Polymer Journal, Vol. 21, No. 9, pp 689—695 (1989)

Sequence Determination in Acrylic Acid–Methyl Methacrylate Copolymers by ^{13}C and ^{1}H NMR Spectroscopy

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(Received November 8, 1988)

ABSTRACT: Acrylic acid(AA)–methyl methacrylate(MMA) copolymers of varying compositions were prepared in bulk using benzoyl peroxide as an initiator. ^{13}C and ^{1}H NMR spectra of the copolymers were recorded and analyzed. From the observed copolymer composition provided by ^{1}H NMR, reactivity ratios were determined. The compositional triad sequences were determined by using carbonyl and α-methyl resonances. The experimentally determined triad concentrations showed good agreement with theoretical distribution, calculated using Bernoullian statistics and Harwood's program, as the copolymers were random in nature.

KEY WORDS ^{13}C NMR / Triad Sequence / Reactivity Ratios / Bernoullian Statistics / Harwood's Program /

As Bovey reported,[1] the high resolution NMR spectra of polymers have been most widely used for the determination of compositional and configurational sequences in polymers. As the sequential length distribution of comonomers is one of the factors that affects the solution, bulk and chemical properties, sequence determination becomes important. Configurational and compositional sequence information may be important, when the physico-mechanical properties of the copolymers are under consideration. In the case of acrylic acid–methy methacrylate copolymers, the reactivity ratios and hence the monomer sequence distribution is found to be dependent on their copolymerization in bulk or in solvents like dimethyl sulfoxide, acetonitrile etc.[2-4] In our earlier publications, the sequence determination of methyl methacrylate–ethyl methacrylate copolymers,[5,6] methyl methacrylate–styrene copolymers[7] and methyl methacrylate–*n*-butyl methacrylate copolymers[8] by ^{13}C NMR has been reported. In the continuation of our earlier works, in this communication the monomer sequence distribution in acrylic acid(AA)–methyl methacrylate (MMA) copolymers by ^{13}C and ^{1}H NMR and various theoretical models shall be reported.

EXPERIMENTAL

Acrylic acid(AA)–methyl methacrylate (MMA) copolymers of different compositions were prepared in bulk, by taking different feed in mole percent of monomers (Table I). The copolymerization reaction was carried out at 60°C using 1% benzoyl peroxide as initiator in nitrogen atmosphere. The percentage conversion was kept low (≈10—15 percent). Conditions for recording ^{1}H and ^{13}C NMR spectra were same as described in our earlier publications[7,8] except for the solvent which was DMSO-d_6. Resonance signal areas were measured by using a Lorentzian curve fitting program for a ICL-2960 computer.

Molecular weight of copolymers were determined by viscometry. These copolymers are not soluble in methanol or chloroform. The

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intrinsic viscosities of these copolymers were determined in 1 : 1 mixture of chloroform and methanol. Mark–Houwick constants for AA–MMA copolymers have not been reported in literature. The values of Mark–Houwink constants were taken as for polyacrylic acid. Intrinsic vicosities and molecular weights of these copolymer are given in Table I.

Table I. Composition (mole fraction) and intrinsic viscosity data for acrylic acid(AA)–methyl methacrylate(MMA) copolymers[a]

Comonomer mole fraction				Intrinsic viscosity,	Molecular weight
f_{AA}	f_{MMA}	F_{AA}	F_{MMA}	η	$\times 10^{-4}$
0.60	0.40	0.74	0.26	1.013	4.7
0.53	0.47	0.68	0.32	1.026	4.8
0.38	0.62	0.55	0.45	1.042	4.9
0.30	0.70	0.47	0.53	1.060	5.1

[a] f = Mole fraction of comonomer in feed.
F = Mole fraction of comonomer in copolymer determined by ^{1}H NMR spectroscopy.
The values of Mark–Houwink constants for polyacrylic acid in $CHCl_3$ at 30°C: $K = 3.76 \times 10^{-3}$ ml g^{-1}; $a = 0.52$ were used.

