

The effect of crosslinking agents on the copolymerization of styrene and *n*-butyl methacrylate

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SUMMARY

The effect of low concentrations of multifunctional vinyl monomers acting as crosslinking agents, on the properties of poly(styrene-co-*n*-butyl methacrylates) with 30 % wt of *n*-butyl methacrylate obtained by solution polymerization at a monomer conversion of approximately 60 wt % has been investigated. Ethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,1,1-trimethylolpropane trimethacrylate and *p*-divinyl benzene were used as crosslinking agents. The relationship between the gel content, the relative viscosity increment, the weight-average molecular weight, non-uniformity, glass transition temperature, melting volume index and the concentration of the crosslinking agent was determined and discussed.

INTRODUCTION

Although the multifunctional vinyl monomers acting as cross-linking agents are widely used in the production of polymers with special properties, the kinetic foundation of these polymerizations has been extensively investigated only recently. In (1-6), mainly, the polymerization of styrene or methyl methacrylate in the presence of even relatively high concentrations of vinyl monomers acting as crosslinking agents such as oligoglycol dimethacrylates, trimethylolpropane trimethacrylate or divinyl benzene was investigated. The determination of the time-dependant conversion of the polymerization system and the derivation of kinetic models were in the centre of the investigations. (7-11) In the *n*-butyl methacrylate/ethylene glycol dimethacrylate polymerization system, heterogeneities were observed within certain temperature ranges, even before the gel point was reached. (12)

The following will cover the investigation of the effect of different crosslinking agents of a relatively low concentration up to 0.4 % wt (in relation to the monomers) on the styrene/*n*-butyl methacrylate comonomer system. The conversion of approximately 60 wt % which is an interesting

level in the solution polymerization and associated with a noticeable decomposition of the peroxidized initiators was examined. Ethylene glycol dimethacrylate (EGDMA), 1,4-butanediol dimethacrylate (BDDMA), 1,1,1-trimethylolpropane trimethacrylate (TMPTMA) and, for reference, p-divinyl benzene (DVB) were used.

EXPERIMENTAL

The purity of ethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,1,1-trimethylolpropane trimethacrylate and p-divinyl benzene (E. Merck) was tested by chromatography and, depending on their concentration, used for the polymerization.

The polymers were prepared by filling the formulation consisting of 30 % wt of ethyl benzene, 69.86 % wt of styrene and n-butyl methacrylate at a weight ratio 7 : 3 and 0.14 % wt of benzoyl peroxide and, if required, the respective crosslinking agents (in % wt, related to the monomers) into a flask with nitrogen and by carrying out the polymerization at 85 °C with stirring the mixture over a period of 12 hours. The obtained polymer solution was concentrated by evaporation in the vacuum of a laboratory rotary film evaporator. It was then applied as a film to sheet metal and the remaining volatiles were separated in the vacuum-drying oven at 200 °C.

The gel content was found by the determination of the dried component insoluble in toluene after a 12-hour shaking at room temperature. The relative viscosity increments were determined with a 0.5 percent filtered polymer solution in toluene at 25 °C by means of the Ubbelohde viscometer.

The molecular weight was determined by column elution chromatography in a Waters gel chromatograph with styragel columns using tetrahydrofuran as an eluent (feeding rate 1.0 ml . min⁻¹) at 298 K. The RI 410 and UV 490 with a wave length of 254 nm were employed for the detection. Closely arranged polystyrene standards were used for calibration with the conversion being based on the universal calibration principle at equal copolymer composition.

The glass transition temperature (the temperature at which half of the maximum precipitous rise of the specific heat capacity is reached) was determined by the DSC-2 (Perkin-Elmer) in argon at a heating rate of 10 K/min.

The melting volume indices (MVI) were determined at the specified temperatures at a stress of 21.2 N by means of the MP-D Göttfert model.

RESULTS AND DISCUSSION

The dependence of the gel content in the copolymerization of styrene and n-butyl methacrylate with 30 % wt of n-butyl methacrylate dissolved in ethyl benzene on the type and quantity of different multifunctional vinyl monomers acting as crosslinking agents is shown in Fig. 1.

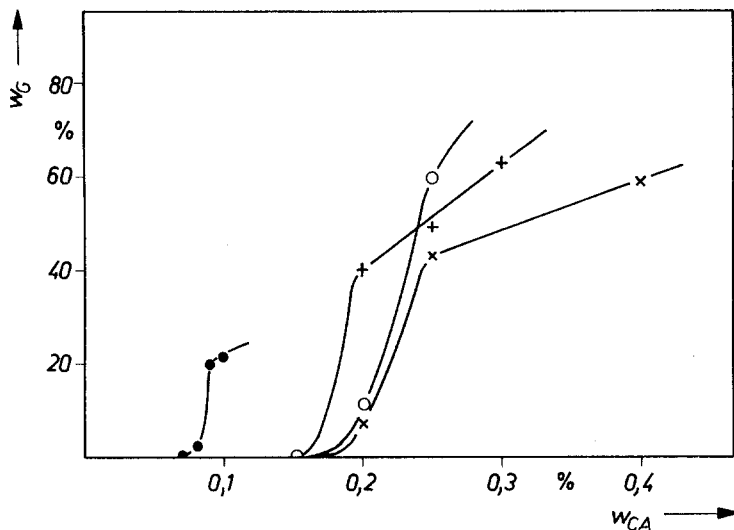


Fig. 1 Relationship between gel content (w_G) of poly(styrene-co-n-butyl methacrylate) and concentration of crosslinking agent (w_{CA}) (\bullet DVB, $+$ BDDMA, \circ TMPTMA, \times EGDMA)

