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Novel aprotic polar polymers

1. Synthesis of aliphatic polysulfoxides

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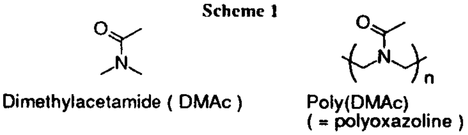
Summary

Aliphatic polysulfoxides having sulfoxide groups in the main chain were prepared by the selective oxidation of aliphatic polysulfides using aqueous hydrogen peroxide in chloroform. Degree of oxidation to sulfoxides was calculated from the integral ratios of methylene protons adjacent to sulfur atoms in ^{1}H-NMR spectra. Poly(hexamethylene sulfoxide) was subjected to Swern oxidation of primary or secondary alcohols, in which 1-octanol and 6-undecanol were oxidized to give octanal and 6-undecanone, respectively, in quantitative yields.

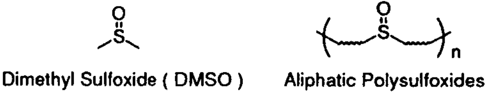
Introduction

Polyoxazoline having amide groups as the repeating units can be regarded as a polymer homolog of dimethylacetamide (DMAc) as shown in Scheme 1 (1). DMAc is known as one of the unique aprotic polar solvents and shows properties such as mixing with water freely and solubilizing several organic polymers. Similarly, polyoxazoline has high hydrophilicity and good compatibility with commodity polar polymers such as poly(vinyl chloride), poly(vinylidene fluoride) or polyamides (1). Thus, polyoxazoline can be regarded as an "aprotic polar polymer".

Scheme 1



Scheme 2



Dimethyl sulfoxide (DMSO) is also known as a unique aprotic polar solvent and is one of the organic solvents having the largest dielectric constant. Many reactions such as Williamson ether synthesis are promoted by using DMSO as a solvent (2). DMSO solubilizes several organic commodity polymers. DMSO is also used as an organic oxidizing reagent (3-7) and as a source of sulfur ylide (8). Therefore, aliphatic polysulfoxides as polymer homologs of DMSO (Scheme 2) are expected to show properties not only as aprotic polar polymers such as compatibility with other polymers but as reactive polymers or polymeric oxidizing reagents.

Sulfoxide compounds are prepared by selective oxidation of corresponding sulfides to avoid overoxidation to sulfones. Thus, aliphatic polysulfoxides as polymer homolog of DMSO are also expected to be prepared by careful oxidation of aliphatic polysulfides. There are several studies on the synthesis of aliphatic polysulfides. Ring-opening polymerizations of thiiranes (9) or thietanes (9b, 10), radical polyaddition of dithiols and diolefins (11), polycondensation of dihalides with dithiols catalyzed by phase transfer catalyst (12) are reported so far. Recently, synthesis of polysulfides by polycondensation of aromatic aldehydes with dithiols was also reported (13). However, there has been few examples of the studies on the oxidation of aliphatic polysulfides to polysulfoxides (14), and no property of the resulting aliphatic polysulfoxides has been reported. In this paper, synthesis of aliphatic polysulfoxides by the effective oxidation of aliphatic polysulfides is described. These new aprotic polar polymers are expected as novel compatibilizer, polymer solvent, polymeric oxidizing reagent and so on. Aliphatic polysulfoxides can

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also be expected as novel reactive polymers. Here, we also present the preliminary results about the possibility as polymeric oxidizing reagents of these aliphatic polysulfoxides.

Results and discussion

Synthesis of aliphatic polysulfides. Aliphatic polysulfides were prepared by polyaddition between aliphatic or aromatic diolefins and aliphatic dithiols using azobis(isobutyronitrile) as a radical initiator (Scheme 3) (11). All reactions were carried out in benzene at 60°C for 12 hours.

Scheme 3. Polyaddition between diolefins and dithiols

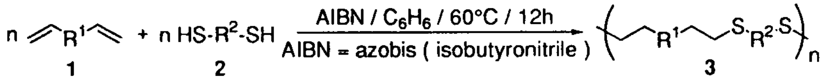
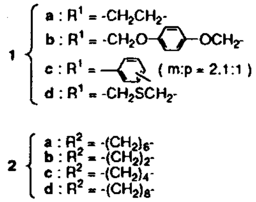


