Topochemistry

Supramolecular Control over the Stereochemistry of Diene Polymers**

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Polymers with different properties can be derived from the same starting monomers by changing the way the repeating units are connected during formation of the polymer. For example, although cellulose, starch, and glycogen consist of glucose as the repeating unit and have a similar repeating structure, and natural rubber and guttapercha are *cis*- and *trans*-1,4-polyisoprenes, respectively, they have different physical and other properties because of their stereochemical structure. Thus, the stereochemistry of polymers, namely, the tacticity, is one of the most important factors for determining the properties of polymeric materials, as well as the repeating unit structure, molecular weight, and molecular-weight distribution. Various catalytic polymerization techniques have been developed since the first discovery of the stereospecific polymerization by Natta and co-workers.[1] As a result, polymer tacticity can now be precisely controlled by the coordination and anionic polymerization of olefins, dienes, and several polar vinyl monomers,[2] as well as by a radical polymerization process.[3,4]

Topochemical polymerization in the crystalline state is the most promising method for controlling the stereochemistry of polymers.[5,6] The structure of polymer chains as well as the polymerization rate are determined by the molecular packing of the monomers in the crystals. Recent amazing developments in supramolecular assembly and crystal engineering now enable us to design and fabricate crystals with a molecular stacking for any function and reaction.[7–10] The rational design of organic crystals has changed topochemical polymerization from a trial-and-error approach to a credible molecular and materials design.[11–13] Here, we report the control that can be achieved over the stereochemical structure of polymers during the solid-state polymerization of 1,3-diene monomers by a novel approach based on crystal engineering. Molecular alignment in the monomer crystals is controlled by several intermolecular interactions, such as strong and weak hydrogen bonds, which leads to the formation of various types of stereoregular polymers through a topochemical polymerization process. This approach to the stereocontrol of polymers differs from other conventional ways of controlling the propagating chain end using catalysts or additives during solution polymerization.

The 1,3-diene dicarboxylic acid derivative muconic acid has three isomers with *Z*,*Z*, *E*,*E*, and *E*,*Z* configurations.[14] 1-Naphthylmethylammonium (*Z*,*Z*)- and (*E*,*E*)-muconates ((*Z*,*Z*)-**1** and (*E*,*E*)-**1**, respectively) with C_2 symmetry favor a translational molecular packing in the crystals. The reacting diene moieties stack in a columnar structure with the aid of two-dimensional (2D) hydrogen-bonding networks at the interface of the muconate anion and countercation layers in the lamella crystals. Topochemical polymerization of (*Z*,*Z*)-**1** and (*E*,*E*)-**1** by UV irradiation in the crystalline state produces the same stereoregular polymer with a *meso*-diisotactic structure.[15] On the other hand, the *Z*,*Z* and *E*,*E* 4-methoxybenzyl muconates (*Z*,*Z*)-**2** and (*E*,*E*)-**2**, respectively, stack alternately in a column through a CH/π interaction between the methoxy protons and the π electrons of the phenyl group, which results in the formation of a *racemo*-disyndiotactic polymer upon photoirradiation.[16]

Topochemical polymerization of the corresponding *E*,*Z* monomers with a different symmetrical structure produced a new type of stereoregular polymer (Scheme 1). The translational molecular packing of 1-naphthylmethylammonium (*E*,*Z*)-muconate ((*E*,*Z*)-**1**) by the interaction of 2D hydrogen-bonding networks gives a *racemo*-diisotactic polymer. Similarly, the alternate stacking of 4-methoxybenzyl (*E*,*Z*)-muconate ((*E*,*Z*)-**2**) results in the formation of a *meso*-disyndiotactic polymer.[17]

