Photocatalyzed Polymerization of Aromatic Dicyanate Esters by Iron–Arene Complexes

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A series of iron–arene complexes with the general formula [CpFe(η^6-arene)]X (Cp = η^5-C_5H_5; arene = toluene, naphthalene; X = PF_6^-, SbF_6^-) are demonstrated to be effective cationic photoinitiators for the polymerization of aromatic dicyanate esters. The photochemically initiated curing reaction has been characterized from thin films of these materials by monitoring *in situ* FTIR spectra; the effects of several different exposure times, various cure temperatures, and different photocatalysts have been investigated. Comparisons of the extent of curing by these iron–arene photoinitiators with the zinc octoate thermal-initiator are also made by FTIR spectroscopy and DSC thermal analysis. In contrast to earlier observations of photocatalysis of epoxy-based materials by these iron–arene systems, the cyanate polymerization is not significantly affected by the nature of the metal complex counterion. The photoinitiation results, however, are consistent with arene dissociation being the primary step in the photochemical mechanism. The [CpFe(toluene)]PF_6 complex is also shown to produce high resolution negative images in thin films of these cyanate esters.

Introduction

Photopolymer materials are of great utility in the electronics industry, especially in the area of photolithography leading to the formulation of high-resolution integrated circuit elements.[1] Photoresist materials containing transition metal compounds as photoinitiators have, in comparison to resists containing organic initiators, received relatively little attention. Organometallic complexes of the type [CpFe(η^6-arene)]$^+$X$^-$ (arene = toluene, naphthalene, pyrene; X$^-$ = BF_4^-, PF_6^-, SbF_6^-) have been demonstrated to act as efficient cationic photoinitiators for the polymerization of epoxy resins.[2] Following irradiation into the lowest energy visible absorption bands these complexes undergo an arene dissociation reaction leaving an unsaturated cationic metal center which, in turn, is available for coordination by up to three oxygen atoms from the epoxide rings. Subsequent thermal treatment of the resin material produces the cross-linked epoxy network (see Scheme 1). The photochemical efficiency of the polymerization reaction is thought to be dependent on the quantum efficiency of the primary process involving arene loss. The reaction has also been determined to be influenced by the nature of the counterion; the

Scheme 1

polymerization product
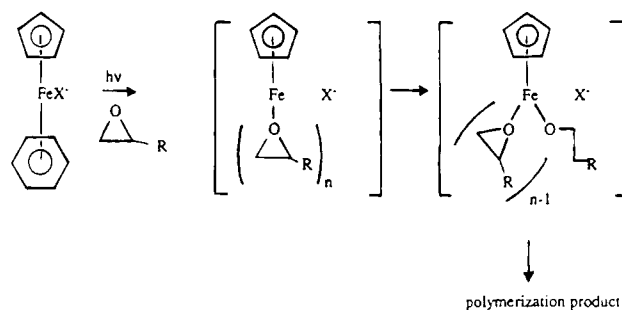
reaction rate in the epoxy resins proceeds 10–100 times faster according to the sequence SbF_6^- > PF_6^- > BF_4^-. Consequently, considerable different exposure times can be employed to cure the resin layers.[2]

Epoxides, polyimides, and acrylates are the dominant materials for resist applications and are used extensively in the microelectronics industry. However, cyanate esters represent another class of materials that possess desirable characteristics.[3] The curing of cyanate esters is usually accelerated with catalysts such as acids, bases or metal salts, the latter normally being

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salts of carboxylic acids, such as zinc octoate. On curing, these monomers or oligomers cross-link to produce triazine-based networks that exhibit low dielectric constants,[3d] excellent thermal stability,[3e] good adhesion to metals and resistance to solvents,[3e,f] and high glass transition temperatures with slightly lower thermal expansion properties than epoxide-based materials.[3e-g]

The mechanism and kinetics of transition-metal catalyzed polycyclotrimerization reaction of aromatic cyanates have been the subject of investigation by Bonetskaya et al.[4] In previous work the kinetics of the thermal cross-linking of a bismaleimide/biscyanate/epoxy blend has been reported.[5] The processes of gel formation in 2,2-bis(4-cyanatophenyl)propane has been studied as a function of different catalysts and their concentrations.[6] In addition, other studies have illustrated that the photoproducts of various transition-metal organometallic complexes can also act as catalytic agents for the cure of cyanate resins;[7] however, the kinetics and mechanisms of these reactions are not well understood and, in fact, the photochemical curing process has been virtually unexplored.[8]

