

# **Copolymerization of Acrylonitrile. I.**

## **Copolymerization with Styrene Derivatives Containing Nitrile Groups in the Side Chain**

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### **Synopsis**

Acrylonitrile was copolymerized in bulk with cinnamonnitrile (I), ethyl benzylidene-cyanoacetate (II), and benzylidenemalononitrile (III) by radical initiation up to low conversions. The conventional scheme of copolymerization fitted all the three copolymer pairs.

### **INTRODUCTION**

Polyacrylonitrile, unlike most other industrial thermoplastic polymers, is actually insoluble in almost all organic solvents and also incompatible with the conventional plasticizers. It is only soluble in very polar solvents such as dimethyl sulfoxide, dimethylformamide, or in concentrated aqueous solution of certain salts. Polyacrylonitrile is stable up to 150–200°C, turning yellow at higher temperature.<sup>1</sup> On ignition it burns only slowly and it has a comparatively good stability in sunlight.

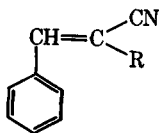
This exceptional high stability of polyacrylonitrile against heat and sunlight and its restricted solubility in highly polar solvents only is due to the structure of the polymer, dominated by the strong dipole–dipole interaction between the nitrile groups.<sup>2,3</sup>

Although these properties of polyacrylonitrile are very advantageous for certain applications, it is just due to this stability and the consequent lack of flow that processing of the homopolymer of acrylonitrile by the conventional molding methods for thermoplastic polymers is very difficult.

In order to overcome these drawbacks, copolymers of acrylonitrile which could be processed by conventional methods, but which had a lower temperature and solvent stability than the homopolymer, were prepared industrially.

It was the object of this investigation to copolymerize acrylonitrile with such polar comonomers, which owing to their bulkiness could act as internal plasticizers without decreasing the stability of the copolymers in comparison to polyacrylonitrile.

The comonomers used have the general formula:



where R is H(I),  $-\text{COOC}_2\text{H}_5$  (II), or  $-\text{CN}$  (III). These comonomers have been previously investigated together with styrene<sup>4-6</sup> and were found to result in improved temperature stability in comparison to homopoly-styrene.

## EXPERIMENTAL

### Materials and Preparation of Monomers

**Acrylonitrile.** Commercial Eastman product was dried over calcium chloride and distilled before use under nitrogen at  $77^\circ\text{C}$ .

**Comonomers.** Cinnamionitrile, ethyl benzylidenecyanoacetate, and benzylidenemalononitrile were prepared as described previously.<sup>4</sup>

**Benzoyl Peroxide.** Eastman pure grade was used after recrystallization from methanol.

**Dimethyl Sulfoxide (DMSO).** Fluka product (purum) was distilled at  $95^\circ\text{C}$  at 25 mm Hg and kept under nitrogen.

### Copolymerization

The parameters of copolymerization were determined by bulk copolymerization with the use of free radicals for initiation. Polymerizations were carried out in Pyrex tubes with a bulb at the lower end and a constriction near the upper end. After flushing with nitrogen, the monomers (10–15 g) and the initiator (benzoyl peroxide: 0.1% by weight) were introduced and frozen immediately in a Dry Ice–acetone mixture. The tubes were flushed three times with nitrogen, evacuated down to 0.3 mm, sealed at the constriction, and kept in the Dry Ice–acetone mixture until the start of polymerization.

The copolymerizations were carried out in a temperature-controlled bath fitted with shaking device in order to keep the reaction mixtures well mixed. At the fixed polymerization temperature ( $70^\circ\text{C}$ ), the starting reaction mixture was a homogeneous solution. The proper time of copolymerization, i.e., the time necessary to polymerize not more than 10% of the mixture, was found by trial and error. After the polymerization, the reaction tubes were cooled to room temperature, opened, and the reaction mixture was poured into methanol. The products were washed with methanol and repeatedly precipitated by methanol from a solution in dimethyl sulfoxide. The purified copolymers were dried at  $80^\circ\text{C}$  under reduced pressure for 24 hr.

