

Viscosity Effects in the Photopolymerization of Two-Monomer Systems

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ABSTRACT: Photopolymerization kinetics and viscosity behavior of five different two-monomer systems forming hydrogen bonds and composed of mixtures of a high viscosity monomer (HVM) and a low viscosity monomer (LVM) at various molar ratios were investigated at six polymerization temperatures. The monomers used were mono- or dimethacrylates. Detailed viscosity measurements of the monomer mixtures showed significant negative deviations from the theoretical values (characterized by excess logarithm viscosities) indicating that interactions between the molecules of the same type (in individual monomers) are stronger than those between two molecules of different types (HVM and LVM). The photopolymerization kinetics were analyzed from the point of view of the appearance, viscosity and temperature behavior of the most

reactive composition (MRC), the one showing the highest value of the maximum polymerization rate within a range of the HVM: LVM ratios. It was found that MRC appearance is determined mainly by the initial viscosity of the two-monomer system, whereas the functionality of the monomers (and network formation) is much less important (MRC is observed even in linear systems). The initial viscosity of all the monomer mixtures showing MRC lay in the range of 0.06–2 Pa s, which is narrow compared to the range of viscosities of the monomers (approximately 10^{-3} – 10^3 Pa s). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 280–287, 2010

Key words: kinetics (polym.); photopolymerization; viscosity

INTRODUCTION

The photopolymerization is nowadays a widespread technique used for preparation of polymeric materials in many branches of industry. Photocurable compositions are based mainly on multifunctional methacrylates and acrylates and are usually composed of highly viscous oligomers (responsible for mechanical properties of the product) and low viscosity monomers (LVM), working as reactive diluents. To the most popular oligomers belong 2,2-bis[4-(2-hydroxymethacryloxypropoxy)phenyl]propane (bis-GMA) and 1,6-bis-(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA), two basic resins used in dental restorative materials.

The very high viscosity of bis-GMA is the main reason of its low polymerization rates and conversions; a dilution with a LVM, like triethylene glycol dimethacrylate (TEGDM), increases the polymerization rate due to the increase in mobility of monomer molecules (causing reduction of diffusional limitations of propagation). However, too large content of the reactive dil-

uent results in another decrease of the polymerization rate due to the increase in the mobility of the macro-radical chain ends and, in consequence, enhanced termination rate.^{1–4} This leads to the appearance of a composition showing a maximum reactivity (the highest value of the maximum polymerization rate R_p^{\max}),^{1,2} in which the ratio of the monomers changes with temperature.¹ Beside bis-GMA/TEGDM system, a similar behavior was also found for other systems, like UDMA/TEGDM, (ethoxylated bisphenol A dimethacrylate)/TEGDM, bis-GMA/(phenyl glycidyl ether methacrylate) and bis-GMA/styrene systems.^{2,5,6} In all these systems the high viscosity component was the crosslinking monomer whereas the reactive diluent was a tetrafunctional or difunctional one (according to Flory's definition difunctional monomers contain one double bond⁷). The importance of the initial viscosity of the system as the main factor to obtain optimum reactivity was indicated in some works^{1,2} but also other explanations were proposed, like different reactivity of functional groups, change in pendant double bond fraction or change in initiator efficiency.⁶

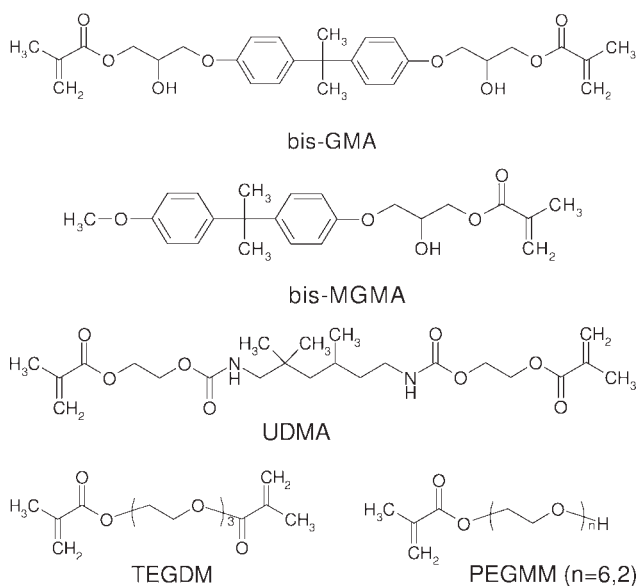
On the other hand, the existence of the most reactive composition (MRC) was also proved for mixtures of two LVMs, one tetra- and one difunctional. In such a case the determining factor is the crosslink density.^{8–11} If two monomers differ both with viscosity and functionality, changes in their ratio in the formulation cause changes both in the initial

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viscosity of the system as well as in the crosslink density of the polymerization product. This in turn will affect the polymerization kinetics and the monomer ratio in MRC. Thus, it is of interest to find out what influences the polymerization kinetics more: changes in viscosity or changes in crosslink density?

