

Monochelic copolymer as a matrix for cholesteric composites with gold nanoparticles



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ABSTRACT

Copolymer based on acrylic acid derivatives containing mesogenic groups in the side chains and thiol group at the end of the backbones has been synthesized to create a liquid crystal cholesteric composite with the gold nanoparticles (NPs). Reversible addition fragmentation chain transfer (RAFT) polymerization carried out using asymmetric agent makes easy producing monochelic macromolecules with mesogenic groups in the side chains and functional end-groups. Modification of the terminal groups of the copolymer does not change the type and properties of its liquid crystal phase. The monochelic copolymer obtained by modifying residue of RAFT agent located at the end of the main chain. The separation of the functional group that binds to NP and the mesogenic groups allows creating liquid crystalline (LC) material containing exceptionally high concentration of (up to 30 wt %) of gold NPs (~4.8 nm in size). The distribution of NPs in the composite film is uniform and does not interfere with the LC order of the matrix. This ordering takes place on a scale which corresponds to at least micron-sized cholesteric domains. The thin films obtained demonstrate the coexistence of optical properties of both cholesteric liquid crystals with a stop band and plasmonic gold nanoparticles.

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1. Introduction

Recently, composite materials based on NPs and LC polymers have attracted a lot of attention. The properties of NPs can be controlled by changing their size and shape. This can be achieved by adjusting the conditions used for the synthesis of NPs. The most striking examples are semiconductor NPs with quantum size effect which provides the control over their optical properties [1]. Other examples include metallic NPs with plasmonic and magnetic properties [2]. One of the most attractive areas of nanomaterials

research appeared in the last decade is chiroplasmonics [3]. Chiral assembly of plasmonic metal nanoparticles into well-controlled nanoarchitectures is the key factor to the development of nanostructured metamaterials and promising applications in biosensor [4,5] nonlinear optics [6,7], negative refraction materials [3], broadband circular polarizers [8] and catalysts [9,10]. A very delicate approach to creating chiroplasmonic systems was developed in several research studies [11–14]. Kumacheva and co-workers have demonstrated a chiral plasmonic solid film made of gold nanorods and chiral nematic ordered cellulose [15] whereas the tunable chiral distribution of the aligned anisotropic silver nanowires with long-range order obtained through the CNCs liquid crystal mediated realignment is shown in Ref. [16].

Thermotropic liquid crystals (both low molecular weight and polymeric) are matrices, that may affect the properties of NPs. The formation of anisotropic medium surrounding NPs may control their optical properties due to orientationally ordered co-alignment of gold nanorods in chiral liquid crystalline phase with polarization

Abbreviations: LC, liquid crystal; NPs, nanoparticles; AuNPs, gold nanoparticles; CP, copolymer; SPR, surface plasmon resonance; TEM, transmission electron microscopy; SAED, selected area electron diffraction; FTIR, Fourier transform infrared spectroscopy; RAFT, reversible addition-fragmentation chain transfer; DSC, differential scanning calorimetry.

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dependent properties [17]. Moreover, as shown in Ref. [18] NP chirality created by chiral ligands attached can be transmitted to the surrounding nematic medium.

However a limited compatibility of NPs and LC matrix imposes considerable restrictions on the properties of these materials. One of the major issues of the combining inorganic NPs with the LC medium is to achieve their compatibility while the anisotropy of matrix is preserved. The common tool considered as a strategy to provide the necessary miscibility of the components is the modification of the NP surface with organic ligands having the chemical structure similar to that of liquid crystals [19–21]. However, even this approach does not work in every case and also depends on the NPs size, ligands length, and the overall composition [22–24]. The content of NPs in LC with no phase separation usually varies from 0.1 to several weight percents. As for NPs in LC polymer matrices, the major amount of research was done on carbon nanotubes (CNT) via dispersing the latter in LC elastomers [25–32]. Nevertheless, the relationship between the amount of embedded NPs and the retention of LC properties of a polymer matrix is still poorly understood. LC polymers have the advantage of being able to generate nonequilibrium composites that retain stability for months [33]. A possible reason for this is a hindered diffusion of NPs in the matrix.

Our approach to embedding NPs in a polymer matrix considers their chemical binding to the functional groups of macromolecules either in the side chains [34,35] or at the end of a backbone. One of the solutions to maintain the LC ordering of a matrix with a high concentration of NPs is the spatial separation of the mesogenic groups and groups capable of binding the surface of NPs. Monochelic polymers with side chains which contain mesogens and terminal functional group for a selective formation of the bond with the surface of the NP may be considered as a model of such macromolecules.

That is why the primary goal of this study was to create nanocomposites based on LC monochelic polymer matrix containing gold NPs with a special attention at the retention of LC properties of the polymer matrix at high concentration of NPs approaching several tenth of weight percents.

