(0.1 mole) of acetophenone oxime in 50 ml. of sulfur dioxide. After the reaction period, the sulfur dioxide was removed as usual and the residue was treated with 25% sodium hydroxide solution. The products were extracted with ether; the ether solution was dried and evaporated to yield 14.8 g. of material. Trituration with ether gave 7.9 g. of soluble material and 6.9 g. of colorless residue, m.p. *ca.* 155°, which was recrystallized from benzene to give a crystalline product with m.p. 164–165.5°, not depressed on mixture with authentic *p*-bromoacetanilide.

When the reaction was repeated on the same scale with a chlorine–bromine mixture, a yield of 14.5 g. of crude mixed products was obtained. This was triturated with benzene–ligroin (6.3 g. was soluble) to give 7.9 g. of colorless residue. Fractional crystallization from water gave 4.4 g. of material melting at about 100° and 3.8 g. of material melting at about 165°. Each fraction was crystallized from benzene; the products were identified as acetanilide (m.p. and mixed m.p. 113–114°) and *p*-chloroacetanilide (m.p. and mixed m.p. 171–172.5°).

The reaction with benzophenone oxime (19.7 g., 0.1 mole) was carried out in the usual way in 100-ml. total volume of sulfur dioxide. The yield of 18.7 g. of crude product was triturated in ether (4.4 g. of soluble material) to give 14.3 g. of orange powder, m.p. 201–202°. The m.p. was not depressed on mixture with authentic N-benzoyl-*p*-bromoaniline.

When a chlorine–bromine mixture was used with 0.1 mole of benzophenone oxime, crude product amounted to 20.3 g. This was triturated with benzene, and the benzene solution yielded 6.6 g. of N-benzoyl-*o*-chloroaniline, m.p. and mixed m.p. 99–101° after recrystallization from ethanol. The benzene-insoluble residue was fractionally crystallized to give 12 g. of N-benzoyl-*p*-chloroaniline, m.p. and mixed m.p. 187–188.5°, and an unidentified material (1.7 g.) with m.p. 150–152°.

Satisfactory nitrogen analyses were obtained for all reaction products.

Reactions with Bromine–Water Mixture.—When a bromine–water mixture was used in sulfur dioxide with cyclohexanone oxime, a rearrangement did not occur (Table I). Cyclohexanone and cyclohexanone oxime were recovered. For the reactions in Table I, the recovery of oxime was 74.0 and 87.6%.

SENDAI, JAPAN

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, POLYMER CORPORATION LTD.]

The Synthesis and Identification of Block Polymers of Butadiene and Styrene

BY R. J. ORR AND H. LEVERNE WILLIAMS

RECEIVED NOVEMBER 21, 1956

A method of synthesizing polymeric dihydroperoxides in which the hydroperoxy groups are terminal has been evolved. The monomers are polymerized in emulsion at 12.8° using sufficiently large quantities of complexed iron(II) and *p*-diisopropylbenzene dihydroperoxide that mutual termination is dominant. The molecular weight of the polymeric dihydroperoxide is controlled by adjusting the emulsifier, the dihydroperoxide and the iron(II) sulfate concentrations. The residual hydroperoxide group on the polymer is protected from reaction by the short residence time in the aqueous phase. Such polymers after purification will initiate polymerization of a second monomer. The iodine monochloride adduct of butadiene–styrene copolymers is insoluble in carbon tetrachloride for high-butadiene polymers and soluble for low-butadiene polymers. This permitted verification that the polymers produced by initiating styrene polymerization with polybutadiene dihydroperoxide were not mixtures of polystyrene and polybutadiene but were composed of chemically linked blocks of polymers of the two compositions. This was supported by fractionation experiments which indicated that some bound styrene could not be extracted after cross-linking such a polymer. Evidence is presented that such results do not arise from chain transfer.

Introduction

Active interest in the field of block and graft polymers is comparatively recent, stimulated by the potential economic value of some novel product. While methods of grafting are numerous, since they depend only on placing side chains randomly along the main chain, the methods of forming block polymers are few due to the restriction on the location of the points of union of the blocks in the molecule. Several reviews[1–3] summarize methods. The methods have the defect that if they are simple and commercially feasible they offer little control over the structure of the final polymer. The problem of exerting control over the process and product seems to be the major difficulty.

