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The effect of interpenetrating polymer network formation on polymerization kinetics in an epoxy-acrylate system

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Abstract

The kinetics of thermally initiated cationic epoxy polymerization and free radical acrylate photopolymerization were studied using photo-differential scanning calorimetry. The reactions of the neat monomers and diluted monomers as well as interpenetrating polymer networks (IPNs) were studied as a function of dilution by the other monomer and temperature. The reaction sequence was also varied to study its effect on the kinetics of formation of the simultaneous IPN's. Both reactions quickly become diffusion controlled. The effects of increasing temperature and dilution on the acrylate polymerization rate profiles are similar, leading to reduced polymerization rate and longer polymerization times. The dilution effect on the epoxy polymerization is similar to that of the acrylate. However, unlike the acrylate reaction the epoxy polymerization rate increases strongly with temperature. The preexistence of one polymer has a significant effect on the polymerization of the second monomer. This effect is larger for the acrylate than for the epoxy polymerization. New kinetic models are needed to capture these complex behaviors.

Keywords: Interpenetrating polymer network; Kinetics; Epoxy-acrylate

1. Introduction

Interpenetrating polymer networks (IPNs) are formed when two distinct multi-functional polymers become entangled at the molecular level [1]. This is achieved when at least one of the multi-functional monomers is reacted in the presence of the other polymer. When one of the monomers is added to an existing polymer and reacted in situ the IPN is classified as sequential. When the polymerization is started from a mixture of the monomers the IPN is classified as simultaneous [2]. IPNs are used in a wide variety of materials from automobile parts to contact lenses to controlled drug delivery capsules to vibration damping pads [3].

In a comprehensive review by Suthar et al. [4] it was found that for a variety of IPN chemistries the morphology and properties of the IPNs were significantly affected by the polymerization kinetics and the presence of the second polymer. The most homogenous IPNs were made when the reaction rates of the two monomers were simultaneous. Complete conversion of one monomer could be achieved in an IPN while in contrast it was not reached during homopolymerization. This was attributed to the second monomer and polymer acting as diluents and delaying or preventing the cage effect that occurs at high conversion when the reaction becomes diffusion controlled with high viscosity. Phase separation was found to begin at low conversions. The kinetics of phase separation is slow because of the viscosity, thus the phase separation does not affect the reaction kinetics. Therefore complete phase separation does not occur.

More recent literature supports these observations. For a polyurethane–poly(butyl methacrylate) IPN the reaction kinetics was demonstrated to control the final morphology due to microphase separation [5]. For a similar system the reaction kinetics was affected by the addition of a 'compatibilizer' [6]. Depending on the chemistry of the compatibilizer the IPN could be formed in one phase or driven to rapidly separate into two distinct phases. The addition of a compatibilizer to incompatible polyurethane–polystyrene IPN resulted in the formation of one phase [7].

Depending on the amine used in the formation of a methacrylate and bisphenol A epoxy semi-IPN, either one or two phases were formed [8]. Interestingly, the slowest amine in this study resulted in one phase. This suggests that the amine was acting both as a compatibilizer and as a crosslinking agent.

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In a series of experiments with IPNs and semi-IPNs based on a variety of acrylate–bisphenol A epoxies, the reaction rate of both monomers was reduced and the activation energy increased during IPN formation [9–13]. Similar observations were made during IPN formation of bisphenol A acrylate and bisphenol A epoxy networks. The reaction rates were slow due to dilution in the other monomer. The final acrylate conversion was observed to be higher due to plasticization by the epoxy, and the epoxy final conversion was reduced due to mobility restrains caused by the quicker forming acrylate network [14,15]. In contrast, when a diacrylate was photopolymerized together with a cycloaliphatic epoxy the acrylate polymerization went to higher conversion in the IPN compared to homopolymerization. In addition the epoxy conversion was not affected by the more rapidly formed acrylate network [16,17]. With an IPN formed from a butyl acrylate and epoxy anhydride, the polymerization rate decreased with increased dilution. The kinetics was affected by the gelation of each phase and by phase separation. The phase behavior and the composition is also a function of the relative reaction rates and the reaction path [2]. The reaction sequence of the monomers during IPN formation has also been demonstrated to affect the final materials properties of an epoxy-methacrylate IPN [18]. In addition to changing the reaction sequence, the monomers can also be reacted simultaneously. It is known that the final properties of the material would then depend on the relative polymerization rates, particularly if phase separation occurs [2]. A phase inversion was suggested from transmission electron microscopy images between IPNs formed with ratios of 50:50 and 25:75 polyethylene glycol 600 diacrylate/bisphenol A epoxy as the continuous phase changed from acrylate to epoxy [19]. Differential scanning calorimetry was used to study formation of an acrylate-epoxy IPN for use in powder coatings [20].

The reaction kinetics during IPN formation plays an important role in the final properties of the IPN. Reaction rates are affected by catalyst concentration, viscosity, reaction sequence and concentrations. The morphology, phase separation, and composition are determined by the reaction kinetics and chemical compatibility. Thus, understanding the reaction kinetics becomes important to engineer final material properties.

The objective of this study is to investigate the polymerization kinetics of a difunctional acrylate and diepoxy during IPN formation. The reaction sequence is controlled by using a free radical polymerization for the acrylate and a thermally initiated cationic polymerization for the epoxy. The photopolymerization kinetics of multifunctional monomers and coating systems has been recently reviewed [21,22] and the kinetics of multifunctional (meth)acrylates continues to be studied [23–26] and modeled [27–30]. The effect of dilution or solvent on the propagation kinetics of radical polymerizations has also been studied [31,32]. Epoxy polymerizations have been widely studied, with cationic epoxy polymerizations receiving less attention than anionic polymerizations. However cationic polymerizations that are photoinitiated are generating renewed interest due to several reasons; the reactions are solvent free, there are no residual amines, and the reaction is carried out at low temperature. Recent investigations have evaluated rate constants [33–35], the effects of different catalyst and catalyst concentration on physical properties and reaction rates [36–41], different initiation methods [42], reaction mechanisms [43], and the reactivity of different epoxide monomers [44]. Hybrid cationic/free-radical polymerization using a photosensitizer, electron donor and diaryliodonum salt to sequentially cure first an acrylate and then an epoxy have also been recently investigated [45]. The formation of a methacrylate/epoxy IPN was studied using photoinitiated free radicals and cations. The presence of the non-reacting monomer was found to plasticize the polymerization. It was also found that the use of a photoinitiator was not necessary [46]. The effect of poly(methylmethacrylate) on the polymerization of a tetrafunctional epoxy was studied during pseudo-IPN formation. It was found that the presence of the methacrylate reduced the reaction rate [47]. By using different azo initiators the reaction sequence in the simultaneous dimethacrylate/epoxy IPN formation was controlled. Reaction rates during IPN formation were lower than neat resins. The initial conversions were also lower when compared to neat resins, after post curing the final conversion were very close to the neat resins [48].

