Relative Photoactivities of Iodonium Tetrakis(pentafluorophenyl)gallates Measured by Fluorescence Probe Techniques

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ABSTRACT: A series of iodonium tetrakis(pentafluorophenyl)gallate photoinitiators were employed to catalyze the photopolymerization of three typical epoxy resins. Rates of photoacid release were compared using Quinaldine Red as acid indicator in either acetonitrile or ethanol. A new fluorescence probe technique was successfully employed to follow the cross-linking kinetics of the epoxysilicone oligomer in real time. The results show that these new salts are the most soluble, most reactive photoinitiators with the desirable stability in monomer formulations in this family.

Introduction

Iodonium tetrakis(pentafluorophenyl)gallates are highly attractive photoinitiators for cationic polymerization due to their excellent solubility and high photosensitivity.[2] Of industrial interest is that these novel gallate photoinitiators can be used for the photopolymerization in nonpolar media. This is a problem with most of commercial cationic photoinitiators. Epoxy silicone resins of low polarity, especially, are used in release coatings for pressure-sensitive adhesives.[3] When we investigated the performance of such iodonium gallates (Figure 1) in epoxy silicone resins by routine FTIR,[4,5] the kinetics of their polymerization could not be monitored since the IR band of the epoxy group overlapped with that of the siloxane functions, causing the usual FTIR method to be insensitive. In addition, the FTIR method also has other limitations that limit film thickness and the transmission of the substrates.

In recent years, fluorescence probe techniques have been intensively studied in this laboratory to monitor the kinetics of radical photopolymerizations in real time.[6−14] There also have been a few reports in the fluorescence probes for monitoring the cationic polymerization of epoxy resins induced by heat[15] or by light.[6] A rapid scan fluorimeter, the CM 1000, has also been developed commercially for this application. One of the keys to applying this technique successfully is the selection of the proper fluorescence probe. Compounds useful for monitoring polymerization display a unique blue shift in the fluorescence emission during conversion of monomer into polymer. Our group has discovered that several different mechanisms cause the blue shift of different probes, including twisted intramolecular charge transfer,[13] charge transfer,[9,11] excimer formation,[14] and organic salt ionization.[10] As far as we know, the most commonly used probes are coumarin 1, DASB (5-(dimethylamino)naphthalene-1-sulfonyl-*n*-butylamide) (Figure 2), and derivatives. In each case the addition of amines must be acceptable as it is when monitoring acrylates and other polymers. However, amines are unacceptable for use in cationic polymerization, because they may inhibit acid-catalyzed polymerization. This drawback has been overcome recently with the discovery of a new class of compounds that do not contain a proton reactive group,[16] for example, *N*-dodecyl-1-hydroxy-2-naphthalenecarboxamide (DDHNA). This compound displays characteristic fluorescence changes that occur in parallel with cationic cure. Because of its long branch chain, the compound is soluble at a limited concentration in a wide variety of resins, including epoxy silicones, cycloaliphatic epoxides, and bisphenol A derivatives.

In a previous paper, we reported the synthesis, characterization, and photolysis of iodonium tetrakis(pentafluorophenyl)gallates.[2] Herein, we successfully apply fluorescence probe techniques to evaluate these gallate salts in a typical epoxy silicone oligomers (**I**) and two other typical resins (**II, III**) (Figure 3), combining this with the evaluation of the rate of their photoacid release by using a fast analysis technique in solution previously developed in our group.[17−19] The results indicate that the larger sized and less nucleophilic tetrakis(pentafluorophenyl)gallate anion renders the iodonium salt more photosensitive. These novel salts show excellent polymerization characteristics.

Experimental Section

Materials. Reagents and solvents were purchased from Aldrich and used without further purification. (4-Isopropylphenyl)-4-methylphenyliodonium tetrakis(pentafluorophenyl)borate (**2b**) (Rhodorsil 2074) was obtained from Rhodia. (4-Octyloxyphenyl)phenyliodonium hexafluoroantimonate (**3e**) (OPPI) was provided by GE Silicones. (4-Octyloxyphenyl)phenyliodonium tetrakis(pentafluorophenyl)borate (**2e**), (4-isopropylphenyl)-4-methylphenyliodonium hexafluoroantimonate (**3b**), and (4-isopropylphenyl)-4-methylphenyliodonium choloride (**4b**) were prepared as described previously.[5,20] All of iodonium tetrakis(pentafluorophenyl)gallates were prepared according to procedures reported in another paper.[2]

Epoxy silicone oligomer UV 9315 (**I**) was supplied by GE Silicones. Bisphenol A derivative DER 332 (**II**) was obtained from Dow Chemical Co. Cycloaliphatic epoxide UVR 6110 (**III**) was purchased from Union Carbide Co.

