JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 1
1984

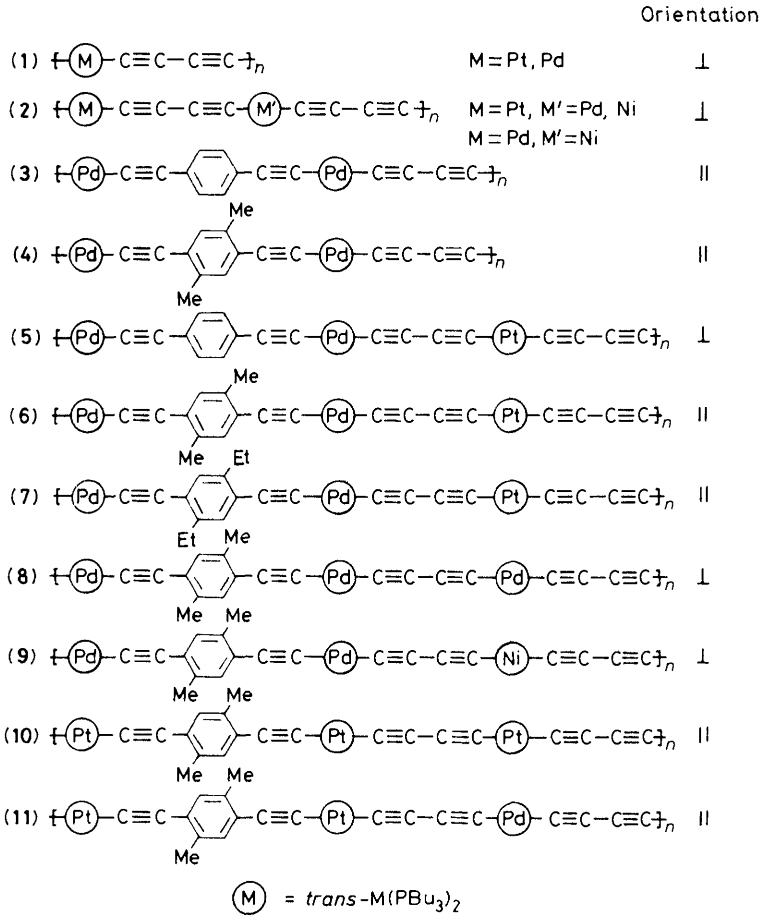
Liquid Crystals formed by Transition Metal–Poly(yne) Polymers: a Relation between Magnetic Anisotropy and Polymer Structure

Shigetoshi Takahashi,*[a] Yoshio Takai,[a] Hideko Morimoto,[a] and Kenkichi Sonogashira[b]

[a] *The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan*
[b] *Research Institute for Atomic Energy, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan*

High resolution ^{31}P n.m.r. studies of lyotropic liquid crystals formed by transition metal–poly(yne) polymers indicates that the magnetic anisotropy of the polymers may be systematically controlled by including different transition metal atoms in the polymer structure.

In recent years, organometallic polymers have attracted much attention particularly in terms of their physical and catalytic properties.[1] We previously reported that a new extended organometallic polymer (**1**) formed lyotropic liquid crystals which exhibited a response to magnetic and electric fields. An experiment using ^{31}P n.m.r. showed that polymer (**1**) aligned



Magnetic ordering of transition metal-poly(yne) polymers in an anisotropic phase. 'Orientation' refers to the direction of the main chain of polymers with respect to the magnetic field of the spectrometer.

