Styrene—Acrylonitrile Copolymerization: Effect of Remote Units on the Reactivity of the Styrene-Ended Radicals

A. Guyot[a]; J. Guillot[a]

[a] C.N.R.S. INSTITUT DE RECHERCHES SUR LA CATALYSE, VILLEURBANNE, FRANCE

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C.N.R.S. INSTITUT DE RECHERCHES SUR LA CATALYSE
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Summary

Application of the gas-liquid chromatographic method to the analysis of the process of styrene–acrylonitrile radical copolymerization, especially with a monomer mixture rich in styrene, provided evidence for penultimate and antepenultimate effects. Methods are given for the determination of the corresponding reactivity ratios:

$$r_A \simeq 0, \quad r_{AS} \simeq 0.55, \quad r_{ASS} = 0.50, \quad r_{SSS} = 0.25$$

Measurements of the reactivity ratios in radical copolymerization of styrene with acrylonitrile have been published by several authors (1–9). The results, somewhat dispersed, are reported in Table 1.

Owing to the large difference in polarity of the two monomers, Ham (10) has suggested the possible occurrence of a penultimate effect for the styryl radical. He has applied the methods proposed by Barb (11) to account for the styrene–maleic anhydride and other systems.

In place of the Lewis and Mayo equation

$$n = (r_1 x + 1)/[(r_2/x) + 1] \tag{1}$$

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, Barb has used the equation proposed by Alfrey (12),

$$n = \frac{1 + [r_1' x (r_1 x + 1)]/(r_1' x + 1)}{1 + (r_2'/x)[(r_2 + x)/(r_2' + x)]} \tag{1'}$$

TABLE 1

Monomer Reactivity Ratios in Copolymerization of Styrene
(S) with Acrylonitrile (A)

r_S	r_A	T, °C	Ref.
0.41 ± 0.08	0.04 ± 0.04	60	1
0.41 ± 0.08	0.03 ± 0.03	75	2
0.37 ± 0.03	0.07 ± 0.006	50	3
0.37 ± 0.02	0.05 ± 0.02	50	4
0.40 ± 0.05	0.04 ± 0.04	60	5
0.38 ± 0.03	0.05 ± 0.02	41.5	6
0.45 ± 0.03	0.02 ± 0.02	65	6
0.47 ± 0.03	0.02 ± 0.02	86.5	6
0.3 ± 0.08	0.02 ± 0.02	40	7
0.39 ± 0.02	0.06 ± 0.01	99	8
0.33 ± 0.03	0.00 ± 0.02	50	9

where $r_1 = r_{AA}$, $r_1' = r_{BA}$, $r_2 = r_{BB}$, and $r_2' = r_{AB}$. In the systems investigated by Barb, the reactivity ratios of B radicals were null and Eq. (1') reduced to

$$n - 1 = r'x(1 + rx)/(1 + r'x) \qquad (2)$$

Ham (10) has used this equation implicitly, assuming that, in the case of the system styrene–acrylonitrile, it was possible to equate the denominator of (1') with unity. Using this simplified form of (2) in the two cases $x \to \infty$ and $x \to 0$, Ham has obtained

$$r' = r_{AS} = 0.45 \qquad \text{and} \qquad r = r_{SS} = 0.30$$

Actually, the denominator of (1') is rigourously equal to 1 only if $r_A = 0$. But, if r_A has a finite value, which is the case since acrylonitrile can be homopolymerized, the error obtained may be important when $x \to 0$. For this case, Ham's value of r_{AS} is probably too low.

To obtain the accurate values of r_{AS} and r_{SS}, one may use Eq. (2) in a range of high values of x where the term r_2'/x is negligible; then, it is convenient to use the linear form already proposed by Barb (11):

$$r = (n - 2)/x + (1/r')(n - 1)/x^2 \qquad (3)$$

Graphically, it is possible to use either a diagram of r_{SS} vs. $1/r_{AS}$ (as

in the intersection method proposed by Lewis and Mayo (*13*) for the determination of reactivity ratios) or a diagram of $[(n-2)/x]$ vs. $[(n-1)/x^2]$ (by analogy with the Finemann and Ross plot) (*14*).