RESULTS AND DISCUSSION

^{1}H NMR Studies

A typical ^{1}H NMR spectrum of AA–MMA copolymer (AA mol% is 38.0) is shown in Figure 1. The methane resonance of AA at δ 2.5 ppm has been observed as a multiplet. The methylene peaks of AA and MMA overlap each other and appear at δ 1.5—2.0 ppm. Methoxy protons resonance at δ 3.5 ppm are less sensitive to sequence distribution as compared to α-methyl protons at δ 0.8—1.0 ppm. Methoxy proton NMR signal contains a strong peak due to the presence of water absorbed by the NMR solvent DMSO-d_6. The relative comonomer concentration in the copolymers was determined using integrated intensities of the methine protons of AA and α-methyl protons of MMA, as follows:

$$\text{Fraction of AA} = \frac{I(\text{CH})}{I(\text{CH}) + 1/3\, I(\alpha\text{-CH}_3)}$$

where I(CH) and $I(\alpha\text{-CH}_3)$ are the intensities of methine and α-methyl peaks, respectively. The composition of copolymers as determined by

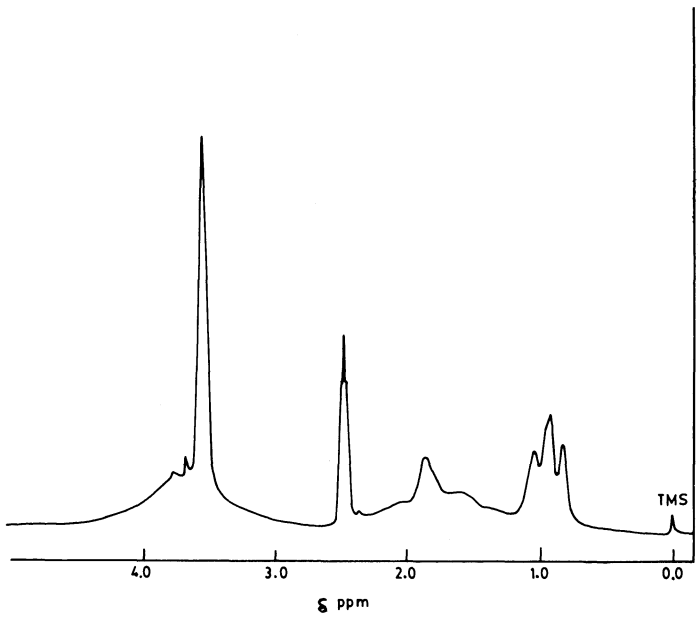

Figure 1. ^{1}H NMR spectrum of AA–MMA (AA = 38.0 mol%) copolymer recorded at 100°C in DMSO-d_6.

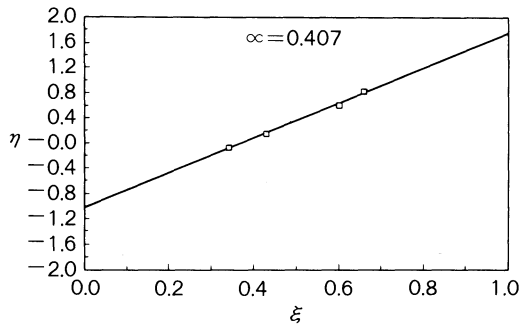

Figure 2. Kelen–Tüdös plot for AA–MMA copolymer system with $\alpha=0.407$.

^{1}H NMR along with feed in composition is given in Table I. The reactivity ratios were determined by the method of Kelen and Tüdös.[9] The values of r_1 (AA) and r_2 (MMA) were found to be 1.76 and 0.42, respectively. Figure 2 shows the corresponding Kelen–Tüdös plot for the AA–MMA copolymer system. The reactivity ratios were computed from the two intercepts ($\delta=0$, 1) of the best straight line according to the recommended expression:

$$\eta=(r_1+r_2/\alpha)\varepsilon-(r_2/\alpha)$$

where $\eta=G/\alpha+F$ and $\varepsilon=F/\alpha+F$

$$G=x(y-1)/y \quad \text{and} \quad F=x^2y$$

and

$x=M_1/M_2$, *i.e.*, monomer ratio in feed.

