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Synthesis and Characterization of Poly(1,2-dithiane)

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ABSTRACT: Polymerization of 1,2-dithiane (DT) and the characterization of the polymer were investigated. Bulk polymerization of DT proceeded readily without initiators above the melting point of DT, giving a polymer in high yield. The polymerization of DT was strongly affected by the presence of small amounts of thiols. The molecular weight of polymers obtained from the polymerization of DT could be controlled by the addition of benzyl mercaptan (BM). The ^{13}C and ^{1}H NMR spectra of the poly(DT) suggest that the poly(DT) has a macrocyclic structure containing disulfide bonds in the main chain, in contrast to the linear polymers that were obtained from polymerization of DT in the presence of thiols. The poly(DT) obtained from polymerization of DT was characterized by the interconversion between thiol and disulfide bonds, thermal properties, dynamic viscoelasticity, stress−strain test, solubility, and photodegradation of the poly(DT) and was found to have unusual properties. In the polymerization of DT in the presence of the cyclic poly(oxyethylene) (CPO), the product included a catenane structure of cyclic poly(DT) and CPO entangled with each other. From the results obtained in this study, we presume that the poly(DT) obtained from polymerization of DT includes a polycatenane structure.

Introduction

Many approaches have been reported to prepare polymers containing disulfide bonds in the main chains, including polycondensations of α,ω-dihalides with sulfur, oxidative polymerizations of α,ω-dithiols, and ring-opening polymerizations of cyclic disulfides.[1−10] Among them, ring-opening polymerization is a useful process for synthesizing high molecular weight polymers bearing disulfide bonds in the main chain. Polymerizations of cyclic disulfides have been reported,[2−8] and torsional strain of the −C−S−S−C− bond angle was also asserted to be one driving force to induce the ring-opening polymerization.[9−11] It is difficult to isolate monomeric cyclic disulfides because of their high reactivity. However, 1,2-dithiane (DT) seems to be a suitable monomer to study the polymerization of cyclic disulfide because the enthalpy of the ring-opening polymerization of DT was reported to be negative even though it is a six-membered cyclic disulfide.[8]

Recently, much attention has been paid to preparing cyclic polymers from the points of not only their interesting properties but also as an element of topological polymers such as catenanes and rotaxanes.[12−16] Large cyclic polymers were synthesized by intramolecular cyclizations of difunctional living dianions with α,ω-alkyl dihalides[17−20] and intramolecular cyclizations of α,ω-heterotelechelic polymers produced by living polymerizations.[21−26] It was also reported that an anionic polymerization of β-DL-butyrolactone or DL-lactide with cyclic dibutyltin initiators gave cyclic polymers. [27]

Although many studies of polymerizations of cyclic disulfides have been reported,[1−11] the detailed structures of the resulting polymers have not been carefully investigated. We found that DT gave an unusual polymer structure from the polymerization of DT without added initiators. The polymerization of DT in the absence of any initiators seems to provide a unique method for preparing cyclic polymers with special properties based on unusual polymer structures.

Experimental Part

Materials. 1,4-Butanedithiol (BDT) and benzyl mercaptan (BM) (Aldrich Chem., reagent grade) were used without further purification. Other reagents were purified by conventional methods before use. DT was synthesized from BDT according to a reported procedure.[7] The product was concentrated at reduced pressure to remove $CHCl_3$ solvent, giving a pale yellow liquid (yield 86%). Because it included monomer, oligomer, and polymer, it was purified by fractional distillation (60 °C/4 Torr). The distillate was collected in an ice−water trap. In the ^{13}C NMR spectrum of the distillate, peaks appeared at 33.1 ppm from methylene carbons neighboring a sulfur atom and at 27.6 ppm from CH_2 carbons between CH_2 groups, which identified the product as DT. The purity of the synthesized DT determined by HPLC was 99.6%, and BDT was detected as a contaminant. The distilled DT was further purified by recrystallization from methanol several times to remove BDT completely. After recrystallization several times from methanol, the purity of DT determined by HPLC was >99.9%; mp 31.0−31.5 °C (mp 31−32 °C[28]). ^{1}H NMR ($CDCl_3$): 2.85 ppm (s, 2H), 1.97 ppm (s, 2H). ^{13}C NMR ($CDCl_3$): 27.7 ppm, 33.2 ppm. The highly purified DT was used as the monomer for polymerization.

The cyclic poly(oxyethylene) (M_n = 720) was synthesized according to the literature.[2,4] Because polymer produced by intermolecular reaction (cyclic or linear) was less soluble than the required product,[4] it could be separated by a precipitation−fractionation procedure. The reaction product (ca. 5 g) was dissolved in toluene (250 mL) at 25 °C. *n*-Hexane was slowly added until the stirred solution became cloudy. Equilibrium phase separation was ensured by heating the cloudy solution until it cleared and then cooling it slowly with gentle stirring to 25 °C. The required product was isolated by evaporating the solvent, and it was confirmed to be cyclic poly(oxyethylene) (CPO) by comparison with the ESI-MS chart of the product as reported previously.[29]

Polymerization Procedure. Polymerization was carried out in a sealed Pyrex tube. After the required amounts of reagents were charged, the tube was degassed, and then sealed

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below 0.1 Torr. After polymerization at constant temperature for a given time in a thermostat, the contents of the tube were poured into a large amount of *n*-hexane to precipitate the polymer formed. The polymer was washed well with *n*-hexane and dried under 1 Torr at room temperature. The polymer yield was determined by gravimetry.

