Polyesters Containing Sulfur. I. Products of Melt Polycondensation of Diphenylmethane-4,4′-Di(methylthioacetic Acid) with Some Diols

ANNA KULTYS and WAWRZYNIEC PODKOSCIELNY, *Institute of Chemistry, Maria Curie-Skłodowska University Lublin, Poland*

Synopsis

Several new polyesters containing sulfur in the main chain were obtained by melt polycondensation of diphenylmethane-4,4′-di(methylthioacetic acid) with ethanediol, 1,3-propane diol, 1,4-butanediol, 1,5-pentenediol, 1,6-hexanediol, 1,2-propanediol, and 2,2′-oxydiethanol. The structure of all polyesters was determined from elemental analysis and infrared (IR) spectra. Yield, reduced viscosity, molecular weight, and softening temperature for reaction products have been found. Initial decomposition and initial intensive decomposition temperature were defined from the curves of thermogravimetric analysis.

INTRODUCTION

Linear polyesters being one of the main group of polymers were thoroughly investigated several years ago with regard to their synthesis, structure, and properties. They are obtained mainly from dicarboxylic acids, their esters or acid dichlorides, by means of melt polycondensation, low- and high-temperature solution polycondensation as well as by interfacial polycondensation.[1-3]

Until now not much research has been done on polyesters containing sulfur in the main chain. Linear polyesters containing sulfur in their structure are obtained by polycondensation of thiodicarboxylic acids or their esters with diols by using melt method.

Korshak and Vinagradova[4] obtained thipoliesters with the use of diethyl ester of the thiodivaleric acid and some polymethylene diols. The reaction was carried out by melt polycondensation using equimolar amounts of reagents. At the first stage of polycondensation the reaction mixture was gradually heated at the atmospheric pressure to temperature 190°C and, next, for several hours at temperature range of 190–250°C under reduced pressure (1–3 mm Hg). Depending on the conditions of the reaction the polyesters obtained possessed various, molecular weights in the range of 1600–6600.

Colonge and Stuchlik[5] obtained thiopoliesters from thiodiacetic acid and thiodiethanol by using melt polycondensation. The reaction was carried out in two stages, at first by heating diacid with a small excess of diol at temperature 160–180°C. In the next stage, the low-molecular polyester obtained earlier was submitted to transesterification by heating at temperature 200–250°C under reduced pressure.

As early as in 1948 Lowe[6] published a method for obtaining thiopolyesters with the use of dimethyl ester of the 4,4′-thiodibenzoic acid with some

Journal of Applied Polymer Science, Vol. 39, 715–720 (1990)
© 1990 John Wiley & Sons, Inc.
CCC 0021-8995/90/030715-06$04.00

polymethylene diols, the reaction being carried out by melt polycondensation. Further interesting information concerning the synthesis, properties and directions of application of thiopolyesters was published by Weesner.[7] The process was carried out by melt polycondensation in the presence of the catalyst, at first at atmospheric pressure in the presence of nitrogen or other inert gas at temperature range of 140–210°C, and next under reduced pressure depending on the kind of monomers used.

Esterification catalysts were either lead oxide or a commonly known basic catalyst. These included amines like pyridine, triethyl amine, etc., or alkali or alkaline earth metals or their alkoxides hydrides and halides. Acid catalysts like *p*-toluenesulphonic acid or benzenesulphonic acid were also used. During the progress of the polycondensation process, water and excess of glycols were removed by evaporation under reduced pressure. In this way increase of chains in the forming thiopolyester was provoked.

Furthermore, Weesner showed many possibilities of application of polyesters containing sulfur in their structure. They are useful as nonvolutile plasticizers for poly(vinyl chloride), rubber modifiers, and the like. They are also useful for modifying or plasticing elemental sulfur. By heating a mixture of sulfur and thiopolyester useful caulking compounds or products to be added to compositions for stripping or marling highways are produced.

Molecular weights of the thiopolyesters were in the wide range of 2000–10,000 and their reduced viscosity of about 0.2 to 0.4 in 1% concentration in ethylene dichloride. Besides, one should mention a paper by Schweiker and Robitschek,[8] in which the authors described elastomers showing chemical resistance.

These resins were obtained by polycondensation of fluorine-containing diols with 3,6-dithiooctanedioic acid or 3,5-dithioheptanedioic acid. As is evident from the literature surveyed, till now in the synthesis of thiopolyesters with diols, mainly aliphatic or aromatic thiodiacids were used. In view of this, it seems suitable and interesting to conduct studies on the synthesis, structure, and properties of new thiopolyesters by using aliphatic–aromaticthioalkane carboxylic acids.

The present paper describes the process of melt polycondensation of diphenylmethane-4,4′-di(methylthioacetic acid) with some diols such as ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, and 2,2′-oxydiethanol.

EXPERIMENTAL

Reagents

Diphenylmethane-4,4′-di(methyltioacetic acid), mp 166–167°C (after crystallization from ethanol), was obtained from 4,4′-di(mercaptomethyl)diphenylmethane by condensation with monochloric acid.

