Model Reaction for Functionalization of Water-soluble Polymers －Reactivity of An Epoxy Compound with Tertiary Amines in Water－

Susumu Harashima, and Toshihiko Matsumoto*
Department of Life Science and Sustainable Chemistry, Tokyo Polytechnic University
1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan E-mail: matumoto@chem.t-kougei.ac.jp

Introduction

Recently, much attention has been paid to non-solvent or in-water reaction from the perspective of environmental protection.[1] In the present study, as a model reaction for functionalization of water-soluble polymers, the reactivity of an epoxy compound, glycidylmethacrylate (GMA), with water-soluble tertiary amines in water was investigated using NMR and FT-IR spectoroscopies.

Experimental

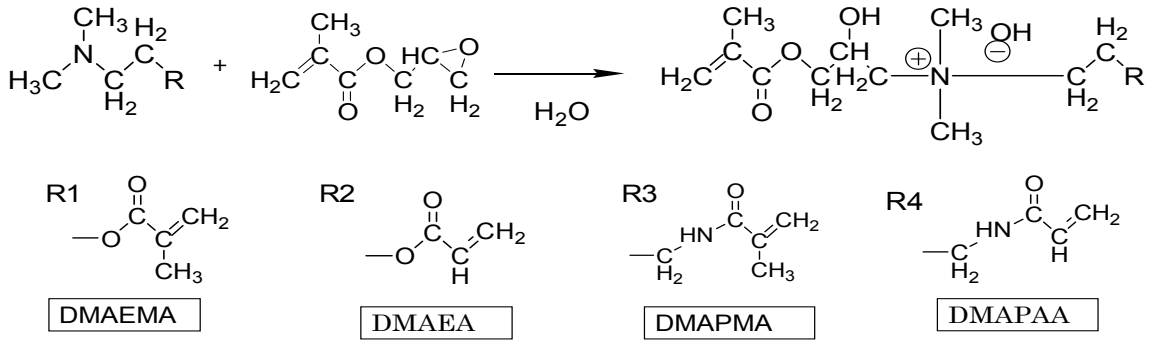
1. Reagents and Model reaction Glycidylmethacrylate (GMA), an epoxy compound having a polymerizable vinyl group, was reacted in water at room temperature for 6-15 hours with water-soluble tertiary amines such as dimethylaminopropylmethacrylamide (DMAPMA), dimethylaminopropylacrylamide (DMAPAA), dimethylaminoethylmethacrylate (DMAEMA), and dimethylaminoethyl acrylate (DMAEA). All the reagents were purchased from Wako Pure Chemical Industries Ltd., and Tokyo Chemical Industry Co. Ltd., and used without further purification.

2. Measurement FT-IR spectra were measured using a JASCO Plus 460 spectrophotometer. The NMR data were recorded on a JEOL JNM-LA 500 spectrometer with sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 as an internal standard in D_2O.

Results and Discussion

1. Analysis of the reaction products

The reactions of GMA with four kinds of water-soluble amines having a vinyl group, DMAPMA, DMAPAA, DMAEMA and DMAEA in water gave β-hydroxytetraalkylammonium hydroxides quantitatively (**Scheme 1**).



Scheme 1. Reactions of GMA with water-soluble tertiary amines in water.

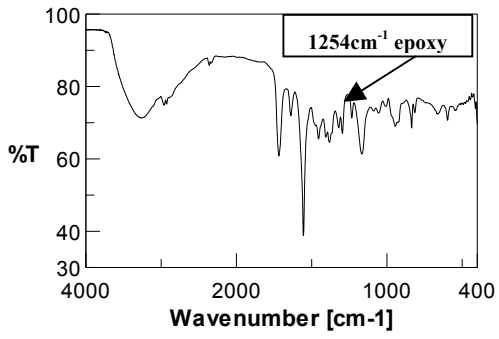


Figure 1. FT-IR spectrum of the product obtained from the reaction of GMA with DMAEMA in water.

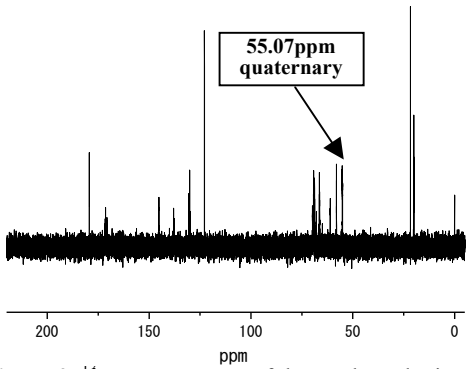


Figure 2. ^{13}NMR spectrum of the product obtained from the reaction of GMA with DMAEMA in water.

In the FT-IR spectrum (**Figure 1**) of the reaction product between DMAEMA and GMA, the peak 1254 cm^{-1} assigned to epoxy group is disappeared, and in the ^{13}C-NMR and CH-cosy spectra (**Figure 2** and **3**), a signal at 55.07 ppm assign to methyl group attached to nitrogen atom of quaternary amine

(β-hydroxytetraalkylammonium hydroxide) is observed. The chemical shift estimated roughly using the MO calculation is 47.5 ppm as illustrated in **Figure 3**. It is known that epoxy compounds undergo the ring-opening polymerization by a tertiary amine in bulk or in organic solvents. However, in water β-hydroxytetraalkylammonium hydroxides were generated by addition of the tertiary amine to the epoxy-ring instead of ring-open polymerization.

