Controlled Radical Alternating Copolymerization of *N*-Phenyl Maleimide with Ethyl *α*-Ethylacrylate by Reversible Addition Fragmentation Chain-Transfer Process

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ABSTRACT: The alternating copolymerization of *N*-phenyl maleimide (NPMI) with ethyl *α*-ethylacrylate (EEA) by the reversible addition fragmentation chain-transfer process was investigated. The monomer reactivity ratios were measured and $r_1 = 0.19 \pm 0.03$ for NPMI and $r_2 = 0.20 \pm 0.04$ for EEA. It was found that before about 45% of the comonomer conversion, the molecular weight of the copolymer increased with the conversion, the molecular weight distribution was rather narrow, and the molecular weight of the copolymer approached a constant value, irrespective of the length of the polymerization time. Electronic spin resonance determined that the radical signal disappeared quickly after the conversion of comonomer exceeded 45%, which may be attributed to the coupling termination of the propagating polymer chains with the EEA end with the intermediate radicals when the concentration of comonomers decreased. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2376–2382, 2004

Key words: copolymerization; reversible addition fragmentation chain transfer (RAFT); *N*-phenyl maleimide; ethyl *α*-ethylacrylate; ESR/EPR

INTRODUCTION

Recently, "controlled" or "living"-radical polymerizations have been of considerable academic and industrial interest. Their promising important applications in providing new and facile synthetic routes to form well-defined, low-polydispersity polymers have proved that they are superior to those produced by conventional radical polymerization.[1,2] Among these methods, reversible addition fragmentation chain transfer (RAFT)–based living-radical polymerization, which can be used with a wide range of monomers and reaction conditions, seems to be an ideal technique to prepare various polymers with various architectures.[3] Currently, many studies focusing on the RAFT system are reported. However, only a few studies describe the synthesis of copolymers possessing controlled sequences.[4,5]

N-Phenyl maleimide (NPMI) and other N-substituted maleimides are known to be able to copolymerize with styrene by the charge transfer complex (CTC) mechanism,[6] and the incorporation of NPMI units into thermoplastic resins may greatly improve the heat resistance and chemical stability of the products.[7] On the other hand, the *α*-substituted acrylates, such as phenyl,[8] ethyl, propyl,[9] and hydromethyl-substituted acrylate,[10] constitute a new kind of monomers, some of them showing physiological reactivity in the human body.[11,12] In the investigation of copolymerization of ethyl *α*-phenylacrylate with *N*-phenyl maleimide,[13] it was observed that the spontaneous alternating copolymers were formed, although no CTC was detected. It was believed that copolymerization for this system underwent a process in which a contact-type CTC was formed for monomer pairs. This type of systems containing monomers composed of a weak electron donor and acceptor is of great interest for the investigation of their kinetic behavior of copolymerization by RAFT.

This article reports the controlled/"living" copolymerization of NPMI with ethyl *α*-ethylacrylate (EEA) by RAFT techniques, in which a weak electron donor and acceptor are presented. Some special phenomena in the copolymerization are discussed.

EXPERIMENTAL

Materials

Diethyl malonate (Shanghai Third Reagent Factory, China) was purified by distillation at reduced pressure. The fraction of 82°C/7 mmHg was collected. Maleic anhydride (Shanghai Third Reagent Factory, China) and urea (Wuxi Mingfeng Reagent Factory,

China) were used as obtained. AIBN was recrystallized from methanol. Dioxane was treated with fresh sodium and distilled. All other reagents were purified by standard methods.

Monomer preparation

NPMI (M_1) was prepared according to a literature-reported method[14] at a yield of 89%, mp: 89–90°C. EEA (M_2) was also prepared according to the literature[15] and purified by distillation at reduced pressure, at a yield of 46%, bp: 64–65°C (15 mmHg).

