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Bis-Type Modifiers in Polymerization. I. Behavior of Various Disulfides in Bulk Styrene Polymerization*

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INTRODUCTION

This paper is concerned with a study of the relative modifier activity (chain growth regulator effectiveness) of disulfides having certain representative structures and of the mechanism of cleavage of some of them in styrene polymerization.

The use of modifiers of bis-type structures would offer a most convenient method of conferring desired groups onto both ends of each primary chain for emulsion polymers of $\bar{M}_n$ of 10^5 or less, providing that it can be established that the modifier confers one-half of itself onto each of the terminated and initiated chain ends, *viz.*, that the transfer process can be represented as:

$$\underset{\substack{\text{Growing}\\\text{polymer}\\\text{chain}}}{\text{P}\cdot} + \underset{\substack{\text{Bis-type}\\\text{modifier}}}{\text{RX-XR}} \longrightarrow \underset{\substack{\text{Terminated}\\\text{chain}}}{\text{PXR}} + \underset{\substack{\text{Radical}\\\text{from}\\\text{modifier}}}{\text{RX}\cdot} \xrightarrow{\text{Monomer}} \underset{\substack{\text{New}\\\text{chain}}}{\text{RXM}\cdot} \qquad (1)$$

where X-X is a comparatively weak link, such as a disulfide. The objectives sought in preparing addition polymers (especially elastomers) containing end groups capable of further reaction in a fashion which eliminates the "free" chain ends have been discussed earlier,[2] as have the advantages of the use of bis-type modifiers over other methods for incorporation of such groups.

The evaluation of modifier effectiveness of various compounds was carried out in bulk styrene in the present work, although the primary interest in the use of bis-type modifiers is contemplated to be in the improvement of resilience of GR-S emulsion polymers. Measurements made in bulk styrene were deemed more useful for this preliminary phase of the work on addition polymers with reactive end groups because effects on apparent activity due to diffusion properties of the modifier—properties which are always a factor in emulsion polymerization[3-5]—do not have to be taken into account; also, number average molecular weight-intrinsic viscosity relationships are more accurately known for polystyrene than for any other polymer. Moreover, at 50°C. the contribution of thermal polymerization or of transfer reactions with monomer, polymer, or with

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initiators such as azoisobutyronitrile to the total number of chain ends (at number average molecular weights of substantially less than 10^6) is known to be so slight that for practical purposes all chain ends can be considered to have arisen from either the initiation reaction or the transfer reaction with modifier.

Insofar as the reported work on the behavior of true "transfer agents" (those not affecting rate) is concerned, comparatively little study seems to have been devoted to bis-type modifiers as such. In one of the early and more exhaustive of the studies on mercaptans,[6] Snyder and co-workers listed some data on the number of sulfur atoms per molecule of styrene polymers modified with bisisopropyl xanthogen disulfide (Dixie). These varied over a wide range, a factor which may have been due to the comparatively inexact means for measuring $\overline{M}_n$ that were available. The qualitative effectiveness of various disulfides in Mutual GR-S recipe polymerizations was reviewed in the summary paper of Marvel and co-authors.[7] Gregg and Mayo's recent publication[8] listing the transfer constants of a large number of compounds in styrene polymerization includes a couple of disulfides and a diselenide. The latter compound, dibenzyl diselenide, had a transfer constant 200 times its sulfur counterpart. The extent to which various common initiators participate in transfer reactions has been studied by various authors,[9–14] and Cass in particular has shown that aryl and aroyl peroxides are cleaved by radicals derived from ethers by a reaction similar to that shown in equation (1), where the oxygen-oxygen bond would correspond to the X-X bond of the equation. The behavior of disulfides in reactions not involving polymer radicals has also been the subject of appreciable experimental work.[15–17]

Gannon, Fettes, and Tobolsky[17a] used various dihalo compounds such as ethylene dichloride, chloroacetyl chloride, and the like, in bulk styrene polymerizations. While the structure of some of their compounds led them to believe that the resulting polymers contained halogen groups at both ends, their experiments were not carried to the point of demonstrating this. Also, they point out that transfer mechanisms involving hydrogen, rather than halogen atoms were likely to occur with many of their compounds, leading to two halogen atoms on one end and none on the other.

Since the present work was undertaken Stockmayer and co-authors[18] and Tobolsky and Baysal[19] have shown for vinyl acetate and for styrene, respectively, that disulfides must cleave according to equation (1), in that the use of cyclic disulfides led to polymers of high molecular weight containing appreciably more than two sulfur atoms per polymer molecule. Tobolsky and Baysal also prepared two styrene polymers using high contents of dibutyl disulfide in the charge and determined from their sulfur contents that 2.7 and 3.8 sulfur atoms per polymer molecule had become combined. However, these polymerizations were carried to conversions well beyond the point where the ratio of the unreacted modifier to unreacted monomer concentration was essentially that in the charge, and the use of the Gregg-Mayo equation for calculating $\overline{M}_n$ from intrinsic viscosity was probably not well justified. This latter point is discussed in the experimental section of the present paper.

In this paper, chain transfer activity has been evaluated by a technique essentially that evolved by Mayo and co-workers,[20] and the determination of the number of fragments per molecule has been carried out by comparing the concentration of identifiable end groups with the number average molecular weight. For the latter purpose, some comparisons have also been made on polymers prepared with thiol modifiers containing similar groups, in order that the determination of the number of fragments imparted by the bis-type modifiers be as independent as possible of a knowledge of the absolute value of the $\bar{M}_n$ or of the concentration per unit weight of the group to be analyzed for.

EXPERIMENTAL

A. Units; Parameters Measured

The measurement of chain growth regulator effectiveness used is that of Mayo and co-workers.[20] The transfer constant, C, is defined as:

$$C = \frac{M}{R}\left(\frac{1}{P} - \frac{1}{P_0}\right) \tag{2}$$

where M and R are, respectively, the initial concentrations in moles of monomer and chain growth regulator (modifier); P and P_0 are, respectively, the degrees of polymerization in the presence and absence of regulator. The $1/P_0$ term corrects for the contribution of the initiator and of thermal initiation to the modifiers of high activity. No attempt has been made to compute transfer constants of less than 0.01, nor even to take all the steps of elaborate purification of ingredients necessary to the detection of very low orders of transfer activity. Those materials considered to have a negligible activity, so far as our interests are concerned, are listed as less than 0.005. The degree of polymerization was calculated from intrinsic viscosities measured in benzene, using the relation developed by Gregg and Mayo:[21]

$$\bar{M}_n = 184{,}000[\eta]^{1.40} \tag{3}$$

(The revised expression, $\bar{M}_n = 167{,}000[\eta]^{1.37}$, proposed in a later paper[9] gives values differing so little from those derived from the earlier equation in the molecular weight range of interest that the earlier version was used exclusively.) The validity of equation (3) was verified on two low conversion polymers modified with 2-mercaptomethyl naphthalene, whose number average molecular weights were checked independently by two other methods: osmotic pressure measurements and determinations of the concentration of naphthyl end groups. These results are described in Table I. (All polymerizations were carried out in bulk at 50°C., with 0.05% of bisazoisobutyronitrile (AIBN) initiator, as described in the experimental section.)

It should be noted that equations relating intrinsic viscosity to $\bar{M}_n$ are applicable only to polymers prepared under substantially "constant"

TABLE I

COMPARISON OF VISCOMETRICALLY DETERMINED $\bar{M}_n$ WITH VALUES OBTAINED BY OTHER METHODS

				$\bar{M}_n \times 10^{-3}$		
Polymer No.	Parts MMN[a]	% Convn.	$[\eta]$	Calcd. from equation (3)	Calcd. from end groups[b]	Osmotic[c]
2124-28A	0	3.8	1.52	340	—	—
-28B	0.0056	3.8	0.84	145	141	117
-28C	0.0148	3.7	0.51	71.0	67.5	68.7

[a] 2-Mercaptomethyl naphthalene.

[b] Corrected for contribution of the initiator terminated ends, *i.e.*, $\frac{1}{\bar{M}_n(\text{corr.})} = \frac{1}{\bar{M}_n(\text{act.})} - \frac{1}{\bar{M}_{n0}}$, where $\bar{M}_n$ (act.) is the actual $\bar{M}_n$ of the sample, $\bar{M}_n$ (corr.) the value calculated from the end group determination by ultraviolet absorption, and $\bar{M}_{n0}$ the molecular weight of the polymer (28A) prepared in the absence of modifier. Based on ultraviolet spectra of a considerable number of specially prepared sulfides with naphthalene and phenyl groups, a specific extinction coefficient of 30.0 at 286 mμ was used for the calculations. The transfer constant (calculated in terms of moles and degree of polymerization, P) was *ca.* 13; at 2.8% conversion it was 17.

