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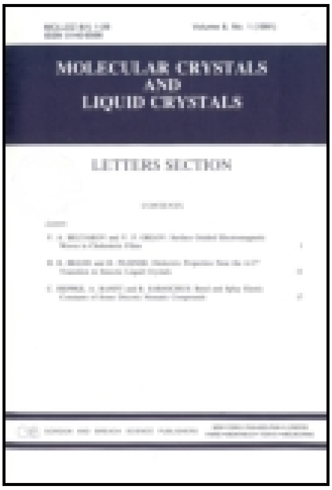

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Star polymers with sulfonyl groups in the central core were prepared by ATRP and the degradation of their cores was investigated. The core of the star polymer was efficiently and selectively decomposed by piperidine. Furthermore, the star polymer with mesogens in the side chain showed almost the same LC-isotropic phase transition temperature as the resulting degradation product, demonstrating the independence of polymer architecture on LC properties.

Keywords Atom transfer radical polymerization; degradable initiators; liquid crystals; star polymers; sulfonyl groups

Introduction

Recently, well-defined polymers with sophisticated architectures have found increasing attention and applications in functional materials [1]. In particular, star polymers composed of a single branch point as the core and two or more linear chains (arms) are the simplest models of branched polymers, and such polymers containing functional arms have been prepared in hopes of attaining both functionality and unique properties arising from the polymer architecture [2–4]. Star polymers can be classified into core-shell structured star polymers and multi-arm star polymers based on the size of the central core. Core-shell structured star polymers, which have a large number of arms tethered to a macroscopic core of cross-linked or aggregated polymers, have been applied as drug carriers [5–7] and reaction sites [8], for example, because they behave like ultrasoft colloidal particles in solution [9] and functionality can be introduced in both the macroscopic core and arms. The relationship between polymer architecture and properties has been explored from both theoretical and experimental standpoints in multi-arm star polymers with small molecule cores. Chen et al. reported that the incorporation of a bulky core in an eight-arm star polymer inhibited the aggregation of polyfluorene arms as compared with linear polymers, resulting in improvement of thermal and optoelectronic properties in organic light-emitting diodes [10]. Kricheldorf et al. and Polk et al. demonstrated that a liquid crystalline (LC) star polymer with mesogens in the main chain showed low crystallinity

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*Address correspondence to Yumiko Naka, Department of Chemical, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan. Tel.: +81-3-5228-8277. E-mail: sasaki@rs.kagu.tus.ac.jp due to its branched structure [11, 12]. In a side-chain LC polymer, it was observed that the transition temperature was prone to decrease with increasing branching. Interestingly, it was recently proven using well-defined branched polymers that the broad LC-isotropic phase transition observed in general polymers resulted from the limited miscibility of the mixture of branched structures rather than the wide polydispersity of molecular weight [13–16]. Generally, side-chain LC polymers have been studied as advanced functional materials due to their responsiveness to external stimuli induced by self-organizing nature, cooperative motion, anisotropy and so on [17]. Furthermore, investigating the effects of polymer architecture on LC properties is particularly relevant in side-chain LC polymers. However, it is difficult to directly explore slight influences of polymer architecture on LC properties in side-chain LC polymers because there are multiple factors that affect the properties, such as molecular weight, type of end group, polydispersity, and tacticity.

Degradable polymers have been extensively studied in the field of polymer science [18]. Degradability is generally introduced via the monomer repeating units, the cross-linkers, or the initiated fragment in the polymer. We previously reported the depolymerization of poly(olefin sulfone)s possessing sulfonyl groups as degradable groups in the main chain [19]. The depolymerization was induced by the base abstraction of protons on carbon atoms adjacent to the sulfonyl group and the subsequent chain reaction. These reactions took place at ambient temperature in solution or films. Accordingly, strongly electron-withdrawing sulfonyl groups may act as cleavable groups under mild conditions, although they are not generally known as labile groups [18]. If well-defined star polymers with sulfonyl groups in the core are cleaved at a precise central location, linear chains with identical properties as one arm of the primary star polymers are produced, enabling us to obtain a better understanding of the relationship between the polymer architecture and LC properties without complicating factors such as polydispersity or tacticity. In this study, four-arm star polymers with sulfonyl groups in the core were prepared by atom transfer radical polymerization (ATRP), and their degradability was investigated by treatment with bases. Furthermore, LC properties of a star polymer possessing cyanobiphenyl mesogens in the side chain were compared with those of the linear polymer obtained by degradation of the corresponding four-arm star polymer.

