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Anionic Copolymerization of ε-Caprolactam with ω-Laurolactam

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Summary: Polyamide 6/12 copolymers were prepared by employing two different initiation systems containing activator N-benzoyl-ε-caprolactam (BzCL) and initiator either sodium salt of ε-caprolactam (CLNa) or ε-caprolactam magnesium bromide (CLMgBr). Materials prepared by initiation with CLNa show one melting endotherm and are random copolymers. Materials prepared by initiation with CLMgBr show two melting endotherms and are probably composed from random copolymer and block copolymer containing blocks of random copolymer and blocks of copolymer with ε-caprolactam rich segments. The character of copolymers and fractionalized materials was evaluated by means of DSC and NMR.

Keywords: copolymerization; DSC; ε-caprolactam; NMR; ω-laurolactam

Introduction

Polyamide 6 (PA 6) is prepared by ring opening polymerization of ε-caprolactam and possesses outstanding mechanical and chemical properties.[1] PA 6 is commonly known as a high quality fiber forming material but one third of its world production is used as engineering plastic.[2] To increase the scale of its utilizations it is necessary to tailor its properties by copolymerization. ε-Caprolactam can be copolymerized with all its analogues but only ω-laurolactam is industrially accessible. Anionic lactam (co)polymerization is fast and can be performed above and below the melting temperature of (co)polymer. Activated anionic copolymerization of ε-caprolactam with ω-laurolactam has been initiated preferably with sodium compounds.[3,4] Less basic magnesium initiators were studied only marginally.[5–7] The detailed comparison of activity of Na and Mg initiator and properties of copolymers prepared has been the aim of this study.

Experimental Part

Copolymerizations of ε-caprolactam (CL) with ω-laurolactam (LL) activated with N-benzoyl-ε-caprolactam (BzCL) and initiated either with sodium salt of ε-caprolactam (CLNa) or ε-caprolactam magnesium bromide (CLMgBr) were performed according to ref. [8] in test tubes, polymerization time was 30 minutes. Polymer yields were evaluated by extraction with methanol at laboratory temperature. Materials extracted with methanol were then fractionated with boiling ethanol. Thermal properties of samples were evaluated by DSC 2920 (TA Instruments) in the temperature range of 20–240 °C at a heating rate of 10 °C/min and nitrogen purge (50 $cm^3 \cdot min^{-1}$) (1st heating scan). ^{13}C NMR measurements at 75.5 MHz were performed at 330 K in 2,2,2-trifluoroethanol-d_3/LiCl solutions with an upgraded Bruker Avance DPX300 spectrometer.

Results and Discussion

The detailed study of CL and LL copolymerization in the whole concentration range of polymerization feed composition at 150 °C was described in paper.[8] Materi-

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als prepared by initiation with CLNa showed one melting endotherm in the whole concentration range of comonomers in polymerization feed. Such a polymerization behavior has been proved in literature[3,4,9] and materials prepared were random copolymers. Materials prepared by initiation with CLMgBr for 30–70 mol% CL in polymerization feed displayed different behavior and exhibited two melting endotherms at ~140 and ~210 °C (Figure 1).

In this paper we have concentrated on the influence of polymerization temperature on polymerization process. Copolymerization of an equimolar mixture of CL and LL was studied in the temperature interval 140–210 °C. Polymerization time was 30 minutes in all cases. Materials prepared by initiation with CLNa exhibited again one melting endotherm at all polymerization temperatures (Figure 2) and are undoubtedly random copolymers. The shift of melting endotherms 140 → 129 °C is caused by an increasing content of incorporated LL into the copolymer at 210 °C in comparizon to 180 and 150 °C – difference in polymer yield 20 % (72.7 vs. 90.6%).[8] The higher polymerization temperature probably increases the rate of transacylation reactions –higher randomisation of system could also decreases melting temperature.

