

The Diffusion of Gases and Water Vapor Through Grafted Polyoxymethylene

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Synopsis

Polyoxymethylene was successfully grafted with styrene, butadiene, and acrylonitrile by the mutual irradiation method in the monomer containing 18% of dimethyl formamide. The CO₂ and water vapor permeabilities and diffusivities were determined in the case of the butadiene- and acrylonitrile-grafted products. The former grafts had higher permeabilities than the ungrafted materials. However, the acrylonitrile grafts showed considerably reduced water vapor permeability and diffusivity compared to the ungrafted polyoxymethylene. Films made by grafting to polymer powder and compression molding showed lower permeabilities compared to those made by direct grafting to polyoxymethylene films.

INTRODUCTION

The successful synthesis of thermally stable polyoxymethylenes formed by capping with appropriate endgroups or by the introduction of a few per cent of a suitable comonomer has led to its widespread use as a plastic material with many useful properties. Its use in various packaging applications has been somewhat reduced, however, by its high water-vapor transmission rate.^{1,2} Thus, at 25°C even at low humidities, it has a permeability constant of 90×10^{-9} ccs STP per cm² per cm per sec per cm Hg. This compares with corresponding values of 27.5 and 9.0×10^{-9} for poly(vinyl chloride) and low-density polyethylene, respectively. Furthermore, the water vapor permeability increases with increasing humidity to a permeability constant value of almost 140×10^{-9} with liquid water. The reason is the comparatively high solubility of water, about 1% at saturation, and also a rather high diffusivity of water in the polymer, about 2.8×10^{-8} cm per second at 25°C. It is not easy to devise methods for reducing these values. One possible method is to graft a hydrophobic polymer to the polyoxymethylene backbone. In addition to possibly reducing the overall water solubility, grafting may lead to closer packing of the polymer chains, i.e., to a decrease in the free volume. Since the diffusivity reacts exponentially to change in the free volume, small effects could be quite beneficial. Some evidence that this could be a possibility may be found in the

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work of Harmer³ with styrene-grafted polyvinylchloride. It was found that the density actually increased on grafting up to 10% of polystyrene even though the grafted polymer has a much lower density. These experiments were made by molding grafted granules; the work of Takamatsu⁴ was carried out by grafting styrene directly onto poly(vinyl chloride) film and showed only a continuous decrease in density with grafting. The

