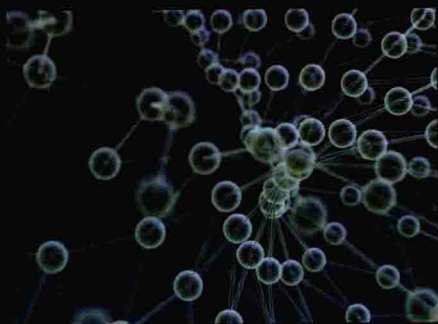
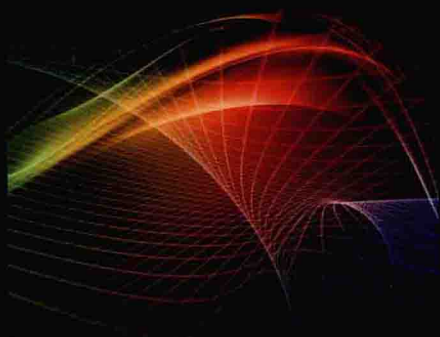




# Photopolymers

Photoresist  
Materials,  
Processes, and  
Applications



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**Kenichiro Nakamura**



**CRC Press**  
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# Photopolymers

## Photoresist Materials, Processes, and Applications



Kenichiro Nakamura



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# Photopolymers

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# Introduction

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Recent development of photopolymers has highly contributed to the improvement of sophisticated industries, especially in the electronics, optical engineering, and medical fields. Photopolymerization, photodegradation, and photo-crosslinking are basic ideas for photopolymers. The progress of lithography technology, in which photofabrications are performed by images of photopolymers, has given high densities to micro-products. Large-scale integrated (LSI) circuits are produced by lithography technology. Giga-scale electronic circuits are applied to central parts of computers.

Microminiaturization made it possible to employ millions of transistors in a single circuit. The reduction in size of transistors has dramatically lowered the cost of production and increased the speed of running electronic circuits. The first integrated circuit (IC) was 64 kilo-bits random access memory (RAM) by lithography technology in 1960. Since 1960, the growth in the number of components per chips has increased by  $10^7$ .

Resolution of photofabrication is limited by wavelength of exposure. The less time the wavelength is exposed, the higher the resolution is expected to be. In those 30 years, wavelength shifted from i-line (365 nm) via ArF (193 nm) to EUV (13 nm). It is projected to soon reach T memory (tera  $10^{12}$ ).

Photopolymers are applied to many fields including semiconductor device manufacturing, printing boards, optical engineering, medical materials, curing, printing plates, and microelectromechanical systems (MEMSs). Application fields are still expanding because of developing photopolymers. In this book, the progress of photopolymers will be summarized and reviewed, from basic idea to industrial application.

I thank the many persons who supported the publication of this book by Taylor & Francis. I express great pleasure to Prof. Moriaki Wakaki of Tokai University for suggesting this book be published. I thank Prof. Minoru Tsuda of Chiba University and Prof. C. Grant Willson of Texas University for their help in expanding my knowledge of photopolymers. I express many thanks to my son, Sohichiro Nakamura, and wife, Yukiko Nakamura, for supporting me during the preparation of this book.

**Kenichiro Nakamura**

*Tokyo*

*November 2013*



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## About the Author

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**Kenichiro Nakamura** graduated from Kanazawa University in 1963 and from the University of Tokyo with his doctorate in engineering in 1968. He received his postdoctoral fellowship from the University of Texas at Austin in 1968–1970. His work experience includes working for Prof. Albert Noyes in photochemistry and holding the positions of associate professor, Tokai University (1970–1978), professor, Tokai University (1978–2010), honorary professor, Tokai University (since 2010), and editor in chief of the *Journal of Photopolymer Science and Technology* (since 1998).

