

Kinetic Investigation of the Free-radical Cross-linking Copolymerization of Methyl Methacrylate and Ethylene Glycol Dimethacrylate by Using Bifunctional Initiator

Hamid Javaherian Naghash^{1,*} and Shadpour Mallakpour²

(1) Department of Chemistry, Shahreza Islamic Azad University, Shahreza-84145-311
Isfahan, I.R. Iran

(2) Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University
of Technology, Isfahan-84156, I.R. Iran

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ABSTRACT

Both photo and thermal initiated free-radical cross-linking copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) have been investigated in toluene at a monomer concentration of 3.5 molar and at 60°C and 27°C for azo and benzoin groups, respectively. The bifunctional initiator used was 4,4'-azo-bis-(4-cyanopentanoyl)-bis benzoin (ACPB). Conversion of monomer and pendant vinyl groups and the size of the pre-gel polymers were measured as a function of the reaction time up to the onset of macrogelation. Approximately 97% of the pendant vinyl groups were found to be consumed by cyclization reactions. The fraction of units in cycles is independent of the EGDM concentration. As a result of the cyclization reactions, the accessibility of the radical centres and pendant vinyl groups for other polymer molecules is strongly reduced. Consequently, both termination and cross-linking reactions are controlled by the segmental diffusion of the polymer radicals. Calculations indicate 1-2 orders of magnitude decrease in the average reactivity of pendant vinyls for intermolecular reactions compared to the monomeric vinyls. This drastic decrease in pendant reactivity is mainly responsible for the delay in the gel point. Contrary to gelation theories, the size distribution curves of the pre-gel polymers change from monomodal to bimodal distributions as polymerization proceeds. This finding confirms the coagulation-type gelation mechanism of compact primary particles and indicates the polydispersity shape of the pre-gel polymers. Virtually we observed the same kinetic behaviour in the MMA-EGDM polymer gel systems by bifunctional initiator the same way we had found before with photo and thermal initiators.

Key Words:

free radical cross-linking copolymerization;
bifunctional initiator;
methyl methacrylate;
ethylene glycol dimethacrylate.

INTRODUCTION

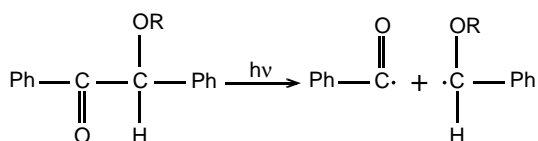
Benzoin and its derivatives are well known, and they are extensively used as photoinitiators for free radical polymerization[1]. Upon photo-excitation, these compounds undergo α -scission with high quantum efficiencies according to reaction of

Scheme I [2].

Onen and Yagci [3] reported the synthesis and initiator properties of azo-benzoin initiators as in Scheme II.

These bifunctional low molar mass initiators contain two chromophoric groups, the azo and ben-

(*) To whom correspondence should be addressed.
E-mail: hamid_J_N@yahoo.com



Scheme I

zoin groups, that differ significantly in thermal and photoactivity.

In this study we used the 4,4'-azo-bis-(4-cyanopentanoyl)-bis benzoin (ACPB) through thermolysis of the azo group and subsequent photolysis of the benzoin group in the presence of methyl methacrylate and ethylene glycol dimethacrylate. This paper is concerned with the utilization of azo-benzoin initiator for the formation and characterization of gels of mentioned monomers.

On the other hand the bulk photopolymerization of multifunctional (meth) acrylates leads to the formation of highly cross-linked polymer networks. These networks have found applications in various fields such as furniture finishing, printing, metal, information technology decorating and packaging [4-7]. More recent applications are the manufacturing of optical discs [8,9] of aspherical lenses [10-11] and the in-line coating of optical fibres [12-13]. In many of these applications glassy materials are required vitrification, which strongly reduces the rate of polymerization and, therefore, incomplete conversion of double bonds is often observed.

