

LIQUID CRYSTALLINE BEHAVIOR OF HYDROXYPROPYL CELLULOSE ESTERIFIED WITH 4-ALKOXYBENZOIC ACID

Nahla A. El-Wakil,^{a*} Yehia Fahmy,^a Ragab E. Abou-Zeid,^{a,b} Alain Dufresne,^b and Samya El-Sherbiny^c

A series of 4-alkoxybenzoyloxypropyl cellulose (ABPC-*n*) samples was synthesized via the esterification of hydroxypropyl cellulose (HPC) with 4-alkoxybenzoic acid bearing different numbers of carbon atoms. The molecular structure of the ABPC-*n* was confirmed by Fourier transform infrared (FT-IR) spectroscopy and ¹H NMR spectroscopy. The liquid crystalline (LC) phases and transitions behaviors were investigated using differential scanning calorimetry (DSC), polarized light microscopy (PLM), and refractometry. It was found that the glass transition (T_g) and clearing (T_c) temperatures decrease with increase of the alkoxy chain length. It was observed that the derivatives with an odd number of carbon atoms are non-mesomorphic. This series of ABPC-*n* polymers exhibit characteristic features of cholesteric LC phases between their glass transition and isotropization temperatures.

Contact information: a: Cellulose and Paper Department, National Research Center, El-Tahrir St., Giza, Egypt; b: Grenoble Institute of Technology (INP) - The International School of Paper, Print Media and Biomaterials (PAGORA), BP 65, 38402 Saint Martin d'Hères cédex, Grenoble, France; c: Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt; *Corresponding author: nawakil@hotmail.com

Keywords: HPC 4-alkoxybenzoic acid; Mesophase behavior; Refractive index

INTRODUCTION

Due to their remarkable reflection of light at specific wavelengths, cholesteric liquid crystals are of great scientific and technological interest. These materials exhibit unique selective reflection of light at characteristic wavelengths with a specific pitch length.

Attention has been paid towards modification of many polymeric materials to impart new properties to the product. Cellulose derivatization leads to new products whose properties are well controlled at the molecular level and can be tailored to suit the application required (Tianhui et al. 2010).

The force of the formation of liquid crystals for cellulose and its derivatives is attributed to both their semi-rigid backbone and molecular interactions in the system (Huang et al. 1995). The study on liquid crystal phases of cellulose esters or ethers becomes attractive owing to their potential advantages, such as toughness and processibility. On the other hand, the liquid crystalline properties of cellulose in electro-optical applications opens new horizons for these traditional materials.

A cholesteric phase of hydroxypropyl cellulose (HPC) in aqueous solutions was first reported by Werbowyl and Gray (1976). HPC itself (Shimamura et al. 1981), HPC derivatives (Gray 1983), and other fully substituted cellulose derivatives (Yamagishi et

al. 1988, 1989, 1990, and 1991) with flexible side chains have been reported to melt readily, forming thermotropic liquid crystalline mesophases.

Actually it was shown that HPC is able to form both lyotropic and thermotropic mesophases (Shimamura et al. 1981; Zugenmaier et al. 1989). Liquid crystalline behaviors of modified HPC were reported in previous works (Tseng et al. 1981, 1982; Bhadani et al. 1983; Lee et al. 1997a, 1997, and 1989). Investigations of the thermotropic cholesteric properties of several HPC esters were also reported (Tseng et al. 1981, 1982; Bhadani et al. 1983).

The goal of the present study is to modify HPC via esterification with benzoic acid bearing a terminal alkoxy chain to correlate the mesophase behavior of the resulting esters with the alkoxy chain length.

The prepared samples were alkoxybenzoyloxypropyl cellulose coded as ABPC-*n*, where *n* refers to the number of carbon atoms in the alkoxy chain (Fig. 1).

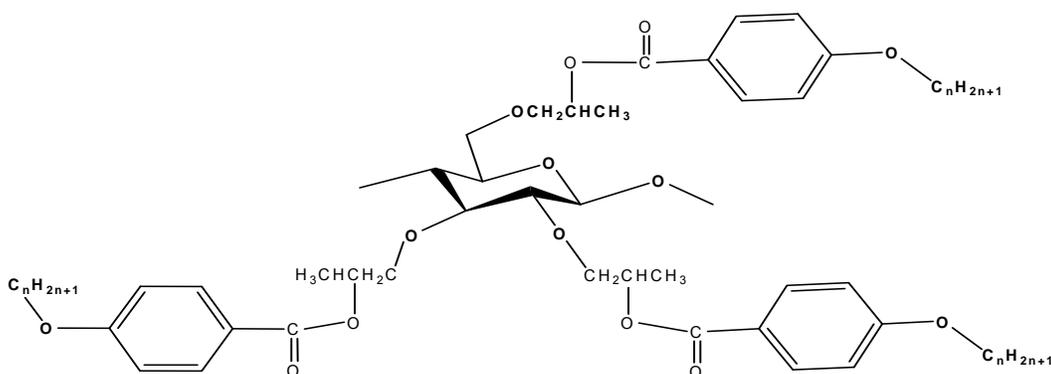


Fig. 1. Idealized structure for a substituted anhydroglucose unit of 4-alkoxybenzoyloxypropyl Cellulose; degree of etherification = 3, Degree of esterification = 3

