Macromolecules **1996,** *29,* 6673−6675 **6673**

Hexagonal Columns of Poly(*n*-alkyl propiolate) Produced with Rhodium Complex Catalyst. X-ray Analysis and Oxygen Permeability

M. Tabata,* Y. Sadahiro, Y. Nozaki, Y. Inaba, and K. Yokota

Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060, Japan

Received April 19, 1996
Revised Manuscript Received July 9, 1996

Introduction

Polymer membranes, e.g., poly(dimethylsiloxane), PDMS,[1] poly[(*tri*-methylsilyl)propyne], PTMS,[2] and poly(*tert*-butylacetylene), (PTBA),[3] have received not only scientific but also industrial interest due to a rather high oxygen permeability among the existing polymers. These polymers are glassy materials, and some of them are difficult to fabricate as films.

Despite important factors in the gas separation,[2,3] the geometrical structure with respect to the C═C bond in such substituted polyacetylenes is not completely understood nor can the secondary structure at the solid phase be controlled due to the generation of amorphous polymers. Further, it has been believed, in general, that polyacetylenes are oxidized in air[4] and the associated structural relaxation, e.g., crystallization, takes place during film use, decreasing the ability of the film to function as a filter.[5]

Recently we found that stereoregular poly(*n*-alkyl propiolate), (PAP), was obtained from *n*-alkyl propiolate (AP) using a [Rh(norbornadiene)Cl]$_2$, [Rh(NBD)Cl]$_2$, complex catalyst[6] and the resulting polymers were neither oxidized in air, even for more than 2 years, nor structurally relaxed.

In this note, we report that the stereoregularly polymerized PAP polymers have pseudohexagonal packing structures as self-organizations or assemblies called columnar structures together with the oxygen permeability. Therefore, this is a new series of columnar polymers which we expect to play an important role in oxygen enrichment.

Polymerizations of the AP monomers with different alkyl chain lengths, $n = 3-14$, were performed with the Rh complex in the presence of an alcohol such as methanol according to our method described in previous reports.[6,7] The alcohol was also considered to dissociate the dimer catalyst, [(Rh(NBD)Cl]$_2$, into the monomeric species responsible for propagating the species in this polymerization in which cis−transoid forms were selectively formed, as shown Scheme 1. The preliminary characterization of the resulting PAP polymers using IR and laser Raman spectroscopic methods is shown in our previous paper.[6] The polymers were soluble in toluene, chloroform, and tetrahydrofuran (THF) but insoluble in *n*-hexane and methanol. The PAP polymers were found to have molecular weight, M_w, *ca.* 19 500−83 600 with molecular weight dispersity, $M_w/M_n \approx 2-4$. The polymer colors were also found to change from a pale yellow to orange with increasing alkyl chain length. These polymers showed ^{1}H NMR spectra with fairly narrow line widths, unlike those of polymers polymerized with a metathesis catalyst like WCl$_6$;[8,9] e.g., ^{1}H NMR signals observed at 0.8 (3H), 1.3 (6H), 3.8 (2H), and 6.8 (1H) ppm in CDCl$_3$ solvent could be clearly assigned to the CH_3, inner $-CH_2-$, OCH_2, and C═CH protons in poly(*n*-pentyl propiolate), PPP, respectively, suggesting formation of stereoregular PPP polymer,as reported in the poly(pentynoate) polymer.[8]