### Analyses of Products

All the copolymers were obtained as yellowish powders. The composition of the copolymers was determined by microanalyses for C, H, N, and O. In all cases, residues (2.5–5%) were obtained after combustion, and the compositions of the copolymers were calculated accordingly.

### Melting Ranges

Attempts to determine the melting range of the various copolymers in capillaries under air and under nitrogen were unsuccessful. All the copolymers showed a color change to brown and then to black and were carbonized above 300°C.

### Solubility

All copolymers are soluble in dimethyl sulfoxide.

## RESULTS AND DISCUSSION

The conditions and results of the various copolymerizations are summarized in Tables I–III.

TABLE I  
Acrylonitrile ( $M_1$ ) and Cinnamionitrile I ( $M_2$ )

| Experiment no. | $M_2$ , mole fraction of monomer 2 | Time of polymerization, min | Conversion, % | Nitrogen content of copolymer, % | $m_2$ , mole fraction in copolymer |
|----------------|------------------------------------|-----------------------------|---------------|----------------------------------|------------------------------------|
| 69/2           | 0.8                                | 1210                        | 0.9           | 16.2                             | 0.45                               |
| 69/3           | 0.7                                | 505                         | 2.4           | 18.9                             | 0.28                               |
| 69/4           | 0.54                               | 155                         | 1.8           | 22.0                             | 0.15                               |
| 69/6           | 0.4                                | 140                         | 2.5           | 23.5                             | 0.09                               |
| 69/7           | 0.3                                | 63                          | 2.1           | 23.45                            | 0.09                               |
| 69/8           | 0.2                                | 50                          | 2.2           | 25.4                             | 0.03                               |
| 69/9           | 0.1                                | 30                          | 3.2           | 23.35                            | 0.09                               |

The calculation of the reactivity ratios for the various copolymers were based on the elementary analyses of the products. It was therefore of greatest importance to free the copolymers from any residual monomer. In order to prevent the inclusion of any monomer in the copolymers during purification, precipitation of the copolymers was carried out in a Waring Blender.

A further problem was the complete removal of the solvent, dimethyl sulfoxide, which tends to be bound to the polar groups of the polymer. Only by heating the copolymer at 80°C under reduced pressure (0.5 mm Hg) for at least 10 hr could the last traces of the solvent be removed.

Infrared spectra were obtained after purification of the polymers.

TABLE II  
Acrylonitrile ( $M_1$ ) and Ethyl Benzyldenecyanoacetate II ( $M_2$ )

| Experiment no. | $M_2$ , mole fraction of monomer 2 | Time of polymerization, min | Conversion, % | Nitrogen content of copolymer, % | $m_2$ , mole fraction in copolymer |
|----------------|------------------------------------|-----------------------------|---------------|----------------------------------|------------------------------------|
| 63/1           | 0.9                                | 690                         | 2.8           | 21.7                             | 0.077                              |
| 63/2           | 0.8                                | 690                         | 3.8           | 21.7                             | 0.077                              |
| 63/3           | 0.7                                | 120                         | 1.05          | 23.6                             | 0.0435                             |
| 63/4           | 0.6                                | 72                          | 1.7           | 23.25                            | 0.048                              |
| 63/5           | 0.5                                | 40                          | 0.9           | 24.0                             | 0.035                              |
| 63/6           | 0.4                                | 50                          | 3.0           | 24.0                             | 0.035                              |
| 63/7           | 0.3                                | 40                          | 1.85          | 24.6                             | 0.025                              |
| 63/8           | 0.2                                | 40                          | 7.0           | 24.15                            | 0.032                              |
| 63/9           | 0.1                                | 7                           | 1.02          | 25.2                             | 0.015                              |