Irradiation of the crystals of (*E*,*Z*)-**1** with UV light afforded an atactic polymer as a result of the simultaneous occurrence of isomerization and polymerization, while no reaction occurred with (*E*,*Z*)-**2** (Table 1). However, polymerization of (*E*,*Z*)-**1** and (*E*,*Z*)-**2** with γ-radiation at 200 kGy provided polymers in yields of 61 and 96%, respectively, without any isomerization to form the *E*,*E* isomers. The powder X-ray diffraction profiles of the monomers and the polymers showed that the polymerizations proceed by a topochemical reaction process in which a similar and highly crystalline structure is maintained (see the Supporting Information). The structure of the *racemo*-diisotactic polymer obtained from (*E*,*Z*)-**1** was confirmed by the solid-state hydrolysis of the corresponding poly(muconic acid) derived from the ammonium polymers. A pair of adjacent carboxy groups of the *racemo*-diisotactic poly(muconic acid) are located in the same direction along the main chain, while the carboxy groups of the *meso*-diisotactic polymer are on opposite sides of the polymer chain. Heating the *racemo* polymer at 250 °C resulted in a weight loss as a consequence of the formation of the five-membered ring acid anhydride; in contrast no weight loss was observed for the *meso* polymers at the same temperature. The stereospecific dehydration was also confirmed by IR spectroscopy by the appearance of new peaks at 1864, 1777, and 921 cm^{-1}.

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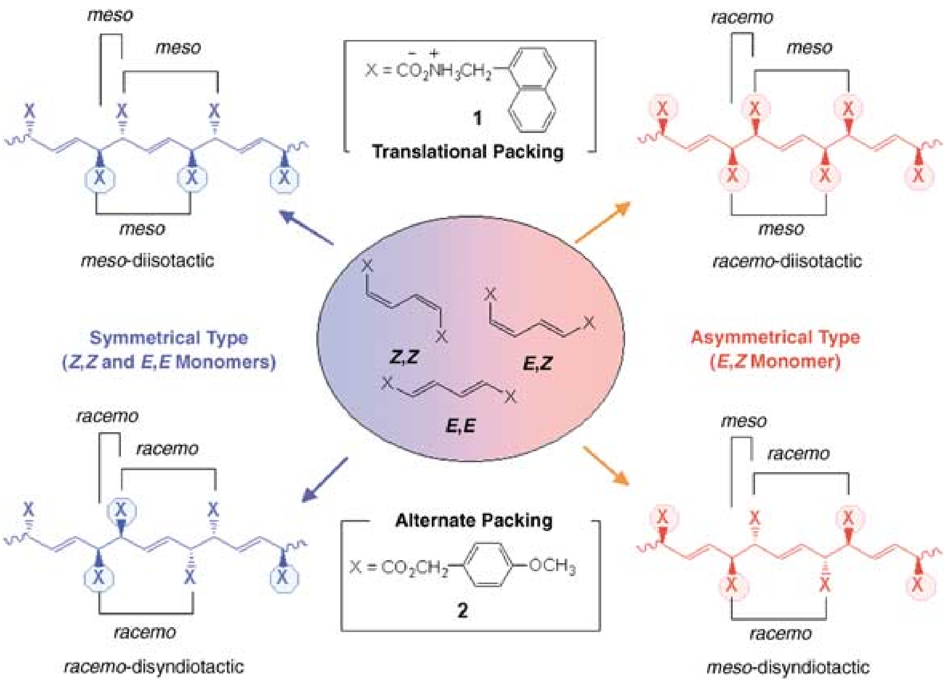

Scheme 1. Stereoregular polymer sequences for *trans*-1,4-polymers obtained from 1,3-diene dicarboxylic acid derivatives.

Table 1: Radiation polymerization of muconates in the crystalline state.[a]

Monomer	UV irradiation Polymer structure	Yield [%]	γ-radiation Polymer structure	Yield [%]
(*Z*,*Z*)-**1**	*meso*-diisotactic	90	*meso*-diisotactic	96
(*E*,*E*)-**1**	*meso*-diisotactic	71	*meso*-diisotactic	99
(*E*,*Z*)-**1**	atactic	8[b]	*racemo*-diisotactic	61
(*Z*,*Z*)-**2**	*racemo*-disyndiotactic	93	*racemo*-disyndiotactic	ca. 100
(*E*,*E*)-**2**	*racemo*-disyndiotactic	81	*racemo*-disyndiotactic	ca. 100
(*E*,*Z*)-**2**	no reaction	0	*meso*-disyndiotactic	96

[a] UV irradiation was carried out using a high-pressure mercury lamp for 8 h at room temperature. γ-Radiation was carried out using ^{60}Co at a dose of 200 kGy. [b] UV irradiation for 40 h. An atactic polymer was formed by the *E*,*Z* isomerization of (*E*,*Z*)-**1** and the subsequent copolymerization of the *E*,*Z* and *E*,*E* isomers.

