

Methyl Methacrylate/*N*-(*o*-/*m*-/*p*-Chlorophenyl) Itaconimide Copolymers: Microstructure Determination by NMR Spectroscopy

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ABSTRACT: Homopolymerization and copolymerization of *N*-(*o*-/*m*-/*p*-chlorophenyl) itaconimide with methyl methacrylate was carried out by taking varying mole fractions (0.1 to 0.5) of *N*-aryl substituted itaconimide monomers in the initial feed using azobisisobutyronitrile as an initiator and tetrahydrofuran as the solvent. The copolymer composition was determined by ¹H-NMR spectroscopy using the ratio of proton resonance signal intensity attributed to -OCH₃ of MMA ($\delta = 3.5\text{--}3.8$ ppm) and the aromatic protons ($\delta = 7.0\text{--}7.5$ ppm) of *N*-(*o*-/*m*-/*p*-chlorophenyl) itaconimide. The comonomer reactivity ratios were determined using Kelen-Tüdös and nonlinear error in variable methods. The reactivity ratios obtained by nonlinear error in variable methods were r_1 (PI) = 1.26/ r_2 (MMA) = 0.35; r_1 (MI)

= 1.21/ r_2 (MMA) = 0.34; and r_1 (OI) = 0.78/ r_2 (MMA) = 0.34. The carbonyl carbon signals of MMA (M) as well as *N*-aryl itaconimide (I) copolymers were used for the determination of the sequence distribution of M- and I-centered triads. The sequence distribution of M- and I-centered triads determined from ¹³C{¹H}-NMR spectra of the copolymers are in good agreement with the triad concentrations calculated using the Alfrey-Mayo statistical model and Monte Carlo simulation method. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2016–2027, 2004

Key words: *N*-aryl itaconimide; microstructure; reactivity ratio; NMR; copolymerization

INTRODUCTION

The physical and chemical properties of polymers are influenced by their microstructure, which involves the monomer distribution in the polymer chain and the stereochemical arrangement^{1–3} of the various groups. Microstructural studies of copolymers are of immense help in establishing the structure–property relationship.^{4,5} ¹³C-NMR spectroscopy has been used extensively to determine the microstructure of vinyl copolymers.^{6–12} However no reports are available on the microstructural characterization of MMA : *N*-aryl itaconimide copolymers. In our previous articles, we reported the copolymerization behavior of *N*-aryl itaconimides with MMA and investigated the effect of copolymer composition on the thermal behavior.^{13,14} Because properties of a copolymer can be varied to a large extent by the microstructure the present studies were thus undertaken with the aim of investigating the microstructure of *N*-(*o*-/*m*-/*p*-chlorophenyl) itac-

onimide : methyl methacrylate copolymers. Structural characterization of copolymers was done by using ¹H, ¹³C{¹H}, and distortionless enhancement by polarization transfer (DEPT)-NMR experiments. The comonomer reactivity ratios were determined by both Kelen-Tüdös¹⁵ and nonlinear error in variable model methods,¹⁶ using RREVM computer program.¹² The carbonyl carbon signals of MMA (M) as well as *N*-aryl itaconimide (I) copolymers were used for the determination of the sequence distribution of M- and I-centered triads. The triad concentrations were calculated theoretically using the Alfrey-Mayo statistical model and Monte Carlo simulation method and experimentally from ¹³C{¹H}-NMR spectra.

EXPERIMENTAL

Materials

Itaconic acid (Merck, Darmstadt, Germany), *p*-chloroaniline (Merck), methanol (S.D. Fine Chemicals, Mumbai, India), chloroform (S.D. Fine Chemicals), phosphorus pentoxide (Qualigens), and silica gel for column chromatography (CDH) were used as supplied. *m*-Chloroaniline (Merck) and *o*-chloroaniline (Merck) were distilled under reduced pressure before

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

System	Kelen-Tüdös		RREVM	
	r_1	r_2	r_1	r_2
PI:MMA	1.24 ± 0.13	0.35 ± 0.02	1.26	0.35
MI:MMA	1.18 ± 0.20	0.33 ± 0.04	1.21	0.34
OI:MMA	0.77 ± 0.11	0.34 ± 0.01	0.78	0.34

use. Acetone (Qualigens) was dried overnight over potassium carbonate followed by distillation. Acetic anhydride (S.D. Fine Chemicals) was used after distillation. Anhydrous sodium acetate (CDH) was obtained by fusion.

Tetrahydrofuran (THF; CDH) was purified by passing it through an alumina column. It was then dried by refluxing with metallic sodium and benzophenone followed by distillation. Azobisisobutyronitrile (AIBN; High Polymer Labs) was recrystallized using

chloroform. Methyl methacrylate (MMA; Merck) was washed with dilute sodium hydroxide to remove the inhibitor, followed by repeated washings with distilled water until neutral. It was dried over anhydrous sodium sulfate overnight and distilled under reduced pressure.

N-(*o*-/*m*-/*p*-Chlorophenyl) itaconimide monomers were prepared by reacting itaconic anhydride with the corresponding amine and the detailed procedure is reported elsewhere.¹³

Preparation of polymer

Homopolymerization and copolymerization of *N*-(*o*-/*m*-/*p*-chlorophenyl) itaconimide with MMA was carried out in THF using AIBN as an initiator at 60°C under nitrogen atmosphere. The mole fraction of *N*-aryl itaconimides in the initial feed was varied from 0.1 to 0.5. Polymerization was carried out by taking 30% (w/v) solution of monomers in THF using 0.5% of AIBN as an initiator. The reaction was stopped at

