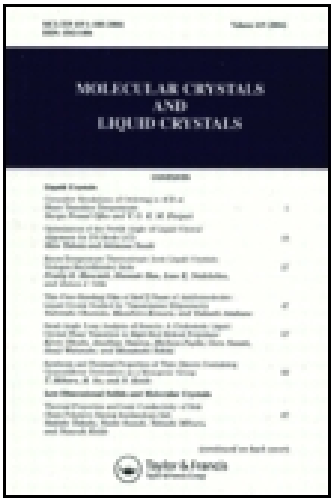

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# Polymer Crystal Engineering for Control of Stereochemical Structure of Polymers: Stereospecific Monomer Synthesis and Stereospecific Solid-State Polymerization

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# Polymer Crystal Engineering for Control of Stereochemical Structure of Polymers: Stereospecific Monomer Synthesis and Stereospecific Solid-State Polymerization

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*We have successfully synthesized diisotactic and disyndiotactic polymers of (Z,Z)- and (E,E)-muconates with various benzyl ester groups. Muconic acid was conveniently converted into its corresponding ester derivatives without EZ isomerization when reacted with benzyl bromides in the presence of potassium carbonate in hexamethylphosphoramide (HMPA) at room temperature. Several monomers undergo photopolymerization in the crystalline state to give stereoregular polymers according to the monomer configuration and the ester substituents. X-ray single crystal structure analysis of the monomer and polymer crystals has revealed the process of the topochemical polymerization. In the monomer crystals with 4-alkoxybenzyl groups as the ester substituents, a columnar structure is formed by the alternate stacking of monomer molecules with the aid of weak hydrogen bonds such as CH/π and CH/O intermolecular interactions. The alternate stacking is appropriate for syndiotactic polymerization, being different from the crystal structures of many other ester monomers which provide a diisotactic polymer due to the translational monomer stacking in a column, as is seen in the crystals of the 4-chloro-, 4-bromo-, and 4-nitro-substituted benzyl esters. Weak and flexible intermolecular interactions provide a variety of crystal structures and different type of molecular stacking leading to the different tacticity of the polymers.*

**Keywords:** crystal engineering; CH/π interaction; controlled radical polymerization; isotactic polymer; solid-state photoreaction; syndiotactic polymer; tacticity; topochemical polymerization; weak hydrogen bond; X-ray structure

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## INTRODUCTION

We have recently investigated polymer structure control and organic material design based on polymer crystal engineering [1,2]. The structures and properties of crystalline materials are designed using pre-organized molecules through various intermolecular interactions such as hydrogen bonds, $\pi/\pi$, CH/$\pi$, CH/O, and halogen interactions [3–5]. In the previous papers [6–9], we have reported the features and mechanisms of the topochemical polymerization of 1,3-diene monomers including some ester, ammonium, and amide derivatives of muconic and sorbic acids. We have already proposed the topochemical polymerization principles for diene monomers on the basis of the crystallographic data accumulated for various kinds of diene monomers. The combination of several intermolecular interactions is useful for the construction of molecular packing appropriate for 5 Å stacking in order to facilitate the topochemical polymerization in the crystalline state [6]. Furthermore, we have successfully synthesized a novel disyndiotactic polymer of di(4-alkoxybenzyl) (*Z,Z*)- and (*E,E*)-muconates [10]. To understand the relationship between the crystal structure and the solid-state reactivity is most important for further development and a more sophisticated design of new crystalline materials by polymer crystal engineering. Actually, however, the EZ isomerism of muconic derivatives importantly influences the photoreaction behavior in the crystalline state. Consequently, the stereoselective synthesis of muconic esters as monomers is necessary for the design and control of polymer structures. The ZZ isomers of muconic derivatives readily isomerize to the corresponding EZ and EE isomers, but the reverse hardly proceeds. A few synthetic routes have been reported for ZZ muconic derivatives without EZ isomerization [11,12].

