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Free-radical polymerization of lauryl methacrylate by differential scanning calorimetry.
Part 1. Enthalpy of polymerization

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Abstract

The free-radical bulk polymerization of lauryl methacrylate (LMA) in the presence of 2,2′-azobisisobutyronitrile (AIBN) has been studied by differential scanning calorimetry (DSC) in dynamic and isothermal modes. The measured heats of reaction ΔH, increased with the concentration of the initiator. The enthalpy of polymerization in the presence of a large excess of AIBN was obtained by extrapolation. At low concentrations of AIBN, a constant heat of polymerization of LMA ($-41.7\ \mathrm{kJ\ mol^{-1}}$) was obtained after correcting for both the incomplete conversion to polymer and the decomposition enthalpy of AIBN.

INTRODUCTION

Calorimetry is a powerful method for the direct measurement of the rate of an exothermic polymerization. Differential scanning calorimetry (DSC) has been used with success to follow the course of free-radical polymerizations with bulk monomer using either an isothermal or scanning method [1–6].

A knowledge of the rate of free-radical bulk polymerization of a monomer up to high conversion is of both technical and scientific interest. Lauryl methacrylate (LMA) can be polymerized by free-radical initiators such as benzoyl peroxide or 2,2′-azobisisobutyronitrile (AIBN) but calorimetric studies on the free-radical polymerization of LMA in bulk monomer are scarce. Nor have any enthalpic studies of this reaction been reported. This DSC study intends to add to the existing knowledge on the free-radical homopolymerization of LMA in bulk.

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EXPERIMENTAL

Lauryl methacrylate (LMA) was prepared by esterification of methacrylic acid with lauryl alcohol (Henkel, KGaa) (purity >99%) in an excess of methacrylic acid (Merck). The latter was purified by distillation under a reduced pressure of nitrogen. The esterification was carried out in the presence of *p*-toluene sulphonic acid in benzene solution. Hydroquinone was used as an inhibitor. The unreacted acid was removed by washing with dilute alkali and subsequently with distilled water until the washings were neutral. The LMA was further purified by distillation under a reduced pressure of nitrogen (b.p. 140°C/4 mmHg). The purity of the LMA obtained was found to be >99.5% by gas-liquid chromatography (GLC). The 2,2′-azobisisobutyronitrile (AIBN) (BDH) was recrystallized twice from ethanol.

The calorimetric measurements, dynamic as well as isothermal, were performed using a Perkin-Elmer PC series 7 differential scanning calorimeter calibrated for temperature and enthalpy response with indium. The enthalpy measurements were accurate to within 2% reproducibility. The measurements were performed under nitrogen in aluminium pans filled with 10 mg of the reaction mixture (monomer + initiator) for each polymerization experiment. Dynamic and isothermal polymerization were carried out by placing the aluminium pans containing the reaction mixture into the DSC cell. A nitrogen flow rate of 20 $cm^3 min^{-1}$/min was used throughout.

Immediately after each run, the contents of the pans were dissolved in tetrahydrofuran (THF) for the determination of molecular weight distribution and percent conversion by gel permeation chromatograph (GPC). A Waters GPC was used, with columns of porosity 10^6, 10^5, 10^4 and 500 Å in series. The GPC was calibrated with narrow-distribution polystyrene samples. The monomer portion was separated clearly and the areas under the polymer and monomer GPC curves were integrated using a Waters data module. A flow rate of 1 $cm^3 min^{-1}$ of THF was used.

RESULTS

The polymerization of LMA in bulk at various molar ratios of [LMA]/[AIBN] was carried out under isothermal conditions at 383 K. The investigation was carried out over the conventional initiator concentration range as used in typical dilatometry [7]. The reaction did not occur to any measurable extent below a concentration of 5.5×10^{-4} mol dm^{-3} of AIBN under isothermal conditions at 383 K, even after 120 min. This eliminates the possibility of free radical self-initiated bulk polymerization of LMA at this temperature. Furthermore, the polymerization did not occur to any measurable extent at temperatures below 348 K. This behaviour agrees well with that reported by Severini and Gallo [8] according to which the

