

Studies on the Microstructure of Vinyl/*N*-Phenylmaleimide Copolymers by NMR and Their Applications

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Received 13 January 1999; accepted 23 May 1999

ABSTRACT: The micro- and stereostructures and sequence distribution of methyl methacrylate (MMA)/*N*-phenylmaleimide (PMI) and styrene (St)-PMI copolymers were studied in detail with NMR spectroscopy. The MMA-PMI copolymer was in a random sequence distribution and the St-PMI copolymer was alternating in structure. Some micro- and stereoinformation of the MMA-PMI copolymers could be obtained from ^1H -NMR spectra. The average number sequence length obtained from the copolymer triad by ^{13}C -NMR spectra was in agreement with that calculated from the reactivity ratios measured by an elemental analyzer. From the triad fraction of the copolymer measured by ^{13}C -NMR, the copolymer chain of MMA-PMI was proved to be a one-order Markov chain. More suitable propagation reactions were proposed from the deviation of sequence distribution of the St-PMI copolymer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2581–2587, 2000

Key words: vinyl monomer; *N*-phenylmaleimide; copolymer; NMR; application

INTRODUCTION

The homopolymer of *N*-phenylmaleimide has high heat resistance,¹ but it cannot be used as an engineering plastic because its high glass transition temperature leads to difficulty in processing. However, *N*-phenylmaleimide (PMI) may easily copolymerize with common monomers to improve the heat-resistant properties of general-purpose plastics. Several articles^{2–4} have recently reported on kinetics and treatment models for vinyl/PMI copolymerization and their copolymer properties.

The properties of copolymers with the same molecular weight and composition may be different in their microstructure and sequence distribution. The heat-resistant properties, such as the glass transition temperature, will be largely dependent not only on the copolymer composition but also on the sequence distribution in the copol-

mer.^{5–7} The high probability of PMI-PMI unit connections will lead to two glass transition temperatures of the copolymer, causing very difficult processing and a very low Vicat softening point of this copolymer material. Unfortunately, the microstructure and sequence distribution of vinyls/PMI copolymers have been seldom studied.

Studies of the microstructure and sequence distribution may reveal the mechanism of copolymerization. From the triad distributions and sequence length, the free-radical attacking site and the propagation reaction of copolymerization can be inferred.

There are many methods to characterize the microstructure and sequence distribution of the copolymer, such as IR and NMR. The statistical or Monte Carlo methods can also be used to estimate the sequence distribution from the reactivity ratios and monomer feed fraction. But, NMR is usually used among these methods. In this article, ^1H -NMR and ^{13}C -NMR will be used to investigate the micro- and stereostructures and sequence distribution of methyl methacrylate (MMA)-PMI and styrene (St)-PMI copolymers.

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Journal of Applied Polymer Science, Vol. 77, 2581–2587 (2000)
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Table I Composition of MMA-PMI Copolymers

| f_1 | Conversion (wt %) | F_1 (Measured by EA) ^a | F_1 (Measured by ¹ H-NMR) |
|-------|-------------------|-------------------------------------|--|
| 0.9 | 6.73 | 0.9583 | 0.9357 |
| 0.8 | 13.92 | 0.8920 | 0.8732 |
| 0.7 | 12.66 | 0.8331 | 0.8380 |
| 0.6 | 12.87 | 0.7822 | 0.7677 |
| 0.5 | 9.27 | 0.7080 | 0.7129 |
| 0.4 | 10.84 | 0.6536 | 0.6504 |
| 0.3 | 14.46 | 0.5585 | 0.5780 |
| 0.2 | 11.70 | 0.4881 | 0.4969 |
| 0.1 | 6.61 | 0.3322 | 0.3313 |

EA, elemental analysis.

EXPERIMENTAL

The copolymers of MMA-PMI and St-PMI were prepared by the method described earlier in the literature.² The compositions of the MMA-PMI and St-PMI copolymers were calculated on the basis of the nitrogen content in the copolymers measured by an elemental analyzer (Carlo Erba-1106). From the ¹H-NMR spectra of the MMA-PMI copolymer, the composition of the MMA-PMI copolymer could also be obtained.

