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Photo-differential scanning calorimetry studies of cationic polymerizations of divinyl ethers

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Photo-differential scanning calorimetry experiments were used to determine effective kinetic constants for propagation and termination for a series of unsteady-state divinyl ether polymerizations at different temperatures and light intensities. For these cationic photopolymerizations the reaction rate and limiting conversion were both found to increase as the reaction temperature was increased. At all temperatures the profile for the propagation rate constant k_p exhibited a dramatic increase at the start of the reaction, plateaued at a value between 5 and 30 l mol^{-1} s^{-1} (depending upon temperature) and then decreased as the reaction reached a limiting conversion owing to trapping of the active centres. The effective termination rate constant k_t was very low, with active centre lifetimes approaching 20 min. The overall activation energy for polymerization was found to be 26.5 ± 3.2 kJ mol^{-1}.

(Keywords: p.d.s.c.; cationic; photopolymerization)

INTRODUCTION

In general, carbocationic polymerization kinetics are complex and vary from system to system. Therefore a simple, coherent, kinetic expression of general validity is not available for cationic polymerizations[1]. There are several difficulties that contribute to this deficiency. First, the reactivity of the carbocationic centre depends strongly on the proximity of the counterion, and a number of propagating species may be identified, including ion pairs, solvated ions or aggregates. The reactivities of the separated or solvated cations are greatly increased over ion pairs and have different chemical characteristics[1]. Second, the pseudo-steady-state active centre concentration assumption is invalid for cationic polymerizations. In contrast to free radical polymerizations, combination of active centres does not occur, and termination is generally suppressed in cationic polymerizations. Therefore, in most cases, the rates of initiation and termination are not equal, and non-steady-state calculations are required[1]. In addition, transfer reactions are typically important in cationic polymerizations, and the polymerization rate constants are affected by the nature of the counterion and solvent. Kinetic analysis of cationic polymerizations is not impossible, but requires careful individual consideration for each system under investigation.

Photo-differential scanning calorimetry (p.d.s.c.) offers a simple method to characterize the kinetics of photopolymerization reactions. Because the polymerizations are highly exothermic, the reaction rate may be measured by monitoring the rate at which heat is released from the polymerizing sample. Therefore, the profiles of reaction heat *versus* time provided by p.d.s.c. may be used to characterize the reaction kinetics and evaluate polymerization rate constants[2]. Several authors have used p.d.s.c. to characterize free radical photopolymerizations[2-6]; however, application of the technique to cationic photopolymerizations of divinyl ethers is more problematic. First, the polymerizations of divinyl ethers proceed very rapidly, and care must be taken to ensure that the reaction rate does not exceed the time resolution of the instrument. Since the d.s.c. response time[7,8] is of the order of 2-3 s, relatively low light intensities must be used to increase the reaction time for the divinyl ether photopolymerizations[9]. Second, photopolymerizations of divinyl ethers are highly exothermic; therefore, to maintain isothermal conditions during the reactions, very small sample sizes must be used (0.5-1.5 mg). If larger sample sizes are used, the heat evolved during the reaction generally cannot be removed on the time-scale of the reaction.

In the present work, p.d.s.c. was used to study the photosensitized cationic homopolymerization of a model divinyl ether monomer. Divinyl ethers have received increased attention in recent years because they generally exhibit very low vapour pressures, relatively low viscosities and low toxicity[10]. Divinyl ethers also

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*To whom correspondence should be addressed polymerize very rapidly to form films that exhibit excellent clarity, adhesion and solvent resistance. There are now a number of commercially available divinyl ether monomers; however, relatively few detailed kinetic studies have been reported. Understanding the kinetics of these cationic photopolymerizations is important owing to the increasing number of applications for rapid, solvent-free curing of polymer films. This recent surge in applications of u.v.-initiated photopolymerizations has been motivated by at least two factors: environmental concerns about the production of volatile organic emissions and the need for high-speed reactions to enhance production rates[3,10–12].

