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Kinetics studies of hybrid structure formation by controlled photopolymerization

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Abstract

Real-time FT-NIR spectroscopy was used to monitor the individual monomer photopolymerization kinetics within the hybrid methacrylate/vinyl ether system composed of 2-phenoxyethyl methacrylate and tri(ethylene glycol) methyl vinyl ether. Photopolymerization processing conditions, such as light intensity, photoinitiator type (both free radical and cationic) and initiator ratios and concentrations, that provide preferential direction of polymer formation based on individual monomer photopolymerization kinetics and overall conversion have been evaluated. Single source UV-light irradiation was employed to produce either single or dual-stage hybrid polymerization, validating the potential of one-step, one-pot methodology for initiating stage-curable polymerizations.

Keywords: Hybrid photopolymerization; Methacrylate; Vinyl ether

1. Introduction

Hybrid polymers, which form from a combination of comonomers with different reactive groups and curing mechanisms, can be considered as a special class of polymer blends. The main advantage of hybrid polymers is that they often synergistically combine the properties of the two constituent homopolymers. A possible way to produce hybrid structure is by copolymerization of functionally different monomers, and especially those that cure by separate initiation mechanisms, which offers the potential for additional kinetic control that can appreciably affect the resulting polymer structures and properties. For example, the combination of two different polymerization processes such as free radical and cationic polymerizations has led to the preparation of a variety of unusual hybrid polymer structures such as multi-block [1–4], graft [5,6], and random [7–9] copolymers and the interpenetrating polymer networks (IPNs) [10,11]. This strategy provides a possible way to combine or modify properties such as glass transition temperature, melting temperature, strength and toughness as well as the surface properties of the corresponding homopolymers.

The aim of the paper is to report a further example of methods to control and analyze the complex hybrid polymerization process. The synthesis of a hybrid polymer based on methacrylate/vinyl ether comonomer system is described. Vinyl ethers, which appear to be very interesting monomers for UV-curable systems because they combine high reactivity and absence of oxygen inhibition with low toxicity and irritation properties [12,13], are readily photopolymerized by a cationic mechanism in the presence of suitable photo-acid generating initiators. Methacrylates, which polymerize by a free radical mechanism, are another type of vinyl monomer widely used in UV-radiation curing, primarily due to the excellent mechanical properties the polymers can provide under ambient photopolymerization conditions [14]. Moreover, in this hybrid system, photoinitiation can provide a unique method to generate each polymer either simultaneously or sequentially [15].

1.1. Simultaneous vs. sequential polymerization

Polymerization sequence control, which can lead to

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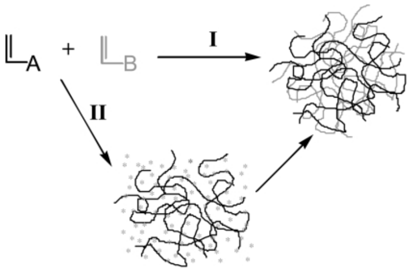


Fig. 1. Hybrid polymerization—I: simultaneous vs. II: sequential.

polymer structure/property control, is a practically important aspect in hybrid polymer formation. It is apparent that, with the selected free radical/cationic hybrid system, the two polymers could be generated in either a sequential or a simultaneous way by a proper selection of processing conditions, as shown in Fig. 1. The main interest of inducing the stage-curable polymerization of free radical/cationic hybrid system lies in its possible potential to not only reduce oxygen and water sensitivity in the respective free radical and cationic processes, but also to favorably affect polymerization shrinkage as well as stress development. In semi- and full-IPN systems, structural features associated with the different photopolymerization profiles could potentially be locked into the final polymer morphology and be used to controllably alter polymer properties. Recently, Decker [11,16] reported that a multiple-stage photopolymerization of (meth)acrylate/epoxide hybrid systems could be achieved through the use of separate irradiation sources at different wavelength ranges or by removal of a filter from a single source. This provided temporally controlled dual wavelength initiation.

In recent years, one-step, one-pot methodology has been introduced to synthetic polymer chemistry as an elegant way to prepare hybrid polymers from comonomers that polymerize by different chemistries [1–4,8,9,17]. In this concept, a bifunctional initiator system containing different reactive sites initiates two different polymerizations independently in a concurrent or sequential manner. Important requirements for the success of such systems are that any step of each polymerization should not interfere with any other step and that both polymerizations should be compatible [4]. Several examples involving different polymerization mechanisms employed in a one-pot, one-step concept have been reported, and corresponding hybrid polymers were prepared in a straightforward manner. Degirmenci et al. [4] successfully prepared block copolymer of cyclohexene oxide and methyl methacrylate initiated simultaneously by photolysis of benzoin in the presence of an oxidizing onium salt. Hawker et al. [2] reported dual living free radial and ring-opening polymerizations from a single initiating molecule with two different functional groups. However, there has been little investigation of sequential polymerization by one-step, one-pot initiation of free radical/cationic hybrid system.

This work examines how variations in initiation conditions can impact the photopolymerization kinetics of hybrid systems and explores the use of a single UV-light to initiate sequential polymerization of methacrylate/vinyl ether system in a one-pot, one-step manner. It is important to monitor the individual monomer polymerization kinetics, since when extended beyond the monovinyl model systems described here, the formation sequence can affect the final polymer structure and ultimately, the hybrid polymer properties.

