JOURNAL OF MATERIALS SCIENCE **36** (2001) 3599 – 3605

Photopolymerization behavior of di(meth)acrylate oligomers

Q. YU
Department of Chemical Engineering, McMaster University,
Hamilton, Ontario, Canada L8S 4L7

S. NAUMAN
Rehabilitation Engineering Department, Bloorview MacMillan Centre,
Toronto, Canada, M4G 1R8

J. P. SANTERRE
Faculty of Dentistry, University of Toronto, Totonto, Canada, M5G 1G6

S. ZHU*
Department of Chemical Engineering, McMaster University, Hamilton,
Ontario, Canada L8S 4L7
E-mail: zhuship@mcmaster.ca

Photo-initiated polymerizations of two series of di(meth)acrylate oligomers, one bisphenol-A based and the other ethylene glycol based, with a camphorquinone/tertiary amine radical photo-initiator system were studied using differential scanning calorimetry. Bisphenol-A based oligomers polymerized much faster than ethylene glycol based oligomers because the higher viscosity of E-bis-A oligomers induced an autoacceleration upon exposure to ultraviolet (UV) radiation; however, higher vinyl conversions were observed with ethylene glycol oligomers due to their greater segmental mobility and elastomeric character of the cured networks. The two series also showed very different temperature dependence for vinyl group conversion. The polymerization rate of E-bis-A DMA oligomers increased when the number of oxyethyl units increased from four to six, but the rate decreased when the spacer length further increased. The exponential factors of the rate dependence on the CQ concentration for all the oligomers were smaller than 0.5. Below 70°C, the maximum rate of polymerization increased with temperature, and yielded apparent activation energies between 10.3–11.6 kJ/mol. At temperatures ≥80°C, the reduced viscosity and improved segmental mobility suppressed autoacceleration, causing the maximum rate to decrease with an increase of temperature.

---

1. Introduction

Photo-initiated polymerization of multifunctional vinyl monomers leads to highly crosslinked polymer networks. High crosslink densities increase dimensional stability, mechanical strength, thermal resistance, and decrease solvent penetration for the networks. Because of the excellent physical properties and rapid reaction rates, the photopolymerization of multifunctional vinyl monomers has found a wide range of applications including dental restorative materials, microelectronic devices, laser video discs, and optical fiber coatings [1–4].

The photopolymerization of di(meth)acrylate monomers with a camphorquinone/amine initiator system proceeds via a free-radical chain growth mechanism. Typical polymerization rate versus reaction time curve shows a sharp increase in the rate from the beginning of the reaction, caused by a dramatic reduction in radical termination due to chain entanglements and crosslinking. A rapid decrease follows as a result of diffusion-controlled propagation as well as monomer depletion. The reaction virtually stops at a certain level of the conversion as the mobility of reactive species is severely reduced by vitrification. The polymerization kinetics and vinyl group conversion depends mainly on the curing temperature and the monomer type, as well as the camphorquinone/amine system [5–9].

Over the years, a range of (meth)acrylate end-capped oligomers have been developed in order to meet specific requirements in different applications. These oligomers differ by the functionalities, the type of functional groups, and the chemical structures in the spacer, which

---

[*] Author to whom all correspondence should be addressed.

have strong influence on the polymerization rate, vinyl group conversion, and network structure. Because of the technological importance of the materials' physical properties, it then becomes important to understand the photopolymerization behavior of these oligomers. In this paper, the UV initiated photopolymerizations of two series of di(meth)acrylate oligomers, one bisphenol A based and the other ethylene glycol based, were investigated using differential scanning calorimetry (DSC). Their polymerization behavior was compared, based on the reaction rate and vinyl group conversion. The effects of curing temperature and photo-initiator concentration on the polymerization were also studied in order to provide further insight into the mechanisms and kinetics of these photopolymerization systems.

2. Experimental

2.1. Materials

The chemical structures for the multifunctional oligomers are shown in Fig. 1. These oligomers can be classified into two categories: bisphenol A based oligomers and ethylene(or propylene) glycol based oligomers. All oligomers were supplied by Sartomer Inc., USA, except for E-bis-A DMA-4 and PPGDMA, which were supplied by Aldrich, Oakville, ON, Canada. The average numbers of ethylene (propylene) oxide units between divinyl groups in the oligomers were determined by ^{1}H n.m.r analysis, from which the molecular weights and the vinyl group concentrations could be calculated. The glass transition temperatures for the cured polymer networks were measured by DSC at a heating rate of 5 °C/min. It should be noted that, due to the broadened transition region, the T_g values for some cured networks with higher crosslinking densities were not readily discerned in the DSC thermogram, and they were then measured using a dynamic mechanical method at a frequency of 1 Hz and a heating rate of 5 °C/min. These parameters are presented in Table I.

