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### Some Recent Advances in Pure and Applied Aspects of Graft Copolymers

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## Some Recent Advances in Pure and Applied Aspects of Graft Copolymers

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### SUMMARY

In recent years more attention has been given to the preparation and characterization of graft copolymers and an examination of their properties than to developing novel methods of synthesis. In particular, these property studies can be used to develop applications of graft copolymers. The methods used to prepare and characterize better defined grafts are briefly reviewed. The structure of most graft copolymers is such that considerable amounts of one polymer can be grafted to another without affecting greatly the main properties of that polymer. In this way, the properties of one polymer such as higher water absorption can be imparted to another without changing the mechanical properties, for example, of the second polymer.

Some other inherent properties of graft copolymers are discussed, including their compatibility with the parent homopolymers, their possible conformational changes, and other features. Finally, the use of the special nature of graft copolymers for the modification of the barrier properties of film and membranes is discussed as one possible general field of application.

### INTRODUCTION

From the time the first grafting reactions were described in 1946 until the early 1960's, the main emphasis of research in this field was on devising

new ways of syntheses of graft copolymers and on learning more details of these grafting reactions already known. Although studies of this kind are continuing, more recently the emphasis has shifted into the preparation and characterization of purer and better defined graft copolymers. With these materials becoming available more meaningful property studies are now being undertaken and more detailed work into possible applications is being conducted.

Studies of the preparation, purification, and characterization of better defined graft copolymers have followed two main lines. The initial approach was to prepare graft copolymers by a more random approach such as radiation and then to purify them and characterize them as well as possible. This was the approach followed by the author and his colleagues using the cellulose acetate-styrene system. By choosing different and well-defined molecular weight cellulose acetates and by changing the conditions of radiation grafting, different molecular weight side chain and backbone grafts could be prepared. The changes in the molecular weight of the cellulose acetate itself with the different grafting conditions was followed by substituting  $\alpha$ -methyl styrene for styrene in the grafting mixture [1].  $\alpha$ -Methyl styrene was found to have similar swelling and solvent powers to styrene and is also known to have similar radical affinities. On the other hand, it does not propagate mainly due to steric hindrance and so one can simulate all the grafting conditions, without actually grafting, and measure the resulting changes in the cellulose acetate backbone. The graft polymers themselves had sufficient solubility changes for the two homopolymers to make their separation rather straightforward. The final purity of such a graft copolymer was demonstrated by means of density gradient ultracentrifugation [2]. The pure graft copolymers could be acid hydrolyzed, leaving behind the polystyrene side chains. These, like the treated cellulose acetate backbone, could be fractionated and the molecular weight distributions determined so that a good deal could be known about the composition and molecular weight of such grafts. Most of the work with this system was aimed at elucidating the kinetic and other features of both the pre-irradiation and mutual radiation grafting methods. However, the approach used did result in the isolation of some rather pure and well-defined graft copolymers, and interesting property studies were conducted with these materials [3]. Some of the results obtained will be described later.

A second and much more powerful approach to the synthesis of well-defined graft copolymers is the use of "living" polymers developed by Szwarc. Rempp and his colleagues have pioneered and developed this approach with considerable success [4]. In our laboratories work has also

been carried out [5, 6], particularly on the styrene-2-vinyl pyridine system. The best approach is to couple living polymeric side chains directly to a previously prepared backbone polymer. The carbanionic method of preparing polymers, if carried out under suitable conditions, leads to a very narrow molecular weight distribution. This lends a valuable extra feature to the well-defined character of the graft copolymers prepared by this technique. The experimental methods used make it easy to simultaneously isolate samples of the backbone and side chain polymers as well as the coupled graft copolymers. This makes comparative studies of the grafts with either the homopolymers or physical mixtures of the same composition of the graft particularly meaningful. Corresponding studies with well-defined block polymers prepared by these techniques are now being extensively pursued in many laboratories [7].

