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Synthesis of Polyanhydrides. XI.¹

Synthesis and Properties of New Polythioetherpolyanhydrides

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SUMMARY:

Four groups of new aromatic and aliphatic a,ω -dicarboxythioethers of the following general structures have been synthesized and the optimum reaction condition has been determined.

$$HOOC(CH_2)_y S(CH_2)_x S(CH_2)_y COOH$$
(I)

$$HOOC(CH_2)_yS(CH_2)_x - \langle \rangle - (CH_2)_xS(CH_2)_yCOOH$$
(II)

$$HOOC(CH_2)_{x}S - S(CH_2)_{x}COOH$$
(III)

$$HOOC(CH_2)_x S(CH_2)_x COOH$$
 (IV)

Polycondensation reactions of a,ω -dicarboxythioethers, carried out with acetic anhydride, afforded new linear and crystalline polythioetherpolyanhydrides. It was confirmed from the physical properties that the flexibility of the polymer chain was markedly enhanced by substituting methylene groups for thioether linkages in the monomer molecule. The experimental evidence supports the observations previously reported for polyetherpolyanhydrides²).

The polymer structure was determined by means of infrared spectra and X-ray diffraction studies and the properties of the new polythioetherpolyanhydrides were investigated. Furthermore, the influence of the molecular structure on the physical properties of these polymers is discussed.

ZUSAMMENFASSUNG:

Vier Gruppen von neuartigen aromatischen und aliphatischen a, ω -Dicarboxythioäthern der allgemeinen Formeln

$$HOOC(CH_2)_yS(CH_2)_xS(CH_2)_yCOOH$$
(1)

$$HOOC(CH_2)_yS(CH_2)_x - \langle \rangle - (CH_2)_xS(CH_2)_yCOOH$$
(II)

 $HOOC(CH_2)_{x}S(CH_2)_{x}COOH$ (III)

wurden dargestellt und die optimalen Reaktionsbedingungen bestimmt.

Die Polykondensationsreaktion von α,ω -Dicarboxylthioäthern, die mit Essigsäureanhydrid durchgeführt wurde, ergab neuartige lineare, kristalline Polythioätherpolyanhydride. Die physikalischen Eigenschaften ließen erkennen, daß die Beweglichkeit der Polymerenkette durch Einführung von Methylengruppen statt Thioäthergruppen merklich verstärkt wird. Die experimentellen Ergebnisse stützen auch die in der vorigen Mitteilung beschriebenen Beobachtungen über Polyätherpolyanhydride²).

Struktur und Eigenschaften der neuartigen Polythioätherpolyanhydride wurden mittels Infrarot- und Röntgenspektren studiert. Ferner wurde der Einfluß der Struktur auf die physikalischen Eigenschaften dieser Polymeren diskutiert.

A. Introduction

It has been reported in a previous paper which deals with linear polyanhydrides containing sulphur in the molecule, that five-membered heterocyclic thiophene polyanhydrides possess fiber- and film-forming properties and are elastic in nature³⁾.

Extending this research further on the synthesis of sulphur containing linear polyanhydrides, the author investigated the polycondensation of α,ω -dicarboxythioethers in which one of the methylene groups of the aliphatic chain within the molecule was replaced by sulphur. Thus, four groups of new aromatic and aliphatic α,ω -dicarboxythioethers of the following general structures have been synthesized and the optimum reaction condition determined.

HOOC(CH₂)_yS(CH₂)_xS(CH₂)_yCOOH (I)
$$x = 1, 2, 3 \cdots y = 1, 2, 3 \cdots$$

HOOC(CH₂)_yS(CH₂)_x – (CH₂)_xS(CH₂)_yCOOH (II)

$$\mathbf{x} = 1, 2, 3 \cdots \mathbf{y} = 1, 2, 3 \cdots$$

HOOC(CH₂)_xS-
$$-$$
S(CH₂)_xCOOH (III)
x = 1, 2, 3...

$$HOOC(CH_2)_x S(CH_2)_x COOH$$
(IV)
x = 1, 2, 3...

As to the preparation of monomers, the interaction of thioglycolic acid and α,ω -alkylene dihalides was studied and new compounds were synthesized. By a similar route HORN⁴) obtained α,ω -dicarboxysulfones by the oxidation of thioethers.

