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POLYMERIZATION OF n-DODECYL METHACRYLATE INTO HIGH CONVERSION

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ABSTRACT

Bulk polymerization of n-dodecyl methacrylate initiated by 2,2'-azobis-(isobutyronitrile) proceeds with low gel effect and formation of a crosslinked polymer in the temperature region from 60 to 90°C. The polymerization conversion, at which an insoluble polymer fraction begins to form, decreases with decreasing polymerization temperature and initiator concentration. A considerable suppressing of the gel effect and formation of a crosslinked structure is most probably related to the transfer reaction of the propagation radical onto the alkyl group of the ester. The formed crosslinked structure is a very loose network. At the highest degree of crosslinking, the samples swelled in toluene 30 to 35 times their original volume at ambient temperature.

Key Words: Radical polymerization; AIBN initiation; n-Dodecyl methacrylate polymerization; Crosslinking; Temperature effect on crosslinking

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INTRODUCTION

The general concept of the mechanism and kinetics of free radical polymerization seems to be completed. In spite of this relatively mature level of knowledge, there needs to be a continual enhancement and refinement in this area of macromolecular chemistry. This particularly concerns monomers that were not investigated in detail until now, but also those in which the observations of polymerization behavior have been in discrepancy.

To that kind of knowledge can be included a question concerning the influence of the structure of the ester group of methacrylic monomers on their gelation behavior.^[1] Particular attention should be given to the observed marked increase in the polymerization rate and molecular weight that occurs in high viscosity polymerization media.

If we generally consider the structure of the alkyl methacrylate propagating macroradicals having various alkyl groups, a very similar delocalization of the unpaired electron can be assumed, and, by this fact, also a comparable reactivity in elementary reactions of the polymerization. Rate constants of the appropriate reactions should be effected above all by sterical parameters of various substituents, primarily if there are big differences in the length of alkyl groups. The increase in length of the ester alkyl group has been related to a decrease in the termination rate constant of polyalkyl methacrylate macroradicals.^[2-5] On the other hand, it is interesting that the longer alkyl substituent in dodecyl methacrylate has been indicated as the reason for the higher value of the propagating rate constant in comparison with the methyl methacrylate.^[3,6-11] In this case, it seems that, in addition to the small polarity differences of the monomers and their derived macroradicals, the longer substituent in the ester group contributes to the more favorable arrangement of the reactants. An effect of "self-arrangement" of the monomers at various conditions in a mixture of methyl methacrylate and dodecyl methacrylate can account for a relatively great difference in the values of copolymerization parameters determined by various research groups^[12-14] (Table 1).

We assume that a possible "self-arrangement" of suitably shaped reactants (monomers) can take part in the propagation step at different

Table 1. Copolymerization Parameters of MMA/DMA

r (MMA)	r (DMA)	Lit.
1.22	0.84	[12]
0.25	0.63	[13]
1.58	1.88	[14]
1.67	1.95	[14]

conditions (presence or absence of solvent, method of preparation of the copolymerization mixture, polymerization rate, and so on) and can result in the formation of micellar associates or homogeneous reaction micro assemblies. Different degrees of homogeneity of reacting monomers can lead to different values of copolymerization parameter determination.

The decrease in the termination rate with increasing length of alkyl group in alkyl methacrylates is described to enhanced monomer viscosity.^[2] Although this fact certainly affects the mentioned dependence in that way, the viscosity increase of the medium by the presence of forming macromolecules does not substantially change the polymerization rate of alkyl methacrylates with long alkyl groups.^[15,16,21] It should be mentioned that a clear gel effect is a typical kinetic property of methyl methacrylate and has been investigated elsewhere.^[17-19]

The absence of a gel effect upon increasing the alkyl-length in methacrylate monomers^[16] is accounted for by an assumption of a higher rate of radical chain transfer to the monomer having alkyl groups longer than methyl. From a model study,^[20] it follows that the gel effect will be zero at a chain transfer constant on monomer (C_M) of $>10^{-3}$. However, this has been found to be in discrepancy with C_M for hexyl methacrylate.^[15] In this case, the chain transfer constant on monomer, C_M , is very low ($C_M = 7.5 \times 10^{-6}$), and in spite this, the gel effect is strongly reduced.

