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TEMPERATURE AND EXTERNAL ELECTROSTATIC FIELD INFLUENCE ON LYOTROPIC LIQUID CRYSTALS LAYERS STUDIED BY FTIR TECHNIQUE

Irina DUMITRASCU[1], Gabriel Grigore MARICIUC[2], Irina MACOVEI[3], Leonas DUMITRASCU[1] and Dana Ortansa DOROHOI[1]

The influence of temperature and the external electrostatic field on the phase transition of lyotropic liquid crystal PolyPhenyl MethAcrylic Ester of CetylOxyBenzoic acid (PPMAECOBA) in Tetra ChloroMethane (TCM) was studied with FTIR technique. The phase transition temperature was monitored by using the frequencies of the symmetric and antisymmetric vibration modes of –CH_2 *groups from the hydrophobic hydrocarbon endings of the polymer side chains. The main phase transition temperature was determined in the absence and in the presence of an external electrostatic field. An increase in the main phase transition temperature in the presence of the external field was revealed. The phenomenon was explained by the orientation of linear side chains of polymer perpendicular on the electric field intensity.*

Keywords: PPMAECOBA in TCM; lyotropic liquid crystal; FTIR spectra; vibration modes of -CH_2 groups; main phase transition.

1. Introduction

The liquid crystalline phases present both properties specific to liquids (flowing, forming drop, lack of form) and solids (anisotropy, ordering of component particles). The substances which are in a liquid crystalline phase, in given thermo dynamical conditions, are named mesogenes. As thermo dynamical parameters are modified, mesogenes have the ability to pass through different thermodynamic states, called mesophases.

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[1] ”Alexandru Ioan Cuza” University, Faculty of Physics, 11A, Carol I Bdv., RO700506, Iasi, Romania, e-mail: irina_dumitrascu2000@yahoo.com

[2] ”Gr.T. Popa” University of Medicine and Pharmacy, Faculty of General Medicine, 16, Universității Street, RO 7000115, Iași, Romania, e-mail: grigmariciuc@yahoo.com

[3] ˝Gr.T. Popa” University of Medicine and Pharmacy, Faculty of Pharmacy, 16, Universității Street, RO 7000115, Iași, Romania, e-mail: iricoman@yahoo.com

[4] ”Alexandru Ioan Cuza” University, Faculty of Physics, 11A, Carol I Bdv., RO700506, Iasi, Romania, e-mail: leonas_dumitrascu@yahoo.com

[5] ”Alexandru Ioan Cuza” University, Faculty of Physics, 11A, Carol I Bdv., RO700506, Iasi, Romania, e-mail: ddorohoi@uaic.ro

As function on the parameters controlling their properties, liquid crystals can be classified in thermotropic and lyotropic [1-3]. The thermotropic liquid crystals are obtained by melting crystals, while the lyotropic ones are obtained by mixing mesogenic molecules (usually amphiliophilic) with polar (water) or non-polar (tetra chloromethane) liquids.

The parameter controlling the thermotropic liquid crystalline phases is temperature, while liquid lyotropic crystals are obtained for given concentrations of the mixed components.

The main characteristic of the liquid crystalline phase is the gentile thermo dynamical equilibrium between the order and disorder, which can be easily modified by external parameters such as fields of forces (mechanical, electrical, magnetical) or temperature variation. Various applications [4-7] covering areas from medicine to electro optics were developed in the last years.

The permanent or induced electric dipole moments of the mesogenic molecules can be oriented either parallel or perpendicular to the molecular axis. The mesogenic molecules having their dipole moment parallel to the long axis tend to orient along the electric field lines. Contrarily, the mesogene molecules having the electric dipole moment perpendicular on their long axis tend to orient perpendicularly on the electric field lines. The liquid crystal molecules react collectively to the action of the electric field determining the rotation of their long axis until it becomes parallel or perpendicular on the lines of the electric field applied.

