

NOTES

**Preparation of Block Copolymer Consisting of Poly(2-methyl-2-oxazoline) and Poly(propylene oxide) Blocks.  
A New Nonionic Surfactant**

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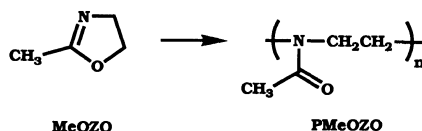
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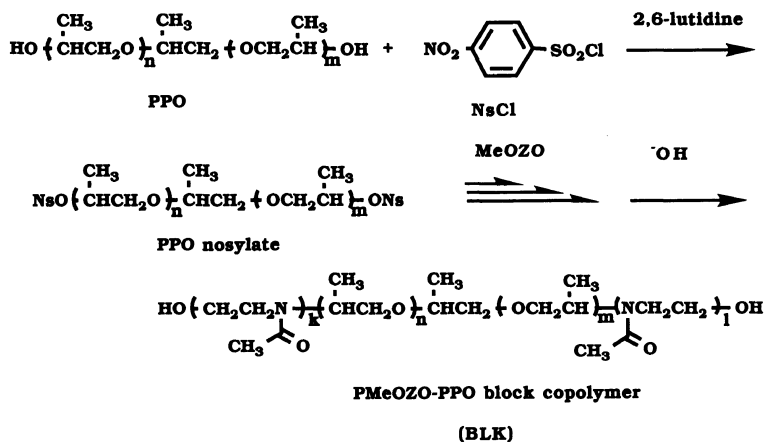
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Poly(2-methyl-2-oxazoline) (PMeOZO) has a structure of Poly[*N*-acetyl(2-imino)ethylene] which may be regarded as a polymer homologue of *N,N*-dimethylacetamide (DMAc). On the analogy of DMAc, PMeOZO has been shown to possess a strong affinity toward water



Scheme 1.



Scheme 2.

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and a high compatibility with various synthetic organic polymers.<sup>1-6</sup> The present paper describes a new class of nonionic surfactants by the combination of PMeOZO as a hydrophilic component and poly(propylene oxide) (PPO) as a hydrophobic component. It somewhat resembles to a nonionic surfactant of block copolymer of poly(ethylene oxide) (PEO) with PPO which has been commercialized under a trade name of "Pluronics". The new block copolymer was prepared by the polymerization of MeOZO with PPO having *p*-nitrobenzenesulfonate ester end groups.

## EXPERIMENTAL

### Materials

PPOs#425 (PPO-1), #1000 (PPO-2), and #3000 (PPO-3) were purchased from Aldrich Chem. Co., which were dried *in vacuo* before use; the molecular weights were determined by VPO. MeOZO and 2,6-lutidine were commercial reagents, which were purified by distillation over KOH pellets. Nitromethane was purified by distillation and dried over molecular sieves 4 Å. *p*-Nitrobenzenesulfonyl chloride (NsCl) was also a commercial reagent and was used without further purification.

### Instrumentations

<sup>1</sup>H NMR spectra were recorded on a 60 MHz Hitachi R-600 spectrometer. IR spectra were obtained on a Hitachi 260-50 infrared spectrometer. GPC analysis was performed by using a Shodex A803 column in chloroform. Molecular weight was measured by a vapor pressure osmometer (Hitachi Model 114) in chloroform at 40°C.

### Preparation of PPO Nosylate

A typical run was as follows: *p*-Nitrobenzenesulfonyl chloride (nosyl chloride) (1.4 g, 6.5 mmol) was added to a stirred solution of PPO-2 (3.5 g, 2.7 mmol) in 20 ml of 2,6-lutidine under cooling with ice, and, the mixture was stirred at room temperature for 3 days. Then,

the mixture was diluted with 150 ml of diethyl ether and shaken with 50 ml of cold 1*N* aq H<sub>2</sub>SO<sub>4</sub> three times. The ethereal layer was dried over MgSO<sub>4</sub>. After filtration, the solvent was evaporated. The resulting crude product was further purified by repeated reprecipitation from ether to hexane under nitrogen. Pale brown liquid was obtained (84% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.8—1.3 (CH<sub>3</sub>), 1.37 (d, CH<sub>3</sub> protons at β position to the ester group), 3.2—3.7 (—CHCH<sub>2</sub>—O), 3.62 (d, CH<sub>2</sub>—ONs), 4.78 (m, CH—ONs), and 8.10 ppm (dd, aromatic protons).

### Preparation of Block Copolymer (BLK)

A typical procedure was as follows: In a test tube equipped with a three-way stopcock and a stirrer bar chip were placed 0.25 g (0.15 mmol) of PPO-2 nosylate and 2 ml of nitromethane under nitrogen. Then 0.75 g (8.8 mmol) of MeOZO was added and the tube was sealed. The mixture was allowed to react at 80°C with stirring. After 7 h, the mixture was diluted with methanol and was treated with 1.2 g of Amberlite IRA-410 (1.5 mequiv/g) for 2 h. After filtration, the solvent was removed by evaporation. The resulting crude product was further purified by repeated reprecipitation from chloroform (solvent) to ether (non-solvent). Pale brown viscous liquid or pale brown solid depending on the molecular weight was obtained.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.8—1.3 (CH<sub>3</sub> of PPO block), 1.8—2.3 (CH<sub>3</sub>CO), and 3.2—3.8 ppm (—CHCH<sub>2</sub>O— and CH<sub>2</sub>N).

