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*Linear polythioesters. XXVII. Products of interfacial
polycondensation of bis(4-mercaptomethylphenyl) ether
with some aliphatic and isomeric phthaloyl dichlorides*

Liniowe politioestry. XXVII. Produkty polikondensacji międzyfazowej
bis(4-merkaptometylofenylo) eteru z alifatycznymi
i izomerycznymi ftaloilowymi chlorkami

1. INTRODUCTION

Systematic studies on the synthesis, structure and properties of polythioesters created by polycondensation of dithiols with aliphatic and isomeric phthaloyl dichlorides were carried out in our laboratory during the last twenty years.

For synthesis of polythioesters two kinds of dithiols were used. The first ones are dithiols which show strong acid character due to the fact that –SH groups are attached directly to the aromatic ring. In this case polycondensation of dithiol derivatives of benzophenone [1], biphenyl [2], diphenylether [3], diphenylsulfide [4] and 2,3,5,6-tetramethylbenzene [5] was applied. The second kind are these with smaller acidity of dithiols, where SH groups are attached to a benzene ring through the –CH₂– group and, among others, bis(mercaptomethyl) derivatives of benzene [6], xylenes [7], naphthalene [8] and diphenylmethane [9] are used.

Syntheses of polythioesters were carried out by means of interfacial, low temperature and high-temperature polycondensation, but interfacial polycondensation proved to be most useful [7].

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Moreover, this research was undertaken to prove that properties of polymers mentioned above are considerably, and sometimes significantly, influenced by a number of various factors such as the quality of reagents, the type of the organic phase, concentration of monomers, excess of hydrochloride acceptor, temperature and time of reaction and also the contribution of type, and quantity of the catalyst.

In most cases the best results for the polycondensation were obtained at molar concentration of monomers 0.1 M, ratio of aqueous to organic phase 1:1, temperature 20°C, and period for acid chloride addition 5–20 min. There was a marked improvement of the results of polycondensation when 50–100 % molar excess of hydrogen chloride acceptor (NaOH) was used.

The aim of this study was to obtain new polythioesters, to determine their structure and fundamental physicochemical properties by using for this purpose bis(4-mercaptomethylphenyl) ether never applied so far. We obtained polythioesters by interfacial polycondensation of above mentioned dithiol with succinyl, adipoyl, sebacyl, terephthaloyl and isophthaloyl chlorides. To define optimal conditions of polycondensation, the example of adipoyl chloride was studied. As an organic phase benzene was applied because it yields the best results of homologous polycondensation of bis(4-mercapto-phenyl)ether with adipoyl chloride [3]. Next, the influence of the following factors on the value of reduced viscosity and the yield were taken into consideration: ratio of aqueous to organic phase, period for acid chloride addition, excess of hydrochloride acceptor, time of the reaction, and the contribution of catalyst and emulsifier.

It is necessary to note that bis(4-mercaptomethylphenyl) ether, although not described until now, was successfully used in our laboratory for the synthesis of thioetherglycidyl resin [10]. Apart from only two notices about bis(4-mercaptomethyl) ether applied, nothing more was said on it in literature. The first one informs about synthesis of dithiol by reaction of bis(chloromethylphenyl)ether with hydrosulphide sodium in methanol but without giving basic properties of dithiol, and it is restricted only to determine proportional contents of sulphur in products of this reaction. Another patent [12] described application of the bis(4-mercaptomethylphenyl) ether for synthesis of sugar dithioacetal polysulphides.

No information about isolation and purification or, properties and structure of object dithiol is included in these two cases. Therefore, it appears desirable to describe the useful method of bis(4-mercaptomethylphenyl)ether synthesis.

2. EXPERIMENTAL

REAGENTS

Adipoyl dichloride, b.p. 128°C/24hPa and sebacoyl dichloride, b.p. 166°C/15hPa were obtained by the reaction of thionyl chloride with corresponding acids. Succinyl dichloride, b.p. 103–104°C/34hPa, isophthaloyl dichloride, b.p. 168–170°C/34hPa and terephthaloyl dichloride, m.p. 80–83°C (after crystallization from hexane) were obtained by the reactions of phosphorus pentachloride with appropriate acids.

Bis(4-mercaptomethylphenyl) ether, m.p. 44–45.5°C was obtained from bis(4-chloromethylphenyl) ether [3] via the thiouronic salt. Essential information about the synthesis of the mentioned dithiol is given below.

