Selective Synthesis of Macrocyclic Ethylene Isophthalate Dimer

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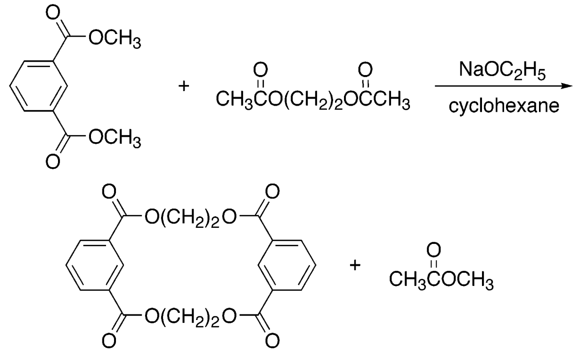
Aromatic polyesters (PET, PBT, PEN, etc.) are extensively employed thermoplastic polymers, used either alone or in blends for application in textile and film manufacturing, food packaging, and information support for the computer industry. New synthetic routes for polyesters via environmentally friendly entropically driven ring-opening polymerization of macrocyclic oligomers have been attracting increasing research attention.[1−7] In this new method, chain ring-opening polymerization of macrocyclic precursors proceeds without elimination, leading to two major benefits: industrial processes will no longer need to emit unwanted reaction byproducts, and energy losses will be drastically reduced. Furthermore, high-quality products without impurities originating in eliminated byproducts are expected to be obtained. In conventional high-temperature synthetic processes, polymeric products are affected by hydrolysis and thermal degradation, making it difficult to prevent discoloration and deterioration of mechanical properties.

We have already demonstrated that the solid-phase ring-opening polymerization of polycarbonates and poly(ethylene terephthalate) gave high-quality polymers.[8,9] When the macrocyclic precursors are strained small ring size compounds, ring-opening polymerization progresses at temperatures much lower than their melting points without solvent. We have also reported that, in the case of macrocyclic oligomers with low tension in the ring, the growth reaction of the polymer chain and the transesterification reaction proceed simultaneously, interfering with formation of high molecular weight polymers. These results may provide an important guiding principle in further molecular design of oligomers.

Concerning the synthesis of ethylene isophthalate copolymers, our knowledge of solid phase ring-opening polymerization of aromatic polyesters suggests that cyclic dimer with high melting point is suitable. Oligomers with a larger ring size show less strain in the molecules, and the reaction leading to the ring-opening polymerization does not usually progress efficiently. To our knowledge, to this date no simple and effective methods for the selective synthesis of macrocyclic ethylene isophthalate dimer have been reported in the literature. With the high-dilution (or pseudo-high-dilution) method, even though mixtures of cyclic oligomers were desired, the highest yield of dimer is not greater than 65% accompanied by considerable amounts of higher oligomers.[3b,5] Recently, new synthetic approaches using cyclo-depolymerization have been reported.[5,10] Although these are significant advances from the viewpoint of material recycling of polyesters, they are unsuitable for our requirements because of either low dimer yields[5] or usage of chlorinated solvents and long reaction times.[10]

In this communication, we report a simple method for the selective and quantitative synthesis of macrocyclic ethylene isophthalate dimer. In this method, the most important factor is the selection of the solvent and the leaving groups of substrates. The key point of this method is that the reaction progresses efficiently in the form of an azeotropic mixture.



Ethylene glycol diacetate (EGA, distilled in vacuo, 2.34 g, 16 mmol) and isophthalic acid dimethyl ester (recrystallized from methanol, 3.88 g, 20 mmol) were stirred in 30 mL of cyclohexane (previously dried over calcium hydride, bp 80.8 °C) at 65 °C and treated with sodium ethoxide (freshly prepared just before the experiment by adding metal sodium to dry ethanol followed by drying in vacuo, 4.6 mg, 0.2 mmol) in EGA (0.56 g, 4 mmol). The reaction that immediately followed started with the clouding of the solution, in which methyl acetate (bp 57.8 °C) was evaporated at 55.5 °C by producing an azeotropic mixture with cyclohexane.[11] After 2 h of stirring, the reaction mixture was cooled to room temperature. White precipitate was filtrated and dried. On the basis of unreacted monomers in the filtrate, the conversion was found to be 97.6%. The purity of the white powder, as measured by GC,[12a] was 98.4%. Low molecular weight impurity was completely removed by recrystallization from DMF, producing white crystals of mp = 390−401 °C.[13] Complete absence of molecules larger than the dimer was proved by SEC.[12b] The structure was confirmed by elemental analysis[12c] and high-resolution ESI mass spectrum analysis.[12d]

Previously, we reported a new synthetic method for oligo(ethylene terephthalate) by ester−ester exchange reaction between diethyl terephthalate and ethylene glycol diacetate in hydrocarbon solutions using an alkali metal alkoxide as a catalyst, which was based on the similar idea as described here.[14] Comparing various combinations of solvents and esters, it was found that in nonazeotropic conditions efficiencies of ester−ester exchange reactions deteriorate remarkably. A special

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feature of this method is that no components in the system release protons, as a result of which the alkali metal alkoxide shows high activity as catalyst. Accordingly, impurities that risk becoming sources of proton emission, such as water, alcohol, and/or carboxylic acid, should be completely removed from the substrate and solvent before use, and it is essential to remove water from the atmosphere under which the reaction takes place.

In summary, the new method of macrocyclic ethylene isophthalate dimer synthesis described herein compares favorably with heretofore-reported methodologies, especially in terms of dimer yield and selectivity, simple apparatus and procedure, short reaction time, and nonreliance on halogenated solvents.

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(12) (a) Gas chromatography conditions. Column: HP-5 (30 m × 0.32 mm × 0.25 μm); oven: programmed from 100 to 300 °C at a rate of 10 °C/min; detector: FID; carrier gas: 2.4 mL/min, helium (constant flow). (b) Size exclusion chromatography conditions. Column: KF802 (Shodex); eluant: 1.0 mL/min, chloroform; detector: UV (254 nm). (c) Anal. Calcd for $C_{20}H_{16}O_8$: C, 62.50; H, 4.20; O, 33.30. Found: C, 62.53; H, 4.05; O, 33.27. (d) High-resolution mass (ESI; $M + H^+$) calcd for $C_{20}H_{16}O_8H^+$: 385.0918. Found: 385.0892.
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