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A Study on the Ordering of Intercalated Solvents in Poly-benzyl-L-glutamate; In-situ Raman and X-ray Scattering Investigations

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SUMMARY: A polymer/solvent system can form a gel due to specific interactions between the polymer and the solvent. For poly-benzyl-L-glutamate/solvent systems, gelation can be based on carbonyl or phenyl ring interactions, depending on the solvent. The present paper describes X-ray scattering and Raman investigations on cast films of poly-benzyl-L-glutamate (PBLG) and benzylmethacrylate (BzMA). The studies indicate that in the cast samples separate zones of PBLG and BzMA are present. Upon heating, the system homogenises and the PBLG molecules pack in a pseudo hexagonal lattice. At approximately 150 °C a new reflection at 11.4 Å in the WAXS pattern arises. This reflection is attributed to structural ordering of the solvent, due to intercalation of the solvent molecules within the helices of PBLG. The observed changes in the WAXS pattern upon heating are supported by Raman experiments.

Introduction

Poly-benzyl-L-glutamate (PBLG), first synthesised in the 1930s, is a polypeptide with the side group $-(CH_2)_2-(C{=}O)-O-CH_2-C_6H_5$. It is well known that in solution hydrogen bonds can be formed between the oxygen of a carbonyl-group and the hydrogen of an amide-group four groups further down the main-chain[1]. As a result, a α-helical crystal structure, with 18-residue-5-turn (18/5), is obtained. Crystallisation of the PBLG from 1,2 dichloromethane solutions results in the formation of the so-called C-form[2] in which the α-helical molecules are packed in a rather irregular pseudo hexagonal lattice ($a = 15.2$ Å, $b = 14.3$ Å, $c = 27$ Å and $\gamma = 118°$).

Gelation of a polymer/solvent system can occur due to specific interactions between the polymer and the solvent. For PBLG, gelation in benzylalcohol can occur due to phenyl ring interactions between the solvent and the side chain of the polymer, while in dimethylformamide the gelation is based on carbonyl interactions.

In this paper time-resolved X-ray scattering and Raman spectroscopy investigations on the system PBLG/benzylmethacrylate (BzMA) will be presented. Benzylmethacrylate is chosen as solvent for the following two reasons. First, due to the similarity in structure between BzMA and the side chain of PBLG there is a possibility for both carbonyl and phenyl ring

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interactions. Moreover, as a result of the presence of a C=C double bond, the intercalated BzMA solvent can be polymerised to make unique polymer blends, as will be described in a subsequent paper[3].

Experimental Section

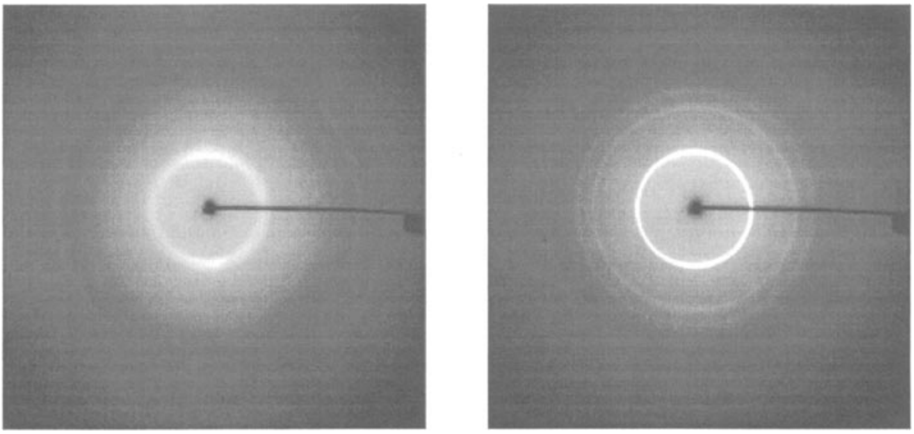
PBLG with a molecular weight between 150.000 and 350.000 was obtained from Sigma Chemical Laboratory. Benzylmethacrylate and dichloromethane were purchased from Aldrich Chemical Company and used without purification. Aldrich Chemical Company also supplied Benzoquinone (inhibitor).

Samples were prepared by dissolving both PBLG and BzMA (with inhibitor) in dichloromethane. The solutions, in which the concentration of PBLG was varied between 20 and 100 wt%, were poured into a petri dish. After drying in air, the films were sealed into Lindemann capillaries.

Raman spectra were obtained with a Dilor LabRaman system, coupled with an air-cooled CCD array detector. Time-resolved WAXS experiments upon heating the samples were performed on ID11/BL2 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The applied wavelength was 0.93 Å.

