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Preliminary communication

Optical isotropic mesophase in side chain copolymers containing isophthalic acid groups

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Random side chain copolymers, containing cyanobiphenyl mesogenic units and 37–58 mol % of isophthalic acid monomer units, possess an unusual ability to produce optically isotropic mesophases. This is demonstrated by the absence of birefringence and by high optical transparency of their films. At the same time, corresponding DSC curves show a well pronounced first order transition with a heat of fusion of 1.5–2.34 kJ mol⁻¹. A key reason behind the formation of an optically isotropic mesophase is likely to be related to the microphase separation between side groups of the copolymers.

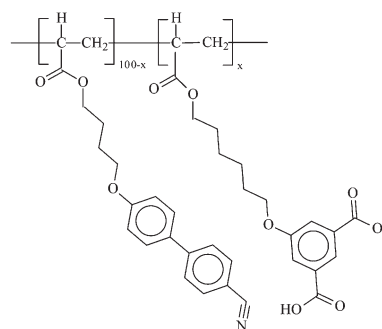
Birefringence is one of the most important fundamental characteristics of liquid crystalline compounds [1]. This parameter reflects the dependence of refractive index on the direction of light passage in anisotropic media. However multiple accounts of the discovery of so-called optically isotropic mesophases (OIMs) are already present in the literature [2–13]. The compounds studied are able to produce thermodynamically stable mesophases with different supramolecular structures, a fact unequivocally proved by DSC measurements and X-ray studies. At the same time, these mesophases are optically isotropic.

Cubic or blue phases are known to comprise the most common types of optically isotropic structures. In this case, the absence of birefringence is explained by high symmetry of their molecular packing. Thermotropic cubic phases were initially found for the derivatives of 4'-*n*-alkoxy-3'-nitrophenyl-4-carboxylic acid [2, 3]. The formation of OIM is now observed for many compounds, including polycatenar and swallow-tailed compounds, dendrimers, folic acid derivatives, polyhydroxy amphiphiles, hydrogen-bonded siloxane-containing acid/base complexes, etc. [4]. All these compounds are characterized by their well pronounced amphiphilic character, i.e. their chemical structure contains at least two continuous fragments with different polarities. Seemingly, a strong microphase separation between hydrophilic and hydrophobic parts is a key factor for the formation of cubic phases [5].

In the case of high-molar-mass compounds, the development of OIM was observed for several comb-shaped polymers containing optically active (chiral) fragments in their side chains [12, 13]. The absence of birefringence in such compounds is related to the formation of specific TGB-like amorphous smectic structure with extremely short helical pitch ($\lambda \sim 200$ nm).

The study of the reasons behind the formation and specific features of such mesophases presents a challenging problem of fundamental science. Furthermore, this knowledge will offer a new approach for the preparation of advanced polymer materials that combine high transparency in their thick films and unique liquid crystalline properties. In our opinion, such substances may find some interesting applications in areas of nonlinear optics and holography.

This work presents results concerning the formation of OIMs in random side-chain copolymers containing mesogenic fragments and functional carboxylic groups of isophthalic acid. Their chemical structure is:



CB ($x=0$ mol %); AA6 ($x=100$ mol %); CB-AA6- x ; $M_w=9-14 \times 10^3$

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The selection of the above monomers was motivated by the results of our earlier work concerning the specific features of phase behaviour [14], structure, and orientational ordering [15] in LC copolymers with various functional fragments. Typically, either acrylic acid or derivatives of *n*-alkyloxybenzoic acid containing aliphatic spacers of different lengths were used as functional co-monomers. It was found that hydrogen bonding between functional carboxylic groups plays an important role in mesophase formation. So, originally this work was focused on studying the effect of the concentration of dibasic isophthalic acid on the phase behaviour and structure of comb-shaped LC copolymers.

Figure 1 presents the phase diagram for CB-AA6 copolymers. In the homopolymer CB, a nematic mesophase is formed due to the presence of rigid anisometric fragments of cyanobiphenyl in its side chains. Let us emphasize that homopolymer AA6 is also capable of forming a LC phase, even though it contains no anisometric groups. The formation of mesogenic fragments due to hydrogen bonding of end carboxylic groups is usually considered to explain the development of smectic phases by the derivatives of *n*-substituted oxybenzoic acids. However, in this case, spatial hindrances (geometric features) prevent this possibility. The development of a LC phase in AA6 is likely to be related to microphase separation of hydrophobic polymer chains and polar end groups of isophthalic acid, as in the case of lyotropic liquid crystals and lamellar phases of polymer and low-molar-mass surfactants.

