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MULTIMONOMER AND CROSS-LINKED POLYMERS FORMED BY ITS COPOLYMERIZATION
Thermal studies

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Abstract

Differential scanning calorimetry (DSC) and thermogravimetry (TG) were used to examine the thermal behavior of the multimonomer poly[2-(10-undecenoyloxy)ethyl methacrylate] (PUDEM) within the temperature range from –80 to 400°C. DSC measurements indicated that the polymer side chains were able to crystallize in paraffinic phase. PUDEM, added to methyl methacrylate (MM), can effectively copolymerize with essentially no homopolymer produced as shown by DSC (single T_g). The value of T_g depends on the PUDEM content, degree of cross-linking and the presence of free MM in the cross-linked product.

Keywords: DSC, methyl methacrylate, poly[2-(10-undecenoyloxy)ethyl methacrylate], thermoset, TG

Introduction

Cross-linked polymers have been an interesting subject of research for many years due to their use in fields such as dentistry, microelectronics, information storage systems or as absorbents in medicine and chemistry. These materials can be prepared by polymerization or copolymerization of appropriate vinyl monomers in the presence of low-molecular-mass cross-linking compounds. The most frequently used cross-linking compounds include divinyl monomers such as divinylbenzene and diol (dimeth)acrylates [1–9]. It is generally known that considerable influence on the thermostability of polymers is exerted by their chemical structure – the strength of bonds between atoms of macromolecules. The thermal stability of polymers depends also to a great extent on the character of the macromolecular structure (linear, branched or cross-linked) [10]. As a rule, branched polymers are less thermally resistant than linear polymers, while cross-linking increases thermostability.

In the previous work [11], we reported the results of synthesis and characterization of poly[2-(10-undecenoyloxy)ethyl methacrylate] (PUDEM). In the present paper, the

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thermal properties of PUDEM and cross-linked polymers resulted from the free-radical copolymerization of MM and PUDEM were examined by means of DSC and TG.

Experimental

Materials

Methyl methacrylate (MMA) was purified 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 poly[2-(10-undecenoyloxy)ethyl methacrylate] (PUDEM) 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 [11]. The number average molecular mass of PUDEM determined by use membrane osmometer was Mn=27500 g mol^{-1}.

Synthesis of cross-linked PMMA

The free-radical polymerization of MMA in the presence of AIBN as initiator and variable amounts of the PUDEM as cross-linking agent was carried out for 24 h, gradually raising the process temperature from 40 to 75°C. Typical course of this process was as follows: 4.4 cm^3 of MMA, 0.02 g AIBN and the cross-linking agent in amounts ranging from 0.5 to 6.3% mol (calculated per single double bonds of cross-linkers) in relation to the monomer were placed between glass plates (100x50x0.9 mm), previously siliconised with a dimethyldichlorosilane. The polymerization was carried out in a laboratory drier under the following conditions: 2 h at 40°C, 2 h at 55°C and 16 h at 75°C. The gradual temperature raising prevented blister formation in the cross-linked PMMA samples. Solid transparent products were obtained.

Measuring methods

The thermal properties of PUDEM and MM-PUDEM copolymers were measured by DSC, using a DSC-7 Perkin Elmer calorimeter operating with 1020 Series DSC-7 Thermal Analysis System.

The calorimeter was temperature calibrated using dodecane, indium and zinc standards. The heat emission rate axis was calibrated using the heat of fusion of indium (28.45 J g^{-1}) as a standard.

Dynamic measurements were carried out within the temperature range of –80 to 400°C depending on the value being measured, at a heating rate of 10 or 20°C min^{-1} under nitrogen passing at a rate of 25 cm^3 min^{-1}. Weighed samples of 3–15 mg were used. Volatile samples were put in aluminium, airtight sealed vessels. PUDEM was heated in vessels under atmospheric pressure.

Thermogravimetric measurements were carried out using a TGA-7 thermobalance of Perkin-Elmer under nitrogen (heating rate 20°C min^{-1}).

Results and discussion

Figure 1 shows the DSC curves of PUDEM heated, cooled and reheated from –80 to 50°C. In the DSC heating curves (curves a, c), there is an endothermic peak with the heat effect of ΔH=16 J g^{-1}, while the cooling curve (curve b) shows an exothermic peak at –37.7°C. The exothermic and endothermic peaks are connected with the crystallization and fusion of the crystalline phase formed due to the ordered state of the multimonomer side chains, which is in agreement with literature data [12–14].

