A Photo-Degradable Helix: Synthesis, Structure, and Photolysis of Optically Active Poly[2,7-bis(4-*t*-butylphenyl)-9-methylfluoren-9-yl Acrylate]

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ABSTRACT: 2,7-Bis(4-*t*-butylphenyl)-9-methylfluoren-9-yl acrylate (**BBPMFA**) was synthesized and polymerized using α, α' -azobisisobutyronitrile or *n*-Bu₃B-air as a radical initiator and using the complex of 9-fluorenyllithium with (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine as an optically active anionic initiator. Although the radical polymerization led to rather low-molecular-weight products at low yields, the anionic polymerization afforded polymers with higher molecular weights in higher yields. The poly(**BBPMFA**) obtained by the anionic polymerization was slightly rich in isotacticity (meso diad 57%) and showed an intense circular dichroism (CD) spectrum and large dextrorotation. The intensity of the CD spectrum and magnitude of optical activity increased with an increase in M_{nr} , suggesting that the polymer possesses a preferred-handed helical conformation. The CD spectrum disappeared within 1 s on irradiation to

INTRODUCTION Chiral polymers are important not only from the view of basic polymer stereochemistry but also from a practical view because such polymers have high potentialities in applications such as chiral separation, nonlinear optical devices, and chiral catalysts.¹ One of the most extensively and systematically studied classes of chiral polymers is a helical polymer. Optically active, helical polymers with single-handed or preferred-handed helicity can be typically prepared by asymmetric polymerization of a properly designed achiral or chiral monomer (helix-sense-selective polymerization) as well as the other methods including supramolecular interaction control between an achiral polymer and chiral added molecules,1(j-m) or by chain folding control of "foldamers."1(g,h) Helix-sense-selective polymerization of vinyl monomer was first realized for bulky triphenylmethyl methacrylate,²⁻⁴ and thereafter, many bulky acrylic monomers were designed and subjected for this type of polymerization.^{1(a-f),5}

The stability of single-handed helix of acrylic polymers depends on the structure of side-chain group. As for polymethacrylates, triphenylmethyl ester does not undergo sterthe polymer in a CHCl₃ solution using a 500-W Hg-Xe lamp. This was ascribed to fast photolysis of the ester linkage leading to a loss of helical conformation of the entire chain. Photolysis products of poly(**BBPMFA**) were poly(acrylic acid) and 2,7-bis(4-*t*-butylphenyl)-9-methylenefluorene (2,7-bis(4-*t*-butylphenyl)dibenzofulvene). The photolysis reaction seemed to proceed through the "unzipping" mechanism. The rate constant of photolysis of poly(**BBPMFA**) under irradiation at monochromated 325 nm was around 0.01 s⁻¹ independent of molecular weight. Photolysis at 325 nm was approximately 2400 times faster than that for chemical ester solvolysis under a neutral condition in the dark. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 945–956, 2011

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eomutation on heating in a solution while less bulky esters including diphenyl-2-pyridylmethyl ester⁶ undergo helix-helix transition leading to a remarkable change in chiroptical properties. As the first example of a helical polymer that undergoes photo-induced helix-helix transition without any changes in chemical bonding such as isomerization of a double bond or bond cleavage and formation, we recently synthesized poly[2,7-bis(4-*t*-butylphenyl)-9-fluoren-9-yl acrylate] [poly(**BBPFA**)]⁷ (Chart 1). The conformation of this polymer is stable on heating in a solution but the polymer readily undergoes helix-helix transition upon photo irradiation leading to complete racemization of preferred-handed helix constructed through the polymerization process. It was proposed that the helix-helix transition of the chain is triggered by twist-to-coplanar, local conformational transition of the side-chain biphenyl moieties of poly(BBPFA) on photo excitation.

Stimulated by the behavior of poly(**BBPFA**), in this work, we synthesized and polymerized 2,7-bis(4-*t*-butylphenyl)-9-methylfluoren-9-yl acrylate (**BBPMFA**) with an additional methyl group at the 9-position of fluorene ring of **BBPFA**

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CHART 1 Structures of poly(BBPFA) and poly(BBPMFA).

and investigated the resulting polymer's structural transition through the interaction with light. Although our original intention was to tune the rate of photo-induced helix-helix transition by steric effects of the additional methyl group, helical poly(**BBPMFA**) unexpectedly underwent very fast photolysis. The photolysis took place through the cleavage of side-chain ester bonding and the products consisted mainly of 2,7-bis(4-*t*-butylphenyl)-9-methylenefluorene and poly (acrylic acid). The reaction completed within 1 s on irradiation using a 500-W Hg-Xe lamp. This may be one of the fastest example among macromolecular reactions so far reported. Here, we report the full details of synthesis and polymerization of **BBPMFA** and photolysis of helical poly(**BBPMFA**).

EXPERIMENTAL

Materials

Acryloyl chloride (Wako Chemical) was purified by distillation under N2 atmosphere. Fluorene (Nacalai Tesque) was first recrystallized from ethanol and then from hexane; m.p. 104.5–105.0 °C. The chiral ligand, (S)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine (PMP) (Aldrich), was dried over CaH₂ and distilled under reduced pressure. $\alpha_{,\alpha}$ '-Azobis(isobutyronitrile) (AIBN) (Wako) was recrystallized from an ethanol solution at room temperature. n-Bu₃B (1.0 M, a tetrahydrofuran (THF) solution, Aldrich) was used as obtained. MeMgBr (3.0 M, a Et₂O solution, Aldrich) was used as obtained. n-BuLi (1.6 M, a hexane solution, Kanto Chemical) was used after titration. Dithranol (Aldrich) and silver trifluoroacetate (Aldrich) were used as obtained. THF (Wako) and benzene (Wako) were refluxed over sodium benzophenone ketyl and distilled under N₂ atmosphere. CH₂Cl₂ was refluxed over P_2O_5 and distilled under N_2 atmosphere. Et₃N was refluxed over CaH_2 and distilled under N_2 atmosphere. Toluene used for anionic polymerization was purified in the usual manner, mixed with a small amount of n-BuLi, and distilled under high vacuum immediately before use.

