STUDY OF THE ISOTHERMAL FREE RADICAL POLYMERIZATION OF SOME HIGHER *n*-ALKYL METHACRYLATES

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The free radical polymerizations of higher *n*-alkyl methacrylates were not investigated in detail until now. In this work, the courses of the isothermal free radical bulk polymerization of dodecyl, quatrodecyl and hexadecyl methacrylates were investigated by differential scanning calorimetry. The effects of the polymerization temperature and the alkyl group length in the esters on the monomer conversions during polymerization were studied. It was found that the polymerization rate *vs.* time curves have two maxima. The free radical polymerizations of above-mentioned monomers proceed with slightly expressed gel effect at the temperatures below 90°C, at initiator concentration 1 mass% in monomer.

Keywords: DSC, higher n-alkyl methacrylates, polymerization

Introduction

The higher polyalkyl mathacrylates have a significant practical application. They are used as the additives to improve the lubricating oils properties: viscosities, thermooxidative stability, shear resistance, etc. [1, 2]. From the other point of view the investigation of the courses of corresponding monomers polymerizations are important because of the autoacceleration phenomenon.

The free radical polymerizations of *n*-alkyl methacrylates, and especially that of methyl methacrylate, have been frequently investigated because of the autoacceleration in rate of reaction, known as the gel effect or the Norrish–Trommsdorf effect [3–6]. A number of studies of alkyl methacrylates polymerizations have been published, and many models have been developed with a view to explaining the onset of the gel effect [7–14]. The first to study the course and kinetics of the bulk polymerization of methyl methacrylate by differential scanning calorimetry (DSC) were Horie *et al.* [15]. The kinetics of polymerization of some other alkyl methacrylates were investigated by many authors too [16–20].

In our previous paper [21] we have presented the results of the investigation of lower *n*-alkyl methacrylates (methyl, ethyl and butyl) polymerizations by DSC. The free radical bulk polymerization of above methacrylates are characterized by a strong autoacceleration and with five characteristic events in polymerization rate *vs.* time curves: point M (the onset of autoacceleration), point S (maximum in the polymerization rate), point K (end of the polymerization), and points P and R (maximum and minimum of auto-

acceleration). It was found that the conversion in point M depends similarly on the polymerization temperature and the alkyl group length in the ester. The positions of other characteristic events depend more on the polymerization temperature than on the alkyl group length in the methacrylate [21].

The polymerizations of higher *n*-alkyl methacrylates were not investigated in detail until now. It was found that the overall rate constant of polymerization and the final conversion increase with the increasing of alkyl group length in ester [20]. With increasing length of the alkyl group in the methacrylic ester, the intensity of the gel effect decreases and the conversion at the onset of the gel effect increases [20, 22]. In the polymerization of hexyl methacrylate the gel effect was not observed [20]. A series of polyalkyl methacrylates were prepared from monomer of high purity and subjected to gamma irradiation [23]. Gelation in the *n*-alkyl series was detected at lower doses as the length of the alkyl group increased [23]. In the current literature most of the published data are related to the investigation of the free radical propagation rate coefficients (k_p) of higher alkyl methacrylates polymerizations. The k_p values for the free radical polymerization of dodecyl methacrylate from electron spin resonance spectroscopy analysis [24] are in excellent agreement with the corresponding data from pulsed laser polymerization, the IUPAC-recommended procedure for reliable k_p measurement [25, 26]. Zammit *et al.* [27] concluded that the differences in activation energy for dodecyl methacrylate, from the lower methacrylates are significant (a much lower activation energy for dodecyl methacrylate leads to a higher k_p).

