

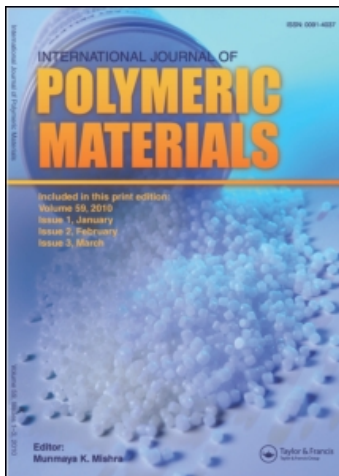
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# Water Sorption by Graft Copolymers of Polyamide and Poly-N,N-Dimethylaminoethyl Methacrylate

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This paper deals with the investigation of sorption and structural properties of graft copolymers of polycaproamide and poly-N,N-dimethylaminoethyl methacrylate. It is shown that the portion of hydrolyzing amide groups does not exchange after grafting. All samples have equal solubility, but diffusion coefficients depend on grafting degrees, and the zero coefficient is a function of CONH-group concentration.

**KEY WORDS** Sorption, graft copolymers, polyamides, poly-N,N-dimethylaminoethyl methacrylate

The method of graft polymerization of fibers of ionogenic monomers and monomers involving reactive groups that enable the incorporation of ionogenic groups into fibers as a result of certain conversions is widely used in the production of chemisorbing material.<sup>1</sup>

The grafting of such monomers ultimately determines the sorption-diffusion characteristics of fibers that are to a great extent responsible for the service of grafted monomers.<sup>2</sup> Such is the rate of various compounds' chemisorption by fibrous materials. At the same time the sorption properties of graft copolymers are as yet insufficiently studied.

One type of chemisorption fibers is obtained by the authors and represents an anion exchange fiber produced from a graft polycaproamide copolymer (PCA) and polydimethylaminoethyl methacrylate (PDMAEMA) which appears to be a very effective sorbent of acid gases. Therefore, these copolymers undergo acid hydrolysis by service conditions. Hence, investigations of sorption-diffusion properties in polymer-water systems is necessary to predict the longevity of polymer articles.

## EXPERIMENTAL DATA

In order to verify the reliability of the information obtained, PCA films with various contents of graft polymer are studied along with the PCA fibers.

Use is made of industrial PCA PC-4 film 50–70 mkm thick purified of low molecular compounds, a nylon-6 film of the “Bayer” firm 20 mkm thick (nonoriented), and a PDMAEMA film obtained from a solution of PDMAEMA in ethyl alcohol by evaporation of the solvent in a teflon cell.

The PCA-PDMAEMA copolymers are produced as a film by grafting PDMAEMA directly to the above-mentioned PCA film using the redox system  $\text{Cu}^{2+}$ - $\text{Na}_2\text{S}$ - $\text{H}_2\text{O}_2$ .<sup>3,4</sup> The amount of graft polymer was controlled by varying the preparation conditions.

In ascertaining the dependence of the water diffusion coefficients in the PDMAEMA-modified fibers, the water vapor sorption is studied by the interval method at 25°C using the McBain balance.<sup>3</sup> The shot is 20–30 mg, the quartz spiral sensitivity 0.778 mg/mm and the water diffusion coefficient is calculated by the equation

$$\frac{M_t}{M} = 1 - \frac{8}{n^2} \exp(n^2 D t / l^2) \quad (1)$$

where  $M_t$  and  $M$  are the changes in the film weight at the instant  $t$  and in the state of sorption equilibrium, respectively,  $l$  is the film thickness and  $D$  is the differential diffusion coefficient.

The integral diffusion coefficient  $\bar{D}$  over the range of relative vapor pressures  $P/P_0$  from 0 to 0.8 is calculated by equation (5):

$$\bar{D} = \left[ \int_{c_2}^{c_1} D(c) dc \right] / (c_1 - c_2) \quad (2)$$

where  $c_1$  and  $c_2$  are the extreme concentrations of the studied diffusion range.

The functional dependence of the diffusion coefficient on concentration  $D(c)$  is found by the matching method up to the best coincidence of the experimental and calculated data. The polymer accessibility to water molecules is found by the isotope H→D exchange method. It consists of the fact that heavy water penetrating into the polymer matrix becomes involved in the isotope exchange reaction with the mobile hydrogen atom of the amide group.

