

New Aspects of Viscosity Effects on the Photopolymerization Kinetics of the 2,2-Bis[4-(2-hydroxymethacryloxypropoxy)phenyl]propane/Triethylene Glycol Dimethacrylate Monomer System

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ABSTRACT: The photopolymerization kinetics and viscosity behavior of 11 2,2-bis[4-(2-hydroxymethacryloxypropoxy)phenyl]propane/triethylene glycol dimethacrylate mixtures were investigated. The viscosity was studied at six temperatures (20–70°C), and the activation energies for the viscosity were determined. The excess logarithm viscosities were calculated and found to be negative over the whole composition and temperature ranges; they were fitted to the Redlich–Kister polynomial equation. The kinetic analysis of the photopolymerization was carried out at three polymerization temperatures (20, 40, and 60°C). The results proved the existence of the most reactive composition (reaching the highest value of the maximum polymer-

ization rate), but the ratio of the monomers in this composition, close to equimolar, showed a tendency to change with the polymerization temperature. The viscosities of the most reactive compositions lay in the range of about 0.1–1.2 Pa s, which was narrow in comparison with the range of viscosities of all the compositions used in the kinetic studies (from 3×10^{-3} to 1.5×10^3 Pa s). The activation energies for the polymerization rates were calculated and correlated with the viscosity changes. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2780–2786, 2008

Key words: activation energy; dental polymers; kinetics (polym.); photopolymerization; viscosity

INTRODUCTION

Dimethacrylate-based networks formed during photopolymerization are frequently used in high-performance applications such as dental restorative materials and information storage systems. Substantial effort has been devoted to understanding how varying the structure of methacrylate comonomers and the conditions of photopolymerization impacts the polymerization kinetics.^{1,2}

A system that has been intensively studied during the last several years is a mixture of two monomers: highly viscous 2,2-bis[4-(2-hydroxymethacryloxypropoxy)phenyl]propane (bis-GMA) and low-viscosity triethylene glycol dimethacrylate (TEGDM). Their mixtures are often used as the organic phase of dental restorative materials.^{3,4} Some kinetic studies have shown that both the addition of TEGDM to bis-

GMA and the dilution of bis-GMA with TEGDM increase the maximum polymerization rate (R_p^{\max}) in comparison with the neat monomers. This leads to the appearance of a composition showing the maximum reactivity (the highest value of R_p^{\max}). Although most often the composition of the most reactive resin is close to the equimolar mixture of the two monomers,^{4–6} the number of investigated compositions with various monomer ratios is rather limited, and only in one case has it been as high as 9.⁴

However, one can expect the composition of the most reactive mixture to be sensitive also to the initiation rate (the type of initiating system used and the intensity of the incident light) as well as the polymerization temperature (mainly due to viscosity changes). In our study, we took into account the latter factor and investigated the photopolymerization kinetics for 11 comonomer ratios at three polymerization temperatures. Special attention was paid to the viscosity behavior of the bis-GMA/TEGDM monomer mixtures at six temperatures.

EXPERIMENTAL

TEGDM was purchased from Aldrich (St. Louis, MO) and was purified by column chromatography before use. The removal of the inhibitor is important

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TABLE I
 η Values of the Bis-GMA/TEGDM Mixtures at Six Temperatures

Temperature (°C)	η (Pa·s)										
	TEGDM content (mol %)										
	0	10	20	30	40	50	60	70	80	90	100
20	1480	243	52.4	13.87	3.82	1.20	0.431	0.144	0.055	0.022	0.010
30	159	38.1	11.06	3.83	1.21	0.448	0.181	0.071	0.031	0.014	0.007
40	26.99	8.60	2.99	1.18	0.486	0.198	0.089	0.039	0.019	0.009	0.005
50	6.44	2.42	1.02	0.459	0.202	0.098	0.048	0.024	0.012	0.007	0.004
60	1.98	0.853	0.409	0.207	0.102	0.055	0.029	0.016	0.009	0.005	0.003
70	0.734	0.373	0.197	0.108	0.057	0.033	0.018	0.011	0.006	0.004	0.002

for kinetic studies because its content changes during storage; the results obtained for the unpurified monomer depended on the batch number and were different than those for the inhibitor-free monomer. Because of difficulties with the purification of bis-GMA (Polysciences Inc., Warrington, PA), it was used as received.