$y=dM_1/dM_2$ *i.e.*, monomer ratio in copolymer.

α being an adjustable parameter for uniform distribution of experimental data.

The values of reactivity ratios reported in the literature[10] are r_1(AA)=1.51 and r_2 (MMA)=0.48. Small difference in the value of r_1 may be due to the use of different initiator and temperature of polymerization.

Splitting in the α-methyl signal can be used to calculate the MMA-centred sequence distribution. Three signals in α-methyl region are attributed to the three possible MMA-centred triads; 121 (δ1.05 ppm), 122 (δ 0.933 ppm), and 222 (δ 0.892 ppm), where 1 represents AA unit and 2 represents MMA unit. Small shoulders on the α-methyl proton NMR peaks are due to tacticity whthin a particular comonomer triad sequence. Relative concentrations of MMA-centred triads were determined from the ^{1}H-NMR spectrum and are given in Table II. As the concentration of MMA increases in the copolymer, the concentration of 221, 222 triads increases. The triad concentrations were also calculated theoretically from the reactivity ratios and copolymer compositions using the method described by Bovey.[1] The following equations were used for the calculation of MMA-centred triads concentration:

$$P_{11}=\frac{r_1f_1}{1-f_1(1-r_1)}$$

$$P_{22}=\frac{r_2f_2}{1-f_2(1-r_2)}$$

where p_{11} is the probability that a chain ending in monomer 1 will add to 1 and P_{22} is the probability that chain ending in monomer 2

Table II. Calculated and observed distribution of MMA-centred triads using α-methyl proton resonance

f_{AA}	Triad	Triad concentration		
		A	B	C
0.60	[121]	0.54	0.55	0.62
	[122]	0.40	0.38	0.34
	[222]	0.06	0.07	0.04
0.53	[121]	0.46	0.46	0.53
	[122]	0.44	0.44	0.40
	[222]	0.10	0.10	0.07
0.38	[121]	0.26	0.30	0.35
	[122]	0.47	0.50	0.48
	[222]	0.27	0.20	0.16
0.30	[121]	0.15	0.22	0.25
	[122]	0.47	0.50	0.50
	[222]	0.38	0.28	0.25

1, acrylic acid; 2, methyl methacrylate; A, by ^{1}H NMR spectroscopy; B, from Bernoullian statistics; C, from reactivity ratios ($r_1=1.76$, $r_2=0.42$).

will add to 2. Where r_1 and r_2 are the values of reactivity ratios for AA and MMA respectively; f_1 and f_2 are the feed mole fraction for monomers 1 and 2, respectively.

The MMA (2)-centred triad concentrations can be given as:

$$[222]=F_2[P_{22}]^2$$

$$[122]=2F_2[P_{22}(1-P_{22})]$$

$$[121]=F_1[(1-P_{11})(1-P_{22})]$$

Here F_1, F_2 are the mole fraction of monomers 1 and 2, respectively, in the copolymers. MMA-centred triad concentrations determined from ^{1}H NMR and those calculated from the reactivity ratio and Bernoullian statistics are in good agreement (Table II). This shows that the monomer placement is random in nature.

^{13}C NMR Studies

A typical proton decoupled ^{13}C NMR spectrum of AA–MMA (AA mol% is 30.0) copolymer is shown in Figure 3. α-Methyl resonance (δ17—21 ppm) in this case is a multiplet and seems to be pentad sesitive to the various monomer placements. Since some bands in this region are not well resolved for our analysis, we did not calculate sequence distribution using α-methyl resonance. The quaternary carbon (–C–) resonance seems monomeric and configurational sequence insensitive since it does not show any splitting. The solvent DMSO-d_6 peaks overlap with methine (–CH) carbon-13 resonance signal of acrylic acid.