The selection of gold NPs was made for two reasons. First, the optical properties of gold NPs strongly depend on the inter-particle distance, especially when it becomes comparable with the size of NPs [36,37]. Therefore, the aggregation of the NPs can be observed by optical methods directly in the process of composites preparation. Second, it is possible to synthesize a polymer with mesogenic groups which do not participate in the formation of a bond with NPs and remain free for a LC ordering, whereas the thiol group at the end of a macromolecule may react with the surface of the gold. Several attempts were described to prepare LC polymer molecules with functionalized end-groups using reversible addition fragmentation chain transfer (RAFT) polymerization [38–44]. The use of RAFT polymerization allows us to synthesize the polymer monochelic macromolecules that carry a functional thiol group. We can further follow any change in the LC mesophase structure and properties of LC polymer/NP composites which are prepared with the contribution of the thiol functional groups at the end of polymer backbones in the reaction with the NP surface.

The choice of the LC polymer structure was motivated by the fact that composites containing gold NPs in the LC matrix show that these particles are displaced in the structural defects [45–47]. It is particularly true for cholesteric matrices in which the generation of large number of defects containing NPs would not allow for creating the preferential planar orientation and the observation of the stop band which is characteristic for such liquid crystals. That is why the acrylic cholesteric copolymer (CP) containing 4-methoxyphenyl-4-(6-acryloyloxy-hexyloxy)benzoate (MPHb-6A), 4-(6-acryloyloxy) hexyloxy cholesteryl benzoate (BACH-6A) and 4-(ω-

acryloyloxy) hexyloxy benzoic acid (BA-6A) monomeric units CP (5-75-20) (see Chart 1) was chosen. As we demonstrated before, copolymers of that family possess cholesteric order in a broad temperature range when they are prepared via conventional radical polymerization in solution [48].

2. Results and discussion

2.1. Chemical structure and molar mass characteristics of the synthesized LC copolymer

LC CP has been prepared by RAFT polymerization using 2-cyano-2-propyl dodecyl trithiocarbonate (CPDTC) as a chain transfer agent (CTA) and AIBN as an initiator, and subjected to modification aiming at the synthesis of thiol-functionalized LC polymers. According to the synthetic strategy chosen, one needs the formation of majority of the chains bearing trithiocarbonate terminal group. This may become possible only if the following conditions are met: 1) CTA agent should be effective for the given monomer; 2) CTA/initiator molar ratio should be as high as possible. Thus, for carrying out the synthesis we have chosen CPDTC that according to literary data, has no influence on the polymerization kinetics and contains cyanoisopropyl leaving group, which is known as a “good” leaving group for majority of methacrylates [43].

The choice of CTA/initiator molar ratio and their absolute concentrations depends on the targeted molecular weight of the polymer and the reasonable values of polymerization rate can be achieved. Due to limitation of monomer solubility (<2 mol/L) in organic solvents CTA and AIBN concentration were taken as 0.01 and 0.001 mol/L, respectively. The average molecular weights of the synthesized polymers and their molecular weight distribution, obtained by gel permeation chromatography are summarized in Table 1.

The NMR of the spectrum of CP is presented in Fig. S1–S1. Comonomer composition was calculated by using integrated peaks 8.07 ppm (2H MPHb-6A, “I1”), 7.95 ppm (2H BA-6A plus 2H BACH-6A, “I2”) and 5.37 ppm (1H BACH-6A, “I3”). The calculated ratio of the comonomer units m:n:k is 4:73:23 which is in good agreement with the monomers composition, prepared in solution before the polymerization (5:75:20).

As shown by Ledin et al. [49], the presence of the thioester group in RAFT-synthesized macromolecules can be detected by UV spectroscopy with a peak at about 310–320 nm. Unfortunately, the UV spectra of CP (5-75-20) and CP (5-75-20)-SH in solution do not

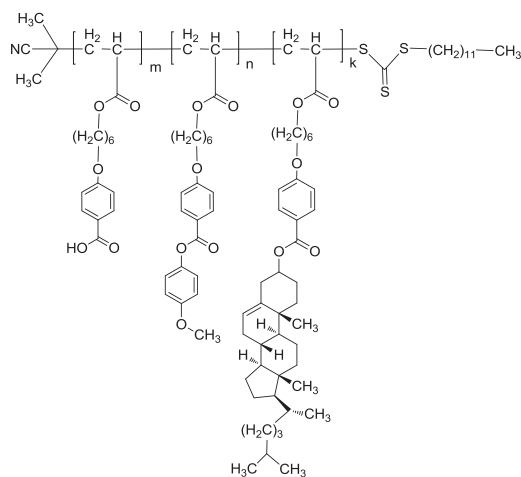


Chart 1. Structure of copolymer prepared via RAFT polymerization. Ratio m:n:k = 5:75:20.

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