Reactivity of Polar Monomers in Copolymerization

GEORGE E. HAM, *The Chemstrand Corporation, Decatur, Alabama*

As a consequence of a detailed study of the copolymer system styrene–fumaronitrile,[1] the investigators were led to the conclusion that the high reactivity of fumaronitrile monomer with a styrene free radical relative to styrene monomer underwent a marked decrease as the fumaronitrile content of the copolymer increased. This result was not in keeping with the predictions of the conventional Lewis and Mayo copolymerization equation:[2]

$$\frac{m_1}{m_2} = \left(\frac{M_1}{M_2}\right) \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \tag{1}$$

where m_1/m_2 is the composition of the initial copolymer and M_1 and M_2 are the monomer concentrations. This effect was attributed to electrostatic repulsion between adding fumaronitrile monomer and chains rich in fumaronitrile. The observed data were later interpreted in the light of a copolymer composition equation, which allowed for the effect of the penultimate unit in the growing free radical, previously derived by Merz, Alfrey, and Goldfinger:[3]

$$\frac{a}{b} = \frac{1 + \dfrac{A}{\alpha_1 B}\left(\dfrac{\alpha_1 B + A}{\alpha_2 B + A}\right)}{1 + \dfrac{\beta_1 B}{A}\left(\dfrac{\beta_2 B + A}{\beta_1 B + A}\right)} \tag{2}$$

where a/b is the composition of the initial copolymer, A and B are the initial monomer concentrations, and:

$$\alpha_1 = \frac{k_2^{aab}}{k_2^{aaa}} \qquad \alpha_2 = \frac{k_2^{bab}}{k_2^{baa}}$$

$$\beta_1 = \frac{k_2^{abb}}{k_2^{aba}} \qquad \beta_2 = \frac{k_2^{bbb}}{k_2^{bba}}$$

The various ratios involving rate constants k refer to propagative reactions. Thus k_2^{aab} is rate constant for the addition of monomer B to a chain ending in two molecules of A.

This interpretation[4] led to a simplified equation which assumed r_2 and r_2' values of 0:

$$n - 1 = r'x(1 + rx)/(1 + r'x) \tag{3}$$

where x is the molar ratio of monomer 1/monomer 2 in the reaction mixture and n is the molar ratio of monomer 1/monomer 2 in the copolymer; and where r is the reactivity ratio for a radical with similar penultimate and terminal unit, and r' the ratio for a radical with dissimilar units. Though this equation neglects a small, but significant, effect of units farther removed than the penultimate unit, it is useful in interpreting copolymerization systems exhibiting electrostatic repulsion or steric phenomena.

Since it was now established that electrostatic repulsion of nonterminal units played an important part in the copolymerization of styrene with polar 1,2-disubstituted monomers, it was of interest to reexamine the copolymerization behavior of polar monosubstituted monomers for a similar effect. Published data on copolymerization systems involving acrylonitrile, methacrylonitrile, methyl acrylate, acrylic acid, and methacrylic
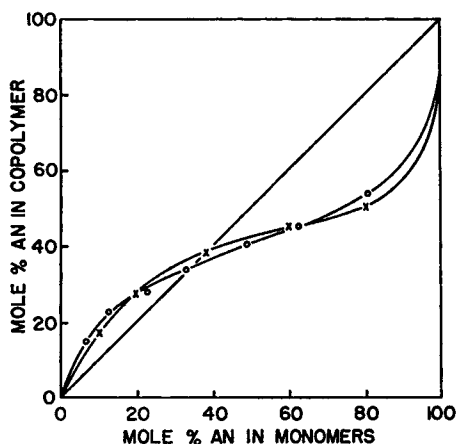

Fig. 1. Composition of styrene–acrylonitrile copolymers:
(○) experimental mass-polymerization points; (×) theoretical curve
of $r_1 = 0.4 \pm 0.08$, $r_2 = 0.03 \pm 0.03$.

acid were studied for such an effect. Only acrylonitrile was found to exhibit electrostatic repulsion between polar monomer and chains rich in the same monomer (exclusive of terminal unit). This behavior was noted in the copolymerization of acrylonitrile with styrene, α-methylstyrene, and α-acetoxystyrene. As expected, the degree of repulsion is much less pronounced than in those cases in which the adding monomer possesses polar groups on both carbons separated by a double bond.

Perhaps the most complete copolymerization data reported at a single temperature for styrene and acrylonitrile were obtained by Fordyce and Chapin.[5] A plot of monomer *versus* copolymer composition produces a curve which is somewhat similar in shape at low acrylonitrile concentrations to the styrene–fumaronitrile curve. Damping of acrylonitrile reactivity as the acrylonitrile content of the copolymer increases is definite, though considerably less pronounced than in the case of fumaronitrile. The re-

ported reactivity ratios for styrene–acrylonitrile ($r_1 = 0.41 \pm 0.08$, $r_2 = 0.03 \pm 0.03$)[5] represent the best fit of the experimental data assuming no contributions to reactivity by acrylonitrile units other than at the chain end. The deviation between the experimental and calculated curve is shown in Figure 1.

