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Size distribution of polymers during the photoinitiated free-radical copolymerization of methyl methacrylate and ethylene glycol dimethacrylate

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Summary

Photoinitiated methyl methacrylate - ethylene glycol dimethacrylate (MMA / EGDM) copolymerization has been investigated in toluene at a monomer concentration of 35 w/v %. Diphenyl-2,4,6-trimethylbenzoylphosphine oxide (DPTPO) was used as a photoinitiator at 0.3 wt % concentration. Monomer conversions and the size distribution of the polymer molecules were measured as a function of the reaction time up to the onset of macrogelation. Compared to the photoinitiators benzoin or benzoin derivatives, gelation process proceeds at much higher rates in the presence of DPTPO. The size distribution curves obtained by size-exclusion chromatography (SEC) change from monomodal to bimodal distributions as the polymerization proceeds. Strongly bimodal SEC curves were obtained in the close vicinity of the gel point. This finding confirms the coagulation type gelation mechanism of compact primary particles. It also indicates that the present gelation theories cannot describe the structure dependent kinetics of free-radical crosslinking copolymerization.

Introduction

There are several theories of network formation to describe the relations among the molecular weight of polymers and the conversion or reaction time during crosslinking. These theories include statistical (1-7) and kinetic methods (8-17), and simulation in n-dimensional space, such as the percolation method (18-20). In the past half century, statistical and kinetic approaches have been extensively used to describe polymeric gelation in free-radical crosslinking copolymerization (FCC). Generally, kinetic theories give satisfactory predictions for the average properties of the species in the pregel regime, such as the average molecular weights of the polymers. These theories also give molecular weight distributions (MWD's) of sol polymers, which are predicted to be unimodal in the whole course of the free-radical crosslinking copolymerization reactions. Recently, Teymour and Campbell (21) proposed a "numerical fractionation" technique, that predicts bimodal MWD's in the pregel regime of FCC. According to this technique the overall polymer population is divided into different generations according to their size. Transfer from the *nth* to the *(n+1)*st generation occurs when two polymer molecules of the *n*th generation react together to form a single molecule. The overall MWD of the sol polymer is calculated by summing up the MWD's of all the generations. More recently, Arzamendi and Asua showed that the bimodal MWD predicted by the numerical fractionation technique is an artifact of the method due to the transfer rules from one

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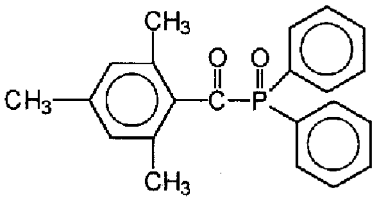
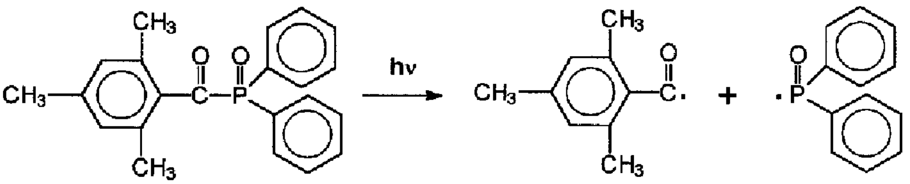
generation to the other (22). After corrections this technique also leads to unimodal MWD's for the pregel regime of FCC.

The experimental data reported in the literature for the actual MWD of polymers in free-radical copolymerization of vinyl and divinyl monomers are rather scarce. The MWD of the pregel polymers was mainly analyzed using size-exclusion chromatography (SEC) coupled with refractometry. Previously, bimodal distributions have been observed (23-25), but also, in some studies monomodal SEC curves have been reported (26,27). In this study a monovinyl - divinyl monomer system with nearly equal monomeric vinyl group reactivity (28,29), namely methyl methacrylate (MMA) / ethylene glycol dimethacrylate (EGDM) was selected. An acylphosphine oxide, namely diphenyl-2,4,6-trimethylbenzoylphosphine oxide (DPTPO), of the following structure was used as the photoinitiator:



These type of photoinitiators are particularly interesting because of their high extinction coefficients in near u.v. wavelength range, efficiency in curing of the formulations containing acrylates as monomers (30). The pronounced initiating capability of these compounds is based on the fact that, upon irradiation with u.v. light, they readily undergo α-scission according to the following reaction, e.g. for DPTPO:



Scheme 1

In our work, u.v. photopolymerizations were carried out at 35 w/v % monomer concentration in toluene and using 0.3 wt % of the photoinitiator DPTPO. The size distribution of the polymers was followed using SEC as a function of the monomer conversion up to the onset of a macrogelation. The variation of the shape of the distribution curves with the crosslinker concentration was examined. It is the purpose of this paper to test the prediction of the gelation theories for the size distribution of the pregel polymers.

