Scientific Paper

Copolymerization of Methyl Methacrylate and Dodecyl Methacrylate Initiated by Bifunctional Peroxide[†]

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[†] Dedicated to the memory of Prof. Dr. Tatjana Malavašič

Abstract

This paper deals with the kinetic study of methyl methacrylate (MMA) and dodecyl methacrylate (DDMA) free radical polymerization initiated with the bifunctional initiator 1,1-di(tert-butylperoxy)cyclohexane (BPCH). The reactions were carried out in xylene solution up to high conversions in an isothermal reaction calorimeter. The results were compared with values obtained by using dibenzoyl peroxide as a conventional monofunctional initiator. The influence of monomer mixture composition and initiator functionality on initial reaction rate, conversion and polymer molecular mass distribution was described and discussed. The polymerization rate was found to be in the order: DDMA > DDMA/MMA > MMA for both type of initiators, with significantly higher values obtained by using BPCH. It was established that in polymerizations initiated with BPCH high reaction rates and high polymer molecular masses were achieved simultaneously. As a result, the short-cycle reactions with reduction in polymerization time of up to 50% were accomplished with the bifunctional initiator at appropriate polymerization temperature.

Key words: methyl methacrylate, dodecyl methacrylate, bifunctional peroxide initiator, polymerization, kinetics

Introduction

Most of the synthetic polymeric materials are produced by the free radical initiated polymerization; however, due to the nature of its mechanism it is not possible to simultaneously obtain high polymerization rates and high molecular mass in bulk, suspension or solution processes.[1] Recently, it was shown that in the bulk polymerization of styrene this problem can be overcome by using initiators with two peroxide groups of different thermal stabilities.[2–7] Such initiators undergo a sequential decomposition, which generates primary radicals continuously as polymerization proceeds, giving simultaneously, at suitable reaction conditions, high monomer conversion, high molecular mass and narrower molecular mass distribution. Due to these advantages, the polymerization reaction time can be reduced significantly with no need for any modification of reactor equipment.[8] However, most of the published results on bifunctional peroxide initiation are concerned with the kinetics of styrene bulk homopolymerization.[2–8] In few cases methyl methacrylate homopolymerization was studied,[2,9] whereas homopolymerization of dodecyl methacrylate or its copolymerization with methyl methacrylate using bifunctional initiators have not been reported so far.

Methacrylate copolymers of controlled molecular architecture have attracted continuous attention because they have found important applications, such as rheology modifiers for liquids, particularly as viscosity improvers for lubricating mineral oils.[10,11] Usually, they are copolymers of methacrylic acid esters with short, intermediate and long alkyl side groups. Because these monomers showed very similar copolymerization reactivity ratios,[12] a noticeable tendency towards ideal copolymerization reaction giving homogeneous copolymer composition in all ranges of conversion was found. Such polymers, besides exhibiting high solution viscosities, should also be stable against high shear rates developed in lubricating conditions. Moreover, for the equal polymer molecular mass, the shear stability is higher when a polymer of a narrower molecular mass distribution is applied.[13]

In this paper, the reaction kinetics of methyl methacrylate and dodecyl methacrylate free radical homo- and co-polymerization in xylene solution using the bifunctional initiator 1,1-di(tert-butylperoxy)cyclohexane was investigated up to high conversions. The kinetic results and structural properties of obtained polymers are discussed and compared with the values obtained by using dibenzoyl peroxide as a conventional monofunctional initiator.

Experimental

Materials

Methyl methacrylate (MMA) and dodecyl methacrylate (DDMA) (RohMax Chem. Co.) monomers were freed from polymerization inhibitor by washing with 5% (w/v) aqueous sodium hydroxide solution followed by several washing with water. Further, monomers were dried over anhydrous sodium sulfate and distilled under nitrogen atmosphere at reduced pressure before use. Benzoyl peroxide (BPO) (Lucidol, Akzo Nobel) was purified by repeated crystallization from methanol. 1,1-Di(tert-butylperoxy)cyclohexane (BPCH) (Trigonox 22, Akzo Nobel) and solvents were used as received. The initiator half-lives, $t_{1/2}$, in xylene solution have been established by a differential scanning calorimeter,[14] Perkin Elmer DSC-7; for bifunctional BPCH $t_{1/2}$ = 1 h at 113 °C whereas for BPO $t_{1/2}$ = 1 h at 92 °C. The obtained values are in good agreement with literature data.[15]

