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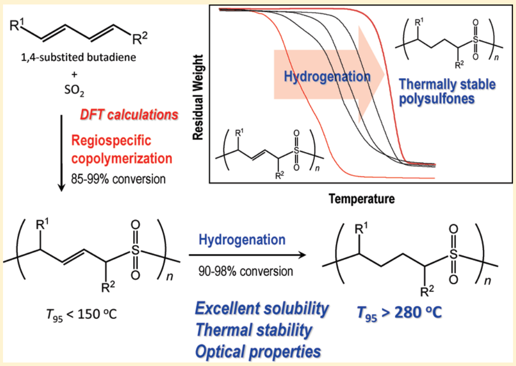
Thermally Stable Polysulfones Obtained by Regiospecific Radical Copolymerization of Various Acyclic and Cyclic 1,3-Diene Monomers with Sulfur Dioxide and Subsequent Hydrogenation

Naruki Tanaka, Eriko Sato, 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

Supporting Information

ABSTRACT: We synthesized the thermally stable alternating copolymers from various acyclic and cyclic alkyl-substituted 1,3-diene monomers with sulfur dioxide (SO_2) as the starting comonomers by radical copolymerization and subsequent hydrogenation. It was revealed based on the DFT calculation results using model reactions as well as the thermodynamic analysis of polymerization that some propagation steps were reversible and the highly 1,4-regiospecific sequences of the poly(diene sulfone)s (PDSs) were consequently produced via a free radical propagation mechanism. The stereochemical structures of the PDSs obtained from cyclic 1,3-diene monomers, such as 1,3-cyclopentadiene and 1,3-cyclohexadiene, were also estimated based on the DFT calculations. Transparent films with a refractive index of 1.53−1.55 were readily obtained by casting the PDS solutions, being confirmed to be amorphous by wide-angle X-ray diffraction measurements. The decomposition of the PDSs started below 150 °C, but hydrogenation produced thermally stable polymers, of which the onset temperatures of decomposition were higher than 280 °C. The hydrogenation conversion significantly depended on the position of an alkyl substituent on the polymer main chain. A ternary copolymerization system consisting of both cyclic and acyclic diene monomers with SO_2 was carried out in order to simultaneously modify the thermal properties as well as the solubility of the resulting polymers.



■ INTRODUCTION

Recent progress in optoelectronics has demanded high-performance polymers with excellent thermal stabilities as well as optical, electronic, and other physical properties. Thermally stable aromatic polysulfones are obtained by condensation polymerization and used as engineering plastics for the mechanical and electrical parts of machines and automobiles, functional membranes for separation and fuel cells, and optical materials such as lens and films.[1] In contrast, poly(olefin sulfone)s[2−4] are synthesized by the radical copolymerization of olefins with sulfur dioxide (SO_2) and they have been developed as resist materials because of their readily degradable properties.[5−8] Radical chain polymerization has a significant potential for controlled polymer syntheses with a well-designed chain structure, such as sequential, regio-, and stereocontrolled repeating structures[9−14] as well as molecular weight, molecular weight distribution, and chain-end structures. Especially, the regiospecific polymerization of diene monomers is required because the physical properties of diene polymers significantly depend on the repeating structure of the diene monomer units.[15−17] Highly regiospecific propagation has recently been reported for the alternating radical copolymerization of 1,3-diene monomers with O_2 and SO_2.[18−21] It was demonstrated in our previous study that poly(diene sulfone) (PDS) could be synthesized by the regiospecific radical copolymerization of 2,4-hexadiene (**M5** in Chart 1) with SO_2 and the transformation of the PDS into a thermally stable polymer by the hydrogenation of the carbon-to-carbon double bond of the main chain.[20] Very few reports on the copolymerization of other diene monomers with SO_2 as well as the properties of the resulting PDSs have been published,[22−30] being in contrast to the high number of studies on the synthesis and characterization of the PDSs produced from olefins.[2−4]

In the present study, we systematically investigated the synthesis of PDSs using various types of alkyl-substituted 1,3-diene monomers, as shown in Chart 1 and characterized their structure, solubility, thermal stability, optical properties, and reactivity for hydrogenation. The solubility and hydrogenation reactivity significantly depended on the position of the alkyl substituents of the polymers. We have revealed that the solubility of PDS is also related to the repeating structure of the polymer chains, i.e., the stereochemical and head-to-tail structures. The PDSs were converted into thermally stable polymers when the

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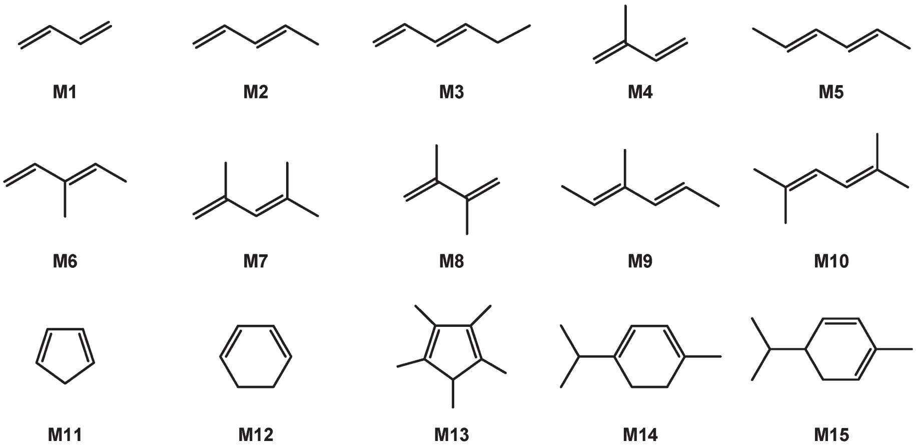
Chart 1



double bond in the main chain was hydrogenated. The butadiene derivatives having an alkyl substituent on their α- and δ-positions were valid for the synthesis of the soluble and thermally stable polysulfones via radical copolymerization with SO_2 and subsequent hydrogenation in a high yield. We have fabricated the terpolymers consisting of cyclic and acyclic diene monomers with SO_2 in order to modify their thermal stability and solubility.

EXPERIMENTAL SECTION

General Procedures. The NMR spectra were recorded using a Bruker AV300N spectrometer in $CDCl_3$, dimethyl sulfoxide-d_6 (DMSO-d_6), and trifluoroacetic acid-d_1 (TFA-d_1). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (M_w/M_n) were determined by size exclusion chromatography (SEC) 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 maximum temperature of decomposition (T_{max}) was determined using the derivatives of the TG 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. Differential scanning calorimetry (DSC) was carried out using a Seiko DSC-6200 at the heating and cooling rates of 10 °C/min in order to determine the glass transition temperature (T_g). The UV–vis spectra were recorded using a JASCO V-550 spectrophotometer. The wide-angle X-ray diffraction (XRD) data were collected using a Rigaku RINT-Ultima 2100 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å, 40 kV, 40 mA) at the scanning rate of 0.25 degree/min. The refractive indices (n_D, n_F, and n_C) of the PDS films were measured at the wavelengths of 486, 589, and 656 nm, respectively, using an Abbe-type refractometer (Atago DR-M2, 1-bromonaphthalene, a halogen lamp). The Abbe number (ν_D) was calculated as follows.

$$\nu_D = (n_D - 1)/(n_F - n_C) \tag{1}$$

Materials. The 1,3-diene monomers, 1,3-butadiene (**M1**), 1,3-pentadiene (**M2**), 1,3-hexadiene (**M3**), isoprene (**M4**), **M5**, 3-methyl-1,3-pentadiene (**M6**), 2,4-dimethyl-1,3-pentadiene (**M7**), 2,3-dimethyl-1,3-butadiene (**M8**), 3-methyl-2,4-hexadiene (**M9**), 2,5-dimethyl-2,4-hexadiene (**M10**), 1,3-cyclopentadiene (**M11**), 1,3-cyclohexadiene (**M12**), pentamethyl-1,3-cyclopentadiene (**M13**), 1-isoropyl-4-methyl-1,3-cyclohexadine (**M14**), and 2-methyl-5-isopropyl-1,3-cyclohexadiene (**M15**) (purchased from Tokyo Chemical Industry Corporation, Ltd., Sigma-Aldrich Corporation, Ltd., or Wako Pure Chemical Industries, Ltd.), SO_2 (Sumitomo Seika Chemicals Corporation, Ltd.), *tert*-butyl hydroperoxide (Sigma-Aldrich Corporation, Ltd.), and *p*-toluenesulfonyl hydrazide (TSH) (Wako Pure Chemical Industries, Ltd.) were used as received without further purification. The **M4** and the solvents were distilled before use. The **M2**, **M5**, and **M6** were used as a mixture of the *EZ* isomers; E/Z = 75/25 for **M2**, $EE/EZ/ZZ$ = 57/39/4 for **M5**, and E/Z = 62/38 for **M6**. A pure EE isomer was used for **M3** and **M7**. The **M11** was obtained by the thermal decomposition of the commercial dicyclopentadiene and purified by repeated distillation.

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. 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 PDSs were purified by repeated reprecipitation using chloroform or DMSO as the solvent and methanol as the precipitant.

Poly(1,3-pentadiene-*alt*-SO_2) (P2). ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.75–5.99 (m, $CH{=}CHCH_2$, 2H), 3.83–4.29 (m, $CHCH{=}CHCH_2$, 3H), 1.13–1.62 (m, $CH(CH_3)CH{=}CH$, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 133.01 ($C(CH_3)CH{=}CH$), 123.88 ($C(CH_3)CH{=}CH$), 59.39 ($C(CH_3)CH{=}CH$), 52.75 ($CH{=}CHCH_2SO_2$), 11.41–12.30 ($C(CH_3)CH{=}CH$). IR (KBr): 2984, 2938, 1811, 1634, 1456, 1407, 1302, 1128, 1021, 976, 922, 885, 830, and 736 cm^{-1}.