Table 1. Radical Polyaddition between Dienes (1) and Dithiols (2)

entry	1	2	AIBN (mol%)	3	yield (%)	M_n	M_w / M_n
1	a	a	1	a	78	6200	1.91
2	a	b	0.5	b	75	2400	2.04
3	a	c	0.5	c	92	8000	1.88
4	a	d	1	d	98	3300	2.01
5	b	a	1	e	98	2000	1.65
6	c	a	1	f	98	3200	3.35
7	d	a	1		no polymerization		



The results are summarized in Table 1. In the reactions between 1,6-hexadiene **1a** and aliphatic dithiols **2a-2d** (entries 1-4), aliphatic polysulfides **3a-3d** with molecular weights between 2400 and 8000 were obtained in fair to good yields. This relatively low molecular weight would be due to the influence of residual oxygen in the reaction vessel. Previous literature said that the molecular weight of polysulfides prepared by polyaddition between diynes and dithiols reached tens of thousands in the system in which oxygen was completely removed (15). When aromatic diolefins were used as shown in entries 5 and 6, the corresponding polysulfides **3e** and **3f** were prepared in good yields.

As a typical example, ^{1}H-NMR spectrum of poly(hexamethylene sulfide) **3a** is shown in Figure 1, in which a small doublet peak is observed at 1.26ppm. This result indicates that only a few thiol groups (4.7%) were reacted in Markovnikov addition. In other aliphatic polysulfides, only small or no peak due to Markovnikov addition was observed except for **3f**, in which about 18% of thiol groups were found to react in Markovnikov addition. Thus, the main structures in polysulfides **3** were proved to be anti-Markovnikov addition products as illustrated in Scheme 3.

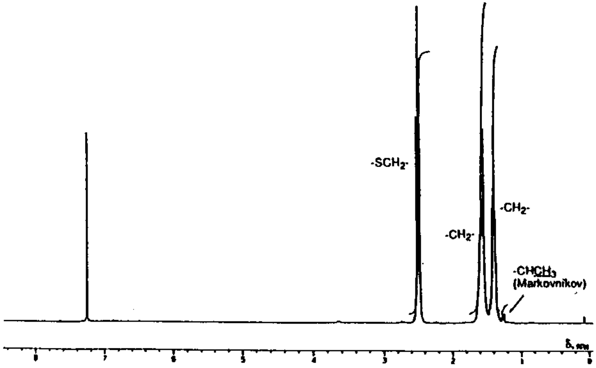


Figure 1. ^{1}H-NMR Spectrum of Poly(hexamethylene sulfide) **3a**.

Oxidation of aliphatic polysulfides. Poly(hexamethylene sulfide) **3a** was typically used as a the starting polysulfide for the preparation of polysulfoxide. All oxidation reactions were carried out with 30% aqueous hydrogen peroxide in chloroform (Scheme 4) (14a). The degree of oxidation was calculated from integral ratios of methylene protons adjacent to sulfur atoms by ^{1}H-NMR spectrum (Figure 2, *vide infra*). Comparison of molecular weights was carried out by using crude products. Table 2

Scheme 4. Oxidation of Poly(hexamethylene sulfide) 3a.

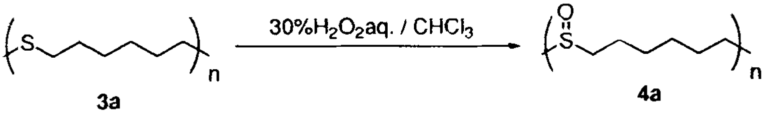


Table 2. Oxidation of 3a to 4a by Aqueous Hydrogen Peroxide

entry	H_2O_2 (eq.)	time (hrs)	temp.	yield (%)	-S- : -SO- : -SO_2- [a]	M_n (3a → 4a) [b]	M_w / M_n
1	1	17	r.t.	48	30 : 70 : 0	4200 → 2200	1.27
2	1	35	r.t.	70	32 : 68 : 0		
3	1	5	reflux	82	0 : 78 : 22		
4	10	17	r.t.	63	20 : 80 : 0		
5	20	17	r.t.	77	**5 : 92 : 3**	3100 → 2300	1.28
6	30	17	r.t.	47	6 : 89 : 5		

a) The ratio was determined from the results of ^{1}H - NMR spectra.
b) M_ns of **4a** are of crude products.

summarizes the results. The reaction with 20 equivalents of H_2O_2 for 17 hours at room temperature gave the best result, that is, the production of the polymer having 92% of sulfoxide units in the main chain with little formation of sulfone units (entry 5). The comparison of the molecular weight of crude **4a** prepared under this condition with that of the starting polysulfide **3a** showed that the decrease of molecular weight during oxidation was not so serious. It can be said that main-chain scission by oxidizing reagent is not very significant. The effective oxidation of sulfide groups to sulfoxides would be explained by assuming that the over-contact of polymer molecules with oxidizing reagent is suppressed by two-phase reaction of polymer-containing chloroform layer and H_2O_2-containing water layer (14a).