Consequently, we have carried out a systematic investigation into the role of a series of photosensitive transition-metal organometallic complexes with the general formula $[CpFe(\eta^6\text{-arene})]X$ (Cp = cyclopentadienyl $(\eta^5\text{-}C_5H_5)$; arene = toluene, naphthalene; X = PF_6^-, SbF_6^-) in the cure of thin films containing cyanate ester monomers and oligomers. The effects of these iron arene photocatalysts on the curing characteristics of cyanate ester thin films have been measured by recording *in situ* FTIR spectra and by DSC thermal analysis. A preliminary mechanistic interpretation of the photochemistry is also presented.

Experimental Section

Materials. Ferrocene was purchased from Pressure Chemical Co. and recrystallized prior to use. Aluminum powder and anhydrous aluminum trichloride were obtained from Baker Chemical Co. in high purity (>99%). The acids hydrogen hexafluoroantimonate and hydrogen hexafluorophosphate were used as 60% solutions (Alfa Chemical Co.) The liquid dicyanate monomer AroCy L-10 and resin AroCy B-30 were obtained from Hi-Tek Polymers, Inc. Zinc octoate was purchased from Mooney Chemicals, Inc. as an 8% solution of zinc metal in mineral spirits.

Syntheses. The [CpFe(toluene)]X [Cp = $\eta^5\text{-}C_5H_5$; X = PF_6^-, SbF_6^-) complexes were synthesized according to the method of Nesmeyanov et al.[9] Ferrocene (5.0 g), AlCl$_3$ (7.1 g), and Al powder (0.7 g) were refluxed in toluene under argon for 4 h. After the mixture had cooled to room temperature, it was further cooled in an ice bath and then 200 mL of ice water

was added. The mixture was stirred rapidly for 20 min to ensure complete hydrolysis. Upon separation of the aqueous phase and subsequent addition of HPF$_6$ or HSbF$_6$ a yellow precipitate was collected and dried under vacuum. The iron arene complexes were characterized by comparison of the proton NMR spectra with the reported values; ^{1}H NMR δ 6.3 (5H, arene) δ 5.3 (5H, Cp), δ 2.4 (3H, CH$_3$).[10] The [CpFe-(naphthalene)]X (Cp = $\eta^5\text{-}C_5H_5$; X = PF_6^-, SbF_6^-) complexes were synthesized similarly by refluxing ferrocene (5.0 g), naphthalene (3.5 g), AlCl$_3$ (8.0 g), and Al powder (0.8 g), in Decalin (60 mL) for 90 min. The complexes were isolated as described above for [CpFe(toluene)]X. Purity was established by comparison with the reported UV−visible absorption spectra.[2a]

Thin-Film Preparation. The thin films were typically prepared by dissolving 10^{-4} moles of the iron−arene photocatalyst in 5 g of the difunctional cyanate AroCy L-10 material; zinc octoate was used at a concentration of 800 ppm. In the photoimaging work 2-mil-thick films of AroCy B-30 containing 0.5 wt % of the iron−arene compound and zinc octoate (800 ppm) were coated onto the treated side of 1.4-mil-thickness copper foil using a coating knife. The films were B-staged (partially cured) by baking at 393 K for approximately 15 min. Exposure of the resulting dry film to imaging radiation was performed through a Stouffer 1-T resolution guide. Samples were prepared for infrared analysis by spin coating the solutions onto 25 × 5 mm round NaCl plates using a Headway Research Inc. Model 1-EC101D-R485 photoresist spinner.

