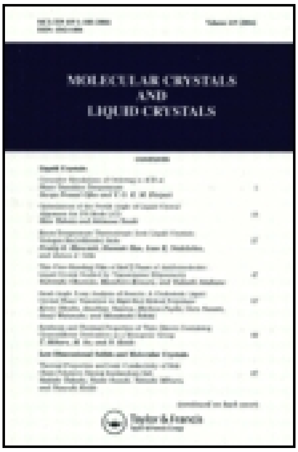

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Novel Characteristics of Poly(1,6-Heptadiyne) Derivatives with Long Side Chains in Liquid Crystalline Phase

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NOVEL CHARACTERISTICS OF POLY(1,6-HEPTADIYNE) DERIVATIVES WITH LONG SIDE CHAINS IN LIQUID CRYSTALLINE PHASE

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Abstract Poly(1,6-heptadiyne) derivatives substituted with long side chains containing mesogen units such as poly(bis(4-methoxy-4'-hexyloxybiphenyl)-dipropargyl malonate) (PMHBDPM) exhibit unique characteristics typical to both liquid crystal and conducting polymer. PMHBDPM exhibits smectic A phase in consistent with temperature dependence of X-ray diffraction. Two stages of electrochemical doping corresponding to the charge transfers between dopants and polymer main chain and also between dopants and the core of the mesogen unit in the side chain are observed. Diffusion coefficient of dopants also exhibits drastic change at the phase transition between smectic A phase and isotropic phase. These characteristics have been discussed in terms of molecular orientations of both polymer main chains and substituted side chains. Unique dielectric properties and X-ray diffraction characteristics have been observed in a mixture of PMHBDPM with ferroelectric liquid crystal of low molecular weight.

INTRODUCTION

Recently, liquid crystalline polymers with side chains containing mesogen units have attracted much attention. In these new class of polymers the polymer main chain is composed of flexible saturated bonds such as siloxane bond. On the other hand, polymers with rigid unsaturated main chains have been extensively studied, because these polymers named as conducting polymer exhibit various novel properties such as insulator-metal transition and thermochromism and also various types of functional applications such as secondary battery and display devices have been proposed.[1-6]

In the present paper, we describe novel electrical, electrochemical and optical properties in liquid crystalline phase of a poly(1,6-heptadiyne) derivative with long side chains containing mesogen units such as poly(bis(4-methoxy-4'-hexyloxy biphenyl)-dipropargyl malonate) (PMHBDPM) whose structure is shown in Figure 1 are discussed.

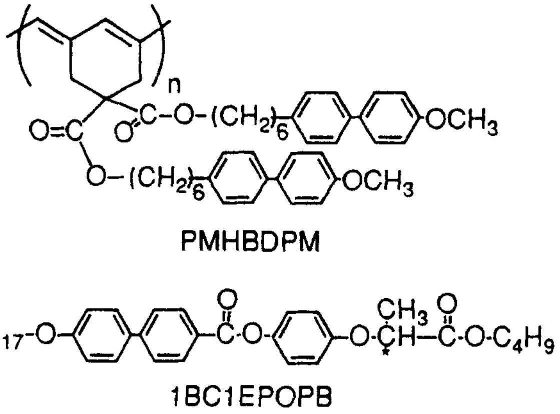

FIGURE 1 Molecular structures of PMHBDPM and 1BC1EPOPB

EXPERIMENTAL

PMHBDPM was prepared by metathesis polymerization with transition metal catalysts and purified by the method already reported.[7,8]