When α,ω -dicarboxythioethers thus obtained are treated with acetic anhydride to form diacetates, and heated *in vacuo* at 200–240 °C. under nitrogen, it was found that new polythioetherpolyanhydrides of linear crystalline structures were obtained. The thioether group within the molecule was detected by C-S stretching vibration mode in the infrared spectrum, $600-700 \text{ cm}^{-1}$, $(14.0-14.5 \,\mu)^{8)}$ and anhydride group was confirmed by two characteristic carbonyl stretching modes in the infrared spectra in $5.65-5.90 \,\mu$ region.

The flexibility of the polymer was markedly enhanced, as postulated, by substituting methylene groups for thioether linkages in the molecule.

The experimental evidence supports the observations previously reported for polyetherpolyanhydrides²). There has been no publications so far for the synthesis of sulphur containing linear polyanhydrides, and in this present study the new synthesis of polythioetherpolyanhydrides is described in detail, and the influence of the molecular structure on the physical properties of these polymers is discussed.

B. Experimental and Results*)

1. Synthesis of a, ω -dicarboxythioethers

 α,ω -dicarboxythioethers were prepared by dehydrohalogenation of thioglycol and alkylene halides. All of the α,ω -dicarboxythioethers except β -thiopropionic acid were unknown compounds, and optimum reaction condition was determined by changing reaction time and temperature.

a) 3,3'-(ethylenedithio)-dipropionic acid

By the interaction of 2 moles of β -mercaptopropionic acid and 1 mole of ethylene chloride, 3,3'-(ethylenedithio)dipropionic acid was prepared in 83% yield.

$2 \operatorname{SH}(\operatorname{CH}_2)_2 \operatorname{COOH} + \operatorname{Cl}(\operatorname{CH}_2)_2 \operatorname{Cl} \rightarrow \operatorname{HOOC}(\operatorname{CH}_2)_2 \operatorname{S}(\operatorname{CH}_2)_2 \operatorname{S}(\operatorname{CH}_2)_2 \operatorname{COOH} + 2 \operatorname{HCl}$

21.0 g. (0.20 mole) of β -mercaptopropionic acid (b.p.₅: 105–108 °C.) were added to 200 ml. of 20% aqueous ethanol containing 16.0 g. of sodium hydroxide. The reaction vessel was heated at 90 °C., and 13.0 g. (0.13 mole) of ethylene chloride were added and stirring was continued for 5 hrs. at 90 °C. After removal of ethanol under reduced pressure, the solution was acidified with hydrochloric acid. The precipitate was filtered and recrystallized from acetone/ethyl acetate to afford crystalline solid (m.p. 156 °C.) in 83% yield. The infrared spectrum, Fig. 1, shows that the carbonyl stretching band corresponding to carboxylic acid is at $\lambda_{max}^{C=O} = 5.89 \,\mu$ and C–S stretching absorption band at $\lambda_{max}^{-C-S} = 14.01 \,\mu$.

C₈H₁₄O₄S₂ (238.14) Calcd.: C 40.33 H 5.88 S 26.90 Found: C 39.53 H 6.91 S 26.05

^{*)} Melting points were recorded on a ZEISS polarizing microscope and were corrected.



Fig. 1. Infrared spectrum of 3,3'-(ethylenedithio)-dipropionic acid; m.p. 155°C. (Nujol) HOOC(CH₂)₂S(CH₂)₂S(CH₂)₂COOH

b) 2,2'-(ethylenedithio)-diacetic acid
2 SHCH₂COOH + Cl(CH₂)₂Cl
$$\rightarrow$$
 HOOCCH₂S(CH₂)₂SCH₂COOH + 2 HCl

To a solution of 200 ml. of 20% aqueous ethanol containing 16.0 g. of sodium hydroxide and 18 g. (0.2 mole) of β -mercaptoacetic acid (b.p.₁₆: 107-108°C.), 13 g. (0.13 mole) of ethylene chloride were added at 90°C. After stirring for 16 hrs. at 80-85°C., the ethanol was removed, acidified with hydrochloric acid and the product extracted with ether to afford colorless needles, m.p. 103°C. in 62% yield. Infrared spectrum (Fig. 2) indicates carbonyl stretching absorption band at $\lambda_{max}^{C=O} = 5.82$, 5.95 μ , C-S stretching band at $\lambda_{max}^{-C-S} = 14.22 \mu$

