Controlled Composition in Emulsion Copolymerization Application to Butadiene-Acrylonitrile Copolymers

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ABSTRACT

The use of gas chromatographic analysis of the actual monomer mixture at fixed time intervals to monitor the composition of copolymers in emulsion copolymerization has been described previously. The design has been now improved by the insertion of a dilution cell to avoid flocculation problems in the loop carrying the reaction medium from the reactor to the injection kit of the chromatograph. Then the copolymerization can be monitored up to completion. This system has been applied to the copolymerization of butadiene and acrylonitrile, and constant composition runs have been compared to the batch. Two main differences are observed. (1) Constant composition copolymers show a unique glass transition interval of limited width instead of two or at least one broad temperature interval for the copolymer produced in batch. (2) In the monitored copolymerizations, the production of insoluble gels is delayed and sometimes totally avoided. The production of the gels is related to the formation of 1,2-butadiene units which appear to be preferentially present in long sequences of butadiene units. The cross-linking process involves the consumption of the pendent vinyl groups by copolymerization with the monomers.

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INTRODUCTION

Improved nitrile rubbers are now produced through control of co-
polymer composition and molecular weight [1]. A drift in the compo-
sition of a copolymer can be avoided by incremental addition of acrylo-
nitrile monomer during polymerization; the resulting copolymers show
a unique glass transition temperature with a narrower transition inter-
val than for copolymers produced in batch [2]. In our laboratory an ap-
paratus designed to monitor the composition of a copolymer through
automatic measurement and correction of the composition of the mono-
mer mixture analyzed by gas chromatography has been created [3] and
was recently applied to the emulsion copolymerization of styrene and
acrylonitrile [4, 5]. The system has now been applied to butadiene-
acrylonitrile copolymerization with some improvement in order to
avoid the mechanical flocculation problem encountered when the solid
content is higher than 20%.

EXPERIMENTAL

Copolymerization was carried out at 5°C using t-dodecyl mercaptan
as the chain regulator, introduced in toluene which can be used as a
calibration additive for gas chromatographic measurements. The ini-
tiator is the redox system diisopropylbenzene hydroperoxide and fer-
rous sulfate.

A kinetic study was carried out by gas chromatographic (GC) analy-
sis (Instersmat IGC 12 F with flame ionization detector) using a carbo-
wax columne (3 m) at 120°C. A typical chromatogram is shown in Fig.
1. The apparatus used for producing constant composition copolymers
has been described previously [3, 6]. Basically, samples of the reac-
tion medium are injected at regular time intervals in the GC apparatus.
Signals from the two comonomers are compared and the differential
signal is used, through a special interface after the integrator of the
GC signal, to monitor a metering system (electrically driven perfusor)
for introducing the monomer which is consumed more rapidly (acrylo-
nitrile on the present study). Flocculation problems due to mechanical
stress are encountered in the pump or the tubing or the injection valve
between the reactor and the GC apparatus as soon as the solid content
of the emulsion is over 20%. In order to avoid that problem, a dilu-
tion device, shown in Fig. 2, has been fixed at the bottom of the reac-
tor. A compressed-air-driven piston is used to take the sample from
the reactor and introduce it into the dilution chamber. Water is intro-
duced to the chamber through a nitrogen pressure and carries the di-
luted sample to the sampling valve of the GC. A cycle of sampling,
dilution, injection, and washing operations is carried out by pressure
changes governed by a two-position valve (Fig. 3) and an electronically
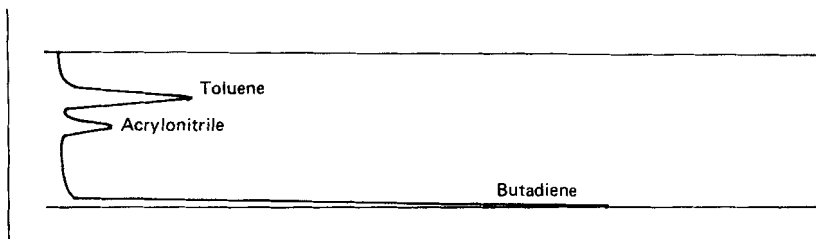monitored system. (Details are available on request.)

