Effect of Intramolecular Hydroxyls on Electron Beam Polymerization and Photopolymerization of Acrylate Monomers

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Synopsis

The effect of intramolecular hydroxyls on the electron beam polymerization and photopolymerization of monoacrylate monomers has been studied. In both polymerization methods, the rate of polymerization of monoacrylate monomers containing a hydroxyl was several times faster than those without hydroxyls. This can be partly explained by the higher viscosity of the hydroxyl containing monomer, resulting in a decrease in the termination rate constant to increase the polymerization rate. In electron beam polymerization, an increase in initiating species by the generation of radicals from the hydroxyls can also accelerate the polymerization.

INTRODUCTION

In a previous paper,[1] filler effect on the dynamic mechanical properties of electron beam (EB) cured hard paint films has been studied. The formulation of matrix resins consisted mainly of pentaerythritol triacrylate (PETA) or trimethylolpropane triacrylate (TMPTA). As the two triacrylate monomers are accepted to contain three acryloyloxymethyl groups attached to a quaternary carbon, they were expected to give polymers with the same crosslink density on EB irradiation. However, the polymer from PETA showed 20–40% greater modulus and hardness than that from TMPTA. Structural analysis showed that triacrylate monomers were mixtures of di-, tri-, and tetra-acrylates, resulting in a deviation of their average functionality from three. However, differences in average functionality did not affect the curing behavior significantly, but the hydroxyls contained in the monomer were proved to give polymers of higher hardness.[2]

In this work, therefore, EB polymerization and photopolymerization of monoacrylate monomers have been studied to clarify the effect of intramolecular hydroxyls. The rate of polymerization of monoacrylates containing a hydroxyl was several times faster than those without hydroxyls. Acceleration of polymerization can be explained by higher viscosity of the hydroxyl-containing monomer, and by an increase in initiating species by the generation of radicals from the hydroxyls.

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EXPERIMENTAL

Materials

Commercially available monoacrylate monomers (Toagosei) were used: 3-phenoxy-2-hydroxypropyl acrylate (PHPA) and diethyleneglycol monophenylether acrylate (DEPA). These monomers were treated with NaOH solution to remove inhibitors, washed, and dried over anhydrous sodium sulfate.

The OH group contained in PHPA was further deactivated by acetylation; 55.5 g (0.25 mol) of PHPA and 28.3 mL (0.35 mol) of pyridine were dissolved in 100 mL of dry ether. To the stirred ether solution is slowly added dropwise 25 mL (0.35 mol) of acetyl chloride. Then the mixture was warmed on a 30°C water bath for 2 h and then allowed to stand for one night. The ether layer was separated from the pyridine hydrochloride solid precipitate before washing with 10% sulfuric acid, and was then dried over anhydrous sodium sulfate. The ether was removed by distillation to yield acetylated PHPA (PHPA–AC).

Triethylamine (Hayashi Pure Chemical), 2-phenyl ethanol (Wako Pure Chemical), and 1,1-diphenyl-2-picrylhydrazyl (DPPH, Tokyo Kasei) were used as received. Photoinitiators used were 1-hydroxycyclohexylphenylketone (HCPK, Ciba-Geigy; Irgacure 184) and 2,2′-azobisisobutyronitrile (AIBN).

Procedures

Monomers coated on a flat substrate were irradiated with either EB or ultraviolet (UV) light. EB irradiation was carried out using a Nissin High Voltage area beam type electron beam accelerator at room temperature under nitrogen. It was operated at 175 kV, at beam currents ranging from 0.1 to 1.9 mA, which correspond to dose rates from 0.165 to 3.14 Mrad/s, and with line speeds varying from 3 to 60 m/min. Electron beam dose was measured using a cellulose triacetate film.

UV light was irradiated by a 80 or 120 W/cm high pressure mercury lamp with line speeds varying from 0.5 to 13 m/min. To eliminate oxygen inhibition, poly(ethylene terephthalate) films of 100 μm thickness were overlaid onto the coated monomer before irradiation. UV light intensity was measured by Ushio Electric model UIT-101 irradiance meter at 365 nm.

The percent conversion was determined by infrared spectra using a Digilab FTS-20E Fourier transform infrared spectrometer. Spectra of 10 μm thick films coated on a NaCl crystal was measured before and after irradiation, and the conversion was calculated from the intensity of olefin stretching band at 1640 cm^{-1}.

Gel permeation chromatography (GPC) was carried out using a Shimadzu Model LC-6A system. Molecular weights were determined relative to polystyrene standards. The viscosity of the monomers was obtained by a Brookfield LVT type viscometer.

