Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 5965–5975 **5965**
DOI: 10.1021/ma9006297

Photopolymerization of Vinyl Ether Networks Using an Iodonium Initiator: Effect of Radiation Intensity and Iodonium Concentration

Shaohua Chen, Wayne D. Cook,* and Fei Chen

Department of Materials Engineering, Monash University, Wellington Road, Clayton 3800, Victoria, Australia

Received March 24, 2009; Revised Manuscript Received June 28, 2009

ABSTRACT: Photo-differential scanning calorimetry (photo-DSC) was used to investigate the photocuring kinetics of visible light initiated cationic photopolymerization of triethylene glycol divinyl ether (TEGDVE) with a diphenyl iodonium salt initiator and the three photosensitizers: 1-chloro-4-propoxy-9*H*-thioxanthen-9-one (CPTXO), camphorquinone (CQ), and acridine orange (AO). The effects of water, a tertiary amine, and a radical scavenger were used to probe the photocuring mechanism. The rate of photopolymerization was approximately proportional to the incident light intensity, and in each system, the final conversions, as measured by photo-DSC, also increased with raised incident light intensity. The power-law dependence of the reaction rate on the concentration of iodonium salt with CPTXO and AO was ~1.5, while the order is nearly unity with CQ as the photosensitizer, suggesting that these photosensitizers do not follow the same sensitization mechanism. For the three photosensitizers, the final conversions all increased with higher iodonium salt concentrations. After cessation of irradiation, a dark reaction was observed—although the rate of this process decreased rapidly with time (as shown by photo-DSC), the polymerization continued very slowly over a long period of time.

Introduction

Ultraviolet (UV) and visible light induced photopolymerizations have received considerable attention due to their numerous advantages including their rapid curing even at ambient temperatures and their freedom from solvents, and this has led to many important applications, including composite production, prototyping, coatings, adhesives, inks, and electronics.[1−4] Cationic photopolymerization has several advantages over free radical photopolymerization. Because bimolecular termination between cations does not occur, the systems can exhibit dark cure behavior in which the monomers continue to react slowly upon storage of the sample in the dark after the irradiation has ceased.[3,5−8] Also, due to the absence of reactions between cations and oxygen, cationic polymerization is generally insensitive to the presence of air. Vinyl ethers can be rapidly cured via the cationic mechanism with onium salts, and these systems have the advantages of relatively low toxicity, low viscosities, and low shrinkage.[3] There are several studies on the photopolymerization of vinyl ethers with onium photoinitiators by UV light[6,9−12]and electron beam.[13−15] Because the onium photoinitiators generally only absorb in the deep-UV region, photopolymerization with visible light can be attained only by the use of a photosensitizer which absorbs visible or near-UV radiation and so produces an excited state which then reacts with the onium salt acting as a co-initiator.[1,16−21] This photosensitization can occur either by an energy transfer process[22,23] or by a photoinduced redox reaction[16,24] (see Scheme 1), resulting in the generation of a carbocation or superacid which can initiate the cationic polymerization. Scheme 1 also includes the unsensitized photodecomposition mechanism of diaryliodonium salts which has been summarized by Crivello and Lam.[25]

Despite the importance of photosensitizers to the application of photocationic polymerization with onium salts, there have been no detailed investigations of the effect of radiation intensity or initiator concentrations on the photopolymerization kinetics, and so a deep understanding of the specific mechanisms involved is still lacking, Therefore, in this work and a companion paper,[26] we study the cationic photopolymerization of tri(ethylene glycol) divinyl ether (TEGDVE) via photo-DSC, photo-FTIR, and steady-state UV−vis spectrometry with three types of photosensitizers: an aromatic ketone, 1-chloro-4-propoxy-9*H*-thioxanthen-9-one (CPTXO), an aliphatic diketone, camphorquinone (CQ), and a heteropolycyclic amine, acridine orange (AO). The photosensitization of iodonium salt photopolymerization of epoxy resins using AO was demonstrated many years ago by Crivello and Lam,[25] and the photosensitization of an iodonium salt by anthracene (which has a similar structure to AO) for divinyl ether photopolymerization has been studied.[20,27−29] Crivello and Sangermano[16] used CQ as a photosensitizer in the iodonium cationic polymerizations of epoxy and vinyl ethers, while CPTXO has also been reported as a photosensitizer of iodonium salts for acrylate[30] and vinyl ether[19] polymerization. However, there have been no detailed studies of the influence of incident light intensity or of the effect of concentration of iodonium salt and photosensitizer on the kinetics of photopolymerization of vinyl ethers. Thus, here we investigate the effect of cationic initiator concentration and of the visible radiation intensity (and, in a companion paper,[26] the effect of the photosensitizer concentrations) on the polymerization rate and provide mechanisms that are consistent with these observations.

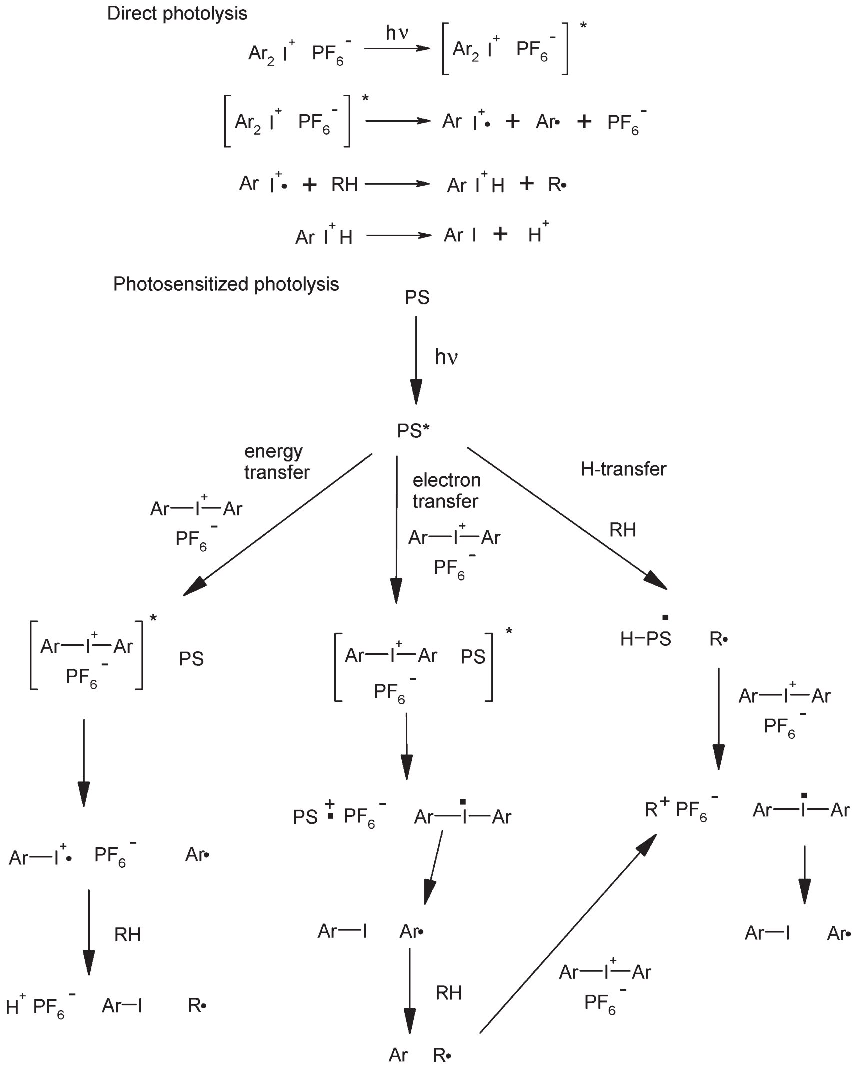
Experimental Section

Materials. Tri(ethylene glycol) divinyl ether (TEGDVE, Sigma-Aldrich Pty Ltd.) was used as the monomer. Occasionally, monomers that are sensitive to cationic polymerization are stabilized by small amounts of alkalis[31]—simple pH tests of aqueous solutions of the monomer did not reveal the presence of any detectable level of bases (pH ≈ 7). Over long storage in the

---

*Corresponding author. E-mail: wayne.cook@eng.monash.edu.au.

