Kinetics and Mechanism of Grafting of Crotonic Acid onto Acrylonitrile–Butadiene–Styrene Terpolymer

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ABSTRACT: The grafting of crotonic acid onto acrylonitrile–butadiene–styrene terpolymer (ABS) was initiated by benzoyl peroxide (BPO) in 1,2-dichloroethane solution. The infrared spectra confirmed that crotonic acid was successfully grafted onto ABS backbone. The influences of the concentration of crotonic acid, BPO, and ABS on grafting were studied. The graft occurred at the butadiene region of ABS. A reaction mechanism was proposed: the grafting most likely took place by cross-termination of poly(crotonic acid) radicals with ABS macroradicals. The initial rate of grafting could be written as: $R_p = 2.02 \times 10^{-4}[P][M]^2[I_2]^{0.5}/([M] + 1.05[P])^2$. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 726–733, 2002

Key words: acrylonitrile–butadiene–styrene terpolymer; grafting; crotonic acid; kinetics; mechanism

INTRODUCTION

Functionalized polymers are useful in various applications such as reactive compatibilization of polymer blends. Functionalized polymers may be obtained by grafting of functional monomers with existing polymers. Acrylic acid, methacrylic acid, maleic anhydride, glycidyl methacrylate, and the like are the most commonly used monomers. To date, crotonic acid has not been used as grafting monomer for polymers in published studies.

Huang et al.[1–4] grafted styrene, benzyl acrylate, and benzyl methacrylate onto polybutadiene (PB) in benzene solution at 60°C with benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) as initiators. They found for styrene and benzyl methacrylate monomers, graft site formation was attributed to the initiator radical attacking PB by allylic hydrogen abstraction, whereas for benzyl acrylate monomer the grafting was attributed to the homopolymer radical attacking the double bond of PB. They thought this phenomenon resulted from the reactivity difference in monomer and homopolymer radicals.

Cameron et al.[5–8] grafted styrene onto PB in benzene solution at 60°C with BPO as initiator. They proposed a grafting mechanism of primary radicals attacking PB by abstraction of allylic hydrogen.

Manaresi et al.[9] studied the grafting of styrene onto PB in bulk at 100°C with α-dicumyl peroxide as initiator. They proposed that the graft site was formed evidently through direct hydrogen abstraction or chain-transfer reaction.

Chandrasiri et al.[10] grafted acrylic acid onto ABS in chloroform using BPO and AIBN as initiators. They also investigated the grafting of acrylic acid onto polystyrene, polyacrylonitrile, and PB. They concluded that the graft reaction

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occurred by addition of monomer to the double bond of the butadiene region of ABS.

Abdel-Razik et al.[11,12] investigated the photoinduced grafting of acrylamide onto ABS in chloroform in the presence of benzophenone or 4-acetyldiphenyl. Irradiation of benzophenone or 4-acetyldiphenyl produced a radical that abstracted an allylic hydrogen and/or added to the double bond of the butadiene portion of the polymer to generate the radical site for grafting.

The work reported here is an attempt to study the grafting of crotonic acid onto ABS and to investigate the kinetics and mechanism of radical graft reaction of crotonic acid onto ABS.

EXPERIMENTAL

Materials

The ABS used in this study was a product of Taiwan Qimei Co. (M_n = 49,000, M_w = 134,000, M_w/M_n = 2.72, containing 2.7 wt % additives, 22.4 wt % acrylonitrile, 13.5 wt % butadiene, and 61.4 wt % styrene, as determined by elementary analysis and solvent separation method). BPO (Shanghai Zhongli Chemical Factory) was purified by dissolving in chloroform at room temperature and precipitating in cool methanol. AIBN, supplied by Shanghai No. 4 Reagent Factory, was recrystallized from ethanol before use. Crotonic acid, 1,2-dichloroethane, ethanol, acetone, and cyclohexane were obtained from Shanghai Chemical Reagent Company and used as received without further purification.