The ¹H-NMR spectra of the MMA-PMI copolymer were determined on the Bruker DPX-400 NMR spectrometer at room temperature with CDCl₃ as a solvent. The ¹³C-NMR spectra of the MMA-PMI copolymer were recorded on the Bruker DPX-400 NMR spectrometer at room temperature in 10-mm-o.d. NMR tubes. Solutions up to 20 w/v % in CDCl₃ were used. To have a quantitative response, the ¹³C-NMR spectra were recorded by using a 10-s pulse cycle. The conditions ensure the complete relaxation of all the nuclei analyzed.

The ¹³C-NMR spectra of the St-PMI copolymer were measured on a JEOL FX-90Q NMR spectrometer at 120°C in 10-mm-o.d. NMR tubes. Solutions up to 15 w/v % in *o*-dichlorobenzene-*d*₄ were used. To have a quantitative response, the ¹³C-NMR spectra were recorded using a 3-s pulse cycle. These conditions ensure the complete relaxation of all the nuclei analyzed.

RESULTS AND DISCUSSION

Copolymer Composition

The experimentally determined compositions of the MMA-PMI copolymer are given in Table I, together with the corresponding initial monomer feed fractions and the monomer conversions.

These data were fitted to the terminal model using the nonlinear least-squares (NLLS) method. The 95 and 99% confidence intervals of the reactivity ratios for MMA/PMI copolymerization is shown in Figure 1. The relationship between initial monomer feed fraction and composition of the St-PMI copolymer and the 95 and 99% confidence intervals of the reactivity ratios of the St/PMI copolymerization were reported in the literature.² The reactivity ratios for these two copolymerization systems are given in Table II.

Microstructural Analysis of MMA-PMI Copolymer

There are 10 possible types of stereotriad structures with MMA located at the center of triads in the MMA-PMI copolymer as follows:

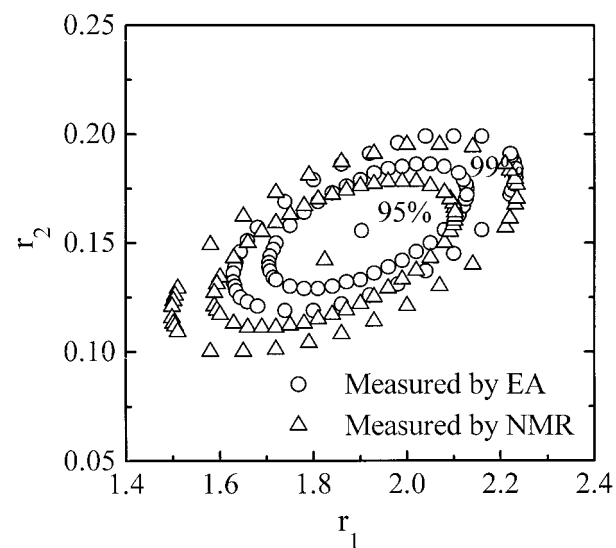
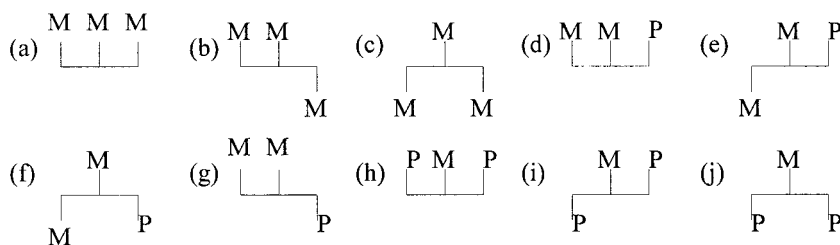


Figure 1 The 95 and 99% confidence intervals of reactivity ratios for MMA/PMI copolymerization in CHCl₃ at 50°C with AIBN as the initiator.

Table II Results of Reactivity Ratio

| Copolymerization System | Measured Method | r_1 | r_2 |
|-------------------------|------------------|-------------------------|-------------------------|
| MMA/PMI | EA | 1.9030 | 0.1556 |
| MMA/PMI | $^1\text{H-NMR}$ | 1.8240 | 0.1419 |
| St/PMI | EA | 5.1667×10^{-2} | 7.0982×10^{-3} |



where M and P represent the units of MMA and PMI in the MMA-PMI copolymer.