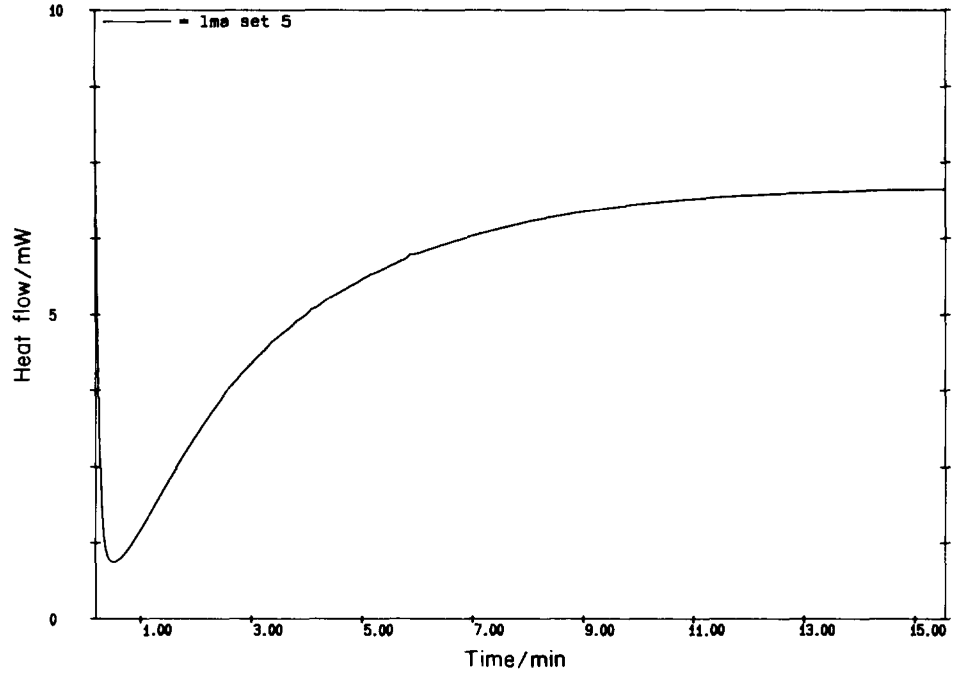

Fig. 1. Typical DSC curve at 383 K of an LMA–AIBN mixture with [LMA]/[AIBN] = 70.

decomposition reaction of AIBN is significant in DSC only at or above 353 K. Figure 1 shows a typical DSC trace at 383 K of an LMA–AIBN mixture with a molar ratio of 70. Figure 2 shows the change in reaction heat with the molar ratio. It is evident from Fig. 2 that a finite value of ΔH cannot be obtained when the curve is extrapolated to a molar ratio zero.

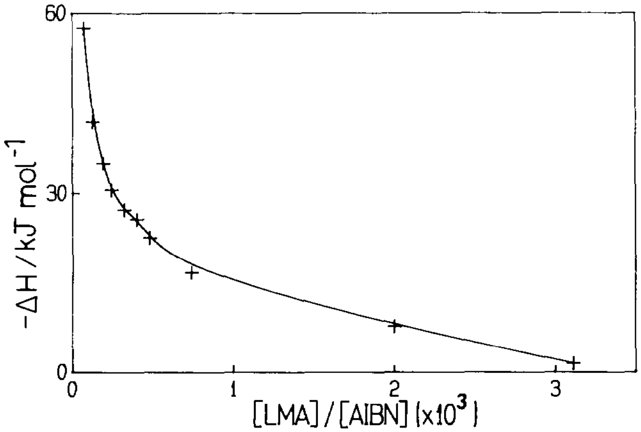

Fig. 2. Change in the uncorrected reaction enthalpy with molar ratio [LMA]/[AIBN] (reaction temperature 383 K).

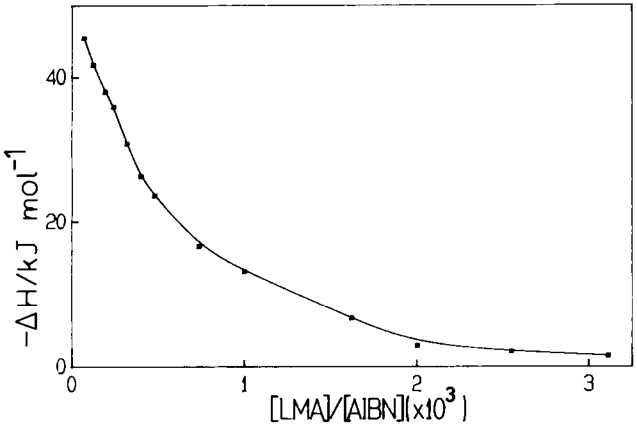

Fig. 3. Change in the reaction enthalpy (corrected for the decomposition enthalpy of AIBN) with molar ratio [LMA]/[AIBN] (reaction temperature 383 K).

