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Analysis of sequence distribution in methyl methacrylate–methyl acrylate copolymers by ^{13}C NMR spectroscopy

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Abstract

Methyl methacrylate (MMA)–methyl acrylate (MA) copolymers, prepared in bulk at 50 °C using AIBN as initiator, were characterized by 150 MHz ^{13}C NMR spectroscopy, including use of the Distortionless Enhancement by Polarization Transfer (DEPT) experiment to obtain methylene and methine carbon resonances as subspectra. Dyad, triad, tetrad and partial pentad distributions were measured from the α-methyl, methine and methylene carbon resonances. These were in good agreement with distributions calculated for the copolymers based on monomer feed compositions, conversions and reactivity ratios of 2.60 and 0.27 for methyl methacrylate and methyl acrylate, respectively.

Keywords: ^{13}C NMR; Acrylate copolymer; Methacrylate copolymer

1. Introduction

Knowledge about the compositions and arrangements of monomer units in copolymers derived from acrylate and methacrylate monomers is important for studies on their physical properties and the chemistry involved in their formation. A number of papers describe the use of ^{1}H- and ^{13}C NMR spectroscopy to characterize the compositions and microstructures of such copolymers. The α-methyl proton resonance patterns of methyl methacrylate–methyl acrylate copolymers have been studied by several groups [1–3], but it has been difficult to obtain quantitative sequence information from them because they are badly overlapped. Methoxy proton resonance was shown to be useful for characterizing MMA-centered sequences in butyl acrylate–MMA copolymers [4] and the compositions of ethyl acrylate–butyl methacrylate copolymers have also been investigated by ^{1}H NMR [5]. Most investigators have employed ^{13}C NMR to characterize acrylate–methacrylate copolymers [4,6–16] particularly ethyl acrylate–methyl methacrylate [4,6–10] and butyl acrylate–methyl methacrylate [4,11,12] copolymers. Mostly, the carbonyl and quaternary carbon resonance patterns have been investigated in these studies, but the α-methyl carbon resonances have also been studied in a few instances.

The purpose of the present paper is to report an investigation of the 150 MHz methylene, methine and α-carbon resonances of methyl acrylate–methyl methacrylate copolymers and their use to characterize the distributions of monomer unit sequences in them. With the exception of a dissertation authored by one of us [17], there are no reports on the ^{13}C NMR spectra of methyl acrylate–methyl methacrylate copolymers. The copolymers studied were prepared in low conversions by bulk polymerization of methyl acrylate–methyl methacrylate mixtures using AIBN as initiator. In this study, the Distortionless Enhancement by Polarization Transfer (DEPT) pulse sequence [18] was used to separate the methine and methylene carbon resonances. These were then assigned and used to characterize dyad, triad, tetrad and partial pentad sequences in the copolymers. Matlengiewicz et al. recently called attention to the value of β-CH_2 carbon resonances in ethyl acrylate–methyl methacrylate copolymers for microstructure characterization [7]. Our results add support to this approach for acrylic copolymer microstructure analysis and also show that the methine carbon resonance patterns are very valuable for this purpose.

2. Experimental

2.1. Copolymer synthesis

Methyl methacrylate was distilled under vacuum (bp 37 °C/70 mmHg; lit. bp 47 °C/100 mmHg) [19]. Methyl acrylate was fractionally distilled under vacuum (bp

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Table 1
Preparation of methyl methacrylate–methyl acrylate copolymers

Methyl methacrylate (mol%)			Conversion (wt%)	Polymerization time (min)
Monomer mixture	Copolymer			
	Experimental[a]	Calculated[b]		
79.9	90	91.4	2.9	120
70.0	85	86.3	2.3	120
59.9	80	80.3	4.4	180
49.9	75	73.4	5.2	180
40.0	67	65.7	2.8	210
20.0	43	43.5	4.2	130

[a] Data from 150 MHz ^{13}C NMR spectra.
[b] Calculated using wt% conversions, monomer feeds and reactivity ratios of 2.60 and 0.27 for methyl methacrylate and methyl acrylate, respectively.

26 °C/89 mmHg; lit. bp 28 °C/100 mmHg) [19]. The distillates were stored in a freezer prior to being used. The free radical initiator AIBN was recrystallized from methanol, dried in a desiccator, and stored in a freezer until used.

A series of methyl methacrylate (MMA)–methyl acrylate (MA) copolymers, poly(methyl methacrylate), PMMA, and poly(methyl acrylate), PMA, were prepared in low conversion at 50 °C from bulk monomers using AIBN (0.05 mol%) as initiator. The polymerization mixtures were diluted with acetone and poured into a large volume of a water–methanol mixture to precipitate the copolymers. They were washed with methanol and vacuum dried to constant weight. Table 1 lists the compositions of the copolymerization mixtures, the polymerization times, the copolymer compositions, and the yields of the copolymers obtained.

