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INFLUENCE OF DIFFERENT INITIATORS ON METHYL METHACRYLATE POLYMERIZATION, STUDIED BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

Differential scanning calorimetry (DSC) was used to measure the decomposition rates of four commercially used initiators, 2,2′-azobis(isobutyronitrile) 2,2′-azobis(2,4-dimethylvaleronitrile), dilauroyl peroxide and bis(4-t-butylcyclohexyl)peroxydicarbonate, in dynamic mode, while the courses of methyl methacrylate polymerization with the listed initiators at 65, 75 and 85°C were measured isothermally. From the DSC curves, the polymerization enthalpies, the overall reaction rate constants and the activation energies for the initial steady-state polymerization were calculated. It was found that the polymerization enthalpy and the kinetic parameters depended on the type of the initiator. An initiator with a shorter decomposition half-lifetime shifted the onset of the gel effect to a higher conversion, intensified it and decreased the average molar mass of the polymer.

Keywords: differential scanning calorimetry, initiators, kinetics, methyl methacrylate, polymerization

Introduction

Differential scanning calorimetry (DSC) has been shown to be a fast and simple method for investigation of the radical polymerization of methyl methacrylate (MMA) [1]. While 2,2′-azobis(isobutyronitrile) (AIBN) is the major initiator used in research, for the industrial polymerization of MMA other initiators, with different decomposition temperatures and different decomposition rate constants, may be interesting. In this work, the influence of four initiators, 2,2′-azobis(isobutyronitrile) (AIBN), 2,2′-azobis(2,4-dimethylvaleronitrile) (V-65), dilauroyl peroxide (LPO) and bis(4-t-butylcyclohexyl)peroxydicarbonate (P-16), on the course and reaction rate constants of MMA polymerization was investigated, with the aim of using the results in the manu-

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facture of poly(methacrylate) sheets. The courses of the polymerization were measured by DSC in the isothermal mode at three different temperatures.

Experimental

Materials

Commercially supplied inhibited MMA (ICI) was used without further purification to meet the conditions during industrial polymerization process. The initiators AIBN (Akzo), LPO (Akzo), P-16 (Akzo) and V-65 (Wako) were recrystallized from chloroform with methanol, vacuum-dried overnight at room temperature and stored in the dark at –25°C.

Methods

All kinetic measurements were performed with a Perkin-Elmer differential scanning calorimeter DSC 7.

The temperature intervals and the rates of initiator decomposition were measured by heating the samples from 30 to 150°C at a rate of 5 $\text{deg}\cdot\text{min}^{-1}$. To avoid a violent reaction and induced decomposition, initiators were dissolved in di-*n*-butyl phthalate at a concentration of 0.06 to 0.2 mol/l. For measurements, Perkin-Elmer volatile-sample pans with a small hole in the lid were used. Kinetic parameters were calculated by the non-isothermal differential method based on the multiple regression technique with the Perkin-Elmer Kinetics Software [2–4].

The basic rate equation $dx/dt=k(1-x)^n$ and the Arrhenius equation for the temperature dependence of k were combined:

$$\frac{dx}{dt} = Z\cdot\exp(-E_a/RT)(1-x)^n, \tag{1}$$

where x is the degree of conversion, n is the order of reaction, k is the reaction rate constant, t is time, Z is the pre-exponential factor, E_a is the Arrhenius activation energy, R is the universal gas constant, and T is the absolute temperature.

In DSC, the temperature varies linearly with time and Eq. (1) can be rewritten:

$$\frac{dT}{dt}\cdot\frac{dx}{dT} = Z\cdot\exp(-E_a/RT)(1-x)^n \tag{2}$$

The value of x is obtained via the ratio of the partial enthalpy ΔH_p to the total enthalpy of reaction ΔH. The values of enthalpies are evaluated from the partial area to time $t(\Delta H_p)$ and from the total area (ΔH) under the DSC curve.

