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Polymerisation of Intercalated Solvents in Gels; an Attempt to Obtain Molecular Blending

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SUMMARY: Recent studies performed on gels like syndiotactic polystyrene /benzylmethacrylate and poly-benzyl-L-glutamate/benzylmethacrylate indicate that the solvent molecules can be intercalated between or within the helices of the polymer. The present paper describes the UV polymerisation of these intercalated solvents. It was found that for both systems the solvent stays intercalated between the helices after polymerisation. This method can therefore be used to blend two immiscible polymers on a molecular scale.

Introduction

In general, the X-ray pattern of amorphous methacrylate polymers shows two halos, of which one corresponds to an average Bragg distance between the neighbouring main chains.[1] The Bragg distance varies with the size of the side chain of the polymer. The X-ray reflection as observed in these amorphous polymers can also be observed for some methacrylate solvents in polymer/solvent gels. The regularity in these solvent molecules has recently been observed for gels of syndiotactic polystyrene (sPS) with benzylmethacrylate (BzMA) and for gels of poly-benzyl-L-glutamate (PBLG) with BzMA[2,3].

SPS is a polymer that can adopt two different conformations. Crystallisation of the pure material leads to the formation of a zigzag phase, while in presence of a solvent a helical conformation can be obtained. A possible modification of the helical conformation is the δ-phase, a phase in which the helices of sPS include some solvent molecules. It was recognised by Guenet et al. that the δ-phase is a polymer-solvent compound[4]. Recent studies indicated the existence of two different forms in this δ-phase, depending on the ordering of the intercalated solvent[2]. Upon quenching, a helical phase in which the phenyl rings of BzMA are intercalated within the phenyl rings of sPS is obtained. Due to this intercalation a regular ordering of the solvent molecules is achieved. The X-ray reflection at 12.05 Å, which arises due to this regular ordering, matches the size of the BzMA molecules. This phase is called the δ'-phase. Upon heating the δ'-phase the ordering of the solvent molecules is lost and a different form of the δ-phase is obtained, the δ''-phase. This δ''-phase is described as a helical phase in which the solvent is still present between the helices, though the structural order between the solvent molecules no longer exists.

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Poly-benzyl-L-glutamate is a polypeptide with $-(CH_2)_2-(C{=}O)-O-CH_2-C_6H_5$ as its side chain. Due to hydrogen bonds formed in the main chain between the oxygen of a carbonyl group and the hydrogen of an amide group, a α-helical structure is obtained. Upon heating cast films of PBLG/BzMA the α-helices pack themselves most probably in a hexagonal lattice. This packing is followed by an ordering of the solvent molecules[3]. In the WAXS pattern, the ordering in the solvent molecules gives rise to a Bragg distance which is in close correspondence with the size of the solvent molecule, similar as in the sPS/BzMA system. Due to the similarity in structure between BzMA and the side chain of PBLG it is proposed that the BzMA molecule is residing within the helices of PBLG. As a result, the intercalation will not only be based on phenyl ring interactions, like in the sPS/BzMA system, but also on carbonyl interactions between BzMA molecules and the side chain of PBLG[3].

In this paper the UV polymerisation of benzylmethacrylate in the sPS/BzMA and PBLG/BzMA gels will be described. The aim of the work is to achieve blending of polymers at the molecular level.

Experimental section

PBLG and sPS were obtained from Sigma Chemical Laboratory and Dow Chemical respectively. Benzylmethacrylate (used without purification), dichloromethane and 2,2 dimethoxy-2-phenyl-acetophenone (UV initiator) were supplied by Aldrich.

SPS/BzMA samples were prepared by dissolving the polymer and the UV-initiator near the boiling point of the solvent. The solutions were quenched in liquid nitrogen. PBLG/BzMA samples were prepared by dissolving PBLG, BzMA and the UV-initiator in dichloromethane. The solutions were poured into a petri dish and dried in the air. Both gels were transferred into Lindemann capillaries.