2.2. ^{13}C NMR studies

^{13}C NMR spectra were recorded at 150 MHz at 30 °C using a Varian Unity*plus* 600 NMR spectrometer. Measurements were made on 10% w/v solutions of polymer. The quantitative spectra were obtained with a 15 s delay (D1), a 90° pulse width and a gated decoupler (DM = NNY). The intensities of each resonance for the homopolymers of methyl methacrylate and methyl acrylate were compared with the expected values to assure that the spectra were suitable for quantitative work.

150 MHz DEPT [18] spectra were recorded at 150 MHz at 30 °C using a Varian Unity*plus* 600 NMR spectrometer to separate the backbone methylene and methine carbon resonances of the polymer samples. The parameters used for the experiments were as follows: 0.497 s acquisition time, 7915 Hz spectral window, 16.2 μs ^{13}C pulse width, 45.0 μs decoupler 90° pulse width, 3.5 ms τ delay (J_{CH} = 140 Hz). The experiment was conducted by varying the third pulse width (θ) for ^{1}H at 45, 90 and 135°.

2.3. Reactivity ratio determinations

Monomer reactivity ratios for methyl acrylate, r_A, and methyl methacrylate, r_M, were calculated from the data in Table 1 using the non-linear least squares method described by Mortimer and Tidwell [20].

2.4. Sequence distribution calculations

Copolymer compositions, *n*-add distributions of monomer sequences, monomer centered triad fractions and monomer centered pentad fractions were calculated from copolymerization mixture composition data, conversions and reactivity ratios of 0.27 and 2.60 for methyl acrylate and methyl methacrylate, respectively, using the computer program previously described by Harwood [21].

3. Results and discussion

Fig. 1 shows the ^{13}C NMR spectra of poly(methyl methacrylate), poly(methyl acrylate) and a 75/25 MMA/MA copolymer. The observed relative intensities of the resonance peaks for the homopolymers were in good agreement with the expected values, assuring that the conditions employed to record the polymer and copolymer spectra were adequate to obtain quantitative ^{13}C NMR data. In the spectrum of the copolymer, the resonances of carbonyl, methine and α-methyl carbons are observed in the same regions as in the homopolymers, but signals not evident in the homopolymer spectra are also present. These signals provide information about how the monomer units are arranged along the copolymer chain. Particular interest may be drawn to the resonance of backbone methylene carbons which occurs as many new signals covering a range of about 22 ppm in chemical shifts (34–56 ppm). These signals are rich in information about monomer unit sequence distributions.

In studies on the copolymer spectra, their compositions were determined from the carbonyl and α-methyl carbon resonance spectra and used to calculate monomer reactivity ratios for the methyl acrylate (A)–methyl methacrylate (M) copolymerization system. The values obtained were 0.27 ± 0.13 for methyl acrylate and 2.60 ± 0.07 for methyl

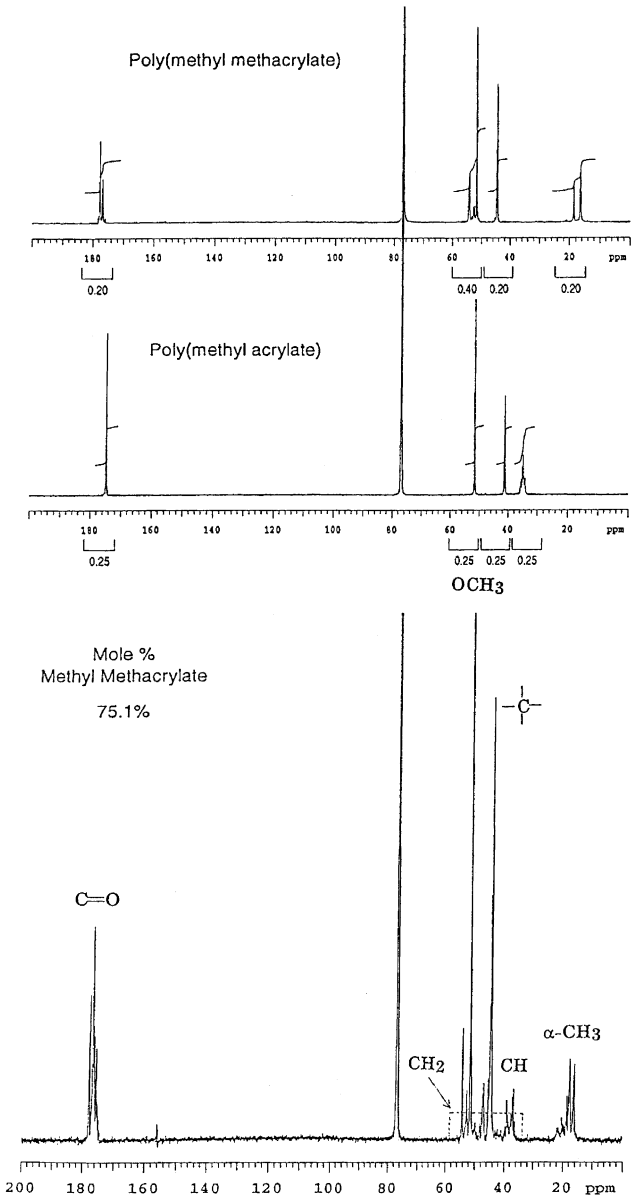


Fig. 1. 150 MHz ^{13}C NMR spectra of poly(methyl methacrylate), poly(methyl acrylate) and a MMA–MA copolymer containing 75.1 mol% methyl methacrylate.

