Macromolecules 1991, *24*, 6238-6243

Phase Behavior and Molecular Ordering of Semiflexible Poly(yne)-Platinum Polymers in Trichloroethylene

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Received March 11, 1991; Revised Manuscript Received July 9, 1991

ABSTRACT: Poly(yne)-platinum polymers having the structure $-Pt(PBu_3)_2-C{\equiv}C-C{\equiv}C-Pt(PBu_3)_2-C{\equiv}C-C_6H_4-C{\equiv}C-$ have been prepared according to the prescription developed by Hagihara, Takahashi, et al. The orientational characteristics of these polymers in the lyotropic nematic mesophase (trichloroethylene) were studied in relation to their phase behavior. The volume fractions, v'_p and v''_p, in the coexisting isotropic and anisotropic mesophase were found to be around 0.29 and 0.43, respectively. These values tend to be slightly higher in the low molecular weight region. The molecular weight distributions remain practically identical between the two conjugate phases. The orientational order parameter S was determined for partially deuterated polymers in the lyotropic liquid crystalline state (v_p = 0.4-0.6) by using the ^{2}H NMR technique. Experimental S-v_p curves tend to increase more rapidly toward higher concentrations (i.e., concave upward), suggesting that the persistence of orientational correlation along the chain increases as a function of concentration. All these observations indicate that the polymer chain is considerably flexible. Experimental results were compared with those of theoretical calculations: a persistence length q = 13 nm was adopted from Teramoto et al.'s work. The phase equilibrium data are reasonably well reproduced by Flory's Kuhn-chain model, which however failed to predict correct values for S. The persistent-chain model of Khokhlov and Semenov somewhat overestimates the values of v'_p and v''_p, indicating the need of consideration for higher virial terms in the theory. Further elaborations are required in theories for a quantitative description of the S-v_p relation.

Introduction

The synthesis and properties of extended polymers having a backbone composed of conjugated poly(yne) structures linked together by platinum metal atoms were reported by Hagihara, Takahashi, and their collaborators[1,2] some years ago. Spectral studies including ^{31}P NMR indicated that the polymers have square-planar trans configurations at the metal moieties leading to an extended chain conformation.[2] The architecture of the polymer is unique in the sense that the principal axis of the polarizability tensor lies exactly along the skeletal backbone. Polymers are soluble in conventional organic solvents and exhibit a lyotropic mesophase under certain conditions.[3] Trichloroethylene (TCE) has been extensively employed in the investigation of the liquid crystallinity of these polymers.

The solution properties of poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl] (I) have been

$$-\!\!\!\left[\, Pt(PBu_3)_2-C{\equiv}C-C{\equiv}C \,\right]\!\!\!-_x$$

I

reported by Fujita, Teramoto, et al.[4] The results of viscosity and sedimentation velocity mesaurements in *n*-heptane were analyzed in terms of the Yamakawa-Fujii theories. The value of the persistence length q was found to be 13 ± 3 nm, suggesting that the polymer can be represented as a wormlike chain. Light-scattering measurements on the same polymers have been carried out by Ikeda et al.[5] All these studies indicate that an isolated polymer may be approximated by a Kuhn-chain model except when its molecular weight is extremely low.

In previous studies[6,7] we have demonstrated that the deuterium NMR technique is useful in studying the orientational characteristics of α-helical poly(γ-benzyl L-glutamate) (PBLG) in the lyotropic liquid crystalline state. Deuterium labeles were introduced at the amide or α-methine group to elucidate the order parameter S of the backbone. The values observed at the critical concentration (B point) were compared with those derived from various thermodynamic theories.[7] The Flory lattice theory[8] predicted S_{crit} = 0.92, being somewhat inconsistent with experimental observations. Experimental values of S_{crit} (ca. 0.80) were most closely reproduced by the Onsager virial theory,[9] but the corresponding critical concentrations were much too low. The skeletal backbone of the α-helical PBLG molecule is known to be comparatively stiff ($q \cong$ 150 nm) among real polymer systems.[10] Nevertheless, it still substantially deviates from a perfect rigidity. The order parameter determined by the ^{2}H NMR method may include the effect arising from local fluctuations along the chain, leading to an underestimate of the S value as compared with those calculated for a strictly rigid-rod particle. The semiflexibility of polymeric chains has been considered in the Khokhlov-Semenov (K-S) theory[11] within the framework of the Onsager scheme. Adoption of a persistence length of 150 nm in the Khokhlov-Semenov-Odijk (K-S-O) expression[12] was found to improve the agreement in the critical concentrations but led to a *significant underestimate of the orientational order parameter*.

