

Polymers Containing Sulfur in the Side Chain

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SYNOPSIS

We synthesized new thiodicarboxylic acids, *p*-tolylmethylthiomethylsuccinic acid and 1-naphthylmethylthiomethylsuccinic acid, and thiodiols, 2-(*p*-tolylmethylthiomethyl)-1,4-butanediol and 2-(1-naphthylmethylthiomethyl)-1,4-butanediol, by the addition of dimethyl itaconate with *p*-tolylmethanethiol or 1-naphthylmethanethiol, followed by hydrolysis or reduction, respectively, of the resultant dimethyl esters. These difunctional monomers were used for the synthesis of new linear polyesters and polyurethanes containing sulfur in the side chain. The polyesters were synthesized by melt polycondensation of the obtained acids with 2,2'-oxydiethanol. We found reduced viscosity, molecular weight (by GPC), and softening temperature for the reaction products. Low molecular weights, low softening temperature, and very good solubility in organic solvents are their characteristics. The polyurethanes were prepared by polyaddition diols with hexamethylene diisocyanate and tolylene diisocyanate in benzene. They were characterized by reduced viscosity and some tensile properties. The polyurethane derived from 2-(*p*-tolylmethylthiomethyl)-1,4-butanediol and hexamethylene diisocyanate (η_{red} 1.17 dL/g) behaves like a high elasticity thermoplastic elastomer. Thermal stability of all polymers was determined by thermogravimetric analysis. The structure of the monomers and polymers were confirmed by elemental analysis and FTIR and ¹H-NMR spectroscopy. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Among the polymers containing sulfur in their structure, chemical compounds of linear structure occupy the main position. Poly-(polysulfide)s, poly(phenylene)sulfides, and polysulfones are especially interesting because of their excellent physicochemical or mechanical properties. A considerable number of articles and patents concerned the structure, properties, and possibilities of application of the above-mentioned polymers, as well as others containing sulfur in the main chain, have been reviewed in available monographs¹⁻⁴ and encyclopedias,^{5,6} and, lately, presented very clearly in a chapter in the *Handbook of Polymer Synthesis* by Spassky et al.⁷

Sulfur atoms are also present in the side chains of polymers, which play an essential role in biochemical processes as, for instance, in polypeptides with S-containing α -amino acids. In S—S bridges,

sulfur atoms play a decisive role in the formation of the three-dimensional structures of enzymes (e.g., insulin) and antibodies. It has been established that compounds having sulfhydryl groups are the most efficient protectors of living organisms against ionizing radiation.

Overberger and co-workers are pioneers of the object synthesis of polymers containing sulfur in the side chain as well other kinds with a free sulfhydryl group. Investigations concerning the above-mentioned problem have been described in their articles in some detail.⁸⁻¹⁰ The purpose of our research was investigations inspired by Overberger¹¹ concerning the synthesis and properties of polyesters and polyurethanes containing sulfur in the side chain, which have been obtained on the basis of new monomers.

EXPERIMENTAL

Materials

p-Tolylmethanethiol, bp 89–90°C/11 mmHg, and 1-naphthylmethanethiol, bp 174°C/15 mmHg, were

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obtained from suitable bromomethyl and chloromethyl compounds through thiouronic salts.^{12,13} Dimethyl itaconate, bp 105°C/12 mmHg, was obtained by reaction of itaconate acid with dimethyl sulfate in the presence of the methanol solution of sodium hydroxide.¹⁴ 2,2'-Oxydiethanol (Merck) was purified by distillation under reduced pressure; bp 128°C/10 mmHg. Commercial solvents (benzene, ether) were dried over sodium metal before use. Other reagents such as Izocyn T-80 (TDI-80, i.e., the mixture of tolylene 2,4-diisocyanate [80% wt] and tolylene 2,6-diisocyanate [20% wt], "Zachem," Bydgoszcz [Poland]), hexamethylene diisocyanate (HDI, Merck), *p*-toluenesulfonic acid (POCH, Gliwice, Poland), and dibutyltin dilaurate (Merck) were used as received.

Monomer Synthesis

Dimethyl *p*-Tolylmethylthiomethylsuccinate (DTMTMS)

To a stirred mixture of 5 g of anhydrous potassium carbonate in 89 g (0.5 mol) of dimethyl itaconate added dropwise was, with ice-bath cooling, 69 g (0.5 mol) of *p*-tolylmethanethiol. The hydroquinone present as a polymerization inhibitor in the ester was not removed. After the addition was completed, the reaction mixture was stirred for 18 h, diluted with benzene (50 mL), and filtered. After removing benzene, the oily residue was distilled under reduced pressure. Colorless oil; bp 170–172°C (1 mmHg); yield 141 g (86%).