General Procedure for Measurement of Rate of Acid Release. Solutions of iodonium salts containing ∼10 ppm of quinaldine red (QR) in acetonitrile or ethanol were prepared

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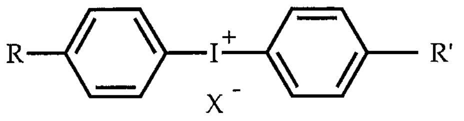


1: X = $Ga(C_6F_5)_4$

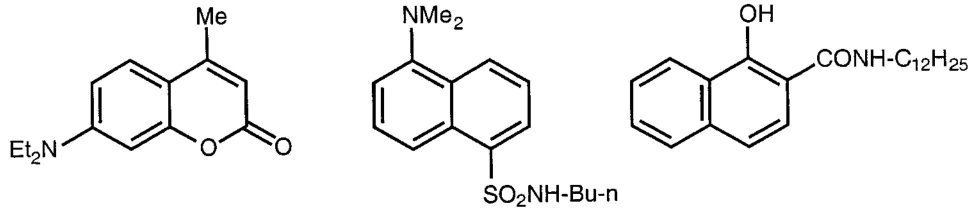
2: X = $B(C_6F_5)_4$

3: X = SbF_6

4: X = Cl, or OTs

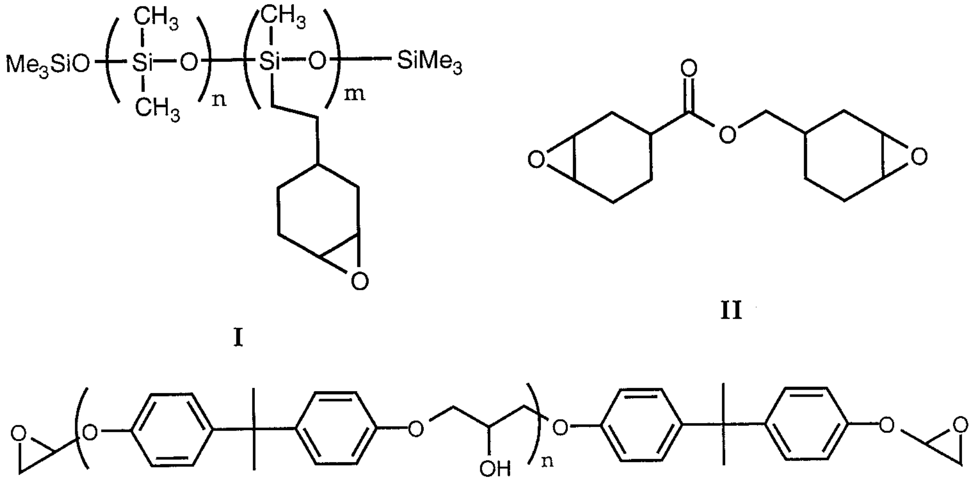
	R	R′
a	H	H
b	CH_3	i-C_3H_7
c	i-C_3H_7	i-C_3H_7
d	$C_{12}H_{25}$-n	$C_{12}H_{25}$-n
e	H	OC_8H_{17}-n
f	H	$O(CH_2)_3Si(CH_3)_3$
g	H	$OCH_2CH(OH)C_{12}H_{25}$-n

Figure 1. Structures of initiators used.



Coumarin-1 DASB DDHNA

Figure 2. Fluorescence probes.



I

II

III

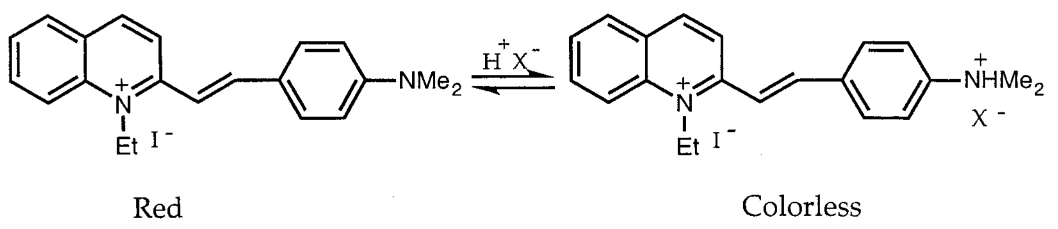
Figure 3. Structures of oligomers or monomer used.

