Molecular Design of Diene Monomers Containing an Ester Functional Group for the Synthesis of Poly(diene sulfone)s by Radical Alternating Copolymerization with Sulfur Dioxide

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ABSTRACT: Functional poly(diene sulfone)s are prepared by the radical alternating copolymerization of 1,3-diene monomers containing an ester substituent with sulfur dioxide. Methyl 3,5-hexadienoate (MH) and methyl 5,7-octadienoate (MO) with both an alkylene spacer and a terminal diene structure are suitable to produce a high-molecular-weight copolymer in a high yield, while the copolymerization of 5,7-nonadienoic acid, ethyl 2,4-pentadienoate, and ethyl 4-methyl-2,4-pentadienoate including either an alkylene spacer or a terminal diene structure lead to unsuccessful results. The ^{13}C NMR chemical shift values of MH and MO suggest a high electron density at their reacting α-carbon for exhibiting a high copolymerization reactivity. Fluorene-containing diene monomers, 9-fluorenyl 3,5-hexadienoate (FH) and 9-fluorenyl 5,7-octadienoate (FO), are also prepared and copolymerized with sulfur dioxide. The thermal and optical properties of the poly(diene sulfone)s containing the methyl and fluorenyl ester substituents in the side chain are investigated. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *00*, 000–000

KEYWORDS: alternating copolymer; high performance polymers; radical polymerization; refractive index; transparency

INTRODUCTION Recent optoelectronic applications have demanded high-performance polymers with excellent thermal stability as well as optical, electronic, and other physical properties.[1–6] Aromatic polysulfones are synthesized by condensation polymerization and used as the engineering plastics for the mechanical and electric parts of machines, separation membranes, and also optical materials, such as lenses and films, due to their excellent thermal and mechanical properties.[7] In contrast, poly(olefin sulfone)s[8,9] and poly(diene sulfone)s[10–13] are synthesized by the radical alternating copolymerization of olefin and diene monomers with sulfur dioxide (SO_2) and they are used as the degradable polymers, such as resist materials for electron-beam and X-ray radiation lithography. The resulting poly(diene sulfone)s are also expected to be used as optical materials due to their high transparency, good film processability, and excellent thermal stability after hydrogenation.[11–13] We started on the investigation of the copolymerization of diene monomers containing an ester moiety with SO_2 because the introduction of a functional group in the side chain of poly(diene sulfone)s can modify the physical properties of the copolymers. The copolymerization using commercially available methyl sorbate (MS) as the first trial test resulted in the production of the corresponding poly(diene sulfone) in only a low yield. In this study, therefore, functional diene monomers shown in Figure 1 were newly synthesized and copolymerized with SO_2. As a result, we revealed that methyl 3,5-hexadienoate (MH) and methyl 5,7-octadienoate (MO) with both an alkylene spacer and a terminal diene structure were suitable to produce a high-molecular-weight copolymer in a high yield, while the copolymerization of 5,7-nonadienoic acid (NA), ethyl 2,4-pentadienoate (EP), and ethyl 4-methyl-2,4-pentadienoate (EMP) including either an alkylene spacer or a terminal diene structure led to unsuccessful results. The thermal and optical properties of poly(diene sulfone)s containing the methyl and fluorenyl ester substituents in the side chain were investigated.

EXPERIMENTAL

General Procedures

The NMR spectra were recorded in $CDCl_3$ using Bruker AV300N and AV600 and JEOL JNM-A400 spectrometers. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (M_w/M_n) were

Additional Supporting Information may be found in the online version of this article.

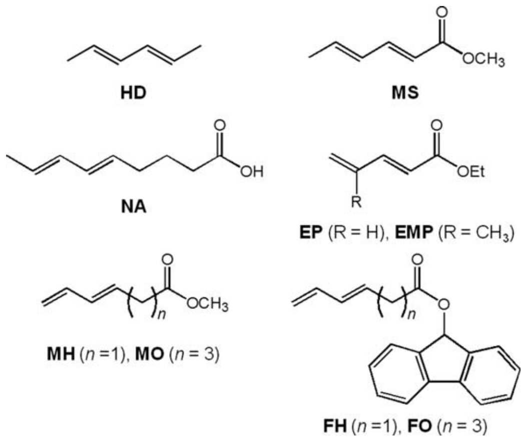


FIGURE 1 Chemical structures of 1,3-diene monomers used in this study. MS, EP, EMP, MH, and FH were used as the pure (*E*)-isomer. HD, NA, MO, and FO were used as the mixture of (*E*)- and (*Z*)-isomers. All the monomers are shown as the isomers with an (*E*)-configuration for simplification. See the experimental section and Table 1 for the detailed isomeric structures.

determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF) or chloroform using a Tosoh 8020 series and calibration with standard polystyrenes. The thermogravimetric and differential thermal analyses (TG/DTA) were carried out using a Seiko TG/DTA 6200 in a nitrogen stream (200 mL/min) at the heating rate of 10 °C/min in the temperature range of 30−500 °C. The onset temperature of decomposition was evaluated as the 5% weight-loss temperature (T_{d5}) in the TG analysis. The maximum temperature of decomposition (T_{max}) was determined using the derivatives of the TG curves. Differential scanning calorimetry (DSC) was carried out using a Seiko DSC-6200 in a nitrogen stream at the heating rate of 10 °C/min to determine the glass transition temperature (T_g). The UV-Vis spectra were recorded using a JASCO V-550 spectrophotometer. The polymer films were prepared by casting of the 5 wt % chloroform solution and drying at 20 °C overnight, then further dried under reduced pressure at room temperature. The refractive indices (n_F, n_D, and n_C) were measured at the wavelengths of 486, 589, and 656 nm, respectively, using an Abbe-type Atago DR-M2 refractometer with a zinc dichloride aqueous saturated solution and a halogen lamp. The average value of five measurements was typically recorded. The Abbe number (ν_D) was calculated as follows: $\nu_D = (n_D - 1)/(n_F - n_C)$.

