Microstructure Determination of Methyl Methacrylate-*N*-Arylsubstituted Itaconimide Copolymers by NMR Spectroscopy

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ABSTRACT: This article describes the homopolymerization and copolymerization of methyl methacrylate with *N*-(5-chloro-2-methoxyphenyl)itaconimide (OMCPI)/*N*-(5-chloro-3-methoxyphenyl)itaconimide (MCPI) monomers using AIBN as an initiator and THF as solvent at 60°C. Feed compositions having varying mole fractions of OMCPI and MCPI ranging from 0.1 to 0.5 were taken to prepare copolymers. Structural characterization of homopolymers and copolymers thus obtained was done using FT-IR, ^{1}H-NMR, and elemental analysis. Copolymer composition was determined using percent nitrogen content. Comonomer reactivity ratios were determined using Kelen-Tüdos and non-linear error in variable model (EVM) method using RREVM computer program. Carbonyl carbon signals of MMA (M) as well as *N*-aryl itaconimide (I) copolymers in the $^{13}C\{^{1}H\}$-NMR spectra were used for the determination of sequence distribution of *M*-and *I*-centered triads. Sequence distribution of *M*- and *I*-centered triads calculated using $^{13}C\{^{1}H\}$-NMR spectra are in good agreement with the theoretically calculated values using Harwood's model. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 491–497, 2010

Key words: methyl methacrylate; *N*-arylsubstituted itaconimide; microstructure; copolymerization

INTRODUCTION

Microstructural studies in copolymers are of immense help in establishing structure-property relationships.[1,2] The microstructure of the polymers can be investigated by nuclear magnetic resonance (NMR) spectroscopy.[3–5] Polymer microstructure allows elucidation of the mechanism of polymerization and polymer dynamics. In studies of copolymerization kinetics and polymer microstructures, the organization and interpretation of reaction probability models can be done.[1,6,7] These statistical models fall into two categories: those where the chain end of the propagating polymer chain influences the addition of next monomer unit (so-called chain-end control), and those where the catalyst/initiator determines the addition (catalytic-site control). The most common chain-end-controlled models are Bernoullian (B) and first- and second-order Markovian (M1 and M2) models.

The present article describes the microstructure analysis of copolymers of MMA with *N*-(5-chloro-2-methoxyphenyl) itaconimide (OMCPI)/*N*-(5-chloro-3-methoxyphenyl) itaconimide (MCPI) monomers using Harwood's statistical model program and experimentally using ^{13}C-NMR spectroscopy.

EXPERIMENTAL

Materials

OMCPI and MCPI were synthesized and purified in the laboratory using the procedure reported in one of our earlier articles.[8] Tetrahydrofuran (THF) (CDH, India) was dried by refluxing with metallic sodium and benzophenone followed by distillation. Azobisisobutyronitrile (AIBN) (High Polymer Labs, India) was recrystallized using chloroform. Methyl methacrylate (MMA) (Merck, India) was washed with dilute sodium hydroxide to remove the inhibitor, followed by repeated washing with distilled water until neutral. It was dried over anhydrous sodium sulfate overnight and distilled under reduced pressure. Methanol (s.d. Fine Chem., India), chloroform (s.d. Fine Chem., India), and silica gel for column chromatography (CDH, India) were used as supplied.

Preparation of homopolymers and copolymers of OMCPI/ MCPI and MMA

Homopolymerization and copolymerization of *N*-arylsubstituted itaconimides with MMA was carried out at 60°C under nitrogen atmosphere in

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solution using THF as solvent and AIBN as an initiator. Ten to thirty percent (w/v) solution of the monomers in THF was placed in a three necked round bottom flask equipped with a reflux condenser, CaCl$_2$ drying tube, and a nitrogen gas inlet tube. The whole assembly was placed in a thermostatted bath and stirred with a magnetic stirrer. Reaction mixture was purged with nitrogen and the temperature was raised to 60°C. Polymerization was initiated by adding AIBN [1% (w/w) of monomers] to the monomer solution. Reaction was stopped at low conversion (∼ 10–15%) by pouring the contents of the flask into large excess of methanol. The precipitated polymer was washed repeatedly with hot methanol to remove unreacted monomer and was dried under vacuum. Homopolymers of OMCPI and MCPI are designated as OMCPI-10 and MCPI-10, respectively.