(7.8×10^{-3} M). The initial absorbance was ~1.6 at 520 nm (in acetonitrile) or 530 nm (in ethanol). The solutions were irradiated using different doses (IL390B light radiometer from International Light Inc.) under an UV lamp (System LC-06-T3 from American Ultraviolet Co.), while the absorbance of QR at 520 nm (MeCN) or 530 nm (EtOH) was measured. Conversion was calculated from the following eq 1, where A_0 was the absorbance at the beginning and A_n was the absorbance at dose n:

$$\text{conversion} = (1 - A_n/A_0) \times 100\% \tag{1}$$

General Procedure for Kinetic Measurement of the Photopolymerizations Rate. Solutions of each of the pho-

Scheme 1



toinitiators in oligomer **I** and **III** or monomer **II** containing 0.1% (w/w) DDHNA (*N*-dodecyl-1-hydroxy-2-naphthalenecarboxamide) were prepared.

A 0.1 mm film of each solution was prepared by sandwiching a drop of solution between two glass slides (75 × 25 × 1 mm). The sample was placed directly under the sensor head of the CM 1000 optical fiber fluorometer (commercially available from Spectra Group Limited, Inc.) and held in an upward position shielded from stray light by means of a dark box. A small spot on the layer was cured with the 350 nm excitation beam of the CM 1000, and a fluorescence intensity ratio measured at two monitoring wavelengths, 527 and 420 nm, selected from the differences in the fluorescence intensities before and after complete polymerization was achieved. Under these optimal test conditions, real-time kinetic profiles for different photoinitiators to polymerize selected epoxy oligomers and monomer could be obtained. All measurements were performed at ambient temperature (about 23 °C).

Correlation of Fluorescence Intensity Ratio and Cure Degree Using FTIR. A drop of 1.0% (w/w) solution of **1b** in monomer **II** containing 0.1% (w/w) of DDHNA was placed between two NaCl plates spaced with a Teflon spacer (0.015 mm). The liquid film was irradiated at different doses under an UV lamp (System LC-06-T3 from American Ultraviolet Co.), and the fluorescence intensity ratio at 527 and 420 nm was monitored. Peaks at 790 and 1730 cm^{-1} were followed by FTIR and integrated as a function of dose. The peak at 1730 cm^{-1} was selected as the internal standard, and the conversion was calculated from eq 2, where $(A_{790}/A_{1730})_0$ and $(A_{790}/A_{1730})_n$ are the area ratios of peaks at 790 and 1730 cm^{-1} at beginning and at dose *n*, respectively.

$$\text{conversion} = [1 - (A_{790}/A_{1730})_0/(A_{790}/A_{1730})_n\ ] \times 100\% \qquad (2)$$

Storage Stability of Iodonium Tetrakis(pentafluorophenyl)gallate Compositions. Compound **1e** was dissolved at 0.40% (w/w) in about 20 g of resins **I**, **II**, and **III** and used as a standard. Solutions of **2e** and **3e** were prepared at molar concentrations equal to **1e**. The solutions were kept in an oven at 65 °C. Their viscosities were measured by viscometer (model LVF from Brookfield Engineering Laboratories, Inc.).

Solutions of **1c** in oligomer **I** were prepared at different concentrations ranging from 0.05 to 2.00 wt %. These formulations were stored in the dark at room temperature to observe the change of their viscosities. Gel times were recorded.

Results and Discussion

Comparison of the Rate of Acid Release. Several sensitive analytical methods have been reported to determine the amount of Brønsted acid generated from the photolysis of iodonium salts. The most effective in our hands is the system quinaldine red in acetonitrile or ethanol (Scheme 1).[18] We observe that the photobleaching rate of QR in acetonitrile correlates well with the basicity of the anions, while that in ethanol correlates well with the photosensitivity of the iodonium cations.

