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Soluble and Thermally Stable Polysulfones Prepared by the Regiospecific and Alternating Radical Copolymerization of 2,4-Hexadiene with Sulfur Dioxide

Tomoaki Kitamura, Naruki Tanaka, Asako Mihashi, and Akikazu Matsumoto*

Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

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ABSTRACT: We synthesized the alternating copolymers of 1,3-diene monomers with sulfur dioxide (SO_2) as a new class of thermally stable polymers by the radical copolymerization process and the subsequent hydrogenation. The copolymerizations of 2,4-hexadiene (HD), 1,3-butadiene (BD), and isoprene (IP) with SO_2 were carried out at −78 to 0 °C in toluene in the presence of *tert*-butyl hydroperoxide, which acts as one component in the redox initiating system in combination with SO_2. The resulting poly(diene-*alt*-SO_2)s were found to consist of highly controlled repeating units, that is, an alternating and 1,4-regiospecific repeating structure. Poly(HD-*alt*-SO_2) was soluble in several organic solvents, such as chloroform, nitromethane, tetrahydrofuran, acetone, and dimethyl sulfoxide. In contrast, poly(IP-*alt*-SO_2) was soluble only in dimethyl sulfoxide, whereas poly(BD-*alt*-SO_2) was insoluble in all of the solvents. The poly(diene-*alt*-SO_2)s readily degraded upon heating because of the expected fast depolymerization. We have demonstrated that the thermal stability of the poly(diene-*alt*-SO_2)s is modified by the hydrogenation of the double bond in the polymer main chain. The hydrogenation of poly(HD-*alt*-SO_2) resulted in a drastic increase in the 5% weight-loss temperature from 135 to 317 °C.

Introduction

Recent progress in the development of materials for optoelectronics demands a new kind of polymer with an excellent thermal stability as well as optical and electric properties. Polysulfones are defined as the polymers that include a sulfonyl group ($-SO_2-$) in the main chain.[1] The sulfonyl groups are connected to aliphatic, cycloaliphatic, or aromatic groups as the other repeating units. Aromatic polyether sulfones are some of the important engineering plastics, which are prepared by condensation polymerization and used in a wide range of application fields. Poly(vinyl sulfone)s, that is, poly(alkylene sulfone)s, are obtained by the free-radical copolymerization of olefins or cycloolefins with sulfur dioxide (SO_2).[2−4] Many kinds of vinyl monomers, such as styrene, vinyl chloride, and acrylic monomers, have been used for the synthesis of poly(vinyl sulfone)s.[5−15] The resulting poly(vinyl sulfone)s contain weak sulfur−carbon bonds, which are readily cleaved and induce a fast depolymerization (Scheme 1). The copolymerization is usually performed at a low temperature below a ceiling temperature using a redox initiator to obtain a high-molecular-weight polymer. The readily degradable poly(vinyl sulfone)s have been developed as resist materials rather than thermoplastics.[16,17] Therefore, the characteristic of the poly(vinyl sulfone)s is different from the features of aromatic polysulfones obtained by condensation polymerization as thermally stable plastics.

In contrast with the significant number of investigations for the synthesis and characterization of the poly(vinyl sulfone)s, only a few reports have been published regarding the poly(diene sulfone)s, which were prepared by the copolymerization of 1,3-diene monomers with SO_2. For example, the alternating radical copolymerization of 1,3-butadiene (BD),[18−23] isoprene (IP),[21] and 1,3-cycloalkadienes[24−27] as well as the random copolymerization of chloroprene[28] with SO_2 were reported, but the details of the structure and properties of the copolymers have not been investigated. In 1970, Bauer et al.[22] reported the high crystallinity and the poor solubility of poly(butadiene sulfone) prepared by emulsion polymerization. They also carried out the hydrogenation of poly(butadiene sulfone) using a tris(triphenylphosphine)-rhodium chloride catalyst at 120 °C. The structure and thermal decomposition properties of the hydrogenated poly(butadiene sulfone) were compared with those of the poly(tetramethylene sulfone) obtained from the oxidation of poly(tetramethylene sulfide). These two polymers showed similar structures and properties. The onset temperature of the poly(tetramethylene sulfone)s was approximately 100 °C higher than that of poly(butadiene sulfone). The thermal stability of the poly(tetramethylene sulfone) was first suggested by Noethe[29] in 1958, and more recently, Wudl and coworkers[30] revealed the thermal decomposition mechanism of polysulfones based on DFT calculations. Wudl et al. also reported the remarkable thermal stability of the polysulfones with a five-carbon linker between the sulfone groups in the chain. Davies and Daly[31,32] reported the synthesis of the poly(diene sulfone)s using BD, IP, and the other diene monomers by the redox polymerization and their application to X-ray lithography resists.

