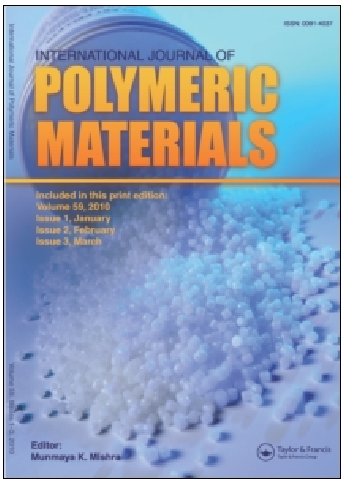


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Polyesters containing sulfur, X: The use of new hydroxyl-terminated thiopolyesters with diphenylmethane unit in their structure for polyurethane preparation

Anna Kultys[a]
[a] Department of Organic Chemistry and Technology, Maria Curie-Skltodowska University, Lublin, Poland

To cite this Article Kultys, Anna(2003) 'Polyesters containing sulfur, X: The use of new hydroxyl-terminated thiopolyesters with diphenylmethane unit in their structure for polyurethane preparation', International Journal of Polymeric Materials, 52: 9, 773 — 783

To link to this Article: DOI: 10.1080/713743709

URL: http://dx.doi.org/10.1080/713743709

International Journal of Polymeric Materials, 52:773–783, 2003

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390225093

POLYESTERS CONTAINING SULFUR, X: THE USE OF NEW HYDROXYL-TERMINATED THIOPOLYESTERS WITH DIPHENYLMETHANE UNIT IN THEIR STRUCTURE FOR POLYURETHANE PREPARATION

Anna Kultys
Department of Organic Chemistry and Technology,
Maria Curie-Skłtodowska University, Lublin, Poland

The new linear hydroxyl-terminated thiopolyesters (PEs) containing thioether linkages in the main chain were prepared by melt polymerization of newly obtained diphenylmethane-4,4′-bis(methylthioacetic acid) with excess of 1,4-butanediol, 1,5-pentanediol (PD), and 1,6-hexanediol. All these PEs ($\bar{M}_n$ *of* $\sim$*1900–2500) were converted to thiopoly(ester-urethane)s (PEUs) by addition reaction with hexamethylene diisocyanate (HDI) or 4,4′-diphenylmethane diisocyanate (MDI) which was carried out in melt at the ratio of* $NCO/OH = 1.05$*. The PEUs obtained were elastomeric products, completely amorphous from MDI or with a little tendency to crystallize from HDI. Their characteristics were* $\eta_{red} = 0.65$–0.93 *dL/g, glass transition temperatures ranging from* -12.7 *to* -0.9*°C, tensile strength of* $0.4-2.3$ *MPa, elongation at break of 650–2000%, and thermal stabilities of up to* $230-260$*°C. Segmented PEUs (hard segment content* $\sim$*50 wt.%) prepared by using the PD-based PE, HDI or MDI, and bis[4-(6-hydroxyhexylthio)phenyl] ether as a chain extender were elastomeric materials, particularly those from MDI, with tensile strength of 10.6 or 13.8 MPa and elongation at break of 120 or 250%, respectively. The structures of the polymers were determined by Fourier transform infrared and* H^1*-NMR.*

Keywords: Diphenylmethane, linear thiopolyester diols, melt polymerization, thiopoly(ester-urethane)s, thermoplastic elastomers, thermal and tensile properties

Received 16 April 2001; in final form 22 April 2001.