Scheme 1. Direct Photolysis Mechanism of Diaryliodonium Salt[25] and a Generalized Scheme of Energy Transfer[22,23] or Electron/Hydrogen Transfer[16,24] between the Photosensitizer (PS) and the Onium Salt (in This Case, Ph_2IPF_6) in the Presence of Abstractable Hydrogens



presence of oxygen, ethers can develop peroxides, but simple tests for peroxides by addition of iodide/starch solutions did not show significant levels of peroxide (<0.005 wt %). Diphenyliodonium hexafluorophosphate (Ph_2IPF_6, Sigma-Aldrich Pty Ltd.) was used as the co-initiator at different concentrations. 1-Chloro-4-propoxy-9*H*-thioxanthen-9-one (CPTXO, Sigma-Aldrich Pty Ltd.), camphorquinone (CQ, Sigma-Aldrich Pty Ltd.), and acridine orange base, 3,6-bis(dimethylamino)acridine (AO, Sigma-Aldrich Pty Ltd.), were used as photosensitizers. Because of the widely varying absorption coefficients of the photosensitizers, the limited dynamic range of the measurement of the heat flow, and the complexity of systems with two initiator components, we selected as "standard initiating systems" for TEGDVE the ratios 0.1 wt % CPTXO/0.1 wt % Ph_2IPF_6, 0.8 wt % CQ/0.8 wt % Ph_2IPF_6 and 0.2 wt % AO/0.2 wt % Ph_2IPF_6 however these concentrations were varied in some of the studies, but in all cases the concentration of photosensitizer exceeded that of the iodonium salt. The tertiary amine, *N*,*N*,3,5-tetramethylaniline (TMA, Sigma-Aldrich Pty Ltd.), and 2,6-di-*tert*-butyl-4-methylphenol (BHT, Sigma-Aldrich Pty Ltd.) were used to confirm the cationic nature of the photopolymerization. The structures of these chemicals are shown in Figure 1, all of which were used as received.

Photo-Differential Scanning Calorimetry. The isothermal photopolymerization studies were performed on ca. 6 mg samples (equivalent to ca. 0.4 mm thickness in the DSC pan) under a N_2 atmosphere in a Perkin-Elmer DSC-7 which had been modified[32] to allow the uniform irradiation of both the sample and reference pans. A Visilux-2 visible light dental curing unit (3M Co.) was used as the radiation source—this lamp produces radiation from 380 to 510 nm with a peak at 470 nm.[33] A stream of air was used to cool the lamp and prevent it from overheating.

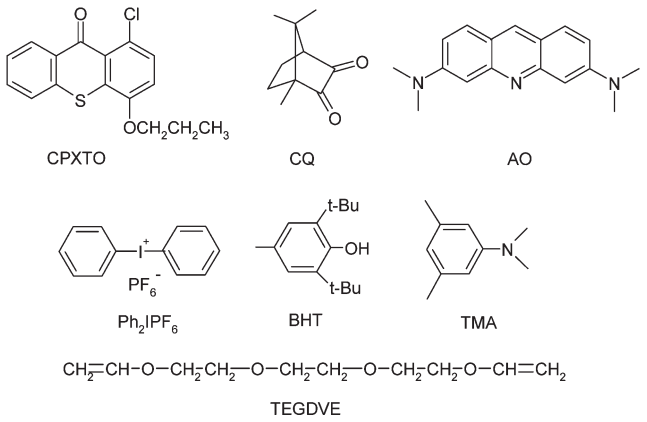


Figure 1. Chemical structures of CPTXO, CQ, Ph_2IPF_6, AO, TEGDVE, BHT, and TMA.

A bifurcated glass fiber-optic light guide (7 mm diameter entry window, 5 mm diameter exit windows) was used to pass the radiation from the light source through a PMMA block (replacing the metal block normally used in the DSC) and onto the reference and sample DSC pans. Glass neutral density filters (Schott, Germany) were used to vary the incident light intensity—in some cases the photopolymerization was so rapid under the full intensity of the Visilux lamp that glass neutral density filters had to be used to maintain thermal control of the photo-DSC. The spectral distribution of the Visilux-2 emitted at the base of the DSC pan was measured with a USB2000 fiber-optic spectroradiometer (Ocean Optics, Inc.). The relative radiation intensity (I_{rel}) quoted is relative to the unattenuated intensity of the lamp at the base of the sample pan. Prior to irradiation, the sample chamber was purged with nitrogen for several minutes, and then the lamp was turned on for 30 s to stabilize its output. The irradiation time was controlled by a shutter between the radiation source and the light guide. Fine aluminum rings were placed on the ledge in each sample pan holder, and two 0.05 mm thick PET covers (6 mm diameter) with two vent holes were used to cover the DSC pan holders—this provided a stable baseline (by avoidance of flow turbulence of the purge gas).[34]

The irradiation of both the sample and reference pans, and the use of a fully polymerized sample in the reference pan, minimized the effect of thermal heating from the lamp on the measured heat flux. In addition, any residual thermal heating effects due to small imbalances of the lamp irradiation (often of the order of 1 mW) were eliminated after each experiment by repeating the isothermal photo-DSC experiment with the now cured sample and subtracting the data from that obtained in the first photocuring experiment. The time response of the Perkin-Elmer DSC was obtained by irradiating only the sample pan (containing a fully cured sample) and then monitoring the change in heat flow when the shutter was inserted. According to Gray,[35] for a power compensation DSC operated in isothermal mode (such as that used here), the rate of heat flow ($\mathrm{d}q/\mathrm{d}t$) detected by the DSC is given by the equation

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{\mathrm{d}q}{\mathrm{d}t} + \tau\frac{\mathrm{d}^2q}{\mathrm{d}t^2} \qquad (1)$$

where $\mathrm{d}h/\mathrm{d}t$ is the power generated by the sample and τ is the response time which depends on the thermal resistance of the DSC cell and the heat capacity of the sample chamber. For the experiment described above, when the lamp is turned off (so $\mathrm{d}h/\mathrm{d}t$ is zero), this equation predicts an exponential decay in $\mathrm{d}q/\mathrm{d}t$, which is analogous to Newton's law of cooling. This was found to be the case, and the exponential time constant of the instrument was measured to be 3.5 ± 0.5 s.

FTIR Spectroscopy of the Dark Reaction. A Perkin-Elmer 1600 FTIR was used in conjunction with a Graesby-Specac temperature-controlled cell to monitor the long-term photopolymerization behavior. A sample of the formulated resin was placed between two KBr disks, and the change in the absorbance of the vinyl peak at 1618 cm^{-1} was monitored at 40 °C for several hours following a short period (10 s) of irradiation with a relative intensity of 0.1.

UV–Vis Spectrometry. A Cary 3000-Bio (Varian) spectrometer was used to measure the UV–vis spectra of the photosensitizers and the iodonium salt in ethanol at room temperature, using 10 mm thick quartz cells with an identical cell containing ethanol as the reference.

Results and Discussion

Confirmation of Cationic Nature of the Photopolymerization. As discussed above and illustrated in Scheme 1, the photosensitized decomposition of iodonium salts produces both cations and radicals, and so the possibility of radical polymerization (which is slow for vinyl ethers[36] but does occur) needs to be excluded. As discussed in more detail in a companion paper,[26] addition of 0.03 wt % of the basic amine TMA was found to completely prevent or significantly reduce the photopolymerization of the systems TEGDVE/0.1 wt % CPTXO/0.1 wt % $\mathrm{Ph_2IPF_6}$, TEGDVE/0.2 wt % CQ/0.2 wt % $\mathrm{Ph_2IPF_6}$, and TEGDVE/0.2 wt % AO/0.2 wt % $\mathrm{Ph_2IPF_6}$, at a relative radiation intensity of 1.0, confirming that a cationic mechanism is responsible for the photopolymerization. The addition of 0.03 wt % BHT radical inhibitor to the same CPTXO and AO systems retarded the photopolymerization, and the final conversion was reduced in the presence of BHT, implying that the production of cations from the radical-induced decomposition of $\mathrm{Ph_2IPF_6}$ is an important mechanism for the photopolymerization of TEGDVE when CPTXO and AO are used as the photosensitizers. In contrast, the same amount of BHT did not retard the photopolymerization of TEGDVE/0.2 wt % CQ/0.2 wt % $\mathrm{Ph_2IPF_6}$, and a similar final conversion was obtained with or without 0.03 wt % BHT, suggesting a slightly different initiation mechanism, as discussed in more detail in a companion paper.[26]

Some studies[37−39] have suggested that cationic polymerization using the photosensitized onium systems requires water to proceed; however, addition of varying levels of water (0−1 wt %) to the TEGDVE/0.1 wt % CPTXO/0.1 wt % $\mathrm{Ph_2IPF_6}$ system which had been previously dried with activated 4 Å molecular sieves had no significant effect on the photo-DSC polymerization rate. This suggests that if an electron or hydrogen transfer process is involved in the photoinitiation, then it does not involve water and, further, that if the propagating cation reacts with water (as a base), the proton generated is active enough to reinitiate the polymerization.

Further information can be obtained about the photoredox reaction from the Rhem−Weller equation,[40] which can be used to predict the possibility of electron transfer from the free energy of electron transfer:

$$\Delta G_{\mathrm{et}} = F[E^{\mathrm{ox}}(\mathrm{D/D^{\bullet+}}) - E^{\mathrm{red}}(\mathrm{A/A^{\bullet-}})] - E^* \qquad (2)$$

where F is the Faraday constant, $E^{\mathrm{ox}}(\mathrm{D/D^{\bullet+}})$ is the half-wave oxidation potential of the donor (photosensitizer), $E^{\mathrm{red}}(\mathrm{A/A^{\bullet-}})$ is the reduction potential of the acceptor (−0.2 V/SCE for the iodonium salt[41]), and E^* represents the excited state energy of the sensitizer (typically the triplet state). If the free energy change is negative, then the reaction is thermodynamically feasible. Table 1 lists the parameters for the reaction of the excited photosensitizers with the iodonium salt. The radical cations of thioxanthones[42] (of which CPTXO is a member) and AO[43] are known in the literature, and values of $E^{\mathrm{ox}}(\mathrm{D/D^{\bullet+}})$ for chlorothioxanthone[44] (an analogue of CPTXO) and AO[45] are available; however, reports for the oxidation of CQ[46,47] do not suggest the formation of a radical cation, and no values of $E^{\mathrm{ox}}(\mathrm{D/D^{\bullet+}})$ were found in the literature. From Table 1, it can be seen that the oxidation of the excited states of CPTXO and AO by $\mathrm{Ph_2IPF_6}$ to form the corresponding radical cations is thermodynamically feasible.

