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Photoinduced Depolymerization of Poly(olefin sulfone)s Possessing Photobase Generating Groups in the Side Chain

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ABSTRACT: A series of poly(olefin sulfone)s possessing photobase generating groups was synthesized, and photochemically induced depolymerization was investigated. The photobase generating groups used in this study produce primary or secondary amino groups by UV irradiation. The photochemically produced base extracts protons from the main chain of the poly(olefin sulfone) and induces a depolymerization reaction.

Introduction

Polymers that change their physical and/or chemical properties through absorption of light are called photopolymers.¹ There have been a number of studies on photopolymers; however, few have been known that exhibit photoinduced conversion to monomers under mild conditions. If the irradiated part of the polymer is converted completely into monomers, not only a decrease in the average molecular weight, such a process enables and has the potential for sophisticated device processing including stereolithography without the use of solvents. Polymers that can be depolymerized under mild conditions are expected to be reusable, which is a key element in green (sustainable) chemistry. However, most depolymerizable polymers known so far require γ -rays or electron beam irradiation for the depolymerization process.^{2,3} There are only a few that are known to exhibit depolymerization by low-energy irradiation.^{4–10} The unzipping degradation of a polymer main chain by irradiation was achieved in polymers containing heteroatoms in a main chain. It has been known that in the case of a poly-(1-butene sulfone), a partial depolymerization occurs, and olefins are involved in the gas produced by γ -rays or electron-beam irradiation.^{11,12} A poly(olefin sulfone) possesses sulfonyl groups ($-\text{SO}_2-$) in the main chain, and they are easily synthesized by radical polymerization of an olefin monomer in a liquefied sulfur dioxide.^{13,14} The olefin radical is unstable; however, the sulfonyl radical is fairly stable. The olefin radical generated in liquefied sulfur dioxide immediately reacts with a sulfur dioxide molecule and results in an alkylated sulfonyl radical. The sulfonyl radicals react with the olefin monomers, and a polymer chain is generated. The sulfur atom of the sulfonyl radical is positively charged, so that it cannot react with the positively charged sulfur atom of sulfur dioxide. Thus, the resulting poly(olefin sulfone) is a 1:1 alternating copolymer of olefin monomers and sulfur dioxides.¹⁵ The degradation of a poly(olefin sulfone) doped with a photosensitizer has been investigated. The degradation of poly-(1-butene sulfone) doped with pyridine *N*-oxide was induced by 300 nm irradiation.¹⁶ However, in this system, in addition to the degradation of the main chain, a crosslinking reaction also occurs. The number of photoinduced breaks in the main chain in this system was reported to be 10–12.

A sulfonyl group is a strong electron-withdrawing moiety. The electrons on the carbon atoms next to SO_2 are attracted by

SO_2 , and protons on that carbon can easily be withdrawn by bases.¹⁷ When a proton on this carbon is withdrawn, a chain reaction occurs in which the main chain of a poly(olefin sulfone) is depolymerized to the olefin monomer and sulfur dioxide (Scheme 1). The main chain of poly(olefin sulfone) decomposes when mixed with bases such as piperidine, methylamine, and triethylamine. Thus, if a poly(olefin sulfone) possessing a photobase-generating group is synthesized, it should exhibit depolymerization by photoirradiation (Figure 1). In this study, a series of poly(olefin sulfone)s that possess several photobase generating groups were synthesized, and their photochemical behavior was investigated.

Experimental Section

Samples. The structures of poly(olefin sulfone)s investigated in this study are shown in Schemes 2 and 3. Four types of photobase generating groups were incorporated, including the *o*-acyl oxime group (polymer **1**), 3,5-dimethoxybenzyloxy carbonyl group (polymers **2** and **8**), oxime urethane group (polymers **3**, **4**, and **9**), and [(*o*-nitrobenzyl)oxy]carbonyl group (polymers **5–7** and **10–13**). All these photobase generating groups exhibit a decarboxylation reaction and produce primary- or secondary-amino groups. The olefin monomers were synthesized according to procedures described in literature.^{18–22}

Acetophenone *o*-3-Butenoyloxime (1).¹⁸ Monomer **1** was obtained as white crystals, mp 45–46 °C. ¹H NMR (DMSO-*d*₆, 500 MHz): δ 2.38 (s, 3H, $-\text{CH}_3$), 3.38 (d, 2H, $-\text{CH}_2-$), 5.23 (dd, 2H, $-\text{CH}=\text{CH}_2$), 5.95 (m, 1H, $-\text{CH}=\text{CH}_2$), 7.50 (m, 3H, ArH), 7.75 (d, 2H, ArH). IR (KBr): 1757 (s, C=O), 1116 cm^{-1} (s, C–O). Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$ (203.24): C 70.92, H 6.45, N 6.89. Found: C 70.21, H 6.32, N 6.68. UV: λ_{max} 244 nm, ϵ_{365} 4, ϵ_{244} 13 833, ϵ_{254} 11 095.

***N*-Allyl-[(3, 5-dimethoxybenzyl)oxy]carbonyl Amine (2).**¹⁹ Monomer **2** was obtained as a transparent oil. ¹H NMR (CDCl_3 , 500 MHz): δ 3.78 (s, 6H, $-\text{OCH}_3$), 3.82 (t, 2H, $-\text{CH}_2-$), 4.90 (s, br, 1H, $-\text{NH}-$), 5.05 (s, 2H, $-\text{CH}_2-$), 5.15 (dd, 2H, $\text{CH}_2=\text{CH}-$), 5.85 (m, 1H, $\text{CH}_2=\text{CH}-$), 6.40 (t, 1H, ArH), 6.50 (d, 2H, ArH). IR (KBr): 3340 (s, N–H), 1707 (s, C=O), 1599 cm^{-1} (s, NH–CO). UV: λ_{max} 277 nm, ϵ_{365} 23, ϵ_{277} 2656, ϵ_{254} 1190.