Scheme 1

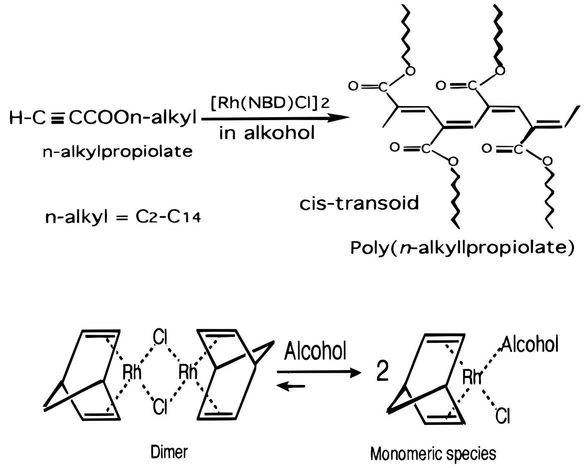

Figure 1 shows X-ray diffraction (XRD) spectra of poly(*n*-pentyl propiolate), PPP, and poly(*n*-octyl propiolate), POCP, polymers as examples of the typical polymers polymerized with the Rh complex catalyst in methanol at 40 °C, respectively. The lower angle side peak at $d = 15.44$ Å in the POCP polymer was ascribed to the (100) reflection in the polymer. The small peaks at $d = 8.99$ Å and $d = 7.73$ Å in POCP can be assigned to the (110) and (200) reflections, respectively. The broad peak at $d = 4.65$ Å should be assigned to that of not the amorphous halo but the akyl side chains distances, i.e., the cis POCP back-born spacing. On the basis of these results it was concluded, therefore, that POCP has a pseudohexagonal packing structure at room temperature which is composed of seven polymer chains called a columnar having a diameter 17.83 Å, as shown in Figure 1c. Similar assignments were also made for the peaks in the PPP polymer, except for the peak at $d = 3.41$ Å, which may be due to the (310) reflection. The peak at $d = 3.41$ Å was found to disappear completely when the polymer was warmed to *ca.* 130−140 °C, giving rise to a spectrum similar to that in Figure 1b, suggesting that a phase transformation occurred, i.e., formation of the pseudohexagonal structure. Therefore we concluded that PPP and POCP, as well as other PAP polymers examined, have pseudohexagonal packing structures at room temperature, indicating the formation of new self-ordered materials with a specific secondary structure called a self-organization or supramolecule. Similar columnar polymers have been reported to date, e.g., poly(di-*n*-alkylsiloxane),[10] poly(dialkylphosphazene),[11] and poly[(*o*-methoxyphenyl)acetylene][12] where a mesophase with birefringence may be observed between the solid and isotropic phases, as well as PAP polymers.

Figure 2 shows the diameter dependencies of the columns on the *n*-alkyl chain length, $n = 3-14$, in the PAP polymers. This curve indicates that the diameter increases linearly with increasing carbon number. The increment ratio was found to saturate at around $n = 14$, suggesting that the *n*-alkyl chain in the polymer has not an extended trans planar zigzag chain but a fold or gauche chain where odd and even carbon number effects on the parameters such as phase transition temperature were not observed, unlike the cases of ordinary liquid crystals.[13]

S0024-9297(96)00583-9 CCC: $12.00

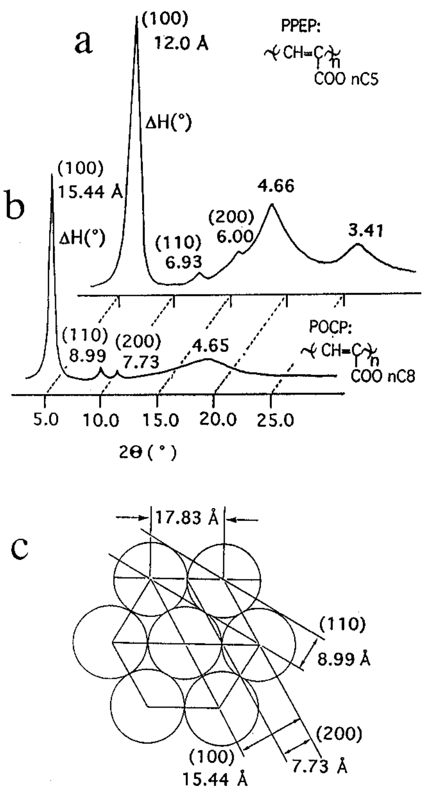

Figure 1. X-ray diffraction spectra of poly(*n*-pentyl propiolate), PPP (a) and poly(*n*-octyl propiolate), POCP (b), observed at room temperature using Cu Kα. The *d* (Å) spacing in the polymers was calculated using the Bragg equation. (c) represents the pseudohexagonal packing structure for the POCP polymer together with Miller's indices.

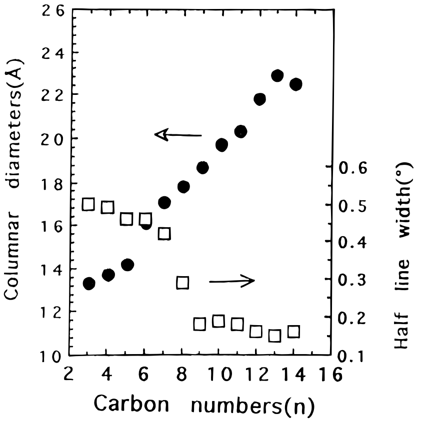

Figure 2. Dependencies of the columnar diameter (●) and half line width, Δ*H* (□), of the (100) reflection peak on the *n*-alkyl chain length in the PAP polymers. The diameter was also calculated by putting *θ* (°) into the Bragg equation and assuming a pseudohexagonal structure.

The half line width, Δ*H*(°), in the lowest angle peak of each polymer was also plotted as a function of the carbon number in order to know the degree of self-organization order in the columnar polymers, which is also shown in Figure 2. This curve shows the inverse tendency; i.e., the line width does not depend on the carbon number in the alkyl chain but instead decreases with increasing chain length in the polymer. In particular the line width decreases rapidly at around $n = 6$ where semisolid polymers are formed even at room temperature. Such decreases in line widths may reflect the formation of more ordered columnars. Conversely, the columnar polymer with shorter side chains is loosely bundled to make disordered structures, as depicted in Figure 3.