In general, the $^1\text{H-NMR}$ spectra of α -methyl or methene groups were applied to research the micro- and stereostructures of PMMA. The $^1\text{H-NMR}$ spectra of α -methyl or methene groups for the MMA-PMI copolymer were very complex, because the micro- and stereostructures of PMMA would affect the chemical shifts of these two groups. They will be influenced by the micro- and stereostructure of the MMA unit in the MMA-PMI copolymer. It is difficult to discern the effect of the PMI unit existence on the chemical shift of the MMA unit. The $^1\text{H-NMR}$ spectrum of the methoxy group for the MMA-PMI copolymer is a single band. The chemical-shift range of the methoxy group is 2.1–3.7 ppm. The $^1\text{H-NMR}$ spectrum of the methoxy group will change with the shielding effect of the PMI unit, so it is selected to characterize the effect of the PMI unit existence on the chemical shift of the MMA unit.

The $^1\text{H-NMR}$ spectra at 2.0–4.0 ppm for the MMA-PMI copolymers at various initial monomer feed fractions are shown in Figure 2. Peak I, the methenyl group spectrum of PMI unit, increases and covers peak II with the content of the PMI unit in the MMA-PMI copolymer. Among the PMP triads, the shielding effect of the PMI unit on the MMA unit at the same side will be larger than that at the different side, so the chemical shift of the (h) stereostructure will shift to the highest field (band VI); the (i) and (j) stereostructures will locate at bands V and III, respectively. Among the MMM triads, the chemical shifts of

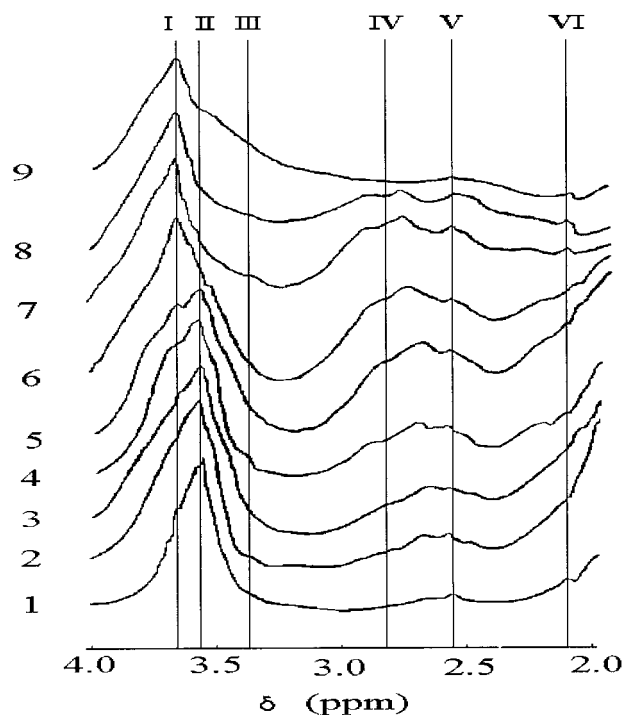


Figure 2 $^1\text{H-NMR}$ spectra of the MMA-PMI copolymer ($f_1 = 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1$, corresponding to numbers of 1–9).

the (a)–(c) stereostructures are the same as that of the PMMA (band II). But, among the MMP triads, the shielding effect of the PMI unit to the MMA unit at the different side is very weak, so the chemical shifts of the (f) and (g) stereostructures will adhere to band II. The chemical shifts of the (d) and (e) stereostructures will shift to a

Table III Hydrogen Assignments of $^1\text{H-NMR}$ Spectra for MMA-PMI Copolymers

| Peak No. | Chemical Shift (ppm) | Assignment |
|----------|----------------------|-----------------------------|
| I | 3.66 | $>\text{CH}-\text{CH}<$ |
| II | 3.57 | (a), (b), (c), (f), and (g) |
| III | 3.37 | (j) |
| IV | 2.82 | (d) and (e) |
| V | 2.55 | (i) |
| VI | 2.10 | (h) |

higher field (band IV) for the strong same-side shielding effect of the PMI unit to the MMA unit among the MMP triads.

