

# Analysis of DSC curve of dodecyl methacrylate polymerization by two-peak deconvolution method

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**Abstract** Free radical polymerization of *n*-dodecyl methacrylate (DDMA) in bulk has been investigated by differential scanning calorimetry (DSC). Autoacceleration of reaction was observed at the temperatures 70, 80, and 90 °C, with 0.25, 0.5, and 1 wt% of initiator, and was absent at 100 °C. DSC curves obtained at the temperatures below 100 °C were characterized by two maxima. Two-peak deconvolution was used to separate DSC curve into two constitutive unimodal curves, i.e., to calculate the contribution of polydodecyl methacrylate formed before (first maximum) and after (second maximum) the onset of autoacceleration. The share of second maximum decreases as the polymerization temperature and initiator concentration are increased. As the organization of monomer is known to decrease with increasing temperature, it can be expected that the fraction of polymerized disordered phase of monomer (first maximum in DSC curve) is the highest at 90 °C. Our results confirm this prediction and are in good agreement with those observed from conversion versus time curves of DDMA polymerization.

**Keywords** Autoacceleration · Dodecyl methacrylate · DSC · Free radical polymerization · Two-peak deconvolution

## Introduction

Autoacceleration in the rate of the polymerization is the phenomenon that often occurs during the free radical

polymerization of vinyl monomers in bulk at intermediate or high degrees of conversion [1–3]. Autoacceleration in the polymerization of some alkyl methacrylates, especially that of methyl methacrylate, has been observed by many investigators [4–7], and many models have been developed with a view to explain the onset of that phenomenon. The conversion at the onset of autoacceleration increases with increasing the length of the alkyl group in the ester [8, 9]. Interest in the polymerization of dodecyl methacrylate (DDMA) results primarily from the significant commercial importance of polydodecyl methacrylate as the additive for improvement of lubricating oils properties [10] and, from a more fundamental viewpoint, the fact that autoacceleration phenomenon is observed in the bulk polymerization of DDMA [9, 11].

The kinetics of free radical polymerization of DDMA was studied at 60 and 80 °C in bulk and in benzene solution [12]. The analysis of the data showed the kinetic results deviated from classical behavior and that this deviation could be explained by the chain length dependence on the diffusion controlled termination rate constant [12]. It was found that the free radical polymerizations of some higher *n*-alkyl methacrylates (dodecyl, quaterdecyl, and hexadecyl methacrylates) are characterized by non-intensive autoacceleration at temperatures below 90 °C [9]. The intensity of autoacceleration decreases as the alkyl group length in the esters increases [9]. Bulk polymerization of DDMA initiated by 2,2-azobisisobutyronitrile (AIBN) proceeds with low autoacceleration and formation of a cross-linked polymer in the temperature region from 60 to 90 °C [11]. The polymerization conversion, at which an insoluble polymer fraction begins to form, decreases with decreasing polymerization temperature and initiator concentration [11]. The free radical bulk polymerization of DDMA in the presence of AIBN has been studied by

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differential scanning calorimetry (DSC) and it was found that the measured heat of reaction increased with the concentration of the initiator [13]. In the article of Kale et al. [14], the free radical polymerization of DDMA has been studied using a combination of rheological and kinetic methods. Simultaneous measurements provided the data for correlating changes in the kinetics with changes in the rheology of the polymerizing system. Controlled polymerization of higher alkyl methacrylates, e.g. DDMA and stearyl methacrylate, has been successfully achieved by atom transfer radical polymerization (ATRP) at ambient temperature [15]. Dinitroalkyl acrylates and methacrylates were synthesized and the kinetics of their free radical polymerizations in the presence of AIBN was investigated by DSC in the non-isothermal mode [16]. DDMA star-like polymers were synthesized by ATRP, and the influence of the experimental parameters on the structures of synthesized polymers was studied [17].

The intention of this article was to study the course of DDMA free radical isothermal polymerization in bulk by DSC method. The contribution of polydodecyl methacrylate formed before and after the onset of autoacceleration was calculated by two-peak deconvolution of experimental curves.