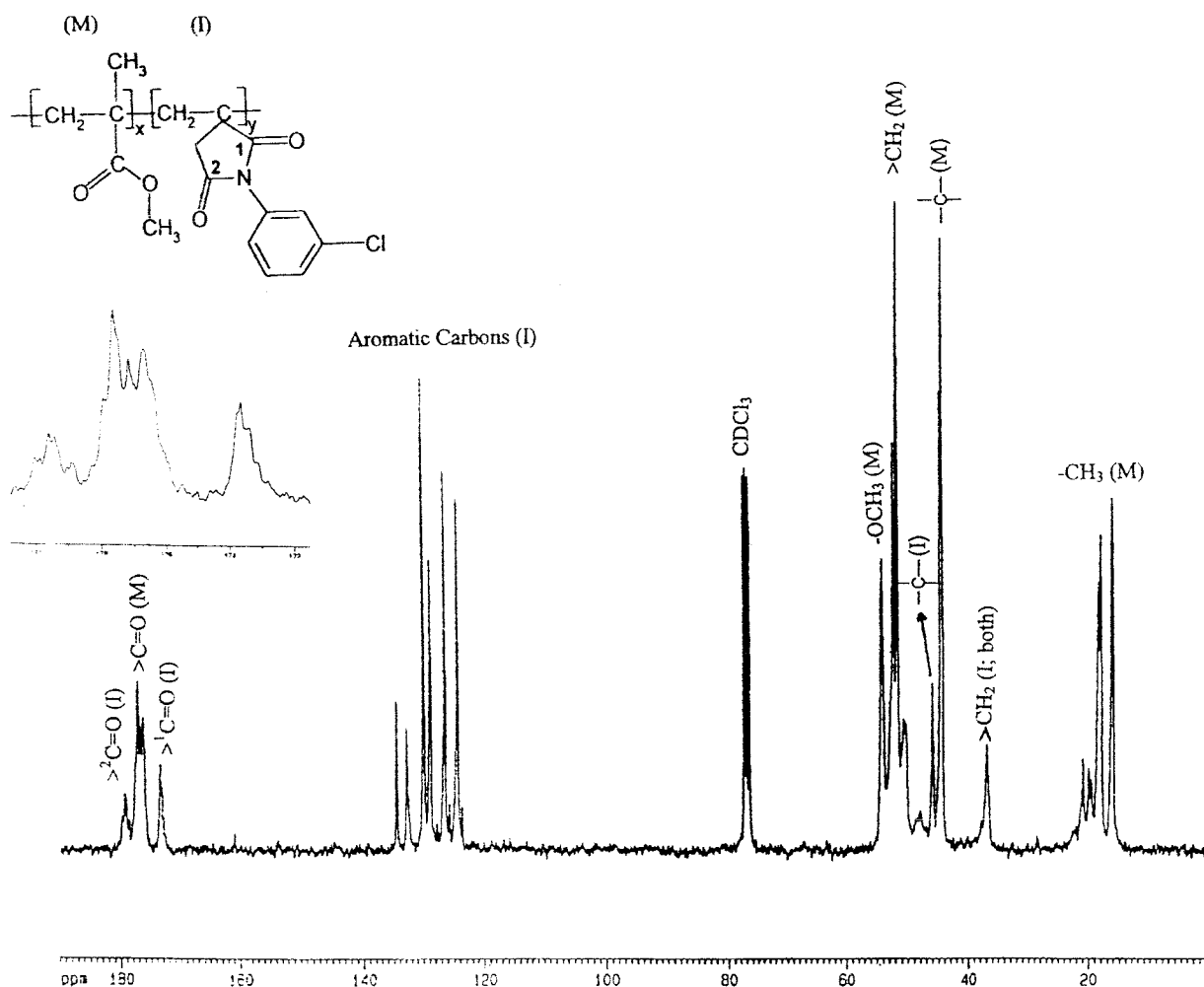


Figure 1 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PMI-1 copolymer.

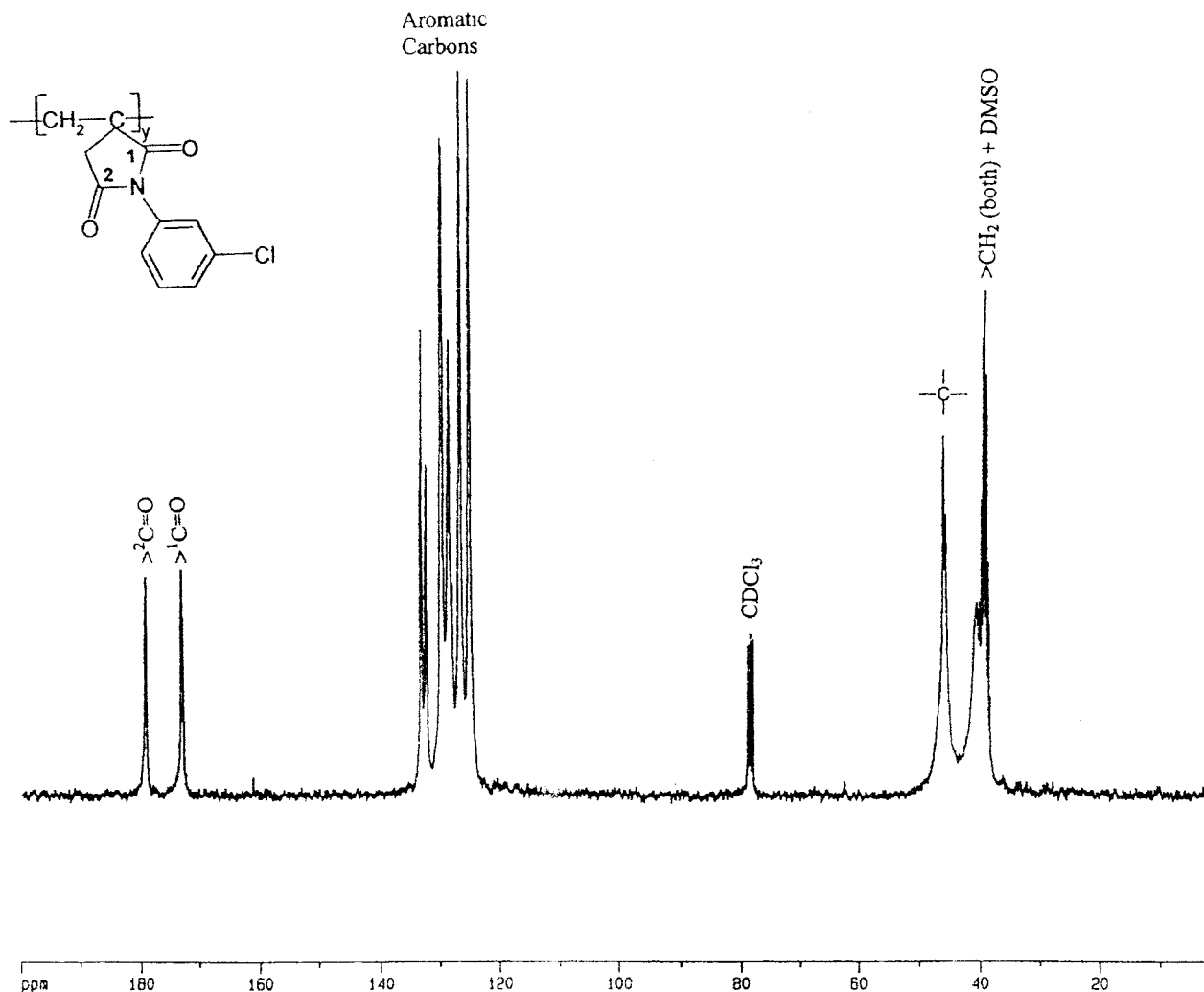


Figure 2 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PMI homopolymer.

low conversion ($\leq 15\%$) by pouring the contents of the flask into a large excess of methanol. The precipitated polymer was washed repeatedly with hot methanol to remove unreacted monomers and was dried in a vacuum oven.

Copolymers were designated by adding a prefix P to the monomer designation of *N*-aryl itaconimides followed by a numerical suffix indicating the mole fraction of itaconimides multiplied by 10. For example, a copolymer prepared by taking 0.2 mol fraction of PI, MI, and OI was designated as PPI-2, PMI-2, and POI-2, respectively. Homopolymers were designated by adding a prefix P to the monomer designation of *N*-aryl itaconimides.

