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The use of sequence distributions to determine monomer feed compositions in the emulsion copolymerization of chlorotrifluoroethylene with vinyl acetate and vinyl propionate

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Emulsion copolymerizations of chlorotrifluoroethylene (CTFE) with vinyl acetate (VAc) and vinyl propionate (VPr) under redox initiation conditions were investigated. Reactivity ratios (r) determined for VAc and CTFE in the VAc/CTFE system were 0.68 ± 0.11 and 0.04 ± 0.02, respectively. The reactivity ratios for VPr and CTFE in the VPr/CTFE system were 0.63 ± 0.04 and 0.08 ± 0.01, respectively. Vinyl ester-centred triad distributions of the copolymers were measured by ^{1}H nuclear magnetic resonance spectroscopy and were used to calculate conditional probabilities for monomer placements. These values were compared to conditional probabilities calculated from reactivity ratios, conversions and monomer feed compositions. Significant differences between the experimental and calculated conditional probabilities were observed. The variations in the conditional probabilities could be attributed to the dissimilar comonomer solubilities, which results in a different monomer concentration at the site of polymerization than is expected based on the amounts added to the reactor. This work cites the danger of using emulsion polymerization to obtain r values for monomer pairs. By using sequence distribution information, the concentration of monomers at the site of polymerization can be calculated, which is useful for investigating the location of polymerization.

(Keywords: emulsion copolymerization; sequence distributions; monomer feed compositions)

INTRODUCTION

The copolymerization of two monomers (A and B) is a widely used technique by which polymers are produced with a variety of properties. The properties of copolymers depend not only on the nature of the comonomers and the overall composition, but also on the distribution of monomer units along the chain. Models to describe the copolymerization process have been proposed with the intent of predicting both the concentration and sequencing of the monomer units within the chains. In general, all copolymerization models portray the copolymerization process as depending on the reactivity of various propagating chain ends towards each monomer and the relative concentrations of monomers in the copolymerization feed. The differences in the models are based on suppositions made in regard to the number of different propagating radicals involved, the reversibility of the propagating radicals and the participation of monomer complexes in the propagation step. The most widely used copolymerization model is one in which the reactivity of the chain end depends on the last monomer addition. This model is fittingly called the terminal model. The initial details of this model were worked out by Mayo and Lewis[1], who showed that the copolymerization can be characterized by two reactivity ratios that reflect the preferences of the two possible propagating radicals towards each monomer. Their resulting equation is the well known copolymer equation[1]:

$$\frac{d[A]}{d[B]} = \frac{[A](r_A[A] + [B])}{[B](r_B[B] + [A])} \tag{1}$$

where [A] is the concentration of monomer A, [B] is the concentration of monomer B, r_A is the reactivity ratio of monomer A and r_B is the reactivity ratio of monomer B. Copolymers that obey the terminal model have monomer unit sequence distributions that can be described by first-order Markoffian statistics[2].

Early studies to determine the reactivity ratios of monomer pairs showed that calculated r values can vary depending on the method of polymerization. Fordyce and Chapin[3] determined the reactivity ratios for styrene/acrylonitrile copolymerizations in bulk and emulsion

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polymerizations, and found slight differences in the monomer–polymer composition curves. For a given feed ratio, the copolymer produced by emulsion polymerization contained less acrylonitrile than that prepared by bulk polymerization. This led the authors to conclude that polymerization in the emulsion system occurred mainly in the oil phase and a substantial portion of the acrylonitrile, which is quite water-soluble, was partitioned into the water phase. Wall *et al.*[4] determined the reactivity ratios for styrene and methyl methacrylate in solution and emulsion. As with the styrene/acrylonitrile system, the authors obtained different reactivity ratios for the two polymerization techniques. The authors attempted to apply a correction factor, directly to the reactivity ratios, to correct for partitioning of the monomers among the phases. This approach overestimated the slight changes observed in the reactivity ratios. Bovey *et al.*[5] pointed out a small, but consistent, difference in monomer reactivity ratios for styrene and butadiene when copolymerized in bulk and emulsion. Again, the authors attributed these variations to differences in the solubility of the monomers in water, micelles and monomer-swollen polymer particles. Due to the complexity of the solubility of butadiene in all the possible phases, it was not possible to account for this effect quantitatively. In an attempt to probe the location of polymerization during interval I, Nomura *et al.*[6] investigated the composition of low-conversion (less that 8%) styrene/methyl methacrylate copolymers prepared by emulsion polymerization. Differences in the early copolymer compositions were observed that reflected the differences in water solubility of the monomers. In addition, different polymer compositions were reported for polymerizations performed in the presence and absence of micelles. Clearly the multiplicity of polymerization sites in an emulsion polymerization system contributes to the differences observed in copolymer compositions relative to other polymerization techniques.

