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The Radiation-Induced Copolymerization of Methyl Methacrylate with Di- and Trimethacrylates

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ABSTRACT

The rates and gel formation of the radiation-induced copolymerization of a number of dimethacrylates and trimethylol propane trimethacrylate with methyl methacrylate has been studied in detail. The rates were found to be linked to the nature and amount of gel formed rather than to differences in the reactivities of the monomers.

INTRODUCTION

The previous papers in this series [1, 2] were concerned with the radiation-induced polymerization of styrene and methyl methacrylate at high dose rates. Studies of the kinetics at high dose rates are complicated by the accompanying heat effects due both to beam heating and the exotherm associated with such rapid polymerizations. The kinetics are further complicated in electron beam studies by the complex dose-depth relationships and the use of scanned beams [1-3].

Practical aspects of such studies are concerned with the growing use of electron beams for curing reactive coating compositions consisting of mixtures of unsaturated polymers and vinyl monomers. The present paper describes the results of extending the simple monomer systems to mixtures of di- and trivinyl compounds with the corresponding simple vinyl monomer. Specifically, the radiation-induced copolymerization of di- and trimethacrylates with methyl methacrylate was studied. With such rapidly gelling polymerizations the heat effects at high dose rates are very large and the major proportion of this investigation was therefore conducted at lower dose rates using a ^{60}Co source.

The chemical reactivity of each double bond in the entire system should be equivalent. Differences in the reaction rates for the various multifunctional methacrylates would be expected to be due to differences in the steric resistance in a diffusion-controlled reaction plus any special features of the radiolysis on the initiation step. The relationship between the development of cross-links and the autoacceleration in the rates of polymerization should therefore be particularly meaningful. The effect of cross-linking on the onset of autoacceleration was first reported by Hayden and Melville [4] in their studies of the copolymerization of methyl methacrylate and ethylene glycol dimethacrylate. Increasing the proportion of the dimethacrylate increased the number of cross-links at a given conversion and caused the onset of autoacceleration to occur at lower conversions. The present studies include the effects of changes in both the structure and the concentration of the dimethacrylates and of one trimethacrylate, at dose rates varying from 240 to 2.8×10^6 rads/sec, on the kinetics of copolymerization, autoacceleration, cross-linking, and gel formation.

EXPERIMENTAL

Methyl methacrylate (MMA) was obtained from the Rohm and Haas Co. Ethylene glycol dimethacrylate (EGDM), 1,3-butylene glycol dimethacrylate (BGDM), 1,4-tetramethylene glycol dimethacrylate (TMGDM), 1,6-hexamethylene glycol dimethacrylate (HMGDM), diethylene glycol dimethacylate (DEGDM), and diisopropylene glycol dimethacrylate (DIPGDM) were all obtained from the Monomer-Polymer Division, Borden Chemical Co. 1,10-Decamethylene glycol dimethacrylate (DMGDM), 2,2-propane diol dimethacrylate (PDDM), and 1,1,1-trimethylol propane trimethacrylate (TMPTM) were obtained from Polysciences, Inc. They were all freed from inhibitors by passing through an Amberlyst A.27 (Rohm and Haas Co.) ion exchange column. This treatment was previously found to be satisfactory with methyl methacrylate [2]. The purified MMA or the mixture of MMA and the cross-linking monomers were then placed in 10 ml ampules. Degassing was carried out by repeatedly freezing the tube contents under 10^{-5} Torr followed by thawing. The tubes were then flame sealed and exposed to γ-rays from ^{60}Co of intensity 0.85 Mrad/hr (240 rads/sec) at 25°C. In addition, high dose rate studies were carried out using the 3 MeV Dynamitron at the Columbia Research Corp. Full details on this radiation source were presented in the first paper of this series.

After irradiation, the ampules were kept in liquid nitrogen until opened, and their contents were poured into methanol containing benzoquinone inhibitor. Both the methanol and the monomers were then decanted and vacuum evaporated away from the precipitated polymer at 60°C. The percent conversion was calculated from the weight of the dried polymer and the weight of the original monomers.

The percent gel of the copolymers formed was determined by a modification of a procedure described by Nuenke and Milgrom [5]. The polymer sample (about 1.2 g) was placed in the bottom four of five trays. The latter consist of disks of wire cloth (80 mesh) welded to metal rims. Sections of metal tubing (1/4 in.) were used as tray separators. The trays were placed in an extraction thimble made of stainless steel wire cloth (180 mesh). The thimbles were placed in a jar and sufficient benzene added to cover the top tray in the thimble (approximately 120 ml), the jar was then tightly covered and allowed to stand at room temperature in the dark for 72 hr, during which time the solvent was changed every 24 hr. The insoluble part was then dried in a vacuum oven at 100°C for 48 hr and weighed. The percent gel was calculated from the weight of the insoluble part of the sample and from the initial weight before extraction.