Characterization of polymers

^1H , $^{13}\text{C}\{^1\text{H}\}$, and DEPT NMR experiments were carried out on a Bruker DPX 300 MHz spectrometer (Bruker Instruments, Billerica, MA) using standard

pulse sequences as reported in the Bruker pulse program library. The ^1H -NMR spectra for all the homo- and copolymers were recorded at a frequency of 300.13 MHz. The 32K data points were accumulated with 5 s as delay time between 16 successive scans. $^{13}\text{C}\{^1\text{H}\}$ -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 16K data points using Waltz-16 broad band decoupler. The Carbon-13 DEPT measurements were carried out using the standard pulse sequence with a J modulation time of 3.7 ms ($J_{\text{CH}} = 135$ Hz) with 2 s as delay time. A total of 6000 scans were accumulated over 16K data points. The 90° pulse was calibrated for each sample that was used for the DEPT-135 experiments. The recording conditions were kept similar for all the samples. The relative areas of resonance signals were determined using a nonlinear least-square Lorentzian line shape deconvolution program.⁹ In all cases the fitting was considered valid only at $\chi^2 < 1$.

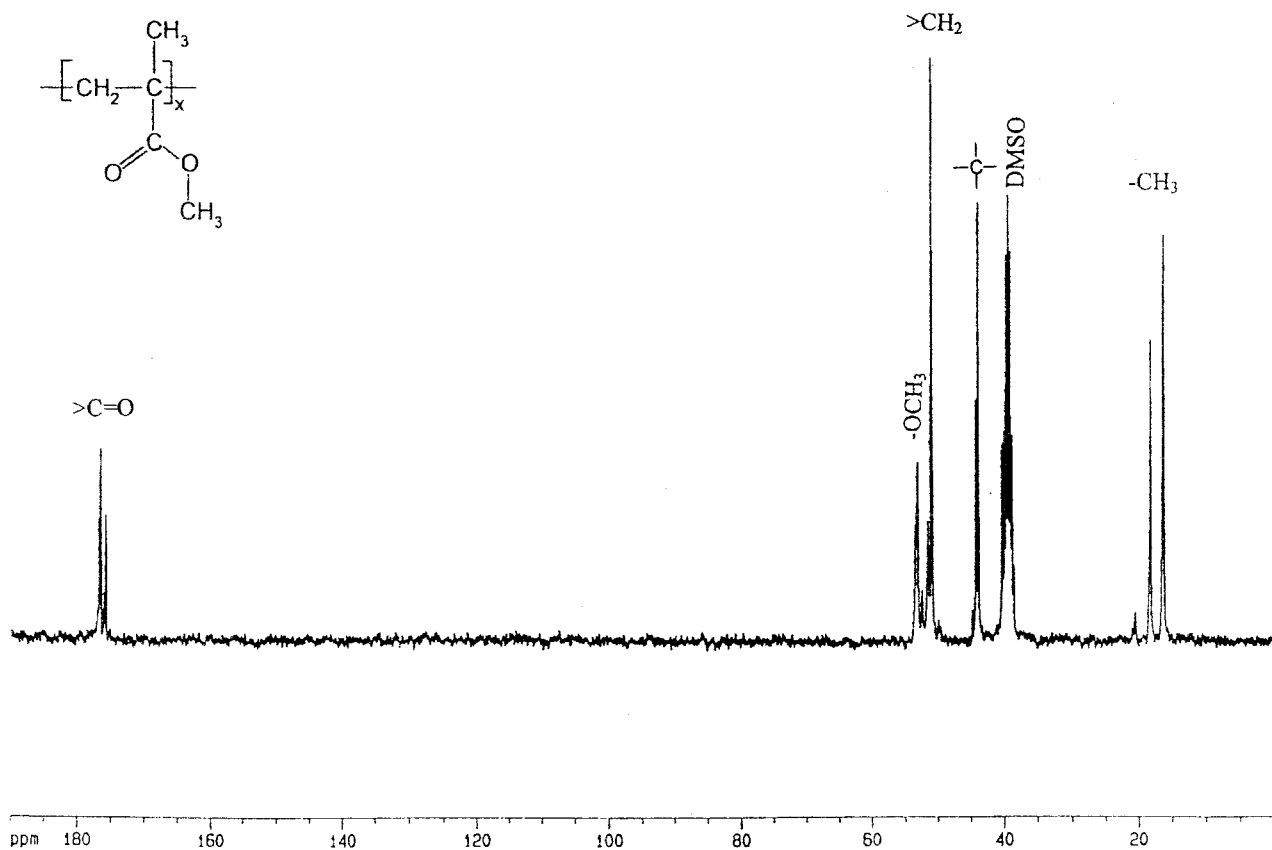


Figure 3 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PMMA.

