

value of $\alpha = 0.5$ results in a ρ_v value approximately equal to that for phenol. In addition, a better fit of experimental points is obtained, as shown by the standard differences in Table II.

It is of interest to note that the ρ_v values for

phenols in carbon tetrachloride and tetrachloroethylene are found to be approximately the same (-12.6 and -13.2) when only data for the same compounds in each solvent are used.

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

Carbanionic Copolymerization Studies

BY FREDERICK C. FOSTER

Relative reactivity ratios have been determined for the carbanionic polymerization of vinyl butyl sulfone-acrylonitrile catalyzed by sodium in liquid ammonia. Similar data were obtained on the carbanionic copolymerization of styrene-acrylonitrile and methyl methacrylate-acrylonitrile; however, reactivity ratios could not be determined in these systems because of a side reaction in the former system and the large difference in monomer reactivities in the latter system. The relative reactivity of vinyl butyl sulfone in carbanionic copolymerization is consistent with the proposed effect of structure on reactivity. Steric effects have been suggested as a possible explanation of the tendency for alternation of monomer units in the vinyl butyl sulfone-acrylonitrile copolymerization.

Recent work¹ has clearly shown the large differences in relative monomer reactivities in the three mechanisms of vinyl polymerization: free radical, carbonium ion and carbanion. In fact, copolymer composition affords the most direct method of determining polymerization mechanism.

The free radical mechanism of polymerization has been so extensively studied that an adequate theory of monomer reactivity has been established which effects a theoretical correlation of these data and can be used to predict, fairly accurately, monomer reactivity ratios in systems that have not been experimentally investigated.

However, very little experimental work has been done on the determination of monomer reactivity ratios for copolymerizations catalyzed by ionic mechanisms. There are many reasons for this. The number of monomers that readily polymerize by either a carbonium ion or a carbanion mechanism is small. In addition, differences in reactivity between individual monomers are so large that few monomer pairs easily yield copolymers containing appreciable proportions of both monomers. Also, both carbanion and carbonium ion polymerizations yield low molecular weight polymers in a large proportion of the possible systems, especially when the less reactive monomers are used. All of these factors account largely for the general lack of technical interest in ionic catalyzed copolymers.

The present work includes studies on the carbanionic copolymerization of three monomer pairs using sodium in liquid ammonia as catalyst.

Experimental

Acrylonitrile obtained from American Cyanamide Corporation was distilled before use. Physical constants found were b.p. 77.0° at 740 mm., n_D^{20} 1.3916.

Methyl methacrylate obtained from Resinous Products and Chemical Co. was distilled before use. Physical constants found were b.p. 100.2° at 733 mm., n_D^{20} 1.4150.

Styrene obtained from Koppers Company, Inc., was distilled under reduced pressure. Physical constant found was n_D^{20} 1.5450.

Vinyl butyl sulfone was prepared in this Laboratory. Physical constants found were b.p. $115-116^\circ$ (4 mm.), n_D^{20} 1.4632, molecular refraction 37.62 (calcd.), 38.04 (obsd.).

All monomers were tested for the absence of polymer before use by adding a sample to methanol.

The experimental procedure was the same as that described in a previous publication² with the following exceptions. The copolymerizations of acrylonitrile-vinyl butyl sulfone were conducted at -78° . The copolymerizations of styrene-acrylonitrile were conducted at -40° , and 140 cc. of ether was added as solvent. The higher temperature and the ether were necessary to make the reaction mixture one phase. The copolymerizations of acrylonitrile-methyl methacrylate were run at the temperature of the previous experiments, -55° . In the purification of the copolymers by reprecipitation, dimethylformamide was used as solvent and methanol as precipitant for many of the copolymers.

The compositions of all copolymers were determined by nitrogen analyses, using the theoretical per cent. nitrogen for acrylonitrile, 26.40.