Acetophenone Oxime Allylurethane (3).²⁰ Monomer **3** was obtained as white crystals, mp 40–41 °C. ¹H NMR (DMSO-*d*₆, 500 MHz): δ 2.36 (s, 3H, $-\text{CH}_3$), 3.76 (t, 2H, $-\text{CH}_2-$), 5.12 (dd, 2H, $-\text{CH}=\text{CH}_2$), 5.86 (m, 1H, $-\text{CH}=\text{CH}_2$), 7.48 (m, 3H, ArH), 7.79 (t, 1H, $-\text{NH}-$), 7.87 (d, 2H, ArH). IR (KBr): 3364 (s, N–H), 1715 (s, C=O), 1497 cm^{-1} (s, NH–CO). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2$ (218.25): C 66.04, H 6.47, N 12.84. Found: C 64.65, H 6.41, N 12.45. UV: λ_{max} 245 nm, ϵ_{254} 12 403, ϵ_{245} 14 808.

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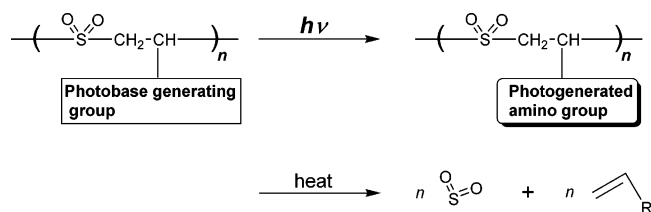
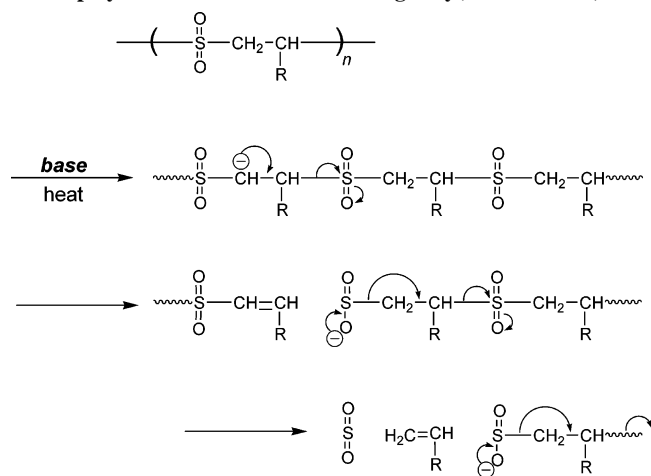


Figure 1. Photoinduced depolymerization of 1:1 alternating poly(olefin sulfone)s containing photobase generating groups in the side chain.

Scheme 1. Proposed Mechanism of Base-Catalyzed Thermal Depolymerization of 1:1 Alternating Poly(olefin sulfone)s



Depolymerization chain reaction

Benzophenone Oxime Allylurethane (4).²⁰ Monomer **4** was obtained as transparent yellow crystals, mp 107–108 °C. ¹H NMR (DMSO-*d*₆, 500 MHz): δ 3.72 (t, 2H, –CH₂–), 5.11 (dd, 2H, CH₂=CH–), 5.84 (m, 1H, CH₂=CH–), 7.34 (2H, ArH), 7.45 (2H, ArH), 7.53 (6H, ArH), 7.84 (1H, –NH–). IR (KBr): 3379 (s, N–H), 1717 (s, C=O), 1529 cm^{–1} (s, NH–CO). Anal. Calcd for C₁₇H₁₆N₂O₂ (280.32): C 72.84, H 5.75, N 9.99. Found: C 72.50, H 5.83, N 9.72. UV: λ_{max} 254 nm, ε₂₅₄ 15 190.

N-Allyl-[(*o*-Nitrobenzyl)oxy]carbonyl Amine (5).^{21,22} Monomer **5** was obtained as white crystals, mp 59–62 °C. ¹H NMR (DMSO-*d*₆, 500 MHz): δ 3.64 (t, 2H, –CH₂–), 5.09 (dd, 2H, CH₂=CH–), 5.37 (s, 2H, –CH₂–), 5.80 (m, 1H, CH₂=CH–), 7.25 (s, 1H, –NH–), 7.64 (m, 2H, ArH), 7.81 (t, 1H, ArH), 8.11 (d, 1H, ArH). IR (KBr): 3315 (s, N–H str), 1698 (s, C=O str), 1523 (s, asym N–O str), 1341 cm^{–1} (s, sym N–O str). Anal. Calcd for C₁₁H₁₂N₂O₄ (236.22): C 55.93, H 5.12, N 11.86. Found: C 55.20, H 5.01, N 11.73. UV: λ_{max} 258 nm, ε₃₆₅ 157, ε₂₅₄ 5981, ε₂₅₈ 6166.

N-Allyl-[methyl(2-nitrobenzyl)oxy]carbonyl Amine (6).^{21,22} Monomer **6** was obtained as a transparent oil. ¹H NMR (DMSO-*d*₆, 500 MHz): δ 1.55 (d, 3H, –CH₃), 3.54 (t, 2H, –CH₂–), 3.68 (s, 1H, –NH–), 5.03 (dd, 2H, CH₂=CH–), 5.72 (m, 1H, CH₂=CH–), 5.99 (m, 1H, –CH(CH₃)–), 7.56 (t, 1H, ArH), 7.69 (d, 1H, ArH), 7.97 (t, 1H, ArH), 7.67 (d, 1H, ArH). IR (KBr): 3336 (s, N–H str), 1702 (s, C=O str), 1524 (s, asym N–O str), 1349 cm^{–1} (s, sym N–O str). UV: λ_{max} 255 nm, ε₃₆₅ 400, ε₂₅₄ 5914, ε₂₅₅ 5923.

N-Allyl-[(2-nitro-4,5-dimethoxybenzyl)oxy]carbonyl Amine (7).^{21,22} Monomer **7** was obtained as white crystals, mp 108–109 °C. ¹H NMR (DMSO-*d*₆, 500 MHz): δ 3.66 (t, 2H, –CH₂–), 3.87 (d, 6H, OCH₃), 5.10 (dd, 2H, CH₂=CH–), 5.34 (s, 2H, –CH₂–), 5.81 (m, 1H, CH₂=CH–), 7.21 (s, 1H, ArH), 7.67 (s, 1H, –NH–), 7.70 (s, 1H, ArH). IR (KBr): 3340 (s, N–H str), 1707 (s, C=O str), 1527 (s, asym N–O str), 1345 cm^{–1} (s, sym N–O str). Anal. Calcd for C₁₃H₁₆N₂O₆ (296.28): C 52.70, H 5.44, N 9.46. Found: C 55.20, H 5.55, N 9.18. UV: λ_{max} 241 nm, ε₃₆₅ 4789, ε₂₅₄ 5480, ε₂₄₁ 12 713.

