Highly Asymmetric and Anionic Polymerizations of Achiral Methacrylate by Using Axially Chiral Ligands

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Highly Asymmetric and Anionic Polymerizations of Achiral Methacrylate by Using Axially Chiral Ligands

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61470105

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Single-year Grants

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高分子合成

Research Institution

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Research Abstract

The asymmetric polymerization of achiral methacrylates having bulky ester groups was achieved successfully by using the following chiral anionic initiators. Thus, we synthesized optically active tetramethylethylenediamine (TMEDA) derivatives modified with C_2-chiral substituents derived from tartaric acid having asymmetric carbons, or more preferentially from atropisomeric biphenyls and binaphthyls. These ligands were complexed effectively to various organolithium compounds. The resulting chiral complexes polymerized triphenylmethyl methacrylate (TrMA) in toluene at -78° C. The produced polymers

showed high optical rotations owing to the helical conformation, which was formed with high stereosectivity through the polymerization. The rotation values and senses of the polymers were strongly depending upon the structures of the used ligands. Although reaher complicated stereochemical product/ligand correlations were observed, they were consistently explained in terms of the stereoelectronic interaction between the propagating end of the polymer chain and the chiral ligand complexed to the counter lithium cation. One of the most effective ligands was a biphenyl-monosubstituted TMEDA. Its lithium complexes served as effective initiators for the polymerization of not only TrMA but also its 2- pyridyl derivative. The polymers produced quantitatively had almost pure one-handed heliciy, and have so limited molecular weights as to be easily soluble in tetrahydrofuran. The optically active and solvent-soluble polymers were useful as chiral packing materials for HPLC. On the other hand, when less bulky methacrylates of methyl and benzyl alcohols were polymerized with the above initiators, the produced isotactic polymers showed negligible rotations. From this result, we now consider that such poly(ester)s can't form helical conformation being enough stable in solutions.

Research Products (11 results)

All | Other

All | Publications (11 results)

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[Publications] Shigeyoshi Kanoh: Die Makromolekulare Chemic. 187. 53-59 (1986)

[Publications] Shigeyoshi Kanoh: Die Makromolekulare Chemie. 188. 463-474 (1987)

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