

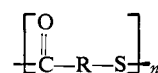
Anionic Ring-Opening Polymerization of Thiolactones¹C. G. Overberger^{2a} and Jurgen K. Weise^{2b}*Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201. Received July 27, 1967*

Abstract: Thiepan-2-one (ϵ -thiocaprolactone) was prepared by cyclization of 6-mercaptohexanoic acid and polymerized by a base-catalyzed ring-opening reaction to a linear poly(thiol ester). Poly- ϵ -thiocaprolactone is crystalline and has a high molecular weight (intrinsic viscosity, 0.5–1.0 dl/g in chloroform. Its crystalline melting point is 105°; it has a second-order transition at +19° and is soluble in several common solvents, especially in partially halogenated hydrocarbons. When oriented by drawing, it has a fiber period of 17.8 Å, which corresponds to the length of two extended thiol ester repeat units (14 atoms in the backbone). Thian-2-one (δ -thiovalerolactone) can also be converted to a crystalline polymer, but thiolan-2-one (γ -thiobutyrolactone) does not react under these conditions. The reactivity of the thiolactones toward polymerization catalysts is, therefore, dependent on ring size in a manner which is analogous to the behavior of lactones but which is different from that of lactams.

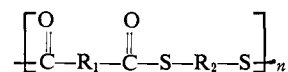
Thiolan-2-one (γ -thiobutyrolactone, I)³ and thian-2-one (δ -thiovalerolactone, II)⁴ have been known for several years; a number of the more stable alkyl-substituted compounds of both types had already been studied in 1912.⁵ These γ - and δ -thiolactones can be conveniently prepared by distillation of the corresponding mercapto acids^{3,4,6} or by reaction of the corresponding lactone with hydrogen sulfide in the presence of a sodium sulfide catalyst.⁷ In some cases the spontaneous cyclization of an unsubstituted thiol acid⁸ or the reaction of a lactone with phosphorus pentasulfide⁵ can be used. None of these methods, however, appears to have been successfully employed with thiol esters having rings of four, or more than six, atoms. The preparation of thietan-2-one (β -thiopropiolactone) from β -bromopropionyl chloride and dry sodium sulfide has been reported in a patent,⁹ and several alkyl- and halogen-substituted β -thiolactones have been prepared in a similar manner¹⁰ or by treating the mercapto acid with ethyl chloroformate.¹¹

Polymerizations of thiolactones have been reported only for four-membered rings (β -thiolactones). Knunyants, Linkova, and coworkers polymerized 4,4-dimethylthietan-2-one (β -methyl- β -thiobutyrolactone) by heating it with a trace of water. They also observed that some α -substituted and α,α -disubstituted β -thiolactones polymerized at room temperature in the presence of catalytic amounts of bases.¹⁰ Schöberl¹² obtained

polythioglycolides of high molecular weight from cyclic dithioglycolide. Other polymers of the type



(A–B type) were prepared by Korte and Christoph,⁸ who obtained products of low molecular weight by spontaneous reaction of certain ω -unsaturated thiol acids. On the other hand, linear poly(thiol esters) of the type



where R₁ and R₂ are various alkylene and arylene groups (A–A,B–B type) are well known.^{13,14} They are stable fiber-forming polymers of high molecular weight.

The preparation of thiepan-2-one (ϵ -thiocaprolactone, IV) and its polymerization by an anionic ring-opening reaction were reported in a preliminary communication from this laboratory.¹⁵ The present paper comprises a detailed description of these results as well as an extended study of the polymerization reaction. The polymerizability of a series of unsubstituted thiolactones is discussed as a function of ring size. The polymerization reaction was also employed for the preparation of certain asymmetric, structurally homogeneous poly(thiol esters), as will be reported in a separate paper.

Results and Discussion

Synthesis. γ -Mercaptobutyric acid was prepared according to the procedure of Schotte¹⁶ and was distilled at atmospheric pressure to yield thiolan-2-one (I). Thian-2-one (II) was prepared according to the method of Korte and Büchel⁶ from 5-mercaptovaleric acid. The latter was obtained by hydrolysis of 5-bromovaleronitrile followed by reaction with thiourea.

Cyclization of 6-mercaptohexanoic acid (III) to give thiepan-2-one (IV) was effected by slow distillation of

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(2) (a) Author to whom inquiries should be sent at The University of Michigan, Ann Arbor, Mich. 48104. (b) This paper comprises a portion of a dissertation submitted by J. K. Weise in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry) to the Graduate School of the Polytechnic Institute of Brooklyn, 1966.

(3) B. Holmberg and E. Schjanberg, *Arkiv. Kemi, Mineral. Geol.*, **14A**, 22 (1940).

(4) E. Schjanberg, *Ber.*, **74**, 1755 (1941).