Sample was sandwiched between indium-tin oxide (ITO) covered glass plates with appropriate polyethyleneterephtharate (PET) spacers for the optical observation utilizing polarized optical microscope and the electrical measurement. Absorption spectrum was measured utilizing a Hitachi 330 spectrophotometer. Dielectric constant was measured with an impedance analyzer (HP, 4192A). Electrical conductivity was measured by both the two and the four probe methods. Electrochemical doping was carried out by the common three electrode cell utilizing acetonitrile solution containing tetrabutylammonium fluoroborate ($TBABF_4$) as an electrolyte. Electrochemical measurements such as cyclic voltammetry and chronoamperometry were performed using an arbitrary function generator HB104 and a potentiostat HA301 (Hokuto Denko). In situ absorption and electron spin resonance (ESR) measurements were carried out utilizing a spectrophotometer Hitachi 330 and a Bruker ESP-300 systems, respectively. X-ray diffraction measurements were carried out utilizing the RINT 1100 system (Rigaku) with X-ray of 1.54 Å in wavelength. The temperature of the sample was controlled by a Mettler FP-82. Anisotropy of absorption spectrum and its temperature dependence were studied utilizing a microscopic spectrometer system (Otsuka Electronics, IMUC7000G; Nikon, OPTIPHOT2).

A ferroelectric liquid crystal of low molecular weight, (R)-4'-(1-butoxycarbonyl-1-ethoxy)phenyl 4-[4-(*n*-octyloxy)phenyl]benzoate (1BC1EPOPB) whose molecular structure is also shown in Figure 1 was prepared by the method already reported and mixed with PMHBDPM for various measurements.[9] 1BC1EPOPB exhibits phase sequence of 22 Sm* 55 Sm*C 71 SmA 119 Iso.

RESULTS AND DISCUSSION

From the polarized optical microscope observations, PMHBDPM is found to exhibit the smectic A phase at the temperature range around 85-115 °C. The smectic phase was also confirmed by the small-angle X-ray diffraction measurements.

The film of PMHBDPM was red in color, which is consistent with the absorption spectrum shown in Figure 2.

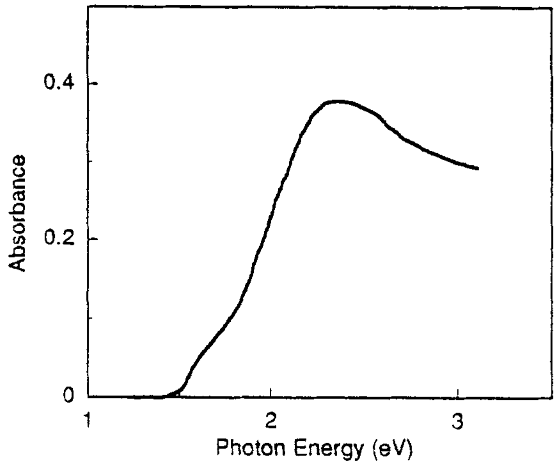

FIGURE 2 Absorption spectrum of PMHBDPM film

Anisotropy of absorption spectrum was also studied utilizing the aligned sample by giving shear stress in smectic A phase. As evident in figure 3, clear anisotropy was observed in the smectic A phase but it disappeared in the isotropic liquid phase.

In the smectic A phase, large absorption was observed for the light polarized perpendicular to the director which corresponds to the direction of alignment of side chain mesogen units. This fact means that the absorption is predominant for the light polarized along the conjugation of the main chain.

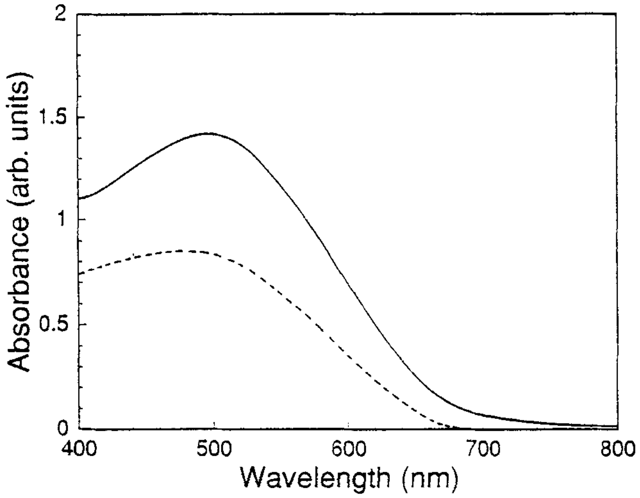

FIGURE 3 Anisotropy of absorption in an aligned domain of PMHBDPM; solid line: polarization is perpendicular to the director, broken line: polarization is parallel to the director.

