

PHOTOPOLYMERIZATION

ROGER PHILLIPS

Research and Development Division, Metal Box PLC, Wantage, Oxon. OX12 9BP (Gt. Britain)

(Received December 22, 1983)

There are two major classes of reactions involved in photopolymerization [1]. In type 1 each increase in molecular weight involves an intermediate excited state. Practical applications usually involve the formation of cross-links between pre-existing polymer chains. The photochemically active cross-linking group may be part of the chain, appended to it, or part of a separate difunctional cross-linking agent. It is the cross-linking group which is excited, either by direct absorption of a photon or by energy transfer from a photosensitizer. The photo-cross-linking reaction finds its main use in photoresist technology, to insolubilize resist materials used in the preparation of printing plates, printed circuit boards and integrated circuits. The last few years have seen a dramatic expansion in the use of photoresists and a growth in the use of synthetic materials at the expense of systems based on natural colloids such as gelatin. The demands made on materials and methods are constantly increasing and have brought about rapid developments and an extensive patent literature. The most common photo-cross-linking types in current use are those based on the photodimerization of pendant cinnamate groups and the use of bisazides to cross link cyclized rubbers.

In type 2 photopolymerization an excited photoinitiator molecule yields an initiating species, a radical or an ion, which interacts with monomer to give polymer by a chain reaction. Type 2 photopolymerization is used for photoresists, but its main practical application has been for the drying and hardening of protective and decorative surface coatings, a process known as "UV curing".

The potential of UV curing as a method of eliminating non-reactive solvents and time-consuming or energy-intensive drying processes was realized in the late 1940s, but early experiments based on drying oils in combination with free-radical generators such as carbon tetrabromide were unsuccessful. The first viable systems were developed in the early 1960s and were in widespread use in the woodfinishing industry by the late 1960s. They were based on unsaturated polyester resins combined with available vinyl-type monomers, such as styrene, and using photoinitiators such as sulphonyl chlorides and benzoin ethers. These early formulations were similar to existing thermally curing systems based on unsaturated polyesters, the only significant difference being the substitution of a photoinitiator for

the thermal radical generator. Although these early formulations worked reasonably well on slow woodfinishing lines they had limitations which prevented more widespread use, particularly in the high speed printing and coating operations used in the packaging industry. Cure was slow, oxygen inhibition of cure pronounced, the cured resin often rather brittle and the monomers were volatile and odorous. Styrene, being a powerful triplet quencher, prevented the use of several promising ketone-amine photoinitiator systems.

Around 1970 a new generation of UV curing formulations appeared. These were based on the free-radical addition polymerization of the acrylate double bond, which, once initiated, takes place very rapidly at ambient temperature. Whereas previous formulations had used materials already available, for this new generation it was necessary to synthesize special oligomer resins with acrylate functional groups. These were made by attaching acrylate groups to resin types commonly used in surface coating technology, such as epoxides, urethanes and polyesters. A wide range became available to allow the formulator to obtain the functional performance required in the cured coating. Available acrylate monomers were monofunctional and rather volatile, and therefore it was necessary to synthesize special acrylate esters of low volatility to be used as reactive diluents. It was realized that a polyfunctional monomer would allow more rapid cure and a more highly cross-linked cured polymer, and therefore these special diluents were prepared by reacting polyols such as trimethylolpropane with acrylic acid.

The use of the acrylate functional group allowed the use of ketone-amine systems as photoinitiators. The ability of excited ketones to abstract hydrogen from amines via the formation of charge transfer complexes had been the subject of intensive academic study in the late 1960s, which laid the foundations for the use of aromatic ketones and tertiary amines as radical-generating photoinitiators. A mix of benzophenone and Michler's ketone was found to be particularly effective, especially in pigmented formulations. The better photocleavage-type initiators gave faster cure at low concentrations than combinations of ketones and aliphatic amines, but amines were found to provide some protection against oxygen inhibition effects [2].

The majority of the UV curing formulations used today are still of the acrylate type, but there have been many refinements made since the early 1970s. The concern for health and safety in the working environment has been a major influence. Acrylate monomers were investigated for their skin and eye irritation potential, and some of those used in the early days were later replaced by types with lower Draize values. Michler's ketone came under suspicion as a possible carcinogen and its use was discontinued by many formulators. Another aromatic tertiary amine, ethyl-4-dimethylaminobenzoate, was found to be effective, and as this had been used for many years in skin lotions it was felt to be a safer alternative.

