

Diffusion of Unreacted Monomers Detected by ATR FTIR Spectroscopy in a Photosensitive Printing Plate After the Photoreaction

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ABSTRACT: A water-developable flexographic printing plate consisting of poly(acrylonitrile-co-butadiene), polybutadiene, and carboxylated polyurethane as a polymer matrix, hexanediol dimethacrylate and polybutadiene diacrylate as reactive monomers, and benzildimethylketal as a photoinitiator was prepared and its photoreaction followed by structural change caused by the diffusion of unreacted monomers was characterized. Analysis combined ^{13}C -NMR and attenuated total reflection (ATR) FTIR showed the photoreaction occurred predominantly at the surface of exposure to the light at first, and then the reaction proceeded to

the direction of the opposite surface with an increase in the exposure time. Diffusion of unreacted monomers after the photoreaction from the unexposed side to the exposed side was monitored by ATR FTIR. The diffusivity of unreacted monomers was dependent on the extent of photoreaction in the plate and the molecular weight of diffusing monomers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2903–2907, 2004

Key words: diffusion; FTIR; photopolymerization; monomers; NMR

INTRODUCTION

As an application of photosensitive image forming materials, photosensitive flexographic printing is used for rotary printing with sheet-like elastic relief plate and fast drying ink such as water- or alcohol-based ink.¹ The flexographic printing has the next largest shear to offset printing in the global printing markets because of its wide applicability and high productivity.² While halogenated organic solvents were used as developer in this field, water-developable plates are appearing as alternatives from the viewpoint of a safety issue.^{3–5} The water-developable plates should satisfy two opposite requirements: one requirement is hydrophilicity to be essential for water developing; the other requirement is hydrophobicity to resist the corrosion by hydrophilic ink. For this objective, we reported the photosensitive compositions consisting of linear hydrophilic polymers and linear hydrophobic polymers with (meth)acrylate monomers.^{6–11} Phase separation exists in these photosensitive flexographic compositions, because they comprise polymers with different chemical structures.

Control of photochemical reaction in the phase-separated system is one of the keys to obtain the printing

plates with high resolution. Furthermore, understanding of the time dependence of structural change after the photoreaction is also important because the printing plate is used with several processes of exposures and posttreatments.

In previous articles, we reported that combination of overall reactivity evaluated by ^{13}C -NMR measurement and reactivity near the surface obtained by attenuated total reflection (ATR) FTIR spectroscopy was useful to understand the distribution of photoreaction in the direction of thickness for flexographic printing plates.^{12,13} This new approach to understand the photochemical reaction in printing plates can be applied not only to compare the characteristics among the plates with different compositions, but also to chase the diffusion of unreacted monomers in the plates after the exposure to the radiation. In this article, the time dependence of structural change in a flexographic printing plate after the photoreaction evaluated by ATR FTIR will be reported.

EXPERIMENTAL

Materials

An experimental printing plate was prepared as follows. Carboxylated polyurethane (11 g), polybutadiene diacrylate (weight average molecular weight ~ 8000) (26 g) (Kyoeisha Chemical Co., Ltd., Osaka, Japan), poly(acrylonitrile-co-butadiene) (41 g), polybutadiene (12 g) (JSR Corp., Tokyo, Japan), 1,6-hex-

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anediol dimethacrylate (8 g) (Shinnakamura Kagaku Co., Wakayama, Japan), and benzildimethylketal (2 g) (Nihon SiberHegner K. K., Tokyo, Japan) were mixed with 50 g of toluene (Idemitsu Petrochemical Co., Ltd., Tokyo, Japan) and 10 g of water at 105°C, and then the toluene and water were evaporated under reduced pressure. To prepare a photosensitive composition plate with 2.8 mm of thickness, the composition obtained was heat-pressed between polyethylene terephthalate (PET) films (Toyobo Co., Ltd., Osaka, Japan) under 100 kg cm⁻² of pressure at 105°C (one of the PET films was coated with an adhesive layer, and the other was coated with a release layer).

