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The effect of cross-linking density on the termination mechanism in network radical polymerization

RAPID COMMUNICATION

Summary — The diffusion control of termination in radical polymerization involving multivinyl monomers results in an alternative mechanism of bimolecular termination, namely in the reaction diffusion. By studying photoinitiated polymerization and copolymerization of mono- and dimethacrylates, the influence of polymer cross-linking density and monomer structure on reaction diffusion parameter *R* was determined. A reduction of cross-linking density results in the shift of reaction diffusion controlled termination towards high conversion. In loosely cross-linked systems, the reaction diffusion may not control the termination. It is proposed that the apparent increase in *R* with conversion beyond its steady value that begins at the conversion range of maximum polymerization rate is associated with a change of termination mechanism. Then the rate equations for bimolecular reaction fail to describe the process.

Key words: radical polymerization, termination mechanism, reaction diffusion, multivinyl monomers, cross-linking density.

The termination in free-radical polymerization is controlled by diffusion from the very beginning of the process. This makes the rate coefficient of bimolecular termination, k_t^b, in the reaction:

$$P_i^\bullet + P_j^\bullet \xrightarrow{k_t^b} \text{Polymer} \tag{1}$$

varying with conversion due to increase of viscosity during polymerization and/or network formation. For cross-linking systems, diffusional limitations of movement, both on macroradicals as well as on monomer molecules, lead to an additional way of eliminating of radicals from further reaction, namely to radical trapping (which is a monomolecular process characterized by the monomolecular termination rate coefficient k_t^m) [1, 2]:

$$P_i^\bullet \xrightarrow{k_t^m} (P_j^\bullet)_{\text{trapped}} \tag{2}$$

An alternative mechanism of bimolecular termination is the reaction diffusion [1—4]. This mechanism becomes important after the onset of autoacceleration. At this reaction stage virtually all free radicals are immobilized by entanglements or by polymer network to such an extent that their centers of mass are essentially immobile on the time scale of propagation, and the only possible diffusive motion of radical chain ends becomes the propagation reaction. The rate coefficient for termination by reaction diffusion, $k_{t,RD}$, is proportional to the rate coefficient for propagation k_p and the concentration of double bonds $[M]$:

$$k_{t,RD} = R \cdot k_p \cdot [M] \tag{3}$$

where *R is the reaction diffusion parameter.*

The overall bimolecular termination rate coefficient is the sum of k_t^b and $k_{t,RD}$.

The reaction diffusion parameter *R* first decreases with the increase of conversion, but starting from the conversion when the reaction diffusion begins to dominate the termination process (*i.e.*, $k_t^b << k_{t,RD}$), the value of *R* remains constant. For multimethacrylates the plateau level of *R* of the order of 2—3 L/mol was found [3].

The reaction diffusion parameters can be conveniently determined from the postpolymerization curves (recorded for the reaction continuing in the absence of initiation, *i.e.*, for the light-induced polymerization, when after stopping irradiation the process occurs in the

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dark). Assuming bimolecular termination, R can be calculated from the following equation:

$$\frac{1}{(R_p)_1}-\frac{1}{(R_p)_0}=2\cdot R\cdot(t_1-t_0) \qquad (4)$$

where: R_p *is the polymerization rate,* t *is the polymerization time, subscripts* 0 *and* 1 *denote the parameters at the moment of stopping the irradiation and after the time of the reaction in the dark, respectively.*

When the bimolecular reaction is the only termination mechanism, a constant R value should be observed in the whole range of conversions with the reaction diffusion control of termination, (*i.e.* up to the end of the reaction). However, the data presented in some works showed that R value may increase with conversion after its plateau range [3, 4]. Since the mobility of the system decreases with the increase of conversion, such an effect may, in our opinion, be associated with a change in termination mechanism, which causes the bimolecular reaction rate equations to fail to describe the process correctly.

The aim of this work was to find how the monomer structure and cross-linking density affect the reaction diffusion parameter and its dependence on conversion in free radical polymerization involving a multivinyl monomer.

EXPERIMENTAL

(Ethylene glycol) dimethacrylate (EGDM, n = 1), (diethylene glycol) dimethacrylate (DEGDM, n = 2), (tetraethylene glycol) dimethacrylate (TETGDM, n = 4), all of formula I, and lauryl methacrylate (LM, formula II) were supplied by Aldrich; 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (bis-GMA, formula III) was supplied by Polysciences and the photoinitiator (Irgacure 651) by Ciba. All the monomers (except of bis-GMA) were purified by column chromatography before use.

The reaction rate profiles and conversions were determined at 40°C in argon atmosphere with differential scanning photocalorimetry as described previously [5]. For the determination of R, series of experiments were performed in which the initiating light was switched off at a given time (degree of double bond conversion), but the polymerization rate was still monitored on the DSC even in the dark period. The decrease of the reaction rate over 100 s reaction time after the light was removed [$t_1 - t_0 = 100$ in Eq. (4)] was used to calculate a value of R.

