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NMR Study of the Chain Microstructure of P(MMA-co-MAA)

Abstract: The usefulness of proton and carbon-13 NMR spectroscopy in characterizing the chain microstructure (i.e., sequence distribution and tacticity) of methyl methacrylate-methacrylic acid (MMA-MAA) copolymers has been investigated. Because the comonomers have such similar structures, assessment of chain tacticity and sequence distribution required computer simulation of spectra to circumvent the problems of resonance overlap. The computer analysis used ^{1}H and ^{13}C chemical shift data on homopolymers and "sterically-defined" copolymers, Bernoullian and Markovian statistics for the respective tactic and sequence distributions, and a Lorentzian lineshape program to generate a theoretical spectrum. The generating parameters that produced simulation of both the ^{1}H and ^{13}C spectra provided the basis for describing the triad microstructure of the copolymers. This method of characterizing the microstructure was applied to copolymers of similar composition but different preparative histories. The results indicated that free-radical polymerization in toluene yielded a heterogeneous copolymer system while free-radical polymerization in tetrahydrofuran (THF) and emulsion polymerization yielded relatively homogeneous systems.

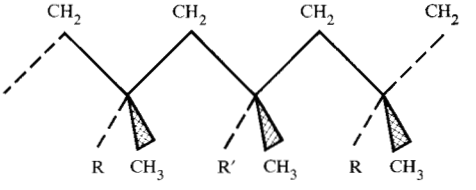
Introduction

It is well-established that the physical, mechanical, and, to some extent, chemical properties of vinyl and diene homopolymers depend upon their chain configuration or tacticity [1, 2], i.e., the stereochemical relationship between the repeat units. In copolymers of these materials, the sequence distribution, i.e., the placement of comonomer units along the chain, as well as the tacticity, influences the copolymer's properties. Clearly, knowledge of these so-called microstructural features of a polymer is fundamental to understanding the relationship of polymer properties to molecular structure. In turn, the development of this understanding is essential to the design of materials with specific physical properties.

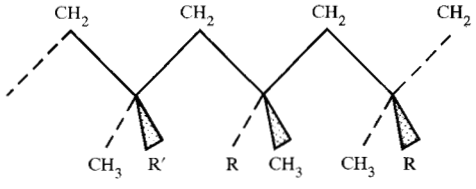
For a copolymer, the simplest description of the chain microstructure is the delineation of the chemical and stereochemical nature of the neighboring units of a monomer, i.e., knowledge of the distribution of copolymer *triads*. If the copolymer is composed of comonomers each having an asymmetric carbon, triad units are defined by the sequence of the three constituent repeat units and the two tactic relationships, each of which can be either racemic (r) or meso (m). Permutations of triad sequence and tacticity produce twenty-eight such structures, two of which are shown in Fig. 1 for the methyl methacrylate-methacrylic acid (MMA-MAA) copolymer system.

At present, the experimental technique most amenable to the detection of triad structural units is nuclear magnetic resonance (NMR) spectroscopy. The magnitude of the local magnetic field (and, thereby, the chemical shift) experienced by a magnetic nucleus in a monomer unit of a polymer chain is a function of the chemical and stereochemical nature of neighboring units. Copolymer

Figure 1 Schematic representation of two of the possible twenty triads arising from sequence and tactic effects in poly(MMA-MAA) systems. Symbols: A – methacrylic acid unit; E – methyl methacrylate unit; m – meso relationship; r – racemic relationship; R – COOH; R′ – $COOCH_3$.



$A^{m}E^{m}A$ triad



$E^{r}A^{r}A$ triad

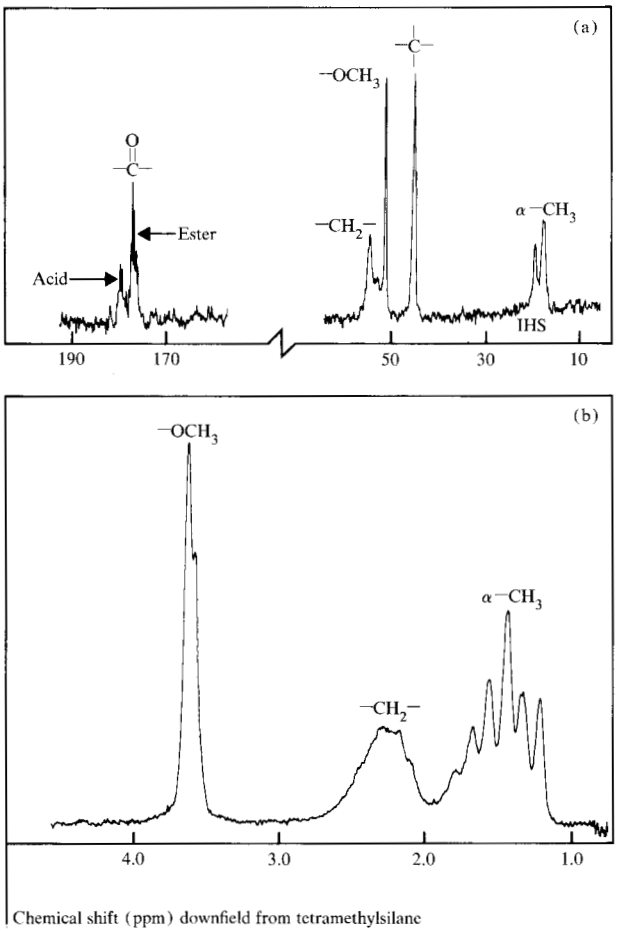


Figure 2 (a) 20.0 MHz ^{13}C spectrum of pyridine-d_5 solution of poly(MMA-MAA), 65-35 composition, T = 311 K. Carbon assignments are indicated for the appropriate resonance region. Symbols: I – isotactic triad; H – heterotactic triad; S – syndiotactic triad. (b) 100 MHz ^{1}H spectrum of the same copolymer, $T = 373$ K. Proton assignments are given above the appropriate resonance regions.

triad structure gives rise to twenty potentially distinguishable magnetic environments. (Of the twenty-eight possible structures, eight are degenerate.) In principle, each of these environments produces a unique resonance line, which can be assigned to the proper triad. Measurement of the relative intensities of the triad resonances therefore provides a statistical description of the copolymer triad character.