EXPERIMENTAL

Materials

Hydroxypropylcellulose (HPC) (Aldrich, Mw = 100,000 gmol⁻¹) was dried under vacuum at 50°C for about 48h before use. Para-toluenesulfonylchloride (TsCl), anhydrous pyridine, dimethyl acetamide (DMA), and 4-Alkoxybenzoic acid (C_nH_{2n+1}OC₆H₄CO₂H, n= 1, 2, 3, 4, 5, 7, 8, 12 were all purchased from Aldrich and used as received.

Synthesis of 4-alkoxybenzoyloxypropyl Cellulose (ABPC-*n*).

HPC (2.0 g) corresponding to 16.14 mmol based on hydroxypropyl unit was stirred in DMA (20g/L). 4-Alkoxybenzoic acid (6 molar equivalent) was added as well as pyridine and TsCl and stirred for at least 24 h at 80 °C. The reaction mixture was then poured into excess water. The ABPC-*n* separated as a white sticky mass. For purification, the filtered precipitate was dissolved in acetone, and then reprecipitated with cold methanol to get rid of all unreacted acid and other byproducts. The derivatives were

purified at least four times by dissolutions and reprecipitation, and finally the product was dried under vacuum at 60°C.

Physical Characterization

IR spectra were measured, in KBr disc, on a JASCO 300-E Fourier transform infrared (FTIR) spectrometer. ^1H NMR spectra were recorded in dimethylsulfoxide (DMSO) using tetramethylsilane (TMS) as reference, on a JEOL AS 500 MHz spectrometer. Differential scanning calorimeter (DSC Q100 TA Instruments, USA) measurements were carried out for samples (around 6 mg) placed in a sealed aluminum pan. All thermograms were carried out at a heating rate $5\text{ }^\circ\text{C min}^{-1}$ in an inert atmosphere of nitrogen. Transition temperatures were checked, and types of mesophases were identified, for samples investigated with THMS600 polarized-light microscope (PLM) equipped with a hot stage. To investigate the lyotropic properties, samples were kept in the solvent dimethylacetamide (DMA), (40 wt% and 60 wt%) for at least one week before measurements. Refractive indices were performed on an Abbe 60 refractometer attached to an ultrathermostat and recorded at 25 °C.

RESULTS AND DISCUSSION

Molecular Structure and Liquid Crystalline Properties

The molecular structure of some modified HPC has been described in previous publications (Tseng et al. 1982; Bhadani et al. 1983; Hou et al. 2002). In the present study, the degree of substitution (DS) is referred to as the degree of esterification of hydroxyl groups per repeating unit of HPC. DS is usually determined either from elemental analysis, IR spectroscopy, or ^1H NMR. In this contribution, it was determined by ^1H NMR (Ritcey et al 1988). In these ester derivatives, it was found that 2.0 to 2.4 hydroxyl groups of the HPC were substituted on average. The long alkyl/alkoxy chains add flexibility to the rigid core structure that tends to be exhibited. Additionally the alkyl/alkoxy chains are believed to be responsible for stabilizing the molecular orientation necessary for LC phase generation (Peter et al. 1997). The overall chain structure becomes semi-rigid; therefore, thermotropic or lyotropic cholesteric LC phases may be developed in bulk with certain temperature regions (thermotropic) or in high ABPC-*n* concentration solutions (lyotropic) (Huang et al. 2007).

There is a difference in the solubility between more rigid HPC and less rigid ABPC-*n*; therefore further evidence of the esterification of HPC with 4-Alkoxy benzoic acid was noted from the increased solubility of the ester derivatives in organic solvents such as DMA, and tetrahydrofuran (THF).

FTIR spectra

To confirm the substitution reactions of cellulose and its derivatives, IR spectra were measured. Figure 2 displays the FTIR spectra for the HPC and some selected derivatives namely, (ABPC-8 and ABPC-12).

