

Kinetic study of free radical copolymerization of dodecyl methacrylate and styrene using diperoxide initiator

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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 can 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 the most commonly used method for the synthesis and production of the synthetic polymeric materials [1] with broad variety of applications. From the free radical theory, it is well known that molecular weight is inversely proportional to the rate of polymerization [2]. 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 [3]. In recent studies, mostly for bulk homopolymerization of styrene [4-7], it was shown that the solutions to these problems are initiators with two or more functional peroxide groups with different thermal stabilities [8]. They provide several advantages, such as production of high molecular weight polymers at high temperatures with well-defined structure and complete conversion of monomers. Beside, the reaction time can be significantly reduced and process can be performed by a simple, entirely batch routine [9]. 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 [10]. To our knowledge, most of the published results on diperoxide initiation are concerned with the kinetics of styrene bulk homopolymerization, whereas homo- and copolymerizations of other monomers are only rarely investigated [11], particularly those including long-chain alkyl methacrylates such as dodecyl methacrylate. 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 structural properties 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, where they serve as viscosity index improvers and pour point depressants [12,13].

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 [14]: $k_d / s^{-1} = 1.54 \times 10^{14} \exp [-124\,900 / (RT)]$ and $k_d / s^{-1} = 7.59 \times 10^{13} \exp [-127\,520 / (RT)]$ 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 initiators (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 and number-average molecular weight 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 diperoxide initiator 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane and monofunctional initiator *tert*-butyl peroxy-2-ethylhexanoate. 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 (ST) and dodecyl methacrylate (DDMA) initiated with mono- at 91 and 105 °C and diperoxide initiator at 105 and 115 °C (Figs 1-4). Copolymerization reactions were carried out at exact temperatures chosen to conform to the initiators half-lives of one hour.

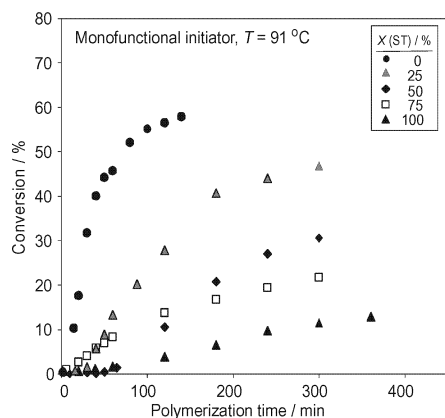


Figure 1. The effect of monomer mixture composition on conversion in the copolymerization of styrene and dodecyl methacrylate using monofunctional initiator Trigonox 21[®] in xylene solution at 91 °C.

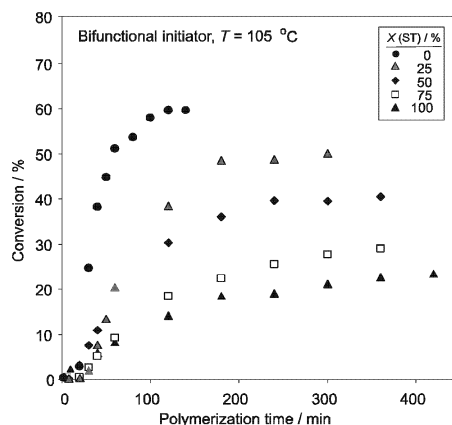


Figure 2. The effect of monomer mixture composition on conversion in the copolymerization of styrene and dodecyl methacrylate using bifunctional initiator Trigonox 29[®] in xylene solution at 105 °C.

In all the copolymerization experiments, when both initiators are employed at identical concentrations, it was observed that with a usage of diperoxide initiator a higher rate of polymerization and higher monomer conversions were achieved in comparison with results obtained by using conventional monofunctional initiator. For copolymerization system with 50 mol. % of styrene (Figs. 1 and 2), it was observed that, in a first hour of the copolymerization reaction, accomplished monomer conversion was 27.9 % with the usage of bifunctional initiator at 105 °C which is much higher than 1.3 % achieved with the monofunctional initiator at 91 °C. Also, the temperature influence on overall reaction rate is more pronounced in systems initiated with monofunctional peroxide initiator. Monomer conversion accomplished for the same copolymerization system in a first hour of the reaction with monofunctional initiator at 105 °C was 17.0 % and with bifunctional initiator at 115 °C was 17.7 % (Figs 3 and 4).

