

Dilute gelling systems: copolymers of styrene and glycol dimethacrylates

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(Received 23 November 1979)

Gelation properties of the copolymers of styrene with various proportions of ^{14}C labelled ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate and polyethylene glycol (MW = 400) dimethacrylate have been studied. The thermal copolymerizations were carried out in 15% (v/v) solution in toluene. The rates of polymerization were found to increase with larger proportions of dimethacrylate crosslinking agents. The conversion at the gel point was surprisingly constant over a wide range of crosslinker concentration. The fraction of crosslinker saturated at both ends was found to increase in the order ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate and polyethylene glycol 400 dimethacrylate. The proportion of completely reacted crosslinker increased only slowly with conversion. At very high concentrations of crosslinker, the onset of inhomogeneity was observed as described previously by Storey³ and Dusek¹⁸.

INTRODUCTION

The gel forming behaviour of vinyl-divinyl copolymerization has been extensively studied by several research workers¹⁻⁵, and it has become apparent that substantial deviations occur from the theory of polyfunctional polymerization reaction as proposed by Flory and Stockmayer⁶. A clear reason for this deviation, which was originally investigated by Simpson and coworkers, lies in the occurrence of intramolecular cyclization⁷⁻⁹. Work in the present series of papers has aimed at determining precisely the amount of internal cyclization by extrapolating polymer structures to zero conversion¹⁰⁻¹². In this paper we study the gelation of styrene-glycol and polyglycol dimethacrylate copolymers for which some information on internal cyclization is already available. The results extend the apparently unlikely conclusions of Storey³ and Dušek⁴ regarding the insensitivity of conversion at the gel point to the concentration of crosslinking agent.

EXPERIMENTAL

Chemicals

Styrene and toluene were purified immediately prior to each polymerization, exactly as described in the preceding paper¹².

The glycol dimethacrylates were synthesized as before¹² by the reaction of ^{14}C radioactive NaCN with acetone, followed by hydrolysis to methacrylic acid, which when reacted with the appropriate glycol, produced the glycol dimethacrylate. The three methacrylates used were:

- 1 Ethylene glycol dimethacrylate (EGDM)
- 2 Tetraethylene glycol dimethacrylate (TEGDM)
- 3 Polyethylene glycol (MW400) dimethacrylate (PEG (400) DM)

Polymerizations

Polymerizations were carried out at $95^\circ \pm 0.1^\circ\text{C}$, in glass Carius tubes exactly as before¹². First the polymerizations were carried out with inactive crosslinking agents to establish a rough idea of gel points. The experiments were then repeated with radioactive crosslinkers and the gel-points were observed visually.

Copolymer analyses

The copolymers were characterized in the same way as described in the preceding paper¹².

RESULTS AND DISCUSSION

The main aspects of the investigation include the study of the overall rates of polymerization, the time taken to gelation and the conversion at gelation. The incorporation of the crosslinkers into the copolymers, and the fraction of the incorporated crosslinker reacted at both ends at various stages of the reaction is of particular interest for the determination of the amounts of intermolecular crosslinking and intramolecular cyclization reactions taking place in the course of the polymerization.

The polymerizations described here were carried out with 10–20 mol % dimethacrylate crosslinker feed concentrations, so extending the previous work which was limited to 4 mol %. All the rates of polymerization showed pronounced increases on the incorporation of the crosslinker, but with the higher concentrations used here increases in rate of up to 3–4 times were observed (*Figure 1*). Comparison of the results with the three different methacrylates showed that the one based on PEG 400 gave the greatest increase in reaction rates. Results of a similar type have previously been observed with styrene-divinyl benzene (for example, references 3, 10) and are generally ascribed to the limitation

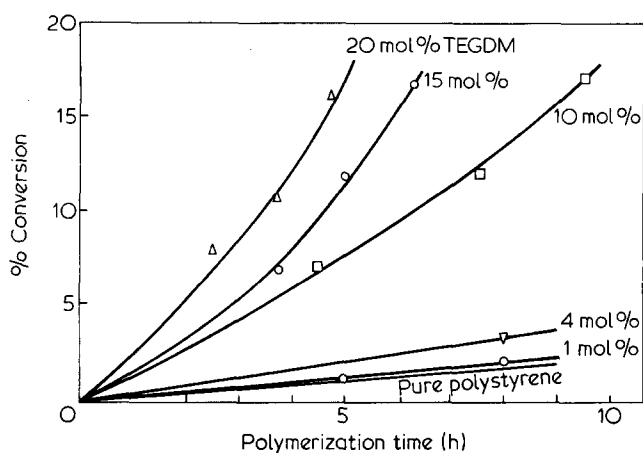


Figure 1 The effect of tetraethylene glycol dimethacrylate concentration on the rate of polymerization

