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Biopolymers Summit 2018: Synthesis of bio-based polyesters from 2,5-furandicarboxylic acid (2,5-FDCA): From completely amorphous to high crystallinity-Xiaoqing Liu-Ningbo Institute of Material Technology and Engineering

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Introduction:

A serials of fully bio-based poly(ethylene dodecanedioate-2,5-furandicarboxylate) (PEDF) were synthesized from Dodecanedioic acid (DDCA), 2,5-Furandicarboxylic acid (2,5-FDCA), and ethylene glycol through a two-step procedure consisted of trans-esterification and polycondensation. After their chemical structures were confirmed by Nuclear Magnetic Resonance and Fourier Transform Infrared Spectroscopy, their thermal, mechanical, and biodegradation properties were investigated in detail. Results showed that the chemical composition of PEDFs could be easily controlled by the feeding mole ratio of DDCA to FDCA and they possessed the characteristic of random copolyester with the intrinsic viscosity ranged from 0.82 to 1.2 dL/g. With the varied mole ratio of DDCA to FDCA, PEDFs could be changed from semi-crystalline thermoplastic to the completely amorphous elastomer, indicated by the elongation at break ranged from 4 for poly(ethylene 2,5-furandicarboxylate) to 1500% for amorphous PEDF-40. The amorphousPEDF-30 and PEDF-40 showed satisfactory shape recovery after cyclic tensile test, which was the typical behaviour for elastomer. Enzymatic degradation test indicated that all the PEDFs were biodegradable and the degradation rate was heavily affected by their chemical compositions.

In recent years, due to the rapid depletion of fossil resource sand worsening environmental pollution, using renewable resource as the raw material to produce the biodegradable or biobased polymers via environment friendly method has attracted much more attention, both in the industrial and academic community.1,2Up to now, several kinds of bio-based or biodegradable polyesters, including poly(lactic acid),3poly(butylene succinate),4and poly(butylene adipate co butylene terephthalate),5have been commercialized successfully and widely used as food package, agricultural ground film, and garbage bag. And the great potential of bio-based polyesters has been fully recognized.

Experimental Materials:

DDCA, EG (99%), and lipase from porcine pancreas were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Antimony trioxide(III, 99.99%), zinc acetate (99%), trifuoroaceticacid, phenol, and tetrachloroethane were purchased from Sino-pharm Chemical Reagent Co. Ltd (Shanghai, China). FDCA was purchased from Chem target Technologies Co. Ltd (Mianyang, China). All the chemicals were used as received without any further treatment

Synthesis of Dimethyl Furan-2,5-Dicarboxylate

78.0 g FDCA together with 320.0 g methanol and 2 mL of concentrated sulfuric acid as the catalyst were added in a round-bottom flask equipped with mechanical stirrer. The mixture was refluxed at 90degrees for 5 h. The excess methanol was distilled out of the flask and the dimethyl ester was precipitated after cooling to room temperature. After the white precipitate was collected via filtration and washed with distilled water for several times, it was dried in the vacuum oven and further purified by sublimating at 120 8C in order to obtain the pure dimethyl furan-2,5-dicarboxylate (DMFD) crystal. The yield was calculated to be 89% and its chemical structure was confirmed by ^{1}H-NMR and ^{13}C-NMR.

Synthesis of Dimethyl Dodecanedioate 40.0 g of DDCA

300ml methanol and 0.4 g of p-toluenesulfonic acid as the catalyst were added into a 500 ml round-bottom flask equipped with a magnetic stirring. The mixture was refluxed at 90 8C for about 5 h. After cooling to room temperature, the mixture was neutralized by the addition of saturated sodium bicarbonate (NaHCO3) solution until the pH was increased to about 8. Then dichloromethane (CH2Cl2) and distilled water were used to extract the pure dimethyl dodecanedioate (DMDC) from the mixture. After the organic phase was dried with anhydrous magnesium sulfate (MgSO4), the solvent was removed in the rotary evaporator and the target product DMDC was obtained. The yield was calculated to be about 96%

Synthesis of Copolyesters (PEDFs)

The different copolyesters PEDFs were synthesized by a two-step transesterification and polycondensation process, with the molar ratio of EG: (DMDC 1DMFD) was 1.6:1 (in order to ensure the sufficient transesterification). For the first transesterification step, predetermined EG, DMDC, DMFD(DMDC 1DMFD, 0.30 mol) and first portion of catalyst (Zincacetate, 0.2 mol % based on diester) were added into a three-necked round bottom flask equipped with a mechanical stirrer with torque indicator.

Characterizations:

Intrinsic viscosity of the synthesized polyester was calculated from the elution time of the copolyesters solution and solvent measured in an Ubbelodhe viscometer with the capillary tube diameter of 0.792 mm in a water bath at 258C. The mixture of phenol and tetrachloroethane (1/1, W/W) was

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used as the solvent and the concentration of the copolyester was 5 mg/mL. The equation [h]5[(1 11.4hsp)1/2– 1]/0.7c was used to calculate the intrinsic viscosity [h], where hsp5(t1–t0)/t0,t0is the elution time of solvent and t1is the elution time of co-polyesters solutions. Due to the fact that PEF, PEDF, and PED cannot be dissolved in the same solvent, such as the mixture of chloroform and 2-chlorophenol (V/V59:1), it is difficult to compare the GPC results of PEDFs and PED with that of PEF.

Results and Discussion:

Synthesis and Characterization of PEF, PED, and PEDFs in full composition range were synthesized following a two-step procedure consisted of transesterification and polycondensation (Scheme 1). The esterification between diacids (2,5-FDCA and DDCA) and methanol was conducted at first. After the transesterification between the diesters (DMFD and DMDC)and EG was finished, which was indicated by the distillation of more than 95% theoretical methanol, the polycondensation was conducted at 230–240°C for 3–4 h to get the copolyesters with similar viscosity. For the synthesis of different copolyesters, the varied feeding compositions were summarized. The chemical structure and compositions of PEDFs were characterized by 1H-NMR, 13C-NMR, and FTIR.

Conclusion:

SA serial of bio-based copolyesters PEDFs in full composition range derived from bio-based DDCA, FDCA, and EG were successfully synthesized through a two-step polycondensation procedure. As determined by ^{1}H NMR and ^{13}C NMR, PEDFs showed the typical characteristics of random copolymers and their compositions could be easily controlled by the feeding stoichiometry. With the increasing content of DDCA unit, PEDFs were varied from amorphous elastomers to semi-crystalline plastics. From the results of cycle tensile testing, PEDF-30, and PEDF-40 demonstrated recovery ratio higher than 90% after five cycles, which was higher than some other poly(ether–ester) elastomer reported in literatures. The trade-off effect between FDCA content and the crystallizability of PEDFs on the biodegradability was observed, and it was the FDCA content playing a determining role. We hope that, with the rapid development of bio-technology and chemical industry, the overall properties of PEDFs could be improved further and practical applications could be found in the future.

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