SHORT COMMUNICATIONS

Orientational Characteristics of Semiflexible Poly(yne)–Platinum Polymers as Studied by Deuterium NMR

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The synthesis and properties of extended polymers having a backbone composed of conjugated poly(yn)e structures linked together by platinum metal atoms have been reported by Hagihara, Takahashi, and their collaborators.¹ The architecture of the polymer is unique in the sense that the principal axis of the polarizability tensor lies exactly along the skeletal backbone.¹ In this work, we have attempted to elucidate orientational characteristics of these polymers in the lyotropic nematic mesophase in relation to their phase behaviors. In order to apply the ^2H NMR technique to these polymer systems, an alternate copolymer such as

was prepared, with deuterium labels introduced on the phenylene rings.

Fujita, Teramoto *et al.*² have reported solution properties of poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadienediyl]

The results of viscosity and sedimentation velocity measurements in *n*-heptane were analyzed in terms of the Yamakawa–Fujii theory for the wormlike chain. The value of the persistence length q was found to be

13 ± 3 nm, suggesting that the polymer can be represented as wormlike chains. Solution properties of the same polymer have been examined by Ikeda *et al.*,³ who carried out light-scattering measurements as well. All these studies indicate that an isolated polymer may be approximated by a Kuhn-chain model except when its molecular weight is extremely low.

These poly(yn)e–platinum polymers are known to form lyotropic nematic liquid crystals in trichloroethylene (TCE).⁴ In the nematic state, polymer (I) tends to align in the direction parallel to the applied magnetic field in contrast to polymer (II), which orients vertically with respect to the field. In the former system, deuterons situated on the phenylene groups along the chain skeleton should provide information regarding the molecular ordering of polymers.

EXPERIMENTAL

Polymer samples were prepared according to the prescription described by Takahashi *et al.*¹ Deuterium labels were introduced on the phenylene rings by reacting 1,4-diethynylbenzene-*d*₄ with bis[*trans*-chlorobis(tri-*n*-butylphosphine)platinum(II)]-1,4-butadienediyl. As-polymerized samples were fractionated by

precipitation from benzene solution by using methanol as a precipitant. The samples were freeze-dried from benzene and stored in a refrigerator.

The ^2H NMR spectra of liquid crystalline solutions were recorded at 41.25 and 76.55 MHz, respectively, on JEOL GSX-270 and GSX-500 spectrometers. Measurements were carried out under a complete proton decoupling and nonspinning mode.

RESULTS AND DISCUSSION

Molecular Characteristics of the Polymer

The molecular weights of samples were estimated from intrinsic viscosities measured in *n*-heptane at 25°C. The viscosity-molecular weight relation has been established for polymer (II) in the same solvent system by Motowoka *et al.*²:

$$[\eta] = 5.64 \times 10^{-4} M_w^{1.07} \quad (1)$$

where M_w denotes the weight-average molecular weight derived from sedimentation velocity measurements. Since polymer (I) differs little from (II) in the chemical constitution, adoption of this expression may be justified. Gel permeation chromatography (GPC) (HLC-803D manufactured by Toyosoda Co.) provided a very efficient technique in determining the molecular weight and molecular weight distribution from a limited amount of samples. In order to establish a calibration curve, polymer samples of narrow molecular weight distributions were prepared by the fractional-precipitation method. A linear relation was obtained between the elution volume V_e and the corresponding molecular weight M determined by using eq 1:

$$V_e = 63.57 - 6.266 \times \ln M \quad (2)$$

These measurements were carried out in tetrahydrofuran at room temperature. The molecular weight distributions were estimated from the chromatogram by using the mensuration-by-parts methods.

Figure 1. Molecular weight dependence of the intrinsic viscosity determined in TCE at 25°C. Molecular weights were estimated from the GPC data.

In Takahashi *et al.*'s work,⁴ liquid crystalline properties of the polymer have been extensively studied in TCE. The same solvent was found to be most suited for our deuterium NMR studies of the liquid crystal. With this reason, intrinsic viscosities were also measured for several polymer samples in TCE at 25°C. The values of M_w were estimated for the corresponding samples as prescribed above. The results are shown in Figure 1, which leads to a relation such as $[\eta] = 1.3 \times 10^{-3} M_w^{1.0}$. Although the range of M_w studied is somewhat limited, the exponent in the Mark-Houwink-Sakurada equation was found to be in the range 1.0 ± 0.1 . This value is sufficiently close to that mentioned above for polymer (II) (*cf.* eq 1), suggesting that the stiffness of the skeletal backbone is little affected by the insertion of a phenylene group in every two repeating units.

