

SULFUR-CONTAINING POLYMERS

1. Introduction

In the last decade of the twentieth century, sulfur-containing polymers have increasingly come into attention because of their interesting properties that make them useful in a wide range of applications. They can be used as high performance engineering plastics, chemically stable ion-exchange membranes in electromembrane processes, proton-conducting electrolytes, and optical, optoelectronic, and photochemical materials. Some polymers are employed in biomedical applications, eg, sulfopolymers as biomembranes and blood-compatible materials, and polysulfates and polysulfonates as antithrombotic or antiviral agents. The presence of sulfur, particularly in the form of disulfide bridges, plays an important role in biopolymers.

The purpose of this review is mainly to present recent advances in the area of sulfur-containing polymers that may not yet have commercial applications. Nevertheless, older but still significant material has been included at the beginning of the discussion of each class (see also ;).

2. Poly(monosulfide)s

Polymers containing a monosulfide linkage in both the main chain and the pendent group are the subject of many detailed studies. A few reviews of the synthesis and properties of all types of polymers have been published (1,2,3,4); the nearest one covering polymer with sulfur in the main chain appeared in 1992 (3). Polysulfides with controlled and well-defined structures are easily prepared. Nevertheless, the only commercial poly(monosulfide) is Ryton [Philips Petroleum Co., poly(thio-1,4-phenylene) more frequently referred to as poly(*p*-phenylene sulfide) or poly(phenylene sulfide) (PPS)].

Much effort has been devoted to preparing aromatic compounds in view of their significance as reactive intermediates for the synthesis of high performance linear aromatic polymers by ring-opening polymerization (ROP) (5). In an attempt to develop a novel synthetic method for the preparation of high molecular weight poly(thioarylene)s, macrocyclic aromatic sulfides and disulfides have been intensively prepared (6,7,8,9,10, 11,12,13,14). The coordination chemistry of macrocyclic polysulfides has also received considerable attention during the past years. The thiacyclic ether polymer ligands can be used as ion-exchange resins, metal ion adsorbents, and polymeric phase-transfer catalysts (15,16). Molecular systems in which tetrathiafulvalene is incorporated into macrocycles with supplementary donor atoms are potential electroactive cation sensors (17). The π -conjugated polymers have been extensively studied because of their attractive electronic properties.

2 SULFUR-CONTAINING POLYMERS

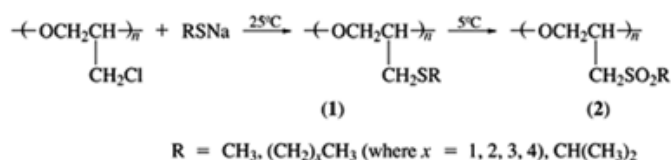
2.1. Aliphatic Poly(monosulfide)s

High molecular weight polymers may be obtained easily by ring-opening chain-growth polymerization of the smaller rings (episulfides with three and four atoms, thiiranes, and thietanes, respectively) (3,4). Nevertheless, polymers with larger aliphatic groups have been prepared only by step-growth polymerization (1,3).

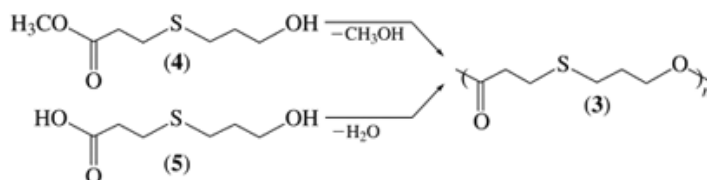
The most important here have been the addition of dithiols to diolefins (3,18) and the condensation of alkali metal sulfides or dithiolates with dihalides (3,19).

In the last decade, only a few new wholly aliphatic or mixed aliphatic–aromatic poly(monosulfide)s have been reported.

A series of poly(oxyalkylene)s such as poly[oxy((alkylthio)methyl)ethylene] (1), poly[oxy((alkylthio)methyl)ethylen-co-oxyethylene], and poly[oxy-2,2-bis((alkylthio)methyl)trimethylene] containing (alkylthio)methyl side groups were prepared from corresponding chloromethyl compounds with sodium alkanethiolates, using *N,N*-dimethylacetamide (DMAc) as a solvent and tetrabutylphosphonium bromide (tetra-*n*-butylphosphonium bromide) [3115-68-2] as a phase-transfer catalyst at 25 or 140°C (20). This substitution reaction gave 100% conversion with little, if any, backbone cleavage. The obtained (alkylthio)methyl-substituted polymers [intrinsic viscosities ($[\eta]$) from 1.10 to 2.68 dL/g and glass-transition temperatures (T_g) from -6 to -71°C] were successfully oxidized under mild conditions to highly polar (alkylsulfonyl)methyl-substituted poly(oxyalkylene)s (eg, (2)). The effectiveness and simplicity of these reactions make it possible to synthesize copolymers with chloro- and thioether, and/or sulfone side groups; this opens unlimited possibilities for making new polymers for various applications, including liquid crystalline polymers (21).



The novel partially crystalline polymer (3) with number-average molecular weight (M_n) of up to 5700 was prepared under various conditions by catalyzed self-condensation of 3-hydroxypropyl methoxycarbonyl ethyl sulfide (4) or 3-hydroxypropyl carboxyethyl sulfide (5) (22). The degree of crystallinity, melting temperature (T_m), T_g , and temperature of initial decomposition (T_d) were 36–46%, 37–47°C, -61 to -70°C , and 164–260°C, respectively. The monomers (4) and (5) were prepared by an addition of methyl 3-mercaptopropionate and 3-mercaptopropionic acid with allyl alcohol [107-18-6] catalyzed by AIBN [2,2'-azobis(2-methylpropionitrile), azobisisobutyronitrile, azodiisobutyrodinitrile, 2,2'-azobis(2-methylpropanenitrile), α,α' -azodiisobutyronitrile, 2,2'-azo-bis(isobutyronitrile), 2,2'-dicyano-2,2'-azopropane, Porofo-57, 2,2'-dimethyl-2,2'-azodipropionitrile, 2,2(-azobis(2-methylpropionitrile))] [78-67-1].



An addition of conjugate 1,4-benzenedithiol (A) to 1,4-divinylbenzene (1,4-diethenylbenzene, *p*-divinylbenzene) (B) [105-06-6] was investigated in detail in the presence of the AIBN initiator in toluene at 75°C (23). It was found that the polymerization proceeded without an induction period, to give a white

polymer with a high molecular weight [weight-average molecular weight (M_w) = 110,000] in ~90% yield for 2 h. In addition, it was confirmed by ^1H nmr, ir, and the sulfur contents that the polymer had an alternating structure of A and B units.

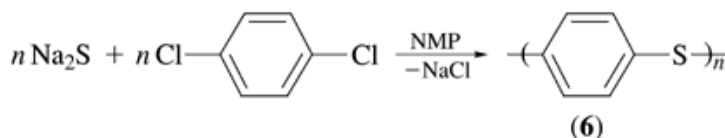
The synthesis and radical addition behavior of optically active cysteine-based monomers with mercapto and olefin groups have also been studied (24). *N*-4-vinylbenzoyl-L-cysteine methyl ester polymerized satisfactorily to afford the corresponding polysulfide (with M_n in the range of 7000–23,000) in good yields.

A novel one-pot synthesis of sulfur-containing polymers including poly(monosulfide)s (polythioethers), poly(disulfide)s, polythioesters, and polythiourethanes from a five-membered cyclic dithiocarbonate (5-phenoxymethyl-1,3-oxathiolane-2-thione) and diamines has been examined. Polythioethers with M_n = 2600–17,700 were obtained by condensation of *in situ* forming dithiol with α,α' -dibromo-*p*-xylene [623-24-5] (25). A synthesis by using a bifunctional five-membered cyclic dicarbonate and benzylamine [100-46-9] has also been reported (26).

High temperature solution condensation of 4,4'-bis(mercaptomethyl)biphenyl (MMB) (**88d**) or 4,4'-dimercaptobiphenyl (4,4'-biphenyldithiol) (MB) with various aliphatic and aromatic-aliphatic dihalogen hydrocarbons has been studied in detail. Polymers with reduced viscosity (η_{red}) = 0.18–0.54 dL/g and in ~78–99% yield were obtained under optimum conditions. Their characteristics were T_m = 104–248°C from MMB, 215–345°C from MB and T_d = 230–270°C from MMB, 290–340°C from MB. All the polymers showed good chemical resistance. Some mechanical and electrical properties of the selected polymers were examined (27).

2.2. Poly(arylene sulfide)s

The best-known polymer in this class is PPS (**6**). The commercial product produced from dichlorobenzene and sodium sulfide (Na_2S) by polymerization in a polar solvent, eg, *N*-methyl-2-pyrrolidinone (NMP) [872-50-4], contains up to a few percent of disulfide linkages.



Linear PPS is a crystalline material with T_m ~285°C and T_g = 85°C for a degree of polymerization of ~200. PPS shows a rather good chemical and thermal resistance (T_d = 370°C) and finds a wide range of applications as a high performance thermoplastic with excellent mechanical properties (3,28,29).

The main types of preparation of poly(arylene sulfide)s can broadly be classified into electrophilic and nucleophilic reactions; the latter are much more developed. In addition, many other polycondensation, oxidation, irradiation, or electroinitiated reactions were developed for the synthesis of various aromatic or aromatic-aliphatic materials (3).

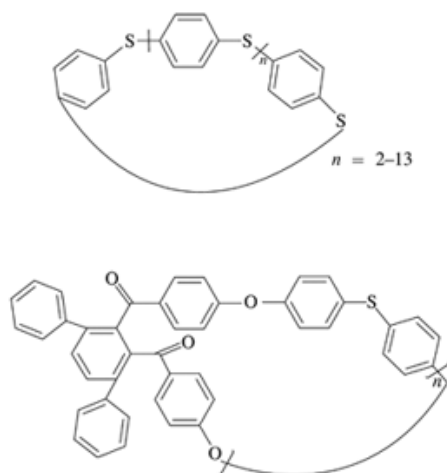
2.2.1. Ring-Opening Polymerization (ROP)

Free-radical ROP of various macrocyclic oligomers containing an aromatic sulfide linkage has recently been intensively studied as a new facile route to obtaining high performance thermoplastic polymers. The advantageous aspects of ROP over the conventional condensation methods are the elimination of solvents, the absence of by-products, and the rapid formation of high molecular weight polymers in high yields. Another noticeable attractive feature in using cycles is their much lower melt viscosity compared with that of the polymers, which facilitates reactive injection molding (14).

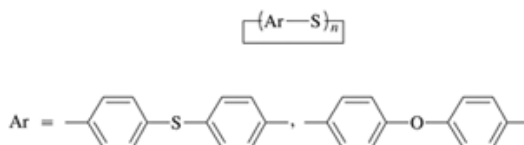
It was found that heating cyclic oligomers which contain an aromatic sulfide linkage in the presence of elemental sulfur or an aromatic disulfide, eg, 2,2'-dithiobis(benzothiazole) (MBTS, 2-mercaptobenzothiazole

4 SULFUR-CONTAINING POLYMERS

disulfide, etc) [120-78-5] readily yields high molecular weight polymers by ROP which proceed via a free-radical mechanism (8). The free-radical nature of the polymerization was confirmed by electron spin resonance (esr) spectroscopy. Melt polymerization of the cyclic hexakis(thio-1,4-phenylene) gave only a low molecular weight polymer (12,14,30) whereas that of a lower melting mixture of cyclic oligomers (**1**) led to the formation of highly crystalline high molecular weight poly(thio-1,4-phenylene), which is compared with that of commercial PPS. Other macrocycles, eg, (**2**), also gave high polymers ($M_n \sim 30,000$) (8).



Free-radical ROP of cyclic oligo(thioarylene)s (**3**) in the presence of a small amount of an initiator (elemental sulfur or MBTS) in melt at 300°C has been studied (14).



Linear poly(thioarylene)s obtained (yield 91–100%) were rather low-molecular-weight polymers ($M_n = 1500-2100$ with polydispersity 2.2–3.1). Their T_m s were 195–250°C, temperatures of the 10% weight loss (T_{d10}) $\sim 490^\circ\text{C}$.

2.2.2. Other Methods

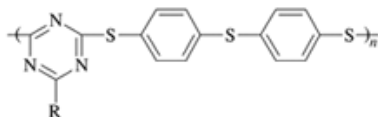
The electrophilic reaction of sulfur dichloride (SCl_2) or sulfur chloride (S_2Cl_2) with phenyl sulfide (diphenyl sulfide, diphenylthioether, 1,1'-thiobisbenzene) [139-66-2] in dichloromethane [75-09-2] solution at room temperature was studied in the presence of various catalysts (31). The resulting oligomeric products contained a linear structure linked by sulfide and disulfide bonds. It was found that SCl_2 showed higher reactivity than S_2Cl_2 . The quantitative yield was achieved among other things with a catalyst, such as Fe, SnCl_4 , TiCl_4 , or ZnCl_2 . An Fe catalyst gave a white product containing no elemental sulfur.

It has been reported that tris(2,2'-bipyridine)ruthenium(II) chloride catalyzed the photooxidative polymerization of diaryl disulfides by O_2 , by which poly(thioarylene)s were efficiently prepared. The polymerization proceeded through the electrophilic reaction of the sulfonium cation which was produced selectively by the pho-

toredox system. The ruthenium(II) complex provided the first photocatalytic system for the polymerization of diphenyl disulfide. The linear structures of the obtained polymers were confirmed (32).

Linear perfluorinated PPS was successfully prepared in 100% yield by the new method condensation of the corresponding fluorinated aryl sulfoxide via the poly(arylenesulfonium salt) as a precursor (33). The polymer had a significantly higher T_m (373°C) than that of PPS (285°C). The contact angle measurements showed that the surface energy of the polymer ($\sigma_s = 41$ mN/m) is comparable to those of poly(ethylene terephthalate) [25038-59-9] and polystyrene [9003-53-6]. High molecular weight PPS is also synthesized by this method.

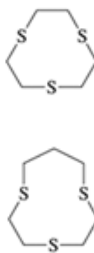
New aromatic poly(monosulfide)s (**4**) (34) containing a 1,3,5-triazine ring were readily prepared with moderate yields by the aromatic nucleophilic substitution polymerization of 2,4-dichloro-1,3,5-triazine derivatives with bis(4-mercaptophenyl) sulfide (4,4'-thiodibenzenethiol) [19362-77-7] under mild conditions in the presence of a base in tetrahydrofuran (THF) [109-99-9] solution or in the *o*-dichlorobenzene/water two-phase system by using phase-transfer catalyst. The resulting polymers showed highly crystalline structures and high thermal stability ($T_d \sim 330$ –410).



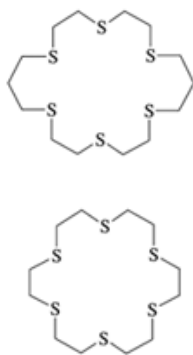
Preliminary investigations of the thermal polymerization reactions of newly obtained cyclic aromatic disulfides with *p*-diiodobenzene [624-38-4] and dibromobenzene [26249-12-7], or bis(4-bromophenyl) ether (4,4'-dibromodiphenylether, bis-*p*-bromophenyl ether, *p,p'*-dibromodiphenyl ether) [2050-47-7] as a new alternative approach to PPS and other polysulfides have been reported (9). The reactions were carried out in diphenyl ether solution at 270°C giving polymers with ~96% yield.