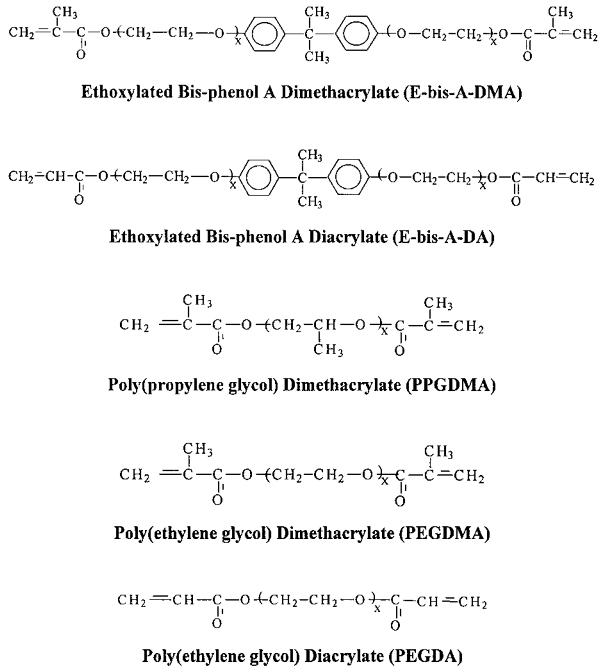


Figure 1 Chemical structures of the oligomers studied.

The photopolymerizations were initiated with camphorquinone (CQ, initiator, Aldrich, Oakville, ON, Canada) and 2-(dimethylamino)ethyl methacrylate (DMAEM, co-initiator, Aldrich, Oakville, ON, Canada). All chemicals were used as received.

2.2. Characterization of the polymerization

CQ and DMAEM were dissolved in the oligomers in darkness and at room temperature for five hours. For a standard formulation, 0.02 mol CQ and 0.04 mol DMAEM per kg resin were used. To assess the effect of initiator concentration, CQ was varied from 0.005 to 0.04 mol and the ratio of DMAEM to CQ was fixed at 2 (mol/eq).

The photopolymerizations were carried out in a differential scanning calorimeter capped with a UV radiation unit (DSC 2910, TA Instruments). The light intensity was measured at the sample level by a radiometer and it was 710 W/m^2. Approximately 10 mg of sample mixture was placed as a thin layer in an open aluminum pan having a diameter of 4.5 mm. In order to minimize the effect of dissolved oxygen on the polymerization the DSC cell was purged with nitrogen gas for 10 min prior to exposing the sample pan to radiation.

Heat flow versus time (DSC thermogram) was recorded in an isothermal mode under a flow of nitrogen (50 ml/min). The heat liberated in the polymerization is directly proportional to the number of vinyl groups reacted within the system. By integrating the area under the exothermic peak in the DSC thermogram, vinyl group conversion (C) or the extent of reaction could be determined according to:

TABLE I Parameters of the oligomers and their polymers used in this work

Oligomer code	Average number of oxyethyl (or oxypropyl) units	Molecular weight, M_n	Viscosity (Pa.s. 25°C)	T_g of the cured network (°C)
E-bis-A DMA-1	4.2	550	0.55	110
E-bis-A DMA-2	6.0	628	0.445	70
E-bis-A DMA-3	10.4	820	0.418	5
E-bis-A DMA-4	30	1680	0.610	−40
E-bis-A DA	4	474	1.08	60
PPGDMA	7	560	0.065	−22
PEGDMA	9.3	563	0.085	−25
PEGDA	9.9	560	0.075	3

$C = \Delta H_t / \Delta H_0^{\text{theor}}$, where ΔH_t is the reaction heat evolved up to time t, and $\Delta H_0^{\text{theor}}$ is the theoretical heat for complete conversion. For the methacrylate double bond, $\Delta H_0^{\text{theor}} = 54.85$ kJ/mol, and for the acrylate double bond, $\Delta H_0^{\text{theor}} = 86.25$ kJ/mol [10]. As well, the polymerization rate (R_p) was directly related to the heat flow (dH/dt): $R_p = dC/dt = (dH/dt)/\Delta H_0^{\text{theor}}$.

After photopolymerization, the cured sample was immediately placed into acetone for 72 hours in order to extract unreacted monomers and linear polymers. The insoluble portion was defined as the gel fraction and was reported as a percent value relative to the total amount of resin incorporated in the original sample.

3. Results and discussion

3.1. Polymerization behavior

Fig. 2 shows the polymerization rate profiles for five different oligomers obtained from the isothermal photopolymerization experiments conducted at 30 °C in the DSC. The maximum rates for E-bis-A DA and PEGDA were double as those for their counterparts, E-bis-A DMA-1 and PEGDMA. This rate difference is attributed to the increased reactivity of the acrylate group. These observations are in agreement with the literature that the propagation and termination kinetic constants, k_p and k_t, of acrylate are many times higher than that of methacrylate [10].

