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Poly(thioester)s

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REVIEW ARTICLE

Poly(thioester)s

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Syntheses and properties of aliphatic and aromatic polythioesters (PTEs) were reviewed including polythiocarbonates and polythiourethanes. The content is subdivided into the following sections: PTEs of aliphatic α-mercapto carboxylic acid, PTEs of ω-mercapto carboxylic acids, PTEs derived from α,ω-dimercapto alkanes, aromatic poly(thioester)s, aliphatic poly(thiocarbonate)s, aliphatic poly(thiourethane)s and aromatic polythiocarbonates. The synthetic strategies reviewed in this article include anionic and cationic ring-opening polymerizations, polycondensations in bulk, polycondensations in solutions, interfacial polycondensations and in vitro enzymatic polycondensations.

Keywords: polyesters; polycarbonates; polyurethanes; polycondensation; ring-opening polymerization

1 Introduction

Over the past fifty years, polyesters have found immense interest by both academic researchers and chemical companies and numerous polyesters were commercialized. Most widely produced are semi-aromatic polyesters such as poly(ethylene terephthalate) and poly(butylenes terephthalate), the production volume of which reaches more than one million tons per year worldwide. In contrast, fully aromatic polyesters, such as Vectra® or Sumicosuper®, which are processed from a nematic melt, are niche products. However, these polyesters possess a unique combination of thermal and mechanical properties, which is particularly useful for the electronic industry. Another much more important class of fully aromatic polyesters with a much broader application are polycarbonates, which are mainly based on bisphenol-A as monomer. More recently, aliphatic polyesters have attracted great interest under the aspect of biodegradable materials. These aliphatic polyesters may be subdivided into two groups, namely those derived from ω-hydroxy carboxylic acids (e.g. lactic acid or ε-hydroxycaproic acid) and polyesters based on diols and dicarboxylic acids. Representatives of both groups were technically produced and commercialized during the past decade.

In contrast to these normal polyesters, polyesters containing at least one sulfur atom in the ester group (summarized under the term "polythioesters") have attracted little interest. To the best of our knowledge, not even one polythioester has been technically produced and commercialized. However, four factors may stimulate increasing interest in polythioesters; first, the booming activities in the field of biodegradable and biocompatible materials; second, the relatively high refractive index of sulfur-containing polymers which is of interest for optical applications, and third, the discovery of Steinbüchel and coworkers (1–8) that certain microorganisms possess enzymes which are capable to incorporate β-mercaptocarboxylic acids into poly(β-oxyalkanoate)s so that copolyesters of β-hydroxy-and β-mercapto carboxylic acids are formed and even the homopolyester of 3-mercaptopropionic acid was obtained. Finally, the discovery that a certain group of the extremophilic microorganisms possesses a metabolism based on sulfur chemistry instead on oxidation of organic substrates. The purpose of this article is to summarize the broadly scattered publications on polythioesters hoping that such a review will contribute to an intensification of research activities in this neglected working field.

1.1 Structure, Nomenclature and Reactivity

The term polythioester is a rather superficial and inaccurate label for a diversified group of polymers, and therefore, well suited as a title of a review article, but not suited as an

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accurate denomination or description of a chemical structure. This inaccuracy has two sources. First, the term ester itself needs definition and second, sulfur atoms may replace O-atoms in two or three different positions so that the diversity of thioesters is far greater than that of ester groups. All the thioester groups discussed in this article can be summarized by formula **1**. This means, this review is focused on thioanalogs of carboxylic–and carbonic acid esters, but excludes polymers containing thiophosphate, thiophosphonate, thiosulfate and thiosulfonate groups (most of which are unknown anyway).
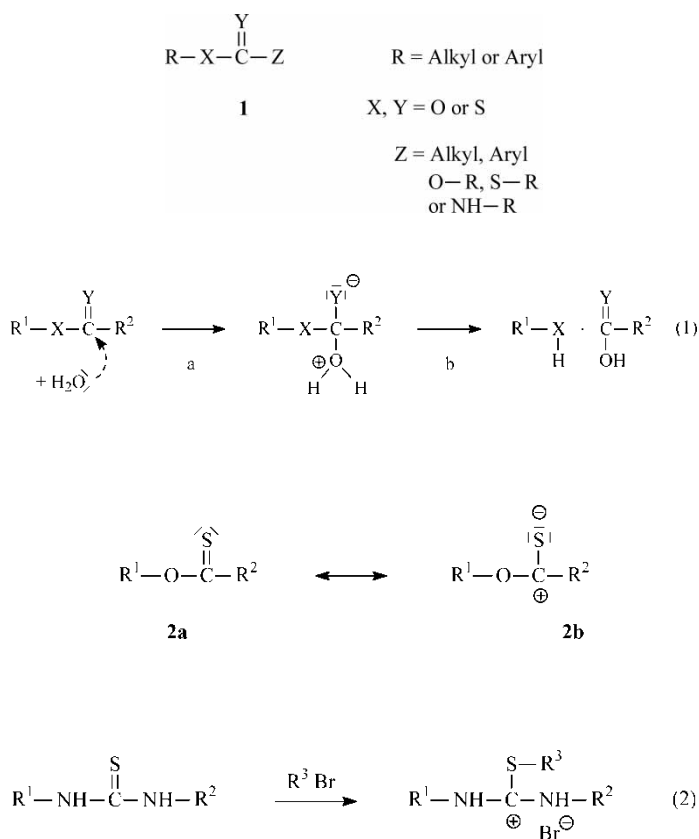
When in formula **1** Z is an alkyl or aryl group and Y═O, the term thiolester may be used. With X = O and Y = S, the lable is thionoester, whereas with X = S and Y = S, the simplest term is dithioester. Analogously, urethanes (Z = NH-R) may be called thiol urethane (or carbamate) for X = S, Y = O, thionourethane (or carbamate) for X = O, Y = S and dithiourethane (dithiocarbamate) for X, Y = S. In the case of carbonate groups, the diversity is even higher because with Z = S-R and X, Y = S, even trithio carbonates may exist.

When the reactivity of thiolesters is compared to that of a normal ester group, the result depends on the reaction mechanism. A nucleophilic substitution proceeds in two steps (Eq. (1), which may be distinguished as addition (1a) and elimination steps (1b). When the addition step is rate-determining, as is true for poor nucleophiles such as water, the thiolesters are less reactive. The electrons of the S-atom repel the nucleophile more efficiently, because the diameter of the S-atom is greater than that of the O-atom. Yet, in the case of a strong nucleophile such as OH$^{\ominus}$ the elimination step may be rate-determining. Now the thiolester is more reactive, because the sulfide ion is more stable than a corresponding oxide ion, and thus, it is the better leaving group. This difference is evident from the higher acidity of H_2S relative to H_2O or from the higher acidity of thiophenols relative to phenols. The high reactivity of S-acetyl Coenzyme-A as acyl transfer agent is also based on this property. In summary, thiolesters are less sensitive to hydrolysis in neutral or weakly acidic water, but more sensitive to alkaline hydrolysis or to reactions with aliphatic amines.

Thionoesters (Y = S) differ from thiol esters (X = S) in two points. First, the electron (nucleophile) repelling effect no longer exists. Second, the C═S double bond is more polarized than the C═O double bond, due to the different diameters of C and S which reduce the overlapping of their p-orbitals. The higher polarity of the C═S group (see mesomeric formula **2b**), eases the additional step of nucleophilic attack. Furthermore, the sulfur itself can play the role of nucleophile and in the case of thiono carbonates, thiono urethanes and thio(no) ureas, alkylation with alkyl bromides (or tosylates) is rather easy to achieve. Eq. (2) illustrates such a reaction for the long known synthesis of isothiouronium bromides.

Another interesting aspect is the thermostability of polythioesters relative to normal polyesters. If the thermal

degradation mainly occurs via β-elimination (Tsugaew Elimination, Eq. (3), thiolesters (R-CO-SR′) might be more stable, because the back-reaction, i.e., the addition of the mercapto group onto the double bond should be faster. In the case of thionoesters (Y═S, X═O), the higher polarity favors rupture of the O-CH$_2$ bond, but the C═S group is a weaker base than C═O. Both hemolytic cleavage Eq. (4) and heterolytic cleavage Eq. (5) of ester groups should be favored in thiolesters. Sulfur radicals are more stable than analogous alkoxy or aryloxy radicals and the same is true for sulfide anions compared to oxide anions. For long-term use in air, the oxidative stability is more important than thermostability. It is a general trend in organic chemistry and polymer chemistry that sulfur-containing compounds are more sensitive to oxidative degradation than analogous oxygen compounds. However, systematic studies of oxidative or thermal degradation of polythioesters are scarce, to the best knowledge of the authors.
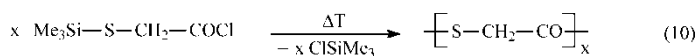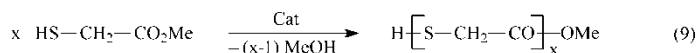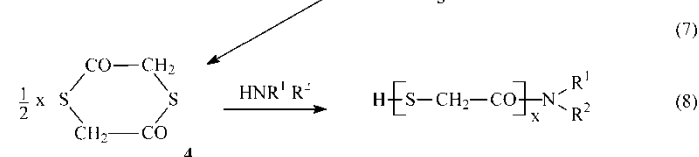

$$R-X-\overset{\overset{\displaystyle Y}{\|}}{C}-Z \qquad R = \text{Alkyl or Aryl}$$

1   X, Y = O or S

Z = Alkyl, Aryl
O—R, S—R
or NH—R

$$R^1-X-\overset{\overset{\displaystyle Y}{\|}}{C}-R^2 \xrightarrow{a} R^1-X-\overset{\overset{\displaystyle \overset{\ominus}{Y}}{|}}{\underset{\overset{\oplus}{O}}{\underset{\overset{/\ \backslash}{H\ \ H}}{C}}}-R^2 \xrightarrow{b} R^1-X\ \cdot\ \overset{\overset{\displaystyle Y}{\|}}{\underset{\overset{|}{OH}}{\underset{H}{C}}}-R^2 \quad (1)$$
+ H$_2$O

$$R^1-O-\overset{\overset{\displaystyle S}{\|}}{C}-R^2 \longleftrightarrow R^1-O-\overset{\overset{\displaystyle \overset{\ominus}{S}}{|}}{\underset{\oplus}{C}}-R^2$$

2a   **2b**

$$R^1-NH-\overset{\overset{\displaystyle S}{\|}}{C}-NH-R^2 \xrightarrow{R^3\,Br} R^1-NH-\overset{\overset{\displaystyle S-R^3}{|}}{\underset{\oplus}{C}}-NH-R^2 \quad (2)$$
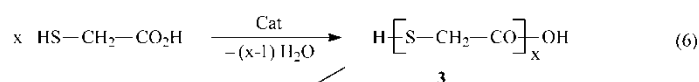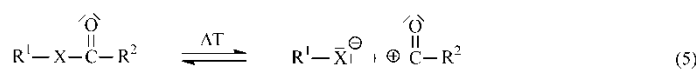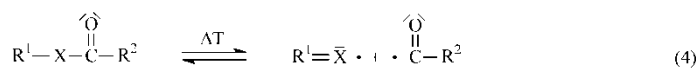Br$^{\ominus}$

1.2 Aliphatic Polyesters of α-Mercapto Carboxylic Acids

First systematic studies of poly(thio glycolide) **3** were conducted by Schöberl and coworkers (9−14). The first synthetic approach explored by those authors was based on the polycondensation of mercaptoacetic acid Eq. (6). Most of these polycondensations were performed at 130−140°C with removal of the liberated water *in vacuo* or by azeotropic distillation. No catalyst was found allowing for an acceleration

of this slow process without causing significant side reactions. Regardless of the reaction conditions, only mixtures of oligomers with average degrees of polymerizations (P_n's) around 6 were obtained. Fractionation by extraction with different solvents yielded fractions having P_n's up to 20. The melting temperature rapidly increased with the P_n's up to values around 120°C. Elias and Bührer (15) later discovered that the limitation of the $\bar{P}_n$ mainly resulted from cyclization, because the cyclic dithioglycolide **4** was found in quantities up to 20%. Presumably higher cyclic oligomers were also formed, but the analytical methods of that time did not allow for the detection of higher cyclic oligomers in complex reaction mixtures. Schöberl (13) also reported that all his attempts to prepare polythioesters by polycondensations of other α- or β- mercaptocarboxylic acids were unsuccessful.

Another interesting finding of Schöberl et al. concerned the thermal degradation of the oligothioglycolides, which gave high yields of dithioglycolide **4** when this compound was immediately distilled off *in vacuo* (14). The cyclic dithioglycolide proved, in turn, to be a useful monomer for the preparation of polythioglycolide by ring-opening polymerization at 20–25°C. Primary and secondary aliphatic amines proved to be the best initiators and number average molecular weights (M_ns) up to 18 000 Da were apparently obtained (12, 13, 15). With increasing M_ns, higher T_ms were found with a maximum at 170°C.

$$R^1—C{\overset{\bar{Y}\,\cdot\,\cdot\,H}{\underset{\bar{X}—CH_2}{\Big\langle}}}CH—R^2 \quad \underset{}{\overset{\Delta T}{\rightleftharpoons}} \quad R—C{\overset{I\bar{Y}—H}{\underset{\bar{X}\,I}{\Big\langle}}} \;+\; {\overset{}{\underset{CH_2}{\Big\|}}}CH—R^2 \qquad (3)$$

$$R^1—{\overset{\overset{\frown}{O}}{\underset{}{\overset{\|}{C}}}}—R^2 \quad \overset{\Delta T}{\rightleftharpoons} \quad R^1=\bar{X}\,\cdot\,\cdot\,{\overset{\overset{\frown}{O}}{\underset{}{\overset{\|}{C}}}}—R^2 \qquad (4)$$

$$R^1—X—{\overset{\overset{\frown}{O}}{\underset{}{\overset{\|}{C}}}}—R^2 \quad \overset{\Delta T}{\rightleftharpoons} \quad R^1—\bar{X}^{\ominus}\,I\;\oplus\,{\overset{\overset{\frown}{O}}{\underset{}{\overset{\|}{C}}}}—R^2 \qquad (5)$$

$$x\;\;HS—CH_2—CO_2H \quad \xrightarrow[-(x-1)\,H_2O]{Cat} \quad H{\Big[}S—CH_2—CO{\Big]}_x OH \qquad (6)$$

3

$$(7)$$

$$\tfrac{1}{2}\,x\;\; S{\overset{CO—CH_2}{\underset{CH_2—CO}{\Big\langle\Big\rangle}}}S \quad \xrightarrow{HNR^1R^2} \quad H{\Big[}S—CH_2—CO{\Big]}_x N{\overset{R^1}{\underset{R^2}{\langle}}} \qquad (8)$$

4

$$x\;\;HS—CH_2—CO_2Me \quad \xrightarrow[-(x-1)\,MeOH]{Cat} \quad H{\Big[}S—CH_2—CO{\Big]}_x OMe \qquad (9)$$

$$x\;\;Me_3Si—S—CH_2—COCl \quad \xrightarrow[-\,x\,ClSiMe_3]{\Delta T} \quad {\Big[}S—CH_2—CO{\Big]}_x \qquad (10)$$
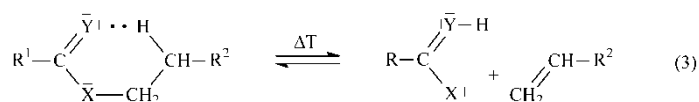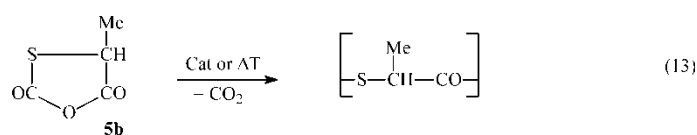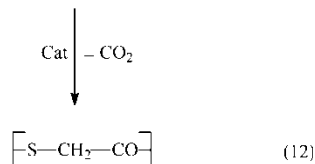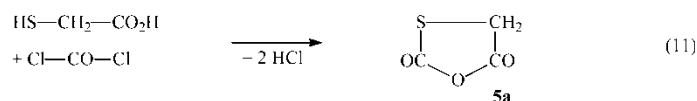
Polycondensations of methyl mercaptoacetate Eq. (9) were also described (15), but regardless of the transesterification catalyst, only low oligomers were obtained quite analogous to polycondensations of the mercaptoacetic acid itself. A short notice in Reference 15 also says that high molar mass polythioglycolide may be prepared by polycondensation of S-trimethylsilyl mercaptoacetyl chloride Eq. (10), but experimental details were never published.

The numerous experiments of Schöberl (9–14) (later reinvestigated by Elias and Bührer (15) suggested that ring-opening polymerization might be a more promising approach to the preparation of high molar mass polythioglycolide than polycondensation methods. Therefore, Schöberl (13) also attempted to polymerize the S-carboxyanhydride **5a** (2,5-dioxo-1,3-oxathiolane) which was for the first time - synthesized (via Eq. (11) by Davies (16, 17) (but not polymerized). Schöberl (13) used traces of water, primary or secondary aliphatic amines, N,N-dimethylaniline and pyridine as initiators, whereby the strongest catalytic effect was found for pyridine. Unfortunately, neither yields nor $\bar{P}_n$s or M_ns of the individual polymers were reported and the nature of the endgroups also remained obscure Eq. (13). This situation prompted other authors (10, 18, 19) to explore the ROP of **5a** and its methyl analog **5b** Eq. (13) in more detail.

Elias and Bührer studied the usefulness of a broad variety of potential initiators in dioxane at 25°C. The only strong acid, $BF_3 \cdot Et_2O$, proved to be inactive and the weakly basic protic nucleophiles, water, mercaptoacetic acid and 4-bromoaniline were likewise inactive. n-Hexylamine gave a moderate yield of a few molar mass poly(thioglycolide)s. Tertiary amines and strong bases such as $NaBH_4$ or $NaOCH_3$ gave the highest yields and molar masses. On the basis of these results, triethylamine-catalyzed polymerizations were studied in more detail. When the monomer/catalyst (M/C) ratio was varied, the molar masses increased with higher M/C ratios, but the effect was poor. A stronger influence was found for a variation of the temperature between −50 and 100°C. The highest molar mass (and a conversion of 93%) was found at the lowest temperature. When the time was varied at 25°C in dioxane with a M/C ratio of 400/1, both conversion and molar mass showed a weak maximum at 6 h.

Whereas Schöberl reported that low molar mass polythioglycolide is soluble in DMF, pyridine, phenol or hot cyclohexanone, Elias and Bührer found among hundred inert solvents only two which dissolved high molar mass polythioglycolide, namely dichloroacetic acid (DCA) and hexafluoroacetone sesquihydrate. Using light-scattering measurements in DCA, those authors elaborated the Mark-Houwink equation (14).

The highest T_m determined by DSC measurements was 157°C, which is considerably lower than the T_m of polyglycolide which amounts to 220–225°C.

$$HS—CH_2—CO_2H + Cl—CO—Cl \xrightarrow{-2\ HCl} \mathbf{5a} \quad (11)$$

$$\xrightarrow{Cat,\ -CO_2}$$

$$[S—CH_2—CO] \quad (12)$$

$$\mathbf{5b} \xrightarrow{Cat\ or\ \Delta T,\ -CO_2} [S—CH—CO] \quad (13)$$

$$[\eta] = 0.018 \times M_w^{0.72} \quad (mL/g) \quad (14)$$

Reinvestigation of the tert.amine-catalyzed polymerization of the SCA **5** by the authors (18) showed that the efficiency of the amines (i.e., the rate of polymerization) increased with their basicity. Triethylamine-catalyzed polymerizations in tetrahydrofuran with a variation of the temperature again gave the highest yield at the lowest temperature. Particularly interesting is the variation of the purity of both monomer **5** and reaction medium (dioxane). As demonstrated by the results listed in Table 1 (experiments Nos. 1–5), the presence of impurities (most likely protic compounds like H_2O, -CH_2OH and -CH_2SH-groups)

causes a drastic reduction of the molar mass. These findings suggest the following hypothetical polymerization mechanism. The triethylamine deprotonates a protic impurity or the monomer itself Eq. (15) and the resulting anion initiates an anionic ROP (Eqs. 16–18). Protonation and decarboxylation of the thiocarbonate chain end generates an inactive mercaptogroup, and thus, a termination step Eqs. (19) and (20).