A number of p.d.s.c. experiments were performed on cationic photopolymerizations of a divinyl ether initiated with a diaryliodonium hexafluoroantimonate salt photosensitized by anthracene. The photosensitizer allowed the initiating wavelength to be shifted from the deep u.v. region of the spectrum to the near u.v. region[13] at approximately 350 nm. Isothermal p.d.s.c. experiments were performed for a series of reaction temperatures and light intensities. The profiles were used in conjunction with previously determined photosensitization rate constants[13] to determine the kinetic constant for propagation. The kinetic constant for termination was determined from a series of unsteady-state 'dark cure' reactions at different temperatures and light exposure times. The resulting profiles for the propagation and termination rate constants as functions of conversion provide important insight into the nature of the cationic photopolymerizations.

EXPERIMENTAL

Materials

In these studies, 3,6,9,12-tetraoxatetradeca-1,13-diene (DVE-3, ISP) was used as the monomer. The monomer was dried over molecular sieves to remove any traces of water. As in previous spectroscopic studies[13,14], a commercially available initiator (UV9310C, GE Silicones) was used. The initiator formulation included 5–10 wt% linear alkylate dodecylbenzene, ~ 50 wt% 2-ethyl-1,3-hexanediol and ~ 50 wt% bis(4-dodecylphenyl)iodonium hexafluoroantimonate. Initiator concentrations specified in the remainder of this paper correspond to the total UV9310C concentration. The photosensitizer anthracene was purchased from Aldrich and was used as received. A representative reaction sample contained 0.01 wt% anthracene and 1 wt% initiator in DVE-3.

P.d.s.c. experiments

The p.d.s.c. experiments were conducted using a differential scanning calorimeter equipped with a photocalorimetric accessory (Perkin–Elmer, DSC-DPA 7). The photocalorimetric accessory included transfer optics to produce full-beam u.v. light of varying intensity and a monochromator to produce light of a given wavelength. The initiation light source was a 100 W mercury arc lamp used in conjunction with neutral density filters (Melles Griot) to control the intensity of the incident light. The strong mercury line at 365 nm was used to excite the anthracene photosensitizer. The polymerization reactions were run isothermally by means of a refrigerated recirculating chiller (NESLAB, CFT-25) maintained at 5°C. Small sample sizes (0.5–1.5 mg) were required in order to limit the total heat released during the polymerization reaction so that isothermal conditions could be maintained. The samples were placed in uncovered aluminium d.s.c. pans and cured with u.v. light intensities in the range 0.4–1.6 mW cm^{-2} at various reaction temperatures.

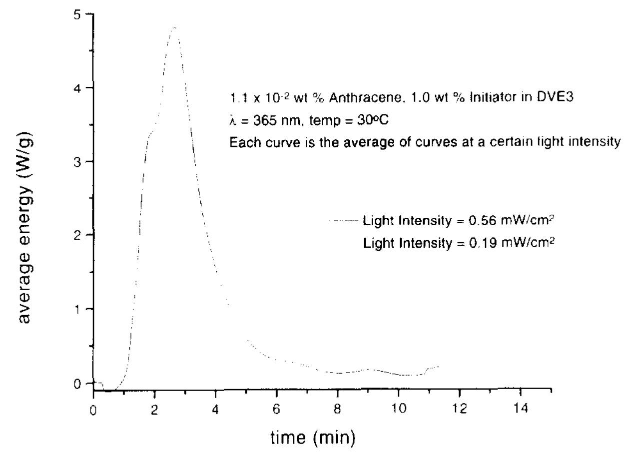

Figure 1 P.d.s.c. exotherms for the cationic polymerization of DVE-3 at different light intensity values

RESULTS AND DISCUSSION

Effect of light intensity

Experiments were performed at several different excitation intensities in order to determine the effect of light intensity on the reaction profiles. The light intensity at 365 nm was adjusted by placing a neutral density filter after the excitation monochromator. Optical densities in the range 0.5–2.0 were required to adjust the light intensity. At optical densities less than 0.5 the reaction proceeded very rapidly, which prevented isothermal conditions. Optical densities greater than 2.0 resulted in very slow reactions, limiting the number of reactions that could be completed in a reasonable time.

