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GRAFT POLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE ONTO PLASMA PRETREATED COTTON, SILK, AND POLYESTER FIBERS

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ABSTRACT

Graft polymerization of 2-hydroxyethyl methacrylate was made onto plasma pretreated fabrics of cotton, silk, and polyester. Homopolymerization also took place during the graft polymerization, but the percent of the homopolymer formation was comparatively small. Therefore, kinetic analyses of graft polymerization were undertaken based on the first-order reaction of the monomer. Through a comparison of the rate constants which were obtained from the rate equation of the graft polymerization of 2-hydroxyethyl methacrylate, the dependence of plasma pretreatment on various factors and the resulting polymerization were clarified. Polymerizability was compared to that obtained with the Ce(IV) catalyst and without catalysts.

INTRODUCTION

Many activated species such as radicals and ions are formed in a glow discharge plasma, and they lead to characteristic chemical reactions [1, 2]. Polymer radicals generated by the opening of C—X bonds ($X = H,$

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C, halogen, etc.) on the surface of plasma-treated substrates can initiate graft polymerization of some vinyl monomers [3]. The graft polymer layer obtained by such procedures is in general formed in the vicinity of the surface of the plasma-treated substrates. The technique has been applied in various fields of surface modification such as textile finishing and the preparation of separation membranes. We have applied this technique to obtain composite membranes for liquid-vapor separation and pervaporation in water-ethanol separation. Dehydration was achieved with membranes grafted by hydrophilic monomers such as acrylic acid (AA) [4], methacrylic acid [5], AA-acrylamide [6], 2-hydroxyethyl methacrylate (HEMA) [7], etc.

Grafting is, of course, dependent on both plasma pretreatment conditions and postpolymerization as well as on the reactivity of the starting monomer. A problem often encountered in the operation of graft polymerization during the preparation of composite materials is the simultaneous production of homopolymers, and this also makes reaction analysis more complicated. However, in the cases where homopolymerization is comparatively small, the kinetics of graft polymerization can be studied more simply by the procedure used in conventional radical polymerization [8]. According to the mechanism in which the rate of polymerization is proportional to the monomer concentration, graft polymerization of several vinyl monomers onto cellulosic materials such as cotton, with and without catalysts, was investigated by using the reaction kinetics of Imoto et al. [9].

In the present paper we report the results of the kinetic analyses of plasma graft polymerization of HEMA onto fabric substrates of cotton, silk, and polyester (PET). The rate constants of the graft polymerization are estimated from the dependence of monomer consumption on the reaction period. By using the rate constants, the reactivity of HEMA is discussed from the standpoint of plasma treatment conditions and the resulting polymerization. In addition, the polymerizability of HEMA by plasma activation is compared with those initiated by cerium ammonium nitrate and those without catalysts.

EXPERIMENTAL

Materials

HEMA was purified by distillation under reduced pressure and used for graft polymerization.

Fabrics of cotton and PET as test samples were obtained based on

the Japan Industrial Standard (JIS) for colorfastness measurements. Silk fabrics were woven in the Kyoto Consulting Institute for Fabrics, Kyoto Prefecture. Weights of the fabrics were about 11.3, 12.3, and 6.6 mg/cm² for cotton, silk, and PET, respectively. The diameters of these original fibers, as estimated by scanning electron microscopy (SEM), were 17.5–22.5, 11.4–17, and 14.5 μm , respectively.

Procedure of Plasma Graft Polymerization

The method of plasma graft polymerization was principally the same as described previously [4–7]. The general procedure for plasma graft polymerization of HEMA was as follows.

A sheet of fabric (4 cm \times 4 cm) was placed in a reactor (30 mm i.d., 24 cm length), and initially treated with the inductively coupled plasma of residual gas by a radio frequency of 13.56 MHz. In the present work, the residual gas was used as the plasma source and was mainly composed of hydrogen released from the substrates during plasma irradiation [10]. Graft polymerization of HEMA was followed by plasma activation of the substrate fibers by reaction in an aqueous monomer solution (40 mL) with shaking in a water-bath. After termination of graft polymerization, the products were washed in water and the homopolymers were removed. Grafting of HEMA onto these fibers was estimated by the weight increase per unit area of the fabrics after complete drying in vacuum.