While the most widely used magnetic nucleus in studying the microstructural features of polymers has been the proton [2], the advent of Fourier transform NMR [3] has made it possible to obtain high resolution natural abundance carbon-13 spectra of macromolecules either in solution or in the bulk at a temperature above the glass-transition temperature. Most often the ^{13}C data supplement the ^{1}H results; however, in some instances, a ^{13}C spectrum yields information not available from a ^{1}H spectrum [4]. Thus, it is desirable to couple NMR data from both ^{1}H and ^{13}C in attempting to assess copolymer microstructure. In this paper, we report results on the application of ^{1}H and ^{13}C NMR to the study of triad microstructure in poly(MMA-MAA) systems prepared by different synthetic routes.

Experimental

• *NMR spectra*

The ^{1}H NMR spectra at 100 MHz were obtained at 373 K on pyridine-d_5 solutions of the MMA-MAA copolymers using a Varian HA-100 NMR spectrometer operating in the continuous-wave mode. The ^{13}C NMR spectra on 50/50 V/V pyridine/pyridine-d_5 solutions of the copolymers were obtained at 20 MHz and 311 K. The ^{13}C spectra were recorded on a Varian CFT-20 NMR spectrometer operating in the pulse Fourier transform mode. This spectrometer was equipped with random-noise proton decoupling, decoupler-gating options, and a 16K-word (K ≡ 1024) minicomputer for Fourier transformation and data manipulation. The ^{13}C spectra used for assignments of chemical shifts were obtained under full proton-decoupled conditions. Spectra used for quantitative purposes were obtained with gated proton decoupling, where the decoupler was on only during acquisition of the free induction decay. Because the carboxyl-carbonyl relaxation times T_1 were found to be in the range 0.8-1.1s, the use of a 60° pulse, a pulse delay of 3 s between the 1-s data acquisitions (i.e., total time between successive pulses equaled 4 s) and the decoupler gating ensured a ^{13}C spectrum in which all intensities were quantitative. Recent arguments by Opella et al. [5] and Canet [6] concerning the use of gated-decoupling to determine nuclear Overhauser enhancement (NOE) values indicate that if significant differences existed between ester and acid carbonyl NOE values, a pulse delay greater than that required to negate the effects of differential relaxation on quantitation would be required. For the MMA-MAA copolymers, the NOE values of the carbonyl carbons are all about equal (1.7-1.9), thus the pulse delay of 3.0 s was sufficient for quantitation. One method of checking that the spectrometer conditions indeed were sufficient to yield quantitative data was to compare the total integral of the carbonyl region with those obtained for α-CH_3, $-\overset{|}{\underset{|}{C}}-$, CH_2, since all integrals should be the same under quantitative conditions. In all cases examined, the integral values for all four resonance regions were within 2–3 percent. Additionally, comparison of compositions from NMR analysis and acid titration data were found to be in excellent agreement for a series of MMA/MAA copolymers [7].

• *Sample preparation*

Samples for ^{1}H analysis were prepared by dissolving about 0.05 g of copolymer in about 0.3 g of solvent. The solution components were weighed directly into 5mm outside diameter (o.d.) NMR tubes. Samples for ^{13}C analysis were prepared in a like manner except about 0.3 g of copolymer and about 2 g of solvent were weighed into 10mm (o.d.) NMR tubes. The MMA-MAA copolymers used in the study were prepared by three different synthetic procedures: 1) free-radical polymerization of monomers in tetrahydrofuran (THF), 2) free-radical polymerization in toluene, and 3) emulsion polymerization.

• *Computer generation of spectra*

Experimental FORTRAN programs were written to calculate triad and pentad structure probabilities, to compute spectra based on these probabilities and Lorentzian lineshapes, and to plot calculated spectra. A minicomputer was used as a buffer/interface between the CPU and the HA-100 spectrometer whose recorder was used to plot the computed spectra. In addition, experimental ^{1}H spectra were digitized and stored in the CPU file using the minicomputer for data acquisition and data transfer.

Results and discussion

• *Sensitivity of ^{1}H and ^{13}C spectra to triad structure*

The respective ^{13}C and ^{1}H spectra of poly(MMA-MAA) 35 mole-percent acid are shown in Figs. 2(a) and 2(b). The proton spectra of MMA-MAA copolymers have been treated in detail by Klesper et al. [8, 9], who have found that 1) the α-methyl protons are sensitive to triad sequence and triad tacticity; 2) the methylene protons are sensitive to tetrad effects; and 3) the ester methoxy protons appear to be little affected by microstructure (at least in pyridine). Since the methylene spectral region, Fig. 2(b), is largely unresolved, only the α-methyl region offers potential microstructural information. Unfortunately, even in this region, the twenty triads give rise to only six resolvable resonance lines.

Because the ^{13}C spectra of MMA-MAA copolymers have only recently been reported [9], sensitivity of the various carbons to microstructural features of the polymer chain is not well defined. The ^{13}C spectra of homopolymers of ester [10–12] and acid [13] have revealed the following tactic sensitivities: 1) The α-methyl and the quaternary carbons are sensitive to triad tacticity; 2) the carbonyl and carboxyl carbon resonances reveal pentad tactic effects; 3) the methylene carbons are presumably sensitive to tetrad effects; and 4) as in the ^{1}H spectrum, the ester methoxy is not influenced by tactic effects. However, effects of sequence may be such as to cancel some of the tactic sensitivity [4]; thus, the same tactic sensitivity may not be found in copolymers.