4-[N-Allylcarbamoxy]oxy-N-[(3,5-dimethoxybenzyl)oxy]carbonyl]piperidine (8).¹⁹ Monomer **8** was obtained as white crystals, mp 78–80 °C. ¹H NMR (CDCl₃, 500 MHz): δ 1.63 (br, 2H, cyclo), 1.88 (br, 2H, cyclo), 3.31 (br, 2H, cyclo), 3.79 (10H, –CH₂–, cyclo, –OCH₃), 4.75 (br, 1H, cyclo), 4.85 (s, 1H, –NH–), 5.06 (s, 2H, –CH₂–), 5.16 (dd, 2H, CH₂=CH–), 5.84 (m, 1H, CH₂=CH–), 6.41 (s, 1H, ArH), 6.50 (s, 2H, ArH). IR (KBr): 3306 (s, N–H), 1687 (s, C=O), 1543 cm^{–1} (s, NH–CO). Anal. Calcd for C₁₉H₂₆N₂O₆ (378.42): C 60.30, H 6.93, N 7.40. Found: C 59.67, H 6.79, N 7.62. UV: λ_{max} 278 nm, ε₃₆₅ 331, ε₂₇₈ 2891, ε₂₅₄ 1137.

XX4-[N-Allylcarbamoxy]oxy-N-[acetophenoneoxime Urethane]piperidine (9).²⁰ Monomer **9** was obtained as white crystals, mp 102–103 °C. ¹H NMR (CDCl₃, 500 MHz): δ 1.71 (br, 2H, cyclo), 1.96 (br, 2H, cyclo), 2.36 (s, 3H, –CH₃), 3.42 (br, 2H, cyclo), 3.82 (br, 4H, –CH₂–, cyclo), 4.79 (s, 1H, cyclo), 4.90 (s, 1H, –NH–), 5.17 (dd, 2H, CH₂=CH–), 5.86 (m, 1H, CH₂=CH–), 7.40 (m, 3H, ArH), 7.75 (d, 2H, ArH). IR (KBr): 3332 (s, N–H), 1725 (s, C=O), 1544 cm^{–1} (s, NH–CO). Anal. Calcd for C₁₈H₂₃N₃O₄ (345.39): C 62.59, H 6.71, N 12.17. Found: C 63.84, H 6.72, N 12.29. UV: λ_{max} 245 nm, ε₃₆₅ 207, ε₂₄₅ 17056, ε₂₅₄ 14299.

4-[N-Allylcarbamoxy]oxy-N-[(*o*-nitrobenzyl)oxy]carbonyl]piperidine (10).^{21,22} Monomer **10** was obtained as white crystals, mp 79–81 °C. ¹H NMR (CDCl₃, 500 MHz): δ 1.47 (br, 2H, cyclo), 1.83 (br, 2H, cyclo), 3.21 (br, 2H, cyclo), 3.60 (t, 2H, –CH₂–), 3.7 (br, 2H, cyclo), 4.7 (m, 1H, cyclo), 5.08 (dd, 2H, CH₂=CH–), 5.38 (s, 2H, –CH₂–), 5.8 (m, 1H, CH₂=CH–), 7.34 (t, 1H, –NH–), 7.64 (m, 2H, ArH), 7.79 (t, 1H, ArH), 8.09 (d, 1H, ArH). IR (KBr): 3275 (s, N–H str), 1708 (s, C=O str), 1521 (s, asym N–O str), 1338 cm^{–1} (s, sym N–O str). Anal. Calcd for C₁₇H₂₁N₃O₆ (363.37): C 56.19, H 5.83, N 11.56. Found: C 55.46, H 5.66, N 11.50. UV: λ_{max} 258 nm, ε₃₆₅ 331, ε₂₅₄ 5801.

