

nate could be due to a small contribution of structures such as II; this explanation is made doubtful by the observed decrement in the case of *p*-nitrophenyl thiocyanate.

An alternative explanation of the observed increments might be that they arise from an abnormally large vibration polarization¹² such as is found in *p*-dinitrobenzene. The large increments observed here and, especially, the large differences between the thio- and selenocyanates suggests that these are principally resonance effects.

(12) L. E. Sutton, *Annual Reports Chem. Soc.*, **37**, 36 (1940).

Summary

The electric moments of some *para* substituted phenylthiocyanates and phenylselenocyanates have been measured in benzene solution at 25°; the substituents used were the amino, dimethylamino, nitro, and methoxyl groups. A rather large enhancement of resonance is observed when the thiocyno- and, to a smaller extent, the selenocyno- group is *para* to an electron-receiving group. The results have been briefly discussed in terms of resonance.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Properties of Polymers as Functions of Conversion. IV. Composition Studies of Rubber-like Copolymers¹

BY F. T. WALL, R. W. POWERS,² G. D. SANDS³ AND G. S. STENT

It is generally recognized that the products obtained at different stages of conversion in a polymerization reaction will exhibit wide variations in chemical and physical properties. For example, the intrinsic viscosity can show changes of several hundred per cent.,⁴ and the molecular weight can likewise vary several fold.⁵ In the case of copolymers, the composition of the product, which is generally different from that of the reaction mixture, can also change during the conversion.

Numerous copolymer systems have been investigated from a composition standpoint by Mayo,⁶ Alfrey⁷ and others. For bulk and solution polymerizations, relatively simple theories have been devised for the compositional relationships,^{6a,7a,8} but for emulsion systems, the situation is much more complicated. A considerable amount of experimental work, however, has been done on emulsion copolymerizations. For example, Meehan⁹ studied the GR-S system in some detail and observed that the styrene content varied from 17 to 25% in the course of a reaction when the initial charge was 25% styrene. Fordyce and Chapin¹⁰ also have investigated several emulsion systems. The investigations here reported deal with the de-

pendence of composition on conversion for a number of rubber-like copolymers other than GR-S.

Theory

During recent years considerable thought has been given to the theoretical aspects of the compositional relationships in copolymers.^{6a,7a,8} These theories ultimately give rise to a basic differential equation governing the relative rates of disappearance of the monomers. This differential equation, which is valid for single phase polymerizations, is

$$\frac{dM_1}{dM_2} = \frac{M_1(r_1M_1 + M_2)}{M_2(M_1 + r_2M_2)} \quad (1)$$

where M_1 and M_2 equal the number of moles of unreacted monomer and the parameters r_1 and r_2 represent the ratios of certain specific reaction rate constants for the chain growth steps.¹¹ The general validity of equation (1) has been established by many experiments, although it is not obvious that it should be valid for emulsion reactions. However, it will be seen later that an equation of the same type does empirically agree with the observations for many emulsion systems, although considerable doubt can be raised as to its full validity in some cases. Actually it is possible to derive such an equation for emulsion systems by making certain assumptions such as the following:

(1) It is first supposed that the reaction does not take place in the oil phase of the emulsion. (If the reaction occurs in the oil phase, then equation (1) would be expected to hold right off and the present discussion would be irrelevant except for the perturbing effect of the monomer solubility in water.)

(2) Secondly, it is assumed that the amount of monomeric material in the actual reaction environment (supposed not to be the oil phase) repre-

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program (first reported in March, 1947).

(2) Present address: Cryogenic Laboratory, Ohio State University, Columbus 10, Ohio.

(3) Present address: Chemical and Physical Research Laboratories, Firestone Tire and Rubber Company, Akron 17, Ohio.

(4) F. T. Wall, R. W. Powers, G. D. Sands and G. S. Stent, *THIS JOURNAL*, **69**, 904 (1947).

(5) F. T. Wall and L. F. Beste, *ibid.*, **69**, 1761 (1947).

(6) (a) F. R. Mayo and T. M. Lewis, *ibid.*, **66**, 1594 (1944); (b) T. M. Lewis, F. R. Mayo and W. F. Hulse, *ibid.*, **67**, 1701 (1945).

(7) (a) T. Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) T. Alfrey and J. G. Harrison, Jr., *THIS JOURNAL*, **68**, 299 (1946).

(8) F. T. Wall, *ibid.*, **66**, 2050 (1944).