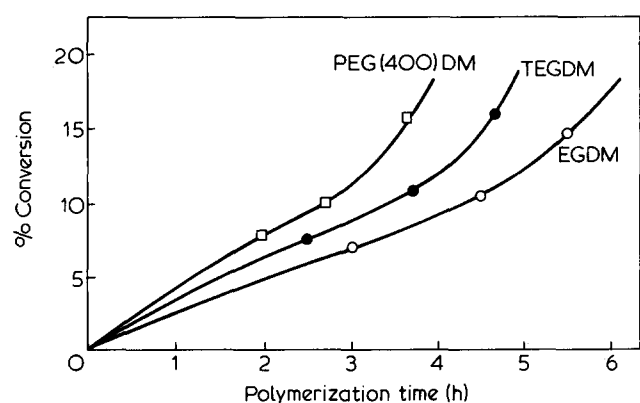


Figure 2 Comparison of the rates of copolymerization at 20% crosslinker feed for different comonomers

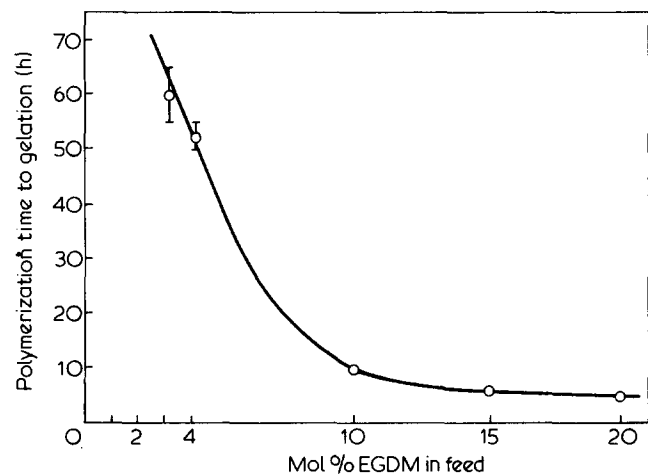


Figure 3 Polymerization time required for gelation in relation to the mol % EGDM in feed

of the chain termination reaction as originally proposed by Norrish and Smith^{13,14}. In the present system, however, the effect will be reduced by the presence of a transfer reaction (to toluene) that effectively controls the initial polymer molecular weight¹⁰. For this reason, gel formation occurs much more quickly with higher dimethacrylate concentrations (Figures 3–5), though the extent of reaction at gelation remains more or less the same (about 15% conversion) in all the polymerization systems ranging from 1 mol % to

20 mol % crosslinker feed concentrations, and for all the three dimethacrylate crosslinkers under investigation (Figure 6). These results fall generally into line with the results of Malinsky, Klaban and Dusek⁴, who studied styrene divinyl benzene polymerizations, and reported that conversions at gelation did not depend on the concentration of divinyl benzene over the range 10–100 mol % *p*-DVB. Similar results were reported by Storey³ over the range 8–100 mol % *p*-DVB. Thus there seems no reason to doubt the correctness of this otherwise unexpected conclusion.

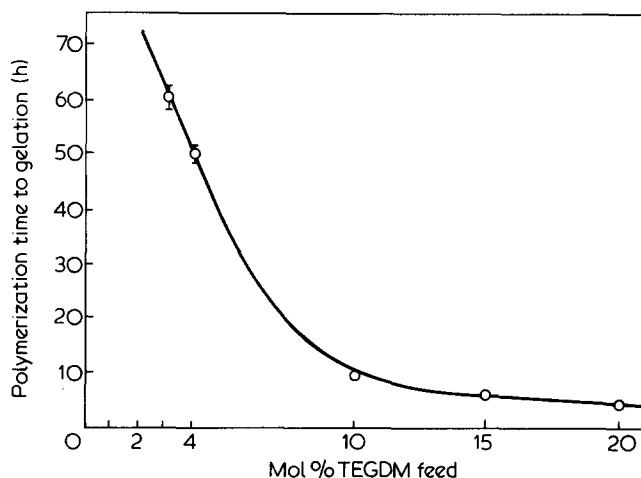


Figure 4 Polymerization time required for gelation in relation to the mol % TEGDM in feed