In this paper we explore the complex reaction kinetics during formation of an epoxy-acrylate IPN. These reactions are studied first by diluting the reacting monomer with the other monomer and reacting. Next sequential polymerization of the monomers is explored and finally a concurrent polymerization is studied. The effects of monomer concentration, reaction temperature, reaction sequence and dilution with unreacted monomer are studied. The effects of these different reaction sequences, dilution, and temperature will be discussed as they relate to reaction mechanisms. Based on these studies, a mechanism of IPN formation is proposed.

2. Experimental

2.1. Materials

Polyethylene glycol 200 diacrylate (PEG200DA) a multifunctional acrylate (marketed under the trade designation ‘SR-259’) was purchased from Sartomer (Exton, PA) and bisphenol A-ephichlorohydrin epoxy resin (DGEBA), a multifunctional epoxy (marketed under the trade designation ‘EPON 828’), was purchased from Resolution Performance Products (Houston, TX). The acrylate was polymerized using α,α-dimethoxy-α-phenylacetophenone (DMPA), a free radical photoinitiator (marketed under the trade designation ‘Irgacure 651’), from Ciba Specialty Chemicals (Basel, Switzerland). The epoxy was reacted using a thermal activated cationic catalyst, a proprietary ammonium antimony hexafluoride (marketed under the trade designation ‘XC-7231’) from King Industries (Norwalk, CT). The chemical structures of the acrylate, epoxy, and photoinitiator are shown in Fig. 1. All materials were used as received.

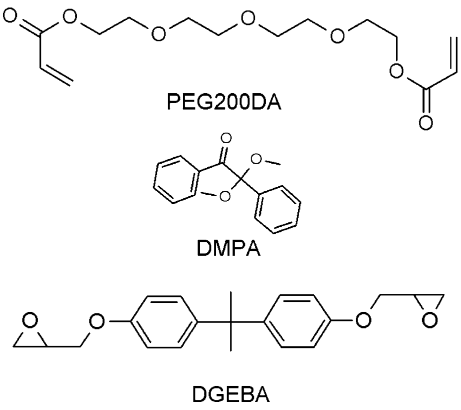

Fig. 1. Chemical structures of: the acrylate, polyethylene glycol 200 diacrylate (PEG200DA), SR-259; the photoinitiator, α,α-dimethoxy-α-phenylacetophenone (DMPA), Irgacure 651; and the epoxy, diglycidal ether of bisphenol-A (DGEBA), Epon 828.

2.2. Sample preparation

Samples were weighed and mixed at room temperature. The photoinitiator is miscible with the diacrylate, and was added in low light conditions (i.e. in a dark room). The XC-7231 was stirred into the DGEBA and readily dissolved. Blends of epoxy and acrylate were also miscible. Samples were stored in dark bottles. For differential scanning calorimetry (DSC) experiments, samples weighing 1–5 mg were micropipetted into standard DSC pans.

2.3. Reaction measurements

2.3.1. Photo DSC

A thermal analyzer marketed under the trade designation 'DSC Q1000' from TA Instruments (New Castle, DE) with a PCA UV light accessory was used to react the samples and study the kinetics and physical properties. In order to accurately track the heat evolved it was necessary to develop a test method for reacting the acrylate. It was found for a sample weighing less than 10 mg, that a light intensity of 3 mW/cm^2 with a nitrogen purge of 15 ml/min is needed so that the DSC can track the reaction heat during the acrylate reaction.

It is difficult to study the epoxy reaction isothermally. The two techniques commonly used are either to preheat the DSC cell to the isothermal temperature and then rapidly open the cover and place the sample in the cell or to rapidly ramp the DSC to the temperature of interest [49]. Both of these methods were explored. It was determined that the rapid ramp to the final temperature retained more of the reaction profile than the other method.

In order to track the epoxy reaction isothermally, the sample was first equilibrated at 25 °C, and then the temperature was rapidly ramped up to the reaction temperature, followed by holding the temperature for the reaction period (15 min). Then the temperature was ramped down to −50 °C at 20 °C/min. After holding at this temperature for 2 min, the sample was returned to the equilibration temperature for 5 min. This was followed by raising the temperature to the reaction temperature a second time, holding for reaction time, and ramping down to −50 °C. This method is similar to Isothermal Method 1 described by Prime [49]. The heat generation and the reaction temperature were recorded as a function of reaction time.

A similar procedure was followed for the acrylate polymerization diluted in epoxy with the exception that the UV light source was unshuttered after the sample had equilibrated at the reaction temperature and the reaction period was reduced to 10 min.

These techniques were applied to study kinetics of IPN formation when the monomers were reacted sequentially. The IPN samples were made at 100 and 130 °C. In the first sequence the acrylate reaction was carried out in the presence of light at 25 °C for 10 min, followed by a jump to the isothermal temperature for 15 min and a ramp down to −50 °C. As before, a re-jump sequence was used to determine the baseline. In the second sequence the sample was heated to the isothermal reaction temperature for the epoxy reaction to occur, and after 15 min the light was turned on for 10 min, followed by the ramp down to −50 °C and retraced.

