

## Polymers in Imaging Systems

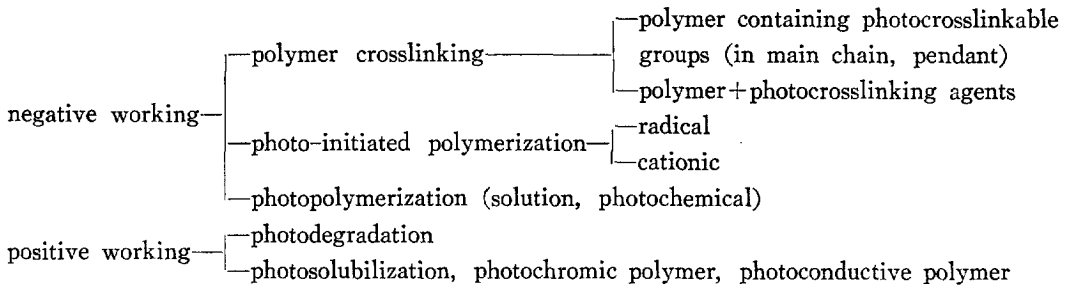
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### Introduction

Photopolymer systems have been well investigated and applied to the imaging technology. The term photopolymer system includes a

number of processes which use polymers for image-formation, but, which are quite different photochemically. These systems are classified conveniently as follows:

#### Classification of Photopolymer Systems



The photopolymer systems are capable of producing results of good image quality with a short access time and a simple or dry processing. The image-formation processes of the photopolymer systems are based on differences between the exposed and the unexposed regions in the photosensitive layer being in their physical properties, namely, in their solubility, thermal transition, tackiness, adhesion, cohesion, diffusion, and light scattering, etc. Special readout methods are, therefore, necessary to produce images.

The photopolymer imaging systems have the following characteristics:

(i) These systems can mostly be photochemically sensitized by adding chemical sensitizers (e. g., aromatic ketones) or organic dyes to

extend their spectral sensitivities from uv to visible region.

(ii) These systems have a relatively high resolution as compared to other unconventional imaging systems, and have a high contrast (inferior in tone reproduction).

The image-forming photopolymer systems have been widely applied to practical uses, namely, in the manufacturing of printing plates (relief, lithographic, and flexographic plates), photore-sists, screen inks, and solder resists, etc.

### Photo-initiated Polymerization

When polymerization is induced by initiating species produced by light, it is termed photo-initiated polymerization<sup>1</sup>. Photo-initiated polymerization involves a chain reaction, and hence, photographic amplification can be expected. Formation of polymerization-initiating species is

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a key step, which can be sensitized by adding suitable sensitizers.

In the most practical systems, the basic composition of the photosensitive layer is as follows: (i) ethylenically unsaturated multi-functional monomers or prepolymers, (ii) photo-initiators (sensitizers), (iii) thermal polymerization inhibitors, and (iv) organic polymeric binders. Adhesives, plastisizers, fillers, colourants and antihalation agents, etc, may be added optionally for particular purposes.

Choice of monomers is particularly important because monomers play an important role in governing chemical reactivities of the system and physical properties of the resulting polymers, e. g. hardness and crosslinked density etc<sup>2</sup>. Branched and polyfunctional monomers are generally considered to result in the formation of highly crosslinked polymers with low flexibility. Whereas monomers having the flexible chains such as polyethylene glycol derivatives give flexible polymers with low crosslinked density.

A wide variety of methods of photo-initiation has been proposed. As a whole, the free radical capable of initiating polymerization may be generated by one of the following photochemical reactions: (i) photodecomposition, (ii) hydrogen transfer, and (iii) electron transfer.

Free radical formations by decompositions of excited photoinitiators account for polymerizations initiated by benzoin derivatives, peroxides, disulfides, organic halides, and azo-compounds. These initiators are usually thermally unstable and hence, they shorten shelf-lives of the photosensitive coatings.

Aromatic carbonyl compounds having  $n-\pi^*$  triplet states as the low-lying excited states such as benzophenones, and quinones have been reported as good initiators for the vinyl polymerizations<sup>3</sup>. This fact is accounted for on the

following ground. Namely, the  $n-\pi^*$  triplet excited molecules can easily abstract hydrogens from the surroundings with high quantum efficiencies to produce free radicals which initiate polymerizations. Whereas the aromatic carbonyl compounds having  $\pi-\pi^*$  triplet states as the low-lying excited states abstract hydrogens with quite low efficiencies, so that they are supposed to be poor initiators. However, combinations of such aromatic ketones with electron rich donors, aromatic or aliphatic amines, are found to be quite efficient polymerization initiators<sup>4</sup>. These aromatic compounds are exemplified by fluorenone, xanthone, and naphthyl carbonyl compounds. This sensitization can be understood on the following base. Namely, such aromatic compounds are excited to the low-lying  $\pi-\pi^*$  triplet states on irradiation and then the triplet molecules interact with electron rich amines to form the corresponding exciplexes, which decompose by electron transfer processes to give radical cations and radical anions. The ionic radicals are finally transformed to free radicals via hydrogen transfer reactions, and initiate polymerizations. Therefore, these systems are called photoredox polymerization initiating systems<sup>5</sup>.