RESULTS AND DISCUSSION

In Figure 1 are plotted total polymerization rates R_p for EB polymerization at dose rates ranging from 0.165 to 3.14 Mrad/s. R_p was derived from the
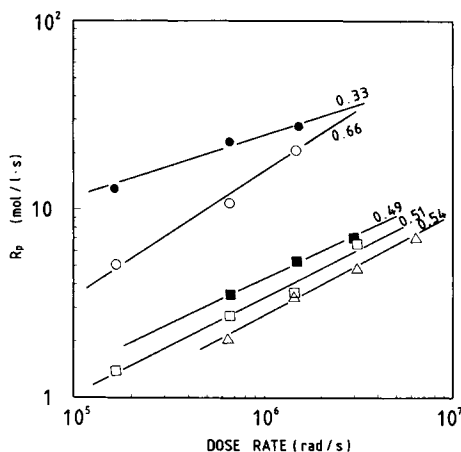
Fig. 1. Effect of dose rate upon the rate of polymerization of monoacrylate monomers: (○) PHPA;(●) PHPA/triethylamine (10 mol %); (□) PHPA—AC, (■) PHPA—AC/2-phenyl-ethanol(50 mol %); (△) DEPA. Numbers refer to slope of the lines.

slope of the percent conversion–dose curve at initial stage. R_p of PHPA containing a hydroxyl was about five times greater than that of DEPA, which does not contain hydroxyls.

R_p of PHPA–AC was determined to verify the rate enhancement effect of OH groups. The OH stretching band at about 3500 cm^{-1} has disappeared in the infrared spectrum of PHPA–AC. Viscosity was reduced from 140 cP of PHPA to 62 cP of PHPA–AC. These data indicate that the OH group in PHPA is effectively deactivated by acetylation. R_p of PHPA–AC shown in Figure 1 are almost the same as that of DEPA. The dose necessary to achieve 95% conversion at the dose rate of 1.49 Mrad/s was 2.0 Mrad for DEPA and PHPA–AC, whereas that was only 0.6–0.8 Mrad for PHPA. Therefore, OH groups are proved to accelerate the rate of polymerization in EB polymerization of monoacrylate mononers.

A simple free radical mechanism including bimolecular termination leads to the following relationship for the rate of polymerization under steady state conditions[3]:

$$R_p = \frac{k_p R_i^{0.5}[\mathrm{M}]}{k_t^{0.5}} \propto r^{0.5} \tag{1}$$

where k_p is the propagation rate constant, k_t is the termination rate constant, R_i is the rate of initiation, [M] is the monomer concentration, and r is the EB dose rate. Since the rate of initiation is directly proportional to the dose rate, it is clear that R_p is proportional to the square root of the dose rate. Dose rate exponent will be less than 0.5 when termination by primary radicals is included, and will be greater than 0.5 when monomolecular termination comes into play.[4] The dose rate exponent, decided from the slope of the lines in Figure 1, is 0.54 for DEPA and 0.51 for PHPA–AC. These values are close to the one-half order expected from eq. (1). However, R_p of PHPA is proportional to $r^{0.66}$, suggesting the monomolecular termination contribution.
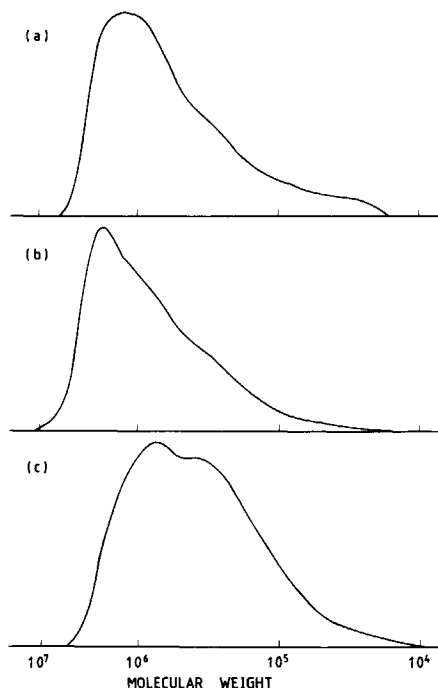
Fig. 2. GPC curves of electon beam polymerized monoacrylates at dose rate of 0.165 Mrad/s: (a) PHPA (THF soluble); (b) PHPA-AC; (c) PHPA-AC/2-phenylethanol (50 mol %).