ANAL: Calcd for C₁₅H₂₀O₄S: C, 61.20%; H, 6.85%; S, 10.89%;

Found: C, 61.45%; H, 6.61%; S, 10.65%.

p-Tolylmethylthiomethylsuccinic Acid (TMTMSA)

To a solution of 19 g (0.3 mol) potassium hydroxide in 200 mL of ethanol, 27 g (0.1 mol) of dimethyl *p*-tolylmethylthiomethylsuccinate was added and the resulting mixture was refluxed for 10 h. After this time, 150 mL of ethanol was removed, then 30 mL of water was added and the mixture heated to boiling and filtered. The filtrate was acidified with dilute (1 : 1) hydrochloric acid and the white precipitate formed was collected by filtration. The crude compound (24 g) was recrystallized from water (500 mL). Colorless needles; mp 132–133°C; yield 19 g (78%).

IR (KBr, cm⁻¹): 3300–2300 (O—H 0 stretching, s), 1713 (C=O stretching, s), 942 (O—H 0 bending, m), 1299 (C—O stretching, s), 1420 (C—H bending of CH₂—S, m), 1514 (benzene ring, m), 827 (C—H bending of *p*-substituted benzene ring, s).

¹H-NMR (δ in CH₃COCH₃-*d*₆, ppm): 2.29 (s, 3H, CH₃), 2.54–3.13 (m, 5H, SCH₂CHCH₂), 3.75 (s, 2H, SCH₂C₆H₄), 7.13; 7.22 (dd, 4H, *p*-phenylene ring protons, *J* = 8 Hz), 10.24 (s, 2H, COOH).

ANAL: Calcd for C₁₃H₁₆O₄S: C, 58.18%; H, 6.09%; S, 11.95%;

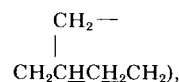
Found: C, 58.27%; H, 5.85%; S, 11.87%.

2-(*p*-Tolylmethylthiomethyl)-1,4-butanediol (TMTMBD)

A solution of 26.2 g (0.69 mol) of lithium aluminum hydride in 1000 mL of anhydrous ether was refluxed for 3 h, after which a solution of 176.6 g (0.60 mol) of dimethyl *p*-tolylmethylthiomethylsuccinate in 200 mL of anhydrous ether was added dropwise with stirring. The resulting mixture was refluxed for 48 h, the salt decomposed by dropwise addition of water, and all solids removed by filtration. The ether layer was dried over anhydrous magnesium sulfate. After ether was evaporated on a rotary evaporator, the crude product (80 g) was recrystallized from carbon tetrachloride (150 mL). Colorless needles; mp 77°C; yield 65 g (45%).

IR (KBr, cm⁻¹): 3284 (O—H 0 stretching, s), 1029 (C—O stretching, s), 1421 (C—H bending of CH₂—S, m), 1513 (benzene ring, m), 827 (C—H bending of *p*-substituted benzene ring, s).

¹H-NMR (δ in CHCl₃-*d*₁, ppm): 1.65–1.73 (m, 3H,



2.32 (s, 3H, CH₃), 2.41; 2.43 (2d, 2H, SCH₂CH, *J*_{vic} = 6.0 Hz and 7.1 Hz), 3.41 (s, 2H, OH), 3.54–3.71 (m, 6H, C₆H₄—CH₂S, 2 CH₂OH), 7.09; 7.19 (dd, 4H, *p*-phenylene ring protons, *J* = 8 Hz).

ANAL: Calcd for C₁₃H₂₀O₂S: C, 64.95%; H, 8.39%; S, 13.34%;

Found: C, 65.11%; H, 8.46%; S, 13.21%.

Dimethyl 1-Naphthylmethylthiomethylsuccinate (DNMTMS)

The same procedure as that for DTMTMS was employed. Dimethyl itaconate (89 g, 0.5 mol), 1-naphthylmethanethiol (87 g, 0.5 mol), and anhydrous potassium carbonate (5 g) were used. Colorless oil; bp 230°C (2 mmHg); yield 140 g (85%).

