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RADIATION-INDUCED GRAFTING OF 2,3-EPOXYPROPYL METHACRYLATE ON POLYPROPYLENE FABRIC, AND AMINATION ONTO THE COPOLYMERS

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ABSTRACT

The grafting of 2,3-epoxypropyl methacrylate on polypropylene fabric was carried out by the γ-ray preirradiation grafting technique. The grafting extent was found to be dependent on the storage condition of the irradiated polypropylene fabric, the preirradiation dose, the reaction time and temperature, and the addition of solvent. 2,3-Epoxypropyl methacrylate-grafted polypropylene fabric was reacted with ammonia and various types of amines for different reaction times and temperatures. The amination extent followed the order dimethyl amine, trimethyl amine > methyl amine > ammonia.

INTRODUCTION

It is known that free radicals created by irradiation in a solid polymer may be immobilized and remain trapped for a considerable length of time [1]. In the preirradiation process the polymeric material is irradiated, and subsequently the deaerated monomer is contacted with the irradiated polymer. Grafting is induced by macroradicals trapped in the irradiated polymer. Preirradiation of the polymer produces relatively stable trapped free radicals [2, 3]. Virtually little homopolymer is produced by this method, and there is no limitation to any particular polymer/monomer combination since the monomer itself is not irradiated. Although the method has been successfully used for grafting various vinyl monomers onto polypropylene [4, 5], the grafting yield obtained by this method depends on the efficiency of trapped radicals.

The main factor governing the trapping of radicals is the physical state of the irradiated polymer. In the case of rubbery and noncrystalline polymers, the mobility of radicals is fairly significant, and their survival time after irradiation is not long compared to polymers having high crystallinity. The usefulness of the grafting method depends largely on the crystallinity of the polymer, the relative reaction rates of monomer with trapped radicals, and the thermal decay of radicals at the temperature required for grafting [6]. If initiating radicals are quickly depleted by decay at an elevated temperature, the efficiency of the grafting is impaired. The preirradiation technique has been extensively applied to some crystalline polymer. There are very few studies of preirradiation grafting of 2,3-epoxypropyl methacrylate (EPMA) onto polypropylene fabric. Graft polymerization of EPMA onto polymer substrates is attractive because the epoxy group of EPMA reacts to impart some desirable functions, such as ion exchange and the adsorption of toxic gases, without having much effect on the original properties. For this study, attempts were made to graft EPMA onto polypropylene fabric and to introduce various amine groups onto the EPMA-grafted polypropylene fabric.

EXPERIMENTAL

Material

Commercial polypropylene fabrics of 140 g/m^2 (Chonbang Industries Co.) were used as a substrate for graft polymerization. EPMA (Merck) was used without further treatment. Other chemicals were reagent grade.

Irradiation

γ-Ray irradiation from Co-60 was carried out at an exposure rate of 6.2×10^3 Gy/h in air.

Grafting Procedure

The grafting experiments were performed in glass ampules with a cock. The solvent was added first, followed by monomer to a total volume of 50 mL. The irradiated fabric (3 × 5 cm) was immersed in the monomer solution and purged by bubbling nitrogen for 20 minutes. The grafting reaction was carried out by placing the ampules in a water bath set at the relevant temperature. After completion of the grafting reaction the grafted fabrics were removed from the monomer solution in the glass ampule and extracted with tetrahydrofuran to remove the attached homopolymer. The amount of homopolymer was calculated by evaporating most of unreacted monomer in a fume-hood and then in a vacuum oven at 50°C until constant weight was reached. The degree of grafting (%) was determined by

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where W_g and W_0 are the weights of the grafted and the ungrafted fabric, respectively.

Homopolymer content (%) and grafting efficiency (%) were estimated by

$$\text{Homopolymer (\%)} = \frac{W_h}{W_m} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{W_g}{W_g + W_h} \times 100$$

where W_h and W_m are the weights of homopolymer and monomer, respectively.

Amination Procedure

EPMA-grafted polypropylene fabric was reacted with ammonia and various amines in 20 mL glass ampules at various temperatures and times. All the amines in this experiment were used as 30% aqueous solutions.

