of the polymers obtained at $[M]_0 = 0.4$ M was comparable to that of the anionic polymerization products. This is consistent with the conclusion in the conclusion that the oligomers obtained at $[M]_0 = 0.08$ M have a partially defective conformation.

In the fluorescence spectra (Figure 9), the radical polymerization products obtained at $[M]_0 = 0.4$ M (run 1 in Table 1) indicated exclusive intramolecular dimer (excimer) emission (ca. 400 nm) which is characteristic of a π-stacked structure while the products obtained at $[M]_0 = 0.08$ M (run 10 in Table 1) indicated both monomer (ca. 305−320 nm) and dimer (excimer) emis-

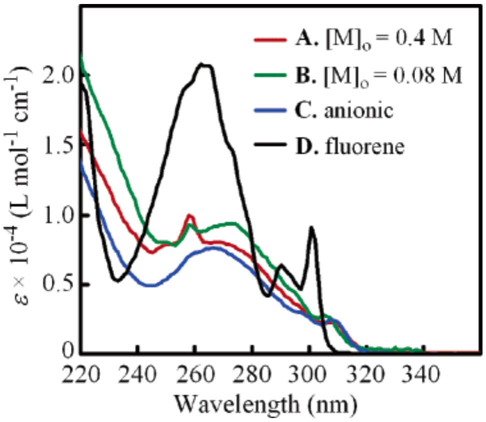


Figure 8. Absorption spectra of the radical polymerization products obtained at $[M]_0 = 0.4$ M (run 1 in Table 1) (A) and 0.08 M (run 10 in Table 1), the polymer having ethyl groups at the chain terminals obtained by anionic polymerization (M_n 1890, available from our recent work[2]) (C), and fluorene as model monomeric unit (D) [THF, rt]. The molar extinction coefficients are based on the molar concentration of fluorene moieties in the samples.

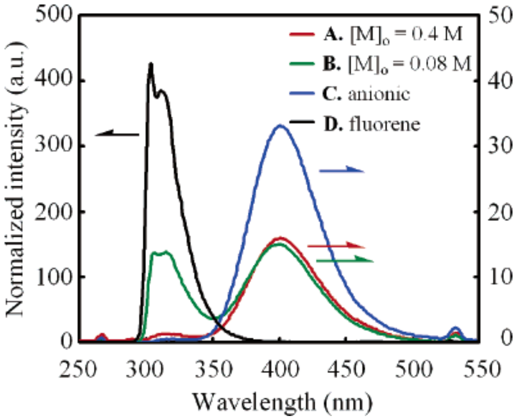


Figure 9. Fluorescent spectra of the $CHCl_3$-soluble, radical polymerization products obtained at $[M]_0 = 0.4$ M (run 1 in Table 1) (A) and 0.08 M (run 10 in Table 1) (B), the anionic polymerization products (M_n 1890, available from our recent work[2]) (C), and fluorene as model monomeric unit (D). The intensity was corrected to a constant absorbance at 267 nm [THF, rt, $\lambda_{ex} = 267$ nm].

Table 2. Fluorescence Quantum Yields (Φ_F) for Spectra in Figure 9[a]

spectrum	monomer emission (300−350 nm)	excimer emission (350−500 nm)
A		0.060
B	0.025	0.056
C		0.12
D	0.69	

[a] Determined with reference to 9,10-diphenylanthracene (Φ_F 0.90).[18]

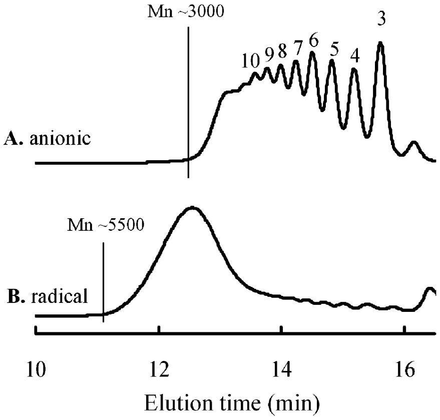


Figure 10. SEC curves of the $CHCl_3$-soluble poly(DBF)s obtained by the anionic polymerization using FlLi at $[M]_0/[I]_0 = 10$ in THF[2] (A) and by the radical polymerization in hexane (run 8 in Table 1) (B).

sions. The monomer emission should have nothing to do with the low DPs of the products at $[M]_0 = 0.08$ M and is considered to arise from the conformationally defective parts because a DBF dimer having terminal ethyl groups with a π-stacked structure showed only dimer (excimer) emission.

It is notable that the emission intensity of the products obtained at $[M]_0 = 0.4$ M (run 1 in Table 1) was approximately half that of the anionic polymerization product. This may be because the π-stacked structure constructed by radical polymerization is not as regular as that produced by anionic polymerization and has a small amount of defective conformations incorporated in a π-stacked sequence. Such a conformational defect might act as a built-in quenching site. Also, the terminal −CN group originating from AIBN might possibly quench the emission although this possibility has not been investigated in detail.

Solubility. A clear difference between the anionic and radical polymerization products was found in solubility. Although both the radical and anionic products are only partially soluble in solvents, the M_n range of the highest-molecular-weight fractions of $CHCl_3$-soluble part was found to be much higher for the radical polymerization products (run 8 in Table 1) than the anionic polymerization products prepared in THF at −78 °C using fluorenyllithium (FlLi) at $[M]_0/[I]_0 = 20$,[2] as shown in Figure 10. As well as the lower fluorescent efficiency, this also may be explained by minor structural defects in the mostly π-stacked chain prepared by radical polymerization. A slight conformational irregularity may make molecular packing less tight in the formation of the insoluble aggregates.

Conclusions. Radical polymerization of DBF was carried out under various conditions, and the structure and properties of the obtained polymers and oligomers were investigated. It was shown that (i) radical polymerization of DBF proceeded through a vinyl addition mode, (ii) the polymers had a mostly π-stacked conformation with a small amount of defective parts, (iii) the polymers showed lower fluorescent efficiency and higher solubility compared with those of the poly(DBF) synthesized by anionic polymerization possibly due to a small amount of defective conformations, and (iv) a lower monomer concentration and a higher temperature led to defective conformations, which was explained by a proposed reaction mechanism involving two interchangeable conformers of the growing radical with different conformation specificity on monomer addition.

Although regulated and stable π-stacked structures have been realized for several types of polymers other than poly(DBF) and its derivatives, the examples are still limited, and their synthesis generally requires more laborious procedures than simple vinyl polymerization.[27−31] This study opens a way to synthesize a π-stacked polymer by radical polymerization method which is especially facile among various vinyl polymerization techniques. In addition, it is implicated that conformational modification is possible to a certain extent by controlling reaction conditions (monomer concentration and reaction temperature). This feature may be used to modify not only the solubility discussed here but also other physical properties of π-stacked poly(DBF) such as charge mobility and conductivity.

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