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Copolymerization of Lipoic Acid with 1,2-Dithiane and Characterization of the Copolymer as an Interlocked Cyclic Polymer

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ABSTRACT: Copolymerization of lipoic acid (LPA) and 1,2-dithiane (DT) and characterization of the resulting product were investigated. The copolymerization induced readily to give high-molecular-weight polymers in high yields. The difference in the polymerization reactivity between the two monomers may originate from the strain energies of the monomers. The mechanical properties of poly(LPA-*co*-DT) demonstrated that the polymers contains polycatenane structures. The molecular weight entanglement (M_e) of poly(LPA-*co*-DT) estimated from a dynamic viscoelasticity measurement was in good agreement with the half value of the molecular weight of a noninterlocked cyclic polymer estimated from the photodecomposition of poly(LPA-*co*-DT).

Introduction

Recently, much attention has been paid to topologically unique macromolecules containing a single cyclic or multicyclic polymer unit from the viewpoints of not only the distinctive properties from linear polymers but also elements of architecturally complex polymers and interlocked macromolecules such as polyrotaxanes and polycatenanes.[1−3]

For synthesizing cyclic polymers, many approaches such as backbiting process by ring−chain equilibriums of poly(dimethylsiloxane)s,[4] the cyclization by intermolecular coupling reaction of a bifunctionally living anionic polymer precursor with a complementarily reactive bifunctional reagent,[5,6] and unimolecular process such as the cyclization by intramolecular reactions of an α,ω-heterobifunctional telechelic polymer precursor[7,8] have been developed. Other methods using the anionic polymerization of β-DL-butyrolactone or DL-lactide with cyclic dibutyltin initiators,[9] the "electrostatic self-assembly and covalent fixation",[10,11] and ring-opening metathesis polymerization of *cis*-cyclooctene using the cyclic type of the Ru complex[12] were also reported.

Although many methods of the syntheses of cyclic polymers have been investigated, characteristic functions for cyclic polymers have been hardly found in the literature.[2,3,6,8,13]

Although it is expected to show specific characters based on the structures,[14] it is difficult to synthesize polymers with polycatenane structure, because the formation of a catenane structure should be followed by an intramolecluar cyclization after the chain passed through a inside of cycle chain formed during polymerization. Namely, we have to design a suitable polymerization system, in which a cyclization by backbiting and coupling reactions is induced frequently to form catenane. Taking these conditions into consideration, we investigate polymerizations of cyclic disulfides.

Many approaches have been reported to prepare polymers containing disulfide linkages in the main chain have been reported.[15] Among them, ring-opening polymerization of cyclic disulfides is an interesting method for synthesizing such polymers. Although syntheses and polymerizations of cyclic disulfides have been investigated since the second half of the 1940s,[15] characterization and structural analyses of the polymers have not been investigated in detail for a long time. Since 1,2-dithiane (DT) is relative stable monomer, we studied on polymerization of 1,2-dithiane (DT) to investigate a structure of the formed polymers.[16,17] From the polymerization mechanism in polymerization of DT without initiators, the solubility and the photodecomposition behavior of the formed polymer, the polymerization in the presence of other cyclic polymer, the properties of the polymers estimated from DSC and dynamic viscoelasticity, and the polymer obtained from polymerization of DT without initiators using highly purified monomer contains polycatenane structure composed of interlocking system by entanglements with cyclic polymers, as illustrated in Scheme 1.[17]

Such structure will be maintained even when the copolymerization between cyclic disulfides. Moreover, if we use lipoic acid (LPA) which is five-membered cyclic disulfide with a carboxyl group at the side chain, such a copolymer can be applied as a functional copolymer to develop new polymer structures. In this article, we report on copolymerization of LPA with DT and the characterization of the resulting copolymer in detail.

Experimental Section

Reagents. 1,4-Butanedithiol (BDT, Tokyo Kasei Kogyo, Japan) and *p*-toluenesulfonyl-*N*-methyl-*N*-nitrosoamide (Tokyo Kasei Kogyo, Japan) were used without further purification. LPA (Tokyo Kasei Kogyo, Japan) was purified by recrystallization from cyclohexane: mp 61.3−62.0 °C (lit.[18] mp 61−62 °C). Other reagents and solvents were purified by conventional methods. DT was synthesized from BDT as described in a previous paper,[19] and the purity of DT determined by HPLC was above 99.9%.

