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# Compound Formation and Solvent (Dis)ordering in Syndiotactic Polystyrene/Benzylmethacrylate Systems

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SUMMARY: In-situ small- and wide-angle X-ray scattering (SAXS and WAXS) experiments combined with Raman spectroscopy have been performed to study the phase behaviour of syndiotactic polystyrene (sPS) and benzylmethacrylate (BzMA). In the quenched gels, sPS adopts a helical conformation which is stabilised by the solvent molecules, in fact compound formation occurs. From the combined experimental data it was concluded that two different structural modifications exist within the solvent-included helical δ-phase, respectively the δ' phase in which the solvent molecules are intercalated and ordered between the phenyl rings of sPS and a δ" phase where this solvent ordering is lost.

## Introduction

Syndiotactic polystyrene (sPS) is a fast crystallising polymer possessing a high melting temperature of 275°C. Various studies have been dealt with crystallisation of sPS, both from the melt and solution, and several conformations in the crystalline state have been reported and confirmed[1,2,3]. SPS can crystallise in four crystalline modifications, α, β, γ and δ. In the α– and β–modifications, the chains adopt a $T_4$ all-trans zigzag conformation, which can be subdivided into α', α", β', and β"[2,3,4,5]. In the γ– and δ– modifications, the chains adopt a $T_2G_2$ helical conformation, where the δ-phase is considered to be a solvent-included phase and the γ-phase a solvent-free phase. The helical modification can only be prepared in the presence of a solvent. It was recognised by Guenet[6] that the occurrence of an invariant liquid-solid line, independent of polymer concentration, in the temperature-concentration phase diagram is indicative for the formation of a polymer-solvent compound. For sPS, it has been stated that solvents may intercalate with this polymer resulting in compound formation[1,2,3,4,5,6]. If monomers are employed, polymerisation in the sPS/solvent compounds could lead to unique polymer blends, e.g. molecularly dispersed polymer blends. In this paper we present results concerning the phase behaviour of sPS and the monomer benzylmethacrylate (BzMA), using in-situ X-ray scattering (SAXS and WAXS) experiments combined with Raman spectroscopy. This monomer was chosen as a model system to show the importance of the interaction between the phenyl rings of the solvent and the polymer[7].

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## Experimental part

SPS ($M_w$ = 400 kg • $mol^{-1}$) (DOW) and the monomer BzMA (Aldrich) were used as received. Solutions were prepared in sealed test-tubes by dissolving the polymer near the boiling point of the monomers. The solutions were then transferred into disposable pipettes and quenched in liquid nitrogen. The gels obtained were transferred into Lindemann capillaries for further analysis. To follow in-situ the morphological and structural changes during the phase transformations in the sPS gels, simultaneous time resolved SAXS and WAXS in combination with Raman spectroscopy experiments were performed. Experimental details of the measurements are described elsewhere[7,8,9)].

## Results on phase behaviour of sPS and benzylmethacrylate (BzMA)

Some results of the WAXS and SAXS experiments obtained during the heating scan of the 40 wt% sPS system are depicted in Fig. 1d, 1e and 2a, respectively. The sPS chains adopt a helical δ-conformation in the quenched material at -20°C. This is characterised by rather sharp reflections at *d* = 15.17, 8.59, 4.5, 3.9, 3.76, 3.54 and 3.18 Å[7)]. We have marked several reflections which correspond to distinct *d*-values. The existence of the δ-phase implies that BzMA can form a molecular compound with sPS. At approx. 50°C, two broad reflections centred around *d* = 12.05 Å (marked as 1) and 4.91 Å (marked as 2) appear simultaneously (see Fig. 1d). On continued heating (Fig. 1e, T = 115°C), the reflection at *d* = 12.05 Å disappears and the reflection at *d* = 4.91 Å shifts to higher angles, while a sharp reflection around *d* = 5.43 Å appears (marked as 3). Simultaneously, the reflection at *d* = 8.59 Å (marked as 4) gradually shifts to lower angles and the sharpness of this reflection decreases[7)]. These changes are related to transformations within the helical δ-phase. On heating beyond 130°C, we observe that the reflections corresponding to the helical phase disappear with a subsequent incoming of sharp reflections associated to the crystalline β''-phase[3)] (see Fig. 1f).