Table 1. Calculation of the Free Energy Change for Oxidation of the Excited Photosensitizers by Iodonium Salt

	$\mathrm{PS^* + Ph_2I^+ \rightarrow PS^{\bullet+} + Ph_2I^\bullet}$		
PS oxidation by $\mathrm{Ph_2I^+PF_6^-}$	CPTXO	AO	CQ
$E^{\mathrm{ox}}(\mathrm{PS})$ (V)	1.57[a]	1.47[c]	
$E^*(\mathrm{PS})$ (kJ/mol)	274[a]	203[b]	211[d]
ΔG (kJ/mol)	−104	−42	

[a] From ref 44. [b] From ref 45. [c] From ref 48. [d] From ref 49.

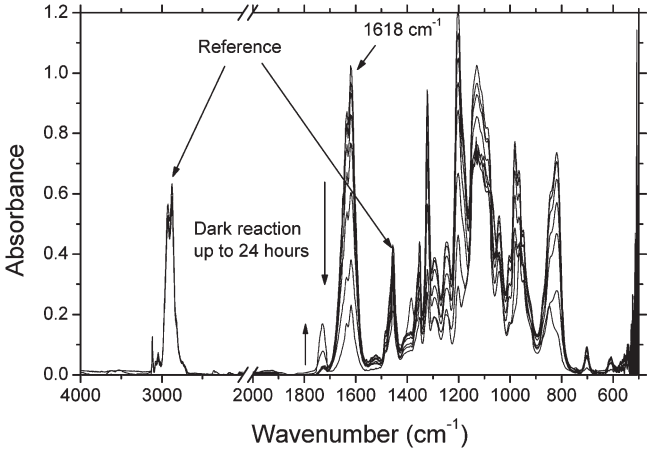


Figure 2. FTIR spectra at 40 °C of TEGDVE/0.1 wt % CPTXO/0.1 wt % Ph$_2$IPF$_6$ in the dark after 10 s irradiation with a relative intensity of 0.1.

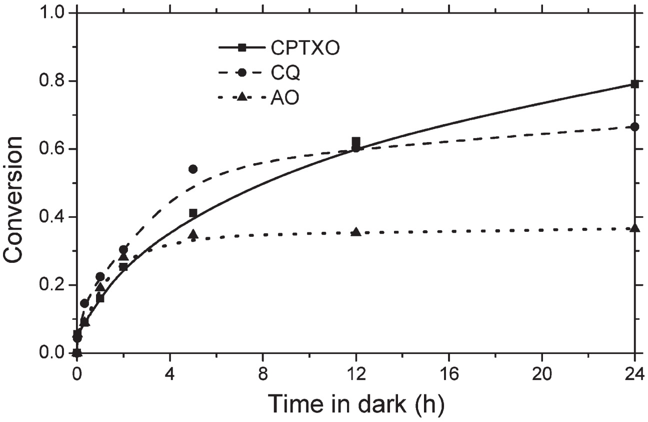


Figure 3. Double-bond conversion determined by FTIR at 40 °C of TEGDVE/0.1 wt % CPTXO/0.1 wt % Ph$_2$IPF$_6$, TEGDVE/1.0 wt % CQ/1.0 wt % Ph$_2$IPF$_6$, and TEGDVE/0.2 wt % AO/0.2 wt % Ph$_2$IPF$_6$ in the dark after 10 s irradiation with a relative intensity of 0.1.

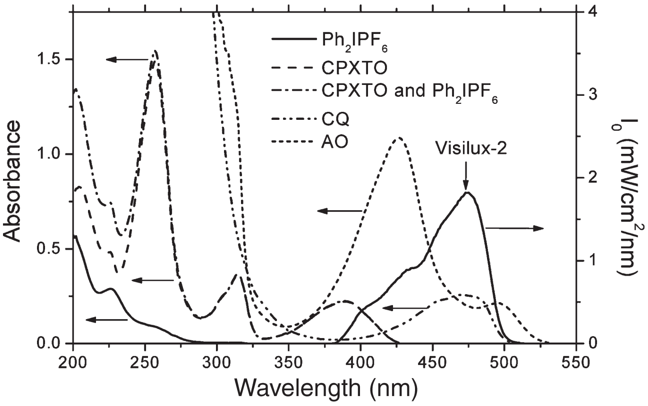


Figure 4. UV−vis absorption spectra for Ph$_2$IPF$_6$, CPTXO, CQ, and AO at concentrations of 0.001 25, 0.001 25, 0.2, and 0.002 wt %, respectively. Also included is the spectrum of a mixture of 0.001 25 wt % CPTXO and 0.001 25 wt % Ph$_2$IPF$_6$. All solutions were in ethanol using a path length of 10 mm. The spectral distribution (at the surface of the DSC pan) for the Visilux-2 source is also shown.

Dark Reaction. It has been previously shown[3,5−8] that cationic photopolymerization can continue after cessation of irradiation. For TEGDVE/0.05 wt % CPTXO/0.05 wt % Ph$_2$IPF$_6$, photo-DSC studies showed evidence of a dark reaction because the polymerization continues slowly after the radiation was terminated. It is clear that this effect was not an artifact of the DSC since the response time was measured as 3.5 s while the first-order rate decay times observed varied from 5 to 15 s as the irradiation time varied from 10 s (corresponding to ca. 20% conversion) to 30 s (corresponding to about 70% conversion)—the decay times increased with larger photoirradiation times presumably because the cations formed at a later stage of the reaction were longer living. Nelson et al.[5] also observed the dark reaction by photo-DSC using TEGDVE with 1 wt % of an iodonium initiator and 0.01 wt % anthracene as the photosensitizer, but in this study the decay time was 17 min. The reason for the large difference with the present work is not known; however, it was noticed that even after 5 min, the polymerization of TEGDVE/0.05% CPTXO/0.05% Ph$_2$IPF$_6$ had not stopped but was continuing at a low rate. Since DSC is an excellent technique to monitor fast reactions but is insensitive for slow reactions, the same system was studied by FTIR. Figure 2 shows the mid-FTIR spectra of TEGDVE/0.05% CPTXO/0.05% Ph$_2$IPF$_6$ following a 10 s irradiation at a relative intensity of 0.1. The change in the vinyl peak absorbance at 1618 cm^{-1} indicates that only a small amount of polymerization occurs during the irradiation but that the polymerization continues for many hours in the dark due to the presence of some long-lived cations. In addition, between 2 and 12 h in the dark reaction for the CPTXO- and CQ-sensitized systems, a peak appeared at 1726 cm^{-1}, suggesting the formation of aldehyde[50] perhaps due a the acid-catalyzed hydrolysis reaction[39] or rearrangement of the cation adduct of the vinyl ether ($R-CH_2-CH^+-O-R'$) to form an aldehyde ($R-CH_2-CH{=}O$) and a carbocation (R'^+). Figure 3 shows the time-dependent conversion during the dark reaction period. The conversions of the CQ- and AO-sensitized systems appear to have reached a plateau after 12 h, but the CPTXO system is still curing slowly. The lower level of conversion attained during the dark reaction for the AO system may be due to the role of AO as both a photosensitizer and a terminator of the cationic polymerization through its amine functionality, as will be discussed elsewhere.[26]

Absorption Spectra. The absorption spectra for Ph$_2$IPF$_6$, CPTXO, CQ, and AO are shown in Figure 4. Ph$_2$IPF$_6$ absorbs in the 200−300 nm region, but not above 300 nm, while CPTXO absorbs strongly in the 200−290 nm region and has two other maxima at 315 and 390 nm. The spectra of mixtures of Ph$_2$IPF$_6$ with either CPTXO, CQ, or AO are the additive result of the individual components, suggesting that there is no ground-state charge transfer between these species. CQ exhibits strongly in the 375−500 nm region and has a maximum at 470 nm. Figure 4 also shows that AO has a maximum at 425 nm (and a smaller peak at 495 nm, shown elsewhere[26] to be due to a small amount of oxidized AO impurity) and absorbs very strongly in the visible region. This figure also includes the spectral distribution of the dental Visilux source which shows that while the source is well tuned to the absorption spectra of CQ and AO, only a fraction of its energy is available to CPTXO.