Synthesis of 2,7-bis(4-*t*-butylphenyl)-9methylfluoren-9-ol

The reactions were performed under N_2 atmosphere. 2,7-Bis(4-t-butylphenyl)-9-methylfluorenone was available from our recent work.⁷ This ketone (40.0 g, 90.6 mmol) was dissolved in THF (300 mL) in a 500-mL flask equipped with a dropping funnel. To this solution was added MeMgBr (60.0 mL, 180 mmol), and the reaction mixture was stirred at room temperature for 3 h. The reaction was quenched by

adding saturated aq. NH₄Cl (300 mL). The product was extracted with CHCl₃, and the organic layer was dried on MgSO₄. Concentration of the dried organic layer afforded a crude oily material. The crude material was recrystallized from a mixture of CHCl₃ and MeOH (1/1, v/v) to give a colorless crystalline material (39.5 g, 95.0%). Anal: m.p. 266 °C (decomp.); ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ 1.36 (s, 18H, -Bu^t), 2.04 (s, 1H, -OH), 1.80 (s, 3H, -CH₃ attached to the fluorene ring), 7.46–7.47 (m, 4H, aromatic H), 7.58–7.61 (m, 6H, aromatic H), 7.66–7.68 (d, 2H, aromatic H), 7.79–7.80 (d, 2H, aromatic H); HRMS (EI) Calcd for C₃₄H₃₆O₁ 460.27661, found 460.27595.

Synthesis of BBPMFA

In a 1-L flask equipped with a dropping funnel and a reflux condenser flushed with N₂ gas was placed 2,7-bis(4-t-butylphenyl)-9-methylfluoren-9-ol (30.0 g, 65.2 mmol). CH₂Cl₂ (200 mL) and Et₃N (13.2 g, 130 mmol) were introduced to dissolve the alcohol. Acryloyl chloride (10.0 g, 111 mmol) was slowly added to the solution of alcohol cooled at 0 °C. The mixture was warmed to room temperature and stirred for 30 min, and it was then heated to 40 °C and stirred for 1.5 h. The reaction mixture was decomposed by adding water. The product was extracted with CHCl3-water. The organic layer was washed with saturated aq. Na₂CO₃ and with brine in this order and was then dried on MgSO₄. Removal of solvents gave a crude material. This material was recrystallized from a mixture of toluene and MeOH (10/1, v/v) to afford a colorless crystalline product (18.1 g, 54.0%). Anal: m.p. 235 °C; ¹H NMR (270 MHz, CDCl₃, Me₄Si) δ 1.35 (s, 18H, $-Bu^{t}$), 1.91 (s, 3H, $-CH_{3}$ attached to the fluorene ring), 1.99 (s, 3H, $-CH_3$), 5.70-5.74 (dd, I = 1.7 Hz, 10.3 Hz, 1H, vinyl H), 6.00–6.11 (dd, J = 10.3 Hz, 1H, 16.8 Hz, vinyl H), 6.21-6.28 (dd, 1.7 Hz, 16.8 Hz, 1H, vinyl H), 7.44-7.47 (m, 4H, aromatic H), 7.55-7.62 (m, 6H, aromatic H), 7.70-7.73 (m, 4H, aromatic H); HRMS (EI) Calcd for C₃₇H₃₈O₂ 514.28718, found 514.28541.

Synthesis of 2,7-bis(4-*t*-butylphenyl)-9-methylenefluorene (2,7-bis(4-*t*butylphenyl)dibenzofulvene)

In a 1-L flask equipped with a dropping funnel, 2,7-bis(4-tbutylphenyl)-9-methylfluoren-9-ol (10.0 g, 21.7 mmol) was dissolved in benzene (500 mL) and the solution was heated at 80 °C. p-TsOH-H₂O (2.10 g, 10.9 mmol) was added to the solution and the mixture was stirred under refluxing for 20 min. The reaction was decomposed by adding saturated aq. NaHCO₃ (300 mL). The product was extracted twice with benzene and the combined organic layer was washed with brine and was then dried on MgSO4. Removal of solvents gave a crude material (9.64 g, 99.4%). Recrystallization of the crude material from a mixture of benzene and hexane (10/1, v/v) afforded a pure crystalline product (6.40 g, 66.0%). Anal: m.p. 256 °C; ¹H NMR (270 MHz, CDCl₃, Me₄Si) δ 1.37 (s, 18H, -Bu^t), 6.16 (s, 1H, vinyl H), 7.47-7.50 (m, 4H, aromatic H), 7.58-7.62 (m, 6H, aromatic H), 7.72-7.75 (d, J = 7.8 Hz, 2H, aromatic H), 7.93–7.94 (d, J = 2.2 Hz, 2H, aromatic H); HRMS (EI) Calcd for C34H34 442.26605, found 442.26482.