Nakamura has written several papers in his field that have been published in journals such as the *Bulletin of the Chemical Society of Japan*, *Journal of Applied Photographic Engineering*, and *Journal of Photopolymer Science and Technology*, among many others. He has also published many books, including *Photographic Science* (Kogakusha Press, 2004), *Fundamentals of Quantum Physical Chemistry* (Tokai University Press, 1996), and *Activities of Light* (Dainippon Library Co., 1993).





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# 1

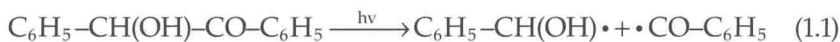
## *Basic Idea of Photopolymerization*

### 1.1 Introduction

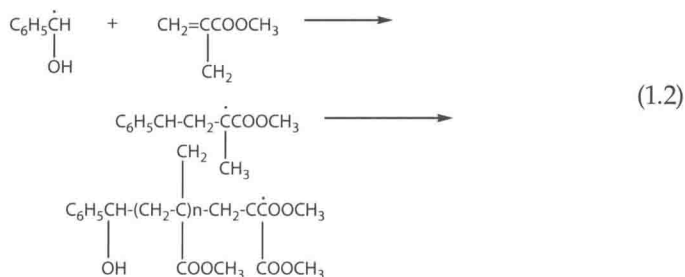
Photopolymerization is caused by radical or cationic initiation. It induces various changes in solubilities, adhesion, melting points, phases, and chemical and physical properties. Photopolymers were historically applied to photography and printing materials, and they have recently been applied to ultra-fine fabrication of electronic and mechanical devices. The photo-curing of paints, the curing of printing ink, and photo-adhesive agents are also performed by photopolymerization. Photo-crosslinking gives larger effects in solubilities of polymers. Therefore, photo-crosslinking is also an important field in photopolymerization. Photo-dissociation degrades molecular weight in polymers. Therefore, photo-dissociation must be included in photopolymerization. Those phenomena are discussed in this chapter.

### 1.2 Radical Polymerization

Many vinyl monomers are polymerized by light irradiation.<sup>1-3</sup> Photoinitiators are effective with polymerization. Irradiation to benzoin produces radicals:



Those radicals initiate polymerization of vinyl monomers. For example, methylmethacrylate is polymerized by the benzoin radical as follows:

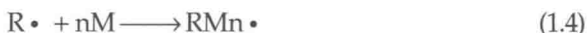


Thus, free radicals are emitted from benzoin propagate polymerization of an acryl monomer.

The scheme of photopolymerization is shown below:

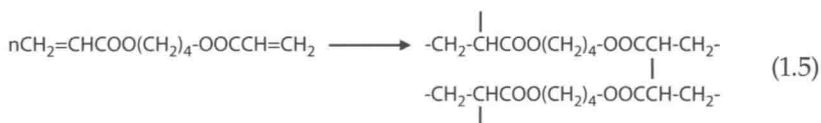


where  $A-R$  is a photoinitiator and  $R\cdot$  is a radical. The concentration of the radical is proportional to the intensity of the absorbed photon. More photons are absorbed on the surface of the coated layer than on the bottom of a thick layer. The radical induces polymerization of monomer.



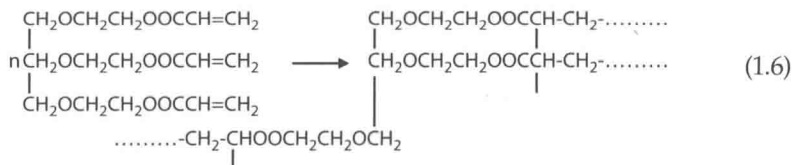
The polymerization is interrupted by radical scavengers such as oxygen or impurities existing in the coated monomer layer. Oxygen is a strong scavenger for radical polymerization. It invades the layer from the surface. Therefore, polymerization is disturbed, especially on the surface.

Acrylic acids and methacrylic acids are mostly applied to polymerize monomers. However, esters of their acids are generally used. Monofunctional monomers are basic monomers for photopolymerization and are used for dilution because of low viscosity. Bifunctional monomers induce crosslinking and hard coating. Polymerization of 1,4-butanediol diacrylate (BDDA) is shown below:



Network structures are induced by polymerization of bifunctional monomers.

