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Bis-Type Modifiers in Polymerization. II. Comparison of Effectiveness of Various Compounds in Emulsion Butadiene and Bulk Styrene Polymerizations*

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INTRODUCTION AND PURPOSE

The present paper evaluates further the effects of structure and of incorporation of functional groups onto compounds of bis-type structure when used as modifiers in the bulk polymerization of styrene and in emulsion polymerization of butadiene. The general objective of this work, which is similar to objectives which have been set forth in detail elsewhere,[1,2] is the screening of compounds which may serve to incorporate desired functional groups onto the highest possible fraction of the chain ends of elastomeric polymers. Elastomers with end groups which can be reacted after polymer formation are of interest in efforts to determine what improvement in resilience and other properties of the network results from elimination of the so-called "free end fraction."

Although the principal impetus for the use of modifiers containing functional groups has been based on the improvement of high diene emulsion polymers, the evaluation in bulk styrene was continued because of the value of this method in affording a quantitative rating of modifier effectiveness, and because such ratings could be obtained under conditions where diffusion properties were not a factor. These advantages are not attainable in any single standard screening evaluation method that might be selected for high diene emulsion polymerizations, and hence the chief usefulness of the information gained from the bulk styrene data is to know whether or not it is worth while to seek emulsion polymerization conditions which attain the maximum efficiency from a modifier, such as by the use of charging or other conditions which tend to increase or retard the over-all diffusion rate of the modifier. This approach is based on the thesis that the reactivity of various radicals with styrene and with butadiene, and of the radicals of these monomers with compounds capable of yielding radicals,

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is generally similar. The latter thesis seems to have been well supported in the considerable literature on monomer reactivity ratios, and also by the present work.

EXPERIMENTAL

A. Bulk Styrene Polymerizations

The units, parameters measured, and techniques are the same as those employed in the companion paper.[1] It will be noted that some pyridine was necessary in a few of the bulk polymerizations in order to keep the modifier in solution; the contribution of the pyridine to lowering of $\bar{M}_n$—which was very slight—has been taken account of in the P_0.

No attempt has been made to calculate transfer constants less than 0.01; modifiers of such low transfer constants are not of interest for the present purposes, and those compounds having no detectable effect on $\bar{M}_n$ are simply listed as <0.005, the approximate lower limit of accuracy of this method of evaluation.

B. Butadiene Emulsion Polymerizations

The initial evaluations were carried out at 50°C. in a variant of the Mutual formula at the standard 70–80% conversion. Since many compounds were showing no modifier activity where, from the results obtained in bulk styrene tests, some activity was anticipated, a method was devised which minimized the effects of the diffusion factor in retarding the rate of modifier consumption. This involved adding a solution of the modifier in twenty parts of a water-soluble solvent to the remainder of the aqueous phase (including soap) prior to charging, so as to yield a fine particle size dispersion of the modifier. This was done just before adding butadiene, so that the polymerization bottle could be placed on the bath promptly. The three solvents tried with each modifier were pyridine, isopropanol, and acetone. The few modifiers which were evaluated in a cold recipe were also charged in this manner, using isopropanol only.

That the predispersion of modifier in the aqueous phase, and not the solvent used for it, was the important feature in enhancing the apparent modifier activity of slow-diffusing compounds was shown in some separate runs (not shown in Table II) with *n*-hexadecyl mercaptan, where introduction of this mercaptan by the predispersing technique using 20 parts of isopropanol gave a 27% conversion polymer of 100% solubility whereas addition of the modifier in the monomers to a charge containing the same amount of isopropanol gave a polymer that was 27% soluble and had a gel of SV = 50 (compared with 5% soluble and SV = 19 for a control with no solvent and no predispersion).

Each of the solvents used, in the absence of modifier (Table III), appears to contain impurities which contribute very slightly to the over-all modification process.

The polymerization recipes used were as follows (all using a 20 g. monomer charge in 4 oz. screw cap bottles):

Recipe A (50°C.)

Butadiene	100 parts
Water (or water plus solvent)	200 "
OSR Soap Flakes	5.0 "
Bis-azoisobutyronitrile (AIBN)	0.3 "
Modifier	Varied (usually 1.0)

Recipe B (50°C.). Same as recipe *A*, except 5.0 parts of Duponol G, a sodium alkyl sulfonate type emulsifier, used in place of OSR Soap Flakes.

Recipe C (50°C.)

Butadiene	100 parts
Water (or water plus solvent)	200 "
Diazoaminobenzene	1.0 "
Hydroquinone	0.5 "
Duponol G	5.0 "
Modifier	Varied (usually 1.0 part)

Recipe D (5°C.)

Butadiene	100 parts
Water	200 "
Dresinate 214	2.25 "
KOSR Soap Flakes	2.25 "
Tamol N	0.15 "
$Na_3PO_4 \cdot 12H_2O$	0.5 "
$FeSO_4 \cdot 7H_2O$	0.10 "
$K_4P_2O_7$	0.12 "
p-Menthane hydroperoxide	0.15 "
Modifier	Varied (see Table III)

Except for the method of adding modifier, noted above, the charging techniques followed conventional practices.

In isolating the polymers, the latices were coagulated in alcohol containing phenyl-β-naphthylamine, and dried at moderate temperature (75°C.) in an air oven. The dried crumb was given four or five passes through a coarsely set mill with equal speed rolls in order to "mass" the microgel. Experience showed that unless this were done, polymers which by appearance and feel were known to be very high in gel content would apparently be completely soluble, though giving turbid "solutions." Tests showed the mill treatment to have negligible degrading effects on soluble polymers. The solubility and swell volume of the gel were obtained by conventional techniques.

Since the information gained from the evaluations in emulsion butadiene polymerization does not lend itself to expression in a single quantitative value which would be analogous to the transfer constant derived from the bulk styrene measurements, the following arbitrary rating system was devised, based on the comparative effectiveness of a compound:

Excellent—equivalent to, or nearly so, the best results obtainable with C_{16} mercaptan by predispersing.

Good—100% soluble, DSV's of less than 2.5 when 1.0 part modifier used.

Fair—from 50 to 100% soluble.

Slight—20–50% soluble.
None—not significantly better than control.

In listing results in Tables II and III, the ratings obtained under conditions giving less than maximum effectiveness attained are indicated in parentheses.

C. Preparations

Bis-(4-aminophenyl) Disulfide

Bis-(4-aminophenyl) disulfide (m.p. 77–78°C.) was prepared according to the method of Price and Stacey.[3]

Dibenzyl Disulfide

A sample of dibenzyl disulfide from a supply available in the University of Illinois Laboratory was recrystallized from ethanol to give white crystals, m.p. 74–75°C.

Dithiosalicylic Acid (Bis-(2-carboxyphenyl) Disulfide)

Dithiosalicylic acid was prepared according to the method of Allen and MacKay.[4] Recrystallization of the crude acid from dioxane yielded granules, m.p. 289–292°C.

Dibenzoyl Disulfide

Dibenzoyl disulfide was prepared according to the method of Shelton and Rider.[5] Three recrystallizations of the crude disulfide from ethanol yielded white solid, m.p. 134–135°C.