RESULTS AND DISCUSSION

Graft polymerization can be carried out by ionization radiation, UV, plasmas, or chemical initiators. Of these techniques, radiation-induced grafting is one of the most effective methods because of the uniform creation of radical sites in the polymer matrix. The grafting reaction in this experiment was carried out by means of a preirradiation technique in which the substrate polymer of polypropylene fabric was preirradiated with γ-rays in air. When polypropylene is irradiated by γ-ray in air, the following radical reactions take place.

$$R\sim\sim\sim\sim \longrightarrow R\cdot \tag{1}$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \tag{2}$$

$$RO_2\cdot + RH \longrightarrow ROOH + R\cdot \tag{3}$$

$$RO_2\cdot + RO_2\cdot \longrightarrow ROOR + O_2 \tag{4}$$

$$R\cdot + R\cdot \longrightarrow R{-}R \tag{5}$$

In these schemes, R represents the polypropylene chain and R· represents the radicals produced by irradiation. It is known that free radicals created by irradiation in solid polymers are immobilized and may remain trapped for a considerable length of time. The major factor governing the trapping of radicals is the physical state of the irradiated polymer.

The lifetime of the trapped free radical depends on the temperature of storage because it can affect the mobility of polymer radicals. The relation between grafting reaction and the storage time and storage temperature is important from the viewpoint of practical application.

The polypropylene fabrics were stored at various storage conditions for a certain time immediately after irradiation. Figure 1 shows the effect of storage temperature and time on the grafting of 2,3-epoxypropyl methacrylate onto polypropylene fabric preirradiated to a total dose of 50 kGy. The grafting yield in the irradiated polypropylene fabric stored at room temperature was found to decrease rapidly with storage time. On the other hand, the grafting yield at storage temperatures ranging from −20 to −78°C remained nearly constant up to 135 hours, then decreased slightly up to 360 hours. There was no significant difference between storage temperatures of −20 and −78°C up to 135 hours of storage time, with a little low grafting yield at −20°C compared with −78°C. The reason why a large grafting yield was attained even after 360 hours of storage at −20 and −78°C can be attributed to the decrease in termination of free radicals (Eq. 5) which comes from the high crystallinity of polypropylene and the restriction of chain segmental motion at low temperatures. Termination of various active sites increases with increasing storage temperature of irradiated polymer. The grafting efficiency and extent of homopolymer were evaluated in this experiment. The amount of homopolymer was extremely low in all experimental conditions. As shown in Table 1, the amount of homopolymer was only 0.06% at an irradiation dose of 50 kGy and a reaction temperature of 70°C.

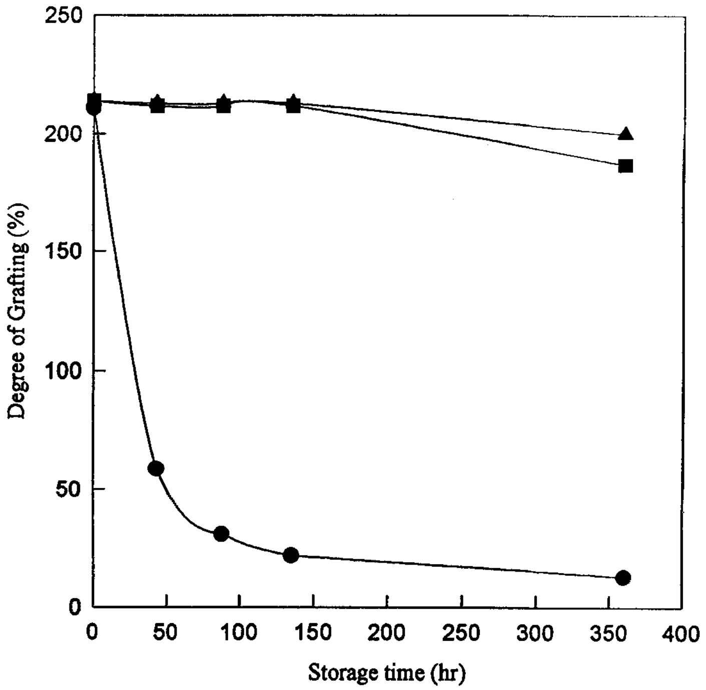


FIG. 1. Effect of storage temperature and time on the grafting of EPMA onto polypropylene fabric preirradiated to a total dose of 50 kGy. Grafting reaction: 70°C for 3 hours. (●) Room temperature, (■) −20°C, (▲) −78°C.

