Reactivity Ratios of Conjugated Dienes Copolymerized in Emulsion at 5°[1]

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The copolymerization of isoprene and dimethylbutadiene with butadiene and of butadiene with styrene was studied in an emulsion system at 5°. From the combining ratio of the monomers at low conversion the reactivity ratios of the copolymerizing pairs were calculated. From these, estimates of the values of Q and e for butadiene, isoprene and dimethylbutadiene were made. A terpolymer of butadiene–isoprene–dimethylbutadiene was prepared and compared with polybutadiene. It was found to have a higher freeze point but superior retraction properties at low temperatures.

Introduction

Studies of the relative reactivities of vinyl monomers have been numerous[3] but information on conjugated diene monomers is less extensive. Butadiene is a major constituent of general purpose rubbers and isoprene or dimethylbutadiene have interesting commercial possibilities. Hence it was desirable to obtain more information relating to these three monomers, in particular their reactivity ratios when copolymerized in pairs or with styrene.

Recent publications have shown marked temperature dependence of the reactivity ratios. Mitchell and Williams[4] found that $r_1 = 1.83$ and $r_2 = 0.65$ when butadiene (M_1) was copolymerized with styrene (M_2) at 45° in emulsion. Orr and Williams[5,6] observed that polymerization at $-18°$ yielded a polymer which indicated $r_1 = 1.37$ and $r_2 = 0.38$ when butadiene is monomer-1 and styrene is monomer-2.

The values of Q and e changed from 1.83 to 1.38 and -0.8 to 0.008, respectively. Also at $-18°$ Orr and Williams[7] found that the reactivity ratios in the copolymerization of isoprene (M_1) and styrene (M_2) were $r_1 = 1.30$ and $r_2 = 0.48$, and in the copolymerization of dimethylbutadiene (M_1) and styrene (M_2) were $r_1 = 0.92$ and $r_2 = 0.42$. The Q and e values for isoprene and dimethylbutadiene were 1.19 and -0.112 and 1.09 and 0.181, respectively.

Although it was desirable to synthesize the polymers under conditions where side reactions are minimized, as at $-18°$, reactions at this temperature are not yet considered completely suitable for large scale production of copolymers. Considerably more data are available on polymerization reactions at higher temperatures. It was of importance to extend the above studies particularly to an intermediate temperature. This was chosen as 5°.

Results

The Phillips "Custom" (X-478) recipe,[8] developed for the copolymerization of butadiene and styrene at 5°, was found to give reasonable rates of conversion for the copolymerization of butadiene

with isoprene and of butadiene with 2,3-dimethyl-1,3-butadiene (Table I).

TABLE I
POLYMERIZATION OF BUTADIENE/ISOPRENE AND BUTADIENE/2,3-DIMETHYL-1,3-BUTADIENE (DMBd)

Charge ratio	Conversion, %	Time, hours
90/10 Bd/isoprene	77.5	21.0
75/25 Bd/isoprene	83.5	27.0
50/50 Bd/isoprene	63.2	19.0
0/100 Bd/isoprene	48.7	24.7
75/25 Bd/DMBd	94.3	69.0
50/50 Bd/DMBd	100.0	73.0
0/100 Bd/DMBd	88.3	48.8

Some variations in the recipe were investigated using a charge ratio of butadiene/isoprene, 90/10. The pH of the sugar–soap solution, and the concentration of ferrous sulfate were varied (Tables II and III). Fryling and St. John[9] reported that increased rates of conversion were obtained for the copolymerization of butadiene and styrene when the potassium chloride was added to the activator solution previous to aging rather than to the sugar–soap solution. However, their results could not be duplicated for butadiene/isoprene, 90/10

TABLE II
POLYMERIZATION OF BUTADIENE/ISOPRENE, 90/10. VARIATION OF pH OF SUGAR–SOAP SOLUTION (UNBUFFERED CHARGES)

pH	Conversion in 21 hours, %
9.45	61.5
9.60	62.4
9.95	66.5
10.30	67.4
10.60	71.5
10.70	71.9
11.60	49.8