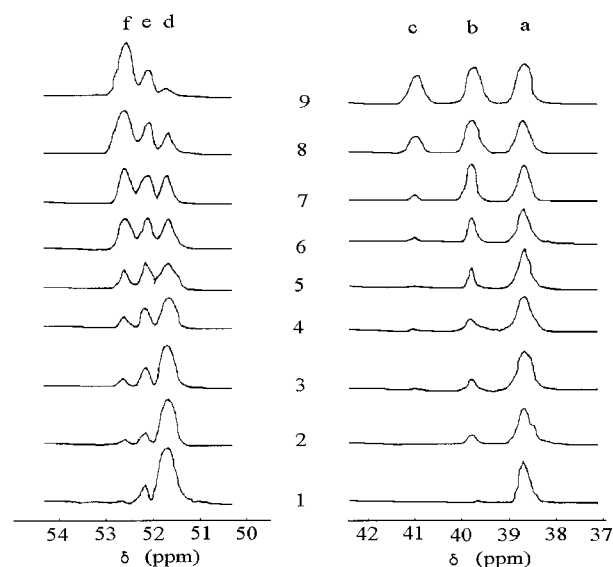
From the $^1\text{H-NMR}$ spectra of the methoxy group for the MMA-PMI copolymers measured at various initial monomer feed fractions, the micro- and stereostructures of the MMA-PMI copolymer will appear. The hydrogen assignments are put together in Table III.

MMA-PMI Copolymer Sequence Distribution

The $^{13}\text{C-NMR}$ spectra are usually used to determine the copolymer sequence distribution. However, as the chemical shift will be affected by the micro- and stereostructure of the copolymer, it is necessary to remove the micro- and stereostructure effects on the triads' information. From the $^{13}\text{C-NMR}$ spectra of the MMA-PMI copolymers, there is no band at about 22.1 ppm for the α -methyl group, indicating that all the MMA units in the MMM triads of the MMA-PMI copolymer are syndiotactic. In the $^{13}\text{C-NMR}$ spectrum of homopoly(*N*-phenylmaleimide), no band appears when the chemical shift is below 40.98 ppm. So, the bands that appear below the 40.98 ppm (methenyl group of the PMI unit) and the upper 51.70 ppm bands (methylene of the MMA unit) are not being interfered with by the micro- and stereostructure can be regarded as information on the triads.

The $^{13}\text{C-NMR}$ spectra at 37–42 and 50–54 ppm for the MMA-PMI copolymers at various initial monomer feed fractions are shown in Figure 3. The carbon assignments for the $^{13}\text{C-NMR}$ spectra are given in Table IV.

The triad fractions (F_{111} , $F_{112+211}$, F_{212} , F_{222} , $F_{221+122}$, and F_{121}) can be calculated according to the areas of peak. The effects of the initial monomer feed fraction on the triad fractions are shown in Figures 4 and 5.

**Figure 3** $^{13}\text{C-NMR}$ spectra for MMA-PMI copolymer triads ($f_1 = 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1$, corresponding to numbers 1–9).

The average number sequence length of MMA (M_1) and PMI (M_2) in the MMA-PMI copolymer, $\langle L_1 \rangle_n$ and $\langle L_2 \rangle_n$, can be expressed as follows:

$$\langle L_1 \rangle_n = \frac{F_{111} + F_{112+211} + F_{212}}{F_{212} + 0.5F_{112+211}} \quad (1)$$

$$\langle L_2 \rangle_n = \frac{F_{222} + F_{221+122} + F_{121}}{F_{121} + 0.5F_{221+122}} \quad (2)$$

The effects of the initial monomer feed fraction on the average number sequence length of MMA and PMI in the MMA-PMI copolymer are given in Figure 6 (experimental data). Using the reactivity ratios obtained by the elemental analyzer in Table II ($r_1 = 1.9030$, $r_2 = 0.1556$) and introducing these reactivity ratios into the terminal

Table IV Carbon Assignments of $^{13}\text{C-NMR}$ Spectra for MMA-PMI Copolymer Triads

| Peak No. | Chemical Shift (ppm) | Assignments |
|----------|----------------------------|-------------------------------|
| a | 38.66 (38.40) ⁸ | $>\text{CH}$, MPM |
| b | 39.76 | $>\text{CH}$, MPP + PPM |
| c | 40.98 (41.0) ⁹ | $>\text{CH}$, PPP |
| d | 51.70 (51.9) ¹⁰ | $>\text{CH}_2$, syndio-(MMM) |
| e | 52.19 | $>\text{CH}_2$, MMP + PMM |
| f | 52.63 | $>\text{CH}_2$, PMP |