## RESULTS AND DISCUSSION

### Preparation of End-Functionalized PPO

The end group of PPO consists of primary and secondary hydroxy groups, and the percentage of secondary hydroxy group increases with increasing the molecular weight of PPO.<sup>7</sup> Sulfonate esterification of secondary hydroxy groups is generally troublesome because of its reduced reactivity. In the present

study *p*-nitrobenzenesulfonyl chloride (NsCl) was used as the esterification agent to increase the extent of esterification.

Three commercial PPO polymers with different molecular weights were employed. The molecular weights of PPO determined by VPO and the molecular weight distributions determined by GPC were shown in Table I. The esterification of PPO was carried out with a slight excess molar amount of NsCl (1.2 eq) in the presence of 2,6-lutidine at room temperature. The product sulfonate of PPO (PPO nosylate) was isolated by reprecipitation from ether (solvent) to hexane (non-solvent) after excess lutidine was removed by washing with dil. H<sub>2</sub>SO<sub>4</sub>. The yields were not quantitative due to the loss during reprecipita-

tion process. The extent of sulfonate esterification was determined by <sup>1</sup>H NMR, which are also shown in Table I. The functionality of the nosylate end group was not quantitative, and decreased with increasing the molecular weight of the starting PPO. It may be due to the low reactivity of secondary hydroxy group.

#### Block Copolymerization

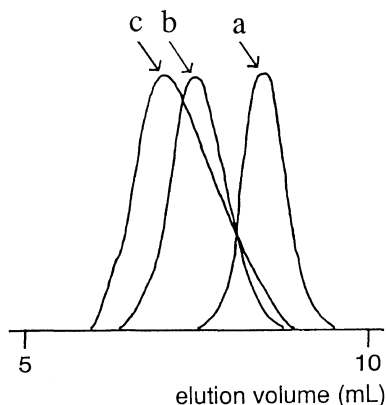
Polymerization of MeOZO with the initiator of PPO nosylate was carried out in nitromethane at 80°C with varying monomer/initiator ratios in feed. The product polymer was purified by reprecipitation using chloro-

**Table I.** Preparation of PPO nosylates<sup>a</sup>

	PPO		Product	
	<i>M<sub>n</sub></i> (VPO)	<i>M<sub>w</sub>/M<sub>n</sub></i> (GPC)	Yield wt%	EF <sup>b</sup>
PPO-1	460	1.15	79	1.72
PPO-2	1,300	1.15	84	1.80
PPO-3	2,800	1.19	77	1.50

<sup>a</sup> PPO was reacted with 1.2 eq. NsCl in 2,6-lutidine at room temperature for 3 days.

<sup>b</sup> Extent of Functionalization per PPO.



**Figure 1.** GPC charts of PPO-2 (a), BLK-2 (b), and BLK-3 (c); Shodex A803 column, chloroform eluent.

**Table II.** Preparation of block copolymers<sup>a</sup>

BLK	Starting PPO nosylate	[M] [I]	Product copolymer			
			Yield wt%	<i>M<sub>n</sub></i> <sup>b</sup>	Unit ratio <sup>c</sup> PPO : PMeOZO	PMeOZO content/wt%
BLK-1	PPO-1	11	91	1100	8 : 14	74
BLK-2	PPO-2	24	62	2900	22 : 46	75
BLK-3	PPO-2	58	76	5000	22 : 85	85
BLK-4	PPO-2	202	90	8600	22 : 170	92
BLK-5	PPO-3	49	77	15000	47 : 220	87

<sup>a</sup> In nitromethane, at 80°C, for 7 h.

<sup>b</sup> Determined by VPO.

<sup>c</sup> Numbers indicate the combined lengths of the respective blocks of ABA and AB block copolymers, which were calculated from integral ratios of <sup>1</sup>H NMR spectra.

form (solvent) and diethyl ether (non-solvent) after the removal of *p*-nitrobenzenesulfonic acid with Amberlite IRA-410 (hydroxide form) in methanol solution. All the block copolymer products were soluble in water and in common organic solvents except for hydrocarbons. GPC analysis showed that the polymer products consisted exclusively of block copolymer. Representative GPC charts are shown in Figure 1. From the structure of PPO nosylate, it is assumed that the product of block copolymerization is a mixture of block copolymers of ABA and AB types (A, PMeOZO; B, PPO). In GPC analysis, block copolymers of ABA and AB types have not been separated from each other.