TABLE III
POLYMERIZATION OF BUTADIENE/ISOPRENE, 90/10. VARIATION OF FERROUS SULFATE CONCENTRATION

Part FeSO₄·7H₂O	Conversion in 21 hours, %

Part $FeSO_4 \cdot 7H_2O$	Conversion in 21 hours, %
A. KCl in soap master batch	
0.110	57.1
.140	71.9
.166	74.7
.194	59.3
B. KCl in activator solution	
0.110	53.4
.140	63.8
.166	69.5

(1) Sponsored by the Defence Research Board, Ottawa, Ontario. Presented before the Division of High Polymer Chemistry, American Chemical Society, Buffalo, New York, March 23–27, 1952.

(2) Defence Research Board.

(3) F. R. Mayo and C. Walling, Chem. Revs., 46, 191 (1950).

(4) J. M. Mitchell and H. L. Williams, Can. J. Research, 275, 35 (1949).

(5) R. J. Orr and H. L. Williams, Can. J. Tech., 29, 29 (1951).

(6) R. J. Orr and H. L. Williams, Can. J. Chem., 29, 270 (1951).

(7) R. J. Orr and H. L. Williams, ibid., 30, in press (1952).

(8) J. M. Mitchell, R. Spolsky and H. L. Williams, Ind. Eng. Chem., 41, 1592 (1949).

(9) C. F. Fryling and W. M. St. John, Jr., ibid., 42, 2164 (1950).

(Table III). The original recipe gave the optimal results in all the cases investigated.

The isoprene used in these studies was commercial material that was redistilled once and stored in the refrigerator before use. The 2,3-dimethyl-1,3-butadiene was synthesized, and was likewise redistilled and stored in the refrigerator before use. It had a refractive index of $n^{25}D$ 1.4354, and gave a 72.5% yield of cis-4,5-dimethyl-1,2,3,6-tetrahydrophthalic anhydride on reaction with maleic anhydride.

The determination of the Q and e values of a monomer involves its copolymerization with a monomer of known Q and e values, and the estimation of the reactivity ratios (r_1 and r_2) from the composition of the copolymer. Then Q and e can be calculated from the Alfrey–Price equations.[10]

$$r_1 = Q_1/Q_2 e^{-e_1(e_1 - e_2)} \qquad (1)$$

$$r_2 = Q_2/Q_1 e^{-e_2(e_2 - e_1)} \qquad (2)$$

The Q and e values of butadiene have been determined[4,6,11] using styrene as a reference monomer. All of these determinations were made at temperatures other than 5° the temperature of polymerization chosen for this particular investigation. The temperature dependence of the reactivity ratios has already been noted. The initial step was to determine the reactivity ratios of butadiene at 5° using styrene as a reference monomer. Butadiene in turn was used as a reference monomer to determine the reactivity ratios of isoprene and 2,3-dimethylbutadiene. Before any copolymerization studies could be undertaken it was necessary to have a method of determining the composition of the copolymers.

As the carbon–hydrogen content of butadiene, isoprene and 2,3-dimethyl-1,3-butadiene are very similar, micro-analysis of their copolymers or terpolymers would not be feasible. Chemical analyses of copolymers is not satisfactory. Burger, Donaldson and Baty[12] devised a procedure for the determination of isoprene in polymers based on the fact that chromic acid oxidation of the structure

$$\begin{array}{c} CH_3 \\ | \\ -CH_2-C=CH- \end{array}$$
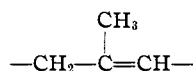
formed a molecule of acetic acid which may be separated and estimated. Using natural rubber they only obtained a 75% yield of acetic acid.

The most promising approach to the problem seemed to be analysis by infrared methods. There are a considerable number of reports on quantitative analysis by infrared, but there is not a great deal published in the open literature on analysis of polymers. Barnes and co-workers[13] developed an analysis of natural rubber Buna S blends using the C–CH₃ absorption peak at 7.27 μ. Their accuracy was limited to 5–10% because of the inability to make their samples of constant thickness.

