

Grafting of Long-Chain Unsaturated Carboxylic Acids onto Acrylonitrile–Butadiene–Styrene Terpolymer

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Received 16 November 2000; accepted 13 January 2001

ABSTRACT: The graft copolymerization of undecylenic acid, oleic acid, and crotonic acid onto acrylonitrile–butadiene–styrene terpolymer (ABS) was initiated by benzoyl peroxide (BPO) in 1,2-dichloroethane solution. The infrared spectra confirmed that undecylenic acid, oleic acid, and crotonic acid were successfully grafted onto the ABS backbone. The grafting occurred at the butadiene region of the ABS. The grafting degree increased with increasing monomer concentration, but it decreased after monomer concentration, reaching 0.30 mol/L in undecylenic acid and oleic acid systems. The grafting degree increased rapidly with increasing initiator concentration, but slowed down at about 0.012 mol/L of initiator concentration. The grafting degree decreased considerably with increasing ABS concentration; however, the total amount of grafted monomer increased. Increasing reaction time and temperature led to an increase in grafting degree. The chain length of the monomer has a great influence on grafting. The grafting degree decreases with increasing the chain length due to a steric hindrance and monomer cage effect, which is in agreement with activation energy calculation. The overall activation energy of crotonic acid, undecylenic acid, and oleic acid systems are 118, 122, and 134 kJ/mol, respectively. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1934–1939, 2002

Key words: functionalization of polymers; modification; resins; ABS; long chain carboxylic acid

INTRODUCTION

The acrylonitrile–butadiene–styrene terpolymer is a good example of the combination of rigidity of plastics and elasticity of rubber. It is widely used nowadays in mobile industry, consumer products, etc. Several reports have recently appeared on the subject of the grafting of vinyl monomers onto ABS with various methods. Abdel-Razik et al.^{1,2} investigated the photoinduced graft copolymerization of acrylamide onto ABS in chloroform in

the presence of benzophenone or 4-acetyldiphenyl. Irradiation of benzophenone or 4-acetyldiphenyl produces a radical that abstracts an allylic hydrogen and/or adds to the double bond of the butadiene portion of the polymer to generate the radical site for grafting. Wilkie et al.^{3–6} have reported the graft copolymerization of acrylic acid onto ABS by using both BPO and azobisisobutyronitrile (AIBN) as initiators; they also studied the grafting of methacrylic acid, acrylamide, and acrylic acid onto ABS from an aqueous solution, which was initiated by the thermal decomposition of polymeric hydroperoxides formed from UV irradiation of ABS containing anthracene. They found that the thermal degradation property of ABS grafted with methacrylic acid, which was

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Contract grant sponsor: Ministry of Education.

Journal of Applied Polymer Science, Vol. 83, 1934–1939 (2002)
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DOI 10.1002/app.10089

turned to sodium salt, was improved greatly by forming an adherent coating of the sodium salt of methacrylic acid on the surface of ABS, but this result was not observed in the acrylic acid system.

Maleic anhydride is another important monomer for ABS grafting. Carrot et al.⁷ and Rao et al.⁸ carried out the grafting of maleic anhydride onto ABS in a molten state and in solution, respectively. Rodriguez-Gonzalez et al.⁹ also studied the grafting of maleic anhydride onto ABS in a Brabender mixing chamber, and they found that FTIR spectroscopy, potentiometry, and elemental analysis were all reasonable methods to determine the grafting degree of graft copolymer. The maleic anhydride modified ABS was mainly used in polymer blends such as ABS/Nylon,^{10,11} ABS/Polycarbonate,^{12,13} and ABS/Poly(ethylene terephthalate).¹⁴ The mechanical properties of maleated ABS blends were better than that of unmodified ABS blends due to the compatibilization of the modified ABS.

Long-chain unsaturated carboxylic acid, such as undecylenic acid and oleic acid, has rarely been found to be used as a graft monomer in published articles so far. In this work, undecylenic acid, oleic acid, and crotonic acid were grafted onto ABS in solution using BPO as initiator. The effects of various factors such as monomer chain length and concentration, initiator concentration and type, ABS concentration, reaction time, and reaction temperature on the grafting degree were discussed.

