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Microstructure Elucidation of Glycidyl Methacrylate–Alkyl Acrylate Copolymers by ^{13}C NMR Spectroscopy

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ABSTRACT: A detailed study of the microstructures of glycidyl methacrylate (GMA), *n*-butyl acrylate (nBA), and isobutyl acrylate (iBA) copolymers was carried out by using ^{13}C NMR spectroscopy. The NMR spectra of the carbonyl region are well resolved and represent the compositional triad distribution in the copolymers. This has been studied with varying composition of the copolymers. The number-average sequence lengths of the monomers in the copolymers have been calculated from reactivity ratios as well as from experimental triad fractions, which show good agreement with each other.

Introduction

The microstructure of polymers, which involves the distribution of monomers in the copolymers and the stereochemical arrangement of various groups pendant to the polymer backbone, fundamentally influences their physical and chemical properties.[1] High-resolution NMR spectroscopy, particularly the proton noise decoupled ^{13}C technique, has been proved effective in the elucidation of the microstructure of synthetic polymers.[2,3]

In recent years, copolymers based on glycidyl methacrylate have received increasing attention due to their versatile applications.[4-6] The literature concerning microstructure determination of glycidyl methacrylate based copolymers is scanty. In the present study, we have investigated the monomer sequence distribution of glycidyl methacrylate–*n*-butyl acrylate and –isobutyl acrylate copolymers by means of ^{13}C NMR spectroscopy. The following features of this copolymer system have been considered: (i) interpretation of the spectra of the homopolymers; (ii) estimation of the composition of the copolymers to calculate monomer reactivity ratios; (iii) determination of sequence distribution of the monomers in the copolymers.

Experimental Section

Synthesis of Copolymers. Glycidyl methacrylate (GMA), *n*-butyl acrylate (nBA), and isobutyl acrylate (iBA) were obtained from Fluka AG. The two batches of copolymers, i.e. GMA–nBA and GMA–iBA, were prepared in bulk. The detailed methods of purification of monomers and synthesis of copolymers were described elsehwere.[7]

NMR Measurements. ^{13}C NMR spectra were measured with a JEOL JNM-FX100 NMR spectrometer operating at 25.05 MHz. The copolymer samples were examined as 15–20% (w/v) solutions in $CDCl_3$. The detail conditions of operations are as follows: temperature of the probe, 50 °C; reference, center peak of $CDCl_3$, assigned as 77.0 ppm; pulse width, 6 μs (30° flip angle); pulse delay, 5 s; spectral width, 6250 Hz; 16K data points for Fourier transform; mode of decoupling, gated. These experimental conditions ensure the complete relaxation of all the ^{13}C carbons.[8] Since NOE and T_1 are the same for different carbons in or near the polymer main chain, the relative peak areas have been considered to be proportional to the number of contributing carbons.[9] Besides, as the gated decoupling method was employed, the quantitative NMR study was done more precisely. The relative peak intensities were measured from integrated peak areas calculated by means of a computer.

Results and Discussion

Table I
Relative Pentad Intensities and Peak Chemical Shifts from the Carbonyl Carbon Resonance of Poly(glycidyl methacrylate)

pentad	chem shift,[a] ppm	rel intens	
rrrr	176.68	0.39	0.66
rrrm	176.0	0.21	
rrmr	176.05	0.06	
mrmr			
mrrm	177.02	0.29	
mmrr			
rmmr			
mmmr			
mmrm	177.46	0.03	
mmmm			

[a] Relative to center peak of $CDCl_3$ (77.0 ppm).