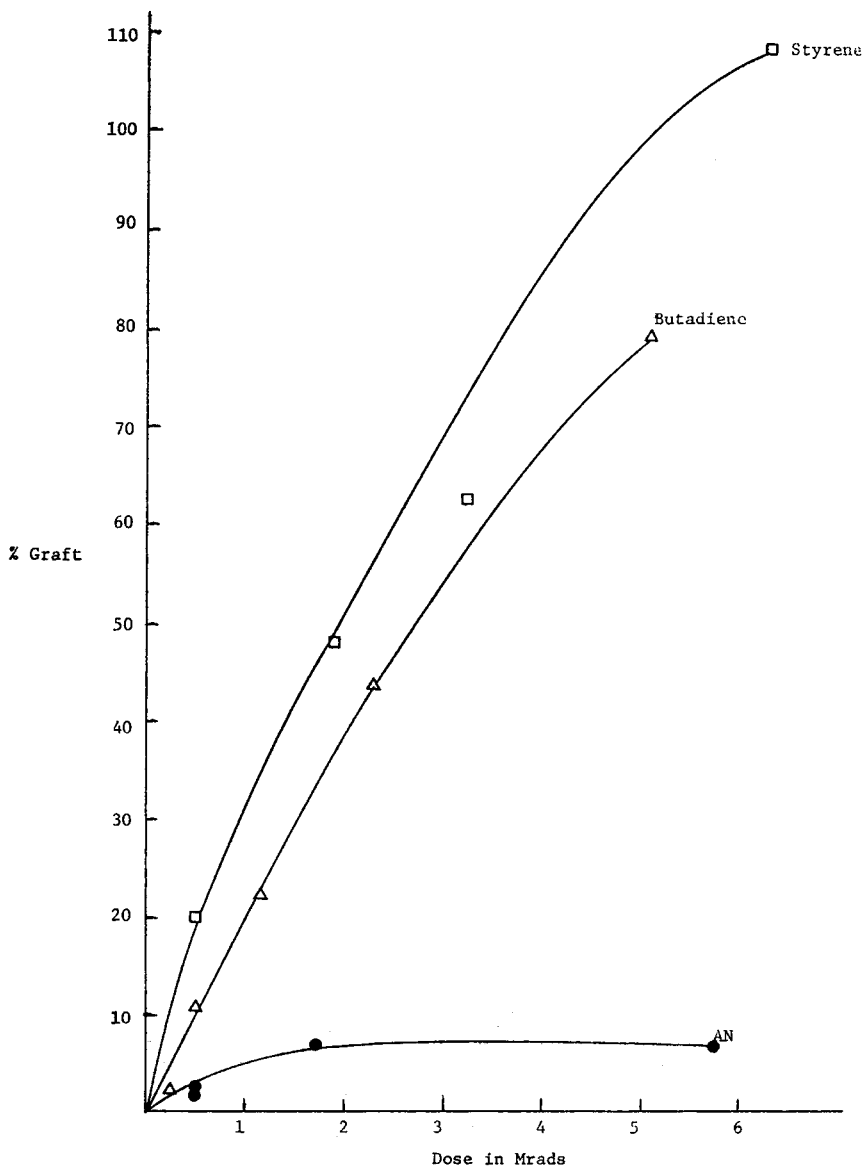


Fig. 1. Grafting of various monomers to POM film in the presence of 18% DMF at 25°C. Dose rate 0.01 Mrad/hr.

present paper describes the results of some preliminary attempts to change the barrier properties of polyoxymethylene by graft polymerization.

EXPERIMENTAL

The polyoxymethylene used in this study was obtained from the Celanese Corporation in the form of extruded films or fine granules and contained less than 5% of copolymerized oxymethylene units. The density was 1.405 and films of 0.10 and 0.45 mm were used.

The permeability and time-lag diffusion constants were measured using the modified high vacuum technique.⁵ Water vapor sorption isotherms were obtained using a conventional quartz helix microbalance and a recording Cahn RG electronic microbalance.

Grafting experiments were carried out in sealed glass ampoules which contained previously degassed monomer and solvent in direct contact with the sample. Degassing was achieved by the usual freeze-thaw method. The sample tubes were irradiated from a cobalt-60 source to the desired