Time resolved WAXS experiments were performed on station ID11/BL2 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Raman spectra were obtained with a Dilor LabRaman system, coupled with an air-cooled CCD array detector.

Results and Discussion

Polymerisation of sPS/BzMA Systems

Polymerisation of sPS/BzMA gels is performed for systems with sPS concentrations between 20 and 50 wt%. For the different concentrations the same trends in results are observed and therefore only the results of the 20 wt% sPS samples will be presented in this paper. Figure 1a shows the 2-D WAXS patterns at 60 °C before and after UV-irradiation. The reflections at $2\theta = 4.9$ and 9.6° (corresponding to Bragg distances $d = 8.85$ and 4.5 Å resp.), as observed for the starting material, are indicative for the presence of the δ'-phase[2]. Upon UV-irradiation, the incoming of a broad reflection at 3.7° (d-spacing 11.7 Å) is observed. This reflection, which is also observed by Miller et al.[1], matches the size of the side-chain of polybenzylmethacrylate (PBzMA). The reflection can therefore be considered as an indication for the polymerisation of BzMA.

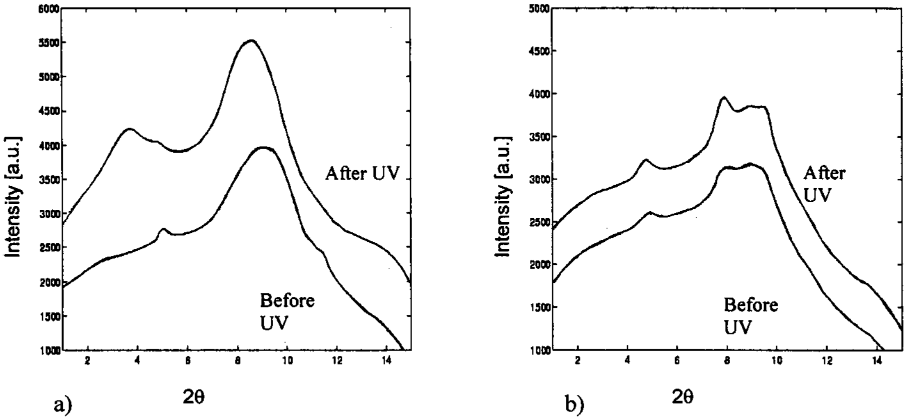

Fig 1. 2-D WAXS data upon UV-irradiation of a 20/80 wt% sPS/BzMA sample: a) T = 60 °C b) T = 80 °C. Applied wavelength λ = 0.757 Å.

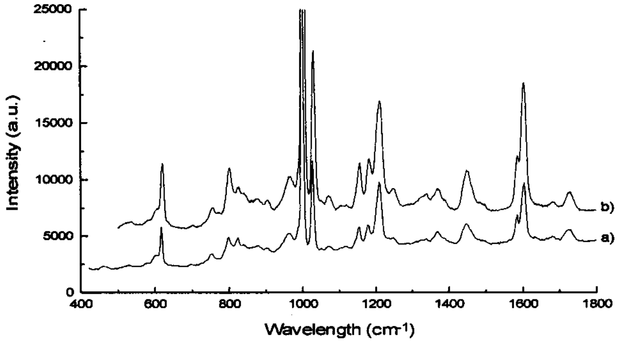

Fig 2. Raman spectra of polymerised 20/80 wt% sPS/BzMA samples: a) polymerised at 60 °C b) polymerised at 80 °C.