[c] Based on least squares line (no curvature observed).

polymerization conditions, *i.e.*, prepared to low extents of depletion of any ingredients affecting molecular weight. Such polymers are presumed to have molecular weight distributions of the "most probable" type, where:

$$\bar{M}_w/\bar{M}_n \cong 2$$

Intrinsic viscosities were calculated from specific viscosity measurements made (usually) at a single concentration in benzene, using the expression of Tingey and Smith:[22]

$$\eta_{sp}/c_v = [\eta] + 0.375[\eta]^2 c_v$$

This relationship was checked experimentally on several polymers in the present work, and found to apply accurately. Measurements were made in a viscometer with a flow time of 93 seconds for benzene, and having negligible kinetic energy corrections.

B. Polymerizations

Commercial 99.5+ % styrene was distilled and dried with anhydrous sodium sulfate, and kept in a refrigerator under a nitrogen atmosphere until ready for use. Polymerizations were carried out for the most part in 16 cc. screw cap vials fitted with aluminum foil gaskets. 10.0 g. monomer charges were employed, the free space above the liquid being kept flushed with lamp-grade nitrogen during the capping operation. 0.1 weight per cent of azoisobutyronitrile was used as the initiator in all except a few runs, where 0.05% was used. The latter are indicated. The polymerization temperature used for obtaining the data of Tables I to VIII and the figures was 50°C. Conversions were measured either by the conventional solids method of drying down a very small aliquot in an aluminum weighing cup on an open hot plate, or by the refractive index method of Smith.[5] Agreement between these two methods was excellent. Reproducibility of polymerization rate was generally quite satisfactory. On each occasion when a single modifier or set of modifier charges was being run, a control polymerization containing AIBN initiator only was also run, and the P_0 of this particular control was used in all computations involving the modifiers or modifiers being investigated. Reproducibility of P_0's from one series to the next was good.

In order to utilize the Gregg-Mayo equation relating intrinsic viscosity and $\bar{M}_n$ with impunity, conversions were kept below the point where the ratio of residual monomer to residual modifier had changed appreciably from the ratio in the original charge. The extent to which the ratio of $\bar{M}_w/\bar{M}_n$ changes as a function of conversion and transfer constant has been calculated by Bardwell and Winkler.[23] The applicability of the $\bar{M}_n$-$[\eta]$ equation decreases with conversion or with the value of the transfer constant, an effect which is shown quantitatively in Figure 1. Here the "apparent transfer constant" calculated from equations (2) and (3) is shown as a function of conversion for a comparatively low transfer constant modifier (di-o-tolyl disulfide), a modifier of quite high transfer constant (bis-(2-aminophenyl) disulfide), and one of very high transfer constant (1-mercaptomethyl naphthalene). Attainment of a high degree of accuracy for the transfer constant of very active materials (such as primary thiols) would require extrapolation to zero conversion. This refinement was not resorted to for the present work, since the Bardwell-Winkler equations

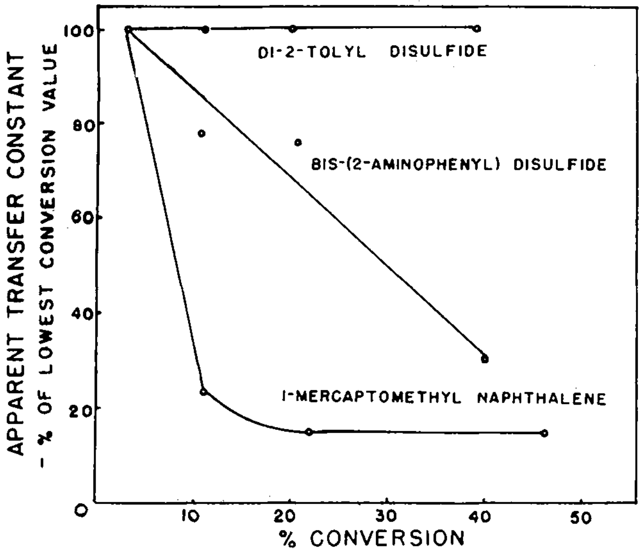


Fig. 1. Change in the apparent transfer constant as a function of conversion for modifiers having a wide range in chain transfer activity. At conversions of 2.5–2.9%, the di-2-tolyl and bis-(2-aminophenyl) disulfides, and 1-mercaptomethylnaphthalene gave transfer constant values of 0.27, 3.7, and 17.0, respectively.

demonstrate that a change in the cumulative $\bar{M}_w/\bar{M}_n$ of only *ca.* 10% occurs when the ratio of residual modifier to residual monomer has changed 50% from the initial value. This accounts at the same time for the reasons why the error in the value for a primary thiol (C = 17–20) is small if conversions are kept down to 2–2.5%, as well as why the observed value of low activity materials does not deviate significantly from the initial value even if observations are made at quite high conversions. For the present work conversions were restricted to 10–14% for modifiers of moderate activity, and to less than 3% for the primary thiols. Fettes, Tobolsky, and Johnson[23a] have derived quantitative relations from the Bardwell-Winkler equations which demonstrate this same point.

The low solubility in styrene of some of the modifiers necessitated the use of an added solvent in order to keep them in solution. Pyridine was found the most generally effective solvent for this purpose, and was accordingly used whenever a solvent was necessary. In such cases control runs with the same concentration of pyridine and with no modifier were used as the basis for calculating P_0. The latter values differed only slightly from those obtained in the absence of pyridine. The transfer constant of the grade of C.P. pyridine used was in the range of 0.0003–0.0008. Gregg and Mayo report a value of 6×10^{-5},[8] so that our comparatively high value probably is due to impurities in the solvent.

Concentrations of modifiers are listed in parts per 100 parts of styrene. Calculations of transfer constants, however, were made on the basis of Mayo's original nomenclature: moles of transfer agent per mole of monomer.

C. Analysis of End Groups

Naphthyl Groups

The modifiers di-2-naphthyl disulfide and 1-mercaptomethyl naphthalene were employed in comparisons of the modification mechanism of disulfides and of thiols, in order to utilize the strongly absorbing naphthyl group as a means of analyzing very low concentrations of end groups by ultraviolet spectra. Various sulfur-containing "model" compounds having structures similar to those expected to be present on the ends of polystyrene chains using these modifiers were prepared, and their spectra measured in a Beckman model DU spectrophotometer.[24] On the basis of these measurements the compounds 2-naphthyl benzyl sulfide (E_{molar} = 8350 at 285 mμ) and 1-naphthylmethyl benzyl sulfide (E_{molar} = 7920 at 286 mμ) were used to "calibrate" the measurements made on the polymers of Table IV.

Carboxyl Groups

Carboxyl groups conferred onto polymers by either bis-type modifiers or by the thiol, β-mercaptopropionic acid, were analyzed by titration with standard sodium methoxide in 90/10 benzene/alcohol solution, the polymer being dissolved in benzene. The use of thymol blue as indicator proved to give sharp end points at very low molar levels of carboxyl groups, as determined initially on highly diluted benzene solutions of oleic acid of known concentration.

Amine Groups

Amine groups present on polymer chain ends, as imparted by the use of bis-(2-aminophenyl) disulfide, or the 4-isomer, were analyzed by titration of benzene solutions with standard perchloric acid (in glacial acetic acid) using methyl violet as indicator. The sensitivity attainable with this method was such that the titers of polymers of $\bar{M}_n$ of 10^5 was believed to be reliable within *ca.* 5%.

Benzothiazyl Groups

Polymers prepared with di-(2-benzothiazyl) disulfide (Altax) were also analyzed by ultraviolet absorption. The model compound employed, as representing fairly closely the configuration of the end group, was 2-benzylthio-benzothiazole ($E_{\text{molar}} = 12{,}600$ at 282 mμ).

D. Preparations

Bis-(2-ethyl hexyl) Disulfide

A sample of 2-ethyl hexyl mercaptan (Hooker), containing 20.1% mercaptan sulfur, was oxidized with iodine, at room temperature, in 70/30 isopropanol/water. When a faint yellow color persisted, a large excess of water was added, and the oil that separated was taken up in petroleum ether. Evaporation of the latter left a slightly yellow oil, n_D^{30} 1.4772, which gave a negative test for mercaptan.

Dibenzyl Disulfide

Benzyl mercaptan (Hooker) was oxidized with solid iodine in 2B alcohol, and precipitated by diluting with water. The white crystals were used without further treatment. No mercaptan could be detected. A later preparation from the University of Illinois[1] was believed purer, on the basis of the latter's lower transfer constant.

Bis-chlorobenzyl Disulfide

Chlorobenzyl mercaptan (a Hooker product containing a mixture of isomers) was oxidized as above, diluted with water, and taken up in chloroform. Removal of chloroform left a faintly orange oil, n_D^{27} 1.6300, which gave a negative test for mercaptan.

Bis-(2-pyridyl-β-ethyl) Disulfide

A sample of 2-(β-mercaptoethyl) pyridine (Reilly) was iodine oxidized in alcohol, precipitated with water, taken up in chloroform, and the latter vacuum evaporated. The pale yellow oil could not be crystallized from solvents, even at very low temperatures, and was employed without further purification.