Polymerization Procedure. Polymerization was carried out in a sealed glass tube. After ca. 1.0 g of comonomer was charged, the tube was degassed and then sealed under high vacuum. After polymerization at constant temperature for a given time in thermostat, the tube was opened, and the contents in the tube were poured into a large amount of cyclohexane or *n*-hexane to precipitate the polymer formed. The polymer was washed well with a large amount of cyclohexane or *n*-hexane and dried in vacuo at room temperature for overnight. The isolated polymer yield was determined gravimetrically.

Methyl Esterification of Polymers. The resulting polymer (0.5 g) was dissolved or swollen in 50 mL of THF. To this, ca. 5 mL

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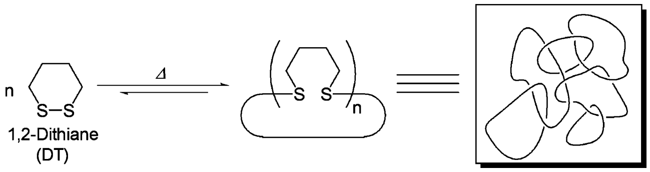
Scheme 1. Thermal Polymerization of DT and Illustration for Polycatenane Structure



of diazomethane solution of diethyl ether, which was synthesized from *p*-toluenesulfonyl-*N*-methyl-*N*-nitrosamide, was added under stirring at room temperature, and then bubbles were generated. After diazomethane solution was added until no bubbles from the solution were generated, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. The polymers were washed well with an excess of methanol and dried in vacuo at room temperature for overnight.

Preparation of Casting Samples. The casting film of the polymer was prepared from a chloroform solution of the polymer. Poly(DT) washed well with a large amount of *n*-hexane and dried completely was dissolved in chloroform (1−2 wt %). The chloroform solution of poly(DT) was poured into a glass mold whose size 100 (L) × 5 (W) × 5 (T) mm in the dark. The solvent was dried in at atmospheric pressure at room temperature in the dark, and then thin film was obtained. After such operation was repeated to make samples with predetermined thickness, they were dried in vacuo at room temperature for overnight.

Polymer Characterization. The number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the molecular weight distributions (M_w/M_n) of the obtained polymer were determined by GPC at 38 °C in tetrahydrofuran (THF) as an eluent using a Tosoh GPC-8000 series system. The calibration of molecular weight of the polymers was established with standard polystyrenes. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL A-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard at room temperature. IR spectra were taken by use of a JASCO FT/IR 430 spectrometer. The polymer samples were prepared according to following procedure: the polymer was dissolved in a solvent, and the polymer solution was added dropwise onto a NaBr plate. DSC measurement was carried out with a SEIKO Instruments Inc. DSC 6200 in a nitrogen stream at a heating and cooling rate of 10 °C/min. The sample weights for DSC were ca. 10 mg. TG/DTA measurement was carried out with a SEIKO Instruments Inc. TG/DTA 6200 at a heating rate of 10 °C/min in a nitrogen stream. The sample weights for TG/DTA were ca. 5 mg.

Dynamic mechanical measurement of poly(LPA-*co*-DT) was performed by use of a SEIKO Instruments Inc. DMS 6100 in the shear mode operating at a frequency of 0.1 to 20 Hz. The dimensions of the testing sample are 32 (L) × 5 (W) × 1.5 (T) mm. Nitrogen gas was circulated in the environment chamber to prevent the testing sample from degrading during the measurement. The shear storage modulus (E'), the shear loss modulus (E''), and the loss factor (tan δ) were obtained at a heating rate of 2 °C/min in the range from −120 to 100 °C.

Wide-angle X-ray diffraction patterns in the range $2\theta = 3-45°$ were measured on a Shimadzu XD-610 diffractometer and a RIGAKU X-ray diffractometer RINT-Ultima with Cu Kα radiation.