Figure 1 shows the relationship between reaction rate and light intensity. As expected, an increase in the initiating light intensity resulted in an increased reaction rate, as indicated by the exotherm reaching its maximum more rapidly. For example, at 0.56 mW cm^{-2} the heat flux reached the maximum at 2.5 ± 0.7 min with an average peak area of 660 ± 59 J g^{-1}, while for an initiating intensity of 0.19 mW cm^{-2} the maximum was reached at 5.4 ± 0.7 min and had an average area of 553 ± 14 J g^{-1}. Each of the curves in *Figure 1* is an average of several profiles obtained at each light intensity, and therefore the average curves are slightly shorter and wider than the original data. However, the average curves represent the general shape and provide the correct average time at the peak maximum and the average area.

Effect of temperature

Reactions were performed at a series of temperatures between 20 and 50°C in order to determine an overall activation energy for the polymerization reaction. A maximum temperature of 50°C was used to ensure that no thermal initiation occurred. An average initial reaction rate was determined for each temperature by

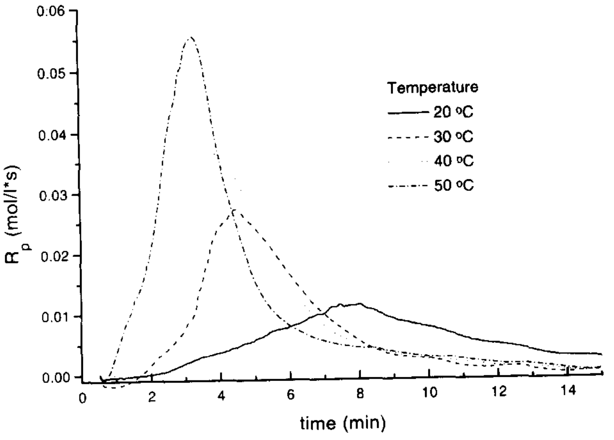

Figure 2 P.d.s.c. exotherms for the cationic polymerization of DVE-3 at temperatures ranging from 20 to 50°C

measuring the time required to reach 20% conversion. This conversion was chosen since it represents the maximum conversion for the lowest-temperature experiment. The activation energy was determined from an Arrhenius fit to the data.

Figure 2 shows p.d.s.c. exotherms for the cationic polymerization of DVE-3 photosensitized with 0.01 wt% anthracene and 1 wt% initiator and controlled at temperatures from 20 to 50°C. As expected, the reaction rate and total conversion increased with increasing temperature, as illustrated by the fact that the exotherms reach the maximum in a shorter time and exhibit larger integrated heat as the temperature is increased. Based upon an Arrhenius fit, the overall activation energy for the cationic polymerization was determined to be $26.5 \pm 3.2\,\mathrm{kJ\,mol^{-1}}$. Since p.d.s.c. measures the total heat of reaction, this value represents an overall activation energy including initiation, propagation and termination

$$E_R = E_P + E_I - E_T \qquad (1)$$

For equation (1) to be valid, the active centre production must continue throughout the reaction. Based upon previous measurements of the kinetic constants for photosensitization[13], the photosensitizer is not completely consumed until well after the time for the peak maximum, and therefore the active centre concentration continues to increase at the peak maximum (the point where the reaction rate was measured). Therefore equation (1) can be used to represent the overall activation energy for the photopolymerization reaction.