IPNs with concurrent polymerization were made by heating the sample to the reaction temperature. Thirty seconds after the jump, the UV exposure was started. The reactions that depend on UV radiation for initiation then occur concurrently with the thermal polymerization. The sample temperature was then ramped down to −50 °C and the process repeated to create a baseline.

The DSC traces were further processed using the program marketed under the trade designation 'Universal Analysis' from TA Instruments, New Castle, DE. The heat evolved during the second isothermal period was used as a base line and subtracted from the heat evolved during the first isothermal period. The baseline was corrected to zero. The conversion rate was calculated by dividing the heat flow by the total heat of reaction. The heat of reaction is 532 J/g for PEG200DA [50] and 502 J/g for DGEBA [43,51] respectively. The total conversion was calculated by integrating the conversion rate. A linear or extrapolated baseline was used for the integration depending on the shape of the curve. A running integral of the conversion rate curve was used to create profiles of conversion versus time.

3. Results and discussion

3.1. Reaction mechanisms

Acrylate reaction scheme

$\mathrm{PI} + h\nu \rightarrow 2\mathrm{R}^{\cdot}$ Activation

$\mathrm{R}^{\cdot} + \mathrm{PEG(200)DA} \rightarrow \mathrm{PEG(200)DA}^{\cdot}$ Initiation

$(\mathrm{PEG(200)DA})_n\cdot + \mathrm{PEG(200)DA} \rightarrow \mathrm{PEG(200)DA}_{n+1}\cdot$

Propagation

$\mathrm{R}^{\cdot} + \mathrm{R}^{\cdot} \rightarrow \mathrm{R{-}R}$ Termination

The acrylate polymerization is a fast photo-initiated free radical polymerization. In the above reaction scheme, PI is the photoinitiator, $R^{\cdot}$ is a free radical, and $(PEG(200)DA)_n\cdot$ is a macroradical. The reaction rate quickly falls off when the photo-initiation stops as the free radicals are rapidly scavenged and no more are generated. This scheme shows one of many termination mechanisms [51,52]. Free radical scavengers such as oxygen can also hinder the start of the initiation or reduce the propagation.

Neat acrylate and methacrylate polymerizations have been widely studied [21–32]. Acrylates are commercially important as they are converted from a liquid to a solid coating rapidly without the use of solvents. Methacrylates are used in place of acrylates, even though reaction rates for methacrylates are much slower, because of the lower toxicity of the methacrylates. Acrylate photopolymerizations are characterized by autoacceleration. The autoacceleration is attributed to a reduction in radical termination rate as termination quickly becomes diffusion controlled. The two radicals formed during initiation rapidly move away from each other by polymerizing with available monomer to become macroradicals. The reaction peaks and begins to decelerate. The propagation reaction also becomes diffusion controlled as polymerization proceeds and the monomer concentration drops. The changes to diffusion control for both termination and propagation are due to both the reduction in relative concentrations but also more importantly due to the rapid increase in system viscosity in these solvent-free systems. Autocatalytic models are frequently used to describe acrylate polymerizations. Autocatalytic models are usually not sufficient to completely describe the reaction profiles and conversion [53] so chain length dependent termination and propagation rate constants are also commonly used [24–26].

Epoxy reaction scheme

$$XC + \Delta \rightarrow SA^{+} + SbF_6^{-} \qquad \text{Activation}$$

$$SA^{+} + DGEBA \rightarrow DGEBA^{+} \qquad \text{Initiation}$$

$$DGEBA_n^{+} + DGEBA \rightarrow DBEBA_{n+1}^{+} \qquad \text{Propagation}$$

The XC-7231, XC, thermally disassociates into a super acid, SA^{+}, and hexafluoroantimonate, SbF_6^{-}. The super acid attacks the epoxide to initiate polymerization. Impurities such as hydroxyls or water act as chain transfer agents. This has the effect of speeding the reaction, depending on how the polymerization is measured, but decreasing the ultimate crosslink density, glass transition temperature (T_g) and mechanical properties [54]. The polymer chain remains as an active cation (i.e. 'living' polymer) after vitrification [52]. If the temperature is raised above the T_g the propagation will continue.

Neat epoxy polymerizations are frequently autocatalytic due to the liberated heat and the high temperature sensitivity of the reaction. The rate profiles are often fit to an autocatalytic model with an Arrhenius temperature dependence [39,40,49]. Recently acceleration in the cationic polymerization rate of glycidyl ethers has been observed when polymerized with a free radical donor [44]. A delayed reacceleration of the polymerization has also been reported when the viscosity of the system becomes high enough for the propagating cation to escape from the anion by reaction diffusion. This escape results in a more active cation and an increase in the polymerization rate [33].

Autocatalytic models fit both the epoxy and acrylate reaction profiles. Barring large viscosity effects due to temperature, the acrylate polymerization has relatively low temperature dependence. In contrast, the epoxy reaction is very temperature sensitive. The autocatalytic model fits these reaction profiles but the reasons for the profile shapes arise from different mechanisms.

3.2. Acrylate reaction and kinetics

The acrylate reaction was studied by reaction blends of acrylate and photoinitiator with epoxy resin. These reactions were carried out at 25, 100 and 130 °C. The composition of the blends ranged from 25 to 100% (by mass) of acrylate. The photoinitiator concentration was kept constant at 1% (by mass) of acrylate. To compare the reaction profiles the heat flow from the DSC was converted to reaction rate by dividing by the heat of the acrylate reaction and mass fraction of acrylate. A typical reaction rate profile as a function of acrylate concentration at 130 °C is shown in Fig. 2(a).

From Fig. 2(a), at a given temperature as the acrylate fraction decreases the autoacceleration decreases slightly. More significantly, the deceleration declines sharply. The maximum polymerization rate is much lower at lower acrylate fractions but the final conversion is higher, increasing from 85% for neat acrylate to 89–91% for diluted acrylates. The higher conversion is due to the lower viscosity in the dilute system which allows monomer and macroradical mobility to be maintained allowing for more complete reaction. Propagation continues as the monomer concentration remains relatively high compared to the propagating macroradicals. The final conversion peaks at a mass fraction of 0.75. The trends due to acrylate mass fraction were consistent at 25 and 100 °C.

