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DIRECT N.M.R. OBSERVATION OF LYOTROPIC LIQUID CRYSTALS FORMED BY TRANSITION METAL-POLY-YNE POLYMERS

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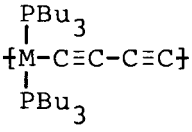
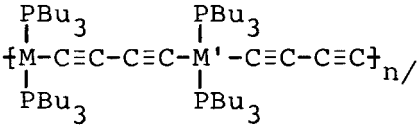
ABSTRACT: The lyotropic liquid crystals formed by metal-poly-yne polymers I and II have been directly detected by high resolution ^{31}P-n.m.r. method which has revealed that the main chain of the polymers aligns itself in the direction perpendicular to an applied magnetic field.

There have been some reports on high resolution n.m.r. studies of lyotropic liquid crystals formed by synthetic polymers such as poly-γ-benzyl-L-glutamate(PBLG).[1] However, most of them seem to be limited to the analysis of solvent signals observed in the liquid crystalline phases since the polymer signals are usually too broad and too intricate to be defined because of the very large intramolecular nuclear dipolar interactions. Therefore, behavior of the polymer molecules composing liquid crystals was unable to be investigated directly by a n.m.r. method without a special modification like labelling

polymers with deuterium.[2] Here we report a direct n.m.r. observation of polymer molecules composing a liquid crystal and their behavior towards magnetic fields.

Recently, we have shown that poly[*trans*-bis-(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl], Ia, and the analogues, IIa-c, provide the first examples of lyotropic liquid crystalline materials having transition metals.[3] They form liquid crystals





Ia: M=Pt (Pt-D^1)
Ib: M=Pd (Pd-D^1)

IIa: M=Pt, M'=Pd (Pt-D^1-Pd-D^1)
IIb: M=Pt, M'=Ni (Pt-D^1-Ni-D^1)
IIc: M=Pd, M'=Ni (Pd-D^1-Ni-D^1)

in solvents such as trichloroethylene, methylene chloride, THF and furan when the polymer concentration exceeds a certain limiting value depending on the molecular weight of the polymer. The $^{31}P\{^1H\}$-n.m.r. spectrum of a dilute solution (1 w/w%) of Pt-D^1 polymer ($\bar{M}w$=65000, n=100) in trichloroethylene exhibited a sharp signal at -4.34 p.p.m.[4] with attendant satellites due to coupling with ^{195}Pt(J_{Pt-P} = 2416 Hz). A concentrated solution (35 w/w%) of the same sample of Pt-D^1, which contained both isotropic and anisotropic (liquid crystals) phases, was placed in a spectrometer magnetic field (23.5 kilogauss) at 25°C. The high resolution $^{31}P\{^1H\}$-n.m.r. spectrum (S-1 in Figure) which was recorded after 30 min. without spinning showed a new broad signal at 17.2 p.p.m. and satellites($\Delta\nu_{Pt-P}$=2346 Hz) along with ordinary signals attributable to the polymer in an isotropic state. The former signal