Experimental Methods

Synthesis of Initiator with Sulfonyl Groups

*Tetrakis[(2-hydroxyethylthio)methyl]methane (Compound **1**).* A solution of 1,3-dibromo-2,2-bis(bromomethyl)propane (4.0 g, 52 mmol) in 200 mL of methanol was added dropwise over 30 min with stirring to a mixture of 2-mercaptoethanol (4.0 g, 52 mmol) and 11 M NaOH (7.1 mL, 77 mmol). The reaction mixture was stirred at 90 °C for 3 hr. The solvent was evaporated under vacuum, and the residue was poured in water and extracted with diethyl ether. The combined ether extracts were washed with saturated $NaCl_{aq}$, dried over anhydrous $MgSO_4$, and filtered. The filtrate was evaporated under vacuum.

*Tetrakis{[2-(2-bromoisobutyryloxy)ethylthio]methyl}methane (Compound **2**).* Unpurified compound **1** (1.7 g, 4.6 mmol) was dissolved in dry tetrahydrofuran (THF) and triethylamine (9.3 mL, 92 mmol). The solution was slowly added dropwise at 0 °C to a solution of 2-bromoisobutyryl bromide (21 g, 92 mmol) in THF and the reaction mixture was stirred at room temperature overnight. After the reaction, the solvent was evaporated under vacuum.

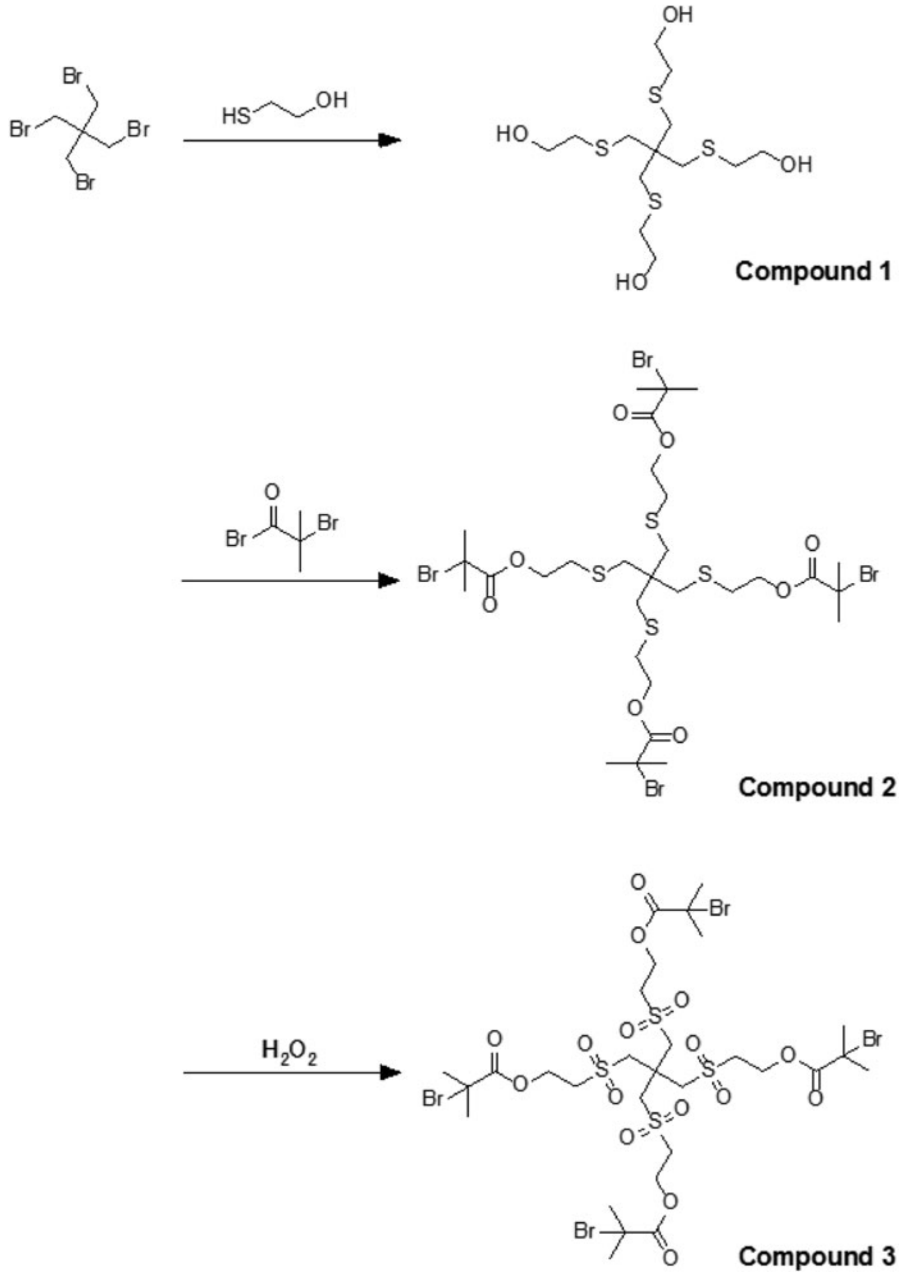
The product dissolved in chloroform was washed with saturated $NaHCO_{3aq}$, dried over anhydrous $MgSO_4$, and filtered. The oil was purified by column chromatography (silica gel, chloroform as eluent) to yield 4.8 g (> 12%) of light yellow oil. ^1H NMR (300 MHz, $CDCl_3$, δ): 1.96 (s, 24H), 2.80 (s, 8H), 2.87 (t, $J = 6.8$ Hz, 8H), 4.33 (t, $J = 6.8$ Hz, 8H).