Recently, we synthesized the polysulfones by the alternating radical copolymerization using several 1,3-diene monomers and SO_2 as the starting materials to obtain thermally stable polysulfones by the subsequent polymer reaction for the hydrogenation of the double bond in the main chain using *p*-toluene sulfonyl hydrazide (TSH)[33,34] (Scheme 2). The TSH is often used for the hydrogenation of polybutadiene[36,37] and other polymers[38−41] involving unsaturated groups. The radical alternating copolymerization is one of the most convenient and useful methods for

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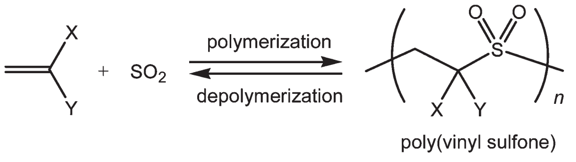
*Corresponding author. E-mail: matsumoto@a-chem.eng.osaka-cu.ac.jp.

the polymer synthesis because of the merits of their polymerization features; for example, the use of a wide range of monomers including materials other than vinyl monomers and inorganic compounds, such as SO_2 and O_2, the facile synthesis of a high molecular weight polymer with a high yield, the well-defined polymer repeating structures independent of the copolymerization conditions (monomer composition, solvent, and temperature), and the polymer properties different from those of the random copolymers and homopolymers. Furthermore, we determined the formation of the polymers with a regiocontrolled structure during the radical copolymerization of dienes with SO_2. In general, the control of stereochemical and regiostructures is still difficult during the conventional radical polymerization,[42,43] although several successful results have recently been reported for solid-state[42,44] and template[43,45] polymerizations and the controlled polymerization using Lewis acids.[42,43] In the present study, we carried out the highly regiospecific and alternating radical copolymerization of 2,4-hexadiene (HD), BD, and IP with SO_2 as the comonomer using a redox-initiating system. The structure and properties of the resulting poly(diene sulfone)s as well as the modification of the thermal stability of the polymers by hydrogenation were investigated.

Experimental Section

General Procedures. The NMR spectra were recorded using a Bruker AV300N spectrometer in $CDCl_3$ and dimethyl sulfoxide-d_6 (DMSO-d_6). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (M_w/M_n) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. The FT-IR spectra were recorded by a JASCO FT/IR 430 spectrometer using the KBr pellet method. The thermogravimetric and differential thermal analyses (TG/DTA) were carried out using a Seiko TG/DTA 6200 with a nitrogen stream at the heating rate of 10 °C/min. The onset and maximum temperatures of decomposition (T_{init} and T_{max}) were determined as the onset and maximum rate temperatures of decomposition, respectively, using the derivatives of the TG and DTA curves. The decomposition characteristic was also evaluated as the 5 and 50% weight-loss temperatures (T_{95} and T_{50}, respectively) in the TG analysis. The differential scanning calorimetry (DSC) was carried out using a Seiko DSC-6200 at the heating and cooling rates of 10 °C/min. The UV−vis spectra were recorded using a JASCO V-550 spectrophotometer. The wide-angle X-ray diffraction data were collected using a Rigaku RINT-Ultima 2100 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å).

Scheme 1



Materials. HD (Tokyo Chemical Industry), BD (Tokyo Chemical Industry), SO_2 (Sumitomo Seika Chemicals), *tert*-butyl hydroperoxide (Sigma-Aldrich), and TSH (Wako Pure Chemical Industries) were used as received without further purification. IP (Wako Pure Chemical Industries) and the solvents were distilled before use.

Polymerization. A diene monomer (20 mmol) and *tert*-butyl hydroperoxide (0.04 mL, 0.2 mmol) in toluene (10 mL) were placed in a glass ampule. The solution was degassed by the freeze−thaw technique. The cycle was repeated three times; then, SO_2 (2.0 mL, 50 mmol) was added by vacuum distillation, and finally the ampule was sealed. For the copolymerization of BD, the BD monomer was added by vacuum distillation after the freeze−thaw procedure. After polymerization for a given time at −78, −20, or 0 °C, the polymerization mixture was poured in 200 mL of methanol. The polymer was filtered, washed with methanol, and then dried in vacuo at room temperature. The yield of the polymers was gravimetrically determined on the basis of the amount of the charged diene monomers. Poly(HD-*alt*-SO_2) and poly(IP-*alt*-SO_2) were purified by repeated reprecipitation using chloroform and DMSO as the solvent, respectively, and methanol as the precipitant.

Poly(HD-alt-SO_2). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 5.89 (m, $CH{=}CH$, 1H), 4.00 (m, $CH(CH_3)CH{=}CH$, 1H), 1.50 (m, $SO_2CH(CH_3)CH$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 129.20 ($CH{=}CH$), 56.99 ($CH(CH_3)SO_2$), 12.55 ($CH(CH_3)SO_2$). IR (KBr; cm^{-1}): 2986, 2940, 2877, 1638, 1456, 1382, 1299, 1128, 1059, 1018, 975, 911, 846, 744, 601, 510, 448.

Poly(BD-alt-SO_2). Insoluble; IR (KBr; cm^{-1}): 2977, 2922, 1651, 1407, 1295, 1254, 1188, 1115, 1077, 974, 882.

Poly(IP-alt-SO_2). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 5.62−5.65 (m, $C{=}CHCH_2$, 1H), 3.98−4.03 (m, $CH_2C(CH_3){=}CHCH_2$, 4H), 1.86 (s, $C(CH_3){=}CH$, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 133.50 ($CH_2C(CH_3){=}CH$), 120.20 ($C{=}CHCH_2$), 60.87 ($SO_2CH_2C{=}CH$), 51.44 ($CH{=}CH_2SO_2$), 17.49 ($CH_3C{=}CH$). IR (KBr; cm^{-1}): 2982, 2928, 1638, 1411, 1306, 1256, 891, 795.