A plot of $n - 1$ vs. x (Fig. 2) was utilized to assign values of r_1 and r_1' using the method of Barb.[4] The experimental curve exhibits slope r' at $x = 0$ and slope r as $x \to \infty$. It is assumed that addition of acrylonitrile monomer to radicals ending in acrylonitrile at less than 50 mole per cent acrylonitrile is negligible. (This assumption is valid if $r_1 r_2$ is very small.) This effect is further minimized by taking the slope of the tangent drawn
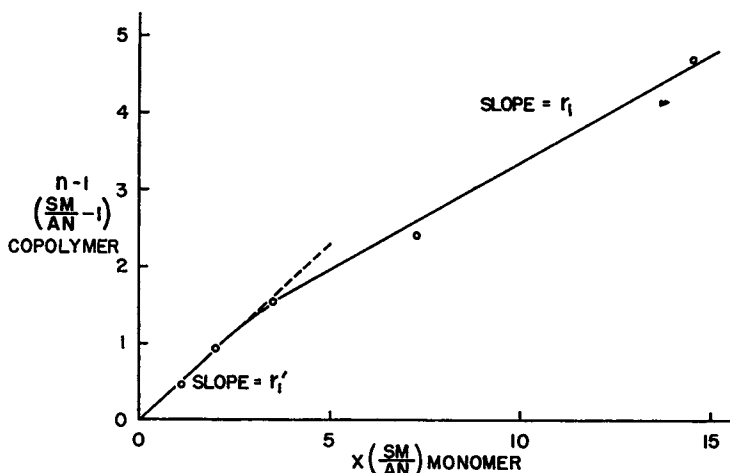

Fig. 2. Copolymerization of styrene–acrylonitrile: $r_1 = 0.30 \pm 0.02$, $r_1' = 0.45 \pm 0.02$, $r_2 = 0.03 \pm 0.03$.

from the origin to the curve as r'. Values of $r_1 = 0.30 \pm 0.02$ and $r_1' = 0.45 \pm 0.02$ were obtained for the system styrene–acrylonitrile. Slight effects of acrylonitrile units other than the terminal and penultimate units are neglected in the assignment of these values. The meager data at greater than 50 mole % acrylonitrile prevent assignment or justification of separate r_2 and r' values. For our present purposes it is assumed that $r_2 = r_2' = 0.03$.

The ratio r_1'/r_1 may be used as a measure of the relative repelling tendencies of polar monomers. Thus, in the system styrene–acrylonitrile $r_1'/r_1 = 1.5$. This compares with approximately 15 for fumaronitrile and 3–4 for maleic anhydride and maleate esters in copolymerization with styrene.[4] It is reasonable that r_1'/r_1 for acrylonitrile is low, since there is only one polar group per molecule and the unsubstituted end is presented for reaction with the free radical. Hence, repulsion is at longer range than in the case of fumaronitrile or maleic anhydride.

The system α-methylstyrene–acrylonitrile[6] was examined in a similar
way. Values for $r_1 = 0.055 \pm 0.005$ and $r_1' = 0.093 \pm 0.005$ were ob-
tained (Fig. 3). The ratio r_1'/r_1 in this case is 1.69, which is close to the
value of 1.5 obtained in the styrene–acrylonitrile system. Since the repell-
ing tendency is almost exclusively due to acrylonitrile it is reasonable that
the values be similar.

The system α-acetoxystyrene–acrylonitrile[7] was also examined, although
the reported data are not sufficient for firm conclusions. Estimated values
of $r_1 = 0.09 \pm 0.01$ and $r_1' = 0.47 + 0.10$ were obtained, compared with
the literature value of $r_1 = 0.4 \pm 0.05$. The ratio of r_1'/r_1 was 5.2 which
may be considered the result of the strong alternating tendency in this sys-
tem as well as repulsion of penultimate acrylonitrile units from adding
acrylonitrile monomer. Similar examination of the systems vinyl acetate–
acrylonitrile[6] ($r_1 = 0.02 \pm 0.02$, $r_2 = 6 \pm 2$) and vinyl chloride–acryloni-
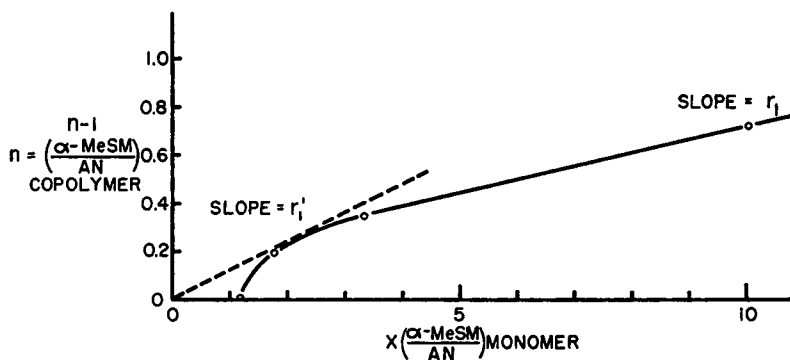trile[8] ($r_1 = 0.074$, $r_2 = 3.7$) for possible differences between r_1 and r_1' was