Di-o-nitrophenyl Disulfide

Di-*o*-nitrophenyl disulfide (m.p. 193–194.5°C., recrystallized from dioxane) was prepared according to the procedure of Bogert and Stoll.[6]

Di-tert-butyl Disulfide

Di-*tert*-butyl disulfide was prepared by oxidation of *tert*-butyl mercaptan according to the method of Rheinboldt.[7] A sample, twice distilled, had the following properties b.p. 75.5–76°C. at 10 mm.; $n_D^{20.5} = 1.4898$.

Di-sec-butyl Disulfide

Analogously, di-*sec*-butyl disulfide, b.p. 91°C. at 10 mm., $n_D^{20} = 1.4927$, was prepared by oxidation of *sec*-butyl mercaptan.

Tetraphenylsuccinodinitrile

This compound was prepared according to the method of Auwers and Meyer.[8] 23 grams (1 mole) of freshly cut sodium was dissolved in 2 l. absolute ethanol. To the stirred solution was added in portions 193 g. (1 mole) of diphenylacetonitrile[9] followed by 128 g. (0.5 mole) of iodine in 1 l. of absolute ethanol. At the end of the addition, the white solid which had formed was collected on a filter and washed several times with water and then with hot alcohol. A white powdery substance melting at 188–190°C. was obtained. This powder was triturated six times with hot distilled water and hot alcohol. When dry the material melted at 210–212 °C. with sintering at 208 °C. Yield, 180 g. 96%.

ANALYSIS: *Calcd. for* $C_{28}H_{20}N_2$, C, 87.50; H, 5.21; N, 7.29. *Found,* C, 87.57; H, 5.10; N, 7.22.

Hexacarboethoxyethane

A sample of crude hexacarboethoxyethane (m.p. 75–85 °C.) available at the University of Illinois was triturated thoroughly with three portions of boiling petroleum ether. This treatment served to extract an impurity smelling somewhat like ethyl malonate, possibly tricarboethoxyethane. The nearly odorless white solid was dissolved in hot commercial absolute ethanol and recrystallized therefrom as a powdery white solid, m.p. 106–107 °C.

ANALYSIS: *Calcd. for* $C_{20}H_{30}O_{12}$, C, 51.96; H, 6.55. *Found,* C, 52.14; H, 6.67.

Dimesityl Disulfide

Dimesityl disulfide was prepared according to the method of Holtmeyer.[10] 80 grams of mesitylenesulfonic acid dihydrate[11] was heated under reduced pressure for three hours over a steam cone. 100 grams of phosphorus pentachloride was added portionwise, and the dark liquid heated for another hour. The dark mass was poured onto ice, and the grayish solid which formed was collected on a filter. Recrystallization from ether yielded 40 g. of mesitylenesulfonyl chloride, white crystals, m.p. 60 °C. (*cf.* Holtmeyer, m.p. 57 °C.), yield 45%. (The low yield was probably due to the prolonged heating of the acid dihydrate, which causes its hydrolysis to mesitylene.)

30 grams (0.138 mole) of mesitylenesulfonyl chloride was added to a cold mixture of 300 g. of ice and 52 ml. of concentrated sulfuric acid. The temperature was maintained at −5 to 0 °C. while 70 g. of zinc was added portionwise, with stirring. Steam distillation of the reaction mixture yielded an oil, which was taken up in ether and dried over anhydrous sodium sulfate. After removal of the ether by distillation, the oil was treated with an excess of methanolic iodine. The resulting solid, dimesityl disulfide, was recrystallized from ethanol: m.p. 125 °C. (*cf.* Holtmeyer, m.p. 125 °C.); yield 5 g., 37%.

Di-p-anisyl Disulfide

14 grams (0.1 mole) of *p*-methoxythiophenol,[12] b.p. 78–81 °C./5.0 mm., n_D^{20} 1.5826, was added to a solution of 4 g. of sodium hydroxide in 100 ml. of ethanol. Iodine, 12.8 g., was added portionwise to the boiling solution. When all had been added the solution was heated under reflux for two hours. The solution was concentrated by distillation and washed with sodium bisulfite solution. The oil obtained was dissolved in ether and dried over anhydrous sodium sulfate. Evaporation of the ether left an oil which could not be recrystallized from a number of solvents. Distillation under reduced pressure yielded 10 g. of a viscous liquid which crystallized after standing overnight at 0 °C. This solid was recrystallized from petroleum ether to give 7 g. of white crystalline solid, m.p. 44–45 °C.

Bis-(2-hydroxymethyl-phenyl) Disulfide

o-Mercaptobenzoic acid (15.0 g., 0.1 mole, Eastman technical grade, m.p. 163 °C.) was reduced with 7 g. of lithium aluminum hydride in 500 ml. of anhydrous ether. The Soxhlet technique was used, and the reaction allowed to proceed overnight. Excess hydride was decomposed with water, and 10% HCl was added to the stirred mixture to decompose the complex. The ether layer was separated, washed twice with water, and dried with anhydrous Na_2SO_4. The filtered ether solution was concentrated to *ca.* 150 ml., and 12.7 g. (0.05 mole) of iodine added. The mixture was heated over a steam cone for an hour with occasional stirring, the solution cooled, and then shaken with saturated sodium bisulfite solution to remove iodine. The solid remaining after removal of ether was recrystallized from aqueous ethanol to give a white solid, m.p. 137–138 °C., yield 8 g., 57%.

ANALYSIS: *Calcd. for* $C_{14}H_{14}S_2O_2$, C, 60.38; H, 5.08. *Found*, C, 60.41; H, 5.16.

Further recrystallization from aqueous ethanol in the Goodyear Laboratory yielded crystals melting at 141.6–142.6 °C. (The melting point of this compound, as prepared by Reichert and Crämer, *Ber.*, **B61**, 2555–66, 1928, in 73% yield, by coupling diazotized 2-aminobenzyl alcohol with sodium disulfide and recrystallized from benzene, was 144 °C.)

Bis-(4-carboxymethyl-phenyl) Disulfide

Sodium sulfide nonahydrate (52.8 g., 0.22 mole) was dissolved in 60 ml. of boiling water; to the solution was added, portionwise, 7 g. of sulfur (0.22 mole). Boiling was continued until a dark red-brown viscous solution was obtained. To the solution was added 8 g. of sodium hydroxide (0.20 mole) dissolved in 40 ml. of water. The solution was cooled to 3 °C.

p-Aminophenylacetic acid (30.2 g., 0.20 mole) was mixed with 40 ml. of concentrated hydrochloric acid and 200 ml. water. The solution was cooled to 3 °C. To the stirred suspension was added, in portions, a solution of 17 g. of sodium nitrite in 56 ml. of water cooled to 3 °C. The temperature was maintained between 0 and 4 °C. by addition of pieces of ice. The diazo solution so prepared gave an immediate test with potassium iodide-starch paper.

The diazo solution was maintained at 3 °C. and added, with stirring, to the alkaline sodium disulfide solution. Throughout the addition the temperature was maintained between 0 and 4 °C. by adding ice when necessary. The frothing solution was allowed to stand for five minutes in an ice bath and then at room temperature for two hours. The solution was separated from solid material by filtration and then acidified with concentrated hydrochloric acid to Congo red. The precipitate was collected on a filter, washed with water, and dissolved with saturated potassium carbonate solution. The solution was again filtered from residual sulfur and re-acidified with hydrochloric acid to Congo red to give a pink solid, which was washed with water until the washings gave a neutral test with litmus paper. The product was dried as completely as possible on a suction filter and then spread out to dry. The crude product so obtained weighed 26 g., m.p.