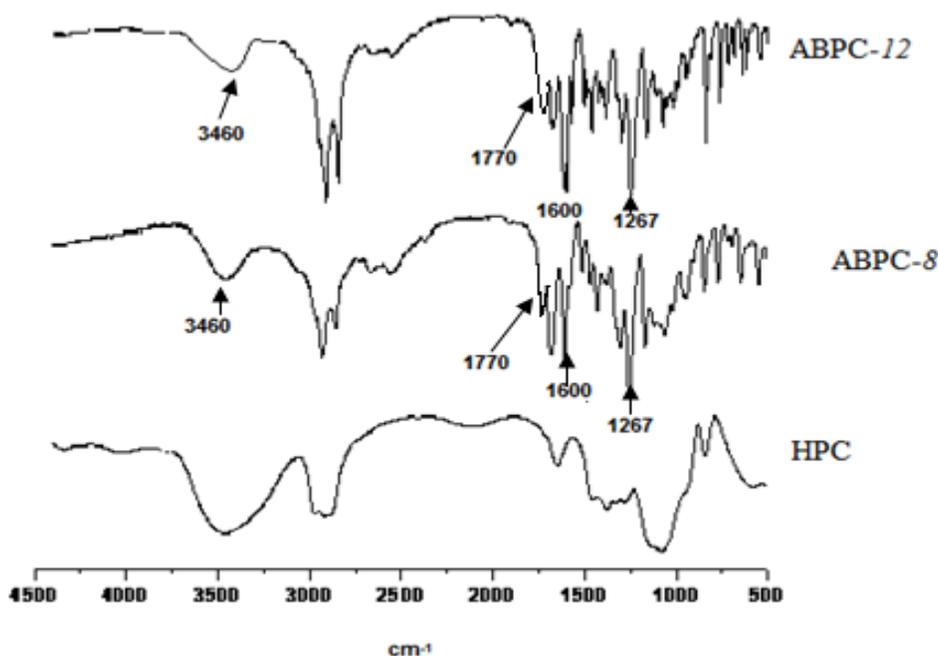


Fig. 2. FTIR spectra of HPC, ABPC-8 and ABPC-12

The FTIR spectrum of HPC shows a broad peak at 3460 cm^{-1} assigned to the O-H stretching vibration, which intensity decreased upon esterification. The peak detected at 2935 cm^{-1} is assigned to C-H asymmetric stretching vibration; the intensity of this peak increased with an increase of the alkoxy chain length with C-H stretching due to the difference in the number of CH_2 groups. Upon substitution, new peaks appeared. The peaks observed at 1770 cm^{-1} , 1267 cm^{-1} , 1600 cm^{-1} , and 700 cm^{-1} are assigned to C=O stretching, C-O stretching, aromatic C-C stretching, and aromatic C-H bending, respectively.

^1H NMR spectra

The benzylation of HPC was further confirmed with ^1H NMR. Figure 3 represents the ^1H NMR spectra of HPC, (ABPC-8, and ABPC-12) as examples.

^1H NMR spectrum (in DMSO) analysis of ABPC-12 was established, and the obtained bands were assigned as follows: 0.96 ppm for the protons in terminal CH_3 in the alkoxy chain length; 1.33 ppm and 1.29 ppm for the protons CH_2 CH_3 in the alkoxy chain length and for the protons $\text{O}(\text{CH}_2)_8\text{CH}_2\text{CH}_3$, respectively. From 3 to 5.25 ppm for the protons of the anhydroglucose ring and 6.8 and 7.88 ppm for the aromatic protons. For the ABPC-8 is the same except for the chain length.

For the HPC spectrum, the signals of the proton of the terminal methyl group were detected at 1.0 ppm and all the other protons were merged in the broad multiplets from 3.1 to 4.2 ppm. The spectra were also used to determine the DS for substituted samples by the method described by Ritcey et al. 1988, and the results are collected in Table 1.