RESULTS AND DISCUSSION

A change of the cross-linking density may be achieved by increasing the length of spacer groups between two unsaturations in the monomer molecule or by copolymerization of a multifunctional monomer with various amounts of a difunctional (monovinyl) one. In this work both methods were used.

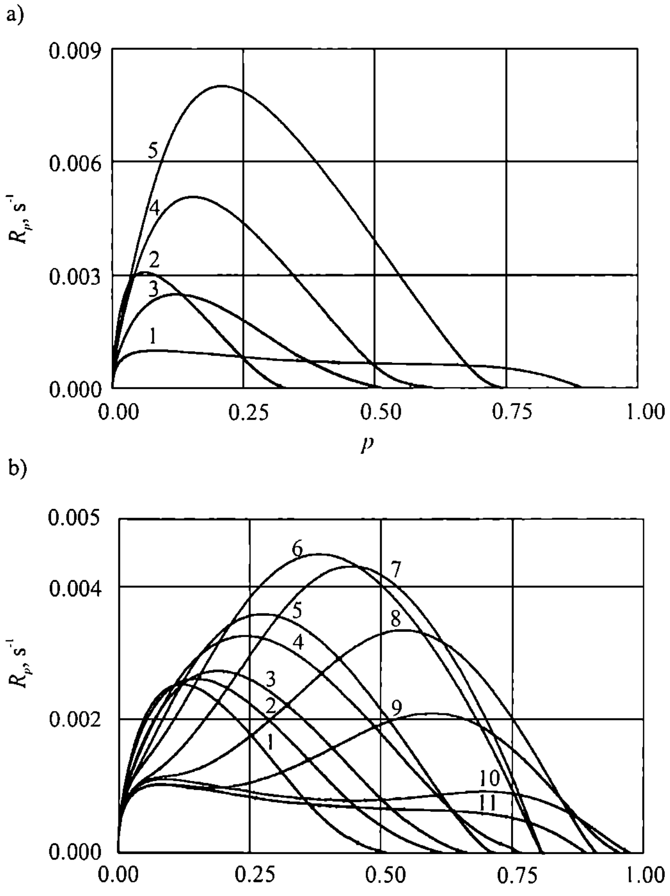
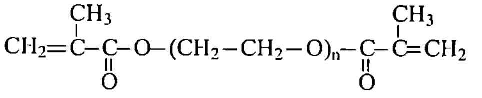
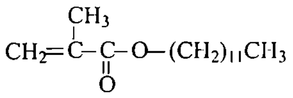


Fig. 1. Polymerization rate (R_p) *vs. double bond conversion (p) kinetic curves for the photoinitiated polymerization of: (a) various methacrylates: 1 — LM, 2 — bis-GMA, 3 — EGDM, 4 — DEGDM, 5 — TETGDM; (b) EGDM/LM mixtures at various molar ratios: 1 — 100/0; 2 — 80/20; 3 — 60/40; 4 — 50/50; 5 — 40/60; 6 — 30/70; 7 — 20/80; 8 — 10/90; 9 — 5/95; 10 — 1/99; 11 — 0/100*



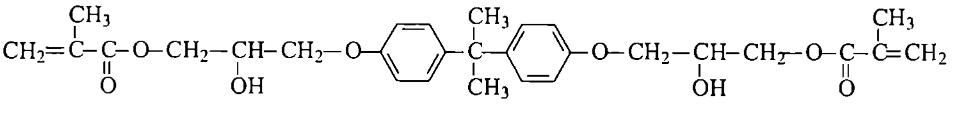
$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle O}{\|}}{C}-O-(CH_2-CH_2-O)_n-\underset{\underset{\displaystyle O}{\|}}{C}-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$$

(I)



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle O}{\|}}{C}-O-(CH_2)_{11}CH_3$$

(II)



(III)

The kinetic curves of the photoinitiated polymerization of multiethylene glycol dimethacrylates are shown in Fig. 1a together with the kinetic curves of polymerization of monovinyl LM that yields linear polymer (all monomers have similar viscosities) and for bis-GMA (viscosity higher by about 1000 times). The data presented in Fig. 1a confirm that autoacceleration is enhanced by network formation and that higher cross-linking density or higher viscosity of the system reduce both the polymerization rate and the conversion degree of double bonds.

Figure 1b presents the kinetic curves obtained for copolymerization of EGDM with various amounts of LM. A decrease of cross-linking density by adding LM to EGDM results in an increase and then the decrease of the maximum polymerization rate (R_p^{max}). The highest R_p^{max} value occurs at the EGDM/LM molar ratio equal to 30:70 (curve 6). However, the attainable double bond conversion decreases with the increase of cross-linking density.

