

NOVEL SULPHONATED POLYSILOXANE POLYUREA-URETHANE IONOMERS

CHEN Lei (陈雷) YU Xuehai (余学海) and YANG Changzheng (杨昌正)

(*Institute of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210008*)

ABSTRACT

A series of novel polysiloxane polyurea-urethane blockcopolymers based on methylene bis(p-phenylisocyanate (MDI), sodium-s-1,2-dihydroxy propyl sulphonate (SDPS) and aminopropyl-terminated polydimethylsiloxane (ATPS) was synthesized with varying length of soft segments and neutralizing cation. The effect of the chemical composition and the cation on the morphology and mechanical properties of the samples were studied.

It was found that the SDPS chain extender based samples have definite chemical structure (-MDI-SDPS-MDI-ATPS-). As the length of the soft segment increases, an improvement of phase separation was observed. In addition, when SO_3Na was translated into SO_3H or the sulphonic acid groups were neutralized with different charge cations (Na^+ , Zn^{2+} and Al^{3+}), the morphology and mechanical properties changed greatly.

INTRODUCTION

The morphology and properties of polysiloxane polyurethane blockcopolymers have been extensively investigated over the past decade^[1-6]. The degree of microphase separation is affected by the length of segment, copolymer composition, crystallization ability of either segments, and the methods of sample fabrication^[6].

Introducing ions into polymeric materials is a useful way to alter polymer morphology and physical properties^[7]. Polyurethane ionomers are a new class of blockcopolymers usually containing a relatively small number of ionic groups in polymer backbone or side chains. Several methods of introducing ionic centers into the polymers have been reported^[8-10]. In our laboratory, a series of sulphonated polyether polyurethane ionomers have been synthesized by using bimolecular nucleophilic displacement of the urethane hydrogen with sodium hydride followed by reaction with γ -propane sultone^[11]. This method has the advantage of obtaining higher ionic contents because there are more ionization sites per hard segment, but the ionic content cannot be controlled strictly and this nucleophilic displacement reaction cannot be

applied to polysiloxane containing systems. There are only a few reports on the synthesis of sulphonated polysiloxane ionomers.

In this paper, diol sodium-*s*-1, 2-dihydroxypropyl sulphonate (SDPS) was used as chain extender. With this new chain extender a series of polysiloxane polyurea-urethane ionomers was successfully synthesized. In addition, the structures of these ionomers were also studied.

EXPERIMENTAL

Materials

Methylene bis(*p*-phenylisocyanate) (MDI) and cyclic octamethyl-tetrasiloxane (D_4) were vacuum distilled. Sodium sulphite, 3-chloropropane-1, 2-diol (CPD), diethyl ether, anhydrous *N*, *N'*-dimethylacetamide (DMAc), tetrahydrofuran (THF) and tetramethyl ammonium hydroxide were further dehydrated. 1, 3-bis (γ -aminopropyl) tetramethyl-disiloxane (AT) (Silar Lab), stannous octoate and strongly sulphonic acidic macro reticular resin (Aldrich) etc, were used as received.

*Synthesis of sodium-*s*-1, 2-dihydroxypropylsulphonate (SDPS)*

Sodium sulphite 37.8g was dissolved in 60 cm³ of water and then 22.1g CPD in 60 cm³ water was added. The solution was refluxed for 2.5h and cooled. Diethyl ether 40ml was added to extract any traces of unreacted CPD. Water was then removed by rotary evaporation. At the end of the reaction white solid was obtained. After cooling, SDPS was extracted from the white solid with warm DMAc (90ml). The DMAc was then removed by rotary evaporator under vacuum. The product was washed with 300ml acetone and then dried in a vacuum desiccator at room temperature for 48h.

