

STRUCTURAL MODEL OF A POLY(VINYL-ALCOHOL) FILM UNIAXIALLY STRETCHED IN WATER

Recently, liquid crystal displays (LCD) have been widely used in various industrial applications, such as televisions and the monitors in cellular phones. Poly(vinyl alcohol) (PVA) has been promising as a substrate for the polarizers used in LCD, because it possesses a high ability of PVA-iodine complex formation in the film microstructure. When PVA films are soaked in a KI/I_2 aqueous solution, adsorbed polyiodine ions are one-dimensionally aligned along the PVA chains, which are oriented by film drawing, resulting in the formation of PVA-iodine complexes, which show excellent dichromatic performance. It was suggested that PVA-iodine complexes are formed in amorphous regions in PVA films when the films are soaked in KI/I_2 aqueous solution with a relatively low iodine concentration [1,2]. Therefore, it is very important to investigate the orientation of the molecular chains in the film microstructure, particularly in the amorphous regions, because the high dichromatic performance of the polarizers is attributed to the PVA-iodine complexes with a high degree of orientation in amorphous regions.

To elucidate the development of the orientation in PVA molecular chains in the amorphous regions with the strain, we investigated the structural changes in PVA films during uniaxial deformation in water without molecular chain relaxation by simultaneous measurements of small-angle X-ray scattering (SAXS) and the tensile stress-strain (S-S) relationship. Simultaneous SAXS and S-S were performed at beamline **BL40B2** with our newly developed stretch machine with a water bath, which can be jacked up and down so as to enclose and disclose the film

sample to examine a film sample in water, as schematically shown in Fig. 1. The experimental setup at BL40B2 is shown in Fig. 2. This stretch machine allows a film sample to be stretched laterally to receive X-ray radiation at the same position of the sample during deformation. A typical stretching speed and data acquisition time of a two-dimensional scattering pattern obtained using a CCD detector system with an image intensifier are 5 mm/min and 15 s, respectively.

PVA films with a degree of polymerization of 2400 were used in this study. The thickness of the films is 0.075 mm. In a previous work, we studied the swelling behavior of the film with water. It was concluded that only amorphous regions in the film are swollen in water, while the crystalline domains do not absorb water.

A S-S curve and typical two-dimensional (2D) SAXS patterns obtained simultaneously during uniaxial deformation in water at 298 K are shown in Fig. 3 [3]. We examined the longitudinal and transversal 1D scattering slices of 2D patterns, which describe the actual microstructural parameters in the film, and the mechanical transition is shown in the S-S curve.

Consequently, we determined the microstructure changes associated with the film stretching, as follows [3]. Below the strain of 70%, the crystalline lamellae are oriented in the direction perpendicular to the stretching direction, and the intervening amorphous regions swollen with water are elastically deformed in proportion to the macroscopic film deformation. Beyond the strain of 70%, the molecular chains in the

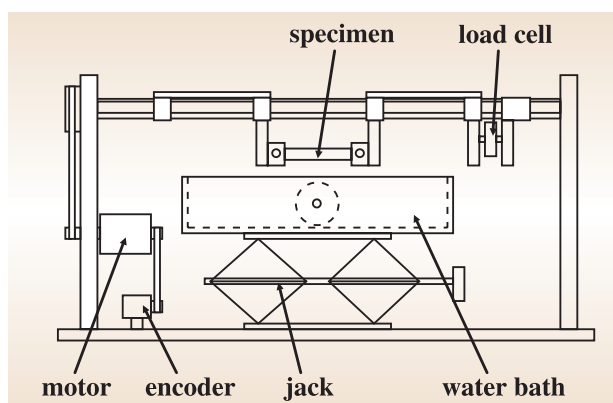


Fig. 1. Schematic drawing of the newly developed stretch machine for *in situ* SAXS measurements during uniaxial deformation of PVA films in water.