175–183 °C. Treatment with decolorizing charcoal and recrystallization from aqueous methanol raised the melting point to 196–197 °C.

ANALYSIS: *Calcd. for* $C_{16}H_{14}S_2O_4$, C, 57.46; H, 4.18; S, 19.16. *Found,* C, 57.22; H, 4.40; S, 19.06.

A molecular weight determination by the Rast camphor method indicated a molecular weight of 333; the theoretical value is 334.

Bis-(10-carbomethoxy-n-decyl) Disulfide

A. Methyl Undecylenate. 368 grams of undecylenic acid (EKC) was dissolved in 600 ml. of methanol. 10 ml. of sulfuric acid was added slowly, with shaking, and the mixture refluxed overnight. Excess methanol was removed by distillation at reduced pressure; the residue was neutralized with saturated sodium bicarbonate solution and then washed twice with water. The ester was dried over anhydrous sodium sulfate. Fractionation at reduced pressure yielded 300 g. of methyl undecylenate, b.p. 124–125 °C. at 10 mm.; n_D^{20} 1.4390; 80% yield.

B. Methyl 11-Thioacetoxyhendecanoate. In a 200-ml. round-bottomed quartz flask were placed 59.4 g. (0.3 mole) of methyl undecylenate and 22.8 g. (0.3 mole) of thiolacetic acid. After several minutes the mixture began to get warm, and the flask was cooled under running water. The evolution of heat ceased after about five minutes, and 0.5 ml. of acetone was added. The cloudy solution was irradiated under an ultraviolet lamp for six minutes. The mixture solidified after being cooled in an ice bath. The solid was triturated with saturated sodium carbonate solution and then three times with water. The crude product melted at 30–34 °C. A small portion which was recrystallized three times from methanol melted at 39–40 °C. The bulk of the ester was used in the next step with no further purification.

ANALYSIS: *Calcd. for* $C_{14}H_{26}O_3S$, C, 61.26; H, 9.57; S, 11.68. *Found,* C, 61.30; H, 9.73; S, 11.62.

C. Lead Salt of Methyl 11-Mercaptohendecanoate. The crude methyl 11-thioacetoxyhendecanoate formed above was dissolved in 300 ml. of methanol. 2 ml. sulfuric acid was added, and the mixture was refluxed overnight. After the theoretical amount of methanol-methyl acetate azeotrope, b.p. 53–55 °C., had been removed by fractionation through a 12 in. packed column, the volume was reduced to about 200 ml. by distillation of methyl alcohol. The cooled methanolic solution was neutralized with 3.5 g. of sodium bicarbonate and then poured into 200 ml. of cold water. The oil which separated was washed twice with cold water and then added dropwise, with stirring, to a boiling methanolic solution of 114 g. (0.3 mole) of lead acetate trihydrate in 300 ml. of methanol. A light brown solid separated in clumps. The mixture was diluted to about 1500 ml. with methanol, and digested for two hours on a steam bath. The now yellow solid was then collected on a filter. It was washed several times with cold water, and then five times with hot acetone, until no more material appeared to dissolve. After washing twice with anhydrous ether and drying, the lead salt was obtained as a golden-yellow, free flowing powder, m.p. 93–97 °C., 65 g. (69% yield).

D. Bis-(10-carbomethoxy-n-decyl) Disulfide. 20 grams (0.3 mole) of the lead salt of methyl mercaptohendecanoate was dissolved in 600 ml. of glacial acetic acid in a 1-l., 3-necked, round-bottomed flask equipped with mechanical stirrer, reflux condenser, and dropping funnel, and the mixture was heated to 80 °C. The solution had a gray-black appearance. 9 grams of iodine dissolved in 250 ml. glacial acetic acid was added dropwise to the stirred, heated (80–90 °C.) solution. Lead iodide precipitated during the addition, which required forty-five minutes. The mixture was stirred and heated for two more hours. The hot acetic acid solution was filtered rapidly with suction. The filtrate was poured into 1 l. of cold water, and the white solid which separated was collected on a filter. Recrystallization from glacial acetic acid yielded 12.5 g. (92%) of white crystals, m.p. 55–56 °C.

ANALYSIS: *Calcd. for* $C_{24}H_{46}S_2O_4$, C, 62.34; H, 9.96; S, 13.85. *Found*, C, 62.18; H, 10.14; S, 13.57.

Bis-(4-carboxy-2-aminophenyl) Disulfide

A. 4-Bromo-3-nitrobenzoic Acid. 200 grams (1 mole) of *p*-bromobenzoic acid (EKC White Label) was suspended in 350 ml. of concentrated sulfuric acid in a 2-l. 3-necked flask equipped with dropping funnel, mechanical stirrer, and thermometer. The suspension was then cooled in an ice bath to about 10 °C. A mixture of 83 ml. of concentrated nitric acid and 83 ml. of concentrated sulfuric acid was added dropwise to the stirred suspension, the temperature being maintained between 10 and 20 °C. After completion of the addition the white pasty mass was stirred for two hours more and then poured, with stirring, onto ice. The solid which separated was collected on a filter and recrystallized from ethanol-water mixture to yield 235 g. of 4-bromo-3-nitrobenzoic acid (m.p. 194–197 °C.) in 92% yield.

B. Bis-(4-carboxy-2-aminophenyl) Disulfide. In a 1-l. round-bottomed flask was dissolved 24.6 g. (0.1 mole) of 4-bromo-3-nitrobenzoic acid in 500 ml. of water containing four grams of sodium hydroxide. Sodium sulfide nonahydrate (63.5 g., 0.26 mole) was added to the solution with shaking, and the resulting solution was heated overnight over a steam cone. The dark red solution was transferred to a 1-l. 3-necked flask equipped with mechanical stirrer, dropping funnel, and thermometer. The stirred solution was heated to 60 °C., and 17 ml. of 30% hydrogen peroxide was added dropwise. After completion of the addition the solution was stirred at 60 °C. for an hour more. The light brown solution was then separated from a small amount of solid by filtration and acidified to Congo red end point with about 20 ml. of concentrated hydrochloric acid. The crude yellow product which separated was collected on a filter. It was soluble in both acid and alkali, and when dry melted at 180–193 °C. Treatment with decolorizing charcoal (Darco) and recrystallization from aqueous ethanol: light yellow solid (m.p. 224–226 °C., 15.4 g.) in 46% yield.

A sample recrystallized several times from aqueous ethanol melted at 227–229 °C.

ANALYSIS: *Calcd. for* $C_{14}H_{12}O_4N_2S_2$, C, 49.90; H, 3.60; S, 19.06; N, 8.33. *Found,* C, 50.07; H, 3.93; S, 18.95; N, 8.36.

Molecular weight, as determined by the Rast camphor method, was 352. The calculated value is 336.

