Synthesis and microscopy studies of polymer nanostructures

L. Poláková[1], Z. Sedláková[1], P. Látalová[1], and H. Valentová[2]

1. Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Heyrovský Sq. 2, Prague, Czech Republic, 162 06
2. Faculty of Mathematics and Physics, Charles University,V Holešovičkách 2, Prague, Czech Republic, 180 00

polakova@imc.cas.cz
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Liquid-crystalline (LC) polymers are attractive materials. Due to their properties, they can be used in photonic, ferroelectric and antiferroelectric applications or in non-linear optics [1-2]. Introduction of a mesogen into polymer side chains usually leads to the preparation of such polymers. Azobenzene-based mesogens belong to an important class of photochromic materials with properties based on cis/trans isomerization of azochromophore group [3-4].

Mesogenic thiols with azobenzene as a rigid part and with various substituent (H-, methoxy-, butoxy- or octyloxy-, **Figure 1**) in *para*-position of azobenzene ring were synthesized by multi-step syntheses. The thiols were grafted onto double bonds of telechelic poly(butadiene)diol (M_n ~ 2 400, functionality f_n = 2, 60 mol. % of 1,2-butadiene units) via radical addition in the presence of 2,2´-azobis(2-methylpropionitrile) (AIBN). Initial mole ratio of thiol/double bonds varied in the range of 0.2 to 1.0. Influence of the azobenzene subtituent on the extent of modification reaction was estimated using elemental analysis, size-exclusion chromatography and ^{1}H NMR-spectroscopy.

Generally, LC materials (polymer or low-molecular) are anizotropic substances showing many important properties, among them optical birefringence [5]. Due to this phenomena, polarizing optical microscopy is one of the physical method allowing characterization of matter LC-state. Using the above mentioned type of microscopy, temperature-dependent formation of characteristic LC-textures was observed (**Figure 2**). The detection of the LC-state and mesophase types were confirmed by differential scanning calorimetry and X-ray analysis, too. It was found that the substituent on mesogen plays an important role in thermal behavior of both the thiols and the obtained comb-like polymers.

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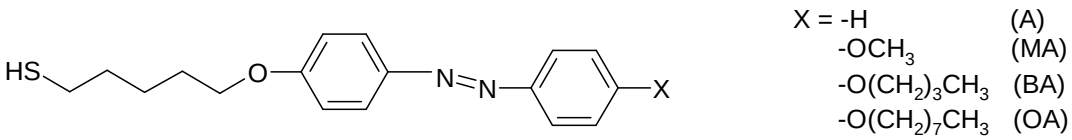
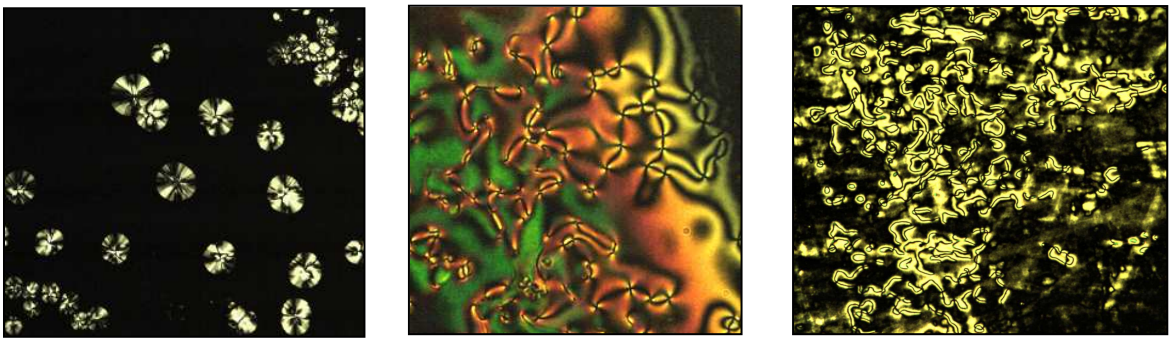


Figure 1. The synthesized liquid-crystalline units. All of them possess a 1,5-pentane-diyl spacer terminated with thiol group and azobenzene as a rigid, mesogenic part. The thiols designation is written in brackets.



A. B. C.

Figure 2. Nematic textures of the poly(butadiene)diols grafted by thiol MA with various ratio SH/double bonds in the feed (A – 0.2, B – 0.6, C – 0.8). Width of the images is about 300 μm. The textures were observed during a cooling regime (5°C/min) at related temperatures (25°C – A and B, 72°C – C).

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