Phase behaviors have also been extensively studied for other stiff-chain systems such as schizophyllan in water (q = 200 nm)[13] and poly(n-hexyl isocyanate) (PHIC) in toluene (q = 40 nm) as well as in dichloromethane (q = 21 nm).[14,15] As the stiffness of the skeletal chain decreases, the isotropic-anisotropic phase transition tends to occur in higher concentrations. From a careful analysis of their experimental data, Teramoto et al.[16] have concluded that the agreement between the K-S theory and experiment is only moderate for the latter two systems, where the validity of the second virial approximation is questionable. When the stiffness of a polymer molecule is relatively low, the orientational correlation along the chain may also be affected by the strength of the external field imposed by the intermolecular interactions in higher concentrations.

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This is one of the interests of the present investigation.

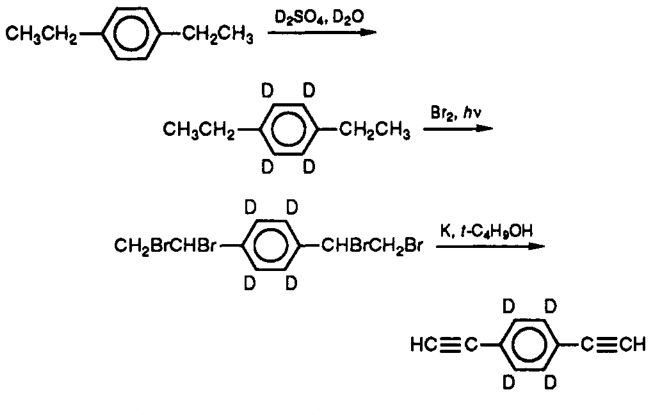
In this study, we have attempted to elucidate the orientational characteristics of poly(yne)-platinum polymers in the lyotropic nematic mesophase in relation to their phase behaviors. As stated above, the chain backbone is locally rectilinear, but an accumulation of bond-angle fluctuations makes it only moderately stiff over a long range. These polymers are very different from PBLG in the chemical constitution as well as in the stiffness of the chain. To apply the ^{2}H NMR technique to these polymer systems, an alternate copolymer such as that depicted in Figure 1 has been prepared (hereafter called polymer II or simply the polymer when it can be unambiguously identified).[17] The molecular dimensions of the polymer estimated from the crystallographic data reported for relevant short-chain model compounds[18,19] are included in the figure.

Polymer II is also known to form a lyotropic nematic mesophase in TCE.[3] In the liquid crystalline state, polymer II tends to align in the direction parallel to the applied magnetic field, in contrast to polymer I, which orients vertically with respect to the field.[3] Deuterons situated on the phenylene groups along the chain skeleton should provide information regarding the molecular ordering of polymers. The applicability of the ^{2}H NMR technique to this problem has been briefly reported in our preliminary communications.[20] The phase behaviors of polymer II were investigated in the same solvent. Statistical thermodynamic theories developed for semirigid polymers are used to predict the isotropic-nematic phase equilibrium as well as the orientational order parameter at the critical concentration, the results of calculations being compared with experimental observations.

Experimental Section

Preparation of Samples. Polymer. Several samples of polymer II were prepared according to the prescription established by Takahashi et al.[1,2] The configuration of the polymer was confirmed from ^{31}P NMR spectra taken in dichloromethane at room temperature. The observed value of the chemical shift $\delta = 3.52$ (relative to the external 85% H_3PO_4 standard) and the coupling constant $J_{\text{Pt-P}} = 2385$ Hz were found to be nearly identical with those reported in the literature.[2] The polymer was quite stable when stored in the solid state. In solution, addition of a trace amount of tributylphosphine was required to prevent some possible gradual decomposition. GPC examination indicated that the polymer samples remained stable, at least for several days in the lyotropic liquid crystalline state, provided that such a precaution was taken.