methacrylate. These were then used to calculate monomer contents and monomer unit sequence distributions for the copolymers. As can be seen in Table 1, copolymer compositions calculated this way agree well with experimentally determined compositions. The α-methyl carbon resonance patterns of the copolymers were then analyzed in terms of methyl methacrylate centered triad fractions and the probabilities of *meso* MM placements (σ). The DEPT experiment [18] was then used to record methine carbon and methylene carbon resonances for the copolymers. These were then analyzed in terms of sequence distribution information calculated for the copolymers. The DEPT experiment has been employed successfully in many previously reported copolymer microstructure studies [22–30] to separate methine or methoxy and methylene carbon resonances of copolymers.

3.1. Copolymer compositions

The resonances of carbonyl and α-methyl carbons are well separated from other resonances and their relative resonance areas can be easily measured. Since the carbonyl carbon resonance is due to both monomers, but the α-methyl carbon resonance is due only to methyl methacrylate units, the ratio of the relative areas of α-methyl ($A_{\alpha\text{-methyl}}$) to carbonyl (A_{carbonyl}) carbon resonance can be used to calculate the mole fraction of methyl methacrylate (F_M) in the copolymer. This is easily expressed by the following equation.

$$\frac{A_{\alpha\text{-methyl}}}{A_{\text{carbonyl}}} = \frac{F_M}{F_M + (1 - F_M)} = F_M$$

Alternatively, the copolymer compositions can be obtained from the ratio of the α-methyl carbon resonance area to the combined areas of all other resonances except the α-methyl and carbonyl carbon resonances, (A_{rest}) by using the following relationships.

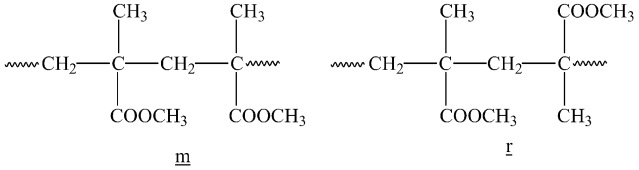
$$\frac{A_{\alpha\text{-methyl}}}{A_{\text{rest}}} = \frac{F_M}{3F_M + 3(1 - F_M)} = \frac{F_M}{3}$$

$$F_M = 3\left(\frac{A_{\alpha\text{-methyl}}}{A_{\text{rest}}}\right)$$

The copolymer compositions obtained by these two approaches agreed within 2%, indicating that the spectra were suitable for quantitative study. For simplicity, the copolymer compositions were calculated by the first expression using the resonance areas of the carbonyl and α-methyl carbons. The compositions of the copolymers determined this way are listed in Table 1.

3.2. Sequence analysis

The resonances of various carbons in the copolymers can be influenced by monomer units, monomer units present as nearest and next nearest neighbors and by stereochemical effects. To simplify notation, methyl methacrylate units will be represented by M and methyl acrylate units will be represented by A. Since only the configurations of M–M placements seem to have a significant effect on the resonances of carbons in sequences containing them, Bovey's σ parameter [31] will be used to represent the probability an M–M placement is *meso* or *m*, as defined below.



The resonances of carbonyl, methine and α-methyl

carbons in the copolymers can be related to the relative amounts of monomer units centered in various triad or pentad sequences. These will be referred to as triad or pentad fractions and designated, for example, as f_{AAA}, $f_{(AAM+MAA)}$ and f_{MAM} for methyl acrylate centered triads or as f_{AAAAA}, f_{MAAAM} or f_{AMAMA} for some of the methyl acrylate centered pentads. Methods for calculating these quantities for copolymerization data or copolymer characterization parameters are covered abundantly in the literature. In this work, they were calculated using the computer program we have described previously [21].

When M–M placements are present in the triads, it is necessary to also indicate their configurations. Thus, M-centered triad concentrations will be represented as mm-MMM, (mr + rm)MMM, rr-(MMM), m-(MMA + AMM), r-(MMA + AMM) and AMA triads, their relative amounts being represented as appropriate triad fractions.

Backbone methylene carbons must be viewed as connecting monomer units rather than being associated with a specific monomer unit. They are present in the center of various dyad, tetrad or larger even-numbered sequences of monomer units. The relative amounts of such carbons or sequences can be represented by probabilities such as $P(AA)$, $P(AM + MA)$, m-$P(MM) = \sigma P(MM)$ and r-$P(MM) = (1 - \sigma)P(MM)$ for dyads. In this investigation, attempts were made to measure dyad distributions from the backbone methylene carbon resonance patterns.

On the basis of the above considerations, the carbonyl, α-methyl, methylene and methine carbon resonances of the copolymers may now be discussed.