EXPERIMENTAL

Material

The ABS used in this study was a product of Taiwan Qimei Co. Ltd. ($M_n = 49,000$, $M_w = 134,000$, $M_w/M_n = 2.72$, containing 2.7 wt % additives, 22.4 wt % acrylonitrile, 13.5 wt % butadiene, and 61.4 wt % styrene, as determined by elementary analysis and the solvent separation method). BPO was a product of the Shanghai Zhongli Chemical Factory, it 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 using. Undecylenic acid, oleic acid, crotonic acid, 1,2-dichloroethane, ethanol, acetone, and cyclohexane were obtained from Shanghai Chemical Reagent Company, and used as received without further purification.

Graft Copolymerization

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, precise amount of ABS (2.50 g) was dissolved in 50 mL 1,2-dichloroethane in the reaction vessel with constant stirring. Desired amounts of monomer and BPO were added when the resin was completely dissolved, then the vessel was put into a water bath, which was already adjusted to the desired reaction temperature. The reaction proceeded under N_2 . The reaction mixture was poured into 10-fold volume of ethanol under vigorous stirring after the reaction was deemed complete, followed by drying of the precipitated polymer. The precipitated polymer was purified by dissolving in 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.

Characterization

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

Determination of Grafting degree and Grafted Monomer

The grafting degree and grafted monomer were determined by a back titration procedure. A 0.15-g sample was dissolved in 50 mL acetone, and then 10 mL of a 0.1 mol/L sodium hydroxide (NaOH) ethanol solution was added. The solution was refluxed for 30 min with stirring to assure that the grafted acid completely reacted with NaOH. The surplus NaOH was back-titrated with 0.1 mol/L hydrochloric acid (HCl) using methyl red as an indicator. A control sample of pure ABS undergoing exactly the same back-titration procedure was used.

To compare the grafting information of three monomers, the grafting degree (GD) was defined as the molar amount of monomer grafted per weight of ABS and calculated by:

$$\text{GD (mol/g)} = \frac{(V_0 - V_1) \times 10^{-3} \times C}{W - (V_0 - V_1) \times 10^{-3} \times C \times M} \quad (1)$$

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

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

$$G \text{ (mol/l)} = \frac{(V_0 - V_1) \times 10^{-3} \times C \times W_0}{W} \times \frac{1000}{V} \quad (2)$$

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

Phase Separation of ABS and Grafted ABS

To obtain further information of grafted ABS, it was separated into three fractions by using the solvent fractionation method similar to Gesner's.¹⁵ Pure ABS was first dissolved in 1,2-dichloroethane and precipitated in ethanol to get fine powder polymer. A 1.0 g of the fine powder of ABS or grafted ABS 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 a fume hood under a nitrogen purge. The residue was weighed, redissolved in cyclohexane, and smeared on a KBr salt plate for FTIR analysis. The cyclohexane-insoluble material was

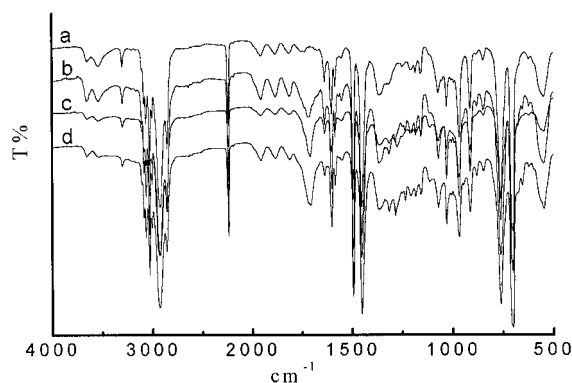


Figure 1 Infrared spectra of ABS and grafted ABS. (a) ABS; (b) ABS-*g*-oleic acid; (c) ABS-*g*-undecylenic acid; (d) ABS-*g*-crotonic acid.