The phenothiazine dye(photo-oxidant)/organic sulfinic acid (reductant)-acrylic monomers has been known to be a photoredox photo-initiated polymerization systems<sup>6</sup>.

One of the disadvantages of photo-initiated polymerization reactions is that free radicals may react more rapidly with oxygen than with monomers. This results in an induction period during which time oxygen contained in the polymerizable coating is consumed and in extreme case may prevent polymerization from occurring if oxygen diffuses into the coating during the exposure<sup>7</sup>. Several methods have been proposed to remove the oxygen effect in photo-

initiated polymerizations. Addition of trialkyl phosphites as reducing agents minimizes the oxygen effect because such reducing agents effectively react with molecular oxygen<sup>8</sup>. An electron rich compound such as 1,3-diphenylisobenzofuran is often added to the coatings as a singlet oxygen scavenger<sup>9</sup>.

Photo-initiated polymerizations have been widely applied for graphic arts technology such as lithographic printing plates, letterpress plates, resists, and colour proofings.

### Photo-initiated Cationic Polymerization

Certain electron rich monomers are polymerizable in the presence of cationic initiators. When such cationic initiators are produced by light, the system is termed photo-initiated cationic polymerization.

In contrast to photo-initiated radical polymerizations, the cationic polymerizations are not inhibited by oxygen. The initiators used in this system are "onium" salts<sup>10,11</sup> such as phenyl diazonium, diphenyliodonium, and triphenyl sulfonium salts having complex metal halides as counter anions, e.g.  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ , and  $\text{SbF}_6^-$ , etc. These onium salts easily decompose on irradiation to afford Lewis acids or Brønsted acids, which initiate cationic polymerizations. Some of such initiators, e.g. iodonium and sulfonium salts, are sensitized by common sensitizers such as anthracene, perylene, phenothiazine, and Michler's ketone.

There has been reported an elegant application of photopolymer systems called "Bell & Howell's camera-speed photo-initiated polymerization system"<sup>12</sup>. This system is a combination of N-vinylcarbazole and  $\text{CBr}_4$  dispersed in a gelatin matrix as droplets of 0.5 to  $20\mu\text{m}$ . The image-formation is performed by the following two successive photo-irradiations. Namely, the first image-wise visible light exposure with low

intensity causes a photo-initiated polymerization of N-vinylcarbazoles (colourless change of the monomer) by initiators formed by photodecomposition of N-vinylcarbazole- $\text{CBr}_4$  charge-transfer complex which is sensitive to visible light. The initiator could be  $\text{Br}^\cdot$ ,  $\text{CBr}_3^\cdot$  and/or  $\text{HBr}$ . A great number of N-vinylcarbazole monomers is efficiently deactivated by such polymerization reaction in the exposed region. Then, this photosensitive layer is subjected to the second over-all uv exposure with high intensity. In this process, a very large number of photo-activated molecules and photodecomposition products of  $\text{CBr}_4$  are present, and mutual reactions by substitution in preferential positions of carbazole nuclei give rise to colour formation.

The photographic characteristics are as follows: (i) high sensitivity, ca  $300\text{ erg/cm}^2$ , (ii) dry processing, (iii) continuous tone reproduction, (iv) positive working, (v) short shelf-life.

### Photopolymerization

Photopolymerizations can be defined as a process in which every polymerization step involves a photon absorption, and are exemplified by photochemical cycloadditions of monomers having dichloromophoric moieties with give rise to the polymer containing a repeated cycloalkane unit structure<sup>1</sup>.

The photopolymerizations occur in solutions, in amorphous matrices, or in crystalline states. These photopolymerizations are formally classified into four types of basic reactions:

(i) [2+2]cycloaddition, (ii) [4+2]cycloaddition (Diels-Alder type reaction). (iii) [4+4] cyclo addition, and (iv) oxetane formation reaction (Paterno-Büchi reaction).

The [2+2] cycloaddition involves the photochemical cyclobutane formation reaction and is exemplified by photopolymerizations of 2,5-distyryl pyrazines, phenylene diacrylic acids<sup>13</sup>,

N, N'-polymethylene-bis-dichloromaleimides<sup>14</sup>, and bis-coumarines<sup>15</sup>.