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(7) K. Heinz (Badische Anilin- und Soda-Fabrik), German Patent 859,456 (1952); *Chem. Abstr.*, **47**, 11233 (1953).

(8) F. Korte and H. Christoph, *Ber.*, **94**, 1966 (1961).

(9) B. F. Goodrich Company, British Patent 840,658 (1960); *Chem. Abstr.*, **55**, 1452 (1961).

(10) I. L. Knunyants, M. G. Linkova, and N. D. Kuleshova, *Izv. Acad. Nauk SSSR, Ser. Khim.*, 644 (1964); *Chem. Abstr.*, **61**, 2966 (1964).

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(12) A. Schöberl, *Makromol. Chem.*, **37**, 64 (1960).

(13) P. J. Flory, British Patent 630,625 (1949); *Chem. Abstr.*, **44**, 3741 (1950); U.S. Patent 2,510,567 (1950); *Chem. Abstr.*, **46**, 1301 (1952); W. A. Murphy, U. S. Patent 2,870,126 (1959); *Chem. Abstr.*, **53**, 6642 (1959); J. W. Stimpson, British Patent 853,730 (1960); *Chem. Abstr.*, **55**, 20505 (1961).

(14) C. S. Marvel and A. Kotch, *J. Amer. Chem. Soc.*, **73**, 1100 (1951); C. S. Marvel and E. A. Kraiman, *J. Org. Chem.*, **18**, 707, 1664 (1953).

(15) C. G. Overberger and J. Weise, *J. Polymer Sci.*, **B**, **2**, 239 (1964).

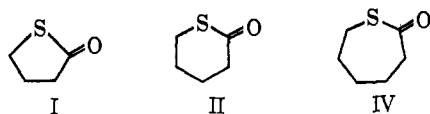
(16) L. Schotte, *Arkiv Kemi*, **8**, 460 (1955).

Table I. Polymerization of Thiolactones

Monomer (thiolactone)	Initiator, mole %	Temp, °C	Time, hr	Method ^a	$[\eta]^{25}_{\text{CHCl}_3}$, dl/g	Conversion, ^b %
I	<i>t</i> -BuOK, 0.3	155	17	A	No polymer	
II	<i>t</i> -BuOK, 0.23	155	17	A	0.147	21
IV	No initiator	155	15	A	No polymer	
	<i>t</i> -BuOK, 2.9	155	17	A	0.731	78
	<i>t</i> -BuOK, 0.4	179	17	A	0.680	90
	<i>t</i> -BuOK, 0.47	110-150	7	B	0.900	100 ^c
	<i>n</i> -BuLi, 1.5	Ca. 25	20	C	0.612	58
	<i>n</i> -BuLi, 1.0	25	40	D	0.558	86
	<i>n</i> -BuLi, 2.3	25	40	D	0.353	78
	<i>n</i> -BuLi, 3.0	110	14	A	0.386	73
	Na dispersion, 1.6	155	15	A	0.720	77
	Al(Et) ₃ in THF soln, 0.68	56	39	A	Cross-linked	
	K ₂ CO ₃ , 0.72	179	17	A	0.354	82
	H ₂ O, 1.5 + AlCl ₃ , 1.2	179	17	A	Cross-linked ^d	
	CH ₃ I, 1.7	155	15	A	0.181	77 ^d
	<i>t</i> -BuOK, 1.6 + CH ₃ I, 2.5	110	14	A	0.102	18 ^d

^a The capital letters used here for denoting the method of polymerization correspond to the paragraph headings in the Experimental Section, where these methods are described in detail: A, in a sealed tube placed in a vapor bath; B, with nitrogen capillary in a side-arm polymerization tube connected to a vacuum system; C, by shaking in a flask at room temperature; D, in tetrahydrofuran solution. ^b Determined as polymer yield after reprecipitation and drying. In some cases the mechanical losses during work-up were considerable. ^c The polymer was not reprecipitated and had the same physical (and optical) properties as polymer which had been freed from monomer by precipitation. Due to the high vacuum and the elevated temperatures and purging during polymerization, a small amount of monomer was carried off with the nitrogen stream. ^d The polymer is colored.

the acid from phosphorus pentoxide. A temperature of 190-220° was found to give the highest yield (48%), and the pressure was adjusted accordingly. This method appears to be preferable to the use of other dehydrating catalysts or other techniques. Compound



III was prepared by treating 6-bromohexanoic acid with either potassium hydrosulfide or thiourea, the bromo acid being obtained either by hydrolysis of ϵ -caprolactam followed by diazotization or from hydrolysis of 6-bromohexanonitrile. Methyl 6-mercaptohexanoate (V) was prepared from methyl 6-bromohexanoate and anhydrous potassium hydrosulfide in methanol. It could not be cyclized to IV in a satisfactory yield.