TABLE 1. Grafting of 2,3-Epoxypropyl Methacrylate onto Polypropylene Fabric[a]

Irradiation dose, kGy	Graft, %	Homopolymer, %	Grafting efficiency, %
30	183	0.05	99.97
40	253	0.05	99.98
50	353	0.06	99.98

[a] Reaction temperature 70°C, reaction time 300 minutes.

The reaction temperature is one of the important factors to control the grafting. As shown in Figure 2, the grafting yield at 70°C was much higher than that at 50°C, with being much lower grafting yield in 30°C.

Most of the grafting reaction, at particularly low reaction temperature can be attributable to the trapped radicals of Eq. (1). On the other hand, it is possible that the reactive sites on the backbone polymer can be generated by the decomposition of hydroperoxide (Eq. 3) or diperoxide (Eq. 4) at high temperature, leading to the grafting reaction.

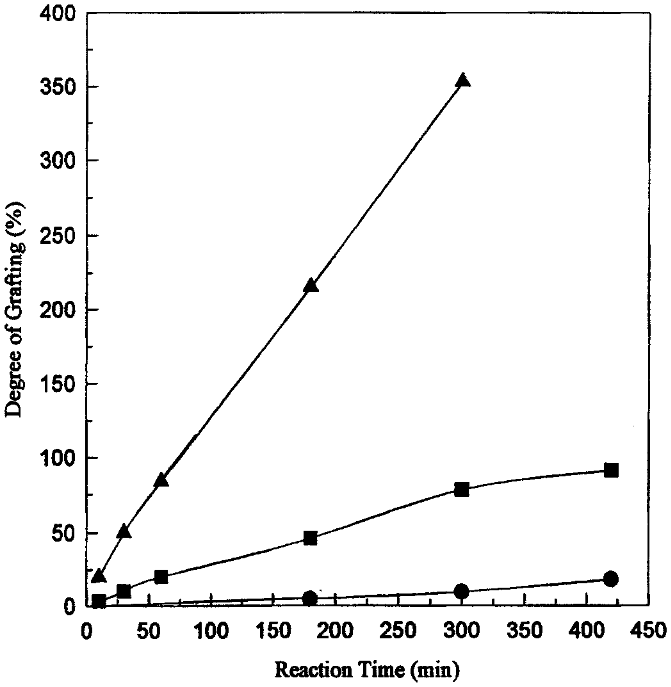


FIG. 2. Effect of reaction temperature on the grafting of EPMA onto polypropylene fabric irradiated to a total dose of 50 kGy. Grafting time: 3 hours. (●) 30°C, (■) 50°C, (▲) 70°C.

Based on the data in Fig. 2, logarithmic plots of the grafting rate against the reciprocal temperature are shown in Fig. 3. The increase in grafting rate with temperature follows the Arrhenius relationship:

$$\text{Log } K = \log A - \frac{E_a}{2.3RT}$$

where K is the reaction rate, A is a temperature-independent constant, E_a is the activation energy, R is Boltzmann's constant, and T is the absolute temperature. Based on the slopes of the Arrhenius plots, the activation energy of grafting was 21.8 kcal/mol. This value is apparently too high for a reaction of free radicals with vinyl monomer. Therefore, the high apparent activation energy may mainly be due to a monomer diffusion process.

Figure 4 shows the effect of reaction time and irradiation dose on the grafting of EPMA onto polypropylene fabric at a reaction temperature of 70°C. The grafting yield was found to increase with increasing irradiation dose and reaction time.

