

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Emulsion Copolymerization of Styrene with Multifunctional Monomer

Viera Chrástová^a; H. S. Nguyen^a; Ján Bartus^b; Peter Zarras^c

^a Faculty of Chemical Technology, Slovak Technical University, Bratislav, Slovak Republic ^b Nashua Corporation, Merrimack, NH ^c Research Technology Division, CA, China Lake

To cite this Article Chrástová, Viera , Nguyen, H. S. , Bartus, Ján and Zarras, Peter(1997) 'Emulsion Copolymerization of Styrene with Multifunctional Monomer', *Journal of Macromolecular Science, Part A*, 34: 8, 1311 – 1323

To link to this Article: DOI: 10.1080/10601329708011046

URL: <http://dx.doi.org/10.1080/10601329708011046>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

EMULSION COPOLYMERIZATION OF STYRENE WITH MULTIFUNCTIONAL MONOMER

Viera Chrástová and H. S. Nguyen

Faculty of Chemical Technology
Slovak Technical University
812 37 Bratislava, Slovak Republic

Ján Bartus*

Nashua Corporation
RTE 3, Merrimack, NH 03054

Peter Zarras

Research Technology Division
Code 4B22000
NAWCWPNS
China Lake, CA 93555

Key Words: Emulsion Copolymerization; Multifunctional Monomer; Crosslinking Agent; Latex Particle Size; Styrene; Ethylene Glycol Dimethacrylate; Reactivity Ratio.

ABSTRACT

The concentration effect of crosslinking agents divinylbenzene, ethylene glycol dimethacrylate (EGDMA) and trimethylolpropane trimethacrylate on the emulsion copolymerization rate with styrene initiated by $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ system was investigated. The latex particle size, the gel content and the polymer viscosity numbers were also determined. In the case of styrene - EGDMA, the crosslinker concentration varied from 0.036 to 1.13 mol/L. We found that the EGDMA concentration does not influence the crosslinking rate of as much as the gel fraction content. High gel

content was observed at the beginning of copolymerization. For styrene - EGDMA the reactivity ratios were calculated as: $r_1 = 0.28$ and $r_2 = 0.98$.

INTRODUCTION

Multifunctional monomers have broad use in radical emulsion polymerization of vinyl monomers. In such systems, crosslinking reaction products have been found useful technologically as e.g. sorbents, ion-exchanging resins, column chromatography packaging materials and dispersions for water-based coatings, etc.

Crosslinking reactions in emulsion systems are not only interesting from an application point of view but also for theoretical studies. According to the classical theory of Flory [1] and Stockmayer [2] it was assumed that the crosslinked polymers are formed in three stages. In the first stage, only linear macromolecules with pendant side groups are formed. In the second stage, the monomers conversion increases with polymer chain branching and finally crosslinking takes place. Based on this theory, different statistical models were formulated. Considerable deviations from these models were observed [3] in the styrene (ST) copolymerization with divinylbenzene (DVB) or ethylene glycol dimethacrylate (EGDMA) initiated by $K_2S_2O_8$. Microgels with different particle size and distribution were prepared from these systems. The presence of linear or branched chains was not observed. Only highly intramolecular crosslinked polymer was isolated. The study of thermally initiated emulsion polymerization of DVB [4] revealed another unique behavior of emulsion polymerization with multifunctional monomer: the polymerization (R_p) rate is inversely proportional to the emulsifier concentration and the particle size is proportional to the emulsifier concentration. This is opposite to the classical theory of emulsion polymerization. Considerable differences were observed in the parameters characterized the emulsion homopolymerization of individual multifunctional monomers (DVB, EGDMA) compared with the crosslinking copolymerization of ST with EGDMA [5].

The newest kinetic models of emulsion crosslinking copolymerization developed by Tobita et al. enables one to predict the network density [6], distribution of molecular weight [7] and the system behavior near the gel point [8].

In this study, we report the investigation results of different types of multifunctional monomers on the course of emulsion polymerization of styrene. In the case of the binary system styrene - ethylene glycol dimethacrylate, the total crosslinker and styrene concentrations were kept constant. In this crosslinking

emulsion copolymerization the bifunctional monomer concentration influence on the reaction rate and gel content was investigated.