FIG. 1. GC chromatogram of an acrylonitrile (A) butadiene mono-
mer mixture with X_A = [A]/[B] = 0.058. Carbowax (3 m), 120 C.
Internal standard: toluene.
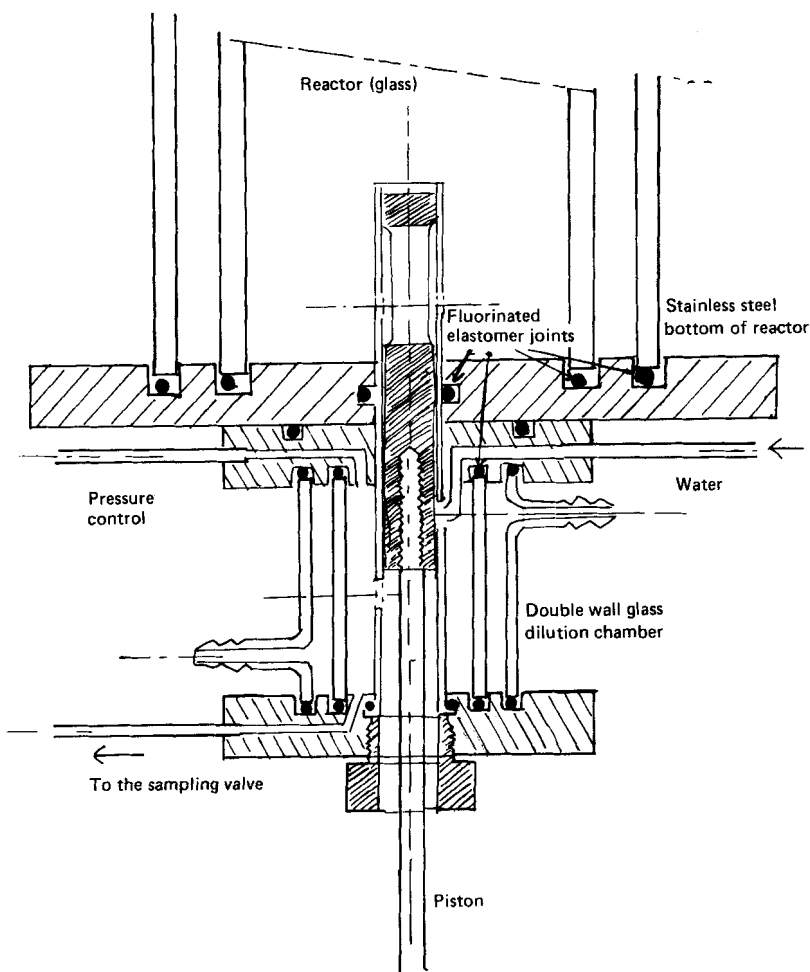
FIG. 2. Cross section of the monitored dilution device developed
for automatic injection of the reaction emulsion.
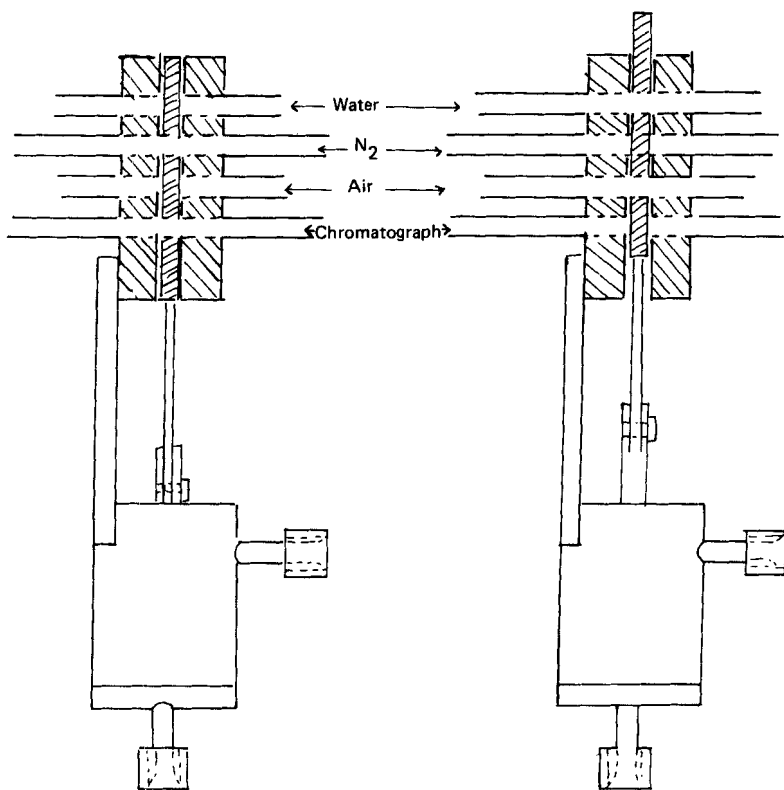
FIG. 3. Pneumatic valve for fluid distribution in the two possible positions corresponding to filling and emptying the dilution cell.

After flocculation and washing, the copolymers were dissolved to determine their gel content upon filtering, drying, and weighing. They were analyzed by IR (Perkin-Elmer) and ^{13}C-NMR (Bruker WP80) for their structure, and finally by DSC (Dupont 990) for measuring their glass transition temperature T_g.