Similarly, copolymerization of OMCPI/MCPI with MMA was carried out in nitrogen atmosphere at 60°C using AIBN as an initiator and THF as solvent. The mole fraction of imides in the initial feed was varied from 0.1 to 0.5, respectively. Copolymers have been designated as OMCPI and MCPI followed by a numerical suffix indicating the mol fraction of the itaconimide in the feed multiplied by 10. For example, a copolymer prepared by taking 0.2-mol fraction of OMCPI and MCPI has been designated as OMCPI-2 and MCPI-2, respectively.

Characterization techniques

FT-IR spectra of polymers were recorded as thin films using Nicolet FT-IR spectrophotometer. Elementar Vario EL was used for C, H, and N analysis.

^{1}H and ^{13}C{^{1}H}-NMR experiments were carried out on a Bruker DPX 300 MHz spectrometer using standard pulse sequences as reported in Bruker pulse program library. ^{1}H-NMR spectra for all the homo and copolymers were recorded at a frequency of 300.13 MHz. The 32 k data points were accumulated with a 5 s delay time for 16 successive scans. ^{13}C{^{1}H}-NMR spectra of all the homo and copolymers were recorded at 75.5 MHz. A total of 6000 scans were accumulated with a relaxation delay of 2 s containing 16 k data points using Waltz-16 broad band decoupler. The relative areas of resonance signals were determined using a non-linear least square Lorentzian line shape deconvolution program.[9] In all the cases, fitting was considered valid only when $\chi^2 < 1$.

RESULTS AND DISCUSSION

FT-IR

In FT-IR spectra of the MMA-N-arylsubstituted itaconimide copolymers, the two characteristic

absorption bands due to imide groups were observed in the region 1700–1800 cm^{-1}. The absence of peak around 1640 cm^{-1} in all the copolymer samples showed the absence of double bond and thus the absence of monomers.

^{1}H-NMR

In ^{1}H-NMR spectra of MMA-N-arylsubstituted itaconimide copolymers, resonance signals due to ─OCH$_3$ protons of MMA and aromatic protons of N-arylsubstituted itaconimide were observed at δ = 3.7–3.6 ppm and δ = 7.3–6.9 ppm, respectively. The other characteristic signals observed at δ = 2.0–1.6 ppm and 1.2–0.8 ppm were due to ─CH$_2$ and ─CH$_3$ protons of MMA, respectively. The intensity of signals due to aromatic protons increased with increasing concentration of itaconimide in the initial feed. The signal due to ─OCH$_3$ of MMA got merged with the signal due to ─OCH$_3$ substituent of aromatic ring making it difficult to calculate the copolymer composition from ^{1}H-NMR. Therefore, in present work copolymer composition was determined from percent nitrogen content.

Copolymer composition and reactivity ratio determination

From the results of % nitrogen, copolymer composition was determined using following equation:

$$\%N = \frac{14na}{M_1a + M_2(1 - a)} \tag{1}$$

where, a = mole fraction of N-arylitaconimide monomer in the copolymer.

TABLE I
Details of Feed Composition and Results of Copolymer Composition Determined from % Nitrogen Content in MMA-N-Arylsubstituted Itaconimide Copolymers

Sample designation	Nitrogen (%)	Mole fraction of N-arylsubstituted itaconimide in	
		Feed	Copolymers
MCPI-1	2.26	0.10	0.21
MCPI-2	3.31	0.20	0.37
MCPI-3	4.29	0.30	0.57
MCPI-4	4.01	0.40	0.51
MCPI-5	5.33	0.50	0.58
OMCPI-1	3.03	0.10	0.32
OMCPI-2	3.50	0.20	0.40
OMCPI-3	4.34	0.30	0.58
OMCPI-4	4.24	0.40	0.56
OMCPI-5	4.70	0.50	0.68

TABLE II
Reactivity Ratio of *N*-Aryl Itaconimides (r_1) and MMA (r_2)

Copolymer system	Kelen Tüdos		RREVM	
	r_1	r_2	r_1	r_2
MMA–MCPI	1.60	0.28	1.54	0.32
MMA–OMCPI	1.41	0.17	1.23	0.15

M_1 and M_2 are the molecular weights of *N*-arylitaconimide and MMA, respectively.

