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EFFECTS OF OXYGEN EXPOSURE ON PLASMA GRAFT POLYMERIZATION OF SOME HYDROPHILIC MONOMERS ONTO POLYPROPYLENE FILMS

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ABSTRACT

Graft polymerization of hydrophilic monomers was made onto O_2-exposed polypropylene films that had been previously treated by glow discharge plasma of Ar, and the influence of oxidation on the grafting was investigated. The grafting yield decreased with an increase of O_2 exposure time (~1000 minutes) when the reaction occurred at 60°C. The yield was very dependent on the reaction temperature, and the temperature for maximal grafting amounts of 2-hydroxyethyl methacrylate onto oxidized films was shifted to around 75°C. It was believed that the dissociation of peroxide group on substrate films took place effectively near this temperature. The oxidized substrates were also activated when the reaction was carried out in the presence of metal ions in their reduced state (e.g., Fe^{2+}). The generated oxiradicals should participate effectively in the initiation of graft polymerization.

INTRODUCTION

Graft polymerization of vinyl monomers onto a plasma-pretreated polymer is an effective procedure for the preparation of surface functional polymers. The advantage in plasma graft polymerization lies in the formation of regular chain polymers that are chemically bonded to substrates, and as a result, durable composite polymer materials can be produced. However, the control of grafting condition is not easy and so much care is necessary for the effective polymerization of monomers; i.e., the grafting yields are very dependent on the pretreatment and postpolymerization conditions as well as on the monomer reactivity. In spite of these difficulties, the products have some advantages in their characteristic structures and properties, various aspects of which have been applied. For example, applications previously investigated include pervaporation membranes for the separation of aqueous solvents [1-3], adsorbent materials of metal ions [4], substrate materials for enzyme immobilization [5], modified textile fibers [6-8], polymer materials containing cationic surfaces [9], and so forth.

We have recently applied the process to the preparation of composite membranes for pervaporation of water-ethanol separation by graft polymerization of hydrophilic monomers such as acrylic acid, acrylamide, 2-hydroxyethyl methacrylate, and so forth [1-3]. The process was employed for the purpose of improving the stability and durability of membranes. More effective separation was achieved with some composite membranes involving hydrophilic grafted polymers immobilized by chemical bonds to the substrates.

We carried out the entire graft polymerization process in vacuum for the effective grafting of monomers. However, grafting can be effective even after air exposure of the plasma-pretreated polymer substrates if the pretreatment and the graft polymerization are handled independently. In those cases the processing should be more convenient and easier.

When plasma-treated polymer substrates are exposed to air, the radicals react with O_2 and oxides are formed on the polymer surface. The state of radicals on plasma-treated polymer substrates has been extensively investigated using ESR by Kuzuya et al., and new peaks of the peroxy groups have been observed after air exposure [10-12]. Thus, radicals on plasma-activated polymer substrates are very reactive toward O_2, and this is the reason for the change in the initiation ability of graft polymerization. However, some reports have described the grafting process of monomers onto such air-exposed polymer substrates [13-20], and some researchers have insisted on the role of oxiradicals generated after contact to O_2 or air as the initiation sites for the graft polymerization of monomers.

In the present study the effects of O_2 exposure of plasma-pretreated polypropylene films on the grafting ability with some hydrophilic monomers were investigated because the influence of oxidation has not been hitherto studied extensively. For this purpose, Ar-plasma-pretreated substrates were exposed to O_2 at atmospheric pressure for up to 1000 minutes, and then the graft polymerization of monomers was again done in vacuum. The initiation ability of these oxidized polymer film surfaces was compared, and the effect of O_2 exposure time was investigated. The graft polymerization of monomers was carried out in vacuum by again evacuating the system. The inhibition effects of graft polymerization by O_2 were thus excluded by shutting out air during the polymerization process. (In fact, grafting did not proceed satisfactorily when the reaction was carried out in air.)

The yield on the O_2-exposed substrate films actually decreased with exposure time when the grafting of monomers was carried out in the lower temperature range. In order to increase the initiation ability, graft polymerization was done using 2-hydroxyethyl methacrylate at higher temperatures and in the presence of some metal ions in their reduced states. The mechanism of regeneration of grafting ability was considered from thermal dissociation of peroxy groups and through redox reactions by the metal ions.