2.3. Macrocyclic Polythioethers

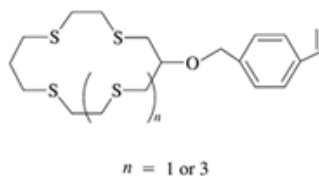
During the past decade, intensive studies have taken place of the complexation of transition metal ions with crown thioether ligands, mainly 1,4,7-trithiacyclononane (9S3) (**5**) as well as 1,4,7-trithiacyclodecane (10S3) (**6**), 1,4,7,11,14,17-hexathiacycloeicosane (20S6) (**7**), and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) (**8**), and many articles (35,36,37,38,39,40,41,42), including reviews (35,36,37,38,39), dealing with the coordination chemistry of these ligand systems have been published. The crown thioether complexes of the soft metal ions exhibit unusual stereochemical, spectroscopic, and electrochemical properties, such as the ability to stabilize uncommon oxidation states including Pd(III), Pt(III), Au(II), and Rh(II), the ability to force metals ions into unusual geometries such as octahedral Rh(I) and Au(III), the formation of metal–carbon bonds, and the ability to activate carbon–hydrogen bonds in ring-opening reactions (41).



6 SULFUR-CONTAINING POLYMERS



The thiacrown ether monomers (**9**) were polymerized and copolymerized with styrene [100-42-5] and *N*-vinyl-2-pyrrolidinone (*N*-vinyl-2-pyrrolidone, *N*-vinylpyrrolidone, 1-vinyl-2-pyrrolidone, 1-vinyl-2-pyrrolidinone, vinylbutyrolactam, etc) [88-12-0] by radical polymerization, giving the thiacrown ether polymer ligands which had binding selectivity for Ag(I) and Hg(II) ions. These polymers are likely to be efficient sorbents for the heavy metal ions under industrial conditions, since they can be used repeatedly under acidic conditions (15,16).



A new method has been reported of the synthesis of thiocrowned and oxothiocrowned 1,3-dithiole-2-thiones from the key starting compound of 4,5-bis(benzylthio)-1,3-dithiole-2-thione. Intramolecular phosphite coupling reaction yielded the new tetrathiafulvalene (TTF) [31366-25-3] derivatives incorporated into thiacrown as well as oxathiacrown ether macrocycles in moderate yields. This procedure permits the isolation of asymmetric sulfur/oxygen donors not accessible by other methods (43). TTF-containing macrocycles with sulfur and selenium soft donor atoms were obtained by using a similar method (17). The cyclic voltammograms of these TTFs were discussed.

2.4. Polythiophenes

Polythiophene and its alkyl derivatives are the first class of conducting polymers with a good stability toward oxygen and moisture (3,44,45,46). High molecular weight polymers are successfully produced by the chemical oxidations (Lewis acid), the organometallic coupling (chemical), and the electropolymerization methods. Good-quality films are afforded by electropolymerization.

The synthesis of 3-(perfluoro)-thiophenes and 3-(polyfluoro)-thiophenes as precursors to electrically conductive polymers has been reported (47,48,49,50,51,52,53). The incorporation of a significant percentage of fluorine into the polymer is anticipated to allow greater control over its oxidation potential and provide better long-term chemical and thermal stability in the electrochemical environment over that of the nonfluorinated polythiophene analogs.

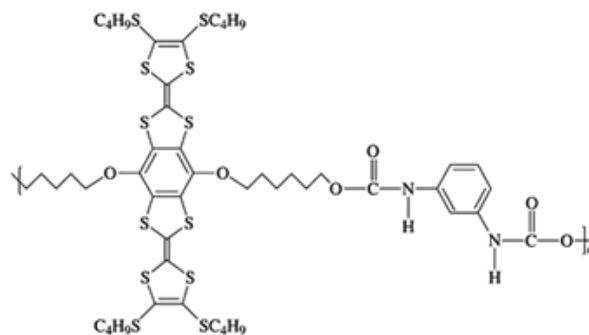
The novel functionalized polythiophenes, poly[3-(6-hydroxyhexyl)thiophene] and poly(3-octanethio-2,2'-bithiophene), have been used as selective coating materials for quartz crystal microbalance (QCM) sensors.

These Langmuir–Blodgett film coated QCM sensors are useful in detecting heavy metal ions in aqueous solution, which are major pollutants in wastewater (54).

2.5. Tetrathiafulvalene Polymers

TTF and its derivatives form highly conductive anisotropic (quasi one-dimensional) charge-transfer complexes and radical cation salts. To obtain materials with three-dimensional conductivity, good processability, and film-forming properties, the polymeric forms of TTF are prepared. TTF can be incorporated into the polymer backbones via condensation to polyesters, polyamides, polyurethanes, and polysulfonates (55).

Several main-chain and side-chain TTF polymers have been synthesized via a multistep synthesis (55). They combine the unique properties of high molecular weight polymers, such as processability, with the outstanding electron-donating properties of TTF systems. Doping the polyurethane-type polymer (**10**) with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane led to a free-standing, processable film exhibiting a moderately high electrical conductivity of $8 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, which is comparable to iodine-doped nonordered polythiophene.



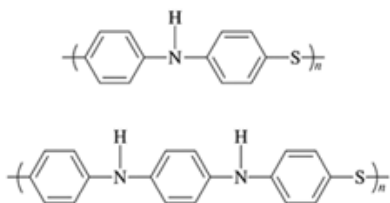
The synthesis of a fully conjugated, planar, and sulfur-rich TTF polymer, which should increase the dimensionality of the conduction process in the doped state, was also reported (55).

2.6. Conjugated Polymers

Sulfur-containing conjugated polymers have played a major role in the development of temperature-stable thermoplastic materials and in the search for materials being suitable as active components of optoelectronic and photonic devices. The new synthetic approaches to these polymers, including poly(phenantrolinebisthiazole), poly(phenylene sulfide-phenyleneamine) (PPSA), poly(tetrathiafulvalene), sulfur-containing [n]acenes, and donor-acceptor substituted poly(phenylenevinylene), were presented in a review article in 1997 (56). Two different strategies have been taken. The first one comprises the synthesis of suitably functionalized monomeric building blocks, which can be easily polymerized by common polymerization methods; the second one is based on novel methods of carbon–carbon and carbon–sulfur bond formation.

High molecular weight PPSA ($M_n = 150,000$) (**11**) and poly(phenylene sulfide-phenyleneamine-phenyleneamine) (PPSAA) ($M_n = 68,000$) (**12**) have been synthesized in high yields via their poly(sulfonium) cations through the acid-induced condensation reaction (57,58). These novel polymers represent the first hybrid structures of PPS and polyaniline (PAni). Both polymers are structurally well-defined and exhibit exceptional solubility in many solvents, including THF, *N,N*-dimethylformamide (DMF) [68-12-2], dimethylsulfoxide (DMSO) [67-68-5], and NMP, contrary to PPS and PAni. The electronic properties of polymer (**11**) that define this material as a prominent candidate for efficient hole-transport ability in light-emitting diodes (LEDs) have already been studied.

8 SULFUR-CONTAINING POLYMERS



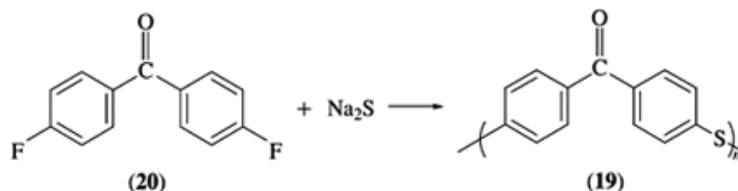
The first π -conjugated TTF polymer composed entirely of vinylogous, linearly fused TTF moieties was achieved by oxidative polymerization of 2-5-di(benzylidene)-1,3,4,6-tetrathiapentalene (59).

The syntheses of the first sulfonio-bridged, *p*-phenylene ladder oligomers (**19**) that have a planar ribbon-type structure have also been reported (60).

2.7. Poly(monosulfide ketone)s

Aromatic poly(monosulfide ketone)s [poly(thioether ketone)s] have been investigated in view of their potential use as high performance thermoplastics.

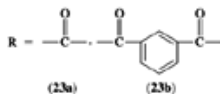
Poly(*p*-phenylene sulfide ketone) (**19**) (61) was prepared under different conditions by polymerization of 4,4'-difluorobenzophenone [345-92-6] (**20**) with sodium sulfide (Na_2S). Since the reaction involves nucleophilic aromatic substitution, it should be facilitated in aprotic polar solvents by increased dianion reactivity. A high molecular weight polymer [inherent viscosity (η_{inh}) = 0.95 dL/g] was obtained in solution of *N*-cyclohexyl-2-pyrrolidinone (*N*-cyclohexyl-2-pyrrolidone, 1-cyclohexyl-2-pyrrolidinone, 1-cyclohexyl-2-pyrrolidone, CHP) [6837-24-7], using freshly crystallized and dehydrated Na_2S . The polymer was high melting, $T_m = 335^\circ\text{C}$ and $T_g = 152^\circ\text{C}$.



Random copoly(*p*-phenylene sulfide sulfone/ketone)s were easily prepared in high yield (~95–99%) by the solution (NMP) condensation of sodium hydrosulfide (NaSH) with bis(4-chlorophenyl) sulfone (4,4'-dichlorodiphenyl sulfone) [80-07-9] and 4,4'-dichlorobenzophenone [98-98-2]. Copolymers with sulfone/ketone molar ratios $> 25:75$ were amorphous, whereas those with ratios $\leq 25:75$ were crystalline. These materials form tough, creaseable films and exhibit a linear increase in the T_g from 144 to 215°C , with increasing sulfone content (62).

A series of poly(thioether ketone)s or poly(thioether ether ketone)s ($\eta_{\text{inh}} = 0.1\text{--}0.73$ dL/g) were synthesized by condensation of aromatic dicarboxylic acids with aryl compounds containing ether or sulfide structures using phosphorous pentoxide/methanesulfonic acid as the condensing agent and solvent. The polymers showed $T_{\text{d}10}$ in the range of $420\text{--}485^\circ\text{C}$ in air and nitrogen atmospheres (63).

Poly(thioether ketone)s (**21**) ($\eta_{\text{inh}} = 0.3\text{--}0.54$ dL/g, tetrachloroethane, 0.5%) were also prepared in good yield (92–94%) from masked bithiophenol (**22**) and difluoro-compounds (**23**) such as 4,4'-difluorobenzophenone [345-92-6] (**23a**) or 1,3-bis(4-fluorobenzoyl)benzene (**23b**) by solution (NMP) polymerization in the presence of KHCO_3 . The polymers showed $T_g = 106\text{--}121^\circ\text{C}$ and excellent thermal stability ($T_{\text{d}10} \sim 460\text{--}515^\circ\text{C}$ in N_2 and air). This novel method eliminates the problem associated with the conventional procedure in handling the unstable bithiophenol monomers (64).



Chemical structures of the polyimides are shown below:

Structure 1 (top): A polyimide with a central benzophenone core. The core is substituted with two 4-fluorophenyl groups and a 4-(4-phenylthiophenylthio)phenyl group. The repeating unit is shown in parentheses with a subscript n .

Structure 2 (bottom): A polyimide with a central benzophenone core. The core is substituted with two 4-phenylthiophenyl groups and a 4-(4-phenylthiophenylthio)phenyl group. The repeating unit is shown in parentheses with a subscript n .

3. Poly(disulfide)s

During the last several decades, aliphatic poly(polysulfide)s, including poly(disulfide)s, have been extensively investigated because of their interesting properties resulting from the presence of polysulfide linkages. The properties such as good resistance to solvents and hydrocarbon fuels, resistance to dissolution for linear polymers and to swelling for cross-linked polymers, as well as generally good low temperature properties have given them a particular position among specialty elastomers. The Thiokol Co. in the United States marketed the first synthetic polysulfide rubber under the trade name Thiokol A [poly(ethylene tetrasulfide)]. Rohm and Haas now produces and distributes Thiokols. Aliphatic poly(disulfide)s, eg. Thiokol D [poly(ethyl

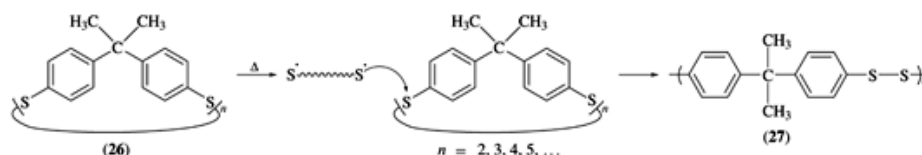
10 SULFUR-CONTAINING POLYMERS

ether disulfide], have also been produced commercially (71,72). There are several reviews of the synthesis and properties of this class of polymers (2,3,73,74) (see).

In the last decade, extensive efforts have been devoted to the synthesis of cyclic oligomers as precursors for the preparation of high molecular weight polymers by ROP. Although it is routine to prepare aliphatic poly(disulfide)s by ROP (75), little attention has been given to the ROP study of cyclic (aromatic disulfide)s (3,76).

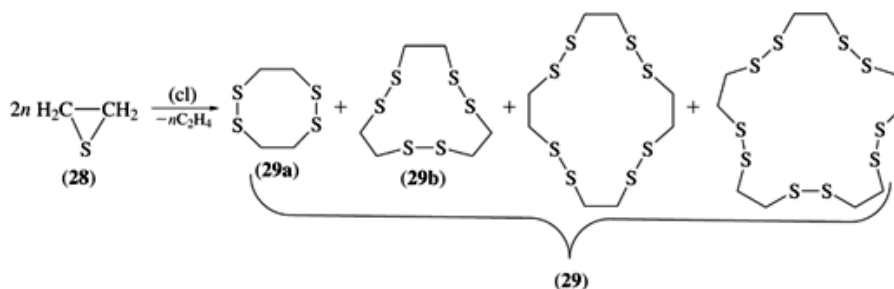
A series of cyclic (aromatic disulfide) oligomers have been synthesized in high yields by a copper-catalyzed oxidation with oxygen of arenedithiols in DMAc solution (10). The aryl groups contained moieties such as isopropylidene, ketone, sulfone, ether, thioether, and phenylphosphine oxide groups. In general, these cyclic oligomers with up to nine repeating units were soluble in common organic solvents and had sharp melting points. Contrary to earlier-described cyclization reactions, which were run over 16 h under high dilution conditions, this one was complete in 3–4 h at room temperature (10).

The ROP reaction of the cyclic oligomers mixture (26) derived from 2,2-bis(4-mercaptophenyl)propane (4,4'-isopropylidene bisthiophenol) was studied in both diphenyl ether solution and melt without adding any catalyst. It was found that ROP began at $\sim 150^\circ\text{C}$ in solution and at $\sim 200^\circ\text{C}$ in melt. It may be supposed that the reaction is initiated by forming upon heating the radical species of (26). The highest molecular weight polymers (27) ($M_n = 64,000\text{--}88,000$) were formed at 200°C with conversion of cycles $\sim 80\%$ in solution and $\sim 98\%$ in melt. A ^{13}C nmr study indicated that structurally regular polymers were formed below 250°C (77).



Earlier attempts of ROP without adding any catalyst were performed on some cyclic bis(arylene tetrasulfide)s upon heating (78) and 1,2,3-trithiane [3325-33-5] upon standing at room temperature (77). Some cyclic (arylene) disulfides were already prepared earlier by using iodine or DMSO as oxidizing agent, mainly to study their structural geometry and their potential for complexation (79,80,81,82,83,84).

A new easier approach to cyclic poly(aliphatic disulfide)s by catalytic transformation of thiiranes by (thiirane) $\text{W}(\text{CO})_5$ complexes has been studied (85,86). For this purpose, the new thiirane complexes such as $\text{W}(\text{CO})_5(\text{thiirane})$ (c1), $\text{W}(\text{CO})_5(\text{cis-dimethylthiirane})$ (c2), and $\text{W}(\text{CO})_5(\text{trans-dimethylthiirane})$ (c3) were prepared and characterized. It was found that c1, as $\text{W}(\text{CO})_5(\text{NCMe})$ (87) used earlier, transforms free thiirane (thiacyclopropane, ethylene sulfide) [420-12-2] (28) into a mixture of cyclic poly(disulfide)s (29), and ethylene, catalytically; the compound (29a) was the major product ($\sim 66\%$). Also, *cis*- and *trans*-dimethylthiirane were catalytically transformed by c2 and c3 with the formation of small amounts of cyclic disulfides. The mechanism of these reactions has been proposed.



