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IR Spectroscopic Study on Differences between Diastereoisomeric Monomers in Solvent-Free Polycondensation

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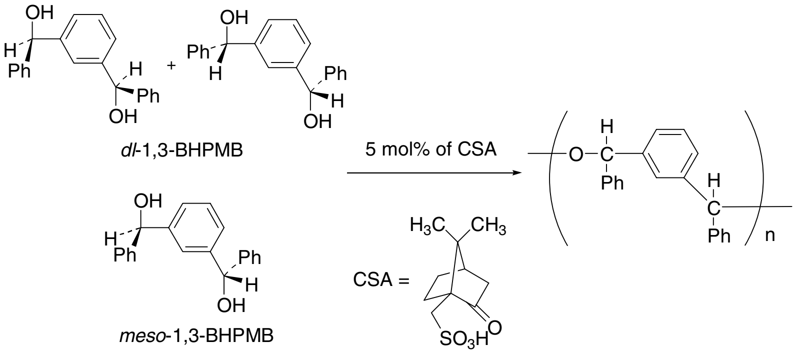
Summary

To shed light on dramatic differences between *dl*- and *meso*-1,3-bis(hydroxyphenylmethyl)benzenes in the solvent-free polycondensation, which takes place below the melting point of each monomer and gives the polyether, IR spectroscopic study of these monomers has been performed at variable temperature. The dl monomer proved to have stronger hydrogen-bonding networks in the crystalline state than the meso monomer, while these diastereoisomeric monomers showed quite identical IR spectra in the fusion state. These findings correspond with the polymerization behavior of these monomers; the dl monomer yields the higher molecular weight polymer in the solvent-free polymerization, while these two monomers are indistinguishable in the solution polymerization. The changes in the IR spectra with increasing temperature were found to take place all at once at the melting point of each monomer, supporting the differences between these monomers in the solvent-free polycondensation.

Introduction

There are known various kinds of solid-state polymerizations, however, which are not so popular. Among them, topochemical polymerization, as is termed, is absolutely governed by molecular arrangement in a monomer crystal, which is directly transformed to a polymer crystal.[1-3] However, even on some non-topochemical polymerizations, where the crystal lattices of monomer are broken with the progress of the polymerization, the original molecular arrangement in a monomer crystal can exert significant influence.[4-9]
On the course of our project to develop novel solid-state polymerizations, our very recent articles revealed that *dl*- and *meso*-1,3-bis(hydroxyphenylmethyl)benzenes (BHPMBs) undergo novel solvent-free polycondensation with the aid of an acid catalyst (Scheme 1).[10][11] The crystals of *dl*- or *meso*-1,3-BHPMB were ground with the powdery (*1S*)-10-camphorsulfonic acid (CSA, 5 mol%) in a motor and heated below the melting point of each monomer, resultantly forming the

corresponding polyether. As compared with the dl monomer (mp 158-160 °C), the meso monomer (mp 96-98 °C) was found to be polymerizable at a lower temperature, however, producing the much lower molecular weight polymer. Molecular mobility in a crystal lattice is larger for the lower melting point material, reducing the reaction temperature in the solid state. In contrast with the solvent-free conditions, these two diastereoisomeric monomers in the solutions showed the almost same polymerization behavior. Therefore, molecular packing in the monomer crystals should govern this novel solvent-free polymerization, however, which is a non-topochemical system.



Scheme 1. Solid-State Polycondensation of 1,3-BHPMBs.

As described in our previous article,[11] we made efforts to prepare adequate crystals of *dl*- and *meso*-1,3-BHPMBs for X-ray crystallography, but in vain; the former gives fibrous crystals like cotton, and the latter presents mould-like crystals. Accordingly, to elucidate the above differences in the polymerization behavior between *dl*- and *meso*-1,3-BHPMBs, we planed to study the hydrogen bonding of these molecules in crystals by means of IR spectroscopy. Since this polycondensation proceeds via the dehydration between the benzhydrol moieties, the strength of the hydrogen bonding between the reaction sites could be one of the important factors to determine the reactivity in the solid state.