*Tetrakis{[2-(2-bromoisobutyryloxy)ethylsulfonyl]methyl}methane (Compound **3**).* Compound **2** (2.0 g, 2.1 mmol) was dissolved in 2 mL of a 50–50 mixture of glacial acetic acid and acetic anhydride, and then 30% hydrogen peroxide (2.0 g, 17 mmol) was added to the solution. The reaction mixture was stirred at 60 °C for 10 hr. After the reaction, the product was extracted with chloroform, and then washed with saturated $NaHCO_{3aq}$. The chloroform solution was dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent gave a residue which was dried at room temperature for a long time to afford a white solid. ^1H NMR (500 MHz, $CDCl_3$, δ): 1.95 (s, 24H), 3.49 (t, J = 5.6 Hz, 8H), 4.23 (s, 8H), 4.63 (t, J = 5.6 Hz, 8H); GCMS (FAB) m/z: $[M]^+$ calcd for $C_{28}H_{38}N_2O_3$, 1100.56; found, 1101. Anal. calcd. for $C_{28}H_{38}N_2O_3$: C 31.65, H 4.40, O 23.26, Br 29.04, S 11.65; found: C 31.55; H 4.03.

Synthesis of Star Polymers

Star-PMMA. Star polymers were prepared by ATRP using compound **3**. To remove the stabilizer (hydroquinone, 0.005%), commercially available methyl methacrylate (MMA, 98%) was washed with an aqueous solution of sodium sulfite (pH 4), sodium hydroxide (5%), and sodium chloride (5%), then stirred over anhydrous magnesium sulfate overnight and distilled under vacuum. Copper (I) bromide [Cu(I)Br, Wako Pure Chemical Industries Ltd.] as catalyst was purified as described in the literature [20]. 1,1,4,7,10,10-Hexamethyltriethlyenetetramine (HMTETA, Aldrich) and dry THF were used without further purification. After compound **3** (0.100 g, 0.092 mmol), MMA (3.87 g, 38.7 mmol), Cu(I)Br (13.2 mg, 0.093 mmol), HMTETA (25.3 μL, 0.093 mmol), and THF (1.5 mL) were mixed, the mixture was degassed using freeze-pump-thaw cycles and sealed under nitrogen, then stirred for 30 min at room temperature. The reaction was carried out in a preheated oil bath at 90 °C for 3 hr. Next, the ampule was opened and quickly placed in an ice bath. The polymer solution was passed through a column (silica gel) with chloroform as eluent to remove the catalyst, and star-PMMA was precipitated in a large excess of hexane and finally dried under vacuum. A white solid product was obtained in a yield of 67%.

