Sequence Determination in Methyl Methacrylate–n-Butyl Methacrylate Copolymers by ^{13}C NMR Spectroscopy

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ABSTRACT: Methyl methacrylate (MMA) and n-butyl methacrylate (n-BuMA) were bulk copolymerized at 70°C using benzoyl peroxide as an initiator. The composition of the copolymer samples was estimated by ^{1}H NMR spectroscopic technique. Reactivity ratios were calculated by Tüdös method. ^{13}C [^{1}H] NMR spectra were used to study the monomer sequence distribution in copolymers. Various triads fractions were calculated by using the carbonyl resonance. The experimental triad concentrations showed good agreement with calculated values from Bernoullian and Harwood statistical programs.

KEY WORDS Methyl Methacrylate / n-Butyl Methacrylate / Triad Sequence / ^{13}C NMR / Bernoullian Statistics / Harwood Statistics /

Recent advances in nuclear magnetic resonance spectroscopy have led to more exact characterization of copolymers including determination of stereochemical configuration and sequence length distribution. NMR spectroscopy has been used to study the copolymer composition and monomer sequence distribution for several copolymers: vinyl chloride–vinylidene chloride,[1] ethylene–vinylacetate,[2] methacrylic acid–(dimethylamino)ethyl methacrylate,[3] tetrahydrofuran–3,3-dimethyloxetane,[4] methyl methacrylate–acrylic acid.[5] In our previous publications, the sequence distribution of methyl methacrylate–ethyl methacrylate copolymer,[6] methyl methacrylate–acrylic acid copolymers[7] and methyl methacrylate–styrene copolymers[8] have been reported by ^{13}C NMR spectroscopy. In the continuation of our previous work, in this manuscript, we report the sequence distribution in methyl methacrylate–n-butyl methacrylate copolymers by using NMR spectroscopy, Bernoullian and Harwood statistical program.[9]

EXPERIMENTAL

Methyl methacrylate and n-butyl methacrylate were distilled under vacuum and stored below 5°C. Benzoylperoxide (0.1%) was mixed with the monomers in a three neck flask. Molar feed ratios from 0 to 100% methyl methacrylate were used. The polymerization was carried out at 70°C and a slow stream of purified nitrogen was passed in. The copolymerization was terminated at a conversion of less than 5% by precipitation into excess of methanol.

Conditions for recording ^{1}H NMR and ^{13}C NMR spectra, and curve fitting have been reported in the previous papers.[6-8] The molecular weights of the copolymers were determined by viscometry at 39 ± 0.1°C in toluene.

RESULTS AND DISCUSSION

^{1}H NMR spectrum of methyl methacrylate–n-butyl methacrylate copolymer is shown in Figure 1. The resonance band at δ 3.96 can be
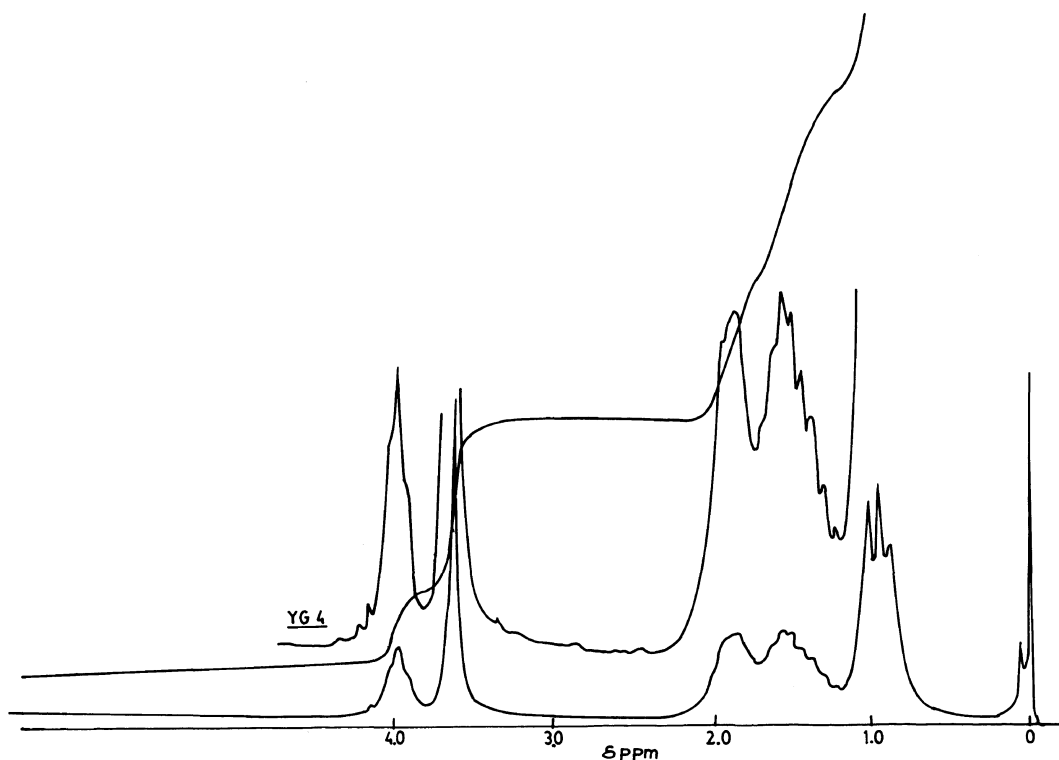
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Figure 1.   99.55 MHz ^{1}H NMR spectrum of MMA–n-BuMA (39%) copolymer in CDCl$_3$ at 25°C.