^{13}C Resonances of Poly(GMA). The ^{13}C NMR spectrum of poly(GMA) is shown in Figure 1. The assignment of various resonance peaks due to different carbon atoms has been made on the basis of results of off-resonance decoupling as well as by comparison with analogous groups from the literature.[10] The neatly resolved spectrum provides information regarding the configurational differences in the polymer backbone. The carbon atoms sensitive to configurational changes are α-methyl (17.36–19.2 ppm), backbone quaternary carbon atom (44.75–45.42 ppm), and carbonyl (176.0–177.46 ppm) carbon atoms. The expanded spectra of these three carbon resonances are shown in Figure 2. The three peaks due to quaternary carbon atom have been considered for configurational triad assignments, with isotactic (mm), heterotactic (mr + rm), and syndiotactic (rr) from low to high field. This assignment has been made on the basis of the assignments made for the quaternary carbon resonances for poly(methyl methacrylate) by Reynolds[11] and for poly(α-chloroacrylates) by Hatada et al.,[12] who observed that the syndiotactic resonance appears at higher field. The estimation of tacticity indicates a random distribution of triads obeying Bernoullian statistics with a P_m value 0.24. The carbonyl carbon and α-methyl carbon resonances showed resolution of six and nine peaks, respectively. The assignment of various peaks due to different configurational pentads for these carbon atoms is summarized in Tables I and II, which show the polymer to consist of a variety of configurational sequences having a higher tendency for the syndiotactic mode of chain propagation. Because of peak overlap, precise quantitative estimation was not possible for carbonyl carbon resonances.

The validity of the assignments of various peaks is further supported by calculation of the specific persistence ratio, $\rho = 2(m)(r)/(mr)$, which expresses the tendency of

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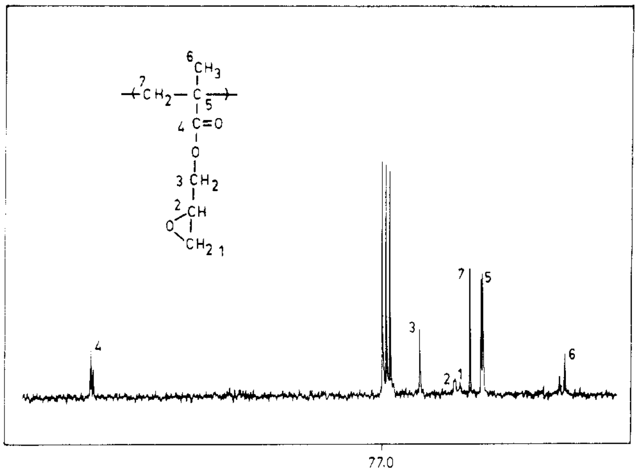

Figure 1. ^{13}C spectrum (25.05 MHz) of poly(glycidyl methacrylate).

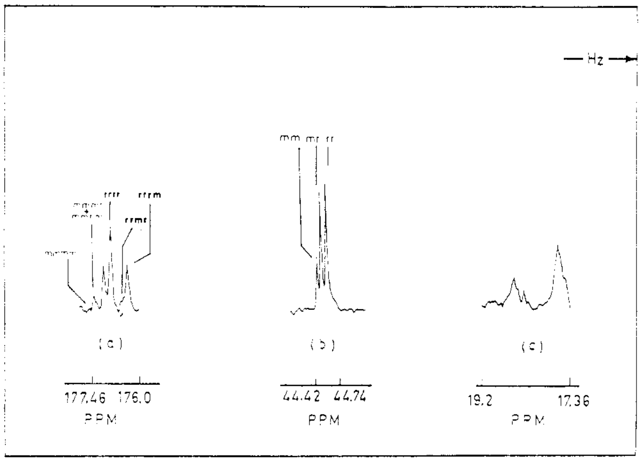

Figure 2. Expanded spectra of the carbonyl carbon (a), quaternary carbon (b), and α-methyl carbon (c) regions of poly(GMA).

Table II
Relative Pentad Intensities and Peak Chemical Shifts from the α-Methyl Carbon Resonance of Poly(glycidyl methacrylate)

pentad	chem shift,[a] ppm	rel intens	
rrrr	17.36	0.28	0.58
rrrm	17.31	0.12	
rrmr	17.27	0.18	
mrmr	18.77	0.09	0.37
mmrr	19.0	0.10	
mrrm	19.15	0.13	
rmmr	19.2	0.04	
mmmr	19.7	0.02	0.05
mmrm	19.8	0.03	
mmmm	—		

[a] Relative to center peak of $CDCl_3$ (77.0 ppm).