Because of the absorption in the visible region by CQ, it is often used in dentistry with tetramethylaniline (TMA) as photoredox initiator system for polymerizing dimethacrylates by irradiation with visible light;[32,51] however, no significant free-radical vinyl ether photopolymerization was observed by photo-DSC during irradiation of TEGDVE/CQ/TMA with the Visilux lamp. This confirms that TEGDVE polymerization by free radicals is not significant in the TEGDVE/CQ/Ph$_2$IPF$_6$ system—in fact, TEGDVE was found to polymerize only slowly and partly by free radical polymerization using an azo initiator at elevated temperatures[36]—and that the

Table 2. Effect of Relative Radiation Intensity on the Isothermal Photo-DSC Curing of TEGDVE with 0.1 or 0.2 wt % CPTXO and with 0.2 or 0.8 wt % Ph_2IPF_6, with 0.2 or 0.8 wt % AO and with 0.2 or 0.8 wt % Ph_2IPF_6, and with 0.8 wt % CQ and with 0.8 wt % Ph_2IPF_6

relative radiation intensity (I_{rel})	max heat flow (W/g)	induction time (s)	peak maximum (s)	final conversion (%)
0.1 wt % CPTXO (and 0.1 wt % Ph_2IPF_6)				
1.0	51.2	2	10	81
0.5	25.6	4	18	68
0.25	12.5	8	46	62
0.1	5.1	22	92	57
0.05	2.2	80	160	45
0.2 wt % CPTXO (and 0.2 wt % Ph_2IPF_6)				
0.10	40.5	9.8	19.6	78
0.050	26.9	10.8	25.6	77
0.025	11.7	17.6	22.4	76
0.010	5.3	47.2	108.0	66
0.0050	2.2	77.6	163.6	44
0.2 wt % AO (and 0.2 wt % Ph_2IPF_6)				
1.0	36.1	4	11	54
0.5	17.8	14	34	50
0.25	10.7	36	69	44
0.1	3.6	69	130	57
0.05	2.0	173	299	48
0.8 wt % AO (and 0.8 wt % Ph_2IPF_6)				
0.1	58.2	2	11	86
0.05	33.7	12	31	93
0.025	22.5	36	69	88
0.01	8.5	73	139	96
0.005	4.1	174	323	92
0.8 wt % CQ (and 0.8 wt % Ph_2IPF_6)				
1.0	45.1	27	56	100
0.5	28.1	60	91	98
0.25	12.0	82	141	94
0.1	4.2	95	215	91

photopolymerization of TEGDVE with CQ/Ph_2IPF_6 is a cationic process.

Effect of Radiation Intensity. In photo-DSC, the measured heat flow is usually assumed to be proportional to the conversion rate; therefore, the rate of conversion can be defined as follows:[51,52]

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{tot}}\left(\frac{dH}{dt}\right)_T \tag{3}$$

where $d\alpha/dt$ is the conversion rate or the polymerization rate, $(dH/dt)_T$ is the measured heat flow at a constant temperature T, and ΔH_{tot} is the total exothermic heat of reaction. Using the heat of polymerization of butyl vinyl ether[53,54] of 60 kJ/mol, the expected heat of polymerization of TEGDVE is 593 J/g using its theoretical molecular weight. This value is also close to those obtained by Nelson et al.[20] for the same monomer. This value was used to calculate the conversion rate and the conversion (α) which was obtained by integrating eq 3.

The effect of the variation of incident light intensity on the rate of polymerization of the TEGDVE was studied for the three systems. Initially, the systems containing CPTXO and AO were formulated with 0.2 wt % CPTXO/0.2 wt % Ph_2IPF_6 and 0.8 wt % AO/0.8 wt % Ph_2IPF_6, and the analyses of the photo-DSC traces are listed in Table 2. The maximum rate of polymerization measured directly by photo-DSC decreases with lower incident light intensity (with a power-law dependence of 1.01 ± 0.04 and 0.88 ± 0.05 for CPTXO and AO, respectively), while the time taken to reach the maximum peak heat flow increases, as expected. For both systems the conversion is relatively high and constant except at low radiation intensities as discussed below. More quantitative analysis of the data in Table 2 is limited because calculations based on the absorption spectra and the spectral distribution of the Visilux lamp shown in Figure 4 reveal that for the TEGDVE/CPTXO/Ph_2IPF_6 system containing 0.2 wt % CPTXO only 7% of the radiation at 400 nm (the wavelength where most of the energy is absorbed) is transmitted by the 0.4 mm thick DSC film. Even though CPTXO photobleaches[26] at 400 nm and so the radiation attenuation effect is not as significant as initially expected, this self-screening of the radiation may cause errors in the calculation of the exponent for the irradiation intensity. Similarly, for a system with 0.8 wt % AO, only 0.04% of the radiation is transmitted through 0.4 mm thickness at 470 nm and virtually zero at the second absorption maximum of 420 nm, and so the DSC data for this system were significantly affected by radiation attenuation effects and can only be considered as qualitative. These calculations show the importance of relating the concentration of photoinitiator and its absorption spectra with the radiation source spectral distribution and the specimen thickness so that high-quality photopolymerization studies can be undertaken. For these reasons, studies of the influence of radiation intensity were repeated with lower concentrations of photosensitized as described below.

The photo-DSC behavior of TEGDVE/0.1 wt % CPTXO/0.1 wt % Ph_2IPF_6, TEGDVE/0.8 wt % CQ/0.8 wt % Ph_2IPF_6, and TEGDVE/0.2 wt % AO/0.2 wt % Ph_2IPF_6 are illustrated in Figures 5, 6, and 7, respectively. An induction time before the commencement of polymerization

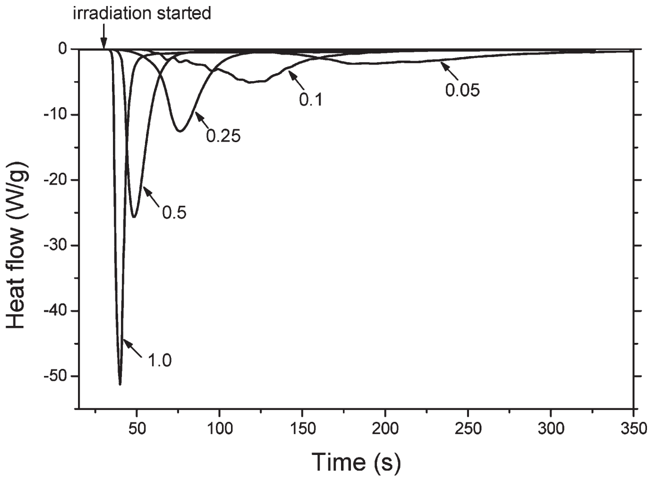


Figure 5. Heat flow versus time for TEGDVE photocured with 0.1 wt % Ph_2IPF_6 and 0.1 wt % CPTXO at 40 °C with various relative intensities (as shown).

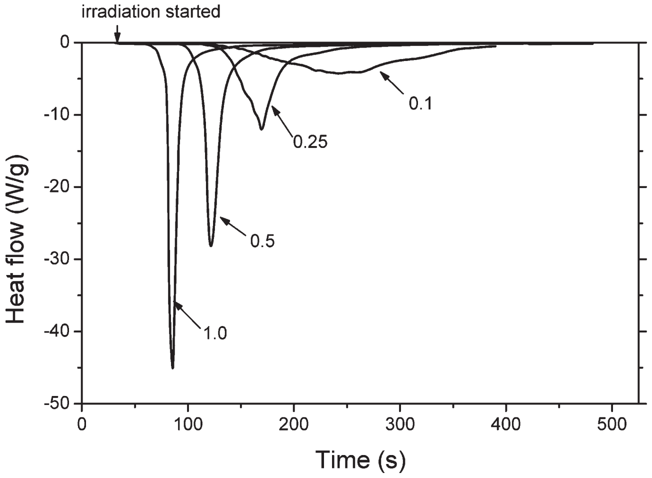


Figure 6. Heat flow versus time for TEGDVE photocured with 0.8 wt % Ph_2IPF_6 and 0.8 wt % CQ at 40 °C with various relative intensities (as shown).

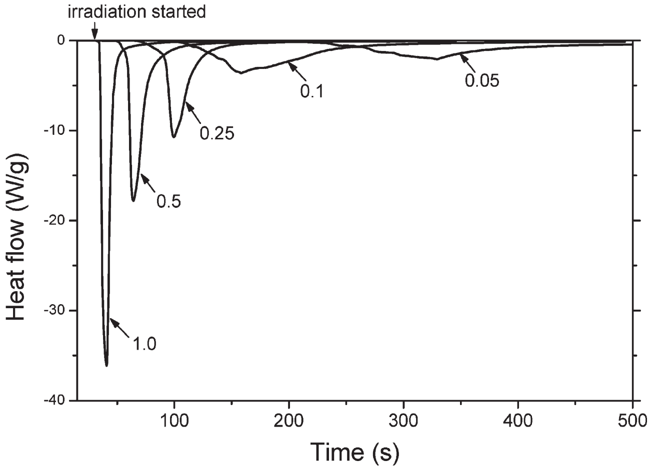


Figure 7. Heat flow versus time for TEGDVE photocured with 0.2 wt % Ph_2IPF_6 and 0.2 wt % AO at 40 °C with various relative intensities (as shown).