Poly(1,3-hexadiene-*alt*-SO_2) (P3). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.66–6.12 (m, $CH{=}CH$, 2H), 3.98, 3.82 (m, $CH{=}CHCH_2SO_2$, 2H), 3.65 (m, $CH(CH_2CH_3)CH{=}CH$, 1H), 1.50–2.32 (m, $CH(CH_2CH_3)$, 2H), 0.72–1.27 (m, $CH(CH_2CH_3)$, 3H).

Table 1. Synthesis of PDS by the Radical Copolymerization of Various 1,3-Diene Monomers with SO_2[a]

monomer	time (h)	yield[b] (%)	T_{95}[c] (°C)	T_g (°C)	M_n[d] × 10^{-4}	M_w/M_n[d]
M1	24	99.9[e]	233	f	g	g
M2	12	99.9	141	f	g	g
M3	24	95.3	138	f	g	g
M4	12	92.9[e]	156[e]	93.4[e]	g	g
M5	24	96.5[e]	135[e]	f	11.1[e]	2.0[e]
M6	12	66.0	133	f	g	g
M7	24	13.2	130	f	g	g
M8	12	98.4	166	f	g	g
M9	24	84.8	164	f	13.3	1.7
M10	24	0 (0)[h]				
M11	24	42.9	141	f	g	g
M12	12	92.9	156	f	g	g
M13	12	0				
M14	24	0				
M15	24	4.9				

[a] Copolymerization conditions: [diene monomer] = 2.0 mol/L, [SO_2] = 5.0 mol/L, [t-BuOOH] = 20 mmol/L in toluene at −78 °C. [b] On the basis of diene monomers. [c] The T_{95} is the 5% weight-loss temperature at the heating rate at 10 °C/min in a nitrogen stream. [d] Determined by SEC calibrated with standard polystyrenes in THF. [e] Reference 20. [f] T_g was not detected by DSC in a temperature range below T_{95}. [g] Insoluble in THF. [h] 0 °C for 24 h.

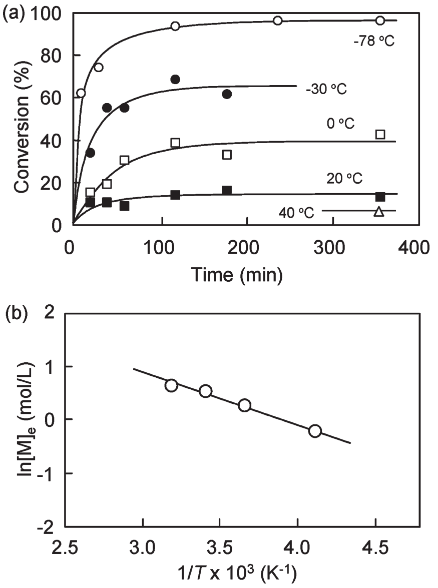


Figure 1. (a) Time−conversion curves for the copolymerization of **M5** and SO_2 at various temperatures. Copolymerization conditions: [**M5**] = 2.0 mol/L, [SO_2] = 5.0 mol/L, [t-BuOOH] = 20 mmol/L in toluene and (b) plot of ln[M]$_e$ versus 1/*T*.

^{13}C NMR (75 MHz, $CDCl_3$): δ 131.97−133.44 ($CH{=}CHCH_2$), 124.11−126.27 ($CH{=}CHCH_2$), 66.39−68.20 (CH_3CH_2CH), 52.96−54.36 ($CH{=}CHCH_2$), 19.07−20.30 (CH_3CH_2CH), 11.24 (CH_3CH_2CH). IR (KBr): 2973, 2937, 2886, 1637, 1460, 1408, 1287, 1132, 1055, 976, 888, 752, 614, and 532 cm^{-1}.

Poly(3-methyl-1,3-pentadiene-*alt*-SO_2) (P6). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.68−5.88 (m, $C(CH_3){=}CHCH_2$, 1H), 3.69−4.16 (m, $(CH_3)CH(CH_3)C{=}CHCH_2$, 3H), 1.91 (s, $(CH_3)C{=}CH$, 3H), 1.40−1.71 (m, $SO_2CH(CH_3)CH$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.29 ($CH{=}C(CH_3)$), 118.85 ($CH{=}C(CH_3)$), 61.77−67.00 ($CH(CH_3)SO_2$), 49.19−53.37 ($CH_2CH{=}C(CH_3)$), 14.56 ($CH{=}C(CH_3)$), 10.83−13.16 ($CH(CH_3)SO_2$). IR (KBr): 2988, 2938, 1650, 1454, 1306, 1239, 1127, 898, and 780 cm^{-1}.

Poly(2,4-dimethyl-1,3-pentadiene-*alt*-SO_2) (P7). ^{1}H NMR (300 MHz, TFA-d_1): δ 5.80−6.11 (m, $C(CH_3){=}CH$, 1H), 3.97−4.46 (m, $CH_2C(CH_3){=}CH$, 2H), 2.26 (s, $CH_2C(CH_3){=}CH$, 3H) 1.81 (s, $C(CH_3)_2SO_2$, 6H). ^{13}C NMR (75 MHz, TFA-d_1): δ 139.90 ($C(CH_3){=}CH$), 134.12 ($C(CH_3){=}CH$), 68.41 (CH_2SO_2), 60.04 ($C(CH_3)_2SO_2$), 23.37 ($C(CH_3)_2SO_2$), 20.95 ($C(CH_3){=}CH$). IR (KBr): 2982, 2937, 1649, 1472, 1291, 1155, 1104, 1028, 849, 791, 735, 677, 594, and 516 cm^{-1}.

Poly(2,3-dimethyl-1,3-butadiene-*alt*-SO_2) (P8). Insoluble. IR (KBr): 2995, 2934, 1637, 1419, 1306, 1217, 1122, 863, and 714 cm^{-1}.

Poly(3-methyl-2,4-hexadiene-*alt*-SO_2) (P9). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.37−5.83 (m, $C(CH_3){=}CH$, 1H), 3.71−4.60 (m, $CH(CH_3)C(CH_3){=}CHCH_2(CH_3)$, 3H), 1.88 (s, $C(CH_3){=}CH$, 3H), 1.46 (m, $SO_2CH(CH_3)CH{=}C(CH_3)CH(CH_3)$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.83 ($C(CH_3){=}CH$), 127.44 $C(CH_3){=}CH$, 64,55 ($CH(CH_3)SO_2$), 55.34 ($C(CH_3){=}CH$), 14.56 ($CH(CH_3)SO_2$). IR (KBr): 2986, 2939, 2876, 1655, 1456, 1383, 1303, 1235, 1131, 1081, 1020, 968, 906, 872, 803, and 748 cm^{-1}.

Poly(1,3-cyclopentadiene-*alt*-SO_2) (P11). ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.18−6.41 (m, $CH{=}CH$, 2H), 4.81 (m, CH, 2H), 2.67 (m, CH_2, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 131.56 ($CH{=}CH$), 67.39 ($CHSO_2$), 24.98 (CH_2). IR (KBr): 3085, 2939, 1631, 1442, 1304, 1243, 1175, 1123, 1063, 1015, 943, 791, 724, 659, and 485 cm^{-1}.

Poly(1,3-cyclohexadiene-*alt*-SO_2) (P12). Insoluble. IR (KBr): 2926, 1634, 1448, 1295, 1122, 985, 894, 817, 741, 656, and 517 cm^{-1}.

Poly[(1,3-cyclohexadiene/1,3-pentadiene)-*alt*-SO_2] [P(12/2)]. ^{1}H NMR (300 MHz, TFA-d_1): δ 6.33−6.66 (m, $CH{=}CH$, 2H), 6.04− 6.33 (m, $CH{=}CHCH_2$, 2H), 3.97−4.61 (m, $CHSO_2$, $CHCH{=}CHCH_2$, 5H), 2.14−2.91 (m, $CHCH_2CH_2CH$, 4H), 1.53−1.84 (m, $CH(CH_3)CH{=}CH$, 3H)). ^{13}C NMR (75 MHz, TFA-d_1): δ 135.49−136.76 ($C(CH_3)CH{=}CH$), 126.97−128.74 ($CHCHCHCHSO_2$), 124.58−126.26 ($C(CH_3)CH{=}CH$), 61.45−64.40 ($C(CH_3)CH{=}CH$), 57.37−60.74 ($CHCH_2CH_2CHSO_2$), 54.82−55.93 ($CH{=}CHCH_2SO_2$), 20.22−21.94 ($CHCH_2CH_2CHSO_2$), 12.58−14.22 ($C(CH_3)CH{=}CH$). IR (KBr): 3588, 2938, 1636, 1456, 1406, 1300, 1123, 1021, 977, 893, 817, and 742 cm^{-1}.

Poly[(1,3-cyclohexadiene/2,4-hexadiene)-*alt*-SO_2] [P(12/5)]. ^{1}H NMR (300 MHz, TFA-d_1): δ 6.32−6.45 (m, $CH{=}CH$, 2H), 5.96−6.32 (m, $CH{=}CH$, 2H), 3.96−4.66 (m, $CHSO_2$, $CH(CH_3)CH{=}CH$, 4H), 2.02−2.99 (m, $CHCH_2CH_2CH$, 4H), 1.33−1.95 (m, $SO_2CH(CH_3)CH$, 6H). ^{13}C NMR (75 MHz, TFA-d_1): δ 132.00−133.92 ($CH{=}CH$), 127.03−128.66 ($CHCHCHSO_2$), 60.54−62.41 ($CH(CH_3)SO_2$), 57.39−60.33 ($CHCH_2CH_2CHSO_2$), 20.36−21.75 ($CHCH_2CH_2CHSO_2$), 12.93−14.63 ($CH(CH_3)SO_2$). IR (KBr): 3567, 2940, 1636, 1456, 1298, 1124, 1018, 978, 894, 817, and 742 cm^{-1}.