Experimental Section

Preparation of 1,3-BHPMBs

Two diastereomers of *dl*- and *meso*-1,3-BHPMBs were prepared by the reduction of 1,3-dibenzoylbenzene with $NaBH_4$ and subsequently isolated through repetitious recrystallization with toluene. The details are described in our previous article.[11] The diastereomeric purity of *dl*- and *meso*-1,3-BHPMBs was evaluated by means of HPLC (eluent: n-hexane/2-propanol = 1/1 v/v) equipped with a chiral column of CHIRACEL OD-H (Daicel Co.)

FT-IR measurement

ATR (Attenuated Total Reflection) IR spectra of *dl*- and *meso*-1,3-BHPMB crystals were recorded on a Jasco FT/IR 460plus spectrometer (a resolution power = 2 cm^{-1}) equipped with a ATR PRO400-S module (a ZnSe prism; a incident angle = 45°; one time reflection). Transmittance microscopic IR spectra were measured by a Jasco

MFT-2000 spectrometer (an MCT detector, a resolution power = 4 cm^{-1}) equipped with a MHC-500 hot stage (a heating rate = 5 °C/min); the crystals of *dl*- and *meso*-1,3-BHPMBs were pressed (200 Kg/cm^2) between two KBr plates and then subjected to the measurement.

Results and Discussion

Figure 1 shows the ATR IR spectra of *dl*- and *meso*-1,3-BHPMB crystals. There are observed absorption bands due to O-H stretching vibrations to be different in shapes and positions for these diastereomers. Shoulder peaks are involved in both bands, suggesting that different kinds of hydrogen bonding are included in crystalline molecular networks. Showing the υOH band at the smaller wave number, the dl isomer has proved to have the stronger hydrogen bonding networks in the crystalline state than the meso isomer.

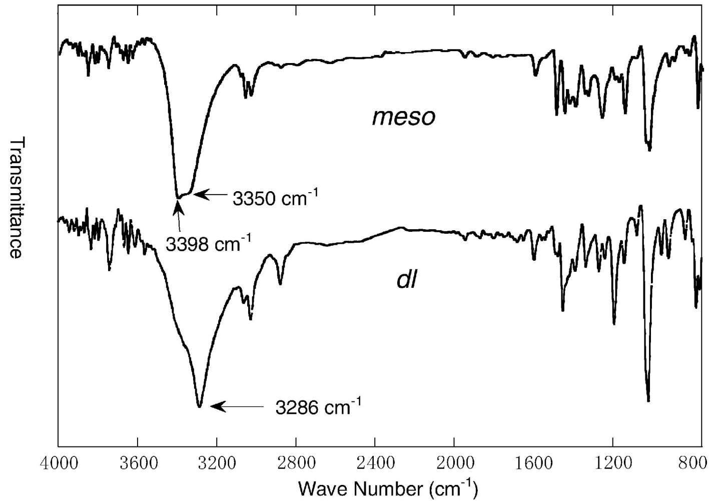


Figure 1. ATR IR spectra of *dl*- and *meso*-1,3-BHPMB crystals.

Figure 2 shows transmittance microscopic IR spectra of these diastereomers. As compared with the corresponding ATR spectra (Figure 1), absorption peaks due to O-H stretching vibrations shift to a little larger wave numbers in both cases. This is ascribable to the sample preparation process for the microscopic IR measurement; the crystalline compounds are exposed to a high pressure of 200 Kg/cm^2, which could affect the molecular networks in the crystals.

