

KINETIC STUDY OF FREE RADICAL COPOLYMERIZATION OF DODECYL METHACRYLATE AND STYRENE USING DIPEROXIDE INITIATOR

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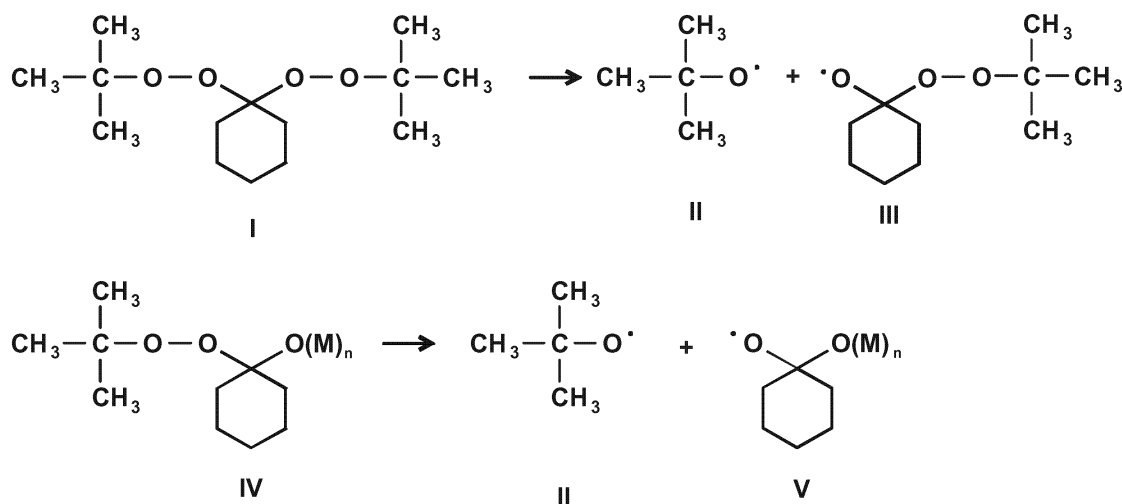
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In this study kinetics of the free radical copolymerization of styrene and dodecyl methacrylate in xylene solution using diperoxide initiator, up to high conversions, was investigated. Kinetic results and structural properties of the synthesized polymers were compared with values obtained for homopolymerization and copolymerization systems initiated with conventional monofunctional initiator. It was established that higher polymerization rates could be achieved by using diperoxide initiator while maintaining high values of molecular weight and a relatively narrow polydispersity index. However, in copolymerization systems with higher mole fractions of dodecyl methacrylate in initial feed, the fall of diperoxide initiator efficiency was observed.