RESULTS

The kinetic study led to the reactivity ratio through a Fineman-Ross plot [7] (Fig. 4). The values obtained are $r_B = 0.3$ (butadiene) and $r_A = 0.04$ (acrylonitrile). These values are in good agreement with the literature data of Kates and Evans [8]. These authors show

FIG. 4. Fineman-Ross plot of butadiene-acrylonitrile kinetic data.

that their values (r_B = 0.28 and r_A = 0.02) have to be corrected (r_B = 0.18 and r_A = 0.03) to take into account the high water solubility of acrylonitrile (1.75 mol/L). The corrected values, in turn, are in good agreement with the literature values of Embree et al. [9]. The rather large difference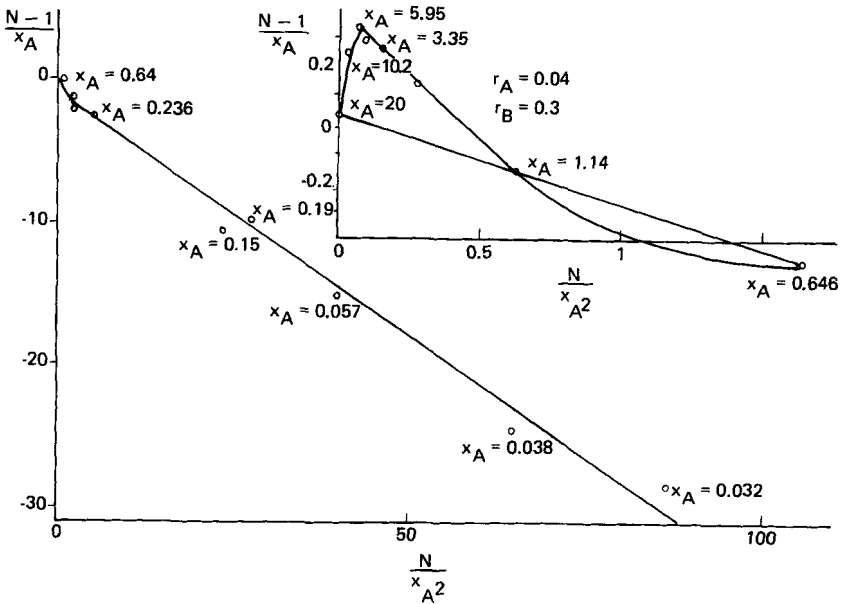 in reactivity ratio means that in a batch procedure there is a rather large composition drift during polymerization. Examples of that drift are shown in Fig. 5. The acrylonitrile-butadiene ratio incorporated into the copolymer decreases rapidly as conversion proceeds. For the two compositions studied, which correspond to typical commercial production, the instantaneous product is practically pure polybutadiene above 80% conversion.

When the constant composition device is used, acrylonitrile is introduced to compensate for rapid conversion. Figure 6 shows examples of the amounts of acrylonitrile introduced as conversion proceeds. The total amount of acrylonitrile introduced corresponds to a large proportion of the whole monomer used.

This automatic corrected batch process allows for a very large reduction of the gel contents. Typical results are shown in Fig. 7. When the acrylonitrile content is high enough, there is no gel in the copolymer, even at conversion as high as 97%.