Bis-(4-carboethoxyaminophenyl) Disulfide

8 grams of bis-(4-aminophenyl) disulfide was dissolved in 300 ml. of dry benzene and mixed with 15 ml. of ethyl chloroformate. An almost immediate precipitation of nearly white solid formed. Recrystallization from ethanol yielded white crystals, m.p. 140–142 °C. An analytical sample melted at 141–142 °C.

ANALYSIS: *Calcd. for* $C_{16}H_{20}O_4N_2S_2$, C, 55.07; H, 5.15; N, 7.14; S, 16.34. *Found,* C, 55.27; H, 5.37; N, 7.30; S, 16.10.

Bis-(4-n-dodecylaminophenyl) Disulfide

A. Bis-(4-n-dodecanoylamidophenyl) Disulfide. 100 grams of lauric acid (0.50 mole) (Eastman), m.p. 44–45 °C., was dissolved in 100 ml. of thionyl chloride and refluxed overnight. Excess thionyl chloride was removed by distillation at reduced pressure and 50 g. (0.21 mole) of bis-(4-aminophenyl) disulfide, m.p. 75–76 °C., was added, with shaking, to the dark brown acid chloride. A tan solid soon formed; the mixture was heated with occasional shaking over a steam cone for one hour. The tan solid was triturated several times with ether and then with ethanol; it was then dissolved in dimethyl formamide, treated with decolorizing charcoal, and recrystallized thereform. The nearly white sample was completely decolorized by trituration with ethanol; yield 44 g. 72%; m.p. 179–180 °C. An analytical sample melted at 181–182 °C.

ANALYSIS: *Calcd. for* $C_{36}H_{56}N_2O_2S_2$, C, 70.54; H, 9.22; N, 4.57. *Found,* C, 70.10; H, 9.10; N, 4.47.

B. Bis-(4-n-dodecylaminophenyl) Disulfide. 26 grams of bis-(4-*n*-dodecanoylamidophenyl) disulfide was reduced with 6 g. of lithium aluminum hydride in tetrahydrofuran. Oxidation of the reaction product with 7 g. of iodine gave bis-(4-*n*-dodecylaminophenyl) disulfide which, after recrystallization from 95% ethanol, melted at 63–64 °C.; yield 7 g., 30%.

ANALYSIS: *Calcd. for* $C_{36}H_{60}N_2S_2$, C, 73.89; H, 10.36; N, 4.78. *Found,* C, 73.75; H, 10.25; N, 4.84.

Bis-(2,4,6-triisopropylphenyl) Disulfide

A. 2,4,6 - Triisopropylphenyl Mercaptan. Triisopropylbenzenesulfonyl chloride, m.p. 135–137 °C. (anilide found to contain 3.66% N; calcd. for $C_{21}H_{29}NO_2S$, 3.90% N), 18.37 g., was mixed with 10.6 g. of potassium iodide, 5.0 of red phosphorus, and 106 ml. of phosphoric acid. The mixture was heated, slowly at first, since at one stage the reaction became most vigorous, depositing much iodine in the reflux condenser. When the reaction abated somewhat the mixture was heated to reflux and maintained at reflux for six hours. The nearly clear mixture was cooled and extracted twice with ether. The dried ether solution was concentrated and distilled at reduced pressure. 2,4,6-Triisopropylphenyl mercaptan, 10.46 g. (70%), b.p. 76–85 °C. at 0.3 mm., $n_D^{20.3}$ 1.5324, was obtained as a clear, viscous oil. Two fractionations afforded material boiling at 81 °C. at 0.2 mm. and having an index of refraction n_D^{20} 1.5335.

Analysis: *Calcd. for* $C_{15}H_{24}S$, C, 76.19; H, 10.25; S, 13.56. *Found*, C, 76.00; H. 10.02; S, 13.52.

Infrared absorption indicated the presence of —SH (3460 cm.$^{-1}$) and isopropyl (1370, 1398^{-1}) groups.

B. Bis - (2,4,6-triisopropylphenyl) Disulfide. 2,4,6-Triisopropylphenyl mercaptan, 10.46 g., was dissolved in 70 ml. of methanol containing 1.82 g. of sodium hydroxide. To this solution was added 5.75 g. of iodine. 10 ml. of water was added, and the mixture stirred for ten minutes, during which time the color of iodine disappeared and a yellowish oil separated. After standing overnight the oil solidified, and when dry weighed 10.02 g. After four recrystallizations from methanol nearly white solid was obtained, 7.5 g. (67%), m.p. 79.0–79.5 °C.

Analysis: *Calcd. for* $C_{30}H_{46}S$, C, 76.52; H, 9.86; S, 13.62. *Found*, C, 76.62; H, 9.98; S, 13.57.

The sources or preparations used for diphenyl disulfide, di-*o*-tolyl disulfide, di-*p*-tolyl disulfide, bis-(4-carboxyphenyl) disulfide, bis-(4-carboethoxyphenyl) disulfide, bis-(2-aminophenyl) disulfide, carbonyl bis-(thioglycolic acid), and bis-(4-hydroxymethylphenyl) disulfide are described in another paper.[1] The di-α-naphthoyl disulfide was a preparation of Frank and co-workers.[22] The bis-(2-carboethoxyphenyl) disulfide was prepared by A. H. Weinstein, who esterified the acid by conventional procedures to yield white crystals, m.p. 118.7–119.7 °C. The di-2-pyridyl disulfide (m.p. 57–58 °C.), di-2-quinolyl disulfide (m.p. 131–132 °C.), and di-2-lepidyl disulfide (m.p. 165–166.5 °C.) were prepared by R. Leshin of the Goodyear laboratory.

RESULTS AND DISCUSSION

Table I lists the intrinsic viscosities, $\bar{M}_n$ values, and calculated transfer constants of the modifiers when evaluated in 50 °C. bulk styrene polymerizations. For the sake of completeness in making comparisons, some of the compounds prepared and evaluated in another paper[1] are also included in Table I. Table II depicts the results obtained with the various modifiers in 50 °C. emulsion butadiene polymerizations; however, in order to restrict the information to comprehensible proportions, only the results obtained with the most effective of the predispersing solvents are listed. For comparison, Table II also includes some of the results obtained at both low and high conversion in the absence of a predispersing solvent. Table III shows data on a few of the modifiers evaluated in a 5 °C. iron-pyrophosphate emulsion formula with butadiene.

As pointed out in the introduction, the chief purpose of acquiring information in bulk styrene polymerization was that it offered the only means of obtaining a simple quantitative measure of modifier effectiveness under conditions where diffusion effects could play no part, and would thus be valuable in guiding efforts to attain the maximum efficiency from modifiers of various structure in emulsion polymerization. That the effectiveness of a modifier in emulsion polymerization is a function both of its reactivity to the attacking polymer radical and of its diffusing properties was pointed out early by Reynolds[13] who coined the term "diffox product." Various experimental investigations with mercaptans have borne out this concept.[14-17] The ease with which it is possible to adjust charging conditions, agitation, or other factors to obtain mercaptan disappearance curves which are either concave or convex toward the conversion axis in standard cold recipes was shown in a recent investigation,[16] and is amply illustrated at the end of Table II, where *n*-hexadecyl mercaptan—traditionally considered a "poor" modifier—is converted to a "good" modifier by simply predispersing it. In the present work, it was not feasible to make for each modifier an exhaustive investigation of conditions in the emulsion polymerization of butadiene which produced maximum effectiveness, so that the data obtained in emulsion polymerization might be subject to some considerable improvement for those modifiers whose structures will warrant further investigation in this program.