ANAL: Calcd for C₁₈H₂₀O₄S: C, 65.04%; H, 6.06%; S, 9.65%;

Found: C, 64.89%; H, 5.87%; S, 9.42%.

1-Naphthylmethylthiomethylsuccinic Acid (NMTMSA)

Dimethyl-1-naphthylmethylthiomethylsuccinate, 33.2 g (0.1 mol), was converted into 1-naphthylmethylthiomethylsuccinic acid according to the same procedure as that described for TMTMSA. The crude compound (27 g) was recrystallized from toluene (400 mL). Colorless needles; mp 143–144°C; yield 22 g (72%).

IR (KBr, cm^{-1}): 3300–2500 (O—H ν stretching, s), 1734 (C=O stretching, s), 887 (O—H δ bending, m), 1247 (C—O stretching, s), 1422 (C—H bending of CH_2 —S, m), 1510 (naphthalene ring, m), 779 (C—H bending of α -substituted naphthalene, s).

$^1\text{H-NMR}$ (δ in CH_3COCH_3 - d_6 , ppm): 2.61–3.15 (m, 5H, $\text{SCH}_2\text{CHCH}_2$), 4.29 (s, 2H, $\text{SCH}_2\text{C}_{10}\text{H}_7$), 7.33–8.27 (m, 7H, naphthyl ring protons), 9.90 (s, 2H, COOH).

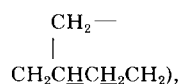
ANAL: Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{S}$: C, 63.10%; H, 5.25%; S, 10.53%;
Found: C, 62.82%; H, 4.99%; S, 10.27%.

2-(1-Naphthylmethylthiomethyl)-1,4-butanediol (NMTMBD)

The same procedure as that for TMTMBD was employed. Lithium aluminum hydride (26.2 g, 0.69 mol) and dimethyl 1-naphthylmethyl-thiomethylsuccinate (199.4 g, 0.60 mol) were used. The crude compound (99.7 g) was recrystallized from toluene (210 mL). Colorless needles; mp 65–67°C; yield 69 g (42%).

IR (KBr, cm^{-1}): 3269 (O—H ν stretching, s), 1027 (C—O stretching, s), 1419 (C—H bending of CH_2 —S, m), 1510 (naphthalene ring, m), 780 (C—H bending of α -substituted naphthalene, s).

$^1\text{H-NMR}$ (δ in CHCl_3 - d_1 , ppm): 1.51–1.80 (m, 3H,



2.44; 2.46 (2d, 2H, SCH_2CH , $J_{\text{vic.}} = 6.1$ Hz and 7.1 Hz), 3.36–3.67 [m, 6H, 2 CH_2OH ; 3.61 (s, 2H, OH)], 4.11 (s, 2H, $\text{SCH}_2\text{C}_{10}\text{H}_7$), 7.31–8.15 (m, 7H, naphthyl ring protons).

ANAL: Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{S}$: C, 69.52%; H, 7.29%; S, 11.60%;
Found: C, 69.31%; H, 7.05%; S, 11.42%.

Polymer Synthesis

Polyesters

The polyesters were synthesized using melt polycondensation. *p*-Tolylmethylthiomethylsuccinic

acid (TMTMSA) (10.74 g, 0.04 mol) or 1-naphthylmethylthiomethylsuccinic acid (NMTMSA) (12.18 g, 0.04 mol), and 2,2'-oxydiethanol (4.46 g, 0.042 mol) were used. The reaction of polycondensation was carried out under nitrogen in two variants: (1) without a catalyst by heating of the reagents at 160–170°C for 26 h, and (2) with the presence of the catalyst (*p*-toluenesulfonic acid, 0.152 g and 0.162 g, respectively) by heating of the reagents at 140–150°C for 6 h.

ANAL: PE I: Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_5\text{S}$: C, 60.33%; H, 6.55%; S, 9.47%;

Found: C, 59.49%; H, 6.12%; S, 9.72%.

PE II: Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_5\text{S}$: C, 60.33%; H, 6.55%; S, 9.47%;

Found: C, 59.42%; H, 6.25%; S, 9.58%.

PE III: Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5\text{S}$: C, 64.15%; H, 5.92%; S, 8.56%;

Found: C, 63.35%; H, 5.78%; S, 9.08%.

PE IV: Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5\text{S}$: C, 64.15%; H, 5.92%; S, 8.56%;

Found: C, 63.75%; H, 5.90%; S, 8.89%.