1. INTRODUCTION

Free radical copolymerization is one of the most common and useful reaction mechanisms for making copolymers from two or more vinyl monomers (Moad and Solomon, 1996). Because of their operational simplicity and production adaptability in comparison with other reaction mechanisms, it has a very large industrial application (Tomašek *et al.*, 2005) and most of the synthetic polymeric materials with broad variety of applications are produced on such way (McGreavy, 1993). The main limitation of this mechanism is a small ability to influence on the molar mass distribution and structural properties of the synthesized copolymers (Hammouri *et al.*, 1999). From the free radical theory, it is well known that molecular weight is inversely proportional to the rate of polymerization (Odian, 2004). As such, it is not possible to simultaneously obtain high reaction rates and high polymer molecular weights for bulk, suspension and solution processes with a usage of a conventional monofunctional initiator (Scorah *et al.*, 2005). In recent studies, mostly for bulk homopolymerization of styrene (Choi *et al.*, 1987; Villalobos *et al.*, 1991; González *et al.*, 1996), it was shown that the solutions to these problems are initiators with two or more functional peroxide groups with different thermal stabilities (Gao *et al.*, 2004). They provide several advantages, such as production of high molecular weight polymers at high temperatures with well-defined structure and complete conversion of monomers. Besides, the reaction time can be significantly reduced and process can be performed by a simple, entirely batch routine (Prasad *et al.*, 2002). Such an effect is a consequence of the sequential decomposition of the second peroxide group during the polymerization reaction that allows repeated initiation (reinitiation) of the macromolecular species produced in the earlier stage of the process (Benbachir and Benjelloun, 2001). Decomposition mechanism of diperoxide initiator is presented at Scheme 1. In a first stage (I), two different primary radicals are formed - one similar to the monofunctional initiator (II) and the other is bearing undecomposed peroxide group (III). This unreacted peroxide group in polymers (IV) decomposes further and new radical species are generated (II, V) and distributed via elementary chain polymerization reactions (Asteasuain *et al.*, 2004). To our knowledge, most of the published results on diperoxide initiation are concerned with the kinetics of styrene bulk homopolymerization, whereas homo- and copolymerization of other monomers are only rarely investigated (Dhib *et al.*, 2000), particularly those including long-chain alkyl methacrylates such as dodecyl methacrylate. Methacrylate-based copolymers are one of the most efficient and most commonly used polymeric rheology modifiers, especially for lubricating mineral oils where they serve as viscosity index improvers and pour point depressants (Mortimer and Orsulik, 1997; Florea *et al.*, 1999). Mainly, they are copolymers of methacrylic acid esters with short, intermediate and/or long alkyl side groups (Jukić *et al.*, 2007).

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Scheme 1. Sequential decomposition of diperoxide initiator

As such, they need to fulfill certain requirements since viscosity, shear stability and pour point depression as main lubricating oil rheological properties are highly dependent on the structural properties of the applied copolymers. Recently, the styrene was used as a comonomer for modifying the poly(alkyl methacrylate) additive to increase its thermal and oxidation stability (Vidović *et al.*, 2002; Luca *et al.*, 1997; Jukić *et al.*, 2007). Besides, such copolymers should also be stable against shear rates developed in lubricating conditions. Based on the so-called Critical-Stress-to-Fracture (CSF) theory, it is well known that shear stability is higher when polymers of narrow molar mass distribution and low polydispersity index are applied (Schulz and Glass, 1991). In this work, copolymerization kinetics of styrene and dodecyl methacrylate in xylene solution using diperoxide initiator, up to high conversions, was investigated. The kinetic results and molar mass distribution of synthesized polymers were compared with values obtained for homo- and copolymerization systems initiated with monofunctional initiator. These results were gathered in order to obtain copolymers of defined composition and structure, responsive to their application as rheology modifiers for lubricating mineral oils.

2. EXPERIMENTAL

2.1 Materials

Polymerization grade monomers, styrene and dodecyl methacrylate (RohMax Chem.) were passed through a column of activated basic aluminium oxide (Aldrich) and purged with high-purity nitrogen prior to use. The initiators, monofunctional *tert*-butyl peroxy-2-ethylhexanoate (Trigonox 21[®], 70 wt. % solution, Akzo Chemie) and bifunctional 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (Trigonox 29[®], 90 wt. % solution, Akzo Chemie) were used as received, as well as the reagent grade solvents xylene, toluene and methanol. Initiator decomposition rate coefficients were given as temperature functions (Product Data Sheet, Akzonobel, 2006): $k_d / \text{s}^{-1} = 1.54 \times 10^{14} \exp [-124\,900 / (RT)]$ and $k_d / \text{s}^{-1} = 7.59 \times 10^{13} \exp [-127\,520 / (RT)]$ for monofunctional and bifunctional initiator, respectively.