Experimental

Commercially available methyl methacrylate (MMA) , ethylene glycol dimethacrylate (EGDM) monomers, and the photoinitiator diphenyl-2,4,6-trimethylbenzoylphosphine oxide (DPTPO) (BASF) were purified by usual methods. The polymerization solvent toluene (Merck p.a.) was twice distilled before use. Photoinitiated copolymerization of MMA and EGDM was carried out in toluene at 27 ± 0.1 °C. The conversion of the monomers up to the onset of macrogelation was followed by dilatometry. The dilatometers constructed in this laboratory 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 thickness of the dilatometers was less than 6 mm to ensure the applicability of the thin film approximation and uniform light intensity across the sample. The reaction mixture was flushed with nitrogen 20 min prior to the polymerization. Polymerization was initiated with u.v. light of intensity 3.8×10^{-9} einsteins generated using a medium mercury lamp. The meniscus of the polymerizing solution was measured throughout the experiment with a millimetric paper to 0.2 mm. The polymerization technique used was described in detail elsewhere (31). 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%. The initial concentrations of the monomers and the initiator were held constant at 3.5 M (35 w/v %) and 0.3 wt % (with respect to the monomers), respectively, while the crosslinker ratio was varied in a wide range.

The polymer samples for SEC measurements were obtained by a gravimetric technique. For this purpose, a 15-mL three-neck flask of 0.7 mm thickness containing a magnetic stirrer bar fitted with a nitrogen inlet and pipette outlet was filled with the liquid mixture. After degassing of the mixture, polymerization was initiated with the u.v. light of the mercury lamp at 27 ± 0.1 °C. After predetermined polymerization times, samples were withdrawn from the reactor, rapidly cooled in order to quench the reaction, and then, they were diluted in THF. The size distribution of the pregel polymers were obtained by size exclusion chromatography (Waters, Model M-6000A), equipped with refractive index detector, using two polystyrene gel columns (500, 10,000 A) at a flow rate of 1.0 mL / min in THF at 40°C, and using polystyrene standards.

Results and discussion

Figure 1 shows conversion - time histories for MMA / EGDM copolymerization at different EGDM concentrations up to the macrogelation point. The EGDM concentration varies from 0 to 50 mol %. The rate of polymerization increases with increasing EGDM

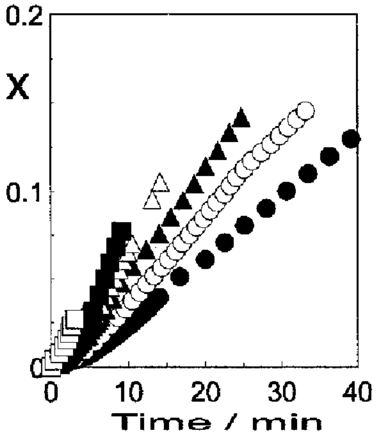


Fig. 1. Monomer conversion x versus time histories in MMA/EGDM copolymerization at 0 (●); 6.4 (O); 9.3 (▲); 15.1 (Δ); 25 (■); and 50 mol % EGDM (❑).

