

Spontaneous Copolymerization of *N*-Butyl Maleimide and Ethyl α -Phenyl Acrylate with High Alternating Tendency

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ABSTRACT: The copolymerization of *N*-butyl maleimide (BMI) and ethyl α -phenyl acrylate (EPA) was successfully carried out without an initiator. A high alternating tendency was observed. The Q , e values were derived by Alfrey–Price equations: $Q = 0.09$, $e = 0.81$ for BMI and $Q = 0.21$, $e = -0.5$ for EPA, and the monomer reactivity ratios were $r_{\text{BMI}} = 0.15 \pm 0.01$ and $r_{\text{EPA}} = 0.18 \pm 0.08$, respectively. In this system BMI was donor and EPA was acceptor. The maximum copolymerization rate and molecular weight appeared at 70

mol % (BMI) in the feed ratio. The spontaneous alternating copolymerization was considered to be completed by a contact-type charge-transfer complex formed by the monomer pairs. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 355–360, 2004

Key words: copolymerization; charge transfer; UV–vis spectroscopy; initiators; Alfrey–Price equations

INTRODUCTION

During the early period of polymer science it was quickly recognized that copolymerization possessed some unique features quite different from those of homopolymerization, which means the interpretation for copolymerization is more complicated than that for homopolymerization. For example, some monomers, such as stilbene and maleic anhydride,¹ which are very difficult to homopolymerize, can easily be copolymerized. In contrast, in some cases, such as styrene and vinyl acetate, when they were placed together for copolymerization, only corresponding homopolymers were obtained.² Therefore copolymerization is a complicated process, the knowledge of the copolymerization is far from perfect, and there are still some very significant areas that must be investigated further.

N-substituted maleimide ranks among the group of useful monomers because, when their units were inserted into some polymer chains as thermoplastic resins,³ the heat-resistant, solvent-resistant, chemical stability, and other properties of these materials were greatly improved. Sakurai et al.⁴ found that maleimide (MI) and its derivatives show biological activity; Gam et al.⁵ evaluated antitumor activities of poly(*N*-glycinylnmaleimide-*co*-methacrylate acid) and poly(*N*-glyci-

nylmaleimide-*co*-vinyl acetate) *in vivo*. These results have opened up a new field for MI investigation.

On the other hand, *N*-substituted acrylates are also very interesting monomers. They are difficult to be homopolymerized by radicals other than methacrylate,⁶ but in specific conditions, some of them could be copolymerized with electron donors such as styrene (St).⁷ It was found that the homopolymers of α -substituted acrylate, for example, poly(ethyl α -ethylacrylate) prepared by anionic polymerization, demonstrated high physiological activities in the human body.⁸

Our purpose in this study was to seek a method of combining the merits of *N*-substituted maleimide and *N*-substituted acrylate to obtain some useful materials with some special properties.

With respect to copolymerization, alternating copolymerization induced by charge-transfer complex (CTC) is a kind of specific and complex reaction. There are two mechanisms that explain the alternating tendency: (1) the cross-reaction of the free monomers⁹ and (2) the homopolymerization of a CTC formed between monomer pairs.¹⁰

Although the CTC could be determined by many methods,¹¹ the most important evidence is the existence of a red shift peak in UV.¹² However, most of the reported CTC systems were constituted by strong electron donors and strong electron acceptors; the systems composed of weak donors and weak acceptors are relatively rarer.¹³ In some systems, alternating copolymerization was observed, but no evidence of CTC was found. For example, Barrales-rienda et al.¹⁴ found that the alternating copolymerization of *N*-phenyl ma-