EXPERIMENTAL

Materials

Monomers used in the present study were 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AA), acrylamide (AAm), and *N*-isopropyl acrylamide (NiPAAm). Liquid monomers, HEMA and AA, were purified by distillation under reduced pressure, and crystalline monomers, AAm and NiPAAm, were purified by recrystallization.

Metal salts such as $FeCl_2$, $FeCl_3$, $FeSO_4$, and ferrous ammonium sulfate were all of reagent grade and used as supplied.

Commercially available Celgard 2400 and 2500 films (Hoechst Celanese Co.) made of isotactic polypropylene were used for the substrates of graft polymerization [21]. (They are abbreviated PP-1 and PP-2, respectively.)

Procedure of Plasma Graft Polymerization

The method and apparatus for plasma graft polymerization were principally the same as described before [1-3].

Plasma was generated by an inductively coupled discharge using the radio frequency of 13.56 MHz. The substrate PP films (6 × 6 cm) were first treated with Ar-gas plasma (2.7 Pa, 10 W, 60 seconds) in a reactor made of Pyrex tubing (3.0-cm diameter, 24-cm length), and then O_2 at atmospheric pressure was introduced into the reactor. The inert plasma gas Ar was chosen to prevent the oxidative degradation of the substrate films. After leaving the films in O_2 at atmospheric pressure for a certain time period up to 1000 minutes, the reactor system was evacuated again and graft polymerization was done in vacuum using aqueous monomer solutions at 60°C for 4 hours unless otherwise noted. The concentration of a monomer was in the range of 1 to 5%, depending on the monomer reactivity.

After the finish of graft polymerization, the product films were soaked with water (for AA, AAm, and NiPAAm) or with ethanol (for HEMA) to wash off the unreacted monomers and homopolymers. Almost all the ungrafted portion could be removed by this washing procedure. The films were then dried in air and then in vacuum, and the grafting yield was evaluated by the weight increase of dried graft polymers.

The temperature dependence of graft polymerization of HEMA was investigated in the 40 to 80°C range. Graft polymerization was also done by mixing some metal salts in aqueous monomer solutions, and the effects on grafting yield were investigated.

RESULTS AND DISCUSSION

Effect of Oxygen Exposure on Graft Polymerization

Monomer Reactivity

The grafting yield was, of course, dependent on the starting monomer, and HEMA and NiPAAm are more graft polymerized in spite of having bulky side groups. AAM and AA were less graft polymerized in spite of their smaller steric hindrance. The order of reactivity was not changed on the substrate PP film even after oxidation. In general, HEMA was considerably graft polymerized in vacuum at a concentration of more than 2%, and the graft polymers formed penetrated into the inner layer of the PP film from the surface. As a result, deformation of substrate films resulted beyond a certain grafted amount.

By considering the graft polymerization of a monomer onto the surface of substrates to be by first-order kinetics, we obtained the rate constants of some monomers onto plasma-pretreated textile fabrics [22]. When the amount of homopolymer formed is very small, as in the case of the reaction of HEMA, the rate constant of graft polymerization (k_g) is obtained from the initial monomer concentration ($[M_0]$) and the grafted amount at the reaction time of t($[M_{gt}]$) as follows:

$$k_g = -\ln(1 - [M_{gt}]/[M_0])/t \qquad (1)$$

The rate constant of graft polymerization of HEMA onto plasma-pretreated PP films without contact with O_2 was estimated as 10^{-6} to 10^{-5} s^{-1}. The order of constants was comparable to that obtained onto plasma-pretreated textile fibers such as cotton [22].

For the smaller reactivities of AAm and AA, the competitive reactions between graft polymerization and homopolymerization must be taken into account. Aqueous solutions of AA and AAm gradually became viscous during the graft polymerization process, and the formation of homopolymers was suggested.

Plasma-pretreated PP films were exposed to O_2 at atmospheric pressure before graft polymerization under vacuum, and the effects of oxidation on the yield were next investigated. Figures 1 and 2 show the dependence of the yield of grafted polymers on O_2-exposure time up to 1000 minutes onto PP-1 and PP-2, respectively. The monomers were reacted at concentrations of 1% for HEMA, 3% for NiPAAm,