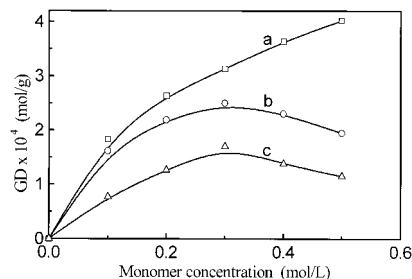


Figure 2 Effect of monomer concentration on grafting degree: ([BPO] = 0.021 mol/L, [ABS] = 50 g/L, t = 5 h, T = 84°C). (a) Crotonic acid; (b) undecylenic acid; (c) oleic acid.

stirred in 200 mL cold acetone for 2 h, 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.

RESULTS AND DISCUSSION

Evidence of Grafting

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

Effect of Monomer Concentration

The effects of monomer concentration on the grafting degree are shown in Figure 2. The grafting degree increases with increasing monomer concentration, but it decreases when monomer concentration is higher than 0.30 mol/L in undecylenic acid and oleic acid systems. Increasing

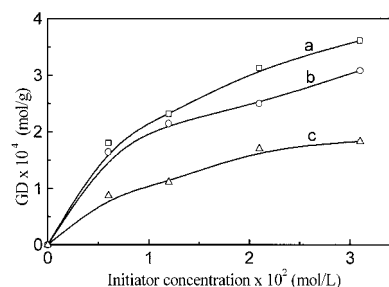


Figure 3 Effect of initiator concentration on grafting degree: ([M] = 0.30 mol/L, [ABS] = 50 g/L, t = 5 h, T = 84°C). (a) Crotonic acid; (b) undecylenic acid; (c) oleic acid.

Table I Effect of Initiator Type on Grafting Degree

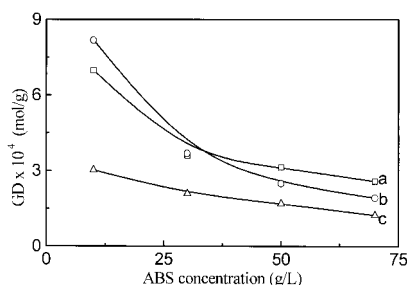
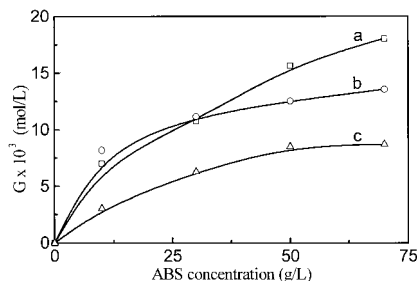
Monomer	Grafting Degree $\times 10^4$ mol/g	
	BPO	AIBN
Undecylenic acid	2.50	2.20
Crotonic acid	3.13	0.63
Oleic acid	1.70	0.04

monomer concentration increases the chance of monomer to react with the backbone; therefore, the grafting degree increases. The decrease of grafting degree in undecylenic acid and oleic acid systems at high monomer concentrations could be due to the monomer cage effects as a result of a long molecular chain of the monomers. The monomer cage effect is generally proportional to the monomer concentration.¹⁶

It can also be observed from Figure 2 that the grafting degree decreases with increasing the chain length of the monomer; this may probably be a result of high steric hindrance and monomer cage effects in the long-chain monomers.

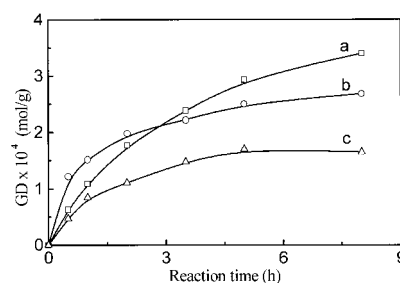
Effect of Initiator Concentration and Type

Figure 3 shows the effect of the initiator concentration on the grafting degree. Grafting did not take place to a significant amount in the absence of the initiator under nitrogen. The grafting degree increases rapidly initially with increasing the initiator concentration, then slows down at about 0.012 mol/L of the initiator concentration. With increasing the initiator concentration, increasing the amount of primary radicals are generated; the chance of monomer grafting onto ABS