The role of solvents is one of the most important variables which influences the grafting yield. It is known that those components in a grafting solution which wet and swell the polymer substrate assist the grafting reaction. In order for grafting in a grafting solution to be effective, the preirradiated polymer must be in contact with a homogeneous solution. Therefore, first property of the solvent chosen should be that it will disolve the monomer. The effect of EPMA concentration in the solvent on grafting yield is shown in Fig. 5. Methanol and tetrahydrofuran were

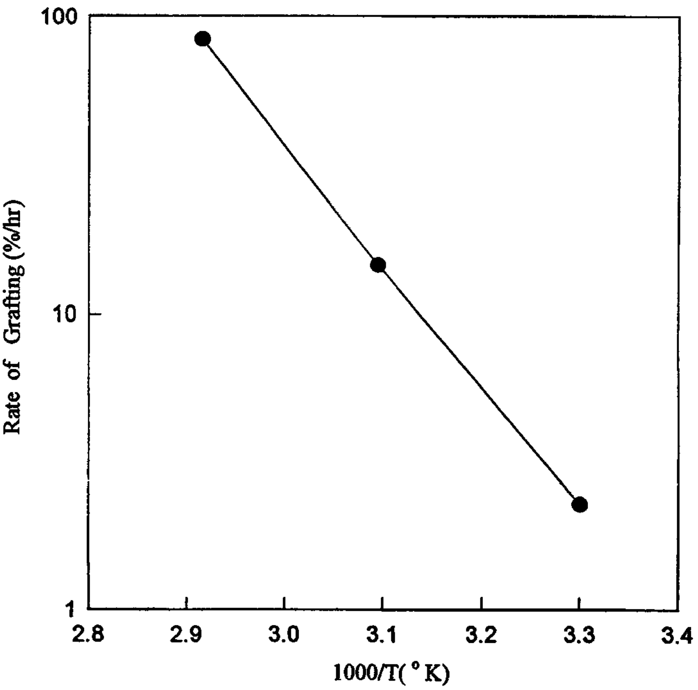


FIG. 3. Logarithmic plots of rate vs reciprocal of grafting temperature. Grafting conditions are the same as in Fig. 2.

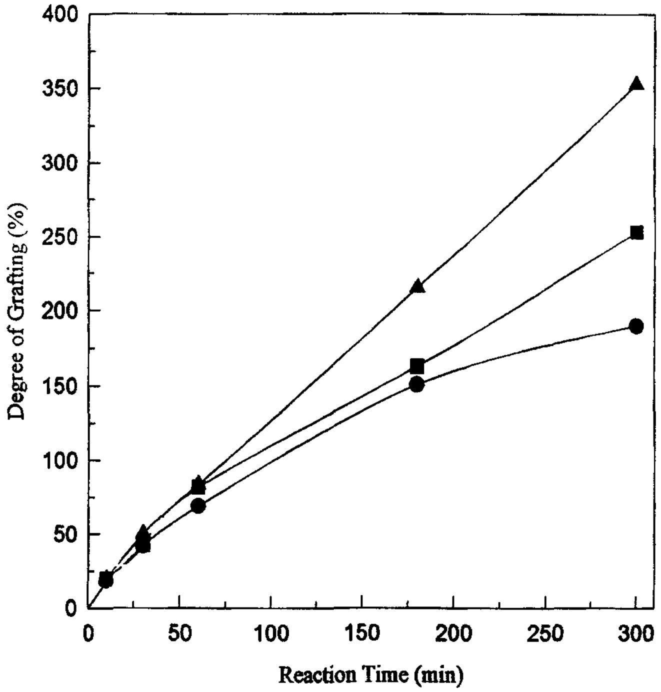
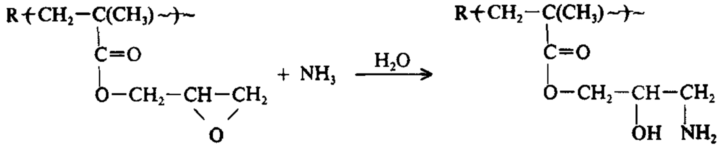