Solvent choice has also been reported to have an important influence on calculated reactivity ratios when monomers with polar substituents or with substituents capable of hydrogen bonding are employed. Plochocka[7] has reviewed earlier work in this area. Recently, monomer sequence distribution measurements have led to a partial understanding of such solvent effects[2]. Systems in which the polarity of the monomers vary greatly such as styrene/methacrylic acid[8,9], styrene/acrylic acid[10,11], styrene/acrylamide[12] and vinylidene chloride/methacrylonitrile[13,14] have monomer–polymer composition curves that vary as the solvent employed for copolymerization is changed. However, for a given polymerization system, copolymers having the same compositions were shown to have the same distributions of monomer sequences irrespective of the solvent used to prepare them. This demonstrated that the same conditional probabilities (i.e. reactivity ratios) governed the formation of the copolymers in the various solvents. Therefore, they concluded that the local concentration of the monomers at the polymerization site varies with the solvent employed for polymerization. This so-called 'bootstrap' effect[2] in solution polymerization demonstrates the importance of local concentration variations during polymerization.

The purpose of this investigation was to explore the copolymerization of monomers having differing water solubilities in emulsion polymerization. Sequence distributions along with copolymer composition data were used to obtain information on both the reactivity ratios and the concentration of monomer at the polymerization site.

EXPERIMENTAL

Materials

Chlorotrifluoroethylene (CTFE; PCR Inc.) was flash distilled into the reactors prior to polymerization. Vinyl acetate (VAc; Aldrich Chemical Co.) and vinyl propionate (VPr; Polysciences Inc.) were distilled under N_2 to remove the inhibitor and were then refrigerated. Water was deionized and filtered through a 2 μm filter using a Corning MegaPure DF water purification system. The specific resistivity of the water was greater than 15 MΩ cm in all cases. The surfactant, ammonium perfluorooctanoate (FC-143, 3M Corp.), was recrystallized from a 5/2 chloroform/acetone solution. The redox initiation system consisted of ammonium persulfate (Aldrich Chemical Co., ACS reagent), ammonium bisulfate (Aldrich Chemical Co.) and ferrous sulfate heptahydrate (Aldrich Chemical Co., ACS reagent), all used as received.

Polymerization procedure

The polymerizations were carried out in 40 ml stainless-steel pressure bombs. These reactors were constructed from 40 ml stainless-steel gas sampling cylinders to which was connected stainless-steel self-sealing quick-connect valves (Swagelok Co.)[15]. The reaction vessels were pressurized with N_2 several times and then evacuated. The proper amounts of the vinyl ester and Fe^{2+}/bisulfate solution were introduced into the reactor under vacuum via a removable septum. The reaction vessel was cooled in a dry ice/isopropanol bath to retard the redox system. With the contents frozen, the proper amount of ammonium persulfate dissolved in water was added. The reaction vessel was then returned to the dry ice bath and CTFE was flash distilled into it using the set-up shown in *Figure 1*. The vessel was clamped into a thermoregulated water bath at 25°C and rotated end-over-end at 45 rev min^{-1}. The conditions and amounts of each reaction are summarized in *Table 1*.

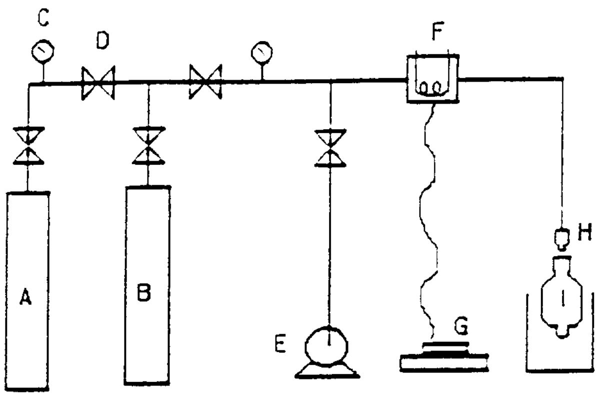


Figure 1 Schematic diagram of polymerization set-up: A, CTFE cylinder; B, nitrogen cylinder; C, pressure gauge; D, valve; E, vacuum pump; F, TCD flow meter; G, strip chart recorder; H, quick connect; I, reaction bomb; J, dry ice bath

Table 1 General recipe and conditions for the copolymerizations

Deionized H_2O	100 g
CTFE	Variable
Vinyl ester	Variable
Total monomer	20 g
Ammonium perfluorooctanoate	0.3 g
Ammonium persulfate	4.75×10^{-3} M
Ammonium bisulfate	4.75×10^{-3} M
Fe^{2+}	100 ppm
Temperature	25°C
Rotation	45 rev min^{-1}

The polymerizations were stopped by venting the excess CTFE in a hood and coagulating the polymer in an aluminium sulfate solution. The precipitated polymers were washed several times with deionized water and dried. The weights of the polymers were recorded and conversions determined. The polymers were than reprecipitated from acetone into water.

