k_x/k_y the contribution from the zero point energy effect will be less than 1% for processes of the type involved in this reaction at 350°. It has been shown that the reduced mass effect is unity if similar bonds are made and ruptured in the transition state.[7] Therefore there will be no reduced mass contribution to the ratio k_x/k_y and as a result its value should be unity within less than 1%. Thus an analysis of mechanism B predicts no fractionation of carbon isotopes during the pyrolysis, which is in agreement with experiment. Almost any concerted reaction mechanism for the pyrolysis will lead to this same result.

UPTON, LONG ISLAND, N. Y.

[CONTRIBUTION FROM CHEMICAL AND PHYSICAL RESEARCH LABORATORIES, THE FIRESTONE TIRE AND RUBBER COMPANY]

The Effect of Comonomer on the Microstructure of Butadiene Copolymers

BY FREDERICK C. FOSTER AND JOHN L. BINDER

RECEIVED OCTOBER 30, 1952

The microstructure of butadiene–styrene copolymers having a wide range of styrene contents has been determined by infrared absorption. The results demonstrate that the percentage of *trans*-1,4-addition increases, the 1,2-addition decreases and the *cis*-1,4-addition decreases as the styrene content is increased. Similar measurements on five other butadiene copolymer systems indicate that all of these vinyl monomers, acrylonitrile, methacrylonitrile, methyl vinyl ketone, vinylpyridine and α-methylstyrene, change the microstructure in the same direction as styrene, differing only in the magnitude of their effect. A theoretical explanation, consistent with the experimental results obtained, is given for the change in microstructure with comonomer content.

It is well-known that butadiene polymerizes by 1,2-addition to produce side vinyl ($—CH=CH_2$) groups and by 1,4-addition to produce double bonds in the polymer chain with *cis* and *trans* configurations. With butadiene–vinyl copolymers the diene portion of the copolymer chain may also have any or all of the three microstructures mentioned above. It is known[1] that, in general, increasing the temperature of polymerization, for both types of polymers, increases the amount of *cis*-1,4-addition and decreases the amount of *trans*-1,4-addition. It is also known that a variation in the mechanism of polymerization causes a change in the microstructure of butadiene polymers; thus, 1,2-addition predominates in sodium-catalyzed butadiene polymers.

Little or nothing is known about the effect of the kind or concentration of the vinyl comonomer on the microstructure of the diene polymer. Thus early workers[2] by ozonolysis concluded that copolymers of butadiene with methyl methacrylate and methacrylonitrile probably contained more 1,4-addition than polybutadiene. Early infrared work[3] indicated that butadiene–styrene or butadiene–acrylonitrile copolymers had smaller amounts of 1,2-addition than polybutadiene. However, Kolthoff, Lee and Mairs,[4] using the perbenzoic acid method, reported that the amount of 1,2-addition did not vary with kind or concentration of the comonomer in butadiene copolymers. Hart and Meyer[5] on the basis of infrared measurements, concluded that the amount of styrene had no effect on the amounts of 1,2- and 1,4-addition in the butadiene portion of butadiene–styrene copolymers. However, their data show a slight increase of *trans*-1,4-addition with a corresponding decrease of *cis*-1,4-addition as the styrene concentration was increased from 0 to 23%.

With many of the butadiene copolymers reported above the range of concentration of the comonomer was small and the experimental uncertainties too large to show small trends. Therefore, the effect of kind and concentration of the comonomer in butadiene–vinyl copolymers was investigated, in the present work, using large concentration ranges. Because of the dependence of microstructure on temperature and polymerization mechanism, all of the polymers reported here were prepared at the same temperature using free radical catalysis.

Experimental

All vinyl monomers were purified by distillation before use. Monomers were tested for the absence of polymer before use. Physical constants found for the monomers were: acrylonitrile, $n^{20}D$ 1.3916; methacrylonitrile, $n^{20}D$ 1.4005; α-methylstyrene, $n^{20}D$ 1.5386, methyl vinyl ketone, $n^{20}D$ 1.4117; 2-vinylpyridine, $n^{20}D$ 1.5482 and styrene, $n^{20}D$ 1.5468.

Butadiene, supplied by Koppers Company and meeting Rubber Reserve standards of purity, was merely condensed before use.

All copolymerizations were conducted at 50° using the following recipe

Water	180
Monomers	100
S F Flakes	5
Potassium persulfate	0.3
Dodecanethiol	0.75

Conversions were varied from low to complete conversion.

