PREPARATION AND PHOTO REACTION OF POLYMERS CONTAINING BENZOYLFORMYLATED NOVOLACs

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1. Introduction
Resists for micro lithography are indispensable for manufacturing integrated circuits and large-scale integrated chips. It is known that cinnamate and quinone diazide are useful functional groups for negative and positive tone image lithograph, respectively. Recently, new type of functions such as diazo isopropylidene malonate for deep ultra-violet (UV) resists[1] and 2-methylpentene for electron beam resists[2] have been developed.

We have reported peculiar formylated novolacs which showed both positive and negative tone images by selecting a suitable developing agent[3]. It is anticipated that benzoylformyl group is more reactive than formyl group by deep UV irradiation because benzoyl group can act as an excellent chromophore. In this paper, we describe the preparation and photoreaction of benzoylformyl novolacs as well as the model reaction.

2. Results and discussion
Preparation of benzoylformylated (BzF-Nov) was carried out by the reaction of novolacs (Nov) with benzoylformic acid-acetic anhydride in the presence of pyridine. The degree of the benzoylformylation was estimated from the $^1$H NMR spectrum of the resulting BzF-Nov on the basis of the ratio of phenyl protons of benzoyl group (7.4-8.2 ppm) to methylene protons (3.4-4.0 ppm) and/or phenyl protons of Nov, as shown in Fig. 1. The degree of benzoylformylation decreased with the increase of the reaction temperature whose result was in good agreement with that of formylated Nov [3].

As the model reaction, photolysis of 2,6-dimethylphenyl benzoylformate (PhBzF) was performed in n-hexane by irradiation of deep UV for 3 min. The gaschromatogram of the reaction mixture indicated that reaction products consisted of two main components and
Isolation of the main products was carried out by thin layer chromatograph. Mass spectroscopic analysis of the products showed that the mass numbers (m/e) of the two main products are 210 and 226. IR spectra showed the characteristic absorption of ketone carbonyl at 1665 cm\(^{-1}\) and ester carbonyl at 1738 cm\(^{-1}\), respectively. These spectra strongly suggested that not only the decarbonylation but also the decarboxylation of PhBzF took place to yield 2,6-dimethylbenzophenone (BzPh) and 2,6-dimethylphenyl benzoate (PhBz) (Scheme 1).

Then, photolysis of BzF-Nov was carried out. The IR spectral changes of BzF-Nov before and after irradiation of deep UV were shown in Fig. 2. The absorption at 1670 cm\(^{-1}\) assignable to the ketone carbonyl of keto ester completely diminished and the peak ascribed to ester carbonyl shifted from 1745 cm\(^{-1}\) to 1730 cm\(^{-1}\) at the same time. These spectral changes accomplished by only 100 mJ cm\(^{-2}\). The \(^{13}\)C NMR spectra of BzF-Nov before and after deep UV irradiation also revealed that decarbonylation completely took place within 100 sec from the disappearance of the signal due to keto carbonyl at 185 ppm. The apparent quantum yield for photolysis of BzF-Nov was estimated to be 0.3, which is 30 times greater than that of poly(methyl vinyl ketone). Therefore, it was concluded that photolysis of BzF-Nov proceeds through only the decarbonylation to produce benzoyle novolacs (Bz-Nov) (Scheme 2). Further studies aimed at the application of BzF-Nov for micro lithography by using the difference of the reactivity between keto ester and ester with suitable primary amine are now in progress.

References