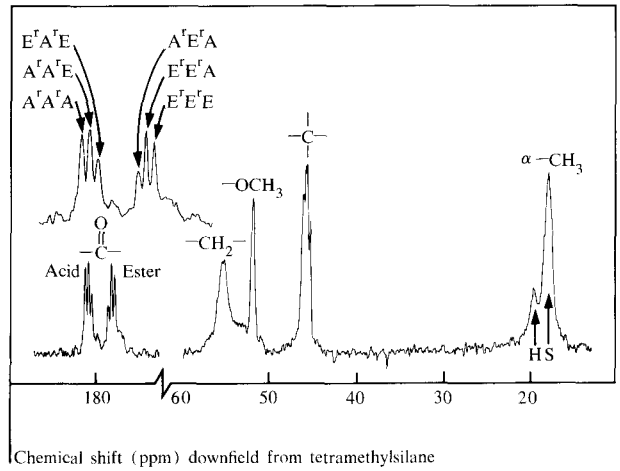


Figure 3 ^{13}C spectrum of predominantly syndiotactic (86 percent racemic dyads) poly(MMA-MAA), 50-50 composition. Carbon assignments are indicated above each group of resonances. In the upper left corner is the expansion of the carbonyl-carboxyl region and the appropriate assignments to ester (E)- and acid (A)-centered sequence triads. Symbols: H – heterotactic triad; S – syndiotactic triad.

The gross features of the ^{13}C spectra of the copolymers do not differ greatly from the homopolymer spectra because the comonomer units are structurally similar. This similarity serves to negate one of the principal advantages of ^{13}C NMR over ^{1}H NMR, i.e., the greater spectral dispersion. Nonetheless, it is possible to obtain some microstructural information from the MMA-MAA copolymer carbon spectrum. As in the case of each of the homopolymers, the α-methyl carbon region, Fig. 2(a), appears to divide among tactic triads. The assignment of the resonance lines to syndiotactic, heterotactic, and isotactic stereochemical triads is based on the study of model compounds and chemical shifts of other polymers [4]. The broader α-methyl resonance lines of the copolymers relative to homopolymers indicate that small effects due to chain sequence are superimposed on the chemical shifts induced by tactic effects. Proof of this result has been demonstrated in two ways. First, the hydrolysis of poly(MMA) to give MMA-MAA copolymers was carried out for different degrees of hydrolysis. At each degree of hydrolysis, the relative intensities of the three α-methyl resonances remained the same; however, some distortions in the lineshapes occurred, presumably due to sequence changes. Secondly, the ^{13}C spectrum of a primarily cosyndiotactic copolymer of 50/50 composition (Fig. 3) was recorded and yielded only syndiotactic and small heterotactic resonances in the α-methyl carbon region. Thus, it is clear that the α-methyl region of the ^{13}C spectrum is dominated by tactic effects and this region can be used as a monitor of total triad tacticities of the MMA-MAA copolymers.

Table 1 Definitions of generation parameters for the intensity of microstructural triads in MMA-MAA copolymers.

Reactivity ratios	r_E	Ratio of the second-order rate constant for an ester unit to add another ester unit to that for ester to add acid
	r_A	Ratio of the second-order rate constant for an acid unit to add another acid unit to that for acid to add ester
Feed ratios	f_E	Mole fraction of ester in the initial monomer feed
	f_A	Mole fraction of acid in the initial monomer feed
Sequence probabilities	P_{EE}	Probability an ester unit adds to an ester unit in the presence of acid; defined as $P_{EE} = \frac{r_E f_E}{(1-f_E) + r_E f_E}$
	P_{AA}	Probability an acid unit adds to an acid unit in the presence of ester; defined as $P_{AA} = \frac{r_A f_A}{(1-f_A) + r_A f_A}$
	P_{EA}	Probability an ester unit adds to an acid unit; defined as $(1 - P_{EE})$
	P_{AE}	Probability an acid unit adds to an ester unit; defined as $(1 - P_{AA})$
Tactic probabilities	σ_m^{EE}	Probability for an ester unit to add an ester unit in a meso stereochemical relationship
	σ_m^{EA}	Probability for an ester unit to add an acid unit in a meso relationship
	σ_m^{AE}	Probability for an acid unit to add an ester unit in a meso relationship
	σ_m^{AA}	Probability for an acid unit to add an acid unit in a meso relationship
		Note: $1 - \sigma_m^{XY}$ is the probability a monomer X adds to a monomer Y in a racemic relationship.)

Combination of the P's and σ's yields the twenty relationships for the triad intensities. A recent compilation of the equations is given in reference [16].

As evidenced by the several resonance lines at about 45 ppm in the spectrum of the cosyndiotactic copolymer (Fig. 3), the quaternary carbon is sensitive to sequence effects. However, the total range of chemical shifts (about 1 ppm) is too small to provide sequence information in copolymers of more random stereochemistry, since the additional tactic effects (which are of the same magnitude as the sequence effects) lead to a largely unresolved resonance [see Fig. 2(a)]. The methylene region is even more intractable, and the ester methoxy is apparently unaffected by sequence or by tacticity. The carbonyl-carboxyl resonance region does offer some information because the acid carboxyl resonances are all downfield of the ester carbonyl resonances when the copolymers are dissolved in pyridine. In solvents such as dimethyl sulfoxide (DMSO) and $HCCl_3$ there is overlap of these resonances. Apparently, the association of pyridine with the acid carboxyl group shifts the carboxyl resonance downfield. From Fig. 3 it is clear that the carbonyl and carboxyl carbons are sensitive to the triad sequence. Because the copolymer is highly stereoregular (i.e., tactic effects are absent), the six major resonance lines in the carbonyl-carboxyl region must arise from the six possible triad sequence permutations. However, in less stereoregular copolymers, the accompanying effects of tacticity give rise to resonance overlap of triad structures, which hinders obtaining quantitative microstructural data from this spectral region in much the same manner as in the α-methyl region of the ^1H spectrum.

From the preceding, it is obvious that due to resonance overlap neither the ^1H nor the ^{13}C spectrum provides a *direct* account of the triad microstructure in the MMA-MAA copolymers. Thus, to attempt to determine in more detail the distribution of microstructural triads in these copolymers, an experimental computer routine was devised in which calculated distributions of triads were used to simulate experimental spectra.