In figure 1b the WAXS patterns before and after UV-irradiation at 80 °C are depicted. The presence of a reflection at 7.9° (d-spacing 5.5 Å) indicates the existence of the δ''-phase[2]. In contrast to the samples starting from the δ'-phase, no changes which can be attributed to polymerisation are observed in the WAXS patterns after UV-irradiation of the sample (figure 1b). This can suggest that polymerisation does not occur if the δ''-phase is the initial modification. However, the (nearly complete) absence of the peak at 1637 cm^{-1} (C=C stretching vibration) in the Raman spectra (figure 2) indicates that for both samples, independent of the helical modification (δ' or δ''), BzMA has been polymerised. A possible explanation for the absence (in case of δ'') and presence (in case of δ') of the polymerisation reflection in the WAXS pattern can be as follows. The δ'-phase is the phase in which the BzMA molecules possess a regular packing within the helical structure of sPS, due to the intercalation of the phenyl rings of BzMA within the phenyl rings of sPS[2]. Because of this ordered structure, a correlation is observed between the BzMA molecules and polymerisation is reflected by the incoming of a broad reflection at 2θ = 3.7° (figure 1). On the contrary, the δ''-phase is described as a helical phase in which the BzMA molecules are also present between the helices but without any structural order between the solvent molecules[2]. Although BzMA is polymerised upon UV-irradiation, this will not be observed in the WAXS pattern, as a result of the absence of the correlation.

Due to the low miscibility of the polymers sPS and PBzMA, it is anticipated that upon polymerisation phase separation occurs, followed by the crystallisation of sPS into the planar zigzag phase. However, the WAXS patterns after UV-irradiation show no reflections corresponding to the planar zigzag phase. This indicates that phase separation does not occur after polymerisation, which leads to the conclusion that the BzMA molecules before and after polymerisation are indeed interlocked between the helices of sPS.

Polymerisation of PBLG/BzMA Systems

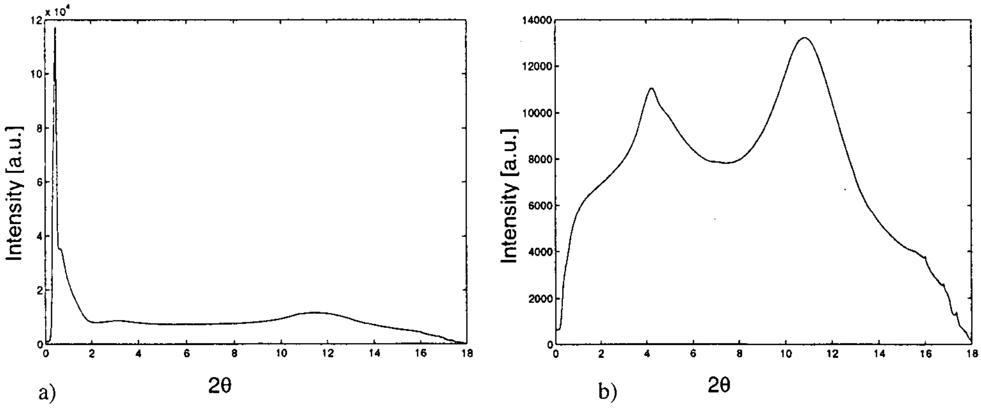

Fig 3. 2-D WAXS data at room temperature of a 20/80 wt% PBLG/BzMA sample a) casted from dichloromethane b) cast film which has been heated till 150 °C and cooled down to room temperature; applied wavelength λ = 0.93 Å.

Like for the sPS/BzMA systems, the polymerisation of PBLG/BzMA systems is performed for samples with different PBLG concentrations. Only the results for the 20 wt% PBLG sample will be presented. For the other concentrations similar results have been obtained. Results, presented in a different paper by the same authors[2], indicate that upon casting a PBLG/BzMA sample from dichloromethane separate zones of PBLG and BzMA are obtained. Due to electron density differences between PBLG and BzMA these zones give rise to a high intensity close to the beam stop (see figure 3a). Upon heating these samples intercalation of the solvent into the helices of PBLG occurs, by which a homogeneous system is obtained. As a result, the high intensity in the small angle region disappears, while packing of the α-helices (relative sharp reflection at $2\theta = 4°$, corresponding Bragg distance d = 13.2 Å), and at the same time an ordering of the solvent molecules ($2\theta = 4.6°$, corresponding d= 11.6 Å), is observed (figure 3b).