Dodecyl methacrylate is a logical candidate monomer to use for study of the origin of gel-effect depression by long-chain alkyl methacrylates.^[21] This monomer has been known for some time to result in long-chain branching during solution polymerization.^[22] It is possible to speculate that in the case of long-chain alkyl methacrylates the crosslinking and the suppression of the gel effect have a common reason.

In our previous work,^[21] dibenzoyl peroxide was used as polymerization initiator for n-dodecyl methacrylate. Its benzoyloxy free radicals are sufficiently reactive for a quick chain transfer reaction on alkyl groups of the alkyl methacrylate monomer. Such chain transfer by primary radicals can somewhat complicate a discussion about crosslinking reactions of n-dodecyl methacrylate polymerization. For this reason, the conditions of n-dodecyl methacrylate crosslinking behavior during polymerization were investigated using azobis(isobutyronitrile) as initiator, which is known to be practically inactive in chain-transfer reactions. Thus, we hope to obtain more useful data about the mechanism of n-dodecyl methacrylate crosslinking from this study.

EXPERIMENTAL

Chemicals

n-Dodecyl methacrylate (DMA), 96%, was a commercial product (Aldrich). It was shaken before polymerization with a water solution of sodium

hydroxide and then dried over calcium chloride. Initiator 2,2'-azobis(isobutyronitrile) (AIBN), 98%, was a commercial product (Fluka). It was recrystallized from methanol before use.

METHODS

Determination of Monomer Conversion

An amount of DMA, close to 1 g, with a proper content of initiator AIBN was placed into ampoules and sealed under nitrogen. The ampoules were placed in a water bath maintained at the desired reaction temperature. After the reaction time at a given temperature, the ampoule was opened, the reaction mixture was diluted with toluene, and the solution was poured into ethanol containing hydroquinone, where the polymer was precipitated. Polymer was separated by filtration, washed, and dried in a vacuum dryer to constant mass.

Determination of Crosslinked Poly(Dodecyl Methacrylate) and Degree of Its Swelling

The sample of polymerized DMA, which was obtained from the polymerization mixture was extracted in 100 cm³ of toluene at room temperature for 120 hours. After 72 hours of extraction, the toluene solution (containing soluble polymer) was separated and to the remaining portion of the insoluble polymer, more pure toluene was added and the extraction continued another 48 hours. After a second separation of toluene solution from the insoluble fraction, the insoluble (i.e., crosslinked) polymer was weighed out and then vacuum dried to a constant weight. From these data, the amount of insoluble fraction of the polymer—poly(dodecyl methacrylate) (PDMA)—and the degree of swelling, as a ratio of the weight of swollen polymer to the weight of dried PDMA, was calculated.

RESULTS AND DISCUSSION

Polymerization Rate as a Function of Monomer Conversion

Conversion curves of bulk polymerization of DMA, shown in Fig. 1, are continuous and do not show a clear acceleration of the polymerization rate as is observed with an analogous methyl methacrylate polymerization. A clear acceleration of the polymerization rate of DMA is observed after 10 to 30% conversion only at 60°C. A linear increase of the conversion, as is seen on curves A and B (Fig. 1), are observed in many other cases having a wide range of initial concentrations of AIBN (0.005 till 0.3 wt%) at temperatures