Figure 3 shows the transmittance microscopic IR spectra at 170 °C that is above the melting points of both *dl*- and *meso*-1,3-BHPMBs: 158-160 and 96-98 °C, respectively. Interestingly, the fusion state makes the IR spectra of these diastereomers almost identical, indicating that *dl*- and *meso*-1,3-BHPMBs in the fusion state form the same hydrogen bonding networks. In contrast with the crystalline state where weaker intermolecular interactions than hydrogen bonding effectively work for molecular arrangement, the fusion state could not allow such interactions as to distinguish the diastereomers having the chiral centers at the 1,3-positions of the benzene ring. Figures 2 and 3 allow the comparison between

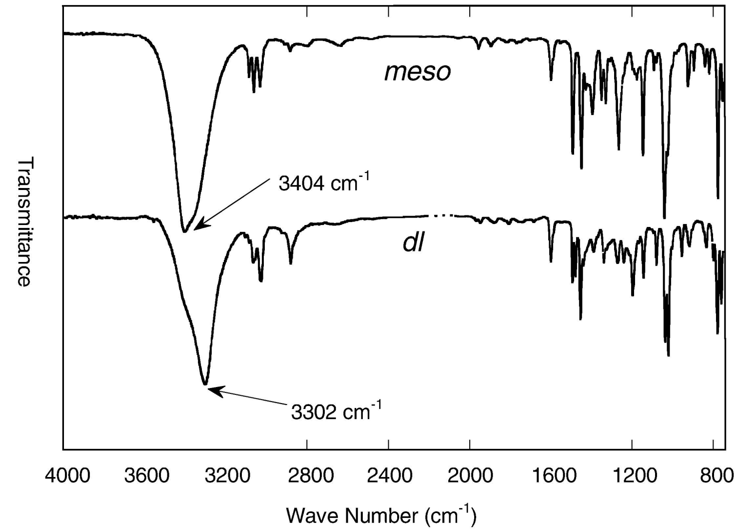


Figure 2. Transmittance microscopic IR spectra of *dl*- and *meso*-1,3-BHPMB crystals.

crystalline and fusion states of each diastereomer. There are observed big differences on the absorption band due to the O-H stretching vibration, which shifts onto the larger wave number area, showing a bimodal peak. These findings suggest that, as usual, the hydrogen bonding networks in the fusion state are weaker than those in the crystalline state and that two types of hydrogen bonding are involved in the fusion state.

Figure 4 shows transitions of the IR spectra (2500~4000 cm^{-1}) of *dl*- and *meso*-1,3-BHPMBs with increasing temperature. In either case, the dramatic change in the spectra takes place just above the melting points. Representatively, the peak of the

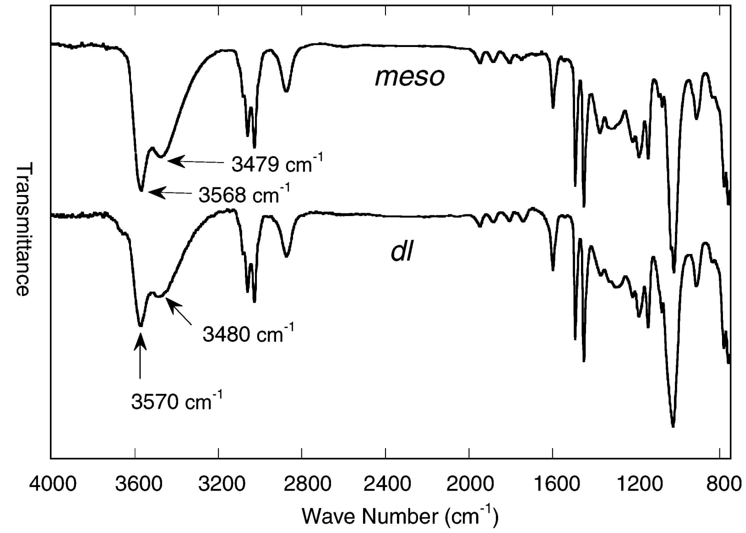


Figure 3. Transmittance microscopic IR spectra of *dl*- and *meso*-1,3-BHPMBs in the fusion state at 170 °C.