2.2 Methods

Homopolymerizations and copolymerizations of styrene and dodecyl methacrylate were performed in 2 mol L⁻¹ xylene solution at constant concentration of the initiator (0.01 mol L⁻¹). Polymerization temperatures were 91 °C and 105 °C for reactions initiated with Trigonox 21[®], and 105 °C and 115 °C for reactions initiated with Trigonox 29[®]. The experiments were carried out in double jacket glass reactor (0.25 L) connected to thermostated bath, equipped with a mechanical stirrer (200 rpm) and nitrogen inlet and outlet. Reaction

mixture samples were taken directly from reactor and polymer was isolated by precipitation in excess of methanol; final conversions were determined gravimetrically. Weight-average molecular weight (M_w) and number-average molecular weight (M_n) were determined at room temperature using GPC-20 Polymer Laboratories size exclusion chromatograph. Measurements were performed in toluene as an eluent with a flow of 1.0 mL min^{-1} and the calibration curve was based on polystyrene standards (EasyCal PS-1B, 580-2,560,000 g mol^{-1}) with narrow distribution.

3. RESULTS AND DISCUSSION

3.1 Copolymerization kinetics

The free radical (co)polymerizations of styrene (ST) and dodecyl methacrylate (DDMA) were performed in xylene solutions using bifunctional initiator 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane and monofunctional initiator *tert*-butyl peroxy-2-ethyl-hexanoate. In order to study the effect of diperoxide initiator on comonomer feed, experiments were completed with 100-0 mol. %, 75-25 mol. %, 50-50 mol. %, 25-75 mol. % and 0-100 mol. % mixtures of styrene and dodecyl methacrylate initiated with mono- at 91°C and 105°C and diperoxide initiator at 105°C and 115°C . Reaction temperatures, 91°C for monoperoxide and 105°C for diperoxide are chosen to confirm the initiators half-lives ($t_{1/2}$) of approximately 60 min. In order to investigate temperature influence on initiator decomposition rate, additional study was made for ST-DDMA copolymerization system and experiments were performed at higher temperatures; 105°C for monoperoxide and 115°C for diperoxide. Those temperatures correspond to the initiator half-lives of around 20 min. Based on simulation data that presents initiator concentration (c_i) as a function of reaction time (t_p) at different temperatures (Fig 1), it can be observed that both initiator types decompose faster at higher temperatures. Also, concentration curves are quite similar and comparable. Calculation was performed by using chemical process simulation software ChemCAD i.e. its integrated module CC-Polymer.

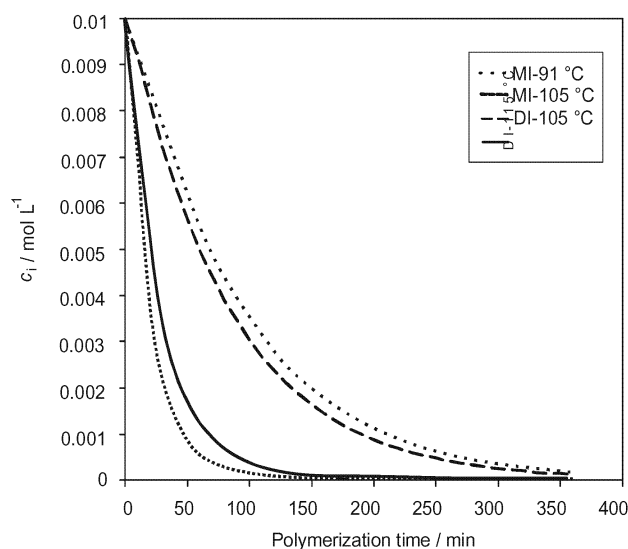


Figure 1. Initiator concentration (c_i) as a function of polymerization time (t_p) at two different temperatures for both initiated systems (simulation data); MI – monofunctional initiator, DI – diperoxide initiator.

For solution homopolymerization of styrene when both initiators are employed at identical concentration, it can be observed that with a usage of diperoxide initiator, a higher rate of polymerization and higher monomer conversion were achieved in comparison with results obtained with conventional monofunctional initiator

(Fig 2). These benefits are the consequence of the sequential decomposition of the second peroxide group during the polymerization reaction that allows repeated initiation (*reinitiation*) of the macromolecular species produced in the earlier stage of the process. Also, it can be observed that the temperature influence is more pronounced in system initiated with mono- than with diperoxide initiator.

