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First Disyndiotactic Polymer from a 1,4-Disubstituted Butadiene by Alternate Molecular Stacking in the Crystalline State

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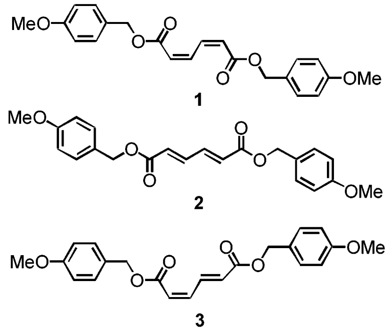
The control of polymer chain structures in polymer synthesis can hardly be overestimated for the architecture of advanced polymeric materials, because all of the features and functions of polymers as organic solids importantly depend on chain structures and, also, the structure of the polymer chain assembly. Especially, the stereochemistry of polymers has received significant attention in both fundamental and applied fields ever since the first discoveries of stereoregular polymers. Highly controlled stereospecific polymerization has already been well established by coordination polymerization of olefins and diene monomers, and by anionic polymerization of certain types of polar monomers.[1] Radical polymerization is the most important and convenient process for the production of various kinds of vinyl and diene polymers due to recent achievements of well-controlled polymerizations in addition to the classical advantages of the radical process. It includes two fundamentally different approaches to stereochemical control of polymers: one is the catalytic control[2] of the propagating chain end using Lewis acids, solvents, and chiral auxiliaries, and another is the use of polymerizations in organized and constrained media.[3] Topochemical polymerizations of organized monomers are useful not only for the control of polymer tacticity, but also for the fabrication of polymer composites designed on the basis of supramolecular architecture and crystal engineering.[4]

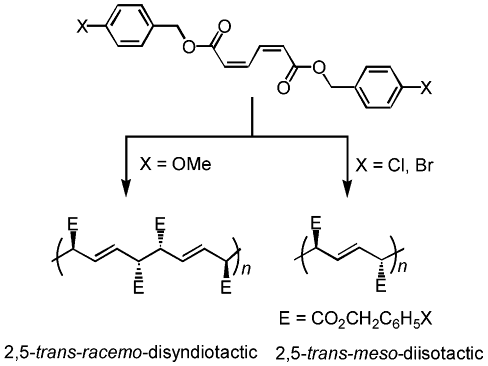
In general, the stereochemical structure of 1,4-disubstituted butadienes is represented not only by 1,2-, 1,4-, and cis−trans isomerism but also by isotactic−syndiotactic and meso−racemo (or erythro−threo) relationships. These polymers are referred to as tritactic polymers due to the presence of three elements of stereoisomerism for each monomer unit, that is, two pseudoasymmetric carbon centers and a double bond.[5] During the topochemical polymerization of 1,3-diene mono- and dicarboxylates including muconic and sorbic acid derivatives, 2,5-*trans-meso*-diisotactic polymers were always produced due to the translational molecular packing in a column with an appropriate stacking distance of 5 Å in the crystals.[6−8] Recently, however, we have confirmed that a different type of molecular packing is formed in the crystals of the 4-methoxy substituted benzyl ester monomers (Scheme 1) and that the molecular packing leads to the formation of another type of stereoregular polymer.

Here, we report the first synthesis of a *trans*-disyndiotactic polymer as the tritactic polymer through topochemical polymerization using di(4-methoxybenzyl) muconate as the 1,3-diene dicarboxylate monomer. It provides a 2,5-*trans-racemo*-disyndiotactic polymer under photoirradiation in the crystalline state (Scheme 2), as a result of the alternating molecular stacking in a column formed in the crystals with aid of weak hydrogen bonds such as CH/π and CH···O intermolecular interactions,[9] while di(4-chlorobenzyl) and di(4-bromobenzyl) (*Z,Z*)-muconates[10] provide diisotactic polymers due to the translational molecular stacking supported by the CH/π and halogen−halogen interactions.

Scheme 1



Scheme 2



The photoirradiation of **1** and **2** in the crystalline state for 8 h provided the identically structured polymer in 93 and 81% yield, respectively, via a radical chain reaction mechanism, while the *EZ*-derivative **3** had no reaction under similar conditions. The polymer was produced quantitatively under γ-radiation with a dose of 200 kGy. The single-crystal structures of **1** and **2** revealed that monomer molecules are packed in a column in the alternate fashion[11] (Figure 1). In the crystal of **3**, no columnar structure was observed. The stacking distance (d_s) of monomer molecules, which was evaluated as the distance between the mass centers of adjacent monomer molecules, is 4.74 and 4.87 Å, and the carbon-to-carbon distance between C2 and C5′ carbons is 3.44 and 3.32 Å for **1** and **2**, respectively. These values are very similar to the values previously reported for other diene monomers providing isotactic polymers.[8]

The single-crystal structure analysis of **1** and poly(**1**) indicates that the propagation reaction proceeds to make a polymer chain accompanying a change in the type of chemical bonds, but with a minimum movement of atoms. The conformational structures are similar to each other before and after polymerization, being

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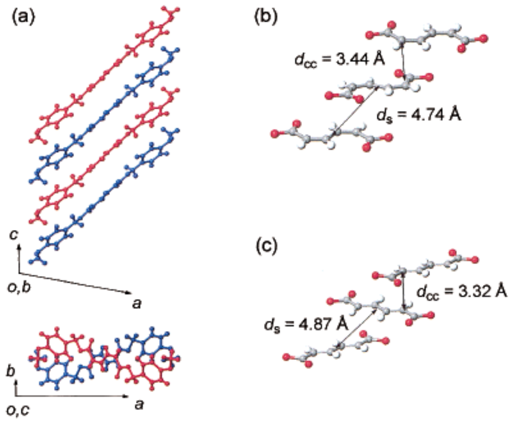

Figure 1. Crystal structures of **1** (a) and monomer stacking structure in a column in the crystals of **1** (b) and **2** (c).