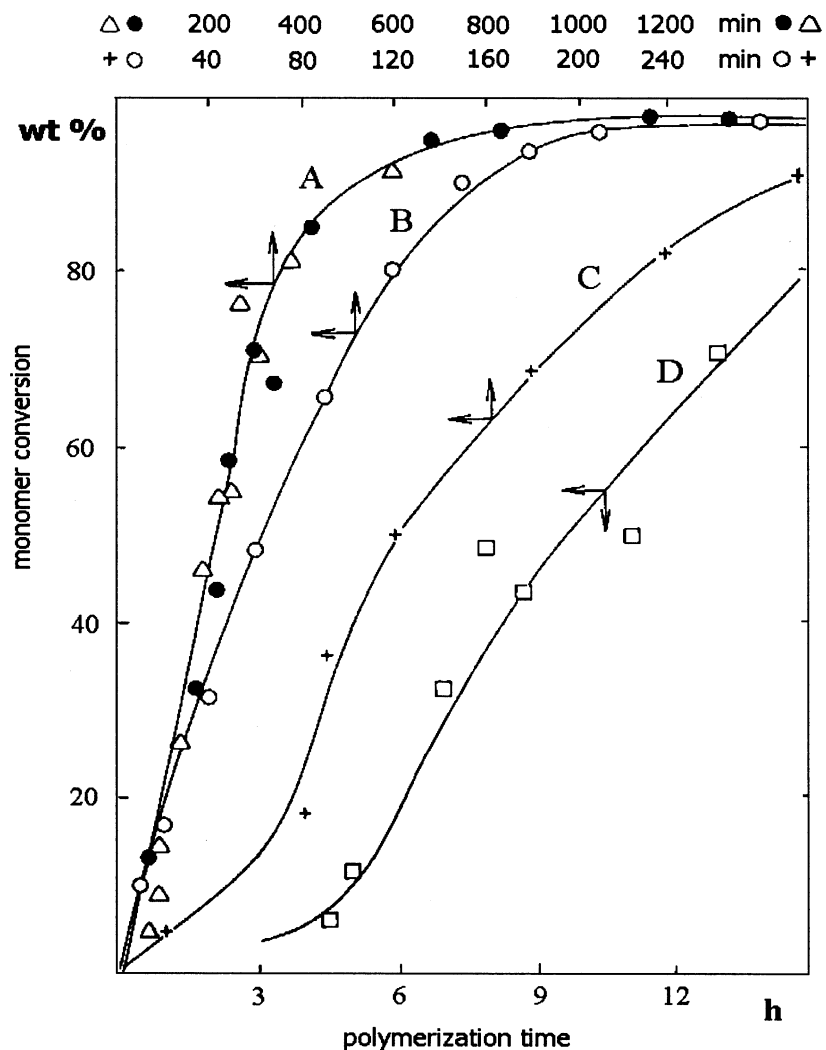


Figure 1. Polymerization curves of DMA at different wt% of initiator (AIBN) content/at different temperatures: A: $\triangle = 0.025$ wt%/60°C; $\bullet = 0.005$ wt%/70°C; B: $\circ = 0.01$ wt%/80°C; C: $\square = 0.005$ wt%/60°C; D: $+$ = 0.05 wt%/60°C.

70, 80, and 90°C. Under these conditions, the course of polymerizations is very similar to the case of hexyl methacrylate, which was measured only at 70°C.^[15] Also, it is worth commenting that the linear conversion dependences contain a “hidden” gel effect, which could be judged from the dependence of the polymerization rate on conversion. However, from the graphically illustrated dependence of the total polymerization rate (calculated as a ratio of instantaneous conversion to the reaction time) on conversion, it follows (Fig. 2) that the reaction rate increases gradually but consistently with increasing