3.3. Carbonyl carbon resonance

Since methyl methacrylate and methyl acrylate both contain carbonyl carbons, and their resonances overlap, the resonance patterns of carbonyl carbons in the copolymers are rather complicated combinations of both M-centered and A-centered triad or pentads, including various possible configurations. This makes interpretation of the carbonyl carbon resonance region very difficult.

Other investigators [8,9] have relied on empirical chemical shift rules and spectral simulation techniques to make assignments for the carbonyl carbon resonances in related polymers and have been reasonably successful. We have elected to ignore this region because of the complexity involved, but recognize and appreciate the value of the approach others have used in studies on the carbonyl carbon resonances.

3.4. α-Methyl carbon resonance patterns

Previously, the α-methyl carbon resonance of ethyl acrylate–methyl methacrylate copolymers was reported [10] to consist of five resonance areas that can be attributed to M units centered in rr-, (mr + rm)-, and mm- configurations of MMM triads, (MMA + AMM) and MAM triads. The α-methyl carbon resonances of methyl acrylate–methyl methacrylate copolymers are similar to those reported for ethyl acrylate–methyl methacrylate copolymers but we prefer to take into account separate contributions from r- and m- (MMA + AMM) triads. Fig. 2 shows the α-methyl carbon resonance patterns of poly(methyl methacrylate) and of several methyl acrylate–methyl methacrylate copolymers. It proved convenient to divide the patterns into five areas that were assigned as shown in Table 2.

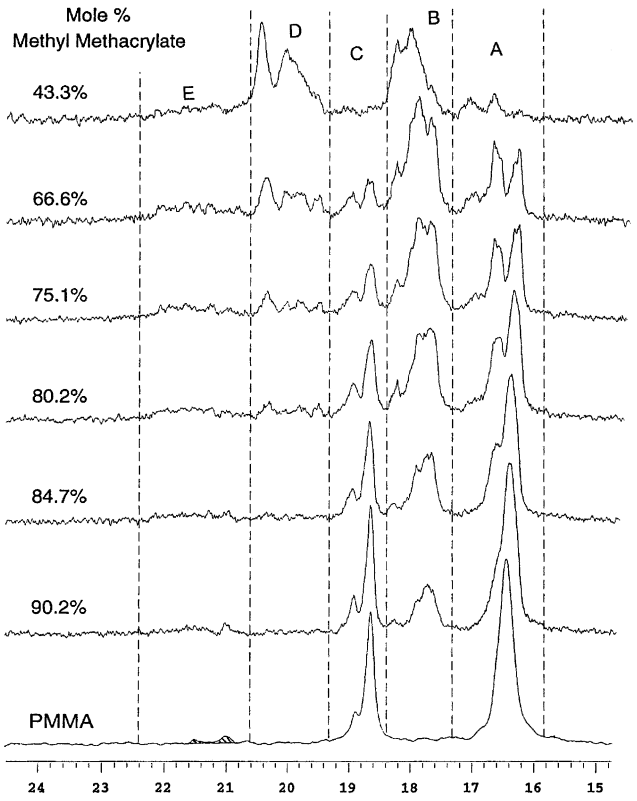


Fig. 2. 150 MHz α-methyl carbon resonance patterns of poly(methyl methacrylate) and MMA–MA copolymers.

Support for these assignments is provided by the fact that the resonance of rr-, (mr + rm)- and mm- triads in poly (methyl methacrylate) occur in areas A, C and E and by the fact that the ratios of areas A to C and of B to E were approximately two and four, respectively in all the spectra. Based on the value of σ determined for PMMA in this study (0.20), and neglecting the minor contribution of mm-MMM triad resonance to all the spectra, the ratio of areas A to C and of B to E should be two and four, respectively.

Table 2
Assignment of α-methyl carbon resonance patterns (r and m refer to configurations of M–M placements in these triads)

Resonance area	Assignment
A (15.8–17.3 ppm)	rr-MMM
B (17.3–18.4 ppm)	r-(MMA + AMM)
C (18.4–19.3 ppm)	(rm + mr)-MMM
D (19.3–20.6 ppm)	AMA
E (20.6–22.4 ppm)	mm-MMM + m-(MMA + AMM)

Table 3
Methyl methacrylate-centered triad fractions determined from the α-methyl carbon resonance patterns

Methyl methacrylate (mol%)	Triad fractions					
	Observed[a]			Calculated[b]		
	MMM	MMA + AMM	AMA	MMM	MMA + AMM	AMA
90	0.79	0.18	0.03	0.830	0.162	0.008
85	0.69	0.26	0.05	0.735	0.245	0.020
80	0.58	0.35	0.07	0.628	0.329	0.043
75	0.48	0.41	0.11	0.513	0.406	0.080
67	0.37	0.47	0.16	0.398	0.466	0.136
43	0.15	0.46	0.39	0.149	0.474	0.376

[a] $\sigma = 0.20$.
[b] On the basis of reactivity ratios of 2.60 and 0.27 for methyl methacrylate and methyl acrylate, respectively.