TABLE III  
Acrylonitrile ( $M_1$ ) and Benzyldenemalononitrile III ( $M_2$ )

| Experiment no. | $M_2$ , mole fraction of monomer 2 | Time of polymerization, min | Conversion, % | Nitrogen content of copolymer, % | $m_2$ , mole fraction in copolymer |
|----------------|------------------------------------|-----------------------------|---------------|----------------------------------|------------------------------------|
| 66/3           | 0.7                                | 600                         | 3.8           | 24.4                             | 0.100                              |
| 66/4           | 0.6                                | 465                         | 1.8           | 25.5                             | 0.035                              |
| 66/6           | 0.4                                | 255                         | 5.2           | 25.8                             | 0.025                              |
| 66/7           | 0.3                                | 120                         | 8.5           | 25.7                             | 0.03                               |
| 66/8           | 0.2                                | 60                          | 3.9           | 25.4                             | 0.045                              |
| 66/9           | 0.1                                | 30                          | 3.0           | 25.75                            | 0.028                              |

The reactivity ratios  $r_1$  and  $r_2$  were determined by the graphical method<sup>7</sup> (Figs. 1-3) by using the equation (1):

$$r_2 = (M_1/M_2) \{ (m_2/m_1) [1 + (M_1/M_2)r_1] - 1 \} \quad (1)$$

which is the linear form of

$$m_1/m_2 = (M_1/M_2) [(r_1M_1 + M_2)/(r_2M_2 + M_1)] \quad (2)$$

The negative values obtained for  $r_2$  are due to some inaccuracies in the elementary analyses and in the graphical method. Actually  $r_2 = 0$  for all three comonomers was reported previously,<sup>4</sup> and no homopolymers were obtained by radical initiation.

As there exists a penultimate effect for all three comonomers in copolymerization with styrene, the possibility of such an effect was also examined for copolymerization with acrylonitrile by use of the scheme of Merz<sup>8</sup> and Barb's notation:<sup>9</sup>

$$r_1 = [(n-1)/x^2] (1/r_1') + (n-2)/x \quad (3)$$

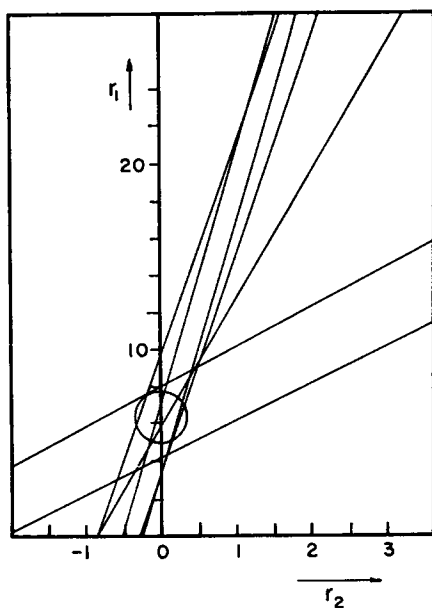


Fig. 1. Copolymerization of acrylonitrile ( $M_1$ ) with cinnamionitrile ( $M_2$ ). Determination of  $r_1$  and  $r_2$  by using eq. (1).  $r_1 = 6.4 \pm 1$ ;  $r_2 = 0 \pm 0.5$ .

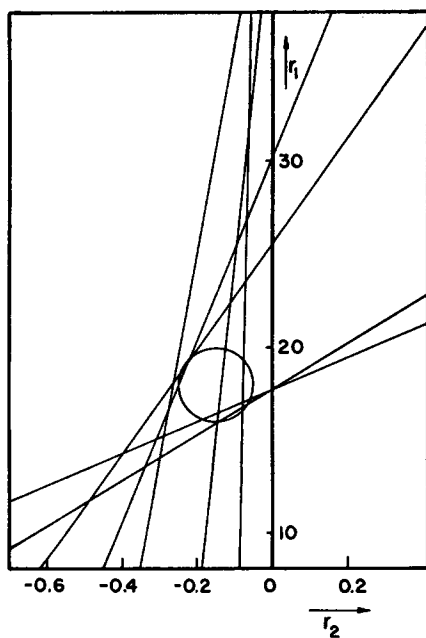


Fig. 2. Copolymerization of acrylonitrile ( $M_1$ ) with ethyl benzylidenecyanoacetate ( $M_2$ ). Determination of  $r_1$  and  $r_2$  by using eq. (1).  $r_1 = 18 \pm 2$ ;  $r_2 = -0.15 \pm 0.1$ .

