Radiation-Induced Grafting of Methacrylic Acid onto Polyurethane in the Presence of Solvents

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Synopsis

The radiation-induced grafting of methacrylic acid onto polyurethane has been carried out in the presence of solvents. The swelling of polyurethane was highest when the solubility parameter of the monomer solution was 11.0. The molecular weight of polyurethane did not change with the irradiation dose up to 30 Mrad in the absence of solvent. The irradiation in the presence of solvent, on the other hand, decreased the molecular weight. The grafting yield in CCl₄, benzene, and n-hexane decreased monotonously with the decrease in monomer concentration. The large decrease of the grafting yield in CCl₄ was proved to be due to the high possibility of chain transfer to CCl₄. When such solvents as water, methanol, and DMF were used, on the other hand, a maximum grafting yield was obtained when the monomer concentration was ca. 75%. The hydrogen bonding among polyurethane, methacrylic acid, and solvent was found to affect both the swelling and the grafting yield.

INTRODUCTION

Polyurethane has been used as a trunk polymer for grafting of such hydrophilic monomers as hydroxyethyl methacrylate, acrylamide, N-vinylpyrrolidone, acrylic acid, and methacrylic acid mainly to obtain polyurethanes with a better quality for biomedical applications.[1-7]

In most cases with these studies, the swelling behavior of polyurethane with monomer or monomer solution was an important factor in controlling grafting behavior. However, it is not clear how the swelling of polyurethane and the grafting of the monomers are related to the polymer structure of polyurethane. Since polyurethane has urethane groups in its polymer structure, it is extensively hydrogen-bonded. When the above-mentioned monomers and such solvents as water and methanol which have the ability of hydrogen bonding are added to polyurethane, the swelling behavior of polyurethane and the grafting yield of these monomers onto polyurethane are expected to be affected by hydrogen bondings among polyurethane, monomer, and solvent.

In the present paper, the radiation-induced grafting of methacrylic acid was carried out in the presence of various kinds of solvents and the effect of solvent on both the swelling of polyurethane and the grafting yield of methacrylic acid onto polyurethane was studied and discussed in connection with hydrogen bondings.

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EXPERIMENTAL

A hard segment type polyurethane powder which was prepared by a solution polymerization of p,p'-diphenylmethane diisocyanate (TDI) and butanediol (BD) using N-methyl pyrrolidinone/dimethyl sulfoxide cosolvent system was supplied by Union Carbide. Methacrylic acid (Eastman) was purified before use by a usual distillation method. The solvents listed in Table I were used without further purification.

The sieved polyurethane powder (ca. 28 mesh) was immersed in a monomer–solvent mixture for the prescribed period and was interposed with filter papers for a short period (less than 30 s). The contribution of solvent entrained between powder particles was minimized by scrubbing the particles with filter papers.[8] The weight decrease was followed with time by a microbalance. The degree of swelling was obtained from the extraporated weight at $t = 0$.

About 1 g of polyurethane powder was introduced into a glass ampoule and was sealed under vacuum (ca. 1×10^{-4} mm Hg). The irradiation was carried out in a ^{60}Co γ-ray source at room temperature. The dose rate was 0.2×10^6 rad/h. The viscosity of the irradiated polyurethane dissolved in DMF was measured with an Ostwald-Fenske type viscometer at 25.0 ± 0.02°C.

The mixture of polyurethane powder and methacrylic acid solutions in a glass ampoule was evacuated by repeating freeze–thaw cycles at least three times and was irradiated in a Co source. The homopolymer and the unreacted monomer were extracted by boiling the irradiated mixture with a large amount of water for at least 3 days. The grafting yield was obtained from the weight increase of the glass crusible which filtrated the water. The blank test showed no loss of polyurethane powder with this procedure.