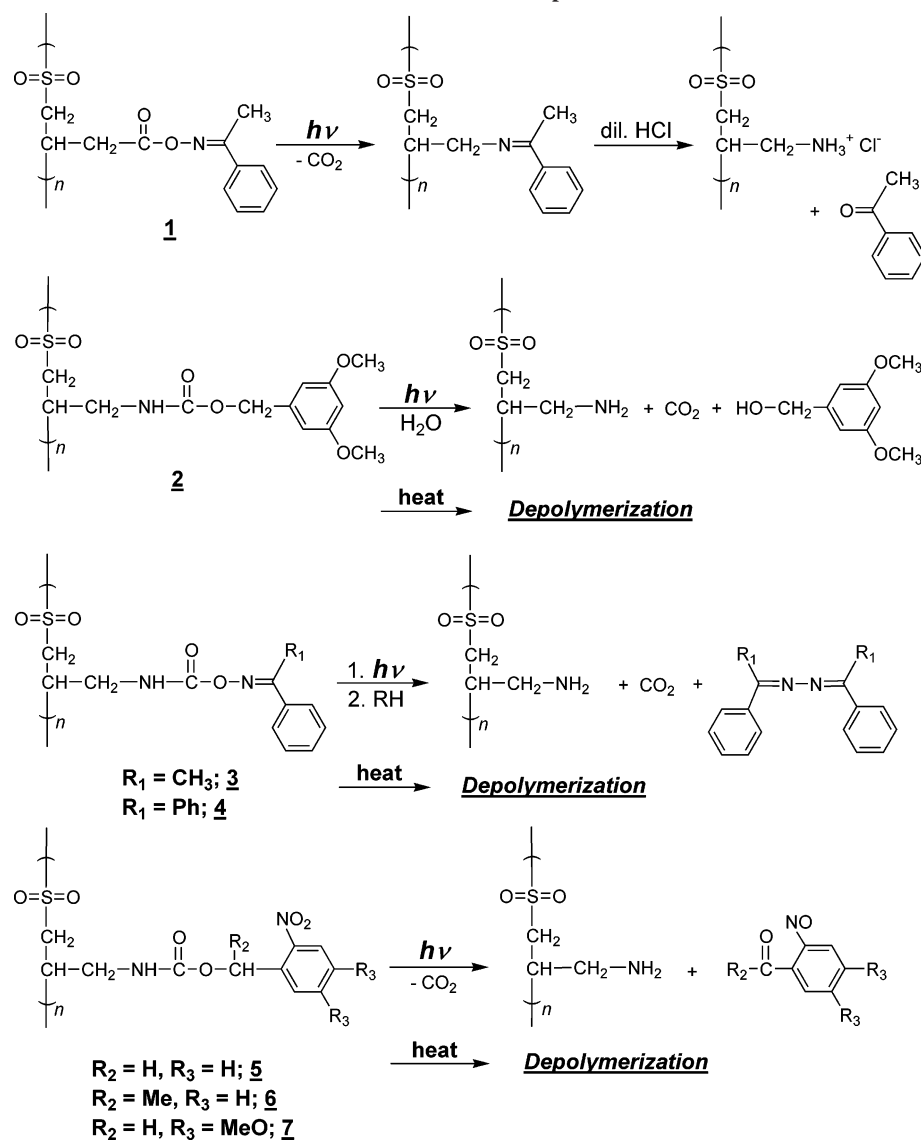
4-[N-Allylcarbamoxy]oxy-N-[[methyl(*o*-nitrobenzyl)oxy]carbonyl]piperidine (11).^{21,22} Monomer **11** was obtained as a transparent oil. ¹H NMR (CDCl₃, 500 MHz): δ 1.49 (br, 5H, cyclo, –CH₃), 1.83 (br, 2H, cyclo), 3.34 (br, 2H, cyclo), 3.61 (s, 2H, –CH₂–), 3.80 (br, 2H, cyclo), 4.7 (m, 1H, cyclo), 5.08 (dd, 2H, CH₂=CH–), 5.8 (m, 1H, CH₂=CH–), 6.0 (m, 1H, –CH(CH₃)–), 7.33 (s, 1H, –NH–), 7.56 (t, 1H, ArH), 7.72 (d, 1H, ArH), 7.78 (t, 1H, ArH), 7.95 (d, 1H, ArH). IR (KBr): 3323 (s, N–H str), 1708 (s, C=O str), 1525 (s, asym N–O str), 1321 cm^{–1} (s, sym N–O str).

4-[N-Allylcarbamoxy]oxy-N-[(2-nitro-4,5-dimethoxybenzyl)oxy]carbonyl]piperidine (12).^{21,22} Monomer **12** was obtained as yellow crystals, mp 119–120 °C. ¹H NMR (CDCl₃, 500 MHz): δ 1.65 (br, 2H, cyclo), 1.89 (br, 2H, cyclo), 3.34 (br, 2H, cyclo), 3.81 (br, 4H, –CH₂–, cyclo), 3.95 (d, 6H, –OCH₃), 4.74 (br, 1H, cyclo), 4.86 (s, 1H, –NH–), 5.17 (dd, 2H, CH₂=CH–), 5.52 (s, 2H, –CH₂–), 5.84 (m, 1H, CH₂=CH–), 6.97 (s, 1H, ArH), 7.70 (s, 1H, ArH). IR (KBr): 3324 (s, N–H str), 1709 (s, C=O str), 1525 (s, asym N–O str), 1321 cm^{–1} (s, sym N–O str). Anal. Calcd for C₁₉H₂₅N₃O₈ (423.42): C 53.90, H 5.95, N 9.92. Found: C 54.49, H 5.96, N 9.95. UV: λ_{max} 241 nm, ε₃₆₅ 3835, ε₂₄₁ 11 526, ε₂₅₄ 5107.

4-[Allylcarbonyl]oxy-N-[(*o*-nitrobenzyl)oxy]carbonyl]piperidine (13).^{21,22} Monomer **13** was obtained as a transparent oil. ¹H NMR (CDCl₃, 500 MHz): δ 1.68 (br, 2H, cyclo), 1.90 (br, 2H, cyclo), 3.11 (d, 2H, –CH₂–), 3.38 (br, 2H, cyclo), 3.75 (br, 2H, cyclo), 4.99 (m, 1H, cyclo), 5.18 (d, 2H, CH₂=CH–), 5.53 (s, 2H, –CH₂–), 5.92 (m, 1H, CH₂=CH–), 7.49 (t, 1H, ArH), 7.55 (d, 1H, ArH), 7.64 (t, 1H, ArH), 8.06 (d, 1H, ArH). IR (KBr): 1705 (s, C=O str), 1526 (s, asym N–O str), 1340 cm^{–1} (s, sym N–O str). UV: λ_{max} 255 nm, ε₃₆₅ 287, ε₂₅₅ 5266, ε₂₅₄ 5243.

Polymerization of the Poly(olefin sulfone)s. A polymerization tube (glass tube) containing 1 g of an olefin monomer and 3.2 × 10^{–4} mol of *tert*-butyl hydroperoxide (a redox initiator) was connected to a vacuum line and cooled in liquefied nitrogen. The tube was evacuated, and 6 g of sulfur dioxide was added by transfer via a vacuum line. The mixture was stirred for 24 h at –13 °C. The resulting polymer was reprecipitated in methanol. The polymer was washed several times with methanol and dried in vacuum at room temperature. The presence of SO₂ in a polymer was confirmed

Scheme 2. Structures of Poly(olefin sulfone)s That Generate Primary Amines by Photoirradiation and the Photochemical Reactions of the Pendant Group