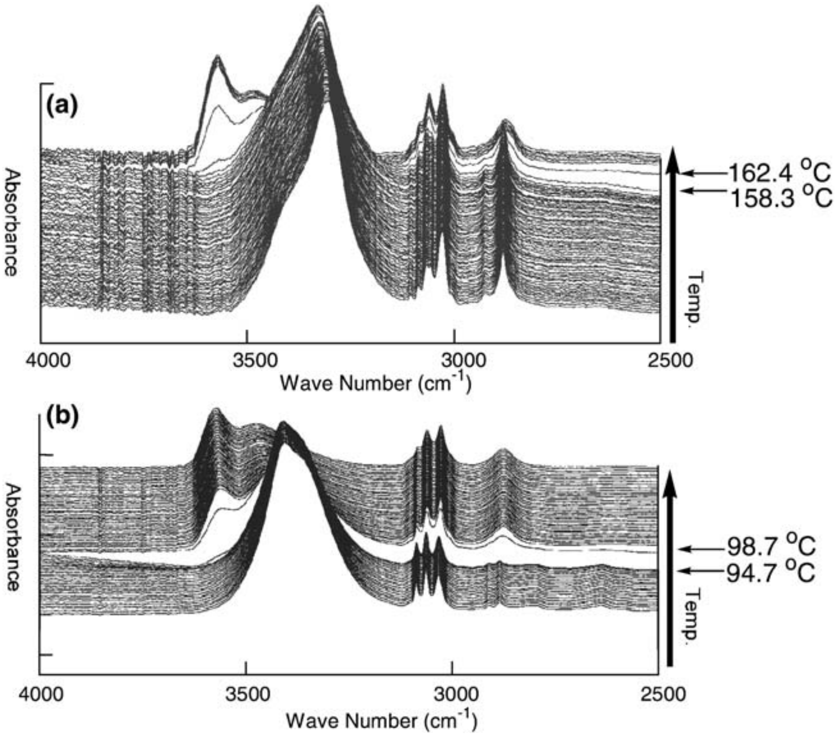


Figure 4. Expanded microscopic IR spectra of *dl*- (a) and *meso*- (b) 1,3-BHPMBs with increasing temperature.

O-H stretching vibration band shows drastic shift through the phase transition. This process is clearly specified by Figure 5, where the wave numbers of these peak tops are plotted on a function of temperature. There are observed the plot lines jumping at the melting points. The increase rate of the wave number with increasing temperature is very small in the crystalline state and then becomes larger, after the jump, in the fusion state. Increasing temperature weakens the hydrogen bonding and this effect is obviously stronger in the fusion state than in the crystalline state.

In Figure 6, ratios of the absorbance at 3570 cm^{-1} to that at 1600 cm^{-1} are plotted on a function of temperature. These two wave numbers are the peak positions of the O-H stretching vibration in the fusion state and of the aromatic C-C stretching vibration, respectively; the latter peak undergoes no shift through the phase transition, as observed in Figures 2 and 3 for both stereoisomers. Figure 6 shows that the absorbance at 3570 cm^{-1} is constantly zero before melting and then jumps to certain values just at the melting points. This means that the transformation of the hydrogen bonding takes place all at once, same as the phase transition.

As described in Introduction, we conducted this study to get information about the solvent-free polymerization of *dl*- and *meso*-1,3-BHPMBs. In consequence, compared with the latter monomer, the former has proved to have stronger hydrogen bonding and therefore smaller molecular distance between the reaction sites in the crystalline state (Figures 1 and 2). This can be a favorable factor for the solvent-free polycondensation to yield the higher molecular weight polymer.[10][11] The dramatic difference in the polymerization behavior of these diastereomers in the solid