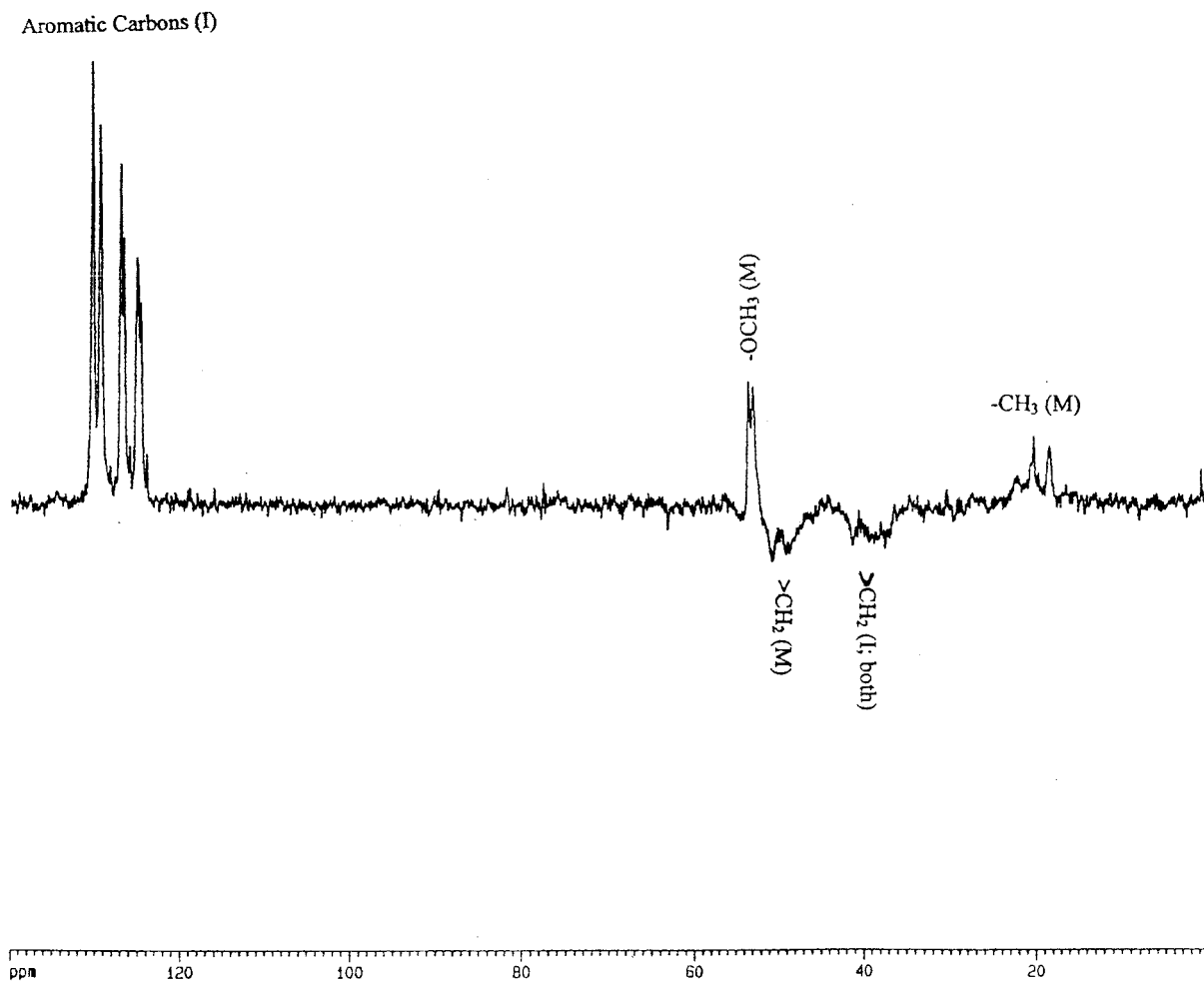


Figure 4 DEPT-135 NMR spectrum of PMI-5 copolymer.

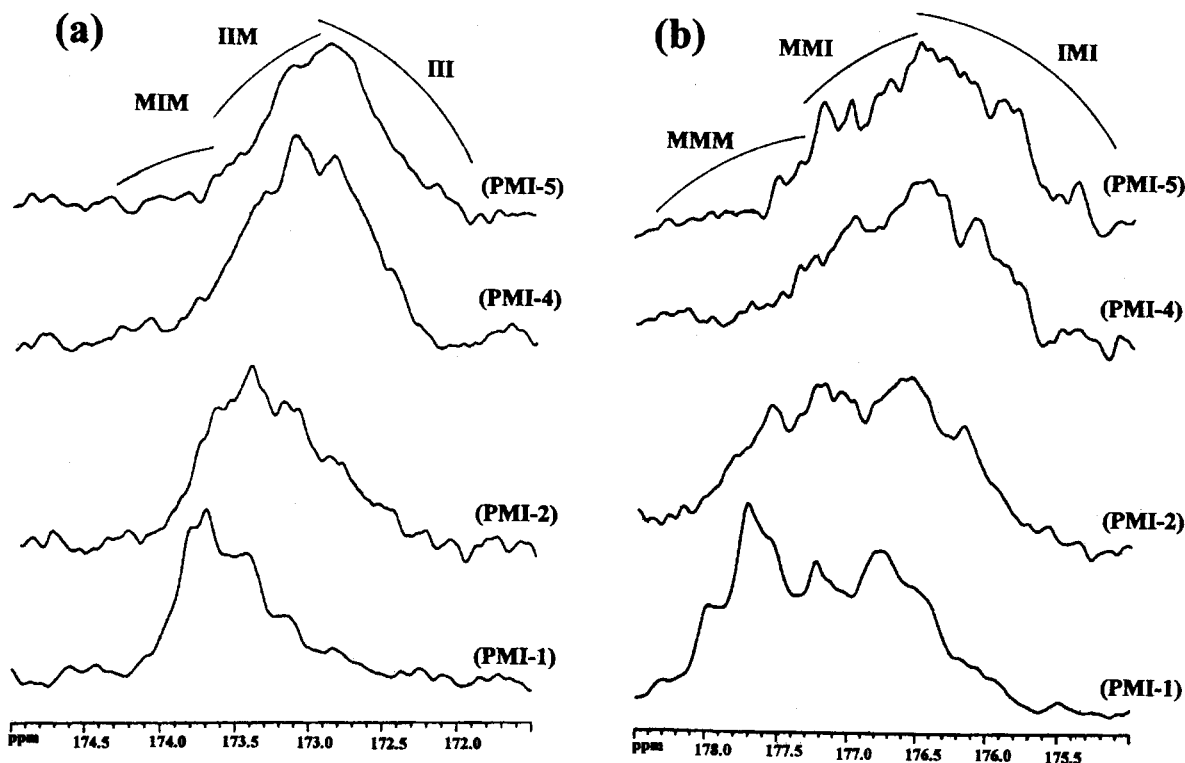


Figure 5 Carbonyl carbons in $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of PMI copolymers (a) I-Centered and (b) M-Centered.

RESULTS AND DISCUSSION

^1H -NMR studies

In the ^1H -NMR spectra of copolymers, resonance signals attributed to the $-\text{OCH}_3$ protons of MMA and aromatic protons of *N*-aryl itaconimides were present at $\delta = 3.5\text{--}3.8$ and $7.0\text{--}7.5$ ppm, respectively. The intensity of the signal assigned to aromatic protons increased with increasing *N*-aryl itaconimide content in the copolymers. The copolymer composition was determined by taking the ratio of the intensity of signals attributed to methoxy protons of MMA and aromatic protons of *N*-aryl itaconimides. Copolymer composition was also determined from the % nitrogen content in the copolymers. A good correlation was observed between the values obtained by ^1H -NMR and elemental analysis.

Reactivity ratio determination

The copolymer composition data were used to calculate the reactivity ratio using the Kelen–Tüdös method. These reactivity ratio values along with the copolymer composition data were used to calculate the reactivity ratios from the nonlinear error in variable model (EVM) method using the RREVM computer program. These results clearly show that the reactivity of MMA is less than that of the *N*-aryl itac-

onimides monomers toward homo/cross propagation. The reactivity ratio values obtained by both methods are summarized in Table I.

$^{13}\text{C}\{^1\text{H}\}$ -NMR studies

The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PMI-1 copolymer in CDCl_3 is shown in Figure 1. All resonance signals in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PMI-1 copolymer were assigned with the help of $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of homopolymer of MI and MMA. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PMI homopolymer (Fig. 2) was recorded in the mixture of $\text{DMSO-}d_6$ and CDCl_3 , whereas that of PMMA (Fig. 3) was recorded in $\text{DMSO-}d_6$. The resonance signals attributed to the carbonyl carbon of PMI homopolymer were observed at $\delta = 172.3\text{--}174.0$ ppm ($>^1\text{C}=\text{O}$) and $\delta = 178.6\text{--}180.2$ ppm ($>^2\text{C}=\text{O}$) (Fig. 1). The aromatic carbon of PMI homopolymer resonates at $\delta = 123.7\text{--}134.4$ ppm. The resonance signal attributed to the carbonyl carbon of PMMA was observed at $\delta = 175.1\text{--}177.2$ ppm and shows a multiplet attributed to tacticity. In copolymers the carbonyl carbon of MMA resonates at $\delta = 175.0\text{--}178.4$ ppm and of *N*-aryl itaconimide at $\delta = 171.9\text{--}174.2$ ppm ($>^1\text{C}=\text{O}$) and $\delta = 178.6\text{--}180.9$ ppm ($>^2\text{C}=\text{O}$). The methyl carbon of MMA and aromatic carbon of *N*-aryl itaconimide were observed at $\delta = 16.0\text{--}21.0$ and $123.0\text{--}135.0$ ppm, respectively. The region between $\delta = 30.0$ and $\delta = 60.0$