Bis(4-isothiuroniummethylphenyl) ether

To 26.7g (0.1 mol) of bis(4-chloromethylphenyl) ether dissolved in 100ml of dioxane the hot solution of 19.03g (0.25 mol) thiourea in 50ml of 80% ethanol was added, and the resulting mixture was stirred under reflux for 1h. After a few minutes all the thiourea dissolved and white precipitate of isothiouronic salt began to form. After the reaction was over, the reaction mixture was cooled to room temperature and the product was isolated by filtration. The crude compound was crystallized from water (75ml). The obtained product given colourless lenses, m.p. 235–236°C (decomp.), yield 31.7g (75%).

Analysis:

For $C_{16}H_{20}Cl_2N_4OS_2$ (419.40)

calcd.: 45.81% C, 4.80% H, 13.36% N;

found: 46.02% C, 4.85% H, 13.35% N.

Bis(4-mercaptomethylphenyl) ether

The isothiuronium salt 20.97g (0.05 mol) was dissolved in 100ml of water and 45ml of 20% aqueous solution of sodium hydroxide, and the resulting mixture was heated to reflux for 2h, then the hot reaction mixture was filtered. The cooled filtrate was acidified with dilute (1:1) hydrochloric acid to form oil, which quickly solidified. The precipitate was collected by filtration, washed with water and dried under the reduced pressure (20hPa) at room temperature, m.p. 44–44.5°C, yield 11.9g (90%).

The purity of the compound obtained in this manner was checked by elemental analysis, FT-infrared and ^1H NMR spectroscopies (see Figures 1 and 2) as determined in the following.

Analysis:

For $\text{C}_{14}\text{H}_{14}\text{OS}_2$ (262.38)

calcd.: 64.08% C, 5.38% H, 24.44% S;

found: 63.67% C, 5.40% H, 24.08% S.

IR (KBr, cm^{-1}) 1602, 1500 $\nu(\text{C}_{\text{Ar}}=\text{C}_{\text{Ar}})$, 3032 ν , 837 $\delta(\text{C}_{\text{Ar}}-\text{H})$, 1240 (as), 1015 $\nu_s(-\text{C}-\text{O}-\text{C}-)$, 2561 $\nu(\text{S}-\text{H})$, 2926 ν , 1425 $\delta(\text{C}-\text{H}(\text{CH}_2))$.

^1H NMR (ppm, CDCl_3) 1.76 t, $J = 7.5\text{Hz}$ 2H(SH); 3.72 d, $J = 7.5\text{Hz}$ 4H($-\text{CH}_2-$); 6.93 d, $J = 8.8\text{Hz}$ 4H(orto); 7.27 d, $J = 8.8\text{Hz}$ 4H(meta).

Synthesis of polythioesters

The syntheses of polythioesters by interfacial polycondensation of bis(4-mercaptomethylphenyl)ether with aliphatic and aromatic dichlorides were carried out as follows.

In a 500ml of three-necked round-bottom flask equipped with mechanical stirrer (1800rpm), thermometer and dropping funnel 0.02 mol dithiol, 100ml benzene and sodium hydroxide (0.08 mol) dissolved in 40ml of water were located. During through mixing 0.022 mol of acid chloride in 100ml benzene was added within 15–20 min. After the addition of the acid chloride was completed, the stirring was continued for 20min., and the mixture was then acidified with hydrochloric acid (Congo red). The isolated polycondensation product was filtered, washed with hot water (2x50 ml) and acetone (30ml) and dried to constant weight under reduced pressure (20hPa) at 40–80°C.

MEASUREMENT OF PROPERTIES

Melting point determinations were made on a Böetius apparatus at a heating rate of $6^\circ\text{C}/\text{min}^{-1}$. The reduced viscosity (dl/g) of a 1% solution of polythioesters in a phenol/tetrachloroethane mixture (1:3, V/V) or tetrachloroethane was measured with an Ubbelohde viscometer at 25°C.

Infrared (IR) spectra were recorded in KBr discs with a FT 1725 X Perkin-Elmer spectrophotometer.

The ^1H NMR spectra were determined using BS 567 A Tesla 100MHz spectrometer with TMS as an internal standard. Samples were run in CDCl_3 solutions.