Polyurethanes

The polyurethanes were prepared according to the following procedure: To a solution of 4.81 g (0.02 mol) of 2-(*p*-tolylmethylthiomethyl)-1,4-butanediol (TMTMBD) or 5.53 g (0.02 mol) of 2-(1-naphthylmethylthiomethyl)-1,4-butanediol (NMTMBD) in 40 mL of anhydrous benzene and 3 drops of dibutyltin dilaurate added dropwise with stirring was a solution of 3.36 g (0.02 mol) of hexamethylene diisocyanate (HDI) or 3.49 g (0.02 mol) of tolylene diisocyanate (TDI-80) in 10 mL of anhydrous benzene. After the addition was completed, the heating and stirring of the reaction mixture was continued for 2 h. The precipitate oil product was separated by decantation of the supernatant liquid and dried under vacuum at 80°C.

ANAL: PU I: Calcd for $\text{C}_{21}\text{H}_{32}\text{O}_4\text{N}_2\text{S}$: C, 61.75%; H, 7.90%; N, 6.86%;

Found: C, 61.25%; H, 7.56%; N, 7.06%.

PU II: Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_2\text{N}_2\text{S}$: C, 63.75%; H, 6.32%; N, 6.76%;

Found: C, 64.04%; H, 6.34%; N, 7.12%.

PU III: Calcd for $\text{C}_{24}\text{H}_{32}\text{O}_4\text{N}_2\text{S}$: C, 64.84%; H, 7.26%; S, 6.30%;

Found: C, 64.78%; H, 6.95%; S, 6.27%.

Measurement of Properties

Spectral Analysis

FTIR spectra were obtained with a Perkin-Elmer 1725 \times FTIR spectrophotometer using KBr discs or

thin films, as appropriate. The $^1\text{H-NMR}$ spectra were obtained with a Tesla BS-567-17 spectrometer at 100 MHz using TMS as an internal reference. Samples were run in CHCl_3-d_1 or $\text{CH}_3\text{COCH}_3-d_6$ solutions, as appropriate.

Viscosity

Reduced viscosity (dL/g) of 1% solutions of polymers in tetrachloroethane was measured in Ubbelohde viscometer at 25°C .

Molecular Weights

Molecular weights were obtained using a Knauer gel chromatograph equipped with 10^6 , 10^5 , 10^4 , 10^3 , and 10^2 Å PL-Gel columns with an RI detector. Tetrahydrofuran was used as the eluent (flow rate was 1.0 mL/min), and numerical values for the molecular weights were obtained by comparison to polystyrene standards.

Thermogravimetric Analysis

Measurement of weight loss was conducted in a MOM Budapest-3427 derivatograph at a heating rate of $10^\circ\text{C}/\text{min}$ in air.

Softening Temperature

Measurement of the softening temperature of polyesters was taken by the "Ring-Ball" method according to Polish Standard PN/C-04020.

Hardness

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

Tensile Tests

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

X-ray Analysis

Diffraction measurements were performed using a DRON-3 X-ray apparatus with a Cu tube and Ni filter. X-ray patterns of the investigated samples were obtained by measuring the number of impulses within a given angle over 10 s. The measurements were taken every 0.04° .

