# Characterization of Photochemical Reaction in Photosensitive Printing Plates by $^{13}$C NMR in the Bulk State and ATR FTIR Spectroscopy

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Photochemical reaction in a flexographic printing plate was characterized. The distribution of photochemical reaction in the direction of thickness was successfully understood by the combination of overall reactivity obtained by $^{13}$C NMR measurement and reactivity near the surface obtained by ATR FTIR spectroscopy.

One of the application of photosensitive image forming materials is photosensitive flexographic printing, which is used for rotary printing with sheet-like elastic relief plate and fast drying ink such as water- or alcohol-based ink.[1] While halogenated organic solvents have been used as developer in this field, water-developable plates are appearing as alternatives from the viewpoint of safety issue.[2–5] As water-developable photosensitive flexographic printing plates comprise several polymers and low molecular weight compounds with hydrophilic and hydrophobic properties, phase separation exists in these compositions.[6] Control of photochemical reaction in the phase separated system is necessary to obtain the printing plates with high resolution. In these systems, reactivity of monomers in the compositions and transparency of plates are important factors to control the depth of relief. Characterization of photo-reacted flexographic printing plates has been carried out by practical evaluation such as printing performance, surface hardness and relief depth. Although fundamental understanding of the photochemical reactions based on chemical analysis is important for designing a high-quality flexographic plate composition, no works from this point of view have been reported to our knowledge.

In this paper, in order to establish an analytical method to understand the photochemical reaction in a rubber-state printing plate of a few millimeter thickness, Cyrel® AQS (Du Pont Co., thickness: 2.8 mm), a commercial water-developable photosensitive flexographic printing plate, was chosen to be characterized.

First, the composition of Cyrel® AQS was analyzed by using soxhlet extraction with methanol in the dark condition. The extract was separated into several fractions with GPC. Each fraction and the residue of extraction were characterized with IR and $^{1}$H NMR (solvent: $CDCl_3$), respectively. The analytical results of Cyrel® AQS was as follows: poly(styrene-co-butadiene) and hydrophilic poly(styrene-co-butadiene) as polymer components, 85 wt%; 1,6-hexanediol dimethacrylate as a reactive monomer, 12 wt%; benzildimethylketal and benzophenone as initiators, 3 wt% and 0.3 wt%, respectively.

After the cover films and coating layers were removed from the both surfaces of the Cyrel® AQS printing plate, exposure of the plate to the light radiation was carried out by using a UV lamp (FR20T12-BL-9-BP, Anderson A Veeland Co., 17.5 W/cm$^2$ at 365 nm) for several radiation times. The exposed plates were kept in the dark and provided for the characterization.

$^{13}$C NMR measurement in the bulk state was carried out for the plate filled directly in a 10 mm$\phi$ NMR sample tube with a Varian Unity-500 NMR Spectrometer. Measuring condition was similar to general solution NMR measurement, except no NMR-lock was used and longer recycle delay was selected. Changes in $^{13}$C NMR spectra of the Cyrel® AQS with exposure time are shown in Figure 1. The printing plates before the exposure are in the rubber state, so that the molecular mobility of each component is high enough for $^{13}$C NMR measurement even in the bulk state. Signals of 1,6-hexanediol dimethacrylate are found at 167 ppm and 65 ppm, which are assigned to the carbonyl of methacrylate and the methylene bonded to oxygen, respectively. These signals decreased with the progress of polymerization. Decrease in the mobility of reacted species with polymerization decreased the signal intensity as the result of increase in dipole interaction and spin-lattice relaxation time. Changes in the integral intensity of these signals were used to evaluate the progress of photopolymerization of the monomers as the whole plate. Quantification of unreacted monomers in the exposure measurements was also carried out by soxhlet extraction of the exposed plate by ethyl acetate in the dark and the following $^{1}$H NMR measurement of the extracts in $CDCl_3$. The validity of determination based on NMR