The range of validity of Eq. (2) corresponds to high values of x, i.e., low concentrations of acrylonitrile. But the usual methods of determination of the copolymer composition at low conversion are not sufficiently accurate in this case. Recently we have proposed (*15*) a new method to follow the kinetics of polymerization or copolymerization by gas-liquid chromatographic analysis of samples taken from the reaction mixture containing the monomers and an inert compound which is used as a calibration standard. We have applied this method for the copolymerization of styrene and acrylonitrile. The polymerizations were carried out at 60°C in toluene solutions (which served as the calibration standard) and were initiated by azobisisobutyronitrile. We have reported in Table 2 the initial compositions for four experiments. The chromatographic

TABLE 2

Initial Compositions

No.	Toluene, moles	Catalyst, moles	Styrene, moles	Acrylonitrile, moles	$S/A = x$, moles/mole
1	3.00	0.52×10^{-2}	0.575	0.372	1.54
2	4.60	0.70×10^{-2}	1.26	0.262	4.80
3	2.50	0.49×10^{-2}	0.83	0.036	23.0
4	2.60	0.56×10^{-2}	0.98	0.018	54.0

analysis of the reactants showed that toluene contained an impurity (500 ppm) which had the same retention time as acrylonitrile. The necessary correction was always made, which was important when the acrylonitrile concentration was very low. The accuracy required was obtained using a disc integrator or a digital automatic integrator.

The conversion curves obtained in two of the four experiments are reported in Figs. 1 and 2. It is possible to obtain with good accuracy the initial rates and their ratios. As shown in Fig. 3, we determined the reactivity ratios using either the Lewis and Mayo method or the Finemann and Ross plot. Using the results of the three experiments with the highest concentration in acrylonitrile,

it is possible to obtain a reactivity ratio $r_S = 0.32$, somewhat lower than the average value of Table 1. But the corresponding value of r_A is definitely negative, and the results of the fourth experiment ($x = 54.0$) are not consistent with the other results. Thus it is confirmed that the simple treatment of Lewis and Mayo is not valid for the styrene–acrylonitrile system.
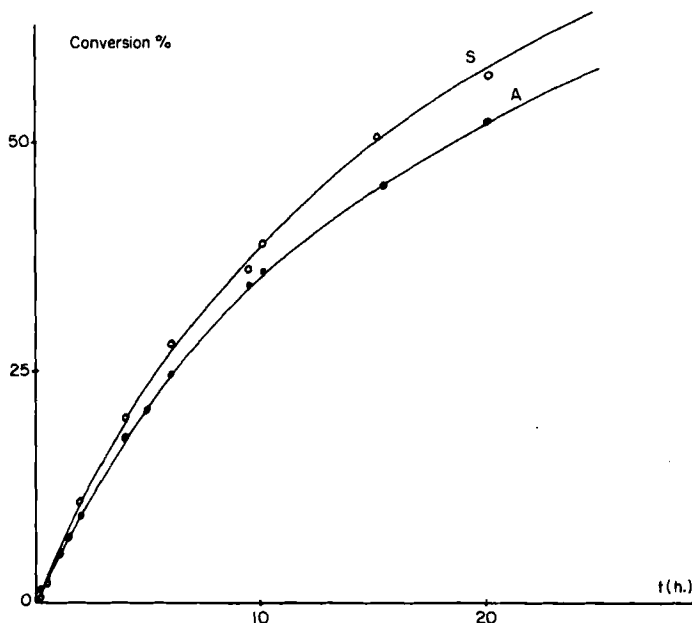
FIG. 1. Styrene–acrylonitrile copolymerization conversion curves for experiment 1 ($x_0 = 1.54$): styrene, ○; acrylonitrile, ●.