It is observed in Fig. 2 that the bisphenol A based oligomers polymerized much faster than the ethylene glycol based oligomers. The major difference between the two series is that the former has a rigid bisphenol A group while the latter contains flexible ethylene or propylene oxide segments. It seems unlikely that the inductive effect of bisphenol A could be transferred to the vinyl groups because of the long spacer between them. Hence, an alternate explanation for the difference is believed to be related to the difference in the viscosity of the oligomers. In the photopolymerization of multifunctional monomers, the rate of polymerization increases dramatically at the beginning of the reaction caused by the hindered mobility of the macroradicals. The viscosity of the liquid oligomer influences the onset and development of the autoacceleration because the "reduction effect" of viscosity is more pronounced on k_t than on k_p. A study has shown [11] that the polymerization rate increased as the initial viscosity of the formulation was increased. For the E-bis-A oligomers, because of their relatively high viscosities, the reaction became diffusion-controlled immediately upon exposure to UV radiation, resulting in a dramatic autoacceleration that gave rise to a higher polymerization rate. However, in the case of PEGDMA or PPGDMA, the lower viscosity allowed the reaction to occur in a less restricted environment. The diffusion-controlled reaction was postponed and the autoacceleration was partially suppressed, leading to a relatively slower and less erratic polymerization behavior.

Fig. 3 illustrates the polymerization rate as a function of vinyl conversion for the same photopolymerizations reported in Fig. 2. It is observed that the final conversions for the two E-bis-A oligomers were much lower than those of the three ethylene or propylene glycol oligomers (Table II). The difference in the extent of reaction can be explained by the physical state of the cured polymer network. The five oligomers can be divided into two groups based on their T_g data presented in Table I: glass-forming systems for E-bis-A DMA and E-bis-A DA, and elastomer-forming systems for PPGDMA, PEGDMA, and PEGDA. When the polymerization proceeds beyond the $R_p^{\max}$, the rate begins to decrease because of the reduced monomer mobility. In the glass-forming system an additional decrease in the rate is expected when the sample vitrifies (i.e. the T_g of the resulting network is higher than the reaction temperature) during the polymerization. The vitrification will freeze the free volume, reduce the mobility of

TABLE II Vinyl group conversion and gel fraction of the oligomers

	E-bis-A DMA-1	E-bis-A DA	PPGDMA	PEGDMA	PEGDA
Conversion (%)	56.0	51.7	87.7	90.1	78.1
Gel Fraction (%)	86.5	81.0	98.5	99.1	98.2

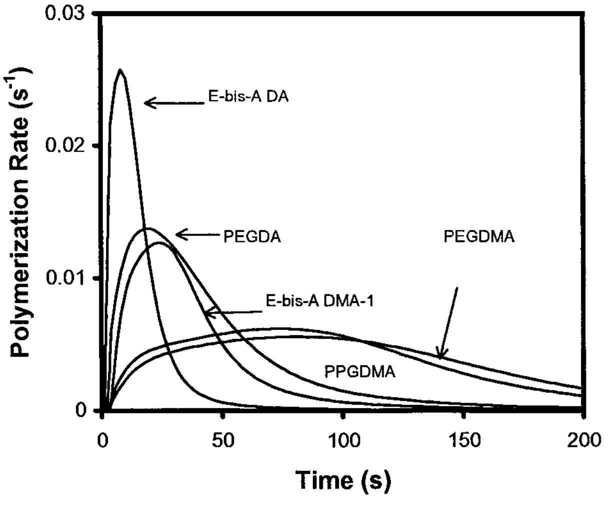


Figure 2 Polymerization rate profiles for different oligomers, cured at 30°C with UV light intensity of 710 W/m^2.

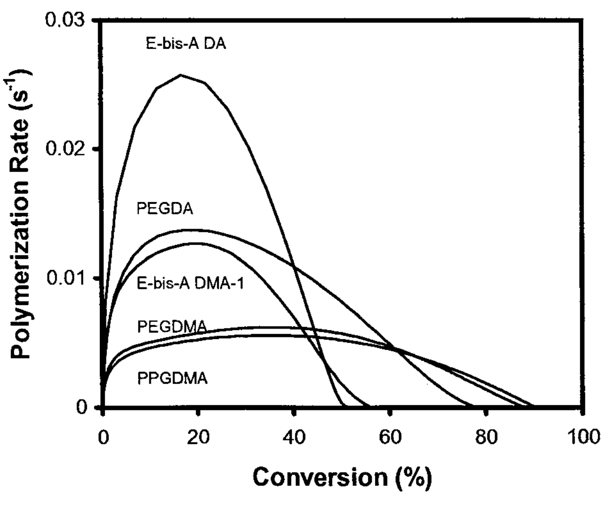


Figure 3 Polymerization rate as a function of vinyl group conversion for different oligomers, cured at 30°C with UV light intensity of 710 W/m^2.

the reactive species, and finally stop the polymerization, giving rise to a lower vinyl group conversion. In an elastomer-forming system, although the formation of the polymer network restricts the mobility of the reactive species, leading to a progressive decrease in the rate, the diffusion of macroradicals and the motion of chain segments can still occur, allowing the reaction to continue. In this case, a high vinyl group conversion can be achieved within an adequate reaction time period.