ppm is complex and was resolved with the help of DEPT-135 experiment, where the methyl carbon signals have positive phase and methylene carbon signals have negative phase. Figure 4 shows the DEPT-135 spectrum of PMI-5 copolymer. Thus signals observed at $\delta = 54.3, 50.5\text{--}52.5,$ and 44.7 ppm in $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of copolymers were assigned to $-\text{OCH}_3,$ $>\text{CH}_2,$ and quaternary carbon of MMA, respectively. The quaternary carbon of *N*-aryl itaconimide was observed at $\delta = 46.2$ ppm and both $>\text{CH}_2$ (backbone and side-chain ring methylene carbon) of *N*-aryl itaconimide resonate at $\delta = 36.9\text{--}38.8$ ppm.

The carbonyl carbon signals of MMA (M) ($\delta = 175.0\text{--}178.4$ ppm) as well as of *N*-aryl itaconimide (I) ($\delta = 171.9\text{--}174.2$ ppm) in $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of copolymers show multiplets, indicating sensitivity to compositional and configurational sequences and hence were used for the determination of the sequence distribution of M- and I-centered triads. Figure 5 shows the I- and M-centered carbonyl region in $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra for the series of PMI copolymers of different copolymer compositions. The MMA carbonyl region is divided into three broad envelopes. The carbonyl carbon resonance signals in the region $\delta = 177.4\text{--}178.4$ ppm, which decrease in intensity as the MMA content in the copolymer decreases, are assigned to the MMM triad. The intensity of the carbonyl signals in the region $\delta = 175.1\text{--}176.5$ ppm increases as the MMA content in the copolymer decreases and are therefore assigned to the IMI triad compositional sequence. The region around $\delta = 176.5\text{--}177.4$ ppm is assigned to the MMI compositional triad, which first increases and then decreases with the increase in *N*-(*m*-chlorophenyl) itaconimide content in the copolymer.

Similarly the I-centered carbonyl region ($\delta = 171.9\text{--}174.2$ ppm) is also divided into three broad envelopes. The region that increases and decreases with the increasing *N*-(*m*-chlorophenyl) itaconimide content was assigned as III ($\delta = 171.9\text{--}172.9$) and MIM ($\delta = 173.6\text{--}174.2$) compositional triad regions, respectively. The region first increases and then decreases with increasing *N*-(*m*-chlorophenyl) itaconimide content and was thus assigned as the MII ($\delta = 172.9\text{--}173.6$) compositional triad. Similarly for other series the compositional triad concentrations were assigned.

The concentration of various compositional triad fractions was calculated from the relative areas of the resonance signals. The relative areas of resonance signals were determined using a nonlinear least-square Lorentzian line shape deconvoluting program. In all these cases the fitting was considered valid only at $\chi^2 < 1$. Assuming the Alfrey–Mayo (first-order Markov terminal model)³ to be valid at any moment of the low-conversion copolymers, the triad fractions can be calculated using the terminal model reactivity ratio of

TABLE II
Various Triad Compositions Calculated from NMR Spectra and Theoretically from Alfrey–Mayo Statistical Model and Monte Carlo Simulation for PPI Copolymers

Sample	Triad	Triad concentrations by		
		$^{13}\text{C}\{^1\text{H}\}$ -NMR	Alfrey–Mayo	Monte Carlo
PPI-1	MMM	0.62	0.58	0.71
	MMI	0.31	0.36	0.27
	IMI	0.07	0.06	0.02
	III	0.02	0.01	0.01
	IIM	0.22	0.22	0.14
	MIM	0.76	0.77	0.85
PPI-2	MMM	0.41	0.35	0.43
	MMI	0.43	0.48	0.46
	IMI	0.16	0.17	0.11
	III	0.05	0.06	0.02
	IIM	0.32	0.36	0.26
	MIM	0.63	0.58	0.72
PPI-3	MMM	0.23	0.20	0.18
	MMI	0.44	0.49	0.49
	IMI	0.33	0.31	0.33
	III	0.08	0.12	0.07
	IIM	0.47	0.46	0.39
	MIM	0.45	0.42	0.54
PPI-4	MMM	0.15	0.12	0.08
	MMI	0.48	0.46	0.39
	IMI	0.37	0.42	0.53
	III	0.22	0.21	0.16
	IIM	0.51	0.50	0.48
	MIM	0.27	0.29	0.36
PPI-5	MMM	0.10	0.07	0.04
	MMI	0.42	0.39	0.29
	IMI	0.48	0.54	0.67
	III	0.29	0.31	0.34
	IIM	0.48	0.49	0.49
	MIM	0.23	0.20	0.17

the monomers. Tables II–IV show the M- and I-centered triad fractions for all the copolymers calculated from the Alfrey–Mayo model using Harwood’s statistical model program¹⁷ and the experimentally (from $^{13}\text{C}\{^1\text{H}\}$ -NMR) determined triad fractions. A good agreement between the calculated and the experimentally determined triad concentrations shows that the copolymer formation follows the first-order Markov model.

Figure 6 shows the plot of normalized M- and I-centered triad fractions for all the copolymers versus *N*-aryl itaconimide in the feed. The solid lines represent the theoretically calculated triad fractions using the Alfrey–Mayo statistical model, whereas symbols represent the experimentally determined ($^{13}\text{C}\{^1\text{H}\}$ -NMR) triad fractions. It may be observed from Figure 6 that the MMI triad fraction reaches a maximum in the range of 0.2–0.3 feed composition, whereas the IIM triad fraction shows broad maxima over a range of 0.3–0.6 feed composition. A good agreement between experimentally determined values and values calculated using the Alfrey–Mayo statistical model is seen

from Tables II–IV and Figure 6. Because experimental points were calculated only up to a 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. The triad fraction depends on the reactivity ratio of the monomers. Thus the MIM triad concentration in POI copolymers is slightly higher than that in the other copolymers, whereas the III triad concentration is slightly lower because of its lower reactivity ratio compared to that of other itaconimides.