Cyclic disulfides have been shown to exhibit a variety of antimicrobial properties (85,88). The compounds 1,2,5,6-tetrathiacyclooctane (**29a**) and 1,2,5,6,9,10-hexathiacyclododecane (**29b**) were tested for antimicrobial activity, using a standard disk diffusion assay. The compound (**29a**) exhibited moderate antimicrobial activity toward *Escherichia coli*.

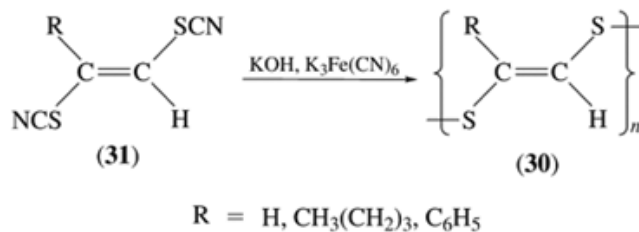
Contrary to the extensive studies on the coordination properties of polythioether macrocycles (35,36,37,38, 39,40,41,42), little information is available about cyclic poly(disulfide)s. The first reaction which was performed with compound (**29a**) and $\text{Ru}_3(\text{CO})_{12}$ led to the formation of two isomers of $\text{Ru}_3(\text{CO})_7(\mu\text{-SCH}_2\text{CH}_2\text{S})_2$, which contained bridging ethanedithiolate ligands formed by cleavage of both of the disulfide S—S bonds (89). Attempts to prepare complexes of (**29a**) and (**29b**) without cleavage of disulfide bonds were performed by reaction with CuI in acetonitrile [75-05-8] (90). Two new compounds obtained in yields of 75 and 61%, respectively, were characterized crystallographically. They exhibited interesting extended structures in the solid state that were created by the formation of bridging ligands involving η^2 -coordination of the cyclic disulfides.

An interesting new approach to poly(disulfide)s with a variety of main-chain structures by one-pot oxidation polymerization of dithiols forming *in situ* from monofunctional (25) and bifunctional (91) five-membered cyclic dithiocarbonates and diamines or amines, respectively, has recently been reported. Polymers with M_n up to ~20,000 and a good yield (up to 98%) were obtained. The starting dithiocarbonates can be easily synthesized by incorporation of CS_2 into epoxides in the presence of metal halides under mild conditions (92,93).

Other oxidation processes leading to poly(disulfide)s, namely the electrochemical (anodic) oxidation of Bunte salts (bisthiosulfates) (94) as well as oligomerization and cyclization of 1,2-ethanedithiol [540-63-6] by selenium dioxide [7446-08-4] or iodine, have also been studied (95).

Poly- and copoly(disulfide)s as electroactive materials have been used successfully in the lithium/poly(ethylene oxide)/(solid redox polymerization electrodes) (Li/PEO/SRPE) battery system (96). The high level of performance of these polymeric materials in thin-film Li/PEO batteries demonstrates the versatility of the SRPE and indicates that such batteries may be useful for a wide range of applications.

Water-insoluble ethylenic poly(disulfide)s (**30**) were prepared, for the first time, by the treatment of dithiocyanates (**31**) with KOH and $\text{K}_3\text{Fe}(\text{CN})_6$ in aqueous solution, and characterized. These simple-structure polymers become semiconductive upon chemical doping (97).



The importance of disulfide bridges in peptides and proteins is well known, and many elegant ways to form these structures have been reported (98,99). In contrast, the corresponding “trisulfide” variants reflect a rather newly appreciated area of chemical and biological interest (100).

4. Sulfonium Polymers

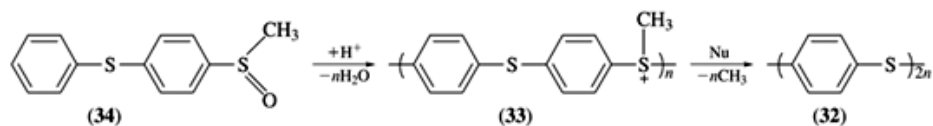
Polysulfonium salts have been extensively studied because of the versatile possibilities of their application. They can be used as ion-exchange resins, polymer supports in peptide synthesis, polymeric reagents, and conducting materials (101). The poly(sulfonium cation) is chemically stable and soluble in common solvents,

12 SULFUR-CONTAINING POLYMERS

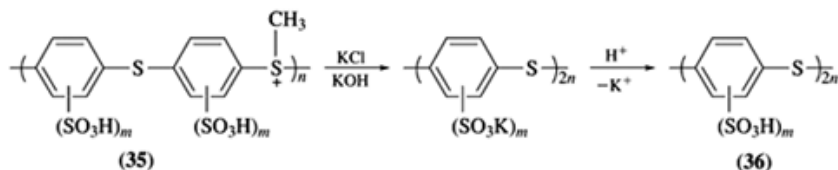
such as acetone, acetonitrile, or protic acid. These properties are applicable to the modification of the polymer in a homogeneous solution under moderate conditions.

There have been reports of examples of polymers with sulfonium salt moieties applied as a catalyst to organic reactions (102) and precursors of such polymers as PPS (103,104,105,106,107), perfluorinated PPS (33), poly(*p*-phenylene vinylene) (PPV) (108,109,110,111) and its derivatives (112), as well as PPSA and PPSAA (57,58).

For example, the high molecular weight PPS (**32**) ($M_w > 200,000$) was synthesized via soluble poly[methyl-4-(phenylthio)phenylsulfonium cation] (**33**) through oxidative polymerization of methyl-4-(phenylthio)phenyl sulfoxide (**34**). The polymerization process carried out in trifluoromethanesulfonic acid (triflic acid, $\text{CF}_3\text{SO}_3\text{H}$) [1493-13-6] and in the presence of P_2O_5 as dehydrate agent at room temperature for 24 h quantitatively produced the high molecular weight polymer (**33**) which was converted, also quantitatively, to PPS (**32**) by nucleophilic demethylation in pyridine [110-86-1] (104,105). The polymerization of (**34**) in sulfuric acid, particularly at elevated temperature and extended reaction time, resulted in a slight sulfonation on the phenylene ring in the polymer chain.



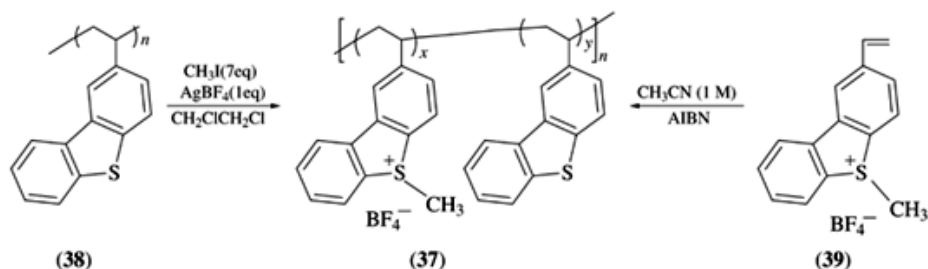
The highly sulfonated polysulfonium salt (**35**) synthesized by the polymerization of (**34**) in the presence of SO_3 can be converted by nucleophilic demethylation with aqueous KCl to the highly sulfonated PPS (**36**) exhibiting excellent proton conductivity (113).



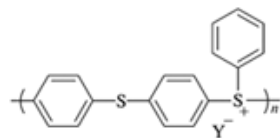
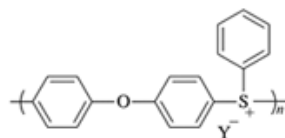
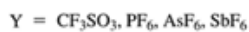
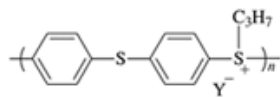
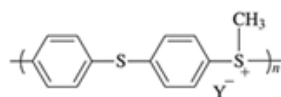
Poly(arylenesulfonium salt)s are employed as new polymeric alkylation reagents because, after the dealkylation, they are converted to insoluble PPS that can easily be removed from the reaction mixture (114,115).

Thiophenium salt derivatives can be utilized as powerful alkylating reagents because of their remarkable instability in nucleophilic solvents (116,117). In order to investigate a similar application of poly(thiophenium salt)s, new polymers having pendent *S*-alkyldibenzothiophenium salt moieties have been, for the first time, synthesized and characterized (118,119,120). Two synthetic routes to polymer (**37**) were investigated: the polymer reaction of poly(2-vinyldibenzothiophene) (**38**) with methyl iodide [74-88-4] and silver tetrafluoroborate [14104-20-2] carried out in 1,2-dichloroethane [107-06-2] at room temperature, and the radical polymerization of a vinyl monomer bearing dibenzothiophenium moieties, ie, 5-methyl-2-vinyldibenzothiophenium tetrafluoroborate (**39**), carried out in acetonitrile with an AIBN catalyst at 60°C. The former method gave the polymer in 96% yield with 71% substitution of the methyldibenzothiophenium tetrafluoroborate units, whereas the latter in 88% yield with 79% substitution. The analogous polymer with 63% substitution was also prepared by the polymer reaction of poly[2-(*p*-vinylbenzyl)dibenzothiophene] (120). The attempts of demethylation showed that the complete demethylation of the dibenzothiophenium units in polymer (**37**) was achieved at 80°C for 48 h by the reaction in acetonitrile (119). In addition, it was found that thermal decomposition of the polysulfonium polymers obtained took place in two steps; the first step was associated with demethylation. These properties

suggest the possibility of utilizing these polymers as an alkylating reagent and an initiator of the cationic polymerization.



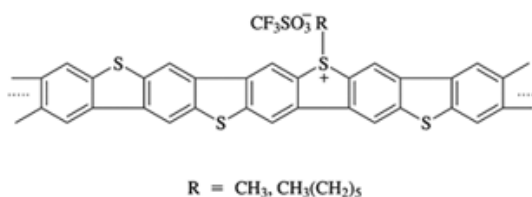
Attention has been paid to the polysulfonium salts as a new type of photochemical polymeric materials (121,122). Several kinds of poly(arylenesulfonium salt)s having methyl (**15**) propyl (**16**), and phenyl substituents ((**17**), (**18**)) including a novel class of polyelectrolytes having triphenylsulfonio groups in the main chain ((**17**), (**18**)) were synthesized in yield up to 100% by the sulfoxide-acid system reaction from the corresponding alkyl and aryl sulfoxide monomers (105,107,115,122).



14 SULFUR-CONTAINING POLYMERS

They showed good solubility in protic acids, including formic acid [64-18-6], sulfuric acid, and $\text{CF}_3\text{SO}_3\text{H}$ and polar organic solvents, including methanol, acetonitrile, DMF, DMSO, etc. The photochemical reactivities of the resulting polymeric sulfonium salts, eg, photolysis (photodegradation), photoinitiated polymerization, and quantum yields, were investigated in detail with comparison to those of the corresponding monomeric compounds. It was found that the photo-irradiation of ultraviolet light at the $\pi-\pi^*$ transition band resulted in the selective degradation of the polymer to the corresponding aryl or alkyl sulfide monomer. The photodegradation was accompanied by proton generation, which could be useful for the photoinitiated polymerization of epoxy compounds. The polymeric sulfonium salts were more effective than the monomeric ones because of a larger extinction coefficient at the irradiation wavelength (122).

The synthesis of the first sulfonio-bridged, *p*-phenylene ladder oligomers (**19**) that have a planar ribbon-type structure have been reported (60).



The oligomers are soluble in formic acid, sulfuric acid, and $\text{CF}_3\text{SO}_3\text{H}$ but insoluble in common organic solvents, including methanol, acetone, acetonitrile, and chloroform. In the presence of an extended π -conjugation, two-dimensional planar structures have electronic advantages, for example, as a lower bandgap material (123).

5. Poly(sulfonic acid)s and Their Derivatives

Polymers substituted by sulfo groups have a wide range of applications because of their unusual properties. Water-soluble polymers are used as emulsifiers, flocculants, thickeners, tanning agents, wetting or cleaning agents, etc. They are also applied in the paint industry and in dye manufacturing (124,125). Introduction of the sulfo groups into fibers (eg, polyester fiber by using sodium-5-sulfo-dimethylisophthalate as ionic comonomer) (126) improves dyeability and imparts antistatic properties. Another important area of application is in construction engineering, eg, concrete technology as high range water reducers (superplasticizers). Lignosulfates, sulfonated melamine-formaldehyde and naphthalene-formaldehyde condensates are typical superplasticizers used commercially (127,128). Poly(3-alkylsulfonate thiophene)s (129), sulfonatoalkoxy-substituted poly(*p*-phenylene) (130), highly sulfonated PPS (113), and PANi (131) are water-soluble conductive polymers. The polyelectrolyte block copolymers, eg, poly(alkyl methacrylate)-*b*-poly(sulfonated glycidyl methacrylate) (132) and poly(ethylethylene)-*b*-poly(styrenesulfonate) (133), were found to be effective stabilizers in emulsion polymerization. Insoluble polymers are used as ion-exchange resins and they find application as membrane materials, eg, Nafion (DuPont, a sulfonated perfluoropolymer) (134,135). A great demand for chemically stable ion-exchange membranes for electromembrane processes, such as electrodialysis, polymer electrolyte membrane electrolysis, and polymer electrolyte fuel cells, has, in the past years, stimulated investigations dealing with the developing of the sulfonation process of thermally and chemically stable engineering plastics.

Sulfopolymers are employed in biomedical systems. Much effort has been expended to improve blood-contacting biomaterials, eg, segmented polyurethanes, and develop various polysulfates and polysulfonates as antithrombotic or antiviral agents.

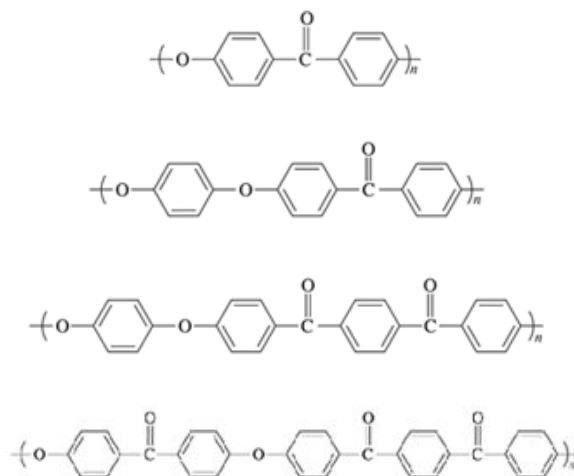
Sulfo groups (as a free acid, salt, or ester) can be introduced into polymers by homo- or copolymerization of monomers containing sulfo groups, or by direct sulfonation of the polymer.

5.1. Poly(sulfonic acid)s

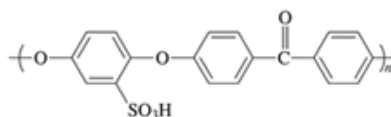
There are many reports on the sulfonation of commercially available, high performance engineering plastics, including poly(*p*-phenylene) (PPP) (130), Udel [Union Carbide, poly(ether ether sulfone)] (136,137), poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) [poly(phenylene ether ether ketone) (PEEK)] (138, 139,140,141,142,143,144), and PPS (103,113,145,146,147,148), etc. (see).

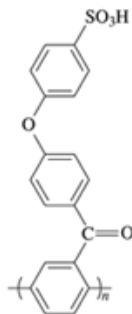
The sulfonation of PEEK (**21**) in concentrated sulfuric acid or in its mixture with methanesulfonic acid [75-72-2] gives polymeric material which is soluble in organic solvents, eg, DMF (138), and good membranes with interesting properties were obtained by processing from these solutions (139,140,141,142).

The sulfonation reaction of several kinds of commercially available poly(aryl ether ketone)s with various ether/carbonyl group ratio (0.67–2.0) ((**20**), (**21**), (**22**), and (**23**)) by mixtures of sulfuric acid and oleum was studied (143). It appeared that with decreasing amounts of ether links in the polymer backbone the sulfonation is hindered, and to obtain products with the same degree of sulfonation, the SO₃ concentration of the reaction mixture has to be increased. Depending on the polymer structure, polymers with contents of sulfonate groups ~1.2–2.0 meq·g⁻¹ polymer were well soluble in DMF or NMP. The cationic exchange membranes with permselectivities >96% and electrical resistances <2 Ω·cm⁻² from the polymers with a high degree of sulfonation were produced. The electrical and mechanical properties of these membranes compare very well with other membrane materials.