It should be noted that, this paper is aimed at fundamental studies to give some insight into the reaction kinetics and molecular interactions involved in the selected hybrid system. Therefore, for the ease of monitoring all kinds of interactions, including initiator/initiator, initiator/-monomer and initiator/polymer interactions, relatively low light intensity and initiator concentration compared with those employed in industrial applications were employed to control the photopolymerization process and amplify the differences encountered.

1.2. Analytical technique

Several analytical methods exist for measurement of monomer conversion during polymerization. Differential scanning calorimetry provides a measure of monomer conversion based on the enthalpy of the exothermic polymerization process [18,19]. But with the selected methacrylate/vinyl ether hybrid system, photo-DSC cannot differentiate individual monomer conversion. To study the hybrid polymerization process of (meth)acrylate/epoxide systems, Decker and Moussa [20] have developed a powerful technique based on real-time infrared (RTIR) spectroscopy that allows one to monitor the polymerization of each monomer type in the mixture. Existing references [4,10–12,16,20–22] have emphasized the use of mid-infrared spectroscopy to follow polymerization kinetics. However, mid-infrared analytical techniques limit the samples to thin films, typically 5–30 μm thick, due to strong molar absorption coefficients [23] in this spectral region. The surface regions only of thicker specimens can be probed with reflectance-based mid-IR techniques. Mid-IR is also often difficult to use in many monomer systems due to complexity arising from overlapping absorption.

There are alternative spectroscopic methods to the use of the mid-IR spectral region for direct measurement of monomer conversion, such as Raman spectroscopy and near-IR. The non-destructive analysis of conversion in dental resins by NIR offers advantages of convenience, practical specimen dimensions and precision compared with standard mid-IR analytical procedures [24]. However, the use of NIR for the analysis of conversion in hybrid polymerization system has received relatively little attention [25,26].

The objective of the present work was to develop real-time near-infrared (NIR) spectroscopy as an alternative analytical method to individually monitor the polymerization kinetics of vinyl ether and methacrylate monomers

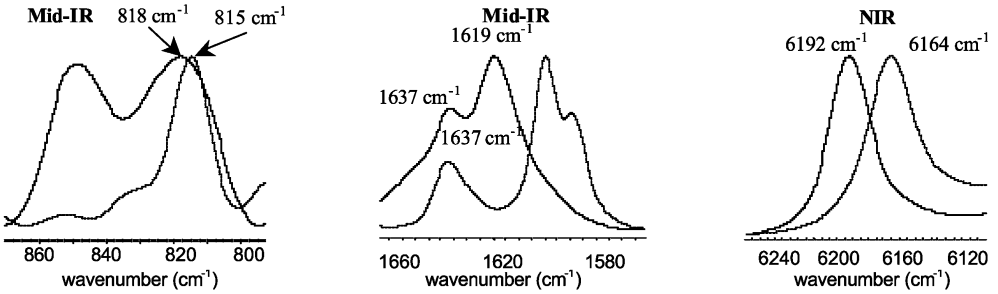


Fig. 2. Vinyl-related absorptions of POEMA (dotted lines) and TEGMVE (solid lines) monomers in Mid-IR and NIR (*Y*-axis: arbitrary absorbance units).

during the photopolymerizations. All potential interactions between coinitiators, comonomers, additives and light sources will be explored to identify conditions that allow the structural development of the hybrid polymers to be systematically controlled.

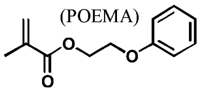
2. Experimental

2.1. Materials

The following compounds were used in this study:

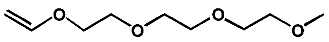
- monomers: 2-phenoxyethyl methacrylate (POEMA, Esstech) and tri(ethylene glycol) methyl vinyl ether (TEGMVE, Aldrich) were used as received;

(POEMA)



2-phenoxyethyl methacrylate

(TEGMVE)



tri(ethylene glycol) methyl vinyl ether

- free radical type initiators: 2,2-dimethoxy-phenylacetophenone (DMPA, Aldrich) and bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (IC, Irgacure 819®, Ciba Specialty Chemicals);
- cationic type initiators and amine additive: (4-((2-hydroxytetradecyl)oxy)phenyl)phenyl iodonium hexafluoroantimonate (iodonium salt), (tert-butoxycarbonylmethoxynaphthyl)diphenylsulfonium triflate (sulfonium salt) and ethyl 4-dimethylaminobenzoate (amine) (all from Aldrich).

The reason for the selection of methacrylate rather than acrylate for polymerization with vinyl ether is that minimized copolymerization is expected to occur between methacrylate and vinyl ether under free radical initiation conditions based on the unfavorable reactivity ratios (methyl methacrylate/ethyl vinyl ether: $r_1 = 37$; $r_2 = 0.01$) compared with the acrylate and vinyl ether combination (methyl acrylate/ethyl vinyl ether: $r_1 = 3.3$; $r_2 = 0$) [27] (See Fig. 7). With the selected monomethacrylate and monovinyl ether monomers used here, phase separation does not occur and the specimens remain transparent before and after UV polymerization.

