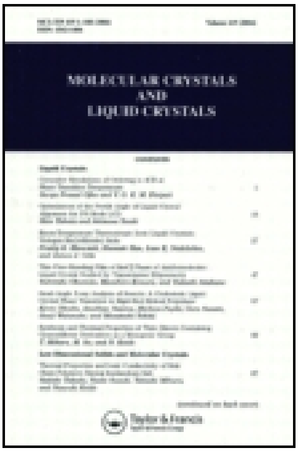

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Unique Liquid Crystalline Behavior of Conducting Polyacetylene Derivatives

Katsumi Yoshino [a] , Kentaro Kobayashi [a] , Katsunori Myojin [a] , Tsuyoshi Kawai [a] , Hiroshi Moritake [a] , Masanori Ozaki [a] , Kazuo Akagi [b] , Hiromasa Goto [b] & Hideki Shirakawa [b]

[a] Department of Electronic Engineering, Faculty of Engineering, Osaka University 2-1 Yamada-Oka, Suita, Osaka, 565, Japan

[b] Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, 305, Japan

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UNIQUE LIQUID CRYSTALLINE BEHAVIOR OF CONDUCTING POLYACETYLENE DERIVATIVES

KATSUMI YOSHINO, KENTARO KOBAYASHI, KATSUNORI MYOJIN,
TSUYOSHI KAWAI, HIROSHI MORITAKE AND MASANORI OZAKI
Department of Electronic Engineering, Faculty of Engineering, Osaka University
2-1 Yamada-Oka, Suita, Osaka 565, Japan

KAZUO AKAGI, HIROMASA GOTO AND HIDEKI SHIRAKAWA
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Abstract Unique liquid crystalline behaviors have been observed in polyacetylene derivatives substituted with long side chains containing mesogen unit such as poly [5- (*p*- (*trans* -4'- *n*- octylcyclohexyl) phenoxy) -1- pentyne] (PPCH803A) with phenylcyclohexyl mesogenic moiety. Texture typical to smectic liquid crystal has been confirmed by optical microscopic observation. Smectic structure has also been confirmed by X-ray diffraction. Anisotropy of optical absorption spectrum consistent with X-ray diffraction has been observed, from which the band gap of PPCH803A has also been evaluated to be 2.7 eV. Dielectric constant of PPCH803A in the smectic phase (90-150° C) is about 2.8 and changes at phase transition temperature in step wise.

The mixture of PPCH803A with ferroelectric liquid crystal of low molecular weight exhibits large dielectric constant and unique ferroelectric behavior in the temperature range of the smectic phase of PPCH803A.

INTRODUCTION

Recently, polymeric liquid crystals with flexible main chains and side chains containing mesogen units have been extensively studied. However, only few papers have been reported on the synthesis and characterization of polymeric liquid crystals with rigid main chains have been reported.[1,2] On the other hand, conducting polymers with conjugated main chains which are rigid have attracted much attention from both fundamental scientific and practical points of view, because various novel physical behaviors have been observed and also various unique fundamental applications have been proposed.[3-7] Here, in this paper, unique electrical and optical properties in liquid crystalline phase of polyacetylene derivatives substituted with long side chains containing mesogen unit poly[5-(*p*-(*trans*-4'-*n*-octylcyclohexyl)phenoxy)-1-pentyne] (PPCH803A)[8] whose molecular structure is shown in Figure 1 are discussed. Ferroelectric behavior in the mixture of PPCH803A and (R)-4'-(1-methoxycarbonyl-1-ethoxy)phenyl 4-[4-(*n*-octyloxy)phenyl]benzoate (1MC1EPOPB)[9] whose molecular structure is also indicated in Figure 1, is also discussed.

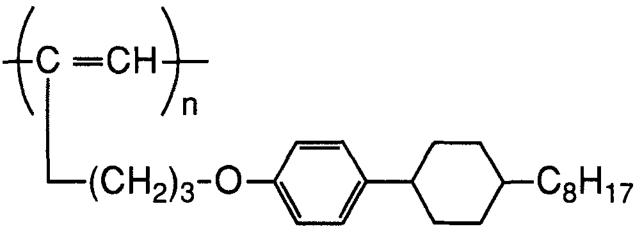

FIGURE 1 Molecular structures of PPCH803A and 1MC1EPOPB.