Termination rate constant

To determine the termination rate constant k_t for the polymerization of DVE-3, dark cure experiments were performed. In these studies, the polymerization samples were exposed to the initiating light for a short period of time, after which the light source was removed. The remaining cure was monitored with no exposure to the light source, and the reaction rate was found to decay exponentially. Samples that were exposed for 2 min or less had total double-bond conversions of less than 5%. Since the change in the vinyl bond concentration during the dark cure was small, it was assumed that the reduction in the polymerization rate was caused by the decline in the number of active centres as a result of termination and not by depletion of monomer.

The p.d.s.c. exotherms were fitted with an exponential decay curve from the point at which the excitation source was removed with an average exponential time constant of 17.3 ± 0.4 min. Therefore the termination rate constant k_t was calculated to be $0.0010 \pm 0.0002\,\mathrm{s^{-1}}$. These results illustrate that the cationic centres exhibit a relatively long lifetime and relatively small termination rate constants compared to free radical systems. This arises from the fact that in contrast to free radicals, cationic centres do not terminate with one another. Termination in cationic systems typically occurs through combination with the counterion or other nucleophilic species. As will be shown later, the termination rate constant for the polymerization reaction was determined to be approximately five times lower than the initiation rate constant.

Initiation rate constant

In these photopolymerizations, active cationic centres are produced through a photosensitization reaction in which an electron is transferred from an excited-state anthracene molecule to the initiator[13]. Although the reaction proceeds by a multistep photochemical mechanism[13], the rate of generation of active centres may be described by the following simple expression

$$\text{rate of active centre generation} = k_i[\mathrm{A}][\mathrm{I}] \qquad (2)$$

where [A] is the anthracene concentration, [I] is the initiator concentration and k_i is an initiation rate constant which accounts for a number of photophysical steps including excitation, intersystem crossing, exciplex formation and electron transfer[13]. According to this convention, k_i is dependent on the incident light intensity. In our reactions, the initiator (diaryliodonium salt) concentration greatly exceeds the anthracene concentration and can be assumed to be constant[13]. Therefore a pseudo-first-order kinetic constant $k_i^*(= k_i[\mathrm{I}])$ may be used to describe the rate of generation of active centres. The above analysis is based upon the assumptions that one active centre is produced per photosensitizer and initiator molecule and that all reactive centres are capable of propagating, as indicated by previous fluorescence measurements[14].

The overall rate of change of the active centre concentration $[\mathrm{M}^+]$ may be derived by combining the rate of generation by photosensitization with the rate of consumption by termination

$$\frac{\mathrm{d}[\mathrm{M}^+]}{\mathrm{d}t} = k_i^*[\mathrm{A}] - k_t[\mathrm{M}^+] \qquad (3)$$

This equation may be integrated (with the initial condition $[\mathrm{M}^+]_0 = 0$ and the exponentially decreasing anthracene concentration) to yield

$$[\mathrm{M}^+] = [\mathrm{A}]_0 \frac{k_i^*}{k_t - k_i^*}\left(\mathrm{e}^{-k_i^* t} - \mathrm{e}^{-k_t t}\right) \qquad (4)$$

For this equation, the termination rate constant k_t was evaluated above, while the initiation rate constant k_i may be determined by solving the photophysical rate expressions as described in earlier work[13]. For the p.d.s.c. experiments, the incident light intensity used in this calculation was determined by measuring the energy absorbed by graphite discs placed in the sample and reference cells. Using the incident light intensity value, k_i^* was determined to be 0.00403 s^{-1} at 25°C by solving the corresponding set of rate expressions[13].

The activation energy for the photosensitization reaction was determined from fluorescence measurements of the photosensitization reaction between anthracene and the diaryliodonium salt. The rate constant k_i was determined for several different temperatures and fitted to an Arrhenius equation to yield an activation energy E_I of $28.5 \pm 1.6\,\mathrm{kJ\,mol^{-1}}$. Using this activation energy, the temperature dependence of k_i^* was described. Based upon the values of k_t, k_i^*, E_I and $[A]_0$, equation (4) was used to obtain profiles of the active centre concentration $[M^+]$ as a function of time for each of the p.d.s.c. reactions.