The spectral data for **P1**, **P4**, and **P5** were already reported in the previous paper.[20]

Table 2. Solubility of the PDSs Produced from Various 1,3-Diene Monomers and SO_2[a]

PDS	TFA	DMSO	$CHCl_3$	acetone	THF	DEE
P1	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
P2	soluble	soluble	swelling	swelling	insoluble	insoluble
P3	soluble	soluble	soluble	insoluble	swelling	insoluble
P4	soluble	soluble	insoluble	insoluble	insoluble	insoluble
P5	soluble	soluble	soluble	soluble	soluble	swelling
P6	soluble	soluble	soluble	soluble	insoluble	insoluble
P7	soluble	insoluble	insoluble	insoluble	insoluble	insoluble
P8	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
P9	soluble	soluble	soluble	soluble	soluble	insoluble
P11	soluble	soluble	insoluble	insoluble	insoluble	insoluble
P12	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble

[a] TFA: trifluoroacetic acid. DMSO: dimethyl sulfoxide. THF: tetrahydrofuran. DEE: 1,2-diethoxyethane. See Figure 3 for the polymer repeating structures.

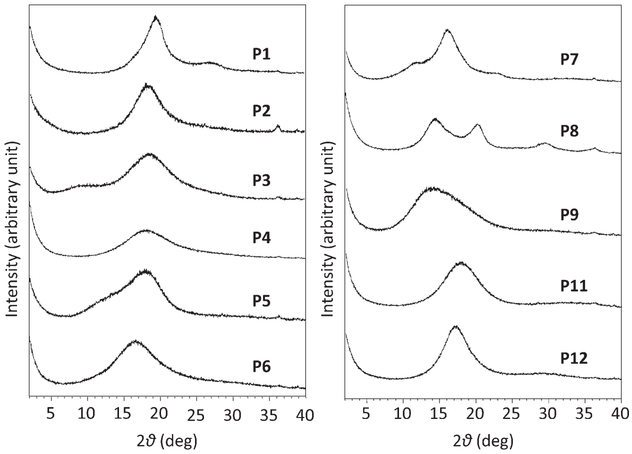


Figure 2. XRD profiles of the PDSs.

Hydrogenation. The PDS (typically, 0.2 g) and TSH (3.7 g, 20 mmol) were stirred in 1,2-diethoxyethane (10 mL) at 100 °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.

Hydrogenated Poly(1,3-pentadiene-*alt*-SO_2) (P2H). ^1H NMR (300 MHz, TFA-d_1): δ 3.25−3.67 (m, $(CH_3)CHCH{=}CHCH_2$, 3H), 1.82−2.49 (m, $CH{=}CH$, 2H), 1.49−1.72 (m, $(CH_3)CHCH{=}CH$, 3H). ^{13}C NMR (75 MHz, TFA-d_1): δ 60.45 ($SO_2(CH_3)CH$), 50.88 ($CH_2CH_2SO_2$), 29.31 ($(CH_3)CHCH_2$), 20.18 ($CH_2CH_2SO_2$), 13.83 ($SO_2(CH_3)CH$). IR (KBr): 2929, 2877, 1638, 1460, 1411, 1385, 1293, 1113, 1029, 894, 835, 726, and 603 cm^{-1}.

Hydrogenated Poly(1,3-hexadiene-*alt*-SO_2) (P3H). ^1H NMR (300 MHz, DMSO-d_6): δ 2.89−3.28 (m, $(CH_3CH_2)CHCH_2CH_2CH_2$, 3H), 1.47−2.17 (m, $(CH_3CH_2)CHCH_2CH_2CH_2$, 6H), 0.81−1.18 (m, $(CH_3CH_2)CH$, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 61.14 ($(CH_3CH_2)CH$), 49.17 (CH_2SO_2), 24.90 ($(CH_3CH_2)CHCH_2$), 19.91 ($(CH_3CH_2)CH$), 18.29 ($CH_2CH_2SO_2$), 10.60 ($(CH_3CH_2)CH$). IR (KBr): 2921, 1633, 1464, 1415, 1388, 1109, 1022, 979, 729, and 601 cm^{-1}.

Hydrogenated Poly(1,3-cyclopentadiene-*alt*-SO_2) (P11H). ^1H NMR (300 MHz, DMSO-d_6): δ 3.75−3.95 (m, $CHSO_2$, 2H), 2.30−2.45 (m, $CHCH_2CH$, 2H), 1.90−2.62 (m, $CHCH_2CH_2CH$, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 58.27 (CH), 25.88−26.35 (CH_2). IR (KBr): 2952, 2874, 1633, 1445, 1300, 1257, 1119, 919, 738, 665, 607, 474, and 429 cm^{-1}.

Hydrogenated Poly(1,3-cyclohexadiene-*alt*-SO_2) (P12H). Insoluble. IR (KBr): 2941, 2871, 1636, 1455, 1288, 1124, 996, 889, 816, 738, 634, and 535 cm^{-1}.

Hydrogenated Poly[(1,3-cyclohexadiene/1,3-pentadiene)-*alt*-SO_2] [P(12/2)H]. IR (KBr): 2941, 1636, 1456, 1289, 1123, 995, 890, 818, and 740 cm^{-1}.

Hydrogenated Poly[(1,3-cyclohexadiene/2,4-hexadiene)-*alt*-SO_2] [P(12/5)H]. IR (KBr): 2942, 1636, 1456, 1290, 1123, 998, 890, 816, and 741 cm^{-1}.

The spectral data for hydrogenated poly(2,4-hexadiene-*alt*-SO_2) (**P5H**) were already reported in the previous paper.[20]

RESULTS AND DISCUSSION

Synthesis of PDSs. The radical alternating copolymerization of various 1,3-diene monomers was carried out using an excess amount of SO_2 ($[SO_2]/[\text{diene monomer}] = 2.5$ molar ratio) in toluene at −78 °C in the presence of *tert*-butyl hydroperoxide as the redox initiator. The SO_2 dually functions as the comonomer for propagation and the reducing agent for initiation. The results of the copolymerization are summarized in Table 1. The copolymerization of the acyclic monomers rapidly occurred and the PDSs were isolated as a colorless solid in a high yield, except for the sterically hindered **M7** and **M10**. It is well-known that a polymer obtained from 1,1-disubstituted ethylenes is thermodynamically unstable due to steric repulsion.[31] Similar steric repulsion probably resulted in the low yield and no formation of the corresponding polymers from **M7** and **M10**, respectively, in this study. When **M11** and **M12** as the cyclic diene monomers were copolymerized with SO_2, their copolymerization reactivity sensitively changed depending on the alkyl carbon numbers of these cyclic monomers. The **M12** as the 6-membered cyclic monomer produced a polymer in quantitative yield, while the 5-membered **M11** produced a polymer only in ca. 50% yield. The cyclic monomers with sterically hindered alkyl substituents, such as **M13**, **M14**, and **M15** (see Chart 1 for the structures), showed low polymerization reactivities, as shown in Table 1.

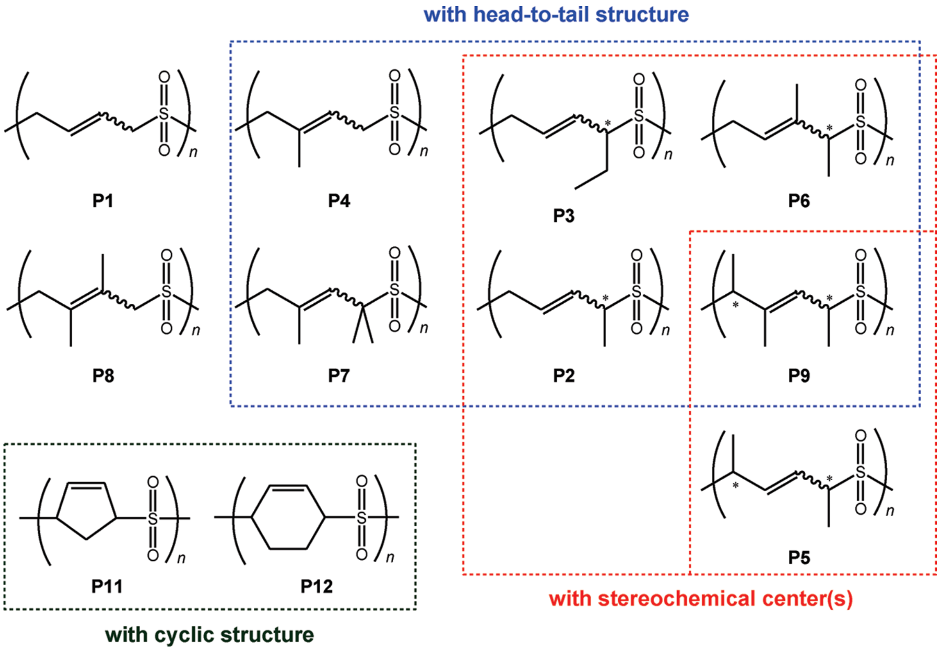


Figure 3. Repeating structures of the PDSs obtained in this study. Only head-to-tail repeating structures are shown for clarity.