'*n*' represents the number of nitrogen atoms in nitrogen containing monomer. Here, $n = 1$ in all the cases.

The results are summarized in Table I.

From the knowledge of copolymer composition, reactivity ratios were calculated using Kelen Tüdos method. These reactivity ratios along with copolymer composition data were used to calculate the reactivity ratios from the non-linear error in variable model (EVM) method using RREVM computer program.[10] The results are summarized in Table II. The error in determining the monomer composition in feed and copolymer was estimated to be 1% and 3%, respectively. The monomer reactivity ratio data shows that reactivity of MMA is lower as compared to *N*-aryl itaconimide monomers towards homo/cross-propagation.

^{13}C{^{1}H}-NMR studies

Structural characterization

The ^{13}C{^{1}H}-NMR spectra of MMA–MCPI and MMA–OMCPI copolymers and the homopolymers of MCPI and OMCPI were recorded using CDCl$_3$ as solvent. ^{13}C{^{1}H}-NMR spectrum of PMMA was recorded using DMSO as solvent. The ^{13}C{^{1}H}-NMR spectra of homopolymers (PMMA, MCPI-10, and OMCPI-10) and copolymers (MCPI-5 and OMCPI-5) are shown in (Figs. 1–3).

In the ^{13}C{^{1}H}-NMR spectrum of PMMA (Fig. 1) the resonance signal due to the carbonyl carbon was observed in the region $\delta = 177.0–175.0$ ppm and shows a multiplicity due to tacticity. The —OCH$_3$, —CH$_2$—, and quaternary carbons were observed at $\delta = 53.0$, 52.0 and 44.0 ppm, respectively. The —CH$_3$ carbon of the side chain shows multiplicity due to tacticity and was observed in the region $\delta = 20–14$ ppm.

The resonance signals due to the carbonyl carbons of MCPI homopolymer [Fig. 2(a)] were observed at $\delta = 176.5–171.0$ ppm ($>^1$C=O) and $\delta = 182.0–177.2$ ppm ($>^2$C=O). Aromatic carbons of MCPI homopolymer resonate in the region $\delta = 160.0–110.0$ ppm and methoxy carbon and vinylidene carbons of itaconimide were observed in the region $\delta = 60.0$
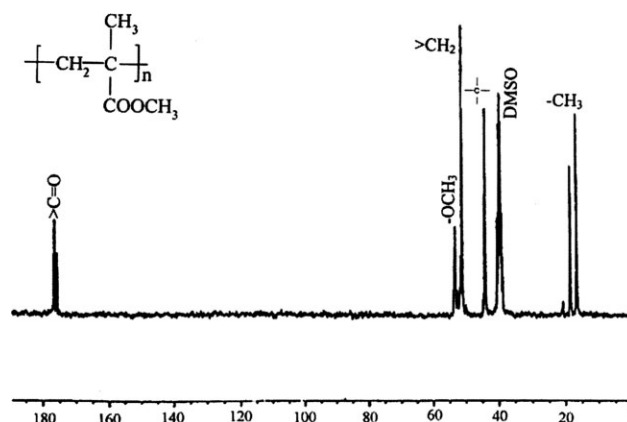

Figure 1 ^{13}C{^{1}H}-NMR Spectrum of PMMA.

and 45.0 ppm, respectively. The signals corresponding to the backbone carbon atoms and methylene carbon of imide were observed in the region $\delta = 55.0–22.0$ ppm.

Similarly, in the ^{13}C{^{1}H}-NMR spectrum of OMCPI homopolymer [Fig. 2(b)], carbonyl carbons were observed in the region $\delta = 176.5–171.0$ ppm ($>^1$C=O) and $\delta = 182.0–177.0$ ppm ($>^2$C=O). Aromatic carbons were observed in the region $\delta = 158.0–95.0$ ppm and methoxy, vinylidene, and the backbone carbons were observed in the region $\delta = 60.0–45.0$ ppm.