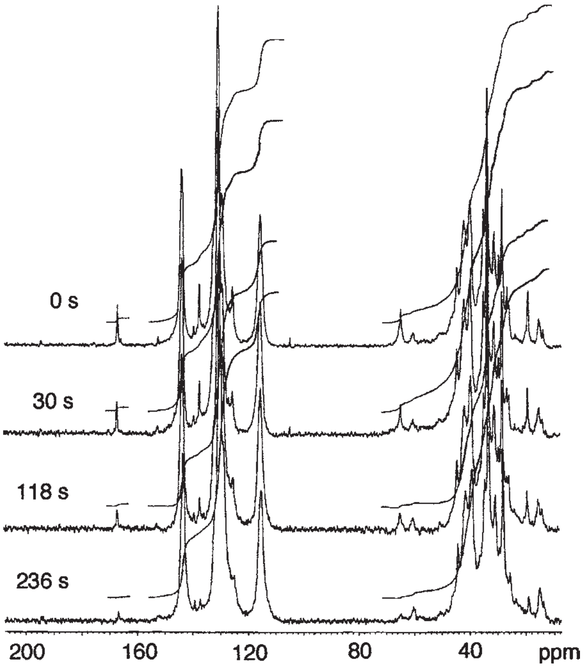

**Figure 1.** Changes in $^{13}$C NMR spectrum of Cyrel® AQS with exposure time.

was ascertained by comparing the results each other as shown in Table 1.

**Table 1.** Conversion in photoreaction of 1,6-hexanediol dimethacrylate with exposure time

| Exposure time/sec | 30 | 59 | 118 | 236 |
|---|---|---|---|---|
| Conversion by NMR/% | 25 | 34 | 50 | 76 |
| Conversion by extraction/% | 28 | 39 | 53 | 75 |

As the printing plate has 2.8 mm of thickness, it is difficult to obtain an IR spectrum based on the whole sample. Therefore, attenuated total reflection (ATR) FTIR spectra for surface region of the plates were measured with a Biorad FTS-60 spectrometer. As a 45 ° germanium prism was used, infrared absorption from the surface to ca. 1 $\mu$m depth was detected. Figure 2 shows the changes in ATR FTIR spectra of Cyrel® AQS with exposure time. A peak at 810 $cm^{-1}$ is out-of-plane bending vibration of C–H bonds on carbon-carbon double bond in 1,6-hexanediol dimethacrylate. This absorption at the exposed side decreased with exposure time. On the other hand, almost no change was detected at the opposite side of exposure, which means the light did not reach the opposite surface. 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 polymerization. Here, the out-of-plane bending vibration for aromatic ring in polystyrene at 760 $cm^{-1}$ was selected as the reference.

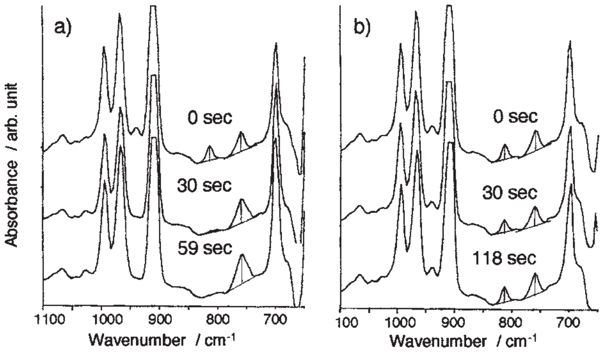

**Figure 2.** Changes in ATR FTIR spectrum of Cyrel® AQS with exposure time; a) at the surface of exposure, b) at the opposite surface of exposure.

Figure 3 shows the progress of reaction with exposure time, as the whole printing plate determined by $^{13}$C NMR measurements and at the surface of exposed side determined by ATR measurement. Although 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.

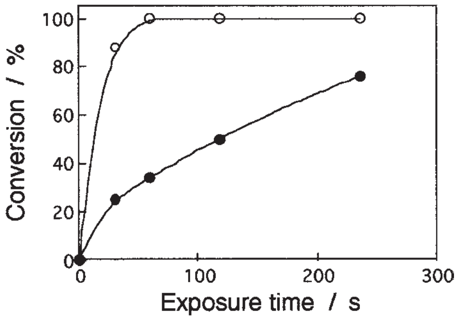

**Figure 3.** Progress of photoreaction of Cyrel® AQS with exposure time; (○) at the exposed surface, (●): as the whole sample.

As shown in this study, it was demonstrated that combination of $^{13}$C NMR and ATR FTIR analysis is useful to understand the distribution of photoreaction in the direction of thickness, that has influence on the relief formation in the photosensitive flexographic printing plates. This new approach to understand the photochemical reaction in printing plates is 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. These properties are related to the change in phase conditions of the components in the plates. Further study utilizing this analytical method is now in progress to design a high-quality photosensitive image forming composition.

## References

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