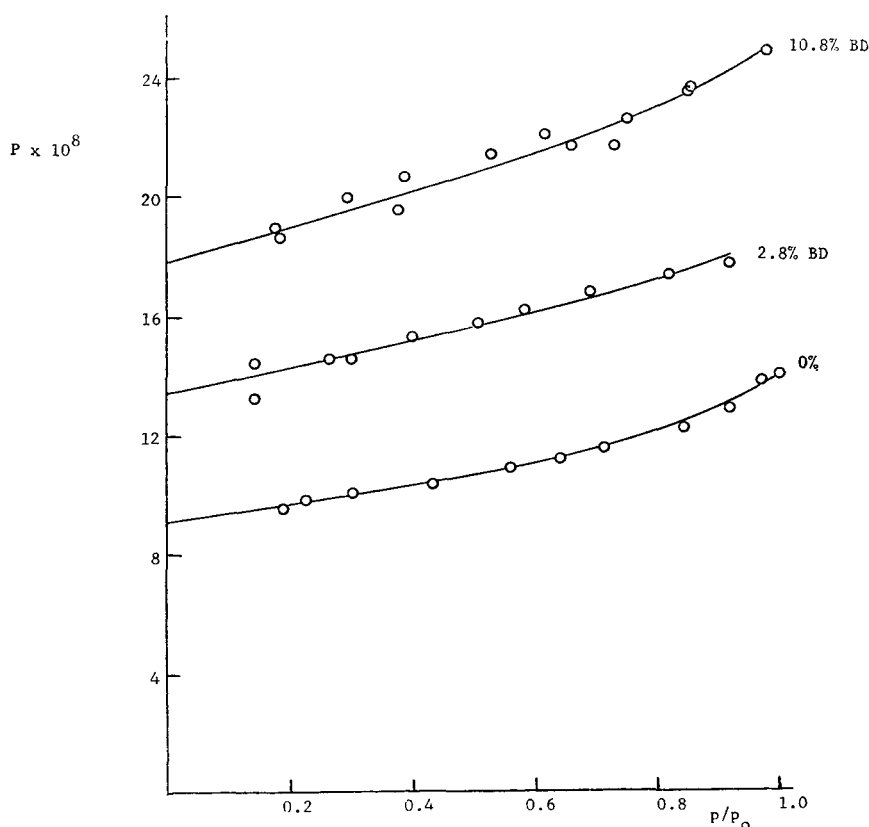


Fig. 2. Concentrated dependence of the permeability constants for water vapor in POM, 2.8% butadiene-grafted POM, and 10.8% butadiene-grafted POM. All at 25°C.

dose. After grafting, the samples were Soxhlet-extracted with a suitable solvent to constant weight. Benzene was used as the extraction solvent for all grafts except the acrylonitrile, which required dimethylformamide. The per cent grafting was taken to be the percentage increase in weight from that of the dry material.

RESULTS AND DISCUSSION

In order to try and reduce the water vapor permeability of polyoxymethylene, mutual irradiation grafting experiments were carried out with two different monomers in the presence of a suitable solvent. These monomers, differing widely in properties, were butadiene and acrylonitrile. Each monomer was found to graft readily in the presence of dimethylformamide.

The results of the grafting experiments for butadiene, styrene, and acrylonitrile are shown in Figure 1. It is clear that grafting continues to increase with dose with butadiene and styrene over the range of doses studied. Such behavior was not, however, exhibited by acrylonitrile. Instead,

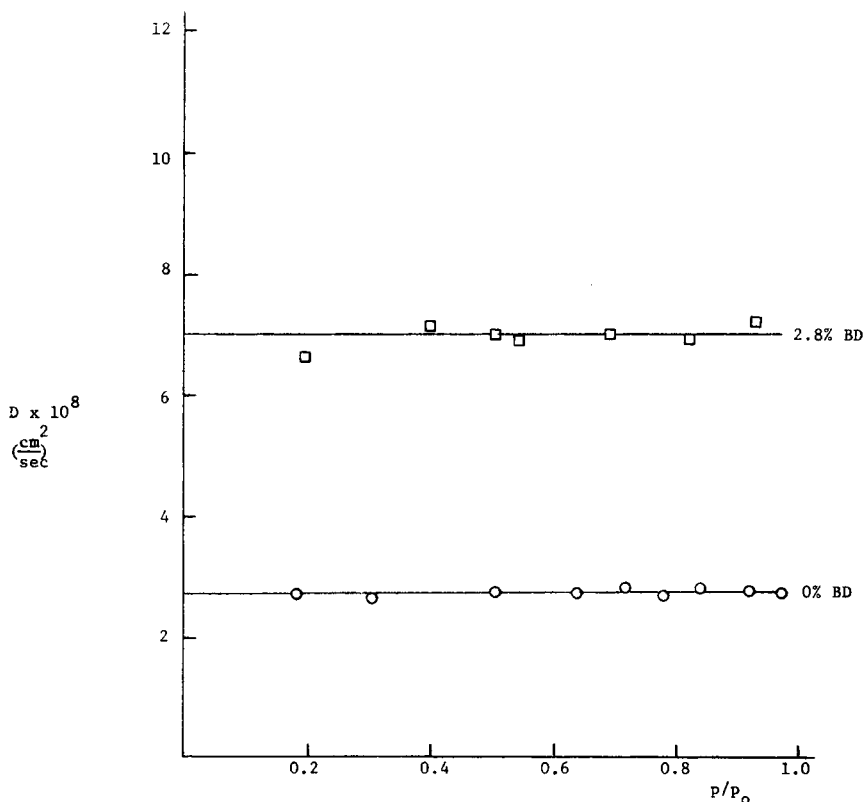


Fig. 3. Concentration dependence of the diffusion constants for water vapor in POM and 2.8% butadiene-grafted POM. All at 25°C.