EXPERIMENTAL

PPCH803A synthesized by the method already reported from monosubstituted acetylene monomer 1-[*p*-(*trans*-4'-*n*-octylcyclohexyl)phenoxy]-1-pentyne utilizing Ziegler-Natta catalysts[8] and 1MC1EPOPB also synthesized and purified by the method already reported[9] were used in this study.

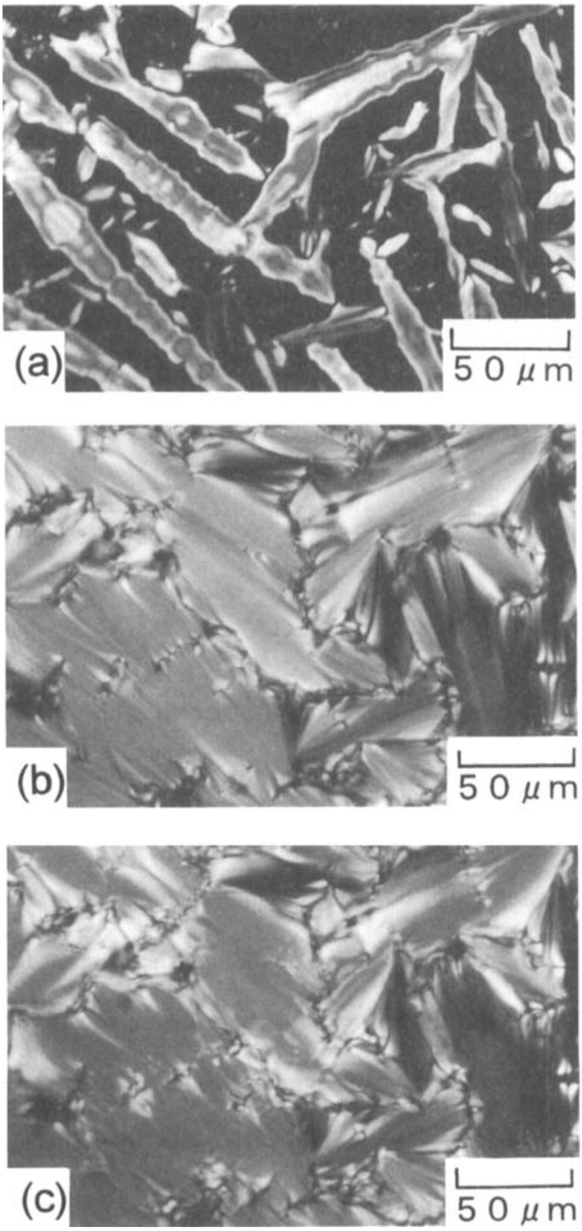

FIGURE 2. Polarized optical microphotographs of PPCH803A at (a)150°C, (b)100°C and (c)50°C. See Color Plate XV.

This sample was sandwiched between In-Sn oxide (ITO) coated glass plates with appropriate polyethyleneterephthalate (PET) spacers. Texture of the sample was observed utilizing polarized optical microscope (Nikon, OPTIPHOT2-POL). Absorption spectrum was measured utilizing microscopic spectrometer system (Otsuka Electronics, IMUC7000G; Nikon,OPTIPHOT2). X-ray diffraction measurements were carried out utilizing the RINT 1100 system with X-rays of 1.54Å in wavelength. The dielectric constant and spontaneous polarization were measured with an impedance analyzer (YHP, 4192A) and by a triangular shaped voltage method, respectively. Transmission of AlGaAs semiconductor laser light (780nm) through the sample was also studied.

RESULTS AND DISCUSSION

Figure 2 (a), (b) and (c) show the photographs observed with the polarized optical microscope at 150°C, 100°C and 50°C, respectively. As is evident from Figure 2(a), with decreasing temperature of PPCH803A from the isotropic phase, rod like structures which is compound of assembly of liquid crystal molecules start to appear at the phase transition temperature from the isotropic phase to the smectic phases at 151°C. As also shown in Figure 2(b), at 100°C, the broken fan-shaped texture was observed, which is the typical texture observed in homogeneously aligned smectic-A phase. It should also be noted in Figure 2(c) that, even in the solid state below the transition temperature from the smectic-A phase to the solid state, still similar texture was maintained, which may originate in the rigid structure of the polymer. In this polarized microscope observation, color also changed remarkably with decreasing temperature due to the change in retardation *Δnd*. For constant cell thickness *d*, the change in retardation should reflect the change in the birefringence *Δn*, which may be originated in the change in the effective conjugation length of conjugated polymer main chain but not simply in the change in the conformation of side chain mesogen units. Even in conducting polymer such as poly(3-alkylthiophene), the change in effective conjugation length is known to be induced associating with the change in the conformation of side chains.[10]

Figure 3 shows the temperature dependence of transmission intensity of semiconductor laser light (780nm) through PPCH803A. As is evident from this figure, the transmission intensity changes drastically at the phase transition temperatures, originating from the change in light scattering in different phases.