• *Simulation of ^1H α-methyl spectra*

Klesper et al. [8] have assigned each of the twenty triad resonances to one of the six resonance lines in the α-methyl proton spectrum by using a combination of specific deuteration studies, stereoregular copolymer studies, and variable solvent studies. These proton chemical shifts and assignments were used as a basis for our simulation of the α-methyl spectrum. Relative intensities of the twenty triad lines were machine-generated from equations derived by Bovey [14]. These equations are based on Bernoullian statistics for polymer tacticity and first-order Markov statistics for sequence distribution. The set of equations relates the triad intensities to three parameters: 1) the reactivity ratios of the two two monomers, r_E and r_A; 2) σ_m, which is the probability that a monomer will add to another in a coisotactic or meso (m) fashion; and 3) the monomer feed ratio f at the start of polymerization. (A further description of these parameters is given in Table 1.) To account for the changing copolymer composition and monomer feed ratio with the extent of copolymerization, provision was made in the computer program to calculate triad intensities and recalculate monomer feed ratio at one-percent conversion intervals. Triad line intensities at the desired degree of copolymerization were obtained by summing the line intensities over the conversion intervals. The intensity, chemical shift, and linewidth at half-height for each triad were then used as input parameters for a Lorentzian

Table 2 Final input parameters for computer simulation of poly (MMA-MAA), 52-48 composition[a].

Reactivity ratios	$r_E = 1.05$
	$r_A = 0.95$
Tactic probabilities	$\sigma_m^{EE} = 0.2$[b]
	$\sigma_m^{AA} = 0.2$
	$\sigma_m^{EA} = 0.2$[c]
	$\sigma_m^{AE} = 0.2$
Monomer feed ratios	$f_E = 0.5$
	$f_A = 0.5$
Linewidths[d]	Ester: 7.5 Hz[e]
	Acid: 9.0 Hz[f]

[a]Polymer prepared by solution polymerization in THF.
[b]Determined from homopolymer spectra.
[c]From α-methyl carbon data.
[d]Linewidth at half-height.
[e]From E^rE^rE resonance line of α-methyl protons.
[f]From differential relaxation rates between ester and acid.

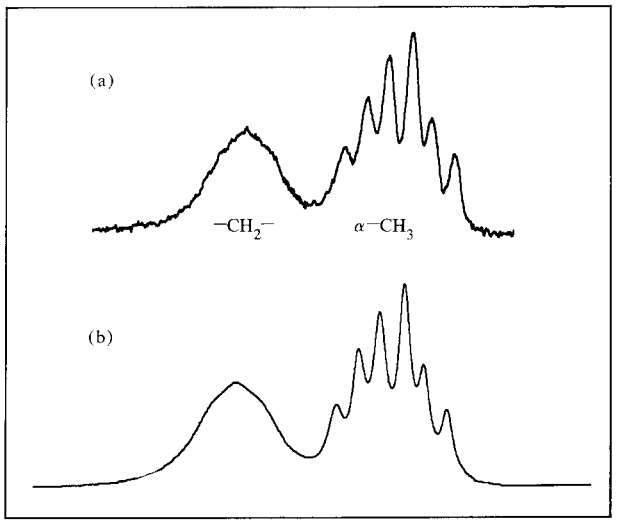


Figure 4 (a) Experimental spectrum of the α-methyl region of the ^1H spectrum of poly(MMA-MAA), 52-48 composition (copolymer prepared in solution in THF). (b) Calculated spectrum.

lineshape generation program [15] which produced a proton spectrum that could be compared to the experimental spectrum.

An example of the result obtained from the simulation procedure is given in Fig. 4, where the experimental and computer-generated spectra for a 52-48 MMA-MAA copolymer prepared by solution synthesis in THF are compared. The degree of conversion was 30 percent based on the total copolymer weight relative to the initial weight of the reactants. Values of the respective reactivity ratios, tactic probabilities, linewidths, and other parameters used to compute the spectrum are given in Table 2. The percentage of each triad in the copolymer chain obtained from this analysis is listed in Table 3. There might be other sets of input parameters that would produce a reasonable simulation of the spectrum; however, not all would be consistent with the available spectral information. For example, the same set of generating parameters yielded good simulations of the ^1H spectra for THF-prepared MMA-MAA copolymers at 35 and 25 percent acid content. In addition, the α-methyl region of the ^{13}C spectrum of the copolymers at each acid composition indicated a tactic distribution of about four percent isotactic, 33 percent heterotactic, and 63 percent syndiotactic. Noting that this is the same distribution found for each of the respective homopolymers when prepared by free-radical polymerization, it is obvious that each of the four tactic probabilities that enter the calculation [16] must be nearly equal (independent of sequence) and be confined to the probability region $\sigma_m \approx 0.2$. Since the composition ratios of the copolymers were nearly the same as the monomer charge ratios, the reactivity ratios also had to be similar. Finally, an estimate of the block character as judged from the triblock resonance lines (see later discussion) in the

Table 3 Triad composition of poly(MMA-MAA)[a,b], 52-48, from computer analysis.

Ester-centered triad	*Probability*[c]	*Acid-centered triad*	*Probability*
E^rE^rE	0.090	A^rA^rA	0.070
E^rE^mE	0.045	A^rA^mA	0.035
E^mE^mE	0.006	A^mA^mA	0.004
E^rE^rA	0.166	A^rA^rE	0.153
E^rE^mA	0.042	A^rA^mE	0.038
E^mE^rA	0.042	A^mA^rE	0.038
E^mE^mA	0.010	A^mA^mE	0.010
A^rE^rA	0.077	E^rA^rE	0.083
A^rE^mA	0.038	E^rA^mE	0.042
A^mE^mA	0.005	E^mA^mE	0.005

[a]Polymer prepared by solution polymerization in THF.
[b]Extent of conversion is 30 percent.
[c]Total probability normalized to unity.

proton spectrum indicated that the reactivity ratios were close to unity. This set of constraints considerably limited the search for the generating parameters to simulate the spectrum. Of course, a further test of the validity of the generation parameters in describing the microstructural characteristics of the copolymer is the degree to which they reproduce the carboxyl-carbonyl region of the ^{13}C spectrum of the copolymer.