The [4+2] cycloaddition is also called Diels-Alder type polymerization and basically forms a six-membered ring by a light-induced thermal reaction. Irradiation of bis-maleimides in the presence of benzene forms a tricyclo[2, 2, 2]-octane system as a primary photoproduct followed by a photochemical [2+2] cycloaddition to lead a photocondensed complex polymers<sup>16</sup>. Photodimerizations of bis-anthracenes follow [4+4] cycloaddition<sup>17</sup>.

Oxetane formation reactions also lead to polymerization of aromatic diketones in the presence of diolefinic compounds (tetramethylallene, or furan<sup>18</sup>) via  $n-\pi^*$  triplet states.

Solid state polymerizations were recently reported and should be classified as photopolymerization reaction. The polymerizations of monomers having conjugated triple bonds turn out to be a versatile method for synthesis of crystalline polymers of high molecular weight exhibiting a fully conjugated backbone<sup>19</sup>. The reaction is best described as an 1,4-addition polymerization of the conjugated triple bonds giving rise to a polymer with three cumulated double bonds per repeating unit. The all trans configurations of the double bonds is a consequence of the solid state reaction mechanism and of the packing of the molecule in the monomer lattice. The solid state polymerization is expected to be used as a new dry process-recording material for a real time holography.

### Photocrosslinking

Photocrosslinking reactions involve radiation-induced crosslinking of polymer chains either by monomers or by radiation-sensitive crosslinking agent incorporated in a polymer matrix or by the use of polymers which have photocrosslinkable groups attached to the polymer chain.

Dichromated colloids are examples of the former process and polymeric azide compounds are examples of the latter system. Photocrosslinking reactions are the reactions leading to insolubilization of polymers in exposed areas. The attachment of photodimerizable functional groups to a polymer skeleton therefore provides a means of crosslinking and insolubilizing the polymer on exposure to light. This reaction leads to a three-dimensional insoluble network resulting from multiple dimerization reactions. The most well known photodimerizable group is the cinnamoyl group which undergoes cyclodimerization to form a cyclobutane ring between the chains containing the group. The polymers having cinnamylidenes, chalcones, coumarins, or stilbazoliums<sup>20</sup> as photodimerizable groups result in photocrosslinking reactions on irradiation. Recently, a kodak research group reported a new type of photocrosslinkable polymers having 1,2-diphenylcyclopropene-3-carboxylate<sup>21</sup>.

Photocrosslinking induced by nitrene radicals produced photochemically from aryl azides or arylsulfonylazides is also very important in the practical application. Photochemically formed nitrene radicals are extremely reactive and can give rise to crosslinking of polymer chains by various reactions, e. g. insertions to C-H bonds, hydrogen abstractions, and additions to double bonds, etc.

These reactive azides can be either used as lateral substitutions on polymer chains or added to suitable polymer binders as a bifunctional derivative represented by  $N_3-Ar-N_3$ .

By addition of the suitable sensitizers, the photosensitivity of the photo-imaging systems based upon photocrosslinking reactions greatly increases and the spectral response of such systems is also extended to much longer wave lengths. Effective sensitizers are found to be aromatic nitro and keto compounds via probably

a triplet-triplet energy transfer mechanism.

The general requirements for the photosensitizer are as follows: (i) triplet energy of the sensitizer has to be larger than that of energy acceptor (photodimerizable functional group or crosslinking agent), (ii) sensitizer has to have a high triplet quantum yield, and (iii) long triplet life-time of sensitizer is preferable.

Recently, 2-benzoylmethylene-1-methyl- $\beta$ -naphthothiazoline<sup>22</sup> and triphenyl pyrylium salt derivatives<sup>23</sup> having triplet energy of ca 51-56 Kcal/mol were found to be excellent sensitizers for photocrosslinkable systems as well as photo-initiated polymerizations.

Chemistry of diazonium salts have been extensively studied and practically applied to the imaging technology. These salts decompose photochemically to liberate nitrogen gas depending on the structures and the reaction media. These salts react easily with electron rich phenolic compounds or aromatic amines, called coupler, to result azo dyes.

The polymers containing diazonium salts are water soluble because of their ionic character, whereas these polymers become insoluble on exposure to light because of decomposition of the hydrophilic diazonium functions. Various imaging processes have been developed on these chemical properties.

### Photodegradation

Photochemical degradation reactions of polymers are well known processes. In general, polymers having polyvinylidene type structures ( $-\text{CH}_2-\text{CR}_1\text{R}_2-$ ) photochemically degrade, but polymers having polyethylene type structures ( $-\text{CH}_2-\text{CHR}-$  or  $-\text{CH}_2-\text{CH}_2-$ ) result in crosslinking reactions on irradiation<sup>24</sup>.

The polymers having the carbonyl groups are photosensitive and degrade by Norrish type bond cleavage reactions. The photochemical primary

products are radical species which cause the subsequent bond scission reactions to fragment the polymer structure, and initiate oxidations (hydrogen abstractions) to result in the formation of additional chromophores. The resulting chromophores are usually sensitive to photo-oxygenation and accelerate the degradation reactions.