Materials

Commercially available methyl sorbate (MS, Tokyo Chemical Industry Co., Ltd., Tokyo) and monoethyl malonate (90%, Sigma-Aldrich Japan Co., Tokyo) were distilled under reduced pressure before use. Diisopropylamine was purchased from Wako Pure Chemicals Co., Ltd., Osaka, and distilled before use. (4-Carboxybutyl)triphenylphosphonium bromide, sodium hydride, 4-dimethylaminopyridine (DMAP), and pyridine were purchased from Wako Pure Chemicals Co., Ltd., Osaka, and used as received. 2,4-Hexadiene (HD, >95%), crotonaldehyde (98%), acrolein (90%), δ-valerolactone (98%), pyridinium chlorochromate (PCC, 98%), allyltriphenylphosphonium bromide (98%), 9-fluorenol, and tetraethyl orthotitanate were purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, and used as received. Anhydrous dimethyl sulfoxide (DMSO) and *n*-butyllithium (1.6 mol/L in *n*-hexane) were purchased from Kanto Chemical Co., Inc., Tokyo, and used as received. Methacrolein (95%), *tert*-butylhydroperoxide (tBuOOH), and hexamethylphosphoramide were purchased from Sigma-Aldrich Japan Co., Tokyo, and used as received. The solvents were distilled before use. Sulfur dioxide was purchased from Sumitomo Seika Chemicals Co., Ltd., and distilled and collected at −196 °C using liquid nitrogen.

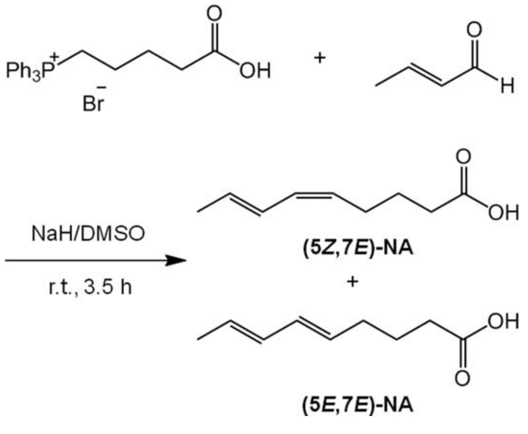
The synthetic procedures of the diene monomers used in this study are described below. The spectral data are shown in Supporting Information.

Synthesis of 5,7-Nonadienoic Acid (NA)

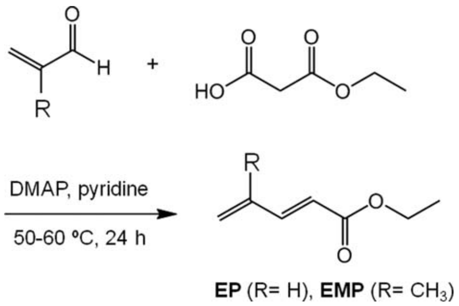
Sodium hydride (1.10 g, 0.046 mol) was slowly added with vigorous stirring to anhydrous DMSO (40 mL) maintained at 75 °C, then the (4-carboxybutyl)triphenylphosphonium bromide (13.3 g, 0.030 mol) in anhydrous DMSO (60 mL) was dropwise added at 25 °C (Scheme 1). After stirring for 20 min, crotonaldehyde (2.1 g, 0.030 mol) in anhydrous DMSO (5 mL) was dropwise added. After further stirring for 2.5 h at room temperature, the mixture was poured into diethyl ether. The pH of the solution was kept at 3.0 using aq. sodium hydrogen sulfate (2.0 mol/L) and then the oil phase was extracted with diethyl ether, and dried over anhydrous sodium sulfate. The crude product was purified by silica gel chromatography using diethyl ether and ethyl acetate (6/5 volume ratio) and distilled under reduced pressure (140 °C/0.5 mmHg). Yield: 13.8%; colorless liquid.

Synthesis of Ethyl 2,4-Pentadienoate (EP) and Ethyl 4-Methyl-2,4-pentadienoate (EMP)

EP and EMP were synthesized by the following reaction procedures.[14] For the synthesis of EP, acrolein (0.56 g, 0.010 mol) and DMAP (0.092 g, 0. 75 mmol) were added to monomethyl malonate (1.98 g, 0.015 mol) in pyridine (5 mL), and the mixture was stirred at 50−60 °C for 24 h (Scheme 2).



SCHEME 1 Synthesis of 5,7-nonadienoic acid (NA).



SCHEME 2 Synthesis of ethyl 2,4-pentadienoate (EP) and ethyl 4-methyl-2,4-pentadienoate (EMP).

The mixture was then poured into water (20 mL) and the product was extracted with diethyl ether (10 mL, three times). The solution was washed with 15% aq. hydrochloric acid (15 mL, three times) and saturated aq. sodium bicarbonate, then dried over anhydrous sodium sulfate. The EP as the product was isolated by distillation under reduced pressure (30 °C/1.0 mmHg). EMP was similarly synthesized using methacyrolein.

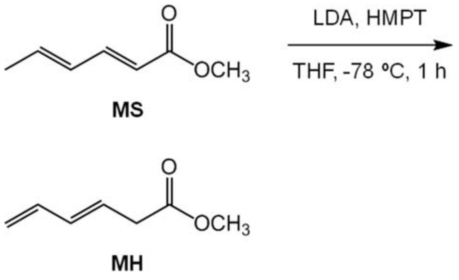
Synthesis of Methyl 3,5-Hexadienoate (MH)

To fresh diisopropylamine (2.45 g, 24 mmol) and distilled THF (40 mL) in a degassed Schlenk flask, *n*-BuLi in *n*-hexane (1.6 mol/L, 15 mL, 24 mmol) was slowly added at −78 °C (Scheme 3). The temperature of the solution was raised to 0 °C for 15 min, cooled to −78 °C, then several drops of HMPT were added and stirred for 30 min. To this solution, MS (2.53 g, 20 mmol) was slowly added over 2 h at −78 °C, and further stirred for 1 h. The mixture was poured into aq. acetic acid cooled at 0 °C, the product extracted with *n*-hexane, washed with water, then distilled under reduced pressure.