The order of photobleaching rates in acetonitrile is **1b** > **2b** > **3b** > **4b** (Figure 4). This indicates that the larger sized and less nucleophilic tetrakis(pentafluorophenyl)gallate anion renders the iodonium cation more photosensitive. The Brønsted acid released is also stronger. It is apparent from Figure 5 that the photobleaching rates of the iodonium gallates in ethanol are divided into three groups, while there is no difference between **1b** and **2b**. Iodonium salts with long alkoxy chains (**1e**, **1f**, and **1g**) show the highest rates due to the red shift of UV maximum absorption wavelength (~250 nm). The rates of the iodonium salts with the symmetric alkyl straight chain (**1a** and **1d**) are the lowest (λ_{max} = 236 nm). The compounds with isopropyl group (**1b** and **1c**) display a higher rate than do **1a** and **1d**. This is likely related either to the more stable isopropylphenyl radical or to the more active α-H of isopropylbenzene formed from the photolysis of **1b** and **1c**.

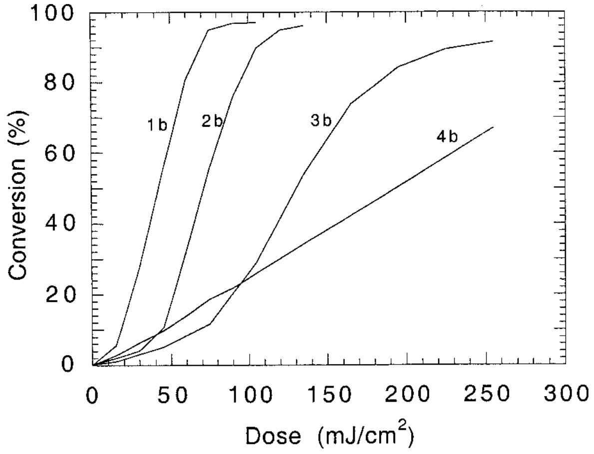


Figure 4. Rate of acid release of iodonium salts (b) in acetonitrile.

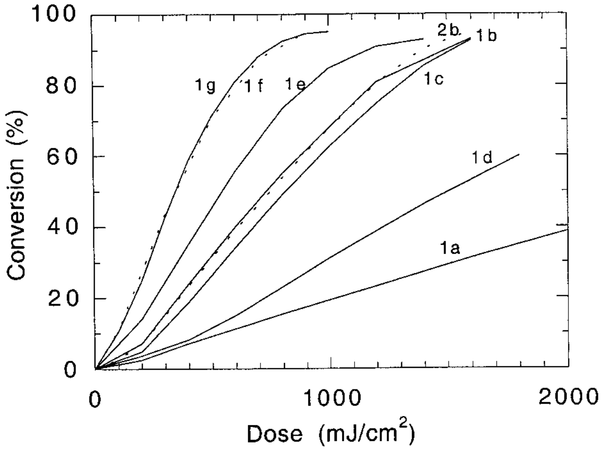


Figure 5. Rate of acid release of gallate salts in ethanol.

Optimization of Monitor Conditions Using Fluorescence Probe DDHNA. To accurately and quickly determine the cure degree of a film by using fluorescence techniques, it is necessary to optimize the test

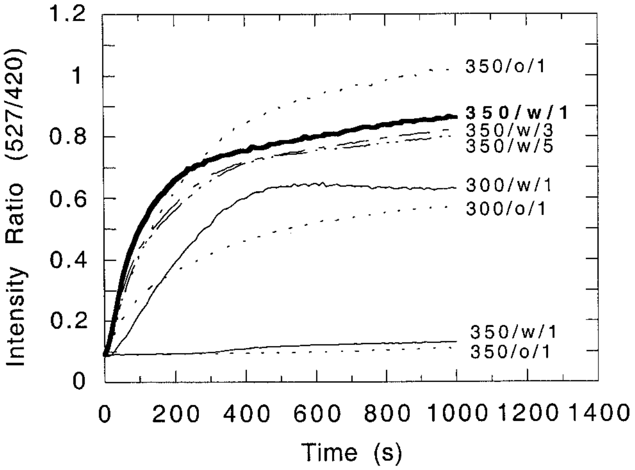


Figure 6. Optimization of cure monitor conditions with 1b. 350/w/3: 3 × 0.1 mm of film covered with a glass slide was irradiated at 350 nm; 300/o/1: 1 × 0.1 mm of film without a glass cover was irradiated at 300 nm.

