

Synthesis and Characteristics of Aqueous Reactive Urethane Oligomer Containing Sulfoisophthalate Sodium Salt

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ABSTRACT: This research studied urethane oligomers, which contains the sulfonic acid group and different reactive groups. First, the transesterification of dimethyl 5-sulfoisophthalate sodium salt were performed with ethylene glycol or polyethylene glycol of different molecular weights to produce PEG soft chains possessing sulfonic acid group. Subsequently, isophorone diisocyanate used as a hard chain was connected to the two terminals of the sulfonated diols, which finally were blocked by methyl ethyl ketoxime or hydroxyethyl methacrylate or 2, 3-epoxy-1-propanol to form three kinds of aqueous reactive urethane oligomers (MSE, HSE, and OSE). The MSE oligomer had the greatest particle diameter, particle variance, and streaming current readings; the HSE oligomer, and the OSE oligomer had the second

large and the smallest readings of the aforementioned measurements, respectively; whereas the contact angle and surface tension appeared with an opposite trend. Within the thermal properties of oligomer, the T_g of oligomer followed the trend: OSE < HSE < MSE; however, T_m and ΔH show an opposite tendency. With regard to the reactivity of the oligomers toward PET fabric, the add-on for the variety of oligomers was in the quantity order of MSE > HSE > OSE series, and the washing durability was rated in the order of HSE > MSE > OSE series. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2907–2916, 2007

Key words: dimethyl 5-sulfoisophthalate sodium salt; reactive urethane oligomer; sulfonated diol

INTRODUCTION

Urethane oligomer is widely applied in adhesive, painting, and biomedical sciences for the products having advantages such as excellent wear-resistance, weatherproof quality, elasticity, and peel bond strength.^{1–2} To improve the reactivity of urethane oligomer, the isocyanate type^{3–8} was generally produced by capping the NCO group of PU prepolymer. Currently, other types of reactive urethane oligomer such as acrylic type^{9–19} containing vinyl group and epoxy type^{20–29} containing epoxide group have been developed. In past studies of isocyanate type, for example, Roy and Kumar³ have used phenol, bisphenol, and hydroquinone as capping agent to synthesize reactive urethane oligomer. They studied the effects of PEG molecular weight and the variety of capping agents to the adhesive property and shock resistance of the formative substances. The bisphenol-A blocked polyurethane adhesive specimens showed higher impact strength and a desirable quality of clarity and rubbery nature. In the acrylic type, for example, Lai and Baccei⁹ used 2-hydroxyethyl methacrylate to synthesize UV-curable PU prepolymer, and studied the influence of PPG molecular weight to the gas perme-

ability and tear strength of the formative substances. As for the researches of epoxy type, Ma and coworkers^{20–22} synthesized glycidol-terminated polyurethane using glycidol to investigate the thermal properties and mechanical properties of the formative substances. Except the reactive group, the characteristics of urethane oligomer should be related to the composition of the internal structure.

In the past few years, some reports have been published that sulfonic acid group is used as the dispersing center^{30–42} in ionic PU, and the formative products are used in the application of electrical conductive materials and thin membranes for biomedical sciences. Cooper and coworkers^{30–32} compared the properties of PU composed of sulfonic acid group and carboxyl acid group as the ionic center. It was pinpointed that sodium sulfonic acid group has strong negative electrical charge in the absence of neutralization. The ζ electric potential of the dispersing solution of PU containing sulfonic acid group is lower than that containing carboxyl acid, so its particle diameter is smaller. In addition to this, it was found that the one containing sulfonic acid group has a better stability of hydrolysis resistance and water resistance, and because of the low phase separation, the extensibility and strength of the membrane is larger. It was previously assumed that the ionic PU containing sulfonic acid group almost belonged to solvent-base and the polymer type,^{33–41} rather than

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the oligomer type. Only a recent report suggested that it belonged to the aqueous urethane oligomer. Lewandoski et al.⁴² used dimethyl 5-sulfoisophthalate sodium salt to undertake transesterification with polycaprolactone or caprolactone to produce sulfonated diol, and subsequently allowed the diol to react with various types of hard segments to form nonreactive aqueous urethane oligomer, followed by terminal blocking with 3-aminopropyltriethoxysilane, and emulsification in water to form a sulfo-urethane silanol dispersing solution. They further studied the impact of hard chain content to mechanical properties of the formative substance. However, the PU prepolymer did not possess any reactivity, and the research about aqueous reactive urethane oligomer containing sulfonic group is not yet available.

This research focuses on the urethane oligomer containing sulfonic acid group and different reactive groups. First, the transesterification of dimethyl 5-sulfoisophthalate sodium salt (SIP) was allowed to proceed with ethylene glycol (EG) or Polyethylene glycol (PEG) of different molecular weights to synthesize PEG soft chain containing sulfonic acid group (sulfonated diol, SE). Each terminal of SE was connected to isophorone diisocyanate (IPDI) as the hard chains, and finally methyl ethyl ketoxime (MEKO) or hydroxyethyl methacrylate (HEMA) or 2,3-Epoxy-1-propanol (EPO) respectively, were used to cap the terminals to form three kinds of aqueous reactive urethane oligomer. Its thermal properties and solution properties, and the reactivity to PET fibers were investigated.

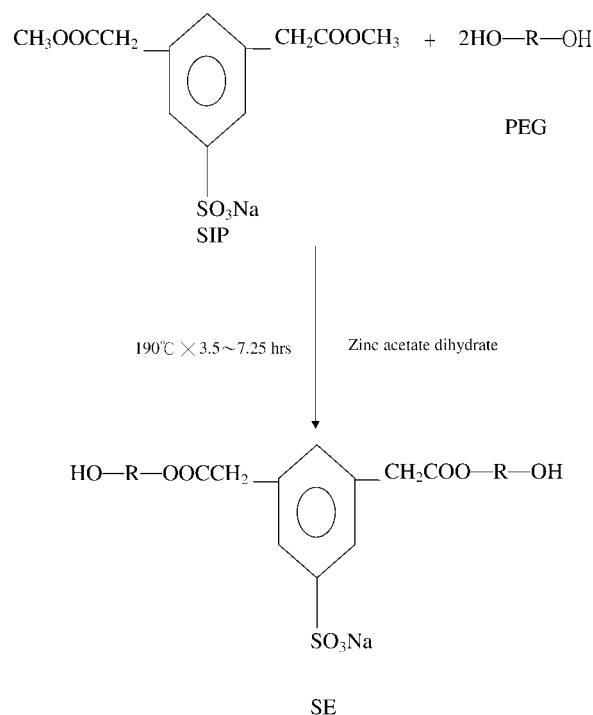
EXPERIMENTAL

Preparation of sulfonated diol

To synthesize urethane oligomer, first, sulfonated diol was synthesized according to the method of Wei et al.⁴³ One mole of dimethyl 5-sulfoisophthalate sodium salt (SIPM, GR grade, Acros) and 2 mol of EG (GR grade, Acros), or PEG (molecular weight 400, 1000, 2000, 3000, GR grade, Acros) were mixed and dehydrated in vacuum. Zinc acetate dehydrate (GR grade, Acros) as the catalyst was subsequently added and incubated with ambient nitrogen gas at 190°C for 3.5–7.25 h for transesterification to produce sulfonated diols (SE). The synthesized products were confirmed by titration of OH and FTIR analysis. The reaction equation is shown in Scheme 1, and the composition of the synthesized products and code names are listed in Table I.