• *Effect of triethylamine on ^{13}C spectra*

To produce a simulation of the carboxyl-carbonyl region, ^{13}C chemical shifts for the various triads were required. A useful method for obtaining shift information

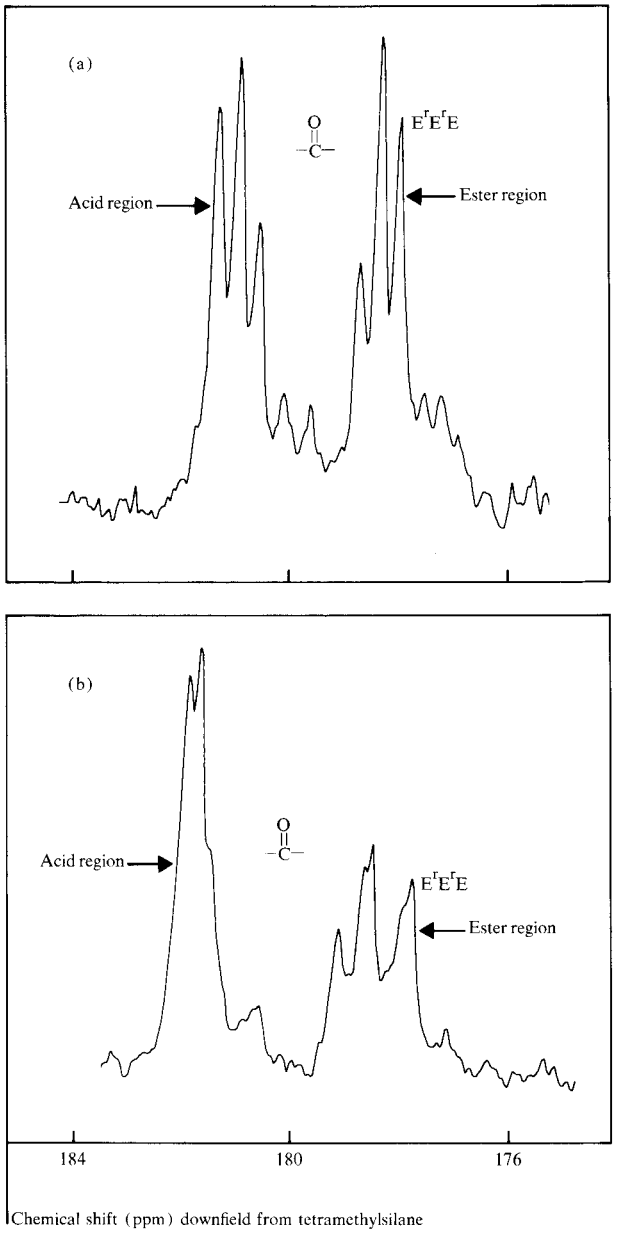


Figure 5 (a) ^{13}C spectrum of carboxyl-carbonyl region of predominantly syndiotactic poly(MMA-MAA), 50-50 composition. (b) ^{13}C spectrum of the same copolymer with triethylamine (TEA) added. The triblock ester sequence (EEE) is marked in each spectrum.

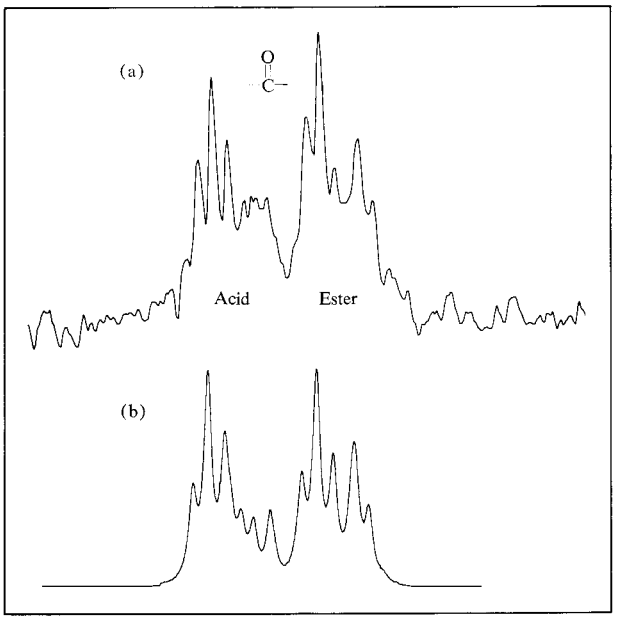


Figure 6 (a) ^{13}C spectrum of the carboxyl-carbonyl region of poly(MMA-MAA), 52-48 composition (copolymer prepared in solution in THF). (b) Computer-calculated spectrum based on triad statistics obtained from simulation of α-methyl region of the ^{1}H spectrum.

and assignments was the addition of triethylamine (TEA) to the MMA-MAA copolymer solutions. It was anticipated that addition of TEA, a stronger base than pyridine, would result in TEA displacing pyridine in the association with the methacrylic acid carboxyl carbon. (TEA was added to the copolymer solution in 20 mole-percent excess of acid present in the copolymer.) This displacement could sufficiently alter the electronic structure of the carboxyl bond to produce a chemical shift of acid residues and also perhaps of carbonyl carbons in neighboring ester units. In this manner, shifted resonance lines in the ester carbonyl region could be assigned to sequence triads in which the ester had one or two acid neighbors.

To test the hypothesis outlined in the preceding paragraph, TEA was added to the highly syndiotactic 50-50 copolymer discussed earlier. The spectra of the carboxyl-carbonyl region before and after addition of TEA are shown in Figs. 5(a) and 5(b) respectively. There is an obvious effect in the acid region as evidenced by the loss of resolution and the shift of resonance lines downfield. In the ester region the resonance lines that were previously assigned to A^rE^rE and A^rE^rA triads (see Fig. 3) are moved downfield while the E^rE^rE triad line is not greatly affected. (Spectral integration of the ester region, before and after addition of TEA, yielded the same results; there was therefore no ester hydrolysis due to amine addition.) Thus, ester units with acid neighbors were readily identified by the addition of TEA. This procedure allowed chemical shift assignments to be made in the heterotactic region of the carbonyl spectrum and allowed verification of assignments in the syndiotactic and isotactic regions.