(9) E. J. Meehan, *J. Polymer Sci.*, **1**, 318 (1946).

(10) R. G. Fordyce and E. C. Chapin, *THIS JOURNAL*, **69**, 581 (1947).

(11) T. Alfrey, F. R. Mayo and F. T. Wall, *J. Polymer Sci.*, **1**, 581 (1946).

sents only a small fraction of the total monomer present.

(3) Finally it is postulated that the distribution of monomers between the oil and reaction phases is subject to the ideal solution laws. This is equivalent to assuming that the ratio of the reactants in the oil phase is proportional to (but not necessarily equal to) their ratio in the reaction phase. Although we speak of "reaction phase," it must be understood that the reaction may take place in the neighborhood of some interface or in soap micelles as well as in a distinct phase of the system.

In accordance with the above assumptions, the desired relationship can readily be derived. Letting M_1 and M_2 represent the total amounts of the monomers, and letting M'_1 and M'_2 equal the amounts in the reaction phase, we can write the following differential equation for the relative rates of disappearance of the two monomers

$$\frac{dM_1}{dM_2} = \frac{M'_1(r_1M'_1 + M'_2)}{M'_2(M'_1 + r_2M'_2)} \quad (2)$$

According to the ideal solution laws

$$\frac{M'_1}{M'_2} = k \frac{M_1}{M_2} \quad (3)$$

it being assumed that M'_1 and M'_2 are very small compared to M_1 and M_2 . Substituting the above relationship (3) into the differential equation (2), we find

$$\frac{dM_1}{dM_2} = \frac{M_1(kr_1M_1 + M_2)}{M_2(M_1 + r_2/kM_2)} = \frac{M_1(r'_1M_1 + M_2)}{M_2(M_1 + r'_2M_2)} \quad (4)$$

where $r'_1 = kr_1$ and $r'_2 = r_2/k$. This equation has the same form as the basic relationship valid for single phase polymerizations, except that r_1 and r_2 are respectively multiplied and divided by the distribution coefficient k . The above derivation suggests that the copolymerization equation might be applicable to emulsion systems even if the polymerization occurs outside the oil phase. Accordingly the results here reported will be interpreted on that basis. To emphasize the fact that the copolymerization parameters for emulsion systems are not necessarily ratios of specific reaction rate constants, they will be represented as primed quantities (r'_1 and r'_2). Of course if the reaction occurs in the oil phase, this distinction is unnecessary.

Partial Conversion Composition

In earlier publications^{4,5} the concept of partial conversion properties of polymers was introduced using intrinsic viscosities and molecular weights as examples. At this time it is appropriate to define what we shall mean by the partial conversion composition of a copolymer. If \bar{F}_i represents the average weight fraction of monomer i in the copolymer, then the partial conversion composition, $\bar{\bar{F}}_i$ will be given by the relationship

$$\bar{\bar{F}}_i = \bar{F}_i + W \frac{d\bar{F}_i}{dW} \quad (5)$$

where W is the weight conversion. Taking account of the definitions of \bar{F}_i and W , it can be shown from (5) that

$$\bar{\bar{F}}_i = \frac{m_i dM_i}{m_1 dM_1 + m_2 dM_2} \quad (6)$$

where M_1 and M_2 are the molecular weights of the monomers. It is evident that $\bar{\bar{F}}_i$ represents the composition of the copolymer increment which forms at any given instant during the reaction. Assuming the validity of differential equation (4), this can be rewritten as

$$\bar{\bar{F}}_1 = \frac{M_1 M_1 (r'_1 M_1 + M_2)}{M_1 r'_1 M_1^2 + (M_1 + M_2) M_1 M_2 + M_2 r'_2 M_2^2} \quad (7)$$

Experimental Section

The polymerizations studied include butadiene with 2,5-dichlorostyrene, with *p*-chlorostyrene, with acrylonitrile, and with 1-cyanobutadiene. Using dodecyl mercaptan as a modifier and Procter and Gamble SF Flakes as the emulsifying agent, these copolymerizations were carried out for various initial charges. In every case, potassium persulfate was the catalyst used.

The polymerizations were carried out in 12 and 28-ounce beverage bottles fitted with special self-sealing caps. During the polymerizations the reaction bottles were immersed in a water-bath maintained at $50 \pm 0.02^\circ$, and were rotated end-over-end at the rate of 20 revolutions per minute. Samples of the latex were removed at various times by means of a brass syringe, the needle of which was inserted into the latex through the self-sealing bottle cap.¹² The polymers were coagulated by adding the latex dropwise to absolute ethanol with vigorous mechanical stirring.