Bis-(2-chloroethyl) Disulfide

A sample of 2-mercaptoethanol (Carbide and Carbon) was oxidized with the theoretical amount of concentrated hydrogen peroxide. After agitating at 34°C. for 45 minutes and 50°C. for one hour, 100 ml. of concentrated

TABLE II

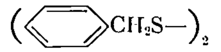
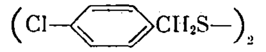
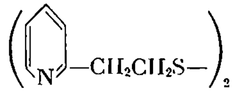
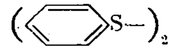
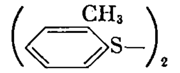
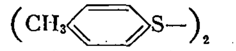
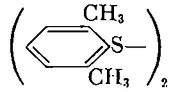
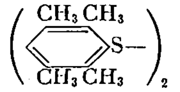
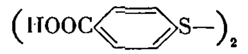
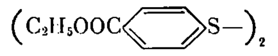
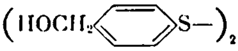
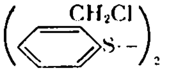
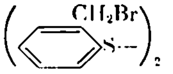
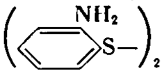
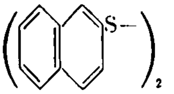
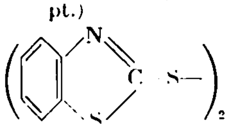
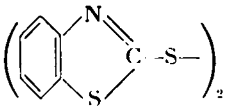
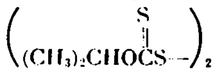
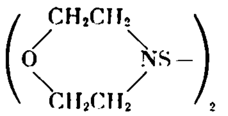
Expt. No.	Compound[a]	% Convn. 17 hrs. at 50°C.	[η]	$\overline{M}_n \times 10^{-3}$	Transfer Constant, C
	None—0.1 AIBN	10.5	1.21–1.28	240–260	—
1844-49B	Bis-(2-ethyl hexyl) disulfide (0.72 pt.) $(C_4H_9(C_2H_5)CHCH_2S—)_2$	10.5	1.15	223	<0.005
1844-56D	*Dibenzyl disulfide (0.62 pt.)* 	12.5	1.10	210	0.03
1844-56E	Bis-(chlorobenzyl) disulfide (0.79 pt.) 	11.6	1.20	240	<0.005
2124-57E	Bis-(2-pyridyl-β-ethyl) disulfide 	11.4	1.00	190	0.03
1979-101B	Bis-(β-chloroethyl) disulfide (2.22 pt.) $(ClCH_2CH_2S—)_2$	10.7	1.00	190	0.01
2209-49-2	Bis-(β-hydroxethyl) disulfide $(HOCH_2CH_2—)_2$	7.5	1.16	230	<0.005
1844-56J	Dithiodiacetic acid (0.46 pt.) $(HOOCCH_2S—)_2$	11.2	1.19	240	<0.005
1844-46H	Esters of bis-(β-carboxyethyl) disulfide $(ROOCCH_2CH_2S—)_2$ (R = C_3)	13.5	1.30	270	<0.005
1844-46J	Bis-(β-chloroacetoxyethyl) disulfide $(ClCH_2CH_2COOCH_2CH_2S)_2$	13.8	1.31	270	<0.005
2051-60F	Diphenyl disulfide 	11.1	0.84	145	0.06
2051-60G	Di-*o*-tolyl disulfide 	11.1	0.52	74	0.23
2051-84F	Di-*p*-tolyl disulfide 	10.9	0.73	120	0.11
2209-75-2	Bis-(2,6-xylyl) disulfide 	10.3	0.29	33	0.69
2293-48-2	Bis-(2,3,5,6-tetramethyl phenyl) disulfide 	10.1	0.32	38	0.73
2051-67C	Bis-(4-carboxyphenyl) disulfide[b] 	11.0	0.70	115	0.11
2051-94B	Bis-(4-carboethoxyphenyl) disulfide 	11.5	0.79	135	0.11

TABLE II (*continued*)

Expt. No.	Compound^a	% Convn. 17 hrs. at 50°C.	[η]	M_n × 10^{-3}	Transfer Constant, C
2124-106B	Bis-(4-hydroxymethyl phenyl disulfide^b 	10.8	0.70	115	0.09
2209-41-2	Bis-(2-chloromethyl phenyl) disulfide 	10.5	0.22	22.5	1.3
2209-130B	Bis-(2-bromomethyl phenyl) disulfide (0.50 pt.) 	12.2	0.44	59	1.0
2124-31EL	Bis-(2-aminophenyl) disulfide 	5.7	0.22	22	3.0
2051-110F	Di-2-naphthyl disulfide 	10.7	0.63	98	0.19
2051-106C	Di-2-benzothiazyl disulfide (0.32 pt.) 	5.9	0.36	45	2.1
1979-104C	Di-2-benzothiazyl sulfide (1.19 pt.) 	11.9	1.18	230	<0.005
2124-112-2	Bis-(isopropyl-xanthogen) disulfide (Dixie)  $\left((CH_3)_2CHO\overset{S}{\overset{\|}{C}}S-\right)_2$	10.0	0.08	5	5.3
1979	4,4′-Dithiodimorpholine disulfide 	9.7	1.17	227	<0.005
2124-57-C	Carbonyl bis-(thioglycolic acid)^b $(HOOCCH_2S-)_2C=O$	7.7	0.37	46	0.36
2124-57-B	Thiocarbonyl bis-(thioglycolic acid)^b $(HOOCCH_2S-)_2$ C=S	8.3	0.50	70	0.21
2124-57-E	Tetraphenylhydrazine Ph_2NNPh_2	Negligible	—	—	—

[a] 1.0 weight per cent used except where indicated otherwise.

[b] These compounds required 30 parts (or less) of pyridine in order to keep in solution. The P_0 of a control containing the same amount of pyridine was used in computing transfer constants.

HCl was added and the mixture heated at 90 °C. for 1.5 hours. The colorless lower layer was removed and dried. Mercaptan could not be detected in this clear yellow oil.

ANALYSIS: *Calcd. for* $C_2H_4Cl_2$, Cl, 37.11; S, 33.55. *Found,* Cl, 36.73, 36.79; S, 33.81, 33.52.

Dithiodiacetic Acid

This was prepared by hydrogen peroxide oxidation of the purest available grade of thioglycolic acid, and recrystallized twice from ether-chloroform mixtures. Neutral equivalent was 103% of theoretical.

Esters of Bis-(β-carboxyethyl) Disulfide $(ROOCCH_2CH_2S)_2$

A sample of β-mercaptopropionic acid (Goodrich) was oxidized with H_2O_2 to the disulfide. The dimethyl, di-*n*-propyl, and bis-(2-chloroethyl) esters were prepared in very small amounts by heating the di-acid at 95 °C. with the appropriate alcohol (ten-fold excess), in the presence of *p*-toluene sulfonic acid for a sufficiently long time to reduce the acid numbers to very low values, evaporating off excess alcohol slowly, taking up in ether, removing unreacted acid with bicarbonate, and finally removing ether under vacuum. All were yellow oils. Since none gave any detectable degree of modification, only the result with the di-*n*-propyl ester is shown in Table II.

ANALYSIS: *Calcd. for* $C_3H_7O_2S$ (dimethyl ester), S, 27.9. *Found,* S, 27.1. *Calcd. for* $C_5H_{11}O_2S$ (di-*n*-propyl ester), S, 21.8. *Found,* S, 22.3. *Calcd. for* $C_4H_8ClO_2S$ (bis-2-chloroethyl ester), Cl, 21.2; S, 19.1. *Found,* Cl, 20.2; S, 18.7.

Bis-(2-chloroacetoxyethyl) Disulfide $(ClCH_2\ COOCH_2\ CH_2S)_2$

A sample of 2-mercaptoethanol (having 94% of theoretical mercaptan sulfur) was oxidized with an equivalent amount of hydrogen peroxide, the disulfide dried by evaporation under high vacuum, and taken up in chloroform. To this was added slowly a chloroform solution of chloroacetyl chloride at 10–12 °C. Two phases were present initially, and the liquid was allowed to warm to room temperature with stirring. After it had become homogeneous, HCl and chloroform were pumped off, finally under a high vacuum. A pale oil, which contained no detectable mercaptan, remained. The product was used without further purification.

Di-o-tolyl Disulfide

This was prepared in 91.6% yield of product, m.p. 34.5–35.5 °C. by iodine oxidation of *o*-thiocresol (Eastman Kodak white label). The melting point of the product was improved only slightly to m.p. 34.8–35.3 °C. after two recrystallizations from 93% aqueous ethanol.

Bis-(4-carboxyphenyl) Disulfide

This compound was prepared by two methods. In the first, the compound was prepared from *p*-toluene sulfonic acid by the method of Smiles[25] via permanganate oxidation to *p*-carboxysodiobenzene sulfonate; conversion to the chlorosulfonyl derivative by treatment with chlorosulfonic acid; reduction to *p*-mercaptobenzoic acid by treatment with zinc and HCl-HAc); and oxidation of the mercapto acid to the disulfide dicarboxylic acid by heating in air for several hours at 100°C. The product prepared in this manner decomposed at 320°C.

