

## Copolymerization of Styrene with Dodecyl Methacrylate and Octadecyl Methacrylate

*Elvira Vidović, Karla Sarić, and Zvonimir Janović\**

*Faculty of Chemical Engineering and Technology, University of Zagreb,  
Marulićev trg 19, 10 000 Zagreb, Croatia*

Received October 8, 2001; revised February 7, 2002; accepted February 22, 2002

Styrene (Sty) was copolymerized with dodecyl methacrylate (DDMA) and with octadecyl methacrylate (ODMA) in toluene solution using 2,2'-azobis(isobutyronitrile) (AIBN) as a free radical initiator over a wide composition and conversion range. The copolymer composition was determined from  $^1\text{H}$  NMR spectra. The copolymerization reactivity ratios were found to be  $r_1 = 0.52$  (Sty) and  $r_2 = 0.42$  (DDMA) for the Sty–DDMA system, and  $r_1 = 0.58$  (Sty) and  $r_2 = 0.45$  (ODMA) for the Sty–ODMA system, showing a tendency toward ideal copolymerization reactions. The  $Q$  and  $e$  values were also calculated according to the Greenly method. The initial polymerization rate,  $R_p$ , was found to be in the order ODMA > DDMA >> Sty and sharply decreased for both copolymerization systems as the content of Sty in the monomer mixture increased. Similar behaviour was also recorded for the molecular weights and intrinsic viscosities of the copolymers as their values significantly decreased with increasing the Sty fraction in the monomer mixture. Polymer viscosity in toluene solution determined at 30 to 90 °C slightly increased with the temperature for homopolymers of the alkyl methacrylates and reached the local maximum value at higher temperature, showing a constant value for the polystyrene, whereas the copolymer values were intermediate between those of homopolymers. Also, the copolymers showed an increase in thermal stability with increasing the Sty content.

**Key words:** styrene, dodecyl methacrylate, octadecyl methacrylate, copolymerization, copolymers, viscosity improvers.

---

\* Author to whom correspondence should be addressed. (E-mail: Janovic@marie.fkit.hr)

## INTRODUCTION

Free radical copolymerization of styrene and methacrylic acid esters have been studied extensively and described in many publications, showing their similar reactivity that somewhat depends on the polarity of the methacrylate alkyl side group giving random copolymers and forming azeotropic compositions.<sup>1-4</sup> Most of the published results are concerned with the styrene-methyl methacrylate system, which is in many studies treated as a theoretical copolymerization model,<sup>5-7</sup> whereas only a few treat long side chain alkyl methacrylate as a comonomer.<sup>3,6,8</sup> The copolymerization reactivity ratios of styrene (Sty) with dodecyl methacrylate (DDMA) have been reported<sup>3,8</sup> but copolymerization kinetics and major properties of the copolymers, particularly of Sty and octadecyl methacrylate (ODMA), have not been investigated. In anionic polymerization, a block copolymer of St-ODMA was prepared by sequential addition of monomers.<sup>9</sup> The copolymers of methacrylates with long alkyl side groups and of controlled molecular architecture have attracted special attention with a renewal of interest because they have found important applications, particularly as lubricating oil rheology modifiers.<sup>10-12</sup> They are usually copolymers of mixed methacrylic esters with short, intermediate and long alkyl side groups,<sup>11-14</sup> but other vinyl comonomers, such as Sty, maleic acid esters, maleimides *N*-vinyl-pyrrolidone or *N*-vinyl-imidazole and others, have been also employed.<sup>10</sup> Termination kinetic modelling in the terpolymerization reaction of acrylate or methacrylate systems has been recently described.<sup>13</sup>

This paper describes the reaction kinetics of styrene with dodecyl methacrylate and octadecyl methacrylate by free radical initiation in toluene solution. Measurements of some characteristic properties of the obtained copolymers, particularly their molecular weights, viscosities at different temperatures as well as thermal behaviour have been also made.

## EXPERIMENTAL

### *Materials*

Commercial monomers: styrene (Sty) (Org. Kem. Ind., Zagreb), dodecyl methacrylate (DDMA) and octadecyl methacrylate (ODMA) (RohMax, Chem. Co., Germany) were deprived of the inhibitor by washing with sodium hydroxide solution, washed several times with water, dried and purified. Sty and DDMA were purified by distillation under nitrogen and reduced pressure whereas ODMA was purified by repeated crystallization from methanol solution. Initiator 2,2'-azobis(isobutironitrile) (AIBN) was recrystallized from methanol. Solvents were purified in the usual way.

### *Measurements*

The  $^1\text{H}$  NMR spectra of the copolymers were recorded on a 90 MHz Varian EM-360 spectrometer at room temperature as 10–15 g L<sup>-1</sup> solutions, in deuterated chloroform with TMS as internal standard.