Elemental analysis

Carbon, hydrogen and fluorine contents of the copolymers were determined by Galbraith Laboratories Inc. (Knoxville, TN).

Thermal properties

The thermal characteristics of the copolymers were measured using a DuPont 910 differential scanning calorimeter. Samples were run in aluminium pans and scanned at a heating rate of $10°C\,min^{-1}$ in N_2. Two heating cycles were necessary to remove the enthalpy relaxation from the T_g transition.

N.m.r. spectra

The ^1H n.m.r. spectra of the copolymers were obtained using a Varian 200 MHz n.m.r. spectrometer. Five weight per cent solutions of the copolymers were made in deuterated chloroform. Delay times of 3 s were employed. Integration of the resonance areas was performed using the software supplied with the system.

RESULTS AND DISCUSSION

Results

All the copolymers produced by these experiments were soluble in common solvents such as methanol, acetone and chloroform. The d.s.c. thermal traces of the copolymers showed no sign of crystallinity and a single glass transition temperature (T_g). The T_g values of the copolymers were a linear function of the monomer weight fraction in the polymer (*Figure 2*), indicating a non-blocky structure for the copolymers[16]. Monomer–polymer composition curves were constructed from the elemental analysis results of *Table 2*. The monomer–polymer composition curve for the vinyl acetate/CTFE copolymerization is nearly matched by the vinyl propionate/CTFE copolymerization curve (*Figure 3*). The reactivity ratios were then calculated using the method described by Kelen and Tüdös[17,18]. The *r* values by this method were 0.67 ± 0.27 and 0.01 ± 0.05 for vinyl acetate and CTFE, respectively. Vinyl propionate and

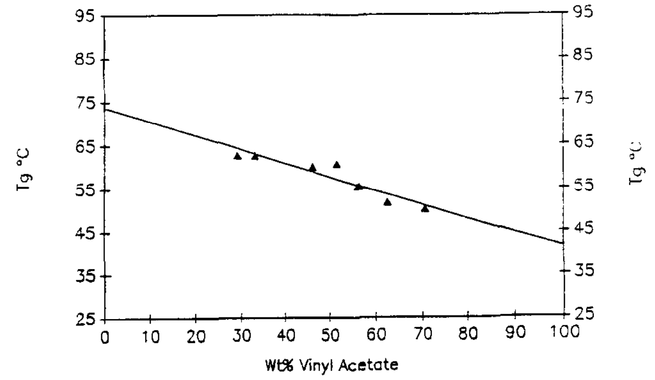


Figure 2 The T_g of poly(vinyl acetate-*co*-CTFE) as a function of weight percentage vinyl acetate in the copolymer

Table 2 Monomer–polymer composition results for the copolymerization of vinyl acetate (VAc) and vinyl propionate (VPr) with chlorotrifluoroethylene (CTFE)

VAc in feed (mol%)	Conv. (wt%)	VAc in copolymer (mol%)		
		by C%	by H%	by F%
9.7	18.0	36.8	35.6	40.7
13.7	23.0	39.5	39.8	46.3
35.4	20.0	54.2	53.6	61.5
39.1	23.0	60.2	59.0	64.2
51.5	9.0	63.1	63.6	66.8
72.9	10.0	72.4	69.3	74.6
81.8	16.0	75.9	74.6	77.7

VPr in feed (mol%)	Conv. (wt%)	VPr in copolymer (mol%)		
		by C%	by H%	by F%
7.2	16.0	29.3	29.3	–
10.1	17.0	34.5	33.0	–
30.7	11.0	50.8	55.8	–
41.2	19.0	54.2	59.5	–
54.2	27.0	60.2	61.3	–
61.2	7.0	66.1	71.8	

CTFE gave similar results with r values of 0.66 ± 0.14 and 0.08 ± 0.01, respectively. The r values were then refined by the method outlined by Mortimer and Tidwell[19]. This method, in which conversion was better accounted for, gave r values of 0.68 ± 0.11 and 0.04 ± 0.02 for vinyl acetate with CTFE and 0.63 ± 0.04 and 0.08 ± 0.01 for vinyl propionate with CTFE. The two methods were in good agreement, and the values of the Mortimer and Tidwell method were chosen for all further calculations.

A typical ^{1}H n.m.r. spectrum of a poly(vinyl acetate-*co*-CTFE) sample is shown in *Figure 4*. The resonance of the methine protons is observed at $\delta = 4.5$–6.5 ppm as a complex pattern that provides information about the vinyl acetate-centred triad distribution and the stereosequence distributions of such triads. The methylene and methyl proton resonances are overlapped in the $\delta = 1.5$–3.0 ppm region. The combined resonance area of this region is five times the methine proton resonance area, as should be the case. While the methylene proton region contains fine structure that may also provide sequence distribution and stereosequence distribution information, it was not investigated because it is poorly defined and is overlapped by the methyl proton resonance.