Molecular weights were obtained using a Knauer gel chromatograph equipped with 10^5 , 10^4 , 10^3 , 10^2 Å and 50μ . PL-Gel columns with a refractometric detector. Tetrahydrofuran was used as the eluent (flow rate was 1.0ml/min., and numerical values for the molecular weight were obtained by comparison to polystyrene standards.

X-ray diffraction measurements were performed using DRON-3 x-ray apparatus with 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 seconds. The measurements were taken every 0.02° .

Thermogravimetric analysis was performed on a MOM Budapest-3427 derivatograph at heating rate of $10^\circ\text{C}/\text{min}$. in air.

Chemical resistance was determined in a 50ml flask by dissolving 0.2g of polythioester in 15ml of different solvents at room temperature during 48h.

3. RESULTS AND DISCUSSION

Determination of optimum conditions of interfacial polycondensation

To determine optimum conditions for interfacial polycondensation of bis(4-mercaptomethylphenyl)ether with acid dichlorides, adipoyl chloride was chosen as the model system.

In the choice of optimal conditions the highest value of reduced viscosity and the highest yield of the process were taken into consideration. The influence of the following factors on the results of interfacial polycondensation was studied: concentration and molar ratio of reagents, the quantitative ratio aqueous to organic phase, concentration of hydrogen chloride acceptor excess, rate of addition of acid dichloride and contribution of catalyst and emulsifier.

The initial reaction conditions were: organic solvent: benzene; concentration of dithiol: 0.1M; concentration of acid chloride: 0.11M; hydrogen chloride acceptor: 0.2M NaOH; rate of acid chloride addition: 5min.; temperature of reaction 20°C .

Influence of the dithiol concentration and the ratio of organic to aqueous phase on the value of reduced viscosity and the yield of the polythioesters were studied with different quantities of water at a constant volume of organic phase. The ratios were from 1:1 to 1:0.1, and correspond to concentration of

1–0.1 mol/l of dithiol in aqueous basic phase. Table 1 shows that the highest value of reduced viscosity and the best yield of polythioester were obtained with 0.2M solution of dithiol (phase ratio 2:1). The effects of the period of addition of acid chloride in the range 2–20 min. on reduced viscosity and yield are shown in Table 2. The optimum time of acid dichloride addition is 15–20 min. Either longer or shorter times cause decrease in the reduced viscosity and yield.

Tab. 1. Influence of the concentration of dithiol in the aqueous basic phase on the reduced viscosity and yield of polythioester from bis(4-mercaptomethylphenyl)ether with adipoyl dichloride
Wpływ stężenia ditiolu na lepkość zredukowaną i wydajność politioestru z eteru bis(4-merkaptometylofenylowego) i chlorku adypilu

Concentration of dithiol [M]	Ratio organic to aqueous phase	η_{red} [dl/g]	Yield [%]
0.1	1:1	0.48	24
0.2	1:0.5	0.55	35
0.4	1:0.25	0.52	20
0.5	1:0.2	0.50	17
1.0	1:0.1	0.46	11

Reaction conditions: organic phase benzene; reagents ratio 1:1.1; period for acid chloride addition 5min.; temperature 20°C; NaOH stoichiometrically

Warunki reakcji: faza organiczna – benzen; stosunek molowy reagentów – 1:1,1; czas dodawania chlorku – 5min; temp. reakcji – 20°C; NaOH – ilość stechiometryczna

In the further optimization process, the influence of excess sodium hydroxide as a hydrogen chloride acceptor was studied considering the results of polycondensation. As shown in Table 3, the use of excess sodium hydroxide in relation to the amount stoichiometrically necessary at first increases and then decreases the value of reduced viscosity. The advantageous influence of excess of sodium hydroxide may be explained by increased activity of thiolane with a simultaneous increase in its solubility. It seems that reaction rate of thiolane with acid chloride is higher than hydrolysis rate of COCl groups.