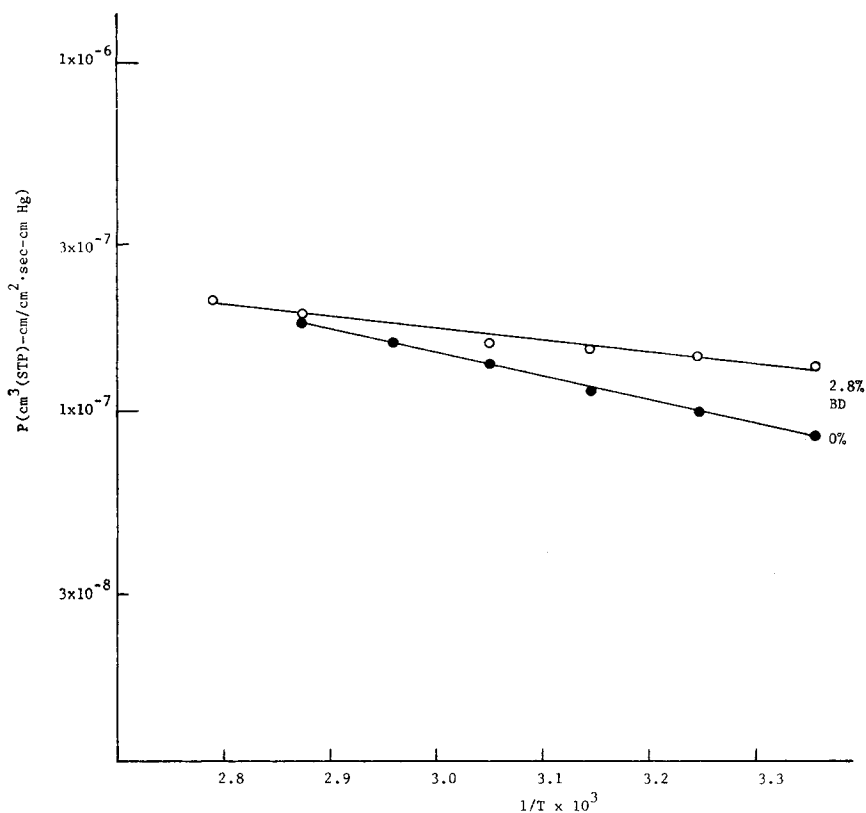


Fig. 4. Temperature dependence for the permeability of water vapor in butadiene-grafted POM.

grafting yields leveled off after about 1.5 Mrad, as can be seen in Figure 1. Irradiation to higher total doses did not result in any significant increases in the grafting level of acrylonitrile.

The reasons for the differences in the grafting behavior with the monomers is undoubtedly due to the differences in the solubility of the homopolymers in their respective monomers.

Polybutadiene is quite soluble in the monomer solution used, and, as grafting proceeds in the lightly swollen substrate, the polymer continues to swell and grafting proceeds smoothly to substantial yields. Styrene behaves quite similarly, as shown by the curve included in Figure 1 and in the work of Kimura et al.⁶ The swelling forces are sufficient to overcome the cohesive forces of the polymer; it is reasonable to expect, therefore, that the free volume of the grafted polymer might be actually increased depending on the packing on one hand and the disruption of the polymer structure on the other.

Polyacrylonitrile, by contrast, is quite insoluble and only slightly swollen by the monomer solution used. The cohesive forces of the polyoxymethyl-