Hydrogenation. The PDS (typically, 0.2 g) and TSH (3.7 g, 20 mmol) were stirred in 1,2-diethoxyethane (10 mL) at 60−100 °C for 12−48 h under a nitrogen atmosphere. After the reaction, the reaction mixture was poured in 200 mL of methanol. The precipitated polymers were filtered, washed with methanol, and then dried in vacuo at room temperature. The yield of the recovered polymers was gravimetrically determined. The conversion was determined by ^{1}H NMR spectroscopy for the reactions of poly(HD-*alt*-SO_2) and poly(IP-*alt*-SO_2) and IR spectroscopy for the reaction of poly(BD-*alt*-SO_2).

Poly(HD-alt-SO_2)-H. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.39−3.49 (m, CH, 1H), 1.34−2.01 (m, CH_2, 2H), 1.24 (m, CH_3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 52.7 (CH), 25.6−26.5 (CH_2), 24.6−25.6 (CH_2), 13.1−14.0 (CH_3), 11.7−13.1 (CH_3). IR (KBr; cm^{-1}) 3436, 2925, 1633, 1462, 1296, 1124, 721, 604.

Results and Discussion

Copolymerization of Dienes with SO_2. The radical copolymerization of the diene monomers was carried out using an excess amount of SO_2 ([SO_2]/[diene] = 2.5 or 1.9 molar ratio) in toluene in the presence of *tert*-butyl hydroperoxide, which

Scheme 2

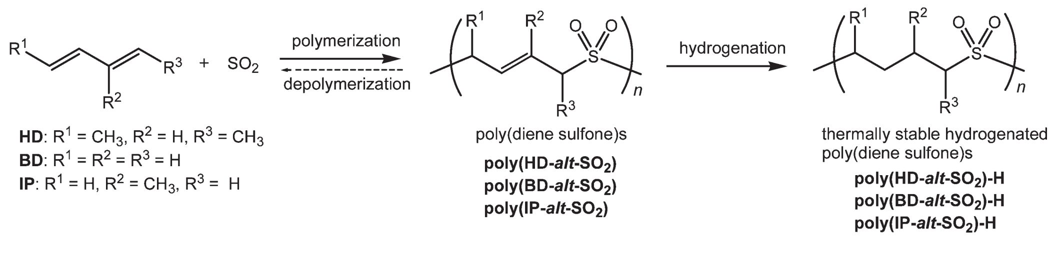


Table 1. Synthesis of Poly(diene sulfone)s by the Radical Copolymerization of 1,3-Diene Monomers with SO_2[a]

1,3-diene monomer	temp (°C)	$[SO_2]/[diene]$	time (h)	yield (%)[b]	T_{95} (°C)[c]	T_g (°C)	$M_n \times 10^{-4}$[d]	M_w/M_n
HD	−78	2.5	0.5	73.9	134	[e]	9.9	1.90
	−78	2.5	2	93.6	124	[e]	14.5	1.74
	−78	2.5	4	96.0	129	[e]	10.1	1.78
	−78	2.5	24	96.5	135	[e]	11.1	2.00
	−20	2.5	12	60.2				
	0	2.5	12	17.8				
BD	−78	1.9	2	80.4	212	[e]	[f]	[f]
	−78	1.9	8	88.8	217	[e]	[f]	[f]
	−78	1.9	24	99.9	224	[e]	[f]	[f]
	−20	1.9	12	52.4	233	[e]	[f]	[f]
IP	−78	2.5	0.5	37.0	164	94.6	[f]	[f]
	−78	2.5	2	94.1			[f]	[f]
	−78	2.5	6	94.8			[f]	[f]
	−78	2.5	24	92.9	156	93.4	[f]	[f]
	−20	2.5	12	80.1			[f]	[f]
	−20	1.7	12	64.3	136		[f]	[f]
	−20	0.83	12	24.1	147	93.1	[f]	[f]
	−20	0.42	12	28.2	136	92.3	[f]	[f]

[a] Polymerization conditions: [HD or IP] = 2.0 mol/L, [BD] = 2.6 mol/L, [*t*-BuOOH] = 20 mmol/L in toluene. [b] Based on diene monomers. [c] T_{95} is the 5% weight-loss temperature. Heating rate at 10 °C/min in a nitrogen stream. [d] Determined by GPC calibrated with standard polystyrenes. [e] Not detected below the decomposition temperature. [f] Insoluble in THF.

effectively acts as the redox initiator in combination with SO_2 even at a low temperature. For all copolymerization systems, the reaction heterogeneously proceeded because the resulting copolymers were insoluble in toluene. After the polymerization, the polymerization mixture was poured in a large amount of methanol, and the copolymer was isolated as a colorless solid after filtration and drying. The results of the copolymerization are summarized in Table 1.