When a propagation step is reversible and the reverse reaction (depropagation) is not negligible, polymerization does not achieve a 100% yield even after a long time reaction. This is because the rate of the reverse reaction depends on the polymerization temperature and the monomer concentration, and the propagation rate is apparently equal to zero at the equilibrium monomer concentration ($[\mathrm{M}]_e$) or the ceiling temperature (T_c).[32−34] The $[\mathrm{M}]_e$ and T_c are related to the temperature by the following equations, respectively;

$$\ln[\mathrm{M}]_e = (\Delta H/RT) - \Delta S°/R \tag{2}$$

or

$$T_c = \Delta H/(\Delta S° + R\ln[\mathrm{M}]) \tag{3}$$

where ΔH is the enthalpy of polymerization, $\Delta S°$ is the entropy change at the standard state ($[\mathrm{M}]_e$ = 1 mol/L), and R is the gas constant.

It has been reported that the reverse reaction is not negligible for the addition polymerization of various 1,1-disubsituted ethylene monomers,[34] such as α-methylstyrene, isobutene, and α-substituted acrylates[35,36] and for the copolymerization of olefins or dienes with SO_2,[37,38] as well as for the ring-opening polymerization of cyclic monomers.[33,34,39] In the present study, we experimentally determined the T_c value for the copolymerization of **M5** with SO_2, of which the initial concentrations were 2.0 and 5.0 mol/L, respectively, in toluene. The time−conversion curves obtained during the copolymerization at different temperatures are shown in Figure 1a. The copolymerization quickly proceeded during the initial stage but the conversion remained constant (dead-end type polymerization) at a certain value for each temperature. The $[\mathrm{M}]_e$ values were evaluated from the infinite conversions as a function of the polymerization temperature. When the polymerization temperature increased, the $[\mathrm{M}]_e$ increased; for example, the $[\mathrm{M}]_e$ values were <0.1 and 1.68 mol/L at −78 and +20 °C, respectively, under the conditions used in this study. From the results in Figure 1, the ΔH and $\Delta S°$ values were determined to be −7.95 kJ/mol and −31.0 J/ mol·K, respectively. The absolute ΔH value is lower than the values reported for the copolymerization of olefins and SO_2 (−18.7 to −21.7 kJ/mol),[38] indicating a significant depropagation during the copolymerization of diene monomers. The T_c value of the copolymerization of **M5** and SO_2 was estimated to be 42 °C at the conditions of [**M5**] = 2.0 mol/L and [SO_2] = 5.0 mol/L, based on eq 3. These results indicate that a difference in the polymer yields depending on the monomer structure in Table 1 was produced by thermodynamically controlled factors rather than kinetic one. The low polymer yield obtained during the copolymerization of **M11** is possibly ascribed to the effect of a more significant depropagation, as discussed later based on the DFT calculation results.

The PDSs produced from **M5** and **M9** were soluble in THF and their M_n and M_w/M_n values were determined by SEC; M_n = (1.1−1.3) × 10^5 and M_w/M_n = 1.7−2.0. The other PDSs were insoluble in THF. The PDSs readily decomposed upon heating; the T_{95} values were 130−166 °C for the PDSs obtained from all the substituted butadiene monomers in this study, while **P1** showed the highest T_{95} value (233 °C) due to the reduced steric repulsion in the polymers. The lower the infinite yield of the PDS during the copolymerization the lower the T_{95} values, due to the significant contribution of depropagation by steric hindrance, as shown in Table 1. The T_g value for **P4** was determined to be 93.4 °C and no clear transition was observed below the onset temperatures of decomposition for the other PDSs based on the results of the DSC measurements. The **P2**−**P5**, which were obtained from acyclic diene monomers, apparently softened upon heating in the temperature range near their decomposition temperatures, while **P11** and **P12**, containing cyclic repeating structures, decomposed without softening.

Solubility. The solubility of the PDSs was dependent on the polymer structure, i.e., the position and the number of alkyl substituents on the polymer main chains, in other words, the substituents on the dienyl group of the starting monomers.

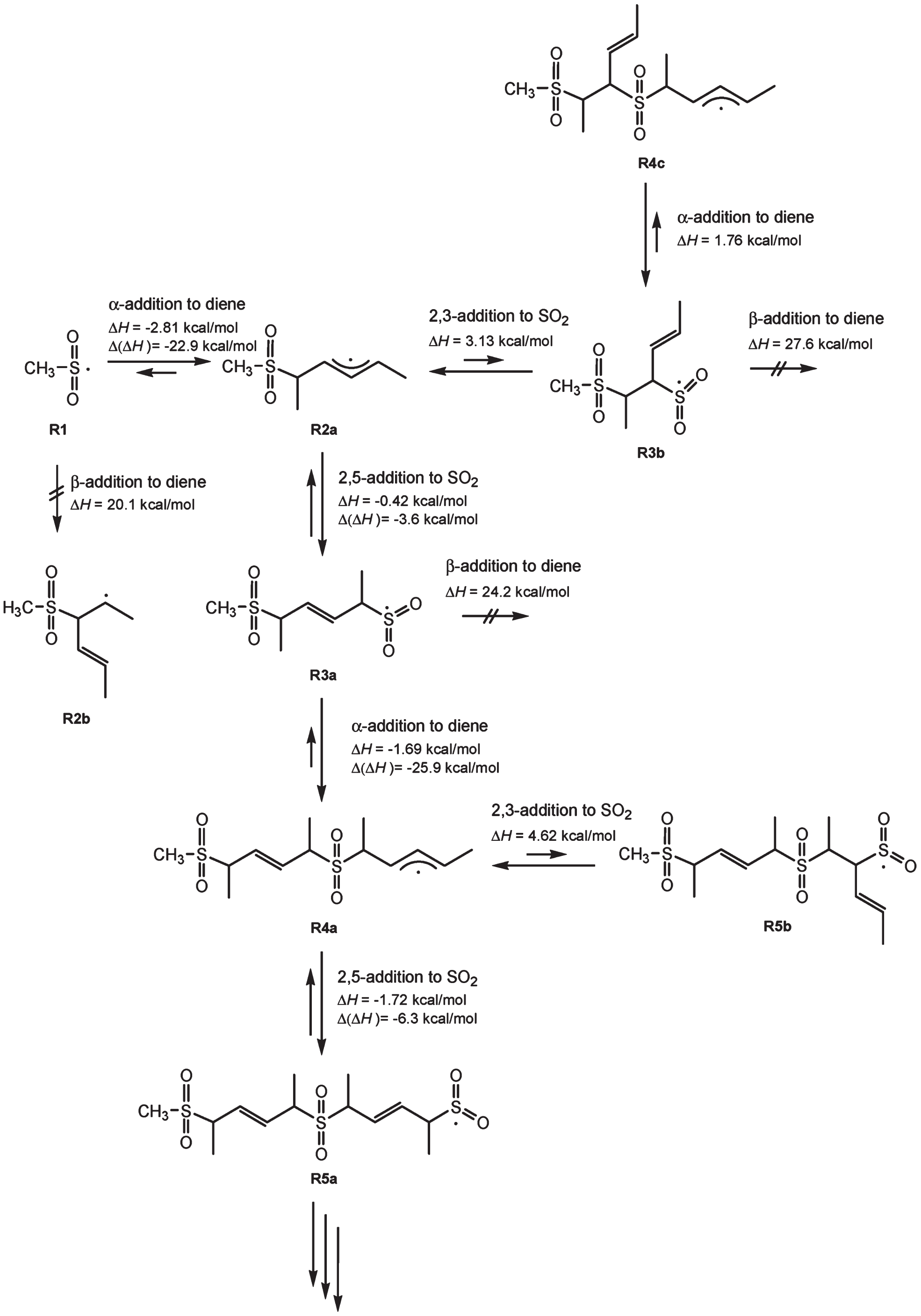


Figure 4. Regiospecific propagations for the copolymerization of **M5** and SO_2 estimated by the DFT calculations at the B3LYP/6-311++G(3df, 3pd) level.

The solubility results are shown in Table 2. The **P5**, **P6**, and **P9** were soluble in TFA, DMSO, chloroform, and acetone, and insoluble in toluene, methanol, diethyl ether, and *n*-hexane. The **P5** and **P9** were also soluble in THF, as already described. The **P4** was soluble in TFA and DMSO and **P7** was soluble in TFA, but they were insoluble in the other solvents. The **P1** and **P8** were insoluble in all the solvents. The **P2** and **P3** showed intermediate solubilities. All the PDSs were amorphous, based on the results of the XRD measurement (Figure 2). The PDSs provided broad diffraction profiles in the region of 2θ = 10−25°, while several peaks due to partial crystallization were observed for **P1**, **P7**, and **P8** with the poor solubilities.