With these qualifying remarks in mind, some comments which can be made on the data of Tables I to III are as follows:

Disulfides of substituted *n*-alkyl mercaptans failed to show any activity in either bulk styrene or emulsion butadiene polymerization, confirming the results obtained in an earlier paper and by others.[1,18,19]

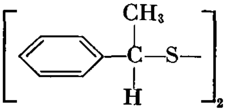
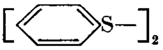
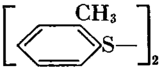
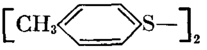
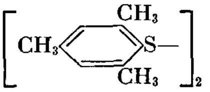
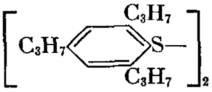
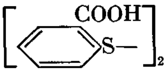
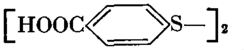
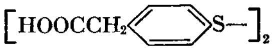
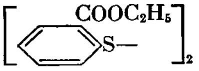
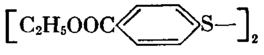
Disulfides of secondary and tertiary butyl mercaptans likewise did not show significant activity, and hence no disulfides of other secondary or tertiary mercaptans were prepared.

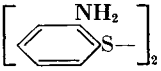
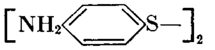
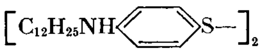
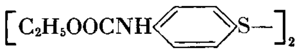
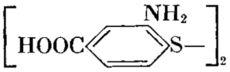
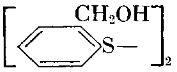
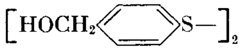
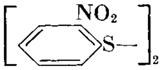
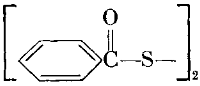
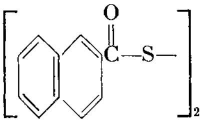
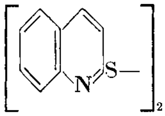
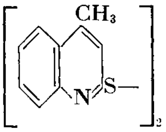
The low transfer constant obtained with dibenzyl disulfide in bulk styrene proved to be of the same order as that reported by Gregg and Mayo,[19] and the comparative absence of activity in emulsion butadiene polymerization made it apparent that the preparation of ring substituted derivatives would appear to hold little promise. The lack of any significant activity with the modifier derived from substituting a methyl group on the methylene carbons of benzyl disulfide, bis-(α-phenethyl) disulfide, was rather surprising in view of the evidence for some slight activity (in bulk styrene) for benzyl disulfide itself.

Symmetrically methyl substituted derivatives of phenyl disulfide show increased activity over phenyl disulfide itself, with substitution of one group in the ortho position showing more effect than substitution in the para position, and a quite high activity being attained when both of the ortho positions and the para position are filled (dimesityl disulfide). When isopropyl groups are incorporated in place of the methyl groups of dimesityl disulfide (*cf.* results on bis-(2,4,6-triisopropylphenyl) disulfide), the modify-

TABLE I

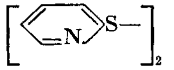
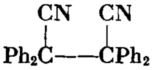
Transfer Constants of Bis-Type Compounds in 50°C. Bulk Styrene Polymerization

Expt. No.	Compound[a]	% convn. 17 hrs. at 50°C.	$[\eta]$	$\overline{M}_n$ $\times 10^{-3}$	Transfer constant, C
	None—0.1 AIBN	11–12	1.21– 1.28	240– 260	—
2051-74B	Bis-(10-carbomethoxy-*n*-decyl) disulfide $[CH_3OOC(CH_2)_{10}S—]_2$	11.0	1.27	260	<0.005
1416-96-4	Dibenzyl disulfide 	12.0	1.06	200	0.02
2293-43-2	Bis-(α-phenethyl) disulfide 	11.1	1.25	260	<0.005
2209-52B	Di-*sec*-butyl disulfide	12.1	1.15	230	<0.005
2209-52C	Di-*tert*-butyl disulfide	12.0	1.18	235	<0.005
2051-60-F	Diphenyl disulfide 	11.1	0.84	145	0.06
2051-60-G	Di-*o*-tolyl disulfide 	11.1	0.52	74	0.23
2051-84-F	Di-*p*-tolyl disulfide 	10.9	0.73	120	0.11
1416-96-2	Bis-(2,4,6-trimethyl phenyl) disulfide (Dimesityl disulfide) 	12.0	0.34	41	0.69
2209-151-2	Bis-(2,4,6-triisopropylphenyl) disulfide 	11.4	0.86	150	0.12
2051-110-C	Bis-(2-carboxyphenyl) disulfide[b] 	3.3	0.92	165	0.01
2051-126-C	Bis-(4-carboxyphenyl) disulfide[b] 	6.3	0.63	98	0.17
2051-145-Z	Bis-(4-carboxymethyl phenyl) disulfide[b] 	6.4	0.57	85	0.24
2051-115-B	Bis-(2-carboethoxyphenyl) disulfide 	10.7	1.24	250	<0.005
2051-94-B	Bis-(4-carboethoxyphenyl) disulfide 	11.5	0.79	135	0.11

Expt. No.	Compound[a]	% convn. 17 hrs. at 50°C.	[η]	$\bar{M}_n$ $\times 10^{-3}$	Transfer constant, C
2124-31 EL	Bis-(2-aminophenyl) disulfide[c] 	5.7[c]	0.22	22	3.0
2051-126-E	Bis-(4-aminophenyl) disulfide 	10.4	0.52	74	0.24
2124-82-2	Bis-(4-*n*-dodecylaminophenyl) disulfide 	9.5	0.78	130	0.21
2124-12-B	Bis-(4-*N*-carboethoxyaminophenyl) disulfide 	11.0	0.63	98	0.24
2124-35-Z	Bis-(4-carboxy-2-aminophenyl) disulfide[b] 	4.5	0.13	10.5	3.0
2124-115-2	Bis-(2-hydroxymethyl phenyl) disulfide[b] 	10.0	0.33	39	0.58
2124-106-B	Bis-(4-hydroxymethyl phenyl) disulfide[b] 	10.8	0.70	115	0.09
2124-82-3	Di-*p*-anisyl disulfide 	11.2	0.61	94	0.18
2051-110-D	Di-*o*-nitrophenyl disulfide 	Nil	—	—	—
2051-110-B	Dibenzoyl disulfide 	10.4	1.26	260	<0.005
2051-110-E	Di-α-naphthoyl disulfide 	6.3	0.54	78	0.34
2209-60-B	Di-2-quinolyl disulfide 	10.4	0.99	185	0.05
2209-60-C	Di-2-lepidyl disulfide 	10.8	1.06	200	0.04

(*table continued*)

TABLE I (*continued*)

Expt. No.	Compound[a]	% convn. 17 hrs. at 50°C.	[η]	$\bar{M}_n$ $\times 10^{-3}$	Transfer constant, *C*
2209-60D	Di-2-pyridyl disulfide 	11.5	1.16	230	0.01
2051-74-C	Hexacarboethoxyethane $(C_2H_5OOC)_3C—C(COOC_2H_5)_3$	10.0	1.32	270	<0.005
2051-56-E	Tetraphenylsuccinodinitrile  $Ph_2C(CN)—C(CN)Ph_2$	4.5	0.15	13	2.8

[a] 1.0 weight per cent of compound used.