Photodecomposition of Polymers. Photodecomposition of polymers dissolved in THF (1 wt %) was carried out in a sealed glass tube under UV irradiation at a distance of 10 cm from tube. UV irradiation was performed using a Toshiba SHL-100-2, 100 W, as a high-pressure mercury lamp. The ca. 10 mL of the THF solution of the polymer was charged, and then the tube was degassed and sealed under high vacuum. After photodecomposition at room temperature for a given time, the tube was opened, and then the contents in the tube were poured into a large amount of methanol to precipitate degradation products. The degradation products were washed well with methanol and dried in vacuo at room temperature. The molecular weight of the isolated product was measured by GPC.

Table 1. Thermal Copolymerization of LPA with DT in Bulk at 80 °C for 6 h

[LPA] in comonomer (mol %)	polymer yield (%)	[LPA] in copolymer (mol %)	$M_n \times 10^{-4\,a}$	M_w/M_n^{a}
100	80.3	100.0	41.6	2.35
70	70.1	77.9	55.0	2.10
50	61.3	58.1	36.5	1.99
30	58.0	37.6	20.1	1.45
20	47.8	25.2	25.3	1.61
0	35.8	0.0	16.8	1.43

[a] Determined by GPC.

Table 2. Solubilities of the Copolymers for Various Solvents at 25 °C before Methyl Esterification[a]

	[LPA] content in comonomer (mol %)					
solvent	100	70	50	30	20	0
THF	○	○	○	○	○	○
pyridine	○	○	○	○	○	Δ
DMF	○	○	○	○	Δ	×
DMSO	Δ	Δ	Δ	Δ	×	×
acetone	○	×	×	×	×	×
chloroform	×	×	×	×	×	○
methanol	×	×	×	×	×	×

[a] Symbols: ○ = soluble, Δ = swelling, and × = insoluble.

Results and Discussion

Thermal Copolymerization of LPA with DT. Polymerization of both LPA (bp 61−62 °C) and DT (bp 31−32 °C) proceeds without initiators above the melting points of each monomer, but they did not polymerize below their melting points.[16,17,20,21] The results suggest that the thermal copolymerization of two cyclic disulfides will be induced, when the copolymerization is carried out above the melting points of both monomers. The copolymerization of DT and LPA in bulk was conducted at 80 °C, and the results are shown in Table 1. The copolymerization gave a product, and the yields increased with an increase of LPA concentration in the feed.

Table 2 shows the solubility of the reaction product for various solvents. Each homopolymer can dissolve in both acetone and chloroform, but the copolymerization products did not dissolve in the solvents. In addition, the solubility of the product to DMSO and DMF has changed gradually with decreasing of LPA composition in the feed, indicating that the copolymerization of LPA and DT proceeds to give the copolymers.

The typical ^{1}H NMR spectra of the polymers after methyl esterification are shown in Figure 1. Copolymer composition calculated from the integration ratio of ***h*** and **2** peaks based on methyl of LPA unit and methylene at β-position of DT unit are also listed in Table 1. On the basis of the data, the comonomer−copolymer composition curve was obtained, and the results are depicted in Figure 2. The reactivity of LPA comonomer was found to be slightly higher than that of DT, which may be explained by a difference in the ring strains between monomers.[19,22]

Since a crystallinity and thermal properties of polymers should change by introduction of another monomer units in the main chain, X-ray diffraction and DSC measurement for poly(LPA-*co*-DT) with various copolymer compositions were examined, and the results are listed in Table 3. The crystallinity decreased gradually with an increase of the LPA contents in the copolymer. Both the melting point (T_m) and the melting peak area of the

