SHORT COMMUNICATIONS

Topochemical Polymerization of 1-Naphthylmethylammonium Sorbate and Characterization of the Resulting Stereoregular Polymer

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The control of the chain structures of polymers have been carried out by the polymerization in organized media including liquid crystallines, vesicles and bilayers, Langmuir-Blodgett films, inclusion and intercalated systems.¹ We have recently discovered that the crystals of diethyl (*Z,Z*)-muconate (diethyl (*Z,Z*)-2,4-hexadienedioate) provide polymer crystals under UV irradiation, and that the polymer produced consists of a highly regulated stereochemical structure because the polymerization proceeds in the crystalline state *via* a topochemical polymerization mechanism.² This polymerization was confirmed to be the first evident example as the topochemical polymerization of 1,3-diene compounds. Similar topochemical polymerization was also found to be applied for the derivatives other than the diethyl ester, *e.g.*, benzyl- and long-chain alkylammonium (*Z,Z*)-muconates.³ Furthermore, it is expected that a variety of diene compounds other than the muconic derivatives also can provide polymers with highly controlled chain structures during polymerization in the crystalline state. In 1985, Tieke⁴ reported the solid-state polymerization of long-alkyl chain derivatives of sorbic acid ((*E,E*)-2,4-hexadienoic acid) under UV or γ -ray irradiation, which resulted in the polymer with a *trans*-2,5-structure in a high yield. More recently, it was disclosed that the alternating copolymerization of octadecyl sorbate with oxygen proceeded in the crystalline state under UV irradiation, and that the polymerization behavior depended on the reaction conditions, *i.e.*, in the absence or presence of oxygen and the kind of recrystallization solvents.⁵ The γ -ray polymerization of the diene derivatives in the solid state has been also reported, dependent on the kind of the irradiation, *i.e.*, UV light or γ -ray.^{6,7} However, there is no direct evidence for the formation of a stereoregular polymer in these literatures previously reported as to the crystalline-state polymerization of sorbic acid derivatives.

We examined the photochemical behavior of some alkylammonium sorbates in the crystalline state and found that the derivative containing a naphthalene moiety proceeds topochemical polymerization to yield a stereoregular polymer. In this paper, the preliminary results of the polymerization as well as the characterization of the polymer obtained are described.

The photoirradiation of various alkylammonium sor-

bates was carried out in the crystalline state with a high-pressure mercury lamp. **1e** provided an insoluble product in a quantitative yield for 8-h irradiation at 30°C as shown in Table I, whereas the other salts including isopropyl, *n*-butyl, *t*-butyl, and benzylammoniums were inert under UV irradiation.⁸ Other derivatives containing a naphthyl group were also prepared, but the ammonium salt **1f** and the ester **2** were isolated as liquid at room temperature, and the crystals of the amide **3** was inert to the photoirradiation. The photoproduct obtained from **1e** was insoluble in any solvents; for example, organic solvents such as *n*-hexane, toluene, chloroform, acetone, tetrahydrofuran, dimethyl sulfoxide, ethanol, methanol, trifluoroacetic acid, and acid or alkali, *i.e.*, dilute HCl and NaOH aqueous solutions as well as water. The IR

Scheme 1.

Table I. Photoreaction of alkylammonium sorbates in the crystalline state^a

Substrate	Alkylammonium	Photoproduct	Yield/%
1a	<i>n</i> -Butylammonium	No reaction	0
1b	Isopropylammonium	No reaction	0
1c	<i>t</i> -Butylammonium	No reaction	0
1d	Benzylammonium	No reaction	0
1e	1-Naphthylmethylammonium	Polymer	98
1f	1-(1-Naphthyl)ethylammonium	— ^b	—
2	— ^c	— ^b	—
3	— ^d	No reaction	0

^a Under photoirradiation with a high-pressure mercury lamp (Pyrex filter) at 30°C for 8 h. ^b Melting point is below room temperature.

^c 1-Naphthylmethyl sorbate. ^d *N*-(1-Naphthylmethyl)sorbamide.

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Figure 1. IR spectra of (a) **1e** monomer, (b) poly(**1e**) as the photoproduct, and (c) poly(sorbic acid) derived by the solid-state transformation.

