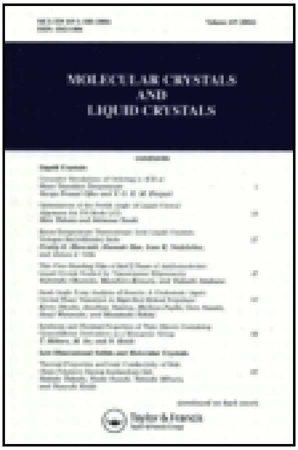

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Characterization of Biphenylethynylbenzene Type Discotic Liquid Crystal

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To cite this article: Daisuke Suzuki & Naoyuki Koide (2001): Synthesis and Characterization of Biphenylethynylbenzene Type Discotic Liquid Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 364:1, 635-645

To link to this article: http://dx.doi.org/10.1080/10587250108025033

Mol. Cryst. and Liq. Cryst., 2001, Vol. 364, pp. 635-645
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Synthesis and Characterization of Biphenylethynylbenzene Type Discotic Liquid Crystal

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Novel discotic liquid crystalline compound containing five rigid biphenyl moieties was synthesized by coupling reaction using palladium catalyst. Thermal and optical properties of the obtained compound were examined. We also examined the mesomorphic properties for the mixtures of the synthesized disk-shaped mesogen doped with 2,4,7-trinitrofluoren-9-on (TNF). The synthesized discotic liquid crystalline compound with a hydroxy group exhibited a schlieren texture characteristic of nematic phase, while the mixtures of the disk-shaped compound with TNF displayed a focal conic fan or a broken fan texture. The charge transfer absorption band of the mixture was observed about 550 nm by UV-vis absorption spectroscopy measurements. Furthermore, we examined thermal and optical properties of novel discotic liquid crystalline polymers prepared by photopolymerization.

Keywords: discotic liquid crystal; diphenylethynylbenzene; charge transfer complex; photopolymerization; discotic liquid crystalline polymer

INTRODUCTION

Discotic liquid crystals are usually composed of disk-like molecules containing a rigid flat or nearly flat cores, such as triphenylenes [1], benzenes [2], phthalocyanines or phenylacetylene derivatives surrounded by six or eight, or sometimes four, flexible alkyl chain substituents. Moreover, disk-like molecules have considerable interests in their mesomorphic properties and their unique molecular arrangements. Recently, a discotic columnar phase is important for turning their electrical properties such as the rapid carrier mobility. [3,4]

The vast majority of discotic materials exhibit columnar phases, some additionally show the discotic nematic (N_D) phase, and very few exhibit only the N_D phase. The generation of the N_D phase requires that the intermolecular attractions between molecules are weakened, correlated with the balance of the intermolecular force of rigid cores and flexible terminal chains. [5]

Only a few examples of discotic mesogens are known containing one terminal reactive function for the synthesis of the discotic side group polymers. For example, they are based on the monoacetates of a hexahydroxytriphenylene derivative with penta-ether groups, and they can be obtained in relatively low chemical yield. [6]

On the other hand, disk-shaped compound containing an electron donor unit can be doped with an acceptor molecule to form the charge transfer complexes. Using even a non-liquid-crystalline disk-shaped electron donor molecule, the columnar mesophase would be induced by such doping. [7] Moreover, a columnar hexagonal mesophase can be induced from N_D phase. [8] Recently, it was found that a few disk-shaped materials generated a columnar nematic (N_C) phase.[9] The N_C phase consists of short columns of a few molecules adopted a discotic nematic packing arrangement.

In this study, we synthesized a novel disk-shaped mesogen containing one terminal reactive function and novel polymers containing disk-shaped molecule. Their thermal and optical properties are demonstrated.

In addition, we also examined the mesomorphic properties for the mixtures of the synthesized disk-shaped mesogenic compound with TNF. Previously, Wendorff and coworkers reported a disc-shaped donor mesogen exhibiting the N_C phase doped with TNF.[7,9] However, in our study, the novel discotic compound itself exhibited the N_C phase.

EXPERIMENTAL

Materials

Synthesized novel disk-shaped polymers were shown in Scheme 1.