RESULTS AND DISCUSSION

Graft Polymerization of HEMA

Figure 1 shows the dependence of the degree of grafting of HEMA on the reaction period (0–8 h) onto cotton, silk, and PET. Grafting is expressed by the percent increase of weight based on the weight of the original fabric. The fabrics were treated with residual gas plasma of 0.02 torr at 20 W for 30 s, and the graft polymerization of HEMA was made with the 2-wt% aqueous solution at 50°C.

From the results shown in Fig. 1, the characteristic polymerization behavior of HEMA includes:

1. Grafting of HEMA increases with reaction time.

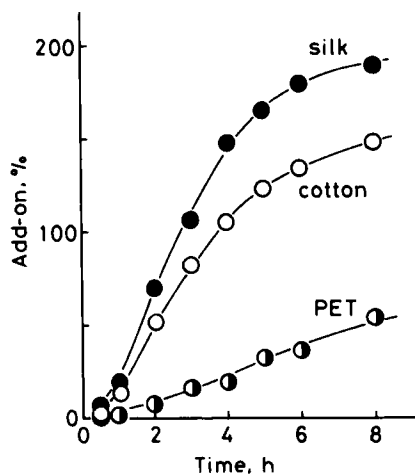


FIG. 1. Dependence of graft polymerization of HEMA on the grafting period at 50°C.

2. Cotton and silk are more reactive in the graft polymerization than is PET.

3. A time lag of ~ 30 min appeared at the first stage of the reaction.

4. The weight increase leveled off beyond 6 h.

It is well known that plasma surface treatment is a kind of etching process. Substrates with greater surface areas, such as fabrics and fibers, should be more susceptible to plasma. However, in the present cases, the decrease of weight due to etching was small. The decreasing rate was estimated to be 2.0×10^{-6} , 1.1×10^{-6} , and 0.25×10^{-6} g/cm² (fabric), respectively, for cotton, silk, and PET for the same plasma treatment as was used for the initiation of graft polymerization.

Homopolymerization accompanied by graft polymerization can be considered a kind of plasma-initiated polymerization. It has been studied by Osada et al. [11]. Whether graft polymerization or homopolymerization prevails is, of course, dependent on the reactivity of the starting monomer. The initiation of homopolymerization of a monomer should take place through the transfer of radicals to a monomer from activated polymeric substrates during contact. This mechanism was confirmed by the fact that the formation of homopolymers was negligible in the reaction system when a fabric was not exposed to plasma.

Kinetic Analyses of Graft Polymerization

A kinetic study based on the results of the reaction period dependence of graft polymerization of HEMA (Fig. 1) was made.

In the case of free radical polymerization catalyzed by an initiator which decomposes to yield a pair of free radicals, e.g., benzoyl peroxide or 2,2'-azobisisobutyronitrile, the rate of polymerization (R_p) is represented by

$$R_p = k_p(fk_d[I]/k_t)^{1/2}[M] \quad (1)$$

where $[M]$ and $[I]$ are the concentrations of a monomer and an initiator, respectively. The rate constants of propagation and termination of polymerization are given by k_p and k_t , respectively. The rate constant of decomposition of an initiator is k_d , and f is the fraction of the primary radicals which participate in the initiation of the polymerization [8].

Since the propagation of graft polymerization proceeds via a radical chain step, the reaction can be analyzed by first-order kinetics. The rate of polymer formation, which is composed of graft polymerization and homopolymerization, is based on the monomer decreasing rate:

$$R_p = -d[M_t]/dt = (k_g + k_h)[M_t] \quad (2)$$

where k_g and k_h are the rate constants of graft polymerization and homopolymerization, respectively, and $[M_t]$ is the monomer concentration at time t .

As suggested by Eq. (1), the initiator concentration and the fraction should strongly influence the rate of free radical polymerization. However, in the following discussion on plasma graft polymerization, the effects of these factors are included in the rate constant k_g .

If graft polymerization prevails over homopolymerization, Eq. (2) takes the form

$$R_p = -d[M_t]/dt = k_g[M_t] \quad (3)$$

In such cases, the monomer concentration at time t , $[M_t]$, is calculated from the initial concentration, $[M_0]$, and the amount of monomer consumed by graft polymerization at time t , $[M_{gt}]$:

$$[M_t] = [M_0] - [M_{gt}] \quad (4)$$

Constant k_g can be obtained from these equations by

$$\begin{aligned}
 k_g &= -\ln(M_t/M_0)/t \\
 &= -\ln(1 - [M_{gt}]/[M_0])/t
 \end{aligned}
 \quad (5)$$

By using the results of the reaction period dependence of the graft polymerization of HEMA (Fig. 1), the rate constant k_g is given by Eq. (5).

