Studies of dimethylacrylates as crosslinkers for styrene

Ashok C. Shah, Ian Holdaway, Ian W. Parsons and Robert N. Haward
Department of Chemistry, University of Birmingham, P. O. Box 363, Edgbaston, Birmingham B15 2TT, UK

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Styrene has been thermally copolymerized to low conversions with small quantities of ^{14}C labelled ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate and poly(ethylene glycol) (mol. wt $\approx$ 400) dimethacrylate. The competition between intramolecular cyclization and intermolecular crosslinking has been examined via studies of intrinsic viscosity, variation of the proportion of the crosslinker reacted at both vinyl groups with conversion, and changes in the polydispersity ratio. These studies indicate that in the early stages of reaction, reductions in intrinsic viscosity are found to be maximum in PEG(400)DM copolymers, followed by TEGDM–styrene copolymers and least in the EGDM–styrene system. Also, in zero conversion extrapolation analysis, the fraction of the crosslinker reacted at both the ends increases with the molecular weight of the ethylene glycol unit. These observations imply that intramolecular cyclization is favoured by increasing the distance of separation between the two vinyl end groups of the dimethacrylate crosslinker. The increase in the fraction of the crosslinker reacted at both ends with conversion is found to be most rapid in the PEG(400)DM–styrene copolymers and least in the EGDM–styrene copolymers. The increase in polydispersity ratio with conversion is also found to fall into the same sequence. These observations suggest that intermolecular crosslinking is also favoured by increasing separation between the two vinyl groups of the crosslinker, i.e. the reactivity of the double bond attached to the polymer chain is greater both for cyclization and intermolecular reaction when the length of the poly(ethylene glycol) unit is increased.

INTRODUCTION

The commercial importance of the copolymerization of styrene with difunctional monomers, such as mixed divinylbenzene isomers, in the manufacture of ion exchange resins and also in gel permeation chromatography has led several workers to seek to understand the various factors controlling the behaviour of different divinyl monomers with a view to ensuring efficient usage of the crosslinking agent. The study of the competition between intermolecular crosslinking and intramolecular cyclization has been a subject of particular interest to several workers. Staudinger[1] showed formation of insoluble networks caused by crosslinking. Haward and Simpson[2] carried out styrene–divinylbenzene copolymerizations to low conversions and showed the presence of internal cyclizations. Later, Zimm, Price and Bianchi[3] carried out similar work and tried to predict gel points. Storey[4] studied the styrene–*p*-divinylbenzene system and established a relationship between gel points and intramolecular cyclization. Also, a great deal of fundamental work has been undertaken[5,6] to study the physical properties of these copolymers.

Soper, Haward and White[7] have studied copolymerization of styrene with *p*-divinylbenzene at low conversions in solution, to estimate the extent of cyclization taking place. They observed that an appreciable proportion of the crosslinker reacted at both ends and this was accompanied by reduction in intrinsic viscosity, indicating a substantial amount of cyclization in the early stages of the reaction. They also estimated the size of the rings formed as 6–12 styrene units, and estimated the consumption of vinyl groups during interchain crosslinking. In a preliminary study using *N,N' bis(p*-methacryl-oxybenzylidene)-1,2-diaminoethane[8], it was inferred that by increasing the distance between the two vinyl end groups of a divinyl monomer, early gel points and greater extents of interchain crosslinking would generally be obtained.

Later, Holdaway, Parsons and Haward[9] studied the copolymerization of styrene with 4,4'-divinyl diphenyl and 4,4'-diisopropenyl diphenyl in toluene solution. In this work, the competition between intermolecular crosslinking and intramolecular cyclization was studied via intrinsic viscosity measurements and molecular weight distributions. They reported that the effect of the inter-vinyl group distance of the crosslinker on the crosslinking behaviour was not as marked as predicted earlier.

It was initially presumed that rather longer chain aliphatic compounds might show quite different crosslinking behaviour owing to their flexibility, and studies using such aliphatic crosslinkers of variable length might lead to some interesting conclusions. Because of the probable equal reactivity of both vinyl end groups, and the easy availability of various chain lengths of glycols, oligomeric ethylene glycol dimethacrylates seemed to be a suitable choice for crosslinkers in the present work.

EXPERIMENTAL

Chemicals

Styrene was purified immediately prior to each polymerization by washing three times with equal volumes of KOH

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solution (2N) to remove the inhibitor (*p*-tert butyl catechol), followed by similar washings with water, drying over $CaCl_2$ and distillation at 10 mmHg pressure under N_2. A middle fraction boiling at 27°–31°C was collected. PTFE sleeves were used on all joints of the apparatus.

Toluene was refluxed for 16 h with $LiAlH_4$ under nitrogen, and finally distilled at 109°C using a 30 cm Vigreux column and stored over 4A type molecular sieve.