The influence of CLMgBr initiator (in combination with the same activator as in the case of CLNa) on copolymerization of equimolar ratio of CL an LL in polymerization feed is more interesting. Two melting endotherms were detected only for polymerization temperature interval 150–180 °C. The peak area (enthalpy of fusion) is changed depending on polymerization temperature (Figure 3). The higher the polymerization temperature is, the larger is the area of melting endotherm at ~140 °C, (Figure 3). This melting endotherm could be tentatively assigned to random copolymer in analogy with the result of copolymerization by initiation with CLNa (Figure 1). Melting

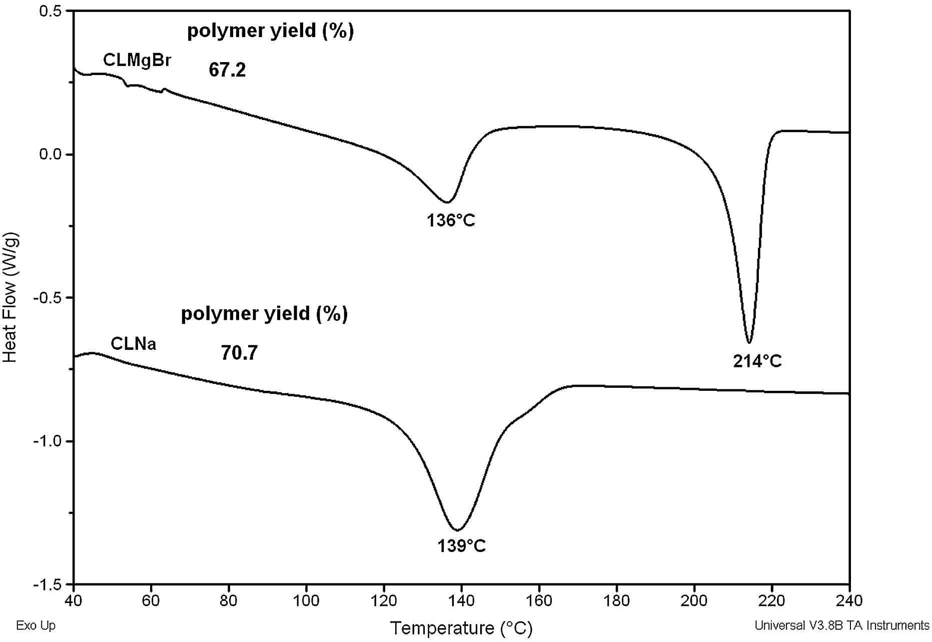

Figure 1.
DSC traces of copolymers prepared from equimolar mixture of CL and LL activated with 0.5 mol% BzCL and initiated either with 0.5 mol% CLMgBr or 0.5 mol% CLNa at 150 °C, polymerization time 30 min.

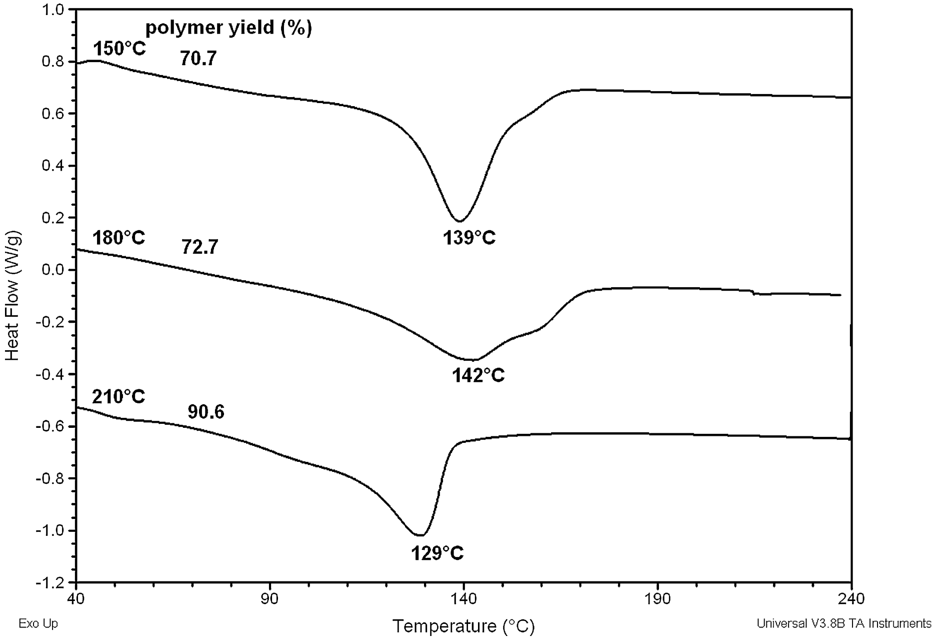

Figure 2.

DSC traces of copolymers prepared from equimolar mixture of CL and LL activated with 0.5 mol% BzCL and initiated with 0.5 mol% CLNa, polymerization time 30 min.