In this paper, we report the stereospecific monomer synthesis and solid-state polymerization of various benzyl muconate derivatives to reveal the molecular stacking in the crystals as well as the tacticity of the resulting polymers during topochemical polymerization.

## EXPERIMENTAL

### Monomer Synthesis

The general procedure for the esterifications using a phase transfer catalyst is as follows. (*Z,Z*)-Muconic acid (711 mg, 5.0 mmol), tetrabutylammonium hydrosulfate (3.73 g, 11 mmol), and potassium hydroxide (1.23 g, 22 mmol) were dissolved in 20 mL of 1,2-dichloroethane and 20 mL of water in a 100-mL flask. 4-Bromobenzyl bromide (2.75 g,

11 mmol) was added and the mixture stirred at room temperature for 3 days. The reaction mixture was poured into 100 mL of water, and the crude product was extracted with two portions of 100 mL of chloroform. After the chloroform solution was washed with water and then dried over sodium sulfate, the chloroform was evaporated under reduced pressure, providing a crude white solid. The solid was subjected to short-path silica gel column chromatography using chloroform, providing di(4-bromobenzyl) muconate. Yield 20.1 g (84%), isomer ratio of ZZ:EZ = 82:18 (determined by $^1$H NMR spectroscopy).

The general procedure for the esterification with HMPA is as follows. To (*Z,Z*)-muconic acid (1.01 g, 7.11 mmol) in 10 mL of HMPA in a 150-mL flask equipped with a calcium chloride tube, were added 4-bromobenzyl bromide (3.91 g, 15.6 mmol) and potassium carbonate (1.47 g, 10.6 mmol) and the mixture stirred at room temperature for 1 day. The reaction mixture was poured into 100 mL of water, and the crude product was washed with methanol to afford di(4-bromobenzyl) muconate, yield 2.70 g (79%), with an isomer ratio of ZZ:EZ = ~100:0. The product obtained was further purified by recrystallization. The EZ-muconates can be prepared from (*E,Z*)-muconic acid, similarly.

For the synthesis of EE-monomers, the crude products (as a mixture of isomers in chloroform) were photoirradiated with a high-pressure mercury lamp at room temperature in the presence of a small amount of iodide. The ester derivatives other than 4-bromobenzyl esters were prepared similarly.

## Polymerization

The monomer crystals were photoirradiated with a high-pressure mercury lamp (Toshiba SHL-100-2, 100 W, Pyrex filter) at a distance of 10 cm under atmospheric conditions at room temperature. After irradiation, the polymers were isolated by removal of the unreacted monomer with chloroform.

## X-ray Crystallography

Single crystal X-ray data were collected on a Rigaku R-AXIS RAPID Imaging Plate diffractometer using Mo-$K_\alpha$ radiation monochromated by graphite. The structures were solved by a direct method with the program SIR92 and refined using full-matrix least-squares procedures. All calculations were performed using the Crystal Structure crystallographic software package from the Molecular Structure Corporation.

## RESULTS AND DISCUSSION

### Stereospecific Monomer Synthesis

Table 1 summarizes the results for the synthesis of di(4-bromobenzyl) muconate using (*Z,Z*)-muconic acid as the starting material. When muconic esters were prepared by classic methods, it was difficult to obtain ZZ isomers efficiently without EZ isomerization. For example, the dehydration of muconic acid and 4-bromobenzyl alcohol in the presence of a catalytic amount of sulfuric acid under reflux in benzene for 3 h resulted in ester formation in a low yield (8%) with a molar ratio of ZZ:EZ = 4:96 (run 6). When the muconic acid chloride was prepared from (*Z,Z*)-muconic acid and thionyl chloride by reflux in dichloromethane for 1 h and was then allowed to react with 4-bromobenzyl alcohol in the presence of triethylamine, a mixture of the esters was isolated in 28% yield (ZZ:EZ:EE = 82:14:4) (run 5). The ZZ isomer was isolated by silica gel chromatography, but the EZ and EE isomers can hardly be separated from each other.