Address correspondence to Anna Kultys, Department of Organic Chemistry and Technology, Maria Curie-Sktodowska University, ul. Gliniana 33, 20-614 Lublin, Poland. E-mail: akultys@hermes.umcs.lublin.pl

INTRODUCTION

Recently, my colleagues and I have reported on the possibility of using the newly obtained linear hydroxyl-terminated aliphatic-aromatic thiopolyesters (PEs) containing thioether linkages in the main chain for synthesis of thermoplastic polyurethane elastomers by extension with both 4,4′-diphenylmethane diisocyanate (MDI) and hexamethylene diisocyanate (HDI) [1–4]. The PEs ($\bar{M}_n$ of 1600–2900) were prepared by melt polymerization of the various aliphatic–aromatic diacids, including naphthalene-1,4-bis(methylthioacetic acid) (N14AA), naphthalene-1,5-bis(methylthioacetic acid) (N15AA) [1], benzophenone-4,4′-bis(methylthioacetic acid) (BAA) [2], or diphenylmethane-4,4′-bis(methylthiopropionic acid) (DPA) [3] with 1,4-butanediol (BD), 1,5-pentanediol (PD), or 1,6-hexanediol (HD) as well as DPA or diphenylmethane-4,4′-bis(methylthioacetic acid) (DAA) with aliphatic–aromatic thiodiol bis[4-(2-hydroxyethylthiomethyl)phenyl]-methane [4].

HDI-based thiopoly(ester-urethane)s (PEUs) prepared by melt polymerization at the ratio of NCO/OH ~ 1 were thermoplastic elastomeric materials, partially crystalline or amorphous, showing reduced viscosities in the range of 0.4–1.1 dL/g, glass transition temperatures (T_g) from -22 to 17°C, tensile strength $\sim$2–17 MPa, and good thermal resistance (up to 235–265°C). In general, PEUs from N15AA-based PEs showed the highest tensile strength, whereas those from DPA-based PEs the lowest T_gs. The analogous MDI-based PEUs obtained in the same conditions were, as expected, completely amorphous elastomers, showing the higher tensile strength but the lower thermal resistance and the higher T_gs than those from HDI. The PEUs derived from DPA and DAA-based PEs bearing diphenylmethane units with active methylene groups, were new potentially peroxide-curable polyurethanes including HDI-based ones [5]. A convenient way of introducing an active methylene group is by the use of MDI as chain-extending diisocyanate. Peroxide curing potential may also be introduced into polyurethane elastomers by the incorporation of the olefinic $-C{=}C-$ groups into the structure, usually as the allyl ether group, $CH_2{=}CH{-}CH_2{-}O-$ [6, 7].

The purpose of the work in this paper was to synthesize new linear hydroxyl-terminated PEs containing diphenylmethane units in their structure as new oligoester diol components for production of the potentially peroxide-curable polyurethane elastomers. The PEs prepared from DAA and BD, PD or HD were converted to PEUs by addition reaction with HDI or MDI. Their thermal and tensile properties were determined and compared. The properties of the segmented PEUs (SPEUs) with the hard segment content of ~ 50 wt.% prepared from chosen PE as the soft segment, the newly obtained thiodiol bis[4-(6-hydroxyhexylthio)phenyl] ether (HPE) as a chain extender, and HDI or MDI were also described.

EXPERIMENTAL

Materials

DAA (m.p. = 166–167°C after crystallization from acetic acid) was obtained by condensation reaction of bis[4-(mercaptomethyl)phenyl] methane with monochloric acetic acid [8].

HPE (m.p. = 71 – 72°C after crystallization from benzene) was obtained by condensation reaction of bis(4-mercaptophenyl) ether with 6-chloro-1-hexanol [9].

The commercial diols, including BD (b.p. = 230–232°C), PD (b.p. = 241–243°C), and HD (b.p. = 253–260, m.p. = 41–43°C) from Fluka Chemie AG (Busch, Switzerland) were all purified by vacuum distillation before using.

MDI by Farbenfabriken Bayer was purified by vacuum distillation. Distillation fraction was collected at 148–150°C/0.12 mm Hg.

Other reagents such as HDI and dibutyltin dilaurate (DBTDL) from Merck-Schuchardt (Hohenbrunn, Germany) were used as received.

Measurements of Properties

Reduced viscosities (η_{red}, dL/g) of 0.5% polymer solution in tetrachloroethane (TChE) were measured in an Ubbelohde viscometer at 25°C.

Number-average molecular weights ($\bar{M}_n$) of PEs were obtained using a Hewlett Packard osmometer 302 B. The measurements were performed in chloroform at 37°C.