The repeating structure of the polymers was of exclusively alternating and 1,4-structures, irrespective of the structure of the used monomers, based on the NMR and IR spectroscopy results. The configuration of the carbon-to-carbon double bond in the polymer main chain was random, i.e., both the *E* and Z (trans and cis) forms of the double bond are included in the polymer chain because of the free-radical addition of an allyl radical during the propagation, similar to the formation of atactic polybutadienes with nonspecific regio structures during the radical polymerization. The solubility of the PDSs can be accounted for by the tacticity and the head-to-tail repeating structure. The repeating

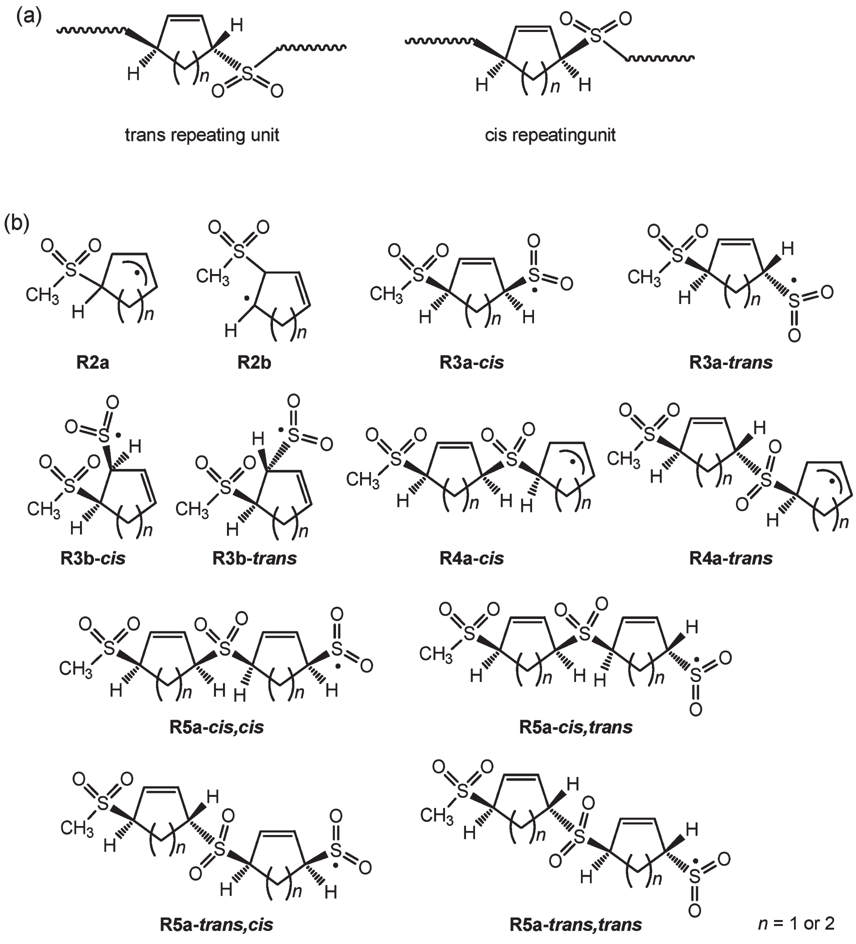


Figure 5. (a) Trans and cis repeating units produced from the cyclic diene monomers during the alternating copolymerization with SO_2. The configuration of the double bond in the cyclic units is fixed as the Z form. (b) Model radicals used for the DFT calculations.

Table 3. Results of DFT Calculations (B3LYP) for the Model Reactions of Radical Alternating Copolymerization of Cyclic Diene Monomers with SO_2

		Δ*H* (kcal/mol) for **M11**		Δ*H* (kcal/mol) for **M12**	
reacting radical	product radical	6-311G (d, p)	6-311++G (3df, 3pd)	6-311G (d, p)	6-311++G (3df, 3pd)
R1	**R2a**	−7.41	−5.53	−12.2	−9.18
	R2b	17.5	16.6	12.5	15.2
R2	**R3a**-*cis*	0.50	2.50	−2.23	−0.05
	R3a-*trans*	−1.81	−0.20	0.12	2.14
	R3b-*cis*	7.11	9.91	2.18	4.26
	R3b-*trans*	1.07	1.91	3.35	5.04
R3a-*cis*	**R4a**-*cis*	−7.34	−4.95	−7.64	−5.33
R3a-*trans*	**R4a**-*trans*	−1.79	0.81	−7.89	−5.55
R4a-*cis*	**R5a**-*cis,cis*	−2.29	0.12	−2.94	−0.39
	R5a-*cis,trans*	−2.32	−0.15	−0.50	1.37
R4a-*trans*	**R5a**-*trans,trans*	−3.98	−2.14	1.02	3.27
	R5a-*trans,cis*	−4.61	−2.14	−4.00	−1.18

unit structures of the PDSs are summarized in Figure 3. The PDSs randomly include head-to-tail, head-to-head, and tail-to-tail sequences due to no or less selectivity for monomer addition during the propagating step. For the PDSs produced from several butadiene monomers with a substituent on the 1- or 4-position, such as **P2**, **P3**, **P5**, **P6**, and **P9**, isotactic (meso) and syndiotactic (racemo) repeating structures should also be considered. Actually, complicated and split peaks were observed in the ^1H and ^{13}C NMR spectra of the PDSs (see Supporting Information). On the other hand, **P1** and **P8** have no asymmetric carbon center in

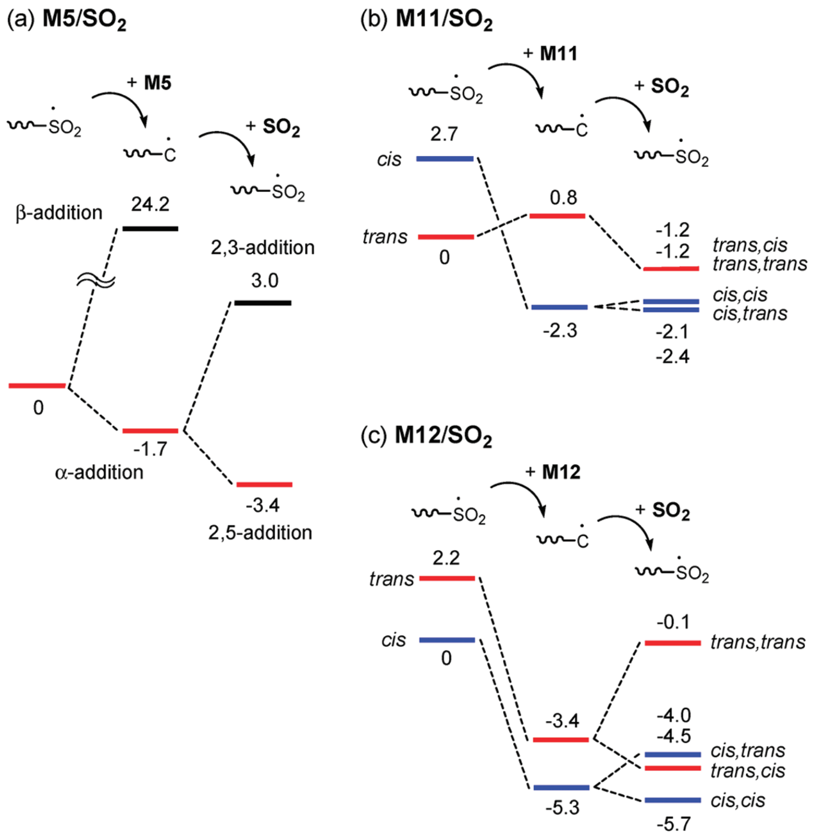


Figure 6. Energy diagrams for alternating propagation steps during the regiospecific copolymerization of diene monomers with SO$_2$ at the B3LYP/6-311++G(3df, 3pd) level. The unit for the energies is kcal/mol. Key: (a) **M5**/SO$_2$, (b) **M11**/SO$_2$, and (c) **M12**/SO$_2$. The energies for the α-addition to the diene monomer and 1,4-addition to SO$_2$ are shown for clarity in the diagrams for the **M11** and **M12** copolymerization with SO$_2$. See Figure 5 for the chemical structure of the radicals used for the calculations.

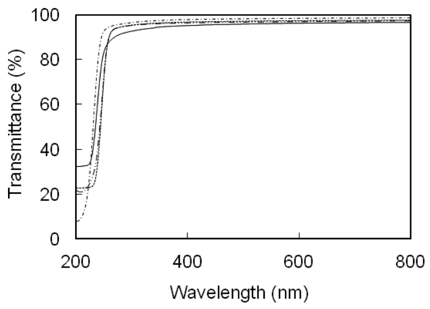


Figure 7. Transmittance of visible light for the PDS films. (— - —) **P3**, (——) **P5**, (- - - -) **P6**, and (— - - —) **P9**. Thickness 20 μm.

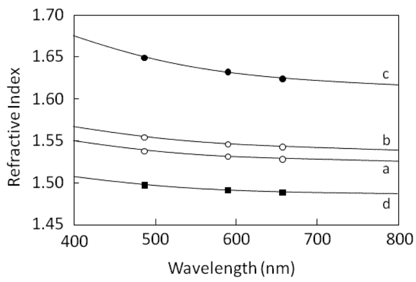


Figure 8. Wavelength dependence of the refractive index of (a) **P3**, (b) **P6**, (c) polysulfone, and (d) PMMA. The curves are drawn based on the calculations using eq 4 with the n_∞ and D parameters in Table 4.

the main chain and no head-to-tail structure. The solubility of the PDSs with a cyclic structure is completely different from the results of the PDSs obtained from the acyclic diene monomers. The **P11** and **P12** showed very poor solubilities. As shown in Table 2, **P11** was soluble in TFA and DMSO, while **P12** was insoluble in all the solvents.

The solubility of the PDSs is divided into the following several categories; (i) the PDSs insoluble in any solvent, consisting of a highly symmetric repeating structure, such as **P1** and **P8**, (ii) the PDSs soluble in TFA or DMSO and insoluble in the other solvents, including head-to-tail structure, such as **P4** and **P7**, (iii) the PDSs soluble in several kinds of solvents, including a head-to-tail structure and a stereochemical center, such as **P2**, **P3**, and **P6**, (iv) the PDSs soluble in many solvents, including two stereochemical centers, such as **P5** and **P9**, and (v) the PDSs with poor solubilities obtained from cyclic diene monomers, such as **P11** and **P12**.

