

SYNTHESIS OF PHOTOBASE GENERATORS AND THEIR USE FOR DESIGN OF POLYMERIC PHOTSENSITIVE SYSTEMS

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Photoacid generators are now one of the key materials in photoresists and UV curings. On the other hand, photobase generators are also promising compounds in the microlithography and surface finishing technology. For example, new photobase generators sensitive to 366 or 436 nm-light are required as a catalyst for imidization of photosensitive polyimides and UV curings of epoxides by photobase generators are very promising in the surface finishing technology.^{1,2)}

We have investigated novel photobase generators for design of polymeric photosensitive systems and found that oxime derivatives are promising as photobase generators. In this paper we report synthesis and photochemistry of oxime derivatives and design of polymeric photosensitive systems.

O-Acyloximes (**1**) and O-carbamoyloximes (**2**) in Scheme 1 were prepared by the reaction of oximes with acid chlorides and isocyanates, respectively. Their photolysis was carried out in a solution or in polystyrene (PSt) films at room temperature in air or under nitrogen. A medium pressure mercury lamp (100 W) was used as a light source without filters unless otherwise mentioned.

In the photolysis of **1** in PSt films in the presence of benzophenone under nitrogen the main product was benzylamine and the yields for **1a** and **1b** were 70 and 90 %, respectively. Their yields decreased to 43 and 57 % in benzene, respectively. Quantum yields of photolysis of acetophenone O-acyloximes (**1a**) and 2-acetylnaphthalene (**1b**) in PSt films were 0.41 and 0.58 at 366 nm, respectively.³⁾

In the photolysis of **2a** at 254 nm under nitrogen, aniline and phenylhydrazine were detected with other products. Their yields were 30 % each in a tetrahydrofuran (THF) solution and those in poly(methyl methacrylate) films were 7 % for aniline and 35 % for phenylhydrazine. In the photolysis of **2b** in a THF solution, the yield of cyclohexylamine was 30%.

Resulting amines and hydrazine derivatives were used as crosslinkers for poly(glycidyl methacrylate) films.

Polymeric photobase generators bearing acyloxyimino (AOI) groups were prepared by the copolymerization of acetophenone O-acryloyloxime (AAPO) with comonomers. In the photolysis of AAPO(30)-St copolymer films, pendant amino groups were introduced effectively and the yield from AOI to amino groups was 70 % (Scheme 2). Irradiated copolymer films were soluble in organic solvents and the transformation of amino groups to ammonium groups made it possible for them to be soluble in polar solvents such as MeOH/water solutions. Furthermore, the irradiated films turned insoluble after the bake at temperatures over their glass transition temperature.⁴⁾

When AAPO copolymer films were irradiated in the presence of p-benzoquinone, irradiated films turned insoluble in organic solvents and the degree of insolubilization was