The Monte Carlo (MC) simulation method was also used to monitor the changes in copolymer sequence behavior during the course of polymerization and the M- and I-centered triad fraction obtained using this method (Tables II–IV) are also in good agreement with the experimental values. The Monte Carlo method can also be used to calculate the triad concentrations at various levels of conversion. Figures 7–9 show the variation of M- and I-centered triad concentrations as a function of fractional conversion for copolymers

TABLE III
Various Triad Compositions Calculated from NMR Spectra and Theoretically from Alfrey–Mayo Statistical Model and Monte Carlo Simulation for PMI Copolymers

Sample	Triad	Triad concentrations by		
		$^{13}\text{C}\{^1\text{H}\}$ -NMR	Alfrey–Mayo	Monte Carlo
PMI-1	MMM	0.59	0.56	0.70
	MMI	0.35	0.38	0.27
	IMI	0.06	0.06	0.03
	III	0.01	0.01	0.01
	IIM	0.20	0.21	0.13
	MIM	0.79	0.78	0.86
PMI-2	MMM	0.36	0.33	0.41
	MMI	0.47	0.49	0.46
	IMI	0.17	0.18	0.13
	III	0.07	0.05	0.02
	IIM	0.37	0.36	0.24
	MIM	0.56	0.59	0.74
PMI-3	MMM	0.14	0.19	0.17
	MMI	0.50	0.49	0.48
	IMI	0.36	0.32	0.35
	III	0.12	0.12	0.06
	IIM	0.44	0.45	0.38
	MIM	0.44	0.43	0.56
PMI-4	MMM	0.11	0.11	0.07
	MMI	0.45	0.45	0.39
	IMI	0.44	0.44	0.54
	III	0.15	0.20	0.15
	IIM	0.48	0.49	0.48
	MIM	0.37	0.31	0.37
PMI-5	MMM	0.08	0.06	0.03
	MMI	0.37	0.38	0.29
	IMI	0.55	0.56	0.68
	III	0.21	0.30	0.33
	IIM	0.51	0.50	0.49
	MIM	0.28	0.20	0.18

TABLE IV
Various Triad Compositions Calculated from NMR Spectra and Theoretically from Alfrey–Mayo Statistical Model and Monte Carlo Simulation for POI Copolymers

Sample	Triad	Triad Concentrations by		
		$^{13}\text{C}\{^1\text{H}\}$ -NMR	Alfrey–Mayo	Monte Carlo
POI-1	MMM	0.55	0.57	0.70
	MMI	0.36	0.37	0.27
	IMI	0.09	0.06	0.03
	III	0.01	0.01	0.00
	IIM	0.16	0.15	0.09
	MIM	0.83	0.84	0.91
POI-2	MMM	0.32	0.33	0.41
	MMI	0.52	0.49	0.46
	IMI	0.16	0.18	0.13
	III	0.02	0.03	0.01
	IIM	0.25	0.27	0.17
	MIM	0.73	0.70	0.82
POI-3	MMM	0.17	0.19	0.16
	MMI	0.48	0.49	0.48
	IMI	0.35	0.32	0.36
	III	0.08	0.06	0.03
	IIM	0.34	0.38	0.27
	MIM	0.58	0.56	0.70
POI-4	MMM	0.10	0.11	0.07
	MMI	0.47	0.45	0.38
	IMI	0.43	0.44	0.55
	III	0.15	0.12	0.07
	IIM	0.45	0.45	0.39
	MIM	0.40	0.43	0.54
POI-5	MMM	0.05	0.07	0.03
	MMI	0.35	0.38	0.30
	IMI	0.60	0.55	0.67
	III	0.16	0.18	0.14
	IIM	0.53	0.49	0.47
	MIM	0.31	0.33	0.39

having feed compositions in the range of 0.1 to 0.5 mol fraction.

It may be observed that with the progress of copolymerization, monomers with higher reactivity ratio (i.e., *N*-aryl itaconimides) are consumed faster than MMA. This is also seen from Figures 7–9, where the MMM triad fraction increased with % conversion; similarly the III triad fraction decreased as % conversion increased. As the amount of itaconimide in the feed increases, the MMM triad fraction increases only at higher conversion because *N*-aryl itaconimide is consumed faster than MMA during the initial stages of polymerization. The concentration of MMI triad fraction first increases, goes through a maximum, and then decreases as the % conversion increases. The IMI triad fraction decreases as the fractional conversion increases. At greater amounts of itaconimide in the feed, the IMI triad concentration is formed initially because the reactivity ratio of itaconimide is higher than that of MMA, but at higher conversion it decreases much more sharply because itaconimide is consumed at a faster rate. The de-