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Cross-linking during free radical polymerization of dodecyl methacrylate (DDMA) was invesigated [28, 29]. Bulk polymerization of DDMA initiated by 2,2'-azobisisobutyronitrile proceeds with low gel effect and formation of a cross-linked polymer in the temperature region from 60 to 90°C [29]. The polymerization conversion, at which an insoluble polymer fraction begins to form, decreases with decreasing polymerization temperature and initiator concentration. Korolev *et al.* [30] were done computer simulation of the structure and thermal stability of higher alkyl methacrylate associates. Obtained results are consistent with the model of regular, kinetically active associates. Methyl methacrylate and higher esters of the methacrylic acid were polymerized at low temperatures [31]. The transition to higher alkyl methacrylates changes the size of the monomer molecules and thus their diffusibilities. The free radical bulk polymerization of lauryl methacrylate in the presence of 2,2'-azobisisobutyronitrile has been studied by DSC in dynamic and isothermal modes [32]. The measured heats of reaction increased with the concentration of the initiator [32]. In the paper of Hempel *et al.* [33] is shown that amorphous as well as semicrystalline polyalkyl methacrylates (with C=12, 16 and 18 alkyl carbons per side chain) can be understood as nanophase-separated polymers with alkyl nanodomains having a typical dimension of 1–2 nm. The kinetics of free radical cross-linking polymerization of methyl methacrylate in the presence of poly[2-(10-undecenoyloxy)ethyl methacrylate as a macromolecular cross-linker has been examined using the DSC [34]. In the paper of Kurmaz *et al.* [35] are shown the results of free radical copolymerization of ethylene glycol dimethacrylate with alkyl methacrylates of various structures and macromolecular design of copolymers. There is some results about the thermomechanical properties of polymeric composites based on alkyl methacrylates [36].

The intention of the present work was a study of some higher *n*-alkyl methacrylates polymerizations which are insufficiently examined. The courses of the isothermal free radical polymerizations of dodecyl, quatrodecyl and hexadecyl methacrylates were investigated by DSC method. The effects of the polymerization temperature and the alkyl group length in the esters on the monomer conversions during polymerization were studied.

Experimental

Chemicals

- Dodecyl methacrylate (DDMA),
  $CH_2=C(CH_3)COO(CH_2)_{11}CH_3$, Merck;

- quatrodecyl methacrylate (QDMA),
  $CH_2=C(CH_3)COO(CH_2)_{13}CH_3$ and
- hexadecyl methacrylate (HDMA),
  $CH_2=C(CH_3)COO(CH_2)_{15}CH_3$ were synthesized.

The monomers were freed of inhibitor before use [21, 29].

- Initiator: 2,2'-azobisisobutyronitrile (AIBN), p.a., Merck, was recrystallized from methanol.

Methods

The bulk polymerizations of DDMA, QDMA and HDMA were studied by DSC, with a DuPont Model 910 instrument. The polymerizations were carried out under isothermal conditions in the temperature range 70–90°C. The initiator concentration was 1 mass%.

The declination on ordinate (*h* in mm, Figs 1 and 2) is proportional to the increase of enthalpy with time, $h=dH/d\tau$ [14, 21]. The heats evolved in the reaction (proportional to the amount of polymerized monomer) were calculated from the areas between the DSC curve and the baseline which was obtained by back-extrapolation of the horizontal straight line, recorded after the polymerization was finished [20, 21, 34]. The amount of unreacted monomer was determined by prolonging the polymerizaton in the dynamic thermal range (from the temperature of isothermal polymerization to 220°C [21].

Results and discussion

DSC curves of monomers polymerization are given in Figs 1 and 2. It is evident that the courses of the higher *n*-alkyl methacrylates polymerizations are different from those of lower *n*-alkyl methacrylates shown in our previous paper [21]. The onset of auto-acceleration (defined as the minimum in the DSC
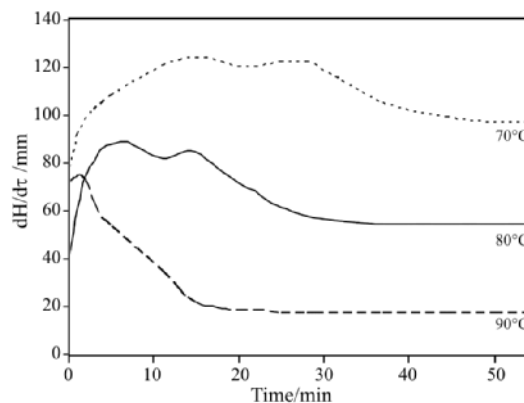

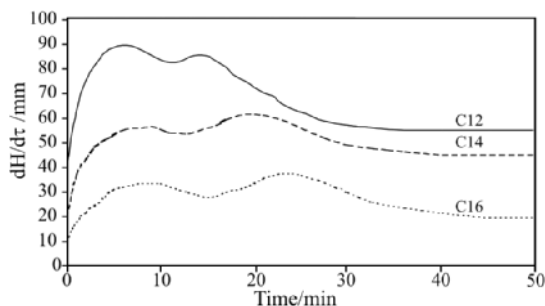**Fig. 1** DSC curves of DDMA polymerization. Effect of polymerization temperature (1 mass% AIBN)