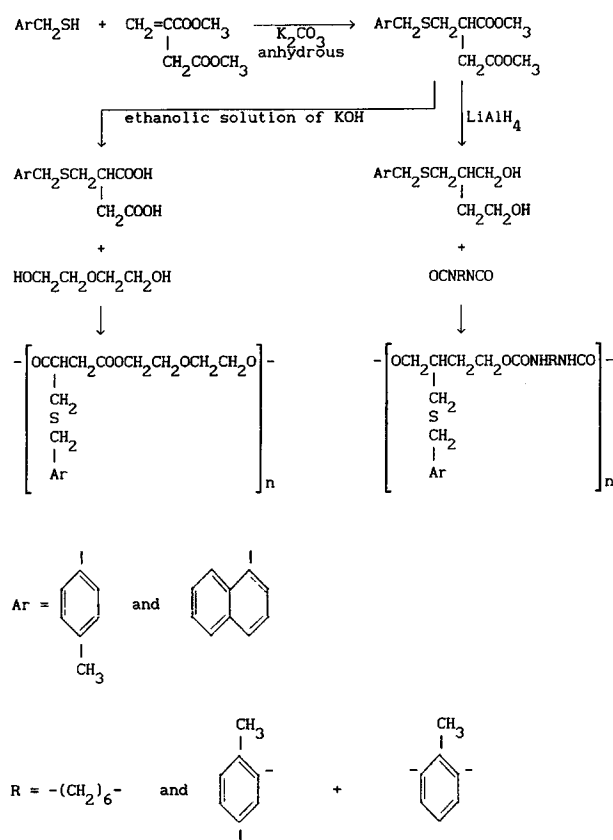
RESULTS AND DISCUSSION

Monomer Synthesis

New polymer-forming thiodicarboxylic acids and thiodiols, *p*-tolylmethylthiomethylsuccinic acid (TMTMSA), 1-naphthylmethylthiomethylsuccinic acid (NMTMSA), 1-(*p*-tolylmethylthiomethyl)-1,4-butanediol (TMTMBD), and 2-(1-naphthylmethylthiomethyl)-1,4-butanediol (NMTMBD), were successfully synthesized from *p*-tolylmethanethiol and 1-naphthylmethanethiol, respectively, as starting materials according to synthetic Scheme 1.

Thus, addition of the suitable thiol to dimethyl itaconate by the method of Knuth et al.¹⁵ yielded dimethyl *p*-tolylmethylthiomethylsuccinate and dimethyl 1-naphthylmethylthiomethylsuccinate, respectively. The required thiodiacids were obtained by hydrolysis of newly obtained dimethyl esters by means of an ethanolic solution of potassium hydroxide, whereas the thiodiols were obtained by reduction of these esters with lithium aluminum hydride.¹¹

Chemical structures of the synthesized acids and diols were confirmed using elemental analysis and



FTIR and $^1\text{H-NMR}$ spectroscopic techniques. FTIR and $^1\text{H-NMR}$ spectra were consistent with the proposed structures of monomers. Elemental analysis of all of these compounds agreed also with the calculated values.

Polymer Synthesis and Characterization

New polyesters (PE I–IV) containing sulfur in the side chain were obtained according to Scheme 1 from TMTMSA or NMTMSA and 2,2'-oxydiethanol using melt polycondensation. The reaction was carried out either without a catalyst or its presence (*p*-toluene-sulfonic acid) using some excess of the diol.

The polyesters obtained are light brown oils (PE I and II) or rubberlike products (PE III and IV). They are very well soluble in common organic solvents like benzene, dioxane, chloroform, methylene and ethylene chloride, tetrachloromethane, DMF, THF, DMSO, and nitrobenzene. Polyesters synthesized from TMTMSA are also soluble in acetone.

Polymerization conditions and the basic physicochemical properties of the obtained polyesters are presented in Table I. They are characterized by low molecular weights and low softening temperature. The use of catalyst significantly decreases the time of reaction and increases the molecular weight of the obtained polyesters. The structure of all polyesters was confirmed using elemental analysis and FTIR and $^1\text{H-NMR}$ spectroscopy. The elemental analysis values of these polyesters were in good agreement with the calculated values for the proposed structures.

FTIR spectra of all polyesters showed strong absorption at $1735\text{--}1734\text{ cm}^{-1}$, which is characteristic of the $\text{C}=\text{O}$ stretching vibration of the ester group; at $1420\text{--}1418\text{ cm}^{-1}$, characteristic of the $\text{C}-\text{H}$ bending vibration of the CH_2-S group; and at $1514\text{--}1510\text{ cm}^{-1}$, characteristic of aromatic ring vibration. The bands at ca. 820 cm^{-1} are attributed to the $\text{C}-\text{H}$ bending vibration of the *p*-substituted

benzene ring in the case of PE I and II, whereas the bands at ca. 780 cm^{-1} are attributed to the $\text{C}-\text{H}$ bending vibration of α -substituted naphthalene in the case of PE III and IV.

$^1\text{H-NMR}$ spectra (δ in $\text{CHCl}_3\text{-}d_1$) of PE I and II reveal a sharp resonance at δ 2.31 ppm attributed to CH_3 protons, multiple resonance at 2.54–3.13 ppm due to protons of the CH_2CHCH_2 group, a single resonance at 3.66 ppm due to protons of CH_2OCH_2 with protons of $\text{SCH}_2\text{C}_6\text{H}_4$ groups, a single resonance at 4.22 ppm due to protons of the CH_2OOC group, and a doublet of doublets at 7.12 and 7.20 ppm ($J = 8\text{ Hz}$) attributed to nonequivalent *p*-phenylene ring protons.