To check the validity of the sampling technique, a special experiment was conducted using butadiene with 2,5-dichlorostyrene. In this experiment the composition of a very high conversion sample obtained from a 12-ounce bottle, from which several samples had been removed in the course of the reaction, was compared with the composition of a polymer formed in a 4-ounce bottle from which no low conversion samples had been taken. The experiment was carried out for three different initial monomer ratios, *i. e.*, 85/15, 60/40, and 40/60 by weight. As long as the final percentage conversion was the same, no significant composition differences were observed between the products obtained in the two different ways. This suggests that the sampling technique is truly representative; if unrepresentative samples had been removed, the effect would have been evident in the composition of the final product.

The following materials were used in these studies: 1. Butadiene: Phillips "Research Grade" 1,3-butadiene was used throughout the investigation. 2. 2,5-Dichlorostyrene: This material was obtained from the Monsanto Chemical Company. It was redistilled immediately before use, as were all other liquid monomers employed in this investigation. At a pressure of 1–2 mm., it boiled between 57 and 58° . 3. *p*-Chlorostyrene: The *p*-chlorostyrene used in this study was obtained from the Dow Chemical Company and boiled at 114° at 6 mm. pressure. 4. Acrylonitrile: Redistilled Eastman "Practical Grade" acrylonitrile was used for this investigation. At atmospheric pressure, it was distilled at 77° . 5. 1-Cyanobutadiene: This chemical consisted mostly of the *trans*-isomer and was obtained from the Organic Division at the University of Illinois. It distilled at 49° under a pressure of 31 mm. 6. *n*-Dodecyl Mercaptan: Very pure *n*-dodecyl mercaptan was prepared by the Organic Division at the University of Illinois by the hydrolysis of

(12) R. L. Frank, C. E. Adams, J. R. Blegen, R. Deanin and P. V. Smith, *Ind. Eng. Chem.*, **39**, 887 (1947).

n-dodecylisothiuronium chloride prepared from pure *n*-dodecyl bromide. The boiling range of this mercaptan was 127–129° at 9 mm., and the material was believed to be 99.5% pure.

Two samples from each batch of latex removed from the reactor were used to determine the conversion by a method of total solids. The composition of the copolymers of butadiene with chloro-substituted styrenes was determined by chlorine analyses. These analyses were accomplished by fusing the copolymer samples with sodium and titrating the chloride formed with silver nitrate, using the amperometric technique of Laitinen and Kolthoff.¹³ The compositions of butadiene-acrylonitrile copolymers were determined by nitrogen analyses carried out by a macro-Kjeldahl method.¹⁴

Discussion and Analysis of Results

Each monomer pair investigated will be considered separately, with each set of data, calculations, and conclusions treated as a unit. In every case, butadiene will be considered the first monomer of the pair and will be given the subscript "1."

To determine the copolymerization parameters for butadiene with 2,5-dichlorostyrene, three different monomer ratios were used. These ratios were 85/15, 70/30, and 50/50 parts of butadiene to parts of 2,5-dichlorostyrene by weight. Samples were taken from the polymerization bottle at intervals corresponding roughly to 10, 20, 30, and 40% conversion. As indicated earlier, the conversions were determined in duplicate, whereas the compositions were measured either in triplicate or duplicate for each sample. The results for this system are given in Tables I-A, I-B, and I-C. From a knowledge of the composition as a function of conversion, it is possible to determine the copolymerization parameters.

Theoretically, a single run with analyses corresponding to several conversions should suffice to determine the parameters. In practice, however, it is much better to use each of several dif-

TABLE I-A

Initial charge in 12-oz. bottle			Weight fraction of dichlorostyrene in polymer		
68.0	g. butadiene				
12.01	g. 2,5-dichlorostyrene				
0.2814	g. dodecyl mercaptan				
140.0	g. 3% solution of P. & G. SF Flakes				
8.0	ml. 3% solution of K ₂ S ₂ O ₈				
Reaction time, hr.	Fractional conversion				
0	0				
1.9	0.131 } .131	0.131	0.2546 } .2554 .2570		0.2557
3.2	.227 } .233	.230	.2434 } .2436		.2435
4.4	.304 } .304	.304	.2335 } .2369		.2352
5.7	.361 } .364	.362	.2244 } .2293 .2293		.2277