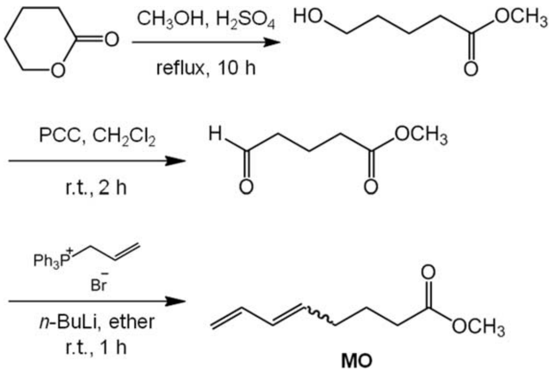
Synthesis of Methyl 5-Hydroxypentanoate

To δ-valerolactone (4.03 g, 40 mmol) and methanol (6 mL) in a flask equipped with a condenser, concentrated sulfonic acid (0.07 mL, 1.31 mmol) was dropwise added with stirring at room temperature (Scheme 4).[15] After reflux for 10 h, sodium
S4 hydrogen carbonate (0.04 g) was added at 0 °C. Silica gel chromatography provided methyl 5-hydroxypentanoate as a colorless liquid.

Yield: 55%. ^{1}H NMR (300 MHz, $CDCl_3$ δ, ppm): 3.68 (*s*, OCH_3, 3H), 3.67−3.62 (*t*, CH_2OH, 2H), 2.39−2.34 (*t*, $CH_2C(=O)O$, 2H), 1.75−1.57 (*m*, CH_2CH_2, 4H).



SCHEME 3 Synthesis of methyl 3,5-hexadienoate (MH).



SCHEME 4 Synthesis of methyl 5-hydroxypentanoate.[15] Synthesis of methyl 5-oxopentanoate.[16] Synthesis of methyl 5,7-octadienoate (MO).[17]

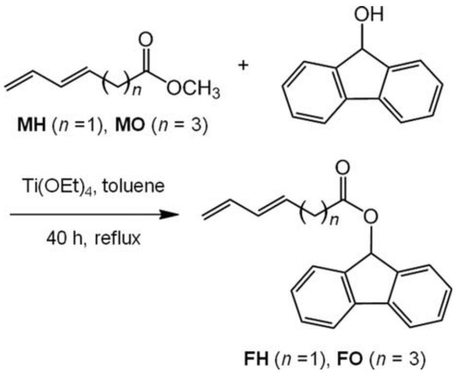
Synthesis of Methyl 5-Oxopentanoate

To pyridinium chlorochromate (PCC, 6.1 g, 28 mmol) and distilled dichloromethane (11 mL), methyl 5-hydroxypentanoate (2.5 g, 19 mmol) in dichloromethane (11 mL) was dropwise added at room temperature with vigorous stirring (Scheme 4).[16] S4
The filtrate was concentrated and passed through a silica gel column to isolate the methyl 5-oxopentanoate as a liquid.

Yield: 44%. ^{1}H NMR (300 MHz, $CDCl_3$ δ, ppm): 9.78 (*s*, CH_2CHO, 1H), 3.68 (*s*, OCH_3, 3H), 2.57−2.52 (*t*, $CH_2C(=O)O$, 2H), 2.39−2.36 (*t*, CH_2CHO, 2H), 1.98−1.94 (*m*, $CH_2CH_2CH_2$, 2H).

Synthesis of Methyl 5,7-Octadienoate (MO)

To allyltriphenylphosphonium bromide (5.0 g, 13mmol) in diethyl ether (70 mL), *n*-BuLi in *n*-hexane (1.6 mol/L, 8.2 mL, 13 mmol) was slowly added at 0−5 °C, and further
stirred for 1 h (Scheme 4).[17] To this solution, methyl S4
5-oxopentanoate (1.54 g, 11.8 mmol) in diethyl ether (15 mL) was dropwise added, and stirred for 1 h at room temperature. The mixture was washed with water and the product was extracted with diethyl ether. MO was purified by silica gel column chromatography and distillation under reduced pressure. The MO was obtained as the mixture of the (5*E*,7*E*) and (5*Z*,7*E*)-isomers, (5*E*,7*E*)/(5*Z*,7*E*) = 4/3.



SCHEME 5 Synthesis of 9-fluorenyl 3,5-hexadienoate (FH) and 9-fluorenyl 5,7-octadienoate (FO).

TABLE 1 Results of Copolymerization of Diene Monomers with Sulfur Dioxide and ^{13}C NMR Chemical Shifts for the Diene Moieties[a]

Diene Monomer	[Diene] (mol/L)	Copolymer Yield (%)	$M_n/10^4$	M_w/M_n	^{13}C NMR Chemical Shift in $CDCl_3$ (ppm, 10 vol %)				
					Isomer	α	β	γ	δ
MS	2	1.0	[b]	[b]	2*E*,4*E*	139.4	129.7	145.1	118.5
NA[c]	2	2.5	0.13[d]	1.4[d]	5*E*,7*E*	129.8	126.7	129.8	127.8
					5*Z*,7*E*	127.5	131.4	131.5	130.1
EP	Bulk[e]	0.3	0.29[d]	2.3[d]	3*E*	125.6	134.9	134.9	122.4
EMP	Bulk[e]	5.8	0.94[d]	2.1[d]	3*E*	124.4	140.7	147.1	118.9
MH	Bulk[e]	25.5	4.7	2.2	5*E*,7*E*	117.2	136.4	134.5	125.6
MO[c]	Bulk[e]	61.6	[b]	[b]	5*E*,7*E*	115.4	137.1	132.0	133.9
					5*Z*,7*E*	117.5	132.1	130.4	131.3
FH	0.5	47.1	3.5	2.1	5*E*,7*E*	117.3	136.4	134.8	125.4
FO[c]	0.3	77.7	4.5	2.2	5*E*,7*E*	115.5	137.1	132.1	133.8
					5*Z*,7*E*	117.6	132.1	130.5	131.2
FH/HD-3/1[f]	2	59.1(65.8)[g]	2.4	3.1					
FH/HD-1/1[f]	2	79.9(37.7)[g]	3.2	2.7					
FH/HD-1/3[f]	2	74.4(21.1)[g]	4.7	2.5					

[a] Copolymerization conditions: $[SO_2] = 5$ mol/L, $[tBuOOH] = 0.02$ mol/L in toluene at −78 °C for 24 h. The copolymer yield was determined on the basis of the amount of the charged diene monomers. M_n and M_w/M_n values were determined by SEC in chloroform.

[b] Not determined.

[c] For the polymerization of a mixture of isomers.