The acid numbers were determined by standard titrimetric method (Polish Standard PN-79/C-89406) described in an earlier work [4]. The hydroxyl numbers were calculated using the formula $\bar{M}_n = 56.1 \times 2 \times 1000/(\text{hydroxyl number} + \text{acid number})$.

Thermogravimetric analysis (TGA) was performed on a MOM 3427 derivatograph (Paulik, Paulik and Erdey, Budapest, Hungary) at the heating rate of 10 K/min in air; measurement relative to Al_2O_3.

Differential scanning calorimetry (DSC) thermograms were obtained with a DuPont 2000 TA calorimeter at the heating rate of 10 K/min. T_gs for the polymer samples were taken as the inflection point on the curves of the heat-capacity changes.

The hardness of the PEUs was measured by the Shore A/D method at 25°C; values were taken after 15 s.

Tensile testing was performed on a TIRA Test 2200 tensile-testing machine according to Polish Standard PN-81/C-89034 at the speed of 100 mm/min at 23°C; the tensile test pieces 1 mm thick and 6 mm wide (for the section measured) were cut from the pressed sheet.

Fourier transform infrared (FTIR) spectra were obtained with a Perkin-Elmer 1725 X FTIR spectrophotometer using thin films.

The ^{1}H-NMR spectra were obtained with a Tesla BS-567-A spectrometer at 100 MHz with tetramethylsilane as internal reference. Samples were run in $CDCl_3$ or CD_3SOCD_3 solutions.

Polymer Synthesis

PEs

All the PEs were prepared by melt polymerization of 60 mmol (22.59 g) of DAA and 78 mmol (7.03, 8.12, 9.22 g) of BD, PD, and HD, respectively.

The reaction was carried out under nitrogen at 150–170°C for about 16 h, the last 6 h under reduced pressure. In these conditions esterification water and excess of diol were being removed by distillation.

The PEs obtained after cooling to room temperature were almost colorless thick oils from which only BD-based PE solidified and crystallized after some time at room temperature.

FTIR (film): 1730 (vs, C=O), 1278–1274 (s, C–O), 3547–3540 (OH), 1416 (CH of CH_2S), 2956–2934 and 2936–2860 (CH of CH_2), 1610 and 1510–1511 cm^{-1} (benzene ring).

^{1}H NMR ($CDCl_3$): $\delta = 1.40 - 1.79$ (m, H^f, $(CH_2)_{2,3 \text{ or } 4}$), 3.06 (s, H^d), 3.64–3.67 (t, H^h, $J \sim 6$ Hz), 3.78–3.79 (s, H^c), 3.93 (s, H^a), 4.08–4.20 (m or t, H^c, $J \sim 6$ Hz), 7.13 and 7.23 (dd, H^b, $J = 8.3$ Hz); (CD_3SOCD_3) $\delta = 4.37 - 4.45$ ppm (t, H^g $J \sim 5$ Hz).

PEUs

All the PEUs were prepared by melt polymerization at the ratio of NCO/OH = 1.05. PEs: B, P. and H (each in the amount of 5.0 g) and HDI (respectively 0.4071, 0.3525, 0.4580 g) or MDI (respectively 0.6057, 0.5245, 0.6815 g) were used.

The general procedure for synthesis of the PEUs by this method was as follows. PE and diisocyanate were gradually heated with stirring under dry nitrogen up to about 140°C and polymerization was continued at this temperature under vigorous stirring for 2 h. Using HDI, DBTDL ($\sim$0.5 wt.;%) was added after the temperature of the mixture reached 90°C. The PEUs obtained were light-yellow elastomeric products.

FTIR (film): 1730–1728 (HDI) or 1732–1729 (MDI) (s, bonded C=O stretching of the urethane group), 1522–1521 (HDI) or 1530–1528 (MDI) (NH bending of the urethane group), 3392–3322 (HDI) or 3351–3350 (MDI) (bonded NH stretching of the urethane group), about 1730 cm^{-1} (vs, C=O stretching of the ester group).