2.2. Equipment

The polymerization reaction was followed in situ by FT-NIR (Nicolet Magna 750 equipped with an extended range KBr beam-splitter, a white light source and a MCT/A detector). A UV-light source (Novacure, EXFO, Mississauga, Ontario, Canada) filtered to 320–390 nm was directed to the sample with a liquid light guide. A horizontal accessory [28] placed in the sample compartment of the IR was used to position the sample mold perpendicular to the incident light with the irradiation intensity at the sample controlled at either 5 or 20 mW/cm^2 as measured with a radiometer. All photopolymerizations were conducted at room temperature.

2.3. Polymerization

For NIR measurement, an equimolar mixture of the two monomers containing the various photoinitiator combinations was put in the rectangular mold made from glass slides at a thickness of 0.5 mm and a width of 12 mm. The $=CH_2$ first overtone absorption bands at 6164 and 6192 cm^{-1} in the NIR were used to follow the concentration of methacrylate and vinyl ether double bonds, respectively. During the photopolymerization, the spectrum acquired at each 0.9 s sampling interval represents the sum of four individual scans at 4 cm^{-1} resolution. The transmission mode spectral series collection coupled with data processing using the IR/NIR's software (OMNIC, Nicolet) provided the conversion vs. time curves.

3. Analytical technique

3.1. Near-IR

In the mid-IR, the methacrylate C=C absorption at 1637 cm^{-1} is completely enveloped by the two vinyl ether C=C absorption bands at 1619, 1637 cm^{-1}, as shown in Fig. 2. The aromatic absorptions at 1582 and 1609 cm^{-1} due to POEMA further complicate analysis of the hybrid polymerization results obtained in this region [24]. Similar overlapping methacrylate and vinyl ether absorptions are observed at around 815 cm^{-1}.

However, the NIR spectra of TEGMVE/POEMA mixtures present partially resolved single $=CH_2-$ based absorption bands for each of the comonomers with nearly 30 wavenumber separation between the peak maxima (Fig. 2).

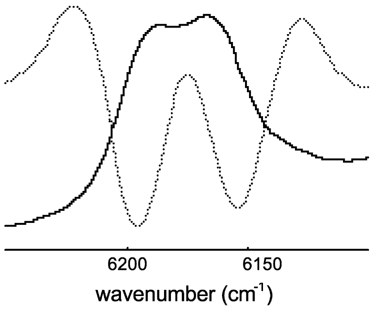


Fig. 3. Examples of original NIR and second-derivative spectra (solid line: NIR absorption band of comonomers; dotted line: second-derivative spectrum).

The NIR analytical technique can be readily applied to study bulk polymerizations with transmission mode spectra using specimen geometries ranging from approximately 0.25 to > 5 mm [24] in thickness. This provides a method to follow bulk polymerization kinetics and determine final conversion values non-destructively directly on specimens designated for other analytical characterization such as mechanical property testing. The NIR method can accommodate a variety of sample preparation configurations including compatibility with glass substrates.

3.2. Evolution of vinyl ether and methacrylate double-bond conversions

The two =CH_2 absorption bands at 6164 and 6192 cm^{-1} in the NIR region were used to follow the concentration of methacrylate and vinyl ether double bonds, respectively, during polymerization. The absorbance peak area method was used to calculate conversion. A second-derivative deconvolution method allows the calculation of conversion for the individual monomers during the polymerization separately. An example of the second-derivative spectra is shown in Fig. 3. The precision of this conversion-analysis method was validated previously by a comparison of the conversion values obtained with the automated second-derivative deconvolution approach with the results based on peak-fitting deconvolution (PeakFit®, SPSS Inc.) of selected individual spectra taken from the series [29,30].

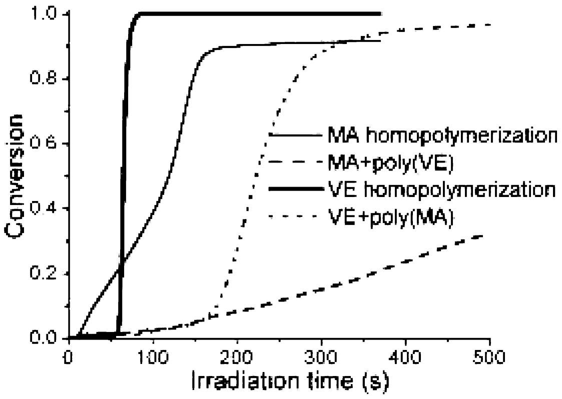


Fig. 4. Homopolymerizations (POEMA + 0.2 wt% DMPA; TEGMVE + 0.2 wt% iodonium salt) vs. sequential polymerizations (POEMA + 0.2 wt% DMPA with prepolymerized TEGMVE; TEGMVE + 0.2 wt% iodonium salt with prepolymerized POEMA) (Light intensity: 5 mW/cm^2).