Grafting

The reactions were carried out in a 250-mL three-neck flask equipped with a condenser, a stirrer, and a gas inlet. In a typical reaction, a precise amount of ABS (2.50 g) was dissolved in 50 mL 1,2-dichloroethane in the reaction vessel with constant stirring. The desired amount of monomer and BPO were added when the resin was completely dissolved, after which the vessel was put into a water bath that was already adjusted to the desired reaction temperature. The reaction proceeded under N_2. Samples were taken out from the reaction mixture for characterization at different times of reaction. Each time, 5 mL of reaction mixture was withdrawn and poured into a 10-fold volume of ethanol under vigorous stirring, followed by drying of the precipitated polymer. The precipitated polymer was purified by dissolving in 10 mL 1,2-dichloroethane, followed by precipitation in ethanol. The purified polymer was collected and dried to constant weight in a vacuum oven at 80°C.

Polymerization conditions for the entire series of experiments are summarized in Table I.

Characterization

Samples were cast into films (0.010–0.015 mm thick) using chloroform as solvent. Infrared spectroscopic information of ABS and the grafted ABS were obtained using a Perkin–Elmer Paragon 1000 FTIR spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT). No significant changes were observed in the FTIR spectrum of the grafted ABS after further purification, indicating that the purification procedure was effective.

The molecular weight of the homopolymer of crotonic acid was determined using a vapor pressure osmometer (K-7000; Knaver Co., Berlin, Germany). The solvent was ethanol and the standard sample was polyglycol.

Determination of Grafted Crotonic Acid

The grafted crotonic acid and grafting degree were determined by a back-titration procedure. A 0.15-g sample was dissolved in 50 mL acetone, and then 10 mL 0.1 mol/L sodium hydroxide (NaOH) ethanol solution was added. The solution was refluxed for 30 min with stirring and back-titrated with 0.1 mol/L hydrochloric acid (HCl) using methyl red as indicator.

The grafting degree (GD) was defined as the amount of acid grafted as a percentage of ABS, calculated by

$$GD\ (\%) = \frac{(V_0 - V_1) \times 10^{-3} \times C \times M}{W - (V_0 - V_1) \times 10^{-3} \times C \times M} \times 100 \quad (1)$$

where V_0 is the amount of HCl consumed by using pure ABS as reference (mL), V_1 is the amount of HCl consumed by grafted sample (mL), C is the molar concentration of HCl (mol/L), M is the molecular weight of crotonic acid, and W is the weight of the sample (g).

The amount of grafted acid (G) was calculated as follows in terms of concentration in the reaction solution:

Table I Experimental Conditions, Grafting Degree, and Initial Rates of Grafting[a]

Run Number	Monomer Concentration (mol/L)	Initiator Concentration (mol/L)	ABS Concentration[b] (mol/L)	GD[c] (%)	$R_p \times 10^6$ (mol L^{-1} s^{-1})
A1	0.10	0.021	0.125	1.6	0.69
A2	0.20	0.021	0.125	2.3	1.33
A3	0.30	0.021	0.125	2.7	1.75
A4	0.40	0.021	0.125	3.1	2.06
A5	0.50	0.021	0.125	3.5	2.29
B1	0.30	0.021	0.025	6.0	0.60
B2	0.30	0.021	0.075	3.1	1.34
B3	0.30	0.021	0.125	2.7	1.75
B4	0.30	0.021	0.175	2.2	2.01
C1	0.30	0.006	0.125	1.5	0.87
C2	0.30	0.012	0.125	2.0	1.22
C3	0.30	0.021	0.125	2.7	1.75
C4	0.30	0.031	0.125	3.1	2.18
D1[c]	0.30	0.021	0		
E1	0.30	0.021 (AIBN)	0.125		

[a] Temperature, 84°C; solvent, 1,2-dichloroethane in all experiments; initiator = BPO in series A, B, and C.
[b] The ABS concentration is defined as butadiene section concentration.
[c] Reaction time, 5 h.

$$G\ (\text{mol/L}) = \frac{(V_0 - V_1) \times 10^{-3} \times C \times W_0}{\dfrac{W}{1 + GD \times 10^{-2}}} \times \frac{1000}{V} \tag{2}$$

where V_0, V_1, C, and W are the same as in eq. (1); W_0 is the weight of ABS added in the reaction (g); and V is the volume of reaction mixture at room temperature (mL).

