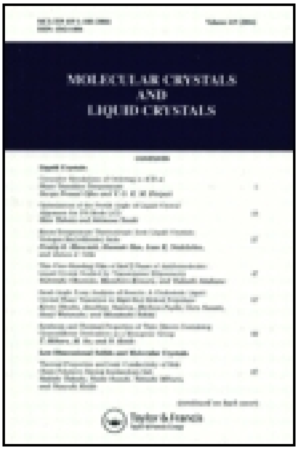


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Photopolymer Systems for Lithographic Applications

J. Finter [a]

[a] Central Research Laboratories, CIBA - GEIGY AG, CH 4002, Basle, Switzerland

Version of record first published: 13 Dec 2006.

To cite this article: J. Finter (1988): Photopolymer Systems for Lithographic Applications, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 161:1, 231-253

To link to this article: http://dx.doi.org/10.1080/00268948808070251

Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 1988, Vol. 161, pp. 231–253
Reprints available directly from the publisher.
Photocopying permitted by license only.

Printed in the United States of America

Photopolymer Systems for Lithographic Applications

J. Finter
Central Research Laboratories, CIBA - GEIGY AG,
CH 4002 Basle, Switzerland

Summary

Photopolymers play an important role in technical imaging systems. Several basic principles of photopolymer crosslinking and photoinduced radical polymerization systems will be reviewed.

Photopolymers are amorphous solids and the photo crosslinking reaction (e.g. increase in molecular weight) takes place in the glassy state. Their ultimate photographic speed may be calculated from basic physical properties of the irradiated areas. A continuous decrease of quantum yield during irradiation is characteristic for the photoreaction. The response to light is made possible by built in or added chromophores that can undergo different reactions depending upon their nature.

In a photoinduced polymerization the photo initiator decays into a radical pair when exposed to radiation. The photochemical reaction is amplified by a subsequent polymerization with multi functional reactive monomers to form an insoluble network. The photographic speed is governed by several factors including the quantum yield of cleavage and the rates of initiator decay, propagation and termination of the growing chain. The extent of conversion is diffusion controlled and therefore temperature dependent.

I. INTRODUCTION [1)]

Photoimaging, especially imaging with photopolymers, is the most important industrial use of photochemical processes in the solid state. Some basic principles of polymer imaging systems and their relevance to solid state chemistry will be reviewed. This paper is confined to photo crosslinkable polymers and radical photopolymerization systems leading to relief images. These systems cover about 90% of the applications of photopolymers for relief imaging.

Although the field of polymer imaging is large and more than a thousand papers and patents have been published in the last ten years, all of the known systems still fit the scheme (Fig. 1) suggested by J.L.R. Williams et al. in 1976 [2)]. This scheme classifies polymer imaging systems according to their chemistry as well as to their imaging applications

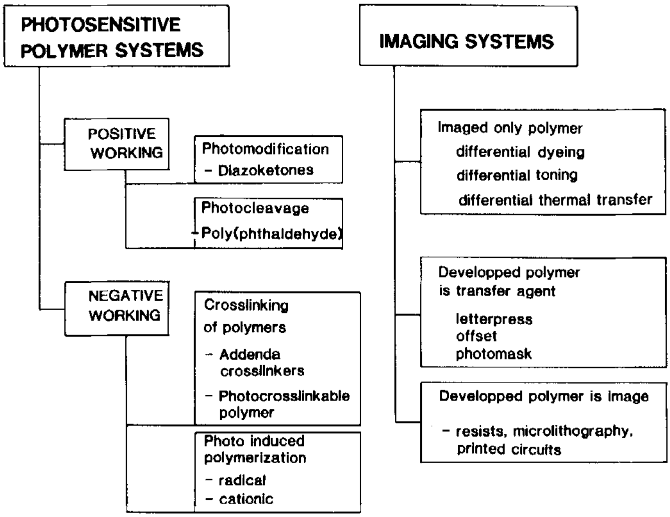


Fig. 1. Classification of Photosensitive Polymer Systems

We discriminate between positive and negative working systems. The typical applications of a photopolymer, as shown in Fig. 2, involve irradiation through a mask followed by a development step. If the resulting pattern is a positve image of the mask (e.g. if the irradiated parts are rendered soluble) the process is called positive. If the resulting pattern is the reverse, the process is considered negative, having rendered the irradiated areas insoluble.

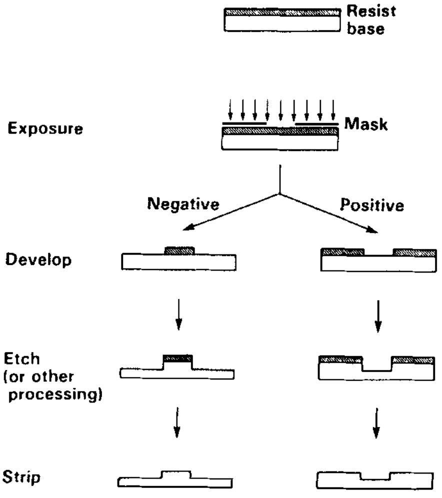


Fig. 2. Lithographic Process

At each stage of the lithographic process imaging applications may be found for a variety of different purposes as indicated in Fig. 1.

1. Positive Systems

Most of the presently availyble commercial positive systems are based on mixtures of naphthodiazo - quinone derivatives and novolack resins, these mixtures being insoluble in alkaline developers. Upon irradiation the diazoquinones undergo a Wolff rearrangement to the alkaline soluble indene carboxylic acid. This polarity change renders the exposed areas of the mixture soluble$^{3)}$.