Fig. 2 DSC curves of DDMA, QDMA and HDMA polymerizations at 80°C (1 mass% AIBN)

Fig. 4 Conversion *vs.* time curves of DDMA, QDMA and HDMA polymerizations at 80°C (1 mass% AIBN)

curve) can not be clearly observed in obtained curves. There are two maxima in polymerization curves. With the increase of polymerization temperature (Fig. 1) and the alkyl group length in the esters (Fig. 2) the ratio of the first maximum (at lower conversion) decreases while the ratio of the second maximum (at higher conversion) increases.

Conversion *vs.* time curves of DDMA polymerizations (Fig. 3) do not show a strong autoacceleration in rate of reaction as it was observed with an analogous lower *n*-alkyl methacrylates. The slopes of the conversion *vs.* time curves of DDMA polymerization increase with increase of the polymerization temperature what was expected [21, 28]. Bulk polymerization of DDMA proceeds with low gel effect in temperature range 70–80°C, at concentration of AIBN 1 mass% in monomer. The conversion *vs.* time curves at 70 and 80°C have 'S' shape (characteristic for autoacceleration, Fig. 3). Autoacceleration of DDMA polymerization is observed after about 15 mass% conversion at 80°C, and after 10 mass% conversion at 70°C. Conversion *vs.* time curve of DDMA polymerization at 90°C is continuous and the gel effect is not observed on it. The conversion at the onset of the gel effect increases with increase of the polymerization temperature in accordance with published data for lower *n*-alkyl methacrylates [20, 21, 38] and with the theory of polymerization of organized monomer systems [39]. The theory [39] states that the organization of monomers decreases with increase of the temperature, resulting in shifting the onset of autoacceleration to higher value.
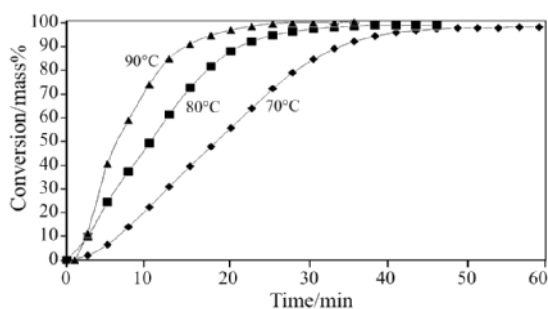

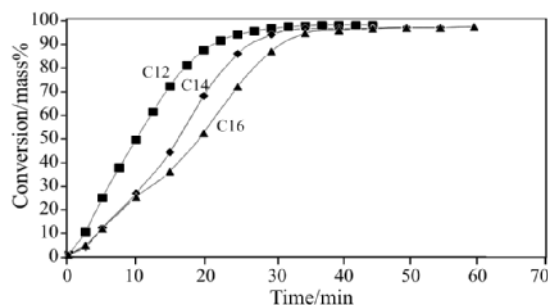**Fig. 3** Conversion *vs.* time curves of DDMA polymerization (1 mass% AIBN)

The slope of the conversion vs. time curve of DDMA polymerization at 80°C is steeper than those of QDMA and HDMA polymerization (Fig. 4). From the 'S'-shapes of presented curves we presume that bulk polymerization of above-mentioned monomers at 80°C are characterized by the gel effect. The autoacceleration of DDMA polymerization starts at conversion of about 15 mass%, in the case of QDMA at conversion of about 30 mass% and in HDMA polymerization at conversion of about 35 mass% (Fig. 4). It can be expected that the degree of organization of monomers will decrease with an increase in alkyl group length. Hence, according to Kargin and Kabanov [39] the autoacceleration will decrease too. Our results confirm this prediction (Fig. 4), since the degree of organization of DDMA is higher than that of QDMA and HDMA, thus the gel effect is stronger expressive in DDMA than in QDMA and HDMA polymerization. Some authors [30, 40] have found that the longer alkyl group in methacrylic ester enables more regularly associative packing of monomer molecules resulting in increase of organization of monomers with an increase in alkyl group length.