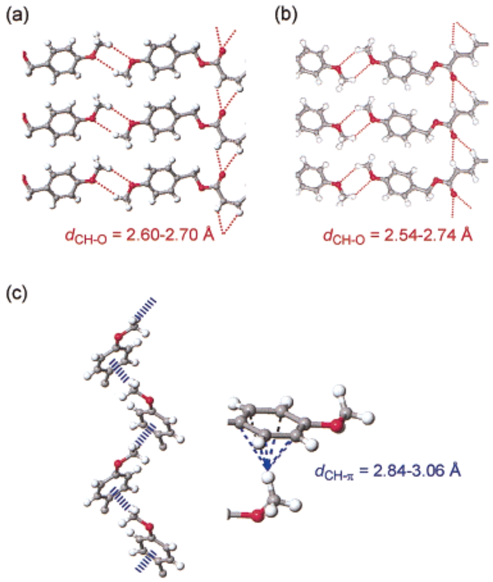

Figure 2. Intercolumn CH···O interaction in the crystals of **1** (a) and poly(**1**) (b), and CH/π interaction in a column in the crystal of **1** (c).

supported by the weak intermolecular interaction between adjacent monomer molecules in a column and intercolumns. The adjacent columns are linked to each other by the CH···O interaction between the methoxy groups to make a sheet structure, and between the carbonyl oxygen and the hydrogen of a butadiene moiety, as shown in Figure 2a and b. The molecular sheets stack alternately to fabricate the molecular stacking structure appropriate for the syndiotactic polymerization in the crystals. In the column along the *c*-axis, close CH/π contact (e.g., 2.84−3.06 Å for **1**) is observed between the benzene ring and the methoxy group (Figure 2c). The CH···O and CH/π interactions are maintained during the polymerization.

In conclusion, we have demonstrated that the combination of weak interactions is useful for the design of topochemical polymerization to yield a new type of stereoregular polymer. In a previous paper,[10] we reported that the halogen−halogen interaction as the supramolecular synthon has a significant potential for rational crystal design of the diene monomers in combination with other weak interactions. Thus, the weak intermolecular interactions are tolerant to a variety of crystal structure formations to induce a different molecular stacking leading to the different tacticity of polymers, being different from the strong hydrogen bond network, which is robust and credible but inflexible, for the ammonium derivatives.[7] The physical properties of disyndiotactic polymers will be investigated and appear elsewhere in the future.

Supporting Information Available: Preparation methods, spectra, powder X-ray diffraction profiles, ORTEP, and detailed crystallographic data (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal structure for **1**: $C_{22}H_{22}O_6$, 382.41, colorless plates, monoclinic, space group $C2/c$, $a = 36.026(3)$ Å, $b = 5.6019(4)$ Å, $c = 9.4840(7)$ Å, $\beta = 100.27(1)$ deg, $V = 1883.4(2)$ Å^3, $Z = 4$, reflns measured 7901, unique reflns 2151, $R_{merge} = 0.087$, no observed ($I > 2\sigma(I)$) 1269, parameter ratio 7.42, $R = 0.070$, $R_w = 0.104$, GOF = 1.18, temp −70 °C. For **2**: $C_{22}H_{22}O_6$, 382.41, colorless plates, monoclinic, space group $C2/c$, $a = 35.644(4)$ Å, $b = 5.6923(4)$ Å, $c = 9.7803(6)$ Å, $\beta = 100.533(3)$ deg, $V = 1951.0(2)$ Å^3, $Z = 4$, reflns measured 7791, unique reflns 2098, $R_{merge} = 0.032$, no observed ($I > 2\sigma(I)$) 1726, parameter ratio 10.46, $R = 0.048$, $R_w = 0.100$, GOF = 0.96, temp −70 °C. For **3**: $C_{22}H_{22}O_6$, 382.41, colorless plates, triclinic, space group $P\bar{1}$, $a = 6.6919(1)$ Å, $b = 10.784(1)$ Å, $c = 14.0070(8)$ Å, $\alpha = 107.237(5)$ deg, $\beta = 99.272(3)$ deg, $\gamma = 93.847(4)$ deg, $V = 945.7(1)$ Å^3, $Z = 2$, reflns measured 7491, unique reflns 4039, $R_{merge} = 0.048$, no observed ($I > 2\sigma(I)$) 2635, parameter ratio 9.80, $R = 0.136$, $R_w = 0.209$, GOF = 1.98, temp 23 °C, methoxy methyl groups are disordered. For poly(**1**): $C_{22}H_{22}O_6$, $(382.41)_n$, colorless plates, monoclinic, space group $C2/c$, $a = 35.117(4)$ Å, $b = 5.7980(6)$ Å, $c = 9.436(1)$ Å, $\beta = 99.321(2)$ deg, $V = 1895.9(3)$ Å^3, $Z = 4$, reflns measured 6714, unique reflns 2151, $R_{merge} = 0.033$, no observed ($I > 2\sigma(I)$) 1620, parameter ratio 9.47, $R = 0.043$, $R_w = 0.071$, GOF = 0.89, temp 23 °C.

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