Reaction rate profiles and conversions were determined by isothermal differential scanning calorimetry with a Unipan-Termal 605 (Warsaw, Poland) M apparatus. Throughout the experiments, the differential scanning calorimetry unit was operated isothermally with an accuracy of $\pm 0.01^\circ\text{C}$. The polymerization was initiated with the light of a medium-pressure Hg lamp (glass filter = 366 nm, light intensity = 1 mW/cm^2) and was carried out in an Ar atmosphere. As the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (Ciba Chemicals, Basel, Switzerland) at a concentration of 0.2 wt % was used. The sample mass was 10 mg. For computations, the heat of polymerization was taken to be 56 kJ/mol of double bonds.⁷ Other details of the experiment were analogous to those described in ref. 8.

The viscosities of the investigated compositions were measured with a Brookfield DV-II+ PRO (Brookfield Viscometers Ltd., Harlow, UK) rheometer. The results for the neat monomers and comonomer mixtures at six polymerization temperatures and their activation energy for viscosity (E_a^η) values are given in Table I and Figure 1.

The theoretical viscosities of the bis-GMA/TEGDM binary mixtures were calculated with eq. (1),^{9,10} and the excess logarithm viscosity ($\ln \eta$)^E values were calculated with eq. (2):¹¹

$$\ln \eta_{\text{mix}} = \sum_{i=1}^2 x_i \ln \eta_i \quad (1)$$

$$(\ln \eta)^E = \ln \eta_{\text{mix}} - \sum_{i=1}^2 x_i \ln \eta_i \quad (2)$$

where η_{mix} is the mixture viscosity, x_i represents the molar fractions, and η_i represents the individual component viscosities.

The calculated $(\ln \eta)^E$ values were fitted to the Redlich–Kister polynomial equation:^{12–14}

$$Y(x) = x_1 x_2 \sum_{i=1}^n A_i (x_1 - x_2)^i \quad (3)$$

where $Y(x) = (\ln \eta)^E$, A_i is the polynomial coefficient, and x_1 and x_2 are monomer molar fractions.

Diffusion rate coefficient [k_{diff} ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)] values were calculated with the following well-known relation:¹⁵

$$k_{\text{diff}} = \frac{8000RT}{3\eta} \quad (4)$$

where R is the gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), and η is the system viscosity (Pa s).

RESULTS AND DISCUSSION

The most striking difference between the two investigated monomers is their viscosity: bis-GMA is

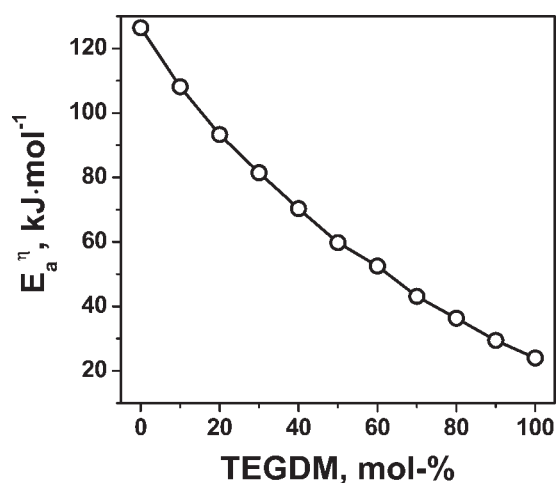


Figure 1 E_a^η of the bis-GMA/TEGDM system as a function of the TEGDM content.