Fig. 3. Copolymerization of α-methylstyrene–acrylonitrile: $r_1 = 0.055$
± 0.005, $r_1' = 0.093 \pm 0.005$, $r_2 = 0.06 \pm 0.02$.

made. It was found that a difference of at least 50% in the value of r_1
could be made without appreciable change in the shape of the curves.
Hence, differences between r_1 and r_1' of this order could not be justified
experimentally. These results follow from the very low value of r_1 in these
systems. However, the product $r_1 r_2$ in both cases is appreciably less than
1, and is taken as evidence of "repulsion" of chains rich in acrylonitrile
from adding acrylonitrile monomer. However, the $r_1 r_2$ products in the
cases of vinyl acetate–acrylonitrile (0.12) and vinyl chloride–acrylonitrile
(0.274) are much greater than in the case of styrene–acrylonitrile (0.009),
so application of the analytical method of Barb in the first two cases may
be questioned. A more general method applicable to any copolymeriza-
tion system is outlined in the next paragraph.

Testing of all of the new values of r_1 and r_1' was made possible by modifi-
cation of the equation of Merz, Alfrey, and Goldfinger.[3] Since r_2 and r_2'
were assumed to be equal, the equation was simplified somewhat:

$$\frac{m_1}{m_2} = \frac{1 + \dfrac{r_1 M_1}{M_2}\left[\dfrac{(M_2/r_1) + M_1}{(M_2/r_1') + M_1}\right]}{1 + (r_2 M_2/M_1)} \tag{4}$$

Literature values for r_2 were assumed to be correct in all cases. The new values for r_1 and r_1' gave theoretical curves much closer to experimental values than those obtained with r_1 and r_2 values alone. However, it was noted that "damping" due to units behind the penultimate unit was still evident. It is believed that equations which would completely account for this behavior would be too complicated for convenient use.

A convenient means of estimating r_1 and r_2 for trial in the above equation as well as in the conventional Lewis and Mayo equation is not believed to be generally known. The slope as $M_2/(M_1 + M_2) \rightarrow 0$ in a plot of copolymer composition vs. monomer composition as in Figure 1 is equal to $1/r_1$ and the slope as $M_2/(M_1 + M_2) \rightarrow 1$ is $1/r_2$. This relationship may be derived from the Lewis and Mayo equation (1), cited above. Since the ratio $M_2/(M_1 + M_2)$ is required, 1 is added to each side of the equation and the reciprocal taken:

$$\frac{m_2}{m_1 + m_2} = \frac{r_2 M_2 + M_1}{r_1 M_1 + M_2}\left(\frac{M_2}{M_1 + M_2}\right) \tag{5}$$

As $M_2/(M_1 + M_2) \rightarrow 0$ the equation reduces to:

$$\frac{m_2}{m_1 + m_2} = \frac{1}{r_1}\left(\frac{M_2}{M_1 + M_2}\right) \tag{6}$$

and the slope become $1/r_1$.

If the graph is inverted, it may be interpreted as representing a plot of:

$$\frac{m_1}{m_1 + m_2} \quad vs. \quad \frac{M_1}{M_1 + M_2}$$

As $M_1/(M_1 + M_2) \rightarrow 0$ the slope may be shown in a similar way to be $1/r_2$. Interpreted on the basis of the original plot, the slope as $M_2/(M_1 + M_2) \rightarrow 1$ is $1/r_2$.

In the search for possible occurrence of repulsion involving nonterminal methacrylonitrile units, the systems styrene–methacrylonitrile, α-methylstyrene–methacrylonitrile, and vinyl acetate–methacrylonitrile were studied. In all cases it was shown by the methods outlined above that such effects were negligible. The α-methyl group appears to have a "shielding" effect.

To determine whether there are appreciable steric contributions to repulsion involving disubstituted olefins, $n - 1$ vs. x was plotted for the system vinyl acetate–crotonic acid ($r_1 = 0.33$, $r_2 = 0$) (Fig. 4). As expected on the basis of one polar group per molecule (and lack of nonterminal polar effect with acrylic acid) a straight line denoting $r_1 = r'$ was obtained.