EXPERIMENTAL

Materials

Styrene (Kaucuk Kralupy), stabilized. The stabilizer was removed by repeated washing with a 10% NaOH solution in a separatory funnel. The monomer was washed with water and after drying, distilled under an inert argon atmosphere. Divinylbenzene (Slovnaft Bratislava) was purified from stabilizer by the same procedure previously discussed. Pure monomer was kept under inert atmosphere.

Ethylene glycol dimethacrylate (Lachema Brno) was used as received, sparged with argon for 30 minutes before use.

Trimethylolpropane trimethacrylate (Lachema Brno) used as received, sparged with argon for 30 minutes before use.

$K_2S_2O_8$ (Lachema Brno), was used as an aqueous solution with a concentration of 9.2×10^{-2} mol/L.

$Na_2S_2O_4 \cdot 2H_2O$ (Lachema Brno), was used as an aqueous solution with a concentration of 11.4×10^{-2} mol/L.

Mersol H [$CH_3(CH_2)_{14}ONa$] (Leunawerke Merseburg), ionic type emulsifier, was used as an aqueous solution with a concentration of 0.14 mol/L. The oxygen was removed from the solution before use by boiling in an inert atmosphere for 1 hour.

Slovasol 2340 (Chemical Works Nováky) [$CH_3(CH_2)_{23}O(C_2H_4O)_{29}C_2H_4OH$], nonionic emulsifier, was used as an aqueous solution with a concentration of 0.14 mol/L. The oxygen was removed from the solution before use by boiling in an inert atmosphere for 1 hour.

Water, twice distilled, was boiled in an inert atmosphere for 1 hour before use.

Solvents [methanol, acetone, methyl ethyl ketone (MEK)] (Lachema Brno), were used as received.

Procedure

Polymerization of monomers

The batch emulsion copolymerization with crosslinker was performed in a 250 mL glass reactor equipped with a mechanical stirrer, nitrogen inlet and exit and a rubber septum closed sampling neck. The copolymerization temperature was

TABLE 1. Composition of the Polymerization System

	Volume mL	Concentration mol/L _{emulsion}
Water Phase		
Initiator (K ₂ S ₂ O ₈)	12	1.37 · 10 ⁻²
Activator (Na ₂ S ₂ O ₄ · 2H ₂ O)	4	1.99 · 10 ⁻³
Emulsifiers - Slovasol 2430	16	2.90 · 10 ⁻²
Mersol H	16	2.90 · 10 ⁻²
Organic Phase		
Monomers - Crosslinker	X ^{a,b}	
- Styrene ^b	32 -X	

^a The multifunctional monomer (DVB or TRIM) was used in 2% on styrene.

^b In the case of ST - EGDMA copolymerization the amounts of EGDMA monomer were:

EGDMA (mL)	0.55	3.0	6.0	9.0	12.0	16.0	17.0
mol/L _{emulsion}	0.036	0.19	0.39	0.59	0.78	0.78	1.13
wt %	2.0	10.8	21.7	32.5	43.4	43.4	61.4

40°C and the stirring rate was 300 RPM. Analysis samples were taken by a syringe through the septum on the sampling neck.

The reactor was swept by inert gas, for 1 hour before the reaction then water, emulsifiers, and monomers were added. The reactor content was heated under stirring until the required temperature was reached, and 15 minutes later the initiation system was added. The polymerization system composition is given in Table 1.

The polymerization course was followed gravimetrically: at certain time intervals small aliquots (about 1 mL) of emulsion were taken and weighed in closed sampling bottles. The polymer was precipitated from these samples in an excess of methanol, filtered on a frit, washed with water, methanol and dried. The monomers conversion was estimated from the known monomers weight in the mixture. The monomers conversion (in weight %) was calculated according to the following Equation 1:

$$\text{Conv.} = \frac{w_p \cdot w_e}{w_a \cdot w_m} \cdot 100 \quad [\text{wt \%}] \quad (1)$$

where: w_p is the precipitated polymer weight

w_e is the emulsion sample weight

w_a is the sum weight of all polymerization system components

w_m is the monomers weight in the reactor feed.

Characterization

Elemental analysis

The EGDMA crosslinker content in polymer samples was determined by elemental analysis. The measurements were performed on the Elementar Analyzer CHN+O, Model 1102, Carlo Erba, Milan, Italy.

Reactivity Ratio Calculations

Reactivity ratios r_1 and r_2 were calculated from Equation 2:

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \quad (2)$$

using the KOPAR program according to Joshi-Joshi (J-J) [9], Kelen-Tüdös (K-T) [10] and Fineman-Ross (F-R) [11] methods.