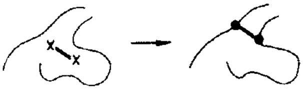
Besides photomodification by a rearrangement reaction, polymer solubilty may be achieved by cleaving polymer bound ester groups with photogenerated Bronsted acids. A series of such systems have been described recently [4].

A third process is the photoinduced depolymerization of polymers with low ceiling temperatures to the monomers. The most prominent example is the photo depolymerization of poly(phthalaldehyde) (PPA) [5].

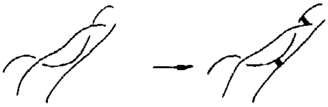
2. Negative Systems

Negative systems can be divided into three basic groups:

1. Crosslinking of polymers via addenda crosslinkers
2. Crosslinking of polymers with covalently bound chromophores
3. Photo induced polymerization



Addenda Crosslinker



Photocrosslinking Polymers

- Step reactions (2+2 Cycloaddition)

- Chain reactions

Fig. 3. Negative Photopolymer Systems

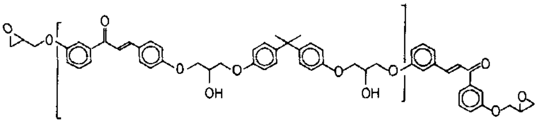
2.1 Addenda Crosslinkers

Addenda photocrosslinkers are added low molecular weight photosensitive molecules reacting chemically with polymer chains. Typical examples are bisazide crosslinkers for cyclisized poly(isoprenes) a system mainly used in microlithography. Upon irradiation, the azide group liberates nitrogen and the formed nitrene inserts itself either into a carbon double bond or a carbon hydrogen bond. Because of the generation of gaseous nitrogen this system may only find applications in very thin films6).

2.2 Crosslinking of Polymers

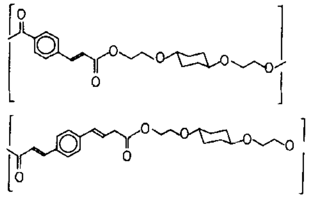
Polymer crosslinking systems involve systems working stepwise by crosslinking via covalently bound chromophores. The most prominent polymers are based on unsaturated esters or ketones crosslinking via [2+2]-cycloaddition upon irradiation. The chromophores may be pendant or linearly built into the polymer backbone. Typical examples are shown in Fig. 4. Another class of polymers undergoing crosslinking reactions by a step-wise mechanism is based upon photo reduction of the benzophenone chromophore followed by crosslinking 9). All these materials are amorphous poymers with T_g's far above room temperature.

TYPICAL PHOTOPOLYMERS WITH BACKBONE CHROMOPHORES



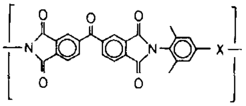
LINEAR POLYEPOXIDE

1c, 7)



α,β - UNSATURATED POLYESTER

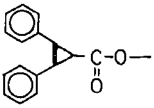
8)



SOLUBLE POLYIMIDE

9)

TYPICAL PHOTOPOLYMERS WITH PENDANT CHROMOPHORES



CYCLOPROPENES

10)

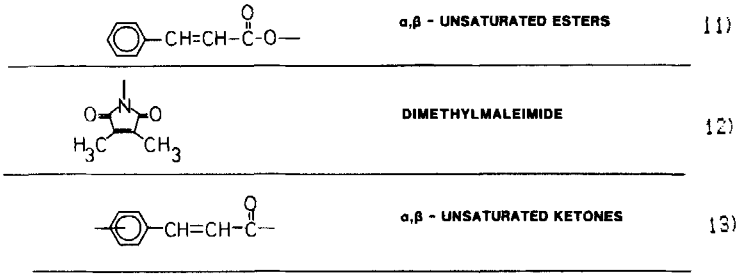


Fig. 4. Formulas of typical industrial photopolymers.

2.3 Photoinduced Polymerization

Photoinduced polymerization converts a reactive highly viscous liquid into a gel and finally a solid. Radical photoinitiators generate radicals, upon irradiation, for the polymerization of olefins. Cationic photoinitiators produce Lewis or Bronsted acids which may induce polymerization of epoxides or vinylethers.

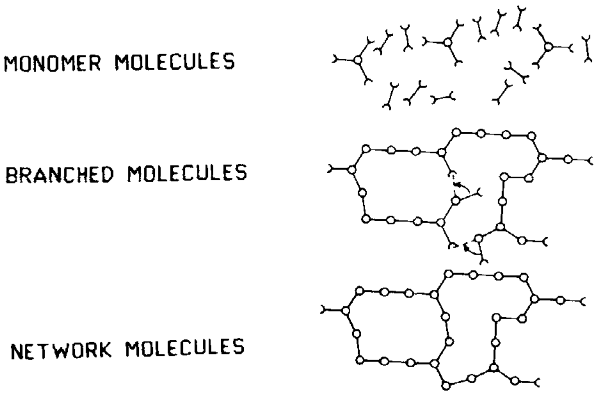


Fig. 5. Network formation from small molecules

3. Properties: Sensitivity, Resolution, Contrast.

Among the most important properties of any imaging system are sensitivity (minimum exposure energy), wavelength range and resolution.

Photopolymers exhibit relatively low sensitivities (Fig. 6). The theoretical limit 14) for crosslinking polymers is about 0.1 mJcm^{-2}. (see II.1). This actual value is, however, two orders of magnitude lower than the minimum exposure energy calculated for an ideal mono photonic photochromic process 15)

Photospeed, though, is not the only parameter of imaging material's performance. When high resolution is required only materials low sensitivity are applicable. Evidently resolution and sensitivity are inversely proportional.
Every high speed imaging process needs some amplification step. In electronic imaging the photon is amplified electronically by the photomultiplier, the resolution being limited by the size of the pixel. Silver halide systems are based upon the chemical amplification of a photolytically generated cluster of at least four silver atoms at the surface of a silver halide crystal. The larger the crystal size the higher the sensitivity but the lower the resolution. In photopolymer imaging the amplification step is an increase in molecular weight either by a chain reaction or crosslinking of high molecular weight polymer chains.