Phase Separation of ABS and Grafted ABS

To get further information of ABS-*g*-crotonic acid copolymer, it was separated into three fractions by using the solvent fractionation method similar to that of Gesner.[13] Pure ABS was first dissolved in 1,2-dichloroethane and precipitated in ethanol to obtain a fine powder polymer. A 1.0-g sample of the fine powder of ABS or grafted ABS (experiment A3, reaction time 5 h, GD = 2.7%) was refluxed in 150 mL cyclohexane for 2 h with stirring, after which the solid residue was filtered away from the hot cyclohexane solution. The cyclohexane extract was evaporated to dryness in the hood under nitrogen purge. The residue was weighed, redissolved in cyclohexane, and smeared on a KBr salt plate for FTIR analysis. The cyclohexane-insoluble material was stirred in 200 mL cold acetone for 2 h and centrifuged at 10,000 rpm for 1 h. The supernatant liquid was removed and cast into a thin film for FTIR analysis. The acetone-insoluble material in the centrifuge tubes was weighed and sandwiched with KBr for FTIR analysis.

REACTION MECHANISM

The degree of polymerization of crotonic acid is 5.6 (experiment D1), as determined using a vapor pressure osmometer. This small number may be attributable to self-inhibition and low reactivity of crotonic acid ($CH_3CH{=}CHCOOH$), which has high steric hindrance. The backbone radicals, formed by primary radicals' attacks, may not be able to further initiate monomer. A mechanism for the grafting of crotonic acid onto ABS may be proposed as follows:

Decomposition of initiator:

$$I_2 \xrightarrow{fk_d} 2I\cdot \tag{3}$$

Radical attack on monomer:

$$I\cdot + M \xrightarrow{k_{i1}} IM\cdot \tag{4}$$

Radical attack on polymer:

$$I\cdot + P \xrightarrow{k_{i2}} P\cdot \tag{5}$$

Propagation of homopolymerization:

$$IM_1\cdot + M \xrightarrow{k_p} IM_2\cdot \tag{6a}$$

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot \tag{6b}$$

Growing homopolymer radicals transfer to monomer:

$$M_n\cdot + M \xrightarrow{k_{tr}} M_nH + M\cdot \tag{7}$$

Termination by recombination:

$$M_n\cdot + M_m\cdot \xrightarrow{k_t} M_{n+m} \tag{8}$$

$$P\cdot + M_n\cdot \xrightarrow{\sigma k_t} PM_n \tag{9}$$

$$P\cdot + P\cdot \xrightarrow{\sigma^2 k_t} P - P \tag{10}$$

Here, I_2, M, and P denote initiator, monomer, and polymer, respectively; $I\cdot$, $M_n\cdot$, and $P\cdot$ denote primary radical, homopolymer radical, and backbone radical, respectively. The cross-termination constant is in eq. (9). For simplicity it may be assumed that a $P\cdot/P\cdot$ termination has a rate constant, which was reported previously by Cameron et al.[8]

Assuming that a stationary state exists for all radicals, the following equations are obtained:

$$\frac{d[I\cdot]}{dt} = 2fk_d[I_2] - k_{i1}[I\cdot][M] - k_{i2}[I\cdot][P] = 0 \tag{11}$$

$$\frac{d[M\cdot]}{dt} = k_{i1}[I\cdot][M] - k_t[M\cdot]^2 - \sigma k_t[M\cdot][P\cdot] = 0 \tag{12}$$

$$\frac{d[P\cdot]}{dt} = k_{i2}[I\cdot][P] - \sigma k_t[M\cdot][P\cdot] - \sigma^2 k_t[P\cdot]^2 = 0 \tag{13}$$

