Journal of Thermal Analysis and Calorimetry, Vol. 78 (2004) 897–904

CALORIMETRIC STUDY OF CROSS-LINKING POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF A MULTIMONOMER

H. Szocik and R. Jantas[*]

Department of Physical Chemistry of Polymers, Technical University of Łódż, 90-924 Łódż, Poland

(Received March 1, 2004; in revised form Apryl 24, 2004)

Abstract

The kinetics of free-radical cross-linking polymerization of methyl methacrylate (MM) in the presence of poly[2-(10-undecenoyloxy)ethyl methacrylate] (PUDEM) as a macromolecular cross-linker has been isothermally examined within the temperature range from 85–100°C using the differential scanning calorimetry (DSC). The activation energy found for this reaction, E_a=89.3 kJ mol^{-1}, exceeds slightly the literature values of activation energy obtained for the mass polymerization of MM without any cross-linking agent. The activation energy has been also determined by the isoconversion method. It has been found that E_a decreases with the increase in the conversion, which may indicate a change in the reaction mechanism.

Keywords: cross-linking, DSC, kinetics MM, multimonomer, polymerization

Introduction

The polymeric network has become a very attractive research area simultaneously combining fundamental and applied topics of great interest [1–4]. Since the physical properties of polymeric networks strongly depend on the polymerization kinetics, an understanding of the network formation kinetics is essential.

In our previous paper we presented the results of studies on cross-linked polymers obtained by methyl methacrylate (MM) polymerization with the use of macromolecular cross-linker, such as poly[2-(10-undecenoyloxy)ethyl methacrylate] (PUDEM) [5]. To get quantitative data concerning this polymerization, kinetic results are necessary. The free-radical polymerization of MM has been studied by many researchers [6–16].

Many published papers concern isothermal polymerization. Recently, the kinetics of polymerization with a high degree of conversion has become of great interest. In many cases, also in our case, the bulk polymerization was carried out below the glass transition temperature of a pure polymer, $T_{g,p}$ which in our case

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[*] Author for correspondence: E-mail: rojan@mail.p.lodz.pl

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

was 122°C [5]. Then the polymerization process is affected also by the formation of the glassy medium of reaction.

It was the aim of the present study to get kinetic data of the cross-linking polymerization of MM with the addition of some PUDEM (1.8 mol%) and to compare them with the literature data of MM polymerization without any cross-linker by using DSC method. It is a great advantage of DSC that small weighed portions may be used, which ensures an isothermal process within the whole conversion range, especially in the area of auto-acceleration. It was a starting point to find kinetic data for the polymerization carried out with low conversion degrees of several percent. In addition to isothermal measurements of the cross-linking polymerization, the isoconversion method was also used in order to estimate if the conversion degree influences the activation energy.

Experimental

Materials

Methyl methacrylate (MM) was freed from its inhibitor by shaking with 5% aqueous KOH, washing with water, and drying over $CaCl_2$. It was then distilled under reduced pressure. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol.

Synthesis of multimonomer – poly[2-(10-undecenoyloxy)ethyl methacrylate] (PUDEM)

Multimonomer was prepared by Schotten–Baumann's esterification of poly(2-hydroxyethyl methacrylate) (PHEMA) with 10-undecenoyl chloride, according to the procedure described in our previous paper [17]. PUDEM was characterized by M_n=27500 g mol^{-1}.

Measuring methods

The cross-linking polymerization of MM with the addition of 1.8 mol% of PUDEM (calculated for single double bonds of cross-linkers) and 1 mass% of AIBN in relation to monomer mass (0.057 mol dm^{-3}) was examined by DSC (DSC-7 Perkin Elmer).

