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Mercaptan-Containing Polymers.

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A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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in partial fulfillment of the
requirements for the degree of

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ABSTRACT

Mercaptan-containing polymers have been synthesized by two general procedures: (a) synthesis and polymerization of monomers containing carbo-t-alkyloxy blocked mercaptan substituents and (b) introduction of mercaptan groups via Bender's salts into preformed polymers containing suitable reactive sites. Three thermally labile Bender's salts ($K^+ - S - \overset{O}{\parallel} C - O - t - R$, $R = t\text{-butyl}$ (1), $t\text{-amyl}$ (2), and cumyl) were synthesized and utilized to effect quantitative S_N2 displacement of primary and secondary halides to form t-alkylthiocarbonate derivatives. Selective displacement of bromide from 1,2-bromochloroethane by 1 or 2 followed by dehydrohalogenation with potassium t-butoxide yielded S-vinyl-O-t-butylthiocarbonate (3) and S-vinyl-O-t-amylthiocarbonate (4), two excellent vinyl precursors of poly(vinyl mercaptans), in 60% and 35% yields respectively. Reactions of 1 with vinylbenzyl chloride yielded S-(vinylbenzyl)-O-t-butylthiocarbonate.

Dilatometric studies of the homopolymerization of S-vinyl-O-t-butylthiocarbonate (3) demonstrated that the polymerization rate was proportional to the free-radical initiator concentration to the 0.765 power. Monomer 3 exhibits a high monomer chain-transfer constant ($C_M = 3.9 \times 10^{-3}$); the molecular weights of the homopolymer and copolymers ranged from 30,000 to 55,000 (GPC). Copolymerization of S-vinyl-O-t-butylthiocarbonate (M_2) with styrene, ($r_1 = 3.0$, $r_2 = 0.2$), methyl

methacrylate ($r_1 = 1.40$, $r_2 = 0.17$) and vinyl acetate ($r_1 = 0.04$, $r_2 = 11.0$) indicated that a sulfur atom adjacent to a vinyl group increases the resonance stability ($Q_2 = 0.5$) and the electron density ($e_2 = -1.4$) of the double bond and the corresponding radical. Water-soluble copolymers could be prepared by incorporating either N-vinylpyrrolidone ($r_1 = 0.12$, $r_2 = 3.94$) or N-isopropylacrylamide ($r_1 = 1.17$, $r_2 = 0.3$) with M_2 . The water solubility of the copolymers decreased markedly when the t-butyloxycarbonyl group was removed.

Pyrolysis of homopolymers containing t-butylthiocarbonate groups yielded polymercaptans and a quantitative loss of isobutylene and carbon dioxide (confirmed by mass spectroscopy). A kinetic study of the pyrolysis of poly(S-vinyl-O-t-butylthiocarbonate) confirmed that the deblocking reaction is a first-order process with $E_a = 31.22$ kcal/mol, and $\Delta S^\ddagger = -2.42$ e.u.

Mercaptan-containing polymers have also been synthesized by the nucleophilic substitution of potassium O-t-butylthiocarbonate on polymers with chloromethyl functional groups such as: chloromethylated polystyrene, poly(epichlorohydrin) (Herclor-H), copoly(epichlorohydrin-ethylene oxide) (Herclor-C), and with poly(vinyl chloride). Spectral and analytical data confirm the presence of t-butylthiocarbonate as well as cyclic dithiocarbonate functional groups on the substrate polymers. The weight-loss patterns from TGA and DTA served as an analytical technique for determining the number of mercaptan groups generated on the chloromethylated polymer substrates.

INTRODUCTION

Mercaptan-containing polymers have been utilized as selective sequestering agents which form stable mercaptides with heavy metals such as Hg, Pb, Ag, Cu, Cd, Fe, Zn, Ni, Pd, and Au. This property has been used for the detection of thiol groups in biological systems as well as for the preparation of exchange resins for the removal of heavy metal ions. Crosslinked poly-(vinylbenzyl mercaptan) prepared by Parrish¹ and crosslinked poly-(p-mercaptostyrene) synthesized by Gregor et al.² both proved effective as sequestering agents. The recovery of the bound metal ions by treatment with ammoniacal 2,3-dimercapto-1-propanol (BAL) illustrates the reversibility of the process.

Thiols are reducing agents according to the reaction

The redox reaction can be reversed with strong reducing agents and thiols can be regenerated from disulfides. Consequently, mercaptan polymers are potentially useful as redox resins.³ The application of poly(p-mercaptostyrene) as a redox resin was explored by Cassidy et al.⁴ but efforts to determine the redox potential were thwarted by precipitation of the polymer during the titration.

Synthetic mercaptan-containing polymers are also interesting in relation to the important role of the thiol function in enzyme

systems⁵ and the catalytic properties of copolymers containing mercaptan and imidazole substituents have been investigated.⁶ Water soluble copolymers have been studied as antiradiation agents.⁷ A short term prophylaxis was observed which was attributed to the ability of mercaptans to inhibit free radical reactions by the formation of stable thiol radicals. A recent ESR study of copolymers of vinyl pyrrolidone and vinyl mercaptan confirm this hypothesis; exposure of these copolymers to ionizing radiation initially produced pyrrolidinyl radicals which rapidly rearranged to exceptionally stable thiyl radicals.⁸

A variety of synthetic methods exist for the preparation of mercaptan-containing polymers. In contrast to vinyl alcohol, vinyl mercaptan can be isolated in very low yield from the addition of hydrogen sulfide to acetylene in the presence of free radical initiators such as peroxides, azo compounds, and UV light.⁹ However

it is useless as a monomer because the sulfhydryl group is too labile, i.e. it is a very efficient chain transfer agent and undergoes trimerization via a tautomeric thioacetaldehyde intermediate.¹⁰ Thus one is forced to resort to indirect synthetic techniques of the following general types: (a) the polymerization of monomers containing a potential mercaptan function which is protected by a subsequently removable "blocking" group, (b) chemical modification of preformed polymers.

Monomer synthesis, followed by polymerization, has the advantage that the composition of the product is known with increased certainty, and that the product is readily characterized. However, the molecular weights of the polymers are usually too low to exhibit good mechanical properties. Thus, the advantages of chemical modification of preformed high molecular weight polymers become apparent, especially when considerations of physical properties, total capacity, and cost are uppermost. Factors such as limited solubility, side reactions and crosslinking generally cause some difficulties in chemical modification of high polymers.^{11,12,13} Frequently, chemical reactions of polymers will not take place due to the increased hinderance imposed by the polymer chains.¹⁴ The choice of which route to take - from monomer, or from preformed polymer - clearly depends upon the ultimate application of the product.

A. Vinyl Mercaptan Precursors

The application of several different blocking groups to polymercaptan synthesis has been thoroughly evaluated. In general, this technique enables one to prepare homopolymers of vinyl mercaptan under conditions where the structure of the polymer can be assigned accurately. For example, vinylthioesters such as S-vinyl thioacetate¹⁵ can be prepared in 43% yield by passing 1 through a glass-packed column heated to 500°. Attempts to duplicate these results revealed that the yields are extremely variable and that the by-products are powerful vesicants.

The polymerization and copolymerization of vinyl thioacetate (2, R=CH₃) has been reported.¹⁸⁻¹⁹ However, monomer (2) exhibit high transfer constant (5.6×10^{-2}) so the molecular weights of their polymers do not exceed 2000. Subsequent hydrolysis of the thioacetate functional group required alkaline conditions and is accompanied by oxidative crosslinking.

Copolymerization with vinylene carbonate¹⁶, methylmethacrylate^{15,20} N-vinylsuccinimide,¹⁸ N-vinylphthalimide,¹⁸ N-vinylcarbazole,¹⁸ styrene,^{15,19} vinylacetate,^{15,19} and methyl acrylate¹⁹ as well as the hydrolysis of these polymers, has been reported. Copolymers of vinyl thioacetate with esters of 1,4-butenedioic acid can be used as coating compounds; their hydrolyzed copolymers can be used in cationic-exchange resins and water softeners.²¹ Polymerization of vinyl thioacetate (2) in liquid ammonia yields poly(vinyl thiol) with intra- or intermolecular disulfide bridges,

the acetate part of the molecule is concomitantly split off to form acetamide.²²

In a similar fashion, vinyl thiobenzoate was synthesized in low yield (~10%) by pyrolysis of β -acetoxyethyl thiobenzoate (**1**, $R = C_6H_5-$) which was derived from thiobenzoic acid and vinyl acetate in the presence of sulfuric acid.²³ The polymerization and copolymerization of **2** ($R = C_6H_5$) were carried out in bulk using azobisisobutyronitrile (AIBN) as initiator. Basic hydrolysis of the polymer yielded poly(vinyl mercaptan). However no sufficient improvement in the degree of polymerization was reported.

Poly(*p*-mercaptostyrene) was prepared by the polymerization of *p*-vinylphenyl thioacetate^{24,25} (**3**) which was synthesized from *p*-aminoacetophenone (**4**). (Scheme I) Conversion of **4** to the

xanthate (5) and reaction with potassium ethyl xanthate, followed by reduction, gave 6. Formation of the diacetate (7) and cleavage of acetic acid gave 2 in ~10% overall yield. This was readily polymerized using AIBN as initiator. Saponification of the resultant homopolymer gave a pure homogeneous alkali soluble polymer. Copolymerization with methyl methacrylate gave, upon saponification, another synthetic mercaptan-containing polymer.

An interesting approach to polymercaptans utilizes the mercaptide ion as a blocking group. Vinylbenzyl thioacetate²⁶ (2) was prepared in 68.5% yield by treating an alkali metal salt of a carbothiolic acid with vinylbenzyl chloride (8a) (70:30 p- to o-isomer). Basic hydrolysis of 2 yielded 42.6% of the corresponding vinylbenzyl mercaptan (11a). Alternatively, S-(4-vinylbenzyl)-isothiourea and isothiuronium chloride²⁷ (10) was prepared by treating pure 4-vinylbenzyl chloride (8b) with thiourea. Subsequent hydrolysis of 10 yielded 78% 4-vinylbenzyl mercaptan (11b).

Heating 11a with AIBN for four days at 100° yielded a poly(vinylbenzyl mercaptan) with 16.6 wt.% of sulfur. Emulsion polymerization of 11b initiated by potassium persulfate in alkaline media yielded the corresponding insoluble mercaptan containing polymer. Alkali metal salts of the polymer from 11a are water soluble and may be oxidized with $\text{Ca}(\text{OCl})_2$ to give insoluble products containing SS linkages between the polymer chains. Detailed characterization of these polymers was not reported, so the efficiency of the mercaptide ion in preventing chain transfer reactions could not be evaluated. However, it is difficult to conceive of a simpler blocking group.

An alternate approach was considered by H. Ringsdorf, et al.²⁸⁻³¹ They prepared vinyl mercaptals by dehydration of the analogous S- β -hydroxyethyl compounds and dehydrohalogenation of S-(β -chloroethyl)monothioacetals. The monomers were polymerized radically with AIBN and cationically with BF_3 -etherate (Scheme II). Only low molecular weight polymers were obtained regardless of the reaction conditions. Further, the polymeric mercaptal could not be hydrolyzed to polymercaptan.

Preparation and cyclopolymerization of S,S'-divinylmercaptals (12) have also been reported by two different groups. Ringsdorf and Overberger^{28,31} found that S,S'-divinyl dithioformal (12, X = S; R = $-\text{CH}=\text{CH}_2$) can be prepared by dehydration of S,S'-(β -hydroxyethyl)-dithioformal. Free radical polymerization of 12 in dilute solution

Scheme II

where $\begin{cases} \text{X} = \text{S}, \text{O}. \end{cases}$

to low conversions favored the formation of linear polydivinylmercaptal containing dithiane repeat units (13). The extremely low molecular weight soluble portion contained approximately 26% residual unsaturation and crosslinked rapidly upon exposure to air.³² Matsuyan and Soakyan³² prepared S,S'-divinyl dithioformal by treatment of ethylene sulfide with hydrogen chloride in the presence of paraformaldehyde to produce S,S'-(β-chloroethyl) dithioformal which was subsequently dehydrogenated. Similarly S,S'-divinyl dithioacetal and S,S'-divinyldithiopropional were synthesized from the

(13)

corresponding aldehydes. The substituted mercaptals cyclopolymerized in bulk but soluble poly(S,S'-divinyldithioformal) could only be obtained by allowing the monomer to stand in the sun for eight months.

The extensive 1,3-dithiane studies by E. J. Corey, et al.³³ showed that one should be able to alkylate polymers containing dithiane rings (13, R = H) by preparing a lithio salt of the polymer with butyl lithium followed by treatment with an alkyl

halide, but all attempts from this laboratory to release the elaborated aldehydes generated by this process failed.

The preparation and cyclopolymerization of S,S' -divinyl-dithiocarbonate has been reported by Ringsdorf and Overberger.³⁴ Their results indicated that this could be a potential monomer for the preparation of stereoregular polymercaptans. Reinvestigation of the monomer synthesis was conducted later by Overberger and Daly.³⁵ Their results showed that dehydrohalogenation of S,S' -(β -chloroethyl)dithiocarbonate (14) with potassium t -butoxide yielded a mixture of S,S' -divinyldithiocarbonate (15), S -vinyl- O - t -butylthiocarbonate (16), S -(β -chloroethyl)- O - t -butylthiocarbonate (17), S -(β -vinylmercapto)ethyl - S' -vinyl-dithiocarbonate (18), and S -vinyl- S' -(β -chloroethyl)dithiocarbonate (19). The complexity

of the reaction mixture is an example of the facile rearrangements that thiocarbonates undergo in basic media. The cyclopolymers initially reported³⁴ were derived from 19, but free radical copolymers of 15 also yielded cyclopolymers of low molecular weight ($[\eta] = 0.05$).³⁶

Since cystamine is one of the most effective radiation prophylactics known, the preparation and polymerization of S-vinyl-N-vinylthiocarbamates³⁷ (21) was utilized in an attempt to prepare alternating poly(vinyl amine-vinylmercaptan) copolymers. (Scheme III). The divinyl monomers were prepared by dehydrochlorination of the respective S-2-chloroethylalkylthiocarbamates (20). The monomers (21) were polymerized under a variety of conditions to yield "terpolymers" (22) composed of the tetrahydro-1,3-thiazin-2-one moiety as well as poly-S-vinyl and poly-N-vinyl units. Attempts to isolate polymeric α -amino γ -thiols (23) formed by hydrolysis of the resultant "terpolymers" (22) proved unsuccessful.

Okawara, et al.³⁸ reported that the addition of sodium N,N-dialkyldithiocarbamate to 1,2-dichloroethane (Scheme IV) in DMF yielded a diadduct (24) which could be cracked to product S-vinyl-N,N-dialkyl dithiocarbamate (25). Monomer 25 could be polymerized under free radical conditions, but it exhibited a high chain transfer constant so the molecular weight of the resultant polymer (26) was rather low. Furthermore, the thermal stability of the polymer was poor, which is not surprising since the polymer structure

Scheme IV

thiocarbonates and vinyl thiocarbamates. The monomers were polymerized by free radical initiation. Several of these derivatives yielded reasonably high molecular weight polymers, but the polymers proved difficult to hydrolyze to the desired polymercaptans.

In 1964, a new monomeric precursor to polymercaptans containing a thermally removable or acid-labile sulfhydryl blocking group was reported by Overberger and Daly.⁴¹ Synthesis of this monomer, S-vinyl-O-t-butylthiocarbonate (16) was achieved by treating 2 moles of potassium t-butoxide with 1 mole of S-(β -chloroethyl)-chlorothioformate (28), effecting a concurrent esterification and dehydrohalogenation, to produce 16 and S-(β -chloroethyl)O-t-butylthiocarbonate (17). The blocking group could be

removed by treatment of the polymer (29) with anhydrous HBr in 6:1 chloroform-tetrachloroethane or by thermolysis at 150° C in N-methylpyrrolidone to yield poly(vinyl mercaptan) (30). The autoxidation of these polymers and related model compounds was studied in an effort to ascertain the influence of the polymer structure on reactivity.⁴²

B. Ring Opening Polymerization of Cyclic Mercaptan Precursors

Since the chain transfer properties of vinyl mercaptan precursors limited the molecular weights attained in addition polymerization, several ring-opening polymerizations of monomers with thio-substituents were evaluated.

Poly-L-cysteine (33) has been prepared by polymerization of S-carbobenzoxy-N-carboxy-L-cysteine anhydride (32), followed by reduction with sodium in liquid ammonia.⁴⁵ The reactivity of the thiol groups in this polymer toward various reagents has been investigated.

Poly-(N-methacrylyl cysteine) has been prepared by using S-thiophenyl or S-benzyl blocking groups to protect the thiol substituent during methacrylation and polymerization.⁴⁶ Treatment of the resultant polymer with sodium in liquid ammonia produced free cysteine residues in 51% yield. Alternatively, N,N'-bis-methacrylyl

cysteine was prepared, polymerized to a crosslinked gel and 79% of the theoretical cysteine residue were liberated on reduction of the disulfide linkage. These polymers should be of interest as a potential radiation prophylactics.

In an effort to improve the mechanical properties of polymercaptans, Goethals turned to cationic polymerization of 3,3-bis(methylenethioester)oxetanes.⁴⁷ Using dithiocarbonates or bis-(thioacetate) derivatives (34), polymers (35) with molecular weights as high as 21,100 could be obtained. Higher molecular weight

materials were prepared by copolymerizing the sulfur containing monomers with β,β -bis(chloromethyl)oxetane but extensive cross-linking occurred during the deblocking step due to the nucleophilic attack of liberated mercaptide ions on residual chloromethyl substituents.

C. Mercaptan-Containing Condensation Polymers

Synthetic methods for the preparation of blocked sulfhydryl monomers and their subsequent condensation polymerization were illustrated by the work of Overberger and Aschkenasy.⁴⁸ Employing the carbobenzoxy blocking group, a mercaptan-containing polyamide (37) of α,α -dithioladipyl chloride (36) and hexamethylenediamine was prepared. Similarly, a polyurethane (39) synthesized from 2-benzylthiomethyl-1,4-butanediol (38) and hexamethylene diisocyanate yielded a polymercaptan on debenzylation.

Polycondensation of thiophenol and derivatives of thioglycolic acid anilide with formaldehyde yielded resins with free thiophenol functions. The oxidation potentials of the polymers were obtained indirectly by Hamamura, et al.⁴⁷ by observing the ability of the polymers to decolorize redox dyes of known potentials.

D. Chemical Introduction of Mercaptan Groups into Preformed Polymers

Cairns and co-workers⁵⁰ introduced a functional group into poly(hexamethylene adipamide) (Nylon 66) by hydroxymethylating the polyamide backbone with formaldehyde and ammonia. Subsequent treatment with thiourea and hydrogen chloride gave an isothiuronium salt from which an alkali soluble polythiol could be obtained.

Okawara, et al.⁵¹ reinvestigated this procedure and found that thiourea treatment followed by saponification yielded a polymercaptan containing only 0.61% SH groups.

Mercaptan-containing polymers derived from poly(vinyl alcohol) (40) prepared in a similar manner by treating 40 with hydrogen bromide and thiourea to give the isothiuronium salt which could be hydrolyzed to an insoluble polymer of vinyl mercaptan.^{53,54} Poly(vinyl mercaptan) was also made by sulfonation of 40 with PhSO_2Cl to activate the polyol before thiourea treatment or thioesterification with MeCOSK and hydrolysis of the thioester.⁵⁴ (Scheme V.) The extent of incorporation of free

mercaptan groups was approximately 42%.

Treatment of poly(vinyl alcohol) with chloroacetaldehyde gave a cyclic acetal with a replaceable chloride (41). Reaction with KSH or thiourea followed by saponification gave a polythiol^{51,54} (42). This approach could lead to hydrophilic polymers with readily accessible mercaptan groups if the acetalization is limited to ~ 10% reaction. Polymers of this type would be useful as enzyme supports.

Polymers (43-45) containing vicinal mercaptan groups were also synthesized from poly(vinyl alcohol).^{54,55} The bromoacetal was elaborated with sodium allyloxide, and the allyl ether formed was converted to a dithiol by addition of bromine followed by substitution with KSH. The incorporation of free mercaptan groups was low (~25%). (Scheme VI.) These materials are polymeric analogs of 2,5-dithiol-1-propanol (BAL) and would probably be very efficient heavy metal scavengers.

Chemical introduction of mercaptan groups into polystyrene derivatives has been extensively examined. Poly(p-mercaptostyrene) (46) was prepared by Gregor, et al.² by treating diazotized polystyrene with potassium ethyl xanthate followed by hydrolysis giving a polymer assaying at 90% of the theoretical sulfur content. The insoluble polymer was swollen by alkaline hydrolysis and was effective

Scheme VI

as an ion-exchange resin. Poly(p-mercaptostyrene) with 55% of the

theoretical sulfur content was made by reducing cross-linked chloro-sulfonated polystyrene.⁵⁶⁻⁵⁸

Alternatively, 46 was prepared by treating polystyrene with 2,4-dinitrophenylsulfenyl chloride followed by alcoholysis. The extent of incorporation of free mercaptan groups was low ($\sim 20\%$).⁵⁶

Poly(p-lithiostyrene), a highly reactive polymer prepared from iodinated polystyrene and lithium, yielded a copolymer containing 62 mol % p-mercaptostyrene when sulfur was added.⁵⁹ Similarly,

treatment of styrene-divinylbenzene copolymers with sulfur and aluminum chloride yielded sulfur-containing polymers in which 21% of the incorporated sulfur is present in the form of mercaptan groups.⁶⁰

Poly(vinylbenzyl mercaptan) has been described by several authors. The synthesis always follows the same path: chloromethylation of polystyrene followed by reaction with thiourea and hydrolysis of the isothiuronium salt.^{1,51,53,61-63} The redox properties of a polymer obtained from chloromethylated styrene-divinylbenzene copolymers have been evaluated.³ Redox capacities given for mercaptyl resins were determined to be 2.40-5.27 milliequivalents of iodine reduced per gram of (dry) resin in aqueous potassium iodide. The oxidized form of the resin could be easily reduced with 10% aqueous sodium bisulfite for a complete redox cycle.

Chloromethylated polystyrene has been used to synthesize polymers containing vicinal mercaptan,⁵⁵ dithiocarbamate,^{64,66} (47) and xanthate groups^{65,66} (48). The photochemical reactions of polymers (47,48) and their model compounds have been extensively studied by Okawara, et al.^{64,68} Photolysis of polymers containing dithiocarbamate groups (47) in the presence of vinyl monomers such as methyl methacrylate (MMA) or styrene generated graft polymers^{66,67} which did not contain sulfur (Scheme VII). In contrast, polymers containing xanthate groups (48) produced polyvinylbenzyl

Scheme VII

thiol radicals upon irradiation^{65,68} and crosslinked via disulfide linkages. The potential applications of these polymers as photoresist resins were considered.

The introduction of N,N-diethyl dithiocarbamate and N-methyl dithiocarbamate groups into poly(vinyl chloride) has been reported.^{11,12} Thermal decomposition of polymers containing N-methyl dithiocarbamate groups (49) failed to produce mercaptan groups, but formed cyclic structure on the polymer matrix (Scheme VIII). Pyrolysis of polymer containing N,N-diethyldithiocarbamate (50) produced polyenes. However, the polymers reacted with nucleophiles such as dimethylamine in dioxane to yield insoluble polymercaptans. LiAlH₄ reduction of 50

Scheme VIII

failed to produce a polymeric thiol. It was also reported that poly(vinyl mercaptan) was prepared from PVC and KSH,⁶⁹ but this reaction was accompanied by extensive dehydrohalogenation.

Gluckman, *et al.*⁷⁰ reacted thioglycolic acid with copolymers containing the glycidyl methacrylate residue to produce resins containing two pendant mercaptan groups for each epoxide group.

Scheme IX

A novel feature of conjugates based on Enzacryl Polythiol (53) is that the coupling can be reversed by treatment with cysteine or mercaptoethanol. Regenerable enzyme carriers have obvious commercial potential. Another feature of 53 is that it may also be activated for enzyme coupling with dicyclohexylcarbodiimide. The activated copolymer, Enzacryl Polythiolactone (54),

may be stored indefinitely under dry conditions.⁷⁷ Enzyme coupling occurs via nucleophilic opening of the thiolactone ring; thus, the conjugate contains free mercaptan groups which may be used to further modify the bound enzyme.