Methyl methacrylate centered triad fractions were calculated from the normalized α-methyl carbon resonance areas as follows:

$$f_{MMM} = \text{Area A}/(1-\sigma)^2 \quad \text{or}$$

$$(\text{Area A} + \text{Area C})/(1-\sigma^2)$$

$$f_{(MMA+AMM)} = \text{Area B} + [\text{Area E} - \sigma^2 f_{MMM}]$$

$$f_{AMA} = \text{Area D}$$

Table 3 compares M-centered triad fractions with theoretical values that were calculated [21] from reactivity ratios, monomer feed compositions and conversions used to make the copolymers. The good agreement between the measured and calculated triad fractions supports the assignments.

In addition to providing information about M-centered triad fractions, the α-methyl carbon resonance region also provided information about several M-centered pentads. Fig. 3 shows assignments for the fine structure observed in the rr-MMM triad region. Table 4 shows that there is reasonable agreement between the measured relative intensities of the three general areas and those calculated from MMMMM, (MMMMA + AMMMM) and AMMMA pentad fractions.

3.5. Methine carbon resonance patterns

Just as the α-methyl carbon resonance patterns provide valuable information about M-centered triad distributions, the methine carbon resonance patterns provide information about A-centered triad distributions. The resonances occurring between 33 and 55 ppm in the ^{13}C NMR spectra of the copolymers contain signals due to the backbone methylene, methoxy, quaternary backbone and methine carbons. For the analysis of backbone methylene and methine carbon resonances, it was necessary to observe those resonances separately to obtain useful sequence distribution information. This was achieved by the use of DEPT pulse sequence [18] which is a ^{13}C NMR method that separates carbon resonance of CH, CH_2 and CH_3 carbons by varying the pulse width of the ^1H pulse by 45, 90 and 135°. In this method, the resonance due to quaternary backbone carbons is suppressed and the resonance of methine carbons is observed separately from the resonance of backbone methylene carbons. Fig. 4 shows this approach. The bottom spectrum (a) contains the resonance signals of methine and methoxy carbons overlapped with the resonance of methylene carbons. The resonance of quaternary backbone carbons that would normally be observed as an intense group of signals at 44–45 ppm is absent from the spectrum. The middle spectrum (b), which is edited to show only CH carbon resonances, shows the resonance of the methine carbons. Also the top spectrum (c), which is a CH_2- only subspectrum shows the resonance of backbone methylene carbons. It was fortunate that this technique could be used to separate the methine and methylene carbon resonances since those resonances are additional valuable sources of information concerning the copolymer structures.

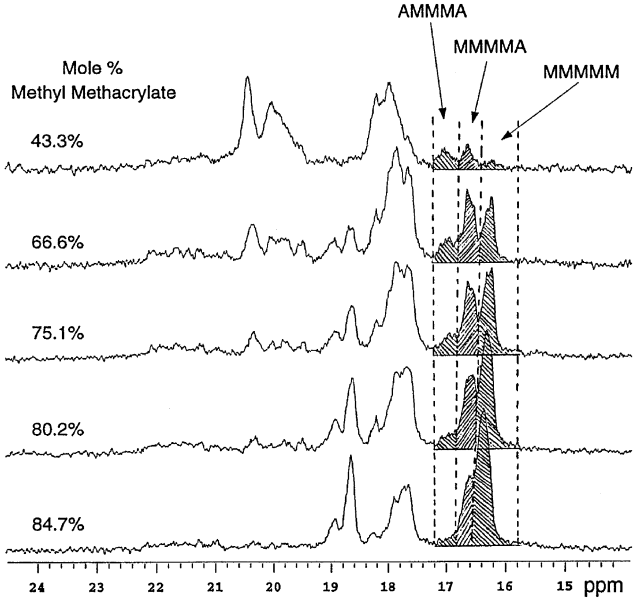


Fig. 3. 150 MHz α-methyl carbon resonance patterns of pentad structures for MMA–MA copolymers.

Table 4
Observed and calculated relative areas of α-methyl proton resonances observed in the rr-MMM triad region (region A)

Methyl methacrylate (mol%)	Observed			Calculated[a]		
	MMMMM	MMMMA	AMMMA	MMMMM	MMMMA	AMMMA
85	0.29	0.12	0.03	0.346	0.115	0.010
80	0.21	0.13	0.04	0.253	0.132	0.017
75	0.14	0.12	0.04	0.169	0.134	0.026
67	0.09	0.11	0.04	0.101	0.118	0.035
43	0.02	0.04	0.03	0.014	0.045	0.034

[a] On the basis of reactivity ratios of 2.60 and 0.27 for methyl methacrylate and methyl acrylate, respectively, and $\sigma = 0.20$.