Except for special cases where intermolecular

action occurs, the amount of light transmitted by a sample is governed by Beer's law

$$I/I_0 = e^{-kcd} \qquad (3)$$

where d is the length of the optical path or thickness of the absorbing layer of the sample. The reproducibility of sample thickness is necessary to obtain desirable accuracy. Dinsmore and Smith[14] repeated the work of Barnes and co-workers and reported an accuracy of $\pm 1\%$. They appear to have prepared samples of more uniform thickness. Also they eliminated d from the spectroscopic function by employing a ratio of extinction coefficients determined at different wave lengths, since d is independent of wave length. They extended their work to include the analysis of acrylonitrile copolymers, and again reported an accuracy of $\pm 1\%$.

The Optical Laboratory group[15] had become interested in the analysis of acrylonitrile copolymers by infrared and developed a superior method of sample preparation. This method was immediately applicable to the present study thus saving time in developing a method of analysis. A great deal of the time was expended in the preparation of samples of polymers for calibration purposes. This involved the preparation of copolymers using various charge ratios of monomers and treating them to 100% conversion, Table IV.

TABLE IV

POLYMERS FOR INFRARED ANALYSIS CALIBRATION

Charge ratio	Conversion, %	Time, hours
	Bd/isoprene	
100/0	76.7	21.5
75/25[a]	100.0	48.0
50/50[a]	100.0	73.5
25/75[a]	100.0	72.0
0/100	67.4	21.5
	Bd/2,3-Dimethyl-1,3-butadiene	
75/25[a]	100.0	95.0
50/50[a]	100.0	48.0
0/100	88.3	48.8
	Styrene/butadiene	
100/0	88.0	23.25
50/50	100.0	47.0
25/75	100.0	49.0
0/100	67.4	21.5
	Bd/isoprene/2,3-dimethyl-1,3-butadiene	
60/20/20	100.0	44.0

[a] Reactivated and recatalyzed at approximately 30 hours.

As these polymers were of known composition, "working curves" could be obtained by plotting the measured extinction ratios against the composition. Once these working curves were established the analysis of copolymers was possible. It has been possible to obtain accurate results for copolymers of butadiene and isoprene (or butadiene and 2,3-dimethyl-1,3-butadiene) containing 50 mole per cent. or less isoprene (or 2,3-dimethyl-1,3-butadiene). Above this concentration the difference in per cent. absorption of the peaks chosen becomes

(10) T. Alfrey, Jr., and C. C. Price, J. Polymer Sci., 2, 101 (1947).

(11) C. C. Price, ibid., 3, 772 (1948).

(12) V. L. Burger, W. E. Donaldson and J. A. Baty, Rubber Chem. and Tech., 16, 660 (1943); ASTM Bull. No. 120, 23 (1943).

(13) R. B. Barnes, V. Z. Williams, A. R. Davis and P. Giesecke, Ind. Eng. Chem., Anal. Ed., 16, 9 (1944).

(14) H. L. Dinsmore and D. C. Smith, Anal. Chem., 20, 11 (1948).

(15) J. D. Sands and G. S. Turner, ibid., 24, 791 (1952).

too small. This places some limitation on the determination of the Q and e values, since a wide range of charge ratios should be used in their determination. This is not serious in practice since butadiene will be the major constituent in most experimental polymers. Phillips 99 mole per cent. pure butadiene and isoprene were used to prepare the copolymers for preparation of the calibration curves for the analysis of this set of copolymers. These pure materials were also used in the determination of the Q and e values of isoprene. A pure grade 2,3-dimethyl-1,3-butadiene was not available commercially. It would have been desirable to use material purified through the sulfone. As there was insufficient material available to carry out the purification on a large enough scale, the monomer purified by distillation was used. Redistilled styrene (99.6% pure) was used throughout these studies.