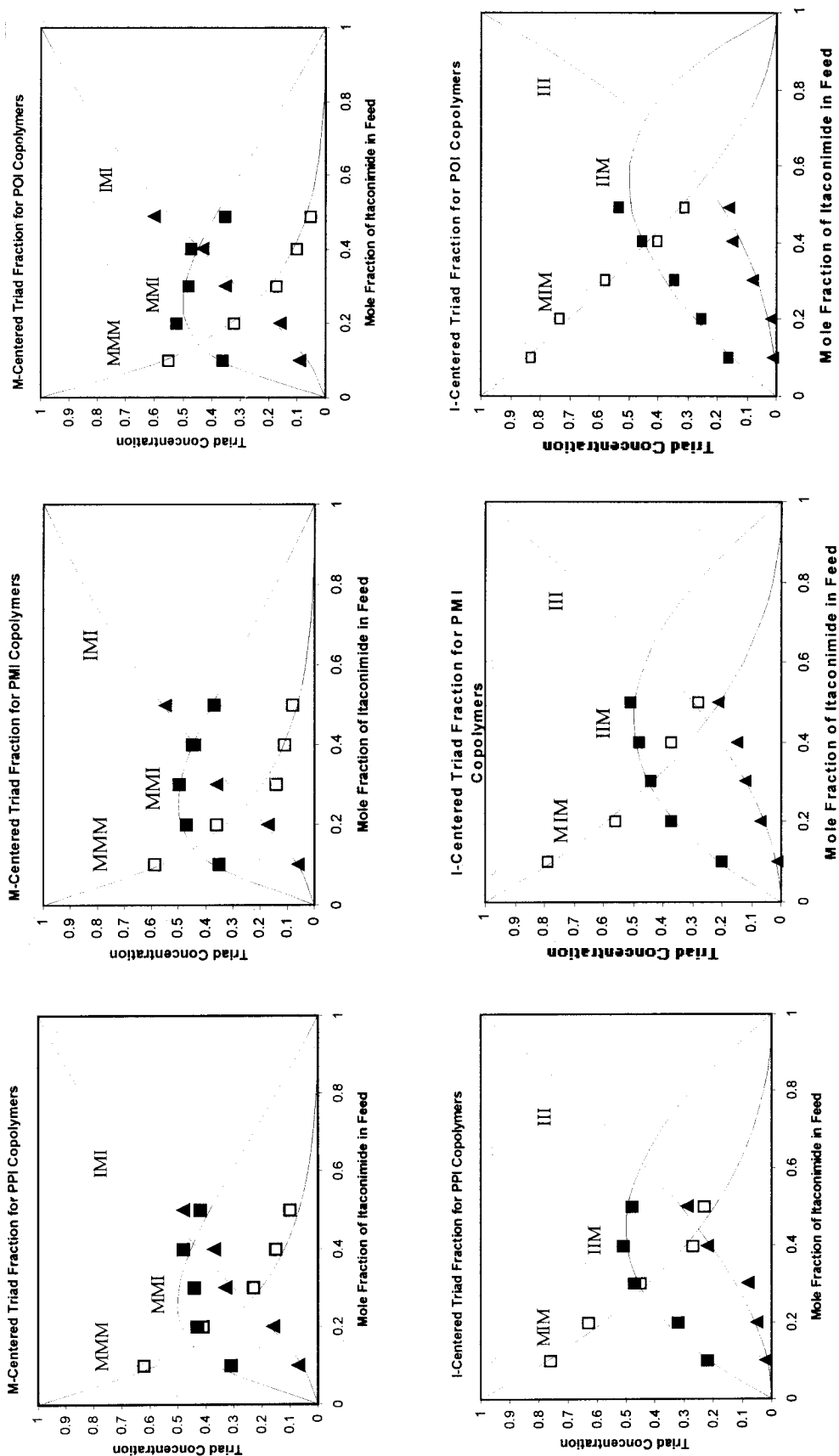


Figure 6 M- and I-centered triad fractions obtained from Alfrey–Mayo statistical model (solid lines) and NMR spectroscopy (symbols) plotted against the mole fraction of itaconimide in feed.

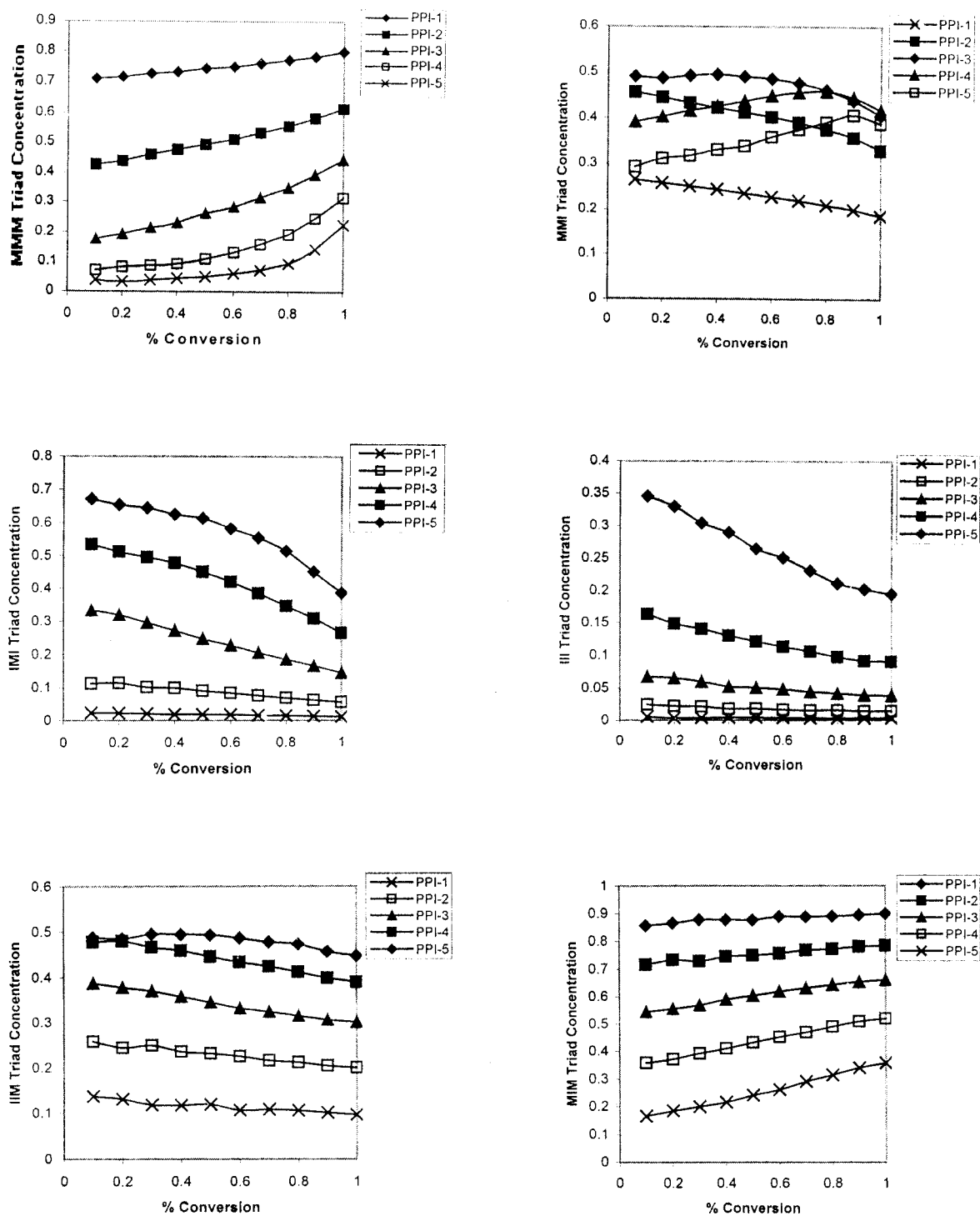


Figure 7 Variation of M- and I-centered triad fractions plotted as a function of fractional conversion for PPI copolymers.

crease in IMI triad fraction is much sharper at higher % conversion for feed having lower mole fractions of MMA.

The III triad concentration decreases as the fractional conversion increases. The IIM triad fraction for the higher feed ratio of itaconimide first increases,

goes through a maximum, and then decreases as the conversion increases. For lower feed ratio of itaconimide, the IIM triad fraction decreases as % conversion increases. The MIM triad fraction increases as the fractional conversion increases. The increase in MIM triad fractions is much sharper at higher % conversion in