4. Results and discussion

With methacrylate/vinyl ether mixtures, the two polymers can be produced either concurrently, or one after the other. Fig. 4 shows the extreme conditions of the two types of sequential polymerizations of the selected hybrid system. When POEMA was UV-irradiated in the presence of the pre-polymerized TEGMVE, which was prepared with the same initiator system as used in its homopolymerization, the POEMA polymerization rate and final conversion (on experimental time scale) were dramatically suppressed compared with the neat monomer. This behavior can be explained by the bulkier, more rigid structure of POEMA, which leads to drastic molecular mobility restrictions in the presence of TEGMVE polymer. On the other hand, the polymerization behavior of TEGMVE, which has more flexible monomeric and polymeric structures than those of POEMA, is much less affected by the prior formation of POEMA polymer. Furthermore, a typical feature of the cationic photopolymerization is the substantial postcure effect observed because of the well-known ‘living’ character of the cationic reaction, which means that TEGMVE continues to polymerize upon storage of the sample in the dark [13,16]. Therefore, to make the hybrid systems polymerize sequentially with maximized final conversion of both monomers, it would be practical to use TEGMVE as a latent reactive diluent or plasticizer during the early polymerization of POEMA. Because of the low conversion values at which the pronounced rate increase in TEGMVE polymerizations occurs, as shown in Fig. 4, it can be assumed that this behavior is due less to mobility restrictions, such as dissociation of the counterion from the active site, and more to the rapid consumption of adventitious moisture, which effectively surpresses the cationic polymerization [31].

The polymerization kinetics depend on a number of parameters, which can be used to control the onset, e.g. simultaneous or sequential, as well as reaction rate and final conversion of each type of polymerization [11]:

- chemical factors: comonomer type and structure, photoinitiator type and its concentration, additives;
- physical factors: irradiation wavelength, light intensity, formulation viscosity, temperature and the sample physical state.

A series of kinetics studies were performed to investigate the effects of chemical or physical factors on the kinetics of homopolymerization of each monomer as well as the dual cure hybrid photopolymerization.

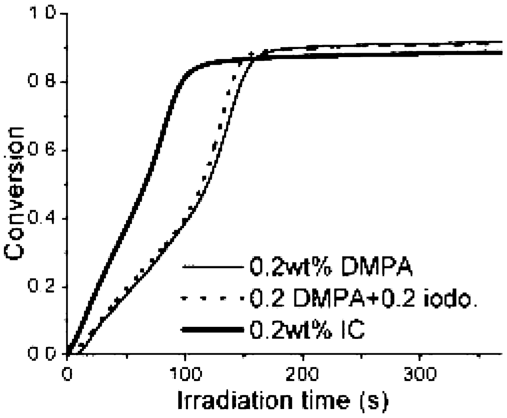


Fig. 5. Effects of initiator type on the conversion profiles for POEMA homopolymerizations (iodo.: iodonium salt) (Light intensity: 5 mW/cm^2).

4.1. *Effects of chemical factors*

4.1.1. Photoinitiator type and its concentration. With the selected hybrid system, photoinitiators play a key role in UV-induced polymerization by controlling both the onset and rate of the polymerization reaction. Figs. 5 and 6 show the homopolymerization profiles recorded by FT-NIR spectroscopy for POEMA and TEGMVE, respectively, upon UV-irradiation in the presence of different photoinitiators and initiator combinations.

Among the free radical type initiators, IC induced significantly higher reactivity in POEMA homopolymerizations compared with DMPA. The presence of the iodonium salt with DMPA had no effect on the free radical methacrylate polymerization profile. For the cationic type initiators, not surprisingly, the sulfonium salt was found to be significantly less reactive than the iodonium salt in TEGMVE polymerizations.

Onium salts (On^+) containing aromatic groups such as diaryliodonium ($Ar_2I^+X^-$) and triarylsulfonium salts ($Ar_3S^+X^-$), represent a large class of compounds that can be used as cationic photoinitiators. These salts effectively act as sources of cation radicals and Lewis acids upon light exposure, as shown in Scheme 1 [4,9,32–39].

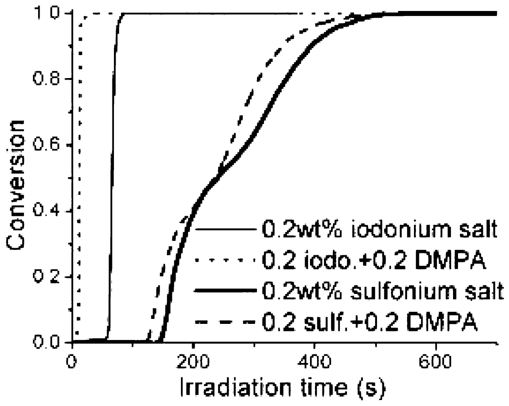


Fig. 6. Effects of initiator type on the conversion profiles for TEGMVE homopolymerizations (Light intensity: 5 mW/cm^2).

Upon irradiation, onium salts decompose to yield a variety of reactive radical, radical-cation and cation intermediates. The cationic species can interact with a proton donor molecule (RH, i.e. monomer or impurity like water) giving rise to the strong Brønsted acid, H^+X^- (Eq. (1)). Initiation proceeds by protonation of the monomer (Eq. (2)) and is followed by polymerization (Eq. (3)). At the same time, aryl radical species produced by photodecomposition of the onium salt can also interact with the monomer in the following two ways. First, the aryl radical can add to an unsaturated monomer (Eq. (4-a)). Alternatively, the radical can abstract a hydrogen atom from the monomer (Eq. (5)). Thereafter, the radical species, $M^{\bullet}_{VE}$ and $ArM^{\bullet}_{VE}$, can be oxidized by the onium salt (Eq. (6-a)) giving rise to carbocations. Subsequently, the diaryliodine (or triarylsulfur) free radical (Eq. (7)) decomposes to generate an iodoaromatic (or sulfoaromatic) compound and an aryl radical. It is obvious from Scheme 1 that the vinyl ether monomer plays an integral role in the overall mechanism by providing not only a polymerizable functional group but also either an abstractable proton or a site of unsaturation, and these sites react subsequently through the previously mentioned redox process to produce initiating carbocations [39].