PMHBDPM can be doped by both gas-phase chemical and also electrochemical doping methods. Electrochemical doping was reversible and in the cyclic voltammogram in TBAFB/AN (acetonitrile solution), two oxidation and reduction waves were observed. Corresponding to this anomalous cyclic voltammogram the absorption spectrum of PMHBDPM exhibited unique complex change with increasing doping potential as indicated in Figure 4.

These unique doping characteristics were interpreted to originate from the interaction of dopant with both the conjugated π-electron system of the main chain and the biphenyl units in the side chains. It should also be mentioned that, corresponding to this spectral change, color of the film changed from dark red to color less and then to blue with increasing doping level. These results clearly indicated that typical characteristics as conducting polymer exist in PMHBDPM.

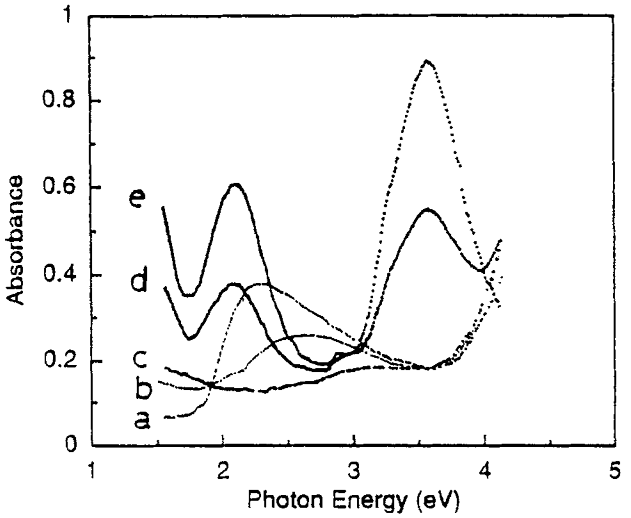

FIGURE 4 Change in absorption spectrum of PMHBDPM at various doping potential. (a) 0.5V (neutral), (b) 0.8V, (c) 1.0V, (d) 1.3V, (e) 1.4V vs Ag.

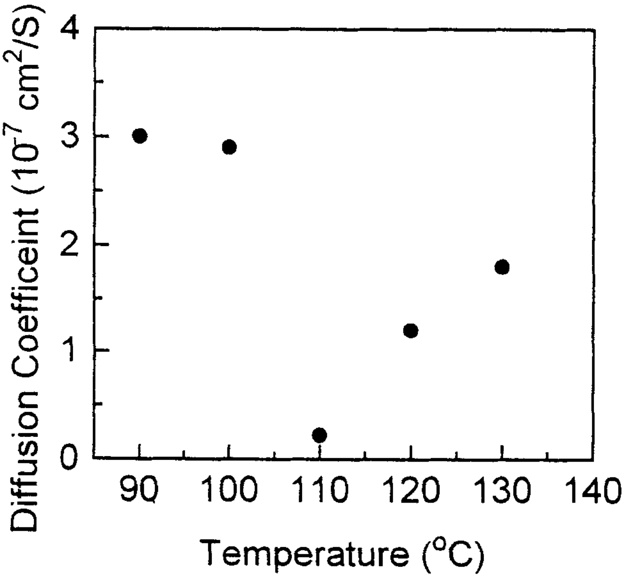

FIGURE 5 Temperature dependence of diffusion coefficient of dopant ion in PMHBDPM layer.

The diffusion coefficient of dopant ion within the polymer layer was also evaluated by the electrochemical technique as a function of temperature.[10] As is evident from Figure 5, with increasing temperature, diffusion coefficient of dopant decreases in stepwise at the transition from the smectic A phase to the isotropic phase and then in the liquid state diffusion coefficient again increases with increasing temperature. These characteristics can be explained by taking change of orientation of side chain mesogen units with temperature. That is, in the present experimental condition the dopant ion migrates parallel to the main chain and therefore also parallel to the smectic layer. This fact indicates that the diffusion coefficient along the smectic layer is larger than that in the isotropic phase, which is consistent with experimental results in low molecular weight liquid crystal. That is, we reported that the mobility of ions along the smectic layer is larger than that perpendicular to the layer and also than that in the isotropic phase.[11]

The electrical and optical properties of the doped state on the polymer main chain were tentatively explained by the soliton model, because the ESR behavior similar to the case of doped polyacetylene was clearly observed.