In these equations $M\cdot$ represents homopolymer radicals (of all lengths) in the system. Equations (11)–(13) are solved to yield

$$[I\cdot] = \frac{2fk_d[I_2]}{k_{i1}[M] + k_{i2}[P]} \tag{14}$$

$$[M\cdot] = \left(\frac{2fk_d}{k_t}\right)^{0.5} \frac{k_{i1}[M][I_2]^{0.5}}{k_{i1}[M] + k_{i2}[P]} \tag{15}$$

$$[P\cdot] = \left(\frac{2fk_d}{k_t}\right)^{0.5} \frac{k_{i2}[P][I_2]^{0.5}}{\sigma(k_{i1}[M] + k_{i2}[P])} \tag{16}$$

Equation (9) is the only graft-forming reaction, so the rate of grafting may be given as

$$R_p = \lambda\sigma k_t[M\cdot][P\cdot] \tag{17}$$

Here λ is the number-average degree of polymerization of the growing poly(crotonic acid) radicals, that is, the kinetic chain length, which is given by

$$\lambda = \frac{\text{rate of growth of poly(crotonic acid) radicals}}{\text{rate of disappearance of poly(crotonic acid) radicals}}$$

$$\lambda = \frac{k_p[M][M\cdot]}{k_t[M\cdot]^2 + \sigma k_t[M\cdot][P\cdot]} \tag{18}$$

By introducing eqs. (15), (16), and (18) into eq. (17), we obtain

$$R_p = \left(\frac{2fk_d}{k_t}\right)^{0.5} \frac{k_p k_{i2}}{k_{i1}} \frac{[P][M]^2[I_2]^{0.5}}{\left([M] + \frac{k_{i2}}{k_{i1}}[P]\right)^2} \quad (19)$$

Equation (19) may be rewritten as

$$R_p = \frac{A[P][M]^2[I_2]^{0.5}}{([M] + B[P])^2} \quad (20)$$

where

$$A = \left(\frac{2fk_d}{k_t}\right)^{0.5} \frac{k_p k_{i2}}{k_{i1}}, \quad B = \frac{k_{i2}}{k_{i1}}$$

Chain transfer to polymer may not be neglected in the above kinetics scheme, according to many investigations.[8,9,14,15] However, it is not important in the grafting of crotonic acid onto ABS, which will be confirmed later.

$$M_n\cdot + P \xrightarrow{k_{trp}} M_n + P\cdot \quad (21)$$

Assuming that a stationary state exists again, R_p can be calculated by the above method as

$$R_p = \frac{k_p\left(\frac{2fk_d}{k_t}\right)^{0.5}[I_2]^{1.5}[M]^2}{\left([I_2]^{0.5} + \frac{k_{trp}}{(2fk_dk_t)^{0.5}}[P]\right)^2\left([M] + \frac{k_{i2}}{k_{i1}}[P]\right)} \times \left[1 - \frac{[I_2]^{0.5}[M]}{\left([I_2]^{0.5} + \frac{k_{trp}}{(2fk_dk_t)^{0.5}}[P]\right)\left([M] + \frac{k_{i2}}{k_{i1}}[P]\right)}\right] \quad (22)$$

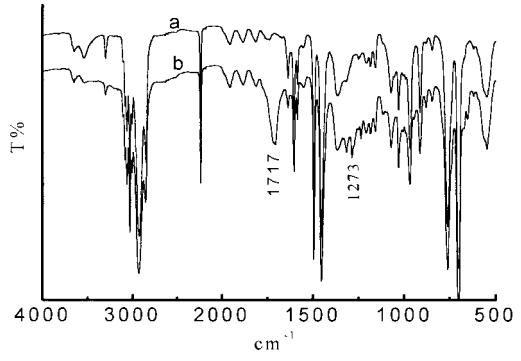

Figure 1 Infrared spectra of (a) ABS and (b) ABS-*g*-crotonic acid.