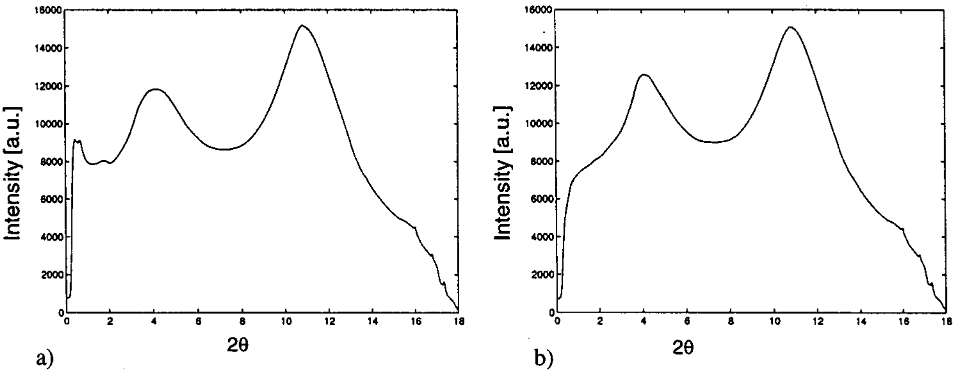

Fig 4. 2-D WAXS data after polymerisation at room temperature of a 20/80 wt% PBLG/BzMA sample a) casted from dichloromethane b) cast film which has been heated till 150 °C and cooled down to room temperature before polymerisation; applied wavelength λ = 0.93 Å.

Polymerisation of the samples, as presented in figures 3a and 3b, is performed at room temperature. Figure 4a shows the WAXS pattern after UV-irradiation of a cast film, in which the separate zones of PBLG and BzMA were present. After polymerisation a relatively low intensity close to the beam stop and three reflections at d = 29.7, 12.9 and 4.9 Å are observed. An explanation for the relative low intensity around the beam stop (compared to the unpolymerised sample, figure 3a) could be found in the fact that the electron density difference between PBLG and PBzMA is much smaller than between PBLG and BzMA. This small electron density difference will give rise to a low intensity. The sample of which the WAXS pattern is depicted in figure 4b has been heated till 150 °C before UV-polymerisation to obtain intercalation of the solvent in the helices of PBLG. After polymerisation the sharp reflection at $2\theta = 4^\circ$ (d = 13.2 Å), which was present in the unpolymerised sample (figure 3b) disappears. The two remaining reflections with Bragg distances at 12.9 and 4.9 Å are in close agreement with the values for PBzMA as found by Miller et al[1]. Due to the immiscibility of most polymers it is anticipated that phase separation would occur upon polymerisation. In the X-ray pattern this should result in a reflection close to the beam stop(like in figure 4a) and to the incoming of reflections as observed for pure PBLG. However, since these reflections are not observed, it can be concluded that no phase separation occurs upon polymerisation. This indicates that the solvent stays intercalated upon polymerisation.

Conclusions

The presented results on the polymerisation of BzMA in the sPS/BzMA systems indicate that, independent of the solvent ordering (δ'- or δ''-phase), the polymerised solvent stays intercalated between the helices of sPS. Also for PBLG/BzMA it is found that when the solvent molecules are intercalated in the helices of PBLG no phase separation occurs upon polymerisation.

It can be concluded that upon polymerisation at room temperature the solvent is frozen in within the initial, intercalated structure. As a result, this applied method can be used to blend two incompatible polymers on a molecular scale.

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[1] Miller, R.L., Boyer, R.F., *J. of Pol. Sci. Pol.Phys. Ed.* **1984**, 22, 2021

[2] Rastogi, S., Goossens, J.G.P., Lemstra, P.J., *Macromolecules* **1998**, 31, 2983

[3] Corstjens, C.S.J., Rastogi, S., Lemstra, P.J. *submitted to Macromolecular Symposia*

[4] Guenet, J.M., *Macromolecules* **1986**, 19,1961