The graphic plots of Eq. (3) are reported in Figs. 4 and 5 (a correction was applied for the first experiment, $x = 1.54$), assuming the average value of Table 1 for the acrylonitrile reactivity ratio in the denominator of (1'). This allowed us to obtain the following values for the two penultimate styryl radicals:

$$r_{AS} = 0.55 \qquad \text{and} \qquad r_{SS} = 0.30$$

The second value is in agreement with the value obtained by Ham, but the first is slightly higher, as expected. However, it can be seen

that these plots do not account any better for the discrepancy pre-
viously observed for the fourth experiment.

The chromatographic analysis of the samples taken during a
polymerization process allowed the calculation not only of the
initial polymerization rate but also of the polymerization rate of
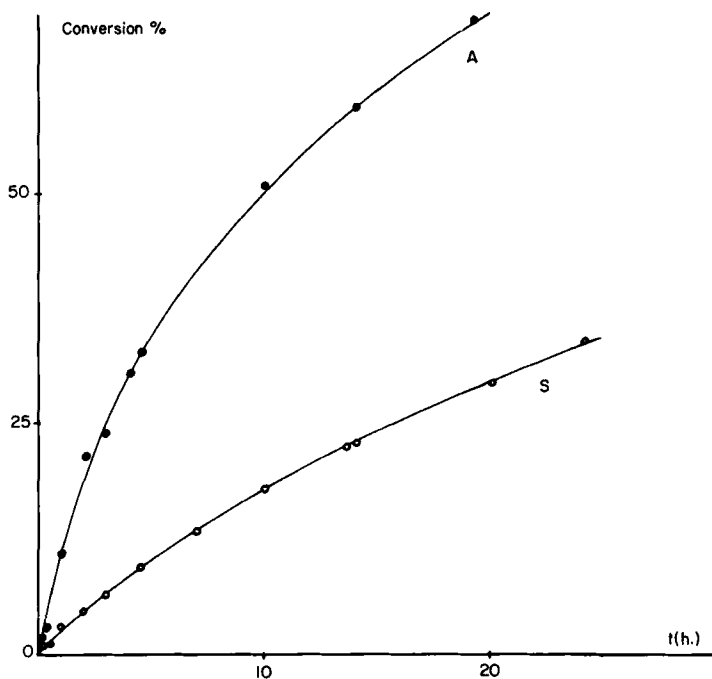each monomer at any time. Thus, as we have already shown, it is

FIG. 2. Styrene–acrylonitrile copolymerization conversion curves for ex-
periment 4 ($x_0 = 54.0$): styrene, ○; acrylonitrile, ●.

possible to determine the two simple reactivity ratios with only
one experiment, since, in a Finemann and Ross plot, for instance,
in place of one point it is possible to have a segment (or a portion
of curve). The application of these methods in the study of the
penultimate effect also give segments in a corresponding Finemann
and Ross plot (Fig. 5). In Fig. 6 it is observed that the segments
deviate from the straight line when x becomes greater than about 7,
i.e., when the conversion increase.

To get a better estimate of all the results, in Fig. 7 we have plotted n vs. x for the four experiments. The four segments so obtained may be accurately fitted by a unique curve which deviates from the straight line C [Eq. (1), $r_A \simeq 0$, $r_S = 0.40$], when x is greater than about 4 and obeys the penultimate curve P [Eq. (2), $r_{AS} = 0.55$, $r_{SS} = 0.31$], only if x is lower than about 20.
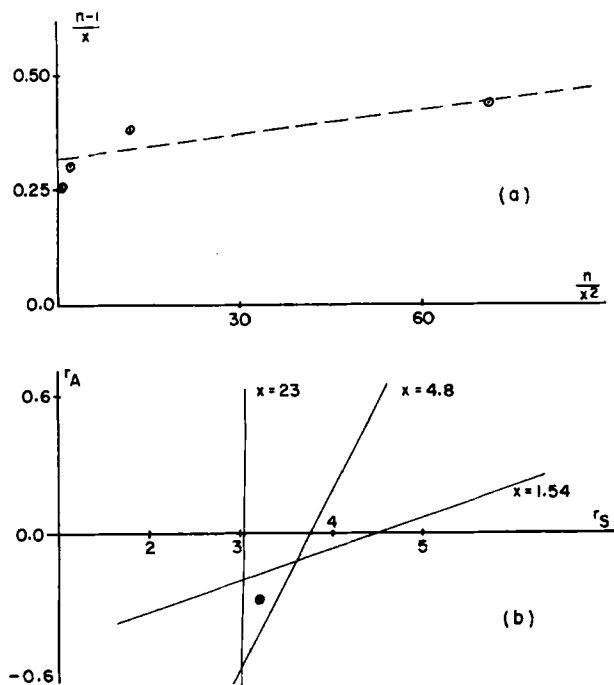

