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Pendant vinyl group reactivity during the free-radical copolymerization of methyl methacrylate and ethylene glycol dimethacrylate

Oguz Okay and Hamid J. Naghash

TUBITAK Marmara Research Center, Department of Chemistry, P.O. Box 21, Gebze, Kocaeli, Turkey

Summary

Methyl methacrylate - ethylene glycol dimethacrylate (MMA-EGDM) copolymerization has been investigated in toluene at a monomer concentration of 22 w/v %. The kinetic models developed recently along with the experimental conversion curve and gel point data provided the calculation of the average reactivity of pendant vinyl groups. It was found that the pendant vinyl reactivity for intermolecular links is much less than the monomeric vinyl reactivity and it decreases further as the EGDM concentration increases. At 5 - 15 mol % EGDM, the average pendant reactivity is 1 - 2 orders of magnitude lower than the monomeric vinyl reactivity. The reduced pendant reactivity is mainly responsible for the shift of the gel point towards higher conversions.

Introduction

Since the pioneering work of network formation in the methyl methacrylate / ethylene glycol dimethacrylate (MMA / EGDM) system by Walling (1), synthesis of these copolymers and their properties have been the subject of a large number of studies. Previous works indicate great discrepancy between the observed behavior of free-radical crosslinking copolymerization of MMA / EGDM system and the prediction using the ideal network formation theories (2). The following differences were reported:

(1) Shift of the gel point by 1 - 2 orders of magnitude towards higher conversions (1,3). At high EGDM contents, the critical conversion at the gel point is largely insensitive to the amounts of EGDM in the initial monomer mixture (1,3).

(2) Pendant vinyl conversion, that is the fraction of EGDM units in the polymer with both vinyls reacted is not zero at zero monomer conversion (4-7). As polymerization proceeds, the increase of the pendant conversion is much faster than that predicted using the ring-free theories (6).

(3) Enhancement of the rate of polymerization with EGDM concentration (3,7,8-10).

(4) Lower intrinsic viscosities of the pre-gel polymers compared to those of linear MMA polymers of the same molecular weight (5). Decrease of the radius of gyration of the pre-gel polymers with conversion (11).

(5) Drastic deviation of the observed critical exponents γ and ν from the predicted mean-field values (3,4).

Walling attributed the observed deviation in the gel point to the diffusion-controlled crosslinking reactions (1). He assumed that cyclization could be neglected. Walling's explanations was contradicted by Gordon and Roe (12); they concluded that cyclization only is responsible for the observed discrepancy between theory and experiment. Later on, Minnema and Staverman (13) demonstrated in the copolymerization of MMA with a degradable crosslinker that the reduced pendant reactivity ("shielding effect") is responsible for the delay in the gel point. It is now generally agreed that both cyclization and reduced pendant reactivity coexist in free-radical crosslinking copolymerizations and they are related each other. On the other hand, as the ideal network formation theories neglect excluded volume effects and concentration fluctuations, which should play an important role in the vicinity of the gel point (14), the observed critical exponents differ drastically from the predictions.

This paper will deal with the evaluation of the average reactivity of pendant vinyl groups in the pre-gel regime of MMA / EGDM copolymerization. For this purpose, a series of experiments with varying amounts of crosslinker EGDM were performed. The total monomer concentration was 22 w/v %. Conversion of monomers and the gel points were determined experimentally by means of the gravimetric technique. The kinetic models developed recently were then used to study the experimental data and to evaluate the reactivity ratio of pendant to monomeric vinyls in MMA/EGDM copolymerization reactions.