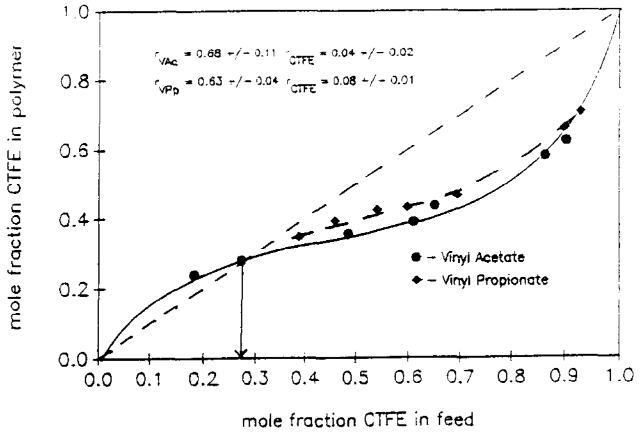


Figure 3 Monomer–polymer composition curves for the emulsion copolymerization of CTFE with vinyl acetate (VAc) and vinyl propionate (VPr)

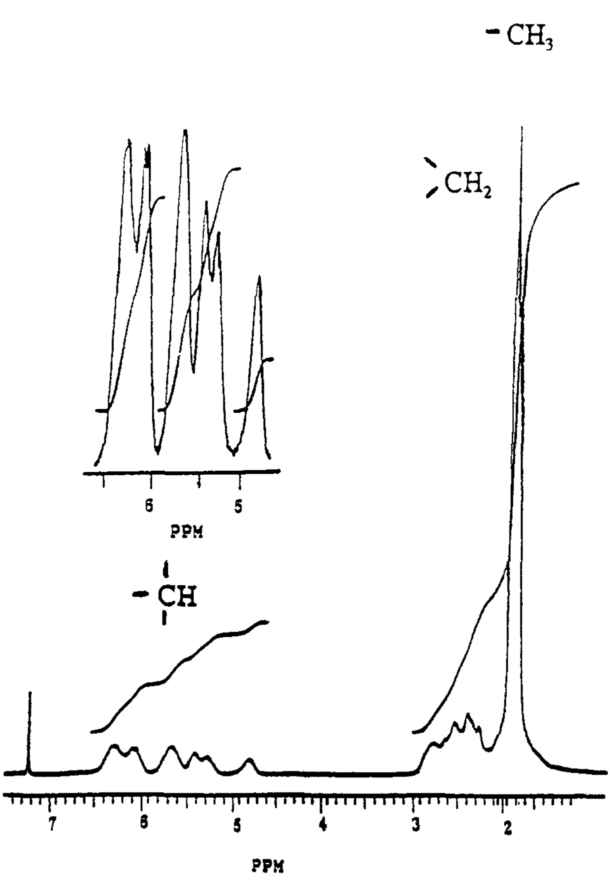
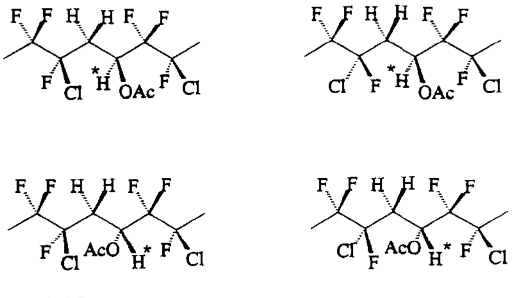


Figure 4 Typical 200 MHz ^{1}H n.m.r. spectrum of poly(vinyl acetate-*co*-CTFE)

The methine proton resonance patterns of a series of poly(VAc-*co*-CTFE) copolymers are shown in greater detail in *Figure 5*. The patterns can be divided into three regions that vary in relative intensity as the copolymer compositions change. Several of these regions contain fine structure that is invariant with copolymer composition, indicating that the fine structure can be attributed to stereosequences. The resonance occuring between $\delta = 4.65$ and 5.15 ppm coincides with the methine resonance for poly(vinyl acetate) and is assigned to vinyl acetate units (A) centred in AAA triads. The resonance occurring between $\delta = 5.85$ and 6.40 ppm increases in relative intensity as the CTFE content of the copolymers increases, and is assigned to the vinyl acetate units having two CTFE (B) neighbours, i.e. BAB triads. The resonance in this region consists of two resonance areas having equal intensities. Although there are four possible stereochemical structures for BAB triads, as shown in *Scheme 1*, apparently two of these are being observed in each of the BAB resonances. This suggests that shielding due to one side of the triads (e.g. the $-CH^*(OAc)-CF_2-CFCL-$ side) may be more influenced by stereochemical configuration than the shielding by the other side (e.g. the $-CFCl-CH_2-CH^*(OAc)$ side). A similar effect has been observed in studies on poly(isobutylene-*co*-CTFE)[20].