TABLE II
 k_{diff} Values of the Three Most Viscous Compositions at 20°C

TEGDM content (mol %)	k_{diff} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
0	4.4×10^3
10	26.7×10^3
20	124×10^3

about 1.5×10^5 more viscous at 20°C and about 5000 times more viscous at 40°C than TEGDM! Thus, it seems that the differences in the polymerization kinetics of formulations containing various ratios of the two monomers will be dominated by viscosity effects.

The polymerization is a complex process consisting of consecutive and parallel reactions. When a reaction rate coefficient is higher than k_{diff} , the reaction becomes diffusion-controlled. The k_{diff} values of the three most viscous compositions are given in Table II. Usually, the propagation rate coefficient of methacrylates is of the order of 3×10^2 – $10^3 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$.¹⁶ Calculations of k_{diff} (Table II) have shown that in the case of neat bis-GMA, the diffusional control of the propagation at 20°C can appear almost from the beginning of the polymerization. This will shorten the time when the polymerization rate increases up to its maximum value. As the TEGDM content in the feed and the polymerization temperature increase, the viscosity rapidly decreases, and the effect of the initial viscosity becomes smaller. The reduction of the viscosity effect with the temperature rise should be highest in the case of compositions rich with bis-GMA because of their high E_a^η values (Fig. 1). E_a^η rapidly decreases with the TEGDM concentration increasing.

The bis-GMA molecule (molecular weight = 512.6), having a large bisphenol A moiety, is almost twice the size of the TEGDM molecule (molecular weight = 286.3), and this leads to a lower concentration of double bonds in the former (at 40°C 4.55 and 7.39 mol/L, respectively). This difference can additionally affect the polymerization kinetics and their changes from one composition to another composition.

Because of the importance of viscosity effects on the polymerization kinetics, we gave more attention to the viscosity behavior of the bis-GMA/TEGDM system. Bis-GMA is strongly associated through hydrogen bonds, which are responsible for its high viscosity.¹⁷ The addition of TEGDM having only dipole–dipole interactions affects hydrogen bonding in bis-GMA. Thus, the measured viscosity of the mixture of the two monomers may deviate from the viscosity predicted by eq. (1) for mixtures of liquids with similar intermolecular interactions and molar volumes. Figure 2 presents the experimental viscos-

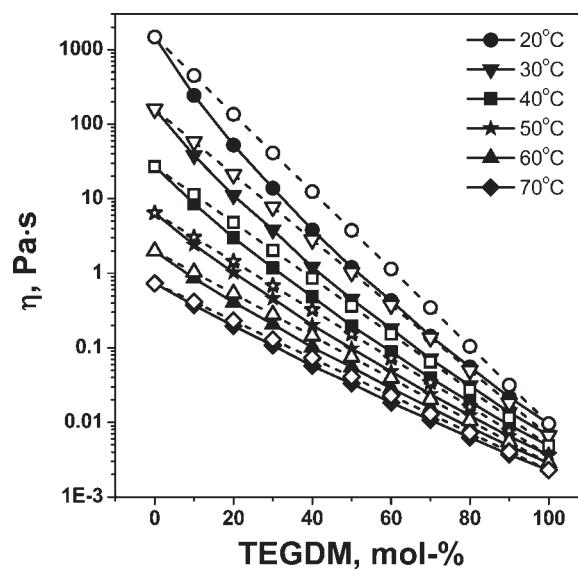


Figure 2 Experimental and calculated η values as a function of the TEGDM molar fraction and temperature. The solid line represents experimental values; the dotted line represents calculated values.

ity values along with those calculated with eq. (1). The logarithmic dependence of the viscosity on the mixture composition is not linear, in contrast to that observed in ref. 4 (at 30°C). Thus, the excess logarithmic viscosities were calculated with eq. (2). An equation of this type is most commonly used to predict the excess physicochemical and thermodynamic properties.¹³ These properties, which depend on the composition and/or temperature, are of great importance in understanding the nature of the molecular aggregation that exists in binary mixtures.¹⁸ The viscosity deviations have been fitted by the third-order Redlich–Kister equation [eq. (3)]; the polynomial coefficients are summarized in Table III.