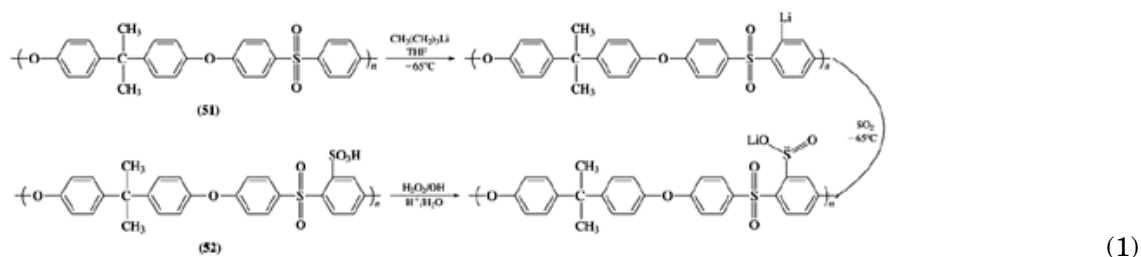


The electrical properties of the thermostable PEEK (**24**) and poly(4-phenoxybenzoyl-1,4-phenylene) (PPBP) (**25**) sulfonated with sulfuric acid and containing 65 mol% sulfonic acid have been studied and compared (144). Sulfonated PPBP showed much higher and more stable proton conductivity than that of sulfonated PEEK, which is in agreement with the strong water absorption of the former polymer, as a consequence of the presence of the flexible pendent side chains. These properties may be important for future design and development of fuel cells based on polymer electrolytes.

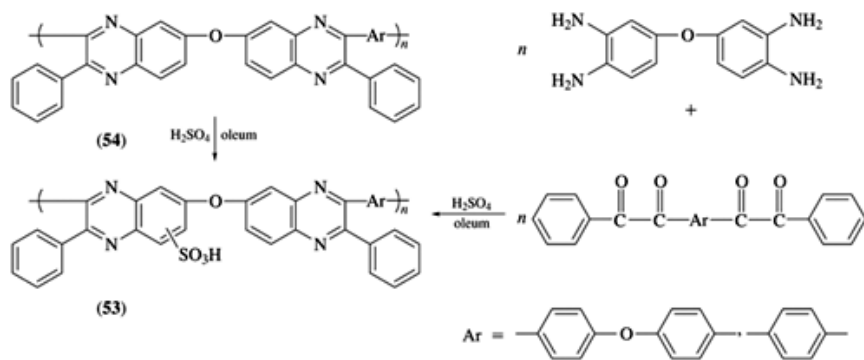




A new process has been developed for the sulfonation of the chemically stable engineering polymer polysulfone Udel (**51**) (137). This multistep sulfonation process described in equation (1) consists of the following steps: lithiation of the polymer at -50 to -80°C , gassing with SO_2 , oxidation of the formed polymeric sulfinate with H_2O_2 , NaOCl , or KMnO_4 , and final ion-exchange of the lithium salt of the sulfonic acid in aqueous HCl . By this method the sulfonic acid group is inserted into the more hydrolysis-stable diarylsulfone part of molecule, contrary to conventional electrophilically sulfonation which it undergoes at position ortho to the ether bridge of the bisphenol A [2,2-bis(4-hydroxyphenyl)propane, *p,p'*-isopropylidenebisphenol, dian, etc] [80-05-7] part (135). The resulting polymer (**52**) has been characterized in terms of ion-exchanges group content, conductivity, and hydrolytic stability. Membranes made from (**52**) showed good conductivity, good permselectivity ($>90\%$), and good hydrolytic stability in $1\text{ }N$ HCl and water at temperatures of up to 80°C . This new sulfonation method can be applied to all the polymers which form soluble lithium salts.



Alternative potential materials for preparation of cation-exchange membranes are sulfonated poly(phenylquinoxaline)s (**53**) (149), which were produced by polymeric reaction sulfonation of poly(phenylquinoxaline)s (**54**) or by synthesis from monomers, directly in the sulfonating medium (eq. 2). In both cases, sulfonation was carried out in a sulfuric acid/oleum mixture (4:1) at 125°C . High strength thermally stable films showing high hydrolytic stability were cast from the solution of (**53**) in DMF. Polymers (**53**) can also be processed by compression molding.



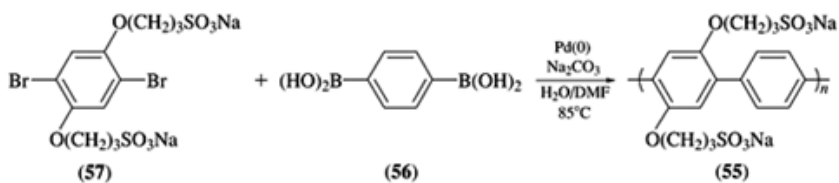
Earlier attempts to prepare highly sulfonated PPS by sulfonation with SO_3 were unsuccessful; the formation of only lightly sulfonated polymers (up to 0.5 sulfonic acid groups per phenylene, m) accompanied by the formation of ladder or cross-linked structures because of the stringent reaction conditions took place (145,146,147,148). The highly sulfonated PPS (m up to 2.0) (**36**) was successfully prepared by the polymerization of methyl-4-(phenylthio)phenyl sulfoxide (**34**) in sulfuric acid via polysulfonium salt as a soluble precursor (113). The sulfonation can be controlled by the reaction time, the temperature, and/or the addition of SO_3 . The sulfonated polymer (**36**), unlike the nonsubstituted polymer, is soluble in water and methanol, and can form a transparent film. It was found that (**36**) exhibits a good water affinity and an excellent proton conductivity of up to $4.5 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 80°C .

Membranes made from homogeneously sulfonated polystyrene exhibited proton conductivity equal to that of Nafion, with methanol permeability about 70% smaller than for this ionomer. This is attractive particularly in relation to the methanol fuel cell technology (150).

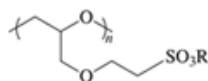
Other proton-exchange membranes bearing sulfonic acid groups were produced by radiation-induced grafting of styrene onto fluorinated polymers and subsequent sulfonation (151,152,153,154,155,156,157,158,159,160,161). Membranes produced from, eg, the high radiation resistance commercial poly(tetrafluoroethylene-*co*-hexafluoropropylene) films having degrees of grafting of 16% and above showed proton conductivity of the magnitude of $10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$ at room temperature, and thermal stability at temperatures up to 290°C under an oxygen atmosphere (151).

A new type of amphiphilic polymer blend comprising polystyrene (PS), poly(ethylene oxide) (PEO), and microspheres of cross-linked polystyrene sulfonic acid (PSSA) was prepared by solution blending and followed by casting. The ir and the differential scanning calorimetry (dsc) studies showed that besides providing protons, PSSA plays a role in enhancing the miscibility of PS and PEO. The influence of the mixing extent between PS and PEO on the proton conductivity has also been studied (162).

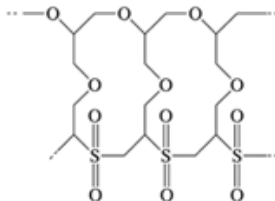
The first water-soluble, electroactive, self-doped sulfonatoalkoxy-substituted PPP, poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-1,4-phenylene] (**55**), was synthesized from 1,4-benzenediboronic acid [4612-26-4] (**56**) and the disodium salt of 1,4-dibromo-2,5-bis(3-sulfonatopropoxy)benzene (**57**) by the homogeneous Suzuki coupling method (130). The polymer purified by dialysis of an aqueous solution was composed exclusively of 1,4-linkages. The ability to utilize a variety of bis(boronic acids) in this polymerization with sulfonate containing aryl halides will lead to a high degree of structural control of the optoelectronic properties of these water-soluble polymers.



As a new approach to sulfonated polymers, sulfonation of oligo(2-propenyloxy)methoxyirane by SO_2 in presence of amines has been studied (163). It was shown that, depending on the reaction conditions, oligomeric sulfo acid or its derivatives (26) as well as crown polysulfonic acid (27) can be synthesized. Crown polysulfonic acid is produced by the copolymerization of SO_2 with double bonds of unsaturated oligomer.



$\text{R} = \text{H, K, Na, Li, NHR}_3^+, \text{R}^1 = \text{organic radical}$



The synthesis, characterization, and some properties of novel unimolecular micelles of hydrophobically modified sodium polysulfonates as well as their potential utility for novel photochemical systems have been reviewed (164).

A novel series of water-soluble amphoteric cyclocopolymers containing the pH-responsive hydrophobic monomer, *N,N*-diallyl-*N*-methylamine [2424-01-3], and the sulfobetaine monomer, 3-(*N,N*-diallyl-*N*-methylammonio)-propanesulfonate, have been prepared in 0.5 *M* NaCl aqueous solution (pH 4.0), using 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959) as the free-radical photoinitiator (165). Equilibrium dialysis experiments demonstrated that they could be utilized to control the sequestration of organic foulants and thus have potential application as polymeric surfactants in micellar-enhanced ultrafiltration processes for water purification.

Numerous copolymers based on the ionizable monomer 2-(acrylamido)-2-methylpropanesulfonate (AMPS, 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propanesulfonic acid) [15214-89-8] and mainly vinyl or acryl comonomers were prepared and characterized because of their various application possibilities. Some of them are mentioned below.

Micelle-forming materials obtained by radical copolymerization of sodium salt of AMPS with 9-vinylphenanthrene and 1-vinylpyrene (AIBN, THF solvent, 60°C) can be used as media for photosensitized electron transfer in aqueous systems (166). Reactive microgels obtained by copolymerization of AMPS with *N,N'*-methyleneacrylamide are suitable for the immobilization of biological materials (167).

Copolymers synthesized by a sodium persulfate-initiated free-radical solution polymerization of acrylamide and AMPS (at different pH values) as a new type of super-absorbent polymer have been studied in terms of swelling or viscosity behavior in water (168).

The reaction of fluoroalkanoyl peroxides with AMPS or AMPS and the comonomers such as trimethylvinylsilane and methyl methacrylate gives novel fluoroalkylated end-capped homo- or copolymers which are able to form gels both in water and organic polar solvents such as methanol, ethanol, DMF, and DMSO under noncross-linked conditions. These AMPS polymer hydrogels have a strong metal ion binding power. Moreover, they are potent and selective inhibitors of the human immunodeficiency virus type 1 (HIV-1) replication in cell culture. One of these gelling polymers was found to possess antibacterial activity against *Staphylococcus aureus* (169).

Copolymers synthesized from AMPS and lauryl methacrylamide in different mole ratios were characterized and used as separation media in electrokinetic chromatography (170).

The new polyacrylic fibers (OHIS, Skopje) contain incorporated AMPS, which gives new and improved dyeing properties to the fiber. It can be dyed in more brilliant hues compared to Malon fiber with itaconic acid as an acidic comonomer (171).

Thermoassociative water-soluble copolymers containing AMPS and poly(ethylene oxide) [25322-68-3] grafts can be applied in the oilfield industry as thickening agents functioning at elevated temperatures (172, 173).

A new water-soluble sulfonated phenolic resin as a potential superplasticizer was prepared from formaldehyde, phenol, and sodium bisulfite (NaHSO_3) through a four-step reaction procedure. It was found that this resin could reduce the water content and improve the workability and compressive strength of concrete. The best results were obtained for concrete containing 2 wt% resin, which are comparable with commercial superplasticizers (128,174,175,176).

Wholly aromatic ionic polyesters such as poly(sulfo-*p*-phenylene terephthalate), poly(sulfo-*p*-phenylene bromoterephthalate), and poly(sulfo-*p*-phenylene nitroterephthalate) containing sulfonate pendent groups have been synthesized, for the first time, by an interfacial condensation procedure from commercially available hydroquinonesulfonic acid potassium salt and terephthaloyl chloride, 2-bromoterephthaloyl chloride or 2-nitroterephthaloyl chloride, respectively (177). It was found that nitro-substituted polyester forms lyotropic liquid crystalline solutions in the wide range of DMSO/water solvent mixtures (15, 30, 50, and 70 vol%), in DMF/water (50 vol%), and in pure water and DMF. Because of their decomposition upon heating at high temperature, these polyesters do not show thermotropic liquid crystal transitions in solid state.

Other lyotropic liquid crystalline polyesters based on poly(sulfo-*p*-phenylene nitroterephthalate) as well as poly(sulfo-*p*-phenylene nitroterephthalamide) have been reported (178).

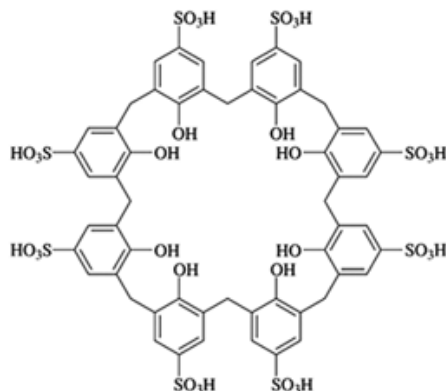
5.1.1. Biomedical Applications

Considerable effort has been focused on the modification of segmented polyurethanes as biomaterials to improve their blood-contacting behavior, eg, preventing the occurrence of thrombosis and thromboembolization. The incorporation of the functional sulfonate groups representing key structural elements of the anticoagulant bioactive molecule, heparin [9005-49-6] (179), is a less difficult type of modification than the incorporation of the molecule itself. The various segmented polyurethanes containing sulfonate groups in the hard (180,181,182, 183,184,185,186) and soft segment (187,188) were synthesized and characterized in order to investigate their anticoagulant effects as the consequence of the platelet adhesion. From this study it appears that incorporation of sulfonate ions into polyurethanes directly affects the blood-contacting response of these materials. However, the effect can be beneficial or deleterious, and it appears to be dependent on the molecular location of the ions and the structure of the polymer.

The effects of the polysulfonic acid derivative 4-*t*-butylcalix[8]arene-*p*-sulfonic acid (GL 522-Y-1, Genelabs, Redwood City, Calif., U.S.) (28) on thrombosis *in vivo* and haemostasis *in vitro* have been investigated. On

20 SULFUR-CONTAINING POLYMERS

the basis of its unique antithrombotic properties, GL 522-Y-1 seems to open a new pathway in the field of antithrombotics; so far it was primarily developed as an antiviral drug (189).



In the past few years, several compounds have been described that exhibit marked activity against respiratory syncytial virus (RSV) *in vitro* (190). Among the most potent and selective RSV inhibitors are various polyanionic substances, including polysulfonates (eg, poly(vinylsulfonate), poly(styrenesulfonate), poly(acrylamidomethylpropanesulfonate), sulfonated derivatized dextrans, etc) and polysulfates (virus adsorption). They have significantly higher selectivity index than Ribavirin (1- β -D-ribofuranosyl-1,2,4-triazole-3-carboxamide, Tribavirin; Virazole; Viramid; RTCA; Vilona; Virazid, etc) [36791-04-5], which is the only antiviral agent approved for the treatment of RSV infections.

5.2. Polysulfonates

Aromatic polysulfonates having the sulfonate ester group in the main chain possess good physical, chemical, electrical, and thermal properties. Their characteristics are high softening and melting temperatures, thermal stability of up to 300°C, resistance to alkali, acids, and oils, and solubility in halogenated aliphatic hydrocarbons. They can be processed by molding, extruding, injection molding, as well as casting from solution. These polymeric materials can be useful as coatings and adhesives (3,191). High molecular weight polysulfonates are easily obtained by step-growth polymerization reaction of aromatic diphenols with aromatic disulfonyl dichlorides using phase-transfer catalyst (3,191,192,193). Wholly aliphatic polysulfonates are prepared by ROP of cyclic sulfonates (3).