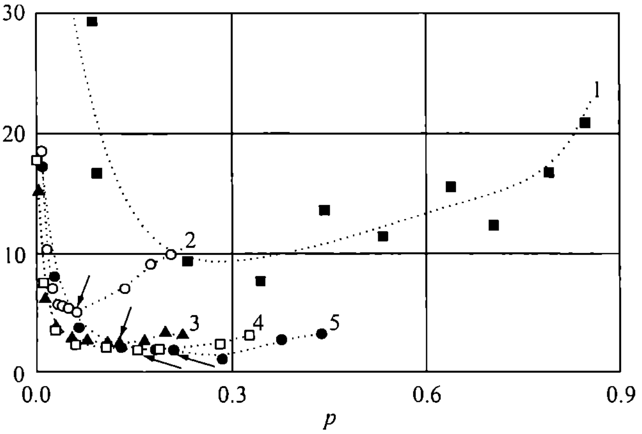


Fig. 2. Dependence of the reaction diffusion parameter (R) on the degree of double bond conversion (p) for the photoinitiated polymerization of various methacrylates: 1 — LM, 2 — bis-GMA, 3 — EGDM, 4 — DEGDM, 5 — TETGDM. Arrows indicate degrees of double bond conversion at which maximum polymerization rate occurs

The calculated R-values for the investigated monomers as a function of double bond conversion are presented in Fig. 2. It is clearly seen that the reaction diffusion parameters for multiethylene glycol dimethacrylates drop rapidly to a constant value 2—3 L/mol as the reaction progresses (curves 3—5). For the monomer with the longest spacer, TETGDM (curve 5), the plateau is shifted towards highest conversion indicating that the lower cross-linking density is, the later reaction diffusion mechanism begins to dominate the process of termination. However, after the range of conversion with steady R-values, an increase of R is observed; the conversion at which the rise starts increases with the length of the spacer group.

Since the calculations of R are based on Eq. (4) derived from the expressions describing bimolecular termination, a deviation from the plateau at high conversion means that Equation (4) no longer describes correctly the processes, which dominate the termination during the dark reaction. On the other hand, it is widely accepted that the contribution of monomolecular reaction [Eq. (2)] to the overall termination process increases as the reaction progresses [1, 6]. Kinetic modeling has shown that radical trapping becomes the main termination mechanism near the maximum polymerization rate [6, 7]. It is noteworthy that the increase of R begins at the conversion degrees that are close to those at which R_p^{max} occurs (Fig. 2). Thus, we may conclude that under the conditions applied in the polymerization of multiethylene glycol dimethacrylates, at the polymerization stage near R_p^{max}, the dominant termination mechanism during the dark reaction (and possibly during illumination) is no longer the bimolecular termination. Most probably the monomolecular one begins to dominate. The R-values for all three monomers at the plateau level are very similar, indicating that the network formation affects their reaction diffusion parameters in the same way.

The dependence of R on conversion for bis-GMA polymerization is quite different (Fig. 2, curve 2). This monomer has a long, but rather stiff spacer and is very viscous. The latter greatly hinders the mobility of the reacting chains from the very beginning of the polymerization. It seems that due to the high initial viscosity and network formation during bis-GMA polymerization its R "has not enough time" to reach a plateau where the termination occurs *via* bimolecular process controlled by reaction diffusion, before another mode of termination begins to dominate.

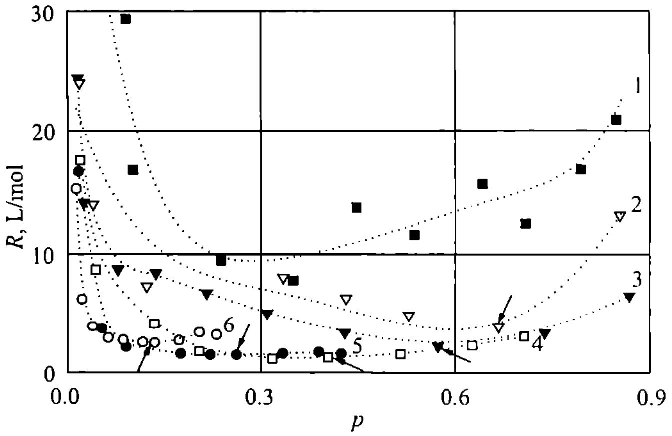


Fig. 3. Dependence of the reaction diffusion parameter (R) on the degree of double bond conversion (p) for the photoinitiated polymerization of EGDM/LM mixtures at various molar ratios: 1 — 0/100, 2 — 5/95, 3 — 10/90, 4 — 30/70, 5 — 50/50, 6 — 100/0. Arrows indicate degrees of double bond conversion at which maximum polymerization rate occurs

The polymerization of LM (curve 1) occurs almost without the gel-effect. Under the conditions used the steady state is observed to the double bond conversion of about 0.35. It is interesting that during LM polymerization a plateau in *R*-values is not observed, which suggests the lack of reaction diffusion control over the termination mechanism. The lowest *R*-value obtained is about 10 L/mol, which corresponds to those for simple methacrylates [1].

The dependence of *R* on double bond conversion for various EGDM/LM molar ratios is shown in Fig. 3. A reduction of cross-linking density by increasing LM content results in a shift of the reaction diffusion controlled termination towards high conversion. The same applies to the point of rise of *R* up from its plateau level. Beginning from 10/90 monomer ratio *R* almost does not plateau which may indicate that the reaction diffusion is not controlling the termination during polymerization of formulations containing more than 90 mol % of LM.

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