Multifunctional monomers give a greater number of network structures. Ethylene-glycolglyceroltriacetate shows a three-dimensional network structure by polymerization:



More functional monomers are possible to apply to polymerization. Pentaeritoltetraacrylate,

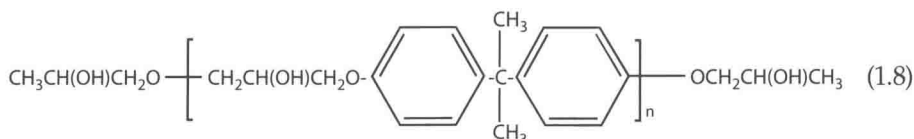


is a tetrafunctional acrylate. Multifunctional monomers give a harder coating than monofunctional monomers.

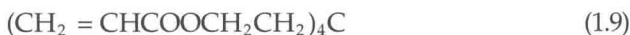
For improving viscosity and the physical properties of a coating layer, the introduction of a prepolymer is quite effective. Prepolymers are oligomers of suitable

molecular weight with photosensitive methacrylate groups. Various types of prepolymers are reported for obtaining physical and chemical properties.

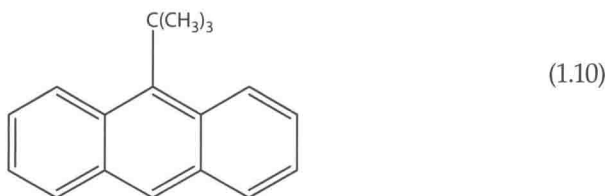
Epoxy prepolymers are widely applied to adhesives, paints, and plastics as thermal hardening resins. Epoxy prepolymers possess a couple of epoxy groups and are polymerized to insoluble by heating with hardening agents of multibasics and diamines. A combination of photosensitive monomers and epoxy prepolymers gives superior characteristics for photopolymerization systems. A combination of a molecular weight of about 1000 of epoxy resin,



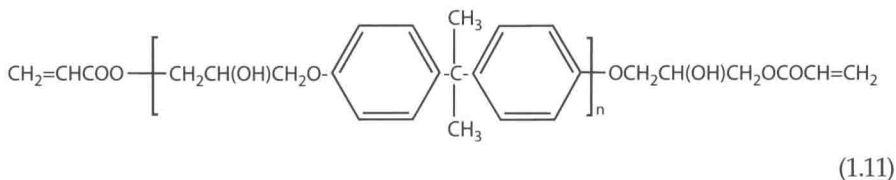
pentaerythritoltetraacrylate,



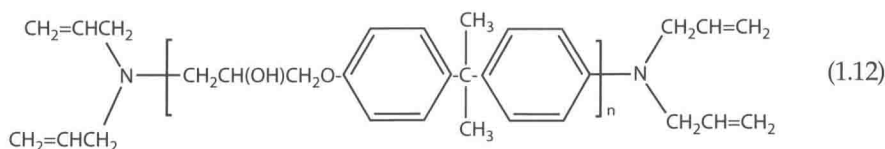
and an initiator of photopolymerization, 2-tert-butylanthraquinone,



give a good photosensitive dielectric layer. An acrylate of epoxy resin, bisphenol A-diglycidylether diacrylate,