Intrinsic viscosities were measured on a Cannon-Fenske capillary viscometer, No. 100, in toluene at different temperatures.

Thermogravimetric analyses were carried out with a Netzsch Sta 409 instrument in nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>.

The average molecular weights of the copolymers were measured by means of gel-permeation chromatography (GPC) using an Aerograph 8500 Varian instrument fitted with a RI detector. Styragel columns (Waters Associates) were used at a flow rate of 1 cm<sup>3</sup> min<sup>-1</sup> of degassed tetrahydrofuran. Retention times were calibrated with the polystyrene fraction.

### *Copolymerization Procedure*

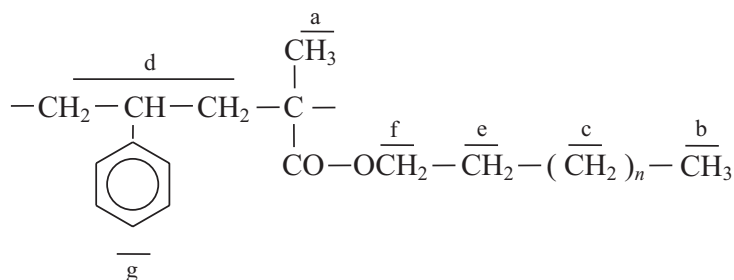
Solution polymerization to low conversion in toluene (50 cm<sup>3</sup> solutions) of monomers (0.1 mol) with AIBN (0.082 g) as initiator at 60 °C was carried out under a constant stream of nitrogen in a 100 cm<sup>3</sup>, double-jacketed glass reactor of 100 cm<sup>3</sup>, equipped with a magnetic stirrer. After an appropriate time interval (10–100 min), the whole reaction mixture was poured into methanol, and the polymer was separated by filtration, dissolved in toluene and reprecipitated twice, and dried at 60 °C under vacuum.

The rate of copolymerization was followed dilatometrically and gravimetrically. Dilatometers (about 20 cm<sup>3</sup>) filled with the toluene solution of the monomer mixture, and the initiator (AIBN) were connected to a high vacuum line and freed of oxygen by freezing-thawing cycles. The dilatometers were then placed in a thermostat bath, and the volume contraction was recorded as a function of time. The reaction was terminated by vacuum suction of the contents and precipitation in excess of methanol. The conversion was determined gravimetrically at the end of each dilatometric experiment.

## RESULTS AND DISCUSSION

### *Copolymerization Reaction*

The free radical copolymerization of styrene (Sty) with dodecyl methacrylate (DDMA) or octadecyl methacrylate (ODMA) was performed in toluene solution using 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator. Compositions of both the Sty–DDMA and Sty–ODMA copolymers were determined by  $^1\text{H}$  NMR spectral analysis. The structure of copolymers and their proton types can be depicted as follows:



where  $n = 9$  in Sty-DDMA and  $n = 15$  in Sty-ODMA copolymer moieties. The chemical shifts of both copolymers (Table I) show combined features of both homopolymers and are very similar to long alkyl methacrylate found by other authors.<sup>15</sup> The mole ratios of the monomers in copolymers were calculated from the ratios of the phenyl group peak area and the area of all aliphatic protons, subtracted from the contribution of three H protons belonging to the styrene backbone part.

TABLE I

<sup>1</sup>H NMR chemical shifts of protons in styrene-dodecyl methacrylate (Sty-DDMA) or styrene-octadecyl methacrylate (Sty-ODMA) copolymers<sup>a</sup>

No.	Proton type	Chemical group	Number of protons	Chemical shift ( $\delta$ /ppm)
1	a	$\alpha$ -CH <sub>3</sub> (backbone)	3	0.73
2	b	-CH <sub>3</sub> (end of alkyl)	3	0.93
3	c	-(CH <sub>2</sub> ) <sub>n</sub> -	18 (30) <sup>b</sup>	1.30
4	d	-CH- , -CH <sub>2</sub> - (backbone)	5	1.35-2.25
5	e	-O-CH <sub>2</sub> -CH <sub>2</sub> -	2	1.94
6	f	-OCH <sub>2</sub> -	2	3.93
7	g	-C <sub>6</sub> H <sub>5</sub> (from styrene)	5	6.57-7.48

<sup>a</sup>The spectra of both Sty-DDMA and Sty-ODMA are identical.

<sup>b</sup>Nine side chain -CH<sub>2</sub>- groups in Sty-DDMA and fifteen -CH<sub>2</sub>- groups in Sty-ODMA copolymers.