The occurrence of homopolymerization in the reaction of fibers of cotton and silk after reaction for 24 h was estimated to be less than 20%, which is not negligible. However, in order to simplify analyses of plasma graft polymerization of HEMA onto these fibers, we used Eq. (5) in an attempt to understand the reactivity. In the case of graft polymerization onto PET, which is much less reactive, the exact amount of homopolymerization could not be estimated, but the same procedure was employed for comparison.

First, the value of $-\ln(1 - [M_{gt}]/[M_0])$ was plotted against the polymerization period (t), and the results are shown in Fig. 2 for cotton, silk, and PET. The value of $-\ln(1 - [M_{gt}]/[M_0])$ increased linearly with t in the range of 1 to 4 h. The constant k_g was obtained from the slope. The deviation of the plots from the linear relationship of $-\ln(1 - [M_{gt}]/[M_0])$ versus t , observed for reaction times in excess of 6 h, is obtained for the reaction system with a fixed amount of monomer. The reaction was not carried out at a constant monomer solution concentration.

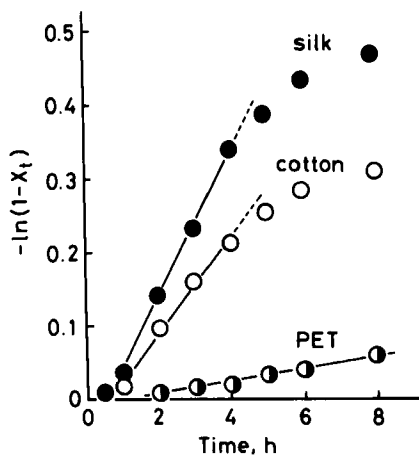


FIG. 2. Relationship between the value of $-\ln(1 - X_t)$ and the grafting period (t), where $X_t = [M_{gt}]/[M_0]$.

By comparing the values of k_g , the graft polymerization of HEMA onto these fabrics was analyzed with respect to the dependence on the factors derived from plasma pretreatment and postpolymerization.

Dependence on Plasma Pretreatment

(a) Discharge Power

Discharge power is directly related to the power imposed on the substrates by the plasma, and therefore should affect the activation for the initiation of graft polymerization. In the present work, plasma activation was performed at a power of 20 W unless otherwise noted. In order to see the effects of discharge power on graft polymerizability, the fabric samples were treated by a residual gas plasma at 10 to 100 W, and the dependence of graft polymerization of HEMA was investigated. Figure 3 shows the results of the power dependence expressed on the k_g rate constants. Here, these textile fabrics were pretreated by the plasma for 30 s at 0.02 torr, followed by the reaction of a 2-wt% aqueous solution of HEMA at 50°C.

Initially, the rate constants k_g increased with discharge power up to 20 W; beyond this power, k_g values level off for all fabric substrates.

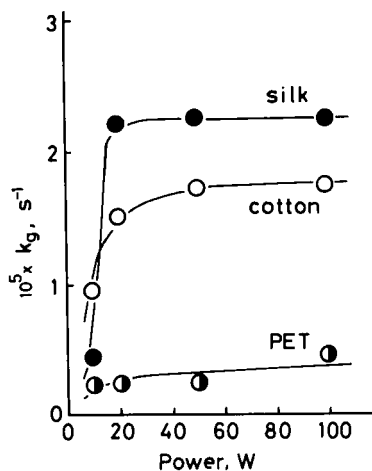


FIG. 3. Dependence of k_g for the graft polymerization of HEMA on the discharge power for plasma pretreatments.

These results indicate that the activity of these fabrics is saturated at this power with respect to the initiation of graft polymerization. Interestingly, similar power effects have been observed in the plasma polymerization of some organic molecules which are not self-degradable in plasma, such as acetylene and ethylene [12]. The reaction mechanism of plasma polymerization is, of course, different from that of initiation for plasma graft polymerization, but it was indicated that the effects of the power required to generate the polymerizations are quite similar. It is also indicated that excessive power, which will cause the degradation of substrates, is not necessary for the effective initiation of graft polymerization.