Finally, the resonance between $\delta = 5.1$ and 5.9 is assigned to vinyl acetate units centred in BAA and AAB triads. This region consists of three areas having relative intensities of 2:1:1. Since eight different BAA and AAB structures are possible, as shown in *Scheme 2*, and since all may be equally likely if the stereochemical enchainment of A–B and B–A placements occurs randomly, it is reasonable to attribute the three areas to various combinations of these structures. However, it is not possible at this time to make specific assignments.

Support for assigning the resonances observed at $\delta = 4.65$–5.15 ppm, $\delta = 5.15$–5.85 ppm and $\delta = 5.85$–6.40 ppm to AAA, AAB + BAA and BAB triads is provided by the fact that their relative areas in the



Scheme 1 BAB stereosequences

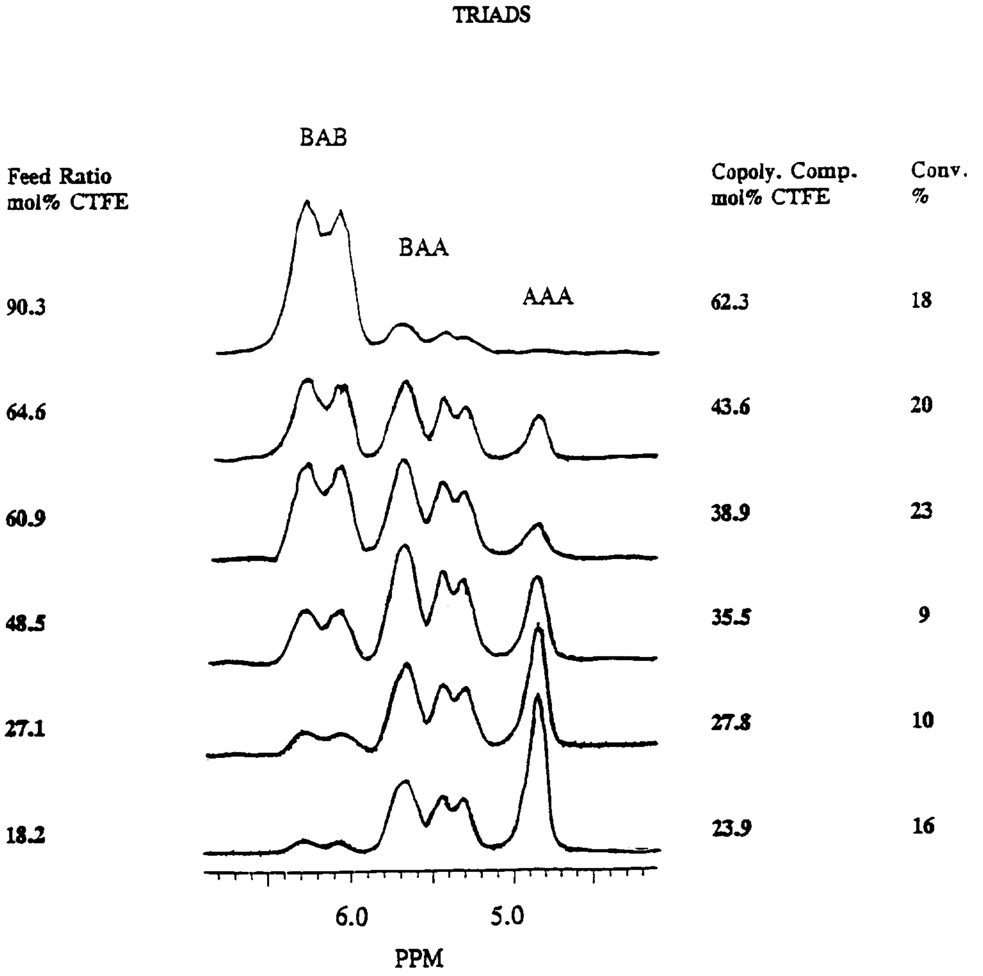
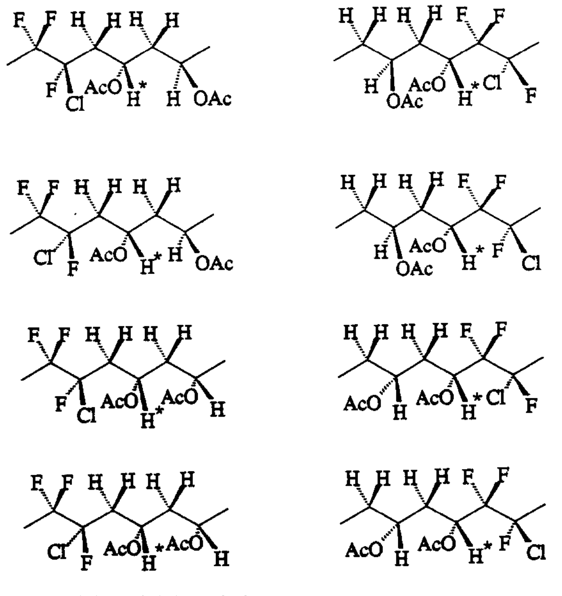