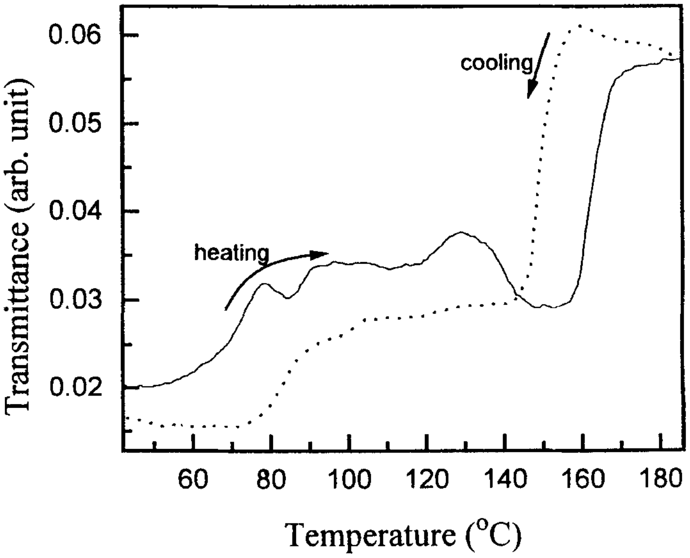

FIGURE 3. Temperature dependence of transmission intensity of laser light (780nm) through the homogeneously aligned PPCH803A.

Figure 4 shows the absorption spectrum of PPCH803A for polarized lights both parallel and perpendicular to the director of liquid crystal in the aligned domain. In the polymeric liquid crystal with mesogen unit in the side chains, the director of the liquid crystal is perpendicular to the polymer main chain in the smectic-A phase. Therefore, observed absorption seems to be originated in the conjugated main chain. The band gap was evaluated from Figure 5 to be 2.7 eV, which is much larger than the band gaps of non-substituted trans- and cis-polyacetylene of 2.0 and 1.5 eV, respectively.[11] This suggests that the polymer main chain is twisted due to the steric hindrance effect induced by the large substituted molecules in the side chain. It is reasonable that absorption for the light polarized parallel to the director, therefore perpendicular to the polymer main chain, is much suppressed.

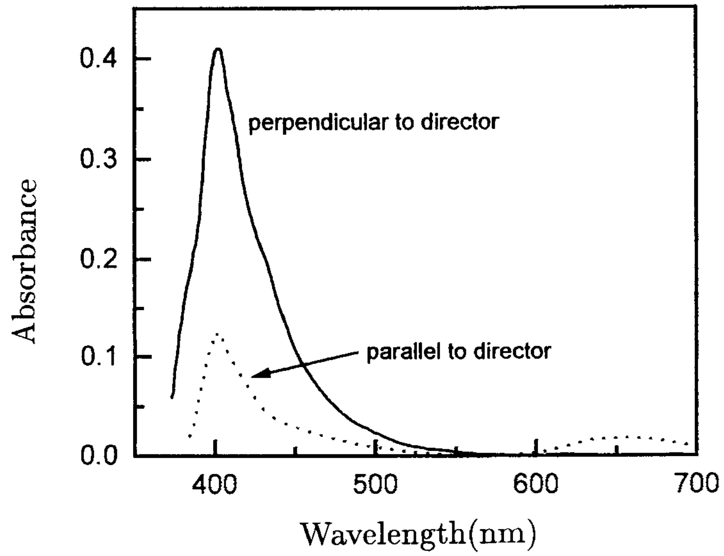

FIGURE 4. Absorption spectrum of PPCH803A in aligned domain for polarized light parallel and perpendicular to the director of liquid crystal.