Results and discussion

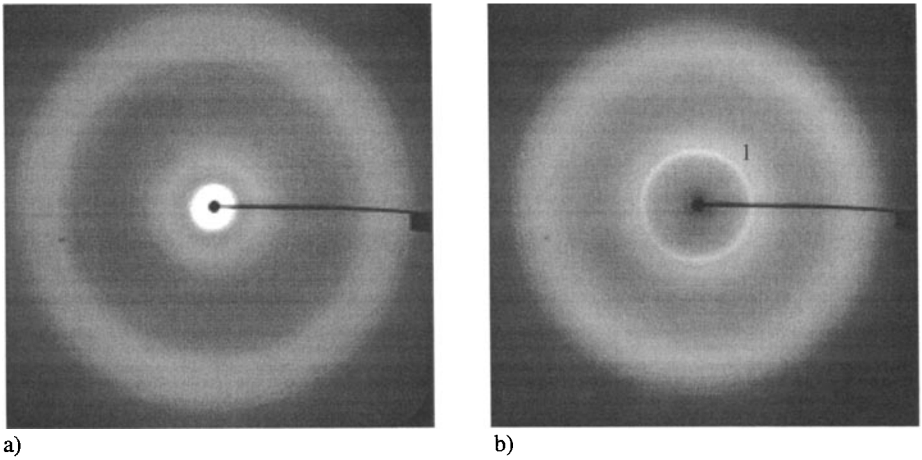
For samples with different ratios PBLG/BzMA similar results were obtained and therefore only the pictures of the most distinghuising concentrations will be presented in this paper.



a)   b)

Fig 1. 2-D WAXS patterns of PBLG, casted from dichloromethane a) $T = 25$ °C b) $T = 150$ °C

Figure 1 presents the WAXS patterns of PBLG, casted from dichloromethane. At room temperature two reflections are observed. The inner broad reflection corresponds to a d-spacing of 13.7 Å, while the d-spacing of the outer reflection is 5.16 Å. Upon heating the sample the inner reflection sharpens and shifts to a lower d-spacing, while also some new reflections develop. The corresponding d-spacings as observed at 150 °C are 13.2 Å, 7.54 Å, 6.46 Å and 5.16 Å. These reflections correspond to the C-form of the α-helical structure as reported by Watanabe et al[2]. The changes upon heating occur due to packing of the α-helices in this pseudo hexagonal lattice.



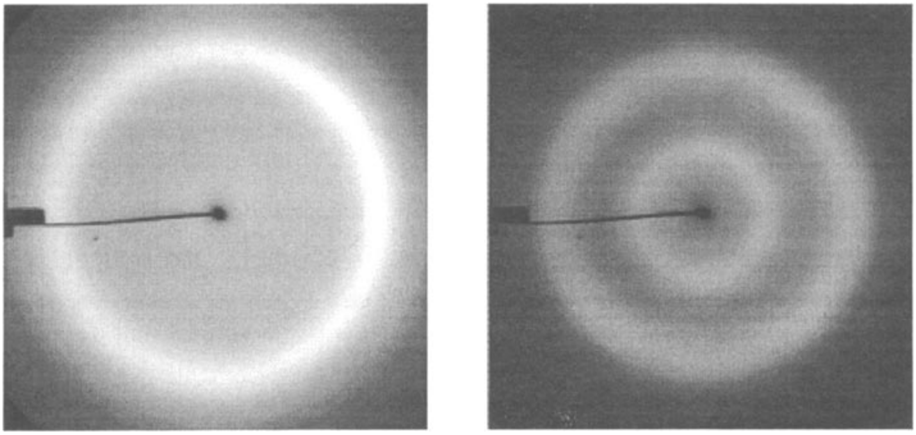
a) b)

Fig 2. 2-D WAXS patterns of PBLG/BzMA 37/63 wt%, casted from dichloromethane
a) T = 25 °C b) T = 150 °C

Casting a solution of dichloromethane which contains PBLG and BzMA (weight ratio 37/63) results in the WAXS patterns as depicted in figure 2. At room temperature two reflections and a high intensity close to the beam stop are present. An explanation for the presence of this high intensity close to the beam stop could be that in the cast samples separate zones of PBLG and BZMA exist. Due to electron density differences between the polymer and the solvent, the presence of separate zones results in a high intensity in the small angle region, close to the beam stop. The d-spacing of the two rather broad reflections are 17.28 and 4.78 Å respectively.

Upon heating the sample, the high intensity around the beam stop disappears while the reflection at 17.28 Å sharpens and shifts to a d-spacing of 13.6 Å. The sharpening of this reflection is accompanied by the incoming of a new, rather broad reflection around 11.4 Å (marked as 1 in figure 2b). Furthermore, the reflection at 4.87 Å shifts to a slightly larger d-spacing (5.18 Å). A possible explanation for these observations can be as follows: Upon heating the sample, a more homogeneous system is obtained and as a result the reflection around the beamstop disappears[4]. The reflection at 13.6 Å is very close to the one as observed for the C-form of pure PBLG[5]. Hence, at 150 °C the PBLG molecules arrange themselves in the pseudo hexagonal lattice. The reflection at 11.4 Å in the PBLG/BzMA system is not observed in pure PBLG and it is therefore concluded that this reflection is arising from the solvent.