Polymer Characterization. The number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the dispersity index (M_w/M_n) of the polymers were determined by GPC using a Tosoh CCPD RE-8000, G2000H, G4000H, and G6000H columns eluted with THF at flow rate of 1 mL/min at 38 °C. Standard polystyrenes purchased from Tosoh Co. Ltd. were used for molecular weight calibration. The structures of polymers were analyzed by ^{1}H and ^{13}C NMR spectroscopy using a JEOL A-400 spectrometer in $CDCl_3$ with TMS as an internal standard.

Fractionation of Low Molecular Weight Poly(DT). The poly(DT) was fractionated by HPLC using a Shimadzu LC-10A and fractional precipitation using a solvent mixture of *n*-hexane-chloroform at various ratios to separate the low molecular weight fraction from the higher molecular weight polymer. The solutions were concentrated at reduced pressure, precipitated with *n*-hexane, and dried at 1 Torr at room temperature.

Reaction of Poly(DT). Reduction of the cyclic poly(DT) obtained from polymerization was carried out in a sealed glass tube. After the required amounts of poly(DT), and other reagents if needed were charged into a glass tube, it was degassed and then sealed under high vacuum. The reaction was carried out under UV irradiation (Toshiba SHL-100-2, 100 W) at 30 °C for 20 min. After the reaction, the tube was opened, and contents of the tube were poured into a large amount of *n*-hexane. The precipitate was washed well with *n*-hexane and dried in high vacuum at room temperature.

Oxidation of linear poly(DT) having thiol groups at both chain ends was carried out according to the literature.[30] The solution of the polymer and triethylamine in chloroform was stirred while adding a solution of I_2 in chloroform at room temperature. The solution was stirred continuously until it became colorless after adding I_2. The reaction mixture was washed with water containing a few percent of sodium thiosulfate, hydrochloric acid, and water. The solutions were concentrated at reduced pressure and then reprecipitated with *n*-hexane and dried in vacuo at room temperature.

Thermal and Mechanical Properties. DSC analysis was carried out with a Seiko instruments DSC 6100 at a heating rate of 10 °C/min. A Shimadzu XD-610 diffractometer was used for powder X-ray diffraction analysis. The stress−strain curve of the polymer was obtained with a Shimadzu Autograph AG-1000D instrument.

Dynamic mechanical measurements were performed with a Rheology DVE-V4 FT rheospectrometer in the shear mode operating at a constant frequency at a constant strain of 0.1%. The dimensions of the testing sample were 40 (L) × 12 (W) × 2 (T) mm. Nitrogen gas was circulated in the environment chamber to prevent degradation of the sample during testing. The storage modulus (E'), shear loss modulus (E''), and loss tangent (tan δ) were obtained at a heating rate of 2 °C/min over the temperature range from −100 to 150 °C.

Degradation of Polymers. The photodegradation of polymers was carried out in Pyrex tube in a THF solution under UV irradiation (Toshiba SHL-100-2, 100 W) at room temperature. After phtodegradation, the contents of the tube were poured into methanol. The methanol-insoluble product was measured by GPC.

Results and Discussion

Thermal Polymerization of DT. Polymerization of DT was conducted in bulk without added initiator, and the results are listed in Table 1. When the polymerization was conducted at a temperature above the melting point of DT, the polymerization proceeded easily. Similar results are reported by Barbee.[31] The polymer obtained from the polymerization of highly purified DT is referred to as poly(DT).

Table 1. Thermal Polymerization of DT in Bulk

temp (°C)	time (h)	yield (%)	$M_w \times 10^{-4\,a}$
0	10	~0.0	
40	8	23.9	81.3
80	8	83.8	28.1

[a] Determined by GPC calibrated with standard polystyrenes.

Table 2. Thermal Bulk Polymerization of DT in the Presence of BM at 80 °C

BM/DT (mole ratio)	time (h)	yield (%)	$M_w \times 10^{-4a}$	$M_w/M_n\,^a$
0.0	8	83.8	28.1	2.5
8.4×10^{-3}	8	2.9	10.4	2.5
1.6×10^{-2}	10	7.2	6.0	2.6
6.2×10^{-2}	50	20.1	0.4	1.9

[a] Determined by GPC calibrated with standard polystyrenes.

Although the polymerization of DT was inhibited by the addition of 1,1-diphenyl-2-picrylhydrazyl (DPPH) as a radical inhibitor, a direct observation of thiyl radicals by ESR even by a spin-trapping method using nitroxide was unsuccessful.

Moreover, taking the −S−S− bond dissociation energy of DT which seems to be similar to that of an aliphatic disulfide (70 kcal/mol) into consideration,[32] the homolysis of the −S−S− bond seems to be difficult at 40 °C. Alternatively, a heterolytic mechanism of thiol−disulfide exchange may be operative, although the initiation mechanism is not clear.