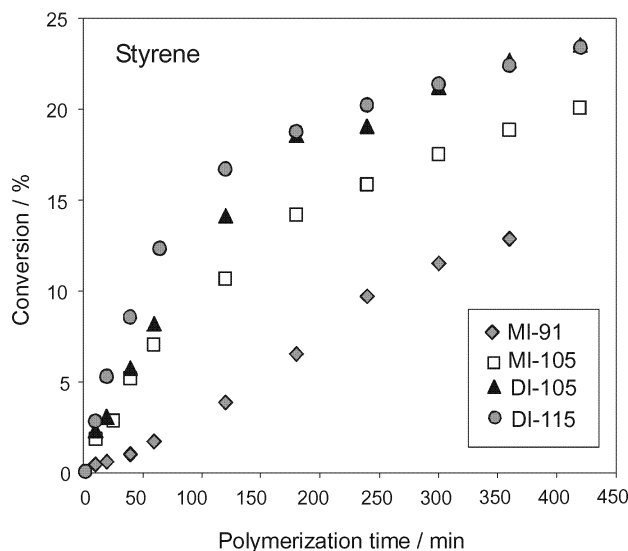


Figure 2. Monomer conversion as a function of time for homopolymerization of styrene with mono- at 91 °C and 105 °C and diperoxide initiator at 105 °C and 115 °C.

Results obtained for ST / DDMA copolymerization system with 75 mol. % of styrene demonstrate also the advantages of using diperoxide initiator over monoperoxide by obtaining higher rate of polymerization and higher monomer conversion (Fig 3). Only, temperature influence on the overall rate of polymerization in system initiated with monoperoxide is a less evident than in the previous.

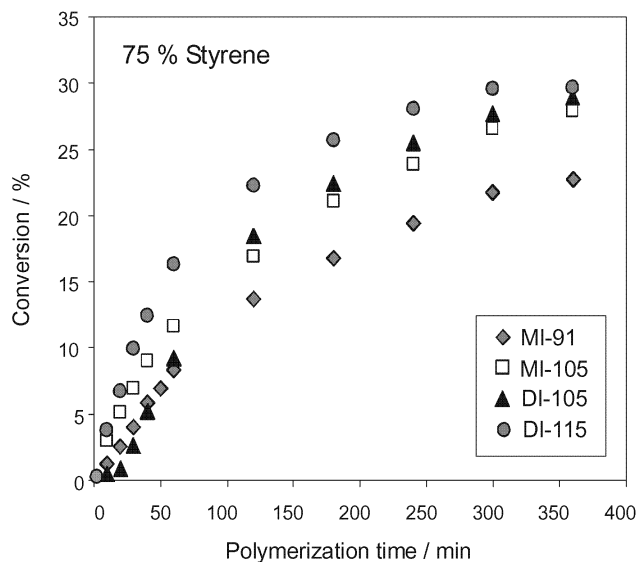


Figure 3. Monomer conversion as a function of time for copolymerization of styrene (75 mol. %) and dodecyl methacrylate (25 mol. %) with mono- at 91 °C and 105 °C and diperoxide initiator at 105 °C and 115 °C.

For ST-DDMA copolymerization system with 50 mol. % of styrene, it was observed that, in a first hour of the copolymerization reaction, accomplished monomer conversion was 17.7 % with the usage of bifunctional initiator at 105 °C which is much higher than 1.3 % achieved with the monofunctional initiator at 91 °C. This low efficiency of the monoperoxide initiator in the first hour of the copolymerization reaction can be explained by the phenomena known in the free radical theory as “cage effect” when the primary radicals are surrounded by a “cage” of solvent and monomer molecules through which they must diffuse to escape from the cage (Hamielec *et al.*, 1992). Also, the temperature influence on overall reaction rate is more pronounced in systems initiated with monofunctional peroxide initiator. Monomer conversion accomplished for this copolymerization system in a first hour of the reaction with monofunctional initiator at 105 °C was 17.1 % and with bifunctional initiator at 115 °C was 27.9 % (Fig 4).