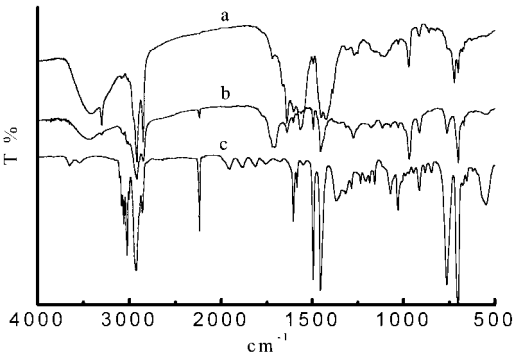

Figure 2 Infrared spectra of three fractions of ABS-*g*-crotonic acid: (a) cyclohexane-soluble fraction; (b) acetone-insoluble fraction; (c) cyclohexane-insoluble acetone-soluble fraction.

Equation (22) may be rewritten as

$$R_p = \frac{\alpha[I_2]^{1.5}[M]^2}{([I_2]^{0.5} + \beta[P])^2([M] + \gamma[P])} \times \left(1 - \frac{[I_2]^{0.5}[M]}{([I_2]^{0.5} + \beta[P])([M] + \gamma[P])}\right) \quad (23)$$

where

$$\alpha = k_p\left(\frac{2fk_d}{k_t}\right)^{0.5}, \quad \beta = \frac{k_{trp}}{(2fk_dk_t)^{0.5}}, \quad \gamma = \frac{k_{i2}}{k_{i1}}$$

RESULTS AND DISCUSSION

Characterization of Grafting

Figure 1 shows the infrared spectra of ABS and grafted ABS. The appearance of new absorbance at 1717 and 1273 cm^{-1} indicates the introduction of C═O and C—O groups of crotonic acid onto ABS.

The infrared spectra of three fractions from solvent separation, shown in Figure 2, indicate that the cyclohexane-soluble fraction was free PB and/or free PB grafted with crotonic acid, the cyclohexane-insoluble but acetone-soluble fraction was styrene–acrylonitrile copolymer (SAN), and the acetone-insoluble fraction was graft copolymer and/or crosslinked PB. As shown in Figure 2, no crotonic acid was grafted onto SAN, but grafting did occur in the cyclohexane-soluble and acetone-insoluble fractions. Therefore, the graft reaction most likely takes place in the butadiene

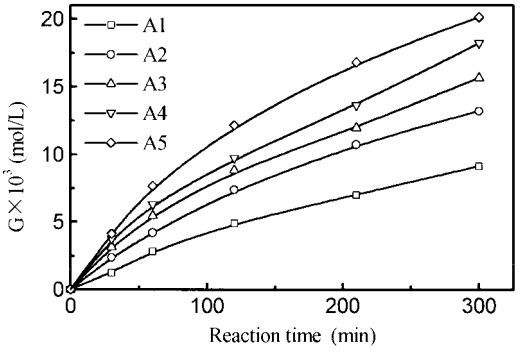

Figure 3 Effect of monomer concentration on the grafting of crotonic acid onto ABS.

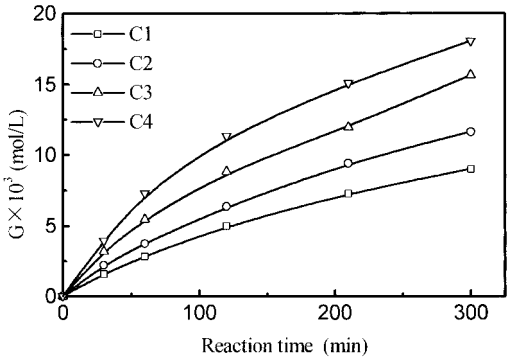

Figure 5 Effect of initiator concentration on the grafting of crotonic acid onto ABS.

region of ABS. This result is in accordance with Chandrasiri's[10] investigation.