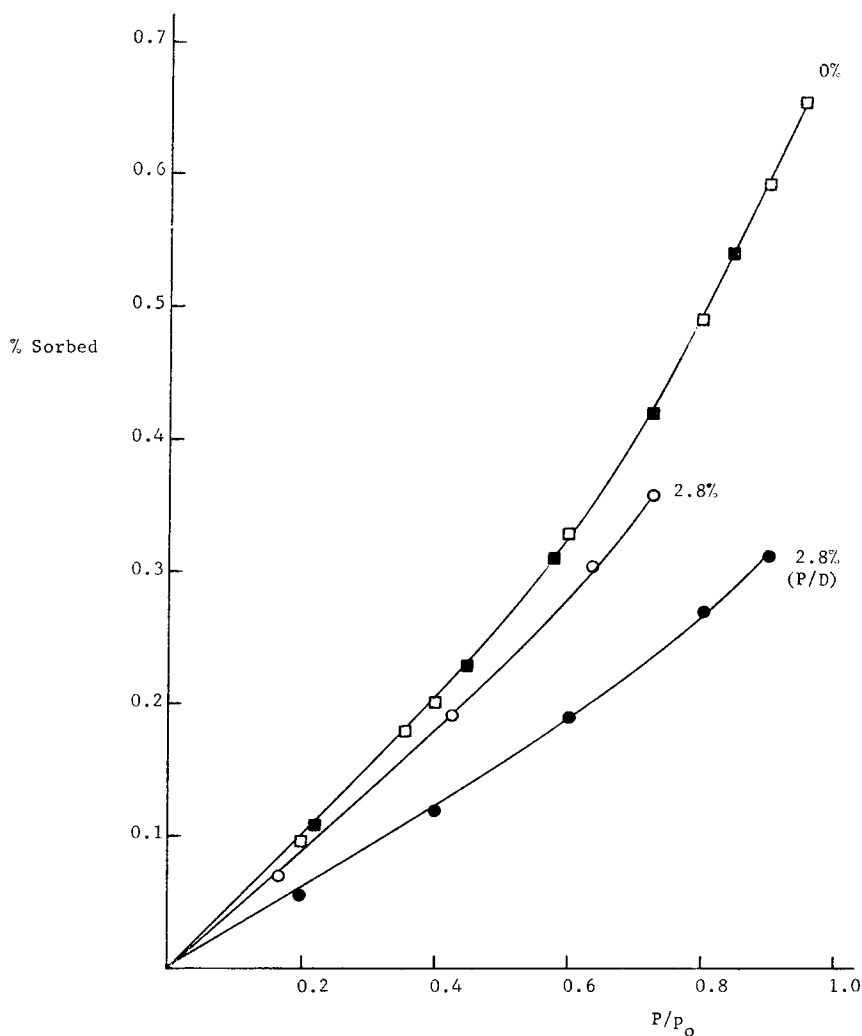


Fig. 5. Sorption isotherm for water in 0% and 2.8% butadiene-grafted POM at 25°C. Filled points are calculated from $P = DS$.

ene substrate are therefore sufficient to prevent such swelling, and the acrylonitrile only grafts to a limited extent. Once the available free volume and surfaces are filled with grafted polymers, no further grafting can take place.

In consideration of the two different types of grafting behavior with polyoxymethylene, butadiene and acrylonitrile grafts were chosen for further water vapor permeability studies.

The permeability behavior of the grafted films were found to be quite different. In the case of butadiene-grafted films, small amounts of graft were found to lead to an increase in both the permeability and diffusivity