The aim of our study was to discuss this question for five two-monomer systems containing monomers of different viscosity and functionality. The high viscosity monomers (HVM) selected for this study were bis-GMA (tetrafunctional), UDMA (tetrafunctional) and 2-[4-(2-hydroxy-3-methacryloxypropoxy)phenylene]-2-[4'-methoxyphenylene]propane (bis-MGMA) (difunctional) and the reactive diluents were TEGDM (tetrafunctional) and polyethylene glycol monomethacrylate (PEGMM) (difunctional).



It should be stressed that all the HVM used are able to form hydrogen bonds, which is the main reason of their high viscosity. Mixing with LVM must drastically influence intermolecular interactions between molecules of the same type (within one monomer) and cause appearance of new interactions between molecules belonging to two different monomers. In our previous article⁷ we described viscosity behavior of bis-GMA/TEGDM system and its influence on the photopolymerization kinetics. In this present article we extended our investigations to other systems of the type (HVM able to form H-bonds)/(LVM, able or not to form H-bonds by itself). Although the polymerization behavior of similar two monomer systems was intensively investigated,^{1-6,12-15} this article presents a new approach taking into account detailed viscosity studies.

EXPERIMENTAL

TEGDM and PEGMM were purchased from Aldrich and were purified by column chromatography

TABLE I
η Values of the Monomers at Six Temperatures

	η, Pa s				
	bis-GMA	bis-MGMA	UDMA	TEGDM	PEGMM
20°C	1420	16.6	18.7	0.01	0.051
30°C	202	2.17	4.9	0.007	0.031
40°C	34.33	0.596	1.37	0.005	0.020
50°C	7.19	0.226	0.511	0.004	0.014
60°C	2.14	0.099	0.228	0.003	0.010
70°C	0.949		0.112	0.002	0.007

before use. Bis-GMA (Polysciences), UDMA (Aldrich) and bis-MGMA (kindly donated by prof. Charmas¹⁶), due to their high viscosity, were used as received.

Reaction rate profiles and conversions were determined by isothermal differential scanning calorimetry (Unipan-Termal 605 M). Throughout the experiments the DSC unit was operated isothermally at the selected temperature kept with accuracy $\pm 0.01^\circ\text{C}$. The polymerization was initiated by the light of a medium pressure Hg lamp (glass filter 366 nm, light intensity 1 mW cm^{-2}) and was carried out in Ar atmosphere. As the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (Ciba) in concentration 0.2 wt % was used. The sample mass was 5 mg. For computations, the heat of polymerization was taken to be 56 kJ mol^{-1} double bonds.¹⁷ Other details of the experiment were analogous to those described in.⁸

Viscosities η of the investigated compositions were measured by DV-II+ PRO Brookfield Rheometer. The results for neat monomers are given in Table I.

Theoretical viscosities of binary mixtures were calculated from eq. (1)^{18,19}:

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

and excess logarithm viscosities $(\ln \eta)^E$ from eq. (2)²⁰:

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

where η_{mix} refers to the mixture viscosity, x_i are mole fractions and η_i are individual component viscosities.

Diffusion rate coefficients k_{diff} were calculated from the well-known relation²¹:

$$k_{\text{diff}} = \frac{8000 \cdot R \cdot T}{3 \cdot \eta} \quad (3)$$

where k_{diff} is expressed in $[\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}]$, R is gas constant $[\text{J mol}^{-1} \text{ K}^{-1}]$, T is temperature $[\text{K}]$, and η is system viscosity $[\text{Pa s}]$.

TABLE II
Two-Monomer Systems Studied in this Work

System	High viscosity monomer		Low viscosity monomer	
	Monomer	Functionality	Monomer	Functionality
1	bis-GMA	4	TEGDM	4
2	UDMA	4	TEGDM	4
3	bis-GMA	4	PEGMM	2
4	bis-MGMA	2	TEGDM	4
5	bis-MGMA	2	PEGMM	2

RESULTS AND DISCUSSION

The monomers in systems HVM/LVM were combined with monomer functionality (f) as follows: 4f /4f, 4f /2f, 2f/4f and 2f/2f, resp., and the systems investigated are defined in Table II.