The carbonyl carbon (>C=O) resonance (δ 175—177 ppm) has been found to be comonomer triad sequence sensitive as six resonance signals were observed for all copolymers. The small shoulders on the main peaks in the carbonyl carbon NMR region are due to the tacticity within a particular comonomer triad sequence. The assignment to various triad sequences has been made by considering the fact that chemical shift differences arising due to different comonomer ssequences are difinitely of the greater magnitude than due to tacticity. Figure 4 shows the expanded carbonyl (>C=O) region spectra for all the copolymer samples. Chemical shifts for various resonances did not change much with the copolymer composition but the effect of copolymer composition is very much evident on the various peaks in the carbonyl carbon resonance

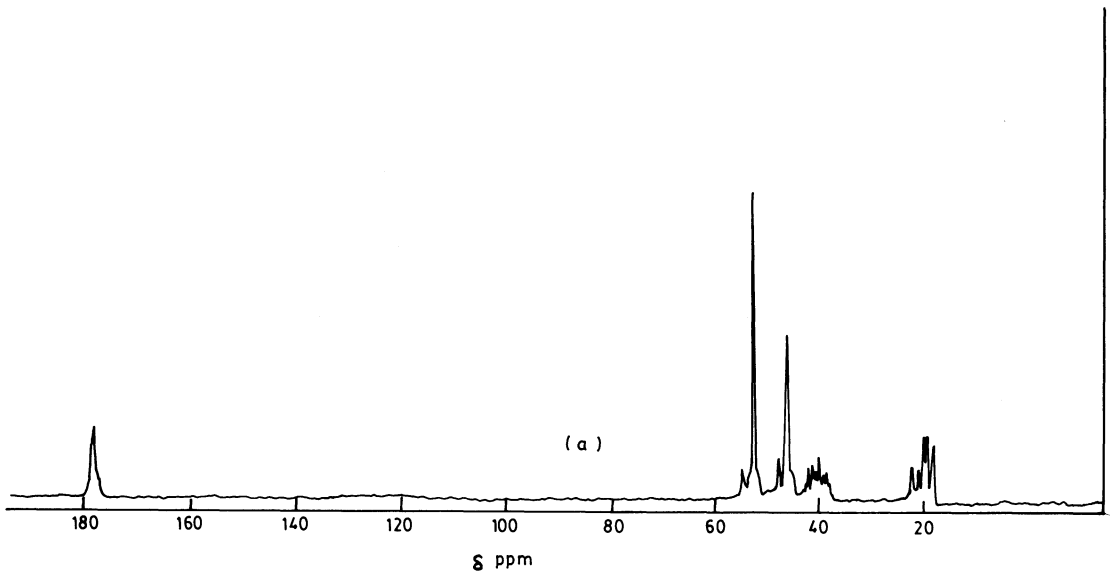

Figure 3. ^{13}C-{^{1}H} NMR spectrum of AA–MMA (AA = 30.0 mol%) copolymer at 100°C in DMSO-d_6.

