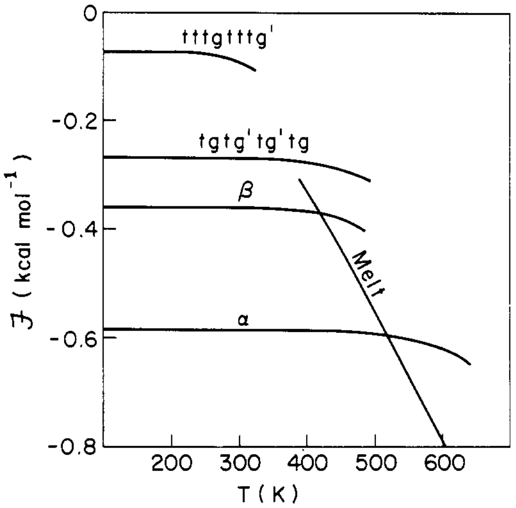

Figure 1. Free-energy minima corresponding to the two suggested chain conformations for a phase III PVF_2 are plotted as a function of temperature. The same quantities for the α, β, and melt phases are also shown for comparison. The termination of each line represents the limit of metastability of that phase.

Table I

chain conformations	repeat distance, Å^a	free energy (300 K), kcal per monomer unit mol
tttgtttg'	9.11	−0.0954
tgtg'tg'tg	8.78	−0.2752
tttttgtg'	9.43	−0.2710
tgtg'tg'tg'	8.66	−0.2740
tttttttg	8.66	−0.2256
tttttgtg	8.66	−0.1184
tttgtgtg'	8.66	−0.1738
tttgtgtg	8.78	−0.0198
tgtg'tgtg' (α phase)	9.11	−0.5869
tttttttt (β phase)	10.33	−0.3405

[a] 112° bond angle.

temperature of 300 K. The eight conformations shown are the same as those arrived at, in I, from consideration of detailed molecular geometry-dependent intrachain energy. We in I, however, disregarded all but *tgtg'tg'tg* and *tttgtttg'*, because these are the only conformations that pack into a unit cell with an *n*-glide-plane symmetry that has been observed in the X-ray data[1] of the phase III sample. The fiber repeat distances of these two conformations are also close to the experimental value of 9.18 Å.

Figure 1 is a plot of the free-energy minima corresponding to these conformations. We find that *tgtg'tg'tg* is more stable than *tttgtttg'* at all temperatures in which they exist. This supports our suggestion in I that the interchain energy may favor *tgtg'tg'tg* over *tttgtttg'*. We note, however, that the difference in free energy of the two conformations is only 0.18 kcal/mol (per monomer unit) at 300 K. This energy is too small to compensate for the valence bond angle deformation energy needed to stretch the repeat distance of *tgtg'tg'tg* to 9.18 Å. The required deformation energy, as shown in I, is approximately 1 kcal per monomer unit mol, over and above that required for the *tttgtttg'* conformation. It may be mentioned in this connection that the infrared data[7] also favor the *tttgtttg'* conformation.

The present theory also predicts the structural phase transition shown in Figure 2. The transition takes *tgtg'tg'tg* into *tttttgtg'* at about 400 K. This breaks the *n*-glide symmetry of the lattice. Consequently, changes should occur in both the X-ray diffraction pattern and in the infrared spectrum of this structure. The observation of this phenomenon would definitely favor *tgtg'tg'tg* as the conformation of phase III.

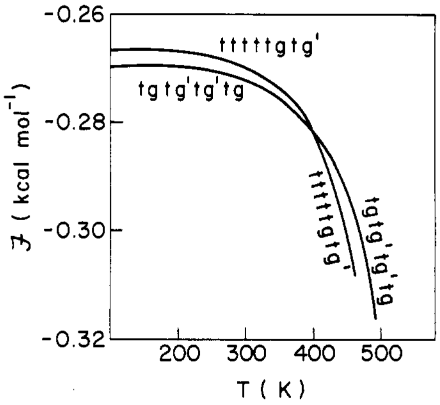

Figure 2. A high-temperature crystal–crystal phase transition, as predicted by the theory, is shown. Two sets of free-energy minima cross at a temperature of about 400 K.