TABLE I-B

Initial charge in 12-oz. bottle			Weight fraction of dichlorostyrene in polymer		
56.0	g. butadiene				
24.02	g. 2,5-dichlorostyrene				
0.2789	g. dodecyl mercaptan				
140.0	g. 3% solution of P. & G. SF Flakes				
8.00	ml. 3% solution of K ₂ S ₂ O ₈				
Reaction time, hr.	Fractional conversion				
0	0				
1.5	0.131 } .133	0.132	0.4181 } .4226 .4251		0.4219
2.5	.240 } .241	.240	.4081 } .4110 .4147		.4113
3.5	.338 } .343	.340	.4014 } .4028 .4083		.4042
4.5	.440 } .450	.445	.3860 } .3900 .3947		.3902

TABLE I-C

Initial charge in 12-oz. bottle			Weight fraction of dichlorostyrene in polymer		
40.0	g. butadiene				
39.99	g. 2,5-dichlorostyrene				
0.2772	g. dodecyl mercaptan				
140.0	g. 3% solution of P. & G. SF Flakes				
8.00	ml. 3% solution of K ₂ S ₂ O ₈				
Reaction time, hr.	Fractional conversion				
0	0				
1.1	0.154 } .154	0.154	0.5874 } .5878 .5906 .5925		0.5896
1.7	.275 } .276	.276	.5734 } .5794 .5795		.5774
2.4	.417 } .419	.418	.5736 } .5742 .5797		.5758
3.1	.544 } .547	.546	.5614 } .5630 .5657 .5678		.5641

ferent initial charging ratios to make the calculations. The procedure finally adopted was the following: The logarithm of the amount of unreacted butadiene was plotted against the logarithm of the amount of unreacted comonomer. It was found empirically that these plots gave straight lines, at least for moderate conversions. Taking the initial slope of such a line, one obtains a relationship between the two parameters, r'_1 and r'_2 . Letting the slope of the log plot equal m , it is readily seen that

$$m = \frac{d \ln M_1}{d \ln M_2} = \frac{r'_1 M_1 + M_2}{M_1 + r'_2 M_2} \quad (8)$$

Evidently if one has experimental data for two different initial charging ratios, one can calculate r'_1 and r'_2 from the two simultaneous equations of

(13) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1941).

(14) The authors are indebted to Dr. H. A. Laitinen and his group for these analyses.

type (8) involving the two m 's. To get an indication of the experimental error, at least three runs were always made, and the best over-all value for the parameters was selected. The procedure adopted was to plot r'_1 versus r'_2 and note the points of intersection for the three (or more) lines so plotted. After inscribing a circle in the triangle resulting from three such lines, one can take the center of that circle to determine the best set of values for the parameters. For purposes of illustration, the graphs will be given for the butadiene-2,5-dichlorostyrene system (Figs. 1-2), but similar plots will not be included for all the other pairs investigated. The procedure employed here differs from that used by Mayo and Lewis,^{6a} who used the integrated form of the equation instead of the differential form.

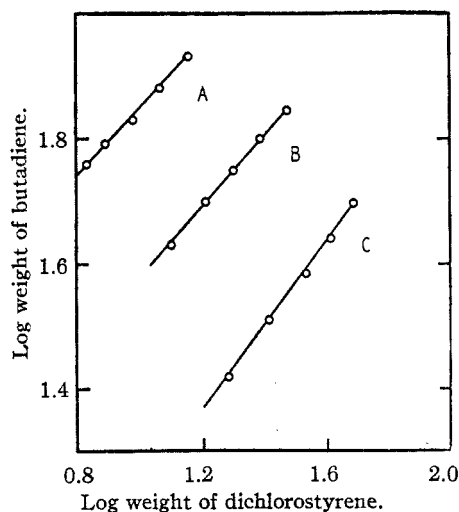


Fig. 1.—Log weight butadiene vs. log weight dichlorostyrene for determining values of m . Curves labeled A, B and C correspond to data in Tables I-A, I-B and I-C.

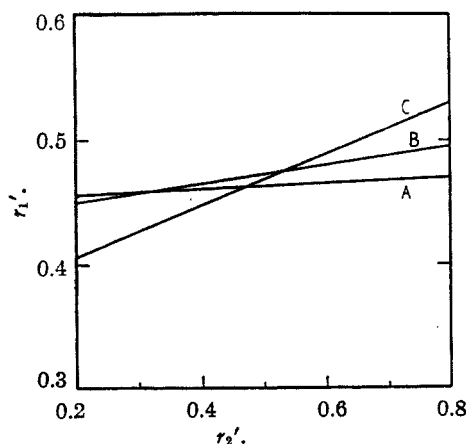


Fig. 2.—Plot for determining copolymerization parameters for dichlorostyrene-butadiene system. Lines A, B and C correspond to data in Tables I-A, I-B and I-C.