Physical Measurements. Samples of the cyanate esters containing the metal complex photoinitiators were irradiated using a 350 W Oriel mercury lamp for the specified times; the lamp intensity was determined to be approximately 3.5 mW/cm^2, measured by means of an International Light Model IL-7000 radiometer. The extent of cyanate ester polymerization was monitored by the heated-cell FTIR method. An Accuspec Corp. Model 20 temperature-controlled sample cell was used for *in situ* analysis; throughout heating the cell was purged with dry nitrogen. The reaction was monitored as a function of irradiation time by determining the decrease in the integrated area of the OCN stretching band in the 2360−2150 cm^{-1} region. The C−H out-of-plane bending vibration of the para-substituted aromatic ring at 1010 cm^{-1} was used as the internal standard. FTIR spectra were acquired on an IBM IR/85 instrument; the spectrometer was programmed to record spectra at 90-s time intervals and with 20 scans/spectra. DSC measurements were made on DuPont Instruments Model 910 DSC equipped with a DuPont Model 1090 thermal analyzer; the onset values were determined by the tangent of the rise in the measured heat flow. Thermal gravimetric analyses were performed on a Perkin-Elmer Model 7 Series thermal analyzer system.

Results and Discussion

In the presence of a suitable metal-containing catalyst, cyanate ester monomers such as AroCy L-10 undergo a polycyclotrimerization reaction upon thermal treatment to form three dimensional triazine polymer networks (see Scheme 2). These materials are becoming increasingly used in the microelectronics industry as they possess thermal and electrical properties surpassing epoxides, polyimides, and bismaleimide triazines (vide supra).[3]

Importantly, the cyanate ester resins are clearly seen to darken following light excitation, which is a dissimilar behavior to the analogous epoxy resin/iron arene photoinitiator system that undergoes photobleaching.[2] This effect has been monitored spectroscopically, and Figure 1 illustrates the UV−visible spectral changes that occur during UV photolysis of

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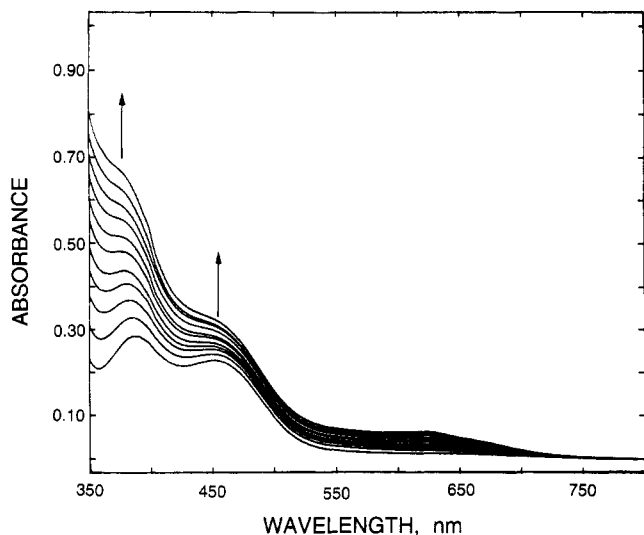
Figure 1. UV–visible absorption spectral changes accompanying the UV photolysis of 2×10^{-3} M [CpFe(toluene)]PF$_6$ in AroCy L-10 cyanate ester solution. Spectra are depicted following 20 s irradiation intervals; initial spectrum recorded prior to photolysis.

Scheme 2
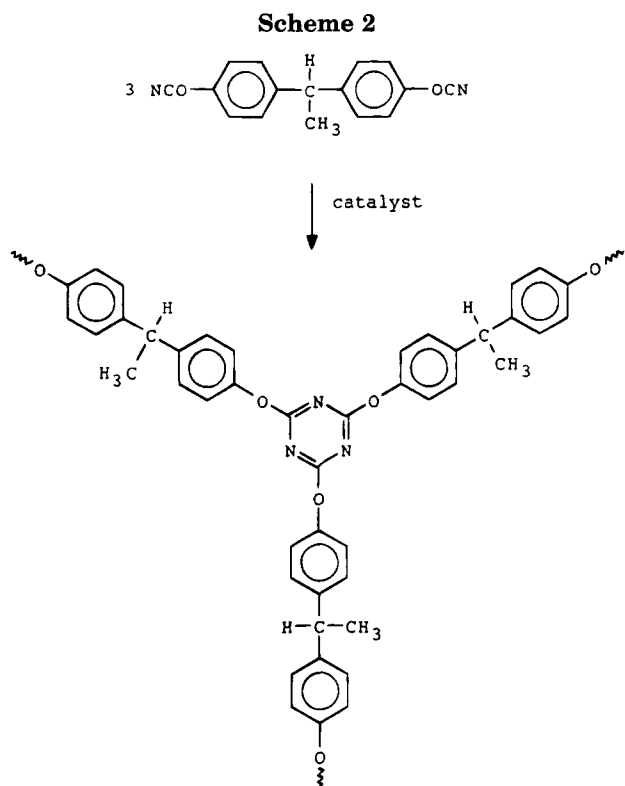
[CpFe(toluene)]PF$_6$ in AroCy L-10 resin. A significant increase can be observed in the light absorbance throughout the visible region. These spectral changes are consistent with ligand field excitation of the [CpFe-(arene)]X complex and subsequent ligand (L) coordination to form the CpFeL$_3$ (L = cyanate ester) cation.[2]

