

DSC INVESTIGATIONS ON THE ALKALINE POLYMERIZATION OF ϵ -CAPROLACTAM

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Both the activated and the non-activated alkaline polymerization of ϵ -caprolactam were studied by DSC. In the latter case, a curve-resolving method was applied to separate the superimposed polymerization and crystallization processes. The counter-ion effect was taken into account in the complexing of the initiator cations by crown compounds.

Both the non-activated and the activated alkaline polymerization of ϵ -caprolactam (CL) can be well studied by DSC, although this method is very rarely used. The superimposed polymerization and crystallization in the DSC traces of the activated anionic polymerization of CL may be separated and quantified by the curve-resolving technique proposed by Karger-Kocsis and Kiss [1]. The method to be presented in the present paper is suitable for study of the counter-ion effect in the anionic polymerization of CL, even if this has been complexed by crown compounds.

Experimental

Samples of freshly-distilled CL were melted under a protecting nitrogen atmosphere in a suitable device, and dehydrated by keeping them at 120–140° and 666 Pa for about 15–20 min. The melt was then cooled to its melting temperature and the calculated amount of alkali metal was added so that the given mole percentage of the alkali metal lactamate (LiL, NaL or KL) initiator was reached. Weighed glass vials fitting into the cell of the DSC equipment were kept in a desiccator until use. Samples for non-activated polymerization were prepared by introducing a known amount of molten CL loaded with initiator into the vial, which was then sealed under nitrogen. For the activated anionic polymerization of CL, N-acetylcaprolactam (NACL) and an aliphatic or aromatic diisocyanate (hexamethylenediisocyanate (HMDI) or 4,4'-diisocyanate-diphenylmethane (MDI) were used as activators. Appropriate amounts of these compounds were weighed into the vials, and the molten initiator containing CL was introduced. Sealing of the vial was preceded by dissolution of the activator in the molten CL by shaking, and followed by quenching in liquid nitrogen. The crown compounds were added either to the molten CL containing initiator [when octamethylcyclotetrasiloxane (D_4) or decamethylcyclopentasiloxane (D_5) was used] or to the activator in the vial (in the case of dibenzo-18-crown-6, DB18C6).

Curves were recorded with Unirelax equipment (Tetrahedron Ass. Inc.) in a modified Calvet heat-conducting DSC cell at a heating or cooling rate of $1.5^\circ/\text{min}$. Composite thermal peaks were resolved into their gaussian components with a DuPont 310 Curve Resolver. The gaussian nature of the peaks in the thermograms was not proved.

Results and discussion

Figure 1 shows the DSC curves characteristic of the non-activated (A) and the activated (B) polymerization of CL.

In DSC records obtained in the heating regime, the endothermic melting peak of the monomer is followed by the exothermic peak of the polymerization (A/a in Fig. 1) or by the common exothermic peak of the polymerization and crystallization, then by the melting peak of the polymeric PA-6 formed (B/a in Fig. 1). The exothermic effect of the crystallization of the molten PA-6 product is shown by the cooling DSC curves (A/b and B/b in Fig. 1). During reheating of this crystallized sample, the endothermic melting process was recorded, as the DSC trace A/c in Fig. 1 shows. Curves B/d in Fig. 1 represent the results from the separation of polymerization and crystallization processes, obtained by subtracting the crystal-

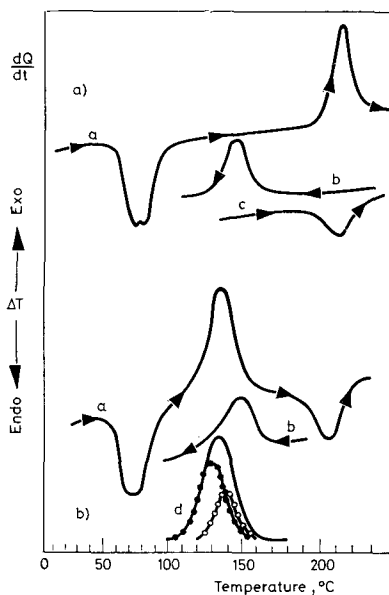


Fig. 1. DSC traces of polymerization of CL initiated by KL (A) non-activated; (B) activated by MDI; (The initiator concentration is 1 mole % in both cases; the activator concentration is 0.5 mole % in the latter system. The sample mass is about 1 g.) Symbols: dQ/dt = heat flux in arbitrary units. T = temperature in $^\circ\text{C}$; a = heating; b = cooling; c = reheating; d = polymerization (— . — . —) and crystallization (— + — + —) given by curve-resolving

lization peak in the cooling regime from the over-all exothermic peak of the heating curve. The subtraction was performed by means of the Curve Resolver. In the activated anionic polymerization initiated by LiL, the polymerization and crystallization processes could be separated merely from the heating curve, without a knowledge of the crystallization peak of the cooling curve [1].

For numerical evaluation of the thermal effects, the melting peak of CL monomer was used as internal standard [2]. For the polymerization heat of CL, $-135 \pm \pm 15$ J/g was obtained by the curve-resolving of DSC curves recorded with samples of various compositions. The corresponding heat of polymerization was -140.8 J/g as determined *via* the combustion heat of PA-6 (3), or -144.5 J/g according to other measurements [4].

It was clearly demonstrated by the calorimetric measurements that the efficiency of the initiator increased from Li^+ to K^+ , confirming the results of Čefelin and Šebenda [5] and those of Šittler and Šebenda [6].

Both the non-activated and the activated polymerization of CL initiated by LiL were highly influenced by the incorporation of organosilicon crown compounds (D_4 , D_5) and macrocyclic polyether (DB18C6). Their effects were much less when Na^+ or K^+ counter-ions were involved. The change in the course of the curves caused by the presence of the crown compounds of complexing ability suggests that a lactamolytic propagation mechanism, as proposed by Champetier and Sekiguchi [7–8], might be involved in the polymerization. Consequently, some configurational prearrangement can be attributed to the counter-ion. The presence of crown compounds results in a shift of the polymerization peaks toward higher temperatures.

Conversion of the polymerization of CL was found to increase slightly as a consequence of the crown compounds, as indicated by the lower monomer content determined by extraction and the higher η_{rel} values of the polymerized samples.

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