Therefore, homopolymers CB and AA6 are capable of the formation of common thermotropic phases with birefringence. The incorporation of a small fraction (18 mol%) of AA6 units into homopolymer CB results in complete distortion of the mesophase. The same

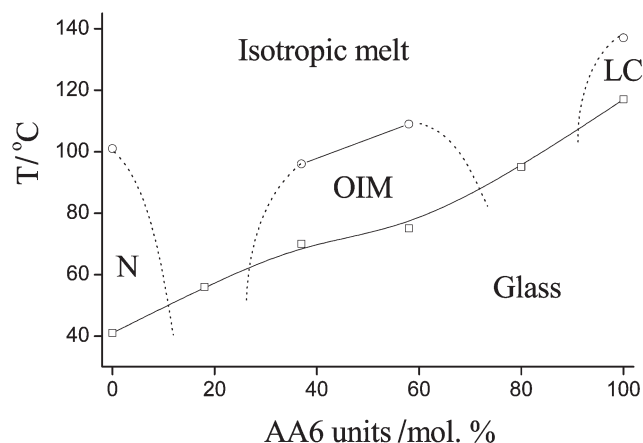


Figure 1. Phase behaviour of copolymers CB-AA6.

effect is observed with the incorporation of nematogenic CB groups into homopolymer pAA6. The mesophase distortion in copolymers CB-AA6-18 and CB-AA6-80 is demonstrated by polarizing microscopy data (absence of birefringence) and degeneration of transitions on DSC curves. However, copolymers containing 37 and 58 mol% of isophthalic acid units AA6 unexpectedly demonstrate OIMs. This is shown by the absence of birefringence (according to the polarizing optical microscopy) and by high transparency (95–97%) of their films (sample thickness is 50 μm) in the visible spectral region at temperatures ranging from 20 to 150°C. At the same time, the corresponding DSC curves of copolymers CB-AA6-37 and CB-AA6-58 exhibit a well pronounced endothermic transition (during heating), its heat of fusion being 1.5–2.3 kJ mol^{-1} . Moreover, DSC scans for CB-AA6-58 (figure 2) clearly show that this transition is reversible and may be reproduced in repeated heating–cooling runs.

One should mention that, for the above-mentioned copolymers, the heat of phase transition is 3–4 times higher than the corresponding values for homopolymers CB (0.38 kJ mol^{-1}) and AA6 (0.51 kJ mol^{-1}). Therefore, copolymers CB-AA6-37 and CB-AA6-58 are able to produce OIM, and its heat of fusion is typical of smectic phases of polymer liquid crystals.

Unfortunately, the X-ray data (figure 3) did not allow us to ascertain the character of packing of side groups in OIMs. The corresponding X-ray patterns of copolymers show only a diffuse halo at wide scattering angles ($d=4.5 \text{ \AA}$), which is typical of mesogenic groups containing aromatic rings. At the same time, these patterns show no small angle peaks that could help to identify the type of organization of side groups in the copolymers.

In our opinion, current speculations in the literature concerning the formation and structure of OIMs cannot be used to explain the absence of optical anisotropy in the copolymers under study. Indeed, the above-mentioned compounds were synthesized by radical copolymerization, and one may hardly expect the formation of cubic or any other high symmetry phases, due to the absence of stereoregularity in the arrangement of monomer units as well as due to compositional inhomogeneity of the copolymers. This conclusion is confirmed by X-ray scattering patterns. Another type of OIM was observed only for optically active copolymers containing chiral fragments in their side groups [12, 13].

At present, experimental and literature data allow one to draw no valid conclusions concerning the mechanism and structure of observed OIMs. In our opinion, OIM formation is primarily induced by the microphase separation between cyanobiphenyl units