Elemental analysis and a molecular weight determination of IV are consistent with the structure of thiepan-2-one. The infrared band at 1665 cm^{-1} is in agreement with the carbonyl absorption bands of cyclic⁶ and linear¹⁷ thiol esters.¹⁸ The ultraviolet spectra with $\lambda_{\text{max}} 234 \pm 3 \mu\text{m}$ and extinction coefficients of ca. 4000 are also typical of thiol esters.¹⁹ The chemical shift of the methylene protons resulting from the cyclic structure IV is larger by 0.2 ppm²⁰ than that of the corresponding open-chain compounds III and VI.

Polymerization. In the absence of water and oxygen, IV was found to react readily with strong bases to yield

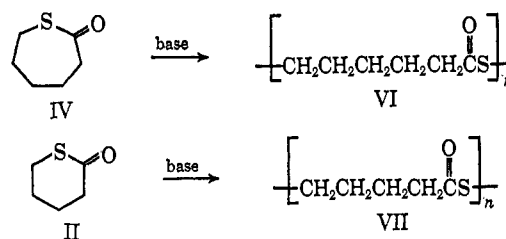
(17) R. A. Nyquist and W. J. Potts, *Spectrochim. Acta*, **15**, 514 (1959).

(18) The frequency of this band will be discussed in greater detail in connection with the optical rotatory dispersion spectra of asymmetric thiepan-2-ones.

(19) B. Sjöberg, *Z. Physik. Chem.*, **52**, 209 (1942).

(20) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 223.

the crystalline high polymer VI. No thermal polymerization takes place at the temperatures employed.²¹ Thus, in contrast to results recently obtained with small-ring lactones and other heterocyclic monomers,²² IV does not polymerize in the absence of ionic initiators. Thian-2-one (II) gives a linear polymer VII which is similar to VI, but which has a lower intrinsic viscosity and which was obtained in lower yield. Under the same conditions thiolan-2-one (I) does not polymerize. Table I summarizes the polymerization results.



Monomer IV was polymerized by four different methods. With catalytic amounts of potassium *t*-butoxide the reaction proceeded equally well in a tube sealed under vacuum and in a side-arm tube agitated by a stream of nitrogen. In the latter case the pressure was gradually lowered to 0.1 mm as the mixture became more viscous. In either case, a temperature of about 150° is best. However, with *n*-butyllithium the reaction proceeds rapidly at room temperature. Within the first minute after addition of the catalyst, solid white polymer precipitates.

(21) Polymeric residues were regularly obtained when the monomer IV or the mercapto acid III was distilled, and a pure sample of polymer VI, $[\eta] = 0.248 \text{ dl/g}$ (25°, chloroform), was obtained from such a residue. This "thermal polymerization," however, is due to autocatalytic polycondensation or ring opening catalyzed by ionic impurities (water, acid, etc.).

(22) H. Ohse, H. Cherdron, and F. Korte, *Makromol. Chem.*, **86**, 312 (1965).

Several other catalysts were employed. Potassium carbonate, sodium dispersion, and sodium hydride produced results similar to those of potassium *t*-butoxide. Methyl iodide, either alone or together with potassium *t*-butoxide, produced colored polymers of low molecular weight. Catalysis by triethylaluminum (in tetrahydrofuran solution) at 56° produced a cross-linked solid plug which swelled but did not dissolve. Aluminum trichloride and water at 179° produced a brown polyester, the major portion of which was soluble in chloroform and appeared to be of low molecular weight.

Strong bases are clearly the best polymerization catalysts. Catalysts which are normally cationic (aluminum trichloride–water, methyl iodide) produced colored polymers of low molecular weight. Both catalysts containing aluminum produced cross-linking, but only the anionic one (triethylaluminum) gives a tough polymer in high conversion. These results are consistent with an ionic ring-opening polymerization initiated by nucleophilic attack at the carbonyl carbon atom and propagated by the sulfur anion. Termination may occur by reaction with water or other ionic impurities. Qualitatively, it was observed that the molecular weight was lower when the monomer was not freshly distilled before polymerization and was therefore, presumably, not dry.²³ This mechanism also agrees with the results of Cherdron, Ohse, and Korte²⁴ on the polymerization of oxepan-2-one and oxan-2-one with anionic catalysts and with the mechanism proposed by the same authors for the ring-opening reaction of these lactones. Moreover, nucleophilic attack at the carbonyl carbon atom is in accordance with the general mechanism for bimolecular, nucleophilic ester hydrolysis with acyl cleavage,²⁵ with the kinetic data on base-catalyzed hydrolysis of unsubstituted lactones with four- to sixteen-membered rings,²⁶ and with similar studies on II and IV.²⁷

The monomer–polymer equilibrium appears to limit the average molecular weight of the samples obtained at elevated temperatures. In the case of the six-membered ring the monomer concentration in the equilibrium mixture is much higher than with the seven-membered ring. This is reflected in the lower molecular weight and yield of VII as compared with VI.