As can be seen, the values of $(\ln \eta)^E$ (Fig. 3) are negative over the whole composition and experimental temperature ranges. The minimum exists at 40–50 mol % TEGDM within the whole range of experimental temperatures. A qualitatively similar but weaker effect has been observed for mixtures of styrene with some *n*-alkanols.¹³ In our case, the strong

TABLE III
Coefficients of the Redlich–Kister Equation for the Excess Logarithm Viscosities of the Bis-GMA/TEGDM System

Temperature (°C)	A_0 (Pa s)	A_1 (Pa s)	A_2 (Pa s)	A_3 (Pa s)
20	−4.480	1.532	−1.455	0.085
30	−3.222	0.540	−0.824	0.656
40	−2.346	0.318	−0.782	0.244
50	−1.781	0.329	−0.524	0.153
60	−1.278	0.265	−0.567	0.224
70	−0.902	0.111	−0.172	−0.128

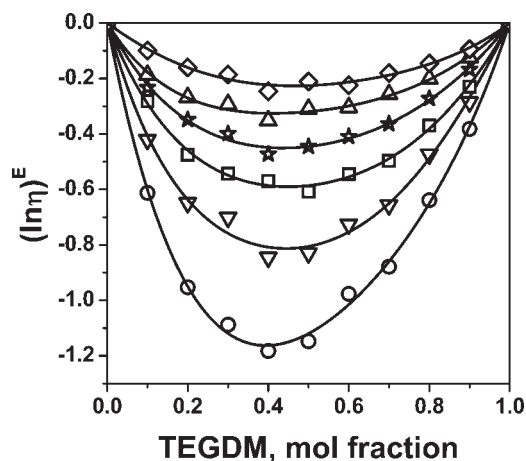


Figure 3 Deviations in $\ln \eta$ versus the molar fraction of TEGDM with bis-GMA: (○) 20, (▽) 30, (□) 40, (☆) 50, (△) 60, and (◇) 70°C. The symbols represent experimental values; the curves were calculated with the Redlich–Kistler equation.

increase in the viscosity deviations with the increase in TEGDM content up to about 40–50 mol % may indicate breaking of hydrogen bonding between hydroxyl groups of bis-GMA, whereas negative values of the deviations suggest that interactions between the molecules of the individual monomers are stronger than those between the molecules of bis-GMA and TEGDM. As the TEGDM content increases above the equimolar amount, the hydrogen bonding diminishes and intermolecular interactions become dominated by those between TEGDM molecules; thus, the viscosity deviation decreases. The values of $(\ln \eta)^E$ become less negative with the temperature rise, as could be expected from the temperature reduction of specific interactions between the molecules.

The kinetics of the photopolymerization have been studied at 20, 40, and 60°C. The kinetic curves of the

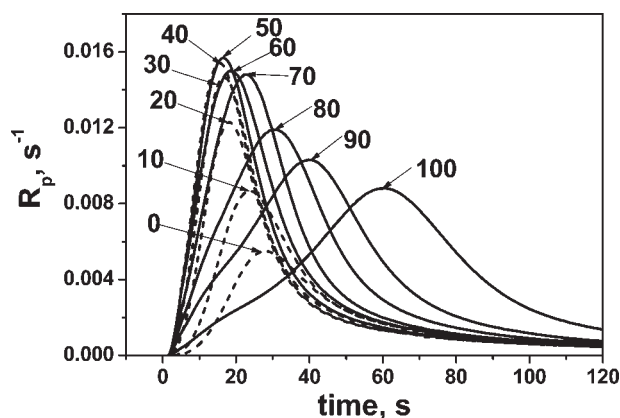


Figure 4 Polymerization rate (R_p) as a function of time for bis-GMA/TEGDM mixtures at 40°C. The numbers indicate the TEGDM content (mol %) in the feed.