FIG. 3. Usual determination of reactivity ratios: a, Finemann and Ross plot; b, Lewis and Mayo method; x (S/A in monomer); n (S/A in copolymer).

To account for the experimental data when the concentration of acrylonitrile is lower than about 3% of the monomer concentration, it appears necessary to consider an antepenultimate effect. Rigorously, one would have eight reactivity ratios such as r_{SSS} (r_1), r_{ASS} (r_1'), r_{SAS} (r_1''), r_{AAS} (r_1'''), r_{SSA} (r_2'''), r_{SAA} (r_2), r_{ASA} (r_2''), r_{AAA} (r_2), and one

would have to use an equation such as (1''):

$$n = \frac{1 + \left[\dfrac{r_1''x(r_1''x+1)}{r_1''x+1}\right]\left[\dfrac{r_1'x(r_1x+1)}{r_1'x+1}\right]\Big/\left[\dfrac{r_1''x(r_1''x+1)}{r_1''x+1}+1\right]}{1 + \dfrac{r_2''}{x}\left(\dfrac{r_2''+x}{r_2''+x}\right)\left[\dfrac{r_2'[(r_2+x)/(r_2'+x)]+x}{r_2''[(r_2''+x)/(r_2'''+x)]+x}\right]} \quad (1'')$$

This equation is too complex to be useful. But in all likelihood the four acrylonitrile reactivity ratios are low and, also, our range of
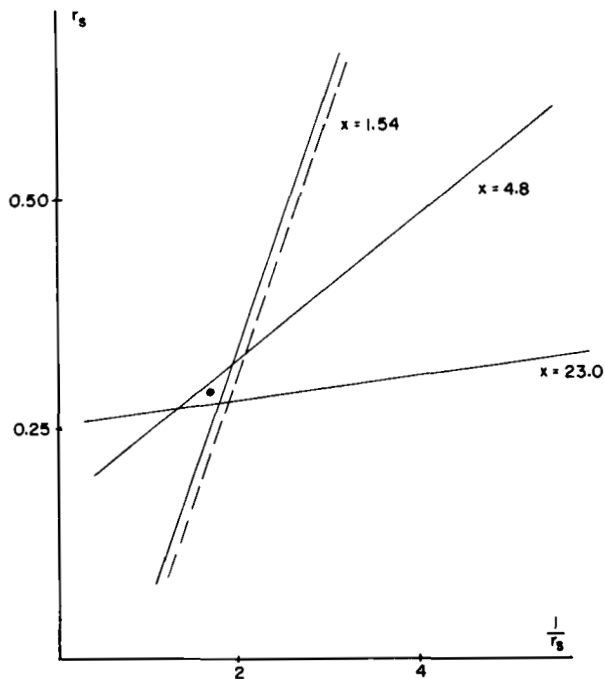

FIG. 4. Lewis and Mayo plot assuming penultimate effect (dashed line denotes uncorrected curve for $x_0 = 1.54$).