Figure 2 shows ^{1}H-NMR spectra of poly(hexamethylene sulfide) **3a** and poly(hexamethylene sulfoxide) **4a**. These NMR charts are of the methylene protons adjacent to sulfur atoms. After the oxidation of polysulfide **3a** to polysulfoxide **4a**, the shift of the peak from 2.5ppm to 2.6-2.8 ppm was observed. The multiplicity of this peak is because two methylene protons adjacent to sulfoxide group are under chemically different environment (Figure 4) and two sets of doublet-doublet peaks are observed in this area. The peak around 3.0 ppm is assigned to that of methylene protons next to the sulfone units. From this result, it is supported that polysulfide was oxidized to polysulfoxide effectively.

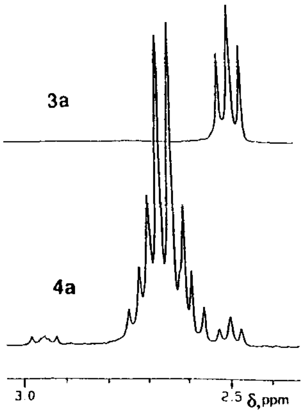


Figure 2. ^{1}H-NMR Spectra of **3a** and **4a**.

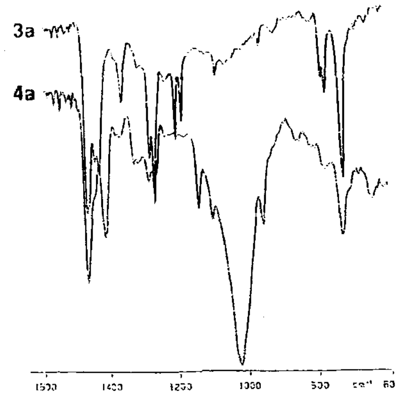


Figure 3. IR Spectra of **3a** and **4a**.

IR spectra of polysulfide **3a** and polysulfoxide **4a** are illustrated in Figure 3. The oxidation of **3a** resulted in the appearance of new absorption around 1,000cm^{-1}, which is assignable to the stretching band of the sulfoxide S=O double bond. From these IR spectra, the formation of polysulfoxide was also supported.

The oxidation of other polysulfides **3** was also examined (Scheme 5). The reactions were carried out under two conditions, that is, (**i**) 20 equivalents of H_2O_2, at room temperature, and 17 hours stirring, and (**ii**) 1 equivalent of H_2O_2, at reflux temperature and 4-6 hours stirring. The degree of oxidation was calculated from integrals of methylene protons adjacent to sulfur atoms by ^{1}H-NMR spectrum as mentioned above.

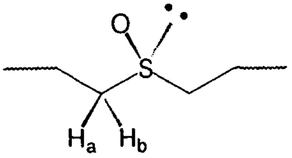
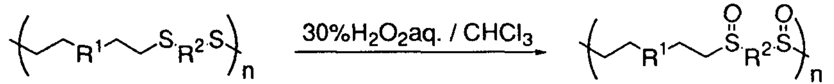


Figure 4. Asymmetry of Two Methylene Protons of Polysulfide Adjacent to a Sulfoxide Group.

Scheme 5. Synthesis of Aliphatic Polysulfoxides 4.

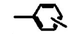


3 **4**

i) 20eq. of H_2O_2 , r.t. , 17h

ii) 1eq. of H_2O_2 , reflux , 4-6h

Table 3. Oxidation of Various Polysulfides **3** to Polysulfoxides **4**.