The calorimeter temperature axis was calibrated using indium and zinc standards. The heat flow rate axis was calibrated using the heat of fusion of indium (28.45 J g^{-1}) as a standard. The polymerization of MM in the presence of 1.8 mol% of PUDEM and 1 mass% of AIBN was examined by the isothermal method 1 [18] at temperatures 85, 90 and 95°C. The process duration was 30 min with the nitrogen flow rate 25 cm^3 min^{-1}. After the isothermal measurement, in order to determine the heat effect from unreacted monomers, the same samples were dynamically heated within the temperature range from 30 to 150°C at a rate of 5°C min^{-1}, and in a subsequent dynamic heating at a heating rate of 20°C min^{-1} the glass transition temperature was determined. The glass transition temperature was measured as the midpoint of the step transition.

About 3 mg of the reaction mixture was weighed in an aluminum calorimetric vessel for volatile substances and was hermetically sealed. The sample was placed in a calorimeter at 50°C and then heated at a rate of 40 K min^{-1} up to the polymerization temperature. The heat of polymerization was determined from the surface area of the exothermic peak between the DSC curve and the baseline established by extrapolation from the trace produced after complete polymerization (no change in the heat produced during the reaction).

In the polymerization carried out at 100°C by the isothermal method 2 [18], the weighed portions of the reaction mixture sealed in calorimetric vessels were isothermally heated at 100°C for 1, 2, 3, 4, 5, 7, 10 min and then they were cooled to 10°C at a rate of 40°C min^{-1} and dynamically reheated to 140–200°C at a rate of 20 K min^{-1}. Based on the exothermic peaks, there was found the thermal effect derived from unreacted monomers in an isothermal measurement (ΔH_r) and possibly T_g. In a subsequent dynamic measurement, T_g was determined for the given reaction conditions.

We have also used the isoconversion (multiple-heating-rate) method [18] that allows one to determine the activation energy from the relationship between heating rate and the temperature of constant conversion. This method is suitable to find out changes in the reaction mechanism through the determination of activation energy at various conversions. We used the following heating rates: 2, 5, 10, 20, 40 K min^{-1}. The activation energy values were found for monomers conversions of 2, 20 and 50%.

Results and discussion

The results of isothermal DSC measurements at 85, 90 and 95°C of the MM polymerization in the presence of 1.8 mol% of PUDEM and 1 mass% of AIBN are given in Table 1. ΔH_i is the enthalpy of MM polymerization with 1.8 mol% of PUDEM determined from the DSC curve obtained during the isothermal heating at appropriate temperature. ΔH_d is the thermal effect obtained in the dynamic heating derived from unreacted monomers during the isothermal heating. The glass transition temperature, T_g, was determined on the basis of a subsequent dynamic heating.

Table 1 Results of DSC isothermal measurements of the MM polymerization with 1.8 mol% of PUDEM and 1 mass% of AIBN

T/°C	ΔH_i/J g^{-1}	ΔH_d/J g^{-1}	$X_{(\Delta H)}$	T_{gexp}/°C	Φ_p	ε	$X(T_g)$
85	–510.2	–8.60	0.930	92.6	0.942	–0.2695	0.950
90	–536.0	–4.40	0.968	103	0.958	–0.2722	0.969
95	–536.3	–4.95	0.970	104	0.961	–0.2750	0.971
100	–	–	–	106	0.965	–0.2778	0.974

[*] $X_{(\Delta H)}$ – final degree of conversion was calculated for the relationship: $X_{(\Delta H)}$ and $X_{(DH)} = (\Delta H_i + \Delta H_d)/\Delta H_\infty$
ΔH_∞ – an average heat of the MM polymerization with the addition of 1.8 mol% of PUDEM and 1 mass% of AIBN, determined from the surface area of exothermic curve peaks obtained by the method of dynamic heating at a rate of 5–10 K min^{-1}, amounting to –558 J g^{-1}