interest corresponded to high values of x. Then the denominator of (1'') may be equated to unity without appreciable error. Also, when the concentration of acrylonitrile is low, the probability of occurrence of AA sequences is neglibible for the same reasons. In this case, the effect of the radical AAS may be neglected and it is
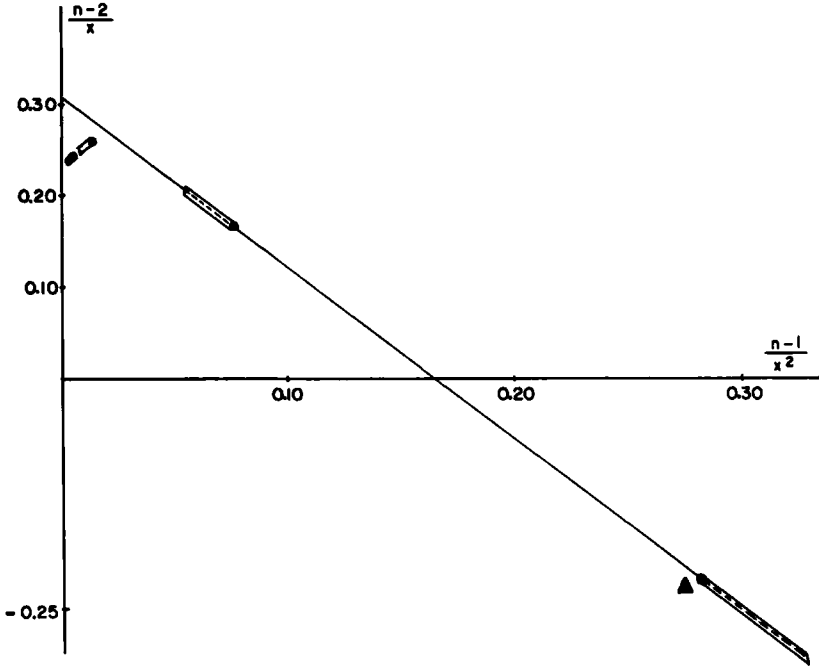
FIG. 5. Finemann and Ross plot assuming penultimate effect (△ denotes uncorrected initial values for $x_0 = 1.54$).
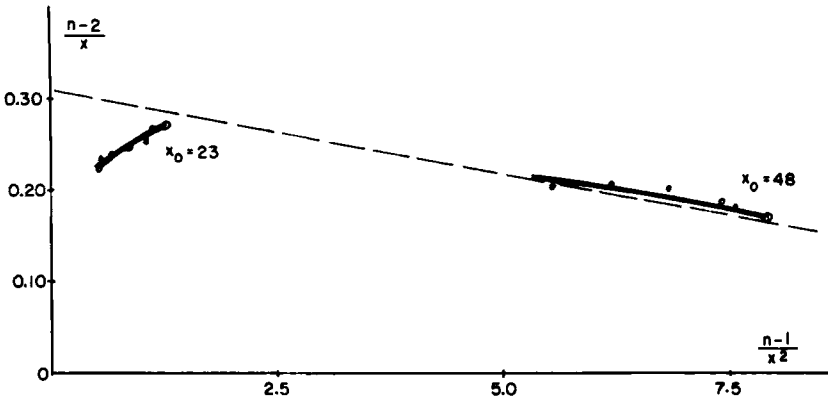
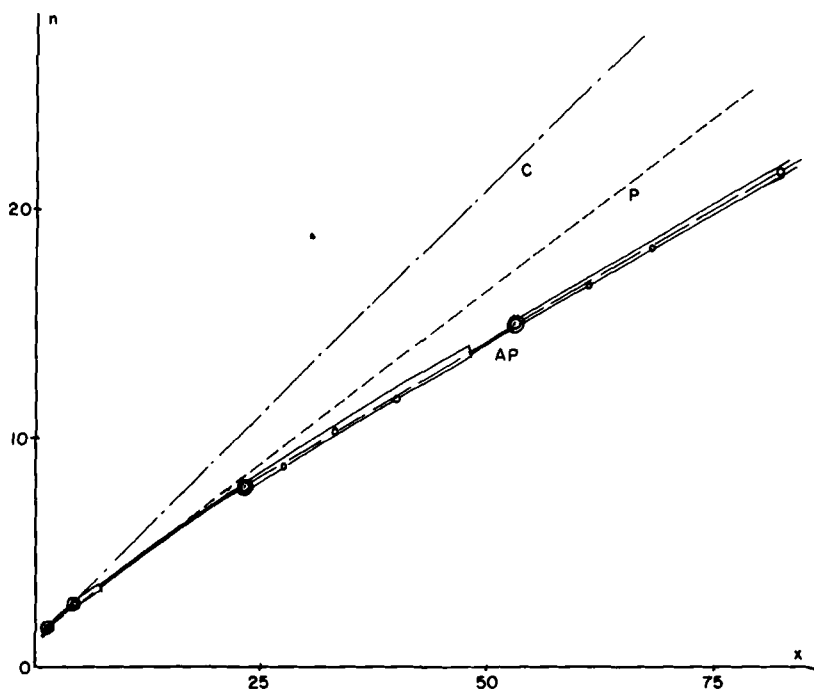**FIG. 6.** Finemann and Ross plot assuming penultimate effect.

