REGULARITIES OF ANIONIC POLYMERIZATION OF ω-DODECALACTAM IN THE PRESENCE OF A POLYMERIC ACTIVATOR

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ABSTRACT

Block copolymers with an elastic polypropyleneoxide (PPO) block in the main chain of polyamide (PA-12), were synthesized via activated anionic polymerization of dodecalactam (DL) in the presence of a basic initiator a sodium salt of hexanelactam (HL) (Na-HL) and a polymeric activator (PAC). The PAC was synthesized on the base of carbamyl derivatives of hydroxyl terminated PPO with isophorone diisocyanate (IPh, 5-isocyanate-1-isocyanatomethyl-1,3,3-trimethylcyclohexane) and blocked with hexanelactam (HL). The isolated copolymers were characterized by 1H-NMR and IR-FT spectroscopy. The regularities of copolymerization was studied as a function of polymerization condition and different DL/PAC ratio.

Keywords: copolyamide, copolymerization, activated anionic polymerization, lactams.

INTRODUCTION

The wide application of polyamides imposes searching of new ways of its modification and synthesis of copolymers on the base of different polyamides with non-polyamide blocks in purpose of combination of their properties. The anionic polymerization of lactams using polymeric activators (PACs) is a suitable method for the preparation of block copolymers with incorporated soft blocks in the main polyamide backbone. Numerous copolymers of polyamides with a variety of non-polyamide blocks (different polyethers [1-3] polybutadiene [4], poly (ether urethane) [5], polycaprolactone [6], polystyrene [7], polydimethylsiloxane [8], polyisoprene [9]) have been prepared in this way. The best-known application of this method is the NyRIM technology (Reaction Injection Molding) producing tough block copolymers of propylene oxide with ε-hexanelactam or ω-dodecalactam [7,8] that have utilization like engineering plastics.

Block copolymers, with an elastic polypropylene oxide (PPO) middle block in the main chain of polyamide 12 (PA-12), were synthesized via activated anionic polymerization of DL in the presence of a basic initiator sodium salt of HL (Na-HL) and a polymeric activator (PAC). The PAC was synthesized on the base of hexanelactam (HL) carbamoyl derivatives of hydroxy terminated PPO and isophorone diisocyanate (IPh). The received block copolymers were analyzed and proved by 1H-NMR and IR-FT spectroscopy.

The purpose of the present work was to study the copolymerization of DL in the presence of the synthesized PAC and the effect of the PAC concentration in the feed composition and polymerization condition on the monomer conversion and molecular weight of the DL/PPO copolymers.
EXPERIMENTAL

Materials
HL (BASF, purum) and DL (Fluka, puriss) were dried in desiccator over $P_2O_5$ at 60°C in vacuo for 3 days before use. The initiator sodium salt of HL (Na-HL) was synthesized and purified by a method that was published according to ref. 10. Polypropylene glycol (Fluka, purum) with a molecular weight (GPC: $M_p=2002$, $M_w=1939$, $M_n=1961$, D=1.01) and hydroxyl value of 44. Isophorone diisocyanate (IPh) (MERCK, synthesis grade) and Sulfuric acid (MERK, Reag. Ph. Eur. 96%) are reagent grades and were used as received.

Polymeric activator preparation
A 250-ml flask fitted with a separated funnel, a stirrer, a reflux condenser, a thermometer and a nitrogen inlet was charged with 2.2 mol of IPh diisocyanate in toluene. PPO (1 mol dissolved in dried toluene) was added drop-wise through the separating funnel under vigorous stirring. The reaction was carried out at 50°C for 5 h in an oil bath. After the reaction completion HL monomer was added in excess (2.2 mol) at 110°C and the mixture was allowed to react for 1 h.

Polymerization
The polymerization was carried out in the temperature range 180-210°C using the ampoule technique [11,12]. PAC and the lactam were added to a glass reactor in a dry nitrogen atmosphere, and the mixture was melted under continuous stirring for 15 min. After homogenization, the initiator Na-HL was added under a vigorous stirring, and the feed was forced into ampoules with $N_2$. The concentration of initiator (Na-HL) was varied from 0.6 to 1 mol %. The PAC was used in concentration range from 2-5 %$_{mol}$ in relation to the lactam. The polymerization process was interrupted at a certain stage and the by-products and unreacted monomers were removed by extraction with methanol in a Soxhlet apparatus for 8 hours. The samples were dried to a constant weight in vacuo at 60°C and the degree of conversion of the monomers was estimated.

Analysis
The $^1$H NMR spectra were obtained on a Bruker AN 400 (400 MHz) spectrometer at 25°C. The isolated copolymers were dissolved in HCOOH/CDC$_3$ (3/2 v/v) solution (HCOOH as an internal standard).

The IR spectra were recorded on a Thermo Nicolet Nexus 670 type FT-IR spectrometer, over the range 750 – 4500 cm$^{-1}$ at a resolution of 4 cm$^{-1}$ and co-addition of 30 scans, using the thin film technique.

The intrinsic viscosity of the block copolymers was obtained in 96% sulfuric acid. The average viscometric molecular weights ($M_v$) were calculated by the Mark- Houwink relationship [13].

RESULTS AND DISCUSSION

The PAC was synthesized by a two –step procedure according to [14]. The first step includes the functionalization of hydroxyl terminated PPO with a molecular weight (GPC: $M_w=1939$) with IPh. The second step includes synthesis of PAC with an N-carbamoilactam structures by the reaction of the isocyanate terminated adduct with an excess of HL. The probable reactions are demonstrated in Schemes 1 and 2. The obtained PAC was dried in a vacuum and stored in a desiccator.

