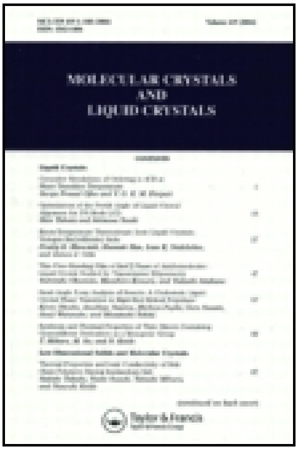

Molecular Crystals and Liquid Crystals

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Lyotropic Liquid-Crystalline Materials Containing Palladium and Nickel

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LYOTROPIC LIQUID-CRYSTALLINE MATERIALS CONTAINING PALLADIUM AND NICKEL

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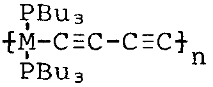
(Submitted for publication July 17, 1981)

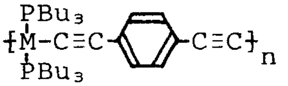
ABSTRACT: Polymers having backbones composed of conjugated acetylenes and palladium- or nickel-atoms have been found to form lyotropic liquid crystals in trichloroethylene of tetrahydrofuran.

Recently, renewed interest has developed in structures and properties of lyotropic liquid crystals formed by rod-like polymers.[1] Although several natural and synthetic polymers such as DNA, cellulose, polyamides and polyisocyanates are known as lyotropic liquid-crystalline materials,[2] none contains transition metals. Even among a large number of thermotropic liquid-crystalline materials only two examples containing transition metals are known.[3] We have recently reported poly[bis(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl] as the first example of lyotropic liquid-crystalline materials containing transition metals.[4] As an extension to other transition metals we prepared and examined metal-polyyne polymers I-V[5] whose main chains are composed of conjugated acetylenes and palladium- or nickel-atoms. Spectral analyses including $^{31}P\{^{1}H\}$-n.m.r. spectra revealed that all the polymers have square-planar *trans*-configurations at the metal moieties and extended chain structures, suggesting that the polymers may form lyotropic liquid crystals in concentrated solutions.

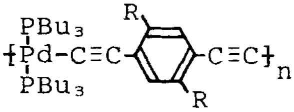


$\left[\overset{\mathrm{PBu_3}}{\underset{\mathrm{PBu_3}}{\mathrm{M}}}-\mathrm{C{\equiv}C-C{\equiv}C}\right]_n$

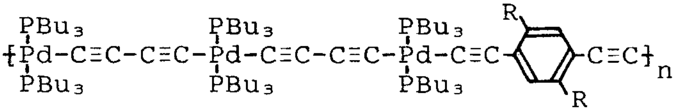
(I) a: $M = Pd$
b: $M = Ni$



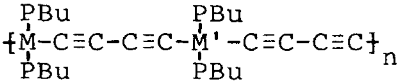
(II) a: $M = Pd$
b: $M = Ni$



(III) a: $R = CH_3$
b: $R = C_2H_5$



(IV) a: $R = H$; b: $R = CH_3$; c: $R = C_2H_5$



$\left[\overset{\mathrm{PBu}}{\underset{\mathrm{PBu}}{\mathrm{M}}}-\mathrm{C{\equiv}C-C{\equiv}C}-\overset{\mathrm{PBu}}{\underset{\mathrm{PBu}}{\mathrm{M'}}}-\mathrm{C{\equiv}C-C{\equiv}C}\right]_n$

(V) a: $M = Pd$, $M' = Pt$; b: $M = Ni$, $M' = Pt$,
b: $M = Pd$, $M' = Ni$

Flory's theory[6] predicts that requisites for formation of lyotropic liquid crystals are a large axial ratio (p) of polymer molecules and a high solubility as well as a rod-like structure of polymers. However, it is difficult to obtain high molecular-weight samples of palladium- or nickel-polyyne polymers because of relatively low solubilities of the sigma-bond between carbon and these metals. Low-molecular-weight polymers, *i.e.*, small p, require very high solubilities for formation of