The absence of a distinct maximum in SAXS (Fig. 2a) prevails up to approx. 100°C. As the structural changes in the helical phase set in, a broad maximum at $q$ = 0.05 $Å^{-1}$ (*d* = 126 Å) appears, which intensifies and shifts to lower angles up to 130°C. On the helical to β transition, the SAXS data show that the maximum decreases in intensity. On subsequent heating, the incoming of a strong maximum at $q$ = 0.03 $Å^{-1}$ (*d* = 209 Å) is indicative for the formation of the lamellar morphology, which shifts to lower *q*-values indicating the increase in the long period before melting.

The WAXS results of the heating scan of the 20 wt% sPS system (Fig. 1a, 1b and 1f) show a few differences in comparison to the 40 wt% sPS system. At approx. 30°C, the incoming of two broad reflections in the WAXS-data centred around $d$ = 12.05 Å and 4.91 Å are observed, which intensify on further heating. These reflections were also present for the 40 wt% system, but are much stronger. The reflection at $d$ = 8.59 Å (marked as 4 in Fig. 1a) is indicative for the presence of the δ-phase at these temperatures. On subsequent heating during the (structural) changes in the helical phase, the reflection at $d$ = 8.59 Å becomes broader, while the reflection centred around $d$ = 12.05 Å disappear and the reflection at 4.91 Å shifts to higher angles in line with the helical-to-helical transformation in the other system as shown in Fig 1b.

The conformational changes were simultaneously followed by Raman spectroscopy and the results of the heating run of the quenched 40 wt% sPS system are shown in Fig. 2b. Differences were found in the 700-800 cm$^{-1}$ region in which the phenyl ring vibration modes have been shown to manifest themselves through the presence of two peaks resulting from conformational changes in the alkyl backbone10,11,12,13). For the planar zigzag conformation, a strong, sharp peak at 770 cm$^{-1}$ with a broad peak at approximately 795 cm$^{-1}$ was attributed to all-trans conformation. The strong peak at 798 cm$^{-1}$ was assigned to the helical phase. The weak peak at 769 cm$^{-1}$ was associated to the mixed trans-gauche conformation. These assignments will be used to follow the phase transitions in our studies as reported below. From the strong peak at 802 cm$^{-1}$ at the starting temperature, it is evident that the chains have adopted the helical conformation in presence of BzMA. On heating, this peak vanishes above approx. 130°C and a new peak at 772 cm$^{-1}$ appears, indicating the incoming of the all-trans planar zigzag conformation, which almost disappears at the melting temperature.