Elias and Bührer also prepared the SCA of thiolactic acid **5b** by phosgenation (19). Using thiolactic acid of different optical purity, a racemic monomer (Tm = 46°C), a monomer containing 29% D-units (T_m = 52°C) and an almost pure D-monomer (T_m = 62°C) were prepared. Oligomeric polythiolactide was prepared by Schöberl and Wiehler via polycondensation of 2-mercaptopropionic acid or its methylester (10), but high molar mass polymers were not obtained. Elias and Bührer studied the ROP of monomer **5b** in dioxane at 25°C with a broad variation of initiator (or catalyst) and variation of the M/C ratio. Unfortunately, neither solvent, temperature, time, or concentration were varied. Compared to the ROP of SCA **5a**, surprising results were obtained, because none of the tert.amines or strong bases catalyzed the polymerization. The best results were achieved with primary aliphatic amines, and even with these initiators, the conversions were low. Complete conversion was observed for thermal polymerization, but no viscosity data were reported. Molar mass or $\bar{P}_n$ measurements are also lacking for all other polythiolactides. For the low molar mass polymer from the D-monomer, a T_m of 152°C was found, while the racemic polythiolactides were amorphous. Optical rotation and circular dichroisms measurements indicated that the polythiolactides adopt a random coil conformation
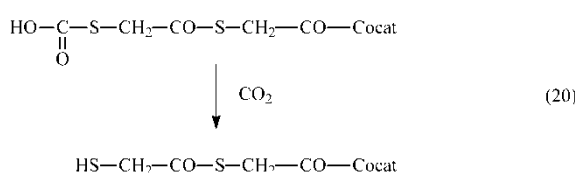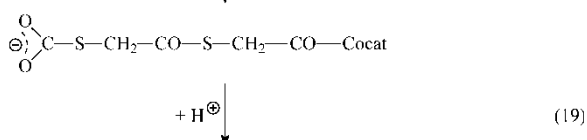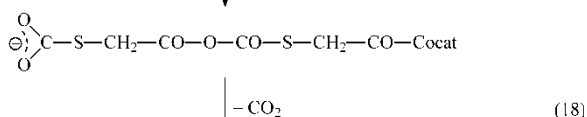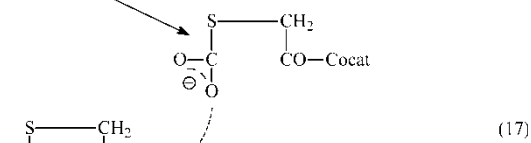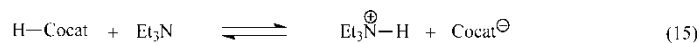
Table 1. Influence of solvent purity on yield and molecular weight (M_v = viscosity average) of poly(thioglycolide), prepared by triethylamine-catalyzed ring-opening polymerization (M/I = 20) in dioxane at 20°C

Exp. No.	Monomer	Purity of dioxane	Yield (%)	$[\eta]^a$ (mL/g)	M_v^b (Da)
1	Oxathiolane-2,5-dione (SCA)	Technical grade	21.5	10.8	7,100
2	"	Uvasol (E. Merck KG)	42.0	11.8	8,100
3	"	1 × dist. over CaH$_2$	52.0	12.0	8,300
4	"	1 × dist. over CaH$_2$ + 2 × dist. over Na	51.0	14.0	10,500
5	"	2 × dist. over Na + 1 × dist. over LiAlHy	63.5	11.0	7,500
6	Dithiolane-2,4-dione (DTD)	Technical grade	48.5	14.0	10,300
7	"	Uvasol (E. Merck KG)	84.0	27.5	26,500
8	"	1 × dist. over CaH$_2$	88.5	52.0	64,000
9	"	1 × dist. over CaH$_2$ + 2 × dist. over Na	92.0	69.0	95,000
10	"	2 × dist. over Na + 1 × dist. over LiAlHy	95.5	78.0	112,000

[a] Measured at 20°C in dichloroacetic acid.
[b] Calculated from $[\eta] = 0.018\ M^{0.72}$.

in chloroform and not a helical secondary structure, regardless of their optical parity.

$$H{-}Cocat \ + \ Et_3N \ \rightleftharpoons \ Et_3\overset{\oplus}{N}{-}H \ + \ Cocat^{\ominus} \qquad (15)$$

$$(16)$$

$$(17)$$

$$(18)$$

$$(19)$$

$$(20)$$

A new class of monomers came into play when Kricheldorf and coworkers succeeded to synthesize the 1,3-dithiolane-2,4-diones **7a–c** (DTDs) (18, 20, 21). The starting materials are α-xanthogen carboxylic acids (**6a–c**), which can easily be prepared from sodium xanthogenate and α-bromocarboxylic acids. When their acid chlorides prepared by means of thionylchloride Eq. (21) are heated, spontaneous cyclization takes place, yielding the 1,3-DTDs Eq. (23). The properties of 1,3-DTDs differ from those of the SCAs **5a,b** in several important aspects. The 1,3-DTDs are chemically and thermally more stable. Therefore, efficient purification is feasible by washing solutions of 1,3-DTDs with water at low temperatures (e.g. $<5°C$). Furthermore, they survive distillation in a good vacuum below $100°C$, and due to their low sensitivity to water, they are stable on storage in a refrigerator. Heating above $100°C$ causes slow polymerization of **7a**, but the molar masses of the resulting polythioglycolides are low and with increasing temperature, increasing amounts of the cyclic dimer **4** are formed.

The racemic substituted monomers **7b** and **7c** are stable for several hours even at $150°C$, but slowly oligomerize and decompose above $170°C$. When polythioesters prepared by means of base-catalyzed polymerizations were heated to

temperatures $>150°C$, the same reaction mixtures (mainly containing cyclic dimers) were obtained. Reactions of various potential catalysts or initiators with **7a** were studied at $20–25°C$. When equimolar amounts of acids such as H_2SO_4, trifluoroacetic acid, $BF_3 \cdot OEt_2$ $ZnCl_2$ or PCl_5 were added to solutions of **7a** in CH_2Cl_2, most of the monomer remained unchanged within 48 h. No polymerization occurred when small amounts ($M/C \leq 10$) of alcohols, mercaptanes or primary aromatic amines were added to solutions of **7a** in dioxane. With a large excess of water, complete hydrolysis was obtained, whereas small amounts of water yielded low oligomers Eq. (24). No reaction was observed with small amounts of alcohols, mercaptanes or primary aromatic amines. Quite analogous to polymerizations of SCA **5a**, tertiary amines and strong bases such as sodium methoxide, potassium tert . butoxide or LiCl in DMF proved to be useful catalysts. Under identical conditions, ethyl diisopropylamine yielded the highest molar masses. A M/C ratio of 100 was more favorable than lower M/C ratios. When triethylamine-catalyzed polymerizations were performed in THF at temperatures between -75 and $50°C$, the highest molar mass was obtained at $-75°C$, but the temperature coefficient was rather small. Particularly interesting were the results obtained from triethylamine-catalyzed polymerizations when the purity of the dioxane was varied. As demonstrated by the data in Table 1 (Nos. 6–10), the purity of the solvent has a tremendous influence on the molar mass. Yet, the most important point is the finding that the 1,3-DTD **7a** yielded much higher molar masses than **5a** under identical reaction conditions. Its higher chemical and thermal stability is thus no hindrance for successful polymerizations, and 1,3-DTDs are in all aspects the more attractive monomers.

$$(21)$$

$$(22)$$

$$(23)$$

6a, 7a : R = H   **6b, 7b** : R = CH_3 **6c, 7c** : R = CH_2CH_3

$$(24)$$
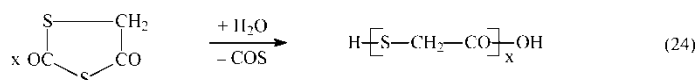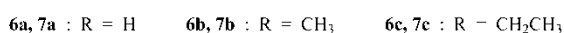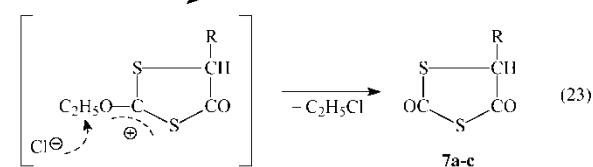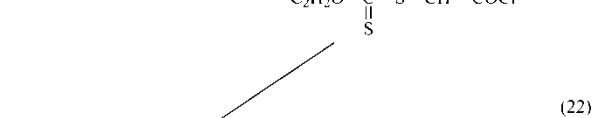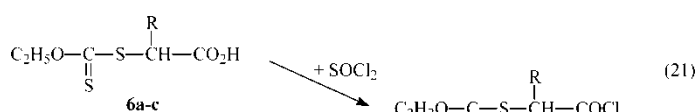
At this point, it should be mentioned that the stability of polythioglycolide in dry dioxane was studied in the

presence of various tert. amines, whereas pyridine had little effect. Strong bases such as triethylamine degraded this poly-thioester quite efficiently, although hydrolytic cleavage could take place. Possibly, back-biting degradation yielding cyclic oligomers is responsible for this effect. In other words, strong bases are not only the most efficient catalysts of the ROP of SCAs and DTDs, they are also powerful degradation catalysts, and thus, optimization of the reaction time is an important prerequisite for a successful polymerization result-ing in high molar masses.

Quite recently, the thermal polymerization and tertiary amine-catalyzed polymerization of DTD **7a** were reinvesti-gated, and the reaction products characterized by MALDI-TOF mass spectrometry (22). Regardless, if pyridine or tri-ethylamine was used as catalyst, cyclic poly(thioglycolide) **8** was the main reaction product in all experiments. Analo-gously, cyclic polypeptides were obtained by thermal-or pyridine-catalyzed polymerization of sarcosine-N-carboxy anhydride and explained by a Zwitterionic polymerization (23). A Zwitterionic mechanism (schematically illustrated in Eqs. (25) and (26) is the most plausible explanation of these results.
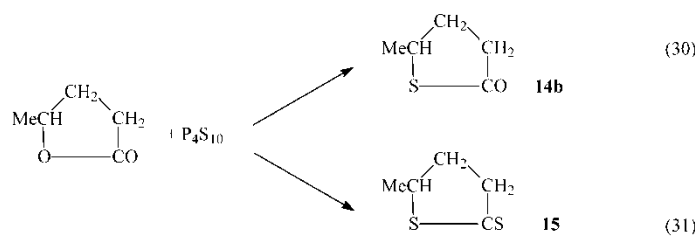
$$(25)$$

$$(26)$$
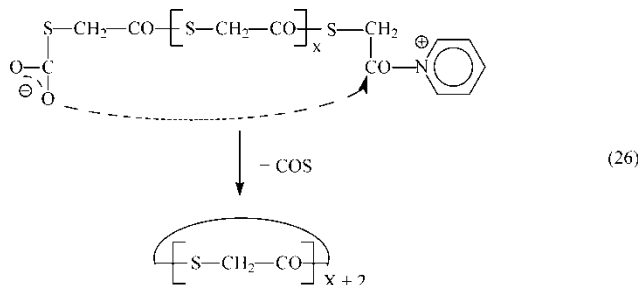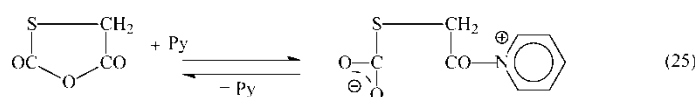
Copolymerization of two different SCAs with each other (e.g. **5a** with **5b**), copolymerization of two different DTDs with each other or copolymerizations of SCAs with similar heterocycles (e.g. α-amino acid N-carboxy anhydrides) were not reported. However, a crystalline copolyester (struc-ture **9**) having an alternating sequence in combination with ethylenglycol and adipic acid was prepared by Kricheldorf and Leppert (24) via alkylation of silylated thioadipic acid Eq. (27). Yet, only one experiment yielding a low molar mass (<3,000 Da) was performed. Furthermore, syntheses of two poly(ester amide)s made up by alternating sequences of mercaptoacetic acid with glycine and 4-aminobenzoic acid were described (25) (structures **11** and **13**, Eqs. (28) and (29)). That study served two purposes. First, it should be found out, if polycondensations of isothiocyanato carboxylic acids (e.g. **10** and **12**) can be performed in such a way that no transesterification or ester-amide interchange occurs. Second, it should be elucidated, if ^{13}C-NMR spectroscopy allows for a
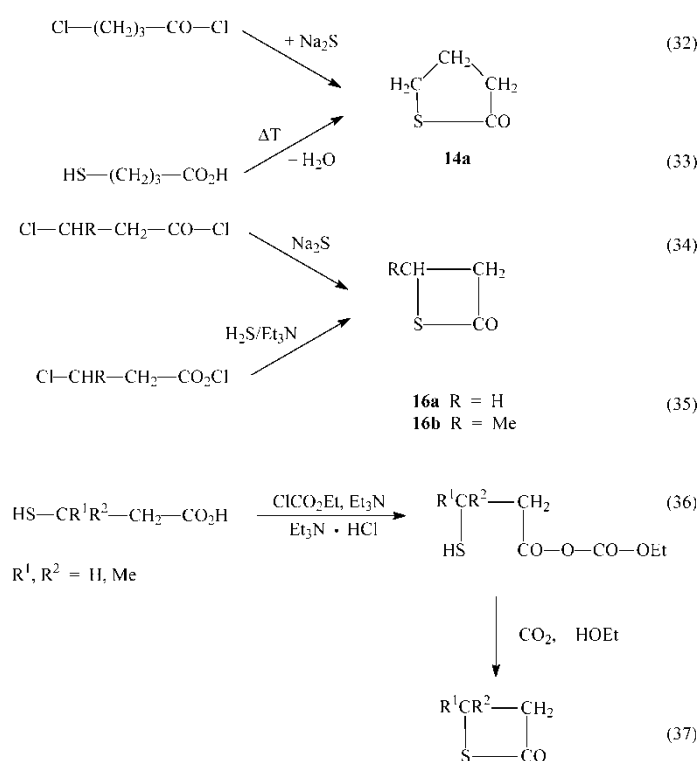
characterization and distinction of isomeric copolyester sequences. The ^{13}C-NMR spectra of **10** and **12** were, indeed, different and displayed three CO-signals, thereby proving the success of both synthetic and analytical method.

$$(27)$$

$$(28)$$

$$(29)$$
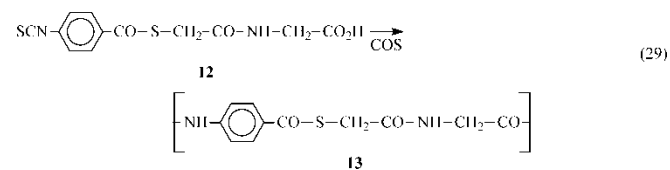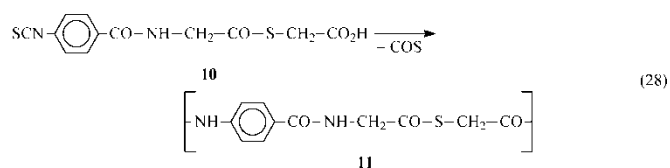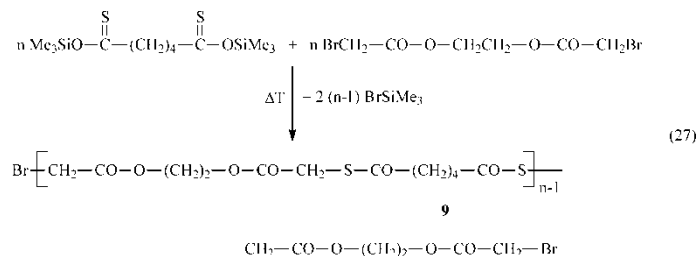
1.3 Polythioesters of Aliphatic ω-Mercapto Carboxylic Acids

The ring-opening polymerization of thiolactones seems to be the most obvious approach to the preparation of PTEs derived from ω-mercapto carboxylic acids. Therefore, syntheses and polymerizations of thiolactones will here be discussed first. The first synthesis of a thiolactone was reported in 1912 (26) and concerned γ-thiovalerolactone **14** Eq. (30) and its thiono analog **15** Eq. (31) which were obtained in low yields by treatment of the corresponding lactones with P_4S_{10}. The unsubstituted γ-thiobutyrolactone **14a** was later prepared by other research groups (27, 28) Eqs. (32) and (33). Yet, γ-butyrolactone itself and all these five-membered thiolactones havein common that they are not homopolymerizable for thermodynamic reasons. Therefore, all studies of ROPs of thiolactones concern four-, six- and seven-membered rings.

$$(30)$$

$$(31)$$

$$\text{Cl}-(\text{CH}_2)_3-\text{CO}-\text{Cl} \quad \xrightarrow{+\ \text{Na}_2\text{S}} \tag{32}$$

$$\text{HS}-(\text{CH}_2)_3-\text{CO}_2\text{H} \quad \xrightarrow[-\ \text{H}_2\text{O}]{\Delta\text{T}} \quad \mathbf{14a} \tag{33}$$

(structure **14a**: five-membered ring with CH_2, H_2C, CH_2, S, CO)

$$\text{Cl}-\text{CHR}-\text{CH}_2-\text{CO}-\text{Cl} \quad \xrightarrow{\text{Na}_2\text{S}} \tag{34}$$

$$\text{Cl}-\text{CHR}-\text{CH}_2-\text{CO}_2\text{Cl} \quad \xrightarrow{\text{H}_2\text{S}/\text{Et}_3\text{N}}$$

(structure: RCH—CH₂ / S—CO)

16a R = H (35)
16b R = Me

$$\text{HS}-\text{CR}^1\text{R}^2-\text{CH}_2-\text{CO}_2\text{H} \quad \xrightarrow[\text{Et}_3\text{N}\cdot\text{HCl}]{\text{ClCO}_2\text{Et},\ \text{Et}_3\text{N}} \quad \tag{36}$$

$$\text{R}^1, \text{R}^2 = \text{H}, \text{Me}$$

(structure: R¹CR²—CH₂ / HS   CO—O—CO—OEt)

$$\downarrow \quad \text{CO}_2, \ \text{HOEt}$$

(structure: R¹CR²—CH₂ / S—CO) (37)

Synthesis and properties of β-thiopropiolactone **16a** were described in a British patent (28). In the same year, a Russian research group headed by Knunyants and Lin'kova also reported on the preparation of various substituted β-thio-lactones (29–36). A little later, the Russian group also reported on the preparation of unsubstituted β-thiopropiolac-tone (37). While the researchers of Goodrich Co. treated β-chloro (or bromo) propionyl chloride with sodium sulfide Eq. (34), the Russian group used the combination of H_2S with triethylamine Eq. (35) for the incorporation of the

sulfide atom (35). The Russian authors also elaborated another synthetic approach based on β-mercapto propionic acids. Treatment with ethylchloroformate and triethylamine at room temperature yielded a mixed anhydride Eq. (36) as unstable intermediate which cyclized spontaneously Eq. (37). This approach proved to be particularly useful for the preparation of substituted thiolactones, whereas in the case of β-mercaptopropionic acid oligoesters but no thiolactone were obtained (37). Despite numerous publications on β-thio-lactones (29–42), polymerization of β-thiopropiolactone was never studied. Other β-thiolactones were polymerized by heating with a trace of water in a sealed tube, whereby low molar mass poly(β-thiolactone)s with variable softening points below 145°C were obtained (33). Exact T_ms or molecular weights were not reported.