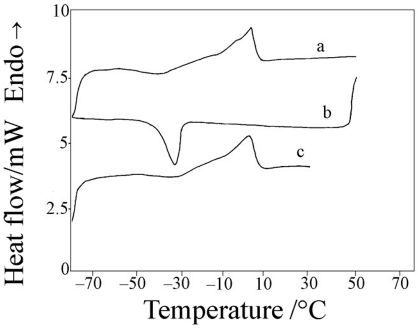

Fig. 1 DSC traces of PUDEM: a – first heating; b – cooling; c – second heating

In our previous paper [11] we found that in the DSC curve of the dynamic heating of PUDEM from 30 to 400°C, there appeared an irregular exothermic peak being a sum of superimposing processes of thermal cross-linking at the expense of multimonomer double bonds (exothermic effect) and the simultaneous decomposition of the sample (endothermic effect). The decomposition was confirmed by the TG analysis. Thus, the heat effect calculated from the peak surface areas amounting to about –150 J g^{-1} cannot be a measure of cross-linking. The heating of PUDEM with an addition of 1% by wt. AIBN divides the cross-linking process (polymerization) into two exothermic peaks with maxima at 130 and 362°C. The first peak corresponds to the cross-linking initiated by the radicals resulted from the initiator decomposition. The second peak, as was previously mentioned, is associated with the thermal cross-linking and degradation [11]. Figure 2a shows the DSC curve of dynamic heating of PUDEM in the presence of 1% by wt. AIBN. The determined thermal effect amounts to –55 J g^{-1} (–16.3 kJ mol^{-1}). This thermal effect is rather low, which means that only some of the PUDEM double bonds are polymerized due to their small accessibility.

Figure 2b shows the DSC curve obtained for the copolymerization of MM with 1.8% mol PUDEM as a macromolecular cross-linking agent and 1% by wt. AIBN taking place during dynamic heating. The heat of MM-PUDEM copolymerization, found on the basis of the peak surface area in curve 2b is –552 J g^{-1}. On the basis of this value, assuming the heat of MM polymerization (–57.5 kJ mol^{-1}) and the PUDEM mole mass 296 g mol^{-1}, the heat of PUDEM polymerization was estimated to be about –70 kJ mol^{-1} (–236 J g^{-1}). Thus, it is almost four times as high as that determined on the basis of the peak of curve 2a. Thus, one may assume that in the case of polymerization of PUDEM itself, only about of 25% mol of double bonds are reacted.

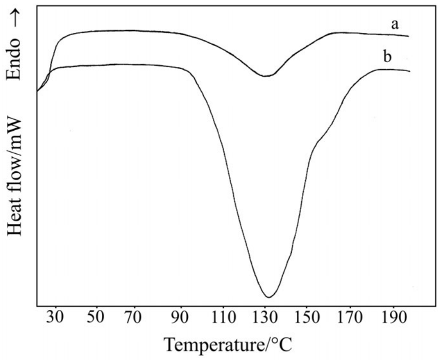

Fig. 2 DSC scans at 20 C min^{-1} on a – PUDEM; b – MM with 1.8% mol PUDEM, in the presence of 1% by wt. AIBN

A sample of PMMA cross-linked with PUDEM (1.8% mol) was subjected to thermogravimetric measurements. Figure 3 shows the TG curves of the cross-linked PMMA (curve a) and untreated PMMA (curve b) prepared and heated under the same conditions. The cross-linked PMMA contains about 4% by wt. of MM. The character of decomposition of both samples is similar and is in agreement with literature data [15, 16]. In the first stage, the branched chain ends, whose number is higher in the cross-linked PMMA, are depolymerized. In the further stage of decomposition, the cross-linked PMMA shows slightly higher thermal stability than PMMA itself.

Glass transition temperatures of the obtained PMMA with various PUDEM contents (0.5, 1.8, 3.6, 6.3% mol) were determined by dynamic heating in the DSC calorimeter. In the first course within the temperature range from 30 to 160°C, there appear exothermic peaks due to the polymerization of unreacted monomers. The glass transition temperatures were determined from the second courses, it measured at midpoint at a heating rate 20°C min^{-1}. The results are given in Table 1.