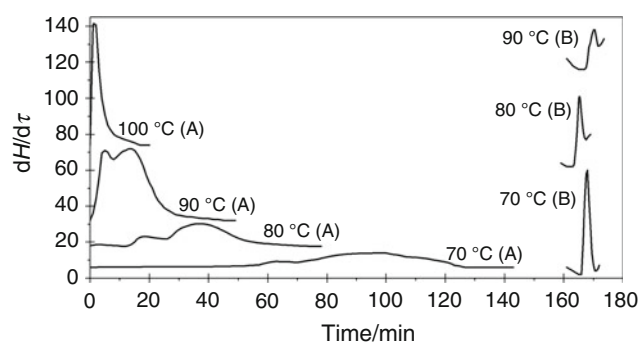
## Experimental

### Chemicals

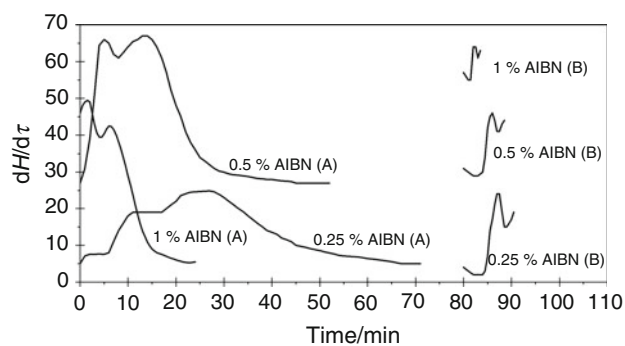
- Dodecyl methacrylate (DDMA),  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_{11}\text{CH}_3$ , Merck, was freed of inhibitor before use. It was washed with 10% aqueous NaOH solution, dried over anhydrous  $\text{CaCl}_2$ , and then vacuum distilled [9, 11].
- Initiator: 2,2'-azobisisobutyronitrile (AIBN), p.a., Merck, was recrystallized from methanol.

### Method

The bulk polymerization of DDMA was carried out in DSC with a TA Model Q20 instrument. The temperature and heat flow scales were calibrated using the melting of high-purity indium. About 5–10 mg of monomer was put into hermetic aluminum DSC pan and sealed with an aluminum lid. Nitrogen was used as purge gas with flow rate of  $50 \text{ mL min}^{-1}$ . The polymerizations of DDMA were performed under isothermal conditions (at 70, 80, 90, and 100 °C). Concentration of the initiator (AIBN) was varied from 0.25 to 1 wt% at 90 °C. The declination on ordinate ( $h$  in mm; Figs. 1, 2) is proportional to the increase of enthalpy with time,  $h = dH/d\tau$  [9]. The amount of polymerized monomer (proportional to the heat evolved in the



**Fig. 1** Isothermal (A) and dynamic (B) DSC curves of DDMA polymerization. Effect of polymerization temperature (0.5 wt% AIBN)



**Fig. 2** Isothermal (A) and dynamic (B) DSC curves of DDMA polymerization. Effect of initiator concentration ( $T = 90 \text{ °C}$ )

reaction) was calculated from the area between the DSC curve and the baseline (Figs. 1A, 2A) using method described in literature [8, 9, 18, 19]. The amount of unreacted monomer was determined by prolonging the polymerization in the dynamic thermal range, from the temperature of isothermal polymerization to  $220 \text{ °C}$  [8, 9] at heating rate  $10 \text{ °C min}^{-1}$ . The total reaction enthalpy of DDMA polymerization is proportional to the sum of areas A (under isothermal DSC curves; Figs. 1A, 2A) and B (under dynamic DSC curves; Figs. 1B, 2B). The area under the dynamic DSC curve (Figs. 1B, 2B) presents the amount of unreacted monomer [8, 9].

## Results and discussion

DSC curves of DDMA isothermal polymerization with 0.5 wt% AIBN are given in Fig. 1A. There are two maxima in polymerization curves at 70, 80, and 90 °C. With the increase of polymerization temperature, the share of the first maximum (at lower time) increases while the share of the second maximum (at higher time) decreases. DSC curve of DDMA polymerization at 100 °C has only one maximum (Fig. 1A).