[b] 10–70 parts (generally 30) of pyridine per 100 styrene used with these compounds in order to keep the modifier in solution. A control with the same amount of pyridine and no modifier was run in each case, and the corresponding P_0 used in the calculations. The adjusted P_0 differed only slightly from the P_0 in the absence of pyridine. The grade of pyridine used (C.P.) did not retard reaction rate significantly and was found to have a transfer constant in the range of 0.0003–0.0008, which comparatively high value may have been due to impurities in the solvent; Gregg and Mayo[18] report a value of 6×10^{-5}.

[c] This run employed 0.05 weight per cent AIBN and 0.36 weight per cent modifier. Control (no modifier) gives about 7.5% conversion with $[\eta] = 1.53$, corresponding to $\bar{M}_n$ of 340,000.

ing effectiveness is decreased fivefold in bulk styrene polymerization, and the activity in emulsion butadiene polymerization reduced correspondingly. This retarding effect of large bulky groups placed adjacent to the bond undergoing cleavage presents a striking example of steric hindrance effects.

A carboxyl group in the ortho position apparently deactivates aryl disulfides nearly completely as modifiers, and this seemed to be the case whether or not the compound was esterified. A carboxyl or a carboethoxy group in the para position appeared to give slightly higher activity than a methyl group. The para carboxymethyl compound had the highest activity of any of the carboxy compounds in bulk styrene polymerization, though this result may be somewhat suspect because the reduction in rate suggests that an impurity may also be contributing to the lowering of molecular weight. The possibility that the effects of benzylic substitution are being manifested also exists here.

Incorporation of an amino group in the ortho position had the most potent effect of any group in activating aryl disulfides as modifiers, and this proved to be true (in the case of bis-(2-aminophenyl) disulfide) in both bulk styrene and emulsion butadiene polymerization. Finding an emulsion polymerization recipe in which any appreciable reaction rate could be attained with this compound was difficult. The rather unique recipe of Stoops,[20] using a combination of diazoaminobenzene and hydroquinone (Recipe C) proved fairly satisfactory, though the rate was greatly retarded at higher concentrations of bis-(2-aminophenyl) disulfide. Unfortunately, no evaluation was obtained in a cold recipe (Table III), since only negligible polymer formation occurred with the one cold recipe tried.

On the other hand, the greatest departure in behavior between the bulk styrene and emulsion butadiene polymerization observed with any of the compounds was noted with bis-(4-carboxy-2-aminophenyl) disulfide, which had about the same high transfer constant in bulk styrene as bis-(2-aminophenyl) disulfide, but no activity under any of the conditions tested with emulsion butadiene polymerizations. Whether the latter result represents an incomplete search for recipes (or conditions) for attaining maximum activity, or whether the incorporation of the carboxy group in the para position completely vitiates the activating effect of the ortho amine group, cannot be stated at present.

An amine group in the para position apparently has only slightly more activating effect than a similarly located methyl group. It is interesting to note that the transfer constants in bulk styrene of bis-(4-aminophenyl) disulfide and of both its *N*-substituted dodecyl and carboethoxy derivatives are all within experimental error of each other. It was of further interest to note that advantage could be taken of the differences in the solubility of amines in media of various pH's in emulsion butadiene polymerizations, in that the bis-(4-aminophenyl) disulfide gave a polymer of lower viscosity at pH 6 than at higher pH's. Unfortunately, reaction rate with this recipe was so retarded at pH's lower than 6 that these could not be investigated, although attempts were made in this direction.

Of the two hydroxymethyl compounds investigated, bis-(2-hydroxymethyl phenyl) disulfide and the 4-isomer, the ortho compound was again much the more effective. The correlation between bulk styrene and 50°C. emulsion butadiene polymerization was good, though the ortho compound proved comparatively ineffective in the single condition tried in 5°C. polymerization.

The rather moderate activity of di-*p*-anisyl disulfide was rather surprising in view of the fact that experience with the earlier discussed compounds would lead one to expect a very high level of activity in compounds with strong electron donating groups. Unfortunately, the ortho isomer was not available.

The absence of any activity for benzoyl disulfide in either bulk styrene or emulsion butadiene polymerization is somewhat at variance with certain of the earlier experience with this compound in the synthetic rubber program, some of which had shown some promise for it and some of which had not. It might be remarked that different methods of preparing this material apparently lead to different impurities, and some of the earlier, less highly purified preparations in the Goodyear laboratory had shown appreciable activity in bulk styrene. Di-α-naphthoyl disulfide showed moderate modiffer effectiveness in both evaluation media.

The presence of a pyridine-type nitrogen atom in the ring did not enhance the activity of disulfides containing it, as can be seen by comparing results obtained with di-2-pyridyl disulfide, di-2-quinolyl disulfide, and di-2-lepidyl disulfide with their nearest aryl analogues.

Hexacarboethoxyethane exhibited negligible activity with either polymerization system.

TABLE II. Bis-Type Modifiers in 50°C. Butadiene Emulsion Polymerizations

Expt. No.	Compound[a]	Recipe	Added solvent (to predisperse)	Hours at 50°C.	% convn.	% sol. in C_6H_6	Swell vol. of gel	DSV of sol	Relative effectiveness as a modifier
2109-88-A	None	A	None	6	26	4	22	—	—
2051-76-C	None	A	None	17	75	4	13	—	—
2180-35-B	None	A	Acetone	8.3	41	31(?)	28	—	—
2180-35-C	None	A	Isopropanol	8.3	39	16	25	—	—
2180-35-D	None	A	Pyridine	8.3	32	11	27	—	—
2051-76-D	Bis-(10-carbomethoxy-*n*-decyl) disulfide	A	None	17	82	4	13	—	—
2180-42-E	"	A	None	5.5	21	6	16	—	—
2180-42-G	"	A	Acetone	8.5	25	15	18	—	None
2180-142-B	Di-*tert*-butyl disulfide	A	None	5	28	38	26	—	Slight
2180-142-D	Di-*sec*-butyl disulfide	A	None	5	25	55	36	—	Slight
2109-114-C	Dibenzyl disulfide	A	None	6	22	6	17	—	None
2308-22-B	Bis-(α-phenethyl) disulfide	A	None	6	34	6	26	—	None
2308-22-C	" "	A	Isopropanol	6	10	6	30	—	None
2180-116-B	Di-*o*-tolyl disulfide	A	None	8	21	100	—	2.91	Fair
2180-28-A	Di-*p*-tolyl disulfide	A	None	8.5	44	38	37	—	(Slight)
2180-28-B	" "	A	Isopropanol	8.5	35	35	64	—	Fair
2180-49-B	Dimesityl disulfide (0.5 pt.)	A	None	7	44	52	50	—	—
2180-49-C	" " "	A	Acetone	7	26	100	—	2.89	—
2180-49-D	" " 1.0	A	None	7	25	100	—	2.91	(Good)
2180-49-D	" " "	A	Acetone	13	32	100	—	1.59	Excellent
2245-108-B	Bis-(2,4,6-triisopropylphenyl) disulfide	A	None	6	31	2	15	—	None
2051-112-F	Bis-(2-carboxyphenyl) disulfide	A	None	16	28	14	35	—	None
2180-30-A	None	B	None	16.5	43	17	—	—	—
2051-147-D	Bis-(4-carboxyphenyl) disulfide	B	None	40	64	6	26	—	None