Analysis of the ^{13}C-NMR spectra of the olefinic carbon –CH gives
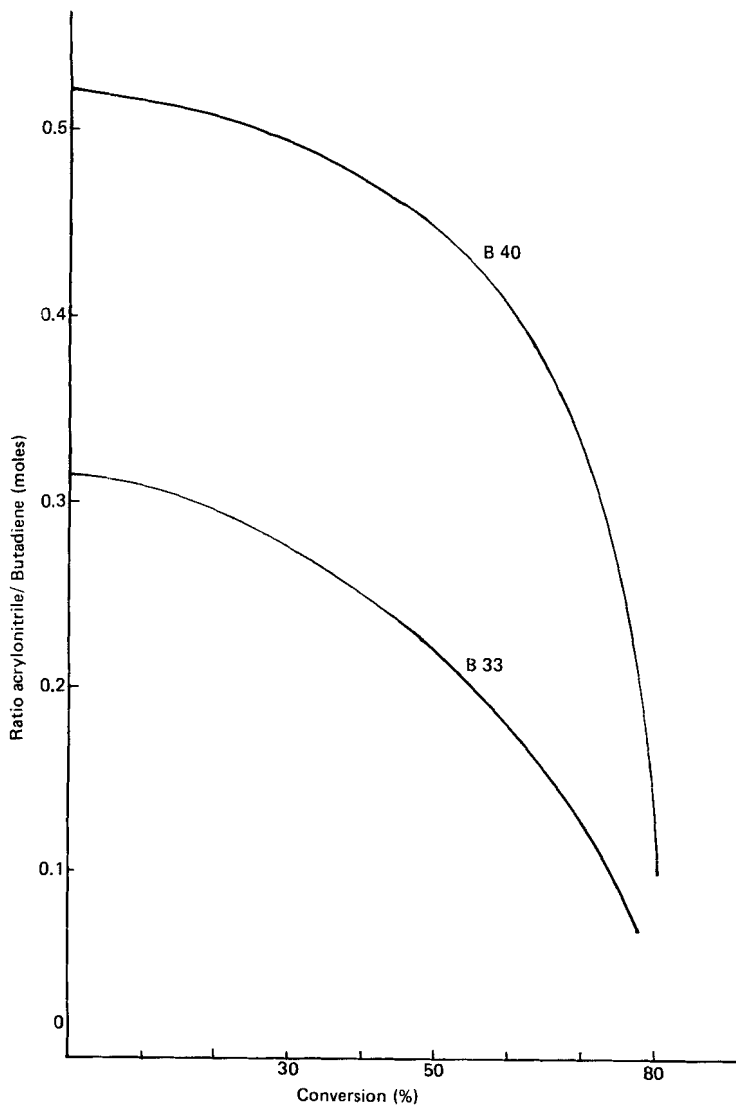
FIG. 5. Change of the acrylonitrile/butadiene ratio versus conversion for various initial monomer feeds in a batch process.
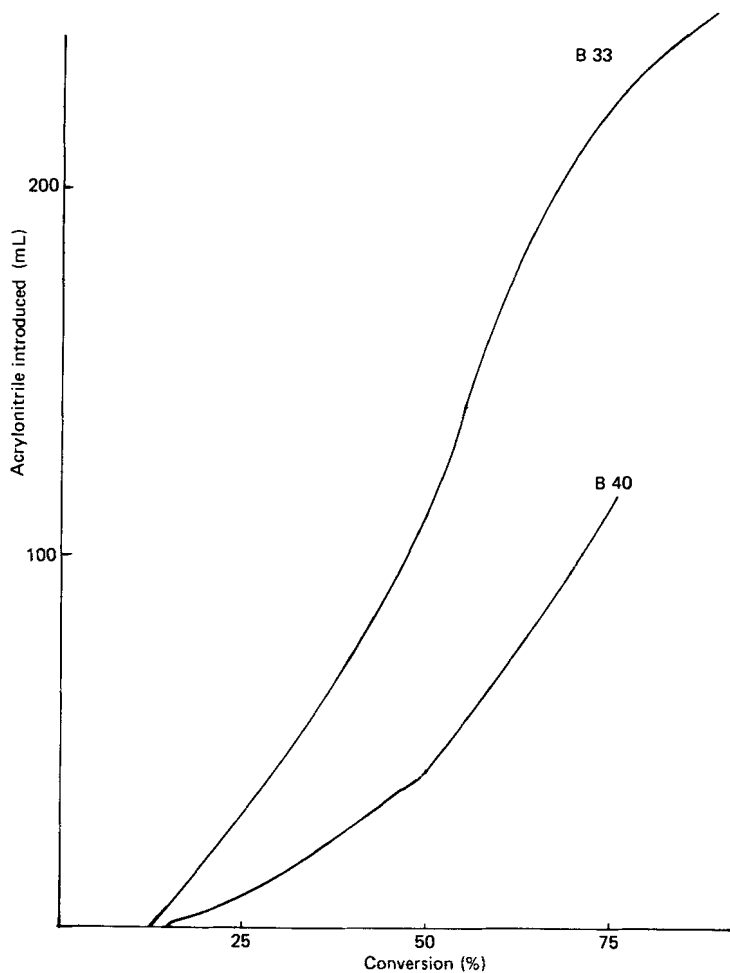
FIG. 6. Program of monitored addition of acrylonitrile monomer (mL) in constant monomer composition reactor experiments.

information about the 1,4 and 1,2 structure content of the butadiene units between 125 and 136 ppm for the 1,4 units and between 142 and 145 ppm for the 1,2 units (Fig. 8). Because the nature of the protons is similar for both structures, the Overhauser effect is supposed to be the same, so that the ratio of the integrated areas, taking into account the number of C atoms involved (1 for the 1,2 and 2 for the 1,4 structure), allows us to obtain the 1,2/1,4 ratio. The results are reported in Table 1 and compared with similar results taken from the

FIG. 7. Gel % content versus conversion for various monomer feeds and processes: B = batch, B-CC = constant composition reactor. No gel in B 40 at full conversion.

FIG. 8. ^{13} C-NMR spectrum of an acrylonitrile/butadiene.