Commercial diols: ethanediol, bp 89°C, 1,3-propanediol, bp 104°C, 1,4-butanediol, bp 118°C, 1,5-pentanediol, bp 128°C, 1,6-hexanediol, bp 135°C, 1,2-propanediol, bp 85°C, and 2,2-oxydiethanol, bp 128°C, were all purified under reduced pressure (at 10 mm Hg).

Measurement of Properties

Viscosity

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

Molecular Weight

The average number molecular weights ($\overline{M}_n$) of polyesters were determined applying Hewlett-Packard vapor–gas osmometer. The investigated polyesters as filtered solution (0.1 g of polymer in 20 cm^3 or 0.5 g polymer in 100 cm^3 methylene chloride) were used. The measurements were carried out at 26°C.

Softening Temperature

Measurement of softening temperature was taken by "ring-ball" method according to Polish Standard PN/C-04020.

Thermogravimetric Analysis

Measurement of weight loss was conducted in a MOM derivatograph (Paulik, Paulik and Erdey, Budapest) at a heating rate of 10°C/min in air.

Infrared Analysis

Infrared spectra were obtained with UNICAM SP-200 spectrophotometer.

RESULTS AND DISCUSSION

New polyesters containing sulfur in the main chain were obtained from diphenylmethane-4,4′-di(methylthioacetic acid) and ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, and 1,2-propanediol as well as 2,2′-oxydiethanol by means of melt polycondensation at equimolar relation of reagents. The reaction of polycondensation was carried out under nitrogen at atmospheric pressure by heating at first at 150–155°C, for 2 h, next at 160–170°C for 10 h, and finally at 170°C for 4 h under reduced pressure (10 mm Hg).

In these conditions esterification water was being removed by distillation. The resins obtained are light-yellow soft solids. They are well soluble in common organic solvents like benzene, chloroform, methylene chloride, ethylene chloride, dioxane, dimethylformamide, dimethylsulfoxide, and nitrobenzene.

The reduced viscosity, softening range, and average molecular weight of all polyesters were determined. Table I presents yield and physicochemical properties of polyesters. Low-molecular weights and low-softening temperature are characteristic for them. The structure of all polyesters was determined by elemental analysis and infrared spectra. The results of elementary analysis are given in Table II.

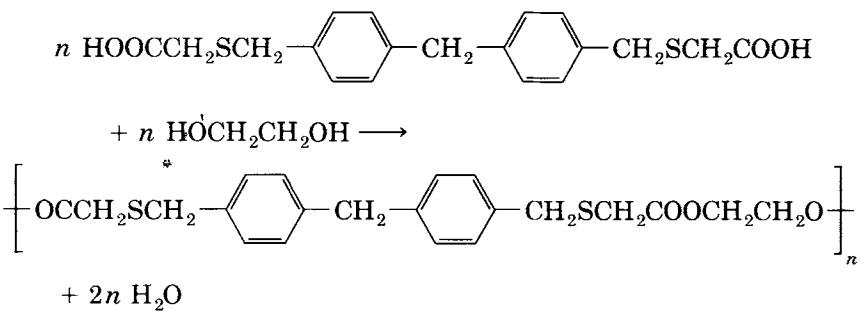
IR spectra polyesters showed strong absorption at 1725–1735 cm^{-1}, which is characteristic of the carbonyl valency bond, at 1510 cm^{-1} characteristic of

TABLE I
The Yields and Some Physicochemical Properties of Polyesters from Diphenylmethane-4,4′-Di(methylthioacetic Acid) and Some Diols

Diols	Yield (%)	η_{red} (dL/g)	Softening temperature (°C)	Molecular weight ($\bar{M}_n$)
Ethanediol	95.5	0.25	51	5665
1,3-Propanediol	95.8	0.30	48	6489
1,4-Butanediol	95.2	0.37	46	4024
1,5-Pentanediol	95.9	0.39	52	4407
1,6-Heksanediol	96.5	0.40	44	3839
1,2-Propanediol	94.7	0.21	48	3850
2,2′-Oxydiethanol	95.6	0.20	38	5066

benzene ring vibration, at 1415–1420 cm^{-1} characteristic of the $-CH_2-S-$ group.

On the basis of good agreement of the calculated and found analytical data (C, H, and S) and IR spectra, the reaction scheme[1] for diphenylmethane-4,4′-di(methylthioacetic acid) and ethanediol was assumed:



Thermal Properties

The polyesters obtained were examined by differential analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial decomposition,

TABLE II
Results of Elementary Analysis of Polyesters from Diphenylmethane-4,4′-Di(Methylthioacetic Acid) and Some Diols