The influence of the Sty mole fraction in the initial monomer mixture ( $f$ ),  $x(\text{Sty})_f$ , on the copolymer composition ( $F$ ),  $x(\text{Sty})_F$ , and some properties of the resulting copolymers obtained at low conversions is presented in Table II

TABLE II

Copolymerization of styrene (Sty) and n-dodecyl methacrylate (DDMA) in solution at low conversion<sup>a</sup>

$x(\text{Sty})_f$ <sup>b</sup>	Conv. %	$x(\text{Sty})_F$ <sup>c</sup>	$\frac{10^5 R_p}{\text{mol dm}^{-3} \text{ s}^{-1}}$	$10^{-3} \overline{M}_w$ <sup>d</sup>	$10^{-3} \overline{M}_n$ <sup>d</sup>	$\frac{[\eta]}{\text{dl g}^{-1}}$ <sup>e</sup>
0.00	12.8	0.00	18.7			0.57
0.10	11.2	0.18	9.7			0.45
0.20	7.7	0.30	6.2	107.5	65.2	0.35
0.30	13.4	0.38	3.9			0.34
0.40	3.9	0.45	2.9	75.7	46.3	0.31
0.50	12.9	0.52	2.4	67.1	40.7	0.26
0.60	7.1	0.58	2.1	51.6	31.2	0.21
0.70	6.6	0.65	1.7			0.19
0.80	9.7	0.74	1.6			0.18
1.00	14.3	1.00	1.5			0.14

<sup>a</sup> Polymerization conditions: toluene solution of monomers,  $c_{\text{tot}} = 2 \text{ mol dm}^{-3}$ ,  $c(\text{AIBN}) = 2 \times 10^{-2} \text{ mol dm}^{-3}$ , 60 °C.

<sup>b</sup> Mole fraction of Sty in the initial monomer mixture.

<sup>c</sup> Mole fraction of Sty in copolymer.

<sup>d</sup>  $\overline{M}_w$  = weight average molecular weight,  $\overline{M}_n$  = number average molecular weight.

<sup>e</sup> Intrinsic viscosity in toluene at 30 °C.

for the Sty–DDMA system and in Table III for the Sty–ODMA system. In both cases, the plots of instantaneous monomer-copolymer composition (Figure 1) show a marked tendency toward an ideal copolymerization reaction and an azeotropic composition forming; for the Sty–DDMA system at mole fractions 0.55 : 0.45 and for Sty–ODMA at 0.56 : 0.44. The type of the copolymer formed will be understood from the values of the reactivity ratio of comonomers. By applying the Fineman-Ross (FR)<sup>16</sup> and two Kelen-Tüdös methods,<sup>17</sup> the low conversion ( $\text{KT}_{\text{LC}}$ ) and the high conversion ( $\text{KT}_{\text{HC}}$ ) method, the copolymerization reactivity ratios of Sty and DDMA or ODMA were evaluated from the monomer feed ratios and the resulting copolymer compositions. The Kelen-Tüdös method is based on the equation:

$$\eta = r_1 \xi - r_2 / \alpha (1 - \xi)$$

where  $\eta$  and  $\xi$  are functions of the monomer mole fraction in the copolymer and in the feed respectively, and  $\alpha$  is an arbitrary parameter. The obtained

TABLE III

Copolymerization of styrene (Sty) and n-octadecyl methacrylate (ODMA) in solution at low conversion<sup>a</sup>

$x(\text{Sty})_f$ <sup>b</sup>	Conv. %	$x(\text{Sty})_F$ <sup>c</sup>	$\frac{10^5 R_p}{\text{mol dm}^{-3} \text{ s}^{-1}}$	$10^{-3} \overline{M}_w$ <sup>d</sup>	$10^{-3} \overline{M}_n$ <sup>d</sup>	$\frac{[\eta]}{\text{dl g}^{-1}}$ <sup>e</sup>
0.00	15.5	0.00	23.4			0.52
0.10	8.7	0.17	11.3			0.46
0.20	10.0	0.29	8.4	128.8	44.7	0.36
0.30	3.0	0.38	5.3			0.28
0.40	9.3	0.45	3.9	93.8	33.9	0.26
0.50	8.5	0.52	3.3			0.24
0.60	13.8	0.59	2.5	77.2	28.6	0.22
0.70	9.2	0.66	2.2	66.2	33.2	0.20
0.80	8.7	0.76	1.7			0.17
1.00	13.3	1.00	1.5			0.14

<sup>a-e</sup> See the corresponding footnotes to Table II.