Kinetic modelling

A kinetic scheme for free-radical crosslinking copolymerization of vinyl/divinyl monomers can be written as follows. Copolymerization of a monovinyl monomer (MVM) with a divinyl monomer having symmetric vinyls (DVM) involves three types of vinyl groups with different reactivities, namely the vinyl groups i) on MVM, ii) on DVM, and iii) on polymer chains, i.e., pendant vinyls. Accordingly, the polymerization system can be considered as a special case of terpolymerization in which one of the vinyl groups (pendant vinyls) is created during the course of the reaction when the vinyl on divinyl monomer reacts (15). The pendant vinyl groups thus formed can then react by cyclization, crosslinking, or multiple crosslinking reactions, or remain pendant. With cyclization the cycle is formed when the macroradical attacks the pendant vinyl groups in the same chain, while with multiple crosslinking it is formed if the radical attacks double bonds pendant on other chains already chemically connected with the growing radical (15,16) (Figure 1).

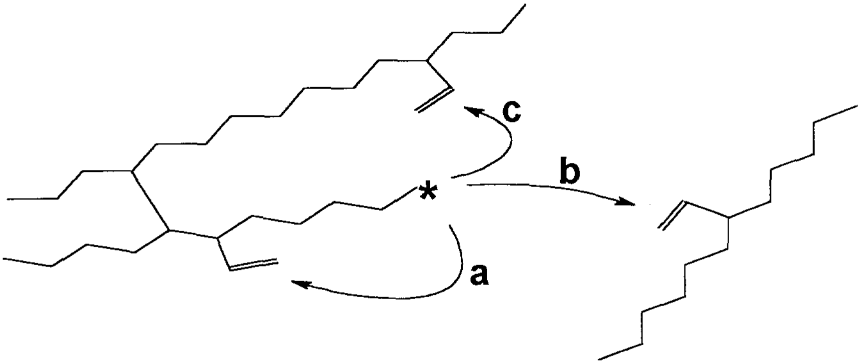

Fig. 1. Schematic representation of the processes of cyclization (a), crosslinking (b) and multiple crosslinking (c) in free-radical crosslinking copolymerization.

Divinyl monomer can thus be found in the polymer as units bearing pendant vinyl groups, cycles, crosslinks or multiple crosslinks. Here, we define the pendant vinyl conversion, x_3, as the fraction of divinyl monomer units with both vinyl groups reacted. Theories neglecting cyclization predict that every divinyl monomer unit in the polymer should initially bear a pendant vinyl group, i.e., $\lim_{x \to 0} x_3 = 0$ where x is the monomer conversion. Since crosslinking is a second-order reaction, deviation from zero indicates the existence of cyclization (6,15-19). On the other hand, the occurrence of multiple crosslinking will be reflected in a greater increase in the pendant vinyl conversion as monomer conversion proceeds than would otherwise occur (16).

Let k_{cyc} be the fraction of pendant vinyls in cycles at zero conversion and k_{mc} be the average number of multiple crosslinkages per crosslink, then, based on the kinetic equations given previously (6,15,20-23), the following rate equations for the weight-average molecular weight $\overline{M}_w$ and the pendant conversion x_3 can be written:

$$\frac{d\left(x\overline{M}_w\right)}{dx} = \overline{M}_w^{\bullet}\left[1 + \frac{r_{21}\bar{r}_{32}\left(1 - x_3\right)\overline{F}_2}{1 + \left(2r_{21} - 1\right)f_2}\left(\frac{x}{1 - x}\right)\frac{\overline{M}_w}{\overline{M}_u}\right]^2 \quad ; \overline{M}_w(0) = \overline{M}_{w,0}^{\bullet} \qquad (1)$$

$$; \overline{M}_w\left(x_c\right) = \infty$$

$$\frac{dx_3}{dx} = \frac{r_{21}}{1 + \left(2r_{21} - 1\right)f_2}\left[\frac{\bar{r}'_{32}\left(1 - x_3\right)}{(1 - x)} - \frac{2f_2}{\overline{F}_2}\frac{\left(x_3 - k_{cyc}\right)}{x}\right] \quad ; x_3(0) = k_{cyc} \qquad (2)$$