Copolymers were coagulated with methanol and washed several times with water and with methanol. Final purification was accomplished by extracting the copolymers under gentle reflux with ethanol–toluene azeotrope (70–30 by volume). Three changes of solvent were used, each extraction lasting an hour. The copolymers were then extracted three times with acetone and dried under vacuum. It was necessary to substitute methanol for acetone in the final extractions of the acrylonitrile copolymers, methacrylonitrile copolymers and the high styrene copolymers in

---

(1) A. W. Meyer, *Ind. Eng. Chem.*, **41**, 1570 (1949).

(2) R. Hill, J. R. Lewis and J. L. Simonson, *Trans. Faraday Soc.*, **35**, 1067, 1073 (1939); E. N. Alekseeva, *J. Gen. Chem. U.S.S.R.*, **11**, 353 (1941); *Rubber Chem. and Technol.*, **15**, 698 (1942).

(3) J. U. White and P. J. Flory, private communication to Office of Rubber Reserve, February 20, 1943.

(4) I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 220 (1947).

(5) E. J. Hart and A. W. Meyer, THIS JOURNAL, **71**, 1980 (1949).

order to avoid dissolving some of the copolymer. In the case of methyl vinyl ketone copolymers, it was necessary to extract only with methanol.

The composition of butadiene–styrene copolymers was determined by refractive index. The method used was essentially that developed by the Bureau of Standards.[6] Copolymers, high in styrene, did not wet the prisms and Thoulet's solution was used to establish contact with the prism in these cases. The relation between refractive index and styrene content, which is not linear over the complete range of compositions, was determined from copolymers of known composition. This relationship agrees with previously determined work.[7]

Copolymer compositions for the systems butadiene–acrylonitrile, butadiene–methacrylonitrile and butadiene–vinyl pyridine were determined by the Friedrich micro-Kjeldahl method for nitrogen analysis. Carbon determination, by combustion, was used in the analysis of butadiene–methyl vinyl ketone copolymers. The composition of one of the butadiene–α-methylstyrene copolymers was calculated from initial charge, having been taken to complete conversion.

The determinations of the amounts of *cis*-1,4-, *trans*-1,4- and 1,2-additions, as well as styrene, were made by a spectroscopic method developed in these laboratories which is partially described elsewhere.[8] Essentially it consists of measuring the intensities of the bands at 10.34, 10.98, 14.7 and 14.29 μ for *trans*-1,4-, 1,2-(terminal vinyl groups), *cis*-1,4- and styrene components, respectively, and assuming that Beer's law holds for the components and the mixture as exemplified by the equation

$$D_i = e_{ij}c_jl + e_{ik}c_kl + e_{im}c_ml + e_{in}c_nl$$

where D_i is the optical density at wave length i, e_{ij}, e_{ik}, etc., are the extinction coefficients at wave length i of components j, k, m, etc., the c's are concentrations in moles/l. or g./l. and l is the length of light path in cm.

In the styrene determinations, it was essential to correct for the deviations from Beer's law, as exhibited by the optical density *vs.* concentration curve for polystyrene, and to purify the polymers by the Bureau of Standards extraction procedure in order to obtain values which agreed with those found by refractive index measurements. The trustworthiness of the results is indicated by the "Total Found," (Column 6 of Table I), which is the amount of polymer found in the solution by the infrared analyses compared with that determined from the total solids of the solution. This value should be equal to or less than 100% depending upon how many of the diene double bonds are saturated. Analyses of polybutadienes by this method have given values for the total unsaturation which agree with those found chemically within the experimental error of the latter method.

The copolymers studied here were analyzed by this method with the following variations in the case of those comonomers for which it was impossible to make calibration curves. The optical densities were measured at the band maxima even though, with some polymers, these may have shifted somewhat from 10.34, 10.98, or 14.70 μ. The α-methylstyrene was considered to absorb the same as styrene at 10.34, 10.98, 14.7 and 14.29 μ and the polymers analyzed as butadiene–styrene copolymers. No correction for the deviation from Beer's law was made for the α-methylstyrene however. The spectra of homopolymers of the other vinyl comonomers showed that there are no other strong bands in the vicinities of the bands at 10.34, 10.98 and 14.7 μ due to polybutadiene, and these copolymers were then analyzed simply as polybutadienes. This means that the contributions of the comonomer absorption at these wave lengths were neglected which should result in the amount of polybutadiene found in the copolymer by the analysis being larger than that found chemically. Actually the two results agree surprisingly well for most of the copolymers studied here which means that the absorptions of the comonomers at the wave lengths used for the polybutadiene analyses must be small. Consequently, it is thought that the results obtained are reliable to about 2%.

