

INFLUENCE OF BACKBONE RIGIDITY ON THE LIQUID CRYSTALLINITY OF MESOGEN-CONTAINING POLYACETYLENES*

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Abstract Two acetylene polymers containing cyanobiphenyl-based mesogens, poly{10-[[((4'-cyano-4-biphenyl)oxy)carbonyl]-1-decyne]} (PA8CN), which has a relatively flexible polyalkyne backbone, and poly {[4-(((12-((4'-cyano-4-biphenyl)oxy)dodecyl)oxy)carbonyl) phenyl)-acetylene} (PB12CN), which has a fairly rigid poly(phenylacetylene) backbone, were synthesized using respectively WCl_6 and $[Rh(nbd)Cl]_2$ as the catalysts. PA8CN exhibits enantiotropic interdigitated smectic A phase (S_{Ad}) over a temperature range as wide as ca. 100°C, whereas PB12CN is non-mesomorphic, demonstrating that the backbone rigidity plays an important role in determining the liquid crystallinity of the polyacetylenes.

Keywords Polyacetylene; Polyalkynes; Poly(phenylacetylene); Substituted polyacetylenes; Liquid crystalline polymers

INTRODUCTION

Polyacetylene has attracted much interest since Shirakawa and co-workers reported a facile synthetic route to the free-standing polyacetylene films^[1,2]. The earlier work in this area was focused on increasing the polymer's electrical conductivity. More recently, a wide range of other potential applications for polyacetylene, its derivatives, and other conjugated polymers have been proposed. Examples include nonlinear optical waveguides^[3], permselective and enantioseparation membranes^[4,5], and optical display systems^[6]. Attachment of mesogenic side chains to the conjugated polyacetylene backbones is of interest because the resulting polymers may

* This work was in part supported by the Hong Kong RGC grants HKUST597/95P and HKUST6149/97P.

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Received October 3, 1997

possess unique electrical and optical properties. For example, the polymers may be both liquid crystalline and electrically conductive, and furthermore, the electrical conductivity may be tuned in the liquid crystalline state under electric and magnetic fields^[6].

Understanding the influence of the backbone rigidity on the mesomorphic behavior is of fundamental importance in designing polyacetylene-based liquid crystals. In this work, we attached cyanobiphenyl-based mesogens to a fairly rigid poly(phenylacetylene) backbone and a relatively flexible polyalkyne backbone, and examined the role of the backbone rigidity in affecting the liquid crystallinity of the resulting polymers.

EXPERIMENTAL

The monomer synthesis and polymerization reactions were carried out according to the procedures published in the previous papers^[7,8]. ¹H-NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer using chloroform-*d* as the solvent. Molecular weights of the polymers were estimated by a GPC system consisted of a Waters 510 HPLC pump, a Waters 486 wavelength-tunable UV/vis detector, and a Waters 410 differential refractometer. A set of monodisperse polystyrene standards was used for calibration purpose. Differential scanning calorimetry (DSC) thermograms of the polymers were recorded on a Setaram DSC 92 under nitrogen at a scanning rate of 10°C/min. An Olympus BX 60 polarizing optical microscope (POM) equipped with a Linkam TMS 92 hot stage was used for the visual observation of thermal behavior of the polymers. X-ray diffraction patterns of the polymer sample was recorded on a Philips PW 1830 powder X-ray diffractometer with a graphite-mono-chromatized Cu K_{α} radiation ($\lambda = 0.154056$ nm). The sample was prepared by melting the polymer powder on a single-crystal silicon wafer, cooling down to its liquid crystal state, and then quenched by liquid nitrogen.

RESULTS AND DISCUSSION

Polymerization behavior

The spacer length in the side-chain liquid crystalline polymers plays an important role in affecting the polymers' liquid crystalline properties. We synthesized two acetylene monomers with long methylene units (Chart 1), in the hope that the flexible spacers may decouple the motion of the polymer backbone from the ordering of the mesogenic groups when the monomers are polymerized.