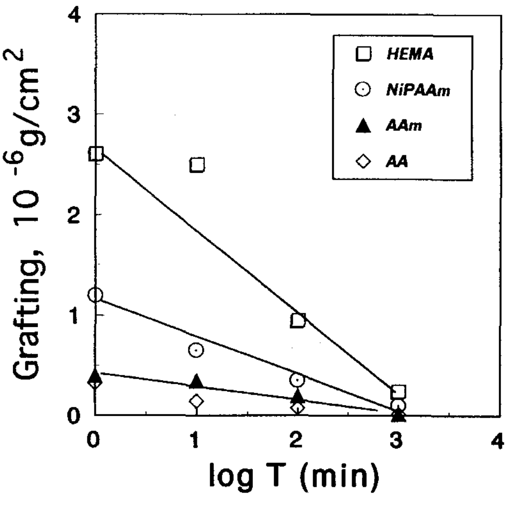

FIG. 1. Dependence of the grafting yield of HEMA (1%), NiPAAm (3%), AAm (5%), and AA (5%) onto Ar-plasma-treated PP-1 film on O_2-exposure time. Grafting conditions: 60°C for 4 hours.

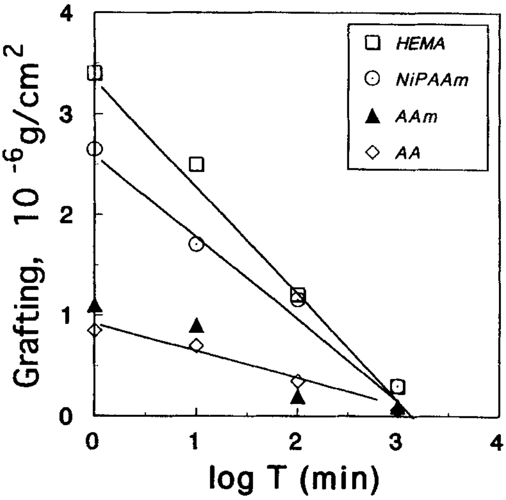

FIG. 2. Dependence of the grafting yield of HEMA (1%), NiPAAm (3%), AAm (5%), and AA (5%) onto Ar-plasma-treated PP-2 film on O_2-exposure time. Grafting conditions: 60°C for 4 hours.

and 5% for AAm and AA. In these figures the abscissa is expressed by the logarithmic value of O_2-exposure time. The monomer solutions were reacted at 60°C for 4 hours.

Analyses of the Decay

The grafting yields decreased with the time of O_2 exposure after plasma treatments under the grafting temperature conditions investigated here. The yield decreased exponentially in these monomers against the O_2-exposure time in general. From the results that the graft polymerization yield decreased reciprocally with the time of O_2-exposure (log T), the equation

$$a_T = -k \times \log T + a_0$$

was derived for a certain range of oxidation time. Here, a_T is the grafting amount at an oxidation time of T, k is a constant, and a_0 is the grafting amount at $\log T = 0$. This equation is somewhat similar to that proposed by Yasuda et al. for the surface mobility factor of modified polymers [23, 24].

The time for $a_T = {}^1/_2 a_0$ may be taken as a kind of half-life of deactivation of the initiation ability in graft polymerization by the oxidation of plasma-pretreated polymer substrates. The half-life period as obtained for these monomers was estimated to be 45–50 minutes for graft polymerization at 60°C, regardless of the type of monomer. It is thus suggested that the initiation ability is exclusively derived from a decrease in the active states on the substrates rather than the monomer reactivity.

Graft Polymerization onto the Substrates Kept in Vacuum

Figure 3 shows the graft polymerization yields of HEMA onto PP-2 films kept for a certain time in vacuum and in contact to O_2. Here again, polymerization grafting was compared for the same reaction conditions of a monomer. The grafting yield was maintained for plasma-treated substrates left in vacuum for 100 minutes but was drastically decreased after exposure to O_2.

Quite similar results of the maintenance of grafting yield were observed in the graft polymerization of NiPAAm. Thus, it was confirmed that the activity of plasma-treated polymers is maintained in vacuum. From these experimental results the deactivation of graft polymerization by oxidation under the critical temperature is suggested. However, when grafting was carried out at a higher temperature, the grafting yield increased again.

Substrate Effects

The polypropylene films (Celgard) used in the present work were highly oriented polymers with a microporous structure [21]. The difference in the grafting abilities onto PP-1 and PP-2 must also be noted. The present films were more graft polymerized by monomers than were flat polypropylene films and other types of polymer films in general. Why the grafting yields changed depending on the type of film cannot be explained at present, but it should be noted that the graft polymers were formed along the extended direction on the substrate Celgard films according to SEM observations [25]. The higher reactivity in graft polymerization may be ascribed in part to the physical structures.