RESULTS AND DISCUSSION

Swelling

Figure 1 shows the degree of swelling of polyurethane expressed in percent by weight when the powder is immersed in various kinds of monomer-

TABLE I
Solubility Parameters of Methacrylic Acid (MA)/Solvent Mixtures[a]

No.	MA/Solvent	Solubility parameter[b] δ_L (cal/cm^3)$^{1/2}$
1	MA/n-hexane	9.5
2	MA/n-heptane	9.5
3	MA/CCl$_4$	10.0
4	MA/ethylbenzene	10.1
5	MA/benzene	10.2
6	MA/tetrahydrofuran	10.3
7	MA/acetone	10.6
8	MA/DMF	11.7
9	MA/methanol	13.0
10	MA/water	18.3

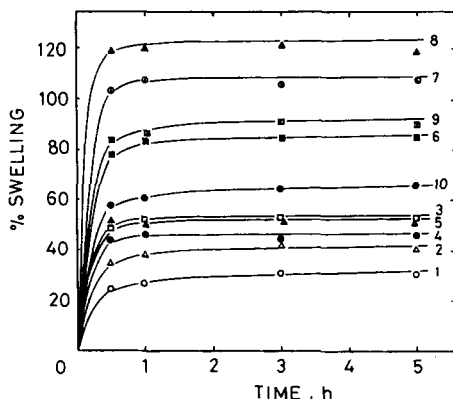[a] Concentration of MA: 50 vol %.
[b] Calculated by eq. (1).

Fig. 1. Degree of swelling of polyurethane powder in various kinds of monomer–solvent 1:1 mixtures at room temperature. The numbers are the same as shown in Table I.

solvent 1:1 mixtures at room temperature. The swelling reaches equilibrium after the initial abrupt increase. It is apparent that both the rate and the equilibrium swelling depend on the solvent. DMF, acetone, and methanol are the solvents which cause swelling to more than 90%, while n-hexane, n-heptane, benzene, ethylbenzene, and CCl$_4$ are the solvents which give the swelling less than 50%.

It has been reported that the degree of swelling of a polymer in liquid is closely related to the difference in solubility parameter between the polymer and the liquid.[8] The smaller the difference, the larger the swelling. Although the solubility parameters of pure substrates are known,[9] those for monomer–solvent mixtures are not known. The solubility parameters for these mixtures are calculated by

$$\delta_L = (\phi_1 \delta_M^2 + \phi_2 \delta_S^2)^{1/2} \tag{1}$$

where δ_L, δ_M, and δ_S are the solubility parameters of the mixture, monomer, and solvent, respectively, and ϕ_1 and ϕ_2 represent the volume fractions of monomer and solvent, respectively. The calculated solubility parameters of the monomer–solvent mixtures used in this study are listed in Table I.

Figure 2 shows the equilibrium swelling plotted against these calculated solubility parameters of various kinds of methacrylic acid–solvent mixtures.
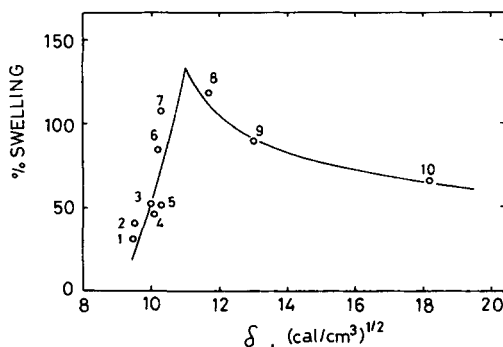

Fig. 2. Equilibrium swelling of polyurethane plotted against solubility parameters of methacrylic acid–solvent mixtures. The numbers are the same as shown in Table I.

The highest swelling is observed at the solubility parameter of ca. 11.0. According to the previous works,[8] the solubility parameter of polymer is defined as the same as that of liquid in which the maximum swelling is observed. Thus, the solubility parameter of the polyurethane, which has not previously been reported, was determined as 11.0.

The solubility parameter of polymer can also be obtained by calculation. The sum of the molar attraction constants, ΣG, for all the atoms and groupings in the repeating unit of the polymer is related to the solubility parameter by

$$\delta = d\Sigma G/M \qquad (2)$$

where δ, d, and M are the solubility parameter of the polymer, density, and molecular weight of the repeating unit, respectively. By adopting the molar attraction constants of Hoy,[10] ΣG was estimated as 3080.82. The calculated solubility parameter of polyurethane by inserting ΣG, d (1.20), and M (340.41) into eq. (2) is 10.9, which is quite comparable to the determined value.

The solubility parameter of polyurethane is close to that of methacrylic acid ($\delta = 11.2$). However, the closeness in solubility parameters between polymer and liquid does not directly mean the high solubility of the polymer in the liquid. In the case of polyurethane, for example, it was not dissolved in methacrylic acid in spite of the small difference in solubility parameter between polyurethane and methacrylic acid. The only solvent which could dissolve polyurethane was DMF ($\delta_{DMF} = 12.1$) among the solvents used in the present study. When DMF was mixed with an equal amount of methacrylic acid, on the other hand, the mixture ($\delta = 11.7$) did not dissolve polyurethane.