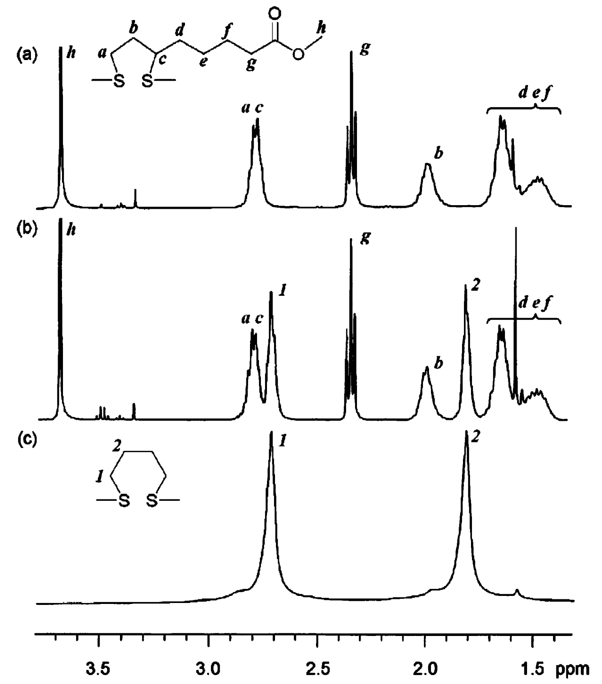


Figure 1. ^{1}H NMR spectra of (a) poly(LPA), (b) the polymer obtained from thermal copolymerization of LPA with DT at comonomer composition 1:1, and (c) poly(DT).

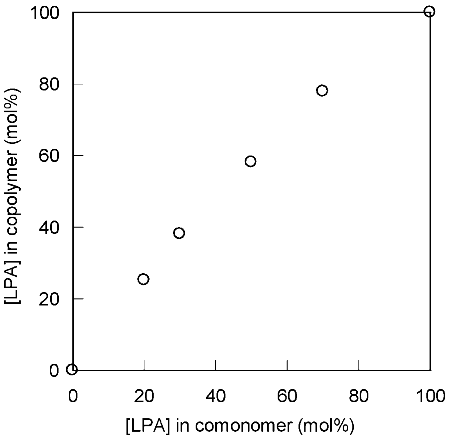


Figure 2. Copolymer composition curve for the thermal copolymerization of LPA with DT.

Table 3. Crystallinity and Thermal Analysis Parameters of Poly(LPA-*co*-DT)s

[LPA] in copolymer (mol %)	crystallinity (%)	T_m[a] (°C)	T_g[b] (°C)
100.0	0.0	–[b]	−37.0
58.1	0.0	–[b]	−43.3
37.6	0.0	–[b]	−49.6
10.2	7.1	30.0	−53.3
3.0	18.5	33.1	−54.8
0.0	31.6	41.5	−55.6

[a] Determined by DSC. [b] T_m was not observed.

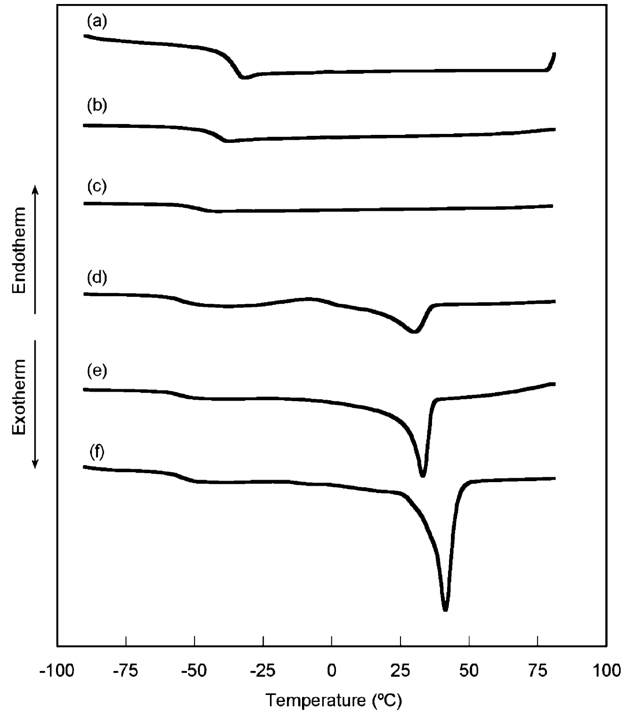


Figure 3. DSC curves of poly(LPA-*co*-DT)s obtained from copolymerization of LPA with DT in bulk at 80 °C for 6 h: [LPA] content of (a) 100, (b) 58.1, (c) 37.6, (d) 10.2, (e) 3.0 and (f) 0 mol % in copolymer at a heating rate of 10 °C/min in nitrogen stream.