The formation of linear and cross-linked macromolecules is accompanied by a considerable increase in the glass transition temperature of the reacting system. In the reaction carried out isothermally in $T<T_{g,p}$, the reacting system may reach a glass

transition temperature that is equal to the reaction temperature T. Then, there occurs a glass transition of the viscous liquid, which causes the segmental motions are slowed in the reaction system. With a very high conversion the reaction mixture is so viscous that the reaction of radical propagation becomes dependent on diffusion and not by chemical factors. The polymerization rate drops to a value close to zero. Finally, the conversion drops below 100% and the final degree of monomer conversion depends on the reaction conditions (T, $T_{g,p}$, calorimetric vessel volume and initiator concentration), which is confirmed by our results given in Table 1. The increase in the polymerization temperature is accompanied by a slight increase in the conversion degree and consequently in $T_{g.}$

The degree of conversion was also calculated using the experimentally found glass transition temperatures. To that end we used the relationship Kelley Bueche Eq. (1) [19] and the volume fraction of the polymer Φ_p related the conversion X Eq. (2).

$$\Phi_p = \frac{\Delta\alpha_M (T_g - T_{g,M})}{\Delta\alpha_M (T_g - T_{g,M}) + \Delta\alpha_p (T_{g,p} - T_g)} \tag{1}$$

$\Delta\alpha_p$ and $\Delta\alpha_M$ are the differences between the volume expansion coefficients in the liquid and in the glassy state of the polymer and monomer, respectively, $T_{g,p}$ and $T_{g,M}$ are the corresponding glass transition temperaures. In this work we have used:

$$\Delta\alpha_M=10^{-3}\ K^{-1},\ \Delta\alpha_p=0.48\cdot10^{-3}\ K^{-1},\ T_{g,M}=-106°C,\ T_{g,p}=122°C$$

The conversion X is related to the volume fraction of the polymer Φ_p by [7]:

$$X=\Phi_P/(1+\varepsilon+\varepsilon\Phi_P) \tag{2}$$

where ε is the volume shrinkage factor; for the polymerization of MM $\varepsilon<0$; its temperature dependence is given by Eq. (3) [14]:

$$-\varepsilon=0.2256+4.81\cdot10^{-4}T+4.1\cdot10^{-7}T^2 \tag{3}$$

where T – polymerization temperature (°C).

Comparing the conversion degrees calculated from the experimental data of polymerization heat and glass transition temperature values, it can be seen that they are consistent (Table 1). Table 2 shows the data obtained during the dynamic heating of reaction mixture samples, previously annealed at 100°C for 1, 2, 3, 4, 4.5, 5, 7, 10 min. Figure 1 shows an example of the curves of the dynamic heating of samples annealed for 3, 4, 4.5, 7 min.

From the presented data it follows that as the conversion degree of double bonds increases to 0.65, the exothermic peaks pass towards lower temperatures. With the conversion degrees from 0.65 to 0.9 the peaks are at the lowest temperatures (85–93°C), while for $X^0_{(\Delta H)}>0.95$ they again reach 123–125°C. This is probably associated with the fact that the viscosity and glass transition temperature of the system increase with the increase in the conversion degree. For the samples with the initial conversion degree lower than 0.6 during the dynamic heating in a calorimeter, the sample temperature is always higher than its glass transition temperature and the

Table 2 Results of DSC dynamic heating of the cross-linked PMMA with various conversion degrees of double bonds

Time heating in 100°C/min	Heating I						Heating II
	T_{onset}/ °C	Peak/ °C	ΔH_r/ J g^{-1}	$X^*_{(\Delta H)}$	T_g/ °C	Final heating temperature	T_g/ °C
1.0	125.3	134.0	–487.0	0.127	–	200	79.0
2.0	122.8	130.0	–428.0	0.230	–	200	79.0
3.0	103.0	110.0	–313.0	0.439	–	180	85.5
4.0	65.0	85.3	–191.0	0.657	-15.0^{**}	200	85.5
4.5	62.0	96.3	–60.0	0.893	62.8^{**}	140	97.0
5.0	54.0	93.0	–54.0	0.903	68.0^{**}	200	90.3
7.0	108.0	123.0	-25.7^{**}	0.954^{**}	94.0	140	97.0
10.0	113.7	125.0	-14.5^{**}	0.974^{**}	106.0	170	97.0