C₆H₁₀O₄S₂ (210.14) Caled.: C 34.88 H 5.53 S 28.51 Found: C 34.45 H 4.50 S 30.45



Fig. 2. Infrared spectrum of 2,2'-(ethylenedithio)-diacetic acid; m.p. 85°C. (Nujol) HOOCCH₂SCH₂SCH₂COOH

c) 3,3'-(p-xylylenedithio)-dipropionic acid 2 SH(CH₂)₂COOH + ClCH₂- \bigcirc -CH₂Cl \rightarrow HOOC(CH₂)₂SCH₂- \bigcirc -CH₂S(CH₂)₂COOH + 2 HCl

21.0 g. (0.2 mole) of β -mercaptopropionic acid (b.p.₅: 105–108 °C.) were added to 200 ml. of 20% aqueous ethanol containing 10 g. of sodium hydroxide. To the solution 25.0 g.

(0.12 mole) of *p*-xylylene dichloride (m.p. 100.5 °C.) dissolved in 200 ml. of ethanol/benzene (1:1) were added. Optimum reaction condition was determined and afforded the dehydrochlorination product in 95% yield. Reaction yields and conditions are summarized in Table 1.

Table 1. Reaction conditions of dehydrochlorination of β -mercaptopropionic acid (0.2 mole) and *p*-xylylene dichloride (0.12 mole) to form 3,3'-(*p*-xylylenedithio)-dipropionic acid. (Solvent: ethanol/benzene 1:1 mole, 200 ml.)

Exp. No.	Reaction time (hrs.)	Temp. (°C.)	Yield (%)
1	3	30	32
2	4	50	45
3	8	70	81
4	11	70	95
5	16	70	94
6	24	70	95
7	30	70.	95

After the reaction was completed, ethanol/benzene was removed, and the product was recrystallized from methanol yielding a crystalline solid, m.p. 138-140 °C. The optimum reaction temperature was found to be 70 °C. in ethanol/benzene as illustrated in Table 1.

Infrared spectrum (Fig. 3) indicates carbonyl absorption band at $\lambda_{\max}^{\infty=0} = 5.89 \,\mu$, thioether stretching band at $\lambda_{\max}^{-C-S} = 14.20 \,\mu$.

C₁₄H₁₈O₄S₂ (314.14) Caled.: C 53.18 H 5.73 S 20.38 Found: C 53.26 H 5.85 S 19.45





$$HOOC(CH_2)_2SCH_2 - CH_2S(CH_2)_2COOH$$

d) 2,2'-(p-xylylenedithio)-diacetic acid 2SHCH₂COOH + ClCH₂- \bigcirc -CH₂Cl \rightarrow HOOCCH₂SCH₂- \bigcirc -CH₂SCH₂COOH To 200 ml. of 20% aqueous ethanol containing 16.0 g. of sodium hydroxide and 18 g. (0.2 mole) of β -mercaptoacetic acid 17.0 g. (0.1 mole) of p-xylylenedichloride dissolved in

160 ml. of ethanol/benzene (5:3) were added. After refluxing was continued at 70°C. for 15 hrs., the solvent was removed, acidified and the precipitate was recrystallized from methanol to afford crystalline solid of m.p. 148–150°C. in 98% yield. Infrared spectrum (Fig. 4) shows carbonyl band at $\lambda_{max}^{C=0} = 5.89 \,\mu$ and thioether band at $\lambda_{max}^{-C-S} = 14.45 \,\mu$.





HOOCCH₂SCH₂-CH₂SCH₂COOH

e) β-thiodipropionic acid⁵⁾

 β -thiodipropionic acid was prepared by the interaction of β -propiolactone with β -mercaptopropionic acid as shown in the following equation:

$$SH(CH_2)_2COOH + CH_2-CH_2 \rightarrow HOOC(CH_2)_2S(CH_2)_2COOH$$
$$| | | O----CO$$

27.0 g. (0.25 mole) of β -mercaptopropionic acid were disolved in 40 ml. of 25% aqueous sodium hydroxide and under ice cooling at 0–5°C. and then, 18.0 g. (0.25 mole) of β -pro-