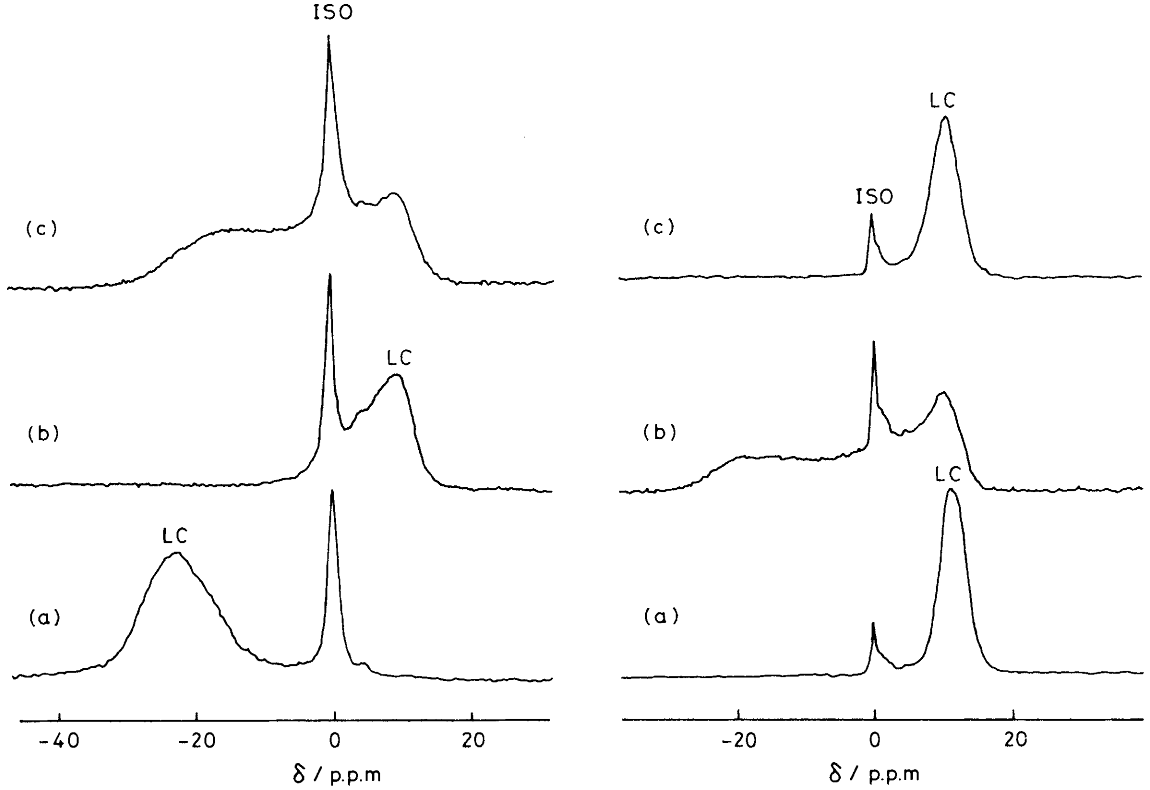


Figure 1. High resolution $^{31}P\{^1H\}$ n.m.r. spectra of concentrated trichloroethylene solutions of transition metal–poly(yne) polymers, (**4**) (left) and (**8**) (right); the symbols, ISO and LC, stand for resonances assigned to the phosphorus on palladium of the polymer molecules in an isotropic and an anisotropic (liquid crystals) phase, respectively.

its main chain in the direction perpendicular to the applied magnetic field.[2] Here we report a relation between the polymer structure and its orientation in a magnetic field.

New polymers (**3**)—(**11**) were synthesized by the method reported previously.[3] All the polymers (**1**)—(**11**) formed nematic liquid crystals in trichloroethylene. N.m.r. experiments[2] revealed that the liquid crystals of (**3**)—(**11**) aligned in a particular direction in the magnetic field of the spectrometer (23.5 kG; 1 G = 10^{-4} T) and the polymers may be divided into two groups on the basis of the preferred direction, *i.e.*, some align their main chain in the direction perpendicular to the applied field and the others parallel to it. Examples of high resolution ^{31}P n.m.r. spectra are shown in Figure 1, they were recorded (a) after a residence time of more than 30 min without spinning the sample tube, (b) immediately after rotating the sample tube through 90° about an axis perpendicular to the magnetic field of the spectrometer, and (c) with continuous spinning of the tube (at *ca.* 7 Hz).