Monomolecular termination occurs (1) in ionic polymerization or (2) seemingly due to the "trapping" of propagating radicals in the crosslinked polymer gel. Electron beam cationic polymerization of styrene is well known to take place simultaneously with radical polymerization under extreme dryness or at high dose rates such as 10^6 rad/s.[3,5,6] Polymerization of butadiene has been reported to proceed only by cationic mechanism.[7] However, methyl methacrylate,[8] methyl acrylate,[9] ethyl acrylate,[9] and butyl acrylate[9] are reported to polymerize only by radical mechanism.

Contribution of cationic mechanism can be identified by two simple ways. First, cationic polymerization results in higher molecular weight of the products than radical reaction. Secondly, cationic polymerization will be suppressed by adding ammonia or amines. Possibility of cationic contribution in the EB polymerization of PHPA was examined from these points. Figure 2(a) shows GPC curve of the THF soluble part of the polymerization product of PHPA at the dose rate of 0.165 Mrad/s. This polymer was crosslinked, and about 70% was insoluble in THF, although PHPA is a monoacrylate. The THF soluble polymer gave a number average molecular weight of 2.61×10^5. Adding 10 mol % of triethylamine to PHPA did not suppress the reaction, but increased R_p as plotted in Figure 1. The product polymerized at 0.165 Mrad/s was completely insoluble in THF, indicating that the molecular weight of the polymer is not reduced. In butadiene,[7] the high molecular weight side of the polymer was greatly reduced by the addition of triethylamine. From these results, it can be deduced that there will be no cationic contribution in the polymerization of PHPA. Rate enhancement by the

addition of an amine may be explained by increased initiating species due to the formation of radicals from the amine as suggested by Takezaki et al.[10] However, molecular weight of the polymer should be reduced if an increase in the number of initiating radical species is only effective. Another explanation is due to the suppression of oxygen inhibition by a chain reaction which allows the amine to consume oxygen.[11] Although the reaction is carried out under nitrogen, some amount of oxygen can be dissolved in the monomer to inhibit radical propagation.

Radical mechanism of the EB polymerization of PHPA was further ascertained by the addition of a radical scavenger. PHPA containing 1 mol % of DPPH was irradiated at the dose rate of 1.49 Mrad/s. As mentioned before, even PHPA–AC or DEPA attains almost 100% conversion at 2.0 Mrad. However, PHPA containing DPPH showed no significant progress of polymerization at this dosage as detected by infrared spectrum and GPC. Therefore, it can be concluded that the electron beam polymerization of PHPA proceeds only by radical mechanism.

The function of hydroxyls was then investigated by adding equimolar alcohol as a model compound to PHPA–AC. 2-Phenylethanol was used as an alcohol. The rate of polymerization was increased by a factor of 1.3 as shown in Figure 1. However, the square root rule was retained. GPC curves of the polymers from PHPA–AC and PHPA–AC/2-phenylethanol mixture irradiated at 0.165 Mrad/s are illustrated in Figures 2(b) and (c), respectively. Although number average molecular weight of the polymer from PHPA–AC was 3.89×10^5, that of the polymer from the alcohol mixture was 1.99×10^5. An increase in R_p and a decrease in molecular weight can be explained by an increase in initiating radical species. Molecular weight reduction of the polymer can be also interpreted by chain transfer to the alcohol.

Effect of 2-phenylethanol on the initiation process was estimated as discussed by Miller and Stannett.[12] When the normal square-root dependency of R_p on the dose rate is found, the ratio of the conversion in unit time with presence of a solvent, C, to that of pure monomer, C_0, may be expressed as shown in reference 12:

$$\frac{C}{C_0} = \left(\frac{m}{m + (1 - m)V_s/V_m m} \right)^{1/2} \left[1 + \phi_{rel}\left(\frac{1 - m}{m} \right) \right]^{1/2} \qquad (2)$$

where m is the mole fraction of monomer, V_s and V_m are the molar volumes of the solvent and monomer, respectively, and ϕ_{rel} represents the relative rate of radical production from the solvent, ϕ_s, and monomer, ϕ_m, respectively, i.e., $\phi_{rel} = \phi_s/\phi_m$. Equation (2) can be rearranged as

$$\phi_{rel} = \left\{ \left(\frac{C}{C_0} \right)^2 \left[\frac{m + (1 - m)V_s/V_m m}{m} \right] - 1 \right\} \frac{m}{1 - m} \qquad (3)$$