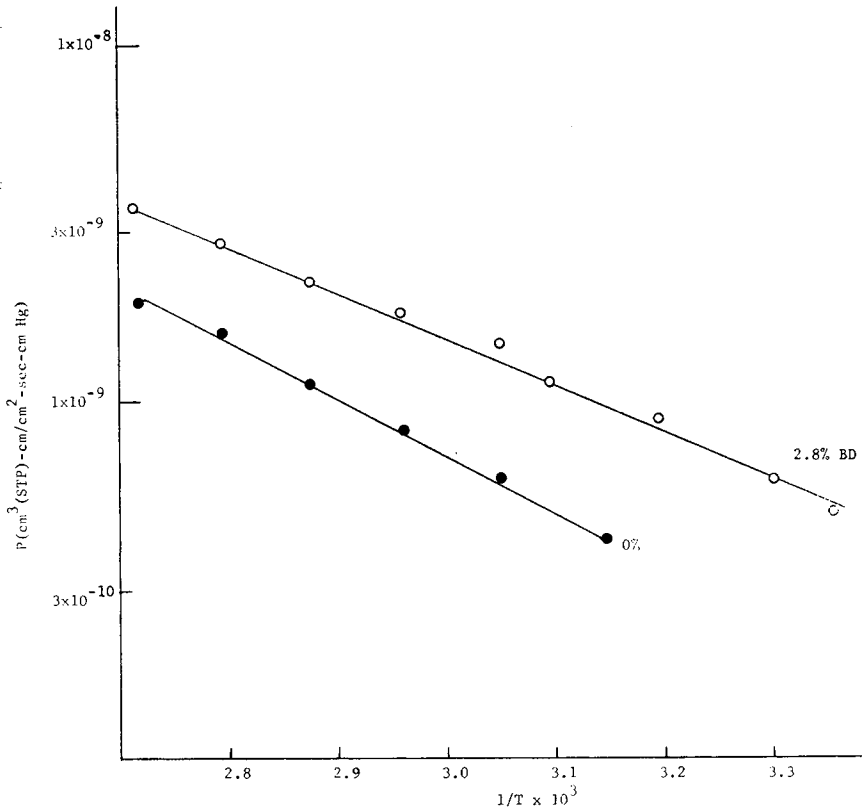


Fig. 6. Temperature dependence for the permeability of carbon dioxide in butadiene-grafted POM,

of water vapor, as can be seen from Figures 2 and 3. As the grafting level was increased from 2.8% to 10.8%, the permeability to water vapor continued to increase. Presumably the grafting in this case has facilitated the diffusion of penetrant by opening up the structure of the polyoxymethylene. Examination of the temperature dependence of the permeability constants

TABLE I
The Effect of Grafting Butadiene to Polyacetal on the
Transport Properties of Water and Carbon Dioxide

Penetrant	Film	$P^a \times 10^8$	$D \times 10^8$, cm ² /sec	P/D	E_p (kcal/ mole)	E_D (kcal/ mole)
H ₂ O	POM	9.1	2.7	3.4	3.1	—
	2.8% BD ^b	13.3	7.0	1.9	1.5	—
CO ₂	POM	1.8	1.4	0.013	7.5	11.7
	2.8% BD ^b	5.1	4.4	0.012	6.0	9.2

^a Units: cm³(STP)-cm/cm²-sec-cm Hg. All values at 25°C.

^b 2.8% Butadiene-grafted POM.

lends some support to this view, as shown in Figure 4. The lower activation energy in the case of the grafted material would indicate that the barrier to diffusion has been lowered somewhat as a result of the graft. The actual values for the activation energies are summarized in Table I.

Water vapor sorption isotherms for the unmodified and 2.0% butadiene-grafted polyoxymethylene films are presented in Figure 5. Clearly, the grafted sample has a lower overall sorption of water than the unmodified

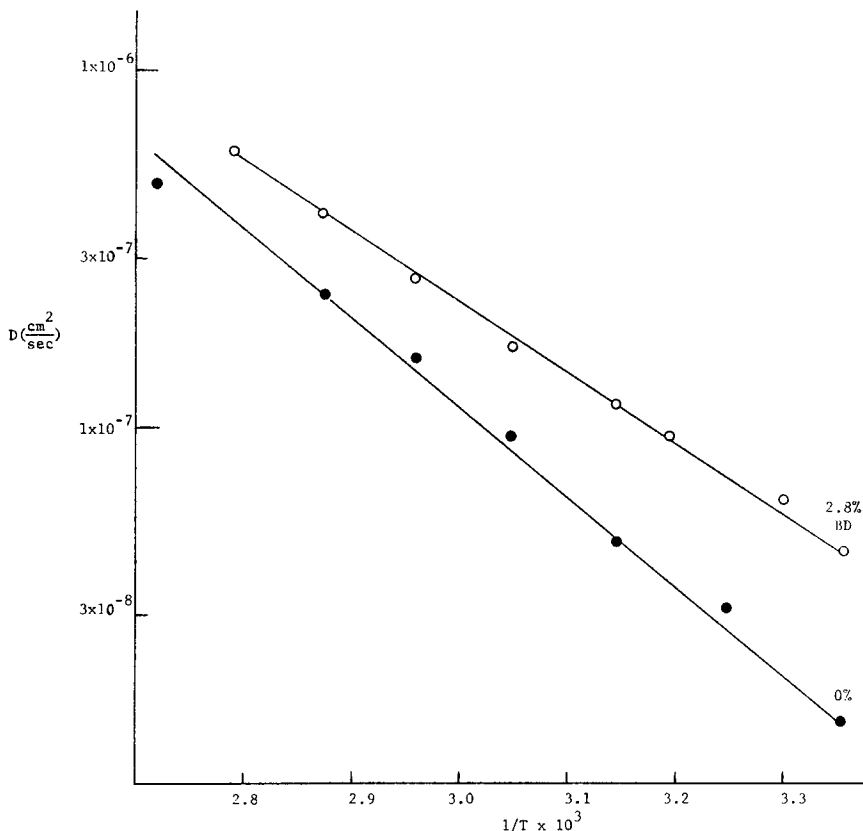


Fig. 7. Temperature dependence for the diffusion of carbon dioxide in butadiene-grafted POM.