where r_{21} is the reactivity ratio of vinyls on divinyl to monovinyl monomers, $\bar{r}_{32}$ and $\bar{r}'_{32}$ are the actual and apparent reactivity ratio of pendant vinyl to monomeric vinyl on divinyl monomer, respectively, f_2 and $\overline{F}_2$ are the accumulated mole fraction of divinyl monomer in the reaction mixture and in the copolymer, respectively, $\overline{M}_u$ is the molecular weight of the repeating unit, $\overline{M}_w^{\bullet}$ is the weight-average molecular weight of the primary chains, and x_c is the critical conversion at the gel point. Please note that the apparent reactivity ratio of pendant to monomeric vinyl $\bar{r}'_{32}$ includes both the contributions of crosslinking and multiple crosslinking reactions, and is related to the actual reactivity ratio through the equation

$$\bar{r}'_{32} = \bar{r}_{32}\left(1 + k_{mc}\right) \qquad (3)$$

It must be noted that the derivation of the equations given above makes the following assumptions: (1) steady-state approximation for the concentration of each radical species; the reactivities are independent of the type of the radical end, (2) both cyclization and multiple crosslinking reactions occur at constant rates, (3) every polymer radical possesses only one radical center, and (4) the mole fraction of pendant vinyl groups is independent of chain length of the polymer molecules. The mole fraction of the divinyl monomer in the reaction mixture f_2 is given by the Skeist equation (24) :

$$\frac{df_2}{dx} = \frac{f_2 - F_2}{1 - x} \quad ; f_2(0) = f_{20} \qquad (4)$$

where f_{20} is the initial mole fraction of the divinyl monomer in the monomer mixture. Moreover, the instantaneous and accumulated mole fraction of the divinyl monomer units in the copolymer, F_2 and $\overline{F}_2$ respectively, can be calculated by the following equations:

$$F_2 = \frac{2r_{21}f_2}{1 + (2r_{21} - 1)f_2} \qquad (5)$$

$$\overline{F}_2 = \frac{1}{x}\left[f_{20} - (1-x)f_2\right] \tag{6}$$

The weight-average molecular weight of the primary chains $\overline{M}^\bullet_w$ is not constant but a function of conversion due to the depletion of monomer and initiator, and due to the diffusion controlled termination reactions. Assuming that the propagation rate constant remains unchanged during polymerization, the drift in the primary chain length can be calculated as follows:

$$\frac{\overline{M}^\bullet_w}{\overline{M}^\bullet_{w,0}} = \frac{(dx/dt)}{(dx/dt)_0}\exp(k_d t) \tag{7}$$

where the subscript o denotes the initial values at the start of the reaction and k_d is the decomposition rate constant of the initiator. As was shown earlier (3,7,9,17), the molecular weight of zero-conversion polymers, $\overline{M}^\bullet_{w,0}$, is also a function of the crosslinker concentration in the reaction mixture. The value of $\overline{M}^\bullet_{w,0}$ can be calculated from the initial rates as

$$\frac{\overline{M}^\bullet_{w,0}}{\overline{M}^\bullet_{w,0,l}} = \frac{(dx/dt)_0}{(dx/dt)_{0,l}}\frac{\overline{M}_{u,0}}{\overline{M}_{u,0,l}} \tag{8}$$

where the subscript l denotes linear polymerization so that $\overline{M}^\bullet_{w,0,l}$ represents the weight-average molecular weight of zero conversion polymers in MMA polymerization and is given by:

$$\overline{M}^\bullet_{w,0,l} = \overline{M}_{u,0,l}\left(2 + \frac{k_{tc}}{k_t}\right)\frac{k_{pl}[M]_0}{k_{t0}[R^*]_0} \tag{9a}$$