Fig. 5. Infrared spectrum of β-thiodipropionic acid; m.p. 116°C. (Nujol) HOOC(CH₂)₂S(CH₂)₂COOH

piolactone (b.p. 146–147 °C.) were added dropwise. The reaction mixture was stirred at 0-5 °C. for 1 hr., and at 20 °C. for 1 hr. followed by acidification, and the product was extracted with 100 ml. ether four times. After removal of ether, it was recrystallized from benzene/methanol giving colorless needles, m.p. 116 °C. (23% yield). Infrared spectrum (Fig. 5) shows carbonyl stretching band at $\lambda_{\text{max}}^{>C=O} = 5.90 \,\mu$ and thioether absorption band at $\lambda_{\text{max}}^{>C=O} = 14.10 \,\mu$.

f) 3,3'-(p-dithiophenyl)-dipropionic acid
2 SH(CH₂)₂COOH + Cl-
$$\bigcirc$$
-Cl \rightarrow HOOC(CH₂)₂S- \bigcirc -S(CH₂)₂COOH + 2 HCl

To 200 ml. of 20% aqueous ethanol containing 16.0 g. of sodium hydroxide and 20.1 g. (0.2 mole) of β -mercaptopropionic acid (b.p.₅: 105–108°C.) 20.0 g. (0.14 mole) of *p*-dichlorobenzene (m.p. 53°C.) dissolved in ethanol/benzene (2:1) were added. The reaction mixture was stirred at 65–70°C. for 20 hrs., after which the solvent was removed, washed with 20% aqueous sodium hydroxide and the unreacted material was removed by extracting with ether. The solution was acidified with hydrochloric acid to afford crystalline solid, which was twice recrystallized from ethyl acetate. m.p. 151°C. (71% yield). Infrared spectrum (Fig. 6) shows bands at $\lambda_{max}^{\times C-O} = 5.87 \mu$ and $\lambda_{max}^{-C-S} = 14.00 \mu$.

C₁₄H₁₈O₄S₂ (314.14) Calcd.: C 50.34 H 4.90 S 20.38 Found: C 49.98 H 5.55 S 20.64



Fig. 6. Infrared spectrum of 3,3'-(p-dithiophenyl)-dipropionic acid; m.p. 154°C. (Nujol) HOOC(CH₂)₂S--S(CH₂)₂COOH

2. Polycondensation of a, ω -dicarboxythioethers with acetic anhydride

a) Polycondensation of 3,3'-(ethylenedithio)-dipropionic acid

12.3 g. (0.60 mole) of carefully recrystallized 3,3'-(ethylenedithio)-dipropionic acid (m.p. 156.0°C.) were dissolved in 200 ml. of acetic anhydride and refluxed at 140-150°C. for 3 hrs. to form the diacetate. The excess of acetic anhydride was removed under reduced pressure, and the resulting diacetate was polycondensed heating *in vacuo* and under nitrogen. The polycondensation procedure is illustrated in Table 2.

Polycond. time	Polycond. temp.		D
(min.)	(°C.)	(Torr)	nemarks
0	125	5	diacetate was heated to melt and dry N_2 gas was introduced
15	130	5	polycondensation starts
30	150	3	viscous solution obtained
60120	150-157	3	polycondensation proceeds
150	158	3	crystalline polymer
180	158	3	polycondensation completed

Table 2. Polycondensation of 3,3'-(ethylenedithio)-dipropionic acid with acetic anhydride

The polyanhydride thus obtained shows spinability. Infrared spectrum of the polymer is shown in Fig. 7.



Fig. 7. Infrared spectrum of poly-(3,3'-(ethylenedithio)-dipropionic acid) anhydride; m.p. 75°C. (KBr) -[-CO(CH₂)₂S(CH₂)₂S(CH₂)₂COO]_n

Carbonyl stretching absorption bands corresponding to anhydride group are observed at $\lambda_{\max}^{C=O} = 5.64 \,\mu$, 5.90 μ , thioether band at $\lambda_{\max}^{-C-S} = 14.01 \,\mu$. Infrared spectral data as well as elementary analysis support the following structure.