Molecular Weight Change with Irradiation

The irradiation of polymer changes its molecular weight through the scission and/or the crosslinking of polymer chains. Solvents affect these reactions by providing radicals and ionic species.[11] In spite of a large amount of works about the irradiation of polymers, little is known about the effect of solvents on the molecular weight change of the irradiated polyurethane.

The molecular weight of polyurethane did not change when irradiated in the absence of solvent as shown in Figure 3. This result indicates that the radicals produced by the irradiation in the polyurethane were consumed by the recombination. When polyurethane was irradiated in the presence of any solvent, on the other hand, the decrease in molecular weight was observed. The decrease observed in methanol was almost the same as that observed in DMF. In this case, the results are explained as follows: The swelling induced by the solvents in the polyurethane allowed more chain mobility and therefore decreased the probability of chains held in rigid crystalline structures "healing" their breaks by direct radical recombination.
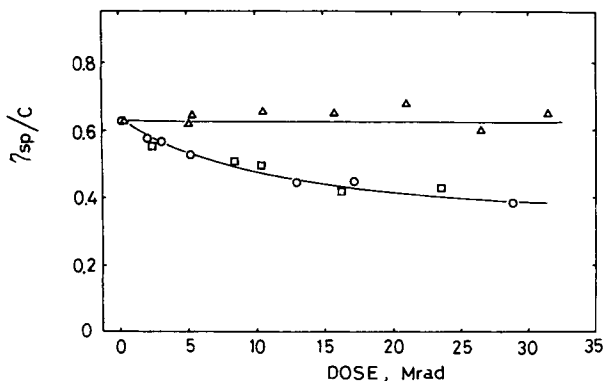
Fig. 3. The change in reduced viscosities of polyurethane with irradiation in the presence of (△) no solvent, (○) DMF, and (□) methanol.

Grafting

The grafting of methacrylic acid onto polyurethane in the presence of solvents was carried out by changing the monomer–solvent ratio. The grafting yield increased with the irradiation dose and attained equilibrium at about 2 Mrad of dose. When such solvents as n-hexane, benzene, and CCl$_4$ which were located at the left-hand side of the curve in Figure 2 were used, a nonlinear decrease in grafting yield with the decrease in monomer concentration was observed as shown in Figure 4.

The grafting yield G is the product of the number of graft chains N and the average degree of polymerization $\bar{x}_n$. N depends on the probability for trunk polymer radicals to react with monomer. On the other hand, $\bar{x}_n$ depends on the probability for growing radicals to react with monomer. Hence, the change in grafting yield is the result of the changes in these probabilities with the change in monomer concentration.

The relation between $\bar{x}_n$ and the monomer concentration [S] is given as[12]

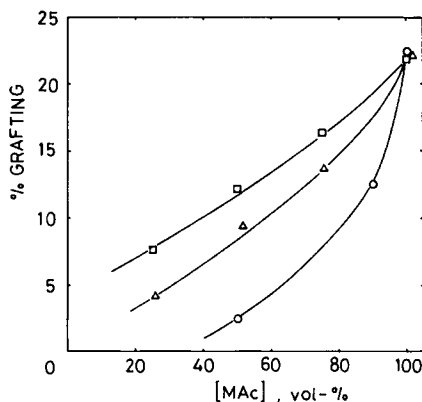$$1/\bar{x}_n = (1/\bar{x}_n)_0 + C_s[S]/[M] \tag{3}$$

Fig. 4. The relation between grafting yield and monomer concentration in the presence of (□) benzene, (△) n-hexane, and (○) CCl$_4$.
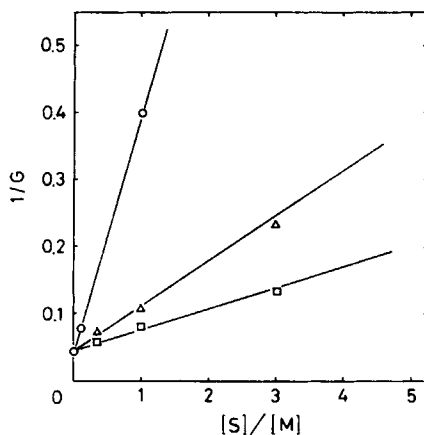
Fig. 5. Plots of $1/G$ vs. [S]/[M]. The symbols are the same as shown in Figure 4.

where $(\bar{x}_n)_0$ and C_s represent degree of polymerization without solvent and chain transfer constant to solvent, respectively. By substituting $\bar{x}_n$ with G $(G = \bar{x}_n \cdot N)$,

$$1/G = (1/G)_0 + (C_s/N)\,[\mathrm{S}]/[\mathrm{M}] \qquad (4)$$

If N is independent of [S]/[M], the plot of $1/G$ vs. [S]/[M] becomes linear and C_s/N is obtained from the slope.