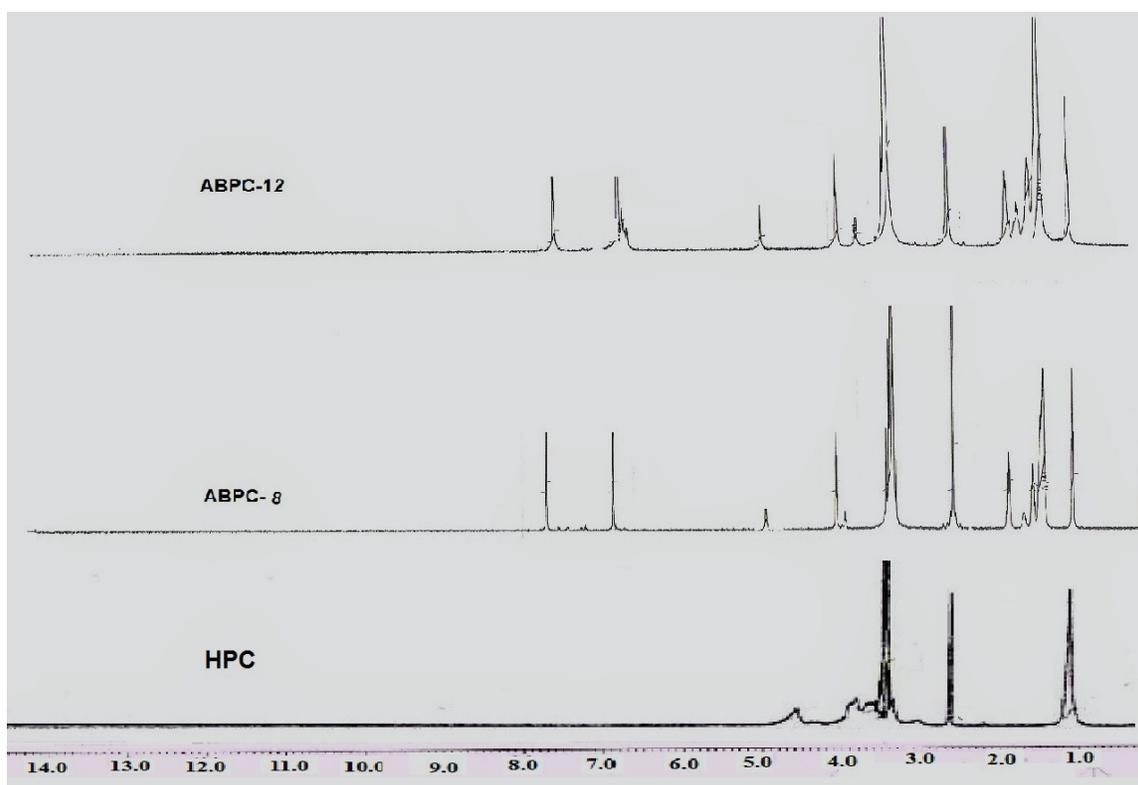


Fig. 3. ^1H NMR spectra of HPC, ABPC-8 and ABPC-12

Phase behavior of ABPC-*n*

Figure 4 shows the DSC heating thermograms for this series of ABPC-*n*. Melting (T_m), glass transition (T_g), and clearing (T_c) temperatures and their corresponding enthalpies (ΔH) are listed in the Table 1. The T_g and T_c values of ABPC-*n* were found to decrease as the length of alkoxy chain increased. These results indicate that not only the backbones but also the side chains are involved in these transitions; the transitions are affected significantly by the length of the alkoxy group. Extending the chain and moving the branch away from the core dilutes the effect of the branch, but LC phase stabilities are still very low when compared to the unbranched analogue, which in fact has a much lower melting point (Peter et al. 1997).

All these observations of the thermal properties of ABPC-*n* indicate that the methylene units in the side chains not only serve as “diluent” but also are involved in these phase transitions by providing contributions to the enthalpy of LC-isotropic transitions (Huang et al. 2007).

The $T_m - T_g$ temperature range was found to decrease when increasing the alkoxy chain length. This indicates that esterification of HPC with alkoxy benzoic acid may improve the processability of the final product.

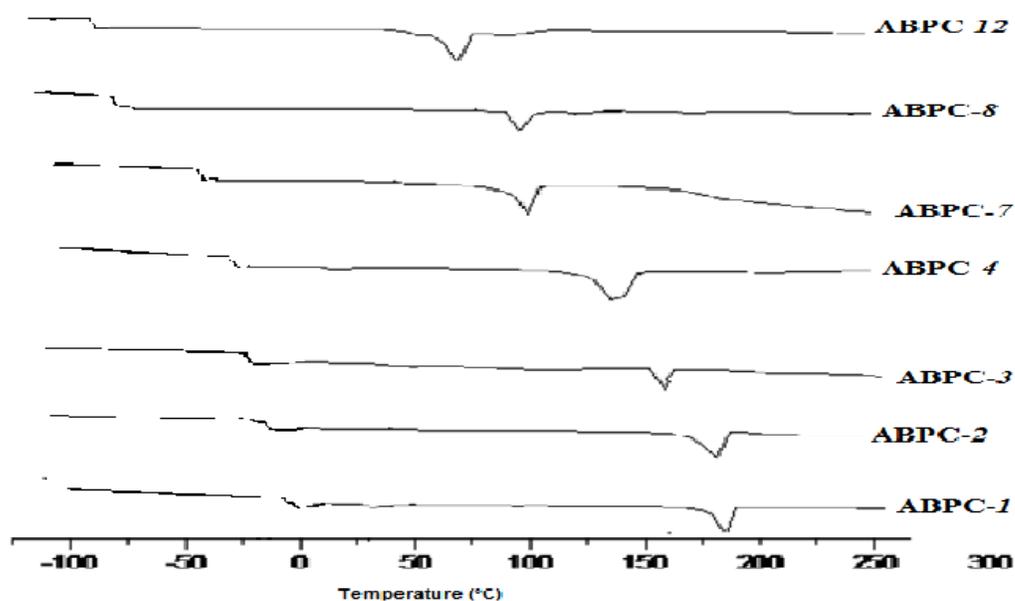


Fig. 4. DSC heating curves of ABPC-*n*

Table 1. Thermal Properties ABPC-*n*

ABPC- <i>n</i>	T_m (°C)	ΔH_m (J/g)	T_g (°C)	ΔH_g (J/g)	DS	T_c (°C)	ΔH_c (J/g)	$\frac{\Delta T(^{\circ}\text{C})}{T_c - T_m}$	$\frac{\Delta T(^{\circ}\text{C})}{T_m - T_g}$
HPC*	130	-	15	-	-	195	-	-	180
ABPC-1	182	184.7	-0.9	1.35	2.4	-	-	-	181.1
ABPC-2	178	131.1	-13.2	1.01	2.3	-	-	-	164.8
ABPC-3	155	118.1	-16.3	0.85	2.3	-	-	-	138.7
ABPC-4	147	89.2	-28.7	0.54	2.0	-	-	-	118.3
ABPC-7	101	109.1	-39.6	0.20	2.1	152.09	6.22	51.3	61.4
ABPC-8	100	38.3	-69.7	0.08	2	149.35	6.55	40.9	30.3
ABPC-12	72	78.8	-70.3	0.07	2	100	2.81	28	1.7