Influence of Reaction Parameters on Grafting

Figures 3–5 show the effect of monomer concentration, ABS concentration, and initiator concentration on graft reaction, respectively. The amount of grafted monomer increases considerably at first, then levels off with reaction time; it also increases with increasing monomer concentration, ABS concentration, and initiator concentration. In this reaction system at constant temperature (84°C), the more the initiator added, the more the primary radicals generated, after which the amount of monomer and backbone radicals increased. Therefore the possibility of monomer to react with polymer was increased. In addition, the chance of monomer to react with polymer also increased with increasing monomer and ABS concentrations.

When the initiator was switched from BPO to AIBN, the results are shown in Figure 6. The extent of grafting of crotonic acid/AIBN/ABS system is much lower than that of the crotonic acid/BPO/ABS system. This is probably attributable to the resonance stability of the primary radical, generated from AIBN, which is incapable of attacking an allylic hydrogen of the butadiene region of ABS.

Table I shows the grafting degree and the initial rates of grafting (R_p) of series A, B, and C. The initial rates of grafting are obtained from the slope of respective curves in the initial periods of the reaction. The grafting degree increases with increasing monomer and initiator concentrations. However, the grafting degree decreases considerably with increasing ABS concentration, which is attributed to competition of grafting on ABS at a fixed level of monomer concentration.

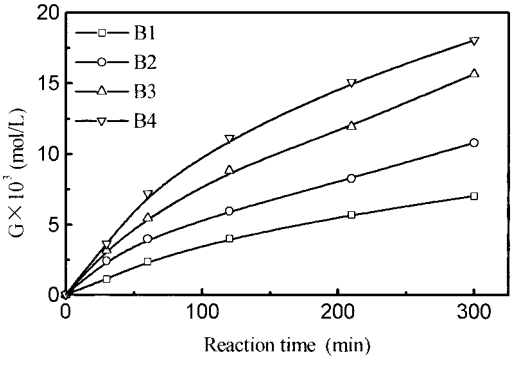

Figure 4 Effect of ABS concentration on the grafting of crotonic acid onto ABS.

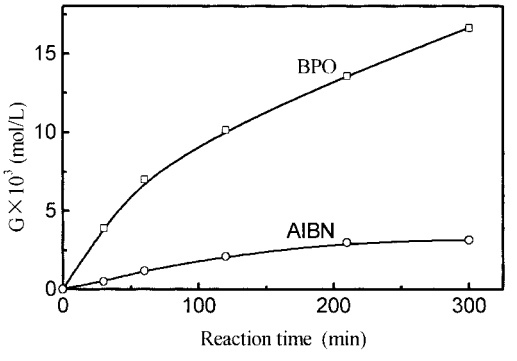

Figure 6 Effect of initiator type on the grafting of crotonic acid onto ABS. Crotonic acid = 0.30 mol/L; initiator = 0.021 mol/L; ABS = 2.50 g; temperature = 84°C; 1,2-dichloroethane = 50 mL.

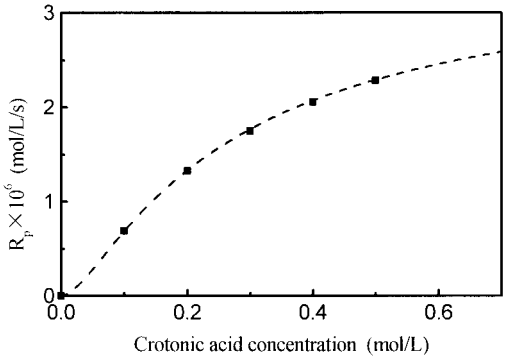

Figure 7 Initial rate of grafting versus monomer concentration: ■, experimental points; – – –, simulation results.

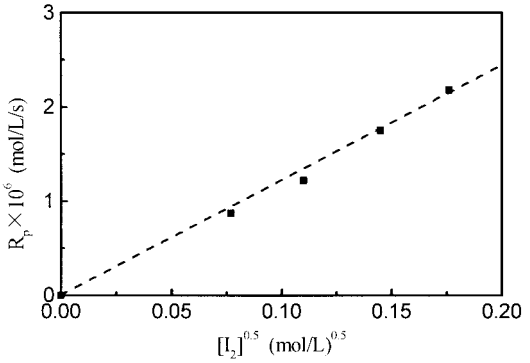

Figure 9 Initial rate of grafting versus initiator concentration: ■, experimental points; – – –, simulation results.