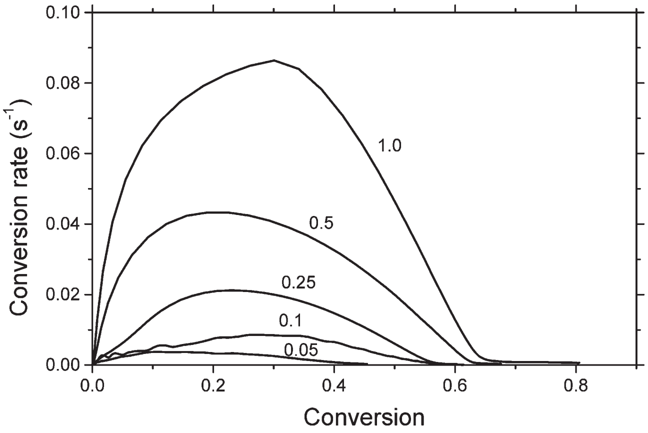


Figure 8. Rate versus conversion for TEGDVE photocured with 0.1 wt % Ph_2IPF_6 and 0.1 wt % CPTXO at 40 °C with various relative intensities (as shown).

occurred in all systems, and as the radiation intensity was decreased, the induction time was found to increase, which is consistent with either the presence of an impurity in the system acting as a cation scavenger or due to the quenching of the excited photosensitizer by an impurity. A reduction of the radiation intensity also increases the time taken to reach the maximum peak heat flow and reduces the maximum rate of polymerization decreases, as expected (see Table 2). Use of the absorption spectra and the spectral distribution of the Visilux lamp (Figure 4) reveals that more than 90% of the radiation at 470 nm is transmitted through a 0.4 mm thick film of TEGDVE/CQ/Ph_2IPF_6 containing 1.0 wt % CQ (the highest concentration studied here) so that light attenuation through the 0.4 mm thick DSC sample was not significant. For TEGDVE/CPTXO/Ph_2IPF_6 containing 0.1 wt % CPTXO (the concentration used in Figure 5) only 31% of the radiation at 400 nm (the wavelength where most of the energy is absorbed) is transmitted by the 0.4 mm thick DSC film. However, as shown elsewhere,[26] CPTXO photobleaches at 400 nm, and so the radiation attenuation effect is not as significant as might be expected. In contrast, for a system with 0.2 wt % AO, only 13% of the radiation is transmitted through 0.4 mm thickness at 470 nm and virtually zero at the second absorption maximum of 420 nm, and so the rate of photopolymerization will vary through the thickness of the photo-DSC specimen due to the radiation attenuation effect and so the kinetic data may be less reliable.

As illustrated in Table 2, for all photosensitizers the final conversion rises with an increase of incident light intensity, particularly for the CPTXO system. Many studies[51,55,56] of the effect of light intensity on free-radical photocuring have observed the same result. One explanation commonly used[57,58] is that with rapid polymerization the volumetric shrinkage lags behind the extent of chemical reaction, providing extra free volume and greater molecular mobility of the reaction sites which raises the conversion correspondingly. This explanation is not applicable here because the polymer is in a rubbery state during the photopolymerization (the T_g was measured by DMTA[36] as 22 °C), and so the rate of reaction and the final conversion should not be significantly dependent on the free volume content. It appears that the reason is more likely related to the presence of adventitious impurities, as discussed above, which are able to quench the excited sensitizer or terminate the cationic reaction when the radiation intensity (and hence the polymerization rate) is low and thus reduce the final conversion. However, as demonstrated by the long-term dark FTIR studies, it must be recognized that it is possible that further polymerization could have occurred after a much longer period where the DSC is insensitive.

Despite this proviso, the FTIR data in Figure 3 do indicate that for the TEGDVE/0.8 wt % CQ/0.8 wt % Ph_2IPF_6 and TEGDVE/0.2 wt % AO/0.2 wt % Ph_2IPF_6 systems described in Table 2 the final conversion is partly limited by loss of initiating cations since complete conversion did not occur even after 24 h.

The rate of reaction versus conversion, derived from Figure 5 for TEGDVE formulated with 0.1 wt % Ph_2IPF_6 and CPTXO, is shown in Figure 8. Aside from the final stages of the reaction, the general shape of the rate−conversion curves are similar for differing radiation intensities, suggesting that the rate expression for the polymerization has the form

$$\text{rate of polymerization} = k[\text{PS}]^x[\text{Ph}_2\text{IPF}_6]^y I_{\text{rel}}{}^z f(1-\alpha) \tag{4}$$

where k is the rate constant, [PS] and $[Ph_2IPF_6]$ are the concentrations of photosensitizer and photoinitiator, I_{rel} is the relevant light intensity, x, y, z are the exponents for the three factors, α is the conversion, and $f(1-\alpha)$ is a function of the monomer concentration remaining.

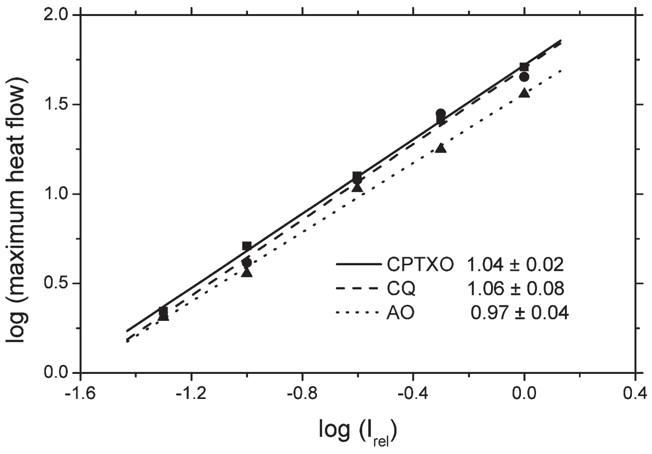


Figure 9. Log−log plot of maximum heat flow (W/g) versus relative intensity (I_{rel}) for TEGDVE/0.1 wt % CPTXO/0.1 wt % Ph_2IPF_6, TEGDVE/0.8 wt % CQ/0.8 wt % Ph_2IPF_6, and TEGDVE/0.2 wt % AO/0.2 wt % Ph_2IPF_6 at 40 °C.

On the basis of the assumption that the initiator concentration is constant, Krzysztof[59] predicted that the cationic polymerization rate should be second order with respect to the monomer concentration. Figure 8 shows that for TEGDVE/0.1 wt % CPTXO/0.1 wt % Ph_2IPF_6 (and the corresponding plots for CQ and AO) the maximum rate of reaction occurs near 20% conversion and that the data are not consistent with the rate being dependent on any simple order of monomer concentration because in all of these cases the maximum rate should occur at 0% conversion. However, the data in Figure 8 do suggest that the cation concentration builds up from the start of the reaction, causing a slow increase in the rate at the start of the reaction as suggested by Nelson et al.[5] before monomer depletion causes the reaction rate to decline.

Figure 9 shows the logarithm of the maximum heat flow versus the logarithm of incident light intensity for the three pairs of initiating systems and reveals that the conversion rate is in direct proportion to the incident light intensity (i.e., the exponents x, y, z in eq 4 are close to unity). In addition, analysis of the data in Table 2 for the CPTXO

Table 3. Effect of Iodonium Salt Concentration on the Isothermal Photo-DSC Curing of TEGDVE with 0.1 or 0.2 wt % CPTXO and with 0.2 or 0.8 wt % AO Using Relative Radiation Intensities of 0.05 or 1.0, Respectively, and with 1.0 wt % CQ Using Relative Radiation Intensities of 0.5 at 40 °C

iodonium salt concn (wt %)	max heat flow (W/g)	induction time (s)	peak maximum (s)	final conversion (%)
0.1 wt % CPTXO (I_{rel} = 1.0)				
0.1	51.2	2	8	79
0.075	40.9	4	11	66
0.05	19.3	7	34	54
0.025	5.8	16	69	47
0.01	1.5	25	81	33
0.2 wt % CPTXO (I_{rel} = 0.05)				
0.2	35.4	2	17	85
0.15	20.2	8	30	59
0.1	9.0	19	56	54
0.075	5.5	26	101	52
0.05	2.1	79	174	39
0.2 wt % AO (I_{rel} = 1.0)				
0.2	36.1	4	12	66
0.15	24.4	15	25	55
0.1	11.2	22	57	46
0.05	4.5	43	88	37
0.8 wt % AO (I_{rel} = 0.05)				
0.1	45.6	2	12	82
0.075	30.8	14	25	78
0.05	8.7	37	91	74
1.0 wt % CQ (I_{rel} = 0.5)				
1.0	32.0	43	83	100
0.5	21.0	72	118	89
0.3	8.8	104	188	82
0.2	6.4	168	261	62
0.1	3.7	226	345	48

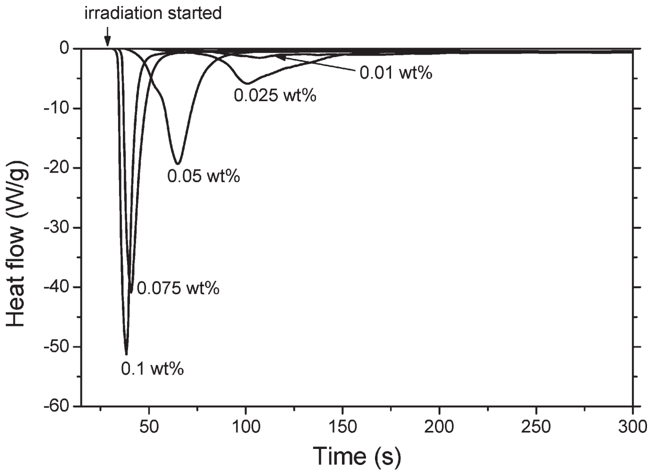


Figure 10. Heat flow versus time for TEGDVE photocured with 0.1 wt % CPTXO and $I_{rel} = 1$ using various concentrations of Ph_2IPF_6 (as shown) at 40 °C.

