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Synthesis of aliphatic polyamide bearing fluorinated groups from ε-caprolactam and modified cyclic lysine

Deniz Tunc [a,b,c,d], Hassen Bouchekif [a,b,c], Bruno Améduri [e], Christine Jérôme [d], Philippe Desbois [f], Philippe Lecomte [d,*], Stéphane Carlotti [a,b,c,*]

[a] *University of Bordeaux, LCPO, UMR 5629, F-33600 Pessac, France*
[b] *CNRS, LCPO, UMR 5629, F-33600 Pessac, France*
[c] *Bordeaux INP, LCPO, UMR 5629, F-33600 Pessac, France*
[d] *Center for Education and Research on Macromolecules, University of Liége, Sart-Tilman, B6a, 4000 Liége, Belgium*
[e] *Engineering and Macromolecular Architectures, Institut Charles Gerhardt, UMR (CNRS) 5253, Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue Ecole Normale, 34296 Montpellier Cedex 5, France*
[f] *BASF SE, Advanced Material and System Research, D-67056 Ludwigshafen, Germany*

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ABSTRACT

Aliphatic polyamide (PA) bearing fluorinated groups was synthesized in bulk with perfluorobutyryl-substituted α-amino-ε-caprolactam and ε-caprolactam by anionic ring-opening polymerization (AROP). The fluorinated monomer was obtained by condensation between cyclic lysine (*i.e.* α-amino-ε-caprolactam) and perfluorobutyryl chloride. The effect of the fluorinated monomer fraction onto the AROP of ε-caprolactam was monitored by the exothermicity of this polymerization *versus* time. The properties and characteristics of the resulting polymers were studied by with differential scanning calorimetry, thermogravimetry, magic angle spinning NMR, FT-IR, and contact angle measurements. Polyamides bearing fluorinated groups exhibited better thermal stability than polyamide 6 (PA6) as well as a higher hydrophobic surface character as evidenced by surface tension measurements. The glass transition temperature of polyamide 6 was 53 °C and rose to 58 °C for a PA bearing fluorinated moieties, while fluorinated monomer insertion induced a decrease of the melting points from 216 to 198 °C. These copolymers displayed a maximum degradation temperature of 390 °C as compared to the 310 °C for PA6, and their surface energies decreased from 49.4 mN cm^{-1} (PA6 value) to 44.1 mN cm^{-1}.

1. Introduction

Fluorinated (co)polymers are endowed with outstanding properties such as better thermal stability, lower surface energy and water absorption [1–5]. Hence, they can be used in many High Tech applications ranging from aerospace, automotive to optics and coatings. These properties stem from the unique characteristics of the fluorine atom: high electronegativity, high ionization potential, and low polarizability [6].

The literature informs that studies on fluorinated aliphatic polyamides [7–10] are quite limited when these polymers are compared to fluorinated aromatic macromolecules [11–15]. Generally, the synthesis of fluorinated copolyamides is achieved from polycondensation but suffers from long polymerization duration and high polymerization temperatures.

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* Corresponding authors at: University of Bordeaux, LCPO, UMR 5629, F-33600 Pessac, France (S. Carlotti).
E-mail addresses: philippe.lecomte@ulg.ac.be (P. Lecomte), carlotti@enscbp.fr (S. Carlotti).

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Fluorine-containing graft copolyamides have also been obtained. Dicarboxyl-terminated poly(perfluoroalkylethyl acrylate) were prepared by radical chain transfer polymerization and copolycondensed with telechelic diamines and dicarboxylic acids [8]. Polyamide 6 films that contained various amounts of this fluorine-containing graft copolyamides were processed by heat pressing. It was shown that 5 wt% of graft copolymers enable making interesting water repellent surfaces.

Hydrolytic ring-opening polymerization [16–19] and anionic ring-opening polymerization (AROP) of ε-caprolactam (CL) [16,17,20–22] are the commonly used techniques to prepare aliphatic polyamides, the latter method enabling to shorter times and lower temperatures. It also allows the synthesis of polyamide-based copolymers offering new materials [23–27]. The AROP of CL is carried out using two reagents: the lactamate anion regarded as the initiator or catalyst, and *N*-acyllactam regarded as the activator. The activator type has an effect both on the kinetics and on the obtained polyamide properties by increasing the polymerization rate and the monomer conversion while reducing molar mass of the polymer. Increasing the initiator amount provides high amount of free anions which can result in faster reaction rates [28,29]. Usually, the literature reports that the activator/initiator molar ratio is 1:1 [20]. This ratio can also vary up to 1:4 or 1:8 minimizing side reactions and resulting in polymers with different properties.