A new synthetic approach was described by the authors (43), who prepared 1,3-dithian-2,4-dione **18** by cyclization of β-xanthogene propionylchloride **18** Eq. (38). The formation of the six-membered monomer **17** is much more difficult to achieve than the formation of the five-membered DTD, and long reaction times or higher temperatures cause decomposition (incl. oligomerization) of this monomer. Therefore, a low yield of 16% was reported and only few polymerization experiments were conducted. Quite analogous to DTD, monomer **17** polymerizes easily when tert. amines were used as catalysts Eq. (39), whereas a stoichiometric reaction occurs with primary amines Eq. (40), (β-thio-propiolactone yields the same products (37), Eq. (41). With triethylamine as catalyst, a polythioester of moderate molecular weight was obtained, the chemical and thermal stability of which was considerably higher than those of polythioglyco-lide (43). Furthermore, a melting temperature around 165°C was found, significantly higher than that of poly(β-propiolac-tone) (see Table 2).
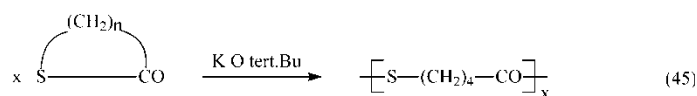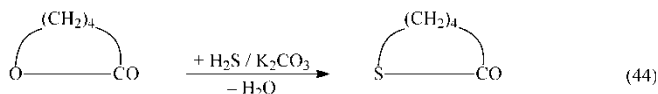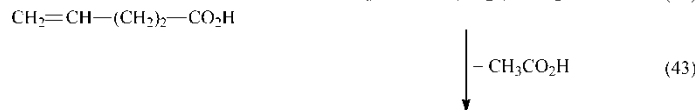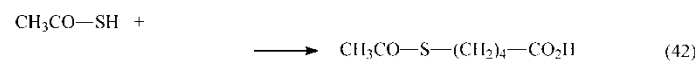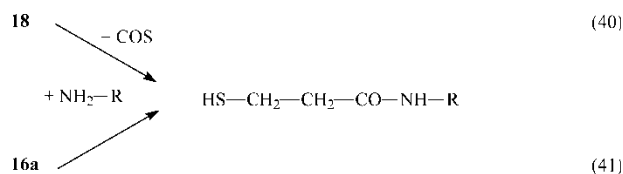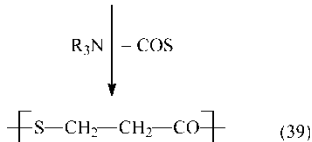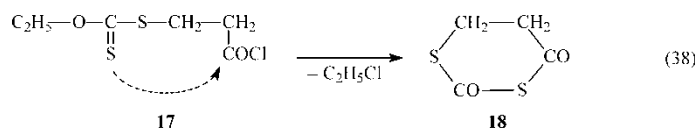
Whereas several papers and patents describe syntheses of δ-thiovalerolactone (44–47), only one publication reports

Table 2. Glass-transitions (Tg) and melting temperatures (Tms) of polythioesters derived from aliphatic ω-mercapto carboxylic acids and their O-analogs

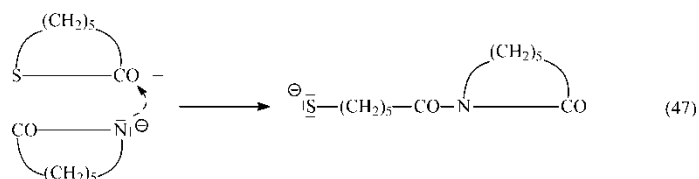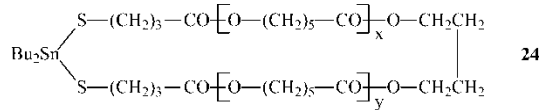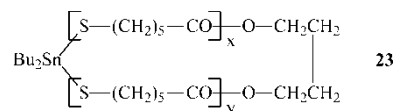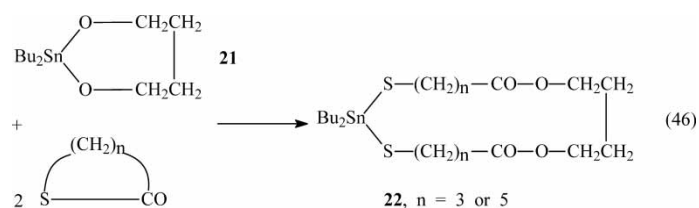| Polythioester of	Tg (°C)	Tm (°C)	Ref.	Polyester of	Tg (°C)	Tm (°C)	Ref.
Mercapto acetic acid	—	137 +155	[15]	Glycolic acid	34	225	[199]
		165 − 169	[13]		45	228	[200]
3-Mercapto propionic acid	—	170	[6]	3-Hydroxy-propionic acid	−10	77	[6]
					−24	93	[199, 200]
4-Mercapto butyric acid	—	90	[61]	4-Hydroxy-butyric acid	−59	65	[199, 200]
		117 − 118	[47]		−63	60	[199]
5-Mercapto valeric acid	—			5-Hydroxy-valeric acid	−66	58	[200]
		105 − 106	[47]		−60	65	[199]
6-Mercapto hexanoic acid	−40	105 − 110	[55]	6-Hydroxy-hexanoic acid	−64	69	[200]
11-Mercapto undecanoic acid	—	105	[72]	11-Hydroxy-undecanoic acid	−46	92	[200]

on its polymerization (47). The δ-thiovalerolactone (**19**) was prepared by cyclization of δ-mercaptovaleric acid which was obtained in two ways. Either thioacetic acid was added onto allylacetic acid, followed by hydrolysis of the acetyl group Eqs. (42) and (43), or δ-chlorovaleric acid was reacted with NaSH or thiourea see Eq. (7). As an alternative method, the treatment of δ-valerolactone with H_2S in the presence of basic catalysts was patented (46) Eq. (44).

three U.S. patents (51–53). Heating of ε-caprolactone with CS_2 and NaOH to 200°C yielded a low molar mass polythioester the thermal depolymerization which in turn yielded the monomeric ε-thiocaprolactone (**20**). This monomer was then homopolymerized, copolymerized with ε-caprolactone and grafted on poly(hydroxy ethyl) methacrylate using manganese-(II)-benzoate as catalyst.
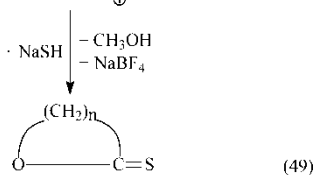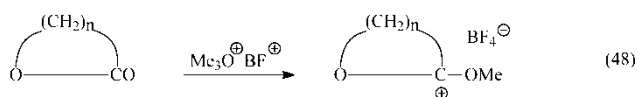

ε-Thiocaprolactone (**20**) was prepared analogously either by cyclization of ε-mercaptohexanoic acid (48, 49) or by treatment of ε-caprolactone with H_2S and a basic catalyst (44). Both δ-thiovalerolactone (**19**, thian-2-one) and ε-thiocaprolactone (**20**, thiepan-2-one) were polymerized in bulk with potassium tert.butoxide at 150–155°C Eq. (45). Only a low yield (21%) and a low molecular weight were obtained for the poly(δ-thiovalerolactone) and a melting temperature of 117–118°C was reported (47). Various polymerization experiments, higher yields (38 or 78%), much higher molecular weights and a T_m of 104–106°C were reported for the polymerization of poly(ε-thiocaprolactone) e.g. Eq. (45) (48, 49). The Overberger group also studied the optical properties of various chiral thiolactones, but without studying their polymerizability (49, 50). Another approach towards the preparation of ε-thiocaprolactone **20** and its polyester was described by Fritze in
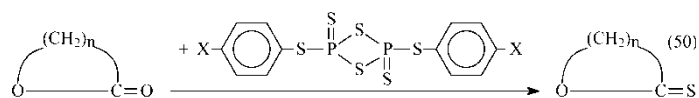
Studies of ring-expansion polymerizations of γ-thiobutyrolactone (**14a**) and ε-thiocaprolactone (**20**) with cyclic tin bisalkoxides were performed by the author (54). When the 2,2-dibutyl-1,3-dioxostannepane **21** was warmed with a double molar amount of the thiolactones, one-step insertions into both Sn-O bonds took place Eq. (46), whereby the macrocycles **22** with the more stable Sn-S bonds were formed Eq. (46). Even a large excess of the γ-thiollactone did not result in further insertion steps because this lactone for thermodynamic reasons does not homopolymerize. In contrast, an excess of ε-thiolactone caused oligomerization yielding the cyclic oligoesters of structure **23**. The cyclic copolyesters **24** were obtained in two steps. At first, ε-caprolactone was polymerized with the initiator **21** followed by two insertion steps
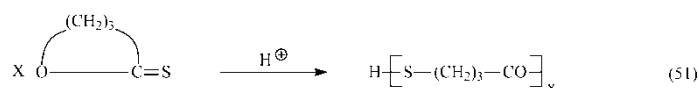
of thiobutyrolactone.

$$\text{(CH}_2\text{)}_n\text{ ring (O—CO)} \xrightarrow{\text{Me}_3\text{O}^{\oplus}\text{BF}^{\oplus}} \text{(CH}_2\text{)}_n\text{ ring (O—}\overset{\oplus}{\text{C}}\text{—OMe)} \; \text{BF}_4^{\ominus} \quad (48)$$

$$\xrightarrow[\substack{-\text{CH}_3\text{OH} \\ -\text{NaBF}_4}]{\cdot\,\text{NaSH}} \text{(CH}_2\text{)}_n\text{ ring (O—C=S)} \quad (49)$$

25 a : n = 3
b : n = 4
c : n = 5

$$\text{(CH}_2\text{)}_n\text{ ring (O—C=O)} + X-\langle\text{C}_6\text{H}_4\rangle-S-\overset{S}{\underset{\parallel}{P}}\underset{S}{\overset{S}{\diamond}}\overset{S}{\underset{\parallel}{P}}-S-\langle\text{C}_6\text{H}_4\rangle-X \longrightarrow \text{(CH}_2\text{)}_n\text{ ring (O—C=S)} \quad (50)$$

25c : n — 5
d : n = 7
e : n — 8
f : n – 15

$$X-\text{(CH}_2\text{)}_5\text{ ring (O—C=S)} \xrightarrow{\text{H}^{\oplus}} \text{H}-[\text{S—(CH}_2\text{)}_3-\text{CO}]_x \quad (51)$$

In connection with ε-thiocaprolactone and its polyester, two physicochemical studies dealing with segmental mobility and glass-transition should be mentioned (55, 56). Furthermore, both thiolactone and poly(t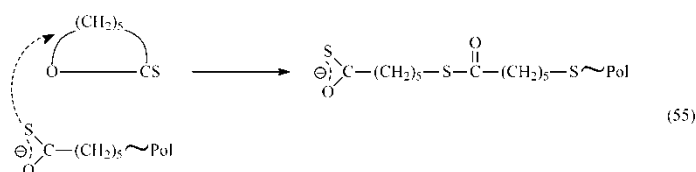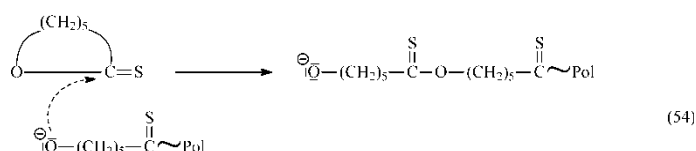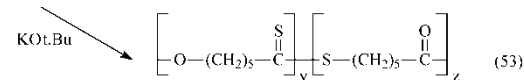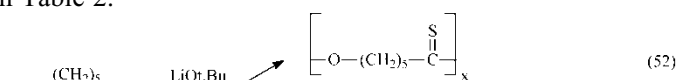hiol ester) were used as electrophilic cocatalysts in anionic polymerizations of ε-caprolactam (57). The initiation reaction formulated in Eq. (47) underlines the relatively high electrophilicity (acylating power) of thiolesters when strong nucleophiles are present.
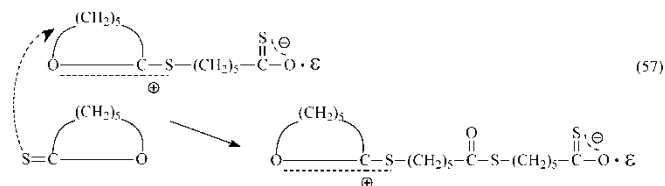
Whereas the chemistry of thiolactones has a long tradition, only few more recent papers deal with syntheses and polymerizations of thionolactones (**25**). Kastounian and coworkers (58, 59) elaborated two synthetic methods, the first one of which is outlined in eqs. (48) and (49). Substituted and unsubstituted five-, six- and seven-membered thionolactones (**25a−c**) were prepared in this way, but those authors did not care about their polymerization. Another group (60) developed the syntheses of **25c−f** illustrated in Eq. (50).

Endo and coworkers (61) compared the polymerizability of γ-thiobutyrolactone **14a** and γ-thionobutyrolactone **25a** using various cationic catalysts. As expected on the basis of previous observations, **14a** did not polymerize, whereas low molar mass poly(thiobutyrolactone) was obtained from **25a** (Eq. (51), ($M_n < 5,000$ Da, the values given in Ref. 58 are too high for reasons mentioned below). The driving force for this polymerization results from rearrangement of the energy rich $>C=S$ group into the more stable $>C=O$ group Eq. (51). This source of exothermic reaction enthalpy is lacking in the case of **14a**. Such rearrangements are well known in organic chemistry from various heterocycles and are not necessarily related to a polymerization process.

The same group also conducted detailed studies of both anionic and cationic polymerizations of ε-thionocaprolactone (62, 63). The course of anionic polymerizations depended very much on the counterion. With Li-alkyls, Li-tert.butoxide and Grignard reagents exclusively poly(thiono ester)s were obtained Eq. (52), whereas K-tert.-butoxide yielded a copolyester mainly consisting of thiol ester groups (Eq. (53)). The question, if a block copolymer or a random sequence was formed, was not discussed, but the ^{13}C-NMR spectra suggest a blocky sequence. The mechanism proposed for the formation of thionoester groups is presented in Eq. (54) and the mechanism yielding thiol ester groups in Eq. (55). Both rates of polymerization and high molecular weights were favored by higher temperatures (up to 100°C). All cationic polymerizations yielded poly(thiol ester)s via a mechanism exemplarily formulated in Eqs. (56) and (57) ($\mathcal{E}$ means electrophilic catalyst). In other words, the growing steps represent alkylation reactions of the C=S group. Yields and molecular weights increased with the temperature as studied in the temperature range of $-78°C$ to 28°C. The highest M_n (57,000 Da) was obtained with $BF_3 \cdot OEt_2$ at 28°C, but all M_ns were determined by polystyrene-calibrated SEC measurements. However, it has been reported by six different research groups (64−71) that such SEC measurements overestimate the real M_ns of aliphatic polyester by 50−100%, and thus, the data provided by Endo's group (and other authors) are certainly too high. This criticism also holds for the M_n and M_w values reported by a Japanese group for poly(11-mercaptoundecanoate) (72). Those authors studied the polycondensation of commercial 11-mercaptoundecanoic acid in bulk at 110°C catalyzed by an immobilized lipase of candida antarctica. Uncorrected M_ns up to 34,000 Da were obtained by this approach. The T_ms of all poly(thio ester)s and their O-analogs were summarized in Table 2.

$$\text{(CH}_2\text{)}_5\text{ ring (O—C=S)} \xrightarrow{\text{LiOt.Bu}} [\text{O—(CH}_2\text{)}_5-\overset{S}{\underset{\parallel}{C}}]_x \quad (52)$$

$$\xrightarrow{\text{KOt.Bu}} [\text{O—(CH}_2\text{)}_5-\overset{S}{\underset{\parallel}{C}}]_y[\text{S—(CH}_2\text{)}_5-\overset{O}{\underset{\parallel}{C}}]_z \quad (53)$$

$$\text{(CH}_2\text{)}_5\text{ ring (O—C=S)} + {}^{\ominus}\text{O—(CH}_2\text{)}_5-\overset{S}{\underset{\parallel}{C}}\sim\text{Pol} \longrightarrow {}^{\ominus}\text{O—(CH}_2\text{)}_5-\overset{S}{\underset{\parallel}{C}}-\text{O—(CH}_2\text{)}_5-\overset{S}{\underset{\parallel}{C}}\sim\text{Pol} \quad (54)$$

$$\text{(CH}_2\text{)}_5\text{ ring (O—CS)} + {}^{\ominus}\overset{S}{\underset{O}{\diamond}}\text{C—(CH}_2\text{)}_5\sim\text{Pol} \longrightarrow {}^{\ominus}\overset{S}{\underset{O}{\diamond}}\text{C—(CH}_2\text{)}_5-\text{S—}\overset{O}{\underset{\parallel}{C}}-\text{(CH}_2\text{)}_5-\text{S}\sim\text{Pol} \quad (55)$$

$$\text{(CH}_2\text{)}_5\text{ ring (O—C=S}\cdot\mathcal{E})_{\delta\oplus} + \text{(CH}_2\text{)}_5\text{ ring (S=C—O)} \longrightarrow \text{(CH}_2\text{)}_5\text{ ring (O—}\overset{\oplus}{\text{C}}\text{—S—(CH}_2\text{)}_5-\overset{S\cdot\ominus}{\underset{\parallel}{C}}-\overset{\ominus}{\text{O}}\cdot\mathcal{E}) \quad (56)$$
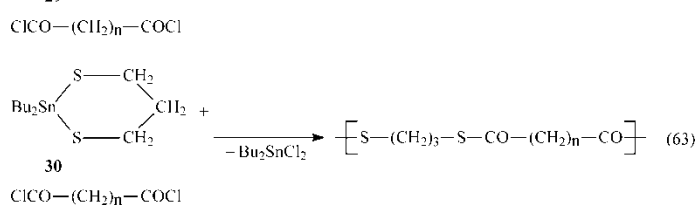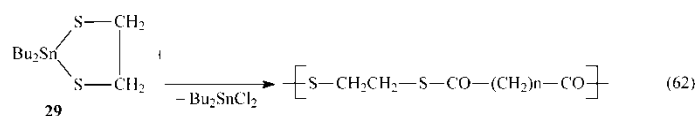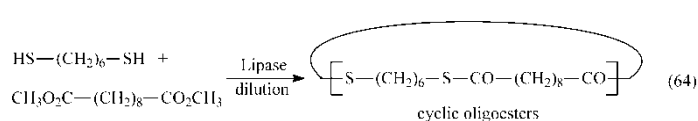
$$(57)$$
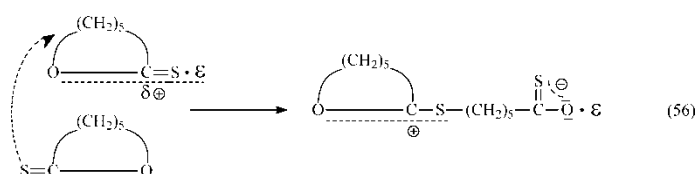
1.4 Poly(thioester)s based on α,ω-Dimercaptoalkanes (Dithiols)

Most research groups reporting on syntheses of PTEs from α,ω-dimercaptoalkanes used both aliphatic and aromatic dicarboxylic acids as comonomers, and thus, this section deals with both classes of PTEs (**26** and **27**). The oldest contribution to this working field is a Flory (73) patent describing polycondensations of α,ω-dimercaptoalkanes (having 2, 4, 6, 8 and 10 CH$_2$ groups) with adipoyl chloride. The reaction partners were heated from 20 to 218°C without the addition of solvents, HCl acceptors or catalysts. The liberated HCl was removed with a permanent stream of dry nitrogen Eqs. (58) and (59). Melting temperatures but no absolute molecular weights and melt viscosities were reported. Another group (74, 75) conducted polycondensations of α,ω-dithiols and aliphatic dicarboxylic dichloride in benzene by addition of pyridine as HCl acceptor and catalyst. The low inherent viscosities suggest that only low molar mass polyesters were obtained. The same group also described a quite different synthetic method, namely polyaddition of aliphatic or aromatic dithiocarboxylic acid onto bisallyl Eqs. (60) and (61). This polyaddition had a UV-light catalyzed radical mechanism and was a clean process in such a sense that isomeric units of structure **28** were not formed. The PTEs resulting from polyaddition Eqs. (60), (61) had nearly the same melting temperatures as those prepared by polycondensation. However, the molecular weights were not significantly higher. One PTE prepared by interfacial polycondensation of 1,2-dimercaptoethane and iso-cinchomeroyl chloride is mentioned in a British patent (76), but without detailed characterization.

$$(61)$$
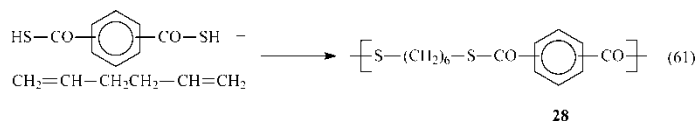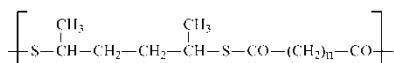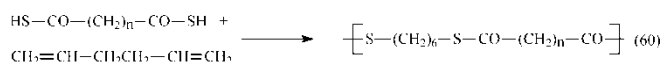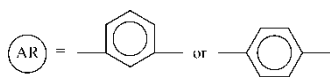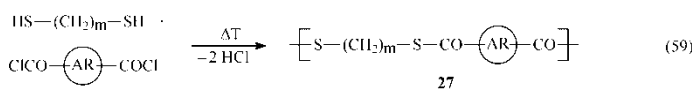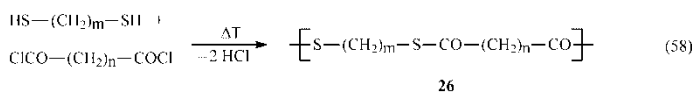
A broader study of interfacial polycondensations of α,ω-dithiols with various aliphatic or aromatic dicarbonyl chlorides (yielding PTEs of structure **26** and **27**) was presented in a U.S. patent (77). Aqueous sodium hydroxide in combination with benzene was used as reaction medium and optimization of the reaction conditions gave PTEs of moderate to high molar masses. Molecular weight data were not reported, but most PTEs allowed for melt-spinning of fibers with good mechanical properties. An unusual synthetic method yielding PTEs of structure **26** was reported by Kricheldorf et al. (78, 79). The cyclic tin derivatives of 1,2-dimercapto ethane **29** (2,2-dibutyl-2-stanna-1,3-ditholane) and of 1,3-dimercapto propane **30** (2,2-dibutyl-2-stanna-1,3-dithiane) served as monomers. These monomers undergo an exothermic ring-opening polycondensation when mixed with aliphatic dicarboxylic acid dichlorides Eqs. (62) and (63). The cyclic monomers **29** and **30** have the advantage to be less sensitive to oxidation than the free dithiols and they are easy to purify by recrystallization. The inherent viscosities indicate that moderate to high molar masses and in several cases SEC measurements were performed which gave uncorrected M_n values up to 30,000 Da. The MALDI-TOF mass spectra proved that these PTEs mainly consisted of cycles and that the chain growth was limited by cyclization. This result agrees perfectly with Kricheldorf's theory of polycondensation (80) which predicts that a clean polycondensation yields 100% cycles when the conversion approaches 100% under optimized reaction conditions. At this point, it should be mentioned that no other research group characterized their PTEs by MALDI-TOF mass spectrometry, so that the question, if cyclic polymers were formed and how the extent of cyclization corresponds to the reaction conditions, was not discussed in any other publication. Another interesting aspect of these studies concerns the thermal properties of the PTEs prepared from monomer **30**. DSC measurements revealed two endotherms and two exotherms in the heating and cooling traces respectively. WAXS measurements with variation of the temperature proved that these PTEs undergo a reversible change of the crystal modification, a physical property which is rarely observed for aliphatic polymers.

$$(58)$$
26

$$(59)$$
27

$$(60)$$

$$(62)$$
29

$$(63)$$
30

$$HS-(CH_2)_6-SH \; + \quad \xrightarrow[\text{dilution}]{\text{Lipase}} \quad \left[S-(CH_2)_6-S-CO-(CH_2)_8-CO \right] \qquad (64)$$
$$CH_3O_2C-(CH_2)_8-CO_2CH_3$$

cyclic oligoesters

Finally, it should be mentioned that PTEs of structure **26** were also prepared by an enzymatically-catalyzed polycondensation process (81). 1,6-Dimercaptohexane was reacted at 120°C with the diethyl esters of various aliphatic dicarboxylic acids in the presence of an immobilized lipase of "candida antarctica" (Novozym 435®). Regardless of the lengths of the dicarboxylic acid (n = 1−8), uncorrected number average molecular weights (M_ns) in the range of 3,000−5,000 Da were determined by SEC. However, the same authors also reported another interesting approach. 1,6-Dimercaptohexane and dimethyl sebacate were polycondensed in solution and cyclic oligoesters were isolated by column chromatography Eq. (64). These cycles were heated with Novozym 435® in bulk to 120°C, and PTE having a M_n around 50,000 Da were obtained. Another group (82, 83) reported on syntheses of oligomers PTEs by polycondensation of 1,6-hexanedithiol with either 1.10-decane dicarboxylic acid or its dimethyl ester in bulk. The immobilized enzyme lipozyme RMIM® was used at 80°C and a reaction time of 384 h was needed.

