The orientation and crystallization of polyethylene terephthalate monitored by its polarized fluorescence

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We have reported the special method to determine the position of fluorescent molecules or groups in films by using polarized fluorescence measurement, and succeeded in the determination of orientation of both guest molecules in a clathrate crystalline form of polymer [1] and molecules doped into polymer films [2]. In the present study, we have applied our method to polyethylene terephthalate (PET) solids and found that PET chains are oriented even in amorphous region once the film was stretched. We stretched PET films prepared by hot-pressed method uniaxially and measured the fluorescence of ground state dimer (GD) that is formed between two phenylene groups of PET only in amorphous region. Figure 1 shows the angular distributions of the polarized fluorescence intensities of GD by rotating the film around the excitation beam. The figure shows that the distribution of GD is oriented. By annealing the films, the cold crystallization should take place. The figure of GD fluorescence after annealing demonstrates that the intensities decreased much and the distribution changed. It suggests that uniaxial stretching below 100°C of a film can orientate PET chains in the amorphous region so much although the X-ray structural analysis cannot find any orientation, and that the cold crystallization by annealing the film at higher temperatures mainly proceeds by this oriented PET chains in the amorphous regions moving a bit for transforming to a crystalline form.

Figure 1. Angular distributions of I₀ (□) and I₉₀ (▲), polarized fluorescence intensities, of the ground state dimer of a PET film stretched uniaxially: drawing ratio is λ ≈ 4.0 before and after annealing at 200°C. The numbers around the outer circle show the angles of setting a film from 0 to 360° around the excitation light beam, while the distance from the center of the circle shows fluorescence intensity.