Electrical conductivity of PMHBDPM increases with increasing temperature and two inflection points are observed at the phase transition points between the smectic phase and other phases. Also in the dielectric measurement, slight enhancement of dielectric constant of PMHBDPM was observed in the smectic phase. However, the increase of the dielectric constant in the smectic phase is small. This relatively small change in dielectric constant may be due to the small component of dipole moment of the side chain perpendicular to the director.

We are also interested in the mixture of conducting polymer liquid crystal with low molecular weight ferroelectric liquid crystal because new functionalities may be realized in the mixture. Influence of added conducting polymer liquid crystal with rigid main chains on dynamic characteristics of ferroelectric liquid crystal (low molecular weight) is also interesting from fundamental view points.

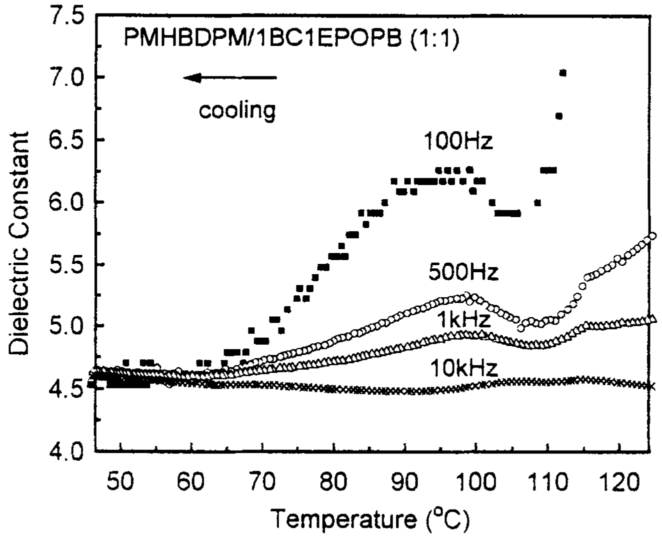

FIGURE 6 Temperature dependence of dielectric constant of mixtureof PMHBDPM and 1BC1EPOPB.

Figure 6 shows the temperature dependence of dielectric constant of the mixture of PMHBDPM and 1BC1EPOPB with the ration of (1:1) at various frequencies. As is evident from this figure, the enhancement of dielectric constant was observed at the phase transition between the smectic phase and the isotropic phase of PMHBDPM with decreasing temperature. In general, ferroelectric liquid crystal shows large dielectric constant in the chiral smectic C phase due to the contribution of the cooperative motion of the spontaneous polarization. In 1BC1EPOPB, the chiral smectic C phase appears below 70°C and the dielectric constant exceeding 1000 is observed.[12] However, the mixture of PMHBDPM and 1BC1EPOPB did not exhibit the enhancement of the dielectric constant which is observed in a pure 1BC1EPOPB even below 70°C. This suggests that in this mixture ferroelectricity was not induced in the conducting polymer liquid crystal and also ferroelectricity of 1BC1EPOPB was suppressed by PMHBDPM.

In the mixture of polyacetylene derivatives with ferroelectric liquid crystal, the ferroelectric behaviors were observed in the smectic phase of the host polymer.[13,14] However, in the mixture studied here, the ferroelectricity was not observed even by the mixing with ferroelectric liquid crystal. This may suggest that 1BC1EPOPB molecules are not well introduced at the side chain of PMHBDPM in the ordered state due to the existence of two long side chains in the each repeating unit of the polymer main chain.