It is important to establish by analytical methods the structure of the polymer postulated from kinetic reasoning. Fractionation of the product of the reaction may be tedious, and success in separating differing polymers depends on the difference in solubilities of the polymers. There is little difference between the solution properties of polybutadiene and polystyrene, so that this approach offers little promise, although some workers report successful fractionations of similar polymer mixtures.[4]

During the course of the study of the decomposition of hydroperoxides by iron(II), *p*-diisopropylbenzene dihydroperoxide was used.[5] This gave a free radical which underwent little side reaction relative to reaction with monomer. Considering the theories of emulsion polymerization as outlined by Harkins[6] and Smith and Ewart[7] suggested that sufficiently rapid decomposition of hydroperoxide might result in appreciable amounts of mutual termination according to the mechanism

$$\mathrm{HOOROOH(aq)} + \mathrm{Fe(II)} \longrightarrow \mathrm{HOORO\cdot(aq)} + \mathrm{Fe(III)}$$

$$\mathrm{HOORO\cdot(aq)} + \mathrm{M(aq)} \longrightarrow$$

$$\mathrm{HOOROM\cdot(aq)} \xrightarrow{(n-1)\mathrm{M}} \mathrm{HOOROM}_n\cdot\mathrm{(oil)}$$

$$\mathrm{HOOROM}_n\mathrm{(oil)} + p\mathrm{M(oil)} \longrightarrow (\mathrm{HOOROM}_{n+p})\mathrm{(oil)}$$

$$\mathrm{HOOROM}_n\mathrm{(oil)} + \mathrm{HOOROM}_{n+p}\mathrm{(oil)} \longrightarrow \mathrm{HOOROM}_{2n+p}\,\mathrm{OROOH}$$

---

(1) H. W. Melville, *Plastics Inst., Trans. and Jour.*, **23**, 146 (1955).

(2) L. Valentine, *Fibres*, **16**, 12, 60 (1955).

(3) H. Mark, *Angew. Chem.*, **61**, 53 (1955).

(4) J. A. Blanchette and L. E. Melsen, *J. Polymer Sci.*, **20**, 317 (1956).

(5) R. J. Orr and H. Leverne Williams, THIS JOURNAL, **78**, 3273 (1956).

(6) W. D. Harkins, *J. Chem. Phys.*, **13**, 581 (1945); THIS JOURNAL, **69**, 1425 (1947); *J. Polymer Sci.*, **5**, 217 (1950).

(7) W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948); THIS JOURNAL, **70**, 3095 (1948).

This would be much more likely with diisopropyl benzene dihydroperoxide than other hydroperoxides since at the high steady state concentrations of hydroperoxy free radicals in the aqueous phase necessary to bring about rapid initiation of polymerization there would be less chance that the free radical would undergo side reactions with iron(II) or with the parent dihydroperoxide. If the residence time of the initiating radical in the aqueous phase be sufficiently short, then little opportunity of reaction of the remaining hydroperoxide group with the water-soluble iron(II) would occur, and a polymeric dihydroperoxide would be formed. Once this is formed, the polymeric hydroperoxide groups would be protected from decomposition by isolation from the water-soluble iron(II). Such a polymer when mixed with another monomer and heated should be capable of forming diradicals which would give rise to block polymer.

Experimental Methods.—The diisopropylbenzene dihydroperoxide (DHP) was obtained in solution in acetone. It was reported as being mostly *para*, although some of the *meta* form may have been present. The product was contaminated with an oil-soluble hydroperoxide, probably diisopropylbenzene monohydroperoxide. No attempt was made to remove it. The compound (DHP) was insoluble in hydrocarbons, probably due to the lipophobic nature of the hydroperoxide groups. The solubility in carbon tetrachloride was less than 0.085%. The solid dihydroperoxide was added to the 7-ounce reaction bottle initially followed by the emulsifier solution and high boiling monomers. The activator (an aqueous solution of iron(II) pyrophosphate) was added. Premature reaction was minimized by the separation of the activator from the dihydroperoxide. Excess volatile monomer was added last and allowed to evaporate to the correct weight to expel residual air. The beginning of agitation of the reaction was taken as zero time. The recipe was composed of 5 parts of potassium fatty acid soap and 320 parts of water per 100 parts of monomer. The large amount of water was necessary to accommodate the catalyst and activator. Reaction temperature was 12.8°.