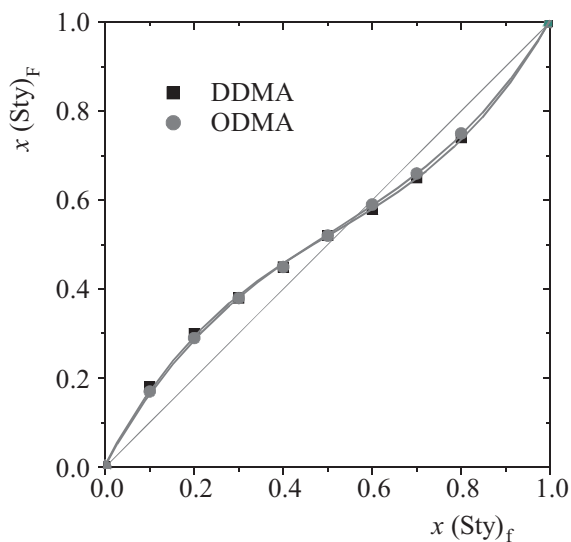


Figure 1. Monomer-copolymer composition curves for copolymerization of styrene with dodecyl methacrylate (Sty-DDMA) or octadecyl methacrylate (Sty-ODMA) in toluene at 60 °C with AIBN.

TABLE IV

Copolymerization parameters for free radical copolymerization of styrene (Sty) with dodecyl methacrylate (DDMA) or octadecyl methacrylate (ODMA)

Monomer	Method	$r_1$	$r_2$	$Q$	$e$
DDMA	(KT) <sub>LC</sub> <sup>a</sup>	0.523 ( $\pm$ 0.016)	0.421 ( $\pm$ 0.018)	0.72	0.43
	(KT) <sub>HC</sub> <sup>b</sup>	0.506 ( $\pm$ 0.016)	0.400 ( $\pm$ 0.018)		
	FR <sup>c</sup>	0.533	0.433		
	Average	0.52	0.42		
ODMA	(KT) <sub>LC</sub>	0.580 ( $\pm$ 0.015)	0.457 ( $\pm$ 0.016)	0.68	0.36
	(KT) <sub>HC</sub>	0.562 ( $\pm$ 0.018)	0.562 ( $\pm$ 0.020)		
	FR	0.583	0.461		
	Average	0.58	0.43		
MMA	(KT) <sub>LC</sub>	0.52	0.46	0.74	0.40

<sup>a</sup> Kelen-Tüdös low conversion method.<sup>17</sup>

<sup>b</sup> Kelen-Tüdös high conversion method.<sup>17</sup>

<sup>c</sup> Fineman-Ross method.<sup>16</sup>

results are presented in Table IV, as related to the polarity ( $e$ ) and the resonance effect ( $Q$ ) in the Alfrey-Price scheme, using the Greenley method<sup>18</sup> and taking additional copolymerization parameters from the literature.<sup>19</sup> For comparison, the values for the Sty-MMA (MMA = methyl methacrylate) copolymerization parameters have been also put together. Graphic presentation was also undertaken for the Kelen-Tüdös low conversion method (Figure 2).<sup>17</sup> Somewhat different values for Sty-DDMA  $r$ -parameters were found by T. Otsu and co-workers,<sup>3</sup> presumably because they used different reaction conditions. The  $Q$  values obtained agree fairly well with those for methyl methacrylate, indicating that the steric effect of the  $n$ -alkyl group in methacrylate esters does not play a significant role in their reactivity. In contrast, the  $e$ -values obtained showed that the electron donating power of  $n$ -alkyl groups increases with the increase of the alkyl chain length, as it was earlier reported for the series of alkyl methacrylates.<sup>3</sup>

The initial copolymerization reaction rates,  $R_p$ , calculated from the dilatometrically measured volume contraction *versus* time<sup>20</sup> for different monomer feed compositions ( $f_1$ ), but at a constant monomer concentration (2 mol dm<sup>-3</sup>), are plotted in Figure 3. They give symmetric curves in both cases, decreasing as the content of styrene in the monomer mixture increases. The initial reaction rate for the homopolymerization reaction also decreased

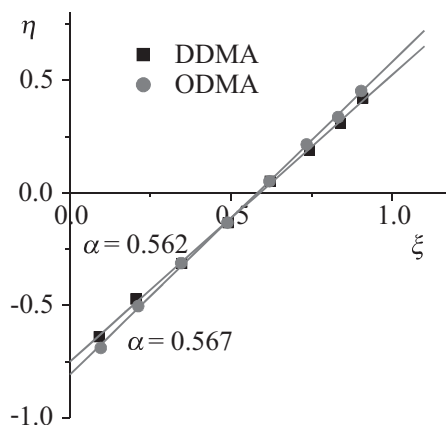


Figure 2. Kelen-Tüdös diagram for the calculation of copolymerization reactivity ratios  $r_1$  and  $r_2$  for the system styrene and dodecyl methacrylate (Sty–DDMA) or octadecyl methacrylate (Sty–ODMA) in toluene. From the straight line,  $r_1$  and  $-r_2 / \alpha$  are the values of  $\eta$  for  $\xi = 1$  and for  $\xi = 0$ , respectively.