As also seen from Scheme 1, radicals (i.e. $Ar^{\bullet}$ and $ArM^{\bullet}_{VE}$) generated by onium salt photolysis can be converted to carbonium ions that can act as initiators for cationic polymerization. Therefore, there is an effective promotion to the onium salt photolysis on considering the number of cationic initiating species generated [4,9,33–36, 39].

From the mechanisms shown in Scheme 2, as well as the data presented in Fig. 6, it is evident that the addition of DMPA to the onium salt initiators, particularly the diaryl iodonium salt, does assist TEGMVE homopolymerization by reducing the induction time, but has little influence on cationic polymerization rate. Again, the induction time in the vinyl ether polymerizations appears to be associated with trace amounts of moisture and the significant reduction in moisture sensitivity under dual cure initiation will be the topic of a separate report.

Under illumination, DMPA molecules decay into free radicals and trigger polymerization reactions of POEMA. Subsequently, it should be noted that, the cationic initiation arising from the addition of low-molecular weight radicals, i.e. $M^{\bullet}_{MA}$, to vinyl ether monomer (Eq. (4–b)) and the following oxidation (Eq. (6-b)), is negligible because POEMA is much more reactive than vinyl ether towards the small radicals [9]. However, the adducts of the growing poly(POEMA) free radicals and electron-donating TEGMVE molecules can be oxidized by onium ions to form cations (Eq. (6-c)), which are capable of initiating cationic polymerization [4,9,33–36,39]. This aspect is particularly attractive because cationic polymerization can be activated by free radical initiators. Since a wide range of onium salts have their principal absorption bands in the

$$Ar_2I^+X^- \xrightarrow{hv} Ar^\bullet + Ar\,\overset{\bullet}{I}{}^+\,X^- \xrightarrow{RH} ArI + R^\bullet + H^+X^- + Ar^\bullet \tag{1-a}$$

$$Ar_3S^+X^- \xrightarrow{hv} Ar^\bullet + Ar_2\,\overset{\bullet}{S}{}^+\,X^- \xrightarrow{RH} Ar_2S + R^\bullet + H^+X^- + Ar^\bullet \tag{1-b}$$

$$H^+X^- + M_{VE} \rightarrow HM_{VE}^+X^- \tag{2}$$

$$HM_{VE}^+X^- + nM_{VE} \rightarrow H(M_{VE})_nM_{VE}^+X^- \tag{3}$$

$$M_{VE} + Ar^\bullet \rightarrow ArM_{VE}^\bullet \tag{4-a}$$

$$M_{VE} - H + Ar^\bullet \rightarrow M_{VE}^\bullet + ArH \tag{5}$$

$$M_{VE}^\bullet + Ar_2I^+X^- \rightarrow M_{VE}^+X^- + Ar_2I^\bullet \tag{6-a}$$

$$Ar_2I^\bullet \rightarrow Ar^\bullet + ArI \tag{7}$$

Scheme 1. Proposed mechanisms of the direct and free-radical-induced decomposition of onium salts in vinyl ether cationic polymerization (M_{VE}: vinyl ether monomer).

short wavelength region (220–310 nm) and many commercially available free radical photoinitiators efficiently absorb wavelengths greater than 300 nm, this offers a flexible way to expand considerably the use of cationic polymerization in applications where longer wavelength irradiation is required [9,34,39].

However, notably, the acceptor strengths of the cationic initiators used, as indicated by their reduction potentials [9], play a key role in the free radical assisted cationic polymerization process. Iodonium salts appear to be more effective serving as oxidant than sulfonium salts, which have less favorable redox potential. In Fig. 6, for TEGMVE homopolymerization, the dual initiator system of DMPA/sulfonium salt has a slightly shorter induction time compared with the sulfonium salt alone. This less efficient sulfonium salt was employed in this paper is because, in some cases, we would like to slow down the cationic polymerization process to induce sequential polymerization within hybrid system. And one might expect that it would be possible to manipulate the relative onset and polymerization rate of each monomer by the use of these initiator combinations.

Fig. 7 shows that with only DMPA as initiator, the extent of TEGMVE consumption by direct free radical copolymerization with POEMA, based on the mechanism shown in Scheme 2, was less than 5%. On the other hand, the POEMA/TEGMVE monomer mixture in the presence of only the iodonium salt initiator did provide some limited degree of POEMA homopolymerization through the radical species generated in the onium salt photolysis process. In this situation, the limiting of conversion (<10%) of POEMA is reached in less than 200 s, which may indicate rapid consumption of the cationic initiator. From these results, it is anticipated that in dual initiation systems, POEMA will not cross over to cationic TEGMVE polymer, but that a small amount of TEGMVE can cross over and copolymerize into the POEMA polymer (Scheme 2).