Experimental

(a) **Molecular Weight of Polymeric Dihydroperoxides.**—The obvious method of controlling molecular weight of the polymeric dihydroperoxide is by changing the rate of free radical production by varying the activator and catalyst concentration in the recipe. The results are in Table I for a 72/28 butadiene/styrene ratio. The branching constants (k') were measured from the slope of the plot of ln $\eta_{r/c}$ *versus* c according to the Mead–Fuoss equation. These compare favorably at the lower molecular weights with those observed for polystyrene.[8]

The polymeric dihydroperoxides were soluble in benzene except when prepared with 0.2 and 0.5 part DHP. The intrinsic viscosity was determined on the soluble fraction of these, which accounts for the decrease in the value of k' from that obtained for the polymer prepared with 1.0 part of dihydroperoxide. The experiments were done using 5.3 parts of emulsifier and conducting the reaction to 100% conversion which was reached by 17 hr. Assuming mutual termination to be responsible for molecular weight control, then the molecular weight at any given rate of free radical production should be dependent on the ratio of the number of particles containing growing chains to the total number of particles. If this ratio be dependent on emulsifier concentration, molecular weight should be dependent on emulsifier concentration. This was investigated. The results are in Table II.

TABLE I

MOLECULAR WEIGHT CONTROL BY ACTIVATOR–CATALYST SYSTEM

Parts DHP	$[\eta]$	k'
0.2	1.64	0.50
0.5	1.01	.53
1.0	0.84	.58
3.0	.83	.46
5.0	.78	..
6.0	.52	.41
7.0	.74	..
10.0	.61	.31

TABLE II

MOLECULAR WEIGHT CONTROL BY VARIATION OF EMULSIFIER CONCENTRATION

100% Conversion in 17 hours; DPH, 10 parts; FESO·$7H_2O/DHP/K_4P_2O_7$,1/1/1

Parts emulsifier	$[\eta]$
7	0.4
10	0.7
15	1.0
20	1.0

(b) **Effect of Monomer Structure on Polymeric Dihydroperoxide Formation.**—Several monomers were polymerized in the preceding recipe containing 10 parts of DHP and $DHP/FeSO_4 \cdot 7H_2O/K_4P_2O_7 = 1$. Those for which intrinsic viscosity data were obtained are in Table III.

TABLE III

FORMATION OF POLYMER DIHYDROPEROXIDES FROM VARIOUS MONOMERS

Initial monomer composition	$[\eta]$
Styrene	0.7
72% butadiene/28% α-methylstyrene	.8
Butadiene	.6
72% isoprene/28% styrene	.7
72% butadiene/28% p-chlorostyrene	.7
72% butadiene/28% vinylpyridine	.3

Other butadiene-containing polymers were prepared with a 72/28 charge ratio of butadiene to acrylonitrile, acrylamide or methyl methacrylate using gel as a criterion for molecular weight changes. The latter two pairs gave gel-free, low molecular weight polymers at 100% conversion. With the first-mentioned pair, it was necessary to reduce the proportion of acrylonitrile in the charge to 5% before the resulting polymer was soluble in benzene or methyl ethyl ketone. On replacing the anionic emulsifier with dodecylamine hydrochloride and reducing the pH to 4.5 with acetic acid, a polymer soluble in methyl ethyl ketone with an intrinsic viscosity of 0.3 in this solvent was obtained. This is believed to be related to a tendency[9] of hydroperoxides to react with acrylonitrile at high pH.