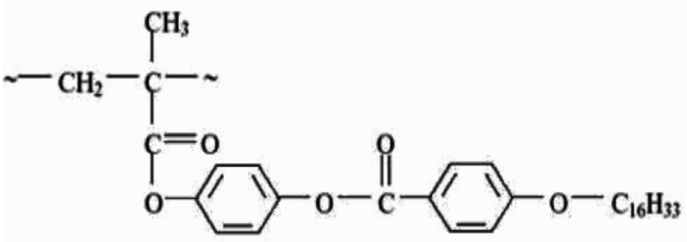
The influence of temperature and external electric field over the degree of order of lyotropic liquid crystals are analyzed in this paper.

The lyotropic liquid crystal has been obtained by mixing PPMAECOBA (Poly Phenyl Meth Acrylic Ester of CetylOxyBenzoic Acid) in Tetra Chloro-Methane (TCM) having a concentration of 10^{-2} g/cm^3 [8,9]. The optical properties of PPMAECOBA in TCM mesophase were characterized at room temperature and the birefringence dispersion was determined by the method of channeled spectra, in the visible range [10-12]. The previous experiments emphasized the dipolar collective orientation of the polymer side chains by the birefringence dependence on the characteristics of the electric field applied to the liquid crystalline layer under the study [11, 12].

The aim of this research is to study the temperature and external electrostatic field influence on the PPMAECOBA 10^{-2} g/cm^3 in TCM layer and to evidence the main phase transition [13, 14] from a more ordered gel phase, to a liquid crystalline phase.

2. Experimental

The lyotropic liquid crystal was obtained by mixing of PPMAECOBA 10^{-2} g/cm^3 in TCM. Structural formula of PPMAECOBA is given in Scheme 1.



Scheme 1 Structural formula of PPMAECOBA

Lyotropic liquid crystal was kept in a special cell of $CaCl_2$ transparent in IR range and temperature resistant. The cell [15] has plan parallel walls covered in interior by a transparent conductive layer which allows an electric field to be applied among them. Supplementary, the interior walls of the cell were covered with a 5% concentration lecithin solution in distilled water, necessary to improve the orientation degree near the cell walls [9, 10]. The walls of the cell are separated by three identical spacers which assure their parallelism. The thickness of the lyotropic crystal layer was 14μm.

The FTIR spectra, recorded with a FTIR BOMEM BM157 spectrometer, were averaged on 100 scans. The registrations were made in the spectral range [2800- 3000] cm^{-1}.

The influence of the solvent spectra was eliminated by subtraction. A Unicam Specac Temperature Controller was used. The FTIR spectra were recorded every 2^{0}C in the interval [26.0- 60.0]^{0}C.

An external electrostatic field obtained by a battery of 1V has been applied between the interior walls of the cell [16, 17].

3. Results and Discussions

The side chains of PPMAECOBA containing alkyl moieties are not solved in TCM and they are ordered by collective interactions. In this way, the polymer main chains are usually disordered, while the polymer side chains determine ordered spaces in mixture [18, 19]. The order in the side chains is determined by dipolar interactions [8, 9].

The lyotropic liquid crystals are very sensible to the action of external fields (mechanical, electrical, magnetic or thermal ones). The improving of order in the lyotropic liquid crystal [9, 15] in an external electrostatic field evidences the dipolar collective interactions between the side chains of PPMAECOBA in TCM.

The non-invasive spectral methods can give indications both about the local changes in the vicinity of the spectral active molecules and about the optical birefringence of the anisotropic sample [17, 20]. In this paper, FTIR spectra (symmetric and antisymmetric vibration modes) of the -CH_2 groups composing the alkyl side-chains of polymer, were used to search the changes in the degree of order of side-chains of PPMAECOBA. The atomic group –CH_2 shows two vibration bands attributed to symmetrical and antisymmetrical vibrations in the infrared range [13, 14].

The measurements in absence of the external electrostatic field had the initial data: $E = 0V/m$; $t = 26.0^0C \;\; \nu_s^0 = 2868.50cm^{-1} \;\; \nu_a^0 = 2938.90cm^{-1}$

When the electrostatic field was applied between the walls of the cell containing liquid crystalline layer the initial conditions were:
$E = 7.1410^4 V/m$; $t = 26.0^0C \;\; \nu_s^0 = 2869.40cm^{-1} \;\; \nu_a^0 = 2940.23cm^{-1}$

When temperature increases, the vibration bands of CH_2 groups from alkyl chains shift to the higher wavenumbers proving an increase in their motion liberty.

