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Effects of cyclization and electrostatic interactions on the termination rate of macroradicals in free-radical crosslinking copolymerization

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Summary

Effects of cyclization and ionic group contents on the termination rate of macroradicals formed at zero monomer conversion were investigated. For this purpose, the pregel regime of free-radical methyl methacrylate / ethylene glycol dimethacrylate (MMA/EGDM) and acrylamide / N,N'-methylenebisacrylamide (AAm/BAAm) copolymerization systems was studied by means of the dilatometric technique. To eliminate the chain-length dependent variation of the termination rates, different sets of experiments were carried out each at a fixed monomer and initiator concentration. At low crosslinker contents, the termination rate of zero-conversion macroradicals was enhanced in crosslinking copolymerizations compared to linear polymerization. This is due to the cyclization reactions which reduce the size of the macroradical coils and thus, enhance the termination rates due to the lowering of the thermodynamic excluded volume effect. As the amount of the crosslinker increases, an enhancement in the initial rate of polymerization is observed in all series of experiments, indicating that steric effects on segmental diffusion dominate at high crosslinker contents. The results also indicate a slower rate of termination of ionic macroradicals compared to the non-ionic radicals of the same molecular weight and points the significance of the thermodynamic excluded volume effect on rising the ionic group content.

Introduction

Free-radical crosslinking copolymerization (henceforth referred as FCC) of vinyl/divinyl monomers is a commonly used procedure for preparing polymer gels. To predict the final properties of polymer gels, their structural characteristics are extremely important, and these in turn depend on the history of the gel formation process by FCC. Previous studies have shown that the mechanism of gel formation in FCC differs appreciably from the prediction of the gel formation theories (1). The difference between the actual and predicted behaviour of FCC has mainly been attributed to cyclization and to diffusion control, which are not properly accounted for in the gel formation theories.

Cyclization is a characteristic feature of FCC especially at zero conversion, at which it strongly influences the polymer structure. A cycle during FCC forms when a macroradical attacks a double bond pendant in the same kinetic chain. Cyclization is responsible for the formation of compact intramolecularly crosslinked structures, called microgels, in the pregel regime of FCC (2). On the other hand, termination reactions during the gel formation process by FCC are known to be diffusion controlled right down

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to zero conversion. It is usual to distinguish two diffusion steps in the termination process (3): (1) translational diffusion of the center-of-mass of the macroradicals toward each other through the solvent, and (2) segmental diffusion of two segments bearing radical ends to a position in which they are able to react each other; this occurs by translational and rotational diffusion or by micro-Brownian motion of these segments. Most evidence points out that the second diffusion step, namely the segmental diffusion is rate controlling at low monomer conversions (4-6). The diffusion rate of segments is affected by both the size and the structure of macroradical coils, which we will define as thermodynamic and steric excluded volume effects, respectively. In larger coils, the segmental diffusion of the radical center out of the coil to encounter another radical becomes difficult; as a result, in larger coils a radical will be found more difficult by other radicals due to the thermodynamic excluded volume effect. On the other hand, in compact macroradicals, the mobility of segments is reduced so that the diffusion of radical centers toward each other is restricted due to the steric excluded volume effect (Figure 1).

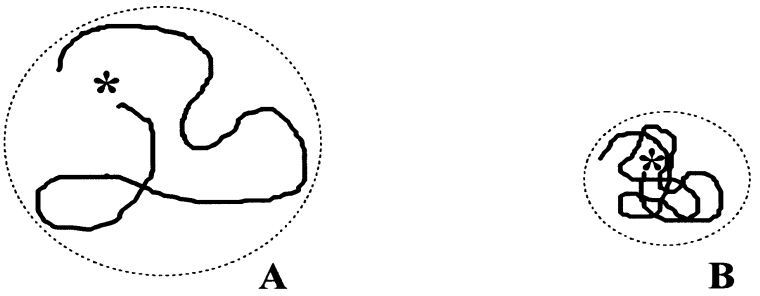

Fig. 1. Two macroradical coils having the same kinetic chain length with expanded (A) and shrinked (B) conformations. Thermodynamic and steric excluded volumes determine the process of the segmental diffusion in coils A and B, respectively.