F. Objectives

From the literature reviewed, it appeared that the potential applications of polymers containing free mercaptan groups as redox resins, crosslinking agents, heavy metal scavengers, radiation prophylactics, enzyme models and polymeric catalysts warranted further investigation of their synthesis techniques. Our initial efforts were devoted to the synthesis of new monomeric mercaptan precursors in an attempt to minimize the synthetic difficulties and reduce the cost of mercaptan polymers. Subsequent work was directed toward the preparation of polymers with good mechanical properties by modification of polymeric substrates.

RESULTS AND DISCUSSION

A. Synthesis of Monomers and Model Compounds.

S-Vinyl-O-t-butylthiocarbonate

The synthesis of poly(vinyl mercaptan)⁷⁸ via S-vinyl-O-t-butylthiocarbonate (16) demonstrated the utility of the carbo-t-butoxy blocking group in mercaptan synthesis and prompted us to investigate the general applicability of this technique for introducing t-alkylthiocarbonate groups ($-S-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-O-t\text{-alkyl}$) into monomer and polymer substrates.

S-Vinyl-O-t-butylthiocarbonate, which had been obtained initially as a by-product of the dehydrohalogenation of S,S'-(β -chloroethyl)dithiocarbonate (14), evolved as the best monomeric precursor for preparing homopolymers and copolymers of poly(vinyl mercaptan). The monomer had been previously synthesized in 5% yield by dehydrohalogenation of S-(β -chloroethyl)-O-t-butylthiocarbonate (17).⁴⁰ A direct synthesis of monomer (16) was developed later by Overberger and Daly.⁴¹ The synthesis required heating ethylene carbonate with an equal molar concentration of potassium thiocyanate to produce pure ethylene sulfide.⁷⁹ Treating ethylene sulfide with a slight excess of condensed phosgene in the presence of pyridine yielded S-(β -chloroethyl)chlorothioformate (28),³⁴ which was concurrently esterified and dehydrogenated with potassium t-butoxide to yield 51% of S-vinyl-O-t-

butylthiocarbonate (16) (Scheme X). By changing the solvent from ether to THF, lowering reaction temperature from 25° to -30°, and increasing the concentration of base (3:1 of *t*-BuOK:28), the yield of monomer was improved to 60%.

One of the problems encountered in working with S-vinyl-O-*t*-butylthiocarbonate was a tendency for this monomer to yield crosslinked polymer. The crosslinking was apparently due to the presence of 3-5% S,S'-divinyldithiocarbonate (15) formed by the reaction sequence shown in Scheme X.

Scheme X

It was very difficult to prevent multiple addition of ethylene-sulfide to phosgene, and the tendency of 28 and 14 to decompose during distillation made separation of the two products difficult. The purity of 16 was estimated by comparing the relative intensity of the vinyl proton region (5.4-6.73δ) to the *t*-butyl group (1.51δ). The major impurity, di-*t*-butylcarbonate (55), produced by the

excess of base, appeared in the nmr spectra as a singlet at 1.42 δ . The structure of 51 was confirmed by an independent synthesis;⁸⁰ 51 is stable at its boiling point, very easily sublimed and is not easily saponified. Thus it is very difficult to quantitatively remove 51 from the monomer by fractional distillation.

S-vinyl-O-t-amylthiocarbonate

After improving the synthesis of S-vinyl-O-t-butylthiocarbonate (16), we became interested in synthesizing similar vinyl monomer using carbo-t-alkyloxy blocking groups [R-(CH₃)₂C-O-C-] to protect the thiol group. Increasing the steric bulk of the t-alkyl substituent should decrease the temperature required for thermolysis of the blocking group.

S-(β -Chloroethyl)chlorothioformate (28) was concurrently esterified and dehydrohalogenated upon addition to a solution of excess sodium 2-methyl-2-butoxide. Purification of the product mixture by fractional distillation through a spinning band column afforded the following components: S-vinyl-O-t-amylthiocarbonate (56), S-(β -chloroethyl)-O-t-amylthiocarbonate (57), di-t-amylcarbonate (58), S,S'-(β -chloroethyl)dithiocarbonate (14), and S,S'-divinyl-dithiocarbonate (15). The composition and yield of

the product mixture was dependent on the reaction conditions; the formation of 56 was favored by using THF as a solvent at lower reaction temperatures as illustrated in Table 1. The reaction usually required excess base (59). Since a tertiary alkoxide can act as both a strong base and a nucleophile, the formation of the chief by-product, di-t-amylcarbonate (58), was anticipated. A nucleophilic attack at the carbonyl group could be enhanced by the formation of a cyclic sulfonium ion⁸¹ which can be displaced as ethylene sulfide.^{35,40} High concentration of base (59)

coupled with long reaction times at higher temperature favored the formation of 58 (Table 1, experiment 1); however, reducing the reaction temperature to -30° favored the formation of the desired monomer. Lower monomer yields than those obtained

TABLE 1

Preparation of S-Vinyl-O-t-amylthiocarbonate (56)

Exp. ^a	Mol ratio, <u>59</u> to <u>28</u>	Reaction conditions			Yield of products, %		
		Solvents	Pot temp., °C	Stirring time, hr.	<u>56</u>	<u>57</u>	<u>58</u>
1	2	Benzene	15	4	16.5	20.4	3.5
2	5	Benzene	15	4	13.4	0	24.9
3	5	Benzene	15	48	0	0	46
4	2.5	Toluene	-20	5	18.3	28.5	2.1
5	3.2	THF	-30	4	31	0	25.3
6	1 ^b	Xylene	-20	5	6.4	48	0.5
7	1 ^c	Toluene and THF	-30	4	7.6	7.9	0
8	1.2 ^d	Xylene and THF	-10	3	13.3	21	0.03
9	1.32 ^e	Toluene and THF	0	4	7	26	1.7
10	2 ^f	Xylene	-5	4	14.4	20.8	3.2

^aExperiments 1 to 6, by adding 28 into the basic solution of 59.
Experiments 7 to 10, by adding 59 into 28.

^b59 Was made by treating t-amyl alcohol with NaH.

^cProducts also contained 9.2% of 28 + 15 + 14.

^dProducts contained 4% of 28 + 15 + 14.

^e3% of .

^f5% of 28.

with potassium *t*-butoxide under identical conditions reflect the reduced basicity of sodium *t*-amyloxide. Therefore, S-(β -chloroethyl)-O-*t*-amylthiocarbonate (57) was synthesized by an alternate procedure (vide infra) and stronger bases were employed for the dehydrohalogenation step.

Dehydrohalogenation of 57 with bulky base such as *t*-butoxide⁴⁰ is expected to yield the corresponding monomer (56), but *t*-BuO⁻K or *t*-Am-O⁻Na usually produced by-product (58), so we were interested in exploring some other bases. Attempted preparation of monomer (56) through dehydrochlorination of 57 by 1,5-diazobicyclo(3.4.0) nonene-5 (60)⁸² proved unsuccessful. The yields from dehydrochlorination of 57 with lithium dicyclo-

hexylamide and/or lithium diisopropylamide in 1,2-dimethoxyethane were discouragingly low.

Spectroscopy analysis of a mixture of 56, 57 and 58 can be achieved by nmr. The chemical shifts for the two tertiary methyl groups of 56, 57, and 58 were detectable as singlets at δ 1.48, 1.45, and 1.42 respectively. The monomer usually contained about 2-5% of di-*t*-amylcarbonate as impurity even after careful distillation through a high efficiency spinning band column.

Synthesis of Thermally Labile Bender's Salts

As described earlier, the synthesis of 16 involved a condensation of ethylene sulfide with phosgene to produce S-(β -chloroethyl)chlorothioformate (28),³⁴ which has limited applicability as a mercaptan precursor. The condensation is difficult to control and the product tends to be contaminated with S,S'-bis(β -chloroethyl)dithiocarbonate (14) which leads to undesirable by-products in the monomer synthesis.³⁵ Furthermore, the inherent experimental problems encountered in working with large quantities of phosgene as well as handling the toxic S-(β -chloroethyl)chlorothioformate limits the application of this technique in large scale monomer synthesis. A new synthetic approach which involved nucleophilic displacement of alkyl halides by thermally labile Bender's salts,⁸³ i.e. potassium-O-t-alkylthiocarbonates, was soon developed to minimize these problems and to extend the preparative scope of the carbo-t-alkyloxy blocking group.

Bender's salts are stable crystalline reagents which can be prepared by treating an alkali metal alcoholate with carbonyl sulfide in an anhydrous solvent mixture of alcohol and dimethylformamide (DMF). In contrast to potassium xanthates, the salts are insoluble in most organic solvents such as: benzene, chloroform, t-butanol, tetrahydrofuran (THF), DMF, and dimethylsulfoxide (DMSO) so it is not possible to maintain a homogeneous system during the preparation. For example, potassium-O-t-butylthiocarbonate (61) precipitates immediately upon introduction of carbonyl sulfide to a

solution of potassium t-butoxide in t-butanol and occludes unreacted alcoholate. Addition of DMF to the reaction mixture increases the yield of the Bender's salt but the mixture remains heterogeneous. The salts can be purified by dissolution in water and precipitation by adding the aqueous solution to ethanol but the purification must be completed rapidly since Bender's salts undergo slow hydrolysis in water.⁸³ Dissolution of 61 in ethylene glycol, 2-methoxyethanol or triethyleneglycol dimethyl ether did not appear to promote decomposition.

Three thermally labile Bender's salts, potassium-O-t-butylthiocarbonate (61), potassium-O-t-(2-methyl-2-butyl)thiocarbonate (62), and potassium-O-(2-phenyl-2-propyl)thiocarbonate (63), were synthesized.

<u>R</u>	<u>Decomp. temp., °C</u>	<u>Wt. loss, %</u>
<u>t</u> -Butyl (<u>61</u>)	255	44.0
<u>t</u> -Amyl (<u>62</u>)	225	54.8
<u>t</u> -Cumyl (<u>63</u>)	195	55.8

The exact nature of the thermal decomposition was not determined, but the presence of more bulky t-alkyl substituents (amyl, cumyl) accelerate the decomposition and reduce the temperature required to remove the blocking group.

The infrared spectra of potassium O-t-alkylthiocarbonates are nearly identical with the exception of strong ring vibrational

modes for t-cumyl derivatives (63). The carbonyl absorptions at $1,900\text{ cm}^{-1}$ of the Bender's salts are much lower than those exhibited by S-alkyl-O-alkylthiocarbonates or dialkylcarbonates ($1700\text{-}1740\text{ cm}^{-1}$), but the values are consistent with the reported values of metal salts of thiol carboxylic acid⁸⁴ and oxyxanthates.⁸⁵ The C-S stretching modes for Bender's salts (695 cm^{-1}) observed were higher than the monothiocarbonate compounds in which C-S stretching appeared at 675 cm^{-1} (Table 2). A literature survey showed that infrared spectra of certain types of sulfur compounds have been unusually variable and difficult to characterize, i.e. values for carbon-sulfur bond stretching range from $650\text{ to }950\text{ cm}^{-1}$.^{84,85,86} Since laser Raman spectroscopy is a complementary analytical tool to infrared for structural elucidation and sulfur containing compounds generally exhibit stronger characteristic bands in the Raman spectra, we have made a study of several thiocarbonates, carbonates, and xanthates in an attempt to clarify the discrepancies reported in the literature. The infrared and laser Raman characteristic group frequencies for these compounds are compiled in Tables 2 and 3 respectively.

The carbonyl stretching frequencies for most of thio-carbonates were lower than dialkylcarbonates. Baker and Harris⁸⁷ have reported that a sulfur adjacent to a carbonyl group usually decreases the basicity of the carbonyl group despite the fact that oxygen has a higher electronegativity than sulfur. Table 4 shows that the carbonyl group frequencies decrease as the number

TABLE 2

Characteristic Infrared Absorptions for S-Alkyl-O-*t*-alkylthiocarbonate, Di-*t*-alkylcarbonate,
and Potassium-O-*t*-alkylcarbonate Compounds. ^{a, b}

Compound	Structure	C-H st.	C=O st.	CH ₃ b. (asym. def.)	<i>t</i> -Alkyl sym. def.	<i>t</i> - Alkyl- O-asym. st.	<i>t</i> -Alkyl def.	<i>t</i> -Alkyl- O-sym. st.	CH ₃ r.k. and/or C-C val.	C-S st.	Other absorptions
5R	$\text{CH}_2=\text{CHSC}(=\text{O})\text{-t-Am}$	2850~ 2970 _s	1690~ 1730 _s	1440 _m , 1460 _m	1360 _m , 1390 _m	1250 _u	1210~ 1180 _s	1110~ 1150 _s	856 _m , 832 _{ms}	674 _u	1600 _s (C=C), 1035 _m (C=C), 962 _m (C=C), 895 _m (C=C), 702 _m (C=C), 1050 _s , 1010 _u , 980 _m , 735 _m .
5Z	$\text{ClCH}_2\text{CH}_2\text{SC}(=\text{O})\text{-t-Am}$	2890~ 2990 _s	1700~ 1730 _s	1440 _m , 1460 _s	1390 _s , 1370 _s	1250 _u	1220~ 1180 _s	1110~ 1150 _s	856 _m , 832 _{ms}	679 _m	1420 _u (CH ₂), 1230 _u (C-Cl), 1060 _s , 1030 _u , 1010 _u , 930 _m , 706 _s (C-Cl)
5R	$\text{t-AmOC}(=\text{O})\text{-t-Am}$	2998 _s , 2900 _s	1750 _s	1465 _s	1380 _s , 1240 _{bs}	1315~ 1240 _{bs}	-----	1120~ 1165 _{bs}	926 _m , 840 _{bs}	-----	1065 _m , 1010 _u , 707 _m .
4R	$\text{CH}_2=\text{CHSC}(=\text{O})\text{-t-Bu}$	2870~ 2940 _s	1690~ 1730 _s	1450 _m , 1470 _m	1370 _m , 1390 _s	1250 _m	1205 _s	1110~ 1150 _s	854 _m , 839 _s	674 _u	1590 _s (C=O), 1035 _m (C=C), 962 _m (C=C), 895 _m (C=C wag), 715 _m (C=C wag.).
4Z	$\text{ClCH}_2\text{CH}_2\text{SC}(=\text{O})\text{-t-Bu}$	2890~ 2960 _s	1690~ 1710 _s	1440 _m , 1450 _m	1360 _m , 1380 _m	1245 _u	1200~ 1180 _s	1110~ 1140 _{vs}	854 _m , 832 _s	674 _u	1410 _u (CH ₂), 1290 _u (C-Cl), 1060 _u (C-Cl), 927 _u (C-Cl), 828 _s (C-Cl), 700 _s (C-S-C val.)
5S	$\text{t-BuOC}(=\text{O})\text{-t-Bu}$	2820~ 2920 _s	1740 _s	1445 _m , 1460 _m	1360 _s , 1380 _m	1305~ 1240 _{bs}	-----	1105~ 1190 _{bs}	926 _u , 900 _s , 850~ 839 _{bs}	-----	792(C-O wag.), 720(C-O wag.) O-C=O wag. or CH ₃ r.k.
6L	$\text{K}^+\text{t-BuCO}_2^-$	2890~ 2950 _m	1590~ 1610 _s	1440 _m , 1470 _u	1365 _m , 1395 _m	1240 _u	-----	1075~ 1125 _{bs}	865 _u , 839 _m	695 _m	

(Table 2 Continued)

82	$\text{K}^{\oplus} \text{S}^{\ominus} \text{CO}-\text{t-Bu}$	2890~ 2940 _m	1590~ 1610 _s	1440 _m , 1460 _m	1360 _m , 1390 _m	1240 _w	-----	1075~ 1125 _{bs}	862 _w , 835 _m	695 _m	1005 _w , 927 _w .
83	$\text{K}^{\oplus} \text{S}^{\ominus} \text{CO}-\text{R}$, $\text{R} = -\text{C}(\text{CH}_3)_2\text{Ph}$	2890~ 2990 _m	1610 _{bs}	1445 _s , 1490 _m	1360 _m	1270 _m	-----	1050~ 1150 _{bs}	860 _m , 838 _s	692 _s	1010 _s and 1030 _s (C=C in plane b.), 932 _w and 938 _w (C=C out of plane b.), 762 _s (C=C ring out of plane b.), 696 _s (ring def.).
85	$\text{RCH}_2\text{CH}_2\text{R}$ where O $\text{R} = \text{t-Bu-OCS}-$	2890~ 2960 _s	1698~ 1720 _s	1450 _m , 1470 _m	1370 _s , 1390 _m	1250 _m	1205 _s	1110~ 1150 _{bs}	860 _s , 839 _s	678 _m	718 _m , 697 _m
86	$\text{HSCH}_2\text{CH}_2\text{SCO}-\text{t-Bu}$	2910~ 2970 _s	1700~ 1725 _s	1460 _m , 1480 _m	1370 _s , 1400 _m	1250 _m	1205 _s	1120~ 1150 _{bs}	860 _m , 840 _s	679 _w	2570 _w (S-H), 1340 _w , 705 _w (C-S-C st.)
87	$\text{CH}_3\text{CH}_2\text{S}-\text{C}-\text{O}-\text{t-Bu}$ O	2880~ 2975 _s	1730~ 1695 _s	1450 _m , 1475 _m	1370 _s , 1390 _m	1250 _m	1205 _s	1110~ 1150 _{bs}	860 _m , 840 _s	679 _m	1060 _m , 1040 _w , 978 _m , 925 _w , 750 _w , 740 _w .
70	$\text{PhCH}_2\text{S}-\text{CO}-\text{t-Bu}$ O	2890~ 2960 _s	1710~ 1685 _s	1450 _m , 1495 _m	1365 _s , 1390 _m	1250 _m	1205 _s	1110~ 1140 _{bs}	855 _m , 836 _s	674 _w	1655 _w and 1585 _w (ring, 1225 _w (C=CH out of plane b.), 772 _w (ring out of plane b.), 700 _{bs} (ring def.))
88		2900~ 2990 _s	1700~ 1725 _s	1450 _w , 1480 _w	1360 _m , 1390 _m	1250 _m	1205 _s	1110~ 1145 _{bs}	857 _m , 837 _s	674 _w	1640 _w (C=C st.), 1610 _w and 1580 _w (phenyl ring), 1405 _w (=CH ₂ def.), 1340 _w (O), 950 _{bs} (C=C), 915 _{bs} (trans CH wag.), 915 _{bs} (=CH ₂ wag.), 822 _m (O), 745 _w , 710 _{bs} (ring def.).

^aAll samples run neat except potassium O-t-alkylcarbonates in KBr disk. All absorptions measured in wavenumber, cm^{-1} . ^bThe following abbreviations will be used in descriptions of infrared in this dissertation: vs - very strong; s = strong; m = medium; b = broad; w = weak; st. = stretching; b. = bending; r.k. = rocking; def. = deformation; asym. = asymmetric; sym. = symmetric; val. = valence; wag. = wagging.

TABLE 3

Laser Raman Characteristic Scatterings for S-Alkyl-O- α -alkylthiocarbonate, Di- α -alkylcarbonate,
and Potassium O- α -Butylthiocarbonate Compounds^{a,b}

Compound	Structure	C-H st.	>C=O	CH ₃ b. (asym. def.)	-CH ₂ -S-	α -Alkyl- O-asym. st.	α -Alkyl def.	α -Alkyl- O-sym. st.	C-O-C asym. val.	C-C Val. for α - alkyl group	CH ₃ r.k. and/or C-C val.	C-O Wag.	C-S	O=C-O out of plane skel. def.	Other scatterings
5a	$\text{CH}_2=\text{CHSCOO}-\alpha\text{-Am}$	3085m and 3040w(CH=OH st.); 2975s(CH ₂ st.); 2938s~ 2875w(α -Amyl st.)	1718w	1446s	-----	1254m	1206w	1132w	1060w 1029m	925m	850w, 825m	735s	705	535w	1595s(C=C), 1378s(C=C), 1303s(α -Amyl def.), 1000s, 835s, 588w, 503s, 456w, 413s, 371m, 269w, 235w.
5c	$\text{ClCHCH}_2\text{SCOO}-\alpha\text{-Am}$	2975vs (CH ₂ st.); 2925s and 2875m(α -Amyl st.)	1710w	1445vs	1412w	1270w	1190m	1132bm	1063m, 1038m	925s	852m, 825m	750vs	700	525m	1295s(-CH ₂ -Cl), 1244w, 975w, 675m and 63m (C-Cl), 500m, 462w, 412w, 335s, 225s.
5b	$\alpha\text{-Am-OCO}-\alpha\text{-Am}$	2975~ 865s	1738w	1450s	-----	1300w	1200w	1165w	1060m	928m	860m	757s	---	----	1238w, 1000w, 550w, 525w, 500w, 450~425bw, 375~338bw, 275~212bw.
1a	$\text{CH}_2=\text{CHSCOO}-\alpha\text{-Bu}$	3025m, 3088w and 3194w(=C-H); 2875s and 2925w (α -Bu)	1725w	1460m	-----	1260m	1215w	1140w	1040m	925w	854s, 837m	750s	712	535w	1599s(C=C), 1382s(C=C), 740w, 463m, 420w, 375s, 325w, 256vs.

(Table 3 Continued)

17		$\text{ClCH}_2\text{CH}_2\text{SC(=O)-t-Bu}$	2954s	1710w	1460s	1412w	1287m	1200w	1140w	1050w	923w	845m, 815m	750s	690m	515m	712m(CH ₂ r.k.), 644m (C-Cl); 485w, 450w, 400w, 320w, 213w.
52		$\text{t-Bu-O-C(=O)-O-t-Bu}$	2887~ 2998s	1738w	1463s	-----	1270m	1200w	-----	1050w	933m	852m	782m	-----	-----	1256m, 531ms, 463m, 353w.
61		$\text{K}^+\text{S-C(=O)-O-t-Bu}$	2937~ 3000s	1581m (sharp)	1463ms	-----	1250w	1190w	-----	1040w 1060w	925w	862ms, 834m	750s	-----	543ms	1450ms (t-Bu asym. def.), 462s, 330s, 297m.
65		$\text{RCH}_2\text{CH}_2\text{R}$ where $\text{O}=\text{C}-\text{S}-\text{O}-\text{t-Bu}$	2950s, 2987s	1600w	1450s	F.	F.	1200m	F.	F.	F.	848m, 825m	740s	-----	503ms	F.
68		$\text{HSCH}_2\text{CH}_2\text{S-C(=O)-O-t-Bu}$	2910~ 2975s	1695~ 1725w	1450ms	1412w	1285w	1200m	1140w	1040w	925m	857ms, 830ms	750s	680w or 640w	518ms	2565ms (S-H), 464w, 413w, 327w, 225m.
69		$\text{CH}_3\text{CH}_2\text{SC(=O)-t-Bu}$	2875~ 2975s	1715w	1468ms	1430w	1262w	1210w	1141w	1070w 1012w	937w	872m, 850m	750s	681m	535m	981w, 475w, 363w, 342w, 267s.
72		$\text{PhCH}_2\text{SC(=O)-t-Bu}$	3050s(C=CH), 2975s (C-H st.), 2925s(CH ₃ st.), 2875s(t-Bu st.).	1725w	1456ms	1420w	1254s	1205s	1165w	1040ms, 1006s	935w	863m, 847m	750ms	697m	525ms	1513s(C=C ring vib.), 1130w and 1165w (t-Bu sym. st.), 825m(ring vib), 779m(ring out of plane b.), 625m(ring vib.), 463m, 425w, 335-313w, 223ms.
88		$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{SC(=O)-t-Bu}$	3020m and 1727~ 3060m(C=CH) 1700w 3000ms and 2975ms(C-H st.), 2925ms (CH ₃ st.).	1450m	1406ms	1253ms	1208m	1181ms	1034w, 1000s	917w	858w, 831m	745m	685w	516w	1532s(C=C ring vib.), 1650s and 1552ms, (1650s), 1312m(ring), 852w(ring vib.), 775ms, 637w(ring), 552w, 456w, 335w, 224w, 213m.	

^aAll samples were recorded using an Argon laser (4880Å) excitation source unless designated otherwise. ^bAll the Raman scatterings were measured in wave-number, $\Delta\nu_{\text{cm}^{-1}}$; abbreviations in laser Raman descriptions are the same as those in Table plus F. = Fluorescence, vib. = vibration, skel. = skeletal.