	Analysis					
	%C		%H		%S	
Diols	Calcd	Found	Calcd	Found	Calcd	Found
Ethanediol	62.66	62.05	5.51	5.11	15.25	15.64
1,3-Propanediol	63.43	62.89	5.81	5.37	14.75	14.21
1,4-Butanediol	64.15	64.74	6.08	6.43	14.30	13.98
1,5-Pentanediol	64.83	64.25	6.34	6.12	13.86	13.14
1,6-Heksanediol	65.46	65.07	6.59	6.29	13.45	13.07
1,2-Propanediol	63.43	62.86	5.81	6.17	14.76	14.16
2,2′-Oxydiethanol	61.85	61.33	5.86	5.42	13.80	14.01

TABLE III
Thermal Properties of Polythioesters

Diols	Thermal analysis[a] T_1 (°C)	U (%)	T_2 (°C)	Mass loss (%) 300°C	350°C	400°C
Ethanediol	270	0.0	330	1.0	35.0	43.5
1,3-Propanediol	280	0.0	330	0.8	29.5	42.5
1,4-Butanediol	290	0.0	330	0.2	28.5	44.0
1,5-Pentanediol	275	0.0	330	0.8	29.0	44.5
1,6-Heksanediol	290	0.0	330	0.8	27.0	44.2
1,2-Propanediol	265	0.0	330	1.0	34.5	47.0
2,2′-Oxydiethanol	265	0.4	330	1.2	37.2	49.5

[a] T_1 = temperature of initial decomposition from the curve DTA (°C), U = mass loss in temperature T_1 (%), and T_2 = temperature of intensive decomposition from curve DTA (°C).

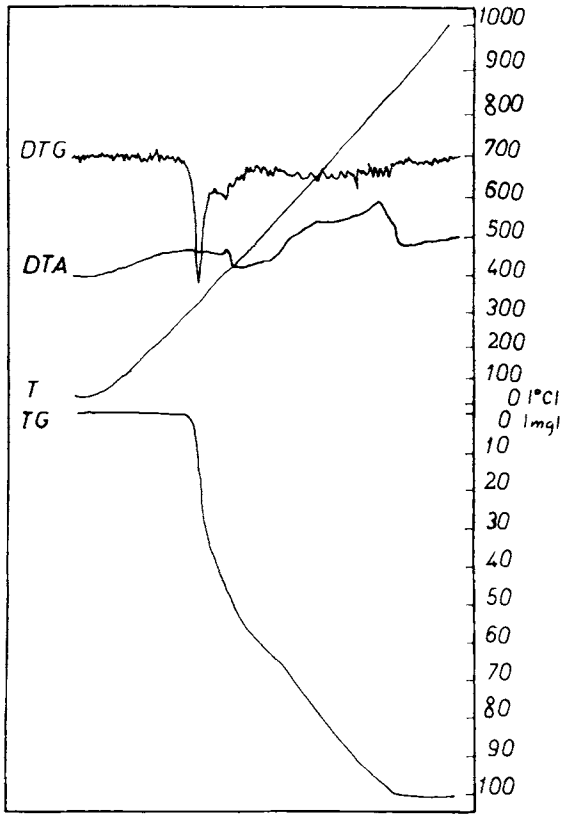


Fig. 1. TGA and DTA polyester from diphenylmethane-4,4′-di(methylthioacetic acid) and 1,4-butanediol: heating time in air, 100 min; measurement relative to Al_2O_3; heating rate, 10°C/min; amount of polyesters, 100 mg.

the percentage of its mass loss, the temperature of the fastest decomposition process, and the percentage of its loss at 300, 350, and 400°C were defined from the curves.

The numerical data are presented in Table III. Polyesters show good thermal stability and relatively high temperature of decomposition.

The results are given as an example of polyester from dithioacid and 1,4-butanediol (Fig. 1), which shows the highest temperature of initial decomposition at 290°C.

CONCLUSION

Linear polyesters containing sulfur in the main chain from diphenylmethane-4,4′-di(methylthioacetic acid) and some diols were obtained in high yield and good thermal stability by melt polycondensation. They are light yellow solids showing low-softening temperature. Because of their good solubility in common organic solvents, polyesters may find use as modifiers and plasticizers of commercial polyesters, epoxy resins, poly(vinyl chloride), and the like. They also may find use for modifying or plasticizing elemental sulfur. Studies on the synthesis and properties of similar polyesters are in progress.

References

1. R. E. Wilfong, *J. Polym. Sci.*, **54**, 385 (1961).
2. P. W. Morgan, *Condensation Polymers by Interfacial and Solution Methods*, Wiley-Interscience, New York, 1965.
3. V. V. Korshak and S. V. Vinogradova, *Usp. Khim.*, **30**, 421 (1961).
4. V. V. Korshak and S. V. Vinogradova, *Zh. Ob. Khim.*, **26**, 732 (1956).
5. J. Colonge and P. Stuchlik, *Bull. Soc., Chim. France*, **17**, 832 (1950).
6. A. R. Lowe, Br. Pat. 604,787 (1948).
7. W. E. Weesner, U.S. Pat. 3,459,797 (1969).
8. G. C. Schweiker and P. Robitschek, *J. Polym. Sci.*, **24**, 33 (1957).

Received January 6, 1989
Accepted January, 17, 1989