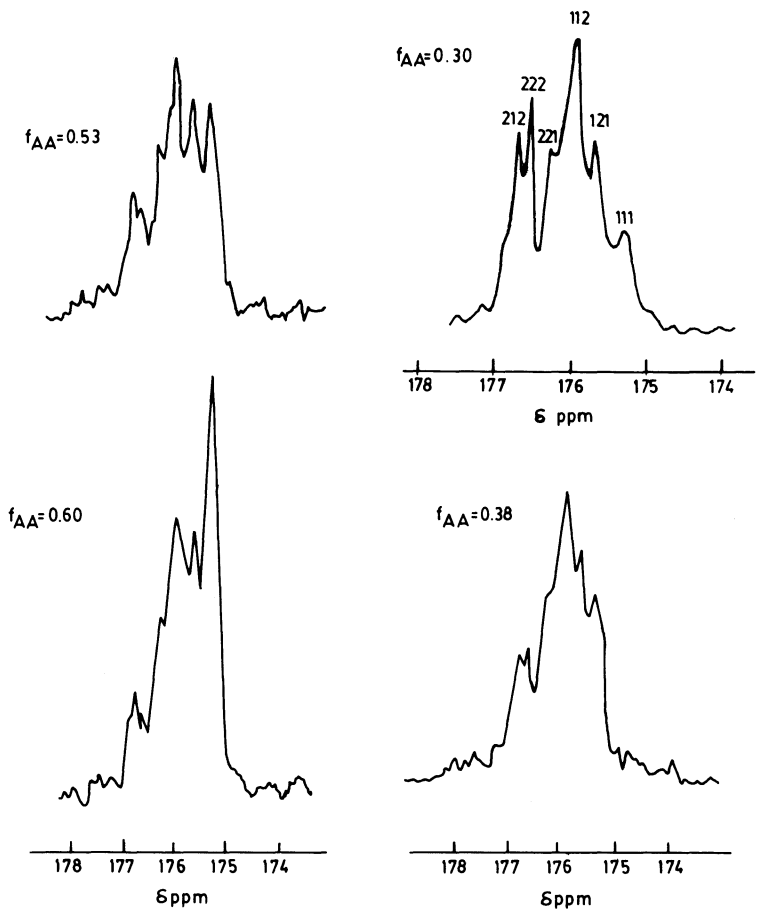

Figure 4. Expanded carbonyl (>C=O) resonance region for all the four copolymer samples: f_{AA} is the mole fraction of acrylic acid: 1, a crylic acid; 2, methyl methacrylate.

Table III. Calculated and observed triad sequence distribution in acrylic acid (**1**)–methyl methacrylate (**2**) copolymers by ^{13}C NMR spectroscopy using carbonyl carbon resonance

Triad	δ ppm*	f_{AA}							
		0.60		0.53		0.38		0.30	
		a	b	a	b	a	b	a	b
[111]	175.42	0.390	0.400	0.351	0.314	0.160	0.166	0.105	0.107
[121]	175.77	0.198	0.143	0.163	0.148	0.145	0.136	0.124	0.117
[112]	176.08	0.275	0.289	0.281	0.296	0.285	0.272	0.287	0.234
[122]	176.35	0.084	0.100	0.129	0.139	0.190	0.223	0.206	0.264
[222]	176.61	0.015	0.018	0.009	0.033	0.110	0.091	0.148	0.148
[212]	176.77	0.038	0.050	0.067	0.070	0.110	0.112	0.130	0.131

a, observed distribution by ^{13}C NMR spectroscopy; b, calculated distribution by Bernoullian statistics.
* Down field from TMS (Me_4Si).

Table IV. Normalized triad sequence distribution by ^{13}C NMR spectroscopy and Harwood's computer program in acrylic acid (**1**)–methyl methacrylate (**2**) copolymers

Triad	f_{AA}							
	0.60		0.53		0.38		0.30	
	a	b	a	b	a	b	a	b
[111]	0.55	0.53	0.50	0.41	0.29	0.29	0.20	0.19
[112]	0.39	0.40	0.40	0.46	0.51	0.50	0.55	0.49
[212]	0.06	0.07	0.10	0.13	0.20	0.21	0.25	0.32
[222]	0.05	0.05	0.03	0.08	0.25	0.15	0.31	0.25
[122]	0.28	0.34	0.43	0.42	0.43	0.47	0.43	0.50
[121]	0.67	0.61	0.54	0.50	0.32	0.38	0.26	0.25

a, observed distribution by ^{13}C NMR spectroscopy; b, calculated distribution by Harwood's program.