Particle size determination

Particle size determination was performed by a light scattering method using the Particle Sizer, model BI - 90 (Brookhaven Instruments Corporation) with He-Ne laser source. The method is based on the intensity of scattered light of dilute dispersions. The samples of lattices were diluted 100 -1000 times by water and the measurement was done at 25°C.

Determination of Gel Content

The content of insoluble portion of polymer after crosslinking (gel) was determined by dissolving samples in methyl ethyl ketone in closed jars for 48 hours at ambient temperature. The insoluble fraction was separated on a frit and dried until constant weight was obtained. The gel content G (in weight %) was determined according to Equation 3:

$$G = \frac{w_g}{w_p} \cdot 100 \quad [\text{wt \%}] \quad (3)$$

where w_g is the weight of insoluble portion in grams
 w_p is the weight of the whole sample in grams

Viscometry

The viscometric measurements were done in MEK at 25°C. The limiting viscosity number $[\eta]$ was obtained from the extrapolation of the dependence (4) to zero concentration.

$$\frac{\eta - \eta_0}{\eta_0 \cdot c} = [\eta] + k_H [\eta]^2 \quad (4)$$

where η , η_0 is the viscosity of solution and the solvent, which is proportional to the flow time of the liquids through a capillary

c is the concentration of solution in g/cm^3
 k_H is the Huggins constant

RESULTS AND DISCUSSION

The crosslinking agent influence on the styrene emulsion copolymerization was investigated for the polymerization system. (Table 1). The crosslinking agent content was kept at 2 wt %. The conversion curves of the styrene polymerization in the presence of two bifunctional monomers (DVB and EGDMA) and one trifunctional (TRIM) are presented in Figure 1. As a result, the presence of crosslinking agent below 2 wt % has a negligible influence on the course of the emulsion polymerization. The overall polymerization (R_p) rate calculated from the stationary part of the curves (20–40% conversion) is slightly lower where crosslinking agents were used compared with pure styrene (Table 2). The dispersions were homogeneous and the polymers particle size, with and without the presence of crosslinking agents, was almost identical (Table 2).

The crosslinked portion - gel was documented from the gel content values on the results obtained using DVB, EGDMA and TRIM. Even more dramatically, the crosslinkers influence was evident from viscometry measurements. The solutions made from crosslinked polymers were partially turbid but the measurements

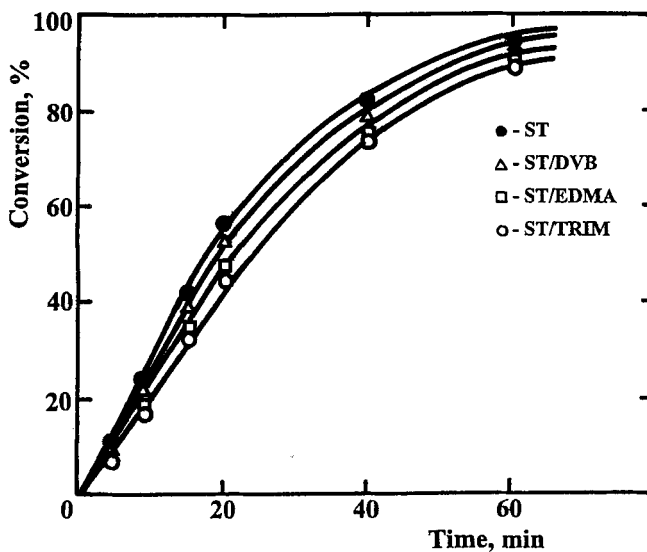


Figure 1. Conversion curves of emulsion copolymerization of styrene at 40°C initiated by $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ system with 2wt % of multifunctional monomer.