## Discussion on structural changes upon heating

The observations made by WAXS during the heating runs on the investigated sPS/solvent systems revealed the presence of different structures within the helical phase (see Fig. 1). It was also observed that in the quenched samples the positions of the reflections assigned to the helical δ-phase depend on the solvent7). On heating the quenched samples of the sPS/BzMA above 50°C, two broad reflections centred around $d$ = 12.05 Å and 4.91 Å are observed, while the other reflections remain the same. These $d$-values are equal to the dimensions of the BzMA molecule. The reflections originate from the regular packing of the BzMA molecules within the confined spaces of the helical structure of sPS and are in close accordance with the local order as observed in PBzMA. The reflection at $d$ = 11.0 Å is attributed to the order between the adjacent main chains and the reflection at $d$ = 5.0 Å is associated to order between the phenyl rings arising from the Van der Waals interactions14). This indicates that a similar local order as observed for PBzMA exists (see Fig. 1c) in the BzMA molecules intercalated within the helices of sPS. This could only be feasible when the phenyl rings of BzMA are intercalated between the phenyl rings of sPS in the same chain along the *b*-axis. The structure of the sPS/BzMA compound is rather different than the sPS/toluene compound, in which the solvent molecules occupy the isolated holes between the polymer chains along the *b*-axis of the unit-cell$^{15)}$. The packing of the solvent molecules, which seems initially absent due to the fast quenching, becomes more regular within the δ-phase on heating. Besides the regular ordering of the solvent molecules within the δ-phase, the WAXS-observations also showed that structural changes occur within the helical phase on further heating. The occurrence of changes within the helical phase was also observed for many other sPS/solvent systems and were related to desiccation of the solvent from the helices, resulting into the solvent-free γ-phase$^{3)}$. The two reflections assigned to BzMA disappear, when the structural changes within the helical phase set in. This can be interpreted either as desiccation of the solvent molecules out of the interstitial regions of the helices leading to the formation of the γ-phase or as a loss in the packing of solvent molecules within the confined space$^{7)}$. The fact that the 010 reflection stays at the same position and 200 reflection shifts to lower angles indicates that no contraction of the unit cell occurs. This implies that the solvent resides within the helices. The disappearance of the reflection at $d$ = 12.05 Å (marked as 1) shows that the order between the adjacent solvent molecules is lost. Simultaneously, changes are observed in the reflection at $d$ = 4.91 Å. This suggests that the observed changes are related to the Van der Waals interactions between the phenyl rings. At the same time, a sharp reflection at $d$ = 5.45 Å appears. The appearance of this sharp reflection, the disappearance of the broad reflection at $d$ = 12.05 Å and the simultaneous shift of the reflection at $d$ = 4.91 Å can be explained by the change in the order of the solvent structure. The sharp reflection at $d$ = 5.45 Å seems to originate from the ordering of the phenyl rings of the sPS chains alone, rather than the ordering of the intercalated phenyl rings between BzMA and sPS as observed at lower temperatures. It is evident that a distinction has to be made within the δ-phase based on the structural (dis)order of the solvent molecules within the confined spaces of the sPS-helices.

## Conclusions

The sPS/BzMA systems clearly demonstrate that in the quenched samples compound formation occurs, resulting into the known δ-phase. Within the δ-phase, the solvent is intercalated between the phenyl rings of the helices. Between the solvent molecules, structural order or disorder can be present, leading to two different modifications of the δ-phase, termed as δ' and δ'', respectively. The phase transformation from the δ' (structural order between the solvent molecules) to the δ" (structural disorder between the solvent molecules) occurs on heating. The interaction between the phenyl rings of the solvent and sPS plays a prominent role in the existence of the δ' and δ" phases. Unlike the known δ (solvent-included phase) to γ (solvent-free phase) transformation on heating, no solvent-free γ-phase was observed in our studies.