Polymer-d_4. Deuterium labels were introduced on the phenylene ring according to the following steps:



1,4-Diethynylbenzene-d_4 thus obtained was reacted with bis[*trans*-chlorobis(tri-*n*-butylphosphine)platinum(II)]-1,4-butadiynediyl to give deuterated polymer samples. The detailed prescriptions are given in the literature cited.[21-23]

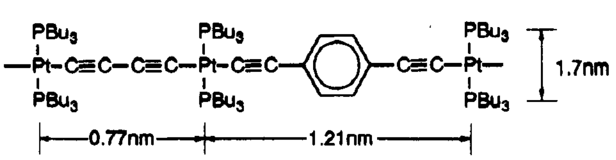


Figure 1. Molecular structure of polymer II. The distances spanning alternative repeating units and the diameter are taken from the crystallographic data reported for relevant model compounds:[18,19] $Cl{-}[Pt(PBu_3)_2{-}C{\equiv}C{-}C{\equiv}C]_2{-}Pt(PBu_3)_2Cl$ and $S{\equiv}C{-}Pt(PEt_3)_2{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}Pt(PEt_3)_2{-}C{\equiv}S$.

Table I
Intrinsic Viscosities, Molecular Weights Estimated Therefrom, and Elution Volumes of GPC for Polymer II Fractions

fraction	$[\eta] \times 10^{-2}$,[a] cm^3 g^{-1}	$M \times 10^{-4}$ [b]	V_e,[c] mL
A-1	0.340	2.93	35.5
A-2	0.538	4.51	34.4
B-1	0.977	7.88	33.2
B-2	1.43	11.2	31.7

[a] Measured in *n*-heptane at 25 °C. [b] Estimated from the relation (eq 1) derived from Motowoka et al.'s data.[4] [c] Values corresponding to the peak position of chromatograms (in THF at 25 °C).

Fractionation of Polymer Samples. The molecular weight distributions of polymers thus obtained were usually broad and found to be in the range $M_w/M_n = 2$–3 by GPC examination (cf. seq.). As-polymerized samples were therefore fractionated by precipitation from benzene solution by using methanol as a precipitant.[4] The samples were freeze-dried from benzene and stored in a refrigerator.

Measurements. Molecular Weight and Molecular Weight Distribution. The molecular weights were estimated for four samples from the intrinsic viscosity measured in *n*-heptane at 25 °C by using Motowoka et al.'s relation, which has been established for fractionated samples of polymer I in the same solvent system:

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

Since polymer II differs little from polymer I in chemical constitution, adoption of this expression may be justified. These results are listed in the second and third columns of Table I. Gel permeation chromatography (GPC) (HLC-803D manufactured by Toyo Soda Co.) has provided a very efficient technique in determining the molecular weight and molecular weight distribution from a limited amount of polymer sample. Shown in the last column of Table I are the elution volumes V_e measured for the aforementioned polymer samples in tetrahydrofuran (THF). The linear relation thus derived

$$V_e = 63.57 - 6.266 \ln M \tag{2}$$

served for the estimation of molecular weights from the GPC data in the present work. The molecular weight distribution conventionally expressed by the ratio of the weight-average and number-average molecular weights M_w/M_n was estimated from the chromatogram according to the mensuration-by-parts method.

NMR. The ^{31}P NMR spectra were recorded either on a JEOL FX-90Q or on a GSX-270 spectrometer. Following Takahashi et al.,[3] the ^{31}P NMR method was used to deduce the alignment of the nematic-domain axis of the liquid crystalline phase under the applied magnetic field. The resonance peak assigned to the liquid crystalline phase exhibited a large downfield shift upon 90° rotation of the sample, indicating that the director of the nematic domain tends to orient parallel to the applied field. The ^{2}H 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

Isotropic-Anisotropic Phase Equilibrium. Following the procedure adopted by Itou et al.[14] and Conio et al.,[15] the critical volume fractions v'_p and v''_p corresponding to the phase boundaries of the biphasic equilibrium