The undesirable results of esterification have prompted us to investigate other methods for suppressing the isomerization. To develop reactions under milder conditions, we first adopted a quaternary ammonium carboxylate salt as the phase transfer catalyst (runs 1–3). Another method is the reaction of the carboxylic acid with benzyl bromides in the presence of bases in a highly polar aprotic solvent such as hexamethylphosphoramide (HMPA) (run 4).

Muconic acid was dissolved with KOH (4.4 equiv.) and tetrabutylammonium hydrosulfate (2.2 equiv.) in 1,2-dichloroethane and water, followed by addition of 2.2 equiv. of 4-bromobenzyl bromide and

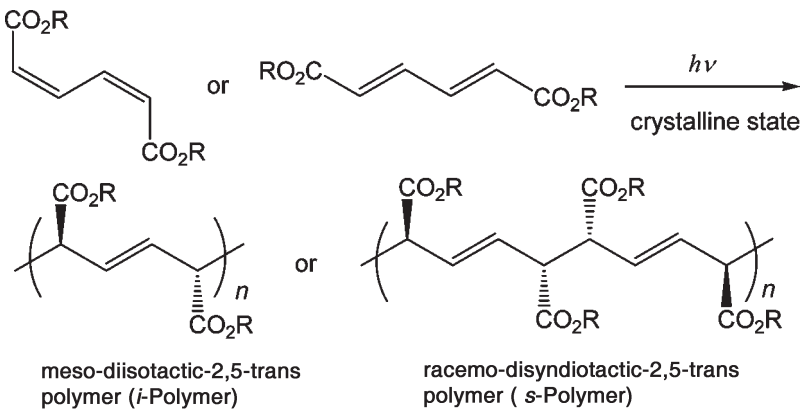
**TABLE 1** Stereospecific Synthesis of Di(4-bromobenzyl) Muconate Monomer

| Run no. | Reaction conditions[a] | Yield (%) | Isomer ratio (ZZ:EZ:EE) |
|---|---|---|---|
| 1 | KOH(4.4 equiv.), PTC, r.t., 3 days | 84 | 30:70:0 |
| 2 | KOH(4.4 equiv.), PTC, reflux, 1 h | 58 | 30:70:0 |
| 3 | $K_2CO_3$(2.2 equiv.), PTC, r.t., 3 days | 56 | 82:18:0 |
| 4 | $K_2CO_3$(1.5 equiv.), HMPA, r.t., 1 day | 79 | ~100:0:0 |
| 5 | $SOCl_2$, $CH_2Cl_2$, reflux, 1 h | 28 | 82:14:4 |
| 6 | $H_2SO_4$(cat), benzene, reflux, 3 h | 8 | 4:96:0 |

[a]Phase transfer catalyst (PTC) method: (*Z,Z*)-muconic acid 1 g, 4-bromobenzyl bromide (2.2 equiv.), tetrabutylammonium hydrosulfate (2.2 equiv.), 1,2-dichloroethane 20 mL, water 20 mL. Hexamethyl-phosphoramide (HMPA) method: (*Z,Z*)-muconic acid 1 g, 4-bromobenzyl bromide (2.2 equiv.), potassium carbonate (1.5 equiv.), HMPA 10 mL.