Synthesis of oligomers

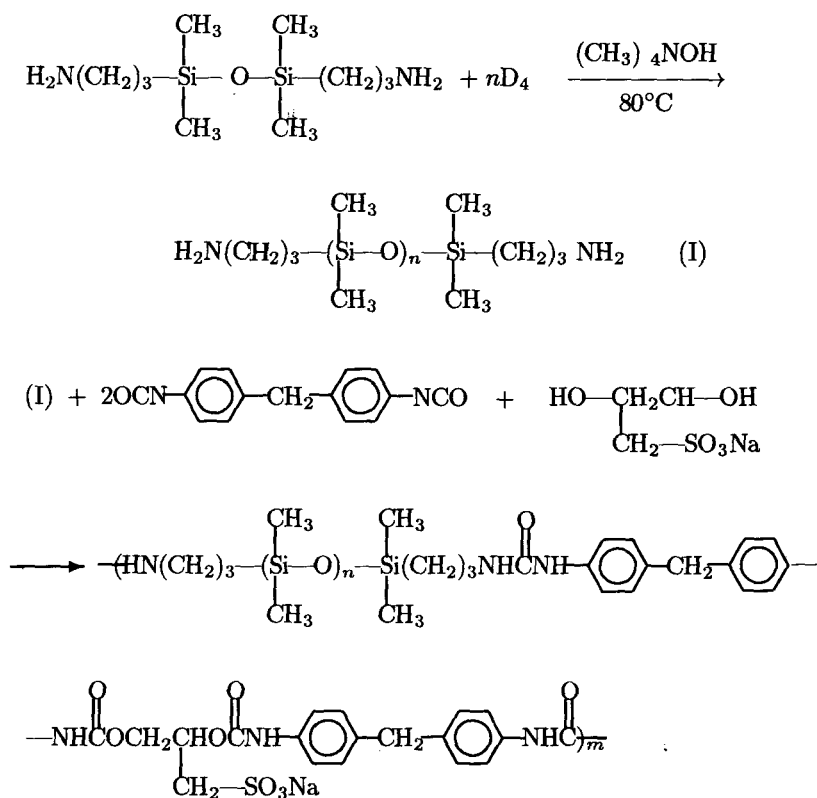
α , γ -Bis (aminopropyl) polydimethylsiloxane oligomers (ATPS) (Scheme 1), were synthesized as described in our previous paper^[2].

The molecular weight of oligomers was listed in Table 1.

Synthesis of ionomers

The segmented polysiloxane polyurea-urethane ionomers used in this study were synthesized by a two-step condensation reaction^[2] in a 1 : 1 THF/DMAc mixed solvent (see Scheme. 1).

Solutions of ATPS and MDI were prepared in THF (20–30 percent w/v). The ATPS solution was added in several portions to the stirred MDI solution at 50°C. After reacting for 1 h, SDPS dissolved in hot DMAc containing 0.15% wt (stannous octoate) was then added and stirred for additional 4 h at 80°C. The products were precipitated in water and dried in a vacuum oven at 70–80°C for at least two days.



Transformation of cation was carried out with sulphonic acidic ion exchange resin by first dissolving the SDPS based polymers in DMAc and then the solution was passed through the resin column drop by drop for about 3h to give the acid form materials. Various metal acetates were added to neutralize the sulphonate groups. All materials studied are described in Table 1.

Table 1 Composition of the materials synthesized

Sample	Hard segment	Soft segment	$\overline{M}_n$ of polysiloxane
	content	type	
PSPU-2-Na	24.9	ATPS-2	2045
PSPU-2-H	24.3	ATPS-2	2045
PSPU-2-Zn	26.1	ATPS-2	2045
PSPU-2-Al	25.0	ATPS-2	2045
PSPU-4-Na	16.5	ATPS-4	3437
PSPU-4-H	16.0	ATPS-4	3437

Characterization

Infrared spectra were recorded with a Nicolet 170-SX FT-IR spectrophotometer purged with dry air. IR samples were prepared by drying dilute polymer solution on NaCl plates under an infrared lamp.

Differential Scanning Calorimeter (DSC) thermograms over the temperature range -150°C to 200°C were recorded using a Perkin-Elmer DSC 2°C at a heating rate of $20^{\circ}\text{C}/\text{min}$ under He purge. Samples were taken directly from the cast film.

Dynamic mechanical data were obtained at 110 Hz using a Rheovibron DDV-II apparatus. Samples were made by casting and the thickness depended on the temperature range being studied. Samples were initially cooled to -140°C and then measured at 2°C intervals with a heating rate of $2^{\circ}\text{C}/\text{min}$.

Room temperature uniaxial stress-strain data were taken on an electric tensile testing device at a speed of 2 mm/min. Samples were prepared using ASTM D412-D standard die.