Figure 2. Powder X-ray diffraction profiles of (a) **1e** and (b) poly(**1e**). Cu-K α , 30 kV, 20 mA, scan speed 1 deg min $^{-1}$.

spectra of **1e** and the photoproduct are shown in Figure 1. After photoirradiation, the peak based on a stretching of the conjugated double bond at 1626 cm $^{-1}$ disappeared and the peak of the carbonyl stretching shifted to the higher wavenumber region from 1507 cm $^{-1}$ to 1537 cm $^{-1}$. These results suggest that the photoproduct is the polymer consisting of a 2,5-structure as the repeating unit, but not a 2,3- or 4,5-structure. Figure 2 shows the powder X-ray diffraction profiles of the monomer **1e** and the resulting polymer. It indicates that the polymer obtained is also crystalline; namely, the polymerization proceeded *via* a crystal-to-crystal process.

Figure 3. 100-MHz ^{13}C NMR spectrum of poly(triethylammonium sorbate) derived from poly(**1e**) by the solid-state polymer transformation. The peak indicated with an asterisk is due to 1,4-dioxane used as the internal standard. Solvent, D $_2$ O. Ambient temperature: (a) whole; (b) expanded spectra.

The resulting polymer was converted to poly(sorbic acid) in dilute HCl aqueous or methanol solution according to the procedure similar to the polymer transformation for the muconic acid derivatives previously reported.³ The polymer structure was confirmed by IR spectroscopy (Figure 1(c)) and elemental analysis because the resulting poly(sorbic acid) was also insoluble in any solvents including alkali aqueous solution. The poor solubility of the polymers formed in the crystalline-state polymerization and the subsequent solid-state polymer transformation is distinguished from the solubility of the atactic polymers prepared by radical polymerization of the sorbic acid derivatives in an isotropic state and of the diisotactic poly(methyl sorbate) prepared by anionic polymerization with alkyllithium in toluene.⁹ The latter was insoluble in benzene, toluene, and tetrahydrofuran, but soluble in chloroform. These results suggest that the stereochemistry of the polymers formed during the crystalline-state polymerization is highly regulated. The tacticity of the polymer was examined by the ^{13}C NMR spectroscopy after the transformation to the triethylammonium salt as the water-soluble polymer. The sharp and single resonances of each carbon of the poly-(triethylammonium sorbate) have revealed that the polymer produced during the crystalline-state polymerization has high stereoregularity (Figure 3). The polymer possibly consists of *erythro*-diisotactic-2,5-*trans*-structure^{9,10} (Scheme 2), which is similar to that of the stereoregular polymers prepared by topochemical polymerization of

Scheme 2.

the muconic derivatives.^{2,3} From geometrical consideration, we can understand that (*Z,Z*)- and (*E,E*)-1,3-diene compounds provide polymers with same configuration by topochemical polymerization when they form a similar column structure by the stacking of monomer molecules in the crystals.¹¹

In conclusion, the photoreaction of alkylammonium sorbates was examined in the crystalline state. The crystals of the 1-naphthylmethylammonium salt of sorbic acid provided an insoluble and crystalline polymer under UV irradiation. This polymer was converted to the water-soluble polymers by the solid-state transformation and revealed to consist of a tritactic structure, indicating that the polymerization proceeds under the crystal-lattice control. Thus, we have demonstrated that the topochemical polymerization of 1,3-diene compounds proceeds not only for muconic acid derivatives but also sorbic acid derivatives. Crystallographic study of the polymerization of 1-naphthylmethylammonium sorbate is now under investigation.

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- 1-Naphthylmethylammonium sorbate (**1e**): needles (methanol), mp 108°C (decomp.); ¹H NMR (400 MHz, CD₃OD) δ 7.34 (m, Ar, 5H), 7.01 (dd, *J* = 15.6 and 11.8 Hz, CH = CHCO₂, 1H), 6.17 (m, CH = CHCH₃, 1H), 6.02 (m, CH = CHCH₃, 1H), 5.78 (d, *J* = 15.6 Hz, CH = CHCO₂, 1H), 4.05 (s, CH₂, 2H), 1.67 (d, *J* = 6.0 Hz, CH₃, 3H); ¹³C NMR (100 MHz, CD₃OD) δ 175.71 (C=O), 142.07, 136.45, 130.76, and 123.75 (C=C), 135.39, 132.36, 131.72, 131.27, 130.04, 128.39, 128.18, 127.41, 126.78, and 126.52 (Ar), 41.46 (CH₂), 18.54 (CH₃); IR (KBr) 1626 (ν_{C=C}), 1507 cm⁻¹ (ν_{C=O}); Anal. Calcd. for C₁₇H₁₉NO₂ (269.34): C, 75.81%; H, 7.11%, N, 5.20%. Found: C, 75.65%; H, 7.31%; N, 5.15%. Poly(**1e**): IR (KBr) 1537 cm⁻¹ (ν_{C=O}); Anal. Calcd. for (C₁₇H₁₉NO₂)_n: C, 75.81%; H, 7.11%, N, 5.20%. Found: C, 75.47%; H, 7.08%; N, 5.16%. Poly(sorbic acid): IR (KBr) 1716 cm⁻¹ (ν_{C=O}); Anal. Calcd. for (C₆H₈O₂)_n: C, 64.26%; H, 7.21%. Found: C, 64.05%; H, 7.36%.
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Conformational Change and Orientation Fluctuations of Isotactic Polystyrene Prior to Crystallization

