

INVESTIGATION OF ISOTHERMAL BULK POLYMERIZATION OF *o*-ALKYLARYL METHACRYLATES BY DSC

D. M. Petrović-Djakov, J. M. Filipović, Lj. P. Vrhovac and J. S. Veličković

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, POB 494,
YU-11000 Belgrade, Yugoslavia

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Abstract

The kinetics of the AIBN-initiated free radical bulk polymerization of five *o*-alkylphenyl methacrylates was studied by means of DSC in the temperature range 353–373 K, and the enthalpy of polymerization, the overall reaction rate constant and the activation energy were determined. The results were compared with those published recently on corresponding *p*-alkylaryl methacrylates. All measured reaction rate constants were found to increase with increasing temperature and to decrease with increasing *o*-alkyl substituent mass and size. It was shown that *o*-substituents influence the rates of polymerization to a greater extent than *p*-substituents. At about 373 K, all differences in rate, most probably resulting from steric hindrance caused by the alkyl groups, disappear in both series, a phenomenon earlier observed for dimethyl phenyl methacrylates.

Keywords: *o*-alkylaryl methacrylates, enthalpies of polymerization, free radical kinetics, temperature dependence

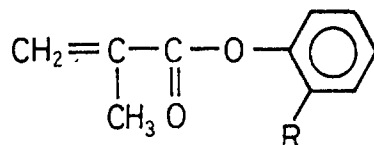
Introduction

The kinetics of the free radical polymerization of alkylaryl methacrylates was studied previously in this laboratory, with the application of dilatometric and occasionally gravimetric techniques [1, 2] in the temperature interval 323–343 K. In a recent investigation [3] of *p*-alkylaryl methacrylates, DSC was applied [4], which allowed study of the polymerization kinetics in the temperature interval 343–383 K. The present investigation is an extension of our previous work on alkylaryl methacrylates, in order to study the influence of the

* Author to whom all correspondence should be addressed.

mass and size of the alkyl substituents on the kinetic parameters in the *o*-series and to compare them with those in the *p*-series.

The monomers investigated in the present investigation have the following general formula:



where the substituents *R* are as in the following listing:

<i>R</i>	<i>Monomer</i>	
H	phenylmethacrylate	(PMA)
CH ₃	<i>o</i> -methylphenyl methacrylate	(<i>o</i> -MPMA)
CH ₂ CH ₃	<i>o</i> -ethylphenyl methacrylate	(<i>o</i> -EPMA)
CH ₂ CH ₂ CH ₃	<i>o</i> -propylphenyl methacrylate	(<i>o</i> -PrPMA)
CH(CH ₃) ₂	<i>o</i> -isopropylphenyl methacrylate	(<i>o</i> - <i>i</i> -PrPMA)
C(CH ₃) ₃	<i>o</i> -tert.-butylphenyl methacrylate	(<i>o</i> - <i>t</i> -BPMA)

Experimental

The experimental work consisted in the synthesis of the corresponding monomers, the investigation of the AIBN-initiated polymerization by DSC and the evaluation of the thermal curves. All experimental details are essentially the same as those outlined previously in the publication on *p*-alkylaryl methacrylates [3].

Results and discussion

The isothermal polymerization of PMA [3], *o*-MPMA, *o*-EPMA, *o*-PrPMA, *o*-*i*-PMA and *o*-*t*-BPMA was studied at 353, 358, 363, 368 and 373K. Figure 1 depicts the course of the polymerization of *o*-EPMA at three different temperatures. From each curve, an induction period can be seen first, followed by the steady-state reaction period, from which the overall rate constant can be calculated, and finally an exothermic peak resulting from the gel effect, at higher conversion after the steady-state reaction. The thermoanalytical curves for all other monomers are similar. The induction period decreases with increasing temperature, and the first slopes observed increase. With increasing substituent size, the curves become flatter and the peaks less pronounced.