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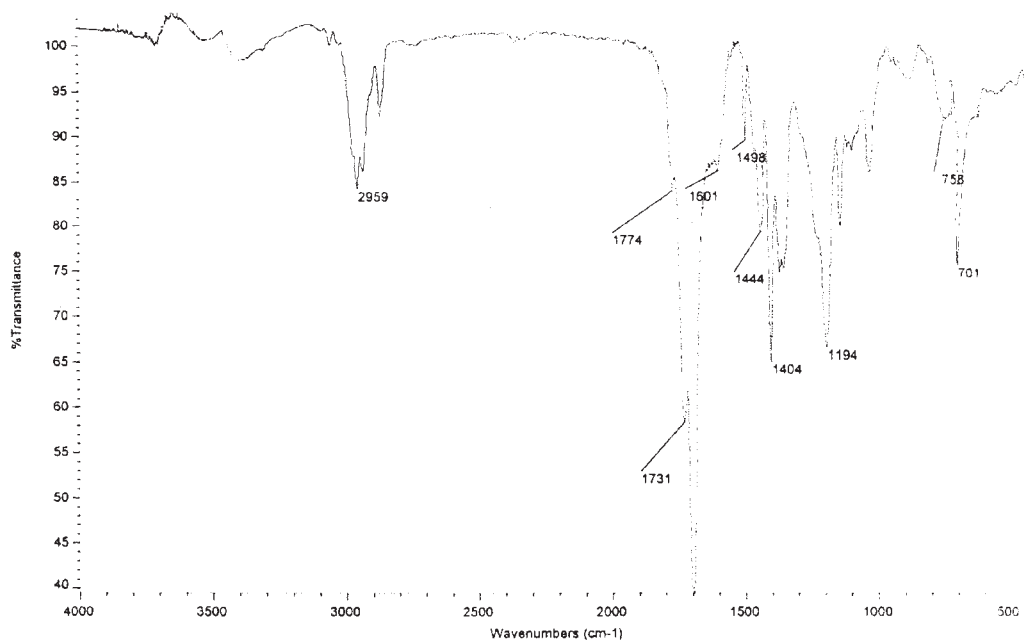


Figure 1 IR spectrum of copolymer.

leimide and styrene could be carried out, but no CTC was detected in cyclohexane; Otsu and Yang¹⁵ also showed that *N*-alkylcitraconimides underwent copolymerization with St, resulting in high molecular weight alternating copolymer, although attempts to adopt the UV technique to detect CTC were not successful.

Ethyl α -phenyl acrylate (EPA) has been commonly regarded as an electron-withdrawing monomer by some authors,⁷ although in our system it was found that EPA serves as an electron donor when it copoly-

merized with *N*-butyl maleimide (BMI), and the spontaneous alternating copolymerization could be carried out.

EXPERIMENTAL

Materials

Ethyl phenylacetate (EPA; Beijing Chemical Factory, China) and diethyl oxalate (DEO; Jiangsu Jincheng Reagent Factory, China) were purified by distillation

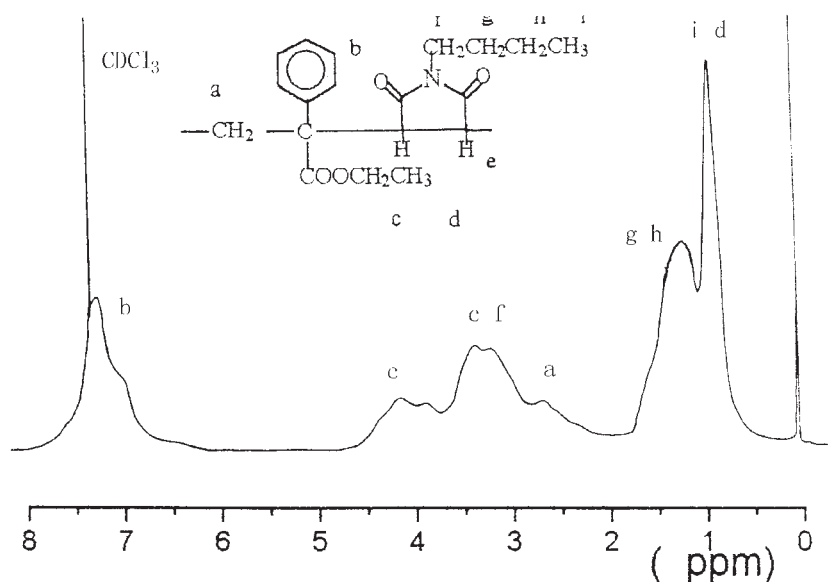


Figure 2 ¹H-NMR spectrum of copolymer.

TABLE I
Effect of Feed Ratio on Copolymerization of MBI and EPA^a

Sample	Feed ratio (mol _{BMI} /mol _{EPA})	M_n ($\times 10^4$)	M_w/M_n	Yield (%)	Composition ^b (BMI mol %)
1	2 : 8	—	—	—	—
2	3 : 7	0.34	1.39	0.99	46.7
3	4 : 6	1.15	1.45	2.12	48.3
4	5 : 5	1.52	1.45	5.60	49.3
5	6 : 4	1.52	1.45	13.50	51.8
6	7 : 3	1.85	1.45	10.16	54.6
7	8 : 2	1.36	1.54	8.80	61.1
8	9 : 1	1.15	1.54	3.87	69.8

^a Copolymerization conditions: 85°C, 10 h, [BMI] + [EPA]: 15 mmol.