The reaction profiles for the same acrylate fraction were also compared at different temperatures. Fig. 2(b) shows an example in which the acrylate mass fraction is 0.50 and the reaction has been carried out at temperatures of 25, 100 and 130 °C. As the temperature increases, the peak reaction rate declines and the rate profile flattens. The final conversion at this mass fraction (88–89%) did not vary with temperature. This mechanism is similar to the dilution effect described above. At higher temperatures, monomer and macroradical mobility is retained allowing for continuing propagation. As the acrylate fraction increases the temperature effect decreases. For example, at an acrylate fraction of 0.75 there is no difference between the rate profiles at 25 and 100 °C. This trend continues to the pure acrylate polymerization where very little temperature effect is observed. This is consistent with previous observations where it was shown that the temperature has little

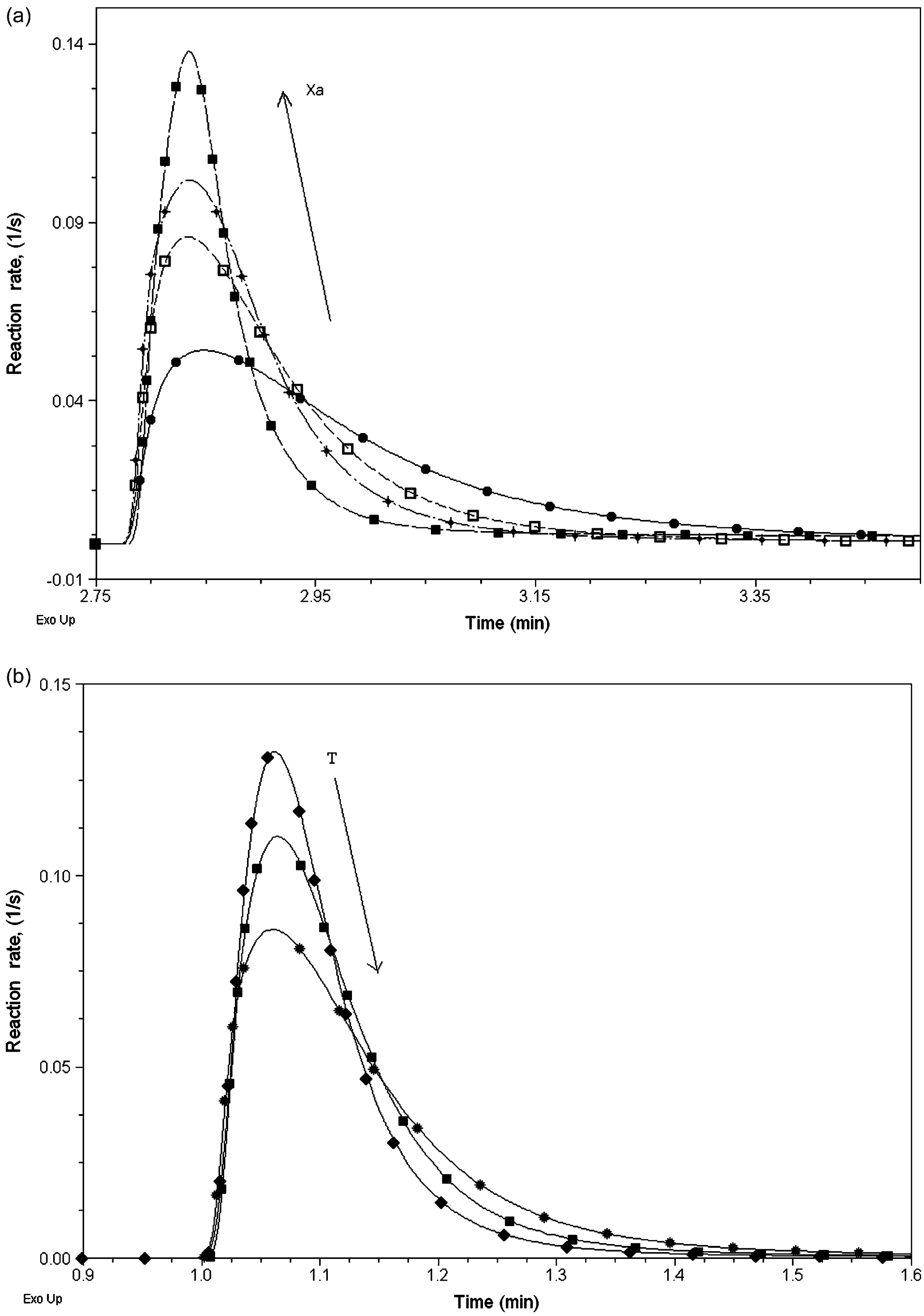

Fig. 2. (a) Reaction rate profiles for the acrylate polymerization diluted with epoxy resin at 130 °C and different acrylate mass fractions. Xa is acrylate fraction; different fractions are represented by 1.0 (■), 0.75 (+), 0.5 (□), and 0.25 (●). Arrow indicates direction of increasing acrylate fraction. (b) Diluted acrylate polymerization reaction rate profiles at different temperatures and an acrylate mass fraction of 0.50. Different temperatures are denoted by (◆) for 25 °C, (■) for 100 °C, and (✸) for 130 °C. Arrow indicates direction of increasing temperature. There was little difference between the two experimental trials at 100 °C. The larger of the two profiles is shown.

effect on the reaction rate, however, a reduction in viscosity allows greater diffusion and mobility [55].

3.3. Epoxy reaction and kinetics

The epoxy reaction was explored by blending the epoxy resin with acrylate and catalyst. Blends of 0.0, 0.25, 0.50 and 0.75 acrylate fraction were studied. The samples were reacted in the DSC at 100 and 130 °C. The catalyst concentration was kept constant at 1% of epoxy. The DSC heat flow curves were converted to reaction rate profiles by dividing by the heat of reaction weighted by the appropriate mass fraction. Contrasted with the acrylate polymerization, the epoxy reaction is slow.