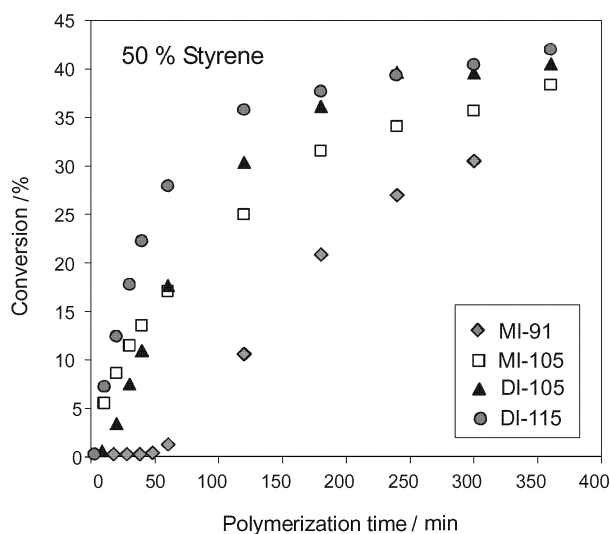


Figure 4. Monomer conversion as a function of time for copolymerization of styrene (50 mol. %) and dodecyl methacrylate (50 mol. %) with mono- at 91 °C and 105 °C and diperoxide initiator at 105 °C and 115 °C.

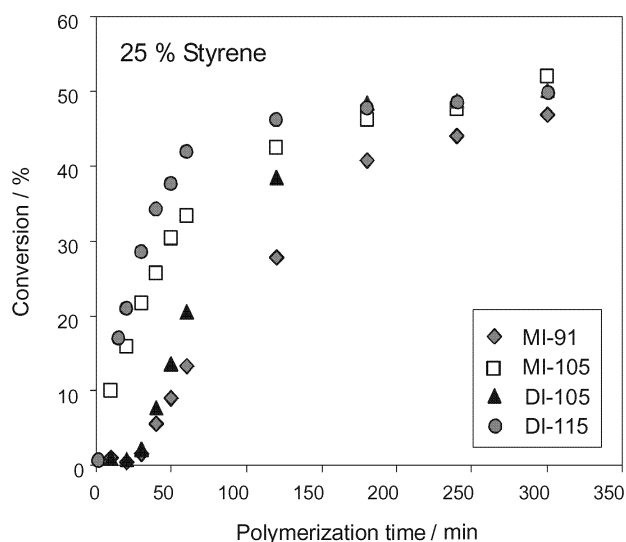


Figure 5. Monomer conversion as a function of time for copolymerization of styrene (25 mol. %) and dodecyl methacrylate (75 mol. %) with mono- at 91 °C and 105 °C and diperoxide initiator at 105 °C and 115 °C.

In copolymerization system with 25 mol. % of styrene, in a first hour of the copolymerization reaction, the low efficiency of both, monofunctionally at 91 °C and bifunctionally at 105 °C initiated systems, was observed. Also, differences between accomplished kinetics results in both cases are very small (Fig 5).

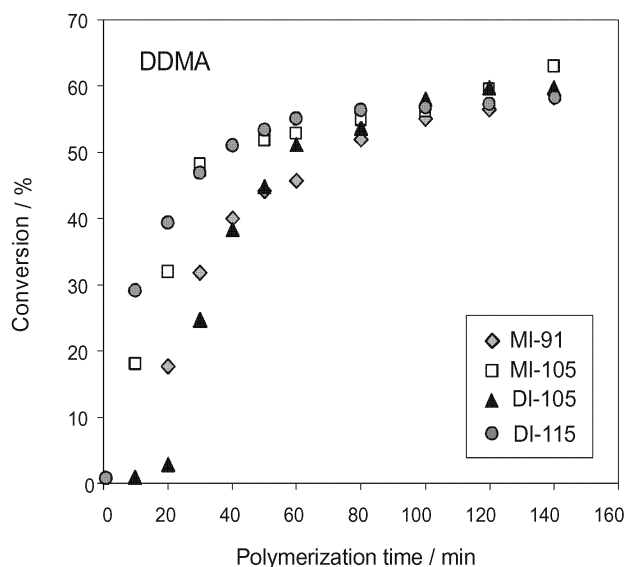


Figure 6. Monomer conversion as a function of time for homopolymerization of dodecyl methacrylate with mono- at 91 °C and 105 °C and diperoxide initiator at 105 °C and 115 °C.