(b) Plasma Exposing Period

Another factor of the activation of substrates is the plasma exposure period. The period was changed from 30 s to 20 min and the effects on graft polymerization of HEMA were examined under the same grafting conditions. The dependence of k_g on the plasma pretreatment period is shown in Fig. 4. Plasma power of 20 W was employed for the comparison because of the threshold energy needed to maximize graft polymerization of HEMA (see Fig. 3).

It is interesting to note that the maximum grafting rate appeared at an exposure period of ~ 5 min; the grafting tendency decreased beyond this time. In addition, the decrease is dependent on the chemical nature of the fabric. The grafting reaction rate was much greater for silk in the first 5 min, but it levels off quickly and decreases. After ~ 6 min its

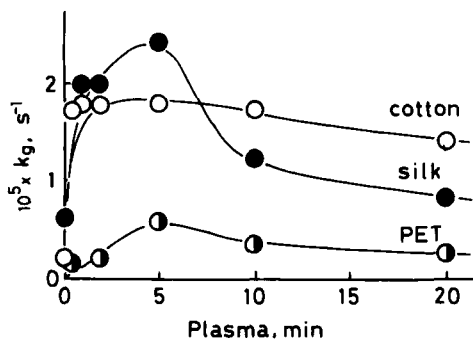


FIG. 4. Dependence of k_g on plasma pretreatment period (20 W).

grafting rate is below that of cotton. This behavior may be the result of radical recombination caused by the high population density of radicals at long exposure times. Suzuki et al. reported similar phenomenon in the plasma graft polymerization of acrylamide onto polyethylene films, but the maximum of grafting appeared at a much shorter period of plasma exposure (5–20 s) [13].

Dependence on Postpolymerization Condition

(a) Monomer Concentration

The previous studies were done at 2 wt% aqueous monomer solution, and dependences on the initiation factors were examined. Lower concentrations were employed in order to suppress the formation of homopolymers and crosslinked products originating from the terminal $-OH$ groups of the monomer. However, the effects of monomer concentration are, of course, important, and for this reason its dependence was investigated by keeping reaction times shorter.

Figure 5 shows the dependence of k_g on the concentration of HEMA in aqueous solution in the 0–10 wt% range. In these experiments the fabric substrates were treated for 30 s with 20 W plasma power at 50°C to affect graft polymerization. The results indicate that the rate constant increases with the monomer concentration and levels off beyond 5 wt%.

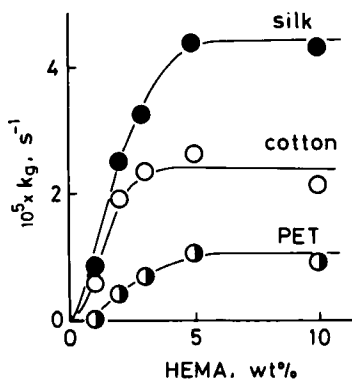


FIG. 5. Dependence of k_g on the concentration of HEMA.

(b) Temperature

As the temperature is raised, polymerization rates should increase below the ceiling temperature. However, in the case of graft polymerization, the influence of temperature should be considered from two aspects: monomer reactivity and the initiation ability of the plasma-activated fiber substrates.

Graft polymerization of HEMA onto fabric substrates was investigated in the temperature range of 40–70°C, and the effects on k_g were investigated. Figure 6 shows the dependence on temperature for graft polymerization. The fabrics were treated by plasma of 20 W for 30 s, and the graft polymerizability was compared by using a 2 wt% HEMA aqueous solution.

The rate constants initially increased with reaction temperature and reached a maximum of 60°C for silk and 50°C for cotton. Above this temperature, graft polymerizability decreased in spite of the increase of monomer reactivity. The deactivation of graft polymerization might be caused by recombination of activated polymer radicals or radical transfer. Deactivation of the substrates has been confirmed by independent experiments on acrylamide [14] carried out with heated polymer substrates after plasma treatments.

(c) Fabric Size

Fabric samples with areas in the range of 4 to 36 cm² were used to determine the influence of surface area on reaction rate constants. Figure

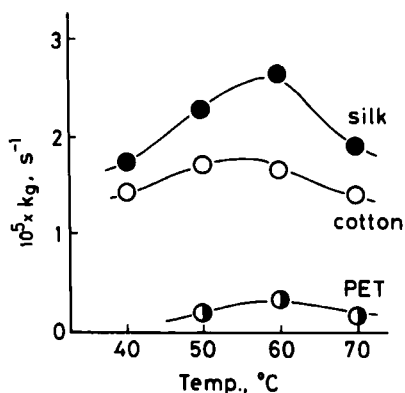


FIG. 6. Dependence of k_g on the grafting temperature.