Hereafter the accessibility  $f$  will mean the portion of the amide groups suffering deuteration. Since water cannot penetrate into the crystalline sites, it can be taken that isotope exchange occurs mainly in amorphous regions. The concentration of the inaccessible amide groups is found from the  $3300 \text{ cm}^{-1}$  absorption band ( $\epsilon_{\text{CONH}} = 16.9 \text{ m}^2/\text{mole}$ ), and of the COND groups from the  $2480 \text{ cm}^{-1}$  absorption band ( $\epsilon_{\text{COND}} = 6.0 \text{ m}^2/\text{mole}$ ). Deuteration is conducted at 25°C for 1–2 days, depending

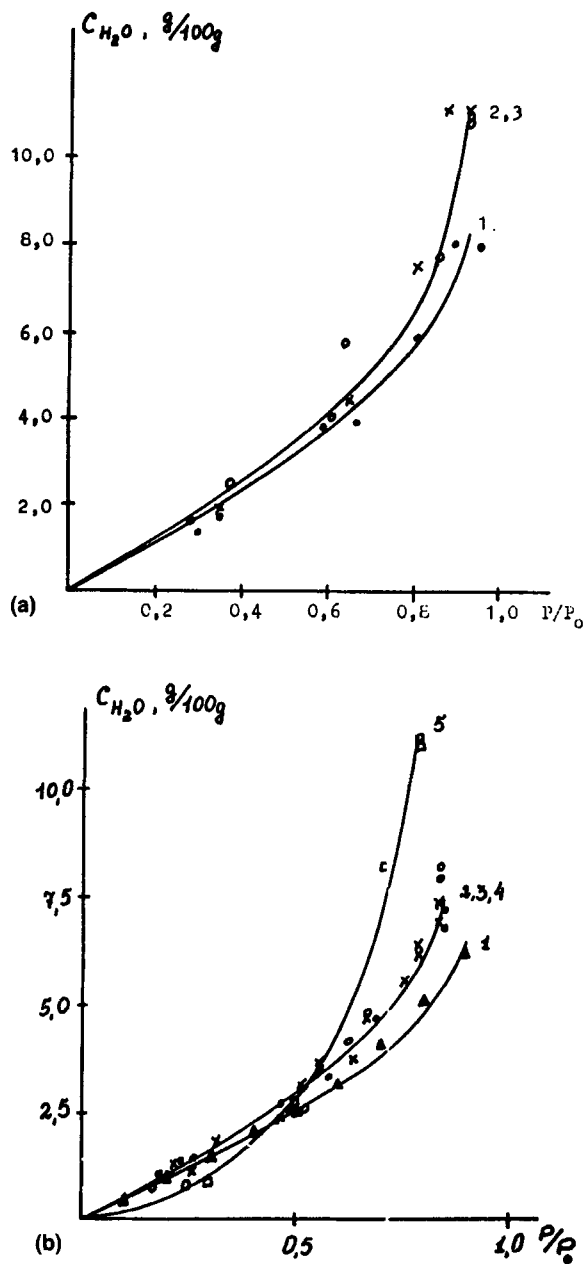


FIGURE 1 Water sorption isotherms by (a) fibers and (b) films of PCA, modified by grafting of PDMAEMA. Quantity of grafted PDMAEMA (% to PCA-mass). (a) (1) 20.3; (2) 60.8; (3) 95.0.

on the graft polymer composition and sample thickness. For a more detailed description see Reference 6.

The infrared spectra are obtained using Perkin Elmer 1600. The sample densities are calculated by the group contribution method proposed by Van Krevelen.

TABLE I

Effect of the grafted PDMAEMA amount on variations in the accessibility of amide groups

Film	Content of grafted PDMAEMA, %	$C_{\text{CONH}}$ mole/l	$C_{\text{CONH}}$ mole/l	$C_{\text{CONH}}^0$ , mole/l		$f^*$
				exp.	calc.	
PC-4	0	—	6.0	—	10.14	0.6
PC-4	11.5	—	4.8	—	8.97	0.54
PC-4	30.8	—	4.3	—	7.60	0.56
PC-4	53.0	—	3.5	—	6.50	0.54
nylon-6	0	5.0	5.0	10.0	10.14	0.50
nylon-6	264.7	1.30	1.15	2.45	2.40	0.47
nylon-6	200.7	1.45	1.45	2.90	2.57	0.50

\*  $f$  is the index of the accessibility of the amide groups, and is calculated as follows:  $f = C_{\text{COND}} / C_{\text{CONH}}^0$ .

TABLE II

Diffusion coefficients for PCA-PDMAEMA copolymers of various composition

Graft polymer percentage	$D_{c=0}$	$\bar{D}$ , cm <sup>2</sup> /s*
0	$7.0 \cdot 10^{-10}$	$0.3 \cdot 10^{-8}$
11.5	$2.5 \cdot 10^{-9}$	$0.8 \cdot 10^{-8}$
30.8	$7.8 \cdot 10^{-9}$	$1.5 \cdot 10^{-8}$
53.0	$21.0 \cdot 10^{-9}$	$3.2 \cdot 10^{-8}$

\*  $\bar{D}$  is calculated over the same  $P/P_0 = 0-0.8$ .