31

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33

34

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36

37

38
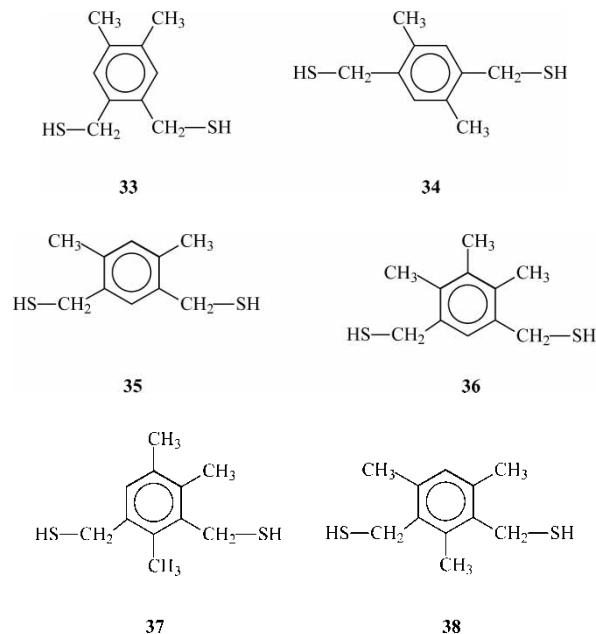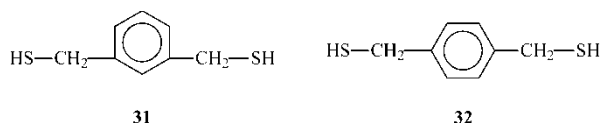
The melting temperatures of all PTEs were compiled in Table 3 together with those of their O-analogs. A comparison of these values demonstrates that in all cases the T_ms of the PTEs were higher.

1.5 Semi-Aromatic and Aromatic Polythioesters

Semi-aromatic PTE means polythioesters containing aromatic and aliphatic groups in the repeat units. According to this simple definition, the aforementioned PTEs of structure **27** also belong to the group of semi-aromatic PTEs. All

Table 3. Glass-transitions (Tg) and melting temperatures (Tms) of Poly(thio)esters derived from α,ω-dimercaptoalkanes or α,ω-dihydroxyalkanes and aliphatic dicarboxylic acids

HS-(A)-SH	HOOC-(A)-COOH	Tg (°C)	Tm (°C)	Ref.	HO-(A)-OH	HOOC-(A)-COOH	Tg (°C)	Tm (°C)	Ref.
-(CH₂)₂-	-(CH₂)₂-	—	194	[78]	-(CH₂)₂-	-(CH₂)₂-	−11	104	[201]
-(CH₂)₂-	-(CH₂)₄-	—	154	[78]	-(CH₂)₂-	-(CH₂)₄-	−47	46	[203]
		—	111−125	[3]			−46	52	[204]
-(CH₂)₂-	-(CH₂)₆-	—	146	[78]	-(CH₂)₂-	-(CH₂)₆-	—	65	[205]
		—						76	[205]
-(CH₂)₂-	-(CH₂)₈-	—	128	[78]	-(CH₂)₂-	-(CH₂)₈-	—	83	[205]
-(CH₂)₂-	-(CH₂)₁₀-	—	126	[78]	-(CH₂)₂-	-(CH₂)₂-	—	82	[208]
-(CH₂)₃-	-(CH₂)₂-	—	126	[79]	-(CH₂)₃-	-(CH₂)₂-	−35	46	[201]
-(CH₂)₃-	-(CH₂)₄-	—	127	[79]	-(CH₂)₃-	-(CH₂)₄-	−59	52	[204]
-(CH₂)₃-	-(CH₂)₆-	—	106	[79]	-(CH₂)₃-	-(CH₂)₆-	—	—	[209]
-(CH₂)₃-	-(CH₂)₈-		94	[79]	-(CH₂)₃-	-(CH₂)₈-	—	—	[209]
-(CH₂)₄-	-(CH₂)₄-	—	109	[74]	-(CH₂)₄-	-(CH₂)₄-	−60	60	[202]
			95−100	[74]			—	64	[206]
							−58	62	[207]
-(CH₂)₄-	-(CH₂)₆-	—	121	[79]	-(CH₂)₄-	-(CH₂)₆-	—	58	[206]
-(CH₂)₆-	-(CH₂)₄-	—	97−104	[74]	-(CH₂)₆-	-(CH₂)₄-	−69	55, 58	[207, 210]
-(CH₂)₆-	-(CH₂)₆-	—	121	[79]	-(CH₂)₆-	-(CH₂)₆-	—	67	[210]
-(CH₂)₁₀-	-(CH₂)₄-	—	70−75	[74]	-(CH₂)₁₀-	-(CH₂)₄-	—	74	[210]

the PTEs discussed in this section (84−114) have in common that they were prepared by interfacial polycondensations. Far most of the studies published in this field were contributed by Podkoscielny and coworkers (84−110). This group prepared semi-aromatic and fully aromatic PTEs by polycondensation of dithiol dissolved in sodium hydroxide with dicarboxylic acid dichlorides dissolved in an organic solvent such as chloroform, benzene or hexane. For most PTEs, those authors optimized the reaction conditions by variation of the organic solvent, variation of the excess of sodium hydroxide, variation of the volume ratio organic phase/aqueous phase, variation of the temperature and addition of an emulsifier (e.g. Mersolan®). The highest yields and molecular weights were usually obtained at low temperatures (5−10°C), with benzene as organic phase and with 100% excess of sodium hydroxide. For several monomers combinations interfacial polycondensations were compared with polycondensations in homogeneous organic solutions (86, 96, 100). Two versions of "solution polycondensations" were studied. The "low-temperature polycondensations" were conducted at 10−20°C with addition of triethylamine as HCl acceptor. Choroform, benzene, chlorobenzene or dioxane were used as solvents. The "high-temperature polycondensations" were performed in boiling xylene without addition of a HCl acceptor. All these studies and comparisons revealed that the highest molar masses resulted from interfacial polycondensations, but no mechanistic explanation was forwarded.

In this context, recent publications (111, 112) of Kricheldorf et al. are of interest, which report on polycondensations of bisphenol-A with diphosgene or bisphenol-A bischloroformate. Tertiary amine promoted polycondensations in homogeneous organic phase (CH_2Cl_2 or dioxane) were compared to interfacial polycondensations (CH_2Cl_2/NaOH) performed at similar temperatures and with identical monomer concentrations. Both methods were carefully optimized and MALDI-TOF mass spectrometry revealed that both methods mainly yielded cyclic polycarbonates, what means that in both cases the chain growth was limited by cyclization. Yet, the interfacial polycondensations yielded much higher molecular weights. For reasons discussed in Ref. 112 the cyclization/chain growth ratio was higher in the homogeneous organic phase and this explanation also seems to be valid for the syntheses of poly(thioester)s studied by Podkoscielny and coworkers.

Podkoscielny and coworkers characterized the structure of the isolated PTEs by elemental analyses, IR-spectra and solution viscosities. The poor solubility of most PTEs in tetrahydrofuran prevented SEC measurement. The evaluation of physical and mechanical properties was performed by DSC and TGA measurements, and by measuring the vicat softening points, tensile strengths, impact strengths, bending strengths, dielectrical constants and dielectrical loss factors. PTEs of the dithiols **31** and **32** were cited in Refs. 99 + 100, PTEs of **33−35** in Refs. 94, 96, 100, PTEs of **36−38** in Refs. 95, 97, 100, PTEs of **39** in Refs. 90, 91,

100, PTEs of **40** and **41** in Refs. 85, 86, PTEs of **42** in Refs. 103 + 108, PTEs of **43** in Ref. 105, PTEs of **44** in Ref. 107, PTEs of **45** in Ref. 109, PTEs of **46** in Refs. 84, 87, 88, PTEs of **47** in Ref. 110, PTEs of **48** in Ref. 106, PTEs of **49** in Refs. 90 + 93, PTEs of **50** in Ref. 101, PTEs of **51** in Ref 93, PTEs of **52** in Refs. 101 and 104 PTE of **53** in Ref. 98.
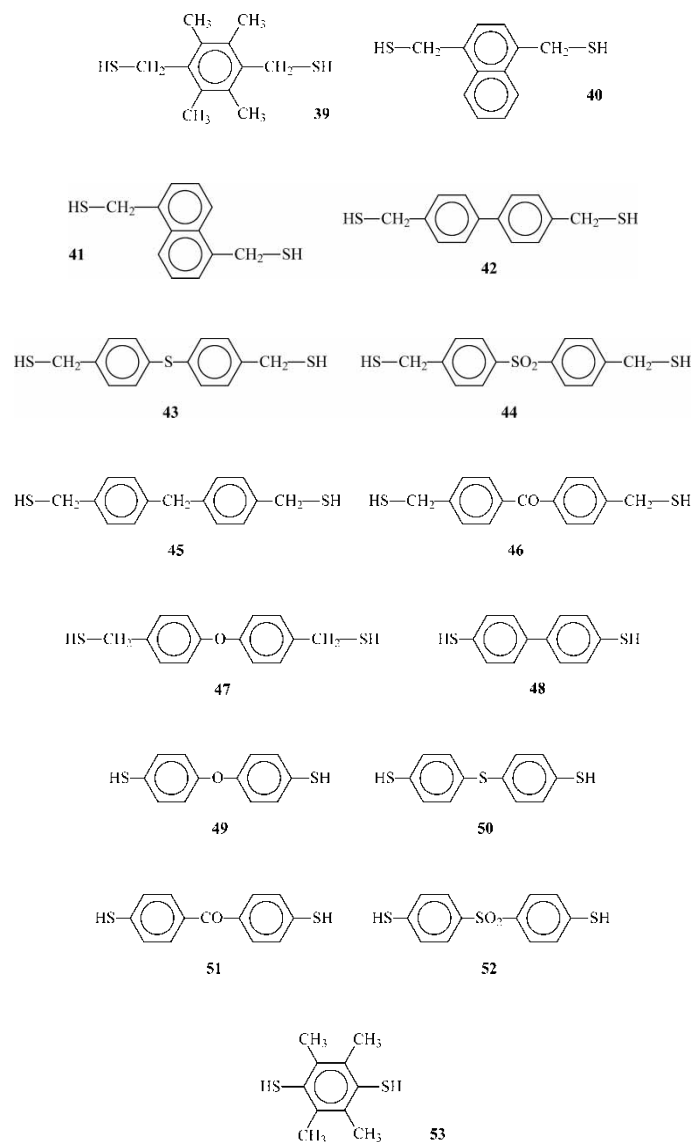
PTEs of 4,4-dimercapto biphenyl (**48**) and aliphatic of α,ω-dicarboxylic acids were also prepared via interfacial polycondensations by an Italian group (113). They were characterized by IR-, ^{1}H-NMR spectroscopy, by SEC, DSC and X-ray scattering measurements. A reversible change of the crystal modification was found by variation of the temperature but no liquid-crystalline phase. Interfacial syntheses of PTEs from 4,4-bis-mercaptodiphenyl sulfide and aliphatic or aromatic dicarboxylic acid dichlorides were also conducted by a Japanese research group (114, 115). M_n values in the range of 10−15 kDa were obtained for the PTEs of the aliphatic

dicarboxylic acids and an odd-even effect for T_g and T_m. Membrane properties such as O_2-permeability were also studied. Finally, the preparation of new PTEs having the structure **54** via an interfacial alkylation process Eq. (65) should be mentioned (116). The purpose of that study was the synthesis of electroconducting materials by cyclization in H_2SO_4, so that fully conjugated polymers having dithia fulvenium groups in the main chain (**55**) were obtained.

(65)

55
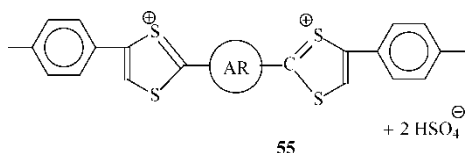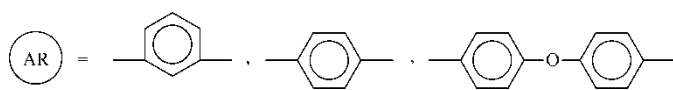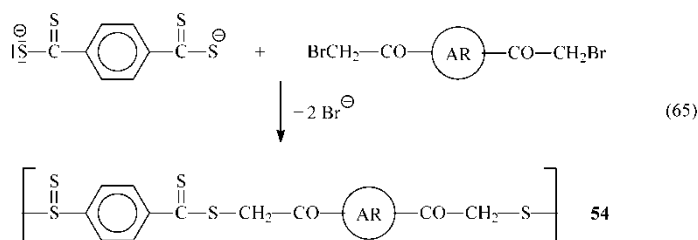
1.6 Various Aromatic Poly(thioester)s

This section is focused on cyclic aromatic oligo-and poly(thio ester)s, on the one hand, and polyesters based on 4-mercapto-benzoic acid, on the other. A first report on cyclic aromatic oligo-and poly(thio ester)s was published in 1987 and deals with syntheses and reactions of benzothiet-2-one (**56**) (117). This highly reactive monomer can be synthesized in various ways as outlined in Scheme 1. Benzothiet-2-one can be stored below $-40°C$, but demerges almost quantitatively when slowly heated to $-40°C$ (Eq. (66). Rapid heating to temperatures $\geq -20°C$ results in formation of cyclic oligoesters and a poly(thio ester) the structure of which was not studied in detail Eq. (67). Yet, the cyclic trimer was isolated and characterized. The same group also synthesized the naphthol-[2,1-b]-thiet-1-one **57** which is more stable than **56** and allows storage at $-18°C$. However, storage at room temperature results in slow polymerization including formation of cyclic oligothioesters. The cyclic dimer was obtained in a yield of 20% Eq. (68), in addition to higher oligomers, when solid **57** was heated to 40°C. Unfortunately, those authors did not made any comment on the mechanism (homolytic or heterolytic) of these oligomerization reactions. A broad variety of cyclic mono-and oligoesters was prepared
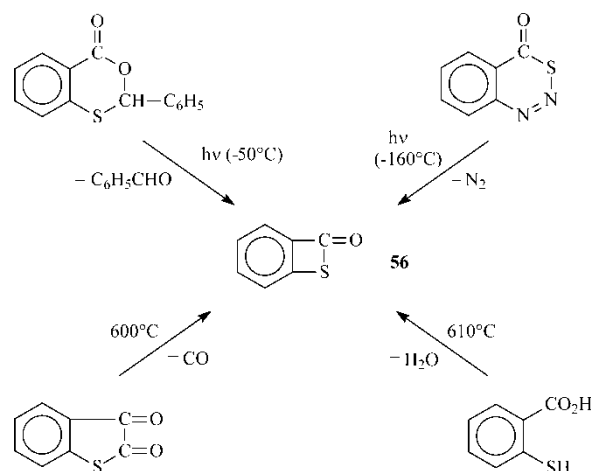
Sch. 1. Syntheses of benzthiet-2-one.

(and characterized) by polycondensation of phthaloyl chloride with catechol, 4-methyl catechol or dithio catechol in THF at 0°C (118). Most of the cyclic oligoesters were extracted from the reaction product by means of diethyl ether and individual cycles were isolated by HPLC. It was found that the monomeric cycles possessed spirocyclic structure **58** in Eq. (69), whereas the higher cyclic oligoesters possessed the normal structure **59** in Eq. (70).

(66)

(67)

(68)
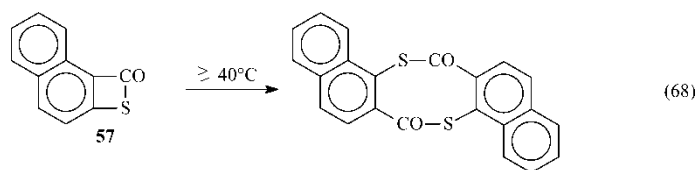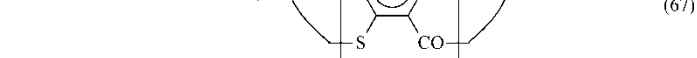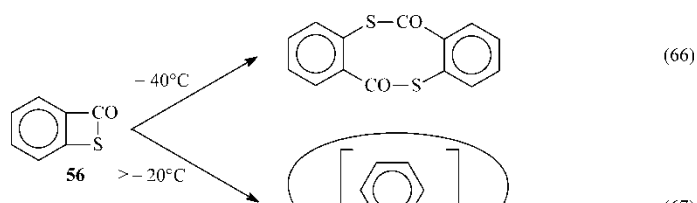
In three papers (119–121) Kameyama et al. reported on syntheses and ring-opening polymerizations of cyclic oligo(thio ester)s **60** and **61**. The syntheses were performed by interfacial polycondensations of the aromatic dithiols with dicarboxylic acid dichlorides Eqs. (71) and (72). The individual cyclic oligoesters were isolated by means of HPLC. They showed melting temperatures in the range of 280–360°C. The authors reported that these cyclic oligomers underwent spontaneous polymerization in the solid state by heating to temperatures well below their melting points (typical reaction temperatures 260 or 280°C). When potassium halide crown

ether complexes were added the initial polymerization temperatures could be lowered to 220 or even 200°C, but the resulting molecular weights were mostly lower. On the other hand, the PTEs prepared in this way were described to the amorphous with T_gs around 180°C (derived from **60**) or 161°C (derived from **61**). Yet, these properties mean that the thermal polymerizations mainly proceeded in polymer melts and not in the solid state as claimed by those authors. High molecular weights were determined by polystyrene-calibrated SEC measurements (M_w values up to 850,000 Da), but never confirmed by light scattering measurements. In one case (121) side reactions via Fries-rearrangement were mentioned, but these PTEs were neither characterized with respect to branching nor with respect to their content of cyclic polymers.

The same group also used the cyclic aromatic oligo(thio ester)s as substrates for an unusual ring-expansion reaction (122). The cyclic dithioester **62** was reacted with phenoxythiirane in hot NMP under the catalytic influence of tetrabutyl ammonium chloride or tetraphenyl phosphonium bromide. The insertion reaction outlined in the simplified equation (73) produced cyclic oligomers and polymers containing thioester and sulfide groups. Due to transesterification reactions complex reaction mixtures with M_n values up to 9,000 Da were obtained. The reaction products were characterized by NMR spectroscopy and MALDI-TOF mass spectrometry.

All publications describing PTEs derived from mercaptobenzoic acids concern 4-mercaptobenzoic acid, whereas studies of PTEs based on 2-mercapto- or 3-mercaptobenzoic acid are still lacking. Kricheldorf et al. (123) were the first who prepared poly(4-thio benzoate) by polycondensation of acetylated 4-mercaptobenzoic acid in thermostable solvent (Marlotherm-S), whereby the crystalline polyester precipitated from the reaction mixture. The time-temperature program was varied and final reaction temperatures up to 400°C were applied. Average degrees of polymerizations up to 200 were determined by ^{1}H-NMR endgroup analyses after hydrolysis of this insoluble PTE. The binary copolyesters **63** and the ternary copolyesters **64** and **65** were prepared analogously or by copolycondensation of mixtures of acetylated hydroxy and mercaptobenzoic acid in bulk catalyzed with MgO. Poly(4-thio benzoate) and its copolyesters with 4-hydroxybenzoic acid (**63**, X = H) were of interest, because SEC measurements and WAXS measurements proved that a reversible change of the crystal modifications occurs at temperatures above 320°C. However, such first order transitions were absent in other copolyesters and no copolyester displayed a liquid-crystalline phase. Regardless of homo-or copolyesters the melting process above 400°C was combined with rapid degradation.