TABLE 2. The Influence of Multifunctional Monomer on the Emulsion Copolymerization with Styrene

Combination a	Rate of Homo- polymerization & Copolymerization $R_p \cdot 10^3, \text{ mol/L} \cdot \text{s}$	Particle Size G D nm	Gel Content ^b		Limiting Viscosity Number, $[\eta]$ dL/g
			G	%	
ST	1.71	59	-		2.14
ST/DVB	.62	58	5.8		0.10
ST/EGDMA	1.32	58	6.7		0.15
ST/TRIM	1.20	54	7.2		0.20

^a The concentration of crosslinker was 2 % wt

^b The gel content was measured at 50 % conversion

in MEK were possible and the limiting viscosity numbers $[\eta]$ were calculated according to Equation 4. It has been shown that the $[\eta]$ values for crosslinked copolymers are much lower than uncrosslinked polystyrene (Table 2). The previous results published by Kasta and Funke [12] or Schellenberg [13] confirm that molecular characteristics ($[\eta]$ and \overline{M}_w) are sensitive to the presence of a crosslinked portion, especially at low crosslinker content and at low conversions. The crosslinking reactions also cause branching of main copolymer chains. The coils of branched copolymer in a good thermodynamic solution assume a smaller hydrodynamic diameter than the linear copolymer macromolecules. The consequence of this is the decreasing of flow time in a viscometer compared with that of a linear polymer. Thus, viscometry can readily provide information about the presence of crosslinks down to a very low level where solutions are non-scattering. In our case, viscometry remains an appropriate technique up to a gel content of about 10%. At higher gel content the solutions were turbid, and the gel had to be removed by filtration which considerably decreased solution concentration. The ratio η/η_0 (or t/t_0) is very low and this leads to an increase in error.

The crosslinker concentration influence on the course of the ST-EGDMA emulsion copolymerization was studied. In a series of copolymerization reactions the EGDMA concentration was changed from 0.036 to 1.05 mol/L (2 to 57 wt %) at a constant comonomer volume. With increasing EGDMA concentration, both monomers were gradually incorporated into a final product. The objective of the study was to investigate the influence of increasing concentration of EGDMA on the overall polymerization R_p rate and on the gel content G .

The monomer conversion dependence as a reaction time function is documented in Figure 2. It has been shown that at a low crosslinker concentration (up to 0.19 mol/L) the polymerization rate decreases, compared with the R_p of pure styrene. The further increase of EGDMA concentration (up to 1.05 mol/L) causes an increase in R_p (Figure 3). Similar results were recently published by Sajjadi [14] for the kinetics of bulk crosslinking copolymerization of styrene with DVB. The rate of polymerization increases with crosslinker content at all used temperatures. In our case, the EGDMA concentration increase above 1.05 mol/L (1.13 mol/L and up) causes the formation of highly crosslinked particles. The resulting emulsion was inhomogeneous and contained macroscopic agglomerates.

In all styrene copolymerizations with EGDMA the gel content dependence was followed as a function of conversion (Figure 4). The gel content increase, as a conversion function for individual polymerizations, is only incremental for different EGDMA concentrations. In all cases, at the beginning of the copoly-

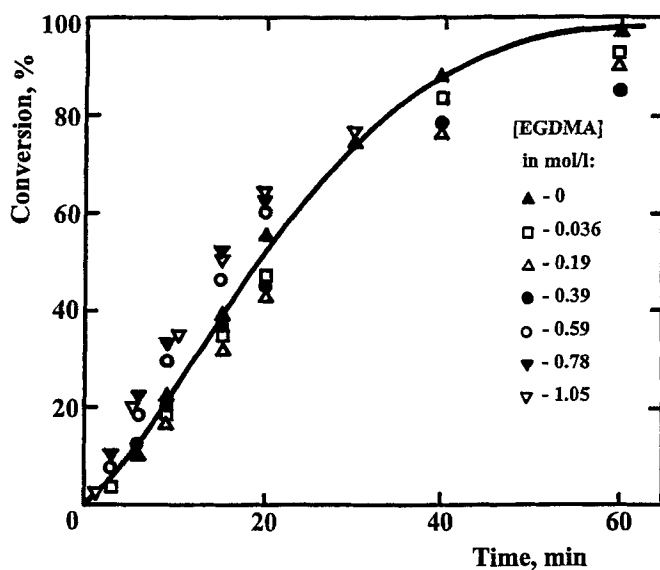


Figure 2. Dependence of monomer conversion as a function of reaction time for emulsion copolymerization of styrene with EGDMA at 40°C initiated by $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$. The full line represent the homopolymerization of styrene.