^b The values derived from the element analysis based on the nitrogen contents.

^c No polymer was detected.

at reduced pressure; fractions of 98–101°C/21 mmHg and 78°C/10 mmHg were collected for EPA and DEO, respectively. *n*-Butyl amine (Shanghai Reagent Purchase Station, China) was distilled before use. Maleic anhydride (Shanghai Third Reagent Factory, China) was used as received. Dioxane was treated with fresh sodium and distilled. All other chemicals were purified by conventional procedures.

Preparation of EPA

EPA was prepared according to procedures reported by Ames and Davey¹⁶ in the yield of 64.8%.

¹H-NMR (δ : ppm): 1.24 (t, 3H, $-\text{CH}_3$), 4.25 (q, 2H, $-\text{CH}_2-$), 5.88 (s, 1H, *trans*-H of $\text{CH}_2=$), 6.34 (s, 1H, *cis*-H of $\text{CH}_2=$), 7.32 (m, 5H, phenyl); IR (cm^{-1}): 1723 (C=O), 1615 (C=C); n_D^{20} : 1.5240.

Preparation of BMI

BMI was also synthesized according to procedures reported in the literature,¹⁷ with some modifications. The procedure may be divided into two steps: (1) To a round-bottom flask, equipped with mechanical stirrer, dropping funnel, and thermometer, maleic anhydride (29.4 g, 0.3 mol) in 600 mL ether was added, then *n*-butylamine (21.9 g, 0.3 mol) in 360 mL ether was added at 0°C with vigorous stirring for 2 h, and the solution was stirred continuously for another hour. After filtration, the solid was washed with ether, dried at 40°C in a vacuum oven for 24 h, and then recrystallized with methanol. Yield: 74%; m.p. of the maleamic acid product: 82–84°C. (2) A 200-mL flask containing 34 g (0.2 mol) maleamic acid, 10 g sodium acetate, and 100 mL 95% acetic anhydride was heated

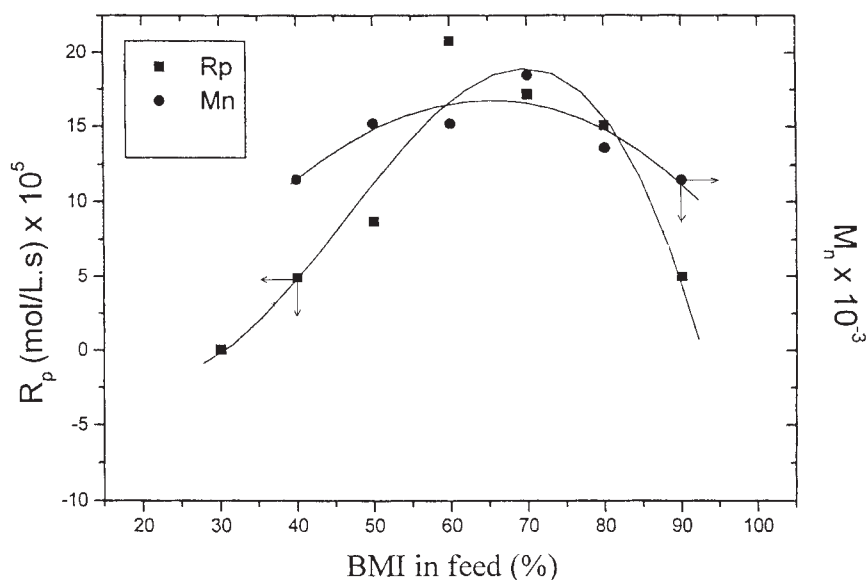


Figure 3 Relationship of polymerization rate and molecular weight with monomer feed ratio (■: copolymerization rate, ●: molecular weight M_n).