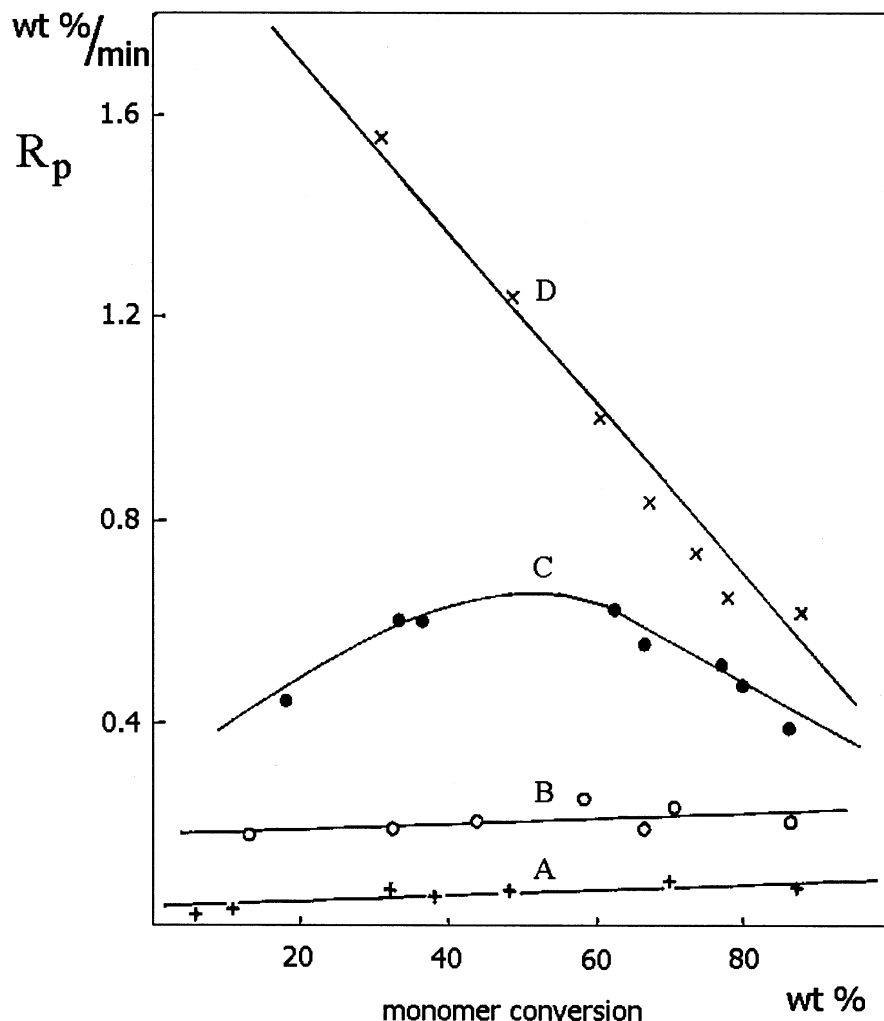


Figure 2. Dependence of polymerization rate – R_p of DMA [wt%/min] on conversion at 60°C the line (A), at 70°C (B), at 80°C (C), and at 90°C (D), and at concentration of AIBN 0.005 wt% in monomer.

polymerization conversion at 60 and 70°C instead of decreasing, as would be expected due to the decreasing monomer concentration in the system. The contrary tendencies, i.e., the viscous medium causing a decrease of the termination reaction rate and increase of polymerization rate, as well as the lower monomer concentration at high conversion causing a decrease of the polymerization rate, are manifested very clearly at 80°C at the initiator concentration used. An expected clear decrease of the polymerization rate with increasing conversion, and so limitation of the gel effect, is seen at AIBN concentration of 0.005 wt% up to a temperature of 90°C. Upon increasing

initiator concentration, onset of the gel effect is shifted to the lower temperature condition. For this reason, we have observed the clear decrease of the dependence of the total polymerization rate on monomer conversion at the higher investigated initiator concentration (0.05 wt% AIBN) already at 80°C.

The thermal dependence of the polymerization rate at 50% conversion, in accordance with the Arrhenius law, is approximately the same for both AIBN concentrations at 0.025 and 0.05 wt%. The mean value of the ratio of activation energy, E , to gas constant, R , is 9780, which approximately corresponds to the value also observed with other alkyl methacrylates.

The relationship of the rising temperature and lowering of the gel effect (enhancement of the negative slope in a dependence of the polymerization rate on conversion) is similar to the relationship of the gel effect and increasing initiator concentration at constant temperature. In Fig. 3, arrows

