

# Novel aprotic polar polymers

## 2. Miscibility of aliphatic polysulfoxides

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### Summary

Miscibility of aliphatic polysulfoxides (**1**, **2**) with other commodity polymers was examined by comparing glass transition temperature(s) ( $T_g$ s) of the mixture of these polymers with  $T_g$ s of the original polymers by differential scanning calorimetry. It was found that the aliphatic polysulfoxides had good miscibility with poly(2-methyl-2-oxazoline) or/and poly(*N*-vinylpyrrolidone).

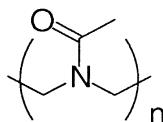
### Introduction

Polymer blends have recently received much attention in connection with developing new composite materials. In blending systems, the miscibility or compatibility of polymers is very important since miscible or compatible polymer blends show the properties of both original polymers, but most of the polymers are known to be incompatible each other. Accordingly, the usefulness of a polymer is increased when the polymer is miscible (compatible) with other polymers. In order to give high miscibility to polymers, it is effective to introduce polar groups in the polymers for interaction between their functional groups. The polymer homologs of aprotic polar solvent (aprotic polar polymers) can be candidates for such polymers. Poly(2-methyl-2-oxazoline) is famous as a polymer homolog of aprotic polar solvent of *N,N*-dimethylacetamide (DMAc) (Scheme 1), and in fact, it is known to show good miscibility with DMAc-soluble commodity polar polymers such as poly(vinyl chloride) and poly(vinylidene fluoride) (1).

### Scheme 1



*N,N*-Dimethylacetamide

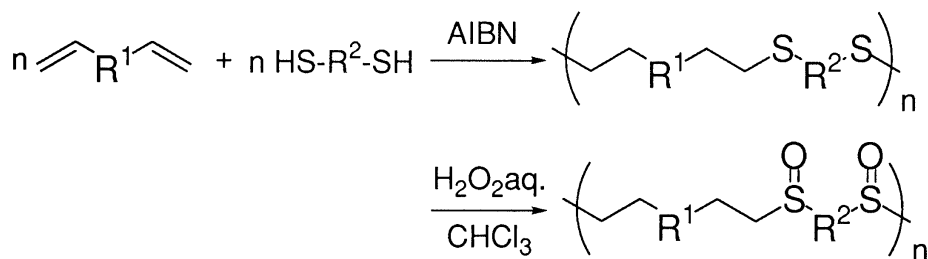


Poly(DMAc)  
(=poly(2-methyl-2-oxazoline))

Thus, it is important to extend the scope of the notion of aprotic polar polymers in order to prepare highly miscible polymers. In the previous paper, we successfully prepared aliphatic polysulfoxides as the polymer homologs of dimethyl sulfoxide (DMSO) which is unique aprotic polar solvent with high dielectric constant (Scheme 2) (2). Therefore it is expected that they have good miscibility with other commodity polar polymers.

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## Scheme 2



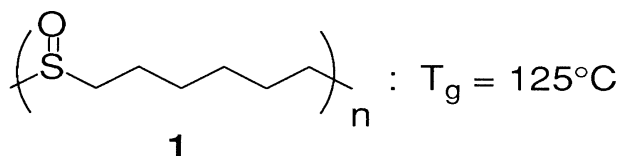
$\text{R}^1 = -\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{OC}_6\text{H}_4\text{OCH}_2-$ ,  $-\text{C}_6\text{H}_4-$ ,

$\text{R}^2 = -(\text{CH}_2)_n-$  ( $n=2, 4, 6, 8$ )

Here, the miscibility of aliphatic polysulfoxides with DMSO-soluble commodity polymers such as poly(vinyl acetate), poly(*N*-vinylpyrrolidone) and poly(2-methyl-2-oxazoline) was studied by differential scanning calorimetry (DSC) method.

### Results and discussion

Samples for DSC analyses were prepared as described in an experimental section. The resulting sample looked homogeneous and was subjected to DSC analysis at heating rate of 15°C/min. The degree of miscibility was estimated by comparing the glass transition temperature(s) of the mixture of two polymers with those of the original polymers.