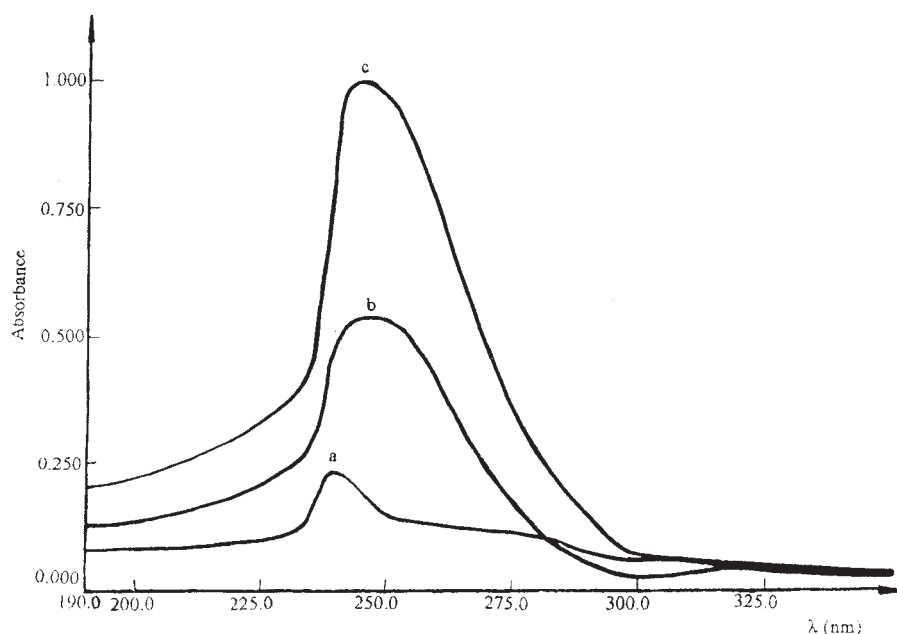


Figure 4 UV spectra of (a) EPA, (b) BMI, (c) mixture of EPA and BMI (solvent: dioxane, concentration: 1.0×10^{-5} mol/L).

at 95–100°C for 1 h, then poured into 300 mL ice water and stirred for 2 h. Potassium carbonate was added until no carbon dioxide was given off. The oil and water layers were separated; the water layer was twice extracted with ether, and the oil layer and extracted solution were merged and dried overnight with sodium sulfate. The BMI product was obtained by distillation under reduced pressure after evaporation of ether, and the fraction of 98–99°C/10 mmHg was collected. Yield: 50%; m.p.: 20°C.

$^1\text{H-NMR}$ (δ : ppm): 0.93 (t, 3H, $-\text{CH}_3$), 1.27–1.34 (sextet, 2H, $-\text{CH}_2\text{CH}_3$), 1.52–1.62 (quintet, 2H, $-\text{NCH}_2-\text{CH}_2-\text{CH}_2-$), 3.52 (t, 2H, $-\text{N}-\text{CH}_2-$), 6.70 (s, 2H, $-\text{CH}=\text{CH}-$); IR (cm^{-1}): 1768, 1706 ($\text{C}=\text{O}$), 1588 ($\text{C}=\text{C}$).

Copolymerization

Copolymerization of BMI and EPA was performed in a glass ampoule using dioxane as solvent. A typical experiment may be described as follows: an ampoule was charged with a given ratio of BMI, EPA, and solvent, and degassed three times by freeze–pump–thaw cycles at 77 K, then sealed under N_2 . The copolymerization using a different monomer feed ratio was carried out at 85°C for a certain time. The copolymer was then precipitated in methanol and purified by dissolution/precipitation with dioxane/methanol, and the purified product could dissolve in many common solvents such as CHCl_3 , tetrahydrofuran (THF), dioxane, and ether.

Measurements

IR spectra were obtained on a Magna-550 FTIR spectrometer (Nicolet Analytical Instruments, Madison,

WI); elemental analyses were determined by a Carlo Erba (Milan, Italy) 1106 elemental analyzer; 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 to 3×10^6); injection volume: 20 μL ; concentration: 1 mg/mL; solvent and eluent: THF (or DMF); flow rate: 0.2–5 mL/min. GPC was calibrated with monodispersed polystyrene standards.