Reaction Kinetics

Figures 7–9 show the relationship of initial rate of grafting with monomer concentration, ABS concentration, and initiator concentration, respectively.

In the case of varying monomer concentration, the concentrations of ABS and BPO are fixed at 0.125 and 0.021 mol/L, respectively. By substituting these values into eq. (20), we obtain

$$R_p = 1.81 \times 10^{-2} \frac{A[M]^2}{(0.125B + [M])^2} \quad (24)$$

The computer simulation with experimental results (as shown in Table I) was performed using the ORIGIN software program, the results of which are shown in Figure 7. One obtains $A = 2.02 \times 10^{-4}$ s^{-1} and $B = 1.05$. That is to say, the ratio of the rate coefficient of the primary radical attacking the polymer to that of monomer molecule was 1.05.

By substituting ABS and BPO concentrations into eq. (23), we get

$$R_p = \frac{3.04 \times 10^{-3}\alpha[M]^2}{(0.145 + 0.125\beta)^2([M] + 0.125\gamma)} \times \left(1 - \frac{0.145[M]}{(0.145 + 0.125\beta)([M] + 0.125\gamma)}\right) \quad (25)$$

After running a computer simulation, one obtains $\alpha = 1.89 \times 10^{-4}$ s^{-1}, $\beta = 0.009$, and $\gamma = 1.05$. Because β is very small, $[I_2]^{0.5}$ and $[P]$ are of the same order of magnitude and the expression $([I_2]^{0.5} + \beta[P])$ in eq. (23) is approximately equal to $[I_2]^{0.5}$. Equation (23) can then be simplified to eq. (20), which confirms that the chain transfer to polymer is not important in the grafting of crotonic acid onto ABS and may be neglected.

When the concentration of monomer and BPO are fixed at 0.30 and 0.021 mol/L, respectively, the relationship between the rate of grafting with ABS concentration can be represented by the following equation, by substituting monomer concentration, BPO concentration, and A and B into eq. (20):

$$R_p = 2.63 \times 10^{-6} \frac{[P]}{(0.30 + 1.05[P])^2} \quad (26)$$

The results of simulation, shown in Figure 8, fit the experimental results well.

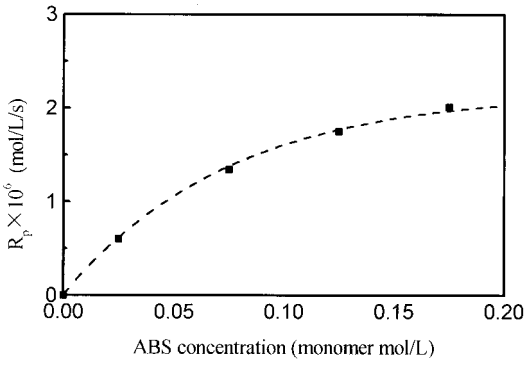

Figure 8 Initial rate of grafting versus ABS concentration: ■, experimental points; – – –, simulation results.

For the variation of the concentration of initiator, the initial rate of grafting should show a half-power dependency on initiator concentration [from eq. (20)] by substituting monomer concentration (0.30 mol/L), ABS concentration (0.125 mol/L), and A and B into eq. (20). The simulation consequence, shown in Figure 9, is in accordance with the experimental results.

CONCLUSIONS

One may successfully graft crotonic acid onto ABS by using BPO as initiator in solution. The graft occurs at the butadiene region of ABS. The graft reaction most likely takes place by cross-termination of poly(crotonic acid) radicals with macroradicals, which are formed by primary radicals attacking backbone. The ratio of the rate coefficient of the primary radical attacking polymer to that of monomer molecule was 1.05. The experimental results of initial rate of grafting polymerization and infrared analysis indicate that the proposed reaction mechanism is feasible.

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