assigned to –OCH$_2$ protons of n-butyl methacrylate unit and at δ 3.59 is due to –OCH$_3$ protons of methyl methacrylate unit. Two broad resonance bands, centered at δ 1.85 and δ 1.56 are due to methylene protons. Resonances at δ 1.02, δ 0.95, and δ 0.88 ppm are due to α-CH$_3$ protons and –CH$_3$ protons in the butyl group. Various resonances in this region can not be distinguished because of overlap due to spin–spin coupling and sensitivity of methyl protons towards tacticity and monomer sequence.

The relative concentration of comonomers in copolymers was determined by comparing the intensities of the –OCH$_2$ and –OCH$_3$ proton resonances. The methyl methacrylate mole fraction (F_1) in the copolymer, can be readily determined by using the relationship:

$$F_1 = \frac{2I(-OCH_3)}{[3I(-OCH_2) + 2I(-OCH_3)]}$$

where $I(-OCH_2)$ and $I(-OCH_3)$ represent the peak intensities of –OCH$_2$ and –OCH$_3$ proton resonance respectively. The comonomer mole fractions, in feed and in copolymers are given in Table I. The reactivity ratios were calculated according to the method of Tüdos et al.[10] The values of reactivity ratios are $r_1 = 0.96$ and $r_2 = 1.04$ (where 1 = MMA and 2 = n-BuMA). In the literature[11,12] lot of discrepancy exists on the values of reactivity ratios for the methyl methacrylate–n-butyl methacrylate copolymer system. The above calculated values seem to be more correct because the structure of methyl methacrylate and n-butyl methacrylate is almost same and so the values of reactivity ratios. Using the data of Table I, Figure 2 represents the corresponding Kelen–Tüdos plot for MMA–n-BuMA copolymer system. To further confirm, reactivity ratios for each sample were calculated by the method of Chûjô.[13] The mole fraction of monomers in

Table I. Copolymerization data of methyl methacrylate (1)–n-butyl methacrylate (2) copolymers prepared at 70°C

Sample	f_1	f_2	F_1	F_2	Conversion wt%	Mol. wt. $M \times 10^{-6}$
A	0.71	0.29	0.70	0.30	3.0	1.22
B	0.61	0.39	0.61	0.39	4.8	1.11
C	0.51	0.49	0.50	0.50	3.5	0.90
D	0.41	0.59	0.40	0.60	5.8	0.69
E	0.31	0.69	0.30	0.70	3.5	1.32