 $\begin{array}{cccc} HoOC(CH_2)_2S(CH_2)_2S(CH_2)_2COOH & & \\ \hline CH_3CO>O & & \\ \hline CH_3CO>O & & \\ \hline Polycondensation & \\ \hline CH_3CO-O-[-CO(CH_2)_2S(CH_2)_2S(CH_2)_2CO-O-COCH_3 & & (1) \\ \hline m.p. \ 75\ ^\circC.; \ [\eta]_{m-cresol}^{25\ \circC.} = 0.23. & & \\ \hline (C_6H_{12}O_3S_2)_n \ (196.26)_n & Calcd.: \ C\ 43.64\ H\ 5.45\ S\ 29.09 \\ \hline Found: \ C\ 45.12\ H\ 5.16\ S\ 29.55 & & \\ \end{array}$

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X-ray diffraction pattern was obtained using nickel-filtered CuK_{α} irradiation which shows discrete DEBYE-SCHERRER's rings as shown in Fig. 8.



Fig. 8. X-ray diffraction pattern of polythioetherpolyanhydride

X-ray radial intensity distribution for poly-[3,3'-(ethylene dithio) dipropionic anhydride] was taken by Norelco X-ray radiation scattering measurement (reflection method), and the degree of crystallization was obtained by computing integrated intensity ratio of crystalline and amorphous radial scattering curves at diffraction angles (20) between 8 and 42°. X-ray radial intensity distribution diagram is shown in Fig. 9.



Fig. 9. X-ray radial intensity distribution diagram of polythioetherpolyanhydride A: crystalline region; B: amorphous region; C: correction for air scattering

In Fig. 9, A and B regions correspond to amorphous and crystalline integrated intensity respectively, and S indicates the correction for air scattering. Thus, by multiplying incoherent factor (0.77) with amorphous integrated intensity, the degree of crystallization was obtained as a ratio of amorphous and crystalline integrated intensity. The degree of crystallization thus calculated was found to be 30 %.

b) Polycondensation of 2,2'-(ethylene dithio)-diacetic acid

A solution of 13.0 g. of purified 2,2'-(ethylenedithio)-diacetic acid (m.p. 103°C.) dissolved in 300 ml. of acetic anhydride was refluxed for 5 hrs. producing the diacetate. The diacetate was worked up in the usual polycondensation process as illustrated in Table 3 and linear polythioetherpolyanhydride was obtained.

Polycond. time	Polycond. temp.		Derech	
(min.)	(°C.) (Torr)		Remarks	
0	100	5	diacetate was heated to melt and dry N_2 gas was introduced	
15	135	5	polycondensation starts	
3060	140	5	viscous solution was obtained	
90-150	150 - 158	4	polycondensation proceeds	
190	158	4	crystalline polymer	
210	158	4	polycondensation completed	

Table 3. Polycondensation of 2,2'-(ethylenedithio)-diacetic acid with acetic anhydride





Infrared spectrum as in Fig. 10 indicates carbonyl stretching bands at of $\lambda_{max}^{C=0} = 5.50 \ \mu$ and $5.84 \ \mu$, $\lambda_{max|}^{C-O-C} = 9.50 \ \mu$, and $\lambda_{max}^{-C-S} = 14.02 \ \mu$. CH₃-CO-O-[-COCH₂S(CH₂)₂SCH₂CO-O-]_n-COCH₃; m.p. 83°C. [η]^{25°C.}_{m-cresol} = 0.21 (C₆H₈O₃S₂)_n (192.26)_n Calcd.: C 37.50 H 4.17 S 23.33 Found: C 38.20 H 5.03 S 32.89

c) Polycondensation of 3,3'-(p-xylylenedithio)-dipropionic acid

A solution of 200 ml. of acetic anhydride containing 12.0 g. of purified 3,3'-(p-xylylenedithio)-dipropionic acid (m.p. 138-140°C.) was refluxed for 3 hrs. to form the diacetate. Polycondensation was carried out in the usual manner as shown in Table 4.

Polycond. time	Polycond. temp.		Dama andra
(min.)	(°C.)	(Torr)	Remarks
0	110	20	diacetate was heated to melt and dry N_2 gas was introduced
10	140	12	polycondensation starts
20-100	150-152	4	viscous solution obtained
160-220	152-158	3	viscosity of the melt increases
250	158	3	fiber-forming polymer
280	158	3	polycondensation completed

Table 4. Polycondensation of 3,3'-(p-xylylenedithio)-dipropionic acid with acetic anhydride

The anhydride carbonyl groups were confirmed by infrared spectrum, Fig. 11. $\lambda_{\text{max}}^{C=0} = 5.50 \,\mu$, $5.75 \,\mu$, $\lambda_{\text{max}}^{C=0-C} = 9.58 \,\mu$.