^cExcitation wavelength of 5145Å.

of the adjacent sulfur atoms increase. Thus, the carbonyl stretching absorptions of carbonates appear at higher frequencies than monothiocarbonates, and the dithiocarbonates appear at lower frequencies. The low carbonyl frequency of Bender's salts (1580 cm^{-1}) is consistent with symmetric and antisymmetric stretching modes of a resonance hybrid which involves $3d$ -orbitals on the sulfur atom.

In turn, this hybridization will also explain the higher stretching mode (695 cm^{-1}) of the Bender's salts than those of most of the S-alkyl-O-t-alkylthiocarbonates. The delocalization of the electron participating in resonance interaction in the ground state through $3d$ -orbitals of the sulfur atom strengthens the C-S bond.

Theoretical calculations showed that the characteristic frequency of C-S linkage^{88,89} should be $\Delta\nu\ 650\text{ cm}^{-1}$ with a force constant 2.14×10^{-5} dynes/cm. Our assignment for the C-S stretchings of $650\text{-}700\text{ cm}^{-1}$ is consistent with those calculations and the data previously reported.^{85,89}

TABLE 4

Frequency Correlations of Carbonyl Compounds

No.	Compound	>C=O Stretch (cm^{-1})	Other absorptions (cm^{-1})	Reference
1		1851		86
2		1757		86
3		1678		86
4	$\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}$	1740-50		this work
5	$\text{R}-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}$	1690-30	679 (C-S)	this work
6	$\text{R}-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-\text{S}-\text{R}$	1640-55		84
7	$\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{S}^- + \text{K}^+$	1570-85	695 (C-S)	this work
8	$\text{R}-\text{O}-\overset{\text{S}}{\parallel}{\text{C}}-\text{S}^- + \text{K}^+$	---	1185-1240 (C=S)	this work
9		1550		84
10		1523		84
11		1727 and 1789		84
12		1680 and 1739		84

Bender's Salts as Nucleophiles

We have found that Bender's salts effect quantitative S_N2 displacement of primary and secondary halides to form O-alkyl-S-alkyl-thiocarbonates.³⁰ Although spectroscopic studies indicate that the charge on the anion is delocalized, no evidence for products

resulting from attack by the oxygen atom was observed. Since carbonyl-alkyl blocking groups can be removed by either thermolysis or acid hydrolysis, selection of potassium-O-alkylthiocarbonates as nucleophiles enables us to introduce a mercaptan precursor on an organic substrate and generate the free mercaptan group in neutral or acidic media. Thus, the rapid, base catalyzed oxidation of mercaptans³¹ and polymercaptans^{36,42} which is a complicating side reaction in the synthesis of polymercaptans via vinyl thioacetate,¹⁵⁻²⁰ isothiuronium salts,⁴³ and S-vinyl-N,N-dialkyldithiocarbamates,^{33,66} is not a problem in our procedure.

The applications of Bender's salts as nucleophiles in the synthesis of O-alkyl-S-alkylthiocarbonate compounds are summarized in Table 5. Exploratory experiments with ethyl bromide and benzyl chloride demonstrated that the best solvent for nucleophilic displacement was DMF containing 1-2% water. Bender's salts form colored complexes with transition metals³² so the reaction mixtures

TABLE 5

Application of Bender's Salts to the Preparation of

Compound	R	R'	Yield %	bp °C/mm	mp °C	Prep. by method ^a
57	ClCH ₂ CH ₂ -	<u>t</u> -Amyl-	93	105/10	-	B
64	ClCH ₂ CH ₂ -	<u>t</u> -Cumyl-	87.5	(dec. temp. 40/10)	-	C
17	ClCH ₂ CH ₂ -	<u>t</u> -Butyl	94	49/0.5	-	B
67	CH ₃ CH ₂ -	<u>t</u> -Butyl	80	39-40/4	-	D
70	C ₆ H ₅ CH ₂ -	<u>t</u> -Butyl	98	105/0.5	-	A
69	CH ₂ =CH CH ₂ -	<u>t</u> -Butyl	100	182/760 (DTA)	-	A
65	-CH ₂ CH ₂ -	<u>t</u> -Butyl	90.8	-	87(dec. temp. 227)	A

a. Reaction conditions: 6 hr. at -5° and 2 hr. at 30° in the following media: A, DMF; B, THF + t-butanol; C, THF + benzene; D, THF.

may be dark-colored during the initial stages of reaction, but the color disappears as the reaction nears completion. As Scheme XI illustrates, selective displacement of bromide in the presence of chloride can be effected in THF:t-butanol (4:1) at -10° .

Scheme XI

Compounds 57, 64, and 17 were synthesized by treating excess of 1,2-bromochloroethane with the corresponding Bender's salts. Nmr and elemental analysis showed that the monosubstitution of the more reactive bromide occurred. Subsequent dehydrohalogenation of these compounds would produce the necessary monomers. Compound 64, S-(β -chloroethyl)-O-(2-phenyl-2-propyl)thiocarbonate, is very unstable. Attempted purification of 64 by fractional distillation at $40^{\circ}/10$ mm Hg yielded α -methylstyrene, 1-mercapto-2-chloro-ethane, carbon dioxide and cumene. Presumably, the extremely low decomposition temperature is due to the formation of a resonance stabilized olefin via a Chugaev reaction.⁹³

Subsequent dehydrohalogenation of 17 with lithium diisopropyl amide yielded 11% of 16; changing the base to potassium t-butoxide

improved the yield to 62%. Similar results were obtained on dehydrohalogenation of 57. No attempt was made to dehydrohalogenate 64 since the monomer would probably decompose under the conditions necessary to effect polymerization.

Initially, we had planned to obtain 16 by vacuum pyrolysis of S,S'-ethylene bis(O-t-butylthiocarbonate) (65) which was made by the reaction of 1 mole of 1,2-dichloroethane with 2 moles of corresponding potassium O-t-butylthiocarbonate (61) (Table 5). However, instead of generating monomer (16), pyrolysis of 65 at 300-325°/70-80 mm yielded S-(β -mercaptoethyl)-O-t-butylthiocarbonate (66). This phenomenon demonstrated that hydrogen abstraction from the

t-alkyl substituent is the only decomposition pathway for carbo-t-butoxy blocking groups. Okawara's successful preparation of S-vinyl-N,N-dialkyl dithiocarbamate by pyrolysis of the corresponding bis-adduct³⁸ (Scheme IV) reflects the difference in stability between C-N and C-O bonds in the blocking group as well as the energy gained by the formation of carbon dioxide in our system.

An alternate preparation of 16 involved nucleophilic displacement of 2-bromoethanol with 61 to yield S-(β -hydroxyethyl)-O-t-butylthiocarbonate (68), mesylation with methane sulfonyl chloride, followed by elimination with triethyl amine in the presence of pyridine, hopefully to yield the corresponding monomer 16. However, this reaction sequence yielded t-butanol, ethylene monothiocarbonate, 1,3-dithiane, di-t-butylcarbonate, and a mixture of unidentified oils instead of the desired monomer.

S-Vinylbenzyl-O-t-butylthiocarbonate

An alternative approach to a monomer synthesis utilizes a commercially available mixture of 60% meta and 40% para-vinyl-benzyl chloride as the substrate. Treatment of the mixture with 61 in DMF produces S-vinylbenzyl-O-t-butylthiocarbonate (69) in quantitative yield. A model compound of 69, S-benzyl-O-t-butylthiocarbonate (70),

was also synthesized in 98% yield as shown in Table 5.

Using the Bender's salt approach, the cost for the synthesis of S-vinyl-O-t-butylthiocarbonate is reduced from \$505/lb. to \$167/lb. In addition to the two-third reduction in cost, the new process eliminates the dangerous phosgene and ethylene sulfide intermediates and

opens a new area for the synthesis of S-alkyl-O-alkylthiocarbonates and their mercaptan derivatives. Thus, the application of Bender's salts to the synthesis of monomer precursors for polymercaptans is the most efficient method for producing low molecular weight, well defined homopolymers and copolymers.

B. Homopolymerization of Vinyl Mercaptan Precursors

Polymerization of S-Vinyl-O-t-butylthiocarbonate. S-Vinyl-O-t-butylthiocarbonate (16) polymerizes readily in bulk or solution in the presence of free radical initiators. Since we used two different methods (Scheme X and XI) to synthesize 16, we conducted a series of dilatometric rate determinations to compare the purity of the monomers obtained. Initially we used the monomer obtained from S-(β -chloroethyl)-chlorothioformate (28) to study the effect of initiator concentration upon the rate of polymerization (R_p). The R_p was evaluated dilatometrically and results are given in experiments 1 to 4 in Table 6. A typical plot of contraction in the dilatometer during polymerization of S-vinyl-O-t-butylthiocarbonate (16) is shown in Figure 1. The usual kinetic rate law for free radical polymerization is:

$$R_p = k_p/k_t^{\frac{1}{2}} (fk_d)^{\frac{1}{2}} [M][I]^{\frac{1}{2}}$$

where k_d , k_p , and k_t are the rate constants for initiator dissociation, chain propagation, and chain termination respectively, and f is an efficiency factor relating initiator decomposition to chain initiation. The unique aspect of this data is the deviation of the rate of polymerization from the square root law for low initiator concentration (Figure 2). A plot of $\ln R_p$ versus $\ln [I]$ (Figure 3) shows that the rate of polymerization is proportional to initiator concentration raised to a power of 0.765, which is similar to the rate law reported for vinyl thioacetate¹⁸ ($R_p \propto [I]^{0.75}$). The effect of monomer concentration on R_p also deviated from the normal (Figure 3); a kinetic study

TABLE 6

Dilatometric Evaluation of S-Vinyl-O-*t*-butylthiocarbonate Polymerization^a

Experiment	$\frac{[M]^b}{\text{mol/l}}$	$\frac{[I] \times 10^2}{\text{mol/l}}$	$\frac{R_p' \times 10^4}{\text{degree of conv./sec}}$	$\frac{R_p \times 10^4}{\text{mol/l-sec}}$	$\frac{R_p/[I]}{\times 10^2}$	$\frac{[\eta]}{(30^\circ, \text{THF})}$	$\frac{\bar{M}_n \times 10^{-4c}}{\text{---}}$
1	5.67	8.295	3.30	18.66	2.25	0.24	2.85
2	5.67	4.265	1.84	10.40	2.44	0.31	3.95
3	5.67	0.825	0.59	3.37	4.09	0.34	4.05
4	5.67	0.498	0.34	1.93	3.89	0.36	4.48(4.9) ^d
5	5.646	1.048	1.86	10.59	10.1	0.40	----
6	5.837	0.684	1.34	7.89	11.5	0.41	----
7	5.406	0.608	0.95	5.21	8.6	0.37	----
8	5.888	0.248	0.39	2.35	9.5	0.35	5.40
9	5.121	0.180	0.44	2.25	12.5	0.39	----

^aPolymerization temperature, 70°; initiator, azobisisobutyronitrile.^bFrom experiment 1 to 4, the monomer was obtained from 28, from experiment 5-9, the monomer was derived from 61.^cEstimated from GPC chromatogram of 0.125% solution in THF except experiment 8 estimated from a 0.125% solution in DMF.^dMeasured in toluene at 30° with Macrolab Model 501 membrane osmometer.

Figure 1:

Typical plot of contraction in the dilatometer during polymerization of S-vinyl-O-t-butylthiocarbonate. Polymerization conditions cited in Table 6, Row 8.

using di-t-butylcarbonate as a diluent revealed that the polymerization is 1.7 order in monomer concentration.

The deviation from normal kinetic relationships could be explained by a change in the efficiency factor, f , in the relationship⁹⁴ between R_p , monomer concentration, $[M]$, and initiator concentration, $[I]$. Matsumoto, et al.⁹⁵ made a study of the chain-transfer properties of vinyl acetate polymerization and attributed the deviation of their system from a normal square root law to the reduction in initiator efficiency at low concentrations of both monomer and initiator. The reason for the reduction in initiator efficiency is not clear, but it seems unlikely that all monomers would behave in an identical fashion. This approach also fails to explain the unusually high order in monomer concentration. A more precise derivation of the kinetic rate law seems to lead to an explanation for our results. Assuming that monomers with a high chain transfer constant act as a solvent at low conversions, one can apply to the problem the kinetics of chain transfer to solvent. Lindemann⁹⁶ derived the following rate equation for polymerization of vinyl acetate in the presence of chain transfer agents:

$$R_p = k_p \left(\frac{R_i}{k_t} \right)^{\frac{1}{2}} [M] \frac{(R_i k_t)^{\frac{1}{2}}}{k_{trs}[S] + (R_i k_t)^{\frac{1}{2}}}$$

The usual definition of terms applies to this expression except that the mode of termination is considered to be the sum of two processes, termination by combination (k_t) and termination by chain

transfer (k_{trs}) to solvent $[S]$. This equation predicts that the dependence of polymerization on initiator concentration will be a power between 0.5 and 1.0. The value of exponent depends on the relative values of $k_{\text{trs}}[S]$ and $(R_i k_t)^{\frac{1}{2}}$. If $(R_i k_t)^{\frac{1}{2}} \gg k_{\text{trs}}[S]$, R_p will follow the normal rate law; but if $k_{\text{trs}}[S] \gg (R_i k_t)^{\frac{1}{2}}$, the order in initiator will increase. S-Vinyl-O-t-butylthiocarbonate shows a "degradative" chain transfer property similar to vinyl acetate, the observed value of $R_p \propto [I]^{0.765}$ for the rate dependence on initiator concentration is consistent with the latter relationship. Further, the solvent in our experiments is actually monomer, so a deviation from first order monomer dependence would be expected if $k_{\text{trs}}[S] \gg (R_i k_t)^{\frac{1}{2}}$. Unusual monomer orders for the polymerization of vinyl acetate in ester solvents were reported by Matsumoto, *et al.*⁹⁵

Homopolymerization of 16 derived from potassium O-t-butylthiocarbonate was also carried out dilatometrically in bulk using low concentrations of AIBN as an initiator. The results are recorded in Table 6 (exp. 5-9) and plotted in Figure 2. The $R_p/[I]$ ratio for this monomer is about six times faster than the monomer prepared by concurrent esterification-dehydrohalogenation. This phenomenon is apparently caused by persistent impurities from the S-(β -chloroethyl)-chlorothioformate, which can not be separated from 16 by multiple distillation. However, the dependence of R_p on the initiator concentration was not changed by the presence of the impurities (Figure 3).

The intrinsic viscosity of the polymer obtained from each experiment was in the range of 0.3 to 0.4 dl/g, regardless of the

Figure 2:

Effect of initiator concentration upon the rate of polymerization (R_p) of S-vinyl-O- $\underline{t}$ -butylthiocarbonate. The intrinsic viscosity of the polymers illustrates the molecular weight dependence. Polymerization conditions: $[M] = 5.6$ mol/l, 70° ; $\bullet$, R_p vs $[I]$; $\blacksquare$, R_p vs $[I]^2$; $\blacktriangle$, $[\eta]$ vs $[I]$ using runs 1-4 in Table 6; $\circ$, R_p vs $[I]$ using runs 5-9 in Table 6.

Figure 3:

Plot of $\ln R_p$ versus $\ln [I]$ and $\ln R_p$ versus $\ln [M]$ for the polymerization of S-vinyl-O-t-butylthiocarbonate (16).

monomer source. A number average molecular weight ($\bar{M}_n$) of 49,000 was determined by osmometry for one of the polymer samples. This appears to be the highest molecular weight attainable under these conditions, but it corresponds to a degree of polymerization of 500, which is about 15 times greater than the DP achieved for poly(vinylthioacetate) under similar conditions.¹⁸ Although these results indicate that 16 is less reactive than vinyl thioacetate as a chain-transfer agent, the molecular weight of the copolymers described later were also rather low (40,000-50,000). The chain-transfer constant to monomer, C_M , was estimated from the intercept of a plot of $1/DP$ vs. R_p (Figure 4) and found to be $C_M = 3.93 \times 10^{-3}$ at 70° . This is about 14.2 times less than that reported for vinyl thioacetate. For comparison, Table 7 shows the chain-transfer constants reported for some vinyl esters and S-vinyl monomers. The chain-transfer characteristics of S-vinyl monomers represent a major disadvantage when high molecular weight copolymers with good mechanical properties are desired.

The ubiquitous presence of di-t-butylcarbonate in the monomer prompted a more thorough study of its influence on the polymerization of S-vinyl-O-t-butylthiocarbonate, the results are summarized in Table 8 and Figure 5. The rate of polymerization and intrinsic viscosity decreased slightly as the concentration of di-t-butylcarbonate increased to concentrations as high as 20%. These results indicated that di-t-butylcarbonate is not an "inhibitor" or "retarder"¹⁰¹ but is simply acting as an inert diluent. Furthermore, 16 was not

Figure 4:

Degree of polymerization of poly(S-vinyl-O-p-butylthiocarbonate) as a function of the polymerization rate at 70°.

TABLE 7

Chain-transfer Constants to Monomer (C_M) for
Some Vinyl Esters and Allyl Monomers

Monomer	Temp., °C	$C_M \times 10^3$	Lit. ref.
S-Vinyl-O- <u>t</u> -butyl- thiocarbonate (16)	70	3.93	This work
Vinyl thioacetate	60	56	18
Vinyl acetate	60(70)	0.15(0.21)	97
Vinyl pelargonate	60(70)	1.5(2.0)	97
Vinyl stearate	60(70)	2.3(3.1)	97
Vinyl benzoate	79.6	0.7	98
Vinyl salicylate	70	8.0	99
Allyl chloride	80	160	100
Allyl acetate	80	70	100

TABLE 8

Dilatometric Evaluation of the Polymerization of
S-Vinyl-O-t-butylthiocarbonate with Di-t-butylcarbonate

Exp.	[M] mol %	[Carbonate] mol %	[AIBN] mol %	$\frac{R_p' \times 10^4}{\text{degree of conv/sec}}$	$\frac{R_p \times 10^4}{\text{mol/l-sec}}$	$[\eta]$ (30° , THF)
1	100	0	0.044	0.40	2.35	0.35 ^b
2	95	5	0.044	0.42	2.30	0.34
3	90.36	9.64	0.044	0.39	2.02	0.31
4	80.11	19.89	0.044	0.36	1.64	0.30
5	89.5	10.5	0.031	0.44	2.26	0.40
6	37.39 ^a	62.61 ^a	0.093	0.42	0.89	0.20

a. Nmr analysis results.

b. $\bar{M}_n = 5.4 \times 10^4$, estimated from GPC of 0.125% solution in DMF.

Figure 5:

Influence of di-*t*-butylcarbonate on intrinsic viscosity and rate of polymerization of S-vinyl-O-*t*-butylthiocarbonate.

responsive to low concentrations of chain-transfer agents such as dodecyl mercaptan, 2-naphthalene thiol, and carbon tetrabromide.³⁶

Free Radical Polymerization of Styrene in the Presence of Additives. Styrene polymerization in the presence of an additive such as di-t-butylcarbonate (55), S-ethyl-O-t-butylthiocarbonate (67), a saturated analog of 16, and poly(S-vinyl-O-t-butylthiocarbonate (71), was studied dilatometrically using AIBN as initiator. The results, as summarized in Table 9, show that no significant chain-transfer property was observed for these compounds. Although the polystyrene radical is not exceptionally reactive, it is unlikely that no effect would be detected if these compounds indeed acted as chain transfer agents in S-vinyl-O-t-butylthiocarbonate polymerization. Thus, the molecular weight limiting feature in homopolymerization and copolymerization of 16 is the chain transfer to monomer.

Polymerization of S-Vinyl-O-t-amylthiocarbonate. S-Vinyl-O-t-amylthiocarbonate (56) polymerized readily in bulk or solution in the presence of free radical initiators. The polymer was soluble in aromatic and halogenated solvents and could be precipitated by addition to aliphatic hydrocarbons or methanol. Isolating and drying the precipitate in vacuo produced a white, flocculent powder (72) with a molecular weight of $\sim 30,000$ (DP = 175). These results are similar to those obtained with S-vinyl-O-t-butylthiocarbonate^{36,78} and better than the DP achieved by polymerizing vinyl thioacetate under similar conditions.¹⁸ The limiting molecular weight is probably

TABLE 9

Effect of "Additive" on the Polymerization of Styrene
Initiated by AIBN^a at 70°

Exp.	Styrene mol/l-sec	Addi- tive	%Conv	$\frac{R'_p \times 10^4}{\text{degree ofconv/sec}}$	$\frac{R_p \times 10^4}{\text{mol/l-sec}}$	$[\eta]$ (30°, Benzene)	$\frac{M_n \times 10^{-4}}{(\text{GPC})^c}$
1	8.291	--	8.963	1.140	9.455	0.930	15.71
2	8.119	55	8.341	1.158	9.406	0.923	-----
3	8.148	67	8.780	1.161	9.421	0.940	-----
4	8.171	71	9.001	1.154	9.429	0.826	13.78

a. Concentration of AIBN: $[\text{AIBN}] \times 10^2 = 0.2336 \text{ mol/l.}$

b. Concentration of additive: $[\text{Additive}] \times 10^2 = 9.586 \text{ mol/l.}$

c. Estimated from GPC of 0.125% solution in DMF.

due to chain transfer to monomer and to the polymer backbone since abstraction of a hydrogen atom adjacent to thio-substituent would result in a radical stabilized by resonance with the sulfur atom.

The differential thermal and thermogravimetric analysis (Figure 6) of the polymer exhibited two major endothermic transitions. The first one, beginning at 222° and reaching a maximum at 230° , presumably corresponds to a thermal deblocking reaction to produce poly(vinyl mercaptan) (30). The second one at 334.5° probably corresponds to a cyclization of 30 accompanied by the release of hydrogen sulfide. A 64.60% (theoretically 65.51%) weight loss (TGA) and the disappearance of t-amyl functional group

in the nmr of the residue were consistent with this interpretation. The thermolysis reaction will be discussed in detail in Section C.

Polymerization of S-Vinylbenzyl-O-t-butylthiocarbonate. S-Vinylbenzyl-O-t-butylthiocarbonate (69) is a very reactive monomer which can be polymerized readily in bulk or solution in the presence of free radical initiators. Polymerization to low conversions yielded 25% crosslinked polymer which swelled rapidly in benzene, THF, and DMF, and 75% benzene soluble poly(S-vinylbenzyl-O-t-butylthiocarbonate) (73) with an intrinsic viscosity of 0.49 dl/g.

Figure 6:

DTA (A) and TGA (B) analysis of poly(S-vinyl-O-t-amylthiocarbonate).

The higher molecular weights of (73) as compared with poly-S-vinyl-O-t-butylthiocarbonate) (71) indicated that the benzyl methylene group shields the growing radical from the d-orbital of the sulfur atom and eliminates the possibility of conjugation with the electrons of the π -bond (d- π conjugation). The free radicals of growing chain from 16 are more stable than 69 radicals, since the expansion of the unpaired electron into the d-orbital of the sulfur atom results in a resonance stabilization.⁴⁰ However, the methylene group is probably a very reactive chain transfer site since the radical formed upon hydrogen abstraction is stabilized. Extensive chain transfer to polymer via the benzyl group is probably responsible for the formation of crosslinked polymer at high conversions. A bulk polymerization which was allowed to go to 100% conversion yielded crosslinked polymer only.

Attempted anionic polymerization of 69 in the presence of n-BuLi at -78° in toluene proved unsuccessful. Polymers from 69 can be decomposed at 222° to form the corresponding poly(vinylbenzyl mercaptan) with subsequent loss of carbon dioxide and isobutylene.

C. Kinetic Studies of the Pyrolysis of Poly(S-vinyl-O- $\underline{t}$ -butylthiocarbonate)

Several examples of the thermal removal of the carbo- $\underline{t}$ -butoxyl blocking group have been reported in literature.¹⁰²⁻¹⁰⁴ Thermal decomposition of poly-(S-vinyl-O- $\underline{t}$ -butylthiocarbonate) was originally investigated by Daly³⁶ by heating a 15% solution of polymer in N-methylpyrrolidone under nitrogen to 160° to induce a vigorous evolution of carbon dioxide and isobutylene. The isobutylene was identified by the formation of N- $\underline{t}$ -butyl benzamide from benzonitrile via the Ritter reaction.¹⁰⁵ Quantitative determination of carbon dioxide by absorption on Ascarite indicated that 89% reaction had occurred after two hours. This was in good agreement with a mercaptan assay of 82% for the poly(vinyl mercaptan) solution. The poly(vinyl mercaptan) was soluble in DMSO, DMF, dioxane and 5% NaOH.