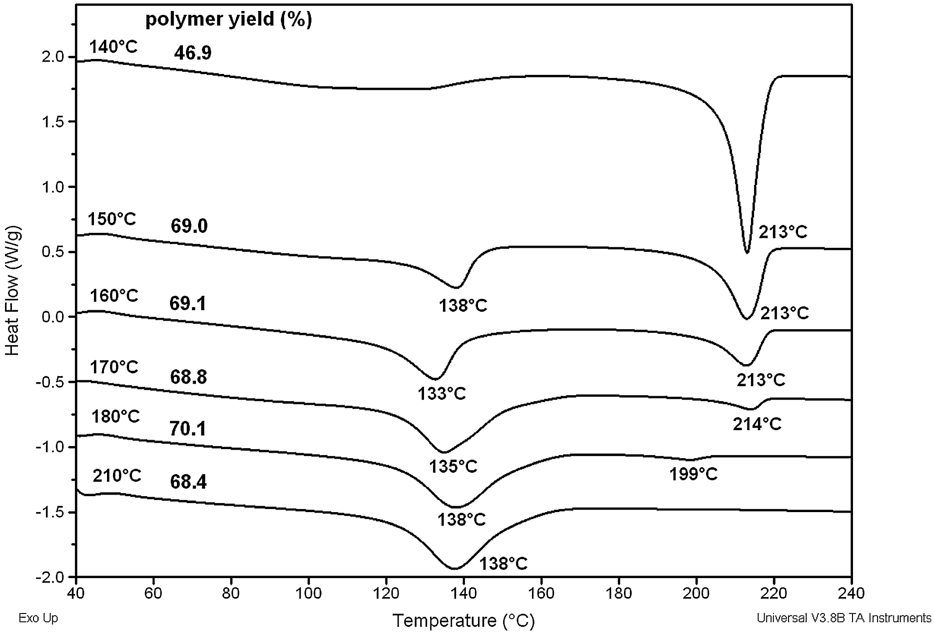

Figure 3.

DSC traces of copolymers prepared from equimolar mixture of CL and LL activated with 0.5 mol% BzCL and initiated with 0.5 mol% CLMgBr, polymerization time 30 min.

endotherm ~210 °C could correspond to homopolymer CL (m.p. of pure PA 6 is ~215 °C).

Material prepared at presence of CLMgBr was separated into two parts equal by weight by extraction with boiling ethanol. The fraction soluble in boiling ethanol exhibited one melting endotherm at 145 °C and the remaining material insoluble in boiling ethanol showed again two melting endotherms at the same position as the virgin material before fractionation (Figure 4).

Subsequent study of the structure of individual fractions was carried out by means of ^{13}C NMR. Spectra of homopolymers of CL and LL (prepared by the anionic polymerization, initiator CLMgBr) and of random copolymer of CL and LL (prepared by the anionic polymerization, initiator CLNa) were used for comparison. It is clearly visible from Figure 5 that the spectrum of the fraction soluble in boiling ethanol is almost identical with the spectrum of random CL/LL copolymer prepared by initiation with CLNa. A more complicated situation arises in the case of the fraction insoluble in boiling ethanol which exhibits two melting endotherms. It is evident from the comparison of spectra (Figure 5) that this fraction contains both homopolymer of CL and random copolymer of CL and LL. The ratio of population of dyads LL-CL/LL-LL is close to unity but that of CL-CL/CL-LL is about 5 according to the deconvolution analysis of carbonyl signals - No 6 of the copolymers (Figure 5). Such results indicate block character of prepared materials with blocks of homopolymer of CL and random copolymer of CL and LL.

Block character was confirmed also by the solubility of the present material. If the block with melting endotherm ~140 °C were not chemically bonded to the homopolymeric CL block, it should be soluble in boiling ethanol - but the material is soluble only in 2,2,2-trifluoroethanol-d3 (good solvent for PA6 block) . Therefore, both blocks have to be linked by a chemical bond. Such type of block copolymer formed