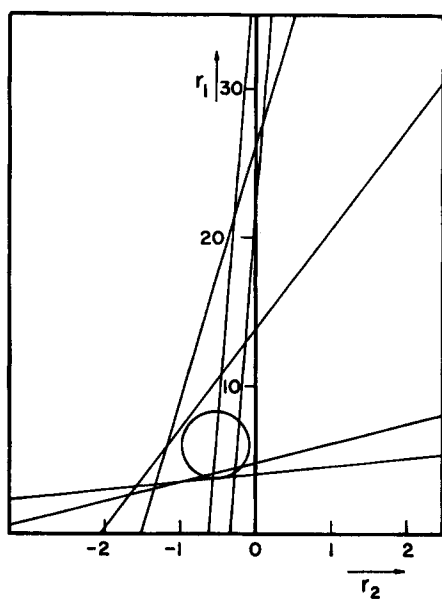


Fig. 3. Copolymerization of acrylonitrile ( $M_1$ ) with benzylidenemalononitrile ( $M_2$ ). Determination of  $r_1$  and  $r_2$  by using eq. (1).  $r_1 = 6.2 \pm 1.8$ ;  $r_2 = -0.5 \pm 0.4$ .

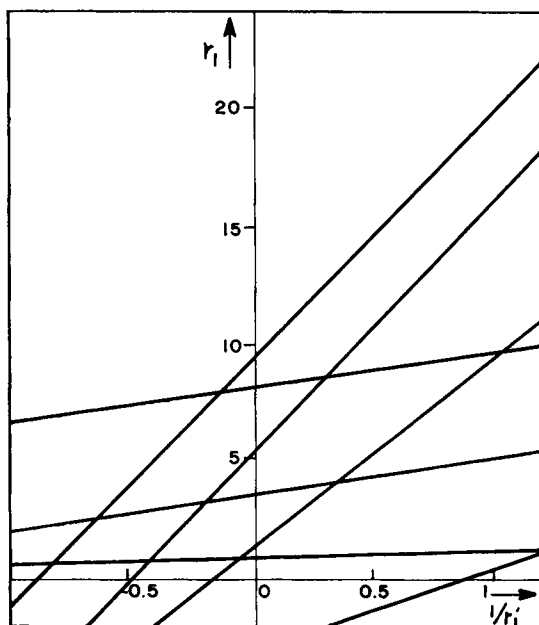


Fig. 4. Copolymerization of acrylonitrile ( $M_1$ ) with cinnamonnitrile ( $M_2$ ). Attempted determination of  $r_1$  and  $r_1'$  by using the enlarged scheme.

