Microstructure study of styrene/n-butyl acrylate emulsion copolymers by ^{13}C nuclear magnetic resonance spectroscopy

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A detailed study of the sequence distribution in styrene (S)/n-butyl acrylate (A) emulsion copolymers using ^{13}C nuclear magnetic resonance spectroscopy is reported. From the interpretation of the spectra of the homopolymers and copolymers, assignment of the carbonyl (A) and quaternary (S) carbon atom resonances has been made. This provides a quantitative estimation of the compositional triad distributions in the copolymers. The results were found to be in relatively good agreement with calculated triad fractions deduced from a simulation program taking into account the actual reactivity ratios and type of emulsion process.

(Keywords: styrene/n-butyl acrylate copolymers; triad distribution; ^{13}C nuclear magnetic resonance; simulation; emulsion process)

INTRODUCTION

The determination of the microstructure in copolymers is of value in establishing structure–properties relationships. N.m.r. spectroscopy, mostly ^{13}C, is one of the more powerful and reliable techniques allowing the characterization of polymer structure (and particularly the monomer sequence distribution in copolymers). Because of interest in many applications, there is an increasing number of papers in the literature concerning the monomer sequence distribution in various types of copolymers[1].

Although styrene/alkyl acrylate copolymers provide an important class of polymers widely used in several applications, mostly in coating processes, only a few works have been devoted to their microstructure analysis. Recently, Johnston *et al.*[2] reported a ^{13}C n.m.r. study of styrene/ethyl acrylate emulsion copolymers in which an accurate measurement of the monomer sequence distribution clearly pointed out differences arising from the use of various types of polymerization process. In that case, such a determination is based on the greater sensitivity of the carbonyl carbon atom ($\simeq 174$ ppm) to the compositional triad sequences than to the configurational effect.

However, in the case of vinyl acetate/n-butyl acrylate copolymers[3], it was found that this carbonyl carbon atom was little affected by the compositional triad distribution; hence the monomer sequence distribution was evaluated in this case from the methine carbon resonance spectra of the copolymers.

With a view to obtaining an accurate characterization of the microstructure in styrene/n-butyl acrylate copolymers by ^{13}C n.m.r., it was interesting to examine further, in this system, which type of carbon atom was favourable to allow such analysis. That was the objective of this paper, which first deals with the assignment of the various ^{13}C resonance peaks in the copolymers and then describes the determination of sequence distribution of the monomers in copolymers of different compositions prepared in two different ways. In order to improve the resolution of the ^{13}C spectrum, we investigated copolymers derived from an emulsifier-free batch technique, a process that provides relatively low molecular weight materials in contrast to the conventional emulsion polymerization process.

EXPERIMENTAL

Preparation of copolymers

Two series of styrene/n-butyl acrylate emulsion copolymers were used in this work. They were prepared using either an emulsifier-free batch technique (series B) or a semicontinuous process that allows one to obtain copolymers with a more homogeneous composition (series SC). Recipes and copolymer compositions are given in *Table 1* and polymerization procedures have already been described elsewhere[4,5]. High-conversion emulsion copolymers were obtained and the final polymers were precipitated and washed by the addition of an excess of methanol, then dried under vacuum at 40°C for 48 h.

Copolymer characterization

Average copolymer composition. The average copolymer composition of the different samples determined by ^{1}H n.m.r. are reported in *Table 1*. The copolymer samples were examined as 5 wt% solutions in deuterated chloroform; the spectra were recorded at 20°C

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using a Varian EM 390 spectrometer (90 MHz). *Figure 1* gives a typical copolymer spectrum. The copolymer composition was calculated from the relative intensities of the phenyl (S_1) and $-OCH_2-$ (S_2) proton resonances, according to the following equation:

$$\text{molar fraction of A} = \frac{S_2/2}{S_2/2 + S_1/5}$$

^{13}C n.m.r. spectroscopy. Fourier transform (*FT*) ^{13}C n.m.r. spectra were recorded at 120°C with a Bruker WP 80 spectrometer operating at 20.1 MHz. The copolymer samples were examined as 15–20 wt% solutions. Several solvents were tried: $CDCl_3$ at 50°C, deuterated nitrobenzene at 125°C and a mixture of tetrachloroethylene and deuterated DMSO (45/55 volume ratio) at 120°C. The last mixture was found to give a slightly better resolution, so that it was adopted throughout the study.

The flip angle was 45° and the repetition time was 0.9 s. A good signal-to-noise ratio was obtained using 30000 pulses. Tetramethylsilane was used as internal reference.

The relative peak intensities were measured by planimetry, according to the proposed separation, as shown on the spectra.

Simulation of triad fractions as a function of conversion and type of emulsion process

In emulsion copolymerization, two aspects have to be taken into account:

(1) Since polymerization proceeds in a heterogeneous medium, monomers are partitioned among the following phases: monomer droplets, water and polymer particles swollen by part of the residual monomer. As this last phase is the main locus of polymerization, it is necessary to know at any time the monomer feed composition within it, since, because of differences in water and polymer solubilities of monomers, the feed composition can be different from one phase to another.

(2) As reactivity ratios are not usually equal to unity, a monomer feed composition drift occurs as polymerization proceeds, except at the azeotropic composition, if any. Hence, the copolymer at a given conversion is a mixture of individual copolymer macromolecules, the complexity of

Table 1 Conversion and average composition of styrene (S)/n-butyl acrylate (A) emulsion copolymers

	Series B (batch)[a]			Series SC (semicontinuous)[b]		
Monomer feed composition (mol% A)	Sample code	Conversion (%)	Average[c] copolymer composition (mol% A)	Sample code	Conversion (%)	Average[c] copolymer composition (mol% A)
17	B 1	85.3	18	SC 1a	97	17
				SC 1b	97	19
35	B 2	84.0	34	SC 2a	96	35.5
				SC 2b	90	37
45				SC 3a	93	44
				SC 3b	87	45
55	B 3	92.5	51	SC 4a	92	55.5
				SC 4b	85	51.5
76.5	B 4	87.4	74.5	SC 5	92	75

[a] Recipe: water 700 g; monomers 50 g; $K_2S_2O_8$ 0.564 g; $NaHCO_3$ 0.5 g; temperature 70°C

[b] Recipe: water 750 g; monomers 300 g; $K_2S_2O_8$ 1.0 g; dodecylmercaptan 1 g; SDS 4.5 g; temperature 60°C

[c] As determined by ^1H n.m.r.