An experiment was conducted to obtain evidence that some of the styrene monomer was not available for copolymerization in the reactions of styrene-acrylonitrile with sodium in liquid ammonia. The experiment was conducted like the other copolymerizations except that an excess of the catalyst was employed. The initial charge consisted of 23.31 g. of acrylonitrile and 23.31 g. of styrene. A yield of 24.29 g. of copolymer was produced. Duplicate nitrogen analyses yielded values of 24.10 and 24.22%, average value 24.16%. The copolymer accounts for 22.23 g. of acrylonitrile and 2.06 g. of styrene. This corresponds to 95.4% of the initial charge of acrylonitrile and 8.8% of the initial charge of styrene. The difficulty in obtaining a complete material balance on the acrylonitrile was probably due to the violence of the reaction. The above data indicate that a large portion of the styrene monomer is not available for copolymerization with acrylonitrile. These data, together with the published work³ on the reaction of styrene with sodium in liquid ammonia, indicate strongly that a large portion of the styrene monomer is reduced to ethylbenzene under the conditions of the present experiments.

Results

Below, in tabular form, are the experimental results obtained in the three copolymerization systems.

TABLE I
STYRENE-ACRYLONITRILE

Initial styrene charge, g.	Initial acrylonitrile charge, g.	Yield, g.	N in copolymer, %
20.04	17.20	0.50	23.04, 23.00
29.08	12.60	3.35	23.22, 23.25
69.39	7.80	2.41	23.20, 23.08
26.32	11.04	0.83	22.95, 23.00
17.98	16.10	0.86	23.00, 23.20

(2) F. C. Foster, THIS JOURNAL, **72**, 1370 (1950).

(3) C. B. Wooster and J. F. Ryan, *ibid.*, **56**, 1133 (1934).

(1) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 277 (1950).

TABLE II
METHYL METHACRYLATE-ACRYLONITRILE

Initial methyl methacrylate charge, g.	Initial acrylonitrile charge, g.	Yield, g.	N in copolymer, %
57.69	10.58	4.19	25.3, 25.5
57.46	10.52	6.48	25.4, 25.6
15.31	33.05	2.47	26.0, 25.8
14.22	32.83	7.08	25.7, 25.7

TABLE III

VINYL BUTYL SULFONE (M_1)-ACRYLONITRILE (M_2)

M_1^0, M_2^0 = initial monomer charges in moles. M_1, M_2 = final monomer charges in moles (calculated from experimental data).

M_1^0	M_2^0	M_1	M_2	N in copolymer, %
0.0720	0.1766	0.0606	0.1330	15.39, 15.10
.2475	.1685	.2137	.1253	8.34, 8.21
.0826 ₃	.6240	.07969	.6002	19.61, 19.60
.0839 ₃	.5963	.07834	.5543	19.19, 19.30

In the copolymerization system styrene-acrylonitrile, the copolymerization equation does not apply because of the complications of a competing reaction, probably the reduction of styrene to ethyl benzene (see Experimental section). A copolymer of the same composition, within experimental error, was produced at low conversions over a wide range of monomer charges. This composition corresponds to a copolymer containing 87.5% acrylonitrile, by weight. The fact that the copolymer produced with an excess of catalyst (Experimental section) contained a higher proportion of acrylonitrile gives a further indication that the styrene monomer is consumed by a competing reaction. Early work³ on the reaction of the phenylethylenes with sodium in liquid ammonia indicated that about 50% of the styrene was reduced to ethylbenzene in this medium.

In the system methyl methacrylate-acrylonitrile, the difference in the reactivities of the two monomers is so large that the relative reactivity ratios cannot be numerically characterized. For example, the low conversion copolymers formed from two experiments at an initial monomer ratio by weight of about 5.5 to 1, methyl methacrylate-acrylonitrile, contained about 96.5% acrylonitrile; two similar experiments at a monomer ratio of about 1 to 2, methyl methacrylate-acrylonitrile, contained about 97.7% acrylonitrile. The difference in copolymer composition is so small that it is only slightly greater than the precision of the nitrogen analy-

ses. Acrylonitrile is obviously so much more reactive than methyl methacrylate in this copolymerization that it can only be stated that r_1 is close to zero and r_2 is very large, methyl methacrylate being designated as monomer 1.