Glycols were purchased from BDH Ltd, and used without further purification.

Glycol dimethacrylates: tetraethylene glycol dimethacrylate (TEGDM)

Preparation of acetone cyanohydrin[10]. Sodium cyanide (25 g) was dissolved in water (60 ml) in a 500 ml flask, and 1 mCi radioactive $Na^{14}CN$ was thoroughly mixed with it. Acetone (45 ml) was added and the contents were converted to acetone cyanohydrin in the usual way[10]. After a standard work-up, a fraction boiling at 65°C (15 mmHg) was collected (yield ~ 60%).

Hydrolysis of acetone cyanohydrin to methacrylic acid[11]. Active acetone cyanohydrin (85 g) was hydrolysed as described in ref 11, maintaining the temperature at about 80°C. After a standard work-up, the acid distilled at 68°–70°C (15 mmHg) (50% yield).

Esterification of methacrylic acid to tetraethylene glycol dimethacrylate. Methacrylic acid (52 g), tetraethylene glycol (59 g), sulphuric acid (3–5 g, 98%), toluene (~ 150ml), hydroquinone (2 g) and benzoquinone (1.5 g) were stirred together in a flask fitted with a Dean and Stark trap. The water was azeotroped out and distillation was continued until no more water separated. The viscous organic liquor was passed through an alumina column (500 g, 3 x 40 cm, Laporte UGl type), and the ester eluted with toluene. The product was stored at –15°C until required. The inhibitors were washed out just before each polymerization (yield 50%). EGDM and PEG(400)DM were prepared similarly.

All the glycol dimethacrylates were characterized spectroscopically: infra-red spectroscopy showed the absence of OH groups; ^1H n.m.r. spectra showed that the ratios of glycol resonances to methacrylate resonances were as expected, and permitted the estimation of residual toluene in the product. Allowance for this has been made in subsequent work.

Pyridine sulphate dibromide

Pyridine sulphate dibromide solution was prepared exactly as described by Rowe, Furnas and Bliss[12].

Polymerizations

Polymerizations were carried out, at 95° ± 0.1°C, in glass Carius tubes sealed under vacuum. The de-inhibited crosslinker was accurately mixed with styrene in the required proportions and 15% (v/v) solutions of total monomer in toluene were used. The solutions were degassed by at least three freeze–thaw cycles before sealing under 10^{-4} mmHg pressure. The polymer was precipated in warm methanol. The suspension was gently boiled to coagulate the polymer which was filtered into a weighed crucible, dried under vacuum at ambient temperature and stored at –10°C.

Viscometry

This was carried out in toluene solutions at 25° ± 0.05°C, using a standard four arm Ubbelhode type dilution viscometer.

Copolymer analyses

Total crosslinker incorporation. The total amount of crosslinker incorporated into each of the copolymers was estimated by radioactivity measurements. The samples were dissolved in Butyl PBD scintillation solution and counted in a liquid scintillation spectrometer (Intertechnique ABAC SL–40), fitted with an on-line computer, programmed with external standard ratio, background rate and quenching factors. This procedure was also used for the active monomers.

Residual (pendant) double bonds. The bromination titration method suggested by Rowe, Furnas and Bliss[12] was used and gave satisfacory results. The weighed sample in solution (in distilled CCl_4) was allowed to react with an excess of pyridine sulphate dibromide solution (in distilled acetic acid) in the presence of mercuric acetate catalyst at room temperature for 16 h. The total reagent was estimated by the usual iodometric titration of a blank with aqueous 0.01 N sodium thiosulphate solution. After absorption, the remaining reagent was estimated and this gave the exact amount of halogen consumed by the sample.

Gel permeation chromatography

G.p.c. analyses were carried out in THF at ambient temperature using 0.25% solutions. The analyses were carried out at the Polymer Supply and Characterization Centre, RAPRA, Shawbury, Shropshire.

RESULTS AND DISCUSSION

The main points of interest lie in studying the overall rates of polymerization, the incorporation of the crosslinkers into the copolymers, and the propertion of incorporated crosslinker reacted at both ends, at various stages of the reaction, also the values of these parameters at zero conversion as obtained by extrapolation of the experimental results. Further, as a check on the other measurements, it is of interest to study the average hydrodynamic radius of the polymer molecules since this is correlated with the observed degree of intramolecular ring formation (which leads to a reduction in the polymer coil volume).