TABLE 1 Polymerization of BBPMFA Using Various Initiators^a

| Run | Initiator | Solvent | [M] [I] | Temp (°C) | Conv. ^b (%) | MeOH-Insoluble Part | | | | |
|-----|---------------------------------|-------------------|------------|--------------|---------------------------|---------------------|------------------------------------|-------------------------------|--|-----------------------------|
| | | | | | | Yield (%) | <i>M</i> _n ^c | $M_{\rm w}/M_{\rm n}^{\rm c}$ | [α] ₄₃₅ ^d (deg) | [α] _D d (deg) |
| 1 | AIBN | CHCl ₃ | 60 | 60 | 20 | 15 | 1200 | 1.40 | - | - |
| 2 | <i>n</i> -Bu₃B-air ^e | THF | 30 | -30 | 8 | 5 | 700 | 1.10 | _ | _ |
| 3 | PMP-FILi | Toluene | 5 | -78 | 74 | 62 | 3100 | 1.12 | +180 | +47 |
| 4 | PMP-FILi | Toluene | 10 | -78 | 69 | 60 | 2800 | 1.12 | +142 | +35 |
| 5 | PMP-FILi | Toluene | 20 | -78 | 42 | 34 | 2300 | 1.18 | +87 | +23 |
| 6 | PMP-FILi | Toluene | 5 | 0 | >99 | 91 | 2800 | 1.36 | +116 | +26 |
| 7 | PMP-FILi | Toluene | 10 | 0 | >99 | 90 | 5400 | 2.26 | +282 | +78 |
| 8 | PMP-FILi | Toluene | 15 | 0 | 62 | 52 | 10,200 | 3.04 | +279 | +75 |
| 9 | PMP-FILi | Toluene | 20 | 0 | 58 | 55 | 1300 ^f | 1.41 | - | _ |

^a Conditions: **BBPMFA**, 0.100 g (run 1), 0.500 g (run 2), and 0.515 g (run 3–9); [**BBPMFA**]₀ = 1.00 M (run 1), 0.65 M (run 2), and 0.080 M (run 3–9); [FILi]/[PMP] = 1.2; polymerization time 12 h (run 1), 6 h (run 2), 24 h (runs 3–9).

^b Determined by ¹H NMR analysis of reaction mixture.

 $^{\rm c}$ Determined by SEC in THF (vs. PSt) (run 1–8) and, in ${\rm CHCl}_3$ (vs. PSt) (run 9).

Polymerization

Radical polymerization using n-Bu₃B was carried out by the literature method.⁸ Preparation of initiator solution and asymmetric anionic polymerization were carried out in dry toluene under dry N2 atmosphere. Polymerization procedure is described for run 6 in Table 1 as an example. Fluorene (0.0898 g, 0.540 mmol) was placed in a flame-dried glass ampoule sealed with a three-way stop cock, which was then evacuated on a vacuum line and flushed with dry N₂ gas. After this procedure was repeated three times, a three-way stop cock was attached to the ampoule and dry toluene (5.10 mL) was introduced with a syringe to dissolve fluorene. n-BuLi in hexane (0.340 mL, 0.540 mmol) and (+)-PMP (0.100 g, 0.650 mmol) were added to the resultant solution with a syringe in this order, and the mixture was left to stand at room temperature for 10 min to obtain an orange-colored PMP-FlLi complex solution (0.100 M). In a similar manner to the preparation of the fluorene solution, BBPMFA (0.515 g, 1.00 mmol) was dried and dissolved in dry toluene (12.5 mL) in a flame-dried glass ampoule sealed with a three-way stop cock. The monomer solution was cooled to 0 °C, and the PMP-FlLi solution (1.01 mL, 0.101 mmoL) was added with a syringe to initiate the polymerization. After 24 h of initiation, the reaction was terminated by adding MeOH (0.5 mL). The reaction mixture was poured into a large excess of MeOH (200 mL), and the MeOH-insoluble part was collected with a centrifuge and dried under high vacuum at 60 °C for 2 h. The MeOH-insoluble product was obtained as colorless powder (0.448 g, yield 89.5%).

Conversion of Poly(BBPMFA) into poly(methyl acrylate)

Poly(**BBPMFA**) ($M_n = 10,200$, $M_w/M_n = 3.04$, run 8 in Table 1) (0.050 g, 0.097 mmol (monomeric unit)) was dissolved in a mixture of CDCl₃ (4.0 mL) and MeOH (0.50 mL) in a 20-

 $^{\rm d}$ In CHCl₃ at room temperature (conc. = 0.50 g/dL; cell length = 1 cm). $^{\rm e}$ Air (5 mL) was bubbled through the monomer solution containing $\textit{n-Bu}_3B.$

^f THF-soluble part only.

mL glass tube with a screw cap in the dark. After the solution was heated at 60 °C for 9 h (conversion 90% by ¹H NMR analysis), 1 mL of MeOH was added to the solution. The reaction was continued at 60 °C for additional 6 h (conversion >99% by ¹H NMR analysis). The solvents were then removed using a rotary evaporator, and the residue was fractionated into MeOH-insoluble and -soluble parts. The MeOH-soluble part was suspended in 0.2 mL of CHCl₃, and CH₂N₂ in ether was added to methylate the sample. The methylated product was subjected to preparative SEC separation to remove side-chain residues from the obtained poly(methyl acrylate) (0.0079 g, 94%).