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ABSTRACT: In order to clarify the preparation process of crystal nucleation of polymers, we have studied the conformational changes and orientation fluctuations of isotactic polystyrene (iPS) in the induction period of crystallization using time-resolved Fourier transform infrared (FT-IR) spectroscopy and depolarized light scattering (DPLS) techniques, respectively. Their measurements were carried out for the so-called cold crystallization, when it was crystallized somewhat above the glass transition temperature $T_g = 100^\circ\text{C}$ from the glassy states. It is found from the time-resolved FT-IR measurements that the polymer chains begin to assume alternate conformations of *trans* (T) and *gauche* (G) in the induction period, which are characteristic to the 3/1 helix in the crystalline state. On the other hand, the time-resolved DPLS observations reveal that orientation fluctuations begin to grow in the induction period after a temperature jump to the crystallization temperature, which means that some rod-like segments of polymer chains actually start to orient parallel to one another prior to crystallization. These results are discussed in terms of the Doi's theory on the isotropic-to-nematic transition of liquid crystals where we assumed that the 3/1 helical segments are stiff and have a persistence length being almost equal to the length of the helix axis. Thus, the growth of the helices involves the increase in persistence length and hence in excluded volume, to cause the parallel ordering of the helix parts as stiff segments.

KEY WORDS Cold Crystallization / Isotactic Polystyrene / Induction Period / Conformational Change / Parallel Orientation /

Recently, the structure formation during the induction period prior to crystal nucleation has received much attention.^{1–8} We investigated the crystallization processes of poly(ethylene terephthalate) (PET) when it was annealed just above the glass transition temperature (T_g) using small-angle X-ray scattering (SAXS),^{4,5} small-angle neutron scattering (SANS)^{6,7} and depolarized light scattering (DPLS)^{6,8} techniques. Surprisingly, we have discovered that a new SAXS peak following the kinetics of spinodal decomposition (SD) appears from the very early stage of the induction period prior to crystallization.^{4,5} Such SD can be understood based on the kinetic theory for the isotropic-to-nematic transition of liquid crystals presented by Doi *et al.*^{9–12}; the parallel orientation of stiff polymer segments induces a SD type microphase separation with a characteristic wavelength being larger than the value corresponding to the SAXS peak.^{4,5} In fact, the parallel orientation was experimentally observed by DPLS measurements.^{6,8} According to this theory, parallel ordering of rod-like polymers is induced only when their length exceeds a critical value. The SANS measurements with deuterium labeling^{6,7} revealed that the persistence length of PET chains, *i.e.* the length of stiff segments, actually increases in the induction period to exceed the critical value.

In the preceding paper,¹³ we investigated the crystallization processes of syndiotactic polystyrene with an extended chain conformation in the crystalline state by annealing at 120°C , *i.e.*, 20°C above T_g by means of time-resolved FT-IR and DPLS techniques. The FT-IR measurements have revealed that the rod-like segments in polymer chains extend as *gauche* conformations trans-

fer to *trans* ones during the induction period before crystallization. It was expected from the Doi's theory^{9–12} that this chain extension causes orientation fluctuations of the stiff segments when their length exceeds a critical value. Such orientation ordering in the induction period was actually confirmed by DPLS measurements.

It is interesting to investigate how the chain conformation changes during the induction period in the case of polymers assuming helical structure in the crystalline state. In this study, we have employed isotactic polystyrene (iPS) with 3/1 helix as an example of helical polymers and investigated the structural changes during the induction period when the polymer was crystallized from the glassy state. The conformational changes were detected by a time-resolved FT-IR spectroscopic method. In this case, it is absolutely necessary that the IR bands concerned should be well characterized. Fortunately, as for isotactic polystyrene, they have been well characterized in terms of tetrad sequences of *trans* and *gauche* by Kobayashi *et al.*^{14,15} The parallel orientation of stiff segments during the induction period has also been measured for iPS by DPLS, and on the basis of these observed results, we discuss the structural formation processes during the induction period of crystallization, focusing on the relation between the 3/1 helix formation and the parallel ordering of 3/1 helix segments.