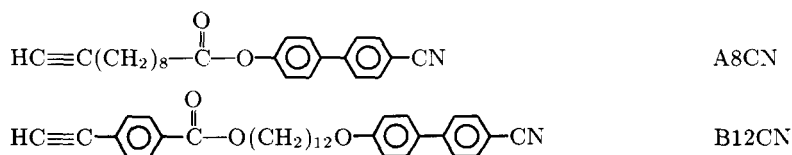


Chart 1

WCl_6 is an effective catalyst for the polymerizations of many acetylene derivatives in toluene and dioxane^[9]. We attempted to polymerize A8CN with WCl_6 in toluene, but no polymer is isolated after stirring the reaction mixture for 24 h (Table 1, no. 1). Changing the solvent to dioxane, a yellowish polymer with an M_w of 23400 is obtained in 56.3% yield (Table 1, no. 2). When Ph_4Sn is used as the cocatalyst, the yield decreases, but the M_w increases to 36100. Increasing the temperature to 80°C leads to high polymer yield and M_w . Thus obviously the polar solvent dioxane is superior to the nonpolar solvent toluene in polymerizing A8CN.

Table 1 Polymreization behavior of A8CN and B12CN^{a)}

No.	Catalyst	Solvent	Yield (%)	$M_w^b)$	$M_w/M_n^b)$
A8CN					
1	WCl_6	toluene	0		
2	WCl_6	dioxane	56.3	23400	1.8
3	$\text{WCl}_6\text{-Ph}_4\text{Sn}$	dioxane	22.0	36100	2.2
4 ^{c)}	$\text{WCl}_6\text{-Ph}_4\text{Sn}$	dioxane	46.8	40500	1.8
B12CN					
5	$\text{WCl}_6\text{-Ph}_4\text{Sn}$	dioxane	0		
6	$[\text{Rh}(\text{nbd})\text{Cl}]_2$	THF/ $\text{Et}_3\text{N}^d)$	59.0 ^{e)}	20300 ^{f)}	4.1 ^{f)}
7	$[\text{Rh}(\text{nbd})\text{Cl}]_2$	DMF	70.0	158000	4.0

a) Polymerized under nitrogen at room temperature for 24 h. $[M]_0 = 0.2 \text{ M}$; for the W catalyst systems, $[\text{cat.}] = [\text{cocat.}] = 20 \text{ mM}$; for the Rh catalyst system, $[\text{cat.}] = 10 \text{ mM}$. b) Determined by GPC in THF on the basis of a polystyrene calibration. c) Polymerized at 80°C. d) Volume ratio of THF to Et_3N : 4:1. e) Partially soluble in THF. f) For the THF-soluble fraction

$\text{WCl}_6\text{-Ph}_4\text{Sn}$ in dioxane, however, fails to polymerize B12CN (Table 1, no. 5), possibly due to the steric effect of the benzene ring directly linked to the acetylene triple bond. $[\text{Rh}(\text{nbd})\text{Cl}]_2$ is known to polymerize phenylacetylene derivatives to stereoregular polymers^[10]. We thus tried to polymerize B12CN using $[\text{Rh}(\text{nbd})\text{Cl}]_2$ in THF/ Et_3N (v/v=4:1). A yellowish polymer is obtained, but the polymer is only partially soluble in THF (Table 1, no. 6). We changed the solvent to DMF, a

completely soluble polymer with an M_w of 158000 is obtained in a high yield (70%).

Structure characterization

Fig. 1A shows the ^1H -NMR spectrum of PA8CN. All the aliphatic and aromatic protons exhibit absorption peaks in the reasonable spectral region, with no unexpected signals being observed. The absorption peak of the *cis* olefin proton of PA8CN appears at around δ 5.9, while the *trans* absorption peak overlaps with those of the aromatic protons. The intensity of the *cis* peak is noticeably weak, suggesting that the majority of the olefin protons are in the *trans* environment or that the polymer is stereochemically *trans*-rich.