X-Ray Crystal Structure Analysis of BBPMFA

Crystal data were collected on a Bruker SMART Apex II CCD diffractometer with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) at 90 K. The crystal structure was solved by direct methods $(SHELXS-97)^9$ and refined by full-matrix least-squares methods on F^2 $(SHELXL-97)^{10}$ with APEX II software. The carbon and oxygen atoms were refined anisotropically. All hydrogen atoms were located at calculated positions and refined isotropically. Crystal data for BBPMFA: $C_{37}H_{38}O_2$; M = 514.67; $0.63 \times 0.38 \times 0.35 \text{ mm}^3$; monoclinic; space group P2₁(no. 4); a = 14.516(3) Å, b =6.3789(15) Å, c = 17.064(4) Å, $\alpha = 90^{\circ}$, $\beta = 112.662(3)^{\circ}$, γ = 90°; V = 1458.0(6) Å³; Z = 2, $\rho_{calcd} = 1.172$ g cm⁻³; $\mu =$ 0.071 mm $^{-1}$; T = 90 K; $2\theta_{max} = 53.46^{\circ}$; reflections collected: 7831, independent reflections: 3367 ($R_{int} = 0.0573$), $R_1(I > 2\sigma) = 0.0508$, $wR_2(I > 2\sigma) = 0.1282$; final difference map within +0.279 and -0.293 eÅ³. CCDC 790370 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.



SCHEME 1 Synthesis of BBPMFA.

Photo Irradiation Experiments

Irradiation experiments were conducted using a Ushio Optical Modulex SX-UID500MAMQQ 500-W Hg-Xe lamp with or without a Shimadzu SPG-120S monochromator.

Measurements

The ¹H NMR spectra were recorded on a JEOL JNM-ECP400 spectrometer (400 MHz for ¹H measurement) and a JEOL INM-EX270 spectrometer (270 MHz for ¹H measurement). SEC was carried out using a chromatographic 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 was performed using a JAI LC-908 preparative recycle chromatograph equipped with JAIGEL-1H and JAIGEL-2H columns connected in series using CHCl₃ as eluent. IR spectra were measured with a Thermo-Fischer Nexus 870 spectrophotometer using KBr pellet samples. Absorption spectra were measured with JASCO V-550 and V-570 spectrophotometers. Circular dichroism (CD) spectra were taken on a JASCO J-820 spectrometer. Specific rotation was measured using a JASCO P-1030 digital polarimeter. MALDI-Mass spectra were obtained with a Bruker Microflex spectrometer using dithranol and silver trifluoroacetate as matrices.

RESULTS AND DISCUSSION

Synthesis and Structure of BBPMFA Monomer

BBPMFA was synthesized by a four-step reaction according to Scheme 1 starting from 2,7-dibromofluorene and was purified by recrystallization to give a material pure enough to be used for anionic polymerization. The monomer structure was confirmed by single-crystal X-ray crystallography (Fig. 1). The most obvious difference between **BBPMFA** and **BBPFA**, the parent compound,⁷ in crystal is in the dihedral angel around the C(9-position of fluorene ring)-O(ester) bonding. While the angle was ca 10° in the **BBPFA** structure,⁷ it was nearly 180° in the **BBPMFA** structure. The complete flip of the acryloyl group in **BBPMFA** in comparison to that in **BBPFA** would be reasonably ascribed to steric repulsion between the carbonyl oxygen and the methyl group at the 9-position of the fluorene ring. Thus, the additional methyl group remarkably affects the monomer conformation.

Polymerization of BBPMFA

The conditions and results of free-radical polymerization using AIBN or *n*-Bu₃B-air and asymmetric anionic polymerization (helix-sense-selective polymerization) using PMP-FlLi are summarized in Table 1. The free-radical polymerizations gave polymers having relatively low M_n s' at low monomer conversions both at 60 °C and -30 °C (run 1 and 2). This is in sharp contrast to the fact that **BBPFA** afforded a polymer with $M_n = 6000$ at 85% conversion (65% MeOH-insoluble yield) by free radical polymerization at 60 °C with AIBN in



FIGURE 1 X-Ray crystal structure of BBPMFA monomer.



FIGURE 2 CD (top panel) and UV (bottom panel) spectra of poly(**BBPMFA**)s having different degrees of polymerization: M_n 10,200 (run 8 in Table 1) (A), M_n 2800 (run 6 in Table 1) (B), and M_n 2,800 (run 6 in Table 1) (C). [conc. 2.00 × 10⁻⁴ M per monomeric residue, in CHCl₃, at room temperature]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CHCl₃ ($[M]_o = 0.11$ M, $[AIBN]_o = 2.2$ mM, time = 12 h).⁷ An increase in bulkiness of **BBPMFA** by the size of a methyl group may seriously retard propagation in the radical polymerization.

Asymmetric anionic polymerization with PMP-FlLi at -78 °C led to optically active polymers with M_ns' in the range of ca. 2000–3000 although the monomer conversion ratios were not quantitative at all [M]/[I] ratios examined (runs 3–5). Under similar conditions with the same initiator system, **BBPFA** quantitatively led to polymers with M_ns' up to 8000.⁷ This again probably means that **BBPMFA** is too bulky to be polymerized as smoothly as **BBPFA** at -78 °C in the anionic polymerization. Hence, the introduction of single methyl group to the side chain resulted in a large decrease in reactivity of **BBPMFA** monomer in both free-radical and anionic modes.

However, in the anionic polymerization, monomer conversions were remarkably improved by raising the reaction temperature to 0 °C (runs 6–9). At [M]/[I] = 5 and 10, the monomer was quantitatively consumed in 24 h at 0 °C. In the range of [M]/[I] = 5-15, M_n of the obtained polymers increased with [M]/[I] up to $M_n = 10,200$ (run 8). At [M]/[I] = 20, most part of the obtained material which probably is of higher molecular weight was insoluble in THF or CHCl₃, and M_n of the soluble part was quite low (1300). In addition, the reaction systems at [M]/[I] = 15 and 20 gelled in the course of polymerization; this may be the main reason why the monomer was not quantitatively polymerized in these two systems.