The curve reflects the monomer conversion of 53.4 to 67.8 % wt after the polymerization with the considerable decomposition of the benzoyl peroxide used as a polymerization initiator. As can be seen, the occurrence of the major gel contents shifts in the order DVB < BDDMA < TMPTMA < EGDMA towards the increasing initial concentrations of the crosslinking agent in the monomer mixture. At a low concentration of the crosslinking agent, no gel formation occurs over wide ranges. However, it vigorously sets in within a small concentration range of the crosslinking agent and rises markedly slowly at higher quantities of the crosslinking agent. Evidently, a complete crosslinking of the copolymers can be prevented by selected reaction conditions.

Unlike the gel content, the relative viscosity increment rises even in the absence of gel components with increasing concentration of crosslinking agents (Fig. 2) and shows a maximum value for low gel contents. The subsequent sharp decrease at a slightly increased quantity of the crosslinking agent is attributed to the high gel content which, due to its separation during the preparation of solutions, is not considered for measurement. Hence, the concentration range of the crosslinking agents can be determined by the determination of the relative viscosity increment and its maximum in a relatively easy and exact way until major gel contents occur in the polymer. This maximum is for DVB 0.08 % wt, for BDDMA 0.15 % wt, for EGDMA 0.2 % wt and for TMPTMA approximately

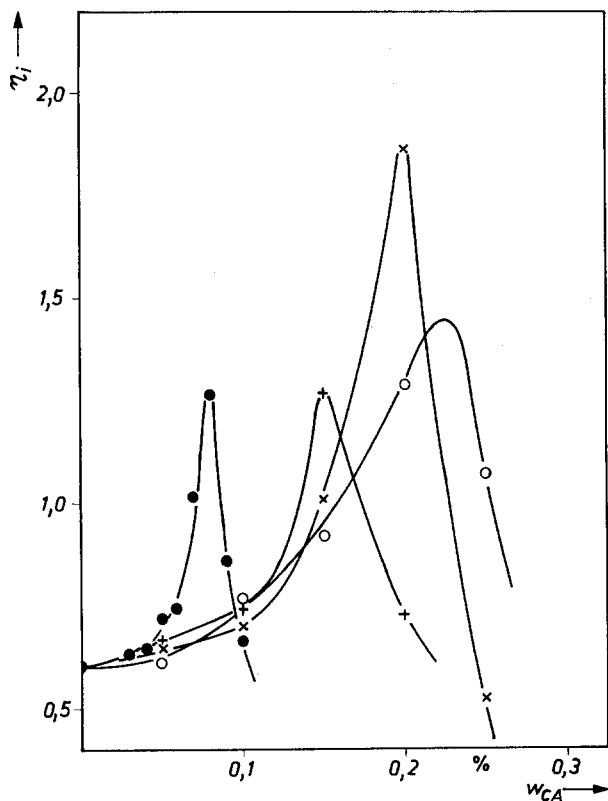


Fig. 2
Relationship
between relative
viscosity
increment
(η_i) and
concentration of
crosslinking
agent (w_{CA}) for
several
crosslinking
agents
(• DVB, + BDDMA,
o TMPTMA, x
EGDMA)

0.225 % wt.

For EGDMA, the viscosity maximum of 0.2 % wt and the monomer conversion of 66.3 % wt correlates with the results of (4) where an increase in the monomer conversion associated with gel formation is shown only for styrene in benzene for the polymerization initiated at 50 °C in the presence of 5 - 15 % mole of EGDMA with the EGDMA quantity in the initial mixture decreasing. A similar relationship applies to the bulk polymerization of methyl methacrylate and EGDMA initiated at 70 °C with and without chain-transfer agent. (7)

The Figures 3 and 4 show the changes of molecular weight and the non-uniformity of the poly(styrene-co-n-butyl methacrylate) prepared in the presence of several crosslinking agents in the particularly interesting range before a major gel content, i. e. crosslinking, occurs. The weight-average molecular weight sharply rises with an increase in the con-

centration of the crosslinking agent. The largest molecular weight increase is reached for BDDMA and TMPTMA under the