The solubilities of **P11** and **P12** were close to those for the polymers classified in categories i and ii, respectively, but it cannot be explained by the diene repeating structures, which imply two stereochemical centers per one repeating unit. The highly symmetrical structure of the repeating unit of **P11** and **P12** including the fixed *Z*-configuration for the cyclic double bond is probably one of the reasons for their poor solubilities. The **P11** and **P12** were also amorphous based on the XRD results (Figure 2) because random addition occurs during the

Table 4. Optical Property of PDSs

polymer	n_F	n_D	n_C	ν_D	n_∞	D
P3	1.5378 ± 0.0006	1.5346 ± 0.0004	1.5278 ± 0.0005	53.6	1.5186	4705
P5	1.5449 ± 0.0002	1.5376 ± 0.0002	1.5319 ± 0.0002	41.5	1.5175	6546
P6	1.5545 ± 0.0005	1.5462 ± 0.0002	1.5431 ± 0.0002	47.8	1.5291	6001
P9	1.5379 ± 0.0002	1.5320 ± 0.0002	1.5274 ± 0.0003	51.0	1.5158	5288
polysulfone	1.6488 ± 0.0003	1.6319 ± 0.0001	1.6234 ± 0.0002	24.9	1.5933	13 152
PMMA	1.4965 ± 0.0003	1.4918 ± 0.0002	1.4878 ± 0.0000	56.5	1.4783	4356

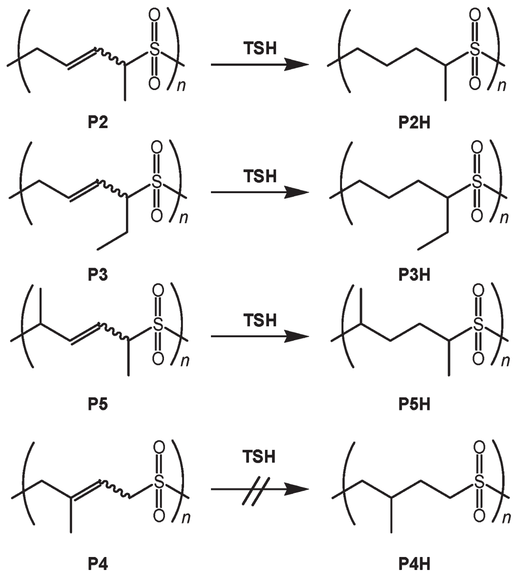


Figure 9. Hydrogenation of the PDSs with TSH and the chemical structures of the hydrogenated PDSs .

propagation, i.e., the stereochemical relationship between the neighboring repeating units is atactic.

DFT Calculations. In our previous study,[21] the DFT calculations were carried out using the model reactions for the copolymerization of **M5** and SO_2 in order to elucidate the highly regiospecific reaction (exclusive 1,4-propagation) via a free radical propagation mechanism. A change in the heat of formation for each propagation step was evaluated using three different basis set levels for the calculations. A summary of the calculated results at the B3LYP/6-311++G(3df, 3pd) level for the regiospecific propagations during the copolymerization of **M5** and SO_2 is illustrated in Figure 4 for understanding the regiospecific copolymerization mechanism. The sulfonyl radical, **R1** exclusively favors a reaction at the α-position of the diene due to the formation of an allyl radical (ΔH = −2.81 kcal/mol). This pathway is more advantageous than the β-addition route (ΔH = 20.1 kcal/mol) and the difference in the ΔH values, i.e., the $\Delta(\Delta H)$ value, was −22.9 kcal/mol. During the addition of the resulting radical **R2a** to SO_2, both the 2,5- and 2,3-propagations should be considered, forming the sulfonyl radicals, **R3a** and **R3b**, respectively. The ΔH value for the former reaction is negative (ΔH = −0.42 kcal/mol) and seems to be favored, while the latter is positive (ΔH = 3.53 kcal/mol). However, the $\Delta(\Delta H)$ value for these reactions is quite small (−3.6 kcal/mol). This suggests that both reaction pathways have a chance of occurring during the copolymerization. The **R3b** radical is unfavorable to further react with **M5** even when the α-addition occurs (ΔH = 1.76 kcal/mol). Consequently, the reverse reaction occurs and reproduces the **R2a** radical again. As a result, the reaction path producing the **R3a** radical is advantageous. Similarly, the **R3a** radical undergoes the α-addition to SO_2 [$\Delta(\Delta H)$ = −25.9 kcal/mol] and the subsequent 2,5-addition to the diene

Table 5. Hydrogenation of PDSs and Thermal Properties of the Obtained Polymers[a]

PDS	time (h)	conv (%)	T_{95} (°C)	T_{50} (°C)	T_{max} (°C)	T_g (°C)
P1	0	0	233	276	249, 290, 307	[b]
	12	57.5[c]	291	393	263, 323, 428	[b]
P2	0	0	141	208	177, 251	[b]
	3	17.7	174	272	274	89.0
	6	31.3	225	296	287	93.7
	12	61.2	267	333	331	76.9
	12	61.5	236	326	330	74.1
	18	94.6	323	366	374	75.7
	18	98.4	322	365	368	60.6
P3	0	0	138	258	175, 269	b
	3	29.6	251	300	298	78.3
	6	49.2	258	307	304	72.8
	9	67.4	275	326	312	59.5
	19	89.7	288	345	351	35.3
P4	0	0	156	240	181, 263	93.4
	36	8.0	206	284	169, 283	82.3
P5	0	0	135	200	157, 235	b
	1	25.0	224	276	211, 279	103.0
	3	34.9	234	282	262, 277	93.5
	6	50.6	246	295	198, 283, 345	97.5
	9	93.6	278	346	347	90.4
	12	98.2	283	340	345	81.7
P9	0	0	164	220	226	b
	12	13.9	202	242	249	b
P11	0	0	141	264	275, 286	b
	6	84.6	279	346	299, 350	b
	9	92.5	284	351	307, 355	b
	12	95.1	291	353	309, 355	b
P12	0	0	156	240	181, 263	b
	3	23.8[c]	206	284	169, 283	b
	6	47.2[c]	164	220	236	b
	9	76.8[c]	274	309	302	b

[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 ^{1}H NMR spectroscopy. [b] No T_g below the decomposition temperature by DSC. [c] Determined by IR spectroscopy.

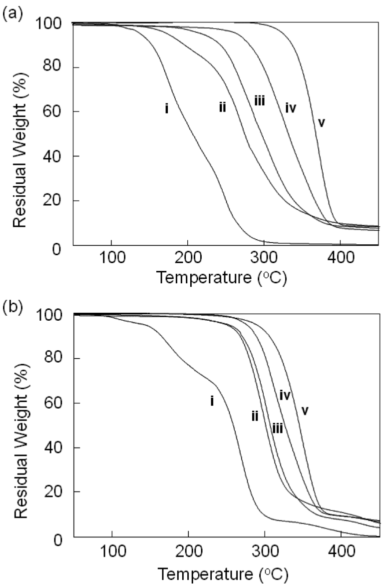


Figure 10. TG curves for the hydrogenated PDSs at different conversions. (a) Transformation of **P2** to **P2H** at (i) 0, (ii) 17.7, (iii) 31.3, (iv) 61.2, and (v) 94.6% conversions. (b) Transformation of **P3** to **P3H** at (i) 0, (ii) 29.6, (iii) 49.2, (iv) 67.4, and (v) 89.7% conversions.

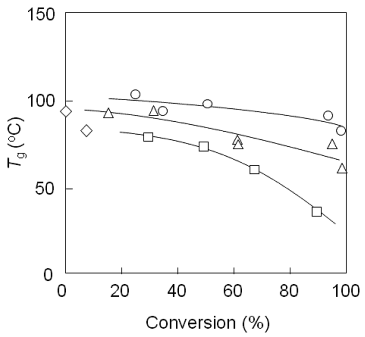


Figure 11. T_g values for the hydrogenated PDSs at different conversions. (△) **P2H**, (□) **P3H**, (◇) **P4H**, and (○) **P5H**.

[$\Delta(\Delta H) = -6.3$ kcal/mol], resulting in the highly regiospecific 1,4-polymer formation.

We also calculated the ΔH values for the model reactions using **M11** and **M12** as the cyclic diene monomers in this study. The calculated results using the B3LYP/6-311G(d, p) and 6-311++G(3df, 3pd) levels are summarized in Table 3. The possible reaction pathways are similar to that for **M5** in Figure 4. During the propagations of the cyclic diene monomers, the configuration of the double bond in the repeating ring structure is exclusively fixed to the *Z*-configuration. The diastereomeric configuration at the 1- and 4-positions of the 5- and 6-membered ring units implies cis and trans ones, as shown in Figure 5a. The structures of the model radicals for each propagation step are also shown in this figure.

The **M11** repeating units including a trans structure is energetically favored but the differences are very small during the reaction of **M11** with SO_2. Overall, the difference in the energies is negligible among the trans,cis-, trans,trans-, cis,cis-, and cis,trans-repeating unit structures, as shown in the energy diagram of Figure 6b. As a result, the **P11** has a highly alternating and fixed *Z*-configuration of the double bond, but the diastereochemical structure is random (atactic) for the configuration of the isomers with a ring structure as the repeating unit. On the other hand, similar calculations suggested the more stable cis,cis-structure of the **M12** ring, which is energetically more favored than the trans,trans-one by 5.6 kcal/mol (Figure 6c), probably leading to the predominant formation of the cis structure of the cyclic diene monomer unit during the copolymerization of **M12** with SO_2. The poor solubility of **P12** is ascribed to the cis-rich diastereochemical structure of the **M12** repeating units. The intermolecular stereochemistry between the adjacent cyclic repeating units is considered to be random, similar to the copolymerization of the acyclic diene monomers.