Analogously with the previous observations[4,9], the polymerization rates showed pronounced initial increases on incorporation of crosslinkers, (*Figure 1*), and this increase, ascribed by us previously to a Tromsdorff–Norrish effect[13,14,15] is greatest for the PEG(400)DM–styrene system

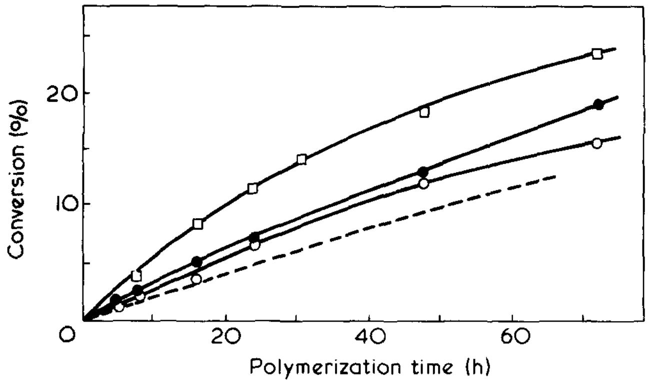


Figure 1 Comparison of the rates of copolymerization at 2 mol % crosslinker feed. Conversion *versus* polymerization time: ○, EGDM; ●, TEGDM; □, PEG(400)DM; — — — —, linear polystyrene

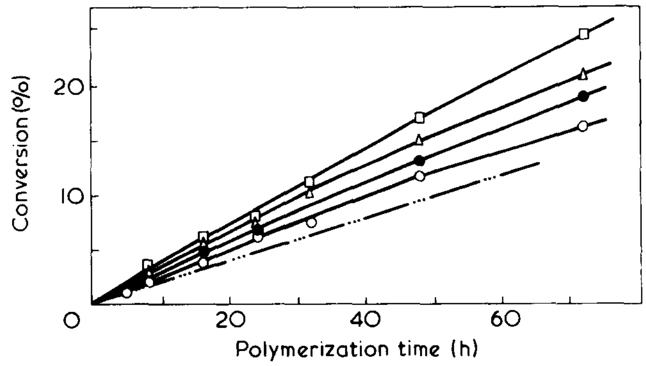
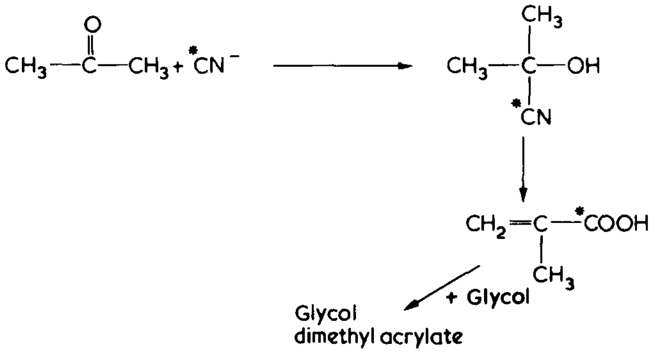


Figure 2 Comparison of the reaction rates with increasing concentrations of TEGDM. Conversion *versus* polymerization time: ○, 1 mol % TEGDM feed; ●, 2 mol % TEGDM feed; △, 3 mol % TEGDM feed; □, 4 mol % TEGDM feed; — · · · — · · · —, linear polystyrene

and least for the EGDM–styrene copolymers. This we take as evidence for faster crosslinking of chains with PEG(400)DM, but an alternative explanation based on a change in the nature of the solution brought about by the relatively high ether group concentration cannot be wholly ruled out. Also, it is observed that the increases in rate are greater with increasing proportions of the crosslinker in the feed (see *Figure 2*). The rates fall off slightly in the later stages of the reaction, presumably owing to depletion of monomers from the system.

The composition of the copolymers was also studied and the variation of this parameter with conversion measured. For this work it was essential to measure separately both the total incorporation of crosslinker and the remaining pendant double bonds. The first objective was attained fairly simply via synthesis of ^{14}C labelled crosslinkers according to the following scheme.



(The chemistry of this sequence is well known, but has apparently not been used before to produce labelled methacrylic acid).

The residual unreacted crosslinker in the polymer samples produced considerable difficulty with the assay of the polymers, and reliable results were obtained only after very prolonged washing of the polymer samples. These results are presented in *Figures 3*, *4* and *5*.

In order to estimate the pendant double bonds, attempts were made to hydrolyse off the pendant ester groups[16]; these proved abortive, and so an alternative analysis for the vinyl groupings was sought. The technique of bromination with pyridine sulphate dibromide[12] proved satisfactory and has been used throughout. These two values (incorporation of crosslinker, and remaining double bonds) for each polymer constituted a complete polymer analysis, and the extrapolations of various interesting quantities to zero conversion are presented in *Table 1*.

An attempt has been made to evaluate the reactivity ratio 'r_1' for the various styrene crosslinker systems using the approximation, for $[M_1] \gg [M_2]$:

$$\underset{\text{(In polymer)}}{\frac{[M_1]}{[M_2]}} = r_1 \underset{\text{(In monomer feed)}}{\frac{[M_1]}{[M_2]}} \quad (\text{clearly } [M_2] = [\text{M\% Dimethacrylate}] \times 2)$$

Extrapolation of calculated r_1 values to zero $[M_2]$ gives an 'ideal' value for r_1 (see *Figure 6*).

