

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Acrylonitrile Copolymerizations. I. Penultimate Effects

A. Guyot^a; J. Guillot^a

^a C.N.R.S. Institut de Recherches sur la Catalyse, Villeurbanne, France

To cite this Article Guyot, A. and Guillot, J.(1968) 'Acrylonitrile Copolymerizations. I. Penultimate Effects', Journal of Macromolecular Science, Part A, 2: 5, 889 – 903

To link to this Article: DOI: 10.1080/10601326808051448

URL: <http://dx.doi.org/10.1080/10601326808051448>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Acrylonitrile Copolymerizations. I. Penultimate Effects

A. GUYOT and J. GUILLOT

*C.N.R.S. Institut de Recherches sur la Catalyse
Villeurbanne, France*

SUMMARY

Kinetics studies, using the gas-chromatographic method, of the two copolymerizations acrylonitrile-methyl methacrylate and styrene-acrylonitrile, show that remote units effects do operate on the reactivity of each radical species. The corresponding reactivity ratios are:

In acrylonitrile (A)-methyl methacrylate (M) copolymerization:

$$r_{AA} = 0.39 \quad r_{MA} = 0.22 \quad r_{AM} = 1.56 \quad r_{MM} = 1.02$$

In styrene (S)-acrylonitrile (A) copolymerization:

$$r_{AA} = 0.33 \quad r_{SA} = 0.08 \quad r_{AS} = 0.55 \quad r_{ASS} = 0.50$$

$$r_{SSS} = 0.25$$

With the mixture rich in acrylonitrile the kinetics are sensible to a dipolar bonding effect between the nitrile groups of the monomer and of the copolymers.

INTRODUCTION

In a preceding paper [1] we have shown that, by means of chromatographic analysis of the reaction medium, it was possible to give evidence for penultimate effects and even antipenultimate effects on the styrene-ended radicals in styrene-acrylonitrile copolymerization. It was quoted that such a system was favorable, owing to the small value of the reactivity ratio of the acrylonitrile; so the de-

nominators of the classical Lewis and Mayo equation (1) or of the Alfrey equation (2) which take in account the penultimate effects may be reduced to unity:

$$n = (r_1 x + 1) / [1 + (r_2/x)] \quad (1)$$

where n is the molar ratio of the two monomers which have been copolymerized at the time t and x is the corresponding ratio of the two monomers in the reaction mixture at the same time:

$$n = \frac{1 + [r'_1 x (r_1 x + 1)] / (r'_1 x + 1)}{1 + (r'_2/x) [(r_2 + x) / (r'_2 + x)]} \quad (2)$$

where r_1 , r_2 , r'_1 , and r'_2 are the reactivity ratio of the different radicals.

The present study is concerned with systems where the second term of the denominators are not necessarily negligible. The couple methyl methacrylate (M)-acrylonitrile (A) has been studied in the whole range of composition; in addition, study of the couple styrene (S)-acrylonitrile (A) has been extended in the range rich in acrylonitrile.

EXPERIMENTAL

The polymerization were carried out at 60°C in solution in either dimethylformamide (DMF) or toluene, under nitrogen atmosphere, with carefully purified monomers, and initiated using azobisisobutyronitrile. With the AM system, 12 experiments were carried out with different initial compositions reported on the Table 1. The corresponding data of the experiments involving the AS system are presented in Table 2.

The chromatographic analyses were performed by means of two kinds of column packing, depending on the solvent used in the polymerization: With toluene solutions the conditions are: column length, 2.5 meters, diameter, 4 mm; 30% silicone 702 on Celite C₂₂; temperature between 70 and 100°C; hydrogen flow, 4 liters/hr. In the case of DMF solution one uses: column length, 1.0 m, diameter, 4 mm; packed with Porapak Q (polystyrene-divinylbenzene beads); between 150 and 170°C; hydrogen flow, 3 liters/hr. The detectors were Gow Mac filaments W2 X catharometers. With the mixtures poor in acrylonitrile, a detector specially sensitive to unsaturated compounds, devised in our laboratory, has been used; it will be described elsewhere [2].