Later the Kimura group studied homo- and copolycondensations of acetylated 4-mercaptobenzoic acid in much detail, mostly using paraffin as liquid reaction medium (124−130). The purpose of those studies was the preparation of needle-like crystals, so-called "whiskers". The influence of the

reaction conditions on the aspect ratio of the whiskers was studied. Longer whiskers were typically obtained by aromatic reaction media. Furthermore, attempts were made to elucidate both polymerization mechanism and crystal growth mechanism. In this connection the four dimers **66**−**69** were also polycondensed to find out, if chain growth and precipitation of crystalline oligomers are fast enough to suppress transesterification and to generate whiskers having an alternating sequence. Furthermore, whiskers having an A-B diblock structure were prepared. At first whiskers of 4-mercaptobenzoic acid were prepared and the polycondensation process was then continued by portionwise addition of 4-acetoxybenzoic acid. The increasing lengths of the resulting whiskers and their thermal properties indicated that indeed diblock copolyesters were obtained (130). Since these whisker crystals consist of bundles of parallel chains they may possess unusual mechanical properties and may, in principle, be useful as reinforcing components of high-performance composites. However, studies in this direction were not reported yet.
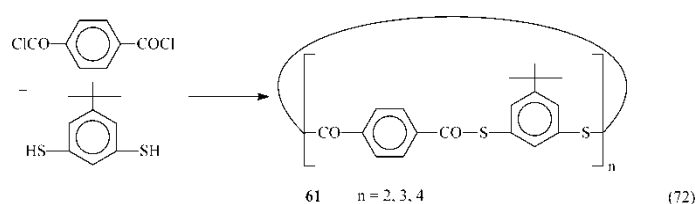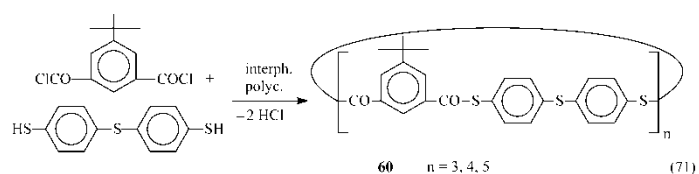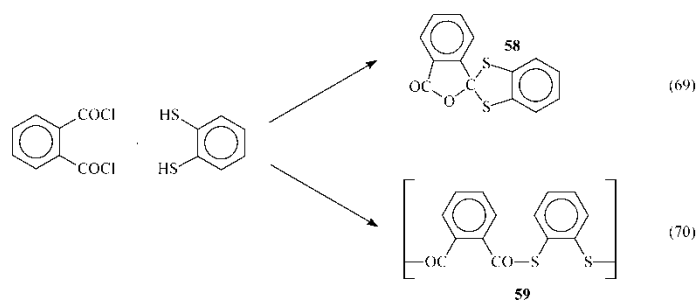
1.4. Aliphatic Polythiocarbonates

Research activities in the field of Polythiocarbonates seemingly begin with the work of Braun and Kissel (131) who studied syntheses of poly(trithiocarbonate)s. Therefore, this section begins with comments on poly(trithiocarbonate)s, whereas a discussion of poly(dithiocarbonate)s and poly(monothiocarbonate)s will follow afterwards.

Braun and Kissel prepared a series of poly(alkylene trithiocarbonate)s by polycondensation of α,ω-dithiols with carbondisulfide catalyzed by tert. amines Eq. (75). The success of this method depended on the length of the alkylene unit, because for n = 2 and n = 3 the monomeric heterocycles **70a** and **70b** were the main products Eq. (76). The viscosity values indicate low molar masses, but molecular weight measurements were not reported. Another approach was described by a Japanese group (132, 133) which studied copolymerizations of ethylene sulfide or 2-methylethylene sulfide (2-methyl thiirane) with carbon disulfide Eq. (77). CdC_2H_5, ZnC and Hg $(S-C_4H_9)_2$ served as catalyst. Low molar mass homo-and copolymers (containing oligoethylenesulfide blocks) were obtained. Those authors also studied model reactions, for instance, the homopolymerization of ethylene trithiocarbonate. Broad variation of the potential catalysts revealed that only conc. H_2SO_4 allowed for an oligomerization of **70a**. Therefore, it was concluded that **70a** may be a byproduct, but not a reactive intermediate in the copolymerization of CS_2 and thiirane.

Two research groups (134−136) reported on the preparation of aliphatic and aromatic poly(trithiocarbonate)s by "polyalkylation" of the trithiocarbonate ion (preformed from CS_2 and Na_2S) by α,ω-dibromoalkanes (eq. (78)) or bis-chloromethyl benzenes (eq. (79)). All these syntheses were conducted by interfacial polycondensations using an excess of CS_2 as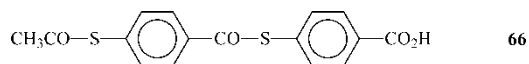 organic phase and tetraalkyl ammonium salts as phase-transfer (PT) catalysts. The solution viscosities suggest low to moderate molar masses. Endgroup analyses were performed assuming two halogen endgroups and without accounting for cyclic oligomers or polymers. A modern version of this approach was recently reported using trithiocarbonate ions bound to an insoluble polymeric support having trimethylammonium groups (136). Dibromoalkanes served as reaction partner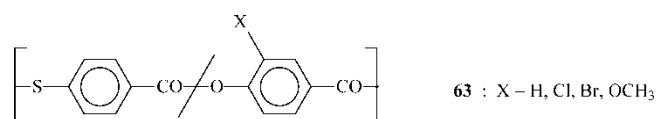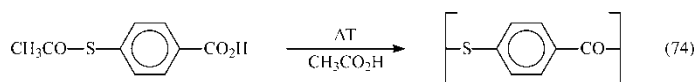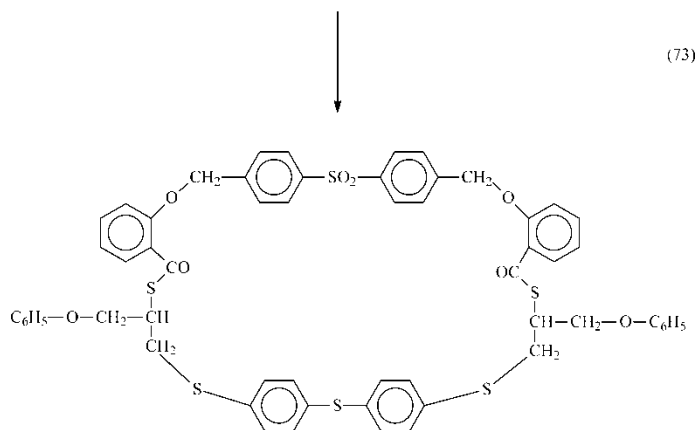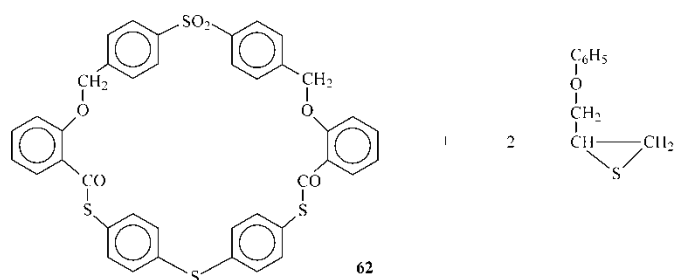s and, depending on the lengths of the dibromoalkanes either cyclic or polymeric trithiocarbonates were obtained. For the polymers M_ns in the range of 3,400 to 11,000 Da were reported, but it is not clear how reliable the calibration of SEC measurements with polystyrene really is. Those authors also calculated P_ns from NMR spectra assuming two Br-endgroups but they did not consider the formation of cyclic oligomers and polymers.

A quite different approach to poly(trithiocarbonate)s was based on the bicyclic tetrathioorthocarbonates **71a−c** which were prepared from $(CH_3S)_4C$ and the corresponding alkane dithiols. The cationic polymerizations of **71a−c** were sluggish even at high temperatures (up to $100°C$) and never yielded clean poly(alkylene trithiocarbonate)s such as **72** or **73**. In the case **71a** (n = 2), degradation was so severe that the polymeric fraction mainly consisted of poly(ethylene sulfide). In the case of **71c,** complex copolymers were obtained seemingly containing repeat units such as those of polymers **72** and **73**. In summary, the spirocycles **71a−c**, proved useless for the preparation of aliphatic

poly(trithiocarbonate)s.

$$HS-(CH_2)_n-SH + CS_2 \xrightarrow{H_2S} \left[S-(CH_2)_n-S-\overset{\overset{\displaystyle S}{\|}}{C} \right] \quad n = 5, 6, 8, 9, 10 \tag{75}$$

$$\xrightarrow{-H_2S} \underset{70a : n = 2}{\overset{(CH_2)_n}{\underset{S}{\overset{S}{\underset{C}{\bigcirc}}}}} \quad 70b : n = 3 \tag{76}$$

$$\underset{R = H, CH_3}{\overset{S}{\underset{CH_2}{\triangle}}\!\!CHR} - CS_2 \xrightarrow{Cat} \left[S-\overset{R}{\underset{}{CH}}-CH_2-S-\overset{\overset{\displaystyle S}{\|}}{C} \right] \tag{77}$$

$$Br-(CH_2)_n-Br + CS_3^{2-} \xrightarrow[(-2\,NaBr)]{PT\text{-}Cat} \left[S-(CH_2)_n-S-\overset{\overset{\displaystyle S}{\|}}{C} \right] \tag{78}$$

$$ClCH_2-\!\!\bigcirc\!\!-CH_2Cl + CS_3^{2-} \xrightarrow[(-2\,NaCl)]{PT\text{-}Cat} \left[S-CH_2-\!\!\bigcirc\!\!-CH_2-S-\overset{\overset{\displaystyle S}{\|}}{C} \right] \tag{79}$$

$$\overset{CH_3}{\underset{O}{CH_2\!\!\triangle\!\!CH}} + CS_2 \longrightarrow \left[CH_2-\overset{CH_3}{\underset{}{CH}}-O \right]_n \left[\overset{\overset{\displaystyle S}{\|}}{C}-S \right]_n \tag{80}$$

$$\underset{\textbf{71a-c} \ (n = 2, 3, 4)}{\overset{S}{\underset{S}{(CH_2)_n}}\!\!C\!\!\overset{S}{\underset{S}{(CH_2)_n}}}$$

$$\left[S-(CH_2)_n-S-\overset{\overset{\displaystyle S}{\|}}{C}-S-(CH_2)_n \right] \quad \textbf{72}$$

$$\left[S-(CH_2)_n-S-\overset{\overset{\displaystyle S}{\|}}{C} \right] \quad \textbf{73}$$

$$x\ HS-(CH_2)_n-SH \xrightarrow[-\,n\ COCl_2]{(CH_2Cl_2/NaOH)} \left[S-(CH_2)_n-S-\overset{\overset{\displaystyle O}{\|}}{C} \right]_x \quad \textbf{76} \tag{81}$$

$$\underset{ClOC-O-\bigcirc\!\!-\!\!|\!\!-\!\!\bigcirc\!\!-O-COCl}{\overset{HS-(CH_2)_n-SH}{\downarrow}} \longrightarrow \left[S-(CH_2)_n-S-\overset{\overset{\displaystyle O}{\|}}{C}-O-\bigcirc\!\!-\!\!|\!\!-\!\!\bigcirc\!\!-O-CO \right] \tag{82}$$

$$\overset{R}{\underset{-CS_2}{CH_2\!\!\triangle\!\!CH}} \xrightarrow{(LiBr)} \underset{\textbf{77 a-l}}{\overset{CH_2-\overset{R}{\underset{}{CH}}}{\underset{S\quad O}{\underset{CS}{\smallfrown}}}} \tag{83}$$

a : R = CH₃

b : R = C₂H₅

c : R = CH₂Cl

d : R = CH₂O—C₆H₅

e : R = CH₂O—COCH₃

f : R = CH₂O—COC₆H₅

g : R = CH₂O—CO—C₆H₄Cl

h : R = CH₂O—CO—C₆H₄OCH₃

i : R = CH₂O—CO—C₆H₄NO₂

k : R = CH₂O—CO—C₆H₄C(CH₃)₃

l : R = CH₂O—CO—(naphthyl)

$$\underset{S\quad O}{\underset{CS}{\overset{CH_2-\overset{R}{\underset{}{CH}}}{\smallfrown}}} \xrightarrow[ZnCl_2]{CF_3SO_3H} \underset{\textbf{78 a-l}}{\overset{CH_2-\overset{R}{\underset{}{CH}}}{\underset{S\quad S}{\underset{CO}{\smallfrown}}}} \tag{84}$$

$$\xrightarrow{CF_3SO_3Me} CH_3-S-CS \left[S-CH_2-\overset{R}{\underset{}{CH}}-S-\overset{\overset{\displaystyle O}{\|}}{C} \right] \quad \textbf{79 a-l} \tag{85}$$

Studies of poly(dithiocarbonate)s began with copolymerizations of epoxides (oxiranes) with carbon disulfide (138, 139). After a short conference report of Inoue et al. (136), Adashi et al. (139) published a detailed study of copolymerizations of propylene oxide and carbon disulfide. Diethyl zink in combination with various bases was used as catalyst. Eq. (80) was presented by those authors, but in addition to ether groups, these copolymers may, in principle, contain six different kinds of dithiocarbonate groups, because partial isomerization of the thiono groups **74a–c** into the carbonate groups **75a–c** was observed by IR spectroscopy (Scheme 2). Yet, with the analytical methods of that time, a full elucidation of composition and sequences was not feasible.

Perfect aliphatic homopolymers having S-CO-S-dithiocarbonate groups (76) were later prepared by an Italian research group (140) via interfacial polycondensations of α,ω-alkane-dithiols Eq. (81). Absolute molar masses were not reported, but the intrinsic viscosities suggest that in individual cases,

$$-CH_2-\overset{CH_3}{\underset{}{CH}}-O-\overset{\overset{\displaystyle S}{\|}}{C}-S-\overset{CH_3}{\underset{}{CH}}-CH_2- \qquad -CH_2-\overset{CH_3}{\underset{}{CH}}-S-\overset{\overset{\displaystyle O}{\|}}{C}-S-\overset{CH_3}{\underset{}{CH}}-CH_2-$$

$$-CH_2-\overset{CH_3}{\underset{}{CH}}-O-\overset{\overset{\displaystyle S}{\|}}{C}-S-CH_2-\overset{CH_3}{\underset{}{CH}}- \qquad -CH_2-\overset{CH_3}{\underset{}{CH}}-S-\overset{\overset{\displaystyle O}{\|}}{C}-S-CH_2-\overset{CH_3}{\underset{}{CH}}-$$

$$-\overset{CH_3}{\underset{}{CH}}-CH_2-O-\overset{\overset{\displaystyle S}{\|}}{C}-S-CH_2-\overset{CH_3}{\underset{}{CH}}- \qquad -\overset{CH_3}{\underset{}{CH}}-CH_2-S-\overset{\overset{\displaystyle O}{\|}}{C}-S-CH_2-\overset{CH_3}{\underset{}{CH}}-$$

$$\textbf{74 a-c} \qquad\qquad\qquad\qquad \textbf{75 a-c}$$
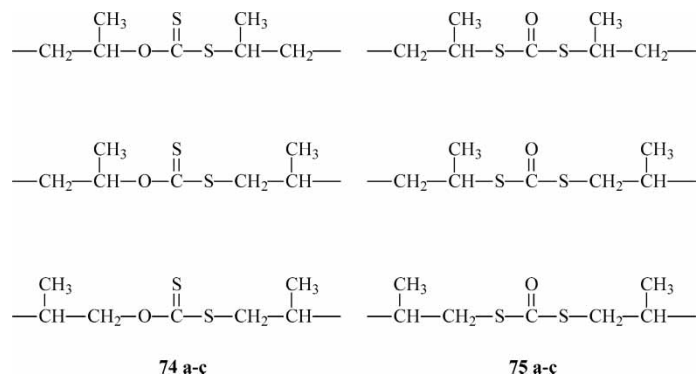
Sch. 2. Isomeric dithiocarbonate groups which may, in principle, result from copolymerization of propylene oxide and CS₂.

high molar masses were obtained. Copoly(monothiocarbonate)s having an alternating sequence of aromatic and aliphatic moieties were analogously prepared by means of bisphenol-A bischloroformate Eq. (82).

Further poly(dithiocarbonate)s having the S-CO-S structure were prepared by Endo and coworkers (141−145) via ring-opening polymerizations of five numbered 1,3-oxathiolane-2-thiones **77a−l**. These heterocycles were prepared from oxiranes and CS_2 in a lithium bromide catalyzed insertion reaction Eq. (83). They were isolated and characterized. Detailed studies of their reactions with acidic (cationic) catalysts revealed the following trends (143−145). With zinc chloride or triflic acid isomerization to the thermodynamically more stable 1,3-dithiolane-2-ones **78a−l** took place. Depending on the substituent, this isomerization reached 100% in several cases Eq. (84). Yet when **77a−l** were treated with methyl or ethyl triflate in bulk, cationic polymerizations yielding poly(dithiocarbonate)s of structure **79a−l** became the main reaction Eq. (85). With $BF_3 \cdot OEt$ monomer **77d** yielded various mixtures of **78d** and **79d**. The polar masses (M_n) of the purified poly(dithiocarbonate)s fell typically into the range of 5,000−11,000 Da as determined by comparison with polystyrene in THF (84, 85). The results of Adachi et al. (139) and Endo (143−146) also mean that even when the still unknown poly(dithiocarbonate)s of structure **80** can be synthesized they are thermodynamically unstable and will isomerize upon heating Eq. (86).

(86)

(87)

(88)

(89)

(90)

(91)

(92)
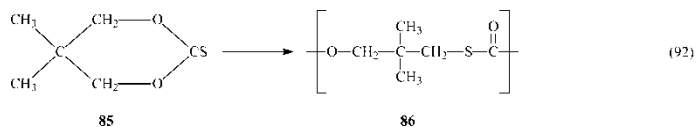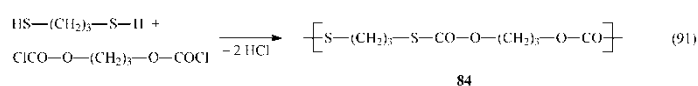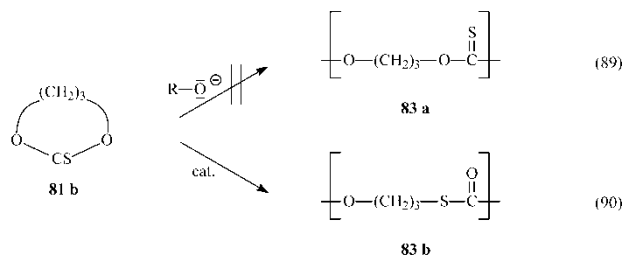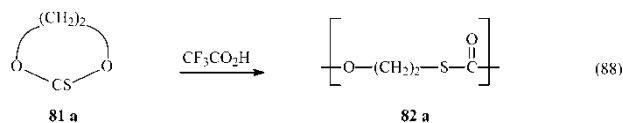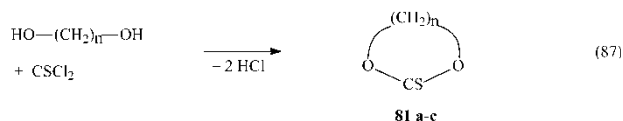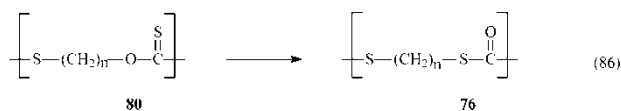
Six papers dealt with syntheses and polymerizations of cyclic monothiocarbonates (147−151). All the monomers described in those papers had the structure of thiono-carbonates (e.g. **81a−c**) and were prepared by cyclization of alkane diols with thiophosgene and pyridine at low concentrations Eq. (87). The first study (147) dealing with this group of monomers was published as early as 1969 and concerned synthesis and polymerization of the five-membered monomer **81a**. Yet, only one cationic polymerization in trifluoroacetic acid yielding oligomers of structure **82a** was performed (147) (Eq. (88)). Almost thirty years later, Kricheldorf et al. (148) reported on synthesis and properties of the six-membered 1,3-dioxane-2-thione **81b**. This monomer proved to be unstable at temperatures of $\geq 20°C$ and underwent slow spontaneous polymerization. The structure of the resulting polythiocarbonate had the structure **83b,** which is easy to distinguish by IR and NMR spectroscopy from that of the "thionopolycarbonate **83a**. Furthermore, the isomeric poly-thiocarbonate **84** was prepared from 1,3-dimercaptopropane Eq. (91). It was demonstrated that ^{13}C-NMR spectroscopy even allows for a distinction between **83b** and **84**. Cationic initiators such as Bu_2SnCl_2, $BuSnCl_3$, $SnCl_4$, $BF_3 \cdot OEt_2$ and methyl triflate greatly accelerated the polymerization of **81b** and yielded the polycarbonate **83b**. Depending on catalyst and purity of the monomer, moderate to high molecular weights were obtained. Surprisingly, even anionic initiators accelerated the polymerization, but no incorporation of the initiator as dead chain was detectable and the resulting polymer had again structure **83b**, a result which is difficult to explain (Eqs. (89), (90)). In contrast to polypropylen carbonate which is amorphous about a M_n of 5,000 Da, the poly(thiocarbonate) **83b** is a rapidly crystallizing material with a T_m around 132°C.