[d] Determined by SEC in tetrahydrofuran.

[e] $[diene]/[SO_2]/[tBuOOH] = 100/250/1$.

[f] Molar ratio of FH to HD in the feed.

[g] Molar fraction of the FH units in the copolymer.

Synthesis of 9-Fluorenyl 3,5-Hexadienoate (FH) and 9-Fluorenyl 5,7-Octadienoate (FO)

For the synthesis of FH, to 0.65 g of MH and 3.45 g of 9-fluorenol in 25 mL of distilled toluene in a 100-mL flask equipped with a condenser, 0.11 g of $Ti(OEt)_4$ as the catalyst was added and refluxed for 40 h (Scheme 5).[18] After the toluene was removed under reduced pressure, the residue was purified by silica gel chromatography with hexane/ethyl acetate = 10/1 in volume ($R_f = 0.6$). Pale yellow solid. Yield: 82.0%.

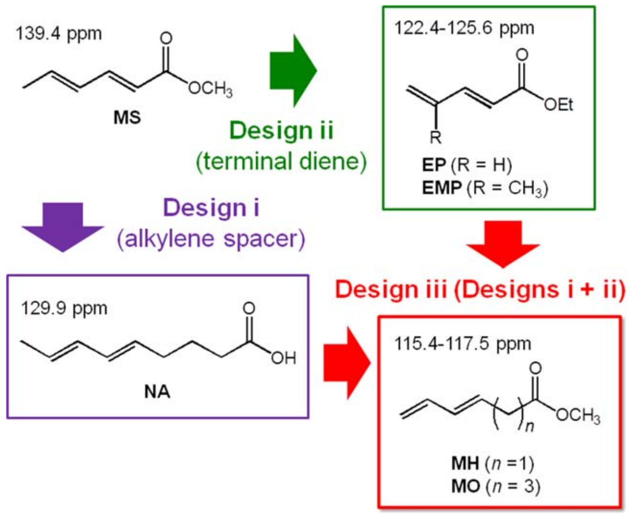


FIGURE 2 Design of diene monomers appropriate for alternating copolymerization with sulfur dioxide. The values indicate the ^{13}C NMR chemical shifts for the α-carbon of diene moieties. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Similarly, FO was synthesized from MO (0.5 g) and purified by silica gel chromatography ($R_f = 0.7-0.8$). The pale yellow solid was isolated as the isomeric mixture [(5*E*,7*E*)-FO/(5*Z*,7*E*)-FO = 4/3]. Yield: 78.3%.

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 ampoule. The solution was degassed by the freeze-thaw technique. This cycle was repeated three times, then SO_2 (2.0 mL, 50 mmol) was added by vacuum distillation, and finally the ampule was sealed. After polymerization for a given time at −78 °C, the polymerization mixture was poured into 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. The soluble poly(diene sulfone)s were purified by repeated reprecipitation using chloroform or dimethyl sulfoxide as the solvent and methanol as the precipitant. The spectral data of the poly(diene sulfone)s are shown in supporting information.

Hydrogenation

The poly(diene sulfone)s (0.05 g) and *p*-toluene sulfonyl hydrazide (15 eq) were stirred in diethylene glycol dimethyl

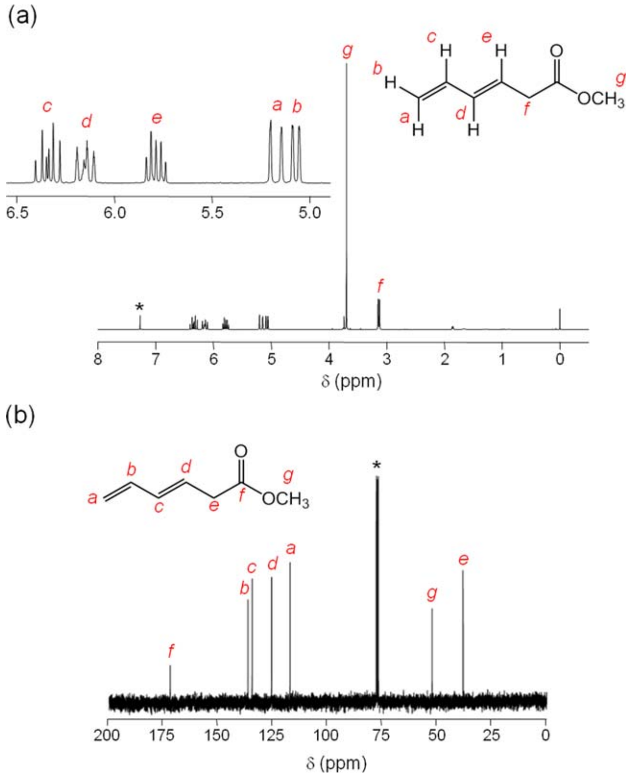


FIGURE 3 (a) ^1H and (b) ^{13}C NMR spectra of MH in $CDCl_3$. An asterisk indicates the peak due to the solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ether (5 mL) at 120 °C under a nitrogen atmosphere. After the reaction, the reaction mixture was poured into 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 ^1H NMR spectroscopy. The conversion was 68–82% during the reaction for 12 h. The spectral data of the hydrogenated poly-(diene sulfone)s are shown in Supporting Information.

RESULTS AND DISCUSSION

We investigated the copolymerization reactivity of MS as the commercially available diene monomer containing an ester group as the preliminary test. The radical copolymerization of MS with SO_2 was carried out in toluene at −78 °C in the presence of tBuOOH as the oxidative agent of a redox initiator system (functioning with SO_2 as the reducing agent) under conditions similar to those for the copolymerization of hydrocarbon diene monomers containing no functional group reported in previous reports.[11] As a result, a copolymer was produced in only a low yield (1.0%), as shown in Table 1. Several reasons were possible for interpreting the low copolymerization reactivity of MS; one was a decrease in the electron density on the diene moiety of the MS monomer and on the carbon of the corresponding propagating MS radical due to the introduction of an electron-withdrawing functional group. The other was a low ceiling temperature for this polymerization.[13,19] For example, the ceiling temperature for the copolymerization of 2,4-hexadiene (HD) and SO_2 was 42 °C for the copolymerization conditions of $[HD] = 2.0$ mol/L and $[SO_2] = 5.0$ mol/L.[13] It was previously concluded that the low ceiling temperature of HD during the copolymerization with SO_2 was due to a small enthalpy change for the copolymerization. Any side reaction of a polar functional group may suppress the copolymer formation with a high molecular weight during the copolymerization, but it was negligible because the radical polymerization implies tolerance to the polar and functional side groups of the monomers and polymers.