Table 1. Methyl Methacrylate (M)-Acrylonitrile (A) Copolymers—Initial Compositions

Gross, mole %	Solvent, moles	Catalyst, moles/liter	M, moles	A, moles	$x_{M,0} = M/A$, moles/mole	$x_{A,0} = A/M$, moles/mole
99-1	Toluene 3.90	10.3×10^{-3}	1.125	0.0122	93.0	0.0107
97.5-2.5	Toluene 3.80	10.4×10^{-3}	1.218	0.0286	42.6	0.0235
97-3	Toluene 1.75	10.8×10^{-3}	1.05	0.0300	35.0	0.0284
85-15	Toluene 3.36	12.9×10^{-3}	0.608	0.103	5.90	0.170
80-20	DMF 3.78	11.0×10^{-3}	1.045	0.280	3.74	0.268
70-30	Toluene 3.53	11.2×10^{-3}	0.629	0.264	2.38	0.42
50-50	DMF 4.75	10.2×10^{-3}	0.815	0.725	1.12	0.89
35-65	DMF 4.80	11.6×10^{-3}	0.442	0.850	0.52	1.925
10-90	DMF 4.50	11.9×10^{-3}	0.116	1.140	0.098	10.2
3-97	DMF 4.75	10.2×10^{-3}	0.039	1.100	0.035	28.0
2-98	DMF 5.05	11.9×10^{-3}	0.0169	0.970	0.0174	57.5
1-99	DMF 4.75	12.4×10^{-3}	0.0120	1.150	0.0104	96.0

Table 2. Styrene (S)-Acrylonitrile (A) Copolymers—Initial Compositions

Gross, mole %	Solvent, moles	Catalyst, moles/liter	S, moles	A, moles	$X_{S,0} = S/A$ moles/mole	$x_{A,0} = A/S$ moles/mole
98-2	Toluene 2.60	5.6×10^{-3}	0.98	0.018	54.0	0.0185
96-4	Toluene 2.50	4.9×10^{-3}	0.83	0.036	23.0	0.0435
80-20	Toluene 4.60	7.0×10^{-3}	1.26	0.262	4.80	0.206
60-40	Toluene 3.00	5.2×10^{-3}	0.575	0.372	1.54	0.65
50-50	DMF 5.50	8.7×10^{-3}	0.487	0.530	0.926	1.08
35-65	DMF 5.10	10.3×10^{-3}	0.370	0.648	0.568	1.76
20-80	DMF 5.50	9.0×10^{-3}	0.236	0.880	0.268	3.73
10-90	DMF 4.80	11.0×10^{-3}	0.117	1.07	0.109	9.15
5-95	DMF 5.00	10.5×10^{-3}	0.056	1.15	0.049	20.5
3-97	DMF 6.00	9.0×10^{-3}	0.037	1.23	0.030	33.0

In all cases the solvents used were internal calibration standard, except in the system SA-DMF, where a small amount of toluene was introduced. The areas under the peaks were measured by an Infotronics CRS-100 electronic integrator.

RESULTS AND DISCUSSIONS

Methyl Methacrylate-Acrylonitrile Copolymers

From the initial slopes of the conversion curves of the two monomers, the initial values of $n_M = dM/dA$ and $n_A = dA/dM$, corresponding to the initial compositions $x_M = M/A$ and $x_A = A/M$ reported in the last columns of the Table 1, have been obtained.

A Lewis and Mayo plot indexed to A and corresponding to the large range $0.17 < x_A < 10$ is illustrated in Fig. 1. It may be seen