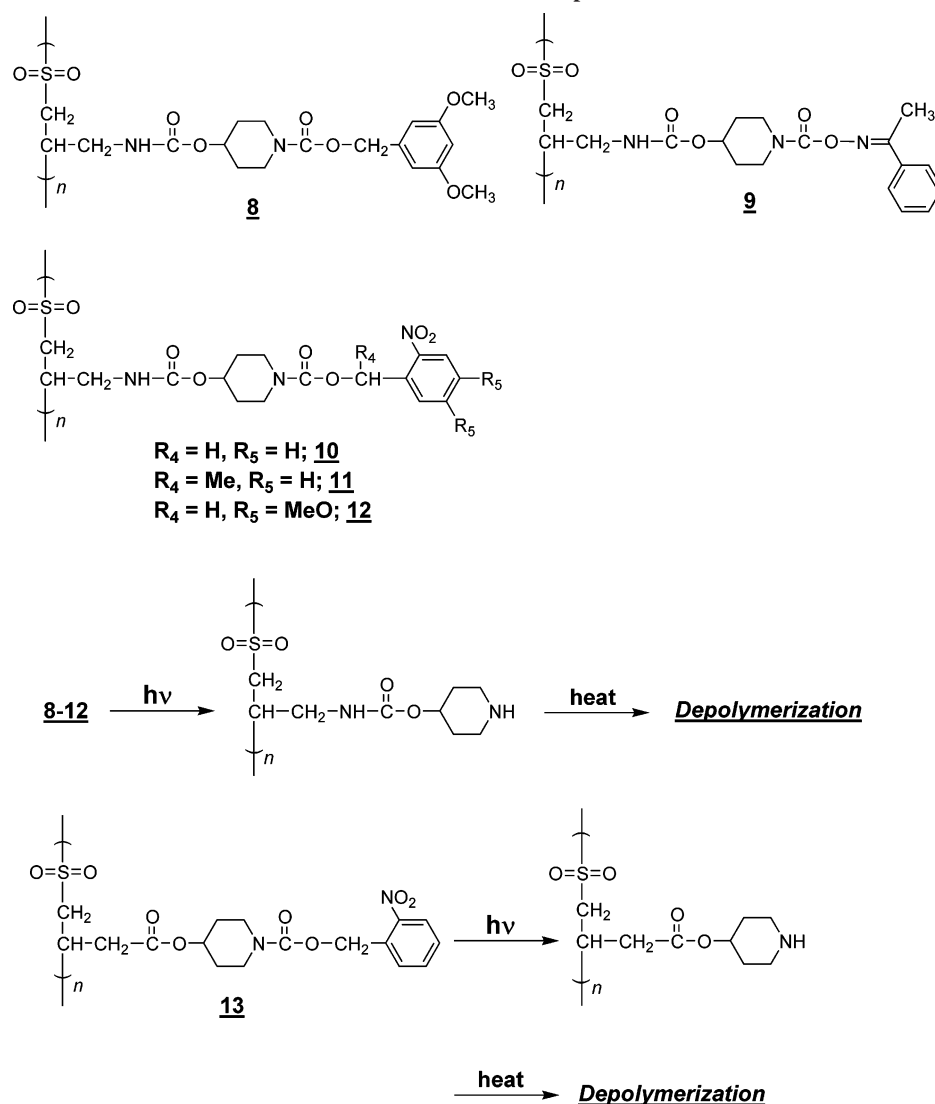
by FT-IR measurements (1311 and 1130 cm^{-1}) and NMR spectra. The copolymerization ratio was examined by elemental analysis. The physical properties of the polymers are listed in Table 1.

Each polymer was dissolved in DMSO, and the solution was spin-coated on a glass plate. The polymer films thus formed were heated on a hot plate at $100\text{ }^\circ\text{C}$ for 10 min. The thickness of the film was measured using an Alpha-step500 (KLA-Tencor) instrument.

Measurements. Infrared spectra were obtained with a JEOL JIR-5500 FT-IR spectrophotometer. The number-average molecular weight (M_n) of the polymer was determined by gel permeation chromatography (GPC; TOSOH HLC-8220 with Super Multipore HZ-M, eluent, THF), and the glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC; Mettler, DSC822e). The decomposition temperature was confirmed by thermogravimetric analysis (TGA, TA instruments, Hi-Res TGA2950). ^1H NMR spectra were measured by a JEOL EX-400 spectrometer (500 MHz). The polymer film was irradiated by a 250 W superhigh-pressure mercury lamp (USHIO, SX-UI250HQ). The intensity of the UV light was maintained at 32 (at 365 nm) and 23 mW/cm 2 (at 254 nm). A color filter (Toshiba, UVD-36C) and an interference filter were used to obtain monochromatic light.

Results and Discussion

Depolymerization of Poly(olefin sulfone)s Induced by Bases in Solutions. The depolymerization of poly(olefin sulfone)s in solutions induced by the addition of bases was investigated. Amino compounds were added to the DMSO- d_6 solutions of poly(*N,N*-diethyl 3-butenic amide sulfone) (DEBA), and the resulting compounds were examined. An amount of 5 mg of DEBA and 4,4'-trimethylenedipiperidine (0.8 mg, 4.0×10^{-3} mmol) were dissolved in DMSO- d_6 (0.7 mL) at room temperature. The solution was heated to $100\text{ }^\circ\text{C}$ for 30 min, and a dark yellow solution was obtained. Figure 2a shows the ^1H NMR spectrum of DEBA before addition of the base. After addition of the base, the ^1H NMR spectrum changed as shown in Figure 2b. Signals of the protons on an olefin were clearly observed. No change was observed in the DEBA solution without the addition of the base. This indicates that DEBA was decomposed by the added base. Figure 2c shows the ^1H NMR spectrum of the olefin monomer (*N,N*-diethyl 3-butenic amide). With the comparison of parts b and c of Figure 2, the major product in the resulting solution can be attributed to the DEBA

Scheme 3. Structures of Poly(olefin sulfone)s That Generate Secondary Amines by Photoirradiation and the Photochemical Reactions of the Pendant Group**Table 1. Physical Properties of the Polymers Used in This Study^a**

polysulfone	M_n^b	M_w/M_n^b	T_g (°C) ^d	T_d (°C) ^e
1	71 000	1.34	93	163
2	<i>c</i>	<i>c</i>	82	166
3	56 000	2.15	120	164
4	36 000	1.95	136	169
5	<i>c</i>	<i>c</i>	93	167
6	<i>c</i>	<i>c</i>	87	125
7	<i>c</i>	<i>c</i>	131	174
8	<i>c</i>	<i>c</i>	105	183
9	<i>c</i>	<i>c</i>	95	170
10	130 000	3.50	106	201
11	12 000	1.49	125	197
12	<i>c</i>	<i>c</i>	112	178
13	6 000	2.85	87	187