The epoxy reaction profiles with different acrylate mass fractions at 130 °C are shown in Fig. 3. The peak reaction rate is highest for the pure monomer. The reaction rate and final

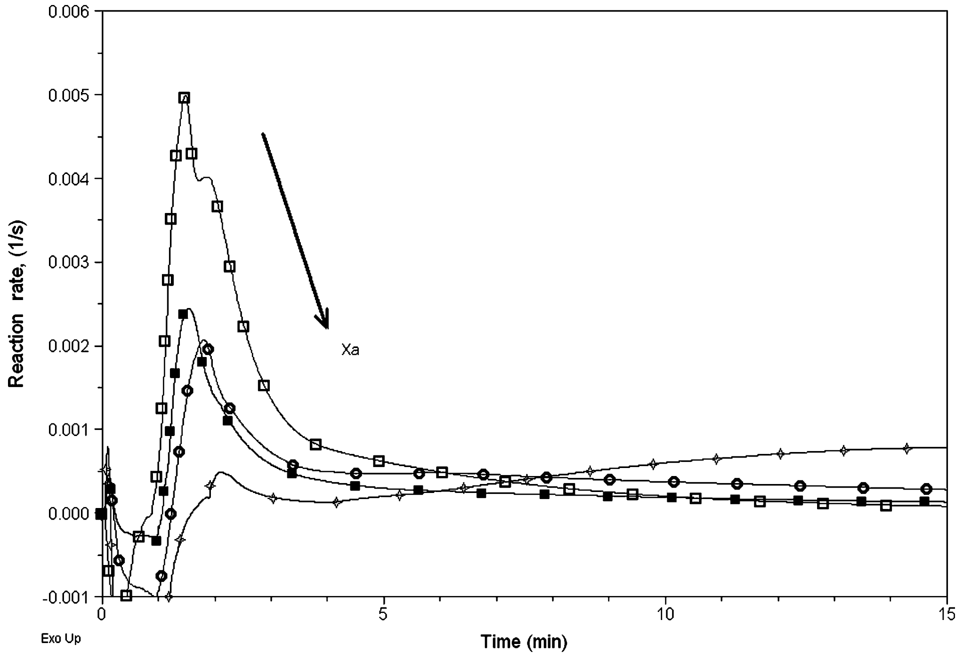

Fig. 3. Epoxy reaction rate profiles diluted in acrylate resin at 130 °C and different acrylate mass fractions, (□) 0, (■) 0.25, (○) 0.50, and (✧) 0.75. Arrow indicates direction of increasing acrylate fraction.

conversion declines as the acrylate concentration increases. There is also indication of a second peak in the neat rate profile, which maybe due to ion separation [34].

4. IPN formation

4.1. Sequential polymerization

Sequential polymerizations with either the acrylate reacting first or the epoxy reacting first were studied at 100 and 130 °C at acrylate mass fractions of 0.25, 0.50, and 0.75. For each sample there are two reaction profiles.

The acrylate polymerization first was done by irradiating the sample at 25 °C for 10 min and then rapidly ramping to the final temperature. The acrylate reaction followed the same pattern as the diluted acrylate polymerization discussed above. As the acrylate is diluted with epoxy the reaction peak declines and the rate profile broadens. The main interest in this reaction sequence is the effect of the previously formed acrylate network on the epoxy reaction. The epoxy reaction rate profiles following the acrylate polymerization at 130 °C and different acrylate fractions are shown in Fig. 4.

The peak reaction rate and final conversion decreases with acrylate concentration. The final conversion is the area under the rate curve. The peak time also increases with the acrylate concentration. The presence of the acrylate network slows the epoxy reaction and reduces the final conversion. The mobility of the propagating cation and monomer are reduced due to the presence of the acrylate gel.

The effect of a preexisting epoxy network on the acrylate polymerization was studied by reacting the epoxy for 15 min and then irradiating the sample. The initial epoxy reactions in this case would be the same as the diluted epoxy reactions. The reactions were conducted at 100 and 130 °C with acrylate fractions of 0.25, 0.50 and 0.75. The epoxy reactions in this case followed the same patterns as the diluted epoxy reactions. The acrylate reaction profiles at 130 °C and at different acrylate fractions are shown in Fig. 5.

The peak reaction rate is highest for an acrylate fraction of 0.75. The lowest peak rate is for the 0.50 acrylate fraction and then increases for the 0.25 acrylate fraction. The reaction deceleration follows this same pattern. The 0.75 acrylate fraction decelerates most steeply followed by the 0.25 and 0.50. The higher reaction rates for the 0.25 and 0.75 fractions may be due to mobility constraints. In the 0.25 acrylate fraction sample, the epoxy has polymerized extensively forming a high viscosity network. After a brief autoacceleration due to a reduction in the termination rate, the reaction decelerates due to a reduction in the diffusion rate in the gel or solid environment on propagation. Similarly, with the 0.75 acrylate, the diffusion limitations are partially due to the previous epoxy reaction but more significantly due to the acrylate polymerization.

4.2. Concurrent IPN formation

Even with different initiation methods for the epoxy and acrylate polymerizations it is not possible to have these reactions occur simultaneously. A concurrent reaction was achieved by rapidly raising the sample temperature, stabilizing for 30 s, and then beginning the UV irradiation. The epoxy reaction begins at about 80 °C. At 100 °C the epoxy reaction is still fairly sluggish. The acrylate reaction begins as soon as the UV light source is turned on.