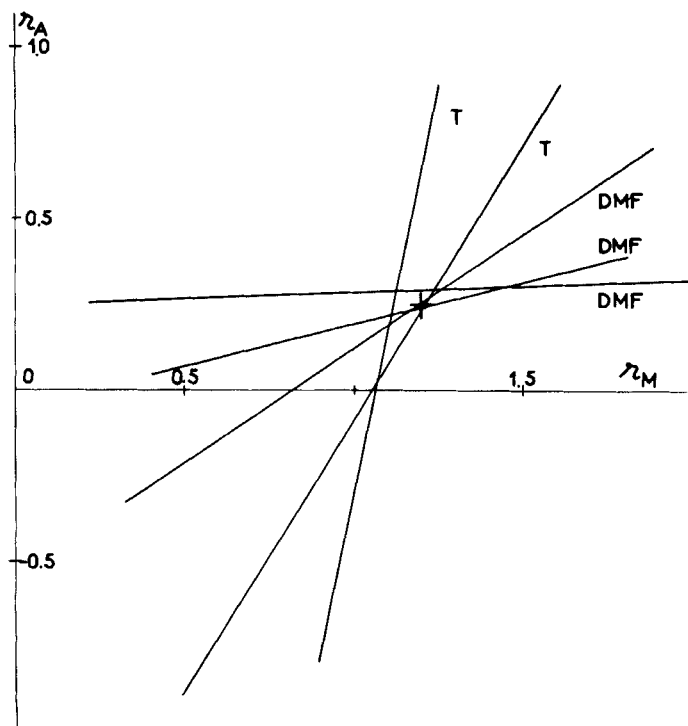


Fig. 1. Methyl methacrylate-acrylonitrile copolymerization. Lewis and Mayo plot for the medium range of composition. Experiments performed in toluene (T) or dimethylformamide (DMF) solutions.

that the lines corresponding to experiments performed in toluene or in DMF cross themselves in the same area, which supports the validity of the classical theory. Thus the reactivity ratios obtained are

$$r_M = 1.20 \pm 0.05 \quad \text{and} \quad r_A = 0.25 \pm 0.04$$

Using a Fineman-Ross plot one obtains

$$r_M = 1.17 \pm 0.05 \quad \text{and} \quad r_A = 0.25 \pm 0.04$$

These values seem to be more precise than the values reported in the literature (see Table 3) except for those of Schmolke et al. [5], which were also obtained from a large range of compositions ($0.04 < x_M < 13$).

Table 3. Monomer Reactivity Ratio in Copolymerization of Acrylonitrile (A) and Methyl Methacrylate (M)

r_A	r_M	T, °C	Ref.
0.100 ± 0.07	1.35 ± 0.13	40	[3]
0.150 ± 0.08	1.22 ± 0.10	80	[3]
0.160 ± 0.10	1.19 ± 0.12	100	[3]
0.150 ± 0.07	1.20 ± 0.14	60	[4]
0.31 ± 0.03	1.15 ± 0.05	50	[5]
0.15 ± 0.03	1.65 ± 0.40	20	[7]

However, the Fig. 2, where a Fineman-Ross plot indexed to M, but corresponding to the extreme composition range, rich in M, definitely proves that the validity of the classical equation is not

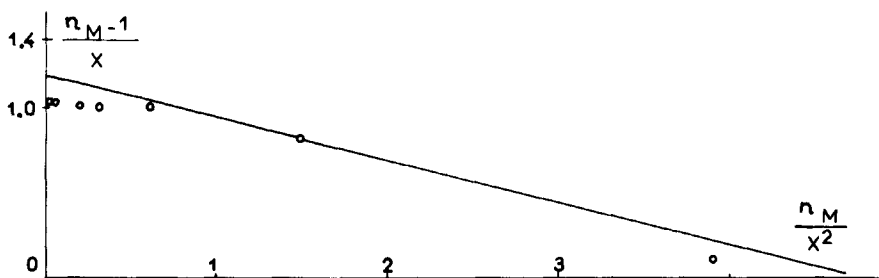


Fig. 2. Mixtures rich in methyl methacrylate, Fineman-Ross plot.

verified for x_M greater than about 5. Then a penultimate effect is indicated. The method used to determine it is similar to that previously described [1], except that correction has been applied to take in account the value of the denominator of Eq. (2). In place of n_M we have used $N_M = n_M (1 + r_A/x_M)$, and the Barb [8] equation is written in its linear form

$$(N_M - 2)/x_M = r_{MM} - (1/r_{AM})[(N_M - 1)/x_M^2] \quad (3)$$

The results plotted in Fig. 3 show that a penultimate effect with

$$r_{MM} = 1.02 \pm 0.01 \quad \text{and} \quad r_{AM} = 1.56 \pm 0.05$$

account very satisfactorily for the experiments, and it seems not necessary to inquire for an antepenultimate effect.