In a second preparation, *p*-mercaptobenzoic acid was prepared by a modification of the method of Thompson[26] who coupled diazotized *p*-aminobenzoic acid with Na_2S_2, and reduced the crude bis-(4-carboxyphenyl) disulfide with iron and concentrated sodium carbonate solution to form *p*-mercaptobenzoic acid. In our preparation, the modification used was that described in *Organic Syntheses*, Coll. Vol. 11, p. 580 for preparation of thiosalicylic acid from anthranilic acid. After reducing the crude disulfide di-acid, obtained in 61.6% yield, to *p*-mercaptobenzoic acid with zinc and HCl-HAcO, as in the first preparation, the mercapto acid was reoxidized to the disulfide at 100°C. in air.

The neutral equivalent obtained by titration of the compound with 0.1 *N* NaOH solution, back titrating with 0.1 *N* H_2SO_4, indicated that 2.69 moles of NaOH were consumed per mole of dicarboxy disulfide during a 10 minute period, indicating that base reacted with the disulfide linkage to a considerable extent.

ANALYSIS: *Calcd. for* $C_{14}H_{10}O_4S_2$, C, 54.88; H, 3.29; S, 20.93. *Found*, using Smiles' method, C, 54.01; 53.92; H, 3.39, 3.27; S, 20.64; 20.61. *Found* by Smiles, C, 54.7; H, 3.6; S, 21.1.

Bis-(4-carbethoxyphenyl) Disulfide

The preceding acid was esterified by refluxing a slurry of 6.81 g. of the acid with 17.0 g. of *p*-toluenesulfonic acid monohydrate in 1.36 l. of absolute ethanol for 22 hours. After removal of most of the ethanol, diluting with water, and cooling, a nearly quantitative yield of crude ester was recovered. By recrystallizing twice from absolute alcohol, a 43% yield of needles, m.p. 66.3°C. (as compared with a product, m.p. 65–66°C. obtained by Kipping[27] by iodine oxidation of ethyl 4-mercaptobenzoate), was obtained.

ANALYSIS: *Calcd. for* $C_{18}H_{18}O_4S_2$, C, 59.66; H, 5.01; S, 17.70. *Found*, C, 59.25, 59.33; H, 5.03, 5.11; S, 17.34, 17.45.

4-Mercaptobenzyl Alcohol

To a slurry of 1.438 g. of lithium aluminum hydride (0.0379 mole) in 120 ml. of anhydrous ether (C.P. and predried over Na) in a 3-neck flask fitted with stirrer, seals, gas bubbler, etc., was added a solution of 4.58 g. (0.0126 mole) of bis-(4-carboethoxyphenyl) disulfide in 50 ml. anhydrous ether over a 1 hr. period, with stirring. After refluxing for an additional 45 minutes, and deactivating with water and 10% aqueous H_2SO_4, the aqueous layer was separated, extracted with ether, and the extract combined with the organic layer. The combined ethereal solutions were washed with saturated brine, dried over anhydrous Na_2SO_4, and evaporated. The greasy solid obtained weighed 1.955 g. or 55.9% yield of crude alcohol. By recrystallizing from a mixture of $CHCl_3$ and *n*-hexane, 1.455 g. of crystalline white 4-mercaptobenzyl alcohol, m.p. 45–47 °C., was obtained.

ANALYSIS: *Calcd. for* C_7H_8OS, C, 59.56; H, 5.75; S, 22.87. *Found*, C, 60.15, 59.90; H, 5.75, 5.78; S, 22.56.

Bis-(4-hydroxymethyl-phenyl) Disulfide

A solution of 1.555 g. of 4-mercaptobenzyl alcohol in methanol was treated with as much iodine (1.815 g., 0.0143 mole) in methanol solution as could be consumed. The product was precipitated by addition of brine. The crude disulfide weighing 1.807 g. m.p. 123–124.5 °C., was obtained in 91.8% yield. A 1.50 g. sample of crude disulfide was recrystallized from 100 ml. of 35% aq. ethanol to a silver colored flaky product weighing 0.897 g., with m.p. 130–131 °C.

Bis-(2-hydroxymethyl-phenyl) Disulfide[1]

This compound was prepared both by lithium aluminum hydride reduction of thiosalicylic acid and subsequent iodine oxidation, following the procedure developed by King[1] (in which case it was isolated in 54% yield of product, m.p. 135.8–139.0°C.), and also by lithium aluminum hydride reduction of dithiosalicylic acid, m.p. 289–292°C. (prepared at the University of Illinois[1]). In the latter case, the over-all yield of product of m.p. 141.7-142.1°C. corr. was 45%.

Bis-(2-carbethoxyphenyl) Disulfide[38]

This compound was prepared in 20% yield of white crystalline solid, m.p. 116–120°C., by direct esterification of the aforementioned dithiosalicylic acid in a manner very similar to that described for preparation of bis-(4-carbethoxyphenyl) disulfide. When recrystallized from abs. ethanol, the product melted at 118.7–119.7°C. (as compared to a melting point of 119–120°C. for this ester as prepared from the bischlorocarbonyl derivative by List and Stein[38]).

Bis-(2-chloromethyl-phenyl) Disulfide

This compound was prepared by treating bis-(2-hydroxymethyl-phenyl) disulfide with an equivalent quantity of phosphorous pentachloride. By cautious addition of 66.5 g. (0.320 moles) of phosphorous pentachloride (Merck reagent grade) to 44.5 g. (0.160 moles) of the bis-hydroxymethyl compound in a 1 l. round bottom flask equipped with a reflux condenser and stirring system and cooled by an ice bath, a vigorous reaction was initiated. After the initial reaction had subsided, the product was warmed on a hot water bath for 1 hour. The resultant brown syrupy mass was decomposed by careful addition of water. The syrup isolated by extracting the product with 350 ml. of benzene, washing and drying the benzene extract, and removing solvent, weighed 49.4 g. (98.0% of theory).

By recrystallizing a 10.5 g. portion of product from 520 ml. of *n*-hexane at −78°C. with the aid of norite, 5.1 g. of white solid, m.p. 38–43°C., were obtained. By recrystallizing this solid further, 2.8 g. (27% over-all yield) of bis-(2-chloromethyl-phenyl) disulfide, m.p. 42.3–44.5°C., was obtained.

ANALYSIS: *Calcd. for* $C_{14}H_{12}Cl_2S_2$, Cl, 22.50; S, 20.34. *Found*, Cl, 21.79, 21.81; S, 20.32, 20.35.

Bis-(2-bromomethyl-phenyl) Disulfide

By treating 0.340 g. (.00123 moles) of bis-(2-hydroxymethyl-phenyl) disulfide in an ether slurry with 0.24 g. (0.00087 moles) of phosphorous tribromide (Merck reagent grade), first at 0°C. for 1 hour, then successively for 1/4 hour at 25°C., 1/4 hour at reflux, and 3 hours at 25°C., an ether soluble product was obtained. From the ethereal solution, a yellow oil weighing 0.395 g. (80% yield of crude dibromide) was obtained. By recrystallizing the oil from 8.5 ml. of 24% chloroform in *n*-hexane at −78°C., 0.246 g. (19.8% yield) of white crystalline product, m.p. 64–66°C., was obtained. By recrystallizing this product from *n*-hexane at −78°C., a white, needle-like product, m.p. 66.5–67.2°C., was obtained.

ANALYSIS: *Calcd. for* $C_{14}H_{12}Br_2S_2$, C, 41.60; H, 2.99; Br, 39.54. *Found*, C, 41.89, 42.16; H, 2.80, 2.94; Br, 38.53, 38.52.

Tetraphenyl Hydrazine

Following the method of Gatterman and Wieland,[28] 16.9 g. (0.05 mole) of diphenyl amine (Eastman Kodak white label) in 100 cc. of acetone was oxidized at 0–5°C. with *ca.* 8 g. of $KMnO_4$ over a 1.5 hour period, additions of permanganate being made in small amounts. After removal from the ice bath, additional permanganate was added at room temperature until a total of 15 g. had been added. The slurry was filtered to remove MnO_2, the filtrate evaporated and the residue recrystallized from benzene.

2-Benzylthio-benzothiazole

This compound was obtained by treatment of an ethanolic potassium hydroxide solution of 2-mercaptobenzothiazole with an equivalent quantity of benzyl chloride, refluxing for several hours, removing KCl and ethanol. Although the product was obtained in 99.4% yield of crude oil, only a 22.3% yield of pure compound, m.p. 38–9°C., could be obtained by repeated low-temperature fractional crystallizations from ethanol, ethanol-ether, and petroleum ether at −78°C.

ANALYSIS: *Calcd. for* $C_{14}H_{11}NS$, S, 24.91; N, 5.44. *Found*, S, 25.20, 24.90; N, 5.45, 5.43. *Found* by Moore and Waight,[29] S, 24.6; N, 5.6, 5.75.

The molar extinction values of the ultraviolet absorption spectra of this compound, at peak wave lengths, corresponded closely with those obtained by Moore and Waight[29] for a compound similarly prepared, having m.p. 39.5–40.5°C.