Tab. 2. Influence of time of acid chloride addition on the reduced viscosity and yield of polythioester from bis(4-mercaptomethylphenyl) ether with adipoyl dichloride

Wpływ czasu wkraplania chlorku kwasowego na lepkość zredukowaną i wydajność politioestru z eteru bis(4-merkaptometylofenylowego) i chlorku adypilu

Time [min]	η_{red} [dl/g]	Yield [%]
2	0.53	20
5	0.55	35
10	0.67	38
15	0.85	40
20	0.82	36

Reaction conditions: organic phase benzene; phase ratio 2:1, reagents ratio 1:1:1; temperature 20°C; NaOH stoichiometrically

Warunki reakcji: faza organiczna – benzen; stosunek fazy wodnej/organicznej – 2:1; stosunek molowy reagentów – 1:1,1; temp. reakcji – 20°C; NaOH – ilość stechiometryczna

Tab. 3. Influence of excess of hydrogen chloride acceptor (NaOH) on the reduced viscosity and yield of polythioester from bis(4-mercaptomethylphenyl) ether with adipoyl dichloride

Wpływ nadmiaru akceptora chlorowodoru (NaOH) na lepkość zredukowaną i wydajność politioestru z eteru bis(4-merkaptometylowego) i chlorku adypilu

Excess of NaOH [%]	η_{red} [dl/g]	Yield [%]
0	0.85	40
50	0.91	43
100	1.10	50
150	0.98	54
200	0.85	52

Reaction conditions: organic phase benzene; phase ratio 2:1, reagents ratio 1:1:1; period for acid chloride addition 15min.; temperature 20°C

Warunki reakcji: faza organiczna – benzen; stosunek fazy wodnej/organicznej – 2:1; stosunek molowy reagentów – 1:1,1; czas dodawania chlorku kwasowego – 15min.; temp. reakcji – 20°C

Studying the influence of benzyltriethylammonium chloride as catalyst used in amount of 5% in relation to dithiol, we do not notice any clear effect on the reduced viscosity of the polyreaction products.

In the case of using emulsifier (Mersolan), values of reduced viscosity and yield of polythioesters decreased.

Polythioesters syntheses from dithiol and succinyl, sebacoyl, isophthaloyl and terephthaloyl dichlorides were carried out according to the experimentally defined conditions for adipoyl chloride. Table 4 shows the values of reduced viscosity, yields, softening ranges and molecular weights of all polythioesters synthesized.

Tab. 4. Some physicochemical properties of polythioesters derivatives of bis(4-mercaptomethylphenyl) ether and acid dichlorides
Właściwości fizykochemiczne politioestrów z eteru bis(4-merkaptometylofenylowego) i dichlorków kwasowych

Polythioester No	Acid dichloride	M.p. [°C]	η_{red} [dl/g]	Yield [%]	GPC data		
					\overline{M}_n	\overline{M}_w	$\overline{M}_n/\overline{M}_w$
I	Succinyl	135–143	0.36 ^a	70	2510	6220	2.47
II	Adipoyl	122–156	1.10 ^a	50	–	–	–
III	Sebacoyl	79–88	0.45 ^a	57	4360	14700	3.36
IV	Isophthaloyl	255–274	–	61	–	–	–
V	Terephthaloyl	210–236	0.70 ^b	70	–	–	–

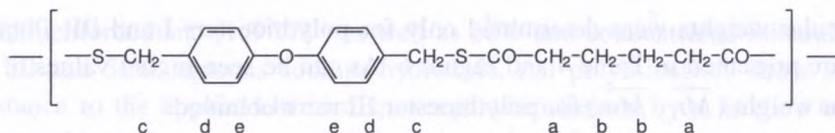
^{a,b} – solvent used: tetrachloroethane, phenol/tetrachloroethane mixture

^{a,b} – rozpuszczalniki: tetrachloroetan, mieszanina fenol/tetrachloroetan

Structure of polythioesters

The structures of all polythioesters obtained under the model conditions were determined by elemental analysis, infrared (IR) and nuclear magnetic resonance (¹HNMR) spectroscopies and X-ray analysis. The results of elemental analyses are given in Table 5.

IR spectra of polythioesters show strong absorptions at 1688–1661 cm⁻¹ which are characteristic of carbonyl valency band. In the range at 971–957 cm⁻¹ absorptions vibration are attributed to the COS function. The absorption bands at 1424–1407 cm⁻¹ are attributed to deformation vibration, 2932–2911 cm⁻¹ and 2876–2849 cm⁻¹ are characteristic of valency of the –CH₂– group. The absorption bands at 847–836 cm⁻¹ is characteristic of 1,4- disubstituted of benzene ring. Absorption band at 1240 cm⁻¹ is characteristic of ether band. In Figure 3 IR spectrum only for the example of polythioester (III) is presented, while Figure 4 shows ¹HNMR only for polythioester II.