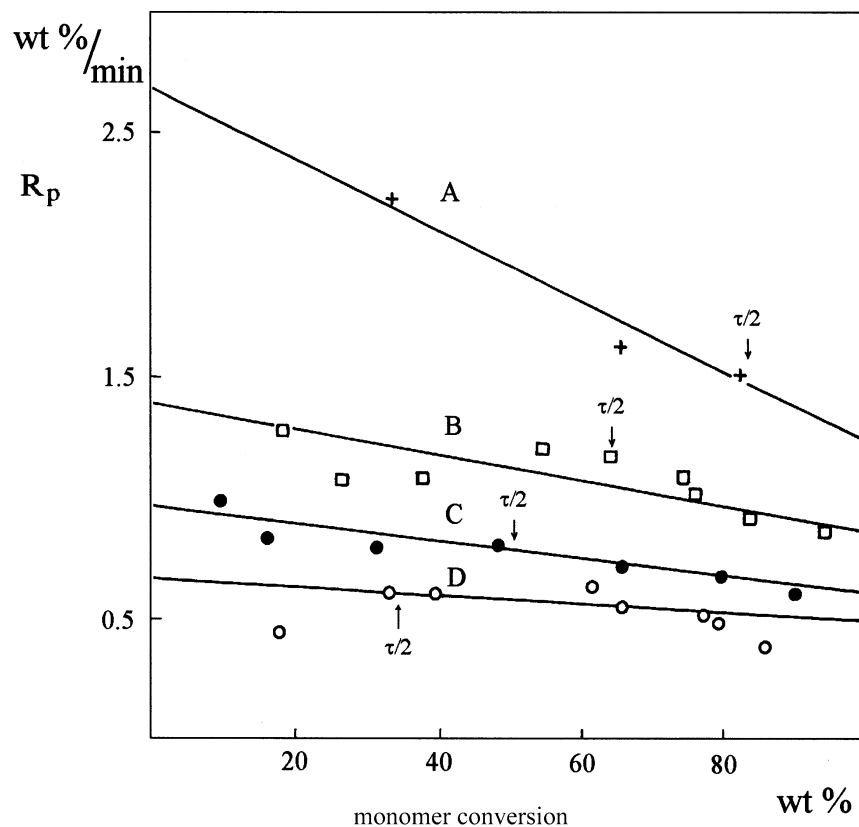


Figure 3. Dependence of polymerization rate – R_p of DMA [wt%/min] on monomer conversion [wt%] at 80°C for various starting AIBN concentrations: line: A – 0.05 wt%; B – 0.025 wt%; C – 0.01 wt%; D – 0.005 wt%. Arrows indicate the conversion at which half of added initiator should be decomposed (calculated according to decomposition rate of initiator).

mark values of the conversion at which the theoretical half-life of AIBN decomposition is attained (calculated from known rate constants determined in low-molecular solutions). Even if it might be assumed that in a polymerizing system with increasing viscosity the decomposition of AIBN will be slower, nothing changes the processes (other than shifting of the arrows to the higher conversion) that we wish to stress. To reach a certain conversion (e.g., 50%), an increasing degree of decomposition of the initiator at this lower concentration is needed. On the other hand, the consumed molar amount of the initiator needed to reach the same conversion is the lowest at the lowest starting concentration. That corresponds to the largest kinetic chain length of the reaction.

Polymerization rates (R_p) measured at 50% conversion (where reaction rates are more accurately determined—see Fig. 3) show a square root dependence on initiator concentration.

$$R_p = k \cdot [\text{AIBN}]^n \quad (1)$$

where k = complex polymerization constant.

The determined exponent of AIBN concentration, $n = 0.46$, is based on initial initiator concentrations. After the starting concentrations were recalculated to the values that can be assumed at 50% monomer conversion, the dependence turns out to be an accurate square root dependence (exponent $n = 0.5$). The square root dependence also holds at 90°C, which means that at this condition, the free propagation radicals disappear by mutual interaction (termination).

An analogous determination of exponential dependence on initiator at a polymerization temperature of 70°C yields a value of $n = 0.61$. At the lowest investigated polymerization temperature (60°C; Fig. 4) at which the gel effect is most clear, the exponent is enhanced to $n = 0.72$. As seen on the individual curves in Fig. 4, increasing the initial AIBN concentration results in a clear shift of the maximal rate to lower conversion. These curves also show a greater polymerization rate decrease with decreasing monomer concentration. There the limitation of the gel effect is influenced by the increased initiator concentration in the polymerization mixture.

The enhancement of the exponent value of the initiator concentration in relation to polymerization rate at 50% of conversion is worth special attention. These elevated values of n are a reflection of a greater limitation of macroradical termination. The exponent enhancement over the value 0.5 results from an increase of the monomolecular decay of propagating radicals in the termination reactions. It is worth mentioning that if the disappearance of the propagating radicals were controlled only by monomolecular mechanism, then the exponent n would have been equal to one. Pseudomonomolecular disappearance can be visualized as a relatively slow intramolecular (Sch. 1) or intermolecular transfer from the propagating radical onto an alkyl

