

# Investigation of the structure and thermal behaviour of polymer liquid crystal / single wall carbon nanotubes nanocomposite

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**Abstract.** In the present work, nanocomposite of thermotropic polymer liquid crystal poly(heptane-1,7-diyl biphenyl-4,4'-dicarboxilate) and single wall carbon nanotubes was investigated. Nanocomposite films were casted from solution blended polymer liquid crystal and nanotubes. The structure and thermal behaviour of the nanocomposite were investigated by means of X-ray scattering and differential scanning calorimetry. The results show that there are two phase transitions on cooling and a single one on subsequent heating for both the neat polymer liquid crystal and nanocomposite. Hence, the smectic order of the polymer liquid crystal as well as its monotropic behaviour are preserved in the nanocomposite. The isotropic melt - smectic transition temperature in the nanocomposite is several degrees higher and the enthalpy of this process is much lower, suggesting heterogeneous nucleation of this phase on the surface of the nanotubes. The temperature of crystal structure formation during further cooling decreases in the nanocomposite showing a stabilization effect of the nanotubes on the smectic phase. Judging from the smaller enthalpy of the smectic-crystal phase transition and the new crystalline peak in the X-ray scattering patterns of the nanocomposite one could suggest a new crystalline form formation and this crystalline phase coexistence with smectic phases at lower temperatures.

## 1. Introduction

Invention of one and two dimensional nanomaterials, such as nanotubes, nanofibers, fullerenes and graphene open the challenging opportunity of developing new functional materials with improved or altered physical properties. Point of great scientific interest has become especially carbon nanotubes, CNT in their single wall, SW, and multi wall, MW, types because of their excellent mechanical, thermal, electrical and optical properties. By adding them into polymer matrices as nanofillers, one may design new nanocomposites [1-3]. In these new class of materials, new properties and morphologies were established and in many cases appropriate technological applications are already found. Polymer nanocomposites were mainly designed by solution blending, melt processing, and in situ polymerization [1,3]. The weak point in most cases is still the inhomogeneous dispersion and strong CNT aggregation



tendency. Attempts to orient and align CNT in polymer nanocomposites by infiltration, applying magnetic or electric field, shear force or mechanical stretching are widely probed but they still do not represent general and very effective way of achieving the goal. In many cases to overcome the low miscibility and to increase to polymer - CNT interactions CNT are modified by acid oxidation, plasma modification and radical reaction and adding functional groups [2] but such approach bears the risk of introducing number of defects in the original nanotube structure and this might alter the initial nanotube properties.

In the last decades, some attempts to explore the interaction between nanotubes and liquid crystals, LC, are also made [4-11]. In some cases, a layer of aligned nanotubes has been used to align and orient LC molecules in smectic [5] or nematic [6] phases on its surface. Some authors [7] also discuss that LC provide a distinctive environment for controlling the alignment CNT but CNT from the other side are important for the enhancement and fine-tuning of LC properties. In some cases, CNT may improve the thermal stability without altering the LC texture [8]. Gursel et al. [9] report to be able to tune the nematic LC molecules alignment by variation in the CNT concentration. The dispersion and possible alignment of CNT via magnetic field in presence of LC has been also discussed [10]. In present, some authors report already some applications of LC- CNT blends [11].

Even though, the polymer liquid crystals, PLC, combine the excellent mechanical properties with the strong tendency of self-organization in variety of different mesophases giving rise to excellent anisotropic physical properties, the possibility to combine them with nanofiller is just in its infancy and the number of scientific publications on this topic is very limited [12,13]. Such nanomaterials will have the additional advantage of easy processing and convenient molecular tailoring. PLC might be used in both respects to disperse/align the nanotubes and/or to influence and to give us the way to tune the PLC nanocomposite properties. The aim of the present work is to contribute to the investigations on polymer liquid crystal / carbon nanotube nanocomposites.