The $^1\text{H-NMR}$ spectra (δ in $\text{CHCl}_3\text{-}d_1$) of PE III and IV reveals a broad multiple resonance of 2.49–3.20 ppm due to protons of the CH_2CHCH_2 group, a triplet at 3.59 ppm ($J = 5.0\text{ Hz}$) due to protons of the CH_2OCH_2 group, a single resonance at 4.12 ppm due to protons of CH_2OOC with protons of $\text{SCH}_2\text{C}_{10}\text{H}_7$ groups, and a broad multiple resonance at 7.33–8.27 ppm attributed to naphthyl ring protons.

GPC analysis, however, showed that apart from the main linear polymer a small quantity of low molecular products are formed (probably including cyclics). This is reflected in the broad molecular weight distribution (MWD) up to > 8.0 . MWD curves are shown in Figure 1, as an instance, for PE III and IV.

The thermal behavior of the polyesters was evaluated using differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Figure 2 shows typical TGA and DTA curves of PE II, and the thermal behavior data of the polyesters are given in Table I.

All the polyesters are stable in the $210\text{--}280^\circ\text{C}$ temperature range in air atmosphere, taking T_1 (1% decomposition temperature) as the criteria for thermal stability. PE III and IV (derived from NMTMSA) exhibit higher thermal stability than

Table I Properties of Polyesters

PE No.	Acid	Reaction		Softening Temperature ($^\circ\text{C}$)	GPC Data			Thermal Properties ^a ($^\circ\text{C}$)			
		Time (h)	η_{red} (dL/g)		\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	T_1	T_{10}	T_{50}	T_{max}
I	TMTMSA	26	0.16	—	2820	8010	2.84	210	295	335	335, 510
II	TMTMSA	6 ^b	0.27	41	4380	15,500	3.53	220	300	345	340, 520
III	NMTMSA	26	0.11	52	2030	5570	2.74	260	305	345	330, 570
IV	NMTMSA	6 ^b	0.23	62	3240	26,100	8.05	280	310	380	335, 595

^a With catalyst.

^b T_1 , T_{10} , T_{50} , and T_{max} are temperatures of 1, 10, and 50% and the maximum rate of weight loss, respectively.

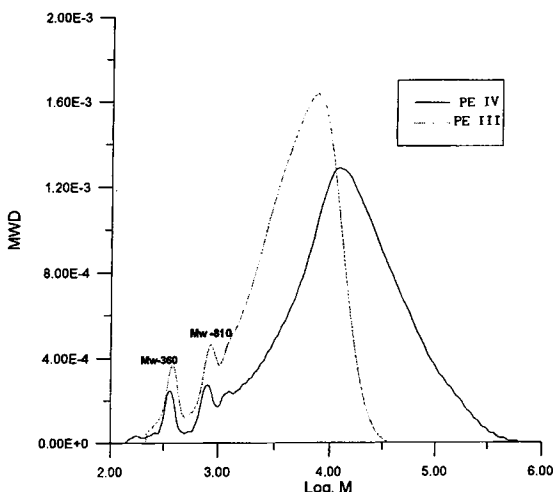


Figure 1 MWD curves of PE III and IV.

do PE I and II (derived from TMTMSA). All the polyesters exhibit two T_{max} values: the first in the 330–335°C and the second in the 510–595°C temperature ranges. The two T_{max} values indicate a two-stage decomposition.

Polyurethanes

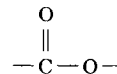
New linear polyurethanes (PU I–III) containing sulfur in the side chain were prepared according to Scheme 1 by treating equimolar quantities of TMTMBD or NMTMBD with diisocyanates (TDI-80 or HDI) in the presence of the catalyst (dibutyltin dilaurate).

Polyurethanes obtained are colorless soft solids: rubberlike derived from HDI and brittle derived from TDI. They all are well soluble in tetrachloroethane and pyridine, with PU II, also in THF and DMSO.

The molecular weight parameters were determined only for PU II (\bar{M}_n 13420, \bar{M}_w 26020, \bar{M}_w/\bar{M}_n 1.94), well soluble in THF, while reduced viscosity values (Table II) were determined for all polyurethanes. The obtained data point to formation of the high molecular weight product (PU I) from TMTMB and HDI.