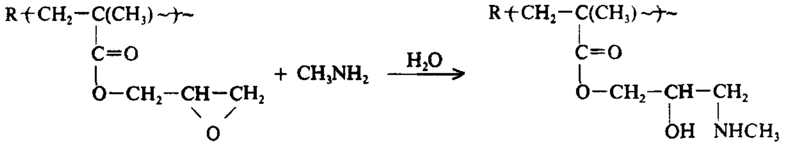
FIG. 4. Effect of reaction time and irradiation dose on the grafting of EPMA onto preirradiated polypropylene fabric. Grafting temperature: 70°C. (●) 30 kGy, (■) 40 kGy, (△) 50 kGy.

used as grafting solvents. A significant difference between the two solvents was not observed in the grafting reaction. The maximum grafting yield was observed around 60% monomer concentration, presumably due to a Trommsdorff-type effect [7, 8]. The pronounced maximum at a certain concentration of monomer can also be explained partially by an increased rate of swelling of the grafted layer in a reaction medium of this composition [9].

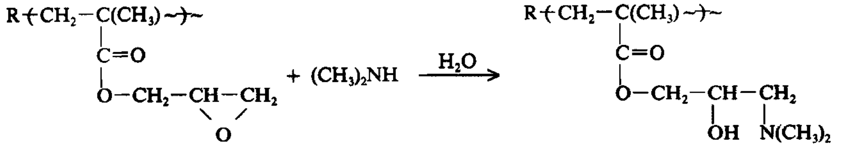
It is known that epoxide reacts with ammonia and amines in aqueous solution. EPMA-grafted polypropylene fabric was reacted with ammonia, methyl amine, dimethyl amine, and trimethyl amine at given temperatures. Their reactions are described in Eqs. (6), (7), (8), and (9).



(6)

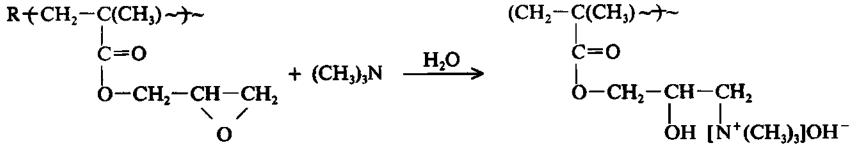


(7)



$$R\text{+}CH_2-C(CH_3)\text{+}\sim(C{=}O)(O-CH_2-CH-CH_2,\ \text{epoxide }O) + (CH_3)_2NH \xrightarrow{H_2O} R\text{+}CH_2-C(CH_3)\text{+}\sim(C{=}O)(O-CH_2-CH(OH)-CH_2N(CH_3)_2)$$

(8)



$$R\text{+}CH_2-C(CH_3)\text{+}\sim(C{=}O)(O-CH_2-CH-CH_2,\ \text{epoxide }O) + (CH_3)_3N \xrightarrow{H_2O} (CH_2-C(CH_3)\text{+}\sim(C{=}O)(O-CH_2-CH(OH)-CH_2[N^+(CH_3)_3]OH^-)$$

(9)

Figure 6 shows the extent of amination (mmol/g) of EPMA-grafted polypropylene fabric with ammonia and the different types of amines at 50°C. It was shown that reactions of methyl amine, dimethyl amine, and trimethyl amine initially proceed rapidly and then level off. On the other hand, the reaction of ammonia did not occur for 30 minutes and after the proceeded slowly. The amination extent followed the order dimethyl amine, trimethyl amine > methyl amine > ammonia. The difference of reactivity between epoxide and amines can be attributable to the different rate of solubilities, ionization constants, and side reactions such as crosslinking. Figure 7 shows the extent of amination of EPMA-grafted polypropylene fabric with various amines at 70°C. Amination of trimethyl amine proceeded rapidly initially, and then decreased continuously with increasing reaction time.

