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Synthesis and photopolymerization kinetics of linear alicyclic urethane acrylate macromonomer in presence of reactive diluents

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Abstract This study deals with the photopolymerization of a macromonomer in the presence of reactive diluents using Photo Differential Scanning Calorimetry or Photo DSC. The kinetic profiles of these systems showed that the rate of photopolymerization rapidly increases at very early stages of the reaction. The rate of reaction was further found to increase with the addition of crosslinking agents. The addition of trifunctional crosslinking agent to the macromonomeric formulation resulted in a higher polymerization rate and conversion than that of a difunctional crosslinking agent. From the heat flow profiles, the kinetic parameters such as induction time, time to attain peak maximum, rate of maximum polymerization, and final conversion were noted for all the formulations. The initiation of photopolymerization was found to depend on the functionality while the in situ viscosity controlled the time scale for reaction diffusion which resulted in varying levels of conversions. Other parameters such as effect of temperature and concentration of photoinitiator on photocuring kinetics are also discussed.

Introduction

The effects of reactive diluents on the photopolymerization of macromonomers are well documented [1]. Acrylate-based macromonomers mostly include polyester [2], polyurethane [3, 4], and epoxy acrylates [5]. Photo DSC [6, 7] is one of the methods to study the radical [8, 9] and cationic photopolymerizations [10, 11]. The photopolymerization kinetics has been studied extensively for many such systems [12, 13]. The number of photopolymerizable ends per mole of the photopolymerizable macromonomer is an important factor that controls the rate of photopolymerization. The addition of crosslinking agents also influences the kinetics of the system. It is known that photopolymerization reactions have particular behaviors, such as autoacceleration [14, 15], incomplete functional group conversion [16], vitrification [17], unequal functional group reactivity [18], and temporary free volume excess [19]. UV cured samples in most cases have free radicals trapped within the material [20], and the radical trapping is more pronounced at lower isothermal conditions [21]. Studies have shown that the reaction is highly accelerated by moderate heating [22]. Substantial free radical concentration on cured methacrylates has been reported [23]. The photopolymerization kinetics in a photo DSC measurement can depend on many factors such as concentration of photo initiator, type of monomers used, reaction temperature, nature of purge gas, type of crosslinking agent, intensity, and wavelength of irradiation. Further during photopolymerization, diffusion processes such as translational, segmental, and reaction diffusions gets involved [21] at different times depending on the physical factors mentioned above. The temporary free volume increase during the initial stages of photopolymerization will increase the radical diffusivity with an initial increase in rate of conversion [24]. However, the polymerization rate will get reduced with time due to limitation in radical diffusion caused by an increase in viscosity of the system with conversion.

This article deals with the evaluation of kinetic parameters of a rigid and linear alicyclic-based urethane acrylate macromonomer (mentioned as macromonomer) in the

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presence of reactive diluents using photo DSC. The addition of monofunctional reactive diluent resulted in providing an optimum viscosity for photopolymerization. The addition of low concentration of di and triacrylate crosslinkers on the macromonomer containing monofunctional reactive diluent showed an enhancement in rate and conversion profiles. The functionality as well as in situ viscosity has effect on these profiles at different stages of the cure reaction. It was observed that the rate of initiation was found to depend on the functionality while the final cure rate and conversion were controlled by the viscosity-dependant reaction diffusion.

Experimental

Materials

Isophorone diisocyanate (IPDI, from Fluka), 4,4′-cyclohexane dimethanol (CHDM, from Fluka), 2-hydroxy ethyl acrylate (HEA, from Aldrich), 1,4-diazabicyclo [2.2.2.] octane (DABCO, from Aldrich), hydroquinone monomethyl ether (HQME, from Fluka), 1-hydroxycyclohexyl phenyl ketone (IRGACURE 184*, from Aldrich), *bis*(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (IRGACURE 819*, from Aldrich), neopentyl glycol propoxylate diacrylate (NPGPDA, from Aldrich), and trimethylol propane triacrylate (TMPTA, from Aldrich) were used as received. * Trademark of Ciba Specialty Chemicals, Switzerland.