Expt. No.	Compound[a]	Recipe	Added solvent (to predisperse)	Hours at 50°C.	% convn.	% sol. in C_6H_6	Swell vol. of gel	DSV of sol	Relative effectiveness as a modifier
2051-141-C	Bis-(4-carboxymethyl phenyl) disulfide	B	None	40	39	20	65	—	Slight
2180-116-D	Bis-(4-carboethoxyphenyl) disulfide	A	None	8	22	56	84	—	Fair
2109-116-A	None	C	None	1	38	2	17	—	—
2109-116-D	Bis-(2-aminophenyl) disulfide (0.1 pt.)	C	None	1.5	27	100	—	1.31	Excellent
2109-116-F	Bis-(2-aminophenyl) disulfide (0.3 pt.)	C	None	3.5	22	100	—	0.62	
2109-116-I	Bis-(2-aminophenyl) disulfide (1.0 pt.)	C	None	50	18	100	—	0.25	
2109-70-C	Bis-(4-aminophenyl) disulfide	B (pH = 6)	None	20	9	100	—	0.72	Good
2109-70	“ “	B (pH = 8)	None	20	25	100	—	1.80	
2109-70	“ “	B (pH = 10)	None	20	25	100	—	1.80	
2180-33-E	“ “	A	None	8.5	17	18	27	—	(None)
2180-33-G	Bis-(4-*n*-dodecylaminophenyl) disulfide	A	None	8.5	29	5	21	—	(None)
2180-33-GI	“	A	Isopropanol	12.5	30	99	—	3.43	Fair
2109-137-A	“	A	None	17	80	3.5	—	22	(None)
2180-28-C	Bis-(4-*N*-carboethoxyaminophenyl) disulfide	A	None	8.5	34	10	29	—	(None)
2180-28-CI	“	A	Isopropanol	8.5	21	62	51	—	Fair
2180-28-D	Bis-(4-carboxy-2-aminophenyl) disulfide	A	None	8.5	19	7	26	—	None
2180-28-DI	“ “	A	Isopropanol	8.5	18	4	30	—	None
2180-28-DP	“	A	Pyridine	14	22	7	27	—	None
2180-94-B	Bis-(2-hydroxymethyl phenyl) disulfide	A	None	28	15	100	—	2.24	Fair
2180-116-E	Bis-(4-hydroxymethyl phenyl) disulfide	A	Isopropanol	8	0	(no emulsion formed)			—
2180-33-H	Di-*p*-anisyl disulfide	A	None	8.5	22	3	19	—	(None)
2180-33-HA	“ “	A	Acetone	8.5	29	100	—	3.22	Fair

(table continued)

TABLE II (*continued*)

Expt. No.	Compound[a]	Recipe	Added solvent (to predisperse)	Hours at 50°C.	% convn.	% sol. in C_6H_6	Swell vol. of gel	DSV of sol	Relative effectiveness as a modifier
2051-112-E	Di-*o*-nitrophenyl disulfide	A	None	16	<5	—	—	—	—
2109-112-C	Di-2-naphthyl disulfide	A	None	8	10	100	—	2.41	Fair
2109-82-B	" "	A	None	9	37	89	—	—	Fair
2051-112-G	Dibenzoyl disulfide	A	None	16	74	5	14	—	None
2180-42-B	" "	A	None	4.5	19	13	24	—	None
2180-42-D	" "	A	Isopropanol	8.5	31	7	20	—	None
2180-33-F	Di-α-naphthoyl disulfide	A	None	8.5	32	47	130	—	(Slight)
2180-33-FA	" "	A	Acetone	12.5	35	92	100	2.86	Fair
2180-148-B	Di-2-lepidyl disulfide	A	None	5	23	10	20	—	None
2180-148-C	Di-2-pyridyl disulfide	A	None	5	21	20	26	—	None
2245-10-C	" (Init. pH 11.1; final = 4.0)	B	None	7.5	19	100	—	2.16	Good
2051-76-E	Hexacarboethoxy ethane	A	None	17	77	3	14	—	None
2051-76-C	Tetraphenylsuccinodinitrile	A	None	17	75	8	13	—	None
2180-42-H	"	A	None	5.5	21	6	16	—	None
2180-42-I	"	A	Acetone	8.5	17	14	17	—	None
2180-30-D	Carbonyl bis-(thioglycolic acid) $(HOOCCH_2S—)_2C = 0$	B	None	16.5	15	100	—	1.51	Excellent
2180-35-E	Sulfole (0.5 pt.)	A	None	5.3	30	100	—	0.55	—
2180-35	" " "	A	Pyridine	5.3	30	100	—	0.50	—
2180-9-A	*n*-Hexadecyl mercaptan (0.5 pt.)	A	None	5	24	8	26	—	(None)
2180-9-B	" " "	A	Acetone	8	26	100	—	2.57	(Good)
2180-10-E	" " "	A	Isopropanol	8	32	100	—	1.78	Excellent

[a] 1.0 part used except where indicated.

TABLE III. BIS-TYPE MODIFIERS IN 5°C. BUTADIENE EMULSION POLYMERIZATION

(Recipe D: Fe-pyrophosphate hydroperoxide)

Expt. No.	Compound	Added solvent (to predisperse)	Hours at 5°C.	% convn.	% sol. in C_6H_6	Swell vol. of gel	DSV of sol	Relative effectiveness as a modifier[a]
2180-121	None	None	3	26	63	27	—	—
2180-104A	0.5 Sulfole	None	4.3	45	100	—	1.04	—
2180-104B	0.5 Sulfole	Isopropanol	4.3	39	100	—	0.52	—
2180-104C	0.5 bis-(2-aminophenyl) disulfide	"	27	3	—	—	—	—
2180-104D	1.0 tetraphenylsuccinodinitrile	"	27	37	57	125	—	Slight
2180-104E	1.0 bis-(2-hydroxymethyl phenyl) disulfide	"	4.3	20	71	54	—	Slight
2180-104F	1.0 dimesityl disulfide	"	4.3	22	100	—	2.45	Fair

[a] Ratings are based on the control with no modifier. The "activity" ratings of runs 104D and 104E are based mostly on the increased swell volumes over that of the control.

The behavior of the tetraphenylsuccinodinitrile in bulk styrene is unique, and appears from the meager data to place this compound in a class with hexaphenylethane, whose function as both an inhibitor and a transfer agent has been discussed by Gregg and Mayo.[21] The explanation appears to lie in the fact that radicals formed from dissociation of compounds of this type do not form as many new radicals as they terminate chains—*i.e.*, that low molecular weight polymers are attainable only at the considerable sacrifice of reaction rate. The lack of any detectable activity in the butadiene polymerizations would indicate that its behavior with butadiene radicals is somewhat different.

