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Influence of silver nanoparticles on the order parameter of liquid crystalline polymers

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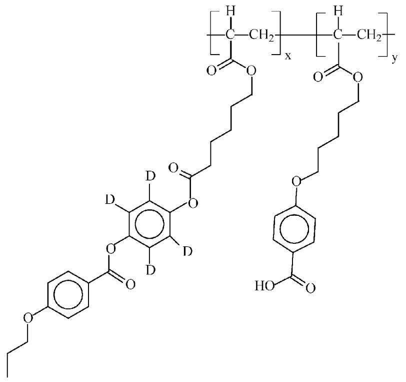
New polymer nematic nanocomposites are prepared containing 1.43–4.64 wt% of silver nanoparticles whose mean dimensions are 2–4 nm. According to ^{2}H NMR spectroscopic measurements, on increasing the content of metallic nanoparticles, the orientational order parameter S_{zz} of the nematic phase shown by the nanocomposites increases.

1. Introduction

A challenging direction in the modern physical chemistry of polymers concerns the development of advanced approaches for the preparation of a new class of mesomorphic polymer nanocomposites, which combine the properties of liquid crystals, polymers and specific characteristics of nanoscale objects [1–3]. In previous work [1] we described a novel approach for the preparation of this class of compound based on comb-shaped liquid crystalline (LC) polymers and silver nanoparticles, which are dispersed within the polymer matrix. The phase behaviour (type and temperature interval of mesophase) of such polymer nanocomposites depends on the content of silver nanoparticles. On increasing the concentration of metal particles in the LC copolymer, the glass transition temperature is found to increase, but the temperature interval of the LC phase decreases. This behaviour may be explained by chemical adsorption of cyanobiphenyl and carboxylate groups of the polymer on to the surface of the silver nanoparticles.

In this work, we studied for the first time the orientational behaviour of polymer LC nanocomposites containing silver nanoparticles in the presence of a magnetic field. The effect of nanoparticles on the phase behaviour and order parameter of LC polymers was also investigated. For this study we chose a random nematic copolymer, P, containing mesogenic groups of 4-{[6-(acryloyloxy)hexanoyl]oxy}phenyl-d_4 4-propoxybenzoate and fragments of 4-{[6-(acryloyloxy)hexyl]oxy}benzoic acid, and using them prepared a number of nanocomposites with different content of silver nanoparticles:



P (y=28 mol %) M_W=8×10^3; polydispersity 1.4, y = 29 mol %

2. Experimental

The syntheses of the monomers and copolymers were described in our previous publication [4]. LC nanocomposites P-Ag(z) (z denotes the concentration of silver nanoparticles) containing 1.43, 2.97, and 4.64 wt% of silver particles were prepared by the thermal reduction of silver ions from their complexes with diene molecules [1, 3]. In this procedure, to a solution of copolymer P in freshly distilled anhydrous tetrahydrofuran (THF) (1 wt%) the appropriate amount of (1,5-cyclooctadiene)-(hexafluoroacetylacetonato) silver(I) (Aldrich) was added. The solution was mixed using a magnetic

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stirrer for 24 h at room temperature, and the solvent was then evaporated on a rotory evaporator. For *in situ* reduction of metal ions the composite was held at 95°C for 7 days at normal pressure and then 48 h under vacuum.

The morphology of the synthesized nanoparticles was observed using a LEO 912AB OMEGA transmission electron microscope (TEM). The samples were prepared by dropping THF solution of the silver nanoparticles onto the Cu grids and observing at an accelerating voltage of 60–120 kV. Microcalorimetry studies were performed with a Mettler differential scanning calorimeter TA4000 with heating rate 10 K min^{-1}. Polarizing optical microscopy (POM) observations were made with a Zeiss polarizing microscope equipped with a Mettler FP-82HT hot stage controlled by a Mettler FP90 unit. X-ray diffraction patterns (XRD) were obtained from a 2 mm diameter capillary sample with a modified STOE STADI 2 diffractometer using Ni-filtered CuK$_\alpha$ radiation and a PSD linear position scanning detector. The UV spectra were recorded using a Unicam UV 500 spectrometer in the region 250–900 nm at a spectral resolution of 2 nm. IR spectra were recorded using a FTIR spectrometer (Biorad FTS 6000) in the region 400–4000 cm^{-1} at a spectral resolution of 1–4 cm^{-1} and an uncertainty <5% in absorbance.