The polymers obtained at 0 °C were optically active as well as those obtained at -78 °C. The ones obtained at [M]/[I] = 10 and 15 with higher $M_{\rm n}$ s' ($M_{\rm n} =$ 5400 and 10,200, respectively) showed much larger dextrootation than the one obtained at [M]/[I] = 5 with a lower $M_{\rm n}$ ($M_{\rm n} =$ 2800). In

addition, these polymers showed intense CD spectra (Fig. 2) whose intensity increased with an increase in $M_{\rm n}$. These results strongly suggest that the observed chiroptical properties of poly(**BBPMFA**)s obtained using PMP-FILi arise from preferred-handed helical conformation. Although the CD spectral pattern of poly(**BBPMFA**) was very similar to that of poly(**BBPFA**), *g* value for poly(**BBPMFA**) (3.75×10^{-4} at 344 nm ($M_{\rm n}$ 5400)) was greater than that for poly(**BBPFA**) (2.02×10^{-4} at 334 nm ($M_{\rm n}$ 12,730)).⁷ This may mean that poly(**BBPMFA**) has a greater preferred handedness than poly (**BBPFA**). The CD spectral intensities of the two polymers may be directly compared because the two polymers have the same side-chain chromophore.

For the purpose of tacticity analysis, the polymer from run 8 in Table 1 was converted to poly(methyl acrylate) by solvolysis in a mixture of CHCl₃ and MeOH followed by methylation with CH₂N₂. Solvolysis of (meth)acrylic polymers having bulky side groups can be performed using an acid such as HCl and H₂SO₄. However, main-chain racemization has been reported for the side-chain hydrolysis reaction of helical poly (*N*,*N*-diphenylacrylamide) under acidic conditions.¹¹ Hence, in order to avoid possible main-chain racemization, solvolysis of poly(BBPMFA) was carried out under a neutral condition. Figure 3 shows the ¹H NMR spectrum of poly(methyl acrylate) obtained from poly(BBPMFA). From the ratio of the peak areas of main-chain methylene signals due to meso and racemo diads, diad tacticity was estimated to be m/r =57/43. This indicates that poly(BBPMFA) obtained by anionic polymerization is only slightly isotactic. This result is in a sharp contrast to the fact that most helical (meth)acrylic polymers so far reported are highly isotactic. In the polymerization of BBPMFA using PMP-FlLi, only conformational control may be achieved unlike helix-sense-selective polymerizations of other (meth)acrylic monomers including that of triphenylmethyl methacrylate where both conformation and configuration are simultaneously, perfectly controlled.⁴

Structural Transition of Helical Poly(BBPMFA) Through the Interaction with Light (Photolysis)

As mentioned earlier, preferred-handed helical, optically active poly(**BBPFA**) is readily transformed into racemic form through helix-helix transition induced by light although the



FIGURE 3 ¹H NMR spectrum of poly(methyl acrylate) derived from the poly(**BBPMFA**) ($M_n = 10,200$, run 8 in Table 1). × denotes impurities. [400 MHz, CDCl₃, 60 °C].



FIGURE 4 Change in CD (top panel) and UV (bottom panel) spectra of the poly(**BBPMFA**) ($M_n = 5400$, run 7 in Table 1) upon irradiation to the sample in a CHCl₃ solution in a 1-mm quartz cell using a 500-W Hg-Xe lamp without monochromating for 0 s (A), 0.5 s (B), and 1 s (C). [conc. 2.00×10^{-4} M per monomeric residue, at room temperature]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer helix is stable on heating.⁷ Because a similar conformational transition would be plausible for poly (**BBPMFA**) synthesized in this work, its conformational and structural stability was examined.

Prior to the photo-induced structural studies, stability of poly(**BBPMFA**) toward thermal stimulus was tested. Structural changes were monitored by CD and UV spectra. A CHCl₃ solution of the poly(**BBPMFA**) ($M_n = 5400$, run 7 in Table 1) (conc. 2.00×10^{-4} M per monomeric residue) was heated at 60 °C for 24 h. Before and after heating, no clear change was observed in either CD or UV, indicating that the helical conformation and its preferred handedness were unaffected by heat under the conditions in this work.

However, upon irradiation to a CHCl₃ solution of poly (**BBPMFA**) ($M_n = 5400$, run 7 in Table 1) (conc. 2.00 × 10⁻⁴ M per monomeric residue, 1-mm quartz cell) using a 500-W Hg-Xe lamp, CD absorption bands completely disappeared within 1 s (Fig. 4). At the same time, the UV spectral pattern largely altered, indicating that chemical transformation had taken place to the polymer. In the case of photo-induced helix-helix transition of poly(**BBPFA**), no clear change was found in UV spectra on irradiation.

The chemical transformation was evidenced by SEC, ¹H NMR, and IR analyses (Figs. 5, 6, and 7, respectively). The peak position in the SEC chromatogram shifted to lower-molecular-weight ranges (Fig. 5). This indicates that a rigid, helical polymer chain transformed into a compact shape or that lower-molecular-weight compounds were formed from the original polymer through photochemical reactions. The latter would be more plausible based on the remarkable change in the UV spectrum of the polymer.