In comparing the polymerizabilities of thiolactones with the known polymerizabilities of the corresponding lactones and lactams, it is evident that in all three series the compounds with four^{28–30} and seven-membered³¹

rings do polymerize. In both the lactone and the thiolactone series, the six-membered³¹ rings can be polymerized, but the five-membered³¹ rings cannot. In the lactam series, however, the six-membered ring is the least reactive toward common polymerization catalysts. In this respect thiolactones resemble lactones and not lactams.

Polymer Characterization. The melting point of poly- ϵ -thiocaprolactone is 108–109°, as determined with a polarizing microscope.³² It does not vary appreciably with the method of synthesis or the molecular weight of the polymer, provided that its intrinsic viscosity is at least 0.25 dl/g. Thus, the melting point of polythiol ester VI is intermediate between those of the corresponding polyester and polyamide. While it is 48° higher than that of poly- ϵ -caprolactone (60°),³³ it is much lower than that of the hydrogen-bonded nylon 6 (215°).³⁴ A differential thermal analysis of VI indicates a second-order transition at +19°. Decomposition begins at 325° and reaches a maximum at 386°.

Poly- ϵ -thiocaprolactone (VI) is soluble in cold, partially halogenated hydrocarbons such as chloroform, methylene bromide, or 1,1,2-trichloroethane, but is insoluble in acetone, ethyl acetate, and other solvents which dissolve poly- ϵ -caprolactone.³⁵ However, VI is much more soluble than nylon 6. Dioxane, 1,2,3,4-tetrahydronaphthalene, tetrahydrofuran, and benzene dissolve VI only on warming.

The infrared spectrum of VI was recorded in a variable-temperature cell. The polymer film was first scanned at room temperature, then melted and again scanned. The bands of the crystalline polymer are not only sharper but many of them are shifted to higher or lower frequencies. In addition, there are several bands which do not appear to correspond to absorptions of the amorphous (molten) sample: $\bar{\nu}_{\max}$ 1355, 1253, 953, 778, and 722 cm⁻¹. These absorptions are presumed to be due to crystalline order.

Further evidence of the crystallinity of VI comes from X-ray photographs. A diagram of an unoriented sample shows diffractions corresponding to $d = 5.61$ (weak), 4.56 (strong), 3.74 (strong), 2.35 (weak), 2.21 (weak), 2.06 (weak), and 1.90 Å (weak). A sample with an intrinsic viscosity of 0.976 dl/g was obtained by fractionation with chloroform–methanol (5:4) and was oriented by drawing at *ca.* 80°. A standard rotation photograph of this uniaxially oriented sample was taken with the X-ray beam perpendicular to the fiber axis. Tilt photographs ($\alpha = 10, 20^\circ$) were also taken and, in addition, oscillation photographs ($\alpha = 0, \pm 15^\circ$) in which the axis of oscillation was perpendicular to the fiber axis. The first layer line of the polymer shows that the fiber period is about 18 Å; this is confirmed by the

(23) In some cases redistillation of the monomer before polymerization was carried out in the presence of lower boiling phenyl isocyanate or higher boiling isocyanates such as triphenylmethane triisocyanate (Möbay Chemical Co.). This treatment appeared to offer no advantage over vacuum distillation and was therefore abandoned in subsequent polymerizations.

(24) H. Cherdron, H. Ohse, and F. Korte, *Makromol. Chem.*, **56**, 183, 187 (1962).

(25) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 314.

(26) R. Hulsgen and H. Ott, *Tetrahedron*, **6**, 253 (1959).

(27) C. G. Overberger and R. Brand, unpublished results.

(28) H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **80**, 6404 (1958).

(29) Preparation of the four-membered thiolactone is reported in B. F. Goodrich Company, British Patent 840,658 (1960); *Chem. Abstr.*, **55**, 1452 (1961). A polymeric solid was formed during its preparation from β -bromopropionyl chloride with sodium sulfide, but polymerization of the purified thiolactone was not studied. However, several halogen- and alkyl-substituted thietan-2-ones are reported to polymerize readily: M. G. Linkova, O. V. Kildisheva, and I. L. Knunyants, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 507 (1955); *Chem. Abstr.*, **50**, 6312 (1956); I. L. Knunyants, E. Y. Perova, M. G. Linkova, and O. V. Kildisheva, *Khim. Nauka i Promy.*, **3**, 278 (1958); *Chem.*

Abstr., **52**, 19929 (1958); I. L. Knunyants, M. G. Linkova, and N. D. Kuleshova, *Izv. Acad. Nauk SSSR, Ser. Khim.*, 644 (1964); *Chem. Abstr.*, **61**, 2966 (1964).

(30) H. Ohse, H. Cherdron, and F. Korte, *Makromol. Chem.*, **86**, 312 (1965); H. Zaugg, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p 326.