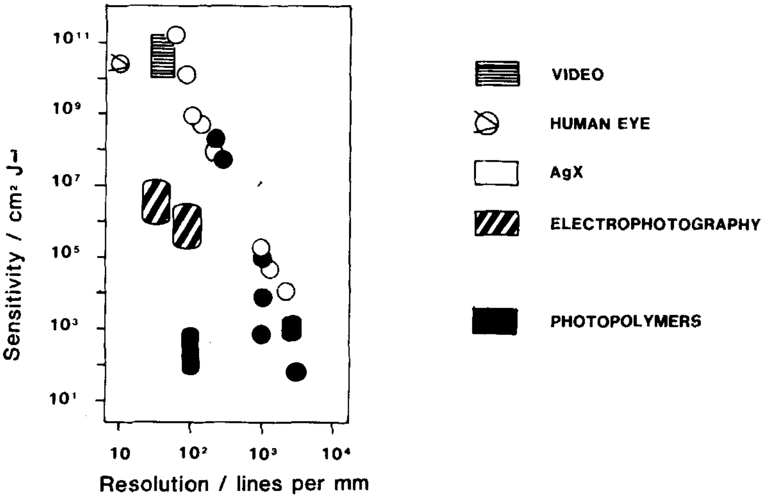


Fig. 6. Resolution and photographic sensitivities for typical imaging systems.

The imaging resolution is limited only by the wave length of irradiation. The limits of resolution may only be reached with 'molecular' homogeneous systems like photopolymers. In heterogeneous silver halide or electrophotographic materials the resolution is limited by the grain size of the crystals or the toner particles, respectively.

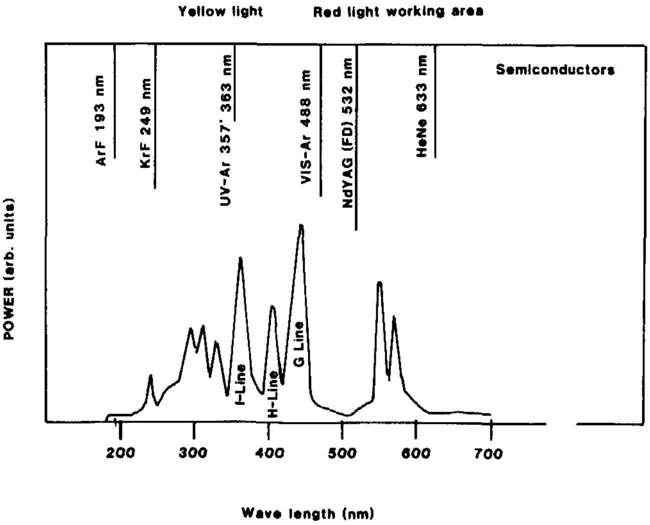


Fig. 7. Emission spectrum of a high pressure mercury lamp and typical high intensity Laser wavelengths.

For technical imaging systems daylight sensitive materials are not desired because they can only be handled in a darkroom. Most photopolymer systems used in industry are sensitive to UV/VIS light of 360 to 440 nm and can be handled under yellow light. Typical exposure equipment uses mercury arcs, Their emission spectrum is shown in Fig. 7 together with the emission lines of some powerful lasers.

Lasers are now available for a large number of different wave lengths. The interest in using lasers in photopolymer imaging stems from two advantages;

Coherence of the Laser beam: the possibility of imaging without a photomask by computer driven scanning devices like laser printers 16)

Monochromaticity of Laser Light: high intensity monochromatic deep UV irradiation for high resolution projection printers (wafer steppers) in microelectronics [17]

High power lasers at a reasonable cost are only available for certain wavelengths outside the emission lines of mercury lamps. Photoresists for use with laser equipment have to be tailored specifically to the laser wavelength. At present there are only a few photopolymer systems available which are sensitive enough for high scanning speeds.

II CHEMISTRY AND PHOTOPHYSICS OF NEGATIVE SYSTEMS

1. The Gelpoint Exposure and Crosslinking Theory

The theoretical photosensitivity of a photo - crosslinkable polymer may be calculated from the kinetics of the photo reaction as well as from the crosslinking theory of polymers.

According to Reiser and Pitts [14] the gel point exposure energy E_{Gel} of a photopolymer is given by

$$(1) \quad E_{Gel} = d \,/\, 2.303\ e \cdot m \cdot \overline{M_w} \cdot \phi_{Gel} \quad (\text{Einstein cm}^{-2})$$

where ϕ_{Gel} is the quantum yield of the crosslinking reaction defined as

$$(2) \quad \phi_{Gel} = \frac{\text{number of crosslinked monomer units}}{\text{number of absorbed quanta of radiation}}$$

d is the density, e is the decadic molar extinction coefficient of the chromophore and m its molarity in the solid film. This formula is independent of the chemical structure and valid for all crosslinking polymers. Three important conclusions can be drawn from equation 1:

1.) There is a linear relationship between Eg and $\overline{M_w}$. Fig. 8 shows typical experimental proof .