As the range of applications of UV curing expanded, the demands on the photoinitiator systems used became more severe. Ideally the photo-

initiator system should respond well to the spectral output of an available light source, and in particular that of the medium pressure mercury lamp [3], and give a high yield of reactive radicals even when used at low concentrations. Its photolysis products should not detract from the properties of the cured coating by being coloured, odorous or toxic, or likely to cause degradation of the cured polymer. It must of course be soluble in the oligomer-resin mix. It should be a poor thermal initiator, so that premature gellation before use does not take place. For some applications involving high pigment concentrations a photoinitiator with a high absorption in a spectral region of reasonable pigment transmission is required. Almost all commercially successful photoinitiators have been aromatic carbonyl compounds. These have absorption spectra which allow them to respond well to the wavelengths emitted by the medium pressure mercury lamp, and a high rate of intersystem crossing favours the formation of a metastable chemically reactive triplet state. The majority of photoinitiators operating by a hydrogen abstraction mechanism can be notionally derived from benzophenone, and those operating by a cleavage mechanism from acetophenone. Benzoin ethers were found to give premature gellation, a problem associated with the benzylic α hydrogen atom, and a logical development was the synthesis of acetophenone derivatives without both a hydrogen atom and an aromatic ring as α substituents, to give, for example, α,α -dimethoxy- α -phenylacetophenone, α,α -diethoxyacetophenone and more recently a range of hydroxyalkylphenones. It has been possible to improve cure by generating more reactive radicals, and to reduce residual odour and unwanted yellowing. Perhaps the most significant developments in hydrogen abstracting photoinitiators have involved the modification of structure to give greater absorption at wavelengths above 350 nm to provide improved performance in heavily pigmented formulations, particularly those containing titanium dioxide. Anthraquinones and thioxanthenes are examples.

Although most applications of photoinitiated polymerization involve a free-radical mechanism there are inherent problems associated with radical polymerization as applied to surface coatings. The high surface-to-volume ratio aggravates the effects of oxygen inhibition, although methods of eliminating or minimizing it are available, *e.g.* inerting, the use of amines, exuding waxes and thiol-ene systems [4] and the use of photosensitizers to convert triplet oxygen to singlet oxygen followed by scavenging [5]. Polymerization via double bonds involves shrinkage which often affects adhesion to impermeable substrates. It is possible in principle to avoid these and other problems associated with free-radical polymerization by using photoinitiated cationic ring opening polymerization. Photoinitiation of cationic polymerization via charge transfer complex formation has been known since the 1960s [6], but the first practical systems were developed by the American Can Company in the early 1970s, using aromatic diazonium salts with non-nucleophilic anions such as PF_6^- as photoinitiators for the ambient temperature polymerization of cycloaliphatic and other epoxides

[7]. Diazonium salts unfortunately generate nitrogen gas on photolysis, and also tend to cause premature gellation. Although they do have some unique attractions as cationic photoinitiators, particularly in that a highly absorbing (and coloured) chromophore can be converted to a colourless residue by the loss of the diazonium group, there was an incentive to examine other onium salts, and aromatic iodonium and sulphonium salts were found to be effective [8]. These became available as epoxy curatives in development quantities in the late 1970s. It has not been possible to synthesize iodonium salts with strong absorption in the UVA, but sensitivity to wavelengths stretching into the visible region can be obtained by use of photosensitizing molecules which work by an electron transfer mechanism [9]. The potential attractions of cationic systems have been effectively demonstrated, but the range of applications has been limited for various commercial and technical reasons. A very serious problem is the ease with which the propagating cation can be terminated by traces of basic impurity.

What of the future? It seems likely that technological applications of photoinitiated polymerization will rely primarily on the acrylate group, and on photoinitiator systems currently available, for several more years. A growth in the use of cationic systems may be expected, and also in the use of hybrid systems, *i.e.* those involving both free-radical and cationic mechanisms, or both photoinitiated and thermal polymerization, in order to overcome the performance limitations or high costs of current materials. The growth of UV curing has been supported by an enthusiastic research and development effort, mainly in the synthesis and exploitation of new materials, and improved sources of radiation [3]. Although fundamental studies of photopolymerization have been carried out, the conditions have usually been far removed from those found in UV curing. The kinetics of the very rapid processes taking place in thin sections, with high viscosities, high concentrations of photoinitiator and polyfunctional monomer, high degrees of polymerization attained and high photon flux densities, remain largely unexplored and present a formidable challenge.

References

- 1 G. A. Delzenne, *Makromol. Chem., Suppl.* 2, (1979) 169 - 188.
- 2 G. Plews and R. Phillips, *J. Coat. Technol.*, 51 (648) (1979) 69 - 77.
- 3 R. Phillips, *Sources and Applications of Ultraviolet Radiation*, Academic Press, London, 1983.
- 4 C. R. Morgan and A. D. Ketley, *J. Radiat. Curing*, 7 (2) (1980) 10 - 13.
- 5 C. Decker, J. Faure, M. Fizet and L. Rychla, *Photogr. Sci. Eng.*, 23 (1979) 137 - 140.
- 6 S. Tazuke, M. Asai, S. Ikeda and S. Okamura, *J. Polym. Sci. B*, 5 (1967) 453 - 457.
- 7 S. I. Schlesinger, *Photogr. Sci. Eng.*, 18 (1974) 387 - 393.
- 8 J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Symp.*, 56 (1976) 383 - 395; *Macromolecules*, 10 (1977) 1307 - 1315; *Am. Chem. Soc., Div. Org. Coat. Plast. Chem., Pap.*, 39 (1978) 31 - 35; *ACS Symp. Ser. 114* (1978) 1 - 16; *J. Polym. Sci., Polym. Chem. Edn.*, 17 (1979) 977 - 999.
- 9 S. P. Pappas and J. H. Jilek, *Photogr. Sci. Eng.*, 23 (1979) 140 - 143.