The influence of exposure dose on the extent of polycyclotrimerization of the cyanate ester has been investigated. Figure 2 illustrates the results obtained from AroCy L-10 containing the [CpFe(toluene)]PF$_6$ complex as photoinitiator following different excitation periods and then a cure at 423 K. It is clearly apparent that the extent of the polymerization reaction is directly proportional to the amount of light irradiation and,
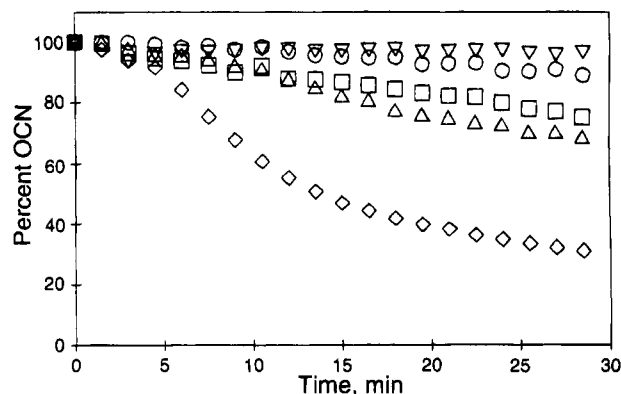
Figure 2. Normalized percent cyanate ester remaining versus cure time at 423 K following various prior irradiation times for 0.5 wt % [CpFe(toluene)]PF$_6$ in AroCy L-10 cyanate ester solution. Irradiation times: (∇) 0 s; (○) 10 s; (□) 30 s; (△) 60 s; (◇) 120 s.
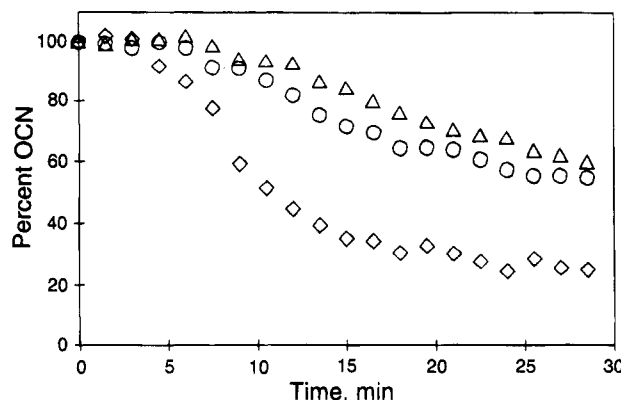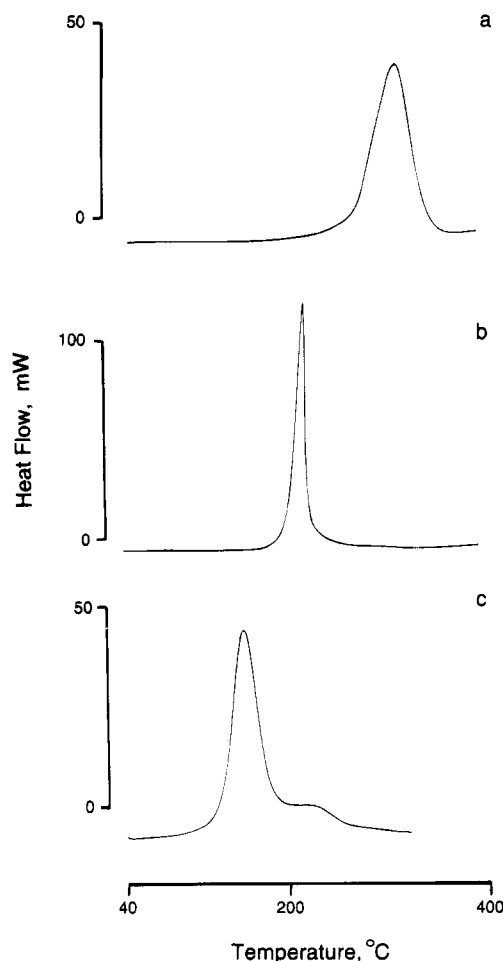