^{2}H NMR spectroscopy measurements were performed in a field of 11.7 T at a frequency of 76.75 MHz (Bruker MSL 500 spectrometer). Single pulse excitation without proton decoupling with a spectral width of 45 kHz was used. The number of scans varied between 40 and 100; a standard temperature unit allowed control of temperature in the range of 300–450 K with an accuracy of 0.1 K. The orientation of samples was performed by slow cooling (1 K min^{-1}) of samples from isotropic melt to mesophase in the magnetic field of the NMR spectrometer ($\mathbf{H}=11.7$ T). The order parameter was calculated from the analysis of quadruplet splitting of the corresponding ^{2}H NMR spectra [5].

3. Results and discussion

In the present work, to obtain LC nanocomposites we used a procedure based on the *in situ* reduction of silver ions. During heat treatment of the LC polymer mixture P with silver–diene complexes the formation of metal nanoparticles is the result of oxidation of organic olefin ligands by Ag$^+$ ions. The formation of silver nanoparticles was proved by the appearance of a wide band in the UV spectra of both solutions and films of the P-Ag composites; this band is due to the plasmon resonance of conducting electrons, and maximum absorption is seen at 418–428 nm (figure 1). Transmission electron microscopy revealed that the silver nanoparticles are spherical. The mean diameter of nanoscale particles is 2–4 nm (figure 2); this parameter increases slightly with increasing silver content in the P-Ag nanocomposites. The XRD patterns of the composites contain several peaks at $2\theta=38.1$, 44.2, 64.4 corresponding to the reflections of [1 1 1], [2 0 0] and [2 2 0] planes for the cubic Ag phase. The lattice constant for the cubic cell was calculated to be 4.087 Å, which is in good agreement with the reported data for pure silver.

The phase behaviour of the LC nanocomposites was studied using DSC and POM. On increasing the content of silver nanoparticles in the P-Ag composite (figure 3), the clearing temperatures (T_C) decreased somewhat. The LC copolymer and nanocomposites show a nematic phase. This is confirmed by the low associated enthalpy change (1.1–1.7 J g^{-1}) and by the presence of a marble texture, which is typical of a nematic phase.

Figure 4 shows characteristic ^{2}H NMR spectra of an LC nanocomposite P-Ag(2.97). In the case of an

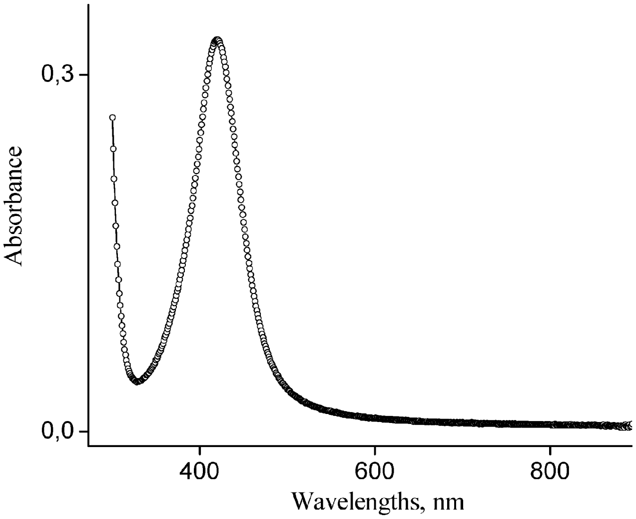

Figure 1. UV-Vis spectra for LC nanocomposite P-Ag (2.97) in THF.

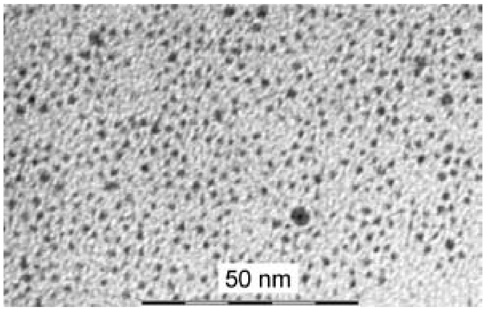

Figure 2. Transmission electron microscopy image of nanocomposites P-Ag(1.43).