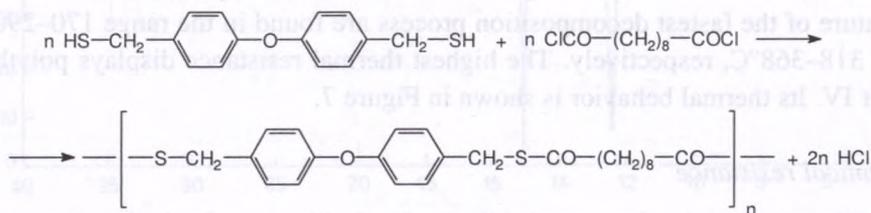
$^1\text{H NMR}$ ppm (CDCl_3): 7.22 d, $J = 8.6\text{Hz}$ 4H(d); 6.89 d, $J = 8.6\text{Hz}$ 4H(e); 4.08 s, 4H(c); 2.64–2.35 m 4H(a); 1.72–1.46 m 4H(b).

Tab. 5. Results of elemental analyses of polythioesters from bis(4-mercaptomethylphenyl)ether and acid dichlorides

Polythio- ester No	Analysis					
	C		H		S	
	calcd.	found	calcd.	found	calcd.	found
I	62.76	62.44	4.68	4.80	18.61	18.35
II	64.48	64.94	5.41	5.88	17.21	17.60
III	67.25	66.48	6.59	6.52	14.96	14.56
IV	67.32	66.48	4.11	4.02	16.34	16.22
V	67.32	66.61	4.11	4.19	16.34	16.59

As follows from X-ray data analysis all polythioesters indicate various degrees of crystallinity (Fig. 5). Polythioesters derivatives of succinyl (I), adipoyl (II) and sebacoyl dichlorides show a sharp peak of diffraction which determined their high degree of crystallinity. Polythioester obtained from terephthaloyl chloride (V) shows only weakly determined diffraction peak which indicates insignificant degree of its crystallinity. Polythioester from dithiol and isophthaloyl chloride (IV) shows wide peak, characteristic of amorphous state.

On the basis of good agreement between calculated and found analytical data (Table 5) and IR and $^1\text{H NMR}$ spectra reaction scheme for bis(4-mercaptomethylphenyl)methane and sebacoyl chloride as an example was taken as:



For all polythioesters obtained molecular weight determination was impossible, because of the low solubility in tetrahydrofuran at room temperature.

Molecular weights were determined only for polythioesters I and III. Obtained data are presented in Table 4 and Figure 6. As can be seen higher values of molecular weight (\overline{Mn} , \overline{Mw}) for polythioester III were obtained.

Tab. 6. Thermal properties of polythioesters
Własności termiczne politioestrów

Polithio- ester No	Thermal analysis			Mass loss [%]				
	T ₁	T ₂	T ₃	Temperature [°C]				
	[°C]	[°C]	[%]	300	350	400	450	500
I	170	320	23	8	40	45	47	49
II	250	318	26	13	37	46	49	52
III	275	368	24	5	17	48	57	66
IV	290	340	8	1	12	19	23	28
V	210	327	18	4	25	29	32	36

T₁ – temperature of initial decomposition from the curve TG

T₂ – temperature of maximum velocity of decomposition from the curve DTG

U – mass loss from the curve TG at temperature T₂

T₁ – temp. początku rozkładu z krzywej TG

T₂ – temp. max. szybkości rozkładu z krzywej DTG

U – ubytek masy w temp. T₂ z krzywej TG

Thermal properties

The thermal resistance of polythioesters was examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial decomposition, its mass loss in percent, the temperature of the fastest decomposition process and percentage mass loss at 300–500 °C were deduced from the curves. Numerical data are presented in Table 6. The results of the examination show that the temperature of initial decomposition and the temperature of the fastest decomposition process are found in the range 170–290°C and 318–368°C, respectively. The highest thermal resistance displays polythioester IV. Its thermal behavior is shown in Figure 7.