During the purification of DT, a small amount of BDT (less than 0.5%) was detected in the distilled materials. When we use it as a monomer, the polymer yield and the M_n of the polymer were suppressed significantly.[31] We refer to this type of polymer as poly(DT−BDT). To check further the effect of thiols, the effect of BM on the polymerization of DT was examined. The results are listed in Table 2. The polymerization of DT was suppressed strongly by addition of BM, and the M_n of the resulting polymers decreased BM concentration increased in the feed. We refer to this polymer as poly(DT−BM).

Structure of Resulting Polymers. The structure of the resulting polymers was examined byNMR spectroscopy. Figure 1a shows the ^{13}C NMR spectrum of the polymers obtained from the polymerization of the highly purified DT. Only two peaks appeared at 27.8 and 38.3 ppm that can be assigned to the methylene carbon atom in the chain. Figure 1b,c shows the polymer obtained from polymerization of DT in the presence of BDT or BM. In the ^{13}C NMR spectra of poly(DT−BDT) and poly(DT−BM), the small signals at 24.2 ppm ($\sim CH_2{-}\mathit{C}H_2{-}SH$) and 32.5 ppm ($\sim \mathit{C}H_2{-}CH_2{-}SH$ at the chain end)[33] are observed besides the peaks at 27.8 and 38.3 ppm of the methylene carbons atom in the main chain. Moreover, in the ^{13}C NMR spectrum of the poly(DT−BM), the signal at 43.5 ppm due to ω-benzylic carbon atom was observed.

In the ^{1}H NMR spectrum of the poly(DT), only two peaks at 1.82 and 2.73 ppm based on the methylene protons in the main chain were observed in poly(DT). On the other hand, the peaks based on thiol groups were observed at 1.38 ppm in addition to methylene protons in the main chain in poly(DT−BDT). These results suggest that the resulting poly(DT) consisted of repeating $-S-(CH_2)_4-S-$ units and no chain ends.

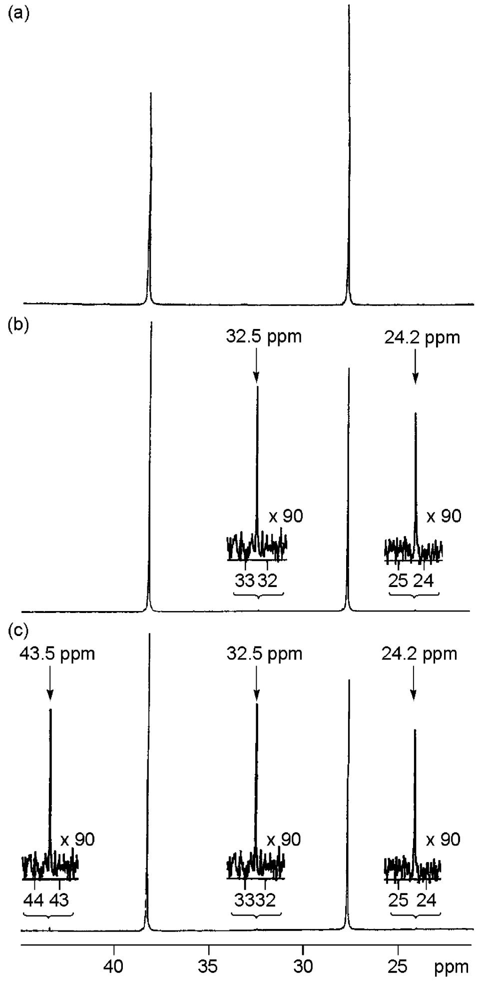


Figure 1. ^{13}C NMR spectra of poly(DT) (a) obtained from highly purified DT, (b) obtained from DT in the presence of BDT, and (c) obtained from DT in the presence of BM.

The M_n of the polymer poly(DT−BDT) obtained from the polymerization of DT in the presence of a small amount of BDT was determined to be 10.3×10^3 from the area ratios of the thiol protons at the chain ends to the methylene protons of the main chains in the ^1H NMR spectrum of the polymer, which was consistent with that determined by GPC measurement ($M_n = 9.6 \times 10^3$). It is clear, thus, that the poly(DT−BDT) is a linear polymer with thiol groups at both chain ends.

Although we could not detect chain ends in the ^{13}C and ^1H NMR spectra of poly(DT), this may be due to the high molecular weight of the polymer examined. To clarify the absence of polymer chain ends, a low molecular weight fraction of the poly(DT) was isolated and characterized. A low molecular weight fraction was obtained by a fractional precipitation with a mixture of *n*-hexane/chloroform solvent (1/5 volume ratio). The M_n and M_w/M_n of the low molecular weight poly(DT)s determined by GPC were 1.4 and 1.1×10^3, respectively. In the low molecular weight poly(DT) obtained from fractionation, the signal due to the chain end was not observed in the ^1H NMR spectra of the polymers. The cyclic structure of the poly(DT) with low molecular weight was confirmed by ESI-MS spectroscopy, as reported previously.[29]