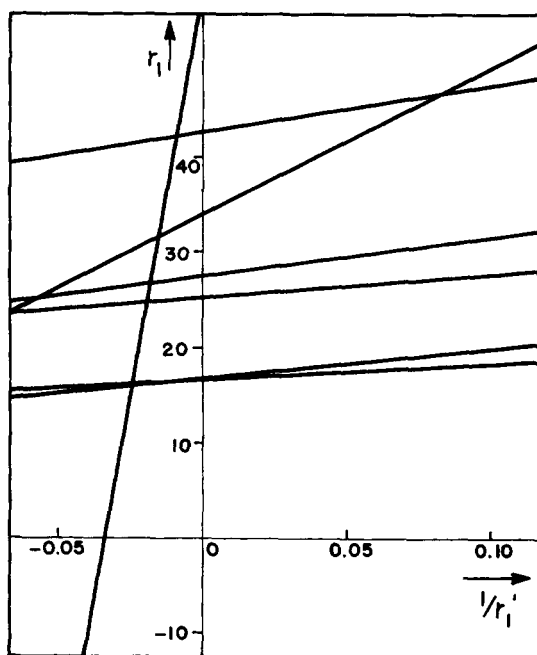


Fig. 5. Copolymerization of acrylonitrile ( $M_1$ ) with ethyl benzylidenecyanoacetate ( $M_2$ ). Attempted determination of  $r_1$  and  $r_1'$  by using the enlarged scheme.

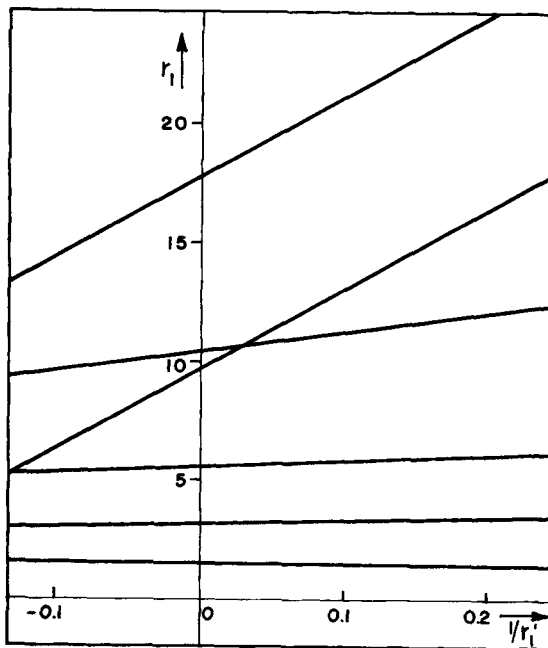


Fig. 6. Copolymerization of acrylonitrile ( $M_1$ ) with benzylidenemalononitrile ( $M_2$ ). Attempted determination of  $r_1$  and  $r_1'$  by using the enlarged scheme.

where  $x = M_1/M_2$  and  $n = m_1/m_2$ . Graphs for  $r_1$  against  $1/r_1'$  yielded widely scattered lines, and thus there seems to be no penultimate effect for these copolymers (Figs. 4-6). Thus this effect exists for the copolymerizations of the three comonomers with styrene (a nonpolar monomer<sup>4</sup>) but not, as expected, for their copolymerization with acrylonitrile, when the whole copolymer chain consists of monomers of similar polarity.

The Alfrey-Price  $Q_2$  and  $e_2$  values<sup>10</sup> (Table IV) were calculated according to the equation

$$r_1 = (Q_1/Q_2) \exp\{-e_1(e_1 - e_2)\} \quad (4)$$

The  $r_1$  values used, were obtained from the copolymerization of the three comonomers with acrylonitrile (present paper) and from their copolymerization with styrene either according to the improved scheme<sup>4</sup> or according to the simple kinetic scheme.\* It was assumed that  $Q_1 = 1.0$  and  $e_1 = -0.8$  for styrene and  $Q_1 = 0.60$  and  $e_1 = 1.20$  for acrylonitrile.