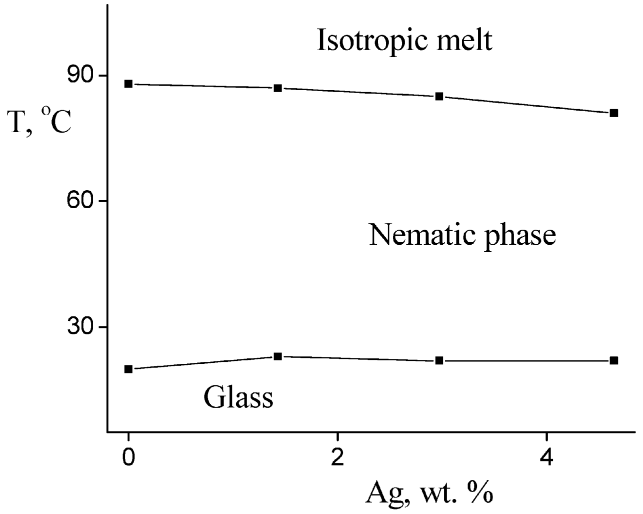

Figure 3. Phase behaviour of polymer LC nanocomposites P-Ag.

isotropic melt (at 362 K), the spectrum consists of a singlet with a half-width at a maximum of ~1.2 kHz. On cooling the LC polymers under the action of a magnetic field, the signal is split into two components. The split signal, corresponding to the deuterons of the aromatic ring and the specific line shape of the corresponding NMR spectra, clearly indicates the orientation of an LC nanocomposite. It is interesting to note that for copolymer P and nanocomposite, the transition of the isotropic melt to the nematic phase is associated with a narrow biphasic region (1–2°C). This is seen clearly in the spectra recorded at 357 and 358 K.

The temperature dependence of the order parameter S_{zz} for the LC copolymer P and the P-Ag nanocomposites are shown to be virtually identical (figure 5). In the vicinity of the (liquid crystal)–(isotropic melt) phase transition, S_{zz} changes abruptly. At the point of the phase transition, the order parameter S_{zz} is equal to 0.36–0.40; as the temperature is decreased, S_{zz} increases.

Let us consider the effect of the content of silver nanoparticles on the orientational characteristics of the LC polymer P. As found for the first time in this work, the silver nanoparticles do not prevent the orientation of the mesogenic groups of the comb-shaped LC copolymer in the presence of a magnetic field. Furthermore, with increasing content of metallic particles, the order parameter S_{zz} markedly increases (figure 6).

In our opinion, the orientational behaviour of the LC nanocomposites is rather surprising. In the presence of minor amounts of silver nanoparticles (below 4.64 wt%), the order parameter increases by ~15 %. The above effect of the content of silver nanoparticles on order parameter may be expected for rod-like ferromagnetic particles [6]. As is well known, anisotropic ferromagnetic particles are able to arrange in the magnetic field; therefore, they can improve the orientation of mesogenic groups and decrease the time of director reorientation of a liquid crystal in the presence of a magnetic field. However, the silver nanoparticles studied here are known to be nonmagnetic and spherical. In other words, the magnetic field should exert no orientational effect on silver

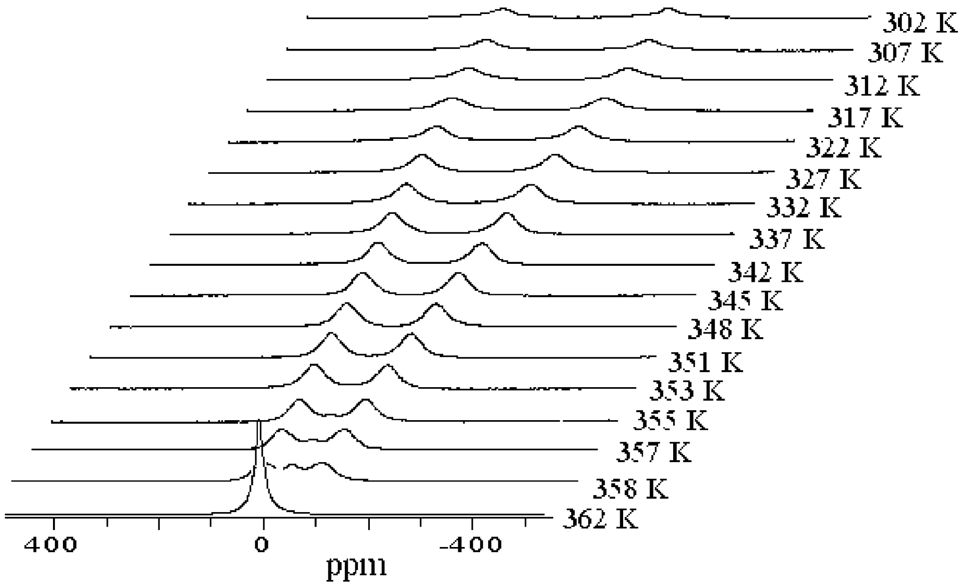

Figure 4. The temperature dependence of ^{2}H NMR spectra of LC nanocomposite P-Ag (2.97).