The enthalpies of polymerization $-\Delta H_p$, presented in Table 1, were calculated from the areas under the DSC curves after correction for the amount of

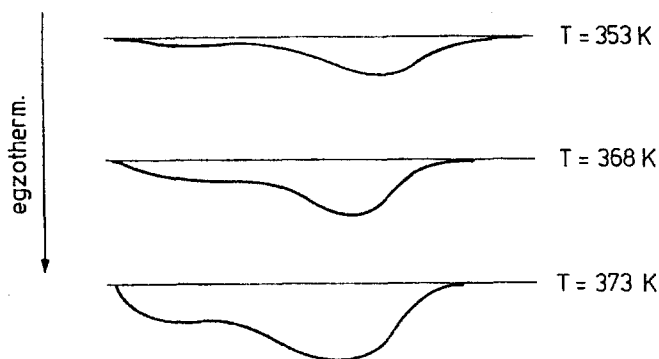


Fig. 1 Integral curves of *o*-EPMA at three temperatures

Table 1 Enthalpies of polymerization of *o*-alkylphenyl methacrylates

Monomer	PMA	<i>o</i> -MPMA	<i>o</i> -EPMA	<i>o</i> -PrPMA	<i>o</i> - <i>i</i> -PrPMA	<i>o</i> - <i>t</i> -BPMA
<i>T</i> /K	$-\Delta H/\text{kJ mol}^{-1}$					
353	57.2	49.3	54.6	—	56.9	—
358	56.5	52.0	57.7	50.1	52.3	24.3
363	56.8	53.6	55.6	54.7	57.1	25.8
368	59.3	51.9	55.6	52.2	54.1	22.6
373	58.8	51.9	55.7	52.0	55.8	21.0
mean value	57.7	51.7	56.2	52.3	55.3	23.4

residual monomer content. All enthalpies were in the range -52 to -56 kJ mol^{-1} , in good agreement with enthalpies of polymerization published previously for *p*-alkylaryl methacrylates [3] and a series of six dimethylphenyl methacrylates [6] investigated in the same way. The only exception in this respect was the low $-\Delta H_p$ of only 25 kJ mol^{-1} for *o*-*t*-BPMA. A similarly low enthalpy of polymerization was earlier observed in a study of the kinetics of six differently substituted dimethylphenyl methacrylates [6], where only the 2,6-substituted isomer with the highest hindrance to free rotation, displayed an enthalpy of polymerization lower by about one-third with respect to the other five members of the series. In contrast with these observations, all enthalpies of polymerization in the *p*-substituted series were similar and close to -55 kJ mol^{-1} [3], indicating that a bulky substituent in the *p*-position on the phenyl ring, i.e. far enough from the macroradical polymerization site, does not affect the reaction rate. The lower enthalpy in the two former cases may be explained by the consumption of energy necessary to overcome the barriers to free rotation of substituted aryl, imposed by the bulky alkyl substituents.

With the assumption that the heat of polymerization evolved up to time τ is proportional to the monomer conversion and that the reaction in the steady state

is first order with respect to the monomer concentration, the overall rate constants k were calculated according to the following equation:

$$\ln(M_0/M) = \ln[A/(A-a)] = k_p(fk_d/k_p)^{1/2}[I_0] \tau = k\tau$$

where M_0 = initial monomer concentration, corresponding to

A = total area under the DSC curve, corrected for the residual monomer content,

a = partial area under the DSC curve, corresponding to time τ ,

M = monomer concentration at time τ , corresponding to area $A-a$, and

k = overall rate constant,

where k_p , k_d , k_t , f and $[I_0]$ have the meanings standard in polymer kinetics.

Table 2 Overall rate constants and activation energies of polymerization of *o*-alkylphenyl methacrylates

Monomer	PMA	<i>o</i> -MPMA	<i>o</i> -EPMA	<i>o</i> -PrPMA	<i>o</i> - <i>i</i> -PrPMA	<i>o</i> - <i>t</i> -BPMA
<i>T</i> /K	$k \cdot 10^4 / s^{-1}$					
353	2.71	1.54	1.67	—	1.75	—
358	3.55	2.73	2.40	2.57	2.62	1.74
363	4.94	3.67	3.39	3.45	3.90	3.23
368	6.24	5.37	5.20	5.44	5.28	4.63
373	9.05	9.57	8.08	8.34	9.17	9.04
$E_a / kJ mol^{-1}$	62	82	81	82	80	107