The photoinitiated cationic ROP of the more stable 5,5-dimethyl-1,3-dioxane-2-thione (**85**) was studied by Endo and coworkers (149) Eq. (92). All polymerizations yielded a polymer of structure **86** having M_ns up to 18,000 Da. In the case of the adamantane-based five-membered thionocarbonate **87**, cationic polymerizations may, in principle, involve two modes of ring-opening Eqs. (93) and (94) (150). Regardless, if Et_3OBF_4, $BF_3 \cdot OH_2$, triflic acid or its methyl ester were used as catalysts, all polymers had the structure **89** and not **88**. M_n values up to 10,600 Da were obtained, a volume expansion of 14% was observed during the polymerization. The eight-membered monomer **81c** was again polymerized in CH_2Cl_2 with cationic catalysts such as $BF_3 \cdot OEt_2$, triflic acid and methyl triflate (151). Uniform poly(thiocarbonate)s of structure **82c** having M_n values 29,100 Da were isolated. The satisfactory control of M_n via the monomer/catalyst ratio was achieved. More complex

but interesting results were obtained when the thionocarbonate **81c** was treated with basic or nucleophilic initiators and catalysts (152). With pyridine, triethylamine or potassium tert.butoxide, the resulting poly(thiocarbonate) had the structure **82c** in analogy to the cationic polymerizations. This finding agrees with the observation of Kricheldorf et al. that **81a** also yields a similar poly(thiocarbonate) when confronted with basic initiators (148). However, when basic 1,3-diazabicyclo[5,4,0]-undecene-7 (DBU) was added to **81c**, a copolymer (**90**) was isolated which combined the repeat units of structures **82** and **83** Eq. (96). With primary, secondary or tert.butyl lithium as initiators, partially insoluble reaction products were formed, which were extracted with tetrahydrofuran. The soluble fractions were identified as poly(thiocarbonate)s of structure **83c** and the insoluble polymer gave the same IR-spectrum and elemental analyses. The reasons for the insolubility were not elucidated and the endgroups of the soluble fraction were not identified. In summary, Endo and coworkers proved (152) that from one monomer (i.e. **81c**) two isomeric kinds of poly(thiocarbonate)s can be prepared just by proper variation of initiator and polymerization mechanism.
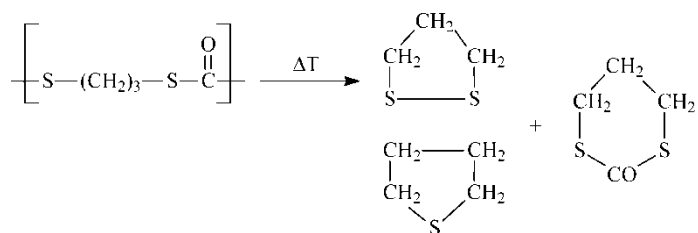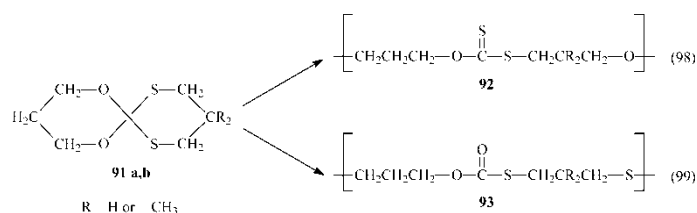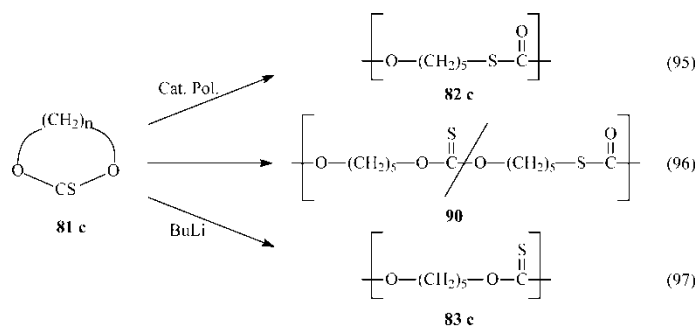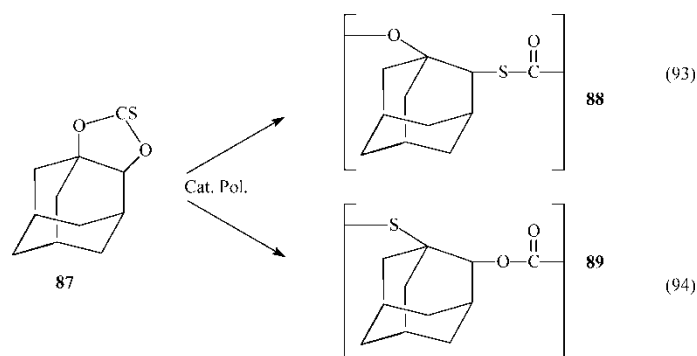
Sch. 3. Reaction product of the thermal degradation of poly(trimethylene dithiocarbonate).

Another research group studied the cationic polymerization of the spirocyclic monomers **91a** and **b** using trityl tetrafluoroborate as initiator (153). Double (or tandem) ring-opening may, in principle, again yield two kinds of isomeric poly(thiocarbonate)s (**92** or **93**) in Eqs. (98) and (99). As expected from the thermodynamic control of this polymerization, exclusively the "polysulfide" **93** having a C=O group was formed.

Finally, two publications should be mentioned which deal with the degradation of poly(dithiocarbonate). In the earlier work (154), thermal degradation of three aliphatic poly(dithiocarbonate)s was studied by pyrolysis/mass spectrometry. As exemplarily outlined in Scheme 3 for poly(trimethylene dithiocarbonate), a cyclic disulfide, a cyclic sulfide and the cyclic monomer were the typical degradation products of all three poly(dithiocarbonate)s. The second work (155) dealt with the cationic polymerization of cyclic thionodicarbonates followed by the acid-catalyzed depolymerization of the resulting poly(dithiocarbonate). In this way, the non-polymerizable isomeric dithiocarbonate was obtained as the main product. ZnCl$_2$ and triflic acid were the preferentially used catalysts.

At the end of this section, a review article should be mentioned (156) which focuses on ring-opening polymerizations involving volume expansion. This article also includes various examples of sulfur-containing polycarbonates.
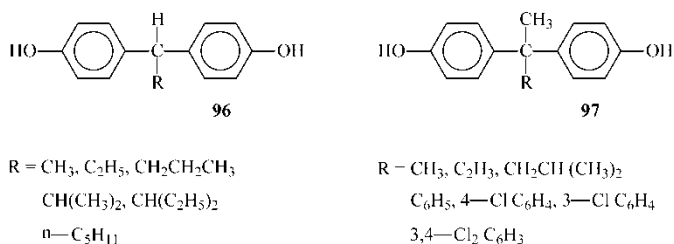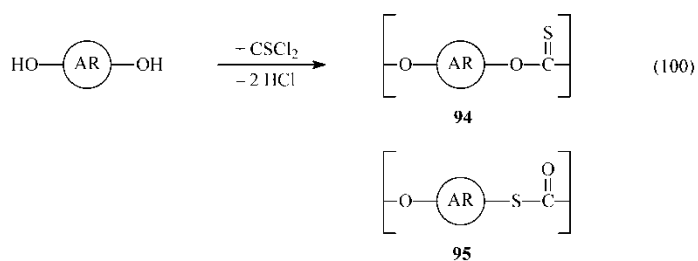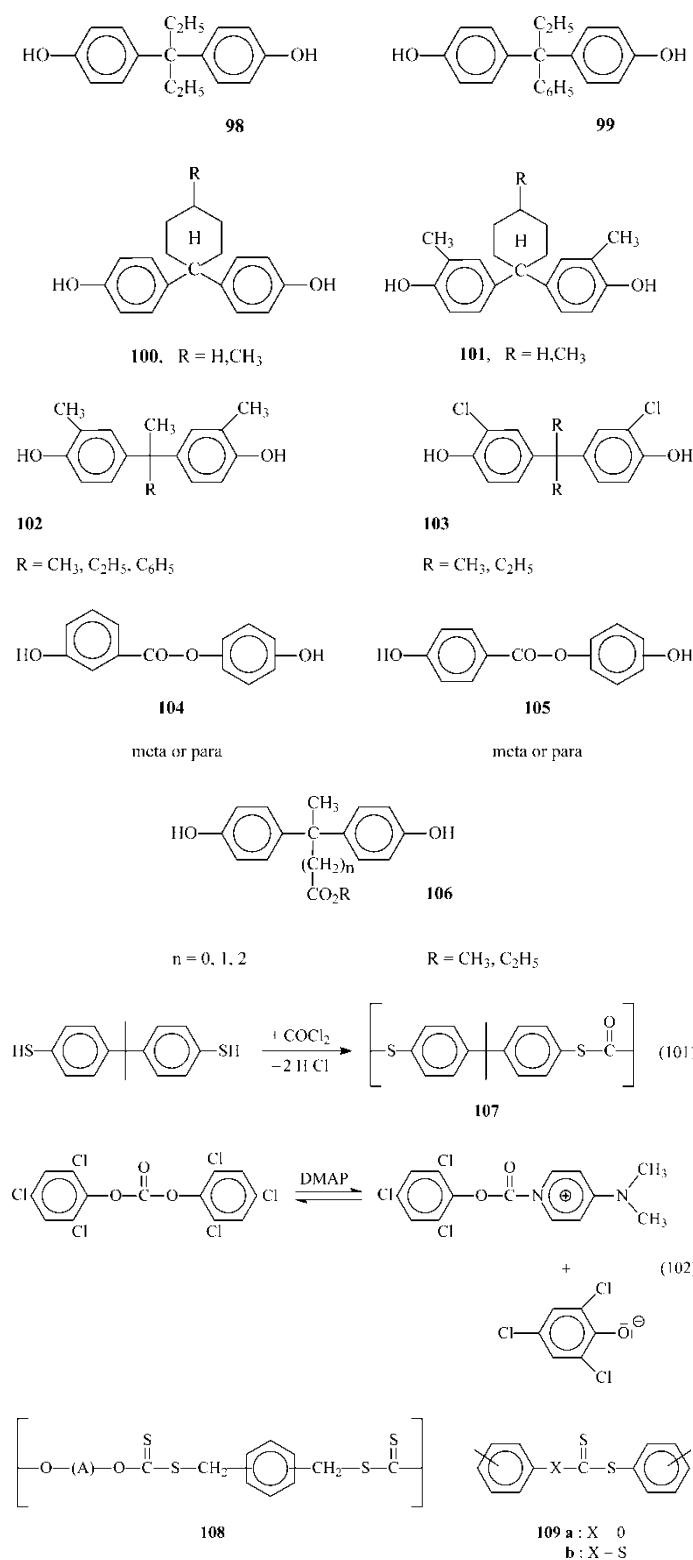
(93)

(94)

(95)

(96)

(97)

(100)

(98)

(99)

R = CH$_3$, C$_2$H$_5$, CH$_2$CH$_2$CH$_3$
CH(CH$_3$)$_2$, CH(C$_2$H$_5$)$_2$
n—C$_5$H$_{11}$

R = CH$_3$, C$_2$H$_5$, CH$_2$CH (CH$_3$)$_2$
C$_6$H$_5$, 4—Cl C$_6$H$_4$, 3—Cl C$_6$H$_4$
3,4—Cl$_2$ C$_6$H$_3$

first polythionocarbonate was prepared by Schlott et al. (157) by polycondensation of bisphenol-A with thiophosgen and triethylamine in dry dichloromethane Eq. (100). Moderate to high molar masses were obtained. The best samples form tough films, and various mechanical properties were measured. Far most studies of poly(thionocarbonate)s were contributed by Tagle and coworkers (158−167). All syntheses were performed by interfacial polycondensations of diphenols with thiophosgene. The influence of various experimental parameters on yield and molecular weights was investigated in much detail. For instance, it was found that the addition of all thiophosgen from the beginning gives higher molar masses than a dropwise addition. Furthermore, relatively hydrophilic phase transfer catalysts were more effective in combination with relatively lipophilic diphenols and lipophilic catalysts in combination with relatively hydrophilic diphenols. The numerous diphenols used in the work of Tagle et al. are summarized under the formula numbers **96− 106**. The syntheses of poly(ester-thiocarbonate)s having ester groups in the main chain on the basis of the isomeric diphenols **104** and **105** are remarkable. Even more surprising are successful interfacial polycondensations of the diphenols **106**, because the aliphatic ester groups in the side chains are more susceptible to alkaline hydrolysis than the aromatic ester groups in the main chain.

Several Chilenian researchers concentrated on the characterization of the poly(thiono carbonate)s prepared by Tagle's group (168−173). For instance, the unperturbed dimensions were determined and Mark-Houwink-Sakurada equations were elaborated (168, 169). Furthermore, dipole moments were measured and glass-transitions were determined and compared to those of S-free polycarbonates (170−173).

Syntheses of aromatic poly(dithiocarbonate)s of structure **107** were shortly mentioned in two patents (174, 175) and more explicitly described in two publications (176, 177). Most syntheses were conducted by interfacial phosgenation of dithiophenols Eq. (101) and included syntheses of copolymers from mixtures of dithiophenols and diphenols (176). 1,3-Dimercaptobenzene and isopropylidene dibenzene thiol were used as "SH-monomers". The patent of Ueda et al. (175) is remarkable, because those authors used reactive substituted diphenyl carbonates as substitutes of the highly poisonous phosgene. In this case, N,N-dimethyl-4-aminopyridine is needed as catalyst, presumably because it activates these carbonates by charge separation Eq. (102). Two papers (178, 179) of an Italian research group dealt with characteristic properties of poly(thiono-carbonate)s and poly(dithio carbonate)s. The refractive indices were determined, because polymers having particularly high refractive indices may be of interest for optical applications (e.g. lenses or fibers). Furthermore, thermal properties of numerous poly (dithio carbonate)s, including semiaromatic species were studied by means of thermogravimetry and pyrolysis mass spectrometry (179).

Finally, it should be mentioned that semi-aromatic poly (dithio carbonate)s (of structure **108**) were prepared from

98

99

100. R = H,CH₃

101, R = H,CH₃

102
R = CH₃, C₂H₅, C₆H₅

103
R = CH₃, C₂H₅

104
meta or para

105
meta or para

106
n = 0, 1, 2   R = CH₃, C₂H₅

107

(101)

(102)

108

109 a : X O
b : X − S

1.7   Aromatic Poly(thiocarbonate)s

All aromatic poly(thiocarbonate)s containing one sulfur atom per repeat unit described so far have the structure **94**, whereas the isomeric polymers of structure **95** are still unknown. The

diols or diphenols and carbondisulfide by alkylation with bis(chloromethyl) or bis(bromomethyl) or bis(bromomethyl)-benzenes (180). However, analogous fully aromatic dithiocarbonates (structure **109a**) or aromatic poly(trithiocarbonate)s (structure **109b**) are seemingly unknown.

1.8 Poly(thio urethane)s

Poly(thio urethane)s were prepared via two completely different synthetic strategies. Strategy I is based on ring-opening polymerizations of cyclic thiourethanes (and will be discussed first), whereas strategy II is based on polyaddition reactions involving a step-growth kinetic.

A first study of synthesis and polymerization of cyclic thionourethanes was published as early as 1966 (181). The monomer **110a** (3-phenyl-1,3-oxazolidine-2-thione) was prepared from 2-phenylaminoethanol and thiophosgene. It was found that this monomer polymerizes just by heating in bulk to temperatures above 140°C. Furthermore, cationic polymerization in nitrobenzene with $BF_3 \cdot OEt_3$ as catalyst proved successful. On the basis of elemental analyses and IR spectra, the poly(thio urethanes) obtained by both polymerization methods had the same structure (**111a**) resulting from a rearrangement of the thiourethane group. In this connection it should be mentioned that before 1966, ^{1}H-NMR spectroscopy was still in its infancy and ^{13}C-NMR spectroscopy or MALDI-TOF mass spectrometry did not exist yet.

Nearly forty years later, Endo and coworkers began with a systematic elaboration of this working field (182–189). It was found that the $BF_3 \cdot OEt_3$ catalyzed polymerization of the N-benzyl perhydro oxazolidine-thione **110b** in nitrobenzene at 100°C had a living character Eq. (104) (182). Polydispersities < 1.10 were found along with a satisfactory control of the molecular weight. When the N-benzylated six-ring monomer **112** was polymerized with methyl triflate or $BF_3 \cdot OEt$ in CH_2Cl_2 or nitrobenzene, the best results were again achieved with $BF_3 \cdot OEt_3$ in nitrobenzene (polymer **113)**, Eq. (105) (183). Again a living polymerization was found which certainly involves the mechanism outlined in the equation (106). These results enabled those authors to prepare the diblock copolymers **114** starting out from the five-membered monomer **110b** or to prepare the A-B-A triblock copolymers **115** beginning with the homopolymerization of **112** (182).

(103)

110 a   **111 a**

(104)

110 b   **111 b**

(105)

112   **113**

(106)

114
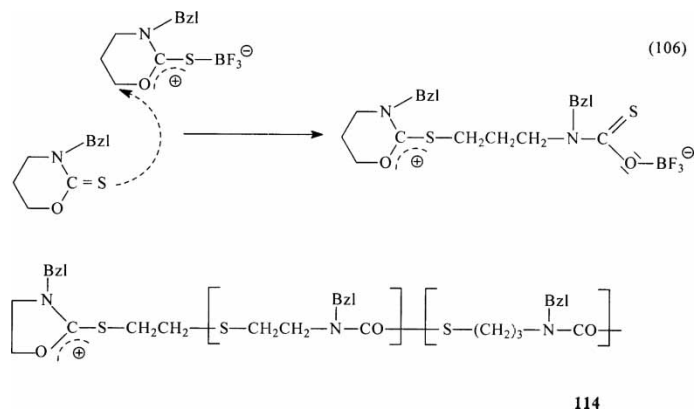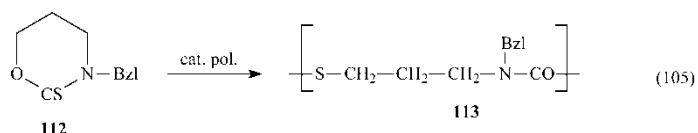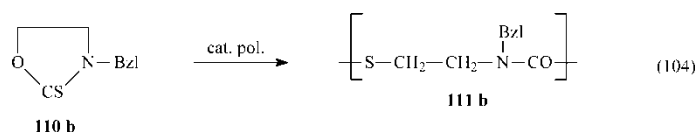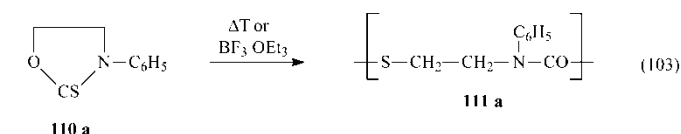
A highly interesting class of cyclic five-membered thionourethanes (**116a**–**d**) was prepared from the methyl ester of L-serine Eq. (107) or of N-substituted L-serines 184–188). Methyl triflate-initiated polymerizations in CH_2Cl_2 gave the best results with almost quantitative yields (structure **117**, Eq. (108) (184). Furthermore, a good control of the molecular weights and polydispersities < 1.10 were achieved. Starting out from L-serine, a chiral initiator which was stable on storage and insensitive to moisture was also synthesized (structure **118**) (185). An analogous reaction pathway (including Eq. (109) was used for the preparation of the cationic initiator **119** which contains a C-C double bond (186). Polymerization of the L-serine based monomer **116a** Eq. (110) yielded a chiral macromer (**120**) which was transformed into a comb-like copolymer by radical polymerization of the styrene group (187). Finally, a detailed MALDI-TOF mass spectrometric analysis of telechelic poly(thio urethane)s should be mentioned (188), which were prepared by cationic polymerizations of the corresponding cyclic thionourethanes. All the expected endgroups were found.

