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ISOTHERMAL BULK POLYMERIZATION OF *p*-ALKYLARYL METHACRYLATES BY DSC

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The course and kinetics of free radical polymerization in bulk of *p*-alkylphenyl methacrylates with AIBN initiator were studied by DSC, in the temperature range 348–373 K. The enthalpy of polymerization, the residual monomer content, as well as the overall reaction rate constants and the activation energies were determined. The similar values of the overall rate constants indicate that the relatively small alkyl substituents in *p*-position of the phenyl ring affect the polymerization rate to a very small, if any, extent.

Keywords: enthalpy of polymerization, free radical polymerization, kinetics, *p*-alkylphenyl methacrylates

Introduction

The kinetics of free radical polymerization of alkylaryl methacrylates has been studied in this laboratory, applying dilatometric and, occasionally, gravimetric techniques [1, 2]. The aim was to determine the influence of the size and the position of alkyl substituents in pendent aryl groups of the monomer molecule on kinetic parameters. The present investigation is an extension of this work using differential scanning calorimetry (DSC), which has proved to be convenient for studying the polymerization of vinyl monomers [3–8]. The rate of polymerization is determined directly, continuously and even in a gel or solid state [3].

The monomers investigated are: *p*-methylphenyl methacrylate (*p*-MPMA), *p*-ethylphenyl methacrylate (*p*-EPMA), *p*-isopropylphenyl methacrylate (*p*-i-PPMA) and *p*-tert-butylphenyl methacrylate (*p*-t-BPMA), represented by the general formula:

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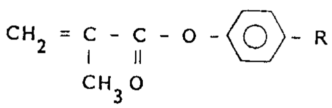

Phenyl methacrylate has been included into the investigation for comparison.

Experimental

The monomers were synthesized as described previously [1] and their purity checked by elemental analysis and IR spectroscopy. AIBN, crystallized twice from methanol and dried in vacuum, was used as an initiator (0.05 mol/dm^3). In order to determine the optimal temperature range the polymerization was carried out dynamically from 323 to 523 K, and then isothermally in the temperature range 348–373 K. The unreacted monomer content was determined after each isothermal run by heating the sample from 323 to 493 K [3]. The exothermal peak, due to the residual monomer polymerization, appeared just when the temperature exceeded that of isothermal polymerization. A Perkin-Elmer DSC 2 thermoanalyser, calibrated by measuring the heat of fusion of indium, was used in all experiments.

Results and discussion

The isothermal polymerization of PMA, *p*-MPMA, *p*-EPMA, *p*-i-PPMA and *p*-t-BPMA has been studied at 348, 353, 358, 363, 368 and 373 K. Figure 1 shows the course of polymerization of *p*-EPMA at different temperatures. The thermal curves for all the methacrylates studied are similar i.e. the gel effects sets in after the steady-state reaction at the beginning of the process. The induction period and the reaction time decrease with increasing temperature.

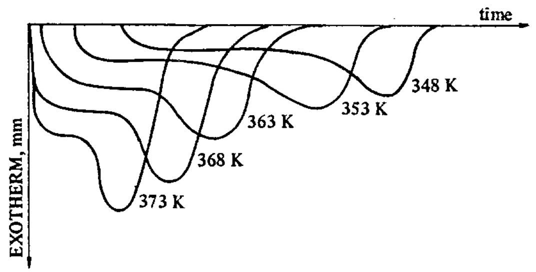

Fig. 1 Course of polymerization of *p*-EPMA at different temperatures

The polymerization enthalpies ΔH_p (Table 1) have been calculated from the areas under the DSC curves, after correcting for the residual monomer content. The values of ΔH_p are between –55 and –58 kJ/mol, similar to those for other methacrylic monomers [4–8]. No temperature dependence of the polymerization enthalpies in the temperature range 348–373 K has been observed.