Synthesis of urethane oligomer

To synthesize the aqueous reactive urethane oligomer, 1 mol of SE as soft chain was dissolved in



R: PEG ($M_n=62, 400, 1000, 2000, 3000$)

Scheme 1 The synthesis of sulfonated diols.

N,N-dimethylformamide (DMF) and dehydrated in a vacuum, and reacted with 2 mol of Isophorone Diisocyanate (IPDI, GR grade, Aldrich) with Dibutyltin dilaurate (DBTDL, GR grade, Aldrich) as a catalyst under ambient nitrogen gas at 45°C for 2–3.5 h. The temperature was subsequently increased to 60°C, and 2 mol of Methyl ethyl ketoxime (MEKO, GR grade, Acros) or hydroxyethyl methacrylate (HEMA, GR grade, Acros) or 2,3-Epoxy-1-propanol (EPO, GR grade, Acros) was added for 60 min to proceed NCO blocking, followed by cooling in a water bath for 15 min. The emulsified dispersion of three kinds of waterborne urethane polymers containing different reactive terminals (MSE,289; HSE, and OSE) were obtained by adding water. The reaction equation is shown in Scheme 2, and the composition and the symbols of the synthesized products are displayed in Table II.

Analysis of structure

FTIR spectra was taken within the scanning range of 400 ~ 4000 nm for 16 times at 25°C NCO titration and Hydroxyl number analysis were performed according to the methods of David⁴⁴ and potassium hydroxide, respectively. Gel Permeation Chromatography (GPC) test, using Polystyrene as the standard and the 100 μ m sample at a concentration of 7 ~ 8 mg/mL

TABLE I
The Compositions and Molecular Weights of Synthesized Sulfonated Diols and Oligomers

Synthetic type	Symbol	Composition (wt%)							Molecular weight	
		Soft segment (SE)			Hard segment	Reactive group			Theo.	Exp.
		SIP	Mn	ratio		IPDI	HEMA	MEKO		
			PEG							
Sulfonated diol	SE62	84.0	62	16.0	0	0	0	0	422	438
	SE400	28.2	400	71.2	0	0	0	0	1112	1146
	SE1000	13.3	1000	86.7	0	0	0	0	2380	2430
	SE2000	7.0	2000	93.0	0	0	0	0	4789	4860
	SE3000	4.8	3000	95.2	0	0	0	0	6802	6920
Acrylic type urethane oligomer	HSE62	28.0	62	11.7	42.0	24.7	0	0	1060	1152
	HSE400	17.1	400	46.2	25.6	15.0	0	0	1736	1892
	HSE1000	10.1	1000	68.2	15.1	8.9	0	0	2936	3220
	HSE2000	6.6	2000	86.6	9.8	5.8	0	0	4936	5140
	HSE3000	4.2	3000	88.6	6.4	3.8	0	0	6936	7130
Isocyanate type urethane oligomer	MSE62	30.5	62	12.8	45.8	0	17.9	0	974	1082
	MSE400	18.0	400	48.6	27.0	0	10.6	0	1650	1703
	MSE1000	10.4	1000	70.2	15.6	0	6.1	0	2850	3030
	MSE2000	6.1	2000	82.5	9.1	0	3.6	0	4850	5020
	MSE3000	4.3	3000	87.6	6.5	0	2.5	0	6850	7020
Epoxy type urethane oligomer	OSE62	31.3	62	13.1	47.0	0	0	15.7	592	612
	OSE400	18.3	400	49.4	27.4	0	0	9.1	1624	1720
	OSE1000	10.5	1000	70.9	15.7	0	0	5.2	2824	2920
	OSE2000	6.1	2000	83.0	9.2	0	0	30.7	4824	5030
	OSE3000	4.3	3000	87.9	6.5	0	0	2.2	6824	6920

The Reac., Prod., Theo. are abbreviations of Exp. reactant, product, theory.

S, E and number in symbol represent SIPM, PEG and molecular weight of PEG, respectively.

HSE, MSE, and OSE in symbol represent acrylic type, isocyanate type and epoxy type respectively.

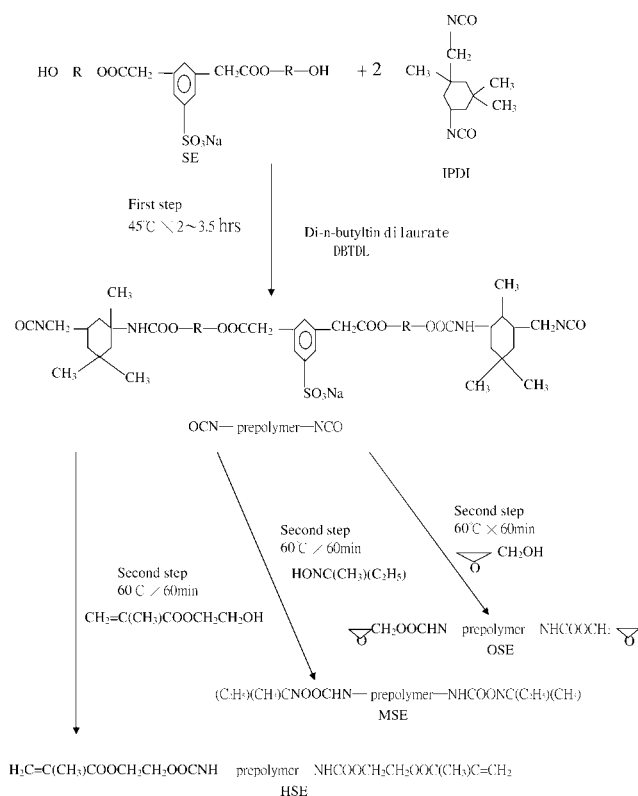
was performed (Water RI-6000 at a speed of 1 mL/min) to determine the molecular weight and distribution of oligomers.