Propagation rate constant

As previously mentioned, the rate of propagation R_p is directly proportional to the rate at which heat is released from the polymerizing sample and is therefore proportional to the height of the d.s.c. exotherm measured in watts per gram. For a propagation rate in units of moles of double bonds per second, the proportionality constant is the density ρ (of the reaction mixture) divided by the heat of polymerization ΔH_p, and the instantaneous rate of propagation may be calculated from

$$R_p = \frac{d[M]}{dt} = \frac{\text{height of exotherm (W g}^{-1}) \times \rho}{\Delta H_p} \qquad (5)$$

According to kinetic analysis, the rate of propagation is given by a propagation rate constant multiplied by the active centre concentration $[M^+]$ and the vinyl bond concentration [M]

$$R_p = \frac{d[M]}{dt} = k_p[M][M^+] = [A]_0 \frac{k_p k_i^*}{k_t - k_i^*}(e^{-k_i^* t} - e^{-k_t t})[M] \qquad (6)$$

If a number of propagating centres with different reactivities exist, this equation may be used to fit the polymerization data to yield an apparent propagation constant that comprises all types of propagating centres (e.g. ion pairs, separated ions, etc.). In this paper, we will use this approach to interpret changes in the value of the apparent propagation constant k_p.

The vinyl bond concentration [M] and the conversion may be calculated from the integral of the reaction rate profile (equation (5)). Therefore the instantaneous double-bond concentration may be calculated from the p.d.s.c. profile using

$$[M] = [M]_0 - \frac{\text{exotherm area (J g}^{-1}) \times \rho}{\Delta H_p} \qquad (7)$$

$$\text{conversion} = \frac{\text{exotherm area (J g}^{-1}) \times \rho}{\Delta H_p [M]_0} \qquad (8)$$

Equation (7) gives the vinyl bond concentration in moles per litre when ρ is the density of the reaction mixture. The heat of reaction for the vinyl bond was determined to be 75 $\mathrm{kJ\,mol^{-1}}$ by reacting a monovinyl ether to high conversion. A complete profile of the double-bond concentration or conversion may be obtained by determining the area under the d.s.c. curve as a function of time and applying equation (7) or (8).

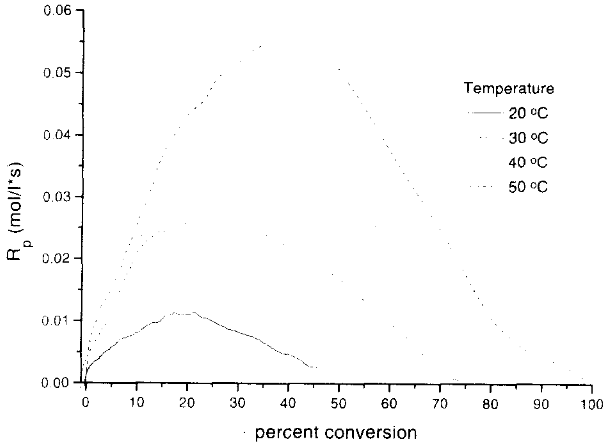

Figure 3 Overall rate of propagation *versus* conversion for DVE-3 photosensitized with 0.01 wt% anthracene and 1 wt% initiator

For each p.d.s.c. exotherm, a profile of the quantity $k_p[M^+]$ may be obtained using the empirical profiles of R_p and [M]. Based only on the p.d.s.c. data, this product may be determined using the following version of equation (6)

$$k_p[M^+] = \frac{R_p}{[M]} \qquad (9)$$

Profiles of the rate of polymerization (propagation) obtained by applying equations (5) and (8) to a set of p.d.s.c. exotherms are shown in *Figure 3*. This figure illustrates that as the temperature is increased, the maximum value of R_p increases accordingly. Furthermore, the conversion at the peak maximum is shifted to higher values as the temperature increases. Therefore *Figure 3* verifies the importance of temperature during the cationic photopolymerization of DVE-3, as characterized by the increase in conversion and rate of reaction with temperature.