2,6-Xylyl Mercaptan

This compound was prepared, essentially, by the method used by Tarbell and Fukushima[30] for preparation of meta-thiocresol from meta toluidine.

By diazotizing a 20.7 g. (0.150 mole) portion of 2,6-xylidine (Eastman Kodak white label), and adding the cold diazonium solution to an aqueous solution of potassium ethyl xanthate (Eastman Kodak white label) maintained at 40–45 °C., and working up the product according to the Tarbell procedure, a 31.2 g. quantity of 92.0% yield of crude 2,6-xylyl ethyl xanthate was isolated as a red oil.

A 17.5 g. quantity of crude 2,6-xylyl mercaptan of 71.5% purity (as determined potentiometrically by G. E. Meyer of this laboratory with standardized $AgNO_3$ solution by a modification of the method of Tamale[31] *et al.*, substituting a silver electrode sensitized by treatment with an ammoniacal alcoholic solution of dodecyl mercaptan for the prescribed silver sulfide electrode) was isolated by hydrolyzing the xanthate with alcoholic KOH, acidifying with dil. H_2SO_4, and extracting from saturated brine solution with ether.

Di-(2,6-xylyl) Disulfide

To 16.7 g. of the crude mercaptan (containing 0.0863 mole mercaptan) in a 500 ml. flask, 200 ml. methanol was added, followed by 11.0 g. (0.0870 gram atoms) iodine, thus precipitating out the disulfide. After removing most of the methanol at reduced pressure, the slurry was poured onto 50 ml. of ice water, and the tan solid collected. The solid was washed with sodium bisulfite solution, then twice with water, and vacuum dried. The yellow product, weighing 12.4 g., was recrystallized from 150 ml. of *n*-hexane, with the aid of "norite," by cooling to −78 °C. A crystalline product, m.p. 103.0–104.2 °C., was collected in 9.0 g. (76.3% yield from mercaptan or 46.5% yield from the xylidine) quantity. By recrystallizing the disulfide from *n*-hexane, crops of 8.0 g., m.p. 105.5–106.0 °C., and 0.55 g., m.p. 104.8–105.5 °C., were obtained.[39]

ANALYSIS: *Calcd. for* C_8H_9S, C, 70.03; H, 6.60; S, 23.37. *Found,* C, 69.75, 69.70; H, 6.51, 6.57; S, 23.30, 23.26.

Durene Sulfonyl Chloride

This was prepared in 96.5% yield of product, m.p. 99–100 °C., by chlorosulfonating durene, m.p. 80.2–81.2 °C. (Edcan laboratories), according to the method of Huntress and Autenrieth.[32]

Duryl Mercaptan

A. This was first prepared in 15% yield of crude product, m.p. 57.5–61.0 °C., by treatment of durene sulfonyl chloride with zinc and dilute sulfuric acid, first at 0 °C. and then at 70 °C. The product was isolated by extracting the reaction mixture with ether. The melting point of the product was improved to 59.5–61.0 °C. by recrystallizing from 53% aq. ethanol, but could not be improved further by a second recrystallization from abs. ethanol at −78 °C.

B. A 95% yield of the crude mercaptan was obtained later by reducing durene sulfonyl chloride with lithium aluminum hydride. A 7.9 g. (0.034 mole) portion of durene sulfonyl chloride, m.p. 99–100 °C., was added spatula-wise, with stirring, to a slurry of 5.7 g. (0.15 mole) of $LiAlH_4$ in 250 ml. anhydrous ether (C.P. dried over sodium) at a rate to maintain gentle reflux. The mixture was refluxed on a water bath for an additional 90 minutes. After decomposing the lithium derivatives with water, and then with 10% H_2SO_4, a 5.3 g. quantity of crude solid mercaptan was isolated from the washed and dried ether extract.

ANALYSIS: *Calcd. for* $C_{10}H_{14}S$, C, 72.22; H, 8.48; S, 19.28. *Found,* C, 71.75, 71.95; H, 8.33, 8.38; S, 18.95, 18.82.

Bis-(2,3,5,6-tetramethyl-phenyl) Disulfide (Di-duryl Disulfide)

By treating the 5.3 g. of crude duryl mercaptan obtained in experiment B with 4.1 g. (0.032 gram atoms) of iodine in ethanol solution, and precipitating the concentrated ethanol solution into ice water, a crude yellow disulfide was obtained. By washing the product with water, aqueous $NaHSO_3$, and water successively, 5.3 g. of disulfide was obtained. By recrystallizing from *n*-hexane at −78°C., the melting point was improved to 100.0–100.6°C.

Pure samples of di-(2-benzothiazyl) disulfide, di-(2-benzothiazyl) monosulfide, 2-mercaptobenzothiazole, and 4,4′-dithiodimorpholine were kindly supplied by A. F. Hardman of this laboratory. The bis-(2-aminophenyl) disulfide was recrystallized twice from 60% aqueous ethanol of American Cyanamide commercial product to yield yellow crystals, m.p. 92–93°C. Diphenyl disulfide and di-*p*-tolyl disulfide were Eastman white label materials. The carbonyl bis-(thioglycolic acid) and thiocarbonyl bis-(thioglycolic acid) were from Stauffer Chemical Co. and were twice recrystallized from glacial acetic acid prior to use. *t*-Dodecyl mercaptan was the RFC Sulfole grade. The β-mercaptopropionic acid was a highly purified grade from B. F. Goodrich Chemical Co., and was found, by analysis, to have within a few per cent of the theoretical equivalent weight, by both iodine titration and acid number determination. The preparation and properties of the di-2-naphthyl disulfide, 1-mercaptomethyl naphthalene, 2-naphthyl benzyl sulfide, and 1-naphthylmethyl benzyl sulfide are described elsewhere.[24] The bis-(4-carboxymethyl phenyl) disulfide and bis-(4-aminophenyl) disulfide (Tables V and VI) are preparations supplied by the University of Illinois.[1] B. F. Goodrich's diisopropyl xanthogen disulfide was recrystallized twice from aqueous ethanol to a product of m.p. 58.3–59.3°C. The bis-(B-hydroxyethyl) disulfide used was obtained by courtesy of E. M. Fettes, Thiokol Corp.

RESULTS AND DISCUSSION

A. Evaluation of Modifier Effectiveness

Results and Discussion

In Table II are listed the molecular weight and calculated transfer constant data obtained in 50°C. bulk styrene polymerizations on all the bis-type compounds tested. The results shown in Table II are those derived from measurements made with one weight per cent of modifier (except where indicated otherwise). Some of the compounds were also tested over a wide range of concentrations (Tables IV–VIII). Table III depicts similar data for the several thiols examined.

None of alkyl disulfide derivatives in Table II (the first eight compounds listed) proved to have enough activity as modifiers to merit consideration as potential sources of incorporating desired functional groups onto polymers of low $\bar{M}_n$. While the purity of some of these compounds is doubtless of a lower order than the majority of the preparations, none possessed sufficient activity to be of practical interest, and hence exhaustive purifications were not undertaken. The true values can only be lower than those shown. It would appear that any further efforts in the direction of preparing alkyl disulfide derivatives of high activity might best be limited to substitution on the alpha carbon atoms.

Derivatives of diphenyl disulfide attained much higher transfer constants than did the alkyl disulfides, though still low in comparison to primary thiols. Of the few simple derivatives examined (the next seven compounds) methyl substitution in one ortho position of each ring more effectively facilitated cleavage of the sulfur-sulfur bond than did substitution in the para position. Introduction of methyl groups into both ortho positions of each ring—bis-(2,6-xylyl) disulfide and bis-(2,3,5,6-tetramethyl phenyl) disulfide—more than tripled the modifier activity over that of di-*o*-tolyl disulfide, in conformance with observations made on bis-(2,4,6-trimethyl phenyl) disulfide, a compound prepared earlier by Charles King of the University of Illinois.[1]

A carboxyl group or a carboethoxy group in the para position failed to increase the modifier activity level over that of a methyl group. (The carboxy compound proved, in several preparations in the Goodyear and University of Illinois laboratories, to be quite difficult to prepare in pure form, and varying effects on reaction rate were noted with the several preparations.)

Incorporation of a hydroxyl group on a para-methyl group—number 2124-106B, bis-(4-hydroxymethyl phenyl) disulfide—likewise had no significant effect on activity.

It was of some interest to note the marked increase in activity when a halogen atom was incorporated onto a single ortho group attached to each ring—*cf.* results with bis-(2-chloromethyl phenyl) disulfide and the corresponding bromo compound *vs.* di-*o*-tolyl disulfide.

Bis-(2-aminophenyl) disulfide proved to be far the most effective modifier of the simple derivatives of diphenyl disulfide, being of the same order of activity as tertiary mercaptans (*cf.* Table III).

Di-2-naphthyl disulfide had approximately the same order of activity as di-*o*-tolyl disulfide.