region as intesities of the peaks were found to be affected by the copolymer composition. As there is a considerable overlap in resonance signals of AA and MMA carbonyls, the assignment of different AA and MMA-centred triad sequences to various carbonyl resonance peaks were made by observing the composition dependence of resonance signals and comparing the triad concentrations obtained by ^{13}C–$\{^1H\}$ NMR studies with those from the Bernoullian statistical model. Peak assignment and sequence distribution of the six possible triads, as determined by ^{13}C NMR using carbonyl resonances, along with the theoretical distribution are given in Table III. The observed and calculated values are well within the experimental error. Monomer sequence distribution can also be calculated by Harwood's computer program[11] which takes into account the monomer reactivity ratios, feed in monomer concentrations, molecular weights of the monomer and the percentage conversion. Terminal model was taken into consideration while carrying out the calculations using Harwood's program. Table IV gives the observed AA and MMA-centred triad distribution along with the calculated distribution using Harwood's program. Fairly good agreements is seen between the two distributions. AA and MMA-centred triad fractions were each normalized to unity to form a basis for comparison.

Table V. Reactivity ratios for individual AA–MMA copolymer samples determined by the method of Chûjo[12]

f_{AA}	r_{AA}	r_{MMA}
0.60	1.44	0.74
0.53	1.43	0.60
0.38	1.38	0.70
0.30	1.41	0.60

Reactivity ratios can also be determined for individual sample by the method of Chûjo.[12] The mole fraction of monomeric units in the feed and dyad concentrations are used to calculate the reactivity ratios for each sample. The dyad concentrations were evaluated from the triad concentration data obtained using carbonyl carbon resonance signal. Following equations relating the dyad-triad concentrations were used to calculated the dyad concentrations.

$$[22]=[222]+1/2[221]$$

$$[12]=[122]+2[121]=[112]+2[212]$$

and

$$[11]=[111]+1/2[112]$$

The reactivity ratios calculated by this method, given in Table V, differ from those calculated by Kelen and Tüdös method, but are in good

Table VI. Mean sequence lengths (l) for acrylic acid (**1**)–methyl methacrylate (**2**) copolymers

f_{AA}	(l_1)		(l_2)		$(l_1/l_2)_{Obsd}$	$(l_1/l_2)_{Calcd}$
	Observed	Calculated	Observed	Calculated		
0.60	3.25	3.64	1.35	1.63	2.40	2.23
0.53	3.18	2.95	1.46	1.38	2.18	2.14
0.38	2.11	2.08	1.90	1.68	1.11	1.24
0.30	1.85	1.75	2.18	1.98	0.85	0.88

agreement with each other for all four copolymer samples. Kelen–Tüdös method uses only mole fractions of monomers in feed and in the copolymer, whereas Chüjo's method uses the mole factions of monomers in feed and the dyad sequence fractions, resulting in the different values of reactivity ratios. But it can not be said that which of the values are more correct because of the excellent linearity of Kelen–Tüdös plot and the excellent agreement between the reactivity ratios values obtained for the individual samples by Chûjô's method. Observed compositions of AA in copolymer and the values of reactivity ratios show the preferential addition of acrylic acid over methyl methacrylate.

Basic kinetic equation valid for low conversions can be applied to determine the mean sequence length (l). The mean sequence length of structural unit, *e.g.*, M_1 or M_2 increases with an increase in the particular monomer in the monomer mixture and in the copolymer also. The (l) may be estimated by following equations:

$$l_1 = r_1[f_1]/[f_2] + 1$$

$$l_2 = r_2[f_2]/[f_1] + 1$$

where r_1 and r_2 are the reactivity ratios of AA and MMA respectively and $[f_1]/[f_2]$ represents the monomer concentration ratio of AA and MMA in the monomer mixture. Table VI shows the mean sequence length l_1 and l_2 calculated using above equations, for the formation of AA and MMA units respectively, along with those calculated from the experimental triad concentrations.[13] The reactivity ratios used were those calculated by Kelen–Tüdös method. A good agreement can be seen between the two values. The ratio of the mean sequence lengths l_1/l_2, which theoretically correspond to monomer ratio in the copolymer is listed in Table VI. As the mole fraction of AA in the copolymer is increasing, the l_1 is also increasing, resulting in the rapid build up of AA in the copolymer.

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