

Photosensitive Resins Containing *p*-Dimethylaminobenzylidene Derivatives and Diphenyliodonium Salt as Photoinitiators

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Synopsis

A series of *p*-dimethylaminobenzylidene derivatives was able to sensitize the photodecomposition of diphenyliodonium salt to afford highly photosensitive negative-type resins. When a polymer-bearing methacryloylated group in the side chain was sensitized with a combination of the *p*-dimethylaminobenzylidene compounds and the iodonium salt, the polymer demonstrated high sensitivity even to 488 nm light emitted from an Argon laser. The same photoinitiator systems were applicable to insolubilize poly(glycidyl methacrylate) through cationic photopolymerization. The storage stability of these types of photoinitiators depends on the structure of the benzylidene compounds; decreasing the basicity of the amino group enhanced the thermal stability.

INTRODUCTION

It is well known that photolysis of diaryliodonium salts affords radical species as well as strong acid, which are effectively applicable to cure resins.¹⁻³ Diaryliodonium salts so far reported possess absorption bands at shorter wavelengths, and the photosensitive resins containing iodonium salts as photoinitiator are sensitive only to ultraviolet (UV) light. In order to expand the spectral sensitivity of iodonium salts, it is necessary to sensitize the decomposition of the salt by suitable sensitizers.^{3,4}

Sensitization of the onium salts may take place through triplet energy transfer, electron transfer, and exciplex-induced bond cleavage.³ According to Pappas and co-workers, the sensitized decomposition of diaryliodonium salt involves two modes of electron transfer; direct electron transfer from sensitizer to the salt and indirect electron transfer from radicals generated from photoexcited benzophenone to the salt.⁵ Considering the role of the iodonium salts as a component for an electron acceptor, the direct electron transfer mechanism is attractive since a variety of donor dyes may be employed whenever the electron transfer process is thermodynamically favorable.³ In addition to aromatic hydrocarbons, some dyes are known to act as sensitizer for the decomposition of the iodonium salt.⁴ Bis(*p*-dialkylamino)benzophenone is also an effective sensitizer, as described in a patent literature.⁶ These

sensitizers have the common molecular structure in which dialkylamino group substituted on phenyl ring is conjugated with electron-withdrawing group to form intramolecular charge transfer structure and possibly induce the decomposition of diaryliodonium salts through the electron transfer mechanism. This paper deals with the effectiveness of a series of *p*-dialkylaminobenzylidene derivatives as sensitizer for the decomposition of the iodonium salt and their applicability for visible light-sensitive resins, which are insolubilized via photoinitiated radical and cationic polymerization.

EXPERIMENTAL

Materials

p-Dimethylaminobenzylidene derivatives were prepared by the Knoevenagel condensation.⁷ 1-[1-Benzoyl-2-(*p*-dimethylaminophenyl)ethenyl]pyridinium hexafluorophosphate was prepared as follows; 1-Phenacylpyridinium bromide (3.56 g) and *p*-dimethylaminobenzaldehyde (1.65 g) were heated in 30 cm³ acetic anhydride at 130°C for 30 min. To the solution was added 300 cm³ ether to precipitate an oily substance which was separated by decantation. The oil was dissolved in 40 cm³ water and mixed with 1.89 g of potassium hexafluorophosphate in water to produce an orange precipitate, which was collected by filtration and washed with water and ether to afford 3.00 g 1-[1-benzoyl-2-(2-dimethylaminophenyl)ethenyl]pyridinium hexafluorophosphate of mp 120–122°C. The structure was confirmed by the infrared (IR) spectrum and elementary analysis.

Copolymer of Methacryloyloxystyrene and Methyl Methacrylate

A 1 : 1 copolymer of chloromethylstyrene (CMS) and methyl methacrylate (MMA) (1.26 g) was dissolved in 20 cm³ dimethylacetamide, and 0.83 g potassium methacrylate was added to the solution. The mixture was stirred at 80°C for 5 h and poured into methanol to precipitate the polymer which was dried in vacuo. The polymer was dissolved in 2-ethoxyethyl acetate in 10 wt% for evaluation of photoinitiation efficiency of dye-diphenyliodonium salt system.

Sensitivity Determination

To a 10 wt% solution of the copolymer of methacryloyloxymethylstyrene and MMA in 2-ethoxyethyl acetate was added sensitizer dye and diphenyliodonium hexafluorophosphate (DPI). The weight ratio of the polymer : sensitizer : iodonium salt was 1 : 0.1 : 0.1. The solution was diluted with the same solvent up to 5 wt% and coated on an aluminum plate with a spin coater. The thin film on a plate was exposed to a Xe arc, followed by soaking in 2-ethoxyethyl acetate. The sensitivity was measured by the gray scale method.⁸ The sensitivity to Ar laser was performed as described in our previous paper.⁸ The polymer thin film coated on an aluminum plate was exposed to 488 nm light beam emitted from Ar laser of NEC GLC 3000, and the diameter of insolubilized spot image was plotted against exposure energy

in mJ/cm^2 required to form a spot having the same diameter as that of the laser beam.

