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

# The Anionic Copolymerization of Methyl Methacrylate–Methacrylonitrile

BY FREDERICK C. FOSTER

Considerable experimental work has been done on the determination of monomer reactivity ratios in free radical copolymerizations. Recently similar studies[1] were reported on copolymerizations catalyzed by Friedel–Crafts, or cationic, catalysts. The present paper reports the determination of relative reactivity ratios for the copolymerization of methyl methacrylate–methacrylonitrile by an anionic type catalyst.

The recent work of Beaman[2] made available a convenient method of conducting anionic polymerizations by the use of sodium in liquid ammonia as basic catalyst. Certain changes were made in the experimental procedure of Beaman in order to stop the copolymerizations at low conversions.

## Experimental

Methyl methacrylate obtained from Rohm and Haas Company was distilled before use. Physical constants found were b. p. 100.7° at 734 mm., $n^{25}\text{D}$ 1.4127.

Methacrylonitrile obtained from Shell Development Company was distilled before use. Physical constants found were b. p. 89.6 at 734 mm., $n^{20}\text{D}$ 1.4006.

The copolymerizations were conducted by first weighing the monomers into a 2" by 8.5" test-tube. The test-tube was then immersed in a Dewar flask containing acetone maintained at −55° with dry ice. Approximately 55 cc. of liquid ammonia was added as a solvent for the reaction. The test-tube was equipped with a glass stirrer; and, while the reaction mixture was stirred, a solution of sodium in liquid ammonia was added increment-wise until a small amount of copolymer precipitated from the reaction mixture. A small amount of ammonium chloride was added to decompose any sodium compounds, and the ammonia allowed to evaporate. The copolymer was washed several times with methanol and water. After a final methanol wash, the copolymer was vacuum dried overnight and weighed to determine per cent. conversion.

As a precaution against any impurities in the copolymer sample, the samples above were dissolved in acetone, precipitated in petroleum ether, washed with methanol, and dried as usual before submitting for nitrogen analysis. This precaution was probably unnecessary since one of the samples was analyzed before and after the above purification procedure and gave the same analysis for nitrogen within the precision of the duplicate analyses for each sample.

The composition of copolymer was calculated from experimental nitrogen analyses of the homopolymers in this system rather than using theoretical values. This method has been commonly used in such investigations.[3] Friedrich micro-Kjeldahl determinations on the homopolymers in this system showed the absence of nitrogen in methyl methacrylate polymer, within the experimental limits; three sets of duplicate analyses on two samples of polymethacrylonitrile yielded values of 19.90, 19.95; 20.10, 19.80; 20.15, 20.10% for nitrogen. The average of the above six values, 20.00, was used for polymethacrylonitrile in calculating copolymer composition; this amounted to a correction of about 5% on the theoretical values of 20.88.

## Results

Below is a table of the experimental results obtained in the five copolymerizations.

TABLE I

| Conversion, % | N in copolymer, % | $M_1°$[a] | $M_1$[b] | $m_1$[c] |
|---|---|---|---|---|
| 16.5 | 11.95, 12.05 | 0.556 | 0.611 | 0.309 |
| 3.9 | 12.90, 13.20 | .541 | .554 | .263 |
| 13.6 | 17.05, 17.25 | .308 | .346 | .100 |
| 1.4 | 6.46, 6.50 | .782 | .785 | .584 |
| 14.0 | 13.20, 13.39 | .533 | .586 | .253 |

[a] $M_1°$ = mole fraction of methyl methacrylate in initial monomer charge. [b] $M_1$ = mole fraction of methyl methacrylate in final monomer charge (calculated from experimental data). [c] $m_1$ = mole fraction of methyl methacrylate in copolymer.

The above data were used to calculate the relative reactivity ratios, $r_1$ and $r_2$, for the anionic copolymerization of methyl methacrylate–methacrylonitrile. The integrated equation of Mayo and Lewis[4] 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 0.67 ± 0.2 and 5.2 ± 1.0, respectively. The experimental error given above is defined by the areas of intersection in the plot of $r_1$ *vs.* $r_2$.[4]

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 equation[4]

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

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 agreement between the experimental points and the calculated curve is about as good as can be expected from the nitrogen analyses.

Figure 1 also gives the monomer–polymer compo-

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(1) T. Alfrey, Jr., and H. Wechsler, THIS JOURNAL, **70**, 4268 (1948).

(2) R. G. Beaman, *ibid.*, **70**, 3115 (1948).

(3) Lewis, Walling, Cummings, Briggs and Mayo, THIS JOURNAL, **70**, 1521 (1948); Nozaki, *J. Polymer Sci.*, **1**, 455 (1946).