The enthalpy changes can also be discussed based on the DFT calculation results. The ΔH values for the formation of the repeating unit of the diene with SO_2 were -3.4 kcal/mol for the copolymerization of **M5** with SO_2. Similarly, the estimated exothermic magnitude was -4.0 to -5.7 kcal/mol for the copolymerization of **M12** with SO_2, except for the trans,trans-repeating unit formation. In contrast, the ΔH values were -1.2 to -2.4 kcal/mol for the **M11** copolymerization, being disadvantageous for the propagation process in the forward direction. The low conversion observed for the copolymerization of **M11** with SO_2 (Table 1) is due to the ceiling temperature being lower than those for the copolymerization of **M5** and **M12**.

Optical Properties. Transparent films were prepared by casting the chloroform solutions of several PDSs and drying at room temperature. The PDS films showed an excellent transparency toward visible light. The transmittance was greater than 95% at 400 nm for the films with a 20-μm thickness (Figure 7). The refractive index was measured at three different wavelengths, i.e., 486, 589, and 656 nm. The obtained n_F, n_D, and n_C values as well as the Abbe numbers (ν_D) are summarized in Table 4. The PDSs have n_D values of 1.53−1.55 and ν_D values of 42−54 with a moderate wavelength dependence. These values are intermediate between those for commercial polysulfone ($n_D = 1.63$ and $\nu_D = 25$) and poly(methyl methacrylate) ($n_D = 1.49$ and $\nu_D = 57$). The wavelength dependence of the refractive index for these polymers was well simulated using a two-parameter analysis based on eq 4,[40] as shown in Figure 8. The determined parameters, n_∞ and D, are shown in Table 4.

$$n_\lambda = n_\infty + D/\lambda^2 \tag{4}$$

Thermal Stability. The PDSs start to readily decompose below 150 °C upon heating. The main decomposition products were the corresponding diene monomers and SO_2. The thermal stability of the PDSs is modified by the hydrogenation of the double bonds in the main chain. The TSH decomposes to quickly produce hydrazide in a quantitative yield at 120 °C,[41−43] but the decomposition of the unreacted PDSs also competitively occurs. In the present study, therefore, hydrogenation was carried out using a large excess amount of TSH at 100 °C in order to avoid the decomposition of the polymers during the hydrogenation reaction. The structures of the hydrogenated PDSs are shown in Figure 9. The results of the modified thermal stability of the polymers are summarized in Table 5. All the T_{95}, T_{50}, and T_{max} values increased according to the increase in the content of the hydrogenated repeating structures. For example, the T_{95} value increased from 135−141 °C for the original PDSs to 283−322 °C after the hydrogenation at a 90−98% conversion for **P2**, **P3**, **P5**, and **P11**. The change in

Table 6. Solubility of the Hydrogenated PDSs [a]

hydrogenated PDS	TFA	DMSO	$CHCl_3$	acetone	THF	DEE
P2H	soluble	insoluble	insoluble	insoluble	insoluble	insoluble
P3H	soluble	soluble	soluble	insoluble	insoluble	insoluble
P5H	soluble	soluble	soluble	insoluble	insoluble	insoluble
P11H	soluble	soluble	insoluble	insoluble	insoluble	insoluble
P12H	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble

[a] TFA: trifluoroacetic acid. DMSO: dimethyl sulfoxide. THF: tetrahydrofuran. DEE: 1,2-diethoxyethane.

Table 7. Synthesis and Characterization of Three-Component PDSs[a]

			PDSs before hydrogenation											
polymerization conditions								solubility[c]				after hydrogenation[b]		
comonomer	**M12** mol%	time (h)	yield (%)	M12 mol %	T_{95} (°C)	T_{50} (°C)	T_g (°C)	TFA	DMSO	$CHCl_3$	THF	T_{95} (°C)	T_{50} (°C)	T_g (°C)
M2	75	24	84.1	80	184	262	*d*	sol	insol	insol	insol	264	313	*d*
	50	24	90.1	53	166	245	*d*	sol	sol	insol	insol	244	338	*d*
	25	24	92.6	26	145	229	*d*	sol	sol	insol	insol	282	355	73.5
M5	75	0.5	39.6	90	180	261	*d*							
		3	62.3	88	178	255	*d*							
		24	82.2	81	178	262	*d*	sol	insol	insol	insol	242	316	*d*
	50	0.5	43.5	64	182	259	*d*							
		3	70.6	63	171	335	*d*							
		24	90.1	53	185	257	*d*	sol	sol	insol	insol	218	283	*d*
	25	0.5	58.7	40	162	235	*d*							
		3	82.7	38	155	225	*d*							
		24	96.1	25	142	199	*d*	sol	sol	insol	insol	222	298	92.2

[a] Polymerization conditions: [diene monomers] = 2.0 mol/L, $[SO_2]$ = 5.0 mol/L, [*t*-BuOOH] = 20 mmol/L in toluene at −78 °C. The yield was determined based on the diene monomers. [b] Hydrogenation conditions: PDS 0.2 g, TSH 13 equiv, and 1,2-diethoxyethane 10 mL at 100 °C for 12 h. [c] TFA: trifluoroacetic acid. DMSO: dimethyl sulfoxide. THF: tetrahydrofuran. [d] No T_g below the decomposition temperature by DSC.

the TG traces is shown in Figure 10 for the hydrogenation of **P2** and **P3** at the different conversions. No depolymerization occurs for the hydrogenated PDSs, resulting in an excellent thermal stability. The complicated decomposition products obtained from the hydrogenated PDSs suggest a random scission of the polymer chains during the degradation in the high temperature region. In contrast to the quantitative hydrogenation of the most PDSs, the hydrogenation hardly occurred for the PDS having a substituent on the double bond in the main chain, such as **P4** and **P9**. Only a low conversion to the hydrogenated structures and a small increase in the decomposition temperature were observed for the previously mentioned compounds. A similar interruption of the hydrogenation was previously reported for polyisoprene and its random copolymer prepared by anionic and radical polymerizations.

The change in the T_g values was also investigated for the hydrogenated PDSs at various conversions. For all the polymers, the T_g values decreased according to an increase in the conversion of hydrogenation, as shown in Figure 11. This corresponds to the change in the repeating chain structures from the rigid carbon-to-carbon double bond to the flexible ethylene units by the hydrogenation. No effect of crystallization was observed for the amorphous PDSs and their hydrogenated polymers in this study.[44,45] The hydrogenated PDSs showed a solubility similar to those for the corresponding PDSs before hydrogenation (Table 6).

Ternary Copolymerization Systems. The **P12** was insoluble in all the solvents, but the solubility was modified by the incorporation of acyclic diene monomer units, such as **M2** and **M5**. The results of the three-component copolymerization, i.e., **M12**/**M2**/SO_2 or **M12**/**M5**/SO_2 are summarized in Table 7, which lists the solubility and thermal properties of the obtained PDSs. The copolymerization was carried out at three different **M12** contents in the feed, at which the total diene monomer concentration was constant as 2.0 mol/L. The regiospecific alternating copolymerization proceeded in these systems and some **M12** monomer units were substituted by the acyclic diene monomer units in the copolymer chains. The polymer yield increased according to an increase in the acyclic monomer content in the feed. This suggests that the infinite copolymer yields for the copolymerization of the acyclic monomers are higher than those for the cyclic one, i.e., the T_c of the copolymerization of **M12** with SO_2 is lower than those for the copolymerization of **M2** and **M5** with SO_2. It was revealed that the **M12** content in the obtained copolymers was always higher than the content in the feed, indicating that the reactivity of **M12** as the monomer is greater than that of **M2** and **M5** during the terpolymerization. In other words, the addition of the SO_2-terminated polymer radical to **M12** is faster than that to **M2** or **M5**. Thus, it has been clarified that the polymer yield is determined depending on the T_c values and the copolymer composition depended on the monomer reactivity during the ternary copolymerizations.

This ternary copolymerization system provided the PDSs soluble in TFA and DMSO depending on the amount of the acyclic diene monomers incorporated into the copolymers, as shown in Table 7. The T_g value was dependent on the compositions of the diene monomer units; the T_g value was determined to be 73.5 and 92.2 °C for the PDSs with the **M12**/**M2** = 3/1 and **M12**/**M5** =3/1 compositions, respectively, after the hydrogenation. These T_g values are higher than those for the hydrogenated polymers, **P2H** and **P5H**, i.e., 60.6 and 81.7 °C, respectively (see Table 5). When the **M12** content increased, no T_g was observed. Thus, the three component copolymerization has been revealed to be valid for the synthesis of soluble and thermally stable polysulfones.

CONCLUSIONS

We investigated the effect of the alkyl substituent of the butadiene moiety on the polymerization reactivity as well as the polymer properties, such as solubility and thermal stability. The highly regiospecific and alternating copolymers were obtained due to the low ceiling temperatures and some reversible propagations via a free radical polymerization mechanism. The solubility and hydrogenation reactivity sensitively depended on the position of the alkyl substituents on the polymer. The hydrogenated PDSs are expected to be used as new types of transparent heat-resistant polymers. We have revealed that the soluble and thermally stable polysulfones are synthesized in a high yield from the butadiene derivatives having an alkyl substituent on their α- and δ-positions via radical copolymerization with SO_2 and subsequent hydrogenation. The PDS will be further modified by the introduction of a functional group into the polymer repeating structures, i.e., the appropriate position of the butadiene monomer, without suppressing the polymerization and hydrogenation reactivity.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** NMR and IR spectra and TG/DTA curves. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES

(1) Elias, H.-G. *Macromolecules vol 2, Industrial Polymer and Syntheses*: Wiley-VCH: Weinheim, Germany, 2007; pp 436−441.