115

(107)

116 a

(108)

116   **117**

$$\text{CF}_3\text{SO}_3^{\ominus} \quad \text{NH}-\text{CH}-\text{CH}_2-\text{O}-\text{CO}-\langle\bigcirc\rangle$$
$$\text{CH}_3-\text{S}-\overset{\oplus}{\text{C}} \quad \quad \text{O}-\text{CH}_2 \quad \textbf{118}$$
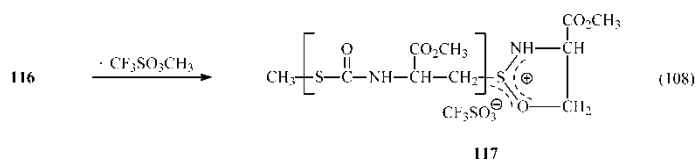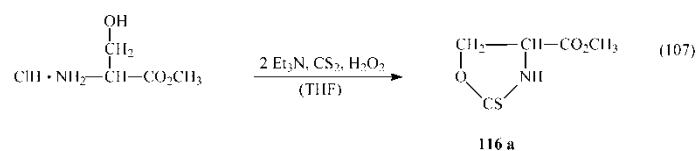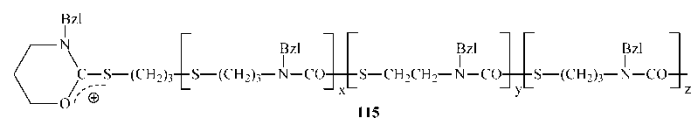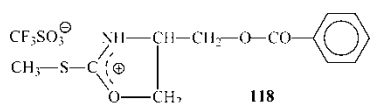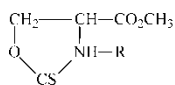
$$\text{CH}_2-\text{CH}-\text{CO}_2\text{CH}_3$$
$$\text{O} \quad \text{NH}-\text{R}$$
$$\text{CS} \quad \textbf{116}$$

b : R $\text{CH}_2\text{C}_6\text{H}_5$
c : R = CO—CH$_3$
d : R – CO—C$_6$H$_5$

$$\begin{array}{ccc}
\text{CH}_3-\text{CH}-\text{CH}_2\text{OH} & & \text{CH}_3-\text{CH}-\text{CH}_2-\text{O}_2\text{C}-\langle\bigcirc\rangle-\text{CH}=\text{CH}_2\\
\text{O} \quad \text{NH} & \xrightarrow[\text{2) CF}_3\text{SO}_3\text{CH}_3]{\text{1) Py (−HCl)}} & \text{O} \quad \text{NH}\\
\text{CS} & & \overset{\oplus}{\text{C}} \quad \text{CF}_3\text{SO}_3^{\ominus}\\
+ & & \text{S}-\text{CH}_3\\
\text{Cl}-\text{CO}-\langle\bigcirc\rangle-\text{CH}=\text{CH}_2 & & \textbf{119}
\end{array} \quad (109)$$

The first syntheses of poly(thio urethane)s were achieved via strategy II shortly mentioned in two patents granted 1942 to E.I. DuPont de Nemours (189, 190). As a concrete example, the addition of dimercaptodecane onto diisocyanatodecane **121a** and Eq. (111) by heating in bulk was described. A broader and more detailed study was then published in 1960 (191). In addition to various α,ω-dimercaptoalkanes, the dimercaptanes **122–124** were used as monomers in combination with 1,6-hexamethylene-diisocyanate or bis(4-isocyanatophenyl) methane. The same authors also explored an alternative approach, namely interfacial polycondensations of α,ω-diaminohexanes with bischloroformiates of the α,ω-dimercapto-alkanes Eq. (112). According to the solution viscosities, low to moderately high molar masses were obtained by both methods, but the second method Eq. (112) gave the better results. A later publication (192) dealing again with the polyaddition of aliphatic dimercaptanes onto diisocyanates was focused on the preparation of telechelics. Starting out from the oligomeric diisocyanate **125**, the telechelic oligomers **126–129** were prepared (Scheme 4).

$$\text{OCN}-(\text{A})\left[\text{NH}-\text{CO}-\text{S}-(\text{CH}_2\text{CH}_2\text{O})-\text{CH}_2\text{CH}_2\text{S}-\text{CO}-\text{NH}-(\text{A})\right]_x\text{NCO}$$
$$\textbf{125}$$
$$\text{PTU}$$

$$\begin{array}{cc}
\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{CO}-\langle\bigcirc\rangle-\text{CH}=\text{CH}_2 & \text{CH}_2-\text{CH}-\text{CO}_2\text{CH}_3\\
\text{O} \quad \overset{\oplus}{\text{N}} & - \text{n} \quad \text{O} \quad \text{NH}\\
\text{C} \quad \text{CH}_3\text{SO}_3^{\ominus} \quad \textbf{120} & \text{CS}\\
\text{S}-\text{CH}_3 &
\end{array}$$

$$\downarrow \quad (110)$$

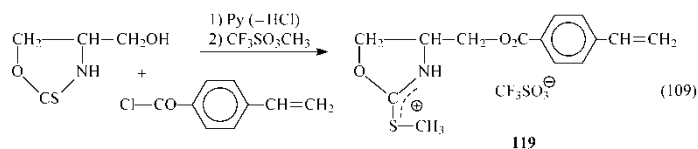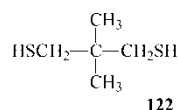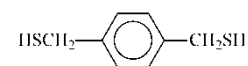$$\text{CH}_3-\text{S}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{NH}-\text{CH}-\text{CH}_2-\left[\text{S}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{NH}-\overset{\text{CO}_2\text{CH}_3}{\text{CH}}-\text{CH}_2\right]$$
$$\text{CH}_2$$
$$\text{O}-\text{CO}-\langle\bigcirc\rangle-\text{CH}=\text{CH}_2$$

$$\text{HSCH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2\text{SH} \quad\quad \text{HSCH}_2-\langle\bigcirc\rangle-\text{CH}_2\text{SH}$$
$$\textbf{122} \quad\quad\quad\quad\quad\quad \textbf{123}$$

$$\text{HSCH}_2-\text{CO}-\text{O}-\text{CH}_2\text{CH}_2\text{O}-\text{CO}-\text{CH}_2\text{SH} \quad \textbf{124}$$

$$\begin{array}{c}
\text{NH}_2-(\text{CH}_2)_m-\text{NH}_2 \quad -\\
\text{ClCO}-\text{S}-(\text{CH}_2)_n-\text{S}-\text{COCl}
\end{array} \xrightarrow[\substack{-2\text{ NaCl}\\-1\text{ H}_2\text{O}}]{2\text{ NaOH}} \left[\text{S}-(\text{CH}_2)n-\text{S}-\text{CO}-\text{NH}-(\text{CH}_2)m-\text{NH}-\text{CO}\right]$$
$$\textbf{121} \quad (112)$$

$$\begin{array}{c}
\text{HS}-(\text{CH}_2)_{10}-\text{SH} \,+\\
\text{OCN}-(\text{CH}_2)_{10}\text{NCO}
\end{array} \xrightarrow{\Delta T} \left[\text{S}-(\text{CH}_2)_{10}-\text{S}-\text{CO}-\text{NH}-(\text{CH}_2)_{10}-\text{NH}-\text{CO}\right] \quad (111)$$
$$\textbf{121 a}$$
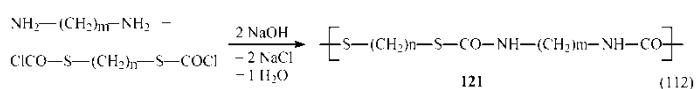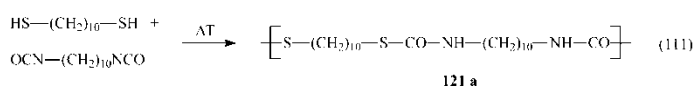
More recently, Endo et al. published three papers (193–195), describing syntheses of various complex poly(thio urethane)s. In all cases, cyclic five-membered

$$\text{HSCH}_2\text{CH}_2-(\text{OCH}_2\text{CH}_2)_2\text{S}-\text{CO}-\text{NH}-(\text{A})-\boxed{\text{PTU}}-\text{NH}-\text{CO}-\text{S}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\text{SH}$$
$$\textbf{126}$$

$$\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CO}-\text{NH}-(\text{A})-\boxed{\text{PTU}}-\text{NH}-\text{CO}-\text{O}-\text{CH}=\text{CH}_2$$
$$\textbf{127}$$

$$\text{CH}_2=\overset{\text{CH}_3}{\underset{}{\text{C}}}-\text{CO}_2-(\text{CH}_2)_2-\text{O}-\text{CO}-\text{NH}-(\text{A})-\boxed{\text{PTU}}-\text{NH}-\text{CO}-(\text{CH}_2)_2-\text{O}_2\text{C}-\overset{\text{CH}_3}{\underset{}{\text{C}}}=\text{CH}_2$$
$$\textbf{128}$$

$$\overset{\text{CH}_2=\text{CH}-\text{CH}_2}{\underset{\text{CH}_2=\text{CH}-\text{CH}_2}{}}\text{N}-\text{CO}-\text{NH}-(\text{A})-\boxed{\text{PTU}}-\text{NH}-\text{CO}-\text{N}\overset{\text{CH}_2-\text{CH}=\text{CH}_2}{\underset{\text{CH}_2-\text{CH}=\text{CH}_2}{}}$$
$$\textbf{129}$$

$$(\text{A}) - \text{—}(\text{CH}_2)_6\text{—}$$

$$-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{CH}_2\text{—}$$
$$+ \text{ Isomer}$$
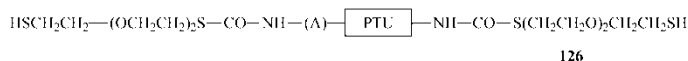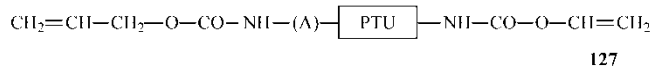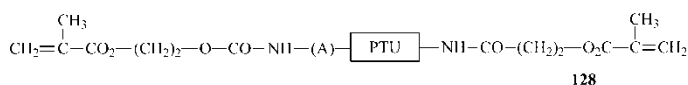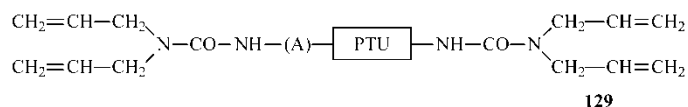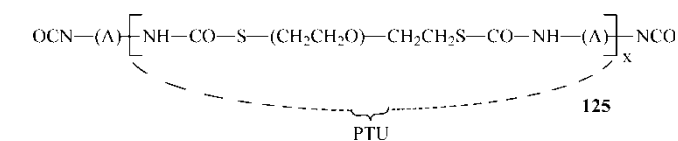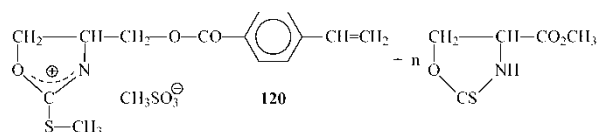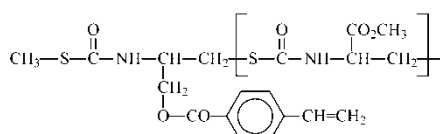
Sch. 4. Telechelic poly(thiourethane)s based on oligo(ethylene oxides)s.
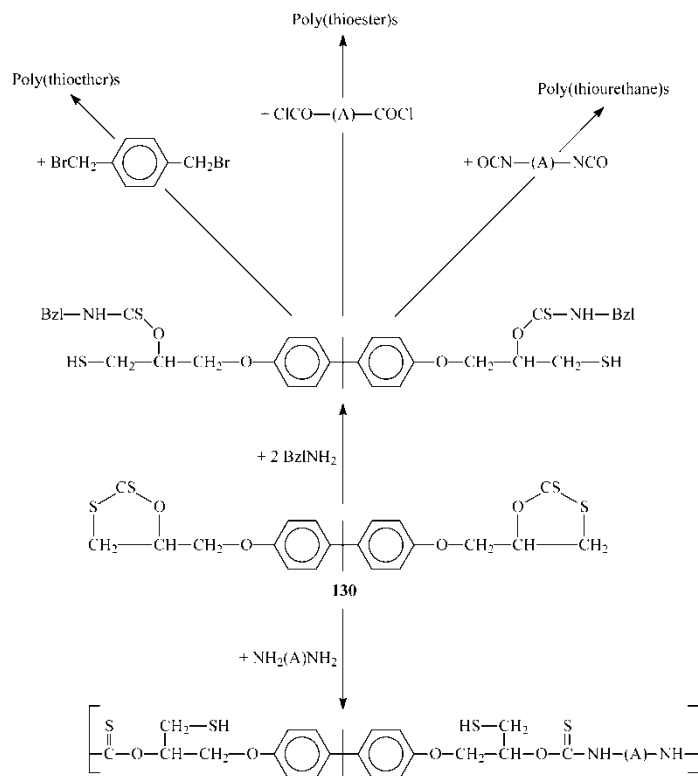
Sch. 5. Syntheses of poly(thiourethane)s and other polymers from a difunctional 1,6-thiolane-2-thione.

dithiocarbonates were used as starting materials. Scheme 5 illustrates how a difunctional thiolane-2-thione **130** can be used for the preparation of various poly(thio urethane)s and for syntheses of poly(thioester)s and poly(thioether)s having thionourethane side groups (193, 194). The trifunctional thiolone-2-thione **131** was analogously reacted with various diamines to yield poly(thio urethane)s networks (195) Eq. (113). In three more papers (196–198), Endo et al. reported on syntheses of polymers bearing thiourethane side chains. In all cases, cyclic dithiocarbonate groups served again as starting materials. The poly(methacrylate)s **132–134** were formulated as examples (197) Eq. (114). In summary, three synthetic methods were described, illustrating the versatility of strategy II.

2 References

1. Lütke-Eversloh, T., Bergander, K., Luftmann, H. and Steinbüchel, A. (2001) *Microbiology* (Reading UK), **147**, 11.
2. Lütke-Eversloh, T. and Steinbüchel, A. (2005) *Microbiol. Lett.*, **221**, 191.
3. Lütke-Eversloh, T., Kawada, I., Marchessault, R.H. and Steinbüchel, A. (2002) *Biomacromolecules*, **3**, 159.
4. Lütke-Eversloh, T., Bergander, K., Luftmann, H. and Steinbüchel, A. (2001) *Biomacromolecules*, **2**, 1061.
5. Lütke-Eversloh, T., Fischer, A., Remminghorst, U., Kawada, I., Marchessault, R.H., Bögershausen, A., Kalwei, M., Eckert, H., Reichelt, R., Liu, S. and Steinbüchel, A. (2003) *Nat. Mater.*, **1**, 236.
6. Kawada, I., Lütke-Eversloh, T., Steinbüchel, A. and Marchessault, R.H. (2003) *Biomacromolecules*, **4**, 1698.
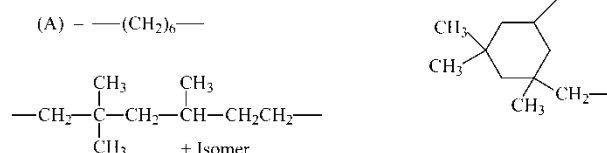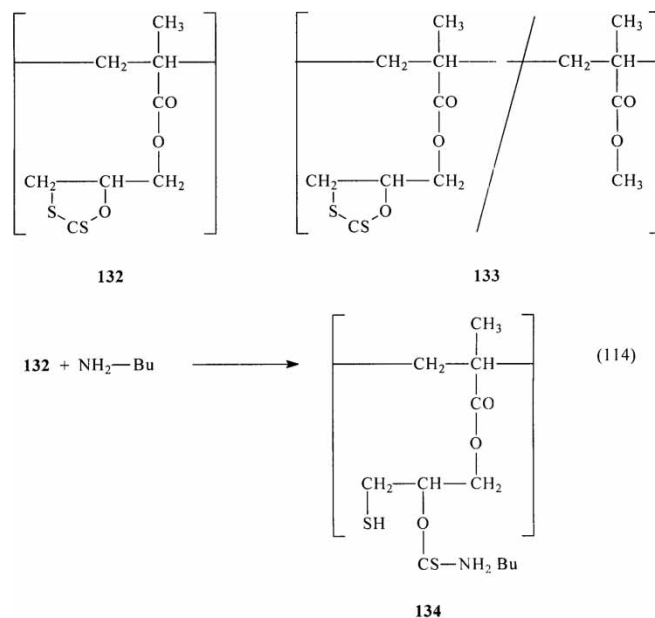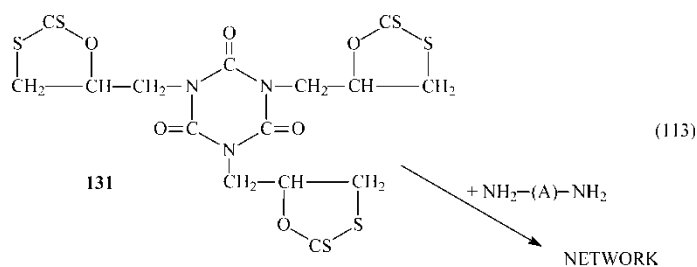7. Lütke-Eversloh, T. and Steinbüchel, A. (2004) *Macromol. Biosc.*, **4**, 165.
8. Kim, D.Y., Lütke-Eversloh, T., Elbana, K., Thakor, N. and Steinbüchel, A. (2005) *Biomacromolecules*, **6**, 897.
9. Schöberl, A. and Krumey, F. (1944) *Ber. Dtsch. Chem. Ges.*, **77**, 1.
10. Schöberl, A. and Wiehler, G. (1954) *Angew. Chem.*, **66**, 273.
11. Schöberl, A. and Wiehler, G. (1955) *Liebigs Ann. Chem.*, **595**, 101.
12. Schöberl, A. (1955) Ger. Pat., **903**, 557.
13. Schöberl, A. (1960) *Macromol. Chem.*, **37**, 64.
14. Schöberl, A. (1948) *Angew. Chem.*, **60**, 7.
15. Elias, H.-G and Bührer, H.G. (1970) *Makromol. Chem.*, **140**, 21.
16. Davies, W.H. (1951) *J. Chem. Soc*; (London), 1357.
17. Davies, W.H. (1951) Brit. Pat. 650003 to I.C.I. Ltd.
18. Kricheldorf, H.R. and Bösinger, K. (1973) *Makromol. Chem.*, **173**, 67.
19. Bührer, H.G. and Elias, H.-G (1970) *Makromol. Chem.*, **140**, 41.
20. Kricheldorf, H.R. (1971) *Angew. Chem.*, **83**, 793.
21. Kricheldorf, H.R., Bösinger, K. and Schwarz, G. (1973) *Makromol. Chem.*, **173**, 43.

22. Kricheldorf, H.R., Lomadze, N. and Schwarz, G. *Macromolecules*, in press.

23. Kricheldorf, H.R., v. Lossow, C. and Schwarz, G. (2005) *Macromolecules*, **38**, 5513.

24. Kricheldorf, H.R. and Leppert, E. (1972) *Macromol. Chem.*, **158**, 223.

25. Kricheldorf, H.R. and Kaschig, J. (1978) *Eur. Polym. J.*, **14**, 923.

26. Fries, K. and Mengl, H. (1912) *Ber. Dtsch. Chem. Ges.*, **45**, 3408.

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

28. Goodrich, B.F. Co. (1956) Brit. Pat. 840.658.

29. Lin'kova, M.G., Kil'disheva, O.V. and Knunyants, I.L. (1955) *Izv. Akad Nauke USSR Ser. Khim.*, 569.

30. Lin'kova, M.G., Kil'disheva, O.V. and Knunyants, I.L. (1955) *Bull. Acad. Sci. USSR. Div. Chem. Sci.*, 507.

31. Knunyants, I.L., Kil'disheva, O.V. and Pervova, E.Y. (1955) *Izv. Akad. Nauke USSR, Ser. Khim.*, 689.

32. Knunyants, I.L., Kil'disheva, O.V. and Pervova, E.Y. (1955) *Bull. Acad. Sci. USSR. Div. Chem. Sci.*, 613.

33. Knunyants, I.L., Pervova, E.Y., Lin'kova, M.G. and Kil'disheva, O.V. (1958) *Khim. Nauke i Promyshlenost*, **3**, 278.

34. Lin'kova, M.G., Patrina, N.D. and Knunyants, I.L. (1959) *Dokl. Akad. Nauk SSSR*, **127**, 564.

35. Lin'kova, M.G., Patrina, N.D. and Knunyants, I.L. (1960) *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1825.

36. Knunyants, I.L., Lin'kova, M.G. and Kuleshova, N.D. (1969) *Izv. Akad. Nauk SSSR, Ser. Khim.*, **4**, 644.

37. Knunyants, I.L., Kuleshova, N.D. and Lin'kova, M.G. (1965) *Izv. Akad. Nauk SSSR, Ser. Khim.*, **6**, 1081.

38. Lin'kova, M.G., Orlov, A.M. and Knunyants, I.L. (1966) *Dokl. Akad. Nauk SSSR*, **170**, 96.

39. Kuleshova, N.D., Lin'kova, M.G., Orlov, A.M. and Knunyants, I.L. (1966) *Izv. Akad. Nauk SSSR, Ser. Khim.*, **116**, 2025.

40. Lin'kova, M.G. and Knunyants, I.L. (1968) *Izv. Akad. Nauk SSSR, Ser. Khim.*, **8**, 1889.

41. Gapanovich, L.I., Lin'kova, M.G., Kil'disheva, O.V. and Knunyants, I.L. (1974) *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1**, 152.