Preparation of chain-transfer agents

2-Phenylprop-2-yl dithiobenzoate (PPDB) was prepared according to a published procedure[1] with the yield of 32%; the product was an oily liquid with a dark purple color. [NMR (CDCl$_3$; ppm): 2.05 (s, 6H), 7.20–7.60 (m, 8H), 8.06 (m, 2H)]

Copolymerization

The accurately weighed NPMI, EEA, AIBN, PPDB, and a given amount of dioxane were introduced to a 100-mL glass ampoule, degassed three times by freeze–pump–thaw cycles at 77 K, and sealed off under N_2. The copolymerization reactions, with different monomer feed ratios, were performed at 70 ± 1°C. After a given time, the ampoules were removed from the oil bath and dipped in liquid nitrogen to stop the copolymerization. The copolymer was purified twice by a dissolution/precipitation procedure with dioxane/ether and extracted with ether for 24 h.

Measurements

^{1}H-NMR spectra were recorded on a Bruker DMX-500 nuclear magnetic resonance (NMR) instrument (Bruker, Darmstadt, Germany) with tetramethylsilane (TMS) as an internal standard and CDCl$_3$ as solvent. IR spectra were scanned by a Magna-550 FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI). Elemental analysis was determined by a Carlo Erba (Milan, Italy) 1106 elemental analyzer. Electron spin resonance (ESR) measurements were performed by placing the degassed sealed tube containing refined comonomers, AIBN initiator, RAFT agent, and benzene in the preheated cavity of the ESR spectrometer at 80°C using an ER 200D-SRC Bruker ESR spectrometer, operating at X-band (9.67 GHz) with a TE mode cavity. Molecular weight and molecular weight distribution were derived with an Agilent 1100 GPC (Agilent Technologies, Palo Alto, CA) with refractive index detector and UV–vis detector (wavelength 190–950 nm); filler: two Mix-C PL-gel columns (500 Å, relative molecular weight 500–3 × 10^6); injection volume: 20 μL; solvent and eluent: THF; flow rate: 0.2–5 mL/min.

GPC was calibrated with monodispersed polystyrene standards.

RESULTS AND DISCUSSION

Synthesis and characterization of poly(NPMI-*co*-EEA)

The copolymerization of NPMI with EEA was carried out in dioxane at 70°C in the presence of AIBN and PPDB, at a ratio of [PPDB] : [AIBN] of about 3 : 1. The product was a pale pink powder and soluble in chloroform, dimethylformamide (DMF), DMSO, THF, and dioxane. Both poly(EEA) and poly(MI) homopolymers, however, were not soluble in dioxane, so it was easy to separate them from the copolymerization product.

The IR spectra of the copolymers showed the characteristic bands of NPMI and EEA: the peaks at 2975 (–CH$_2$–) and 1709 cm^{-1} (C=O) are attributed to the EAA component, and those at 1777 (C=O) and 3065, 1493, 1451, 747, and 689 cm^{-1} (–Ph) to the NPMI component. The ^{1}H-NMR spectrum of the copolymer, shown in Figure 1, indicates the proton signals of –COOCH$_2$ –group of EEA at 4.1 ppm and the *N*-phenyl group of NPMI at 7.1–7.4 ppm, respectively.

Kinetic behavior of living copolymerization

There exist some experimental criteria to diagnose a controlled/"living" polymerization,[16] for example, narrow molecular weight distribution, controlled molecular weight, linear relationship between molecular weight and monomer conversion, and constant concentration of active centers during the polymerization. To investigate the relation of molecular weights with conversion for the copolymerization of NPMI and EEA in the presence of PPDB and AIBN, the copolymerization kinetics was investigated by gravimetric method.

Figure 2 shows the plots of molecular weights M_n and polydispersities M_w/M_n versus conversion. The plots indicate that the molecular weight increases linearly with conversion, and the experimental values are close to the theoretical ones, assuming quantitative initiation. In all cases the molecular weight distribution is less than 1.5. This behavior shows that the RAFT copolymerization of NPMI with EEA is controlled. Figure 3 is the semilogarithmic curve of conversion with time, which shows that, when the conversion is lower than about 45%, the rate of polymerization increases linearly with time. However, when the conversion approached about 45% the polymerization seemed to cease, showing that the molecular weight of the copolymer is no longer variable with the time.