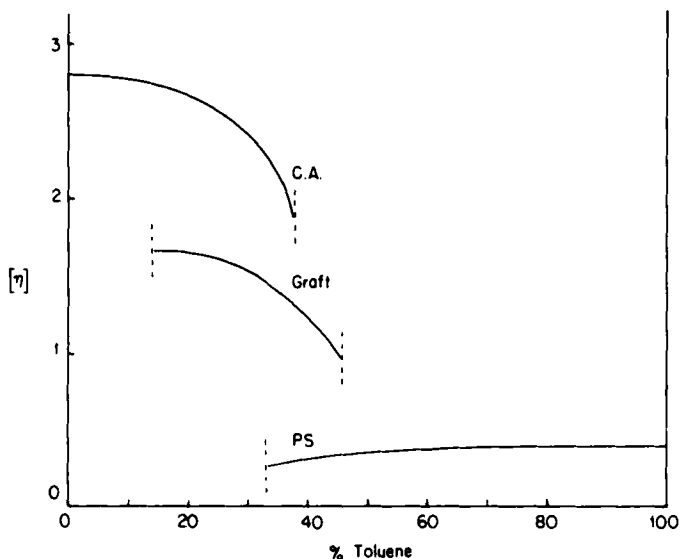
At this point it is well to describe certain general features of graft copolymers which are not always recognized.

Even with multibranching grafts, there are comparatively few branch points per monomer unit in the backbone chain and most methods of grafting give very few. This means that the main properties of the base polymer, such as crystallinity, melting point, glass temperature, and modulus, are essentially unchanged. In practice up to about 15% of another polymer can be grafted without affecting the main properties much. At the same time, if the grafted polymer has very different properties, it couples these with those of the main polymer. A good example is the grafting of 8-12% of polyacrylic acid onto high density polyethylene [8, 9]. The melting point and crystallinity were essentially unchanged, and the modulus and the softening point raised somewhat. Random copolymerization of acrylic acid would, on the other hand, reduce the crystallinity, modulus, and softening point. The water sorption and permeability, however, were markedly increased by the grafting and the grafted polymer had excellent adhesion to aluminum. Thus grafting can be seen to be, perhaps, the only method by which certain properties can be introduced permanently into a polymer without affecting its chief performance characteristics. Such considerations are often behind the extensive researches into the modification of material and synthetic fibers by grafting where it is hoped that properties such as soil release and antistatic behavior can be introduced into a textile fiber, for example, without affecting its strength, softening point, and other desirable characteristics.

Leaving now such lightly grafted polymers and considering the whole range of compositions, there are a number of other features worth discussing, each in turn.

## SOLUBILITY AND COMPATIBILITY

The solubility of a 50:50 cellulose acetate-polystyrene graft copolymer and of the two parent homopolymers in mixtures of solvent, each of which is only a solvent for one component, is shown in Fig. 1. As non-



**Fig. 1.** Intrinsic viscosities and solubility limits of secondary cellulose acetate, polystyrene, and a 44.1% polystyrene grafted cellulose acetate in a mixture of acetone and toluene.

solvent is added, the intrinsic viscosity of that polymer is reduced until it precipitates. The graft copolymer, on the other hand, is not soluble in either solvent alone. At a certain composition, however, the copolymer suddenly becomes soluble and only precipitates again at much higher proportion of the second solvent. In other words, the copolymer is soluble only in a certain range of solvent mixture compositions. The changes in intrinsic viscosity of the homo and graft copolymers with solvent composition will be discussed in more detail later. The capacity of a graft copolymer to be compatible with solvent mixtures, each of which is only a solvent for one component, is also reflected in their behavior with polymer blends. Thus, secondary cellulose acetate is highly incompatible with

polystyrene and even a few per cent of one polymer mixed with the other gives white opaque films on casting from solvents. The addition of a graft copolymer of the two, however, at comparatively low percentages causes compatibilization in the sense that clear transparent films are formed. In Fig. 2 is shown a plot of the light transmission of films of a 50:50 mixture by weight of secondary cellulose acetate and polystyrene to which increasing amounts of a graft copolymer consisting of roughly equal proportions of cellulose acetate and polystyrene have been blended. It can be seen that the excellent clarity of the cast pure graft film is maintained up