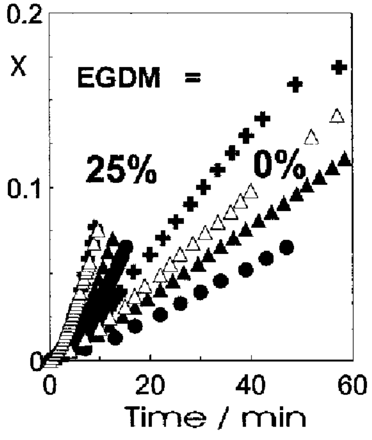


Fig. 2. Comparison of conversion versus time data for the initiators benzoin (●), benzoin ethyl ether (▲), 2,2-dimethoxy-2-phenylacetophenone (Δ) and DPTPO (+).

concentration. It is known that EGDM monomer can incorporate into the polymer during FCC as units bearing pendant vinyl groups (p), cycles (c), crosslinks (μ), and multiple crosslinks (mc). We define pendant conversion x_3 as the fraction of EGDM units with both vinyls reacted, i.e., $x_3 = 1 - p/(p + c + \mu + mc)$. Since crosslinking and multiple crosslinking reactions are second-order reactions, the value x_3 at zero monomer conversion, i.e., $\lim_{x \to 0} x_3$ corresponds to the fraction of EGDM units consumed by cyclization reactions at zero monomer conversion (11). Using pendant vinyl group measurements by bromination method (32), we found for the present system $x_3 = 0.27 \pm 0.06$ for different conversions and EGDM concentrations up to the gel point. Thus, 27 % of the EGDM units in the sol polymers act as cyclic units and, the polymer molecules are intramolecularly crosslinked. Increasing crosslinker content increases the compactness of the structures formed; this will result a decrease in the mobility of chain segments and therefore suppresses diffusion controlled termination of radicals. Thus, termination rate constant decreases as the crosslinker concentration increases which results in the observed enhancement of the rate of polymerization with EGDM concentration.

Figure 2 compares conversion versus time data for the initiators DPTPO, benzoin (B), benzoin ethyl ether (BEE), and 2,2-dimethoxy-2-phenylacetophenone (DMPA). The experimental data for the initiators B, BEE, and DMPA were taken from the literature (32). Compared to the photoinitiators benzoin or benzoin derivatives, MMA/EGDM copolymerization proceeds at much higher rates in the presence of the photoinitiator DPTPO. This may be attributed to the higher absorptivity of DPTPO and to the much higher reactivity of phosphonyl radicals toward olefinic monomers (33-35). Typical value of the rate constant for the reaction of diphenyl phosphonyl radical formed according to scheme 1 with MMA is two orders of magnitude higher than values of rate constants for reactions of carbon centered radicals that are generated by the cleavage of benzoin derivatives. (6×10^7 vs 10^5 $l.mol^{-1}.s^{-1}$). According to ESR studies, phosphonyl radicals possess a tetrahedral structure and the site of the unpaired electron is readily accessible for the monomers.

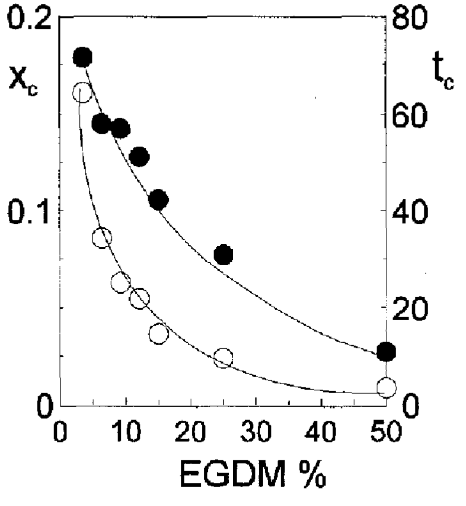


Fig. 3. Critical conversion at the gel point x_c (●) and the gelation times t_c in minutes (O) shown as a function of the EGDM concentration.

The gel points determined using both gravimetric and falling ball methods (32,36) are shown in Figure 3 as a function of the EGDM concentration. Calculations using the kinetic model (15,16) predict the actual gel points shown in Figure 3 if the reactivity ratio of pendant to monomeric vinyls is much less than unity. We calculated that the average pendant reactivity is 1 - 2 orders of magnitude lower than the monomeric vinyl reactivity. In accord with our previous observations (37,38), the drastically reduced reactivity of the pendant vinyl groups suggests formation of compact mutually impenetrable microgel particles as intermediates in free-radical MMA-EGDM copolymerization.