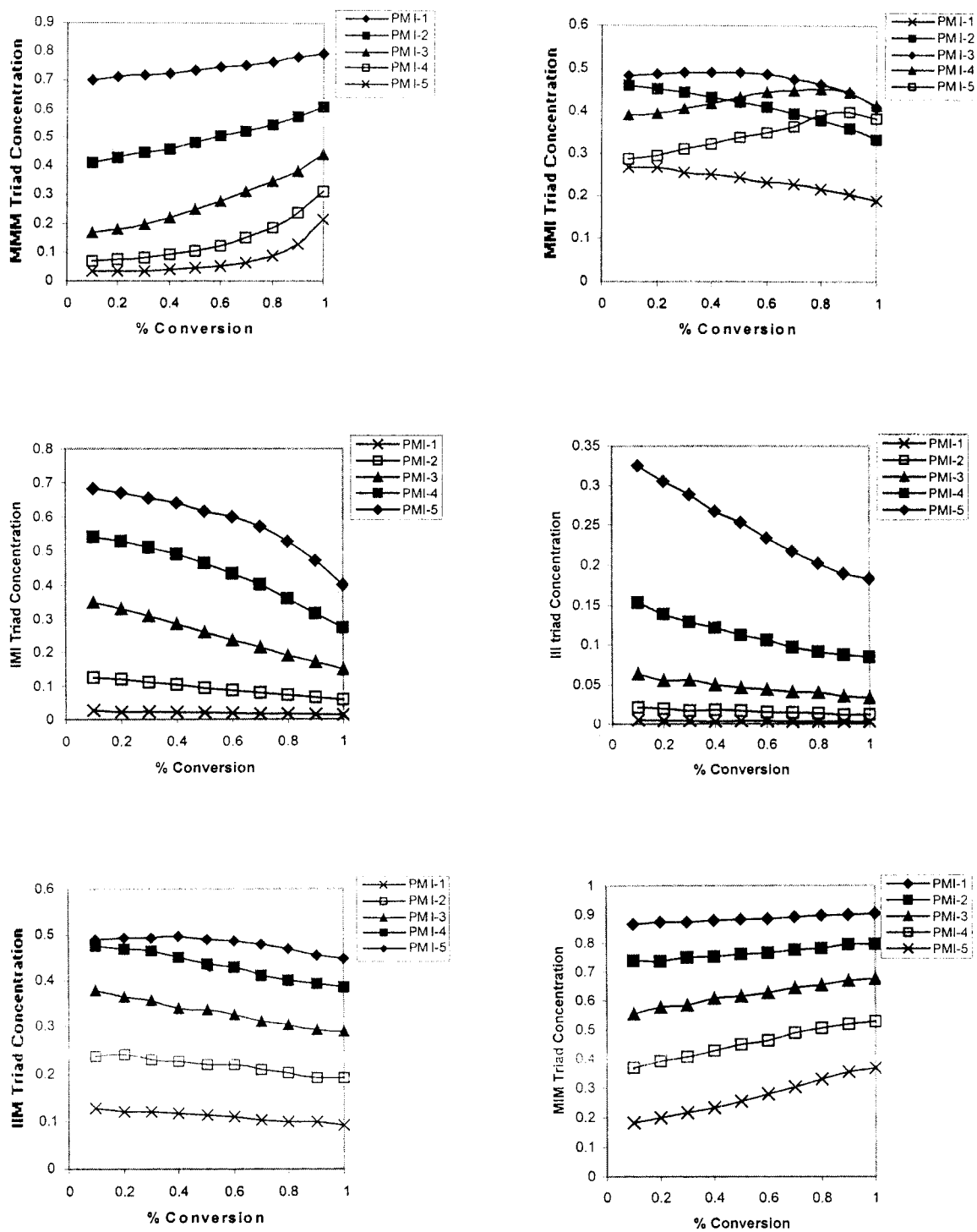


Figure 8 Variation of M- and I-centered triad fractions plotted as a function of fractional conversion for PMI copolymers.

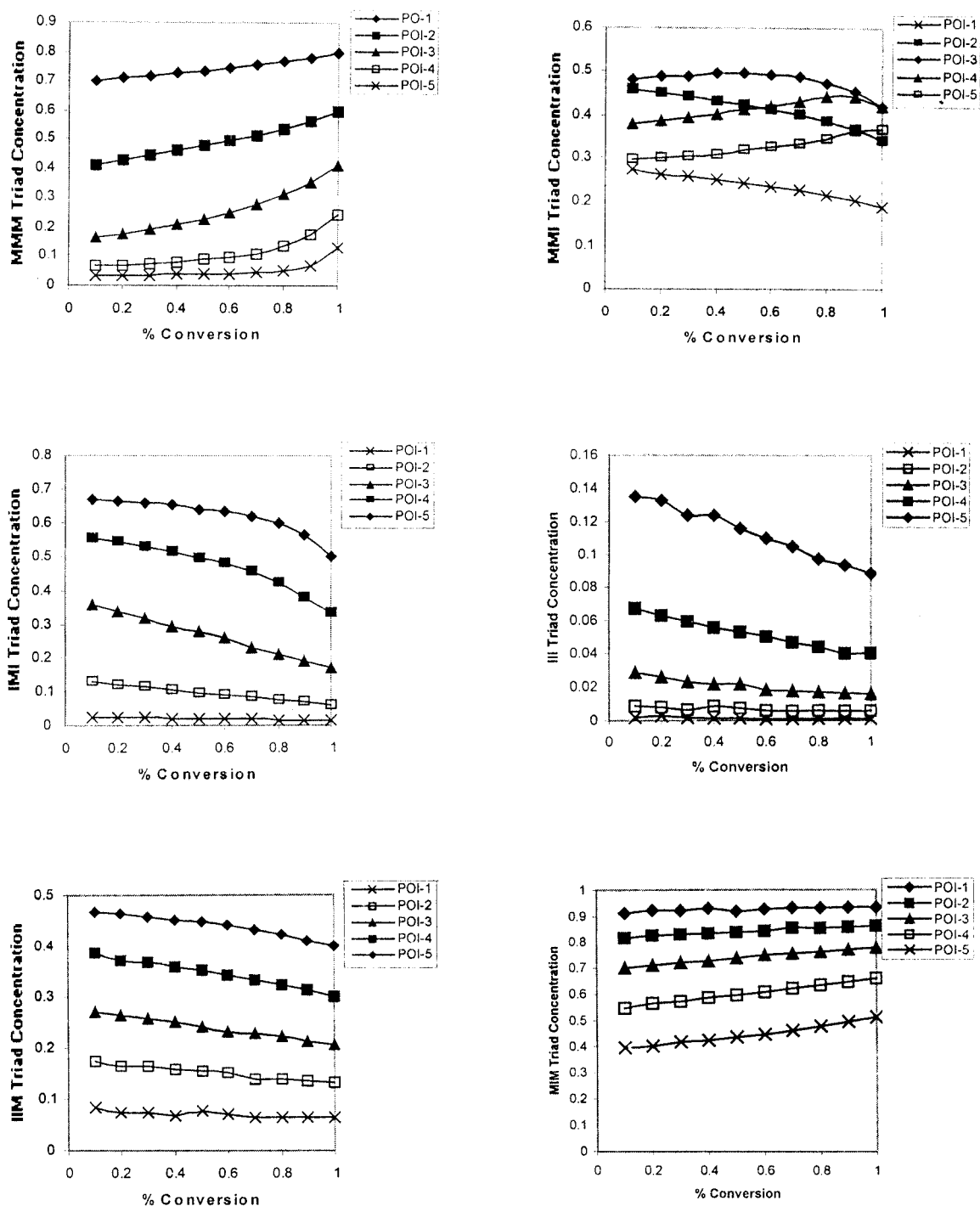


Figure 9 Variation of M- and I-centered triad fractions plotted as a function of fractional conversion for POI copolymers.

the case of copolymerization having lower mole fraction of MMA because the reactivity ratio of MMA is lower compared to that of *N*-aryl itaconimide.

CONCLUSIONS

Various M- and I-centered triad concentrations of MMA : *N*-(*o*-/*m*-/*p*-chlorophenyl) itaconimide copol-

ymers were determined from $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the copolymers (experimentally) and theoretically by using Harwood's program and Monte Carlo simulation program. Triad concentrations determined experimentally from $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the copolymers were in good agreement with the triad concentration calculated theoretically using the Alfrey-Mayo statistical model.

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