To go further in terms of properties, lactam derivatives may offer a real interest. For example, α-Amino-ε-caprolactam produced from L-lysine, obtained from bacterial fermentation [30], is one of them. Mathias et al. [31] reported that vinyl derivatives of α-amino-ε-caprolactam, obtained from various diacid chlorides and diisocyanates, yielded new polymers by free radical polymerization and bearing pendant ε-caprolactam. Among these monomers, bis- and tetra-caprolactams derivatives are polymerized to form self-assembled polymers and networks *via* hydrogen bonding with good thermo-mechanical properties. Our team also proposed controlled [32] or reversible thermal and photo-chemical [33] crosslinking of polyamide 6, by AROP of CL and new bis-monomers synthesized from α-amino-ε-caprolactam.

The objectives of this work deal with the synthesis of aliphatic polyamides that bear pendant fluorinated groups from a novel fluorinated lactam and ε-caprolactam by AROP, instead of the usual polycondensation chemistry. A focus is also given on the limitation of this approach because of side reactions. In addition, thermal properties, crystallinity, and surface tension have been studied and discussed.

2. Experimental part

2.1. Materials

DL-α-amino-ε-caprolactam (>98%, BASF) was purified by solubilization in toluene and filtered to eliminate non-soluble residues. A white product was obtained after evaporation of toluene. Perfluorobutyryl chloride (98%) and triethylamine (>99.5%) were purchased from Sigma–Aldrich and used without further purification. ε-Caprolactam (CL) (BASF, 99%) was recrystallized from dry cyclohexane prior to use. Brüggolen® C20 (17% w/w of isocyanate in CL, *N*,*N*′-hexamethylenebis (2-oxo-1-azepanylcarboxamide) or hexamethylene-1,6-dicarbamoylcaprolactam in CL, Brüggemann Chemical), Brüggolen® C10 (~18% w/w of sodium ε-caprolactamate in CL, Brüggemann Chemical) and 1,1,1,3,3,3-hexafluoro-2-propanol (or 1,1,1,3,3,3-hexafluoro isopropanol, HFIP) (Acros Organics, ⩾99.7%) were used without any further purification.

2.2. Measurements

^{1}H NMR spectra of reactants were recorded by using a Bruker AC250 instrument at a proton frequency of 250 MHz at room temperature. ^{19}F solid state NMR spectra were recorded on a Bruker 400 Avance I 376.46 MHz spectrometer at room temperature. During experiments, magic angle spinning (MAS) rate was 30 kHz using a Bruker 2.5 mm HX probe. Number of co-added transients was 256 and recycle delay was 5s. Single-pulse experiment (90 degree pulse of duration) was 1.8 µs, FID acquisition time was 41 ms. Rate of polymerization was monitored by temperature *vs* time using an ALMEMO2590 AHLBORN thermocouple. The Fourier Transform Infrared (FTIR) spectra were recorded using Nicolet Nexus with an Attenuated Total Reflectance (ATR) accessory by continuum microscope provided with an ATR Germanium (Ge) crystal. Differential scanning calorimetry (DSC) measurements of PA6 samples (~10 mg) were achieved on a Perkin–Elmer Diamond DSC with a heating–cooling rate of 10 °C min^{-1} under nitrogen flow (10 mL min^{-1}) with aluminum pans. Results were obtained from the second run that led to the T_g values assessed from the inflexion point in the heat capacity jump. Thermo-gravimetric analysis (TGA) was performed on a Perkin–Elmer Diamond TA/TGA with a heating rate of 10 °C min^{-1} under nitrogen flow. For surface characterization, thin films of PA6 precursors were spin coated (Specialty Coating Systems, P67080 Spin Coater) on glass plates from 5% solutions in HFIP at 2000 rpm for 5 min and then dried at 80 °C overnight under vacuum. Water, ethylene glycol, and diiodomethane contact angles were measured using the sessile drop method with a drop volume of 2 µl, on a contact angle system by Krüss DSA 100 at 25 °C. More than four drops of the same liquid located at different positions were measured on a given sample and then averaged to lead to the values reported in this study. Measurements were taken 2 days after copolymerization. 1 day was needed for purification while another one was required to prepare dried films of polyamides by spin-coating.

For water uptake measurements, all polymer slides were prepared by heat pressing. The thicknesses of P1-P5 samples were 0.137, 0.121, 0.153, 0.125, and 0.124 mm, respectively. Water uptake was determined by the ratio $100 \times (W - W_0)/W_0$, where W and W_0 stand for the weights of polymer sample after standing in water at 80 °C for 24 h and of polymer sample after being dried under vacuum at 100 °C, respectively.