with $V_s/V_m = 0.462$ in the present PHPA–AC/2-phenylethanol mixture. ϕ_{rel} was calculated to be 2.06 at the dose rate of 1.0 Mrad/s. This means that about two times initiating radicals are formed from the alcohol compared with those from the monomer.
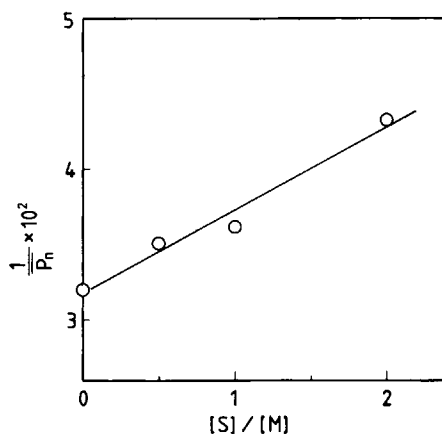
Fig. 3. Dependence of molecular weight on the 2-phenylethanol concentration at 107°C initiated with AIBN.

Chain transfer constant to 2-phenylethanol was then determined for DEPA. To avoid the complication due to the participation of the alcohol in the initiation process, photopolymerization was carried out. Chain transfer constant of a solvent, C_s, can be calculated by Mayo's equation[13]:

$$\frac{1}{\overline{P_n}} = \frac{1}{\overline{P_{n0}}} + C_s \frac{[S]}{[M]} \tag{4}$$

where $\overline{P_n}$ and $\overline{P_{n0}}$ are number average degrees of polymerization with and without presence of a solvent, respectively. [S] is solvent concentration. AIBN was chosen as a photoinitiator since chain transfer to this initiator does not occur. The actual polymerization rates were kept essentially constant by maintaining a constant ratio of monomer concentration to the square root of the initiator concentration. Due to the lower reactivity of AIBN compared with the usual photoinitiators such as HCPK, greater UV irradiation was required to initiate the reaction. This resulted in an increase in reaction temperature by the radiant heat from mercury lamps.

From the slope of $1/\overline{P_n}$ vs. [S]/[M] plot shown in Figure 3, C_s was found to be 5.48×10^{-3} at 107°C. Values of C_s obtained by varying the temperature are plotted as an Arrhenius plot in Figure 4. Extrapolation leads to values of C_s at 25°C of 1.02×10^{-4}, at 30°C of 1.43×10^{-4}, and at 40°C of 2.63×10^{-4}. The activation energy of C_s was found to be 11.1 kcal/mol.

The C_s value is calculated to be 6.9×10^{-4} if the molecular weight reduction of the EB polymerized polymer with presence of 2-phenylethanol shown in Figure 2 is caused only by chain transfer to the alcohol. As the reaction temperature of the EB polymerization is less than 30°C, this value is several times greater than the value found. In the EB polymerization with presence of an alcohol solvent, therefore, radical formation from the alcohol plays a significant role to increase the initiating radical concentration.

From these observations, the high EB polymerization rate of PHPA can be explained by additional formation of initiating radicals from the intramolecu-
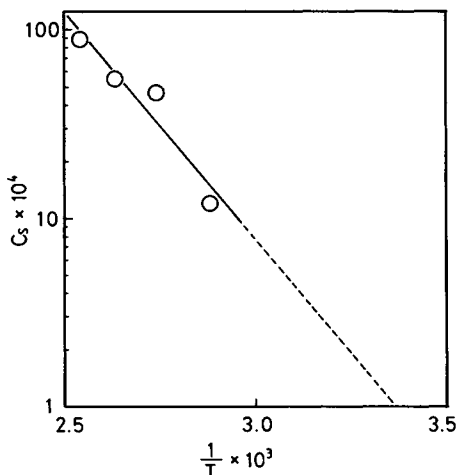
Fig. 4. Temperature dependence of the chain transfer constant of 2-phenylethanol and DEPA.

lar hydroxyls. Enhanced gellation of the PHPA polymer can be interpreted by chain transfer to the polymer.

Photopolymerization rates of PHPA and DEPA were then compared using HCPK as a photoinitiator. In Figure 5 is plotted R_p as a function of initiator concentration. As the polymerization is initiated by photofragmentation of the initiator, the above-discussed radical formation from hydroxyls can not be taken into account. As illustrated in Figure 5, however, PHPA still showed a greater polymerization rate than DEPA. This can be explained by the effect of viscosity of the reaction system. It is accepted that, in viscous media, the termination reaction, involving two radical chains, becomes diffusion controlled, whereas the slower propagation reaction, involving the relatively small monomer molecule, is little affected. In the photopolymerization of methyl-methacrylate in viscous solvents, North and Reed[14] have reported that k_t of 1.60×10^7 L/mol s at the solution viscosity of 0.4 cP was reduced to
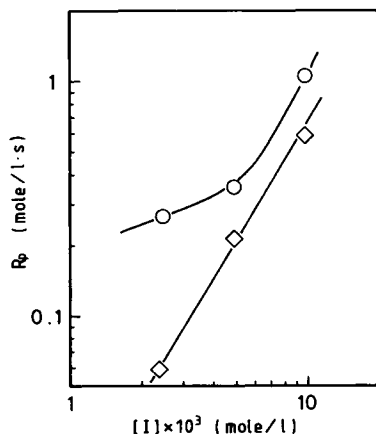