3.2. Effect of spacer length

Four E-bis-A DMA oligomers with different lengths of spacer units were selected to investigate the effect of the spacer on the polymerization behavior. The average numbers of oxyethyl units in the oligomers were $X = 4$, 6, 10, and 30, respectively. Fig. 4 shows the relationship between the polymerization rate and vinyl conversion for these four oligomers, at 30°C. The maximum rate follows the order: E-bis-A DMA-2 ($X = 6$) > E-bis-A DMA-1 ($X = 4$) > E-bis-A DMA-3 ($X = 10$) > E-bis-A DMA-4 ($X = 30$). A similar trend was also observed over a range of curing temperatures. Since these oligomers have different molecular weights, the reduced rate, $(\mathrm{d}c/\mathrm{d}t)/(1 - c)$, is used to compare their polymerization reactivities. This reduced rate is given by $k_p(fR_i/k_t)^{1/2}$ and is often denoted as the apparent rate constant [12], where R_i is the initiation rate, f is the initiation efficiency, k_p and k_t are the propagation and termination rate constants. When expressed as $(\mathrm{d}c/\mathrm{d}t)/(1 - c)$ at the peak maximum, the data shows the same order in the reactivities.

There have been several reports on the influence of the length of spacer on the rate of polymerization. Cook [7] studied the photopolymerization kinetics of a series of bisphenol A based dimethacrylate monomers where the oxyethyl units ranged between zero to four. It was found that the maximum polymerization rate increased with the increase of the length of the spacer and this was attributed to the decreased mobility of the pendant double bonds and the steric shield effect by the close proximity of the bulky bisphenol A as the spacer length was reduced. In other work by Scranton *et al.* [13], with a series of ethylene glycol dimethacrylates, it was shown that while an increase in the ethylene glycol unit from one to four repeating units resulted in an increase in the maximum reaction rate, a decrease of the maximum rate was observed when the repeating unit was increased from four to nine. Based on these findings and our experimental results, it seems that there is a critical spacer length for E-bis-A DMA oligomers. This value lies between six to ten oxyethyl units. When the length of spacer is lower than the critical value, increasing the ethylene glycol chain length provides greater mobility of the pendant double bonds, leading to a faster polymerization. However, when the spacer length is over the critical value, the mobility and accessibility of the pendant double bonds become insensitive to the number of spacer units. The increased units of ethylene glycol chains then act as an inert "solvent" to reduce the effective concentration of the reactive species, which results in a decrease in the rate of polymerization.