The values of the overall rate constants k obtained are presented in Table 2. The bottom row of the Table includes the activation energies of polymerization E_a , obtained from the slopes of conventional Arrhenius plots. The results show that PMA, with no substituent on the phenyl ring, is the fastest polymerizing monomer, but the rate constants of the following four monomers, with rather small substituents, are slightly lower from that of unsubstituted PMA. An obvious exception is *o*-*t*-BPMA, at least at lower temperatures; however, at 373 K any lowering of the polymerization rates due to the bulky *p*-*t*-butyl substituent vanishes. At this temperature, the rate constants for all six investigated monomers are practically equal and close to $9 \cdot 10^{-4} s^{-1}$. This result is very important because it suggests that at 373 K any influence of the substituents on the propagation rate in the *o*-series vanishes. It is further significant that in the previous publication relating to the corresponding *p*-series [3], the rate constants of all five examined monomers also tend towards a value of $9-10 \cdot 10^{-4} s^{-1}$, indicating that at 373 K any influence of the alkyl substituents in either the *o*- or the *p*-position vanishes. Expressed in a different way, all ratios of k for any substituted monomer vs. k_{PMA} approach 1 as the temperature reaches 373 K.

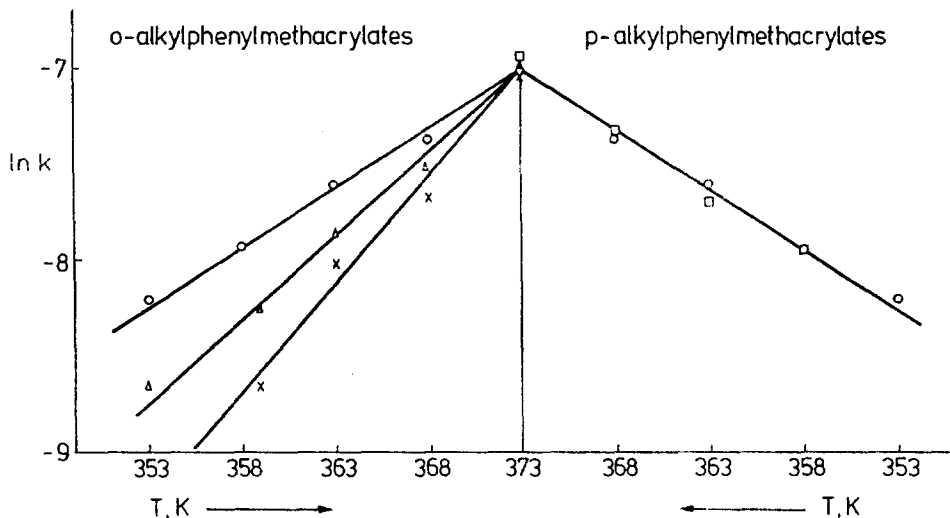


Fig. 2 The dependence of $\ln k$ vs. temperature for PMA(o), *o*-*i*-PrPMA(Δ), *o*-*t*-BMA(x) and *p*-*t*-BMA(\square)

The dependence of $\ln k$ on temperature is presented graphically in Fig. 2. The left-hand part of the Figure depicts the dependence of k on temperature for several *o*-alkylphenyl methacrylates, and the right-hand side that for *p*-substituted alkylphenyl methacrylates [3]. The lowest slope is observed for PMA; in the *o*-substitution part, the plots of alkyl-substituted monomers are steeper, the steepest being observed for *o*-*t*-BPMA, indicating that in this case the influence of the bulky substituent is very pronounced at lower temperatures, but it fades away when the thermal energy of the molecules seems readily to overcome any barriers preventing the monomer from attaining conformations suitable for the propagation step. On the right-hand side of the diagram, relating to *p*-substituted monomers, the rate constants k of the five investigated monomers practically coincide, indicating the absence of any influence of the substituent on the rate. However, all plots from both parts approach a common intersection at about 373 K, i.e. at this temperature any influence caused by the substituents vanishes.

Conclusions

DSC can be applied successfully to the study of polymerization kinetics of alkylphenyl methacrylates in the temperature range 353–373 K. In *o*-substituted alkylphenyl methacrylate monomers, the overall rate constants k depend on the alkyl substituents: the constant decreases with increase in size of the alkyl substituent. However, the difference vanishes with increasing temperature

and at 373 K the rates for the substituted compounds and the unsubstituted monomer are practically equal. The results for *p*-substituted monomers, published previously, fit very well into this general picture.

The enthalpies of polymerization are practically independent of the type of substituent, with the exception of *o*-tert.-butylphenyl methacrylate (*o*-*t*-PBMA); its enthalpy is lower and its activation energy is much higher than those for the other monomers investigated.

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