A kinetic study of the thermolysis of poly(S-vinyl-O- $\underline{t}$ -butylthiocarbonate) (71) was conducted using isothermal time base thermogravimetric analysis (TGA). Table 16 summarizes the isothermal weight-loss data for 71 in a dry nitrogen stream. The results, as shown in Figure 7, confirmed that the reaction is first order and an Arrhenius plot (Figure 8) exhibits a linear temperature dependence in the range from 170-250° with $E_a = 31.22$ kcal/mol, $A = 2.302 \times 10^{12} \text{ sec}^{-1}$, and $\Delta S^\ddagger = -2.42$ e.u. The low activation energy and negative entropy of activation are consistent with the cyclic transition state usually proposed for Chugaev reactions.³³

Figure 7:

Typical curves of isothermal decomposition (TGA) of poly(S-vinyl-O-t-butylthiocarbonate) at 207°, 217°, and 231°.

Figure 8:

Arrhenius plot for thermal deblocking reaction of poly(S-vinyl-O-t-butylthiocarbonate).

The total weight loss averaged over ten isothermal runs was $62.60 \pm 0.1\%$ (calc'd 62.5%). Mass spectral analysis of the gas mixture evolved showed that it was composed of carbon dioxide and isobutylene only, which is consistent with the deblocking mechanism proposed (Scheme XII).

SCHEME XII

Mechanism of Thermolysis

D. Copolymerization of S-Vinyl-O-*t*-butylthiocarbonate

Copolymerization with Styrene, Methyl Methacrylate, and Vinyl Acetate - The copolymerization characteristics of S-vinyl-O-*t*-butylthiocarbonate were determined by measuring the relative reactivity of ~ 16 toward styrene, methyl methacrylate and vinyl acetate. These comonomers represent a wide range of copolymerizabilities, extending from the resonance stabilized styrene with

negative polarity ($Q, 1.0; e, -0.8$) through the negatively polarized non-stabilized vinyl acetate ($Q, 0.028; e, -0.3$) to the positively polarized methyl methacrylate ($Q, 0.74; e, 0.4$)¹⁰⁶. Thus, the reactivity ratios observed when 16 was copolymerized with each of these comonomers should define the Q, e parameters for 16 and indicate the types of comonomers which would yield random copolymers.

The copolymerizations were run with neat monomer mixtures using 0.5 mole % azobisisobutyronitrile as an initiator. In spite of all precautions, the copolymerizations frequently proceeded so rapidly that conversions greater than 10% were obtained. In these cases the initial monomer concentration in the feed was used to obtain a first approximation of the reactivity ratios and then the computer program¹⁰⁷ for generating an integrated copolymer composition at all conversions was used to refine the values. The copolymer composition was determined by two independent techniques, elemental analysis and either ultraviolet or nmr spectrometry. The data obtained was analyzed by the method of Fineman and Ross¹⁰⁸ (Method 1) using one of the following two forms of the copolymerization equation:

$$F - (F/f) = r_1(F^2/f) - r_2 \quad (1)$$

$$\frac{f-1}{F} = -r_2(f/F^2) + r_1 \quad (2)$$

where F is the initial feed ratio, M_1/M_2 , and f is the ratio of monomers incorporated into the copolymer, m_2/m_1 . Both forms of the equation were plotted and the form yielding the best straight

line was used to evaluate r_1 and r_2 . The calculation was checked and refined by the curve fitting technique¹⁰⁹ (Method 2) with a computer program (see Appendix I) using the Mayo and Lewis equation¹¹⁰ to calculate the average composition of the copolymers at the precise percent conversion obtained experimentally. After a

$$\frac{m_1}{m_2} = \frac{r_1 \left(\frac{M_1}{M_2}\right)^2 + \left(\frac{M_1}{M_2}\right)}{\left(\frac{M_1}{M_2}\right) + r_2} \quad (3)$$

satisfactory pair of reactivity ratios was obtained, the program (see Appendix II) was used to generate the instantaneous copolymer composition curve for copolymerization carried to five percent conversion. The copolymer composition curve for styrene (M_1) and S-vinyl-O-t-butylthiocarbonate (M_2) is shown in Figure 9; similar curves for methyl methacrylate and vinyl acetate copolymerizations with 16 are depicted in Figure 10. The reactivity ratios calculated by both Method 1 and Method 2 for each set of analytical data are summarized in Table 10. The values obtained from nmr measurements correlate well with those derived from the elemental analysis and provide addition information on the sequence distribution in the copolymers.

The data obtained from the copolymerization of 16 were used to calculate the Q and e copolymerization parameters employing equations 4 and 5.¹⁰⁶ As Table 11 indicates, a rather broad range

Figure 9:

Copolymer composition curve for the copolymerization of S-vinyl-O-t-butylthiocarbonate (M_2) with styrene (M_1): (■) Experimental; (○) instantaneous copolymer composition at 5% conversion calculated from reactivity ratios cited.

Figure 10:

Copolymer composition curve for the copolymerization of S-vinyl-O-t-butylthiocarbonate (M_2) with ($\blacktriangle$) methyl methacrylate (M_1) and ($\bullet$) vinyl acetate (M_1); ($\circ$) calculated compositions.

TABLE 10

Reactivity Ratios of S-Vinyl-O-t-butylthiocarbonate (M_2)
with Comonomers (M_1)

M_1	Method of calculation	r_1	r_2
Styrene	1	$1.95^{+0.1}$	$0.21^{+0.05}$
	1	$2.15^{+0.2^a}$	$0.15^{+0.05^a}$
	2	$2.50^{+0.1}$	$0.35^{+0.05}$
	2	$3.0^{+0.1^a}$	$0.20^{+0.05^a}$
Methyl methacrylate	1	$1.25^{+0.05}$	$0.25^{+0.05}$
	1	$1.20^{+0.1}$	$0.22^{+0.05}$
	2	$1.40^{+0.05}$	$0.17^{+0.05}$
	2	$1.28^{+0.05^b}$	$0.20^{+0.05^b}$
Vinyl acetate	1	$0.06^{+0.01}$	$11.0^{+1.0}$
	2	$0.04^{+0.01}$	$11.0^{+1.0}$
N-Vinylpyrrolidone	1	$0.12^{+0.02}$	$3.9^{+0.1}$
	2	$0.12^{+0.01}$	$3.94^{+0.05}$
N-Isopropylacrylamide	1	$1.11^{+0.05}$	$0.30^{+0.05}$
	2	$1.17^{+0.05}$	$0.30^{+0.05}$
N-Vinyl-O- <u>t</u> -butyl- carbamate	1	$0.13^{+0.05}$	$5.30^{+0.1}$
	2	$0.12^{+0.05}$	$5.10^{+0.1}$
<u>t</u> -Butyl methacrylate	1	$1.85^{+0.1}$	$0.19^{+0.05}$
	2	$1.70^{+0.05}$	$0.15^{+0.05}$

a. Spectrophotometric determination of styrene content at 260 m μ .

b. Estimated by quantitative nmr analysis of copolymers.

TABLE 11
Copolymerization Parameters of S-Vinyl-O-*t*-butylthiocarbonate
and Related Monomers

M ₁	Q ₁ ^a	e ₁ ^a	M ₂	r ₁	r ₂	Q ₂	e ₂	Ref.
Styrene	1.0	-0.80	$\text{CH}_2=\text{CH}-\text{S}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\text{C}(\text{CH}_3)_3$	3.0	0.2	0.59	-1.51	This work
Methyl methacrylate	0.74	0.40	"	1.4	0.17	0.33	-0.80	"
Vinyl acetate	0.026	-0.22	"	0.04	11.0	0.65	-1.13	"
Styrene	1.0	-0.80	$\text{CH}_2=\text{CH}-\text{S}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{N}(\text{C}_2\text{H}_5)_2$	4.4	0.14	0.40	-1.49	40
Styrene	1.0	-0.80	$\text{CH}_2=\text{CH}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{N}(\text{C}_2\text{H}_5)_2$	32	0.03	0.019	-1.10	40
Styrene	1.0	-0.80	$\text{CH}_2=\text{CH}-\text{S}-\overset{\text{S}}{\underset{\text{O}}{\text{C}}}-\text{N}(\text{C}_2\text{H}_5)_2$	4.05	0.143	0.45	-1.54	36
Styrene	1.0	-0.80	$\text{CH}_2=\text{CH}-\text{S}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_3$	4.0	0.25	0.25	-0.8	18
N-Vinylpyrrolidone	0.14	-1.14	$\text{CH}_2=\text{CH}-\text{S}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\text{C}(\text{CH}_3)_3$	0.12	3.94	0.53	0.027	This work
<i>t</i> -Butylmethacrylate	0.91	-0.44	"	1.70	0.15	0.52	-1.61	"

a. Data from Mayo and Lewis.¹¹⁰

values is obtained but this is not unusual because the errors inherent to the reactivity ratios are compounded in the calculation.

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{\frac{1}{2}} \quad (4)$$

$$Q_2 = Q_1 / r_1 \exp^{-e_1 (e_1 - e_2)} \quad (5)$$

The relative high values obtained for Q_2 confirm the stabilizing influence of a sulfur atom adjacent to double bond and a radical. This phenomena has been attributed to the ability of sulfur to expand its octet and participate in d- π orbital overlap with the double bond and has been confirmed spectrophotometrically.^{19,28} A similar rational can be applied to the stabilization of the growing radical.

The e parameter was originally conceived to account for electrostatic interactions by assuming that the product $e_1 e_2$ represents the attraction or repulsion of static charges. Subsequent efforts to establish this correlation quantitatively have failed but the qualitative concept of the e value has been retained. Thus, the negative values of e_2 observed for 16 indicate that the adjacent sulfur atom enhances the electron

density of the double bond. However, large fluxuations in the e values do not significantly influence the copolymerization ratios observed because the Q factor essentially determines the relative polymerizability of the monomer. The last two entries in Table 11 illustrate this point, both values are negative yet there is a marked difference in the copolymerizability of the corresponding monomers.

The predominate stabilizing influence is the adjacent sulfur atom. Although there is a very significant difference between the Q_2 values of S-vinyl- and O-vinyl-N,N-diethylcarbamates, very little change is noted upon either replacing the carbonyl function with a thiocarbonyl (S-vinyl-N,N-diethyldithiocarbonate) or varying the carbonyl substituent from alkyl to O-alkyl. This indicates that the polymerizability of all S-vinyl-carbonyl derivatives will be similar regardless of the nature of the other substituents on the rest of the molecule. Thus selection of an S-vinyl monomer as a precursor to a poly(vinyl mercaptan) should be based upon the relative ease of removing the blocking group from polymer. In this respect, S-vinyl-O-t-butylthiocarbonate has a distinct advantage because the t-butyloxycarbonyl blocking group can be removed by either acid hydrolysis or mild thermolysis.

Water-Soluble Copolymers¹¹¹ Since most physiological application of polymercaptans required a water soluble polymeric substrate, the copolymerization of S-vinyl-O-t-butylthiocarbonate

Figure 11:

Copolymer composition curve for the copolymerization of S-vinyl-O-t-butylthiocarbonate with ($\blacksquare$) N-isopropylacrylamide (M_1) and ($\blacktriangle$) N-vinylpyrrolidone (M_1); (O) calculated compositions.

copolymers with structure 74 containing $\geq 60\%$ of N-vinyl pyrrolidone were water soluble but the corresponding polymercaptans, 75 were insoluble in aqueous media. Dissolution of 75 in methanol, chloroform, dimethylformamide, dimethyl sulfoxide and 5% aqueous sodium hydroxide occurred rapidly at room temperature indicating that disulfide crosslinks were not responsible for the poor aqueous solubility properties. The sulfhydryl groups appear to be more hydrophobic than their t-butyloxycarbonyl precursor and force the copolymer out of solution, indeed a 95 mole % N-vinyl pyrrolidone content was required to achieve solubility in neutral aqueous media.

N-isopropylacrylamide has also been utilized to enhance the water solubility of copolymers. Conceivably the secondary structure of the isopropylamide substituent is more hydrophilic than the tertiary amide structure found in N-vinylpyrrolidone and water soluble copolymers with $\geq 5\%$ vinyl mercaptan compositions could be prepared. The acrylamide structure is resistant to the hydrolytic action of both strong acids and bases so the properties of the vinyl mercaptan copolymers could be studied over the entire pH range. Copolymerization of N-isopropylacrylamide (M_1) with S-vinyl-O-t-butylthiocarbonate (M_2) proceeded smoothly (Figure 11) and the N-isopropylacrylamide proved to be more reactive than 16 ($r_1 = 1.17$; $r_2 = 0.3$). Water soluble copolymers were obtained but removal of the t-butyloxycarbonyl blocking group by either acid hydrolysis or thermolysis yield insoluble vinyl mercaptan

copolymers. In addition, the isopropylamide moiety seemed to increase the reactivity of the mercaptan group because the polymers darkened very rapidly and became insoluble in dimethylsulfoxide. Thus, N-vinyl pyrrolidone remains the best comonomer for producing a water-soluble polymercaptan substrate.

Polyfunctional Vinylmercaptan Copolymers.¹¹¹ The possibility of preparing amino-mercaptan copolymers for model enzyme substrates evaluation was also explored. N-Vinyl-O-t-butylcarbamate (M_1) was prepared from vinyl isocyanate and t-butanol and copolymerized with the analogous S-vinyl compound (M_2). The copolymerization results were erratic but copolymers could be obtained for all feed ratios (Figure 12). It was difficult to obtain copolymers containing high percentages of the N-vinyl monomer due to the large difference in the reactivity ratios, i.e. $r_1 = 0.13$; $r_2 = 5.10$. The copolymers probably contain long blocks of poly(S-vinyl-O-t-butylthiocarbonate) coupled by isolated N-vinyl-O-t-butyl carbamate linkages rather than a random distribution of comonomers.

The removal of the t-butoxycarbonyl blocking group is complicated by the reactivity of the amino substituent. Thermolytic cleavage lead to a crosslinked resin due to the formation of urea linkages.¹¹² The isolation of the N-vinyl moieties mitigates against cyclic urea formation and leads to insoluble resins at a relatively low extent of blocking group removal. Acid hydrolysis

Figure 12:

Copolymer composition curve for the copolymerization of S-vinyl-O-t-butylthiocarbonate (M_2) with (●) t-butyl methacrylate (M_1) and (▲) N-vinyl-O-t-butylcarbamate (M_1); (○) calculated compositions.

yield the amine hydrobromide salt which could be converted to the free poly (vinylamine - vinyl mercaptan) copolymer by treatment with an ion-exchange resin but the recovery of copolymer from the resin was extremely difficult.

Poly(t-butyl methacrylate-S-vinyl-O-t-butylthiocarbonate) copolymers were prepared as potential precursors to a poly (methacrylic acid-vinyl mercaptan) substrate. The copolymerization results confirm the superior reactivity of acrylic or methacrylic monomers over the S-vinyl-O-t-butylthiocarbonate (M_2) ($r_1 = 1.70$, $r_2 = 0.15$) but copolymers could be obtained over the entire range of feed ratios (Figure 12).

E. Chemical Modification of Polymeric Substrate with Bender's Salts

In section A of this chapter we described a thermally labile Bender's salt which was utilized for preparation of monomers containing "blocked" mercaptan groups. Although the monomer synthesis has many advantages,⁷⁸ the major disadvantage is the inherent chain-transfer or inhibitor properties of sulfur containing functional groups, i.e. S-vinyl-O-t-butylthiocarbonate (16) exhibits a $C_M = 3.9 \times 10^{-3}$. The polymers and copolymers of 16 were

relatively low molecular weight materials, but the versatility of the carbo-t-butoxy blocking group in polymercaptan synthesis was demonstrated.⁴¹ In this section, we describe a method for introducing t-butylthiocarbonate groups into polymers containing chloromethyl functional groups such as: chloromethylated polystyrene, poly(epichlorohydrin) (Herclor-H), copoly(epichlorohydrin-ethylene oxide) (Herclor-C), and poly(vinyl chloride). Displacement of the chloride leaving group with potassium O-t-butylthiocarbonate (61) yields a polymeric mercaptan precursor which can be converted to polymercaptan by thermolysis.

Bender's Salts as Nucleophiles. Bender's salts as described previously can be prepared by treating potassium alcoholates with carbonyl sulfide and DMF. Addition of 1-2% water to DMF produces a good solvent mixture for the displacement reactions; all of the polymer substrates used in this work dissolve in DMF, and the displacement reaction occurs initially in a homogeneous media. However, the mixture soon becomes heterogeneous as both potassium chloride and substituted polymer precipitate from solution. In

most cases, the substitution was nearly quantitative based upon residual chlorine content (Table 12); and strong carbonyl absorptions at $1685\text{--}1710\text{ cm}^{-1}$, *t*-butyl absorptions at $1205\text{--}1250\text{ cm}^{-1}$ and C-S stretching at 675 cm^{-1} (Figure 13 and 14) are consistent with the introduction of *t*-butylthiocarbonate groups. However, sulfur analysis revealed that the substitution is accompanied by side reactions which further increase the sulfur content of the products when the reactive sites are attached to a flexible backbone such as poly(oxyethylene). The polymer derivatives are no longer soluble, but swell rapidly in benzene, THF, and cyclohexanone indicating that crosslinking has occurred during the displacement reaction. Careful exclusion of oxygen and light and using low concentrations of 61 failed to inhibit the crosslinking process. The reaction conditions are too mild to effect thermal deblocking of the carbo-*t*-butoxy blocking group so crosslink probably occurs via a series of nucleophilic reactions. The crosslinking mechanism postulated in Scheme XIII is consistent with the experimental observation that di-*t*-butylcarbonate and *t*-butanol are by-products of the reaction. The dithiocarbonate structure (80) has a higher sulfur composition than the S-alkyl-O-*t*-butylthiocarbonate substituents which would account for the high sulfur content of the substituted polymers. However precise elucidation of the crosslink structure will require further investigation.

TABLE 12

SUBSTITUTION EFFICIENCY

Substrate		Product			
Structure	Initial Cl Content, %	Cl Content, %	Extent of Subst.	S Content, % Found	Calcd.
21.46	1.17	92	11.65	12.17
$\sim\text{CH}_2-\underset{\text{Cl}}{\text{CH}}\sim$	56.69	13.93	54.6	18.96	20.0
$\sim\text{CH}_2-\underset{\text{CH}_2\text{Cl}}{\text{CH}}-\text{O}\sim$	38.24	2.02	95	23.65	16.84
$\sim\text{CH}_2-\underset{\text{CH}_2\text{Cl}}{\text{CH}}-\text{O}\sim$	25.18	7.23	67.6	14.20	13.42
Copolymer with styrene oxide

Figure 13:

Infrared spectra of S-vinylbenzyl-O-t-butylthiocarbonate derivatives.

A, ir of 73; B, ir of 76; C, ir of 70.

Figure 14:

Infrared spectra of PVC derivative (79) compared with poly(S-vinyl-O-t-butylthiocarbonate) (71) and (67). A, ir of 79; B, ir of 71; c, ir of 67.

Scheme XIII

It is possible to reduce the extent of crosslink formation by using lower mole ratios of Bender's salts to reactive functional groups in the substitution reactions. Since quantitative conversion is impossible under these conditions the resultant copolymers still contain active functional groups which will react with sulfhydryl substituents as soon as they are liberated. Thus polymercaptans derived from flexible substrates will be crosslinked inevitably and high free mercaptan contents can not be attained with this technique.

Thermal Analysis of Polymercaptan Precursors. The extent of O-t-butylthiocarbonate substitution and thermolysis efficiency

could be determined quantitatively by thermal gravimetric analysis as shown in Table 13. Differential thermal analysis (DTA) reveals that the deblocking process begins around 200° for all of the polymeric derivatives (Figure 15, 16, and 17). This is consistent with the isothermal TGA kinetic analysis of the thermolysis of poly(S-vinyl-O-t-butylthiocarbonate (71) in the range from 170-250° (Table 16 and Figure 8).

Mass spectral analysis of the gas mixture evolved for all the polymeric derivatives showed that it was composed of CO₂ and isobutylene only. The deblocking reaction is essentially quantitative for polymer substrates containing only O-t-butylthiocarbonate substituents. This fact coupled with the low chlorine content of polymers (76), (77), (79), gives some insight into the nature of the crosslinking reaction. Chloromethylated polystyrene, although slightly crosslinked, has undergone the expected substitution reaction since the chloromethyl groups are practically isolated from each other. However, the more flexible polymers with neighboring chloride leaving groups appear to have incorporated cyclic functional groups. Thus, polymers 77, 78, and 79 exhibit a smaller break than expected at 202° and continue to degrade slowly from 250-475° (Figure 15 and 16). The cyclic structures are more stable to thermolysis and do not appear to degrade to polymercaptans.

TABLE 15

THERMOLYSIS EFFICIENCY

Substrate	Decomp. t °C	Weight loss, %	Calcd. wt ^a loss, %	Calcd. SH ^b content, %
Poly(S-vinyl-O-t-butylthiocarbonate)	215	62.60	62.5	100
Poly(S-vinyl-O-t-amylthiocarbonate)	222	64.60	65.51	98.6
Poly(vinylbenzylthiocarbonate)	222	35.5	40.0	89
Chloromethylated polystyrene	223	35.23	38.02	92.5
Poly(vinyl chloride)	202	19.5	47.17	41.3
Herchlor-H	214	20.0	51.3	39.0
Herchlor-C	220	4.07	32.69	12.4

a. Based upon the residual chlorine content.

b. Based upon the actual weight loss.

Figure 15:

TGA and DTA of Herclor-H and derivative 77. A, TGA of Herclor-H. B, TGA of 77. C, DTA of 77.

Figure 16:

Thermogravimetric analysis of polythiocarbonates: A, TGA of polyvinyl chloride (PVC); B, TGA of thiocarbonate derivative prepared from PVC; C, TGA of poly(S-vinyl-O-t-butylthiocarbonate) (71); D, DTA of 71.

Figure 17a:

TGA of polystyrene (A), compared with derivative 76 (B) and poly(S-vinylbenzyl-O-t-butylthiocarbonate) (73) (C).

Figure 17b:

DTA (A) and TGA (B) of thiocarbonate derivative (76) prepared from chloromethylated polystyrene.

EXPERIMENTAL

All boiling points and melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, or by Mr. Ralph Seab, Louisiana State University-Baton Rouge. Infrared spectra were obtained on a Perkin-Elmer 137 spectrometer. Nmr spectra of CDCl_3 , CCl_4 , $\text{Cl}_2\text{C}=\text{CCl}_2$ or D_2O solutions were recorded on a Varian Associates HA-60 or HA-100 spectrometer; all chemical shifts are given relative to internal tetramethylsilane (TMS) reference (minus indicates downfield) or DHO ($\delta = 4.61$) in D_2O . Laser Raman spectra were recorded on a JEOL Spectrophotometer equipped with an Argon laser using an excitation wavelength of 4880 Å or 5145 Å. Thermal analyses were conducted with a DuPont 900 differential thermal analyser (DTA) equipped with a 950 thermal gravimetric analyser (TGA) attachment. Mass spectra were obtained on a Varian Associate M 66 instrument by Cheryl White and a Hitachi Perkin-Elmer Model RMS-4 Mass Spectrometer with ionization energy of 70 eV by Paula B. Watts. The intrinsic viscosities of the polymers were measured in THF (concentration = 0.25g/25ml THF) at 30° using Cannon-Ubbelohde viscometer. Intrinsic viscosities were determined by extrapolation of specific viscosities (η_{sp}) to infinite dilution. The molecular

weight distributions were obtained on a Waters Associates Model 200 Gel-Permeation Chromatograph (GPC) equipped with automatic injection and collection unit. A 0.125% solution (10 ml) in THF of each of the polymer samples was prepared. A computer program (see Appendix I and II) was used to calculate the weight average molecular weight ($\bar{M}_w$), number average molecular weight ($\bar{M}_n$), and the molecular weight distribution ($MWD = \bar{M}_w/\bar{M}_n$). Number-average molecular weights were determined in toluene at 30° by using SS-08 membranes in a Hewlett-Packard 501 High Speed Membrane Osmometer.