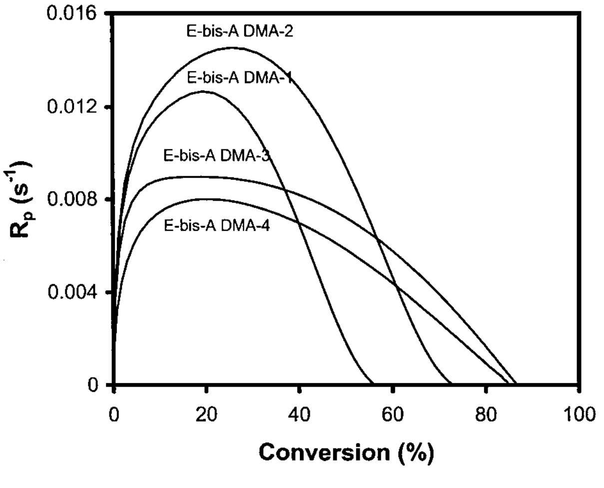


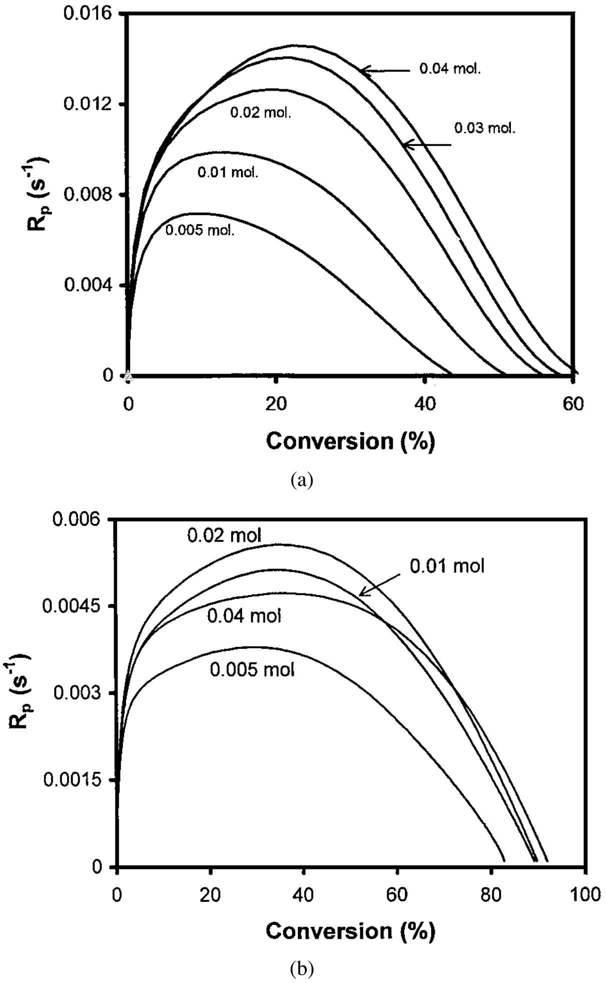
Figure 4 Polymerization rate vs. vinyl group conversion for the four E-bis-A DMA oligomers with different spacer lengths, cured at 30°C with UV light intensity of 710 W/m^2 (oxyethyl units are 4, 6, 10, and 30 for E-bis-A DMA-1, E-bis-A DMA-2, E-bis-A DMA-3, and E-bis-A DMA-4, respectively).

With the increase of ethylene glycol units in E-bis-A DMA oligomers, segmental mobility is improved and crosslinking density is reduced, which benefits further reaction of the pendant double bonds. As a result, the final vinyl conversion is increased from 56% for E-bis-A DMA-1 system to 86.5% for E-bis-A DMA-4 system (Fig. 4). At the same time, the cured polymer materials become more rubbery.

3.3. Effect of initiator concentration

For a photo-initiated radical polymerization based on a steady-state hypothesis, the rate can be expressed as [14]: $R_p = -\mathrm{d}[M]/\mathrm{d}t = k_p/k_t^{1/2}[M](\phi\varepsilon I_o[A])^{1/2}$, where k_p and k_t are the propagation and termination rate constants, $[M]$ is the molar concentration of methacrylate group, ϕ is the initiator efficiency, ε is the absorption coefficient, I_o is the incident light intensity, and $[A]$ is the photoinitiator concentration. According to this equation, the photopolymerization rate is proportional to $[A]^{1/2}$ and it must increase as the initiator concentration increases.

Fig. 5 presents the polymerization rate as a function of vinyl conversion at various CQ concentrations for E-bis-A DMA-1 (Fig. 5a) and PEGDMA (Fig. 5b). The polymerization rate of E-bis-A DMA-1 increased with CQ concentration. However, the increase slowed down at high CQ concentrations. This trend becomes even more evident in the PEGDMA curing system, where an obvious decrease of polymerization rate was observed when the CQ concentration was higher than 0.02 mol. per kg resin. This phenomenon contradicts the prediction of the equation. It should be noted that the photopolymerization rate is also affected by the initiation efficiency, ϕ, which corresponds not only to the dissociation efficiency of the photoinitiator but also to the recombination of the primary radicals (a cage effect) [14, 15]. With the increase in CQ concentration, more primary radicals are generated in a short period of time, and the probability of primary radical recombination



(a)

(b)

Figure 5 (a) Polymerization rate vs. vinyl group conversion at various CQ concentrations for E-bis-A DMA-1; (b) Polymerization rate vs. vinyl group conversion at various CQ concentrations for PEGDMA, cured at 30°C with UV light intensity of 710 W/m^2.

increases, and this yields a smaller ϕ. The reduced initiation efficiency ϕ unavoidably reduces the polymerization rate. However, it is still unclear as to why the drop in the initiation efficiency for the PEGDMA system was greater than that for the E-bis-A DMA-1 system.

The theoretical exponent for the relationship between polymerization rate and initiator concentration is 0.5, based on the bimolecular termination mechanism described above. Table III lists the experimental data for the different oligomers, which were obtained by plotting log R_p versus log[CQ]. All the exponents are less than the theoretical value and they increase at high conversions. The deviation of the exponents from 0.5 is believed to be caused by the recombination of primary radicals [16], which is more likely to occur at high initiation rates. As the network develops, radicals in the matrix become less and less mobile, leading the exponent to increase [5, 17].

TABLE III Exponential factors for the CQ concentration dependence

	E-bis-A DMA-1	E-bis-A DA	PPGDMA	PEGDMA
At 10 % conversion	0.30	0.25	0.35	0.20
At peak rate conversion	0.40	0.34	0.42	0.28

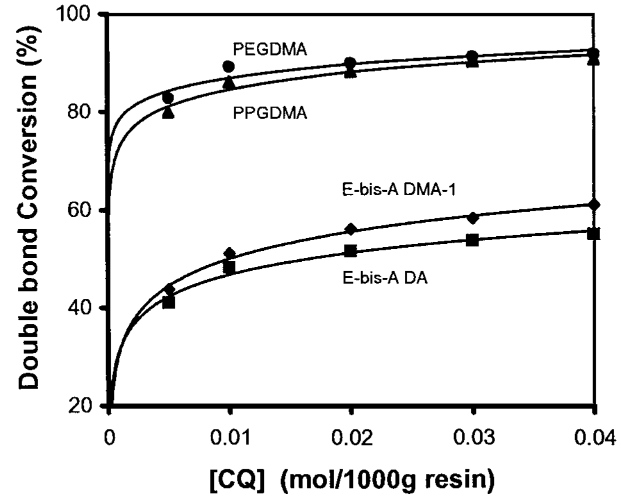


Figure 6 Effect of CQ concentration on the final vinyl group conversion, cured at 30°C with UV light intensity of 710 W/m^2.