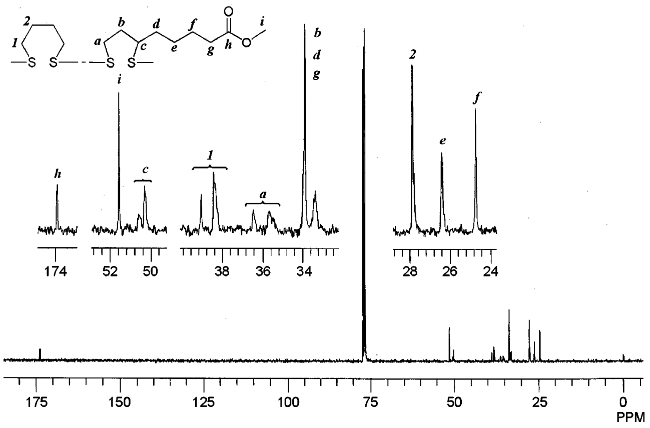


Figure 4. ^{13}C NMR spectra of poly(LPA-*co*-DT) ([LPA] in copolymer; 58.1 mol %) obtained from thermal copolymerization of LPA with DT in bulk at 60 °C for 6 h.

copolymer decreased with an increase of LPA contents, as shown in Figure 3. The melting peak area disappeared completely when the LPA composition of the copolymer was above 37.6 mol %. On the other hand, the glass transition temperature (T_g) of the copolymers gradually increased with an increase of the LPA contents in the copolymer. This also supports that the copolymerization products are the copolymer of LPA and DT.

Structural Analysis of Copolymer. The structure of the resulting copolymer after methyl esterification was examined by NMR spectroscopy. Figure 4 shows a typical ^{13}C NMR spectrum of methyl ester of poly(LPA-*co*-DT). Each peak can be assigned as indicated on the figure. Moreover, the structure of copolymers consisting of LPA with DT units was elucidated from the ^{1}H NMR spectrum of methyl ester of poly(LPA-*co*-DT). The ^{1}H NMR spectra of methyl ester of poly(LPA-*co*-DT) and the expanded spectra of the expected peak region based on the end groups for assuming a linear polymer are shown in Figure 5. In the ^{1}H NMR spectrum of each linear methyl ester polymer of poly(LPA-*co*-DT) synthesized by the polymerization in the presence of BDT, the peak based on thiol end groups appeared at 0.85 and 1.38 ppm, and two methylene protons based on adjoining thiol ends appeared at 2.5−2.6 ppm should be observed, but such peaks due to the linear chain ends were not observed in the copolymers. These results suggest that the poly(LPA-*co*-DT) consists of cyclic structure as well as poly(DT).

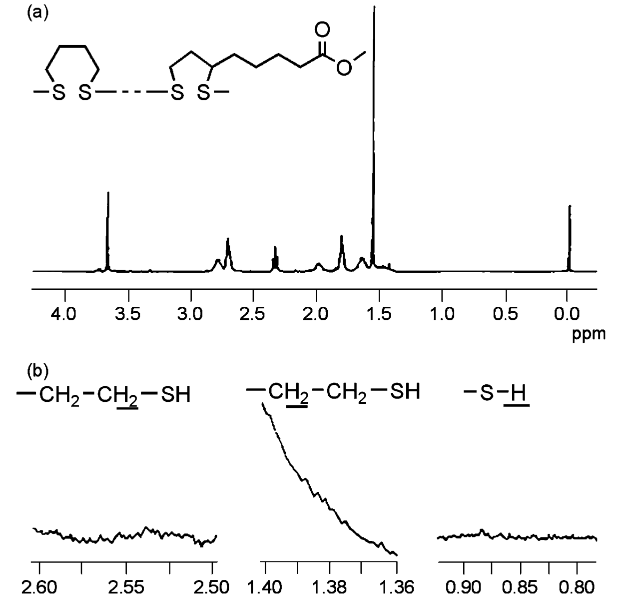


Figure 5. ^{1}H NMR spectra of poly(LPA-*co*-DT) ([LPA] in copolymer; 58.1 mol %) obtained from thermal copolymerization of LPA with DT in bulk at 80 °C for 6 h: (a) the whole and (b) the expanded spectra.