The data in Table III were used to calculate the relative reactivity ratios, r_1 and r_2 , for the carbanionic copolymerization of vinyl butyl sulfone-acrylonitrile. The integrated equation of Mayo and Lewis⁴ was used to calculate the values of r_1 and r_2 . The values of r_1 and r_2 selected from the experimental data were 0.2 ± 0.1 and 1.1 ± 0.2 , respectively. The values of r_1 and r_2 and the experimental error given above are based on the areas of intersection in the plot of r_1 vs. r_2 ⁴ with extra weight given to the three experiments, the last three in Table III, that intersect over a very small area.

The values of r_1 and r_2 define the relation between monomer charge and the composition of copolymer forming at any instant by the following differential equation⁴

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \times \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad (1)$$

In the above equation, dM_1/dM_2 expresses the molar ratio of the two monomers in the copolymer forming at any instant and M_1 and M_2 are the corresponding monomer charges, in molar units.

The calculated, solid curve in Fig. 1 was obtained by inserting the experimentally determined values of r_1 and r_2 in equation (1). The experimental points corresponding to each copolymerization are also plotted in Fig. 1. The copolymer compositions are plotted against the average of the initial and final monomer concentrations. Since all of the reactions were stopped at relatively low conversions, the initial composition from this average monomer concentration is very closely represented by the total copolymer formed.

The plot in Fig. 1 shows that the average deviation of the experimental points from the calculated curve is only slightly greater than the precision of the nitrogen analyses.

The values of r_1 and r_2 for the free radical initiated copolymerization of the same monomer pair are not known so no comparison can be made between relative monomer reactivities in the two types of polymerization. Preliminary experiments in this Laboratory indicate that vinyl butyl sulfone and acrylonitrile do copolymerize in a free radical system, consistent with the work of Mighton.⁵

Discussion

The relative reactivity ratios obtained for the carbanionic copolymerization of vinyl butyl sulfone-acrylonitrile demonstrate that acrylonitrile monomer is somewhat more reactive than vinyl butyl sulfone monomer in this system. A growing chain with a terminal vinyl butyl sulfone group prefers to react with acrylonitrile monomer rather than with vinyl butyl sulfone monomer by a factor of about 5 to 1. However, a growing chain with a terminal acrylonitrile group has about the same tendency to react with acrylonitrile monomer as with vinyl butyl sulfone monomer.

Previous work¹ in carbanionic copolymerizations has established an order of reactivity in this type of polymerization. This order of reactivity is acrylonitrile > methacrylonitrile > methyl methacrylate > styrene > butadiene. From the results above, vinyl butyl sulfone probably occupies a position between acrylonitrile and methacrylonitrile. It has been pointed out that this order of reactivity can be correlated with the ability of substituents to withdraw electrons from the monomer double bond. Thus, a correlation exists between the above order of reactivity and the σ -values of Hammett⁶ or the

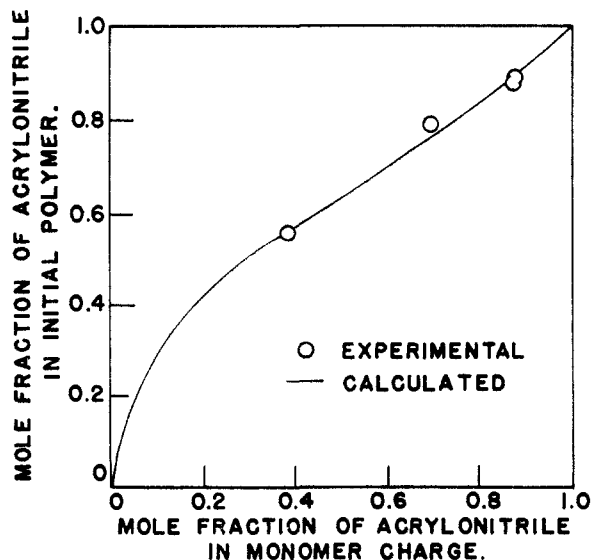


Fig. 1.—Monomer-polymer composition curve of vinyl butyl sulfone-acrylonitrile.