The parameters r'_1 and r'_2 were each found to equal 0.46 for butadiene with 2,5-dichlorostyrene.

This suggests that the system butadiene with 2,5-dichlorostyrene can form an azeotropic copolymer⁸ of composition 75 parts 2,5-dichlorostyrene to 25 parts of butadiene by weight (this is a one-to-one molar ratio). To test this prediction, an experiment was carried out with that initial charge. The results are given in Table II. It will be observed that the composition was indeed very constant over a wide range of conversion, justifying the theory in this connection.

TABLE II

Initial charge in 12-oz. bottle				
	60.92	g. 2,5-dichlorostyrene		
	19.1	g. butadiene		
	0.2832	g. dodecyl mercaptan		
	140.0	g. 3% solution of P. & G. SF Flakes		
	8.00	ml. 3% solution of $K_2S_2O_8$		
Reaction time, hr.	Fractional conversion		Weight fraction of dichlorostyrene in polymer	
0.5	0.032	0.037	0.7743	0.7766
	.42		.7788	
1.1	.286	.288	.7766	.7784
	.290		.7766	
1.6	.519	.522	.7742	.7772
	.524		.7782	
6.0	.946	.948	.7489	.7496
	.950		.7502	

The validity of the theory was further tested by carrying out a special experiment involving a 3 to 1 weight charging ratio of butadiene with 2,5-dichlorostyrene, and comparing the observed compositions with those calculated using the parameters obtained from the experiments described earlier. The results are shown in Fig. 3, which gives the calculated average and partial conversion compositions together with the observed average compositions. Bearing in mind the fact that the parameters were determined by completely independent experiments not involving use of any of the points included in Fig. 3, it is

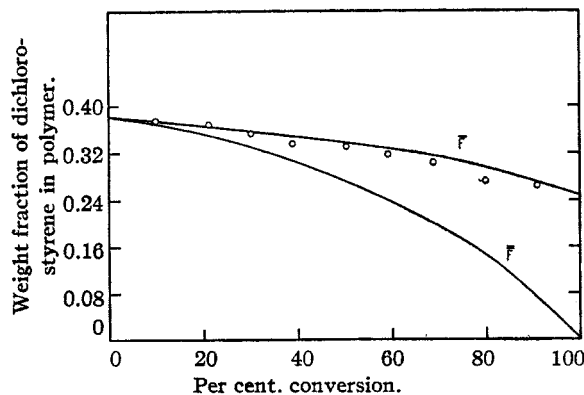


Fig. 3.—Predicted (\bar{F}) and partial conversion (F) compositions of dichlorostyrene in copolymer with butadiene together with experimental average compositions (indicated by circles).

clear that the theory agrees well with observation. It will be noted that although the composition of the charge was only 25% (by weight) of the substituted styrene, the partial conversion composition was initially 38%. This figure falls off with conversion, finally ending up at zero.

Butadiene and *p*-chlorostyrene were polymerized for charging ratios of 80/20, 60/40, and 40/

60, butadiene to the substituted styrene, by weight. The results for this system are given in Tables III-A, III-B, and III-C. The values for r'_1 and r'_2 were found to be 1.07 and 0.42, respectively.

Butadiene and acrylonitrile were copolymerized in the weight ratios 85/15, 75/25, and 65/35. The data for these polymerizations are compiled in Tables IV-A, IV-B, and IV-C. The values of the parameters r'_1 and r'_2 appear to be 0.4 and -0.1. The negative value found for r'_2 is of course meaningless as far as the theory is concerned. Nevertheless, the agreement for the several compositions was excellent, as seen in Fig. 4, demonstrating that the copolymerization equation may have only empirical significance for emulsion systems. The negative value in the case of the acrylo-

TABLE III-A

Initial charge in 12-oz. bottle		16.01 g. <i>p</i> -chlorostyrene 64.0 g. butadiene 0.2827 g. dodecyl mercaptan 140.0 g. 3% solution of P. & G. SF Flakes 8.00 ml. 3% solution of $K_2S_2O_8$			
Reaction time, hr.	Fractional conversion	Weight fraction of <i>p</i> -chlorostyrene in polymer			
0					
2.5	0.149	0.150	0.1820	0.1824	
	.152		.1829		
4	.252	.254	.1835	.1859	
	.256		.1858		
5.5	.356	.356	.1933	.1933	
	.356		.1933		
7	.481	.482	.1878	.1892	
	.484		.1906		

