Synthesis of Optically Active Polyamides with Molecularly Asymmetric Units

Hongzhi Tang

School of Materials Science,
Japan Advanced Institute of Science and Technology

(Supervised by Yusuke Kawakami)

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Abstract

Specific conformation like helix of an optically active polymer plays an important role in the potential applications of the polymer in chiral chromatographic separation or in catalyst for asymmetric induction. Conformationally optically active polymer can be synthesized by introduction of an optically active monomer into polymer main chains. Among the optically active monomers, C2-symmetric units such as binaphthyl led to numbers of optically active polymers taking helical structures. In this study, a novel type of molecular asymmetric unit as spiro[3.3]heptane-2,6-dicarboxylic acid was noticed, in which two functional carboxylic acid groups twist 90^o $strictly due to the twisting of the two cyclobutane rings. Thus, introd$
$direction, and the obtained polymers are expected to take ordered conformations in solution.$

$Spiro[3.3]heptane-2,6-dicarboxylic acid was synthesized starting from pentaerythritol, and the opti$
$+18.8^o(c = 5.3, acetone). Using\ ^{13}CNMR, its optical purity was estimated to be 90$

$In order to obtain optically pure spiro[3.3]heptane-2,6-dicarboxylic acid, a series of spiro[3.3]heptane$
$2,6-dicarboxylic acid esters were synthesized, and chromatographic separations of the mona optically ac$
$2,6-dicarboxylate can be separated by chiral HPLC. Especially, dicinnamyl esters showed high solubility in$
$propanol solvent system and high separationability by HPLC on cellulose carbamate stationary phase. Opti$
$+1.84^o(c = 1.74, CHCl3) and [\alpha]D26 = -1.84^o(c = 1.74, CHCl3), respectively. Optically pure spiro[3.3]$
$2,6-dicarboxylic acid were first obtained by hydrolysis of the optically pure dicinnamyl esters with hydroch$
$+21.1^o(c = 5.32, acetone) and [\phi]40527 = -21.1^o(c = 5.33, acetone) for the two isomers, respectively.$

$Optically active polyamides were synthesized by NMP solution polycondensation of diamines and optic$
$2,6-dicarboxylic acid chloride. Comparing with suitable model compound and oligomers, the conformatio$
$phenylenediamine, 2',5'-diamino-4-(dimethylamino)-4'-nitro-stilbene, 3,3'-$
$dimethoxybenzidine took ordered conformations in solution.$

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