and followed the order ODMA > DDMA  $\gg$  Sty. Under the experimental conditions used, the polymerization rate of ODMA is about 1.25 times higher than that of DDMA and about fifteen times higher than that of styrene. Si-

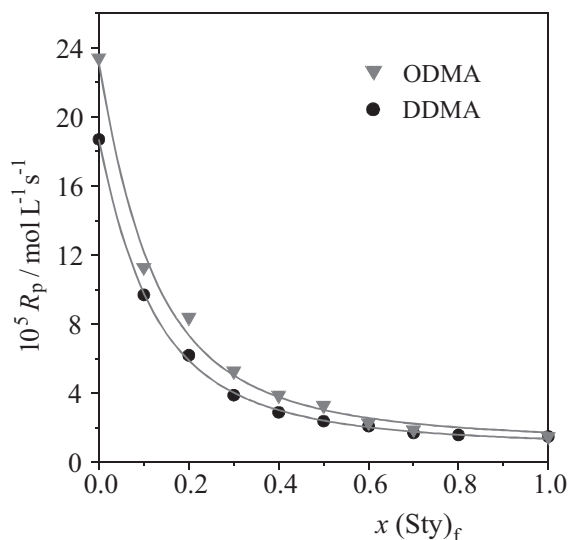


Figure 3. Dependence of the initial reaction rate ( $R_p$ ) on the mole fraction of styrene in the initial monomer mixture,  $x(\text{Sty})_f$ , in copolymerization of styrene and dodecyl methacrylate (Sty–DDMA) or octadecyl methacrylate (Sty–ODMA): total concentration of monomers,  $c_{\text{tot}} = 2 \text{ mol dm}^{-3}$ ,  $c(\text{AIBN}) = 2 \times 10^{-2} \text{ mol dm}^{-3}$ , in toluene at  $60^\circ \text{C}$ .



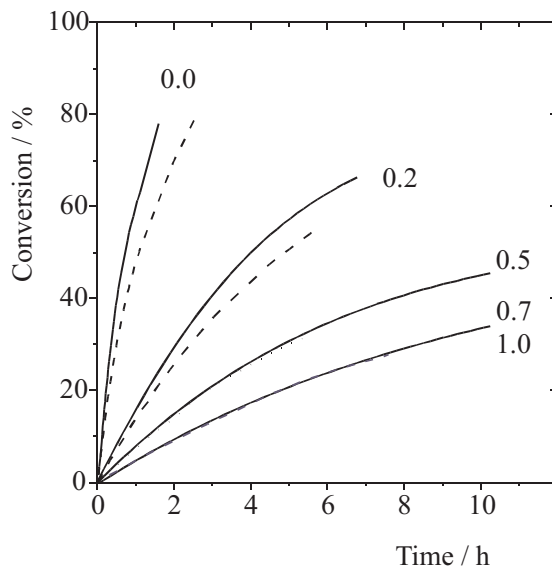


Figure 4. Influence of the monomer mixture composition on the conversion *versus* reaction time in copolymerization of styrene with octadecyl methacrylate (Sty-ODMA, —), and dodecyl methacrylate (Sty-DDMA, ---):  $c_{\text{tot}} = 0.5 \text{ mol dm}^{-3}$ ,  $c(\text{AIBN}) = 1 \times 10^{-2} \text{ mol dm}^{-3}$ , in toluene at  $70 \text{ }^\circ\text{C}$ .

milar reactivity of DDMA and ODMA in free radical polymerization has been reported.<sup>21</sup>

The molecular weight and viscosity of copolymers (Tables II and III) also decrease with an increase of the Sty content in the feed, following the same order.

The course of copolymerizations in toluene solution to a high conversion for different monomer feed ratios, but at a constant total monomer concentration ( $0.5 \text{ mol dm}^{-3}$ ), is represented by integral time-conversion curves (Figure 4). The familiar pattern of the curves showed an increase in conversion as the whole fraction of DDMA or ODMA increased in the monomer mixture. Comparison of the examined copolymerization systems showed that a higher conversion was obtained with ODMA as a comonomer for the same reaction time, particularly at a lower Sty content in the monomer mixture.