The poly(phenylacetylenes) produced by the $[\text{Rh}(\text{nbd})\text{Cl}]_2$ catalyst often possess high stereoregularity. The ^1H -NMR spectrum of PB12CN is shown in Fig. 1B. The spectra peaks are noticeably sharp, indicative of the high stereoregularity of the polymer.

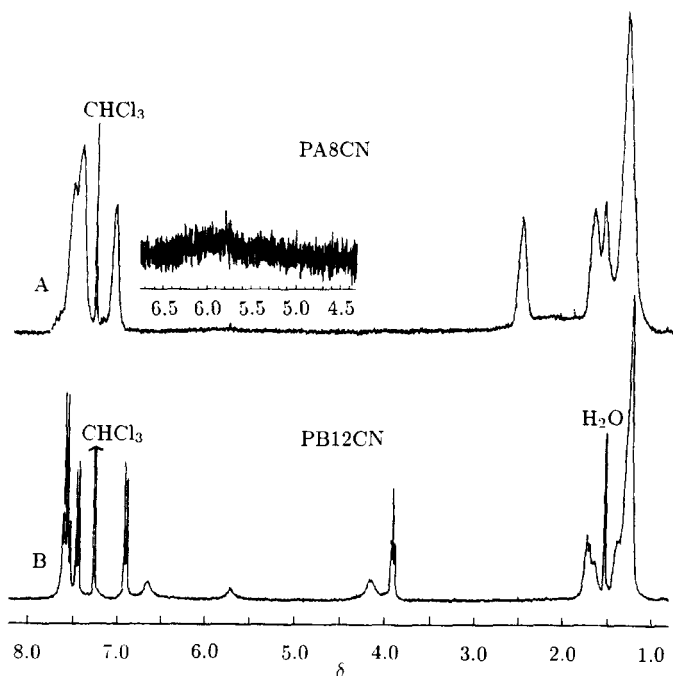


Fig. 1 ^1H -NMR spectra of PA8CN (A) and PB12CN (B) in chloroform- d

Mesomorphic properties

Fig. 2A shows DSC thermograms of PA8CN. Two peaks appear at 85.6 and 192.5°C during the second heating scan, which correspond to the melting and clearing transitions, respectively. The transition peaks recorded during the first cooling

scan slightly shift to the lower temperatures. Thus the phase transitions are enantiotropic.

Fig. 2B shows DSC curves of PB12CN. The first cooling scan detects a sharp exothermic peak centered at 123.0°C, while the second heating scan records an endothermic peak of similar size at 131.1°C. To check the origin of the DSC peak, we conducted POM measurements of the polymer sample. When PB12CN is heated in the POM hot stage, the solid powders completely melt at 138.5°C. When the sample is cooled down, the liquid starts to solidify at 133.0°C. The POM observation thus confirms that the DSC peaks correspond to the melting/crystallization transitions of PB12CN. No liquid crystalline state is detected by either POM or DSC analysis.

POM also was used to identify the mesophases associated with the observed liquid crystalline transitions of PA8CN. Upon cooling PA8CN from the clear point to 191°C, a bâtonnet texture is observed (Fig. 3A), which has been well documented as the evidence for a smectic A phase. Further cooling PA8CN to 185°C, a focal-conical texture appears (Fig. 3B), confirming that PA8CN forms S_A phase.