Monteiro and de Brouwer[17] found the rate retardation in process of RAFT, and presumed that it was related with concentration of the RAFT agent. They
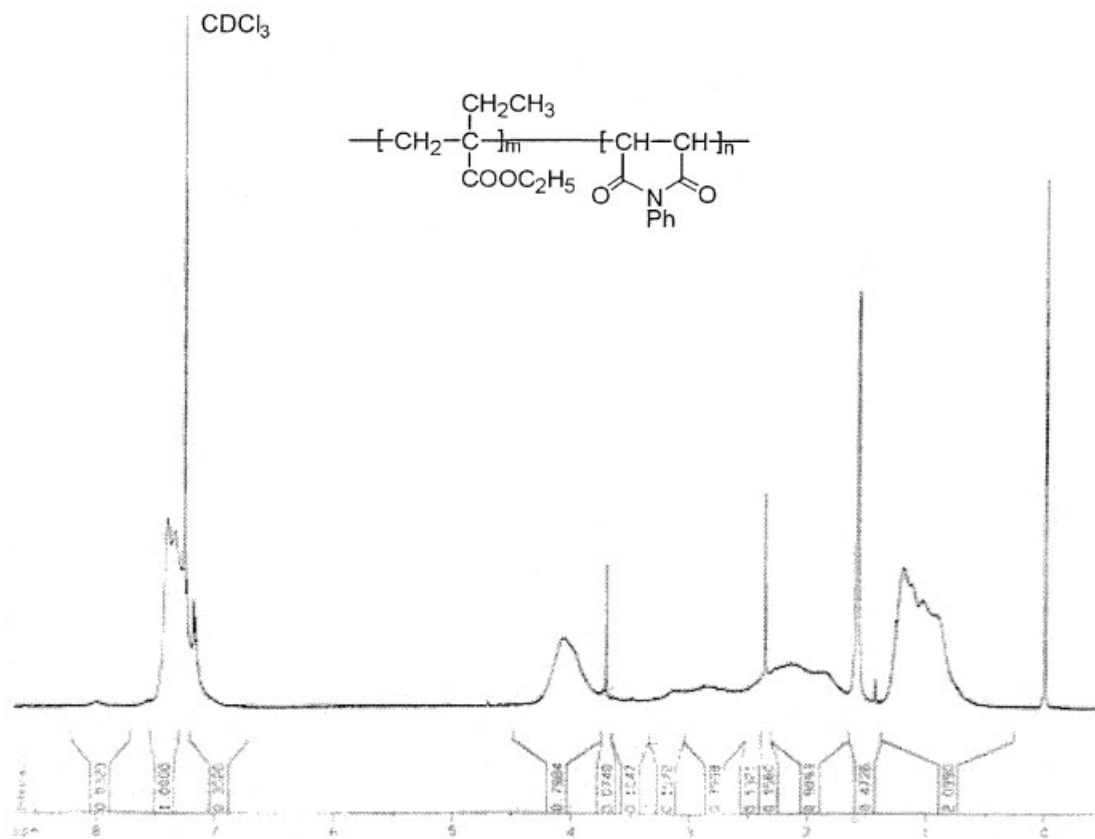
Figure 1 ^{1}H-NMR spectrum of poly(NPMI-*co*-EEA). $M_n = 4.3 \times 10^3$, $M_w/M_n = 1.4$, N = 4.18%.