As the intramolecular cyclization can be equated with the amount of doubly reacted crosslinker at zero conversions, the values in *Table 1* permit comparison of the degrees of cyclization for each crosslinker.

Originally it was supposed that a greater distance between the reactive groups would lead to less intramolecular ring formation, but the data presented in *Table 1* and *Figure 6* do not support this; indeed they demonstrate clearly that the reverse is true in this case since at zero conversion PEG(400)DM is doubly reacted to a greater degree for all

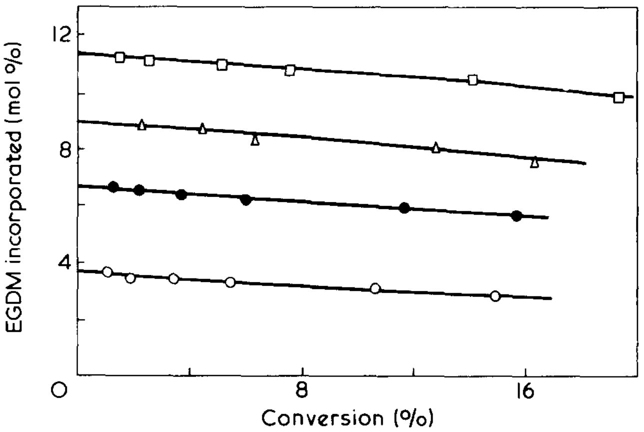


Figure 3 Thermal copolymerization of ethylene glycol dimethacrylate and styrene at 95°C; 15% total monomer (v/v) in toluene. Mol % total crosslinker *versus* conversion: ○, 1 mol % EGDM feed; ●, 2 mol % EGDM feed; △, 3 mol % EGDM feed; □, 4 mol % EGDM feed

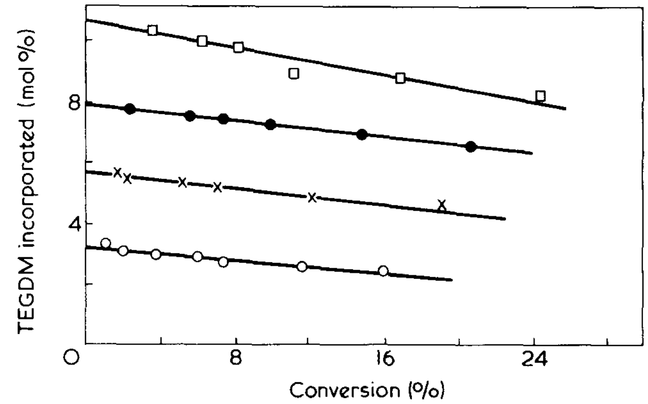


Figure 4 Thermal copolymerization of tetraethylene glycol dimethacrylate styrene at 95°C; 15% total monomer. Mol % total crosslinker *versus* conversion: ○, 1 mol % TEGDM feed; X, 2 mol % TEGDM feed; ●, 3 mol % TEGDM feed; □, 4 mol % TEGDM feed

feed ratios and hence incorporations. If intramolecular cyclizations may be assumed to continue at almost the same rate throughout the early stages of the reaction, the increase in the fraction of the saturated crosslinker with conversion can be attributed to intermolecular crosslinking. From the data in *Figures 8, 9* and *10*, it is clear that the intermolecular crosslinking efficiency of these monomers also increases with the increasing molecular length of the crosslinker.

The results of the intrinsic viscosity measurements (*Figures 11, 12* and *13*) also confirm the above observations. Striking reductions in the values of [η] are observed in the early stages of the reaction, confirming the predominance of intramolecular cyclizations in earlier stages of the reaction (*Figure 14*). A rapid build up in [η] with conversion clearly points to the increasing degree of intermolecular crosslinking.

For confirmation of the above observations, we adduce some selected g.p.c. results. In low conversion polymers, the g.p.c. curves show a slight shift towards higher elution counts (i.e. lower hydrodynamic volume) with increasing incorporation of the crosslinker (*Figure 15*). This obviously shows more intramolecular cyclization in the early stages of reaction. As conversion proceeds, the retention volumes are slightly decreased in all the cases, and are more markedly decreased at higher crosslinker incorporations, indicating increasing hydrodynamic volumes due to intermolecular crosslinking. The polydispersity ratios also increase with conversion and the distribution curves change from single peaks to wider, bimodal distributions. These changes may be attributed to agglomeration of the microgel structures to larger species due to intermolecular crosslinking.