TABLE 1

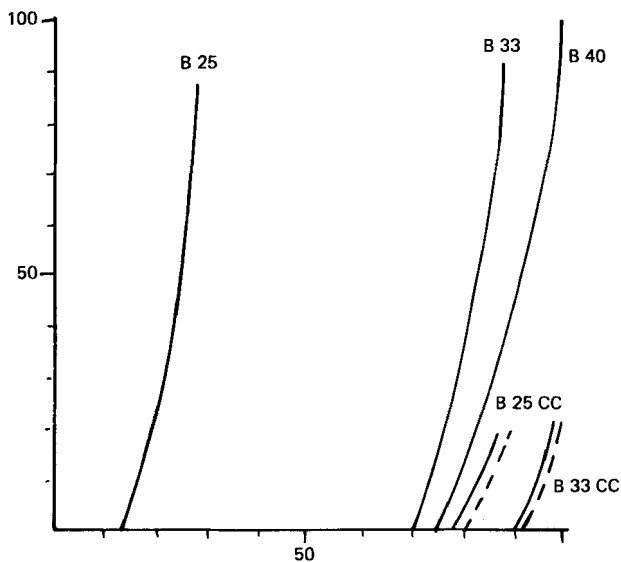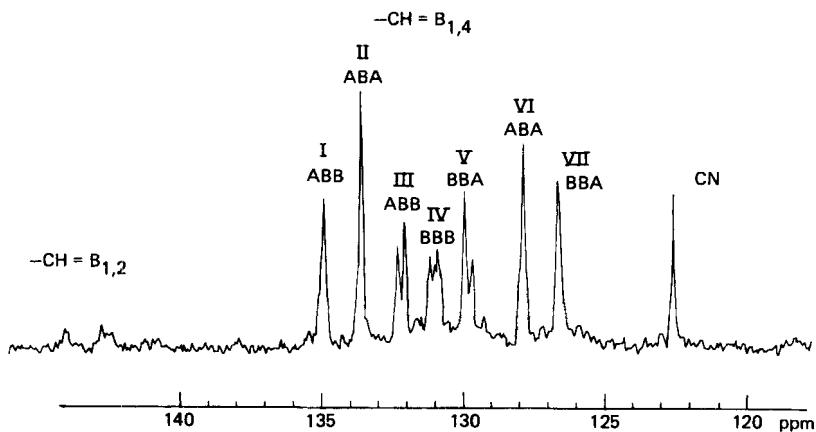|			% 1,2/1,4 RMN		% 1,2/1,4 IR	
B 25		15%		11.8		
		20%	S	17.5	S	16.4
B 25 CC	(b)	10.5%		12.3		
	(a)	50%		12.0		
	(b)	54%				13.3
	(a)	84%	Gel			14.4
B 33	(a)	27%		7.3		
	(b)	34%				8.2
	(b)	54%				14.2
	(b)	70%	First gel			16.5
	(a)	75%	S	13.7		
	(b)	86%	G	13.3	S	13.9
B 33 CC		20%				6.6
		55%				9.6
		88%		8.4		9.8
B 40		6%				12.1
		17%		6.9 (cross-linking?)		
		75%		12.4 first gel		11.9
		87%				12.3
		97%				15.8
		99%	G	11.6 (cross-linking?)	G	14.6
B 40 CC		73%		12		(3)
B 45		65%	S	7.2		
			G	5.9		
		80%	S	6.4		(16.4)
			G	1.8		(15.8)

analysis of the infrared spectra according to Morero et al. [10]. When gel was present, both the gel and the sol fraction were analyzed. Two main features are clear: for the polymer produced in batch, the 1,2/ 1,4 ratio increases with conversion, while in the case of constant co- polymer composition, the value does not change much. In addition, in the sol fraction, and when cross-linking becomes important, the amount of 1,2 decreases. It may thus be concluded that the vinyl double bonds are preferentially involved in the cross-linking process.

The resolution of the NMR spectra between 125 and 136 ppm gives

TABLE 2

x x x CH = CH x x x x x CH = CH x x x x x CH = CH x x x x x CH = CH x x x CH = CH x x x x

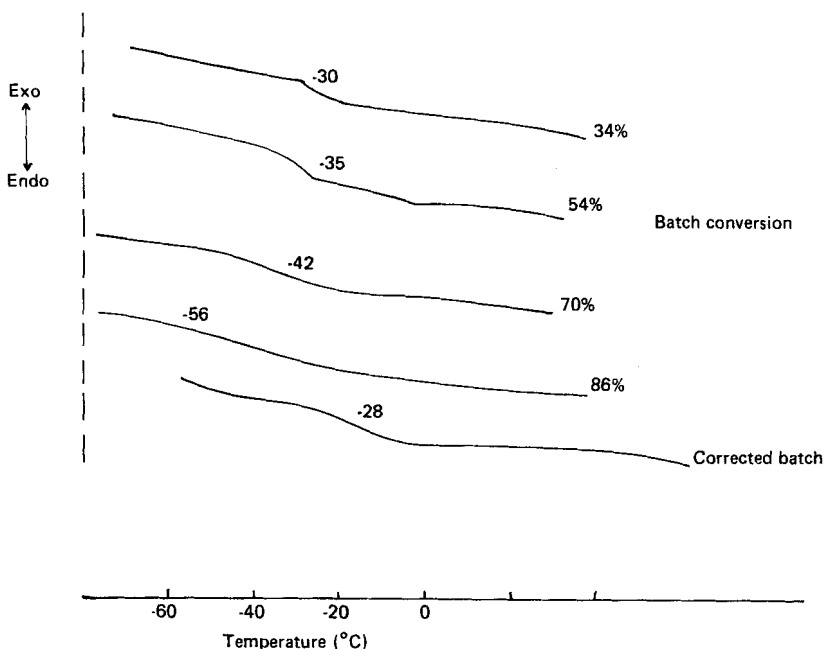|	CN			CN				CN		
Peak	II	VI	I	III	V	VII	I	III	IV	V	VII
Triad	ABA	ABA	ABB	ABB	BBA	BBA	ABB	ABB	BBB	BBB	BBA	BBA
ppm (DMF 390 K)	133.4	127.8	134.7	132.0	129.7	126.7			130.8		

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FIG. 9. DSC thermograms of samples of the B 33 copolymers at various conversions and from a constant composition experiment. Apparatus: DuBut 990. Heating rate: 5°C/min.

information about the distribution of the triads centered on a 1,4 butadiene unit (B_4). The assignments given in Table 2 are in agreement with a Markov I distribution. For instance, for the spectrum shown in Fig. 8, the probability of a B_4A diad is 0.40.