postulated an additional intermediate radical termination mechanism (Scheme 1) to explain this phenomenon on the basis of a combination of simulations and experimental evidence. However, the cessation of polymerization during the RAFT process as our system has never been reported.
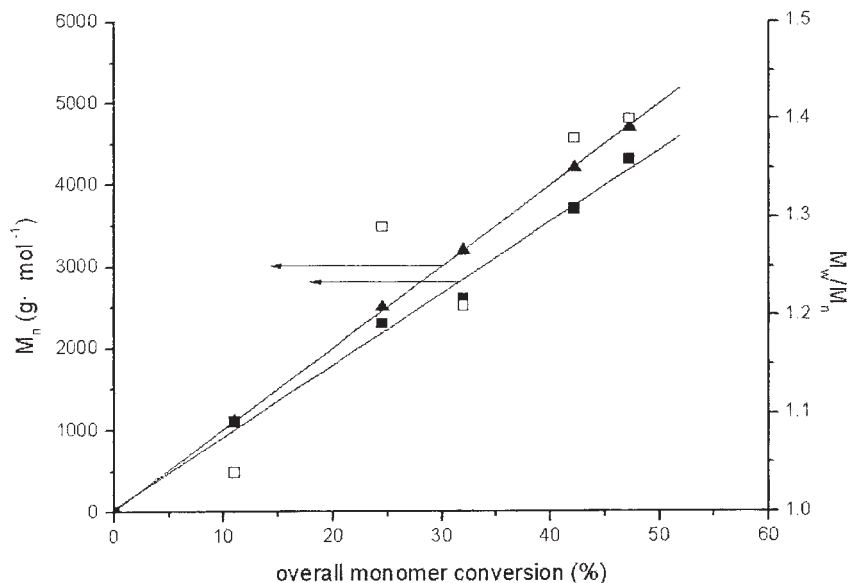

Figure 2   Experimental number-average molecular weight M_n (■), theoretical number-average molecular weight M_n (▲), and polydispersity index M_w/M_n (□) as a function of overall monomer conversion (conv.). $[NPMI]_0 = 4.2$ mol/L; $[EEA]_0 = 4.2$ mol/L; $[AIBN]_0 = 2.6 \times 10^{-2}$ mol/L; $[BDTB]_0 = 7.8 \times 10^{-2}$ mol/L. Theoretical $M_n = ([M]_0 + [S]_0)(conv.)(1.73.17 + 128.17)/\{2(2[AIBN]_0 + [BDTB]_0)\}$.
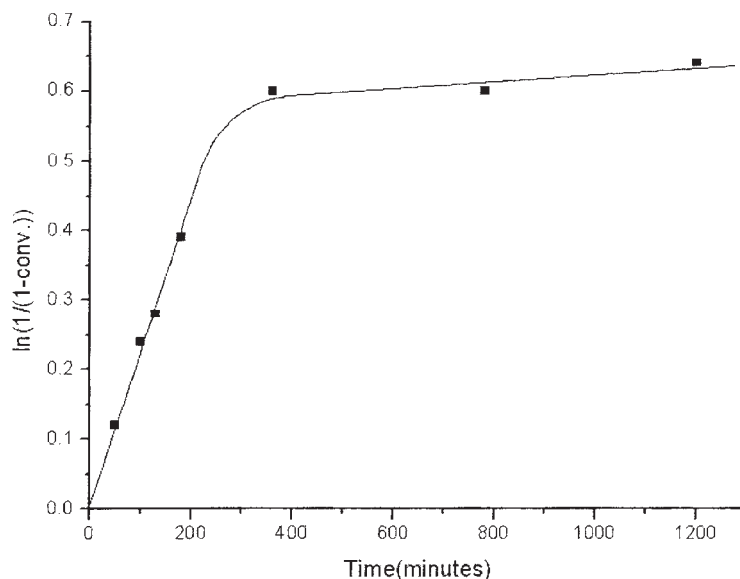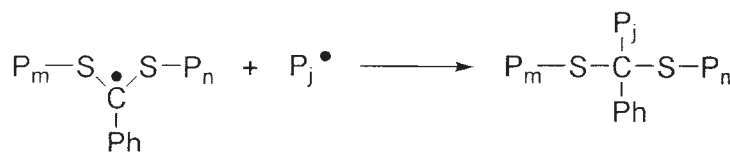
Figure 3 Plot of $\ln[1/(1 - \text{conv.})]$ versus time for the copolymerization of NPMI with EEA at 70°C. Experimental conditions are identical to those in Figure 2.