RESULTS AND DISCUSSION

Infrared spectroscopy

The bands near 3300 (N—H stretch), 1650 (C=O stretch) 1540 (C—N—H bending), and 1310cm^{-1} (N—C—O stretch) are characteristic for polyurethane hard segments. The presence of the peaks at 1260 (sym CH_3 bending) and 1060 (Si—O—Si stretch) indicates the inclusion of the siloxane chains in the final polymer. For this system the S=O absorption peak at about 1040cm^{-1} , observed in the IR spectra of polybutadiene-urethane zwitterionomers^[13], was not detectable because there was a large siloxane absorption peak near this region. Another S=O absorption peak which should be situated near 1150 — 1220cm^{-1} was also overlapped by other peaks. The assignments of FT-IR bands in this work agree with the literature^[14]. Infrared spectra of all samples showed that the stretching vibration of NH (3315cm^{-1}) appears to be primarily hydrogen bonded, because the free (non hydrogen bonded) NH vibration band at 3460cm^{-1} was detected only as a very small shoulder. In the carbonyl region (1600 — 1800cm^{-1}), free C=O stretching should appear as a shoulder at 1730cm^{-1} , but the real peak was at 1647cm^{-1} due to the effect of H-bond. If it is assumed that the extinction coefficients of free and bonded C=O were the same in the polyurethanes, the dominance of the bonded C=O and NH peaks indicated that nearly all the hard segments were hydrogen bonded. IR spectra like this was expected for highly phase-separated polyurethanes. The spectra of Zn^{2+} and Al^{3+} based analogues were similar to that of PSPU-2-Na.

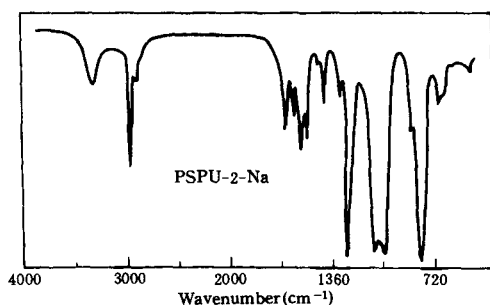


Fig.1 FT-IR spectrum of the sample

On the other hand, the choice of cation also has effect on the FT-IR spectrum. The bands of NH and C=O of the samples neutralized with multi-valence were at lower wave numbers as compared with Na^+ based ionomer. This observation suggests that the polyurea-urethane domains composed of multi valence cations are closer than that of Na based samples. It should be noted that the above peaks of PSPU-2-Al were in the middle of Zn^{2+} and Na^+ based samples. The feature is due to that the Al^{3+} is a neutral metal ion and the force between sulphonic acid and Al^{3+} is weak. It is postulated that the Al^{3+} containing microdomain was impure and that were still some acetate groups in these domains.

Thermal analysis

The film samples were obtained by casting from DMAc in polytetrafluoroethylene plates and dried in an oven at 70°C for 10h and then in a vacuum oven at 50°C for 2 days. Film thickness ranged from 5 to $250\mu\text{m}$, depending upon the test and test conditions. All films were transparent to visible light.

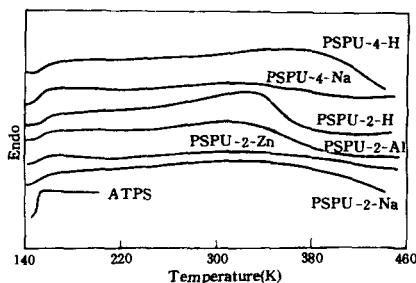


Fig.2 DSC curves for the oligomer and ionomers

DSC curves for different samples are shown in Fig.2 respectively, and their thermal transition data were summarized in Table 2. All DSC data were calculated from the first heating of the samples. The breadth of the soft domain glass tran-

sition provides a qualitative measure of soft phase homogeneity and the variation in the magnitude of T_g indicates the degree of microphase separation. The transition zone width increases with T_g . This transition temperature and its zone width increase with the decrease of the length of the soft segment. The curves of SO_3Zn and SO_3Al based samples are similar to that of SO_3Na based samples. It is noteworthy that there is a broad endotherms for PSPU-2-H and PSPU-4-H respectively, this peak shifts to high temperature with the purity of hard segment increases. In contrast, none of the metal ion based samples exhibits this endotherm showing that this endotherm was not due to the hard segment crystallisation, it was assigned to the hydrogen bond caused by SO_3H . The metal cations have some effects on the value of T_g of the soft segment. It is found that the T_g of PSPU-2-Zn was lower than those of the other two samples. According to the FT-IR results the ion aggregates in PSPU-2-Zn were closer than those of PSPU-2-Na and PSPU-2-Al.