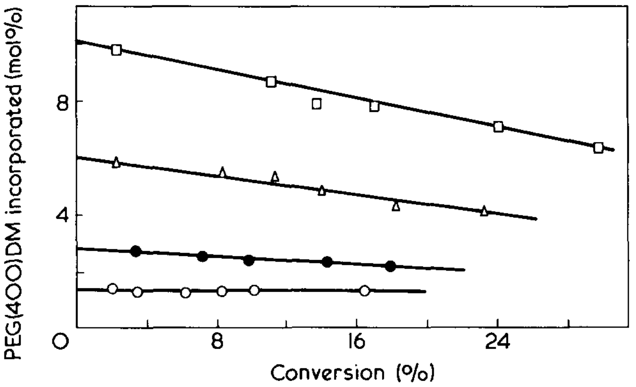


Figure 5 Thermal copolymerization of poly(ethylene glycol) (400) dimethacrylate and styrene at 95°C; 15% total monomer v/v in toluene. Mol % total crosslinker *versus* conversion: ○, 0.5 mol % PEG(400)DM feed; ●, 1 mol % PEG(400)DM feed; △, 2 mol % PEG(400) feed; □, 4 mol % PEG(400)DM feed

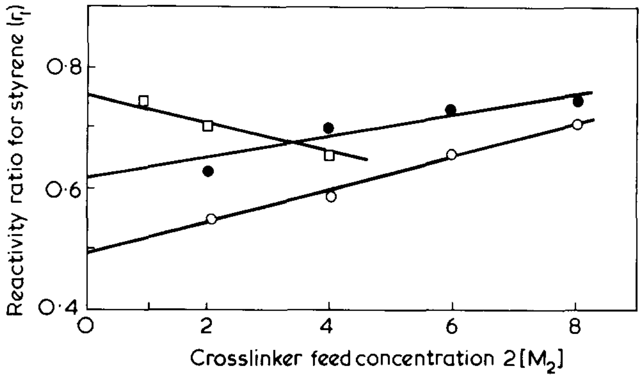


Figure 6 Reactivity ratio 'r' for styrene *versus* comonomer feed concentration: ○, EGDM; ●, TEGDM; □, PEG(400)DM

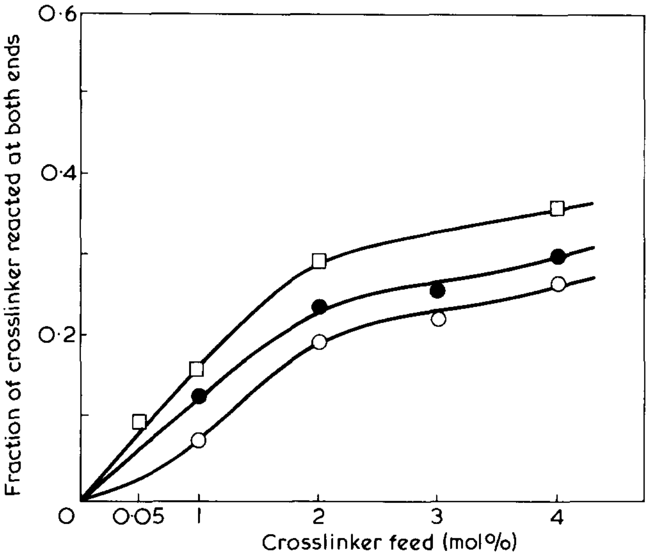


Figure 7 Zero conversion copolymer analysis. Fraction of crosslinker reacted at both ends *versus* mol % crosslinker in feed: ○, EGDM; ●, TEGDM; □, PEG(400)DM

Table 1 Extrapolated analyses of zero conversion polymers

Crosslinker	Mol % in feed	Mol % in copolymers	Mol % reacted at both the ends	Fraction of crosslinker reacted at both the ends	[η] (dl/g)	r_1
EGDM	1	3.64	0.30	0.075	1.00	0.54
	2	6.70	1.35	0.195	0.91	0.58
	3	9.00	1.97	0.22	0.84	0.63
	4	11.35	3.10	0.27	0.75	0.68
TEGDM	1	3.2	0.43	0.13	0.81	0.61
	2	5.65	1.35	0.24	0.71	0.685
	3	7.9	2.01	0.255	0.615	0.71
	4	10.7	3.25	0.30	0.46	0.72
PEG(400)DM	0.5	1.35	0.14	0.10	0.975	0.74
	1	2.85	0.45	0.16	0.665	0.69
	2	6.10	1.85	0.295	0.52	0.64
	4	10.10	3.65	0.36	0.405	–*