The high transfer constant of dibenzothiazyl disulfide is interesting, in light of its well-known activity as an accelerator of sulfur vulcanization

TABLE III

TRANSFER CONSTANTS AT 50°C. OF VARIOUS THIOLS

Expt. No.	Modifier, pt.	Time, hrs.	% conv.	$[\eta]$	$\bar{M}_n \times 10^{-3}$	C
2209-32-M-2[a]	1-Mercaptomethyl naphthalene (0.0116)	4.25	2.8	0.45	61	18.3
2209-30-S-2[a]	*t*-Dodecyl mercaptan (0.063) (Sulfole)	8	5.1	0.53	76	2.9
2124-102-2[b]	β-Mercaptopropionic acid (0.0083)	5	2.6	0.76	127	6.0
1979-110-D[c]	2-Mercaptobenzothiazole (4.8)	32	10.4	0.49	68	0.03

[a] Based on control employing 0.10 AIBN — $\bar{M}_{n_0} = 250{,}000$.

[b] Based on control employing 0.05 AIBN — $\bar{M}_{n_0} = 340{,}000$.

[c] Made in a series in which 100 parts of pyridine used for all runs, though not necessary for solution of mercaptobenzothiazole. The pyridine containing control for this run had an $\bar{M}_n$ of 145,000.

and the demonstration by Cutforth and Selwood[38] that it thermally dissociates into radicals at comparatively low temperatures. That the sulfur-sulfur bond is involved in the cleavage is shown by comparison with the negligibly low transfer constant of the dibenzothiazyl monosulfide.

The high transfer constant characteristic of bis-isopropyl xanthogen disulfide (Dixie) is consistent with the long-known effectiveness of this compound in butadiene copolymer emulsion polymerization.

Trivalent nitrogen attached directly to the sulfur atoms (1979-104B, 4,4′-dithiodimorpholine) apparently does not increase the susceptibility of the disulfide bond to cleavage by styryl radicals, though this compound is known as capable of vulcanizing diene rubbers.

Two interesting materials showing significant activity as modifiers, but which were not true bis-type compounds, were carbonyl bis-(thioglycolic acid) and thiocarbonyl bis-(thioglycolic acid). The likelihood that the cleavage mechanism must be other than that suggested by equation (1) is discussed in connection with the data of Table VIII in section B of the discussion.

The inability to obtain polymerization with tetraphenylhydrazine was disappointing, especially so since the diphenyl amine from which it was made supported polymerization at a rate about half that of the controls. It would suggest that the hydrazine derivative is cleaved to yield a fragment reacting either with initiator or growing polymer radicals, but that the remaining fragment is incapable of initiating new chains. Whether tetraphenylhydrazine cleaves to yield radicals or ions has been discussed by Cain and Wiselogle,[34] and by Lewis and co-authors.[35]

The transfer constants obtained (Table III) with 1-mercaptomethyl naphthalene and with *t*-dodecyl mercaptan (Sulfole) are consistent with values obtained (at 60°C.) by Smith[5] and by Gregg *et al.*,[36] on normal and tertiary alkyl mercaptans. The very low transfer constant obtained with mercaptobenzothiazole might appear remarkable in light of the high value obtained with its disulfide, but would be in agreement with evidence of Koch[37] that mercaptobenzothiazole exists largely in the thioketo form in nonpolar media, rather than in the thiol form. An attempt to convert the material to a "salt" of the thiol by use of some alcohol and KOH in the polymerization (though not sufficient to cause formation of a separate phase) did not increase its modifier activity.

The lower value obtained with β-mercaptopropionic acid, in comparison with alkyl primary thiols, would appear to indicate that the carboxyl group is exerting a "de-activating" effect; but this would not be consistent with the observation of Gregg and co-workers[36] that ethyl thioglycolate has a much higher transfer constant than alkyl thiols. The latter based their calculations on mercaptan disappearance measurements, however, and the two sets of observations might be reconciled if it were shown that carboxyl groups (or esters) increased the tendency for the thiol to add to the double bond to give a nonradical product.

B. Mechanism of Cleavage of Disulfides

Tables IV, V, VI, and VII depict the data directed toward proving that equation (1) correctly describes the mechanism of chain transfer with disulfides. Each is based on the analysis of a particular type of end group incorporated onto polymers varying over a wide range of molecular weight ($2\text{–}30 \times 10^4$). The data shown are only those pertinent to the calculation of the number of analyzed groups per molecule, the latter being indicated in the last column of each table.

Actually, the general method of analysis used does not rule out the possibility of mechanisms of cleavage other than scission at the sulfur-sulfur bond, such as

$$P^{\cdot} + RS\text{—}SR \longrightarrow PR + R^{\cdot} + S_2^{\cdot}, \text{ or } P^{\cdot} + RS\text{—}SR \longrightarrow PSSR + R^{\cdot}$$

However, there appears to be little if any support in the literature for the possibility of either of these mechanisms occurring (*cf.* review by Tarbell and Harnish[17]). For the purposes for which this study was undertaken—using disulfides to confer groups onto each end of the polymer chains—it would in fact make little difference whether either of these alternative mechanisms occurred, so long as the principal portion of each "half" of the disulfide is incorporated onto the chain end.

A number of earlier attempts had been made to pursue these same objectives, by what would seem, superficially at least, to be simpler approaches from an analytical standpoint—namely, the use of very high amounts of experimental modifiers to give very low $\bar{M}_n$ polymers (1000–5000). The problems of isolation of such low molecular weight polymers without partial fractionation, and of measuring cryoscopic molecular weights accurately, proved to be so great that this general approach was abandoned.

In Table IV the comparison between the concentration of naphthyl groups in polymers modified with di-2-naphthyl disulfide and 1-mercaptomethyl naphthalene shows in an unequivocal fashion that this disulfide imparts—within experimental error—twice as many naphthyl end groups

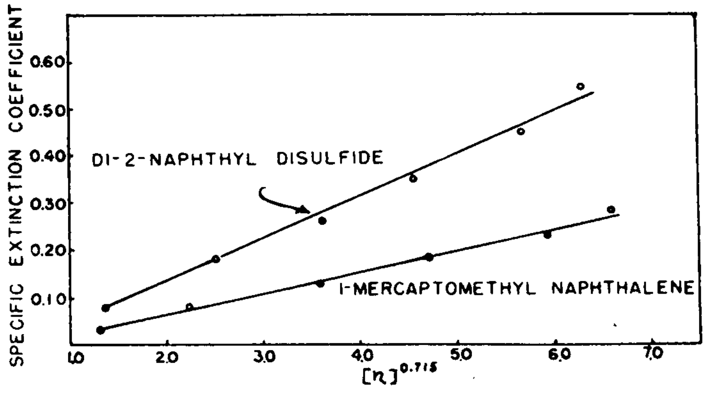


Fig. 2. Concentration of sulfide end groups containing a naphthalene chromophore as a function of $[\eta]^{0.715}$. The slopes of the curves for the disulfide and mercaptan modified series are 0.880 and 0.445, respectively.

TABLE IV

DETERMINATION OF NAPHTHYL END GROUP CONCENTRATIONS IN POLYMERS MODIFIED WITH DI-2-NAPHTHYL DISULFIDE AND WITH 1-MERCAPTOMETHYL NAPHTHALENE

Polymer	Parts modifier/ 100 g. styrene	$[\eta]$	$\bar{M}_n \times 10^{-3}$		Specific extinction coeff.[b]	Calcd. no. of naphthyl end groups per polymer molecules
			Obs.	Corr.[a]		
	Series modified with di-2-naphthyl disulfide[c]					
2051-118B	5.7	0.27	30	33.1	0.539	2.14
C	4.7	0.29	33	36.8	0.446	1.96
D	3.7	0.34	41	47.0	0.354	1.99
E	2.7	0.40	52	62.0	0.258	1.92
F	1.7	0.52	74	96.3	0.178	2.05
G	0.72	0.81	140	249	0.074	2.20
Average						*2.04*
	Series modified with 1-mercaptomethyl-naphthalene[c]					
2124-8B	0.042	0.26	28	30.4	0.289	1.10
C	0.035	0.28	31	34.0	0.242	1.04
D	0.027	0.33	39	43.9	0.195	1.07
E	0.020	0.40	52	61.1	0.136	1.05
F	0.013	0.56	82	107.	0.082	1.11
G	0.005	0.84	145	248.	0.034	1.08
Average						*1.08*

[a] Corrected for the contribution of the catalyst to lowering of molecular weight, *i.e.*, by $\frac{1}{\bar{M}_n(\text{corr.})} = \frac{1}{\bar{M}_n(\text{obs.})} - \frac{1}{\bar{M}_{n_0}}$, where $\bar{M}_{n_0}$ = mol. wt. of polymer prepared with no modifier (av. = 260,000).

[b] Corrected for the absorption of polystyrene at 285 mμ (0.023 av. specific extinction).