⁴ F. R. Mayo and F. M. Lewis, *THIS JOURNAL*, **66**, 1594 (1944).

⁵ C. J. Mighton, U. S. Patent 2,472,672 (1949).

⁶ L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, chap. VII.

e -values of Alfrey and Price.⁷ It is noteworthy that the position of vinyl butyl sulfone in the reactivity series is consistent with the above concept. The e -value of methyl vinyl sulfone⁸ has been determined to be 1.2. The e -value for vinyl butyl sulfone should be almost identical to this value. Values of e for acrylonitrile⁷ range from 0.9–1.6 depending on the co-monomer from which it is calculated. Values of e for methacrylonitrile⁷ are, similarly, 0.9–1.2. Thus, the high reactivity of vinyl butyl sulfone in carbanionic copolymerizations is consistent with the proposed effect of substituents on reactivity.

The considerable data¹ on free radical initiated copolymerizations have indicated a strong tendency for alternation of monomer units. The r_1r_2 product is less than 1 for practically all copolymerizations studied and it is very common for both reactivity ratios to be less than 1 in free radical initiated copolymerizations. There is considerable evidence that the alternation phenomenon in free radical copolymerizations is primarily polar in origin, although in a few cases steric considerations are almost certainly important.

Since, in a free radical copolymerization, neither the monomers nor the growing polymer chains carry a formal charge, it is reasonable that a growing polymer chain with a partial negative charge at the growing end should prefer to react with a monomer that has a partial positive charge in the vicinity of the double bond, and *vice versa*. Thus, α -methylstyrene and acrylonitrile, having approximately identical Q -values, alternate strongly because one has a highly negative e -value and the other a highly positive e -value.⁷

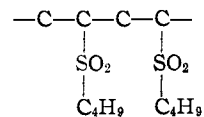
It is of interest that the product, r_1r_2 , is less than 1 for the vinyl butyl sulfone–acrylonitrile copolymerization, indicating some tendency for alternation of monomer units in the copolymer. This is unusual in ionic initiated copolymerizations. For example, of the ionic initiated copolymerization systems^{1,9,10} for which relative reactivity ratios previously have been determined, only two copolymerization systems have an r_1r_2 product less than 1, beyond the limits of error. In none of the ionic initiated copolymerization systems have both reactivity ratios been less than 1.¹¹

A tendency toward alternation of monomer units would not be expected in ionic copolymerizations on theoretical considerations. In the case of ionic initiated copolymerizations, the growing polymer chains carry a formal charge at the growing end of the chain. This charge is +1 for carbonium ion copolymerizations and –1 for carbanion copolymerizations. In these cases, a substituent that polarizes the monomer to yield a partial charge at the double bond opposite to the formal charge of the growing chain not only facilitates the approach and reaction

of the two reactants but also stabilizes the resultant adduct. This view of ionic copolymerizations would predict an order of reactivity of monomers independent of the nature of the attacking ion, *i.e.*, a r_1r_2 product of 1 in all reactions.

The above description of ionic copolymerizations is consistent, as mentioned previously, with the general order of monomer reactivities found in these systems and also with the fact that r_1r_2 products are quite frequently close to 1. However, these same considerations make it difficult to explain any specificity of reactivity found in ionic copolymerizations, *e.g.*, r_1r_2 products deviating appreciably from 1. Further evidence that a specificity of reactivity is superimposed upon a general order of reactivity lies in the fact that styrene, in spite of a side reaction of reduction, showed greater reactivity in copolymerization with acrylonitrile than did methyl methacrylate with acrylonitrile. Yet, in the copolymerization of styrene–methyl methacrylate,¹² methyl methacrylate was much more reactive.

