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Věc: Oponentský posudek disertační práce
Název práce:
Structure, Thermal and Physical Properties of Liquid Crystalline Polymers
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Presented thesis "Structure, Thermal and Physical Properties of Liquid Crystalline Polymers" deals with experimental results obtained for side-chain liquid crystalline polybutadienes (SCLCPB). The topic of the presented thesis is really novel and attractive. Thermotropic liquid-crystalline polymeric compounds are prospective materials for applications. Such compounds could combine the property of low mass liquid crystals (anisotropy of the electrical, mechanical and magnetic properties) with the promising physical properties of polymers (stability, mechanical integrity, high flexibility, elasticity).

Two types of liquid crystalline compounds were used for grafting of polybutadiene: first with cyanobiphenol and second with azobenzene mesogenic group. I expect that the motivation for liquid crystalline compound with azo group is its photosensitivity. For azo-compounds the cis-trans izomerization takes place under the illumination of UV light; consequently, the molecular structure transformation that implies changes in the physical properties and promises numerous applications. So I found the choice of subject very prospective and topical.

Formally, presented thesis is divided into several parts as Introduction, Theoretical review, Aim of the thesis, Methods of measurements, Results and discussions, Conclusions. I enclose a list of equivocalness, omissions or formal errors.

Concerning theoretical review (chapter 2.), I miss more information about side-chain polymers, their preparation and structures. For example:

1. What does it mean comb-like architecture of side-chain polymers and how to reach or influence it?

2. Concerning dielectric spectroscopy, it is not necessary to describe in detail dipole moment. More important would be to refer deeply about dynamical dielectric measurements, which results will be presented later. The most important Havriliak-Negami function is only mentioned on the page 25. It was referred as (28), which is not true number (it is 35). In principle, it is not possible to refer the equation (for example Vogel-Fulcher-Talmmann formula referred as (38) in page 25) if the equation will be presented later, in next paragraph).

3. In part 2.4. I feel a lack of deeper information about X-ray scattering, even if you will present some results later in your thesis. It is not necessary to repeat Bragg law, but it would

be nice to be more general and not to refer only about wide-angle X-ray. In principle, the whole paragraph 2.4. Macroscopic structure characterization does not fit ideally to the chapter "2. Theoretical Review", and is partially repeated in the next chapter "4. Methods and Measurements."

4. Differential scanning calorimetry study is described in 2.4.1. as a method consisting of the specific heat measurements, but in the presented results only the heat flow temperature dependencies are shown. Was specific heat measured and what was the method? If not, I'd prefer information about enthalpy and heat flow behaviour for different types of phase transition.

The aims of the thesis are formulated slightly vaguely, even when the term "degree of modification were not explained" before. Last sentence, in which it is claimed that one studied material was used in some optical measurements and promising results were found, fits better to Conclusions. If these results serve as a motivation for presented work, it should be written exactly what was found and why to study especially this material. I'd appreciate some description of optical properties in Introduction, when you write you believe these compounds will find optical application.

In the experimental results:

1. I don't understand the abbreviation GPC and don't know what time scale is used in the Fig.8 (lack of units).

2. I miss the information about mesomorphic properties of thiol 1, it means what type of mesophase has been observed?

3. Is there really specific heat c_p in Table1 or Table 2? In this case the units are not OK (c_p cannot be in same unit as ΔH). c_p should be in J/(g.K), better specification is in J/(mol.K).

4. Calorimetric measurements: Why was not pure thiol 1 measured for lower temperatures? In principle it is possible to obtain the crystallization for some temperature bellow RT?

5. In Fig.12 the temperature dependences of storage modulus (G) and loss tangent are presented. But it is not clear what curve corresponds to what axis. From the text it is possible to guess it from the information about temperature behaviour (decrease of G with temperature). Nevertheless, the straightforward figure caption is necessary. In connection with figure 12: it is written in text that on temperature dependences of loss tangent a maximum located at lowest temperatures (what temperatures?) corresponds to glass transition. I see only a plateau, I need some explanation. Additionally, the term neat polybutadien is not explained

and why expected liquid-like behaviour at highest temperatures is observed (page 43) only for it.

6. Concerning Fig.13, I need explanation how was the temperature T_0 chosen, why just 20°C because in the comment to equation (11) it is written that C_1 and C_2 depend on T_0. What type of superposition and how it is connected with enthalpy value (page 44)? You distinguish two different types of shift factor (page 44), but in Theoretical Review I have found only temperature shift factor a_T (equation 11 in page 16). I feel a lack of information about vertical shift factor b_T and so I cannot understand Fig.13b and comment it properly. I think that the slope of theoretical line is driven by T_0 value. On contrary, is it possible to derive T_0 value by fitting the obtained data? The y-scale in Fig. 13.b is uselessly large and it is difficult to distinguish how much the data follow linear dependence.

7. In Fig.16 it is not clear what curve corresponds to what temperature (two different temperatures, two different symbols are not specified). Inset is too small, practically illegible and there is no information about the inset in the figure caption.

8. The term "frequency peak maxima" or "absorption frequency peak" are slightly misleading (page 51 and Fig. 19 caption). Reading the frequency corresponding to ε'' maxima is not very precise, I'd prefer some fitting procedure. In Fig.19 the discussed part corresponding to δ-relaxation, fitted by Arrhenius equation with two activation energies, is small and hardly distinguishable.

9. I have not found the term "magnitude of dielectric absorption" ($\Delta\varepsilon.T$) and how it is defined. So I cannot properly understand Fig. 20.

10. In Table 5, there are bad units for specific heat.

11. No proper explanation of formalism concerning the electric modulus M (only definition on page 34) and no explanation about interfacial Maxwell-Wagner-Sillars polarization have been presented. So I can hardly review Figs. 32-34. Formally, description of x-axis in square brackets is inconsistent with other figure description, which was used in the rest of thesis.

Nevertheless, regardless of the formal mistakes, I think the author of presented thesis, Mgr. A. Jigounov, showed the ability for creative scientific work and his thesis deserves to be defended.

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