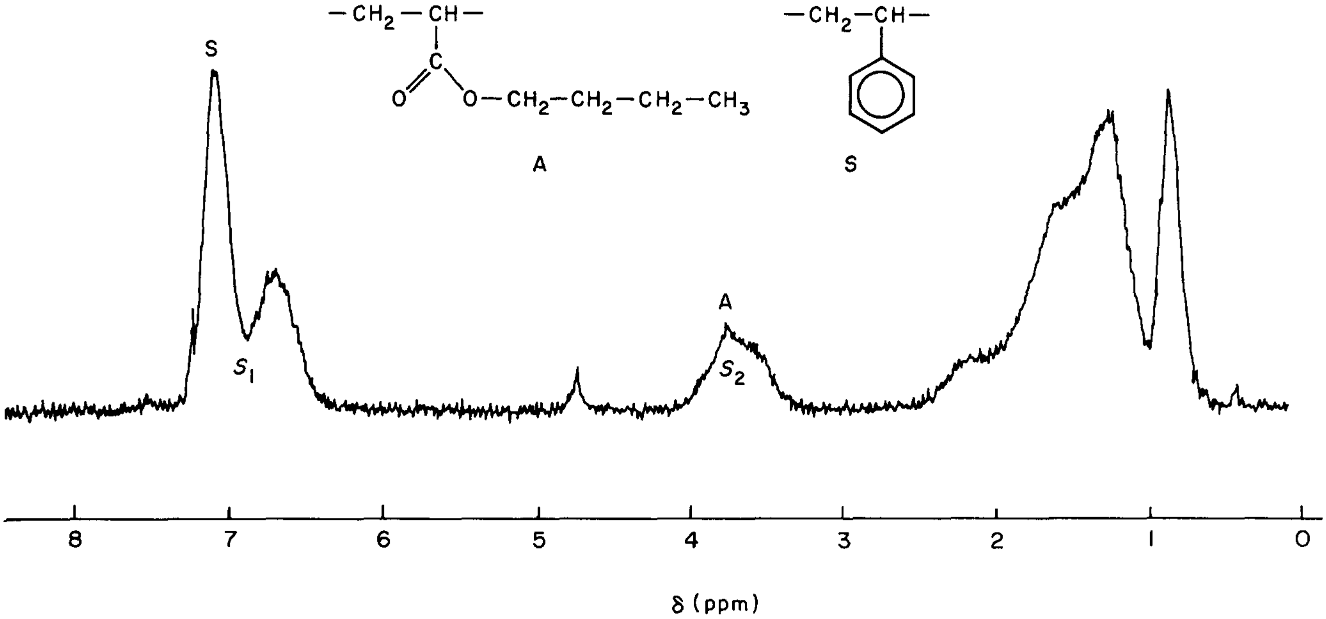

Figure 1 ^1H spectrum (90 MHz) of styrene (S)/n-butyl acrylate (A) copolymer with 55 mol% A

which depends on feed composition and reactivity ratios. As a consequence, the interpretation of n.m.r. spectra needs to take into account, first, the instantaneous microstructure (sequence distribution) of the copolymer arising at any time and, secondly, the average values of the microstructure, for the technique accesses only an 'average' polymer (which has no actual physical meaning).

Simulation of monomer partition. This is based on partition coefficients[6]. Some simplifications have been made and they were found acceptable within the limits of experimental accuracy:

(a) Only one organic phase has been considered, for, as generally observed, the polymer does not greatly affect monomer partitioning, in contrast to the monomer/water ratio, which plays a very important role. Hence, monomer composition is practically the same in droplets and polymer particles.

(b) Partition coefficients are defined as ratios of the volume fractions of a monomer in water and organic phases and are determined experimentally.

(c) The maximum swelling of particles by monomers and its changes *versus* copolymer composition can also be determined experimentally and introduced in the BASIC computation program.

The sequence distribution. This is calculated for a terminal (first-order Markov process) copolymerization model, as proposed by Ito and Yamashita[7] and by Pyun[8]. All the sequence distributions in the instantaneous copolymer can be easily computed from knowledge of the conditional probabilities, P_{ij}, which are simple functions of reactivity ratios and actual monomer feed composition at the polymerization locus. A numerical integration procedure allows one to compute, as conversion increases, the new monomer partition and the resulting instantaneous and average sequence distributions.

From their definition P_{ij} are expressed as, for instance:

$$P_{as}=\frac{K_{as}[A^*][S]}{K_{as}[A^*][S]+K_{aa}[A^*][A]}=\frac{1}{1+r_A[A]/[S]}$$

$$P_{sa}=\frac{1}{1+r_S[S]/[A]}$$

where r_A, r_S are reactivity ratios; [A], [S] are molar concentrations of butyl acrylate and styrene. Obviously

$$P_{aa}=1-P_{as} \qquad \text{and} \qquad P_{ss}=1-P_{sa}$$

Proportions of the various A- or S-centred triads are easily derived for instantaneous copolymer:

$$\begin{array}{ll} (AAA)=P_{aa}^2 & (SSS)=P_{ss}^2 \\ (AAS)=P_{aa}P_{as} & (SSA)=P_{ss}P_{sa} \\ (SAS)=P_{as}^2 & (ASA)=P_{sa}^2 \end{array}$$

RESULTS AND DISCUSSION

Assignment of the various resonance peaks

Principle of the method. Except in some special cases, it is generally observed that the compositional microstructure analysis of a radical-initiated copolymer (AB for instance) appears quite complex because of overlapping of the compositional and configurational sequence resonances, and depends on the spectrometer frequency.

For example, let us consider the case of the $C_\alpha(A)$ methine carbon chemical shift, which is sensitive to the tacticity, at the triad level, in the homopolymer, and thus exhibits three peaks related to the mm, (mr + rm) and rr triads. In a copolymer AB, for a given configuration, if the compositional effect is at the triad level, it gives rise to three different triads, viz. AAA, (BAA + AAB) and BAB. But taking into account both effects leads to 10 different compositional–configurational A-centred triads, when considering the symmetry ($A_mA_rA \equiv A_rA_mA$, $B_rA_mA \equiv A_mA_rB$, etc.). In fact, because of overlapping, the microstructure analysis can only be done in some particular cases, based on the following 'formalism' approach.

At the triad level, let us define $\Delta\delta_{CF}$ as the configurational effect on the methine carbon, which can be estimated from the A homopolymer spectrum, assuming ($\delta_{A_mA_mA} - \delta_{A_mA_rA}$) to be almost equal to ($\delta_{A_mA_rA} - \delta_{A_rA_rA}$) (i.e. the change in chemical shift when, in a triad, a dyad m is replaced by a dyad r, regardless of the environment). This value ($\Delta\delta_{CF}$) is found to be either negative (PVC, for instance) or positive (poly(vinyl alcohol)).

Now, if $\Delta\delta_{CP}$ is defined as the change in chemical shift due to the compositional effect (i.e. $\Delta\delta_{CP}=\delta_{AAA}-\delta_{BAA}$ or $\delta_{BAA}-\delta_{BAB}$), the interpretation of the compositional triad distribution should then be possible in the case when $\Delta\delta_{CP} \gg \Delta\delta_{CF}$ (which means that the compositional effect is more important than the configurational effect).

Such a situation was found to predominate in several copolymer systems[1], which made the compositional triad assignment easier, and thus the analysis of the monomer sequence distribution. In some other cases, particularly in copolymers of methyl methacrylate, $\Delta\delta_{CF}$ is no longer negligible compared with $\Delta\delta_{CP}$ (it could even be larger); when these two effects are of the same order, the composition triad distribution cannot be generally achieved. However, in methyl methacrylate/methacrylic acid copolymers, peak assignment has been made[9,10], and the spectral characteristics were successfully related to the copolymer microstructure owing to a rapid and selective counting procedure[11]. At the opposite extreme, in some cases the compositional effect is found to be almost negligible ($\delta_{AAA}=\delta_{BAA}=\delta_{BAB}$); in such a case, n.m.r. analysis of the A-centred triads in the copolymers gives the configurational triad distribution but not the compositional one[12].