The influence of the CQ concentration on the final vinyl group conversion is shown in Fig. 6 for the four oligomer systems. The increase in the extent of reaction with initiator concentration has been observed in many photopolymerization systems and it is attributed to a volume relaxation effect [15, 18, 19]. The delay in volume shrinkage due to the development of the network generates an excess free volume, which increases the mobility of the reactive species in the system and leads to a higher conversion. Our experiments showed that the volume relaxation effect is more evident when the monomers are rigid like E-bis-A DMA-1 and E-bis-A DA. For ethylene glycol oligomers, the flexible chain and good segmental mobility make the volume relaxation almost instantaneous. Therefore they show a very weak conversion dependence on CQ concentration.

3.4. Effect of curing temperature

Fig. 7 shows the photopolymerization rate versus time for E-bis-A DMA-1 at various curing temperatures. The maximum rate shifted to longer reaction times

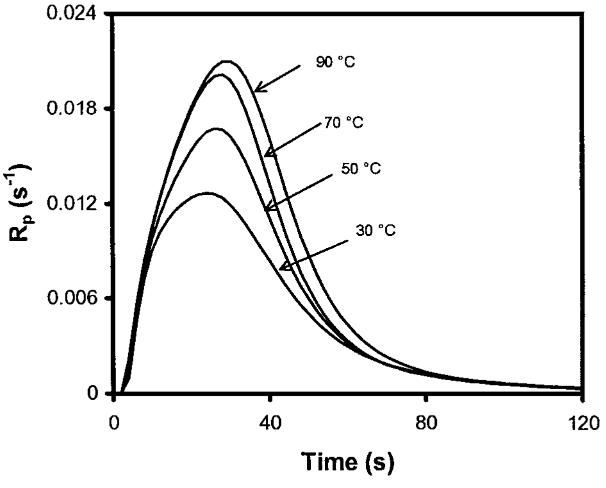


Figure 7 Polymerization rate profiles for E-bis-A DMA-1 at various reaction temperatures, cured with UV light intensity of 710 W/m^2, CQ = 0.02 mol/kg resin.

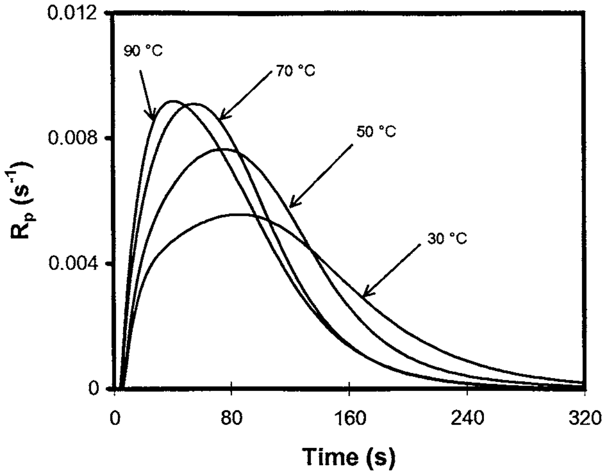


Figure 8 Polymerization rate profiles for PEGDMA at various reaction temperatures, cured with UV light intensity of 710 W/m^2, CQ = 0.02 mol/kg resin.

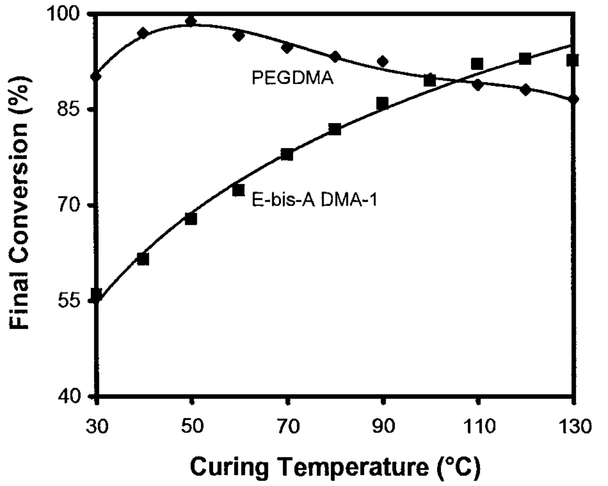


Figure 9 Influence of reaction temperature on the final vinyl group conversion in E-bis-A DMA-1 and PEGDMA systems, CQ = 0.02 mol/kg resin.