Finally, as shown in Fig. 9, the glass transition of the copolymers produced in batch decreases when conversion is increasing. Further, the glass transition interval becomes broader and broader. On the other hand, a narrow glass transition interval is obtained when a constant composition copolymer is produced. Similar results have been described by Ambler [2] who avoided a too large composition drift by incremental addition of monomer during polymerization.
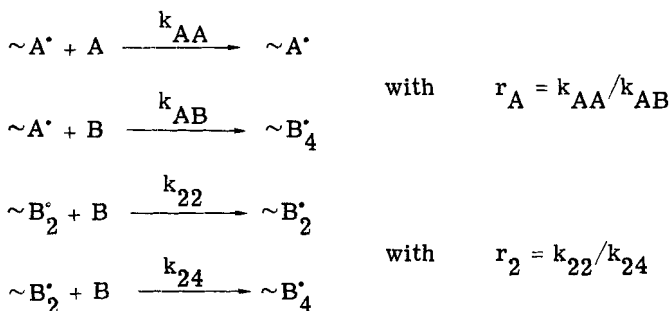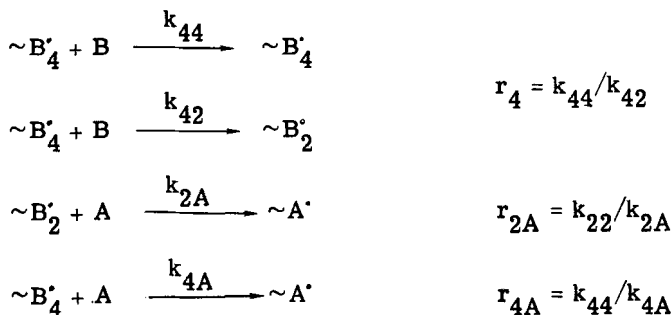
DISCUSSION

All the results presented above tend to demonstrate that the structure of the polymer produced by controlling the composition is different from those of polymers produced in batch, not only due to a difference in the whole composition but also due to a difference in the dis-

tribution of the butadiene units. That is, the 1,2/1,4 ratio is lower for the constant composition copolymer. The reason is simple. It has been shown previously [11] that acrylonitrile radicals add to a butadiene unit B_4. In a batch copolymer, owing to composition drift (i.e., acrylonitrile is consumed preferentially), the monomer mixture becomes richer and richer in butadiene and the copolymer tends to be closer and closer to butadiene homopolymerization in which a rather high proportion (actually 0.2) of butadiene units have the 1,2 structure. On the other hand, the continuous addition of acrylonitrile in constant composition copolymerization will limit the length of the butadiene unit sequences and then the proportion of the 1,2 sequences.

The formation of gel during the homopolymerization of butadiene is admittedly caused by the polymerization reactivity of the residual double bond of the structural unit. The relative competitivity of that residual double bond increases with conversion because of its accumulation and of the depletion of the monomer. It also increases with temperature as the 1,2/1,4 ratio and the 1,4-cis/1,4-trans ratio [12] percent. A recent study by Hayes [13, 14] of the copolymerization of styrene and acrylonitrile in the presence of various polybutadienes concluded that the grafting of the St-AN copolymer onto the polybutadiene occurs through copolymerization with the residual double bond and that the 1,2 unit is much more reactive than the 1,4 unit. The decrease in the 1,2/1,4 ratio in the gel, observed in the present study, is in agreement with Hayes' conclusion. Further, it may also be concluded that the decrease in the gel formation by using the constant composition system can be explained by the fact that the continuous addition of acrylonitrile orientates the incorporated butadiene unit to the 1,4 structure because the sequence length of the butadiene unit is kept small.

The use of a computer allows prediction of the course of a copolymerization as soon as the proper reactivity ratios are known. Various papers have dealt with that problem, including some from our laboratory [15-17]. In the present case the following copolymerization steps are significant. Using, respectively, $A^{\bullet}$, $B_2^{\bullet}$, and $B_4^{\bullet}$ for the radicals from acrylonitrile, butadiene 1,2, and butadiene 1,4 terminal units, and A and B as the corresponding monomer units, we have

$$\sim A^{\bullet} + A \xrightarrow{\quad k_{AA} \quad} \sim A^{\bullet}$$

$$\sim A^{\bullet} + B \xrightarrow{\quad k_{AB} \quad} \sim B_4^{\bullet} \qquad \text{with} \qquad r_A = k_{AA}/k_{AB}$$

$$\sim B_2^{\bullet} + B \xrightarrow{\quad k_{22} \quad} \sim B_2^{\bullet}$$

$$\sim B_2^{\bullet} + B \xrightarrow{\quad k_{24} \quad} \sim B_4^{\bullet} \qquad \text{with} \qquad r_2 = k_{22}/k_{24}$$

$$\sim B_4^{\cdot} + B \xrightarrow{\ k_{44}\ } \sim B_4^{\cdot} \qquad\qquad r_4 = k_{44}/k_{42}$$

$$\sim B_4^{\cdot} + B \xrightarrow{\ k_{42}\ } \sim B_2^{\circ}$$

$$\sim B_2^{\cdot} + A \xrightarrow{\ k_{2A}\ } \sim A^{\cdot} \qquad\qquad r_{2A} = k_{22}/k_{2A}$$

$$\sim B_4^{\cdot} + A \xrightarrow{\ k_{4A}\ } \sim A^{\cdot} \qquad\qquad r_{4A} = k_{44}/k_{4A}$$