#### *Properties of Copolymers*

The average molecular weight and intrinsic viscosity of copolymers obtained at a low conversion and at their constant concentration ( $c = 2.0 \text{ mol dm}^{-3}$ ) but different composition (Tables II and III) significantly decrease as

the styrene content in the monomer mixture, *e.g.* copolymer, increase (Figure 5). The results are in good correlation with the value of the initial reaction rates, since they also decreased as the styrene content in the monomer mixture increased. These measurements suggest that the propagation reaction rate is essentially reduced when styrene units are at the end of the propagation species, as it was also found for the copolymerization of styrene with other alkyl methacrylates, particularly with adamantyl methacrylate.<sup>22</sup>

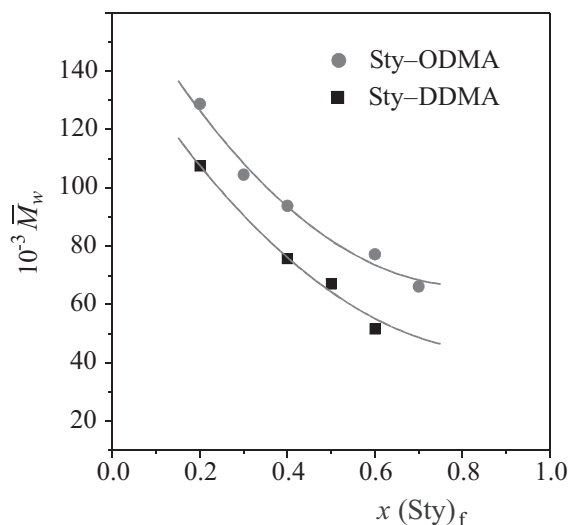


Figure 5. Dependence of weight average molecular weights ( $\bar{M}_w$ ) of styrene–dodecyl methacrylate (Sty–DDMA) and styrene–octadecyl methacrylate (Sty–ODMA) copolymers on the monomer mixture composition,  $x(\text{Sty})_f$  (data from Tables II and III).

The influence of the temperature on the intrinsic viscosity of the homo- and copolymers in toluene solution for the Sty–DDMA and Sty–ODMA are presented in Figures 6 and 7, respectively. Such measurements are directly related to the thickening power of polymer solutions at various temperatures, as one of the most important features of polymers used as viscosity index improvers.<sup>12</sup> The obtained results for both systems show that the viscosities slightly increased with the temperature for the alkyl methacrylate homopolymers and reached the local maximum value at a higher temperature, showing a constant value for the polystyrene whereas the copolymers fall intermediate between those of homopolymers. These results are in agreement with the findings that poly(alkyl methacrylates) showed increasing viscosity with the increase of temperature,<sup>23</sup> and that they are also average molecular weight dependant.

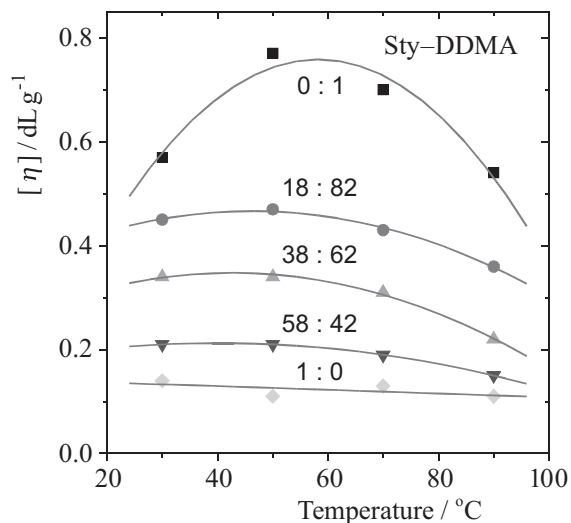


Figure 6. Temperature dependence of intrinsic viscosity ( $[\eta]$ ) at different copolymer compositions of styrene and dodecyl methacrylate (Sty-DDMA) in toluene solution.

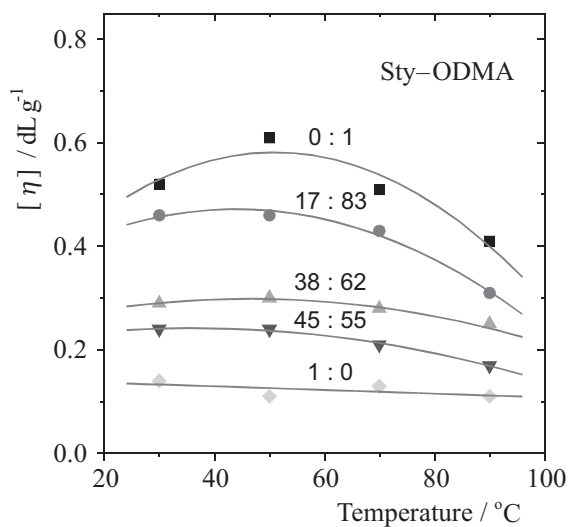


Figure 7. Temperature dependence of intrinsic viscosity ( $[\eta]$ ) at different copolymer compositions of styrene and octadecyl methacrylate (Sty-ODMA) in toluene solution.