* Rutt et al. 1991

Rutt et al. (1991), reported that the T_g of unmodified HPC is 15°C . Upon heating, HPC becomes soft and then melts, leading to the formation of a mesophase at approximately 130°C (Charlet et al. 1987) and becomes isotropic at about 195 °C. As can be seen from Table 1, modification of HPC by 4-alkoxy benzoic acid led to a decrease in both T_g and T_m values, dependent on the length of the alkoxy chain. This further decrease in T_g and T_m values indicates that the side chain participates in enhancing the liquid crystalline properties of the HPC (Rutt et al. 1991).

From Table 1, it is clear that the samples ABPC-1, 2, 3, 4 did not show any thermotropic mesophase. Nevertheless they still exhibited lyotropic LC. On the other hand, the samples ABPC-7, 8, 12 showed both lyotropic and thermotropic liquid crystal behavior, as detected by both DSC and the PLM.

Figure 5 illustrates the DSC heating and cooling cycles of the sample ABPC-12, as an example, and their corresponding PLM images. The endothermic peak appearing at 56.7°C during the heating cycle is attributed to a transition between two solid modifications, since both phases below and above this temperature are solids.

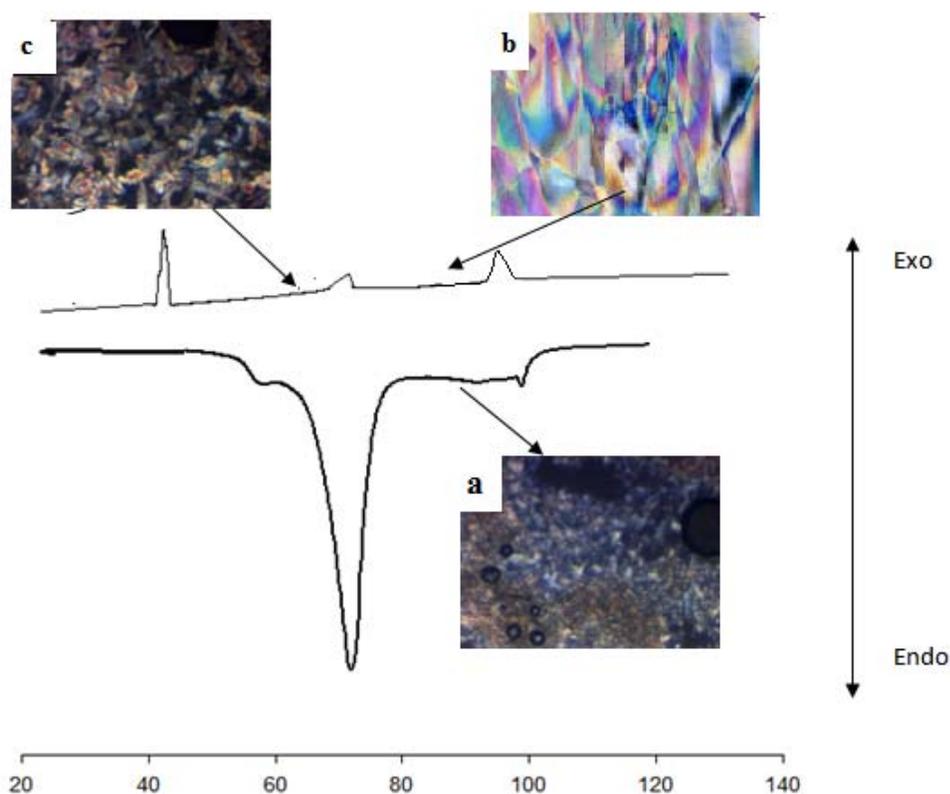


Fig. 5. DSC thermograms and the observed PLM images for ABPC-12 on heating; a) 85.0 °C, and on cooling b) 85.0 °C and c) 65.0 °C

The cholesteric phase appeared on heating at 72 °C and remained until it was transformed to the isotropic phase. On cooling, the thermogram showed the smectic A phase that started at 97.9°C, was transformed to cholesteric at 71.7° C, and finally solidified at 42.4°C. The behavior of the ABPC-*n* reveals that both the backbone of cellulose and the alkoxy chains of the acid have affected the formation of the liquid crystalline phase (Guo et al. 1989; Lenz 1985). Figure 6 shows the effect of the alkoxy-chain length on the phase behavior of the modified HPC prepared. As can be seen from the figure, both melt and clearing temperature decreased with increasing the chain length (*n*).