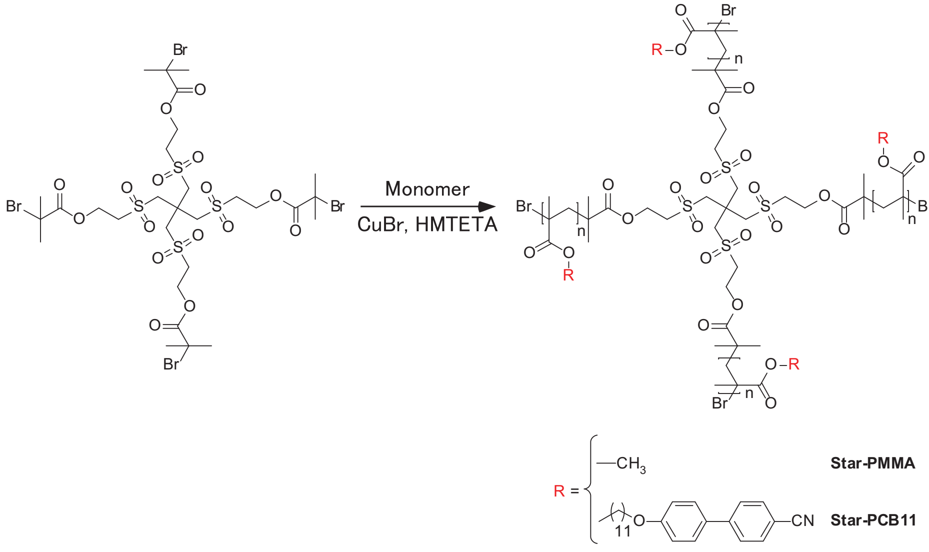
Star-PCB11. An LC star polymer was prepared by ATRP in a similar manner as above. First, an LC monomer, 11-[4-(4-cyanobiphenyl)oxy]undecyl methacrylate (CB11), was synthesized by the Schötten-Baumann reaction between methacryloyl chloride and (4-cyano-4′-biphenyloxy)undecyl-1-ol. ^1H NMR (300 MHz, $CDCl_3$, δ): 1.23–1.84 (m, 34 H), 3.65 (t, $J = 7$ Hz, 2H), 4.03 (t, $J = 7$ Hz, 4H), 4.16 (t, $J = 7$ Hz, 2H), 5.81 (dd, $J = 10, 2$ Hz, 1H), 6.12 (dd, $J = 17, 10$ Hz, 1H), 6.40 (dd, $J = 17, 2$ Hz, 1H), 6.98 (m, 4H), 7.86 (m, 4H); Anal. calcd. for $C_{28}H_{35}NO_3$: C 77.56, H 8.14, N 3.23; found: C 77.24, H 8.02, N 2.96. The DSC thermograms indicated phase transition peaks at 72 and 74 °C upon heating, and 63 °C upon cooling at a scanning rate of 3 °C/min. Compound **3** (2.6 mg, 2.4×10^{-6} mol), CB11 (0.201 g, 0.46 mmol), Cu(I)Br (4.9 mg, 0.035 mmol), HMTETA (9.4 μL, 0.035 mmol), and THF (2.0 mL) were mixed in a 50 mL ampule equipped with a reflux condenser, which was degassed and filled with nitrogen. The mixture was stirred at 80 °C for 24 hr and purified in a similar manner as above. A white solid product was obtained in a yield of 65%.



Scheme 1. Synthetic route of an initiator with sulfonyl groups.