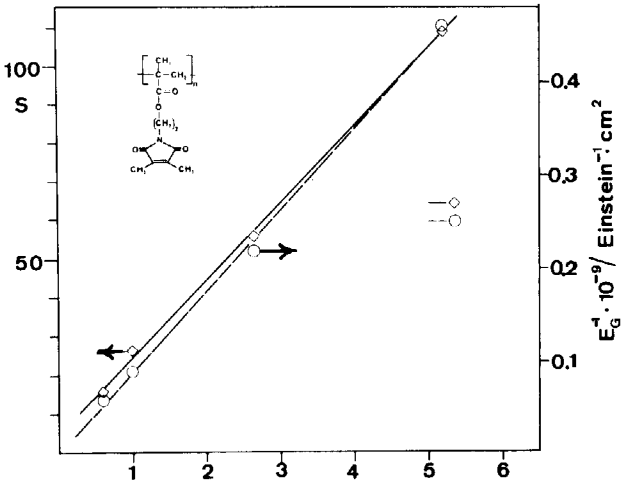


Fig. 8. Linear relation between gel point exposure E_g (O) and molecular weight M_w. For comparison, the relative sensitivity S (◇) is also shown. Data from 12)

2.) The quantum yield for gelation considers only reactions contributing to gel formation. A comparision between the quantum yield for gelation calculated from gel points and quantum yield for conversion determined by other methods should yield information about the amount of chromophores actually consumed in non gel forming reactions.

3.) From this equation, which is valid for all photopolymers, an absolute speed limit may be calculated. Assuming $\overline{M_w} = 10^5$, molarity m of the chromophore m=4 mol/l, extinction coefficient 2500 l/mol cm, density d=1.15 g/cm and quantum yield 0=2 we obtain $E_{Gel} = 0.25\cdot10^{-9}$ Einstein cm^{-2} corresponding to 0.1 mJ cm^{-2} at 360 nm 14).

According to eqn. 1 the photo speed may be increased by three ways ;

- chain reactions with quantum yields higher than 2,
- higher molecular weights,
- larger extinction coefficients.

However, there are several severe drawbacks. High extinction coefficients limit the systems to very thin films, high molecular weights will cause problems of swelling and reduced solubility and chain reactions of pendant monomers will lose efficiency due to trapping of reactive sites by vitrification.

Gel points are determined from gel curves (amount of crosslinked material at a given irradiation dose). They can be measured by a simple experiment (Fig. 9).

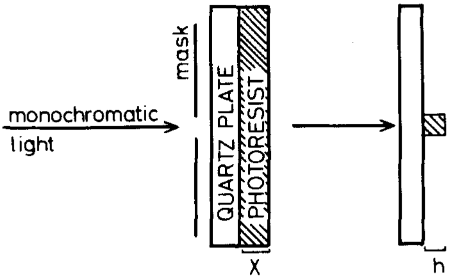


Fig. 9. Gel point experiment

A photopolymer composition is coated on a glass plate and irradiated through the back increasing the doses of light for each trial. After development in a suitable solvent the thickness of the remaining gelled layer is measured and plotted. From such a curve the gel point may be extrapolated. Typical experimental data together with the calculated curve are shown in Fig. 10. The intercept with the x-axis is a function of equation 1, but the slope and the shape of the curve are a function of the molecular weight distribution of the polymer as well.

Unlike the example shown in Fig. 10, in most cases only few points in the vicinity of the gel point are obtained. Therefore the gel point may only be extrapolated by comparison with the calculated curve 14). A numerical method is given in ref. 18)

The gel curve may be calculated by a combination of the photochemical balance with the Flory equation for the crosslink density distribution of any given molecular weight distribution 14). Considering several molecular weight distributions we get a series of curves, as shown in Fig. 11 in dimensionless form for a

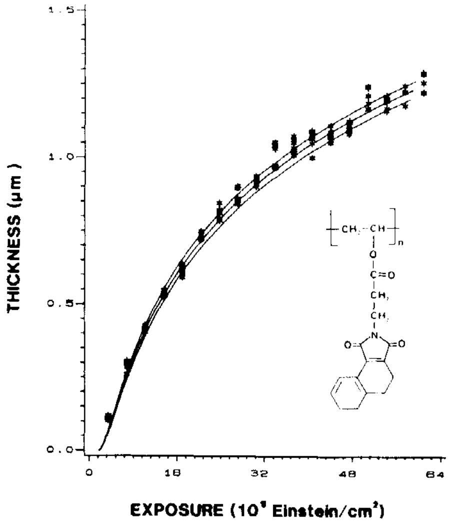


Fig.10. Gel curve [18]. Asterics: experimental points. --- Calculated curves for three different dispersities of the molecular weight.

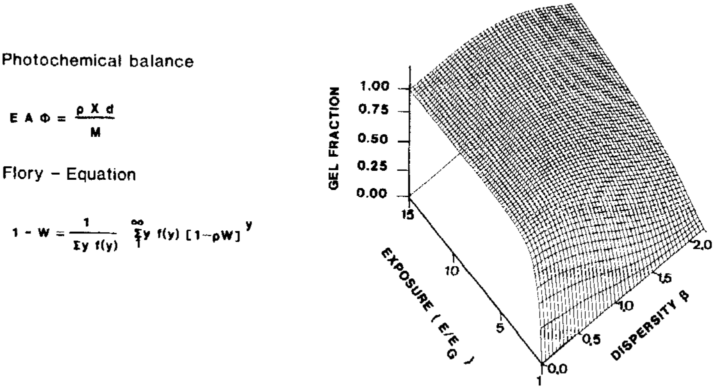


Fig.11 Dimensionless calculated gel curves obtained by combination of the photochemical balance with the Flory equation relating the weight fraction of gel w with the molecular weight distribution y and the crosslink density ρ.

polymer with lognormal distribution. β is the halfwidth of the molecular weight distribution. The broader the molecular weight distribution the smaller is the slope of the gel curve. At very broad distributions a fully crosslinked layer may not be obtained within finite exposure.
Photopolymers show striking similarities to silver halide photography insofar as the sensitivity, determined by M_w, corresponds to the the grain size of the silver halide and the contrast or shape of the characteristic curve determined by the molecular weight distribution corresponds to the particle size distribution of the grains.