Instruments

The NMR spectra were recorded using Bruker 500MHz NMR spectrophotometer. The IR spectra were recorded using a Perkin Elmer Spectrum GX, Infrared spectrophotometer. The molecular weight of the macromonomer was determined using Knauer K-7000 vapor pressure osmometer (VPO) using chloroform as solvent. The Brookfield viscosity of the crosslinkers as well as the macromonomeric formulations were measured using a variable speed (5–1000 rpm) cone and plate viscometer (Brookfield CAP 2000+ viscometer) with spindle # 4 at 80 rpm. DSC Q 100 differential scanning calorimeter connected to Q Series PCA (TA instruments, USA) was used for the online monitoring of the photopolymerization processes. The thermogravimetric analyses were carried out using a TGA 5000 thermogravimetric analyzer provided with an auto sampler (TA Instruments, USA). The glass transition temperatures (T_g) of the photocured polymers were measured in a DSC Q 10 differential scanning calorimeter (TA Instruments, USA).

Procedure for synthesis

Synthesis of prepolymer

A 100 mL three-necked round bottomed flask was used. The flask was provided with a half moon stirrer through a stuffing box and connected to an overhead stirrer through the central neck. It was initially dried and flushed with nitrogen through one side neck. 14.67 g (65.6 mmol) of isophorone diisocyanate was added to it and stirred at 40 °C at 80 rpm. 8.6526 g (60 mmol) of cyclohexane-1,4-dimethanol was solvated in 30 mL of chloroform and added to the flask using a dropping funnel at a flow rate of 1 mL/min so that the ratio of NCO:OH was 1.1:1. During addition, the system was homogenized by increasing the stirring speed to 150 rpm. The temperature was further increased to 70 °C and stirred under nitrogen purge at 100 rpm for 18 h to obtain the prepolymer. The residual isocyanate content was noted using ASTM D 2572 to be 2.49%.

^{13}C NMR (CDCl$_3$): 27.57 (CH$_3$(gem) isophorone ring), 28.75 (ring CH$_2$, cyclohexane ring), 34.99 ($\underline{C}$H, cyclohexane ring), 37.38 ($\underline{C}$H, isophorone ring), 41.84, 46.51(=CH$_2$, isophorone ring), 56.92 ($\underline{C}$H$_2$–NCO), 69.59 (NH–CO–O–$\underline{C}$H$_2$, (exo) cyclohexane ring), 121.67 (NCO), 157.17 (CH$_2$–NH–$\underline{C}$O–O–CH$_2$–), 155.97 (CH$_2$–NH–$\underline{C}$O–O) ppm.

IR: 1699 (C=O, urethane), 2268 (NCO), 3333 and 1520 (N–H, urethane), 1134 (C–O), 3008, 2925, 2857 (C–H) cm^{-1}.

Synthesis of macromonomer

To 22 g of synthesized prepolymer was added 1.3949 g (12 mmol) of 2-hydroxy ethyl acrylate followed by addition of 0.1092 g (0.9735 mmol) of DABCO as catalyst. 200 ppm of HQME was added as stabilizer, and the temperature was raised to 60 °C. The reaction was continued at 100 rpm under nitrogen purge for 20 h until all the isocyanate groups were completely consumed in IR spectroscopy. 40 mL of 1:1 mixture of chloroform and acetone was added to the contents of the flask and mixed well. 10 mL of petroleum ether was added to it and poured in 250 mL water taken in a 500 mL beaker. The precipitated macromonomer was further washed three times with water and initially dried in vacuum at room temperature for 12 h and further dried in vacuum oven for a period of 10 h at 60 °C.