Profiles of $k_p[M^+]$ obtained in this manner are shown in *Figure 4*. As shown in this figure, $k_p[M^+]$ initially increases sharply and then levels off at a plateau value between 0.001 and 0.01 s^{-1} depending upon the reaction temperature (as the temperature is increased, a higher value of $k_p[M^+]$ is observed). Finally, the value of $k_p[M^+]$

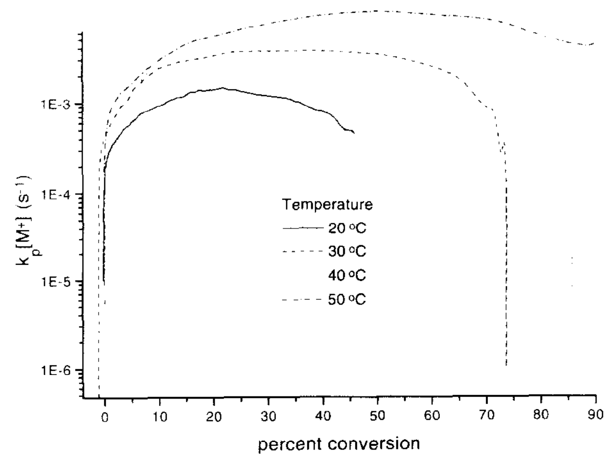

Figure 4 Plots of $k_p[M^+]$ *versus* conversion for the cationic photopolymerization of DVE-3 at temperatures ranging from 20 to 50°C

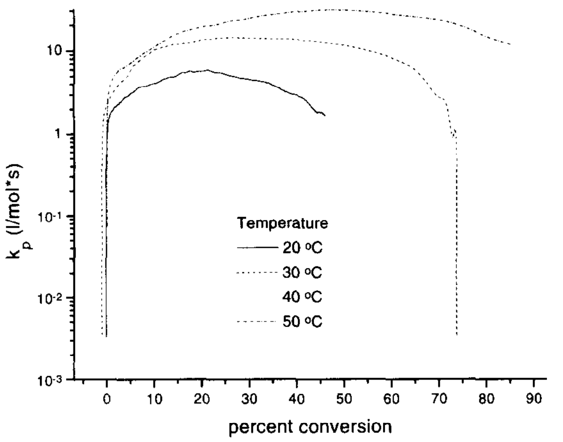

Figure 5 Plots of k_p *versus* conversion for the photopolymerization of DVE-3 at various temperatures

decreases as a limiting conversion is reached. The shape of the profiles in *Figure 4* indicates that the apparent propagation rate constant k_p changes as the reaction proceeds. If k_p remained constant throughout the reaction, this change in $k_p[M^+]$ would be governed by the active centre concentration. Therefore the $k_p[M^+]$ value would increase monotonically until it reached a maximum when all of the photosensitizer was consumed.

More information about the behaviour of k_p may be obtained by coupling the p.d.s.c. data with the k_i^* and k_t values discussed previously. Profiles of the apparent propagation rate constant k_p were obtained by substituting the values of $[A]_0, k_i^*$ and k_t, along with the empirically determined profiles of [M] and R_p, into equation (6). *Figure 5* shows k_p as a function of vinyl bond conversion. The curves exhibit a similar characteristic shape to the $k_p[M^+]$ profiles of *Figure 4*, although the plateau value is much higher owing to the small active centre concentration. The similarity in shape indicates that the relative changes in k_p are much larger than those for $[M^+]$. The final values obtained for k_p were between 5 and $30 \, l \, mol^{-1} \, s^{-1}$, which compare satisfactorily with values from the literature[15].