The structure of all polyurethanes was confirmed by elemental analysis and FTIR spectroscopy. Elemental analysis values of these polyurethanes were in good agreement with the values calculated for the proposed structures. The FTIR spectra of all the polyurethanes showed strong absorption at 1708–1698 cm^{-1} , which is characteristic of the bonded C=O stretching vibration (the amide I band); at 1531–1530 cm^{-1} , characteristic of the N—H bend-

ing vibration of the urethane group (the amide II band); and at 3333–3310 cm^{-1} , characteristic of the bonded N—H stretching vibration. The bands at 1251–1221 cm^{-1} are attributed to the



group.

The thermal behavior of the polyurethanes was evaluated by DTA and TGA. Figure 3 shows typical TGA and DTA curves of PU I, and the thermal behavior data of the polyurethanes are given in Table II. All the polyurethanes are stable up to 250°C in air atmosphere, taking T_{10} (10% decomposition temperature) as the criteria for thermal stability.

As expected, PU I and III (derived from aliphatic diisocyanate) exhibited higher thermal stability than that of PU II (derived from aromatic diisocyanate). A two- and three-stage decomposition is characteristic for them.

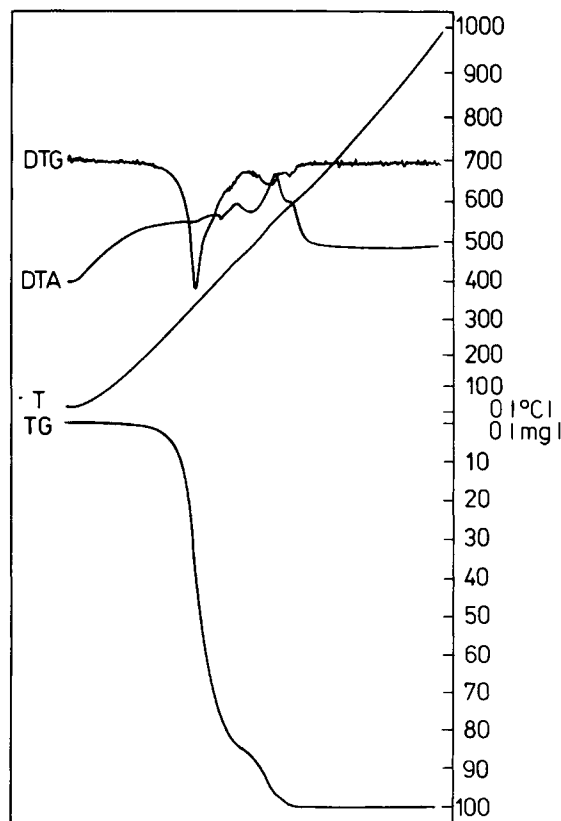


Figure 2 TGA and DTA of PE II: heating time in air, 100 min; measurement relative to Al_2O_3 ; heating rate, 10°C/min; amount of PE, 100 mg.

Table II Properties of Polyurethanes

PU No.	Components		η_{red} (dL/g)	Thermal Properties ^a (°C)			Mechanical Properties				
	Diol	Diisocyanate		T_{10}	T_{50}	T_{max}	Hardness (Shore A/D)	Tensile Strength (MPa)	Elongation at Break (%)	Modulus of Elasticity at Elongation (MPa)	
										300%	500%
I	TMTMBD	HDI	1.17	295	340	320, 375, 555	84/23	2.20	782	0.77	0.96
II	TMTMBD	TDI-80	0.16	250	310	290, 596,	—	—	—	—	—
III	NMTMBD	HDI	0.21	265	330	315, 370, 560	25/4	—	—	—	—

^a T_{10} , T_{50} , and T_{max} are temperatures of 10 and 50% and the maximum rate of weight loss, respectively.

Some mechanical properties of the polyurethanes were studied after pressing at 40–50°C under the pressure of ca. 10 MPa.

Brittle plates were obtained in the case of PU II and, hence, the measurement of the polymer was impossible. Table II shows the hardness of PU I and III as well as the tensile properties of PU I (poly-

urethane with a highest value of reduced viscosity), and Figure 4 shows the stress–strain curve of PU I.

PU I (derived from TMTMBD and HDI) behaved like a high elasticity thermoplastic elastomer. The stress–strain curve points to some capacity for the racking of this polymer, which is confirmed by the presented (Fig. 5) X-ray diffraction patterns obtained for the sample of PU I before and after tension. For the sample without tension, only one broad peak occurs, whereas for the tension sample, a small but visible diffraction peak under $2\theta = 21^\circ$ angle also occurs.