Table III
Comparison of Experimentally Determined Triad Tacticities (Quaternary Carbon Atom) with Those Calculated from Pentad and Configurational Statistics of Poly(glycidyl methacrylate)

triad	exptl value	calcd from pentad	m	r	ρ	Z
rr	0.63	0.64	0.22	0.78	1.02	0.93
mr + rm	0.33	0.29				
mm	0.04	0.07				

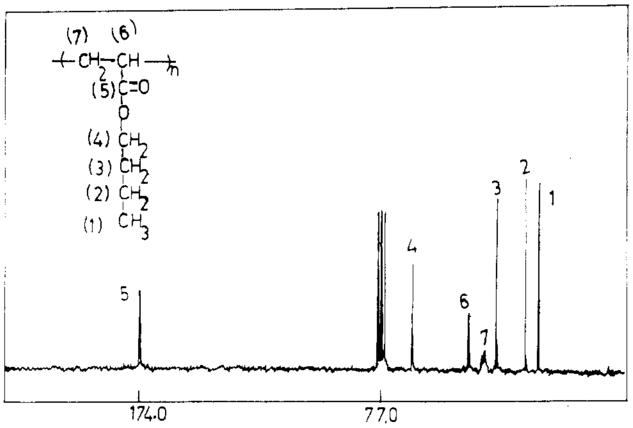

Figure 3. ^{13}C spectrum (25.05 MHz) of poly(*n*-butyl acrylate).

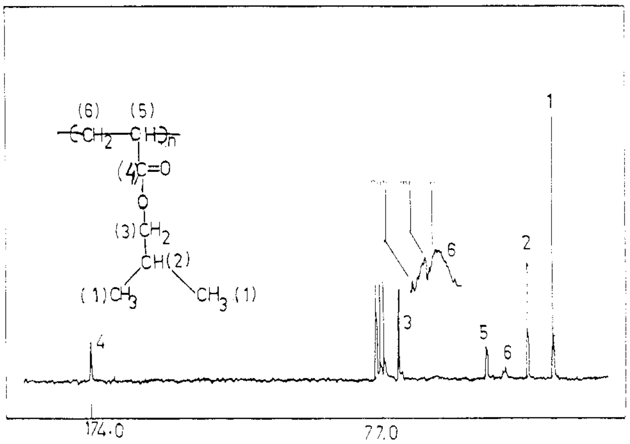

Figure 4. ^{13}C spectrum (25.05 MHz) of poly(isobutyl acrylate) and expanded spectrum of the backbone β-methylene carbon resonances (6).

the r and m units to propagate themselves preferentially. The value of ρ obtained was 1.02, which is nearly equal to unity, obeying Bernoullian statistics for a random distribution.[13,14] Besides, an additional criterion for Bernoullion statistics is that the quantity $Z = 4(\mathrm{mm})(\mathrm{rr})/(\mathrm{mr})^2$ should be either close to or equal to unity.[15] The value of Z was close to unity, further confirming that the system follows Bernoullian statistics. The triad values obtained from quaternary carbon resonances are in excellent agreement with those calculated from pentad sequences. All these values are summarized in Table III. Besides, it is expected that in radical polymerization, the polymer chain has an atactic distribution, with a bias for syndiotacticity and preference for Bernoullian statistics.[16,17]

^{13}C Resonances of Poly(nBA). The poly(nBA) ^{13}C NMR spectrum is shown in Figure 3. The carbonyl carbon atom resonance (174.35 ppm) of this polymer does not reveal any tacticity phenomenon. However, the backbone methylene carbon atom (35.65–36.65 ppm) shows splitting due to configurational effects; the splitting is at the dyad level, with the atactic fraction predominant.

^{13}C Resonances of Poly(iBA). Figure 4 depicts the ^{13}C NMR spectrum of poly(iBA) polymer, which unlike poly(GMA) does not give any information regarding configurational changes at the ^{13}C resonance of the carbonyl carbon atom (174.1 ppm). The backbone methylene carbon resonance splits, indicating a dyad tactic distribution, with the atactic fraction predominant.