In fact, the ^{13}C NMR chemical shift was determined to be high as 139.4 ppm for the α-carbon of the diene moiety of MS, being much higher than those reported for the hydrocarbon diene monomers with high copolymerization reactivities (124–128 ppm for the HDs and 110–117 ppm for the other monomers, see Supporting Information Table S1). This suggested a low electron density on the reacting carbon of MS, which was disadvantageous for the addition of an electron-

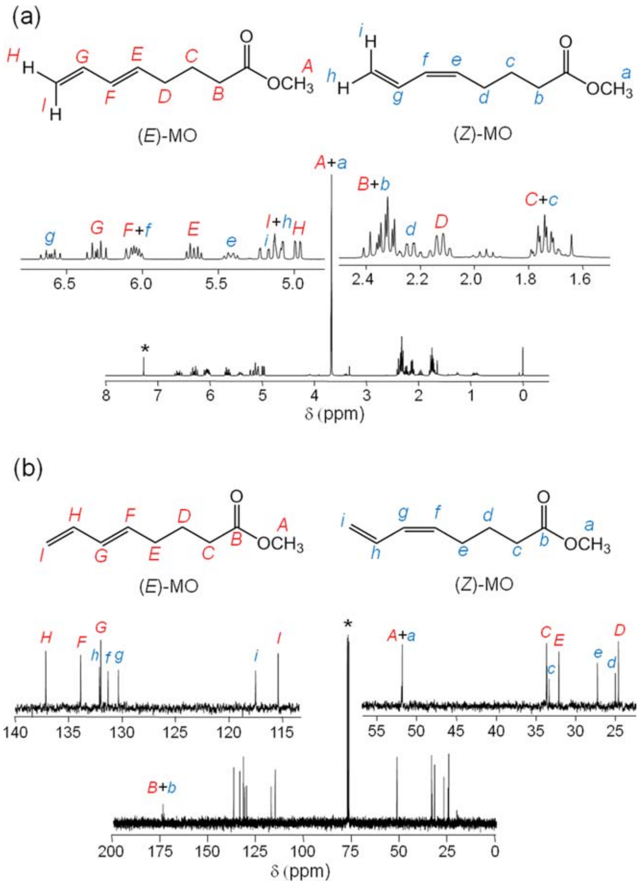
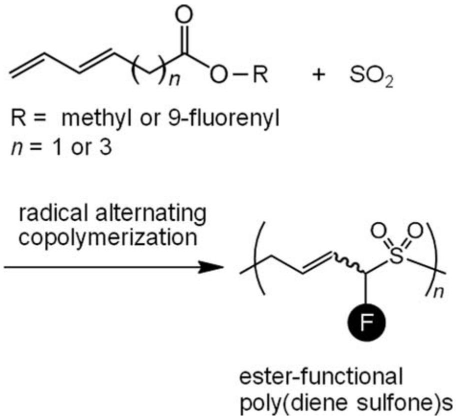


FIGURE 4 (a) ^1H and (b) ^{13}C NMR spectra of MO in $CDCl_3$. An asterisk indicates the peak due to the solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 6 Synthesis of functional poly(diene sulfones) by the radical alternating copolymerization of diene monomers containing an ester group.

deficient sulfonyl radical during the copolymerization. The linear relationship between the ^{13}C NMR chemical shift values and the *e* values of various vinyl monomers was previously reported and their reactivity during polymerization was discussed in the literature.[20] The electron-donating characteristic of diene monomers is required for the successful process of the radical alternating copolymerization with SO_2. At the same time, steric hindrance between a propagating radical and an attacking monomer during the cross-propagation reactions must be avoided in a strategy for the design of diene monomers used for the copolymerization system.

The chemical structures of diene monomers appropriate for the copolymerization with SO_2 was designed according to the following two approaches for decreasing in the steric repulsion and increasing in the electron density on a diene moiety; (i) the introduction of an alkyl spacer between the dienyl and ester groups, and (ii) a change in the internal diene structure to the terminal one (Fig. 2). NA with an alkyl spacer and EP and EMP with a terminal diene moiety were first synthesized by the reactions shown in Schemes 1 and 2, respectively. NA was obtained as the mixture of the (5*E*,7*Z*)- and (5*E*,7*E*)-isomers due to no regioselectivity of the Wittig reaction for the synthesis[21] (see Figs. S1 and S2 in Supporting Information for the NMR spectra of NA). EP and EMP were isolated as pure (3*E*)-isomers[14] in this study (see Figs. S3 to S6 in Supporting Information).

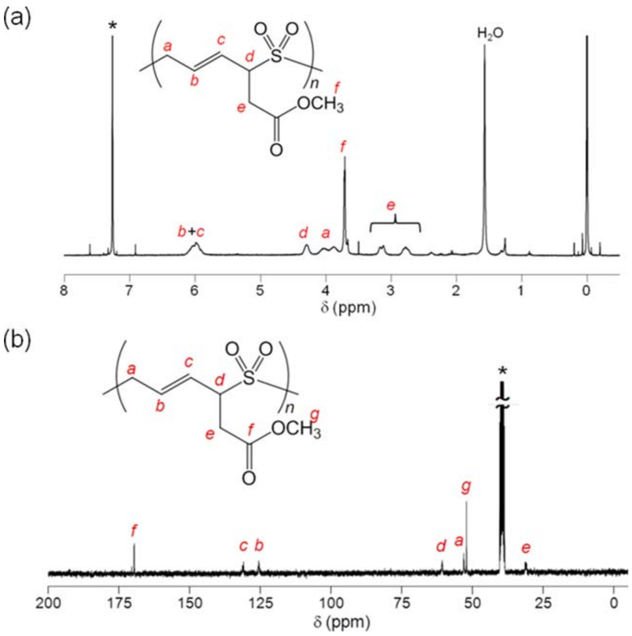


FIGURE 5 (a) ^{1}H and (b) ^{13}C NMR spectra of poly(MH-*alt*-SO_2) in $CDCl_3$ and DMSO-d_6, respectively. An asterisk indicates the peak due to the solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