FIG. 7. Composition of styrene–acrylonitrile copolymers: C, theoretical curve based on $r_S = 0.40$, $r_A = 0.03$; P, theoretical curve assuming penulti-mate effect ($r_{SS} = 0.30$, $r_{AS} = 0.55$, $r_A = 0.03$); AP, theoretical curve assuming antepenultimate effect ($r_{SSS} = 0.25$, $r_{ASS} = 0.50$, $r_{AS} = 0.55$, $r_A = 0.03$). The boxed area denotes experimental segments and the beginning of an experiment.

sufficient to consider only one radical AS. Then Eq. (1″) reduces to (4), which was used by Ham (16) in the study of systems con-taining α-methylstyrene:

$$n - 1 = \frac{r_{AS}x}{r_{AS}x + 1} \left[1 + \frac{r_{ASS}x(r_{SSS}x + 1)}{r_{ASS}x + 1} \right] \tag{4}$$

Equation (4) may also be rewritten in linear form:

$$\frac{r_{AS}x^2}{(n - 1)(r_{AS}x + 1) - r_{AS}x} \, x = \frac{1}{r_{ASS}r_{SSS}}$$
$$+ \frac{1}{r_{SSS}} \left[x - \frac{r_{AS}x^2}{(n - 1)(r_{AS}x + 1) - r_{AS}x} \right] \tag{5}$$

or, more simply

$$P = \frac{1}{r_{ASS}r_{SSS}} + \frac{1}{r_{SSS}} Q \qquad (6)$$

Therefore, if we assume that the value of r_{AS} is known, P and Q can be obtained from experimental results. The corresponding Finemann and Ross plot is given in Fig. 8, where the four experimental segments are reported. The results give a straight-line plot in accord with Eq. (6) and the calculated values

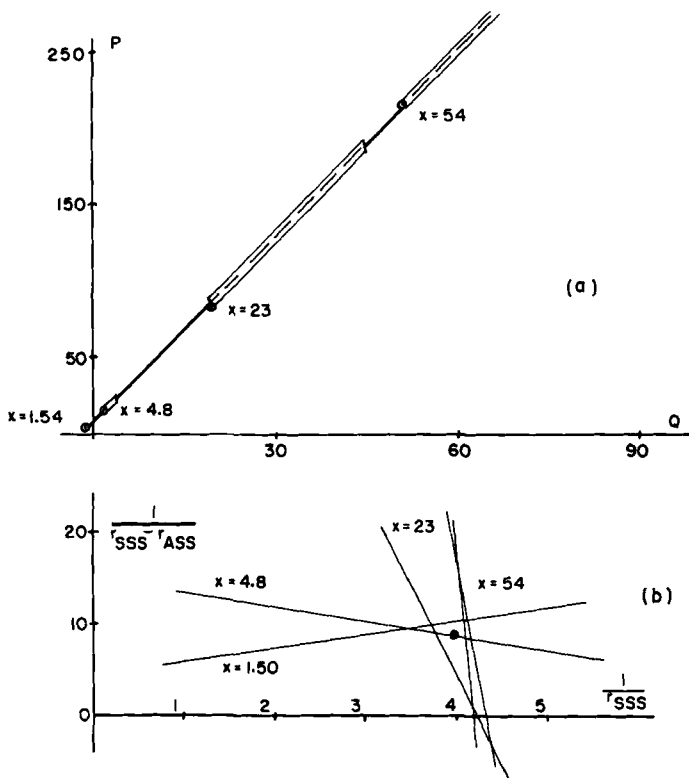$$r_{SSS} = 0.25 \qquad \text{and} \qquad r_{ASS} = 0.50$$