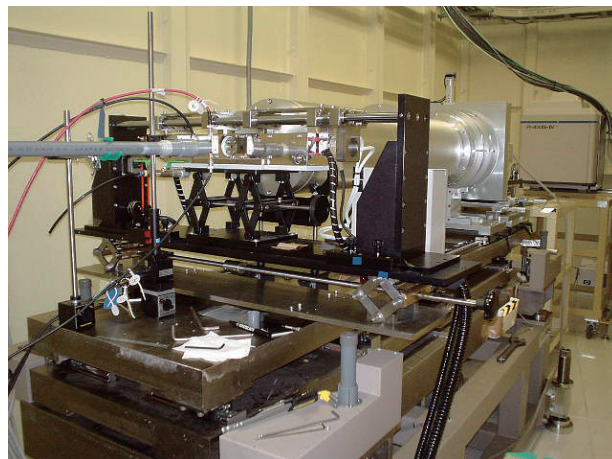


Fig. 2. Experimental setup at BL40B2.

intermediate amorphous region are relaxed owing to lamellar breakup. Above 180% strain, the structural transition of the lamellar structure to a microfibrillar structure takes place, as suggested by the appearance of the transversal streak scattering shown in Fig. 3 and the mechanical transition at the strain of 180%. Moreover, the interfibrillar interaction of the adjacent microfibrils decreases with the film deformation by the pulling-out of the tie chains, which penetrate the adjacent microfibrils, leading to the further stress relaxation of most of the microfibrils. Finally, a network with long-range connectivity

composed of the relaxed microfibrils and the interfibrillar extended amorphous chains exists prior to the breaking of film break.

It is thought that these interfibrillar amorphous chains play an important role in the structure the highly oriented PVA-iodine complexes in the film microstructure. That is to say, it is suggested that highly oriented PVA-iodine complexes, which contribute to the high dichromatic performance of polarizers, are formed in these interfibrillar extended amorphous regions.

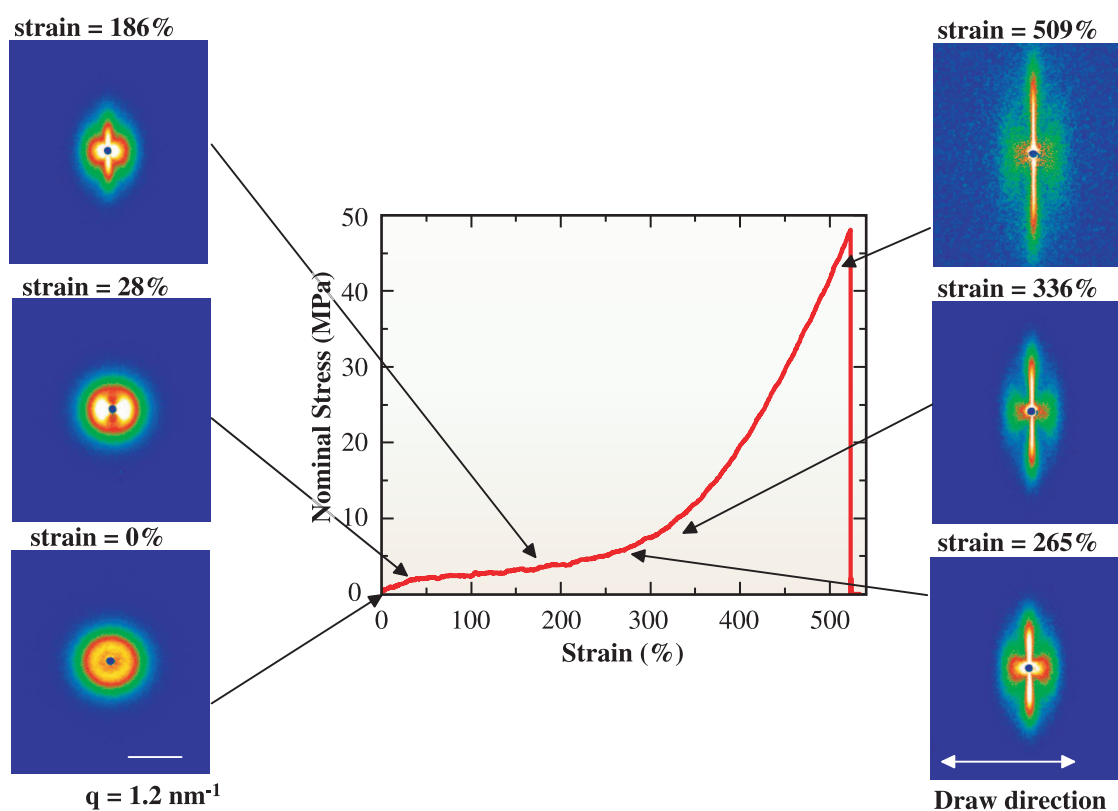


Fig. 3. Stress-strain curve and typical 2D patterns collected during uniaxial deformation in water at 298 K. Each pattern was obtained in 15 s from the point indicated by each arrow.

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References

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