All the resonance signals in ^{13}C{^{1}H}-NMR spectra of the copolymers were assigned with the help of
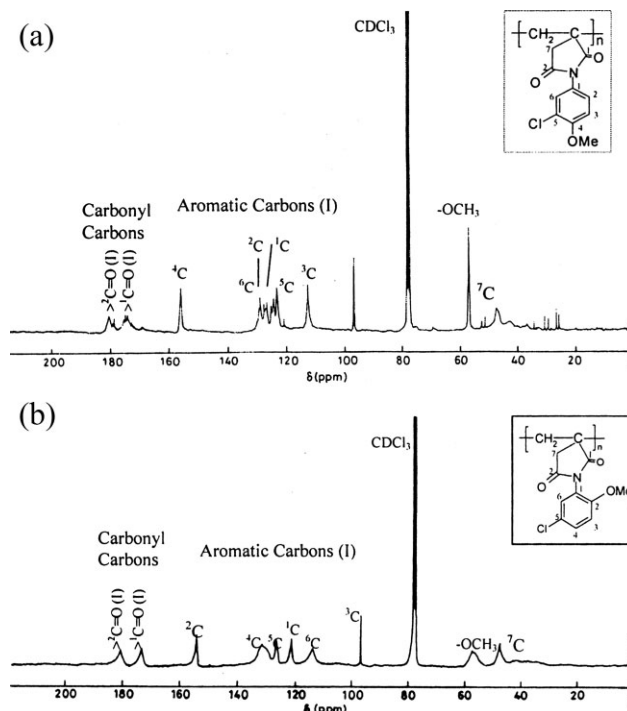
Figure 2 ^{13}C{^{1}H}-NMR Spectra of (a) MCPI-10 (b) OMCPI-10.

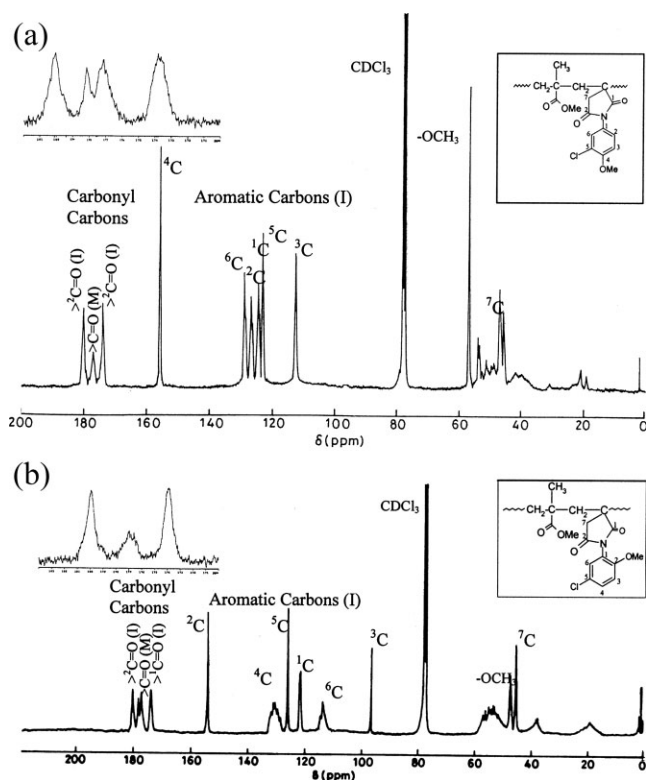**Figure 3** ^{13}C{^{1}H}-NMR Spectra of (a) MCPI-5 (b) OMCPI-5.

^{13}C{^{1}H}-NMR spectra of homopolymers of both the monomers. The ^{13}C{^{1}H}-NMR spectra of MCPI-5 and OMCPI-5 copolymers are shown in Figure 3. In the ^{13}C{^{1}H}-NMR spectra of MMA–MCPI copolymers, the carbonyl carbon of MMA was observed in the region δ = 178.8–176.0 ppm and of N-aryl itaconimide in the region δ = 182.0–177.2 ppm ($>^{2}$C=O) and δ = 175.0–172.7 ppm ($>^{1}$C=O). The aromatic carbons of itaconimide were observed in the region δ = 160.0–110.0 ppm. The signals corresponding to —OCH$_3$ of itaconimide and MMA were observed at δ = 57.1 and 54.2 ppm, respectively. The signals for other carbons in the backbone and the side chain were observed in the region δ = 53.0–15.0 ppm. Similarly, for MMA–OMCPI copolymers the carbonyl carbon of MMA was observed in the region δ = 178.7–175.8 ppm and for N-aryl itaconimide at δ = 182.0–179.0 ppm ($>^{2}$C=O) and δ = 174.6–172.0 ppm ($>^{1}$C=O). The aromatic carbons of itaconimide were observed in the region δ = 157.0–95.0 ppm. The signals corresponding to —OCH$_3$ of itaconimide and MMA and for other carbons in the backbone and the side chain were observed in the region δ = 60.0–15.0 ppm.