Equation (2) can be reduced to a linear form

$$\ln\left(\frac{\mathrm{d}T}{\mathrm{d}t}\cdot\frac{\mathrm{d}x}{\mathrm{d}T}\right) = \ln Z - E_a/RT + n\cdot\ln(1-x). \tag{3}$$

Multilinear regression is performed by using $\ln\left(\frac{\mathrm{d}T}{\mathrm{d}t}\cdot\frac{\mathrm{d}x}{\mathrm{d}T}\right)$, $-1/RT$ and $\ln(1-x)$ as variables and solving for Z, E_a and n.

The polymerization of MMA with the four selected initiators at a concentration of 50 mmol/l was measured isothermally at 65, 75 and 85°C, described in detail elsewhere [5]. The enthalpies of polymerization and the composite rate constants were calculated from the areas between the DSC curves and the baseline, which was obtained by back-extrapolation of the straight line after the polymerization was terminated. As the samples were polymerized at temperatures below the glass transition temperature of the polymer, they were subsequently heated to 150°C at a rate of 5 deg·min^{-1}, to attain polymerization of the unreacted monomer. Its quantity was calculated from the extent of the exothermic reaction [5, 6].

The reaction rate was proportional to the ordinate displacement of the DSC curves. In the first part of the reaction, the ordinate displacement was nearly constant, *i.e.* the polymerization was stationary. For this first part, the overall polymerization rate constants for the first reaction order as regards the monomer concentration, k':

$$k' = k_p\left(\frac{fk_dI_0}{k_t}\right)^{1/2}$$

were calculated from plots of $\ln[\Delta H/(\Delta H-\Delta H_p)]$ *vs.* t(k_p, k_d and k_t) being the rate constants for propagation, initiator decomposition and termination, f the initiator efficiency, and I_0 its initial concentration), while the activation energies were calculated by using the Arrhenius equation [5].

The gel effect was specified by the critical conversion (x_c) at the onset of the autoacceleration, *i.e.* at the sharp increase of the reaction rate in the DSC curve, and by its intensity in terms of the heat flow at the maximum in the DSC curve [7, 8].

The molar mass averages of the synthesized polymers were measured by gel permeation chromatography (GPC) relative to polystyrene standards on a Perkin-Elmer gel chromatograph, using μ-Styragel columns (pore size 10^{-5}, 10^{-6}, 10^{-7} and 5×10^{-8} m). A differential refractometer was used as detector, and tetrahydrofurane at a flow rate of 60 ml/h as the mobile phase.

Results and discussion

Decomposition of initiators

The first-order kinetics for the thermal decomposition of an initiator is an approximation that is valid only for the infinitely dilute solutions, where induced decomposition does not take place. In practice, to avoid induced decomposition and consequently a higher reaction order, the concentration of the initiator should be kept as low as possible and should not exceed 0.2 mol/l [9–11].

DSC curves for the thermal decompositions of AIBN, LPO, V-65 and P-16 are shown in Fig. 1. Kinetic data calculated from these curves are given in Table 1. For AIBN, the decomposition exotherm is preceded by the melting endotherm.