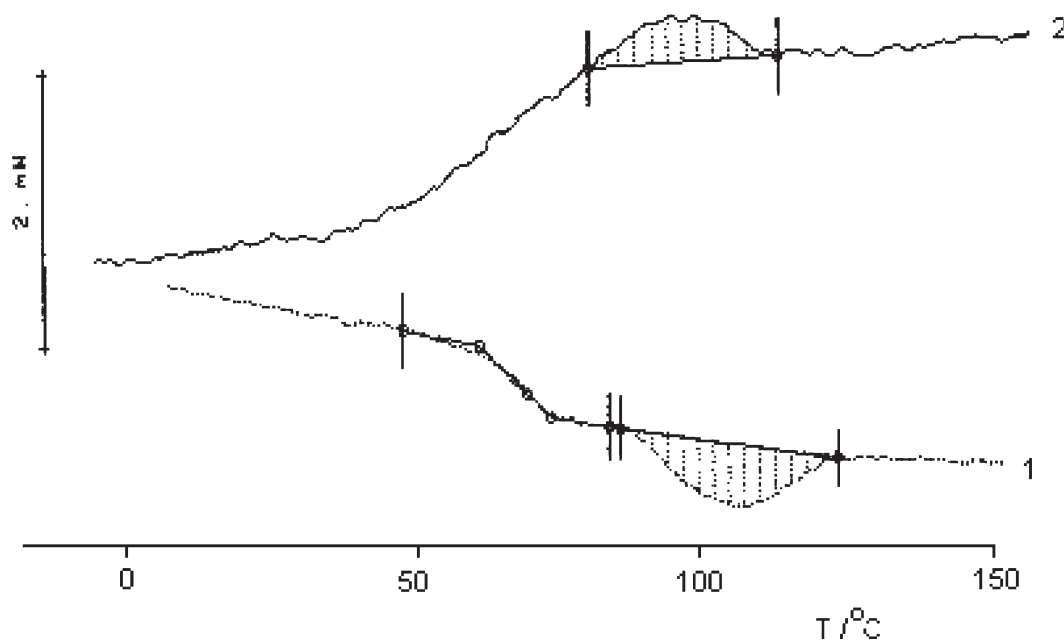


Figure 2. DSC curves for copolymer CB-AA6-58 under heating (1) and cooling (2) regimes.

and fragments of isophthalic acid, which are characterized by appreciably different hydrophobic and hydrophilic properties. These processes may entail the formation of mesomorphic domains with typical dimensions below the wavelength of visible light. The latter fact may be used to explain the absence of birefringence in copolymers CB-AA6-37 and CB-AA6-58. Hydrogen bonding is, presumably, another key factor that controls OIM formation in such systems. A detailed study of hydrogen bonds in copolymers CB-AA6 will be presented in forthcoming publications.

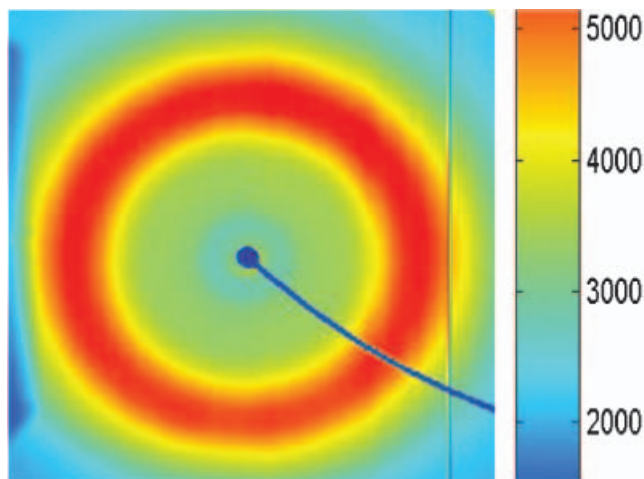


Figure 3. X-ray diffraction images for copolymer CB-AA6-58 at 20°C.

The monomers 4-[(4'-cyano-1,1'-biphenyl-4-yl)oxy]butyl acrylate (M1) and 5-[6-(acryloyloxy)hexyloxy]isophthalic acid (M2) were synthesized according to standard procedures. M1: $^1\text{H NMR}$ (CDCl_3) δ , ppm 7.97 (d, 2H, Ph, $J=8.85$ Hz); 7.67 (d, 2H, Ph, $J=8.55$ Hz); 7.62 (d, 2H, Ph, $J=8.51$ Hz); 7.51 (d, 2H, Ph, $J=8.81$ Hz); 6.35 (dd, 1H, $\text{CH}_2=\text{CH}-$, $J=1.65$, 17.65 Hz); 6.12 (dd, 1H, $\text{CH}_2=\text{CH}-$, $J=10.3$, 17.31 Hz); 5.81 (dd, 1H, $\text{CH}_2=\text{CH}-$, $J=1.65$, 10.3 Hz); 4.21 (t, 2H, $\text{O}-\text{CH}_2$); 4.02 (t, 2H, $-\text{CH}_2-\text{O}$); 1.89 (4H, $-\text{CH}_2-\text{CH}_2-$). M2: $^1\text{H NMR}$ ($\text{DMSO}-d_6$) δ , ppm: 12.8 (2H, $-\text{COOH}$), 8.06 (m, 1H, Ph), 7.63 (m, 2H, Ph), 8.06 (dd, 1H, $\text{CH}_2=\text{CH}-$), 6.11 (dd, 1H, $\text{CH}_2=\text{CH}-$), 5.88 (dd, 1H, $\text{CH}_2=\text{CH}$), 4.12–4.04 (m, 4H, CH_2), 1.76–1.38 (m, 8H, CH_2).