Kinetic Scheme

A kinetic scheme for chain cross-linking polymerization of vinyl divinyl monomers can be written as follows [14]. The polymerization system involves three types of vinyl groups, those on vinyl, divinyl monomers and those on polymer chains, i.e. pendant vinyls. Accordingly the polymerization system can be

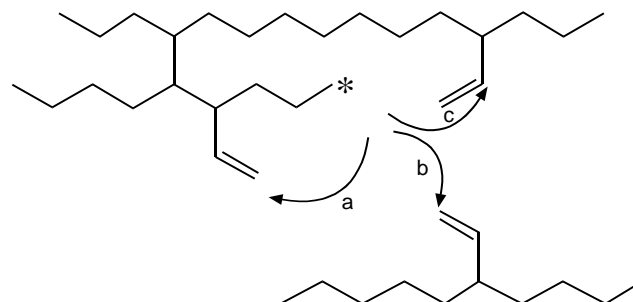


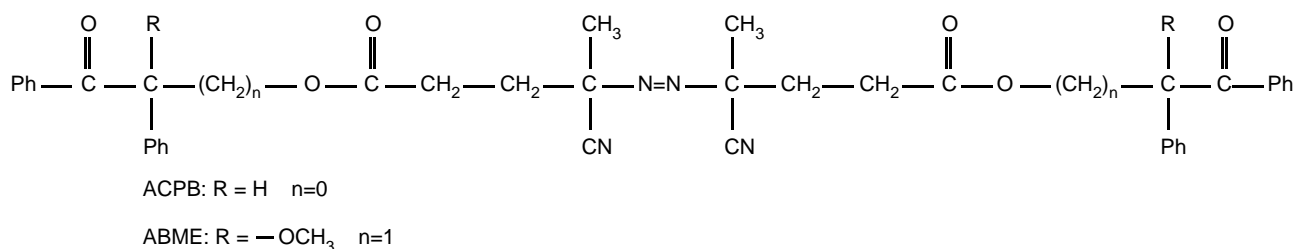
Figure 1. Schematic representation of the processes of cyclization: (a) cross-linking, (b) multiple cross-linking, and (c) in free-radical cross-linking copolymerization.

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 the divinyl monomer reacts. The pendant vinyl groups thus formed can then react by cyclization, cross-linking or multiple cross-linking reactions, or remain pendant. With cyclization the cycle is formed when the macro-radical attacks the pendant vinyl groups in the same kinetic chain. While with multiple cross-linking cyclization is formed if the radical attacks double bonds pendant on the other chains [14-16] already chemically connected to the growing radical (Figure 1). It should be noted that cyclization and multiple cross-linking were recently re-defined as primary and secondary cyclizations, respectively [16].

EXPERIMENTAL

Materials and Equipment

The monomer, methyl methacrylate (MMA, Merck), was washed with 5% aqueous sodium hydroxide to remove inhibitor, followed by several washings with deionized water. After drying successively with anhydrous sodium sulphate and 4A (40 nm) molecular



Scheme II

sieves, it was distilled under reduced pressure. The middle fraction was collected. The cross-linker, ethylene glycol dimethacrylate (EGDM, Aldrich), was washed similarly and then distilled under reduced pressure. The fraction boiling at about 77 C was collected. The initiator 4,4'-azo-bis(4-cyanopentanoyl)-bis-benzoin (ACPB) was synthesized by Onen et al. [3] at the Istanbul Technical University, Istanbul, Turkey. The polymerization solvent, toluene, (Merck) was distilled twice over sodium.

Fourier transform infrared spectroscopy (FTIR) analysis was performed with a Nicolet Impact 400D Model spectro photometer using KBr pellets. Spectra were obtained over the wavenumber range from 500-4000 cm^{-1} at a resolution of 2 cm^{-1} using a MCT detector with co-addition of 64 scans.

Methods

Both photo and thermal initiated copolymerization of MMA and EGDM were carried out in toluene at 60 C and 27 C for azo and benzoin groups, respectively.

The initiator used was ACPB. The conversion of the monomers up to the onset of macrogelation was followed by dilatometry. The dilatometers, constructed in the Marmara Research Center, Istanbul, Turkey, 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 and the thickness of 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 to eliminate dissolved oxygen in the system and the solution was transferred to dilatometer by a 100-mL special round-bottom three-connected valve flask, fitted with a nitrogen inlet, vacuum pump, and dilatometer. A vacuum was created in the flask by opening and closing the valve successively and slanting the vessel. As a result the dilatometer was filled with the reaction mixture. It should be mentioned that the vessel containing solution was kept in the ice bath during the degassing and filling.