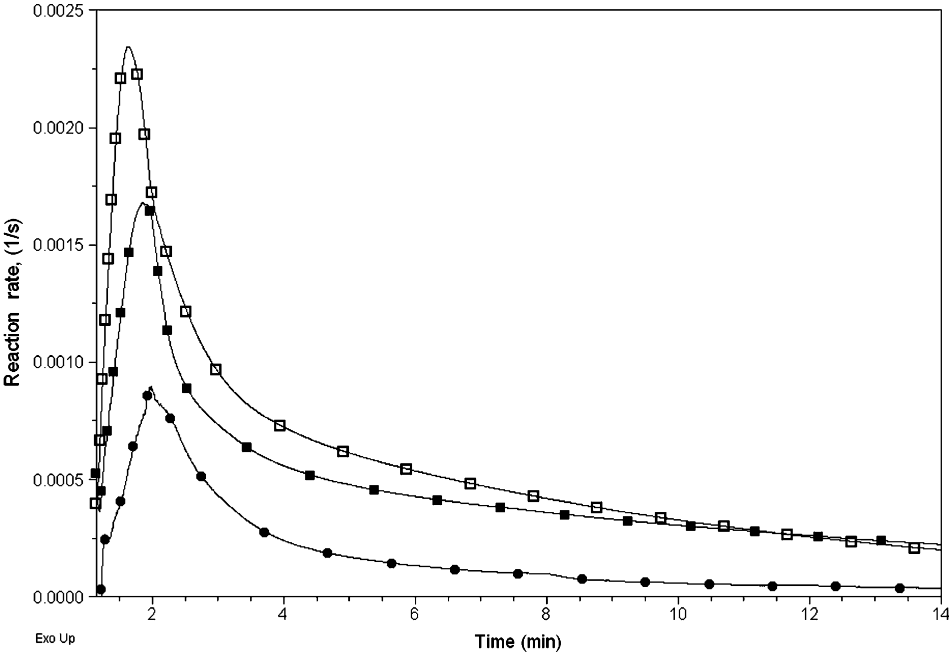

Fig. 4. Epoxy reaction rate profiles following the acrylate polymerization at 130 °C and acrylate fractions of 0.25 (□), 0.5 (■) and 0.75 (●). The median of three trials is shown for the 0.5 acrylate fraction.

The reactions after the light is turned on cannot be separated. It appears that the majority of the exotherm after the light is turned on is due to the acrylate polymerization. There is the possibility of synergy with the free radical formation and enhancement of the epoxy reaction [44]. The reaction rate profiles were determined by dividing the heat flow curves for each reaction separately by the appropriately weighted reaction enthalpy. These reactions were studied at 100 and 130 °C and acrylate fractions of 0.25, 0.50 and 0.75, and the data is shown in Fig. 6.

From Fig. 6, during the concurrent polymerization as the temperature is increased the reaction curve broadens and the peak reaction rate is reduced. A severe reduction in reaction rate is shown for the 0.25 acrylate at 130 °C. At high

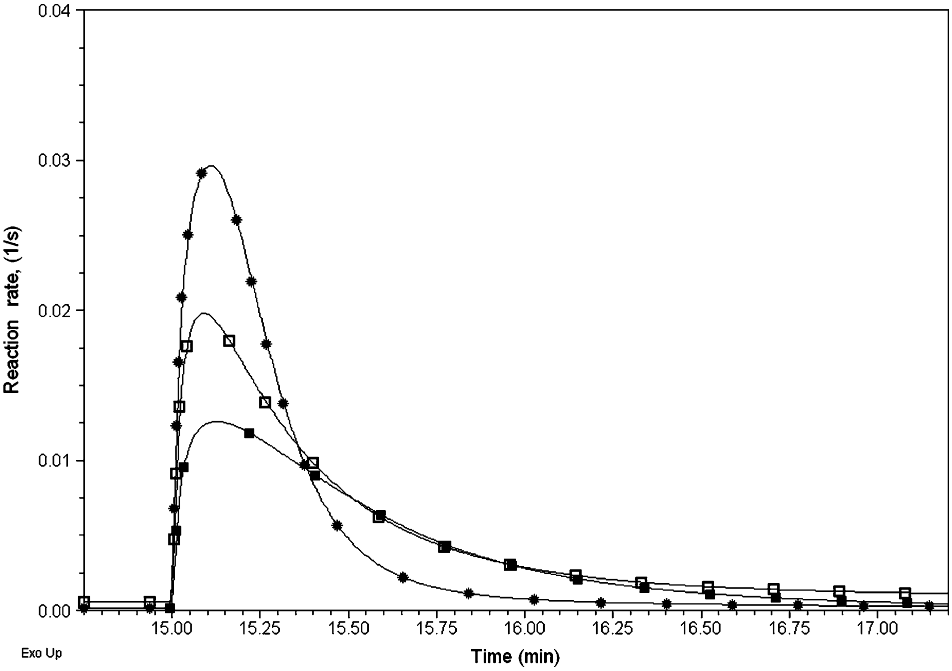

Fig. 5. Acrylate reaction rate profiles at a temperature of 130 °C and acrylate fractions of 0.25 (□), 0.5 (■) and 0.75 (●). These rate profiles are after the epoxy has polymerized. The larger of two trials is shown for the 0.25 acrylate fraction and the median of five trials for the 0.75 acrylate fraction is shown.

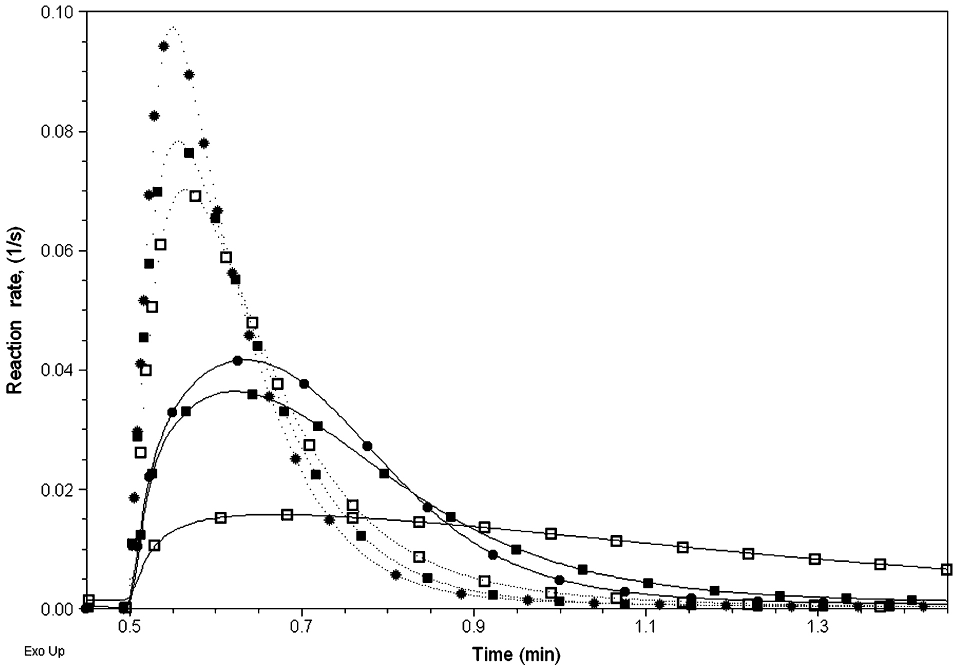

Fig. 6. Acrylate reaction rate profiles during irradiation at 100 °C (dotted line) and 130 °C (solid line) and acrylate mass fractions of 0.25 (□), 0.5 (■) and 0.75 (●) during concurrent polymerization. The larger of duplicate trials is shown for all acrylate fractions at 100 °C.