42. Knunyants, I.L., Kil'disheva, O.V., Lin'kova, M.G. and Vasil'eva, T.P. (1975) *Dokl. Akad. Nauk SSSR*, **224**, 99.

43. Kricheldorf, H.R. (1973) *Makromol. Chem.*, **173**, 81.

44. Schönberg, E. (1941) *Ber. Dtsch. Chem. Ges.*, **74**, 1751.

45. Korte, F. and Löhmer, K.H. (1958) *Ber. Dtsch. Chem. Ges.*, **91**, 1397.

46. Heinz, K., (1952) Ger. Pat. 859, 456 to BASF AG, C.A. (1953), 47:11233.

47. Overberger, C.G. and Weiss, J.K. (1968) *J. Am. Chem. Soc.*, **90**, 3533.

48. Overberger, C.G. and Weiss, J.K. (1964) *Polym. L.H.*, **2**, 329.

49. Overberger, C.G. and Weiss, J.K. (1968) *J. Am. Chem. Soc.*, **90**, 3525.

50. Overberger, C.G., Charles, G. and Weiss, J.K. (1968) *J. Am. Chem. Soc.*, **90**, 3538.

51. Fritze, P.E. and Brode, G.L. (1973) U.S. Pat. 3732250 to Union Carbide, C.A., **79**:5279.

52. Fritze, P.E. (1974) U.S. Pat. 3786066 to Union Carbide, C.A., **80**:1080020.

53. Fritze, P.E. (1973) U.S. Pat. 3755268 to Union Carbide, C.A., **79**:147091.

54. Kricheldorf, H.R., Lee, S.R. and Schittenhelm, N. (1998) *Macromol. Chem. Phys.*, **199**, 273.

55. Seefried, C.G., Jr. and Koleske, J.V. (1976) *Polym. Engin. Sci.*, **16**, 526.

56. Seefried, C.G., Jr. and Koleske, J.V. (1974) *J. Macromol. Sci. Phys.*, **B10**, 579.

57. Matzner, M., McGrath, J.E., Chow, S.W., Koleske, J.V. and Robeson, L.M. (1973) *J. Appl. Polym. Sci.*, **17**, 983.

58. Kaloustian, M.K. and Khouri, F. (1981) *Tetrahedron Letters*, **23**, 413.

59. Nader, R.B. and Kaloustian, M.K. (1979) *Tetrahedron Letters*, **17**, 1477.

60. Nicolau, K.I., McCarry, D.C., Somer, P.K., Kim, B.H., Ogilvie, W.W., Yoannikouros, G., Prasad, C.V.C., Veale, C.A. and Hork, R.R. (1990) *J. Am. Chem. Soc.*, **112**, 6263.

61. Kikuchi, H., Tsubokawa, N. and Endo, T. (2005) *Chemistry Letters*, **34**, 376.

62. Sanda, F., Jirankanjana, D., Mitori, M. and Endo, T. (1999) *Macromolecules*, **32**, 8010.

63. Sanda, F., Jirankanjana, D. and Endo, T. (2000) *J. Polym. Sci. Part A, Polym. Chem.*, **38**, 4057.

64. Schindler, A., Hibionada, Y.M. and Pitt, C.G. (1983) *J. Polym. Sci. Polym. Polym. Chem. Ed.*, **20**, 319.

65. McLain, S.J. and Drysdale, N.E. (1992) *Preprints of the ACS Polym. Div.*, **33**(1), 174.

66. Pasch, H. and Rode, K. (1995) *J. Chromatogr. A*, **699**, 24.

67. Duda, A. and Penczek, S. (1990) *Macromolecules*, **23**, 1636.

68. Kowalski, A., Duda, A. and Penczek, S. (1998) *Macromolecules*, **31**, 2114.

69. Kricheldorf, H.R. and Eggerstedt, S. (1998) *Macromol. Chem. Phys.*, **199**, 283.

70. Kricheldorf, H.R. and Rost, S. (2005) *Polymer*, **46**, 3248.

71. Save, M., Schappacher, M. and Soum, A. (2002) *Macromol. Chem. Phys.*, **203**, 889.

72. Kato, M., Toshima, K. and Matsumara, S. (2005) *Biomacromolecules*, **6**, 2275.

73. Flory, P.J. (1950) U.S. Pat. 2.510.567 to Wingfoot Corp., C.A (1952), **46**:7504.

74. Marvel, C.S. and Kotch, A. (1951) *J. Am. Chem. Soc.*, **83**, 1100.

75. Marvel, C.S. and Kraiman, E.A. (1953) *J. Org. Chem.*, **18**, 707.

76. Stimpson, J.W. Brit. Pat. 853.730 C.A. (1961) **55**:109150.

77. Murphey, W.A. (1959) U.S. Pat. 2.870.126. to E.I. DuPont de Nemours, C.A. (1959) **53**:37212.

78. Al-Masri, M., Schwarz, G. and Kricheldorf, H.R. (2001) *J.M.S. Pure Appl. Chem.*, **A38**, 1007.

79. Kricheldorf, H.R., Probst, N., Schwarz, G., Schulz, G. and Krüger, R.-P (2000) *J. Polym. Sci. Part A. Polym. Chem.*, **36**, 3656.

80. Kricheldorf, H.R. and Schwarz, G. (2003) *Macromol. Rapid Commun.*, **24**, 359.

81. Kato, M., Toshima, K. and Matsumura, S. (2006) *Macromol. Rapid Commun.*, **27**, 605.

82. Weber, N., Bergander, K., Fehling, E., Klein, E. and Mukherjee, K.D. (2006) *Appl. Microbiol. Biotech.*, **70**, 290.

83. Weber, N., Klein, E., Mukherjee, K.D., Fehling, E. and Vosmann, K. (2005) DE 102004026012 A1, C.A. (2005) **144**: 35375.

84. Podkoscielny, W. and Kultys, A. (1976) *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 855.

85. Podkoscielny, W. and Charmas, W. (1979) *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 2429.

86. Podkoscielny, W. and Charmas, W. (1979) *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 3811.

87. Podkoscielny, W. and Kultys, A. (1981) *J. Appl. Polym. Sci.*, **26**, 1143.

88. Podkoscielny, W. and Kultys, A. (1981) *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 2167.

89. Podkoscielny, W. and Wdowicka, D. (1983) *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2961.

90. Podkoscielny, W. and Kowalewska, W. (1984) *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 1025.

91. Podkoscielny, W. and Kowalewska, W. (1984) *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 1579.

92. Podkoscielny, W. and Kultys, A. (1984) *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 1025.

93. Podkoscielny, W. and Wdowicka, D. (1985) *J. Appl. Polym. Sci.*, **30**, 1579.

94. Podkoscielny, W. and Szubinska, S. (1986) *J. Appl. Polym. Sci.*, **32**, 77.

95. Podkoscielny, W. and Szubinska, S. (1987) *J. Appl. Polym. Sci.*, **34**, 143.

96. Podkoscielny, W. and Szubinska, S. (1988) *J. Appl. Polym. Sci.*, **35**, 85.

97. Podkoscielny, W. and Szubinska, S. (1988) *J. Appl. Polym. Sci.*, **35**, 1853.

98. Podkoscielny, W. and Kowalewska, W. (1990) *J. Appl. Polym. Sci.*, **39**, 1649.

99. Podkoscielny, W. (1992) *Ann. Univ. Mariae Curie Sklodowska Sectio AA: Chemia, 42−43, 157,* C.A. (1993) **118**, 255433.

100. Podkoscielny, W. (1992) *Ann. Univ. Mariae Curie Sklodowska Sectio AA: Chemia, 42−43: 167,* C.A. (1993) **119**, 50002.

101. Podkoscielny, W. and Rudz, W. (1993) *J. Appl. Polym. Sci.*, **47**, 1523.

102. Podkoscielny, W. and Kultys, A. (1995) *Ann. Univ. Mariae Curie Sklodowska Sectio AA: Chemia, 46−47, 9,* C.A. (1996) **125**, 196549.

103. Podkoscielny, W. and Tarasiuk, B. (1993) *Angew. Makromol. Chem.*, **204**, 139.

104. Podkoscielny, W. and Rudz, W. (1993) *Eur. Polym. J.*, **29**, 69.

105. Podkoscielny, W. and Rudz, W. (1994) *J. Appl. Polym. Sci.*, **53**, 815.

106. Podkoscielny, W. and Tarasiuk, B. (1993) *Angew. Makromol. Chem.*, **207**, 173.

107. Podkoscielny, W. and Rudz, W. (1993) *Eur. Polym. J.*, **29**, 1115.

108. Podkoscielny, W. and Rudz, W. (1994) *J. Appl. Polym. Sci.*, **53**, 815.

109. Podkoscielny, W. and Podgorski, M. (1996) *Angew. Makromol. Chem.*, **241**, 135.

110. Podkoscielny, W., Mazarczyk, H. and Wdowicka, D. (1998) *Ann. Univ. Marie Curie-Skdodowska, Sectio AA, Chemia, 52−53: 39,* **131**, 214656.

111. Berti, C., Mananucci, E., Pilati, F., Roviello, A. and Sirigu, A. (1999) *Macromolecules*, **23**, 3505.

112. Hirano, H., Watase, S. and Tanaka, M. (2005) *J. Appl. Polym. Sci.*, **96**, 508.

113. Hirano, H., Tanaka, M., Kadota, J., Agari, Y. and Hasegawa, K. (2005) *Nippon Setchaku, Gakhaishi, 41: 259,* C.A. (2005) **144**, 293806.

114. Mulvaney, J.E. and Figueroa, F.R. (1986) *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 147.

115. Kricheldorf, H.R., Böhme, S. and Schwarz, G. (2005) *Macromol. Chem. Phys.*, **206**, 432.

116. Kricheldorf, H.R., Böhme, S. and Schwarz, G. (2006) *Macromolecules*, **39**, 3210.

117. Wentrop, C., Bender, H. and Gross, G. (1987) *J. Org. Chem.*, **52**, 3838.

118. Scampomino, E., Mancino, F. and Vitalini, D. (1995) *Macromolecules*, **28**, 5419.

119. Kameyama, A., Kimura, K. and Nishikubo, T. (2001) *High Perform. Polym.*, **13**, 5181.

120. Kameyama, A., Kimura, K. and Nishikubo, T. (2001) *J. Polym. Sci. Part A. Polym. Chem.*, **39**, 951.

121. Kameyama, A., Ide, T. and Nishikubo, T. (2003) *High Perform. Polym.*, **15**, 207.

122. Kudo, H., Mukino, S., Kameyama, K. and Nishikubo, S. (2005) *Macromolecules*, **38**, 5964.

123. Kricheldorf, H.R. and Conradi, A. (1989) *Macromolecules*, **22**, 14.

124. Kimura, K. and Yamashita, Y. (1994) *Polymer*, **15**, 3311.

125. Kimura, K., Nakajima, D., Kobashi, K., Uchida, T., Yamashita, Y. and Sakaguchi, Y. (2000) *Polym. Adv. Technol.*, **11**, 747.

126. Kobashi, K., Kimura, K., Yamashita, Y., Uchida, T. and Sakaguchi, Y. (2003) *Macromolecules*, **36**, 4268.

127. Kobashi, K., Kimura, K. and Yamashita, Y. (2004) *Polymer*, **45**, 7099.

128. Kobashi, K., Kimura, K. and Yamashita, Y. (2004) *Macromolecules*, **37**, 7570.

129. Kobashi, K., Kimura, K., Uchida, T., Yamashita, Y. and Shimamura, K. (2005) *Polymer*, **46**, 2191.

130. Kimura, K., Nakajima, D., Kobashi, K., Kohama, S., Uchida, T. and Yamashita, Y. (2005) *Polymer J.* (Japan), **37**, 471.

131. Braun, D. and Kissel, M. (1965) *Monatsh. Chem.*, **96**, 631.

132. Soga, K., Imamura, H., Sato, M. and Ikeda, S. (1975) *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 167.

133. Soga, K., Imamura, H., Sato, M. and Ikeda, S. (1976) *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 677.

134. Albert, W.M., Chan, H.W. and Wong, H.C. (1988) *Synth. Commun.*, **18**, 1531.

135. Leung, L.M., Chan, W.H. and Leung, S.K. (1992) *J. Polym. Sci. Part A. Polym. Chem.*, **31**, 1799.

136. You, Y.-Z, Hon, C.-Y and Pan, C.-Y (2002) *Macromol. Rapid Commun.*, **23**, 776.

137. Takatu, T. and Endo, T. (1988) *Macromolecules*, **21**, 2314.

138. Inoue, S., Koinuma, H. and Tsurata, T. (1968) *Paper presented at the 17th Polym. Sym. Japan, Preprints,* p. 383.

139. Adachi, N., Kida, Y. and Shikata, K. (1977) *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 739.

140. Berti, C., Marianucci, C. and Pilati, F. (1988) *Makromol. Chem.*, **189**, 1323.

141. Kihara, N., Hane, N. and Endo, T. (1993) *J. Org. Chem.*, **58**, 6198.

142. Kihara, N., Nakawaki, Y. and Endo, T. (1995) *J. Org. Chem.*, **60**, 473.

143. Choi, W., Sanda, F., Kihara, N. and Endo, T. (1997) *J. Polym. Sci. Part A. Polym. Chem.*, **35**, 3853.

144. Sanda, F., Shinjo, T., Choi, W. and Endo, T. (2001) *Macromol. Rapid. Commun.*, **22**, 363.

145. Choi, W., Sanda, F. and Endo, T. (1998) *Macromolecules*, **31**, 2454.

146. Steblyanko, A., Choi, W., Sanda, F. and Endo, T. (2001) *J. Polym. Sci. Part A. Polym. Chem.*, **39**, 3967.

147. Jones, F.N. and Andreades, J. (1969) *J. Org. Chem.*, **34**, 3011.

148. Kricheldorf, H.R. and Damrau, D.-O (1998) *Macromol. Chem. Phys.*, **199**, 2589.

149. Yonet, N., Yaci, Y., Ochiai, B. and Endo, T. (2003) *Macromolecules*, **36**, 9257.

150. Komeshima, H., Nemoto, N., Sanda, F. and Endo, T. (2002) *Macromolecules*, **35**, 5769.
151. Ochiai, B., Yoshie, K., Nagai, D. and Endo, T. (2005) *J. Polym. Sci. Part A. Polym. Chem.*, **43**, 1014.
152. Ochiai, B., Yoshie, K., Nagai, D. and Endo, T. (2004) *Macromolecules*, **37**, 2329.
153. Bromley, M.K. and Solomon, D.H. (1999) *Polymer*, **40**, 6539.
154. Montando, G., Puglisi, C., Berti, C., Marianucci, E. and Pilati, F. (1989) *J. Polym. Sci. Part A., Polym. Chem.*, **27**, 2277.
155. Endo, T. and Nagai, O. (2005) *Macromol. Symp.*, **226**, 79.
156. Takata, T. and Endo, T. (1993) *Progress Polym. Sci.*, **18**, 839.
157. Schlott, R.J., Scandiglia, T., Goldberg, E.P. and Hoeg, D.F. (1972) *Macromol. Synth.*, **3**:63, (1975) *Chem. Abstr.*, **83**:28622s.
158. Tagle, L.H., Diaz, F.R., Vega, J.C. and Alquinta, P.J. (1985) *Makromol. Chem.*, **186**, 915.
159. Tagle, L.H., Diaz, F.R. and Riveros, P. (1986) *Polym. J.*, **18**, 501.
160. Tagle, L.H., Diaz, F.R. and Valdebonito, N. (1987) *Polym. Bull.*, **18**, 479.
161. Tagle, L.H., Diaz, F.R. and Salas, P. (1989) *J. Macromol. Sci.*, **A26**, 1321.
162. Tagle, L.H., Diaz, F.R. and Margozzoni, C. (1991) *Polym. Bull.*, **25**, 319.
163. Tagle, L.H., Diaz, F.R. and Jinanez, M.L. (1992) *Polym. Bull.*, **28**, 645.
164. Tagle, L.H., Diaz, F.R. and Cisternas, H. (1993) *Int. J. Polym. Mater.*, **20**, 159.
165. Tagle, L.H., Diaz, F.R. and Cisternas, H. (1994) *Bol. Soc. Qim.*, **39**, 279.
166. Tagle, L.H., Diaz, F.R. and Fuenzalida, R. (1994) *J. Macromol. Sci. Pure Appl. Chem.*, **131**, 283.
167. Tagle, L.H., Diaz, F.R. and Donosco, A. (1990) *J. Macromol. Sci. Pure Appl. Chem.*, **A33**, 1643.
168. Gargallo, L., Soto, E., Diaz, F.R., Tagle, L.H. and Radic, D. (1987) *Eur. Polym. J.*, **23**, 571.
169. Gargallo, L., Soto, E., Tagle, L.H. and Radic, D. (1988) *Eur. Polym. J.*, **12**, 1119.
170. Fabre, M.J., Hernández-Fuentes, I., Gargallo, L. and Radic, D. (1992) *Polymer*, **33**, 194.
171. Mogen, J., Abradelo, C., Rey-Stolle, M.F., Tagle, L.H. and Hernândez-Fuentes, I. (1992) *Eur. Polym. J.*, **28**, 187.
172. Rey-Stolle, M.F., Fernández-Martin, F., Tagle, L.H. and Hernández-Fuentes, I. (1997) *Eur. Polym. J.*, **33**, 295.
173. Rey-Stolle, M.F., Fernández-Martin, F., Tagle, L.H. and Hernández-Fuentes, I. (1998) *Polym. Intern.*, **46**, 93.
174. Jaquiss, D.B.G., Martz, V. and Mitchell, L.C. (1987) Ger. Pat. 3.044.654 to General El. C.A. (1981), **95**:98627a.
175. Ueda, M., Sugano, T., and Iguchi, Y. (1988) Jpn. Pat. 02 153 928 to Daicel Chem. Ind. C.A (1990)., **113**:192 191.
176. Berti, C., Marianucci, E. and Pilati, F. (1985) *Polym. Bull.*, **14**, 82.
177. Bondiera, M., Berti, C. and Manaresi, P. (1993) *Makromol. Chem.*, **194**, 2453.
178. Marianucci, E., Berti, C., Pilati, F., Manaresi, P., Guartu, M. and Chionatore, O. (1994) *Polymer*, **35**, 1564.
179. Montando, G., Pugliso, C., Berti, C., Marianucci, E. and Pilati, F. (1989) *J. Polym. Sci. Part A. Polym. Chem.*, **27**, 2657.
180. Leung, L.M., Chan, W.H., Leung, S.K. and Fung, S.M. (1994) *J.M.S. Pure Appl. Chem.*, **A31**, 495.
181. Mukajama, T., Kuwajima, I. and Mizui, K. (1966) *J. Org. Chem.*, **31**, 32.
182. Nagai, D., Sato, M., Ochiai, B. and Endo, T. (2006) *J. Polym. Sci. Part A. Polym. Chem.*, **44**, 4795.
183. Nagai, D., Sato, M., Ochiai, B. and Endo, T. (2004) *Macromolecules*, **37**, 3523.
184. Nagai, D., Miyagawa, T., Kudo, H. and Endo, T. (2003) *Macromolecules*, **36**, 9335.
185. Nagai, D., Ochiai, B. and Endo, T. (2003) *Chem. Commun.*, 3018.
186. Nagai, D., Ochiai, B. and Endo, T. (2004) *Macromolecules*, **37**, 4417.
187. Nagai, D., Ochiai, B. and Endo, T. (2004) *Macromolecules*, **37**, 7538.
188. Nagai, D., Sato, M., Ochiai, B. and Endo, T. (2006) *J. Polym. Sci. Part A: Polym. Chem.*, **44**, 4281.
189. Hanford, W.E. and Holmes, D.F. (1942) U.S. Pat. 2.284.896 to E.I.
190. Catlin, W.E. (1942) U.S. Pat. 2284637 to E.I. DuPont, C.A. (1942) **36**:42250.
191. Dyer, E. and Osborne, D.W. (1960) *J. Polym. Sci.*, **47**, 361.
192. Klemm, E. and Stockl, C. (1991) *Makromol. Chem.*, **192**, 153.
193. Choi, W., Sanda, F. and Endo, T. (1998) *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 1189.
194. Moriguchi, T. and Endo, T. (1995) *Macromolecules*, **28**, 5386.
195. Suzuki, A., Nagai, D., Ochiai, B. and Endo, T. (2004) *J. Polym. Sci. Part A: Polym. Chem.*, **42**, 5983.
196. Kihara, N., Tochigi, H. and Endo, T. (1995) *J. Polym. Sci. Part A: Polym. Chem.*, **33**, 1005.
197. Suzuki, A., Nagai, D., Ochiai, B. and Endo, T. (2004) *Macromolecules*, **37**, 8823.
198. Uenishi, K., Sudo, A. and Endo, T. (2005) *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 4422.
199. Lou, X., Detrembleur, C. and Jerome, R. (2003) *Macromol. Rapid Commun.*, **24**, 161.
200. Lebedev, B. and Yevstropov, A. (1984) *Makromol.Chem.*, **185**, 1235−1253.
201. Papageorgiou, G.Z. and Bikiaris, D.N. (2005) *Polymer*, **46**, 12081−12092.
202. Ahn, B.D., Kim, S.H. and Yang, J.S. (2001) *J. Appl. Polym. Sci.*, **82**, 2808−2826.
203. Jin, H.J., Park, J.K., Park, K.H., Kim, M.N. and Yoon, J.S. (2000) *J. Appl. Polym. Sci.*, **77**, 547−555.
204. Ellis, T.S. (1995) *Macromolecules*, **28**, 1882−1886.
205. Schultze-Gebhardt, F. (1987) *Acta Polymerica*, **38**, 36−42.
206. Kricheldorf, H.R., Langanke, D., Spickermann, J. and Schmidt, M. (1999) *Macromolecules*, **32**, 3559−3564.
207. Tetsuka, H., Doi, Y. and Abe, H. (2006) *Macromolecules*, **39**, 2875−2885.
208. Hori, Y., Hongo, H. and Hagiwara, T. (1999) *Macromolecules*, **32**, 3537−3539.
209. Khalatur, P.G. (1979) *Vysokomol. Soed. Ser.*, **21**, 2190−2196.
210. Maglio, G., Marchetta, C., Botta, A., Palumbo, R. and Pracella, M. (1979) *Europ. Polym. J.*, **15**, 695−699.