$$DMPA \xrightarrow{hv} R^\bullet$$

$$R^\bullet + M_{MA} \rightarrow M_{MA}^\bullet \xrightarrow{M_{MA}} \cdots \xrightarrow{M_{MA}} \sim M_{MA}^\bullet$$

$$M_{MA}^\bullet + M_{VE} \rightarrow M_{MA}M_{VE}^\bullet \tag{4-b}$$

$$\sim M_{MA}^\bullet + M_{VE} \rightarrow \ \sim M_{MA}M_{VE}^\bullet \tag{4-c}$$

$$M_{MA}M_{VE}^\bullet + Ar_2I^+X^- \rightarrow M_{MA}M_{VE}^+X^- + Ar_2I^\bullet \tag{6-b}$$

$$\sim M_{MA}M_{VE}^\bullet + Ar_2I^+X^- \rightarrow \ \sim M_{MA}M_{VE}^+X^- + Ar_2I^\bullet \tag{6-c}$$

Scheme 2. Proposed mechanisms of the photodecomposition of dual DMPA/onium salt initiator system in methacrylate/vinyl ether hybrid polymerization (M_{MA}: methacrylate monomer; M_{VE}: vinyl ether monomer. Similar equations as shown in Scheme 1 are not repeated).

Fig. 8 shows some clear examples that the two polymerizations can occur simultaneously (case 3) or sequentially (cases 1 and 2) by varying initiator formulations. As expected, the polymerization of the POEMA proceeds faster and more extensively than that of the TEGMVE when the DMPA concentration largely exceeds that of the iodonium salt. On the other hand, quite different behaviors of TEGMVE were observed by varying the ratios of DMPA to iodonium salt in these dual initiation systems. It should be noted that 0.05 wt% iodonium salt on its own did not initiate TEGMVE homopolymerization, but it did

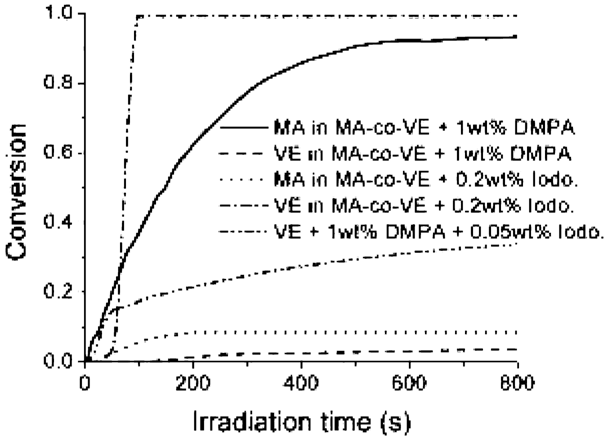


Fig. 7. Effects of initiator concentrations on the conversion profiles for POEMA/TEGMVE hybrid polymerizations and TEGMVE homopolymerization (Light intensity: 5 mW/cm^2).

$$PS^* + (RCH_2)_2NCH_2R' \rightarrow (RCH_2)_2N\dot{C}HR' + (PS)H$$

Scheme 3. Radical formation.

provide a moderate degree of TEGMVE conversion in conjunction with DMPA under homopolymerization conditions (Fig. 7). Moreover, considerably higher levels of TEGMVE conversion were obtained in hybrid polymerizaton systems with 0.05 wt% iodonium salt and various amounts of DMPA, as represented in Fig. 8, due to the reasons discussed above.

4.1.2. Amine additive

4.1.2.1. Influence on free radical polymerization. The beneficial role of amines in UV-initiated free radical polymerization has been well recognized. Tertiary amines have been used widely to promote fast cure and to reduce the inhibition effects of atmospheric oxygen on surface cure performance [40].

First, they are able to donate a proton to photoinitiators or photosensitizers (PS, Scheme 3) that rely on a hydrogen abstraction process. The resultant free radicals are available to initiate polymerization in the UV cure process. Secondly, as seen from Scheme 4, another free radical is produced in the process of oxygen scavenging reaction. Since the samples used here were photopolymerized between glass slides, only dissolved oxygen already present in the monomers is involved. The modest increase in rate observed in the POEMA homopolymerization with added amine (Fig. 9), and particularly the maximized rate at intermediate amine concentration (Fig. 9(b)), is a clear indication that initiating radicals have been produced more effectively under those conditions.

4.1.2.2. Influence on cationic polymerization. Obviously, basic or alkaline materials, like amines, will passivate the protons, which are active for cationic initiation, generated from photolysis of the initiator and the cure will be dramatically slowed or even stopped. For example, the addition of even small amounts of amine dramatically extends the induction period of the TEGMVE homopolymerizations (Fig. 10). In addition, as previously mentioned, the moisture content in TEGMVE monomer or hybrid systems can also be used to extend the induction time of cationic photopolymerizations [31].

4.1.2.3. Influence on hybrid system. Similar results were obtained when the hybrid system was UV-irradiated in the presence of the amine, as shown in Fig. 11. The induction period of TEGMVE could be greatly prolonged with addition of amine because of the base inhibitory effect of amine on cationic polymerization. It is particularly pronounced in the present case because of the comparatively small amount of cationic photoinitiator. The initial protons generated by the photolysis of iodonium salt are preferentially consumed through reaction with the amine in the sample until the amine concentration is reduced to low enough levels to allow the vinyl ether monomer to compete successfully for the initiating protons. For the POEMA, the free radical polymerization remains essentially unaffected by the addition of amine and this is reasonable considering the high concentration of free radical initiator, IC, with respect to amine.