Thermal property of urethane oligomer

The differential scanning calorimetric (DSC) analysis was performed using a differential scanning calorimeter (Perkin-Elmer) to measure the heat variation at an increasing temperature rate of 10°C/min. The measurement range of this analysis was set between -100 and 100°C.

Solution property of urethane oligomer

Laser scattering-based particle sizer of Master Sizer X (Malvern) and a Japan Kaimenagaku CBVP-a3 surface tension meter were employed to determine the particle size and surface tension, respectively. To determine contact angle, a syringe containing a 0.2 wt % solution of oligomer was used to dispense several drops of this solution on the surface of an acrylic plastic sheet and PET fabric. The test of streaming current reading was performed by an ECA2000 electrokinetic charge analyzer.



Scheme 2 The synthesis of reactive urethane oligomers.

TABLE II
The Solution Properties and Thermal Properties of Synthesized Sulfonated Diols and Oligomers

Symbol	Solution properties					Thermal properties			
	Particle		Surface tension (dyne/cm)	Streaming current reading	Contact angle (°)		T_g (°C)	T_m (°C)	ΔH (J/g)
	Size (μm)	Variance (%)			Acrylic plate	PET fabric			
SIPM	1.42	8.4	49.9	-0.16	108	154	-	265	-
SE62	60.14	53.6	49.2	-0.10	125	140	-41	-	-
SE400	52.57	47.9	47.5	-0.18	119	134	-55	-	-
SE1000	30.62	36.9	44.3	-0.58	110	130	-66	34	83
SE2000	58.98	24.5	48.2	-0.42	120	126	-	46	103
SE3000	68.81	22.4	49.3	-0.34	130	132	-	57	145
HSE62	90.21	74.2	34.8	-0.33	88	128	-18	-	-
HSE400	80.31	63.3	37.1	-0.41	92	130	-21	-	-
HSE1000	63.45	50.8	39.7	-0.79	96	136	-25	-	-
HSE2000	55.97	49.8	41.5	-0.95	108	139	-	38	70
HSE3000	45.12	40.3	43.9	-1.22	120	142	-	52	96
MSE62	98.40	84.1	33.1	-0.25	90	118	-25	-	-
MSE400	84.41	72.1	34.4	-0.28	94	120	-27	-	-
MSE1000	73.55	65.0	37.1	-0.34	110	126	-31	-	-
MSE2000	61.35	52.0	39.2	-0.50	112	130	-	31	57
MSE3000	57.32	48.3	42.1	-0.83	125	136	-	44	83
OSE62	71.21	51.4	36.1	-0.84	92	130	-28	-	-
OSE400	60.11	43.3	40.1	-0.92	96	138	-30	-	-
OSE1000	48.37	32.8	42.2	-1.15	104	144	-38	-	-
OSE2000	26.49	31.1	43.7	-1.31	126	148	-	40	81
OSE3000	23.66	29.1	45.4	-1.50	138	152	-	54	107

All tests of solution properties were proceeded at concentration 0.2%.
DSC analysis for T_g , T_m , and ΔH .

Reactivity and washing durability of oligomer to PET fiber

The treated solution constituted of oligomer and cosolvent of water and *N,N*-dimethylformamide (DMF). In the case of the HSE solution, benzoyl peroxide (BPO 1% of oligomer weight) was added as the initiator, and in the MSE type, CAT32 (0.05% of oligomer) was added as the catalyst of finishing. Pad-Dry-Cure process was employed in this study. PET fabric (75/72S.D.W \times 75/72S.D.F, Everest) was padded by the two-dip-two-nip (85% pick up); predried at 90°C for 5 min, and cured at 150°C for 3 min. The treated fabrics were washed by sodium carbonate solution of 2g/L at 60°C for 20 min. After drying, the add-on and physical properties of the treated fabric were tested. The durability of washing was tested by AATCC 135.

RESULTS AND DISCUSSION

Synthesis and identification

At the aspect of PEG soft chain containing sulfonic acid group (sulfonated diol; SE), the dimethyl 5-sulfoisophthalate sodium salt (SIP) was allowed transesterification with PEG of different molecular weights, and the residual OH value versus reaction time is depicted in Figure 1. The transesterification of SIP to glycols is at 190°C (From room temperature to 190°C

it is in the speed of 10°C per minute) with Zinc acetate dehydrate as a catalyst. While the residual OH value reached one half of the reactants, it indicates the completion of transesterification. From the diagram, the reaction time increased upon the increasing PEG molecular weight such as that the PEG of molecular weight 62 requires 3.5 h to finish the reaction and

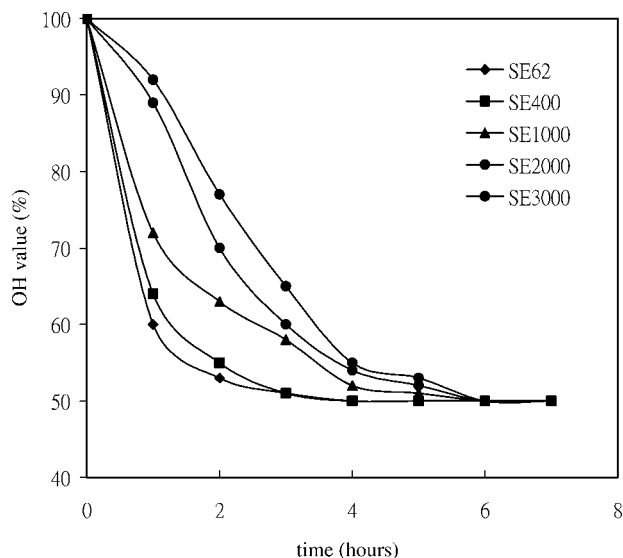


Figure 1 The residual ratio of OH value of PEG synthesized by SIPM for sulfonated diols under different reaction time of transesterification.