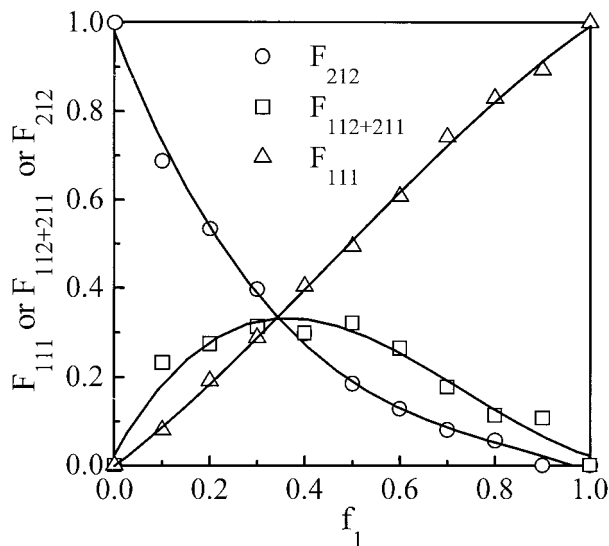


Figure 4 Feed ratios versus the triad fractions for MMA-PMI copolymer.

model, the modeling average number sequence length of MMA and PMI in the MMA-PMI copolymer can be estimated as follows:

$$\langle \bar{L}_1 \rangle_n = 1 + r_1 f_1 / f_2 \quad (3)$$

$$\langle \bar{L}_2 \rangle_n = 1 + r_2 f_2 / f_1 \quad (4)$$

The modeling average number sequence length of MMA and PMI in the MMA-PMI copolymer are in good agreement with the experimental data as

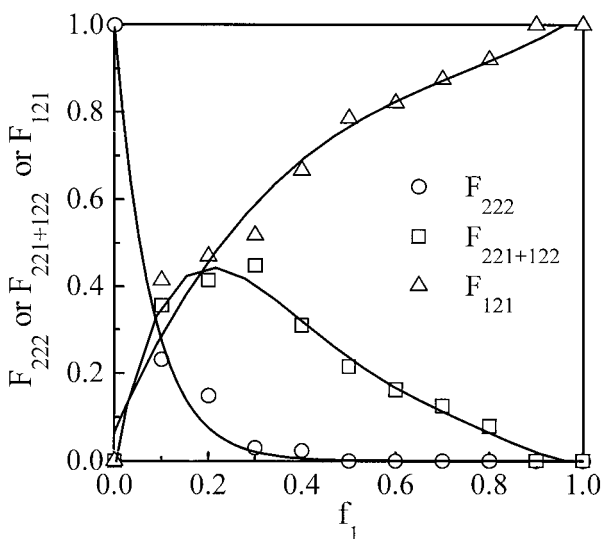


Figure 5 Feed ratios versus the triad fractions for MMA-PMI copolymer.

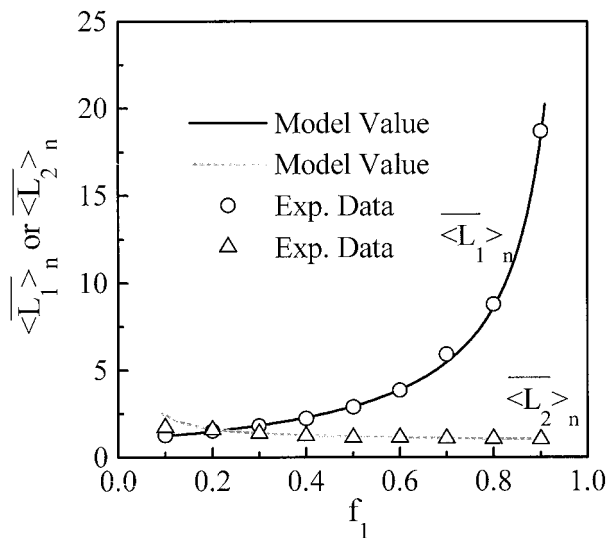


Figure 6 Feed fractions versus the number-average sequence length of the MMA-PMI copolymer.

shown in Figure 6 (point is the experimental data, and the solid line is modeling value).