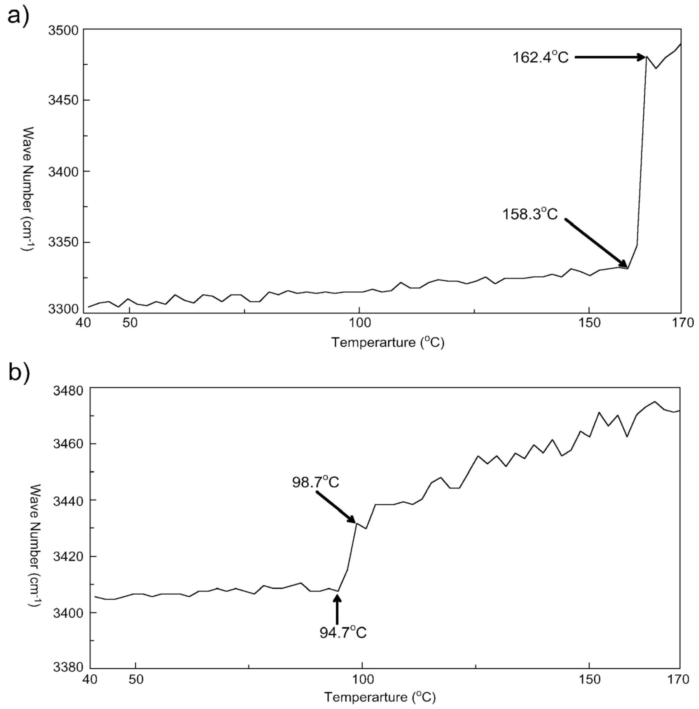


Figure 5. Wave numbers at the peak tops of OH stretching vibration bands on a function of temperature, in IR spectra of *dl*- (a) and *meso*- (b) 1,3-BHPMBs.

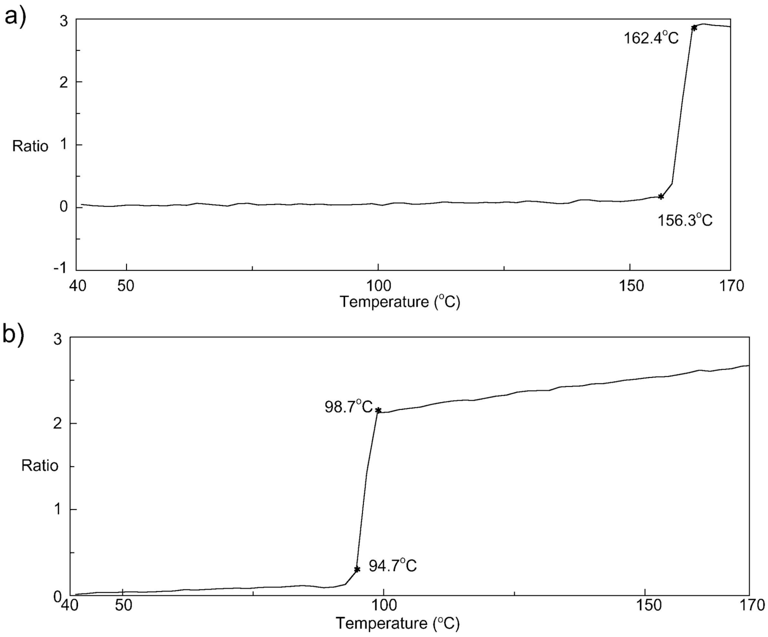


Figure 6. Absorbance ratios (3570 cm^{-1} / 1600 cm^{-1}) on a function of temperature, in IR spectra of *dl*- (a) and *meso*- (b) 1,3-BHPMBs.

state is also supported by Figures 4, 5, and 6; no rearrangement of the molecular networks takes place with increasing temperature below the melting points. In addition, the finding that the identical IR spectra are observed in the fusion state for this diastereomeric couple (Figure 3) is also in good agreement with the previous one that these monomers show the same polymerization behavior in the solution.[11]

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