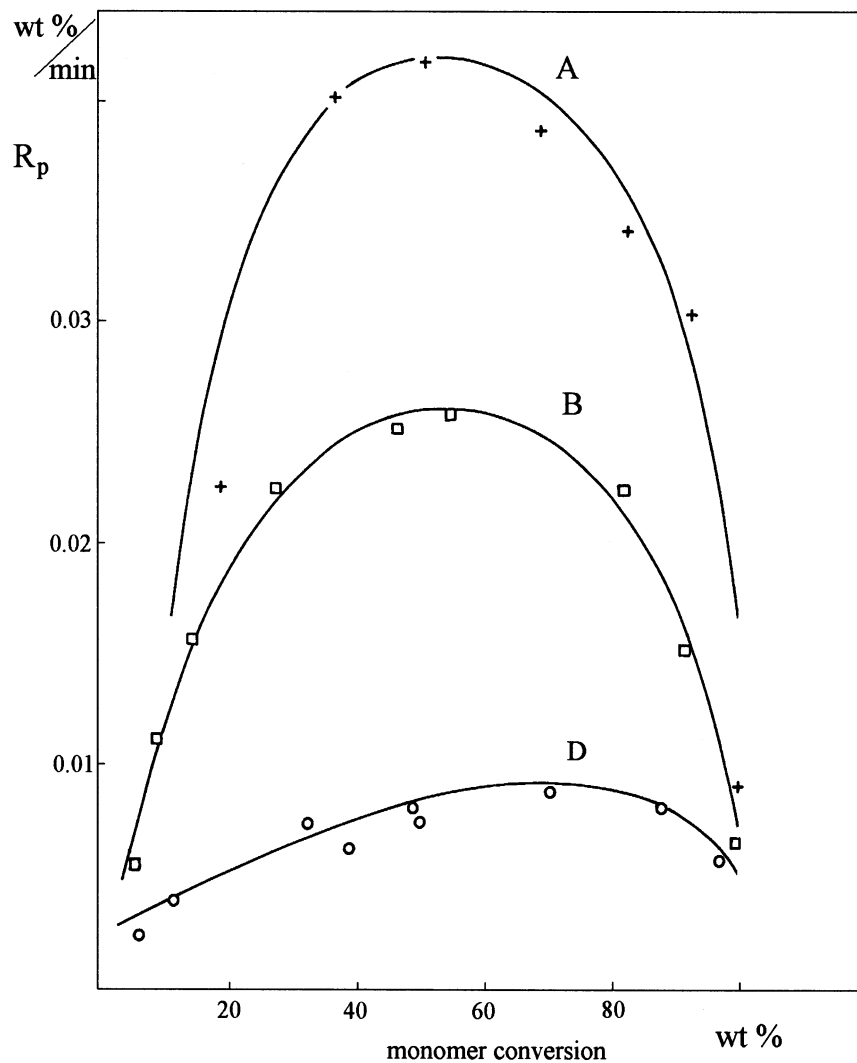
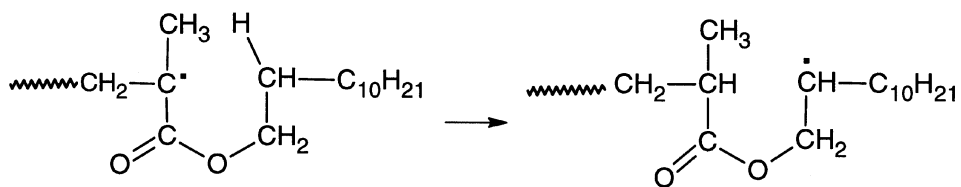


Figure 4. Polymerization rate of DMA [wt%/min] as a function of monomer conversion [wt%] at temperature 60°C for various AIBN concentrations: line A – 0.05 wt%; B – 0.025 wt%; D – 0.005 wt%.



Scheme 1.

group of the ester with subsequent rapid termination of radicals. Transfer reactions are kinetically considered as monomolecular reactions, which are slower, arrange the subsequent faster termination reaction of the radicals arising at transfer reactions. Since the slower monomolecular reactions (at temperatures lower than 80°C and concentrations of AIBN till 0.05 wt%) partially control the bimolecular disappearance of the free radicals, the resulting appearance of the assumed transformation of free radicals will be an increase of the n value in Eq. 1 over 0.5.

It should be mentioned that under the conditions of hard mutual interactions of the propagating radicals, the low molecular free radicals that arose at the transfer of the free radical to the monomer play a key role. They can quickly react with the macroradicals. The macroradical formation with the free radical center placed on the alkyl group can explain the acceleration