Carbonyl region for copolymer samples prepared using varying amounts of MCPI/OMCPI in the feed are shown in Figures 4 and 5. Relative intensity of the signals due to carbonyl carbon of itaconimide increased with respect to the intensity of carbonyl

carbon of MMA as the amount of itaconimide in feed was increased.

Triad concentration determination

Carbonyl carbon signals of MMA (*M*) as well as of N-arylsubstituted itaconimide (*I*) in copolymers show a multiplet indicating that they are sensitive to compositional and configurational sequences and hence were used for the determination of the sequence distribution of *M*- and *I*- centered triads.

Carbonyl region of MMA in ^{13}C{^{1}H}-NMR spectra for the series of MMA–MCPI copolymers of different copolymer composition is divided into three broad envelopes. Carbonyl carbon resonance signal in the region δ = 178.8–177.9 ppm, which decreases in intensity as the MMA content in the copolymer decreases, is assigned to MMM triad and that in the region δ = 177.9–177.0 ppm, which first increases and then decreases is assigned as MMI triad. Intensity of the carbonyl signals in the region δ = 177.0–176.0 ppm increases as the MMA content in the copolymer decreases, and therefore, assigned to IMI triad compositional sequence. Similar assignment of *I*-centered triad regions could not be accomplished due to overlapping of three envelopes.
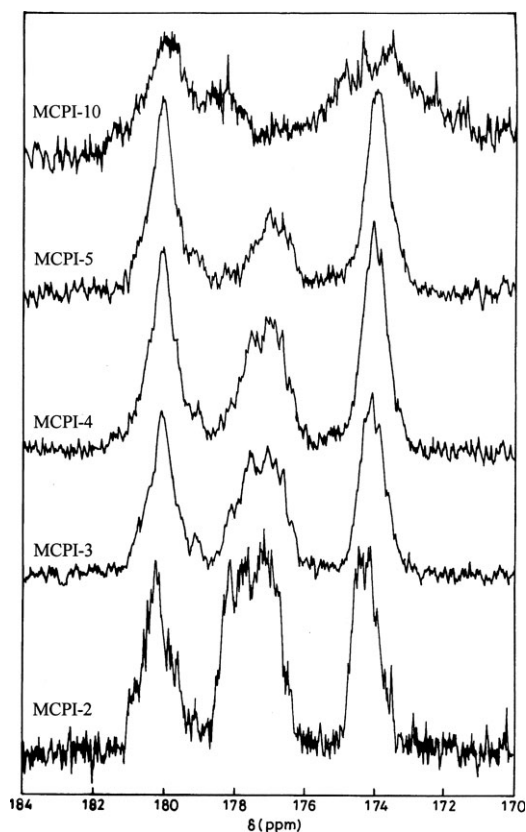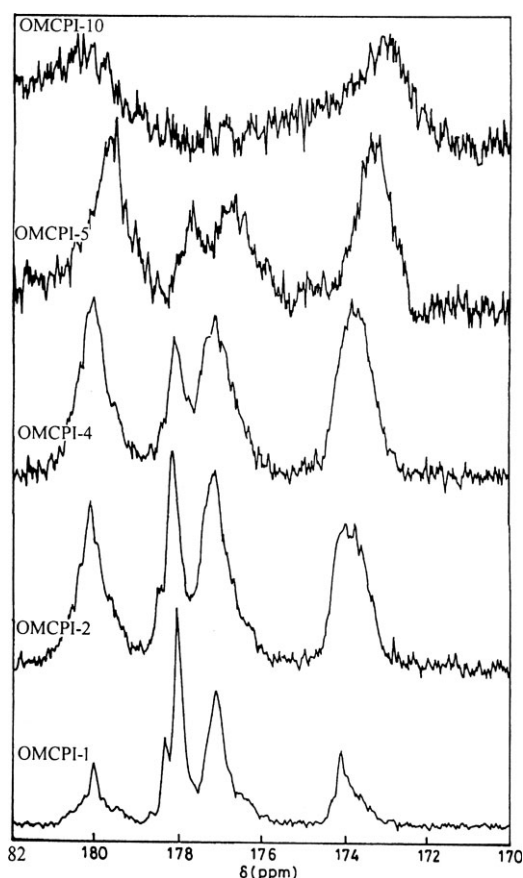