SPEUs

The SPEUs were prepared by one-step melt polymerization process at the ratio of NCO/OH = 1.05 at the temperature range of 120–150°C according to the procedure described for PEUs. PE P (5.0100 g, 2.03 mmol), HPE (3.4773 g, 8.00 mmol) and HDI (1.7661 g, 10.50 mmol) or MDI (2.6277 g, 10.50 mmol) were used.

The SPEUs obtained were light-yellow elastomeric materials.

FTIR (film): about 1725 and 1685 (HDI) or 1732 and 1681 (MDI) (s, bonded C=O stretching of the urethane group), 1538 (HDI) or 1597 (MDI) (NH bending of the urethane group), 3327 (HDI) or 3340 (MDI) (bonded NH stretching of the urethane group), about 1730 (vs, C=O stretching of the ester group), about 1260 (vs, C–O stretching of diaryl ether) cm^{-1}.

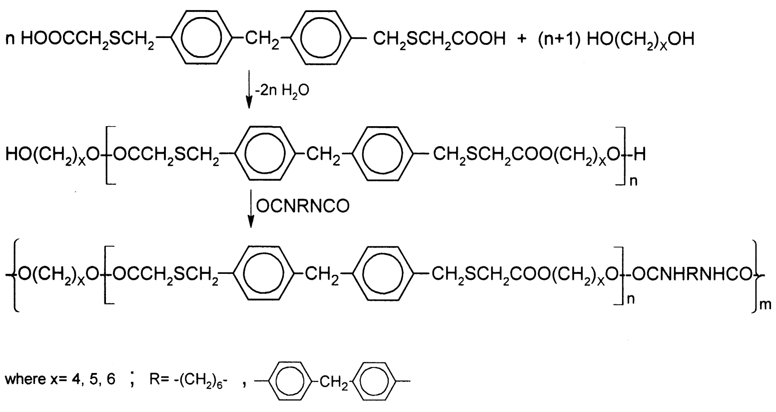
RESULTS AND DISCUSSION

PE Synthesis and Characterization

The new linear PEs (B, P, and H) were prepared according to Scheme 1 by step-growth polymerization of DAA with 0.3 molar excess of BD, PD, or HD. These condensation reactions were conducted in the melt without using a catalyst until products with acid number below 1 mg KOH/g were formed. The excess diol was removed by the application of vacuum. Acid numbers, hydroxyl numbers, number-average functionalities (f_n) of all the PEs as well as $\bar{M}_n$ and reduced viscosities are given in Table 1.

The PEs obtained were thick oils (from PD and HD) or solid (from BD). All the PEs were soluble in common organic solvents like dioxane, chloroform, methylene and ethylene chloride, TChE, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), dimethylsulfoxide, tetrahydrofuran, and nitrobenzene at room temperature.

The chemical structures of all the PEs were examined by FTIR and ^{1}H-NMR. The typical ^{1}H-NMR spectrum of the PE H is shown in Figure 1.



SCHEME 1

Thermal Properties

Thermal behavior of all the PEs was examined by DSC and TGA, and the results are summarized in Table 2.

The T_gs of all the PEs were observed in the range of -23.7 to -17.9°C; they decreased with the increase in the number of methylene groups in the diol component. The DSC thermogram of the PE B without the glass transition showed the melting endotherm with the peak at 32.2°C and heat of fusion (ΔH) 17.3 J/g indicating its partially crystalline structure. In Figure 2, A and B, the thermograms of the PE B and P are presented.

The PEs showed good thermal stability and did not show appreciable decomposition until the 260–270°C temperature range in air.