^{13}C Resonances of the Copolymers. Composition Analysis and Monomer Reactivity Ratios. The ^{13}C NMR spectra of GMA–nBA (A–B) copolymers and GMA–iBA (A–B) copolymers are shown in Figures 5 and 6, respectively. With the help of the spectra of homopolymers, the resonance peaks due to various carbon atoms

Table IV
Copolymer Composition of Glycidyl Methacrylate (M_1)-*n*-Butyl Acrylate and -Isobutyl Acrylate (M_2) Copolymers

sample code	conv, %	av copolymer comp mole fraction (M_1)	init monomer feed comp mole fraction (M_1)
		GMA-nBA System	
nB1	7.5	0.792	0.677
nB2	6.4	0.676	0.474
nB3	6.5	0.484	0.278
		GMA-iBA System	
iB1	6.0	0.766	0.677
iB2	5.5	0.656	0.474
iB3	6.0	0.436	0.278

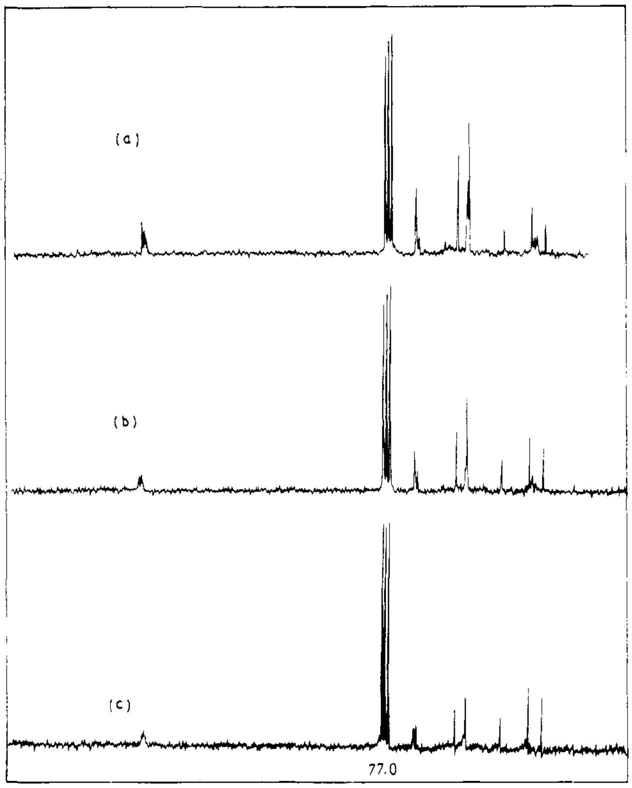

Figure 5. ^{13}C NMR spectra (25.05 MHz) of GMA (A)-nBA (B) Copolymers with A = 79.2% (a), 67.6% (b), and 48.4% (c).

of the copolymers have been assigned. For the quantitative estimation of the compositions of the monomers in the copolymers, the integrated peak intensity due to OCH_2 groups of the monomer components has been considered. This has been justified by the fact that, these carbons being similar, the T_1 values are same for them in each monomer unit. Moreover, as the experiments were carried out by gated decoupling, the possibility of NOE accumulation is alleviated and the quantitative estimation is unambiguous. In GMA-nBA copolymers, the carbon resonances of OCH_2 of GMA and nBA appear at 65.89 and 64.68 ppm, respectively. But in the case of GMA-iBA copolymers, these peaks appear at 65.89 and 71.0 ppm, respectively. Taking the composition of the copolymers and initial feed into account, the monomer reactivity ratios have been calculated by using the YBR method.[18] All values regarding composition and monomer reactivity ratios are summarized in Tables IV and V. The data indicate that GMA in either copolymerization system is more reactive than the alkyl acrylate comonomers. Further, the reactivity of iBA is greater than the reactivity of nBA toward the poly(GMA) radical. The reactivity ratios obtained from chemical analysis[7] and NMR for GMA-iBA copolymers are in good agreement. However, in the case of GMA-nBA copolymers, greater variation in r_1 and r_2 values was found.