To obtain information on the change in chemical structure of the polymer, the reaction was conducted in CDCl_3 (conc. 2.00

 $\times 10^{-2}$ M per monomeric residue, 1-cm quartz cell) by irradiation with a 500-W Hg-Xe lamp and was monitored by ¹H NMR spectroscopy [Fig. 6(A)]. A similar experiment was also performed for **BBPMFA** monomer [Fig. 6(B)]. The polymer showed broad, rather structureless peaks in the aliphatic and aromatic regions [Fig. 6(A-1)]. The broad peaks can be ascribed to a rigid, helical polymer structure that results in a relatively short relaxation time in the ¹H NMR experiment. After irradiation for 5 min, some sharp peaks that seem to be based on low-molecular-weight compounds emerged and the originally broad, aliphatic and aromatic peaks became narrower [Fig. 6(A-2)]. The most characteristic in the spectrum after irradiation was the sharp, singlet signal at 6.17 ppm in the olefinic proton signals region for vinyl monomers. This signal and most of the sharp peaks in the aromatic region coincided in chemical shift with those of 2,7-bis(4-t-butylphenyl)-9-methylenefluorene (2,7-bis(4-*t*-butylphenyl)dibenzofulvene) [Fig. 6(C)]. The authentic sample of this olefin compound was synthesized from 2,7-bis(4-t-butylphenyl)-9-methylfluoren-9ol, the source compound for the BBPMFA monomer synthesis. In addition, MALDI-mass spectra of the irradiated sample indicated a clear signal at m/e = 442 corresponding to the molecular weight of the olefin compound. Therefore, it is assumed that irradiation of the polymer causes photolysis of the ester linkage giving the olefin.

The lowest-molecular-weight peak observed in the SEC curve after irradiation shown in Figure 5 is based on this olefin. This was confirmed by analyzing the authentic olefin by SEC as a reference compound. Although the compounds showing other low-molecular-weight peaks in SEC have not yet been identified, they could contain photo reaction products obtained from the olefin.^{12,13}

Also in the spectrum of the irradiated **BBPMFA** monomer sample in CDCl₃, the vinyl signal of the olefinic compound is



FIGURE 5 SEC curves of poly(**BBPMFA**) ($M_n = 5400$, run 7 in Table 1) (A) and the products obtained from the polymer upon irradiation using a 500-W Hg-Xe lamp without monochromating for 1 s (B). The samples were obtained from the irradiation experiment for Figure 4. SEC curves were obtained by UV detection at 254 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 6 ¹H NMR spectra of poly(**BBPMFA**) ($M_n = 5400$, run 7 in Table 1) (A-1) and the products obtained from the polymer upon irradiation for 5 min (A-2), those of **BBPMFA** monomer (B-1 and B-1') and the products obtained from the monomer upon irradiation for 5 min (B-2 and B-2'), and that of 2,7-bis(4-*t*-butylphenyl)-9-methylenefluorene (2,7-bis(4-*t*-butylphenyl)dibenzofulvene) (C). × denotes impurities. Irradiation experiments were performed in CDCl₃ at 2.00 × 10⁻² M concentration (per monomeric residue) in a 1-cm quartz cell for the polymer and the monomer using a 500-W Hg-Xe lamp without monochromating. [270 MHz, CDCl₃, room temperature].

clearly seen [Fig. 6(B-2')]. The other signals in the olefinic proton signals region after irradiation to the monomer are assigned to those of **BBPMFA** monomer and those of acrylic acid. These results confirm that irradiation causes a photolytic ester linkage cleavage leading the olefin and acid. Based on these results, the products of the polymer photolysis are reasonably identified as a mixture of the olefin and poly (acrylic acid) (Scheme 2). Photolysis of 9-methyl- or 9-alkyl-fluorene derivatives leading to olefin compounds has been reported.^{12,13} The intermediates of such reactions have been proposed to be a fluorenyl cation.

It should be noted here that the polymer photolysis reaction shown in Figure 6(A) seems much slower than the spectral



FIGURE 7 FT-IR spectra of poly(**BBPMFA**) ($M_n = 5400$, run 7 in Table 1) and the products obtained from the polymer upon irradiation using a 500-W Hg-Xe lamp without monochromating for 5 min. The samples were obtained from the irradiation experiment for Figure 6A. [KBr pellet].

change shown in Figure 4. This may be partially because a higher-concentration sample undergoes slower transformation possibly due to intermolecular interaction and partially because a sufficient number of photons was not supplied for the sample due to the existence of too many absorbing molecules at the concentration of 2.00×10^{-2} M per residue.

The production of poly(acrylic acid) on photolysis of the polymer was supported by the IR spectrum of the photolysis products indicating the —OH signal around 3500 cm⁻¹ and the broadened carbonyl stretching signals shifted to the lower-wave number direction (Fig. 7). The products may be a mixture of unreacted ester, acid, and 2,7-bis(4-*t*-butyl-phenyl)-9-methylenefluorene.

Kinetic Aspects of Photolysis

Photolysis of poly(**BBPMFA**) and **BBPMFA** monomer can be monitored by UV spectra as well as ¹H NMR and IR spectra. This is because 2,7-bis(4-*t*-butylphenyl)-9-methylenefluorene and 2,7-bis(4-*t*-butylphenyl)-9-methylfluoren-9-yl ester show distinguishable spectral patterns. Figure 8 shows the UV spectra of poly(**BBPMFA**), **BBPMFA** monomer and corresponding photolysis reaction mixtures obtained by irradiation at 325 nm for various periods of time and that of 2, 7-bis(4-*t*-butylphenyl)-9-methylenefluorene. 2,7-Bis(4-*t*-butylphenyl)-9-methylenefluorene shows characteristic absorption bands in the range of 260–290 nm with the peak maximum at 280 nm. In this range, no clear, overlapping peaks due to 2,7-bis(4-*t*-butylphenyl)-9-methylfluoren-9-yl ester are observed.