(31) H. K. Hall, Jr., and A. K. Schneider, *J. Amer. Chem.*, **80**, 6409 (1958).

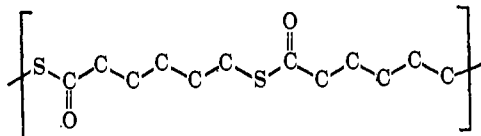
(32) This melting point was measured with oriented specimens. The previously reported value of 104.5–106° was obtained with undrawn samples. Differential thermal analysis gave a melting point of 105° for the undrawn polymer.

(33) Union Carbide Corporation, private communication.

(34) W. E. Hanford and R. M. Joyce, *J. Polymer Sci.*, **3**, 167 (1948).

(35) F. J. Van Natta, J. W. Hill, and W. H. Carothers, *J. Amer. Chem. Soc.*, **56**, 455 (1934).

second layer line, which has a repeat length of about 9 Å. For the 14th meridional reflection a spacing of 1.265 Å was measured. Another meridional reflection, possibly the 12th, corresponding to a spacing of 1.495 Å, was observed. Hence the fiber period of this polymer is 17.8 Å. The theoretical values calculated for two thiol ester repeat units in a fully extended polymer chain is 18.3 Å, which is in good agreement with the observed fiber period. We therefore conclude that there are two monomeric repeat units (14 atoms in the backbone) per fiber period and that the polymer has an essentially



planar structure with extended chains, possibly with slight rotations around one or several of the bonds in each repeat unit. In a planar, extended chain consecutive carbonyl groups will point in opposite directions. Since the measured fiber period and the calculated value are nearly equal, distortion from the planar structure must be small, and a coiled or helical structure in the solid state can be ruled out.

The above results resemble those obtained for the analogous polyamide, nylon 6. This polymer occurs in two crystalline modifications: in the α form with fully extended antiparallel chains the fiber period is 17.24 Å;³⁶ in the γ form, in which all the chains of the same sheet are parallel,³⁷ the unit cell length is 16.70 Å.³⁸ The contraction of 0.54 Å in the γ form is caused by tilting of the amide plane with respect to the fiber axis and is necessary in order to accommodate perfect hydrogen bonding between parallel chains. The contraction observed in VI is of comparable magnitude (0.5 Å). This analogy suggests that the structure of poly(thiol ester) VI resembles the γ form of nylon 6 which has parallel chains in its hydrogen-bonded sheets. However, since the data obtained so far are limited, such correlations are speculative; the nature of the secondary bonding in thiol esters is different from that in amides and cannot be as readily assessed.

Experimental Section²⁹

6-Bromohexanoic Acid. A. **From Caprolactam.** The procedure of West⁴⁰ was used, except that the solution of ϵ -caprolactam,

(36) D. R. Holmes, C. W. Bunn, and D. J. Smith, *J. Polymer Sci.*, **17**, 159 (1955).

(37) Y. Kinoshita, *Makromol. Chem.*, **33**, 1 (1959).

(38) E. M. Bradbury, L. Brown, A. Elliott, and D. A. D. Parry, *Polymer*, **6**, 465 (1965).

(39) Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are corrected. Polymer melting points were observed with a hot-stage polarizing microscope and are also corrected. Unless otherwise indicated, they were obtained for nonoriented samples. Viscosities were measured in Ubbelohde viscometers each equipped with a sintered-glass filter at the bottom of the mixing bulb. Reagent grade chloroform was used at $25 \pm 0.1^\circ$, and flow times were at least 85 sec. Elemental analyses were performed by Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany. Ultraviolet spectra were determined with a Cary 14 spectrophotometer; infrared spectra were recorded on Perkin-Elmer spectrophotometers, Models 21 or 521; the wave numbers reported are the $\bar{\nu}_{\max}$ of strong and medium bands, or important shoulders. Nmr spectra of dissolved samples were taken in deuteriochloroform with tetramethylsilane as the internal standard with a Varian HR-60 spectrometer. A Perkin-Elmer vapor fractometer, Model 154-D, was used for analytical vpc and a Wilkens Aerograph Model A-700 for preparative work. The reported retention times are for samples of 1 μ l at pressures of 15 psi on the Perkin-Elmer instrument, with helium as carrier gas.

(40) H. West, *Faserforsch. Textiltech.*, **5**, 150 (1954).

452 g (4.0 mol), in 500 ml of water and 900 ml of hydrobromic acid (48%, 8.0 mol) was stirred overnight before diazotization, yield 78 g (10%), mp 33–34° (lit.⁴¹ mp 35°); $\bar{\nu}_{\max}$ 3050 (broad, acid dimer), 2950, 2880 (C–H), and 1712 cm^{-1} (acid C=O), consistent with the structure of 6-bromohexanoic acid.