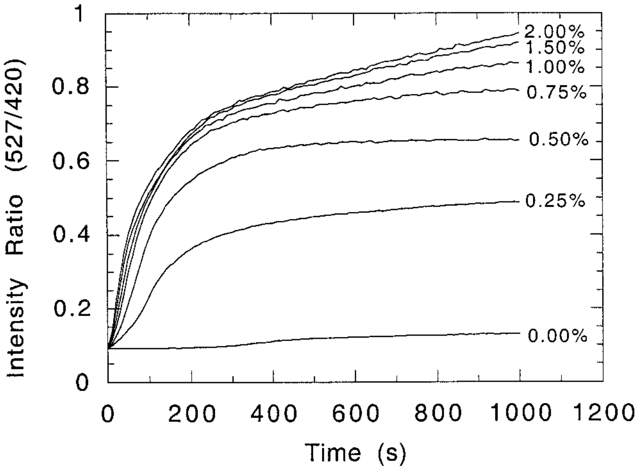


Figure 7. DDHNA (0.1%) in resin I at different concentrations of 1b.

conditions including the emission spectra of the probe before and after cure, the concentration of the probe and photoinitiators, the thickness of film, the substrate, the wavelength of the probe excitation, and initiator activation. As described previously,[16] the concentration of DDHNA was maintained at 0.1 wt % and the fluorescence intensity ratio at 527 and 420 nm monitored. Other test conditions were optimized (Figure 6), such that the concentration of **1b** in resin **I** was 1.0 wt %, the films were prepared on a glass slide with or without a glass slide cover, the thickness of films was 0.1, 0.3, and 0.5 mm, and the wavelength of the beam of the CM 1000 was 300 or 350 nm. It was found that the film need be covered with another glass slide, since moisture affects the cationic polymerization if no cover was present. The CM 1000 beam at 350 nm performed better than that at 300 nm, because the transmission of the glass slide was 45% at 300 nm and 90% at 350 nm. The optimal thickness of film was 0.1 mm. Only minimal change in intensity ratio was observed for the control experiments of no photoinitiator at 350 nm.

The optimization of the concentration of photoinitiator **1b**, where other test conditions were set up according to the above, is given. As expected, the rate of cure in Figure 7 is dependent on the initiator concentration, increasing with a higher concentration of photoinitiator.

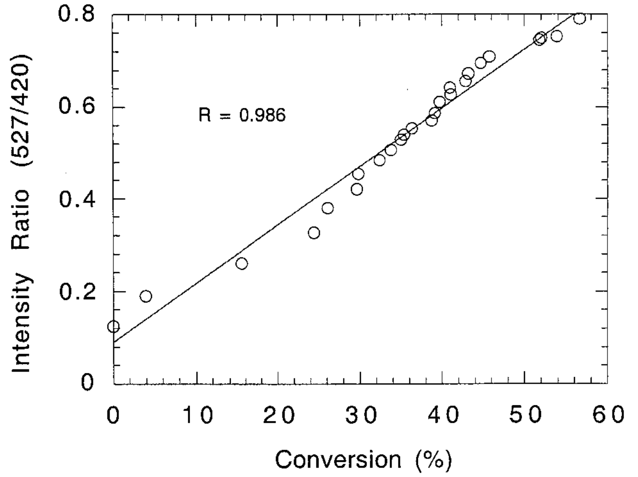


Figure 8. Correlation between fluorescence intensity ratio and conversion measured by FTIR.

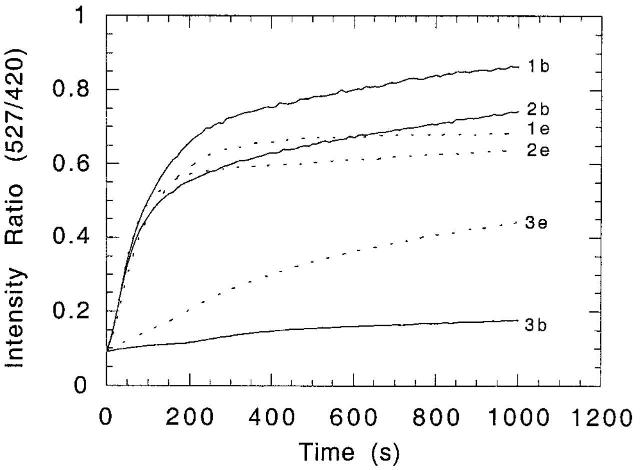


Figure 9. Comparison of iodonium salts differing in anions in resin I.

It was observed that the optimal concentration was 1.0 wt % and that only a little of the increase in intensity ratio was obtained at higher concentration than 1.0%.