^{13}C NMR (CDCl$_3$): 27.56 (CH$_3$(gem) isophorone ring), 28.75 (ring CH$_2$, cyclohexane ring), 34.99 ($\underline{C}$H, cyclohexane ring), 37.37 ($\underline{C}$H, isophorone ring), 41.86, 46.50 (=CH$_2$, isophorone ring), 69.52 (NH–CO–O–$\underline{C}$H$_2$, (exo) cyclohexane ring), 127.95 (CH$_2$=$\underline{C}$H–CO–O), 131.31

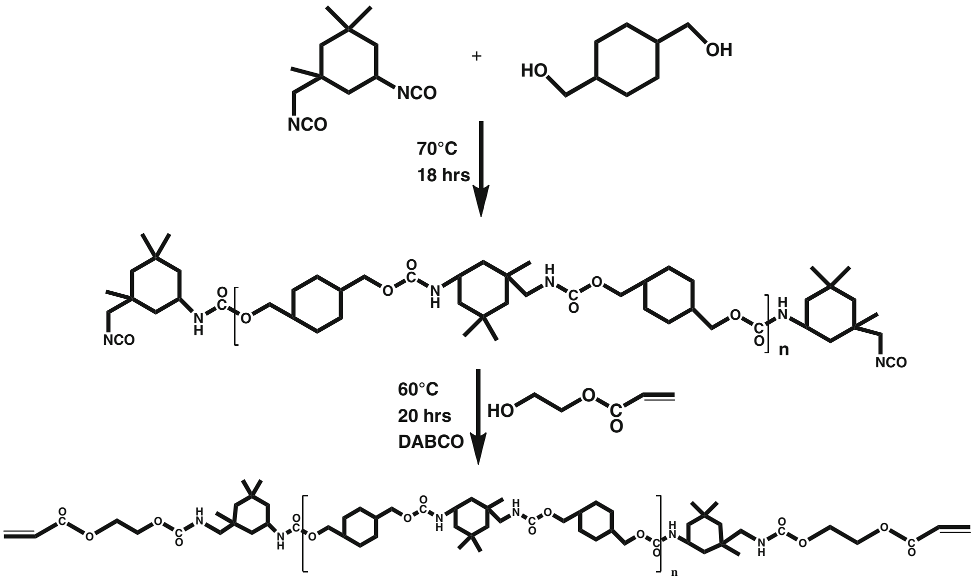

Fig. 1 Synthesis pathway of the macromonomer

($\underline{C}H_2$=CH–CO–O) 157.17 (CH_2–NH–$\underline{C}$O–O–CH_2–), 155.97 (CH_2–NH–$\underline{C}$O–O), 165.90 (CH_2=CH–$\underline{C}$O–O) ppm.

IR: 1698 (C=O, urethane), 3332 and 1524 (N–H, urethane), 1637 and 809 (C=C, acrylate), 1134 and 1196 (C–O), 3000, 2924, 2853(C–H) cm^{-1}.

The synthesis pathway of the macromonomer is given in Fig. 1

Formulations

The photoinitiators of choice were IRGACURE 184 (α-hydroxy alkylphenone type) and IRGACURE 819 (acylphosphine oxide type). The mixing was done in 5-ml glass vials. The M_n of the macromonomer was found to be 5929 g/mol by VPO. 1 g (0.1687 mmol) of macromonomer and 10 wt% (0.8612 mmol) of HEA were added to the vial followed by solvation in minimum amount of chloroform. 0.5 and 2 wt% of the above photoinitiators with respect to the weight of macromonomer and reactive diluent were added to obtain four photopolymerizable formulations. Two more sets of formulations with photoinitiators were made in similar way by adding 5 wt% (0.1524 mmol) of neopentyl glycol propoxylate diacrylate and (0.1687 mmol) trimethylol propane triacrylate as difunctional and trifunctional crosslinkers, respectively, with respect to the weight of the macromonomer to the macromonomeric formulation containing 10% HEA. Each of the twelve formulations thus obtained were homogenized again for 5 min in a vibrating mill. Vacuum was applied for a period of 6 h at 50 °C to remove traces of chloroform from the formulations, as traces of chloroform can lead to chain transfer during the photopolymerization process. The formulations were stored overnight in dark.