Figure 5 ^{1}H n.m.r. spectra of the methine region of poly(vinyl acetate-*co*-CTFE) of different compositions



Scheme 2 BAA and AAB triad stereosequences

spectra obey a simple probability relationship. Thus assuming the triad distributions obey first-order Markoffian statistics, as would be expected for copolymers prepared according to the terminal copolymerization model, the relative areas of the regions should be given by the following relationships:

$$A_{\mathrm{AAA}} = [1 - P(\mathrm{B/A})]^2 = P(\mathrm{A/A})_2 \qquad (2)$$

$$A_{\mathrm{BAB}} = P(\mathrm{B/A})^2 = [1 - P(\mathrm{A/A})]^2 \qquad (3)$$

$$A_{\mathrm{AAB+BAA}} = 2P(\mathrm{A/A})[1 - P(\mathrm{B/A})] = 2P(\mathrm{B/A})[1 - P(\mathrm{A/A})] \qquad (4)$$

where A_{AAA}, $A_{\mathrm{AAB+BAA}}$ and A_{BAB} represent the relative areas of the resonances assigned to AAA, AAB + BAA and BAB triads respectively. $P(\mathrm{B/A})$ is the probability that a B unit follows an A unit in the copolymer, and for a copolymer obeying first-order Markoffian statistics, $P(\mathrm{B/A})$ is also the probability that a B unit precedes an A unit. Using these relationships, $P(\mathrm{B/A})$ or $P(\mathrm{A/A})$values were calculated from the larger of the AAA or BAB relative areas observed in each spectrum and these probabilities were used to calculate the relative areas of the other signals. As can be seen in *Table 3*, the relative areas of the resonances attributed to AAA, AAB + BAA and BAB agree with those calculated using the measured $P(\mathrm{B/A})$ or $P(\mathrm{A/A})$ values.

It is interesting to compare the values of the conditional probabilities evaluated for the copolymers from the methine proton resonance patterns with those calculated from the monomer reactivity ratios that are based on monomer feed/copolymer composition results. The latter can be calculated for a particular ratio of monomer A to monomer B (i.e. $[A]_f/[B]_f$) in the feed mixture as follows:

$$P(B/A) = \frac{1}{(1 + r_A[A]_f/[B]_f)} \tag{5}$$

Another way to calculate $P(B/A)$ is from the run number[21], R, and the mole fraction (or probability) of monomer A in the copolymer, $P(A)$, using the following equations:

$$P(B/A) = \frac{R}{2P(A)} \tag{6}$$

$$R = \frac{200}{2 + r_A[A]_f/[B]_f + r_B[B_f]/[A]_f} \tag{7}$$

$$\frac{P(A)}{1 - P(A)} = \frac{[A]_f}{[B]_f}\,\frac{r_A[A]_f + [B]_f}{[A]_f + r_B[B]_f} \tag{8}$$

These equations are appropriate when the $[A]_f/[B]_f$ ratio does not change. However, when copolymers are prepared at high conversion, the ratio may change, and it is necessary to calculate $P(B/A)$ from average values of the run number (R) and $P(A)$ from the values that prevail during various conversion increments. A computer program has been previously written to calculate these values and was employed to calculate $P(B/A)$ values for the copolymers from monomer reactivity ratios, conversions and initial monomer concentration ratios[22]. From these probabilities, an apparent average concentration of monomers that governed the copolymer composition at the site of polymerization can be calculated using equation (5). The values obtained for the VAc/CTFE system (*Table 4*) reveal that the apparent concentration of monomer at the polymerization site can differ as much as 10% from the value calculated based on the amount added to the reactor.