Results

Table I gives the analyses of butadiene–styrene copolymers by the spectroscopic method and also the amount of styrene found by refractive index. In this table the values under the headings BD = 100 refer to the composition of the butadiene portion of the polymer. The average deviation of the styrene determined spectroscopically and by refractive index is 1.7%. Most of the high totals shown in the table are due to the larger amounts of styrene found spectroscopically. The two exceptions are the two polymers with the highest totals; these were low conversion polymers and the presence of a small amount of styrene monomer might explain both the high totals and the anomalous microstructure values. The actual percentages of the three diene structures may be computed from Table I by subtracting the value in column 4 from the value in column 6 and multiplying the quantity by the value in each of the first three columns.

TABLE I

COMPOSITIONS OF BUTADIENE–STYRENE COPOLYMERS BY INFRARED METHOD

cis-1,4 BD = 100, %	*trans*-1,4 BD = 100, %	1,2 BD = 100, %	Styrene by infrared, %	Styrene by refractive index, %	Total styrene and diene by infrared, %	
13.4	77.6	9.2	87.0	86.3	99.4	
12.3	77.6	10.1	86.8	85.5	102.8	
14.0	75.2	10.9	80.5	78.5	103.2	
14.1	73.9	12.0	72.9	71.7	97.6	
13.6	73.0	13.4	59.9	60.1	95.9	
16.2	70.0	13.7	64.1	59.0	101.7	
12.0	70.0	18.2	55.8	57.1	103.9	
17.5	67.6	14.9	50.3	49.0	101.5	
16.0	68.5	15.5	41.9	40.1	99.3	
17.4	66.9	15.6	30.8	27.7	103.5	
16.7	65.8	17.6	23.9	22.7	100.1	
15.3	65.7	19.1	21.1	21.7	104.0	
19.6	63.4	17.0	0		96.0	Duplicate analyses
19.0	63.7	17.4	0		94.8	

The data show that, as the amount of styrene in the polymer increases, the proportion of *trans*-1,4-addition increases and the proportions of *cis*-1,4- and 1,2-additions decrease. Enough polymerizations were run to various conversions to establish that the conversion has no effect on the microstructure of the polymers.

Figure 1 shows graphically the relationships between the amount of styrene (by refractive index) in the copolymer and the amounts of *cis*-1,4-, *trans*-1,4- and 1,2-additions in the butadiene portion of the polymer. These relationships are linear within experimental error.

Table II gives experimental results of microstructures of several other butadiene copolymer systems. All of the comonomers investigated apparently are similar to styrene in their effect on microstructure and differ only in the magnitude of this effect. For these copolymers the ranges of concentration and the analytical accuracy are not great enough to show unambiguously the effect of dif-

---

(6) A. Arnold, I. Madorsky and L. A. Wood, *Anal. Chem.*, **23**, 1656 (1951).

(7) J. D. D'Ianni, L. D. Hess and W. C. Mast, *Ind. Eng. Chem.*, **43**, 319 (1951). A. T. McPherson, private communication to Office of Rubber Reserve, January 31, 1950.

(8) John L. Binder, private communication to Office of Rubber Reserve, June 25, 1951.

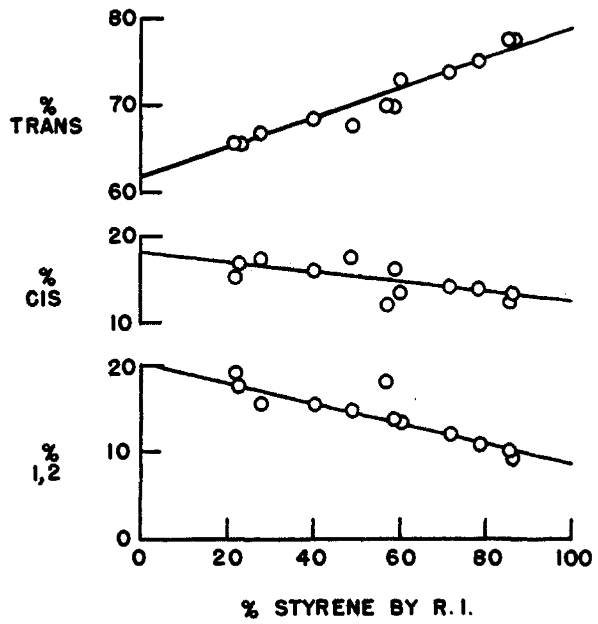

Fig. 1.—Microstructure *vs.* styrene content of butadiene–styrene copolymers.

ferent concentrations of comonomer. The effect of kind of comonomer is clearly shown, however, by comparing these copolymers either with polybutadiene or butadiene–styrene copolymers of similar butadiene content given in Table II.