Another method was used for the determination of percent gel for 1,10-decamethylene dimethacrylate, 2,2-propane diol dimethacrylate, and 1,1,1-trimethylol propane trimethacrylate. In this procedure a fritted glass filter crucible and a Celite analytical filter aid were utilized as follows. The polymer sample (0.2 g) was allowed to stand in contact with 200 ml of benzene overnight, after which it was filtered under suction through a weighed, fine fritted glass filter crucible containing a Celite filter aid bed (3-4 g). The sample was then washed with benzene and dried in a vacuum oven at 150°C for 24 hr. It was washed and dried under the same conditions once more and finally weighed. The results obtained with this technique and with the metal thimble procedure are in reasonable agreement, as can be noted from Table 1.

TABLE 1. Determination of Percent Gel of the System MMA-DMPDMA by Two Methods

% Conversion	Fritted glass crucible with Celite	Metal thimble
6.1	31.0	25.5
7.3	54.6	51.4
20.0	80.0	78.9
30.8	82.7	86.8
35.0	0	0

RESULTS

The effect of varying the concentration of ethylene glycol dimethacrylate in methyl methacrylate on the conversion was studied and the results are summarized in Fig. 1. The conversion curves show an interesting but expected tendency; as the percent of divinyl monomer is increased, the gel effect begins earlier in the reaction leading to higher conversions. Even 4.55 mole % of ethylene glycol dimethacrylate increases the conversion in 30 min (0.425 Mrad) from 7.5 to 35%, thus showing the enormous importance of the gel effect on conversion in this type of polymerization. The corresponding effect on the total dose needed for complete conversion can become very significant indeed.

The effects of the percent of ethylene glycol dimethacrylate on the gel formation are shown in Fig. 2. In general the results from the gel measurements were more scattered than the conversions. Increasing proportions of the dimethacrylate rapidly decreases the time for the beginning of gel formation. Thus, again with only 4.55 mole % of the dimethacrylate, more than 90% gel is formed in 30 min whereas gel is only just beginning to be formed with 1.07 mole % of dimethacrylate. However, the onset of autoacceleration of the rate itself begins later than the onset of gel formation. It is interesting that although gel formation is substantial in 1 hr with only 1.07% of dimethacrylate, no signs of autoacceleration can be seen at the low conversions reached.

A number of dimethacrylates and one trimethacrylate were investigated at the same molar concentration of methacrylate groups. The structures of these compounds are shown in Table 2. Percent

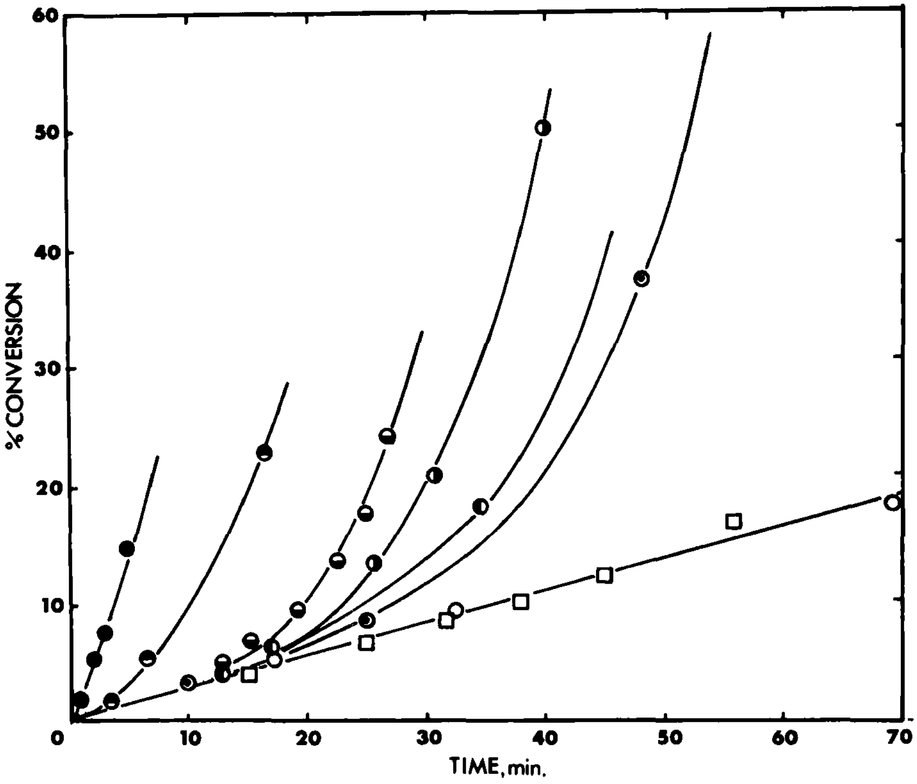


FIG. 1. Rates of radiation-induced copolymerization of ethylene glycol dimethacrylate and methyl methacrylate. Dose rate at 240 rad/sec. (●) 100% EGDM, (⊖) 10% EGDM, (◒) 4.5% EGDM, (◑) 3.4% EGDM, (◐) 3% EGDM, (◉) 2% EGDM, (○) 1% EGDM, and (□) 100% MMA.

conversion and percent gel data for each monomer after 30 min exposure to the ^{60}Co source are also presented in Table 2.