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$$\begin{array}{c} \mathrm{CH_{3}CO-O-[-CO(CH_{2})_{2}SCH_{2}-} & -\mathrm{CH_{2}S(CH_{2})_{2}CO-O-]_{\overline{n}}COCH_{3};} \\ \mathrm{m.p. \ 91^{\circ}C. \ [\eta]_{\mathit{m-cresol}}^{25^{\circ}C.} = \ 0.11.} \\ (C_{14}\mathrm{H_{16}O_{3}S_{2}})_{n} \ (298.42)_{n} \quad \mathrm{Calcd.: \ C \ 56.76 \ H \ 5.41 \ S \ 21.62} \\ \mathrm{Found: \ C \ 56.51 \ H \ 4.98 \ S \ 23.02} \end{array}$$

d) Polycondensation of 2,2'-(p-xylylenedithio)-diacetic acid

A solution of 200 ml. of acetic anhydride containing 10.0 g. of purified 2,2'-(p-xylylene-dithio)-diacetic acid (m.p. 148-150°C.) was refluxed at 155-160°C. for 4 hrs. The polycondensation process is illustrated in Table 5.

Table 5. Polycondensation of 2,2'-(p-xylylenedithio)-diacetic acid with acetic anhydride

Polycond. time	Polycond. temp.		Pb.
(min.)	(°C.)	(Torr)	Remarks
0	115	15	diacetate was heated to melt and dry N_2 gas was introduced
10	125	8	polycondensation starts
25-55	130-140	4	viscous solution obtained
85-145	148-155	4-3	polycondensation proceeds
175	155	3	elastic polymer obtained
200	155	3	polycondensation completed

Polyanhydride thus obtained has elastic properties. It was observed by X-ray diffraction that the crystallinity increases after spinning. Infrared spectrum (Fig. 12) shows anhydride carbonyl absorption bands at $\lambda_{max}^{C=0} = 5.50 \,\mu$, $5.76 \,\mu$, $\lambda_{max}^{C=0-C} = 9.50 \,\mu$ and $\lambda_{max}^{C=S} = 14.15 \,\mu$





$$CH_{3}CO-O-[-COCH_{2}SCH_{2}-CH_{2}SCH_{2}CO-O-]_{\overline{n}}-COCH_{3};$$

m.p. 88°C. $[\eta]_{m-cresol}^{25°C.} = 0.28.$

X-ray diffraction pattern of the polymer in Fig. 13 shows descrete DEBYE-SCHERRER's rings and crystallinity of the polymer is found to be 45-50 % which is presumably affected by aromatic rings in the polymer chain.

(C₁₂H₁₂O₃S₂)_n (268.35)_n Calcd.: C 53.73 H 4.48 S 23.88 Found: C 54.13 H 4.62 S 24.66



Fig. 13. X-ray diffraction pattern of polythioetherpolyanhydride

e) Polycondensation of \beta-thiopropionic acid

12.0 g. of β -thiodipropionic acid (m.p. 116°C.) were dissolved in 150 ml. of acetic anhydride and refluxed at 150–160°C. for 5 hrs. to form the diacetate. The detailed procedure is illustrated in Table 6.

Polycond. time	Polycond. temp.		Beneralia	
(min.)	(°C.)	(Torr)	Remarks	
0	130	10	diacetate was heated to melt and dry N_2 gas was introduced	
15	135	4	polycondensation starts	
30-120	140 - 145	3	viscous solution obtained	
150 - 240	150-153	3	polycondensation proceeds	
270	156	3	fiber-forming polymer	
300	156	· 3	polycondensation completed	

Table 6. Polycondensation of \beta-thiodipropionic acid with acetic anhydride

The infrared spectrum of the resulting polyanhydride (Fig. 14) shows anhydride carbonyl absorption bands at $\lambda_{max}^{SC=O} = 5.50 \,\mu$, $5.80 \,\mu$, and $\lambda_{max}^{C-O-C} = 9.50 \,\mu$, and thioether band at $\lambda_{max}^{C-S} = 14.30 \,\mu$.