Using the information on the triads, the copolymer chain type can be determined. If $p_{12} + p_{21} = 1$, p_{12} , and p_{21} are the probabilities of monomer unit 1 connecting with unit 2 and monomer unit 2 connecting unit 1, the copolymer chain is a type of Bernoulli chain. However, if $F_{111} = (1 - p_{12})^2 p_{21} / (p_{12} + p_{21})$, the copolymer chain is a type of a one-order Markov chain. The relationships between the triad fractions and probabilities are

$$p_{12} = \frac{0.5F_{112+211}}{F_{111} + 0.5F_{112+211}} \quad (5)$$

$$p_{21} = \frac{0.5F_{221+122}}{F_{222} + 0.5F_{221+122}} \quad (6)$$

The results of p_{12} , p_{21} , $(1 - p_{12})^2 p_{21} / (p_{12} + p_{21})$, F_{111} , and $p_{12} + p_{21}$ for the MMA-PMI copolymer are listed in Table V. It is obvious that $F_{111} \approx (1 - p_{12})^2 p_{21} / (p_{12} + p_{21})$ under all initial monomer feed fractions. It indicates that the MMA-PMI copolymer chain is a type of one-order Markov chain. This result is in agreement with the sequence distribution of the MMA-PMI copolymer that can be calculated using the terminal model.

St-PMI Copolymer Sequence Distribution

The ^{13}C -NMR spectra of the St-PMI copolymer are simpler than that of the MMA-PMI copoly-

Table V Determination of Copolymer Chain Type

| f_1 | p_{12} | p_{21} | $(1 - p_{12})^2 p_{21} / (p_{12} + p_{21})$ | F_{111} | $p_{12} + p_{21}$ |
|-------|----------|----------|---|-----------|-------------------|
| 0.1 | 0.5944 | 0.4348 | 0.0695 | 0.0795 | 1.0292 |
| 0.2 | 0.4191 | 0.5833 | 0.1964 | 0.1913 | 1.0024 |
| 0.3 | 0.3532 | 0.8810 | 0.2986 | 0.2881 | 1.2342 |
| 0.4 | 0.2703 | 0.8674 | 0.4060 | 0.4030 | 1.1377 |
| 0.5 | 0.2457 | 1.0 | 0.4567 | 0.4928 | 1.2457 |
| 0.6 | 0.1795 | 1.0 | 0.5708 | 0.6066 | 1.1795 |
| 0.7 | 0.1068 | 1.0 | 0.7208 | 0.7419 | 1.1068 |
| 0.8 | 0.0641 | 1.0 | 0.8231 | 0.8294 | 1.0641 |
| 0.9 | 0.0565 | 1.0 | 0.8426 | 0.8930 | 1.0565 |

mer. There is no band from 130 to 142 ppm in the ^{13}C -NMR spectrum of polystyrene and from 133 to 170 ppm in the ^{13}C -NMR spectrum of poly(*N*-phenylmaleimide). The bands from 133 to 142 ppm can be regarded as information on the triads.

The ^{13}C -NMR spectra at 137–144 ppm for the St-PMI copolymers at various initial monomer feed fractions are shown in Figure 7. The carbon assignments for the ^{13}C -NMR spectra are given in Table VI.

From the ^{13}C -NMR spectra, the bands of PSS + SSP and SSS triads do not appear until the initial monomer feed fraction of St is higher than 0.9. It is certain that the tendency to form an alternating copolymer is very high for the St/PMI copolymerization system.

The average number sequence lengths of St and PMI in the St-PMI copolymer at various

initial monomer feed fractions can be calculated with eqs. (1) and (2) and are given in Figure 8 (experimental data). Using the reactivity ratios obtained by the elemental analyzer in Table II ($r_1 = 5.1667 \times 10^{-2}$, $r_2 = 7.0982 \times 10^{-3}$), one can introduce these reactivity ratios into eqs. (3) and (4) to estimate the modeling average number sequence length of St and PMI in the St-PMI copolymer as shown in Figure 8 (point is the experimental data, and solid line is the modeling value).