PEU Synthesis and Characterization

New thermoplastic PEUs were prepared, according to Scheme 1, by step-growth polymerization of the newly obtained PEs: B, P, H and HDI (B/H, P/H, H/H) or MDI (B/M, P/M, H/M). The addition reac-

TABLE 1 Some Physicochemical Properties of PEs

PE	Diol	η_{red}(dL/g)	$\bar{M}_n$	Acid number (mg/g)	Hydroxyl number (mg/g)	f_n
B	BD	0.14	2140	0.70	51.74	1.9733
P	PD	0.16	2470	0.63	44.80	1.9723
H	HD	0.16	1910	0.48	58.21	1.9836

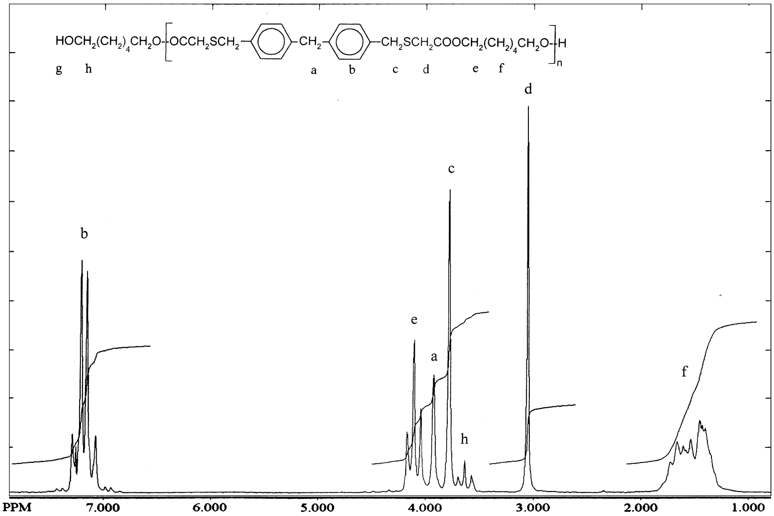


FIGURE 1 ^{1}H-NMR spectrum (in $CDCl_3$) of the PE H; H^g, $\delta = 4.40$ ppm (in CD_3SOCD_3).

TABLE 2 Thermal Properties of PEs, PEUs, and SPEUs

		TGA (°C)			
Polymer	T_g (°C)	T_d[a]	T_{10}[b]	T_{50}[c]	T_{max}[d]
PE					
B	– 17.9	270	335	430	340
P	– 19.7	260	335	430	340
H	– 23.7	270	330	425	335
PEU					
B/H	– 6.7	260	345	410	355
P/H	– 9.4	250	350	415	360
H/H	– 12.7	250	355	425	375
B/M	– 0.9	230	330	460	345
P/M	– 1.5	240	330	450	340
H/M	– 2.9	240	340	475	350
SPEU					
sP/H	– 12.3	230	335	405	365, 410
sP/M	– 7.5, 16.4	200	330	430	355, 410

[a] The temperature of initial decomposition from the thermogravimetric (TG) curve.

[b] The temperature of 10% weight loss from the TG curve.

[c] The temperature of 50% weight loss from the TG curve.

[d] The temperature of the maximum rate of weight loss from the differential TG curve.

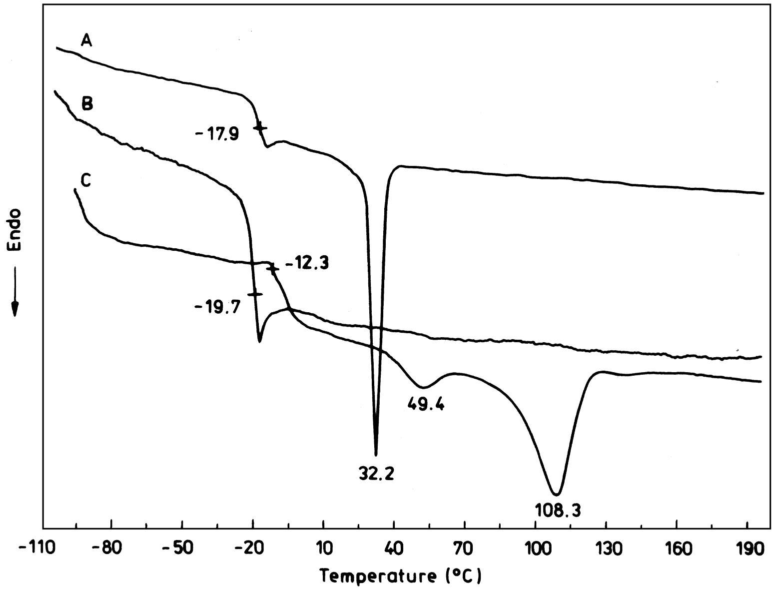


FIGURE 2 DSC thermograms of the PE (A) B and (B) P, and (C) the SPEU sP/H.