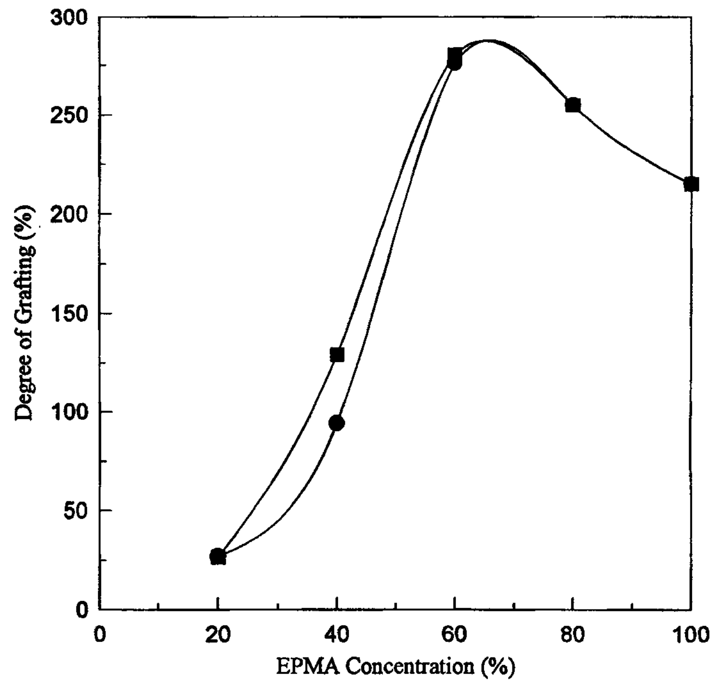


FIG. 5. Effect of EPMA concentration in solvents on the grafting of EPMA onto polypropylene fabric preirradiated to 50 kGy. Grafting reaction: 70°C for 3 hours. (●) Methanol, (■) tetrahydrofuran.

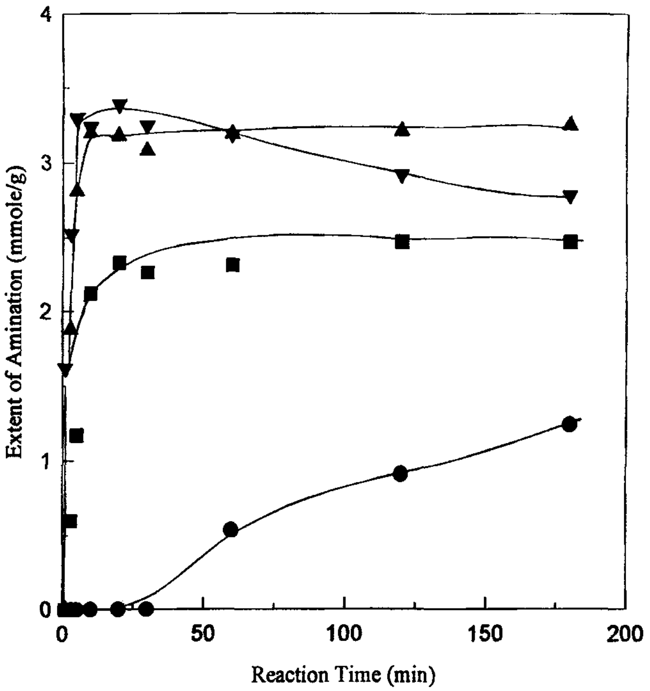


FIG. 6. Extent of amination of EPMA-grafted polypropylene fabric with 30% amine solutions at 50°C. (●) Ammonia, (■) methyl amine, (▲) dimethyl amine, (▼) trimethyl amine.

From these results it is assumed that tetramethyl ammonium (quaternary ammonium compounds) formed from amination of trimethyl amine onto EPMA-grafted polypropylene is sensitive at high temperatures and is easily decomposed. It is well known that quaternary ammonium in a polystyrene-based anion ion exchanger is relatively weak at high temperatures compared with a strong cation ion exchanger. The induction time of the reaction of ammonia with EPMA-grafted polypropylene at 70°C was shortened, and the extent of amination was high compared with that at 50°C. These characteristics were profound at a reaction temperature of 85°C (Fig. 8).

Ethyl amine, diethyl amine, and triethyl amine were reacted with EPMA-grafted polypropylene fabric in 30% amine solution at 50°C (Fig. 9). The extent of amination of triethyl amine was lower than those of ethyl amine and diethyl amine. The extent of amination of triethyl amine was also lower than that of trimethyl amine, and the reaction time did not change at 85°C (Fig. 10). This phenomenon can be attributed to steric hinderance of triethyl amine which has a higher molecular weight than trimethyl amine.