f = mole fraction of comonomers in feed.
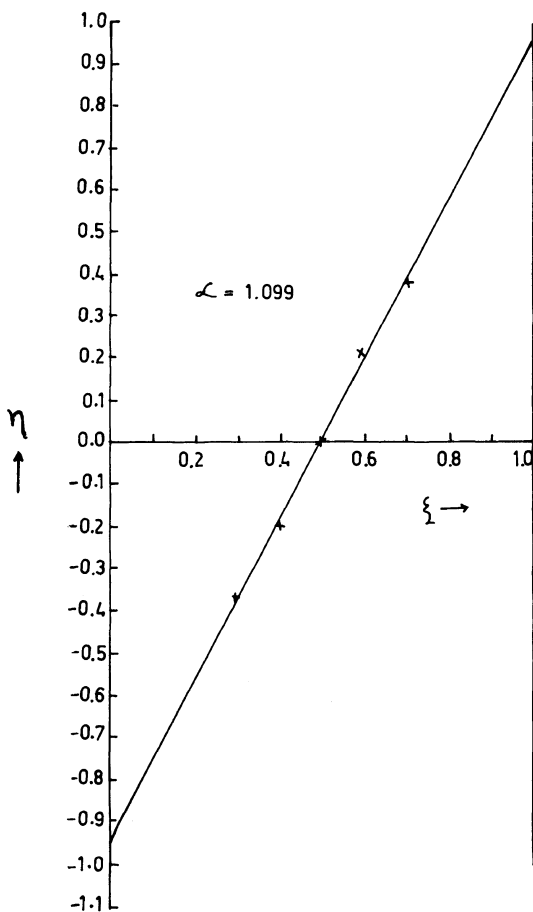F = mole fractions of comonomers in copolymer (by ^{1}H NMR).

Table II. Reactivity ratios for individual samples by the method of Chûjô[13]

Sample	F_1	r_1	r_2
A	0.70	0.98	1.03
B	0.61	0.99	0.98
C	0.50	0.96	1.04
D	0.40	0.98	1.02
E	0.30	0.98	1.02

F_1 = mole fraction of methyl methacrylate in copolymer; r_1 = methyl methacrylate; r_2 = n-butyl methacrylate.
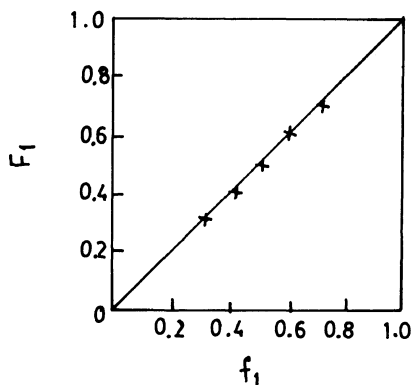

Figure 3. Copolymer composition (mole fraction F_1) as a function of monomer composition (mole fraction f_1): (———), theoretical behavior; (— × —), experimental points.

Figure 2. Kelen Tüdös plot for MMA–n-BuMA copolymer system.

copolymers, as determined by ^{1}H NMR and dyad concentrations were used to calculate the reactivity ratios for each sample. The reactivity ratios as determined by above method are given in Table II. The r_1 varies from 0.96 to 0.98 and r_2 varies from 0.98 to 1.04 and the values are in close agreement with those calculated by Tüdös method. The values of reactivity ratios and their product (0.998), indicate that copolymerization is almost ideal and copolymer composition is always equal to the monomer feed composition. Figure 3, represents calculated composition plot for MMA–n-BuMA copolymer system.