CH₃CO-O-[-CO(CH₂)₂S(CH₂)₂CO-O-]_{\overline{n}}COCH₃; m.p. 55.0°C. [η]^{25°C.} (C₆H₈O₃S)_n (160.19)_n Calcd.: C 45.00 H 5.00 S 20.00 Found: C 45.32 H 5.61 S 19.92



Fig. 14. Infrared spectrum of poly-(β -thiodipropionic acid) anhydride; m.p. 55°C. (KBr) -[-CO(CH₂)₂S(CH₂)₂COO-]_n

X-ray diffraction pattern of the polymer shows descrete DEBYE-SCHERRER's rings confirming that a crystalline polymer was obtained.



Fig. 15. X-ray diffraction pattern of polythioetherpolyanhydride

f) Polycondensation of 3,3'-(p-dithiophenyl)-dipropionic acid

12.0 g. of purified 3,3'-(p-dithiophenyl)-dipropionic acid were dissolved in 300 ml. of acetic anhydride and refluxed for 4 hrs. The detailed procedure is shown in Table 7.

Polycond. time	Polycond. temp.		Barraha
(min.)	(°C.) (Torr)		nemarks
0	95	25	diacetate was heated to melt and dry N_2 gas was introduced
30	100	7	polycondensation starts
90-110	110-135	4	viscous solution obtained
170 - 230	140-145	3	polycondensation proceeds
290	145	3	amorphous polymer
320	145	3	polycondensation completed

Table 7. Polycondensation of 3,3'-(p-dithiophenyl)-dipropionic acid with acetic anhydride

The resulting polymer is low melting, 45-55 °C., and amorphous. Infrared spectrum as recorded in Fig. 16 contains anhydride carbonyl absorption bands at $\lambda_{max}^{\mathcal{C}=O} = 5.65 \,\mu$, 5.78 μ and $\lambda_{max}^{\mathcal{C}=\mathcal{S}} = 14.40 \,\mu$, $\lambda_{max}^{\mathcal{C}=O-\mathcal{C}} = 9.53 \,\mu$.

CH₃CO-O-[-CO(CH₂)₂S-
$$-S(CH_2)_2CO-O-]_{\overline{n}}$$
-COCH₃;
m.p. 45-55°C. $[\eta]_{m-cresol}^{25°C.} = 0.26.$

(C12H13O3S2)n (269.36)n Calcd.: C 53.73 H 4.48 S 23.88 Found: C 53.61 H 5.23 S 22.79





C. Discussions

Polycondensation mechanism of polythioetherpolyanhydrides

When aromatic and aliphatic α,ω -carboxythioethers are polycondensed by treating them with acetic anhydride at 200–240 °C. *in vacuo* under nitrogen, it is reasonably presumed that the polycondensation takes place in three steps as illustrated below:



Structure and properties of aromatic and aliphatic α,ω -dicarboxythioethers synthesized in the present study are summarized in Table 8. These new α,ω -dicarboxythioethers which are new except for No. 5 were successfully obtained in 95–98 % yields.

Structure and properties of polythioetherpolyanhydrides

Polymer properties of various polythioetherpolyanhydrides are summarized in Table 9. As shown in Table 9, the mobility of polymer molecule increases by introducing thioether linkage -C-S-C- in the polymer chain, a depression in melting point was observed when compared with the corresponding methylene linkage $-CH_2-$. The similar tendency has already been reported for polyetherpolyanhydrides with ether linkage -C-O-C- in the polymer chain⁶). The observation that the flexibility

No.	Structure of dicarboxylic acid	m.p. (°C.)	Yield (%)	Infrared characteristic bands (µ)
1	HOOC(CH ₂) ₂ S(CH ₂) ₂ S(CH ₂) ₂ COOH	156	83	5.89
				14.00
2	HOOC(CH ₂)S(CH ₂) ₂ S(CH ₂)COOH	103	62	5.82
				5.95
				14.22
3	HOOC(CH ₂) ₂ SCH ₂ - CH ₂ S(CH ₂) ₂ COOH	138~	95	5.89
•		140		14.30
4	HOOC(CH ₂)SCH ₂ - CH ₂ S(CH ₂)COOH	148~	98	5.89
		150.		14.55
5	HOOC(CH ₂) ₂ S(CH ₂) ₂ COOH	116	23	5.90
				14.00
6	HOOC(CH ₂) ₂ S-////////////////////////////////////	151	71	5.87
				14.00