• *Simulation of carboxyl-carbonyl spectra*

By combining the data from the TEA studies with chemical shifts obtained from the spectra of cosyndiotactic

and coisotactic copolymers, a set of ^{13}C chemical shifts for microstructural triads was determined (Table 4) for the carboxyl-carbonyl region. These chemical shifts were used to calculate the ^{13}C spectrum of the same 48 percent acid copolymer whose proton spectrum was calculated in Fig. 4. The set of generating parameters used to produce the intensities in the proton simulation produced the calculated ^{13}C spectrum shown in Fig. 6(b). As evidenced, the simulation, while in reasonable agreement with the experimental spectrum, Fig. 6(a), is not in exact accord with it. For example, there are some obvious intensity differences between the calculated and the experimental spectra. In addition, the chemical shifts for triad units (Table 4) indicate there should be no acid resonance at higher than 181.2 ppm from tetramethylsilane (TMS) and no ester resonance above 178.6 ppm; however, in the experimental spectrum, there are small shoulders at higher ppm values on the most downfield ester and acid lines. The apparent explanation for these features is that although the chemical shifts of the carboxyl and carbonyl carbons are sensitive only to nearest-neighbor sequence effects, they are sensitive to pentad rather than triad tactic effects, i.e., structures such as $X^mE^rE^rA^rY$ and $X^rE^rE^rA^rY$ (where X and Y can be acid or ester) have different chemical shifts. To take account of pentad tacticity and triad sequence requires the chemical shifts of 72 possible resonances. Since the measurement of all these resonances is not possible experimentally, a set of predicted shifts was derived from a set of additivity parameters based on the sequence effects observed in the cotactic copolymers and the tactic chemical shifts from the homopolymers. The conditional tactic probabilities σ_m were used to produce pentad instead of triad configurational distributions. Coupling this data with the triad sequence probabilities to calculate the line intensities produced the ^{13}C spectrum given in Fig. 7(b). With inclusion of pentad effects, the intensities of the calculated spectrum are in accord with experiment and the downfield resonances in both ester and acid are reproduced. Thus, good agreement of the calculated proton and carbon spectra with their respective experimental counterparts could be obtained using the same set of generating parameters for sequence and tacticity (Table 3). This result indicates that the triad microstructure in the MMA-MAA copolymers prepared in THF is defined by a first-order Markovian sequence distribution and Bernoullian tactic distribution.

• *Studies of 50-50 copolymers*

This study of microstructure in MMA-MAA copolymers was prompted by the finding that copolymers of the same acid-ester composition but different preparative histories gave rise to different behavior under the same thermal or chemical treatment. The proton spectra of three 50-50 copolymers—one prepared by free-radical polymerization in toluene, another by free radical polymerization in THF, and the other by emulsion procedures—are compared in Fig. 8. As evidenced, the spectrum of the toluene-prepared material has a more intense resonance at 1.80 ppm (downfield from TMS) and less intense resonance at 1.20 ppm than is found in the spectra of the other copolymers. Klespar et al. [8] assigned the resonance at 1.8 ppm to the three tactic

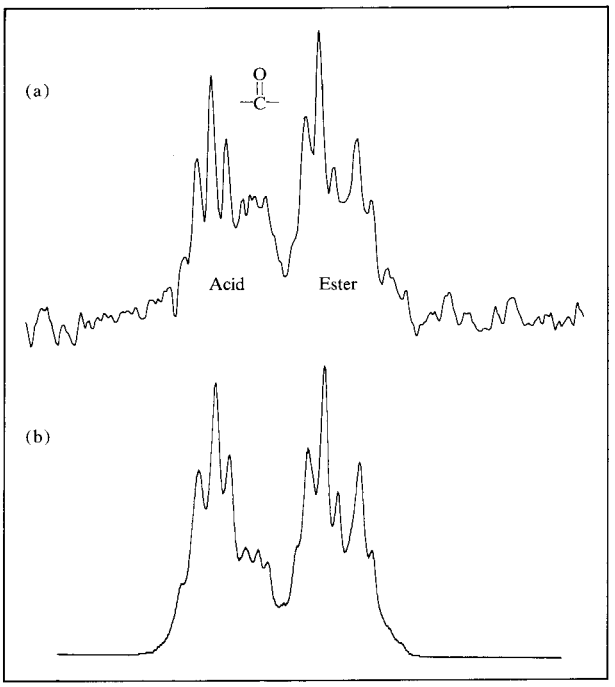


Figure 7 (a) ^{13}C spectrum of the carboxyl-carbonyl region of poly(MMA-MAA), 52-48 composition (copolymer prepared in solution in THF). (b) Computer-calculated spectrum based on triad sequence and pentad tactic effects.

Table 4 ^{13}C chemical shifts for MMA-MAA microstructural triads.

Ester-centered triad	*Chemical shift*[a]	*Acid-centered triad*	*Chemical shift*
E^rE^rE	177.88	A^rA^rA	181.22
E^rE^mE	177.03	A^rA^mA	180.33
E^mE^mE	176.66	A^mA^mA	179.88
E^rE^rA	178.24	A^rA^rE	180.84
E^rE^mA	177.35	A^rA^mE	179.77
E^mE^rA	177.30	A^mA^rE	179.96
E^mE^mA	176.96	A^mA^mE	179.32
A^rE^rA	178.60	E^rA^rE	180.45
A^rE^mA	177.41	E^rA^mE	179.40
A^mE^mA	177.26	E^mA^mE	178.76

[a]In ppm downfield from TMS.