**TABLE 2** Stereospecific Polymerization of Substituted Benzyl Muconates in the Solid State

| Run no. | Configuration | Ester groups (R) | Stacking structure | Photo-product |
|---|---|---|---|---|
| 1 | ZZ- | 2-Methoxybenzyl | – | EE-Isomer |
| 2 | ZZ- | 3-Methoxybenzyl | – | EE-Isomer |
| 3 | ZZ- | 4-Methoxybenzyl | Alternate | *s*-Polymer |
| 4 | ZZ- | 4-Ethoxybenzyl | Alternate | *s*-Polymer |
| 5 | | ZZ- | 4-Butoxybenzyl | Translational |
| | *i*-Polymer | | | |
| 6 | | ZZ- | 4-Chlorobenzyl | Translational |
| | *i*-Polymer | | | |
| 7 | | ZZ- | 4-Bromobenzyl | Translational |
| | *i*-Polymer | | | |
| 8 | | ZZ- | 4-Nitrobenzyl | Translational |
| | *i*-Polymer | | | |
| 9 | | ZZ- | 4-Methylbenzyl | – |
| | No Reaction | | | |
| 10 | EE- | 2-Methoxybenzyl | – | No Reaction |
| 11 | EE- | 3-Methoxybenzyl | Translational | *i*-Polymer |
| 12 | EE- | 4-Methoxybenzyl | Alternate | *s*-Polymer |
| 13 | EE- | 4-Ethoxybenzyl | Alternate | *s*-Polymer |
| 14 | EE- | 4-Butoxybenzyl | – | *s*-Polymer |
| 15 | EE- | 4-Chlorobenzyl | – | No Reaction |
| 16 | EE- | 4-Bromobenzyl | – | No Reaction |
| 17 | EE- | 4-Nitrobenzyl | – | No Reaction |
| 18 | EE- | 4-Methylbenzyl | – | No Reaction |




**SCHEME 1**

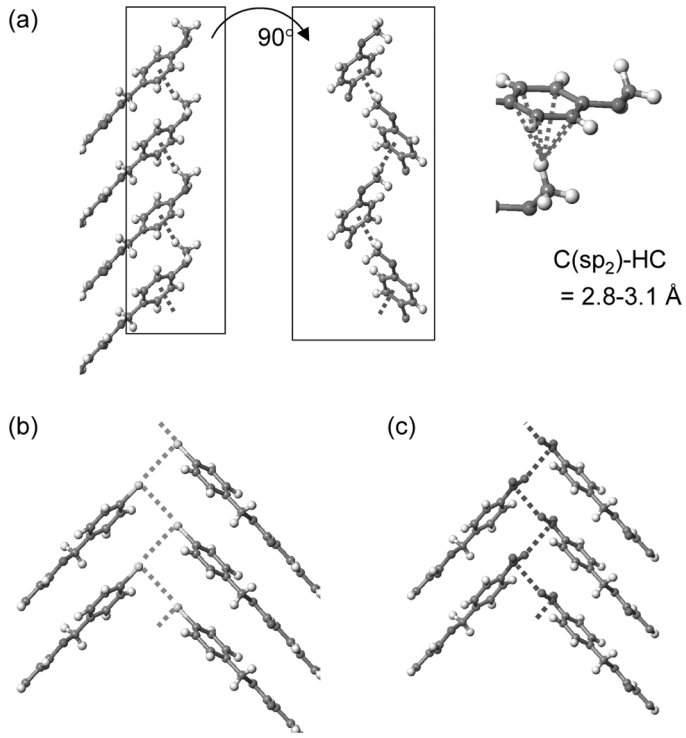



**FIGURE 1** Intermolecular interaction in the monomer crystals. (a) Alternate stacking of di(4-methoxybenzyl) (*Z,Z*)-muconate. (b) Translational stacking of di(4-chlorobenzyl) (*Z,Z*)-muconate. (c) Translational stacking of di (4-nitrobenzyl) (*Z,Z*)-muconate.

stirring for 3 days at room temperature to afford the ester in an isolated yield of 84% with an isomer ratio of ZZ:EZ = 30:70. When $K_2CO_3$ was used as the weak base, the isomerization was suppressed; ZZ:EZ = 82:18. Furthermore, we have found that (*Z,Z*)-muconic acid was readily converted into the corresponding ester without EZ isomerization by the reaction of the potassium muconate with benzyl halides in HMPA [13,14]. This procedure for the esterification and the subsequent isolation was very simple and convenient, as is shown in the experimental section.