The copolymerization of HD with SO_2 rapidly proceeded to reach a quantitative conversion within several hours at −78 °C because of the fast initiating reaction by a redox system. The copolymer yield decreased with an increase in the polymerization temperature, that is, 60.2 and 17.8% at −20 and 0 °C, respectively. The copolymerizations of BD and IP with SO_2 also similarly proceeded, and the copolymers were quantitatively produced during the polymerization at a low temperature. The use of an excess amount of SO_2 resulted in the formation of the copolymer in a high yield, but a decrease in the ratio led to a decrease in the yield. This is mainly due to the reduced initiating rate based on the fact that the resulting copolymers had a similar alternating repeating structure independent of the comonomer ratios in the feed, as described in the following section.

Polymer Repeating Structure. The NMR spectra of the obtained copolymers confirmed the 1,4-repeating structure as the repeating diene unit and the exclusively alternating sequences, as shown in Figure 1. The highly regulated repeating structure was independent of the comonomer ratio in the feed, the polymerization temperature, and the polymer yield. The constant repeating structures of the copolymers were also confirmed by IR spectroscopy. (See the Supporting Information). It is noted that not only HD but also BD and IP gave a highly alternating copolymer, independent of the comonomer composition in the feed, although homopropagation is possible for BD and IP. The facile formation of the alternating copolymers of the electron-donating olefin and diene monomers with SO_2 has been reported in previous studies.[2−4] The experimental results obtained in the present study agree well with the conclusion described in the literature. It was reported by Cais et al.[28] that the composition of the copolymer of chloroprene with SO_2 depended on the copolymerization conditions, such as the comonomer ratio in the feed, the monomer concentration, and the temperature. The electron-donating nature of the dienes is important for the production of the highly alternating copolymers.

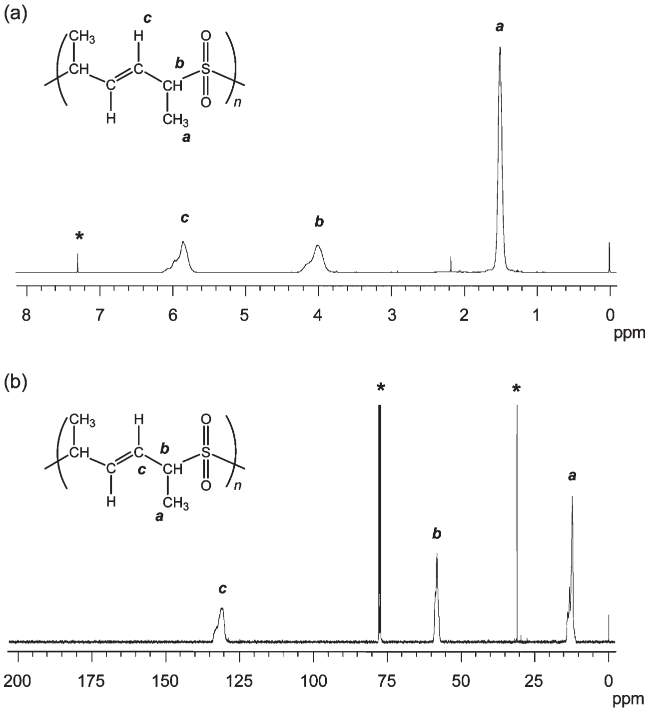


Figure 1. (a) ^1H and (b) ^{13}C NMR spectra of poly(HD-*alt*-SO_2) in $CDCl_3$ at room temperature. Copolymerization conditions: $[SO_2]/[HD]$ = 2.5 in toluene at −78 °C. An asterisk indicates the peak due to the solvent.

It is also noteworthy that the propagation of the diene monomers occurs under regiospecific control, resulting in the exclusive 1,4-repeating unit. The peaks due to the methine and vinylene hydrogens in the main chain were observed at 4.0 and 5.9 ppm, respectively, in the ^1H NMR spectrum of Figure 1. No pendant allyl group, which is produced if the 1,2-propgation occurred, was not detected in the spectrum. The ^{13}C NMR spectrum gave a similar conclusion. A high selectivity in the regiospecificity appeared only during the alternating copolymerization with SO_2, whereas atactic polymers are always produced during the homopolymerization of the diene monomers, such as BD and IP. Recently, the 1,2-regioselective polymerization was determined for the alternating copolymerization of the

Table 2. Solubility of Poly(diene sulfone)s and the Hydrogenated Poly(diene sulfone)s[a]

polymer	$CHCl_3$	CH_3NO_2	THF	acetone	DMSO	DME	DEE
poly(HD-*alt*-SO_2)	soluble	soluble	soluble	soluble	soluble	swelling	swelling
poly(BD-*alt*-SO_2)	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
poly(IP-*alt*-SO_2)	insoluble	insoluble	insoluble	insoluble	soluble	insoluble	insoluble
poly(HD-*alt*-SO_2)-H	soluble	soluble	swelling	swelling	soluble	swelling	insoluble
poly(BD-*alt*-SO_2)-H	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
poly(IP-*alt*-SO_2)-H	insoluble	insoluble	insoluble	insoluble	soluble	insoluble	insoluble

[a] THF: tetrahydrofuran, DMSO: dimethyl sulfoxide, DME: 1,2-dimethoxyethane, DEE: 1,2-diethoxyethane. The hydrogenation conversion was 98.9, 57.5, and 8.0% for poly(HD-*alt*-SO_2)-H, poly(BD-*alt*-SO_2)-H, and poly(IP-*alt*-SO_2)-H, respectively. The detailed conditions are shown in Table 4.