Results and Discussion

A multi-site ATRP initiator with sulfone groups was synthesized in three steps as shown in Scheme 1: introduction of sulfide (-S-) by the reaction between a halide and thiol, addition of bromo end groups by Schötten-Baumann reaction, and oxidation of



Scheme 2. Synthetic route of star polymer by ATRP.

sulfide [21–23]. In the first step, a simple compound with four halides, 1,3-dibromo-2,2-bis(bromomethyl)propane, was reacted with 2-mercaptoethanol in an aqueous alkaline solution. The obtained product (compound **1**) was used for the next reaction without purification because of the ill-smelling unreacted starting material, 2-mercaptoethanol. Thus, a large excess of 2-bromoisobutyryl bromide was added to the system to complete the reaction, and the obtained product was purified by column chromatography on silica gel. Finally, the sulfide was oxidized using a mixture of glacial acetic acid and acetic anhydride with hydrogen peroxide. The introduction of sulfone groups was confirmed by ^{1}H-NMR and IR spectra. In the ^{1}H-NMR spectrum, resonances from the two neighboring protons of the sulfide shifted over 1.4 and 0.6 ppm after the reaction on account of the strong electron-withdrawing sulfone group [Fig.1(a)]. Furthermore, two strong peaks corresponding to sulfone groups at 1130 and 1280 cm^{-1} (O=S=O) appeared in the FT-IR spectrum [Fig.1(b)].

Star poly(methyl methacrylate) (star-PMMA) with a unimodal peak [$M_n = 39{,}000$ and $M_w/M_n = 1.19$ (GPC)] was prepared by ATRP using compound **3** with four initiation sites (Scheme 2). To investigate the decomposition behavior of star-PMMA, the polymer (26 mg) was dissolved in chloroform (2 mL), and then base was added to the polymer solution. After stirring for 24 hr at room temperature, the polymer was precipitated in a large excess of hexane to remove the base. First, piperidine, which promotes effective depolymerization in poly(olefin sulfone)s, was selected as the base. Various amounts of piperidine (10.0, 5.0, 2.0, 0.99, 0.55, 0.09, 0.04, and 0.01 mmol) were added to the star-PMMA solution. In the products obtained by addition of over 0.04 mmol of piperidine, GPC peaks appeared at longer elution times than that of the original polymer as shown in Fig. 2(a), indicating decomposition of the star polymers by piperidine. Next, decomposition behavior by other common bases such as pyridine and triethylamine was investigated [Fig.2(b)]. When star-PMMA was treated with sufficient quantities of pyridine (10 mmol), the GPC elution time did not change. On the other hand, part of the star PMMA decomposed in polymers treated with triethylamine. Upon treating the original polymer ($M_n = 39{,}000$, $M_w/M_n = 1.19$) with