The activity of the received PAC in the anionic polymerization of DL was compared with that of the well known activator N-acylhexanelactam (NAcHL 0.5 mol %).

Anionic ring-opening polymerization of DL follows an activated monomer mechanism as against a conventional activated chain end mechanism of lactam polymerization. The chain growth reaction proceeds by the interaction of an activated monomer (lactam anion) with the N- acylated telechelic oligomer (PAC), on both of its ends. The anionic attack constitutes the rate determining step in the propagation. A typical reaction path for the copolymerization of DL or HL in the presence of PAC is shown in Scheme 3.

![Scheme 1. Functionalization of the hydroxyl terminated telechelic PPO with IPh.](image-url)
The structure of the isolated copolymers (after extraction, see Polymerization) was proved by IR and $^1$H-NMR spectroscopy (Figs. 1, 2). The absorption peaks in the IR spectra appeared at 1642 cm$^{-1}$ due to $n$(Amide I, C-O) vibrations, at 1549 cm$^{-1}$ due to $d$(N-H) + $n$(C-N Amide II) vibrations, at 800 cm$^{-1}$ due to $d$(CONH, Amide IV) vibrations, at 3294 cm$^{-1}$ due to $n$(= N-H stretch vibration, Amide II). In DL/PPO copolymers spectra absorptions around 1080 cm$^{-1}$ appeared due to r(CH$_2$ groups) vibrations distinctive for PA-12, was observed. The strong IR absorption in both spectra of the C-O-C stretching vibration at about 1103 cm$^{-1}$ is due to the incorporated PPO unit. The $^1$H-NMR spectra of the copolymers confirmed that PAC were incorporated into the polymer chain as all peaks distinctive for PA-12, and PPO were observed. The peaks were registered at 1.68 ppm, 1.59 ppm (d) for the CH$_3$ groups, at 2.40 ppm (m) for the CH$_2$-CO group, at 3.3 ppm (s) for the CH$_2$-NH group from PA-12 backbone. The peaks at 1.3 ppm (s) were due to protons from PA-12 methylene groups. The $^1$H-NMR spectra of the copolymers also display three additional peaks at 1.12 (s), 3.65(s), 3.5 (s) ppm due to protons from the PPO segments.
Table 1. Conditions of the DL copolymerization with PAC and characteristics of the obtained copolymers.

<table>
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<tr>
<th>DL/PAC [w/w%]</th>
<th>NaHL [mol%]</th>
<th>N-AcHL [mol%]</th>
<th>Tp [°C]</th>
<th>X⁺ [%]</th>
<th>Mₑ [g/mol]</th>
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* Polymerization temperature; * Degree of conversion; * Viscometric average molecular weight

For estimating the temperature range of the present experiments on the polymerization of DL, homopolymerization at 180 and 210°C was realized (Fig.3). It was observed that the higher polymerization temperature was appropriate for the homopolymerization of DL. In case of copolymerization the concentration of the PAC was varied from 2-5 wt% and the characteristics of the received copolymers were shown in Table 1.

The use of PAC though at 2 %max leads to a significant acceleration of the polymerization process and it starts at the reactor with embarrassed ampoule suction. The resulted copolymer was with degree of conversion, higher than 50 % and with viscometric average molecular weight at about 60000. This could be explained with the higher temperature of the reaction medium due to the higher melting point of DL (149°C) monomer as well as the higher reactivity of the PAC. To get better control on the polymerizability of the DL in the presence of PAC the concentration of the initiator Na-HL was varied from 0.6-1 mol % (Fig.4). As seen from Figure 4 at lower initiator concentrations the degree of conversion strongly decrease. In case of DL/PPO 98/2 the decreasing of the initiator concentration from 1 mol% to 0.8 mol% leads to decreasing of monomer conversion from 70% to 30%, but at higher PAC concentration at the same initiator content the degree of conversion increase. Therefore to achieve higher degree of conversion at lower initiator concentrations the polymerization has to be carried out at higher PAC levels.

All studied polymerizations showed a linear dependence of polymer yield (degree of conversion) on polymerization time until equilibrium of the monomer-polymer conversion was reached. The polymerization of DL in the presence of PAC (Fig. 5) showed that with increasing of PAC concentration the degree of polymerization (X) and average molecular mass (Mₑ) increase. Varying the PAC concentration in the feed must be limited due to the widely accepted side-reactions [15-17]. At 5 %max of PAC the optimum degree of conversion and rate of polymerization was observed.

As seen in Fig. 5 the used PAC activated the anionic polymerization of DL, but if we make a comparison with our previous studies [14], in case of copolymerization of DL with HL, the PAC activity is lower. At same PAC concentration (5 %max) the degree of conversion and the average molecular mass of the
**CONCLUSIONS**

The new PAC synthesized from HL carbamoil derivative of PPO functionalized with IPh was used for the synthesis of block copolymers with soft segments in the main chain of polyamide -12. The structure of the obtained block copolymers were proved by ^1^H NMR and IR. The influence of the activator concentration, reaction conditions on the PAC activity was defined. PAC acted as macroactivator for the anionic polymerization of DL. Was estimated the optimal PAC concentration in the initial polymerization mixture, when an optimum degree of conversion and polymerization rate was observed.

**REFERENCES**