## RESULTS AND DISCUSSION

The data of water sorption by modified PCA fibers show that over a wide range of relative vapor pressures (0.1–1.0) water absorption is, in fact, independent of the graft copolymer content (Figure 1a). This result is rather unexpected, since, as seen from Figure 1b, PDMAEMA is more hydrophilic than PCA. Moreover, according to the general concepts on graft copolymer structures, the graft components loosen the polymer matrix structure.

One of the explanations of this effect is based on the possible decrease in solubility of the graft polymer in comparison with the homopolymer of PDMAEMA due to cross-linking PA-matrix effects. Another reason affecting graft polymer solubility could be a change in the accessibility of amide groups to water molecules in the process of grafting.

In order to verify the latter suggestion, the structural changes of graft copolymers are studied using the H→D isotope exchange method.

The concentration of amide groups accessible to D<sub>2</sub>O molecules on deuteration (Table I) is independent of the graft extent. A good agreement between the  $C_{\text{CONH}}^0$  values calculated from the polymer chemical composition and those found experimentally is noted. The concentration of amide groups for PA films cannot be found experimentally in view of the strong amide group signals. However,

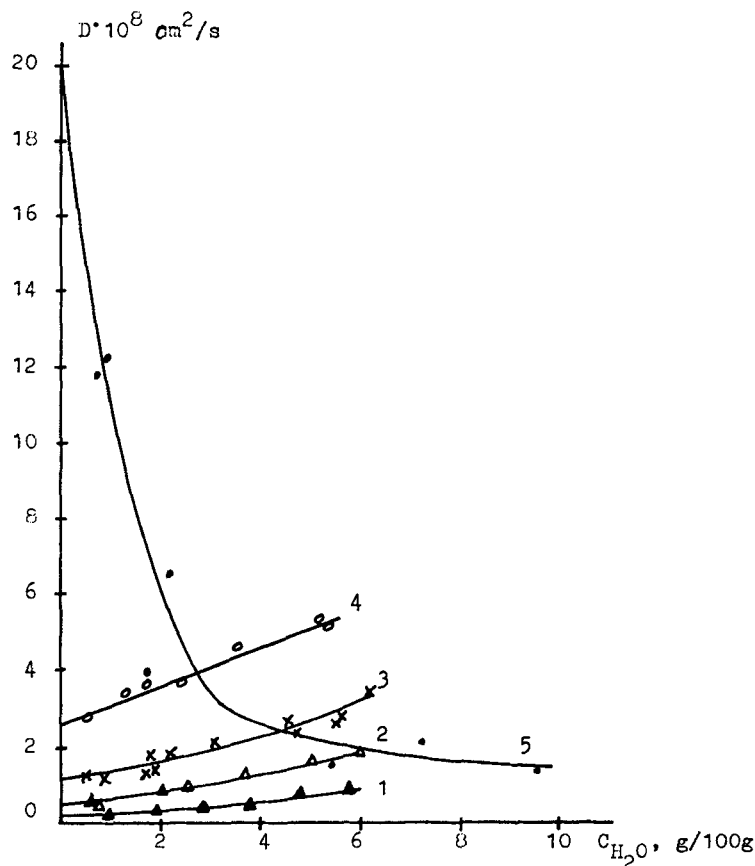


FIGURE 2 Dependence of water diffusion coefficient in graft copolymers of PCA and PDMAEMA on water containing in copolymers. Quantity of grafted PDMAEMA (% to PCA mass): (1) 0; (2) 11.5; (3) 30.8; (4) 53.0; (5) homopolymer of PDMAEMA.

since these films are thicker than the nylon-6 samples, they are used for the study of diffusion processes in the polymer matrix.

As long as the accessibility value is independent of the amount of graft polymer, the regularity of sorption properties seems to be caused by the fact that the decrease in the amide component is compensated for by the increasing PDMAEMA portion.

Things are different with the coefficients of water diffusion into polymers. A marked increase in  $D$  with graft polymer amount is observed for all samples, whatever the water concentration in the matrix (Table II). The only difference is that with a higher water content this distinction becomes smaller. When extrapolating the diffusion coefficient dependence on water concentration  $C_{\text{H}_2\text{O}} \rightarrow 0$  (Figure 2), the values  $D_{c=0}$  of the initial and graft polymers (weight increase 53 mass %) the samples become different by a factor of 30, and at  $C_{\text{H}_2\text{O}} = 5 \text{ g/100 g}$  of the polymer ( $P/P_0 = 0.8$ ) by only 8 (Table II).