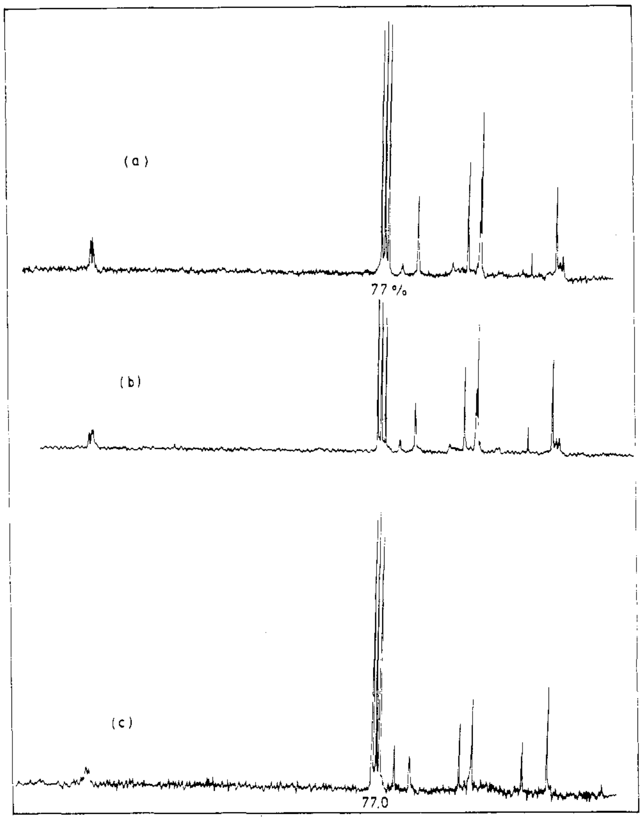

Figure 6. ^{13}C NMR spectra (25.05 MHz) of glycidyl methacrylate (A)-isobutyl acrylate (B) copolymers with A = 76.6% (a), 65.6% (b), and 43.6% (c).

Table V
Monomer Reactivity Ratio Values of Copolymer Systems

copolymer system	r_1	r_2
GMA (1)-nBA (2)	1.608	0.252
GMA (1)-iBA (2)	1.397	0.325

Monomer Sequence Distributions in the Copolymers. The NMR spectra of the copolymers (Figures 5 and 6) reveal the effect of the sequence distribution of monomers on the spectral pattern. The splitting pattern is also influenced by the composition of the copolymers. In both copolymer systems, sequence distribution effects are observed about ^{13}C resonances of the α-methyl group of the GMA unit. Unfortunately, in either case, it has been obscured by the comonomer. In the case of nBA-containing copolymers, the C-2 CH_2 carbon atom of the side alkyl group overlaps the α-methyl resonance of GMA. Similarly, in the case of iBA-containing polymers, the ester methyl groups of iBA overlap the α-methyl ^{13}C resonance peaks (Figure 3 and 4). However, the carbonyl carbon resonances of the homopolymers indicate that these carbon atoms resonate at different frequencies, the chemical shift

Table VI
GMA (A)-Centered Triad Fractions of GMA–nBA and GMA–iBA Copolymers

sample	A/B mole ratios	rel intens AAA	rel intens AAB	rel intens BAB	resp chem shifts, ppm
			GMA–nBA System		
nB1	3.820	0.641	0.207	0.152	175.5–175.9, 176.65, 176.96
nB2	1.970	0.362	0.321	0.317	175.74, 176.05, 176.96
nB3	0.937	0.344	0.347	0.308	175.01, 175.49, 175.68
			GMA–iBA System		
iB1	3.273	0.515	0.316	0.17	175.95–176.1, 176.73, 177.02
iB2	1.940	0.368	0.355	0.297	175.9, 176.68, 177.00
iB3	0.733				

of nBA and iBA being at higher field compared to GMA. This provides a way for assigning the sequence distribution of copolymers. Unlike the spectra of the homopolymers of nBA and iBA, which show a single resonance peak due to the carbonyl carbon atom, the copolymer spectra appear to be well-resolved multiplets, showing both sequence distribution and configurational effects. The backbone quaternary carbon of the GMA unit also shows a triad splitting in the copolymer spectra. However, the intensity pattern of this carbon atom resonance does not change with a change in copolymer composition, indicating it to be independent of the copolymeric effect. This has been more reasonably assigned to GMA-based homotriad sequences (AAA). This cotactic triad is also reflected in the carbonyl carbon resonances in the copolymers containing a higher percentage of GMA. The resolution of this quaternary carbon resonance diminished with decreasing content of GMA in the copolymers.