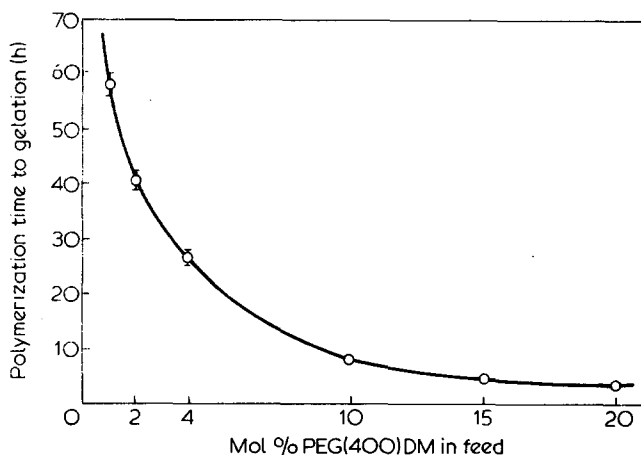


Figure 5 Polymerization time required for gelation in relation to the mol % PEG(400) DM in feed

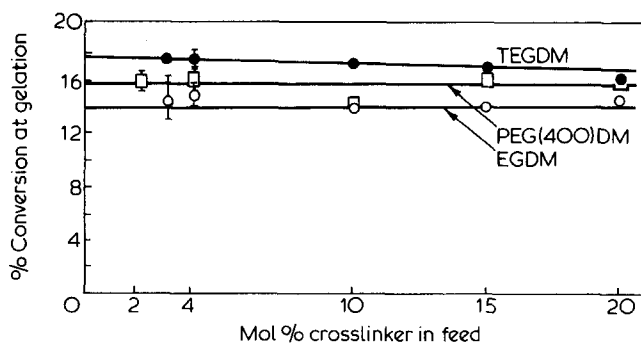


Figure 6 Level of conversion at gelation at different crosslinker feed concentrations

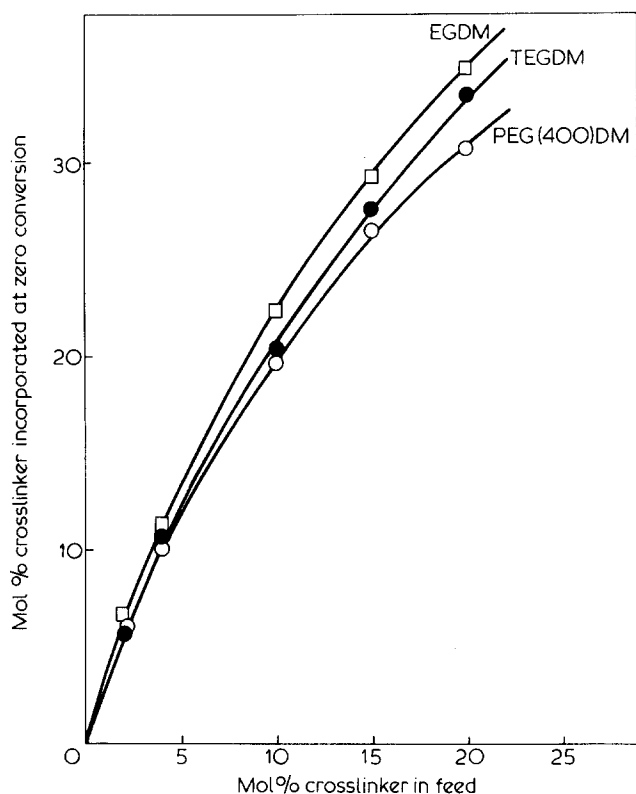


Figure 7 Percent crosslinker incorporated at zero conversion related to mol % in feed

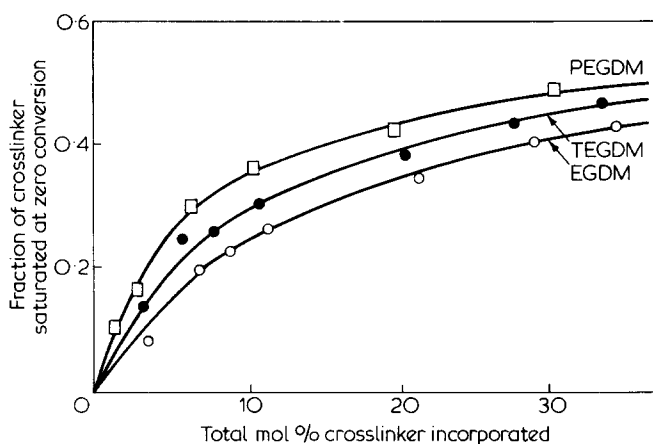


Figure 8 Percent crosslinker incorporated plotted against fraction saturated at both ends at zero conversion

The incorporation of the crosslinker in the copolymer for various crosslinker feed concentrations was measured (Figure 7), showing that EGDM is incorporated in the highest molar proportions followed by TEGDM and PEG (400) DM.