The benefits accomplished with the usage of diperoxide initiator for styrene homopolymerization have not been observed for the homopolymerization of dodecyl methacrylate. The similar was for the copolymerization systems with the high contents of dodecyl methacrylate. Almost the same polymerization rates and final conversions were achieved in both cases. This fall of diperoxide initiator efficiency can be explained by the increase of overall reaction rates in those systems due to higher propagation rates in long-chain alkyl methacrylate systems that have a direct influence on polymerization mechanism. On this circumstances the sequential decomposition of the second peroxide group which usually generates initiator radicals continuously during the polymerization reaction, does not have notable impact.

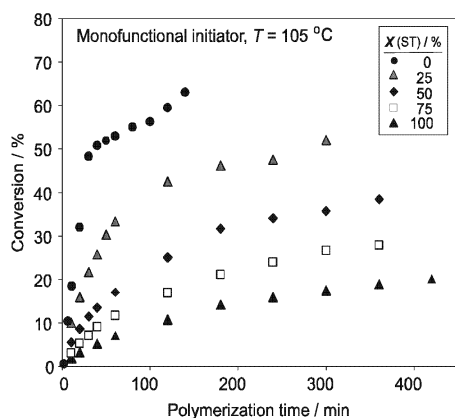


Figure 3. The effect of monomer mixture composition on conversion in the copolymerization of styrene and dodecyl methacrylate using monofunctional initiator Trigonox 21[®] in xylene solution at 105 °C.

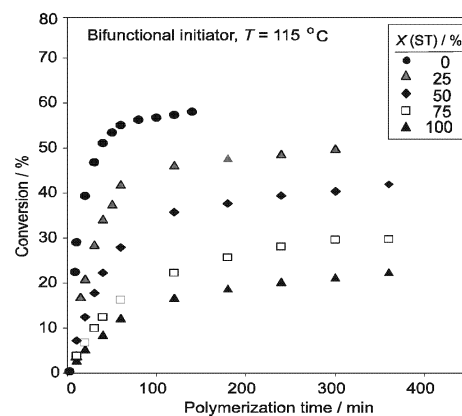


Figure 4. The effect of monomer mixture composition on conversion in the copolymerization of styrene and dodecyl methacrylate using bifunctional initiator Trigonox 29[®] in xylene solution at 115 °C.

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 [15].

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) values are given in Table 1. It can be observed that with increase of mole fraction of dodecyl methacrylate in initial feed mixture, M_n and M_w increases. High values of weight-average molecular weights are required for the application of these copolymers as rheology modifiers in 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. However, 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.

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

System: ST / DDMA	Initiator functionality	$T / ^\circ C$	t_p / min	$X / \%$	$M_n /$ kg mol^{-1}	$M_w /$ kg mol^{-1}	PI
$x(ST) = 100 \%$	*(mono)	91	360	12.90	22.01	42.72	1.94
	*(mono)	105	420	20.06	19.49	35.27	1.81
	** (bi)	105	420	23.55	13.66	30.23	2.21
	** (bi)	115	420	23.51	14.41	28.75	1.99
$x(ST) = 75 \%$	*(mono)	91	300	21.78	33.13	55.93	1.69
	*(mono)	105	360	27.88	34.70	57.91	1.67
	** (bi)	105	360	28.95	32.64	64.35	1.97
	** (bi)	115	360	29.69	29.55	55.56	1.88
$x(ST) = 50 \%$	*(mono)	91	300	30.53	55.66	113.98	2.05
	*(mono)	105	360	38.36	48.08	98.20	2.04
	** (bi)	105	360	40.53	43.95	107.78	2.45
	** (bi)	115	360	41.95	33.59	82.42	2.45
$x(ST) = 25 \%$	*(mono)	91	300	46.84	89.91	183.53	2.04
	*(mono)	105	300	52.02	76.30	140.63	1.84
	** (bi)	105	300	50.16	98.13	251.89	2.56
	** (bi)	115	300	49.91	69.08	139.09	2.01
$x(ST) = 0 \%$	*(mono)	91	140	57.84	140.05	367.33	2.62
	*(mono)	105	140	62.99	80.16	201.76	2.51
	** (bi)	105	140	59.75	126.15	385.63	3.05
	** (bi)	115	140	58.06	66.50	227.03	3.41

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.

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