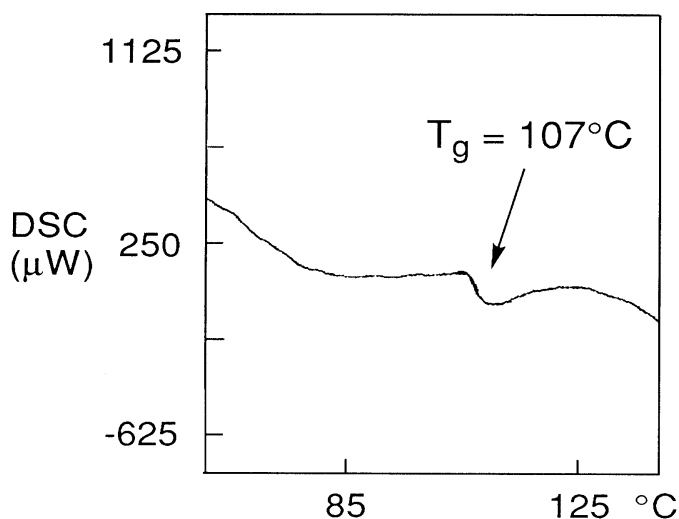


**Table 1.** Miscibility of **1** with Other Polymers.

entry	<b>1</b> ( wt % )	the other polymer ( wt % )	results a) b)
1	50	50	Poly(vinyl acetate) $M_n=8300$ , $T_g = 30^\circ\text{C}$ $T_g = 40$ , $93^\circ\text{C}$ $T_g = 40$ , $104^\circ\text{C}$ $T_g = 40$ , $115^\circ\text{C}$
2	20	80	
3	80	20	
4	50	50	Poly( <i>N</i> -vinylpyrrolidone) $M_n=10000$ , $T_g = 108^\circ\text{C}$ $T_g = 117$ , $124^\circ\text{C}$ $T_g = 100$ , $123^\circ\text{C}$ $T_g = 90$ , $116^\circ\text{C}$
5	20	80	
6	80	20	
7	50	50	Poly(2-methyl-2-oxazoline) $M_n=8500$ , $T_g = 67^\circ\text{C}$ $T_g = 71$ , $121^\circ\text{C}$ $T_g = 73$ , $120^\circ\text{C}$ <b><math>T_g = 107^\circ\text{C}</math></b>
8	20	80	
9	80	20	

a) Two polymers were dissolved in the cosolvent and then reprecipitated.

b) Glass transition temperature was determined by DSC.

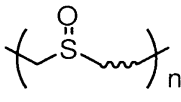
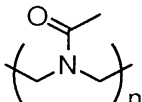
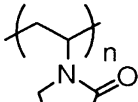
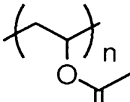


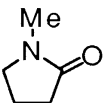
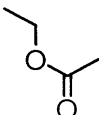


**Figure 1.** DSC Thermogram of the 80:20 Mixture of Polysulfoxide **1** with Poly(2-methyl-2-oxazoline).

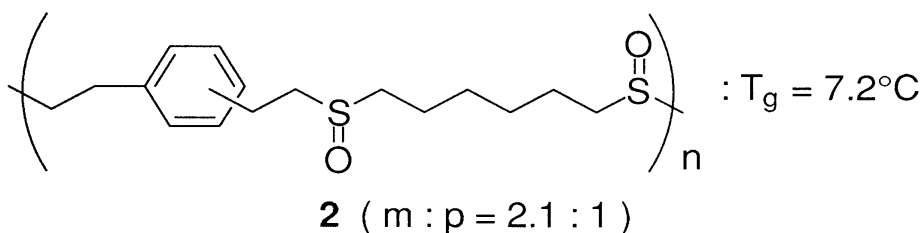
The miscibility of poly(hexamethylene sulfoxide) **1**, which shows the glass transition temperature at 125°C, was examined at first. Table 1 summarizes the results. Some changes of  $T_g$ s were observed in the mixtures with DMSO-soluble polymers such as poly(vinyl acetate), poly(*N*-vinylpyrrolidone) and poly(2-methyl-2-oxazoline) as shown in the table. These results suggest that polysulfoxide **1** is partially miscible with these polymers. In entry 9, when the ratio of **1** to poly(2-methyl-2-oxazoline) was 80:20, the only glass transition temperature of the mixture was observed between two  $T_g$ s of the original polymers.

Figure 1 shows DSC thermogram of the 80:20 mixture of polysulfoxide **1** with poly(2-methyl-2-oxazoline). It follows from this thermogram that polysulfoxide **1** shows good miscibility with poly(2-methyl-2-oxazoline) especially at this ratio. This high miscibility is probably because the polarity of poly(2-methyl-2-oxazoline) can be considered to be higher than other polymers used here. In fact, dielectric constants of model compounds of those commodity polymers are as shown in Figure 2. From this figure, it became clear that the tendency of miscibility of polysulfoxides with other polymers corresponded with an order of decrease of dielectric constant of model compounds. The difference of miscibility might be due to difference of size of side chains in commodity polymers. The reason why miscibility between **1** and poly(2-methyl-2-oxazoline) was highest at the ratio of 80:20 would be explained as follows: poly(hexamethylene sulfoxide) **1** has more methylene groups between functional groups (sulfur atoms) than poly(2-methyl-2-oxazoline) (amide units). Thus, for effective interaction between sulfoxide S=O groups and amide groups of poly(2-methyl-2-oxazoline), the amount of polysulfoxide must exceed that of poly(2-methyl-2-oxazoline).