Catalyzed (benzyltriethylammonium chloride [56-37-1]) interfacial condensation of aromatic-(poly)cycloaliphatic diphenols and their bromoderivatives, including 4,4'-(1-cyclohexylidene)diphenol, 4,4'-(2-norboldidene)diphenol, 4,4'-(1-cyclohexylidene)-di-(2,6-dibromophenol), and 4,4'-(2-norboldidene)-di-(2,6-dibromophenol) with various aromatic dichlorides was studied in detail (191,194). Depending on the reaction conditions and the monomer used, the low crystalline polymers (with $\eta_{red} \sim 0.2\text{--}1.7$ dL/g and softening range of 160–310°C) soluble in halogenated aliphatic and aromatic hydrocarbons and DMF were obtained. They exhibited hydrolytical stability to both mineral acids and bases at room temperature and good thermal stabilities of up to 290–360°C.

More recently, similar polysulfonates, eg, (29) and (30), prepared by conventional interfacial condensation using water-chloroform as an interface, alkali as an acid acceptor, and cetyltrimethylammonium bromide [57-09-0] as an emulsifier have thoroughly been studied (195,196,197,198,199,200,201,202,203,204,205,206). In general, the polymers possess good solubility in common solvents, good acid and alkali resistance, thermal stabilities of up to 355°C, and tensile strength of up to ~ 20 MPa (199).



Polysulfonates with reactive pendent chloromethyl groups (**63**) can be synthesized by solution polymerization of bisepoxides (**64**) with disulfonyl chlorides (**65**) (207).



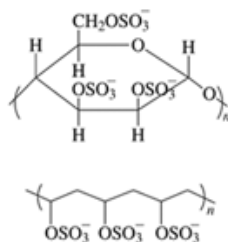
6. Polysulfates

Polysulfates are widely studied because of their potential biomedical applications. Heparin, a naturally occurring sulfated polysaccharide, has antithrombogenic properties and is used in cardiovascular surgery (179,208).

22 SULFUR-CONTAINING POLYMERS

Polysulfates in general, and sulfated polysaccharides in particular, are active against a wide variety of enveloped viruses (209,210).

Various polysulfates, eg, heparin, dextran sulfate, mannan sulfate (**31**), galactan sulfate, xylomannan sulfate, polyacetal polysulfate, poly(vinylalkoholsulfate) (**32**), and poly(acrylic acid vinylalcoholsulfate), are the most potent and selective RSV inhibitors (190).

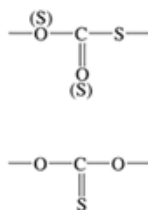


Heparin and other sulfated polysaccharides extracted from sea algae were found to be potent and selective inhibitors of the HIV-1 replication in cell culture as well as various enveloped viruses, including viruses that emerge as opportunistic pathogens (eg, herpes simplex virus and cytomegalovirus) in immunosuppressed [eg, AIDS (the acquired immune deficiency syndrome)] patients. As potential anti-HIV drug candidates, sulfated polysaccharides offer a number of promising features (209,210).

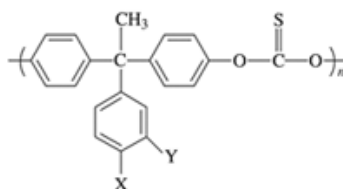
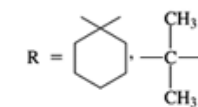
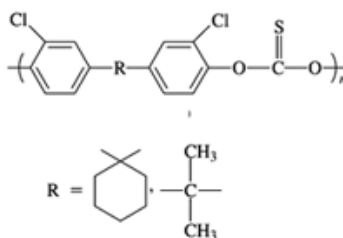
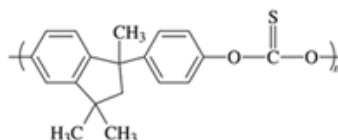
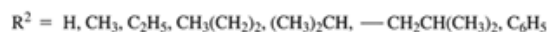
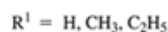
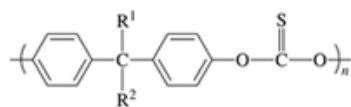
A major commercial sulfated polysaccharide is carrageenan [9000-07-1], used in ice cream and other food products (see Gums).

7. Polythiocarbonates

In general, polythiocarbonates are polymers containing the structural units (**33**) with one to three sulfur atoms and unit (**34**). They are mainly prepared by ROP of the corresponding cyclic monomers, eg, ethylenethiocarbonate (1,3-dioxolan-2-thione) [20628-59-5] or 1,3-oxathiolane-2-thione, or by condensation reactions involving dithiols and adequate difunctional coupling compounds. The synthesis and properties of many kinds of polythiocarbonates were reviewed in 1992 (3).



Poly(monothiocarbonate)s (**35**) (211,212,213,214), (**36**) (215), (**37**) (216), and (**38**) (217) containing oxythiocarbonyloxy linkages (**34**) are prepared from thiophosgene (carbon chlorosulfide, thiocarbonylchloride, carbonothioic dichloride) [463-71-8] and corresponding diphenols under phase-transfer conditions with quaternary ammonium and phosphonium salts as catalysts. The influence of the structure of the bisphenols and the nature of the catalyst on yields and η_{inh} have been studied. Under optimum conditions, polymers in ~ 90 – 97% yields and η_{inh} up to 1.8 (**35**), 0.09 (**36**), 0.24–0.63 (**37**), and 0.24–0.36 dL/g (**38**) (0.5 g/dL, CHCl_3 , at 25°C) were obtained.



The synthesis of related poly(ester-thiocarbonate)s containing the ester group in the main chain (218,219) and in the side chain (220) as well as poly(amide-thiocarbonate)s containing the amide group in both the main (221) and side (222) chains under phase-transfer conditions have also been reported. It has been shown that this technique can be effective to prepare polythiocarbonates derived from diphenols containing Si or Ge, bis(4-hydroxyphenyl)-dimethyl-germane, bis(4-hydroxyphenyl)-diphenyl-germane, bis(4-hydroxyphenyl)-dimethyl-silane, and bis(4-hydroxyphenyl)-diphenyl-silane (223).

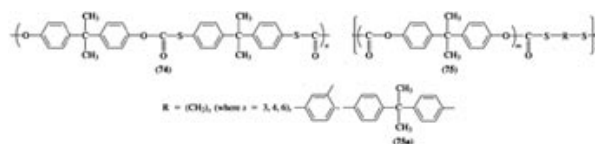
Thermogravimetric (TG) investigations exhibited that the thermal stability of this family of polythiocarbonates is in general lower than that of corresponding polycarbonates (224,225,226). The solution properties (dipole moment and partial specific volume) and chain flexibility of different polymers have been studied (227,228,229,230,231,232,233).

Polymers containing thiocarbonylthio ---S---CO---S--- and oxycarbonylthio ---O---CO---S--- linkages (**33**) were prepared by catalyzed interfacial condensation of aliphatic dithiols, including 1,3-propanedithiol, 1,4-butanedithiol, and 1,6-hexanedithiol (3,234), or aromatic dithiols such as 1,3-dimercaptobenzene (1,3-benzenedithiol) [626-04-0] and 2,2-bis(4-mercaptophenyl)propane (BMP) (3,235,236) with phosgene or bisphenol A bis(chloroformate) [2024-88-6] (235), respectively.

24 SULFUR-CONTAINING POLYMERS

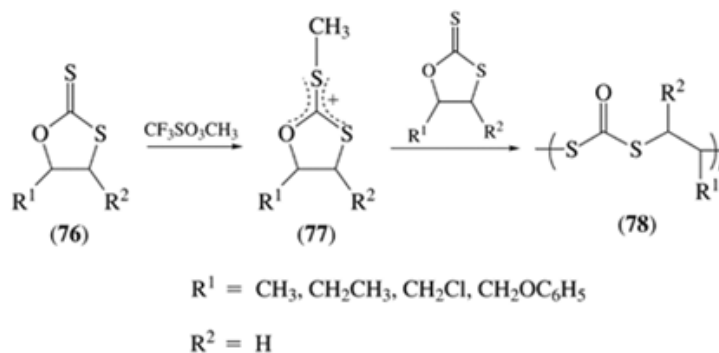
Polymers synthesized from phosgene and dithiols with BTEAC (benzyltriethylammonium chloride) [56-37-1] as phase-transfer catalyst have low $[\eta]$ (up to 0.16 dL/g) and relatively low yields ($\sim 70\%$). This result can be attributed to the low reactivity of the thiocloroformate groups $-\text{SCOCl}$, which derive from the reaction of the thiol groups with phosgene. Using the catalyst DMAP (4-dimethylaminopyridine) [1122-58-3] instead of BTEAC significantly increased molecular weight of the resulting polymers (236).

Polymers with bisphenol A moieties were obtained in high yields and with high molecular weights, particularly those obtained by using DMAP as catalyst and based on BMP ($M_w = 180,000$) (**74**) (236). They exhibited $T_g = 58\text{--}90$ and 154°C for aliphatic and aromatic dithiol BMP, respectively. Coupled block copolymers (**75**) containing both carbonate and thiocarbonate groups synthesized under the same conditions of phase-transfer catalysis in high yields (up to 95%) from the above-mentioned dithiols and bisphenol A polycarbonate oligomers were high molecular weight polymers, particularly those based on BMP (**75a**) ($M_w = 170,000$). Their T_g s were $124\text{--}158^\circ\text{C}$ (234,236).

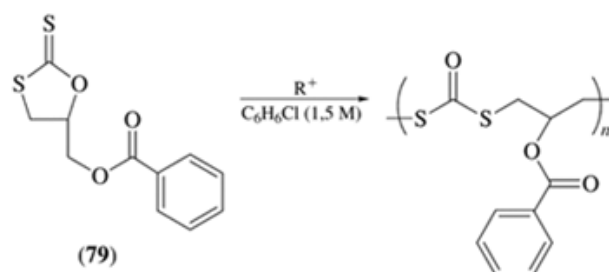


On the basis of the TG analysis, all these polythiocarbonates are, in general, less thermally stable polymers compared with the corresponding polycarbonates (236,237). The high refractive indices observed make these polymers, particularly poly(dithiocarbonate)s, potentially interesting for optical applications (ie, lenses and optical fibers) (238).

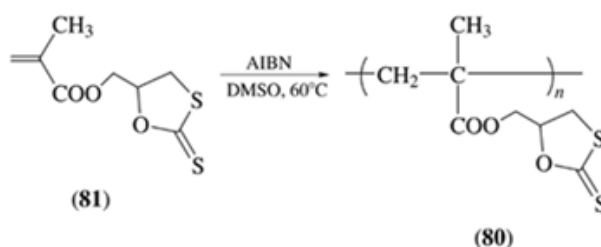
It has been reported that five-membered cyclic dithiocarbonates (**76**) undergo selective ROP with initiators such as $\text{CF}_3\text{SO}_3\text{CH}_3$ [333-27-7] and $\text{CF}_3\text{SO}_3\text{C}_2\text{H}_5$ [425-75-2] through the cyclic carbenium cation (**77**) leading to the formation of the corresponding poly(dithiocarbonate)s (**78**) with thiocarbonylthio linkages (239,240,241).



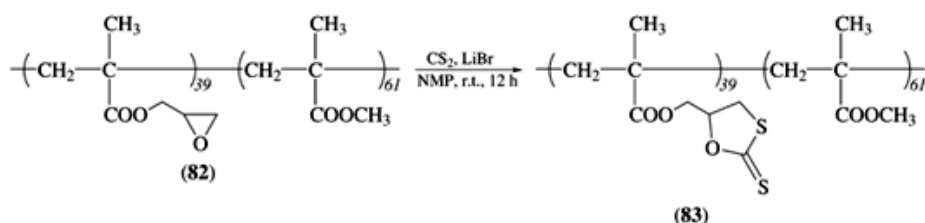
The first example of the controlled living cationic ROP of the five-membered cyclic dithiocarbonate (**79**) based on the neighboring group participation initiated with $\text{CF}_3\text{SO}_3\text{H}$ or $\text{CF}_3\text{SO}_3\text{CH}_3$ has also been demonstrated (234). This new concept of living polymerization may be applied to the design of well-defined novel functional polymers.



The high molecular weight polymethacrylate (**80**) (M_n above 100,000) bearing five-membered cyclic dithiocarbonate groups in the side chain can easily be prepared by AIBN-catalyzed homopolymerization of 5-(methacryloyloxy)methyl-1,3-oxathiolane-2-thione (**81**) (DMSO, 60°C); however the formation of some cross-linked products takes place (243). To avoid the cross-linking reaction, the comonomer methyl methacrylate and more diluted conditions were used.



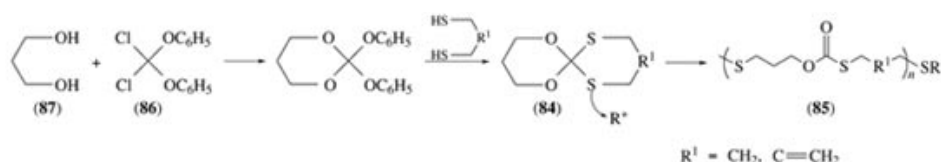
A novel monomer (**81**) was synthesized by the reaction of glycidyl methacrylate [106-91-2] and CS₂ in the presence of LiBr in THF solution at room temperature in 93% yield. The attempts to synthesize polymer (**80**) by polymer reaction of poly(glycidyl methacrylate) with CS₂ were unsuccessful because of the formation of the cross-linking gels. When the copolymer (**82**) (glycidyl methacrylate/methyl methacrylate = 39/61, M_n = 80,000 with polydispersity 1.71) was allowed to react with CS₂ in THF solution and LiBr as catalyst, the yellowish polymer (**83**) (M_n = 114,000 with polydispersity = 5.08) was obtained without cross-linking, soluble in many common organic solvents (243); polymer (**80**) was soluble only in DMSO and DMF. These materials are potentially the most versatile reactive polymers which react with amines to afford a polymethacrylate bearing a thiol group in the side chain as well as potential optical materials, heavy metal-affinity polymers, and photoreactive polymers.



The first cationic polymerization of the sulfur-containing spiro ortocarbonates (**84**) under various initiators both in chlorobenzene [108-90-7] or dichloroethane solution and in the absence of a solvent has been

26 SULFUR-CONTAINING POLYMERS

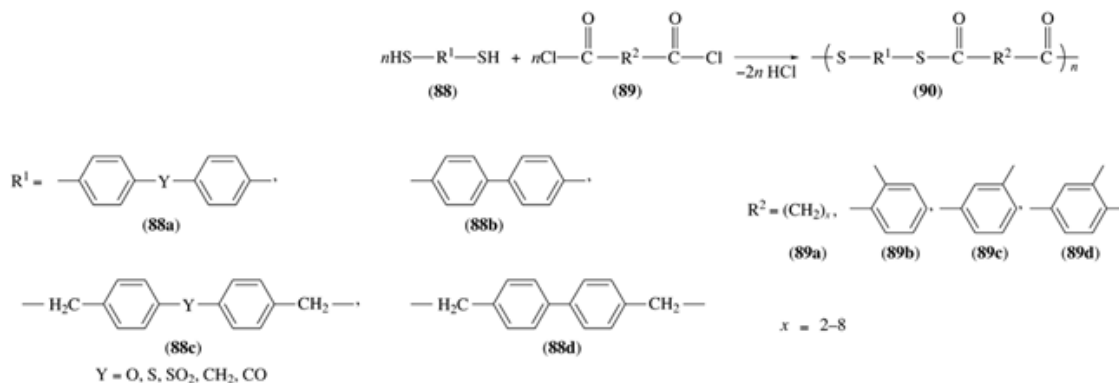
studied (244). The low molecular weight poly(thioether-monothiocarbonate)s (**85**) ($M_n = 700\text{--}2500$ with polydispersity = 3.2–7.8) were obtained. The polymerization is believed to occur via a controlled tandem double ring-opening mechanism. Monomers (**84**) were synthesized via a two-step procedure from 1,1-dichloro-1-diphenoxymethane (**86**) and 1,3-propanediol [504-63-2] (**87**). The relative hydrolytic stability of these monomers is greater than their oxygen analogues.



