Sequence Determination in MMA-EMA Copolymers by ^{13}C NMR

A. S. BRAR* and A. K. SAINI, *Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India*

Synopsis

The ^{13}C nuclear magnetic resonance spectra of MMA-EMA copolymers have been recorded and analyzed. The carbonyl carbon resonance region contains six resonating peaks due to its sensitivity to triad concentrations. From these signals, triad concentrations were determined and compared with calculated values based on Bernoullian and first-order Markovian statistics. Molecular weights were determined by viscosity measurement method.

INTRODUCTION

[1]H nuclear magnetic resonance (NMR) and ^{13}C NMR spectroscopy provides substantial information on the distribution of the monomers and on the nature of the linkages. The sequential length distribution of comonomers is one of the important factors that affects the solution, bulk, and chemical properties of copolymers.[1] Sequence determination of these copolymers is essential due to their long-standing industrial significance. The effects of copolymer composition and monomer sequence distribution on copolymer properties have been investigated for several common pairs: vinyl chloride-vinylidene chloride,[2,3] ethylene-vinyl acetate,[4] methyl methacrylate-methacrylic acid,[5] methacrylic acid-(dimethylamino)ethyl methacrylate,[6] acrylonitrile-styrene,[7] and butadiene-styrene.[8,9] A literature survey reveals that no work has been reported on the sequence determination of methyl methacrylate (MMA)-ethyl methacrylate (EMA) copolymers by using ^{13}C NMR spectroscopy. In this paper the tacticity and sequence determination of copolymers of MMA-EMA are reported.

EXPERIMENTAL

Preparation of Copolymers

Four samples of copolymer were prepared in different proportions of monomers (MMA and EMA), using 1% benzoyl peroxide as an initiator at 50°C. The percentage conversion of monomer was 10% (approximately). The percentage compositions of copolymers are given in Table I.

Mole percentage of monomers in copolymers are given in brackets.

^{13}C NMR AND ^{1}H NMR ANALYSIS

All ^{1}H NMR spectra were obtained with a Jeol FX 100, NMR spectrometer operating at 99.55 MHz in CDCl$_3$ at 25°C with TMS as internal standard.

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*To whom all correspondence may be addressed.

TABLE I
Percentage of Monomers in Copolymer (mol %)

Monomers	A	B	C	D
MMA[a]	20.5 (26)	50.8 (49)	60.7 (64)	80.5 (82)
EMA[a]	79.5 (74)	49.2 (51)	39.3 (36)	19.5 (18)

[a] Mole percentage of monomers in feed.

Number of pulses were given in the range 20–50 and the frequency range was 2000 Hz.

The ^{13}C NMR spectra were also obtained with Jeol FX 100 NMR spectrometer operating at.25 MHz in the pulsed FT-mode with a noise-modulated proton decoupler. The solvent used was $CDCl_3$ with TMS as internal standard. The spectral range was 7500 Hz (300 ppm) with 5000–8000 pulses. The recording was done at 25°C. It was repeated four times and resonance regions were shifted as a whole by ±0.3 to 0.5 ppm, but the resolution was not affected.

In ^{13}C NMR, the peak areas were considered to determine the concentrations of various triad sequence concentration in copolymers. Peak areas were determined by using a Lorentzian curve shape-fitting computer program on ICL-2960 computer at IIT Delhi. In ^{1}H NMR the intensities of the $-OCH_2$ and OCH_3 peaks were taken to calculate the relative concentrations of the comonomers in the copolymers.

VISCOSITY MEASUREMENTS

Chloroform was used as solvent for the viscosity measurements. All the measurements were done at 25 ± 0.1°C. The capillary of the viscometer was 0.5-mm diameter and the time of flow of pure solvent range was 120–150 s.

RESULTS AND DISCUSSION

From the ^{13}C NMR spectra of PMMA and PEMA, it was observed that due to the replacement of $-OCH_3$ group in PMMA by $-OC_2H_5$, there was no
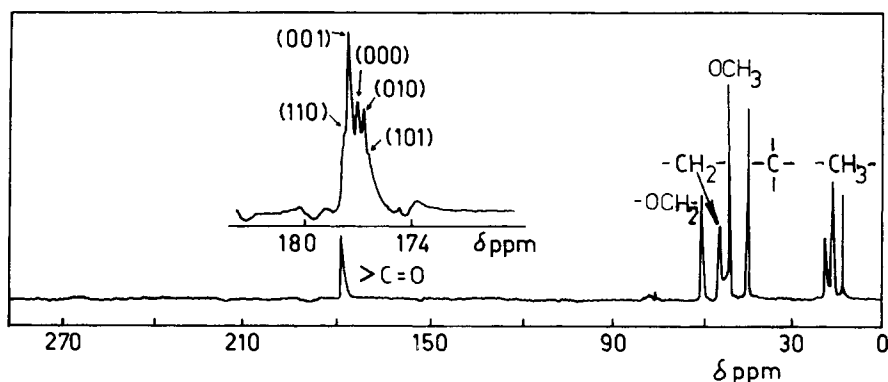