The thermal stabilities of both types of copolymers were determined by means of thermogravimetric measurements recorded in a nitrogen atmosphere, and are presented in Figures 8 and 9. It is evident that both copoly-

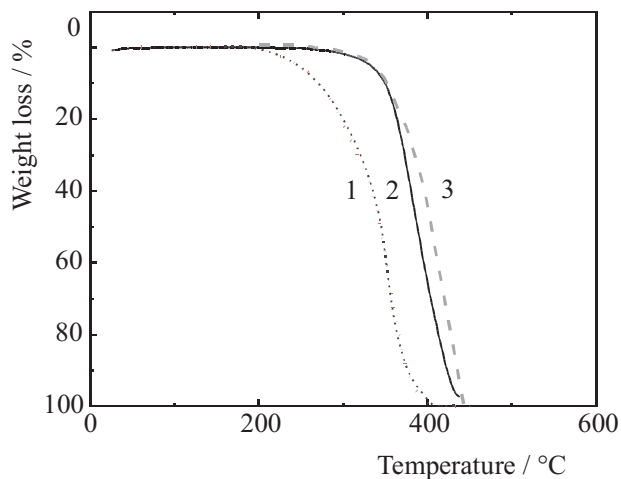


Figure 8. Thermogravimetric analysis of homopolymers of dodecyl methacrylate (1), styrene (3) and their copolymer (2) (Sty–DDMA = 0.52 : 0.48) in a nitrogen atmosphere.

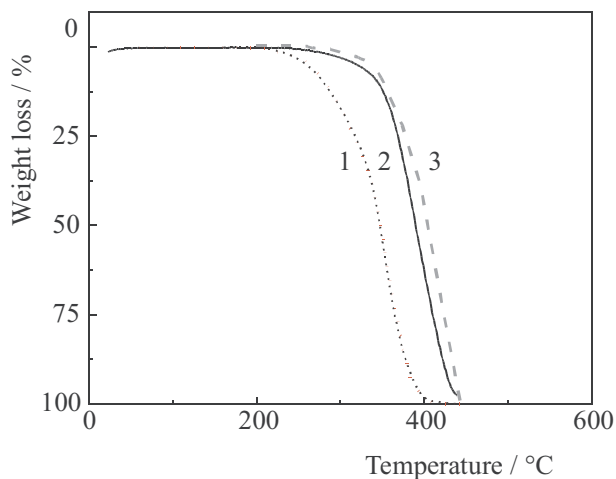


Figure 9. Thermogravimetric analysis of homopolymers of octadecyl methacrylate (1), styrene (3) and their copolymer (2) (Sty–ODMA = 0.52 : 0.48) in a nitrogen atmosphere.

mers decompose by a one-stage mechanism and that their thermal stability falls intermediate between those of methacrylate homopolymers and polystyrene. Sty–DDMA and Sty–ODMA copolymers are stable up to 200 °C and

then the weight loss with rapid decomposition at temperatures  $T_f = 248$  °C (Sty-ODMA) and 264 °C (Sty-DDMA) occurs. The total weight loss was observed at temperatures up to 450 °C. Similar behaviour was observed for the MMA-ODMA and MMA-DDMA copolymers.<sup>15,24</sup>

## CONCLUSION

Copolymerization of styrene and dodecyl methacrylate or octadecyl methacrylate proceeds readily in toluene solutions in the presence of free radical initiators. Similar values of the copolymerization reactivity ratio for both systems showed a marked tendency towards an ideal copolymerization reaction. The initial homopolymerization reaction rate was found to be in the order ODMA > DDMA > Sty whereas the rates of copolymerization reactions sharply decreased as the styrene fraction in the monomer mixture increased. The average molecular weight and the viscosity of the copolymers obtained also decreased with increasing the styrene content in the monomer mixture.

The viscosity of copolymers in toluene solution within a range of 30 to 90 °C slightly increased at the temperature showing a small local maximum, as the content of alkyl methacrylate in copolymer was increased. The thermal stability of copolymers was intermediate between that of less stable alkyl methacrylate homopolymers and more stable polystyrene.

