Macromolecules **1993,** *26,* 559-560 **559**

Communications to the Editor

Preparation of Highly Isotactic Poly(vinyl alcohol)

H. Ohgi* and T. Sato

Central Research Laboratories, Kuraray Company, Sakazu, Kurashiki, Okayama 710, Japan

Received June 30, 1992
Revised Manuscript Received December 7, 1992

Introduction. A lot of investigations have been reported on the synthesis of stereoregular poly(vinyl alcohol)s (PV-OHs) which are rich in syndiotactic and isotactic sequences.[1,2] A marked stereoregularity dependence on their physical properties was recognized, which may be caused by changing of inter- and intramolecular hydrogen bonding. However, the stereoregularity of the PV-OHs still has remained low compared to that of polystyrene or poly(methyl methacrylate).

The present authors studied the polymerization of *tert*-butyl vinyl ether (tBVE) and obtained PV-OH whose isotacticity is the highest of all isotactic PV-OHs reported so far. This PV-OH showed some interesting physical properties different from those of previously reported isotactic PV-OH.

Experimental Section. Materials used were purified and dehydrated carefully by the usual methods. In order to eliminate traces of alcohols, tBVE monomer was washed with water, dehydrated over potassium hydroxide, and distilled over calcium hydride before use.

Polymerization of tBVE was carried out with boron trifluoride etherate in toluene at -78 °C, and the poly(*tert*-butyl vinyl ether) (PtBVE) was converted into PV-OH by cleavage of the ether linkage using hydrogen bromide at 0 °C. Detailed methods of preparation for this polymer are described elsewhere.[3]

All properties were measured on PV-OH films obtained by casting from a DMSO solution at 50 °C.

Results and Discussion. Figure 1 illustrates the ^{1}H-NMR spectrum of PV-OH derived from PtBVE, and Table I shows some physical properties of the PV-OHs. We obtained PV-OHs which have 78-79% triad isotacticity[4] and high molecular weight.[6]

It has been reported that an isotactic PV-OH derived from PtBVE, which is obtained by a process proposed by Okamura et al.,[3] has a triad isotacticity of 55% as determined by ^{1}H-NMR spectroscopy on its solution in DMSO-d_6.[9] It has also been reported that a PV-OH derived from poly(vinyl trimethylsilyl ether) (PVOSi), which is obtained by a process proposed by Murahashi et al.,[10] has a triad isotacticity of 70.2% as determined by ^{1}H-NMR spectroscopy on its solution in DMSO-d_6.[11] No PV-OH having an isotacticity higher than the above has however been obtained yet.

Highly isotactic PV-OHs obtained in this study are more than 20% rich in isotacticity compared to the previously reported PV-OH derived from PtBVE and more than about 8% rich compared to the PV-OH, whose isotacticity was the highest of all isotactic PV-OHs so far, derived from PVOSi.

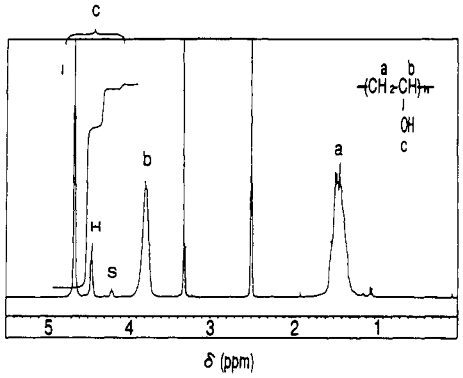
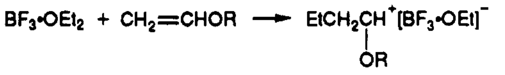


Figure 1. ^{1}H-NMR spectrum of isotactic PV-OH in DMSO-d_6, at 25 °C and 270 MHz. I, H, and S are assigned to isotactic, heterotactic, and syndiotactic triads, respectively.

Table I
Characterization of Isotactic PV-OHs Derived from PtBVE Prepared with $BF_3 \cdot OEt_2$ in Toluene at -78 °C

	tacticity (%)				
sample no.	I	H	S	P_{RAC}	mp (°C)
1	79.1	18.9	2.0	3540	247
2	77.8	19.6	2.6	23800	246

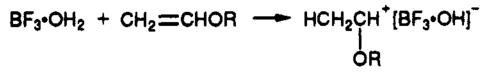
The increase in isotacticity was performed by lowering the catalyst concentration, that is, by controlling the ratio of the catalyst to residual water in toluene. From the kinetic study of the polymerization of alkyl vinyl ether in diethyl ether with $BF_3 \cdot OEt_2$, it has been stated that the initiation of the polymerization occurs with an ion pair formed by the direct reaction between $BF_3 \cdot OEt_2$ and monomer as follows:[12]



$$BF_3 \cdot OEt_2 + CH_2{=}CHOR \longrightarrow EtCH_2\underset{\displaystyle OR}{\underset{|}{C}}H^+[BF_3 \cdot OEt]^- \qquad (1)$$

But in the presence of an equimolar amount of water, the reaction of $BF_3 \cdot OEt_2$ and water shown in eqs 2 and 3 may

$$BF_3 \cdot OEt_2 + H_2O \longrightarrow BF_3 \cdot OH_2 + Et_2O \qquad (2)$$



$$BF_3 \cdot OH_2 + CH_2{=}CHOR \longrightarrow HCH_2\underset{\displaystyle OR}{\underset{|}{C}}H^+[BF_3 \cdot OH]^- \qquad (3)$$

compete with that of eq 1. The former will be dominant in the polymerization reaction when the ratio of the catalyst to residual water in the reaction mixture is low. We consider that the increase in isotacticity may be caused by highly isospecific polymerization with new species generated from ligand exchange of the catalyst from ether to water as shown in eq 2.