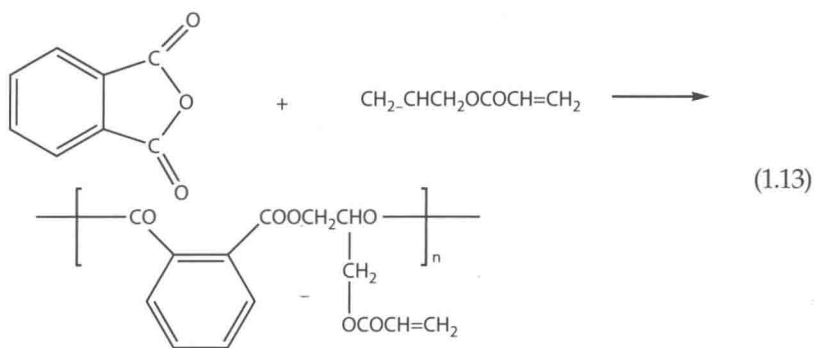


is a prepolymer of photo-hardening paint. A diamine of epoxy resin, bisphenol A-diglycidylether diallyldimaine,

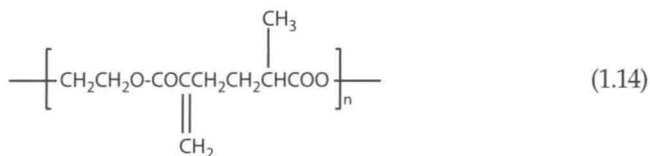


is also a prepolymer of photo-hardening paint.

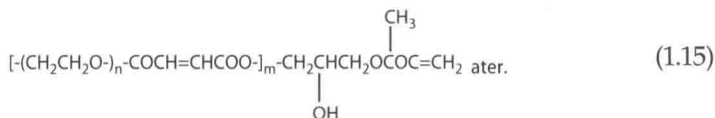
Many polyester acrylates are well known as prepolymers. A copolymerized ester of an open ring reacted on epoxypropylacrylate with phthalic anhydride:



The product is a prepolymer for photo-hardening paint. The ester of ethylene-glycoldiacrylate,

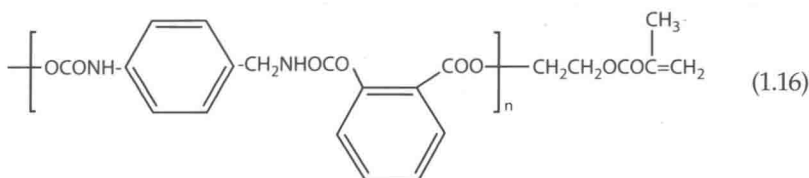


gives a good prepolymer for photo-hardening. An oligomer synthesized from polyethylene-glycol, maleic anhydride, and propyl alcohol of methacrylate,

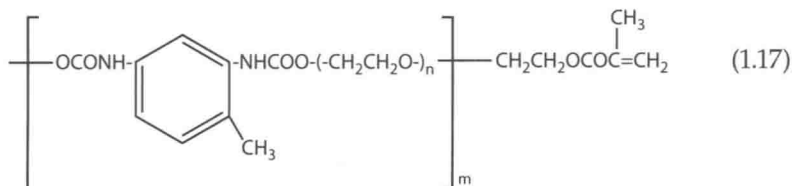


gives a prepolymer for highly sensitive photoresin developable by water.

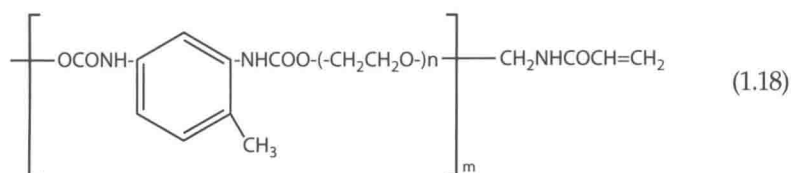
Polyurethans are elastic polymers and applied to photosensitive printing plates. Urethan synthesized from hydroxyethylphtharylmethacrylate and xylene-isocyanate,



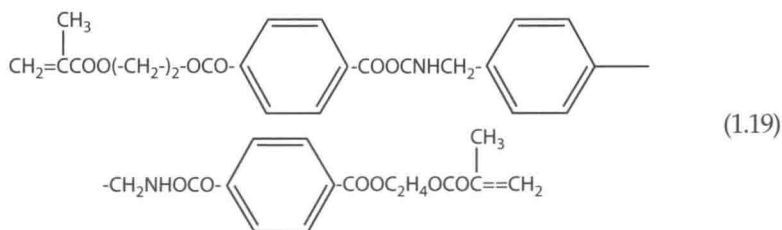
is a prepolymer for photosensitive printing plates. Polyurethan synthesized from polyethylene glycol, 2,4-toluene diisocyanate, and ethylmethacrylate,