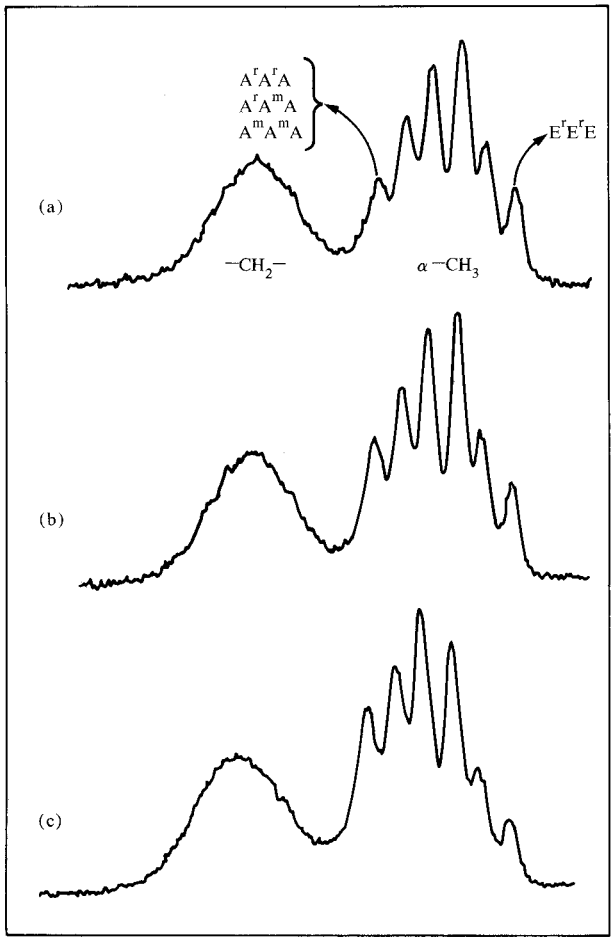


Figure 8 The proton spectrum of the α-methyl region of three MMA-MAA copolymers: (a) prepared in solution in THF, 52-48 composition; (b) prepared by emulsion techniques, 50-50 composition; (c) prepared in solution in toluene, 47-53 composition.

triads of the triblock acid sequence (i.e., the triads A^rA^rA, A^rA^mA, and A^mA^mA) and the resonance at 1.20 ppm to the syndiotactic ester triblock, E^rE^rE. Since the α-methyl region of the carbon spectra of the three polymers indicated each to be highly syndiotactic (about 60 percent), these two resonances yield an estimate of the relative degree of chain blockiness. On this basis, the toluene-prepared copolymer is judged to have a more blocky acid sequence distribution than the other copolymers. To provide further evidence for this conclusion, simulations of the proton spectra were attempted.

The copolymer prepared in THF was that used as the test case for the simulation programs and, as outlined in the preceding section, the proton spectrum was fitted with the parameters listed in Table 2. The reactivity ratios that produced the calculated spectrum are in excellent agreement with the experimental values ($r_E = 1.00 \pm 0.05$ and $r_A = 1.0 \pm 0.2$) determined for MMA-MAA copolymerization in THF by Markert and Pennewiss [17]. Simulation of the proton and carbon spectra of the copolymer prepared by emulsion polymerization was accomplished with the same tactic probabilities as the THF case, but with $r_E = 0.97$ and $r_A = 1.03$. Thus, both the THF and the emulsion syntheses produced copolymers in which the reactivity of the growing chain had little dependence on the nature of the monomer unit at the growing end, i.e., the comonomer feed ratio determined the final polymer composition.

Unlike the relatively homogeneous nature of the copolymers produced by emulsion synthesis or free-radical polymerization in THF, synthesis in toluene yielded a heterogeneous system when carried to high conversion. For the polymer whose proton spectrum is shown in Fig. 9(b), the conversion was carried to 67 percent completion. The best simulation, Fig. 9(c), resulted with $r_E = 0.57$ and $r_A = 1.75$ and tactic probabilities σ_m of 0.3 (determined from the tactic triad intensities in the α-methyl region of the ^{13}C spectrum). The relative reactivity ratios indicate that during the initial stages of polymerization, copolymer chains rich in acid, and thus having a blocky acid structure are produced. For example, at six-percent conversion, the calculated copolymer composition is about 40-60 (MMA-MAA) and yields the triad composition given in Table 5 and the calculated spectrum in Fig. 9(d). At conversion levels near 65 percent, the copolymer chains being produced are calculated to have an MMA-MAA composition of about 54-46. Hence, the experimental spectrum represents a composite of the various chains, and comparison of the experimental spectrum with that in Fig. 9(d) clearly demonstrates the changing relationship of the individual resonance lines as the polymerization proceeds. The calculated triad composition for the composite copolymer (Table 5) gives a normalized triblock acid content of 0.162 relative to a value of 0.212 at six-percent conversion to product. These data compare with a value of 0.109 for the triblock acid content in the THF-polymerized material. The differences in acid sequence between copolymers prepared in THF and toluene could account for the different reactivity of such copolymers toward chemical reagents.

Subsequent measurement of the reactivity ratios in toluene yielded values of r_E and r_A of 0.26 and 0.93, respectively [18]. These data verify the expected heterogeneous nature of the toluene-prepared copolymers; however, the calculated spectrum based on the results [Fig. 9(a)] is in poor agreement with the experimental spectrum, particularly in the triblock sequence regions (resonances at 1.8 and 1.2 ppm). One source of the discrepancy between measured values and values of r deter-

Table 5 Calculated triad composition[a] of MMA-MAA copolymer synthesized in toluene.

	Conversion (percent)	
Ester-centered triad	*6*	*67*
E^rE^rE	0.032	0.048
E^rE^mE	0.028	0.041
E^mE^mE	0.006	0.009
E^rE^rA	0.095	0.111
E^rE^mA	0.041	0.047
E^mE^rA	0.041	0.047
E^mE^mA	0.018	0.020
A^rE^rA	0.070	0.066
A^rE^mA	0.060	0.056
A^mE^mA	0.013	0.012
Acid-centered triad	*6*	*67*
A^rA^rA	0.104	0.079
A^rA^mA	0.089	0.068
A^mA^mA	0.019	0.015
A^rA^rE	0.141	0.131
A^rA^mE	0.060	0.056
A^mA^rE	0.060	0.056
A^mA^mE	0.026	0.024
E^rA^rE	0.048	0.055
E^rA^mE	0.041	0.048
E^mA^mE	0.009	0.010

[a]Calculated with $r_E = 0.57$, $r_A = 1.75$, σ_m's = 0.3, f_E (initial) = 0.54, $f_A = 0.46$. Polymerization carried to 67 percent completion with final product ester-acid composition 47-53.