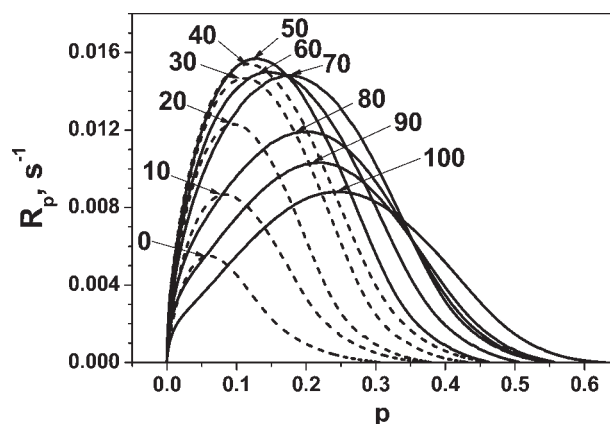


Figure 5 Polymerization rate (R_p) as a function of the fractional conversion (p) for bis-GMA/TEGDM mixtures at 40°C. The numbers indicate the TEGDM content (mol %) in the feed.

investigated bis-GMA/TEGDM mixtures at 40°C are shown in Figures 4 and 5.

Under the conditions used in this work, the highest R_p^{\max} value was obtained at a TEGDM to bis-GMA molar ratio equal to 1 : 1, and this is consistent with the results reported in ref. 4. If the viscosity is the main determining factor, we may suppose that R_p^{\max} increases when bis-GMA is added to TEGDM (up to the equimolar amount) because of the increase in the viscosity, which results in the suppression of termination and enhancement of the gel effect. We believe that the further increase in the viscosity of the initial mixture does not enhance the gel effect because the viscosity becomes so high that it also begins to influence the propagation at low conversions. This in turn leads to a reduction of R_p^{\max} . One may conclude that under such conditions, k_{diff} becomes close to or even lower than the propagation rate coefficient. Thus, the viscosity of the equimolar monomer mixture seems to be optimum for this particular system under the given polymerization conditions.

On the other hand, the final double-bond conversion increases with increasing TEGDM content (Fig. 6), as observed earlier,^{3,5} because of the enhancement of the diffusional ability of the reacting species and delayed vitrification. The same effect is caused by the increase in the polymerization temperature. An analogous trend shows the conversion at R_p^{\max} (p_{peak} ; Fig. 7).

The rise of the polymerization temperature obviously accelerates the polymerization. Figure 8 shows the dependence of R_p^{\max} on the temperature and feed composition. When the polymerization temperature is increased, a shift to a lower TEGDM content in the compositions with the highest R_p^{\max} occurs: from about 50–60 mol % at 20°C to about 30–40 mol % at 60°C (which corresponds to about 36–46 and

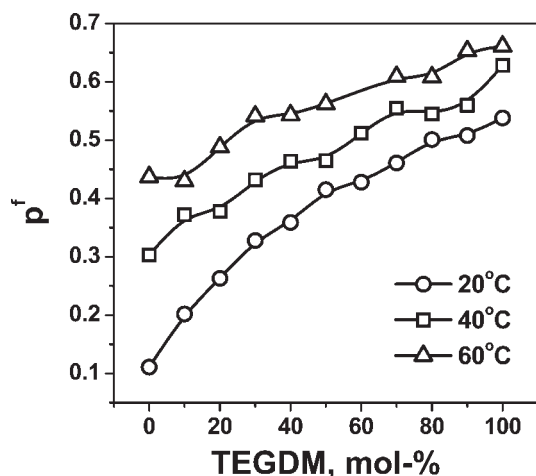


Figure 6 Final double-bond conversion (p_f) as a function of the TEGDM content and polymerization temperature.

19–27 wt %, respectively). The simplest explanation is that the temperature rise reduces the viscosity of the initial monomer mixture and that increasing as the reaction progresses; thus, the initial mixture must contain a larger amount of the more viscous monomer to create optimum conditions for the polymerization.

The time at R_p^{\max} (t_{peak}) reaches the lowest value for the most reactive composition, and this is especially visible at the lowest polymerization temperature (Fig. 9). The changes in t_{peak} with increasing TEGDM content reflect at first the reduction of diffusional limitations (decreasing t_{peak} values) and then the slowing down of the gel effect (increasing t_{peak} values).