Viscosity behavior

Within the group of HVM, bis-GMA stands out from the two remaining monomers: its viscosity is two orders of magnitude higher compared to the viscosities of bis-MGMA and UDMA, which are of the same order (Table I). The high viscosity of bis-GMA results from very strong hydrogen bonding formed by two —OH groups²² and the large size of its molecule. Bis-MGMA with a similar structure but having only one —OH function (and smaller molecule) forms much weaker H-bonds and its viscosity is markedly lower being comparable to the viscosity of UDMA. H-bonds in the latter, formed with the participation of —NH— groups, are weaker than in the case of hydroxyls.^{2,22} On the other hand, within the group of LVM, the viscosity of PEGMM is roughly one order of magnitude higher than that of TEGDM, which results both from larger size of the molecule of the former, as well as from its ability to hydrogen bonding. Generally, HVM are 10^3 – 1.5×10^5 times more viscous than LVM.

When HVM and LVM are mixed together at various molar ratios, the logarithmic dependence of the viscosity on the mixture composition is not linear, as predicted by eq. (1) developed for mixtures of liquids with similar intermolecular interactions and molar volumes. Experimental viscosity values measured at temperature range of 20–70°C along with those calculated from eq. (1) are shown in Figure 1. All the viscosities show deviations from the theoretical values, the higher, the lower the temperature is.

Figure 1 does not show the results for bis-GMA/TEGDM system, which were presented earlier in Ref. 1; however, the general tendency is the same. A qualitatively similar but weaker effect has been observed also for mixtures of styrene with some alkanols.²³ Such deviations are usually described by eq. (2), which is commonly used to predict the excess

physicochemical and thermodynamic properties²³ depending on composition and/or temperature and has great importance in understanding the nature of the molecular aggregation that exists in binary mixtures.²⁴ The exemplary excess logarithm viscosities are presented in Figure 2 for UDMA/TEGDM system; the excess logarithm viscosities for bis-GMA/TEGDM system have been shown in Ref. 1.

The deviations of viscosity from linearity are negative over the whole composition and experimental temperature ranges. Minimum of $(\ln \eta)^E$ values for all the systems studied appears for compositions close to equimolar, within the whole range of experimental temperatures. Similarly as we suggested for bis-GMA/TEGDM system,¹ the strong increase in the viscosity deviations with the decrease in HVM content down to about 80 mol % may indicate breaking of hydrogen bonding between the molecules of HVM, whereas negative values of the deviations suggest that interactions between the molecules of the same type (in individual monomers) are stronger than those between two molecules of different types (HVM and LVM). All the remaining investigated monomer pairs show an analogous behavior.

If the $(\ln \eta)^E$ values could be treated as a measure of changes in intermolecular interactions in two-monomer systems, it would be of interest to compare them for all the monomer pairs investigated in this work. The comparison of $(\ln \eta)^E$ at 20°C is shown in Figure 3.

The comparison shows that deviation of viscosity from the theoretical value for each two-monomer system is substantially different indicating differences in intermolecular interactions between the monomer pairs in these systems. The results suggest that (i) the addition of PEGMM decreases intermolecular interactions between bis-GMA or bis-MGMA molecules to a higher degree than the addition of TEGDM does and/or (ii) possible interactions between HVM and PEGMM molecules are weaker than between HVM and TEGDM molecules. The lowest deviations for UDMA/TEGDM couple result from the weakest H-bonding in UDMA.

POLYMERIZATION KINETICS

Kinetic curves measured at 20°C for all the monomer pairs (exception: bis-GMA/PEGMM at 30°C) are depicted in Fig. 4.

As can be seen, at such polymerization conditions a MRC appears in every system. It is observed even in the linear system (bis-MGMA/PEGMM) where the determining factor is only viscosity. Generally, the propagation becomes diffusion controlled when the diffusion rate coefficient k_{diff} falls below the value of the propagation rate coefficient, k_p . For methacrylates, k_p is of the order of 3×10^2 – $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.²⁵