One possible explanation of a specificity of reactivity in ionic copolymerizations might be based on steric, or entropy, considerations. Two of the three instances, previously cited, in which r_1r_2 products are less than 1 in ionic copolymerizations seem to be amenable to such an explanation. Thus, the r_1r_2 product reported by Alfrey, Arond and Overberger¹³ on the carbonium ion catalyzed copolymerization of anethole–*o*-chlorostyrene can be explained on the basis of a steric inhibition of the highly substituted ethylene, anethole, to react with itself in this copolymerization. Likewise, the deviation from an r_1r_2 product of 1 in the results of the present investigation may be attributed to a steric effect if it is assumed that the following structure would be sterically discouraged



The other system, the carbonium-ion copolymerization of styrene–vinyl acetate investigated by Landler,¹⁰ does not seem to justify an assumption of steric hindrance. It should be pointed out that in the case of anethole–*o*-chlorostyrene and styrene–vinyl acetate, one r -value is very low and the other r -value very high. The r_1r_2 product is subject to more uncertainty in these systems, *i.e.*, a change in one of the r values to make an r_1r_2 product of 1 represents a small change in copolymer composition.

In any case, steric effects, if they do exist, are certainly minor in comparison to polar effects in determining relative monomer reactivities. It is likely that steric effects can best be established in copolymer systems containing monomers of nearly the same general reactivity, as in the present case of vinyl butyl sulfone–acrylonitrile.

Acknowledgment.—The author is indebted to L. J. Gaeta and Miss Maxine Elliott who per-

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

(8) C. C. Price and J. Zomlefer, *THIS JOURNAL*, **72**, 14 (1950).

(9) F. C. Foster, *J. Polymer Sci.*, **5**, 369 (1950).

(10) Y. Landler, *Compt. rend.*, **280**, 539 (1950).

(11) In Landler's paper at the International Congress of Pure and Applied Chemistry, September, 1951, he stated that the previously published¹⁰ numerical values of the reactivity ratios for the carbanionic copolymerization of styrene–vinyl acetate were subject to confirmation.

(12) C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, *THIS JOURNAL*, **72**, 48 (1950).

(13) T. Alfrey, Jr., L. Arond and C. G. Overberger, *J. Polymer Sci.*, **4**, 539 (1949).

formed all of the nitrogen analyses and to Grant Crane who prepared the vinyl butyl sulfone monomer. The author also wishes to express his ap-

preciation to B. L. Johnson for his continued interest in this work.

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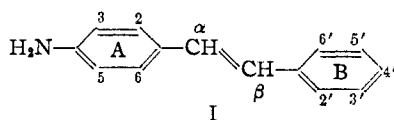
[CONTRIBUTION FROM THE CHESTER BEATTY RESEARCH INSTITUTE, ROYAL CANCER HOSPITAL, LONDON]

The Spectrophotometric Determination of Steric Hindrance in Some Stilbene Derivatives

BY R. N. BEALE AND E. M. F. ROE

The effect of steric hindrance to planarity on the intensity of the longest wave length transition in a number of methyl-derivatives of stilbene and 4-dimethylaminostilbene has been determined by comparison of the oscillator strengths (f) of this band in compounds with substituents in hindering and non-hindering positions in the molecule. A methyl group in a non-hindering position causes either no change or an increment in f -value, *i.e.*, no change at the 3- or 3'-position and a change in f -value of +0.05 at the 4- or 4'-position. In the hindering 2'-position a methyl group causes a decrement in f -value, *i.e.*, a change of -0.04. Successive introductions of further hindering methyl groups causes larger decrements in f of magnitude varying with the position of substitution. It is found that any of these methyl groups exerts its effect on the f -value of this band independently of other groups in the same ring, as though its effect were strictly localized. The changes in f -value are therefore additive for these compounds. A similarly independent effect is exerted by the $-N(CH_3)_2$ group substituted at the 4-position in stilbene, where it causes an increment in f more than twice that produced by a methyl group at that position.