Methods

Polymerizations of methyl methacrylate and dodecyl methacrylate were performed in xylene solution at constant total monomer concentration of 2 molL^{-1} using benzoyl peroxide or 1,1-di(tert-butylperoxy)cyclohexane initiator in concentration of 1 mmol L^{-1}. Polymerization temperature was 95 °C for reactions initiated with BPO, and 115 °C for reactions initiated with BPCH. In all polymerizations reaction volume was 1 L and reaction mixture was stirred at 400 rpm. Reaction mixture samples were taken directly from reactor and polymer was isolated by precipitation in methanol. The vacuum dried samples were dissolved in tetrahydrofurane (THF) and their molecular mass distributions were determined at room temperature using a GPC-20 Polymer Laboratories size exclusion chromatograph and polystyrene samples of narrow polydispersity. The eluent was THF with a flow rate of 1.0 mL min^{-1}.

Polymerization processes were carried out in a Mettler RC1 reaction calorimeter composed of reactor vessel, thermostat and computer units. Four calibrations were made during each experiment in order to calculate the overall heat transfer; two at room temperature, before and after the reaction, and two at reaction temperature, before and after the reaction. At the end of polymerization experiments monomer conversions were determined gravimetrically.

Conversion of the monomer at any polymerization time can be calculated according to equation:[16]

$$X(t) = \frac{\int_{t_0}^{t} \dot{Q}_{\mathrm{chem}}\,\mathrm{d}\,t}{\int_{t_0}^{t_{\mathrm{end}}} \dot{Q}_{\mathrm{chem}}\,\mathrm{d}\,t} \qquad (1)$$

where $X(t)$ is the relative calorimetric conversion. The integral in the numerator is the partial heat of reaction evolved at time t , and the integral in the denominator is the total heat of reaction at the end of polymerization. As one can see, for $t=t_{\mathrm{end}}$, $X(t)$ will be equal to one, which is not likely to be the true for final conversion in solution polymerizations. Thus, to obtain a real calorimetric conversion at any time, $X_{\mathrm{r}}(t)$, it is simply necessary to multiply the relative conversion values given by calorimeter with the value of final monomer conversion, X_{f} , determined by an independent measurement (e.g., gravimetry):

$$X_{\mathrm{r}}(t) = \frac{\int_{t_0}^{t} \dot{Q}_{\mathrm{chem}}\,\mathrm{d}t}{\int_{t_0}^{t_{\mathrm{end}}} \dot{Q}_{\mathrm{chem}}\,\mathrm{d}t} X_{\mathrm{f}} \qquad (2)$$

Furthermore, overall polymerization rate can be also calculated by:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{\dot{Q}_{\mathrm{chem}}}{\int_{t_0}^{t_{\mathrm{end}}} \dot{Q}_{\mathrm{chem}}} \qquad (3)$$

In the all expressions mentioned, it was assumed that the heat of polymerization was linearly dependent on the conversion.

Results and discussion

The free radical polymerization of methyl methacrylate and dodecyl methacrylate was performed in xylene solutions using the bifunctional initiator 1,1-di(tert-butylperoxy) cyclohexane and benzoyl peroxide as the conventional monofunctional initiator. The symmetrical bifunctional initiators like BPCH considered in this study possess two functional peroxide groups of equal thermal stability and show sequential decomposition kinetics. At first, two different primary radicals are formed (Chart 1) – one similar to the monofunctional initiator (II) and the other bearing undecomposed peroxide (III):

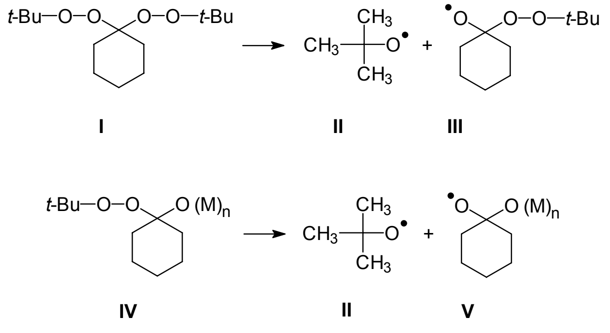

Chart 1

Since the unreacted peroxide group in polymers formed in the early stages of polymerization (IV) decompose further, new radical species are generated (II, V) and distributed via elementary chain polymerization reactions. This multiple reiniciation, propagation and termination phenomenon is responsible for the possibility of achieving simultaneously both high reaction rate and high polymer molecular mass.[2–8]