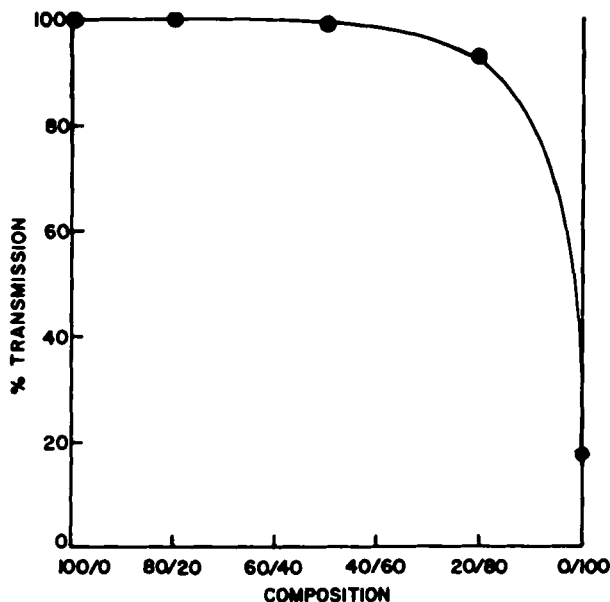


Fig. 2. Light transmission vs composition of films made from a 50:50 blend of secondary cellulose and polystyrene and a 44.1% polystyrene grafted cellulose acetate.

to about 60% of the 50:50 mixture and a good clarity up to about 80%. The complete three component phase diagram, taking 75% light transmission as an arbitrary measure of compatibility, is shown in Fig. 3. Again it can be seen that the graft copolymer has succeeded in compatibilizing a mixture of polystyrene and cellulose acetate over a very wide range of three component compositions. In the same study, however, it was also shown that grafts with too short side chains or backbones did not give a large degree of compatibilization although blends of each type did [3].

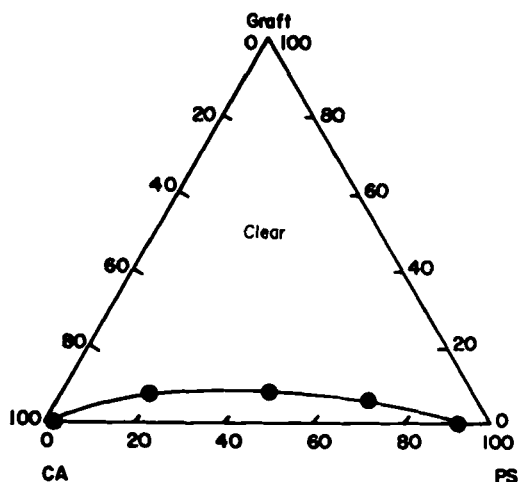


Fig. 3. Phase diagram of blends of secondary cellulose acetate, polystyrene, and a 44.1% polystyrene grafted cellulose acetate. A 75% light transmission of film was selected as an arbitrary compatibility limit.

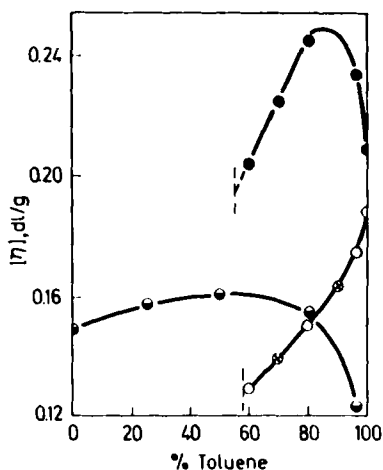
In the above discussion the criteria for compatibility was the clarity of films cast from the various polymer blends. There is evidence, however, that even films cast from pure graft copolymers consist in reality of tiny domains of each type of polymer. Thus, for example, the diffusion constant for water at low activities in cellulose acetate is  $1.8 \times 10^{-8}$  cm<sup>2</sup>/sec compared with  $28.0 \times 10^{-8}$  cm<sup>2</sup>/sec for polystyrene. The diffusion constant for water in a graft copolymer containing 44.1% of combined polystyrene, however, was found to be only  $3.4 \times 10^{-8}$  cm<sup>2</sup>/sec. If the graft copolymer film were molecularly homogeneous, one would expect the diffusivity of the graft approximately intermediate between those of the two homopolymers, i.e., about  $13 \times 10^{-8}$  cm. On the other hand, if the graft copolymer film consisted of isolated domains of each polymeric species, the diffusivity would be governed by the slow diffusion step through the cellulose acetate domains. Since the volume fraction is about 50%, the value would be  $3.6 \times 10^{-8}$  cm<sup>2</sup>/sec, in good agreement with the measured value of 3.4. The implications are clearly that the graft copolymer films are not molecularly homogeneous but consist essentially of domains of each type of polymer. The fact that the films are quite clear is an indication that the domains are extremely small. Since this work was completed, considerable evidence of a similar structure for the case of