The conversion curves are presented in Figs. 3 and 4 for the nine multifunctional methacrylates studied. Substantial differences in the rates can be seen, especially at higher conversions where the gel effect is operative. The trimethacrylate clearly polymerizes the most rapidly. The corresponding gel data is shown in Figs. 5 and 6 for all of the nine monomers studied. The conversions and gel

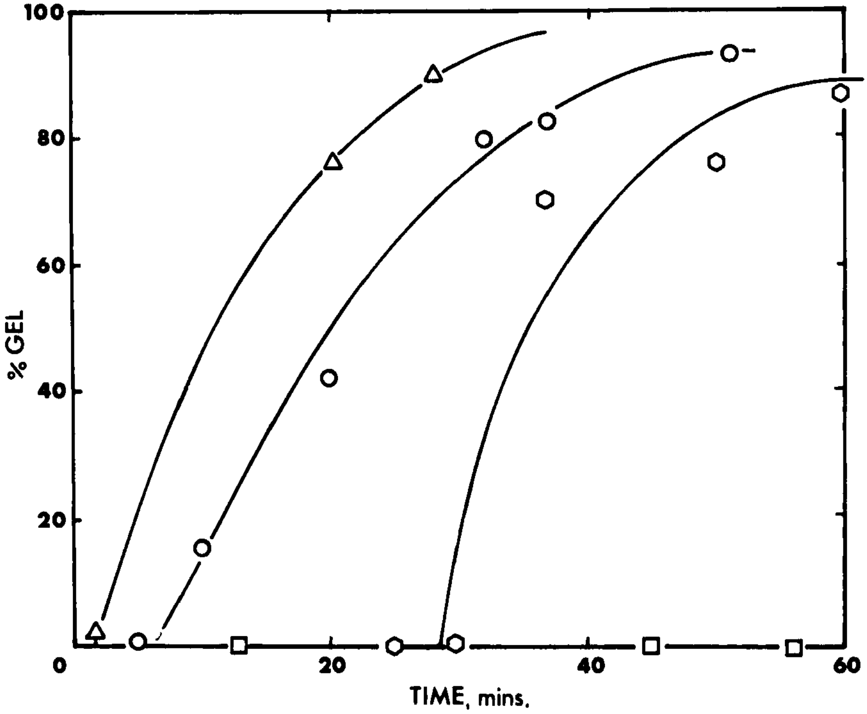
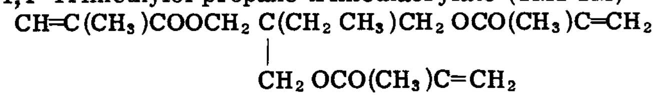


FIG. 2. Rate of gel formation in the radiation-induced copolymerization of ethylene glycol dimethacrylate with methyl methacrylate. Dose rate at 240 rad/sec. (□) MMA, (○) MMA + 1.07 mole % EGDM, (○) MMA + 2.28 mole % EGDM, and (△) MMA + 4.55 mole % EGDM.

contents at 30 min of reaction time are included in Table 2. Again it is clear that the trimethacrylate is the most efficient monomer for promoting gel formation.

Finally, a number of the methacrylate-dimethacrylate systems were studied using an electron accelerator at 2.8 Mrads/sec. The results are summarized in Table 3. One sample with 4% of polymethyl methacrylate is included and demonstrates the accelerating effect of increasing the viscosity of the monomer.

TABLE 2. Radiation-Induced Polymerization of Methyl Methacrylate with 4.55 mole % Functional Group Concentration of Multifunctional Methacrylates at 240 rads/sec for 30 min