2. Distribution of Chromophore Site Reactivities

A photopolymer is a glass with the chromophores statistically distributed. A certain amount is in a favourable position to execute a crosslinking reaction. The first photons entering the matrix will cause photoreactions and produce a gel.

Table 1. Comparison between quantum yield of gelation and quantum yield of conversion.

	$\phi_{C=C}$	ϕ_{Gel}	Ref.
Poly(vinylcinnamate)	0.25	0.26	19)
Poly(DMI)	0.18	0.18	12)
Poly(cyclopropene)	1.70	1.70	10)
Poly(chalcone-ester)	0.26	0.25	19)

Table 1 compares the quantum yields derived from the chromophore conversion with the quantum yields obtained from the gel point exposure measurements. This allows discrimination between reactions leading to intermolecular and intramolecular crosslinks. It is quite surprising that both quantum yields coincide at the gel point. Thus, only interchain crosslinks but no loops are formed.

Prolonged irradiation leads to decrease in quantum yields. Fig. 12 shows the change of quantum yield during irradiation for a typical photopolymer, poly(vinylcinnamate) and crystalline cinnamic acid.

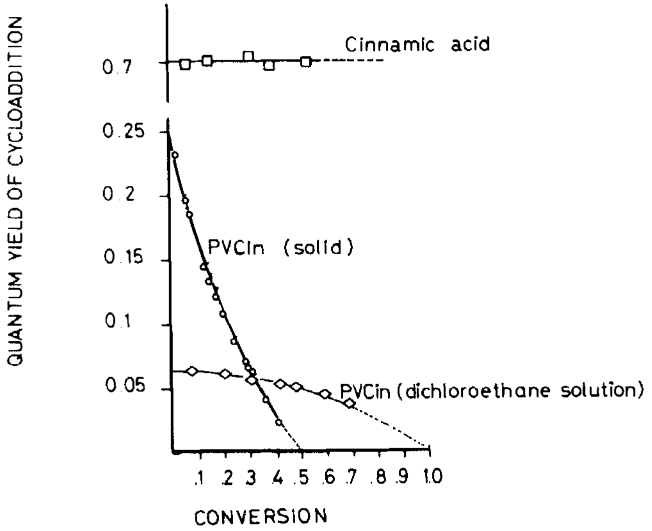


Fig. 12. Quantum yield change during irradiation for Poly(vinylcinnamate) and crystalline cinnamic acid [19]

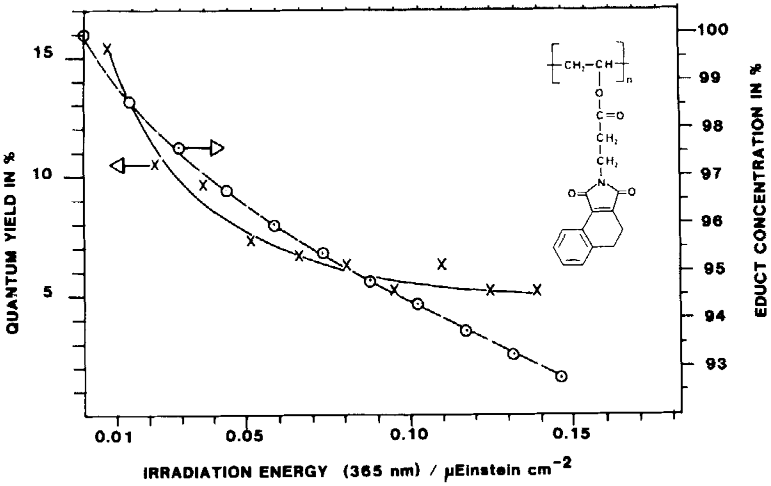


Fig.13. Quantum yield change during irradiation for PNDI polymer [18]

Crystalline cinnamic acid exhibits a constant, high quantum yield of chromophore consumption during irradiation up to high conversions. In contrast, the quantum yield of chromophore consumption for the glassy polymer decreases continuously with exposure time and only partial conversion is achieved, a behavior typical of amorphous photopolymers (see also Fig. 13).

The decrease of quantum yield is interpreted generally by different site reactivities . There may be some highly reactive and many unreactive chromophores, or there may be some sterically hindered chromophores whose reaction probability increases in the course of the reaction. Mathematical modeling of the quantum yield curve may serve as a basis for interpretation of the most probable case for each photopolymer. Based upon photophysical data, Reiser and Pitts 20) performed model calculations on several industrial polymers. A good match between calculated and experimental quantum yield curves was obtained.

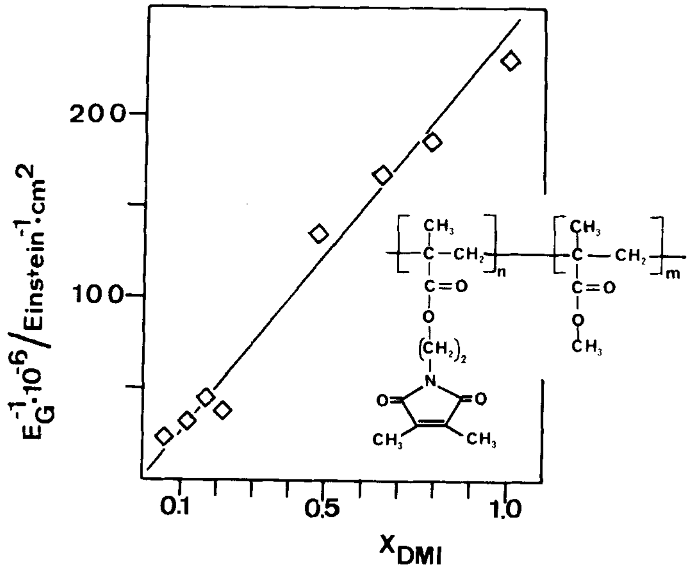


Fig. 14. Sensitivity (reciprocal gel point exposure) as a function of molar fraction of DMI - chromophore in DMI-MMA copolymers.