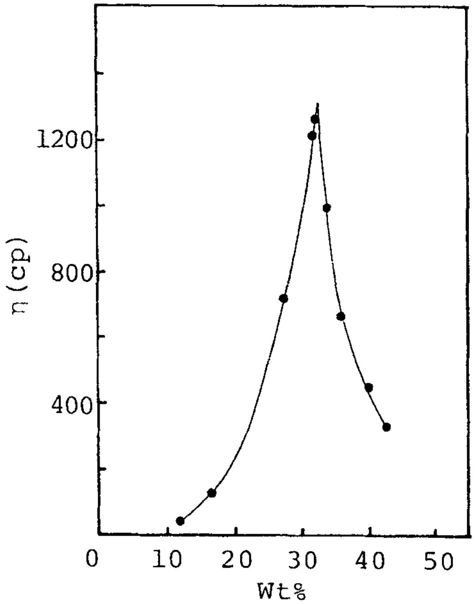


FIGURE 1. Viscosity vs. concentration for the fraction of polymer Ia ($\bar{M}w = 32000$) in trichloroethylene at 20°C.

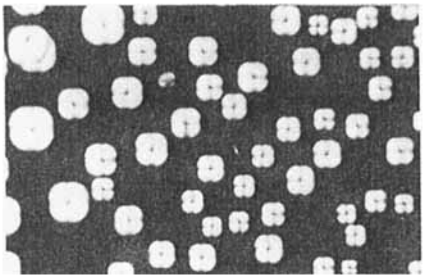


FIGURE 2. Droplets of a liquid-crystalline phase in a dark background of the isotropic phase (a trichloroethylene solution of polymer Vc ($\bar{M}w = 15000$); observed between crossed polarizers at about 200×)

liquid crystals. Polymer Ia with $\overline{M}w = 32000$ showed a satisfactory solubility and formed liquid crystals in a trichloroethylene or tetrahydrofuran solution. Formation of the liquid crystals was confirmed by a characteristic relationship[2] between viscosity and bulk concentration (Fig. 1). But polymers Ib, IIa and IIb having $\overline{M}w = 10000 - 25000$ were not observed to form liquid crystals in concentrated solutions. In order to enhance the solubility of the polymers we attempted to design the polymer structure and found that the introduction of alkyl groups onto the phenyl ring in polymer IIa resulted in favorable increase of the solubility and that polymers IIIa and IIIb exhibited a liquid crystalline behavior. Polymer IV ($\overline{M}w = 10000 - 20000$), which contains two kind of acetylenic segments in a main chain, also showed a good solubility and easily formed liquid crystals in cocentrated solutions.

We could not prepare lyotropic liquid crystals of nickel-polymers Ib ($\overline{M}w = 13000$) and IIb ($\overline{M}w = 10000$) due to their low molecular weight and low solubility which may arise from low stabilities of the Ni-C and Ni-P bonds*. Polymers Vb and Vc, which contain two kinds of metal atoms, nickel and platinum, or nickel and palladium, were more stable and soluble than polymer Ib and were obtained as samples having $\overline{M}w = 15000 - 20000$. They are readily

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*Dissociation of the phosphine ligand from the metal moiety lowers the solubility of polymers because the bulky ligand covers the polymer main chain and prevents an intermolecular interaction between the polymer molecules.

soluble in organic solvents, especially in trichloroethylene and tetrahydrofuran, and easily form liquid crystals. Figure 2 shows droplets of liquid crystals formed by polymer Vc in trichloroethylene. Experiments using a gypsum wedge revealed that the droplets were negative liquid crystals,[4] suggesting that if the refractive index along the *c* axis (parallel to the main chain) of the polymer molecule is higher than along the axes perpendicular to the main chain, which seems most likely, the *c* axes, *i.e.*, molecular direction, of the polymer molecules lie consistently perpendicular to the radius of the spherical liquid-crystalline phase. The same orientation of polymer molecules were also observed in spherical liquid crystals formed by other metal-polyyne polymers, Ia, III and IV.

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