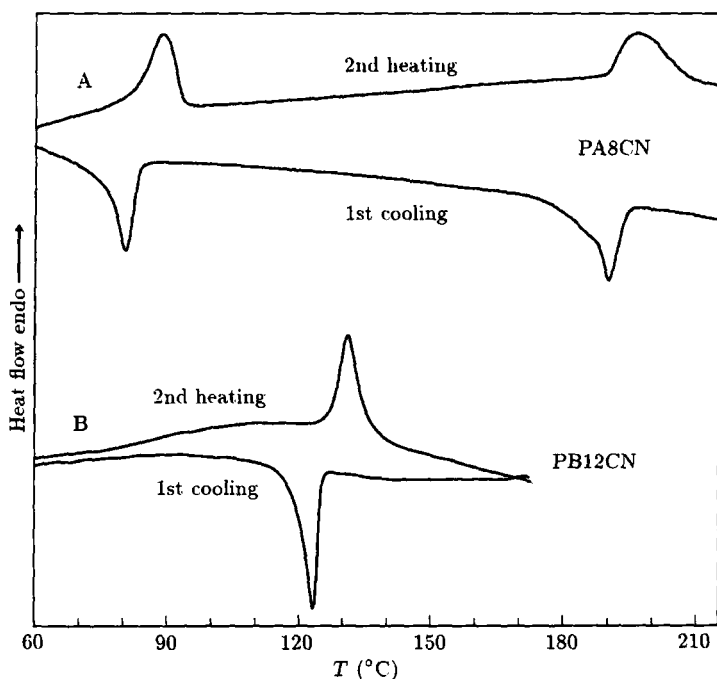


Fig. 2 DSC thermograms of PA8CN (A; sample from Table 1, no. 3) and PB12CN (B; sample from Table 1, no. 7) measured under nitrogen at a scanning rate of 10°C/min

The remarkable difference in the liquid crystallinity of PA8CN and PB12CN may be due to the difference in their backbone rigidity^[11]. The backbone of PB12CN is so rigid that even a spacer consisting of as long as 12 methylene units can not

eliminate its perturbation to the ordering of the mesogenic groups. On the other hand, the relatively flexible PA8CN backbone allows the alignment of the mesogenic groups, giving rise to a well-ordered liquid crystalline phase.

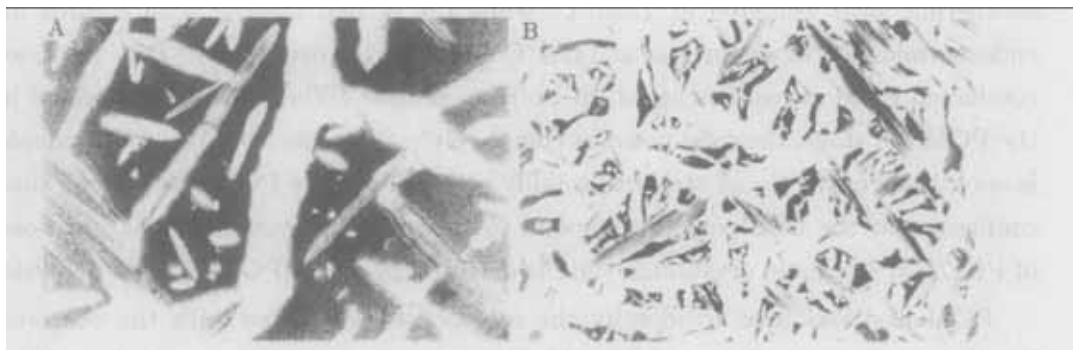


Fig. 3 Polarizing optical micrographs of PA8CN (A) bâtonnets texture at 191°C ($\times 250$) and (B) focal-conical texture at 185°C ($\times 100$)