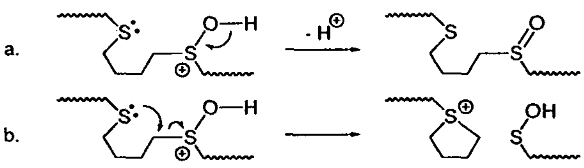
entry	R^1	R^2	condition	yield (%)	-S- : -SO- : -SO$_2$- $^{a)}$	M_n (4)	M_w / M_n
1	-(CH$_2$)$_2$-	-(CH$_2$)$_6$-	i	77 (**4a**)	5 : 92 : 3	2300	1.28
2	-(CH$_2$)$_2$-	-(CH$_2$)$_2$-	i	52 (**4b**)	56 : 44 : 0	3200	2.38
3	-(CH$_2$)$_2$-	-(CH$_2$)$_2$-	ii	32 (**4b**)	46 : 37 : 17	1600	1.71
4	-(CH$_2$)$_2$-	-(CH$_2$)$_4$-	i	24 (**4c**)	12 : 83 : 5	2400	1.26
5	-(CH$_2$)$_2$-	-(CH$_2$)$_8$-	ii	88 (**4d**)	0 : 94 : 6	2600	1.23
6		-(CH$_2$)$_6$-	ii	58 (**4e**)	8 : 92 : 0	3100	2.23
7	 (m:p = 2.1: 1)	-(CH$_2$)$_6$-	ii	74 (**4f**)	12 : 62 : 26	6500	2.77

a) The ratio was determined from the results of ^{1}H-NMR spectra.

The results are summarized in Table 3. When R^2 was two methylene groups as in entries 2 and 3, the effective oxidation failed to occur. This would be because the two sulfur atoms are too close to each other and, as a result, when one of them is oxidized, the other is influenced by the steric or electronic effect of the neighboring sulfoxide group. Thus when R^2 was four or eight methylene groups (entries 4 and 5) or when R^1 had aromatic groups (entry 6), the effective oxidation to polysulfoxides was observed under condition **i** or **ii**, as in the case of poly(hexamethylene sulfoxide) **4a** (entry 1).

When R^2 was four methylene groups (entry 4), the yield of polysulfoxide **4c** was low and the large decrease of molecular weight was observed (8000 →2400). The reason for this low yield and decrease of molecular weight would be because of main chain scission by intramolecular substitution by neighboring sulfur atom as shown in Scheme 6b. This type of back-biting might happen in the oxidation of other polysulfides.

Scheme 6



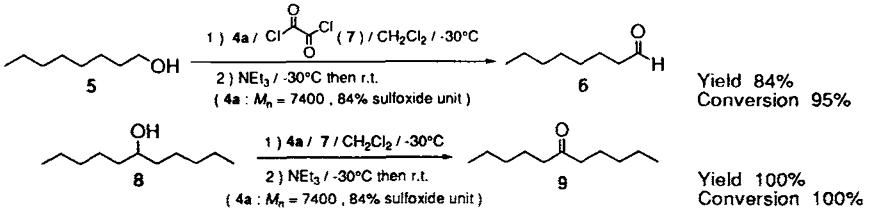
In entry 7, here the polymer had aromatic group in the main chain without ether bond, only moderate degree of oxidation to sulfoxide was achieved. This would be due to large amount of Markovnikov addition structure in the main chain of this polymer and the resulting steric hindrance by methyl group adjacent to sulfur atom. From the results of

Table 3, the two-phase oxidation of aliphatic polysulfides described above is regarded as good method to obtain aliphatic polysulfoxides.

Oxidation of alcohols by poly(hexamethylene sulfoxide). DMSO is known as the organic oxidizing reagent for the oxidation of alkyl halides, alcohols, sulfonates to the corresponding aldehydes or ketones (3-7). Thus, by using polymer homologs of DMSO instead of DMSO itself, the oxidation of alcohols or alkyl halides to the corresponding carbonyl compounds can be expected. Especially, in the oxidation of polymeric alcohols or poly(vinyl halide)s, the enhancement of conversion and/or acceleration of the reaction are expected by the so-called "polymer effect". Recycling of the polymer as an oxidizing reagent is also possible. In the oxidations using DMSO, Swern oxidation, in which alcohols are quantitatively oxidized to carbonyl compounds by using oxalyl chloride as an activator, is one of the most convenient method due to its mild condition, easy handling of reagents and no by-products difficult to separate (5). Here, preliminary attempts to oxidize primary or secondary alcohols by Swern oxidation using poly(hexamethylene sulfoxide) **4a** are investigated.

From the mechanism of Swern oxidation, it is obvious that the hydrogen at carbon(s) next to sulfoxide is needed (5, 16). The aliphatic polysulfoxides obtained in the present study are comfortable in this requirement. So, we examined the oxidation of 1-octanol and 6-undecanol by poly(hexamethylene sulfoxide) **4a**.

Scheme 7. Swern Oxidation of Alcohols by 4a.