(c) **Stability of Polymeric Dihydroperoxides.**—When purifying butadiene-containing polymeric dihydroperoxides, the dry polymer cross-linked easily even after precipitation 3 or 4 times from benzene solution, due to the reactive nature of the polymeric dihydroperoxides. The polymers could be stored as 10% solutions in benzene or toluene at 50° without change of the intrinsic viscosity for at least 72 hr.

A characteristic behavior of the polymeric dihydroperoxides containing butadiene was the tendency for reaction of the double bounds when stored in carbon tetrachloride solution as shown by Fig. 1. After about 50% reaction of the double bonds (as measured by an iodine monochloride titra-

---

[8] J. A. Manson and L. H. Cragg, *Can. J. Chem.*, **30**, 482 (1952).

[9] R. J. Orr and H. Leverne Williams, *Faraday Soc. Disc.*, **14**, 170 (1953).

tion), the polymer began to precipitate. This cannot be due to cross-linking since reaction of less than 5% of the double bonds by such a process should yield 100% gel. It appears reasonable that addition of carbon tetrachloride imparting solvent resistance to the polymer is occurring. To confirm if this were the case, reaction of double bonds of mercaptan-modified polymers in the presence of free hydroperoxide was studied by iodine monochloride titration. It was necessary to treat the remaining hydroperoxide by shaking with aqueous iron(II) sulfate or to carry out a blank titration without polymer since the hydroperoxide reacted with iodine monochloride. With a saturated solution of dihydroperoxide, no reaction of double bonds occurred in 8 days at 50°. With diisopropylbenzene monohydroperoxide higher concentrations of hydroperoxide were attainable. There was an initial reaction of about 4% of the double bonds at 50° in 30 hr. after which time the double bond analysis became constant.

(d) **Initiation by Polymeric Dihydroperoxides.**—Polymeric dihydroperoxides will be formed if the residence time of the hydroperoxy terminated radical in the aqueous phase is sufficiently short that reaction with iron(II) sulfate cannot occur. If this is the case, the polymeric dihydroperoxide should initiate polymerization. To test this the polymer was dissolved in a benzene solution of monomer to give a solution 5.5% polymer and 55% monomer which was heated to 50° for 17 hr. According to Smets and Woodward,[10] the presence of benzene suppresses the formation of branched chains. Since care had to be exercised that the polymerization of the second monomer did not result from peroxidic impurities in the polymer, all polymers were purified by reprecipitation from benzene solution with methanol. In all instances, one precipitation was sufficient to reduce the hydroperoxide concentration in the polymer so that subsequent extraction with methanol did not remove sufficient hydroperoxide to detect by iodimetric methods. Removal of hydroperoxide reflects the insolubility of the free dihydroperoxide in benzene compared with methanol. At least one more purification step was applied to the polymer. Some data on the effect of the number of purifications on the activity of the polymer are in Table IV.

TABLE IV

EFFECT OF PURIFICATION ON POLYMERIZATION ACTIVITY AT 50°

Polymer type	No. of purifications	Increase in total polymer present, %
72/28 Bd/Sty	2	38
	4	10
Polystyrene	2	228
	3	166

The polymer retains initiating activity after concentrations of free hydroperoxide sufficiently large to be detected have disappeared. The difference in activity between the polymeric dihydroperoxides suggests that different structures for the dihydroperoxides must be assigned. This would not be so if free hydroperoxides were catalyzing the reaction. Under comparable condition it was found that a 0.7% solution of dihydroperoxide would polymerize styrene equivalent to only 44% of the total polymer. This amount of hydroperoxide is detectable by iodimetric analysis.