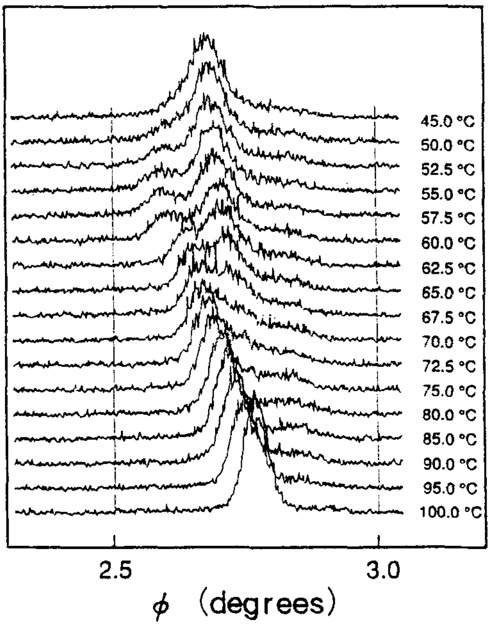

FIGURE 7 X-ray diffraction profiles of PMHBDPM/1BC1EPOPB (1/1) mixture at various temperature.

The result of the X-ray diffraction measurement of the PMHBDPM/1BC1EPOPB mixture is shown in Figure 7. As is evident from this figure, a sharp peak was observed around 2θ=2.8°, which corresponds to the spacing of 32 Å. If this peak originates from the smectic layer structure of 1BC1EPOPB, the narrowing of the layer spacing due to the molecular tilt in the chiral smectic C phase should be observed below 70°C. However, the diffraction peak shifts toward lower angle of 2θ with decreasing temperature, which means the expansion of the layer spacing. Moreover, a new peak appears below 70°C. This suggests that a new layer structure which is different from that of 1BC1EPOPB was induced by mixing 1BC1EPOPB with PMHBDPM.

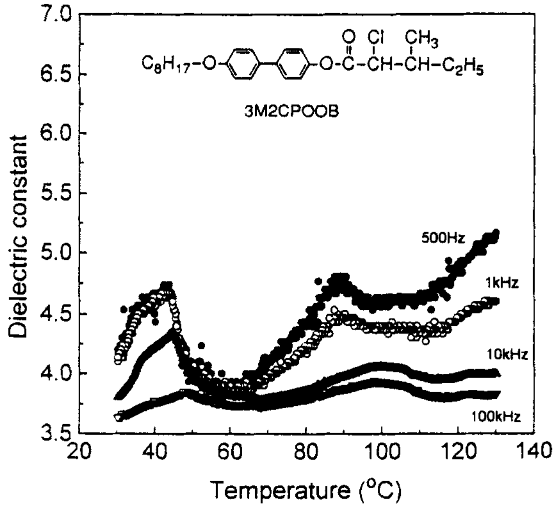

FIGURE 8 Temperature dependence of dielectric constant of PMHBDPM /3M2CPOOB (1/1) mixture. Inset: molecular structure of 3M2CPOOB.

It should also be noted that the length of the 1BC1EPOPB is much longer than the length of the side chain of PMHBDPM. Therefore we have studied mixtures with shorter ferroelectric liquid crystal in length, such as 3M2CPOOB ((25,35)-3-methyl-2-

chloropentanoie acid 4', 4"-alkoxybiphenyl ester), whose molecular structure is shown in the inset of Figure 8.

However, as shown in Figure 8, the (1:1) mixture of PMHBDPM and 3M2CPOOB exhibited just the similar characteristics with that of the (1:1) mixture of PMHBDPM and 1BC1EPOPB.

As also shown in Figures 9 and 10, even with increasing concentration of 3M2CPOOB, ferroelectricity was not induced in the temperature range of the smectic A phase of the undoped PMHBDPM. It is also clear in these figures that the ferroelectricity was observed in the temperature range (36° C~54° C) in which pure 3M2CPOOB exhibits ferroelectricity. On the contrary, it should be pointed out, that the ferroelectricity of 3M2CPOOB was remarkedly suppressed by doping of the conducting polymer liquid crystal PMHBDPM.