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

sition curve (dotted line) for the free radical initiated copolymerization. The values of $r_1$ and $r_2$ used in calculating this curve were taken from the published data of Lewis, Walling, Cummings, Briggs and Wenisch.[5] Values used were 0.67 and 0.65 for $r_1$ and $r_2$, respectively.

## Discussion

The present data indicate a significant difference between the relative reactivity ratios in a free radical initiated copolymerization and the relative reactivity ratios in an anionically initiated copolymerization in the system methyl methacrylate–methacrylonitrile. In the free radical initiated copolymerization, both types of growing free radicals (those with a terminal methyl methacrylate group or those with a terminal methacrylonitrile group) exhibit a preference to alternate monomer units in the growing chain. In the copolymerization of the same two monomers catalyzed by sodium in liquid ammonia both types of growing chains prefer to react with methacrylonitrile rather than methyl methacrylate monomer. This preference is quite pronounced in the case of a growing chain with a terminal methacrylonitrile group.

The results of the present work confirm the mechanism proposed by Beaman[2] for polymerizations of this type and they prove that the reaction mechanism is at least different from the free radical mechanism. In fact, the determination of relative reactivity ratios is one of the best methods of proving that the propagation step in two copolymerizations of the same monomer pair proceeds by an essentially different mechanism. Mayo and Lewis[4] were the first to suggest that constancy of the relative reactivity ratios is a criterion for a single mechanism of chain growth.

The greater reactivity of methacrylonitrile monomer over methyl methacrylate monomer in this anionic chain copolymerization is not surprising. Alfrey and Wechsler[1] suggested that the dominant factor in monomer reactivity in cationic chain copolymerizations is the polarization of the double bond by substituents. They found a correlation between the electronegativity of substituents and the monomer reactivity in copolymerizations studied in the cationic system. According to the mechanism proposed for anionic chain polymerization,[2] the polarization of the double bond by substituents should also be the dominant factor in monomer reactivity in anionic chain copolymerizations. In the anionic system, electron-withdrawing groups attached to the double bond should increase monomer reactivity since the proposed mechanism for chain growth is a nucleophilic attack on the monomer. The greater reactivity of methacrylonitrile monomer over methyl methacrylate monomer in this system would thus be explained by the greater electronegativity of the –CN group over the –COOR group.

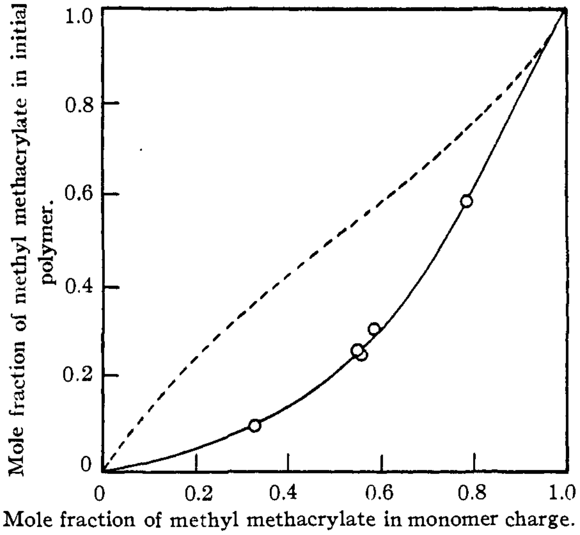

Fig. 1.—Monomer–polymer composition curve of methyl methacrylate–methacrylonitrile: – – –, free radical; ——, anionic; O, experimental.

No practical advantage can be claimed for the production of copolymers of methyl methacrylate–methacrylonitrile in the present system over the ordinary free radical system. In fact, Fig. 1 illustrates that at any monomer charge and at any finite conversion a copolymer of more homogeneous chemical composition is produced in the free radical system. For example, a compositional "azeotrope" is formed in the free radical system from a monomer charge of approximately 0.5 mole fraction of methyl methacrylate. In the anionic system from the same initial charge, the initial copolymer has a composition of about 0.2 mole fraction of methyl methacrylate and the composition of copolymer subsequently formed approaches 1.0 mole fraction of methyl methacrylate as conversion approaches 100%.

Physical properties were determined on the copolymer sample containing 0.1 mole fraction of methyl methacrylate. The intrinsic viscosity of this copolymer was 0.07 in acetone. The sample melted over the range of 115–140°. The plaque pressed at 140° from this copolymer was hard but brittle.

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## Summary

Relative reactivity ratios have been determined for the copolymerization of methyl methacrylate–methacrylonitrile catalyzed by sodium in liquid ammonia. The values are significantly different from those for the free radical copolymerization of the same monomer pair.

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(5) Lewis, Walling, Cummings, Briggs and Wenisch, THIS JOURNAL, 70, 1527 (1948).