CONCLUSIONS

Attempts were made in this study to graft 2,3-epoxypropyl methacrylate onto polypropylene fabric and to introduce various amine groups onto EPMA-grafted polypropylene fabric.

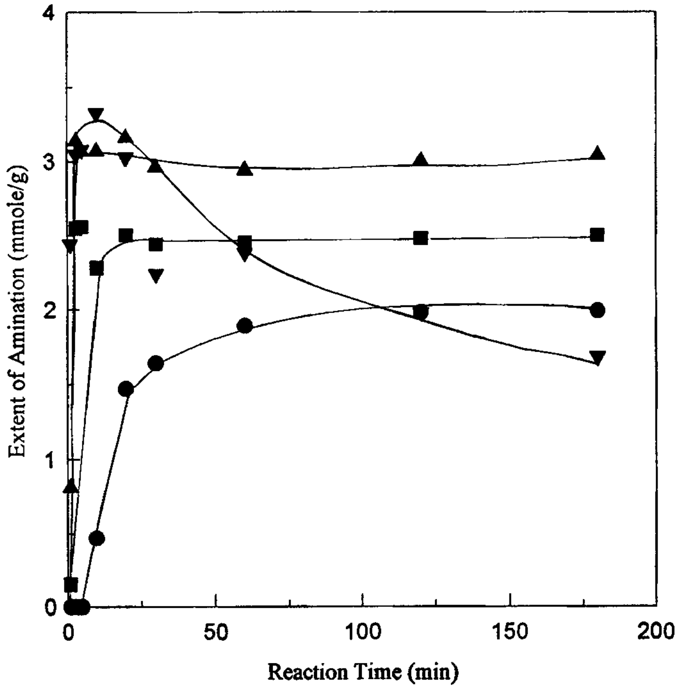


FIG. 7. Extent of amination of EPMA-grafted polypropylene fabric with 30% amine solutions at 70°C. (●) Ammonia, (■) methyl amine, (▲) dimethyl amine, (▼) trimethyl amine.

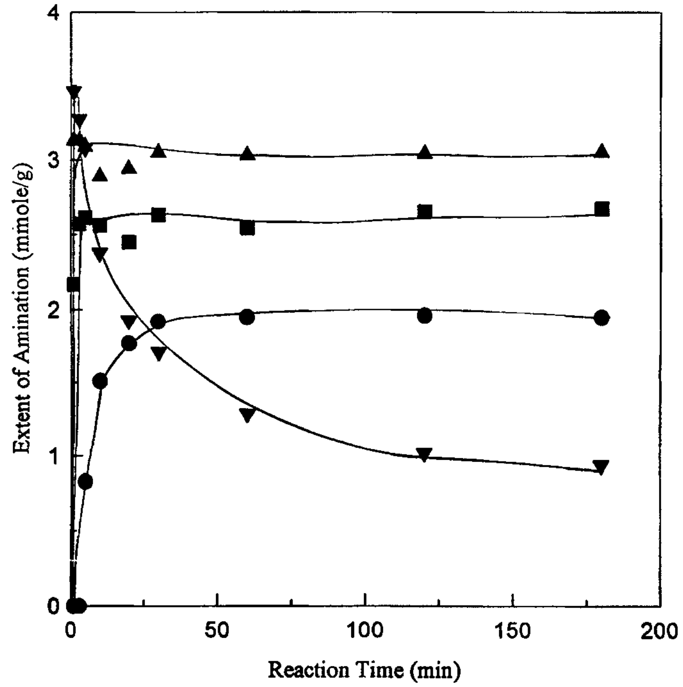


FIG. 8. Extent of amination of EPMA-grafted polypropylene fabric with 30% amine solutions at 85°C. (●) Ammonia, (■) methyl amine, (▲) dimethyl amine, (▼) trimethyl amine.