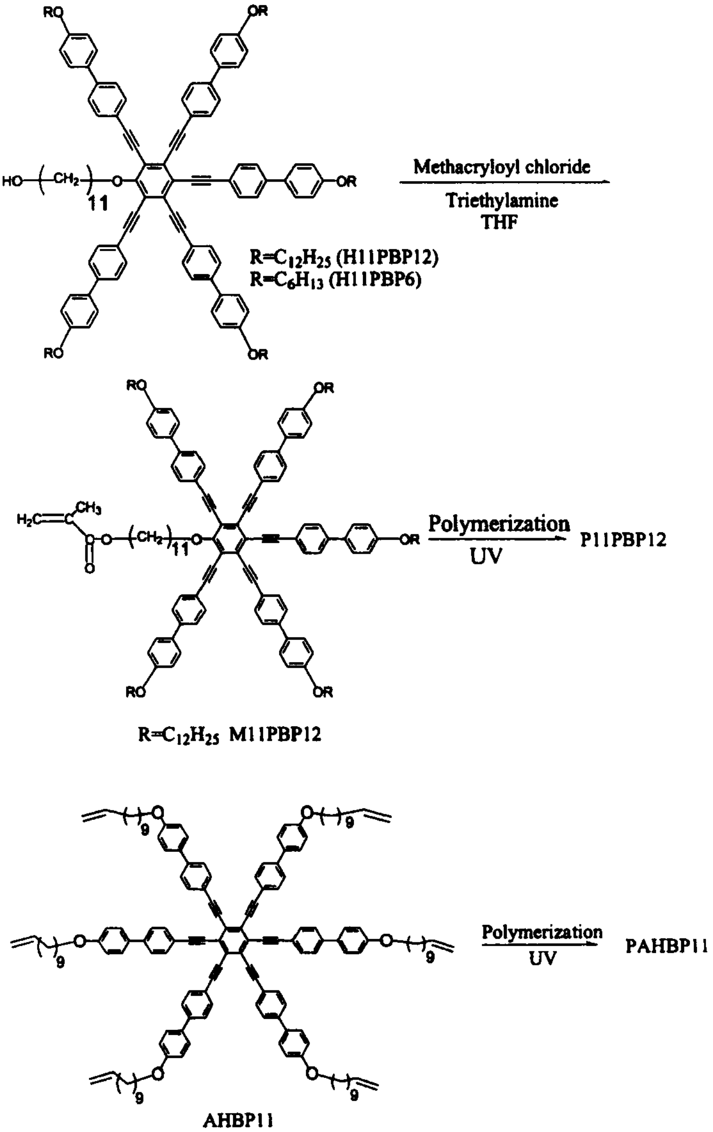
Preparation of the charge transfer (CT) complexes

The CT complexes were prepared by mixing the H11PBP12 with the 2,4,7-trinitrofluoren-9-one (TNF) (recrystallized from ethyl acetate) at the various molar ratios in chloroform solution. After shaking and allowing the mixture to stand for a few minutes, the solvent was removed *in vacuo* to give CT complexes as a dark red solid.

Characterization

^{1}H-NMR spectra were recorded with JNM-LA400(500). IR spectra were obtained with JEOL JIR7000. The physical properties of the samples were examined by using optical microscopy, differential scanning calorimetry (DSC) and X-ray diffraction. Transition temperatures were measured with a Mettler DSC20 system. In all cases the data from the second heating scan were taken. The textures were observed using a Nikon OPTIPHOTO-POL polarizing microscope equipped with a Mettler FP-82 hot stage and Mettler FP-80 thermal controller. For X-ray diffraction measurements, RIGAKU RINT-2500 was used. The samples were prepared in quartz capillaries.

UV-vis absorption spectra were measured by HITACHI U-3410



SCHEME 1 Synthesis of disk-like polymers

spectrophotometer. Samples were prepared as a chloroform (spectroscopic grade) solution, a cast film and a thin film obtained by spin coating on a quartz plate.

Fluorescent spectra were obtained by HITACHI F-4500 fluorescence spectrophotometer. Samples were prepared as chloroform solution and cast film on a quartz plate.