Characterization of photochemical reaction

The printing plates were exposed to the radiation of a lamp (FR20T12-BL-9-BP, Anderson A Veeland Co., 17.5 W/cm² at 365 nm) for several radiation periods. The exposed plates were kept in the dark and provided for the characterization. ¹³C-NMR measurement was carried out for the plates filled directly in a 10 mmϕ NMR sample tube with a Varian Unity-500 NMR spectrometer. Measuring conditions were similar to general solution NMR measurement, except no NMR-lock was used and longer recycle delay was selected. IR spectra for the surface region of the plates were measured with a germanium prism for ATR mode by using a Bio-Rad FTS-60 spectrometer.

Quantification of unreacted monomers was also carried out by Soxhlet extraction of the exposed plate by ethyl acetate in the dark and the following ¹H-NMR measurement of the extracts in CDCl₃ at room temperature.

RESULTS AND DISCUSSION

Distribution of photoreaction

A printing plate composition prepared in this study consists of 41 wt % of poly(acrylonitrile-*co*-butadiene) and 12 wt % of polybutadiene as hydrophobic polymers, 11 wt % of carboxylated polyurethane as hydrophilic polymers, 8 wt % of hexanediol dimethacrylate and 26 wt % polybutadiene diacrylate (weight-average molecular weight: ~ 8000) as reactive monomers, and 2 wt % of benzildimethylketal as a photoinitiator.

Extent of polymerization of reactive monomers by exposure to UV light radiation was evaluated by ¹³C-NMR and ATR FTIR spectroscopy. ¹³C-NMR spectra of the printing plate in the bulk state before and after exposure to light is shown in Figure 1. The printing plate before exposure is in the rubbery state, so that the molecular mobility of each component is high enough for the detection as the usual solution ¹³C-NMR measurement even in the bulk state. Signals around 160 ppm were assigned to the carbonyls of

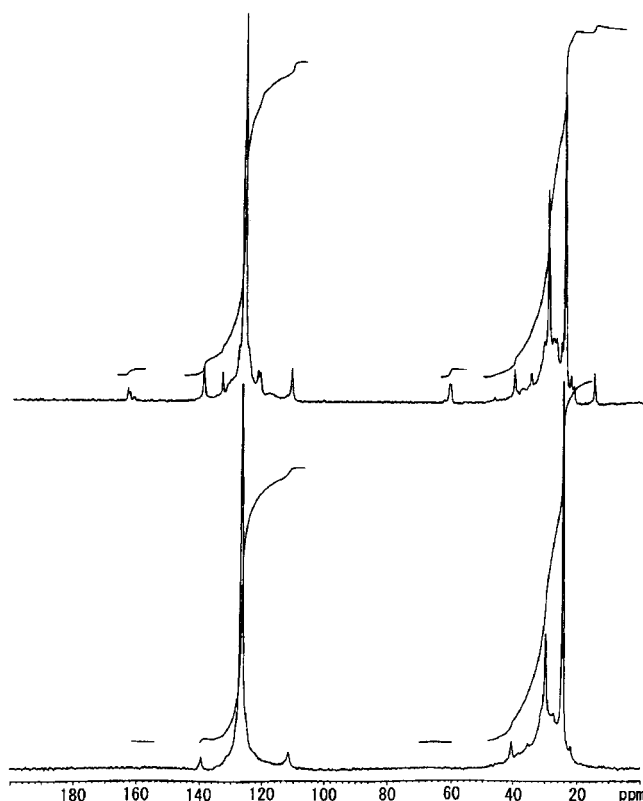


Figure 1 ¹³C-NMR Spectra of the printing plate before (upper) and after (lower) exposure to the radiation for complete photoreaction.

1,6-hexanediol dimethacrylate and polybutadiene diacrylate. Another signal of 1,6-hexanediol dimethacrylate was also found at 65 ppm, which was assigned to the methylene bonded to oxygen. These signals decreased with the progress of polymerization and finally disappeared after long radiation as shown in Figure 1. Decrease in the mobility of reacted species with polymerization decreases the intensity of these signals. Therefore, change in the integral intensity of these signals can be used to evaluate the progress of photopolymerization of the monomers as a whole plate.