The most favourable case is observed when $\Delta\delta_{CP} \gg \Delta\delta_{CF}$; in fact, as soon as $\Delta\delta_{CP} \geqslant 3\Delta\delta_{CF}$ both configurational and compositional sequences can be studied.

Bajaj *et al.*[13], in a recent ^{13}C n.m.r. study of acrylonitrile (A)/haloalkyl acrylate (methacrylate) (M) copolymers, studied the tacticity of AAA and AAM sequences using the fact that both –CH–(A) and –CN(A) exhibit configurational sensitivity at a triad level in the homopolymer A and that in the copolymers $\Delta\delta_{CP} \gg \Delta\delta_{CF}$. They showed that racemic addition is favoured in A–M sequences owing to the presence of bulky substituted acrylate groups.

A recent literature survey and studies in our laboratories suggest that the carbonyl carbon analysis of styrene/n-butyl acrylate copolymers can be classified as the simplest case (i.e. $\Delta\delta_{CF} \ll \Delta\delta_{CP}$ for the carbonyl carbon). A ^{13}C n.m.r. spectrum of a styrene/n-butyl acrylate (55 mol% A) is shown in *Figure 2*. The microstructure analysis of the copolymers is based on a preliminary investigation of the ^{13}C n.m.r. spectra of the corresponding homopolymers, of which the main features are the following.

(a) Polystyrene: At 25.2 MHz, it is well known[1] that the C_α(–CH–) and C_β(–CH_2–) resonances are very close (from 38 to 48 ppm) and that the methine carbon (higher-field part of this region) is not sensitive to the configurational effect[1]. In contrast, the C_1 carbon (quaternary carbon of the aromatic ring) exhibits complex configurational effects with a pentad chemical shift sensitivity. The assignments proposed by different authors are still disputed[1,14].

(b) Poly(n-butyl acrylate): at 20.1 MHz it is known[3] that this polymer exhibits C_β resonances (34 to 38 ppm) affected by configurational effects at a tetrad level. Neither –CO– nor C_α (42.2 ppm) are influenced by the configuration, each of them being a single peak[3].

(c) Styrene (S)/n-butyl acrylate (A) copolymers.

Owing to complex and strong configurational splittings in the homopolymers (A and S), the C_α(A), C_β(S) and C_β(A) resonances are not useful in terms of compositional sequences in the copolymers. The C_α(S), which does not show a configurational effect in the homopolymer and should have some interest for compositional S-centred triads, is in fact overlapped with the C_β(A) resonances. Therefore, the whole resonance region from 33 to 48 ppm cannot be used (regardless of the presence of undesirable resonances coming from the solvent).

So, much attention has been focused (i) on –CO–(A) resonances that do not show configurational effects in the homopolymer and can be used for compositional A-centred triad determination in the copolymer and (ii) on C_1(S) resonances, for, in spite of complex configurational splittings on the homopolymer, an assignment of the compositional S-centred triads in the copolymer is proposed.

–CO–(A) resonances. The carbonyl resonances of butyl acrylate units (A) (from 174 to 175.50 ppm in a TCE/DMSO mixture) consist of three resonance regions rather badly resolved: regions 1, 2 and 3 respectively from high field to low field. These resonances are respectively assigned to AAA, (AAS + SAA) and SAS triads as shown by the effect of the overall copolymer composition on the resonance pattern (*Figure 3*). The determination of the relative amount of A-centred compositional triads is possible (*Figure 3*), but sometimes without much accuracy (*Figure 3b*).

The compositional effect is dependent not only upon the triad composition but probably upon the pentads, since some more splittings are detected: at a high butyl acrylate content (*Figure 3a*), the three main resonances are at 175.20, 174.80 and 174.45 ppm, each of them with a shoulder at higher field. When the butyl acrylate content decreases (*Figure 3b*), the shoulders become the main resonances at 175.0, 174.60 and 174.35 ppm. This probably arises from a complex and overlapping compositional effect at the pentad level, since no configurational effect has been observed on the –CO– resonance of the poly(butyl acrylate) homopolymer (at 20.1 MHz). Nevertheless the A-centred triad distribution is obtained with a good enough accuracy to study the monomer sequence distribution in S/A copolymers as a function of the polymerization conditions.

In *Figure 4a* and *4b* are shown the –CO– resonances obtained in two different solvents for a copolymer composition of 55 mol% A. The overall resonance region

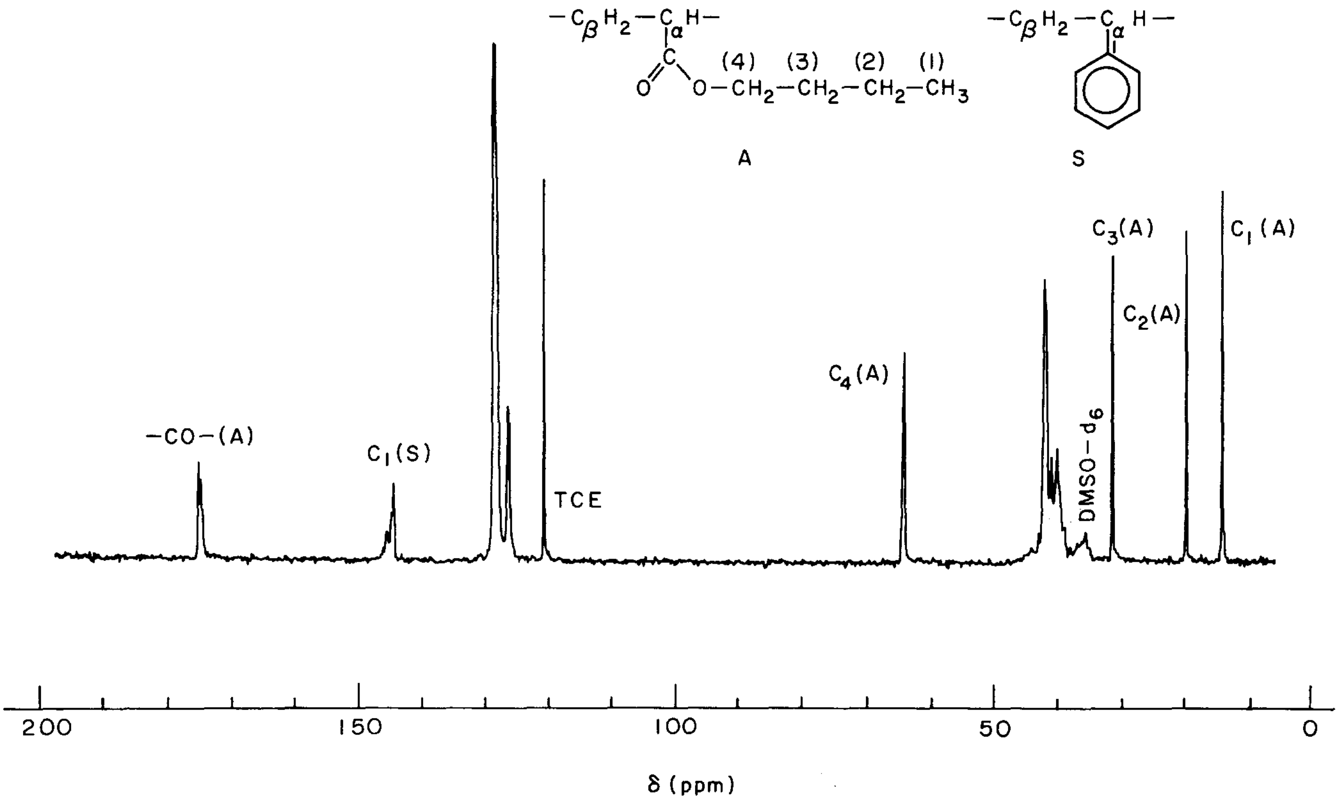

Figure 2 ^{13}C spectrum (20.1 MHz) of styrene (S)/n-butyl acrylate (A) copolymer with 55 mol% A