TABLE III-B

Initial charge in 12-oz. bottle		31.97 g. <i>p</i> -chlorostyrene 48.0 g. butadiene 0.2781 g. dodecyl mercaptan 140.0 g. 3% solution of P. & G. SF Flakes 8.00 ml. 3% solution of $K_2S_2O_8$			
Reaction time, hr.	Fractional conversion	Weight fraction of <i>p</i> -chlorostyrene in polymer			
0	0				
2	0.188	0.190	0.3597	0.3620	
	.192		.3617		
3	.300	.300	.3681	.3693	
	.301		.3705		
4.2	.458	.463	.3627	.3632	
	.468		.3637		
5	.541	.543	.3690	.3699	
	.545		.3708		

TABLE III-C

Initial charge in 12-oz. bottle		48.01 g. <i>p</i> -chlorostyrene 32.0 g. butadiene 0.2759 g. dodecyl mercaptan 140.0 g. 3% solution of P. & G. SF Flakes 8.00 ml. 3% solution of $K_2S_2O_8$			
Reaction time, hr.	Fractional conversion	Weight fraction of <i>p</i> -chlorostyrene in polymer			
0					
1.5	0.218	0.219	0.5326	0.5345	
	.220		.5364		
2.2	.485	.487	.5596	.5607	
	.489		.5617		
4.2	.696	.706	.5654	.5684	
	.716		.5670		
			.5728		

TABLE IV-A

Initial charge in 28-oz. bottles		30.09 g. acrylonitrile 170.0 g. butadiene 0.6970 g. dodecyl mercaptan 350.0 g. 3% solution of P. & G. SF Flakes 20.00 ml. 3% solution of $K_2S_2O_8$			
Reaction time, hr.	Fractional conversion	Nitrogen in polymer, %		Weight fraction of acrylonitrile in polymer	
1	0.209	0.210	5.62	5.64	0.2136
	.212		5.65		
2	.390	.392	5.27	5.31	.2011
	.394		5.35		
2.8	.518	.518	4.79	4.85	.1837
	.519		4.92		
3.5	.654	.654	4.56	4.58	.1735
	.655		4.61		
13.7	.983	.986	3.79	3.81	.1443
	.988		3.83		

TABLE IV-B

Initial charge in 28-oz. bottle		50.02 g. acrylonitrile 150.0 g. butadiene 0.7575 g. dodecyl mercaptan 350.0 g. 3% solution of P. & G. SF Flakes 20.00 ml. 3% solution of $K_2S_2O_8$			
Reaction time, hr.	Fractional conversion	Nitrogen in polymer, %		Weight fraction of acrylonitrile in polymer	
0.5	0.156	0.158	7.93	7.94	0.3008
	.160		7.95		
0.9	.266	.268	7.58	7.60	.2879
	.269		7.62		
1.3	.394	.396	7.55	7.56	.2864
	.398		7.57		
1.8	.528	.528	7.22	7.24	.2742
	.529		7.25		
2.5	.688	.688	6.88	6.92	.2621
	.688		6.95		
3.3	.829	.831	6.69	6.73	.2549
	.833		6.77		
5.0	.949	.949	6.37	6.41	.2428
	.949		6.45		
18.3	1.00	1.00	6.14	6.14	.2330
	1.00		6.15		

TABLE IV-C

Initial charge in 28-oz. bottle	69.90	g. acrylonitrile
	130.0	g. butadiene
	0.6994	g. dodecyl mercaptan
	350.0	g. 3% solution of P. & G. SF Flakes
	20.00	ml. 3% solution of $K_2S_2O_8$

Reaction time, hr.	Fractional conversion	Nitrogen in polymer, %		Weight fraction of acrylonitrile in polymer	
0.2	0.030	0.031	9.54	9.54	0.3614
	.032				
.5	.178	.179	9.40	9.42	.3568
	.180		9.43		
.8	.518	.521	9.05	9.12	.3455
	.524		9.19		
1.0	.631	.632
	.634				
9.0	1.00	1.00	9.03	9.01	.3413
	1.00		8.99		

nitrile copolymer is doubtless due to the appreciable water-solubility of the nitrile, which would render invalid one of the basic assumptions that went into the derivation of the emulsion equation.