block copolymers has been advanced [10, 11]. The compatibility aspects of graft copolymers may have to be somewhat modified in the face of such findings. For example, it may be that graft or block copolymers on their own form clear, apparently homogeneous, films. However, the evidence suggests that these consist of very small domains of each polymeric species. Recent evidence in the case of blocks suggest [10, 11] only about 50-1000 Å size for the domains. Presumably when a given homopolymer is added to a graft or block copolymer, it can blend with the domain of its own kind up to the point when the average domain is large enough to scatter light and begin to show opacity. An extreme of this situation would be when only a small amount of graft copolymer is available but sufficient to form a compatible interface. It now seems clear that the success of blends of opaque rubbery and glassy polymers, such as high impact polystyrene and ABS polymers, is partly due to the deliberate or fortuitious presence of compatibilizing graft copolymers in the blend.

### CONFORMATIONAL CHANGES

It is well known that when a poor solvent is added to a solution of a high polymer in a good solvent, the intrinsic viscosity of the polymer is decreased. This is due to the closer coiling of the polymer chains in the poor solvent leading to a decreased hydrodynamic volume and consequently a lower intrinsic viscosity. In the case of a graft copolymer it is clear that a mixture of two solvents, one good for the side chains and one for the backbone component polymer, should show a maximum in the intrinsic viscosity. Such effects have been studied by Rempp and co-workers [12]. An excellent example of this type of behaviors is shown in Fig. 4 for a polystyrene-poly(2-vinyl pyridine) graft copolymer with about one side chain per polystyrene backbone [13]. The solvent mixture used was toluene and ethanol, good solvents for polystyrene and poly(2-vinyl pyridine), respectively, but nonsolvents for the other polymer. It can be seen that each homopolymer decreases in intrinsic viscosities until precipitation occurs as the proportion of nonsolvent is added. The graft copolymer, on the other hand, first increases to a maximum and then decreases until precipitation occurs at about 40% by volume of ethyl alcohol in toluene. Presumably close to the minimum intrinsic viscosity in pure toluene, the backbone polymer is extended and the side chains coiled whereas in the high alcohol mixture the backbone is more tightly coiled and the side chains extended.





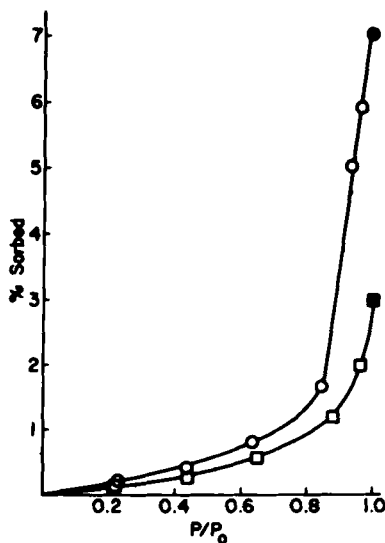
**Fig. 4.** Intrinsic viscosity and solubility limits of polystyrene, poly(2-vinyl pyridine), and graft copolymer of 64.3% polystyrene and 35.7% poly(2-vinyl pyridine) side chains, each component similar to the homopolymers in toluene-ethanol solvent mixtures. ○: Poly(2-vinyl pyridine) side chains. ◐: Polystyrene backbones. ●: Graft copolymers (taken from Ref. 13).