A thin film of PGMA containing sensitizer and DPI was baked at 80°C for 3 min after exposure to a Xe arc or Ar laser. The sensitivity of the resin was evaluated as stated above.

Determination of pKa of Sensitizer

The pKa measurement was undertaken spectrophotometrically in aqueous dioxane acidified with perchloric acid to adjust H_0 value.⁹ A family of spectra of dye solutions in various H_0 showed isosbestic points.

Gelation Time Measurement

The photosensitive resin composition was spin-coated on an aluminum plate and baked at 80°C . The plate was cut into small pieces at intervals and exposed image-wise to a Xe arc, followed by developing with 2-ethoxyethyl acetate. Gelation time was determined as baking time after which a clear negative image was no longer observed.

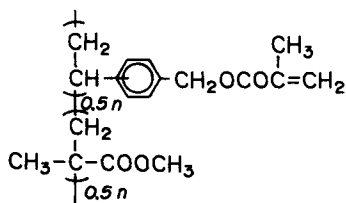
RESULTS AND DISCUSSION

Dye-DPI as Radical Photoinitiator System

Relative efficiency of dye as sensitizer is conveniently evaluated by measuring sensitivity of photopolymerization type polymer (PM) having methacryloyl residue in the side chain (Scheme 1). When *p*-dialkylaminobenzylidene compound and DPI were dissolved in the polymer film, the longest wavelength of electronic absorption bands of dyes suffered red shift, suggesting the formation of the charge transfer. A typical example is shown in Figure 1 for dimethylaminochalcone-DPI.

Exposure of the film to light from a Xe arc resulted in the rapid insolubilization. As shown in the Table I, sensitizers denoted as S-1, S-2, S-5, S-7, S-8, S-11, and S-13 afforded high sensitivity, while the related dyes derived from 3-formylindole (S-14 and S-15) were practically inactive, although they possess conjugated donor and acceptor groups similar to the *p*-dialkylaminobenzylidene derivatives.

The sensitized decomposition of DPI may take place via one electron transfer from the excited sensitizer.³ It is of practical interest to find electron acceptors other than DPI for application to various types of photocurable



PM

Scheme 1.

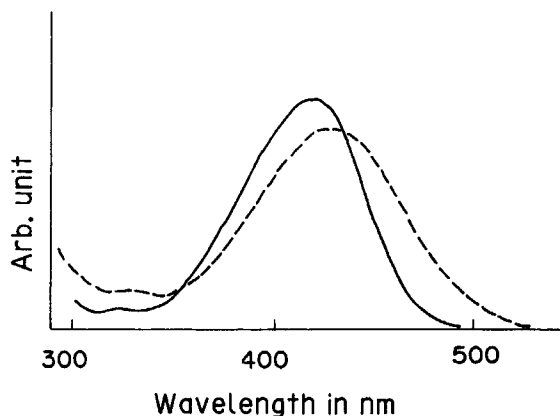


Fig. 1. Electronic absorption spectra of 1-[4-dimethylaminophenyl]-2-[4-methoxyphenyl-carbonyl]ethylene in the methacryloylated polymer in the absence (—) and in the presence (---) of diphenyliodonium hexafluorophosphate.

resins. We have examined the sensitivity of PM containing S-1 and various acceptors. The results are summarized in Table II. As far as we have studied, DPI was the most effective radical-forming compound.

Some sensitizers absorb light at wavelength of 488 nm, and the thin film containing such sensitizers is exposed to an Ar laser to measure sensitivity. The results are also compiled in Table I. Aminochalcones (S-1, S-5, S-8, S-11, and S-13) and the rhodanine derivative (S-7) are particularly suitable for Ar laser-sensitive resin.

Photoinitiator for Cationic Polymerization

We have subsequently studied the crosslinking of PGMA induced by photo-generated acid formed in the dye-DPI system.

Although the sensitizers contain dimethylamino group, which may trap the photogenerated acid to reduce the cationic polymerization efficiency, when a thin film of PGMA containing dye and DPI was exposed to light and subsequent postbaking at 80°C, insolubilization of the polymer was observed. The relative sensitivity was evaluated by the gray scale method and shown in Table III. It was found that the dimethylaminobenzylidene derivatives are all more effective sensitizers than acridine orange.⁴

Prolonged baking caused gelation even in the dark. This indicates that thermal decomposition of DPI is accelerated by the presence of dyes to give acid which catalyses the crosslinking of the epoxide group of PGMA. The rate of thermal insolubilization of PGMA was strongly dependent on the structure of dyes, implying that the nucleophilicity of the dimethylamino group of the dyes plays an essential role in the thermal reaction.

