SHORT COMMUNICATIONS

Stereocomplex Formation between (+)- and (–)-Poly(menthyl methacrylate) in Bulk

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(Received November 1, 1995)

KEY WORDS Stereocomplex / Poly(menthyl methacrylate) / Solubility / Crystallinity /

The mixing of two polymers can lead to the formation of a stereocomplex whose properties may be quite different from those of the parent polymers. A typical example is stereocomplexation between isotactic and syndiotactic poly(methyl methacrylate)s in some solvents and in bulk.^{1,2} Stereocomplexation can also occur in blends of isotactic polymers with opposite configuration, such as poly(α -methylbenzyl methacrylate),³ polylactide,⁴ polyisopropylthiirane,⁵ and more recently, alternating copolymers of α -olefin and carbon monoxide, poly(1,4-ketone)s.⁶ One thing we also have to mention here is that blending two polymers of opposite configuration does not always induce the formation of a stereocomplex, such as the case of polymethylthiirane.⁷

In this work, we found that stereocomplexation took place in bulk between poly((+)-menthyl methacrylate) ((+)-PMnMA) and poly((–)-menthyl methacrylate) ((–)-PMnMA), based on the results of differential scanning calorimetry (DSC), X-ray powder diffraction (XRD), as well as a solubility study.

(+)-Menthyl methacrylate ((+)-MnMA) and (–)-menthyl methacrylate ((–)-MnMA) were prepared by reactions of methacryloyl chloride with the corresponding chiral menthol in pyridine. The specific rotations $[\alpha]_D^{25}$ (neat) were +91.8° and –91.0°, respectively. By initiation with fluorenyllithium (FLi) at –78°C, (+)-MnMA and (–)-MnMA were individually polymerized in toluene to give optically active (+)-PMnMA and (–)-PMnMA.⁸ The number averaged molecular weights were 93300 and 78200 for the polymers. The molecular weight distributions (MWD) were 1.35 and 1.28, respectively. These values were estimated from poly(methyl methacrylate)s (PMMA) derived from the obtained polymers.⁹ The triad tacticity distributions (mm/mr/rr) of PMMAs derived from PMnMAs were 90.2/3.5/6.3 and 93.1/1.8/5.1, respectively. The specific rotations of (+)-PMnMA and (–)-PMnMA were +90.8° and –92.6° in tetrahydrofuran (THF) at D-line and 25°C, respectively.

The ¹H NMR spectra of the polymers were taken on a Unity 400 spectrometer using CDCl₃ as the solvent. Differential scanning calorimeter analysis was performed with Perkin-Elmer DSC-7 apparatus at a heating rate of 10°C min^{–1}. X-Ray powder diffraction measurements were taken on a D/Max IIB instrument. Optical rotation

was measured with a Perkin-Elmer 241 polarimeter. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) on a Shimadzu IC-6A chromatography using THF as eluent (1.0 ml/min). The GPC chromatogram was calibrated against standard polystyrene samples.

(+)-PMnMA and an equal amount of (–)-PMnMA were dissolved in toluene. The solution became transparent readily. After one night of stirring, the solvent was evaporated slowly at room temperature and the resulting film was thoroughly dried under vacuum. The freshly prepared polymer film did not show good solubility as the original polymer mixture and was only partially soluble in toluene. The film became completely insoluble in toluene one week after preparation, but still could be dissolved in chloroform. The same behavior was observed when the blending was done in chloroform. However, film prepared from each individual parent polymer using the same procedure was easily soluble in toluene and chloroform. The difference in solubility strongly implies that a stereocomplex is formed in bulk between (+)-PMnMA and (–)-PMnMA, just as in the case of poly(α -methylbenzyl methacrylate).³

Figure 1 shows the DSC curves of (+)-PMnMA, (–)-PMnMA and the complex between them. (+)-PMnMA and (–)-PMnMA showed endotherms at

Figure 1. DSC curves of (A) (+)-PMnMA, (B) (–)-PMnMA, and (C) the stereocomplex.

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Figure 2. X-Ray powder diffractions of (A) (+)-PMnMA and (B) the stereocomplex.

129°C and 127°C, respectively, corresponding to the glass transition. Both parent polymers had no melting point. On the other hand, no glass transition was observed on the DSC curve of the stereocomplex formed, but there appeared an endotherm at 182°C, corresponding to the melting point of the complex. This clearly indicates that the polymer chains of the complex are associated more closely, thus leading to increased crystallinity.

The decrease in solubility and increase in crystallinity for stereocomplex appeared to be the result of increase in the compactness of the polymer crystalline phases, as hypothesized by Jiang.⁶ The XRD spectra of (+)-PMnMA and stereocomplex were found to be quite distinct (Figure 2). A new sharp reflection at 2θ of about 4.8° appeared in the diffraction pattern of the stereocomplex, besides some small shifts of the other two peaks. Obviously, this new reflection must be attributed

to the crystal structure formed by complexation of (+)- and (–)-PMnMAs. Sakakihara proposed a structural model for racemic isotactic poly(*tert*-butylethylene oxide),¹⁰ where four molecules of helix pass through the unit cell and two pairs of optical antipodes exist in definite positions in the unit cell. However, in our works, it was difficult to determine the structural model of the stereocomplex only from the XRD study. Some conformational analysis may be helpful and the work is in progress.

Acknowledgments. The authors thank the National Natural Science Foundation of China for financial support. We are also grateful to Prof. Zhishen Mu for discussion concerning XRD spectra.

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