The influence of the initial viscosity can be best observed at the beginning of the polymerization at very low conversions. This is shown in Figure 10 for the dependence of the polymerization rate at the 5%

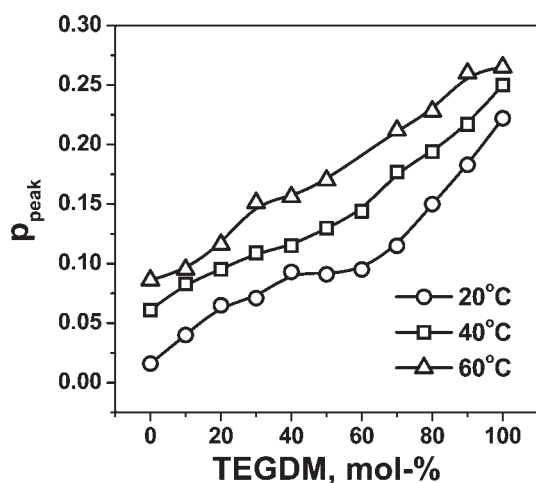


Figure 7 p_{peak} as a function of the TEGDM content and polymerization temperature.

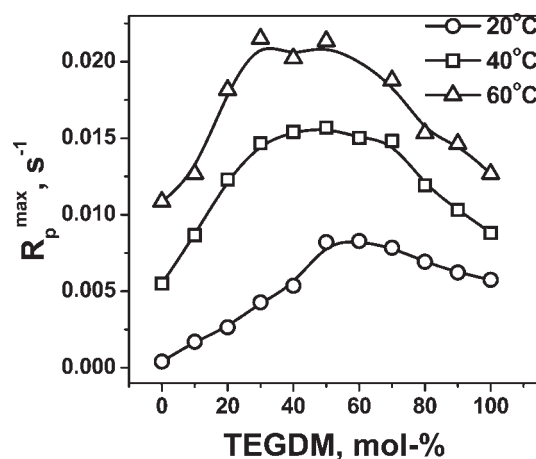


Figure 8 R_p^{\max} as a function of the TEGDM content and polymerization temperature.

double-bond conversion ($R_p^{0.05}$) on the temperature and feed composition. As can be seen, $R_p^{0.05}$ behaves qualitatively similarly to R_p^{\max} . This means that the reaction diffusion-controlled termination and diffusional limitations of propagation take place just at that low conversion (for the polymerization of neat bis-GMA and 10 mol % TEGDM at 20°C, $p_{\text{peak}} < 0.05$). However, the maxima on the plots seem to show a slight tendency to shift to lower TEGDM contents. Because at 5% conversion the viscosity of the polymerizing system is lower than that at R_p^{\max} , to obtain the necessary viscosity level influencing the propagation step, the concentration of the more viscous monomer must be higher.

It is interesting that both the viscosity deviations and the maximum (and at $p = 5\%$) polymerization rates are the highest with the same ranges of monomer ratios. Because the polymerization rate can be influenced by the formation of clusters with a favorable or unfavorable relative orientation of double

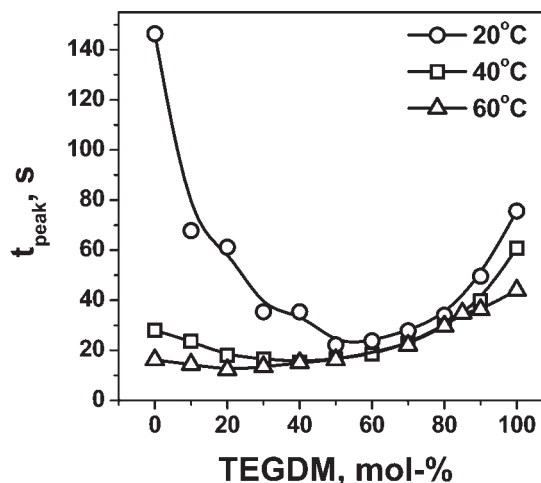


Figure 9 t_{peak} as a function of the TEGDM content and polymerization temperature.