Multifunctional methacrylate	% Conversion	% Gel
Control: Methyl methacrylate (MMA) $CH_2{=}C(CH_3)COOCH_3$	8.1	0
Ethylene glycol dimethaceylate (EGDM) $CH_2{=}(CH_3)COOCH_2CH_2OCO(CH_3)C{=}CH_2$	13	73
Diethylene glycol dimethacrylate (DEGDM) $CH_2{=}C(CH_3)COOCH_2CH_2OCH_2CH_2OCO(CH_3)C{=}CH_2$	15.3	86
1,4-Tetramethylene glycol dimethacrylate (TMGDM) $CH_2{=}C(CH_3)COOCH_2(CH_2)CH_2OCO(CH_3)C{=}CH_2$	8.6	67
1,6-Hexamethylene glycol dimethacrylate (HMGDM) $CH_2(CH_3)COOCH_2(CH_2)_4CH_2OCO(CH_3)C{=}CH_2$	11.2	71
1,10-Decamethylene glycol dimethacrylate (DMGDM) $CH_2{=}C(CH_3)COOCH_2(CH_2)_8CH_2OCO(CH_3)C{=}CH_2$	12.1	71.8
1,3-Butylene glycol dimethacrylate (BGDM) $CH_2{=}C(CH_3)COOCH_2CH_2CH(CH_3)OCO(CH_3)C{=}CH_2$	14	80
2,2-Propane diol dimethacrylate (PDDM) $CH_2{=}C(CH_3)COOC(CH_3)_2OCO(CH_3)C{=}CH_2$		
Di-isopropylene glycol dimethacrylate (DIPGDM) $CH_2{=}C(CH_3)COOC(CH_3)_2OC(CH_3)_2OCOC(CH_3)C{=}CH_2$	15	85
1,1,1-Trimethylol propane trimethacrylate (TMPTM)  $CH{=}C(CH_3)COOCH_2\underset{\displaystyle CH_2OCO(CH_3)C{=}CH_2}{\underset{\vert}{C}}(CH_2CH_3)CH_2OCO(CH_3)C{=}CH_2$	32.2	92

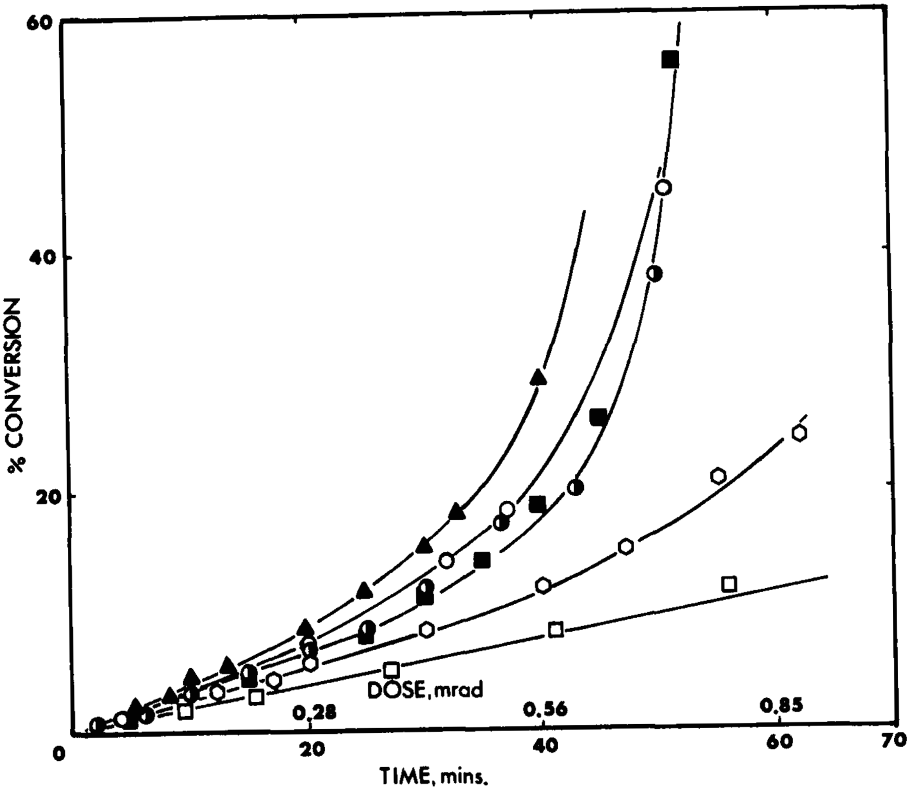


FIG. 3. Rate of radiation-induced copolymerization of methyl methacrylate with various dimethacrylates with functional group concentrations of 4.55 mole %. (□) MMA, (○) TMGDM, (◑) DMGDM, (■) HMGDM, (○) EGDM, and (▲) DEGDM.

DISCUSSION

A rather detailed study was conducted with these systems at two extremes of dose rate. Most of the investigation was carried out at a dose rate of 240 rads/sec followed by a lesser number of experiments at 2.8×10^6 rads/sec. Even at the lower dose rate the increase in temperature due to the exotherm in these rapidly gelling systems become a problem. Since the temperature increases followed the rate