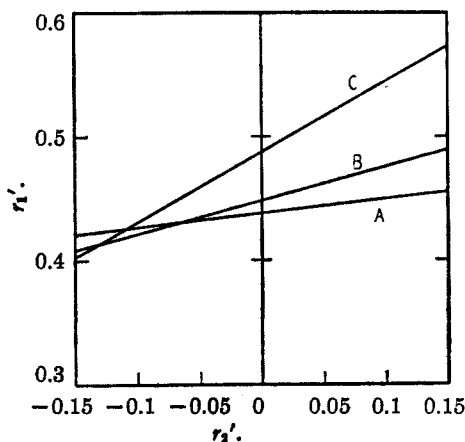


Fig. 4.—Plot for determining copolymerization parameters for acrylonitrile-butadiene system. Lines A, B and C correspond to data in Tables IV-A, IV-B and IV-C.

Butadiene was polymerized with 1-cyanobutadiene in emulsion using weight ratios of 75/25, 60/40, and 40/60, and the results are given in Tables V-A, V-B, and V-C. In this case r_1' was found to be -0.08 , although a value 0 would probably be satisfactory; r_2' was found to have a value of 1.7. This implies that butadiene cannot grow onto a free radical whose last member is a cyanobutadiene unit, although a cyanobutadiene can add onto a butadiene. Accordingly, the first polymer to form will be abnormally high in cyanobutadiene, but as soon as that monomer is depleted, the consumption of butadiene increases. This strange behavior also manifests itself in the conversion *versus* time curve (Fig. 5). The initial rate of conversion is found to be very high, but after about 25% reaction, the rate falls off considerably.

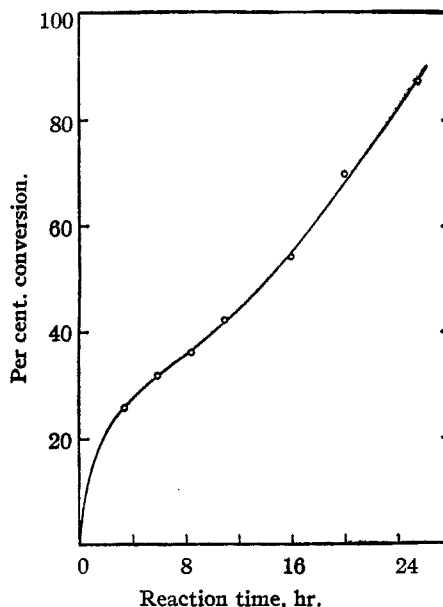


Fig. 5.—Conversion *vs.* reaction time for cyanobutadiene-butadiene copolymer (data in Table V-A).

The experimental results given above demonstrate empirically the validity of the basic copolymerization equation. Theoretically it was shown that the equation might be expected to hold whether the polymerization occurs in the oil or in the aqueous phase. Therefore the experimental observations here reported do not prove which phase the reaction occurs in. As a matter of fact, Fordyce and Chapin¹⁰ have suggested that the oil phase is the seat of the reaction in the case of styrene copolymerized with acrylonitrile. To arrive at a similar conclusion here, it would be

TABLE V-A

Initial charge in 28-oz. bottle	50.03	g. cyanobutadiene
	150.0	g. butadiene
	1.007	g. dodecyl mercaptan
	350.0	g. 3% solution of P. & G. SF Flakes
	20.00	ml. 3% solution of $K_2S_2O_8$

Reaction time, hr.	Fractional conversion	Nitrogen in polymer, %	Weight fraction of cyano- butadiene in polymer
3.5	0.259 } .261 }	11.03 } 11.38 }	11.20 } 0.6325 }
6	.319 } .321 }	10.82 } 10.83 }	10.82 } .6110 }
8.5	.362 } .363 }	10.20 } 10.43 }	10.32 } .5828 }
11	.410 } .411 }	9.87 } 10.02 }	9.94 } .5613 }
16	.539 } .545 }	7.70 } 7.76 }	7.73 } .4365 }
20	.697 } .698 }	5.88 } 5.99 }	5.94 } .3354 }
25.5	.871 } .876 }	4.79 } 4.79 }	4.79 } .2705 }

TABLE V-B

Initial charge in 12-oz. bottle	31.98	g. cyanobutadiene
	48.0	g. butadiene
	0.4511	g. dodecyl mercaptan
	140.0	g. 3% solution of P. & G. SF Flakes
	8.00	ml. 3% solution of $K_2S_2O_8$

Reaction time hr.	Fractional conversion	Nitrogen in polymer, %	Weight fraction of cyano- butadiene in polymer
4.5	0.409 } 0.410		
	.410		
6	.443 } .446	12.08 } 12.12	0.6844
	.449	12.15	
8	.491 } .494	11.69 } 11.72	.6618
	.496	11.76	
10	.543 } .544	11.12 } 11.12	.6279
	.546	11.13	
25.5	.951 } .951	7.74 } 7.77	.4388
		7.80	

necessary to have more data than are available at present.