Table II
Critical Compositions of Phase Separation

sample	$M_w \times 10^{-4}$	M_w/M_n	x	v'_p	v''_p	v''_p/v'_p
C-1	4.57	1.21	55	0.339	0.516	1.52
D-1	5.47	1.29	66	0.227	0.435	1.57
C-2	7.36	1.18	89	0.304	0.431	1.42
E-1	10.5	1.22	127	0.288	0.428	1.49

were estimated from the plot of the overall concentration of polymer v_p against the observed volume fraction of the conjugated isotropic phase ϕ. In this treatment, the partial specific volume of the polymer[1b] and the molar volume of the solvent (TCE) were taken to be 0.79 and 0.68 cm^3 g^{-1}, respectively. Values of v'_p and v''_p obtained at $\phi = 0$ and 1.0 are summarized in Table II, where molecular weight M_w and molecular weight distribution M_w/M_n of the corresponding samples are also included. Critical concentrations v'_p and v''_p were found to be somewhat higher for the lowest molecular weight sample. As shown in the last column, the ratio v''_p/v'_p remains nearly invariant within the range 1.5 ± 0.08, in approximate agreement with those reported for other stiff-chain polymers.[14,24]

A possible fractionation of polymers between the two conjugate phases was investigated for a binary polymer mixture. In Figure 2, GPC chromatograms of the polymer samples collected from the conjugated isotropic and anisotropic phases are compared with that for the whole polymer. As manifestly demonstrated in the diagram, the binodal characteristics of the molecular weight distribution remain nearly identical in all these samples, showing that molecular weight fractionations do not accompany the phase separation. Ciferri et al.[15] have noted a similar Kuhn-chain behavior for a high molecular weight sample ($M_v = 2.8 \times 10^5$) of PHIC. These observations are however at variance with most of those reported for other conventional rodlike polymers.

In the polymer system under investigation, the local rigidity determined by the persistence of orientational correlation along the chain must be the major factor involved in the isotropic to anisotropic phase separation. The contour axial ratios $x = L/d$ estimated from the contour length L and lateral dimension d of the polymer are also included in the fourth column of Table II. The values of L were in turn deduced from the observed molecular weights and the length of the repeating unit (cf. Figure 1): the Pt–Pt distance (0.77 nm) spanning the diacetylene group was derived from the X-ray analysis of a trinuclear complex,[18] and the other Pt–Pt distance (1.21 nm) involving the 1,4-diethynylbenzene group was taken from the X-ray data of an organometallic compound having a relevant chemical structure.[19] The estimate of diameter d ranges from 1.2 ± 0.3 to 1.7 nm. The former value was derived by Motowoka et al. from the Yamakawa–Fujii treatment of the hydrodynamic data of polymer I, while the latter corresponds to the closest packing of molecules in the solid state as estimated from the crystallographic data of a trinuclear complex (cf. Figure 1). As an inspection of a molecular model would suggest, adoption of $d = 1.7$ nm uniformly along the entire molecule may lead to some overestimate of the diameter in solution. In the present treatment, we adopt Motowoka et al.'s value (1.2 nm).

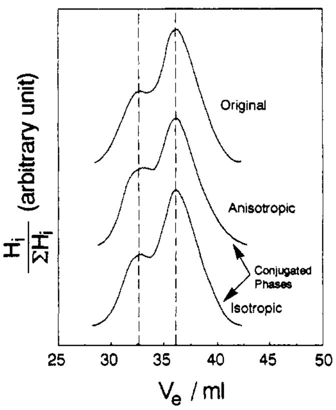


Figure 2. GPC diagrams (in THF at room temperature) for polymers recovered from the conjugate isotropic and anisotropic phases. The uppermost curve corresponds to the whole polymer (a mixture of two fractionated samples) employed in this phase study. The ordinate scale is taken to be arbitrary for comparison purposes.

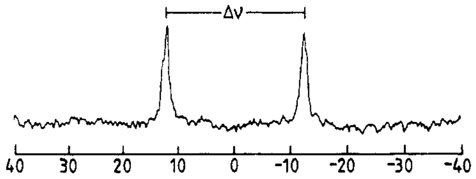


Figure 3. Typical example of the ^{2}H NMR spectrum observed in the nematic liquid crystalline phase (TCE at 30 °C).