Figure 3. Normalized percent cyanate remaining versus cure time at various isothermal holds for 0.5 wt % [CpFe(toluene)]-PF$_6$ in AroCy L-10 solution. In each case the solutions were prior irradiated for 120 s. Cure temperatures: (△) 393 K; (○) 413 K; (◇) 433 K.

hence, the concentration of catalyst generated. The largest degree of curing occurs following 120 s of irradiation. It is important to note that the iron salt is essentially inert with respect to the cure reaction at 423 K when excluded from light, as evidenced by a negligible reaction in the dark.

Variations in the curing temperatures have also been studied. Figure 3 indicates the percent cyanate that remains over time as a function of heating temperature in a sample of AroCy L-10 catalyzed with [CpFe-(toluene)]PF$_6$; in each case samples were irradiated for 120 s prior to heating. The results clearly demonstrate that varying the cure temperature also affects the extent of the polycyclotrimerization reaction. At lower cure temperatures the conversion of cyanate ester is, of course, considerably less than at higher temperatures for any specified cure time. On curing at 433 K it can be seen that a rapid decrease of the cyanate ester concentration begins at approximately 5 min into the cure and subsequently reaches a plateau at approximately 15 minutes of reaction time. Even at a cure temperature of 433 K, however, only about 75% of the cyanate ester has been consumed and further conversion of the cyanate ester requires a higher cure temperature.
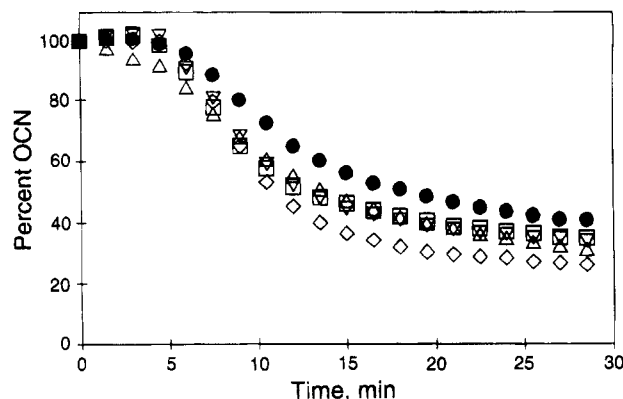
Clearly, the above results demonstrate that the addition and subsequent photolysis of iron–arene salts produce a significant catalytic effect on the curing of

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Figure 5. Normalized percent cyanate remaining versus cure time at 423 K for a series of photochemical and thermal initiators in the AroCy L-10 cyanate ester solution. Samples containing the iron−arene salts were each irradiated for 120 s prior to thermal treatment. Metal complexes: (△) [FeCp-(toluene)]PF$_6$; (▽) [FeCp(toluene)]SbF$_6$; (□) [FeCp(naphtha-lene)]PF$_6$; (◇) [FeCp(naphthalene)]SbF$_6$; (●) Zn octoate.