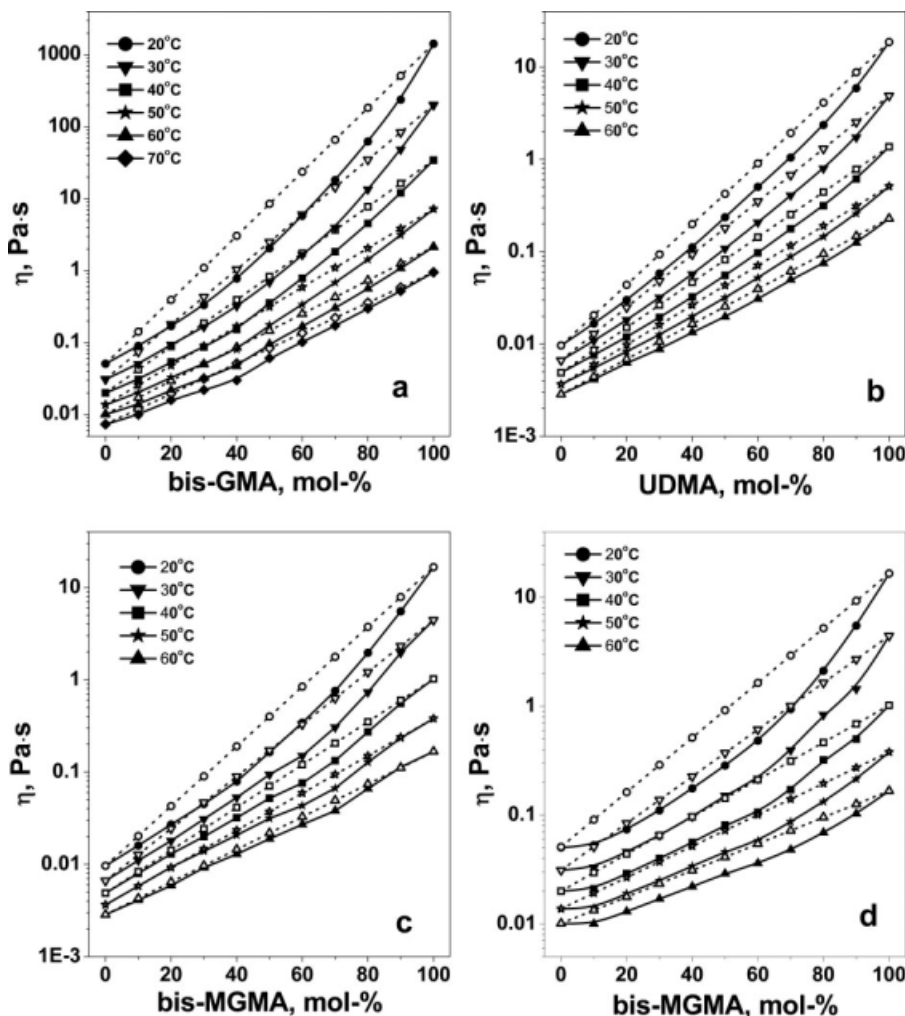


Figure 1 Experimental and calculated η values as a function of the high viscosity monomer molar fraction and temperature. Filled symbols represent experimental values; open symbols represent calculated values. (a) bis-GMA/PEGMM, (b) UDMA/TEGDM, (c) bis-MGMA/TEGDM, (d) bis-MGMA/PEGMM.

Calculations of k_{diff} have shown that diffusional control of the propagation from the beginning of the polymerization is possible only in the case of neat bis-GMA at 20°C ($k_{diff} = 4.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). However, the rapid increase in viscosity of highly viscous systems during the polymerization at relatively low temperatures quickly leads to diffusional limitations of propagation also in other than bis-GMA/TEGDM systems and to the appearance of the MRC. When the polymerization temperature increases, the viscosity drops sharply and the effect of the initial viscosity becomes smaller. This is especially pronounced for systems containing UDMA and bis-MGMA, as can be observed on the plots $R_p^{max} = f(\text{HVM content})$ obtained at various polymerization temperatures (Fig. 5).

For systems of highest viscosity, bis-GMA/TEGDM and bis-GMA/PEGMM, MRCs are observed at all the polymerization temperatures. It is interesting that in these two cases the increase in the polymerization

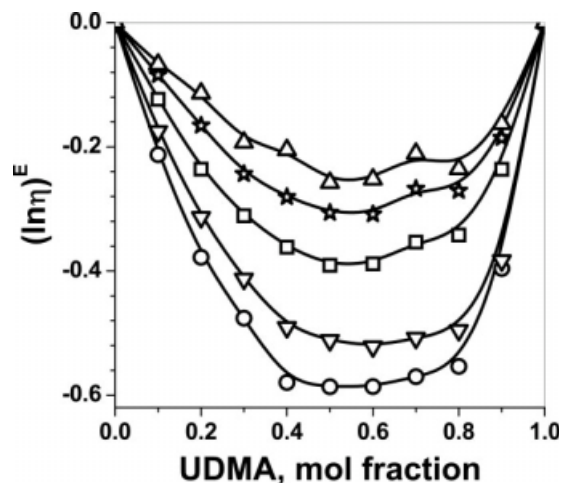


Figure 2 Deviations in $\ln \eta$ versus the molar fraction of UDMA with TEGDM: (○) 20, (▽) 30, (□) 40, (☆) 50, and (Δ) 60°C.