Fig. 5 shows DEPT methine carbon resonance subspectra that were observed for the copolymers. The three general resonance areas observed in these spectra were attributed to A units that are centered in AAA, (AAM + MAA) and MAM triads. Due to the fact that the resonance observed in area A decreased constantly as the mole percent of methyl methacrylate decreased, and the fact that the MAM triad predominated when the copolymer contained mostly methyl methacrylate, the resonance observed in area A must be assigned to MAM triads. In a similar way, the resonance observed in area C must be assigned to AAA triads since this area was very small in the spectra of copolymers containing mostly methyl methacrylate units and it increased constantly as the content of methyl acrylate in the copolymer increased. The resonances observed in area B were then assigned to (MAA + AAM) triads. A-centered triad fractions were determined from the relative areas of the A, B and C areas. These are listed in Table 5 along with calculated values based on the reactivity ratios, monomer mixture compositions and conversions.

The comparison shows generally good agreement between the experimental areas and calculated A-centered triad fractions. The discrepancies observed at high MAM triad fraction values are probably due to the experimental difficulty of measuring C resonance areas which are small when the copolymers have high methyl methacrylate contents. There is generally good agreement between the experimental areas and calculated A-centered triad fractions, although it seems that about 6% of the MAM resonance may be occurring in area B, at least in the copolymers with high MMA contents.

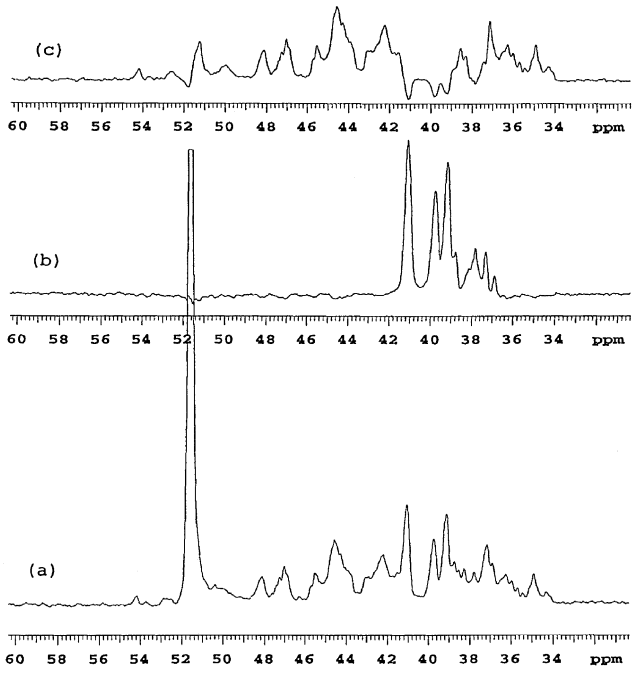


Fig. 4. DEPT NMR spectra of a MMA–MA copolymer containing 43.3 mol% methyl methacrylate: (a) methoxy, methylene and methine resonances, (b) methine resonance, and (c) methylene resonance.

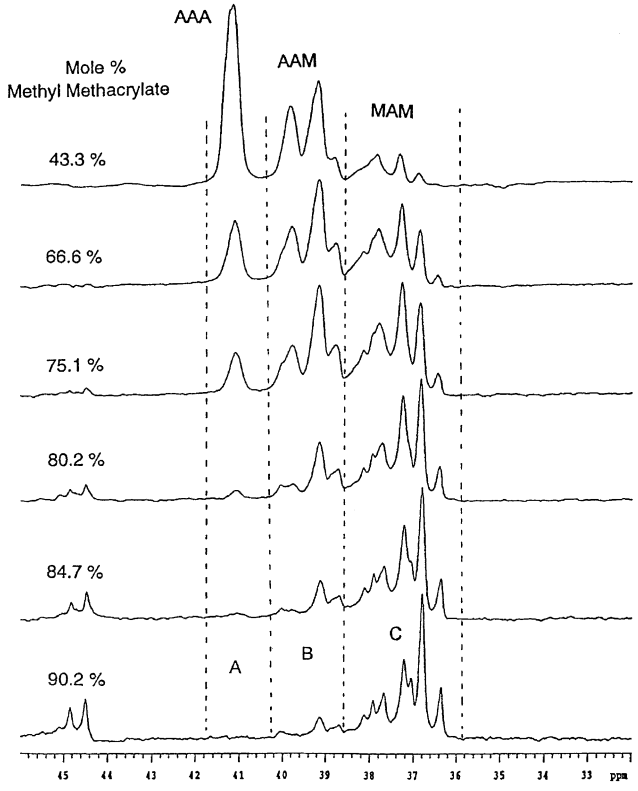


Fig. 5. 150 MHz methine carbon resonance patterns of MMA–MA copolymers.

Table 5
Methyl acrylate-centered triad fractions determined from the methine carbon resonance patterns

Methyl methacrylate (mol%)	Triad fractions					
	Observed[a]			Calculated[b]		
	AAA	AAM	MAM	AAA	AAM	MAM
90	0.02	0.17	0.82	0.004	0.120	0.876
85	0.02	0.24	0.75	0.011	0.187	0.802
80	0.04	0.28	0.67	0.024	0.262	0.714
75	0.06	0.33	0.60	0.047	0.340	0.613
67	0.10	0.40	0.50	0.085	0.413	0.502
43	0.29	0.49	0.23	0.297	0.498	0.223

[a] Measured from the methine carbon resonance DEPT subspectra.
[b] On the basis of reactivity ratios of 2.60 and 0.27 for methyl methacrylate and methyl acrylate, respectively.