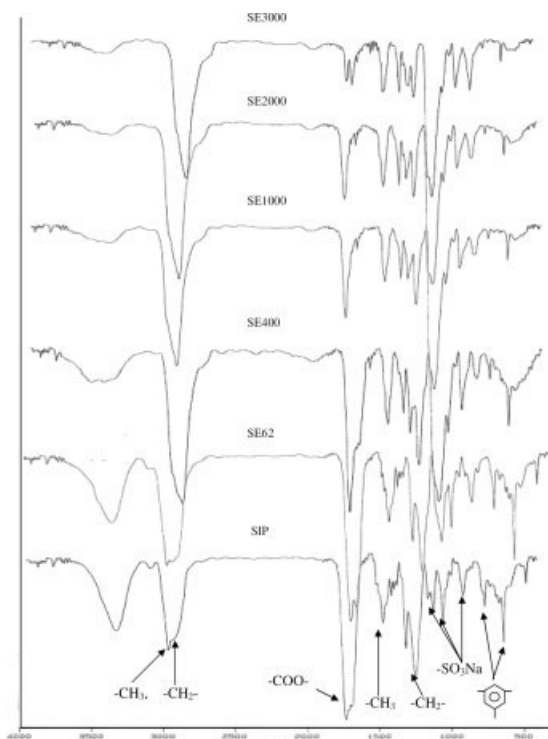


Figure 2 The IR spectra of sulfonated diols.

the PEG of molecular weight 3000 requires 7.5 h. The FTIR spectrum of SE in Figure 2 shows that the raw material SIP possessed absorbance peaks of trisubstituted benzene ring at 700, 850, and 1480 cm^{-1} . The absorptions of sulfonic acid group appeared at 1220, 1040, and 980 cm^{-1} . After the SIP transesterification with PEG to eliminate methanol, $-\text{CH}_3$ of SIP absorption at 1450 cm^{-1} disappeared, and absorption peak of ester group at 1730 cm^{-1} shifted to the right

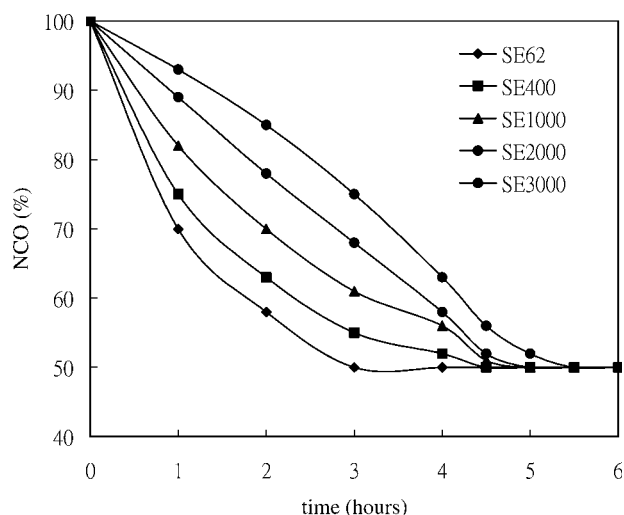


Figure 3 The residual ratio of NCO value of IPDI synthesized with sulfonated diols for the oligomer under different reaction time of first step.

side because more H-bonding were produced between the $-\text{COO}-$ and ethylene oxide of SE. However, the absorption areas of $-\text{O}-$ at 1112 cm^{-1} and $-\text{CH}_2-$ at 3020 cm^{-1} from the amount of EO increased when the PEG molecular weight of sulfonated diol increased, but all the absorption areas of OH group, ester group, phenyl group, and sulfonic group declined.

Urethane oligomer was first synthesized by prepolymerizing IPDI, which was introduced to the end of SE, and then the end of prepolymer was blocked with the MEKO, HEMA, and EPO. Figure 3 and Table II show the results of NCO analysis of urethane oligomer. The Isophorone Diisocyanate (IPDI) reacts with SE at 45°C (from room temperature to 45°C it is in the speed of 1°C per minute) with Dibutyltin dilaurate (DBTDL) as a catalyst. The residual NCO value reached one half of the reactants indicating the completion of prepolymerization. The sulfonated diol containing larger PEG length required a longer reaction time to react with the hard segment IPDI, and the reaction of all kinds of oligomer completed within ~ 2 –3.5 h. Figure 4 shows the FTIR spectra of urethane oligomers. Without regarding the kinds of urethane oligomer, the absorptions of $-\text{NH}-$ at 3400 cm^{-1} , $-\text{C}-\text{N}-$ at 1532 cm^{-1} and 1226 cm^{-1} , and $-\text{COO}$ at 1740 cm^{-1} all revealed the formation of urethane group. In addition to this, different reactive functional groups could be seen from the spectrum, the HSE

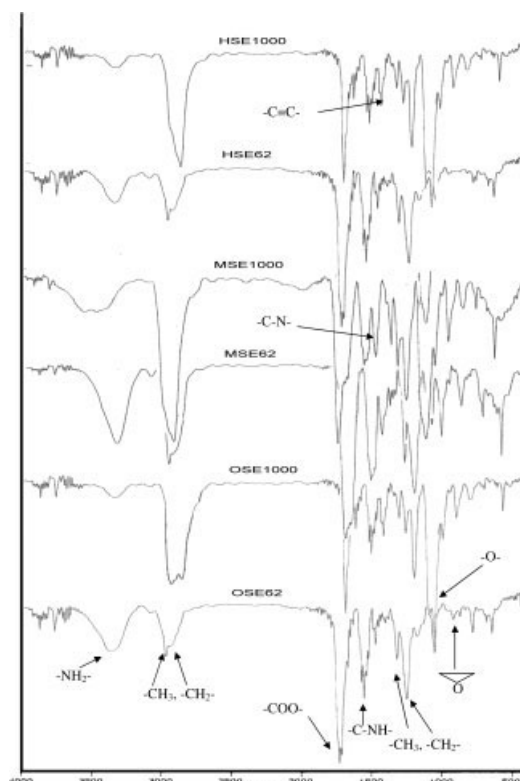


Figure 4 The IR spectra of urethane oligomers.

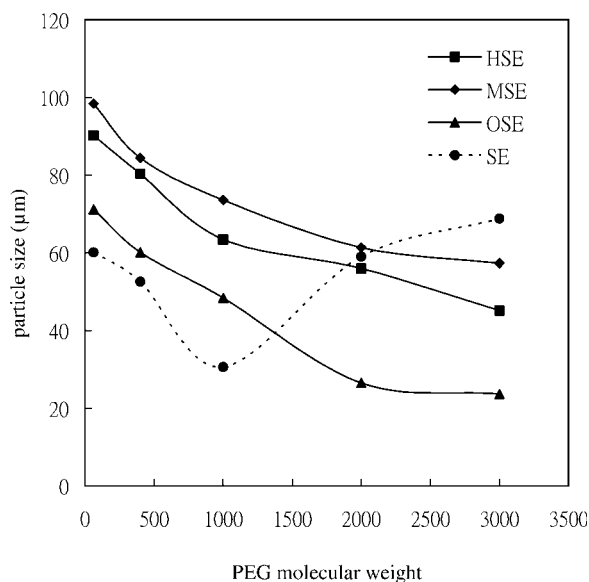


Figure 5 The particle size of solutions of oligomers.

oligomer had an absorption peak of —C=C— at 1650 and 1430 cm^{-1} , and the MSE oligomer had the a —C—N— absorption peak at 1650 cm^{-1} . The epoxide group of OSE oligomer had absorption peaks at 800 and 1250 cm^{-1} . Therefore, the structure of oligomer could be confirmed.