tion was carried out in the melt at the ratio of NCO/OH = 1.05 in the presence of DBTDL as a catalyst, when a less reactive HDI was used.

The PEUs obtained are light-yellow elastomeric materials. The reduced viscosities, ranging from 0.65 to 0.93 dL/g (Table 3), point to the high molecular weights of these polymers. All the HDI-based PEUs and P/M were soluble in TChE, NMP, DMF, DMAc, pyridine, and chloroform at room temperature. The MDI-based polymers B/M and H/M were soluble in TChE, pyridine, DMF, and chloroform at room temperature, whereas in NMP and DMAc at heating.

The chemical structures of the PEUs were examined by FTIR. All the spectra exhibited significant absorptions of the urethane group.

Thermal Properties

Thermal behavior of all the PEUs was examined by DSC and TGA. The T_gs and TGA data of all the polymers are given in Table 2.

The HDI-based PEUs showed lower T_gs (– 12.7 to – 6.7) than the corresponding MDI-based polymers (– 2.9 to – 0.9). In both series these values decreased together with the growing number of the methylene groups in the polymer chain. Only the DSC thermograms of the HDI-based PEU H/P and H/H exhibited a small endotherm at

TABLE 3 Reduced Viscosities and Mechanical Properties of PEUs and SPEUs

Polymer	PE	Diiso-cyanate	η_{red} (dL/g)	Hardness (Shore A/D)	Modulus of elasticity (MPa)	Tensile strength (MPa)	Elongation at break (%)	Pressing temperature (°C)
PEU								
B/H	B	HDI	0.74	28/6	2.6	0.4	730	130
P/H	P	HDI	0.65	24/4	2.3	0.4	1300	120
H/H	H	HDI	0.84	43/6	4.6	1.9	650	150
B/M	B	MDI	0.93	48/8	2.2	1.2	1500	140
P/M	P	MDI	0.72	32/6	1.6	1.3	2000	125
H/M	H	MDI	0.66	42/10	2.9	2.3	800	155
SPEU								
sP/H	P	HDI	0.92	90/37	98.3	10.6	120	135
sP/M	P	MDI	–	81/33	137.2	13.8	250	160

~50°C ($\Delta H = 1.3–2.4$ J/g), which points to their inconsiderable tendency to crystallize.

The PEUs were thermally stable up to 230–260°C. As expected [10], the higher temperatures of initial decomposition (T_d) and 10% of weight loss (T_{10}) were exhibited by HDI-based polymers, whereas the higher temperatures of 50% of weight loss (T_{50}) by polymers derived from MDI.

Mechanical Properties

Shore A/D hardness and tensile properties of all the PEUs were studied after pressing at 120–155°C under a pressure of about 10 MPa. The numerical data are presented in Table 3. The PEUs were high elasticity elastomers with tensile strength in the range of 0.4–2.3 MPa and elongation at break in the range of 650–2000%. All the PEUs from MDI showed a higher tensile strength and elongation at break in comparison with those from HDI.

SPEUs

The SPEUs (sP/H and sP/M, a hard segment content 51, 55 wt.%) were prepared from the PE P, HDI or MDI respectively, and HPE as a chain extender by one-step polymerization process at the ratio of NCO/OH = 1.05. Table 2 gives T_gs and TGA data for both polymers, while their mechanical properties and reduced viscosity of the soluble HDI-based polymer sP/H can be found in Table 3.