Table 1. Polymerization Exotherm Peak Temperatures Obtained by DSC Measurements for the AroCy L-10 Cyanate Ester Resins

| | peak onset, °C | |
complex	no exposure	2 min UV exposure
none	267	267
[CpFe(toluene)]PF$_6$	201	133
[CpFe(toluene)]SbF$_6$	200	138
[CpFe(naphthalene)]PF$_6$	131	111
[CpFe(naphthalene)]SbF$_6$	145	133
Zn octoate	143	143

Figure 4. DSC plots of the polymerization of the AroCy L-10 cyanate ester solutions containing (a) no photoinitiator, (b) 0.5 wt % [CpFe(toluene)]PF$_6$ (no irradiation) and (c) 0.5 wt % [CpFe(toluene)]PF$_6$ (that was prior exposed to UV light for 120 s). Heating rates were 20 °C/min in each case.

the cyanate ester material. This conclusion is further supported by DSC measurements. Figure 4 presents DSC thermal analysis results obtained from the polymerization of the neat AroCy L-10 cyanate ester in three environments: (a) with no photoinitiator present, (b) with [CpFe(toluene)]PF$_6$ but without light excitation, and (c) with [CpFe(toluene)]PF$_6$ and 120 s of irradiation. These DSC data are representative of all the complexes in the iron−arene series studied. It is notable that just the presence of the iron photoinitiator itself significantly lowers the temperature at which the onset of the DSC exotherm is observed and that this effect is even further enhanced with prior light excitation of the catalyst. In the irradiated system a second exotherm is observed at higher temperature which appears to be due to residual (unexposed) Fe arene complex.

The results of DSC measurements of AroCy L-10 containing the complete series of iron−arene salts are summarized in Table 1. Measurements have been obtained with and without prior light exposure and the thermal catalyst zinc octoate is also included for comparison purposes. In each case the onset of the photocatalyzed polymerization exotherm occurs at a much lower temperature than in the neat resin. Also noteworthy is that there is in each case a catalytic effect associated with the purely thermal decomposition of the organometallic complex. This latter effect is consistent

with the thermal decomposition of the respective iron−arene complexes: results obtained from thermal gravimetric analysis reveal decomposition temperatures in air for [CpFe(naphthalene)]PF$_6$, [CpFe(toluene)]PF$_6$, and [CpFe(toluene)]SbF$_6$ at 154, 259, and 275 °C, respectively.

Comparisons of the effect of varying the catalyst on the rate of cyanate conversion have also been made by FTIR spectroscopy; the results are shown in Figure 5. In each case equimolar concentrations of iron−arene salt in AroCy L-10 were irradiated for 120 s and then the resins were cured at 423 K. Importantly, the counterion of the metal complex apparently plays a negligible role in accelerating the rate of cyanate ester polymerization. This is in contrast to the effect observed in epoxy resins where a high degree of counterion dependence has been observed.[2] Instead, our results strongly imply that the primary photoprocess is the same for each iron−arene complex and that the extent of the subsequent polymerization reaction is governed by the efficiency of the arene group dissociation and the formation of the catalytic organometallic intermediate. The primary photochemical step of these iron−arene complexes in the epoxy resin systems is also believed to involve arene dissociation.[2]

It is significant that immediately after photolysis of the cyanate esters containing the Fe photoinitiators (and before heating) no growth was observed in the FTIR bands that are characteristic of the triazine ring. Additionally, no infrared bands appeared in the appropriate frequency region which could be attributed to a nitrogen-bound −OCN moiety acting as a coordinating ligand to the unsaturated iron center. It is suggested therefore that following photolysis and dissociation, the

Scheme 3
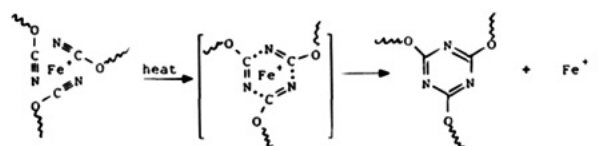
(Here the C_5H_5 ring is omitted for clarity)

cyanate functionalities may coordinate weakly as nucleophilic ligands in a π-fashion to the unsaturated metal center (see Scheme 3). Three such ligand interactions ($2e^-$ donors) are inferred to replace the arene ($6e^-$ donor) that has been photochemically dissociated. Thermal treatment is subsequently needed to form the triazine ring; this observation is consistent with the trimerization reaction occurring in a second endothermic step following the initial coordination of the cyano ligands to the Lewis acid metal center. Additionally, the cyanurate heterocycle formed during the cure (see Scheme 2) can also be expected to act as a ligand for the iron center, and this interaction may actually retard the catalytic process.[11] In an effort to learn more about the mechanisms of these polymerization reactions, we are currently studying the photocatalytic properties of a range of organometallic systems that exhibit varying photochemical behaviors.