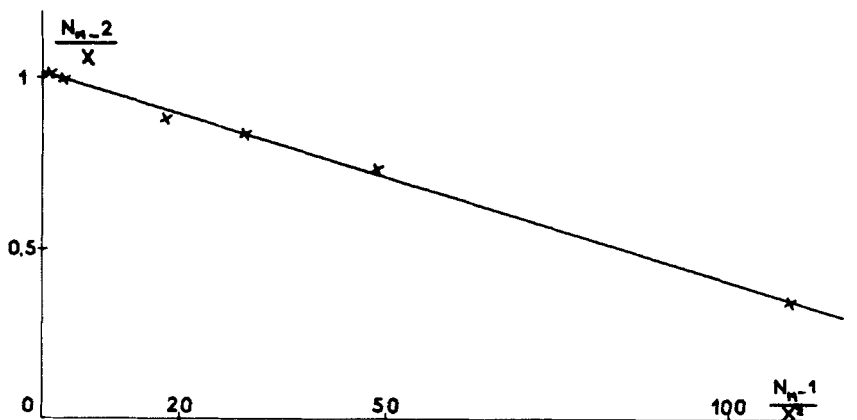


Fig. 3. Fineman-Ross plot of the penultimate effect for methyl methacrylate-ended radicals.

These results may be used to study the second extremity of the composition range. A classical Fineman-Ross plot, indexed now to A, and corresponding to the range $1.9 < x_A < 100$, is illustrated by Fig. 4. The straight line, which gives a good fit with the experiment for the central part of the composition range ($0.1 < x_A < 10$), corresponds to the values of r_M and r_A given above (1.20 and 0.25). Again, a penultimate effect is indicated by the curvature of the extreme part of the plot.

The correction applied here is

$$N_A = n_A \left(1 + \frac{1.56}{x_A} \frac{1.02 + x_A}{1.56 + x_A} \right) \quad (4)$$

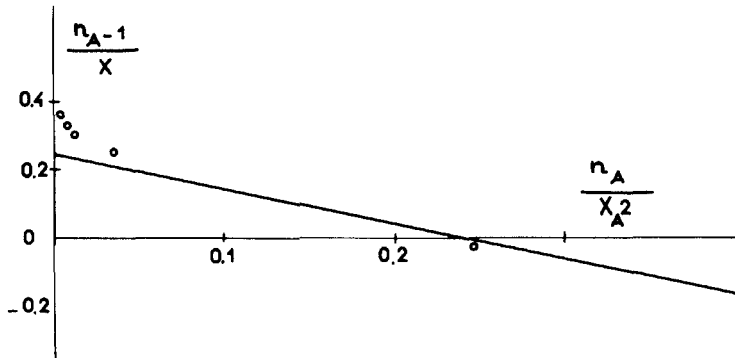


Fig. 4. Mixtures rich in acrylonitrile, Fineman-Ross plot.

which takes in account the penultimate effect determined on the M-ended radicals. Because the two values of r_{AM} and r_{MM} are high, the correction is very important here and N_A can take values as high as $6n_A$. A plot of the linearized Barb equation, illustrated in Fig. 5, also gives a good fit with the straight line, excluding the need for an antepenultimate effect if the M contents are higher than 1%. The values obtained for the reactivity ratios are

$$r_{AA} = 0.39 \pm 0.02 \quad \text{and} \quad r_{MA} = 0.22 \pm 0.05$$

If these values are used in an iterative process to correct the N_M value of Eq. (3) according to the corresponding equation (4), the

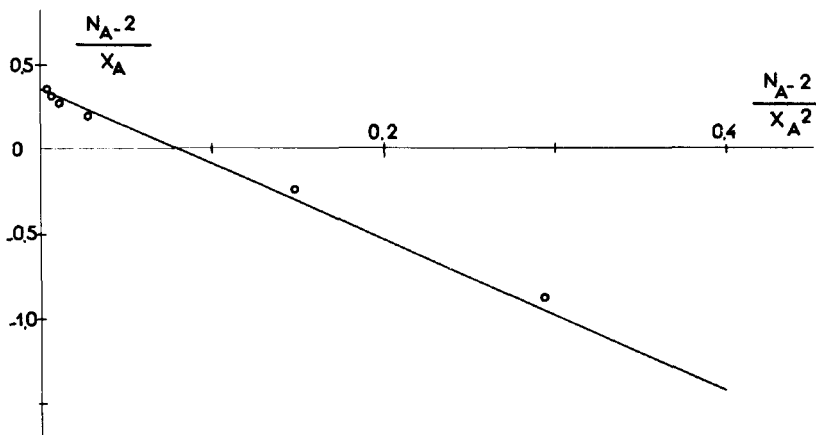


Fig. 5. Fineman-Ross plot of the penultimate effect for acrylonitrile-ended radicals.

values of r_{MM} and r_{AM} are not changed significantly. Thus one may conclude that penultimate effects operate for both kinds of M- or A-ended radicals.