The polymer obtained from the γ radiation of (*E*,*Z*)-**2** was soluble in chloroform despite its high crystallinity. As shown in the molecular stacking structures of (*Z*,*Z*)-**2**, (*E*,*E*)-**2**, and (*E*,*Z*)-**2** in Figure 1, the reactive section of these monomers has an alternate stacking, which leads to formation of the stereoregular polymer with a disyndiotactic structure. The *racemo* and *meso* structures of poly((*Z*,*Z*)-**2**) or poly((*E*,*E*)-**2**) and poly((*E*,*Z*)-**2**), respectively, were confirmed by ^{13}C NMR spectroscopy. Poly((*Z*,*Z*)-**2**) as well as poly((*E*,*E*)-**2**) were insoluble in organic solvents in the highly crystalline forms in which they are obtained by polymerization, but they can be isolated as amorphous and readily soluble solids after the bulk material is heated above their melting points (199 and 195 °C for poly((*Z*,*Z*)-**2**) and poly((*E*,*E*)-**2**), respectively), or from a polar solvent at a high temperature. X-ray diffraction and DSC analyses confirmed the amorphous structure of the polymers recovered after cooling or reprecipitation. A comparison of the NMR data of the related polymers concludes that the chemical shifts for a series of the polymers show they are predominantly determined by the difference in the *meso-racemo* structure rather than that in the diisotactic-disyndiotactic one (see the Supporting Information).

Poly(**2**) compounds in which the benzyl ester groups were substituted by an electron-donating 4-methoxy group were readily converted into poly(muconic acid) by acid-catalyzed hydrolysis. Although diisotactic poly((*Z*,*Z*)-**2**) and poly((*E*,*E*)-**2**) dissolved and then underwent hydrolysis in concentrated sulfuric acid, the disyndiotactic poly((*E*,*Z*)-**2**) underwent heterogeneous hydrolysis in the reaction. Surprisingly, the conversion was quantitative even under mild conditions; completely hydrolyzed poly(muconic acid) was formed within 1 h at room temperature in concentrated sulfuric acid. We previously reported that poly(muconic acid) acts as an organic host compound for an organic intercalating system.[18] Disyndiotactic poly(muconic acid) was also examined as a host polymer for the intercalation of alkyl amines. The repeated intercalation behavior depended on the tacticity and hydrogen-bonding network structure of the polymers: the difference in the tacticity of the host polymer seriously affects the host–guest interactions. We are further investigating the details of the intercalation behavior as well as the physical properties of the polymers with a different stereochemical structure.

In conclusion, we have succeeded in synthesizing all four kinds of stereoregular polymers by controlling the stacking of symmetrical and asymmetrical monomers. This approach contrasts with the difficulty seen in the stereocontrol of diene polymers by catalytic routes.[19]

Experimental Section

(*Z*,*Z*)-Muconic acid was obtained from Mitsubishi Chemical Co., Ltd., Tokyo. Heating and photoirradiation of the *Z*,*Z* acid in solution provided the (*E*,*Z*)- and (*E*,*E*)-muconic acids, respectively. All ammonium monomers were prepared from the corresponding isomer of muconic acid with an amine in quantitative yield. All ester monomers were prepared by the reaction of the muconic acid and corresponding benzyl halides with potassium carbonate in hexamethylphosphoramide. The structures of all the monomers were determined by NMR, IR, and UV spectroscopies.