**Figure 4** Effect of ABS concentration on grafting degree: ($[M] = 0.30$ mol/L, $[BPO] = 0.021$ mol/L, $t = 5$ h, $T = 84^\circ\text{C}$). (a) Crotonic acid; (b) undecylenic acid; (c) oleic acid.**Figure 5** Effect of ABS concentration on grafted monomer: ($[M] = 0.30$ mol/L, $[BPO] = 0.021$ mol/L, $t = 5$ h, $T = 84^\circ\text{C}$). (a) Crotonic acid; (b) undecylenic acid; (c) oleic acid.

is also increased. However, at high initiator concentrations, a significant proportion of homopolymer radicals and/or backbone radicals may be terminated with primary radicals. Therefore, the grafting degree levels off at high initiator concentrations. Figure 3 also shows that the grafting degree decreases with increasing the chain length of the monomer.

The influence of AIBN on the grafting degree is shown in Table I. It is obvious that the results of the three monomers are very different. The grafting degree of undecylenic acid/AIBN/ABS system was close to that of the undecylenic acid/BPO/ABS system, and the grafting degree of the crotonic acid/AIBN/ABS system was much lower than that of the crotonic acid/BPO/ABS system. In the oleic acid/AIBN/ABS system, no significant amount of grafting was obtained. This phenomenon may be due to different reactivities of primary radicals coming from the decomposition of BPO or AIBN and different reaction mechanisms involved in these three monomer reaction systems, which will be discussed in our other articles.

**Figure 6** Effect of reaction time on grafting degree: ($[M] = 0.30$ mol/L, $[BPO] = 0.021$ mol/L, $[ABS] = 50$ g/L, $T = 84^\circ\text{C}$). (a) Crotonic acid; (b) undecylenic acid; (c) oleic acid.

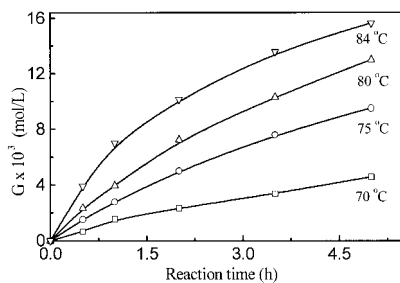


Figure 7 Effect of reaction temperature on the grafting of crotonic acid onto ABS: ($[M] = 0.30$ mol/L, $[BPO] = 0.021$ mol/L, $[ABS] = 50$ g/L).

Effect of ABS Concentration

Figure 4 illustrates the influence of ABS concentration on the grafting degree. The grafting degree decreases considerably with increasing the ABS concentration. However, the total grafted monomer was calculated according to eq. (2) increases with increasing the ABS concentration (Fig. 5). This is due to competition of grafting on ABS at a fixed level of monomer concentration.

Effect of Reaction Time

The effect of reaction time on grafting degree is shown in Figure 6. The grafting degree increases rapidly at first, then levels off with reaction time in undecylenic acid and oleic acid systems, whereas it increases steadily in the crotonic acid system. This may be due to the relatively low steric hindrance in the crotonic acid monomer as a result of the short chain length.

Effect of Reaction Temperature

To investigate the influence of reaction temperature on graft reaction, about 5 mL of reaction mixture was withdrawn according to certain re-

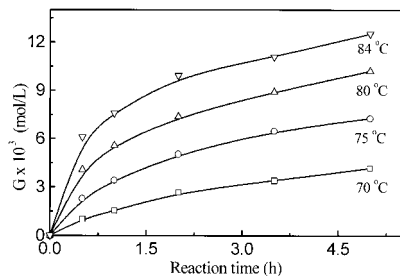


Figure 8 Effect of reaction temperature on the grafting of undecylenic acid onto ABS: ($[M] = 0.30$ mol/L, $[BPO] = 0.021$ mol/L, $[ABS] = 50$ g/L).