The benefits accomplished with the usage of diperoxide initiator for styrene homopolymerization have not been observed for the homopolymerization of dodecyl methacrylate (Fig 6). Almost the same polymerization rates and final conversions were achieved in both cases. This fall of diperoxide initiator efficiency in the systems with higher content of dodecyl methacrylate can be explained by the increase of overall reaction rate in those systems due to higher propagation rates in long-chain alkyl methacrylate systems that have a direct influence on polymerization mechanism (Buback *et al.*, 2007; Šoljić *et al.*, 2008; Šoljić *et al.*, 2009). On this circumstances the sequential decomposition of the second peroxide group that usually generates initiator radicals continuously during the polymerization reaction, does not have notable impact. Also, varying results between two monomers can be explained by their different modes of termination. Styrene experiences termination by combination almost exclusively over a wide range of temperatures. For methacrylate monomers, the combination and disproportionation both occurs at low reaction temperatures, but disproportionation becomes predominant mode at high temperatures (Hamielec *et al.*, 1992).

3.2 Molar mass distribution

Molar mass distributions of synthesized copolymers selected at final conversion were determined by the size exclusion chromatography. The obtained weight-average molecular weight (M_w), number-average (M_n) molecular weight and polydispersity index ($PI = M_w / M_n$) values are given in Table 1. It can be observed that with the increase of mole fraction of dodecyl methacrylate in initial feed mixture, M_w and M_n increases. High values of weight-average molecular weights are required for the application of these copolymers as viscosity index improvers for lubricating oils. In spite of the higher reaction temperatures in bifunctionally initiated systems, average molecular weight results are not significantly different to those obtained when monofunctional initiator is used. Also, at higher conversions and with increase of mole fraction of dodecyl methacrylate in the feed, it was found that bifunctional initiator produced copolymers with somewhat broader molar mass distribution.

Table 1: Effect of monomer mixture composition, $x(\text{ST})$, initiator functionality (*monofunctional, **bifunctional), reaction temperature, T , and polymerization time, t_p , on monomer conversion, X , and structural properties of synthesized polymers: weight-average molecular weight, M_w , number-average molecular weight, M_n , and polydispersity index, PI , for the copolymerization of styrene and dodecyl methacrylate in xylene solution.

System: ST / DDMA	Initiator functionality	$T / ^\circ\text{C}$	t_p / min	$X / \%$	$M_w / \text{kg mol}^{-1}$	$M_n / \text{kg mol}^{-1}$	PI
$x(\text{ST}) = 100 \%$	*mono	91	360	12.9	42.72	22.01	1.94
	*mono	105	420	20.1	35.27	19.49	1.81
	**bi	105	420	23.6	30.23	13.66	2.21
	**bi	115	420	23.5	28.75	14.41	1.99
$x(\text{ST}) = 75 \%$	*mono	91	300	21.8	55.93	33.13	1.69
	*mono	105	360	27.9	57.91	34.70	1.67
	**bi	105	360	28.9	64.35	32.64	1.97
	**bi	115	360	29.7	55.56	29.55	1.88
$x(\text{ST}) = 50 \%$	*mono	91	300	30.5	113.98	55.66	2.05
	*mono	105	360	38.4	98.20	48.08	2.04
	**bi	105	360	40.5	107.78	43.95	2.45
	**bi	115	360	41.9	82.42	33.59	2.45
$x(\text{ST}) = 25 \%$	*mono	91	300	46.8	183.53	89.91	2.04
	*mono	105	300	52.0	140.63	76.30	1.84
	**bi	105	300	50.2	251.89	98.13	2.56
	**bi	115	300	49.9	139.09	69.08	2.01
$x(\text{ST}) = 0 \%$	*mono	91	140	57.8	367.33	140.05	2.62
	*mono	105	140	62.9	201.76	80.16	2.51
	**bi	105	140	59.8	385.63	126.15	3.05
	**bi	115	140	58.1	227.03	66.50	3.41