Photopolymerization studies

DSC Q 100 differential scanning calorimeter connected to Q Series PCA was used for the online monitoring of the photopolymerization process. The intensity of irradiation on either side of the dual light guide system was balanced and adjusted to the required value with blank pans on the DSC platform before the irradiation of sample. The formulations were again homogenized for a period of 2 min in a vibrating mill. Accurately weighed (about 10 mg) sample was placed in the sample pan and kept in the sample platform along with the blank reference pan. The pans were closed by a quartz window to prevent any monomer loss during irradiation. The nitrogen purge in the machine was kept constant at 50 mL/min so as to prevent any effect of oxygen on the system. The sample was preconditioned at the isothermal condition under nitrogen purge for a period of 1 min before irradiation. It was followed by irradiation for a period of 5 min under a constant photo flux from the machine. Light from a 100 W mercury short arc lamp (EXFO-Canada) was passed through the dual light guide system during analysis. End filters were provided in the dual light guide system to reduce the intensity coming from the end of the light guide to 1% of its initial value. The irradiation intensity was kept constant at 4.6 mW/cm^2 throughout the analysis. The isothermal photocalorimetry was studied at 30 and 50 °C using a polychromatic filter (250–450 nm). The major bands for the emission spectrum within the irradiation range appear around 313, 334, 365

(I-line), 404(H-line) and 435 (G-line) nm with a maximum intensity around 365 nm.

Post photopolymerization studies

Measurement of % weight loss

The percentage weight loss during the thermogravimetric analysis was carried out using a TGA 5000 instrument under nitrogen purge at a heating rate of 20 °C/min. The analysis was done from 50 to 650 °C.

Measurement of glass transition temperature

The glass transition temperatures of the photopolymerized systems were studied using a DSC Q 10 instrument on a heat cool heat cycle at a heating rate of 10 °C/min under a nitrogen purge of 50 mL/min from 40 to 250 °C. An equilibration time of 2 min was provided before analysis.

Determination of gel content

The gel contents of the photopolymerized systems were calculated by swelling studies [25] 16 h after photopolymerization. Accurately weighed (about 10 mg) material was extracted with chloroform in a Soxhlet extractor for a period of 24 h and dried in vacuum for 6 h. The procedure was repeated until a constant weight was obtained.

$$\text{Percentage gel content} = W/W_o \times 100$$

where W is the weight of the resin after extraction and W_0 is the weight of the original resin.

Results and discussion

Viscosity studies

Viscosities of the crosslinkers and the macromonomeric formulations without photo initiators were noted using a Brookfield viscometer. The results are given in Table 1.

The above values show that the considered diacrylate is more viscous than triacrylate due to the presence of glycol moiety. Even though the formulation without di or triacrylate as crosslinker has a lower viscosity, a further addition of diacrylate in small amount has increased the viscosity much higher than that for the triacrylate formulation. The above values were noted to understand the initial viscosity of the formulation before photopolymerization.

Photopolymerization studies

The total theoretical heat released in joules per gram of a monomeric multifunctional acrylate on complete polymerization is given by the expression [24, 26, 27]

$$\Delta H_{\text{theor}} = N \times \Delta H_{\text{A}}/\text{MW} = 86190 \times N/\text{MW}$$

where N is the functionality of the acrylate and MW is its molecular weight. The value of H_{A} is calculated based on the observation that 86.19 kJ (20.6 kcal) of heat is released per mole of acrylate double bond undergoing complete polymerization. The total theoretical heat flow for the acrylate formulations involving mixture of two acrylates can thus be calculated as [28]

$$\Delta H_{\text{theor}} = f_1 \times N_1 \times \Delta H_{\text{A}}/\text{MW}_1 + f_2 \times N_2 \times \Delta H_{\text{A}}/\text{MW}_2$$

where f_1 and f_2 are the mass fractions, N_1 and N_2 are the average functionalities, and MW_1 and MW_2 are the average molecular weights of each acrylates in the composition. The rate of photopolymerization (R_{p}) can be calculated from the Photo DSC heat flow measurements. If $\text{d}H/\text{d}t$ represents the heat flow per unit time, then the rate of photopolymerization is given by [29, 30],

$$R_{\text{p}} = (\text{d}H/\text{d}t)/\Delta H_{\text{theor}}$$

The percentage conversion (%C) is thus calculated by integration of the above expression [29]:

$$\%C = (\Delta H_t/\Delta H_{\text{theor}}) \times 100$$

where ΔH_t denotes the heat flow up to a particular time (t) from the starting of the photopolymerization process.