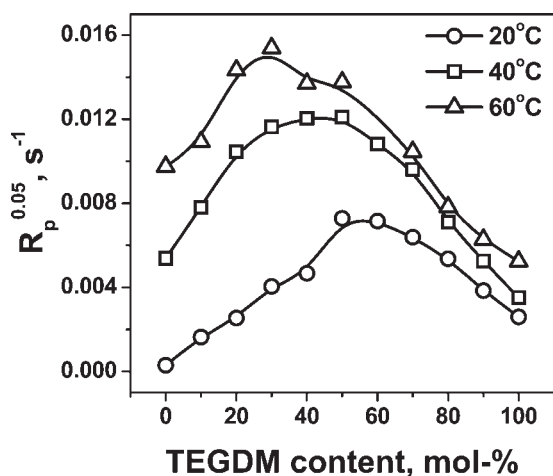


Figure 10 $R_p^{0.05}$ as a function of the TEGDM content and polymerization temperature.

bonds,¹⁹ one can speculate that for the compositions that are close to equimolar, the double-bond orientation is the most favorable for the polymerization.

Monitoring of the polymerization rates at three temperatures enabled the estimation of the composite activation energy for the polymerization rate (E_a^R). The so-calculated E_a^R value is influenced by the viscosity if the viscosity affects the termination and propagation steps. In the case of photochemical initiation, the energy for initiator decomposition is supplied by light quanta, and the activation energy for initiation is close to 0. Calculations were made for both R_p^{\max} and $R_p^{0.05}$. The results are shown in Figure 11.

E_a^R is highest in the case of neat bis-GMA (close to 70 kJ/mol), and this indicates that the influence of the temperature on the polymerization in the absence of any reactive diluent is highest. The strong temperature effect is associated with the high E_a^R value of neat bis-GMA (Fig. 1), which is equal to 126.4 kJ/mol. E_a^R decreases with the initial viscosity and increasing TEGDM content; however, when the TEGDM content reaches about 50 mol %, the changes become very small. This is interesting because below this threshold TEGDM concentration, R_p^{\max} decreases with an increase in the initial viscosity of the formulation (propagation becomes diffusion-controlled at low conversions). At higher TEGDM contents, R_p^{\max} decreases because of the reduction of the gel effect, which is associated with the termination rate. This suggests in turn that E_a^R depends mainly on the activation energy for propagation (E_a^p), which is in agreement with the expression for E_a^R in the case of photochemical initiation: $E_a^R = E_a^p - 0.5E_a^t$, where E_a^t denotes the activation energy for termination. The values of E_a^R increase with the conversion, reflecting a reduction of the mobility of the polymer network being formed. The

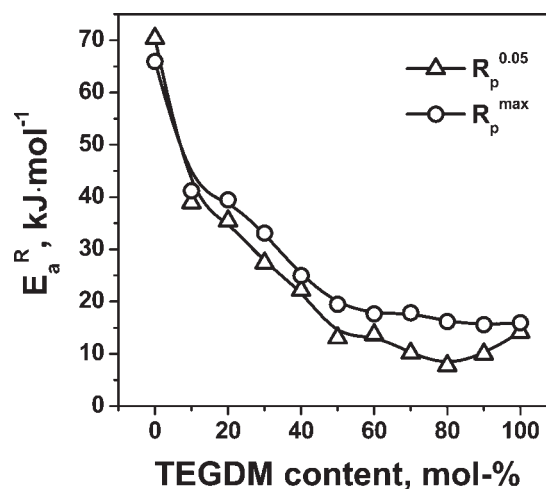


Figure 11 E_a^R at $R_p^{0.05}$ and R_p^{\max} as a function of the TEGDM content.

lowest calculated values (at TEGDM contents > 50 mol %) are of the order of 7–10 kJ/mol. The values obtained by other authors for the photopolymerization process differ markedly, depending on the literature source; for example, for an equimolar bis-GMA/TEGDM mixture at 40% conversion, E_a^R was found to be 25 kJ/mol,²⁰ which is close to the result obtained in our work, whereas for a resin containing 54 mol % TEGDM, E_a^R was found to be ~ 14 kJ/mol.²¹ Generally, the reported activation energies for R_p^{\max} of various methacrylates have been of the order of 3.5–21 kJ/mol,^{22–26} but a possible effect of viscosity has not been considered.