Three equivalents of **4a** and 1.5 equivalents of oxalyl chloride **7** were used in the reactions, and the oxidation was carried out at -30°C for 1 hour followed by stirring with triethylamine for 20 minutes at the same temperature. The results are summarized in Scheme 7. From the results, it was found that 1-octanol and 6-undecanol were oxidized to give octanal and 6-undecanone, respectively, in quantitative yields. These results suggest that aliphatic polysulfoxides are effective oxidizing reagents (5, 16).

Isolation of products was easy and carried out as follows. The reaction mixture was extracted with CH_2Cl_2 and NH_4Claq., the organic layer was dried over $MgSO_4$ and then

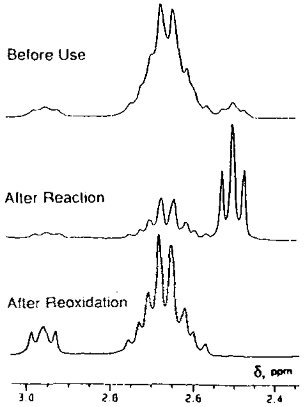


Figure 5. Change of ^{1}H-NMR Spectra of Poly(hexamethylene sulfoxide) **4a**.

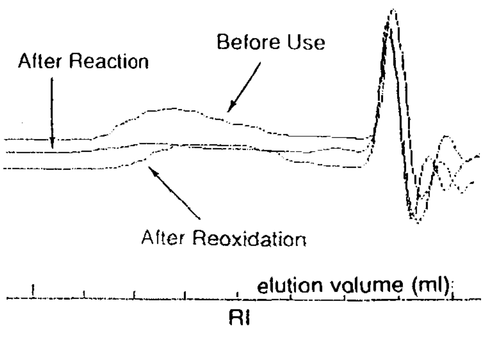


Figure 6. Change of GPC Traces of Poly(hexamethylene sulfoxide) **4a**.

solvent was evaporated. The resulting residue was dissolved in chloroform and poured into n-hexane. By collecting and evaporating the supernatant, the desired carbonyl compound was obtained. Unlike usual Swern oxidation, there is no bad smell derived from dimethyl sulfide in this method. Reoxidation of the polymer used to oxidize 6-undecanol was also investigated. Reoxidation was carried out by the same method as described in the oxidation of aliphatic polysulfides to polysulfoxides, that is, the reaction with 20 equivalents of hydrogen peroxide (30%, aqueous) against S=O units in chloroform. The results are shown in Figure 5 and Figure 6. Figure 5 represents ^{1}H-NMR spectra of poly(hexamethylene sulfoxide) **4a** before use, after Swern oxidation and after the polymer was reoxidized. The increase of sulfide units was observed after the polymer was used for the oxidation of the alcohol. It is also obvious that sulfide units in the polymer were reoxidized to sulfoxide units effectively. Figure 6 shows GPC traces of the polymers used, in which the number average molecular weights M_ns were calculated as 7400 (before use), 7900 (after Swern oxidation) and 2600 (after reoxidation). Decrease of molecular weight was observed when reoxidation was carried out, but the molecular weight of the resulting polymer is sufficient to show the characteristic property as a polymeric oxidizing reagent.

Conclusions

Aliphatic polysulfoxides with various length of methylene chain between sulfurs were prepared by polyaddition of diolefins with dithiols and the following oxidation of the resulting polysulfides. The effective oxidation of polysulfides by using aqueous hydrogen peroxide in chloroform with or without heating resulted in the production of novel aliphatic polysulfoxides. The formation of polysulfoxides was strongly supported by spectroscopic analyses. The compatibility of the aliphatic polysulfoxides with other polymers will be reported in the forthcoming paper.

Preliminary studies to utilize aliphatic polysulfoxides as polymeric oxidizing reagents were also attempted, and the results clearly showed that they would be useful reagents for the oxidation of alcohols to the corresponding carbonyl compounds. These new oxidizing reagents have the advantages that it is recovered and reused after reoxidation of polysulfide moiety. In the oxidation of polymeric compounds, it is expected that reactions are accelerated and/or that conversion is increased by polymer effect, and further studies of oxidation of polymers are under way.

Experimental section

General. ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a JEOL JNM-EX270 spectrometer (270MHz for ^{1}H-NMR and 67.9MHz for ^{13}C-NMR) in chloroform-d. IR spectra were recorded on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh UV-8011 and RI-8000 (Shodex K-803L column) by using chloroform as eluent after calibration with standard polystyrene.