8. Polythioesters

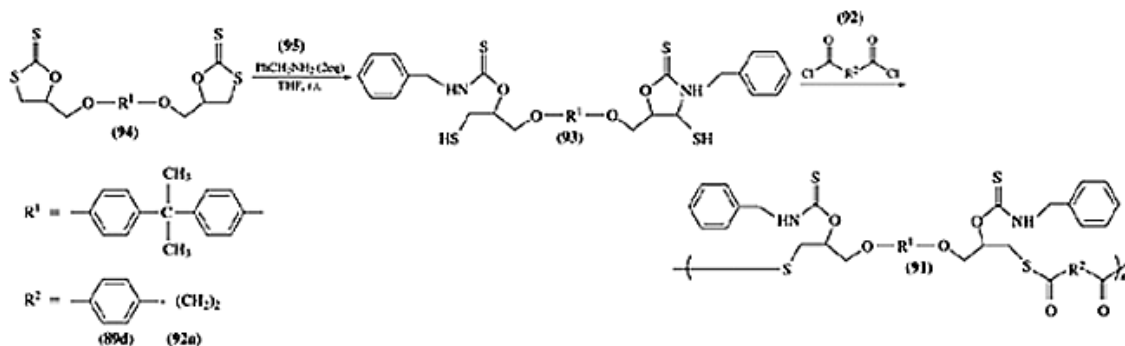
Contrary to their oxygen counterparts polyesters, polythioesters were not commercialized and their research interest has decreased in the last few years. This can partly be due to a more difficult and expensive approach to starting materials, eg, acid dichlorides and dithiols as well as the instability of polymers against alkalis. The synthesis and properties of the polythioesters are reviewed in References 2, 3, and 245.

Interfacial condensation of the two series of dithiols ((**88**)), aromatic ((**88a**) and (**88b**)) (246,247,248,249, 250,251) or aliphatic–aromatic ((**88c**) and (**88d**)) (252,253,254,255,256) with various diacid dichlorides ((**89**)), aliphatic (**89a**) and isomeric phthaloyl chlorides (**89b**), (**89c**), and (**89d**) has been studied in detail as a continuation of an earlier-undertaken systematic study of linear polythioesters. High molecular weight polymers (**90**) (η_{red} up to ~ 2.5 dL/g) in good yields (up to $\sim 99\%$) were obtained under optimum conditions. They were characterized in terms of structures, chemical and thermal resistance, and some mechanical and electrical properties. In general, polymers exhibit a good thermal resistance of up to 450°C . They are resistant to diluted alkali or mineral acids, but decompose when treated with concentrated reagents. Polymers derived from isophthaloyl chloride [99-63-8] (**89c**) and terephthaloyl chloride [100-20-9] (**89d**) are insoluble in common organic solvents, high melting (above 200°C , some even 300°C) and thermal-stable (up to $300\text{--}450^\circ\text{C}$) materials showing good mechanical properties.

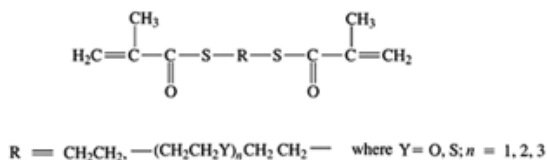


The low temperature solution polymerization of MMB (**88d**) with selected aliphatic and aromatic diacid dichlorides under optimum conditions produced significantly lower molecular weight polymers or copolymers ($\eta_{\text{red}} \sim 0.2\text{--}0.6$ dL/g) in up to 96% yield (257).

Polythioesters (**91**) have been prepared by condensation of terephthaloyl (**89d**) or succinyl chloride [543-20-4] (**92**) with a dithiol (**93**) generated *in situ* from bifunctional five-membered cyclic dithiocarbonate (**94**) and benzylamine [100-46-9] (**95**) in THF solution at room temperature (26). The polymers with $M_n = 5100\text{--}8200$ or 2900 were obtained in the presence of triethylamine [121-44-8] or pyridine [110-86-1], respectively in $\sim 90\%$ yields. Their T_g s were $51\text{--}76^\circ\text{C}$.



It has been reported that the novel bifunctional thiomethacrylates (**41**), which have refractive indices of 1.6 and larger, are very important and useful monomers for high index cross-linkers for optical plastics (258).

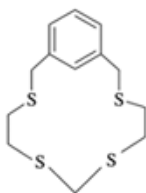
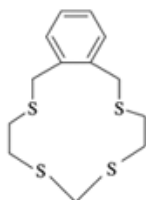
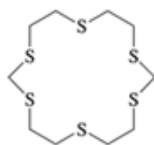


Transparent resins with light weight, a high refractive index, large Abbe number, and excellent impact strength can be produced by using these good copolymerizable (eg, with styrene and acrylonitrile) cross-linking thiomethacrylates. Monomers can be prepared in high yields (84–93%) by phase-transfer catalyzed (tri-*n*-octylmethylammonium chloride [5137-55-3]) interfacial condensation of dithiols and methacryloyl chloride in the chloroform/(H_2O , KOH) system plus inhibitor.

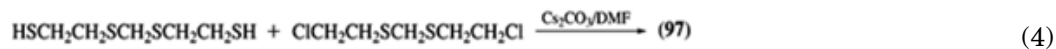
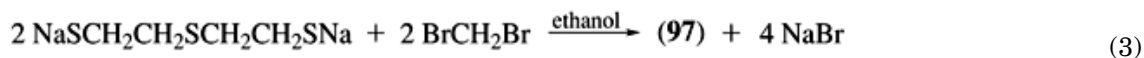
9. Polythioacetals

Earlier studies on polythioacetals, mainly aliphatics, revealed limited possibilities to utilize these materials as potential industrial thermoplastics because of their instability in the molten state as well as an offensive odor of some monomers and degradation products (2,259,260,261). Aromatic polythioacetals (262,263,264) and thiacycrown ethers bearing thioacetal linkages (36,37,262,265,266,267) have recently received increasing attention.

Various macrocycles, eg, (**42**), (**43**), (**44**), (**45**), and (**46**), have been extensively studied in terms of the synthesis, properties, and complexation behavior.

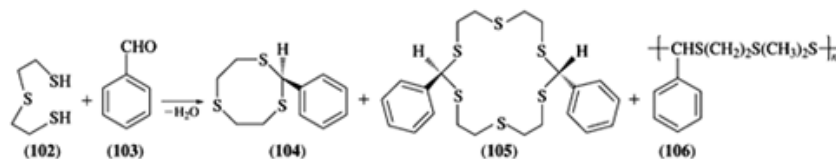


They can be prepared in roughly 50–75% yields by two different synthetic routes described in equations (3) and (4), for example, the synthesis of 1,3,6,9,11,14-hexathiacyclohexadecane (16S6) (**42**) (267). It should be noted, however, that for many cycles the only practical method of synthesis is method (4). Thus, the cycles (**45**) and (**46**) were prepared by the reaction cyclization of the *in situ* generated bis cesium salt of 3,5-dithiaheptane-1,7-dithiol with α,α' -dibromo-*o*-xylene [91-13-4] or α,α' -dibromo-*m*-xylene [626-15-3] in 52 and 63% yield, respectively (266).



It has been found that acid-catalyzed condensation of 2,2'-thiodiethanethiol [3570-55-6] (**102**) with carbonyl compounds (or equivalents thereof) carried out in solution can, under chosen conditions, lead to good yields to thiocrown ethers containing thioacetal units (262). A detailed examination of a prototype reaction

of (102) with benzaldehyde [100-52-7] (103) showed that depending on the reaction conditions, a different distribution of the products [monomer (104), dimer (105), and polymer (106) of $M_n = 11,250$ with polydispersity = 1.9] is achieved. Products (104), (105), and (106) with maximum yields 87, 62, and 99% respectively, can be obtained.

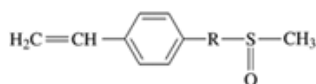


High molecular weight linear polymers with $M_n \sim 9000$ –27,600 in up to 70% yield (after repeated reprecipitation from $CHCl_3$ /ethyl ether) can be obtained by acid-catalyzed (*p*-toluenesulfonic acid [104-15-4]) solution (dichloromethane) polymerization of various aromatic aldehydes such as benzaldehyde and its *p*-substituted (CH_3O –, $CH_2=CHCH_2O$ –, Cl –) derivatives with aliphatic dithiols such as 1,6-hexanedithiol [1191-43-1], 3,6-dioxaoctane-1,8-dithiol [14970-87-7], tetramethylene bis(3-mercaptopropionate), or aromatic dithiol bis(4-mercaptophenyl) ether (263). Nevertheless, the formation of some cyclic side products took place, which have been isolated and identified. Polyrotaxane structures were also found under special conditions (eg, at a shorter reaction period). The linear polymers exhibited $T_g = -31$ to $-13^\circ C$ (from aliphatic dithiols) and $82^\circ C$ (from aromatic dithiol) and T_d above $200^\circ C$. In contrast, the bulk polymerization catalyzed by HPF_6 [16940-81-1] generated *in situ* has produced well-defined thioacetal structure polymers in high yield up to 90% but with low molecular weights of $M_n = 2300$ –5700.

10. Polysulfoxides

Polysulfoxides are polymers containing high reactivity sulfoxide groups towards the free-radical or ionic center and so they are used as functional polymers. Polysulfoxides are a catalyst for reactions conducted under phase-transfer conditions (268,269,270). Poly(sulfinyl acrylate)s exhibit some biological activity (271,272). Membranes bearing sulfoxide moieties are permeable, particularly to polar compounds (273,274). Aliphatic polysulfoxides having sulfoxide groups in the main chain can be used as novel polymeric oxidizing reagents, compatibilizers, and polymer solvents. These novel aprotic polar polymers can also be expected to become novel reactive polymers (18,275). The chiral polysulfoxides can be utilized as stationary phases of chiral hplc column and as polymer reagents (276).

Polysulfoxides with sulfoxide group in the side chain are obtained by polymerization of monomers containing a sulfoxide group linked to the unsaturated carbon–carbon bond via aromatic or aliphatic units (47) (268,269,271,272,277). They are also synthesized by a Michael-type addition of dithiols to diolefins with a double bond activated by an adjacent sulfoxide group (274,278). Both methods were successfully applied to preparation of copolymers (274,277).



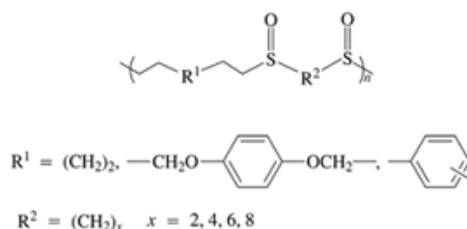
Polysulfoxides containing the sulfoxide group in the main chain are mainly synthesized by controlled oxidation of polysulfides using various oxidizing agents, including nitric acid, *tert*-butyl hydroperoxide [75-91-2], hydrogen peroxide [7722-84-1], peracids, or bromine, but it is difficult to avoid some sulfone formation (3).

30 SULFUR-CONTAINING POLYMERS

Poly(phenylene sulfoxide) of $M_n \sim 8000$ (279) and poly(*p*-phenoxyphenyl sulfoxide) of $M_n = 4800$ (280) containing no sulfone groups were obtained using nitric acid or hydrogen peroxide, respectively, as oxidizing agent. More recently, the selective and quantitative oxidation of atactic poly(propylene sulfide) to its corresponding sulfoxide was conducted by using *m*-chloroperbenzoic acid, hydrogen peroxide, or bromine under stoichiometric conditions either in homogeneous solution or in two-phase process (281).

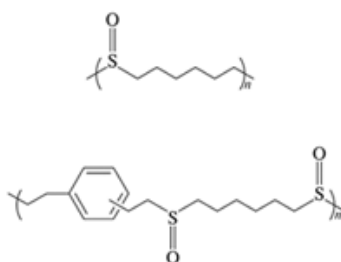
Earlier reports dealing with oxidation of aliphatic polysulfides to polysulfoxides (19,281) contain no information about the properties of the resulting polysulfoxides.

The synthesis, properties, and application of aliphatic polysulfoxides with a methylene chain between sulfur atoms of various length (48) have been reported (18).

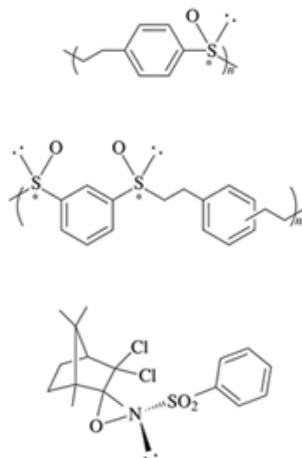


Polymers of $M_n = 1600\text{--}6500$ with polydispersity $\sim 1.2\text{--}2.8$ were prepared by addition of diolefins with dithiols and the following two-phase oxidation of the resulting polydisulfides. The effective oxidation (up to 92% of sulfoxide units) of polysulfides was conducted by using aqueous hydrogen peroxide in chloroform with or without heating. The formation of polysulfoxides was strongly supported by spectroscopic analysis. Poly(hexamethylene sulfoxide) obtained in this way was subject to Swern oxidation of primary or secondary alcohols, in which 1-octanol [111-87-5] and 6-undecanol [23708-56-7] were oxidized to give 1-octanal [124-13-0] and 6-undecanone [927-49-1], respectively, in quantitative yields (18).

The miscibility of aliphatic polysulfoxides (49) and (50) (T_g : 125°C , 7°C) with other commodity polymers was examined by comparing T_g s of the mixture of these polymers with T_g s of the original polymers by dsc. It was found that these polysulfoxides had good miscibility with poly(2-methyl-2-oxazoline) and/or poly(*N*-vinylpyrrolidone) (275).



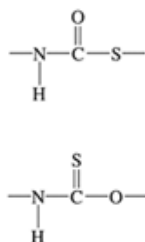
The novel highly optically active polysulfoxides (51) and (52) (276) with chiral sulfonyl groups in the main chain were prepared by asymmetric oxidation of corresponding polysulfides by using chiral *N*-sulfonyloxaziridine. The polysulfoxide with the enantiomeric excess (ee) of up to 91% was obtained in good chemoselectivity when the reaction was carried out with one equivalent of (–)-*N*-sulfonyloxaziridine (53) in chloroform at room temperature followed by reflux.



This asymmetric oxidation is the first example of introduction of chirality in good enantioselectivity into the main chain of a polymer by the polymer reaction, that is, the first example of the control of “tacticity” by polymer reaction. An earlier paper (282) described the synthesis of the liquid crystalline polymers having sulfoxide groups with low enantiomeric excess (25% ee). Another synthetic route to optical active polysulfoxides is the polymerization of optically active vinyl sulfoxides (283,284).

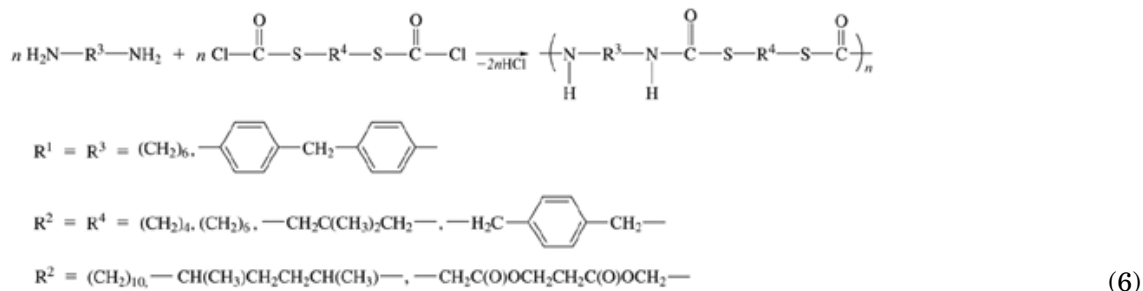
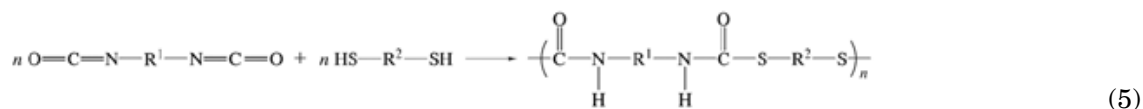
11. Polythiourethanes

Polythiourethanes (polythiocarbamates), the analogues of polyurethanes in which the ethereal or carbonyl oxygen atom of the urethane group has been replaced by sulfur [unit (54) and (55), respectively] are a relatively little-known class of polymers.