The reactivity in a solid matrix is also influenced by the chromophore concentration. The few systematic studies in the literature show that in general, the quantum yield of photocrosslinking and the sensitivity drop significantly when chromophore content is lowered. In the case of poly (DMI-MMA) (Fig. 14), a straight line results indicating linear behavior between molar fraction of DMI and reciprocal gel point exposure (sensitivity) 12). Similiar behavior was observed for polymers with pendant chalcone groups 21). Assuming a bimolecular [2+2] reaction of the chromophore, the experimental points should lie on a parabola stemming from second order kinetics. However, for a reaction in the solid state the second order mechanism is highly unprobable. Since only those chromophore pairs forming a reactive site can react, and the concentration of these sites is fairly low, the crosslinking reaction should follow pseudo first order kinetics.

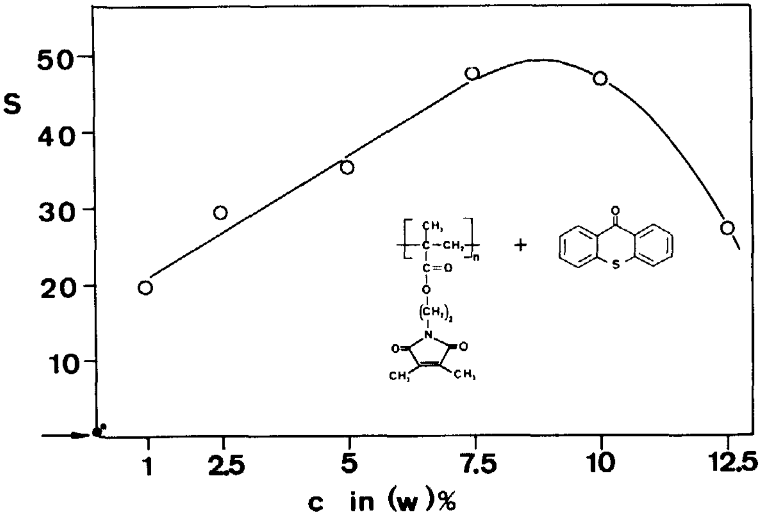


Fig. 15. Sensitivity as function of thioxanthone sensitizer concentration. Arrow: unsensitized polymer.

3. Sensitization

Most crosslinkable chromophores are not sensitive at 360 - 440 nm, the emission maxima of conventional exposure equipment. The addition of triplet sensitizers increases the sensitivity significantly (Fig. 15) 22). General rules for sensitization are:

- the triplet state energy must be higher than that of the unsaturated ester group (50 - 55 kCal/mol)
- the phosphoresence to fluorescence quantum yield must be higher than one
- the lifetime of the triplet state must be longer than 10 ms
- the absorption spectrum should match the emission spectrum of the lamp

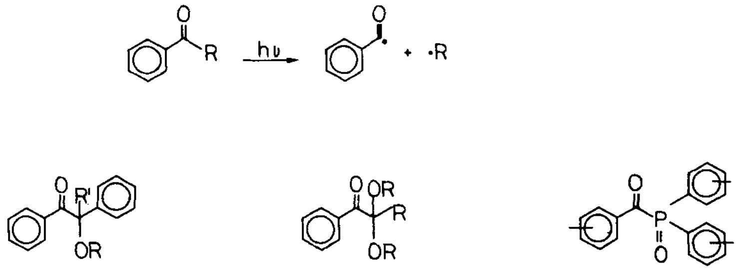
III. Photoinduced polymerization

Photo induced polymerization is completely different from photopolymer crosslinking where one starts with glassy polymers and increases the molecular weight by a solid state reaction. Photopolymerization, however, converts a reactive liquid to a gel and finally to a solid.

1. Photoinitiators 23)

1.1 Unimolecular Cleavage

The most widely used initiator systems producing free radicals involve benzoyl derivatives, e.g. substituted benzoin ethers, acetophenones or, one of the most recent developments, acyl-phosphine oxides. Upon irradiation the benzoyl radical is formed. All these initiators have been studied in detail 24). Besides purely organic initiators metallo organic compounds were also studied and have been reported as initiators 25).



BENZOIN DERIVATIVES ACETOPHENONES ACYLPHOSPHINE OXIDES

Fig. 16. Radical photoinitiators (benzoyl derivatives)

All sensitizers are sensitive to the spectrum of conventional UV-mercury lamps. In some cases sensitization with dyes is also possible.

Benzoyl derivatives show Norrish I unimolecular cleavage (or alpha cleavage) resulting in the creation of two radicals (see Fig. 17). The most reactive radical is the methyl radical [24].