* Not calculated, owing to high concentration of $-CH_2CH_2O-$ groups

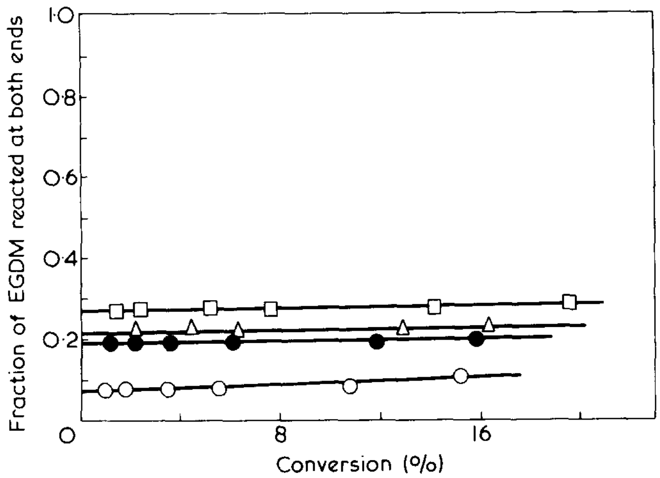


Figure 8 Fraction of EGDM reacted at both ends *versus* conversion: ○, 1 mol % EGDM feed; ●, 2 mol % EGDM feed; △, 3 mol % EGDM feed; □, 4 mol % EGDM feed

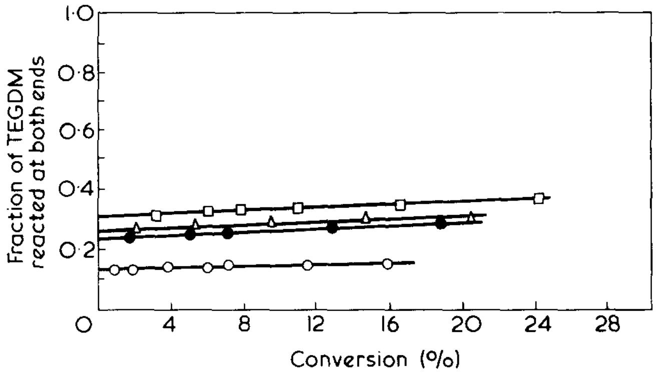


Figure 9 Fraction of TEGDM reacted at both ends *versus* conversion ○, 1 mol % TEGDM feed; ●, 2 mol % TEGDM feed; △, 3 mol % TEGDM feed; □, 4 mol % TEGDM feed

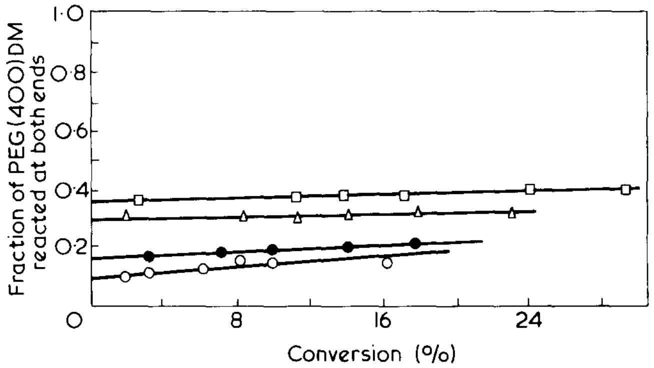


Figure 10 Fraction of PEG(400)DM reacted at both ends *versus* conversion: ○, 0.5 mol % PEG(400)DM feed; ●, 1.0 mol % PEG(400)DM feed; △, 2.0 mol % PEG(400)DM feed; □, 4.0 mol % PEG(400)DM feed

We conclude from the above observations, that the overall length of the crosslinker is important in deciding the type and extent of crosslinking, although not as markedly as one would expect. The present work shows clearly that at least for the monomers studied here, inter- and intramolecular reaction rates are affected in the same sense by the length of

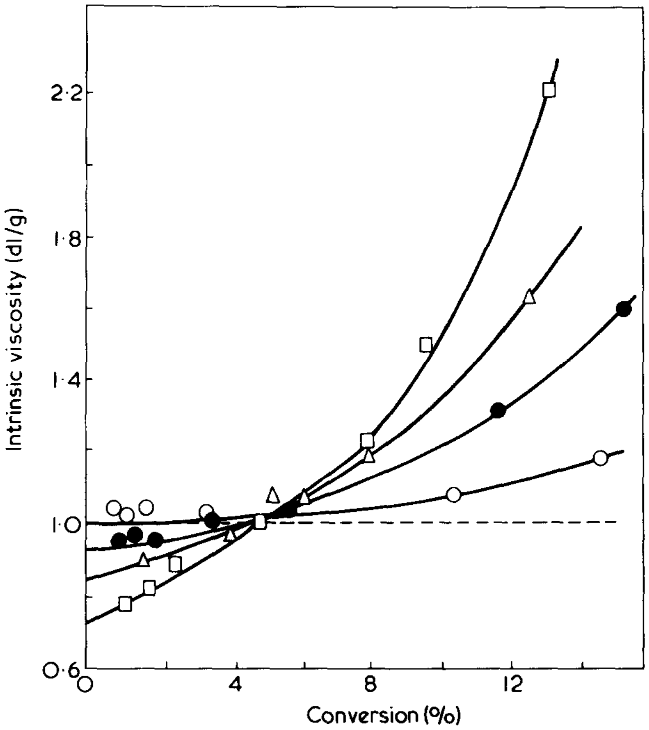


Figure 11 Intrinsic viscosity *versus* conversion for EGDM–styrene copolymers: ○, 1 mol % EGDM feed; ●, 2 mol % EGDM feed; △, 3 mol % EGDM feed; □, 4 mol % EGDM feed; – – – –, linear polystyrene