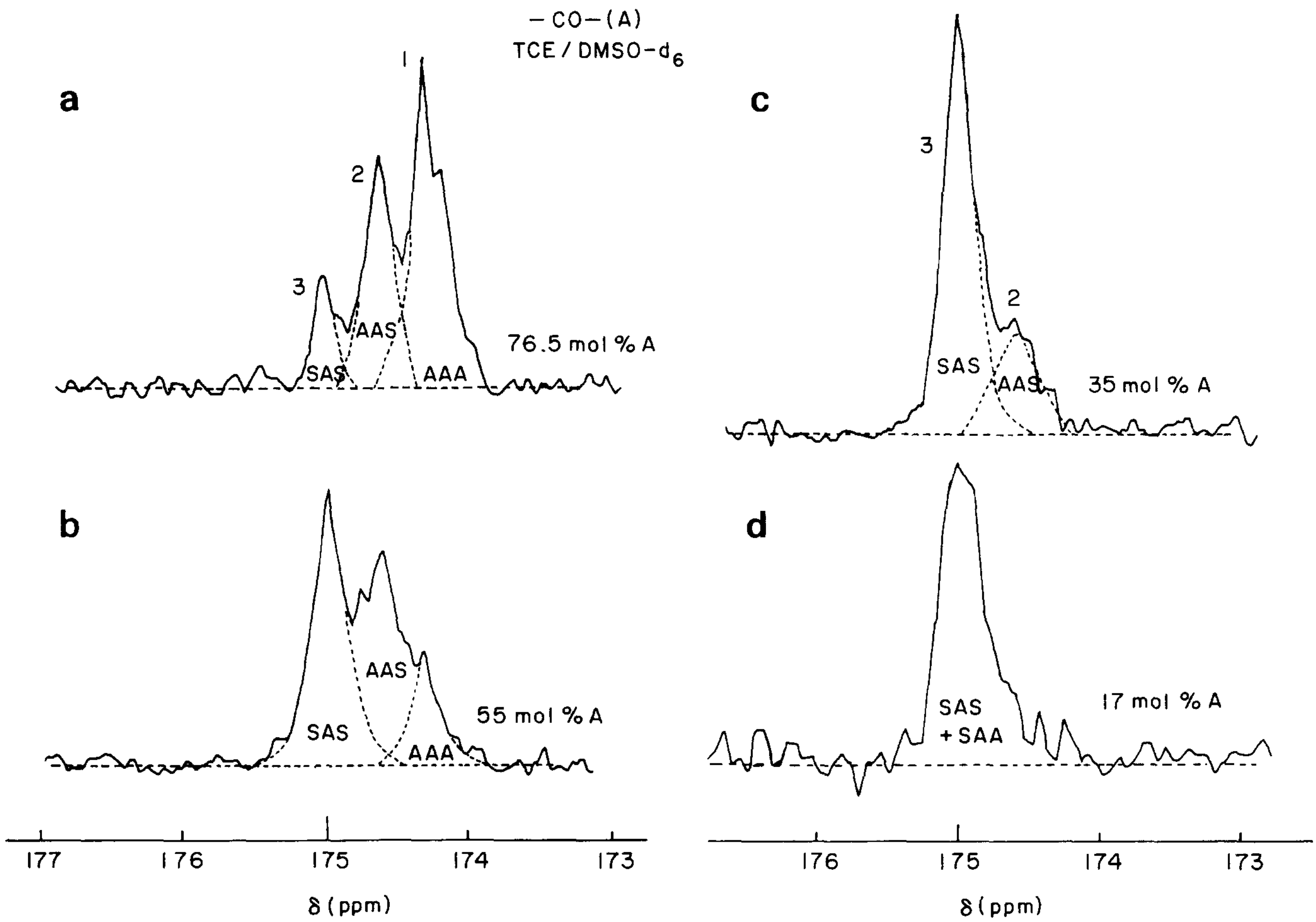

Figure 3 Expanded spectra (20.1 MHz) of the carbonyl carbon region of styrene (S)/n-butyl acrylate (A) copolymer with (a) 76.5, (b) 55, (c) 35, and (d) 17 mol% A

is larger (6 ppm) in $CDCl_3$ than in TCE/DMSO (5 ppm) but the resolution is almost the same, which is true for all compositions. Other solvents have been tested; it appears that, regardless of the solvent, the resolution of the –CO– resonances mostly depends on the nature of the acrylate monomer copolymerized with styrene. Indeed, the resolution falls drastically with increase in the alkyl chain length (from methyl to 2-ethylhexyl acrylate). This point will be discussed elsewhere. The large decrease in –CO– resonance resolution precludes (even when using high-field n.m.r.) the possibility of obtaining results with butyl acrylate as good as those recently reported with ethyl acrylate by Johnston *et al.*[2] That explains why the phenyl C_1 resonances have been investigated in order to gain some information on styrene S-centred triads. From this point of view TCE/DMSO (*Figure 4c*) appears to be slightly better than $CDCl_3$ (*Figure 4d*).

–C_1(S) resonances. Complex and overlapping configurational splittings at the pentad level[1] exist in polystyrene; hence, only an assignment of the observed peaks in terms of compositional S-centred triads is proposed.

The C_1 resonance region between 144 and 147 ppm (at 20.1 MHz in TCE/DMSO) appears to be composed of nine peaks; the influence of copolymer composition on the spectral pattern (*Figure 5*) leads to the following proposed assignments:

SSS triads	peaks 9, 8, 7 and 6
SSA triads	peaks 5, 4 and 3
ASA triads	peaks 2 and 1

The corresponding chemical shift values are given in *Table 1*. These assignments were deduced from the following observations.

(a) At high butyl acrylate content (more than 50%) when ASA triads are the most important ones (*Figures 5a* and *5b*), peak 3 at 144.70 ppm is not visible. Peaks 1 and 2 are obviously assigned to ASA triads.

(b) When the butyl acrylate content decreases, peaks 5 and 4 (SSA triads) increase (*Figures 5b* and *5c*) while peak 3 at 144.70 ppm appears. On this basis, peak 3 has been assigned to SSA triads.

Peaks 2 and 3 being very close together ($\Delta\delta = 0.2$ ppm), the estimation of ASA and SSA triads will be possible only for copolymers with more than 50 mol% butyl acrylate (*Figure 5a* and *5b*).