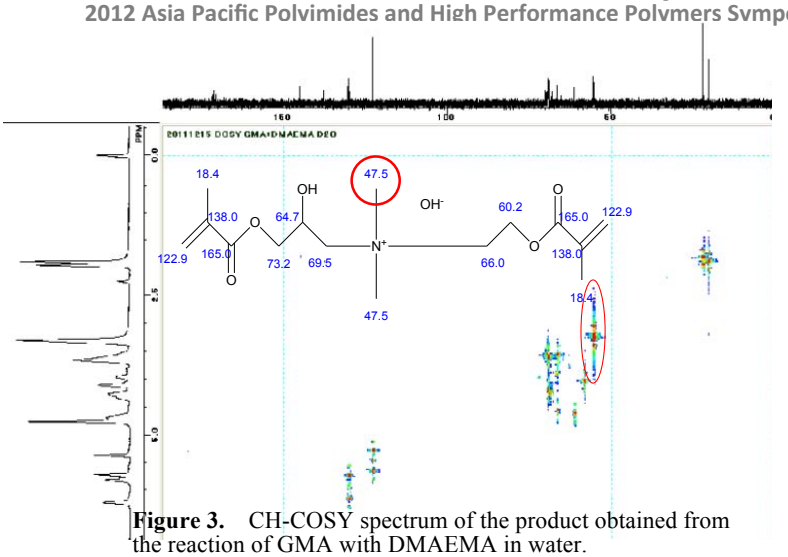


Figure 3. CH-COSY spectrum of the product obtained from the reaction of GMA with DMAEMA in water.

2. Reactivity of GMA with the tertiary amines.

The reaction of GMA with DMAEMA was carried out in an NMR tube. As can be seen from **Figure 4**, the signal intensity of β-hydroxytetraalkylammonium hydroxide increases with a decrease of that of tertiary amine. The reactivity (conversion) was evaluated from the ratio of vinyl-methylene proton of DMAEMA and dimethyl proton of β-hydroxytetraalkylammonium hydroxide in the ^{1}H-NMR spectrum (**Figure 5**). The reaction was completed practically in 2 hours, and the reactions of GMA with DMAPMA, DMAPAA, DMAEMA, DMAEA were proceeded in a similar manner.

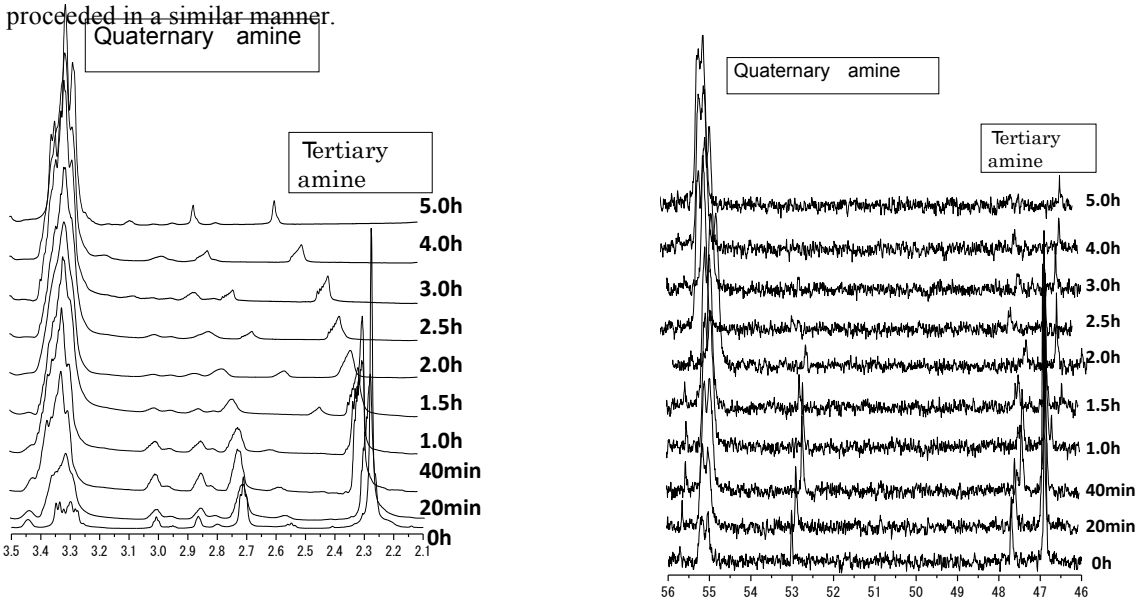


Figure 4. ^{1}H-NMR (left) and ^{13}C-NMR(right) spectra of the reaction mixture between GMA and DMAEMA in D_2O.

Conclusions

The reaction of an epoxy compound (GMA) with water-soluble tertiary amines having a vinyl group were carried out in water and the reaction products were analyzed using FT-IR and NMR spectroscopies. The reactions gave β-hydroxytetraalkylammonium hydroxides quantitatively in 2 hours. These findings are useful for functionalization of water-soluble polymers having a tertiary amine group.

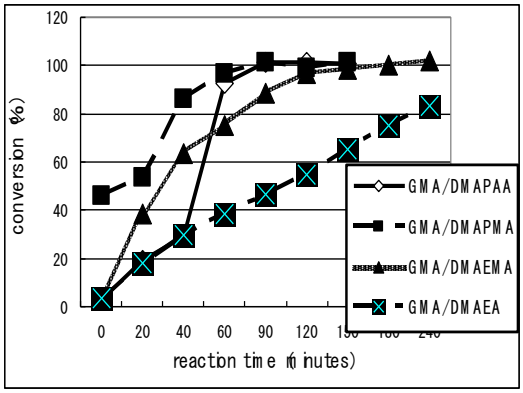


Figure 5. Reactivity of an epoxy compound (GMA) with tertiary amines in water.

Reference

1. Susumu Harashima, Toshihiko Matsumoto, *the Proceedings of Japan Polyimide and advanced Aromatic Conference*, **19**, 170(2012).