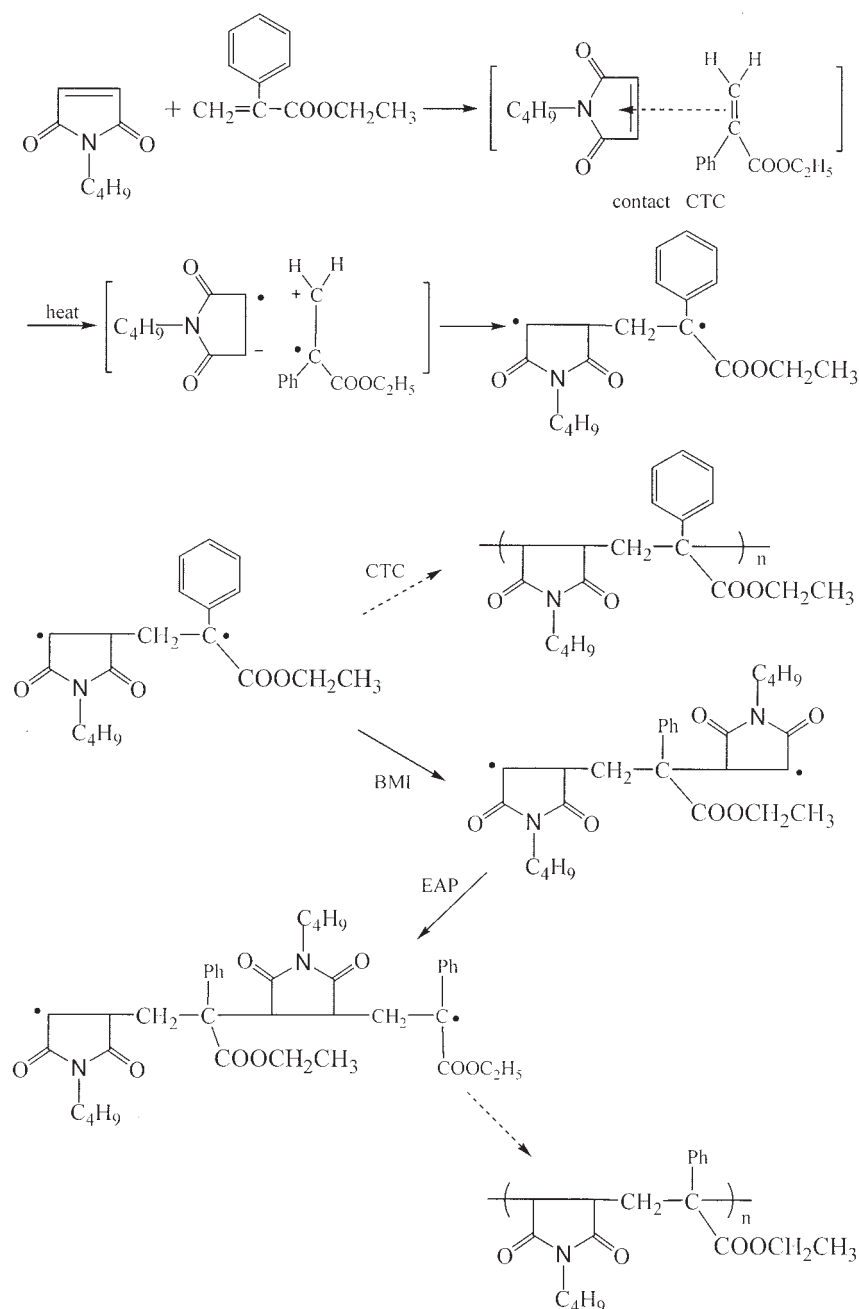
RESULTS AND DISCUSSION

Characterization of copolymer

The copolymer of BMI and EPA is easily soluble in ether, whereas BMI and EPA are not, so the purification procedure is very simple. Figures 1 and 2 show the IR and $^1\text{H-NMR}$ spectra of the copolymer (sample 5 in Table I), respectively. The following could be observed: IR (cm^{-1}) 1774 and 1695 ($\text{C}=\text{O}$), 1404 ($\text{C}-\text{N}$); $^1\text{H-NMR}$ (δ : ppm) 3.4 ($=\text{CH}-$), 3.2 ($-\text{N}-\text{CH}_2-$), 1.6–1.0 ($-\text{CH}_2\text{CH}_2-$), and 0.9 ($-\text{CH}_3$) attributed to BMI; IR (cm^{-1}) 1731 ($\text{C}=\text{O}$), 1498, 758, and 701 (phenyl ring), 1194 ($\text{C}-\text{O}$); $^1\text{H-NMR}$ (δ : ppm) 7.4–6.8 (phenyl ring), 4.2 ($-\text{COOCH}_2-$), and 0.9 ($-\text{CH}_3$) attributed to EPA; and 1617 cm^{-1} , 6.7 ppm and 1588 cm^{-1} , 6.86 ppm for $\text{C}=\text{C}$ of BMI and EPA, respectively, disappeared after copolymerization.