Effect of Grafting Temperature

The effects of oxidation of the substrates films on the initiation ability of graft polymerization became clear from the above experimental results carried out at 60°C. In addition, the graft polymerization of HEMA was examined in the 40–80°C range and the temperature dependence was investigated.

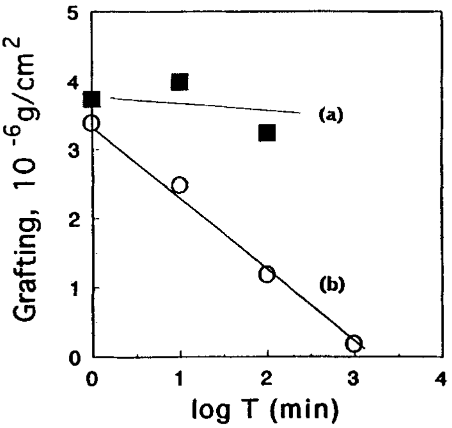

FIG. 3. Comparison of the grafting yield of HEMA (1%, 60°C, 4 hours) onto Ar-plasma-treated PP-2 film kept in vacuum (a) and exposed to O_2 (b).

Figure 4 shows the temperature dependence of the graft polymerization yield of HEMA (1%, 4 hours) under vacuum conditions onto PP-1 film exposed to O_2 for 100 minutes after Ar-plasma treatments. The results are compared with those without exposure to O_2 and also with those polymerized in the presence of Fe^{2+} at a concentration of 0.018 mol/L after O_2 exposure for 100 minutes. Here, a comparatively higher concentration of Fe^{2+} was employed to make sure the effects of metal ion on graft polymerization could be determined.

The maximal yields appeared around 65°C for plasma-treated PP-1 film without contact with O_2. Similar maxima of the amount of grafting have also been observed in other monomers such as acrylamide, and the yield decreased at a higher reaction temperature [26]. The decrease in grafting yield beyond a critical temperature was attributed to the deactivation of radicals.

It should be noted that the grafting yield was smaller at 60°C onto the O_2-exposed films but became greater again to reach a maximum at 75°C, or the maxima were shifted to the higher temperature after O_2-exposure. For the shift of the temperature for the maximal grafting yield of HEMA to 75°C, the following mechanism is proposed: Dissociation of the peroxide radicals (—O—O—) on the substrate films occurred, and the oxiradicals formed are quite effective for the initiation of graft polymerization. It is interesting to compare the maximum temperature of 75°C with the effective polymerization temperature using *t*-butyl peroxide as an initiator. Polymerization using this system takes place effectively under a temperature higher than 80°C [27], which is close to that observed above.

Effect of Metal Ions on Graft Polymerization

With respect to the effect of Fe^{2+} ion, the temperature for the maximal grafting yields at around 70°C was lower than that without ions. This may be because the metal ion in a reduced state assists dissociation of the peroxide group by redox reaction.

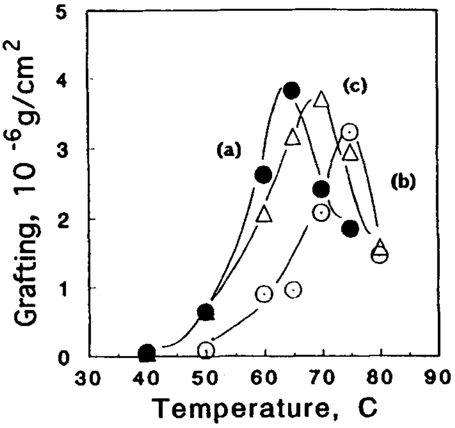

FIG. 4. Temperature dependence of graft polymerization of HEMA (1%, 60°C, 4 hours) carried out immediately onto Ar-plasma-treated PP-1 film (a), after exposure to O_2 for 100 minutes (b), and in the presence of $FeCl_2$ after 100 minutes O_2 exposure (c).

Huglin and Johnson previously investigated the effects of metal ions on the radiation graft polymerization of acrylic acid to nylon using metal salts of Fe^{2+}, Fe^{3+}, and Cu^{2+}, and observed an enhanced graft polymerization yield [28]. Hoffman et al. utilized Cu^{2+} ion to retard homopolymerization of monomers such as HEMA during radiation grafting and achieved effective grafting onto various polymer substrates [29]. They discussed the effects of metal ions mainly from the aspect of the hindrance of homopolymerization taking place during graft polymerization process.