Transformation of Polymers. The disulfide bond is known to transform into a thiol group by UV irradiation or in the presence of a reducing reagent.[34] When the reaction was applied to the poly(DT), it was expected that cyclic poly(DT) should be converted to linear polymer bearing thiol groups at both chain ends. The ^1H NMR spectrum of polymer after the reaction for poly(DT) with a cyclic structure under UV irradiation is shown in Figure 2, from which the signals based on the thiol groups at the chain ends (1.38 ppm, triplet) were observed. If both chain ends are thiol groups, the M_n of the resulting polymer was estimated to be 5.1×10^3 from the ratio of thiol protons of the chain ends to methylene protons of the main chain. The M_n of the polymer determined by ^1H NMR spectroscopy was consistent with that determined by GPC ($M_n = 4.8 \times 10^3$). Thus, it is clear that the cyclic poly(DT) was converted to the corresponding linear polymer having thiol groups at both chain ends.

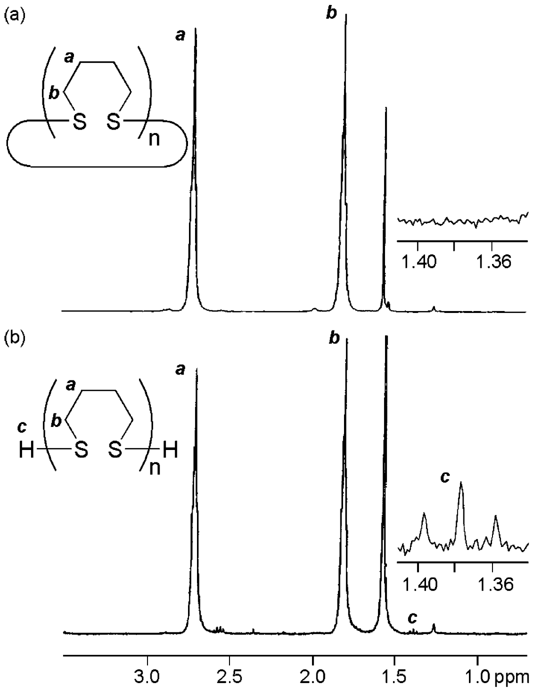


Figure 2. ^1H NMR spectra of polymers (a) obtained from polymerization of highly purified DT and (b) obtained after reduction of poly(DT).

Because it was reported that an intramolecular cyclization of α,ω-bifunctional polymer induced,[35,36] the linear poly(DT-BDT) with thiol groups at both chain ends can also be converted to the corresponding cyclic poly(DT) by an intramolecular oxidation reaction under high dilution conditions (0.05 g of poly(DT−BDT)/10 mL of $CHCl_3$). The ^1H NMR spectra of products after oxidation are shown in Figure 3. The signals of the thiol groups at 1.38 ppm present before the oxidation disappeared completely after the reaction. The M_n of the reaction product determined by GPC was 3.1×10^3 and was ca. 30% smaller than that of the linear polymer before oxidation, which is consistent with the reported results for polystyrene.[18,19] Thus, a change in chain length may not take place during the reaction from linear to cyclic. The results indicate that the linear poly(DT−BDT) was converted into a cyclic polymer by the intramolecular oxidation reaction between the thiol groups at the chain ends. On the basis of these results, the polymerization of DT and reactions of the polymer can be written as Scheme 1.

Although the low molecular weight fraction was confirmed to a cyclic structure, the structure of high

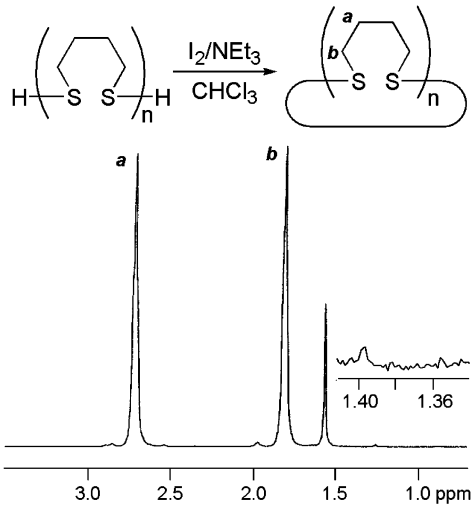
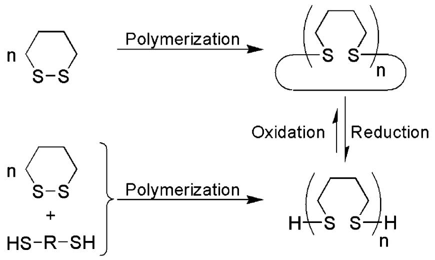


Figure 3. ^{1}H NMR spectrum of the polymer obtained after oxidation of poly(DT-BDT).

Scheme 1. Mechanism of Polymerization of DT



molecular weight poly(DT) determined by GPC cannot conclusively be shown to be a cyclic polymer from NMR spectroscopy and the chemical reactions. Then, we examined high molecular weight poly(DT) by thermal properties, solubility, physical properties, and degradation of the polymer to elucidate the structure of high molecular poly(DT).