Table 8. Infrared characteristic bands and melting points of thioether dicarboxylic acid

Table 9. Structures and properties of polythioetherpolyanhydrides

No.	Polymer structure	m.p. (°C.)	[η] <mark>m-cresol</mark> 25°C	d420	Properties
1	$-[-OCO(CH_2)_2S(CH_2)_2S(CH_2)_2CO-]_{\overline{n}}$	75	0.23	1.386	crystalline polymer
2	$-[-OCO(CH_2) S(CH_2)_2 S(CH_2) CO-]_{\overline{n}}$	83	0.21	-	crystalline polymer
3	$-[-OCO(CH_2)_2SCH_2-CH_2S(CH_2)_2CO-]_{\overline{n}}$	91	0.11	-	fiber-forming polymer
4	$-[-OCO(CH_2)SCH_2 - CH_2S(CH_2)CO -]_{\overline{n}}$	88	0.28	0.28	elastic polymer (fiber-forming and amorphous
5	$-[-OCO(CH_2)_2S(CH_2)_2CO-]_{\overline{n}}$	55	0.31	1.532	crystalline polymer
6	$-[-OCO(CH_2)_2SS(CH_2)_2CO-]_n$	45-55	0.26	1.473	amorphous polymer

zation of polythioetherpolyanhydrides estimated from X-ray intensity diagram of radial scattering was found to be 30 % for undrawn, non-heattreated elastic polymer. Shortly after spinning, however, elasticity is lost and it was confirmed by X-ray diffraction pattern that crystallinity of the polymer increases gradually.

The similar phenomena were observed for heterocyclic polyanhydrides of thiophene ring⁸⁾.

Density of polythioetherpolyanhydride was measured by floating method in carbon tetrachloride/toluene mixture at 25 °C. The results are summarized in Table 9. Specific weight of polythioetherpolyanhydride is in the range of 1.3–1.5, which is rather higher than usual for polycondensation polymers.

C	C–S frequen	cy (Wave length)	D.f
Compound	(cm ⁻¹)	(μ)	nei.
Thiol			
Methyl	705	14.19	
Ethyl	660	15.15	
n-Propyl	553	18.11	
Isopropyl ·	630	15.88	9, 10)
<i>n</i> -Butyl	658	15.20	
Isobutyl	672 or 708	14.90 or 14.12	
tertButyl	587	17.05	
	694	14.45: _s (C-S-C)	
Dimethyl sulfide	742*)	13.46: $a(C-S-C)$	
Methyl ethyl sulfide	652	15.33: s(C-S-C)	
Diethyl sulfide	640	15.62: s(C-S-C)	
CH ₃ -S	705-685	14.19-14.60	
R-CH ₂ -S	660-630	15.15-15.88	11)
RR'CH–S–	630-600	15.88-16.66	
RR'R''C-S	600-570	16.66-17.55	
	763	13.10	r
$CF_3 - S - CF_3 \dots$	761	13.12	12)
	762	13.11	·
$CF_3 - S - S - CF_3 \dots$	759	13.19	1
$CCl_mBr_n-S-CH_3$		15 10 10 40	12)
(m + n = 3)	663-807	15.10-13.40	15)
Ethyl thiolacetate	673	14.85	14)
Ethyl thioltrifluoroacetate	694	14.41	
Ethyl thiolacetaten. n-Butyl thiolacetate		about 9	15, 16)

Table 10. Infrared absorption bands of C-S stretching modes

*) RAMAN line

Infrared absorption spectra of thioether stretching vibrations

As can be seen in Table 10, although the assignments for the C-S stretching modes in dialkyl sulfides, dialkyl disulfides and thiols seem to coincide with one another, some discrepancies are found in alkyl thioethers.

The polythioether polyanhydrides obtained show infrared absorption bands corresponding to C-S stretching modes in Table 10. The polymer structure of these polymers has been established through infrared spectral evidence as well as elementary analysis and X-ray diagrams.

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