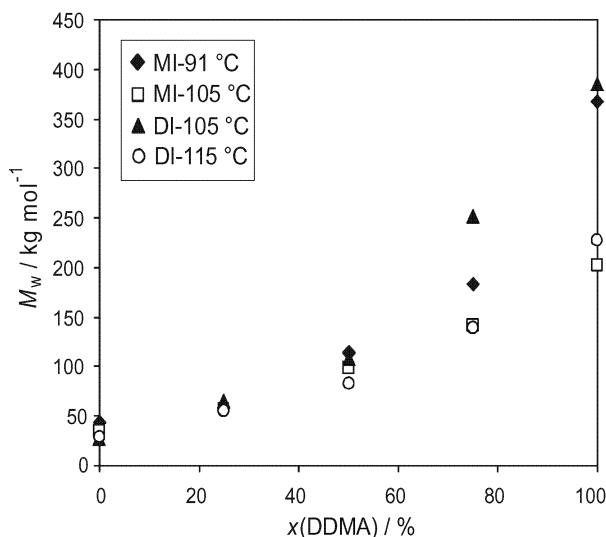


Figure 7. Weight-average molecular weight values (M_w) as a function of mole fraction of dodecyl methacrylate in the initial monomer feed.

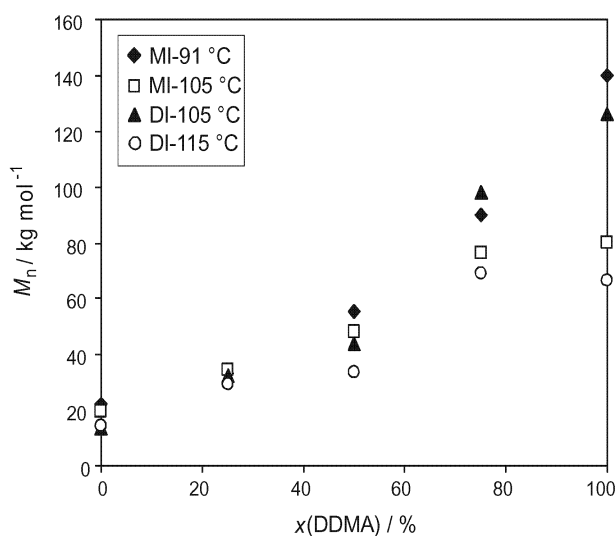


Figure 8. Number-average molecular weight values (M_n) as a function of mole fraction of dodecyl methacrylate in the initial monomer feed.

From the weight-average (M_w) and number-average (M_n) molecular weight values at final conversion as a function of mole fraction of dodecyl methacrylate in the initial feed, it can be observed that with increase of the content of DDMA in the feed mixture, M_w and M_n slightly increases up to 50 mol. % of DDMA and afterwards rise up sharply (Fig 7). Also, with increase of temperature, M_w and M_n slightly decrease in both cases (Fig 8).

Therefore, with the usage of bifunctional initiator the higher polymerization rates can be achieved while maintaining high values of molecular weights and similar polydispersity index values. This enables an increase of productivity through modification of manufacturing process of well-defined polymeric additives for lubricating mineral oils.

4. CONCLUSION

The kinetics of the free radical homopolymerization and copolymerization of styrene and dodecyl methacrylate in xylene solution using bifunctional peroxide initiator, up to high conversions, were investigated. The results were compared with the same copolymerization systems initiated with monofunctional initiator.