Table III
Values of the Quadrupolar Splitting Δν Observed in TCE at 30 °C and the Order Parameters Estimated Therefrom

fraction	$M_w \times 10^4$	M_w/M_n	x	v_p	Δν, kHz	S
G-1	1.8	1.2	21	0.45[a]	21.02	0.731
				0.51	21.77	0.757
				0.63	23.12	0.804
G-2	3.4	1.2	41	0.43[a]	20.02	0.696
				0.52	21.03	0.731
				0.64	24.90	0.866
D-2	7.0	1.2	84	0.39[a]	20.03	0.696
				0.48	21.83	0.759
				0.60	24.99	0.869
F-1	9.2	1.2	111	0.41[a]	22.17	0.771
				0.50	23.21	0.807
				0.60	25.11	0.873

[a] The concentration corresponds to the nematic–isotropic biphasic region.

Orientational Order Parameter. Molecular ordering of the polymer in the mesophase was studied by using samples carrying deuterons on the phenylene groups located along the skeletal backbone. An example of the ^{2}H NMR spectra is shown in Figure 3. Values of the deuterium quadrupolar splitting Δν observed in the liquid crystalline phase (TCE at 30 °C) are listed in Table III, where M_w and M_w/M_n determined by GPC and the corresponding axial ratio x of the polymer sample are also included. As indicated in the table, the observation covers the concentration range (v_p) from ca. 0.4 to 0.6. The lower limit corresponds to the biphasic equilibrium region. The order parameter of the molecular axis S_{ZZ} can be estimated[25] from the observed value of Δν according to the expression

$$\Delta\nu = S_{ZZ}\left(\frac{3q_{bb}}{2}\right)\left(\frac{3\cos^2\gamma - 1}{2} + \frac{\eta}{2}\sin^2\gamma\right) \qquad (3)$$

where

$$\eta = \frac{q_{aa} - q_{cc}}{q_{bb}} \qquad (4)$$

The coordinate systems required for this transformation are defined in Figure 4. Numerical values of the parameters required in this expression were adopted from the literature:[26,27] $\gamma = 60.1°$, $q_{bb} = 183$ kHz, $\eta = 0.06$. The order parameters S_{ZZ} calculated from the observed quadrupolar splittings are listed in the last column of Table

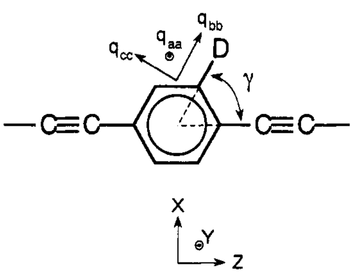


Figure 4. Illustration of the molecular coordinate systems. The quadrupolar coupling constants q_{ii} are defined in the *abc* frame: *b* lies along the C–D bond, while *a* is taken to be perpendicular to the benzene ring. The *XYZ* frame represents the symmetry axes of the molecule: *Z* defines the molecular axis, and *Y* is perpendicular to the ring (thus parallel to *a*).

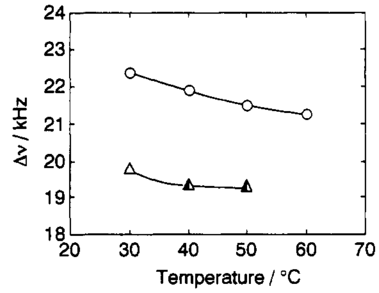


Figure 5. Temperature dependence of the quadrupolar splitting. The values were observed at v_p = 0.5 (○) and 0.6 (△, ▲) for a polymer sample with M_w = 1.8 × 10^4. Half-filled triangles represent the data obtained in the biphasic equilibrium region.

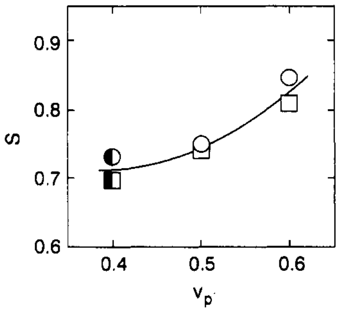


Figure 6. Variation of the order parameter *S* for the deuterated component of a binary mixture as a function of concentration of the whole polymer v_p, observed in TCE at 30 °C: (□, ◧) deuterated (10.6 × 10^4)/nondeuterated (4.5 × 10^4) mixture; (○, ◐) deuterated (4.3 × 10^4)/nondeuterated (10.5 × 10^4) mixture; values in parentheses represent M_w. Open and half-filled circles indicate the values of *S* observed in the stable liquid crystalline and biphasic equilibrium regions, respectively.