EXPERIMENTAL

The sample used for this study was isotactic polystyrene (iPS) with a weight-average molecular weight, $M_w = 4.0 \times 10^5$ and a polydispersity, $M_w/M_n = 2$. The glass transition temperature, T_g , was determined by DSC measurements to be 100°C . Amorphous thin films about

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Figure 1. Annealing time dependence of crystallization isotherm for iPS glass. Annealing temperature was 135°C.

Figure 2. FT-IR spectra of crystalline (upper) and amorphous (lower) iPS in the region 500–1400 cm^{-1} . m indicates the minimum number of monomer units including in the 3/1 helix parts of the polymer chain.

50 μm thick were obtained by quenching the iPS melt into ice-water after being hot-pressed at 290°C for 5 min.

The time-resolved FT-IR measurements were performed on the melt-quenched sample under an isothermal condition at 135°C, *i.e.*, 35°C above T_g in a home-made temperature controlled cell. The IR absorption was recorded using a Nicolet Impact 410 system at 3.0 min intervals.

The time-resolved DPLS measurements were also carried out under the same annealing conditions at 135°C. The samples were irradiated by a plane-polarized He-Ne laser beam ($\lambda = 632.8 \text{ nm}$) on a hot-stage and the scattered light intensity under depolarized conditions was recorded by a photodiode array system at 0.5 min intervals.

RESULTS AND DISCUSSION

Induction Period

Figure 1 shows the crystallization isotherm $\phi(t)$ of iPS measured by differential scanning calorimetry (DSC) using Perkin Elmer DSC 7 as a function of annealing time at 135°C. During the first 70 min, neither exotherm nor endotherm is observed, indicating that it is in the so-called induction period. We also confirmed from wide-angle X-ray diffraction measurements that no crystalline Bragg peaks except for amorphous halos are observed during the induction period; the measurements were carried out on several sample films quenched after annealing for given times before crystallization.

Figure 3. Annealing time dependence of IR spectra of iPS in the region 500–600 cm^{-1} . The bands at 548, 562, 567, and 586 cm^{-1} are assigned to GTTG , TTGG/GTGG , GTGT , and GTGT , respectively.

Detection of Conformational Change by FT-IR

Figure 2 shows the FT-IR spectra of iPS film samples melt-quenched and crystallized at 135°C for 400 min where the resulting crystal modification was the α form.¹⁶ Characteristic differences between the spectra of the amorphous and crystalline iPS films are seen on the bands at around 550 cm^{-1} which are sensitive to the chain conformation with tetrad sequences of *trans* (T) and *gauche* (G)¹⁵ and on the bands between 900 and 1300 cm^{-1} which are sensitive to the length of 3/1 helix conformation.¹⁴

Nakaoki and Kobayashi¹⁵ have assigned the absorption bands of polystyrenes at around 550 cm^{-1} to out-of-plane modes of the phenyl group, whose frequencies depend on the local skeletal conformation in the neighborhood of the phenyl group. These bands are observed in both amorphous and crystalline spectra of iPS as seen in Figure 2 relating to the skeletal conformations with tetrad sequences as will be shown below.

In order to follow the conformational change in the induction period, we have carried out time-resolved FT-IR measurements after a temperature jump to 135°C. Figure 3 shows the time evolution of the enlarged spectra in the frequency range 500 to 600 cm^{-1} when the sample was annealed at 135°C. Here each curve is shifted along the axis of relative absorbance to make it easy to see. Four bands at 548, 562, 567, and 586 cm^{-1} are distinguished and indicated with arrows in Figure 3: the 548 cm^{-1} band has been assigned to GTTG conformation, the 562 cm^{-1} band to TTGG and GGTG , and the 567 and 586 cm^{-1} bands to GTGT , respectively. Here T and G are *trans* and *gauche* conformations, respectively, and the two middle-underlined letters indicate the conformations around the C–C bonds on the both sides of the carbon atom bonded to a phenyl group. For the quantitative analysis, we decomposed the spectra in the region 500–600 cm^{-1} into these four components by assuming a Lorentzian shape for each band as shown in