material. The calculated solubilities, $S = P/D$, from the permeability measurements also indicate an overall lowering of the solubility and are included in Figure 5 along with the calculated solubilities for the unmodified material. It is interesting to note that the calculated solubilities agree with the measured values for the unmodified material, but are slightly lower for the grafted sample. This lack of agreement between measured and calculated sorption isotherms is not unusual and has been discussed in considerable detail in a previous communication.² For comparison, the

initial values are included in Table I for the P/D relationships for the two samples.

Permeability studies made with noncondensable gases also showed values for the unmodified and the butadiene-grafted polyoxymethylenes that had the same relationship as the corresponding values for water. Results of such measurements on the modified films with carbon dioxide are

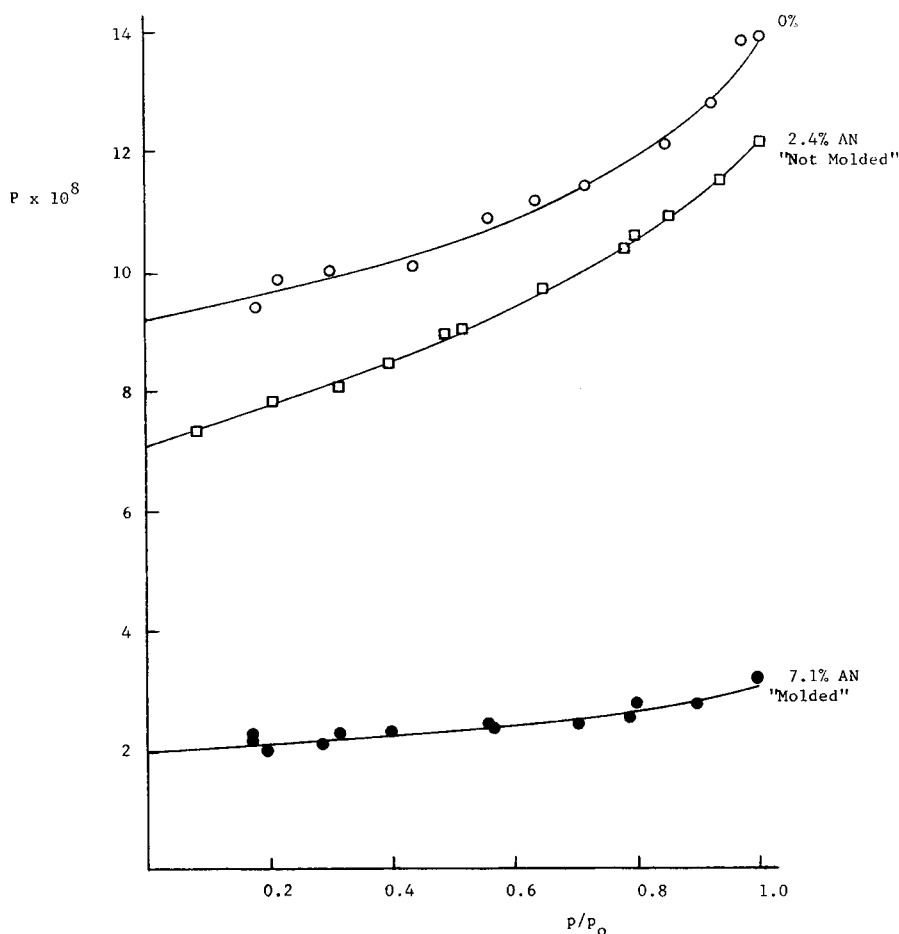


Fig. 8. Concentration dependence of the permeability constants for water vapor in POM, 2.4% acrylonitrile-grafted and 7.1% acrylonitrile-(molded)grafted POM. All at 25°C.

shown in Figures 6 and 7 for the temperature dependence of the permeability and diffusion constants, respectively. The activation energies and other pertinent data for carbon dioxide are summarized along with the corresponding values for water in Table I. It is evident that both penetrants have a lower activation energy and show an increase in permeability in the butadiene-grafted sample in comparison to the unmodified polymer.