Unless otherwise noted, materials were obtained from commercial sources and used after distillation under nitrogen. Benzene was distilled under nitrogen from sodium diphenylketyl, chloroform from P_2O_5. Dichloromethane and triethylamine was distilled under nitrogen from CaH_2. 2,2'-Azobis(isobutyronitrile) was recrystallized from methanol. 30% hydrogen peroxide aqueous solution was used as received. 6-Undecanone was purchased from Tokyo Kasei Kogyo and used as received.

Polyaddition between 1,5-hexadiene (1a) and 1,6-hexanedithiol (2a). To a 60ml benzene solution of azobis(isobutyronitrile) (AIBN, 49.6mg, 0.3mmol) were added **1a** (7.08ml, 60.0mmol) and **2a** (9.18ml, 60.0mmol). The mixture was stirred for 12 hours at 60°C. After cooling, a white precipitate appeared and suction filtration of the mixture gave poly(hexamethylene sulfide) (**3a**) in 78%. All the spectroscopic analyses and GPC measurements were performed without further purification. **3a**: ^{1}H-NMR(δ, ppm) 1.26($-CH_3$, d, J=6.8Hz, trace), 1.39($-CH_2-$, m, 4H), 1.57($-CH_2-$, m, 4H), 2.50($-SCH_2-$, t, J=7.3Hz, 4H); IR(neat) 2932, 2852, 1465, 1353, 1427, 1276, 1262, 1198, 1179, 724cm^{-1}.

Polyaddition between various dienes and dithiols. The following aliphatic polysulfides were prepared in a similar manner as mentioned above. **3b** from **1a** (3.54ml, 30.0mmol) and **2b** (2.52ml, 30.0mmol) in 75% yield: ^{1}H-NMR(δ, ppm) 1.28(-CH_3, trace), 1.40(-CH_2-, m, 4H), 1.59(-CH_2-, m, 4H), 2.54(-SCH_2-, t, J=7.3Hz, 4H), 2.71(-SCH_2CH_2S-, m, 4H). **3c** from **1a** (3.54ml, 30.0mmol) and **2c** (3.52ml, 30.0mmol) in 92% yield: ^{1}H-NMR(δ, ppm) 1.25(-CH_3, trace), 1.40(-CH_2-, m, 4H), 1.58(-CH_2-, m, 4H), 1.68(-CH_2-, m, 4H), 2.51(-SCH_2-, m, 8H). **3d** from **1a** (1.19ml, 10.0mmol) and **2d** (1.85ml, 10.0mmol) in 98% yield: ^{1}H-NMR(δ, ppm) 1.32-1.42(-CH_2-, m, 12H), 1.57(-CH_2-, m, 8H), 2.50(-SCH_2-, t, J=6.8Hz, 8H). **3e** from **1b** (1.91g, 10.0mmol) and **2a** (1.53ml, 10.0mmol) in 85% yield: ^{1}H-NMR(δ, ppm) 1.38(-CH_2-, m, 4H), 1.58(-CH_2-, m, 4H), 2.02(-CH_2-, tt, J=6.8, 6.8Hz, 4H), 2.51(-SCH_2-, t, J=7.2Hz, 4H), 2.68(-SCH_2-, t, J=7.0Hz, 4H), 4.00(-OCH_2-, t, J=6.1Hz, 4H), 6.82(-C_6H_4-, s, 4H). **3f** from **1c** (m : p = 2.1:1, 1.30g, 10.0mmol) and **2a** (1.53ml, 10.0mmol) in 98% yield: ^{1}H-NMR(δ, ppm) 1.14(-CH_3, m, Markovnikov addition(18%)), 1.30(-CH_2-, m, 4H), 1.50(-CH_2-, m, 4H), 2.26(-$CHSCH_2$-, t, J=7.1Hz, Markovnikov addition(18%)), 2.43(-SCH_2-, t, J=7.2Hz, 4H), 2.53(-CHS-, m, Markovnikov addition(18%)), 2.65(-$ArCH_2$-, br, 4H), 2.76(-$ArCH_2CH_2S$-, t, J=7.2Hz, anti-Markovnikov addition (82% of 4H)), 6.80-7.10(-C_6H_4-, m, 4H).