III. The values of S_{ZZ} determined in this manner should implicitly include the effect of local flexibility arising from the bond-angle fluctuation inherent to the skeletal bonding system. In accordance with such consideration, the temperature dependence of the order parameter was found to be fairly large. Examples are shown in Figure 5, where variations of Δν observed in the anisotropic phase are plotted as a function of temperature. The orientational order decreases rapidly with an increase in temperature and eventually reaches a biphasic equilibrium region.

Experiments were also carried out for ternary systems consisting of two polymer components of widely different molecular weights and a solvent. By introducing deuterium labels alternately in these polymer samples, we could determine the order parameters of the polymer components separately. Shown in Figure 6 are the results for a polymer mixture (50% w/w) derived from a combination of samples having M_w = ca. 4.4 × 10^4 and 10.5 × 10^4. In spite of a large disparity in the molecular weight of polymers, the observed S_{ZZ} values are nearly identical between the two components over a wide range of concentration.

Discussion

In this analysis, we have borrowed the values of the persistence length from that measured for polymer I in *n*-heptane by Motowoka et al.[4] In the same work, they also studied the viscosity–molecular weight relation of polymer I in benzene. The exponent in the Mark–Houwink–Sakurada equation was found to be 1.09 in benzene, being consistent with the value (1.07) in *n*-heptane. The results indicate that the stiffness of the polymer chain is similar in these two solvents. For comparison, we measured viscosities of polymer II in TCE at 25 °C. As reported previously,[20] the exponent estimated from a double-logarithmic plot was found to be in the range 1.0 ± 0.1. This value is sufficiently close to those mentioned above for polymer I. The stiffness, or flexibility, of the skeletal backbone is little affected by the insertion of a phenylene group in every two repeating units (cf. Figure 1). These observations are quite compatible with our postulation for the use of eq 1. The experimental results presented above clearly indicate that the polymer chain is considerably flexible, being consistent with the conclusion drawn from studies on the dilute solution properties. According to the Porod–Kratky wormlike chain model[28]

$$2q = b/(1 + \cos\theta) \qquad (5)$$

where *b* and *θ* represent the bond length and the bond angle, respectively. With adoption of b = 0.15 nm for a virtual bond and q = 13 nm for the persistence length of the polymer, we obtain $\cos\theta = -0.994$, corresponding to a continuous deviation of $\Delta\theta$ = ca. 6°. Departure from the rectilinearity is appreciable. A relatively larger deviation from the linearity may be expected for the C–Pt bonds: $l_{\text{C-Pt}}$ = 0.21 nm.

In the Flory lattice theory, the formation of a mesophase is principally determined by the axial ratio of the rigid-rod particle, $x = L/d$. For semiflexible polymer chains with $L \gg q$, Flory[24,29] proposed a particularly simple model in which the tendency to induce formation of a nematic phase is controlled by the Kuhn segment of the chain. In this obviously artificial device, the polymer is effectively replaced by the chain consisting of n_K bonds of appropriate length l_K connected by flexible joints; i.e., $L = n_K l_K$. The axial ratio x_K of the Kuhn segment is given by

$$x_K = l_K/d = 2q/d \qquad (6)$$

Adoption of d = 1.2 nm and q = 13 nm yields x_K = 22. A semiempirical approximation for the critical volume fraction v^*_p for incipience of metastable order has been derived for the condition of equilibrium disorder. In Flory's treatment, the critical volume fraction v^*_p is expressed as a function of the axial ratio of the rigid-rod component. In the framework of the Kuhn model

$$v^*_p = (8/x_K)(1 - 2/x_K) \qquad (7)$$

This relation expresses the volume fraction below which the condition of the order–disorder equilibrium is not fulfilled. Use of x_K = 22 in eq 7 yields v^*_p = 0.3. This value of v^*_p is consistent with the results shown in Table II.