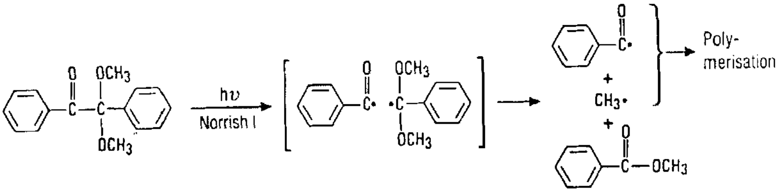


Fig. 17. Generation of radicals by photofragmentation (Norrish I cleavage)

2.2 Photoreduction Systems

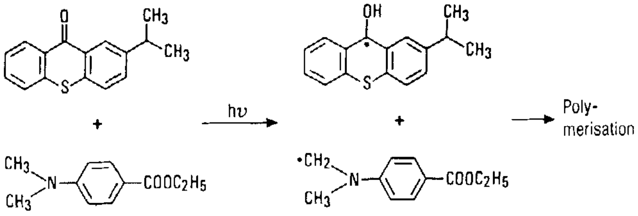


Fig. 18. Generation of radicals by intermolecular photoreduction

Another important type of photoinitiating system is combination of aromatic ketones with donor molecules which produce radicals by a photoreduction mechanism. A typical example is shown in Fig. 18. Upon irradiation the ketone undergoes photoreduction from its exited triplet state with a donor molecule abstracting a hydrogen. Two radicals are produced.

The donor radical is the more reactive.
The broad variety of ketone/donor pairs allows us to tailor the absorption of a photopolymerization system from the deep UV to the visible region of the spectrum. The reactivity of these systems is influenced by the ketone as well by the donor 22).

3. **Monomer Systems**

Olefins are suitable monomers for radical polymerization. Acrylic esters are preferred for their high propagation rates. Typical monomer systems include highly viscous mixtures of multi functional acrylates together with unsaturated oligomers 26). Adhesion, thermal stability , softening temperature (T_g) and chemical stability of the crosslinked image depend on the proper composition of monomers, reactive oligomers and binders, which are often added to soak up the liquid components. To prevent the quenching of the radical polymerization by oxygen, the irradiation is usually performed either under a nitrogen blanket or under an oxygen barrier layer closely adhering to the photosensitive layer, be it a transparent polyester foil or a poly(vinylalcohol) overcoat.

4. **Network Formation**

In photopolymerization it is very difficult to predict gel point exposures and sensitivities from monomer data. Up till now, no complete quantitative description of the photo polymerization reaction, including minimal energy requirements to reach the gel point, can be given. The systems are too highly complex for complete mathematical modeling.

Scheme 1 shows typical values for the quantum yield and the overall rate of polymerization of typical photopolymerization systems. From standard solution or bulk radical photopolymerization kinetics, the overall rate of polymerization Rp and the degree of polymerization DP_n are defined (for the case of low optical densities) by eqns. 3 and 4.

$$(3) \qquad R_p = \frac{k_p}{\sqrt{k_t}} [M] \sqrt{2.303 \cdot I_0 \cdot OD \cdot \Phi_i}$$

(4) $$\overline{DP_n} = \frac{k_p}{\sqrt{k_t}} [M] \Big/ \sqrt{2.303 \cdot I_o \cdot O.D. \cdot \Phi_i}$$

The rate of polymerization R_p should be proportional to the square root of the light intensity. In bulk polymerization, however, this behavior is observed only for the monofunctional monomers whereas multifunctional monomers show a nearly linear dependence between intensity and polymerization rate, as first observed by Decker [27]. This fact may be explained by the absence of termination reactions in the polymerization of multifunctional monomers , e.g. the growing radical that does not find a reaction partner is trapped in the matrix of the network.

There are several experimental proofs for trapped radicals. Free radicals may be detected in the crosslinked networks even days later or postpolymerization may be induced by thermal activation.

$$\phi_P = \frac{\text{double bonds reacted}}{\text{photons absorbed}}$$

$600 < \phi_P < 2'000$ in air

$3'000 < \phi_P < 10'000$ in nitrogen

Conventional Photopolymerization

$R_p \sim I^{0.5}$

monofunctional monomers $R_p \sim I^{0.5}$

multifunctional monomers $R_p \sim I^{0.85}$

Scheme 1: Characteristic parameters of photopolymerization

The kinetics of polymerization in solution and polymerization in the solid state are quite different. In solution polymerization proceeds according to

$$dG = dH - TdS$$

There is a constant heat of polymerization, an entropy that decreases to a constant value after several polymerization steps and a negative free energy of polymerization dG. Normally the reaction does not proceed under equilibrium conditions because the heat of polymerization is usually much higher than the term TdS. The reaction stops when the monomer is consumed.

In the polymerization of monomer single crystals to polymer single crystals there exist only very few examples like diacetylenes or poly(oxymethylene). In this case a complete conversion via a topochemical reaction may also be achieved because there is no great difference in entropy going from one crystalline state to another.

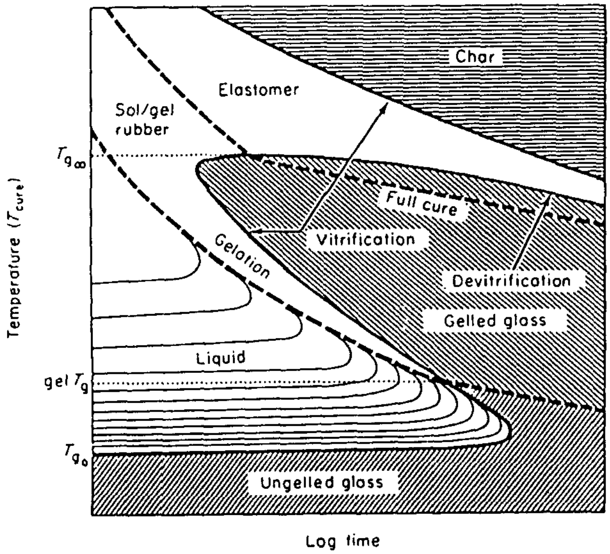


Fig. 19. TTT - (Time, Temperature, Transition) - Diagram

In the polymerization of liquid multifunctional olefins the viscosity increases with conversion until the gel point is reached. Further conversion increases the crosslink density which raises the glass transition temperature T_g. The polymerization stops before completion, at the onset of vitrification. The onset of vitrification occurs when the glass transition temperature of the material coincides with the reaction temperature.