The PV-OH of high molecular weight was prepared when the reagents were sufficiently purified and water, which can function as a chain-transfer agent, was satisfactorily excluded from the reaction mixture.

The highly isotactic PV-OHs did not dissolve in water even at 120 °C at 1%, whereas the isotactic PV-OH derived from PVOSi dissolves in water at 100-110 °C. The degree

0024-9297/93/2226-0559$04.00/0

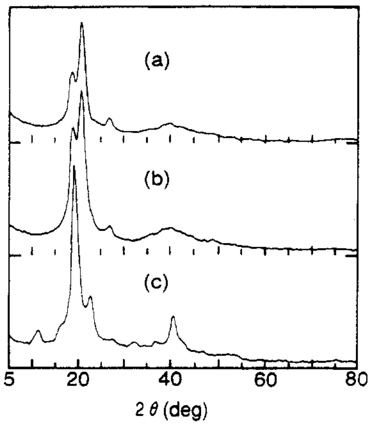


Figure 2. X-ray diffraction patterns of highly isotactic PV-OH treated at 40 (a) and 200 °C (b) and atactic PV-OH treated at 200 °C (c).

of swelling of the highly isotactic PV-OH films was about 1, which was half that of conventional PV-OH (atactic PV-OH). The melting temperature of these highly isotactic PV-OHs was about 15 °C higher than that of PV-OH derived from PVOSi, whose melting temperature was about 235 °C.[1]

As shown in Figure 2, the highly isotactic PV-OH had a sharp X-ray diffraction and its pattern was different from that of atactic PV-OH. It is known that the previously reported isotactic PV-OH has the same crystal structure as that of atactic PV-OH, although their crystallinity is low.[13] This suggests that the highly isotactic PV-OH obtained in this study has high crystallinity and a different crystal structure from the previously reported isotactic PV-OH.

The above characteristics of the highly isotactic PV-OH, high water resistance and high melting temperature, may be due to its specific crystal structure caused by increasing the structural regularity. Further investigations will be carried out.

References and Notes

(1) Fujii, K. *J. Polym. Sci., Part D* **1971**, *5*, 431.
(2) Finch, C. A. *Polyvinyl Alcohol—Developments*; John Wiley & Sons: New York, 1992; Chapter 10.
(3) Okamura, S.; Kodama, T.; Higashimura, T. *Makromol. Chem.* **1962**, *53*, 180.
(4) The Triad tacticity of PV-OH was determined accurately by ^{1}H-NMR spectra of the PV-OH dissolved in DMSO-d_6.[5] The spectra were measured on a JEOL GX-270 at 25 °C.
(5) Moritani, T.; Kuruma, I.; Shibatani, K. *Macromolecules* **1972**, *5*, 577.
(6) In general, the degree of polymerization of PV-OH is calculated from its limiting viscosity measured in water at 30 °C.[7] But it is difficult to dissolve the highly isotactic PV-OH in water, so isotactic PV-OH was converted into poly(vinyl acetate) (PVAc) by reacetylation and its molecular weight was measured. The limiting viscosity ([η]) of PVAc was measured in acetone at 30 °C, and the degree of polymerization of PVAc (P_{RAC}) was determined using Nakajima's equation.[8] $[\eta] = 7.94 \times 10^{-4} P_{RAC}^{0.62}$.
(7) Finch, C. A. *Polyvinyl Alcohol—Developments*; John Wiley & Sons: New York, 1992, p 757.
(8) Nakajima, A. *Kobunshi Kagaku* **1949**, *6*, 451.
(9) DeMember, J. R.; Haas, H. C.; MacDonald, R. L. *J. Polym. Sci., Polym. Lett.* **1972**, *10*, 385.
(10) (a) Murahashi, S.; Nozakura, S.; Sumi, M. *J. Polym. Sci., Polym. Lett.* **1965**, *3*, 245. (b) Murahashi, S.; Nozakura, S.; Sumi, M.; Fuji, S.; Matsumura, K. *Kobunshi Kagaku* **1966**, *23*, 550.
(11) Wu, T. K.; Ovenall, D. W. *Macromolecules* **1973**, *6*, 582.
(12) Plesch, P. H. *The Chemistry of Cationic Polymerization*; Pergamon: Press: New York, 1963; p 392.
(13) Fujii, K.; Mochizuki, T.; Imoto, S.; Ukida, J.; Matsumoto, M. *J. Polym. Sci., Polym. Chem. Ed.* **1964**, 2, 2327.