^a Polymerization was carried out with 54 μL of *t*-BuOOH as a redox initiator in liquid sulfur dioxide at -13°C for 24 h. ^b The molecular weight of the polymers was determined by gel permeation chromatography with polystyrene standards. ^c Insoluble in THF. ^d The glass transition temperature was obtained by differential scanning calorimetry (DSC) with a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 . ^e Measured by thermogravimetric analysis.

monomer. After removal of the $\text{DMSO}-d_6$ solvent, the residue was dissolved in chloroform and was separated by HPLC. The major product was identified to be *N,N*-diethyl 3-butenic amide by ^1H NMR and IR spectra. The decrease in the ^1H NMR signals of the methylene and methine protons of the polymer main chain

Table 2. Decomposition Ratio of DEBA by the Addition of Bases in $\text{DMSO}-d_6$ Solutions^a

base	$\text{p}K_a$	decomposition ratio (%)	depolymerization ratio (%)
triethylamine	11.10	59	44
piperidine	11.12	98	50
cyclohexylamine	10.66	86	42
pyridine	8.80	5	2

^a Reaction conditions: 100°C , 30 min. Base concentration: 6.15 mmol/L. In dimethylsulfoxide- d_6 .

(decomposition ratio) was found to be 98%. The yield of the monomer (depolymerization ratio) was measured to be 50% by ^1H NMR. The decomposition ratio of DEBA induced by the addition of triethylamine, piperidine, cyclohexylamine, and pyridine are summarized in Table 2. The results indicate that secondary amino groups are superior for inducing depolymerization of the poly(olefin sulfone)s.

Photochemical Base-Generation Reaction in the Polymer Films. The base generation reaction in poly(olefin sulfone) films was investigated. Films of polymers **1-3**, **5**, and **10** (Schemes 2 and 3) were irradiated with UV light, and the photochemical reactions of the base-generating groups were examined. The photobase generating moieties incorporated in this study exhibit a decarboxylation reaction when irradiated with UV light and

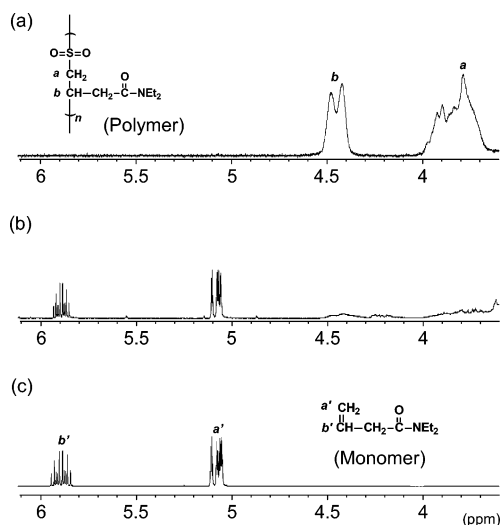


Figure 2. ¹H NMR spectra of DMSO-*d*₆ solutions of (a) DEBA, (b) DEBA mixed with 6.15 mmol/L 4,4'-trimethylenedipiperidine followed by heating at 100 °C for 30 min, and (c) a monomer of DEBA.

yield amino groups. The progress of the photochemical reaction in the 1 μm thick sample films coated on KBr plates were investigated by monitoring the decarboxylation reaction by FT-IR measurements.

When polymer **1** film is exposed to UV light, an *o*-acyl oxime group is photochemically converted into an imino group, which can be changed to an amino group by immersing the polymer film in a dilute HCl solution.^{23,24} It has been reported that the photochemical reaction of the *o*-acyl oxime group occurs most efficiently with 365 nm irradiation in the presence of benzophenone.²³ A film of polymer **1** doped with 10 wt % benzophenone was irradiated with 365 nm light. About 12% of *o*-acyl oxime groups were measured to be converted to imino groups by irradiation of 1 J/cm². The 3,5-dimethoxybenzyloxycarbonyl group (polymers **2** and **8**) directly produce amino groups by UV irradiation.^{19,25,26} A film of polymer **2** was irradiated with 254 nm UV light. The decomposition ratio of the 3,5-dimethoxybenzyloxycarbonyl group was measured to be 1% by irradiation of 1 J/cm². When the oxime urethane group (polymers **3**, **4**, and **9**) is exposed to UV light, an aminyl radical is formed through the photolysis of the oxime urethane group.^{20,27–29} This radical forms an amino group by hydrogen abstraction from RH (e.g., polymers or residual solvent). A film of polymer **3** with 10 wt % of benzophenone added as a sensitizer was irradiated with 365 nm light. About 7% of the oxime urethane groups were converted to amino groups by irradiation of 1 J/cm². The [(*o*-nitrobenzyl)oxy]carbonyl group (polymers **5** and **10**) absorbs 254 nm light and causes an internal oxidation–reduction reaction which produces an amino group.^{21,22,30–32} About 16% of the [(*o*-nitrobenzyl)oxy]carbonyl groups were converted to amino groups by 1 J/cm² irradiation.

The decomposed fractions of the photobase generating groups in polymers **1–3**, **5**, and **10** are plotted as a function of the irradiation energy in Figure 3. The decomposed fraction was increased with increasing irradiation energy. The [(*o*-nitrobenzyl)oxy]carbonyl group (polymers **5** and **10**) exhibited the highest photosensitivity.

Photoinduced Depolymerization of Polyolefinsulfone. The polymers used in this study produce base moieties by photoirradiation at room temperature and exhibit degradation of the main chain when heated to 150 °C. Figure 4 shows the change in the IR spectra of polymer **10** coated on a KBr plate before and after 254 nm light irradiation of 180 mJ/cm² and heating

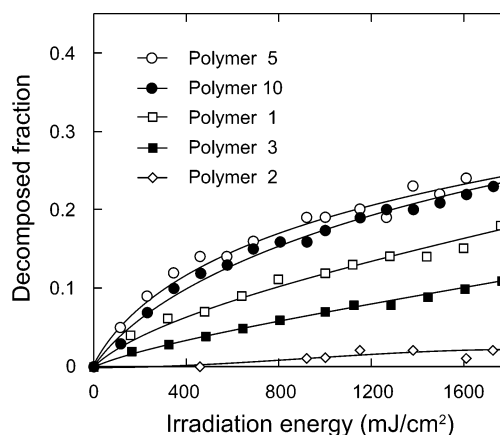


Figure 3. Decomposed fraction of photobase generating groups in the side chain as a function of the irradiation energy. Film thickness was approximately 1 μm.