The greater reactivity of methacrylonitrile over methyl methacrylate in this system supports the previously proposed mechanism of anionic chain growth for polymerizations catalyzed by sodium in liquid ammonia.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# The Oxidation of Styrene

BY HAROLD BOARDMAN[1] AND P. W. SELWOOD

The mechanism of oxygen inhibition in vinyl polymerization has received considerable attention. Thus Barnes[2] showed that the induction period in photopolymerization is accompanied by substantial peroxide formation. The rate of oxygen consumption in styrene polymerization has been studied by Kolthoff and his associates,[3,4] and Medvedev and Zeitlin[5] have examined the ratio of oxidized products (benzaldehyde and formaldehyde) to polymerized products.

Goldfinger and Lauterbach[6] studied the initial rate of thermal polymerization in the presence and absence of oxygen. Samples saturated with air showed an initial higher rate of polymerization, lasting as long as twenty-eight hours, the rate then falling back to normal. An induction period was not observed in the runs in which styrene was saturated with oxygen, although it is questionable if an induction period would be evident, because, as shown in the present investigation, all the oxygen dissolved in the styrene would be consumed within thirty minutes under the experimental conditions. The over-all activation energy was found to be 16 kcal. mol.$^{-1}$.

The rate of oxygen consumption in reacting systems lends itself to measurements of magnetic susceptibility. In this way the disappearance of molecular oxygen may be followed *in situ*, without the necessity for removal and analysis of samples. The method has the added advantage of being extremely sensitive.

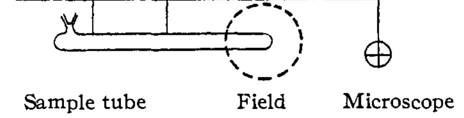

Fig. 1.—Apparatus for magnetic susceptibility measurements.

During the course of the work to be described two publications appeared on the use of magnetic methods for the study of polymerizing systems. Bedwell[7] used magnetic susceptibilities, measured externally, to follow the increase of molecular weight during polymerization of methyl methacrylate. Tanaevsky[8] studied the photopolymerization, in vacuum and with oxygen inhibition, of vinyl acetate.

Some earlier uses of magnetic methods in polymerization studies gave results quite difficult of interpretation.[9-11]

## Experimental Part

**Preparation of Materials.**—Styrene used in this work was Eastman Kodak Company white label material distilled under reduced pressure in a stream of nitrogen before use.

Benzaldehyde was also Eastman material similarly distilled.

Acetic anhydride was J. T. Baker C. P. material similarly distilled.

Sodium iodide was U. S. P. grade, recrystallized from water and dried.

**Magnetic Susceptibility Measurements.**—The design of the apparatus is shown in Fig. 1. A brass sample tube holder was suspended by fine copper wires about 2 meters in length. Each wire was attached at the top to a screw, for vertical adjustment; and the screw was fixed to a microscope stage, for horizontal adjustments. The whole assembly was held in place by wall brackets.

Displacement of the sample tube was measured by a filar micrometer microscope, focussed on cross hairs fixed on a cover slip attached to the brass holder.

The field was supplied by a permanent Alnico magnet,[12] having a 1-inch pole gap, 2-inch pole faces, and a field strength of 8000 gauss.

The sample tube was Pyrex glass, 12 cm. long and 1 cm. external diameter. No advantage was to be gained by using the familiar double tube in this work. In fact, any increase in weight of the sample tube may be shown to decrease the over-all sensitivity of the apparatus.

The force, $f$, acting on a sample of cross-section $A$, which extends from field $H$ to negligible field, is given by $f = 1/2AH^2(\kappa - \kappa')$ where $\kappa$ is the susceptibility per unit volume of the sample, and $\kappa'$ is the susceptibility of the sur-

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[1] Present address: Hercules Powder Company, Wilmington, Delaware.

[2] Barnes, THIS JOURNAL, **67**, 217 (1945).

[3] Kolthoff and Dale, *ibid.*, **69**, 441 (1947).

[4] Bovey and Kolthoff, *ibid.*, **69**, 2143 (1947).

[5] Medvedev and Zeitlin, *Acta Physicochim. U. R. S. S.*, **20**, 3 (1945).

[6] Goldfinger and Lauterbach, *J. Polymer Sci.*, **3**, 145 (1948).

[7] Bedwell, *J. Chem. Soc.*, 1350 (1947).

[8] Tanaevsky, *Compt. rend.*, **225**, 1069 (1947).

[9] Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1936).

[10] Farquharson and Ady, *Nature*, **143**, 1067 (1939).

[11] Bhatnagar, Kapur and Kaur, *J. Indian Chem. Soc.*, **17**, 177 (1940).

[12] The magnet was made for this work by the Indiana Steel Products Company, Chicago, Illinois.