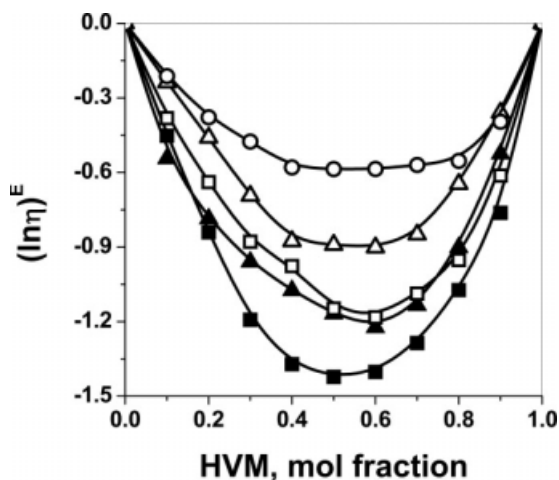


Figure 3 Deviations in $\ln \eta$ at 20°C versus the molar fraction of high viscosity monomer for various monomer pairs: (■) bis-GMA/PEGMM, (▲) bis-MGMA/PEGMM, (□) bis-GMA/TEGDM, (Δ) bis-MGMA/TEGDM, and (○) UDMA/TEGDM.

temperature above 60°C causes a decrease (for bis-GMA/TEGDM) or a suppression of the increase (for bis-GMA/PEGMM) of the R_p^{\max} value, but only in a range of compositions. Generally, a decrease of the polymerization rate with temperature rise at higher polymerization temperatures has been observed in many cases²⁶ but discussion of this phenomenon is beyond the scope of this work.

The monomer ratio in MRC changes with temperature: the higher temperature, the more of HVM in the system is needed to reach the viscosity level nec-

essary for MRC appearance (Fig. 5 and 1). This points to the crucial role of system viscosity in its polymerization behavior. However, in the case of two systems of lower viscosity: bis-MGMA/TEGDM and bis-MGMA/PEGMM at two highest polymerization temperatures (50 and 60°C) no MRC occurred. In these two temperatures elimination of the LVM to increase the viscosity of the system was able only to suppress the termination, which resulted in the increase in R_p^{\max} , but was insufficient to affect the propagation before reaching this polymerization point. The results seem to suggest that the formation of the polymer network, which affects both the termination and propagation processes, was less important, because the general picture of the dependence $R_p^{\max} = f(\text{HVM content})$ for the bis-MGMA/TEGDM (crosslinking) and bis-MGMA/PEGMM (linear) systems is qualitatively similar. Moreover, the increase in the maximum polymerization rate after dilution of the difunctional HVM with the tetrafunctional LVM clearly points to the determining role of the initial viscosity of the system in the MRC appearance. However, the formation of the more dense polymer network in the case of the UDMA/TEGDM system, which viscosity is comparable to the viscosity of the bis-MGMA/TEGDM system, is probably the reason of the MRC appearance even at 60°C.

Because R_p^{\max} is a function of viscosity and the latter is a function of the polymerization temperature, we plotted R_p^{\max} as a function of these two variables (Fig. 6). Figure 6 is analogous to Figure 5, but in the former the viscosity is shown directly on