*initial degree of double bonds conversion $X^0_{(\Delta H)}=(\Delta H_\infty-\Delta H_r)/\Delta H_\infty$
**values calculated on the basis of experimentally found ΔH_r or T_g

polymerization process is chemically controlled. When the initial degree of conversion increases, T_g also increases and the reaction becomes dependent on diffusion, which causes the polymerization rate to decrease. It can be observed that the samples annealed at 100°C for 4.5 and 5 min polymerize in the glassy state during dynamic heating. Under these conditions the quantity of reacted monomer is lower than that if this process were dependent on chemical factors. Hence the determined value of ΔH_r is lower and $(\Delta H_\infty - \Delta H_r)$ and $X_{\Delta H_r}$ are overstated, which causes the calculated initial glass transition temperature to be higher than the real one. For the samples annealed

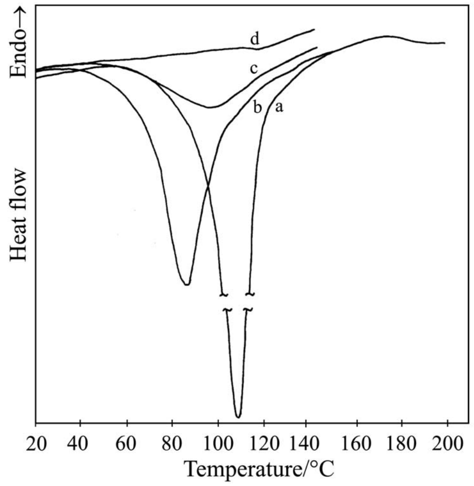

Fig. 1 Example of DSC curves of samples cured isothermally at 100°C for different time: a – 3 min, b – 4 min, c – 4.5 min, d – 7 min

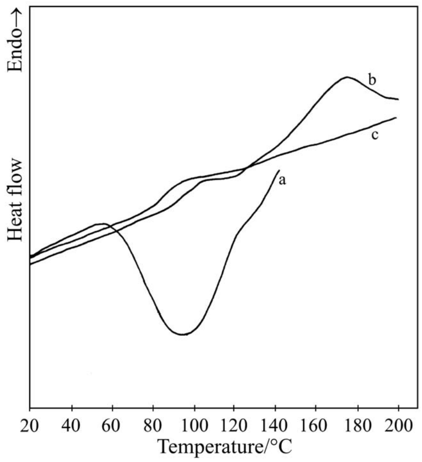

Fig. 2 DSC curves of sample cured isothermally at 100°C for 4.5 min: a – first run, b – second run, c – third run

at 100°C for 7 and 10 min in the dynamic heating curves there appears an endothermic jump corresponding to the glass transition temperatures, below which the polymerization still proceeds. From about 140°C the formed polymer starts to depolymerize as indicated by the endothermic peak (172°C) in DSC profiles (Figs 1 and 2). The following DSC curves of dynamic heating of the reaction system (Fig. 2) show appropriate heat effects, which can be ascribed to the above discussed polymerization, glass transition and depolymerization processes.

For low degrees of conversion (max. 5–6%) the kinetics of radical polymerization in the case of the system under investigation can be described with the use of a conventional kinetic equation of first order:

$$\ln\left(\frac{\Delta H_\infty}{\Delta H_\infty - \Delta H_t}\right) = k^* t \tag{4}$$

where ΔH_∞ – maximal heat of polymerization (–558 J g^{-1}), ΔH_t – polymerization heat released from the beginning of reaction till time t, $k^*=k[\mathrm{I}]^n$, [I] – AIBN concentration, n=0.5, k – the overall constant rate of polymerization.