We have already shown that the chromatographic method allows us to determine the conversion curves of any monomers; thus in a Fineman-Ross plot, each experiment gives not only a point but a segment, as long as the ratios x change during the course of the conversion. With the couple M-A, the segments are very short and quasi-punctual when x_M is greater than 2 if the conversion is not total; in the medium range the segments give a good fit with the straight line of the Fineman-Ross plot. However, in the range rich in A ($x_M < 0.1$), the segments are more and more aside from the experimental curve obtained with the initial slopes, and the effect is more pronounced as the conversion is greater and also as the initial mixture is richer in A. These findings are well illustrated in Fig. 6.

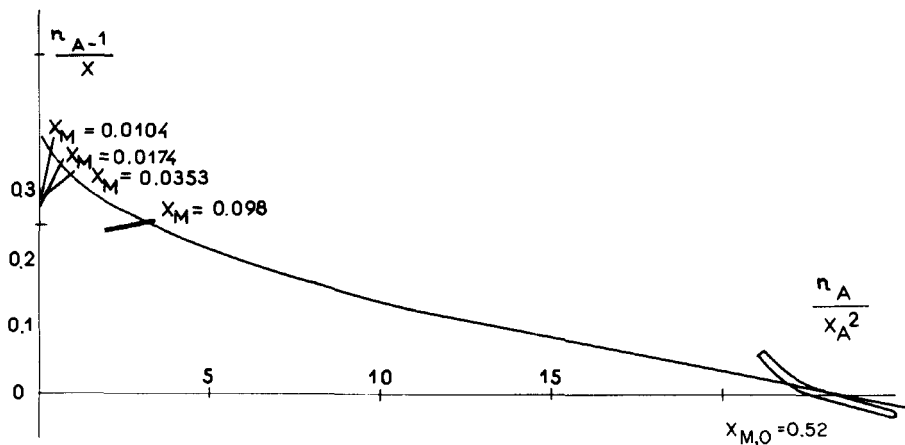


Fig. 6. Deviations from the Fineman-Ross curve of the experimental curve corresponding to the course of the conversion of the mixtures rich in acrylonitrile.

It seems not to be possible to involve a viscosity effect, because the logarithmic plots of $(dM/dt)M$ are linear for the two monomers, independently of the copolymer concentration. The system behaves so that the acrylonitrile polymerization rate decreases when the conversion goes up, also if the A concentration is lower than the measured concentration. We suggest that this effect is due to a dipolar association between the nitrile groups of the monomer and of the polymer. Saum [6] has shown that the organic nitriles are associated not by hydrogen bonding, but by dipolar bonding between the nitrile groups, and also that this dipolar bonding is stronger than hydrogen bonding between the alcohols. These bondings cause the

nitriles to behave like dimers, as shown by their boiling points and other physical properties. Such an association between the nitrile groups of the polymer and of the monomer would cause a relative decrease of the acrylonitrile conversion rate, so that $(n_A - 1)/x_A$ will become lower than the normal values, as observed. The solvent, DMF, which is also highly polar, possibly competes with the nitrile monomer in the bonding with the nitrile group of the polymer; the result is that the number k of acrylonitrile expected to be associated to each polymerized nitrile group is less than or equal to 1, depending on the effect of the DMF. If we denote the conversion ratio of A by ρ_A , the mole percent of A available for polymerization is not $(1 - \rho_A)$ but $[1 - \rho_A(1 + k)]$. And then the value of x_A to be considered at the time t is

$$X_{A,t} = X_{A,0} \frac{1 - \rho_A(1 + k)}{1 - \rho_M}$$

where ρ_M is the conversion ratio of the methyl methacrylate. In Fig. 7 we have plotted the experimental values of $X_{A,t}$ versus n_A