1,3-dienes with molecular oxygen.[46] The selectivity was accounted for by the theoretical calculations using model reactions consisting of two steps involving the addition of a methyl peroxy radical toward a 1,3-diene monomer and the reaction of the resulting allyl radical with oxygen.[47,48] The first step was mainly controlled by the difference in the heat of formation of the intermediate radicals, and the second was determined by the bond dissociation energy of a newly formed C−O bond, which is reversibly cleaved.[49] For the copolymerization of dienes with SO_2 in the present study, we cannot explain the regiospecific reaction by such a simple reaction mechanism. The steric repulsion in the propagating chain end and the contribution of depropagation are important during the copolymerization of SO_2 with a low ceiling temperature. The detailed calculations for the estimation of the heat of formation of the propagation products are now being continued to clarify the regiospecific propagation during the copolymerization of dienes with SO_2.

Solubility of Poly(diene sulfone)s. The solubility of the poly(diene sulfone)s is summarized in Table 2. Poly(HD-*alt*-SO_2) was soluble in chloroform, nitromethane, THF, acetone, and DMSO and insoluble in toluene, methanol, diethyl ether, and *n*-hexane. Poly(IP-*alt*-SO_2) was soluble in DMSO and insoluble in the other solvents, whereas poly(BD-*alt*-SO_2) was insoluble in all organic solvents. Bauer et al.[22] and Davies et al.[31,32] also reported a similar solubility of poly(BD-*alt*-SO_2). The solubility significantly depended on the structure of the used diene monomers but was independent of the polymerization conditions, such as the conversion, the polymerization time, and the polymerization temperature. This indicates that the formation of insoluble polymers is not due to the occurrence of cross-linking reactions during the copolymerization. The resulting poly(diene sulfone)s have double bonds in the main chain (Scheme 2), but they are not incorporated into the propagation because of their reduced reactivity by steric hindrance. The formation of linear polymers is also supported by the constant polydispersity values (M_w/M_n = 1.8 to 2.0) for poly(HD-*alt*-SO_2) even at a high polymer yield after a long polymerization time.

To clarify the relationship between the polymer structure and the solubility, we checked the crystallinity of the poly(diene sulfone)s by wide-angle X-ray diffraction. As a result, only broad reflections were observed at the 2θ values of 10−25° for each polymer (Figure 2). We noted that an exothermic transition appeared at 120 °C in the DTA and DSC thermograms of poly(BD-*alt*-SO_2) during the first heating. No peak was observed during the cooling and the second heating processes for the DSC measurement. When we investigated the X-ray diffraction profiles of poly(BD-*alt*-SO_2) under temperature control, the intensity of the broad diffraction increased with an increase in the temperature up to 120 °C, but no sharp diffraction was observed. This suggests a rearrangement of the poly(BD-*alt*-SO_2) chains upon heating, resulting in partial crystallization.[18] Such an annealing effect was not observed for poly(HD-*alt*-SO_2) and poly(IP-*alt*-SO_2).

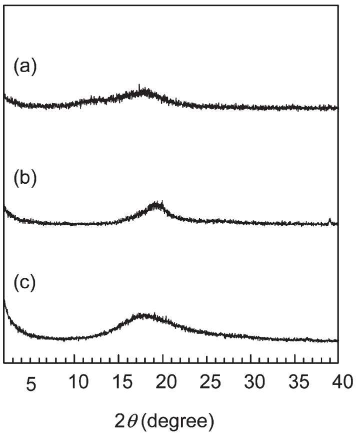


Figure 2. Wide-angle X-ray diffraction profiles of (a) poly(HD-*alt*-SO_2), (b) poly(BD-*alt*-SO_2), and (c) poly(IP-*alt*-SO_2) at room temperature.

Our hypothesis for interpreting the solubility of the poly(diene sulfone)s is as follows: the symmetry of the repeating structure of the diene unit in the polymer chain is related to the solubility. Namely, poly(BD-*alt*-SO_2) has no asymmetric carbon center in the main chain because the diene units exclusively consist of the trans-1,4 repeating structure.[18−26,31,32] Such a symmetric polymer chain structure is favored for partial crystallization, resulting in the poor solubility of poly(BD-*alt*-SO_2). Poly(HD-*alt*-SO_2) includes asymmetric centers in the main chain. The stereochemical structure is atactic. For poly(IP-*alt*-SO_2), the head-to-tail and head-to-head additions of the IP monomer to the sulfonyl radical chain end should be taken into account. The head-to-tail and head-to-head sequences are random for the poly(IP-*alt*-SO_2) because of no selectivity in the direction of the monomer addition. Poly(BD-*alt*-SO_2) has no asymmetric center and no head-to-tail structure in the main chain. This is in contrast with the more complicated repeating chain structures for poly(IP-*alt*-SO_2) involving the head-to-tail and head-to-head (tail-to-tail) structures and poly(HD-*alt*-SO_2) involving two asymmetric centers, as shown in the repeating structure of the poly(diene sulfone)s in Figure 3. Consequently, the latter two polymers are soluble in several solvents. In fact, the solubility of the polymers decreased in the order of poly(HD-*alt*-SO_2) > poly(IP-*alt*-SO_2) > poly(BD-*alt*-SO_2), agreeing well with the symmetry order of the repeating units in the polymer chain and the number and position of the methyl substituent. Davies et al. also reported a similar solubility for the poly(diene sulfone)s; that is, the solubility increased in the order of poly(1,3-hexadiene-*alt*-SO_2) > poly(2-methyl-1,3-pentadiene-*alt*-SO_2) > poly(3-methyl-1,3-pentadiene-*alt*-SO_2) > poly(1,3-pentadiene-*alt*-SO_2) > poly(IP-*alt*-SO_2) > poly(BD-*alt*-SO_2).[31,32]