Figure 8 shows how the fraction of the dimethacrylate reacted at both ends changes with conversion. As might be expected, the fraction of the dimethacrylate reacted at both ends increases with conversion, indicating increasing intermolecular reaction. However, this increase is not much greater than that of similar copolymers containing lesser dimethacrylate contents studied earlier¹². Figure 9 shows the fraction of the dimethacrylate reacted at both ends, extrapolated to zero conversion for the three various crosslinkers under investigation. This fraction is found to increase with greater crosslinker concentrations. At zero conversion conditions, if only intramolecular reactions are assumed to

occur, this implies that intramolecular reactions increase with increasing crosslinker feed concentrations.

Another important observation made was that with higher dimethacrylate feed concentrations, more and more inhomogeneity was observed.

Evidence relating to the gelation process

Taking the present results with those of the previous paper¹², the following conclusions can be drawn;

- (i) at zero conversion the relative incorporation of the three comonomers is not very different and lies in the order EGDM > TEGDM > PEG (400) DM;
- (ii) at zero conversion the effectiveness of an internal crosslink (fully saturated crosslinker) in reducing the limiting viscosity number of the copolymer is in the order *p*-divinyl diphenyl > PEG(400)DM > TEGMA > EGDM¹². Presumably this is due to the formation of larger cyclic structures with the more effective comonomers, so that a greater proportion of the polymer chain is involved in cyclization*.
- (iii) based on number average molecular weight measurements with the styrene-*p*-divinyl benzene system¹⁰, the number of pendant vinyl groups consumed for one effective intermolecular linkage increases with crosslinker content; as this number can be as high as 6 it is clear that the reaction of pendant vinyl groups does not measure effective crosslinkage; the tightly coiled original polymer molecule with a relatively large number of pendant vinyl groups reacts at several points with the first active polymer chains which become attached;
- (iv) in the system used here, the occurrence of chain transfer raises the possibility that fast moving small radicals can detach themselves from a particular polymer molecule; however, as each polymer molecule is a free radical trap a net transfer inwards into preformed polymer molecules or 'microgels' is to be expected;
- (v) in tight molecular coils with a high pendant vinyl population, large numbers of vinyl groups will be effectively shielded from taking part in the first critical crosslinking reaction with a diffusing macroradical;
- (vi) based on a radius of gyration of 20 nm¹⁰, which should be a lower limit for the polymers considered here, the volume of an assembly of polymer coils consisting of the zero conversion polymer, becomes equal to the total

* Taken from Figure 14, Reference 12. It may be noted that the dotted curve for linear polystyrene should not be present on the figure

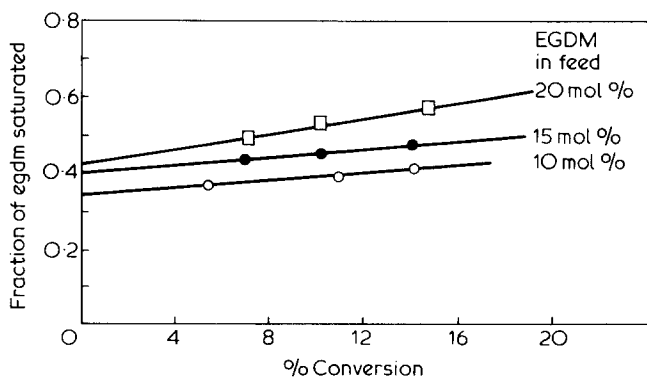


Figure 9 Fraction of crosslinker reacted at both ends in relation to conversion

volume of the solution at a conversion of 6–8%, i.e. a total polymer concentration of ~1%; this concentration would decrease with the more loosely cyclized molecules having higher limiting viscosities.

It is difficult to undertake any precise treatment of all these various factors, but it seems that the following proposition is possible. After each polymer molecule is formed, further pendant vinyl groups will be joined together by the multiple reactions associated with each crosslinking step, and this will lead in turn to a contraction in volume of the original primary coil^{15–17}. With the reduced coil (microgel) volume the rate of the intercoil crosslinking reaction by which two separate molecules (microgels) are united is reduced. This then counteracts the direct effect whereby the crosslinking should be directly related to the concentrations of pendant double bonds.

Thus more complex, tightly-linked molecules are formed as the proportion of pendant vinyl groups on the zero conversion polymers is raised, and the coils grow by the addition of macroradicals, by which they become larger and contain an increased number of immobilized vinyl groups. This will make them still more effective as free radical traps. With the highest concentration of crosslinker, especially with the EGDM copolymers, inhomogeneity was encountered at high conversions, which was easily visible as a pronounced haze. This effect is considered to be almost certainly the same as that seen by Storey³ and Dušek¹⁸ who gave the name of 'microsyneresis' to this effect. According to Dušek this occurs when the maximum degree of swelling of a network in the solvent (which falls as further crosslinks are introduced) drops to the initial degree of swelling. Our observations are in accordance with this concept.

ACKNOWLEDGEMENT

The authors would like to thank Dr. C. A. Barson for assistance with radioactive techniques.

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