## Stereospecific Polymerization in the Solid State

The photopolymerization was carried out under UV irradiation with a high-pressure mercury lamp for 8 h at room temperature. The results

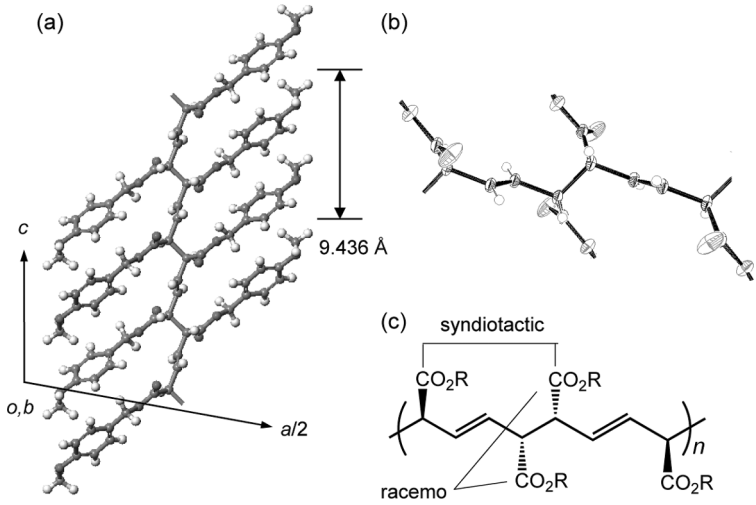



**FIGURE 2** (a) Crystal structure of poly(4-methoxybenzyl muconate). (b) ORTEP drawing. The benzyl moieties are omitted for clarity. (c) Stereochemical relationship for racemo-disynidiotactic polymer.

of the reactions are shown in Table 2. Some ZZ monomers provided the corresponding EE isomers (runs 1, 2). Several other monomers underwent photopolymerization to give polymers with highly controlled stereochemical structures, i.e., meso-diisotactic-2,5-trans and racemo-disyndiotactic-2,5-trans polymers, as shown in Scheme 1.

The X-ray single crystal structure analysis has successfully revealed the stacking structure of the monomer molecules in the crystals and also the stereochemistry of the polymer chains in the polymer crystals [7,10]. Figure 1 shows intermolecular interactions for the alternate and translational molecular stacking of benzyl muconate monomers bearing the methoxy, chloro, and nitro substituents at the para position of their benzyl group. For the alternate stacking, CH/$\pi$ interaction is observed between the benzene ring and the methoxy hydrogens along the specific axis, which is the same direction as that for the formation of polymer chains. The alternate packing of the monomer molecules results in syndiotactic polymerization upon photoirradiation. The 4-methoxy and ethoxy substitutions induce the alternate stacking, irrespective of the monomer configuration (runs 3, 4, 12, and 13), whereas the 4-butoxybenzyl derivatives of ZZ muconate resulted in the translational packing leading to the diisotactic polymerization (run 5), similarly to the 4-chloro, 4-bromo, and 4-nitrobenzyl (*Z,Z*)-muconates (runs 6–8). The corresponding EE

isomers showed no reactions under similar photoirradiation conditions (runs 14–17). The 2-methoxy derivatives (runs 1, 10) and the ZZ isomer of the 3-methoxy derivative (run 2) as well as the 4-methylbenzyl derivatives (runs 9, 18) gave no polymers, but the 3-methoxy (*E,E*)-muconate polymerized to give a diisotactic polymer under $\gamma$-radiation by the appropriate translational monomer stacking in the crystals (run 11). We have directly confirmed the topochemical polymerization process by the single crystal structure analysis of both the monomer and polymer crystals. Figure 2 shows the crystal structure of poly-(4-methoxybenzyl muconate), from which we can determine the stereochemical structure of the polymer chain; i.e., racemo-disyndiotactic-2,5-trans structure as well as a polymer chain assembly in the crystals.

Thus, we have demonstrated that weak intermolecular interactions such as CH/$\pi$ and halogen–halogen interactions are important in constructing of the stacking structures for polymerization and that the stacking structure depends on the position and structure of the substituents in the benzyl groups. Further detailed investigation of crystal structure analysis, molecular packing, and polymer properties will be reported elsewhere in the future.

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