The water solubility of vinyl acetate (2.32×10^{-1} mol l^{-1}) is about three times that of vinyl propionate (8.0×10^{-2} mol l^{-1}). Therefore, owing to its lower water solubility, a different profile of the local monomer concentration at the polymerization site *versus* feed composition would be expected for VPr in comparison to VAc. The n.m.r. spectra of poly(vinyl propionate-*co*-CTFE) were similar to those of the poly(vinyl acetate-*co*-CTFE) (*Figure 6*). In comparing the experimental and calculated conditional probabilities, significant differences were again noted. The apparent concentration of monomers at the polymerization site was calculated in the same manner as for vinyl acetate and the results are displayed in *Table 5*. A comparison was then made of the apparent VPr monomer concentration at the polymerization site to the data for the VAc/CTFE system over the experimental monomer concentration range. Surprisingly, the data for VAc/CTFE and VPr/CTFE systems show the same trend despite their water solubility differences. To enhance this comparison, the difference in the apparent vinyl ester concentration

Table 3 Comparison of the fractional peak areas in the methine region to first-order Markoffian statistics

VAc in feed (mol%)		Peak area fractions		
		A_{AAA}	$A_{AAB+BAA}$	A_{BAB}
9.7	exp.	0.01	0.16	0.18
	calc.	0.00	0.17	0.18[a]
13.7	exp.	0.03	0.27	0.70
	calc.	0.03	0.27	0.70[a]
35.4	exp.	0.10	0.46	0.44
	calc.	0.12	0.44	0.44[a]
39.1	exp.	0.12	0.47	0.41
	calc.	0.13	0.46	0.41[a]
51.5	exp.	0.17	0.58	0.12
	calc.	0.17[a]	0.49	0.18
72.9	exp.	0.32	0.56	0.12
	calc.	0.32[a]	0.50	0.18
81.8	exp.	0.45	0.48	0.07
	calc.	0.45[a]	0.45	0.11

[a] Data were calculated assuming this fraction was correct

Table 4 Comparison of conditional probabilities, $P(B/A)$, from the n.m.r. triad distribution and calculations from copolymer composition data for the CTFE/VAc system

VAc in reactor (mol%)	$P(B/A)$ from copolymer composition data	$P(B/A)$ from n.m.r. triad data	VAc at polymerization site (n.m.r.)
9.7	0.957	0.910	12.7
13.7	0.935	0.832	23.0
35.4	0.750	0.674	41.6
39.1	0.719	0.647	44.5
51.5	0.586	0.548	54.8
72.9	0.354	0.390	67.0
81.8	0.245	0.329	75.6

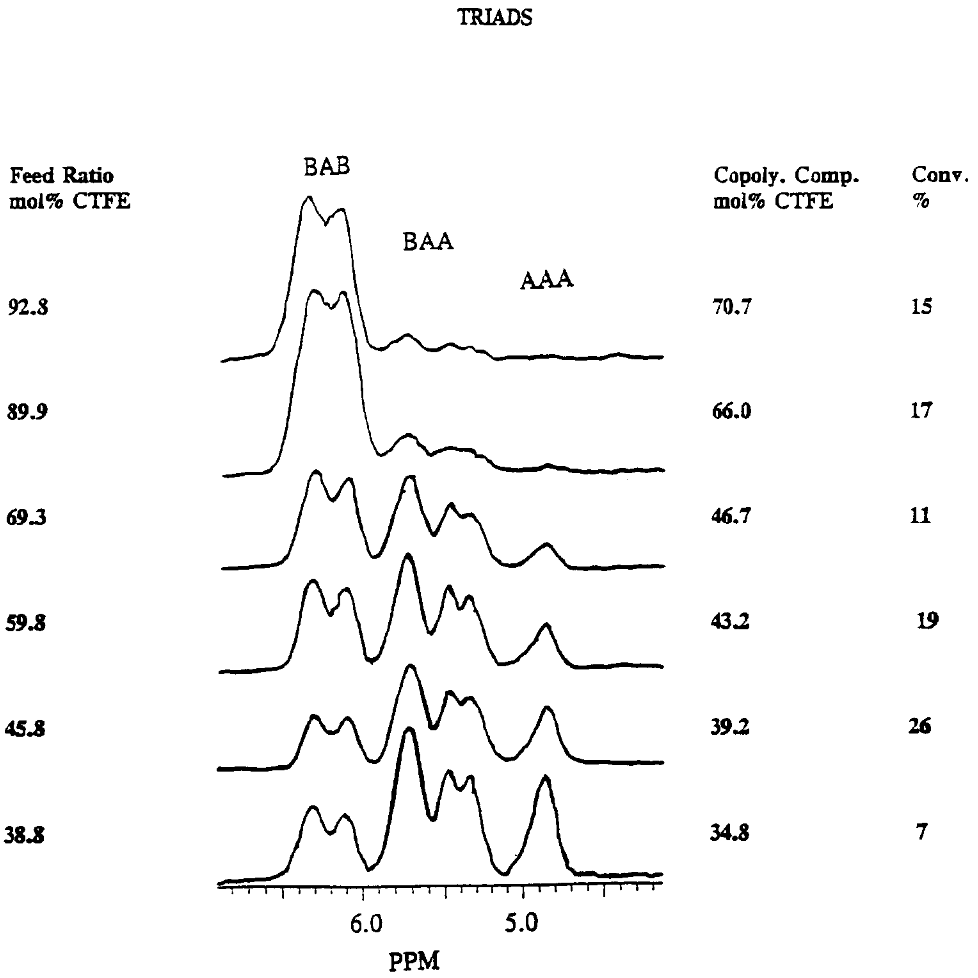


Figure 6 ^{1}H n.m.r. spectra of the methine region of poly(vinyl propionate-*co*-CTFE) of different compositions