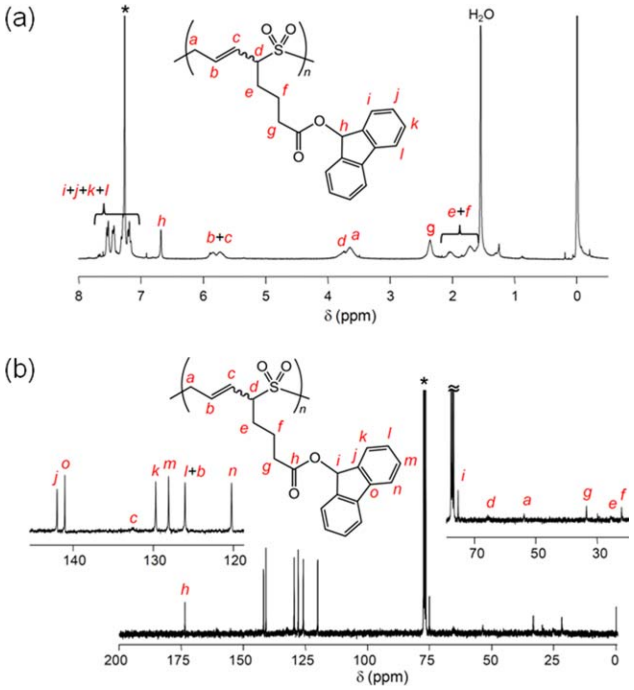


FIGURE 6 (a) ^{1}H and (b) ^{13}C NMR spectra of poly(FO-*alt*-SO_2) in $CDCl_3$. An asterisk indicates the peak due to the solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

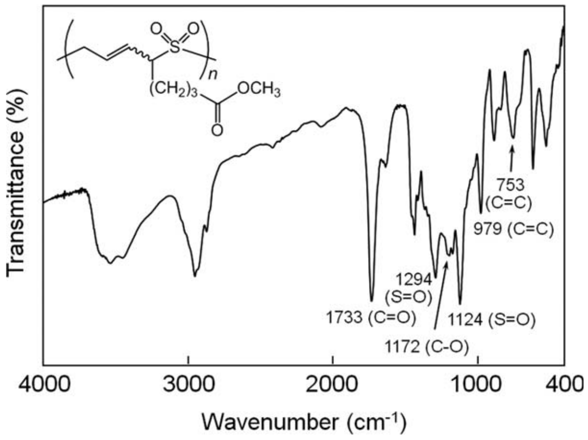
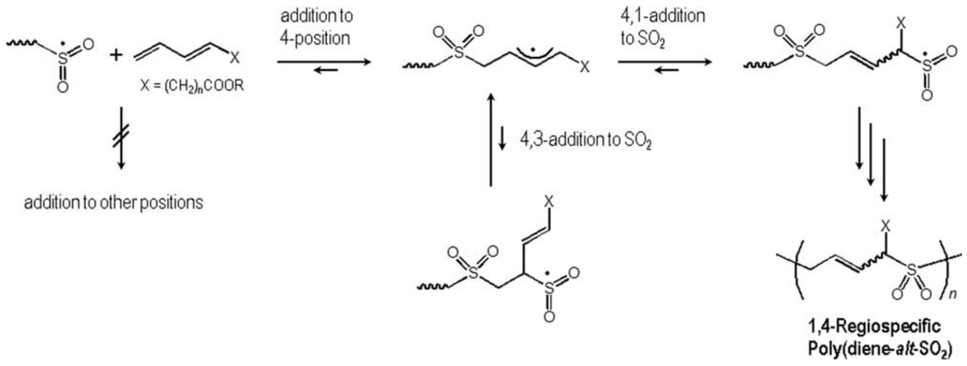


FIGURE 7 IR spectrum of poly(MO-*alt*-SO_2).



SCHEME 7 Reaction mechanism for 1,4-regiospecific propagation during the radical alternating copolymerization of diene monomers with sulfur dioxide.

The results of the copolymerization are shown in Table 1. The ^{1}H NMR and IR spectra of the products confirmed the formation of the copolymers of the diene monomers with SO_2, as shown in Figures S10 and S11 in Supporting Information. However, the copolymer yield of 0.3–5.8% was still low, while the chemical shift values were shifted to 124–130 ppm. Therefore, we further modified the diene monomer structure. Consequently, MH and MO were synthesized according to design iii, in which both key structures were introduced as the monomer design. The synthetic pathways are shown in Schemes 3 and 4. As a result, MH was obtained as the single (3*E*)-isomer, and MO as the mixture of the (5*E*,7*Z*)- and (5*E*,7*E*)-isomers. The ^{1}H and ^{13}C NMR spectra of MH and MO are shown in Figures 3 and 4, respectively (see also Supporting Information Fig. S7).

The copolymerization of these newly synthesized monomers provided the alternating copolymers with SO_2 in high yield, as shown in Scheme 6. The copolymers were produced in 25.5 and 61.6% yield during the copolymerization of MH and MO with SO_2 (Table 1). We further prepared the fluorene-containing monomers, FH and FO, by the transesterification of MH and MO with 9-fluorenol in the presence of the $Ti(OEt)_4$ catalyst[18] (Scheme 5). The fluorene-containing monomers also provided the corresponding copolymers in a high yield, as shown in Table 1. The ^{1}H and ^{13}C NMR and IR spectra of the produced copolymers are shown in Figures 5 to 7 (see also Supporting Information Figs. S12 and S13). The MO and FO monomers with a trimethylene spacer resulted in the copolymer production with higher yields rather than those for the MH and FH with a short methylene spacer. This was due to the avoidance of steric hindrance by the long alkyl spacer between the dienyl and ester moieties.