TABLE IV  
 $Q$  and  $e$  Values

| Monomer                              | $Q_2$ | $e_2$ | Reference               |
|--------------------------------------|-------|-------|-------------------------|
| Cinnamionitrile (I)                  | 0.11  | 1.21  | This paper <sup>a</sup> |
|                                      | 0.11  | 1.19  | This paper <sup>b</sup> |
|                                      | 0.32  | 0.75  | 10                      |
| Ethyl benzylidenecyanoacetate (II)   | 0.13  | 2.70  | This paper <sup>a</sup> |
|                                      | 0.14  | 2.44  | This paper <sup>b</sup> |
|                                      | 1.24  | 0.87  | 10                      |
| Benzylidenemalononitrile (III)       | 0.52  | 2.60  | This paper <sup>a</sup> |
|                                      | 0.38  | 2.35  | This paper <sup>b</sup> |
| Acrylonitrile (AN)                   | 0.60  | 1.20  | 10                      |
| Crotononitrile (CN)                  | 0.009 | 1.13  | 11                      |
| Methyl $\alpha$ -cyanoacrylate (MCA) | 17    | 2.48  | 12                      |
| Vinylidene cyanide (VC)              | 20.13 | 2.58  | 10                      |
| Ethyl cinnamate (EC)                 | 0.18  | 0.46  | 13                      |
| Methyl atropate (MA)                 | 6.1   | 1.3   | 14                      |
| Ethyl atropate (EA)                  | 4.28  | 1.41  | 13                      |
| Diethyl chloromaleate (DCM)          | 0.056 | 1.65  | 10                      |

<sup>a</sup>  $r_1$  from copolymerization with styrene according to improved scheme.

<sup>b</sup>  $r_1$  from copolymerization with styrene according to simple kinetic scheme.

In addition,  $Q_2$  and  $e_2$  for comonomers I and II as reported by Ham<sup>10</sup> are given in Table IV. Our  $Q_2$  and  $e_2$  values differ from those reported by Ham, yet his results were obtained from one set of data only.

For comparison,  $Q_2$  and  $e_2$  of several monomers, having chemical structures similar to those of our three comonomers, are given.

One can see, that the  $Q_2$  of the 1,2-disubstituted vinyl (cinnamionitrile, I) is quite low and similar to the  $Q_2$  values of EC, and the same applies to

\* The values of  $r_1$  for the copolymerization of the comonomers I, II, and III with styrene, calculated by the simple kinetic scheme are: St-I,  $r_1 = 2.3$ ; St-II,  $r_1 = 0.51$ ; St-III,  $r_1 = 0.25$ .



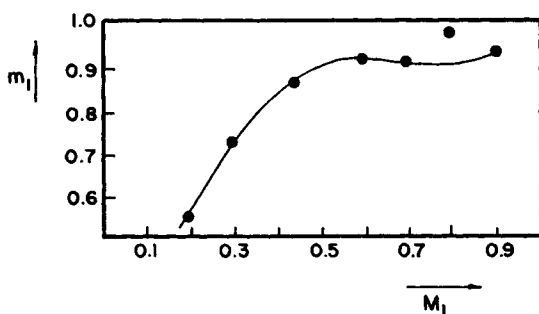


Fig. 7. Copolymerization of acrylonitrile ( $M_1$ ) with cinnamonnitrile ( $M_2$ ). Initial copolymer composition vs. composition of monomer feed.

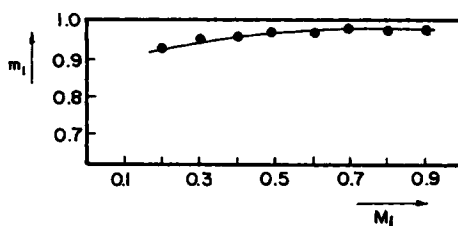


Fig. 8. Copolymerization of acrylonitrile ( $M_1$ ) with ethyl benzylidenecyanoacetate ( $M_2$ ). Initial copolymer composition vs. composition of monomer feed.

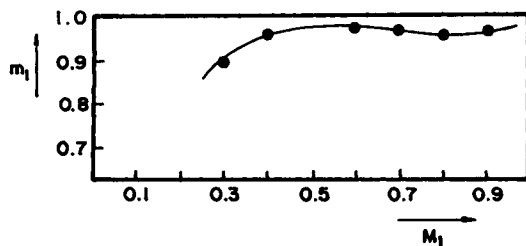


Fig. 9. Copolymerization of acrylonitrile ( $M_1$ ) with benzylidenemalononitrile ( $M_2$ ). Initial copolymer composition vs. composition of monomer feed.