Thermal Stability of Poly(diene sulfone)s. The poly(diene sulfone)s are readily degradable upon heating, similar to the poly(vinyl sulfone)s reported in the literature.[2−4] The onset temperature of decomposition (T_{init}) was ~120 °C for poly(HD-*alt*-SO_2) and poly(IP-*alt*-SO_2) and 220 °C for poly(BD-*alt*-SO_2), determined by TG/DTA analyses at the heating rate of 10 °C in a nitrogen stream. The TG, the first derivative of TG (DTG), and DTA curves obtained for each polymer are shown in Figure 4, and the determined thermal decomposition temperatures are summarized in Table 3. The decomposition occurred via two- or three-step reactions, as shown in the derivative TG curves. The higher decomposition temperature of poly(BD-*alt*-SO_2) than the others is due to the lower steric hindrance of the polymer chain. During the decomposition of the polymers, the scission of the C−S bond in the main chain first occurs below 200 °C, followed by the fast depolymerization that produces the corresponding diene monomer. We actually confirmed by NMR and IR spectroscopy analyses that one of the main decomposition products of poly(HD-*alt*-SO_2) and poly(IP-*alt*-SO_2) is the corresponding diene monomer during the initial stage of the decomposition, and the simultaneous evolution of the SO_2 gas was also observed. The more complicated polymer decomposition occurred in the temperature region over 200 °C.

Hydrogenation of Poly(diene sulfone)s. We carried out the hydrogenation of the poly(diene sulfone)s using TSH[33−35] to improve the thermal stability of the polymers. In the present study, the hydrogenation reaction was performed at a relatively low temperature below 100 °C to avoid the decomposition of the polymers during the reaction. As a result, a drastic increase in the onset temperature of decomposition was observed after the hydrogenation. For example, the T_{95} value for poly(HD-*alt*-SO_2) was 135 °C, whereas the weight loss started over 300 °C and the T_{95} value increased to 317 °C after the quantitative hydrogenation. The thermal

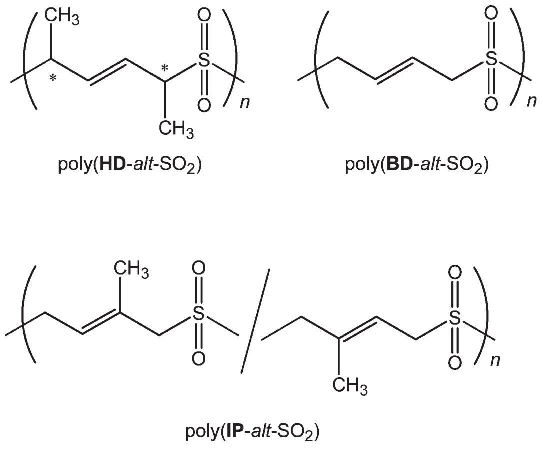


Figure 3. Stereochemical and head-to-tail structures for the repeating unit for poly(HD-*alt*-SO_2), poly(BD-*alt*-SO_2), and poly(IP-*alt*-SO_2). The exclusive 1,4-trans-polymerization occurs during all copolymerizations of these dienes with SO_2.

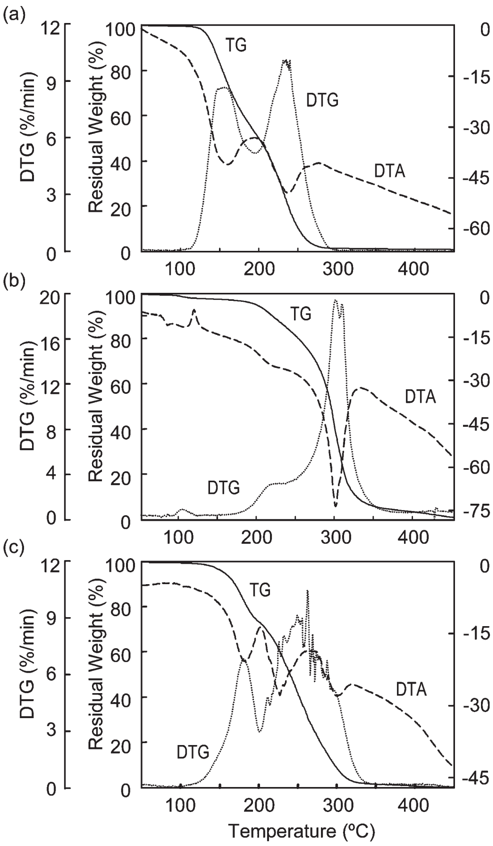


Figure 4. TG, DTG, and DTA curves for (a) poly(HD-*alt*-SO_2), (b) poly(BD-*alt*-SO_2), and (c) poly(IP-*alt*-SO_2) in a nitrogen stream at the heating rate of 10 °C/min.