However, subtraction of the enthalpy of decomposition of AIBN from the measured values for the reaction at that temperature leads to a value of ΔH upon extrapolation to zero molar ratio (Fig. 3). This is in agreement with results obtained by Gallo and Severini [4] from their enthalpic studies on the polymerization of maleic anhydride.

The polymerization of LMA in bulk at various molar ratios was also carried out under dynamic conditions at two scanning rates. Dynamic tests also produced a regular change in reaction heats with the molar ratio. The best results were obtained with a scanning rate of 20 K min^{-1} (Fig. 4). Figure 5, curve a is a plot of ΔH values, obtained by subtracting the decomposition ΔH value of AIBN obtained under the same conditions from the measured ΔH value, against molar ratio.

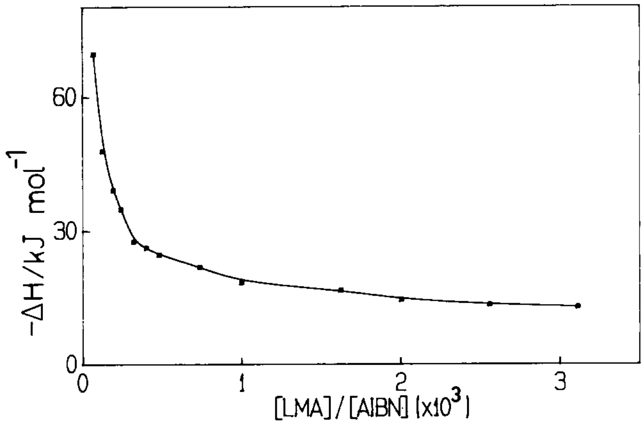

Fig. 4. Change in the uncorrected reaction enthalpy with molar ratio [LMA]/[AIBN] (scanning rate 20 K min^{-1}).

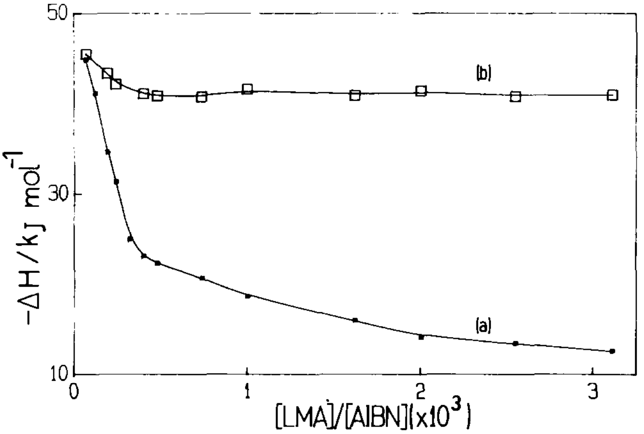

Fig. 5. Curve a. Change in the reaction enthalpy (corrected for the decomposition enthalpy of AIBN) with molar ratio [LMA]/[AIBN] (scanning rate 20 K min^{-1}). Curve b. Change in the reaction enthalpy (corrected for both the decomposition enthalpy of AIBN and for incomplete conversion of monomer to polymer) with molar ratio [LMA]/[AIBN] (scanning rate 20 K min^{-1}).

The total conversion of monomer to polymer was determined by gel permeation chromatography (GPC) for each of the samples obtained from dynamic tests at a scanning rate of 20 K min^{-1}. Figure 5, curve b shows the plot of ΔH, obtained after correcting for both the decomposition ΔH value of AIBN under the same conditions and for incomplete conversion of monomer to polymer, against molar ratio.