Since the basicity of the amino group reflects nucleophilicity when the steric effect is negligible, we have measured pK_a of some dyes, which are stable in strongly acidic solution during the course of the pK_a measurement. As shown in Figure 2, a good relationship exists between pK_a and thermal gelation time. It was confirmed from the results that the introduction of an electron-withdrawing group to the C=C bond makes the photoinitiator sys-

TABLE I
Sensitivity Characteristics of Methacryloylated Polymers Containing Sensitizers and Diphenyliodonium Hexafluorophosphate




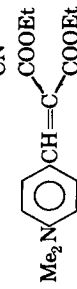
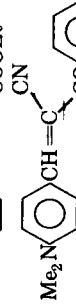


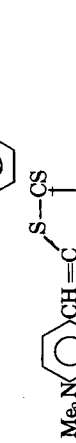
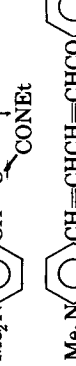
Sample no.	Structure	λ_{\max}		Film	Xe^a	Sensitivity Ar^b (mJ/cm ²)
		CHCl ₃				
S-1		408		418	32	5
S-2		420		426	16	25
S-3		429		435	3	38
S-4		375		379	2	
S-5		440		440	32	5
S-6		[340 390]		[340 388]	4	
S-7		479		473	32	3
S-8		428		435	32	2
S-9		465		472	8	13

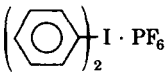
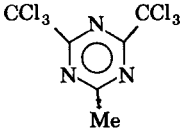
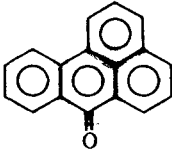


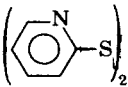
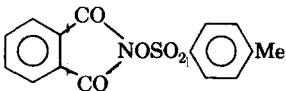
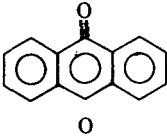
TABLE I. (Continued from the previous page.)

Sample no.	Structure	λ_{\max}		Sensitivity Ar ^b (mJ/cm ²)	
		CHCl ₃	Film		
S-10		490	489	3	21
S-11		422	428	16	5
S-12		498	502	4	7
S-13		440	440	32	1.5
S-14		380	383	-0	
S-15		404	406	0.5	

^a Relative value using sensitized poly(vinyl cinnamate) as a standard.

^b Exposure energy according to the "spot method" (see Experimental).

TABLE II
Relative Sensitivity of the Methacryloylated Polymer Containing 1-[4-Dimethylaminophenyl]-2-[4-Methoxyphenylcarbonyl]ethylene and Various Additives

Additives	Relative sensitivity ^a
	32
	2
	0.25
	0
	0.1
	0
	0.25
	0.1
$(\text{Me}_2\text{NCS})_2\text{S}_2$	0

^aRelative to the sensitivity of sensitized poly(vinyl cinnamate).

tems thermally more stable. In this respect, S-13 acts as an efficient sensitizer for photoinduced cationic polymerization when coupled with DPI.

Sensitivity characteristics of PGMA containing the photoinitiator system were investigated in more detail for optimization, using S-5 and S-7, which are relatively stable in the baking process, as sensitizers.

Figure 3 shows the effect of concentration of the rhodanine derivative (S-7) as well as DPI. The sensitivity reached a maximum value after 10 min postbaking, and the concentration of both the sensitizer and the activator

TABLE III
Sensitivity of Poly(glycidyl Methacrylate) Containing 10 wt% of Diphenyliodonium Hexafluorophosphate and 10 wt% of Various Sensitizers

Sensitizer ^a	Relative sensitivity ^b	pKa
S-1	8	1.99
S-2	3	
S-3	3	
S-5	6	0.94
S-7	4	
S-8	4	2.42
S-10	2	1.79
S-12	2	1.37
S-13	8	
Acridine orange	1	

^aThe structures are shown in Table I.

^bAfter postbaking for 3 min at 80°C.