It was established that higher polymerization rates can be achieved by using bifunctional initiator while maintaining high values of molecular weight and a relatively low polydispersity index values. However, these advantages of using bifunctional initiators can only be achieved for homopolymerization of styrene and copolymerization systems with 25 and 50 % mole fractions of dodecyl methacrylate in the feed. For the copolymerization systems with 75 and 100 % mole fractions of dodecyl methacrylate this benefits have not been observed; almost the same polymerization rates and final conversions were achieved in both cases. This fall of diperoxide initiator efficiency in copolymerization systems with higher mole fractions of dodecyl methacrylate can be explained by the increase of reaction rates and reduction of copolymerization time, when the sequential decomposition of second peroxide group, i.e. reinitiation, does not have notable impact in copolymerization mechanism.

5. REFERENCES

- Moad G., Solomon D. H. (1996). *The Chemistry of Free Radical Polymerization*, Elsevier Science Inc., New York
- Tomašek Lj., Jukić A., Janović Z. (2005). *Acta Chim. Slov.*, 52, 3, 224
- McGreavy C. (1993). *Polymer Reaction Engineering*, Chapman & Hall, New York
- Hammouri H., McKenna T. F., Othman S. (1999). *Ind. Eng. Chem. Res.*, 38, 12, 4815
- Odian G., 2004, *Principles of Polymerization*, Wiley, New York
- Scorah M. J., Dhib R., Penlidis A. (2005). *J. Macromol. Sci. Part A*, 42, 4, 403
- Choi K. Y., Lei G. D. (1987). *AIChE J.* 33, 12, 2067
- Villalobos M. A., Hamielec A. E., Wood P. E. (1991). *J. Appl. Polym. Sci.*, 42, 4, 629
- González I. M., Meira G. R., Oliva H. M. (1996). *J. Appl. Polym. Sci.*, 59, 7, 1015
- Cavin L., Rouge A., Meyer T., Renken A. (2000). *Polymer*, 41, 11, 3925
- Gao J., Hungenberg K. D., Penlidis A. (2004). *Macromol. Symp.*, 206, 1, 509
- Prasad V., Schley M., Russo L. P., Bequette B. W. (2002). *J. Process Control*, 12, 3, 353
- Benbachir M., Benjelloun D. (2001). *Polymer*, 42, 18, 7727
- Asteasuain M., Brandolin A., Sarmoria C. (2004). *Polymer*, 45, 1, 321
- Dhib R., Gao J., Penlidis A. (2000). *Polym. React. Eng.*, 8, 4, 299
- Mortimer R.M. and Orszulik S.Y. (1997). *Chemistry and Technology of Lubricants*, Chapman & Hall, London
- Florea M., Catrinoiu D., Luca P., Balliu S. (1999). *Lubr. Sci.*, 12, 1, 31
- Jukić A., Vidović E., Janović Z. (2007). *Chem. Technol. Fuels & Oils*, 43, 5, 386
- Vidović E., Sarić K., Janović Z. (2002). *Croat. Chem. Acta*, 75, 3, 769
- Luca P., Florea M., Balliu S., Catrinoiu D. (1997) *J. Balkan Trib. Assoc.*, 3, 2, 120
- Jukić A., Rogošić M., Vidović E., Janović Z. (2007). *Polym. Int.*, 56, 1, 112
- Schulz D. N., Glass E.J. (1991). *Polymers as Rheology Modifiers*, American Chemical Society, Washington DC
- Product Data Sheet: Trigonox[®] 21, Trigonox[®] 29, www.akzonobel-polymer-chemicals.com, March 2006.
- Hamielec A. E., Tobita, H., Gerrens H. (1992). *Ullmann's Encyclopedia of Industrial Chemistry: Polymerization processes*, VCH Publishers, New York
- Buback M., Muller E. (2007). *Macromol. Chem. Phys.*, 208, 6, 581
- Šoljić I., Jukić A., Janović Z. (2008). *Polimeri*, 29, 1, 21
- Šoljić I., Jukić A., Janović Z. (2009). *Polym. Int.*, 58, 9, 1014