The results of the copolymerization studies are shown in Tables V, VI and VII. The copolymer ratios, r_1 and r_2, were estimated by use of the copolymerization equation

$$\mathrm{d}M_1/\mathrm{d}M_2 = \frac{M_1(r_1M_1 + M_2)}{M_2(r_2M_2 + M_1)} \qquad (4)$$

This equation may be used if one makes the assumption that the feed is essentially unchanged when the conversion is only carried to a few per cent. Table VIII lists the estimated r_1 and r_2 values (calculated by the method of Fineman and Ross[16]) and the calculated Q and e values for the monomers. The results of earlier studies are included for comparison.[5-7]

Table V

COPOLYMERIZATION OF STYRENE (M_2) WITH BUTADIENE (M_1)

$M_1{}^a$	Time (hours)	Conversion, %	Butadiene in copolymer, %	$\mathrm{d}M_1{}^b$
0.375	3.5	23.5	31.4	0.469
.500	3.5	17.5	43.1	.593
.625	2.0	17.0	56.7	.716
.750	3.5	20.7	68.8	.809
.875	3.0	12.7	87.3	.929

^{a} Mole fraction of butadiene in original monomer mixture. ^{b} Mole fraction of butadiene in copolymer by infrared analysis.

Table VI

COPOLYMERIZATION OF BUTADIENE(M_1) WITH ISOPRENE(M_2)

$M_2{}^a$	Time, hours	Conversion, %	Isoprene in copolymer, %	$\mathrm{d}M_2{}^b$
0.125	2.2	18.3	18.9	0.158
.250	4.0	13.5	32.1	.271
.375	3.5	15.0	40.5	.349
.500	5.0	20.5	57.9	.521
.625	6.0	27.2	^{c}	

^{a} Mole fraction of isoprene in original monomer mixture. ^{b} Mole fraction of isoprene in copolymer by infrared analysis. ^{c} Per cent. isoprene in copolymer too high to analyze.

The Q and e values of butadiene at 5° were calculated using styrene as the reference monomer. The Q and e values of styrene at 60° have been arbitrarily chosen[11] as 1.0 and −0.8, respectively. These reactivity factors of butadiene were in turn

(16) M. Fineman and R. D. Ross, J. Polymer Sci., 5, 259 (1950).

Table VII

COPOLYMERIZATION OF BUTADIENE (M_1) WITH 2,3-DI-METHYL-1,3-BUTADIENE (M_2)

$M_2{}^a$	Time, hours	Conversion, %	2,3-Dimethyl-1,3-butadiene in copolymer, %	$\mathrm{d}M_2{}^b$
0.125	2.5	11.6	19.9	0.134
.250	4.1	24.9	32.1	.222
.375	4.75	19.5	41.6	.303
.500	5.5	21.8	58.0	.465
.625	6.5	20.1	^{c}	

^{a} Mole fraction of 2,3-dimethyl-1,3-butadiene in original monomer mixture. ^{b} Mole fraction of 2,3-dimethyl-1,3-butadiene in copolymer by infrared analysis. ^{c} Per cent. 2,3-dimethyl-1,3-butadiene in copolymer too high to analyze.

used to calculate the Q and e values of isoprene and 2,3-dimethyl-1,3-butadiene using the reactivity ratios (r_1 and r_2) determined.

The value of r_1 for butadiene in the butadiene–styrene reaction is considerably less than that observed at 45° by Mitchell and Williams[3] but agrees well with the results obtained by Meehan.[17] The former worked with monomer ratios containing 50% or more by weight of styrene while the latter based his calculations on results obtained with less than 50 wt. % of styrene. The present data agree also with those obtained in bulk polymerization[18,19] and at −18° by Orr and Williams.[6] The values of r_1 and r_2 for the copolymerization of isoprene and dimethylbutadiene with butadiene are in good qualitative agreement with calculated values from the data obtained in the study of the copolymerization of the three dienes individually with styrene.[5-7]

The interpretation of the Q and e values is more difficult. There are two possible solutions. Price[20] has suggested that the one giving the more negative e value is preferred by him. Both sets of results are in Table VIII. The two sets of results for butadiene can in turn be used to calculate two answers for each set for isoprene and dimethylbutadiene. When the less negative value of e is taken for butadiene either set of answers for isoprene and/or dimethylbutadiene may be considered reasonable. When the more negative value of e is used for butadiene the results with the less negative values of e for isoprene and dimethylbutadiene seem reasonable. Further only the results with the less negative value of e are reasonable for the copolymerization studies at −18°. Thus the more consistent picture is obtained by using only the less negative values of e. As Price suggests the obvious extension to this study is copolymerization of the dienes with a monomer such as acrylonitrile for which some data are available.[21]