TABLE V

EFFECT OF COMPOSITION ON REACTIVITY OF MONOMER–POLYMER PAIR

Monomer	Increment in polymer during reaction, %									
	Chlorostyrene		Styrene		Methyl methacrylate		Vinylpyridine		72/28 Bd/Sty	
Polymer	50°	100°	50°	100°	50°	100°	50°	100°	50°	100°
Butadiene	600	. .	122	. .	0	500	0	. .	0	300
72/28 Bd/Sty	. .	1100	38	332	0	1100	0	200	. .	332
Styrene	. .	1100	228	. .	0	1100	0	119	0	134
72/28 Bd/MMA	0	1100	0	1100	0	1100	0	270	. .	. .
Methyl MA	0	1100	0	615	. .	. .	0	43	0	173

To investigate the factors affecting the activity of the polymeric dihydroperoxide, a series of polymeric dihydroperoxides of varying composition was prepared and chain-extended with a series of monomers with the results shown in Table V. The polymers were purified twice. The value at 1100% polymer increment indicates that polymerization had proceeded till the monomer supply was exhausted. Those reactions which proceeded only at 100° were preaged 17 hr. at 50°. While the data in this table may be affected by the tendency of the polymeric dihydroperoxide to lose activity during purification, there seems to be an inverse correlation between the polarity of the monomer–polymer pair and the reactivity. Experiments containing monomeric dienes proved to be exceptions since they were less reactive than monovinyl compounds.

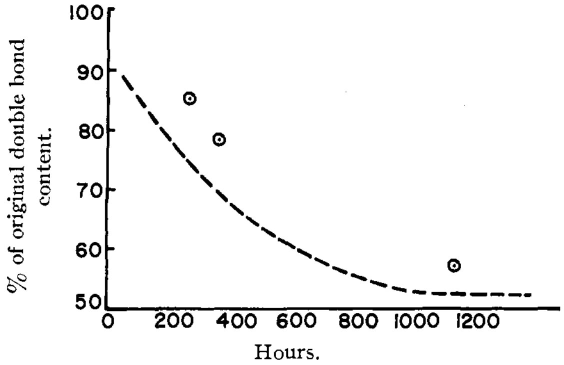

Fig. 1.—Double bond disappearance of polybutadiene dihydroperoxide in CCl_4 at 25°.

(e) **Effect of Iodine Monochloride on Copolymers and Their Mixtures.**—Consideration was given to methods other than fractional precipitation to prove that the polybutadiene chains were chemically linked to polystyrene units. Kemp and Peters[11] utilized iodine monochloride analyses for butadiene in a copolymer. This added quantitatively to the double bond in the polymerized butadiene in dichlorobenzene solution. It was noted that when carbon tetrachloride was used as a solvent, iodine monochloride consumption gave reproducible values for the bound butadiene and that a voluminous white precipitate formed with polymers richer in butadiene. Since no reaction between polymers of monovinyl compounds and iodine monochloride occurred, it was felt that this would be a method for analyzing polymeric mixtures in which one substituent was a polymer or copolymer of a diene.

(f) **Determination of Iodine Monochloride Consumption.**—Since the addition product may weigh nearly four times as much as the polymer from which it is formed, the importance of a precise determination of the iodine monochloride consumption is obvious; 0.05 molar solution iodine monochloride was added to 0.12 g. of polybutadiene or its equivalent so as to give an amount of iodine monochloride 100% in excess of the theoretical requirement. After the reaction proceeds to completion, the residual iodine monochloride was titrated with 0.1 *N* sodium thiosulfate to a starch end-point. With 100% excess, no changes in iodine monochloride reacted occurred between 15 minutes and 1 hr. so that the titration could be made after 15 minutes. A polymer was prepared in a conventional recipe with a charge ratio of 72/28 butadiene/styrene. It was possible to determine the butadiene content (and hence the iodine monochloride

---

(10) G. Smets and A. E. Woodward, *J. Polymer Sci.*, **14**, 127 (1954).

(11) A. R. Kemp and H. Peters, *Ind. Eng. Chem., Anal. Ed.*, **15**, 453 (1943).

content of the precipitate) as 75.28 ± 0.15% based on 12 determinations.

(g) **Filtration of the Addition Product.**—Filtration of the addition products for high molecular weight polymers proved much easier than for low molecular weight compounds. The latter plugged the pores of sintered glass filters and necessitated the use of ground glass as a filtration aid. The precipitate particles were trapped in a thick pad of ground glass over the fritted disk. The precipitate adhered to the walls of the flask if there was water in the reaction flask. Each experiment was done using two identical samples, since filtration could not be done with the sample intended for back titration of the excess iodine monochloride.