Thermal Properties of the Polymers. The thermal properties of the cyclic polymers seem to be different from those of linear materials.[37] To check this point, poly(DT) with different molecular weights were obtained by fractional precipitation of high molecular weight cyclic poly(DT) using a mixed solvent of *n*-hexane/chloroform (50/50 vol %). Linear poly(DT−BM) was synthesized by polymerization of DT in the presence of BM. The T_g of the poly(DT) and the poly(DT−BM) were plotted against the M_n of the polymers, and the results are shown in Figure 4. It is noteworthy that the T_g of the poly(DT) remained almost constant even with an increase of the molecular weight of the poly(DT). In contrast, the T_g of the poly(DT−BM) increased with increasing molecular weight. The difference in the thermal behavior between poly(DT) and poly(DT−BM) may originate from the polymer structure.

To elucidate this point further, we synthesized cyclic poly(oxyethylene) (CPO) according to the literature.[24] The relationships between the T_g and the M_n of the CPO are also shown in Figure 4. In the CPO, the T_g of the CPO increased with increasing molecular weight, which is consistent with that of poly(DT−BM). On the other hand, the melting points of both poly(DT) and poly(DT-BM) were determined to be ca. 44 °C, as shown in Figure 5. The presence of a crystalline part for both polymers was also confirmed by powder X-ray diffraction, as shown in Figure 6. Thus, this peculiar behavior of T_g for the poly(DT) is not due only to a cyclic structure and may be attributed to specific topological interactions.

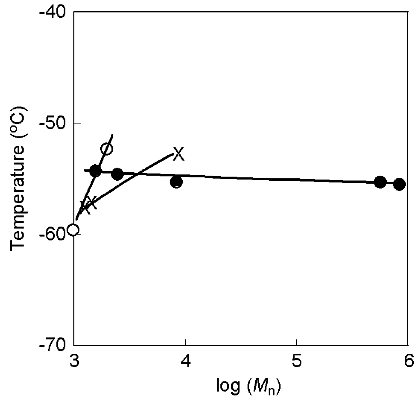


Figure 4. Relationship between M_n and T_g of poly(DT) (●) obtained by fractional precipitation and poly(DT-BM) (×) and cyclic poly(oxyethylene) (○).

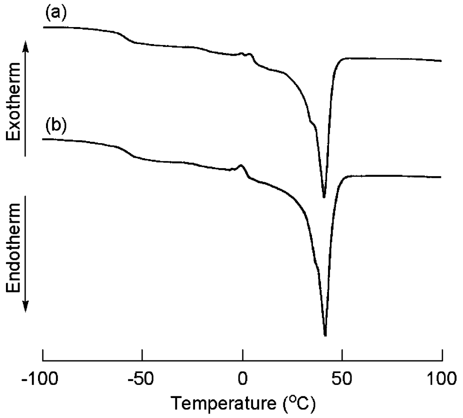


Figure 5. DSC traces of (a) poly(DT) and (b) poly(DT-BM).

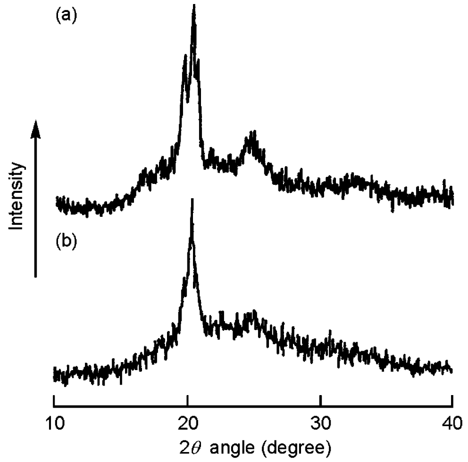


Figure 6. Powder X-ray diffraction patterns of (a) poly(DT) and (b) poly(DT-BM).

Viscoelasticity of the Polymers. Because mechanical properties of polymers are closely associated with the polymer structures, analysis of dynamic viscoelasticity of the poly(DT) should give us useful information about the polymer structure. For this purpose, we measured the temperature dependence of storage modulus (E'), loss modulus (E''), and tan δ of the poly(DT) and the poly(DT−BM) at a frequency of 11 Hz. The results are shown in Figures 7 and 8, respectively. The M_n values of poly(DT) and poly(DT−BM) used were 18.2 $\times$ 10^4 and 9.5 $\times$ 10^4, respectively. In the dynamic

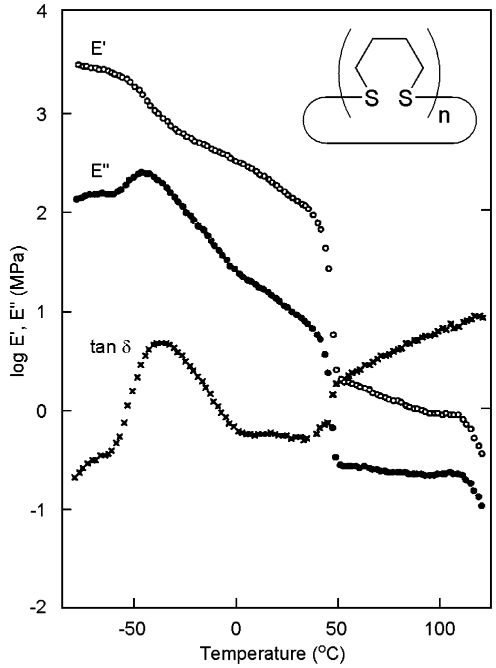


Figure 7. Temperature dependence of E' (○), E'' (●), and tan δ (×) for poly(DT) at 11 Hz; $M_n = 18.2 \times 10^4$, $M_w/M_n = 2.33$.