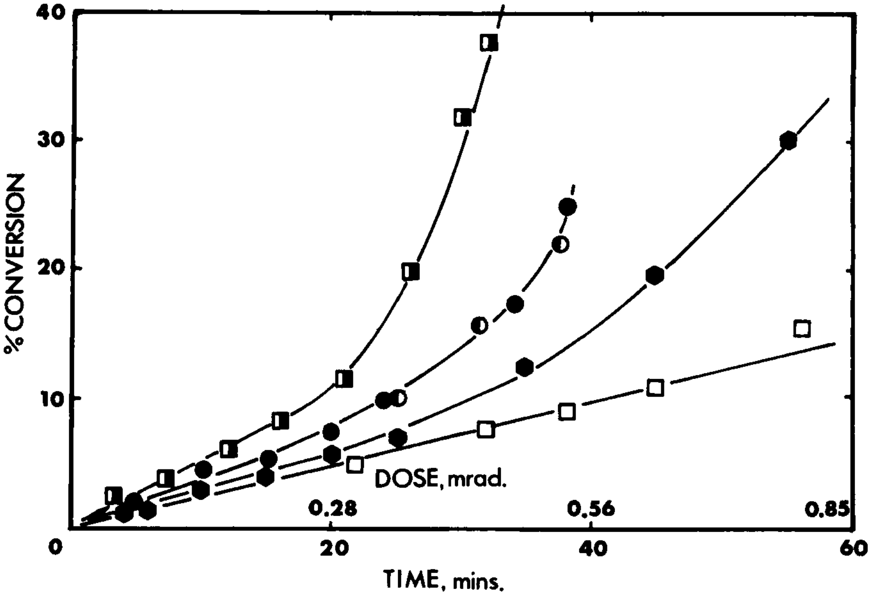


FIG. 4. Rate of radiation-induced copolymerization of methyl methacrylate with various multifunctional methacrylates with functional group concentrations of 4.55 mole %. (□) MMA, (●) PDDM, (•) BGDM, (◘) TMPTM, and (◐) DIPGDM.

of gelling, the orders of reactivity of the various difunctional monomers are very likely correct. In other words, any perturbations due to the difficulty of controlling the temperature tended to exaggerate rather than hide the effect of structure on the reactivity. Later the initial studies in an air bath were repeated in a water-cooled system and indeed did confirm the results, as suggested above. The concentration of the multifunctional methacrylate in the methyl methacrylate was varied and, in addition, a large number of different dimethacrylates and one trimethacrylate were investigated. The overall percent conversion and the percent of gel were measured as a function of dose.

As the percent of the di- or trimethacrylate was increased, the rate of conversion increased. The conversion-dose curves did coincide at very low conversion, i.e., before gelation began. As would be expected, the dose required for the acceleration in rate to begin and the overall rate of gelation increased with increasing concentrations of multifunctional methacrylate.

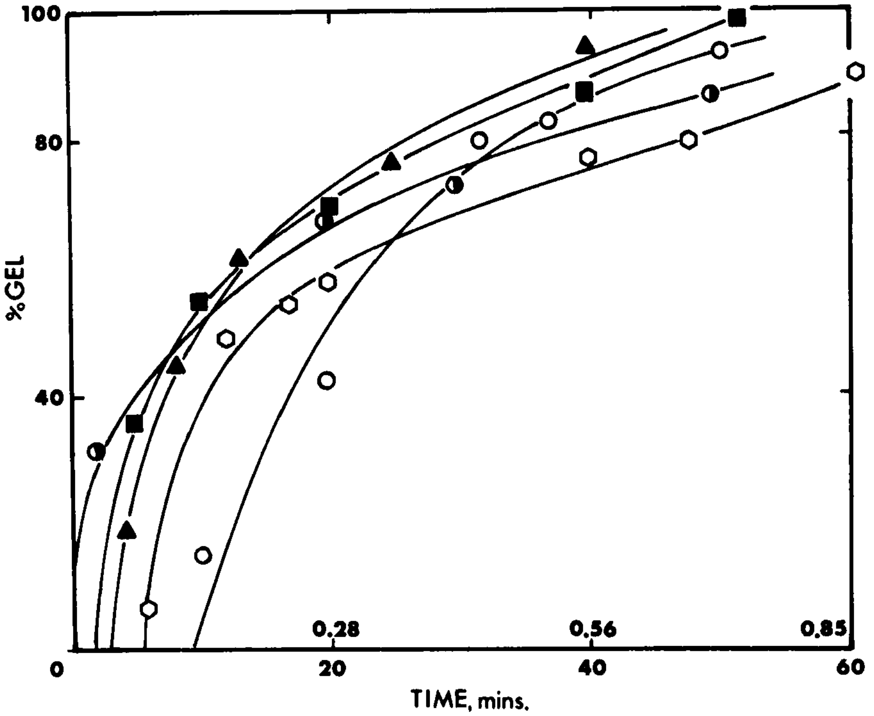


FIG. 5. Effect of increasing the chain length between vinyl groups in the dimethacrylate on the rate of gel formation. (○) MMA + 2.28 mole % EGDM, (o) MMA + 2.28 mole % TMGDM, (▲) MMA + 2.28 mole % DEGDM, (■) MMA + 2.28 mole % HMGDM, (◑) MMA + 2.28 mole % DMGDM.