The assignment of these ^{13}C carbonyl resonances has been attempted in terms of A- and B-centered triads. The number-average sequence lengths ($\bar{N}_1$ and $\bar{N}_2$) have been calculated theoretically by using the reactivity ratios and feed values. The assumption has been made on the basis of the terminal copolymer model, which obeys a first-order Markov process.[19,20] The following relationships have been employed for calculating the number-average sequence lengths:

$$\bar{N}_1 = \frac{1}{P_{12}} = r_1\frac{[\mathrm{M}_1]}{[\mathrm{M}_2]} + 1 \qquad (1)$$

$$\bar{N}_2 = \frac{1}{P_{21}} = r_2\frac{[\mathrm{M}_2]}{[\mathrm{M}_1]} + 1 \qquad (2)$$

where $\bar{N}_1$ and $\bar{N}_2$ are the number-average sequence lengths of the monomers 1 (GMA) and 2 (nBA or iBA), respectively. M_i is the mole fraction of the monomer in the initial feed and r_i is the corresponding reactivity ratio. P_{12} and P_{21} are the conditional probabilities for cross propagation.

Semiquantitative estimation of various fractions of A- and B-centered triads has been made from direct peak area measurements in the carbonyl carbon regions. It has further been observed that while the GMA unit gives a well-resolved triad showing a tacticity phenomenon, the peaks due to nBA and iBA are overlapping, and with an increase in their concentration, the overall resolution of the spectra diminishes (Figures 7 and 8).

In the case of GMA–nBA copolymers (Figure 7a), the carbon resonances due to carbonyl in the range 174–177 ppm have been assigned to various triad fractions. The resonances at 175.5–175.9 ppm have been assigned to the triad consisting of various cotactic sequences. The presence of cotactic triads is further substantiated by the quaternary carbon resonance, which has been assigned to the GMA-centered cotactic triad having a higher syndiotactic content. This assignments is based on the quaternary carbon resonance of poly(GMA), which shows similar intensity lines. The peaks at 176.65 and 176.96 ppm are due to AAB and BAB triads, respectively. The resonances due to B(nBA)-centered triads occur in the 174.5–175.02-ppm region. The peak at 175.02 ppm has been assigned to the ABA triad, and other B-enriched triads have negligible intensity due to the lesser concentration of these components in this copolymer. The triad distributions in the other copolymers containing higher amounts of nBA have been calculated similarly (Figure 7b,c). The values of these fractions are summarized in Table VI.

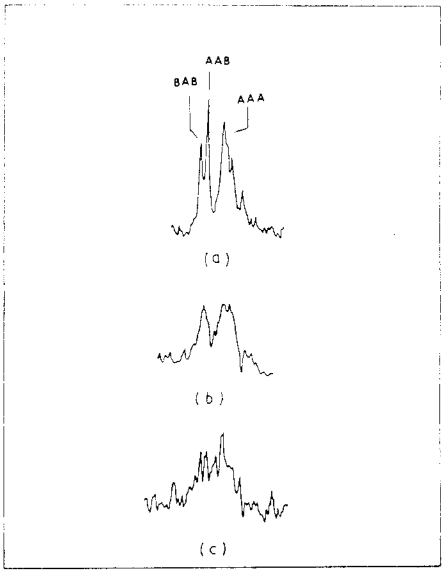

Figure 7. Expanded spectra of the carbonyl carbon region of GMA–nBA copolymers with GMA 79% (a), 67.6% (b), and 48% (c).

