SHORT COMMUNICATION

Complex Formation between Isotactic Polymers of *R*-(+)- and *S*-(-)- α -Methylbenzyl Methacrylates in Bulk and in Solution

Koichi HATADA, Shin-ichi SHIMIZU, Yoshio TERAWAKI,
Koji OHTA, and Heimei YUKI

*Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan.*

(Received December 20, 1980)

KEY WORDS Complex Formation / Association / Poly(*R*-(+)- α -methylbenzyl methacrylate) / Poly(*S*-(-)- α -methylbenzyl methacrylate) / Optical Active Poly(methylbenzyl methacrylate) / ^1H NMR / DSC / Glass Transition Temperature /

It is well known that some macromolecules tend to form complexes in solution. A typical example is the formation of stereocomplexes between isotactic and syndiotactic poly(methyl methacrylate)s in some solvents.^{1,2}

In this work, we found the formation in bulk of a complex between the isotactic poly(*R*-(+)- α -methylbenzyl methacrylate) (poly(*R*-MBMA)) and poly(*S*-(-)- α -methylbenzyl methacrylate) (poly(*S*-MBMA)). We studied this complex by differential scanning calorimetry (DSC). The association between these polymers in solution was also studied by high-resolution NMR spectroscopy.

Poly(*R*-MBMA) and poly(*S*-MBMA) were prepared in toluene by cyclohexylmagnesium chloride-(−)-sparteine at -78°C ,³ and the number averaged molecular weights were 79,300 and 53,800, respectively. The isotacticities of both polymers were found to be almost 100% in triads from the ^1H NMR spectra taken in nitrobenzene- d_5 at 140°C . The specific rotations of the *R*- and *S*-polymers were 377.4 and -351.1° in chloroform at 365 nm and 25°C , respectively.

The ^1H NMR spectra of the polymer were taken in toluene- d_8 on a JEOL JNM-FX-100 spectrometer at 100 MHz . Differential scanning calorimetric analysis was performed with a Rigaku Denki Calorimeter, Model, 8001 SL/C, at a heating rate of 5°C min^{-1} using an aluminum sample pan with lid.

An equal amount mixture of poly(*R*-MBMA) and poly(*S*-MBMA) was dissolved in toluene, and

the solution was evaporated to dryness to form a polymer film under vacuum at room temperature. The polymer mixture was easily soluble in toluene, but the freshly prepared film was only partially soluble and completely insoluble in toluene at room temperature three days after preparation although it was still easily soluble in chloroform. The film prepared similarly from each individual poly(*R*-MBMA) and poly(*S*-MBMA) was easily soluble in toluene as well as in chloroform. This strongly implies the formation in bulk of a complex between poly(*R*-MBMA) and poly(*S*-MBMA).

The film of the complex showed clear polarization under a polarized microscope, indicating high crystallinity. At 228 – 230°C the polarization color disappeared and the complex melted. The film of an individual polymer showed no polarization and liquidized below 160°C .

In Figure 1 are shown the DSC thermograms of poly(*S*-MBMA) and the complex between poly(*S*-MBMA) and poly(*R*-MBMA). The poly(*S*-MBMA) showed two endotherms at 81°C and at about 266°C . The former should be attributed to the glass transition and the latter, to the degradation of polymer chain. On the other hand, no glass transition was observed in the thermogram of the complex, but there appeared an endotherm at 230°C corresponding to the melting point of the complex. The disappearance of the glass transition and the appearance of a melting point were also reported for the formation of a

Figure 1. DSC diagram of (A) poly(*S*-MBMA) and (B) 1:1 mixture of poly(*S*-MBMA) and poly(*R*-MBMA).

Figure 2. Degree of association of poly(*S*-MBMA), poly(*R*-MBMA) and 1:1 mixture, of poly(*S*-MBMA) and poly(*R*-MBMA) in toluene-*d*₈ at various temperatures (47.5 g l⁻¹).

stereocomplex between isotactic and syndiotactic poly(methyl methacrylate)s.⁴ It may thus be concluded that the complex forms between poly(*R*-MBMA) and poly(*S*-MBMA) in bulk.

The association between polymer molecules in solution was elucidated by ¹H NMR for poly(methyl methacrylate).⁵⁻⁷ When association occurs between polymer molecules, the mobility of the protons of the polymer decreases and their high resolution NMR signals become too broad to be detected. The degree of association can be determined from the equation, $1 - I/I_0$. Here I is the observed signal intensity and I_0 , the intensity for the case in which no association takes place in the same solution at the same temperature. In this work, the

value of I_0 was estimated using a solution of octane in toluene-*d*₈ containing the same amount of hydrogen as that in the polymer solution. ¹H NMR spectra were measured for poly(*S*-MBMA), poly(*R*-MBMA) and a 1:1 mixture of poly(*S*-MBMA) and poly(*R*-MBMA) in toluene-*d*₈. The summation of the intensities of all signals was determined at various temperatures. The degree of association, $1 - I/I_0$, is plotted against the temperature in Figure 2. The plots for poly(*S*-MBMA) and poly(*R*-MBMA) are similar to each other, and the degree of association increased below 0°C with a decrease in the temperature. This indicates that association of poly(*S*-MBMA) or poly(*R*-MBMA) in solution occurred at a low temperature as reported for isotactic or syndiotactic poly(methyl methacrylate).⁷ The curve for the polymer mixture suggests that association between poly(*R*-MBMA) and poly(*S*-MBMA) occurs in toluene-*d*₈ at low temperature and that the degree of association between the enantiomeric polymers is higher than that between the individual polymer chains. The complementary interaction between the lateral chains of both polymers might possibly play an important role in the formation of an associated structure.

Additional work is now under way for studying more extensively associated structures in bulk and in solution; and the results will be published in the near future.

Acknowledgment. The authors are grateful to Mrs. F. Yano for her clerical assistance in preparing this manuscript.

REFERENCES

1. W. H. Watanabe, C. F. Ryan, P. C. Fleisher, Jr., and B. S. Garrett, *J. Phys. Chem.*, **65**, 896 (1961).
2. A. M. Liquori, G. Anzuino, V. M. Corio, M. D'Alagni, P. DeSantis, and M. Savino, *Nature (London)*, **206**, 358 (1965).
3. Y. Okamoto, K. Ohta, and H. Yuki, *Macromolecules*, **11**, 724 (1978).
4. E. L. Feitsma, A. de Boer, and G. Challa, *Polymer*, **16**, 515 (1975).
5. J. Spevacek and B. Schneider, *Makromol. Chem.*, **175**, 2939 (1974).
6. J. Spevacek and B. Schneider, *Makromol. Chem.*, **176**, 729 (1975).
7. J. Spevacek and B. Schneider, *Makromol. Chem.*, **176**, 3409 (1975).