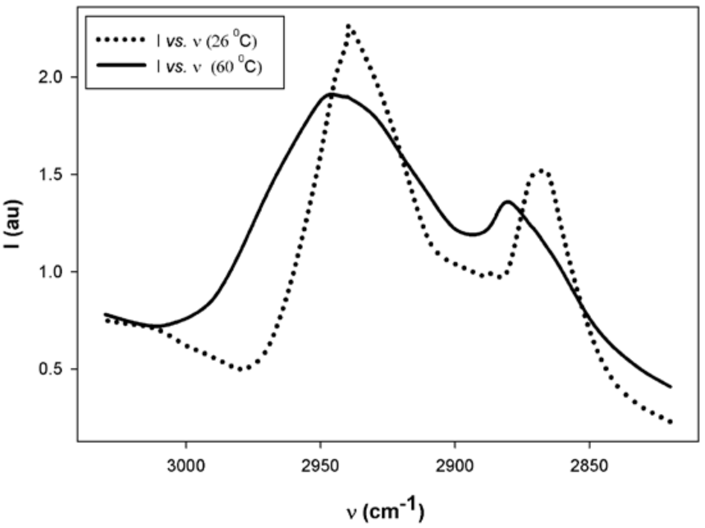


Fig.1 FTIR spectra of PPMAECOBA in TCM in spectral range 2800-3000cm^{-1} in absence of the electrostatic field for 26.0 ^{0}C and for 60.0 ^{0}C.

The dependence of the intensity (expressed in arbitrary units) on the IR radiation wavenumber (cm^{-1}) in the maxima of the vibration bands corresponding to symmetric (s) and antisymmetrical (a) modes of –CH_2 groups is illustrated in Figs.1 and 2 for the sample free of electrostatic field and in the presence of an electrostatic field of E=7.14 10^4 V/m. The plots correspond to the extreme temperatures achieved in our experiments.

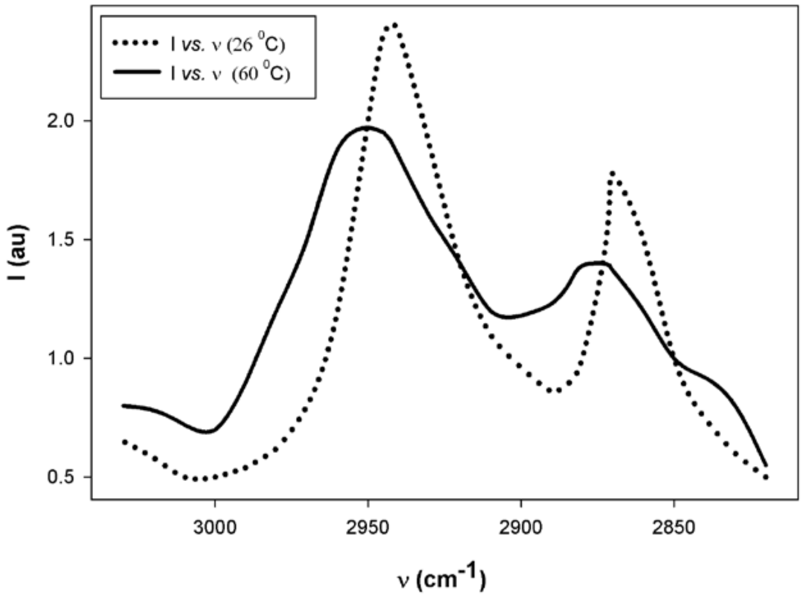


Fig.2 FTIR spectra of PPMAECOBA in TCM in spectral range 2800-3000cm^{-1} in an electrostatic field of 7.14$10^4$ V/m for 26.0 ^{0}C and for 60.0 ^{0}C

The dependence of the wavenumber in the maximum of the symmetric and asymmetric bands of –CH_2 groups of the alkyl side chains on temperature is illustrated in Figures 3 and 4.