$$[R^*]_0 = \left(2f\,k_d[I]_0 / k_{t0}\right)^{0.5} \tag{9b}$$

where k_{pl} is the propagation rate constant, k_{t0} is the initial termination rate constant, k_{tc}/k_t is the fraction of radicals terminating by coupling, f is the initiator efficiency, $[M]_0$ and $[I]_0$ are the initial concentrations of the monomer and initiator respectively. For MMA polymerization at 60°C with 2,2' azobisisobutyronitrile (AIBN) as the initiator, the following values were reported (25,26): $f = 0.44$; $k_d = 0.85\mathrm{x}10^{-5}$ s^{-1}; $k_{pl} = 600$ $L.mol^{-1}.s^{-1}$; $k_{tc} / k_t = 0.5$; $k_{to} = 2.2\mathrm{x}10^7$ $L.mol^{-1}.s^{-1}$ and $\overline{M}_{u,0,l}=100$ g/mol. Thus, using eqs 9 we obtain $\overline{M}^\bullet_{w,0,l} = 1.17\mathrm{x}10^4\ [M]_0 / [I]_0$ g/mol.

Up to the gel point all the molecules present in free-radical crosslinking copolymerization are finite. Thus, the equations given above may be used for calculation of the average reactivity ratio of pendant to monomeric vinyl $\overline{r}_{32}$ as follows: Since $\overline{M}_w$ diverges at the gel point, the value of $\overline{r}_{32}$ satisfying $\overline{M}_w(x_c) = \infty$ may be obtained numerically using simultaneous solution of eqs 1-6. The drift in the primary chain length can be included into the calculations by fitting eqs 7-8 to experimental time-conversion data. Thus, in order to calculate the average reactivity ratio of pendant to monomeric vinyls, experimental monomer and pendant conversions, together with the gel point conversions must first be obtained.

Experimental

The monomers MMA and EGDM were freed from the inhibitor by shaking with 5 % aqueous NaOH, washing with water, and drying over $CaCl_2$. They were then distilled under reduced pressure. The initiator (AIBN) was recrystallized twice from methanol. The polymerization solvent, toluene, was distilled twice over sodium. MMA-EGDM copolymerization was conducted in a 500-mL round bottom, three-neck flask, fitted with a nitrogen inlet, condenser and rubber septum. All reactions were carried out under nitrogen atmosphere and in toluene at 60 ±0.1°C with AIBN as the initiator. The initial concentrations of the monomers and the initiator were held constant at 2.0 - 2.4 M (20 - 24 wt %) and 0.01 M respectively, while the EGDM concentration was varied from 0 to 15 mol %.

The monomers and toluene were pipetted into the round-bottom flask containing a Teflon-covered magnetic stirring bar, and the appropriate amount of AIBN was then added. To eliminate oxygen from the system nitrogen was bubbled through the reaction mixture at room temperature for 30 minutes. Then the reactor was set in a thermostated bath at 60°C. In order to detect the end of the induction period, usually a few minutes, small samples were removed from the reactor by means of a syringe and added into methanol. The time of the first appearance of a stable white color was recorded as t = 0. Then samples were taken at different reaction times via syringes and they were precipitated dropwise into an agitated solution of methanol. The conversion of monomer was determined by drying and weighing the precipitated polymer. The gel point was determined experimentally as the midpoint between the last time at which a soluble polymer was obtained and that at which the mixture was not soluble in toluene.

Figure 2 shows the conversion - time histories for MMA-EGDM copolymerization at 60°C and for different EGDM concentrations. The experimental determined gel points in terms of monomer conversion x_c are shown in Figure 3 as filled circles as a function of the initial EGDM concentration of the reaction mixture.