Figure 2 shows ATR FTIR spectra of the printing plate before and after exposure to the light. As the printing plate has 2.8 mm of thickness, it is difficult to obtain an IR spectrum based on the whole sample. Therefore, ATR FTIR spectra for the surface region of the plates were measured. As a 45° germanium prism was used, infrared absorption from the surface to ~ 1 μm depth was detected. A peak at 810 cm⁻¹ is an out-of-plane bending vibration of C—H bonds on ethylenical double bond in 1,6-hexanediol dimethacrylate and polybutadiene diacrylate. This absorption at the exposed side decreased with the exposure time and finally disappeared. On the other hand, almost no change was detected at the opposite side of exposure

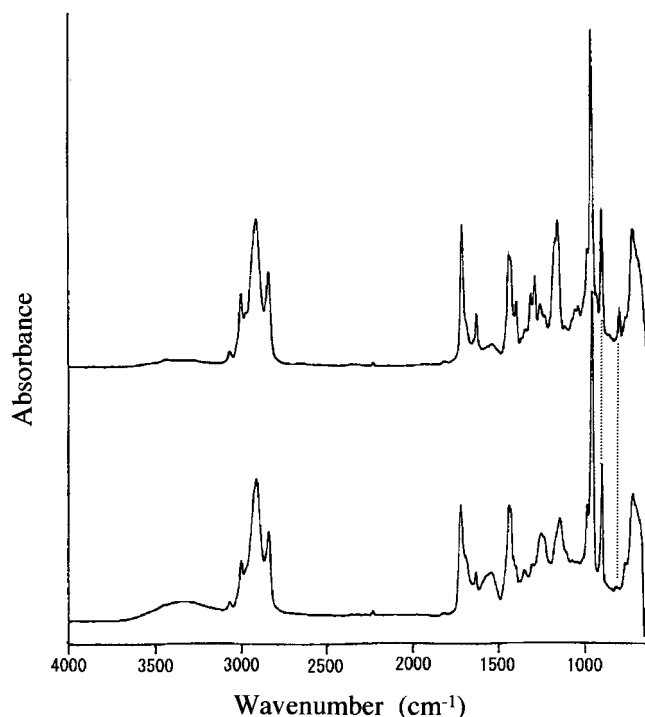


Figure 2 ATR FTIR spectra of the printing plate before (upper) and after (lower) exposure to the radiation for complete photoreaction.

to a certain extent of exposure time, which means the light did not reach the opposite surface sufficiently. Progress of reaction near the exposed surface can be determined by the change in relative intensity of the peak at 810 cm^{-1} to a reference peak of which intensity does not change with the photoreaction. Here, the out-of-plane bending vibration of C—H bonds on carbon-carbon double bond at 912 cm^{-1} in 1,2-polybutadiene unit was selected as the reference.

Table I shows the progress of reaction with exposure time. Both the conversion at the surface exposed and the overall conversion increased with exposure time. It was clearly observed that the polymerization occurred predominantly at the surface of exposed side and resulted in a distribution of reaction in the direction of thickness depending on the exposure time.

Extent of the photoreaction was also evaluated by the characterization of the extracts by Soxhlet with

TABLE I
Reactivity of Monomers in the Printing Plate

Exposure time (s)	Conversion (%)	
	Total ^a	surface ^b
40	25	60
100	50	70

^a Evaluated by bulk ^{13}C -NMR.

^b Evaluated by ATR FTIR at the exposed surface.

