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SHORT COMMUNICATIONS

# Novel Synthesis of Self-Sensitized Photosensitive Polymers by Addition Reaction of Pendant Epoxide Groups in the Polymer with Some Cinnamic Esters

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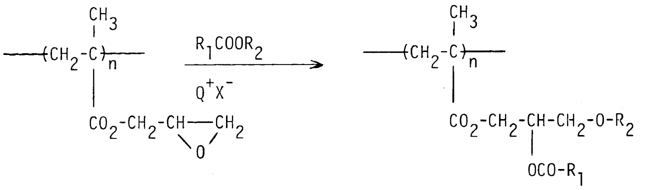
Poly(glycidyl methacrylate) and its copolymers have attracted much attention for their use as reactive polymers.[1] Previously, we reported the synthesis of photosensitive polymers by the addition reaction of poly(glycidyl methacrylate-*co*-methyl methacrylate) (PGMA) with carboxylic acids.[2] However, gel compounds were produced at the final stage of the reaction due to a side reaction of pendant epoxide groups with the resulting hydroxyl groups. Recently, we also reported[3] the synthesis of polymers having pendant cinnamic ester and chloromethyl groups by the addition reaction of PGMA with cinnamoyl chloride. This method has been found best for the synthesis of photosensitive polymers from PGMA, since no gel compounds form during the reaction. However, the polymers with pendant cinnamate groups prepared by these two methods were not sufficiently photosensitive and low molecular weight photosensitizers were necessary.

This communication describe a successful synthesis for highly photoreactive polymers having pendant cinnamate and 4-nitrophenyl or 4-nitro-1-naphthyl ether as photosensitizing groups for the cinnamate group,[4] by the addition reaction of PGMA with 4-nitrophenyl cinnamate[5] (NPC) or 4-nitro-1-naphthyl cinnamate (NNC) using quaternary salts as catalysts.



The PGMA (epoxide equivalent was 251, as determined by the reported method.[5] The inherent viscosity was 0.23, measured at 0.5 g dl$^{-1}$ in DMF at 30°C) 1.004 g (4 mmol) were dissolved in 10 ml of sulfolane followed by the addition of 1.077 g (4 mmol) of NPC and 0.066 g (0.4 mmol) of tetraethylammonium chloride (TEAC). The reaction mixture was stirred at 130°C for 24 h and then poured into ethanol. The reaction product was purified by reprecipitating twice from THF into methanol and finally dried *in vacuo* at 50°C. The yield of the recovered polymer was 1.68 g. The degree of reaction was 95.1 mol% (calculated from the elemental analysis of nitrogen). The inherent viscosity of this polymer was 0.21 (0.5 $\mathrm{g\,dl^{-1}}$ in DMF at 30°C). The IR spectrum (film) of the polymer showed absorptions at 1720 $\mathrm{cm^{-1}}$ due to $\mathrm{C{=}O}$ stretching (s), 1640 $\mathrm{cm^{-1}}$ due to $\mathrm{C{=}C}$ stretching (s), and 1520 and 1340 $\mathrm{cm^{-1}}$ due to $-\mathrm{NO_2}$ stretching (m). The $^1$H NMR spectrum ($\mathrm{CDCl_3}$) of this polymer showed signals of $\mathrm{C{-}CH_3}$ protons at $\delta=0.95$ ppm, $\mathrm{C{-}CH_2{-}C}$ protons of main chain at $\delta=1.90$ ppm, $\mathrm{O{-}CH_3}$ protons of methyl methacrylate at $\delta=3.50$ ppm, $\mathrm{O{-}CH_2{-}C}$ protons of the side chain at $\delta=4.30$ ppm, $\mathrm{C{-}\underset{\underset{C}{|}}{C}H{-}O}$ proton at $\delta=5.50$ ppm, $\mathrm{C{-}CH{=}CH{-}C}$ protons of cinnamate at $\delta=6.4$ and 7.7 (doublet) ppm, and aromatic protons of cinnamate and 4-nitrophenoxide at $\delta=6.95$—8.20 ppm. The degree of addition calculated from the intensity ratio of the $^1$H NMR spectrum was consistent with the value obtained from elemental analysis. Recently, Funahashi[6] reported the selective synthesis of 1-methyl-2-phenoxyethyl acetate by the reaction of methyloxirane with phenyl acetate using basic catalysts. This suggests that poly[2-cinnamoyloxy-3-(4-nitrophenoxy)propyl methacrylate-*co*-methyl methacrylate] (PCNPMA) is synthesized by the selective addition reaction of PGMA with NPC, using TEAC as the catalyst.

Other reactions of PGMA with esters such as NPC, NNC, 4-nitrophenyl benzoate (NPB), 4-chlorophenyl benzoate (CPB), phenyl benzoate (PB), and 4-methoxyphenyl benzoate (MPB) were carried out in a similar way and the reaction products were confirmed by elemental analysis, IR and $^1$H NMR spectra.