Figure 4 ^{13}C{^{1}H}-NMR Spectra of MMA–MCPI Copolymers (carbonyl regions).

Figure 5 ^{13}C{^{1}H}-NMR Spectra of MMA–OMCPI Copolymers (carbonyl regions).

In case of MMA–OMCPI copolymers, the carbonyl region of MMA was observed in the region δ = 178.7–175.8 ppm whereas the carbonyl of itaconimide was observed in the region δ = 182.0–179.0 ppm ($>^2$C=O) and δ = 174.6–172.0 ppm ($>^1$C=O).

The signals resonating around δ = 178.7–177.6 ppm decreases whereas the signal around δ = 177.6–175.8 ppm increases with decrease in MMA content. Therefore, on the basis of these changes in the intensities of the signals with changes in the copolymer composition, the two resonating signals around δ = 178.7–177.6 ppm, δ = 177.6–176.0 ppm are assigned to the MMI and IMI triads, respectively.

On comparing with the ^{13}C{^{1}H}-NMR spectra of poly(methyl methacrylate) it was observed that MMM triad in MMA–OMCPI copolymers resonates in the region δ = 178.7–176.0 ppm and is split into three spectral regions around δ = 178.7–177.5, δ = 177.5–176.3, and δ = 176.3–175.8 ppm, which are assigned to the configurational sequences M_rM_rM, M_mM_rM, and M_mM_mM, respectively.[11]
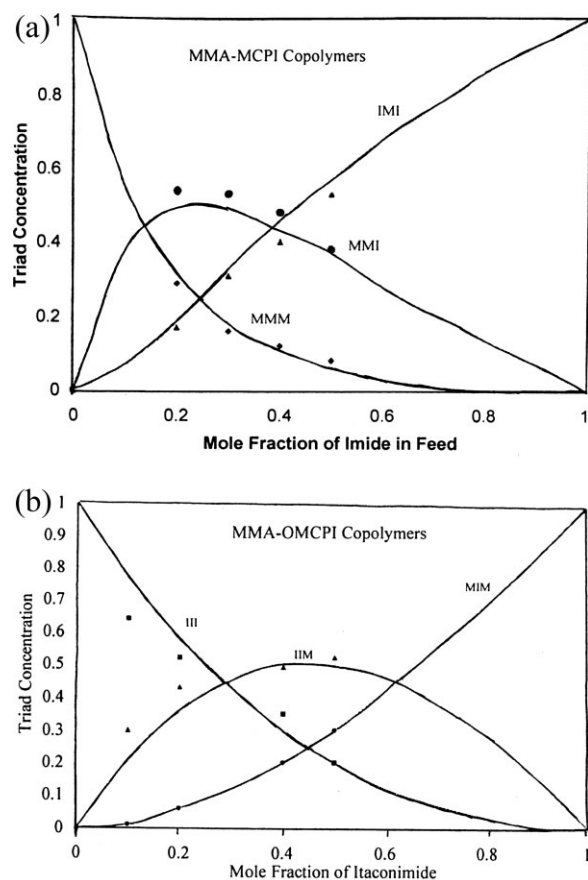
In the ^{13}C{^{1}H}-NMR spectra of MMA–OMCPI copolymers, the signals resonating around δ = 174.6–173.8 ppm decreases with increase in *I*-content, the signals resonating around δ = 173.8–173.0 ppm

TABLE III
Various Triad Compositions Calculated from NMR Spectra and Theoretically from Alfrey-Mayo Model Using Harwood's Statistical Model Program for MMA–MCPI Copolymers

