Influence of chain architecture on self-organization in polymers with semifluorinated side chains

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Structural segments consisting of alkyl and perfluoroalkyl groups covalently linked by a C-C bond, called semifluorinated (SF) compounds, are known for their microphase separation resulting in highly ordered bulk structures [1]. The microphase separation is caused by the thermodynamic immiscibility between alkyl and perfluorinated alkyl segments. The goal of the project was to evaluate the influence of SF-side chains on the bulk structure and the surface properties of polysulfones (PSU’s) with different chain structure. Thus, segmented block copolymers consisting of PSU and semifluorinated aromatic polyester (SF-PES) segments as well as PSU’s having SF-chains randomly distributed over the polymer backbone were synthesized with a different concentration of side chains (chain architecture) (compare Fig.1). Oxydecylperfluorodecyl side chains were used because of their strong tendency for self-organization.

Fig. 1: Schematic representation of the chain architectures; left: segmented block copolymers with PSU and SF-PES segments; right: PSU with randomly distributed SF-side chains

The structure of PSU-SF-PES block copolymers (BCP) is determined by microphase separation which occurs between the amorphous PSU phase and SF-PES domains at very low molecular weights of SF-segments having only a few monomeric units. The reasons therefore are the high interaction parameter between SF-PES and PSU ($\chi \approx 13.6$) [2] as well as the high tendency for self-organization of the SF-PES itself, driving to a highly ordered bulk structure. The structure of the SF-poly($p$-phenylene isophthalate) was reported earlier [3]. By a combination of methods, the structural changes upon heating and cooling could be understood [4,5]. Phase separated BCP’s of PSU and the SF-PES should have both, the glass transition of PSU as indication of an amorphous matrix, as well as the thermal transitions of the SF-PES [5]. Based on the results obtained by DSC, SAXS, and TEM, a structural model was proposed recently [2,6] showing a random distribution of well-ordered SF-domains within an amorphous matrix.

SAXS curves of segmented BCP’s show two scattering maxima at $d_1$ being exactly the layer distance obtained in the pure SF-PES (Fig. 3). The larger scattering maximum $d_2$ refers to the periodic distance between the SF-PES domains in the PSU matrix. A correlation between this distance and the domain size was postulated recently [6]. The random SF-PSU’s show a somewhat different structure compared to the BCP (Fig. 2, Tab. 1). In DSC investigations, only a glass transition can be found, without indications of side chains melting and isotropization. The $T_g$’s strongly depend on the structure of the side chains. The $T_g$ of PSU with COOH-side chains increases slightly with the side chain concentration referring to higher intermolecular interactions. In contrast, the $T_g$’s of PSU with SF-side chains drop down significantly with increasing side chain concentration, showing that the SF-side chains alter the amorphous rigid structure of unmodified PSU.

Tab. 1: Layer distances $d$ in the SF-domains obtained for random SF-PSU’s with different molar concentration of SF-side chains $c_{SF}$ (after the 1st heating to 300 °C and cooling to 25 °C) [7]

<table>
<thead>
<tr>
<th>$c_{SF}$ / (mol%)</th>
<th>Structure at RT?</th>
<th>$d$ / (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>yes</td>
<td>5.2</td>
</tr>
<tr>
<td>42</td>
<td>yes</td>
<td>5.3</td>
</tr>
<tr>
<td>33</td>
<td>no</td>
<td>5.5</td>
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<tr>
<td>25</td>
<td>no</td>
<td>6.6</td>
</tr>
<tr>
<td>0</td>
<td>no</td>
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</table>
BCP with PSU and SF-PES segments show a stronger tendency of self-organization of SF-side chains than PSU’s with randomly distributed ones, which can be understood in terms of a lower distance and therefore higher interaction of the fluorinated parts in the BCP, leading to a higher ordered structure in the bulk.

References