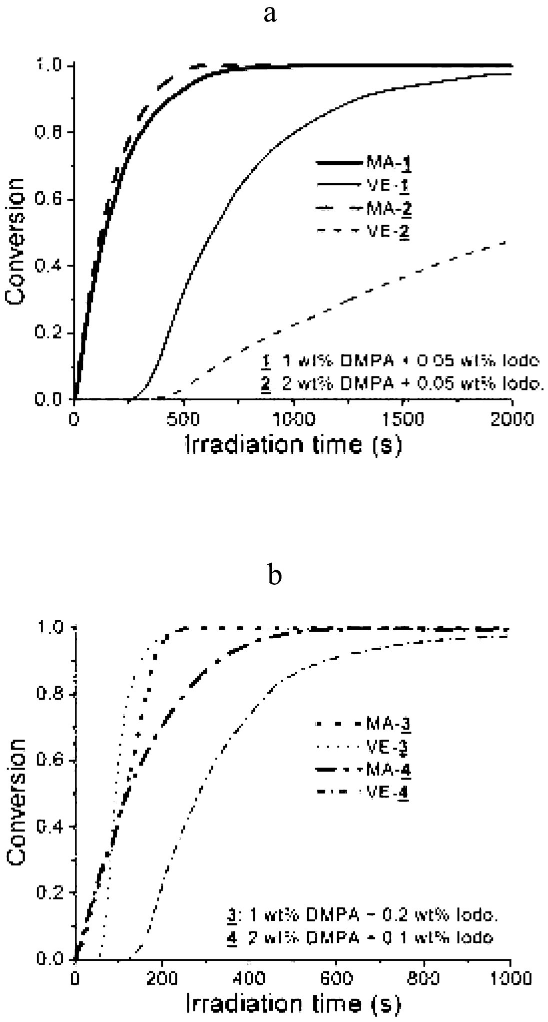
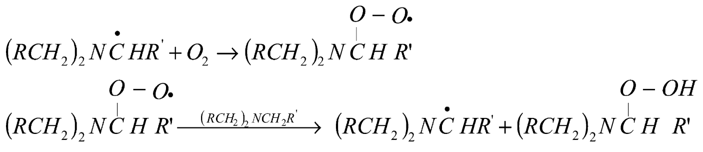


Fig. 8. Effects of initiator concentrations on the conversion profiles for POEMA/TEGMVE hybrid polymerizations (Light intensity: 5 mW/cm^2).



$$(RCH_2)_2N\dot{C}HR' + O_2 \rightarrow (RCH_2)_2N\underset{}{\overset{O-O\bullet}{\overset{|}{C}}}HR'$$

$$(RCH_2)_2N\overset{O-O\bullet}{\overset{|}{C}}HR' \xrightarrow{(RCH_2)_2NCH_2R'} (RCH_2)_2N\dot{C}HR' + (RCH_2)_2N\overset{O-OH}{\overset{|}{C}}HR'$$

Scheme 4. Oxygen scavenging reaction.

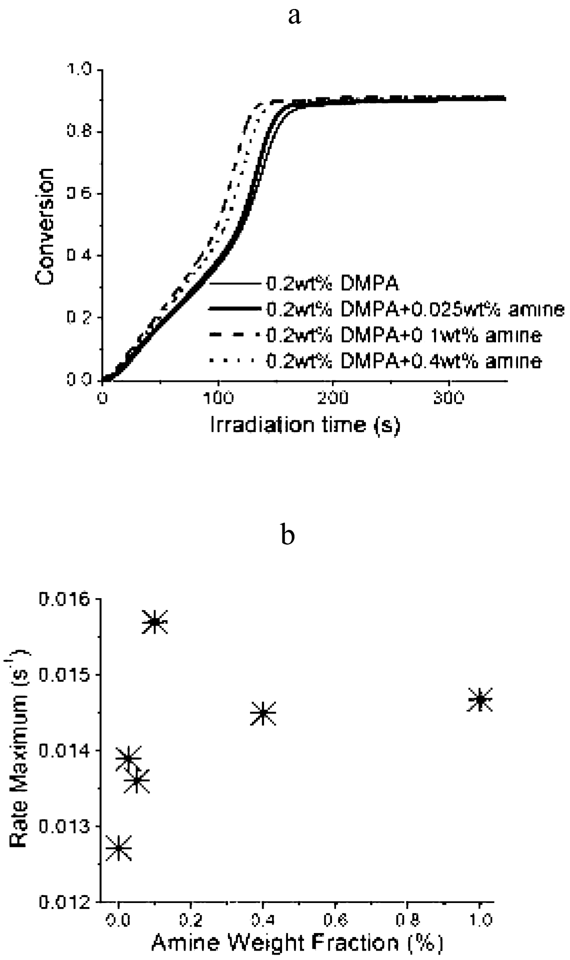


Fig. 9. Effects of amine additives on POEMA homopolymerizations: (a) conversion profiles; (b) rate maximum vs. amine weight fraction (Light intensity: 5 mW/cm^2).