After preparation of the dilatometer with above method the polymerization was initiated first with UV light of intensity 3.8×10^{-9} Einstein s generated using a medium mercury lamp, then the UV light was cut and

the sample was immersed in a bath of 60 C temperature. The meniscus of the polymerizing solution was measured throughout the experiment with a millimetric paper to 0.2 mm.

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 initiator were held constant at 3.5 M and 0.3 wt % (with respect to the monomers), respectively, while the cross-linker concentration was varied for a wide range. The polymer samples for pendant vinyl group and size exclusion chromatography 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 first with the UV light of the mercury lamp at 27 C and then placed in a thermostat with 60 C heat. After predetermined polymerization times, the content of the flask was poured into 100 mL of methanol and allowed to settle. The precipitated polymer was filtered and dried in vacuo to constant weight. Measurement of the number of pendant vinyls MMA/EGDM copolymers was carried out using a bromination method with pyridine sulphate dibromide (PSDB) reagent in the presence of mercury acetate as catalyst [17]. The method is based on the reaction of pendant vinyl groups with bromine produced in situ from the PSDB reagent and back-titration of the excess bromine for the calculation of pendant conversion, the reactivities of monomer vinyls were assumed to be equal. For determined size exclusion chromatography (Waters Model M-6000 A) equipped with refractive index detector, using two polystyrene gel columns (500/10000A) at a flow rate of 1 mL/min in THF at 40 C and using polystyrene standards.

Gel point measurements were carried out using two different methods. First, the gravimetric technique was used to follow the polymerization reactions, the gel was determined as the mid-point between the last time at which the polymer was not soluble in toluene.

For ascertaining the insoluble gel component of samples the latter were treated with an approximately 50-fold excess of toluene at room temperature. The formation of insoluble polymer was detected visually

from the appearance of gel particles in toluene. Second, dilatometers containing a steel sphere of 4.8 mm diameter were used for the gel point measurements. The mid-point between the last time at which the sphere moved magnetically and that at which it stopped moving was taken as the gel point. We found remarkable consistency in the gel point determined using both methods. Each gel point reported in this paper is an average of at least four measurements. Standard deviations were 7%.

RESULTS AND DISCUSSION

The structures of copolymers before gel point were determined by FTIR spectroscopy. Figures 2 and 3 show the spectrum of polymethylmethacrylate homopolymer and methyl methacrylate with ethylene glycol dimethacrylate copolymer, respectively. A decrease in the height of the 775, 843 and 991 cm^{-1} in Figure 3 is indicative of copolymers. Figure 4 shows conversion (%) versus time histories for MMA/EGDM copolymerization by dilatometry at different EGDM concentrations up to the macrogelation point. The bifunctional initiator used was 4,4'-azo-bis-(4-cyanopentanoyl)-bis-benzoin and the EGDM concentration varies from 12-50 mol%. The rate of polymerization increases with increasing EGDM concentration. It is known that EGDM monomer can incorporate into

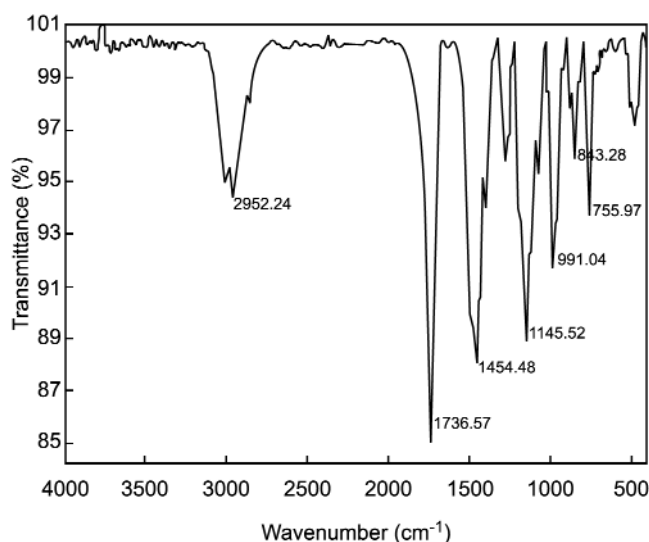


Figure 2. FTIR Spectrum of polymethylmethacrylate homopolymer.