A. Reagents and Materials

Ethylene sulfide may be purchased or synthesized from cyclic ethylene carbonate and potassium thiocyanate according to the procedure of Searles and Lutz.⁷⁹ Phosgene was purchased from Matheson and was used without further purification. *t*-Butyl alcohol and *t*-amyl alcohol were distilled from CaH_2 and stored over Lindas 4-A molecular sieves. Tetrahydrofuran (THF) was passed through a column of basic alumina to remove peroxides, dried by distillation from CaH_2 and stored over molecular sieves. Azobisisobutyronitrile (AIBN) was recrystallized from methanol (mp 102-103° decomp.). Dimethylformamide (DMF) was distilled under reduced pressure. Commercially available carbonyl sulfide was used without further purification. A solution (1-3 molar) of sodium 2-methyl-2-butoxide can be prepared by refluxing a solution of *t*-amyl alcohol in benzene,

toluene, xylene or THF with excess sodium wire or ribbon under nitrogen until evolution of hydrogen ceases. Vinylbenzyl chloride (a 60:40 mixture of meta and para isomer) was obtained from Dow Chemical Company.

B. Preparation of Monomers and Model Compounds

1. S-(β -Chloroethyl)chlorothioformate - The procedure of Ringsdorf and Overberger³⁴ was modified. A 1 l four-necked round bottom flask was fitted with a thermometer, a mechanical stirrer, a sintered glass gas inlet tube and a Dewar condenser cooled with dry ice acetone. The exit gases were vented through a CaCl₂ drying tube, an empty trap to eliminate the possibility of caustic solution sucking back into the reaction vessel, over a solution of 10% NaOH stirred in 1000 ml filter flask, through a solution of 10% NaOH and finally washed down the drain in a good hood. The flask was charged with 272 g (2.7 mol) of phosgene and catalytic amounts of pyridine (0.5 to 1.0 ml), cooled to -10° and stirring was initiated. Ethylene sulfide 150 g (2.5 mol), was added dropwise while the temperature was maintained between -10° and -5° for 4 hrs. The solution was warmed carefully to room temperature and allowed to react for an additional 10 hrs. The excess phosgene was blown out of the reaction mixture with a nitrogen purge and the residue was vacuum distilled to yield 251.5 g (64%) of S-(β -chloroethyl)chlorothioformate (28), bp 60-62° (2 mm); lit.³⁴ bp 67.5°

(5mm), and 16.3 g (3%) of S,S'-bis(β -chloroethyl)dithiocarbonate, bp 124-126° (2 mm). Spectroscopic data for 28 are as follows: Nmr (CDCl_3)¹¹³₈TMS 3.52 (A₂B₂ m, 4, S-CH₂-CH₂-Cl); ir (neat)¹¹⁵ $\nu_{\text{cm}^{-1}}$ 1760_s (C=O), 1430_s (-CH₂-O), 1400_m, 1390_m, 1290_m, 1270_s, (CH₂-Cl wag), 1220_s (-S-CH₂ wag), 1130_w, 1020_w, 932_w, 818-870_{sb} (C-Cl) 750_w and 704_s (C-C-Cl), 675_w, (C-S); laser Raman spectrum¹¹⁴ (Ar 4880 Å) $\Delta\nu_{\text{cm}^{-1}}$ 2945_s and 2925_s (C-H), 1756_w (C=O), 1437.5_w, 1294_m (C-C r.k.), 1194_w and 1137.5_w (C-O), 1031_w (C-O-C), 931_w, 837_w (C-C val.), 732_s (C-O wag.), 643.5 (C-S), 575 _{vs} (C-Cl), 425_s, 318.5_w, 277_w, 225_s.

Anal. Calcd for C₃H₄OSCl₂: C, 22.64; H, 2.51; S, 20.12; Cl, 44.65.

Found: C, 22.83; H, 2.70; S, 20.18; Cl, 44.58.

The product 28 may be stored in a brown, glass stoppered flask in a freezer for at least one year without significant loss of reactivity. Both products and reactants are extremely toxic. In addition, S-(β -chloroethyl)chlorothioformate is an incidious lachrymator and skin irritant. Therefore it is advisable to wear a tightly buttoned lab coat and two pairs of sturdy rubber gloves (neoprene type) and an oxygen mask should be available at all time during the preparation of these compounds. Since it is impossible to quantitatively remove the excess phosgene by sparging, the vacuum pump should be protected with KOH traps and vented into a good hood. The crude product should be isolated by flash distillation of the residue to minimize decomposition catalysed by high boiling by-products.

Subsequent fractional distillation through a 12-inch Vigreux column is sufficient to separate 28 from the major by-product, S,S'-bis(β -chloroethyl)dithiocarbonate.³⁴ Removal of this by-product is essential because it will yield S,S'-divinylthiocarbonate upon treatment with potassium t-butoxide. The divinyl monomer is difficult to separate from S-vinyl-O-t-butylthiocarbonate and acts as a crosslinking agent in the polymerization step.

2. Di-t-butylcarbonate(25) - A solution of potassium t-butoxide was prepared by refluxing 500 ml anhydrous t-butanol over 39.1 g (1 g-atom) of potassium metal at 70°, cooling the mixture to room temperature, and adding 200 ml anhydrous THF. After cooling the solution to -30°, it was slowly added to 44.5 g (0.5 mol) phosgene (phosgene was condensed and weighed in a round bottom flask at -78°). The reaction was extremely exothermic, so care must be taken during the addition. A white precipitate formed immediately after addition of phosgene. The mixture was allowed to warm to room temperature and stirred for 12 hours and finally heated to 65° for 30 min to drive off residual phosgene. The solution was poured into 5 liters of ice water mixture and the crystalline material which separated was isolated, washed three times with ice-water and distilled in vacuo (bp 157.5°). Three recrystallizations of the distillate from 95% ethanol gave flaky, white crystals of 25 which were further purified by sublimation. The yield of sublimed crystals was 36 g (41.4%), mp 40°, lit.⁸⁰

TABLE 14

NMR Data of S-Alkyl-O-t-alkylthiocarbonate and Di-t-alkylcarbonate Compounds[‡]

Compound	Structure		Nmr, δ TMS
	R	R'	
67	$\text{CH}_3\text{CH}_2\text{S}-$ b c	$-\text{CH}_3$ a	2.81 (q, 2, c); 1.48 (s, 9, a); 1.29 (t, 3, b).
70	$\text{Ph}-\text{CH}_2-\text{S}-$ b c	$-\text{CH}_3$ a	7.29 (s, 5, b); 4.05 (s, 2, c); 1.47 (s, 9, a).
17	$\text{Cl}(\text{CH}_2)-\text{S}-$ b	$-\text{CH}_3$ a	3.38 (A_2B_2m , 4, b); 1.50 (s, 9, a).
55	$(\text{CH}_3)_3\text{C}-\text{O}-$ a	$-\text{CH}_3$ a	1.45 (s, 18, a).
57	$\text{Cl}(\text{CH}_2)_2-\text{S}-$ b	$-\text{CH}_2\text{CH}_3$ c d	3.38 (A_2B_2m , 4, b); 1.81 (q, 2, $J_{bc}=7.5$ Hz, c); 1.47 (s, 6, a); 0.91 (t, 3, $J_{cb}=7.5$ Hz, d).
58	$\text{CH}_3\text{CH}_2(\text{CH}_3)_2\text{C}-\text{O}-$ c b a	$-\text{CH}_2\text{CH}_3$ b c	1.72 (q, 2, $J_{bc}=7.5$ Hz, b); 1.43 (s, 6, a); 0.90 (t, 3, $J_{bc}=7.5$ Hz, c).

[‡] s, d, t, q, and m represent singlet, doublet, triplet, quartet, and multiplet respectively.

mp 39.5-40.5°. The nmr, ir, and laser Raman spectra are reported in Tables 14, 2, and 3, respectively.

Anal. Calcd for $C_9H_{18}O_3$: C, 62.07; H, 10.33.

Found: C, 61.89; H, 10.33.

3. Potassium O-*t*-Butylthiocarbonate (61) - A 1.5 M solution of potassium *t*-butoxide was prepared by dissolving 29.8 g (0.762 g-atom) of potassium in 500 ml of anhydrous *t*-butanol. The solution was diluted with 300 ml DMF and 100 ml THF, cooled to -5°, and 60 g (1 mol) of carbonyl sulfide was bubbled slowly into the vigorously stirred mixture. A white precipitate began to form immediately. The slurry was allowed to warm to room temperature, stirred for 2 hr and then poured into 1 l of ether. The precipitate was isolated and dried under vacuum at 30° for 48 hr. A total of 110 g (84%) of 61, dec. temp. 235° (wt. loss 44%) was obtained. Nmr (D_2O) δ_{DHO} (4.61 δ) 1.38 [s, 9, $-C(CH_3)_3$]; ir and laser Raman spectra (see Tables 2 and 3).

Anal. Calcd for $C_5H_8O_2SK$: C, 34.8; H, 5.2; S, 18.6.

Found: C, 32.8; H, 5.04; S, 18.91.

4. Potassium O-(2-Methyl-2-butyl)thiocarbonate (62) was synthesized in a similar manner by bubbling carbonyl sulfide into a DMF/THF solution of potassium 2-methyl-2-butanoxide at -5°. A yield of 80-85% of 62 with dec. temp. 225° (wt. loss 54.8%) was obtained. Nmr (D_2O) δ_{DHO} 0.92 (t, 3, $J_{ab} = 7.5$ Hz, $\underline{CH_3^a-CH_2^b-}$), 1.39 (s, 6, $\underline{CH_3-C-CH_3}$), 1.80 (q, 2, $J_{ba} = 7.5$ Hz, $CH_3^a-\underline{CH_2^b-}$); laser Raman spectrum (fluorescence) $\Delta\nu_{cm^{-1}}$ 2937.5-2987 $\underline{5}$ (C-H),

1583_w (C=O), 1450_s (CH₃ asym. def.), 831.5_m (C-C val.), 727.5_s (C-O wag.), 542.5_s [$\overset{\text{O}}{\underset{\text{S}}{\text{C}}}=\text{O}$, out of plane skeletal def. or C-S]; ir (KBr disk), see Table 2.

Anal. Calcd for C₈H₁₁O₂SK: C, 38.7; H, 5.9; S, 17.17.

Found: C, 35.73; H, 5.42; S, 16.50.

5. Potassium O-(2-Phenyl-2-propyl)thiocarbonate (63) was synthesized by bubbling carbonyl sulfide into a DMF/THF solution of potassium 2-phenyl-2-propanoxide at -5°; 80% of 63 with dec. temp. 195° (wt. loss 55.8%) was obtained. Nmr (D₂O) δ_{DHO} 1.68 (s, 6, $\text{CH}_3-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{CH}_3$), 7.38 (s, 5, C₆H₅-C-); ir (KBr disk), see Table 2.

Anal. Calcd for C₁₀H₁₁O₂SK: C, 52.1; H, 5.21; S, 13.65.

Found: C, 44.34; H, 4.33; S, 13.46.

6. S-Ethyl-O-t-butylthiocarbonate (67) was prepared by stirring 16.3 g (0.15 mol) of ethyl bromide with 14.31 g (0.083 mol) of 61 in 100 ml of anhydrous THF for 6 hr. at 45°. After removing the KBr by centrifugation, the solvent was evaporated under reduced pressure. Fractional distillation of the residue afforded 10.8 g (80%) of 67 bp 39-40° (4 mm); nmr (CDCl₃), see Table 14; ir (neat), see Table 2; laser Raman spectrum (Ar 4880 Å laser), see Table 3.

Anal. Calcd for C₇H₁₄O₂S: C, 51.8; H, 8.65; S, 19.76.

Found: C, 52.08; H, 8.41; S, 18.98.

7. S-Benzyl-O-t-butylthiocarbonate (70) - To a 1.76 g (0.01 mol) of potassium O-t-butylthiocarbonate in 20 ml of anhydrous THF was added 1.52 g (0.012 mol) of benzyl chloride. The mixture

was stirred at 45° for 24 hr., and KCl removed by centrifugation. The solvent was evaporated under reduced pressure; fractional distillation of the residue afforded 1.5 g (65.5%)* of S-benzyl-O-t-butylthiocarbonate (70), bp 105° (0.5 mm); nmr (CDCl₃), see Table 14; ir (neat), see Table 2; laser Raman spectrum (Ar 4880 Å laser), see Table 3.

Anal. Calcd for C₁₂H₁₈O₂S: C, 64.3; H, 7.15; S, 14.5.

Found: C, 64.51; H, 7.23; S, 14.57.

8. S-(β-Chloroethyl)-O-t-amylthiocarbonate (57) - A mixture of 93 g (0.5 mol) of potassium O-t-amylthiocarbonate in 400 ml of THF and 200 ml of t-butanol was cooled to -10°, and 86 g (0.6 mol) of 1,2-bromochloroethane diluted with 40 ml of THF was added rapidly. The mixture was stirred while the temperature was maintained between -10° to -5° for 6 hrs, allowed to warm to room temperature and stirred for 24 hrs. The KBr precipitate was removed by centrifugation and the solvent mixture was evaporated under reduced pressure. Fractional distillation of the residue yield 97.6 g (93%) of 57, bp 105° (10 mm); nmr (CDCl₃) δ_{TMS} 0.89 (t, 3, -CH₂-CH₃), 1.42 (s, 6, CH₃-C-CH₃), 1.79 (q, 2, -CH₂-CH₃), 3.39 (A₂B₂m, 4, -S-CH₂-CH₂-Cl); IR and laser Raman spectrum are reported in Tables 2 and 3 respectively.

* By using DMF instead of THF as solvent, the yield of 70 increased to 98%.

Anal. Calcd for $C_8H_{15}O_2SCl$: C, 45.69; H, 7.13; S, 15.20;
O, 15.20; Cl, 16.85.

Found: C, 45.68; H, 7.41; S, 15.10; O, 14.98; Cl,
16.72.

9. S-(β -Chloroethyl)-O-(2-phenyl-2-propyl)thiocarbonate (64)
was prepared by reacting 117.1 g (0.5 mol) of potassium O-(2-phenyl-2-propyl)thiocarbonate with 93.3 g (0.65 mol) of 1,2-bromochloroethane in 600 ml THF and 100 ml benzene. The mixture was stirred at -5° for 6 hrs, then allowed to warm to room temperature and stirred for 24 hrs. The KBr precipitate was removed by filtration and the solvent was evaporated under reduced pressure. Analysis of the residue showed that 87.5% (~113.1 g) of 64 was obtained, nmr ($CDCl_3$) δ_{TMS} 1.72 (s, 6, $\text{CH}_3-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3$), 3.2 (A_2B_2m , 4, $-\text{CH}_2-\text{CH}_2-$), 7.1 (s, 5, phenyl group). Further purification of the residue was not attempted.

10. S-(β -Chloroethyl)-O-t-butylthiocarbonate (17) - To a mixture of 172.1 g (1 mol) of potassium O-t-butylthiocarbonate (61) in 500 ml THF and 200 ml of t-butanol was cooled to -10° , and 175 g (1.22 mol) of 1,2-bromochloroethane diluted with 50 ml of THF was added rapidly. The mixture was stirred at -5° for 6 hrs, allowed to warm to room temperature and stirred for 24 hrs. After work up, fractional distillation of the residue yielded 184 g (94%) of 17, bp 49° (0.5 mm). The nmr, ir, and laser Raman spectrum are reported in Tables 14, 2, and 3, respectively.

11. Concurrent Esterification - Dehydrohalogenation of S-(β -Chloroethyl)chlorothioformate.

(a) With Potassium *t*-Butoxide - The procedure of Overberger and Daly⁴¹ was modified to improve the yield. A potassium *t*-butoxide solution in 1:1 *t*-butanol-THF was prepared by dissolving 39.1 g (1.0 g-atom) of potassium metal in 550 ml of *t*-butanol at 70° (reflux), cooling the mixture to 20°, and adding 550 ml of anhydrous THF. A 2-liter 4-necked flask was equipped with a mechanical stirrer, a nitrogen inlet, a thermometer, and a pressure equalizing dropping funnel capped with a drying tube. The flask was charged with one mole of potassium *t*-butoxide dissolved in *t*-butanol-THF. The alcoholate solution was cooled to -30° and a solution of 53 g (0.333 mol) S-(β -chloroethyl)chlorothioformate (28) in 200 ml of THF is added dropwise over a two hour interval. After stirring the mixture for an additional two hours at -30°, the mixture was allowed to warm to room temperature, neutralized with glacial acetic acid and worked up immediately. Following removal of the potassium chloride by centrifugation, the solvent was evaporated under reduced pressure from the clear supernatant solution. Fractional distillation of the oily residue through a spinning band column afforded 32 g (60%) of S-vinyl-O-*t*-butylthiocarbonate (16) bp 60-61° (15 mm) lit⁴¹ bp 60.5-61° (15 mm). Nmr, ir, and laser Raman spectrum are reported in Tables 15, 2, and 3, respectively.

Anal. Calcd for C₇H₁₂O₂S: C, 52.47; H, 7.55; S, 20.00.

Found: C, 52.11; H, 7.49; S, 19.73.

One of the by-products from this reaction is S-(β -chloroethyl)-O-t-butylthiocarbonate (17) 3.3g (5%), bp 120° (9mm), lit.³⁴ bp 48-49° (0.5mm). For nmr, ir, and laser Raman spectrum see Tables 14, 2, and 3, respectively. The monomer usually contains a small amount of di-t-butylcarbonate (55), which is detectable in the nmr as a singlet at 1.42 δ . The purity of 16 can be estimated by comparing the relative intensities of the vinyl proton absorption and the absorptions in the methyl region. The monomer assayed routinely between 93-95% pure.

(b) With Sodium 2-Methyl-2-butoxide - The procedure of Overberger and Daly⁴¹ for the synthesis S-vinyl-O-t-butylthiocarbonate (16) was employed using sodium 2-methyl-2-butoxide as the base and varying the reaction conditions (specific condition and yields are given in Table 1). Purification by fractional distillation through a spinning band column afforded the following components:

(i) S-Vinyl-O-t-amylthiocarbonate (56), bp 82-84° (13 mm); n_D^{20} 1.4671; d_4^{25} 0.97451; mass spectrum m/e rel intensity) 174 (0.44) M^+ , 144 (5.33) (M-29)⁺, 131 (5.24) (M-43)⁺, 117 (10.66) (M-57)⁺, 87 (60.44) (M-87)⁺, 71 (100) (M-113)⁺, 59 (7.11), 55 (12.22), 43 (51.55); nmr (100 MHz), see Table 15; ir (neat), see Table 2; laser Raman spectrum (Ar 4880 Å laser), see Table 3.

Anal. Calcd for C₈H₁₄O₂S: C, 55.17; H, 8.06; S, 18.33.

Found: C, 55.28; H, 8.11; S, 18.25.

TABLE 15
NMR Spectra of Vinyl Monomers, *

Compound	Structure R	H _a (δ)	J _{ab} (Hz)	J _{ac} (Hz)	J _{bc} Hz	H _b (δ)	H _c (δ)	Other Protons (δ)
56	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}-\text{C}-\text{O}-\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3 \\ \text{d} \quad \text{e} \quad \text{f} \end{array}$	6.69 (q, 1)	17.5	10.0	-	5.38 (d, 1)	5.37 (d, 1)	1.82 (q, 2, J _{ef} = 7.5Hz, e); 1.48 (s, 6, d); 0.91 (t, 3, J _{fe} = 7.5Hz, f).
16	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}-\text{C}-\text{O}-\text{C}(\text{CH}_3)_3 \\ \text{d} \end{array}$	6.72 (q, 1)	17.6	10.0	-	5.39 (d, 1)	5.38 (d, 1)	1.50 (s, 9, d).
69	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5-\text{CH}_2-\text{S}-\text{C}-\text{O}-\text{C}(\text{CH}_3)_3 \\ \text{d} \quad \text{e} \quad \text{f} \end{array}$	6.69 (q, 1)	17.4	10.6	1.5	5.70 (dd, 1)	5.20 (dd, 1)	7.28 (m, 4, d); 4.03 (s, 2, e); 1.46 (s, 9, f).
15	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}-\text{C}-\text{S}-\text{CH}=\text{CH}_2 \end{array}$	6.87 (q, 1)	17.3	9.7	-	5.60 (d, 1)	5.49 (d, 1)	-----

* Samples run in CDCl₃; TMS as internal standard; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

(ii) S-(β -Chloroethyl)-O-t-amylthiocarbonate (57), bp 89-90° (2.8 mm); n_D^{20} 1.4735; d_4^{25} 1.1161; mass spectrum m/e (rel intensity) 183 (0.53), 181 (2.0), 125 (5.07), 123 (16.4), 71 (100); nmr (100 MHz), ir (neat), and laser Raman spectrum (Ar 4880 Å laser) were consistent with those reported previously.

Anal. Calcd for $C_8H_{15}O_2SCl$: C, 45.61; H, 7.13; S, 15.21; Cl, 16.85

Found: C, 45.69; H, 7.21; S, 15.21; Cl, 16.72.

(iii) Di-t-amylcarbonate (58), bp 89-90.2° (15mm); n_D^{20} 1.41434; d_4^{25} 0.90133; mass spectrum m/e (rel intensity) 71 (100) ($M-131$)⁺, 55 (21.25) ($M-147$)⁺, 43 (63.75), 41 (23.75), 41 (23.75), 29 (28.75); nmr (100 MHz), see Table 14; ir (neat), see Table 2; laser Raman (Ar 4880 Å), see Table 3.

Anal. Calcd for $C_{11}H_{22}O_3$: C, 65.4; H, 10.88.

Found: C, 64.82; H, 10.72.

Small amounts of S,S'-divinyldithiocarbonate (15) and S,S'-(β -chloroethyl)dithiocarbonate (14) were also obtained (see Table 1).

12. Dehydrochlorination of S-(β -Chloroethyl)-O-t-butylthiocarbonate (28).

Method A.- A lithium diisopropylamide solution was prepared by adding 32 ml (0.3 mol) of n-BuLi in hexane to 20.2 g (0.2 mol) of diisopropylamine in 100 ml THF at -30°. The mixture was stirred at -30° for 2 hrs while 34 g (0.17 mol) of 28 in 100 ml THF was added dropwise. No potassium chloride precipitate formed so 10 g

sodium hydride, 125 ml dimethylsulfoxide and 125 ml *t*-BuOH were added to the reaction mixture. After one hour at room temperature the precipitate was removed by centrifugation and the solvent evaporated under reduced pressure. Fractional distillation of the residue afforded 3 g (11%) of S-vinyl-O-*t*-butylthiocarbonate.

Method B. - A 2.2 M solution of potassium *t*-butoxide was prepared by dissolving 46.92 g (1.2 g-atom) of potassium metal in 650 ml of anhydrous *t*-butanol at 70°, cooling the mixture to 20°, and adding 400 ml anhydrous THF. The solution was cooled to -30°, and a solution of 178 g (0.906 mol) 28 in 100 ml of THF was added dropwise. The mixture was stirred at -30° for 3 hrs after addition was completed, allowed to warm to room temperature for 1 hr and then neutralized with glacial acetic acid. The potassium chloride was removed by centrifugation and the solvent evaporated in vacuo. Distillation of the residue through a 30 cm spinning band column yielded S-vinyl-O-*t*-butylthiocarbonate (16), 90 g (62%), bp 60-61° (15 mm). Elemental analysis and spectroscopic data by nmr, ir, and laser Raman were consistent with those previously reported.

13. S,S'-Ethylene Bis(O-*t*-butylthiocarbonate) (65) To a solution of 5.5 g (0.03 mol) of 61 in 150 ml DMF was added 1.5 g (0.015 mol) 1,2-dichloroethane dissolved in 50 ml DMF. The mixture was stirred at 55-58° for 12 hrs. The KCl precipitate was removed by centrifugation and the filtrate was poured into 600 ml of ice water to yield 4 g (90.8%) of 65 as a white precipitate, mp_{DTA} =

87°, 227° (dec. temp.); nmr (CDCl₃), δ_{TMS} 1.49 (s, 18, t-Bu), 3.03 (s, 4, -CH₂-CH₂-); mass spectrum m/e (rel intensity) 294 (0.25) M⁺, 238 (1.72) (M-56)⁺, 224 (0.19) (M-70)⁺, 209 (0.1) (M-85)⁺, 194 (3.49) (M-100)⁺, 182 (1.35) (M-112)⁺, 160 (2.70) (M-134)⁺, 150 (5.76) (M-144)⁺, 138 (10.30) (M-156)⁺, 121 (16.24) (M-173)⁺, 116 (19.00) (M-178)⁺, 105 (3.00), 94 (10.67), 92 (7.54), 73 (1.53), 72 (2.42), 57 (100), 41 (35.25); ir (KBr disk), see Table 2; laser Raman, see Table 3.