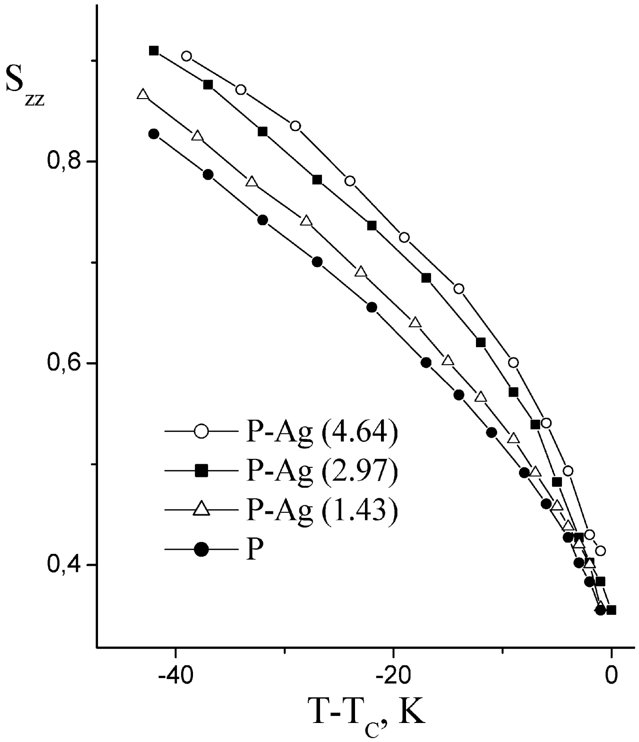

Figure 5. The influence of temperature on order parameter S_{zz} of nematic copolymer P and nanocomposites P-Ag.

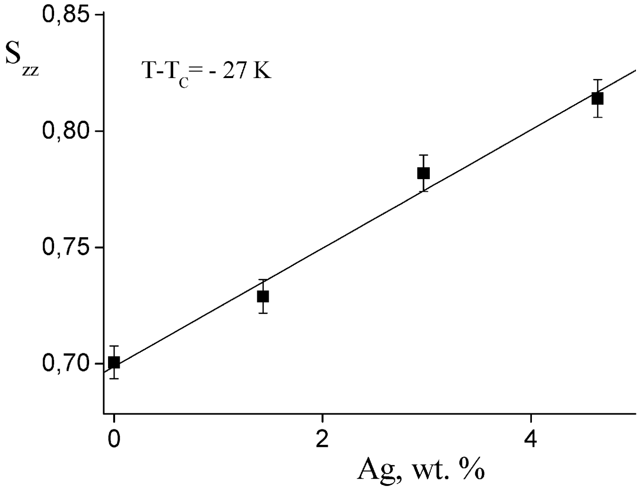

Figure 6. The influence of content of silver nanoparticles on order parameter S_{zz} of nematic nanocomposites P-Ag.

nanoparticles and should not affect the orientation of the mesogenic groups in LC copolymer P.

As a working hypothesis, we believe that the behaviour described may be associated with an improved order of the nematic phase (at the scale of individual domains) in the presence of silver nanoparticles. For example, one of the reasons behind over observations may be an increased smectogenic character of the nematic composites, which is provided by the chemical adsorption of side groups of LC copolymer P on the surface of silver nanoparticles. In other words, we assume that metallic nanoparticles are not just inert fragments in the LC polymer P-Ag nanocomposite, but rahter they are able to exert a marked effect on the LC order of phases in the nanocomposites.

One should note the important role of LC polymer in the stabilization of silver nanophase. The effective interaction of the functional groups of the LC polymer with the silver nanoparticles assists the formation of a protective organic layer on the surface of the silver nanoparticles. This process prevents their agglomeration in the course of the chemical reduction of silver ions and upon the repeated heating–cooling cycles during experimental studies of the phase behaviour of nanocomposites and NMR spectroscopic experiments.