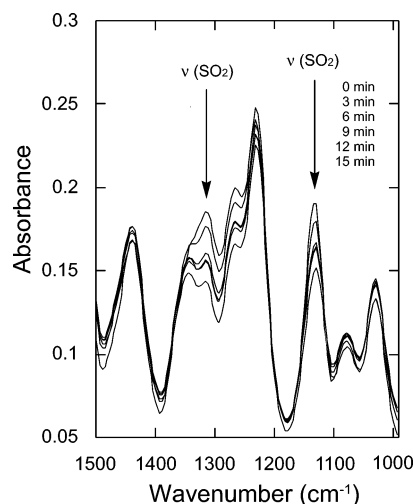


Figure 4. A change in the IR absorption spectrum of the sulfonyl group in polymer **10** coated on a KBr plate. Postexposure bake time was changed from 0 to 15 min at 150 °C after 254 nm irradiation at 180 mJ/cm².

(postexposure bake) at 150 °C for 15 min. The absorption peaks of the sulfonyl stretching band (1311 and 1130 cm⁻¹) decreased with increasing heating time. The decrease of the sulfonyl group in the film indicates decomposition of the main chain.

Photoinduced decomposition of the poly(olefin sulfone)s was investigated by ¹H NMR measurement. Figure 5 shows the ¹H NMR spectra of polymer **10** (part a) before and (part b) after irradiation at 600 mJ/cm² followed by heating at 150 °C for 15 min. The progress of depolymerization was confirmed by observing the disappearance of the methylene and methine protons in the main chain (4.3–3.8 ppm) and the appearance of signals at 5.1 and 5.8 ppm. By comparison with the ¹H NMR spectrum of the monomer (Figure 5c), the signals at 5.1–5.8 ppm can be attributed to the protons on a vinyl group. The decomposition ratio is obtained from a decrease of the main-chain signal (4.3–3.8 ppm). The decomposition ratio of polymer **10** irradiated at 600 mJ/cm² followed by heating at 150 °C for 15 min was estimated to be 95%. The decomposition ratio increased with increasing irradiation energy (Figure 6). The conversion of the polymer to the olefin monomer (depolymerization ratio) was estimated to be 50%. The irradiated film (polymer **10**) after heating was dissolved in THF, and the molecular weight was measured by GPC (Figure 7). The polymer completely disappeared and low-molecular weight species appeared. The retention time of the lowest molecular

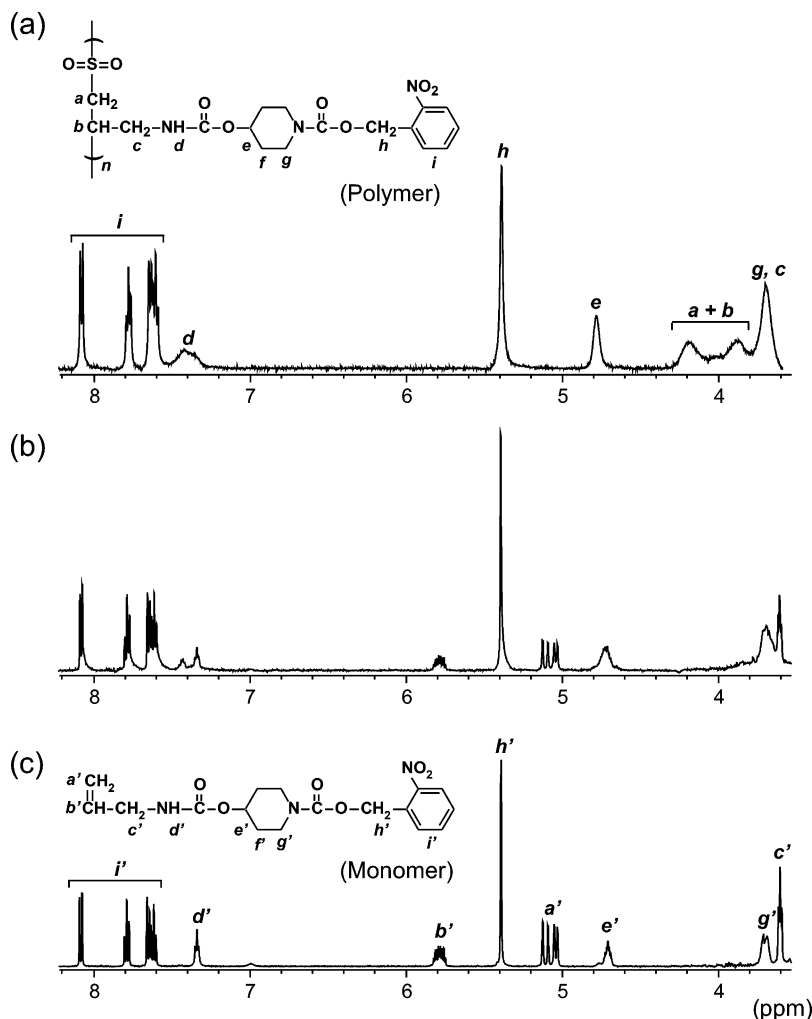


Figure 5. ^1H NMR spectra of polymer **10** in $\text{DMSO-}d_6$ (a) before UV irradiation, (b) after 254 nm irradiation of 600 mJ/cm^2 followed by heating at 150°C for 15 min, and (c) monomer **10**.