Figure 4 shows a set of SEC curves for polymers isolated at different reaction times up to the close vicinity of the gel point. The initial concentrations of EGDM were 0, 9, and 15 mol % for series A, B, and C respectively. As the polymerization time increases, the distribution curves change from single peaks to wider, bimodal distributions. The position of the large elution volume peak which corresponds to the primary molecule is essentially the same irrespective of the polymerization time, while small elution volume peaks are increased significantly as the reaction proceeds. Experiments carried out using other initiator systems such as benzoin derivatives also lead to pregel polymers with bimodal SEC curves (32). Increasing crosslinker concentration results in strongly bimodal SEC curves in the immediate vicinity of the gel point. Calculated results using kinetic (22,39) or statistical theories (40) for the sol phase near the gel point give flat curves extending across the molecular weight (elution volume) axis toward infinity. Monte Carlo simulations also show that the crosslinking reactions tend to produce a unimodal MWD (41). However, as shown in Figure 4, the SEC curves illustrate completely different behavior.

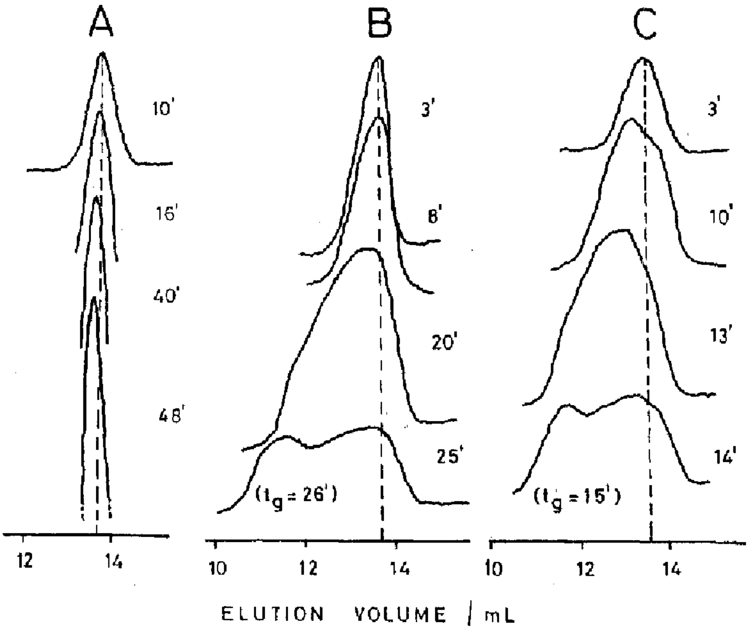


Fig. 4. SEC chromatograms of the pregel polymers isolated at different reaction times in MMA/EGDM copolymerization. Initiator: DPTPO. EGDM mol % = 0 (A), 9 (B), and 15 (C).

It must be pointed out that the SEC chromatography with combined refractive index detection does not allow to establish unique correlations between hydrodynamic volume and molecular weight for the polymers obtained in FCC. Therefore, the prediction of the gelation theories for the MWD of the pregel polymers cannot be disproved from the present experimental data. Since the molecules are separated in SEC columns according to their hydrodynamic volumes, the elution curves in SEC corresponds to the size distribution of polymer molecules. Thus, the molecules with the same molecular weight but different hydrodynamic volumes, i.e., those with shape polydispersity are eluted at different times. Since the mean field theories only consider the molecular weight polydispersity, the difference between theory and experiment can be attributed to the shape polydispersity of the molecules present during the polymerization. One may expect that the large shape polydispersity due to the cyclization reactions results in the observed strongly bimodal curves. Thus, the single peaks that appear at low conversion correspond to the microgels while their aggregates appear as a second peak in the small elution volumes side of the microgel peak.

According to the present results, the structural dependence of crosslinking reactions is important in free-radical crosslinking copolymerization. The results indicate the shape polydispersity of the pregel polymers and the coagulation type gelation mechanism of compact primary particles in FCC. In order to predict correctly the gel formation process it is necessary to consider the size and structure dependent kinetics of free-radical crosslinking copolymerization. Thus, by modifying the rate constants for termination and crosslinking reactions to include their dependence on the structural characteristics of the reacting molecules, the shape polydispersity effects can be included into the mean field model calculations.

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