Anal. Calcd for $\text{C}_6\text{H}_{11}\text{BrO}_2$: C, 36.94; H, 5.69. Found: C, 36.69; H, 5.52.

B. From 6-Bromohexanonitrile. Hydrobromic acid (48%), 200 ml, was stirred overnight with 100 g (0.57 mol) of 6-bromohexanonitrile (Aldrich). The mixture was then refluxed for 3 hr. After cooling, it was filtered to remove ammonium chloride, and the filtrate was extracted with three portions of ether. The acid was extracted from the ether solution with sodium carbonate solution. The combined aqueous extracts were acidified with HCl (congo red) and again extracted with ether. After drying, the solvent was distilled at room temperature, and the product was recrystallized from dry hexane to give 91 g (83%), mp 33–34°.

6-Mercaptohexanoic Acid (III). The procedure of Ivanovics and Vargha⁴² using crystalline potassium hydrosulfide was modified as follows. Hydrogen sulfide, 36 g (1.05 mol), was dissolved in a cooled solution of 62.4 g (1.1 mol) of potassium hydroxide and 750 ml of water. 6-Bromohexanoic acid, 91 g (0.47 mol), was added and the mixture was refluxed for 2 hr. After cooling, the solution was acidified with sulfuric acid and extracted with ether. The solution was dried over sodium sulfate, the ether was evaporated, and the product distilled to give 47.4 g (69%); vpc on silicone oil (Dow Corning 200) at 190° showed that the compound was homogeneous, retention time 8 min, bp 88–89° (0.09 mm) (lit.⁴³ bp 112–116° (0.8 mm)), n_D^{20} 1.4837 (lit.⁴⁴ n_D^{20} 1.4804), mp 13°; $\bar{\nu}_{\max}$ 3050 (broad, acid dimer), 2940, 2870 (C–H), 2560 (S–H), and 1710 cm^{-1} (acid C=O).

Anal. Calcd for $\text{C}_6\text{H}_{12}\text{O}_2\text{S}$: C, 48.62; H, 8.16. Found: C, 48.81; H, 8.10.

Using thiourea, the compound was prepared from 6-bromohexanoic acid in 71% yield, bp 98–100° (0.2 mm), n_D^{20} 1.4811.

Methyl 6-Mercaptohexanoate (V). Potassium, 30 g (0.77 g-atom), was cut in small pieces and added to 400 ml of cooled, agitated methanol under a nitrogen atmosphere. When the metal had completely reacted, hydrogen sulfide, 26 g (0.77 mol), was added through a gas inlet tube, and potassium hydrosulfide precipitated. To this slurry was added 82.0 g (0.39 mol) of methyl 6-bromohexanoate (bp 74–76° (0.8 mm), n_D^{20} 1.4626 (lit.⁴⁵ bp 72° (1.0 mm), n_D^{20} 1.4635)), which had been prepared from 6-bromohexanoic acid. The mixture was refluxed overnight, then concentrated *in vacuo* to 200 ml, diluted with 800 ml of water, and extracted with chloroform. The solution was dried over magnesium sulfate and the solvent evaporated. Fractionation gave 40.8 g (64%); vpc on Carbowax 1540 as the liquid phase showed that the compound was homogeneous, retention time 6 min at 164°, bp 69° (1.0 mm), n_D^{20} 1.4629; $\bar{\nu}_{\max}$ 2940, 2870, 2560 (weak, S–H), 1743, 1437, 1363, 1258, 1200, 1170, and 1050 cm^{-1} ; τ 6.36 (3 H, singlet), 7.41–7.79 (4 H, multiplet), 8.12–8.57 (6 H, multiplet), and 8.77 (1 H, triplet).

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{O}_2\text{S}$: C, 51.82; H, 8.70; S, 19.76. Found: C, 51.81; H, 8.49; S, 19.72.

Thiepan-2-one (IV). 6-Mercaptohexanoic acid, 4.0 g (27 mmol), was placed in a thick-walled, 50-ml erlenmeyer flask modified with a ground-glass joint. Phosphorus pentoxide, 0.8 g, was added, and the flask was quickly fitted with a small distillation head and a receiver and immersed in an oil bath at 190°. The reaction mixture was vigorously agitated with a magnetic stirrer and the pressure was lowered to about 60 mm, allowing crude thiolactone to distill slowly. The rate of distillation was kept steady by gradually lowering the pressure to 0.1 mm and raising the temperature of the oil bath to 220°. Distillation ceased after about 30 min, and the orange contents of the receiver were taken up in ether and washed first with aqueous sodium carbonate and then with water until the latter remained neutral. The ether extracts of several experiments were combined, dried over magnesium sulfate, and fractionally