With increase of the initiator concentration from 0.25 to 1 wt%, at 90 °C (Fig. 2A), the share of the first maximum in DSC curve of DDMA polymerization increases.

On the basis of presented DSC curves (Figs. 1A, 2A), we can assume that the free radical polymerization of DDMA at temperatures below 100 °C is separated into two stages: before and after the onset of autoacceleration. A two-peak deconvolution method [20, 21] used in this study enables deconvolution of bimodal DSC curves by means of two characteristic unimodal curves. The first peak (maximum), located at low time (conversion), characterizes the polymer formed during the first part of the polymerization (up to the onset of autoacceleration); the second peak (maximum), at higher time (conversion), represents the contribution of the polymer fraction which has been formed after autoacceleration (Figs. 1A, 2A). In order to give an estimate of the ratio of both fractions in the final curve, it is necessary to analyze these two peaks separately. Because of overlapping, this is not possible. Deconvolution is a mathematical process of extracting constitutive peaks from the cumulative curve. In this study, Origin 8.0 was used to extract constitutive peaks from DSC curves (Figs. 1A, 2A). When the peaks were identified, numerical integration was applied, resulting in a value for the area under each maximum and under the cumulative curve. Now, simply dividing the area under each peak by the area under cumulative DSC curve gives the percentage of monomer conversion before and after the onset of autoacceleration (Table 1).

The share of second peak which represents the contribution of polymerized DDMA after autoacceleration decreases as the polymerization temperature is increased from 70 to 90 °C. The same happens as initiator concentration is increased from 0.25 to 1 wt% (Table 1). The theory of the polymerization of organized monomers [22] suggests that up to onset of autoacceleration, monomer from the disordered phase is polymerized and, after that moment monomer from the ordered phase is polymerized. As the organization of monomer is known to decrease with increasing temperature [22], it can be expected that the fraction of polymerized disordered phase of monomer (first maximum in DSC curve) is the highest at 90 °C. Our

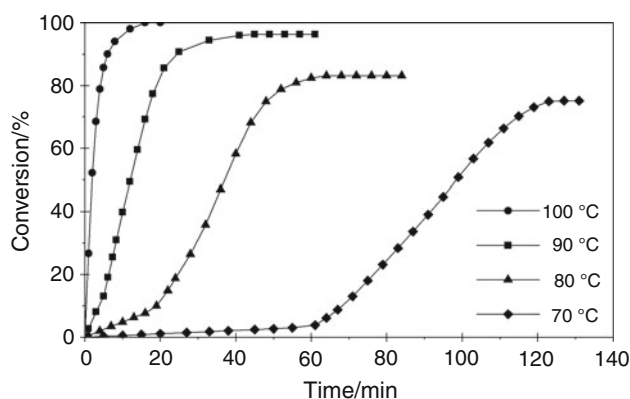
**Table 1** Results obtained by two-peak deconvolution of DSC curves

Concentration of AIBN/wt%	Polymerization temperature/°C	Share of the first peak/%	Share of the second peak/%
0.25	90	6.6	93.4
0.5	70	6.0	94.0
0.5	80	10.3	89.7
0.5	90	13.9	86.1
1	90	37.9	62.1

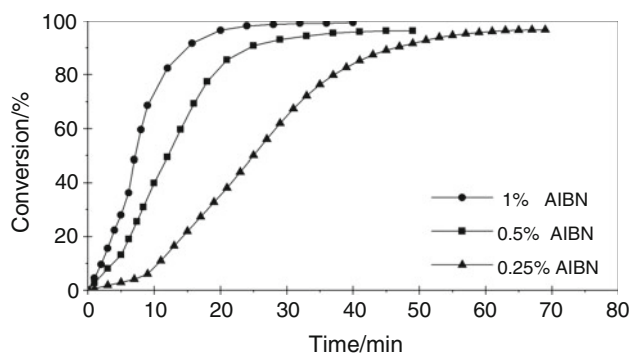
results (Table 1) are in accordance with this prediction. There is some literature data which confirm that DDMA is partially organized monomer [23].