Table 1 Brookfield viscosity with spindle#4 at 80 rpm and 30 °C

Type of crosslinker/formulation	Brookfield viscosity[a] (cP)
NPGPDA	450 ± 9
TMPTA	375 ± 2
Diacrylate terminated macromonomer + 10 wt% HEA	4387 ± 36
Diacrylate terminated macromonomer + 10 wt% HEA + 5 wt% NPGPDA	11630 ± 55
Diacrylate terminated macromonomer + 10 wt% HEA + 5 wt% TMPTA	5481 ± 17

Shear rate 266.4/s

[a] Average of three readings

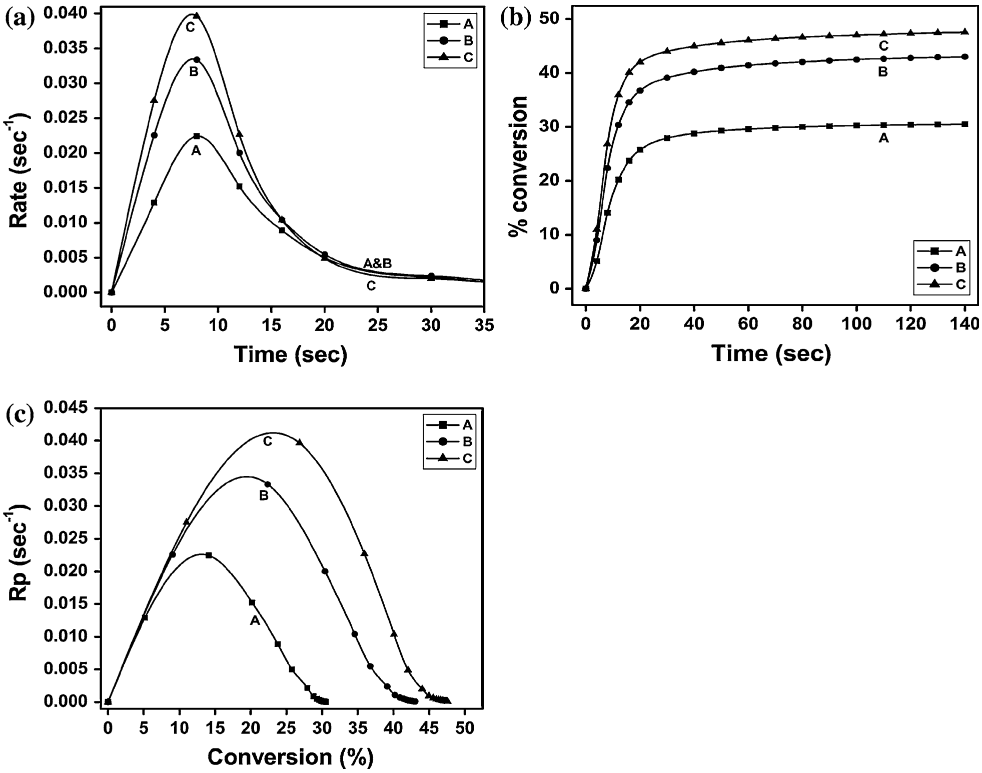

Fig. 2 Time dependent polymerization rates and corresponding conversions with 0.5 wt% of IRG 184 at 50 °C for the macromonomer containing **a** 10% HEA, macromonomeric formulation containing **b** 5 wt% of NPGPDA, and **c** 5 wt% of TMPTA as crosslinkers

The rate and conversion profiles of the in situ photopolymerization process are given in Fig. 2a–c.

Influence of viscosity

Initial system viscosity affects the extent of final conversion [31]. For an acrylate with similar backbone, the viscosity generally increases with increase in acrylate functionality. It has been observed that an increase in functionality can decrease the final conversion during a photocuring process, if all the analysis parameters are kept constant [26]. Here, we made a choice so that the triacrylate has a lower viscosity than the diacrylate. In addition, these acrylates at low concentration were found to impart similar effect on the formulation viscosity (Table 1). On comparison of the thermal signatures in the case of macromonomeric formulations given above in Figs. 2a–c, we can infer that the rate of photopolymerization is found to increase with an increase in functionality of crosslinkers. At higher temperature, unlike low molecular mass multiacrylates, the initial viscosity of the triacrylate formulation being lower than that of diacrylate resulted in a higher final conversion than that of the diacrylate due to low in situ viscosity during initial stages of the reaction.