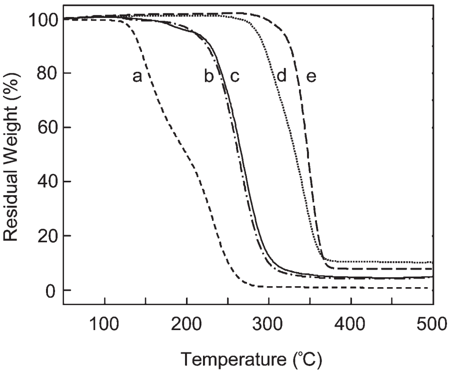


Figure 5. TG curves for the poly(HD-*alt*-SO_2) (a) before and (b−e) after the hydrogenation under various conditions. Hydrogenation conditions and conversions: (b) 60 °C, 12 h, 16.1%; (c) 60 °C, 24 h, 32.3%; (d) 80 °C, 48 h, 71.3%; and (e) 100 °C, 12 h, 98.9%. The TG curves are recorded in a nitrogen stream at the heating rate of 10 °C/min.

Table 3. Thermal Properties of Poly(diene sulfone)s and the Hydrogenated Poly(diene sulfone)s Determined by TGA/DTA at the Heating Rate at 10 °C/min in a Nitrogen Stream[a]

	DTA		TGA				
polymer	T_{init} (°C)	T_{max} (°C)	T_{init} (°C)	T_{max} (°C)	T_{95} (°C)	T_{50} (°C)	residual weight at 450 °C (%)
poly(HD-*alt*-SO_2)	120	161, 237	122	157, 235	135	200	5.0
poly(BD-*alt*-SO_2)	226	248, 295	220	249, 290, 307	233	276	7.6
poly(IP-*alt*-SO_2)	154	183, 227, 300	143	181, 263	156	240	0.4
poly(HD-*alt*-SO_2)-H	321	351	312	351	317	348	7.9
poly(BD-*alt*-SO_2)-H	235	263, 300, 428	229	263, 323, 428	291	393	8.6
poly(IP-*alt*-SO_2)-H	154	171, 283	156	169, 283	206	284	3.1

[a] Hydrogenation was carried out at 100 °C. The hydrogenation conversion was 98.9, 57.5, and 8.0% for poly(HD-*alt*-SO_2)-H, poly(BD-*alt*-SO_2)-H, and poly(IP-*alt*-SO_2)-H, respectively. The detailed conditions are shown in Table 4.

decomposition parameters for the poly(alkylene sulfone)s [poly(diene sulfone)-H] obtained by the hydrogenation of the poly(diene sulfone)s are summarized in Table 3. A drastic increase in the thermal stability of the poly(diene sulfone)s by the hydrogenation is evidence of the occurring 1,4-regioselective propagation of the diene monomers during the copolymerization because an increase in the thermal stability is expected for only the hydrogenation of the 1,4-polymers but not for the 1,2-polymers. The solubility of the poly(diene sulfone)-H slightly decreased compared with the precursor poly(diene sulfone), as shown in Table 2. The poly(diene sulfone)-H was amorphous.

As shown in Figure 5, the decomposition of poly(HD-*alt*-SO_2) occurred in one step after hydrogenation because no depolymerization occurred for the poly(diene sulfone)-H. The decomposition temperature sensitively depended on the hydrogenation conversion, as shown by the TG curves in Figure 5. The conversion was determined on the basis of a decrease in the intensity of the peak because of the double bond of the polymers (Figure 6). For the other poly(diene sulfone)s, the hydrogenation conversion was lower than that for the reaction of poly(HD-*alt*-SO_2) (Table 4) because of the higher crystallinity of poly(BD-*alt*-SO_2) and the steric hindrance of the substituent on the double bond of poly(IP-*alt*-SO_2). A slight increase in the onset temperature of the decomposition was observed for poly(BD-*alt*-SO_2) and poly(IP-*alt*-SO_2). A higher thermal stability will be expected if the hydrogenation proceeds in a quantitative manner. Therefore, the good solubility of poly(HD-*alt*-SO_2) is advantageous for the polymer reaction to obtain thermally stable polysulfones by hydrogenation.