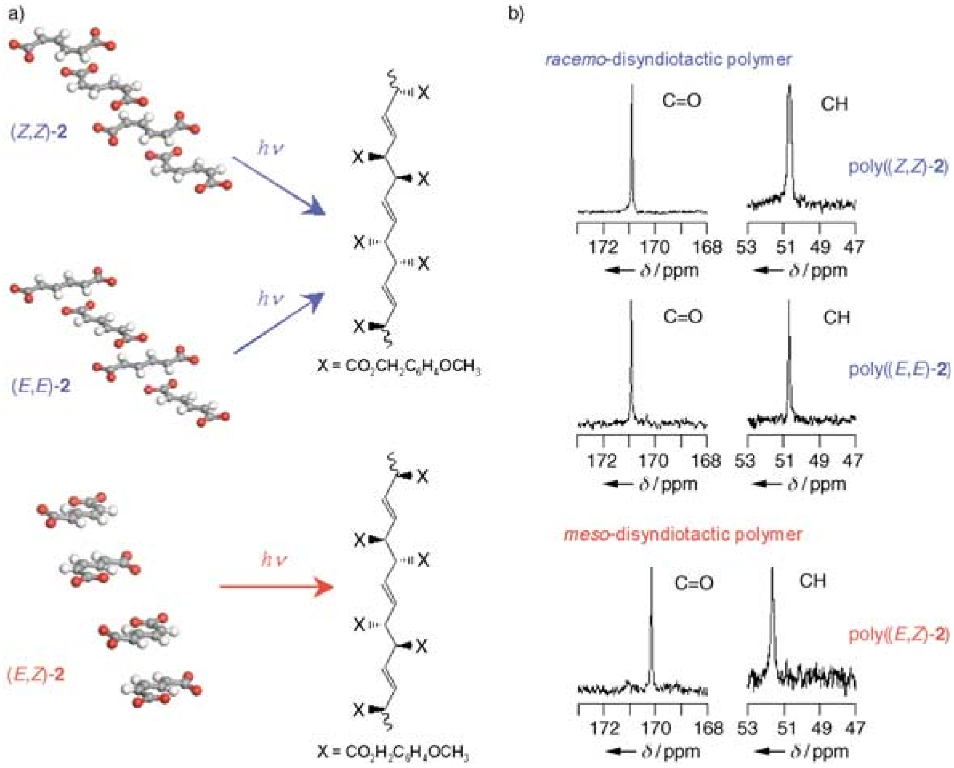

Figure 1. a) Alternate molecular stacking of (*Z,Z*)-**2**, (*E,E*)-**2**, and (*E,Z*)-**2** in a columnar structure in the crystals. The benzyl groups are omitted here for clarity. (*Z,Z*)-**2** and (*E,E*)-**2** produce the same stereoregular polymer, that is, the *racemo*-disyndiotactic-2,5-*trans* polymer, through the topochemical polymerization, while (*E,Z*)-**2** provides a *meso*-disyndiotactic-2,5-*trans* polymer. b) ^{13}C NMR spectra of *racemo*-disyndiotactic poly((*Z,Z*)-**2**) and poly((*E,E*)-**2**) as well as *meso*-disyndiotactic poly((*E,Z*)-**2**).

The monomer crystals were placed in a pyrex tube, which was then degassed and sealed. γ-Radiation was carried out with ^{60}Co at the Research Institute for Advanced Science and Technology, Osaka Prefecture University, Japan. The irradiation dose was 200 kGy at a dose rate of 48.6 kGy h^{-1}. After irradiation, the polymer was isolated by removal of any remaining monomer with methanol. The polymer yield was determined by gravimetric analysis.

NMR, IR, and UV spectra were recorded on a JEOL JMN A-400, JASCO Herschel FT-IR-430, and JASCO V-550 spectrometer, respectively. The powder X-ray diffraction data were collected with a Rigaku RINT-2100 diffractometer with monochromated $\mathrm{Cu_{K\alpha}}$ radiation ($\lambda = 1.5418$ Å, 30 kV, 20 mA, scan speed 1 deg min^{-1}). The thermogravimetric/differential thermal analysis measurements were carried out using a Seiko TG/DTA 6200 in a nitrogen stream at a heating rate of 10 °C min^{-1}.

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[17] The stereochemistry of these polymers is represented by the following two kinds of relationships: 1) the relative configuration between the two repeating monomer units: when all the

repeating units are in a *meso* arrangement the polymer is diisotactic, and when they are *racemo* it is disyndiotactic; 2) the relative configuration between the vicinal carbon centers (also represented by the same term, *meso* and *racemo*): when monomer molecules stack in a translational manner in a column in the crystals, both *Z*,*Z* and *E*,*E* isomers provide an identical *meso*-diisotactic polymer, and the *E*,*Z* isomer provides a *racemo*-diisotactic polymer. On the other hand, both the *Z*,*Z* and *E*,*E* monomers result in the formation of a *racemo*-disyndiotactic polymer when the monomers alternately stack in a column, and the *E*,*Z* monomer produces a *meso*-disyndiotactic polymer. See also refs. [2a] and [15a].

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