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A New Liquid-Crystalline Material. Transition Metal-Poly(yne) Polymers

In recent years, there has been a growth of interest in extended chain polymers.[1] One of the characteristic features of rigid extended polymers is that their concentrated solutions form lyotropic liquid crystals. An example is poly(γ-benzyl L-glutamate), which exhibits cholesteric liquid crystalline behavior in selected solvents.[2] Some synthetic linear polymers such as polyamides,[1,3] polyesters,[1] and polyisocyanates[4] also form liquid-crystalline solutions. We now wish to report a new class of polymers exhibiting lyotropic liquid-crystalline behavior.

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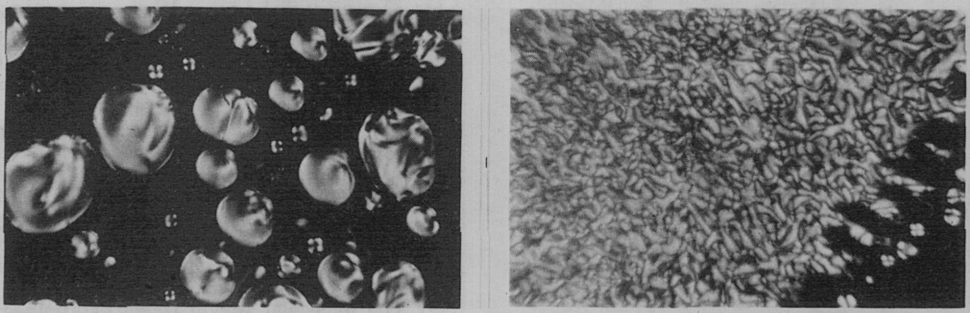
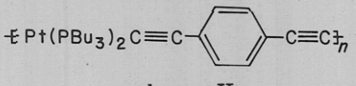


Figure 1. (a, left) Droplets of a liquid-crystalline phase in a dark background of the isotropic phase of a methylene chloride solution (~30 vol %) of polymer I ($\bar{M}_w$ 70 000); observed between crossed polarizers at about 160×. (b, right) A thin layer of a large liquid-crystalline phase of a trichloroethylene solution (~36 vol %) of polymer I ($\bar{M}_w$ 70 000); observed between crossed polarizers at about 160×.

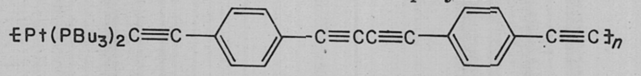
We have recently reported[5] a synthesis of new extended polymers having a backbone composed of conjugated poly(yne) structures linked together by platinum metal atoms and demonstrated on the basis of their dilute solution properties that the metal–poly(yne) polymers might have a rodlike structure. Since anisotropic molecular shape and extended polymer conformation are prerequisites for the formation of a liquid-crystalline phase, we might expect lyotropic liquid crystallinity for the metal–poly(yne) polymers. In fact, we have observed formation of a liquid-crystalline phase in concentrated solutions of polymers I, II, and III. Among the metal–poly(yne) polymers,

$-\!\!\left[\mathrm{Pt(PBu_3)_2C{\equiv}CC{\equiv}C}\right]\!\!-_n$

polymer I



polymer II



polymer III

polymer I was chosen for the present study because it could be prepared easily in the form of high molecular weight samples with sufficient solubility for use in a wide range of concentrations. Thus, solutions in concentrations as high as 50 wt % were prepared without any special additives.

A solution of polymer I in trichloroethylene at concentrations exceeding a certain limiting value exhibits typical liquid-crystalline behavior similar to that described for aromatic polyamides.[6] Thus, a concentrated solution of polymer I ($\bar{M}_w = 10^5$, 35 wt %) appears turbid even though it contains no undissolved material. On gentle stirring of the solution an opalescent appearance is readily observed, and this fades rapidly when stirring ceases.