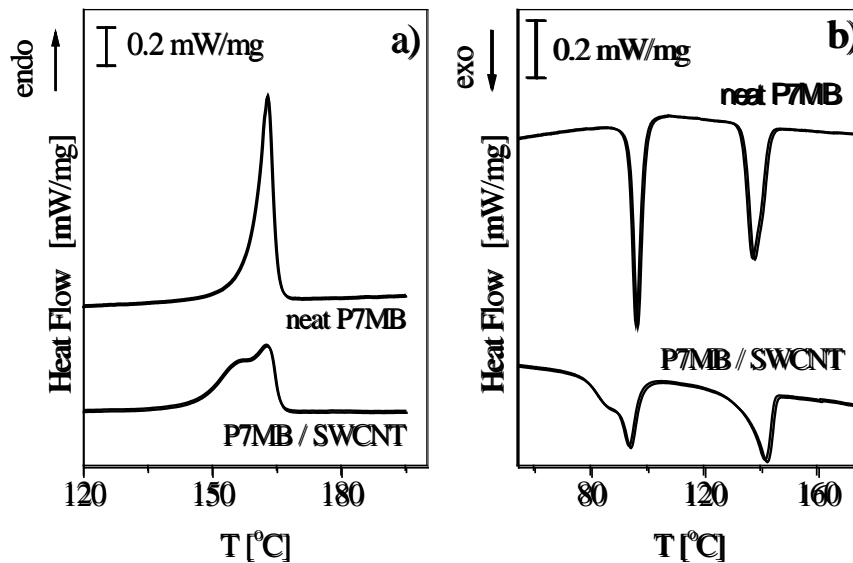
## 2. Experimental part

The nanocomposite was prepared by solution blending. As a first step the PLC poly(heptane-1,7-diyl biphenyl-4,4'-dicarboxylate), P7MB, and the single wall carbon nanotubes were separately dispersed in chloroform. P7MB, which synthesis is discussed elsewhere [14] was dissolved into chloroform (CAS:67-66-3, *Rai-chim, Bulgaria*) in a concentration 21.35 g/ml, at room temperature. The solution was bath-sonicated (*RH52 H, Bandelin Sonorex, Germany*) for 30 mins. Separately, single wall carbon nanotubes, SWCNT, (EC1.0, *Meijo Nano Carbon Co., Japan*) were added to chloroform in a concentration 0.14 mg/ml. The solvent was chosen as it is a second good solvent for SWCNT [15] and it is a common one for P7MB as well. A homogeneous suspension was achieved after 40 minutes of tip-sonication (*UP100 H Ultrasonic processor, Hielscher, Germany*) followed by 4 hours of bath-sonication. The P7MB solution and SWCNT suspension were then mixed and again bath sonicated for 4 hours. From the final suspension, films were casted. The solvent was left to evaporate overnight in a vacuum oven, at room temperature. The nanocomposite films were then heated to 195 °C and kept at this temperature of about 10 min, in order to get an isotropic melt and then either slowly cooled down to room temperature or quenched to room temperature (20°C), which is below the glass transition temperature of the P7MB  $T_g = 41^\circ\text{C}$ .

X-ray scattering experiments were performed at Deutsches Elektronen-Synchrotron DESY, PETRA III station, P12 line (*BioSAXS*). The experimental range of d-space values was from 0.37 to 7.2 nm ( $q = d/2\pi = 0.08722 \div 16.8777 \text{ nm}^{-1}$ ). Neat P7MB, quenched nanocomposite as well as slowly cooled samples were used.

Differential scanning calorimetry (*DSC 204 F1 Phoenix, Netzsch, Germany*), DSC, was employed to investigate the thermal behaviour and the phase transitions of the nanocomposite and to compare them with those of the neat PLC. The DSC equipment was temperature and sensitivity calibrated with 5 different materials. Small samples with a mass of about 5 mg were used. The samples were sealed in a pierced aluminium pan and the experiments were performed under argon atmosphere. The temperature protocol for the neat P7MB and for its composite was exactly the same. All samples were subjected

initially to temperature equilibration of about 30 mins, at 20°C then heated at a linear rate of 10 °C/min up to the isotropization temperature of 195 °C. In order to achieve complete homogenisation and to delete possible thermal prehistory the samples were kept at this temperature for 10 minutes. The melt was then cooled down to 0 °C by applying a linear cooling rate of 10 °C/min. In order to investigate the thermal stability of the nanocomposite, the same temperature protocol was repeated two time after allowing the sample to equilibrate at 20 °C for 30 minutes.



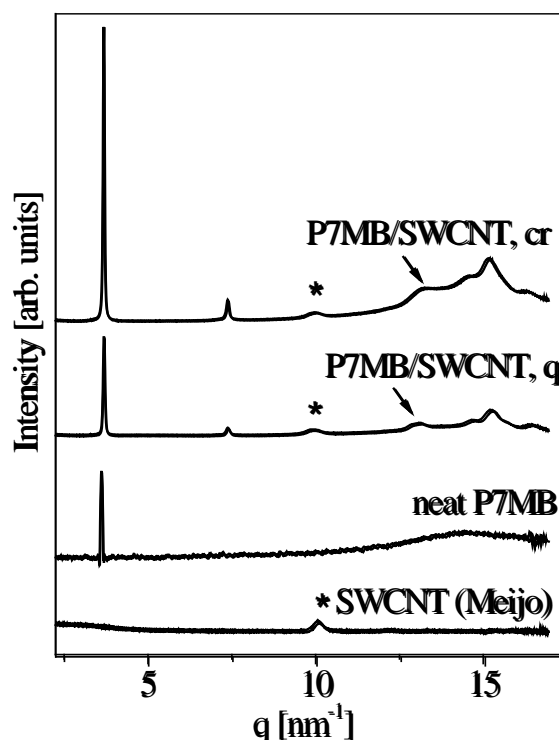
**Figure 1.** Differential scanning calorimetry thermograms of neat P7MB and nanocomposite P7MB / SWCNT: **a)** heating curves with melting endotherm at a heating rate 10 °C/min; **b)** cooling curves at a cooling rate 10 °C/min with two exotherms. The curves are translated vertically for better visualisation.