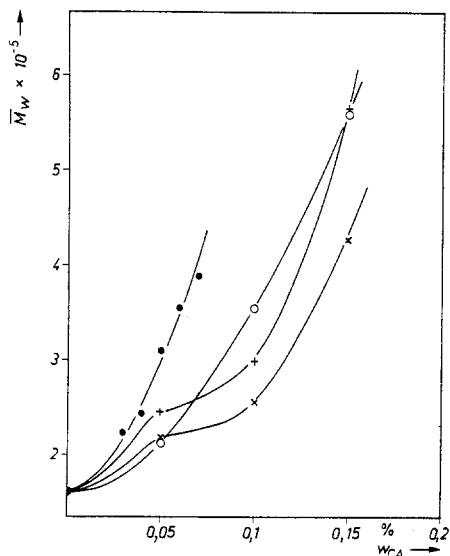


Fig. 3 Relationship between the weight-average molecular weight (\bar{M}_w) and concentration of cross-linking agent (w_{CA}) before major gel quantities occur (• DVB, + BDDMA, o TMPTMA, x EGDMA)

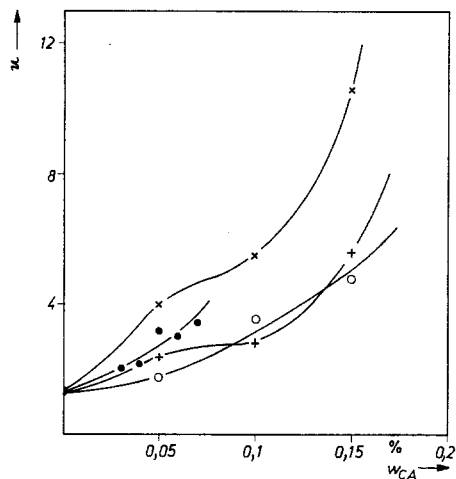


Fig. 4 Effect of the concentration of the crosslinking agent (w_{CA}) on the non-uniformity ($U = (\bar{M}_w/\bar{M}_n) - 1$) of the poly(styrene-co-n-butyl methacrylates) prepared with several crosslinking agents (• DVB, + BDDMA, o TMPTMA, x EGDMA)

prevailing conditions. Also, the non-uniformity of the polymers increases with the increasing concentration of the crosslinking agent under the selected experimental conditions. With DVB, only a slight widening of the molecular weight distribution can be reached, whereas with EGDMA, particularly broadly distributed polymers can be obtained. Hence, a possible increase in the molecular weight of the polymers in the presence of crosslinking agents by increasing the monomer conversion nearly up to the gel point as for example described in (4, 6) can be avoided.

In order to characterize the thermal properties of the poly(styrene-co-n-butyl methacrylates) prepared in the presence of several multifunctional vinyl monomers acting as crosslinking agents, the glass transition temperature of the polymers was investigated. The results are shown in Figure 5 as a function of the concentration of the crosslinking agents. It can be seen that the glass transition temperatures are relatively constant irrespective of the concentration of the crosslinking agents for both the still completely soluble polymers and the polymers with crosslinked components. This confirms that a limit of the glass transition temperature of poly(styrene-co-n-butyl methacrylates) is reached at a higher molecular weight^(13, 14) which is only slightly effected by small quantities of additional multifunctional monomers or by crosslinked polymer components.

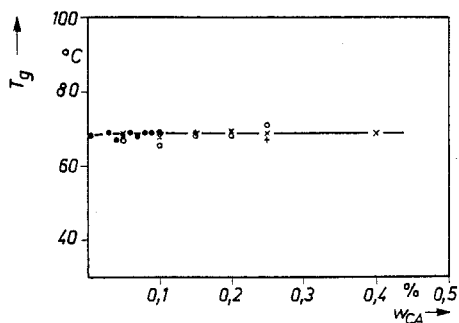


Fig. 5 Relationship between glass transition temperature (T_g) and concentration of crosslinking agent (w_{CA})
(• DVB, + BDDMA, o TMPTMA, x EGDMA)

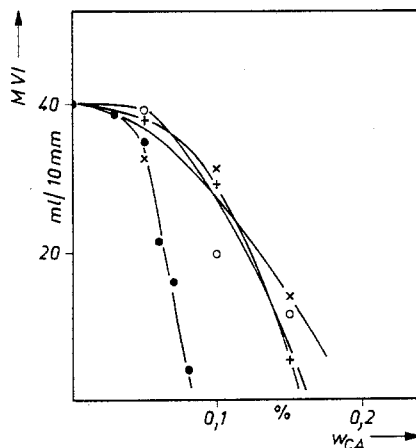


Fig. 6 Relationship between melting volume index (MVI, 210 °, 21.2 N) of the polymers and concentration of crosslinking agent (w_{CA})
(• DVB, + BDDMA, o TMPTMA, x EGDMA)

The flow characteristics of the still free-flowing polymers prepared in the presence of the crosslinking agents are shown in Figure 6 as a function of the melting volume index (210 °C, 21.2 N) on the concentration of the crosslinking agent. The melting volume index of the polymers noticeably decreases with the increasing concentration of the crosslinking agent and the growing molecular weight. The decrease of the melting volume index as a function of the concentration of the crosslinking agent is particularly large for DVB.

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