The photolysis reactions described in this section was intentionally set to be slower than that in Figure 4 to increase accuracy in time axis using the monochromated incident light. Monochromating at 325 nm leads to a lower number and a lower averaged-energy of photons that hit the sample. The lower averaged energy of photons comes from the absence of the UV-range light including the Hg 254 nm line.

The photolysis mixtures obtained from poly(**BBPMFA**) and **BBPMFA** showed an isosbestic points at 295 nm at earlier stages of photolysis, indicating that photolysis systems consist only of original 2,7-bis(4-*t*-butylphenyl)-9-methylfluoren-9-yl ester and resulting 2.7-bis(4-*t*-butylphenyl)-9-methylene-fluorene as chromophores at earlier stages of the reaction. Based on these spectral characteristics, the extent of photolysis was estimated. By monitoring the increment in molar absorptivity at 280 nm with reference to molar absorptivity at 295 nm in the course of irradiation, photolysis conversion versus irradiation time plots were obtained for poly(-**BBPMFA**) samples having different M_n s' (M_n 5400, 10,200, 22,800) and **BBPMFA** monomer (Fig. 9). The polymer sample of $M_n = 22,800$ was obtained by SEC fractionation from the sample of $M_n = 10,200$ (run 8 in Table 1).

Photolysis of **BBPMFA** monomer was faster than that of poly(**BBPMFA**) samples, and polymers having different $M_{n}s'$



SCHEME 2 Photolysis of BBPMFA monomer (top) and poly(BBPMFA) (bottom).

(A) UV spectra of poly(**BBPMFA**) in the course of photolysis



(B) UV spectra of BBPMFA in the course of photolysis



(C) UV spectrum of 2,7-bis(t-butylphenyl)-9-methylenefluorene



FIGURE 8 UV spectra of poly(**BBPMFA**) (M_n 5400, run 7 in Table 1) (A) and BBPFMA monomer (B) upon irradiation to sample solutions in CHCl₃ in a 1-mm quartz cell at 325 nm for different periods of time and that of 2,7-bis(4-*t*-butylphenyl)-9-methylenefluorene (2,7-bis(4-*t*-butylphenyl)dibenzofulvene) in CHCl₃ (C). [conc. 2.00 × 10⁻⁴ M per monomeric residue, at room temperature]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

underwent photolysis at very similar rates. This is consistent with that polymer reactions are generally slower than corresponding reactions involving low-molecular-weight compounds.¹⁴ First-order rate constants (*k*) of photolysis for **BBPMFA** monomer, poly(**BBPMFA**) of $M_n = 5400$, poly (**BBPMFA**) of $M_n = 10,200$, and poly(**BBPMFA**) of $M_n = 22,800$ were 0.028 s^{-1} , 0.011 s^{-1} , 0.011 s^{-1} , and 0.012 s^{-1} , respectively, as estimated from the data shown in Figure 9 according to:

$$\ln([ester]_{o}/[ester]_{t}) = kt$$

where [ester]_o, [ester]_t, k, and t are the initial concentration of 2,7-bis(4-t-butylphenyl)-9-methylfluoren-9-yl ester, concentration of the ester at given reaction time, first-order rate constant, and reaction time, respectively. In this equation, the concentration of photons involved in photolysis is not taken into account. Hence, the rate constant values estimated here are not intrinsic to these particular monomer and polymer compounds and will vary depending on light intensity.

However, it is interesting to compare the rate constants for photolysis with those for chemical solvolysis of the sidechain ester linkage in the dark. The latter values were estimated to be 0.018 h^{-1} for the reaction system under a neutral condition (polymer ($M_{\rm n}=5400$) 10 mg, CDCl₃ 0.8 mL, MeOH 0.1 mL, room temperature) and 0.17 h^{-1} for the reaction system under an acidic condition (polymer ($M_{\rm n} = 5400$) 10 mg, CDCl₃ 0.8 mL, MeOH 0.1 mL, conc. HCl 5 μ L, room temperature) by monitoring the reactions by ¹H NMR. Thus, the photolysis is 250-2400 times faster than the solvolysis. Furthermore, it is faster than reported solvolysis of other helical polymethacrylates under neutral conditions¹⁴ by the order of 10². Although rate constants have not been reported for most polymer reactions,¹⁵ solvolysis of helical polymethacrylates is considered to be a fast class of macromolecular reaction. It has been reported that conversion in hydrolysis reaction of poly(methyl methacrylate) in a mixture of MeOH



FIGURE 9 First-order plots for photolysis of **BBPMFA** monomer (A) and poly(**BBPMFA**) samples having different M_ns' (M_n 5400 (B), 10,200 (C), 22,800 (D)). The reactions were carried out in a CHCl₃ solution at a concentration of 2.00 × 10⁻⁴ M per monomeric residue in a 1-mm quartz cell with irradiation at 325 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 3 Photolysis of a helical polymer by unzipping (A) and random (B) mechanisms. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and water containing NaOH at 80 $\,^\circ\text{C}$ is less than 1% in 3 $h.^{16}$

Because CD and UV spectral changes were complete within 1 s when the irradiation was conducted using a 500-W Hg-Xe lamp without monochromating (Fig. 4), the photolysis of helical poly(**BBPMFA**) may be one of the fastest macromolecular reactions leading to a large change in molecular shape.¹⁴

For side-chain solvolysis of helical poly(meth)acrylates, "unzipping" mechanism¹⁷ has been proposed. According to this mechanism, once an ester bonding is cleaved in a chain (the initial cleavage), typically at the chain terminals, solvolysis along the entire chain proceeds from the initial cleavage point at a much large rate than that of the initial cleavage. This mechanism involving acceleration can be explained by the acidic catalytic effect of the carboxylic acid moiety formed by solvolysis for the neighboring monomeric units. A reaction system in the course of side-chain cleavage reaction through the unzipping mechanism should be, ideally, a mixture of intact helix and completely decomposed products without partially decomposed chains¹⁷ [Scheme 3(A)] while a system with random scission mechanism may contain chains with various degrees of decomposition [Scheme 3(B)]. Figure 10 shows the SEC curves of the irradiated products obtained from the poly(**BBPMFA**) of $M_n = 5400$ at different conversions. Up to 53% photolysis conversion, the position and shape of polymer peaks virtually did not change, the relative intensity of polymer peaks decreased, and the relative intensity of lower-molecular-weight peaks increased. These results indicate that the reaction mixture does not contain partially decomposed chains, establishing the unzipping photolysis mechanism.