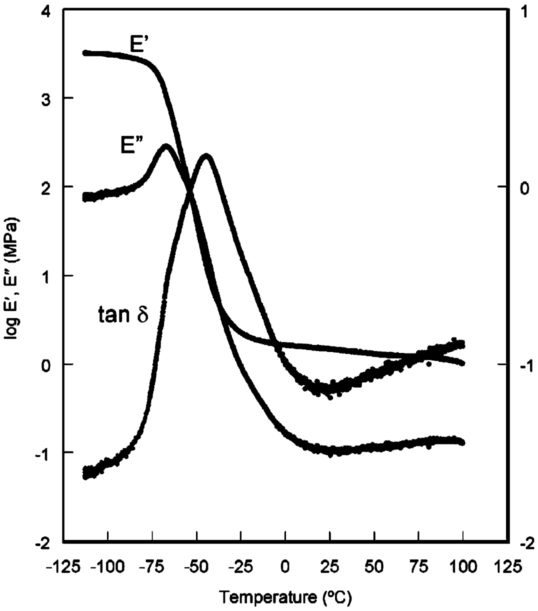


Figure 6. Temperature dependences of E', E'', and tan δ for poly(LPA-*co*-DT) ([LPA] in copolymer; 37.6 mol %) obtained from the thermal polymerization in bulk.

The dynamic viscoelasticity measurement of poly(LPA-*co*-DT) was performed, and the results are shown in Figure 6. The temperature dependences of storage modulus (E'), loss modulus (E''), and tan δ are measured at a frequency of 11 Hz using the copolymer whose the M_n was 4.4 × 10^5 and the LPA content in the poly(LPA-*co*-DT) was 37.6 mol %. In the dynamic viscoelasticity curves, E' and E'' values decreased when the polymer sample was heated from ca. −70 up to ca. 0 °C. On the other hand, E' and E'' values kept almost constant when the polymer sample was heated over ca. 0 °C. Namely, the rubber plateau was observed for the poly(LPA-*co*-DT). As shown in Figure 7, the GPC elution curves of the polymer samples did not change before and after the measurement, suggesting that no reaction occurred during the measurement.

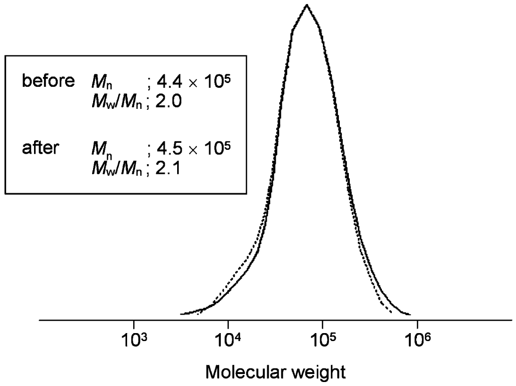


Figure 7. GPC elution curves of the poly(LPA-*co*-DT) ([LPA] in copolymer; 37.6 mol %) before (solid line) and after (dotted line) dynamic viscoelasiticity measurement.

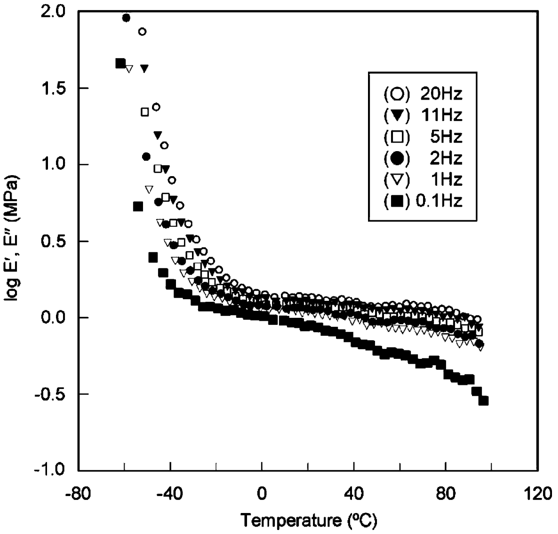


Figure 8. Frequency dependence of E' for the poly(LPA-*co*-DT) ([LPA] in copolymer; 37.6 mol %).