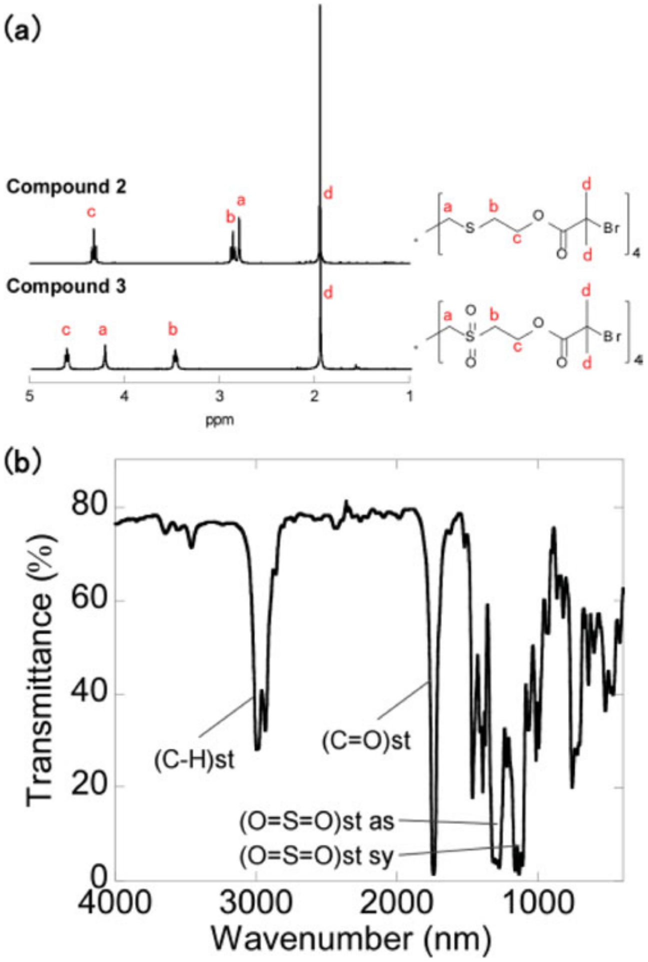


Figure 1. Confirmation of introduction of sulfonyl groups. (a) NMR spectra of compounds **2** and **3**. (b) IR spectra of compound **3**.

piperidine under the same conditions, a polymer with well-defined molecular weight M_n of 16,000 and M_w/M_n of 1.22 was formed. The ^{1}H-NMR spectrum of the cleaved polymer agreed closely with that of the original polymer, with the chemical structure of the repeating units remaining unchanged (Fig. 3). These results suggest that selective cleavage of the central core occurs in star-PMMA with sulfonyl groups without decomposition of the main polymer chain.

Next, an LC polymer bearing cyanobiphenyl moieties in the side chain (star-PCB11) was synthesized by ATRP. The resulting polymer with M_n of 34,000 and narrow molar-mass dispersity of 1.26 was decomposed under the same conditions as star-PMMA. As shown in Fig. 4, the degradation product showed a unimodal peak in the GPC curve and small M_n of 16,000 ($M_w/M_n = 1.22$). ^{1}H-NMR and IR spectra of the polymer were unchanged after addition of piperidine (Fig. 5). From these results, the decomposition of both the main chain and side chain was confirmed. Mesomorphic properties of the original star-PCB11 and degradation product were studied by DSC and polarizing microscopy (POM). Both

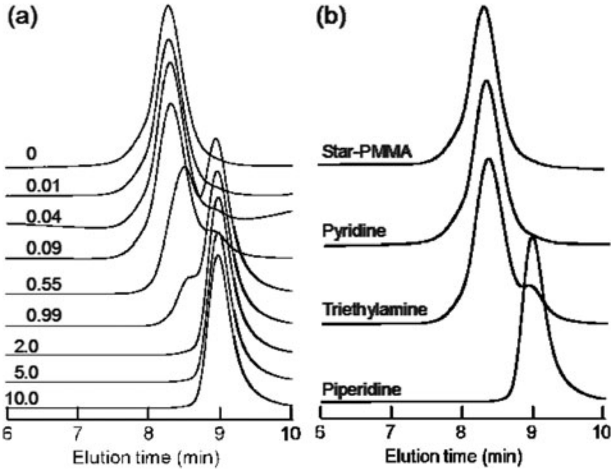


Figure 2. GPC curves of original star-PMMA and its degradation product. (a) To a star-PMMA (26 g) solution was added 0.01, 0.04, 0.09, 0.55, 0.99, 2.0, 5.0, and 10.0 mmol of piperidine. (b) Star-PMMA upon addition of pyridine, piperidine, and triethylamine in chloroform solution.

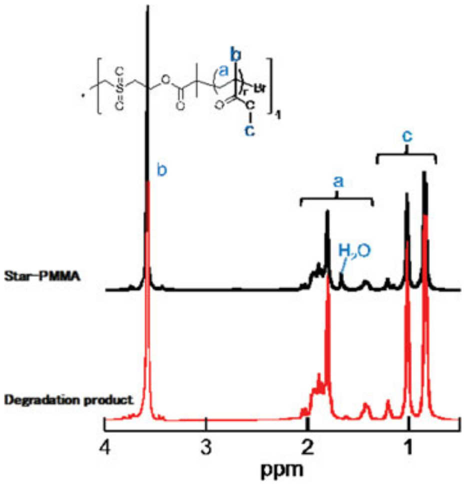


Figure 3. NMR spectra of star-PMMA and its degradation product.