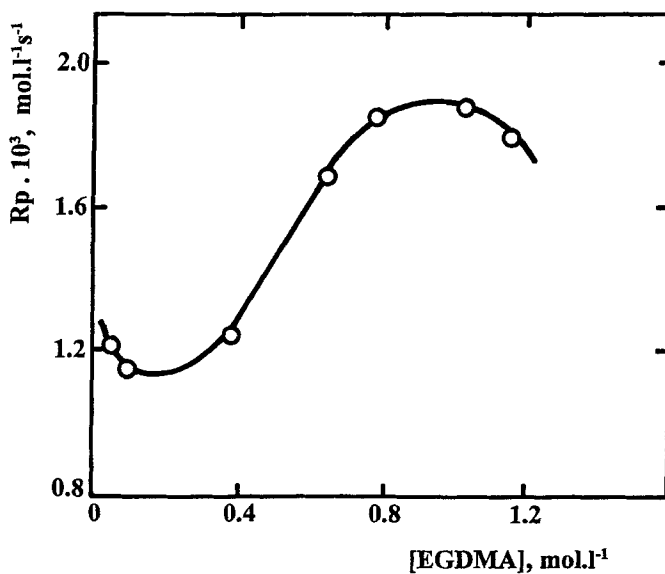


Figure 3. Dependence of overall rate of polymerization R_p as a function of molar concentration of crosslinking monomer for emulsion copolymerization of styrene with EGDMA at 40°C initiated by $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ system.

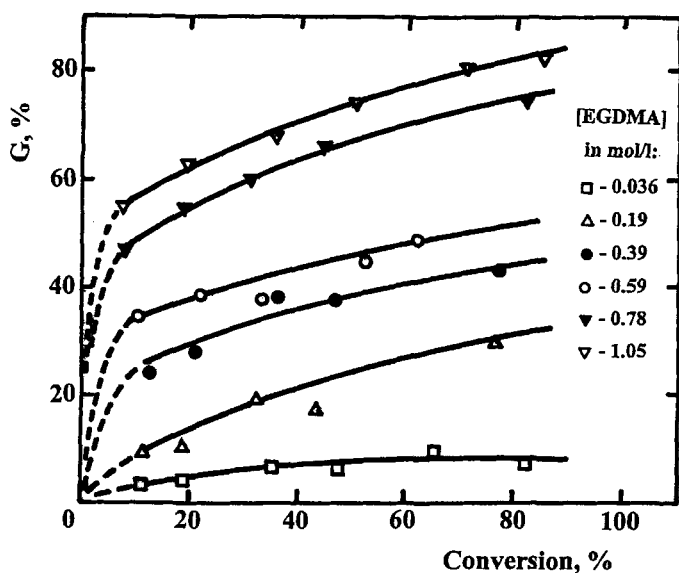


Figure 4. Dependence of gel content G as a function of monomer conversion for emulsion crosslinking copolymerization of styrene with EGDMA at 40°C initiated by $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ system.

erization the gel content is high. This finding is in agreement with the results obtained by kinetics modelling of crosslinking emulsion copolymerization published by Tobita [6]. In simulation experiments using similar kinetic parameters as for bulk polymerization it was found that the crosslink density is much higher in the early stages of an emulsion polymerization system and the polymer network is more heterogeneous compared to that for a bulk system.

In our case, the emulsion crosslinking copolymerization of ST with EGDMA with the water-soluble initiation system ($\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) we assume that the oligomeric radicals formed in the water phase are growing until a certain polymer chain length is reached and they contain the inception of the network. The formation of the crosslinked portion is suppressed by the swelling of created particles by monomers, resulting in the active centers moving from the inside toward the outside core of the particles. The growing macroradical has increasing difficulty reaching unreacted functional groups localized inside the same polymer chain and is more susceptible to reacting with free functional groups of other chains. Therefore, the internal cyclization is suppressed and the efficiency of crosslinking is not diminished in the early stages of polymerization. This results in considerable gel formation at low monomer conversion.

TABLE 3. The Molar Fractions of ST and EGDMA in a Monomer Mixture (f_1 and f_2) and in the Copolymer (F_1 and F_2) in the Emulsion Crosslinking Copolymerization System

	f_1	f_2	F_1	F_2
	0.99	0.01	0.96	0.04
	0.95	0.05	0.86	0.14
	0.88	0.12	0.74	0.26
	0.81	0.19	0.60	0.40
	0.73	0.27	0.56	0.44
	0.62	0.38	0.44	0.56