We propose that by two-peak deconvolution of experimental DSC curve, it is possible to separate the contribution of polydodecyl methacrylate obtained before and after onset of autoacceleration. Calculated percentage of area under the first peak (contribution of polymerized monomer up to the onset of autoacceleration; Table 1) is in good agreement with conversion at the transition point from linear to “S” shape, defined as the onset of autoacceleration [7, 8, 24] in experimental conversion versus time curves of DDMA polymerization (obtained from DSC curves; Figs. 3, 4).

The conversion versus time curves of DDMA polymerization at 70, 80, and 90 °C have “S” shape, that is characteristic for autoacceleration of the polymerization (Fig. 3). The transition from linear to “S” shape of curve, i.e., the onset of autoacceleration is observed after about 4 wt% of monomer conversion at 70 °C, after 9 wt% of monomer conversion at 80 °C, and after about 13.5 wt% of monomer conversion at 90 °C (Fig. 3). Values of monomer



**Fig. 3** Conversion versus time curves of DDMA polymerization. Effect of polymerization temperature (0.5 wt% AIBN)



**Fig. 4** Conversion versus time curves of DDMA polymerization. Effect of initiator concentration ( $T = 90$  °C)

conversions up to the onset of autoacceleration determined from Fig. 3 are similar with data obtained by two-peak deconvolution of DSC curves, presented in Table 1 (share of the first peak). Conversion versus time curve of DDMA polymerization at 100 °C is continuous, and autoacceleration is not observed on it (Fig. 3). This observation is in accordance with obtained DSC curve of DDMA polymerization at 100 °C which has only one maximum (Fig. 1).

Conversion at the onset of autoacceleration increases with increase of initiator concentration (Fig. 4). The onset of autoacceleration at 90 °C is observed after about 5 wt% of DDMA conversion with 0.25 wt% AIBN, after 13.5 wt% of DDMA conversion with 0.5 wt% AIBN, and after about 36.5 wt% of DDMA conversion with 1 wt% AIBN (Fig. 4). These results are in accordance with values of DDMA conversions calculated by two-peak deconvolution (share of the first peak; Table 1).

Good agreement of data calculated by two-peak deconvolution presented in Table 1 and results determined from Figs. 3 and 4 show that simply two-peak deconvolution method can be useful for analysis of DSC curve of isothermal DDMA polymerization at temperatures below 100 °C, respectively, for the study of the effects of polymerization conditions on the onset of autoacceleration in reaction.

## Conclusions

Free radical polymerization of DDMA in bulk is characterized by autoacceleration at the temperatures 70, 80, and 90 °C with used concentrations of AIBN. DSC curves of DDMA isothermal polymerization at temperatures below 100 °C have two maxima. The first maximum corresponds to monomer that was polymerized up to the onset of autoacceleration. The second maximum represents the contribution of the monomer which was polymerized after autoacceleration. Two-peak deconvolution was used to separate DSC curve into two constitutive unimodal curves and calculate the contribution of polydodecyl methacrylate formed before and after autoacceleration. The share of second maximum decreases as the polymerization temperature and initiator concentration are increased. As the organization of monomer is known to decrease with increasing temperature, it can be expected that the fraction of polymerized disordered phase of monomer (first maximum in DSC curve) is the highest at 90 °C. Our results confirm this prediction and are in good agreement with those observed from experimental conversion versus time curves of DDMA polymerization. The data presented in this article show that DSC curve of DDMA polymerization with two maxima can be analyzed by two-peak deconvolution method.