Sample designation	Triads	Triad concentrations	
		^{13}C{^{1}H}-NMR	Harwood's program
MCPI-2	MMM	0.29	0.32
	MMI	0.54	0.49
	IMI	0.17	0.19
	III	–	0.08
	IIM	–	0.40
	MIM	–	0.52
MCPI-3	MMM	0.16	0.18
	MMI	0.53	0.49
	IMI	0.31	0.33
	III	–	0.16
	IIM	–	0.48
	MIM	–	0.36
MCPI-4	MMM	0.12	0.11
	MMI	0.48	0.44
	IMI	0.40	0.46
	III	–	0.26
	IIM	–	0.50
	MIM	–	0.24
MCPI-5	MMM	0.08	0.06
	MMI	0.38	0.37
	IMI	0.53	0.57
	III	–	0.37
	IIM	–	0.48
	MIM	–	0.16

TABLE IV
Various Triad Compositions Calculated from NMR Spectra and Theoretically from Alfrey-Mayo Model Using Harwood's Statistical Model Program for MMA–OMCPI Copolymers

Sample designation	Triads	Triad concentrations	
		^{13}C{^{1}H}-NMR	Harwood's program
OMCPI-1	MMM	–	0.30
	MMI	–	0.49
	IMI	–	0.20
	III	0.06	0.02
	IIM	0.30	0.23
	MIM	0.64	0.76
OMCPI-2	MMM	–	0.14
	MMI	–	0.47
	IMI	–	0.39
	III	0.04	0.06
	IIM	0.43	0.36
	MIM	0.52	0.58
OMCPI-4	MMM	–	0.03
	MMI	–	0.30
	IMI	–	0.67
	III	0.16	0.20
	IIM	0.49	0.50
	MIM	0.35	0.30
OMCPI-5	MMM	–	0.02
	MMI	–	0.23
	IMI	–	0.76
	III	0.28	0.30
	IIM	0.52	0.49
	MIM	0.20	0.20

Figure 6 Triad fractions obtained from Harwood's program (solid lines) and NMR spectroscopy (symbols) plotted against the mole fraction of itaconimide in feed (a) MMA–MCPI copolymers (b) MMA–OMCPI copolymers.

first increase and then decrease in intensity with increasing amount of *I*, and the signals resonating around δ = 173.0–172.0 ppm increase in intensity with increase in *I*-content. Therefore, on the basis of these changes in intensities of the signals with changes in copolymer composition, the three resonating signals around δ = 174.6–173.8 ppm, 173.8–173.0 ppm, and δ = 173.0–172.0 ppm are assigned as MIM, IIM, and III triads respectively.

Concentration of various compositional triad fractions were calculated from the relative areas of

resonance signals. Due to the overlapping of III, IIM, and MIM triad regions in MMA–MCPI copolymers, their concentration could not be determined. Similarly, in case of MMA–OMCPI copolymers, the concentration of *M*-centered triad fractions could not be determined due to overlapping of MMA triad region with MMI and IMI triad regions.

Assuming the Alfrey-Mayo, i.e., first-order Markov terminal model[12] to be valid at any moment in low-conversion copolymers, the triad fractions can be calculated using the terminal model reactivity ratio of monomers. Tables III and IV show the *M*- and *I*- centered triad fractions for all the copolymers determined experimentally from $^{13}C\{^{1}H\}$-NMR spectra and calculated using Harwood's statistical model program.[12]

Good agreements between calculated and experimentally determined triad concentrations show that copolymer formation follows the first-order Markov model [Fig. 6(a,b)]. It is observed that MMI triad fraction reach maximum at the feed composition ranging from 0.2 to 0.3 mole fraction. The reactivity ratios from KT method have been used because triad fractions calculated from this method were in good agreement with those calculated from the NMR spectrum. There is more uncertainty in the reactivity ratios calculated from RREVM program. Since experimental points were calculated only upto feed composition of 0.5 (i.e., MMA: I, 0.5:0.5), a good agreement observed between experimental and theoretical values can be used to predict triad fractions over the whole range of feed composition.[13]