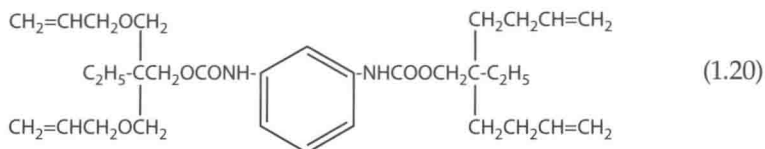
is a prepolymer for photo-hardening paints. Polyurethan synthesized from polyethylene glycol, 2,4-toluene diisocyanate, and N-methylacrylamide,



is also a prepolymer for photo-hardening paint. Dihydroxyethylphthalylmethacrylate xylene diisocyanate,



is a bifunctional urethane prepolymer. Polyurethan synthesized from trimethylolpropane diallylether and toluene-2,4-diisocyanate

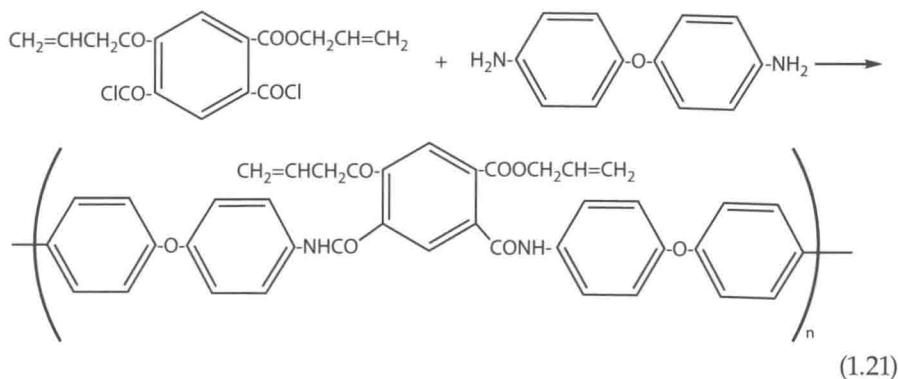


is a prepolymer for solder resistance of printing circuits.

Photopolymerize polymers bound by polyamides are applied to printing plates. They are mixed with polyamides soluble to alcohol

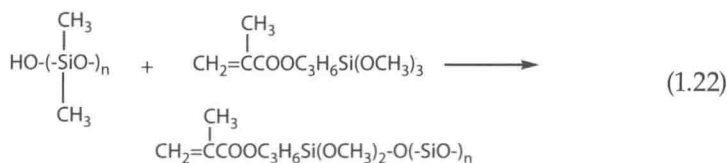


and multifunctional monomers. Dichlorodiallylester of pyromellitic acid reacted with *p,p'*-diaminodiphenylether,

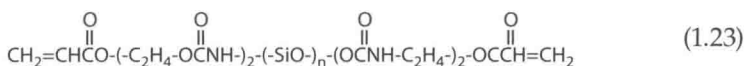


is prepolymer for a heat-resistant photoresist.

Silicone acrylate resists are prepolymers for water and chemical resistivity with inactive surfaces. Silicone resist is applied to a dry-plane printing plate because it is not adhesive with printing ink.<sup>4</sup> A prepolymer synthesized from dimethylpolysiloxane  $\gamma$ -methacryloxypropyltrimethoxysilane is a silicone resist:



Polysiloxane diisocyanate-2-hydroxyethylacrylate,



is a silicone prepolymer for printing boards and coatings. Methylbutylacrylate polysiloxane,



is a photosensitive silicone prepolymer.