Based on the DSC curves of isothermal heating of MM with 1.8 mol% of PUDEM in the presence of 0.057 mol dm^{-3} of AIBN, the overall constants of polymerization rate, k, were determined and compared to corresponding literature data for the polymerization of MM (Table 3) [11, 12]. The activation energy determined from Arrhenius relationship was found to be E_a=89.3 kJ mol^{-1}.

The data given in Table 3 indicate that the addition of PUDEM increases the overall constant of MM polymerization rate within the temperature range under investigation. The literature value of activation energy of the MM radical polymerization ranges from 62 to 87 kJ mol^{-1}, thus being lower than that found by us for the polymerization of MM with the addition of a cross-linker.

Table 3 Rate constants of the MM polymerization and the MM polymerization with 1.8 mol% of PUDEM

T/°C	$k\cdot 10^3$/dm$^{3/2}$ s^{-1} mol$^{-1/2}$		
	MM [12]	MM [11]	MM+PUDEM
85	2.97	2.13	3.61
90	3.5	3.15	5.07
95	–	5.17	8.68
100	–	6.92	11.51

E_a was also determined by the isoconversion method. Its value was calculated from the relationship given by Kissinger [20]:

$$\ln\frac{\Phi}{T_p^2}=\ln\frac{AR}{E_a}-\frac{E_a}{R}\frac{1}{T_p} \tag{5}$$

where Φ – dynamic heating rate, T_p – isoconversion temperature, A – frequency factor.

The following heating rates were used: 2, 5, 10, 20, and 40°C min^{-1}. The thermal effect of the MM polymerization with the addition of 1.8 mol% of PUDEM determined on the basis of the dynamic heating of the reaction mixture did not depend on the heating rates: 5 and 10°C min^{-1}, its average value from several measurements was: $\Delta H_\infty=-558$ J g^{-1}. On the other hand, the thermal effect determined from the DSC curve at a heating rate of 40°C min^{-1} was considerably lower due to the observed depolymerization.

From the relationship $\ln\Phi/T_p^2=f(1/T_p)$ for the conversions 2, 20 and 50% the activation energy and frequency factor were determined (Table 4).

Table 4 Kinetic parameters of the MM polymerization with the use of 1.8 mol% of PUDEM determined by Kissinger's method

X/%	E_a/kJ mol^{-1}	$A\cdot 10^{-10}$ min^{-1}
50	75.6	0.9
20	79.2	6.0
2	81.8	40.5
The isothermal method	89.3	55.0

Ozawa's method [21] used to calculate the activation energy allowed for very close values. The values of activation energy and frequency factor determined by the isoconversion method correlate with the results of isothermal measurements. The decrease in activation energy with increasing conversion degree has been already reported in the literature, for instance Gimenez in the case of cross-linking unsaturated modified poly(vinyl alcohol) [22]. This indicates a change in the reaction mechanism during the process.

Conclusions

The isothermal and isoconversion examinations of the free-radical polymerization of MM with the addition of 1.8 mol% of PUDEM initiated with AIBN indicate the dependence of activation energy on the degree of conversion, which indicates a change in mechanism of the process. The studies on the isothermal polymerization of MM with the addition of 1.8 mol% of PUDEM have shown that similarly as in the case of the MM polymerization without the crosslinker for low conversion degrees, the process can be described as a reaction of the first order. The determined value of activation energy of the MM polymerization in the presence of a macromolecular cross-linking agent is higher than the literature values of activation energy of the MM polymerization without this cross-linker. The isoconversion examinations have shown that the activation energy and the frequency factor decreases with the increase in the conversion degree. The values of rate constant (for the given *T*) determined on the basis of Arrhenius relationship depend on the degree of conversion, with the maximum value being about 2% of conversion.

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This work was partly supported by the Committee for Research (KBN) in the framework of project No. 7 T08E 026 20

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