The M_n values of the copolymers were 3.5 to 4.7 × 10^4, similar to those of the copolymers with HD and other previously reported hydrocarbon diene monomers.[11] The NMR and IR spectra confirmed the formation of the alternating copolymers under highly regioselective control of the diene repeating structure; i.e., the 1,4-repeating structure was predominantly produced (Figs. 5–7, see also Supporting Information).[11–13] Scheme 7 shows a reaction mechanism of the radical alternating copolymerization of diene monomers with SO_2 to produce a highly regioselective 1,4-diene

TABLE 2 Solubility of Poly(diene sulfone)s with Ester Side Groups[a]

Polymer	TFA	DMSO	$CHCl_3$	Acetone	THF	DGDE
Poly(MH-*alt*-SO_2)	Insoluble	Soluble	Soluble	Insoluble	Insoluble	Insoluble
Poly(MO-*alt*-SO_2)	Soluble	Soluble	Soluble	Soluble	Swelling	Soluble
Poly(FH-*alt*-SO_2)	Insoluble	Soluble	Soluble	Swelling	Swelling	Soluble
Poly(FO-*alt*-SO_2)	Insoluble	Soluble	Soluble	Soluble	Soluble	Soluble
Poly(FH/HD-*alt*-SO_2)−66	Insoluble	Soluble	Soluble	Swelling	Soluble	Soluble
Poly(FH/HD-*alt*-SO_2)−38	Insoluble	Soluble	Soluble	Swelling	Soluble	Soluble
Poly(FH/HD-*alt*-SO_2)−21	Soluble	Soluble	Soluble	Soluble	Soluble	Swelling
Poly(HD-*alt*-SO_2)	Soluble	Soluble	Soluble	Soluble	Soluble	Swelling
Poly(MP-*alt*-SO_2)[b,c]	Soluble	Soluble	Soluble	Soluble	Insoluble	Insoluble
Poly(BD-*alt*-SO_2)[c,d]	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble

[a] TFA: trifluoroacetic acid, DMSO: dimethyl sulfoxide, THF: tetrahydrofuran, DGDE: diethylene glycol dimethyl ether.

[b] MP: 3-methyl-1,3-pentadiene.

[c] Cited from a previous article (ref. 13).

[d] BD: butadiene.

TABLE 3 Thermal and Optical Properties of Poly(diene sulfone)s with a Functional Side Group

Polymer	T_{d5} (°C)	T_{d50} (°C)	T_g (°C)	%T at 400 nm	n_F	n_D	n_C	ν_D
Poly(MH-*alt*-SO_2)	136	256	82.0	95.1	1.5381	1.5300	1.5251	40
Poly(MO-*alt*-SO_2)	173	254	47.0	95.9	1.5348	1.5267	1.5205	37
Poly(FH-*alt*-SO_2)	213	367	131.0	–[a]	–[a]	–[a]	–[a]	–[a]
Poly(FO-*alt*-SO_2)	240	383	99.0	95.0	1.6256	1.6107	1.6015	25
Poly(FH/HD-*alt*-SO_2)−66[b]	207	330	129.0	94.9	1.6149	1.6001	1.5938	28
Poly(FH/HD-*alt*-SO_2)−38[b]	159	279	128.0	95.3	1.5912	1.5796	1.5730	32
Poly(FH/HD-*alt*-SO_2)−21[b]	150	252	126.0	95.5	1.5745	1.5635	1.5584	35
Poly(HD-*alt*-SO_2)	135	200	–[a]	95.2	1.5449	1.5377	1.5317	41
Bisphenol A polysulfone					1.6488	1.6319	1.6234	25

[a] Not determined.

[b] The number indicates the molar fraction of the FH units in the copolymer.

repeating structure.[12,13] The DFT calculations were previously carried out using the model reactions in order to elucidate the highly regiospecific reaction via a free radical propagation mechanism.[12,22] It had been pointed out that the thermodynamic analysis is useful for estimating the propagating fashion during the radical alternating copolymerization of a diene monomer with SO_2, in which the contribution of the depropagation is important due to the low ceiling temperatures. As shown in Scheme 7, the sulfonyl propagating radical favors a reaction at the α-position of the diene (i.e., 4-position of a functional diene in the scheme) due to the formation of an allyl radical and the steric hindrance of the substituent X. During the addition of the diene radical to SO_2, both the 4,1- and 4,3-propagations of the allyl radical should be considered. The enthalpy changes (ΔH) value for the former reaction is negative and seems to be favored, while the latter is positive, but the difference in these values is quite small. This suggested that the both reaction pathways have a chance for to occur during the copolymerization. During these propagation steps, the depropagation effect is not negligible because of a low ceiling temperature, as already described. Especially, the addition of the allyl radical to SO_2 is slow and the reverse reaction should be considered. The reversible propagation steps are a key for controlling the regioselectivity during the alternating copolymerizations of diene monomers with SO_2.

The copolymers were soluble in dimethyl sulfoxide and chloroform and the solubility increased by the introduction of the alkylene spacer and the fluorenyl ester group in the order of FO > MO $\simeq$ FH > MH (Table 2). The T_{d5} and T_{d50} values of the poly(diene sulfone)s containing an ester side group were 136–240 °C and 254–383 °C, respectively, as summarized in Table 3. The copolymers including the FH and FO with the fluorenyl substituents in the ester group showed higher decomposition temperatures due to the nonvolatile property of the large fluorenyl moiety. The transmittance spectra of the cast films of poly(diene sulfone)s containing an ester group in the side chain are

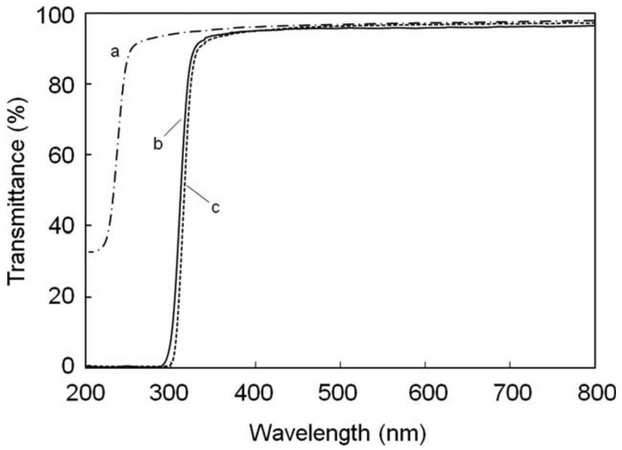


FIGURE 8 Transmittance of UV and visible lights for the poly(diene sulfone)s films. (a) poly(MO-*alt*-SO_2), (b) poly(FH/HD-*alt*-SO_2)−66, and (c) poly(FO-*alt*-SO_2). Film thickness 20 μm.