In the present study, we intend to elucidate the relative contributions of thermodynamic and steric excluded volumes on the termination rate of macroradicals during FCC. For this purpose, we investigated the termination rate of polymer radicals formed at zero monomer conversion, at which the second order reactions such as the crosslinking and multiple crosslinking reactions do not occur. To eliminate chain-length dependent variation of the termination rates, different sets of experiments were carried out each at a fixed monomer and initiator concentration. Macroradicals of the same kinetic chain length but of different sizes and structure were obtained by including into the reaction mixture a crosslinker or an ionic comonomer, both in small quantities. Addition of a crosslinker in the feed leads, at zero monomer conversion, to the formation of cycles, which reduces the size of the macroradicals formed. Addition of an ionic comonomer in the feed causes formation of ionic macroradicals, that exhibit, compared to the nonionic macroradicals, an expanded conformation in solution due to the electrostatic interactions. Two commonly used comonomer systems for the gel synthesis were selected for this purpose, namely methyl methacrylate / ethylene glycol dimethacrylate (MMA/EGDM) and acrylamide / N,N'-methylenebisacrylamide (AAm/BAAm) systems. The pregel regime of FCC reactions was studied by means of the dilatometric technique. Polymerization solvents, toluene and water for MMA/EGDM and AAm/BAAm systems respectively,

were used at a high concentration to ensure that strong cyclization occurs during the reaction (2).

Experimental

Materials

Commercially available NBM, EGDM, AAm, acrylic acid (AAc), 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and BAAm monomers and the initiators 2,2' azobisisobutyronitrile (AIBN) and potassium peroxodisulfate ($K_2S_2O_8$) were purified by usual methods. The ionic comonomers sodium acrylate (NaAc) and AMPS sodium salt (NaAMPS) were prepared *in situ* by adding equimolar amounts of sodium hydroxide and AAc or AMPS in the polymerization mixture, respectively. The polymerization solvents toluene (Merck p.a.) and water were twice distilled before use. Sodium hydrogen carbonate ($NaHCO_3$) and sodium thiosulfate ($Na_2S_2O_3$) (both analytical grades) were used without further purification.

Polymerization procedure

MMA - EGDM copolymerizations were carried out at a monomer concentration of 2.3 M (24.4 v/v %) in toluene at 60±0.1°C with AIBN as the initiator. AAm - BAAm copolymerizations were carried out at a monomer concentration of 0.5 M (35g/L) in water at 40 ± 0.1 °C with $K_2S_2O_8$ / NaS_2O_3 redox initiator system in the presence of $NaHCO_3$ buffer. Concentrations used were $1x10^{-3}$ M for $K_2S_2O_8$, NaS_2O_3, and $NaHCO_3$. NaAc and NaAMPS were used as the ionizable comonomer of AAm. The conversion of monomers up to the onset of macrogelation was followed by dilatometry. The dilatometers consisted of a blown glass bulb, approximately 25 ml in volume connected to a 30 cm length of 1.5 mm precision-bore capillary tubing with a ground-glass joint. The meniscus was read with a millimetric paper to 0.2 mm. The polymerization technique used was described in detail elsewhere (7). The reproducibility of the kinetic data was checked by repeating the experiments. The deviation in the initial slopes of time versus conversion data between two runs was always less than 3%.

Different series of experiments were carried out. In the first series of experiments, monomer ($[M]_0$) and initiator ($[I]_0$) concentrations were held constant while the mole fraction of the crosslinker in the monomer mixture (f_{20}) was varied from 0 to $0.12x10^{-2}$. In the second series of experiments, monomer (AAm), crosslinker (BAAm), and initiator concentrations were held constant while the mole fraction of the ionic comonomer NaAc or NaAMPS was varied from 0 to 0.08. Typical monomer conversion x versus time t plots for various crosslinker (f_{20}) and NaAc contents are shown in Figures 2A and 2B, respectively. The initial polymerization rates, $(dx/dt)_0$, were estimated from the lines drawn through the data points for $x < 0.10$ by using a least-squares fit.

Results and discussion

Figure 3A shows the variation of the initial rate of polymerization $(dx/dt)_0$ in MMA/EGDM and AAm/BAAm systems with the crosslinker concentration (f_{20}). In each series of experiments shown in the figure, the total monomer and the initiator concentrations were held constant, so that the chain length of macroradicals was fixed. At low crosslinker contents, the initial rates are slow compared with the linear polymerization. As the amount of crosslinker increases, an enhancement in the initial rate of polymerization is observed in all series of experiments. The enhancement of the rate of polymerization with increasing f_{20} has also been observed previously for moderate to high

crosslinker concentrations (1,8-12). However, reduced polymerization rate at low crosslinker contents was recently observed by us and the present results shown in Figure 3A confirm this phenomenon (7). Figure 3B shows the initial rates in AAm/BAAm copolymerization plotted as a function of the concentration of the ionic comonomer NaAc and NaAMPS. It is seen that the initial rate strongly depends on the amount of the ionic comonomer and it increases on rising NaAc or NaAMPS concentration in the feed.