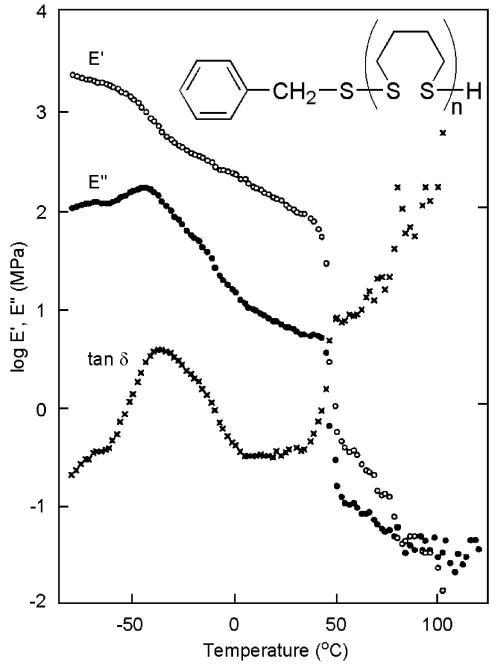


Figure 8. Temperature dependence of E' (○), E'' (●), and tan δ (×) for poly(DT-BM) at 11 Hz; $M_n = 9.5 \times 10^4$, $M_w/M_n = 1.97$.

viscoelasticity curves of poly(DT), E' and E'' values gradually decreased from 10^3 to 10^2 MPa from 0 to ca. 40 °C, which corresponds to the leathery state. At ca. 45 °C, E' and E'' values of both polymers decreased significantly upon melting. Above the melting points, both polymers revealed quite different behavior. In poly(DT), E' remained almost constant at temperatures above 50 °C up to around 100 °C; i.e., the molten state of the poly(DT) revealed a rubber plateau. Moreover, the molecular weight of poly(DT) determined by GPC did not change before and after the measurement. On the contrary, such behavior was not observed for the poly(DT−BM), and the sample was broken at a molten state.

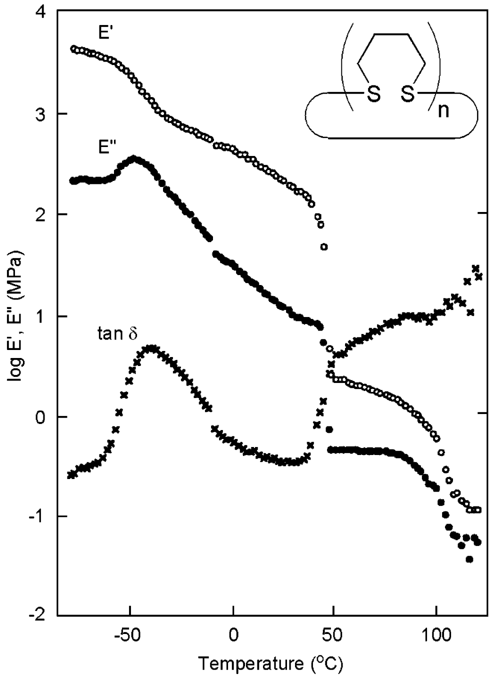


Figure 9. Temperature dependence of E' (○), E'' (●), and tan δ (×) for poly(DT) at 5 Hz; $M_n = 18.2 \times 10^4$, $M_w/M_n = 2.33$.

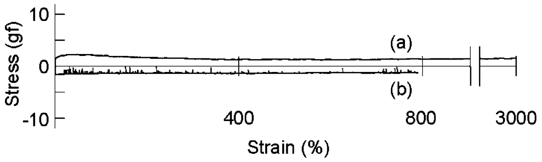


Figure 10. Stress−strain curves of (a) poly(DT) and (b) poly(DT-BM) at 50 °C.

The mechanical properties of the poly(DT) were further analyzed by dynamic viscoelasticity measurement by changing the frequency from 11 to 5 Hz, and the results are shown in Figure 9. Although the modulus curve of the poly(DT) showed the rubbery plateau above 50 °C, the rubbery plateau became shorter.

The difference in the dynamic viscoelasticity behavior between the poly(DT) and the poly(DT−BM) could not be attributed to the molecular weight of both samples because both polymers have similar molecular weights. Because the rubbery properties observed above the melting point have not been reported, to our knowledge, in the measurement of conventional linear polymers, other reasons should be considered. Although vulcanized rubbers and some triblock copolymers such as poly(styrene-*b*-butadiene-*b*-styrene) exhibit a rubbery plateau, the poly(DT) was a homopolymer, and it was not vulcanized. If polymer chains of the poly(DT) are spatially linked, rubbery properties should appear, even in the molten state. Thus, the behavior of poly(DT) above 50 °C might be caused by the entanglement between the cyclic polymer.