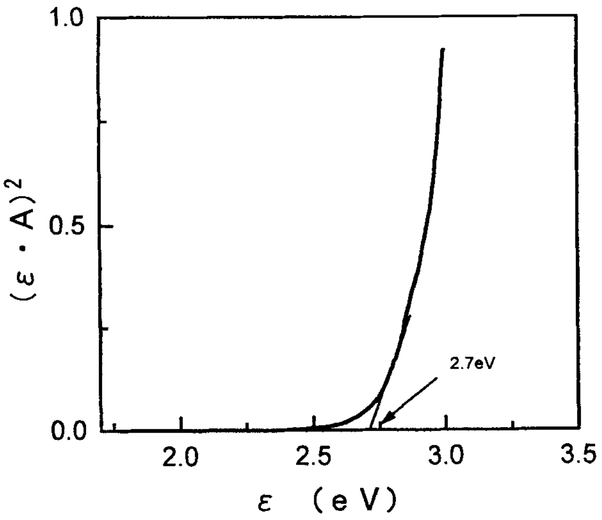

FIGURE 5. Absorption of PPCH803A as a function of photon energy for the evaluation of band gap.

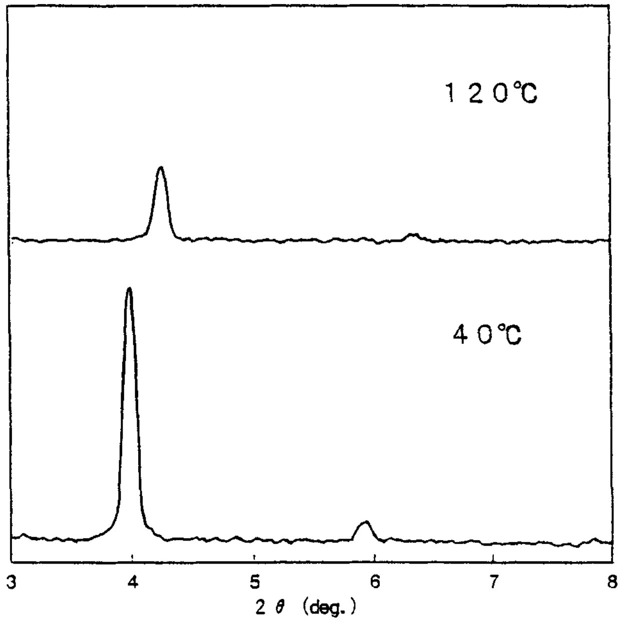

FIGURE 6. X-ray diffraction profiles of PPCH803A at (a) smectic-A phase (120°C) and (b) crystalline phase (40°C).

Clear X-ray diffraction peak was observed as shown in Figure 6 in the smectic-A and solid phases. The layer spacing of about 20Å in the smectic-A phase slightly increases with decreasing temperature. This may be due to the change in conformation of side chains with temperature. That is, at higher temperature, side chain becomes slightly shorter because of trans-gauche conformation change. This layer spacing of about 20Å is comparable to the length of side chain molecules, which suggests either inter-digitating structure or the structure with the side chains on the same side of the main chain.

It should be also noted that, even in the solid state, still layer structure with a little layer spacing is maintained. This coincides with the fact that the broken fan-shaped texture which is characteristic of the smectic phase was observed in the solid phase as shown in Figure 2(c).

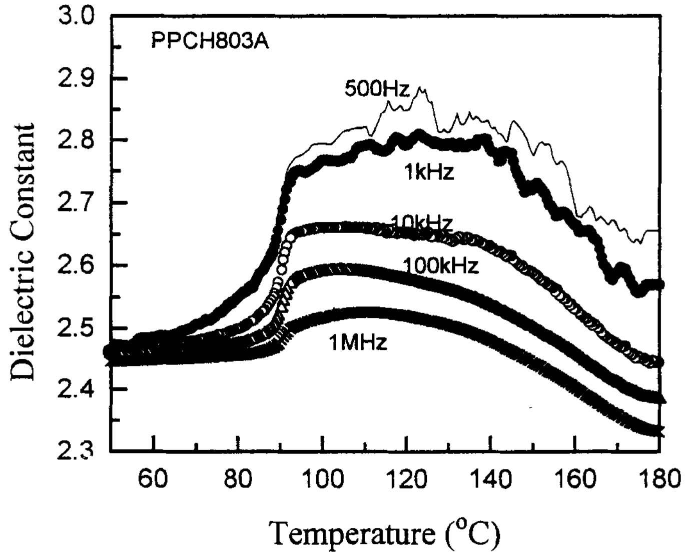

FIGURE 7. Temperature dependence of dielectric constant of PPCH803A at various frequencies.

Figure 7 shows temperature dependence of dielectric constant in PPCH803A of homogeneous alignment at various frequencies. With decreasing temperature, dielectric constant increases in stepwise at the phase transition from the isotropic phase to smectic-A phase. It again decreases at the phase transition from the smectic-A phase to the solid phase. This result suggests that the anisotropy of dielectric constant in this material is negative, suggesting the important contribution of dipole moment originated from oxygen neighboring to the benzene core.