Figure 8 shows the expanded version of the carbonyl and quaternary carbon atom resonances of the GMA–iBA copolymers. In Figure 8a, with 76% GMA, the carbonyl carbon resonances in the region 175.95–176.1 ppm have been assigned to the AAA triad. In this case, the cotacticity effect is taken into account and the three peaks with decreasing field strength have been assigned to rr, mr, and mm cotactic triad due to AAA block in the copolymer. This assignment is further supported by the fact that the quaternary carbon resonates in a similar fashion, giving higher syndiotactic content at upfield (44.75–45.4 ppm). The peaks at 176.73 and 177.02 ppm have been assigned to AAB and BAB, respectively. The resonances at 175.51 and 175.75 ppm, which are well separated, have been assigned to (BBB + BBA) and ABA sequences, respectively. The quantitative estimation of various A-centered triads has been done by considering cotactic components for the AAA triad. In Figure 8b (67% GMA), the peak due to AAA triad appears at 175.9 ppm, which is blurred and does not reveal any cotacticity. It is, however, observed at the quaternary carbon resonance. The peaks at 176.68 and

Table VII
Number-Average Sequence Lengths of GMA–nBA and GMA–iBA Copolymers

	$\bar{N}_1$		$\bar{N}_2$	
sample	exptl	calcd from react ratios	exptl	calcd from react ratios
		GMA–nBA System		
nB1	3.91	4.31	1.02	1.11
nB2	2.14	2.44	1.11	1.28
nB3	1.92	1.65	1.80	1.65
		GMA–iBA System		
iB1	4.16	3.94	1.14	1.16
iB2	2.15	2.26	1.16	1.36
iB3		1.54		1.84

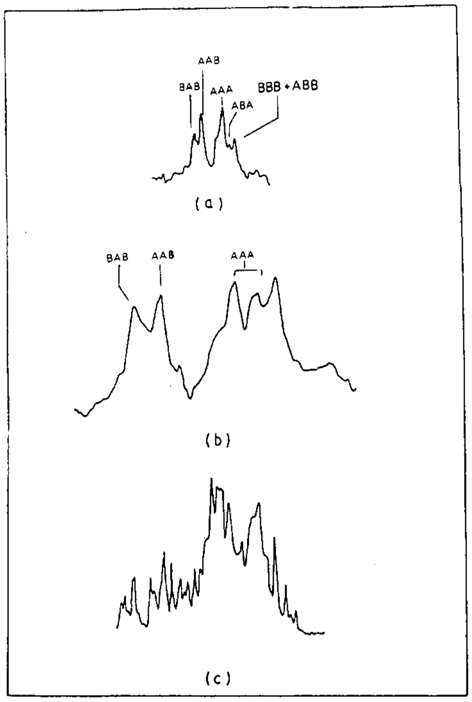

Figure 8. Expanded spectra of the carbonyl carbon region of GMA–iBA copolymers with GMA 76% (a), 65% (b), and 43% (c).

176.97 ppm have been assigned to AAB and BAB triads, respectively. The peaks at 175.47 and 175.71 ppm have been assigned due to (BBB + ABB) and ABA triads, respectively. All the values of A-centered triads are summarized in Table VI. With lesser content of GMA, the copolymer (Figure 8c) does not show any clear resolution of the carbonyl peaks and quantitative estimation of the various triads was not possible.

Taking the various triad fractions into account, the number-average sequence lengths have been determined experimentally. These values have been compared with those calculated from reactivity ratio data. To calculate the sequence length from triad fractions, the pertinent equations are[21]

$$\bar{N}_1 = (f_{212} + f_{112}/2)^{-1} \quad (3)$$

$$\bar{N}_2 = (m_2/m_1)\bar{N}_1 \quad (4)$$

where $f_{111} + f_{211} + f_{212} = 1$ for various GMA(1)-centered triads and m_1 and m_2 are the mole fractions of monomers 1 and 2 in the copolymer. The values of the number-average sequence length obtained from reactivity ratios as well as determined experimentally from triad fractions for varying copolymer conditions are shown in Table VII. The values are in excellent agreement, which supports the assignment of peaks to various monomer sequence triads.

It may be concluded that this polymerization process involves random propagation and that GMA is more reactive than alkyl acrylates. Moreover, GMA forms steric blocks in the copolymer chain with most units in a syndiotactic mode of arrangement.

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Registry No. (GMA)·(nBA) (copolymer), 26660-36-6; (GMA)·(iBA) (copolymer), 87106-09-0.

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