The liquid-crystalline behavior observed under a polarizing microscope is shown in Figure 1a,b. The anisotropic phase is formed spontaneously when the solution exceeds a certain critical point depending on the molecular weight of the polymer. Figure 1a shows the onset of birefringence, where droplets of the liquid-crystalline phase form clear small Maltese crosses[2,4] which are also observed in Figure 1b at the boundary between the isotropic phase and the large anisotropic region. Experiments using a quartz wedge[7] revealed that the small droplets were negative liquid crystals. If the refractive index along the *c* axis (parallel to the main chain) of the polymer molecule is higher than that along the *a* and *b* axes (perpendicular to the main chain), which seems most likely, it may be suggested that the *c* axes, i.e., molecular direction, of the polymer molecules lie consistently perpendicular to the radius of the spherical liquid-crystalline phase.[8] A similar orientation of the *c* axis of the polymer molecule is often observed in spherulites of some polymers such as polyethylene.[7,9] Increasing the polymer concentration resulted in growth of the anisotropic droplets and disappearance of the Maltese cross, implying that the anisotropic phase is organized into microscopic domains of varying size and direction of orientation. The large anisotropic phase exhibits a typically nematic texture (Figure 1b).

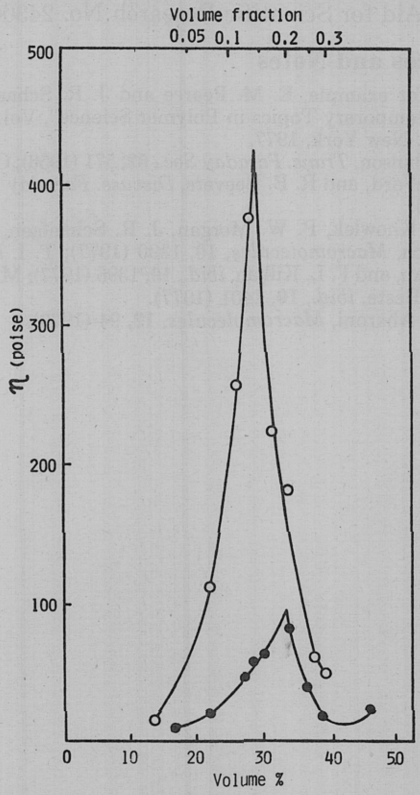


Figure 2. Viscosity[11] vs. concentration for the fractions of polymer I with $\bar{M}_w$[12] 100 000 (○) and 56 000 (●) in trichloroethylene at 20 °C.

It is also known[3,10] that lyotropic liquid-crystalline solutions exhibit a characteristic rheological property, i.e., an abrupt change in viscosity at the transition from an isotropic to an anisotropic phase. Figure 2 shows the relationship between viscosity and concentration of polymer I in trichloroethylene.[11] As the concentration of the polymer increased, the viscosity also increased. When the concentration reached a volume fraction of about 0.20 for a polymer of $\bar{M}_w = 5.6 \times 10^4$, the slope of the curve suddenly changed and the viscosity began to drop due to the formation of two phases, isotropic and anisotropic, the presence of which was also confirmed by means of polarizing microscopy. For the higher molecular weight polymer I, an abrupt viscosity change was observed at a lower concentration (volume fraction, 0.14). These critical concentrations, referred to as the A point, may be treated theoretically in terms of the molecular dimension of polymers.[13] The dependence of critical concentration on the molecular weight of polymer I is consistent with a theory[14] which predicts that increasing the axial ratio of polymer molecules results in a lowering of the critical concentration.[15]

Consequently, it has been shown that metal–poly(yne) polymers with an inherently rigid rodlike structure form liquid-crystalline solutions easily. These polymers may be the first example of lyotropic liquid-crystalline materials having transition metals. Even among a large number of thermotropic liquid crystals only two examples containing transition metals are known.[16]

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