One possible explanation for the initial large increase in the apparent rate constant for propagation is a change in the reactivity of the carbocationic species due to the proximity of the counterion. In the early stages of the reaction, polymerization leads to a large local increase in viscosity which reduces diffusional mobility. The active carbocation retains considerable mobility through propagation since the cation effectively moves through the reaction mixture by reacting with new monomers. This type of mobility has been termed 'reaction diffusion' and may become the dominant mechanism for mobility of the active centre in highly crosslinked polymerizations[5,16]. However, the large hexafluoroantimonate counterion experiences a decrease in mobility as the viscosity increases since it cannot diffuse through the reaction mixture in a similar manner. During this process, the counterion and carbocation become separated, and since separated ions are orders of magnitude more reactive than ion pairs[1], this would lead to a large increase in the apparent propagation rate constant k_p. This type of 'reaction diffusion' is well known for highly crosslinked free radical systems[5,16] and may aid in explaining the shape of the curves in *Figures 4* and *5*. The final decrease in k_p arises from active centre trapping during these highly crosslinked polymerizations. Therefore a limiting conversion at which the reaction ceases is observed despite the presence of active centres. As previously mentioned, the above analysis is based upon the assumptions that one active centre is produced for each photosensitizer molecule consumed and that all reactive centres are capable of propagating[14].

CONCLUSIONS

In the present work, p.d.s.c. was used to monitor cationic photopolymerizations of a divinyl ether. P.d.s.c. offers a direct method for evaluating the heat generated during a polymerization reaction. The heat of reaction profiles provided by p.d.s.c. were used to characterize the reaction kinetics and evaluate polymerization rate constants. However, the reaction system was extremely rapid and highly exothermic, making d.s.c. measurements particularly challenging. To maintain isothermal reaction conditions, low light intensities and very small sample sizes (0.5–1.5 mg) were used to increase the reaction time for the divinyl ether photopolymerizations.

The p.d.s.c. experiments were used to determine kinetic constants for a series of unsteady-state divinyl ether polymerizations at different temperatures and light exposure times. Kinetic constants for propagation and termination were obtained from the p.d.s.c. experiments in conjunction with previously determined photosensitization rate constants. As expected, an increase in the initiating light intensity or an increase in the reaction temperature resulted in an increased reaction rate. This increase in reaction rate was found to result in higher final conversions as determined from the total heat of reaction.

To determine the termination rate constant k_t, p.d.s.c. dark cure exotherms were fitted with an exponential decay from the point at which the excitation source was removed (the exponential time constant was 17.3 ± 0.4 min). The results illustrate that the cationic centres exhibit a relatively long lifetime and relatively small termination rate constants compared to free radical systems, arising from the fact that cationic centres do not terminate by combination with each other.

An apparent propagation rate constant that comprises all types of propagating centres (e.g. ion pairs, separated ions, etc.) with different reactivities was determined from the p.d.s.c. reaction profiles. The apparent propagation rate constant k_p initially increases sharply and then levels off at a plateau value (as the temperature is increased, a higher value of k_p is observed). Finally, the value of k_p decreases as a limiting conversion is reached. This profile shape indicates that the apparent propagation rate constant k_p changes greatly as the reaction proceeds. The initial large increase in the apparent rate constant for propagation may be explained by a change in the reactivity of the carbocationic species due to the proximity of the counterion. During the polymerization, there is a decrease in the mobility of the large hexafluoroantimonate counterion as the viscosity of the system increases. However, the active carbocation retains diffusional mobility by reacting with vinyl bonds, and this may lead to separation of the two species. Since separated ions are orders of magnitude more reactive than ion pairs[1], the apparent value of k_p increases dramatically during the early stages of the reaction. The final decrease in k_p arises from active centre trapping during these highly crosslinked polymerizations. Therefore a limiting conversion at which the reaction ceases is observed despite the presence of active centres.

The p.d.s.c. profiles for the propagation and termination rate constants as functions of conversion provide important insight into the nature of these high-speed cationic photopolymerizations. Understanding the kinetics of these cationic photopolymerizations is important owing to the increasing number of applications for rapid, solvent-free curing of polymer films.

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