Copolymerization kinetics

Copolymerizations of BMI and EPA, with different feed ratios, were performed at 85°C; no corresponding



Scheme 1

homopolymers were detected in control experiments. Table I lists the experimental results of copolymerization, from which the relationship of initial rate of copolymerization and the M_n of the copolymer with monomer feed ratio were derived (Fig. 3). It was found that a maximum initial rate of copolymerization and a maximum M_n occurred at 70 mol % BMI in the feed ratio. The monomer reactivity ratios, $r_{\text{BMI}} = 0.15 \pm 0.01$ and $r_{\text{EPA}} = 0.18 \pm 0.03$, were measured by the Fineman-Ross method.¹⁸ We also found that when the amount of BMI or EPA (especially BMI) is excessive in the feed ratio, the composition of copolymer deviated

from the 1 : 1 ratio. The precise 1 : 1 alternating structure was formed only in the feed ratio range of 5 : 5 to 7 : 3 (mol_{BMI}/mol_{EPA}). The molecular weight of all copolymer samples was low; in most cases the molecular weight was no more than 20,000, which may be attributed to the low reactivity of both samples.

Copolymerization mechanism

The copolymerization of BMI and EPA proceeded smoothly; conversely, the homopolymerization of BMI was conducted slowly and EPA was disinclined

to homopolymerize radically. Alternating copolymerization involving various CTC types have been documented by several authors, and the existence of a new red shift peak in the UV spectrum is always used as strong evidence for CTC. Figure 4 shows the UV spectra of BMI, EPA, and their mixtures. The maximum absorption peaks for EPA and BMI were located at 250 and 238 nm, respectively, and the molar extinguishing efficiency (ϵ_{\max}) was 1.03 and $0.46 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. When they were mixed, no new peak at a long wavelength was observed, and the maximum absorption peak was still at 251 nm; when the strength of the peak increased, however, the ϵ_{\max} was $1.66 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, indicating that a special interaction exists when BMI and EPA are mixed.

The monomer EPA is commonly used as an electron acceptor.⁷ To ascertain its function in our system, the Q and e values, representing the resonance stabilization and polarity of monomers, respectively, were derived by Alfrey-Price equations: the values are $Q = 0.21$, $e = -0.5$ for EPA and $Q = 0.09$, $e = 0.81$ for BMI, using St as reference. Therefore in our system, EPA is the electron donor and BMI is the electron acceptor, and the charge transfer complex should be formed when they are mixed. We also found some similar examples from references in which the alternating copolymerization could be conducted smoothly, although no evidence for CTC could be supplied. For example, in the system of isobutyl vinyl sulfide, a strong electron-donating monomer, and methyl acrylate or acrylonitrile, a weak electron-accepting monomer, no evidence of CTC was found spectroscopically, yet spontaneous copolymerization was observed.²⁰ Therefore the concept of contact-type CTC was developed.¹⁵

As we mentioned earlier, the charge-transfer polymerization proceeded by a pair of monomers involving two types of mechanisms: (1) One is CTC,¹⁰ which means the polymer chain was propagated by using the CTC composed of the pair of monomers as a basic unit. The polymer chain consisted of a strict 1:1 monomer ratio; the maximum polymerization rate and maximum molecular weight of copolymer occur at 1:1 feed ratio and because, in this case, all the monomer pairs constituted the CTC, the concentration of CTC is highest. (2) The other mechanism is the alternating addition of monomers that constitute the CTC.⁹ Then the polymerization rate and molecular weight of copolymer are dependent only on the monomer activity and independent of the monomer feed ratio, and no maximum polymerization rate and molecular weight could be determined.

In the BMI-EPA system shown in Figure 1, however, the derivation was found, and thus the copolymerization did not proceed by a single addition mode, and the dual mechanisms of CTC addition and alternating addition of comonomers could operate simultaneously.

Therefore we propose the following mechanism, as shown in Scheme 1:

The contact type of CTC is formed first by charge transfer between the electron-donor EPA and the electron-acceptor BMI, thus producing a biradical. The propagation occurs by CTC addition, using whole CTC as a unit, and simultaneously alternating addition of EPA and BMI.

CONCLUSIONS

A new spontaneous alternating copolymerization of BMI and EPA was successfully carried out at 85°C, the structure of which was characterized by IR and ¹H-NMR. In this system, the EPA is the electron donor and BMI is the electron acceptor, and interaction between them was confirmed by UV. The values of monomer reactivity ratios were $r_{\text{BMI}} = 0.15 \pm 0.01$ and $r_{\text{EPA}} = 0.18 \pm 0.08$, respectively. The maximum polymerization rate and maximum molecular weight were derived from the feed ratio 1:1 ($\text{mol}_{\text{BMI}}/\text{mol}_{\text{EPA}}$), and occurred at 5:5 to 7:3. The chain propagation might be performed by CTC and alternating addition of monomers.

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