Chemical resistance

We tried to dissolve samples (1g) of polythioesters in 48 hours at room temperature in 50 ml of different solvents such as: acetone, dioxane, methylene chloride, dimethyl sulphoxide, tetrachloroethane and a mixture of phe-

nol/tetrachloroethane (1:3 V/V) as well as 10% and concentrated mineral acids and 10 and 50% aqueous sodium hydroxide. All polythioesters show a great resistance to the applied chemicals, except when treated by a mixture of phenol/tetrachloroethane. Concentrated nitric and sulfuric acids result in a very quick decomposition of polythioesters.

4. CONCLUSION

Polythioesters synthesized by interfacial polycondensation from bis(4-mercaptomethylphenyl) ether with chosen acid dichlorides were obtained with good yield and relatively good reduced viscosity. The best properties of the polymers were obtained with concentration 0.2M of dithiol, ratio aqueous to organic phase (benzene) 2:1 and period for acid chloride addition 15min. Clear improvements of the results of polycondensation were achieved when about 100% molar excess of hydrogen chloride acceptor (NaOH) was used. The obtained polythioesters show good thermal and chemical resistance. The best thermal resistance is characteristic of polythioester from dithiol and isophthaloyl chloride.

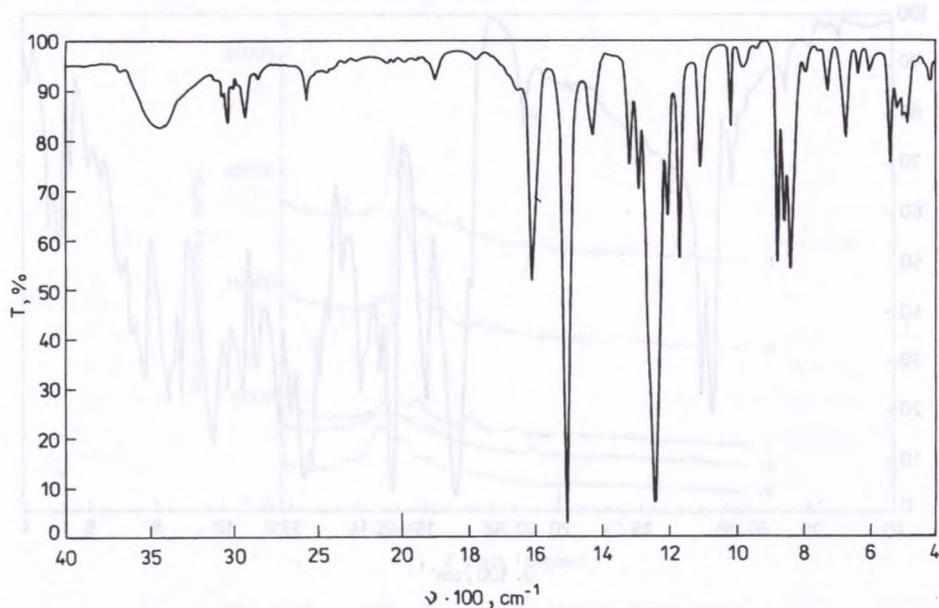


Fig. 1. FT-IR spectrum of the bis(4-mercaptomethylphenyl)ether
Widmo FT-IR eteru bis(4-merkaptometylofenylowego)

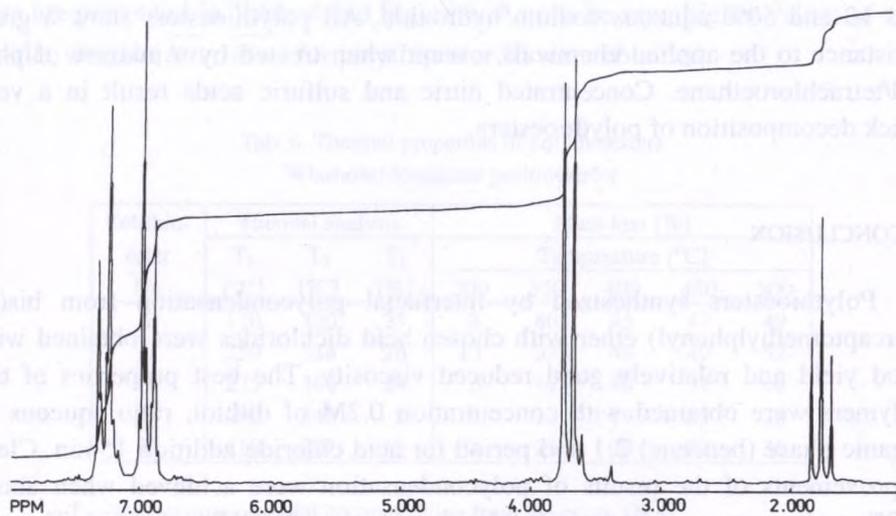


Fig. 2. HNMR spectrum of the bis(4-mercaptomethylphenyl) ether
Widmo HNMR eteru bis(4-merkaptometylofenylowego)