The different methacrylates varied widely in their rate of gelation. The order of efficiency at promoting gelation at a fixed methacrylate group-based molar concentration was: 1,1,1-Trimethylol propanol trimethacrylate > diethylene glycol dimethacrylate > di-isopropylene glycol dimethacrylate > 1,3-butylene glycol dimethacrylate > ethylene glycol dimethacrylate > 1,10-decamethylene glycol dimethacrylate > 1,6-hexamethylene glycol dimethacrylate > 2,2-propane diol dimethacrylate > 1,4-tetramethylene glycol dimethacrylate.

The DPPH method of measuring the rate of radical production was used with methyl methacrylate itself and with one of the fastest gelling systems, diethylene glycol dimethacrylate. The results clearly

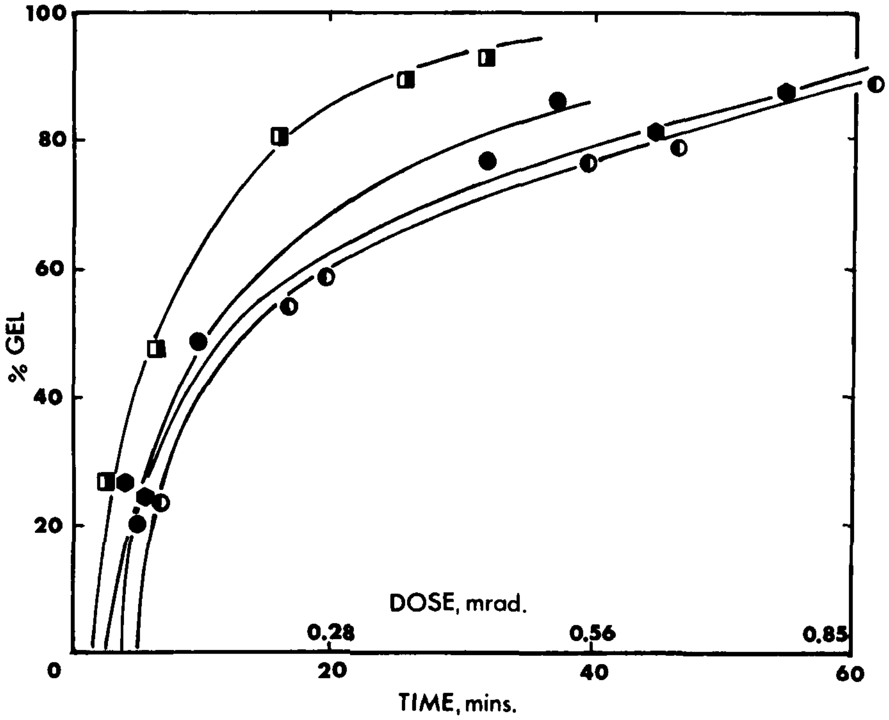


FIG. 6. Effect of the presence of a side group in the polyfunctional monomer on the rate of gel formation of the system MMA-polymethacrylate. (◨) MMA + 1.52 mold % TMPTM, (●) MMA + 2.28 mole % BGDM, (●) MMA + 2.28 mole % PDDM, and (◐) MMA + 2.28 mole % DIPGDM.

indicated that the rate of radical production from the radiolysis was not greatly different with the two systems and was not responsible for the substantial differences in rates of conversion. Since the rates of radical production initially were similar, the interesting conclusion is that the nature of the gel itself is mainly responsible for the considerable differences in reactivity observed. The data indicate that the differences in the effectiveness of the various dimethacrylates is mainly in the different rates of conversion. These, perhaps, might be associated with the lifetime of radicals after the removal of the radiation, posteffects, or with some contribution from the

TABLE 3. Copolymerization of Methyl Methacrylate with Various Dimethacrylates at 2.83 Mrads/sec at 30°C for 4.2 sec

Dimethacrylate	Percent in MMA	Time (sec)	% Conversion	% Gel
Control: Pure MMA	0	4.2	3.47	0
EGDM	25	4.2	32.2	80.5
HMGDM	50	4.2	41.0	69.0
TMGDM	50	4.2	8.3	68.8
HMGDM	50	4.2	9.46	87.5
PDDM	50	4.2	47.2	95.0
Polymethyl methacrylate	4.0	4.2	4.2	0

character of the gel formed such as the tightness of the gel due to shorter connecting links which could lead to more gel effect and higher relative conversions.

The onset of autoacceleration seemed to coincide with the appearance of gel in most of the systems investigated. These results could not be extrapolated to very low concentrations of difunctional methacrylates since methyl methacrylate autoaccelerations without crosslinking at about 20% conversion at the polymerization rates investigated with ^{60}Co. The initial rates were higher in concentrated solutions of ethylene glycol dimethacrylate. For pure ethylene glycol dimethacrylate, the initial rate was 1.9% conversion/min, in contrast to 0.27% conversion/min for methyl methacrylate. These higher initial rates not only induced gelation earlier, but also increased the rates after the onset of autoacceleration. Such effects have a profound effect upon the percent conversion for a fixed dose and therefore upon the economics of curing.