The estimate of diameter d ranges from 1.2 ± 0.3 to 1.7 nm. The former value was derived by Motowoka *et al.*² from the Yamakawa-Fujii treatment of the hydrodynamic data of polymer (II), while the latter corresponds to the closest packing of molecules in the solid state. In the following treatment, we adopt Motowoka *et al.*'s value.

Orientational Ordering in the Liquid Crystalline State

A well-resolved quadrupolar splitting $\Delta\nu$ was observed for a liquid crystalline solution of the polymer in TCE. Orientational order pa-

parameter S of the polymer in the nematic mesophase can be obtained by

$$S = (2/3)(\Delta\nu/q_{zz}) \quad (3)$$

where q_{zz} is the component of the field gradient tensor along the molecular axis. For estimation of the q_{zz} value,⁵ the quadrupolar coupling constant along the aromatic C-D bond was taken to be 183 kHz, with the asymmetry factor $\eta = 0.06$. The structural parameters required were also taken from literatures.⁶ The value of S determined in this manner should include contributions from the overall orientation of the persistent rod as well as local fluctuations arising from the bond-angle deformation.

In accordance with the molecular characteristics observed in dilute solution, the volume fractions in the coexisting isotropic (v_p') and anisotropic mesophase (v_p'') were found to be around 0.3 and 0.4, respectively, being somewhat higher than those reported for the other conventional stiff-chain polymers of comparable contour length.⁷⁻⁹ The values of v_p' and v_p'' were found to be quite insensitive to the molecular weight of the polymer except in the very low-molecular-weight region. Accordingly, the ^2H NMR measurements were carried out for liquid crystalline samples in the concentration range (volume fraction) of $v_p = 0.4$ to 0.6. A typical example of the experimental S - v_p curve is shown in Figure 2, where the data obtained in the homogeneous mesophase and in the biphasic equilibrium region are indicated by open and half-filled circles, respectively. The contour axial ratio x of the sample was estimated to be 111 from the measured molecular weight ($M_w = 9.23 \times 10^4$) and the lateral dimension of the polymer. Shown also in this figure (triangles) are the corresponding results previously reported for poly(γ -benzyl L-glutamate) (PBLG) ($x = 121$) in dimethylformamide.¹⁰ Since the PBLG molecule is more rodlike, the transition to the isotropic phase occurs at lower concentrations. Following our previous treatment,¹⁰ we compare these experimental S - v_p plots with

Figure 2. Variation of the order parameter S with polymer concentration (volume fraction). The values observed for poly(yn)-platinum polymers in TCE are indicated by open circles. Shown for comparison by open triangles are the results previously reported for the PBLG/DMF system. Half-filled symbols designate the order in the biphasic equilibrium region. The corresponding results derived from the Flory-Ronca lattice theory are shown by the solid curves. The curve denoted with $x_k = 22$ was calculated according to the Kuhn-chain assumption. The broken curves indicate some extension into the biphasic region.

those calculated from the Flory-Ronca lattice theory.¹¹ In consideration of the chain flexibility, theoretical calculations for poly(yn)-platinum polymers were carried out on the basis of the Kuhn-chain assumption,¹² the axial ratio of the Kuhn segment x_k being estimated to be 22 from the persistence length and the diameter of the polymer.² The variations of S in the anisotropic phase are illustrated by the solid curves, and the broken curves indicate the results of calculations extended over the concentration range where the biphasic equilibrium should be expected. The values of S at the boundary between these curves define S_{crit} . Although the theory predicts approximately acceptable values for the isotropic-anisotropic phase equilibrium concentration (v_p), a large difference is demonstrated between the calculated and observed order parameters (S). Such a discrepancy may be at least partially attributable to the inability of the theory to take account of the local fluctuation of the chain axis, which should affect the order parameter determined by the ^2H NMR method. In Figure 2, it may be also important to note that the experimental S - v_p

plot of the poly(yne)-platinum polymer (circles) tends to increase more rapidly toward higher concentrations (*i.e.* concave upward). The opposite trend is expected by the theory and also observed in the case of PBLG (triangles). These observations suggest that the stiffness, or more precisely the persistence of orientational correlation along the chain, increase as a function of concentration in the polymer (I)/TCE mesophase. Phenomenologically, this is likely to occur when the skeletal backbone of stiff-polymers is moderately flexible.

A comprehensive paper including the phase behaviors will be published in the near future.

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