[c] Both series employed 0.05 part azoisobutyronitrile. The disulfide and mercaptan modified series were polymerized to *ca.* 7.5 and 3.5% conversion, respectively. The lower conversion of the thiol series was necessitated by the much more rapid disappearance of modifier (transfer constant *ca.* 18).

as the thiol. (Attempts to use thio-2-naphthol to prepare the thiol "reference" series disclosed that this thiol is consumed largely by addition to the styrene double bond, and not in a transfer reaction.) The results are shown graphically in Figure 2 in a form which renders unnecessary even a knowledge of the absolute value of the $\bar{M}_n$; specific extinction is plotted against $[\eta]^{0.715}$ (where the 0.715 is the reciprocal of the 1.40 exponent appearing in the transposed form of the equation) for each series—*i.e.*, the only assumptions involved are that the molar extinction coefficient of the naphthyl groups are approximately equal and that the $\bar{M}_n$ is *proportional* to $[\eta]^{1.40}$. The ratio of the slopes of the straight lines thus obtained is *ca.* 2.

Table V contains similar data on two bis-type carboxylic acid modifiers, bis-(4-carboxyphenyl) disulfide and bis-(4-carboxymethyl phenyl) disulfide, and on the thiol acid, β-mercaptopropionic acid. Again the two-to-one ratio of the concentration of analyzed groups in the series modified with the bis-type acids over that modified with the mono-acid is evident,

TABLE V

DETERMINATION OF CARBOXYL END GROUPS IN POLYMERS MODIFIED WITH DISULFIDE AND THIOL COMPOUNDS CONTAINING CARBOXYL GROUPS

Polymer No.	Parts modifier	% conv.	$[\eta]$	$\bar{M}_n \times 10^{-3}$ [a]		Transfer const., C	Ml. of 0.0070 N NaOCH$_3$/g. polymer [b]	No. of COOH groups per polymer molecule
				Obs.	Corr.			
Polymers modified with bis-(4-carboxyphenyl) disulfide								
2124-84-A*	None	8.3	1.31	275	—	—	(0.12)	—
-B*	1.21	12.0	0.77	130	247	0.10	1.10	1.91
-C*	1.62	12.0	0.70	113	192	0.10	1.69	2.27
-D*	2.40	12.1	0.58	86	125	0.10	2.26	1.98
Average								*2.05*
Polymers modified with bis-(4-carboxymethyl phenyl) disulfide								
2124-95-1*	None	8.5	1.16	230	—	—	(0.15)	—
-95-2*	0.69	11.6	0.72	117	239	0.20	1.19	2.10
-95-3*	0.89	10.5	0.65	102	183	0.20	1.53	2.09
-95-4*	1.25	9.2	0.53	76	114	0.23	2.19	1.85
Average								*2.01*
Polymers modified with β-mercaptopropionic acid								
2124-102-4	None	2.6	1.48	320	—	—	(0.14)	—
-1	0.0116	2.4	0.70	115	179	5.1	1.16	1.10
-2	0.0083	2.6	0.76	127	210	6.0	0.93	1.04
-3	0.0062	2.5	0.82	140	249	6.9	0.92	1.20
Average								*1.11*

* These runs employed 30 pts. pyridine to keep modifier in solution.

[a] Corrected for the contribution of the initiator to lowering of molecular weight as in Table IV, footnote *a*.

[b] Titrations conducted with 0.8 to 1.6 g. of polymer in 30 ml. benzene whose NaOCH$_3$ requirement of 0.10 ml. is subtracted from values tabulated. The titers of each of the acid group terminated polymers have been corrected for the titer of the control in its series.

TABLE VI

DETERMINATION OF AMINE END GROUPS IN POLYMERS MODIFIED WITH BIS-(2- OR 4-AMINOPHENYL) DISULFIDES

Expt. No.	Parts modifier/ 100 g. styrene[a]	[η]	$\overline{M}_n \times 10^{-3}$		Wt. of polymer titrated, g.	Ml. of 0.0056 N $HClO_4$ corr.[c]	NH_2 group per polymer molecule
			Uncorr.	Corr.[b]			
Polymers modified with bis-(4-aminophenyl) disulfide							
2051-139-1	0	1.53	340	—	0.25	(0.05)[c]	—
-2	3.68	0.24	25	27	0.2521	3.60	2.16
-3	1.84	0.38	48	56	0.3811	2.82	2.32
-4	1.15	0.51	72	91.3	0.4429	2.04	2.36
-5	0.81	0.60	91	124.2	0.5197	1.64	2.20
-6	0.59	0.72	117	178.5	0.5590	1.28	2.28
-7	0.44	0.80	137	230	0.6091	0.97	2.05
Average							2.23
Polymer modified with bis-(2-aminophenyl) disulfide							
2124-31 EL	0.36	0.22	22	23.5	0.2417	3.30	1.80

[a] All prepared with 0.05 part azoisobutyronitrile to *ca.* 7% conversion.

[b] Corrected for contribution of catalyst to the lowering of molecular weight, as in Table IV, footnote *a*.

[c] The value of 0.05 ml. obtained on run −1, plus another 0.05 ml. required to neutralize the benzene, was taken as a blank, and was subtracted from the observed titers to give the values reported. The amount of titrant required to give a marked end point change was 0.10–0.15 ml.

In Table VI are recorded the values obtained over a range of $\overline{M}_n$ for polymers modified with bis-(4-aminophenyl) disulfide and for a single polymer prepared with bis-(2-aminophenyl) disulfide. It is not known whether the somewhat lower value of amine groups/molecule obtained with the latter reflects differences which are actual, or is due simply to the greater difficulty of attaining reliable analyses for groups in the ortho posi-

TABLE VII

DETERMINATION OF THE CONCENTRATION OF BENZOTHIAZYL END GROUPS IN POLYMERS MODIFIED WITH DIBENZOTHIAZYL DISULFIDE

Polymer No.	Parts modifier/ 100 g. styrene[a]	[η]	$\overline{M}_n \times 10^{-3}$		Specific extinction coeff.[b]	Calcd. no. of benzothiazyl groups per polymer molecule
			Obs.	Corr.		
2051-106-C	0.32	0.35	43	48.5	0.613	2.36
-D	0.16	0.51	72	89.4	0.312	2.21
-E	0.08	0.74	113	162.5	0.162	2.09
-F	0.04	1.13	220	543	0.079	3.40[c]
Av. of runs C–E						2.24

[a] All polymers prepared to *ca.* 6% conversion with 0.05 part AIBN.

[b] Corrected for the specific extinction of polystyrene (0.026 at 285 mμ).

[c] This value may be in considerable error, due to the large correction required in the $\overline{M}_n$ for the P_0. It was noted that the calculated transfer constant for this run was appreciably lower than those of the first three, which agreed fairly well.

tion. No "reference" thiol with an amine group was available, unfortunately, but the necessity for its use, in the fashion that reference series with thiols were made for Tables IV and V, was considered greatly decreased by the further validation of the $\bar{M}_n$-$[\eta]$ expression of the latter two tables.

Analogous data for polymers modified with di-2-benzothiazyl disulfide are cited in Table VII. The very low level of modifier activity evinced by mercaptobenzothiazole, already referred to, vitiated the use of the latter compound for preparing a reference series here.

A situation distinctly different from that of the disulfides is encountered with the di-acid, carbonyl bis-(thioglycolic acid), $(HOOC\ CH_2S—)_2C=O$. It is evident from the data of Table VIII that not only is the transfer constant dependent on concentration, but so is the number of carboxyl groups which become incorporated per polymer molecule. The structure of this material precludes a reaction similar to that of equation (1), and it is not unlikely that more than one reaction is involved in the attack of this molecule by styryl radicals.

TABLE VIII

DETERMINATION OF TRANSFER CONSTANTS AND CARBOXYL GROUPS PER MOLECULE IN POLYMERS MODIFIED WITH CARBONYL BIS-(THIOGLYCOLIC ACID)

Polymer No.	Parts modifier/100 g. styrene[a]	$[\eta]$	$\bar{M}_n \times 10^{-3}$		Transfer constant, C	Wt. of polymer for titration, g.	Ml. of 0.0077 N $NaOCH_3$ corr.[b]	COOH groups per polymer molecule
			Obs.	Corr.				
2124-71-1	0.41	0.63	96	155	0.31	0.7490	0.66	1.06
-2	0.55	0.59	86	131	0.30	0.7508	1.10	1.48
-3	0.80	0.56	80	117	0.22	0.7050	1.35	1.75
-4	1.31	0.50	68	93.4	0.17	0.6550	1.16	1.82
-5	2.73	0.35	42	52.6	0.15	0.6578	2.83	1.75
-6	None	1.25	250	—	—	0.700	(0.43)	—

[a] 10 parts pyridine required to keep modifier in solution.

[b] All titrations carried out in 25 ml. benzene. The amounts shown are already corrected for the amount of titrant required for the polymer made without modifier (Run 6).