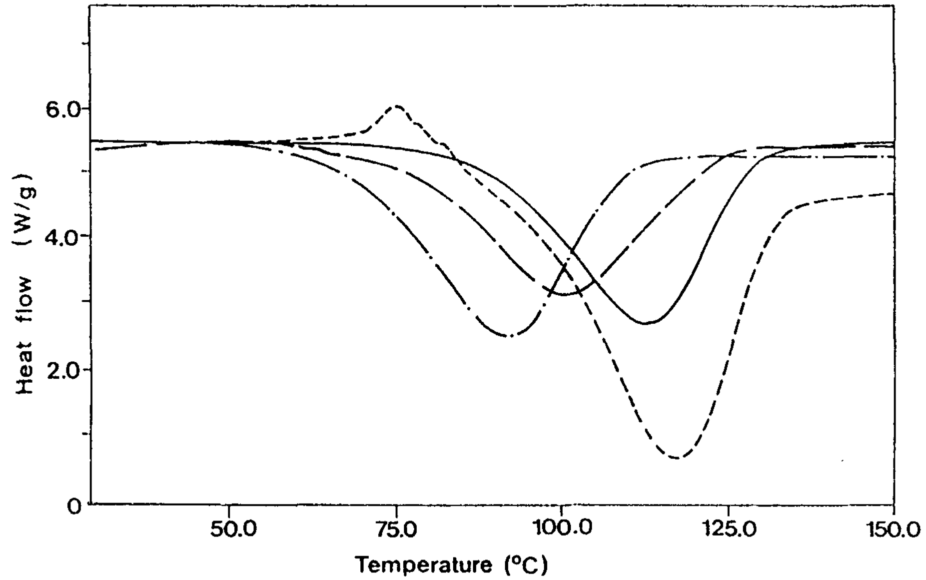

Fig. 1 Courses of the decomposition of AIBN (- - -), LPO (—), V-65 (– –) and P-16 (— - —)

From Fig. 1 and Table 1, it can be seen that the four initiators have different temperature intervals and rates of decomposition, and also different activation energies. The values are in good agreement with the literature data [1, 9] and differ slightly from those given by the producers [12, 13], obtained by another method.

Polymerization of MMA

The polymerization of MMA was measured isothermally at 65, 75 and 85°C. The polymerization was initiated by AIBN, LPO, V-65 or P-16. The courses of

Table 1 Kinetics data for thermal decomposition of initiators

Initiator	T_{max}/	$k_d\times10^4(s^{-1})$ at			E_a/	n	$t_{1/2}$(h)		
	°C	65°C	75°C	85°C	kJ·mol^{-1}		65°C	75°C	85°C
AIBN	118	0.27	0.92	2.92	120.4	1.0	7.6	2.20	0.70
producer[12]	–	0.36	1.15	3.40	112.3	–	5.3	1.70	0.60
LPO	114	0.22	0.88	3.27	135.7	1.1	8.8	2.20	0.60
producer[12]	–	0.28	1.04	3.56	127.3	–	6.8	1.90	0.50
V-65	101	1.00	3.68	12.56	128.4	1.3	2.0	0.50	0.15
producer[13]	–	1.29	4.45	14.33	121.2	–	1.5	0.40	0.13
P-16	93	3.30	12.00	41.00	127.0	1.2	0.6	0.16	0.05
producer[12]	–	3.74	13.30	43.90	124.0	–	0.5	0.15	0.04

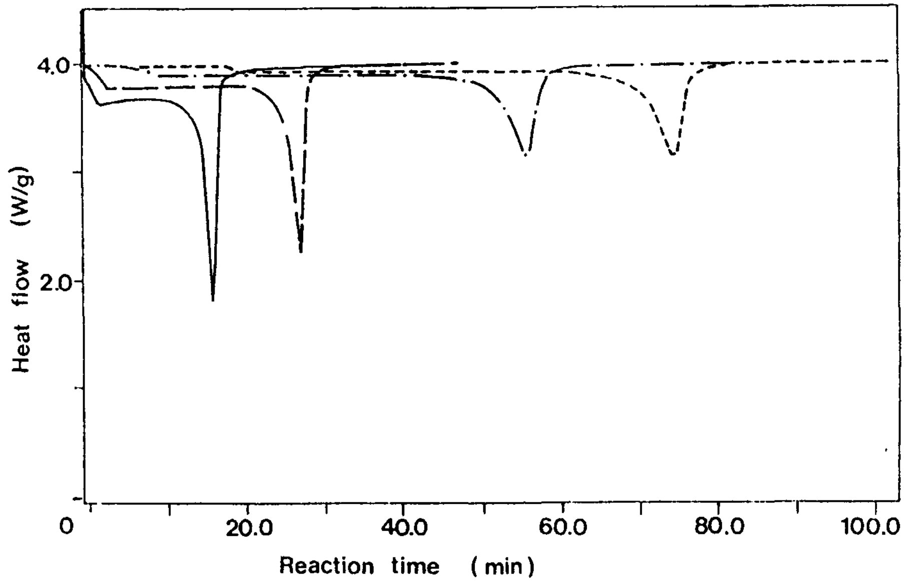

Fig. 2 Courses of the isothermal MMA polymerization at 65°C with AIBN (— - —), LPO (- - -), V-65 (– –) and P-16 (—)