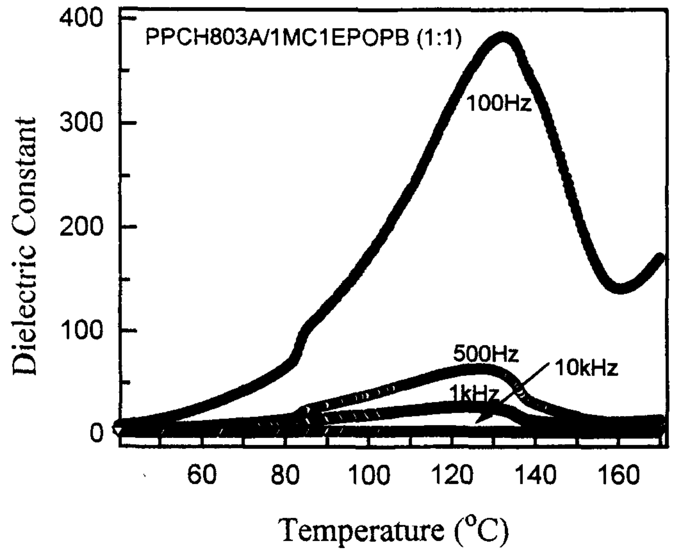

FIGURE 8. Temperature dependence of dielectric constant of PPCH803A-1MC1EPOPB mixture (1:1) at various frequencies.

We have also studied dielectric properties of PPCH803A mixed with chiral smectic liquid crystal, 1MC1EPOPB. As shown in Figure 8, dielectric constant in the (1:1) mixture of PPCH803A and 1MC1EPOPB is extremely larger in the temperature range in which PPCH803A exhibits the smectic-A phase. 1MC1EPOPB is ferroelectric liquid crystal with large spontaneous polarization (170nC/cm^2) and, therefore, shows large dielectric constant in the chiral smectic-C phase (83 -103 °C) as shown in Figure 9.

This result suggests that the ferroelectricity was induced in the temperature range of the smectic phase of host polymer PPCH803A upon the introduction of 1MC1EPOPB with narrower temperature range of ferroelectricity. Detailed characteristics of the mixtures of PPCH803A and 1MC1EPOPB of various concentration and their mechanism are under study.

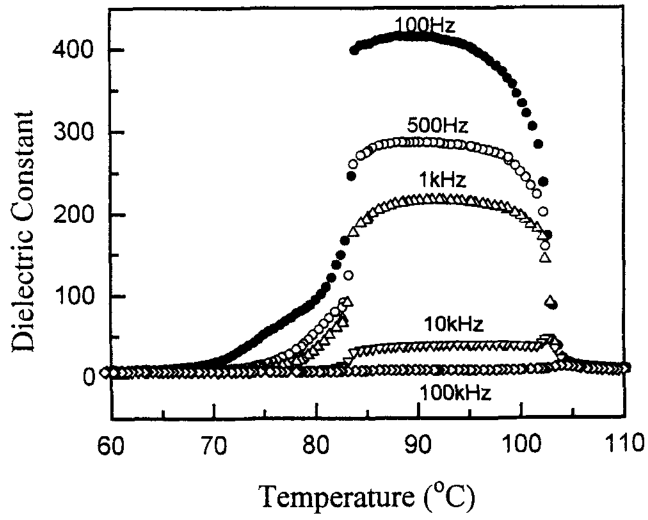

FIGURE 9. Temperature dependence of dielectric constant of ferroelectric liquid crystal, 1MC1EPOPB, at various frequencies.

CONCLUSIONS

In polyacetylene derivatives substituted with long side chains containing mesogen unit with phenylcyclohexyl mesogenic moiety, unique optical and electrical properties in liquid crystalline phase were observed. This polymeric liquid crystal showed typical microscopic texture observed in the smectic-A phase and sharp X-ray diffraction peak due to the smectic layer structure. Anisotropy of optical absorption spectrum originated from the smectic layer structure was observed. The temperature dependence of dielectric constant in PPCH803A reflected the characteristics of phase transition and changes at phase transition temperature in step wise. The mixture of PPCH803A with ferroelectric liquid crystal of low molecular weight exhibited large dielectric constant in the temperature range of the smectic phase of PPCH803A.

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