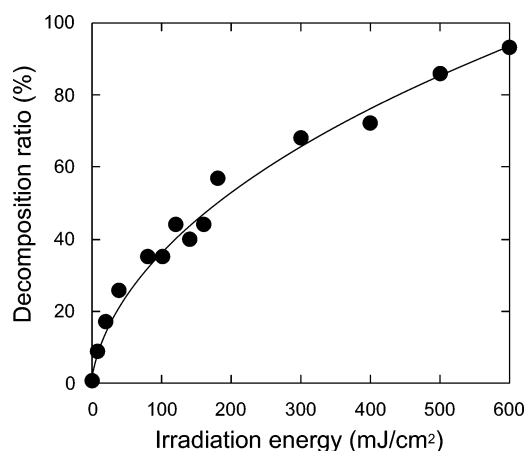


Figure 6. Decomposition ratio of polymer **10** heated at 150°C for 15 min after UV irradiation as a function of irradiation energy.

weight species was coincident with that of the olefin monomer. The number-average molecular weight decreased from 130 000 to 300. Polymers **2–13** exhibited photoinduced depolymerization. However, polymer **1** did not exhibit depolymerization. This was because the *o*-acyl oxime group produces an HCl salt of an amino group in the development process. The depolymerization ratio of polymers **1–13** are summarized in Table 3. The order of the magnitude of the depolymerization ratio of polymers **2–13** is coincident with the photosensitivities of the photobase

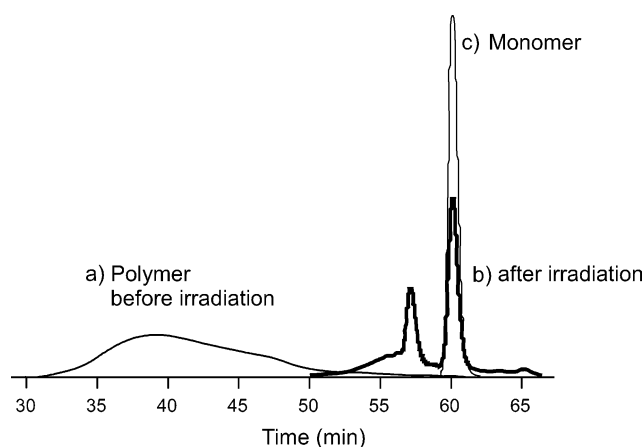


Figure 7. GPC curves of polymer **10** (a) before UV irradiation, (b) after UV irradiation at 600 mJ/cm^2 , followed by heating at 150°C for 15 min, and (c) the corresponding olefin monomer.

generating groups (Figure 3). Coincident with the results of the degradation in the basic solution, the photobase generator which produces a secondary amino group induced the most efficient depolymerization of poly(olefin sulfone)s.

The sensitivities of the polymers were also investigated. The polymer films were exposed to UV light (365 or 254 nm) and developed with 0.012 M HCl aqueous solution after a postexposure bake. The remnant film thicknesses were measured. All

Table 3. Depolymerization of Poly(olefin sulfone)s Induced by Photoirradiation

polysulfone	postexposure bake conditions	depolymerization ratio (%) irradiation energy (mJ/cm ²)		
		180 ^a	180 ^b	1000 ^b
1 ^c	130 °C, 10 min	0.0	0.0	0.0
2	120 °C, 15 min		0.6	0.9
3 ^c	100 °C, 15 min	0.9	0.5	3.0
4 ^c	100 °C, 15 min	0.3	1.6	3.7
5	130 °C, 15 min		4.2	6.9
6	130 °C, 15 min		5.9	6.9
7	120 °C, 15 min	1.5	1.3	1.4
8	120 °C, 15 min		<i>d</i>	<i>d</i>
9	120 °C, 10 min		2.0	3.0
10	150 °C, 15 min	19.5	25.0	50.0
11	140 °C, 15 min		12.9	18.8
12	110 °C, 15 min	6.8	11.2	13.1
13	140 °C, 10 min		12.2	20.4

^a Wavelength at 365 nm. ^b Wavelength at 254 nm. ^c Doped with 10 wt % of benzophenone as a sensitizer. ^d Depolymerization ratio of polysulfone 8 cannot be estimated since it is insoluble in a common deuterium solvent.

Table 4. Sensitivities of the Polymers Used in This Study

polysulfone	sensitivity ^a (mJ/cm ²)	developer
1	1900 ^{b,c}	0.012 M HCl(aq)
2		
3	900 ^{b,c}	0.012 M HCl(aq)
5	133 ^d	0.012 M HCl(aq)
10	98 ^d	0.012 M HCl(aq)

^a Complete film removal. ^b Doped with 10 wt % of benzophenone as a sensitizer. ^c Wavelength at 365 nm. ^d Wavelength at 254 nm.

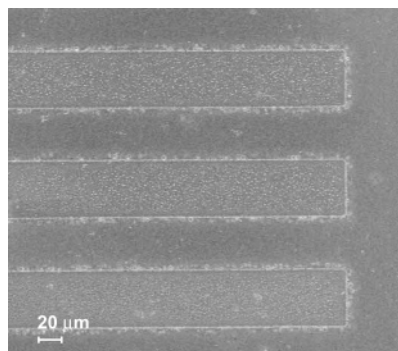


Figure 8. SEM image of polymer 10 film after UV irradiation at 100 mJ/cm², followed by heating at 130 °C for 60 s and washed with 0.012 M HCl(aq).

exposures were performed in air at room temperature. Subsequently, the polymer film was heated to 130 °C for 60 s and washed with 0.012 M HCl for 30 s. The photosensitivity of the polymer film was defined as the irradiation energy required to completely remove the irradiated parts. The sensitivities of polymers 1–3, 5, and 10 are summarized in Table 4. Since the polymers used in this study exhibit both a lowering of the molecular weight as well as a change in the polarity, they showed relatively high sensitivity to UV light.

The lithographic image of a 40 μm line and space on a film of polymer 10 developed with 0.012 M HCl aqueous solution is shown in Figure 8. A clear positive-tone image was obtained. Irradiation of 254 nm light resulted in the generation of a base with the creation of a latent image. The visible image was developed after heating the exposed polymer film to 130 °C for 60 s. Good quality positive images were also obtained for polymers 1–3 and 5.

Conclusions

A series of poly(olefin sulfone)s that possess photobase generating groups was synthesized, and the photochemical behavior was investigated. The poly(olefin sulfone)s exhibit unzipping depolymerization by low-energy irradiation. The decomposition ratio of polymer 10, one of the series, irradiated at 600 mJ/cm² followed by heating was estimated to be 95%. The use of the [(*o*-nitrobenzyl)oxy]carbonyl moiety as a photobase generating group was most effective for the unzipping depolymerization of poly(olefin sulfone)s.

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