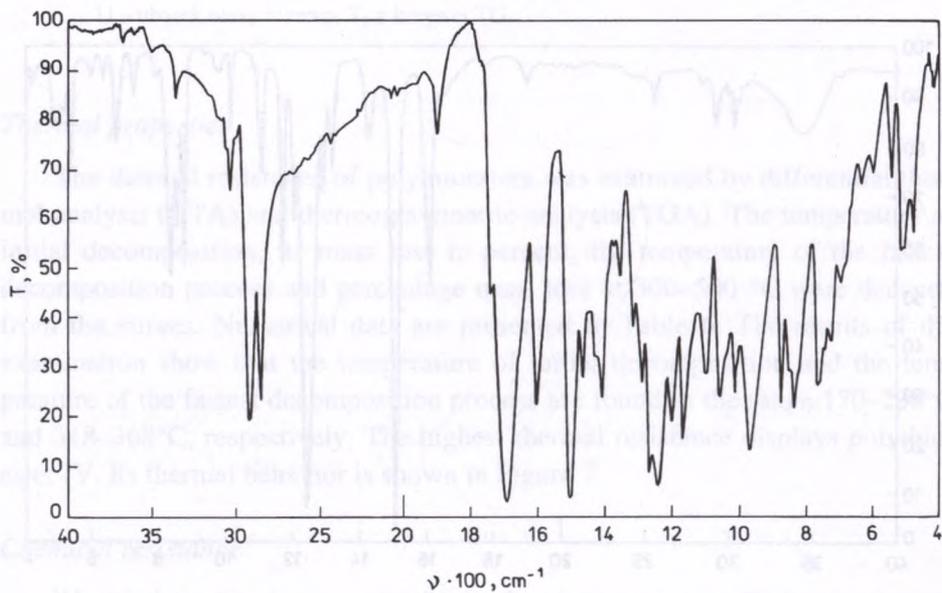


Fig. 3. FT-IR spectrum of the polythioester III
Widmo FT-IR politioestru III

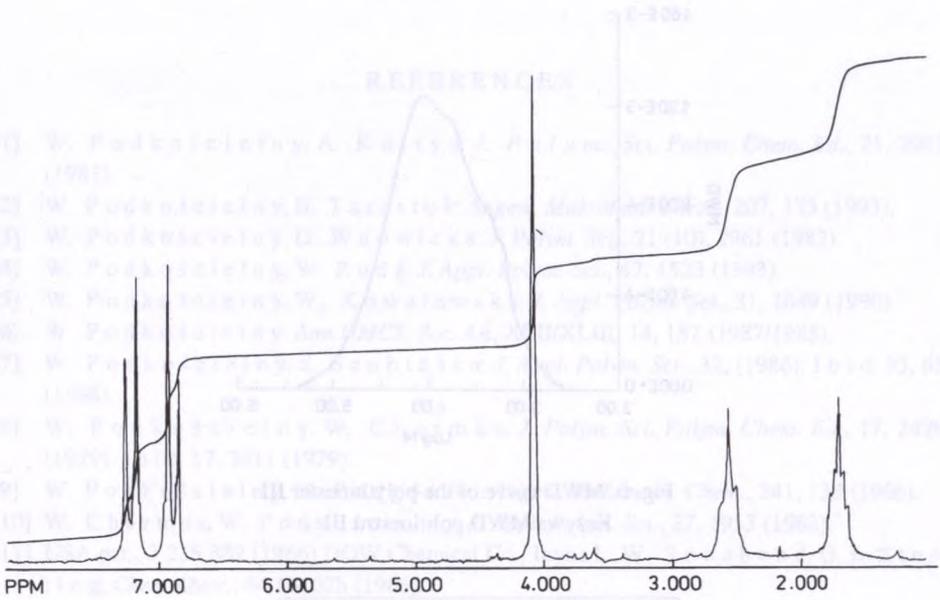


Fig. 4. HNMR spectrum of the polythioester II
Widmo HNMR politioestru II

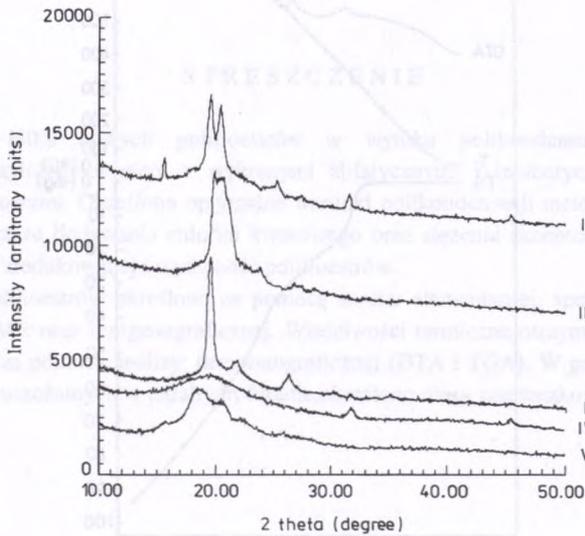


Fig. 5. X-ray diffraction patterns of the polythioesters
Rentgenogramy dyfrakcyjne politioestrów

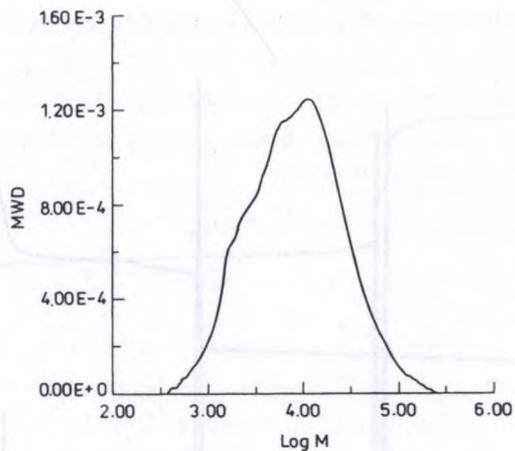


Fig. 6. MWD curve of the polythioester III
Krzywa MWD politioestru III

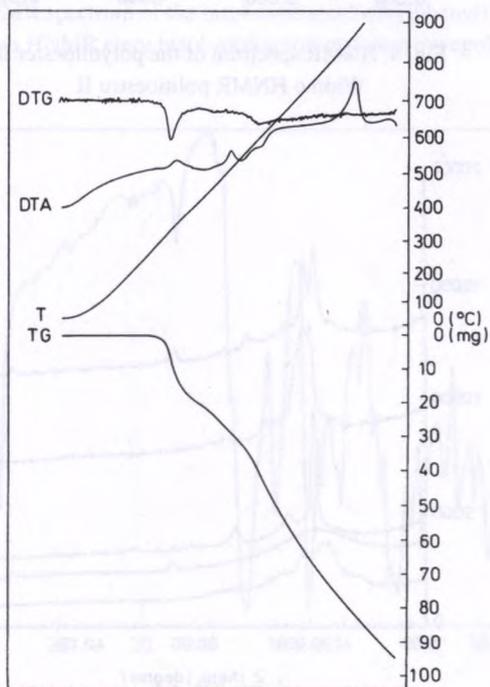


Fig. 7. DTA and TGA of the polythioester IV
DTA i TGA politioestru IV

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STRESZCZENIE

Otrzymano kilka nowych politioestrów w wyniku polikondensacji międzyfazowej bis(4-merkaptometylofenylo) eteru z wybranymi alifatycznymi i izomerycznymi ftaloilowymi dichlorkami kwasowymi. Określono optymalne warunki polikondensacji metodą badania wpływu stężenia ditiolu, czasu dodawania chlorku kwasowego oraz stężenia akceptora chlorowodoru na wielkość lepkości zredukowanej i wydajność politioestrów.

Strukturę politioestrów określono za pomocą analiz: elementarnej, spektralnej w podczerwieni (IR) i ^1H NMR oraz rentgenograficznej. Właściwości termiczne otrzymanych politioestrów zostały określone za pomocą analizy: derywatograficznej (DTA i TGA). W przypadku niektórych politioestrów rozpuszczalnych w tetrahydrofuranie określono masy cząsteczkowe (\overline{M}_n i \overline{M}_w).