(c) At high butyl acrylate content (more than 50%) when the relative amount of SSS triads is very low, a peak is observed at 145.30 ppm (peak 5).

(d) When the butyl acrylate content decreases, peaks 9, 8 and 7 increase and are assigned to SSS triads (*Figure 5*). But peak 6 (145.50 ppm) increases too while peaks 4 and 3 become weak. In the region 145.30–145.50 ppm, there are two peaks: the one at higher field (peak 5), already present at high butyl acrylate content (*Figures 5a* and *5b*), is assigned to SSA triads and the other at slightly lower field (peak 6) (*Figures 5c* and *5d*) is assigned to SSS triads.

At a butyl acrylate content of 35% or more, a limit at about 145.70 ppm (*Table 2* and *Figures 5a–c*, vertical full lines) is convenient to separate the SSS resonance areas.

At a lower butyl acrylate content, the same separation will underestimate the SSS value (since the peak 6 area

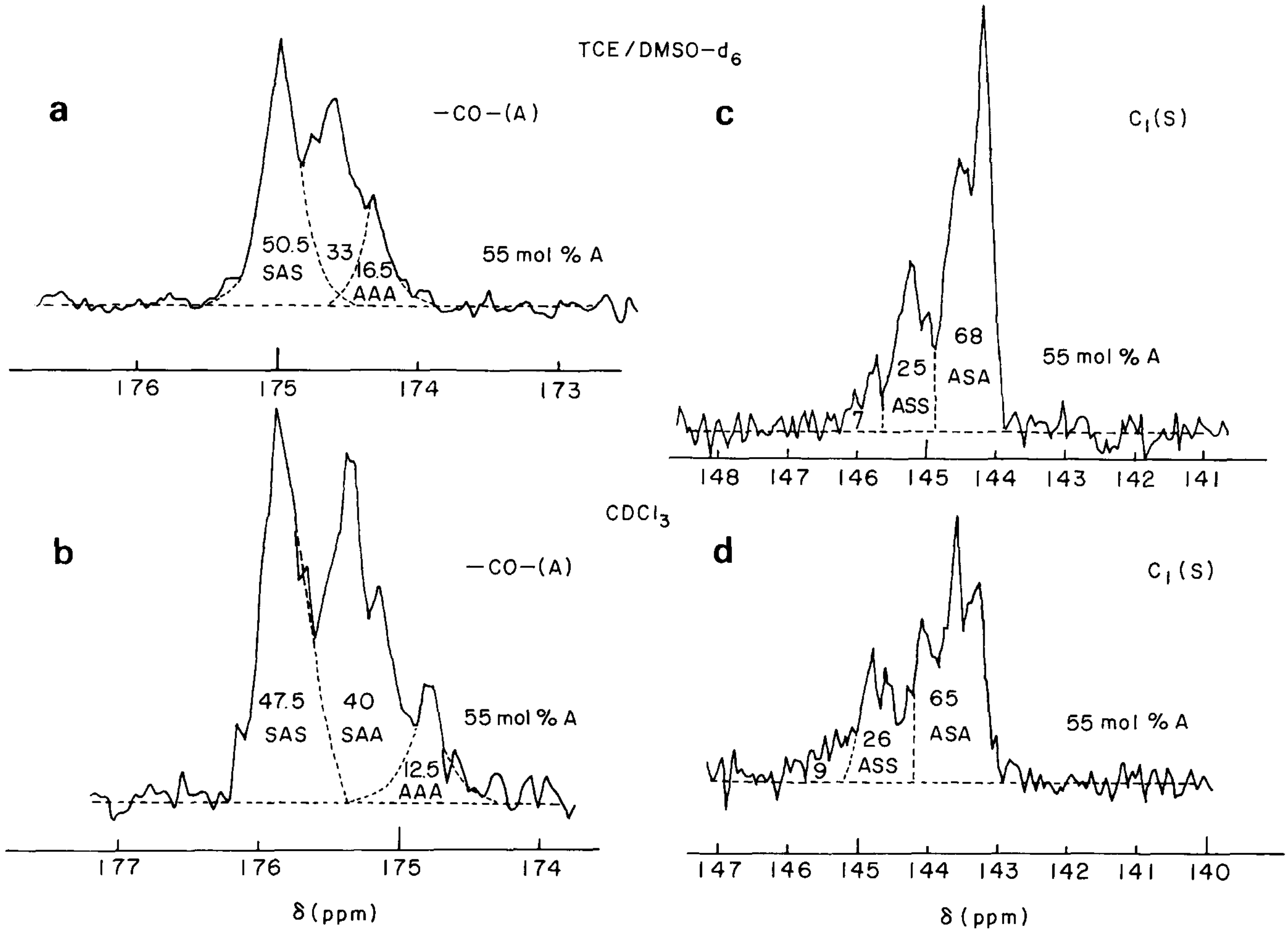

Figure 4 Expanded spectra (20.1 MHz) of the carbonyl carbon –CO–(A) and quaternary carbon C_1(S) resonance regions of a styrene (S)/n-butyl acrylate (A) copolymer with 55 mol% A. Influence of the solvent on the spectrum resolution: (a,c) TCE/DMSO-d_6 mixture; (b,d) $CDCl_3$

contribution is no longer negligible). The other separation at about 145.20 ppm (*Table 2* and *Figure 5d*, vertical broken line) will overestimate the SSS value; in fact the average value provides a good estimation.

At a butyl acrylate content of about 55 mol%, each of the three types of S-centred triads can be evaluated. The separation of the areas is made as shown in *Figure 5b* and *Table 2*, assuming that peak 3 $\ll$ peak 2 and peak 6 $\ll$ peak 5, which is verified as soon as ASA $\gg$ ASS $\gg$ SSS.

Figure 6a shows the C_1 resonances of a copolymer with 17 mol% butyl acrylate at 62.8 MHz (Bruker 250). Compared with the results obtained at 20.1 MHz (*Figure 6b*), it is clearly seen that the determination of the compositional triads is not easy. At 62.8 MHz, the better resolution enhances the separation of peaks 5 and 6 and of peaks 2 and 3.

In conclusion, at 20.1 MHz, both –CO–(A) and C_1(S) resonances of butyl acrylate/styrene copolymers exhibit complex and overlapping splittings at a level higher than a triad sensitivity. A method is proposed in order to evaluate the relative amounts of S-centred and A-centred triads. The results obtained have been compared with theoretical values obtained by simulation.

Monomer sequence distributions in butyl acrylate (A)/styrene (S) copolymers

At first, the microstructure of copolymers was estimated in batch copolymers prepared under emulsifier-free conditions. The values of the six S- and A-centred triad proportions are summarized in *Table 3* and compared with those calculated through a simulation program taking into account the actual reactivity ratios ($r_A = 0.18$, $r_S = 0.66$), as recently determined in our laboratories[15], and the conversion.