When the unzipping mechanism is in effect, the rate-limiting step is the initial cleavage. Hence, the rate constants of photolysis discussed above are actually those for the initial cleavage reaction. Rate constants for the following photolysis should be much larger, i.e., the following photolysis should be much faster although estimating them is beyond the scope of this work.

Helix-Helix Transition (Racemization) versus Photolysis

Does poly(**BBPMFA**) racemize before it decomposes? This question was addressed by CD spectral measurements in the



FIGURE 10 SEC curves of poly(**BBPMFA**) ($M_n = 5400$, run 7 in Table 1) corresponding to the spectral experiments shown in Figure 8A: irradiation time 0 min (conv. 0%) (A), 10 s (conv. 11%) (B), 1 min (conv. 53%) (C), and 10 min (conv. 80%) (D). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

course photolysis (Fig. 11). CD intensity decreased with an increase in photolysis conversion. To examine the change in CD intensity quantitatively, molar ellipticity was plotted against photolysis conversion as shown in Figure 12. In



FIGURE 11 CD (top panel) and UV (bottom panel) spectra of poly(**BBPMFA**) ($M_n = 5400$, run 7 in Table 1) corresponding to the spectral experiments shown in Figure 8A. The UV spectra are identical to those shown in Figure 8A [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 12, the solid line indicates the theoretical relation between the two quantities expected for a system where the decrease in CD intensity is based only by decomposition. If CD intensity is lower than the theoretical line, the decrease is not only on decomposition but also by racemization. In Figure 12, all data points are below the line, indicating that racemization did take place. Racemization precedes photolysis for a chain although the chain may start to decompose before completion of racemization.

The original intention of this work was to design a new polymer that undergoes photo-induced helix-helix transition and to examine how the methyl group introduced at the 9position of fluorene ring affects the stereomutation. Because the polymer decomposes on irradiation as well as racemization, it is difficult to examine and discuss racemization only. However, by irradiating the polymer of $M_{\rm p} = 5400$ at 254 nm, information on the effects of the methyl group on racemization was obtained (Fig. 13). After irradiation at 254 nm for 1 min, the CD intensity decreased to 43% of the original spectrum at 343 nm and the photolysis conversion was only 5%. This means that the large decrease in CD intensity is mainly due to helix-helix transition (racemization). This is in a sharp contrast to the reported result that poly(BBPFA) without an additional methyl group did not show CD spectral changes on irradiation at 254 nm. From these results, it can be concluded that the added methyl group at the 9-position of fluorene ring largely facilitates the stereomutation.

CONCLUSIONS

Preferred-handed helical, optically active poly(**BBPMFA**) was synthesized by helix-sense-selective anionic polymerization of **BBPMFA** monomer. Both the monomer and the polymer were found to readily decompose on irradiation. The apparent, first-order rate constants of polymer photolysis on irradiation at 325 nm were in the order of 10^{-2} s⁻¹ while that for solvolysis in the dark under a neutral condition was as high as 0.018 h⁻¹. Thus, the photolysis confirmed in this work is far much faster than solvolysis. Within 1 s of irradiation with a 500-W Xe-Hg lamp, the polymer completely lost



FIGURE 12 CD intensity at 344 nm versus photolysis conversion plots corresponding to the data shown in Figure 11. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 13 CD (top panel) and absorption (bottom panel) spectra of poly(**BBPMFA**) ($M_n = 5400$, run 7 in Table 1) upon irradiation to sample solutions in CHCl₃ in a 1-mm quartz cell at 254 nm for different periods of time. [conc. 2.00×10^{-4} M per monomeric residue, at room temperature]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

its chirality. The photolysis reaction found in this work may be one of the fastest among polymer reactions most of which are caused mainly by chemical stimuli.

The reason why the additional methyl group at the 9-position of the fluorene ring of **BBPMFA** and poly(**BBPMFA**) makes the monomer so unstable on irradiation is not immediately clear. A possible explanation may be that production of 2,7-bis(4-*t*-butylphenyl)dibenzofulvene is energetically very favorable.

Photolysis of 9-methyl- and 9-alkylfluorene derivatives similar to that found in this work has been reported; however, such reactions have never been used for photo-induced structural transformation of a polymer with an ordered conformation. 2,7-Bis(4-*t*-butylphenyl)-9-methylfluorenyl esters (polymer and monomer) which were first made in this work and were found to be effectively and quickly transformed into an olefin compound and an acid may be applicable for other systems that need fast modification of properties of polymers by remote, photo stimuli. An example is helical template for molecular-imprinting synthesis of chiral crosslinked polymer (gel) where the template needs to be readily degradable.¹⁸

In addition, photolysis of racemic poly(BBPMFA) prepared under achiral conditions using circularly polarized light could possibly be helix-sense-selective. This might be a novel way to obtain a single-handed helical polymer. Further studies on this possibility are under way.

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