The 60/20/20 charge ratio was chosen for the preparation of a terpolymer. It is evident from Table IX that the reaction was quite homogeneous throughout its course and shows that the recipe

(17) E. J. Meehan, ibid., 1, 318 (1946).
(18) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and F. R. Mayo, This Journal, 70, 1527 (1948).
(19) R. Simha and L. A. Wall, J. Research Natl. Bur. Standards, 41, 521 (1948).
(20) Personal communication.
(21) W. H. Embree, J. M. Mitchell and H. L. Williams, Can. J. Chem., 29, 253 (1951).

TABLE VIII
REACTIVITY RATIOS OF DIENES

M_1	M_2	r_1	r_2	Q	e	Q	e
		Copolymerization at 5°					
Butadiene	Styrene	1.38	0.64	1.18	−0.45	2.06	−1.15
Relative to butadiene $Q = 1.18$, $e = -0.45$							
Butadiene	Isoprene	0.75	.85	1.14	.22	2.12	−1.12
Butadiene	Dimethylbutadiene	0.85	.63	0.98	.34	1.98	−1.24
Relative to butadiene $Q = 2.06$, $e = -1.15$							
Butadiene	Isoprene	0.75	.85	1.27	− .48	5.94	−1.82
Butadiene	Dimethylbutadiene	0.85	.63	0.98	− .36	6.01	−1.94
		Copolymerization at −18°					
Butadiene	Styrene	1.37	.38	1.38	.008	5.02	−1.61
Isoprene	Styrene	1.30	.48 ·	1.20	− .112	3.61	−1.49
Dimethylbutadiene	Styrene	0.92	.42	1.10	.181	5.23	−1.78
		Copolymerization at 45°					
Butadiene	Styrene	1.83	.65	1.83	− .8	1.83	−0.8
		Calculated data from copolymerization at −18°					
Butadiene	Isoprene	0.94	1.06				
Butadiene	Dimethylbutadiene	1.26	0.78				

used gave a reasonable rate of polymerization— approximately 6% per hour.

TABLE IX
POLYMERIZATION OF BUTADIENE, ISOPRENE AND 2,3-DI- METHYL-1,3-BUTADIENE 60/20/20

Time, hours	Conversion, %	Butadiene, %
2.5	20.7	54.4
5.0	31.4	55.0
10.0	46.9	54.4
15.0	64.2	54.0
20.0	77.3	54.0
25.0	86.9	55.7

Physical test data obtained on the 60/20/20 copolymer tested in the compounding recipe shown in Table X are given in Table XI. In general the copolymer exhibited higher freeze point but better

TABLE X
COMPOUNDING RECIPE

Polymer	100 parts by weight
NBS-Black (EPC Channel)	40
NBS-Zinc oxide	5
RRC-2 sulfur	2
NBS-Altax (benzothiazole disulfide)	3
RRC-Stearic acid	1.5

TABLE XI
PHYSICAL TEST DATA FOR POLYMER FROM 60/20/20 BUTA- DIENE/ISOPRENE/DIMETHYLBUTADIENE CHARGE

	60/20/20 terpolymer	Polybutadiene
Micro tensile		
Cure at 292°F., min.	25	25
Tensile p.s.i.	3190	3155
Modulus (300%) p.s.i.	1230	750
Elongation, %	540	620
Gehman T-10	−56°C.	approx. −72°C.
Freeze point	−64.5	......
TR test		
TR-10	−57°C.	−57°C.
TR-70	−43°C.	−16.5°C.
Brittle test		
50% break	−67°C.	−73°C.

retraction properties than a polybutadiene of similar properties, i.e., 60% conversion at 5°.