the polymerization at 65°C are shown in Fig. 2. At the beginning, the polymerization is stationary (d*H*/d*t* ~const.), followed by a strong gel effect, with a steep increase in the reaction rate, which is characteristic of MMA polymerization. In the DSC curves of AIBN and LPO (initiators with longer decomposition half-lifetimes) at 65°C, the onset of polymerization is delayed, due to the inhibitor present in the monomer (induction period). The DSC curves reveal that the reaction time to the final conversion, the initial reaction rates, the conversions at the onset of the gel effect, and its intensities, depend on the type of the initiator. From the DSC curves, the polymerization enthalpies were calculated. To obtain the complete enthalpy of polymerization (100% conversion), the polymerization enthalpies of the residual, *i.e.* unreacted monomer were added to the isothermal enthalpy values. The data are given in Table 2.

Table 2 Polymerization enthalpies (ΔH) of MMA initiated by different initiators corrected for the residual monomer (*r.m.*)

	AIBN		LPO		V-65		P-16	
T/ °C	ΔH/ kJ·mol^{-1}	*r.m.*/ %	ΔH/ kJ·mol^{-1}	*r.m.*/ %	ΔH/ kJ·mol^{-1}	*r.m.*/ %	ΔH/ kJ·mol^{-1}	*r.m.*/ %
65	–54.5	4.6	–52.9	2.5	–57.2	6.2	–55.5	3.3
75	–56.7	7.7	–56.4	1.8	–56.8	3.6	–56.3	2.0
85	–57.4	2.9	–56.9	0.3	–56.4	1.6	–52.3	0.6

With AIBN and LPO, the polymerization enthalpies decreased, *i.e.* became more negative, with increase of the reaction temperature, as expected. With the more reactive initiators V-65 and P-16, at higher temperature the reaction started before thermal equilibrium in the apparatus was achieved and the measurement could begin. In this way, part of the polymerization enthalpy was lost and too low values were found.

From the DSC curves, the overall reaction rate constants k' and from k' the Arrhenius activation energies (E_a) were also calculated. The values are given in Table 3.

Table 3 Overall reaction rate constants for the polymerization of MMA with different initiators

Initiator	$k' \times 10^3/\mathrm{s}^{-1}$			E_a/
	65°C	75°C	85°C	kJ·mol^{-1}
AIBN	0.18 ± 0.005	0.31 ± 0.020	0.77 ± 0.042	72.9 ± 6.1
LPO	0.15 ± 0.002	0.31 ± 0.038	0.700.022	76.0 ± 0.7
V-65	0.43 ± 0.040	0.87 ± 0.088	1.64 ± 0.049	67.5 ± 0.4
P-16	0.80 ± 0.038	1.35 ± 0.032	2.86 ± 0.043	64.2 ± 3.9

The type of the initiator is the only variable in the measured reaction systems, and therefore the overall reaction rate in the stationary state is related to $(fk_d)^{1/2}$, and the polymerization with P-16 was found to be the fastest.

The gel effect is stronger in the systems with a higher polymerization rate constant in the stationary state, and its intensity increases with temperature. The conversion at the onset of the gel effect is related to the critical viscosity in the reaction system. Since the viscosity decreases with temperature and increases with increasing molar mass of the polymer, the gel effect onset is expected to shift to a higher conversion at higher isothermal polymerization temperatures and in systems with a lower molar mass average. The molar mass of the polymer, on the other hand, depends on the concentration and on the decomposition half-lifetime of the initiator. An initiator with a shorter decomposition half-lifetime produces a higher concentration of primary radicals per unit time at a given temperature.