(h) **Drying the Addition Product.**—This was done by drawing air through the product or by drying under vacuum. Although high molecular weight compounds reached constant weight readily, lower molecular weight polymers showed a steady decrease in weight after all solvent had apparently vanished (Fig. 2). The precipitate may undergo some thermal change. By choosing the point of inflection in the weight *vs.* time curve as the correct weight, it was possible to account for all polymer present within ±2%. The precision could be improved to that characteristic of analysis of high molecular weight polymers on a relative scale. To determine the amount of styrene which had been blocked onto the ends of a polybutadiene chain, the weight–time curve of the block polymer precipitate was compared with that curve derived from a precipitate of an equal amount of the original polybutadiene. The difference was nearly independent of time. For higher molecular weight products it was possible to recover 99.5% ± 0.6% of the total for four polymer samples.

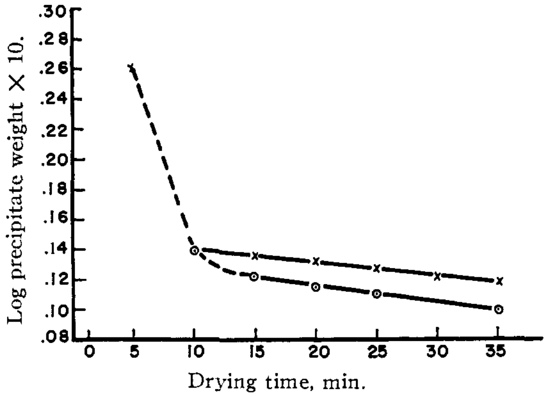

Fig. 2.—Dependence of weight of ICl addition product on drying time for low molecular weight polybutadiene.

(i) **Effect of Styrene Content on Precipitation.**—Polymers were prepared from varying charge ratios, and the effect of styrene content on the tendency to precipitate was investigated. The results are in Table VI. It is interesting that the total change in solubility occurs over a region of less than 10% bound styrene.

TABLE VI

INFLUENCE OF STYRENE CONTENT ON RECOVERY OF PRECIPITATE

Styrene, %	[η]	Theor. ppt., %
0	0.6	100
25	1.5	99.7
40	1.5	100.2
50	1.5	Cloudy
70	1.5	Clear

(j) **Analysis of Mixtures of Polymers and Copolymers of Butadiene and Polystyrene.**—A 75/25 butadiene/styrene copolymer was mixed with twice its weight of polystyrene. The butadiene-containing portion was precipitated with iodine monochloride. Complete recovery of this portion could be made in this fashion when the volume of CCl_4 present was 600 cc. When only 300 cc. was used, it was difficult to wash the precipitate free of polystyrene. The precision of determinations in a volume of 600 cc. is that predicted from the reproducibility of each step in the process, indicating no significant absorption of polystyrene on the precipitate. Polystyrene, when mixed with polybutadiene, showed no effect on recovery up to 4/1 ratio.

(k) **Effect of Various Solvents.**—Carbon tetrachloride was the only suitable solvent found for this precipitation. No precipitation occurred in benzene, chlorobenzene, ether, pentane, ethylene dichloride, chloroform or ethanol–carbon tetrachloride mixes. Addition of the ICl to the double bond occurred in all instances.

(l) **Study of Chain Extension Step by Iodine Monochloride Technique.**—Two aspects were considered: (i) The tendency of the iodine monochloride adduct to become soluble in CCl_4 when chain extension was great. (ii) The degree to which it was possible to recover in this adduct all of the polymer formed when chain extension was little.

