Microscopic Orientation in Uniaxially Stretched Polymers as Studied by Small-angle Light Scattering

Dominguez-Diaz, M, Alvarado-Tenorio, B, Romero- Guzman, ME & Romo-Uribe, A
Laboratorio de Nanopolímeros y Coloides, Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México. Av. Universidad s/n, Cuernavaca, Morelos. C.P. 62210 MÉXICO
aromo-uribe@ce.fis.unam.mx

1. Abstract

A small-angle light scattering (SALS) instrument has been developed in our Laboratory. SALS is especially well suited to studies of systems with a weak scattering power and/or a time-dependent structure evolution in a wide spatial range with sub-micrometer resolution. The technique enables to measure the size, anisotropy, radial periodicity and internal structure of polymer spherulites at a resolution below that achieved by optical microscopy. We will show applications of this instrument to investigate the correlation of microstructure with applied strain in thin polymer films with different thermal histories, the morphological changes in superstructure parallel changes in crystal orientation.

2. Introduction

The small-angle light scattering (SALS) technique was initially developed to characterize polymeric solutions and colloidal suspensions. The usefulness of SALS is now well established and the technique is routinely utilized to investigate soft condensed matter as well as complex fluids. For instance, the spherulitic microstructure of partially crystalline polymers, the microstructure in deformed polyethylene samples, and the influence of thermal annealing on polymer’s crystalline microstructure. There also a number of applications into biological systems. In this work we showed applications of this instrument to investigate the correlation of microstructure with applied strain in thin polymer films subjected to uniaxial tensile deformation.

3. Experimental

3.1 Materials

Nylon 6™ extruded films 35 μm thick were kindly provided by Ticona, the Engineering Polymers Business of Celanese Co. A polyester terpolymer of terephathalic acid and a mixture of 1,4-butanediol and polytetrahydrofuran was also investigated. This material is marketed as Riteflex™ by Ticona and was also obtained as extruded films 35 μm thick. The polyTHF serves as a soft segment in the PBT.

3.2 Small-angle light scattering (SALS)

The SALS apparatus, developed in our Laboratory (Figure 1a) [1], consists of a vertically polarized He-Ne laser (λ=632.8 nm) of 0.8 mW power (model 1500, JDS Uniphase Corp., CA, USA). Scattering patterns were displayed on the color monitor of a PC and recorded via an IMAQ frame grabber (model PCI-1405, National Instruments, USA). Frame grabbing was performed using NI software. SALS was applied to investigate the microstructure in extruded films. The samples were uniaxially deformed along the extrusion direction. The polymer film was clamped at both ends and displaced symmetrically in such a way as the incident beam always impinged at the same point each time.

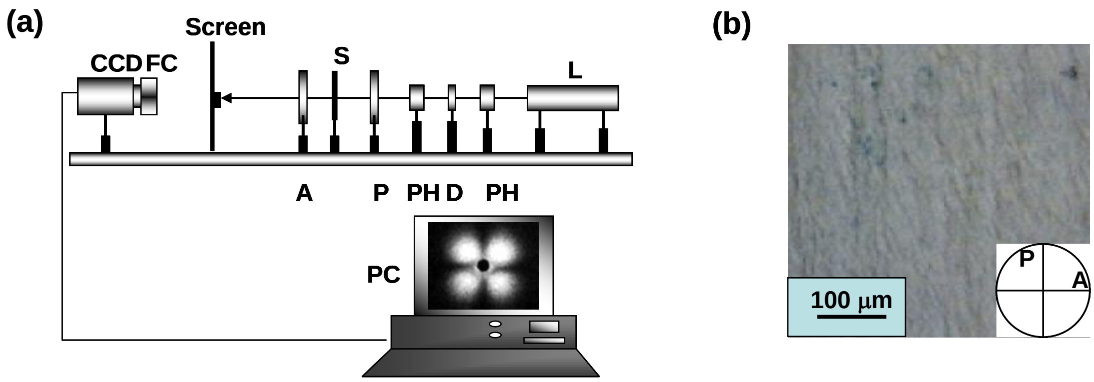

Figure 1. (a) Experimental setup of the small-angle light scattering (SALS) instrument. L: laser, PH: pinhole, D: neutral density filter, P: polarizer, A: analyzer, CCD: charge-coupled device, FC: focusing lens, PC: computer. (b) Optical micrograph under crossed polarizers condition of extruded 35 μm thick Nylon 6 film.