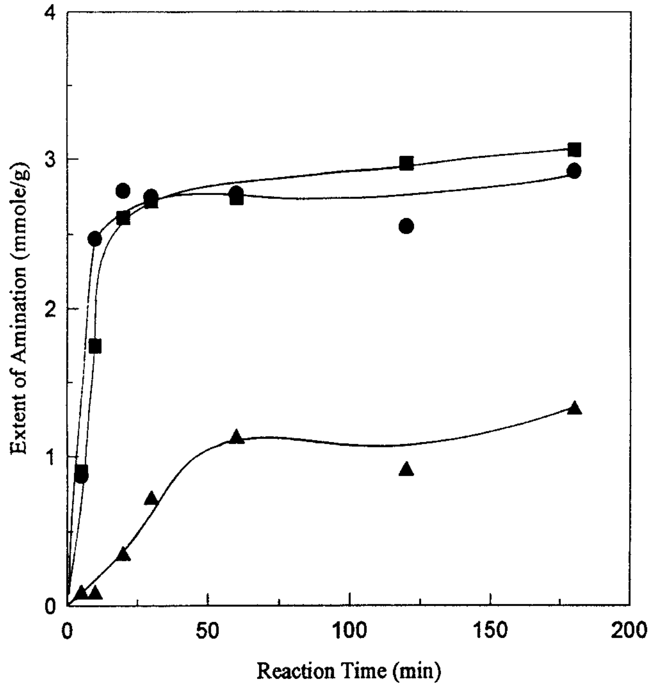


FIG. 9. Extent of amination of EPMA-grafted polypropylene fabric with 30% amine solutions at 50°C. (●) Ethyl amine, (■) diethyl amine, (▲) triethyl amine.

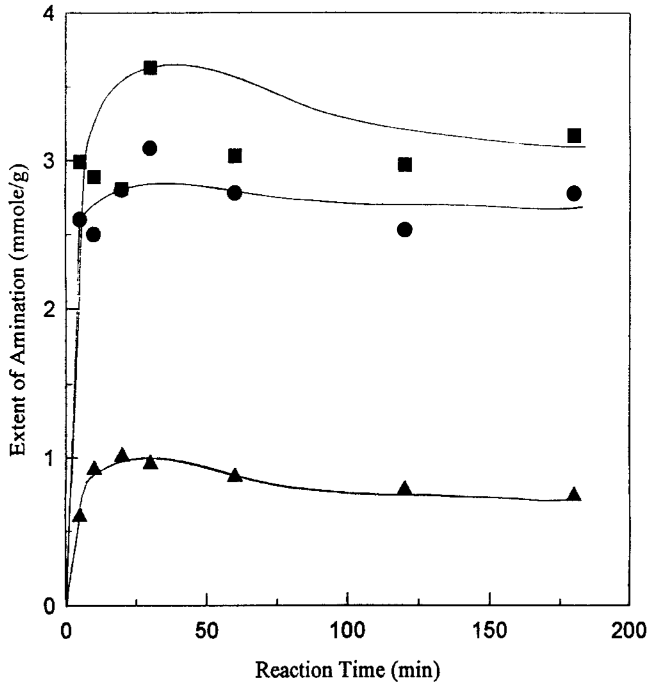


FIG. 10. Extent of amination of EPMA-grafted polypropylene fabric with 30% amine solutions at 85°C. (●) Ethyl amine, (■) diethyl amine, (▲) triethyl amine.

The polypropylene fabrics were stored under various storage conditions for a certain period time immediately after irradiation. The grafting yield in the irradiated polypropylene fabric stored at room temperature was found to decrease rapidly with storage time. On the other hand, the grafting yield for storage temperatures ranging from −20 to −78°C remain nearly constant up to 135 hours and then decreased slightly up to 360 hours. The activation energy of grafting was 21.8 kcal/mol based on logarithmic plots of the grafting rate against the reciprocal temperature.

Methanol and tetrahydrofuran were used as grafting solvents. The maximum grafting yield was observed around 60% monomer concentration.

Ammonia and various amines were reacted with EPMA-grafted polypropylene fabric. The amination extent followed the order dimethyl amine, trimethyl amine > methyl amine > ammonia.

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