From the proton decoupled ^{13}C NMR spectra of poly(MMA) and poly(n-BuMA), it was observed that there were no significant changes in the chemical shift values for the carbonyl
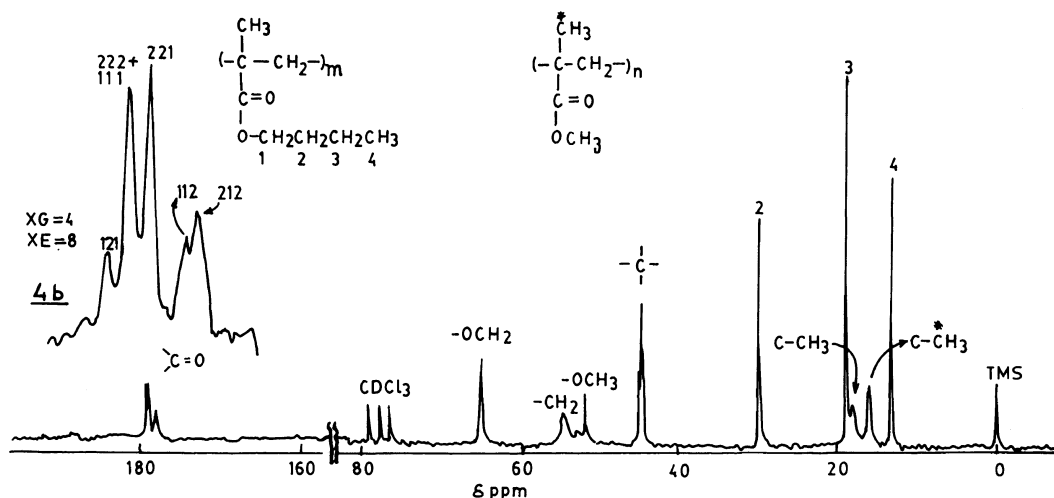
Figure 4. 25 MHz proton decoupled ^{13}C NMR spectrum of MMA–n-BuMA copolymer in CDCl$_3$ at 25°C.

and quaternary carbons. A proton decoupled ^{13}C NMR spectrum for methyl methacrylate–n-butyl methacrylate (69%) copolymer is shown in Figure 4. The various resonance peaks have been assigned by comparing with poly-(methyl methacrylate) and poly(butyl methacrylate). Quaternary, methylene and various methyl carbons are showing single resonance band due to their insensitivity towards monomer and stereo-sequences. Carbonyl resonance is appearing as a multiplet, due to its sensitivity towards various placements of monomers. As resonance frequencies of MMA and n-BuMA overlap, there is no ordering of chemical shift for different triads. Therefore, peak assignment to different triad sequences were made by comparing the experimentally determined triad fraction and those calculated theoretically using Bernoullian and Harwood statisics. The peak assignment to different triads is shown in Figure 4b. Also it is evident that there is no effect of polymer composition on the pattern of the spectrum, only the intensities of the peaks are being affected. The resonance peaks due to 221, 212 triad are growing, as the mole fraction of n-BuMA in the copolymer is increasing. The effect of concentration of n-

BuMA on the resonance peak due to 222 triad is not so significant because resonance peaks of 222 and 111 triads are overlapping. The stereosequence effects on the splitting of carbonyl resonance signals were ruled out by calculating the triad, tetrad and pentad sequence distribution using Harwood statistics. The values for the triad concentrations as calculated by ^{13}C NMR tally well with the theoretical values using Bernoullian and Harwood statistics. This shows, however there is not much difference in the chemical shift of various triad combination but the agreement between ^{13}C NMR data and theoretical data shows that the stereosequence effects are negligible, if any. The observed triad distribution for all the copolymers, along with triad concentrations calculated using Bernoullian and Harwood statistics are given in Table III. A somewhat greater block tendency may be noticed in the calculated distribution, which may be due to the omission of penultimate effects in the calculations. Figure 5 shows the normalised MMA and n-BuMA centered population respectively vs. % methyl methacrylate in the copolymers over a whole range of composition. The curves reflect the monomer distribution of a random

Table III. Observed and calculated triad distribution in methyl methacrylate–n-butyl methacrylate copolymers

Sample Triad	δ ppm*	A			B			C		
		CMR.	BER.	HAR.	CMR.	BER.	HAR.	CMR.	BER.	HAR.
[111]	100.65	0.49	0.49	0.49	0.44	0.37	0.36	0.25	0.25	0.25
[112]	99.65	0.39	42	0.42	0.44	0.48	0.48	0.43	0.50	0.50
[212]	99.51	0.12	0.09	0.09	0.12	0.15	0.16	0.32	0.25	0.25
[222]	100.58	0.08	0.09	0.09	0.16	0.15	0.16	0.39	0.25	0.25
[221]	100.24	0.41	0.42	0.42	0.42	0.48	0.48	0.36	0.50	0.50
[121]	100.92	0.51	0.49	0.49	0.42	0.37	0.36	0.25	0.25	0.25