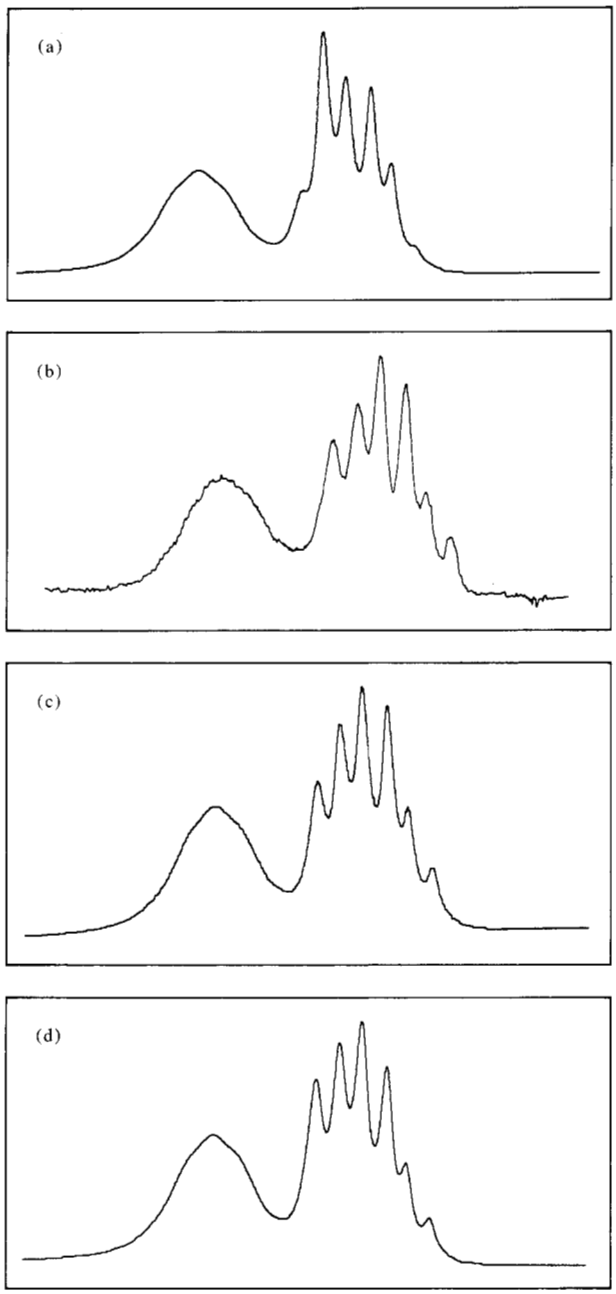


Figure 9 (a) Calculated spectrum of MMA-MAA copolymer polymerized in toluene; $r_E = 0.26$ and $r_A = 0.93$. (b) Experimental spectrum. (c) Calculated spectrum, 67 percent conversion; $r_E = 0.57$ and $r_A = 1.75$. (d) Calculated spectrum, six percent conversion; $r_E = 0.57$ and $r_A = 1.75$.

mined from the simulation is the nature of the acid monomer in toluene. Markert and Pennewiss [17] found that the values of r_E for polymerization of MMA-MAA copolymers in nonpolar solvents is less than in polar solvents, while the opposite is true for r_A. For example, $r_E = r_A = 1.0$ in THF, but in benzene, r_E has been determined to be 0.35 to 0.7 and r_A to be 1.3 to 2.4 [17, 19]. Dimerization of the acid monomers in the nonpolar solvent and association of acid monomer with carboxyl groups in the growing copolymer chain have been suggested as the reasons for the relative values of the reactivity ratios in benzene. Since toluene is a relatively nonpolar solvent, both of these effects could be operative in this polymerization system. The consequence of the presence of association and dimerization is a deviation of the copolymerization process from first-order Markov statistics; i.e., the reactivity of the growing chain is dependent upon more than the nature of the monomer unit at the growing end. The association mechanism would lead to a greater concentration of acid moieties near the growing-end of the polymer, while the dimerization mechanism could lead to the simultaneous incorporation of two acid units (i.e., an acid dyad) into the growing polymer.

Both the association with carboxyl groups in the chain and the self-association of acid monomers would produce a blocky-acid polymer in the initial stages of polymerization; however, as polymerization proceeds and the acid monomer content drops, both mechanisms would become less important. The simulation procedure, which is based on Markov statistics for sequence distribution, attempts to account for the blocky-acid structure

with enhanced acid reactivity ratio relative to ester. Thus, the fitted-spectrum [Fig. 9(c)] represents the best fit based on first-order Markov statistics and simultaneously meeting the constraints of producing the measured copolymer composition (47-53) at 67 percent conversion and the measured triad tactic content. As evidenced in Figs. 9(b) and 9(c), the simulated spectrum underestimates to some degree the triblock character of the experimental spectrum. The important result from the simulation is that it demonstrates that the measured r values cannot account for the experimental spectrum and that effects such as association of the acid must be considered in the polymerization process.

Summary

Currently, we are undertaking additional studies on toluene-prepared materials in an attempt to define more clearly the role of association of acid monomer in affecting the sequence distribution and the measured values of the reactivity ratios. (Clearly, the experimentally determined r values could be in error since association would, in effect, decrease the number of acid moieties present in the feedstock. Thus, calculation of r values based on monomer ratios in the feedstock could lead to errors in the determined values.) Additionally, we are incorporating other statistical schemes [20–22] for tactic and sequence distribution into the computer programs. However, if addition of acid monomer and dimer were both important in the copolymerization process, as they appear to be, the NMR studies alone will not provide sufficient quantitative data to allow a unique characterization of the system by non-Markovian statistics. (The sum of two parallel Markov processes requires a non-Markovian description [23, 24]). Information on long-range sequences can often be obtained by chemical degradation studies; however, attempts to use such techniques on the MMA-MAA copolymers have been largely unsuccessful [25].

Although the resolution of the details of the copolymerization process in toluene may prove difficult, the results of this study indicate that correlation of proton and carbon-13 NMR spectra, coupled with experimental computer simulation schemes based on statistical models for polymerization, can provide information on the triad microstructure of MMA-MAA copolymers and indicate whether polymerization proceeds via a simple Markov process.

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