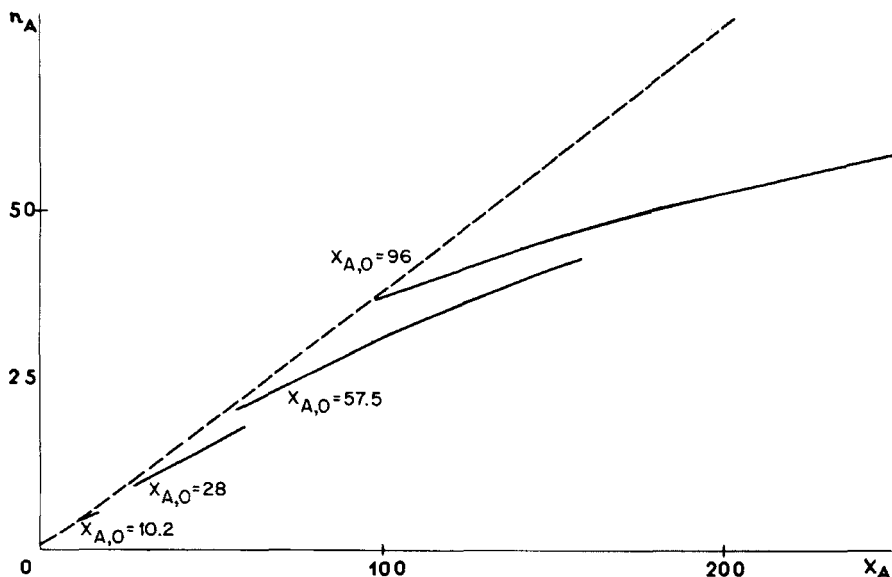


Fig. 7. Copolymer composition ratio n_A versus monomer mixture composition X_A . Experimental curves (—) for various initial feeds $X_{A,0}$; calculated curve (---) according to penultimate effects.

corresponding to the four experiments with higher values of $X_{A,0}$. The dashed curve is the theoretical curve calculated using the above values of r_{AM} , r_{MM} , r_{MA} , and r_{AA} . From the difference between the calculated and experimental values of X_A for the same n_A , one may calculate k :

$$k = (X_{A,t} \text{ obs} - X_{A,t} \text{ calc}) (1 - \rho_M) / X_{A,0} \rho_A$$

It is found, as shown by the curve in Fig. 8, that k is close to 1 at low conversion and decreases smoothly. We may suppose first that the dipolar bonding between nitrile groups is very much stronger than dipolar interaction between DMF and these groups, and, second, that as the conversion increases, dipolar bonding between nitrile groups of A units in the copolymer develops and competes with the bonding with the monomer. Further, the effect becomes less visible when the initial acrylonitrile concentration is smaller. It is possible that the strength of the bonding would be greater for monomer-monomer interaction than for monomer-polymer interaction and further for polymer-polymer interaction due to the effects of the conjugation. Then if the monomer concentration is small, the concentration of unassociated monomer available for bonding with the polymer is too small for the complete development of these bondings.

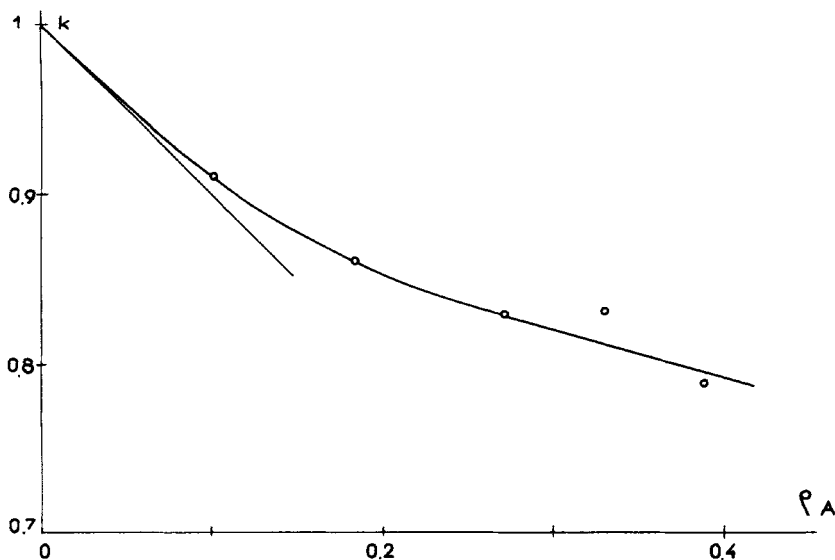


Fig. 8. Ratio k of acrylonitrile fixed on acrylonitrile polymerized versus conversion.

Styrene-Acrylonitrile Copolymers

The study of copolymerization with mixtures rich in styrene ($1.5 < x_S < 100$) has shown that a penultimate and even an ante-penultimate effect must be considered for styrene-ended radicals. In this region attempts to determine the reactivity ratios r_A for acrylonitrile drive them to negative values.