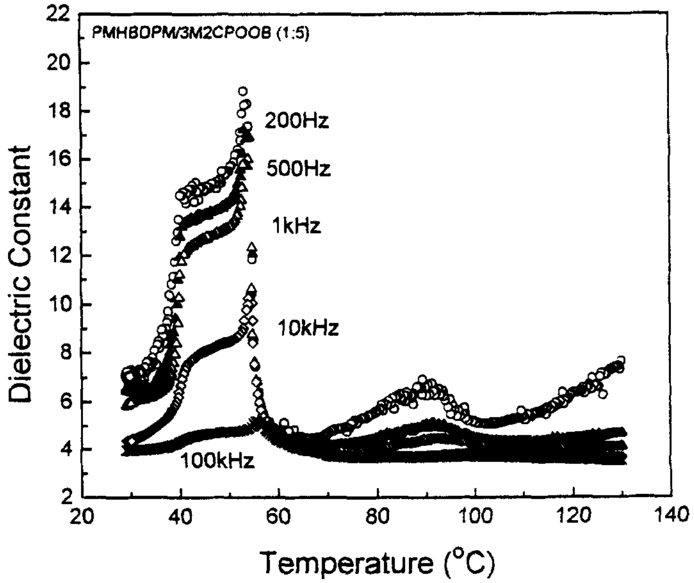

FIGURE 9 Temperature dependence of dielectric constant of the (1/5) mixture of PMHBDPM/3M2CPOOB .

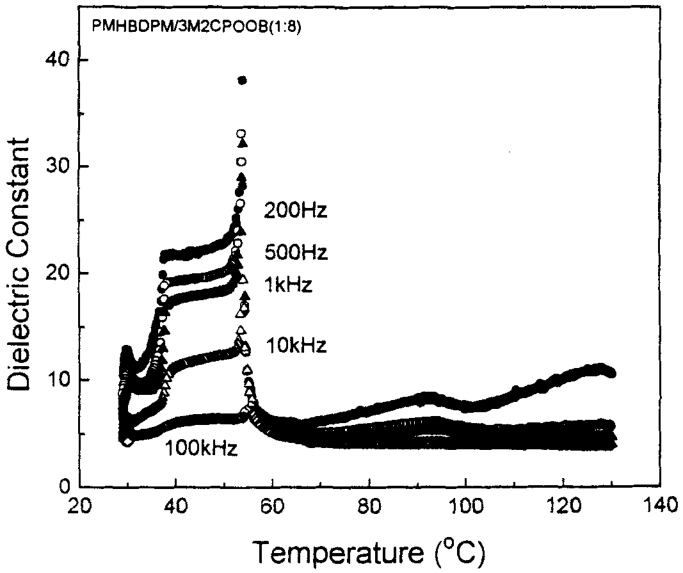

FIGURE 10 Temperature dependence of dielectric constant of the (1/8) mixture PMHBDPM/3M2CPOOB .

CONCLUSIONS

Unique characteristics typical to both liquid crystal and conducting polymer were observed in poly(1,6-heptadiyne) derivatives substituted with long side chains containing mesogen units. PMHBDPM exhibited the smectic A phase, which was confirmed by the optical microscopic observation and the X-ray diffraction measurement. The change in electrical properties such as electrical conductivity and dielectric constant were also observed at the phase transition temperatures. On the other hand, two stages of electrochemical doping were observed. Diffusion coefficient of dopants also exhibited drastic change with the phase transition between the smectic A phase and the isotropic phase.

Dielectric behavior of the mixture of the conducting polymer liquid crystal PMHBDPM and the low molecular weight ferroelectric liquid crystal were also clarified. The enhancement of dielectric constant has been observed in the mixture of PMHBDPM with ferroelectric liquid crystal of low molecular weight. However, ferroelectricity was not induced in the temperature range showing smectic phase of original PMHBDPM. On the contrary, the ferroelectricity of the low molecular weight ferroelectric liquid crystal was suppressed upon introdution of small amount of PMHBDPM.

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