If, for example, films were cast under these extreme conditions, the properties of either the side chain or backbone polymer should predominate. Such effects were first shown by Bateman for grafts of polyethyl methacrylate and natural rubber [14]. According to the solvents used, rubbery or glassy properties could be imparted to the films. In the case of the styrene-2-vinyl pyridine graft copolymers, both polymers are glassy at room temperature but the water sorption is quite different for each polymer. In Fig. 5 the sorption isotherms for films of the same graft copolymer but treated with different solvents are shown. It can be seen that the films treated with methanol, a good solvent for the vinyl pyridine, the hydrophilic component sorbs much more water than the same film treated with toluene only. The water vapor permeabilities of two similarly treated films of the same graft copolymer was also measured. The film treated with methanol had more than eight times the water vapor permeability compared with the film cast directly from benzene solution.

### GRAFT COPOLYMERS IN MEMBRANE TECHNOLOGY

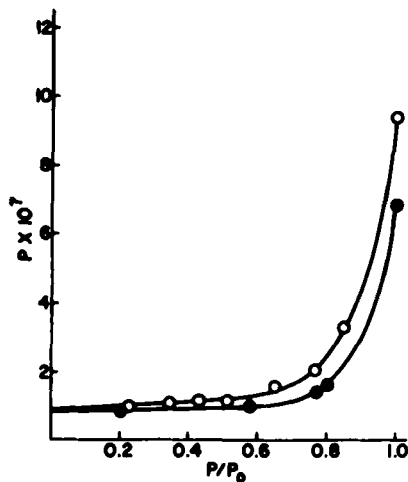
In principle the effect of the conformational changes discussed above can

be used to put a conformational gradient across the thickness of a membrane. If the polymer has a concentration dependent diffusion constant, then a membrane which has a different water vapor permeation rate in one direction than another can be prepared. The principles behind such behavior have been described by Rogers et al. [15]. Such a membrane was prepared by grafting 2-vinyl pyridine to polyethylene since the vinyl



**Fig. 5.** Water vapor isotherms of a graft copolymer of 70% polystyrene backbone and 30% poly(2-vinyl pyridine) side chains cast from benzene.  $\circ$ : Swollen in 75:25 petroleum ether-toluene mixture, solvent exchanged with methanol and dried.  $\square$ : Swollen in 75:25 petroleum ether-toluene mixture and dried. Solid points are with liquid water.

pyridine-styrene graft copolymers were found to have a concentration independent diffusion constant for water vapor. The membrane was treated on the upstream side with hot ethanol vapor in a permeability cell where the downstream side was constantly pumped. In this way a conformational gradient was imposed on the film. The water vapor permeabilities were then measured at a number of vapor pressures, the film inverted in the cell, and remeasured. The results in Fig. 6 show clearly the two directional nature of the water vapor permeability even though the effect is not large [16].



**Fig. 6.** Dependence of the permeability constants for water at 25°C in a poly(2-vinyl pyridine) grafted 0.922 density polyethylene film on the relative humidity. ●: Permeation against direction of the ethanol gradient treatment. ○: Permeation in direction of ethanol gradient. Grafted film consisted of 92% poly(2-vinyl pyridine) grafted to 100 parts polyethylene by weight.

Anisotropy across the thickness of membranes is not usually discussed in molecular terms. The best known anisotropic membranes are the Loeb-Sourirajan cellulose acetate membranes developed for the reverse osmosis process for water purification. These consist of a thin intact skin of cellulose acetate on top of a more spongy open structure. This structure enables high fluxes to be achieved due to the very thin intact layer. However, under the high pressures needed for reverse osmosis, especially with sea water purification, there is a gradual compaction of the structure causing a marked decline in the flux rate.

Since polystyrene has a good resistance to wet creep it was thought of interest to study the effect of grafting styrene to cellulose acetate reverse osmosis membranes. The initial phases of the research has been to determine the effect of grafting polystyrene on the wet tensile creep behavior of films cast from pure graft copolymers. The results are summarized in Table 1 and show that the grafting does indeed reduce the wet tensile creep. It is interesting that shortening the length of the grafted side chains

increases the effectiveness of grafting in reducing the tensile creep. The transport of water in the grafted and ungrafted films are also summarized in Table I and show comparatively small reduction in the water flux with even substantial degrees of grafting. This illustrates further the way in which grafting can build in the properties of a second polymer such as polystyrene without gross changes in those of the first polymer such as cellulose acetate. The grafted films still have to be fully studied under reverse osmosis with Loeb-type membranes but preliminary indications are at least modestly encouraging [17].