The importance of monomer structure on the "gel effect" may be determined from an analysis of the variation of polarity on the polymeric constituents of the polymer chain since the "gel effect" is caused by steric resistance to chain end diffusion. Increasing the polarity of a polymeric constituent will increase the dipole-dipole and the induced dipole interactions. One result of these attractions would be to increase the steric resistance to chain end diffusion, thus increasing the polymerization autoacceleration. The most effective dimethacrylates studied, diisopropylene glycol dimethacrylate and diisopropylene glycol dimethacrylate, each contain an oxygen linkage in the dialcohol component. These dimethacrylates were more autoaccelerating, with the exception of 1,3-butylene dimethacrylate, than the other dimethacrylates. The polarity of the oxygen linkage was expected to increase the interchain attractions.

The oligomethacrylate-methacrylate copolymerization systems varied in their kinetic response to Co irradiation. Factors contributing to this variation may be determined from an examination of the gelation and conversion data for the most reactive and the least reactive systems which were investigated. The most reactive oligomethacrylate which was investigated was trimethanol propane trimethacrylate. The trifunctional nature of this monomer is expected to increase the steric resistance to chain end diffusion and this increase the rate of polymerization. The least reactive oligomethacrylate was tetramethylene glycol dimethacrylate. It was expected to have less reactive pendant groups due to the relatively short chains, and yet form cross-links in which the primary chain "associations" were not especially pronounced.

These two systems both induce gelation at relatively low conversions to polymer. At these low conversions to polymer, the fraction of intramolecular cross-linking was anticipated to be significant. This could explain the similar conversions at the onset of gelation in the two systems, since intramolecular cross-linking sets a lower bound on the conversion to form gel. This constraint on gelation was apparent in the system MMA-EGDM presented in Fig. 2.

Multifunctional methacrylates with long chains between methacrylate units were expected to be more reactive than short chains because of increased pendant mobility associated with the long chain. This expected trend was observed in a homologous series with various chain lengths. The longer chains did induce gelation earlier, the order of the effectiveness of the dimethacrylate being 1,10-decamethylene > 1,6-hexamethylene > diethylene ~ tetramethylene > ethylene. After irradiation times of approximately 40 min, however, the order of polymerization rates was diethylene > ethylene > 1,10-decamethylene > 1,6-hexamethylene > 1,4-tetramethylene. This rearrangement of relative orders was also almost exactly paralleled in the relative gel percentages observed after 40 min. The reversal in the effectiveness of ethylene glycol dimethacrylate could be explained in the nature of the gel itself. Shorter cross-links might produce a "tighter gel" with increased segmental association, and consequently lower termination probability in gelled domains. The longer cross-links associated with 1,10-decamethylene glycol dimethacrylate, for example, would initially generate gel faster, but would be less reactive to form gel in the gel domains.

These observations of the anomalous effect of a side group on the polymerization kinetics at relatively low conversions suggest that the "gel effect" is due to segmental associations which are nonrandom in nature and may be attributed to localized accretions of polymeric segments or gel domains. This postulated mechanism of the gel effect is also indicated by the effect of the chain lengths of the cross-links on autoaccelerations.

The effect of a side group on the dialcohol component of the dimethacrylate was generally to reduce the autoacceleration: diisopropanol dimethacrylate is less effective than diethylene glycol dimethacrylate, 1,3-butylene dimethacrylate is more effective than neopentyl dimethacrylate, and ethylene glycol dimethacrylate is more effective than 2,2-propane diol dimethacrylate. The presence of a side group would be to decrease the flexibility of the cross-link and may serve to physically separate the primary chains.

The effectiveness of a side group to reduce the segmental association associated with the gel effect is well-known for the polymerization of methyl methacrylate and methyl acrylate. The presence of a methyl group on the double bond has a profound effect on the nature of the autoacceleration (ignoring momentarily differences in the chemical reactivities). The monomer with the side group, methyl methacrylate, autoaccelerates after a much higher conversion to polymer than methyl acrylate.

If the "gel effect" is due to increased steric resistance in a randomly dispersed polymer solution, the presence of a side group would only increase the steric resistance. On the other hand, if the "gel effect" is due to increased steric resistance resulting from segmental associations that are nonrandom in nature, the presence of a side group would serve to reduce those primary chain associations. At high conversions, the polymerization medium would be expected to be more random in distribution, and the presence of a side group would increase the diffusional resistance to both the propagation and termination steps. In the case of methyl methacrylate and methyl acrylate, the steric resistance of methyl methacrylate is much greater at high conversions when the polymer distribution would be expected to be random.