Figure 5 shows the plots of $1/G$ vs. [S]/[M] when such solvents as shown in Figure 4 are used. The straight lines in Figure 5 assure the assumption that N is independent of [S]/[M]. This result may be related to the fact that the solubility parameter difference between polyurethane and methacrylic acid is smaller than that between polyurethane and solvent. That is, the contact between polymer radicals and methacrylic acid is little interfered by solvents.

Table II shows the relative values of C_s/N when C_s/N in benzene is taken as unity. The chain transfer to CCl_4 is more than 10 times that to benzene, which is a similar tendency observed in the ordinary polymerization.[9]

When such solvents as water, methanol, and DMF which are located at the right-hand side of the curve in Figure 2 were used, the changes in grafting yield with monomer concentration were quite different from those as shown in Figure 4. Figure 6 shows a maximum when the monomer

TABLE II
C_s/N in Grafting of Methacrylic Acid onto Polyurethane

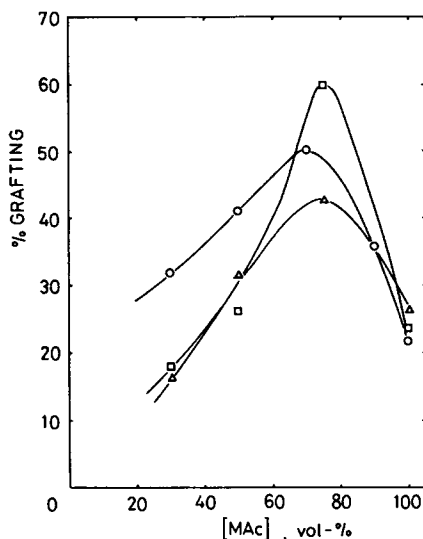| Solvent	C_s/N (a.u.)
Benzene	1
n-Hexane	2.1
CCl_4	11.3

Fig. 6. The relation between grafting yield and monomer concentration in the presence of (□) DMF, (○) methanol, and (△) water.

concentration is ca. 75%. By reference to the results in Figure 2 the order of the maximum value of the grafting yield depends on the difference in solubility parameter between polyurethane and monomer solution. A higher monomer concentration in polyurethane was obtained when the polyurethane and monomer solutions had similar solubility parameters. However, this is not specific to polyurethane–monomer–solvent system. In the case of polyurethane, the polar structure of polyurethane should be considered.[2] When a polar monomer such as methacrylic acid is supplied to a polar polymer such as polyurethane, the monomer is coupled with the polar groups in the polymer, and the grafting is affected by the dipolar coupling.

MacKnight et al. pointed out that about 80–85% of the N—H groups in polyurethane are hydrogen-bonded.[13] The N—H groups of the urethane serves as the proton donor, while the acceptor group is the carbonyl and adjacent oxygen atom in the urethane group. The structure of polyurethane containing hydrogen bonding may be indicated as
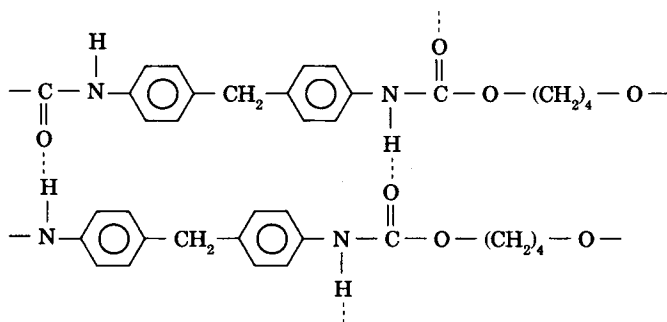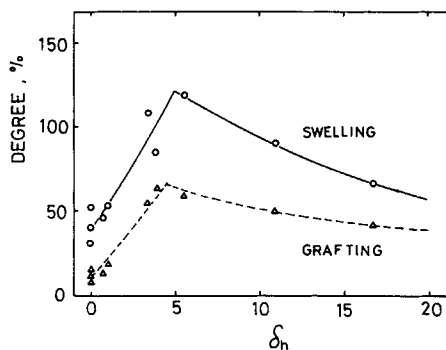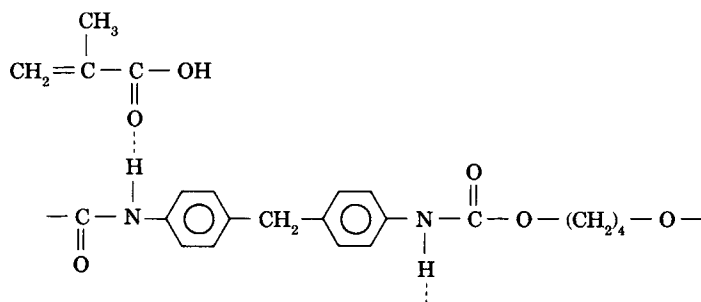
Fig. 7.　Percent swelling and percent grafting plotted against δ_h of solvent.