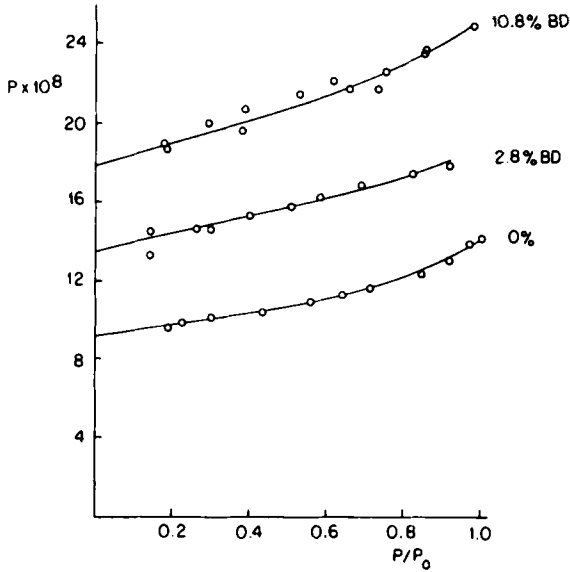
Another area where grafting might change the permeability properties of a membrane would be where small amounts of grafting could in some-way cause tighter packing, reduce the free volume, and decrease the permeability characteristics. Some inkling that this might be realized may be found in the paper by Harmer on grafting styrene to polyvinyl chloride [18]. It was found that grafting a few percent of styrene lead to increases in the film density over that of the original polyvinyl chloride even though polystyrene is of considerably lower density. A number of experiments along these lines were conducted on polyoxymethylene with a view to reducing its water vapor permeability [19]. Two monomers were studied for grafting, butadiene and acrylonitrile. It was found that both could be readily grafted by the mutual radiation method in a dimethyl formamide solution of the monomers. The permeability behaviors of the grafted films was quite different. Small amounts of butadiene were found to lead to polyoxymethylene films with increased permeabilities and diffusivities to water vapor as can be seen from the data plotted in Figs. 7 and 8. Acrylonitrile, on the other hand, leads to decreased permeability and diffusivity to water vapor as can be seen from the data plotted in Figs. 9 and 10. The work of Harmer with styrene grafted to polyvinyl chloride had shown that the increased density of the grafts only occurred when the grafted powder was molded and not when grafted directly on film. With polyoxymethylene, on the other hand, grafting acrylonitrile directly on film also resulted in a marked reduction in both the diffusivity and permeability to water vapor. However, the molded grafted product did seem to be more effective in changing the properties compared with the film as can be seen from Fig. 9. More work is clearly needed to follow this interesting behavior.

In summary it can be seen that graft copolymers are unique structures in that two polymers are connected together in such a way that the properties of each may remain comparatively unaffected. This leads to a

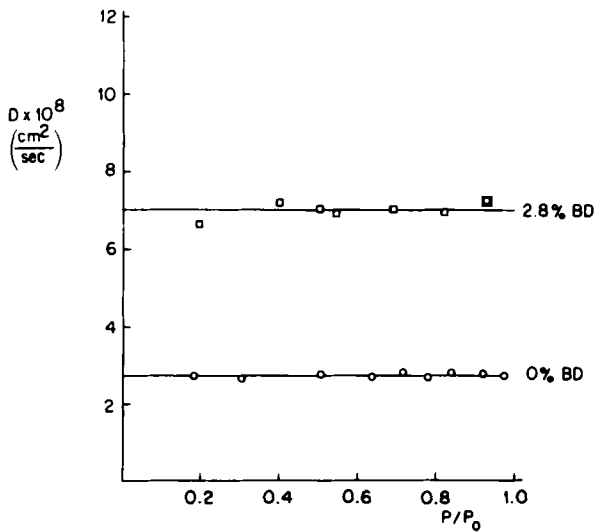
**Table 1. Effect of Grafting Polystyrene on the Reverse Osmosis Performance and Tensile Creep Properties of Cellulose Acetate Films<sup>a</sup>**