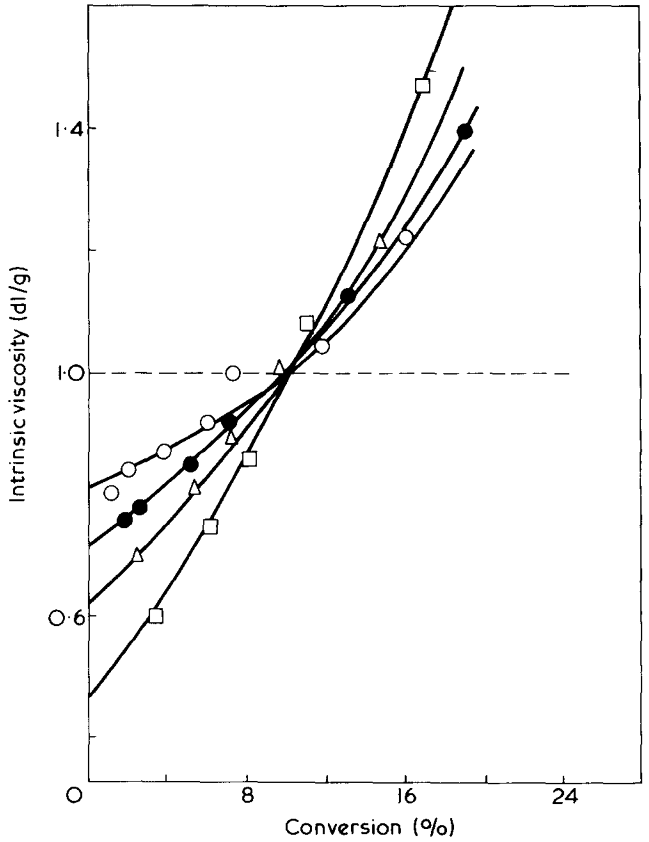


Figure 12 Intrinsic viscosity *versus* conversion for TEGDM–styrene copolymers: ○, 1 mol % TEGDM feed; ●, 2 mol % TEGDM feed; △, 3 mol % TEGDM feed; □, 4 mol % TEGDM feed; – – – –, linear polystyrene

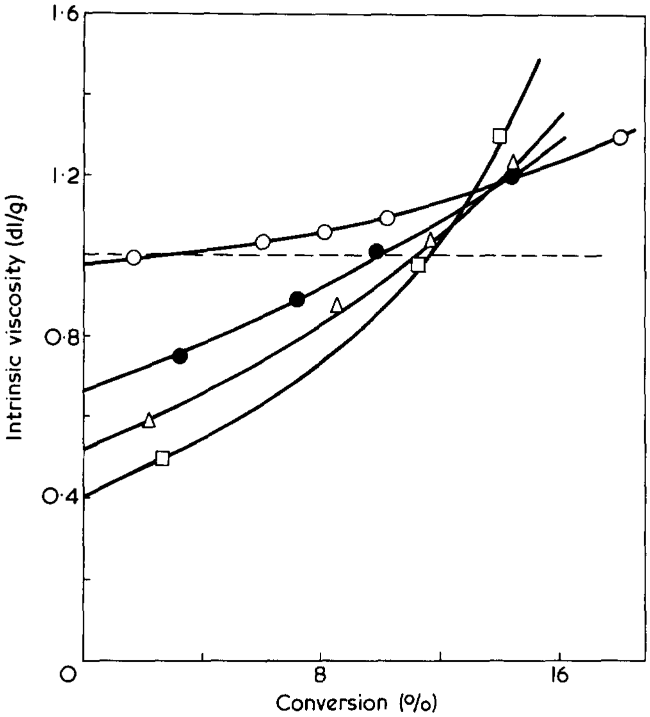


Figure 13 Intrinsic viscosity *versus* conversion for PEG(400)DM–styrene copolymers: ○, 0.5 mol % PEG(400)DM feed; ●, 1.0 mol % PEG(400)DM feed; △, 2.0 mol % PEG(400)DM feed; □, 4.0 mol % PEG(400)DM feed; — — — —, linear polystyrene