Polymer Physical Properties. The stress−strain curves of the poly(DT) and poly(DT−BM) at 50 °C are shown in Figure 10. The sample of poly(DT) was elongated until 3000% without breaking under load. This sample also showed an instant elastic recovery. For poly(DT−BM), such behavior was not observed. This observation indicates that the poly(DT) has a spatially linked structure between the cyclic polymers.

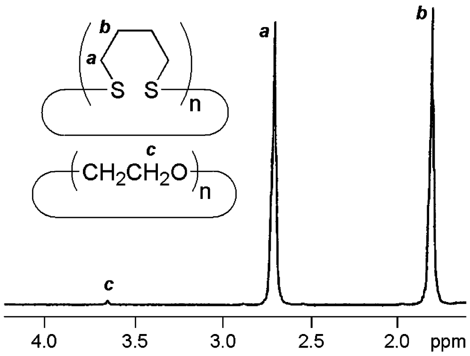


Figure 11. ^{1}H NMR spectrum of the polymer obtained from polymerization of DT in the presence of CPO.

Table 3. Thermal Bulk Polymerization of DT in the Presence of CPO at 60 °C for 5 h

DT/CPO (g/g)	yield (%)	$M_w \times 10^{-4}$	M_w/M_n
5/0	14.7	6.8	1.8
5/1	5.7	4.6	3.0
5/2	3.0	3.1	2.3
5/3	1.4	3.7	2.8

Solubility of Polymers. In the dissolution process of poly(DT), the polymer first swells like a gel, and the volume of the poly(DT) expanded for a long time and eventually dissolved in $CHCl_3$ and THF. On the other hand, poly(DT–BM) with similar molecular weight dissolved instantly in THF and $CHCl_3$, and a gel like state was not observed. The difference in dissolution behavior between these two polymers suggests that the poly(DT) has a spatially linked structure.

Polymerization of DT in the Presence of CPO. If the structure of poly(DT) has spatially linked structure, an interlocking product consisting of two different ring polymers would be synthesized by polymerization of DT in the presence of another cyclic polymer. For this purpose, we used cyclic poly(oxyethylene) (CPO), and the polymerization of DT in the presence of CPO was conducted at 60 °C for 5 h. The results are shown in Table 3. To remove the noninterlocking CPO, the products were extracted with an excess of methanol because CPO dissolves easily in methanol. The yield and the molecular weight of the reaction product decreased with increasing CPO concentrations in the feed.

The ^{1}H NMR spectrum of the reaction product is shown in Figure 11. Not only two signals at 1.8 and 2.7 ppm based on methylene protons in the main chain of poly(DT), but also the signal at 3.7 ppm based on methylene protons in the main chain of CPO was observed. Such observation is possible for only a mixture of both materials. To clarify this point, we carried out GPC measurement of the polymerization product, and the elution curves are shown in Figure 12. In the curve for the polymerization product, no peak corresponding to the molecular weight of CPO was observed. The reaction product, thus, seems to include interlocking materials between CPO with poly(DT), although the amount of the interlocking materials is small judging from the small peak area in the ^{1}H NMR spectra of the reaction materials, as shown in Scheme 2.

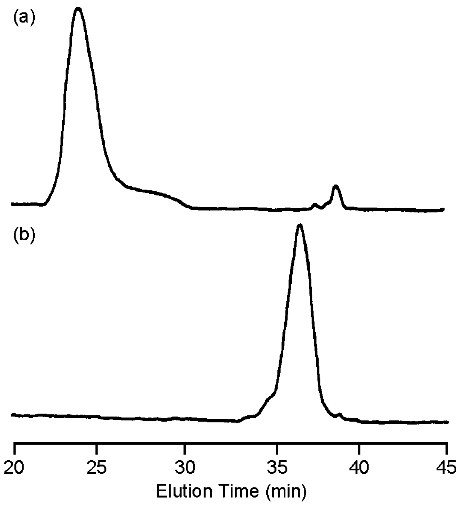


Figure 12. GPC elution curves of (a) the polymer obtained from polymerization of DT in the presence of CPO and (b) CPO.

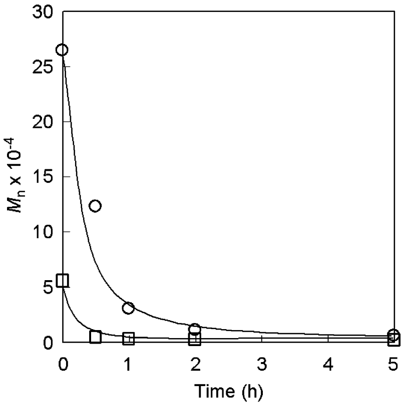
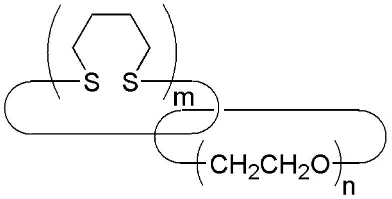


Figure 13. Photodecomposition behavior of poly(DT) in THF; $M_n = 26.8 \times 10^4$ (○), 5.3×10^4 (□).