temperature and dilution, autoacceleration declines as termination remains high due to retained mobility. This higher termination rate at higher temperature and dilution limits the peak propagation rate. Propagation also continues for a longer time due to the lower viscosity at higher temperatures and dilution. The result is that the reaction profile is flat and broadened.

4.3. Comparisons of reaction profiles between reaction sequences

In this section, the same reactions, either acrylate or epoxy, are reviewed at the same mass fraction and temperature yet with different reaction sequences. The only difference between reaction profiles is the sequence. It is expected that when the other monomer has been polymerized previously, the reaction profile would be reduced.

The acrylate reaction sequences that are expected to be similar are the diluted acrylate and acrylate first IPN. For the sequence when the epoxy was reacted first the acrylate reaction is expected to be reduced due to the presence of the epoxy polymer. During the concurrent reaction, the epoxy reaction has been started before the light is turned on. If the light reaction is solely the acrylate, it is expected that this would be hindered by the increased viscosity of the initial epoxy polymerization. If this reaction included an epoxy portion the reaction rate profile could be as large as or larger than the diluted acrylate monomer polymerization.

Similar epoxy reaction profiles are expected from the reaction sequences: diluted epoxy polymerization, the epoxy reaction before the acrylate reaction, and the beginning of the concurrent polymerization before the light is turned on. The epoxy polymerization is expected to be significantly hindered when it occurs after the acrylate reaction.

During the acrylate polymerization the epoxy can be either a diluent or may have already formed a polymer network or be in the process of polymerizing. The effect of the different states of epoxy on the acrylate polymerization profiles is directionally the same regardless of the temperature or acrylate concentration.

From Fig. 7, the acrylate reaction profiles follow the expected order. The diluted monomer reaction has the highest peak reaction rate. This is followed by the concurrent polymerization and the case when the epoxy is prepolymerized. With the epoxy network already in place the reaction peak is broad and peaks at a later time. Even for the concurrent sequence the deceleration after the peak is less than that of the monomer although the autoacceleration has not been greatly affected. Reaction rate profile behavior was similar at 0.25 and 0.75 acrylate fraction. The relative magnitude of the effect at the lower acrylate concentration is not nearly as large. The acrylate reaction in this case is already severely reduced due to the low concentration. At this temperature the epoxy reaction has not progressed very far but is already having a measurable effect on the acrylate polymerization.

The order of the acrylate rate profiles for concurrent polymerization at 130 °C is similar to that at 100 °C. The acrylate polymerization first has the highest reaction rate. This is followed by the concurrent polymerization and then the reaction in the preexisting epoxy network. The autoacceleration for the concurrent and epoxy first reactions are similar. However, the concurrent polymerization during irradiation decelerates faster. The impact on the concurrent rate profile is much larger at 130 °C. This is due to a more substantial build

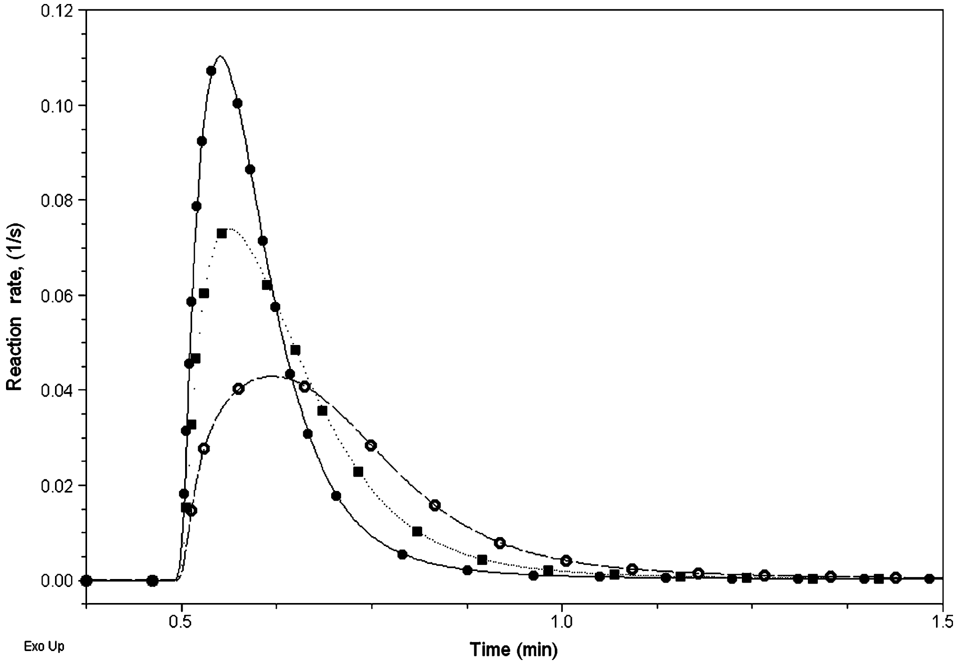

Fig. 7. Acrylate reaction profiles by different reaction sequences at a mass fraction of 0.50 and a temperature of 100 °C. The reaction sequences and the symbols and line style used to denote them are: diluted acrylate reaction (●) and solid line, concurrent polymerization (■) and dashed line, and epoxy reacted first by (○) and dashed line. The larger of duplicate trials is shown for all acrylate fractions.

up in the epoxy network at this temperature compared to 100 °C.