In each series polybutadiene dihydroperoxide was dissolved in benzene, styrene added to the solution and the temperature raised to 50°. In one series, designed for low amounts of chain extensions, the polymer concentration was 2.34% and the polymer/styrene ratio either 85/15 or 50/50. At the required degree of chain extension, the sample containing styrene and its styrene-free control were cooled and the benzene and residual styrene removed by evaporation from aliquots and replaced with CCl_4. Precipitation, when combined with the ICl reaction by an aliquot from which the residual styrene had not been removed, permitted calculation of percentage polymer relative to total polymerization. For higher chain extensions the styrene/polymer ratio was 10, in about 5.5% solution of polymer in benzene–styrene. The polymer was coagulated, purified by reprecipitation and analyzed. After precipitation, all samples of the addition product showed continuous decrease of weight on drying, a characteristic noted previously for polybutadiene. The weight difference between the precipitate of the chain-extended sample and the polybutadiene control was found to be independent of drying time. This weight difference must be equivalent to the weight of styrene bound to the ends of the polybutadiene chain. The precision involved in the determination will be double that of the weighing and filtering processes which was determined as ±0.1%.

Figure 3 shows the percentage recovery of the polymer in the addition product against the total amount of polymerized styrene in the polymer. This is compared with the curve to be expected if subsequent polymerization were formation of polystyrene.

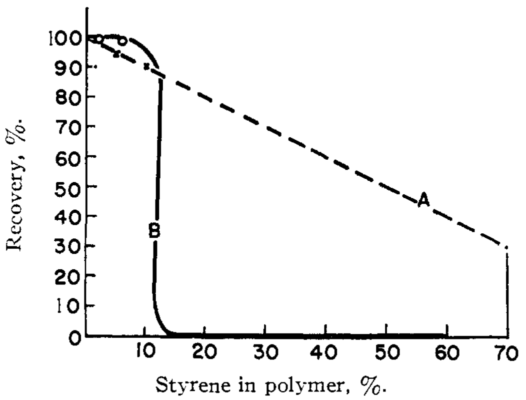

Fig. 3.—Recovery of addition product for block polymers of butadiene and styrene: A, predicted curve for mixtures of homopolymers; B, measured curve for block polymer.

These data demonstrated a number of properties, not only of the process but also of the product. The ability to convert polybutadiene to a polymer which did not precipitate upon addition of iodine monochloride permitted no interpretation other than the elimination of polybutadiene as a separate chemical entity. Previous experiments indicated that up to a 4-to-1 ratio of polystyrene to polybutadiene did not interfere with the recovery of the addition product. The maximum ratio of polystyrene to polybutadiene in the above was 1/1. Such interference could not result from polystyrene. During the initial portion of the reaction the polymerized styrene in the addition product was recovered. However, this ceased to be quantitative after the bound styrene reached about 6%. After this, the amount of addition product and the recovery of the polymer decreased and reached zero at about 10% bound styrene. This indicates that some of the polymer chains contained sufficient styrene to make the iodine monochloride addition product soluble. This effect was also noted with random copolymers in increasing the styrene content, but not until about 50% bound styrene had been reached. The average bound styrene content necessary to make the addition product soluble showed that styrene had a much greater effect when blocked onto the ends of a polymer than when copolymerized randomly. The tendency of the incoming styrene to make the addition product soluble made any estimate of the amount of styrene polymerizing to the homopolymer unrealistic. The possibility of forming graft polymers by chain transfer between a polystyrene radical and polybutadiene was checked by polymerizing a similar amount of styrene with diisopropylbenzene dihydroperoxide in 2.75% polybutadiene solution to give an apparent 95% chain extension. By removal of the gelled fraction and purification of the sol fraction, it was established by the iodine monochloride technique that all the polymerized butadiene present was in the form of polybutadiene. This corresponds with the conclusions drawn by Smets and Woodward.[10]

(m) **Chain Extension of Polybutadiene Dihydroperoxide with Methyl Methacrylate and Analysis of Products.**—In an attempt to obtain more precise results on the rate of homopolymer formation, polybutadiene was chain extended with methyl methacrylate. It was possible to show a minimum of 200% weight increase in the polymer precipitated with iodine monochloride. However, interpretation of these results was complicated by the ability of iodine monochloride to precipitate polymethyl methacrylate from carbon tetrachloride solution, even though there was no chemical reaction between the polymer and iodine monochloride. This method of investigating chain extension may have limitations for polar–non-polar monomer–polymer pairs.