The volume fractions of conjugated phases at biphasic equilibrium were calculated according to Flory's prescription for the Kuhn-chain model with x_K = 22, and the results are compared with those observed in Figure 7, where values of v'_p and v''_p are plotted against the contour axial ratio

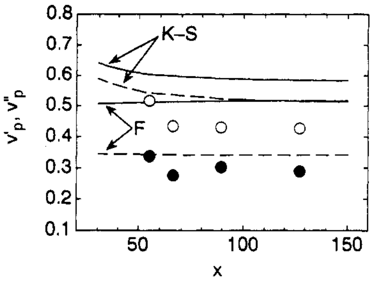


Figure 7. Comparison of the observed and calculated critical concentrations: (●, - - -) for $v'_{\rm p}$; (○, —) for $v''_{\rm p}$. Observed values are taken from Table II. Calculations were carried out for polymer chains with q = 13 nm and d = 1.2 nm, and the results are plotted against x. The theoretical curves obtained from the Flory Kuhn-chain model are indicated by F, and those derived according to the Khokhlov–Semenov theory are designated with K–S.

x. The theoretical values shown by a pair of solid and broken curves (F) remain nearly constant for the range $x \gg x_{\rm K}$. With $x_{\rm K}$ = 22, the theory somewhat overestimates the critical volume fractions. These theoretical calculations lead to an estimate of the ratio $v''_{\rm p}/v'_{\rm p} \cong 1.5$, in good agreement with those observed (cf. Table II). Tentative calculations indicate that a choice of $x_{\rm K}$ = 27 reproduces most satisfactorily the experimental observations.

Khokhlov and Semenov[11] have treated the configurational entropy arising from the semiflexibility of a wormlike chain. The theory overestimates critical concentrations for poly(yne)–platinum polymers, a similar behavior being reported for other flexible chains such as poly(n-hexyl isocyanate). The theoretical curves obtained by using the same set of d and q values as before are shown by a pair of curves denoted as K–S in Figure 7, where the abscissa is expressed by the axial ratio x (=L/d) for comparison purposes. The agreement between theory and experiment may be improved to some extent by adjusting the axial ratio $x_{\rm K}$ (=$2q/d$): e.g., with $x_{\rm K}$ = 35, the calculation yields $v'_{\rm p}$ = 0.334 and $v''_{\rm p}$ = 0.374 for a contour axial ratio x = 100. The ratio $v''_{\rm p}/v'_{\rm p}$ (=1.1) remains unaffected however, indicating that the estimate of the biphasic gap is still too narrow (cf. Table II).

The orientational order parameter of the Kuhn segment can be easily calculated according to the Flory–Ronca scheme[8b] as a function of concentration. The theoretical S–$v_{\rm p}$ curves are compared with experimental values (cf. Table III) determined by the deuterium NMR method in Figure 8a. Computations were carried out for discrete values of $x_{\rm K}$ as indicated by the numerical figures given to each curve. 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 $S_{\rm crit}$. Experimental values of S obtained in the anisotropic phase are shown by open symbols, half-filled symbols being used to indicate values observed in the biphasic equilibrium region. While the theory predicts $S_{\rm crit}$ = 0.9, the values observed in the biphasic region are appreciably lower (ca. 0.7). As noted previously, 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 average orientation of the C–D bond of the aromatic core. The reduction of S arising from this source may be roughly estimated to be of the order of 10% on the basis of the aforementioned Porod–Kratky description (eq 5) of the chain. The limitation inherent to the simple Kuhn-chain model is apparent.

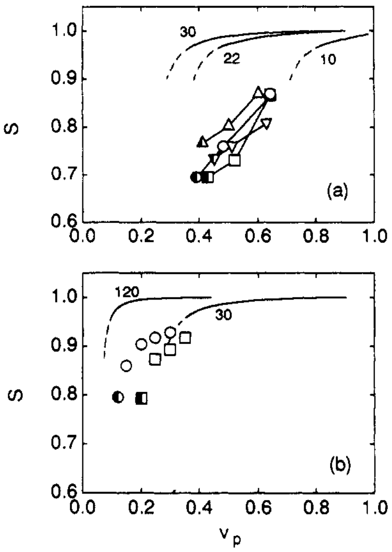


Figure 8. Variation of the order parameter S with concentration $v_{\rm p}$. (a) Polymer II in TCE. Observed values are listed in Table III for the individual samples: F-1 (△), D-2 (○), G-2 (□), and G-1 (▽). The results of calculations according to the Flory–Ronca theory are shown by the solid curves. Values of the Kuhn axial ratio $x_{\rm K}$ used in calculations are given to each curve. The junction between the solid and broken curves corresponds to the nematic–isotropic phase boundary and defines the critical order parameter $S_{\rm crit}$. (b) The corresponding results previously obtained for α-helical PBLG in DMF. Calculations were carried out by assuming perfectly rigid PBLG rods.