The frequency dependence of E' on the dynamic viscoelasiticity was also examined, and the results are shown in Figure 8. The slope of the rubbery region of E' gradually became large with a decrease of the frequency. The rubbery plateau region became shorter with a decrease of the frequency, suggesting that the polymer has a entanglements between interlocked cyclic polymers. Vulcanized rubbers and triblock copolymers such as poly(styrene-*b*-butadiene-*b*-styrene) are known to reveal a rubber plateau originated from the cross-linking and the hard segments, respectively. Despite that, poly(LPA-*co*-DT) is not vulcanized and has only simple repeating units of LPA and DT in the main chain. Thus, we presumed that the poly(LPA-*co*-DT) contains the intermolecular entanglements derived from topologically linked structure of the cyclic component.[17]

Photodegradation of the Copolymer. The photodecomposition of the copolymer of LPA and DT was conducted under UV irradiation at room temperature using a high-pressure Hg lamp. The results are shown in Figure 9, in which the results for each homopolymer are also indicated to comparison. At the early stage of the decomposition, the molecular weight of each polymer decreased remarkably. After a rapid decrease of molecular weights of the polymers at the initial stage of the reaction, they kept on almost constant even for a prolonged time.

The GPC elution curves of the photodecomposition products of the poly(LPA-*co*-DT) ([LPA] = 37.6 mol %) are shown in Figure 10. After high-molecular-weight region on the GPC elution curve disappeared rapidly at the early stage of the decomposition, the curves converged on a certain low-molecular-weight region (the M_n of the product was estimated to be

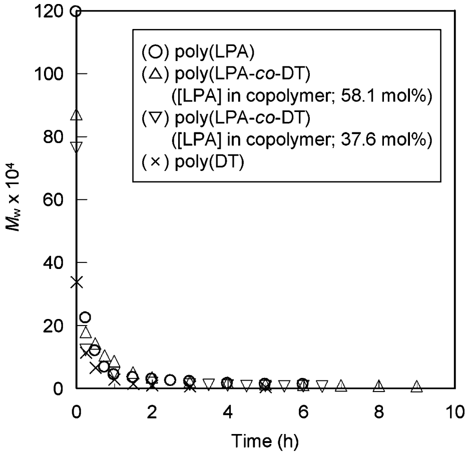


Figure 9. Photodecomposition behaviors of poly(LPA), poly(LPA-*co*-DT)s, and poly(DT) in THF (1% w/w) under irradiation of a high-pressure Hg lamp at 25 °C.

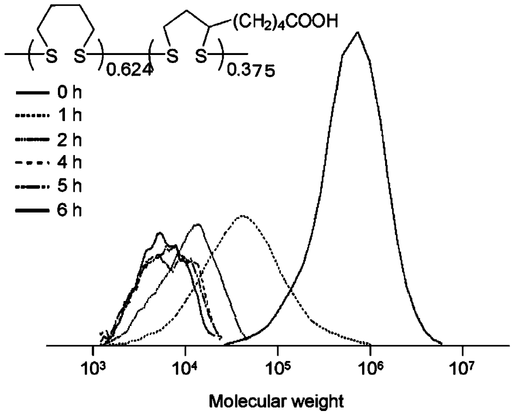
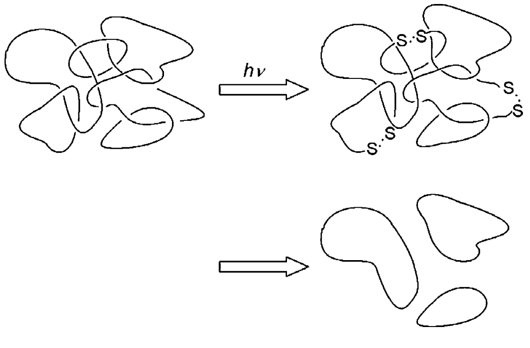