RESULTS AND DISCUSSION

Thermal properties

The synthesized low molecular discotic liquid crystalline compound was highly soluble in organic solvents such as chloroform and tetrahydrofuran.

Thermal properties was summarized in Table 1. H11PBP12 exhibited a nematic columnar phase due to a schlieren texture (Figure 1(a)) and X-ray diffraction pattern (Figure 2(a)). In the X-ray diffraction pattern of H11PBP12, a broad peak was observed in the small angle region. In the wide angle region, a diffuse and broad reflection peak was observed, and the peak was assigned to an intracolumnar reflection. The phase structure of H11PBP12 was the nematic columnar (N_C) phase.

TABLE I Phase transition temperatures of discotic mesogens.

Compounds	Phase transition temperatures (°C)
H11PBP12	$\mathrm{Cr} \underset{93}{\overset{134}{\longleftrightarrow}} \mathrm{N_C} \underset{157}{\overset{158}{\longleftrightarrow}} \mathrm{I}$
H11PBP6	$\mathrm{Cr} \underset{122}{\overset{161}{\longleftrightarrow}} \mathrm{N_D} \underset{208}{\overset{212}{\longleftrightarrow}} \mathrm{I}$
AHBP11	$\mathrm{Cr} \underset{69}{\overset{133}{\longleftrightarrow}} \mathrm{D} \underset{116}{\overset{136}{\longleftrightarrow}} \mathrm{N} \underset{185}{\overset{193}{\longleftrightarrow}} \mathrm{I}$
M11PBP12	$\mathrm{Cr} \underset{88}{\overset{106}{\longleftrightarrow}} \mathrm{N} \underset{142}{\overset{143}{\longleftrightarrow}} \mathrm{I}$

Cr: crystal, N_C: nematic columnar, N_D: nematic discotic, I: Isotropic, D: discotic columnar phase, N: nematic phase

On the other hand, in the X-ray pattern of H11PBP6, no peak was observed in the small angle region. As a result, the phase structure of H11PBP6 was assigned to the nematic discotic phase. The difference of the phase structure between H11PBP12 and H11PBP6 may be attributed

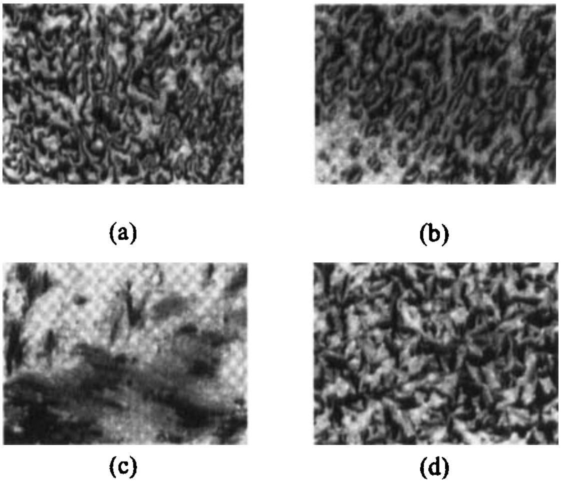
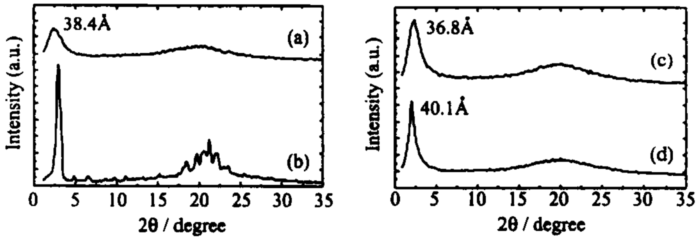


FIGURE 1 Textures of H11PBP12 and mixtures:(a) H11PBP12 at 153.2°C on cooling, (b) TNF 50mol% mixture at 134.7°C on cooling, (c) TNF 50 mol% mixture at 111.6°C on cooling, (d) TNF 70 mol% mixture at 111.3°C on cooling.

to the difference of phase transition enthalpy.