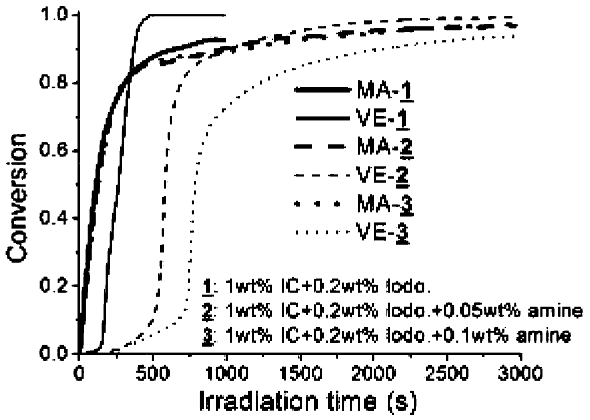


Fig. 11. Effects of amine additives on the conversion profiles for POEMA/TEGMVE hybrid polymerizations (Light intensity: 5 mW/cm^2).

4.2. Effects of physical factor

Fig. 12 represents conversion profiles for both monomers corresponding to two light intensities. The POEMA polymerization with the same coinitiator composition at higher irradiation intensity (I) shows a slight rate enhancement in the low conversion region compared with that obtained at low intensity since the rate of polymerization (R_p) is proportional to $I^{0.5}$ [41]. However, a significantly longer irradiation time is required for POEMA to reach complete conversion with the higher UV light intensity. This occurs at the higher irradiation intensity since the vinyl ether cationic polymerization becomes less sequential due to a dramatically enhanced reaction rate and a shortened induction period since for cationic polymerizations, $R_p \propto I$ [41]. A similar TEGMVE final conversion is observed compared with that obtained at the lower intensity. Fig. 12 also indicates another of the potential interactions encountered in this hybrid polymerization system. It can be seen that, at low irradiation intensity, TEGMVE acts as a reactive diluent or plasticizer at the initial stage of polymerization. This leads to a higher cure rate of POEMA between 75–100% conversion than that at high intensity due to the very low level of TEGMVE conversion achieved during the interval of methacrylate polymerization. While not included in the current study, photopolymerization temperature, which includes both the cure temperature as well as the reaction exotherm, would also be expected to induce different

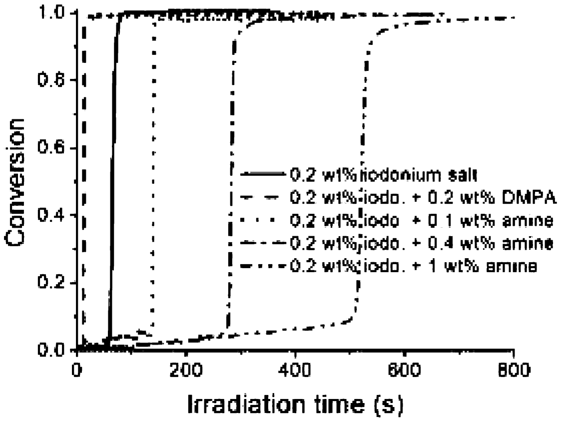


Fig. 10. Effects of amine additives on the conversion profiles for TEGMVE homopolymerizations (Light intensity: 5 mW/cm^2).

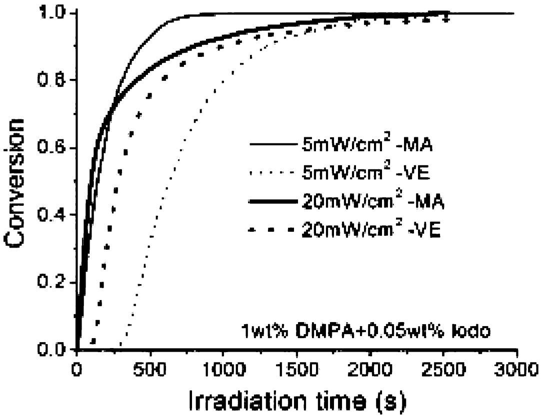


Fig. 12. Effect of light intensity on the conversion profiles for POEMA/TEGMVE hybrid polymerizations.

kinetic effects on radical and cationic polymerization processes and may offer another means to control the individual polymerization reactions.

5. Conclusions

Real-time FT-NIR spectroscopy was successfully used to monitor the individual monomer photopolymerization kinetics within the hybrid methacrylate/vinyl ether system. There are several benefits associated with the use of NIR for conversion analysis in hybrid system. NIR uses a direct transmission technique that gives bulk polymer conversion data on sample geometry compatible with other characterizations. The partially resolved vinyl-based absorbance bands in the NIR spectra allow the direct monitoring of individual monomer kinetics precisely in the hybrid photopolymerization of the methacrylate and vinyl ether monomers.

UV-initiated photopolymerization processing conditions have been explored such that comonomers that polymerize by different mechanisms can be simultaneously or sequentially polymerized in an effort that ultimately aims to controllably alter polymer structure and properties. Initiation formulations, additives and light intensity are all important factors, which could be used to provide preferential direction of polymer formation based on individual monomer photopolymerization kinetics and overall conversion. The use of single source UV-light irradiation afforded simple processing procedure, validating the potential of one-step, one-pot process for initiating multiple-stage polymerizations. Future work will describe the extension of this novel technique to semi-IPN or full IPN systems formed from difunctional monomer combinations.

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