Fig. 1. Proton noise decoupled ^{13}C NMR spectrum at 25 MHz of MMA–EMA copolymer ($P_0 = 0.64$ and $P_1 = 0.36$) in $CDCl_3$ at 25°C. Insert: enlarged carbonyl regions.

significant change in the order of 0.4 ppm, which is within the instrumental error. The chemical shifts for the carbonyl carbon and quaternary carbons for PMMA fall in the 176.50–177.97 ppm and 44.25–45.20 ppm range, respectively, and for PEMA these are 176.33–177.53 ppm and 44.54–45.42 ppm, respectively. The carbonyl frequency shifts to upfield and quaternary carbon frequency shifts downfield in the copolymers.

There was no effect of change of composition of monomer on the pattern of the spectra, only the peak intensities were affected. The chemical shift for the carbonyl carbons of the copolymers fall in the 176.33–177.97 ppm range. The ^{13}C NMR spectrum of sample (C) is shown in Figure 1. As the concentration of EMA was increased the chemical shift values shifted upfield slightly.

Since the reactivities of EMA and MMA are approximately equal, Bernoullian and first-order Markovian statistics can be applied to MMA-EMA copolymers.

Proton-decoupled ^{13}C NMR spectrum obtained for one of the copolymer samples (C) is shown in Figure 1. The expanded C=O region, which is shown in Figure 1(b), reveals the presence of six peaks. Johnson and co-workers[5] observed 18 possible configurational pentad-compositional triad sequences in the case of MMA-MAA copolymers, due to the significant difference in the carbonyl carbon resonance frequencies of MMA and MAA units. Since there was overlap between the carbonyl carbon frequencies of MMA and EMA, 6 resonance peaks were observed due to triad sequences. Peat and Reynolds[10] have reported good agreement between observed triad concentrations with those calculated from Bernoullian and Markovian statistical models in PMMA. They assigned the pentad and triad chemical assignments for the carboxyl carbon from low to high field as mrrm*. rrrm, rrrr, rmrm + mmrm, rmrr + mmrr, mmmm, mmmr, and rmmr. The concentrations of triads were calculated from Bernoullian and Markovian statistical models, which are in good agreement with the observed values. The peaks were assigned to the compositional triads as shown in Figure 1(b). The assignment of triad sequence from carboxyl resonance peaks were verified from Bernoullian and Markovian statistics. The observed triad distributions for the samples are given in Table II along with triad concentrations calculated from the Bernoullian and first-order Markovian statistics.

Bernoullian probability expressions for a comonomer triad distribution of any particular length are given below. 0 and 1 are used for the concentration of methyl methacrylate and ethyl methacrylate in the sequence of copolymer. P_0 and P_1 are mole fractions of MMA and EMA respectively in copolymer.

$$(000) = P_0^3$$

$$(100) + (001) = 2P_0^2(1 - P_0)$$

$$(101) = P_0(1 - P_0)^2$$

$$(010) = P_0^2(1 - P_0)$$

$$(110) + (011) = 2P_0(1 - P_0)^2$$

$$(111) = (1 - P_0)^3$$

*m = meso and r = racemic conformations of polymers (Ref. 1).

TABLE II
Calculated and Observed Sequence Concentrations in Copolymers

Samples	A			B			C			D		
Sequences	Observed conc.	Calculated conc. Bernoullian statistic $P_0 = .26$	Markov statistic $P_{01} = .71$ $P_{10} = .20$	Observed conc.	Calculated conc. Bernoullian Sstatistic $P_0 = .45$	Markov statistic $P_{01} = .62$ $P_{10} = .69$	Observed conc.	Calculated conc. Bernoullian statistic $P_0 = .64$	Markov statistic $P_{01} = .43$ $P_{10} = .66$	Observed conc.	Calculated conc. Bernoullian statistic $P_0 = .82$	Markov statistic $P_{01} = .18$ $P_{10} = .84$
(111)	0.435	0.405	0.499	0.084	0.166	0.045	0.010	0.047	0.045	0.020	0.006	0.005
(110)	0.253	0.284	0.249	0.372	0.272	0.202	0.141	0.166	0.177	0.082	0.053	0.048
(010)	0.036	0.050	0.031	0.110	0.111	0.225	0.169	0.147	0.172	0.247	0.121	0.124
(000)	0.010	0.017	0.018	0.091	0.091	0.076	0.258	0.262	0.196	0.425	0.551	0.554
(001)	0.083	0.100	0.091	0.224	0.223	0.248	0.284	0.295	0.297	0.161	0.242	0.243
(101)	0.202	0.142	0.111	0.136	0.136	0.202	0.138	0.083	0.112	0.059	0.025	0.027

P_0 = Probability of finding MMA unit in copolymers
P_{01} = Probability of addition of 1 to a chain ending in 0.
P_{10} = Probability of addition of 0 to a chain ending in 1.
(0' represent MMA, '1' represent EMA).