Solution properties of urethane oligomer emulsified dispersion

The solution properties and thermal properties of urethane oligomer are shown in Table II, and the particle size of urethane oligomers are shown in Figure 5. All solution properties were performed at a concentration of oligomer 0.2% after a stir until the value tested is constant. The particle size decreased when the PEG molecular weight was less than 1000, but increased when the PEG molecular weight was more than 1000. As the SE containing PEG of molecular weight was 62, the more hydrophobic characteristics caused the SE difficult to disperse into water. While the PEG molecular weight increased to 1000, the more hydrophilic composition caused a greater dispersing status of SE. As the PEG molecular weights were greater than 2000, the molecules tended to attract each other and resulted in entanglement, which prevents water from entering into the internal particle so the particle diameter became larger. As for the situation of reactive urethane oligomers, the particle size dropped as PEG molecular weight was increased. This was not in line with the trend of SE because the reactive groups have blocked oligomer terminals, which constrain the PEG molecules to intertwine with each other. MSE had the largest particle diameter; HSE had the second large particle diameter; and OSE had the smallest

one. The MSE had larger molecular weight and water insolubility. HSE showed the poor water solubility for having —C=C— group, so the particle diameter of HSE was larger than OSE. The epoxy group of OSE, which possesses good water solubility, conferred OSE a smaller particle diameter. Another reason is that MSE and HSE oligomers has larger molecular than that of OSE. Figure 6 shows the particle variance of oligomer solutions, and the large variance value indicated that the particle size of emulsion was not even in the solution. All sulfonated diols or oligomers decreased upon the increase of PEG molecular weight, because more EO group is easy to hydrate with water and evenly disperse in water. The trend of particle variance was the same as the particle size of oligomer type in the order of $\text{MSE} > \text{HSE} > \text{OSE}$. This indicates that the oligomer possesses a great hydrophilic characteristic and can easily disperse evenly.

Figure 7 shows the surface tension of oligomer solutions. The surface tension of oligomer solutions was found to increase along with the increase of PEG molecular weight of oligomer. The oligomer containing PEG of low molecular weight possessed a stronger hydrophobic characteristic, resulting in the formation of micelles easily. Because of the PEG of larger molecular weight, the EO group produced H-bonding with water so the hydrophobic groups of oligomer had difficulty to attract to form micelles. For the oligomer type, the surface tension of solutions of OSE, HSE, and MSE were compared and ranked in the order of $\text{OSE} > \text{HSE} > \text{MSE}$ because of the difference of oligomers in terms of hydrophilic property, and the results were consistent with the particle diameter. Figure 8 shows the results of streaming current reading. While molecular weight of PEG went up, the stream-

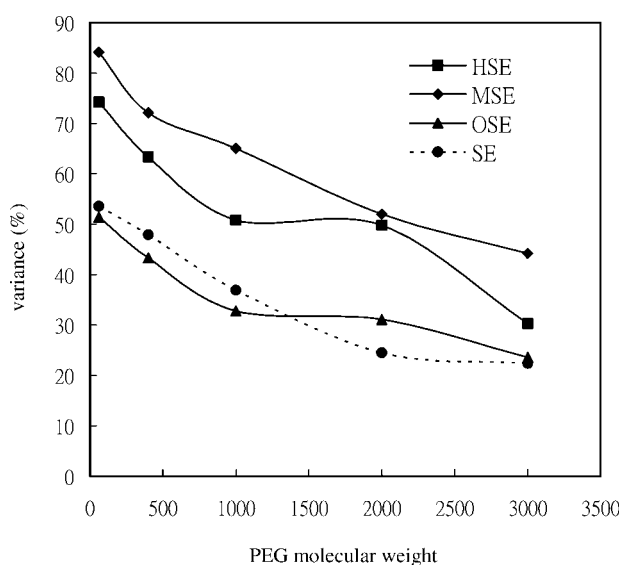


Figure 6 The particle variance of solutions of oligomers.

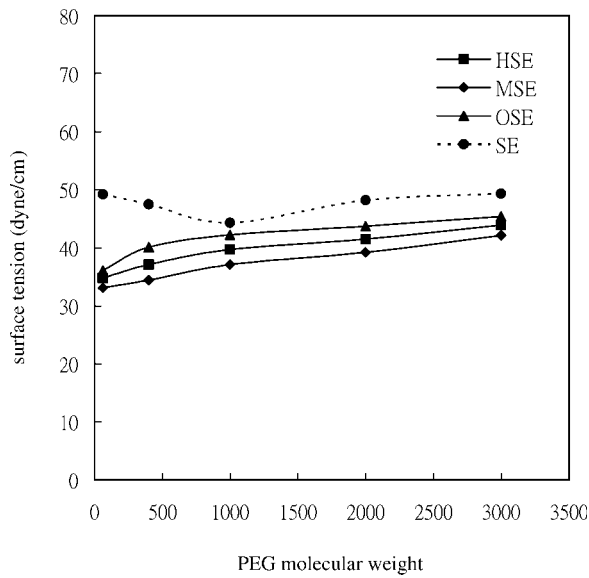


Figure 7 The surface tension of solutions of oligomers.

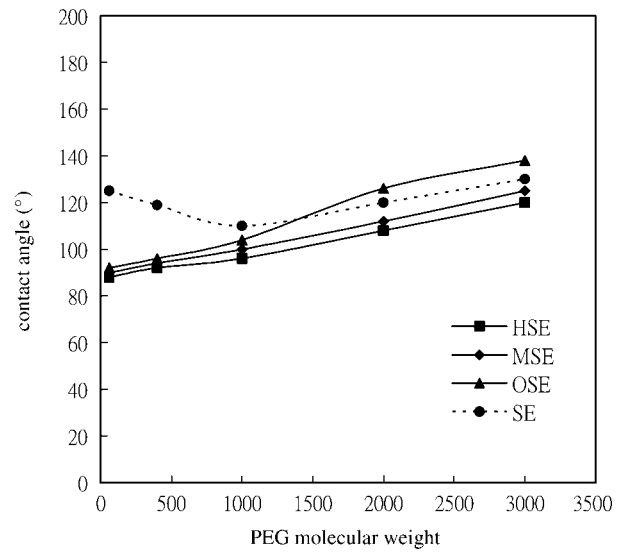


Figure 9 The contact angles of solutions of oligomers on acrylic plate.

ing current reading declined. In general, the streaming current reading was determined by the electric charge on the particle surface. The oligomer containing the PEG of low molecular weight has more ionic groups and causes molecular chains to attract to each other, so it increases the peripheral electric charge surrounding the micelle and shows the highest reading. The value declined as PEG of oligomer became longer due to the smaller electric charge. As for the oligomer type, MSE was the highest, HSE the second, and OSE had the lowest streaming current reading because the hydrophobic property of MSE was stronger causing its micelle larger but OSE had an opposite situation.