% Grafted Polystyrene	MW of grafted polystyrene	Water flux g/d-mil	% Salt rejection	Per cent Elongation	
				1 hr	100 hr
113.6	100,000	0.052	93.5	1.4	2.6
74.00	55,000	0.066	90.0	1.6	4.5
63.00	162,000	0.060	98.2	3.4	5.9
47.5	66,000	0.052	98.5	1.4	4.4
44.7	138,000	—	—	2.8	6.3
0	Control	0.079	96.0	5.7	10.2

<sup>a</sup>Per cent graft is expressed as weight of polystyrene per 100 parts of cellulose acetate. Reverse osmosis conditions 1500 psi, 35000 ppm, NaCl 28°C. Tensile creep 10<sup>8</sup> dynes/cm<sup>2</sup>, 38°C.



**Fig. 7.** Permeability constants for water vapor at 25°C as a function of relative humidity in 0, 2.8, and 10.8% butadiene grafted to polyoxymethylene.



**Fig. 8.** Diffusion constants for water vapor at 25°C as a function of relative humidity in 0 and 2.8% butadiene grafted to polyoxymethylene.

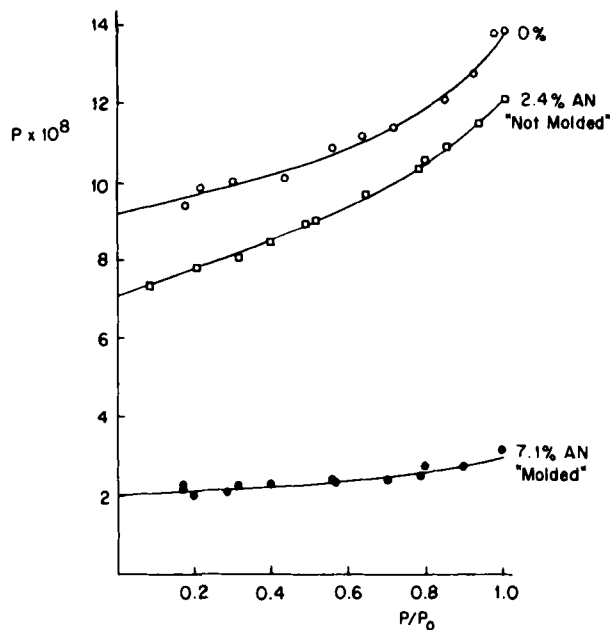


Fig. 9. Permeability constants for water vapor at 25°C as a function of relative humidity in 0, 2.4, and 7.1% acrylonitrile grafted polyoxymethylene.

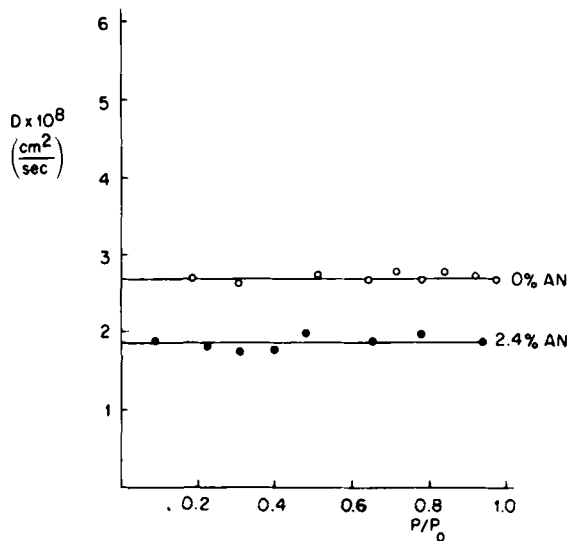


Fig. 10. Diffusion constants for water vapor at 25°C as a function of relative humidity in 0 and 2.4% acrylonitrile grafted polyoxymethylene.

number of unique possibilities for combining the properties of one polymer with those of another together with various other possibilities.

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