To be able to draw a conclusion about the origin of this 11.4 Å reflection, WAXS patterns of unpolymerised BzMA and polymerised BzMA (PBzMA) are measured. These results are depicted in figure 3.



a) b)

Fig 3. 2-D WAXS patterns of BzMA a) unpolymerised sample b) polymerised sample

In the unpolymerised sample (figure 3a) only one reflection is observed. This reflection with a d-spacing of approximately 5 Å corresponds to the interaction between the phenyl rings. Upon polymerisation another reflection is observed at 11.4 Å, corresponding to the size of the side chain in PBzMA (figure 3b). The new reflection as observed in the PBLG/BzMA system (figure 2b) matches the 11.4 Å reflection of PBzMA. A possibility can be that in the PBLG/BzMA system the BzMA is polymerised. However, the presence of the peak at 1637 cm^{-1} (C=C stretching vibration) in the Raman spectrum of PBLG/BZMA (figure 4) indicates that at this temperature the BzMA is not polymerised yet, due to the addition of inhibitor. It is therefore suggested that the reflection arises from solvent ordering due to intercalation. An explanation for this phenomenon can be as follows: Upon heating the PBLG/BzMA system a homogeneous system is obtained. This indicates that the solvent molecules intercalate between or within the helices of PBLG. Since the observed packing of the α-helices is in close accordance with the values of pure PBLG, there is not enough space for the solvent molecules to reside between the helices. This suggests that the solvent molecules are intercalating within the side chains of PBLG. Hence, compound formation occurs. Due to the similarity in the structure between BzMA and the side chain of PBLG, the intercalation will be based on both phenyl ring and carbonyl interactions. Due to the intercalation a regular packing of the solvent molecules is obtained, which results in the reflection at 11.4 Å, like in PBzMA.

The presence of the 930 cm^{-1} band in the Raman spectrum at room temperature (figure 4a) suggest the presence of α-helices in the PBLG/BzMA system[6]. On heating the sample, changes occur around the same temperature as observed in the WAXS experiments (figure 2). The spectrum at 150 °C (figure 4b) shows splitting of peaks in the regions 1600-1800 cm^{-1}. Around 1640 cm^{-1} the C=C stretching vibration of BzMA and the amide I stretching vibration of PBLG[6] are detected as two separated peaks (1637 and 1652 cm^{-1} resp.), while also the carbonyl stretching vibration of BzMA (1719 cm^{-1}) separates from the carbonyl stretching vibration of the side chain of PBLG (1733 cm^{-1})[6]. Also in the region around 950 cm^{-1} splitting of the peaks (927 and 965 cm^{-1}) is observed. The comparison with the WAXS data suggest that these conformational changes should arise from a regular ordering of both the polymer and the solvent.

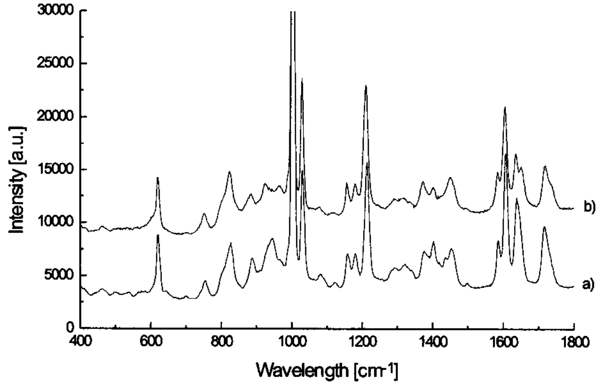


Fig 4. Raman spectrum of PBLG/BzMA 60/40 wt%, casted from dichloromethane a) T=25 °C b) T = 150 °C

Conclusions

From the present results it can be concluded that in the solution-cast films of PBLG/BzMA separate zones of the polymer and the solvent exist. Upon heating, the system homogenises, leading to compound formation. In this compound the PBLG molecules adopt a pseudo hexagonal phase. The unique feature of these investigations is that the solvent molecules are intercalated within the helices of the pseudo hexagonal phase at temperatures around 150 °C, thus being a part of the unit cell. Furthermore, X-ray and Raman studies indicate that due to this intercalation structural ordering of the solvent molecules arises.

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[1] Horton, J.C., Donald, A.M. *Polymer* **1991**, 32, 2418

[2] Watanabe, J., Kazamichi, I., Gehani, R. *J. of Pol. Sci* **1981**, 19, 653

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

[4] Another explanation for the disappearance of the intense reflection close to the beam stop can be an increase in the zone size. The zones can become so large that they can not be detected by X-ray in the present set-up. However, this explanation contradicts the observed results of solvent ordering as explained further in the paper.

[5] In the samples with higher concentration of PBLG (60 wt%) also two weak reflections of the C-form around 7.5 and 6.4 Å are observed together with the reflection at 13.6 Å.

[6] Koening, J.L., *J. of Pol Sci part D* **1972**, 59