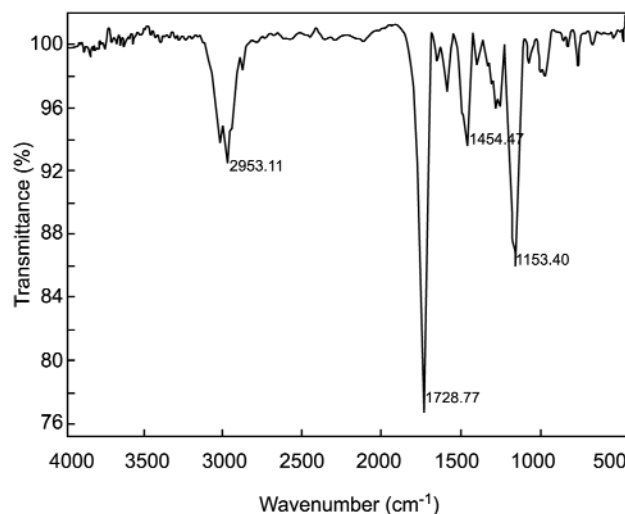


Figure 3. FTIR Spectrum of polymethylmethacrylate with ethylene glycol dimethacrylate copolymer.

the polymer during free radical cross-linking copolymerization as units bearing pendant vinyl groups (p) cycles (c) cross-links (μ) and multiple cross-links (mc) we define pendant conversion X_3 as the fraction of EGDM units with both vinyls reacted [18], i.e:

$$X_3 = 1 - p / (p + c + \mu + mc) \quad (1)$$

Since cross-linking and multiple cross-linking reactions are second-order reactions, the value X_3 at zero monomer conversion, i.e. $\lim X_3$ corresponds to the

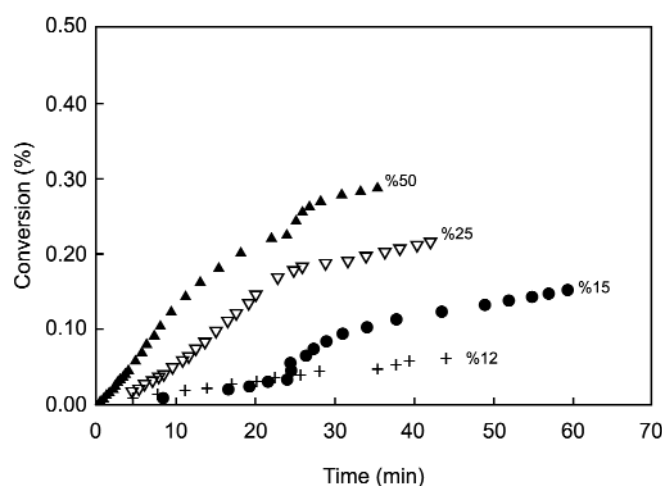


Figure 4. Monomer conversion X versus time histories in MMA/EGDM copolymerization at: 12(+); 15(●); 25(▽); and 50 mol% EGDM(▲).

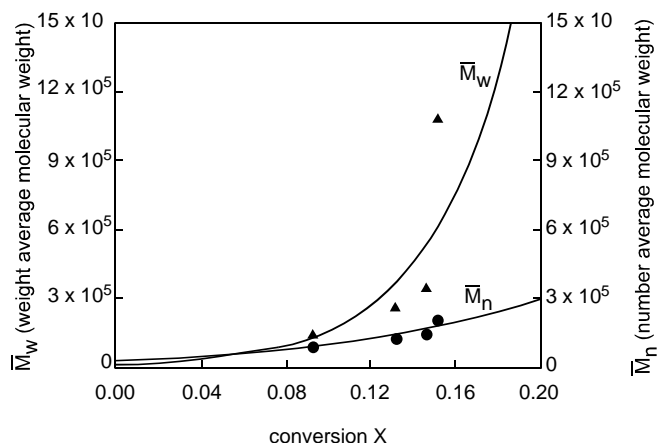


Figure 5. Variation of \bar{M}_w (▲) and \bar{M}_n (●) with monomer conversion X at 50% EGDM concentration in the presence of the bifunctional initiator 4,4'-azo-bis(4-cyanopentanoyl)-bis-benzoin (ACPB).