Figure 2

Polymers				
	Polysulfoxides	PMeOZO	PVP	PVAc
Model Compounds				
	DMSO	DMAc	NMP	AcOEt
Dielectric Constant	48.9 (20°C)	37.8(25°C)	32.0(25°C)	6.0(20°C)

- PMeOZO=poly(2-methyl-2-oxazoline), PVP=poly(*N*-vinylpyrrolidone), PVAc=poly(vinyl acetate)
- DMSO=dimethyl sulfoxide, DMAc=*N,N*-dimethylacetamide, NMP=*N*-methylpyrrolidone



The miscibility of **2**, having aromatic groups in the main chain, was also estimated with poly(2-methyl-2-oxazoline) and poly(*N*-vinylpyrrolidone). Polysulfoxide **2** shows glass transition temperature at 7.2°C, much lower than  $T_g$  of **1**. The main chain of **2** is thought to have more linearity than that of **1** owing to introduction of aromatic groups. As a result, the segment of polysulfoxide **2** would move more easily than **1** due to less entanglement between polymer chains and the freezing point of molecular motion, that is, the glass transition temperature would become low. The results estimating miscibility of **2** are summarized in Table 2. In the system of **2** with poly(2-methyl-2-oxazoline), the largest shift of glass transition temperatures was observed when the weight ratio between **2** and poly(2-methyl-2-oxazoline) was 20:80 as shown in entry 2. On the other hand, polysulfoxide **2** gave the best miscibility in the system where the ratio between **2** and poly(*N*-vinylpyrrolidone) was 50:50. Here the only glass transition temperature was seen between those of the original polymers at 46°C. The ratio that **2** showed good miscibility

**Table 2.** Miscibility of **2** with Other Polymers.

entry	<b>2</b> ( wt % )	the other polymer ( wt % )	results <sup>a) b)</sup>
1	50	50	Poly(2-methyl-2-oxazoline) $M_n = 8500, T_g = 67^\circ\text{C}$
2	20	80	
3	80	20	
4	50	50	Poly( <i>N</i> -vinylpyrrolidone) $M_n = 10000, T_g = 108^\circ\text{C}$
5	20	80	
6	80	20	

a ) Two polymers were dissolved in the cosolvent and then reprecipitated.

b ) Glass transition temperature was determined by DSC.

was different from that of **1**. This would be because the sulfoxide S=O groups of **2** were likely to be stuck out to the surface of interaction due to their rigid main chain structure. Poly(hexamethylene sulfoxide) **1** has long aliphatic main chain and, as a result, it might be difficult for S=O groups of **1** to come at the surface of interaction.

In conclusion, aliphatic polysulfoxides **1** and **2** showed good miscibility with DMSO-soluble commodity polymers. Especially, in systems with poly(*N*-vinylpyrrolidone) and poly(2-methyl-2-oxazoline), high miscibility was observed. These results prove aliphatic polysulfoxides to be regarded as polymer homologs of DMSO. It is also expected that block or graft copolymers of these polysulfoxides, or polysulfoxides themselves can be utilized as compatibilizers. The studies of the possibility of aliphatic polysulfoxides as versatile compatibilizers and of the synthesis of block and graft copolymers are in progress.

### Experimental section

**General.** All DSC analyses were carried out on a Seiko DSC200 instrument by using about 10mg of exactly weighed samples.

Poly(acrylonitrile), poly(vinyl acetate) and poly(*N*-vinylpyrrolidone) were obtained from Aldrich Chemical Co. Poly(2-methyl-2-oxazoline) was prepared by ring-opening polymerization of 2-methyl-2-oxazoline as described in reference (1).

**Synthesis of aliphatic polysulfoxides.** Aliphatic polysulfoxides **1** and **2** were prepared by the oxidation of aliphatic polysulfides, obtained by polyaddition between the corresponding dienes and dithiols, as described in the previous paper (2).

**Differential scanning calorimetry analyses.** Samples for DSC analyses were prepared as follows: A mixture (0.10g) of polysulfoxide with commodity polymer at a desired ratio was dissolved in a small amount of chloroform. The solution was then reprecipitated into large amount of n-hexane to give a colorless solid. After filtration and freeze-drying of the mixture, the resulting solid was dried in *vacuo* at 80°C and the sample was obtained as a colorless powder or gum.

**References**

1. Saegusa T, Chujo Y (1991) Makromol Chem, Macromol Symp 51:1.
2. Oyama T, Ozaki J, Chujo Y (1997) Polym Bull 38:379, and references cited therein.