Table 4 gives critical conversions at the onset of the gel effect (the residual monomer being taken into consideration), the intensities of the gel effect as maximal ordinate displacements and the molar mass averages relative to polystyrene standards.

In the polymerization of MMA in the bulk, the molar mass distribution has been found to be bimodal [8], the first maximum (M_a) relating to the polymer formed before the onset of the gel effect and the second maximum to the polymer formed during the gel effect (M_b). Due to the limited selectivity of the col-

Table 4 Influence of the type of the initiator on the onset (x_c) and on the intesity (d) of the gel effect, as well as on weight average of molar mass (M_w). In the case of bimodal distribution the values for both components, before the gel effect (M_a) and during the gel effect (M_b) are given

T/	AIBN					LPO				
	x_c	d	M_w	M_a	M_b	x_c	d	M_w	M_a	M_b
°C	%	W·g^{-1}		×10^5		%	W·g^{-1}		×10^5	
65	28.3	0.82	2.6	–	–	26.7	0.85	2.1	–	–
75	29.0	1.43	1.8	–	–	33.2	1.64	1.4	–	–
85	36.1	2.64	1.2	–	–	36.2	2.62	1.0	–	–
T/	V-65					P-16				
	x_c	d	M_w	M_a	M_b	x_c	d	M_w	M_a	M_b
°C	%	W·g^{-1}		×10^5		%	W·g^{-1}		×10^5	
65	32.3	1.76	1.2	0.7	1.4	38.4	2.28	0.8	0.5	1.0
75	43.1	2.66	0.9	0.6	1.1	41.3	2.86	0.7	0.4	0.8
85	45.4	3.45	0.6	0.3	0.7	46.1	4.02	0.5	0.3	0.6

umns used, in this work the bimodal distribution was detected only in polymers initiated with V-65 or P-16. In systems with AIBN or LPO, only one broad peak was found.

To obtain an appropriate reaction time for DSC measurements, a relatively high initiator concentration was needed. The molar masses of the polymers were therefore lower than for a typical commercial polymer.

Conclusions

AIBN, LPO, V-65 and P-16 have different temperature intervals and rate constants of decomposition. Consequently, they have a great influence on the overall polymeryzation rate of MMA, on the conversion at the onset of the gel effect and on its intensity, and on the molar mass of the poly(methyl methacrylate) formed at a selected temperature, *i.e.* an initiator with a higher decomposition rate constants moves the onset of the gel effect to a higher conversion and increases its intensity. GPC measurements on the systems with V-65 or P-16 yielded a bimodal distribution curve, indicating the difference in molar mass of the polymer formed before and during the gel effect, while in the systems with AIBN or LPO only one broad peak was observed.

For practical reasons, it is important to know that with P-16 at 65°C a similar course of polymerization is obtained as with AIBN or LPO at 85°C, but the reaction time and the molar mass averages are approximately 30% lower. A lower temperature and a shorter reaction time may improve the economy of the polymerization process.

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Zusammenfassung — Mittels DSC wurde die Zersetzungsgeschwindigkeit von vier handelsüblichen Initiatoren, namentlich 2,2'-Azobis(isobutyronitril), 2,2'-Azobis(2,4-Dimethylvaleronitril), Dilauroylperoxid und Bis(4-*t*-butylcyclohexyl)peroxydikarbonat gemessen, während der Verlauf der Methylmetacrylatpolymerisation mit den angeführten Initiatoren isotherm bei 65, 75 und 85°C gemessen wurde. Anhand der DSC-Kurven wurden Polymerisationsenthalpie, Gesamtreaktionsgeschwindigkeitskonstante und Aktivierungsenergie für die anfängliche Gleichgewichts-Polymerisation berechnet. Man stellte eine Abhängigkeit der Polymerisationsenthalpie und der kinetischen Parameter von der Art des Initiators fest. Ein Initiator mit einer kürzeren Zersetzungshalbwertzeit verschiebt das Einsetzen des Geleffektes in Richtung höherer Umsätze, verstärkt ihn und reduziert die durchschnittliche Molmasse des Polymers.