Correlation between Fluorescence Intensity Ratios and Cure Degree by FTIR. Various spectroscopic methods have been employed for the comparison of photoinitiator efficiencies; the most common are the real-time infrared spectroscopy (RTIR),[4,5] Fourier transform IR spectroscopy (FTIR),[18] Raman spectroscopy,[21] and nuclear magnetic resonance (NMR) spectroscopy.[22] Herein, we chose FTIR to calibrate against the fluorescence technique using **II**. For this purpose, a 1.0 wt % of **1b** solution containing 0.1 wt % DDHNA was sandwiched between two NaCl plates and irradiated. Both data for the IR spectra and cure monitor ratios were measured as a function of light doses. Figure 8 showed the correlation between the fluorescence intensity ratios and the degree of cure attained from the IR spectra. The result confirms that this fluorescence probe technique correlates to FTIR well.

Activity of Iodonium Tetrakis(pentafluorophenyl)gallate Photoinitiators. By using 1.0 wt % **1b** as a standard, other photoinitiators at molar concentrations equal to **1b** were investigated. As one can see from Figure 9, the iodonium gallates show higher photoactivity than the borate salts. The antimonate salts were the slowest in photopolymerization. Since photoinitiator **3e** is more soluble than **3b** in this nonpolar resin, it

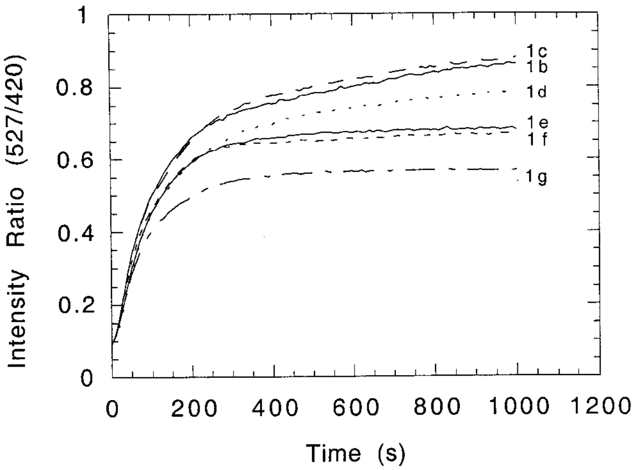


Figure 10. DDHNA (0.1%) in resin I with different iodonium gallates.

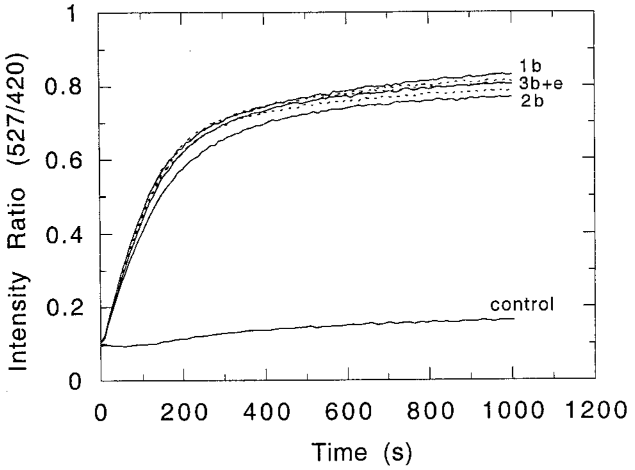


Figure 11. Comparison of iodonium salts differing in anions in resin II.

performed better than **3b**. This result is consistent with that of the acid release in acetonitrile and those deriving from melting point, NMR data, and UV spectra.[2]

Surprisingly, the iodonium gallate or borate with alkyl chains (**1b** or **2b**) displayed better activity than those with an alkoxy chain (**1e** or **2e**). This was further confirmed from a series of other iodonium gallates that **1c** and **1d** also showed better activities than **1f** and **1g** (Figure 10). These results are not consistent with those of the rate of acid release in ethanol.

It is known that the sensitized photolysis of iodonium salts is influenced by the polarity of media and the lipophilic substituents of cations. We suspect that 0.1 wt % of DDHNA not only acts as a fluorescence probe but also functions as a sensitizer. Without this sensitizer, it is impossible for these photoinitiators to catalyze the photopolymerization of epoxy resin at 350 nm, since these iodonium salts almost have no absorption above 300 nm. In nonpolar media, the sensitized photolysis depends on the substituents on the iodonium salts. This can occur through energy or electron transfer controlled by thermodynamic requirements (eq 3). Electron transfer from the exited sensitizer DDHNA to iodonium salts is thermodynamically possible if the free energy obtained from the Rehm−Weller relationship is negative:

$$\Delta G = E_{\mathrm{ox}} - E_{\mathrm{red}} - E^{*} \qquad (3)$$

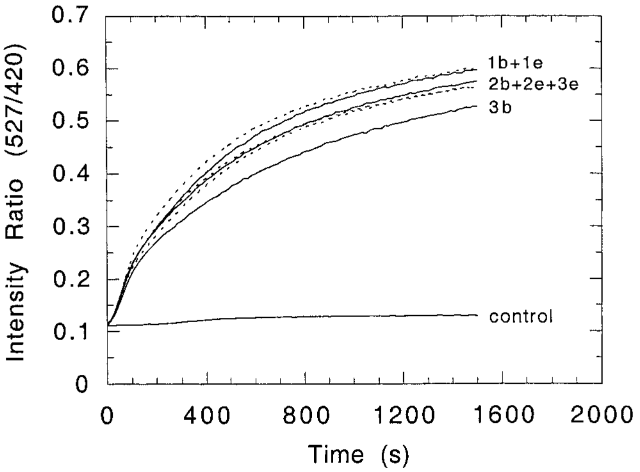


Figure 12. Comparison of iodonium salts differing in anion in resin III.

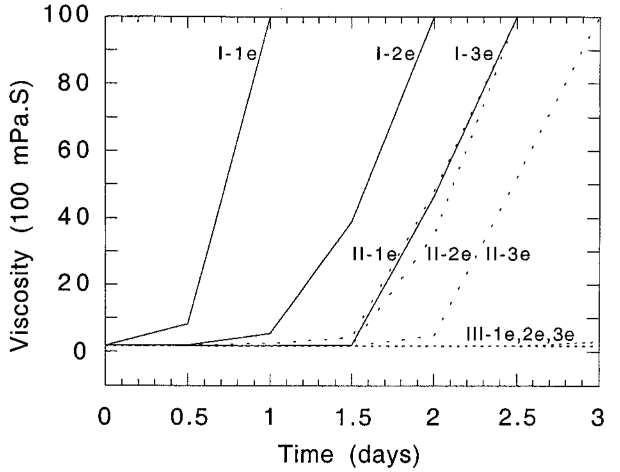


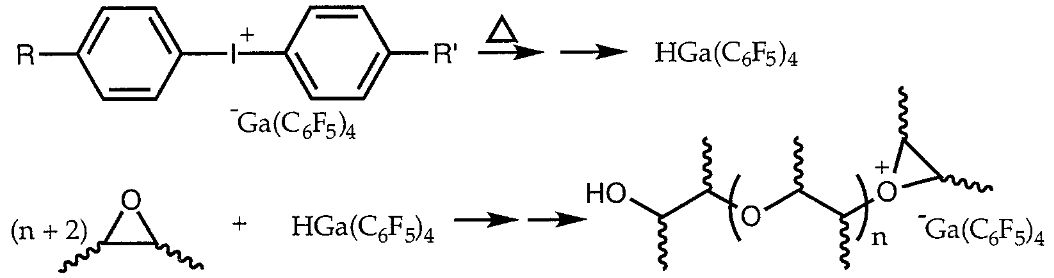
Figure 13. Gel time of iodonium salts solutions in resins at 65 °C.

where ΔG is the free energy of the electron transfer, E_{ox} is the half-wave oxidation potential of the sensitizer DDHNA, and E^{*} is the energy of the excited DDHNA. E_{red} is the half-wave reduction potential of the iodonium salts. As reported recently,[23,24] since the reduction potential of the alkoxy-substituted iodonium salts is more negative than that of alkyl-substituted salts, the corresponding ΔG is less negative. In this case, the direct physical meaning is that the alkyl-substituted iodonium salts were sensitized by the probe DDHNA more efficiently than were the alkoxy-substituted ones. As a result, **1b**, **1c**, and **1d** exhibited the higher cure rates than **1e**, **1f**, and **1g**.

The performance of the iodonium salts differing in anion in two resins of significant polarity, **II** and **III**, was also investigated and compared (Figures 11 and 12). No significant difference was observed. In highly polar media, no matter how different the branched chains of the iodonium salts, their reactivity toward the excited sensitizer DDHNA quenching does not differ,[25] although ΔG is different for these salts. On the other hand, all of the photoinitiators used are soluble. Therefore, their relative activities were approximate in resins **II** and **III**.