Anal. Calcd for C₁₂H₂₂O₄S₂: C, 48.94; H, 7.49; S, 21.78.

Found: C, 48.27; H, 7.47; S, 23.50.

14. S-(β -Mercaptoethyl)-O-t-butylthiocarbonate (66) A 100 ml three-necked round bottom flask was fitted with a thermometer, a dropping funnel, a Vigreux column with a fractional distillation head and a receiver. The exit gases were passed through two dry-ice-acetone traps. The flask was charged half-full with glass beads and heated on a sand bath to 300-325° under 70-80 mm, while 2.37 g (0.08 mol) of 65 in 15 ml tetrachloroethylene was added dropwise. 65 decomposed and 1 g (71%) of 66 gradually distilled into the receiver, bp 203° (760 mm); mass spectrum m/e (rel intensity) 193 (0.0001), 138 (0.007), 121 (0.013), 94 (0.16), 61 (0.12), 57 (100), 41 (43.64); ir (neat), see Table 2; laser Raman spectrum (Ar 4880 Å laser), see Table 3.

Anal. Calcd for C₇H₁₄O₂S₂: C, 43.3; H, 7.22; S, 33.0

Found: C, 43.10; H, 7.15; S, 33.57.

15. S-Vinylbenzyl-O-t-butylthiocarbonate (69) was prepared by stirring 15.3 g (0.1 mol) of vinylbenzyl chloride with 18.6 g (0.108 mol) of potassium O-t-butylthiocarbonate (61) in 200 ml of DMF for 12 hr at 30°. Conversion was essentially quantitative as indicated by nmr of the residue following centrifugation. The DMF solution was poured into 300 ml of water, and extracted three times with 300 ml hexane. The solvent was evaporated under reduced pressure after drying for 5 hrs over 5 g MgSO₄. The yield of monomer (69) was 20.80 g (83.2%), bp 182° (DTA), nmr (CDCl₃), see Table 15 ; ir (neat), see Table 2; laser Raman spectrum (Ar 4880 Å laser), see Table 3.

Anal. Calcd for C₁₄H₁₈SO₂: C, 67.2; H, 7.2; S, 12.8, O, 12.8.

Found: C, 67.26; H, 7.20; S, 13.00; O, 12.71.

C. Homopolymerization

1. Bulk Polymerization of S-Vinyl-O-t-amylthiocarbonate

A dried polymerization tube was charged with 1 g (5.65 mmol) of 56 and 25 mg of azobisisobutyronitrile (AIBN, 2.62 mol%). The mixture was frozen in a dry-ice acetone mixture, the tube is evacuated to 0.1 mm Hg, closed to the vacuum and allowed to warm to room temperature. After repeating this vacuum freeze-thaw degassing process three times, the mixture was frozen and the tube was sealed under vacuum. The sealed tube was immersed in a constant temperature bath at 60° for 12 hrs. The polymerization tube was cooled in an ice bath, opened and the extremely viscous polymer solution was

poured into 10 ml THF. The tube was washed with three 5 ml aliquots of THF, the washings were added to the polymer solution and the polymer was precipitated by adding this solution slowly to 200 ml of vigorously stirred methanol. The polymer was collected on a medium porosity sintered glass filter funnel, redissolved in 15 ml of THF, and reprecipitated into methanol twice. After isolating and drying the precipitate at 40° in vacuo for 48 hours, 0.48 g (48% conversion) of white amorphous polymer, 72, was obtained. Nmr (CDCl_3) δ_{TMS} 0.92 (t, 3, $J_{\text{ba}} = 7.5$ Hz, $-\text{CH}_2^{\text{b}}-\text{CH}_3^{\text{a}}$), 1.46 (s, 6, $\text{CH}_3-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{CH}_3$), 1.82 (q, 2, $J_{\text{ba}} = 7.5$ Hz, $-\text{CH}_2^{\text{b}}-\text{CH}_3^{\text{a}}$), 1.97 [broad s, 2, backbone $\text{-(CH}_2-\overset{\text{I}}{\underset{\text{I}}{\text{CH}}}\text{)}_x$], 3.55 [broad s, 1, backbone $\text{-(CH}_2-\overset{\text{I}}{\underset{\text{I}}{\text{CH}}}\text{)}_x$]; ir (film) $\nu_{\text{cm}^{-1}}$ 2995-2990 $\underline{\text{s}}$ (C-H), 1725-1695 $\underline{\text{s}}$ (C=O), 1455 $\underline{\text{m}}$ and 1440 $\underline{\text{m}}$ (CH_3 asym. def.), 1380 $\underline{\text{m}}$ and 1368 $\underline{\text{m}}$ ($\underline{\text{t}}$ -amyl def.), 1190 $\underline{\text{s}}$ ($\underline{\text{t}}$ -amyl def.), 1140-1110 $\underline{\text{bs}}$ ($\underline{\text{t}}$ -amyl-O-sym st.), 1060 $\underline{\text{m}}$, 1010 $\underline{\text{w}}$, 925 $\underline{\text{m}}$, 855 $\underline{\text{m}}$, (CH_3 r.k.), 830 $\underline{\text{s}}$ (C-C val.), 674 $\underline{\text{w}}$ (C-S); DTA $t_1 = 222^\circ$ to 230° , $t_2 = 334.5^\circ$; TGA % weight loss = 64.60 (theoretically 65.51%); $\bar{M}_{\text{GPC}} = \sim 30,000$.

2. Bulk Polymerization of S-Vinylbenzyl-O- $\underline{\text{t}}$ -butylthio-carbonate - A dried polymerization ampoule was charged with 2.0245 g (8.1×10^{-3} mol) of monomer (69) and 5.05 mg (3.08×10^{-5} mol) of AIBN. The ampoule was degassed in vacuum by three alternate freeze-thaw cycles and then sealed in vacuo. The tube was immersed in a 70° oil bath for 40 min. The polymers were purified by precipitation from benzene into methanol, then freeze dried to yield

0.377 g (18.61 % conversion) of poly[S-vinylbenzyl-O-t-butylthiocarbonate] (73), dec. temp. 222° (wt. loss 35.5%), 75.2% of the polymer was soluble in benzene, THF, and DMF with $[\eta] = 0.49$ dl/g in benzene at 30° ; 24.8% was insoluble-swollen polymer. Ir(KBr disk) $\nu_{\text{cm}^{-1}}$ 1710-1685 $\underline{\text{g}}$ (C=O), 1250-1205 $\underline{\text{m}}$ (t-Bu), 675 $\underline{\text{w}}$ (C-S).

Anal. Calcd for $-(\text{C}_{14}\text{H}_{18}\text{SO}_2)_x-$: C, 67.2; H, 7.2; S, 12.8;
O, 12.8.

Found: C, 67.27; H, 7.10; S, 12.85; O, 12.75.

3. Dilatometric Studies of the Homopolymerization of S-Vinyl-O-t-butylthiocarbonate (16)- Monomer (16) and AIBN catalyst were weighed into a calibrated dilatometer (calibrated by mercury at 24° , $V = 2.97618$ ml), and polymerization was initiated by immersing the dilatometer in a constant temperature oil bath ($T = 70 \pm 0.05^{\circ}$). After following the polymerization for the desired interval, the polymer was isolated by pouring the mixture into methanol, dissolving the polymer in THF, and reprecipitating in methanol. The conversion was calculated from the weight of polymer remaining after drying for 48 hrs at 40° in vacuo. The rate of polymerization was calculated from the initial volume by using the following equation:

$$R_p = \frac{\Delta V}{\Delta T} \left(\frac{1}{VK} \right)$$

where the total contraction K was estimated from gravimetric conversion data to be 14.41. The results are summarized in Table 6.

Dilatometric studies on the influence of di-t-butylcarbonate on the polymerization of S-vinyl-O-t-butylthiocarbonate were conducted by weighing freshly distilled 16 and di-t-butylcarbonate into a calibrated dilatometer with 0.045 mol% of AIBN as initiator. The polymers were precipitated in methanol from 10% THF solution. After reprecipitation twice in methanol from THF and benzene, respectively, the polymers were dried at 40° for 48 hrs in vacuo. The results are summarized in Table 8 and Figure 5.

4. Free Radical Polymerization of Styrene in the Presence of Additives - Styrene was purified by extracting three times with 10% aqueous NaOH to remove the inhibitor, washed three times with distilled water, dried over anhydrous CaCl₂ and distilled in vacuo [bp 31.5° (15mm)] immediately prior to the polymerization experiment; only center cuts were used.

A stock solution was prepared by adding 0.030 g AIBN to 50 ml of styrene. The additive [di-t-butylcarbonate, S-ethyl-O-t-butylthiocarbonate, or poly(S-vinyl-O-t-butylthiocarbonate)], 1.166 mol%, was weighed into a 15 ml volumetric flask, 10 ml of the styrene-AIBN stock solution was added and the mixture was diluted to 15 ml with pure styrene. The polymerization was followed in a calibrated dilatometer at 70°. The polymer was dissolved in 25 ml benzene and precipitated by addition to methanol; reprecipitated twice from THF into methanol and dried at 40° in vacuo for 48 hr. The results were summarized in Table 9.

D. Kinetic Studies of the Pyrolysis of Poly(S-Vinyl-O-*t*-butylthiocarbonate)

Thermal Removal of *t*-Butyloxocarbonyl Blocking Group - All solvents used in this experiment were deionized by passing them through an analytical grade chelating resin¹¹⁵ which had been dried at 80° and 15 mm for 3 days. Poly(S-vinyl-O-*t*-butylthiocarbonate), 0.10 g (0.625 meq), is dissolved in 5 ml of N-methylpyrrolidone. This solution was introduced into a vapor jacketed reaction vessel and stirred by bubbling nitrogen through it. The exit gases were passed through a dry ice-acetone gas trap, a Schwarz tube filled with Drierite, a Nesbitt absorption bulb containing Ascarite CO₂ absorbent, a sulfuric acid bubbler and a potassium hydroxide trap. The polymer solution was heated to 165° in a bath of refluxing N,N-dimethylacetamide for 2 hrs. The weight of CO₂ absorbed indicated that 86.7% of the theoretical CO₂ evolution has occurred within 2 hrs. The polymer solution was allowed to cool, then transferred quantitatively to a 10 ml volumetric flask and diluted to the mark with N-methylpyrrolidone. After thorough purging with nitrogen, this polymer solution can be stored in a dry, oxygen free atmosphere for several days.

The polymer can be isolated for characterization by precipitating into 10:1 methanol-pentane in a dry box or glove bag. The infrared spectrum in KBr contained a strong peak at 2650 cm⁻¹ (SH) and a weak peak 1720 cm⁻¹ (C=O), which is consistent for poly(vinyl mercaptan).

Determination of Mercaptan Groups - 2 ml of the stock solution of poly(vinyl mercaptan) (~ 0.125 meq) in N-methylpyrrolidone was added to 20 ml of a solution of 6.0g mercuric chloride in 300 ml of dimethylsulfoxide. This mixture was stirred for at least 30 min and then 150 ml of an aqueous 0.5 M solution of sodium chloride was added. The mixture was titrated potentiometrically with 0.1N potassium hydroxide. The mercaptan content should be 0.104 meq (83%). This was in close agreement with 86.7% determined by CO_2 evolution.

Isothermal Decomposition of Poly(S-vinyl-O-t-butylthiocarbonate) - An isothermal time base TGA was obtained at a nominal scanning rate of 1 inch/min by setting temperature rate at $5^\circ/\text{min}$ and X-axis scale at 0.4 mv./inch. The results were shown in Figure 8, and Table 16.

Table 16

Isothermal Decomposition of Poly(S-vinyl-O-t-butylthiocarbonate)			
T, $^\circ\text{K}$	$k = \frac{dw}{dt} \times 10^3$ *	$\ln k$	Total weight loss, %**
444	1.04166	-6.86693	-
456	2.51215	-5.98661	61.65
468	6.68369	-5.00808	62.48
475	11.379	-4.47598	68.00
480	17.71428	-4.03338	62.14
485	22.39583	-3.79888	60.38
490	42.29885	-3.16299	62.50
492	33.51648	-3.39571	62.50
498	48.96755	-3.01659	62.02
504	62.45954	-2.77323	62.55
512	86.53846	-2.44716	62.31
517	143.18181	-1.94364	62.37

* k = slope = wt loss (g)/time (sec), estimated at 31.25% weight loss.

** Average value 62.60% total weight loss.

E. Copolymerization of S-Vinyl-O-*t*-butylthiocarbonate (M_2)

1. With Styrene (M_1) - Styrene was purified as described previously. Styrene and S-vinyl-O-*t*-butylthiocarbonate were weighed into 10 ml drying ampoules containing 41 mg (3.94×10^{-4} mol) AIBN. The total molar composition of the monomer mixture was maintained at 0.05 mole, but the feed ratio was varied. The ampoules were degassed in vacuum by three alternate freeze-thaw cycles and then sealed in vacuo. The tubes were immersed in a 70° oil bath until a noticeable increase in viscosity indicated the formation of copolymer. The copolymers were diluted with 10 ml of benzene and precipitated in methanol or petroleum ether, depending on expected polymer composition. The copolymers were reprecipitated twice from THF into methanol. The precipitates were dried in a vacuum oven at 40° for 48 hrs and weighed to determine the extent of conversion. The composition of the copolymers was calculated from their elemental analysis (Table 17). The styrene content was determined spectrophotometrically in CHCl_3 at 260 m μ with a Cary-14 spectrophotometer

The reactivity ratios were estimated by the method of intercepts¹¹⁰ (Figure 18) or the Fineman-Ross method¹⁰⁸ (Figure 19), and refined by a curve fitting technique¹⁰⁹. The copolymer composition curve was shown in Figure 9. A computer program written by Montgomery and Fry¹⁰⁷ was used to generate the integral copolymer composition for the curve-fitting approach. Values of $r_1 = 3.0$ and $r_2 = 0.20$ were obtained.

TABLE 17

Copolymerization of S-Vinyl-O-t-butylthiocarbonate (M_2) with Styrene (M_1)

$M_1 \leftarrow \text{Feed} \rightarrow M_2$				Mole fraction in feed, M_1	Polymerization time ^a (min)	% Conv. ^b	%S	Mole fraction in copolymer	
g	(m. mole)	g	(m. mole)					m_1 ^c	m_1 ^d
0.572	(5.5)	7.21	(45)	0.109	90	6.46	15.54	0.224	0.315
1.022	(9.82)	6.406	(40.0)	0.197	60	2.59	11.33	0.434	0.513
1.606	(15.42)	5.601	(35.0)	0.306	120	9.03			0.587
2.118	(20.35)	4.802	(30.01)	0.404	60	3.38	7.07	0.646	0.726
2.542	(24.43)	4.00	(25.0)	0.494	55	6.84	5.09	0.746	0.746
3.572	(34.3)	2.403	(15.0)	0.696	65	9.85			0.797
4.168	(40.04)	1.601	(10.01)	0.800	30	4.33	2.54	0.873	0.898
4.716	(45.3)	0.8	(5.0)	0.901	75	14.7			0.929
4.683	(45.0)	0.8	(5.0)	0.900	30	5.1			0.866
5.006	(48.09)	0.401	(2.54)	0.951	30	6.93	0.54	0.973	0.894

a. Polymerization temperature, 70°; initiator, 41.0 mg (0.5 mole %) azobisisobutyronitrile.

b. Precipitant, methanol; reprecipitated from THF into methanol.

c. Calculated from elemental analysis.

d. Spectrophotometric determination of styrene content at 260 mμ.

Figure 18:

Method of intersection plot for styrene (M_1) - S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

Figure 19:

Fineman-Ross plot for styrene (M_1) - S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

2. With Methyl Methacrylate (M_1). Methyl methacrylate (MMA) was extracted twice with 5% NaOH, washed with distilled water, dried over anhydrous $MgSO_4$ and distilled from CaH_2 under nitrogen, bp $33-35^\circ$ (60 mm).

The monomers and 5.0 mg (0.05 mol%) AIBN were weighed into polymerization ampoules. The ampoules were degassed, sealed under vacuum and heated at 70° for 18-19 min. The polymers were diluted with 19 ml of benzene and precipitated by addition to either methanol or pentane. The polymers were filtered and reprecipitated in this manner two more times to insure their purity, dried under vacuum at 40° for 48 hrs and weighed. The compositions of the methyl methacrylate copolymers were determined by nmr analysis of 5 wt-% $CDCl_3$ copolymer solutions. Sulfur contents from elemental analysis were also used to calculate the copolymer composition. The results are summarized in Table 18.

The copolymer composition curve is shown in Figure 10, method of intercepts plot in Figure 20, and Fineman-Ross plot in Figure 21. The reactivity ratios were found to be: $r_1 = 1.40$; $r_2 = 0.17$.

3. With Vinyl Acetate (M_1). Vinyl acetate was extracted with 5% NaOH, washed with water, dried over $MgSO_4$ and distilled at atmosphere pressure from CaH_2 under nitrogen, bp $72.2-72.3^\circ$ (760 mm). The monomers and either 0.5 mol% or 0.05 mol% AIBN were weighed into polymerization tubes. The tubes were degassed, sealed under vacuum and heated at 70° for the time indicated. The

TABLE 18

Copolymerization of S-Vinyl-O-t-butylthiocarbonate (M_2) with Methylmethacrylate, (M_1)

$M_1 \leftarrow \text{Feed} \rightarrow M_2$				Mole fraction in feed, M_1	Polymerization time ^a (min.)	% Conv. ^b	%S	Mole fraction in copolymer	
g	(m mole)	g	(m mole)					m_2^c	m_1^d
0.388	(3.88)	4.006	(25.00)	0.135	19	2.98	13.98	.302	0.311
1.087	(10.87)	4.003	(24.98)	0.303	19	5.40	10.20	.491	0.469
2.430	(24.30)	4.004	(24.99)	0.493	19	5.30	7.43	.628	0.607
4.661	(46.61)	3.384	(21.12)	0.688	19	4.28	4.40	.780	0.744
4.669	(46.69)	1.974	(12.36)	0.791	18	4.78	3.03	.848	0.823
4.696	(46.96)	0.880	(5.49)	0.895	18	5.69	1.48	.926	0.928

a. Polymerization temp., 70°, initiator, 5.0 mg (0.05 mole %) azobisisobutyronitrile.

b. Precipitant, methanol; reprecipitated from THF into methanol.

c. Calculated from elemental analysis.

d. Estimated by quantitative nmr measurement at $\delta = 3.65$ ($-\text{OCH}_3$).

Figure 20:

Method of intersection plot for methyl methacrylate (M_1) - S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

Figure 21:

Fineman-Ross plot for methyl methacrylate (M_1) - S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

copolymers were very gummy and difficult to purify, they were precipitated in methanol, then freeze-dried. The results are shown in Table 19, Figure 10 and Figure 22. The reactivity ratios were found to be: $r_1 = 0.04$, $r_2 = 11.0$.

4. With N-Vinylpyrrolidone (M_1)^{1,11} Freshly distilled N-vinylpyrrolidone and S-vinyl-O-t-butyl thiolcarbonate were weighed directly into polymerization tubes, and 0.5% by weight of azo-bis-isobutyronitrile was added as a free radical source. The tubes were degassed, sealed under vacuum and heated in an oil bath at 65° for twenty minutes. The contents of the tubes were diluted with 10 ml. of benzene and precipitated in either methanol, pentane or ether, depending on expected polymer composition. The polymers were reprecipitated and then lyophilized from benzene. Table 20 shows the results.

TABLE 20

Copolymerization of S-Vinyl-O-t-butylthiocarbonate(M_2)
with N-Vinylpyrrolidone(M_1)

Mole fraction in feed, M_1	Polymerization time ^a , min	% Conv.	% N in Polymer	Mole fraction in Polymer, m_1
0.3	20	10.6 ^b	1.38	0.10
0.5	20	13.0 ^c	2.52	0.18
0.7	20	14.0 ^c	4.44	0.32
0.9	20	16.0 ^d	7.80	0.57

a. Polymerization temperature, 65°; initiator, 0.5 wt% AIBN.

b. Precipitant, methanol.

c. Precipitant, pentane.

d. Precipitant, ether.

TABLE 19

Copolymerization of S-Vinyl-O-t-butylthiocarbonate (M_2) with Vinyl Acetate (M_1)

$M_1 \leftarrow \text{Feed} \rightarrow M_2$				Mole fraction in feed M_1	Polymerization time (min)	% Conv. ^c	%S	Mole fraction in polymer, m_1 ^d
g	(m mole)	g	(m mole)					
0.441	(5.12)	7.208	(44.98)	0.102	30 ^a	13.96	20.10	0.0
0.888	(10.3)	6.407	(39.98)	0.205	12	4.95	19.74	0.013
1.292	(15.0)	5.601	(34.95)	0.300	22	8.55	20.56	0.0
2.150	(24.97)	4.005	(24.99)	0.50	21	6.31	20.61	0.0
3.049	(35.42)	2.405	(15.01)	0.702	31	12.66	18.95	0.052
3.853	(44.76)	0.801	(5.00)	0.900	32	14.03	12.98	0.35
4.62	(53.67)	2.165	(13.51)	0.799	125 ^b	15.90	15.13	0.244
5.013	(58.23)	2.282	(14.24)	0.804	50	1.37	14.79	0.261
4.62	(53.67)	1.53	(9.548)	0.849	148	15.5	14.69	0.266
4.62	(53.67)	1.53	(9.548)	0.849	123	13.10	14.00	0.300
5.003	(58.13)	1.612	(10.06)	0.853	50	3.40	13.82	0.309
4.62	(53.67)	0.455	(2.84)	0.95	148	19.20	6.90	0.654
4.62	(53.67)	0.455	(2.84)	0.95	105	6.35	8.50	0.575

a. Polymerization temperature, 70°; initiator, 41 mg (0.5 mole %) AIBN.

b. Initiator concentration decreased to 5.0 mg (0.05 mole %) on the remaining runs.

c. Precipitant, petroleum ether at -20°C, reprecipitated from THF and lyophilized from benzene.

d. Calculated from elemental analysis.

Figure 22:

Fineman-Ross plot for vinyl acetate (M_1) - S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

Based on the differential form of the copolymer equation, the method of intercepts was used to calculate the reactivity rates. Values of $r_1 = 0.119$ and $r_2 = 3.94$ were obtained. The copolymer composition curve is shown in Fig. 11, the reactivity ratio plot in Figure 23, and the Fineman Ross Plot in Figure 24.

5. With N-Isopropylacrylamide (M_1).¹¹¹ N-Isopropylacrylamide was recrystallized twice from hexane to a constant melting point, m.p. 64.5-65° (lit.¹¹⁸ m.p. 62°). The monomers and 0.5 wt. % azobisisobutyronitrile were weighed into polymerization tubes. After adding 10 ml. of benzene to dissolve the monomer mixture, the tubes were degassed, sealed under vacuum and heated at 70° for the times specified. The polymers were precipitated at least twice by addition to pentane and lyophilized from benzene. The results are shown in Table 21, Figure 11 and Figure 25 and 26. The reactivity ratios were found to be: r_1 , 1.17; r_2 , 0.30.

TABLE 21

Copolymerization of S-Vinyl-O-t-butylthiocarbonate(M_2)
with N-Isopropylacrylamide(M_1)

Mole fraction in feed, M_1	Polymerization time ^a , min	% Conv. ^b	% N in Polymer	Mole fraction in polymer, m_1
0.1	180	1.8	3.05	0.246
0.5	65	17.5	7.71	0.625
0.7	40	13.5	9.53	0.770
0.9	60	12.5	10.83	0.877

a. Polymerization temperature, 70°; initiator, 0.5 wt% AIBN; solvent, benzene; $[M]$, 5 mol/l.

b. Precipitant, pentane; lyophilized from benzene.