fraction of EGDM units consumed by cyclization reactions at zero monomer conversion [19, 20]. Using pendant vinyl group measurements by bromination method [14], we found for the present system $X_3 = 0.97$ for different conversions and EGDM concentrations up to the gel point. Thus 97% of the EGDM units in the sol polymers act as cyclic units and, the polymer molecules are intramolecularly cross-linked. Increasing cross-linker

content increases the compactness of the structures formed. This will result in a decrease of the mobility of chain segments and, therefore, suppresses diffusion controlled termination of radicals. Thus termination rate constant decreases as the cross-linker concentration increases which results in the observed enhancement of the rate of polymerization with EGDM concentration. Figure 5 shows the variation of \bar{M}_w and \bar{M}_n with monomer conversion X at 50% EGDM concentration in the presence of the bifunctional initiator 4,4'-azo-bis(4-cyanopentanoyl)-bis-benzoin.

Size Distribution of Sol Molecules

Figure 6 shows a representative set of gel permeation chromatograms (GPC) for reaction products isolated at different reaction times up to the close vicinity of the gel point by bifunctional initiator. The initial concentrations of EGDM were 12, 15 and 50 mol% for series A, B and C, respectively. As the polymerization time in MMA-EGDM copolymerization increases the polydispersity ratios increase and the distribution curves change from single peaks to wider, bimodal distributions.

The shape of the large elution volume peaks is essentially the same, irrespective of the polymerization time while small elution volume peaks are increased