We carried out X-ray diffraction experiments in order to gain further information on the molecular packing arrangements of PA8CN within the mesomorphic phases. The polymer sample was placed on a single-crystal silicon wafer, which was heated to the isotropic state, cooled down and annealed at the liquid crystalline state for 5 min, and then quickly quenched by liquid nitrogen to freeze the molecular alignments. The X-ray diagram of the polymer shows not only a broad diffuse peak in the high-angle region, but also Bragg reflections at the middle and low angles (Fig. 4). The broad hump peak at $2\theta = 20.7^\circ$ ($d = 0.42$ nm) corresponds to the average lateral distance between the molecules in the two-dimension liquid-like intermolecular organization layers. The sharp reflection at $2\theta = 2.7^\circ$ corresponds to a layer spacing occurring in the lateral packing of $d = 3.33$ nm, which is considerably in excess of the molecular length of the repeat unit of the polymer in its most extended conformation ($l = 2.40$ nm). The mesophase of the polymer thus may consist of such a bilayer structure as schematically shown in Chart 2, in which the mesogens arrange in an antiparallel overlapping interdigitated manner, giving a d/l ratio of 1.4, a value often found in the S_{Ad} mesophases of the liquid crystalline molecules containing cyano terminal groups^[12]. The crystal structure of A8CN (monomer) determined by the single crystal X-ray diffraction shows that the cyanobiphenyl groups are partially interdigitated, stabilizing by the electronic interaction between the cyano and the ester groups. From the diffraction at $2\theta = 6.4^\circ$, a d -spacing of 1.38 nm is derived. The calculated length for the interdigitated cyanobiphenyloxycarbonyl groups (or the part between the two carbonyl groups in two adjacent mesogens) in the proposed

bilayer structure of PA8CN is 1.33 nm. The reflection peak at $2\theta = 6.4^\circ$ thus may be related to the regions in which the polarized rigid cyanobiphenyloxycarbonyl groups are interdigitated and well packed, whereas the order of the flexible octyl spacers is perturbed by the aliphatic chain random motion.

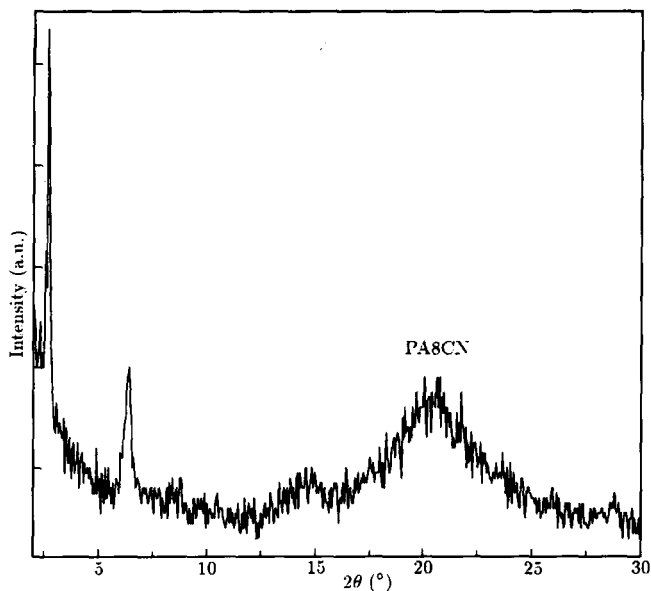
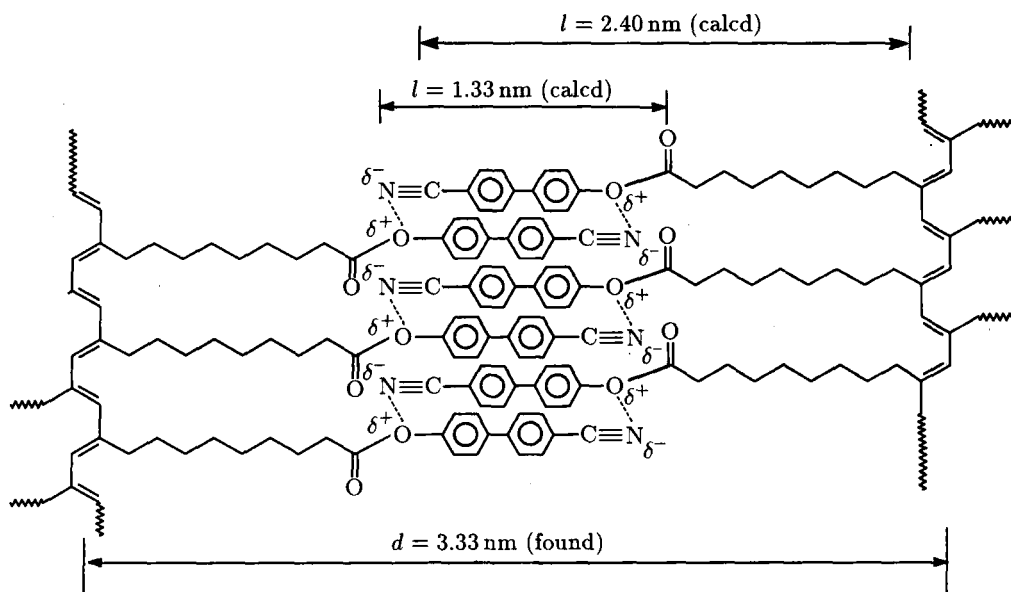