The rate of polymerization of MMA and DDMA using monofunctional and bifunctional peroxide initiator was studied by isothermal reaction calorimetry as it was described in the experimental part. This method has been proven to be very convenient and realizable for the determination of kinetic and thermodynamic data, as well as in the development, scale-up, optimization and safety studies of polymerization reactions and chemical processes.[17–20] Besides homopolymerizations, two different copolymerizations with monomer mixture compositions of the molar ratios of MMA/DDMA = 0.3/0.7 and 0.7/0.3 were examined. Polymerization reactions were carried out at temperatures chosen to conform to the initiator half-life of approximately one hour, a usual condition in the free radical polymerizations; namely, at 95 °C with BPO and 115 °C when BPCH was used as initiator. The conversion versus reaction time relationships established by reaction calorimetry measurements are shown in Figure 1. and Figure 2. Both monofunctionally initiated systems and bifunctionally initiated ones show common pattern of the curves with an increase of conversion (at equal reaction times) as the molar fraction of DDMA in the monomer mixture increases. It was established in a number of pulsed-laser polymerization studies that propagation rate coefficient (k_p) of *n*-alkyl methacrylates increases with ester chain length.[21–23] Therefore, the k_p of DDMA is much higher than for MMA, leading to the higher overall polymerization rate. Hence, alkyl methacrylate monomer reactivity has the following order:

DDMA > DDMA/MMA (0.7/0.3) > DDMA/MMA (0.3/0.7) > MMA

The effect of monomer mixture composition on reaction rate is presented in Figures 3. and 4., for monofunctionally and bifunctionally initiated polymerization systems, respectively. All the curves show an initial sharp increase of reaction rate; eventually it reaches a maximum and than smoothly decreases with time. Also, it is evident that much higher maximum values of reaction rates were obtained when bifunctional initiator was used.

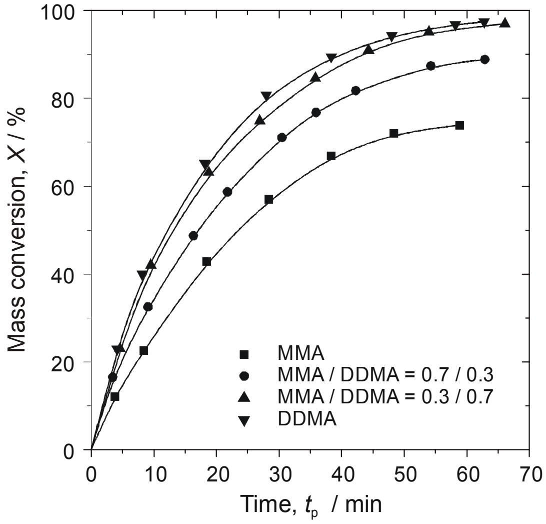

Figure 1. The effect of monomer mixture composition on conversion in the polymerization of methyl methacrylate (MMA) and dodecyl methacrylate (DDMA) with benzoyl peroxide as initiator in xylene solution at 95 °C.

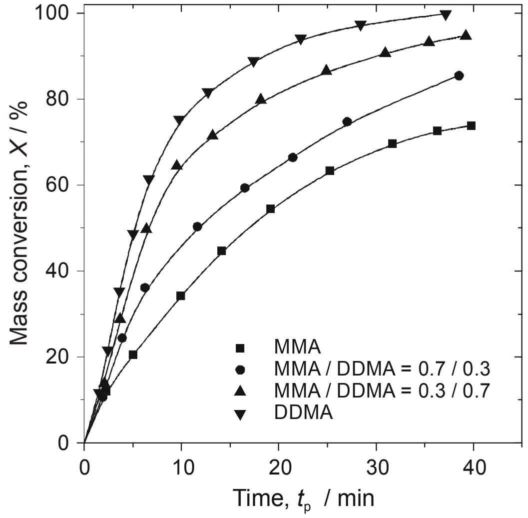

Figure 2. The effect of monomer mixture composition on conversion in the polymerization of methyl methacrylate (MMA) and dodecyl methacrylate (DDMA) with 1,1-di(tert-butylperoxy)cyclohexane as initiator in xylene solution at 115 °C.