The fine structure observed in areas A and B of the methine carbon resonance region could provide information about A-centered pentads, larger A-centered n-ads or stereosequence distributions, but no additional assignments have been made.

3.6. Backbone methylene carbon resonance patterns

The resonance of backbone methylene carbons in the copolymers, being observed over a 20 ppm range, can provide valuable information about dyad, tetrad or even larger monomer sequence and stereosequence distributions. This was demonstrated for ethyl acrylate–methyl methacrylate copolymers by Matlengiewicz et al. [7] who developed empirical rules for calculating methylene carbon chemical shifts based on connected monomer units, their nearest neighbors and their stereochemistries. The 20 parameters involved were evaluated by comparing simulated spectra based on them and calculated sequence distributions with experimental spectra and using a least squares routine to adjust the parameters until the best agreement was obtained. A total of 72 lines were used to represent the contributions of the methylene carbons in various tetrads to the spectrum.

Our approach was simpler than that of Matlengiewicz et al. in that we did not attempt to incorporate stereosequence effects into our analysis. Instead, we used Grant–Paul parameters [32] to calculate the chemical shifts of methylene carbons centered in the 10 possible tetrads. This led to the results in Table 6, which groups the tetrads in the order of decreasing chemical shift. This order was used to group the resonances into contributions from dyads and some tetrads as is shown in Fig. 6. The resonance patterns observed for copolymers with either high (57%) or low (10%) acrylate contents were also used in making assignments for MMMM, (MMMA + AMMM), (MMAM + MAMM), AAAA, AMMA + AAMA and (MAAA + AAAM) tetrads because such copolymers contained only a few tetrads in high concentration. By noticing changes in the relative amounts of various resonance areas with changes in copolymer composition and by comparing relative resonance areas with tetrad distributions calculated for the copolymers, other tetrad assignments were developed. Table 6 lists the assignments made. In general, they correspond very well to the assignments of Matlengiewicz [7], except that the range of chemical shifts observed for the methyl acrylate–methyl methacrylate copolymers is slightly broader than that for ethyl acrylate–methyl methacrylate copolymers.

Table 7 compares the observed resonance areas with those calculated based on the assignments given in Table 6 and tetrad probabilities calculated for the copolymers from monomer feed compositions, conversions and monomer reactivity ratios of 2.70 and 0.27 for methyl

Table 6
Assignment of methylene carbon resonance areas

Chemical shift range (ppm)			
MA–MMA copolymers (this work)		EA–MMA copolymers [7]	
MMMM + MMMA + AMMM	51.2–55.2	MMMM	51.76–54.50
		MMME + EMMM	50.28–52.95
AMMA	48.2–51.2	EMME	48.20–51.20
MMAM + MAMM	46.8–48.2	MMEM + MEMM	45.80–46.75
MMAA + AAMM + AMAM + MAMA	44.0–46.7	MMEE + EEMM + EMEM + MEME	43.85–45.10
AMAA	40.6–43.0	EMEE + EEME	42.35–42.85
MAAM	36.7–39.0	MEEM	39.20–40.10
MAAA + AAAM	35.0–36.7	MEEE + EEEM	36.35–38.45
AAAA	34.0–35.0	EEEE	33.50–37.20

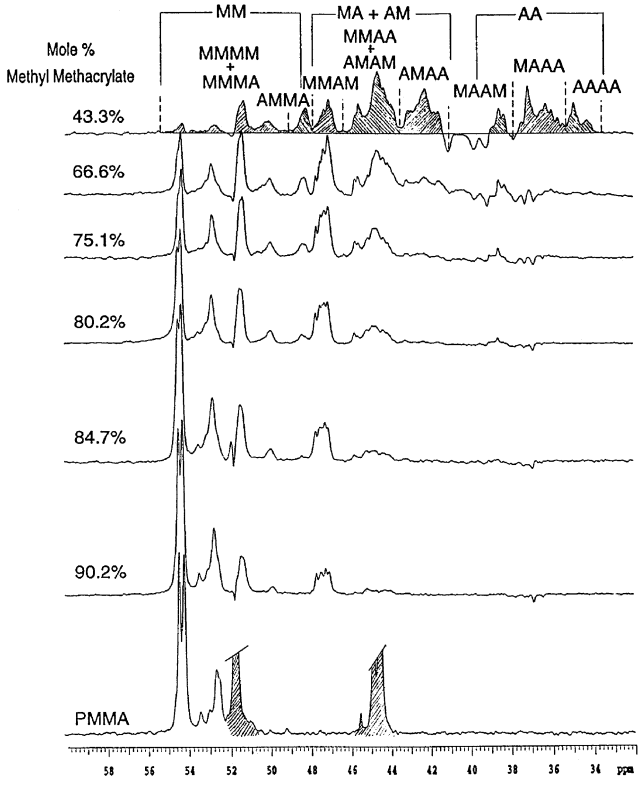


Fig. 6. 150 MHz methylene carbon resonance patterns of poly(methyl methacrylate) and MMA–MA copolymers. Resonances due to quaternary and methoxy carbons in the PMMA spectrum are shaded.

methacrylate and methyl acrylate, respectively. The agreement seems satisfactory.