Using DMF as a solvent we have investigated the other part of the whole range of composition ($0.03 < x_S < 1$). Taking in account all the results, a Fineman-Ross plot corresponding to Eq. (1) was drawn. The straight line on Fig. 9 gives

$$r_A = 0.08 \quad \text{and} \quad r_S = 0.38$$

Similarly a Lewis and Mayo plot gives

$$r_A = 0.06 \pm 0.02 \quad \text{and} \quad r_S = 0.40 \pm 0.03$$

These values are now in agreement with most of the published data (cf. Table I in Ref. [1]).

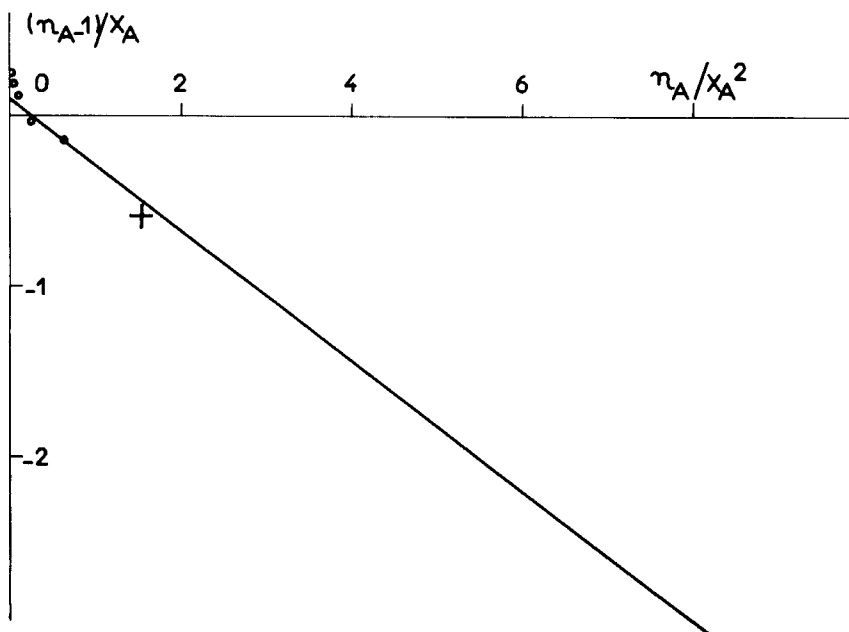


Fig. 9. Fineman-Ross plot for styrene-acrylonitrile copolymerization.

However, it may be seen in Fig. 9 that for $x_A > 4$ ($x_S < 0.25$), the experimental points deviate from the straight line. A penultimate effect was then tested. The corresponding Fineman-Ross plot is given in Fig. 10. Of course, the necessary correction for the denominator of Eq. (2), assuming the values previously determined for r_{AS} (0.55), r_{ASS} (0.50), and r_{SSS} (0.25), was applied. One obtains

$$r_{AA} = 0.33 \pm 0.02 \quad \text{and} \quad r_{SA} = 0.08 \pm 0.02$$

Up to $x_A = 20$ the results fit well with a penultimate effect. Further an antepenultimate effect is possible; but, owing to the difficulties of chromatographic analysis of the mixture DMF-styrene when the styrene is in small amount, the experimental errors do not allow a safe determination.

One may note that an iterative process does not drive to significant correction of the given values of the styrene-ended-radical reactivity ratios.