The kinetic parameters calculated from the heat flow profiles are given in Fig. 3a–d, while the heat of reactions from the photo DSC are given in Fig. 3e. In the case of macromonomeric formulations containing 10 wt% HEA, the $R_{p\ \max}$ was comparatively lower than that of formulations containing di and triacrylate as crosslinkers. Even though these formulations without di or triacrylate showed a longer timescale for reaction diffusion with delayed vitrification, the final ultimate conversion was found to be less due to reduced crosslinking. In the case of formulations containing di and triacrylates, the $R_{p\ \max}$ and final conversions were much higher. It can be expected that the diacrylate system which has the highest initial viscosity must have a higher initial rate of polymerization due to a much faster autoacceleration [32]. This can result in a faster viscosity build up at the expense of the temporary free volume and the polymerization gets immediately controlled by the reaction diffusion resulting in a low value of $R_{p\ \max}$ than the triacrylate formulation.

In the case of the macromonomeric formulations containing triacrylate, the initial system viscosities are lower, and segmental mobility is enhanced. As a result after autoacceleration, the $R_{p\ \max}$ is comparatively higher than the diacrylate formulations due to a slight delay in the onset of reaction diffusion. From Table 2, we can find that the ultimate T_g of the photopolymerized system containing triacrylate was higher that that of the diacrylate, which in turn is higher than that of the macromonomeric system containing 10 wt% HEA. Since the isothermal cure temperatures are much lower than the ultimate T_g, we can expect that the triacrylate vitrifies faster than diacrylate formulation and can be observed from the rate curve in