The effects of Fe^{2+} ion on graft polymerization onto pretreated plasma and then air-exposed polymer substrates have been investigated, and the effects of metal ions have been discussed based on the suppression of the formation of homopolymers [16, 19]. Hsiue and Wang studied the dependence of the amount of grafted poly (AA) on the concentration of Fe^{2+} ion in the 10^{-6} to 10^{-1} mol/L range, and observed the maximum of the grafted amount to be around 1×10^{-3} mol/L [16]. They observed a decrease in the generation of homopolymers with an increasing concentration of the metal-reducing agent, and concluded that homopolymerization was suppressed by metal ions.

On the other hand, metal ions in their reduced states can react with oxidized species, redox reactions should take place, and the radicals formed through the redox reactions must be taken into account in the initiation of graft polymerization. Actually, the radicals generated by the redox reaction in the cellulose-Fe^{2+} system have been applied to the initiation of graft polymerization [30]. Postnikov et al. investigated the grafting of acrylamide onto irradiated polyethylene films after air exposure in the presence of Fe^{2+} ion (10^{-5}–10^{-2} g-ion/L), and observed the initiation of graft polymerization under lower temperatures [31]. A similar function of metals as a redox source should also be considered in the plasma graft polymerization of monomers onto O_2-exposed substrate films.

Comparison of the Effects of Fe^{2+} and Fe^{3+}

Figure 5 shows the grafting yields of HEMA (1%, at 60°C for 4 hours) in the presence of $FeCl_2$ and $FeCl_3$ (0.01 mol/L) to O_2-exposed PP-1 film. The results are compared with those without the addition of metal salts. The yield in the presence of Fe^{2+} was comparable to that onto nonoxidized substrate polymers, and the grafting yield increased with an increase of O_2-exposure time to more than 100 minutes. A similar effect of Fe^{2+} on graft polymerization was observed for NiPAAm as shown in Fig. 6, although the yield profile was somewhat changed from that of HEMA. Thus, the grafting ability was retained by the effects of Fe^{2+}.

In contrast to this, the grafting yield decreased in the presence of Fe^{3+} in quite the same way as without metal ions. It is suggested that the Fe^{3+} ion was not active at all, and so the effect of Fe^{3+} was quite different from that of Fe^{2+} for the initiation of graft polymerization onto O_2-exposed films.

Dependence on Fe^{2+} Concentration

In order to determine the minimal concentration of Fe^{2+} ion that is effective for enhancing graft polymerization, the molar ratios in the aqueous solution were changed and the grafting yields were compared. Figure 7 shows the results of graft

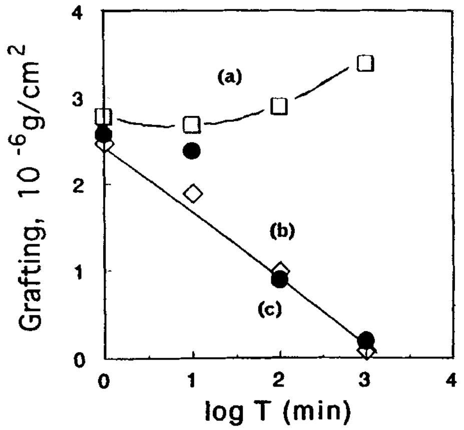

FIG. 5. Comparison of the dependence of grafting yield of HEMA (1%, 60°C, 4 hours) on the O_2-exposure time to PP-1 film in the presence of $FeCl_2$ (a) and $FeCl_3$ (b), and without metal salts (c).

polymerization of HEMA (1%, at 60°C for 4 hours) in the presence of $FeCl_2$ at concentrations up to 0.01 mol/L. The recovery of the grafting yield was evident at concentrations of Fe^{2+} as low as 10^{-3} mol/L. Interestingly, the amount grafted became greater at a concentration of 10^{-2} mol/L to PP films that had been exposed for a period longer than 100–1000 minutes.