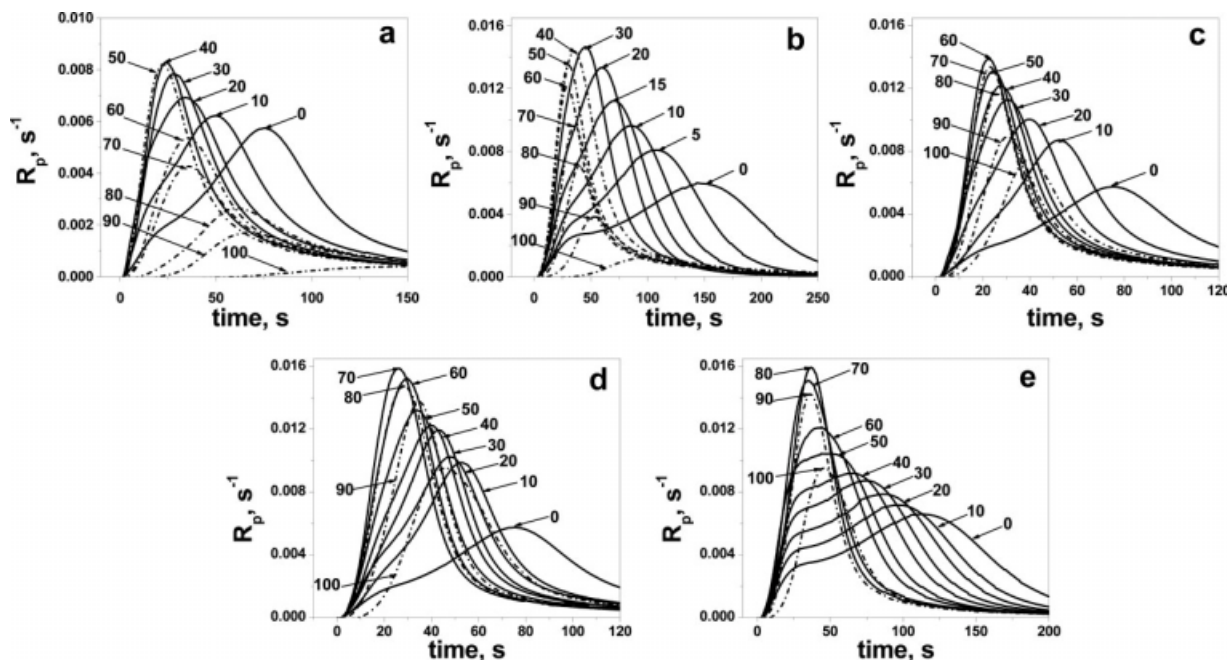


Figure 4 Rate profiles for HVM/LVM polymerization at 20°C: (a) bis-GMA/TEGDM, (b) bis-GMA/PEGMM (at 30°C), (c) UDMA/TEGDM, (d) bis-MGMA/TEGDM, (e) bis-MGMA/PEGMM. The numbers indicate the HVM content (mol %) in the feed.

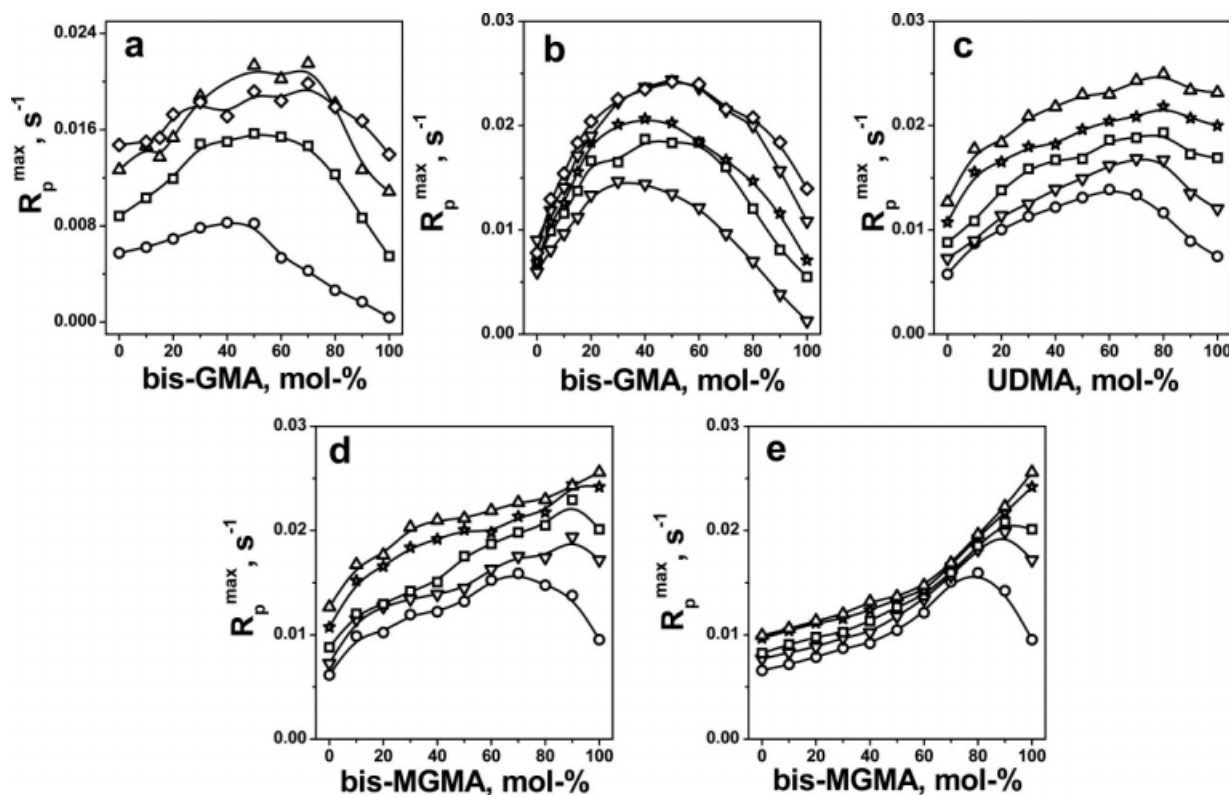


Figure 5 R_p^{\max} as a function of HVM molar fraction and polymerization temperature: (○) 20, (▽) 30, (□) 40, (☆) 50, (Δ) 60, and (◇) 70°C. (a) bis-GMA/TEGDM, (b) bis-GMA/PEGMM, (c) UDMA/TEGDM, (d) bis-MGMA/TEGDM, (e) bis-MGMA/PEGMM.

x axis, whereas in the latter the viscosity is included in the content of the HVM. However, the curves shown in Figures 5 and 6 draw a substantial distinction in trends: although HVM content in the MRC increases with the temperature (Fig. 5), it does not bring the system to the same MRC viscosity as at lower temperature because MRC's initial viscosity decreases when the temperature is raised (Fig. 6).