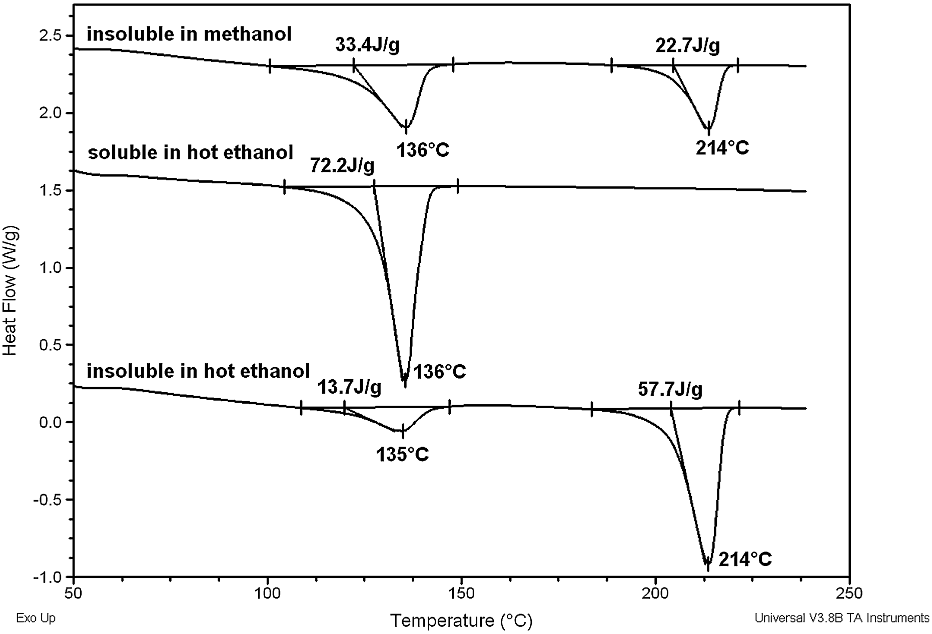

Figure 4.

DSC traces of fractionated copolymer prepared from equimolar mixture of CL and LL activated with 0.5 mol% BzCL and initiated with 0.5 mol% CLMgBr, polymerization time 30 min.

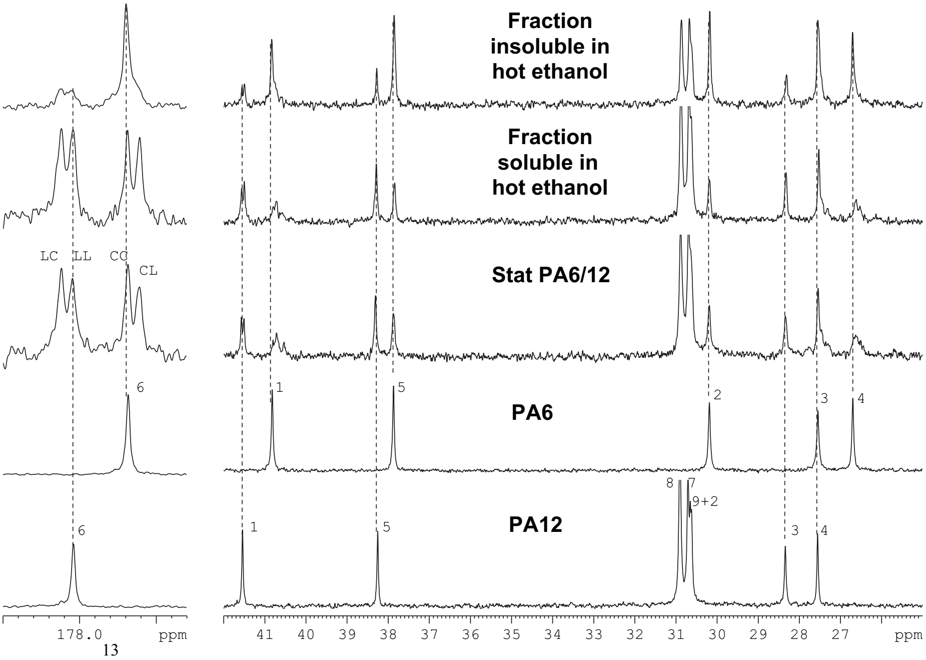

Figure 5.
^{13}C NMR spectra of the homopolymers and copolymers of CL (C) and LL (L).

in situ has not yet been described in literature. The difference between materials prepared by initiation with both initiators is caused by different ratio among propagation, transamidation (catalyzed by base) and side reactions depending on temperature, concentration, type of initiator, growth centers and complex ionic equilibria (association, medium permitivities etc.) for both initiators. Probably PA 6 is preferentially formed at the beginning of polymerization (LL is incorporated by polymerization slowly), random copolymer CL and LL is formed with lower rate and it is continuously bound with PA 6 by transamidation reactions.

Conclusions

The materials prepared by initiation with CLNa exhibit always one melting endotherm and have random character under all polymerization conditions used. The materials prepared by initiation with CLMgBr exhibited two melting endotherms and are probably a mixture of statistic copolymer CL/LL and chains of random copolymer CL/LL containing CL rich blocks.

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