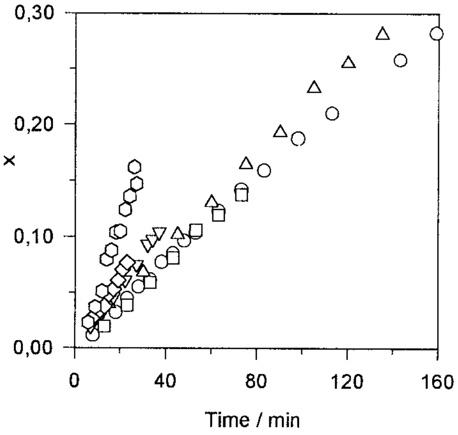

Fig. 2. Monomer conversion x versus time histories in MMA/EGDM copolymerization at 0 (Δ); 0.4 (O); 2 (□); 4.6 (∇); 6.7 (◊); and 14.7 % EGDM (◊). $[M]_0$ = 2.3 M, $[I]_0$ = 0.01 M.

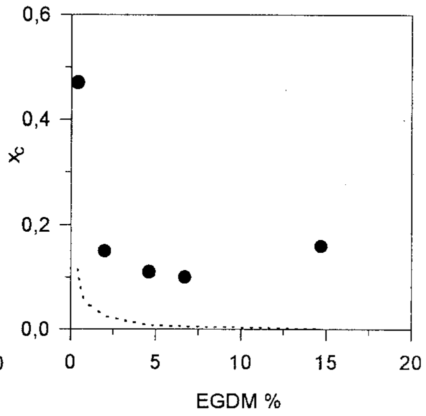

Fig. 3. Critical conversion at the gel point x_c shown as a function of the EGDM concentration. Experimental data points are shown as filled circles. The dotted curve was calculated for r_{32} = 1 (no substitution effect)

Results and discussion

Figure 4 shows the ratio of the weight-average molecular weight of zero conversion polymers in MMA/EGDM copolymerization to that in linear MMA polymerization under the same experimental condition, $\overline{M}^{\bullet}_{w,0}/\overline{M}^{\bullet}_{w,0,l}$, plotted as a function of the EGDM concentration. The values $\overline{M}^{\bullet}_{w,0}/\overline{M}^{\bullet}_{w,0,l}$ were calculated using the initial rates of polymerization and using eq 8. It seems that at low crosslinker contents, zero conversion polymer chains are shorter than those present in linear system. This is probably due to the cyclization reactions which reduce the coil size of macromolecules and thus, increase the radical concentration in the reaction locus (7). However, as the crosslinker concentration further increases, the chains become longer than those present in linear system due to steric reasons.

The drift in the primary chain length is shown in Figure 5 in terms of $\overline{M}^{\bullet}_{w}$ / $\overline{M}^{\bullet}_{w,0}$ plotted against the monomer conversion x. For EGDM contents higher than 2 %, the primary chain length starts to increase at zero conversion indicating that the termination reactions become diffusion controlled right down to zero conversion. Moreover, as expected (10), the results indicate an increasing extent of drift with increasing EGDM concentration.

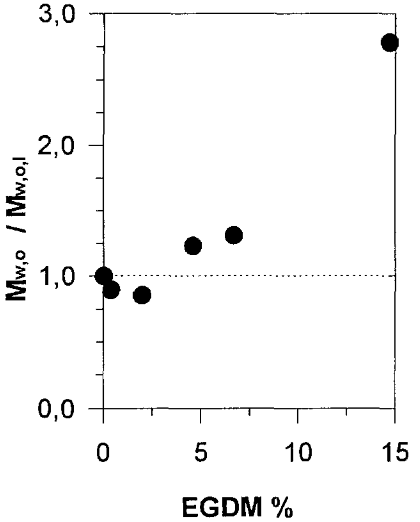

Fig. 4. Variation of the relative weight-average molecular weight of zero conversion polymers with the EGDM concentration.