This effect must be associated with other factors than the initial viscosity. One of them seems to be the change in the double bond conversion degree when R_p^{\max} is reached. This conversion, defined as p_{peak} , can be found from kinetic curves expressed in the $R_p = f(p)$ form (not shown here), where p is double bond conversion depending on the polymerization time. The parameter discussed increases with temperature due to the enhanced mobility of the reacting species. With the increase in polymer concentration (and crosslinking density in crosslinking systems), the viscosity of the polymerizing system at this reaction point also increases, which needs compensation by a reduction of the initial viscosity. An exemplary dependence of p_{peak} on temperature and HVM content for UDMA/TEGDM system is presented in Figure 7. The arrow shows an increasing tendency in MRC's p_{peak} with temperature.

The results presented in Figure 6 suggest that the MRCs occur in a limited range of the initial viscos-

ities. In Figure 8 we put together the values of all the initial viscosities of the MRCs along with viscosities of the neat monomers. Despite the very wide range of the monomer viscosities (approximately 10^{-3} – 10^3 Pa s), the range of MRC initial viscosities is narrow (0.06–2 Pa s) and becomes even narrower for a given polymerization temperature; e.g., at 40°C MRC's viscosities of five different HVM/LVM systems are in the range of only 0.2–0.6 Pa s. In the latter case the differences in MRC initial viscosities are caused only by individual properties of the monomers and their mixtures, like reactivity, hydrogen bonding, crosslinking density, etc.

CONCLUSIONS

The investigations undertaken in this work were aimed to give a better insight into the appearance and behavior of the MRC in two-monomer systems. The kinetic observations were accompanied by detailed viscosity measurements. The latter proved significant negative deviations from the theoretical values (characterized by excess logarithm viscosities) that interactions between the molecules of the same type (in individual monomers) are stronger than those between two molecules of different types (HVM and LVM); this is in agreement with our