The results were interpreted according to the composition range. With an overall butyl acrylate content lower than 50 mol%, owing to a high overlapping of the S-centred triad peak resonances, it is only possible to distinguish unambiguously the SSS triads and the (SSA + ASS) triads. Concerning the A-centred triads, since the amount of AAA triad is found to be negligible, the determination of the SAS and SAA triads is possible for an overall composition of 35 mol% A. It should be mentioned that, in this composition range, the compositional drift mainly affects the S-centred triads. Moreover, for an initial monomer feed of 35 mol% A, the monomer sequence distribution obtained at high conversion (84%) corresponds to the azeotropic distribution, since the simulation shows that, for this composition, all the different triad proportions are nearly constant regardless of the conversion.

In the case of A-rich copolymers, the ^{13}C n.m.r. analysis is found to be more reliable since all the compositional triads can be determined with sufficient accuracy. Above an overall composition of 50 mol% A, the compositional drift, as a result of the faster polymerization of S, causes an increase in the variation of the A-centred triads at the end of polymerization ($\simeq 80\%$). As shown in *Table 3*, there is

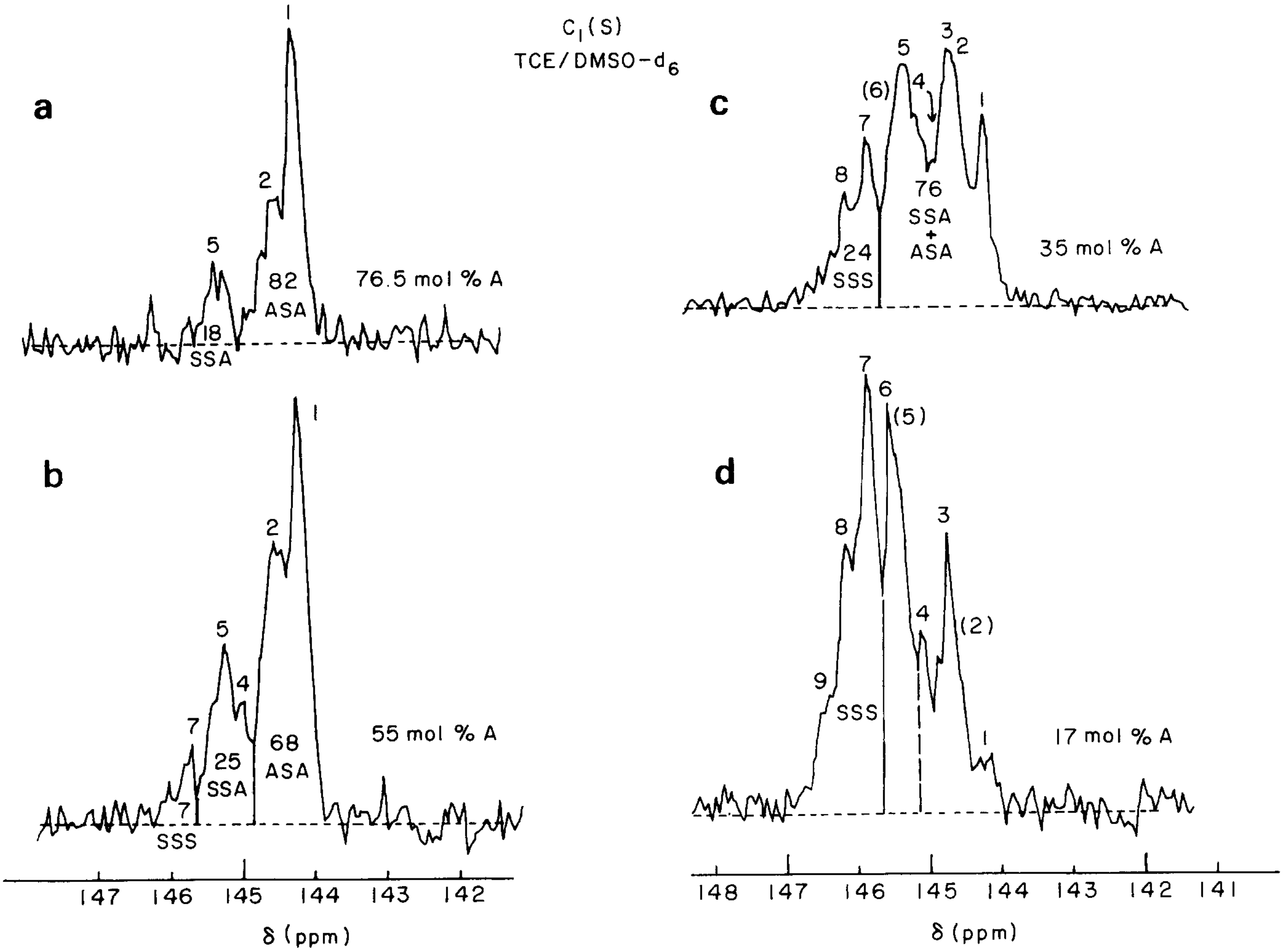

Figure 5 Expanded spectra (20.1 MHz) of the C$_1$(S) resonance region of a styrene (S)/n-butyl acrylate (A) copolymer with (a) 76.5, (b) 55, (c) 35, and (d) 17 mol% A

Table 2 Chemical shifts of the various splittings of C$_1$(S) resonances observed in n-butyl acrylate (A)/styrene (S) copolymers *versus* the copolymer composition. Assignments in terms of compositional triads. Proposal for separation and quantitative estimation of their relative amounts

Copolymer composition (mol% A)	Peaks								
	SSS triads				ASS triads			ASA triads	
	9	8	7	6	5	4	3	2	1
76.5					145.30			144.50	144.20
55					145.30	145.00		144.55	144.20
35		146.20	145.85	← 145.40		→ 145.05	144.70	144.55	144.25
17	146.60	146.20	145.85	145.50		145.10	144.70		144.15
Separation				145.70		145.20	144.80		

good agreement between the experimental and theoretical values. For a composition such as 55 mol%A, the ASA appears to be larger than that expected from the simulation: conversely, the SSA is found to be smaller. Experimental data for A-centred triads, in the case of 55 and 76.5% A, seem to correspond to a batch copolymer of higher conversion than that of the actual copolymer (87.4%). However the discrepancies observed when using two different solvents in the n.m.r. analysis (as reported in *Table 3* for the former copolymer composition (55%)), suggest that this effect might be due to a lack of accuracy in the peak separation coming from bad spectral resolution of the carbonyl resonances.

Based on this first study, it was then attempted to show whether the ^{13}C n.m.r. analysis was sufficiently efficient to investigate the compositional drift effect vs. concentration in batch copolymers where the initial comonomer feed is far from the azeotropic composition (28.5 mol% in butyl acrylate). An initial comonomer feed of 76.5 mol% A was selected and different samples were withdrawn during the batch copolymerization. Values of A- and S-centred triads are collected in *Table 4*, and *Figure 7* reports the change in the six different triad proportions as a function of the conversion derived from the simulation program. It may be seen that, if the S-centred triad (mainly ASA and SSA) percentages do no change drastically with conversion, those related to the butyl acrylate ones exhibit a continuous change, with an increase in the butyl acrylate average sequence length at the end of polymerization, due to styrene monomer depletion in the reaction mixture.