The reaction of PGMA with NPC proceeded to a high degree of conversion using

**Table I.** Addition reaction of PGMA with esters

| Ester (4 mmol) | Catalyst (0.4 mmol) | Solvent (10 ml) | Temp °C | Conversion mol% | $\eta_{\mathrm{sp}/c}$[a] |
|---|---|---|---|---|---|
| NPC | None | Sulfolane | 100 | 12.9 | Gel |
| NPC | TEA | Sulfolane | 100 | 71.4 | 0.52 |
| NPC | TEAB | Sulfolane | 100 | 93.7 | 0.20 |
| NPC | TPAB | Sulfolane | 100 | 92.8 | 0.20 |
| NPC | TBPB | Sulfolane | 100 | 89.0 | 0.18 |
| NPC | TEAC | Sulfolane | 90 | 49.5 | 0.23 |
| NPC | TEAC | Sulfolane | 100 | 59.6 | 0.23 |
| NPC | TEAC | Sulfolane | 130 | 95.1 | 0.21 |
| NPC | TEAC | Diglyme | 90 | 66.3 | 0.23 |
| NPC | TEAC | NMP | 90 | 67.9 | 0.22 |
| NNC | TEAC | Sulfolane | 100 | 34.4 | 6.31 |
| NNC | TEAB | Sulfolane | 100 | 70.5 | 0.33 |
| NNC | TEAC | Sulfolane | 100 | 53.6 | 0.32 |
| NNC | TEAC | Sulfolane | 130 | 83.5 | 0.30 |
| NPB | TBAB | Sulfolane | 100 | 89.4 | — |
| CPB | TBAB | Sulfolane | 100 | 71.8 | — |
| PB | TBAB | Sulfolane | 100 | 8.7 | — |
| MPB | TBAB | Sulfolane | 100 | 2.6 | — |

The reaction was carried out with 4 mmol of PGMA, 4 mmol of an ester and 0.4 mmol of a catalyst in 10 ml of solvent for 24 h.

[a] Measured at 0.5 $\mathrm{g\,dl^{-1}}$ in DMF at 30°C.

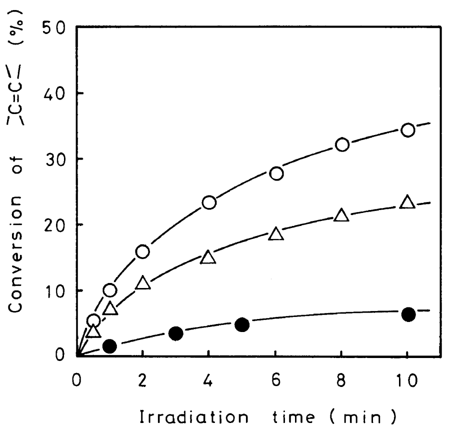


**Figure 1.** The disappearance rate of the C=C group of cinnamate in the polymers: (○), PCNPMA with the cinnamate of 94 mol%; (△), PCNNMA with the cinnamate of 72 mol%; (●), PCCMA with the cinnamate of 99 mol%.

other quaternary salts such as tetraethylammonium bromide (TEAB), tetra-*n*-propylammonium bromide (TPAB), and tetra-*n*-butylphosphonium bromide (TBPB) in sulfolane, diglyme or *N*-methyl-2-pyrrolidone (NMP). In addition, the degree of conversion of this reaction increased with the reaction temperature. The reaction did not proceed to a high degree of conversion in the absence of a catalyst and gel polymer was obtained. PGMA and NPC reacted to give a 71.4 mol% conversion at 100°C in sulfolane using triethylamine (TEA) as the catalyst. The inherent viscosity of the resulting polymer by this reaction was higher than that of the polymer obtained by the reaction using quaternary salts.

The reaction of PGMA with NNC also proceeded at 100—130°C in sulfolane using quaternary salts as catalysts, but gave a polymer with higher viscosity in the presence of TEA. The reactions of PGMA with NPB and CPB took place to relatively high degree of conversion at 100°C in sulfolane using tetra-*n*-butylammonium bromide (TBAB) as a catalyst, while the reactions of PGMA with PB and MPB occurred hardly at all under essentially the same reaction conditions.

The reaction of PGMA with active esters, having electron attractive groups in the phenoxide, is thus very useful for synthesizing polymers with two different functional groups in one step. In addition, some quaternary salts are excellent catalysts for the selective addition of PGMA to esters.

A THF solution of the polymer obtained was cast on a KRS plate and dried. The film (8 $\mu$m) on the plate was irradiated with a high-pressure mercury lamp (Ushio Electric Co., USH-250D) without a filter at a distance of 30 cm. The disappearance rate of the absorption of the C=C group at 1640 $\mathrm{cm}^{-1}$ was measured by IR spectroscopy (JASCO model A-202). As shown in Figure 1, the disappearance rate of the C=C bond of cinnamate in PCNPMA and poly[2-cinnamoyloxy-3-(4-nitro-1-naphthyloxy)propyl methacrylate-*co*-methyl methacrylate] (PCNNMA) was higher than that of the C=C bond in poly-(2-cinnamoyloxy-3-chloropropyl methacrylate-*co*-methyl methacrylate) (PCCMA), prepared by the reaction of PGMA with cinnamoyl chloride according to the reported method.[3] This indicates that the photochemical reaction of the pendant cinnamic ester in PCNPMA and PCNNMA may be sensitized by intramolecular pendant 4-nitrophenoxy and 4-nitro-1-naphthyloxy groups, respectively.

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