Scheme 2. Model for the Catenane Entangled with Cyclic Poly(DT) and CPO



Degradation of Polymers. The photodecomposition of poly(DT) was carried out under UV irradiation at room temperature. The relationships between molecular weight of the polymer and reaction time are shown in Figure 13. The molecular weight of poly(DT) decreased rapidly in the early stages of decomposition. After rapid degradation, the molecular weight of the product remained constant even for a prolonged reaction time regardless of different molecular weights of the original polymers. The GPC elution curves of poly(DT) before and after photodegradation are shown in Figure 14, in which the signal based on DT is omitted. After photodegradation, the reaction product gave a similar monomodal elution curve, regardless of reaction time. Figure 15 shows the ^{1}H NMR spectra of the original poly(DT) and the decomposition product. From a comparison of these two spectra, the decomposition product might be shown to be a cyclic structure. The M_n of the reaction product was estimated to be about 2700 g/mol, which was assumed to be noninterlocking cyclic poly(DT).

Molecular Weight between Entanglements of the Cyclic Polymer. The molecular weight between the points entangled by the cyclic polymer can be calculated by using the following formula (1) derived from properties of the polymer in the rubbery plateau[37]

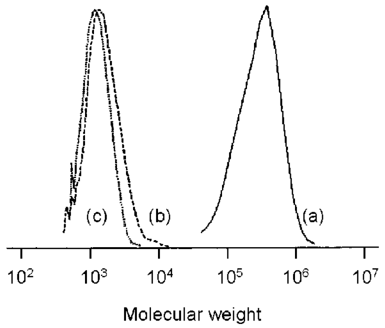


Figure 14. GPC elution curves of poly(DT) before and after photodegradation: reaction time (a) 0, (b) 2, and (c) 5 h.

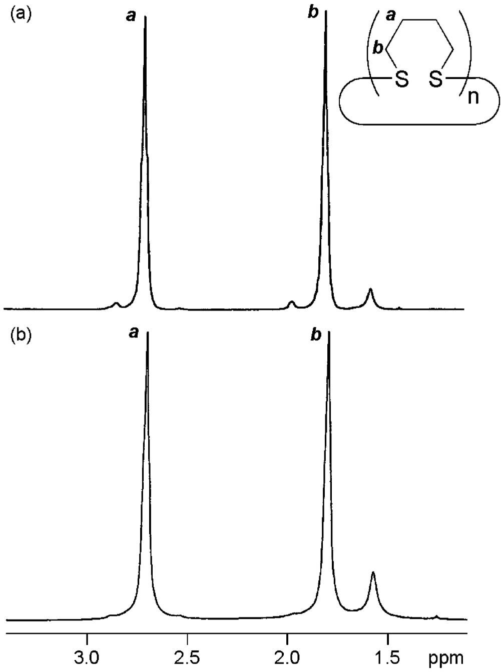


Figure 15. ^{1}H NMR spectra of (a) before decomposition of poly(DT) and (b) the decomposition product insoluble in methanol after UV irradiation for 4 h.

$$G_N{}^\circ = \rho RT/M_e \qquad (1)$$

where $G_N{}^\circ$ is the the pseudo-equilibrium elastic modulus, ρ the polymer density, R the gas constant, T the temperature (K), and M_e the molecular weight between points of entanglement. From the dynamic viscoelastisity measurement of poly(DT), we used 2.2 MPa at 323 K as the pseudo-equilibrium elastic modulus in the rubbery plateau. The density of the polymer sample was measured to be 1.12 g/mL at 323 K. When these values were substituted in formula 1, we obtained 1370 g/mol as the value of M_e.

From photodecomposition of poly(DT), the M_n of the un-interlocked polymer was estimated to be about 2700 g/mol as described above. If the assumption is correct, the molecular weight between the points of entanglement will correspond to half of 2700, as shown in Scheme 3. Thus, the M_n between the points of entanglement by the polymer decomposition method was estimated to be 1350 g/mol. The molecular weight between the points of entanglement of the poly(DT) estimated by dynamic viscoelasticity methods was in a good agreement with that estimated by photodegradation. Accordingly, we presume that the poly(DT) obtained from polymerization of DT includes a polycatenane structure. Such structure might be formed by a backbiting reaction, although the detailed structure is not clear.

Scheme 3. Concept of Molecular Weight between the Points of Entanglement

Conclusion

The polymerization of highly purified DT proceeded easily at reaction temperatures above the melting point of DT, giving high molecular weight polymer. From the structural analysis of the resulting poly(DT), the poly(DT) was found to have large cyclic structure, which is in contrast to that of the polymer obtained from the polymerization of DT in the presence of thiol compounds such as BM, which gave a linear polymer. In dynamic viscoelastic measurements, poly(DT) showed a rubbery plateau in the melt state of the polymer. Such behavior was not observed in poly(DT−BM). The T_g of poly(DT) decreased with increasing M_n of the poly(DT), which is different from that of poly(DT−BM). Different solubility behavior in $CHCl_3$ and THF between the poly(DT) and the poly(DT−BM) was also observed. The M_e determined from both decomposition of the polymer and dynamic viscoelastic measurements was the same. On the basis of these results, we conclude that the poly(DT) obtained from polymerization of DT includes a polycatenane structure.

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