New Photosensitive Polymer Containing *o*-Methylphenacyl Photocage

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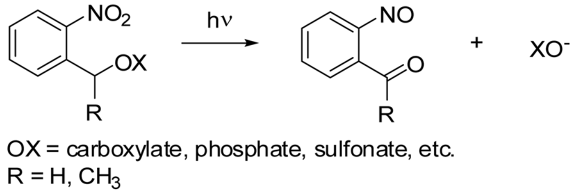
Photopolymers or photofunctional polymers have received much attention due to their application to many areas as photoremovable protecting groups in peptide synthesis, photolithography, photo resist, etc.[1] Such applications mostly exploit the photochemical reactions of the *o*-nitrobenzyl esters.[2] The usage of *o*-nitrobenzyl esters as photoremovable protecting group (also called 'photocage') was first introduced by Engels and Schlaeger[3] and the key reaction is shown in Scheme 1.

Recently many other types of photocage have been developed in organic chemistry.[4] However, the newly developed photochemical reactions have rarely been tested in the field of polymer chemistry. Continuing our efforts to elucidate substituent effects on photoreactivities,[5] we have recently investigated photochemical behaviors of *o*-alkylphenacyl halides and esters. Herein we report on preparation and photochemical property of a new photopolymer containing *o*-methylphenacyl group.

For synthesis of a new photopolymer, we decided to use radical polymerization of a methacrylic acid derivative having *o*-methylphenacyl group instead of using esterification of polymethacrylic acid. The latter method has widely been used in the synthesis of photopolymers with *o*-nitrobenzyl group.[2] The radical method was, however, preferred in our cases because we were also interested in photochemical properties of the monomer itself.

The monomer, *o*-methylphenacyl methacrylate, was prepared by substitution reaction of *o*-methylphenacyl bromide by methacrylic acid as shown in Scheme 2.

Polymerization of the monomer was performed by refluxing THF solution of the monomer containing AIBN as an initiator. The polymer, poly-*o*-methylphenacyl methacrylate (PMPMA), was obtained by precipitation from cold methanol solution of the reaction mixture. The formation of the polymer was evidenced by disappearance of ^{1}H NMR peaks corresponding to vinyl protons of the monomer, and by broadening of other peaks, which is the typical phenomena observed in polymer skeleton due to the reduced mobility. The molecular weight measured by GPC was 5,000.

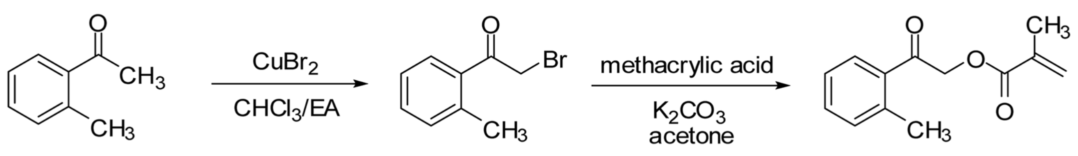


Scheme 1. Photochemical reaction of *o*-nitrobenzyl esters.

Before we investigated photoreactivities of the new polymer PMPMA, we decided to irradiate the monomer first. When the monomer was irradiated in benzene using the Pyrex filtered UV light, white precipitate was formed. IR spectrum of the solid showed the presence of carboxylic acid functionality and the solid turned out to be polymethacrylic acid from comparison with an authentic sample which was prepared separately. The filtrate of the reaction mixture was concentrated to give yellowish oil, which was identified as indanone according to its spectroscopic properties.

In order to obtain the more detailed information about the reaction, the photolysis was repeated using the sample made by dissolving the monomer in benzene-d$_6$ in an NMR tube. The degassed NMR sample was irradiated under the same condition as the above and the reaction was monitored by ^{1}H NMR spectra taken at regular intervals. Once again white precipitate was formed in the NMR scale photolysis, and the only product shown in the ^{1}H NMR was indanone. The result tells us that the indanone is formed before the monomer polymerizes. If the polymerization of the monomer occurs at comparable rate to that of indanone formation, the ^{1}H NMR of the reaction mixture would have shown the corresponding peaks to the polymer PMPMA, *vide infra*.

With photobehavior of the monomer at hand, we decided to irradiate the polymer PMPMA. Since the polymer was readily soluble in benzene, the NMR scale photolysis was done in benzene-d$_6$. Irradiation under the same condition as the above resulted in clean conversion to indanone and polymethacrylic acid which was precipitated out during the photolysis. Figure 1 shows ^{1}H NMR spectra before and after



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Scheme 2. Synthesis of the Monomer.