The very broad signals in the spectra, (**4**)-(c) and (**8**)-(b), which are 2D powder patterns, indicate no regularity in molecular orientation, whereas the peaks designated by the symbol 'LC' reveal a single orientation with respect to the magnetic field.[4a] The change in the spectra depending on the experimental conditions indicates that the director, *i.e.*, the main chain of polymer (**4**) is oriented in the direction parallel to the applied field, while polymer (**8**) aligns in the direction perpendicular to it.[2,4] This assignment has been confirmed by analysis of the ^{31}P n.m.r. spectra recorded on a super-conducting magnet (Bruker WM-360) spectrometer whose spinning axis is parallel to the magnetic field.

In a magnetic field every system aligns itself with the axis of its greatest susceptibility in the direction of the field. The polymers that align at right-angles to the applied field, therefore, have a negative 'diamagnetic anisotropy' ($\Delta_\chi = \Delta_{\chi\|} - \Delta_{\chi\perp} < 0$), whereas those that align parallel to the field have a positive anisotropy ($\Delta_\chi > 0$).† The magnetic anisotropy of the polymers is essentially dependent on the structure, especially on the ratio of carbon–carbon triple bonds to benzene rings in the repeat unit. The magnetic anisotropy of polymers (**1**)—(**4**) may be tentatively interpreted by considering the individual magnetic anisotropy (Δ_χ in erg G^{-2} mol^{-1})‡ of acetylene and benzene, *i.e.*, acetylene has a negative diamagnetic anisotropy of -7×10^{-6}, while benzene has positive anisotropy of $+60 \times 10^{-6}$.[5]

When comparing (**6**) with (**5**), the parallel orientation of the latter polymer can be understood on the basis of Δ_χ ($+68 \times 10^{-6}$ erg G^{-2} mol^{-1}) of *p*-xylene which is a little larger than that of benzene. Comparison of (**6**) with (**8**) or (**9**), and of (**8**) with (**11**), which have the same bridging unit, reveals that the nature of the transition metal atoms in the polymers effectively determines their magnetic properties. This is of particular interest because the magnetic properties observed for different transiton metal–polymer structures reflect the magnetic environment in the vicinity of the metal

---

† The symbols, $\chi_\|$ and $\chi_\perp$, are the diamagnetic susceptibilities parallel and perpendicular to the preferred direction of the long axis of the liquid crystalline molecule.

‡ 1 erg = 10^{-7} J.

atom and depend on the nature of the bonding between the metal atom and the carbon atom of the acetylenic unit.

The authors are grateful to Professor Y. Kyogoku for the Bruker WM-360 n.m.r. spectra.

Received, 19th July 1983; Com. 966

References

1 See, for example, C. E. Carraher, Jr., J. E. Sheats, and C. U. Pittman, Jr., 'Organometallic Polymers,' Academic Press, New York, 1978; N. Hagihara, K. Sonogashira, and S. Takahashi, *Adv. Polym. Sci.*, 1980, **41**, 149.

2 S. Takahashi, Y. Takai, H. Morimoto, K. Sonogashira, and N. Hagihara, *Mol. Cryst. Liq. Cryst.*, 1982, **82**, 139.

3 S. Takahashi, H. Morimoto, E. Murata, S. Kataoka, K. Sonogashira, and N. Hagihara, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 565.

4 (a) S. Sobajima, *J. Phys. Soc. Jpn.*, 1967, **23**, 1070; M. Panar and W. D. Phillips, *J. Am. Chem. Soc.*, 1968, **90**, 3880; E. T. Samulski and A. V. Tobolsky, *Mol. Cryst. Liq. Cryst.*, 1969, **7**, 433; R. D. Orwell and R. L. Vold, *J. Am. Chem. Soc.*, 1971, **93**; 5335; (b) L. Pohl and R. Eidenschink, *Anal. Chem.*, 1978, **50**, 1934; B. J. Forrest and L. W. Reeves, *Chem. Rev.*, 1981, **81**, 1.

5 B. R. Appleman and B. P. Dailey, 'Advances in Magnetic Resonance,' ed. J. S. Waugh, Academic Press, New York, 1974, vol. 7, p. 231.