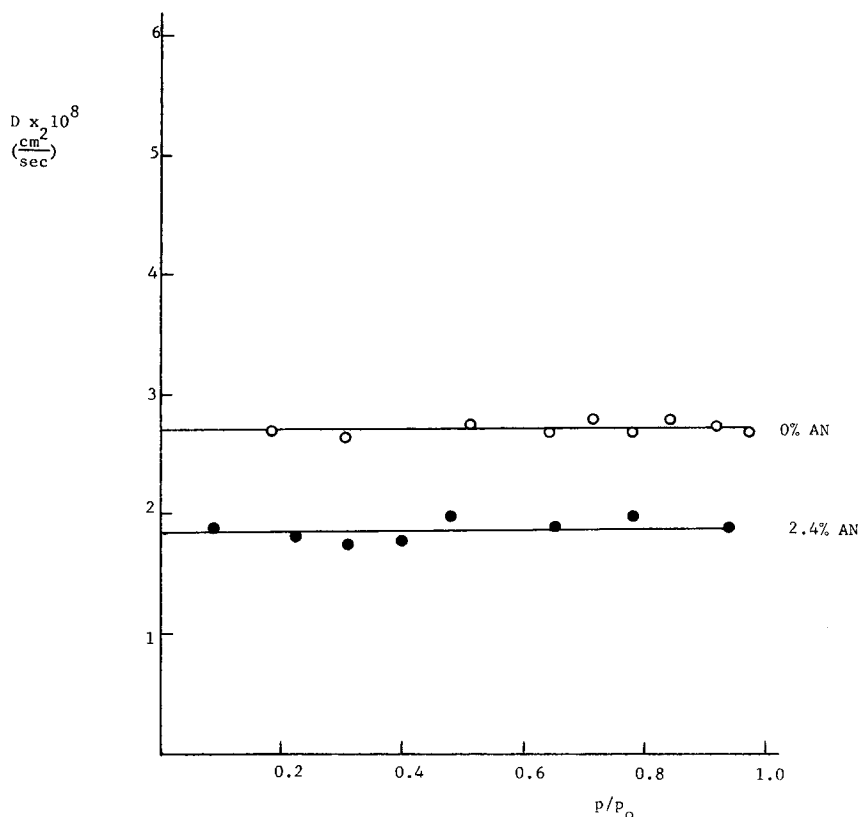


Fig. 9. Concentration dependence of the diffusion constants for water vapor in POM and 2.4% acrylonitrile-grafted POM. All at 25°C.

A quite different behavior in transport properties was exhibited in the second case with the acrylonitrile-grafted polymer. Unlike the butadiene-grafted polymer, the acrylonitrile-grafted sample showed a decrease in both the permeability and diffusion of water, as shown in Figures 8 and 9. If one views the graft in this case as packing in the interstitial regions and thus lowering the net free volume of the polymer, the results would be an increase in diffusion path length and thus a lowering of the diffusion constant as found. The grafting results presented above lend some support to this view. Further support of this viewpoint was indicated recently in a paper by Harmer, referred to previously, on grafting of styrene to polyvinyl chloride.³ It was found that grafting a few per cent of styrene led to an increase in the film density over that of the original polyvinyl chloride even though polystyrene is of considerably lower density.

The work of Harmer³ and Takamatsu⁴ indicated that styrene grafted to polyvinyl chloride showed an increase in film density only when grafting was first carried out on powder and then molded, and not when grafted directly on film. With polyoxymethylene, however, a substantial reduc-

tion in both diffusivity and permeability was found when acrylonitrile was grafted on the film.

Measurements were also carried out on a molded product. Although the molded product contained a higher percentage of acrylonitrile, it did seem to be more effective in changing the properties compared with the film, as can be seen from Figure 8.

In conclusion, it can be stated that grafting small amounts of a suitable polymer can lead to a significant decrease in the permeability of a substrate polymer. Molding the grafted polymer does seem to give larger decreases than direct grafting to the preformed polymer film.

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