TABLE II

MICROSTRUCTURE OF BUTADIENE PORTION OF DIENE–VINYL COPOLYMERS

Vinyl comonomer	*cis*-1,4 BD = 100, %	*trans*-1,4 BD = 100, %	1,2 BD = 100, %	Butadiene by infrared, %	Butadiene chemically, %
α-Methylstyrene	20.1	73.0	6.9	27.6	
	14.2	77.0	8.7	37.6	
	17.8	64.8	17.4	53.7	
	17.6	69.1	13.3	55.8	
	18.8	64.4	16.8	77.7	80.1[a]
Vinylpyridine	18.0	70.4	11.7	24.7	24.6[b]
	14.2	71.6	14.2	50.1	46.5[b]
	16.7	66.5	16.8	61.9	61.2[b]
	18.8	64.9	16.4	68.0	74.6[b]
Methyl vinyl ketone	13.8	72.7	13.5	62.4	59.6[c]
	16.1	69.7	14.2	70.5	68.9[c]
	17.5	67.4	15.0	75.1	71.6[c]
Acrylonitrile	14.6	76.2	9.3	72.0	75.4[b]
	12.4	77.1	10.5	76.9	76.1[b]
	16.7	72.3	11.0	72.8	78.0[b]
Methacrylonitrile	15.9	75.5	8.6	56.8	67.6[b]
	14.9	75.1	10.0	62.8	71.6[b]
	14.1	71.3	14.5	73.1	78.2[b]

[a] Based on initial charge and complete conversion. [b] Nitrogen analyses. [c] Carbon analyses.

Discussion

Alfrey[9] has emphasized that the microstructure of a given butadiene unit is not determined at the time when the butadiene molecule is attacked by the growing chain, but rather at the time of the subsequent propagation step, when the butadiene radical attacks the next monomer. In copolymerization reactions of butadiene, this subsequent propagation step may involve reaction with either butadiene monomer or the comonomer. It does not seem surprising that the structure of the monomer in this latter step would, in general, affect the proportions of the three diene structures in the resultant polymer. Therefore, in general, the percentages of *cis*-1,4-, *trans*-1,4- and 1,2-structures would be expected to be different from those for polybutadiene and, in fact, vary as the type of comonomer is varied. It would also follow that the change in the microstructure of diene copolymers would increase as the comonomer content of the copolymer is increased.

Considering that only the two propagation reactions involving diene free radicals affect microstructure while all four propagation reactions affect copolymer composition, kinetic calculations show that structure should depend linearly on the quantity $1/(1 + r_1[\text{D}]/[\text{V}])$, where r_1 is the reactivity ratio for the diene and [D] and [V] refer to the mole fractions of diene and vinyl monomer, whereas the copolymer composition depends linearly on the quantity $(1 + r_2[\text{V}]/[\text{D}])/(2 + r_1[\text{D}]/[\text{V}] + r_2[\text{V}]/[\text{D}])$. These two quantities become identical only when $r_1 = 1/r_2$. Figure 2 shows the expected relationship of copolymer composition and microstructure for three different types of copolymers. These curves were calculated from the above algebraic expressions which relate to the structure and composition of an initial copolymer (*i.e.*, zero conversion) since they were derived from differential equations. Considering an example in which the polydiene contains 20% of the 1,2-structure and the percentage of 1,2-structure approaches zero as a limit at 100% vinyl content, a 50-50 copolymer, on a mole basis, of type A should contain about 2% 1,2-addition, a similar type B polymer should contain 10% 1,2-addition, and a corresponding type C polymer should contain about 18% 1,2-addition, all based on the diene portion of the copolymer.

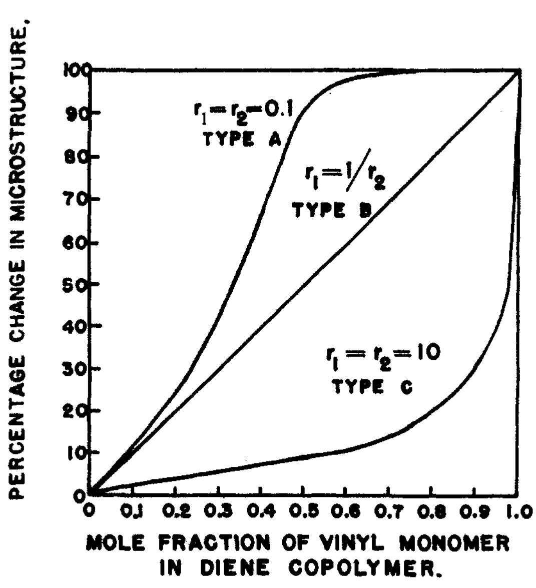

Fig. 2.—Variation of microstructure with composition of initial copolymers.