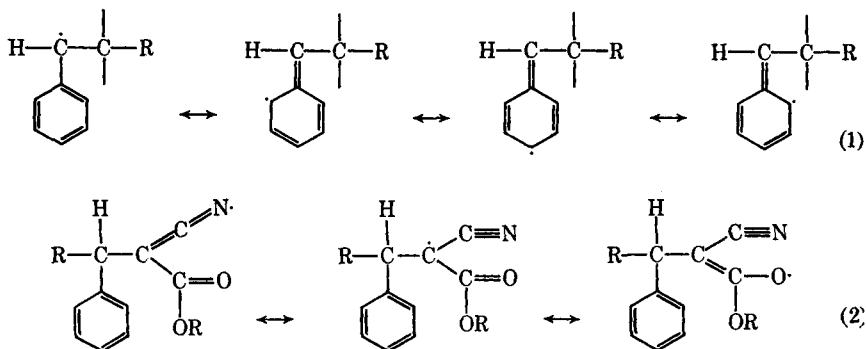
1,1,2-trisubstituted monomers (II, III, DCM). On the other hand, unsymmetrical 1,1-disubstituted monomers with a  $\text{CH}_2=$  group (VC, MCA, MA, EA) have a rather high  $Q_2$ . Regarding  $e_2$ , characterizing the polarity, the values for AN, I, and CN are nearly equal, and the same applies to the corresponding pairs II-MCA and III-VC.

The dependence of the composition of the copolymers  $m_1$  on the composition of the monomer mixture  $M_1$  is given in Figures 7-9. In all three cases, the copolymers show a much higher content of acrylonitrile than the monomer mixtures. As the three comonomers do not homopolymerize under the conditions given above, one can assume that the monomer sequence in the three copolymers consists of larger blocks of acrylonitrile

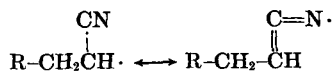
units, interrupted by single comonomer molecules. The dependence of the rates of copolymerization can be summarized for all three pairs as follows. The rates of copolymerization decrease with increasing comonomer content. This rate decrease is about three times up to 30% comonomer content, but becomes much stronger with a comonomer content of up to 80%. However, as the rate of polymerization of acrylonitrile is very high indeed, the addition of small quantities of these comonomers would be even useful for control of the polymerization reaction itself, provided that the copolymers obtained excel the homopolymer regarding certain properties.

The rate of polymerization depends on the polarities of the monomers, on steric factors, and on the resonance stabilization of the radicals. Due to the  $\alpha$  and  $\beta$  substitution of the double bond, there exists a strong steric factor for all three comonomers in comparison to acrylonitrile. Thus at about equal polarity but due to the steric factor, the acrylonitrile radical seems to react preferably with another acrylonitrile molecule than with one of the comonomers.

Due to the presence of a phenyl group, one or two nitrile groups, or an ester group, all three comonomers have a conjugated system. By the attack of free radicals on the  $\alpha,\beta$ -substituted double bond, resonance-stabilized radicals are produced:



The resonance stabilization according to (1) is of course greater, yet both possibilities affect a decrease of the reactivity of the comonomer radicals. The acrylonitrile radical is rather weakly stabilized,



and consequently the composition of the resulting copolymer is determined mainly by the relatively high rate of self-addition of acrylonitrile. Further, the faster diffusion of the acrylonitrile in comparison with the bulky comonomers may have to be considered. In the copolymerization with styrene, where all the monomers are rather bulky and all are highly stabilized, an increase of the rate of polymerization seems to be mainly due to the polarity of the comonomers.

The reluctance of the three comonomers (I, II, and III) to copolymerize with acrylonitrile in comparison to their readiness to copolymerize with styrene is also consistent with their  $Q-e$  values.

This paper is taken in part from a thesis submitted by Samuel H. Ronel to the Department of Chemistry, Technion—Israel Institute of Technology, Haifa, in partial fulfillment of the degree of M.Sc.

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Received January 23, 1969