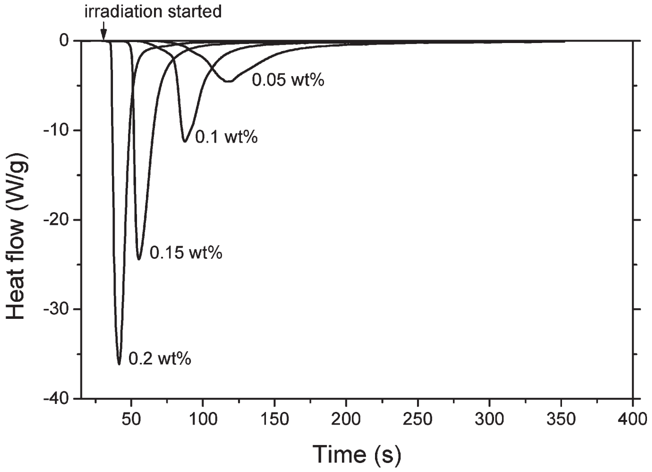


Figure 11. Heat flow versus time for TEGDVE photocured with 0.2 wt % AO and $I_{rel} = 1$ using various concentrations of Ph_2IPF_6 (as shown) at 40 °C.

and AO-sensitized systems gave radiation exponents of 1.01 ± 0.4 and 0.88 ± 0.05, respectively, which are in reasonable agreement with the other data (see Figure 9) despite the occurrence of radiation attenuation through the sample, which may complicate the kinetics. An exponent of unity for the radiation intensity is expected for a polymerization process having a rate-determining step in which the rate is proportional to the radiation intensity. In contrast, free radical photopolymerization usually exhibits a square root dependency on intensity because the radicals are formed and consumed in a steady state.[51]

In determining the rate dependence on relative intensity, effort should also be made to ensure that neither photosensitizer nor initiator is prematurely consumed. As shown in a companion paper,[26] CQ is not significantly consumed during the time scale of the photo-DSC experiment so its loss is not of concern. Unfortunately, attempts at measuring the loss of the iodonium salt in the TEGDVE/CQ/Ph_2IPF_6 by UV−vis spectroscopy was not successful due to strong absorption by the resin and CQ in the regions of iodonium salt absorption. Thus, the simplest method of determining the significance of Ph_2IPF_6 loss is from inspection of the data. Figure 9 does not show any tendency to nonlinearity at high radiation intensities where deviation from a linear relationship due to depletion would be expected, and so it is concluded that the first-order dependency of the rate on radiation intensity is confirmed. UV−vis spectroscopy studies of the photolysis of CPTXO and AO in the formulated TEGDVE/Ph_2IPF_6 systems show that these sensitizers are consumed[26] but that neither is significantly depleted at the maximum polymerization rate or during most of the proceeding reaction.

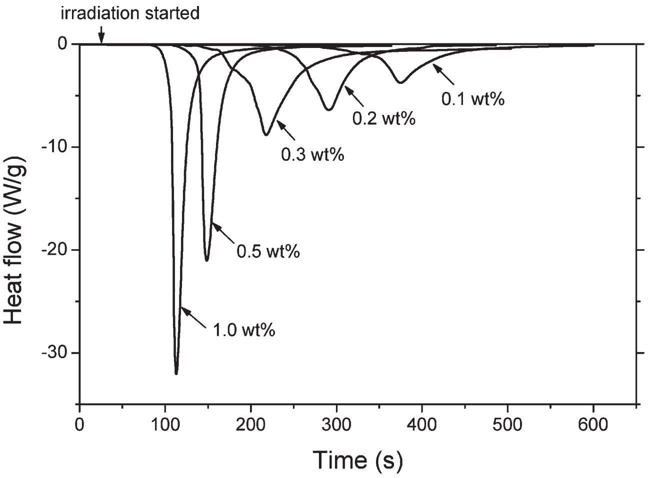


Figure 12. Heat flow versus time for TEGDVE photocured with 1.0 wt % CQ and $I_{rel} = 0.5$ using various concentrations of Ph_2IPF_6 (as shown) at 40 °C.

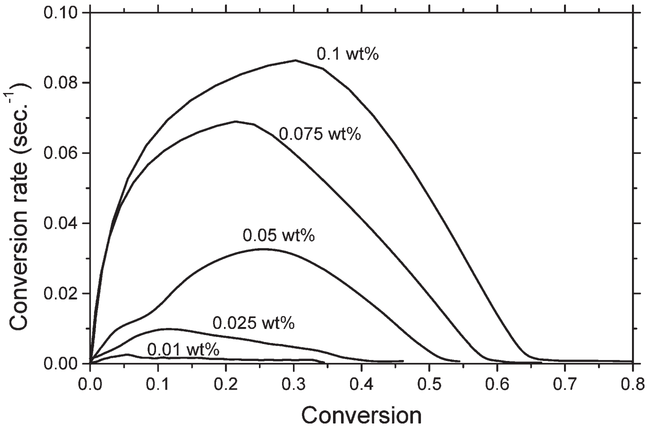


Figure 13. Reaction rate versus conversion for TEGDVE photocured with 0.1 wt % CPTXO and $I_{rel} = 1$ using various concentrations of Ph_2IPF_6 (as shown) at 40 °C.

Effect of Iodonium Salt Concentration. The effect of iodonium salt concentration on the cure behavior of TEGDVE/0.2 wt % CPTXO/Ph_2IPF_6 and TEGDVE/0.8 wt % AO/Ph_2IPF_6 systems was investigated initially, and the data derived from these photo-DSC experiments are tabulated in Table 3. As the iodonium salt concentration decreases, the maximum rate of polymerization measured directly by photo-DSC is reduced while the time taken to reach the maximum peak heat flow increases, as expected. Log−log plots of the dependence of maximum rate on iodonium salt concentration gave iodonium salt exponents of 2.01 ± 0.4 and 2.5 ± 0.5 for the CPTXO and AO systems, respectively, suggesting a iodonium salt order close to two. However, as discussed above, the DSC data for these systems were significantly affected by radiation attenuation effects and so can only be considered as qualitative. For these reasons, studies of the influence of radiation intensity were repeated with lower concentrations of photosensitizer.

Figures 10−12 show the dependence of the photopolymerization on the iodonium salt concentration for the

TEGDVE/0.1 wt % CPTXO/Ph_2IPF_6 (Figure 10), TEGDVE/0.2 wt % AO/Ph_2IPF_6 (Figure 11), and TEGDVE/1 wt % CQ/Ph_2IPF_6 systems (Figure 12), and Table 3 lists the kinetic information. An induction period is also observed in these data, and the induction time increases when the iodonium salt concentration is reduced, which is either consistent with the presence of an impurity in the system acting as a cation scavenger or due to the quenching of the excited photosensitizer by an impurity (since the excited state needs to remain active when the surrounding medium has a lower concentration of iodonium ions). As noted above, as the concentration of Ph_2IPF_6 is reduced, the time to reach the peak reaction rate increases and the photopolymerization rate decreases. Table 3 reveals that the final vinyl conversions are generally less than 100% and decreases as the concentration of the iodonium salt is lowered, particularly for the CPTXO and AO systems. This behavior may be explained by termination of the reaction by a process analogous to dead-end free radical polymerization[60]—if a chain termination process is active, such as reaction with basic species, then the loss of cation activity will be more likely to occur prior to complete polymerization when the initiator concentration is low. Surprisingly, the TEGDVE/0.2 wt % AO/Ph_2IPF_6 systems have very low final conversions in comparison with the other systems. This may be due to the fact that AO has the dual nature of being a photosensitizer and also being a cation trap via its amino moiety.