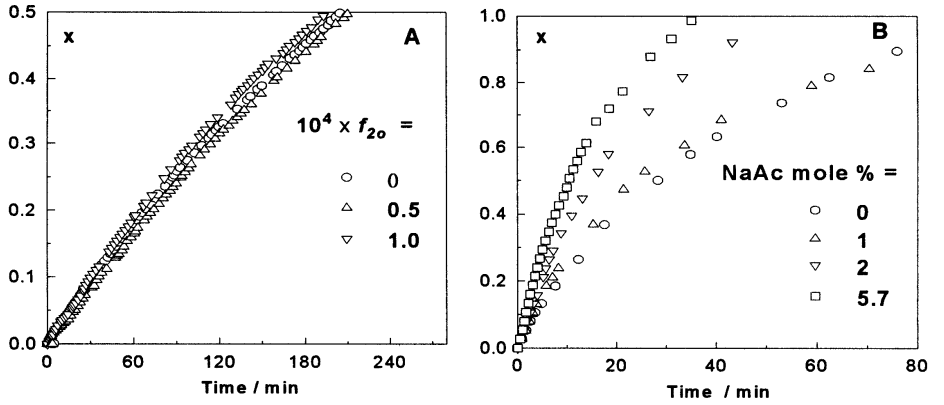

Fig. 2. Variation of the conversion x versus time histories in FCC with the crosslinker (A) and the ionic comonomer concentration (B). **(A)** MMA/EGDM system. $[I]_0 = 0.02$ M. **(B)** AAm/BAAm system. $f_{2o} = 5 \times 10^{-4}$.

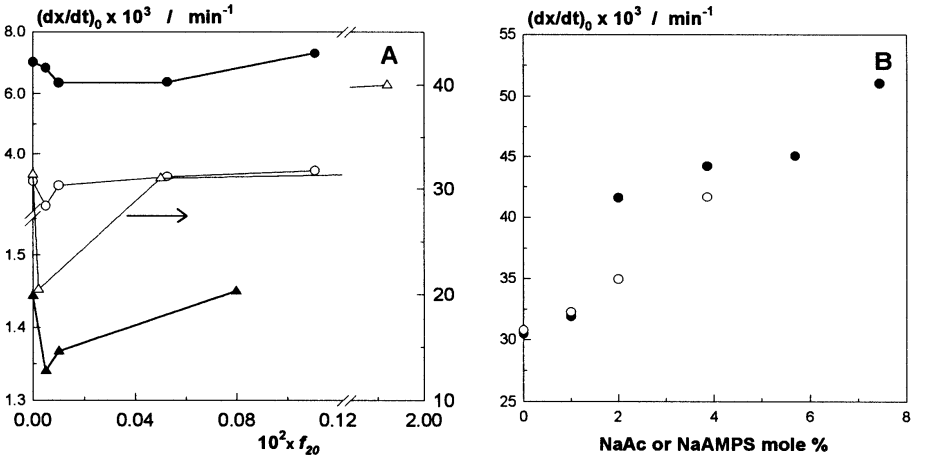

Fig. 3. Variation of the initial rate of polymerization $(dx/dt)_0$ with the crosslinker (f_{20}) and ionic comonomer (NaAc or NaAMPS) concentration. **(A)** MMA/EGDM system: $[I]_0$ = 0.1 (●), 0.02 (○), and 3.75×10^{-3} M (▲). AAm/BAAm system: (Δ). **(B)** AAm/BAAm system: $f_{2o} = 5 \times 10^{-4}$, Ionic comonomer = NaAc (●), NaAMPS (○).

Invoking steady-state approximation for radicals R^*, the expression for the rate of polymerization in FCC is given by (12):

$$dx/dt = k_p[R*](1-x) \quad (1)$$

$$[R*] = \left(2f\ k_d[I]/k_t\right)^{0.5} \quad (1a)$$

where k_p and k_t are the instantaneous rate constants for propagation and termination, respectively, f is the initiator efficiency, and k_d is the decomposition rate constant of the initiator I. The instantaneous propagation rate constant k_p relates to the propagation rate constant for the homopolymerization of monovinyl monomer k_{pl} through the equation (12):

$$k_p = k_{p1}\left[1+\left(2r_{21}-1\right)f_2\right] \quad (1b)$$

where f_2 is the mole fraction of the divinyl monomer (crosslinker) in the reaction mixture, and r_{21} is the reactivity ratio of vinyls on divinyl to monovinyl monomer. The expression for the initial rate of polymerization follows from eq (1) as:

$$\left(dx/dt\right)_0 = k_{p0}[R*]_0 \quad (2)$$

$$[R*]_0 = \left(2f\ k_d[I]_0/k_{t0}\right)^{0.5} \quad (2a)$$

where the subscript o holds for the initial values. Previous experimental studies showed that the vinyl group reactivities in MMA/EGDM and in AAm/BAAm copolymerization systems are almost equal, i.e., $r_{21} \cong 1$ (13-15). Furthermore, since $f_{20} << 1$ in the present study, it is reasonable to assume a constant k_{p0} in each series of experiments (constant initial concentrations of the total monomer and the initiator). Thus, the relative initial termination rate constant, $k_{t0,rel,}$ which is the ratio of k_{t0} of crosslinking polymerization to that of the linear polymerization at the same reaction condition, can be calculated from eq (2) as:

$$k_{t0,rel} = \frac{k_{t0}}{k_{t0,l}} = \left(\frac{\left(dx/dt\right)_{0,l}}{\left(dx/dt\right)_0}\right)^2 \quad (3)$$

where the subscript 1 denotes the linear polymerization. In Figures 4A, $k_{t0,rel}$ values calculated using eq (3) are shown as a function of the crosslinker concentration. $k_{t0,rel}$ is greater than unity at low crosslinker contents, i.e., the termination rate constant of zero conversion macroradicals k_{t0} was enhanced in crosslinking copolymerizations compared to linear polymerization. Since we are dealing with zero conversion polymer radicals, i.e., with the polymer radicals in the absence of preformed polymers, the basic difference between linear and crosslinking copolymerization is the incorporation of cycles in the growing polymer. Cyclization reactions reduce the size of the macroradical coils; this is reflected in Figure 4A with the enhancement of the termination rates due to the lowering of the thermodynamic excluded volume effect. It must be noted that the delayed onset of gelation in good solvents as observed by Matsumoto et al. in several FCC systems is also a

result of this thermodynamic excluded volume effect (16); the reactivity of pendant vinyl groups for intermolecular reactions is much lower in good solvents than in poor solvents due to the excluded volume of the molecule. The present results suggest the significance of the thermodynamic excluded volume effect at very low crosslinker contents ($f_{20} < 1x10^{-4}$). As the crosslinker concentration (f_{20}) further increases, $k_{t0,rel}$ decreases monotonically, indicating that steric effects on segmental diffusion dominate at high crosslinker contents. As f_{20} increases, the local concentration of pendant vinyls within a coil should increase. Thus, the growing radicals would tend to form more cycles and exhibit more compact structure. According to the experimental data, the reduction in the termination rate of radicals due to the steric effects compensates more than the rate enhancement due to the decrease of the coil size.

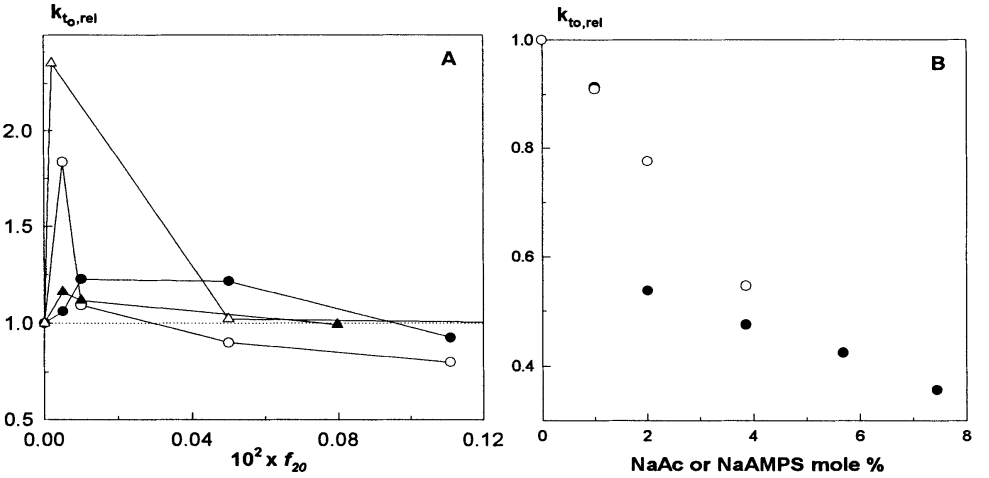

Fig. 4. Variation of the relative termination rate constant of zero conversion polymer radicals, $k_{t0,rel}$, with the crosslinker (f_{20}) and ionic comonomer (NaAc or NaAMPS) concentration. **(A)** MMA/EGDM system: $[I]_0$ = 0.1 (●), 0.02 (○), and $3.75x10^{-3}$ M (▲). AAm/BAAm system: (Δ). **(B)** AAm/BAAm system: $f_{2o} = 5x10^{-4}$, Ionic comonomer = NaAc (●), NaAMPS (○).