#### Surfactant Properties

Surface tension values of some block copolymers at a few varieties of concentrations in water are shown in Figures 2 and 3. The relationship between  $\gamma$  and concentration of the shortest block copolymer, BLK-1, is obviously different from the others and resembles that of a common, surface inactive organic substance, because the block length is not sufficient to reveal the surface activity. As the PPO block becomes longer, the block copolymer shows a better surface activity (Figure 2). The relationship between  $\gamma$  and concentration of the PMeOZO-PPO block copolymers resembles that of PEO-PPO block copolymer at a lower concentration. In Figure 3, three different block copolymers, (PMeOZO-PPO)<sub>s</sub> (BLK-2 and BLK-3) and PEO-PPO (Pluronic F68: PEO: PPO unit ratio = 120:39), having an analogous weight content of hydrophilic block (75, 85, and 80%, respectively) show almost identical behaviors of the  $\gamma$  vs. concentration relationship at under 0.1 wt%. At 1 wt%, on the other hand, (MeOZO-PPO)<sub>s</sub> show better surface activities than PEO-PPO. Among (PMeOZO-PPO)<sub>s</sub> having the same PPO block, the block copolymer becomes less surface active with increasing the length of hydrophilic PMeOZO block (Figure 3). A similar relationship

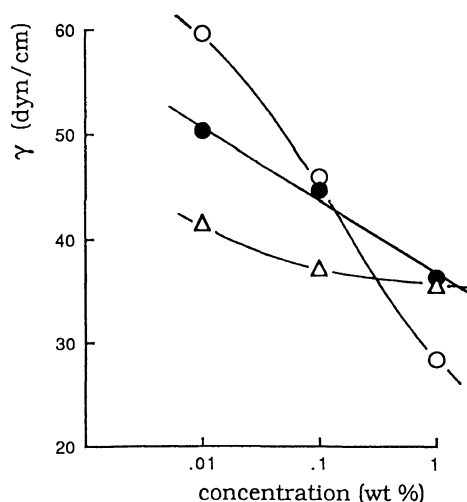


Figure 2. Surface tension curves of block copolymers, BLK-1 (○), BLK-2 (●), and BLK-5 (△) at 20°C.

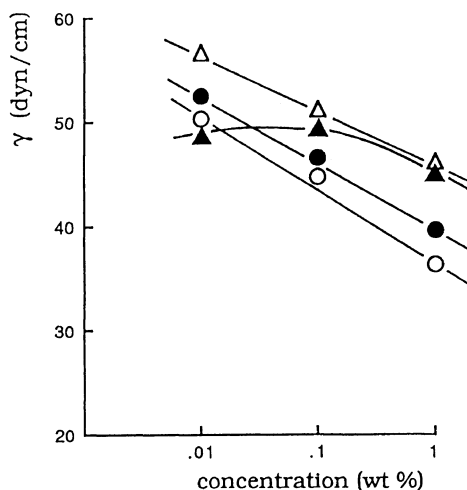


Figure 3. Surface tension curves of BLK-2 (○), BLK-3 (●), BLK-4 (△), and Pluronic F68 (▲) at 20°C.

between the length of hydrophilic PEO block and the surface activity has also been observed in the case of Pluronics.<sup>8</sup>

The PMeOZO-PPO is distinguished from PEO-PPO by a strong affinity toward water. The cloud point of BLK-1 was higher than 130°C while that of a PEO-PPO block copolymer having a analogous unit ratio (Pluronics L35, PPO: PEO unit ratio = 16:23)

has been reported as 81°C.<sup>9</sup> In addition, PMeOZO-PPO may have some other useful characteristics based on the *N,N*-dimethyl-alkylcarbamide structure. For example high compatibility with organic polymers is readily assumed from our previous studies.<sup>1,2</sup>

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#### REFERENCES

1. M. Miyamoto, Y. Sano, T. Saegusa, and S. Kobayashi, *Eur. Polym. J.*, **19**, 955 (1983).
2. S. Kobayashi, M. Kaku, and T. Saegusa, *Macromolecules*, **21**, 334 (1988).
3. M. Miyamoto, K. Aoi, and T. Saegusa, *Macromolecules*, **22**, 3540 (1989).
4. S. Kobayashi, T. Igarashi, Y. Moriuchi, and T. Saegusa, *Macromolecules*, **19**, 535 (1986).
5. H. Keskkula and D. R. Paul, *J. Appl. Polym. Sci.*, **31**, 1189 (1986).
6. M. H. Litt, B. R. Hsieh, I. M. Krieger, T. T. Chen, and H. L. Lu, *J. Colloid Interface Sci.*, **115**, 312 (1987).
7. J. G. Hanna and S. Sigga, *J. Polym. Sci.*, **56**, 297 (1962).
8. T. H. Vaughn, H. R. Suter, L. G. Lundsted, and M. G. Kramer, *J. Am. Oil Chem.*, 294 (1951).
9. L. C. Pizzini and J. T. Patton, Jr., "Encyclopedia of Polymer Science and Technology," Suppl. Vol. 6, Wiley, New York, N.Y., 1976, p 159.