Figure 23:

Method of intersection plot for N-vinylpyrrolidone (M_1) -
S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

Figure 24:

Fineman-Ross plots for N-vinylpyrrolidone (M_1) S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations and N-vinyl-O-t-butylcarbamate (M_1) - S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

Figure 25:

Method of intersection plot for N-isopropylacrylamide (M_1) -
S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

Figure 26:

Fineman-Ross plot for N-isopropylacrylamide (M_1) - S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

6. With N-Vinyl-O-*t*-butylcarbamate (M_1)¹¹¹ N-vinyl-O-*t*-butylcarbamate was prepared from vinylisocyanate and *t*-butanol in 81.5% yield according to the procedure of Schulz and Hartmann.¹¹⁷ Two recrystallizations from hexane produced analytically pure material, m.p. 66.5-67° (lit.¹¹⁸ m.p. 66°).

The monomers and 0.5 wt. % azobisisobutyronitrile were weighed into polymerization tubes and dissolved in 25 ml. of anhydrous benzene. The tubes were degassed, sealed under vacuum and heated at 65° for the times indicated. The polymers were precipitated by addition to either methanol or pentane, reprecipitated and lyophilized from benzene. The results are summarized in Table 22 and Figures 12, 24 and 27. The reactivity ratios were found to be: $r_1 = 0.125$; $r_2 = 5.10$.

TABLE 22

Copolymerization of S-Vinyl-O-*t*-butylthiocarbonate (M_2)
with N-Vinyl-O-*t*-butylcarbamate (M_1)

Mole fraction in feed, M_1	Polymerization time ^a , min	% Conv.	% N in Polymer	Mole fraction in polymer, m_1
0.2	240	8.95 ^b	0.54	0.055
0.4	240	1.3 ^b	0.97	0.099
0.5	240	3.5 ^b	1.54	0.185
0.7	360	1.6 ^c	2.84	0.288
0.9	420	1.9 ^c	5.65	0.575

a. Polymerization temperature, 70°; initiator, 0.5 wt% AIBN; solvent, benzene; $[M]$, 2 mol/l.

b. Precipitant, methanol.

c. Precipitant, pentane.

Figure 27:

Method of intersection plot for N-vinyl-O-t-butylcarbamate (M_1) -
S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

7. With t-Butyl methacrylate(M_1).¹¹¹ t-Butyl methacrylate was washed with 5% aqueous NaOH, water, dried over anhydrous $MgSO_4$ and distilled under vacuum. The copolymerizations were carried out in sealed ampoules and the copolymers were purified by precipitation from benzene into methanol. The results are summarized in Table 23 and Figure 10, 28 and 29. Values of $r_1 = 1.70$, $r_2 = 0.15$, were obtained.

TABLE 23

Copolymerization of S-Vinyl-O-t-butylthiocarbonate (M_2)
with t-Butyl methacrylate (M_1)

Mole fraction in feed, M_1	Feed ratio, M_1/M_2	Mole fraction in polymer, m_1	Copolymer composition ratio, m_1/m_2
0.117	0.132	0.365	0.575
0.329	0.490	0.571	1.332
0.535	1.15	0.735	2.78
0.726	2.65	0.832	4.96
0.908	9.87	0.962	25.37

F. Chemical Modification of Polymeric Substrates with Bender's Salts

Poly(S-vinylbenzyl-O-t-butylthiocarbonate) (76). Poly-styrene ($[\eta] = 0.764$ dl/g) was chloromethylated with chloromethyl methyl ether in the presence of zinc chloride,¹¹⁸ the product contained 21.42% Cl (89% monochloromethylation). Chloromethylated

Figure 28:

Method of intersection plot for t-butyl methacrylate (M_1) - S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

Figure 29:

Fineman-Ross plot for t-butyl methacrylate (M_1) - S-vinyl-O-t-butylthiocarbonate (M_2) copolymerizations.

polystyrene (4.4 g, 0.025 eq) and 5.77 g (0.0335 mol) of potassium O-t-butylthiocarbonate (61) were dissolved in 100 ml of DMF and stirred at 30° for 12 hr under nitrogen. The product was isolated by pouring the DMF into water, reswelling the precipitated 76 in benzene-methanol and washing the swollen polymer with methanol and water. After drying for 48 hrs in vacuo, 6.51 g of 76, dec. temp. 223° (wt loss 35.89%), DTA $T_1 = 88^\circ$, $T_2 = 242^\circ$, $T_3 = 345^\circ$, was obtained, ir (KBr disk) $\nu_{\text{cm}^{-1}}$ 1710-1685s (C=O), 1250m, 12-5s (t-Bu), 675 (C-S), (Figure 13).

Anal. Found: C, 68.81; H, 7.21; S, 11.65; Cl, 1.17.

Assuming a structure of: $-(\text{C}_{14}\text{H}_{18}\text{O}_2\text{S})_x-(\text{C}_9\text{H}_9\text{Cl})_y-(\text{C}_8\text{H}_8)_z-$, the analysis indicates a ratio of $x:y:z = 80:7:13$ and an extent of substitution of 92%.

Nucleophilic Substitution on Herclor-H and Herclor-C.

Poly(epichlorohydrin)(Herclor-H) and copoly(epichlorohydrin-ethylene oxide)(Herclor-C) were supplied by Hercules, Inc. Displacement of the chloride leaving group with potassium O-t-butylthiocarbonate (61) in DMF as described above yielded poly(epichlorohydrin) derivative (77) with dec. temp. 214-256° (wt loss 23%), DTA $T_1 = 224^\circ$; $T_2 = 334^\circ$, and copoly(epichlorohydrinethylene oxide) derivative (78), with dec. temp. 224° (wt loss 4.1%), DTA $T_1 = 233^\circ$, $T_2 = 334^\circ$, ir (KBr disk) $\nu_{\text{cm}^{-1}}$ 1700s (C=O), 1200m (t-Bu def.), 1140-1110bs (t-Bu-O sym. st.), 674w (C-S).

Anal. For 77, Found: C, 45.14; H, 6.57; S, 23.65; Cl, 2.02. Assuming a structure of: $-(C_8H_{14}O_3S)_x-(C_3H_5OCl)_y-$ the analysis of chlorine content indicates a ratio of $x:y = 95:5$ and an extent of substitution of 95%.

For 78, Found: C, 46.35; H, 6.94; S, 14.29; Cl, 7.23. Assuming a structure of: $-(C_8H_{14}O_3S)_x-(C_3H_5OCl)_y-(C_2H_4O)_z-$ the analysis of chlorine content indicates a ratio of $x:y:z = 32.2:15.4:52.4$ and an extent of substitution of 67.65%.

Nucleophilic Substitution on Poly(vinyl chloride). Poly-(vinyl chloride) (PVC) was dissolved in DMF, the solution was centrifuged to remove a small gel fraction and the PVC was precipitated from methanol. The purified PVC 3.126 g, was dissolved in 100 ml DMF, treated with 9.2 g of 61 and stirred at 35° for 12 hr under nitrogen in the dark. The reaction was terminated by slowly adding 1 l of water to the mixture, and stirring for 6 hr. The light yellowish polymer (79) was washed thoroughly with water and methanol. After drying for 48 hr in vacuo, 3.55 g of 79, Dec. temp. $202-239^\circ$ (wt loss 20%), DTA T = 224° was obtained. As shown in Figure 14, ir (KBr disk) absorption bands at ν_{cm}^{-1} 1700_s (C=O), 1370_m and 1390_m (t-Bu sym. def.), 1250_m (t-Bu-O sym. st.), 1205_s (t-Bu def.), 1140-1110_{bs} (t-Bu-O sym. st.), 674_w, (C-S) and laser Raman spectrum (Ar 4880 Å laser source) $\Delta\nu_{cm}^{-1}$ 3060_m, 2675_{ms}, 2275_m, 1750-1722_w, 1544_s, 1150_s, confirm substitution.

Anal. Found: C, 51.73; H, 5.87; S, 18.98; Cl, 13.93. Assuming a structure of: $-(C_7H_{12}O_2S)_x-(C_2H_3Cl)_y-$, the analysis

indicates a ratio of $x:y = 88:12$ and an extent of substitution of 54.6% based on the chlorine content.

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APPENDIX I

COMPUTER PROGRAM FOR CALCULATION OF RELATION OF REACTIVITY RATIOS FROM COMPOSITION-CONVERSION DATA*

For a given pair of monomers, this program accepts two points of composition vs. conversion data and, with the initial monomer compositions corresponding to the given data points and the monomer molecular weights, calculates the relative reactivity ratios (r_1 , r_2) which would result in said compositions at said conversions. A copy of the program (in Fortran IV) and an example of a typical output are attached.

Definitions for the input variables are listed in Table I with the number of spaces (card columns) allocated to each. It may be noted that the total spaces assigned is 72, which allows data for one run to be entered on one card. Each of the variables except N_0 and LIMN requires a decimal point and this is included in the spaces allocated to them. P and DEL may be either positive or negative (but not zero), depending upon the particular case; all others are positive.

*We are indebted to Dr. Charles V. Pittman for sending us this program translated into Fortran IV.

TABLE I
List of Input Variables

Variable	Spaces Allocated	Definition
NØ	3	Arbitrary run number, for identification
XMW1	6	Molecular weight of monomer 1
XMW2	6	Molecular weight of monomer 2
WM1A	4	Initial weight fraction, monomer 1, Case A
WM2A	4	Initial weight fraction, monomer 2, Case A
WM1B	4	Initial weight fraction, monomer 1, Case B
WM2B	4	Initial weight fraction, monomer 2, Case B
CØNVA	4	Fractional conversion, Case A
CØNVA	4	Fractional conversion, Case B
PW1A	4	Weight fraction monomer 1 in polymer, Case A
PW2A	4	Weight fraction monomer 2 in polymer, Case A
PW1B	4	Weight fraction monomer 1 in polymer, Case B
PW2B	4	Weight fraction monomer 2 in polymer, Case B
P	5	Integration variable
DEL	5	Increment applied to P
ULP	4	Upper limit on P
LIMN	3	Limit on N (N - number of cycles during convergence process)

The integrated form of the copolymer equation used [a slightly modified version of the one published by Mayo and Lewis, J. Amer. Chem. Soc., 66, 1594 (1944)] is as follows:

$$r_2 = \frac{\log \frac{M_2^0}{M_2} - \frac{1}{P} \log \frac{1-P \frac{M_1}{M_2} \left(\frac{MW_2}{MW_1} \right)}{1-P \frac{M_1^0}{M_2^0} \left(\frac{MW_2}{MW_1} \right)}}{\log \frac{M_1^0}{M_1} + \log \frac{1-P \frac{M_1}{M_2} \left(\frac{MW_2}{MW_1} \right)}{1-P \frac{M_1^0}{M_2^0} \left(\frac{MW_2}{MW_1} \right)}}, \quad P = \frac{1-r_1}{1-r_2}$$

where M_1^0 = weight fraction of monomer₁ present initially, M_1 = relative weight of monomer₁ remaining at the conversion that the polymer compositions is measured (i.e., $M_1 = M_1^0$ - weight fraction monomer₁ in polymer X fractional conversion), P is an integration variable, and r_1 and r_2 are the conventional relative reactivity ratios.

The program operates by calculating r_2 in terms of the arbitrary P for each of the data points, then incrementing P in such a manner that the two r_2 's converge to the unique value which is common to both points. This r_2 , with the corresponding P is then used to calculate r_1 . The program is currently set to cycle until the difference between r_{2A} and r_{2B} is < 0.00001 , although this can easily be changed to any desired level. ULP and LIMN are simply devices to cause the computer to go on to the next data set if convergence has not been achieved in a reasonable period.

Although arbitrary, the initial values chosen for P and DEL can strongly influence the amount of computational time required. Even very crude estimates of r_1 and r_2 can help in choosing the initial P . Since $P = (1-r_1)/(1-r_2)$, if $r_1, r_2 < 1$, $P > 0$ and large if r_1 is large and/or r_2 is small. Conversely, P decreased as r_1 increases toward 1 and/or r_2 decreases. On the other hand, if $r_1 < 1 < r_2$, or $r_2 < 1 < r_1$, then $P < 0$, with the absolute magnitude of P dependent upon the relative magnitude of r_1 and r_2 in the obvious manner.

The equation has certain obvious mathematical prohibitions, e.g., $r_1 = 1$, $r_2 = 1$, $P \frac{M_1}{M_2} \left(\frac{MW_2}{MW_1} \right) = 1$, $P \frac{M_1^0}{M_2^0} \left(\frac{MW_2}{MW_1} \right) = 1$, $P = 0$, M_1 or $M_2 < 0$, $P \frac{M_1}{M_2} \left(\frac{MW_2}{MW_1} \right) < 1 < P \frac{M_1^0}{M_2^0} \left(\frac{MW_2}{MW_1} \right)$, etc., all lead to indeterminacies, discontinuities, dividing by zero, or attempting to take $\log N$ where $N < 0$. Such situations could arise via errors in entering data or fortuitously during the convergence process. The program is written upon build-in checks so that if one of these mathematically prohibited conditions occurs, the computer will print out a coded error message and go on to the next data set, rather than dump the entire program. The key to the error code is given in Table II. The error message will be the last line printed for a given data set and will have the form

NO = XX ERROR = XXX

When the error number has more than one digit, the last digit indicates whether the program is associated with Case A (1) or Case B (2);

TABLE II
ERROR CODE

Number	
1XX	M_1 is negative, <u>i.e.</u> , initial monomer composition cannot yield composition given at conversion cited.
2XX	$M_1 = 0$, mathematics yields indeterminate form.
3	Molecular weight of monomer ₁ entered negative or zero.
4XX	Initial weight fraction entered negative or zero. (Corresponding conversion or polymer composition would also have to have been entered negative to avoid being kicked out as 1XX.)
5X	$P(M_1^0/M_2^0)(MW_2/MW_1) = 1$.
6	$P = 0$.
7X	Complex ratio zero or negative, <u>i.e.</u> , cannot take log.
8X	Denominator of fraction expressing $r_2 =$ zero.
9	P exceeds ULP.
10	N exceeds LIMN.
20	Not making any progress, <u>i.e.</u> , two successive cycles did not improve convergence.
30	Program error, got into wrong loop during cycle.

if three digits are used, the middle digit specifies which monomer is at fault. The error reported will be the first one encountered and does not guarantee that further errors may not be present.


```

100 *RELATIVE REACTIVITY RATIOS FROM COMPOSITION-CONVERSION DATA
110 IN = 5
120 IF = 6
130 I N=5
140 ISM = 0
150 READ(5,*)NO,XM1,XM2,M1A,M2A,CNVA,M1A,M2A,M1B,M2B,CNVB%
160 P=M1B,M2B,P,DEL,ULP,LIMN
170 100 FORMAT(13,2F6.2,10F4.3,F6.1,F5.2,F5.0,12)
180 WRITE(6,101)NO,XM1,M1A,M2A,CNVA,M1A,M2A
190 101 FORMAT(////1H1,62H RELATIVE REACTIVITY RATIOS FROM COMPOSITION-CONVE%
200 RSION DATA/4HONO=,13/6HONMI=,F6.2,7H M1A=,F5.3,7H M2A=,F5.3,8H C%
210 CNVA=,F5.3,7H P1A=,F5.3,7H P2A=,F5.3)
212 WRITE(6,105)XM2,M1B,M2B,CNVB,P1B,P2B,P,DEL,ULP,LIMN
220 105 FORMAT(6H XM2=,F6.2,7H M1B=,F5.3,7H M2B=,F5.3,8H CNVB=,F5.3,7%
230 7H P1B=,F5.3,7H P2B=,F5.3/34 P=,F6.1,11H DEL=,F6.2,8H ULP=,F5.0,7%
240 9H LIMN=,14//1H0,6X,3H12A,6X,3H12B,6X,1HP,6X,4HDIF=)
250 RM1A=M1A-PM1A-CNVA
260 RM2A=M2A-PM2A-CNVA
270 RM1B=M1B-PM1B-CNVB
280 RM2B=M2B-PM2B-CNVB
290 IF(MM1A)11,12,20
300 11 IERR=111
310 5 WRITE(6,102)NO,IERR
320 102 FORMAT(4HONO=13,9H ERROR=13)
330 GO TO 1
340 12 IERR=211
350 GO TO 5
360 20 IF(RM2A)21,22,30
370 21 IERR=121
380 GO TO 5
390 22 IERR=221
400 GO TO 5
410 30 IF(RM1B)31,32,40
420 31 IERR=112
430 GO TO 5
440 32 IERR=212
450 GO TO 5
460 40 IF(RM2B)41,42,50
470 41 IERR=122
480 GO TO 5
490 42 IERR=222
500 GO TO 5
510 50 RM1A=MM1A/RM1A
520 RM2A=MM2A/RM2A
530 RM1B=MM1B/RM1B
540 RM2B=MM2B/RM2B
550 IF(XM1)51,51,52
560 51 IERR=3
570 GO TO 5
580 52 RM21=XM2/XM1
590 R12A=(M1A/RM2A)*RM21
600 R12B=(M1B/RM2B)*RM21
610 R12A=(RM1A/RM2A)*RM21

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```

620 RM12B=(RM1B/RM2B)*RM21
630 IF (RM1A)53.53,54
640 53 IERR=411
650 GO TO 5
660 54 IF(RM2A)55,55,56
670 55 IERR=421
680 GO TO 5
690 56 IF(RM1B)57,57,58
700 57 IERR=412
710 GO TO 5
720 58 IF(RM2B)59,59,60
730 59 IERR=422
740 GO TO 5
750 60 ALOG1=ALOG(RM1A)
760 ALOG2=ALOG(RM2A)
770 BLOG1=ALOG(RM1B)
780 BLOG2=ALOG(RM2B)
790 81 IF(1.0-P*(RM12A))62,61,62
800 61 IERR=51
810 GO TO 5
820 62 IF(1.0-P*(RM12B))64,63,64
830 63 IERR=52
840 GO TO 5
850 64 IF(P)66,65,66
860 65 IERR=6
870 GO TO 5
880 66 RALB=(1.0-P*(RM12A))/(1.0-P*(RM12A))
890 HALB=(1.0-P*(RM12B))/(1.0-P*(RM12B))
900 IF (KALB)67,67,68
910 67 IERR=71
920 GO TO 5
930 68 IF(HALB)69,69,70
940 69 IERR=72
950 GO TO 5
960 70 ALOGH=ALOG(HALB)
970 BLOGH=ALOG(HALB)
980 IF(ALOG1+ALOGH)72,71,72
990 71 IERR=61
1000 GO TO 5
1010 72 IF(BLOG1+BLOGH)74,73,74
1020 73 IERR=62
1030 GO TO 5
1040 74 H2A=(ALOG2-ALOGH/P)/(ALOG1+ALOGH)
1050 H2B=(BLOG2-BLOGH/P)/(BLOG1+BLOGH)
1060 IF (N-1)75,75,85
1070 75 PD=P+DEL
1080 76 DIH=H2A-H2B
1090 HATE(6,103)H2A,H2B,P,DIFF
1100 103 FORMAT(3H,2F11.5,F10.5,F11.6)
1110 IF(ABS(DIFF)-0.00001)77,77,78
1120 78 N=N+1
1130 P=PD
1140 IF(ABS(P)-ULP)79,79,80
1150 80 IERR=9

```

```

1160 GO TO 5
1170 IF(N-LIMN)81,81,82
1180 82 IERR=10
1190 GO TO 5
1200 85 XDIFP=R2A-R2B
1210 COMP=DIFP-XDIFP
1220 ACOMP=ABS(DIFP)-ABS(XDIFP)
1230 IF(ABS(COMP)-ABS(ACOMP))83,83,84
1240 84 ISW=1
1250 DEL=DEL*(-0.5)
1260 GO TO 75
1270 83 IF(1SW)86,86,87
1280 87 DEL=DEL*0.5
1290 GO TO 75
1300 86 IF(ACOMP)88,88,90
1310 90 PD=P+DEL
1320 GO TO 76
1330 89 IERR=20
1340 GO TO 5
1350 88 DEL=-DEL
1360 PD=P+2.0*DEL
1370 IF(N-3)91,92,92
1380 92 IERR=30
1390 91 GO TO 76
1400 77 R1A=1.0-P*(1.0-R2A)
1410 WRITE(5,104)R0,R1A,R2A
1420 104 FORMAT(8HORIZ NO 13,5H R1=F9.5,5H R2=F9.5//)
1430 GO TO 1
1450 200 END

```

RELATIVE REACTIVITY RATIOS FROM COMPOSITION-CONVERSION DATA

NO= 1

XA1=1.00.00 WA1A=0.135 WA2A=0.865 CUNVA=0.030 PM1A=0.302 PM2A=0.698
 XA12=1.60.23 WA1B=0.303 WA2B=0.697 CUNVB=0.054 PM1B=0.491 PM2B=0.509
 P= -2.5 DEL= -0.10 ULP= 5. LIM= 40

R2A	R2B	P	DIFF
0.33/31	0.46080	-2.50000	-0.123431
0.32/83	0.44173	-2.30000	-0.113692
0.32296	0.43167	-2.20000	-0.106711
0.31802	0.42125	-2.10000	-0.103232
0.31300	0.41044	-2.00000	-0.097437
0.30791	0.39921	-1.90000	-0.091307
0.30274	0.38755	-1.80000	-0.084811
0.29750	0.37543	-1.70000	-0.077934
0.29217	0.36282	-1.60000	-0.070647
0.28677	0.34969	-1.50000	-0.062921
0.28128	0.33601	-1.40000	-0.054726
0.27570	0.32173	-1.30000	-0.046032
0.27004	0.30683	-1.20000	-0.036794
0.26429	0.29127	-1.09999	-0.026980
0.25845	0.27498	-0.99999	-0.016537
0.25251	0.25793	-0.89999	-0.005421
0.24646	0.24006	-0.79999	0.006421
0.24950	0.22411	-0.64999	0.000396
0.25101	0.25354	-0.67499	-0.002528
0.25027	0.25133	-0.66249	-0.001057
0.24986	0.25022	-0.65624	-0.000337
0.24969	0.24967	-0.65312	0.000026
0.24979	0.24994	-0.65466	-0.000152
0.24974	0.24980	-0.65390	-0.000063
0.24972	0.24973	-0.65351	-0.000010

RUN NO 1 A1= 1.64037 A2= 0.24972

RELATIVE REACTIVITY RATIOS FROM COMPOSITION-CONVERSION DATA

RD= 2

XM1=100.00 WM1A=0.303 WM2A=0.697 CONVA=0.054 PW1A=0.491 PW2A=0.509
 XM2=160.23 WM1B=0.493 WM2B=0.507 CONVB=0.053 PW1B=0.628 PW2B=0.372
 P= -2.5 DEL= -0.10 dLP= .5. LIMN= 40

H2A	R2B	P	DIFF
0.46030	0.65409	-2.50000	-0.194086
0.44173	0.63468	-2.30000	-0.193150
0.43167	0.62397	-2.20000	-0.192300
0.42125	0.61240	-2.10000	-0.191147
0.41044	0.60099	-2.00000	-0.189047
0.39921	0.58897	-1.90000	-0.187752
0.38755	0.57296	-1.80000	-0.185404
0.37543	0.55797	-1.70000	-0.182532
0.36262	0.54188	-1.60000	-0.179060
0.34969	0.52458	-1.50000	-0.174694
0.33601	0.50593	-1.40000	-0.169921
0.32173	0.48575	-1.30000	-0.164015
0.30663	0.46335	-1.20000	-0.157015
0.29127	0.44000	-1.09999	-0.148733
0.27498	0.41393	-0.99999	-0.138951
0.25793	0.38532	-0.89999	-0.127390
0.24006	0.35378	-0.79999	-0.113714
0.22131	0.31881	-0.69999	-0.097506
0.20160	0.27985	-0.59999	-0.078252
0.18089	0.23615	-0.49999	-0.055260
0.15903	0.18661	-0.39999	-0.027777
0.13603	0.13066	-0.29999	0.005367
0.14766	0.15967	-0.34999	-0.011980
0.14139	0.14543	-0.32499	-0.003533
0.13694	0.13814	-0.31249	0.000602
0.14045	0.14178	-0.31874	-0.001334
0.13971	0.13995	-0.31562	-0.000239
0.13931	0.13903	-0.31406	0.000285
0.13954	0.13952	-0.31464	0.000016
0.13961	0.13972	-0.31523	-0.000110
0.13956	0.13962	-0.31503	-0.000056
0.13952	0.13954	-0.31494	-0.000018
0.13951	0.13953	-0.31469	-0.000013
0.13951	0.13951	-0.31436	0.000004

RUN NO 2 RI= 1.27094 R2= 0.13951

APPENDIX II

COMPUTER PROGRAM FOR CALCULATION OF COMPOSITION vs. CONVERSION DATA FROM RELATIVE REACTIVITY RATIOS

The programs, written in Fortran IV, calculates instantaneous copolymer composition and average composition of the cumulative copolymer versus per cent conversion for the free radical polymerization of any combination of two monomers for which the appropriate relative reactivity ratios are known or can be calculated with suitable accuracy. (Possible penultimate effects are not treated.) Input is in weight fractions, output is in weight per cents. A copy of the program (in Fortran IV) and an example of a typical output are attached.