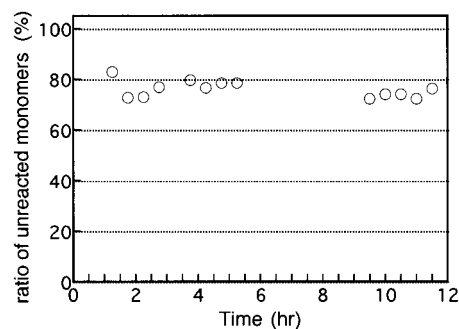


Figure 3 Time dependence of the ratio of unreacted monomers in the printing plate after 40 s exposure to light.

ethyl acetate for the plate exposed for 100 s. Quantification of unreacted monomers in the extract showed that the conversions of 1,6-hexanediol dimethacrylate and polybutadiene diacrylate were 62 and 25%, respectively, and the total conversion of the monomers was 54%. This result was roughly consistent with the result of ^{13}C -NMR and showed that hexanediol dimethacrylate reacted more than twice as fast as polybutadiene diacrylate. It is considered that the radical terminal in the low molecular weight difunctional monomers has the advantage of finding the other reactive terminal in the same molecule, and higher diffusivity of low molecular weight monomers in the polymer matrix is also favorable for the polymerization.

Diffusion of unreacted monomers

Structural change of the photoreacted samples in the dark condition was investigated. ^{13}C -NMR was used to determine the change in the extent of reaction as a whole plate after the photoreaction. Figure 3 shows the time dependence of the ratio of unreacted monomers against all the feed monomers in the printing plate that were exposed to the light for 40 s and kept in an NMR tube in the dark. The total conversion of

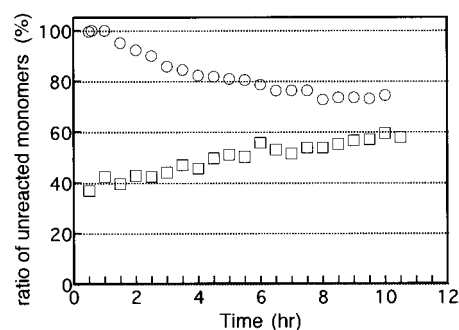


Figure 4 Time dependence of the ratio of unreacted monomers in the printing plate after 40 s exposure to light at the exposed surface (\square) and the unexposed surface (\circ).

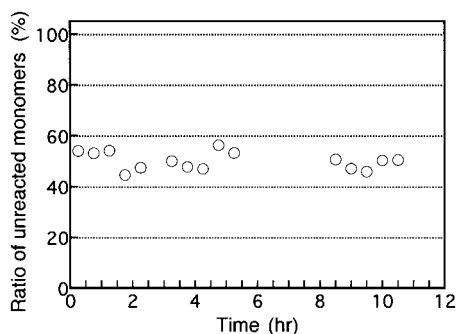


Figure 5 Time dependence of the ratio of unreacted monomers in the printing plate after 100 s exposure to light.

photoreaction for the acrylates and methacrylates with 40 s radiation was $\sim 25\%$, and no further reaction proceeded after the radiation. ATR FTIR was employed for chasing the change in the ratio of unreacted monomers after the photoreaction at the exposed and unexposed surfaces, respectively. Figure 4 shows the results of photoreacted printing plate exposed for 40 s. Although the overall conversion did not increase in the dark after the photoreaction, monomer concentration decreased at the unexposed side and increased gradually at the exposed surfaces. This means that the printing plate was still in the rubbery state after the photoreaction, particularly near the unexposed side, and the diffusion of unreacted monomers was possible from the unexposed side to the exposed side. After 10 h from the photoreaction, the monomer concentrations of both sides approached $\sim 70\%$, which was consistent with total conversion determined by ^{13}C -NMR.

Figures 5 and 6 show the structural change in the printing plate when the sample was kept in the dark after exposure to light for a longer time, 100 s. Total conversion of monomers by photoreaction was $\sim 50\%$ in this experiment. Even in this case, almost no monomers reacted at the opposite side to the exposure, while the conversion was 70% at the exposed surface.