The mixtures of H11PBP12 with TNF were a dark red solids. Figure 3 showed the phase diagram of the mixtures. Only the N_C phase was found in a concentration range between 10 and 40 mol% TNF. When the TNF ratio was 50 mol% and 60 mol%, both schlieren (Figure 1(b)) and broken fan textures (Figure 1(c)) were observed. The TNF 50mol% mixture at 130°C (Figure 2(c)) showed similar results to the X-ray diffraction pattern for the nematic columnar type of mesophase (a broad intercolumnar spacing of 36.8 Å (2θ=2.40)). The TNF 50mol% mixture at 110 °C displayed a sharp reflection in the small angle region with an intercolumnar spacing of 40.1 Å (2θ=2.20) (Figure 2(d)). This induced mesophase was identified as the discotic hexagonal disordered type (D_{hd}). It was considered that H11PBP12 formed charge transfer complexes with TNF and that the energy of the complexed system was stabilized. Thus, with increasing interaction between disk type molecules, the columnar arrange-



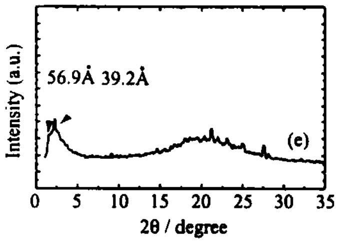


FIGURE 2 X-ray diffraction patterns of H11PBP12 and mixtures,(a)H11PBP12 at 145°C, (b)H11PBP12 at rt, (c)TNF 50mol% at 130°C, (d)TNF 50mol% at 100°C,(e)TNF 80mol% at 105°C.

ment was induced.

When the TNF ratio was above 70 mol%, a schlieren texture was not observed under polarized microscope and a new focal conic fan texture was observed (Figure 1(d)). The X-ray diffraction pattern of the TNF 80 mol% at 105℃ (see Figure 2(e)) displayed a slightly broad intercolumnar reflection in the small angle region with an intercolumnar spacing of 39.2 Å (2θ=2.25) and a small shoulder at 56.9 Å (2θ=1.55). In the wide angle region, a diffuse and broad reflection was observed, and this peak would be originated from

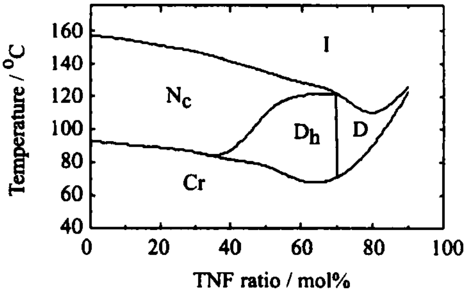


FIGURE 3 Phase diagram of H11PBP12 and mixtures: Cr, crystal; N_c, nematic columnar; I, isotropic; D_h, discotic columnar hexagonal; D, discotic columnar (type not yet clarified)

the intracolumnar reflection. The weak and sharp reflections on the amorphous halo, as shown in Figure 2(e), in the wide angle region were due to crystallized TNF, because phase separation occurred for the mixtures at high concentration of TNF. Therefore, a small peak in the small angle region may be due to crystallization of TNF or an exhibition of discotic columnar rectangular phase.

Table 2 showed thermal properties of polymers. Two kinds of polymer were prepared by photopolymerization. A schlieren texture was exhibited for P11PBP12, while birefringence was observed for PAHBP11. P11PBP12 was soluble in common organic solvents like chloroform and tetrahydrofuran. PAHBP11 was insoluble in organic solvents because of network structure of PAHBP11, formed by crosslinking of aryl groups.

TABLE 2 Thermal properties and molecular weight of polymers.