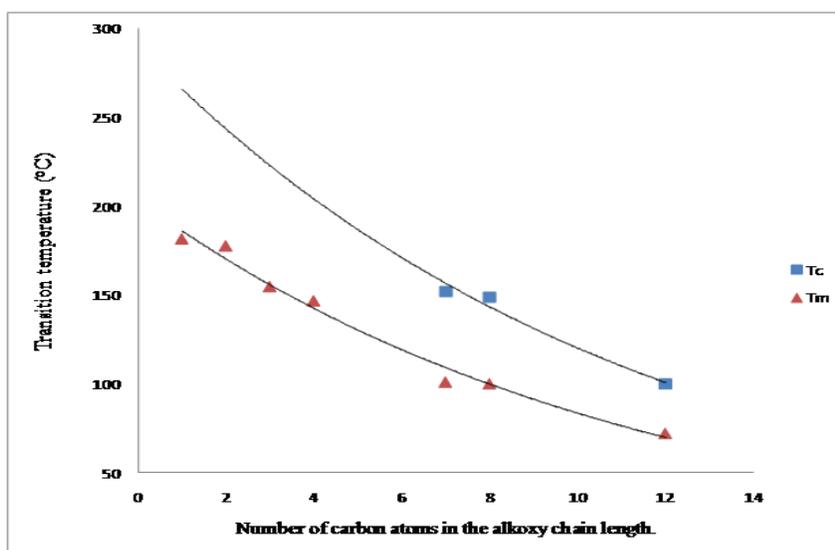


Fig. 6. Effect of alkoxy-chain length in the phase behavior (T_m (▲) and T_c (■)) of derivative ABPC-*n*

Figure 7 shows the lyotropic textures of ABPC-1 and ABPC-3 solutions (60% weight) in DMA. At concentrations lower than 44 and 43 wt% of samples ABPC-1 and ABPC-3, respectively, the mesophase was not formed, indicating that these concentrations are the critical ones for each of the samples, respectively.

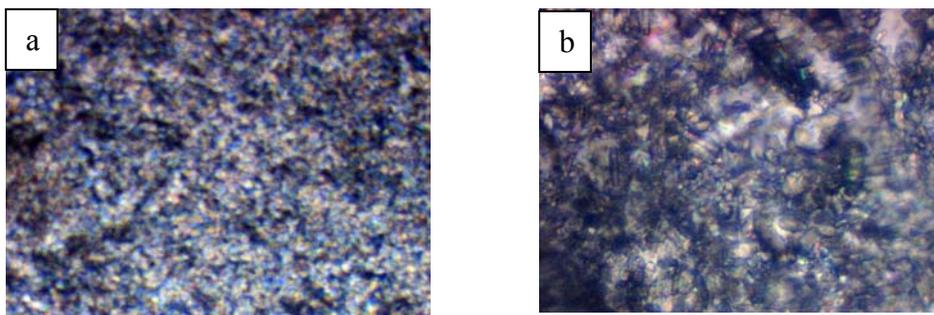


Fig. 7. PLM images of a (ABPC-1) and b (ABPC-3) in 60 wt % DMA at room temperature

By measuring the refractive indices (n) of solutions of DMA the critical concentration can be determined from the plot of the mean refractive index versus concentration (Fig. 8). The critical concentrations of ABPC- n were found to be close to each other in the range from 42% to 46%. It is known that the solution is isotropic at a concentration below the critical concentration, or anisotropic above that concentration.

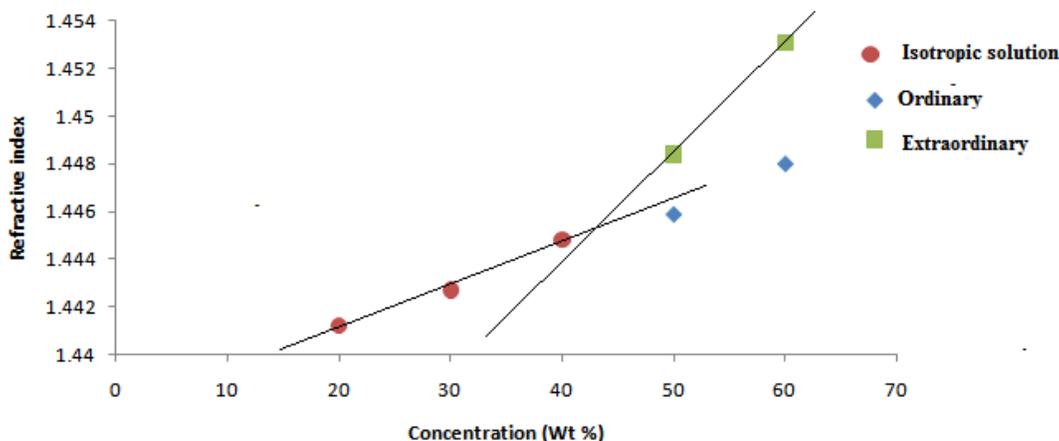


Fig. 8. Plot of the mean refractive index vs. the concentration for ABPC-12

Table (2) represents the extraordinary refractive index (n_e), ordinary refractive index (n_o), birefringence ($\Delta n = n_e - n_o$), average refractive index (n), and the critical concentration of the samples bearing even number of carbon atoms. It is clear from the table that upon increasing the length of alkoxy groups the birefringence (Δn) of ABPC- n decreases and the average refractive index was not varied regularly with the chain length (n).