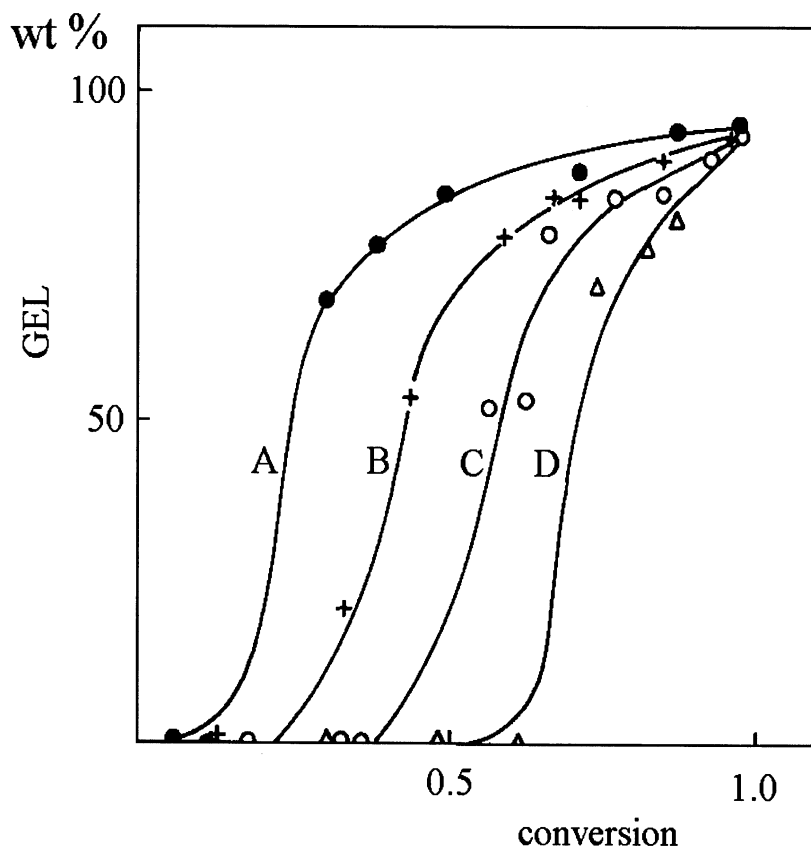


Figure 5. Dependence of insoluble portion [wt%] from the polymerized poly(dodecyl methacrylate) on conversion at AIBN content [wt%] and at polymerization temperature: line (A) – 0.005 wt%/60°C; line (B) – 0.01 wt%/70°C; line (C) – 0.025 wt%/80°C; line D – 0.05 wt%/90°C.

of the termination reaction due to higher mobility of the radical center than in the case of an original macroradical.

Crosslinking During Polymerization

The quantity of the insoluble polymer fraction obtained from the polymerized DMA depends on the polymerization conditions (Fig. 5). The determined gel point (Table 2) occurs at a lower conversion under conditions more suitable for formation of a higher degree of polymerization. Under these conditions, the transfer reactions of macroradicals can be realized and termination reactions take place between the transformed macroradicals.

To favor the crosslinking process, the termination of radicals by combination should be favored over the disproportionation of radicals. It is worth mentioning that during termination of tertiary alkyl radicals, a disproportionation reaction governs, while in the case of secondary alkyl radicals, a combination path is comparable with a disproportionation. Secondary radicals would be generated by transfer to the DMA alkyl group during polymerization of DMA, and high conversion would lead to crosslinking. In the case of methyl methacrylate, only an increase of molecular weight of essentially linear polymer is observed. The transfer reaction from the propagating DMA macroradical to the alkyl of the ester group can explain not only the suppression of the gel effect but also an increase in the tendency toward crosslinking.

Data from solvent swelling studies of crosslinked poly(dodecyl methacrylate) in toluene have been treated with theoretical considerations^[23] that relate the degree of swelling to the density of crosslinks. This indicates that the mean size of crosslinked chains between crosslinks in the gel

Table 2. Interpolated Values of the Conversion of the Polymerization of Dodecyl Methacrylate–DMA (in wt%) at which the First Portion of Crosslinked Polymer Was Formed (Gel Point) at Different Temperatures

Polymerization Temperature [°C]	Gel Point – Conversion of DMA Polymerization [wt%]		
	AIBN [wt%]		
	0.005	0.025	0.05
60	22	46	43
70	23	62	76
80	50	70	a
90	64	a	a

a) At highest conversion (97 to 99 wt%) no insoluble polymer was observed.

fraction is about 170 kDa. The loose network structure is in accord with a crosslinking mechanism as a side reaction in the polymerization process. Crosslinks most probably arise from a copolymerization of a formed macromonomer and a recombination of macroradicals after chain transfer reaction to the preformed polymer, as we have considered earlier.^[21]

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