The dye-sensitized photo-oxidative degradations have been known for a long time. Methylene blue, crystal violet, xanthone and acridine red, etc, are typical sensitizers for photo-oxygenations<sup>25</sup>. The reactive species involved in the photo-oxygenations are the singlet oxygen formed by triplet energy transfer of the sensitizing dyes to the triplet ground state oxygen. The singlet oxygen is highly reactive to the electron rich double bond because of its electron deficient nature. The singlet oxygen reacts with olefinic compounds to yield allylic peroxides or often to give oxetanes, both of which are thermally unstable and decompose to initiate degradations of polymers.

Polyoxymethylene containing o-nitrophenyl groups is reported recently for new facile photodepolymerizable polymers to give positive relief images by dry process<sup>26</sup>. This unique photodepolymerization process is based on thermally metastable polyoxymethylene units decapped by photochemically efficient transformation of o-nitrophenyl chromophore in the exposed area at 350 nm. Development and amplification requires heating above 100°C to cause unzipping of the uncapped polyoxymethylene chain.

### Photosolubilization

This system can be represented by o-quinone diazide in coatings. Photolysis of o-quinone diazides is known as S<sub>1</sub>S reaction. Irradiation of o-quinone diazides affords an indenecarboxylic acid derivative via a photochemically formed ketocarbene intermediate in the presence of

water. The resulting indenecarboxylic acid is soluble in alkaline media, and hence, the preferential elimination of the exposed area is attained. Spectral sensitivity of this system is situated between 300 and 450 nm and efforts to sensitize this system have failed up to now. The intrinsic sensitivity of this system using phenol-formaldehyde resins as binders is approximately  $ca\ 10^5\ \text{erg/cm}^2$ .

O-Quinone diazide photographic systems are mainly used for manufacturing positive working offset printing plates, positive working photoreists in the production of printed or integrated circuits, colour proofing systems, and negative working systems in the special cases. Various efforts to modify the chemical structure of o-quinone diazide resin have been attempted to improve the practical performance.

### Photochromic Polymer

Certain organic compounds show a change in colour when they are exposed to electromagnetic radiation, but return to their original state in the dark. The reversible colour change is called photochromism. The photochromism is mostly a photo-isomerization reaction such as cis-trans isomerizations, tautomerizations, photoenolizations, and photo-induced skeletal rearrangements, etc. The main characteristics of this process is its reversibility which distinguishes it from all other photosensitive imaging systems. Therefore, images produced by photochromism are really of a more transient nature and so far no reliable or satisfactory process has been found to stabilize them in order to produce "hard copies". Fixing is very important in the practical use but no successful methods for fixation have not been developed. Amplification of photochromic process does not appear to be feasible in view of the reversible nature of the process and competing side reactions.

The incorporation of the photochromic compounds in the polymer has been shown to reduce the thermal self-bleaching or reverse reaction, and therefore, offer some advantages in imaging systems. The polymers containing spiropyran<sup>27</sup>, mercuric dithizonates<sup>28</sup>, azobenzenes, and viologens are synthesized and studied for photographic applications.

### Photoconductive Polymer

Photoconductivity in certain polymers is of considerable current interest. Photoconduction involves two distinct processes, namely, photo-carrier generation and photocarrier transportation. When the polymers have these two functions properly, they are called photoconductive polymers<sup>29</sup>.

The photoconductive polymers ever synthesized are divided into three classes from the structural point of view: (i) polymers having highly conjugated bonds in the main chain, (ii) polymers having polynuclear aromatic groups with large  $\pi$  electron systems, and (iii) polymers having diversified aromatic amino groups. Such polymers usually are photosensitive to uv light to generate carriers, and transport charge carriers in the applied electric field. In order to extend their spectral sensitivities into the visible region, cationic dyes or electron acceptors are generally added.

Most of the photoconductive polymers containing an electron rich group such as polyvinyl-carbazole transport holes more efficiently than electrons, and therefore, these materials are coated on organic or inorganic carrier generating materials such as organic pigments or amorphous selenium to increase photoconductivity.

The chemistry of photoconductivity has so far been little understood, and has been extensively investigating.

## Tendencies

The polymer systems except electrophotography have a rather low sensitivity, which restricts a successful penetration in the broad field of photographic applications. Hence, the photopolymer systems have mainly been used in the graphic field. In contrast to other photopolymer systems, the photo-initiated polymerization reaction exhibits an inherent amplification possibility by its intrinsic chain reaction character, but such a polymerization can proceed thermally to shorten the shelf-life of its system. The improvement of the shelf-life in this system remains as an unsolved problem.

Development of spectrally sensitizable and thermally stable photopolymer systems are becoming important because the evolution of laser technology will permit the use of such photopolymeric recording materials.

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