The program operates by calculating the instantaneous copolymer composition for the initial monomer composition, assuming constant composition for a small increment of conversion, then calculating a new monomer composition at the end of the increment and iterating the process. The increments are summed to get the cumulative copolymer composition. This stepwise conversion is, of course, an approximation; the inherent error is cumulative and is more significant at high conversions than at low conversions. The magnitude of the error is dependent upon the size of the increments and upon the specific case being considered, i.e. for cases with widely different r values, smaller increments are required to keep

the error to a "reasonable" level. The increment of conversion (weight per cent) for each step is $100/XNOIN$, e.g. $XNOIN = 100$ specifies 1 per cent increments of conversion. If the r 's do not differ by more than a factor of about 10, this will give good approximations to 80 or 90 per cent conversion. If the r 's are grossly different, say $r_1/r_2 > 100$, one can specify very small increments and cut the calculations after a few per cent conversion, by use of LIMN which counts the number of cycles. This can save considerable computer time in cases where one is concerned only with behavior early in the conversion. For example, with $XNOIN = 5000$ and $LIMN = 250$, one gets the first 5 per cent of conversion in 0.02 per cent increments.

The input variables are defined as follows:

WT_i = initial weight fraction, monomer _{i}

XMW_i = molecular weight, monomer _{i}

$R_i(R_{ij})$ = conventional relative reactivity ratios $r_i(r_{ij})$

$XNOIN$ = number of increments (per cent conversion per increment = $100/XNOIN$)

$LIMN$ = limit on number of cycles before going on to next data set

As indicated by the Format statements, all variables except LIMN require a decimal point.

Mechanically, it is desirable to make the "fastest" monomer (the one which will be completely consumed most rapidly) equal to M_1 . With this arrangement, the program will continue even after one monomer is used up, with "instantaneous" homopolymer and the

appropriate average cumulative composition, as would occur in actual polymerizations. When M_2 is reduced below an arbitrary level, the calculations cease and the next data set is read in.

One further note of caution about the use of these programs is appropriate. The theory used in developing the equations utilized is applicable only to systems where the relative monomer concentrations at the actual site of polymerization are the same as the overall relative monomer concentrations. This is, in general, true for solution polymerizations (if the viscosity does not go too high) but frequently is not true for emulsion (latex) or suspension polymerizations. Therefore, the program should be applied with care to the latter types of polymerization. Even in solution polymerizations, difficulties may be encountered when the polymer precipitates as it is formed.

FORTRAN IV G LEVEL 18

MAIN

DATE = 70352

16/50/14

```

C      WEIGHT PERCENT SOLUTION OF COPOLYMER COMPOSITION VS CONVERSION
0001      IN=5
0002      IO=6
0003      1 CONV=0.
0004      SUM1=0.
0005      SUM2=0.
0006      N=0
0007      READ( 5,100)WT1,WT2,XMW1,XMW2,R1,R2,XNOIN,LIHM
0008      100 FORMAT(2F6.5,2F7.2,2F7.3,F5.0,I4)
0009      WRITE( 6,101)R1,R2,XMW1,XMW2,XNOIN
0010      101 FORMAT(1H1,22X,50HWEIGHT PERCENT COPOLYMER COMPOSITION VS CONVERSI
      10N/5HOR1 =F7.3,7H R2 =F7.3, 15H MOL. WT. 1 =F6.2,16H MOL. W
      2T. 2 =F6.2,23H NO. OF INCREMENTS =F5.0/10HO FWT. M1,7X,7HFWT.
      3M2,4X,10HCONVERSION,5X,6HWT. M1,8X,6HWT. M2,8X,7HCUM. M1,7X,7HCUM.
      4 M2)
0011      DEL=1./XNOIN
0012      10 X=(WT1/WT2)*((R1*WT1*XMW2+WT2*XMW1)/(R2*WT2*XMW1+WT1*XMW2))
0013      X1=(X/(1.+X))*100.
0014      X2=100.-X1
0015      SUM1=SUM1+X1
0016      SUM2=SUM2+X2
0017      DENOM=(CONV+DEL)*XNOIN
0018      CUM1=SUM1/DENOM
0019      CUM2=SUM2/DENOM
0020      WRITE( 6,102)WT1,WT2,CONV,X1,X2,CUM1,CUM2
0021      102 FORMAT(1H ,F9.5,F14.5,2PF12.2,OPF13.2,3F14.2)
0022      N=N+1
0023      IF(N-LIHM)12,12,1
0024      12 WT1=WT1-(X1/100.)*DEL
0025      IF(WT1-.000001)21,20,20
0026      21 WT1=0.
0027      20 WT2=WT2-(X2/100.)*DEL
0028      IF(WT2-.00001)40,30,30
0029      30 CONV=CONV+DEL
0030      IF(CONV-1.110,10,40
0031      40 GO TO 1
0032      50 STOP
0033      END

```

R1 = 3.000 R2 = 0.200 WEIGHT PERCENT COPOLYMER COMPOSITION VS CONVERSION NO. OF INCREMENTS = 500.
MOL. WT. 1 = 104.14 MOL. WT. 2 = 160.24

FWT. M1	FWT. M2	CONVERSION	WT. M1	WT. M2	COP. M1	COP. M2
0.30000	0.10000	0.0	59.76	40.24	59.76	40.24
0.29900	0.09920	0.20	59.70	40.30	59.73	40.27
0.29761	0.09839	0.40	59.64	40.36	59.70	40.30
0.29642	0.09758	0.60	59.58	40.42	59.67	40.31
0.29523	0.09677	0.80	59.51	40.49	59.64	40.36
0.29404	0.09596	1.00	59.45	40.55	59.61	40.39
0.29295	0.09515	1.20	59.39	40.61	59.58	40.42
0.29166	0.09434	1.40	59.33	40.67	59.55	40.45
0.29047	0.09353	1.60	59.27	40.73	59.51	40.49
0.28925	0.09271	1.80	59.20	40.80	59.48	40.52
0.28810	0.09190	2.00	59.14	40.86	59.45	40.55
0.28692	0.09108	2.20	59.08	40.92	59.42	40.59
0.28574	0.09026	2.40	59.01	40.99	59.39	40.61
0.28456	0.08944	2.60	58.95	41.05	59.36	40.64
0.28338	0.08862	2.80	58.88	41.12	59.33	40.67
0.28220	0.08780	3.00	58.82	41.19	59.29	40.71
0.28103	0.08697	3.20	58.75	41.25	59.26	40.74
0.27985	0.08615	3.40	58.69	41.31	59.23	40.77
0.27868	0.08532	3.60	58.62	41.38	59.20	40.80
0.27750	0.08450	3.80	58.56	41.44	59.17	40.83
0.27633	0.08367	4.00	58.49	41.51	59.13	40.87
0.27516	0.08284	4.20	58.43	41.57	59.10	40.90
0.27399	0.08200	4.40	58.36	41.64	59.07	40.93
0.27283	0.08117	4.60	58.30	41.70	59.04	40.96
0.27166	0.08034	4.80	58.23	41.77	59.01	40.99
0.27050	0.07950	5.00	58.16	41.84	58.97	41.03

WEIGHT PERCENT COPOLYMER COMPOSITION VS CONVERSION
 R1 = 3.000 R2 = 0.200 MOL. WT. 1 = 104.14 MOL. WT. 2 = 160.24 NO. OF INCREMENTS = 2000.

FMT. M1	FMT. M2	CONVERSION	WT. M1	WT. M2	CUM. M1	CUM. M2
C.1C900	0.89100	0.0	33.02	66.98	33.02	66.98
0.1C883	0.89067	0.05	33.00	67.00	33.01	66.99
0.1C867	0.89033	0.10	32.98	67.02	33.00	67.00
C.1C850	0.88999	0.15	32.96	67.04	32.99	67.01
C.1C834	0.88966	0.20	32.93	67.07	32.98	67.02
0.1C818	0.88932	0.25	32.91	67.09	32.97	67.03
C.1C801	0.88899	0.30	32.89	67.11	32.96	67.04
C.1C785	0.88865	0.35	32.87	67.13	32.95	67.05
0.1C768	0.88832	0.40	32.85	67.15	32.93	67.07
C.1C752	0.88798	0.45	32.82	67.18	32.92	67.08
C.1C735	0.88765	0.50	32.80	67.20	32.91	67.09
C.1C719	0.88731	0.55	32.78	67.22	32.90	67.10
0.1C703	0.88697	0.60	32.76	67.24	32.89	67.11
C.1C686	0.88664	0.65	32.73	67.27	32.88	67.12
0.1C670	0.88630	0.70	32.71	67.29	32.87	67.13
C.1C653	0.88596	0.75	32.69	67.31	32.86	67.14
0.1C637	0.88563	0.80	32.67	67.33	32.85	67.15
0.1C621	0.88529	0.85	32.65	67.35	32.83	67.17
C.1C604	0.88495	0.90	32.62	67.38	32.82	67.18
0.1C588	0.88462	0.95	32.60	67.40	32.81	67.19
C.1C572	0.88428	1.00	32.58	67.42	32.80	67.20
C.1C556	0.88394	1.05	32.56	67.44	32.79	67.21
C.1C539	0.88361	1.10	32.53	67.47	32.78	67.22
C.1C523	0.88327	1.15	32.51	67.49	32.77	67.23
C.1C507	0.88293	1.20	32.49	67.51	32.76	67.24
0.1C490	0.88259	1.25	32.47	67.53	32.75	67.25
C.1C474	0.88226	1.30	32.44	67.56	32.73	67.27
0.1C458	0.88192	1.35	32.42	67.58	32.72	67.28
C.1C442	0.88158	1.40	32.40	67.60	32.71	67.29
C.1C426	0.88124	1.45	32.38	67.62	32.70	67.30
C.1C409	0.88090	1.50	32.35	67.65	32.69	67.31
C.1C393	0.88057	1.55	32.33	67.67	32.68	67.32
C.1C377	0.88023	1.60	32.31	67.69	32.67	67.33
C.1C361	0.87989	1.65	32.29	67.71	32.66	67.34
C.1C345	0.87955	1.70	32.26	67.74	32.64	67.36
C.1C329	0.87921	1.75	32.24	67.76	32.63	67.37
C.1C312	0.87887	1.80	32.22	67.78	32.62	67.38
C.1C296	0.87853	1.85	32.20	67.80	32.61	67.39
C.1C280	0.87820	1.90	32.17	67.83	32.60	67.40
C.1C264	0.87786	1.95	32.15	67.85	32.59	67.41
C.1C248	0.87752	2.00	32.13	67.87	32.58	67.42
C.1C232	0.87718	2.05	32.11	67.89	32.57	67.43
C.1C216	0.87684	2.10	32.08	67.92	32.56	67.44
C.1C200	0.87650	2.15	32.06	67.94	32.54	67.46
C.1C184	0.87616	2.20	32.04	67.96	32.53	67.47
C.1C168	0.87582	2.25	32.02	67.98	32.52	67.48
C.1C152	0.87548	2.30	31.99	68.01	32.51	67.49
C.1C136	0.87514	2.35	31.97	68.03	32.50	67.50
C.1C120	0.87480	2.40	31.95	68.05	32.49	67.51
C.1C104	0.87446	2.45	31.93	68.07	32.48	67.52
C.1C088	0.87412	2.50	31.90	68.10	32.47	67.53
C.1C072	0.87378	2.55	31.88	68.12	32.45	67.55
0.1C056	0.87344	2.60	31.86	68.14	32.44	67.56
C.1C040	0.87310	2.65	31.83	68.17	32.43	67.57
C.1C024	0.87276	2.70	31.81	68.19	32.42	67.58
0.1C008	0.87241	2.75	31.79	68.21	32.41	67.59

0.09992	0.87207	2.80	31.77	68.23	32.40	67.60
0.09977	0.87173	2.85	31.74	68.26	32.39	67.61
0.09961	0.87139	2.90	31.72	68.20	32.38	67.63
0.09945	0.87105	2.95	31.70	68.30	32.36	67.64
0.09929	0.87071	3.00	31.67	68.33	32.35	67.65
0.09913	0.87037	3.05	31.65	68.35	32.34	67.66
0.09897	0.87002	3.10	31.63	68.37	32.33	67.67
0.09881	0.86968	3.15	31.61	68.39	32.32	67.68
0.09866	0.86934	3.20	31.58	68.42	32.31	67.69
0.09850	0.86900	3.25	31.56	68.44	32.30	67.70
0.09834	0.86866	3.30	31.54	68.46	32.28	67.72
0.09818	0.86831	3.35	31.51	68.49	32.27	67.73
0.09803	0.86797	3.40	31.49	68.51	32.26	67.74
0.09787	0.86763	3.45	31.47	68.53	32.25	67.75
0.09771	0.86729	3.50	31.45	68.55	32.24	67.76
0.09755	0.86694	3.55	31.42	68.58	32.23	67.77
0.09740	0.86660	3.60	31.40	68.60	32.22	67.78
0.09724	0.86626	3.65	31.38	68.62	32.21	67.79
0.09708	0.86591	3.70	31.35	68.65	32.19	67.81
0.09693	0.86557	3.75	31.33	68.67	32.18	67.82
0.09677	0.86523	3.80	31.31	68.69	32.17	67.83
0.09661	0.86488	3.85	31.28	68.72	32.16	67.84
0.09646	0.86454	3.90	31.26	68.74	32.15	67.85
0.09630	0.86420	3.95	31.24	68.76	32.14	67.86
0.09614	0.86385	4.00	31.21	68.79	32.13	67.87
0.09599	0.86351	4.05	31.19	68.81	32.11	67.89
0.09583	0.86316	4.10	31.17	68.83	32.10	67.90
0.09568	0.86282	4.15	31.15	68.85	32.09	67.91
0.09552	0.86248	4.20	31.12	68.88	32.08	67.92
0.09536	0.86213	4.25	31.10	68.90	32.07	67.93
0.09521	0.86179	4.30	31.08	68.92	32.06	67.94
0.09505	0.86144	4.35	31.05	68.95	32.05	67.95
0.09490	0.86110	4.40	31.03	68.97	32.03	67.97
0.09474	0.86075	4.45	31.01	68.99	32.02	67.98
0.09459	0.86041	4.50	30.98	69.02	32.01	67.99
0.09443	0.86006	4.55	30.96	69.04	32.00	68.00
0.09428	0.85972	4.60	30.94	69.06	31.99	68.01
0.09412	0.85937	4.65	30.91	69.09	31.98	68.02
0.09397	0.85903	4.70	30.89	69.11	31.97	68.03
0.09381	0.85868	4.75	30.87	69.13	31.95	68.05
0.09366	0.85834	4.80	30.84	69.16	31.94	68.06
0.09351	0.85799	4.85	30.82	69.18	31.93	68.07
0.09335	0.85764	4.90	30.80	69.20	31.92	68.08
0.09320	0.85730	4.95	30.77	69.23	31.91	68.09
0.09304	0.85695	5.00	30.75	69.25	31.90	68.10
0.09289	0.85661	5.05	30.73	69.27	31.89	68.11
0.09274	0.85626	5.10	30.70	69.30	31.87	68.13
0.09258	0.85591	5.15	30.68	69.32	31.86	68.14
0.09243	0.85557	5.20	30.66	69.34	31.85	68.15
0.09228	0.85522	5.25	30.63	69.37	31.84	68.16
0.09212	0.85487	5.30	30.61	69.39	31.83	68.17
0.09197	0.85453	5.35	30.59	69.41	31.82	68.18
0.09182	0.85418	5.40	30.56	69.44	31.81	68.19
0.09166	0.85383	5.45	30.54	69.46	31.79	68.21
0.09151	0.85348	5.50	30.52	69.48	31.78	68.22
0.09136	0.85314	5.55	30.49	69.51	31.77	68.23
0.09121	0.85279	5.60	30.47	69.53	31.76	68.24
0.09105	0.85244	5.65	30.44	69.56	31.75	68.25
0.09090	0.85209	5.70	30.42	69.58	31.74	68.26
0.09075	0.85175	5.75	30.40	69.60	31.72	68.28

C.09060	0.85140	5.80	30.37	69.63	31.71	68.29
C.09044	0.85105	5.85	30.35	69.65	31.70	68.30
C.09029	0.85070	5.90	30.33	69.67	31.69	68.31
C.09014	0.85035	5.95	30.30	69.70	31.68	68.32
C.08999	0.85000	6.00	30.28	69.72	31.67	68.33
C.08984	0.84966	6.05	30.26	69.74	31.66	68.34
C.08969	0.84931	6.10	30.23	69.77	31.64	68.36
C.08954	0.84896	6.15	30.21	69.79	31.63	68.37
C.08939	0.84861	6.20	30.19	69.81	31.62	68.38
C.08923	0.84826	6.25	30.16	69.84	31.61	68.39
C.08908	0.84791	6.30	30.14	69.86	31.60	68.40
C.08893	0.84756	6.35	30.11	69.89	31.59	68.41
C.08878	0.84721	6.40	30.09	69.91	31.57	68.43
C.08863	0.84686	6.45	30.07	69.93	31.56	68.44
C.08848	0.84651	6.50	30.04	69.96	31.55	68.45
C.08833	0.84616	6.55	30.02	69.98	31.54	68.46
C.08818	0.84581	6.60	30.00	70.00	31.53	68.47
C.08803	0.84546	6.65	29.97	70.03	31.52	68.48
C.08788	0.84511	6.70	29.95	70.05	31.50	68.50
C.08773	0.84476	6.75	29.92	70.08	31.49	68.51
C.08758	0.84441	6.80	29.90	70.10	31.48	68.52
C.08743	0.84406	6.85	29.88	70.12	31.47	68.53
C.08728	0.84371	6.90	29.85	70.15	31.46	68.54
C.08713	0.84336	6.95	29.83	70.17	31.45	68.55
C.08698	0.84301	7.00	29.80	70.20	31.43	68.57
C.08683	0.84266	7.05	29.78	70.22	31.42	68.58
C.08669	0.84231	7.10	29.76	70.24	31.41	68.59
C.08654	0.84196	7.15	29.73	70.27	31.40	68.60
C.08639	0.84160	7.20	29.71	70.29	31.39	68.61
C.08624	0.84125	7.25	29.68	70.32	31.38	68.62
C.08609	0.84090	7.30	29.66	70.34	31.36	68.64
C.08594	0.84055	7.35	29.64	70.36	31.35	68.65
C.08579	0.84020	7.40	29.61	70.39	31.34	68.66
C.08565	0.83985	7.45	29.59	70.41	31.33	68.67
C.08550	0.83949	7.50	29.56	70.44	31.32	68.68
C.08535	0.83914	7.55	29.54	70.46	31.31	68.69
C.08520	0.83879	7.60	29.52	70.48	31.29	68.71
C.08506	0.83844	7.65	29.49	70.51	31.28	68.72
C.08491	0.83808	7.70	29.47	70.53	31.27	68.73
C.08476	0.83773	7.75	29.44	70.56	31.26	68.74
C.08461	0.83738	7.80	29.42	70.58	31.25	68.75
C.08447	0.83703	7.85	29.40	70.60	31.24	68.76
C.08432	0.83667	7.90	29.37	70.63	31.22	68.78
C.08417	0.83632	7.95	29.35	70.65	31.21	68.79
C.08403	0.83597	8.00	29.32	70.68	31.20	68.80
C.08388	0.83561	8.05	29.30	70.70	31.19	68.81
C.08373	0.83526	8.10	29.28	70.72	31.18	68.82
C.08359	0.83491	8.15	29.25	70.75	31.17	68.83
C.08344	0.83455	8.20	29.23	70.77	31.15	68.85
C.08329	0.83420	8.25	29.20	70.80	31.14	68.86
C.08315	0.83384	8.30	29.18	70.82	31.13	68.87
C.08300	0.83349	8.35	29.15	70.85	31.12	68.88
C.08286	0.83314	8.40	29.13	70.87	31.11	68.89
C.08271	0.83278	8.45	29.11	70.89	31.10	68.91
C.08256	0.83243	8.50	29.08	70.92	31.08	68.92
C.08242	0.83207	8.55	29.06	70.94	31.07	68.93
C.08227	0.83172	8.60	29.03	70.97	31.06	68.94
C.08213	0.83136	8.65	29.01	70.99	31.05	68.95
C.08198	0.83101	8.70	28.98	71.02	31.04	68.96
C.08184	0.83065	8.75	28.96	71.04	31.02	68.98

C.08169	0.83030	8.80	28.94	71.06	31.01	68.99
C.08155	0.82994	8.85	28.91	71.09	31.00	69.00
C.08140	0.82959	8.90	28.89	71.11	30.99	69.01
C.08126	0.82923	8.95	28.86	71.14	30.96	69.02
C.08112	0.82887	9.00	28.84	71.16	30.97	69.04
C.08097	0.82852	9.05	28.81	71.19	30.95	69.03
C.08083	0.82816	9.10	28.79	71.21	30.94	69.06
C.08068	0.82781	9.15	28.76	71.24	30.93	69.07
C.08054	0.82745	9.20	28.74	71.26	30.92	69.08
C.08040	0.82709	9.25	28.72	71.28	30.91	69.09
C.08025	0.82674	9.30	28.69	71.31	30.89	69.11
C.08011	0.82638	9.35	28.67	71.33	30.88	69.12
C.07997	0.82602	9.40	28.64	71.36	30.87	69.13
C.07982	0.82567	9.45	28.62	71.38	30.86	69.14
C.07968	0.82531	9.50	28.59	71.41	30.85	69.15
C.07954	0.82495	9.55	28.57	71.43	30.84	69.17
C.07939	0.82460	9.60	28.54	71.46	30.82	69.18
C.07925	0.82424	9.65	28.52	71.48	30.81	69.19
C.07911	0.82388	9.70	28.49	71.51	30.80	69.20
C.07897	0.82352	9.75	28.47	71.53	30.79	69.21
C.07882	0.82317	9.80	28.45	71.55	30.78	69.23
C.07868	0.82281	9.85	28.42	71.58	30.76	69.24
C.07854	0.82245	9.90	28.40	71.60	30.75	69.25
C.07840	0.82209	9.95	28.37	71.63	30.74	69.26
C.07825	0.82173	10.00	28.35	71.65	30.73	69.27

VITA

Chien-Da Stephenson Lee was born in Chengtu, Szuchuan, China, on May 6, 1942. He graduated from Taiwan Provincial 2nd Senior High School in 1961 and received the B.Sc. degree in Chemistry in 1965 from National Cheng Kung University in Tainan, Taiwan. He served as an officer in the Army of the Republic of China followed by a year as Assistant Professor at Cheng Hsiu Institute of Technology in Kaoshiung, Taiwan before entering graduate school at Louisiana State University-Baton Rouge in 1968. He is presently a candidate for the degree of Doctor of Philosophy with a major in organic polymer chemistry and a minor in analytical chemistry.

He is a member of Phi Kappa Phi and Sigma Xi honorary society and of the American Chemical Society. He has accepted a position by the Minnesota Mining and Manufacture Company at St. Paul, Minnesota.

In 1969, he married Jane T. J. Tsang and is now the father of two sons, Terry and David.

EXAMINATION AND THESIS REPORT

Candidate: Chien-Da Stephenson Lee

Major Field: Chemistry

Title of Thesis: Mercaptan-Containing Polymers

Approved:

William H. Daly
Major Professor and Chairman

James G. Layman
Dean of the Graduate School

EXAMINING COMMITTEE:

W. H. Daly

A. W. F. Allen

S. K. Carpenter

K. N. Houk

Date of Examination:

September 28, 1973