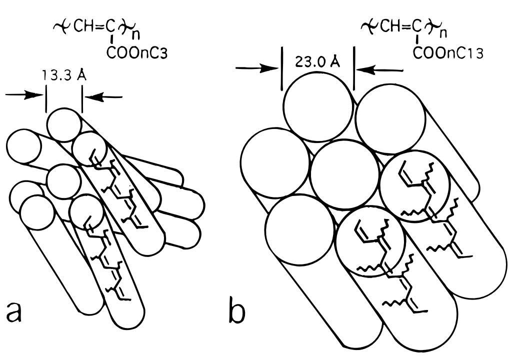

Figure 3. Proposed pseudohexagonal structures in the PAP polymers: poly(*n*-propyl propiolate) (a) and poly(*n*-tridecyl propiolate) (b).

It is necessary to closely pack seven polymer chains in each unit column in order to produce stable columnar structures. Therefore, polymer chains with regular structures, i.e., head to tail structures, are thermodynamically preferred structures to generate more stable columns compared with those of polymers bearing disorder structures such as head to head or tail to tail sequences, as observed in the stereoregular PAP polymer.

Recently, Unger proposed that such hexagonal polymers can be classified as liquid crystals which have no positional long range order (PLRO) in the direction of the molecular axis, although they have been called rotator, condis (conformational disorder) crystalline, smectic, columnar, or simply mesophase.[14]

These findings intrigued us to use the PAP polymer as a new oxygen transfer material because the vacant area in each column tube, which is in part packed with the cis−transoid polyacetylene polymer like a herring backbone, must have a higher affinity to oxygen. In this report the poly(*n*-propyl propiolate), PPRP, polymer with the shortest chain length among the PAP polymers examined was cast using toluene to make a membrane, and O_2 and N_2 permeabilities, P_{O_2} andP_{N_2}, with perselectivty, $P_{O_2}/P_{N_2} = \alpha$, were estimated using a JASCO Gasperm 100 at room temperature. We found that the PPRP polymer has $P_{O_2} = 5.5 \times 10^{-9}$ and $P_{N_2} = 1.6 \times 10^{-9}$, respectively, similar to those of polyacetylene analogues which contain the trimethylsilyl or fluorocarbon moieties required as the membranes, and has a rather high $\alpha = 3.5$. Such high perselectivity compared with those of existing oxygen permeable membrane polymers, e.g., PDMS, PTMS, and PTBA, suggests that the PAP columnar structure having an extremely high cis−transoid form plays an important role in oxygen transfer at the molecular level though no trimethylsilyl or trifluoromethyl and dimethylsilicon moieties are needed in the polymer. We propose, therefore, that such a columnar polymer works as a new and useful enricher of O_2, i.e., may potentially be used in the treatment of respiratory disease and in the separation of other gas or molecules due to the ease of fabrication of large thin films or hollow fiber tubes whose diameters can be precisely controlled. At present, a study of the enrichment mechanism of O_2 and other molecules using polymers with columnar structures is in progress in our laboratory, and the results will be reported elsewhere soon.

Acknowledgment. The authors appreciate the helpful discussion of Professor T. Masuda at Kyoto University and thank Mr. M. Takahashi for taking the gas permeability data in the Shinetsu Polymer Ltd. apparatus. This work was partly supported by the Grant-in-Aid for Scientific Research on Priority Area from the Ministry of Education, Science, and Culture, Japan.

References and Notes

(1) Wolfgang, P.; Walch, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 660.
(2) Masuda, T.; Isobe, E.; Higashimura, T. *J. Am. Chem. Soc.* **1983**, *105*, 7473.
(3) Takada, K.; Masuda, T.; Higashimura, T. *J. Appl. Polym. Sci.* **1985**, *30*, 1605.
(4) Sohma, J.; Tabata, M.; Ebisawa, F.; Hatano, M. *Polym. Degrad. Stab.* **1987**, *17*, 5.
(5) Ichiraku, Y.; Stern, A.; Nakagawa, T. *J. Membr. Sci.* **1987**, *34*, 5.
(6) Tabata, M.; Inaba, Y.; Nozaki, Y.; Yokota, K. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 465.
(7) (a) Tabata, M.; Yang, W.; Yokota, K. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1113. (b) Yang, W.; Tabata, M.; Yokota, K. *Polym. J.* **1991**, *23*, 1135.
(8) Minakawa, H.; Tabata, M.; Yokota, K. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 291.
(9) Nakano, M.; Masuda, T.; Higashimura, T. *Macromolecules* **1994**, *27*, 1344.
(10) Shivaev, V. P.; Plate, N. A. *Adv. Polym. Sci.* **1984**, *60/61*, 173.
(11) Blumstein, A., Ed. *Liquid Crystalline Order in Polymers*; Academic Press: New York, 1978, pp 299−326.
(12) Tabata, M.; Takamura, H.; Yokota, K.; Nozaki, Y.; Hoshina, T.; Minakawa, H.; Kodaira, K. *Macromolecules* **1994**, *27*, 6234.
(13) Kricheldorf, H. R.; Domschke, A. *Macromolecules* **1994**, *27*, 1509.
(14) Unger, G. *Polymer* **1993**, *34*, 2050.

MA960583Q