Oxidation of poly(hexamethylene sulfide)(3a) to poly(hexamethylene sulfoxide)(4a). Poly(hexamethylene sulfide) (**3a**) was prepared as described above and used without further purification. To a chloroform (80ml) solution of **3a** (0.50g, 4.3mmol of sulfur) under nitrogen atmosphere was added 30% aqueous hydrogen peroxide (8.71ml, 86.0 mmol). The reaction mixture was vigorously stirred at room temperature. After 17 hours stirring, the mixture was extracted with chloroform and brine. The drying over magnesium sulfate and the evaporation of the solvent gave a white solid. All the spectroscopic analyses and GPC measurements were carried out without further purification. **4a**: ^{1}H-NMR(δ, ppm) 1.54(-CH_2-, m, 4H), 1.81(-CH_2-, m, 4H), 2.50(-SCH_2-, t, J=7.2Hz, 5% of 4H), 2.60+2.71(-$S(O)CH_2$-, dd+dd, J=13.1, 8.0Hz+13.2, 7.3Hz, 92% of 4H), 2.95(-$S(O)_2CH_2$-, t, J=8.1Hz, 3% of 4H); ^{13}C-NMR(δ, ppm) 8.48, 21.5, 21.7, 22.3, 22.4, 28.0, 28.3, 29.2, 29.4, 31.8, 31.9, 45.7, 52.1, 52.2, 52.5; IR(neat) 2926, 2856, 1653, 1466, 1410, 1356, 1321, 1279, 1259, 1135, 1096, 1024, 951, 730cm^{-1}. **4a** can be purified by reprecipitation from chloroform into n-hexane and following freeze-drying, and was obtained in 77% yield.

Oxidation of other aliphatic polysulfides prepared by polyaddition. By a procedure similar to that described for **4a**, the following aliphatic polysulfoxides were prepared. In cases of **4d**, **4e** and **4f**, the reaction mixture was stirred for 4-6 hours at reflux temperature of chloroform. In the oxidation of **3b**, effective oxidation failed to occur. **4c** from **3c** (1.00g, 9.78mmol): ^{1}H-NMR(δ, ppm) 1.25(-CH_3, m, trace), 1.52(-CH_2-, m), 1.68(-CH_2-, m), 1.78(-CH_2-, m), 1.97(-CH_2-, m, 12H of peaks 1.52-1.97), 2.50(-SCH_2-, m, 12% of 8H), 2.70(-$S(O)CH_2$-, m, 83% of 8H), 2.98(-$S(O)_2CH_2$-, m, 5% of 8H). **4d** from **3d** (0.30g, 2.30mmol): ^{1}H-NMR(δ, ppm) 1.26-1.71(-CH_2-, m, 12H), 1.77(-CH_2-, m, 8H), 2.65(-$S(O)CH_2$-, m, 96% of 8H), 2.95(-$S(O)_2CH_2$-, m, 4% of 8H). **4e** from **3e** (0.30g, 1.76mmol): ^{1}H-NMR(δ, ppm) 1.55(-CH_2-, m, 4H), 1.82(-CH_2-, m, 4H), 2.02(-CH_2-, m, 8% of 4H), 2.25(-CH_2-, tt, J=6.5Hz, 92% of 4H), 2.52(-SCH_2-, m, 8% of 4H), 2.70(-SCH_2- + -$S(O)CH_2$-, m, 8%+92% of 4H), 2.86(-$S(O)$-CH_2-, m, 92% of 4H), 4.06(-OCH_2-, m, 4H), 6.82(-C_6H_4-, s, 4H). **4f** from **3f** (0.81g, 5.78mmol): ^{1}H-NMR(δ, ppm) 1.25(-CH_3, m, Markovnikov addition product), 1.38(-CH_2-, m, 4H), 1.48(-CH_2-, m, 4H), 1.79(-CH_2-, m, 4H), 2.46(-$ArCH_2$-, m, 12% of 4H), 2.64(-$ArCH_2$- + -SCH_2-, m, 62% of 4H+12% of 4H), 2.92(-$S(O)CH_2$-, m, 62% of

4H), 2.99(-$S(O)_2CH_2$-, m, 26% of 4H), 3.07(-$S(O)CH_2$-, m, 62% of 4H), 3.20(-$S(O)_2CH_2$-, m, 26% of 4H), 6.70-7.36(-C_6H_4-, m, 4H).