Figure 9 illustrates the dependence of birefringence (Δn) on chain length. From the figure and table, one can observe that on increasing the length of alkoxy group, the birefringence of ABPC- n decreases and the average refractive index is independent on the chain length. It is notable that the derivatives with alkoxy group of odd number of carbon atoms do not show any mesophase and hence do not appear in Fig. (9).

Table 2. Optical Properties of ABPC- n

ABPC- n	n_e	n_o	Birefringence $\Delta n \times 10^3$	n	Critical Conc. (wt%)
HPC	1.4585	1.4524	6.1	1.4565	46
ABPC-2	1.4524	1.44329	9.11	1.4494	44
ABPC-4	1.4651	1.4579	7.2	1.4627	44
ABPC-8	1.4598	1.4557	4.1	1.4584	43
ABPC-12	1.4531	1.4509	2.2	1.4524	42

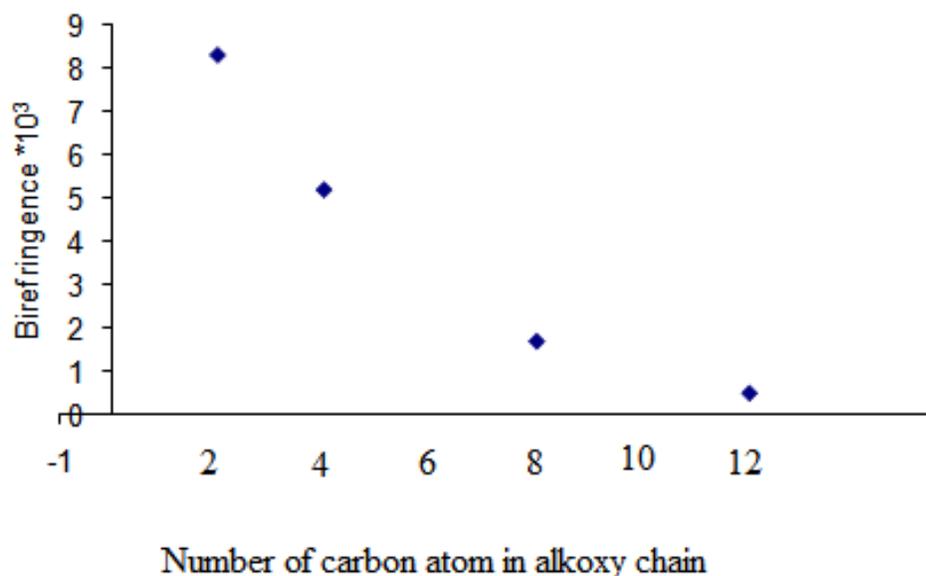


Fig. 9. Dependence of the birefringence on the number of the methylene groups of ABPC-*n*

It was reported by Yamagishi et al. (1990) that the flexible side chain not only assists the melting and the orientation of the cellulose backbone due to an increase in the mobility of the latter, but also plays an important role in the formation of helical structures in cholesteric mesophases. Also, many studies (Werbowj et al. 1976; Gray 1983; Huang et al. 2007) discussed the role of the side chain in the formation of cholesteric mesophase of specifically HPC.

Since HPC is rather hydrophilic, the hydrophilicity or hydrophobicity of substituent in HPC derivative might play an important part to form a cholesteric phase. Other thermotropic derivatives of HPC have been found also to form cholesteric mesophases with a pitch in the visible region (Guo, et al. 1983; Lenz, et al 1985; Yamagishi et al. 1990).

This study will be extended by placing more stress on HPC with increasing number of methylene groups in the alkoxybenzoic acid and study their chiral properties and packing properties to confirm the phase type using WAXRD.

Further investigations will be carried out concerning the liquid crystalline behavior of these cellulosic derivatives using X- ray diffraction, thermal analysis, and application to ready-made paper in the second part of this work.

ACKNOWLEDGMENTS

This work was financially supported by the “EGIDE” and Centre Français de Culture et de Coopération in Egypt. The author would like to thank Prof. Dr. Magdi M. Naoum, Dr. KROUIT Mohammed, and Prof. Dr. BELGACEM Naceur (director of LGP2) for their support.