Figures 9 and 10 show the contact angle of sulfonated diol and oligomer on acrylic plastic sheet and polyester fabric, respectively. Without regarding the contact angle on acrylic sheet or polyester fabric, all oligomers enhanced their contact angles as the PEG molecular weight increased. OSE had the greatest contact angle while HSE came next, and MSE had the smallest. The acrylic plastic sheet and polyester fabric are hydrophobic and the oligomer containing PEG of larger molecular weight had a lower surface tension (Fig. 6) to decrease the surface free energy, so its contact angle was smaller. In addition, since the hydrophilic property of OSE had a greater surface tension so the contact angle was larger.

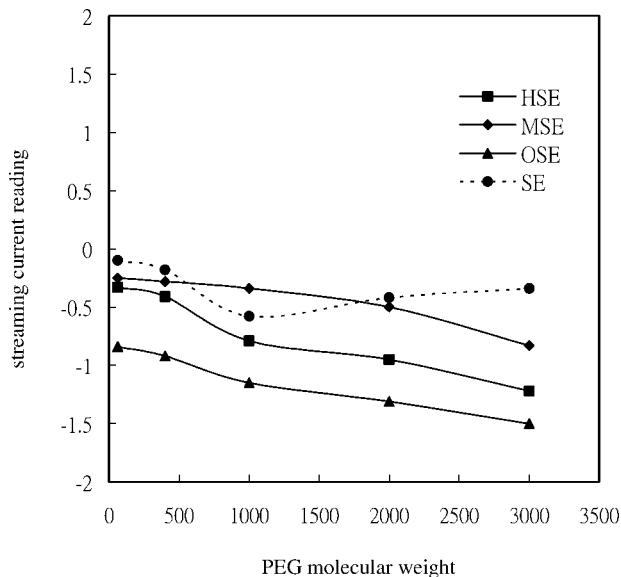


Figure 8 The streaming current reading of solutions of oligomers.

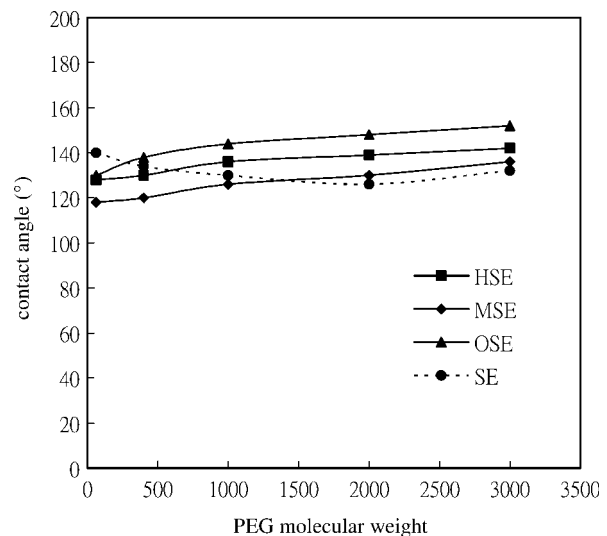


Figure 10 The contact angles of solutions of oligomers on PET fabrics.

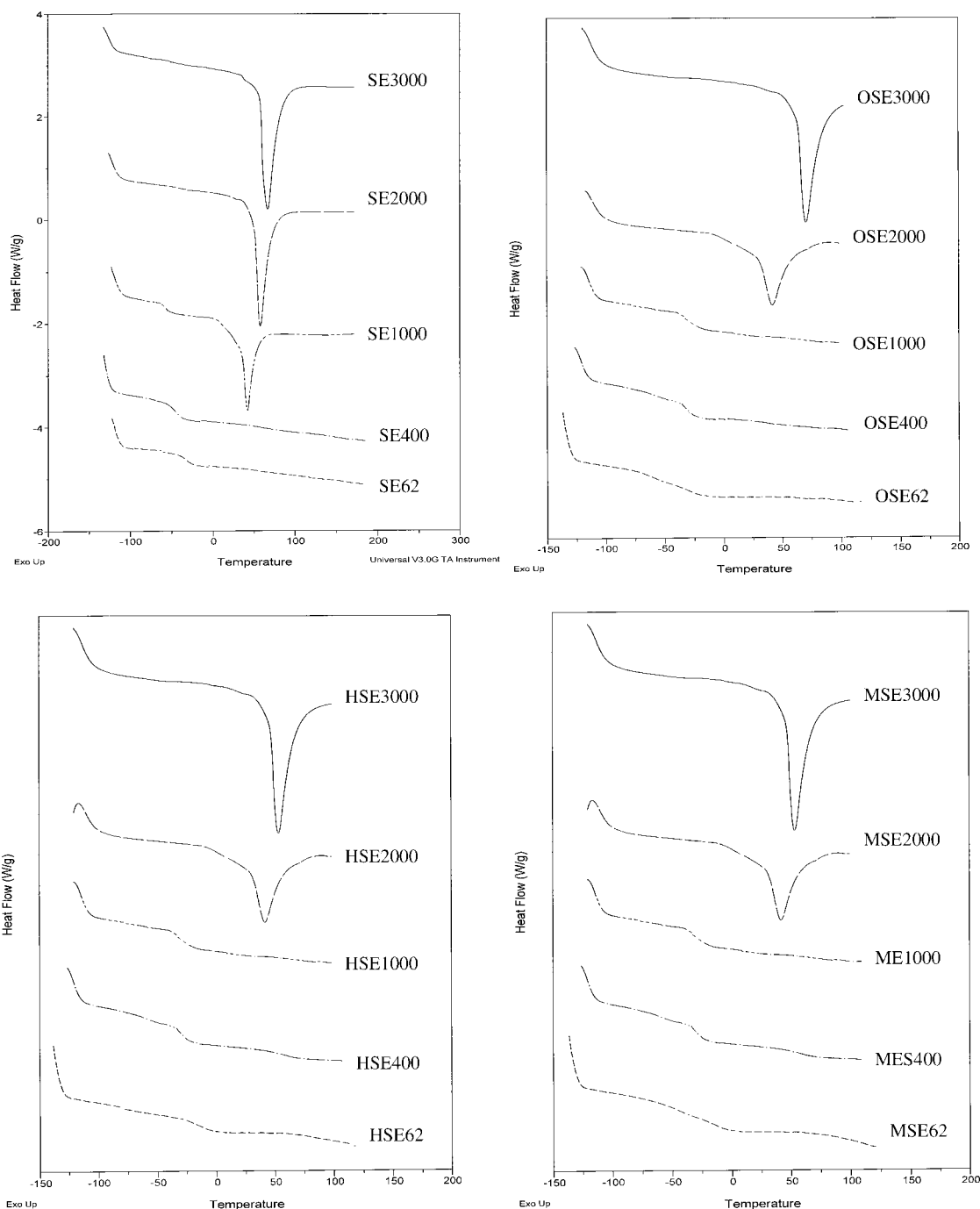


Figure 11 The DSC thermograms of sulfonated diols and urethane oligomers.

