



Poly(hexamethylene terephthalate-co-caprolactone) copolymers: Influence of cycle size on ring-opening polymerization

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ABSTRACT

Poly(hexamethylene terephthalate) was cyclo-depolymerized in solution by heating to yield a fraction of cyclic oligomers of hexamethylene terephthalate ($c(\text{HT})_{2-5}$) with a content around to 95% in dimer to pentamer. Ring-opening polymerization in the melt of $c(\text{HT})_{2-5}$, either neat or in mixtures with ϵ -caprolactone (CL) covering a range of HT/CL ratios from 9/1 to 1/9 was carried out to produce polyesters with molecular weights above 30,000 in high yields. The copolyesters had a comonomer composition according to the feed and the microstructure evolved from random to blocky as the content in CL increases. The thermal and mechanical properties of the copolyesters were evaluated for a variety of compositions. Results obtained in this work were compared to those previously obtained by us in the ring-opening copolymerization of CL with a cyclic oligomeric fraction enriched in hexamer and heptamer ($c(\text{HT})_{6-7}$). Although the polyesters resulting from the use of these two fractions were similar, significant differences were found in polymerization rate evidencing a lower reactivity of $c(\text{HT})_n$ with decreasing values of n .

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1. Introduction

Aromatic polyesters are typically prepared by step-growth polycondensation in the melt [1,2]. A second option is the ring-opening polymerization (ROP) of cyclic oligoesters under solvent free conditions [3]. This methodology is widely used in the synthesis of aliphatic polyesters as polyglycolide and polylactide, poly(ϵ -caprolactone) or poly(p -dioxanone) [4–6]. In this method, the polyester is prepared from low-viscosity precursors by an entropically driven process that evolves without releasing of volatiles or emission of heat. However, the potential of ROP is strongly constrained by the limited availability of suitable cyclic monomers. Increasing attention is being paid recently to the utilization of cyclic oligoesters as feedstock for the synthesis and processing of aromatic polyesters [3,7–9]. One source of cyclic oligoesters of great interest is cyclo-depoly-

merization of linear polyesters, which in combination with ROP, would provide an environmentally friendly route for the chemical recycling of currently important thermoplastics as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and other closely related industrial aromatic polyesters and copolyesters [10–14].

Poly(hexamethylene terephthalate) (PHT) is a semi-crystalline aromatic polyester that has not been industrially used to date. The presence of the hexamethylene segment confers to this polyester a great chain flexibility that is reflected in a relatively low T_g ($\sim 10^\circ\text{C}$) and a moderate T_m ($\sim 140^\circ\text{C}$) as compared to PET [15,16]. Nevertheless, PHT continues exhibiting good mechanical properties and chemical resistance characteristic of aromatic polyesters [17]. PHT is not biodegradable, and as it happens with other poly(phthalate)s, block copolyesters of hexamethylene terephthalate (HT) and ϵ -caprolactone have been explored for their potential as biodegradable materials for packaging [18]. Recently we succeeded in preparing copolyesters of HT and ϵ -caprolactone (CL) by ROP. A fraction of hexamethylene terephthalate cyclic oligomers consisting of a mixture

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of hexamer and heptamer $c(\text{HT})_{6-7}$ prepared by cyclo-depolymerization of PHT was used for this synthesis [19].

In this paper we wish to report again on the preparation of poly(hexamethylene terephthalate-co-caprolactone) copolyesters by ROP, but now using a fraction of cyclic hexamethylene terephthalate oligomers $c(\text{HT})_{2-5}$ enriched in dimer to pentamer. The aim of the work is to evaluate the influence of the size of the cyclic oligoesters on the ring-opening polymerization reaction and on the structure and properties of the resulting polyesters. Firstly the oligomeric $c(\text{HT})_{2-5}$ fraction was prepared by cyclo-depolymerization of PHT and characterized in full detail. Secondly, a series of copolyesters with a ratio of HT to CL ranging from 90/10 to 10/90, in addition to the PHT homopolymer, were prepared by ROP. The progress of the polymerization reaction using one or the other fraction, as well as the chemical structure and thermal properties of the copolyesters generated in each case were comparatively studied.

2. Experimental

2.1. Materials and measurements

Dimethyl terephthalate (DMT) (99%), hexanediol (HD) (99%), ϵ -caprolactone (CL) (>99%), dibutyltin oxide (DBTO) (98%), tin octanoate ($\text{Sn}(\text{Oct})_2$) (95%), and 1,2-dichlorobenzene (DCB) (99%) were purchased from Sigma–Aldrich Co. and were used without further purification. Antimony (III) oxide (97%, Panreac Co.) was reagent grade and used as received. The solvents used for purification and characterization, such as methanol, chloroform, dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether, dichloroacetic acid (DCA), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), were high-purity grade and used as received.