The epoxy reaction profiles at an acrylate fraction of 0.25 and 130 °C is shown in Fig. 8. The epoxy reactions at higher acrylate mass fractions are harder to follow due to a much reduced rate compared to the acrylate reaction. The trends for the reactions are generally the same. The epoxy reaction profiles at 0.25 acrylate fraction and 130 °C, Fig. 8, appear to be nearly identical. The presence of the acrylate network has little effect on the epoxy polymerization.

The reaction profiles for the epoxy first and concurrent reactions should be the same for the first part of the reaction. There are the same components in the same concentrations for both reactions. The diluted monomer reaction profile is also

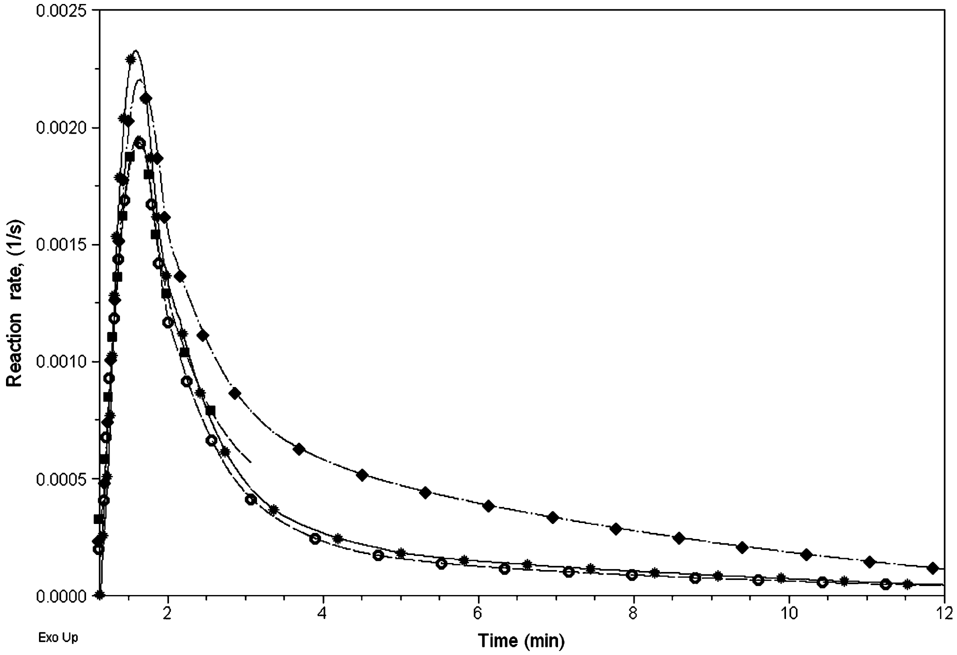

Fig. 8. Epoxy reaction rate profiles at 130 °C and an acrylate mass fraction of 0.25 by different reaction sequences. The reaction sequences and the symbols and line style used to denote them are: diluted epoxy reaction (●) and solid line, concurrent polymerization (■) and dashed line, and epoxy reacted first by (○) and dashed line, acrylate reacted first by (◆) and dot dash line. The larger of two experimental trials is shown for the concurrent and epoxy reacted first sequences.

expected to be similar to the others. It is expected that the preexistence of the acrylate network would hinder the epoxy reaction but this does not appear to be the case.

Based on these experimental observations, the following picture emerges of the reaction mechanisms during IPN formation. Changes in molecular mobility of reaction species during polymerization determine the reaction rates. During polymerization, the reaction environment is constantly changing. Hence a species may become incompatible with the phase in which it is present. When this happens, the diffusivity increases as the molecule is forced to another phase. As the polymer chain grows, the viscosity of the system increases. If a diluent is present, the mobility of the reacting species can be extended for longer time allowing higher conversion when compared to the neat monomer. Increasing the temperature has a similar effect on the free radical polymerization—it reduces the autoacceleration, but increases the reaction species mobility for an extended time allowing for further polymerization and more complete conversion. During sequential IPN formation the prior existence of a polymer network, which causes higher viscosity, reduces the reaction rate of the subsequent polymerization. The epoxy polymerization is less hindered than the acrylate by the existence of a network. The concurrent IPN formation has a similar effect on the acrylate reaction as the preepoxy polymerization. The effect is not as large as when the epoxy reacts completely first. A kinetic model to fully describe all of these phenomena would need to include effects of temperature and dilution, which have similar impact on the rate profiles, as well as allow for the preexistence of a higher viscosity at the onset of polymerization. For the concurrent polymerization, a model would need to account for the continuously changing environment as both monomers polymerize. This will quickly become complex as the viscosity rapidly increases due to both polymerizations and the dilution effect on both polymerizations declines. We are currently developing models to explain these observations.

5. Conclusions

The thermally initiated cationic polymerization of a diepoxy and the photoinitiated free radical polymerization of a diacrylate were studied as pure monomers, diluted monomers, and concurrently reacting monomers polymerized to form homopolymers and IPN's by various reaction sequences with photoDSC. The reactions were studied at isothermal temperatures of 25, 100 and 130 °C and a series of acrylate mass fractions.

When one or both reactions become diffusion controlled, the reaction kinetics during simultaneous IPN formation is very complex. Increasing the temperature and diluting the monomer have similar effects on the acrylate reaction profiles. The autoacceleration is reduced, but the polymerization continues longer as monomer mobility is retained at higher temperatures or with dilution. A similar dilution effect is seen for the epoxy polymerization, but in contrast, the epoxy polymerization strongly increases with temperature. If one polymer is formed before the other, the presence of the first polymer has a significant effect on the subsequent polymerization. If both monomers are polymerized together, or nearly so, the shape of the reaction rate versus time curve is altered. More specifically, the peak reaction rate is reduced and the reaction rate at other times is altered. A kinetic model to capture this complex behavior needs to account for different initial viscosities and changes in dilution and viscosity with conversion of one or both monomers.

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