The slowing down of water sorption with increasing concentration of amide groups has been observed earlier<sup>8,9</sup> in studying the diffusion into linear aliphatic polymers. The dependence of  $-\lg D_{c=0}$  on  $C_{\text{CONH}}$  is markedly linear, the intercept

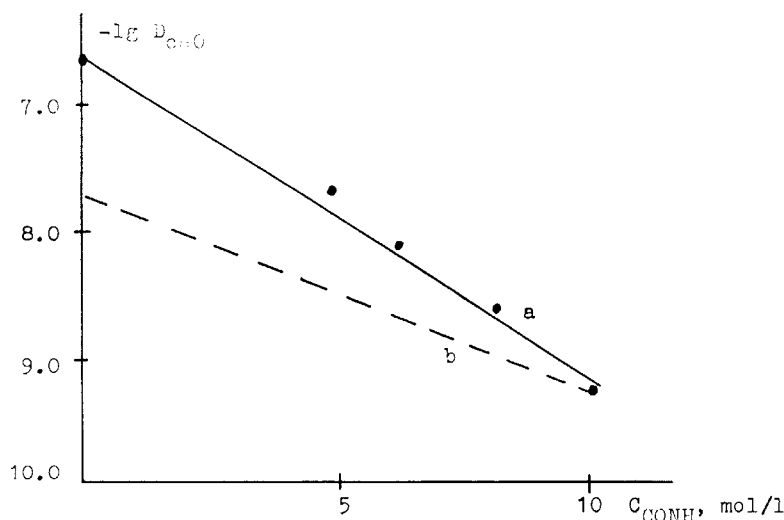


FIGURE 3 Dependence of zero diffusion coefficient in graft copolymers of PCA and PDMAEMA on amide groups containing in copolymers. (a) Graft copolymers of PCA and PDMAEMA. (b) Aliphatic polyamides.

on the  $y$ -axis being similar to the  $\lg D_{c=0}$  of polyethylene. A dependence similar in nature is observed for water diffusion into graft polyamides. The difference consists only of a change in the inclination angle from 0.142 to 0.26, and of the intercept on the  $y$ -axis equaling  $\lg D_{c=0}$  of PDMAEMA (Figure 3). This distinction of the inclination angles is evidence that the concentration of the  $C_{\text{CONH}}$  groups and the matrix structure loosening as a result of PDMAEMA grafting have the same effect on the value of  $D_{c=0}$ .

As to the different diffusion coefficients depending on the water content in the polymer, the diffusion coefficients increase with water concentration for all graft polymers. Yet, while for polyamide this dependence is described by  $D = D_{c=0} (1 + b C_{\text{H}_2\text{O}}^2)$  where  $b = 7.110^{-4} \text{ l}^2/\text{g}$ , for a graft copolymer with, for instance, 53 mass % of grafted PDMAEMA, this dependence is less marked and is of a linear nature (Figure 3).

As the water content in the polymer increases, there occur counterdirected processes such as plastification and clustering. Since the initial PCA film is less loose than that in the graft polymer, the plastification of this film is more appreciable and the dependence of  $D$  on  $C_{\text{H}_2\text{O}}$  is stronger.

An antibatic dependence of the diffusion coefficient on the polymer water content is observed for the PDMAEMA film (Figure 2). This seems to be connected with the stronger effect of water clustering.

The suggestion that the intersection between water molecules in PDMAEMA is stronger than in PCA is also evidenced by the sorption isotherm shape: in the first case it is more concave toward the  $x$ -axis than in other situations. The water clustering (divergence of the dependence  $C_{\text{H}_2\text{O}} = f(P/P_0)$  linearity) in PDMAEMA starts at  $P/P_0 = 0.3$  ( $C_{\text{H}_2\text{O}} = 1 \text{ g}/100 \text{ g}$ ) and for PCA and graft copolymers at  $P/P_0 = 0.5-0.6$  ( $C_{\text{H}_2\text{O}} = 2.5-3.0 \text{ g}/100 \text{ g}$ ).

Thus it is found by study of water diffusion into the PCA graft copolymer that solubility by polyamides virtually does not change with PDMAEMA grafting. However despite the fact that the solubility of the initial and grafted films is the same, in passing to graft polyamides the diffusion coefficient values become higher.

This phenomenon can have an essential effect on the kinetics of chemisorption processes when using such materials as chemisorbents the production of consumer goods.

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