Except in the case of the high-conversion sample (87.5%) where the experimental triad AAA is again slightly higher than expected, the comparison between the experimental and theoretical values is quite close, which confirms the good accuracy obtained in the determination of the reactivity ratios and the validity of the selected method to derive the sequence distribution from the ^{13}C n.m.r. spectra.

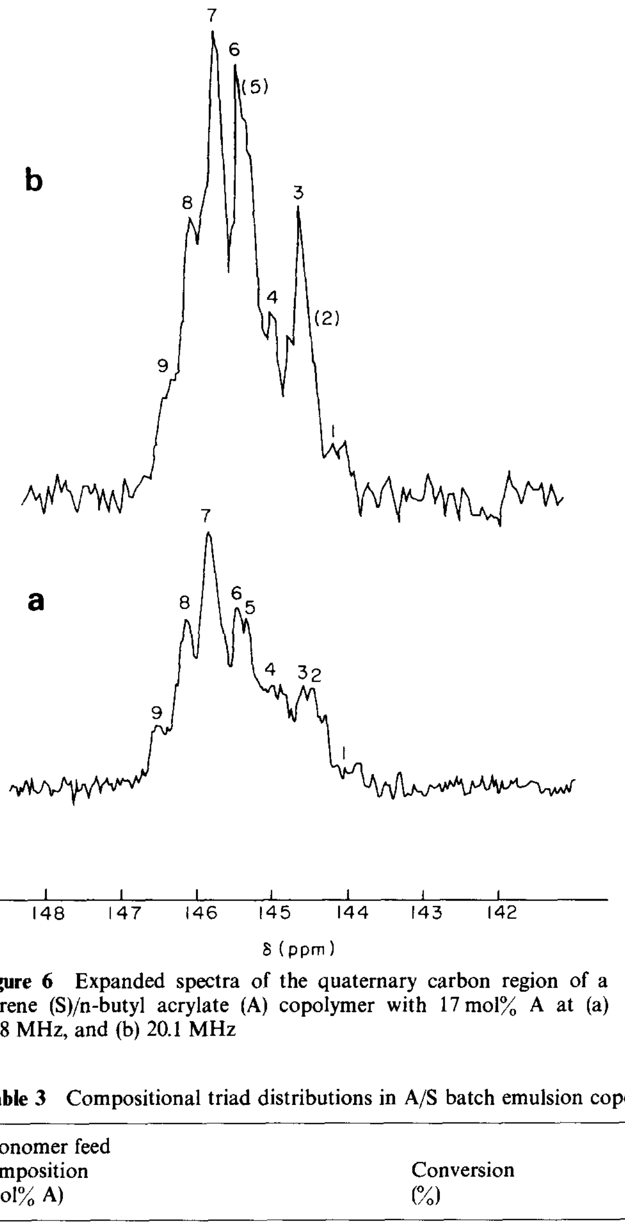

Figure 6 Expanded spectra of the quaternary carbon region of a styrene (S)/n-butyl acrylate (A) copolymer with 17 mol% A at (a) 62.8 MHz, and (b) 20.1 MHz

Owing to the nature of the process, semicontinuous copolymers display a relatively homogeneous copolymer composition, without the compositional drift observed in batch copolymers when reactivity ratios of the two monomers are markedly different. Thus, it was interesting to analyse such copolymers in terms of microstructure, with the same restriction as proposed in the case of the batch series (i.e. bad resolution of the SSA and ASA triads for a feed composition lower than 50 mol% A).

The results are given in *Table 5* for five different initial comonomer feed compositions. Theoretical values of the triad proportions were derived from a modified simulation program taking into account the monomer addition rate and water solubility of the monomers. An example is provided in *Figure 8* for 76.5 mol% A: it may be seen that the monomer sequence distribution is affected early in conversion due to the initial batch period (10% of the overall monomer feed was added into the reactor) but after 25 to 30 mol% conversion, proportions of the different triads remain constant up to high conversion. Final values (*Table 5*) are relatively close to those obtained at 100% conversion in batch copolymerization (*Table 3*), except for the overall compositions far from the azeotropic composition, 28.5 mole% A.

The agreement with the experimental values is again close although, in the copolymer samples having respectively 45 and 55 mol% A, it is pointed out that the SAS and SAA triads differ significantly from the calculated values derived from the simulation at the given conversion. It is difficult to say whether this discrepancy is due to a lack of accuracy in the quantitative analysis (because of peak overlap) or the result of a real effect on the polymerization mechanism. It is well known that, when running semicontinuous emulsion copolymerization, specific kinetic behaviour is found since polymerization takes place in highly converted polymer particles (i.e. a very viscous medium). Snuparek *et al.*[16] referred to the influence of the viscosity inside the polymer–monomer particles on polymerization rate, which is also dependent upon monomer diffusion. They estimated effective reactivity ratios under high feed rates ($r_A = 0.47$, $r_S = 0.66$), accounting for kinetic and physical effects in terms of the nature of the process.

In our case, for the same initial comonomer feed composition, some copolymer samples were prepared at

Table 3 Compositional triad distributions in A/S batch emulsion copolymerization

Monomer feed composition (mol% A)		Conversion (%)	S-centred triads			A-centred triads		
			SSS	SSA	ASA	SAS	SAA	AAA
17	theor.	85.3	62	33.5	4.5	94.0	6.0	0
		100	64	32	4.5			
	exp.	85.3	60[a]	40		100		0
35	theor.	84	27	50	23	81	18	1.0
		100						
	exp.	84	24	76		76	24	0
55	theor.	92.5	8	38.5	54.0	50	38	12
		100				44	34	22
	exp.	92.5	7	25	68	50.5	33	16.5
	exp. ($CDCl_3$)	92.5	9	26	65	47.5	40	12.5
76.5	theor.	87.4	1.0	19	80	15.5	34	50.5
		100				13.5	29	57.5
	exp.	87.4	0	18	82	12	33.5	54.50

[a] SSS corresponds to the mean value between the two evaluations obtained by separating the resonance regions respectively at 145.70 and 145.20 ppm (*Table 2*) (*Figure 5d*)

Table 4 Effect of conversion on the compositional triad distribution and average sequence length ($\overline{LnA}$) in A/S batch emulsion copolymerization (initial monomer feed composition 76.5 mol% A)

Conversion (%)		S-centred triads			A-centred triads			
		SSS	SSA	ASA	SAS	SAA	AAA	$\overline{LnA}$
5	theor.	2.5	27.5	70	39	47	14	1.60
	exp.	3.5	28.5	68	38	45	17	1.65
32.5	theor.	2	24	73.5	33	49	18	1.74
	exp.	0	22	78	32	49	19	1.77
63	theor.	1.5	20	78.5	23	47	30	2.15
	exp.	0	22	78	18.5	46	35.5	2.41
79	theor.	1.5	19	80	18	39	43	2.67
	exp.	0	16.5	83.5	17	38	45	2.78
87.5	theor.	1.5	19	80	15.5	34.5	50	3.00
	exp.	0	18	82	12	33.5	54.5	3.48
100	theor.	1.5	19	80	13	29.5	57.5	3.57