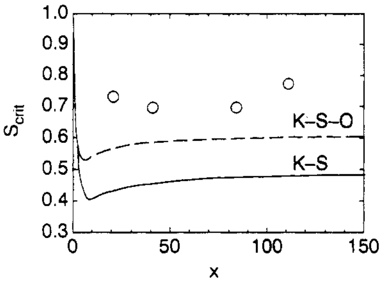


Figure 9. Plots of $S_{\rm crit}$ vs x. Open circles indicate experimental values obtained for polymer II in TCE at 30 °C. The solid curve illustrates the relation derived from the Khokhlov–Semenov (K–S) theory (q = 13 nm, d = 1.2 nm). The theory modified by Odijk (K–S–O) yielded the broken curve.

Shown in Figure 8b for comparison are the corresponding results previously obtained for PBLG in our laboratory.[7] Notations used are similar to those in Figure 8a. Since the PBLG molecule is more rodlike, the transition to the isotropic phase occurs at lower concentrations.[30] A large discrepancy may be noted in the experimentally observed S–$v_{\rm p}$ plots between these two diagrams. While the curves tend to be concave in Figure 8a, the trend is opposite in Figure 8b. The ordinary theories predict the latter behavior for rodlike molecules. Phenomenologically, this is likely to occur when the skeletal backbone of stiff polymers is moderately flexible: i.e., $q \ll L$. Theory has yet to be developed on this interesting issue.[31]

Values of the critical order parameter $S_{\rm crit}$ (at the B point) calculated according to the Khokhlov–Semenov theory[11] are plotted as a function of the contour axial ratio x (solid curve) in Figure 9, where the corresponding experimental values are shown by open circles. In contrast to the aforementioned Kuhn-chain model, the theory underestimates the order parameter $S_{\rm crit}$. As indicated by the broken curve, the agreement was found to be improved somewhat when the expression proposed by Odijk[12] (K–S–O theory) was adopted. The disparity between theory and experiment is still appreciable, however. The difference cannot be remedied by consideration of the local fluctuation.

Another interesting model has been proposed by Ronca and Yoon,[32] who treated the departure from strict rigidity by introducing a concept of the wormlike chain with limiting curvature. In their formulation, steric interactions among anisotropic solutes are taken into account through the Flory lattice model. Some of the numerical results have been reported in the literature by these authors. For $x_a = q/d = 11$, we read $v_p = 0.3$ at the A point and $S_{crit} = 0.7$ $(1/x \rightarrow 0)$ for the low-temperature model (cf. Figures 1 and 3 of ref 32), in approximate agreement with our experimental data. According to the authors, however, this model corresponds to $d \ln \langle r^2 \rangle / d \ln T = 0$ for the dimension, which is unrealistic for the polymer at hand. Furthermore, if we consider the effect of local fluctuation on the order parameter, the prediction of $S_{crit} = 0.7$ seems to be a little too low.

In a recent work, Sato and Teramoto[16] revised the Cotter scaled particle theory[33] by introducing an orientational entropy term as prescribed by Khokhlov and Semenov.[11] Sato et al. have thus achieved an appreciable improvement in the agreement between the theory and experiment on thermodynamic quantities such as the osmotic pressure and the isotropic–anisotropic phase boundary concentrations for the aqueous schizophyllan, PHIC–toluene, and PHIC–dichloromethane systems. As shown in this work, account of the third and higher terms in the virial expansion may become important especially when polymer chains are considerably flexible. Interpretation of the observed ordering behaviors seems to require further elaboration in the development of theories.

Finally, we wish to emphasize that the ^{2}H NMR method provides very accurate information regarding the ordering characteristics of stiff-chain polymers in the mesophase, which is in turn useful for a critical test of the model adopted in thermodynamic theories.

Acknowledgment. We are very grateful to Prof. S. Takahashi for his valuable suggestions on the preparation of poly(yne)–platinum samples. We also like to thank Prof. S. Ikeda for communicating some of his unpublished data and Prof. A. Teramoto for helpful discussions. This work was supported (in part) by a Grant for International Joint Research Project from the NEDO, Japan.

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