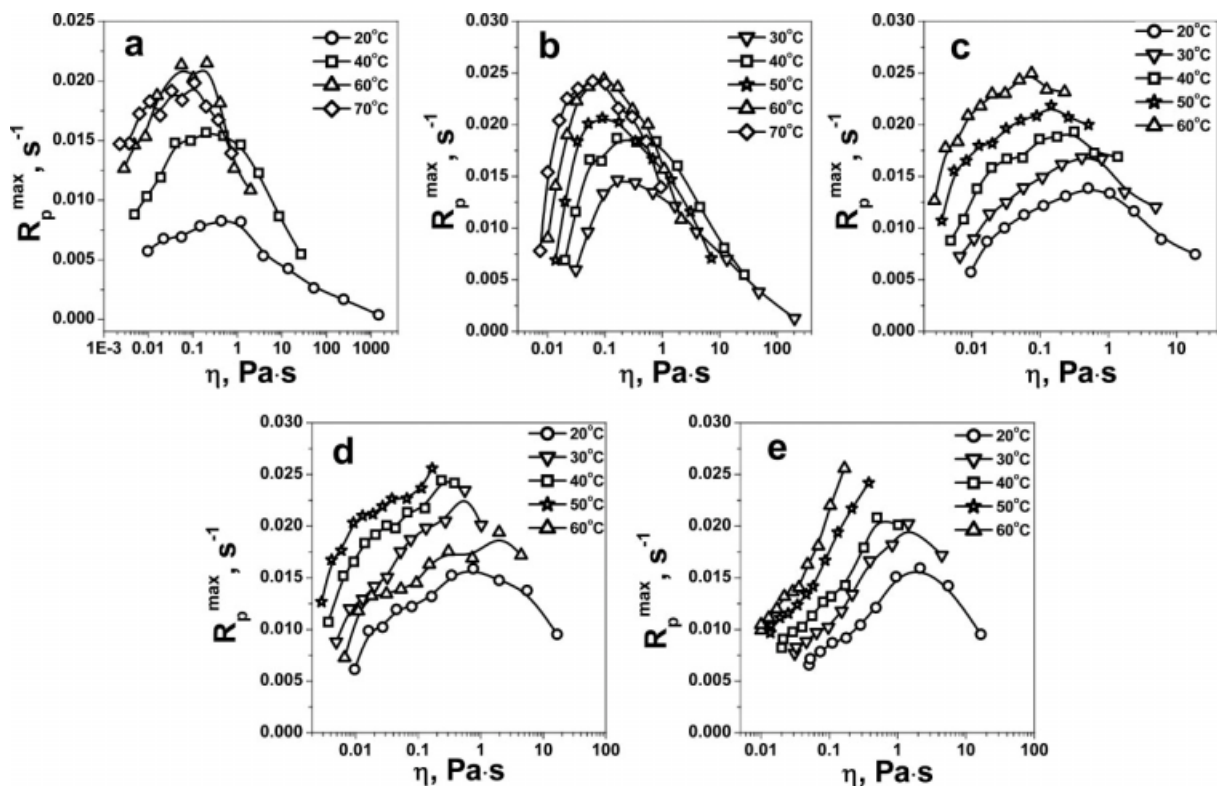


Figure 6 R_p^{\max} as a function of the initial viscosity and polymerization temperature. (a) bis-GMA/TEGDM, (b) bis-GMA/PEGMM, (c) UDMA/TEGDM, (d) bis-MGMA/TEGDM, (e) bis-MGMA/PEGMM.

earlier findings for one only system.¹ The MRC appearance depends mainly on the initial viscosity of the two-monomer system, which controls the mobility of the reacting species and is observed even in linear systems. MRC viscosity corresponds to a viscosity, which is so high that hampers termination markedly but still does not control significantly the propagation. This suggests in turn that the MRC vis-

cosities of different HVM/LVM systems should be similar. This was really observed: the initial viscosity of all the monomer mixtures showing MRC lay in the range of 0.06–2 Pa s (in the whole range of temperatures studied), which is narrow compared to the range of viscosities of the monomers (approximately 10^{-3} – 10^3 Pa s).

The HVM content in MRC increases with the temperature to compensate the reduction of the

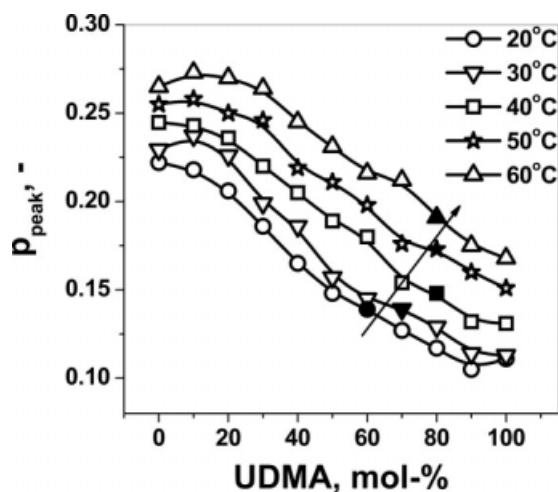


Figure 7 UDMA/TEGDM system: p_{peak} as a function of UDMA molar fraction and polymerization temperature. Filled points correspond to MRCs; the arrow indicates the trend of MRC's p_{peak} changes with temperature increase.

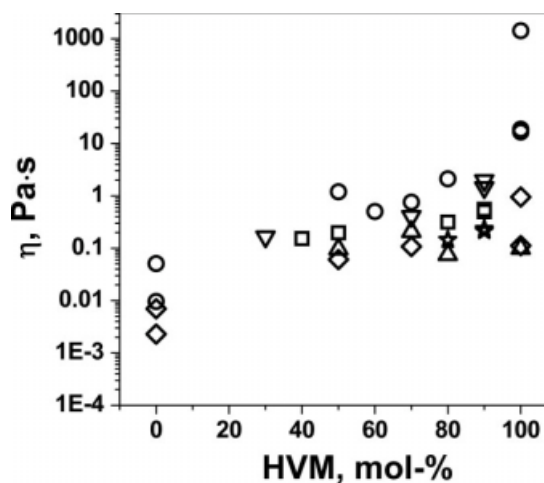


Figure 8 Comparison of the initial viscosities of the most reactive compositions and the neat monomers at various temperatures: (○) 20, (▽) 30, (□) 40, (☆) 50, (Δ) 60, and (◇) 70°C.

viscosity. However, such a compensation is not full, since the MRC's initial viscosity decreases when the temperature is raised. This phenomenon may be partly associated with the increase in conversion degree at the maximum polymerization rate, which results in a higher viscosity of the polymerizing system at this polymerization point. Additional differences in MRC initial viscosities are caused by individual properties of the monomers and their mixtures, like reactivity, hydrogen bonding, cross-linking density, etc.

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