REFERENCES CITED

- Bhadani, S. N., Tseng, D. L., and Gray, D. G. (1983). "Lyotropic and thermotropic phase formation from fractions of a semiflexible cellulosic polymer," *Macromol. Chem.* 184, 1727-1740.
- Charlet, G., and Gray, D. G. (1987). "Solid cholesteric films cast from aqueous (hydroxypropyl) cellulose," *Macromolecules* 20, 33-38.
- Gray, D. G. (1983). "Liquid crystalline cellulose derivatives," *J. Appl. Polym. Sci., Appl. Polym. Symp.* 37, 179.
- Guo, J. X., and Gray, D. G. (1989). "Preparation and liquid crystalline properties of (acetyl) (ethyl) cellulose," *Macromolecules* 22, 2082-2086.
- Hou, H. Q., Reuning, A., Wendorff, J. H., and Greiner, A. (2000). "Tuning of the pitch height of thermotropic cellulose esters," *Macromol Chem Phys.* 201, 2050-2054.
- Huang, B., Ge, J. J., Li, Y. H., and Hou, H. Q. (2007). "Aliphatic acid esters of (2-hydroxypropyl) cellulose. Effect of side chain length on properties of cholesteric liquid crystals," *Polymer*, 48, 264-269.
- Huang, Y., Liang, W., and Shen, J. R. (1995). "Molecular interactions and formation of lyotropic liquid crystals of hydroxyethyl cellulose acetate," *Polymer Bulletin* 35, 357-364.
- Lee, J. L., Pearce, E. M., and Kwei, T. K. (1997a). "Morphological development in alkyl-substituted semiflexible polymers," *Macromolecules* 30, 8233.
- Lee, J. L., Pearce, E. M., and Kwei, T. K. (1997). "Side-chain crystallization in alkyl-substituted semiflexible polymers," (1997). *Macromolecules* 30, 6877-6883.
- Lee, J. L., Pearce, E. M., and Kwei, T. K. (1998). "Liquid crystallinity and side chain order in partially substituted semi-flexible polymers," *Macromol. Chem. Phys.* 199, 1003.
- Lenz, R. W. (1985). "Characterization of thermotropic liquid crystalline polymers," *Pure and Applied Chemistry* 57, 977.
- Collings, P. J., and Hird, M. (1997). *Introduction to Liquid Crystals Chemistry and Physics*, Taylor and Francis Ltd., London and Philadelphia.
- Ritcey, A. M., Holme, K. R., and Gray D. G. (1988). "Cholesteric properties of cellulose acetate and triacetate in trifluoroacetic acid," *Macromolecules* 21, 2914-2917.
- Rutt, J. S., Takahashi, Y., and Karasz, F. E. (1991). "Phase behavior of thermotropic liquid crystalline/conducting polymer blends," *Polymer Bulletin*, 27, 261.
- Shimamura, K., White, J. L., and Fellers, J. F. (1981). "Hydroxypropylcellulose, a thermotropic liquid crystal: Characteristics and structure development in continuous extrusion and melt spinning," *Appl. Polym. Sci.* 26, 2165-2180.
- Tianhui H., Helou X., Jianbo X., Hailiang Z., and Erqiang C. (2010). "Design, synthesis, and characterization of a combined main-chain/side-chain liquid-crystalline polymer based on ethyl cellulose," *Cellulose* 17, 547-558.
- Tseng, S. L., Laivins, G. V., and Gray, D. G. (1982). "The propanoate ester of (2-hydroxypropyl) cellulose: A thermotropic cholesteric polymer that reflects visible light at ambient temperatures," *Macromolecules* 15, 1262-1264.
- Tseng, S. L., Valente A., and Gray, D. G. (1981). "Cholesteric liquid crystalline phases based on (acetoxypopyl)cellulose," *Macromolecules* 14, 715-719.

- Werbowj, R. S., and Gray, D. G. (1976). "Liquid crystalline structure in aqueous hydroxypropyl cellulose solutions," *Liq. Cryst.* 34, 97-103.
- Yamagishi T., Fukuda T., Miyamoto T., and Watanabe J. (1988). "Thermotropic cellulose derivatives with flexible substituents. II. Effect of substituents on thermal properties," *Polym. Bull.* 20(4), 373-377.
- Yamagishi, T., Fukuda, T., Miyamoto, T., and Watanabe, J. (1989). "Thermotropic cellulose derivatives with flexible substituents. I. Preparation of tri-O-(b-methoxyethoxy) ethyl cellulose and its cholesteric mesophase properties," *Mol. Cryst. Liq. Cryst.* 172, 17-25.
- Yamagishi, T., Fukuda, T., Miyamoto, T., Ichizuka, T., and Watanabe, J. (1990). "Thermotropic cellulose derivatives with flexible substituents. IV. Temperature dependence of cholesteric pitches exhibiting a cholesteric sense inversion," *Liq. Cryst.* 7(2), 155-161.
- Yamagishi, T., Fukuda, T., Miyamoto, T., Yakoh, Y., Takashina, Y., and Watanabe, J. (1991). "Thermotropic cellulose derivatives with flexible substituents. IV. Columnar liquid crystals from ester-type derivatives of cellulose," *Liq. Cryst.* 10(4), 467-473.
- Zugenmaier, P. (1998). In: *Handbook of Liquid Crystals*, D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, and V. Vill (eds.), Wiley-VCH, Weinheim, Vol. 3, p. 453.

Article submitted: May 24, 2010; Peer review completed: June 21, 2010; Revised version received: July 12, 2010; Accepted: July 13, 2010; Published: July 15, 2010.