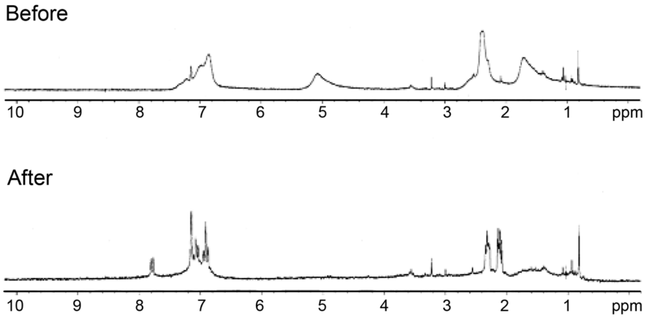


Figure 1. ^{1}H NMR spectra before and after irradiation of PMPMA in benzene d$_6$.

irradiation of PMPMA in benzene d$_6$.

Since the polymer can be more useful if it is photoactive in the solid state, we attempted the solid state photolysis of PMPMA. Samples were prepared in two ways; One way is to put the polymer powder in a sealed container. The other is to dip a thin glass plate in benzene solution of the polymer and to dry to make a thin layer plate. Even after prolonged irradiation, both samples remained unchanged.

Klan and Wirz have studied kinetics of photochemical reactions of 2,5-dimethyl phenacyl esters and reported that the photorelease rate of carboxylic acids is in the order of 10^2 s^{-1} in solution.[1] In our experiment with the monomer, *o*-methylphenacyl methacrylate, the formation of indanone was much faster than polymerization of the monomer. The monomer concentration typically used in our experiment did not exceed 0.02 M. In this low concentration polymerization of the methacrylate ester cannot compete with photorelease of carboxylic acids.

The polymer PMPMA formed indanone efficiently upon photolysis in solution as the monomer did. However, in the solid state, the polymer was inert in the reaction condition. The inertness can find explanation from the reaction mechanism of indanone formation. Scheme 3 summarizes the reaction mechanism suggested previously.[6]

The biradical intermediate formed from the triplet excited state has to rotate 180 degree along the axis connecting benzene ring and the benzylic carbon in order to form the final product indanone. Such a motion will be hindered in the solid state, which makes the formation of *E*-ortho-xylylenol difficult.

Here we have shown that the photocage of *o*-alkylphenacyl groups can be applied to polymer field. Even though the photoreaction of the polymer was successful only in solution, clean separation of polymer portion from solution upon photolysis would still find interesting application by itself. We are currently expanding our search of new photoresponsive polymer to other photocages developed more recently.

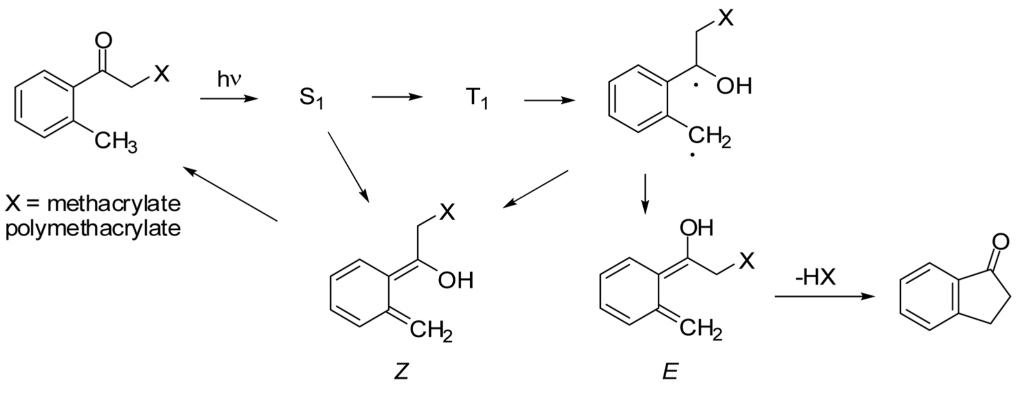
Experimental Section

Procedure for the synthesis of monomer.