The added methacrylic acid may also act as a proton acceptor due to carboxyl groups:

When a solvent is added, therefore, these hydrogen-bonded structures are changed in a different manner according to the ability of hydrogen bonding of the solvent.

According to Hansen,[14] the solubility parameter δ of solvent has three components δ_d, δ_p, and δ_h due to dispersion forces, polar forces, and hydrogen bonding, respectively. When a solvent has a high hydrogen bonding ability, δ_h is large. On the other hand δ_h is small or zero when the hydrogen bonding ability is small. For example, δ_h of water is 16.7, while δ_h of CCl_4 is 0.[9]

Figure 7 shows the effect of δ_h value of solvent on both the swelling of polyurethane and the grafting yield of methacrylic acid onto polyurethane. Both the swelling and the grafting yield are largest when δ_h is about 5. A higher δ_h was not effective to obtain a high swelling and a large grafting yield. Probably, when the δ_h of a solvent is too large, the hydrogen bondings between polyurethane and the solvent as well as between methacrylic acid and solvent are predominant, which limits the hydrogen bonding between polyurethane and methacrylic acid. When δ_h is too small, on the other hand, the hydrophobic solvent interferes with the hydrophilic contact between polyurethane and methacrylic acid. These bring about the decrease in monomer uptake and the resultant decrease in grafting yield. Thus, it is concluded that the hydrogen bonding among polymer, monomer, and solvent is an important factor in controlling both the swelling of polymer and

grafting when a polar monomer such as methacrylic acid is grafted onto a polar polymer such as polyurethane in the presence of solvents.

References

1. C. H. Bamford and I. P. Middleton, *Eur. Polym. J.,* **19**, 1027 (1983).

2. A. Chapiro and M. Lamothe, *Eur. Polym. J.,* **19**, 1117 (1983).

3. S. H. O. Egboh, *J. Macromol. Sci. Chem.,* **A19**, 1041 (1983).

4. B. Jansen and G. Ellinghorst, *Radiat. Phys. Chem.,* **18**, 1195 (1981).

5. B. Jansen and G. Ellinghorst, *J. Polym. Sci., Polym. Symp.,* **66**, 465 (1979).

6. B. D. Ratner, P. K. Weathersby, A. S. Hoffman, M. A. Kelly, and L. H. Scharpen, *J. Appl. Polym. Sci.,* **22**, 643 (1978).

7. W. J. Skraba and J. W. Lynn, *Advances in Chemistry Series No. 66,* R. F. Gould, Ed., Am. Chem. Soc., Washington, DC, 1967.

8. H. Omichi and K Araki, *J. Polym. Sci., Polym. Chem. Ed.,* **17**, 1701 (1979).

9. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook,* 2nd ed., Wiley, New York, 1975.

10. K. L. Hoy, *J. Paint Technol.,* **42**, 76 (1970).

11. A. Henglein and C. Schneider, *Z. Phys. Chem.,* **18**, 56 (1958).

12. F. W. Billmeyer, Jr., Ed., *Textbook of Polymer Chemistry,* Wiley-Interscience, New York, 1957.

13. C. M. Brunette, S. L. Hsu, and W. J. MacKnight, *Macromolecules,* **15**, 71 (1982).

14. C. M. Hansen, *J. Paint Technol.,* **39**, 104 (1967).