Polymers	Phase transition temperatures (°C)	$\overline{M}n$
P11PBP12	$g \underset{?}{\overset{35}{\longleftrightarrow}} N \underset{134}{\overset{140}{\longleftrightarrow}} I$	22,000
PAHBP11	$g \underset{?}{\overset{51}{\longleftrightarrow}} M \xrightarrow{230}$ Decomp.	—[a)]

g: glassy, N: nematic, I: isotropic, M: mesophase, Decomp.:thermal decomposition

a) insoluble in chloroform or THF

Optical properties

Figure 4 shows UV-vis absorption spectra of H11PBP12 and mixtures with cast film. The mixtures with TNF exhibited weak broad absorption bands near 550 nm compared with H11PBP12. This absorption band was due to charge transfer complexes. [10]

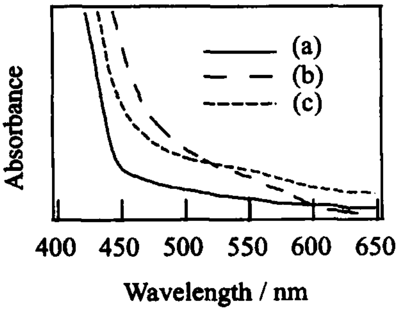


FIGURE 4 UV-vis spectra of H11PBP12 and mixtures, (a)H11PBP12(film), (b) TNF 50mol% mixture(film), (c)TNF 70mol% mixture(film)

Figure 5 shows UV-vis absorption spectra of H11PBP12 at

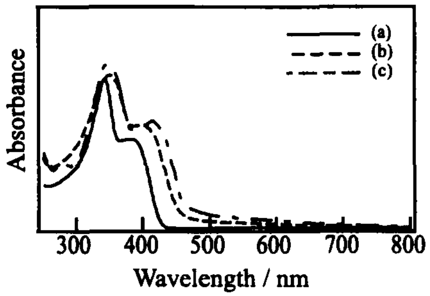


FIGURE 5 UV-vis spectra of H11PBP12, (a)chlorofolm solution, (b) film, (c) film annealed at 130°C.

TABLE 3 UV-vis absorption maxima of compounds.

Compounds	$CHCl_3$ solution (nm)	Film (nm)
H11PBP12	342	350
H11PBP6	339	343
M11PBP12	347	353
P11PBP12	353	364
AHBP11	342	360
PAHBP11	—[a)]	365

a) insoluble in chlorofolm

different sample preparations (chloroform solution, spincoated film and heated film in the liquid crystalline state (130°C)). In the liquid crystalline state, a shoulder peak shifted to about 420 nm. The shift of the shoulder peak would be originated from the intermolecular interaction formed between discotic molecules in the liquid crystalline state. Similar tendency about a red shift of the shoulder peak was observed for the mixture of H11PBP12 with TNF, that exhibited a columnar phase. UV-vis absorp-

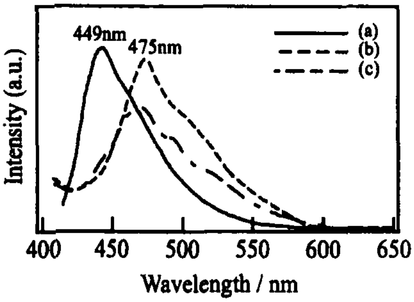


FIGURE 6 Fluorescence spectra of P11PBP12, (a) chlorofolm solution, (b) film, (c) film annealed at 130°C.

TABLE 4 Emission maxima of discotic compounds.

Compounds	$CHCl_3$ solution (nm)	Film (nm)
H11PBP12	434	472
H11PBP6	458	477
M11PBP12	445	469
P11PBP11	449	475
AHBP11	437	476
PAHBP11	—[a)]	480

a) insoluble in chloroform

tion maxima of discotic compounds were summarized in Table 3.

Synthesized discotic compounds had a strong fluorescence property. Figure 6 shows fluorescence spectra of P11PBP12. The fluorescence spectrum of the P11PBP12 film was shifted to longer wavelength about 25 nm than that of chloroform solution. This result indicated that the strong intermolecular interaction would be formed compared to that in chloroform solution due to overlapping of π electron orbit for the discotic molecule in the film. However, the fluorescence intensity in chloroform solution was much larger than that of the film. In particular, the fluorescence intensity decreased in the liquid crystalline state because concentration quenching would occur in the liquid crystalline state, and because temperature was high when these discotic molecules exhibited the liquid crystalline phase. Emission maxima of discotic compounds were summarized in Table 4. The emission maxima of the film for discotic compound is longer wavelength than that of chloroform solution.

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