***o*-Methylphenacyl bromide:** Bromination of *o*-methylacetophenone was performed using a known method.[2] Copper(II) bromide (3.66 g, 17.1 mmol) and ethyl acetate (15 mL) were placed in a round bottomed flask fitted with a reflux condenser. *o*-Methylacetophenone (1.00 g, 7.45 mmol) was dissolved in hot $CHCl_3$ (20 mL) and added to the flask. The reaction mixture was refluxed for 3 hrs. White precipitate was filtered and washed with $CHCl_3$. The organic layer was washed with aqueous $Na_2S_2O_3$, $NaHCO_3$ and distilled water. The aqueous layers were extracted with ether and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to give yellowish oil (1.55 g, 98%). The product was used for the next step without further purification. R_f = 0.51 (*n*-hexane:ethyl acetate = 7:1, v/v); ^{1}H NMR ($CDCl_3$, 200 MHz): δ7.68 (d, 1H, aromatic, J = 9.2 Hz), 7.37 (m, 3H, aromatic), 4.43 (s, 2H, -CH_2), 2.53 (s, 3H, -CH_3).

***o*-Methylphenacyl methacrylate:** A round bottomed flask was charged with methacrylic acid (0.78 g, 9.05 mmol), potassium carbonate (1.25 g, 9.05 mmol) and acetone (20 mL) and the mixture was stirred for 10 min. *o*-Methylphenacyl bromide (1.61 g, 7.54 mmol) dissolved in acetone was added to the flask. The reaction mixture was stirred for 24 hrs at room temperature. Potassium carbonate was filtered out and the filtrate was concentrated by rotary evaporator. The residue was dissolved in ether and washed with distilled water. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo to afford yellowish oil (1.60 g, 97%). The crude product was purified by column chromatography using *n*-hexane and ethyl acetate (7:1, v/v) as eluents.

R_f = 0.43 (ethyl acetate:*n*-hexane = 1:7, v/v); ^{1}H NMR ($CDCl_3$, 200 MHz): δ7.64 (d, 1H, aromatic J = 7.0 Hz), 7.35 (m, 3H, aromatic), 6.26 (d, 1H, =CH, J = 1.2 Hz), 5.67 (d,



Scheme 3. Reaction Mechanism of Formation of Indanone from *o*-Methylphenacyl Photocage.

1H, =CH, J = 1.2 Hz), 5.25 (s, 2H, -CH$_2$), 2.53 (s, 3H, -CH$_3$), 2.01 (s, 3H, -CH$_3$); ^{13}C NMR (CDCl$_3$, 50 MHz): δ 196.1, 166.9, 139.0, 135.7, 134.7, 132.3, 132.1, 128.1, 126.7, 125.8, 67.6, 21.1, 18.3; IR (neat): 1724, 1703, 1161 cm^{-1}.

Polymerization of *o*-methylphenacyl methacrlate. A similar method used by Janda was used.[8] A round bottomed flask was charged with the monomer (1.0 g, 4.58 mmol) and tetrahydrofuran (10 mL) and the solution was purged with argon for 10 min. 2,2'-Azobisisobutyronitrile (0.3 g) was added to the flask and stirred for 40 hrs at 60°C under the atmosphere of argon. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* to approximately 2 mL of THF. The residue was slowly poured to cold methanol. The precipitated polymer was filtered off and washed with cold methanol. Vacuum drying overnight at room temperature afforded 0.72 g of white powder.

Photolysis. *o*-Methylphenacyl methacrylate or poly(*o*-methyl)phenacyl methacrylate (PMPMA) in benzene (typically 0.01-0.02 M) was irradiated in an immersion well with argon bubbling using Pyrex filtered light of a 450 W Hanovia medium pressure mercury arc lamp. White precipitate was filtered off and the filtrate was concentrated at reduced pressure. The reaction product was analyzed by routine spectroscopic measurements. The structures of the precipitate and the product remained in the solution were confirmed by comparing them with authentic samples, polymethacrylic acid and indanone, respectively.

For NMR scale photolysis, an NMR tube containing the monomer or PMPMA in benzene-d$_6$ was degassed and irradiated by attaching it to the side of an immersion well using Pyrex filtered light of a 450 W Hanovia medium pressure mercury arc lamp. ^{1}H NMR spectra were taken at every 20 min.

For solid state photolysis, two different methods were used; Polymer powder was placed in a 10 mL sealed container and attached it to the side of an immersion well, which was irradiated as the above. Or a thin glass plate was coated with the polymer by dipping it into the polymer solution. The dried glass plate coated with the polymer was put in a sample vial and irradiated as the above.

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