These studies reveal that all iodonium tetrakis(pentafluorophenyl)gallates display excellent photosensitivity and solubility in both nonpolar and polar resins. Their performance exceeds that of other photoinitiators

Scheme 2



in this family for the photopolymerization of epoxy silicone resins.

Storage Stability of the Compositions of Iodonium Tetrakis(pentafluorophenyl)gallates. The iodonium tetrakis(pentafluorophenyl)gallates are typically solids or viscous liquids. In practical applications, a liquid form, for ease in handling, has to be prepared by dissolving it in a monomer or oligomer, and these photoinitiator compositions have been maintained for a period of time. Actually, every photoinitiator composition has a tendency to gel and to give a reduced level of performance during the storage period. We compared the influence of the anion of iodonium salts on the storage stability in three typical resins (Figure 13). The results show that the gallate salt made the composition more unstable in the order $^-Ga(C_6F_5)_4 < {}^-B(C_6F_5)_4 < {}^-SbF_6$; the more photoactive resin showed the worse stability in a order **I** < **II** < **III**.

We suspect the less nucleophilic tetrakis(pentafluorophenyl)gallate anion renders the iodonium salt more sensitive not only photochemically but also thermally. Thermal gelling of samples was caused by $HGa(C_6F_5)_4$, which arises from the thermal decomposition of the iodonium cation of the salt; it does not derive from the decomposition of the tetrakis(pentafluorophenyl)gallate anion. In fact, this is a thermally induced cationic polymerization (Scheme 2). This was confirmed by a following experiment. 2.0 wt % of the gelled **1c** solution in resin **I** was kept for 9 days in an oven (65 °C) and 95 days at room temperature without sealing, and the $CDCl_3$ solution extracted from the gel was analyzed by ^{19}F NMR. The result indicated the three fluorine peaks of tetrakis(pentafluorophenyl)gallate did not change, though the cation of the salt had changed in this gelled composition. According to our experience, the different countercations do not affect the fluorine absorption peak of tetrakis(pentafluorophenyl)gallate in ^{19}F NMR spectra. Therefore, the gallate anion was not decomposed in this gelled composition.

An attempt to improve storage stability by adding hindered amine to serve as stabilizer was also carried out.[26] 2.0 wt % of **1e** solution in resin **I** containing 1000 ppm of trioctylamine was stored in the oven (65 °C); the stability increased from 10 h of the control experiment to 40 h.

A further investigation of the **1c** solution in resin **I** showed that a lower concentration of photoinitiator composition gave a longer gel time (Figure 14). For example, a 0.6 wt % of **1c** solution could be stable for over 50 days without gelling. This length of time is acceptable in practical applications.

Conclusion

In this paper, we report that iodonium tetrakis(pentafluorophenyl)gallates show the fastest rate of acid release in this cationic photoinitiator family. This is observed when QR is used as indicator and acetonitrile as solvent. By employing fluorescence probe techniques, the photopolymerization kinetics of epoxy silicone oligomers are successfully followed in real time. It is impossible to monitor this cure process using IR spectrometry. The results confirm the high photoreactivity and excellent solubility of the iodonium gallate salts in both nonpolar and polar media. Various compositions in several typical resins show the desirable storage stability. In a gelled composition of silicone resin, the tetrakis(pentafluorophenyl)gallate anion remains stable. These properties make iodonium tetrakis(pentafluorophenyl)gallate highly attractive for laboratory and commercial applications.

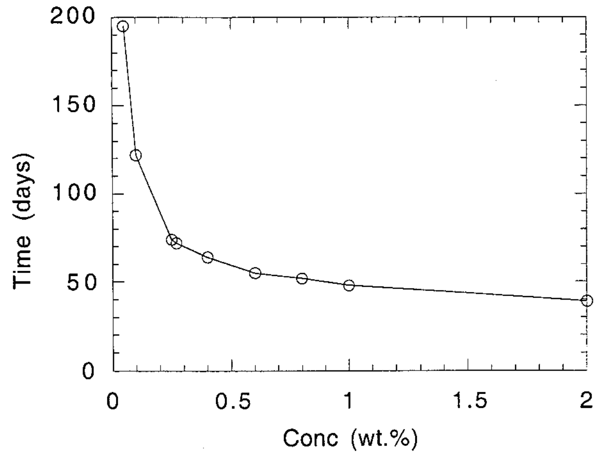


Figure 14. Gel time of 1c at different concentration in resin I.

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