Experimental Techniques

1. **Polymerization Technique.**—All polymerizations were conducted in 8 oz. screw-cap bottles fitted with a gasket[22] for syringe sampling.[23] A soap masterbatch was prepared by dissolving a potassium soap of disproportion-ated rosin known as Dresinate 214 (195 g.) in approximately 1400 ml. of distilled water, and adding KOH (3.75 g.), Daxad 11 (4.2 g.) and KCl (21 g.). Daxad 11 is a dispers-ing agent formed from naphthalene sulfonate condensed with formaldehyde. The solution was boiled for a few minutes, cooled, made up to 1680 g. with distilled water and stored under an atmosphere of nitrogen. Best results were obtained if the mixture was allowed to stand at least a day before using.

Dextrose (5 g.) was dissolved in 195 g. of water and 2 g. of a 10% solution of potassium hydroxide added. This solution was digested on the hot-plate for 20 min., cooled, made up to the original weight with distilled water and added to 200 g. of the soap masterbatch and 477 g. of dis-tilled water. This sugar-soap solution had a pH of 10.7. Each bottle was charged with 88.2 g. of this solution and 0.12 g. (0.13 ml.) of mixed tertiary mercaptan (MTM— Phillips petroleum) was added using a 1-ml. hypodermic syringe and needle. Then the required amount of iso-prene (2,3-dimethyl-1,3-butadiene or styrene) was weighed into each bottle. When isoprene was being charged, the bottles were capped and cooled in the 5° bath for 15 min. before the addition of butadiene. They were then care-fully wiped and the butadiene added. This step was omitted with 2,3-dimethyl-1,3-butadiene and styrene but was con-sidered necessary with isoprene because of the following step and the low b.p. (34°) of isoprene. A slight excess of buta-diene was added and the excess butadiene was allowed to vaporize to drive out the air in the bottle. The bottle was capped when it had reached the correct weight. The bottles were then placed in the constant temperature bath and rotated end over end for 15 min. At that time 5 ml. of the activator solution was injected by syringe and needle and the agitation was resumed for another 15 min., then 0.5 ml. of a solution of cumene hydroperoxide in hexane was injected using a 1-ml. syringe and needle. This catalyst solution was prepared by weighing 1.48 g. of 68% cumene hydroperoxide into a 10-ml. volumetric flask and diluting to the mark with hexane. (There was no difference in the rate of conversion when benzene was substituted for hexane.)

The activator solution was prepared in the following man-ner. Approximately 100 ml. of distilled water was boiled for a few minutes, and nitrogen was bubbled through it while

(22) S. A. Harrison and E. R. Meincke, *Anal. Chem.*, **20**, 47 (1948).
(23) R. J. Houston, *ibid.*, **20**, 49 (1948).

it was cooling. FeSO₄·7H₂O (0.70 g.) and K₄P₂O₇ (0.98 g.) were placed in a 4-oz. screw-cap bottle fitted with a self-sealing gasket, and 50 ml. of the water treated as above was pipetted in. The bottle was lightly capped, the air swept out with nitrogen, securely capped and pressured with 20 p.s.i. of nitrogen pressure. The solution was then heated for 30 min. at 60°. It was allowed to cool to room temperature and thoroughly mixed by shaking before using.

The reactions were stopped at the appropriate times by injecting 2.7 ml. of a 7.5% emulsion of 2,5-di-t-butyl hydroquinone in Dresinate 214, the bottle allowed to rotate an additional 15 min., a sample removed by syringe and needle and a known amount of latex dried to determine the conversion of hydrocarbon to polymer. Nitrogen was introduced into the bottle to maintain a pressure to facilitate sampling.

The sugar-soap solution was adjusted to the desired pH with either 10% potassium hydroxide or approximately 0.1 N hydrochloric acid. When the effect of pH was being studied adjustments were made in the amount of the solution charged to each bottle to compensate for the increased amounts of water.

Exactly the same technique was employed using various amounts of FeSO₄·7H₂O or KCl when the effect of these was being studied. In the second case a soap masterbatch was prepared with potassium chloride omitted. Instead 2.5 g. of potassium chloride was added to the activator solution prior to aging.

The amounts of potassium pyrophosphate and cumene hydroperoxide were adjusted so that molar ratios of 1:1:1 were maintained for the cumene hydroperoxide, ferrous sulfate and potassium pyrophosphate in the above experiments. It has been shown[9] that equality of molar concentrations results in maximal rates of conversion.