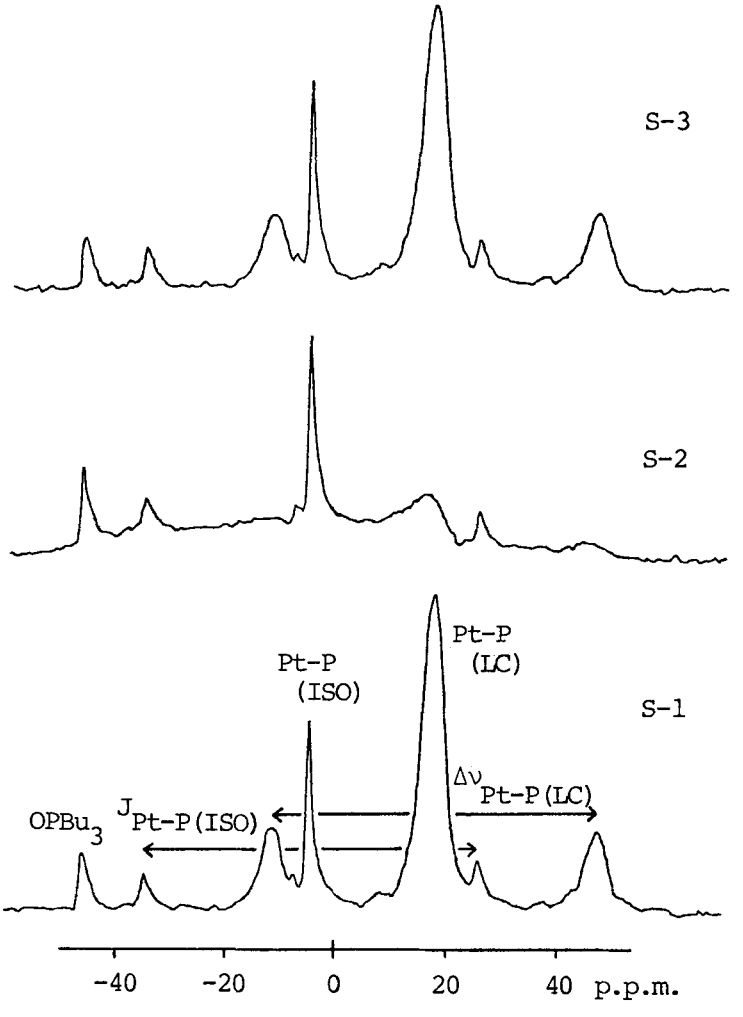


FIGURE. N.m.r. spectra of a concentrated solution of Pt-D[1] in trichloroethylene; recorded on a JEOL FX 100 spectrometer operating at 25°C with ^{1}H-decoupling mode.

could be assigned to the phosphorus on platinum in the polymer molecules composing liquid crystals because the peak intensity was proportional to the liquid crystal content and the signal was not observed in concentrated isotropic solutions (*e.g.*, 20 w/w%).

Similarly, polymers Pd-D^1, Pt-D^1-Pd-D^1 and Pt-D^1-Ni-D^1 showed characteristic resonances in a liquid crystalline state. The polymer in a liquid crystalline state always exhibits the phosphorus resonance at higher field than in an isotropic system with the magnitude of this shift being dependent on the kind of metal atoms; $\Delta\delta$(Pt)=21, $\Delta\delta$(Pd)=11, $\Delta\delta$(Ni)=7 p.p.m.

To investigate the behavior of the liquid crystals in a magnetic field, n.m.r. experiments with a sample tube rotation technique have been made. The sample tube, which showed spectrum S-1 in the Figure, was rotated through 90° about an axis perpendicular to the spectrometer magnetic field. Spectrum S-2 was recorded immediately after the rotation, where the signals due to the liquid crystals broadened and their intensities extremely decreased, whereas the signals based on the isotropic polymer as well as tributylphosphine oxide (internal reference) were almost unaffected. After several minutes the intensities of the former began to recover and the signals regained the initial intensity after *ca.* 30 min. The change in the spectra is reproducible.

Spectra recorded with spinning the sample tube were also analyzed. At the beginning of spinning around an axis perpendicular to the magnetic field, essentially the same spectrum as S-2 was recorded. Continuous spinning at the rate of *ca.* 7 Hz resulted

in a gradual increase in the signal intensities of the liquid crystals and showed spectrum S-3 after 30 min. Interestingly, the same spectrum was obtained immediately after stopping the spin and was no longer affected by rotating the sample tube through 90° about an axis perpendicular to the magnetic field. This behavior of the liquid crystals indicates that the director, *i.e.*, the main chain of the polymer, is oriented in the direction perpendicular to the applied magnetic field,[5] and may be interpreted in terms of the negative magnetic anisotropy of carbon-carbon triple bond.[6]

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