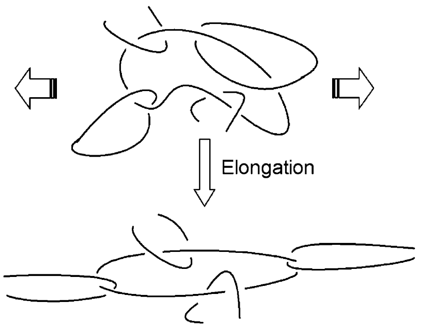
Figure 10. GPC elution curves of the photodecomposition products of poly(LPA-*co*-DT)s ([LPA] = 37.6 mol %) in THF (1 wt %) under irradiation of a high-pressure Hg lamp at at 25 °C.

Scheme 2. Illustration for Photodecomposition Process of Polycatenane Structure



ca. 5.0 × 10^3 g/mol), and such an elution curve did not change during the photodecomposition. The M_n on the converged regions of poly(LPA-*co*-DT) depended on the copolymer composition. The decomposition behavior of poly(LPA-*co*-DT) is in good agreement with that of poly(DT). Thus, the results suggest that the copolymer contains a polycatenane structure consisting of interlocked cyclic polymers, and thus the degradation of the copolymer is illustrated in Scheme 2.

Scheme 3. Concept of Molecular Weight Entanglement



Molecular Weight Entanglement. In general, rubber elasticity is shown under elastic control originated from some meshes of a net formed and relaxation mechanisms being lost. The meshes of a net are formed by an physical linkages, and the physical linkage called it as an entanglement is originated from polymer chains crossing each other and their restricted movements. The modulus strength of the rubbery plateau, that is, pseudo-equilibrium elastic modulus (G_N^0), can be represented by the following formula and estimated by the molecular weight entanglement (M_e) and the number of the main chain bonds between entanglement (N_v).

$$G_N^0 = \rho RT/M_e = \rho RT/M_v N_v \tag{1}$$

where ρ is polymer density, R indicates gas constant, and T is absolute temperature. When the elastic modulus in the range of rubbery plateau obtained by the dynamic viscoelasticity measurement of the poly(LPA-*co*-DT) ([LPA] = 37.6 mol %), the polymer density, gas constant, and temperature were substituted in formula 1, the M_e was calculated to be ca. 2.65 × 10^3 g/mol.

The M_e on polycatenane structure should mean half value of the molecular weight of a noninterlocked cyclic component, as represented schematically in Scheme 3. If the assumption that poly(LPA-*co*-DT) contains such polycatenane structure is correct, the M_e of poly(LPA-*co*-DT) corresponds to the half value of the molecular weight of a single cyclic polymer estimated from the photodecomposition behavior. In the poly(LPA-*co*-DT) ([LPA] = 37.6 mol %), the M_e (ca. 2.65 × 10^3 g/mol) estimated by the dynamic viscoelasticity method was in good agreement with the half value of the molecular weight of a single cyclic component (ca. 5.0 × 10^3 g/mol) estimated by the photodecomposition of the copolymer. Accordingly, it would be concluded that the poly(LPA-*co*-DT) obtained from the copolymerization in bulk contains polycatenane structure.

Conclusion

Thermal copolymerization of LPA with DT was induced readily to give a high molecular weight polymer in a high yield. The reaction products are poly(LPA-*co*-DT) from the ^{13}C NMR spectroscopy and the solubilities of the products. A difference in the polymerization reactivities between two monomers may be originated from the difference in the respective strain energies of the monomers. It was also presumed that the poly(LPA-*co*-DT) consist of cyclic structure as well as poly(DT). The copolymer structure was assumed to be polycatenane structures consisting of the entanglements of cyclic polymer from a photodecomposition and the mechanical properties of poly(LPA-*co*-DT). The M_e of the poly(LPA-*co*-DT) estimated by dynamic viscoelasticity method was in good agreement with the half value of the molecular weight of a noninterlocked cyclic polymer estimated by the photodecomposition behavior of the poly(LPA-*co*-DT). Thus, we concluded that the poly(LPA-*co*-DT) contains a polycatenane structure.

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