---

[9] T. Alfrey, Jr., J. Bohner and H. Mark, "Copolymerization," Interscience Publishers, New York, N. Y., 1952, p. 185.

Type C copolymers, in which both reactivity ratios are greater than 1, do not exist in practice. Type A copolymers, in which both reactivity ratios are less than 1, are quite common. These copolymers are examples of the alternating effect which is so prevalent in free radical copolymerizations. The system butadiene–acrylonitrile is of this type; reactivity ratios are 0.35 and 0.05,[10] respectively. This undoubtedly accounts for the large change in microstructure when approximately 25% acrylonitrile enters a butadiene polymer (see Table II). The change in percentage of 1,2 is larger than could possibly be accounted for on an additive basis, but consistent with the theoretical considerations outlined above.

The reactivity ratios for butadiene–styrene are 1.4 and 0.5,[11] respectively. This system closely approximates Type B in which one reactivity ratio is the reciprocal of the other. Thus, the microstructure theoretically should vary almost linearly with styrene content; experimental data in Fig. 1 are consistent with this.

The data indicate that acrylonitrile monomer causes the greatest change in polybutadiene microstructure, followed by methacrylonitrile. The other four comonomers, styrene, α-methylstyrene, vinylpyridine and methyl vinyl ketone, exert approximately the same effect on microstructure, within the precision of the data. Although this greater change in microstructure associated with acrylonitrile and methacrylonitrile copolymers may be partially explained by the greater alternating tendency in these copolymer systems (Type A in Fig. 2), some of this greater change must be attributed to a greater effect of these two monomers on the diene microstructure. For example, as styrene content approaches 100% the percentage of 1,2-addition approaches about 8% as a limit (see Fig. 1); whereas the 1,2-addition is approaching 0% as a limit as the acrylonitrile or methacrylonitrile content approaches 100%. In fact, the change of per cent 1,2-addition with comonomer content in the case of acrylonitrile copolymers is slightly greater than that theoretically allowable assuming 0% 1,2-addition as the limiting value and indicates some error in either composition or microstructure in this case.

It may be significant that there is an apparent correlation between the magnitude of the effect of a comonomer on butadiene microstructure and the partial charge at the double bond of the comonomer. Thus, of all comonomers studied, acrylonitrile has the most positive e[12] value, with methacrylonitrile the next most positive e value. Further work would be desirable to establish the relationship between comonomer structure and effect on microstructure on a more quantitative basis.

An attempt was made to correlate the effect of comonomers on diene microstructure with deviations from the Q and e theory for these same diene copolymer systems. Wall[13] was the first to point out that the Q and e theory often markedly fails when diene monomers are considered. He suggested addition of a parameter e^* for the diene radical different from the e for the corresponding diene monomer. Although the experimental data on chloroprene copolymerizations do illustrate the defection of the Q and e theory in the case of this diene, the experimental data on butadiene copolymerizations do not support a failure of the Q and e theory in this case, caused either by the difference in polarity between monomer and radical for dienes as proposed by Wall or by the differences in diene microstructure as comonomer is varied that is disclosed in the present work.

Acknowledgment.—The authors are indebted to Maxine Bender, who performed all of the nitrogen and carbon analyses. The authors also wish to express their appreciation to Dr. F. W. Stavely for his continued interest in this work and to the Firestone Tire and Rubber Company for permission to publish these results.

AKRON, OHIO

---

[10] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 218 (1950).

[11] E. J. Meehan, *J. Polymer Sci.*, **1**, 318 (1946). Other values (see ref. 10, p. 212) reported for this system were calculated from an assumption of a linear relationship between refractive index and styrene content. It has been confirmed by several workers[7] that this assumption is incorrect.

[12] C. C. Price, *J. Polymer Sci.*, **3**, 772 (1948); T. Alfrey, Jr., and C.C. Price, *ibid.*, **2**, 101 (1947).

[13] L. A. Wall, *ibid.*, **2**, 542 (1947).