By using the steady-state assumption, it is possible to calculate the 1,2/1,4 ratio and also the probability P_{B_4A} which is experimentally feasible in terms of the four reactivity ratios of butadiene radicals.

$$1,2/1,4 = \frac{1 + \dfrac{r_2}{1 + (A/B)(r_2/r_{2A})}}{1 + r_4 + (A/B)(r_4/r_{4A})} \tag{1}$$

$$P_{B_4A} = \frac{A}{B}\ \frac{r_4}{r_{4A}}\ \frac{1}{1 + r_4} \tag{2}$$

From various experiments at constant composition (A/B constant), the four unknown reactivity ratios can be calculated, with r_A being known (0.04) from the kinetic study.

From Eq. (2), the ratio

$$\frac{P_{B_4A}}{A/B} = \frac{r_4/r_{4A}}{1 + r_4} = \beta$$

is constant. Its value from experiments carried out at constant composition (Table 2) is 1.5.

In the case of butadiene homopolymerization, Eq. 1 is reduced to

$$\frac{1,2}{1,4} = \frac{1 + r_2}{1 + r_4} = \alpha$$

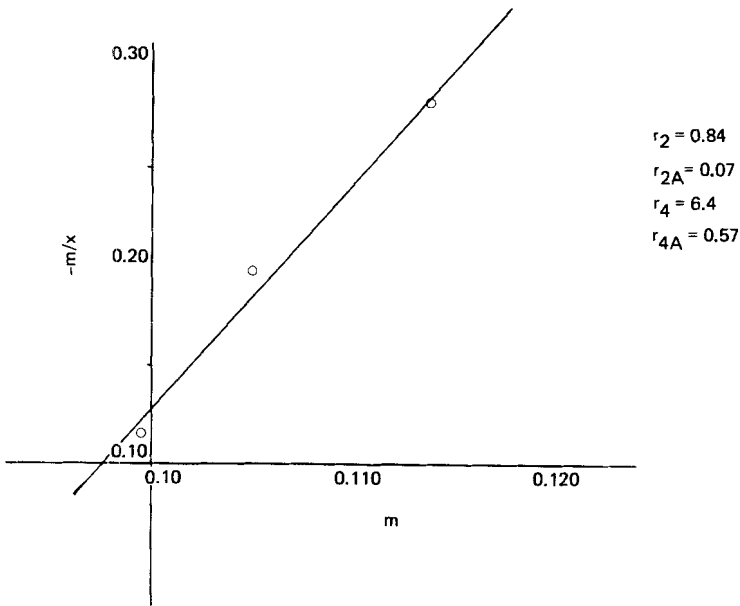and from the literature value [12] $\alpha = 0.2$.

FIG. 10. Plot of the function $(\gamma - m)/x$ versus m as defined in the text (data are referred to $x_A = 0.57$, 0.3, and 0.18, respectively).

Finally, a linear expression of Eq. (1) can be obtained. If $x = A/B$, $\gamma = \alpha/\beta$, and $m = (x + 1/\beta)(1,2/1,4)$, then

$$\frac{\gamma - m}{x} = \left(\frac{r_2}{r_{2A}}\right) m - \frac{r_2/r_{2A}}{r_4/r_{4A}} \qquad (2')$$

Then, from a plot of $(\gamma - m)/x$ versus m (Fig. 10), we can obtain r_2/r_{2A} and then r_4/r_{4A}. Thus, by using the value we have of r_4, we have r_2.

The following set of values has been obtained: $r_2 = 0.33$, $r_4 = 5.7$, $r_{2A} = 0.026$, $r_{4A} = 0.57$.

These values show that the 1,2 unit will be very isolated, as well as the acrylonitrile units ($r_A = 0.04$), but also that the B_4 radicals show a higher reactivity toward acrylonitrile than toward butadiene in 1,2 units.