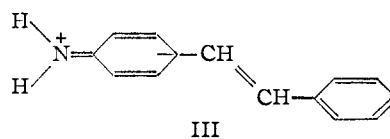
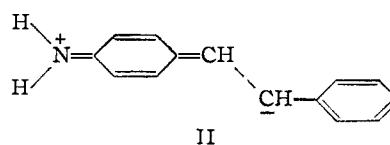
In the course of spectroscopic investigations of the growth-inhibiting and carcinogenic compound,



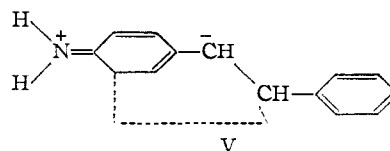
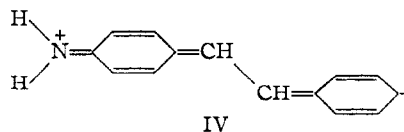
4-aminostilbene (I) and its derivatives,¹ it was observed that the ultraviolet absorption spectra of these compounds show reduction in maximum extinction and in some cases shift to higher frequencies of the long wave length band when substitution causes steric hindrance to the planarity of the molecule. Similar results are found in non-basic stilbene derivatives and examples of the effect are shown in Figs. 1 and 2. In Fig. 1 these progressive changes in extinction and frequency are evident as crowding about the ethylenic double bond is increased from the 2,4,6-trimethyl derivative to the 2,4,6,2',4',6'-hexamethyl derivative of stilbene. The changes are well marked also in the spectrum of 4-dimethylamino-2',4',6'-trimethylstilbene (Fig. 2) but they are more difficult to assess in the case of the corresponding 2'-methyl compound. Similar results have been found by other investigators, for stilbene derivatives² and in further aromatic series.³

In the substituted 4-aminostilbenes with which this investigation is mainly concerned,⁴ the ex-

pected changes in frequency and intensity due to steric hindrance may be discussed in terms of Coulson and Jacobs'⁵ calculations of π -electron charge distribution in the ground state⁶ and lowest excited state of this molecule. Their results were obtained by a simple molecular orbital method and are displayed diagrammatically in Fig. 3. The differences in excess π -electron charge on the atoms are somewhat exaggerated in this diagram. From Fig. 3, the structures expected to be of importance in light absorption would be: (a) in the ground state



and ortho-quinonoid structures corresponding to III; and (b) in the lowest excited state



benes, and resonance structures similar to those postulated for the latter may reasonably be assumed for 4-dimethylaminostilbene. *trans*-Isomers alone are discussed throughout this paper.

(5) C. A. Coulson and J. Jacobs, *J. Chem. Soc.*, 1983 (1949).

(6) Calculations by Pullman⁷ for the ground state of 4-aminostilbene lead to similar conclusions to those of Coulson and Jacobs.

(7) A. Pullman, *Compt. rend.*, 226, 486 (1948).

(1) A. Haddow, R. J. C. Harris, G. A. R. Kon and E. M. F. Roe, *Phil. Trans. Roy. Soc.*, [A] 241, 147 (1948).

(2) H. Ley and F. Rinke, *Ber.*, 56B, 771 (1923); H. Ley and H. Specker, *Z. Wiss. Phot.*, 33, 13 (1939); B. Arends, *Ber.*, 64, 1936 (1931); A. Smakula and A. Wassermann, *Z. physik. Chem.*, 155A, 353 (1931); G. N. Lewis and M. Calvin, *Chem. Revs.*, 25, 273 (1939).

(3) For example: L. W. Pickett, G. F. Walter and H. France, *THIS JOURNAL*, 58, 2296 (1936); W. Theilacker and W. Ozegowski, *Ber.*, 73, 898 (1940); M. T. O'Shaughnessy and W. H. Rodebush, *THIS JOURNAL*, 62, 2906 (1940); R. N. Jones, *ibid.*, 63, 1658 (1941); *ibid.*, 67, 1956 (1945); K. J. Brunings and A. H. Corwin, *ibid.*, 64, 593 (1942); W. R. Remington, *ibid.*, 67, 1838 (1945); L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, Jr., and G. van Zandt, *Chem. Revs.*, 41, 325 (1947).

(4) The spectra investigated are those of derivatives of 4-dimethylaminostilbene, nearly all of which have substituents in ring B. These compounds were of greater biological interest than the 4-aminostil-