

**Concentration Dependence of Diffusion Coefficient of
p-Nitroaniline in Poly(ethylene Terephthalate) and Polyamide**

It is generally accepted that the adsorption isotherm of nonionic dye-disperse dye by synthetic fiber is a so-called Nernst-type partition¹ and that the diffusion coefficient of this system does not depend on the concentration of the penetrant.² Jones³ found that the apparent diffusion coefficient $D(c)$ of azobenzene in cellulose acetate from the vapor phase increases with increasing amount of penetrant, C , represented by

$$D(c) = D_0 (1 + \alpha C) \quad (1)$$

where α is a constant. Sekido and Kojima⁴ have shown that the same relation holds in the diffusion of 4-nitro-4'-hydroxyazobenzene in poly(ethylene terephthalate) (PET) from aqueous solution. The present paper deals with the concentration dependence of *p*-nitroaniline (PNA) as a model compound of disperse dye in synthetic polymers.

The reason for choosing PNA as a penetrant are, firstly, that the ionic character is similar to that of a disperse dye as shown by the pK_a value (about 1.0 in aqueous solution at 25°C), and secondly, that PNA has a fairly high aqueous solubility (e.g., 4.18×10^{-2} mole/liter for PNA compared with 3.15×10^{-5} mole/liter for 1,4-diaminoanthraquinone at 80°C), which makes possible diffusion experiments over a wide range of concentration of dye bath. The diffusion coefficient was determined by the cylindrical film roll method.⁵ The PET used here was Mylar film (du Pont, 5.6 μ thick), the polyamide was nylon 6 film (Unitika Ltd., 27 μ), and the PNA used was GR reagent. Experiments were carried out under following conditions: temperature, 70, 75, 80, 85, 90, and 95°C; PNA concentration, 0.1, 0.25, 0.5, 1.0, 2.0, 3.0 g/500 ml and saturated solution; time, 20 min (95°C saturated solution) and ~ 114 hr, (70°C, 0.1 g/500 ml). Under every set of experiments, the condition of the infinite dye bath was maintained throughout the experiment.

From the concentration profile of the penetrant in the polymer, the diffusion coefficient was calculated by the Boltzman-Matano method.⁶ The concentration dependence of the diffusion coefficient was clearly observed in the case of PET (Fig. 1). In the relatively low concentration range of up to 8×10^{-2} mole/kg PET, D varies with C^n , where n is a constant. In the higher concentration range, D increases with increasing penetrant concentration as follows;

$$D = D_0 \exp(\delta C) \quad (2)$$

where δ is a constant. As was shown in the case of the diffusion of aliphatic hydrocarbon in natural rubber and polyisobutylene, the same type of concentration dependence was observed,⁷ in which δ is a parameter concerning the plasticizing effect of penetrant in polymer substrate. Equation (2) indicates that the increase of diffusion coefficient caused by the penetrant can be superimposed by the displacement of the concentration coordinate. The equation is equivalent to the following formula which is the same type as the Williams-Landel-Ferry equation,⁸

$$\ln a_r = - \frac{A(C - C_0)}{B + C - C_0} \quad (3)$$

where a_r is the ratio of the diffusion coefficient at reference penetrant concentration C_0 to that at concentration C , and A and B are constants. PMA penetrates into an easily accessible amorphous region at low concentration. The penetration reaches a finite value (Fig. 1, I and II): at a higher concentration of PHA, the penetrant may plasticize the PET without changing the total amount of the region available for dyeing. It was suggested that the increase in diffusion coefficient is caused by a minute qualitative change in the amorphous region of PET. This change could not be detected by IR spectroscopy, small-angle x-ray scattering, or dichroism of the dyed film. The tendency

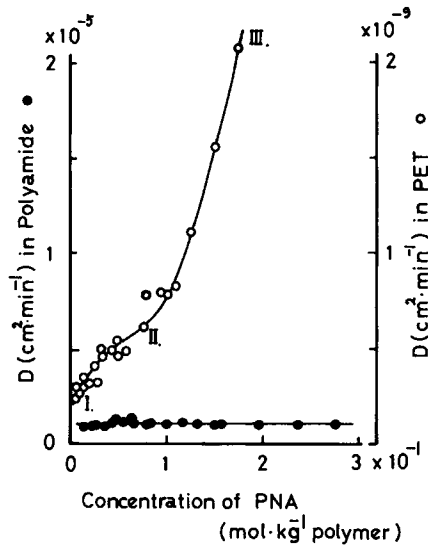


Fig. 1. Concentration dependence of diffusion coefficient (70°C).
(O) PET; (●) Polyamide.

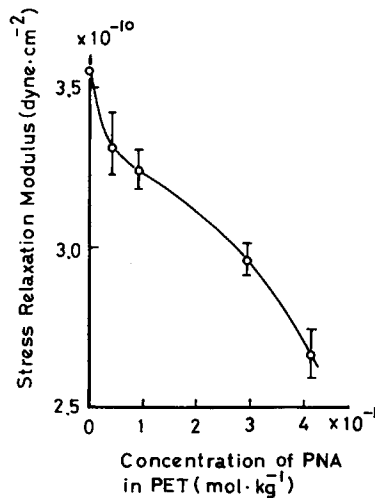


Fig. 2. Stress relaxation modulus of dyed PET (20°C).

of the decrease in stress relaxation modulus corresponds to the tendency of the increase in diffusion coefficient with increasing PNA concentration, as shown in Figure 2.

In contrast to the above results on PET, the concentration dependence was not observed in the case of polyamide as shown in Figure 1, even though the saturation value of PNA in polyamide is almost double that in polyester. Stress relaxation modulus of dyed nylon film did not change over the range of PNA concentration examined. From these results it appears that the penetrant PNA acts in a sense as a plasticizer in polyester substrate owing to the similarity in chemical constitution, i.e., both contain an aromatic nucleus.

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