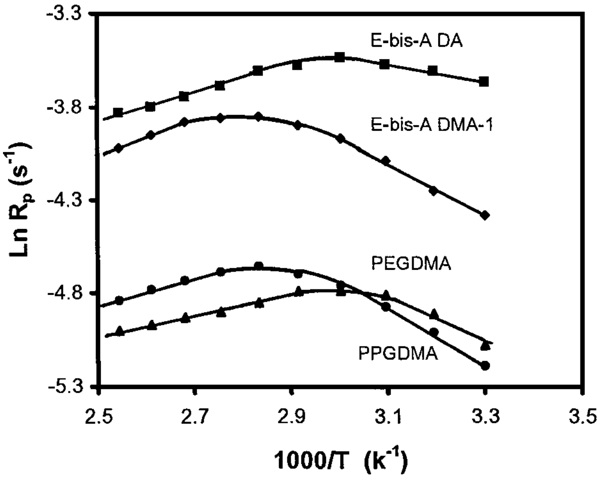


Figure 10 Arrhenius plot of R_p^{max} for the four oligomers.

and the peak became broader as the curing temperature increased. Similar behavior was also observed in the E-bis-A DA system. However, ethylene glycol based oligomers demonstrated a complete opposite temperature dependence in their polymerization rate profiles. As shown in Fig. 8, the maximum in the rate of PEGDMA appeared earlier and the polymerization was completed in a shorter time at the higher curing temperature.

The contrasting temperature dependence profiles are mainly due to the differences in the segmental mobility for oligomers and the proximity of the curing temperature to the T_g of the polymer networks. E-bis-A DMA-1 has a relatively rigid structure and yields a cured network with an elevated T_g. The higher curing temperature improved its segmental mobility and allowed the reaction to continue for a longer period of time before becoming diffusion-controlled. This promoted the maximum rate to occur at later time in the reaction (Fig. 7). Moreover, elevating the temperature lifted the restriction placed on the matrix by its T_g transition and permitted the reaction to further progress to reach a higher conversion (Fig. 9). On the other hand, increasing the temperature provided little improvement for the segment mobility of ethylene glycol oligomers because of their very flexible chains and the low T_g of their cured networks. Nevertheless, the earlier formation of the three-dimensional structure at higher curing temperature exerted extra restriction to the reactivities of the monomeric and the pendant double bonds later in the reaction. Therefore, the final conversions of these systems showed a slight decrease with the curing temperature (Fig. 9).

In the photopolymerization of multifunctional monomers, the temperature effect on the reaction rate is quite complicated [9]. While high temperature always favors chemical activation, leading to an increase in the rate, it reduces the viscosity of the reaction system and suppresses the "gel effect" by enhancing mobility of the reactive species, which may have an opposite effect on the polymerization rate. Fig. 10 gives Arrhenius plots of polymerization rates at the peak maximum (R_p^{max}) for four oligomers. It can been seen that R_p^{max} passes through a maximum with an increase in curing temperature. The maximum polymerization rates appeared near 80–90 °C for E-bis-A DMA-1 and PEGDMA, and near 60–70 °C for E-bis-A DA and PPGDMA.

Apparently, these experimental results are the combined outcome of the chemical activation effect and the effect of "viscosity reduction". In the temperature region below 60–80 °C, the thermal activation mechanism is dominant, resulting in an increase of R_p^{max} as temperature increases. In the higher temperature region (between 80–120°C), the viscosity of reaction system is greatly reduced. Hence, the enhanced segmental mobility and chain translation diffusion lessens the autoacceleration.

Table IV lists the apparent overall activation energies, E_R, obtained from the derivatives of the Arrhenius

TABLE IV Apparent activation energy (kJ/mol) of the photopolymerization at R_p^{max}

	E-bis-A DMA-1	E-bis-A DA	PPGDMA	PEGDMA
Low temperature range	10.6	3.5	10.3	11.6
High temperature range	−8.6	−6.9	−4.6	−4.8

curves in Fig. 10. In the low temperature region, the E_R values were found to be between 10.3–11.6 kJ/mol. for E-bis-A DMA-1, PEGDMA, and PPGDMA, respectively. These values are in a similar range to those reported for other dimethacrylate monomers [15, 20]. However, E-bis-A DA exhibited a very low E_R, 3.5 kJ/mol. In the high temperature region, negative values of E_R were obtained because of the decreased polymeriztion rate.

The reason for the low E_R in the E-bis-A DA curing system is not quite clear. Usually for a more viscous system, the reduced monomer mobility leads to a higher activation energy [21]. In this case, it is presumed that E-bis-A DA exhibited a stronger temperature dependence of viscosity, thus rendering the "viscosity reduction" effect more evident in the low temperature region. This may partially offset the effect of chemical activation, giving rise to a lower apparent activation energy.