Another feature shown in Figure 4A is a much more steeper increase of $k_{t0,rel}$ in AAm/BAAm system compared to the MMA/EGDM system. This is probably due to the higher extent of cyclization in AAm/BAAm copolymerization (80 % compared to 30 % in MMA/EGDM system (7,9,17)), which leads to a greater decrease in the coil size at the same crosslinker concentration. Experimental data obtained at various initiator concentrations give no evidence on the chain-length dependent variation of the thermodynamic excluded volume effect.

For ionic FCC at low ionic comonomer contents, one may define $k_{t0,rel}$ as the ratio of k_{t0} of ionic FCC to that of the non-ionic FCC at the same reaction condition. In Figure 4B, $k_{t0,rel}$ values calculated for AAm/BAAm copolymerization are shown as a function of the concentration of NaAc and NaAMPS. $k_{t0,rel}$ decreases continuously on rising the ionic comonomer concentration. This indicates a slower rate of termination of ionic macroradicals compared to the non-ionic radicals of the same molecular weight and points the significance of the thermodynamic excluded volume effect on rising the ionic group content.

The results presented so far demonstrate separate contributions of thermodynamic and steric excluded volumes of zero-conversion macroradicals on their rate of termination. However, at non-zero monomer conversions, the rate of termination reactions in FCC is mainly determined by the steric effects. Figure 5A shows monomer conversion *x* versus time plots for the homopolymerizations of MMA (open symbols) and EGDM (filled symbols) at two different initial monomer concentrations. It is seen that EGDM polymerizes much more rapidly than MMA and, the difference between their rates of polymerization increases as the initial monomer concentration decreases. Using the experimental data shown in Figure 5A and using eqs (1) - (2), we calculated the normalized termination rate constants k_t / k_{t0}, and they are shown in Figure 5B as a function of the monomer conversion. A steeper decrease in k_t observed at x < 0.05 in EGDM polymerization compared to the MMA polymerization points the significance of the steric effect on the segmental diffusion. In EGDM polymerization, we always observed the appearance of a turbidity in the reaction mixture after a short reaction time. This indicates spatial inhomogeneities in the reaction solution due to the formation of microgels. The crosslink density of microgels is known to increase on rising the degree of dilution (18); this is reflected in Figure 5B with the extent of the diffusion control which is more pronounced at lower monomer concentration.

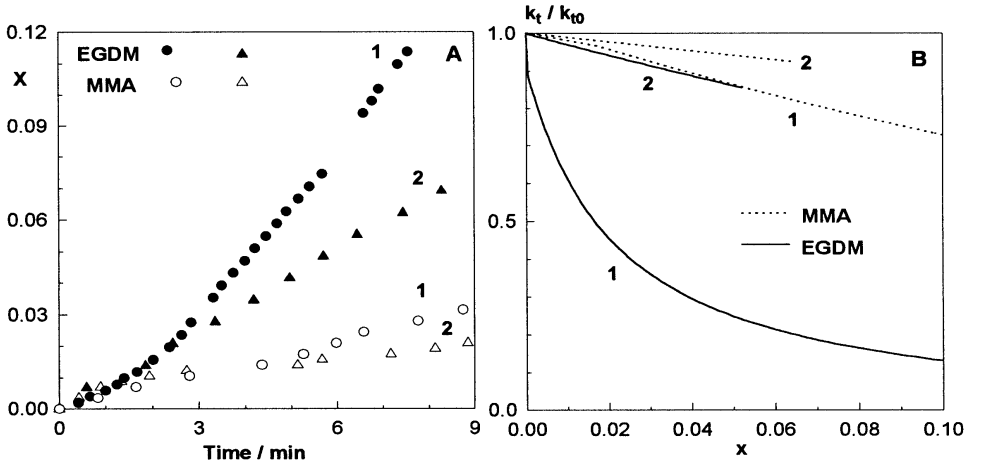

Fig. 5. Variation of the monomer conversion *x* versus time and k_t / k_{t0} versus conversion *x* in MMA and EGDM homopolymerizations. $[M]_0$ = 0.53 (1) and 1.06 M (2). $[I]_0$ = 0.02 M

In summary, the present work introduces a technique that enables to vary the size of macroradical coils while their kinetic chain length remains unchanged. The results presented demonstrate separate contributions of thermodynamic and steric excluded volumes on the termination rate of macroradicals formed at zero monomer conversion. At non-zero monomer conversions, only steric effects determine the termination rates.

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