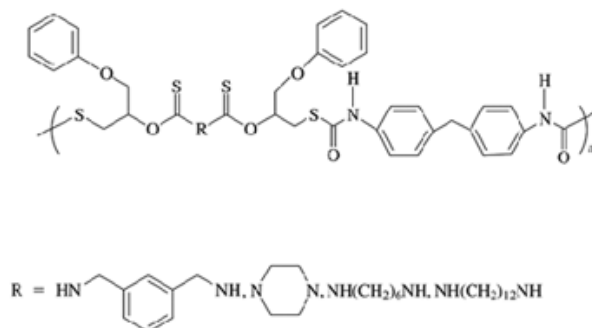
Polymers containing units (54) can be prepared by step-growth polymerization of diisocyanates with dithiols or bischlorothioformates with diamines. Early reports on the synthesis of these polymers concerned the melt polymerization of decamethylene diisocyanate [4538-39-0] and 1,10-decanedithiol [1191-67-9] (285,286).

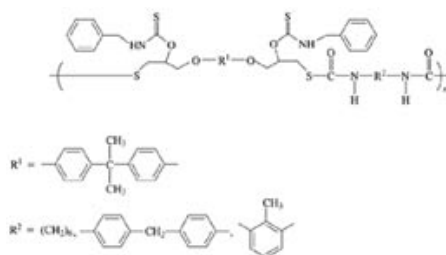
Later, both the methods have been studied and compared, the addition reaction of various diisocyanates and dithiols carried out in chlorobenzene/*o*-dichlorobenzene solution with tri-*n*-propylamine [102-69-2] and DABCO (1,4-diazabicyclo[2.2.2]octane, triethylene diamine, 2,2'-diazabicyclo[2.2.2]octane, TED, BACO) [280-57-9] as catalyst (eq. 5) and interfacial condensation of various diamines and bischlorothioformates in the $\text{CHCl}_3/\text{H}_2\text{O}, \text{Na}_2\text{CO}_3$ system (eq. 6) (287).



In general, the diisocyanate method was found to produce a higher yield (47–87% vs 31–73%) of the lower molecular weight polymers (η_{inh} 0.14–0.33 vs 0.30–1.20 dL/g) than that by the bischlorothioformate method. Polythiourethanes were found to be highly insoluble, odorless white powders which tend to decompose in light, in hot solvents, and in aqueous base. They melt somewhat higher than their oxygen analogues, but are less thermally stable. Some polymers form the pliable films from DMF solution.

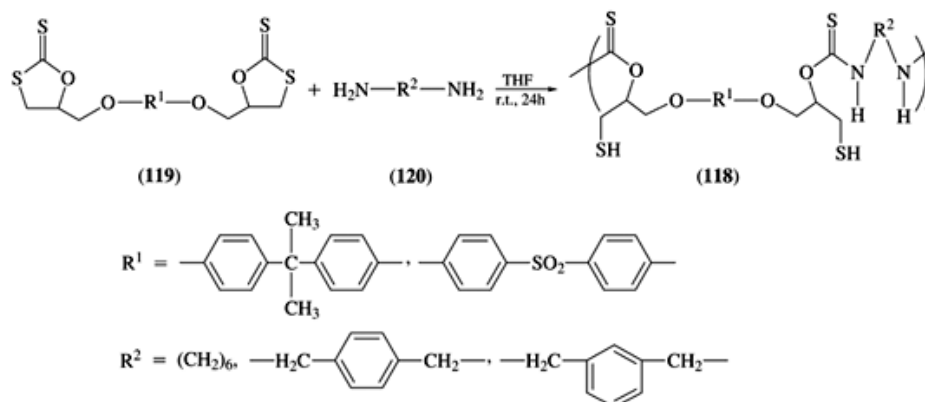
Polythiourethanes (**56**) and (**57**) have been prepared by polymerization of the corresponding diisocyanates, HDI (hexamethylene diisocyanate, 1,6-diisocyanatohexane, 1,6-hexamethylene diisocyanate, hexamethylene-1,6-diisocyanate, HMDI, etc) [822-06-0], MDI (methylenediphenyl diisocyanate, 4,4'-diphenylmethane diisocyanate, diphenylmethane-4,4'-diisocyanate, methylene bis(*p*-phenylene isocyanate), etc) [101-68-8], or 2,6-TDI (toluene-2,6-diisocyanate, 2,6-tolylene diisocyanate, 2,6-toluene diisocyanate, etc) [91-08-7] with dithiols which were formed *in situ* from monofunctional (25) or bifunctional (26) five-membered cyclic dithiocarbonates and various diamines or benzylamine [100-46-9], respectively. The reactions were carried out in THF or THF/DMAC solution with triethylamine [121-44-8] as catalyst at room temperature. The polymers in yield of 74–100% with $M_n = 6000$ –17,200 were obtained; their T_g s were 45–89°C. Contrary to common polythiourethanes showing low solubility even in highly polar organic solvent such as DMF and DMSO, these polymers are soluble in common organic solvents, including acetone and THF.





The SH- and NCO-terminated linear thiourethane telechelics containing units (**54**) ($M_n = 520\text{--}610$) were synthesized by DABCO-catalyzed addition reaction of 3,6-dioxaoctane-1,8-dithiol [14970-87-7] with various diisocyanates, including HDI, the mixture of 2,4,4-trimethylhexamethylene diisocyanate [15646-96-5] and 2,2,4-trimethylhexamethylene diisocyanate [6938-22-0], and isophorone diisocyanate [4098-71-9]. It has been shown that NCO-terminated prepolymers can be transformed into telechelics with olefinic end groups by treating with allyl alcohol [107-18-6], 2-hydroxyethyl methacrylate, or diallylamine [124-02-7] (288).

Polythiourethanes (**118**) containing units (**55**) bearing thiol groups were prepared in yield of up to 96% by the addition reaction of bifunctional five-membered cyclic dithiocarbonates (**119**) with diamines (**120**) carried out at room temperature in THF solution (93).



Their characteristics (after protection of the thiols group by acetylation) are $M_n = 5700\text{--}12,000$ with polydispersity = 1.38–1.65, $T_{d10} = 216\text{--}248^\circ\text{C}$, $T_g = 45\text{--}73^\circ\text{C}$, and the ability to form transparent films. Thus, polythiourethanes may be used as reactive polymers bearing the thiol groups which are sensitive to radical sources and applied to optical materials.

12. Polyesters Containing Sulfur Linkages

Among the thiopolyesters, polymers of linear structure containing S atoms in the main chain occupy the main position. They may find wide application as nonvolatile plasticizers for such polymers as poly(vinyl chloride) and rubber modifiers. They are also useful for modifying or plasticizing elemental sulfur, which may be reacted with them by heating a mixture of the sulfur and polyester to produce such useful products as caulking compounds and compositions for striping or marking highways and other surfaces (289,290,291,292,293,294). Hydroxyl-terminated aliphatic–aromatic thiopolyesters are used as polyol components in the synthesis of high

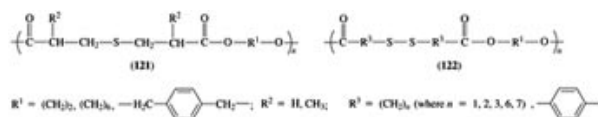
34 SULFUR-CONTAINING POLYMERS

elasticity polyurethane elastomers (293,295,296). Some thiopolyesters with S atom in the side chain are used as intermediates in the synthesis of the polymers containing free thiol groups that might be of considerable usefulness as reducing agents in the thiol-disulfide system (297).

Linear thiopolyesters containing sulfur in the main chain were synthesized by step-growth polymerization of monothio- and dithiocarboxylic acids or their esters with diols and thiodiols mainly by using melt methods.

The earliest reports on thiopolyesters concern the syntheses of the low molecular weight polymers from the diethyl ester of thiodivaleric acid and some polymethylene diols (298), thiodiacetic acid [123-93-3] and 2,2'-thiodiethanol [111-48-8] (299), and dimethyl ester of the 4,4'-thiodibenzoic acid or alkylenedithiodibenzoic acids and some polymethylene diols (300). The highly resistant high molecular weight polymers ($M_n \sim 20,000$) from 3,6-dithiaoctanedioic or 3,5-dithiaheptanedioic acid and fluorine-containing diols have also been described (301). All these reactions were carried out in melt at temperatures in the range of 160–250°C, at the first stage at atmospheric pressure and next under reduced pressure (130–400 Pa).

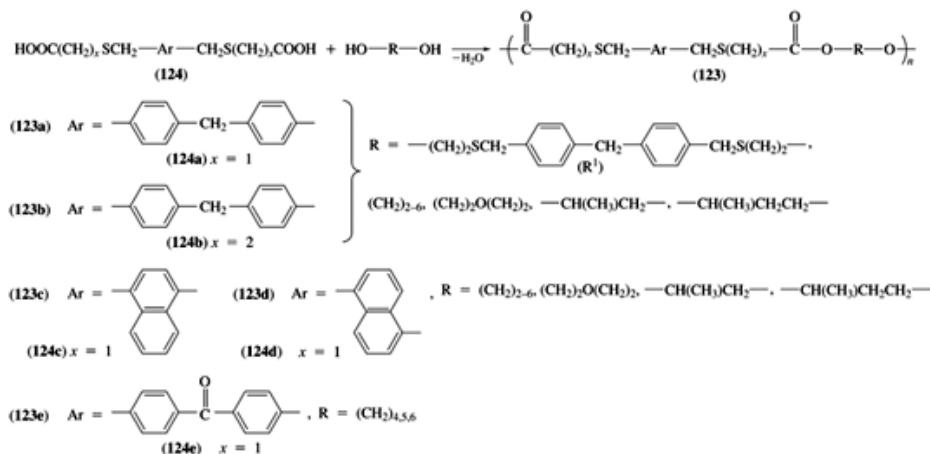
A few years later, various mainly aliphatic monothiopolyesters (**121**) and dithiopolyesters (**122**) (289,290) with M_n up to 10,000 were obtained by melt polymerization of the various monothio- and dithiocarboxylic acids, including 3,3'-thiodipropionic acid [111-17-1], thiodiisobutyric acid, 2,2'-dithiodiacetic acid [505-73-7], 3,3'-dithiodipropionic acid [1119-62-6], 4,4'-dithiodibutyric acid [2906-60-7], 7,7'-dithiodiheptanoic acid, 8,8'-dithiodioctanoic acid, and 4,4'-dithiodibenzoic acid with diols, including 1,2-ethanediol [107-21-1], 1,6-hexanediol [629-11-8], and 1,4-benzenedimethanol [589-29-7]. The process was typically carried out in the presence of nitrogen at temperatures 170–190°C for monothio products and 150–180°C for dithio products in two stages. First the diacid was heated with small excess of diol at atmospheric pressure. In the next stage, the low molecular weight polyester obtained earlier was submitted to transesterification by heating under reduced pressure (26–70 Pa) in the presence of a catalyst (PbO) and inhibitor of cross-linking 4-*tert*-butylcatechol [PTBC, 4-*tert*-butylpyrocatechol, TBC, 4-(1,1-dimethylethyl)-1,2-benzenediol, *tert*-butylcatechol] [98-29-3].



Some of these novel thiopolyesters were used for modifying or plasticizing elemental sulfur. In this order, thiopolyesters were heated with elemental sulfur in amounts of 10–90 wt% at a temperature range of 150–250°C, until a clear melt was obtained. The resulting polyester–sulfur compositions (PSC) showed tensile strength from 0.5 to 10 MPa and elongation at break from 17 to 240%. Their tensile strength was improved by adding such fillers as glass wool and poly(ethylene terephthalate) fiber or by using cross-linked thiopolyesters. The best results in terms of color and flexibility for the wide range of 10–90% sulfur used were achieved by using 3,3'-thiodipropionic acid.

In the last decade, extensive and systematic studies were undertaken of the synthesis structure, properties, and application of linear thiopolyesters (**123**) prepared by melt polymerization from various new aliphatic–aromatic thiodicarboxylic acids and aliphatic diols as well as aliphatic–aromatic bis[4-(2'-hydroxyethylthiomethyl)phenyl]methane (EM) (291,292,293,294,295,296,302,303).

Thiodiacids (**124**), including diphenylmethane-4,4'-bis(methylthioacetic acid) (**124a**), diphenylmethane-4,4'-bis(methylthiopropionic acid) (**124b**), naphthalene-1,4-bis(methylthioacetic acid) (**124c**), naphthalene-1,5-bis(methylthioacetic acid) (**124d**), and benzophenone-4,4'-bis(methylthioacetic acid) (**124e**) ($T_m = 167, 149, 156, 189, 116^\circ\text{C}$, respectively) were prepared from suitable dimercapto compounds by condensation with monochloroacetic acid [79-11-8] or 3-chloropropionic acid [107-94-8] in 10–20% aqueous solution of NaOH.



The kinetics of these esterification reactions was studied at 150, 160, and 170°C. Reaction rate constants and activation parameters from carboxyl group loss were determined using classical methods. The kinetic studies revealed that the rate of the reaction with **(124a)** was more than two times that with **(124b)** (293, 303,304). From the two naphthalene-derived acids, **(124c)** showed a greater reactivity than **(124d)** (295). Thiopolyesters (M_n up to 10,000) are thick oils, waxy solids, or solids; **(123b)** and **(123d)** showed a large tendency to crystallize at room temperature. The relatively low T_g s (~ -30 to -10°C) were shown by **(123a)** and **(123b)** derived from aliphatic diols.

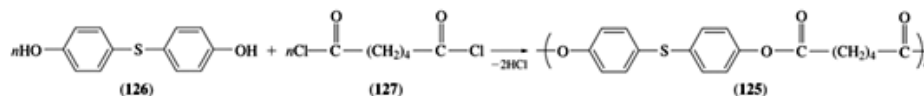
New PSC (291,292,293,294) with increased tensile strength in the form of thermoplastic rubber-like materials with sulfur cross-linked structure were obtained by heating thiopolyester **(123a)** or **(123b)** derived from 1,2-ethanediol [$\text{R}=(\text{CH}_2)_2$], 2,2'-oxydiethanol [111-46-6] [$\text{R}=(\text{CH}_2)_2\text{O}(\text{CH}_2)_2$], or EM ($\text{R}=\text{R}^1$) with 20–80% elemental sulfur at the temperature of about 220°C for 15–25 min. Depending on the nature of the thiopolyester and the amount of sulfur used, products with various degrees of hardness and elasticity characterized by tensile strength and elongation at break in the range of 0.4–21 MPa and 2–340%, respectively, were obtained. A cross-linking effect increasing the tensile strength of the PSC was achieved by introduction of diphenylmethane units with active methylene groups in the polymer chain. The formation of sulfur bridges of thiopolyesters involving these methylene groups was confirmed by solid-state ^{13}C nmr spectroscopy using cross-polarization magic-angle spinning (CP/MAS) and total sideband suppression (TOSS) techniques.

Some hydroxyl-terminated thiopolyesters **(123)** were used for preparing thiopoly(ester-urethane)s (293, 295,296) (see next section). The novel thiopolyesters **(123e)** (M_n of 2000–2600), because of their structures incorporating benzophenone units, may also be considered as new diol components of uv-autopolymerizable polyurethane-(meth)acrylate oligomers.