DISCUSSION AND CONCLUSIONS

The self-initiated bulk polymerization of LMA was not measurable by DSC under isothermal conditions at 383 K, even after 2 h. The free-radical bulk polymerization of LMA could only be detected when the concentration of AIBN exceeded 5.5×10^{-4} mol dm^{-3}. The absolute ΔH value increases with the increase in the concentration of the initiator (Fig. 3 and Fig. 5, curve a). Notable changes are observed from 6.23×10^{-3} mol dm^{-3} of AIBN in the case of the isothermal test, and from 9.35×10^{-3} mol dm^{-3} of AIBN in the case of the dynamic test at a scanning rate of 20 K min^{-1}. When these curves are extrapolated to zero molar ratio, the ΔH values of -50.5 and -51.1 kJ mol^{-1} are obtained from the isothermal and dynamic plots, respectively. The ΔH values obtained by extrapolating the curves of Figs. 2 and 4 to a molar ratio of zero represent the heat generated by the reaction of LMA with a large excess of the radical initiator. The GPC data of the polymer samples formed at high concentration of AIBN indicated the formation of relatively low molecular weight species. This may be due to the chain-transfer reactions of the radical initiator. Thus, at least two

TABLE 1

Enthalpy of polymerization ΔH (uncorrected) and GPC data of polyLMA samples obtained at various initiator concentrations at a scanning rate of 20 K min^{-1}

[AIBN]/ mol dm^{-3}	Conversion in %	$\bar{M}_n$ $\times 10^3$	$\bar{M}_w$ $\times 10^3$	$-\Delta H$/ kJ mol^{-1}
4.71×10^{-2}	85	44	106	53.60
1.37×10^{-2}	79	60	178	36.50
8.31×10^{-3}	61	70	242	27.27
6.93×10^{-3}	53	77	265	23.52
1.15×10^{-4}	28	83	493	12.47
8.06×10^{-4}	19	98	512	8.08

terms contribute to these total values, ΔH of polymerization and ΔH of chain transfer of the initiator [9].

When the conversion of monomer to polymer was taken into consideration and corresponding corrections were made for incomplete conversion to polymer, the ΔH values tended to be approximately constant. This is obvious, because the large variations in ΔH (Fig. 3 and Fig. 5, curve a) with molar ratio, even after correction for the decomposition ΔH of AIBN, arises mainly from the variation in percent conversion of monomer to polymer (Table 1). It can be seen from Table 1 that at relatively lower concentration of AIBN, the percent conversion of monomer to polymer is low.

When the corrected ΔH values obtained from dynamic tests at a scanning rate of 20 K min^{-1} were further corrected for incomplete conversion to polymer, a constant value of $\Delta H(-41.7\ \text{kJ mol}^{-1})$ was obtained in the low concentration range of AIBN (Fig. 5, curve b). At this point, it is quite reasonable to assume that at relatively lower concentrations of AIBN, the contribution of the ΔH of the chain-transfer reactions of the initiator to the obtained ΔH value is negligibly small. Hence, the value -41.7 kJ mol^{-1} may be considered to be the ΔH of polymerization of LMA, ignoring the small contributions from the termination reactions. It is also possible to obtain the ΔH value of -46.6 kJ mol^{-1} when Fig. 5 curve b is extrapolated to zero molar ratio. The difference in the two ΔH values (-4.9 kJ mol^{-1}) may be attributed to the chain-transfer reactions occurring in the presence of a large excess of AIBN.

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REFERENCES

1 K. Horie, I. Mita and H. Kambe, J. Polym. Sci., Part A-1, 6 (1968) 2663.
2 J.R. Ebdon and B.J. Hunt, Anal. Chem., 45 (1973) 804.
3 G.O.R. Alberda Van Ekenstein and Y.Y. Tan, Eur. Polym. J, 17 (1981) 839.
4 R. Gallo and F. Severini, Thermochim. Acta, 147 (1989) 93.
5 F. Severini, R. Gallo and G. Ricca, Thermochim. Acta, 132 (1988) 161.
6 I.A. Katime, F. Palomares, L.C. Cesteros, C. Laborrea and E. Dominguez, Thermochim. Acta, 142 (1989) 317.
7 N.N. Dass, Prog. Polym. Sci., 10 (1984) 51.
8 F. Severini and R. Gallo, J. Therm. Anal., 30 (1985) 841.
9 M.S. Kellou and G. Jenner, Eur. Polym. J., 12 (1976) 883.