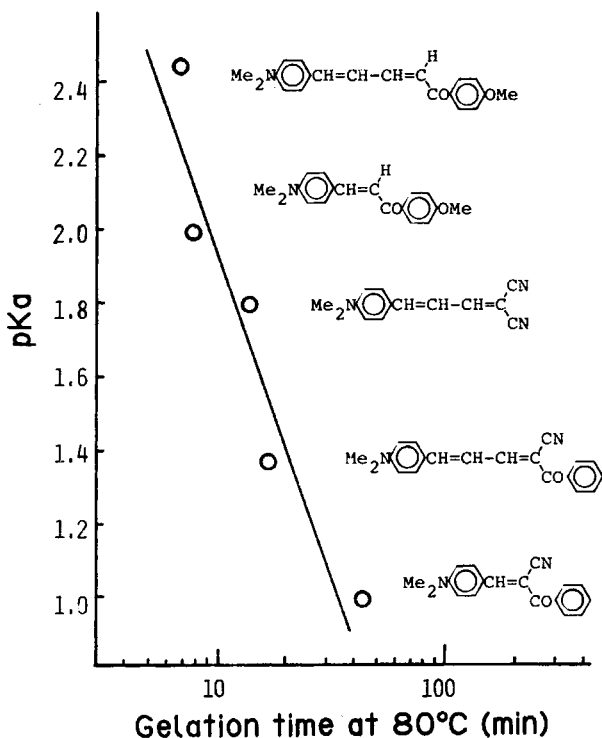


Fig. 2. Dependence of the thermal stability of the methacryloylated polymer containing diphenyliodonium hexafluorophosphate on the pKa of *p*-dimethylaminobenzylidene sensitizers.

(DPI) is sufficient in 10 wt%. This was the same for the cyanosubstituted chalcone (S-5) and DPI system (Fig. 3).

PGMA containing S-5 or S-7 and DPI was sensitive to Ar laser emitting 488 nm light as shown in Figure 4, although the sensitivity was much less than that of the radical polymerization type resin shown in Table I.

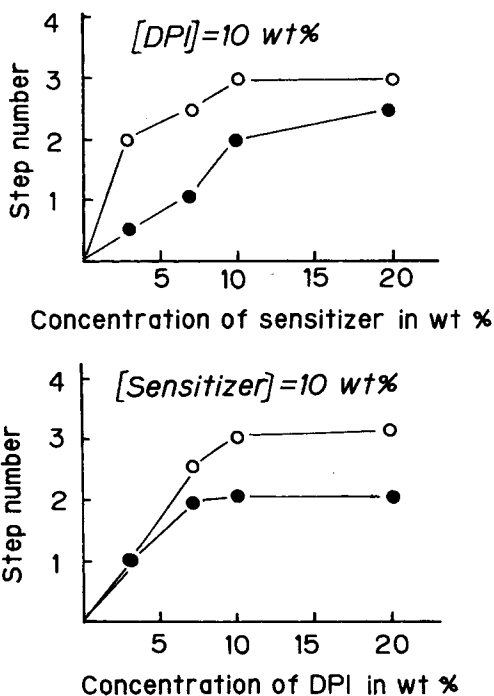


Fig. 3. Concentration effect of sensitizer and diphenyliodonium hexafluorophosphate on the sensitivity of poly(glycidyl methacrylate) after 10 min postbaking (—○—) 2-benzoyl-3-(4-dimethylaminophenyl)-2-propenenitrile (S-5); (—●—) 5-[(4-dimethylaminophenyl)methylene]-4-ethyl-2-thioxo-4-thiazolidinone (S-7).

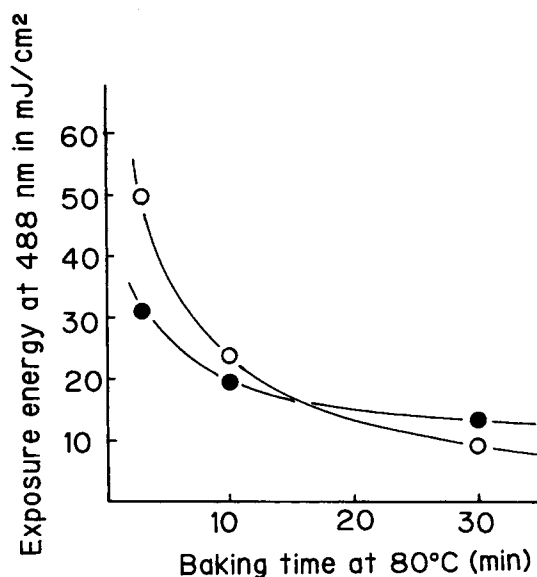


Fig. 4. Sensitivity of poly(glycidyl methacrylate) containing 10 wt% of diphenyliodonium hexafluorophosphate and 10 wt% of the sensitizers to light of 488 nm after post-baking (—○—) 2-benzoyl-3-(4-dimethylaminophenyl)-2-propenenitrile (S-5); (—●—) 5-[(4-dimethylaminophenyl)methylene]-4-ethyl-2-thioxo-4-thiazolidinone (S-7).

In summary, *p*-dialkylaminobenzylidene derivatives conjugated with electron-withdrawing group(s) effectively sensitize the photodecomposition of DPI to offer radical species and strong acid. These photoinitiator systems can be applicable to photocrosslinkable resins sensitive to visible light which are insolubilized in both radical and cationic polymerization.

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