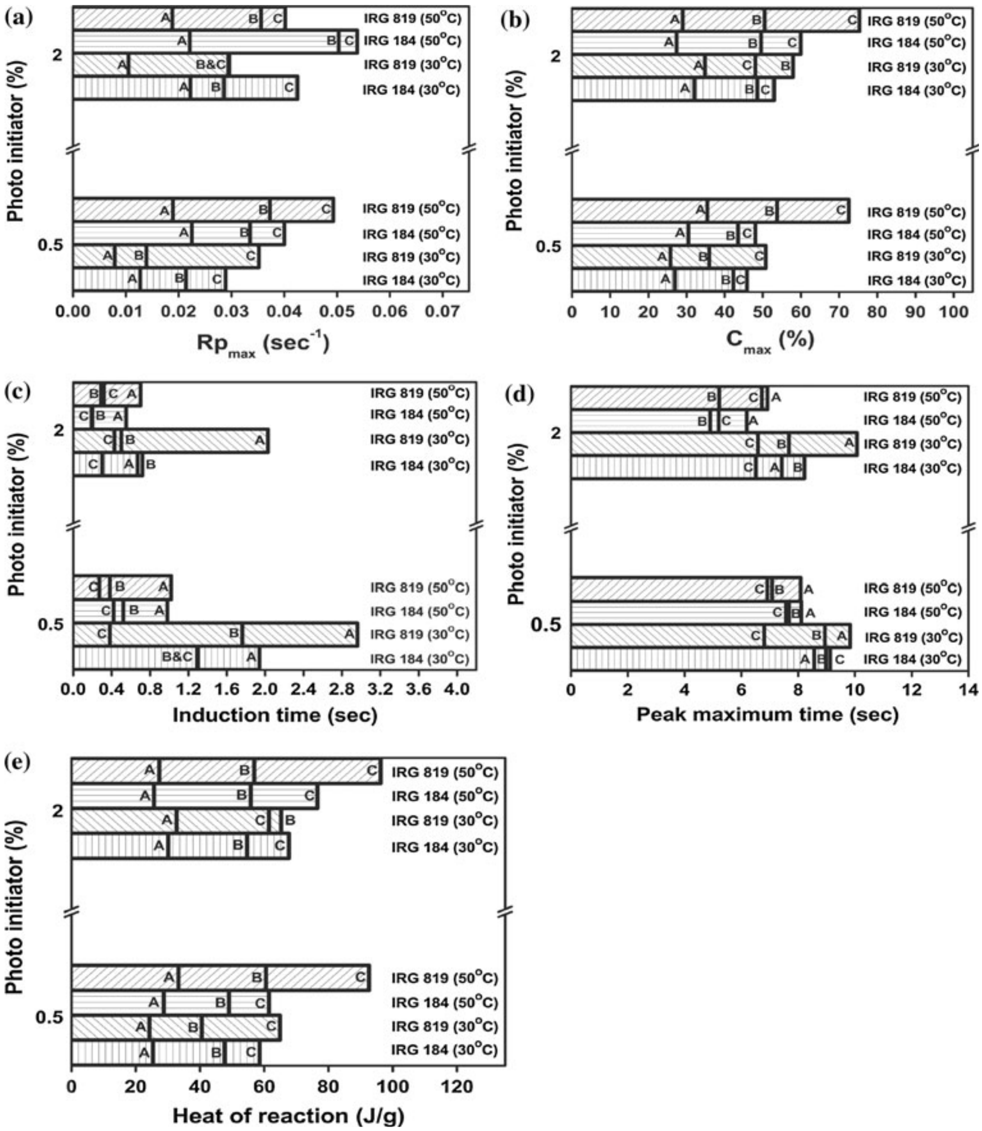

Fig. 3 Time dependent polymerization rates (**a**), corresponding conversions (**b**), induction times (**c**), peak maximum times (**d**), and the heat of reactions (**e**) with 0.5 and 2 wt% of two photo initiators at 30 and 50 °C for the macromonomer containing (*A*) 10% HEA, macromonomeric formulation containing (*B*) 5 wt% of NPGPDA, and (*C*) 5 wt% of TMPTA as crosslinkers

Table 2 Post photopolymerization analysis

Composition[a]	90% weight loss[b] (°C)	T_g^b (°C)	Gel content[b] (%)
Macromonomer with 10% HEA	399 ± 2.1	113 ± 1.2	90 ± 2.6
Macromonomer with 10% HEA and 5% of NPGPDA	432 ± 3.2	117 ± 0.7	93 ± 1.9
Macromonomer with 10% HEA and 5% of TMPTA	449 ± 2.4	125 ± 1.1	93 ± 2.5

[a] With 0.5% IRGACURE 184 as photo initiator cured at 50 °C

[b] Errors based on duplicate analysis

Fig. 2a. Hence a higher final conversion is expected for the diacrylate formulation due to a longer timescale of reaction diffusion coupled with a slight delay in vitrification. However, the final conversions of triacrylate formulations were observed to be slightly higher than that of diacrylates, possibly due to a comparatively lesser in situ viscosity near $R_{p\ max}$.

The induction time (time taken for 1% conversion) is generally found to occur before autoacceleration. During induction time, the in situ viscosity build up is negligible. From the bar charts given in Fig. 3c, it can be understood that the induction time in most cases is the lowest for the triacrylate system followed by diacrylate systems. The macromonomeric formulation containing 10% HEA was found to show the highest induction time. This shows a generally faster initiation rate for the formulation with increase in density of functionality. The effect was not similarly observed in Fig. 3d for the peak maximum time due to the influence of reaction diffusion which occurs soon after autoacceleration resulting in variations. In other words, the onset of reaction diffusion occurs soon after autoacceleration, before the system attains $R_{\mathrm{p\ max}}$.

Influence of photoinitiator and temperature

A comparative higher conversion for formulations containing IRGACURE 819 as compared to IRGACURE 184 was observed. This can be attributed to the more proximity of $\lambda_{\max}$ value of IRGACURE 819 for n–π* transition falling nearer to the major emission line in mercury spectrum at 365 nm [33]. In all the studied formulations, the radical trapping at low temperature has resulted in lower final conversions with 0.5 wt% concentration of photoinitiator. This typical behavior is shown when the amount of radicals produced is within the threshold limit. If the radical concentration is above this optimum level which varies for different systems as per the physical parameters of the formulations, then an increase in temperature can result in either an increase or decrease in final conversions, as the quantum yield of photoinitiation and propagation kinetics involved depends on the competition between the reaction of primary radicals or propagating chains with double bonds as well as in between two primary radicals [29]. When the concentration of photoinitiator was increased to 2 wt%, the final conversion got reduced with increase in temperature for the macromonomeric formulation containing 10% HEA and for the macromonomeric formulation containing diacrylate as crosslinker. The higher concentration of photo initiator results in a larger number of propagating chains with enhanced mobility at high temperature and the system gets vitrified much faster resulting in reduced final conversions. This reduction effect was not observed in the case of triacrylate formulations as these formulations showed a comparatively long segmental mobility than in diacrylate formulations before the reaction diffusion sets in, while for the diacrylate formulations, the propagation kinetics is mostly governed by reaction diffusion from the initial stages of polymerization.

