

Internal Ordered Structure in Syndiotactic Poly(vinyl Alcohol) Solution

류원석, 하완식*, 이철주, 김병철

한국과학기술연구원 고분자연구부, *서울대학교 섬유고분자공학과

To explore the reasons for the spontaneous development of fibrillar structures during saponifying syndiotactic poly(vinyl pivalate) (PVPi) to poly(vinyl alcohol) (PVA), the rheological and rheo-optical properties of PVA solutions in dimethyl sulfoxide (DMSO) were investigated with tacticity, molecular weight, and degree of saponification. Over the frequency range of 10^{-1} to 10^2 rad/sec the high molecular weight (HMW) atactic PVA exhibited almost a Newtonian flow behavior whereas the HMW syndiotactic PVA exhibited a Bingham flow behavior. On the plot of storage modulus against loss modulus the slope of the atactic PVA approached 2 whereas that of syndiotactic PVA approached 1. In the Casson-type plots for the 2g/dl solutions of atactic PVA, all of intercepts reduced to zero whatever the molecular weight of the polymer is. On the other hand, the syndiotactic PVA produced non-zero intercepts on the plot, pointing out existence of yield stress of positive values. In addition, the yield stress notably increased with increasing the molecular weight of the polymer at the identical polymer concentration. The syndiotactic PVA exhibited much longer relaxation time under dynamic shear in comparison with atactic one (Figure 1). An increase in the shear rate notably increased the flow birefringence of the syndiotactic PVA, but it gave rise to only a slight increase in the case of the atactic PVA. The rheological and rheo-optical characterization of atactic and syndiotactic PVA solutions in DMSO provided clues for the *in-situ* formation of fibers during the saponification process of syndiotactic PVPi. Particularly with the syndiotactic PVA solutions the rheological responses revealed heterogeneity, suggesting existence of internal structures with internal orders. This mesophase, which readily develops an oriented structure even by low shear, seemed to play a significant role in the *in-situ* fiber formation.

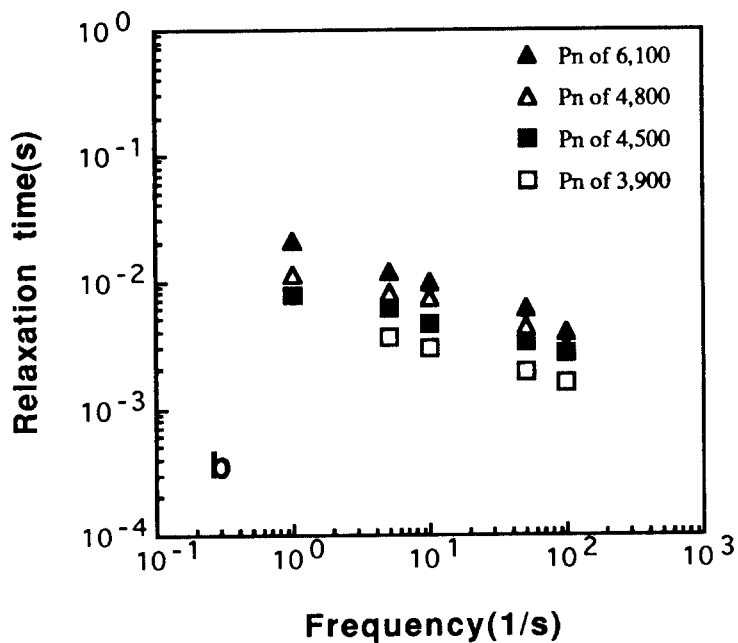
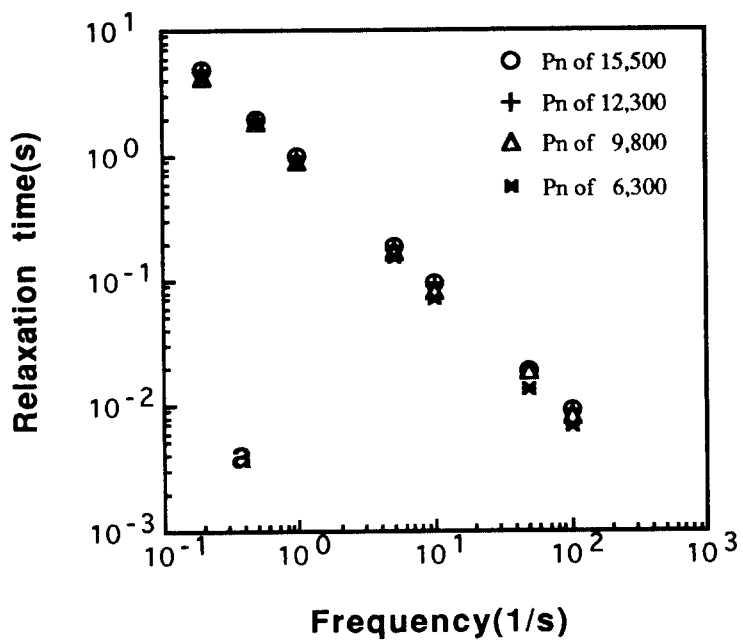


Figure 1. Relaxation times of 2g/dl syndiotactic (a) and atactic (b) PVA solutions as a function of frequency.