As is seen, glass transition temperatures decrease with increasing PUDEM content. The effect of macromolecular cross-linking compound on the properties of cross-linked polymer can be considered from various points of view. Nielsen [17]

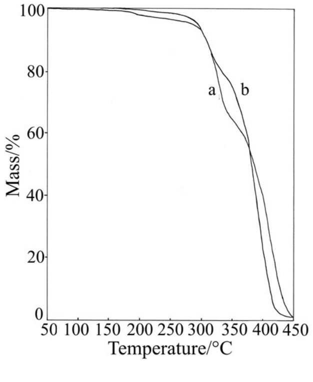

Fig. 3 Thermogravimetry curves of a – cross-linked PMMA; b – untreated PMMA

Table 1 Glass transition temperatures of PMMA with various PUDEM content

Sample	PUDEM /% mol	ΔH / J g^{-1}	$T_{g\,exp}$ / C	$T^{*}_{g\ calc}$/ C
1	0.5	–53.6	109.0	108.6
2	1.8	–9.2	103.0	122.0
3	3.6	–30.1	95.8	139.1
4	6.3	–13.1	91.2	169.2

*calculated with formula (1)

has shown an interesting review of the influences of cross-linking on the physical properties of polymers. In the case of low degrees of cross-linking, this influence is rather low. When more and more cross-linking compound is built into the polymer structure, the polymer chemical composition changes continuously, and so the cross-linking compounds should be treated as comonomer. Changes in T_g are associated with two almost independent effects: the real cross-linking effect, which always results in increased T_g and copolymerization that may either increase or decrease T_g depending on the cross-linking compound structure (in our case it decreases T_g).

Formulas (1) [18, 19] and (2) [20] were used to calculate the glass transition temperature of PMMA cross-linked with PUDEM (1.8% mol).

$$T_{g,\,crl}-T_{g,\,o}=1.2\ T_{g,\,o}\,x_{crl}/(1-x_{crl}) \tag{1}$$

where $T_{g,\,crl}$ – the glass transition temperature of cross-linked PMMA; $T_{g,\,o}$ – the glass transition temperature of uncross-linked PMMA (377 K); x_{crl} – the cross-linking degree calculated as a ratio of the number of cross-linking points to the number of atoms in main chains.

$$T_g=\frac{\alpha_p\Phi_p T_{g_p}+\alpha_m\Phi_m T_{g_m}}{\alpha_p\Phi_p+\alpha_m\Phi_m} \tag{2}$$

where α_p, α_m – differences in the thermal expansion coefficients of polymer and monomer, respectively ($0.48\cdot10^{-3}$ K^{-1} and 10^{-3} K^{-1}) in the liquid and vitrified states; Φ_p, Φ_m – polymer and monomer phase contents, respectively (0.96 and 0.04); T_{g_p}, T_{g_m} – glass transition temperatures of polymer and monomer, respectively (395 K and 167 K).

Formula (2) takes into account the effect of unreacted monomer (MM) on the glass transition temperatures of the polymer-monomer mixture. For a complete reaction x_{crl} =0.036, $T_{g,crl}$=394 K. In the presence of 4% of unreacted MM x_{crl}=0.0375, $\mathrm{T}_{g,crl}$=395 K was taken in formula (2) as T_{g_p} and calculated T_g=376.5 K of the polymer-monomer mixture, which was confirmed experimentally. For the cross-linked PMMA with a higher PUDEM content the values of T_g found experimentally are lower than theoretical values, which may suggest incomplete reaction of PUDEM and consequently a lower degree of cross-linking.

Conclusions

The thermal measurements of PUDEM by DSC have shown the presence of crystalline phase, indicating that polymer side chains are able to crystallize in a paraffinic phase which melts at 2.4°C with ΔH=16 J g^{-1}. During dynamic heating in the DSC calorimeter, the double bonds present in PUDEM are subject to the radical polymerization initiated by AIBN within the temperature range from 90 to 140°C, while the conversion degree of double bonds is about 25%. MM and PUDEM dissolved in it are subject to the radical copolymerization initiated by AIBN. The obtained cross-linked copolymer with a single glass transition temperature indicating a typical single-phase. The value of T_g depends on the PUDEM content, degree of cross-linking and the presence of free MM in the cross-linked product.

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