Table 2 Thermal transition data

Sample code	T_g of polysiloxane ($^{\circ}\text{C}$)		
	DSC	DSC breadth	DMA
ATPS oligomer	-120.85	—	—
PSPU-2-Na	-116.55	12	-113.3
PSPU-2-H	-116.00	11	—
PSPU-2-Zn	-118.45	10	-115.3
PSPU-2-Al	-117.89	10	-117.1
PSPU-4-Na	-119.59	6	-115.1
PSPU-4-H	-119.60	15	—

Dynamic mechanical analysis

The results of dynamic mechanical analysis are showed in Fig.3 and Table 2. The transition temperature of the polyether domain measured by DMA experiments are generally higher than those of DSC due to the differences in heating rate and test frequency. In this paper, the length of hard segment is constant but the molecular weights of the soft segments are quite different. A lower and wider rubbery module plate was observed as the soft segment was increased, indicating that the purity of the hard segment increased with the increasing of the soft segment. The storage module of the ionomer containing Zn^{2+} and Al^{3+} increased greatly and dropped at a higher temperature compared with that of Na^+ based sample. This feature can be attributed to the clustering of the sulphonate groups. As the charge of the cation increases, the average number of sulphonate groups around the cation increases. This result leads to a larger ionic aggregate and a higher plateau module. As mentioned

above, not all of SO_3H groups were neutralized with $\text{Al}_2(\text{Ac})_3$ so the plateau module of PSPU-2-Al decreases compared with that of PSPU-2-Zn. As SO_3Na was transformed to SO_3H in the hard segment, the storage modules dropped at lower temperature in the high temperature range and exhibited a gradual drop-off. According to Hashimoto and Annighofer^[15,16], the block copolymers with significant "domain boundary mixing" exhibit a higher loss factor between the two main transitions, a gradual drop-off of storage modules above the soft segment T_g , and a dependence of transition temperature on the interfacial thickness between the domains. On the

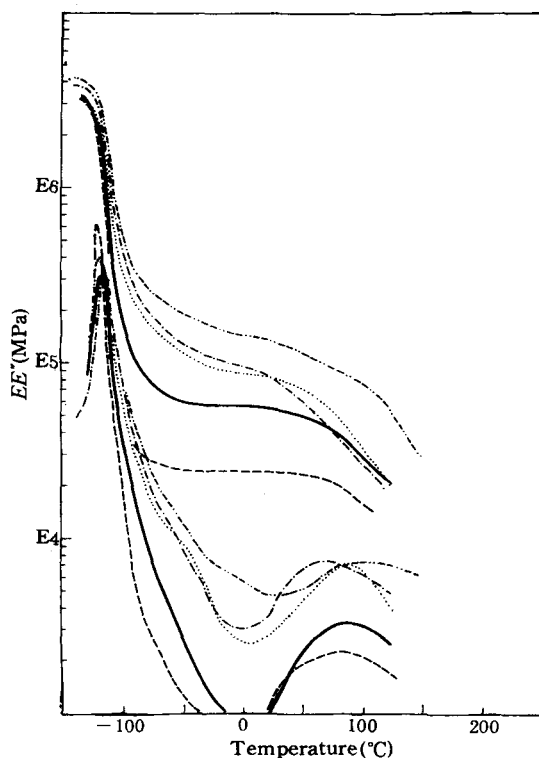


Fig.3 Dynamic mechanical properties of the ionomers

—PSPU-2-Na; - - - PSPU-2-H; · · · · · PSPU-2-Zn;
- · - · - PSPU-4-Na; · · · · · PSPU-2-Al ionomers

other hand, the loss module plate changed with the length of soft segment, meanwhile, the peak of loss module of the soft segment shifted to lower temperature. Clearly the longer soft segment is less compatible with polyurea-urethane segments and the hard segment has an inherently greater tendency to crystallise in well phase separation system. As the ionic charge increased from Na^+ to Zn^{2+} , the peak of T_g of polysiloxane segments shifted to lower temperature and became sharper. The

peaks corresponding to the soft segment glass transition were in consistent with DSC data.

Stress-strain analysis

The stress-strain data for all the samples are shown in Fig.4.