FIG. 8. Determination of reactivity ratios assuming antepenultimate effect ($t_{AS} = 0.55$): a, Finemann and Ross plot, P vs. Q (see the text); b, Lewis and Mayo plot, $1/r_{SSS}r_{ASS}$ vs. $1/r_{SSS}$.

The second part of Fig. 8 represents the corresponding plot using the Lewis and Mayo intersection method. In Fig. 7 the calculated curve AP, which corresponds to this antepenultimate effect, accurately fits the experimental segments.

In the experimental range investigated ($1.5 < x < 100$), it appears unnecessary to look for the effects of units more remote than the antepenultimate. Such effects might possibly be observed if the acrylonitrile concentration was even lower. Then the method applied before would allow, step by step, the calculation of the values of r_{SSSS}, r_{ASSS}, or r_{SASS}.

It should be noted that the use of equations such as (3) or (5) does not stipulate the exact structure of the radicals which are differentiated. Therefore, if it were necessary to replace r_{ASS} by two radicals, it would be probably more exact to consider r_{SSASS} and r_{ASASS} instead of r_{AASS} and r_{SASS}.

In conclusion, we have shown that the gas-liquid chromatographic method facilitates the investigation of the entire range of monomer composition in a copolymerization study and particularly the extreme compositions. In this way it was possible to give a better demonstration of the occurrence of a penultimate effect and also to show the existence of an antepenultimate effect in the case of the styrene–acrylonitrile system. In this connection, it is important that the denominator of equations such as (1') or (1'') could be equated to unity. When one of the two monomers does not homopolymerize, this condition is satisfied in the entire range of composition of the monomer mixture. If one of the two simple reactivity ratios has a low value, the investigation of a penultimate effect may be studied in a rather large range. But when the two reactivity ratios are sufficiently high, the observation of the possible penultimate effects would probably require experiments with a very high value of the concentration ratio x. Additional experiments are in progress to examine the generality of this phenomenon.

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Zusammenfassung

Die Anwendung von Gaschromatographie zur Analyse des Prozesses der Styrol–Acrylnitril–Radikalpolymerisation, unter besonderer Berücksichtigung von Monomerengemischen die reich an Styrol sind, ergab Hinweise für "penultimate" und "antepenultimate" Effekte. Weiterhin werden Methoden zur Bestimmung der entsprechenden Reaktivitätsverhältnisse angegeben:

$$r_A \simeq 0, \quad r_{AS} = 0.55, \quad r_{ASS} = 0.50, \quad r_{SSS} = 0.25$$

Résumé

L'application de la chromatographie gazeuse à l'analyse de l'évaluation de la copolymerisation styrene–Anylonitrile, en particulier dans le case de mélanges riches en styrene, permet de mettre en évidence des effets pénultièmes et antepénultièmes. On décrit les méthodes qui permettent de déterminer les valeurs des taux de réactivité correspondants:

$$r_A \simeq 0, \quad r_{AS} = 0.55, \quad r_{ASS} = 0.50, \quad r_{SSS} = 0.25$$