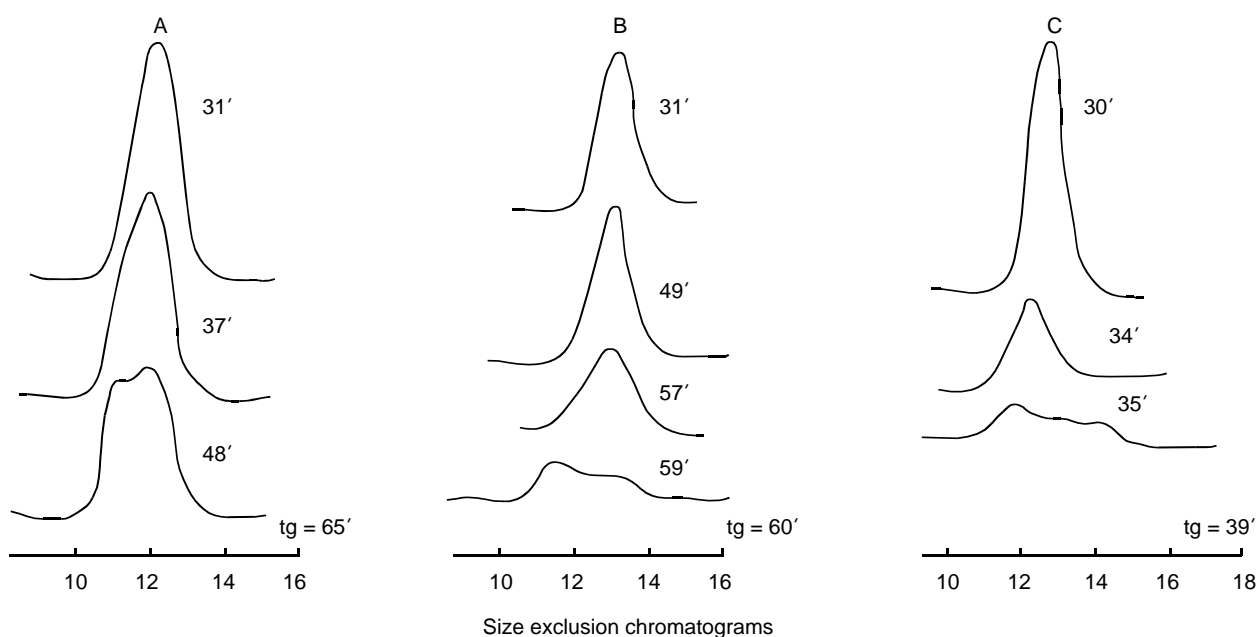


Figure 6. Size exclusion chromatograms of the pre-gel polymers isolated at different reaction times in MMA/EGDM copolymerization. The initiator was 4,4'-azo-bis(4-cyanopentanoyl)-bis-benzoin (ACPB). EGDM Concentration =12(A), 15(B), and 50%(C).

significantly as the reaction proceeds. Increasing cross-linker concentration results in strongly GPC curves in the immediate vicinity of the gel point for free radical systems, bimodal distributions have been observed previously [21,22] but also in some studies monomodal GPC curves have been reported [23,24]. Calculations using statistical [25,26] or kinetic [27-29] theories predict, however, monomodal weight-chain length distributions, which are fundamentally equivalent to the elution curve in the GPC calculated results for the sol phase near the gel point giving flat curves extending across the molecular weight (elution volume) axis toward infinity. However, as shown in Figure 6, the actual behaviour is completely different. It is known that the molecules are separated in the GPC columns according to their hydrodynamic volume. Thus, the molecules with the same molecular weight but different hydrodynamic volumes, i.e. those with polydispersity shape, 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 polydispersity shape, of the molecules present during the polymerization. One may expect that the large shape polydispersity due to the increasing extent of cyclization at high EGDM contents 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.

Cyclization

Figure 7 shows the plot of pendant conversion X_3 versus monomer conversion X for different cross-linker concentrations. Scattering of the data originates from the uncertainty of the method of measurements, which is estimated to be ± 0.1 . Approximately, 97% of the pendant vinyl groups were found to be consumed by cyclization reactions. The fraction of units in cycles is independent of the EGDM concentration.

However, since increasing EGDM concentration also increases the number of divinyl monomer units on the polymer molecules, the higher the EGDM content, the higher is the number of cycles on polymer chains, and therefore, the more compact would be the primary particles.

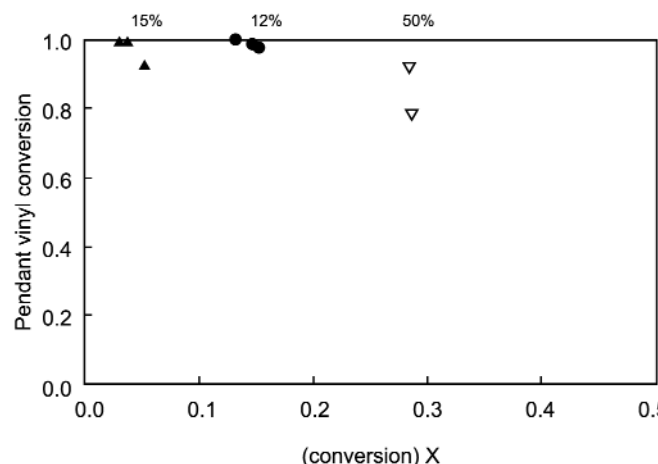


Figure 7. Variation of the pendant vinyl conversion X_3 with the monomer conversion X in MMA/EGDM copolymerization. EGDM Content = 12(●) ; 15(▲) and 50 (▽).

The extent of multiple cross-linkages from experimental data in Figure 4 is because of the experimental error involved in the data points. However, the slight change in polymer unsaturation with conversion indicates that the multiple cross-linking reactions are not important under the experimental conditions. The results on cyclization are in accordance with the reaction rate data of the previous paper [14]. Increasing cross-linker content increases the compactness of the structures formed, this will result in a decrease in the mobility of chain segments and, therefore, suppresses diffusion controlled termination of radicals owing to steric reasons. These phenomena are reflected in the enhancement of the rate of polymerization shown in Figure 4.

Previous percolation-type simulations, called kinetic gelation models [16,31] predicted zero pendant vinyl group conversion at zero monomer conversion. This means that there is no cycle formation at the start of the reaction as the reaction proceeds, the number of cycles increases rapidly and after passing a maximum it decreases again.