Summary

Copolymerizations of butadiene with various other monomers have been carried out in emulsion systems. It is found that the copolymerization equations of Mayo and others have empirical

TABLE V-C

Initial charge in 12-oz. bottle	47.92	g. cyanobutadiene
	32.0	g. butadiene
	0.4256	g. dodecyl mercaptan
	140.0	g. 3% solution of P. & G. SF Flakes
	8.00	ml. 3% solution of $K_2S_2O_8$

Reaction time, hr.	Fractional conversion	Nitrogen in polymer, %	Weight fraction of cyano- butadiene in polymer
0			
4	0.474 } 0.478	13.54 } 13.60	0.7680
	.483	13.66	
5.5	.625 } .626	13.01 } 13.07	.7381
	.627	13.13	
7	.690 } .693	12.77 } 12.77	.7211
	.696	12.77	
8	.730 } .730	12.68 } 12.70	.7172
	.730	12.73	
25.5	.913 } .918	11.06 } 11.09	.6262
	.922	11.12	

validity for all of the systems examined. The equations are also believed to be theoretically significant in most cases, an exception being butadiene with acrylonitrile. The anomalous results obtained for that pair are attributed to the high solubility of acrylonitrile in water.

URBANA, ILLINOIS

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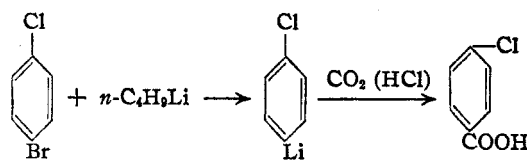
The Application of the Halogen-Metal Interconversion Reaction to Syntheses with Isotopic Carbon¹

BY ARTHUR MURRAY, III, W. W. FOREMAN AND WRIGHT LANGHAM

The extensive application of the halogen-metal interconversion reaction to a wide variety of aryl halides has resulted in the preparation of organometallic compounds having additional functional groups.^{2a,b,c,d}

Because of the rapidity of the reaction, the halogen-metal interconversion between an alkyl-lithium compound and an aryl halide is uniquely suited to the preparation of organolithium compounds with additional functional groups. As an example, *p*-chlorobromobenzene and *n*-butyllithium react to give a 90% yield of *p*-chlorophenyllithium in ten minutes.^{2a} Subsequent carbonation results in the formation of the corresponding carboxylic acids according to the reaction.

The use of isotopic carbon in biological studies is complicated by the relatively small quantities of



isotope available and by the unavoidable high dilution of the isotope when introduced into biological systems. In order to conserve isotopic carbon and to achieve maximum specific activity required for certain investigations, we have adapted the halogen-metal interconversion reaction to the micro synthesis of certain compounds of biological significance.

p-Aminobenzoic acid, labelled with C^{14} in the carboxyl group, was prepared by an adaptation of the reaction of Gilman and Stuckwisch.^{3a,b} The *p*-aminophenyllithium derivative⁴ was isolated and washed free of *n*-butyllithium before carbonation with gaseous $C^{14}O_2$.

(1) This paper is based on work performed under contract W-7405-Eng-36 with the Atomic Energy Commission at the Los Alamos Scientific Laboratory of the University of California.

(2) (a) Gilman, Langham and Moore, *THIS JOURNAL*, **62**, 2327 (1940); (b) Langham, Brewster and Gilman, *ibid.*, **63**, 545 (1941); (c) Gilman, Langham and Willis, *ibid.*, **62**, 346 (1940); (d) Gilman and Gainer, *ibid.*, **69**, 1946 (1947).

(3) (a) Gilman and Stuckwisch, *ibid.*, **63**, 2844 (1941); (b) Gilman and Stuckwisch, *ibid.*, **64**, 1007 (1942).

(4) This compound is believed to be $p\text{-LiC}_6\text{H}_4\text{N}(\text{Li})_2$. C. G. Stuckwisch, private communication.