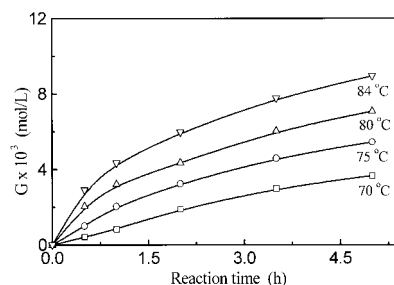


Figure 9 Effect of reaction temperature on the grafting of oleic acid onto ABS: ($[M] = 0.30$ mol/L, $[BPO] = 0.021$ mol/L, $[ABS] = 50$ g/L).

action times during the grafting. The mixture was precipitated and purified by the method described previously. The results are shown in Figures 7–9. A rapid increase in the extent of grafting is observed with increasing temperature due to increasing the rate of initiator decomposition.

The initial rates of graft copolymerization (R_p) of the three monomer systems are obtained from the slope of respective curves in the initial period of the reaction. From the Arrhenius¹⁷ plot of $\log R_p$ vs. $1/T$ (Fig. 10) the overall activation energy of crotonic acid, undecylenic acid, and oleic acid systems are computed to be 118, 122, and 134 kJ/mol, respectively. The activation energy increases with increasing the chain length of the monomer.

Site of Grafting

The grafted ABS was separated into three fractions by using the solvent fractionation method. The infrared spectra of three fractions of ABS-g-crotonic acid ($GD = 3.13 \times 10^{-4}$ mol/g) from solvent separation are shown in Figure 11. This indicated that the cyclohexane-soluble fraction was free PB and/or free PB-grafted with crotonic acid, the cyclohexane-insoluble but acetone-soluble fraction was a styrene-acrylonitrile copolymer

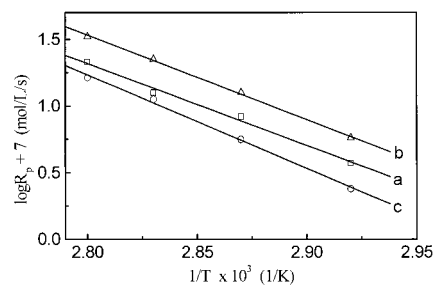


Figure 10 Arrhenius plot of $\log R_p$ vs. $1/T$. (a) Crotonic acid; (b) undecylenic acid; (c) oleic acid.

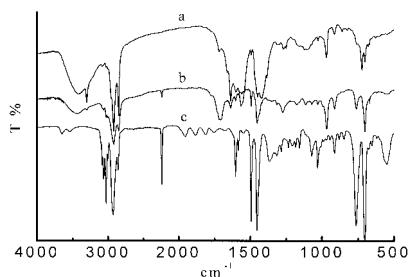


Figure 11 Infrared spectra of three fractions of ABS-*g*-crotonic acid. (a) Cyclohexane soluble fraction; (b) acetone insoluble fraction; (c) cyclohexane insoluble acetone soluble fraction.

(SAN), and the acetone-insoluble fraction was a graft copolymer and/or crosslinked PB. As shown in Figure 11, no crotonic acid was grafted onto SAN, but grafting did occur in cyclohexane-soluble and acetone-insoluble fractions. Therefore, the grafting most probably takes place in the butadiene region of ABS. This result is in accordance with Chandrasiri's reports.³ The infrared spectra of three fractions of ABS-*g*-undecylenic acid and ABS-*g*-oleic acid are almost the same as Figure 11, and are omitted here.

CONCLUSION

It is successful to graft undecylenic acid, oleic acid, and crotonic acid onto ABS by using BPO as an initiator in solution. The grafting occurs at the butadiene region of ABS. Monomer concentration, initiator concentration, ABS concentration, reaction time, and reaction temperature have considerable influences on the grafting degree. The chain length of the monomer has a great influence on the grafting. The grafting degree decreases with increasing the chain length due to steric hindrance and the monomer cage effect, which is in agreement with the activation energy calculation. The overall activation energy of crotonic

acid, undecylenic acid, and oleic acid systems are 118, 122, and 134 kJ/mol, respectively.

The authors would like to acknowledge the Ministry of Education for its financial support.

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