This complex behavior is best pictured in the TTT - (Time, Temperature, Transition) - diagrams introduced by Gillham [27] (Fig. 19). The x-axis shows the reaction time, the y - axis the temperature. We have to deal with a.); the T_g of the unreacted material, b.); the T_g of the completely crosslinked material and c.); the reaction temperature. The reaction goes from the liquid to the solid state , the reaction stops at the vitrification sinodal. Therefore materials with high T_g are not accessible by reaction at room temperature.

Acknowledgements

Thanks are due to Dr. S. Bauer, Dr. K. Dietliker, Dr. J. Pfeifer and Dr. H. Zweifel for helpful discussions.

References

1) G.A. Delzenne, Adv. Photochem. **11**, 1 (1979); H. Vollmann, Angew. Chem. **92**, 95 (1980); G.E. Green, P.B. Stark and S.A. Zahir, J. Macromol. Chem. Revs. Macromol. Chem. **C21**, 187 (1982), W.S. DeForest, Photoresist - Materials and Processing, McGraw Hill Book Company, New York 1975

2) J.L.R. Williams, S.Y. Farid, J.G. Doty, R.C. Daly, D.P. Specht, R. Searle, D.G. Borden, H.J. Chang and P.A. Martic, Pure Appl. Chem: **49**, 523 - 538 (1977)

3) J. Kosar, Light Sensitive Systems, Chapt. 7, J. Wiley & Sons, New York 1965; O. Sues, Liebigs Ann. Chem. **556**, 65 - 84, 84 - 90 (1944)

4) J.M.J. Frechet, E. Eichler, H. Ito, C. G. Willson, Polymer **24**, 995 - 1002 (1983)

5) H. Ito, C. G. Willson, Technical Papers, Soc. Plast. Eng. 1982, 331

6) J. Kosar, Light Sensitive Systems, Chapt. 7, J. Wiley & Sons, New York 1965; V. M. Treushnikov, N. V. Frolova, A. V. Oleinik and Yu. D. Semchikow, Polym. Sci. USSR.:**20**, 2949 - 2957 (1979)

7) S. A. Zahir, J. Appl. Polym. Sci.,**23**, 1355 (1979)

8) A. Reiser and P.L. Egerton, Macromolecules **12**, 670 (1979)

9) J. Pfeifer and O. Rohde, Proc. Sec. Int. Conf. Polyimides, Soc. Plast. Eng., Ellenville NY, Oct. 30 - Nov. 1, 1985, p.

130; A.A. Lin, V.R. Sastri, G. Tesoro, A. Reiser, R. Eachus, to be published

10) M.V. Mijovic, P.J. Beynon, T.J. Shaw, K. Petrak, A. Reiser, A.J. Roberts and D. Phillips, Macromolecules **15**, 1464 - 1471 (1982)

11) L.M. Minsk, US Pat. 2 725 377, 1955

12) J. Berger and H. Zweifel, Angew. Makromol. Chem. **115**, 163 (1983); J. Finter, E. Widmer and H. Zweifel, Angew. Makromol. Chem. **128**, 71 (1984); H. Zweifel, Phot. Sci. Eng. **27**, 114 (1982)

13) D.G. Borden and J.L.R. Williams, Makromol. Chem. **178**, 3035 - 3049 (1977)

14) A. Reiser and E. Pitts, Phot. Sci. Eng. **20**, 225 - 229 (1976); N.J.H. Parham, E. Pitts and A. Reiser, Phot. Sci. Eng. **21**, 145 - 147 (1977); A. Reiser, J. Chim. Phys. Phys.-Chem. Biol. **77**, 469 - 481 (1980)

15) G.A. Delzenne, Adv. Photochem. **11**, 8 (1979)

16) J. Tuck, Circuits Manuf. **1984**, 2, 36 - 42

17) V. Pol, Solid State Techn. **30** (1), 71 (1987)

18) J. Finter, Z. Haniotis, K. Meier and H. Zweifel, J. Imag. Sci. **30**, 259 - 266 (1986)

19) P.L. Egerton, E. Pitts and A. Reiser, Macromolecules **14**, 95 - 100 (1981)

20) E. Pitts and A. Reiser, J. Amer. Chem. Soc. **105**, 5590 - 5593 (1983)

21) C.C. Unruh, J. Appl. Polym. Sci. **2**, 358 (1959)

22) K. Meier and H. Zweifel, J. Photochem. **35**, 353 - 366 (1986)

23) H.J. Hagemann, Prog. Organ. Coat. **13**, 123 - 150 (1985)

24) G. Berner, J. Puglisi, R. Kirchmayr and G. Rist, J. Rad. Curing: **1979**, 2 - 7; A. Borer, R. Kirchmayr and G. Rist, Helv. Chim. Act. **61**, 305 - 324 (1978)

25) A. Roloff, K. Meier and M. Riediker, Pure Appl. Chem. **58**, 1267 - 1272 (1987), J. Finter, M. Riediker, O. Rohde and B. Rotzinger, Proc. Eur. Symp. Polym. Mater. Polym. Electron. Sec. Paper ED03, Lyon, Sept. 14-18 (1987)

26) G.A. Senich and R.E. Florin, J. Macromol. Sci. Rev. Macromol. Chem. Phys. **C24**, 239-324 (1984)

27) C. Decker and K. Moussa, J.Appl. Polym. Sci. **34**, 1603 - 1618 (1987)

28) J.K. Gillham, Br. Polym. J. **17**, 224 - 226 (1985)