Table 1 Enthalpy of polymerization of *p*-alkylphenyl methacrylates, $[I_o]$ =[AIBN$_o$] =0.05 mol/dm^3

MONOMER	PMA	*p*-MPMA	*p*-EPMA	*p*-i-PPMA	*p*-t-BPMA
T / K			$-\Delta H_p$ / kJ·mol^{-1}		
348	58.4	55.8	52.8	54.8	—
353	57.2	55.9	56.0	53.8	—
358	56.5	56.8	57.1	53.8	59.4
363	56.8	56.3	59.4	56.2	52.3
368	59.3	55.8	58.1	56.1	55.4
373	58.8	59.7	59.8	57.7	53.0
Mean value	57.8±1.2	56.7±1.5	57.2±2.6	55.4±1.5	55.0±3.2

Assuming that the reaction in the steady state was first order with respect to the monomer concentration, the overall rate constants were calculated using the equation:

$$\ln [A/(A-a)] = k_p\,(f\cdot k_d/k_t)^{1/2}\,[I_o]^{1/2}\,\tau = k\cdot\tau \qquad (1)$$

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

a = the partial area, up to time τ,

k = the overall rate constant of polymerization during the steady state of the reaction.

The values of the overall rate constants are given in Table 2.

Under the same conditions the process of polymerization of *p*-alkylaryl methacrylates proceeds in a similar way. The values of the overall rate constants are nearly the same, indicating that the relatively small alkyl substituents in the *p*-position of the phenyl ring affect the rate of polymerization to a very small extent. It has been found earlier that the interrelation of k values for the series of substituents in the *p*-position: hydrogen, methyl, ethyl, isopropyl, tert-butyl is close to unity [2]. The results obtained by DSC confirm the conclusion started above.

Using the dependence of the overall rate constant on temperature (Table 2) the overall activation energies of polymerization were obtained from the slopes of conventional Arrhenius plots and the values are summarized in Table 2. The E_a values obtained are similar to those characteristic of alkyl- and substituted phenyl methacrylates [4–7]. In a recently published paper on the kinetics of bulk polymerization of some substituted phenyl methacrylates by DTA [7] an activation energy of 83.4 kJ/mol for *p*-t-BPMA has been reported, in quite good agreement with the result obtained by DSC.

Table 2 The overall rate constants and the activation energies for the polymerization of *p*-alkylphenyl methacrylates, $[I_o] = [AIBN_o] = 0.05$ mol/dm^3

MONOMER	PMA	*p*-MPA	*p*-EPMA	*p*-i-PPMA	*p*-t-BPMA
T / K			$k \cdot 10^4$ / s^{-1}		
348	2.16	2.05	2.16	1.98	—
353	2.71	2.90	2.72	2.83	—
358	3.55	3.35	3.46	3.44	3.54
363	4.94	5.45	5.52	5.05	4.47
368	6.24	7.99	7.70	7.72	6.52
373	9.05	11.3	10.3	9.80	9.75
E_a / kJ·mol^{-1}	62	74	70	70	76

The rate constants of polymerization of the same *p*-alkylaryl methacrylate monomers determined by dilatometry [1, 2] are higher than those obtained by DSC technique. The reasons for this disagreement could be the approximations involved in the derivation of Eq. (1) and the presence of oxygen in the sample pans, but the most probable one is the temperature difference between the dilatometer content and the thermostat, which in the steady state of the polymerization of methylmethacrylate, for example, is proportional to the sample weight [8]. The (DSC) technique, with samples of less than 15 mg, does not suffer from this disadvantage and consequently, gives more reliable results.

Conclusions

The polymerization of *p*-alkylphenyl methacrylates is characterized by a steady-state reaction at the beginning, followed by the gel effect at the later stage of the process. The comparison of the initial rate constants for the steady-state first order reaction with respect to the monomer concentration, determined from the DSC curves, indicates that relatively small alkyl substituents (methyl-, ethyl-, iso-propyl- and tert-butyl-) in *p*-position have no significant effect on the rate of polymerization of *p*-alkyl phenyl methacrylates.

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Zusammenfassung —Mittels DSC wurden im Temperaturbereich 348-373 K Reaktionsweg und Kinetik der radikalischen Raumpolymerisation von *p*-Alkylphenylmethacrylaten mit AIBN Initiator untersucht. Dabei wurden die Polymerisationsenthalpie, der Monomerrest-gehalt als auch die Geschwindigkeitskonstanten und die Aktivierungsenergien der Gesamt-reaktion bestimmt. Ähnliche Werte für die Gesamtgeschwindigkeitskonstanten weisen darauf hin, daß die relativ kleinen Alkylsubstituenten in *p*-Stellung des Phenylringes die Polymerisationsgeschwindigkeit nur in sehr kleinem Maße – wenn überhaupt – beeinflussen.