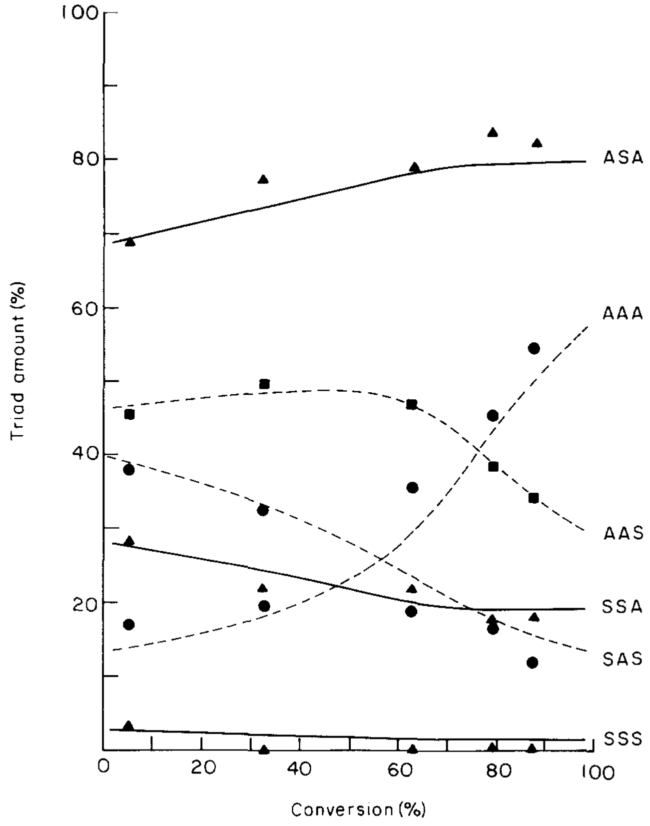

Figure 7 Average triad distributions *versus* conversion in a styrene (S)/n-butyl acrylate (A) batch emulsion copolymerization with an initial monomer feed composition of 76.5 mol% A

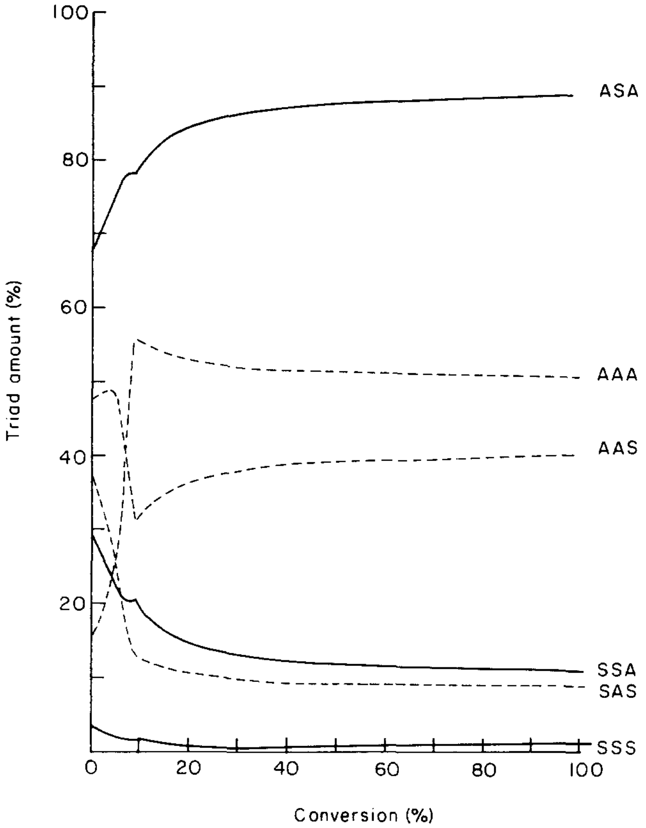

Figure 8 Simulation of the average triad distribution in semicontinuous emulsion copolymerization with 76.5 mol% A; $r_S = 0.66$, $r_A = 0.18$

low feed rates (0.36×10^{-3} mol s^{-1}) or at high feed rates (1.30×10^{-3} mol s^{-1}); the discrepancies observed in the corresponding triad compositions do not clearly show the influence of this experimental parameter, maybe because the range of selected feed rate was not large enough. Moreover, it was found that, when using the reactivity ratios determined by Snuparek in the simulation program, the calculated data do not fit our experimental triad proportions better, regardless of the initial comonomer feed composition.

CONCLUSIONS

It may be concluded that the microstructure of styrene (S)/n-butyl acrylate (A) can be investigated through 20.1 MHz ^{13}C n.m.r. analysis, although the resolution of the carbonyl (A) carbon atom resonance peaks is not as good as in the case of styrene/ethyl acrylate[2]. This suggests that increasing the alkyl chain length of the acrylate causes a drastic change in the spectrum resolution of the corresponding carbon resonances, a

Table 5 Compositional triad distributions in A/S semicontinuous emulsion copolymerization

Sample code	Copolymer composition (mol% A)		S-centred triads			A-centred triads		
			SSS	SSA	ASA	SAS	SAA	AAA
		theor.	64.5	32	3.5	94	6	0
SC 1a[a]	17	exp.	57.5	42.5		86	14	0
SC 1b[b]	19	exp. ($CDCl_3$)	62.5	32.5	5	90	10	0
		theor.	29	50	21	80	19	1
SC 2a	35.5	exp.	22[c]	78		81	19	0
SC 2b	37	exp.	23[c]	77		76	24	0
		theor.	13	45.5	41.5	62	31	7
SC 3a	44	exp.	17	83		63	30	7
SC 3b	45	exp. ($CDCl_3$)	14	86		53	39	8
		theor.	4.5	33	62.5	42.5	42.5	15
SC 4a	55.5	exp.	6	22	72	38	39.5	22.5
SC 4b	51.5	exp.	8.5	27	64.5	55	28	17
		theor.	0.5	12	87.5	9.5	39	51.5
SC 5	75	exp.	0	–[d]	–[d]	14	35.5	50.5

[a] Low feed rate
[b] High feed rate
[c] Underestimated values
[d] Cannot be separately estimated

trend that was confirmed in the case of styrene/2-ethylhexyl acrylate copolymers for which the ^{13}C resonances of the carbonyl spectra exhibit poor resolution. The differences in chemical shift of the –CO– resonances, viz. $\delta_{SAS}-\delta_{AAS}$ and $\delta_{AAS}-\delta_{AAA}$, were the same for ethyl and 2-ethylhexyl acrylate, and the change in resolution could be related to differences in relaxation times found by one of the present authors (M.F.Ll.-D.).

Although a precise quantitative determination was not always possible in the whole composition range because of peak overlap (chiefly in the case of S-centred triads), the determination of the monomer sequence distribution in copolymers was nevertheless carried out. The compositional drift *versus* conversion in batch copolymers due to the difference in the reactivity ratios can be readily seen, mainly when considering the change in the A average sequence length. However, since this composition drift *versus* conversion is not very large for this system, differences in the triad distributions are not so important for copolymers prepared either by a batch process (heterogeneous copolymer composition is expected) or in a semicontinuous process (which allows better control of the compositional homogeneity).

If the peak resolution could be improved, such an experimental microstructure analysis, associated with the corresponding theoretical simulation, might also provide valuable arguments in the discussion of emulsion copolymerization mechanisms as functions of conversion and type of process.

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