C. Effect of Polymerization Temperature on Transfer Constant

A tertiary and a primary thiol and four disulfides were used in polymerizations carried out at 25, 50, and 75°C. in order to find whether the chain transfer reaction with disulfides differed significantly in "apparent" activation energy from that of thiols. Since the transfer constant is the ratio of the rate constant of the transfer reaction to that of the propagation reaction, the "apparent" energy of activation of the transfer constant is actually the difference between the activation energies of the transfer and propagation reactions, $E_t - E_p$. These results are summarized in Table IX. The differences in transfer constants at the different temperatures were not great enough to warrant plotting in the usual form for calculation of apparent activation energies. However, it can be observed qualitatively

TABLE IX

EFFECT OF POLYMERIZATION TEMPERATURE ON TRANSFER CONSTANTS OF VARIOUS THIOLS AND DISULFIDES

Expt. No.	Modifier, pts.	Polymerization temp., °C.	Time, hrs.	% Conv.	$[\eta]$	$\overline{M}_n \times 10^{-3}$	C
2209-28-C-1	None	25	264	12	2.94	820	—
-C-2	"	50	16	12.3	1.10[a]	215	—
-C-3	"	75	1.1	11.2	0.51	72	—
-32-2C-1	"	25	96	1.6	2.70	740	—
-32-2C-2	"	50	4.25	2.7	1.21	240	—
-2C-3	"	75	0.30	3.0	0.51	72	—
-28-N-1	Di-2-naphthyl disulfide (1.64)	25	264	10.0	0.65	102	0.17
-N-2	"	50	16	12.5	0.49	68	0.19
-N-3	"	75	1.1	11.5	0.31	36	0.29
-28-T-1	Di-*o*-tolyl disulfide (0.91)	25	264	9.6	0.66	105	0.22
-T-2	"	50	16	12.4	0.48	66	0.28
-T-3	"	75	1.1	11.2	0.33	39	0.32
-30-A-1	Bis-(2-aminophenyl) disulfide (0.077)	25	192	5.8	0.53	76	3.8
-A-2	"	50	8	5.3	0.49	68	3.4
-A-3	"	75	0.51	5.3	0.35	43	3.0
-30-B-1	Dibenzothiazyl disulfide (0.146)	25	192	5.6	0.59	89	2.3
-B-2	"	50	8	5.3	0.49	68	2.3
-B-3	"	75	0.51	5.3	0.34	41	2.4
-30-S-1	*t*-DDM Sulfole (0.063)	25	192	5.8	0.59	89	3.2
-S-2	"	50	8	5.1	0.53	76	2.9
-S-3	"	75	0.51	5.3	0.37	47	2.4
-32-M-1	1-Mercaptomethyl naphthalene (0.0116)	25	96	3.2	0.65	102	12.7(?)
-M-2	"	50	4.25	2.8	0.45	61	18.3
-M-3	"	75	0.30	2.7	0.34	41	15.7

[a] Value unexplainably low. Dozens of previous runs generally gave $[\eta] = 1.21$–1.28 which is M_n of 240,000–260,000.

that the thiols will exhibit moderate negative apparent energies of activation, agreeing with the observations of Gregg *et al.*[36] The bis-(4-aminophenyl) disulfide, having a transfer constant approximately the same as Sulfole, has about the same low negative activation energy, though the dibenzothiazyl disulfide, having a transfer constant in the same range, appears to have no apparent activation energy at all. Only the two disulfides with comparatively low transfer constants, di-*o*-tolyl disulfide and di-2-naphthyl disulfide, have positive apparent energies of activation, and these are of low order.

CONCLUSIONS

The results on the effectiveness of modifiers of the few bis-type structures that have been examined in this preliminary investigation would confirm that the aryl disulfides would appear to offer much more promise than alkyl disulfides as means of incorporating desired end groups. It has been demonstrated for various aryl disulfides that the cleavage mechanism on attack by styryl radicals is such that one-half of the molecule becomes incorporated onto each end of the polymer molecule. The polymerization temperature does not affect the transfer constant appreciably.

The effects of a number of additional structures—largely, derivatives of diphenyl disulfide—are described in another paper.[1]

We are indebted to R. J. Coleman for the osmotic molecular weight information in Table I. A. F. Hardman supplied several of the highly purified compounds that also have uses as vulcanization accelerators. We thank G. E. Meyer for the analyses on mercaptan purity. The preparations of bis-(4-aminophenyl) disulfide, and bis-(4-carboxymethyl phenyl) disulfide were by Charles King of the University of Illinois, and are described in another paper.[1]

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Synopsis

Modifiers with bis-type structures are of interest as a means for conferring reactive groups onto the highest possible fraction of polymer chain ends. Various disulfides and other bis-type compounds—some with reactive groups attached—were compared as to their effectiveness as modifiers in low conversion bulk styrene polymerizations and studies made of their mechanism of cleavage. Alkyl disulfides of primary thiols had transfer constants too low to be of much interest for this work, even when substituted at carbons near the sulfur-sulfur bond. Aryl disulfides proved to have much higher transfer constants, and substitution on each ring with appropriate groups offered a means both of increasing the transfer constant and of incorporating desired groups.

It has been shown quite conclusively that aryl disulfides cleave so as to confer one-half the molecule onto each end of the polymer. This was demonstrated by analyzing the end group concentrations of styrene polymers of wide molecular weight range which contained various types of end groups—carboxyl, amino, naphthyl, and benzothiazyl—and comparing, wherever possible, with polymers modified with thiols containing similar groups.

Polymerizations carried out at 25, 50, and 75 °C. with certain of the bis-type compounds and with a normal and a tertiary mercaptan showed that activation energies are very slight if the transfer constant is high, and begin to reach significant levels only at low levels of transfer constant.

Résumé

Les modificateurs à structure symétrique double sont intéressants par ce qu'ils permettent d'introduire des groupes terminaux au plus grand nombre possible de molécules de polymère. Différents disulfures et autres composés doubles—dont certains munis de groupes réactionnels—ont été comparés entre eux du point de vue de leur efficacité comme modificateurs des polymérisations en bloc du styrène (aux faibles degrés de conversion) et du point de vue de leur mécanisme de rupture. Les disulfures d'alcoyles de thiols primaires présentent des constantes de transfert trop faibles pour entrer en ligne de compte dans ce travail, même s'ils sont substitués au carbone voisin de la liaison soufre-soufre. Les disulfures d'aryle ont des constantes de transfert plus élevées, et la substitution à chaque noyau par des groupes appropriés permet d'accroître la constante de transfert et également d'introduire les groupes désirés. On a montré ainsi que les disulfures d'aryles se cassent à telle enseigne qu'une demi-molécule se retrouve à chaque extrémité des polymères. Ceci a été démontré en analysant la concentration en groupes terminaux des polymères styréniques présentant une grande gamme de poids moléculaire et contenant différents types de groupes terminaux, savoir carboxylique, aminé, naphtylé et benzothiazyle, et en les comparant, si possible, avec les polymères modifiés avec les thiols contenant des groupes identiques. Les polymérisations effectuées à 25, 50 et 75 °C en présence de certains dérivés à structure symétrique double et avec des mercaptans normaux et tertiaires indiquent que les énergies d'activation sont très faibles si les constantes de transfert sont élevées, et n'atteignent des valeurs appréciables qu'aux faibles constantes de tranferts.

Zusammenfassung

Modifikationsmittel mit bis-Typus Strukturen sind von Interesse als Mittel, um reaktive Gruppen an die höchstmögliche Fraktion von Polymerkettenenden anzufügen. Verschiedene Disulfide und andere Verbindungen vom bis-Typus—einige mit angeschlossenen reaktiven Gruppen—wurden auf ihre Wirksamkeit als Modifikationsmittel in Block-Styrol-Polymerisationen von niedriger Konversion verglichen, und es wurden Untersuchungen ihres Spaltungsmechanismus ausgeführt. Alkyldisulfide primärer Thiole hatten zu niedrige Ubertragungskonstanten, um für dise Arbeit von viel Interesse zu sein, auch wenn sie an den Kohlenwasserstoffen nahe der Schwefel-Schwefel-Bindung substituiert wurden. Aryldisulfide zeigten viel höhere Transferkonstanten, und Substitution an jedem Ring mit geeigneten Gruppen ergab ein Mittel sowohl zur Erhöhung der Transferkonstante als auch zur Einführung gewünschter Gruppen. Es wurde ziemlich endgültig gezeigt, dass sich Aryldisulfide spalten, sodass sie eine Hälfte des Moleküles an jedes Ende des Polymers abgeben können. Dies wurde durch Analyse der Endgruppenkonzentrationen von Styrolpolymeren von weitem Molekulargewichtsbereich gezeigt, welche verschiedene Typen von Endgruppen enthielten—Carboxyl, Amino, Naphthyl und Benzothiazyl—und durch Vergleich, wo dies möglich war, mit Polymeren, die mit Thiolen, die ähnliche Gruppen enthielten, modifiziert worden waren. Bei 25, 50 und 75 °C ausgeführte Polymerisationen mit einigen der bis-Typus-Verbindungen und mit einem normalen und einem tertiären Merkaptan zeigten, dass die Aktivationsenergien sehr klein sind, wenn die Transferkonstante hoch ist, und dass sie erst bei niedrigem niveau der Transferkonstante anfangen, ein erhebliches Niveau zu erreichen.

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