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distilled (Podbielniak column) to give a colorless liquid in 48% yield. It was analyzed by vpc and was found to be homogeneous on silicone oil (Dow Corning 710, retention time 2.2 min at 200°) and polypropylene glycol (24 min at 182°), bp 74–75° (1.0 mm), n_D^{25} 1.5257; $\lambda_{\text{max}}^{\text{cyclohexane}}$ 232 m μ (ϵ 4160); $\lambda_{\text{max}}^{\text{dioxane}}$ 235 m μ (ϵ 3830); $\lambda_{\text{max}}^{\text{MeOH}}$ 237 m μ (ϵ 3850); sharp infrared bands at $\bar{\nu}_{\text{max}}$ 2940, 2860, 1665 (thiol ester C=O), 1447, 1218, 1126, 1104, 1082, 1048, 928, 885, 845, 817, and 788 cm $^{-1}$; τ 7.10 (2 H, triplet), 7.16 (2 H, triplet), and 7.82–8.51 (6 H, multiplet).

Anal. Calcd for C₆H₁₀OS: C, 55.34; H, 7.74; S, 24.63; mol wt, 130.2. Found: C, 55.31; H, 7.74; S, 24.36; mol wt, 130.

Thiolan-2-one (I). 4-Mercaptobutyric acid, bp 98–100° (2.4 mm), n_D^{25} 1.5030 (lit.⁸ bp 102–103° (2.5 mm), n_D^{20} 1.4912), was prepared according to Schotte¹⁶ and cyclized by the procedure of Holmberg and Schjanberg⁸ in 82% yield. Analysis by vpc showed that the product was homogeneous on the following liquid phases: diethylene glycol succinate polyester (retention time 7.2 min at 195°), di-2-ethylhexyl sebacate (20 min at 170°), and silicone oil (Dow Corning 200, 6.5 min at 128°); bp 78–79° (11 mm), n_D^{25} 1.5231 (lit.³ bp 55–56° (3 mm), n_D^{20} 1.5242); $\bar{\nu}_{\text{max}}$ 1705 cm $^{-1}$ (C=O), (lit.⁶ $\bar{\nu}_{\text{max}}$ 1705 cm $^{-1}$).

Anal. Calcd for C₄H₆OS: C, 47.03; H, 5.92; S, 31.29. Found: C, 47.23; H, 5.91; S, 31.36.

5-Mercaptovaleric Acid. 5-Bromovaleronitrile (Aldrich), 200 g, was hydrolyzed with 310 ml of HBr (48%) and separated from the starting material as described above for 6-bromohexanoic acid. After recrystallization from dry hexane, 169 g (75%) of 5-bromovaleric acid was obtained, mp 38–39° (lit.⁴⁶ prepared from 5-phenoxy-pentanoic acid with hydrobromic acid, mp 38–39°). This acid, 126 g (0.685 mol), was treated according to a general method⁴⁷ with 53 g (0.70 mol) of thiourea to yield 59.5 g (64%) of 5-mercaptovaleric acid, bp 96° (0.3 mm), n_D^{25} 1.4873 (lit.⁴ bp 110–112° (0.8 mm), n_D^{21} 1.4882).

Thian-2-one (II). The procedure of Korte and Büchel⁶ was used. After two consecutive vacuum distillations the product was obtained in 70% yield; vpc on Carbowax 1540 showed that it was homogeneous, retention time 7.5 min at 164°, bp 82° (4 mm), n_D^{25} 1.5305 (lit.⁴ bp 79–80° (2.5 mm), n_D^{20} 1.5314); $\bar{\nu}_{\text{max}}$ 1663 cm $^{-1}$ (C=O) (lit.⁶ $\bar{\nu}_{\text{max}}$ 1664 cm $^{-1}$).

Anal. Calcd for C₅H₈OS: C, 51.69; H, 6.94; S, 27.60. Found: C, 51.76; H, 6.93; S, 27.49.

Poly- ϵ -thiocaprolactone (VI). A. In a Sealed Tube. A 10-ml polymerization tube was flamed under vacuum and filled with dry, oxygen-free nitrogen. The tube was evacuated and filled with nitrogen twice more before it was opened briefly in a drybox to add 30.3 mg (2.9 mol % of monomer) of potassium *t*-butoxide. By means of a syringe, redistilled thiepan-2-one (ϵ -thiocaprolactone, IV), 1.2 g (9.2 mmol), was injected through the rubber tubing connecting the tube with the vacuum system. The contents of the tube were frozen and degassed three times by thawing and refreezing under vacuum (with the stopcock connecting the tube with the vacuum pump closed), followed by evacuation (with opened stopcock). The tube was then sealed under vacuum and placed in a vapor bath of cyclohexanone (155°) for 17 hr. Upon cooling, the polymer formed a solid white plug, which was dissolved in 10 ml of chloroform. The solution was added dropwise to 1 l. of agitated methanol, and the polymer precipitated in the form of white flakes, which were filtered and dried under vacuum overnight, yield 78%, mp 104.5–106°, $[\eta]$ 0.763 dl/g; $\lambda_{\text{max}}^{\text{dioxane}}$ 234 m μ (ϵ 4470 at ~50°);

infrared bands of the crystalline polymer (as film) at $\bar{\nu}_{\text{max}}$ 2940, 2870, 1685, 1470, 1410, 1355, 1253, 1108, 1084, 1020, 953, 778, and 722 cm $^{-1}$; bands of the amorphous (molten) polymer at $\bar{\nu}_{\text{max}}$ 2940, 2870, 1697, 1456, 1410, 1084, and 990 cm $^{-1}$; τ 7.11 (2 H, triplet), 7.43 (2 H, triplet), and 8.06–8.68 (6 H, multiplet).