Thermal properties of urethane oligomer

Figure 11 shows DSC thermal analysis of oligomers, and the data of glass-transition point, melting temperature, and enthalpy are summarized in Table II. From these results, the T_g of oligomer and sulfonated diol reduced while PEG molecular weight increased for longer soft chains, which might be less constrained by hard chains, whereas the molecular chains were more easy to move. T_m and enthalpy become greater when PEG molecular weight increased because larger PEG

molecules tend to attract mutually to produce crystallite. For the comparison of urethane oligomer and sulfonated diol, the glass-transition point of sulfonated diols were lower than that of the oligomer, but the melting temperature and ΔH were both higher than those of oligomers because the terminals of sulfonated diol are not blocked, and its chains are more flexible so they could easily fold up to form crystallite. With regard to oligomer type, T_g of MSE was the highest, HSE the next, and OSE was the lowest, and the melting

temperature and ΔH displayed a contrary tendency. This was due to both MSE and HSE containing double-bonded functional groups, whereas the end group has methyl and ethyl groups. Thus higher energy was required for the movement of MSE and HSE oligomer molecules resulting in a higher T_g . OSE that contains softer EPO has lower glass-transition point. Furthermore, the epoxy group of OSE was similar to the EO group of PEG that did not interfere with the crystallization of PEG and thus had the highest T_m and enthalpy. Because of the double-bonded structure of the end groups, the PEG crystallization of MSE and HSE were interfered, and thus had the lowest T_m and enthalpy.

Reactivity and washing durability of oligmer to PET fiber

Figure 12 shows the influence of the PEG molecular weight of urethane oligomer to the reactive add-on of PET treated fabric. It could be seen from the diagram that the add-on for various oligomers was in the quantitative order of MSE > HSE > OSE series. Generally, a smaller contact angle to fiber caused a stronger absorption to enhance the reactivity with fiber. From Figure 10 the contact angle followed the trend: MSE > HSE > OSE, and that indicated that the MSE possessed a strongest absorption to PET fiber. HSE was the next, and OSE was the poorest in absorption. The reactivity of the oligomer containing NCO group was stronger than others containing acrylic group or epoxide group. The add-on had a tendency to decline upon the increase of PEG molecular weight of oligomer because the oligomer contained more hydrophilic PEG to weaken the absorption. Figure 13 shows the situation in the washing durability of treated PET fabrics. HSE fabrics had the greatest

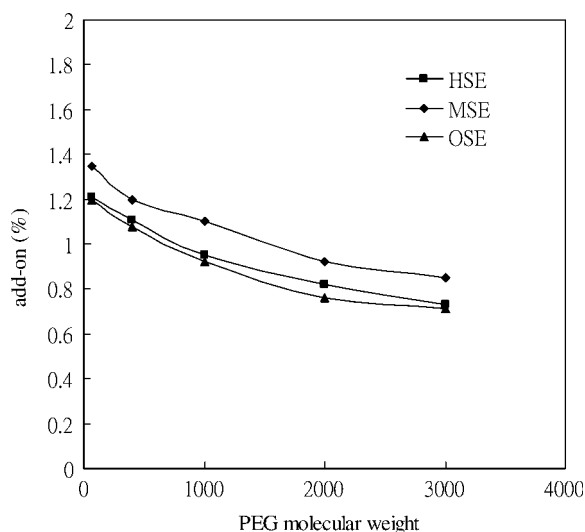


Figure 12 The add-on of PET fabrics treated by oligomers.

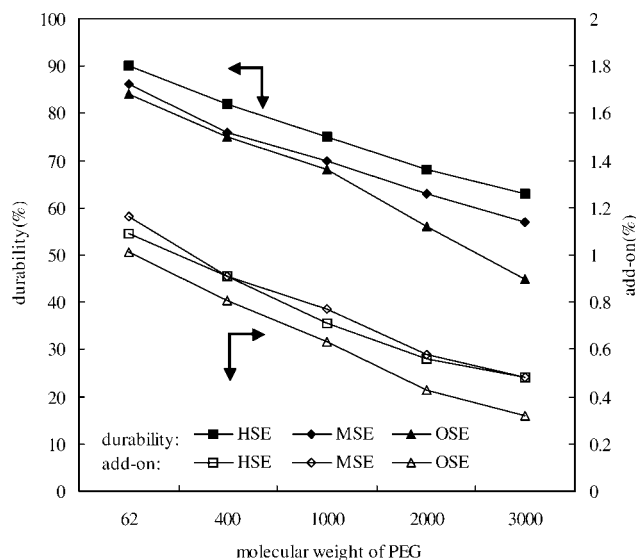


Figure 13 The durability and add-on after washing of PET fabrics treated by oligomers.

durability, and the next was MSE fabrics, followed by OSE fabrics, which were the poorest. In the HSE oligomer, the free radical polymerization could lead to a grafting reaction to PET fiber, and the oligomer could react with fibers to form a firm chemical bonding. As the hydrophobic group of MSE oligomer was strongly adsorbed to PET during the reaction, it could effectively get entangled and reacted with fibers. In the case of OSE oligomer, its hydrophobic and hydrophilic structures were intermixed causing a poor adsorption, and thus the durability of OSE fabric became the poorest.

CONCLUSIONS

This research studied urethane oligomers containing sulfonic acid group and different reactive groups. Their solution properties, thermal properties, and reactivity to PET fibers were investigated. The following conclusion was drawn from the observed results.