Sample Triad	δ ppm*	D			E		
		CMR.	BER.	HAR.	CMR.	BER.	HAR.
[111]	100.65	0.16	0.16	0.16	0.09	0.09	0.09
[112]	99.65	0.43	0.48	0.48	0.40	0.42	0.42
[212]	99.51	0.41	0.36	0.36	0.51	0.49	0.49
[222]	100.58	0.41	0.36	0.36	0.46	0.49	0.49
[221]	100.24	0.45	0.48	0.48	0.44	0.42	0.42
[121]	100.92	0.14	0.16	0.16	0.10	0.09	0.09

* = downfield from $CDCl_3$; 1 = methyl methacrylate; 2 = n-butyl methacrylate; CMR = by ^{13}C NMR spectroscopy; BER = by Bernoullian statistics; HAR = by Harwood statistics.
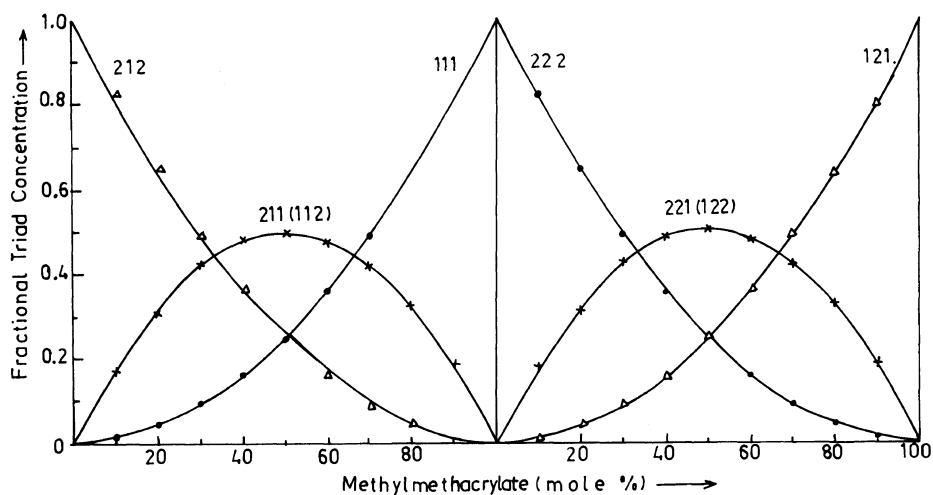

Figure 5. Normalized statistical monomer sequence distribution triad concentrations *vs.* methyl methacrylate (mol%) in methyl methacrylate (1)–n-butyl methacrylate (2) copolymers.

copolymer. The good agreement between the experimental and theoretical distribution allowed us to calculate the tetrad and pentad sequence distribution using Harwood's program. Tetrad and pentad distribution for methyl methacrylate–n-butyl methacrylate copolymer system over a whole range of composition is given in Table IV and V respectively.

Table IV. Calculated tetrad distribution for methyl methacrylate (1)–*n*-butyl methacrylate (2) copolymers by Harwood statistics

Tetrad	Methyl methacrylate (mol%)								
	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0
[1111]	0.000	0.001	0.008	0.026	0.062	0.130	0.242	0.396	0.645
[2111]	0.002	0.012	0.038	0.077	0.125	0.173	0.206	0.206	0.149
[2112]	0.008	0.024	0.044	0.058	0.062	0.058	0.044	0.027	0.009
[1121]	0.002	0.012	0.038	0.077	0.125	0.173	0.206	0.206	0.149
[1122]	0.015	0.049	0.089	0.115	0.125	0.115	0.088	0.054	0.017
[2222]	0.666	0.422	0.238	0.129	0.063	0.025	0.008	0.002	0.000
[1222]	0.142	0.203	0.205	0.173	0.125	0.077	0.037	0.014	0.002
[1221]	0.008	0.024	0.045	0.058	0.063	0.058	0.044	0.027	0.009
[2122]	0.142	0.204	0.206	0.172	0.125	0.077	0.037	0.014	0.003
[2121]	0.015	0.049	0.089	0.115	0.125	0.114	0.088	0.054	0.017

Table V. Pentad distribution for methyl methacrylate (1)–*n*-butyl methacrylate (2) copolymers by Harwood statistics