(n) **Fractionation of Butadiene–Styrene Block Copolymers.**—Polybutadiene, twice purified, was chain extended with styrene as in the preceding experiments. A film was cast from solution and allowed to stand in air at 45° for 72 hr. This polymer was found to be partly gelled. The ge portion was loose and swelled in benzene. Benzene was added until the gel had imbibed its maximum and allowed to come to equilibrium before the soluble fraction was removed. Several extractions were carried out until the extract showed no evidence of dissolved polymer. The sol fraction contained large quantities of bound butadiene as evidenced by reaction with iodine monochloride. The swollen gel fraction was pressed into a film and dried. Refractive index of the film indicated 14% bound styrene which was unextractable. This styrene must have been bound directly to the butadiene in a block and cannot be considered to indicate the total amount of block polymer present, since this will consist of the higher end of the molecular weight distribution which may or may not contain the same proportion of active polymers as does the lower end of the distribution. The film of block polymer was not subjected to quantitative measurements, but it differed from a normal copolymer with 14% bound styrene. It was hard and stiff and not rubbery, which may be a result of a higher second-order transition point.

(o) **Intrinsic Viscosity Changes During Chain Extension.**—The change in intrinsic viscosities during chain extension was investigated. A polymeric dihydroperoxide composed of 72% butadiene and 28% styrene increased in intrinsic viscosity from 0.61 to 1.20 when styrene was blocked on the ends to give a polymer containing 35% styrene. Any polystyrene formation will tend to increase the intrinsic viscosity of the resultant mixture since the intrinsic viscosity of bulk polymerized polystyrene was found to be about 3.0. However, if this be neglected, as the analytical data indicate to be reasonable, then it is possible to calculate the Staudinger K and α values for a block polymer.

The Staudinger equation for the molecular weight of GR-S types at 50° is: $\eta = 5.25 \times 10^4 M^{0.667}$.[12]

Considering the above polymer and postulating that the total number of molecules in the system did not change, then if the system were always monodisperse, the molecular weight would increase from 7.6×10^4 to 1.1×10^5. Each styrene block has a molecular weight of 1.7×10^4 or approximately 1700 styrene units. α does not differ markedly for GR-S and styrene in solution being 0.69 for polystyrene.[13] If α for the block polymer be taken as that of polystyrene, then the Staudinger formula is $4.9 \times 10^4 M^{0.69}$.

Conclusions

This work provides a qualitative confirmation of the mechanisms assigned to emulsion polymerization. Predictions which have been made on the basis of the work of Harkins and Ewart and Smith as well as on our own have been experimentally verified.

The method of synthesis of the polymeric dihydroperoxides conforms to one of the more important requirements for preparing any active polymer to be chain extended, that is, the isolation of such polymers from conditions which may result in destruction of some of the active centers. This is accomplished since the polymeric dihydroperoxide becomes oil-soluble so quickly that there is no significant reaction with the iron(II) sulfate. If this is not done, subsequent deactivation of such active centers will give rise to an inactive polymer and result in contamination of the product. The fact that little of this exists is confirmed by the disappearance of insoluble ICl adduct characteristic of high styrene polymers. The use of the iodine monochloride technique allows rapid analysis of the polymers resulting from non-polar monomer polyperoxide pairs. The method does not appear to be applicable to non-polar–polar pairs, but other methods such as turbidimetric titration[14] exist which are useful.

Acknowledgments.—Helpful discussions were held with Dr. L. A. McLeod of Polymer Corporation Limited and Dr. M. H. Jones of Ontario Research Foundation. R. Wunder was technical assistant. The sample of dihydroperoxide of diisopropylbenzene was supplied by Hercules Powder Co. The authors thank Polymer Corporation Limited for permission to publish this data. Presented at the 130th Meeting, American Chemical Society, Atlantic City, N. J., Sept., 1956.

SARNIA, ONTARIO, CANADA

---

[12] R. L. Scott, W. C. Carter and M. Magat, THIS JOURNAL, **71**, 220 (1949).

[13] T. Alfrey, A. Bartovics and H. Mark, *ibid.*, **65**, 2319 (1943).

[14] H. W. Melville and B. D. Stead, *J. Polymer Sci.*, **16**, 505 (1955).