For temperatures higher than 40 ^{0}C, sudden changes in the wavenumbers appear. The wavenumber in the maxima of the –CH_2 vibration bands of the polymer alkyl side chains vary with about 4.61 cm^{-1} (for symmetric mode) and 5.60 cm^{-1} (for asymmetric mode) in absence of the electrostatic field. When an electrostatic field of E=7.14 10^4 V/m is applied on the liquid crystalline layer, the corresponding spectral shifts are 3.90 cm^{-1} (for symmetric mode) and 4.67 cm^{-1} (for asymmetric mode).

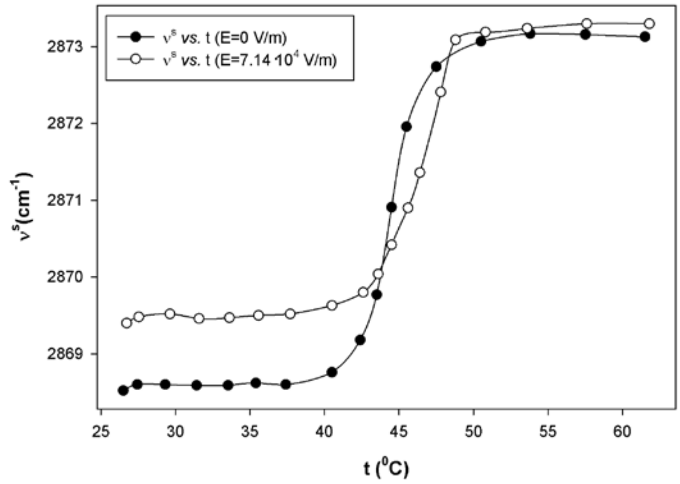


Fig. 3 Wavenumber vs. temperature for symmetric FTIR band of $–CH_2$ groups of PPMAECOBA in TCM sample in absence (E=0V/m) and in presence of electrostatic field (E=7.14 10^4 V/m).

The experimental data contained in Figs. 3 and 4 give information about the temperature of the main phase transition in the lyotropic liquid crystal PPMAEBOBA in TCM, temperature for which the number of the oriented systems in the lyotropic layer equalizes the number of those disordered. In the absence of the external electrostatic field this temperature is 44.5 ^{0}C, while in the presence of the electrostatic field this temperature is 46.5 ^{0}C.

By comparing the results obtained in the absence and in the presence of an external electrostatic field, one can conclude that the electric field increases the degree of order of the polymer side chains. This result has been also confirmed by the measurements of the birefringence of the PPMAECOBA in TCM layers by the method of channeled spectra [11-13].

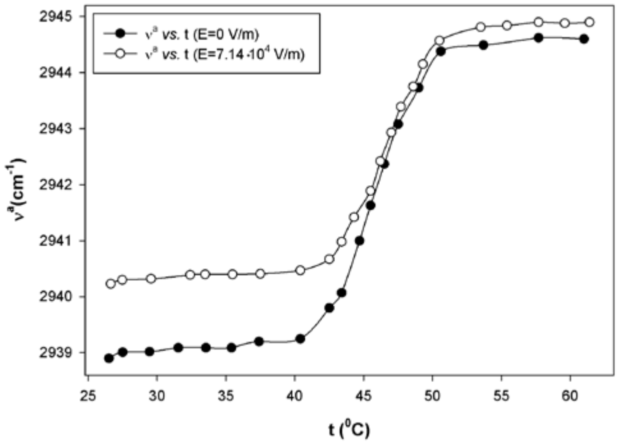


Fig. 4 Wavenumber vs. temperature for asymmetric FTIR band of $–CH_2$ groups of PPMAECOBA in TCM sample in absence (E=0V/m) and in presence of electrostatic field (E=7.14 10^4 V/m).

The electrostatic field increases the transition temperature with 2.0 °C, which is a very low temperature difference. This experiment demonstrates that the liquid crystalline phase of PPMAECOBA in TCM is very sensible to the temperature variations.

4. Conclusions

The experiments described in this paper demonstrate the dipolar character of the collective order in the mixture of PPMAECOBA and TCM.

The external electrostatic field applied on polymer anisotropic layer improves the orientation order and so, it increases the temperature of the main phase transition between the gel phase and the liquid crystalline phase.

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