At the aspect of solution properties, the MSE oligomer had the greatest particle diameter, particle variance, and streaming current readings. The HSE oligomer was the next, and the OSE oligomer showed the smallest value whereas the contact angle and surface tension appeared with an opposite trend. Without regarding the types of oligomer, the particle size, particle variance and streaming current reading of aqueous reactive urethane oligomer decreased, but the surface tension and contact angle were enhanced upon the increase of PEG molecular weight of oligomer. Within the thermal properties of oligomer, the T_g of MSE was the highest, HSE the next, and OSE was the lowest; however T_m and ΔH show an opposite tendency. The glass-transition

point of oligomer declined, but the melting point and enthalpy became enhanced while PEG molecular weight increased. With regard to the reactivity of the oligomers toward PET fabrics, the add-on of MSE was the largest, HSE the next, and OSE was the lowest. HSE possessed the highest durability, MSE the second, and OSE had the lowest. There was a decreasing trend of add-on and washing durability of the treated fabrics as PEG molecular weight increased.

References

1. Hepburn, C. In *Polyurethane Elastomers*; Elsevier Science: New York; 1982; p 225.
2. Szycher, M. In *High Performance Biomaterials* Technomic: Lancaster, 1991; p 51.
3. Roy, S.; Kumar, A. *Poly Eng Sci* 1995, 35, 1046.
4. Thames, S. F.; Boyer, P. C. *J Coat Technol* 1990, 62, 51.
5. Takeichi, T.; Suefuji, K.; Inoue, K. *J Polym Sci Polym Chem* 2002, 40, 3497.
6. Takeichi T.; Suefuji K.; Inoue K. *Polym J* 2002, 34, 455.
7. Zuo, M.; Takeichi, T. *J Polym Sci Polym Chem* 1997, 35, 3745.
8. Zuo, M.; Takeichi, T. *Polymer* 1999, 40, 5153.
9. Lai, Y. C.; Baccei, L. J. *J Appl Polym Sci* 1991, 42, 2039.
10. Nabeth, B.; Gerard, J. F.; Pascault, J. P. *J Appl Polym Sci* 1996, 60, 2113.
11. Lai, Y. C.; Baccei, L. J. *J Appl Polym Sci* 1991, 42, 3173.
12. Clayton, A. B.; Allen, P. E. M.; Williams, D. R. G. *Eur Polym Mater* 1993, 29, 1231.
13. Shama, J A.; Tortorello, A. J. *J Appl Polym Sci* 1991, 43, 699.
14. Hossain, M. A.; Hassan, T.; Khan, M. A.; Ali, M. I. *Polym Plast Technol Eng* 1997, 33, 1.
15. Sreenivasan, K.; Rao, K. V. C. *J Appl Polym Sci* 1992, 44, 1703.
16. Suh, K. D.; Chou, Y. S.; Kim, J. Y. *Polym Bull* 1997, 38, 294.
17. Suh, K. D.; Kim, J. Y. *Colloid Polym* 1996, 274, 920.
18. Grepinet, B.; Pla, F.; Hobbes, P.; Swaels, P.; Monge, T. *J Appl Polym Sci* 2000, 75, 705.
19. Grepinet, B.; Pla, F.; Hobbes, P.; Swaels, P.; Monge, T. *J Appl Polym Sci* 2001, 81, 3149.
20. Li, Y. S.; Li, M. S.; Ma, C. C. M.; Hsia, H. C. *Polym Int* 1994, 35, 371.
21. Li, Y. S.; Li, M. S.; Ma, C. C. M.; Chen, D. S.; Hsia, H. C. *Polym Int* 1994, 35, 361.
22. Li, Y. S.; Li, M. S.; Ma, C. C. M.; Chen, D. S.; Hsia, H. C. *J Appl Polym Sci* 1994, 52, 1137.
23. Ohtsuka, K.; Hasegawa, K.; Fukada, A. *Polym Int* 1994, 33, 93.
24. Wang, H. H.; Chen, J. C. *J Appl Polym Sci* 2001, 82, 2903.
25. Han, J. L.; Chern, Y. C.; Li, K. Y.; Hsieh, K. H. *J Appl Polym Sci* 1998, 70, 529.
26. Tan, S. T.; Wei, C.; Wang, X. Y.; Zhang, M. Q.; Zeng, H. M. *J Appl Polym Sci* 2003, 88, 783.
27. Harani, H.; Fellahi, S.; Bakar, M. *J Appl Polym Sci* 1998, 70, 2603.
28. Chiang, W. Y.; Chang, D. M. *J Mater Sci* 1997, 32, 4085.
29. Wang, H. H.; Chen, J. C. *J Appl Polym Sci* 1995, 57, 671.
30. Visser, S. A.; Cooper, S. L. *Macromolecules* 1991, 24, 2576.
31. Visser, S. A.; Cooper, S. L. *Polymer* 1992, 33, 920.
32. Thompson, A. A.; Yu, X.; Cooper, S. L. *J Appl Polym Sci* 1990, 41, 1831.
33. Wei, X.; Yu, X. *J Polym Sci Polym Phys* 1997, 35, 225.
34. Ho, K. S.; Hsieh, K. H.; Huang, S. K.; Hsieh, T. H. *Synth Metals* 1999, 107, 65.
35. Skarja, G. A.; Brash, J. L. *J Biomed Mater Res* 1997, 34, 439.
36. Santerre, J. P.; Brash, J. L. *Macromolecules* 1991, 24, 5497.
37. Zhu, W.; Tian, L.; Ren, T.; Wang, X.; Tang, X.; Li, G. *J Appl Polym Sci* 2002, 84, 67.
38. Wang, X.; Fang, B.; Wang, L.; Tang, X.; Chang, F. C. *J Appl Polym Sci* 2001, 82, 541.
39. Wang, X.; Wang, L.; Li, H.; Tang, X.; Chang, F. C. *J Appl Polym Sci* 2000, 77, 184.
40. Wang, X.; Li, H.; Tang, X.; Chang, F. C. *J Polym Sci Polym Phys* 1999, 37, 837.
41. Wang, X.; Zhu, W.; Liu, Y.; Tang, X.; Yang, X. *J Appl Polym Sci* 2003, 89, 2369.
42. Lewandowski, K.; Krepski, L. R.; Mickus, D. E.; Roberts, R. R.; Heilmann, S. M.; Laeson, W. K.; Purgett, M. D.; Koecher, S. D.; Johnson, S. A.; McGurran, D. J.; Rueb, C. J.; Pather, S. V.; Thakur, K. A. M. *J Polym Sci Polym Chem* 2002, 40, 3037.
43. Wei, X.; Yu, X. *J Polym Sci Part B Polym Phys* 1997, 35, 225.
44. David, D. J. In *Analytical Chemistry of the Polyurethane*; Wiley-Interscience: New York, 1969; p 86.
45. Barbee, R. B. U.S. Pat. 40,43,753 (1977).