Electronic Supplementary Information

Soft Segment Free Thermoplastic Polyester Elastomer with High Performance

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Experimental

Materials: 1,4-butandiol (BDO), ethanol and titanium(IV) butoxide were purchased from Aladdin Reagent Co. Ltd (Shanghai, China), *trans*-1,4-cyclohexanedicarboxylic acid (*trans*-CHDA) (99%) and *mix*-1,4-cyclohexanedicarboxylic acid (*mix*-CHDA) with a *cis*/*trans* ratio of 50/50 were purchased from Nanjing Chemlin Chemical Industry Co., Ltd. *cis*-CHDA (97%) was obtained by separation and purification of *mix*-CHDA from ethanol according to methods described in the literatures[1,2]. All the chemicals are used as received without further treatment.

Synthesis: In a typical process, CHDA (172.2g, 1.0mol), BDO (180.0g, 2.0mol) and first portion of titanium(IV) butoxide (0.086g, 0.05wt % of CHDA) were added to a 1L autoclave, the mixture was placed under vacuum (0.1kPa) and then purged with N_2 gas. This cycle was repeated for three times. Subsequently, the mixture was heated to 200^{o}C under N_2 until the amount of the distilled water reached 90% of its theoretic amount. A second portion of catalyst (0.086g titanium(IV) butoxide, 0.05wt % of CHDA) was added and the system was sealed and evacuated below 20Pa, and simultaneously heated up to 260^{o}C. This polycondensation reaction was conducted for a certain period time under mechanical stirring until the torque value reached a certain amount to ensure similar molecular weights of the products. The polymer was poured into cooling water and then dried at 50^{o}C under vacuum and kept still for further studies.

Characterization

Molecular weights and molecular weight distributions were measured on PL-GPC220 gel

permeation chromatography (GPC). HPLC grade chloroform was used as elution solvent at 40°C and molecular weight was calibrated with polystyrene standard. The concentration of all samples was about 6.7mg·mL^{-1}.

Structure and the amount of *cis*-CHRM in the polymer chain of PBC were determined by proton nuclear magnetic resonance (^{1}H NMR) in $CDCl_3$ solvent using a Bruker AVIII400 NMR spectrometer at room temperature.

Differential scanning calorimetry (DSC) measurements were performed using differential scanning calorimeter (METTLER-TOLEDO DSC I). Temperature calibration was carried out using an indium standard. Measurements were performed under a nitrogen atmosphere at a flow rate of 50mL·min^{-1}. About 5mg of sample was placed in an alumina sample pan and the measurement was carried out according to the following process: the sample was heated up to 260°C at 10°C min^{-1} and held at this temperature for 4min to erase the heat history. It was then cooled down to -40°C at 10°C·min^{-1}. Subsequently, a second heating scan was performed at 10°C·min^{-1} to 260°C. The melting point (T_m) and heat of fusion (ΔH_m) were obtained from the second heating scan and the crystallization temperature (T_c) was taken from the cooling scan. The degree of crystallinity (χ_c) is calculated according to the following equation:

$$\chi_c(\%)= \frac{\Delta H_m}{f \times \Delta H_m^{\theta}} \times 100\%$$

where f is the weight fraction of *trans*-CHRM in PBC, ΔH_m is the experimental melting heat of fusion, and ΔH_m^{θ} is the heat of fusion of 100% crystalline for PBC with 100% *trans*-CHRM calculated according to the group contribution theory[3], which is 141 J·g^{-1}.

Thermal stability measurements were conducted using a Mettler-Toledo TGA/DSC thermogravimetric analysis (TGA). For each sample, 6.0-10.0mg sample was placed in a ceramic

furnace and the TGA curve was recorded ranging from 50 to 800^{o}C with a heating rate of 10^{o}C min^{-1} under dry nitrogen or air atmosphere with a flow rate of 50mL·min^{-1}. We took the temperature at which the weight loss was 5% ($T_{5\%}$) as an index to evaluate the thermal stability of the sample.

Dynamic mechanical analysis (DMA) was conducted with a METTLER-TOLEDO dynamic mechanical analyzer (DMA/SDTA861^{e}) at a fixed frequency of 1 Hz, operated in the film tension mold. The samples with dimensions of 10.5mm (length), 6.0mm (width) and 0.5mm (thickness) were prepared from press-molding. The temperature range studied was from -110 to 50^{o}C with a heating rate of 3^{o}C·min^{-1}.

Figure S1. Tanδ of PBC plotted as a function of temperature by DMA

Figure S2. storage modulus (E'), loss modulus (E'')and Tanδ of PBC71 plotted as a function of temperature by DMA

Tensile testing was performed in an Instron5567 tensile testing machine with a 500 N load cell. The stretching rate was 100mm·min^{-1} and the test temperature was 25^{o}C. Dumb-bell-shaped sample bars with dimensions of 35.0mm (length), 2.0mm (neck width) and 0.5mm (thickness) were prepared by press-molding at temperature 20^{o}C higher than T_m or T_f of the sample and subsequently cooled down to temperature below its T_c or simply to room temperature, without releasing the pressure. All data were obtained by averaging the data from five parallel measurements.

Cyclic tensile testing was done with an Instron 5567 apparatus. The dumb-bell-shaped sample bars with dimensions of 35.0mm (length), 2.0mm (width), and 0.5mm (thickness) were

stretched to ε_m, 200% elongation at room temperature with a 100mm·min^{-1} stretching rate. Then the clamps began to return with a speed of 50mm·min^{-1} until the force on the sample was 0. After the above two steps, one cycle is complete. Three samples were tested to calculate mean values and standard deviation. Every sample was subjected to 5 cycles and the shape recovery rate (R_r) was calculated according to the following equation.

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N\text{-}1)}$$

where N is the cycle number, ε_m is the maximum strain imposed on the material, $\varepsilon_p(N)$ and $\varepsilon_p(N\text{-}1)$ are the strains of the sample in two successive cycles when the force on the sample is 0 and $R_r(N)$ is based on two successive cycles.

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[2] M. A. Osman, *Macromolecules* **1986**, *19*, 1824.

[3] K. G. Joback, R. C. Reid, *Chem. Eng. Commun.* **1987**, *57*, 233.