These iron–arene complexes have excellent light absorption properties in the ultraviolet region of the spectrum and their absorption characteristics can be tuned in the visible region by structural changes in the arene ligand system.[2,12] We have also determined that it is possible to use the [CpFe(toluene)]PF$_6$ salt to act as a photoinitiator for a negative resist system based upon the AroCy B-30 cyanate resin. Coating formulations for testing were prepared from the resin Arocy B-30 containing 0.5 wt % of the iron–arene salt dissolved in methyl amyl ketone. The resulting solution was cast on copper foil to produce a film with a thickness of approximately 2 mil. It was found to be necessary to partially cure the film (B-Stage) in order to ensure that a tack-free film was placed in contact with the imaging mask. Exposure through a Stouffer 1-T resolution guide and subsequent baking and development produced a negative image of the guide with high resolution (see Figure 6). These photoimaging characteristics, in combination with their excellent thermal, dielectric, adhesive, T_g, and expansion properties, makes these photopolymers most attractive for a variety of electronic applications.

Conclusion

A series of iron–arene complexes are characterized to be effective photoinitiators for the polycyclotrimerization of aromatic dicyanate esters. In the absence of

(11) We are grateful to a reviewer for raising this latter point.
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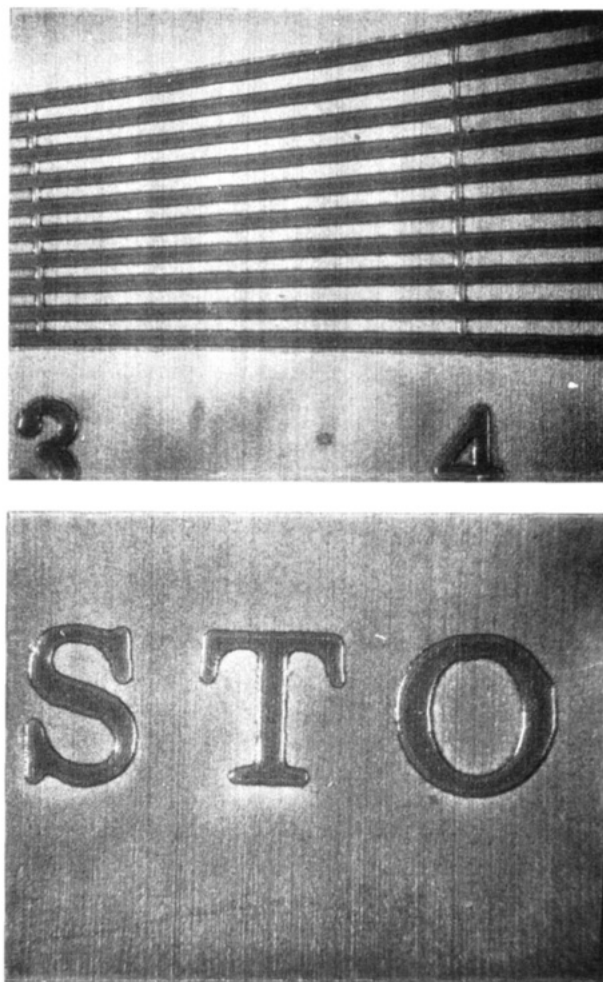
Figure 6. Optical micrographs of negative image photoresists of a UV-exposed AroCy B-30 cyanate ester thin film containing 0.5 wt % [CpFe(toluene)]PF$_6$ photoinitiator. Magnifications are ×25 and ×40 for the upper and lower photographs, respectively.

any metal catalyst this reaction takes place thermally at temperatures above 265 °C. Incorporation of the iron–arene complex, however, lowers this reaction temperature to 130–200 °C, and when the organometallic compound is prior irradiated, the polymerization process occurs at even lower temperatures of 110–140 °C. The results observed on varying the arene ligand and the counterion in these iron complexes are consistent with a photochemical mechanism involving arene dissociation as the initial step. High-resolution negative images have also been obtained following light excitation of the iron–arene system in cyanate ester thin films.

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