It is well known that the RAFT process is accomplished by a conventional radical polymerization in the presence of a (thiocarbonyl) sulfanyl compound with the structure S=C(Z)-SR, which acts as an efficient reversible addition fragmentation chain-transfer agent and confers living-radical characteristics to the polymerization.[1] The existence of this intermediate radical was evidenced by Hawthorne et al.[18] through ESR spectroscopy. To investigate the cause of cessation of our copolymerization system, ESR was also used to monitor the whole RAFT process. Figure 4(A) shows the ESR spectrum acquired by integrating the signal of this system from a reaction time of 24 to 40 min. The signal is well resolved and is clearly distinct from other species that could be present in the system. Compared with the literature g-factor value (g = 2.0043) of the intermediate radical when PPDB was used,[18] the g-factor value in our system was 2.0038, similar to the reported value. The experimental data confirmed that in our system the reactive intermediate radicals are really produced by PPDB. Throughout the whole process of RAFT, ESR spectra were obtained at 1-min intervals and the signal was observed soon after 2 min [Fig. 4(B)]. The intensity of this signal increased with time, passing through a maximum at 11 min [Fig. 4(C)]. Subsequently, the signal intensity remained at a constant level for about 70 min [Fig. 4(D)], then decreased quickly. After about 160 min reaction time the entire signal was masked by noise [Fig. 4(E)]. The quick decrease of signal intensity indicates that the radicals were soon consumed, resulting in a cessation of copolymerization. To explain this phenomenon, the reactivity ratios of comonomers were investigated.

The reactivity ratios r_1 and r_2 for the monomers NPMI and EEA were evaluated by the Kelen–Tüdos method,[19] the values of which were 0.19 ± 0.03 and 0.20 ± 0.04, respectively. The copolymer compositions for the different feed ratios were determined by elemental analysis and are listed in Table I.

Thus the Q and e values of EEA were derived as Q = 0.16 and $e = -0.06$, using the Price–Alfrey equation, and for NPMI, $Q = 0.74$ and $e = 1.75$ were reported from the literature.[20] The Q-value of EEA indicates that in the RAFT system EEA with low activity is disinclined to propagate and the corresponding radical can easily couple with the propagation species. At the beginning of the copolymerization, the concentration of comonomers is high, such that chain propagation is the main reaction; the radicals have little chance to couple with the intermediate radicals. Monteiro and de Brouwer[17] reported that, at first, no retardation and no inhibition phenomena appeared. As the copoly-

$$P_m{-}S{\underset{\underset{Ph}{|}}{\overset{\bullet}{\underset{C}{\diagdown}}}}S{-}P_n \;+\; P_j{}^{\bullet} \longrightarrow P_m{-}S{-}\underset{\underset{Ph}{|}}{\overset{\overset{P_j}{|}}{C}}{-}S{-}P_n$$
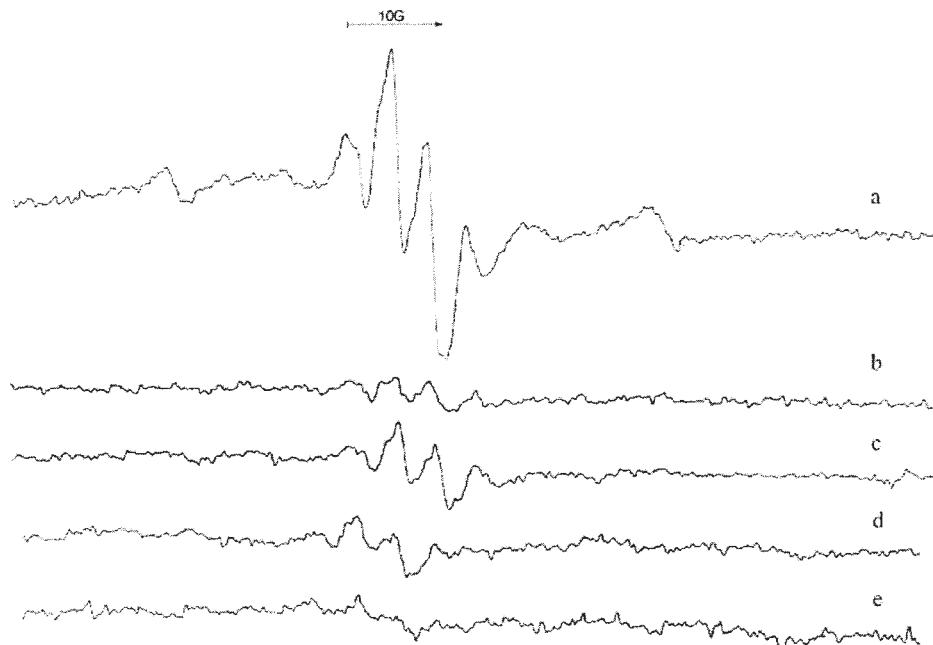
Scheme 1