### 3. Results and discussion

The results from DSC show two phase transitions on cooling and single one on heating (figure 1) for the neat P7MB as well as for the nanocomposite of P7MB/SWCNT. Hence, the smectic order of P7MB is preserved in the nanocomposites as well as its monotropic behaviour. The transition temperatures of isotropic melt – smectic, I-Sm, for the nanocomposite ( $T_{I-Sm}^{P7MB} = 141.7^{\circ}\text{C}$ ) is several degrees higher than that of the neat polymer ( $T_{I-Sm}^{P7MB/SWCNT} = 137.4^{\circ}\text{C}$ ). In addition, the enthalpy of the neat polymer is  $\Delta H_{I-Sm}^{P7MB} = 16.1 \text{ J/g}$  is much higher than that of the nanocomposite, where  $\Delta H_{I-Sm}^{P7MB/SWCNT} = 11.7 \text{ J/g}$ . The reason for the observed difference could be heterogeneous nucleation of the smectic phase on the surface of the nanotubes.

On further cooling, the smectic phase of the neat P7MB crystallizes [14], where the temperature of this transition as obtained from the DSC thermograms (Fig.1) is  $T_{Sm-Cr}^{P7MB} = 96.1^{\circ}\text{C}$  and enthalpy  $\Delta H_{Sm-Cr}^{P7MB} = 16.3 \text{ J/g}$ . It seems that the situation in the nanocomposite is similar and a crystallization takes place but here the transition is presented by two exotherms center at  $T_{Sm-Cr,1}^{P7MB/SWCNT} = 93.7^{\circ}\text{C}$  and  $T_{Sm-Cr,2}^{P7MB/SWCNT} = 85.5^{\circ}\text{C}$ . The total enthalpy for this process is  $\Delta H_{Sm-Cr}^{P7MB/SWCNT} = 13.8 \text{ J/g}$ . The lower temperature suggests the stabilization effect of the nanotubes on the smectic phase. Interestingly, in both cases – quenching and slow cooling, a new crystalline peak appears (figure 2, marked with an arrow). This peak cannot be attributed to the

nanotubes only since they show a single peak, which still persists in the nanocomposite and its position is marked by a star in figure 2. Judging from the smaller enthalpy of the Sm-Cr phase transition and the new crystalline peak in the X-ray scattering patterns one would conclude that the nanofiller hinders the crystallization of the smectic phase and/or a new type of structure is formed. The mesogenic d-spacing for the neat P7MB is 1.73 nm, whereas for both different temperature treatments of the nanocomposite this spacing is 1.70 nm showing better order, expressed in existence of second order or the same d-spacing. The difference supports the idea of observing new crystalline form (or different smectic phase) in the presence of the nanofiller.



**Figure 2.** X-ray scattering curves of P7MB/SWCNT nanocomposite either quenched (q) or slowly cooled (cr) and those of neat P7MB as well as of SWCNT. The curves are translated vertically for better visualisation.

The melting temperature interval (figure 1) is almost the same for the neat polymer liquid crystal, having a maximum at  $T_{Cr-I}^{P7MB} = 162.8^{\circ}\text{C}$  and for its nanocomposite but the melting for the nanocomposite is represented by two endotherms with maxima  $T_{Cr-I,1}^{P7MB} = 156.0^{\circ}\text{C}$  and  $T_{Cr-I,2}^{P7MB} = 162.6^{\circ}\text{C}$ . Comparing the values one can attribute the higher temperature peak to the crystalline phase melting whereas the lower temperature peak should be connected to the coexisting smectic phase.

The temperature behavior of the P7MB/ SWCNT nanocomposite is very reproducible, which was proven by several consecutive DSC runs, where the thermograms did not show any difference.

#### 4. Conclusions

In the present work nanocomposite of PLC poly(heptane-1,7-diyl biphenyl-4,4'-dicarboxylate) and single wall carbon nanotubes were prepared by solution blending. The results show that in the nanocomposite the liquid crystallinity is preserved as well as its monotropic behaviour. The smectic phase appears by the mechanism of heterogeneous nucleation on the surface of the SWCNTs. The nanofiller has a stabilization effect on the smectic phase, shifting the smectic phase transition to higher temperature and crystallization of this smectic phase to lower temperatures. The low temperature phase is suggested to be a new crystalline form coexisting with the smectic phase, which could not undergo a

phase transition. The nanocomposite displays temperature stability in the sense of complete reproducibility at subsequent heating and cooling cycles.

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