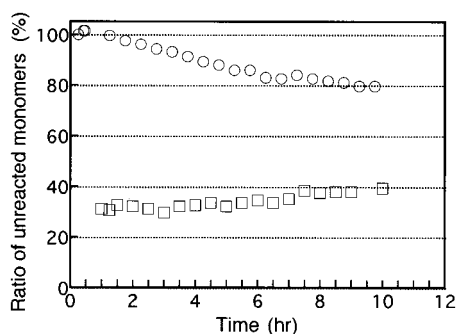


Figure 6 Time dependence of the ratio of unreacted monomers in the printing plate after 100 s exposure to the light at the exposed surface (\square) and the unexposed surface (\circ).

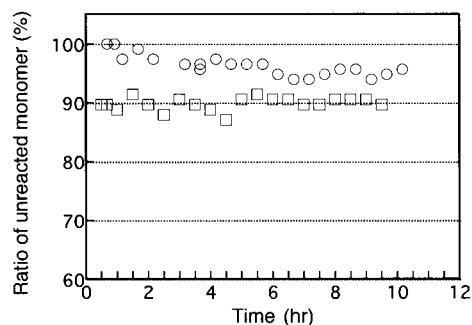


Figure 7 Time dependence of the ratio of unreacted polybutadiene diacrylate in the printing plate after 40 s exposure to the light at the exposed surface (\square) and the unexposed surface (\circ).

Monomer diffusion also occurred in this sample after the photoreaction, although the diffusion was slow and a large difference in the concentration between the both sides, 40%, remained after 10 h. The viscosity of the polymer matrix was an important factor to control the diffusivity of unreacted monomers.

To consider the effect of molecular weight of monomers for diffusion in the printing plate, another experimental composition without 1,6-hexanediol dimethacrylate was prepared and the same experiments described above were carried out. Figures 7 and 8 show the change in unreacted polybutadiene diacrylate after 40 and 100 s exposures to the light, respectively. In these experiments, the extent of photoreaction of the polybutadiene diacrylate was lower than that of mixed monomers, and diffusion of unreacted monomer was also slow. It was confirmed that the molecular weight of monomers has a large influence on their diffusion. In addition, high molecular weight monomers have a disadvantage in reactivity, probably due to the long distance among the reactive points and low mobility of reactive functional groups.

As shown above, the diffusion of unreacted monomers in the printing plates after the photoreaction was

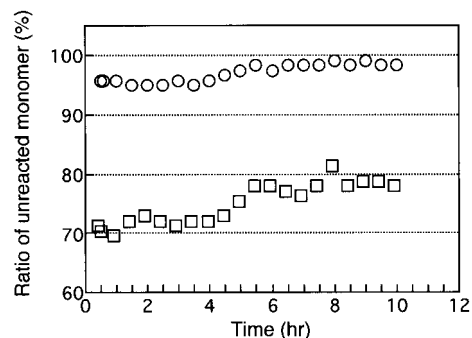


Figure 8 Time dependence of the ratio of unreacted polybutadiene diacrylate in the printing plate after 100 s exposure to the light at the exposed surface (\square) and the unexposed surface (\circ).

successfully monitored by ATR FTIR technique. The diffusivity of unreacted monomers depended not only on the condition of the plates exposed, but also on the structures of monomers. Understanding of the details of these phenomena utilizing chemical analysis will be a good help for designing a high-quality printing plate.

CONCLUSION

A printing plate composition containing two reactive monomers was prepared and its photoreaction followed by structural change caused by the diffusion of unreacted monomers was characterized by bulk ^{13}C -NMR and ATR FTIR spectroscopies.

(1) The photoreaction occurred predominantly at the surface of exposure to the light at first, and then the reaction proceeded to the direction of opposite surface with an increase in the exposure time.

(2) The distribution of photoreaction in the direction of thickness induced the diffusion of unreacted monomers from the unexposed side to the exposed side.

(3) The diffusivity of unreacted monomers was dependent on the extent of photoreaction in the plate and the molecular weight of diffusing monomers.

These new approaches to understand the photochemical reaction in printing plates are helpful to de-

sign a high-quality photosensitive image forming composition in the future.

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