Figure 4 ESR spectrum observed in the copolymerization of NPMI with EEA in the presence of AIBN and BDTB in benzene at 80°C: (a) spectrum integrated from reaction time of 24 to 40 min; (b) spectrum observed at 2 min reaction time; (c) spectrum observed at 11 min reaction time; (d) spectrum observed at 83 min reaction time; (e) spectrum observed at 163 min reaction time. [NPMI] = 2.7 × 10^{-3} mol/L; [EEA] = 2.7 × 10^{-2} mol/L; [AIBN] = 1.6 × 10^{-3} mol/L; [BDTB] = 2.7 × 10^{-3} mol/L.

merization proceeds, the concentration of comonomer radicals decreases and the additional intermediate radical termination begins to be a competitive reaction of chain propagation.[21] Thus, for our system, when the comonomer concentration decreased, the propagating polymer chains with EEA end couple much more easily with the intermediate radicals. Accordingly, cessation of copolymerization is induced.

TABLE I
Radical Copolymerization of NPMI (M_1) with EEA (M_2) in Dioxane by RAFT Process Using AIBN as an Initiator at 70°C[a]

Run	NPMI in feed (f_1) (mol %)	Conv. (%)	Copolymer composition	
			N (%)[b]	NPMI (mol %)[c]
1	30	1.31	4.09	43.05
2	40	6.60	4.30	45.61
3	50	7.97	4.53	48.48
4	60	4.39	5.03	54.86
5	70	4.40	5.14	56.30

[a] $[M_1]_0 + [M_2]_0 = 8.0$ mol/L; $[AIBN]_0 = 4.0 × 10^{-2}$ mol/L; $[BDTB]_0 = 1.2 × 10^{-1}$ mol/L.
[b] The average nitrogen content in the copolymer was obtained by duplicate analysis.
[c] NPMI (mol %) in copolymer was calculated as F_1: $F_1 = (1/\langle 1 + \{[(14/N) - 173.17]/128.17\}\rangle) × 100\%$, where N is the nitrogen content (mol %) in copolymer; 173.17 and 128.17 are the molecular weights of NPMI and EEA, respectively.

Copolymer microstructure and mechanism of alternating copolymerization

Figure 5 (A shows the UV spectra of NPMI, EEA, and their mixtures. The maximum absorption peaks for NPMI and EEA were located at 238, 261, 311; and 236 and 255 nm, respectively. When they were mixed, the maximum absorption peak was still at 242, 254, and 310 nm, and no new peaks were found. However, the product of $r_1r_2 = 0.04$ (≪1), indicating that the copolymerization of NPMI and EEA shows an alternating tendency. There are also some similar examples on the literature in which the alternating copolymerizations could be conducted smoothly, although no evidence for CTC could be supplied.[22]

As shown in Table I, although the feed ratio varies from 3 : 7 to 7 : 3 for NPMI/EEA, the copolymer composition is near 50 : 50. The statistical distribution of the monomer sequences and the content of NPMI–NPMI, EEA–EEA, and NPMI–EEA in copolymer chains were calculated using the following equations[23]:

$$X = \phi_1 - 2\phi_1(1 - \phi_1)$$
$$\div \{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1 - \phi_1)]^{1/2}\} \quad (1)$$

$$Y = (1 - \phi_1) - 2\phi_1(1 - \phi_1)$$
$$\div \{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1 - \phi_1)]^{1/2}\} \quad (2)$$

TABLE II
Structural Data of the NPMI–EEA Copolymers[a]

Run	Copolymer composition (mol %)		Sequence distribution (mol %)		
	NPMI	EEA	NPMI–NPMI (X)	EEA–EEA (Y)	NPMI–EEA (Z)
1[b]	44.2	55.8	4.0	15.5	80.5
2[c]	42.7	57.3	3.2	17.9	78.9