Application

When the initial monomer feed fraction of St is higher than 0.1, the modeling average number sequence lengths of St and PMI in the St-PMI copolymer are in agreement with the experimental data. But when the initial feed fraction of St is lower than 0.1, there is much PMI monomer in the St/PMI copolymerization system. The average number sequence length of PMI in the St-PMI copolymer is still 1.0, as obtained from the experimental data. It indicates that the PMI free radical cannot attack the PMI monomer. The propagation reactions of St/PMI copolymerization in the literature³ can be rewritten as

**Table VI** Carbon Assignment of ^{13}C -NMR Spectra for St-PMI Copolymer Triads

| Peak No. | Chemical Shift (ppm) | Assignments |
|----------|--|--------------------------------|
| d | 134.07 | Ph(C ¹), SPS |
| e | 138.80 | Ph(C ¹), PSP |
| e | 141.10 | Ph(C ¹), PSS + SSP |
| f | 143.20 (142.8) ¹¹ (142.0) ¹² | Ph(C ¹), SSS |

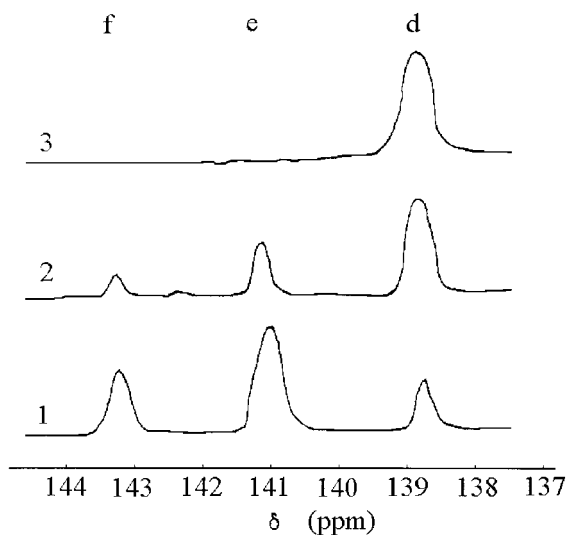


Figure 7 ^{13}C -NMR spectra for St-PMI copolymer triads (1 - $f_1 = 0.97$, 2 - $f_1 = 0.90$, 3 - $f_1 = 0.50$, 0.10, and 0.03).

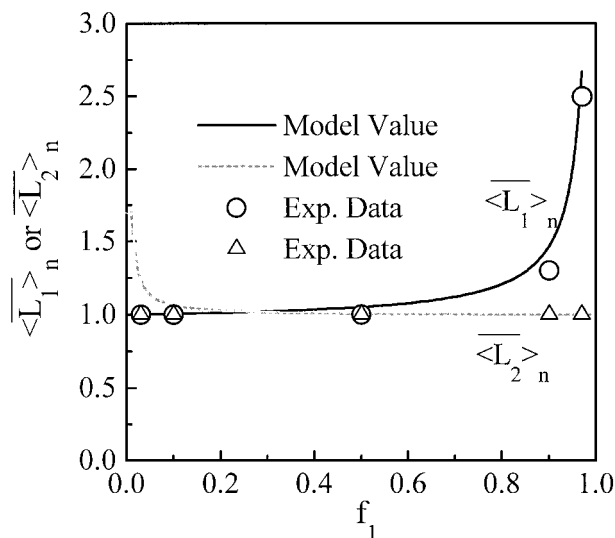


Figure 8 Feed fractions versus the number-average sequence length of St-PMI copolymer.



where the charge-transfer complex (CTC) formation equation is



The propagation reaction, by which PMI free radicals attack the PMI free monomer, will not happen:



CONCLUSIONS

The copolymer compositions of MMA-PMI and St-PMI were measured by EA or NMR. Their reactivity ratios were $r_1 = 1.9030$, $r_2 = 0.1556$ (measured by EA), and $r_1 = 1.8240$, $r_2 = 0.1419$ (measured by $^1\text{H-NMR}$) for MMA/PMI copolymerization and $r_1 = 5.1667 \times 10^{-2}$, $r_2 = 7.0982 \times 10^{-3}$ (measured by EA) for St/PMI copolymerization, and 95 and 99% confidence intervals are given. Using $^1\text{H-NMR}$ spectroscopy, the micro- and stereostructures of the MMA-PMI copolymer were investigated in detail. From the triad fractions of the MMA-PMI copolymer measured by $^{13}\text{C-NMR}$, the average number sequence length is in agreement with that calculated from the reactivity ratios, and the copolymer chain of MMA-PMI was proved to be a one-order Markov chain. From the triad fractions of the St-PMI copolymer measured by $^{13}\text{C-NMR}$, the bands of the PSS + SSP and SSS triads do not appear until the initial monomer feed fraction of St is larger than 0.9. More suitable propagation reactions are proposed from the deviation of sequence distribution of the St-PMI copolymer.

This project was supported by the Doctoral Station Foundation of China Education Commission.

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