TABLE 4. The Reactivity ratios (r_1 and r_2) for Emulsion Copolymerization System ST(1) - EGDMA(2) initiated by $K_2S_2O_8/Na_2S_2O_4 \cdot 2H_2O$ at 40°C

r	J-J	Method		Average	Reference[6]	Reference[15]
		K-T	F-R			
r_1	0.28	0.29	0.28	0.28	0.26	0.32
r_2	1.05	1.11	0.80	0.98	0.92	0.62

The formation of the crosslinked portion during nucleation in the early stages of the synthesis increases with the concentration of EGDMA crosslinker. An additional contributing factor is the higher reactivity of EGDMA monomer as compared with styrene. This was confirmed by the determination of reactivity ratios found from the analysis of composition of the ST/EGDMA copolymers. The data describing the content of ST (F_1) and EGDMA (F_2) in copolymers expressed as molar ratios as a function of molar fraction of styrene (f_1) and EGDMA (f_2) in the monomer mixture are presented in the Table 3. The copolymerization ratios were calculated according to Joshi-Joshi (J-J), Kellen-Tüdös (K-T) and Fineman-Ross (F-R) methods using our program KOPAR and are presented in Table 4. From the results, it is seen that the calculated reactivity ratios (average value) for emulsion copolymerization of ST with EGDMA $r_1 = 0.28$ and $r_2 = 0.98$ are in good agreement with results published earlier [6] determined on the basis of a kinetic model for emulsion copolymerization of ST with EGDMA. Compared with the bulk copolymerization of ST with EGDMA initiated by benzoyl peroxide and run at 60°C [15] our r_1 value is slightly lower and r_2 higher.

A possible explanation for the difference in r_1 and r_2 values can be related to the mechanism of emulsion copolymerization in the presence of a crosslinking comonomer. Here the formation of oligomeric radicals with reactive side groups accessible for interparticle crosslinking [5, 16] can be expected. This is also related to the different mechanism of crosslink formation in emulsion and bulk polymerization. In the emulsion system the oligomeric radicals are formed in the water phase and later are occluded by the emulsifier. As a result, in emulsion system different rate constants are entering into the reactivity ratio formula as in the case of bulk polymerization.

CONCLUSION

From the results of emulsion copolymerization of styrene with low amounts of various types of crosslinking monomers (up to 2 wt %) it can be concluded that the rate of copolymerization is only slightly lower compared with homopolymerization of styrene. We found that EGDMA has a promoting effect on the rate of copolymerization with styrene in the concentration range 10.8 - 57.8 wt %. The crosslinker has a dramatic influence on the content of the crosslinked portion in the copolymer. The gel content is high from the beginning of emulsion copolymerization. This may be related to the kinetics of emulsion copolymerization and to the higher reactivity of crosslinking comonomer as compared to styrene.

REFERENCES

- [1] R. J. Flory: Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 384 (1953).
- [2] W. M. Stockmayer, *J. Chem. Phys.*, *12*, 125 (1944).
- [3] W. Obrecht, U. Seitz, and W. Funke, *Makromol. Chem.*, *177*, 1877 (1976).
- [4] H. Kast and W. Funke, *Makromol. Chem.*, *182*, 1553 (1981).
- [5] M. Nomura and K. Fujita, *Polym. Int.*, *30*, 483 (1993).
- [6] H. Tobita, *Macromolecules*, *25*, 2671 (1992).
- [7] H. Tobita, *Macromolecules*, *26*, 836 (1993).
- [8] H. Tobita and K. Yamamoto, *Macromolecules*, *27*, 3389 (1994).
- [9] R. M. Joshi and S. G. Joshi, *J. Macromol. Sci. - Chem.*, *A5*, 1329 (1971).

- [10] T. Kelen and F. Tüdös, *J. Macromol. Sci.*, *A9*, 1 (1971).
- [11] M. Fineman and S. D. Ross, *J. Polym. Sci.*, *5*, 259 (1950).
- [12] H. Kast and W. Funke, *Makromol. Chem.*, *180*, 1335 (1979).
- [13] J. Schellenberg and B. Hamann, *Polymer Bulletin*, *31*, 479 (1993).
- [14] S. Sajjadi, S. A. M. Keshavarz, and M. Nekoomanesh, *Polymer*, *37*, 4141 (1996).
- [15] R. H. Wiley and E. E. Sale, *J. Polym. Sci.*, *42*, 491 (1960).
- [16] H. Tobita, K. Kimura, K. Fujita, and M. Nomura, *Polymer*, *34*, 2569 (1993).

Received December 20, 1996

Revision Received January 23, 1997