[a] Copolymer was prepared with the feed ratio 5:5 for NPMI/EEA. ($M_n = 4.3 \times 10^3$, $M_w/M_n = 1.4$, N = 4.18%)
[b] This series of data is based on the elemental analysis.
[c] This series of data is based on integrating area of ^{1}H-NMR spectrum of poly(NPMI-co-EEA) (Fig. 1).

$$Z = 4\phi_1(1 - \phi_1)$$
$$\div \{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1 - \phi_1)]^{1/2}\} \quad (3)$$

where r_1 and r_2 are the reactivity ratios of NPMI and EEA, respectively; ϕ_1 is the molar fraction of NPMI in the copolymer; and X, Y, and Z are the mole fractions of the NPMI–NPMI, EEA–EEA, and NPMI–EEA sequences in the copolymer, respectively. The data of NPMI contents (mol %) in the copolymer were obtained by both elemental analysis and ^{1}H-NMR.

For elemental analysis, the following formula was used:

$$\phi_1 = \frac{1}{1 + \dfrac{\dfrac{14}{N} - 173.17}{128.17}} \times 100\% \quad (4)$$

where ϕ_1 is NPMI contents (mol %) in the copolymers; N is the nitrogen content (mol %) in the copolymer; and 173.17 and 128.17 are the molecular weights of NPMI and EEA, respectively. For the ^{1}H-NMR spectrum, as Figure 1 shows, the signals from 7.4 to 7.1 ppm for phenyl rings are used to represent the NPMI fraction in copolymers, and the signals from 1.2 to 1.0 ppm for methyl are representative of the EEA fraction in copolymer. Using the integrating area of these two regions, the NPMI data (mol %) in the copolymer were derived ($\sim$ 42.7%), which is similar to the data obtained from elemental analysis. Comparing the mole fraction of the NPMI–EEA sequence in the copolymer calculated by the two methods, we found that the content of NPMI–EEA alternating sequence in copolymer is as high as 80%, which confirms that poly(N-PMI-co-EEA) is an alternating copolymer.

CONCLUSIONS

The alternating copolymer of NPMI with EEA was prepared by the RAFT process. It was found that before 45% of the comonomer conversion, the molecular weight of the copolymer increased with the conversion, the molecular weight distribution was rather narrow, and the molecular weight of the copolymer approached a constant value, irrespective of the length of polymerization time. In the comonomers, the EEA was indisposed to polymerize, so the propagating polymer chains with the EEA end more easily couple with the intermediate radicals when the comonomer concentration is decreased.

Figure 5 UV absorption spectra of (A) mixture of NPMI and EEA (mol/mol: 1 : 1); (B) NPMI; (C) EEA. Solvent: dioxane, concentration: 5×10^{-4} mol/L.

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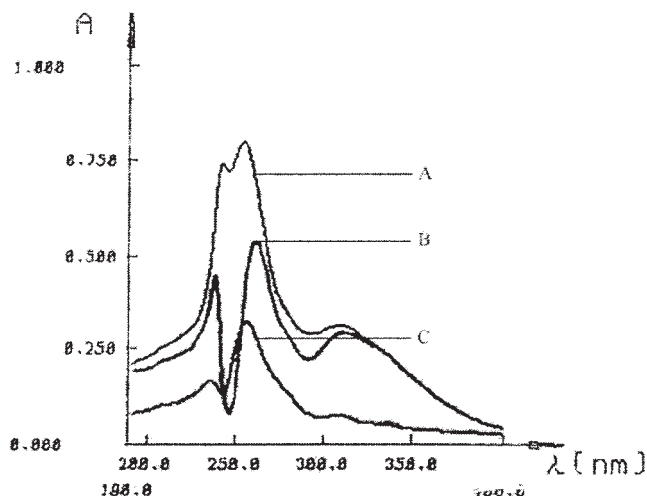6. Brandrup, J.; Immergut, E. H. Polymer Handbook, 2nd ed.; Wiley: New York, 1975; pp II, 105–386.

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