Several basic mechanisms of interaction of functional groups of low molecular mass compounds and polymers with metallic nanoparticles have been described in the literature [7]. The most stable polymer–nanoparticle complex is formed when macromolecules are sorbed on the particles due to the formation of covalent, ionic or coordination bonds. Taking into account the chemical nature of mesogenic groups of copolymer P, one may assume that only carboxylic groups of oxybenzoic acid are able to form strong interactions with the surface of silver nanoparticles. This conclusion is also supported by IR spectroscopy of the P-Ag composites and by the literature data on the related compounds. According to the IR spectra (figure 7), some carboxylic groups of the oxybenzoic acid in the P-Ag nanocomposites exist in their deprotonated state. This conclusion is supported by the presence of two characteristic carboxylate ion absorption bands at 1544 and 1595 cm^{-1}. Interaction of aromatic acids with finely dispersed silver particles has been studied in more detail using IR and Raman spectroscopy [8, 9]. As was shown, this interaction is accompanied by deprotonation of carboxylic groups and formation of organic ions, whose long axes are oriented perpendicular to the surface of the metallic particles. At the same time, a far more efficient interaction is observed for carboxylate ions, including the salts of saturated carbonic acids.

Thus, from studying phase behaviour with optical microscopy or calorimetry one may conclude that silver nanoparticles exert a weak effect on the phase behaviour of nematic copolymer P. However, as the content of silver nanoparticles in the P-Ag composites is increased, the ordering of LC phase of the nanocomposites is markedly improved as shown by NMR

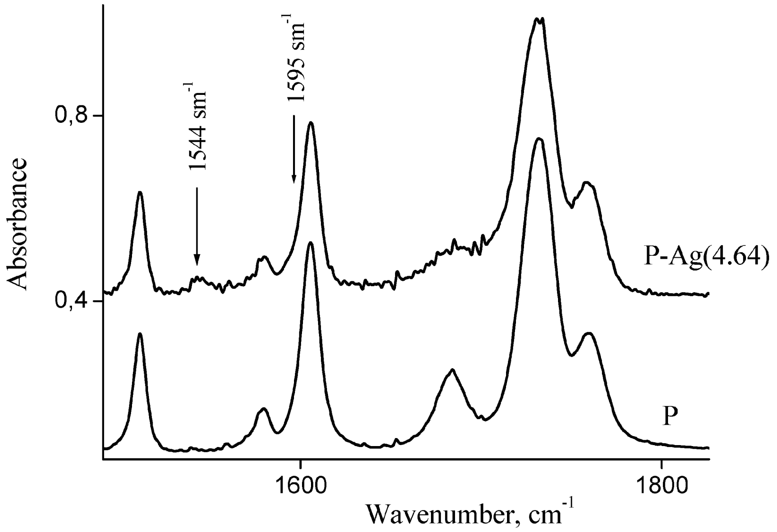

Figure 7. IR spectra for LC copolymer P and nanocomposite P-Ag (4.64).

spectroscopy. Further work will now be focused on studying the mechanism and specific features of this phenomenon.

Undoubtedly, these observations offer new and promising routes for the practical application of polymer LC nanocomposites because they still preserve the characteristic ability of liquid crystals to form oriented structures under the action of external fields. In this case, the polymer matrix not only assists the stabilization of shape and dimensions of nanoparticles, but also exhibits the valuable properties of polymers, including high mechanical characteristics, and film- and fibre-forming properties, as well as the ability to freeze and fix the supramolecular structure of liquid crystals in the glassy state.

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References

[1] E.B. Barmatov, D.A. Pebalk, M.V. Barmatova. *Langmuir*, **20**, 10868 (2004).
[2] G.A. Shandryuk, A.V. Rebrov, R.B. Vasiliev, S.G. Dorofeev, A.S. Merekalov, A.M. Gas'kov, R.V. Talroze. *Polymer Sci. B*, **47**, 266 (2005).
[3] E.B. Barmatov, A.S. Medvedev, D.A. Pebalk, M.V. Barmatova, S.B. Zezin, N.A. Nikonorova, V.P. Shibaev. *Polym. Sci. A*, **A. 48**, 665 (2006).
[4] E.B. Barmatov, Tao Yongjie, G.F. Kolbina, I.N. Stennikova, N. Akhmedov, M.V. Kozlovsky, V.P. Shibaev. *Polym. Sci. A*, **43**, 1 (2001).
[5] E. Barmatov, L. Chiezzi, S. Pizzanelli, C.A. Veracini. *Macromolecules*, **35**, 3076 (2002).
[6] F. Brochard, P.G. de Gennes. *Phys. Fr.*, **31**, 691 (1970).
[7] K.J. Klabunde (Ed.). *Nanoscale Materials in Chemistry*. Wiley, New York (2001).
[8] M.W. Lee, M.S. Kim, K.J. Kim. *Mol. Struct.*, **415**, 93 (1997).
[9] H.S. Han, C.H. Kim, K. Kim. *Appl. Spectrosc.*, **52**, 1047 (1998).