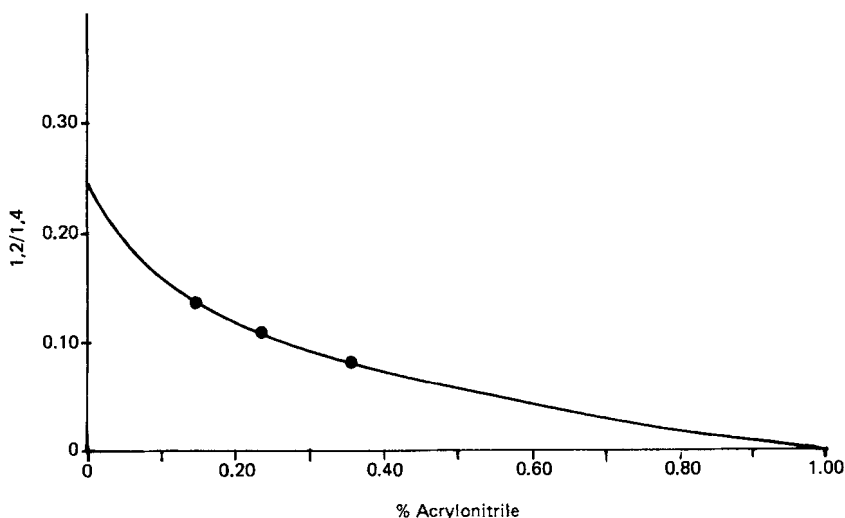Figure 11 is a simulation of the 1,2/1,4 ratio versus the acrylo-

FIG. 11. Recalculated $(1,2)/(1,4)$ ratio versus copolymer composition from the derived reactivity ratios. (●): Experimental mean values from NMR and IR analysis (x_A = 0.57, 0.31, and 0.18).

nitrile content in the monomer mixture, using the above reactivity ratios, which of course give a good agreement with the experimental points.

Another measurement from the kinetic study is r_B which is a function of the four reactivity ratios and the monomer concentrations.

One has

$$k_{BB}B^{\cdot}B = (k_{22} + k_{24})B_2B + (k_{42} + k_{44})B_4^{\cdot}B$$

$$k_{BA}B^{\cdot}A = k_{2A}B_2A + k_{4A}B_4A$$

Again, using the steady-state assumption,

$$r_B = \frac{k_{BB}}{k_{BA}} = \frac{1 + r_2 + (1 + r_4)(B + Ar_2/r_{2A})}{(r_2/r_{2A}) + (r_4/r_{4A})(B + Ar_2/r_{2A})} = 0.2 \qquad (3)$$

Using the above-mentioned set of reactivity ratios, good agreement with the value of r_B is obtained when A + B is kept low as well as when the A/B ratio is decreasing. Actually, in the kinetic study, the value of r_B was derived by extrapolation to low values of A/B.
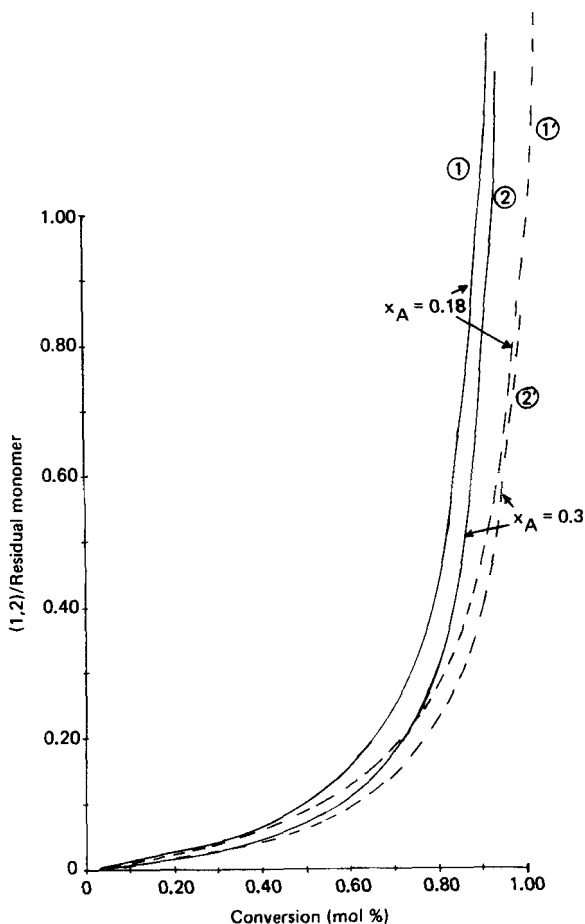
FIG. 12. 1,2 Bonds relative to residual monomers at various conversions in batch and constant composition reactors. Curves 1 and 2: Batch experiments with $(x_A)_0 = 0.18$ and 0.31, respectively. Curves 1' and 2': Constant composition reactor experiments with $(x_A)_0 = 0.18$ and 0.31, respectively.

Knowledge of all the reactivity ratios can be used to simulate the copolymerization in batch conditions [16]. Some typical results are illustrated in Fig. 12 which gives the ratio of the pendent 1,2 double bond in the copolymer and the residual amount of monomer versus the whole conversion for two values of the molar ratio X_A of acrylonitrile on butadiene in the mixture. The simulation is able to compare the

situation in the batch process and in the constant composition experiments. It can be seen that, at the end of the process, the competition between the 1,2 double bond and the monomer for radical reaction becomes more favorable for the 1,2 double bond in the batch process so that the cross-linking process through copolymerization of these pendent double bonds becomes increasingly probable. Comparison with experimental results is difficult because cross-linking obviously takes place upon aging. The simulation also shows how the accumulation of 1,2 units is delayed when the corrected batch process is used.

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