Pentad	Methyl methacrylate (mol%)								
	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0
[11111]	0.000	0.001	0.008	0.026	0.062	0.130	0.242	0.396	0.646
[21111]	0.002	0.012	0.038	0.077	0.125	0.173	0.206	0.206	0.149
[21112]	0.008	0.024	0.044	0.058	0.063	0.058	0.044	0.027	0.009
[12111]	0.002	0.012	0.038	0.077	0.125	0.173	0.206	0.206	0.149
[21121]	0.015	0.049	0.089	0.115	0.125	0.115	0.088	0.054	0.017
[22111]	0.015	0.049	0.089	0.115	0.125	0.115	0.088	0.054	0.017
[22112]	0.142	0.203	0.206	0.172	0.125	0.076	0.037	0.014	0.002
[12121]	0.008	0.024	0.044	0.058	0.063	0.058	0.044	0.027	0.009
[22122]	0.666	0.423	0.238	0.129	0.062	0.025	0.008	0.002	0.000
[22121]	0.142	0.203	0.206	0.173	0.125	0.077	0.037	0.014	0.002
[22222]	0.666	0.422	0.238	0.129	0.062	0.025	0.008	0.002	0.000
[12222]	0.142	0.203	0.205	0.173	0.125	0.076	0.037	0.014	0.002
[12221]	0.008	0.024	0.044	0.058	0.062	0.057	0.044	0.027	0.009
[21222]	0.142	0.203	0.206	0.173	0.125	0.077	0.037	0.014	0.002
[12212]	0.015	0.049	0.089	0.115	0.125	0.115	0.088	0.054	0.017
[11222]	0.015	0.049	0.089	0.115	0.125	0.115	0.087	0.054	0.017
[11221]	0.002	0.012	0.038	0.077	0.125	0.173	0.206	0.206	0.149
[21212]	0.008	0.024	0.044	0.058	0.063	0.058	0.044	0.027	0.009
[11211]	0.000	0.001	0.008	0.026	0.063	0.130	0.242	0.396	0.045
[11212]	0.002	0.012	0.038	0.077	0.125	0.173	0.206	0.206	0.149

MOLECULAR WEIGHT MEASUREMENTS

Since the Mark–Houwink constants for MMA–*n*-BuMA copolymer are not reported, we have taken these constants as equal to that for PMMA from the literature.[14] Mark Houwink constants for PMMA at 39°C in Toluene are $K = 7.24 \times 10^{-3}$ ml g^{-1}, $a = 0.72$. The molecular weights are given in Table I. The values of molecular weights are in order of the million for all the samples.

REFERENCES

1. A. Komoroski and J. P. Shockcor, *Macromolecules,* **16,** 1538 (1983).
2. H. N. Sung and J. H. Noggle, *J. Polym. Sci.,* **19,** 1593 (1981).
3. L. Marle and Y. Marle, *Macromolecules,* **15,** 360 (1982).
4. J. Guzman and E. Riande, *J. Polym. Sci., Polym. Chem. Ed.,* **23,** 2283 (1985).
5. K. I. Ekpenyong, *J. Polym. Sci., Polym. Chem. Ed.,* **23,** 125 (1985).
6. A. S. Brar and A. K. Saini, *J. Appl. Polym. Sci.,* **32,** 4607 (1986).
7. A. S. Brar and E. Arunan, *J. Polym. Sci., Polym. Chem. Ed.,* (communicated).
8. A. S. Brar and G. S. Kapur, *Polym. J.,* **20,** 371 (1988).
9. H. J. Harwood, *J. Polym. Sci., C,* **25,** 37 (1968).
10. T. Kelen and F. Tüdös, *J. Macromol. Sci. Chem.,* **A9,** 1 (1975).
11. J. K. Borchardt, *J. Macromol. Sci.-Chem.,* **A22,** 1717 (1985).
12. R. G. Greenly, *J. Macromol. Sci.-Chem.,* **A14,** 445 (1980).
13. R. Chûjô, *J. Phys. Soc. Jpn.,* **21,** 2669 (1966).
14. J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," Interscience, New York, N. Y., 1966.