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## References

- Norrish RW, Smith RR. Catalysed polymerization of methyl methacrylate in the liquid phase. *Nature*. 1942;150:336–7.
- Trommsdorff E, Kohle H, Lagally P. Zur polymerisation des methacrylsäure-methylesters. *Makromol Chem*. 1948;1: 169–98.
- Cardenas JN, O'Driscoll KF. High-conversion polymerization. I. Theory and application to methyl methacrylate. *J Polym Sci Polym Chem*. 1976;14:883–97.
- Lee H, Turner D. Autoacceleration of free-radical polymerization. 2. Methyl methacrylate. *Macromolecules*. 1977;10: 226–31.
- Burnett GM, Duncan GL. High conversion polymerisation of vinyl systems. I. Methyl methacrylate. *Makromol Chem*. 1962; 51:154–70.
- North AM, Postlethwaite D. The copolymerization of methyl-methacrylate and maleic anhydride. *Polymer*. 1964;5:237–49.
- Otsu T, Ito T, Imoto M. Vinyl polymerization. LXXIX. Effect of the alkyl group on the radical polymerization of alkyl methacrylates. *J Polym Sci A*. 1964;2:2901–6.
- Radičević R, Stoiljković D, Budinski-Simendić J. Characteristic events in free radical polymerization of lower n-alkyl methacrylates. *J Therm Anal Calorim*. 2000;62:237–49.
- Radičević R, Stoiljković D, Budinski-Simendić J. Study of the isothermal free radical polymerization of some higher n-alkyl methacrylates. *J Therm Anal Calorim*. 2007;90:243–7.
- Jukić A, Rogošić M, Janović Z. Miscibility and interactions of polystyrene/polyolefine and polystyrene/poly(n-alkyl methacrylate) mixtures in dilute xylene solutions. *Eur Polym J*. 2006;42: 1105–12.
- Lazár M, Hřčková L, Fiedlerova A, Borsig E. Crosslinking during radical polymerization of dodecyl methacrylate. *Macromol Mater Eng*. 2000;283:88–92.
- Mahabadi HKh, O'Driscoll KF. Free radical polymerization kinetics of n-lauryl methacrylate. *Makromol Chem*. 1978;179: 1921–8.
- Mahato PK, Chanda D, Borthakur A, Raol KU. Free-radical polymerization of lauryl methacrylate by differential scanning calorimetry. I. Enthalpy of polymerization. *Thermochim Acta*. 1993;222:265–71.
- Kale LT, O'Driscoll KF. Rheokinetics of polymerization of N-laurylmethacrylate. *Polym Eng Sci*. 1982;22:402–9.
- Chatterjee DP, Mandal BM. Facile atom transfer radical homo and block copolymerization of higher alkyl methacrylates at ambient temperature using CuCl/PMDTA/quaternaryammonium halide catalyst system. *Polymer*. 2006;47:1812–9.
- Zhang GZ, Du SH, Wang J, Wang XC. Differential scanning calorimetric study on free-radical polymerization of gem-dinitroalkyl acrylates and methacrylates. *J Therm Anal Calorim*. 2009;95:433–6.
- Qiu L, Wang Y, Lin Q, Zhou X. Synthesis of Lauryl methacrylate star-like polymers via ATRP. *Asia Pac J Chem Eng*. 2009. doi: 10.1002/apj.317.
- Szocik H, Jantas R. Calorimetric study of cross-linking polymerization of methyl methacrylate in the presence of a multimonomer. *J Therm Anal Calorim*. 2004;78:897–904.
- Jovičić M, Radičević R, Budinski-Simendić J. Curing of alkyds based on semi-drying oils with melamine resin. *J Therm Anal Calorim*. 2008;94:143–50.

20. Radičević R, Kisin S, Krakovsky I. Analysis of the molecular weight distribution of polystyrene. *Chromatographia*. 2004;59:621–4.
21. Maschio G, Scali C. Analysis of the molecular weight distribution in free radical polymerization: modelling of the *MWD* from the analysis of experimental GPC curves. *Macromol Chem Phys*. 1999;200:1708–21.
22. Kargin VA, Kabanov VA. Polimerizatsiya v strukturirovannykh sistemakh. *Zh Vses Khim Ob*. 1964;9:602–31.
23. Korolev GV, Mogilevich MM, Il'in AA. Assotsiatsiya zhidkikh organicheskikh soedinenii. Moskva: Mir; 2002.
24. Malavašić T, Osredkar U, Anžur I, Vizovišek I. Study of the polymerization of some methacrylic acid esters by differential scanning calorimetry. *J Therm Anal*. 1984;29:697–700.