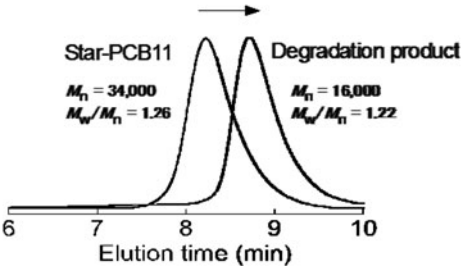


Figure 4. GPC curves of original star-PCB11 and its degradation product.

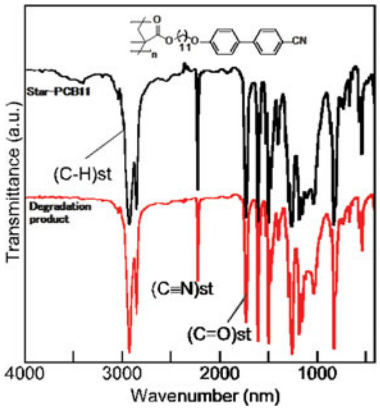


Figure 5. IR spectra of star-PCB11 and its degradation product.

the polymers showed focal conic texture in the POM studies, corresponding to a smectic A phase. The glass transition (T_g) and LC-isotropic phase transition temperatures ($T_{\text{LC-iso}}$) of the degraded product were almost the same as those of the original star-PCB11 (Fig. 6). The polymer obtained by the degradation of the branched polymer is completely identical to the arm of the branched polymer itself (Table 1). This means that only the effects of the branched structure of the polymer on T_g and $T_{\text{LC-iso}}$ contribute to the result. Thus, it can be

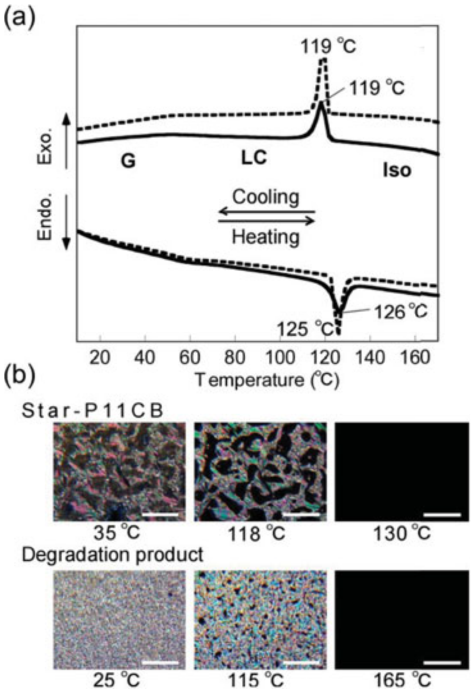


Figure 6. DSC curves (a) and polarizing optical micrographs (b) of star-PCB11 and its degradation product.

Table 1. Glass-Transition Temperatures of Star-PMMA, the Degradation Product of Star-PMMA, Star-PCB11, and the Degradation Product of Star-PCB11

	Star-PMMA	Star-PCB 11
Before degradation	118	51
After degradation	118	48

concluded that molecular weight and branched structures of the polymers had no effect on the transition temperature.

Conclusions

A new compound that possesses four ATRP initiation sites and degradable sulfonyl groups was synthesized. The compound was designed to study decomposition of polymers by bases. The four-arm star poly(methacrylate) with well-defined molecular weight was prepared by ATRP using the obtained initiator. The addition of triethylamine or piperidine to the solution of the star poly(methyl metacrylate) at room temperature produced linear polymers. On the other hand, addition of pyridine did not induce decomposition of the star polymer even when an excessive amount was used. Moreover, liquid-crystalline (LC) properties of the star polymer with cyanobiphenyl mesogens in the side chain were investigated. They showed almost the same LC-isotropic phase transition temperature as the corresponding linear arm polymer with the same polydispersity and tacticity, exhibiting no effect of polymer architecture on LC properties.

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