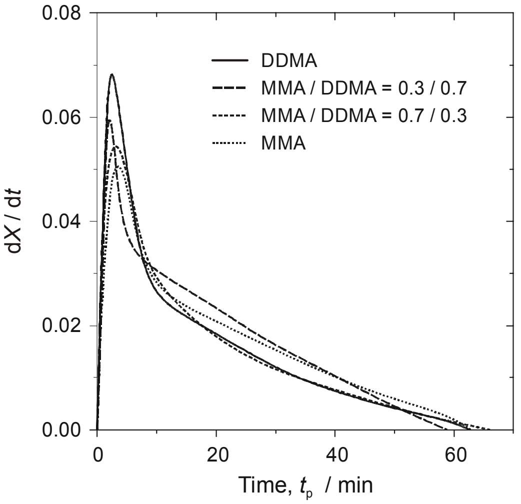

Figure 3. The effect of monomer mixture composition on reaction rate in the polymerization of methyl methacrylate (MMA) and dodecyl methacrylate (DDMA) with benzoyl peroxide as initiator in xylene solution at 95 °C.

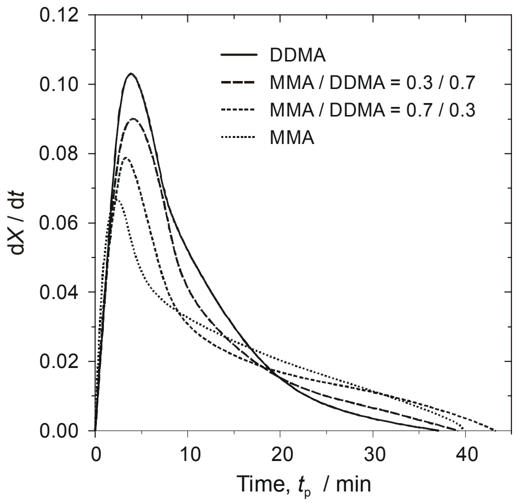

Figure 4. The effect of monomer mixture composition on reaction rate in the polymerization of methyl methacrylate (MMA) and dodecyl methacrylate (DDMA) with 1,1-di(tert-butylperoxy)cyclohexane as initiator in xylene solution at 115 °C.

Initial polymerization rates, R_p, were obtained from the initial (low conversion) slopes of conversion vs. time curves. They were found to follow the same order of reactivity, DDMA > DDMA/MMA > MMA, for both types of initiator; much higher values were obtained by using BPCH, as it is presented in Figure 5. These findings are in good accordance with literature data.[2–7,21–24]

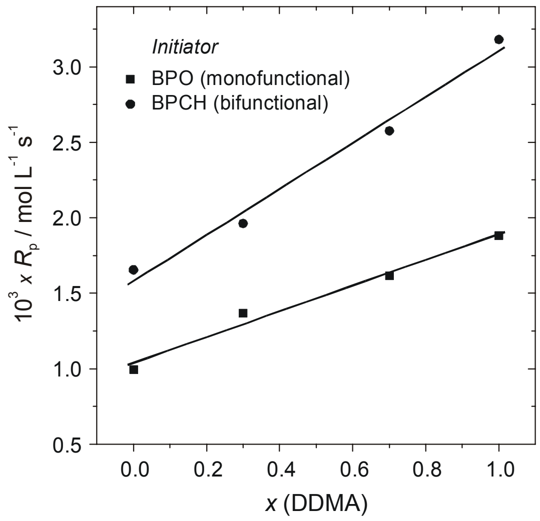

Figure 5. The effect of initiator functionality and monomer mixture composition on initial reaction rate, R_p, in the polymerization of methyl methacrylate (MMA) and dodecyl methacrylate (DDMA) in xylene solution.

It is well known that higher reaction rates may be achieved in free radical polymerization by increasing the reaction temperature, monomer or initiator concentration, but as a rule lower molecular mass is obtained.[1] As can be seen from data given in Table 1, obtained polymers did not show significant differences in average molecular mass values, in spite of the higher reaction temperature in bifunctionally initiated systems. These findings are presented in more details in Figures 6 and 7 for DDMA homopolymerization

Table 1. The effects of monomer mixture composition, initiator functionality and polymerization time on conversion and structural properties of synthesized polymers, i.e. average molecular mass and polydispersity.

Sample	[I]	t_p / min	X / %	$\overline{M}_w$ / kg mol^{-1}	$\overline{M}_n$ / kg mol^{-1}	$PI = \overline{M}_w / \overline{M}_n$
PMMA	*	58.9	73.9	46.6	24.8	1.88
	**	39.8	73.8	42.0	23.3	1.80
MMA/DDMA = 0.7/0.3	*	62.9	88.9	133.7	55.8	2.40
	**	38.5	85.4	103.0	53.5	1.93
MMA/DDMA = 0.3/0.7	*	66.1	97.0	206.6	71.2	2.90
	**	39.2	94.7	188.7	80.4	2.34
PDDMA	*	62.8	97.5	267.2	76.1	3.51
	**	37.2	99.8	248.9	74.8	3.33

* monofunctionally initiated polymerization at 95 °C. ** bifunctionally initiated polymerization at 115 °C.

and DDMA/MMA copolymerization, respectively, where cumulative molecular mass averages are shown as functions of the conversion and type of initiator. By inspecting the polymerization course (Figures 1 and 2) and corresponding molecular mass values (Figures 6 and 7), it is evident that gel-effect did not occur in any of the experiments.