Fig. 4 X-ray diffraction pattern of PA8CN (quenched from its liquid crystalline state by liquid nitrogen)



CONCLUSION

We have synthesized two acetylene monomers, A8CN and B12CN, which are respectively polymerized by WCl_6 and $[\text{Rh}(\text{nbd})\text{Cl}]_2$. The PA8CN with a relatively flexible backbone exhibits a smectic A phase in a wide temperature range, whereas the PB12CN with a relatively rigid backbone shows no mesomorphic properties. Thus the attachment of the mesogenic units to the rigid poly(phenylacetylene) backbone should be avoided. Grubbs and coworkers^[13] have recently investigated the effect of the backbone rigidity on the liquid crystalline properties of polynorbornenes and polybutadienes synthesized by ring-opening metathesis polymerizations. Our work, however, is the first example in studying such effects in the polyacetylene systems, and the insight we gained here may guide the further efforts in the molecular design of new liquid crystalline polyacetylenes.

REFERENCES

- [1] Itoh, T., Shirakawa, H., Ikeda, S., *J. Polym. Sci., Polym. Chem. Ed.*, **1974**, *12*, 11
- [2] Shirakawa, H., Louis, E.J., MacDiamid, A.G., Chiang, C.K., Heeger, A.J., *J. Chem. Soc., Chem. Comm.*, **1977**, 578
- [3] Le Moigne, J., Hilberer, A., Strazielle, C., *Macromolecules*, **1992**, *25*, 6705
- [4] Masuda, T., Higashimura, T., *Adv. Polym. Sci.*, **1987**, *81*, 121
- [5] Aoki, T., Shinohara, T., Oikawa, E., *Makromol. Chem. Rapid Commun.*, **1992**, *13*, 565
- [6] Yoshina, K., Yin, X.H., Mourita, S., Nakazono, M., Kawai, T., Ozaki, M., Jin, S.H., Choi, S.K., *Jpn. J. Appl. Phys.*, **1993**, *32*, L1673
- [7] Tang, B.Z., Kong, X., Wan, X., Feng, X.D., *Macromolecules*, **1997**, *30*, 5620
- [8] Tang, B.Z., Kong, X., Wan, X., Feng, X.D., Kwok, H.S., *Macromolecules*, submitted
- [9] Masuda, T., Higashimura, T., *Acc. Chem. Res.*, **1984**, *17*, 51
- [10] Tang, B.Z., Poon, W.H., Leung, S.M., Leung, W.H., Peng, H., *Macromolecules*, **1997**, *30*, 2209
- [11] Masuda, T., Tang, B.Z., Tanaka, A., Higashimura, T., *Macromolecules*, **1986**, *19*, 1459
- [12] Le Barny, P., Dubois, J.C., Friedrich, C., Noel, C., *Polym. Bull.*, **1986**, *15*, 341
- [13] Maughon, B.R., Weck, M., Mohr, B., Grubbs, R.H., *Macromolecules*, **1997**, *30*, 257