Table 5 Comparison of conditional probabilities, $P(B/A)$, from the n.m.r. triad distribution and calculations from copolymer composition data for the CTFE/VPr system

VPr in reactor (mol%)	$P(B/A)$ from copolymer composition data	$P(B/A)$ from n.m.r. triad data	VPr at polymerization site (n.m.r.)
7.2	0.966	0.956	6.8
10.1	0.950	0.911	13.4
30.7	0.790	0.694	41.2
41.2	0.708	0.638	47.4
54.2	0.585	0.559	55.7
61.2	0.503	0.517	55.7

calculated from the n.m.r. data and actual concentration of the vinyl ester added to the reactor was plotted against the actual vinyl ester concentration in the reactor (*Figure 7*). This comparison reveals that the concentration differences are maximum at low mole percentage of vinyl ester.

Discussion

Calculation of the true reactivity ratios in this copolymerization system is not possible since the exact concentration of the monomers at the polymerization site is not known. The calculation of $P(B/A)$ depends on accurate knowledge of the reactivity ratios; thus the values calculated for the monomer feed ratio at the polymerization site are useful only for comparative analysis and not for a quantitative measurement. This

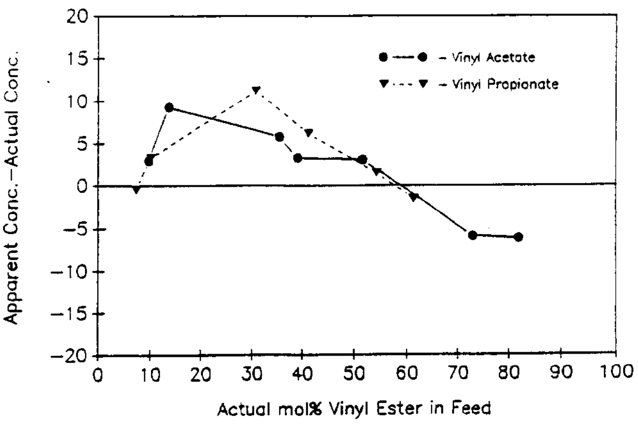


Figure 7 The difference of the apparent vinyl ester concentration at the polymerization site and the actual concentration added to the reactor as a function of copolymerization feed composition

could be overcome by the use of r values determined from a homogeneous polymerization system.

In this emulsion polymerization system, a large difference in the water solubility of the comonomer pairs exists, and since the most likely site of the early-stage polymerization is in the aqueous phase, polymers produced at low conversions should be rich in the more water-soluble vinyl ester. This is especially true when the vinyl ester is present in concentrations below its water solubility limit. Above the solubility limit, a separate vinyl ester phase is present and the amount of vinyl ester in the aqueous phase remains constant with increasing vinyl ester concentration. On initial observations, the results of these experiments are in accordance with this intuitive statement. However, the maximum enrichment of VPr in the VPr/CTFE system occurs at a concentration beyond the solubility limit of VPr in water. This suggests that water solubility is not the only factor that needs to be considered (*Figure 7*).

The solubility of CTFE in the various phases with changing conditions is also an unknown, and the exact reason for the similarities of VAc/CTFE and VPr/CTFE systems cannot be conclusively resolved from these data. However, the similarities in the behaviour of these systems suggest that the same phenomenon is controlling the concentration of monomers at the polymerization site. Micelles and their impact on the polymerization can be ruled out since all polymerizations were carried out below the critical micelle concentration of the perfluoro surfactant. A likely explanation for the similar behaviour of VAc and VPr in these systems may be that the concentration of monomer at the polymerization site is governed by the solubility of the vinyl ester in the CTFE. The solubility of VAc and VPr in CTFE would tend to be more similar than the large difference in their water solubilities.

CONCLUSIONS

This work points out the danger of using emulsion copolymerization data for the determination of reactivity ratios. Attempts to correct for solubility differences by applying a correction factor to the r values is an oversimplification of the problem, since it is the concentration of monomer at the polymerization site that is changing and not the reactivity of the monomers. The use of sequence distribution information can aid in obtaining the concentration of the monomers at the polymerization site, which is useful for determining the location of polymerization in emulsion copolymerization systems. With systems other than CTFE and vinyl esters in which the r values have been determined by homogeneous polymerization systems, the sequence distribution technique could be used to monitor accurate monomer concentrations.

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