The SPEUs obtained were light-yellow elastomeric materials, particularly that from MDI which showed the higher tensile strength and elongation at break. Figure 3 presents the stress–strain curve of the SPEU sP/M. The DSC thermograms of the SPEUs without glass

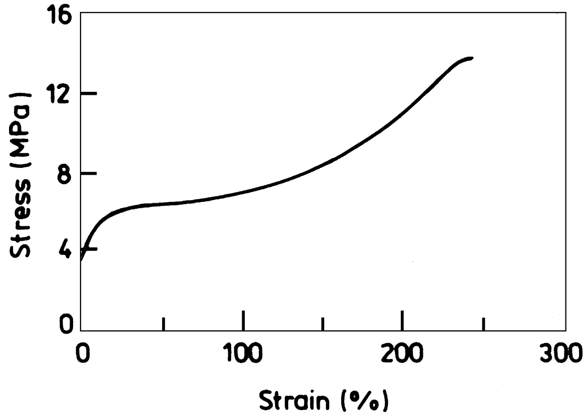


FIGURE 3 The stress–strain curve of the SPEU sP/M.

transitions exhibited two endotherms with peaks at ~50 and 108°C (from HDI) or 153 and 174°C (from MDI) associated with the melting of the hard segment. The higher ΔH value of the HDI-based polymer (20.0 J/g) than MDI-based one (3.5 J/g), point to the higher ability of the former polymer to crystallize. In Figure 2C, the thermogram of the sP/H is presented.

CONCLUSIONS

The step-growth polymerization of the aliphatic–aromatic thiodiacid DAA with excess aliphatic diols such as BD, PD, and HD was carried out in melt at relatively low temperatures (150–170°C) and yielded the almost colorless PEs with $\bar{M}_n$ of ~1900–2500. They showed good solubility in common organic solvents and good thermal stability of up to 260–270°C, similar to the thiopolyesterdiols described earlier. All the PEs exhibited somewhat higher T_gs, ranging from ~−24 to −18°C, than analogous PEs derived from DPA (−34 to −24°C), [3] but considerably lower than those from BAA (−7 to −2°C) [2], N14AA (1 to 5°C), and N15AA (20 to 46°C) [1].

In general, the extension of these partially crystalline aliphatic-aromatic PEs with MDI as well as HDI gave rather amorphous and elastomeric thermoplastic PEUs with relatively low T_gs (−12.7 to −0.9°C). The SPEUs obtained, particularly that from MDI, were also elastomeric materials with tensile strength of up to about 14 MPa. As expected, the HDI-based polyurethanes showed a higher T_d than the corresponding MDI-based ones [10].

Because their polyester segments incorporate diphenylmethane units with active methylene groups, the polyurethanes obtained, including HDI-based ones, can be cured either by peroxides or by both peroxides and diisocyanates.

REFERENCES

[1] Kultys, A., Podkościelny, W. and Pikus, S. (1998). *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 2359.

[2] Kultys, A. (2000). *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 3977.

[3] Kultys, A. (2001). *Macromol. Chem. Phys.*, **202**, 3523.

[4] Kultys, A. (1999). *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 835.

[5] Trappe, G., "Polyurethane Elastomers", In: *Advances in Polyurethane Technology*, 2nd edition, Buist, J. M. and Gudgeon, H., Eds., Elsevier, London, 1970, chapter 2, p. 38.

[6] Hepburn, C., "*Polyurethane Elastomers: Millable Polyurethane Elastomers*", 1st edition, Applied Science Publishers, London and New York, 1982, chapter 7, p.203.

[7] Schroter, A. (1995). *Kautsch. Gummi Kunststt.*, **48**, 44.

[8] Podkościelny, W. and Kultys, A. (1997). *Angew. Makromol. Chem.*, **246**, 71; Podkościelny, W., Podgórski, M., to appear.

[9] Podkościelny, W., Wdowicka, D. and Kultys, A. (2002). *Iran Polym. J.,* **11**, 177.

[10] Pavlova, T. E., Fedorov, A. A., Pominov, I. S. and Sokolov, L. W. (1970). *Zh. Prikl. Spectrosk.*, **13**, 544.