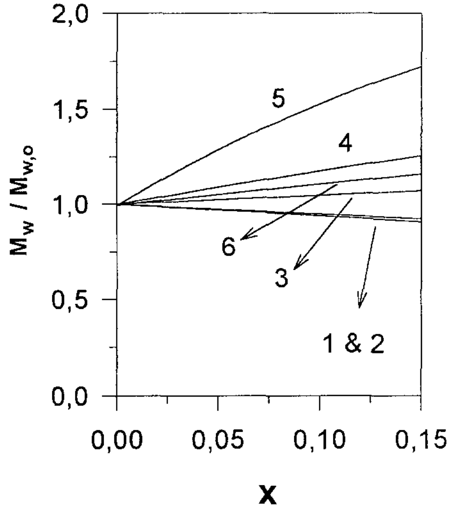

Fig. 5. Drift in the primary chain length shown as a function of conversion x for 0 (1); 0.4 (2); 2 (3); 4.6 (4); 6.7 (5) and 14.7 % EGDM (6).

In the present study, of particular interest to us is the average reactivity of pendant vinyl groups with respect to the monomeric vinyl reactivity, represented by $\overline{r}_{32}$. Our previous pendant vinyl group measurements using ^{1}H-NMR and analytical titration method indicated k_{mc} = 0 for the present system (7). Moreover, nearly half of the pendant vinyl groups was found to be used by cyclization reactions; thus k_{cyc} = 0.5. On the other hand previous experimental data indicate equal reactivity of monomeric vinyls in MMA/EGDM copolymerization, i.e., r_{21} = 1 (4,6). Thus, since we know the values of

k_{mc}, k_{cyc}, r_{21}, $\overline{M}^{\bullet}_{w,0,1}$ and the functional dependence of $\overline{M}^{\bullet}_{w}$ on conversion, eq 1-6 can be solved for $\bar{r}_{32}$ values.

Assuming that the reactivity of the pendant vinyl groups is the same as that of the vinyl groups on EGDM molecule, that is $\bar{r}_{32} = 1$ (no substitution effect), the model predicts gel points shown in Figure 4 as dotted curve. It seems that the actual gel points exceed those predicted for $\bar{r}_{32} = 1$ by 1 - 3 orders of magnitude. The ratio of experimental to theoretical gel points for $\bar{r}_{32} = 1$ increases with increasing amounts of crosslinker. The model predicts actual gel points if the reactivity ratio $\bar{r}_{32}$ is much less than unity. The calculated $\bar{r}_{32}$ values are shown in Figure 6 as function of the EGDM concentration.

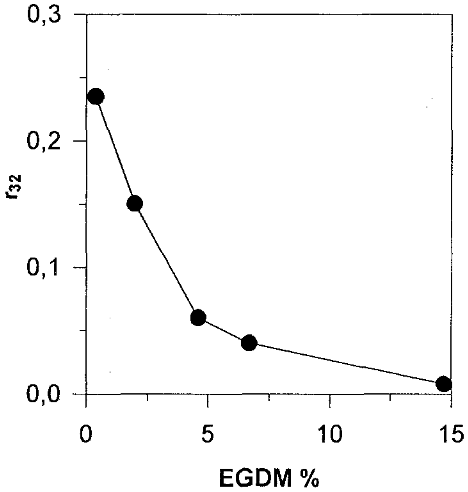

Fig. 6. Variation of the average reactivity of pendant to monomeric vinyls for intermolecular reactions $\bar{r}_{32}$ with the EGDM concentration in MMA/EGDM copolymerization.

The reactivity of pendant vinyls strongly depends on the crosslinker concentration and it decreases as the crosslinker concentration increases. At 5 - 15 mol % EGDM, the average pendant reactivity is 1 - 2 orders of magnitude lower than the monomeric vinyl reactivity. Thus, although both cyclization and reduced pendant reactivity coexist in free-radical crosslinking copolymerizations, the latter is mainly responsible for the delay in the gel point. The consumption of nearly half of the pendant vinyl groups by cyclization reactions and the drastically reduced reactivity of the residual vinyl groups suggest formation of compact mutually impenetrable microgel particles as intermediates in free-radical MMA-EGDM copolymerization.

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