According to our experimental results the cyclization involves only the reactions of polymer radical with its own chain, and so it is reasonable to expect maximum cycle formation at zero monomer conversion. Indeed our present results show that the extrapolated value of pendant vinyl conversion to zero monomer conversion is not always zero, indicating the existence of cycles in the first formed primary molecules.

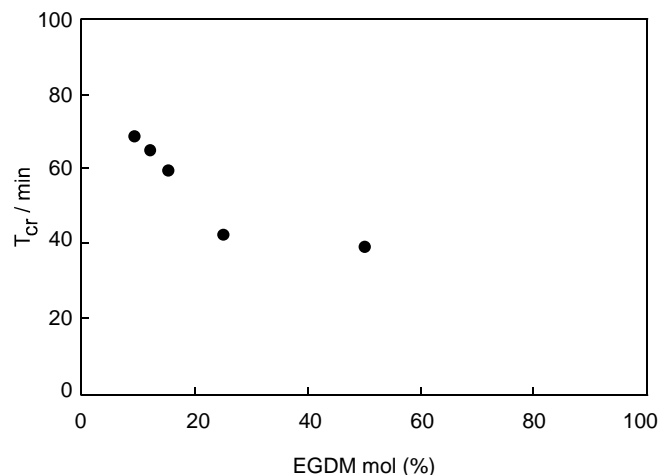


Figure 8. Gel points in terms of the reaction time t_{cr} and as a function of the EGDM concentration. The initiator was 4,4'-azo-bis-(4-cyanopentanoyl) bis-benzoin (ACPB).

Gel Points

Experimentally determined gel points in terms of the reaction time t_{cr} Figure 8 as a function of the EGDM concentration. The initiator used was 4,4'-azobis-(4-cyanopentanoyl) bis-benzoin as thermal and UV initiator. The expected inverse dependence of the gel point on cross-linker concentration is seen for EGDM contents less than 20%. At higher EGDM contents, the gel point becomes insensitive to the amount of cross-linker in the initial monomer mixture.

CONCLUSION

Approximately 97% of the pendant vinyl groups are consumed by cyclization reactions during the pre-gel regime of the copolymerization of MMA and EGDM in toluene solutions by bifunctional initiator employed. The fraction of units in cycles is independent of the EGDM concentration.

However, since increasing EGDM concentration would also increase the number of divinyl monomer units on the polymer molecules, with higher EGDM content, then the higher the number of cycles on polymer chains, and therefore, the more compact would be the primary particles formed.

Due to the cyclization reactions, the accessibility of the radical centres and pendant vinyl groups for other polymer molecules are strongly reduced. As a result

both termination and cross-linking reactions are controlled by the segmental diffusion of the polymer radicals. Variations in the polymerization rate and molecular weight of the primary molecules with EGDM concentration reflect the decrease of the diffusion-controlled termination rate constants with increasing cross-linker concentration. Since cyclization is a first-order reaction, the termination rate constant of zero conversion polymer radicals also depends on the cross-linker content of the monomer mixture. Calculations indicate 1-2 orders of magnitude decrease in the average reactivity of pendant vinyls for intermolecular reactions compared with the monomeric vinyl. In accordance with our previous results[32] this drastic pendant reactivity is mainly responsible for the delay in the gel point. Thus the discrepancy between the observed and calculated gel point, reported already in the literature as early as 1945 [33] is mainly due to the reduced reactivity of pendant vinyl groups.

Contrary to the gelation theories, the size distribution curves of the pre-gel polymers change from monomodal to bimodal distributions as polymerization proceeds. The position and shape of the large elution volume peak corresponding to polymers with small hydrodynamic volumes remain essentially unchanged during the reactions, while a second peak corresponding to small elution volumes appears as the polymerization time approaches the gelation time. This finding confirms the coagulation-type gelation mechanism of compact primary particles and indicates the termination and cross-linking reaction rate constants to include their dependence on the structure of the reacting molecules one may incorporate the size and structure dependent kinetics into the mean field model calculations.

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