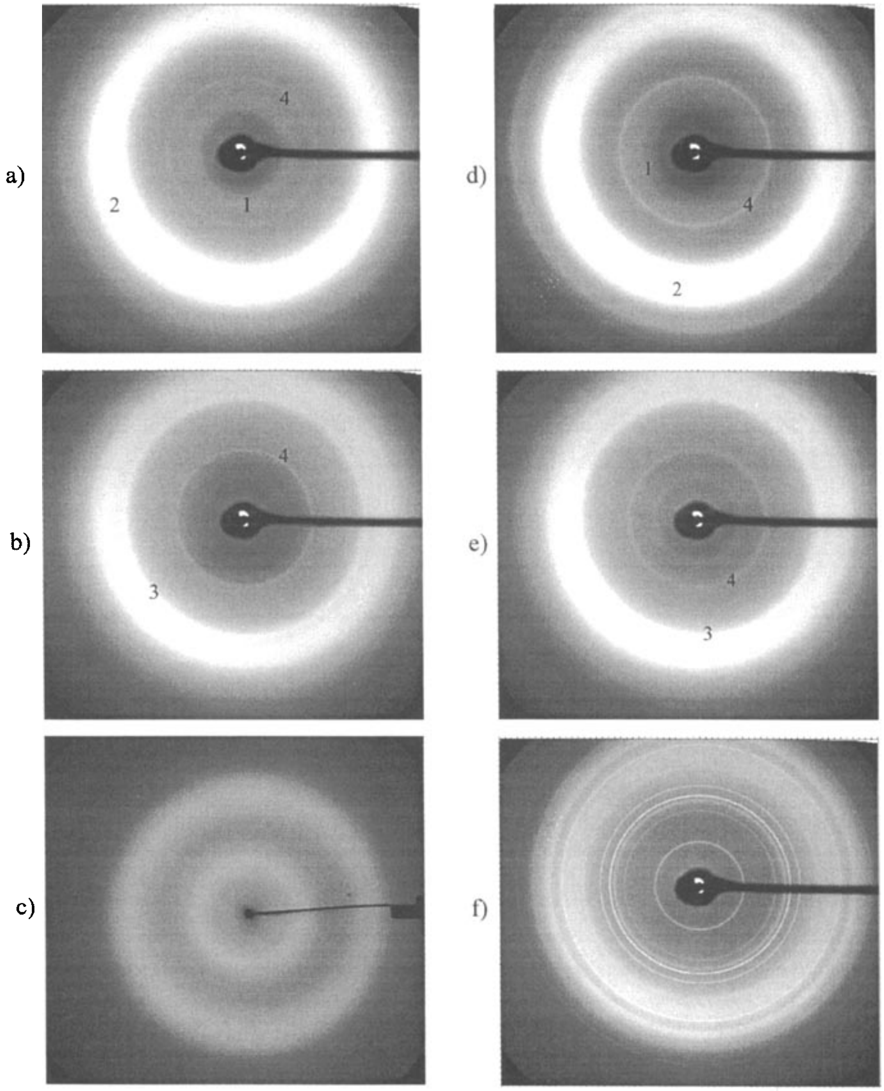

*Figure 1: WAXS data: a ) 20 wt% sPS at 70°C (δ'), b) 20 wt% sPS at 130°C (δ"), c) PBzMA, d) 40 wt% sPS at 55°C (δ'), e) 40 wt% sPS at 115°C (δ"), and f) 20 wt% sPS at 180°C (β').*

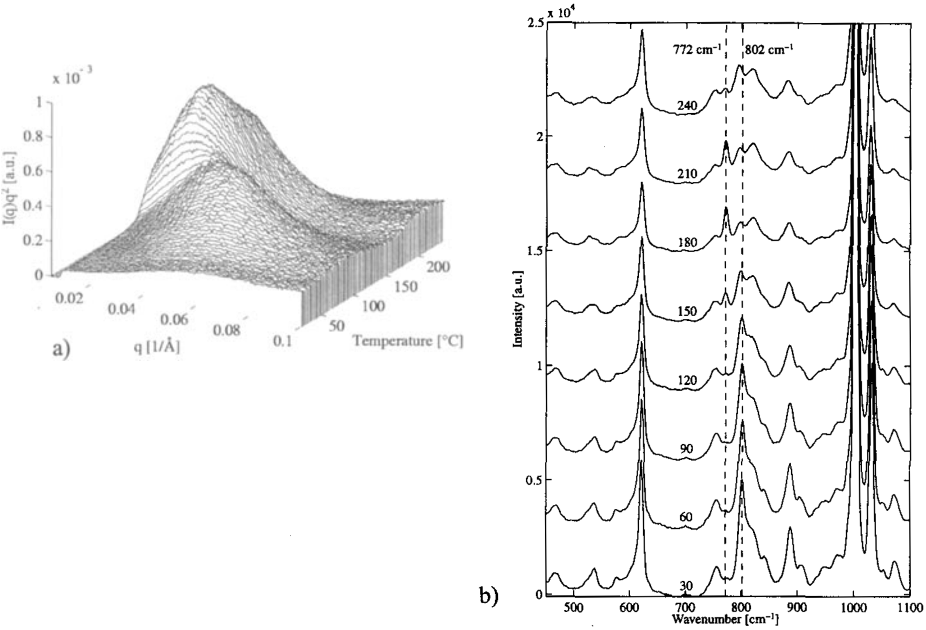

*Figure 2: Results from the heating run from 20 to 230°C at 5°C/min of a quenched 40 wt% sPS/BzMA sample: a) SAXS data and b) Raman data.*

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