The rates of investigated monomers polymerizations were calculated on the basis of the well-known relations from chemical kinetics, using the conversions of monomers determined from DSC curves [41]. Dependence of DDMA polymerization rate on conversion, in temperature range 70–90°C, is given in Fig. 5. From presented curves in Fig. 5 it follows that the polymerization rates at 70 and 80°C are characterized by autoacceleration but much slightly stressed than that was observed with a lower *n*-alkyl methacrylates [21]. The gel effect causes a decrease of the termination reaction rate and increase of the polymerization rate, as well as the lower monomer concentration at high conversion causing a decrease of the polymerization rate (Fig. 5, curves at 70 and 80°C). Clear decrease of the polymerization rate with the increase of conversion, and so limitation of the gel effect, is seen at temperature of 90°C (Fig. 5, curve at 90°C). The polymerization rate *vs.* conversion curves of DDMA, QDMA and HDMA polymerization at 80°C are
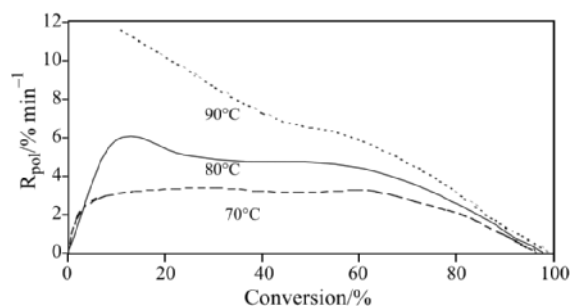
Fig. 5 Polymerization rate *vs*. conversion curves of DDMA polymerization (1 mass% AIBN)
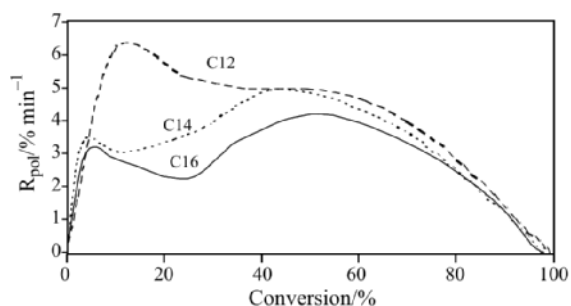

Fig. 6 Polymerization rate *vs*. conversion curves of DDMA, QDMA and HDMA polymerizations at 80°C (1 mass% AIBN)

shown in Fig. 6. From presented curves it is seen that the bulk polymerizations of above-mentioned monomers at 80°C, with 1 mass% of AIBN, are characterized by the gel effect.

The final conversion of DDMA polymerization increases with increase of the reaction temperature (Table 1), in accord with our previous results [21, 41] and with other published data [28, 29]. Values of the final conversions for DDMA vary from 96.9 to 99.1 mass% in temperature range 70–90°C, while for QDMA is 96.5 mass% and for HDMA 97.1 mass% at polymerization temperature 80°C. The alkyl group length does not have a significant effect on the position of the final conversion (Table 1).

Table 1 Final conversions of DDMA, QDMA and HDMA polymerizations (1 mass% AIBN)

Type of monomer	Final conversion/mass% at		
	70°C	80°C	90°C
DDMA	96.9	98.1	99.2
QDMA	–	97.5	–
HDMA	–	97.2	–

All the experimental findings presented in this paper indicate that the free radical polymerizations of DDMA, QDMA and HDMA in bulk are characterized by low gel effect. The onset of the gel effect depends on the polymerization temperature, at the initiator

concentration used, and on the alkyl group length in the ester. It should be noted that shown results provide qualitative information on the courses of some higher *n*-alkyl methacrylates polymerizations and the same could be the basis for the future research on kinetic aspects of that polymerizations. It is necessary to continue this investigation by examination of higher *n*-alkyl methacrylates polymerizations at temperatures below 80°C at which the gel effect should be observed.

Conclusions

The free radical polymerizations of DDMA, QDMA and HDMA in bulk were investigated by DSC. The effects of the polymerization temperature and the alkyl group length in the esters on the monomer conversions during polymerization were studied.

It was found that the free radical polymerizations of above-mentioned monomers are characterized by low gel effect at the temperatures below 90°C, at initiator concentration used. The conversion at the onset of the autoacceleration increases with increase of the polymerization temperature and with increase in the alkyl group length in the methacrylic acid ester.

Acknowledgements

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