7 shows the dependence of k_g on the areas of fabric which were previously treated with glow discharge plasma of 20 W for 30 s. The rate constants for cotton and silk with areas larger than 16 cm² had about the same grafting rate constants.

However, it should be noted that the rate constants are very small for fabrics with surface areas smaller than 9 cm², which indicates that either initiation by substrate radicals is retarded [i.e., f values in Eq. (1) have decreased], or radical recombination is more effective. The results suggest that reasonably sized fabrics are required for the effective initiation and propagation of graft polymerization in order to compare the reactivity.

Comparison of Graft Polymerization

It was thus found that HEMA was effectively graft polymerized onto the plasma-pretreated fabrics of cotton and silk. The higher graft polymerizability is related to the chemical structure of the fibers. Due to the hydroxy and amide functional groups, graft polymerization is possible onto these fibers not only in the presence of catalysts but also in the absence of such catalysts [9]. In order to confirm the effects of plasma pretreatments on the graft polymerization of the fabrics used in this work, the rate constants were obtained for each of the examples and the polymerizability was compared.

Table 1 summarizes the k_g data for the graft polymerization of HEMA initiated by plasma and by cerium ammonium nitrate, and also without

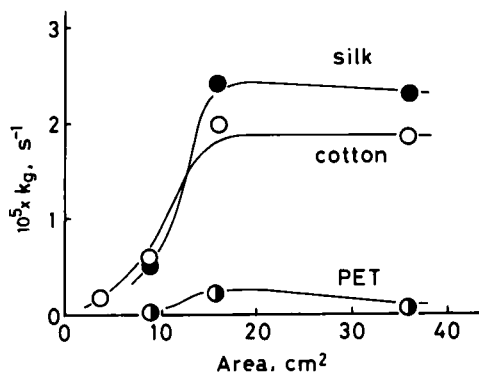


FIG. 7. Dependence of k_g on the fabric size for graft polymerization.

TABLE 1. Comparison of the Rate Constant k_g of Plasma Graft Polymerization onto Cotton, Silk, and PET (at 50°C)

Monomer	Initiation	$k_g \times 10^5, \text{s}^{-1}$		
		Cotton	Silk	PET
(1) HEMA	Plasma ^a	2.4	2.5	0.22
	Ce(IV) ^b	0.45	0.30	0.16
	None	0.10	0.61	0.01
(2) Acrylamide	Plasma	<0.01	<0.01	<0.01
	Ce(IV)	1.9	1.2	0.12
	None	—	—	— ^c
(3) Acrylic acid	Plasma	0.02	<0.01	<0.01
	Ce(IV)	0.02	0.05	0.01
	None	—	—	—

^aPlasma pretreatment at 20 W for 30 s.

^b0.025 mol/L $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$.

^cNo graft polymerization.

using any catalysts. Acrylamide and acrylic acid were also grafted onto these fibers and the polymerizabilities were compared. Postpolymerization was done in vacuum. The results clearly showed that HEMA exhibited the largest values of k_g among the monomers investigated. It was also indicated that plasma treatment was the most effective for the graft polymerization of HEMA. The grafting rate constants were rather small for Ce(IV)-initiated grafting.

CONCLUSION

Graft polymerization of HEMA onto plasma treated fabrics of cotton, silk, and PET was investigated, and the reactivity was analyzed by using grafting rate constants (k_g) obtained by assuming first-order kinetics of polymerization. From this investigation, the following points were found.

1. Plasma exposure was effective in initiating graft polymerization of HEMA, especially on cotton and silk.
2. When the plasma power exceeded a certain wattage (e.g., 20 W), graft polymerization reached saturation.

3. With an increase in the plasma exposure period, grafting increased and reached a maximum around 5 min. Beyond this time, grafting generally decreased. This finding was particularly prominent on silk.

4. Graft polymerization was also affected by postpolymerization conditions. With an increase in temperature up to 50–60°C, grafting increased. However, grafting decreased at higher temperatures.

5. Monomer concentration and the surface area of the fabrics also affected the graft polymerizability of HEMA.

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