Figure 8 shows the dependence of HEMA grafting yield on the concentration of $FeCl_2$ for Ar-plasma-treated PP-1 films without O_2 contact (a), and after exposure to O_2 for 1 (b), 10 (c), 100 (d), and 1000 minutes (e). The enhancing effects on the graft polymerization yield of HEMA by Fe^{2+} was evident with an increase of

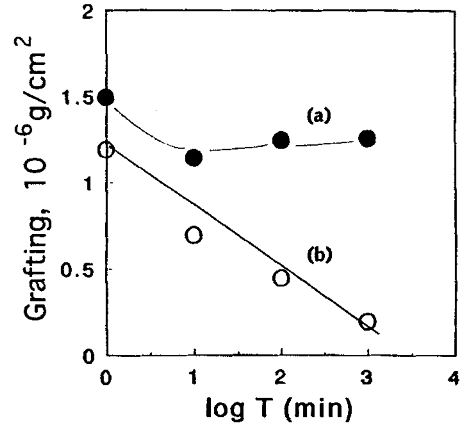

FIG. 6. Comparison of the dependence of grafting yield of NiPAAm (3%, 60°C, 4 hours) on the O_2-exposure time to PP-1 films in the presence of $FeCl_2$ (a) and without metal salts (b).

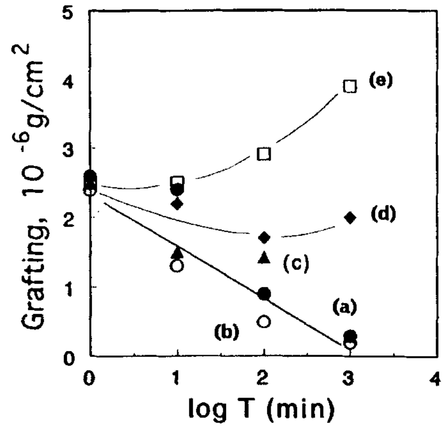

FIG. 7. Effects of graft polymerization yield of HEMA (1%, 60°C, 4 hours) onto O_2-exposed PP-1 films on the concentration of $FeCl_2$; 0 mol/L (a), 10^{-5} mol/L (b), 10^{-4} mol/L (c), 10^{-3} mol/L (d), and 10^{-2} mol/L (e).

the O_2-exposure time. The most prominent change was observed when the substrate film was exposed to O_2 for 1000 minutes.

Effects of Counterions

The experiments described above were all carried out in the presence of $FeCl_2$. The effects of counterions of Fe^{2+} were investigated using ferrous sulfate and ammonium ferrous sulfate. These ferrous salts were all effective for increasing the graft polymerization yields of HEMA, and the dependence on the counter ions was smaller or negligible.

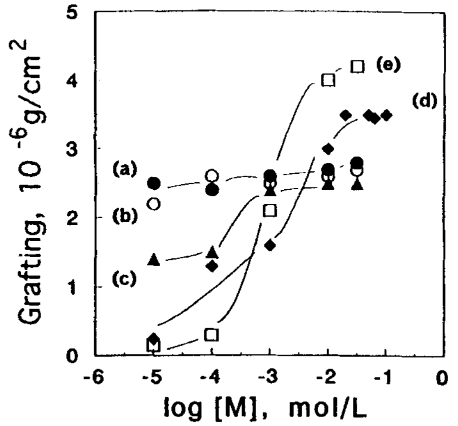

FIG. 8. Dependence of graft polymerization yield of HEMA on the concentration of $FeCl_2$ onto PP-1 film exposed to O_2 for 0 minutes (a), 1 minute (b), 10 minutes (c), 100 minutes (d), and 1000 minutes (e) after Ar-plasma treatments.

CONCLUSION

Graft polymerizations of HEMA and some other vinyl monomers were investigated, and improvements in preferential grafting were observed for the reactions of monomers in the presence of some metal ions in their reduced states. Actually, the effects of metal ions on radiation graft polymerization have been reported, and the suppressing effects of homopolymerization were pointed out before [16, 19]. However, the results described in the present study indicate the important role of the redox reactions of Fe^{2+} on the initiation of graft polymerization onto an oxidized surface of polymers.

These metal ions dissociate the peroxide bonds by redox reactions, and the oxiradicals formed should participate in the initiation of graft polymerization. This mechanism is quite similar to the scheme for Fenton's reagents [30, 32] applied to the initiation of polymerization:

$$Fe^{2+} + H{-}O{-}O{-}H \rightarrow Fe^{3+} + HO^{\cdot} + {}^{\cdot}OH^{-} \qquad (2)$$

Oxidation of the metal ions, and therefore reduction of the peroxides on the polymer substrates, should generate active oxiradical sites for the initiation of graft polymerization.

The nature and concentration of radicals formed on the surface should thus have played an important role in initiation ability, although the states have not been examined for the present cases. We are going to investigate the surface phenomena occurring on the polymer substrates by using ESR, and we will examine the grafting ability of monomers in relation to the surface states.

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