The triad fraction depends on the reactivity ratio of monomers. Higher the incorporation of imide in the polymer backbone, larger will be the splitting of the carbonyl signal of ester. The fraction of MMM triad will decrease with increase in the imide concentration, which is in accordance with the results observed experimentally. Also, MMM triad fraction for the copolymer systems having higher monomer reactivity ratio of itaconimide should be lower. This was again in accordance with the experimentally obtained data in which the MMM triad fraction for the MMM-OMCPI copolymer was lower as

TABLE V
Conditional Probabilities for MMA–MCPI and MMA–OMCPI Copolymers

Sample designation	From statistical calculations				From triad concentrations			
	P_{II}	P_{IM}	P_{MI}	P_{MM}	P_{II}	P_{IM}	P_{MI}	P_{MM}
MCPI-2	0.29	0.71	0.47	0.53	0.28	0.72	0.44	0.56
MCPI-3	0.41	0.59	0.60	0.40	0.40	0.60	0.58	0.42
MCPI-4	0.52	0.48	0.70	0.30	0.51	0.49	0.68	0.32
MCPI-5	0.62	0.38	0.78	0.22	0.60	0.40	0.76	0.24
OMCPI-1	0.14	0.86	0.40	0.60	0.12	0.88	0.43	0.57
OMCPI-2	0.26	0.74	0.60	0.40	0.34	0.66	0.74	0.26
OMCPI-4	0.48	0.52	0.80	0.20	0.45	0.55	0.82	0.18
OMCPI-5	0.59	0.41	0.85	0.15	0.55	0.45	0.87	0.13

TABLE VI
Number Average Sequence Length for
***M*- and *I*-Sequence in MMA- *N*-Arylsubstituted**
Itaconimide Copolymers

Sample designation	From statistical calculations		From triad concentrations	
	$\overline{N}_M$	$\overline{N}_I$	$\overline{N}_M$	$\overline{N}_I$
MCPI-2	2.12	1.40	2.28	1.39
MCPI-3	1.65	1.68	1.75	1.66
MCPI-4	1.42	2.10	1.48	2.03
MCPI-5	1.28	2.60	1.32	2.54
OMCPI-1	2.53	1.16	2.35	1.14
OMCPI-2	1.68	1.35	1.60	1.31
OMCPI-4	1.26	1.94	1.23	1.82
OMCPI-5	1.17	2.41	1.15	2.23

compared to MMA–MCPI copolymer system for the same feed composition (Tables III and IV). Monomer reactivity ratio of OMCPI in MMA–OMCPI copolymer system was higher than MCPI monomer in MMA–MCPI.

Conditional probabilities and sequence length

From the results of composition with respect to various *I*- and *M*-centered triads, conditional probabilities P_{IM}, P_{II}, P_{MI}, and P_{MM} has been calculated using the equations:

$$P_{IM} = \frac{[MIM] + [MII]/2}{[MIM] + [MII] + [III]}$$

$$P_{II} = \frac{[III] + [MII]/2}{[MIM] + [MII] + [III]}$$

$$P_{MI} = \frac{[IMI] + [MMI]/2}{[IMI] + [MMI] + [MMM]}$$

$$P_{MM} = \frac{[MMM] + [MMI]/2}{[IMI] + [MMI] + [MMM]}$$

where P_{IM}, P_{II}, P_{MI}, and P_{MM} are the probabilities for formation of *I-M*, *I-I*, *M-I*, and *M-M* sequences, respectively. Results are given in Table V. Parame-

ters in square brackets are fractions of various triads determined using $^{13}C\{^1H\text{-NMR}\}$-NMR spectroscopy.

Number average sequence lengths ($\overline{N}_M$ and $\overline{N}_I$), which are the reciprocals of the conditional probabilities, can also be obtained and the values are given in Tables V and VI. Average sequence length calculated theoretically (using statistical calculations) and the ones calculated from the triad concentrations determined experimentally are in good agreement. Average sequence length containing MMA monomer units ($\overline{N}_M$) decreases with decrease of MMA in the polymer backbone. Similarly, average sequence length containing the itaconimide monomer units increases with increase of itaconimide in the polymer backbone.

CONCLUSIONS

Microstructure analysis of the MMA–MCPI and MMA–OMCPI copolymers by $^{13}C\{^1H\}$-NMR spectra showed that the copolymer formation follows the first-order Markov model.

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