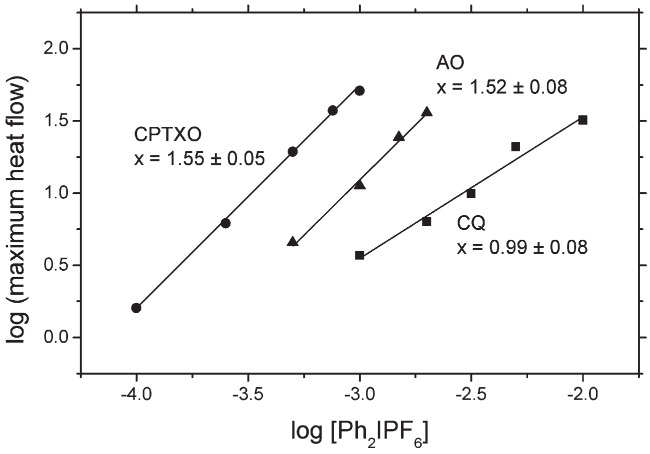
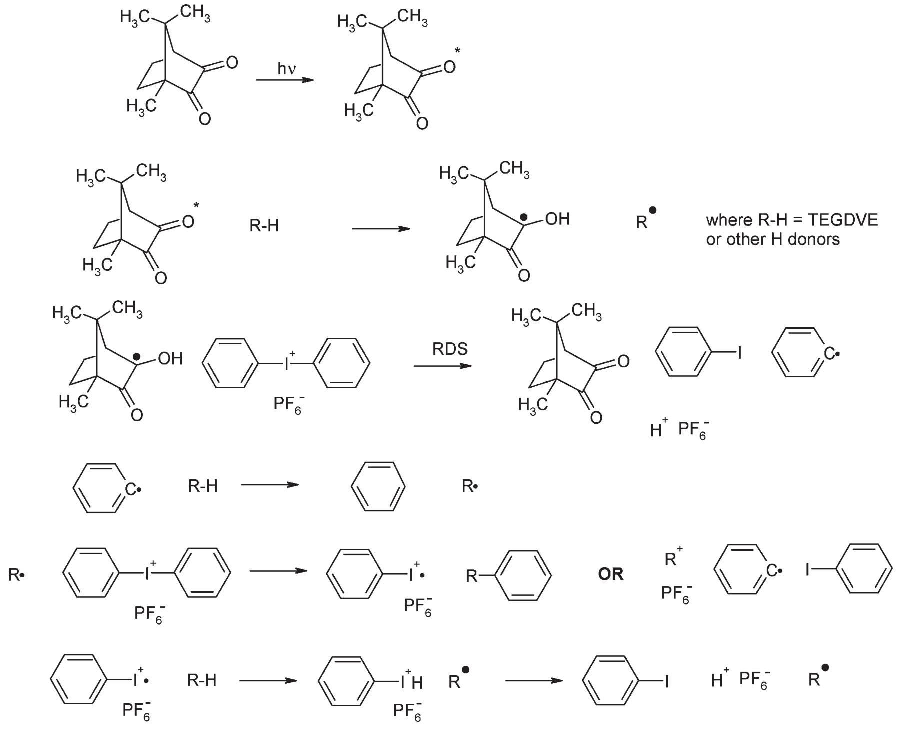


Figure 14. Log−log plot of maximum heat flow (in W/g) versus Ph_2IPF_6 concentration (in weight fraction of total resin) in TEGDVE/0.1 wt % CPTXO/Ph_2IPF_6 and in TEGDVE/0.2 wt % AO/Ph_2IPF_6, using a relative intensity of 1.0 at 40 °C and in TEGDVE/1.0 wt % CQ/Ph_2IPF_6 using a relative intensity of 0.5 at 40 °C.

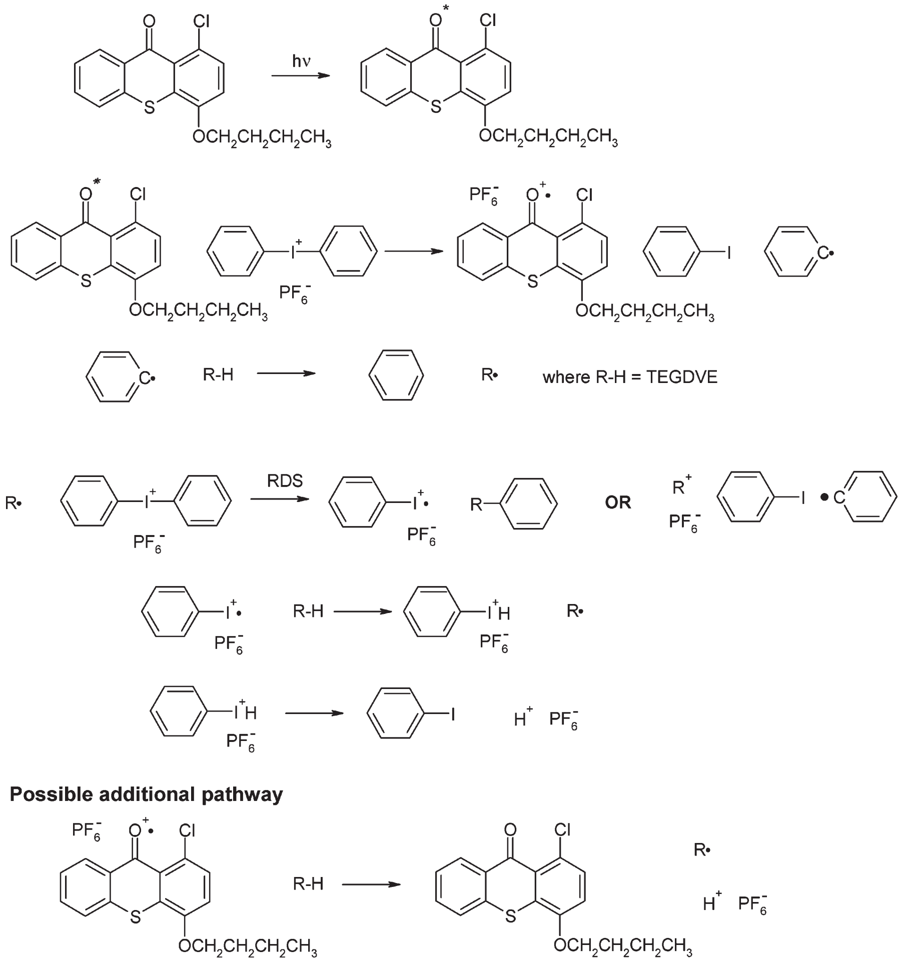
The dependence of the polymerization rate on the conversion for TEGDVE formulated with 0.1 wt % CPTXO and varying amounts of Ph_2IPF_6 is shown in Figure 13. Aside from the final stages of the reaction, the general shapes of the rate−conversion curves are similar, suggesting that the rate expression for the polymerization has the form given by eq 4 for the effect of the iodonium salt concentration. For the CPTXO and AO systems, as shown in Figure 14, the reaction order with respect to the iodonium ion concentration appears to be ~1.5, which is less than the value of ~2.0−2.5 (see above) obtained from the TEGDVE/0.2 wt % CPTXO/Ph_2IPF_6 and TEGDVE/0.8 wt % AO/Ph_2IPF_6 systems in which radiation attenuation through the thickness of the DSC sample was a problem. In contrast, the reaction order of Ph_2IPF_6 in the system TEGDVE/CQ/Ph_2IPF_6 is unity (see Figure 14).

A reason for the different dependencies of the photocuring rate on the iodonium salt concentration for CQ compared with CPTXO and AO is that the photosensitizers are involved in two mechanisms. Thus, it is possible that photoinitiation by CQ involves the H-transfer process shown in Scheme 1. It is well-known that CQ[32] can be reduced to the ketyl (or pinacol) radical, and as suggested in Scheme 2, this ketyl radical may be regenerated by oxidation with the iodonium salt, thus explaining why CQ is not significantly

Scheme 2. Proposed Photoinitiation by CQ Which Accounts for the Very Slow Consumption of CQ during the Photo-DSC Experiment and the First-Order Dependence on the Iodonium Ion Concentration



Scheme 3. Proposed Photoinitiation by CPTXO Which Accounts for Its Consumption during the Photo-DSC Experiment and the Tendency toward a Second-Order Dependence on the Iodonium Salt Concentration (a Similar Mechanism May Apply to AO Also)



consumed during the photo-DSC experiment as discussed in a companion paper.[26] As a result, the mechanism given in Scheme 2 suggests a first-order dependence on the iodonium ion concentration as observed. In contrast, both CPTXO and AO may also photoinitiate via the electron transfer process shown in Scheme 1. As shown in Scheme 3 for CPTXO, the excited photosensitizer is directly oxidized by the iodonium ion, but the formation of the propagating cation requires the involvement of a second iodonium cation and so a second-order dependency of rate on iodonium salt concentration might be expected. While this mechanism explains why the reaction rate is not first order with respect to the iodonium salt, it does not agree with the order of 1.5 found here. This disagreement may be caused by the occurrence of two mechanisms for CPTXO and AO. The first mechanism could be the electron transfer process (see Scheme 1 and the main process in Scheme 3) which produces one carbocation for every two molecules of iodonium ion consumed (a second-order reaction), while the second mechanism (based on the proposals of Rodrigues and Neumann[42] and Denizligil et al.[61]) may involve regeneration of the photosensitizer (see the additional process in Scheme 3) and could produce one proton per iodonium ion consumed (a first-order reaction). Thus, a mixed order for the iodonium ion would be observed. Further evidence for this proposal is given in the companion paper.[26]

Conclusions

The photopolymerization behavior of TEGDVE was investigated using diphenyliodonium hexafluorophosphate as a co-initiator and one of three photosensitizers. Although both radicals and cations are generated during iodonium ion decomposition, the dominance of a cationic cure mechanism was demonstrated. Photo-DSC and photo-FTIR studies show that in most cases the polymerization was incomplete apparently due to consumption of the active cations by basic impurities or due to quenching of the excited state of the photosensitizer.