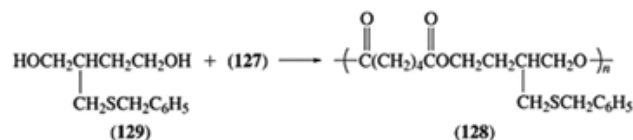
Thiopolyester **(125)** from 4,4'-thiodiphenol [bis(4-hydroxyphenyl) sulfide, 4-hydroxyphenyl sulfide] [2664-63-3] **(126)**, and adipoyl chloride [111-50-2] **(127)** was synthesized by both solution and interfacial condensation, as well as thiocopolyesters from **(126)**, **(127)**, and bisphenol-A (BPA) by interfacial condensation (305). Thiopolyester **(125)** under optimum interfacial polymerization conditions (tetrachloroethane as organic phase, tetra-*n*-butylammonium bromide [1643-19-2] as a phase transfer catalyst) showed a considerably higher specific viscosity value (1.64) than the polymer obtained in solution (0.18); it was a rather brittle material. Comonomer BPA was introduced into the polymer **(125)** chain in order to improve the toughness. Copolymer with the highest yield (93%) and the highest M_n (20,500) was obtained at the molar ratio **(126)**/BPA = 60/40. Its tensile strength

36 SULFUR-CONTAINING POLYMERS

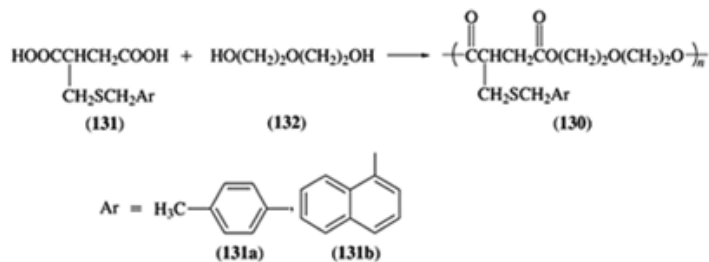
was ~ 44 MPa. Polymers (**126**) with a content above 60 mol% showed a high barrier for oxygen permeability, especially the homopolymer ($1.30 \times 10^{-15} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$).



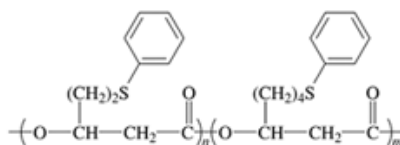
Few thiopolyesters with S atom in the side chain have been reported. The low-molecular-weight polymer (**128**) (297) with side benzylthiomethyl chains was successfully prepared by the condensation of 2-benzylthiomethyl-1,4-butanediol (**129**) with adipoyl chloride (**127**) in refluxing benzene. Attempts to obtain a polymer with free thiol groups through debenylation did not bring satisfactory results because of the simultaneous degradation of the polymer.



Related polymers (**130**), also relatively low molecular weights (M_n up to 4400) and tolylmethylthiomethyl or naphthylmethylthiomethyl side chains, were obtained by uncatalyzed and catalyzed melt condensation of diacids (**131**), *p*-tolymethylthiomethylsuccinic acid (**131a**), or 1-naphthylmethylthiomethylsuccinic acid (**131b**) with 2,2'-oxydiethanol (**132**) (306). Polymers showed thermal stabilities of up to ~ 220 or 280°C , respectively.



Poly(3-hydroxyalkanoate) (**59**) (307) with a thiophenoxy group at the end of the side chain was obtained from *Pseudomonas putida* 27N01, a newly isolated bacterial strain, using 11-thiophenoxyundecanoic acid as the sole carbon source.

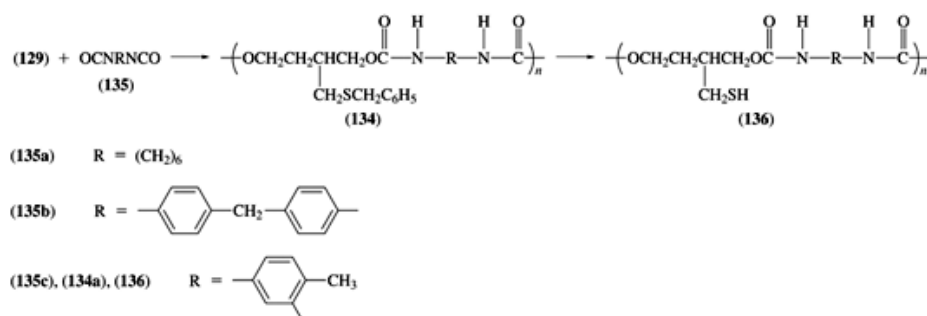


The polymer ($M_n = 81,000$ with polydispersity = 1.8, $T_g = 4^\circ\text{C}$) had a white cream color and was elastomeric. This is the first report of poly(3-hydroxyalkanoates) containing a sulfur atom in the structure produced from bacteria. It may be supposed that (**59**) will usher in a new era of bacterial polymers.

13. Polyurethanes Containing Sulfur Linkages

Earlier studies (297) on the synthesis of thiopolyurethanes were attempted with the aim of obtaining polymers containing free sulfhydryl groups, which are compounds of considerable interest for a variety of reasons, eg, as reducing agents in the thiol-disulfide systems.

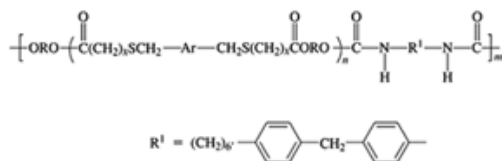
Thiopolyurethanes (**134**) with sulfur in side chain ($[\eta] \sim 0.1\text{--}0.3$ dL/g) prepared by solution (benzene) polymerization of the diol (**129**) with diisocyanates (**135**), HDI (**135a**), MDI (**135b**), or 2,4-TDI (2,4-toluene diisocyanate, 2,4-tolylene diisocyanate, 2,4-diisocyanatotoluene, etc) [584-84-9] (**135c**), were used as the polymeric intermediates for the synthesis of these polymers. The benzyl groups were successfully removed from polymer (**134a**) with sodium in a mixed solvent of liquid ammonium and *n*-propylamine [107-10-8], giving polymer (**136**).



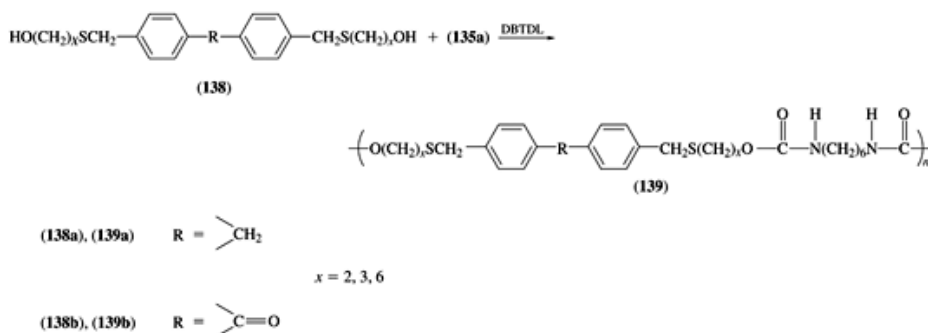
The analogous thiopolyurethanes with the side tolylmethylthiomethyl or naphthylmethylthiomethyl chains (**306**) were obtained from 2-(*p*-tolylmethylthiomethyl)-1,4-butanediol (TB) or 2-(1-naphthylmethylthiomethyl)-1,4-butanediol and HDI or Izocyn T-80 [TDI-80, the mixture of 2,4-TDI (80 wt%) and 2,6-TDI (20 wt%)] by solution (benzene) polymerization in the presence of di-*n*-butyltin dilaurate (DBTDL) [77-58-7] as catalyst. The polymer based on TB and HDI ($\eta_{\text{red}} = 1.17$ dL/g) was a high elasticity thermoplastic elastomer with tensile strength of 2.2 MPa and elongation at break of 780%.

The growing interest in polyurethane elastomers because of their unique properties, as well as in sulfur-containing polymers, prompted scientists in the last decade to undertake studies on the synthesis and properties of a novel class of thiopolyurethanes containing thioether linkages in the main chain, derived from various new diol components as aliphatic–aromatic simple thiodiols (308,309,310,311,312,313,314) and linear thiopolyester diols (293,295,296).

High elasticity thermoplastic thiopoly(ester-urethane)s of general structure (**60**) were prepared from newly obtained hydroxyl-terminated thiopolyesters (**123c**, **123d**, **123e** with $\text{R} = (\text{CH}_2)_{4,5,6}$ and **123a**, **123b** with $\text{R} = (\text{R}^1)$; $M_n = 1600\text{--}2900$) and HDI (**135a**) or MDI (**135b**) at the ratio of $\text{NCO}/\text{OH} = 1$ or 1.05 by melt polymerization at temperature $\sim 130^\circ\text{C}$ in the presence of DBTDL as catalyst, when a less reactive HDI was used. Their characteristics were $\eta_{\text{red}} \sim 0.4\text{--}1.1$ dL/g (1,1,2,2-tetrachlorethane [79-34-5], 0.5–1%), T_g s from -1 to 18°C , tensile strength of 0.6–12 MPa, elongation at break of 500–1400%, and good thermal (up to $220\text{--}260^\circ\text{C}$) and chemical resistance. Polymers from (**123d**) showed the highest tensile strength, whereas those from (**123b**) the lowest T_g s. Thiopolyurethanes from (**123a**) and (**123b**) containing diphenylmethane units with active methylene groups are new, potentially peroxide-curable polymers.



The DBTDL-catalyzed step-growth solution and melt polymerization reaction of the low melting thiodiols (**138**) with HDI (**135a**) at NCO/OH ratio = 1.05 produced thermoplastic nonsegmented thiopolyurethanes (**139a**) (309) and (**139b**) (308) showing partially crystalline structure (T_g s below 40°C, T_m s = 47–124°C). Higher molecular weight polymers ($\eta_{\text{red}} = 0.63\text{--}1.24$ dL/g, tetrachloroethane, 0.5–1%) were obtained by solution (DMF) polymerization. They showed tensile strength in the range of 16–50 MPa and thermal stability of up to 230–240°C.



Thiodiols (**138b**) (315) ($T_m = 38\text{--}76^\circ\text{C}$), including 4,4'-bis(2-hydroxyethylthiomethyl)benzophenone ($x = 2$), 4,4'-bis(3-hydroxypropylthiomethyl)benzophenone ($x = 3$), and 4,4'-bis(6-hydroxyhexylthiomethyl)benzophenone ($x = 6$) and thiodiols (**138a**) (309) ($T_m = 68\text{--}78^\circ\text{C}$), including bis[4-(2-hydroxyethylthiomethyl)phenyl]methane ($x = 2$), bis[4-(3-hydroxypropylthiomethyl)phenyl]methane ($x = 3$), and bis[4-(6-hydroxyhexylthiomethyl)phenyl]methane ($x = 6$) were prepared by condensation reaction of the corresponding dithiols 4,4'-bis(mercaptomethyl)benzophenone or bis[4-(mercaptomethyl)phenyl]methane with 2-chloroethanol [107-07-3], 3-chloro-1-propanol [627-30-5], or 6-chloro-1-hexanol [2009-83-8], respectively, in 10% aqueous solution of sodium hydroxide.

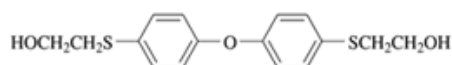
Segmented thiopolyurethanes prepared from thiodiol (**138b**) with $x = 6$ (308) and all thiodiols (**138a**) (310,311) as chain extenders, HDI (**135a**), and 20–80 mol% poly(tetramethylene oxide) (PTMO) [24979-97-3] of $M_n = 1000$ as the soft segment by one-step process in the same conditions as for nonsegmented polymers were thermoplastic elastomers (except those based on 20% PTMO) showing partially crystalline structure. The polymers exhibited definite T_g s (–70 to –60), nearly independent of the hard segment content up to 50 wt% (40–80 mol% PTMO), indicating the existence of mainly microphase-separated soft and hard segments. Higher molecular weight polymers ($M_n = 12,000\text{--}45,000$ with polydispersity $\sim 2\text{--}4$) were produced by the melt polymerization process. They showed tensile strength of 6–17 MPa and elongation at break of 140–680%. In each of the series, the increased PTMO soft-segment content decreased hardness, modulus of elasticity, and tensile strength, whereas elongation at break increased.

Because their structures incorporate diphenylmethane units with active methylene groups, polymers from (**138a**) are new, potentially peroxide-curable, HDI-based thiopolyurethanes, whereas polymers from (**138b**) containing benzophenone units may find use as interesting modifiers of photosensitive polyurethane resins.

Studies on the synthesis and properties of the linear nonsegmented thiopolyurethanes based on thiodiol containing atom S attached directly to aromatic ring bis[4-(2-hydroxyethylthio)phenyl] ether (**61**) ($T_m = 94^\circ\text{C}$)

under melt and solution polymerization conditions at the NCO/OH ratio = 1 showed that these polymers are brittle, hard, or rubber-like solids unsoluble and nonfusible up to 300°C from MDI (**135b**) (312), melting at ~245°C from 2,4-TDI (**135c**) (314), and soluble in DMF and DMSO at heating and melting at ~215°C from HDI (**135a**) (313). Their T_g s were 43–52°C. All the polymers were thermally stable up to 230–270°C. The introduction of comonomer 1,6-hexanediol significantly decreased T_m and T_g , and increased the solubility of the copolymers.

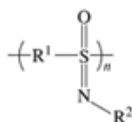
The synthesis and properties of the thermoplastic segmented thiopolyurethanes derived from thiodiol (**61**), 2,4-TDI (**135c**), and 20–80% PTMO of $M_n = 650$ and 1000 under one-step solution (DMF) and melt polymerization conditions (the ratio of NCO/OH = 1, DBTDL as catalyst) have also been reported (314). The most interesting are high molecular weight polymers ($\eta_{red} = 1.42$ –2.30 dL/g) obtained by melt polymerization from PTMO of $M_n = 1000$. They are rubber-like products easily soluble in organic solvents and showing high adhesion to many substrates; these polymers may be useful as glues.



The reactions of some aliphatic thiodiols as 2,2'-thiodiethanol [111-48-8] or 4,4'-thiodibutanol with HDI were investigated many years ago (316).

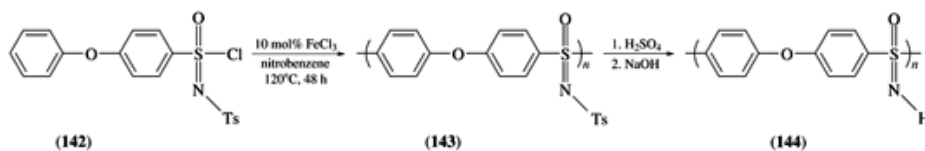
14. Polysulfoximines

The chemical and physical properties of the polysulfoximines are of particular interest because of their rigid and unsymmetrical structure (**62**) and the polymers can be considered as new, potentially high-performance, engineering plastics. In recent years, the first preliminary studies on the synthesis and properties of this novel class of sulfur-containing polymers have been reported (317,318,319,320).



$R^2 = \text{H, alkyl, allyl, aryl, acyl, sulfonyl, etc.}$

The self-condensation of sulfonylimidoyl chlorides such as *N*-tosyl (Ts) derivative of the benzene- and 4-phenoxybenzene-sulfonylimidoyl chloride (**142**) utilizing a catalytic (AlCl_3 or FeCl_3) Friedel–Crafts reaction has been studied as a way to produce these polymers. It has been found that the reaction of the former compound yielded no polymeric product, whereas that of (**142**) produced exclusively methanol-insoluble polymer (**143**) of $M_n = 14,500$ with polydispersity = 1.45 in 80% yield (317).



The treatment of (143) with concentrated sulfuric acid followed by neutralization with NaOH at room temperature gave the corresponding polymer (144) containing the “free” sulfoximine moiety and with M_n nearly equal to that of (143); the T_g s of (143) and (144) were almost equal, namely 335 and 333°C, respectively. Polymer (144) was much more thermally stable than (143) and its thermal stability (20 wt% loss temperature ~550°C) is comparable to that of poly(ether-sulfone).

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44 SULFUR-CONTAINING POLYMERS

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