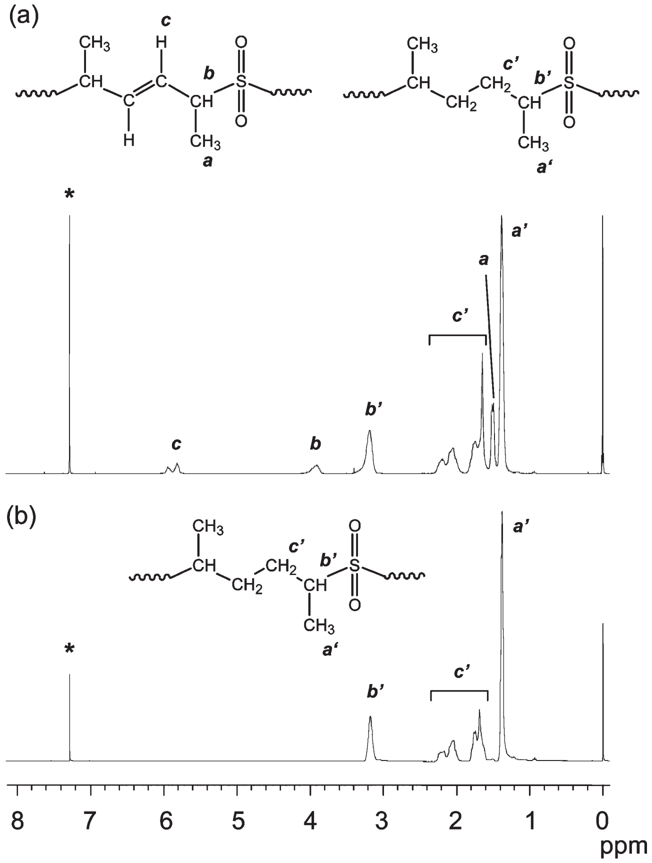


Figure 6. ^1H NMR spectra of poly(HD-*alt*-SO_2) after the hydrogenation under various conditions. Hydrogenation conditions: (a) 80 °C, 48 h, conversion 71.3% and (b) 100 °C, 12 h, conversion 98.9%. The NMR spectra were measured in $CDCl_3$ at room temperature. An asterisk indicates the peak due to the solvent.

On the basis of the results of the DSC analysis, the T_g value was determined to be 94 °C for poly(IP-*alt*-SO_2), whereas poly(HD-*alt*-SO_2) showed no T_g below the decomposition temperature. The poly(IP-*alt*-SO_2)-H (8% conversion) and poly(HD-*alt*-SO_2)-H (99% conversion) obtained after the hydrogenation showed a T_g at 82 and 84 °C, respectively. This suggests that the complete hydrogenation of poly(HD-*alt*-SO_2) decreased the T_g value by at least 20−30 °C because of an increase in the mobility and flexibility of the main chain segment. In contrast, the hydrogenation of the unsaturated groups in the polymer chain often results in an increase in the T_g values of the crystalline polymers in the literature.[39,40,50] The decrease in the T_g values of the poly(diene sulfone)s by the hydrogenation is supposed to be due to a decrease in the partial crystallinity. Transparent and brittle films were obtained by casting the poly(HD-*alt*-SO_2) and poly(HD-*alt*-SO_2)-H solutions, being different from the insoluble poly(BD-*alt*-SO_2) and poly(BD-*alt*-SO_2)-H. The further investigation of the physical properties of the poly(diene sulfone)s and the hydrogenated polymers including those obtained from various kinds of 1,3-diene monomers are now in progress.

Conclusions

In the present study, we synthesized a new type of thermally stable polysulfone by the alternating copolymerization of 1,3-diene monomers with SO_2 and the subsequent hydrogenation of the polymer. It was revealed that the resulting poly(diene-*alt*-SO_2)s consist of a highly controlled alternating and 1,4-regiospecific repeating structure. The solubility and crystallization properties of the copolymers depended on the regularity of the repeating structure. Whereas the poly(diene-*alt*-SO_2)s readily degraded upon heating, the thermal stability of the poly(diene-*alt*-SO_2)s was modified by hydrogenation of the double bond in the polymer main chain. In particular, the hydrogenation of poly(HD-*alt*-SO_2) resulted in a drastic increase in the 5% weight-loss temperature from 135 to 317 °C during the TG analysis. We are now continuing the study of the synthesis of thermally stable

Table 4. Synthesis and Characterization of the Hydrogenated Poly(diene sulfone)s[a]

polymer	temp (°C)	time (h)	conv (%)	T_{95} (°C)	T_{50} (°C)	T_g (°C)
poly(HD-*alt*-SO_2)			0	135	200	$> T_{init}$[b]
	60	12	16.1	208	263	
	60	24	32.3	209	267	
	80	48	71.3	286	333	
	100	12	98.9	317	348	83.8
poly(BD-*alt*-SO_2)			0	233	276	
	100	12	57.5[c]	291	393	
poly(IP-*alt*-SO_2)			0	156	240	93.4
	100	36	8.0	206	284	82.3

[a] Hydrogenation conditions: poly(diene sulfone) (0.2 g), TSH (13 equiv), 1,2-diethoxyethane (10 mL) under a nitrogen stream. The conversion was determined by ^1H NMR spectroscopy. [b] Not detected below the decomposition temperature. [c] Determined by IR spectroscopy.

polysulfones using various 1,3-diene monomers as well as the structure analysis and polymer properties to develop further new types of polysulfones with excellent thermal, mechanical, and optical properties. The details of the synthesis and characterization of various poly(diene sulfone)s will be reported in the future.

Supporting Information Available: NMR and IR spectra, DSC traces, and wide-angle X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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