The effect of incident radiation intensity on the photopolymerization kinetics of TEGDVE was also investigated. The power-law dependences of the polymerization rate on the radiation intensity were nearly unity for the three systems. The final conversions increased with higher radiation intensities, possibly because at higher rates of initiation, and therefore at a higher concentration of cations, there was a lower probability of termination by impurities.

The effect of iodonium salt concentration on the photopolymerization kinetics revealed that for CPTXO and AO the reaction orders for the iodonium salt were ~1.5, while for CQ it was approximately unity, apparently due to different photosensitization mechanisms.

The final conversion of vinyl groups increased with higher Ph_2IPF_6 concentration, presumably because higher polymerization rates reduce the depletion of the cations by anionic impurities in the system.

Acknowledgment. The authors are pleased to acknowledge the ARC Discovery Grant DP0453104 and the 2005 Monash Engineering Research Grant which funded part of this work.

References and Notes

(1) Fouassier, J.-P. *Photoinitiation, Photopolymerization and Photocuring: Fundamentals and Applications*; Hanser Gardner Publications: Cincinnati, OH, 1995.

(2) Roffey, C. G. *Photopolymerization of Surface Coatings*; John Wiley and Sons Ltd.: New York, 1982.

(3) Dufour, P. State-of-the-Art and Trends in the Radiation-Curing Market. In *Radiation Curing in Polymer Science and Technology: Fundamentals and Methods*; Fouassier, J.-P., Rabek, J. F., Eds.; Elsevier Applied Science: London, 1993.

(4) Fouassier, J.-P. *Photoinitiated Polymerisation: Theory and Applications*; Rapra Technology Ltd.: Shawbury, 1998.

(5) Nelson, E. W.; Jacobs, J. L.; Scranton, A. B.; Anseth, K. S.; Bowman, C. N. *Polymer* **1995**, *36*, 4651–4656.

(6) Decker, C.; Bianchi, C.; Decker, D.; Morel, F. *Prog. Org. Coat.* **2001**, *42*, 253–266.

(7) Sipani, V.; Scranton, A. B. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2064–2072.

(8) Wang, T.; Wang, Z. H. *Polym. Bull.* **2005**, *53*, 323–331.

(9) Bongiovanni, R.; Sangermano, M.; Malucelli, G.; Priola, A.; Leonardi, A.; Ameduri, B.; Pollicino, A.; Recca, A. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2890–2897.

(10) Kim, Y. M.; Kostanski, L. K.; MacGregor, J. F. *Polymer* **2003**, *44*, 5103–5109.

(11) Sangermano, M.; Malucelli, G.; Bongiovanni, R.; Priola, A.; Annby, U.; Rehnberg, N. *Eur. Polym. J.* **2002**, *38*, 655–659.

(12) Braun, H.; Yagci, Y.; Nuyken, O. *Eur. Polym. J.* **2002**, *38*, 151–156.

(13) Crivello, J. V. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1999**, *151*, 8–21.

(14) Crivello, J. V. *Radiat. Phys. Chem.* **2002**, *63*, 21–27.

(15) Bo, J.; Yong, Z.; Yang, Z.; Wu, Z.; Huang, G.; Lin, L.; Zhang, X. *J. Appl. Polym. Sci.* **2005**, *98*, 2094–2100.

(16) Crivello, J. V.; Sangermano, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 343–356.

(17) Crivello, J. V.; Kong, S. *Macromolecules* **2000**, *33*, 833–842.

(18) Crivello, J. V. *Annu. Rev. Mater. Sci.* **1983**, *13*, 173–190.

(19) Cho, J. D.; Hong, J. W. *J. Appl. Polym. Sci.* **2005**, *97*, 1345–1351.

(20) Nelson, E. W.; Carter, T. P.; Scranton, A. B. *Macromolecules* **1994**, *27*, 1013–1019.

(21) Yagci, Y.; Reetz, I. *Prog. Polym. Sci.* **1998**, *23*, 1485–1538.

(22) Manivannan, G.; Fouassier, J.-P. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1113–1124.

(23) Devoe, R. J.; Sahyunn, M. R. V.; Serpone, D. K. *Can. J. Chem.* **1987**, *65*, 2342–2349.

(24) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4241–4254.

(25) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2441–2451.

(26) Chen, S.; Cook, W. D.; Chen, F. Photopolymerization of vinyl ether networks using an iodonium initiator – the role of photosensitizers, accepted for publication in *J. Polym. Sci., Part A: Polym. Chem.*

(27) Nelson, E. W.; Carter, T. P.; Scranton, A. B. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 247–256.

(28) Toba, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 982–987.

(29) Cho, J. D.; Kim, E. O.; Kim, H. K.; Hong, J. W. *Polym. Test.* **2002**, *21*, 781–791.

(30) Fouassier, J.-P.; Wu, S. K. *J. Appl. Polym. Sci.* **1992**, *44*, 1779–1786.

(31) Sundell, P. E.; Joensson, S.; Hult, A. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1535–1543.

(32) Cook, W. D. *Polymer* **1992**, *33*, 600–609.

(33) Cook, W. D. *Biomaterials* **1986**, *7*, 449–454.

(34) Scott, T. F.; Cook, W. D.; Forsythe, J. S. *Polymer* **2002**, *43*, 5839–5845.

(35) Gray, A. P. A simple generalized theory for the analysis of dynamic thermal calorimetry. In *Analytical Calorimetry Proceedings*; Porter, R. S., Johnson, R. F., Eds.; Plenum Press: New York, 1968; pp 209–218.

(36) Chen, S.; Cook, W. D.; Chen, F. *Polym. Int.* **2007**, *56*, 1423–1431.

(37) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5405–5410.

(38) Satoh, K.; Nakashima, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 396–401.

(39) Lin, Y.; Stansbury, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1985–1998.

(40) Rehm, D.; Weller, A. *J. Phys. Chem.* **1969**, *73*, 834–839.

(41) Gomez, M. L.; Montejano, H. A.; Previtali, C. M. *J. Photochem. Photobiol., A* **2008**, *197*, 18–24.

(42) Rodrigues, M. R.; Neumann, M. G. *Macromol. Chem. Phys.* **2001**, *202*, 2776–2782.

(43) Kellmann, A. *Photochem. Photobiol.* **1974**, *20*, 101–108.

(44) Fouassier, J.-P.; Burr, D.; Crivello, J. V. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 677–701.

(45) Kurbanyan, K.; Nguyen, K. L.; To, P.; Rivas, E. V.; Lueras, A. M. K.; Kosinski, C.; Steryo, M.; Gonzalez, A.; Mah, D. A.; Stemp, E. D. A. *Biochemistry* **2003**, *42*, 10269–10281.

(46) Meinwald, J.; Klingele, H. O. *J. Am. Chem. Soc.* **1966**, *88*, 2071–2073.

(47) Gream, G. E.; Paice, C.; Ramsay, C. R. *Aust. J. Chem.* **1969**, *22*, 1229–1247.

(48) Kearns, D. R.; Hollins, R. A.; Khan, A. U.; Chambers, R. W.; Radlick, P. *J. Am. Chem. Soc.* **1967**, *89*, 5455–5456.

(49) Nie, J.; Andrzejewska, E.; Rabek, J. F.; Linden, L. A.; Fouassier, J.-P.; Paczkowski, J.; Scigalski, F.; Wrzyszczynski, A. *Macromol. Chem. Phys.* **1999**, *200*, 1692–1701.

(50) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: Chichester, 1991.

(51) Cook, W. D. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1053–1067.

(52) Sawada, H. J. *Macromol. Sci.* **1969**, *C3*, 313–395.

(53) Shostakovskii, M. F.; Bogdanov, I. F. *J. Appl. Chem. Russ.* **1942**, *15*, 249–259.

(54) Zeng, Z.; Zhang, L.; Yang, J.; Chen, Y. *J. Appl. Polym. Sci.* **2005**, *96*, 1930–1935.

(55) Lecamp, L.; Youssef, B.; Bunel, C.; Lebaudy, P. *Polymer* **1997**, *38*, 6089–6096.

(56) Lovell, L. G.; Newman, S. M.; Donaldson, M. M.; Bowman, C. N. *Dent. Mater.* **2003**, *19*, 458–465.

(57) Kloosterboer, J. G.; van de Hei, G. M. M.; Gossink, R. G.; Dortant, G. C. M. *Polym. Commun.* **1984**, *25*, 322–325.

(58) Bowman, C. N.; Peppas, N. A. *Macromolecules* **1991**, *24*, 1914–1920.

(59) Krzysztof, F. *Cationic Polymerizations: Mechanisms, Synthesis, and Applications*; Marcel Dekker: New York, 1996.

(60) O'Driscoll, K. F.; McArdle, S. A. *J. Polym. Sci.* **1959**, *40*, 557–561.

(61) Denizligil, S.; Resul, R.; Yagci, Y.; McArdle, C.; Fouassier, J.-P. *Macromol. Chem. Phys.* **2003**, *197*, 1233–1240.