(2) Fawcett, A. H. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley-Interscience: New York, 1987; Vol. 10, pp 408−432.

(3) Reviews:(a) Florjańczyk, Z. *Prog. Polym. Sci.* **1991**, *16*, 509–560. (b) Soares, B. G. *Prog. Polym. Sci.* **1997**, *22*, 1397–1430. (c) Braun, D.; Hu, F. C. *Prog. Polym. Sci.* **2006**, *31*, 239–276.

(4) (a) Anga, R. S.; Kometani, J. M.; Reichmanis, E.; Hanson, J. E.; Nalamasu, O.; Thompson, L. F.; Heffner, S. A.; Tai, W. W.; Trevor, P. *Chem. Mater.* **1991**, *3*, 660–667. (b) DeSimone, J. M.; York, G. A.; McGrath, J. E.; Gozdz, A. S.; Bowden, M. J. *Macromolecules* **1991**, *24*, 5330–5339. (c) Novembre, A. E.; Tai, W. W.; Kometani, J. M.; Hanson, J. E.; Nalamasu, O.; Taylor, G. N.; Reichmanis, E.; Thompson, L. F. *Chem. Mater.* **1992**, *4*, 278–284. (d) Watanabe, A.; Sakakibara, T.; Ito, S.; Ono, H.; Yoshida, Y.; Tagawa, S.; Matsuda, M. *Macromolecules* **1992**, *25*, 692–697. (e) Fawcett, A. H.; Malcolm, R. K. *Macromolecules* **1997**, *30*, 2997–3004. (f) Date, R. W.; Fawcett, A. H.; Geue, T.; Haferkorn, J.; Malcolm, R. K.; Stumpe, J. *Macromolecules* **1998**, *31*, 4935–4949. (g) Schmidt-Winkel, P.; Wudl, F. *Macromolecules* **1998**, *31*, 2911–2917. (h) Zhao, Y. -L.; Jones, W. H.; Monnat, F.; Wudl, F.; Houk, K. N. *Macromolecules* **2005**, *38*, 10279–10285. (i) Lobez, J. M.; Swager, T. M. *Macromolecules* **2010**, *43*, 10422–10426.

(5) Bowden, M. J.; Allara, D. L.; Vroom, W. I.; Frackoviak, J.; Kelley, L. C.; Falcone, D. R. In *Polymer in Electronics*; Davidson, T., Ed.; ACS Symposium Series 242; American Chemical Society: Washington DC, 1984; pp 135−152.

(6) Willson, C. G. In *Introduction to Microlithography: Theory, Materials, and Processing*; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; ACS Symposium Series 219; American Chemical Society: Washington DC, 1983; pp 87−159.

(7) (a) Davies, J. D.; Daly, W. H. U.S. Patent 5,922,518, issued July 13, 1999. (b) Davies, J. D.; Daly, W. H. U.S. Patent 6,103,866, issued August 15, 2000.

(8) (a) Yaguchi, H.; Sakaki, T.; Matsuda, M. *Chem. Lett.* **2006**, *35*, 760–761. (b) Yaguchi, H.; Sakaki, T. *Macromolecules* **2007**, *40*, 9332–9338.

(9) Matsumoto, A. In *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley: New York, 2002; pp 691−773.

(10) Satoh, K.; Kamigaito, M. *Chem. Rev.* **2009**, *109*, 5120–5156.

(11) Pfeifer, S.; Lutz, J. −F. *J. Am. Chem. Soc.* **2007**, *129*, 9542–9543.

(12) Satoh, K.; Matsuda, K.; Nagai, K.; Kamigaito, M. *J. Am. Chem. Soc.* **2010**, *132*, 10003–10005.

(13) Ida, S.; Ouchi, M.; Sawamoto, M. *J. Am. Chem. Soc.* **2010**, *132*, 14748–14750.

(14) Hibi, Y.; Tokuoka, S.; Terashima, T.; Ouchi, M.; Sawamoto, M. *Polym. Chem.* **2011**, *2*, 341–347.

(15) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223–1252.

(16) Friebe, L.; Nuyken, O.; Obrech, W. *Adv. Polym. Sci.* **2006**, *204*, 1–154.

(17) (a) Matsumoto, A. *Prog. React. Kinet.* **2001**, *26*, 59–109. (b) Matsumoto, A. *Polym. J.* **2003**, *35*, 93–121. (c) Nagahama, S.; Tanaka, T.; Matsumoto, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 3811–3814. (d) Matsumoto, A.; Furukawa, D.; Nakazawa, H. *J. Polym. Sci., Part A, Polym. Chem.* **2006**, *44*, 4952–4965.

(18) Sato, E.; Matsumoto, A. *Chem. Rec.* **2009**, *9*, 247–257.

(19) (a) Matsumoto, A.; Taketani, S. *J. Am. Chem. Soc.* **2006**, *128*, 4566–4567. (b) Sugimoto, Y.; Taketani, S.; Kitamura, T.; Uda, D.; Matsumoto, A. *Macromolecules* **2006**, *39*, 9112–9119.

(20) Kitamura, T.; Tanaka, N.; Mihashi, A.; Matsumoto, A. *Macromolecules* **2010**, *43*, 1800–1806.

(21) Tanaka, N.; Sato, E.; Matsumoto, A. *Org. Biomol. Chem.* **2011**, *9*, 3753–3758.

(22) Fujioka, S.; Shinohara, Y.; Hayashi, K. *Kogyo Kagaku Zasshi* **1956**, *69*, 330–334.

(23) d'Emaus, H. M.; Bray, B.; Martin, J.; Anderson, L. *Ind. Eng. Chem.* **1957**, *49*, 1891–1896.

(24) Minoura, Y.; Nakajima, S. *J. Polym. Sci. Part A-1* **1966**, *4*, 2929–2944.

(25) Kearney, J. J.; Stannett, V.; Clark, H. G. *J. Polym. Sci. Part C* **1968**, 3441–3454.

(26) (a) Yamaguchi, T.; Ono, T. *Chem. Ind.* **1968**, 769–770. (b) Yamaguchi, T.; Nagai, K.; Ono, T. *Kobunshi Kagaku* **1969**, *26*, 463–470. (c) Yamaguchi, T.; Ono, T.; Kudo, E. *Kobunshi Kagaku* **1969**, *26*, 714–720.

(27) Bauer, R. S.; Lunk, H. E.; Youngman, E. A. *J. Polym. Sci., Part A-1* **1970**, *8*, 1915–1920.

(28) Ivin, K. J.; Walker, N. A. *J. Polym. Sci., Part B* **1971**, *9*, 901–906.

(29) Ballard, D. G. H.; Key, J. M. *Eur. Polym. J.* **1975**, *11*, 565–568.

(30) Cais, R. E.; Stuk, G. J. *Macromolecules* **1980**, *13*, 415–426.

(31) Odian, G. *Principles of Polymerization*, 4th ed.; Wiley-Interscience: Hoboken, NJ, 2004; pp 279−281.

(32) Ivin, K. J. *J. Polym. Sci., Part A, Polym. Chem.* **2000**, *38*, 2137–2146.

(33) Ivin, K. J., Saegusa, T. Eds. *Ring-Opening Polymerization*: Elsevier: New York, 1984; pp 1−81.

(34) Ivin, K. J.; Busfield, W. K. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley-Interscience: New York, 1988; Vol. 12, pp 555−605.

(35) (a) Yamada, B.; Kobatake, S. *Prog. Polym. Sci.* **1994**, *19*, 1089–1131. (b) Kobatake, S.; Yamada, B. *J. Polym. Sci., Part A, Polym. Chem.* **1996**, *34*, 95–108.

(36) (a) Ito, H.; Ueda, M. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 551–560. (b) Ueda, M.; Mano, M.; Mori, H.; Ito, H. *J. Polym. Sci., Part A, Polym. Chem.* **1991**, *29*, 1779–1787.

(37) Dainton, F. S.; Diaper, J.; Ivin, K. J.; Sheard, D. R. *Trans. Faraday Soc.* **1957**, *53*, 1269–1284.

(38) Dainton, F. S.; Ivin, K. J. *Q. Rev. Chem. Soc.* **1958**, *12*, 61–92.

(39) (a) Chikaoka, S.; Takata, T.; Endo, T. *Macromolecules* **1991**, *24*, 6557–6562. (b) Nishida, H.; Yamashita, M.; Endo, T.; Tokiwa, Y. *Macromolecules* **2000**, *33*, 6982–6986.

(40) Ando, S.; Watanabe, Y.; Matsuura, T. *Jpn. J. Appl. Phys., Part 1* **2002**, *41*, 5254–5258.

(41) Harwood, H. J.; Russell, D. B.; Verthe, J. J.; Zymonas, J. *Makromol. Chem.* **1973**, *163*, 1–12.

(42) Mango, L. A.; Lenz, R. W. *Makromol. Chem.* **1973**, *163*, 13–36.

(43) Hahn, S. F. *J. Polym. Sci., Part A, Polym. Chem.* **1992**, *30*, 397–408.

(44) Natori, I. *Kobunshi Ronbunshu* **2003**, *60*, 121–127.

(45) Boz, E.; Nemeth, A. J.; Ghiviriga, I.; Jeon, K.; Alamo, R. G.; Wagener, K. B. *Macromolecules* **2007**, *40*, 6545–6551.