^1H and ^{13}C NMR spectra were recorded at 25.0 °C on a Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz, respectively. Both polyesters and cyclic compounds were dissolved in deuterated chloroform or a mixture of deuterated chloroform/trifluoroacetic acid (9/1), and spectra were internally referenced to tetramethylsilane. About 10 and 50 mg of sample in 1 mL of solvent were used for ^1H and ^{13}C , respectively. Sixty-four scans were recorded for ^1H , and between 1000 and 10,000 scans for ^{13}C NMR, with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded in a 4700 Proteomics Analyzer instrument (Applied Biosystems). Spectra acquisition was performed in the MS reflector positive ion mode. About 0.1 mg of sample was dissolved in 50 μL of DCM and 2 μL of this solution were mixed with an equal volume of DCM solution of anthracene (10 mg mL^{-1}) and the mixture left to evaporate to dryness onto the stainless steel plate of the analyzer. The residue was then covered with 2 μL of a solution of 2,5-dihydroxybenzoic acid in acetonitrile/ H_2O (1/1) containing 0.1% TFA and the mixture was left to dry prior to exposition to the laser beam.

High performance liquid chromatography (HPLC) analysis were carried out at 25.0 °C in a Waters apparatus equipped with a UV detector of Applied Biosystems operat-

ing at 254 nm wavelength, and a Scharlau Science column (Si60, 5 μm ; 250 \times 4.6 mm). Cyclic oligomers (1 mg) were dissolved in chloroform (1 mL) and eluted with hexane/1,4-dioxane (70/30 v/v) at a flow rate of 1.0 mL min^{-1} . Molecular weight analysis were performed by GPC using HFIP containing sodium trifluoroacetate (6.8 g L^{-1}) in a Waters equipment provided with RI and UV detectors. 100 μL of 0.1% (w/v) sample solution were injected and chromatographed with a flow of 0.5 mL min^{-1} . HR5E and HR2 Waters linear Styragel columns (7.8 \times 300 mm, pore size 10^3 – 10^4 Å) packed with crosslinked polystyrene and protected with a precolumn (VanGuard, 1.8 μm , 2.1 \times 5 mm) were used. Molecular weight averages and distributions were evaluated against PMMA standards. Intrinsic viscosities were measured from polymer solutions in DCA using an Ubbelohde viscometer thermostatted at 25.0 \pm 0.1 °C.

The thermal behavior of cyclic compounds and polymers was examined by differential scanning calorimetry (DSC), using a Perkin-Elmer Pyris 1 apparatus. Thermograms were obtained from 4–6 mg samples at heating and cooling rates of 10 °C min^{-1} under a nitrogen flow of 20 mL min^{-1} . Indium and zinc were used as standards for temperature and enthalpy calibration, respectively. The glass transition temperature (T_g) was taken as the inflection point of the heating DSC traces recorded at 20 °C min^{-1} from melt-quenched samples, and melting temperature (T_m) was taken as the maximum of the endothermic peak appearing on heating traces. The tensile tests were conducted at room temperature on a Zwick BZ2.5/TN1S universal tensile testing apparatus operating at a constant crosshead speed of 10 mm min^{-1} using a 0.5-N preload and a grip-to-grip separation of 20 mm. All reported tensile data represent an average of at least six independent measurements. Mechanical testing was performed on melt compression samples 4 mm width with an average thickness of 0.16 mm.

2.2. Synthesis of cyclic oligomers $c(\text{HT})_n$ by cyclo-depolymerization of PHT

PHT was synthesized to be used as the source for cyclic oligomers of hexamethylene terephthalate. It was prepared by conventional polycondensation of HD and DMT according to a procedure described by us [19], which was a modification of a procedure previously described in the literature [15]. The PHT was obtained in 84% yield with a weight-average molecular weight of 63,000, a $T_g \sim 10$ °C and a $T_m \sim 140$ °C. NMR (CDCl_3 , 300 MHz): δ (ppm) 8.09 (s, 4H, ArH), 4.36 (t, 4H, OCH_2), 1.83 (q, 4H, OCH_2CH_2), 1.56 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$). ^{13}C (^1H) NMR (CDCl_3 , 75.5 MHz): δ (ppm) 165.8 (C=O), 134.1, 129.5 (ArC), 65.3 (OCH_2), 28.6 (OCH_2CH_2), 25.7 ($\text{OCH}_2\text{CH}_2\text{CH}_2$).

Cyclic oligomers were produced by cyclo-depolymerization of PHT according to the following procedure: PHT (4.96 g, 20 mmol previously dried overnight in a vacuum oven at 60 °C) and DCB (200 mL) containing 3%-mole of DBTO were introduced into a 250 mL round-bottom flask equipped with a condenser. This mixture was stirred vigorously, and the reaction was allowed to proceed under refluxing at a temperature of 180 °C for a period of time between 2 and 8 days, cooled to room temperature and filtered. The clear solution was rapidly evaporated under

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