The above effect can also be described based on rigidity of chains. In general, for soft segmented systems such as polyethyleneoxy linkages, with other analysis parameters remaining constant, an increase in temperature over a wide range can result in enhanced final conversions due to chain flexibility and reduced T_g [9], while a decrease in conversion can also be observed in partially rigid or rigid systems with moderate increase in temperature [26]. Our system being rigid showed variations in conversions mainly due to variations in in situ viscosity after autoacceleration and the above mentioned factors which control the timescale for the overall diffusion processes.

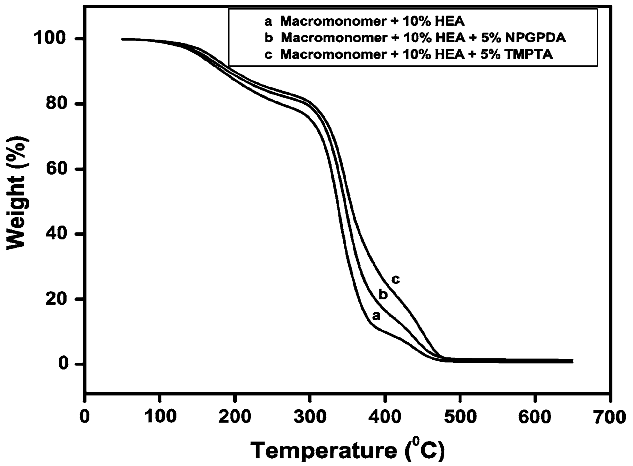

Fig. 4 Thermogravimetric profile of samples photocured at 50 °C using 0.5% of IRGACURE 184

Post polymerization studies

Post polymerization DSC, FTIR, and TGA analysis

The DSC profiles showed an increase in T_g of the composition with an increase in the functionality of the crosslinking agent. The percentage gel content was found to be much closer in all the cases. Even though the macromonomer containing 10% HEA is not much crosslinked as other two systems as per photo DSC heat flow profiles, the percentage gel content for this system after 16 h in dark was also closer to crosslinked systems. Once initiated, photopolymerization can occur in dark at a low rate, which explains this effect [34]. The results are summarized in Table 2.

From post polymerized FTIR analysis, the acrylate peak corresponding to the 1634 cm^{-1} in the composition before irradiation was not clearly distinguishable, and hence the bending peak at 809 cm^{-1} was considered for cure studies. The peak at 809 cm^{-1} vanished from the spectrum, which confirmed the photopolymerization of the end functionalized acrylate moieties. The percentage weight loss in TGA shows that the higher the extent of crosslinking, lesser will be the decomposition profile. Hence the triacrylate has a highest extent of crosslinking and hence is found to have the lowest decomposition rate than other systems (Fig. 4).

Conclusion

The rate of photopolymerization of the macromonomer containing reactive diluent was found to be lower than that of the same system containing crosslinkers. The formulations also showed a comparative increase in final conversions and polymerization rate on addition of crosslinkers. The formulations containing triacrylate crosslinker showed the maximum conversion. Other factors such as radical trapping at lower temperature and optimum concentration of photoinitiators also had influence on the conversion profiles. The rate of initiation was found to depend on the functionality of the formulation, while the autodeceleration step as well as vitrification was found to depend on in situ viscosity. The rate and conversion profile shows that the rate of build up of in situ system viscosity controls the timescale for reaction diffusion which account for the overall effect. The post photopolymerization studies shows a higher extend of crosslinking for the triacrylate system.

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