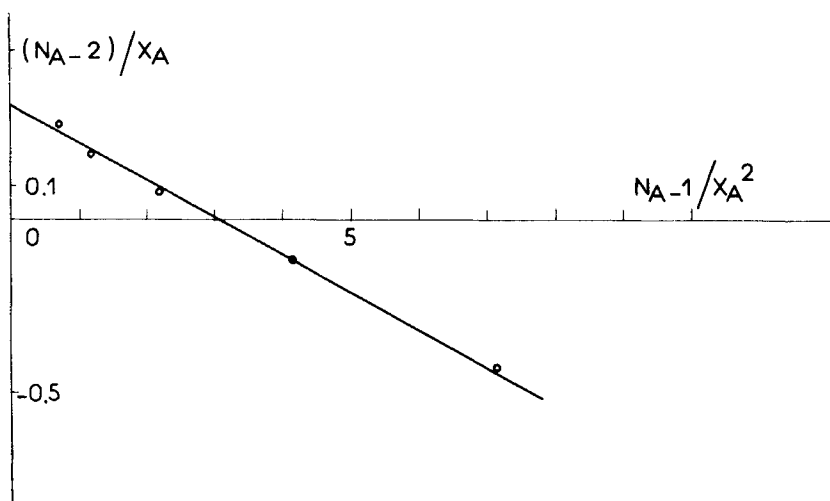


Fig. 10. Fineman-Ross plot for penultimate effect on acrylonitrile-ended radicals in styrene-acrylonitrile copolymerization.

Our results confirm the occurrence of a penultimate effect which has been reported by Ham [9]. However, our data are probably more precise, and the results of Ham, obtained probably from a graphical extrapolation of the plot of the Barb equation (3), seem to overestimate the effect ($r_{AA} = 0.45$ and $r_{SA} = 0.03$).

The dipolar bonding effect is also well observed when the mixture is richest in acrylonitrile, as shown by the curve of Fig. 11. It is found that the value for k is close to unity.

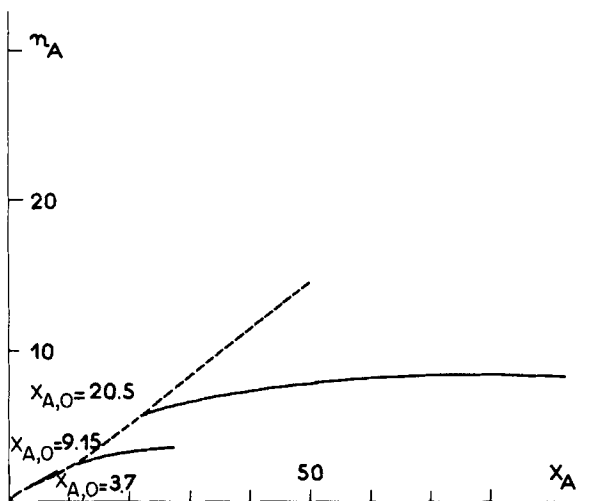


Fig. 11. Copolymer composition n_A versus monomer composition X_A in styrene-acrylonitrile copolymerization. Experimental curves for various initial compositions, $X_{A,0}$ (—); calculated curve according to penultimate effects (----).

CONCLUSION

This study gives support to our previous statement that in copolymerization the remote units may have an influence on the reactivity of all the radicals. The smaller the reactivity ratios of a monomer (as obtained from the classical Fineman-Ross or Lewis and Mayo plots), the broader is the range of composition where the effects do appear. It seems also that the smallest reactivity ratios correspond to the largest penultimate effects. Finally, one may note that the values obtained for r_{AA} in the two couples are close together (0.33 and 0.39). It could be interesting to test the generalization of these observations, because, as pointed by Berger and Kuntz in a theoretical study [10], the remote effects must change the sequence distribution. An NMR and infrared study of the copolymer methyl methacrylate-acrylonitrile was performed in our laboratory and will be published soon.

REFERENCES

- [1] A. Guyot and J. Guillot, *J. Macromol. Sci.*, **A1**, 793 (1967).
- [2] J. Guillot, H. Bottazzi, and A. Guyot, to be published.
- [3] R. M. Joshi and S. L. Kapur, *J. Sci. Ind. Res. (India)*, **16B**, 379 (1957).
- [4] F. M. Lewis, F. R. Mayo, and W. F. Hulse, *J. Am. Chem. Soc.*, **67**, 1701 (1945).
- [5] R. Schmolke, H. Herma, and V. Gröbe, *Faserforsch. Textiltech.*, **16**, 589 (1965).
- [6] A. M. Saum, *J. Polymer Sci.*, **42**, 57 (1960).
- [7] S. Yuguchi and M. Watanabe, *Kobunshi Kagaku*, **15**, 129 (1958).
- [8] W. G. Barb, *J. Polymer Sci.*, **11**, 117 (1953).
- [9] G. E. Ham, *J. Polymer Sci.*, **14**, 87 (1954).
- [10] M. Berger and I. Kuntz, *J. Polymer Sci.*, **A2**, 1687 (1964).

Accepted by editor April 8, 1968

Received for publication May 8, 1968