CONCLUSIONS

Low molecular weight polyesters containing sulfur in the side chain exhibiting good thermal stability, especially PE III and IV, were obtained by melt polycondensation of *p*-tolyl- or 1-naphthylmethylthiomethylsuccinic acid with 2,2'-oxydiethanol. Because of their low softening temperature and excellent solubility in common organic solvents, polyesters may find use as modifiers and plasticizers of commercial polymers [polyesters, poly(vinyl chloride), and the like].

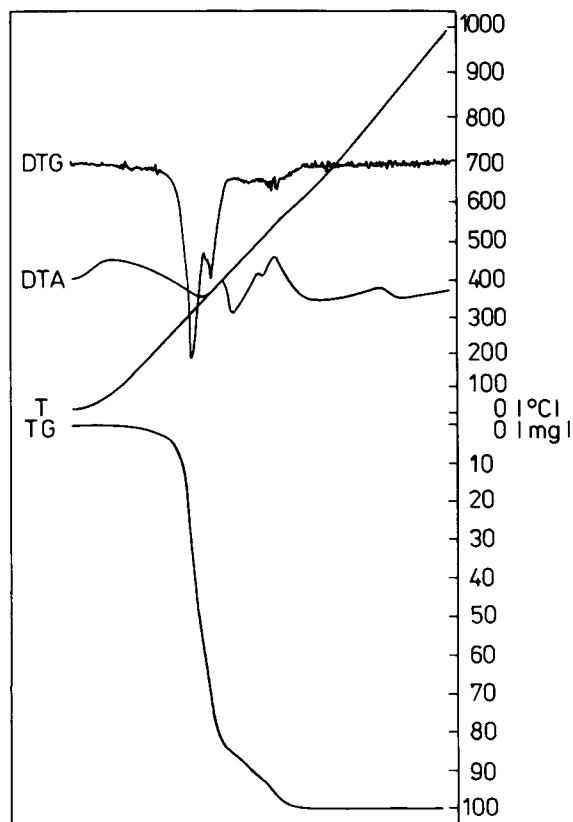


Figure 3 TGA and DTA of PU I: heating time in air, 100 min; measurement relative to Al_2O_3 ; heating rate, 10°C/min; amount of PU, 100 mg.

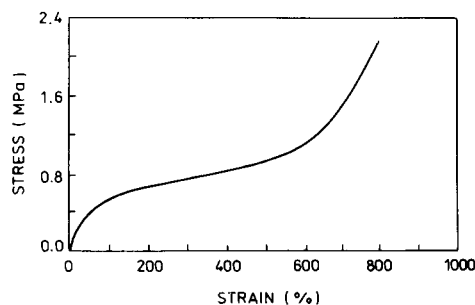


Figure 4 Stress–strain curve of PU I.

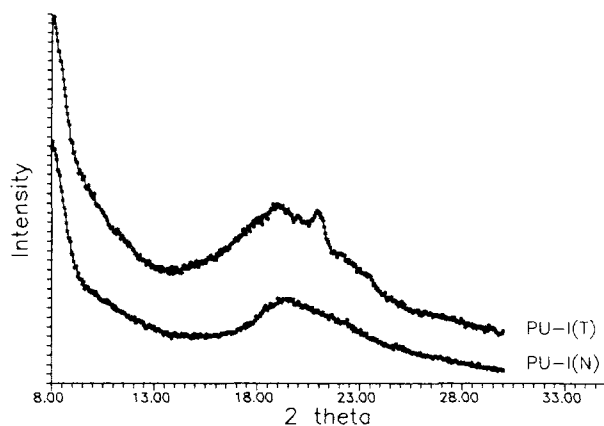


Figure 5 X-ray diffraction patterns of PU I: (N) before tension; (T) after tension.

Thermoplastic polyurethanes containing sulfur in the side chain were prepared by polyaddition of *p*-tolyl- or 1-naphthyl-methylthiomethyl-1,4-butane-diol with HDI and TDI-80. PU I (derived from TMTMBD and HDI, η_{red} 1.17 dL/g), which behaves like a high elasticity thermoplastic elastomer with good thermal stability, proved to be the most interesting. Thus, some of these polyurethanes are considered to be the new promising processable high-elastic polymeric materials.

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