## REFERENCES

1. A. Hamielec and T. Tobita, *Polymerization Processes*, in: *Ullman's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, Vol. A21, 1992, pp. 336–339.
2. D. Hill, G. George, P. Pomery, D. Rogers, and T. Carswell, *Polym. Mat. Sci. Eng.* **66** (1992) 297–298.
3. T. Otsu, T. Ito, and M. Imoto, *J. Polym. Sci. B* **3** (1965) 113–117.
4. M. Coote, M. Zammit, T. Davis, and G. Willett, *Macromolecules* **30** (1997) 8182–8190.
5. A. Kaim, *J. Macromol. Sci., Pure Appl. Chem.* **33** (1996) 1711–1722.
6. T. P. Davis, K. F. O'Driscoll, M. C. Piton, and M. A. Winnik, *Macromolecules* **23** (1990) 2113–2119.
7. T. Fukuda, Y. D. Ma, and H. Inagaki, *Macromolecules* **18** (1985) 17–26.
8. V. P. Budtov and B. V. Revnov, *Vysocamol. Soed. A* **36** (1994) 1061–1066.
9. M. Pitsikalis, E. Sigkali-Kioulafa, and N. Hadjichristidis, *Macromolecules* **33** (2000) 5460–5469.
10. R. M. Mortimer and S. Y. Orszulik (Eds.), *Chemistry and Technology of Lubricants*, 2nd ed., Chapman & Hall, London, 1997, pp. 144–180.
11. G. Ver Strate and M. J. Struglinski, in: D. N. Schulz and J. E. Glass (Eds.), *Polymers as Rheology Modifiers*, American Chemical Society, Washington, 1991, p. 256.

12. C. Neveu and F. Huby, *Lubr. Sci.* **1** (1988) 27–50.
13. M. Buback and C. Kovollik, *Macromol. Chem. Phys.* **200** (1999) 1764–1770.
14. Z. Janović, K. Sarić, and K. Sertić-Bionda, *Chem. Biochem. Eng. Q.* **12** (1998) 19–24.
15. I. K. Warma, M. Warma Nair, V. K. Karan, and D. S. Warma, *Thermochim. Acta* **142** (1989) 189–201.
16. M. Fineman and S. D. Ross, *J. Polymer Sci.* **5** (1950) 259–262.
17. T. Kelen and F. Tüdös, *J. Macromol. Sci., Chem. A* **9** (1975) 1–27.
18. R. Z. Greenley, *J. Macromol. Sci. Chem. A* **9** (1975) 505–516.
19. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Wiley-Interscience, New York, 1989, p. 153–266.
20. P. Wittmer, *Angew. Macromol. Chem.* **39** (1974) 35–57.
21. A. Matsumoto and K. Mizuta, *Polym. Bull.* **33** (1994) 141–148.
22. A. Matsumoto, S. Tanaka, and T. Otsu, *Macromolecules* **24** (1991) 4017–4024.
23. D. Lath, E. Lathova, and M. Bohdanecky, *Pet. Coal* **38** (1996) 34–36.
24. S. Agarwal, V. Choudhary, and K. Varma, *J. Appl. Polym. Sci.* **53** (1994) 1525–1531.

## SAŽETAK

### Kopolimerizacija i kopolimeri stirena s dodecil-metakrilatom i oktadecil-metakrilatom

*Elvira Vidović, Karla Sarić i Zvonimir Janović*

Proučavana je reakcija kopolimerizacije stirena (St) s dodecil-metakrilatom (DDMA) kao i s oktadecil-metakrilatom (ODMA) u otopini toluena uz 2,2'-azobis(isobutironitril) kao slobodno-radikalni inicijator, u širokom rasponu sastava i konverzije. Sastav kopolimera određen je <sup>1</sup>H NMR spektroskopijom. Utvrđene vrijednosti omjera kopolimerizacijske reaktivnosti metodom Kelen-Tüdös-a za niske konverzije iznose: St–DDMA:  $r_1 = 0,52$  (St) i  $r_2 = 0,42$  (DDMA), St–ODMA:  $r_1 = 0,58$  (St) i  $r_2 = 0,45$  (ODMA), pokazujući sklonost prema reakciji idealne kopolimerizacije. Izračunate su i  $Q$  i  $e$  vrijednosti za oba sustava. Početne brzine reakcije polimerizacije,  $R_p$ , nalaze se u poretku: ODMA > DDMA > St i za reakciju kopolimerizacije značajno se smanjuju s porastom St u monomernoj smjesi. Slično ponašanje nađeno je za vrijednosti molekulnih masa. Viskoznost polimernih otopina određena u toluenu pri 30–90 °C pokazuje za metakrilatne homopolimere stanovitu maksimalnu vrijednost, stalnu vrijednost za polistiren i srednje vrijednosti viskoznosti za kopolimere. Toplinska postojanost kopolimera određena metodom DTG raste s porastom udjela stirena.