Anal. Calcd for (C₆H₁₀OS)_n: C, 55.34; H, 7.74; S, 24.63. Found: C, 55.52; H, 7.77; S, 24.82.

A polymer of the same structure (degree of polymerization, 6) was obtained by spontaneous exothermic reaction of 5-hexenethioic acid,¹ mp 80–83°; $\bar{\nu}_{\text{max}}$ 1685 cm $^{-1}$ (C=O).

B. Under Controlled Vacuum and with Agitation by Nitrogen Bubbles. A 10-ml polymerization tube with side arm was flamed under vacuum and flushed with nitrogen. Redistilled IV, 1.4 g (10.7 mmol), and a sealed melting-point capillary containing 5.6 mg (0.47 mol %) of potassium *t*-butoxide were placed in the tube. A thick-walled capillary reaching to the bottom of the tube was inserted carefully, and the space between the capillary and the neck of the polymerization tube was sealed by slipping a piece of rubber tubing over the outer part of the capillary and the neck of the tube. The side arm was connected to the pump, and the system was purged with purified nitrogen for 3 hr. The melting-point capillary containing the catalyst was crushed with the nitrogen inlet and the polymerization tube was immersed in an oil bath at 110°. During 7 hr, the temperature was raised to 150° and the pressure was lowered to 0.5 mm. After cooling, the polymer was obtained as a solid plug and the tube was broken, mp 105–107°, $[\eta]$ 0.900 dl/g. The polymer collected from the upper part of the tube, where there had been less agitation, had $[\eta]$ 0.626 dl/g.

C. At Room Temperature. A 10-ml, long-necked flask was flamed under a stream of dry, oxygen-free nitrogen and closed with a self-sealing rubber cap. Two syringe needles were inserted through the cap; the thicker one reached to the bottom of the flask and was connected to the nitrogen supply. Thiepan-2-one, 1.1 g (8.5 mmol), was injected and purged with nitrogen for 3 hr. *n*-Butyllithium (1.5 mol %) in hexane was added, the syringe needles were removed, and the flask was shaken for 20 hr at room temperature. The polymer was isolated as in part A and obtained in 58% yield, mp 104–106°, $[\eta]$ 0.612 dl/g.

D. In Solution. The solution of 0.94 g (0.72 mmol) of freshly distilled IV (28.5% by weight in anhydrous tetrahydrofuran) was degassed by repeated freezing (liquid N₂) and thawing under vacuum. It was then transferred with a syringe to a 5-ml polymerization tube which had been flamed under vacuum, filled with oxygen-free nitrogen, and covered with a self-sealing rubber cap. *n*-Butyllithium, 7.4 × 10⁻⁵ mol (1 mol %), in hexane was added. The concentration of the catalyst solution had been determined by an independent titration. Some white polymer precipitated within the first few minutes, but the tube was kept at 25 ± 0.2° for 40 hr. The polymer was isolated as in part A, conversion 86%, mp 102–104°, $[\eta]$ 0.558 dl/g.

Anal. Calcd for (C₆H₁₀OS)_n: C, 55.34; H, 7.74; S, 24.63. Found: C, 55.58; H, 7.80; S, 25.02.

Poly- δ -thiovalerolactone (VII). Monomer II, 1.04 g (9 mmol), was polymerized with 0.23 mol % of potassium *t*-butoxide as in the preparation of VI, part A. White granular polymer was obtained in 21% yield, mp 117–118°, $[\eta]$ 0.147 dl/g; $\lambda_{\text{max}}^{\text{dioxane}}$ 233 m μ (ϵ 4470 at ~50°); $\bar{\nu}_{\text{max}}^{\text{KBr}}$ 2935, 2860, 1684, 1455, 1404, 1262, 1062, 1027, 962, and 770 cm $^{-1}$ (lit.⁸ obtained by spontaneous, exothermic reaction of 4-pentenethioic acid, degree of polymerization 9, mp 115–117°); $\lambda_{\text{max}}^{\text{MeOH}}$ 235 m μ ($\log \epsilon$ 3.46); $\bar{\nu}_{\text{max}}$ 1685 cm $^{-1}$ (C=O).

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