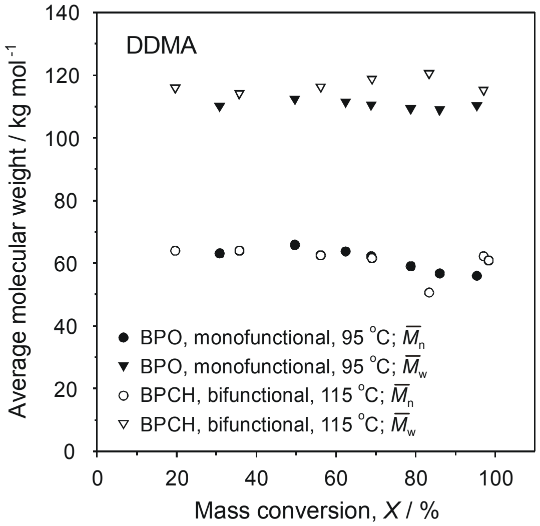

Figure 6. The effect of initiator functionality on polymer molecular mass in the polymerization of dodecyl methacrylate (DDMA) in xylene solution.

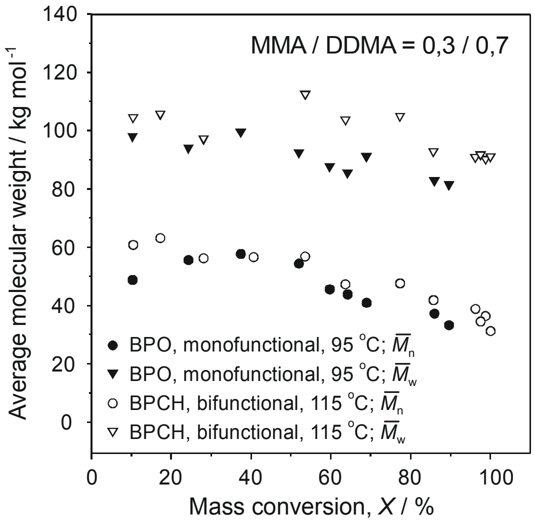

Figure 7. The effect of initiator functionality on polymer molecular mass in the copolymerization of methyl methacrylate (MMA) with dodecyl methacrylate (DDMA) in xylene solution.

A comparison of the examined polymerization systems shows that significantly higher polymerization rates and conversions were obtained with bifunctional initiator (Figures 1 and 2, table 1). Shorter polymerization cycles of ~40 min were achieved with bifunctional initiator, in comparison to ~60 min with monofunctional initiator. Simultaneously, high values of polymer molecular mass were preserved with similar and even lower polydispersity values. Such a behavior can be attributed to the sequential decomposition of two reactive functional groups in bifunctional initiator that generates initiator radicals continuously as polymerization proceeds.

Conclusion

The kinetics of methyl methacrylate and dodecyl methacrylate solution polymerization using the bifunctional initiator 1,1-di(tert-butylperoxy)cyclohexane and monofunctional initiator benzoyl peroxide was investigated and compared. Throughout this study, it was established that high reaction rates, high conversions and significant reductions in polymerization time of up to 50% could be achieved with the bifunctional initiator. At the same time, high molecular masses and polydispersity values of synthesized polymers could be retained.

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Povzetek

Proučevana je kinetika radikalske polimerizacije metil metakrilata (MMA) in dodecil metakrilata (DDMA), inicirana z bifunkcionalnim iniciatorjem 1,1-di(tert-butilperoksi)cikloheksanom (BPCH) do visokih konverzij v raztopini ksilena pod izotermnimi pogoji. Rezultati so primerjani s konvencionalnim monofunkcionalnim iniciatorjem dibenzoil peroksidom. Hitrost polimerizacije je po vrsti: DDMA > DDMA/MMA > MMA za obe vrsti iniciatorjev, vendar ima precej višje vrednosti z BPCH, ki hkrati daje tudi višje molekulske mase polimera. Pri primerni temperaturi reakcije lahko z bifunkcionalnim katalizatorjem skrajšamo čas polimerizacije na polovico.