4. Results y discussion

4.1 Uniaxial deformation in spherulitic morphology

Figure 1b shows the optical micrograph of Nylon 6 film under crossed polarizers, the extrusion direction is vertical. It can be seen that the micrograph shows little contrast if any and certainly no sign of sherulites despite being a semicrystalline polymer. On the other hand, figure 2a shows the H_V SALS pattern of this polymer film, the pattern shows a “four-leaf clover” with intensity maxima at azimuthal angle of ϕ=45º with respect to the extrusion direction. This SALS pattern is typical of spherulitic microstructure in semicrystalline polymers [2]. Stein et al. developed a theory for small-angle scattering from spherulitic polymers by assuming that scattering arises from a homogeneous anisotropic sphere embedded in an isotropic medium [2]. Applying Stein et al. equation we obtained a spherulite radius for the Nylon 6 extruded film of R=10.1 μm. Figure 2 shows a selection of SALS patterns obtained at (0), (b) 30, (c) 66 and (d) 134 % deformation. The scattering pattern at 30 % strain (Figure 2b) shows a slight rotation of the intensity maxima towards the equatorial (horizontal) axis as well as a shifting towards the beam stop. This pattern indicates that the spherulites have been deformed and stretched along the tensile axis. There is additionally an intensity streak along the equatorial axis. This streak arises from an elongated microstructure along the tensile axis. Further stretching the sample up to 66 % strain (Figure 2c) does not change the four lobe morphology indicating that the spherulitic morphology is preserved under the uniaxial elongation. Moreover, the shifting of the lobes towards the beam stop indicates a size increase of the spherulites. It can also be seen that the equatorial streak is more intense and elongated suggesting that more material has been aligned along the tensile axis. Finally, Figure 2d shows the pattern corresponding to 134% strain. The four lobe morphology is still appreciated although the maxima are now concentrated into the beam stop. Furthermore, the equatorial streak has grown in intensity, and it is more elongated along the equatorial axis. It is also noted that the equatorial streak shows some azimuthal broadening. The contraction of the four lobes indicates that the spherulitic microstructure has increased in size.

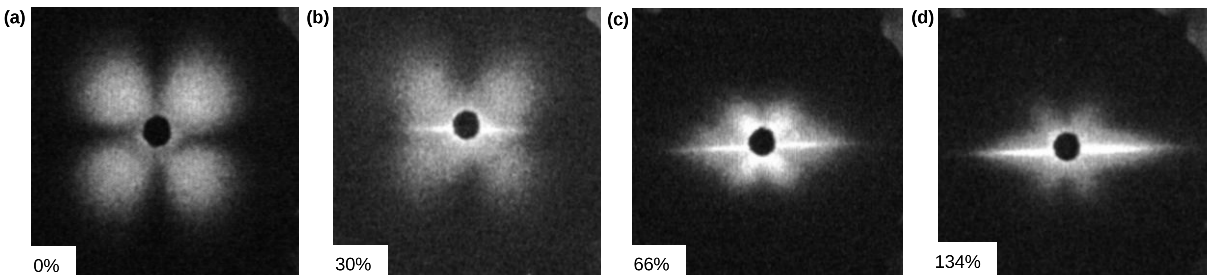

Figure 2. SALS patterns of Nylon 6 film under uniaxial tension along the extrusion (vertical) direction. Patterns correspond to a deformation of (a) 0, (b) 30, (c) 66, and (d) 134%. H_V polarization conditions.