Oxidation of 1-octanol and 6-undecanol by poly(hexamethylene sulfoxide) (4a). A general procedure is described as follows: Poly(hexamethylene sulfoxide) (**4a**) was prepared as described above. To a solution of **4a** (1.8mmol of S=O unit) in dichloromethane (5ml) was added oxalyl chloride (78.5ml, 0.90mmol) at -30°C. The mixture was stirred for 10 minutes and a solution of alcohol (0.6mmol) in dichloromethane (1ml) was added. Stirring was continued for additional 1 hour. Triethylamine (0.418ml, 3.0mmol) was added and the reaction mixture was stirred for 20 minutes and then allowed to warm to room temperature. Aqueous ammonium chloride was added and the mixture was extracted with CH_2Cl_2. The organic layers were combined, washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the resulting residue was dissolved in chloroform and poured into large amount of n-hexane to give a white solid. The supernatant was collected and evaporated to give the corresponding carbonyl compound. From ^{1}H-NMR spectrum, it was proved to be pure without further workup. Octanal (**6**) was prepared from 1-octanol (**5**) in 95% conversion and 84% yield: ^{1}H-NMR(δ, ppm) 0.88(CH_3-, t, J=6.9Hz, 3H), 1.29(-CH_2-, m, 8H), 1.60(-CH_2-, m, 2H), 2.42(-CH_2-, td, J=7.3, 1.8Hz, 2H), 9.76(-C(O)H, t, J=1.8Hz, 1H). 6-Undecanone (**9**) was prepared from 6-undecanol (**8**) in 100% conversion and 100% yield: ^{1}H-NMR(δ, ppm) 0.89(CH_3-, t, J=6.9Hz, 3H), 1.29(-CH_2-, m, 4H), 1.55(-CH_2-, m, 2H), 2.38(-CH_2-, t, J=7.6Hz, 2H). The solid was collected and the ratio of sulfide, sulfoxide and sulfone units was determined by ^{1}H-NMR spectrum as mentioned in the text. Peaks of ethyl protons of triethylammonium salt were also observed at δ1.41(t, J=7.5Hz, 9H) and 3.10(q, J=7.5Hz, 6H)ppm. Ammonium salt was removed by reprecipitation of the polymer into methanol. This used polymer can be reoxidized by aqueous hydrogen peroxide as described in the text.

References and notes

1. Saegusa T, Chujo Y (1991) Makromol Chem, Macromol Symp 51:1.
2. Smith RG, Vanterpool A, Kulak HJ (1969) Can J Chem 47:2015.
3. (a) Johnson AP, Pelter A (1964) J Chem Soc 520. (b) Kornblum N, Jones WJ, Anderson GJ (1959) J Am Chem Soc 81:4113. (c) Epstein WW, Ollinger J (1970) J Chem Soc, D 1338. (d) Ganem B, Boeckman Jr RK (1974) Tetrahedron Lett 917. (e) Baizer MM (1960) J Org Chem 25:670.
4. Pfitzner KE, Moffatt JG (1963) J Am Chem Soc 85:3027.
5. Mancuso AJ, Huang S-L, Swern DJ (1978) J Org Chem 43:2480.
6. Albright JD, Goldman L (1965) J Am Chem Soc 87:4214.
7. Corey EJ, Kim CU (1973) Tetrahedron Lett 919.
8. Corey EJ, Chaykovsky M (1965) J Am Chem Soc 87:1353.
9. (a) Nicco A, Boucheron B (1970) Eur Polym J 6:1477. (b) Sigwalt P, Spassky N (1984) Cyclic compound containing sulfur in the ring. In: Ivin KJ, Saegusa T (ed) Ring-opening polymerization. Elsevier, London and New York (vol. 2, chapter 9).
10. Price CC, Blair EA (1967) J Polym Sci Part A-1 5:171.
11. (a) Marvel CS, Chambers RR (1948) J Am Chem Soc 70:993. (b) Marvel CS, Aldrich PH (1950) J Am Chem Soc 72:1978.
12. Marco C, Fatou JG, Bello A, Perena JM (1984) Makromol Chem 185:1255, and references cited therein.
13. Sensfuß S (1996) Angew Makromol Chem 234:191.
14. (a) Example of effective oxidation of poly(*p*-phenoxyphenyl sulfide) to a polysulfoxide: Fujisawa T, Kakutani M, Kobayashi N (1971) Polym Lett 9:91. (b) Attempts to oxidize aliphatic polysulfides: refs. 10 and 12.
15. (a) Kobayashi E, Ohashi T, Furukawa J (1986) Makromol Chem 187:2525. (b) Kobayashi E, Terada Y, Ohashi T, Furukawa J (1985) Polym Prepr Jpn 34:2045.
16. (a) Mancuso AJ, Swern D (1981) Synthesis 165. (b) Tidwell TT (1990) Synthesis 857, and references cited therein.