The copolymers CB-AA6- x were obtained by free radical copolymerization of the corresponding monomers in absolute tetrahydrofuran (THF) at 65°C; AIBN (2 wt%) was used as initiating agent. These synthesized copolymers were purified by repeated precipitation from THF solutions by hexane. Composition of the copolymers was determined by $^1\text{H NMR}$ spectroscopy.

X-ray measurements were performed using a Rigaku rotating anode, operated at 50 kV and 300 mA with copper as anode target material. For the experiments, the most intense characteristic line from the target with wavelength 1.54 Å was used. A 2D detector system operated with a PC was used for registration of scattering profiles.

Microcalorimetry studies were performed with a Mettler differential scanning calorimeter TA4000 at a scanning rate of $10^{\circ}\text{C min}^{-1}$ from -10 to 180°C in an atmosphere of nitrogen. The DSC cell was calibrated with indium. Polarizing optical microscopy observations were made with a Zeiss polarizing microscope equipped with a Mettler FP-82HT hot stage controlled by a Mettler FP90 unit. Relative molecular masses of the polymers were determined by gel permeation chromatography using a GPC-2 Waters instrument equipped with an LC-100 column oven and a Data Modul-370 data station. Measurements were made using a UV detector, THF as solvent (1 mL min^{-1} , 25°C), a set of PL columns of 100, 500, and 10^3 \AA , and a calibration plot constructed with polystyrene standards.

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References

- [1] D. Demus, J. Goodby, G.W. Grey, H.W. Spiess, V. Vill (Eds). *Handbook of Liquid Crystals* Vols I–IV, Wiley VCH, New York (1998).
- [2] G.W. Gray, B. Jones, F. Narson. *J. chem. Soc.*, 393 (1957).
- [3] D. Demus, G. Kunicke, J. Keelsen, A. Sackmann. *Z. Naturforsch.*, **23a**, 84 (1968).
- [4] E. Nishikawa, J. Yamamoto, H. Yokoyama. *Liq. Cryst.*, **30**, pp. 785, and references therein (2003).
- [5] M. Yoneya, E. Nishikawa, H. Yokoyama. *J. chem. Phys.*, **116**, 5753 (2002).
- [6] J. Billard, H. Zimmermann, R. Poupko, Z. Luz. *J. Phys. (Paris)*, **50**, pp. 539, and references therein (1989).
- [7] V. Percec, M. Lee, J. Heck, H.E. Blackwell, G. Ungar, A. Alvarez-Castro. *J. mater. Chem.*, **2**, 931 (1992).
- [8] W. Weissflog, I. Lekto, G. Pelzl, S. Diele. *Liq. Cryst.*, **18**, 867 (1995).
- [9] A. Yoshizawa, J. Umezawa, N. Ise, R. Sato, Y. Soeda, T. Kusumoto, K. Sato, T. Hiyama, Y. Takanishi, H. Takezoe. *Jpn. J. appl. Phys.*, **37**, 942 (1998).
- [10] E.V. Matukhina, O.I. Shchegolikhina, N.N. Makarova, Y.A. Pozdniakova, D.R. Katsoulis, Y.K. Godovsky. *Liq. Cryst.*, **28**, 869 (2001).
- [11] M. Petrov, E. Anachkova, N. Kirov, H. Ratajczak, J. Baran. *J. mol. Liq.*, **61** (1994).
- [12] L. Bata, K. Fodor-Csorba, J. Szabon, M.V. Kozlovsky, S. Holly. *Ferroelectrics*, **122**, 149 (1991).
- [13] M.V. Kozlovsky, V.P. Shibaev, A.I. Stakhanov, T. Weyrauch, W. Haase. *Liq. Cryst.*, **24**, 759 (1998).
- [14] E.B. Barmatov, D.A. Pebalk, M.V. Barmatova, V.P. Shibaev. *Liq. Cryst.*, **23**, 447 (1997); E.B. Barmatov, A.Yu. Bobrovsky, M.V. Barmatova and V.P. Shibaev. *Liq. Cryst.*, **26**, 581 (1999); M.V. Medvedev, E.B. Barmatov, A.S. Medvedev, V.P. Shibaev, S.A. Ivanov, M. Kozlovsky and J. Stumpe. *Macromolecules*, **38**, 2223 (2005).
- [1] E. Barmatov, S. Grande, A. Filippov, M. Barmatova, F. Kremer, V. Shibaev. *Macromol. Chem. Phys.*, **201**, 2603 (2000); E.B. Barmatov, A.P. Filippov and V.P. Shibaev. *Liq. Cryst.*, **28**, 511 (2001); A.P. Filippov, V.V. Andropov, E.B. Barmatov, F. Kremer, M.V. Barmatova and V.P. Shibaev. *Liq. Cryst.*, **27**, 1585 (2000).