4.2 Uniaxial deformation in non spherulitic morphology

Here it is discussed diffuse scattering arising from a non-spherulitic microstructure in Riteflex extruded film 35 μm thick. The polarized optical micrograph is shown in figure 3a, where a “grainy” microstructure can be appreciated. The H_V SALS pattern of this polymer film shows a diffuse scattering pattern, which can be analyzed using the Debye-Bueche equation in the nonspherically symmetrical form [3]; and from the Guinier-type plots the correlation length can be calculated. Figure 3b shows the plot of correlation length as a function of uniaxial deformation.

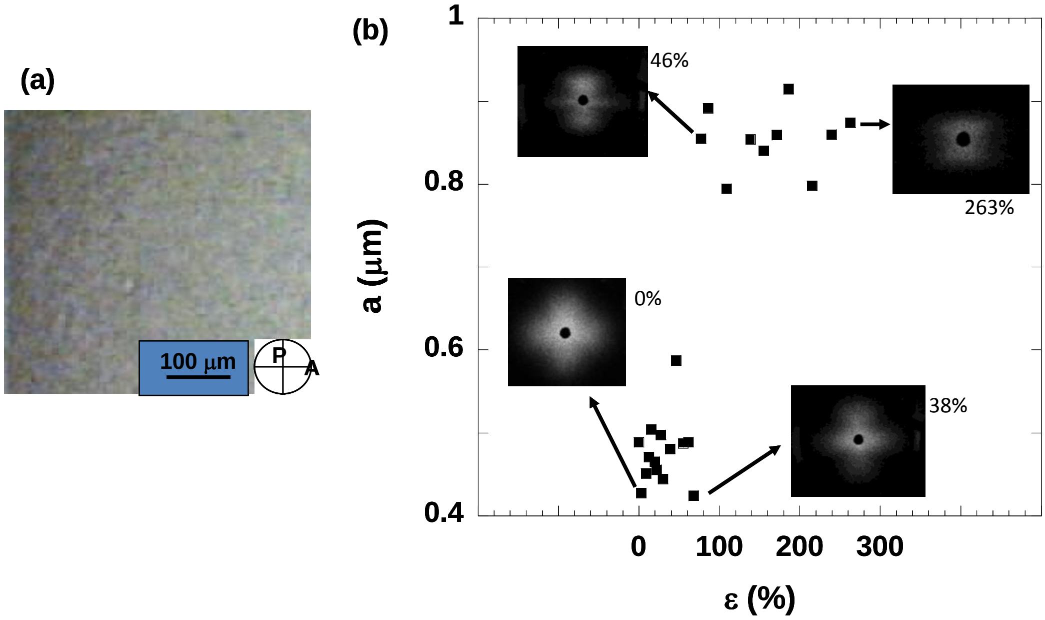

Figure 3. (a) Optical micrograph of 35 µm thick Riteflex film under crossed polarizers condition. (b) The correlation length a, as a function of strain ε, (tension along the extrusion direction) and SALS patterns correspond to a deformation of 0, 38, 46 and 263 %. H_V polarization condition.

5. Conclusions

We have developed a small-angle light scattering instrument that enables characterizing submicron structure in soft condensed matter. The instrument enabled the study of the evolution of the spherulitic microstructure under uniaxial tensile deformation.

M Dominguez-Dìaz and B Alvarado-Tenorio were supported by scholarships from CONACyT. M.E. Romero-Guzmán was supported by a postdoctoral fellowship from DGAPA-UNAM. The authors gratefully acknowledge the financial support of CONACyT (CIAM-2006, grant 58646).

6. References

1. Romo-Uribe A, Alvarado-Tenorio B, Romero-Guzmán ME (2008), submitted.
2. Rhodes MB, Stein RS, *J. Appl. Phys*. 1961; **32**: 2344.
3. Stein RS, Hotta T, *J. Appl. Phys*. 1964; **35**: 2237.