Dyad distributions were calculated for the copolymers by adding tetrad distributions and copolymer compositions were calculated from the dyad distributions. The following relationships were used:

$$P(\mathrm{AA}) = P(\mathrm{MAAM}) + P(\mathrm{MAAA} + \mathrm{AAAM}) + P(\mathrm{AAAA})$$

$$P(\mathrm{AM} + \mathrm{MA}) = P(\mathrm{MMAM} + \mathrm{MAMM}) + P(\mathrm{MMAA} + \mathrm{AAMM}) + P(\mathrm{AMAM} + \mathrm{MAMA}) + P(\mathrm{AMAA} + \mathrm{AAMA})$$

$$P(\mathrm{MM}) = P(\mathrm{MMMM}) + P(\mathrm{MMMA} + \mathrm{AMMM}) + P(\mathrm{AMMA})$$

$$P(\mathrm{M}) = P(\mathrm{MM}) + \frac{1}{2}P(\mathrm{AM} + \mathrm{MA})$$

Table 8 lists the dyad distributions and methyl methacrylate contents of the copolymers that were determined from the tetrad distributions and compare them with calculated quantities. The agreement again is very satisfactory.

4. Conclusions

The 150 MHz ^{13}C NMR spectra of methyl acrylate–methyl methacrylate copolymers were used to characterize their compositions and various structural features. Reactivity ratios for the methyl methacrylate–methyl acrylate copolymerization were determined to be 2.60 ± 0.07 and 0.27 ± 0.13 for methyl methacrylate and methyl acrylate, respectively. The α-methyl carbon resonances of the copolymers provided information about M-centered triad distributions and some pentad distributions. The backbone methylene carbon and methine carbon resonances of the

Table 7
Comparison of experimental and calculated tetrad distributions determined from the methylene carbon resonance patterns

Methyl methacrylate (mol%)	Tetrad distributions							
	MM-centered		MA-centered			AA-centered		
	MMMM + MMMA	AMMA	MMAM	MMAA + AMAM	AMAA	MAAM	MAAA	AAAA
	Observed[a]							
90	0.83	0.01	0.11	0.04	0.00	–	–	–
85	0.72	0.02	0.15	0.09	0.01	–	–	–
80	0.60	0.03	0.19	0.15	0.03	0.01	–	–
75	0.49	0.04	0.20	0.21	0.04	0.01	–	0.01
67	0.35	0.05	0.18	0.27	0.09	0.02	0.02	0.01
43	0.10	0.04	0.08	0.28	0.20	0.05	0.18	0.07
	Calculated[b]							
90	0.826	0.007	0.138	0.023	0.001	0.005	0.001	0.000
85	0.724	0.015	0.189	0.054	0.004	0.012	0.003	0.000
80	0.610	0.027	0.223	0.099	0.011	0.022	0.008	0.001
75	0.484	0.042	0.233	0.157	0.026	0.035	0.020	0.003
67	0.358	0.057	0.217	0.217	0.052	0.050	0.041	0.009
43	0.104	0.063	0.097	0.263	0.173	0.067	0.149	0.083

[a] Measured from the methylene carbon resonance DEPT subspectra.
[b] On the basis of reactivity ratios of 2.60 and 0.27 for methyl methacrylate and methyl acrylate, respectively.

Table 8
Dyad and copolymer compositions determined from the methylene carbon resonance patterns

Methyl methacrylate in copolymer[a] (mol%)	Dyad distributions						Methyl methacrylate in copolymer[b] (mol%)
	Observed[c]			Calculated[d]			
	MM	MA	AA	MM	MA	AA	
90	0.84	0.16	–	0.833	0.162	0.006	92
85	0.74	0.26	–	0.739	0.264	0.014	87
80	0.63	0.36	0.01	0.637	0.333	0.031	81
75	0.52	0.45	0.02	0.526	0.416	0.058	74
67	0.40	0.54	0.06	0.414	0.486	0.100	67
43	0.14	0.56	0.29	0.168	0.534	0.299	42

[a] Data determined from 150 MHz ^{13}C NMR spectra.
[b] Calculated from (1/2)*P*(AM + MA) and *P*(MM).
[c] Measured from the methylene carbon resonance DEPT subspectra.
[d] On the basis of reactivity ratios of 2.60 and 0.27 for methyl methacrylate and methyl acrylate, respectively.

copolymers were badly overlapped but could be separated by the DEPT experiment [18]. The DEPT subspectra of the methine carbon resonance patterns provided information about methyl acrylate-centered triad distributions. The DEPT subspectra of the backbone methylene carbon resonance patterns provided information about dyad and tetrad distributions. The measured sequence distributions were compared with theoretical values that were calculated from reactivity ratios, monomer feed compositions used and the conversions used to make the copolymers. Good agreement was obtained.

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