Fig. 5. Effect of photoinitiator concentration upon the rate of polymerization of acrylate monomers: ($\bigcirc$) PHPA; ($\diamondsuit$) DEPA. Initiator: HCPK, UV dose rate: 17.9 mJ/cm^2 s.

4.00×10^5 L/mol s at the solution viscosity of 28.5 cP. However, k_p was kept unchanged at around 239L/mol s, resulting in an increase in R_p at higher viscosity. Viscosities of PHPA and DEPA are 140 and 15 cP at 23°C, respectively. This difference in viscosity will be large enough to affect the k_t value to make the polymerization rate of PHPA faster.

Greater dose rate exponent than 0.5 in the EB polymerization of PHPA shown in Figure 1 can be interpreted by a seeming monomolecular termination by trapping of polymer radicals into a gel of the crosslinked polymer. Rapid increase in viscosity in the initial stage of the reaction by crosslinking can also make R_p faster at high EB dose rates. These explanations can be also applied to the photopolymerization of PHPA and DEPA at higher initiator concentration plotted in Figure 5.

Although slope for PHPA polymerization in Figure 5 at low initiator concentration is close to the one-half order expected by eq. (1), the slope for the DEPA is greater. Greater UV irradiation was necessary to initiate the photopolymerization of DEPA at the lowest HCPK concentration of 2.45×10^{-3} mol/L. This resulted in an increase in reaction temperature to about 50°C, whereas the temperature rise was not so significant at higher initiator concentration or in PHPA polymerization. As viscosity of DEPA was reduced from 15 cP at 23°C to 6 cP at 50°C, R_p of DEPA at low initiator concentration can be decreased due to the low viscosity.

In conclusion, faster reaction rate in EB polymerization and photopolymerization of hydroxyl-containing acrylate monomer can be partly explained by the higher viscosity of the monomer. In EB polymerization, an increase in initiating radicals by the generation of radicals from the hydroxyls can also accelerate the polymerization rate.

References

1. M. Itoh, T. Shiota, and M. Nishihara, *J. Appl. Polym. Sci.*, **36**, 1417–1431 (1988).

2. M. Itoh, T. Shiota, and M. Nishihara, *Kobunshi Ronbunshu*, **44**, 771–777 (1987).

3. D. R. Squire, J. A. Cleaveland, T. M. A. Hossain, W. Oraby, E. P. Stahel, and V. T. Stannett, *J. Appl. Polym. Sci.*, **16**, 645–661 (1972).

4. T. Otsu, *Kaitei Kobunshi Gosei No Kagaku* (*Chemistry of Polymer Synthesis, Revised Edition*), Kagakudojin, Kyoto, 1979, p. 51.

5. J. Takezaki, T. Okada, and I. Sakurada, *J. Appl. Polym. Sci.*, **21**, 2683–2693 (1977).

6. J. Takezaki, T. Okada, and I. Sakurada, *J. Appl. Polym. Sci.*, **22**, 3311–3325 (1978).

7. K. Hayashi, Y. Tanaka, and S. Okamura, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1435–1443 (1981).

8. C. C. Allen, W. Oraby, T. M. A. Hossain, E. P. Stahel, D. R. Squire, and V. T. Stannett, *J. Appl. Polym. Sci.*, **18**, 709–725 (1974).

9. K. Hayashi and S. Okamura, *Radiat. Phys. Chem.*, **18**, 1133–1142 (1981).

10. J. Takezaki, T. Okada, and I. Sakurada, *Radiat. Phys. Chem.*, **18**, 1125–1132 (1981).

11. R. Phillips, *Source and Applications of Ultraviolet Radiation*, Academic London, 1983. p. 80.

12. L. A. Miller and V. Stannett, *J. Polym. Sci.*, A-1, **7**, 3159–3176 (1969).

13. T. Otsu, *Kaitei Kobunshi Gosei No Kagaku* (*Chemistry of Polymer Synthesis, Revised Edition*), Kagakudojin, Kyoto, 1979, p. 94.

14. A. M. North and G. A. Reed, *Trans. Faraday Soc.*, **57**, 859–870 (1961).