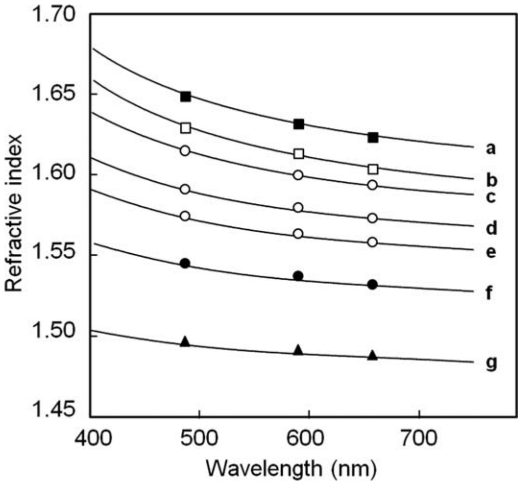


FIGURE 9 Wavelength dependence of the refractive index of (a) conventional bisphenol A polysulfone, (b) poly(FO-*alt*-SO_2), (c) poly(FH/HD-*alt*-SO_2)−66, (d) poly(FH/HD-*alt*-SO_2)−38, (e) poly(FH/HD-*alt*-SO_2)−21, (f) poly(HD-*alt*-SO_2), and (g) poly(methyl methacrylate). The curves were drawn using the following equation with the n_∞ and D parameters: $n_\lambda = n_\infty + D/\lambda^2$ (See also refs. 13 and 25).

TABLE 4 Hydrogenation of Poly(diene sulfone)s with a Functional Side Group and Thermal Properties the Obtained Hydrogenated Polymers[a]

Precursor Polymer	Time (h)	Conversion (%)	T_{d5} (°C)	T_{d50} (°C)	T_g (°C)
Poly(MH-*alt*-SO_2)	6.0	41.3	223	286	57
	12.0	81.6	231	292	47
	18.0	92.1	232	292	46
Poly(MO-*alt*-SO_2)	3.0	27.5	215	301	42
	8.0	44.8	239	308	37
	12.0	68.0	244	330	–[b]
Poly(FH-*alt*-SO_2)	6.0	67.5	248	445	102
Poly(FO-*alt*-SO_2)	6.0	36.7	260	428	88
	12.0	67.5	275	416	86
Poly(FH/HD-*alt*-SO_2)−66[c]	15.0	68.4	236	358	98
	22.0	92.6	250	364	93
Poly(FH/HD-*alt*-SO_2)−38[c]	6.0	60.5	244	326	104
	12.0	80.4	235	341	100
Poly(FH/HD-*alt*-SO_2)−21[c]	12.0	89.7	254	342	93

[a] The hydrogenation was carried out using *p*-toluene sulfonyl hydrazide (15 eq) in diethylene glycol dimethyl ether at 120 °C. The conversion was determined by ^{1}H NMR spectroscopy.
[b] Not determined.
[c] The number indicates the molar fraction of the FH units in the copolymer.

shown in Figure 8. These copolymers exhibited a high transmittance over 95% at 400 nm (see %*T* values in Table 3). The T_g values varied in the temperature range of 47–131 °C, which decreased with the introduction of a longer alkylene spacer and increased with the bulky fluorenyl group. The poly(FH-*alt*-SO_2) film was too brittle to evaluate its optical properties. Therefore, we fabricated the copolymers consisting of ternary repeating units, which were prepared using FH and HD as the diene monomers during the copolymerization with SO_2. The copolymerization results and the copolymer properties are shown in Tables 1 to 3. The poly(FH/HD-*alt*-SO_2)s with a 21.1 to 65.8 mol % FH content were produced as high-molecular-weight copolymers ($M_n = 2.4–4.7 \times 10^4$) with good solubilities. These ternary copolymers included the alternating repeating structure of the diene and SO_2 units. They also produced transparent and tough films by casting of their solutions, similar to the other poly(diene sulfone)s. The wavelength dependence of the refractive indices of the copolymers is shown in Figure 9. The order of the refractive index values was as follows: poly(FO-*alt*-SO_2) >> poly(HD-*alt*-SO_2) ≥ poly(MH-*alt*-SO_2) ≥ poly(MO-*alt*-SO_2). The intermediate refractive index values were observed for a series of the poly(FH/HD-*alt*-SO_2)s, according to the contents of the FH and HD moieties in the copolymers. This result indicated that a refractive index value can be finely controlled by the combination of several diene monomers during the copolymer synthesis. The n_D values were in the range of 1.53–1.61 and the Abbe numbers (ν_D values) were 25–40, being between the values for the conventional aromatic polysulfone and the poly(HD-*alt*-SO_2).

It was previously reported that the onset temperature of the thermal decomposition drastically increased by the hydrogenation of the unsaturated C═C bonds in the copolymer chain.[11] A similar increase in the thermal stability after hydrogenation was observed for the poly(diene sulfone)s containing an ester substituent in this study. The T_{d5} and T_{d50} values were increased to 231–275 °C and 292–445 °C, respectively, when the poly(diene sulfone)s were reacted with hydrazine in diethylene glycol dimethyl ether at 120 °C. The conversion was over 68% after hydrogenation for 12 h, being sufficient for changing the onset temperature of decomposition (Table 4). No change was observed in the ester moiety during the chemical reduction using hydrazine as the reducing agent under the present conditions.

CONCLUSIONS

In this study, we demonstrated that poly(diene sulfone)s including functional ester substituents in their side chain were prepared by the radical alternating copolymerization of the well-designed diene monomers with sulfur dioxide. The obtained functional poly(diene sulfone)s were soluble in organic solvents and the transparent and flexible polymer films were fabricated by casting their solutions. Their refractive index values and Abbe numbers were dependent on the structure of the ester groups and the number of alkylene spacers between the main chain and the ester group. It was also revealed that the physical and optical properties of the copolymers were controlled by the copolymer composition of the ternary copolymerization systems using two different kinds of diene monomers with sulfur dioxide. These functional polysulfones are expected to be used as the new optical polymer materials because the controlled radical polymerization potentially possesses a high number of advantages for structure-controlled polymer syntheses.

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