2. Preparation of Polymers for Infrared Analysis Calibration.—The monomers used were purified as follows. Phillips 99 mole per cent. pure or technical 97.5% pure butadiene was distilled through a short, glass helix-packed column equipped with reflux to remove inhibitor and accumulated dimers. The 99 mole per cent. isoprene was distilled through a stainless steel helix-packed column using a reflux ratio of 20:1 to remove inhibitor. The 2,3-dimethyl-1,3-butadiene was distilled through the same column using a reflux ratio of 20:1. Styrene (99.6% pure) was distilled under reduced pressure (7 mm.) and only the middle fraction collected.

The above described recipe and technique were used with the following modifications. The bottles containing the 100% isoprene and 100% 2,3-dimethyl-1,3-butadiene charges were swept out with nitrogen before capping. The other isoprene charges were cooled in solid carbon dioxide snow just prior to adding the butadiene.

The copolymers were purified in the following manner. The latex was poured, with stirring, into 500 ml. of filtered isopropyl alcohol and the coagulated polymer was allowed to stand overnight. The supernatant liquid was decanted, the polymer cut into small pieces and a representative sample taken. This sample was washed with isopropyl alcohol, collected on a buchner funnel (no filter paper was used) and squeezed as dry as possible with a spatula. It was transferred to a erlenmeyer flask and sufficient filtered benzene (approximately 400 ml.) to dissolve the sample added. After allowing to stand two or three days, it was always found there was a residue of insoluble material. The supernatant liquid was decanted from this residue into 400 ml. of filtered methanol. The precipitated polymer was collected

on the buchner funnel, washed with methanol, squeezed dry as possible, and dried overnight at room temperature under reduced pressure (2 mm.). When butadiene–styrene copolymers were precipitated 0.01 g. of hydroquinone was added to the methanol to inhibit resinification of the polymer on standing.

3. Copolymerization Studies.—Pairs of monomer mixtures containing a total of 0.8 mole of monomers were made up at five equally spaced mole fraction intervals. Due to the present limitations of the analytical method mentioned previously the entire composition range could not be included. The above described recipe and charging technique, with the exception that the isoprene charges were cooled in solid carbon dioxide snow prior to adding the butadiene, were used. The monomers were the same as above and were purified in the same manner. They were weighed to the nearest tenth of a gram on a torsion balance. Polymerization was carried out to as low a conversion as possible and still obtain a suitable coagulum. The charges were stopped by injecting 2,5-di-t-butylhydroquinone, a sample removed by syringe and needle to determine the conversion and the remainder of the charge was coagulated by adding it to 300 ml. of filtered isopropyl alcohol. After allowing to settle overnight the supernatant liquid was decanted, the polymer washed with isopropyl alcohol, and then dissolved in the minimum amount of filtered benzene. The benzene solution was decanted from the insoluble residue into 200 ml. of filtered methanol, the precipitated polymer collected and dried overnight at room temperature under reduced pressure (2 mm.).

4. Preparation of cis-4,5-Dimethyl-1,2,3,6-tetrahydrophthalic Anhydride.—2,3-Dimethyl-1,3-butadiene (4.1 g.) was added in small portions, with cooling to maleic anhydride (4.9 g.). There was an initial vigorous reaction. After allowing the solid reaction mixture to stand overnight it was extracted with boiling methylcyclohexane and the resulting solution filtered to remove a gummy residue. On cooling long colorless needles were deposited, m.p. 78–79° (uncor.). The yield was 6.6 g. (or 72.5% of the theoretical amount). The literature[24] reports m.p. 78°.

5. Preparation of Sample for Micro Compounding and Testing.—Two charges were prepared and stopped at 61.5% conversion with 2,5-di-t-butylhydroquinone. The latex from these two charges was combined and added to a brine-acid solution with vigorous stirring. The brine–acid contained B.L.E. (1.25 parts per 100 parts dry rubber). The coagulated polymer was collected, washed thoroughly with water and then dried for 4 hours at 185°F. in a forced draft oven. The dry weight was 59 g.

(24) E. H. Farmer and F. L. Warren. J. Chem. Soc., 897 (1929).