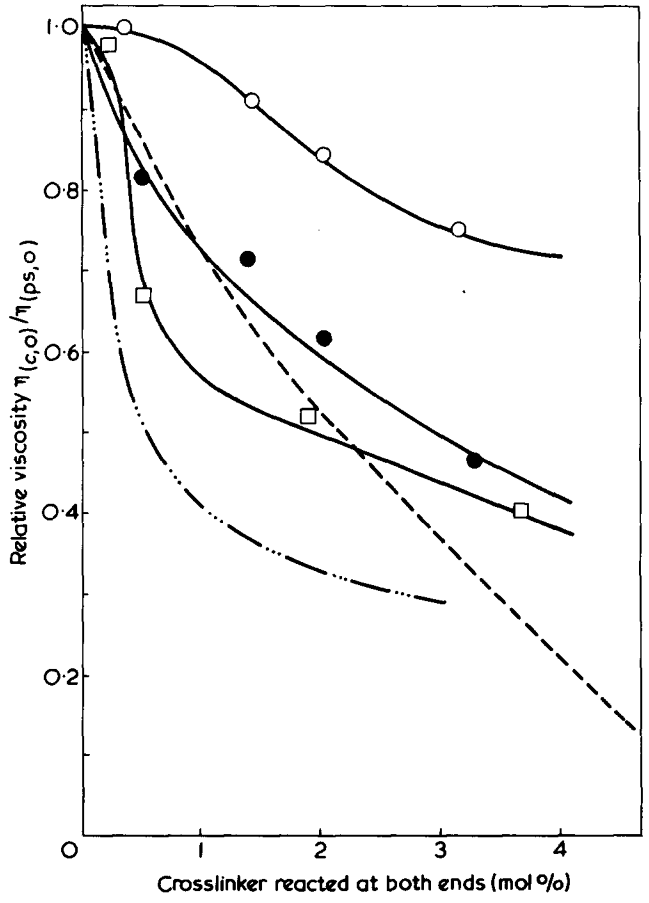


Figure 14 Zero conversion copolymer analysis. Relative viscosities *versus* mol % crosslinker reacted at both ends: ○, EGDM; ●, TEGDM; □, PEG(400)DM; — — — —, linear polystyrene; · · · —, 4,4'-divinyl diphenyl

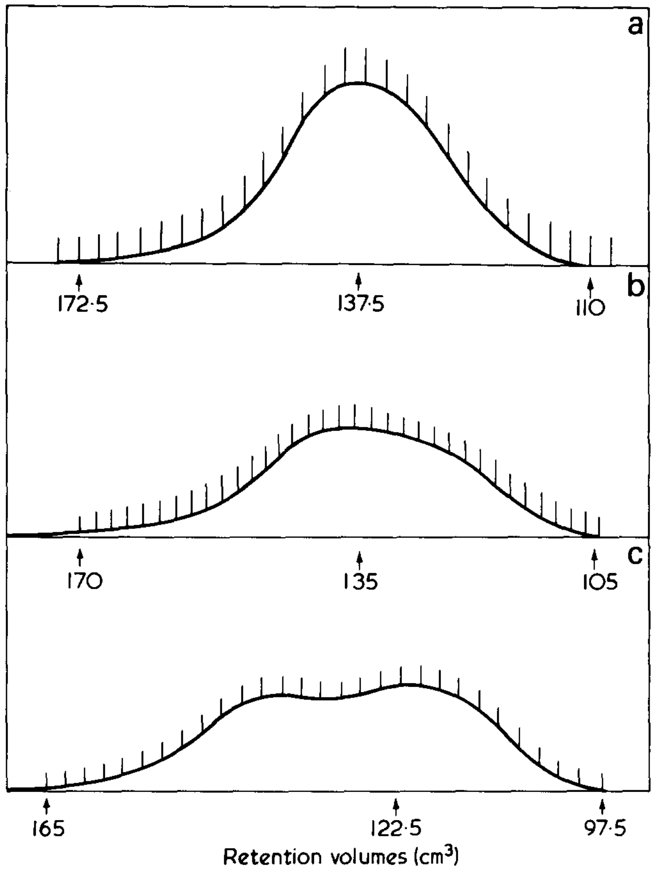


Figure 15 Gel permeation chromatography analysis of copolymers of TEGDM and styrene 4M% TEGDM feed: (a) sample A; (b) sample B; (c) sample C

Sample	Polymerization time (h)	Conversion (%)	[η] (dl/g)	Polydispersity ratio†
A	16	6.00	0.75	3.52
B	32	10.90	1.08	5.52
C	48	16.80	1.47	15.80

† Calculated with no regard for the effect of intramolecular crosslinkers

the chain connecting the reactive group to the 'main' polymer chain, i.e. greater distance between the reactive groups in the crosslinker leads to higher reactivity in these senses. As far as incorporation of crosslinker is concerned, the reverse is true.

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