The effect of a side group on autoacceleration was determined from a study of an isomeric series. For the four carbon isomeric series 1,3-butylene, dimethylene propane, and tetramethylene dimethacrylates, the kinetic and solubility data followed previously expected trends. Autoacceleration in polymerization rates were observed to occur with the onset of gelation. This autoacceleration was considered to be a direct result of an increase in the microviscosity of the medium and the attendant decrease in the chain termination probability. Differences in the molecular structure of the various difunctional monomers would be expected to cause differences in the rates of gel production, as well as differences in the rates of polymerization. The relative reactivities of the dimethacrylates were found to follow the order 1,3-butylene > dimethylene propane > tetramethylene for both polymer and gel production. The more reactive dimethacrylate induced gelation earlier; however, the percent gel did not follow the conventional gelation statistics even with modification for intramolecular cross-linking, particularly at the higher conversions where less gel was formed than was predicted by homogeneous gelation statistics.

The percent gel vs conversion curves of the various dimethacrylates were remarkably similar, except that tetramethylene dimethacrylate had a higher percent gel at the high conversions to polymer. These results are presented in Fig. 7. These data imply that the dimethacrylates in this series had similar reactivities to form gel, but the polymerization rates in the gel were different.

The above remarks relate to the work conducted at a low (240 rads/sec) dose rate. A number of the dimethacrylate systems were also studied at 2.8 Mrads/sec. The initial rates (low conversion to

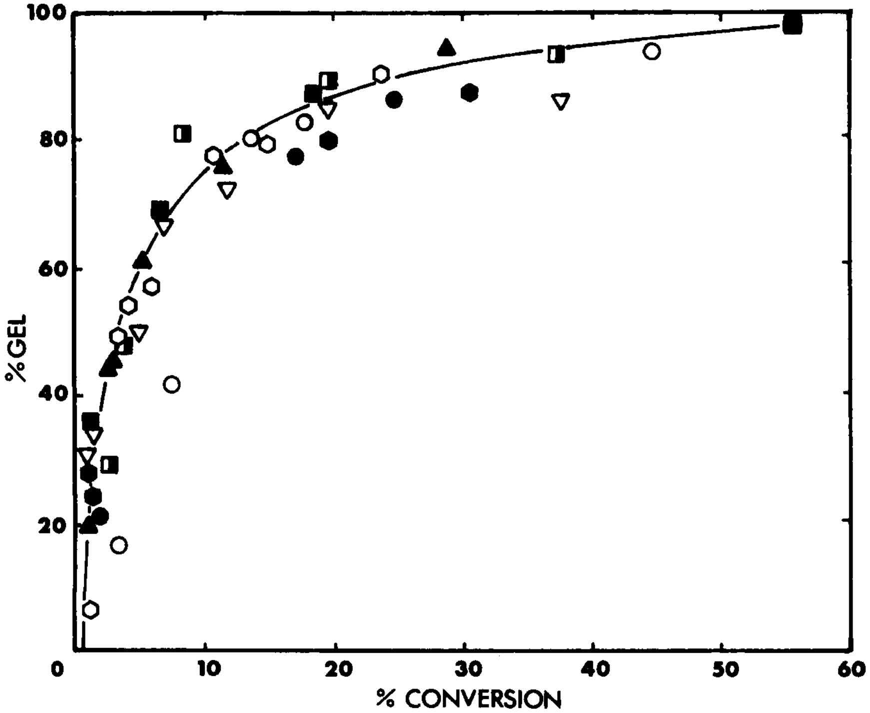


FIG. 7. Percent gel-conversion curves for radiation-induced copolymerization of methyl methacrylate and various polymethacrylates. (○) EGDM, (⬡) TMGDM, (●) BGDM, (■) HMGDM, (▽) DMGDM, (▲) DEGDM, (⬢) PDDM, and (◨) TMPTM.

monomer) of the ethylene glycol dimethacrylate-methyl methacrylate system followed the expected dependency on the square root of the radiation intensity for both high and low EGDM concentrations. The increase in the rate of conversion due to the gel effect was not observed to occur in the systems of low dimethacrylate concentrations, but the gel effect rate acceleration occurred in the systems with high dimethacrylate concentrations (>30%). The reduction in kinetic chain length at high dose rates was expected to reduce the tendency for gel formation and thus prevent the gel effect. This absence of the gel effect due to a reduction in the primary chain length was expected to be much more significant in systems with a low dimethacrylate concentration than in those with high dimethacrylate concentrations with expected gel points at only a few percent conversion.

The order of effectiveness of the various methacrylates studied was ethylene glycol dimethacrylate > hexamethylene glycol dimethacrylate > tetramethylene glycol dimethacrylate > methyl methacrylate, similar to the orders observed at the low dose rate. In the case of ethylene glycol dimethacrylate, the time was determined for the conversion to a solid at 32, 53, 77, and 100% concentrations in methyl methacrylate at both high and low dose rates. Except for the 32% experiment, the times were directly proportional to the square root of the dose rates although these varied over four orders of magnitude.

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