Taking the results as a whole, it appears that derivatives of aryl disulfides offer the most promise in preparing modifiers containing desired functional groups, from the standpoint of combining ease of preparation with the ability to attain high modifier activity through judicious placement of substituting groups. Generally, electron donating groups appear to enhance modifier activity, and a much more pronounced effect is obtained by incorporation in the ortho position than in the para position. The correlation between behavior in bulk styrene and emulsion butadiene polymerizations has generally been quite good—the most notable exception being the results obtained with bis-(4-carboxy-2-aminophenyl) disulfide. No compounds were found which had appreciable modifying activity in butadiene and none in styrene polymerizations.

The present study is by no means to be represented as being exhaustive, insofar as the investigation of the effects of the various possible groups and arrangements of them is concerned. However, from a practical standpoint, it does not appear necessary to extend much further the work on preparation of compounds with new types of groups incorporated on the ring solely for the purpose of attaining enhanced modifier activity, since the addition of methyl groups in each of the available ortho positions of derivatives of diphenyl disulfide appears adequate for achieving satisfactory levels of modifier activity, and leaves open the para position—considered the most desirable for this purpose—for incorporation of desired reactable groups.

Because of the lack of methods for rapidly and accurately measuring the *primary* $\bar{M}_n$ of polybutadiene (*i.e.*, the $\bar{M}_n$ in the absence of crosslinks) and for determining the very low concentration of identifiable end groups imparted by any of the bis-type modifiers studied so far, it has not been possible to extend this study to a determination of the number of modifier halves per primary molecule, as has been done in the case of polystyrene in another paper.[1] Some current research is directed toward this objective.

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Synopsis

The present paper describes the preparation and evaluation of the effectiveness as modifiers of a number of compounds of bis-type structure—principally aryl disulfides—in bulk styrene and emulsion butadiene polymerizations. This work endeavors to explore some of the objectives described in the first paper of this series, and deals primarily with attempts to gain quantitative information on the effect of the nature and location of substituting groups with respect to the dissociating bond. The compounds examined include both those containing reactive groups attached and those lacking such groups. A number of the preparations are now compounds. Evaluations in 50°C. bulk styrene were carried out with the objective of eliminating the complications of the diffusion factor always present in emulsion systems. Generally speaking, the correlation between effectiveness in bulk styrene and 50°C. emulsion butadiene was quite good, though there were exceptions. It was found that the modifier activity of many compounds in emulsion butadiene could be enhanced by predispersing them in the aqueous phase—presumably a result of minimizing the importance of diffusion rate. Some of the modifiers were also tested in a low temperature butadiene emulsion system. Aryl disulfides continue to offer the most promise from the standpoint of combining the features of attaining high transfer constants and ease of incorporating desired reactive groups. Some compounds had adequate activity in emulsion butadiene polymerizations for use as practical modifiers. However, it has not yet been established that these compounds cleave to give one-half the molecule on each end of the butadiene polymer chain, as has been done for styrene polymers.

Résumé

On décrit la préparation et l'évaluation de l'efficacité comme "modificateurs" de nombreux dérivés du type double, tels les disulfures diaryliques, dans le cas de la polymérisation en bloc du styrène et la polymérisation en émulsion du butadiène. Ce travail étudie certains problèmes envisagés antérieurement, et se propose d'obtenir des renseignements quantitatifs concernant la nature et la localisation des groupes substituants par rapport à la liaison rompue. Les composés étudiés comprennent certains dérivés contenant des groupes réactionnels d'autres ne contenant pas de ces groupes. Plusieurs de ces préparations sont nouvellement décrites. Les évaluations au cours de la polymérisation du styrène en bloc à 50 °C ont été effectuées en vue d'éviter les complications dues à des phénomènes de diffusion, toujours présents dans les systèmes en émulsion. De façon générale, la correspondance entre la polymérisation du styrène en bloc à 50 °C et la polymérisation en émulsion du butadiène est bonne, bien qu'il se manifeste certaines exceptions. On a trouvé que l'action modificatrice de certains dérivés en cours de polymérisation en émulsion du butadiène peut être favorisée en dispersant au préalable ces dérivés dans la phase aqueuse, ceci étant vraisemblablenemt à attribuer à une importance moindre de la vitesse de diffusion. Certains modificateurs ont également été essayés dans le sysième en émulsion à basse température dans le cas du butadiène. Les disulfures d'aryle offrent le plus grand intérêt du fait qu'ils permettent de combiner à la fois une constante élevée de transfert de chaîne à une incorporation souhaitable de groupes réactionnels. Certains dérivés présentent une activité intéressante du point de vue pratique pour le cas de la polymérisation en émulsion du butadiène. Toutefois on n'a pas encore établi que ces dérivés se scindaient de telle manière qu'une demi-molécule se retrouvait à l'extrémité d'un butadiène polymérique, ainsi qu'on a pu le démontrer dans le cas du polystyrène.

Zusammenfassung

Die vorliegende Arbeit beschreibt die Herstellung und Evaluierung der Wirksamkeit als Modifikationsmittel einer Anzahl von Verbindungen von bis-Typus Struktur—besonders Aryldisulfide—in Block-Styrol- und Emulsions-Butadien-Polymerisationen. Diese Arbeit versucht, einige der in der ersten Arbeit dieser Reihe beschriebenen Objektive zu erforschen, und behandelt vor allen die Versuche, quantitative Berichte der Wirkung der Natur und Stellung von substituierenden Gruppen in Bezug auf die dissoziierende Bindung zu erhalten. Die untersuchten Verbindungen umschliessen sowohl diejenigen, die angeschlossene reaktive Gruppen enthalten, wie auch diejenigen, denen solche Gruppen fehlen. Eine Anzahl der Herstellungen sind neue Verbindungen. Evaluierungen in 50 °C Block-Styrol wurden mit dem Ziel ausgeführt, die Komplikationen des Diffusionsfaktors zu entfernen, die in Emulsionssystemen immer anwesend sind. Im allgemeine war die Korrelation zwischen Wirksamkeit in Block-Styrol und 50 °C Emulsion-Butadien recht gut, trotzdem Ausnahmen bestanden. Es wurde gefunden, dass die Modifikationsmittel-Aktivität vieler Verbindungen in Emulsion-Butadien dadurch verstärkt werden konnte, dass sie in wässriger Phase vor-dispergiert werden—dies ist wahrscheinlich das Resultat einer Verringerung der Bedeutung der Diffusionsgeschwindigkeit. Einige der Modifikationsmittel wurden auch in einem Butadien-Emulsions system bei niedriger Temperatur geprüft. Aryldisulfide versprechen weiterhin am meisten vom Standpunkt der Vereinigung der Eigenschaften, höhere Transferkonstanten und Leichtigkeit der Vereinigung mit gewünschten reaktiven Gruppen zu erreichen. Einige Verbindungen hatten genügende Aktivität in Emulsions-Butadien-Polymerisationen, um als praktische Modifikationsmittel verwendet zu werden. Es wurde jedoch noch nicht festgestellt, dass sich diese Verbindungen spalten, um ein halbes Molekül an jedem Ende der Butadien-Polymerkatte zu ergeben, wie für Styrolpolymere festgestellt wurde.

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