Looking for a correlation between the photopolymerization kinetics and initial viscosity of the formulation, we put together the values of R_p^{\max} and η (Fig. 12). The obtained dependences suggest that the viscosities of the most reactive compositions in the investigated temperature range lie for this particular

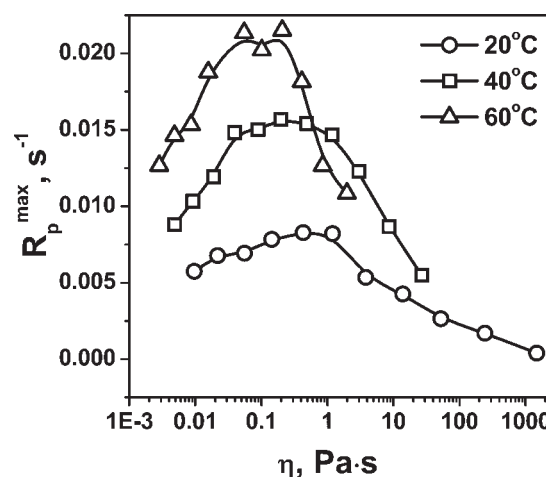


Figure 12 R_p^{\max} as a function of the initial viscosity and temperature.

system in the range of about 0.1–1.2 Pa s, which is narrow in comparison with the range of viscosities of all the compositions used in kinetic studies (from 3×10^{-3} to 1.5×10^3 Pa s). This clearly indicates that the viscosity of the bis-GMA/TEGDM mixture influences its polymerization kinetics more than possible changes in the crosslinking density, reactivity of the monomers, rigidity of the polymer network, and so forth occurring when the temperature is changed. A similar comparison of R_p^{\max} and the initial viscosity (at only 30°C) for mixtures of TEGDM with three high-viscosity resins (including bis-GMA), presented in ref. 4, suggested that the optimum initial viscosity range is 3–5 Pa s. This result differs from that obtained by us, and this may be partly associated with differences in the viscosity values measured in our work and in ref. 4. However, it worth noting that the initial viscosity of the most reactive composition decreases with the polymerization temperature increasing (Fig. 12; a qualitatively analogical dependence was obtained also for $R_p^{0.05}$ values). This means that a simple change in the monomer ratio at a higher temperature to reach the same viscosity as the most reactive composition at a lower temperature is not sufficient to ensure optimum conditions for the polymerization rate at this new, higher temperature. Thus, the conditions that determine the monomer ratio in the most reactive composition, such as the viscosity, hydrogen bonding, reactivity, and crosslinking density (strictly their contributions to the total effect), change with the temperature.

CONCLUSIONS

The investigations undertaken in this work have extended the range of polymerization temperatures at which the photopolymerization kinetics of the popular bis-GMA/TEGDM system have been analyzed. Additionally, the viscosity behavior of mixtures of the two monomers at six temperatures has been studied; the calculated excess logarithm viscosities ($\ln \eta$)^E have been found to be negative over the whole composition and temperature ranges. The kinetic results have proved the existence of a composition showing the highest value of R_p^{\max} and its dependence on the initial viscosity (associated with the monomer ratio) and polymerization temperature. The change in the viscosity of the most reactive

monomer mixture with changes in the polymerization temperature indicates that the conditions that determine the monomer ratio (strictly their contributions to the total effect) also change with the temperature. The high viscosity of bis-GMA (and its high E_a^n value) strongly affects the polymerization (and E_a^R) of mixtures containing less than 50 mol % TEGDM.

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