That acrylonitrile alone, out of numerous polar methylenic monomers examined, should exhibit significantly different r_1 and r_1' values in free radical copolymerization is in line with observations reported by Mayo and Walling[9] on the order of reactivity of various monomers in carbanionic copolymerization.   The order of reactivity was found to be acrylonitrile > methacrylonitrile > methyl methacrylate.   The reactivity of a monomer
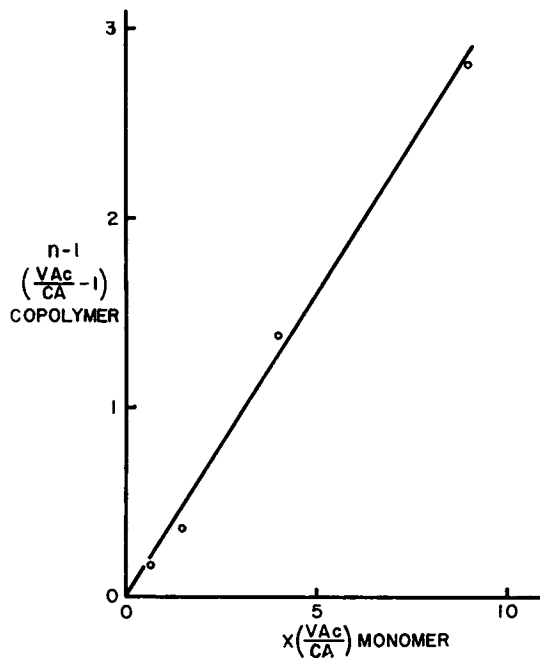

Fig. 4.   Copolymerization of vinyl acetate–crotonic acid: $r_1 = r_1' = 0.33$, $r_2 = 0$.

in carbanionic copolymerization depends on the ability of attached groups to withdraw electrons from the double bond.   Thus, the polar effect in acrylonitrile, which gives rise to r_1' values different from r_1, and is already rather small, disappears almost entirely on going to less polar monomers.

References

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Synopsis

As a consequence of earlier establishment of electrostatic repulsion between non-terminal polar 1,2-disubstituted olefins in polymers and like adding monomer, polar methylenic monomers were examined for such an effect. Acrylonitrile was found to exhibit such behavior in at least three systems: styrene–acrylonitrile, α-methylstyrene–acrylonitrile, and α-acetoxystyrene–acrylonitrile. Absence of such an effect was shown for methacrylonitrile, methyl acrylate, acrylic acid, methacrylic acid, and crotonic acid. A modified copolymerization equation involving r_1, r_1', and r_2 was presented. A convenient means of estimating r_1 and r_2 in this equation as well as in the ordinary copolymerization equation was shown.

Résumé

En conséquence de la répulsion électrostatique existant entre des oléfines 1.2 disubstituées polaires qui ne se trouvent pas en fin de chaîne d'un polymère et de monomères semblables, certains monomères méthyléniques et polaires ont été examinés. L'acrylonitrile témoigne ainsi un tel comportement dans au moins trois systèmes: styrène-acrylonitrile, α-méthylstyrène-acrylonitrile, et α-acétoxystyrène-acrylonitrile. Par contre l'absence de cet effet a été noté pour le méthacrylonitrile, l'acrylate de méthyle, l'acide acrylique, l'acide méthacrylique et l'acide crotonique. Une équation de copolymérisation modifiée comprenant r_1, r_1' et r_2 est présentée; on indique un moyen aisé de déterminer les valeurs r_1 et r_2 de cette équation par une manière analogue à celle utilisée pour l'équation ordinaire de la copolymérisation.

Zusammenfassung

Wie früher festgestellt worden war besteht zwischen nicht-terminalen polaren 1,2-disubstituierten Olefinen in Polymeren und gleicherweise additionierendem Monomer eine elektrostatische Abstossung. Infolgedessen wurden polare Methylen-Monomere auf diese Wirkung untersucht. Es wurde gefunden, dass Acrylonitril dieses Verhalten in mindestens drei Systemen zeigt: Styrol-Acrylonitril, α-Methylstyrol-Acrylonitril und α-Acetoxystyrol-Acrylonitril. Abwesenheit einem solchen Wirkung wurde für Methacrylonitril, Methylacrylate, Acrylsäure, Methacrylsäure und Crotonsäure gezeigt. Eine geänderte Copolymerisationsgleichung, die r_1, r_1' und r_2 behandelt, wurde gegeben. Eine bequeme Methode zur Abschätzung von r_1 und r_2 in dieser Gleichung wie auch in der üblichen Copolymerisationsgleichung wurde gegeben.