

Transport of Noble Gases in Acrylic Polymer

The transport behavior of noble gases in polymers in the region of transition temperature is very interesting in connection with investigations of the diffusivity and solubility of the diffusant itself and also assists in the elucidation of the segmental motion and microstructure of the polymer matrix.

It has been observed that in many amorphous polymers the temperature dependence of diffusivity and solubility of gases is different above and below the glass transition temperature (T_g).¹ Recently, Stannett et al.² reported the permeability and solubility of He, Ne, Ar, and Kr in poly(methyl acrylate), in a temperature range encompassing T_g , and compared it with that in poly(vinyl acetate).

We have already reported on the diffusivity of small molecules in various crystalline polymer substrates in relation to the thermal properties of the polymer.³⁻⁷ There, acrylic polymer shows a specific behavior; i.e., in the case of diffusion from an aqueous or vapor phase, disperse dyes and their model compounds show temperature dependence of the activation energy of diffusion above the T_g . The dependence was clearly represented by the WLF equation by using the T_g of the polymer as reference temperature.⁵

To find a better experimental confirmation of such diffusion behavior in acrylic polymer, the transport of He, Ne, and Ar has been investigated.

Acrylic film used in the experiment was prepared from a copolymer of acrylonitrile and vinyl acetate (93:7 wt) having $\bar{M}_w = 7.2 \times 10^4$ as reported earlier.⁴ The film was cut into a circle 4 cm in diameter. The thickness of the film was about 14 μm and was measured accurately by a Minicom thickness gauge (Tokyo Seimitsu Co. Ltd.) in each set of experiments. The film was checked to be free from pinholes before the experiment. A stainless steel permeation cell was used and sealed with a Viton gasket (1 mm thick). The diffusion cell was kept at constant temperature ($\pm 0.1^\circ\text{C}$) by a thermoregulating Ni-Cr heater mounted in the cell. The amount of permeation of gas was traced by reading the mercury head of a manometer on the vacuum side of the cell. The experiments were carried out at intervals of 10° between 70° and 140°C . The

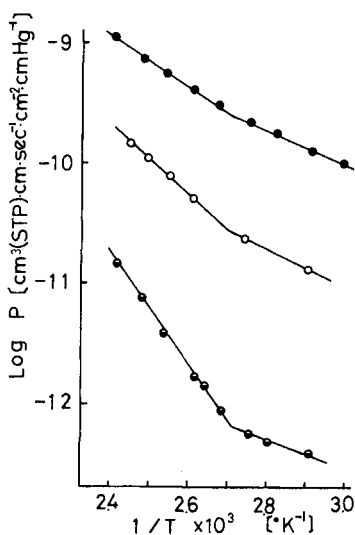


Fig. 1. Temperature dependence of PAN permeability to noble gases: (●) He; (○) Ne; (◐) Ar.

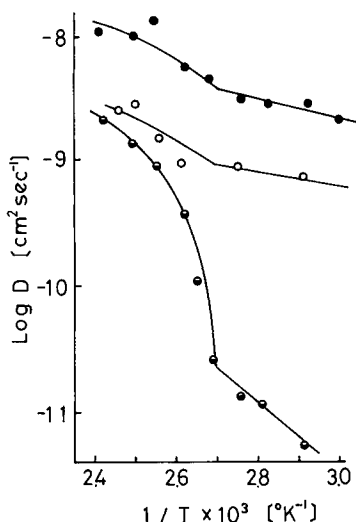


Fig. 2. Temperature dependence of diffusion coefficient of noble gases in PAN: (●) He; (○) Ne; (◐) Ar.

permeability coefficient P was obtained from the gradient of the steady flow. Diffusion coefficients D were calculated by the time lag method.⁸ The results are illustrated in Figures 1 and 2.

As shown in Figure 1, each of the Arrhenius plots of P has two straight lines with inflections at the T_g of this polymer. The Arrhenius plot of D has also a sharp inflection at T_g , above which the slope of the plot changes gradually with rise in temperature (Fig. 2). This pattern is similar to that obtained with Malachite Green⁴ and disperse dyes and their model compounds⁵ in the same polymer. The course of temperature dependence of the diffusion coefficient can be well described by the WLF equation. The values of C_1 and C_2 for Ar were 2.71 and 16.3 (deg), respectively, from which f_g , the fractional free volume at T_g , and $\Delta\alpha$, the difference between the thermal expansion coefficients above and below T_g , are obtained; these were 0.161 and 9.87×10^{-3} (deg⁻¹), respectively. The values are fairly large compared with the universal constants $f_g = 0.025$ and $\Delta\alpha = 4.8 \times 10^{-4}$ (deg⁻¹) and suggest the presence of microvoids⁹ in the acrylic film used.

The authors wish to thank Prof. A. Datyner (U.N.S.W.) for giving advice in writing this paper.

References

1. P. Mears, *J. Amer. Chem. Soc.*, **76**, 3415 (1954); G. J. van Amerongen, *J. Polym. Sci.*, **5**, 307 (1950).
2. W. H. Burgess, H. B. Hopfenberg, and V. T. Stannett, *J. Macromol. Sci.-Phys.*, **B5**(1), 23 (1971).
3. E. Iwahori, T. Iijima, and M. Okazaki, *Sen-i Gakkaishi*, **24**, 118 (1968).
4. T. M. A. Hossain, H. Maeda, T. Iijima, and Z. Morita, *Polym. Lett.*, **5**, 1069 (1967).
5. T. M. A. Hossain, T. Iijima, Z. Morita, and H. Maeda, *J. Appl. Polym. Sci.*, **13**, 541 (1969).

6. T. Shibusawa and T. Iijima, *ibid.*, **14**, 1553 (1970).
7. T. Iijima and S. Ikeda, *Angew. Makromol. Chem.*, **14**, 177 (1970).
8. R. M. Barrer, *Trans. Faraday Soc.*, **35**, 628 (1939).
9. S. Sotton, and A. M. Vialard, *Text. Res. J.* **41**, 834 (1971).

T. IIJIMA
T. TANNO

Department of Polymer Science
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo, Japan

T. NAKAGAWA

Industrial Products Research Institute
Shimomaruko, Ohta-ku, Tokyo, Japan

Received October 10, 1973
Revised November 7, 1973