The number-average sequence lengths of successive 0 or 1 additions are calculated by the expression

$$\bar{n}_0 = 1/1 - P_0$$

$$\bar{n}_1 = 1/P_0$$

The triad equations for the first order Markovian analysis are given in probabilities of P_{01} and P_{10}

$$(000) = P_{10}(1 - P_{01})^2/(P_{01} + P_{10})$$

$$(100) + (001) = 2P_{01}P_{10}(1 - P_{01})/(P_{01} + P_{10})$$

$$(101) = (P_{01})^2 P_{10}/(P_{01} + P_{10})$$

$$(010) = P_{01}(P_{10})^2/(P_{01} + P_{10})$$

$$(011) + (110) = 2P_{01}P_{10}(1 - P_{10})/(P_{01} + P_{10})$$

$$(111) = P_{01}(1 - P_{10})^2/(P_{01} + P_{10})$$

and number average sequences lengths are given by

$$\bar{n}_0 = 1/P_{01}$$

$$\bar{n}_1 = 1/P_{10}$$

Markov parameters P_{01}, P_{10} were calculated from the triad concentrations from NMR spectra, using the above order. Markovian equations triad ratios 110/101 and 001/101 are given in Table III. An examination of a triad distribution shows an agreement with Bernoullian and first-order Markovian statistics in the copolymers (A, B, C). While in sample D (80% MMA) triad distributions observed from ^{13}C NMR spectrum shows deviations. This shows that the presence of higher concentrations of MMA in copolymer.leads to deviations from the Bernoullian behavior. Triad ratios in Table III deviate significantly from 2.0.

TABLE III
Comonomer Triad Ratios of Copolymer (MMA-EMA)

Samples	110/101		001/010	
	Observed	Calculated[a]	Observed	Calculated[a]
A	1.15	2.00	2.31	2.00
B	2.27	2.00	3.23	2.00
C	1.10	2.00	1.68	2.00
D	2.00	2.00	0.66	2.00

[a] Calculated from Bernoullian statistics.

TABLE IV
Number Average Sequence Length for '0' ($\bar{n}_0$)

Samples A	Observed	Calculated from	
		Bernoullian statistics	First-order Markov statistics
A	1.19	1.35	1.41
B	1.67	1.82	1.61
C	2.38	2.78	2.32
D	4.54	5.56	5.56

TABLE V
Number Average Sequence Length for EMA (1) ($\bar{n}_1$)

Sample	Observed	Calculated from	
		Bernoullian statistics	First-order Markov statistics
A	4.72	3.85	5.00
B	2.04	2.22	1.45
C	1.55	1.56	1.51
D	1.07	1.22	1.19

Number average sequence ($\bar{n}_0$) for MMA increases from 1.19 to 4.54 (samples A to D). The number average sequence length for EMA (n_1) decreases from 4.72 to 1.07 in samples A to D. This shows that number average sequence for monomer is dependent on the concentration of that particular monomer. Number average sequence lengths are shown in Tables IV and V. Number average sequence lengths appear to offer better conformity for both first-order Markovian and Bernoullian behavior.

For the quaternary carbons, three peaks were observed in the 44.54–45.42 pm frequency range for all the copolymer samples (A to D). Since the pattern of the spectra and the resonant frequencies for all the copolymers were the same, we can conclude that there is no compositional or sequence distribution effect on the quaternary carbon frequency and that the quaternary carbon resonance pattern cannot be used for obtaining the sequence distribution in the same manner as for PMMA.[10]

TABLE VI
Molecular Weights of Copolymers (Mark-Houwink
Constants K = 4.8×10^{-3} mL/g, a = 0.80)

Sample	Intrinsic viscosity	Mol. wt. $\times 10^{-4}$
A	1.64	2.6
B	1.67	2.7
C	1.77	2.9
D	1.62	2.6

MOLECULAR WEIGHT OF THE COPOLYMERS

Since the Mark-Houwink constants for MMA-EMA copolymer are not reported in the literature, we have taken these constants as equal to that of PMMA from the literature. The molecular weights are given in Table VI. Molecular weight of copolymers were on the order of 2.8×10^4 a.m.u.

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