4. Conclusion

The photopolymeriztion behavior of two series of di(meth)acrylate oligomers with respect to polymerization rate and final vinyl conversion were compared. The effects of the length of spacer, initiator concentration, and curing temperature were also studied. Based on the experimental results, the following conclusions could be made:

1. Acrylates are much more reactive than methacrylates in the photoinitiated polymerization. Although the higher initial viscosity of E-bis-A oligomers induces more dramatic autoaccelerations upon exposure to UV radiation, the greater segmental mobility and elastomeric character of the cured networks for ethylene glycol oligomers yield higher vinyl conversions.
2. For E-bis-A DMA oligomers, there is a critical spacer length determining the polymerization reactivity. The reaction rate initially increases with the increase in the spacer length. When the spacer length is beyond the critical value (six oxyethyl units), the rate starts to decrease.
3. With the increase of CQ concentration, the polymerization rate increases for all the oligomers. However, the exponential factors for the dependence of polymerization rate on CQ concentration are between 0.20 and 0.42, and are not in agreement with the theoretical exponent (0.5). At very high CQ concentrations, the recombination of primary radicals significantly reduces the initiation efficiency, slowing down the polymerization rate.
4. The two series of oligomers show a different temperature dependence of the vinyl conversion. While the final conversions in E-bis-A DMA-1 and E-bis-A DA significantly increase with the increase of temperature due to enhanced chain mobility, the conversions of PEGDMA and PPGDMA slightly decrease with temperature because of an earlier formation of the three-dimensional structure.
5. Elevating the temperature increases the polymerization rate in the low temperature region. The apparent activation energies at R_p^{max} are found to be 10.3–11.6 kJ/mol, except for E-bis-A DA that has an E_R of 3.5 kJ/mol.

Acknowledgement

We would like to thank Materials and Manufacture of Ontario (MMO) and Bloorview-MacMillan Medical Centre for supporting this work. We also thank the Canadian Foundation of Innovation (CFI) for the equipment grant to purchase the DSC.

References

1. G. A. SENICH and R. E. J. FLORIN, *Macromol. Chem. Phys.* **C24** (1984) 239.
2. J. G. KLOOSTERBOER, *Adv. Polym. Sci.* **84** (1988) 1.
3. R. J. M. ZWIERS and G. C. M. DORTANT, *Appl. Opt.* **24** (1985) 4483.
4. H. URABE, K. WAKSAS and M. YAMAKI, *J. Mater. Sci.: Mater. Med.* **1** (1990) 163.
5. J. G. KLOOSTERBOER and G. F. C. M. LIJTEN, *Polymer* **28** (1987) 1149.
6. B. ORIER, G. L. WILKES and K. N. GANESH, *Polym. Prepr.* **26** (1985) 281.
7. W. D. COOK, *Polymer* **33** (1992) 2152.
8. J. NIE, L. A. LINDEN, J. F. RABEK, J. P. FOUASSIER, F. MORLET-SAVARY, F. SCIGALSKI, A. WRZYSZCZYSKI and E. ANDRZEJEWSKA, *Acta Polymerica* **49** (1998) 145.
9. C. DECKER, D. DECKER and F. MOREL, *ACS Symp. Ser.* **673** (1997) 63.
10. K. S. ANSETH, C. M. WANG and C. N. BOWMAN, *Polymer* **35** (1994) 3243.
11. C. DECKER, B. ELZAOUK and D. DECKER, *J. Macromol. Sci., Pure Appl. Chem.* **A33** (1996) 173.
12. P. J. FLORY, in "Principles of Polymer Chemistry" (Cornell University Press, Ithaca, NY, 1953) Ch. 4.
13. A. B. SCRANTON, C. N. BOWMAN, J. KLIER and N. A. PEPPAS, *Polymer* **33** (1992) 1683.
14. G. ODIAN, in "Principles of Polymerization" 2nd ed. (Wiley-Interscience, New York, 1981) p. 182.
15. L. LECAMP, B. YOUSSEF and C. BUNEL, *Polymer* **38** (1997) 6089.
16. U. MULLER, B. STREHMEL and J. NEUENFELD, *Makromol. Chem. Rapid Commun.* **10** (1989) 539.
17. I. R. BELLOBONO, E. SELLI and L. RIGHETTO, *Makromol. Chem.* **190** (1989) 1945.
18. C. N. BOWMAN and N. A. PEPPAS, *Macromolecules* **24** (1991) 1914.
19. W. D. COOK, *J. Polym. Sci., Part A: Polym. Chem.* **31** (1993) 1053.
20. D. J. BROER, G. N. MOL and G. CHALLA, *Polymer* **32** (1991) 691.
21. A. T. DOORNKAMP and Y. Y. TAN, *Polym. Commun.* **23** (1990) 2474.

Received 21 September 2000
and accepted 27 February 2001