The values of Young's modules depended upon the cation charge and agree with those of the dynamic mechanical analysis. The elongation at break was found to decrease significantly upon ionization and decreasing the length of the soft segment. Further more the ultimate elongation is in close relation with cation charge. Clearly the larger the charge of the counter cation is, the shorter the elongation of the sample will be. An abnormal phenomenon is that the stress and the elongation of PSPU-2-H were larger than those of corresponding ionomers. This feature can be attributed to the H-bond between SO_3H and polysiloxane soft segment. On the other hand, the regularity of the samples is also an important factor to determine their mechanical properties. As the ionic cluster containing Zn^{2+} is close and regular, PSPU-2-Zn exhibited a higher ultimate stress than that of the other two ionomers. The poor mechanical properties of PSPU-2-Al may be caused by the remaining acetate groups in the sample.

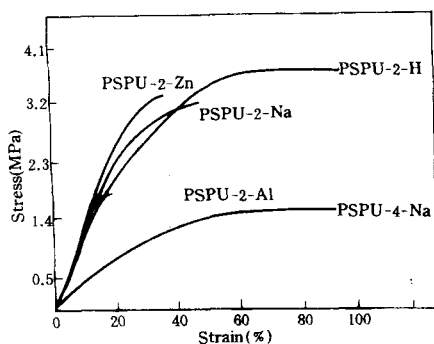


Fig.4 The stress-strain curves of the samples

CONCLUSION

Results of FT-IR, DSC, DMA and stress-strain test showed the effect of the molecular weight of polysiloxane soft segment and the type of the cation on the morphology and mechanical properties of the samples. It is found that the longer soft segment is less compatible with urea-urethane hard segment meanwhile the hard segment has an inherently greater tendency to crystallise in well phase separation system. When SO_3Na was translated to SO_3H , its stress and elongation were greater

than that of the comparable ionomers. The ionic cluster composed of Zn^{2+} is closer and exhibited better thermal stability and ultimate stress than those of the corresponding Na^+ based ionomer. The poor mechanical property of PSPU-2-Al is due to that the Al^{3+} is a neutral metal ion and the Al^{3+} containing microdomain was impure and there may be some acetate groups in this sample.

Keywords:

Polysiloxane; Polyurea; Polyurethane; Ionomers

REFERENCES

- [1] Yu, X.H.; Yang, C.Z. and Chen, L., *Functional Polymer* (in Chinese) **1991**, 4(3): 168.
- [2] Chen, L. and Yu, X.H., *Functional Polymer* (in Chinese) **1991**, 4(1): 19.
- [3] Yu, X.H.; Nagarajan, M.R.; Grasel, T.G., et al., *J. Polym. Sci. B.*, **1985**, 23: 2319.
- [4] Kuckertz, V.H., *Makromol. Chem.*, **1966**, 98: 101.
- [5] Tyagi, D.; McGrath, J.E. and Wilkes, G.L., *Polym. Eng. Sci.*, **1986**, 26(20): 1371.
- [6] Speckhard, T.A. and Cooper, S.L., *Rubber Chemtech*, **1986**, 59: 405.
- [7] Egboth, H.S.; Ghaffar, A.; George, M.H., et al., *J. Polym.* **1982**, 23: 1167.
- [8] Hwang, K.K.S.; Yang, C.Z. and Cooper, S.L., *Polym. Eng. Sci.*, **1981**, 21(15): 1027.
- [9] Seymour, R.W.; Estes, G.M. and Cooper, S.L., *Macromolecules*, **1970**, 3: 597.
- [10] Gu, D.M.; Yang, C.Z. and Yu, X.H., *Chem. J. of Chinese Univ.*, (in Chinese), **1989**, 10(3): 280.
- [11] Yang, C.Z.; Zai, H.L. and Yu, X.H., *Symposium on Polymers Preprints China*, **1989**: 287.
- [12] Tchui, T.Y.; Lam, P.K.H.; George, M.H., et al., *Polym. Comm.*, **1988**, 29: 40.
- [13] Yang, C.Z.; Hwang, K.S.S. and Cooper, S.L., *Makromol. Chem.*, **1983**, 184: 651.
- [14] Li, C.; Yu, X.H.; Speckhard, T.A., et al., *J. Polym. Sci. B. Polym. Phys.*, **1988**, 26: 315.
- [15] Hashimoto, A.; Tsukahra, Y.; Tachi, K., et al., *Macromolecules*, **1983**, 16: 648.
- [16] Annighofer, F. and Gronski, W., *Coll. Polym. Sci.*, **1983**, 261: 15.