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Peculiar Transition Observed on the Temperature Dependence of Water Permeability of a Novel Hydrophilic Polyamide Membrane

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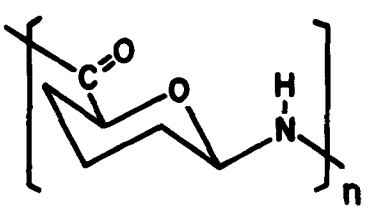
As described in preceding papers, a novel high molecular weight polyamide, poly(tetrahydropyran-2,6-diyliminocarbonyl)(*1*), was easily obtained by anionic ring-opening polymerization of a new class of bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL, *2*) in dimethylsulfoxide at and below room temperatures (SUMITOMO and HASHIMOTO 1973 and 1977a). The hydrophilic poly(BOL) membrane prepared by "casting polymerization" exhibited an excellent fractional solute rejection in the aqueous solution together with an extremely high water permeability (SUMITOMO and HASHIMOTO 1977b and 1978). These conspicuous behaviors, as well as a great capacity for water absorption, may result from some delicate arrangement of polar hydrophilic and nonpolar hydrophobic microdomains probably formed along and between the polymer chains. We wish to report here an unusual transition observed on the temperature dependence of water permeability of the poly(BOL) membrane.



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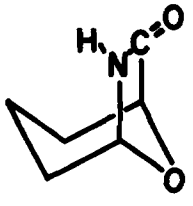

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RESULTS AND DISCUSSION

The poly(BOL) membrane of 0.029 mm thick with the degree of hydration of 0.32 was prepared by drying up at ca. 50°C after casting from the polymer solution in dimethylsulfoxide. The water flux, J_w, of the membrane was determined at various temperatures from 10°C to 45°C under the pressure of 3 kg/cm^2 using a commercial

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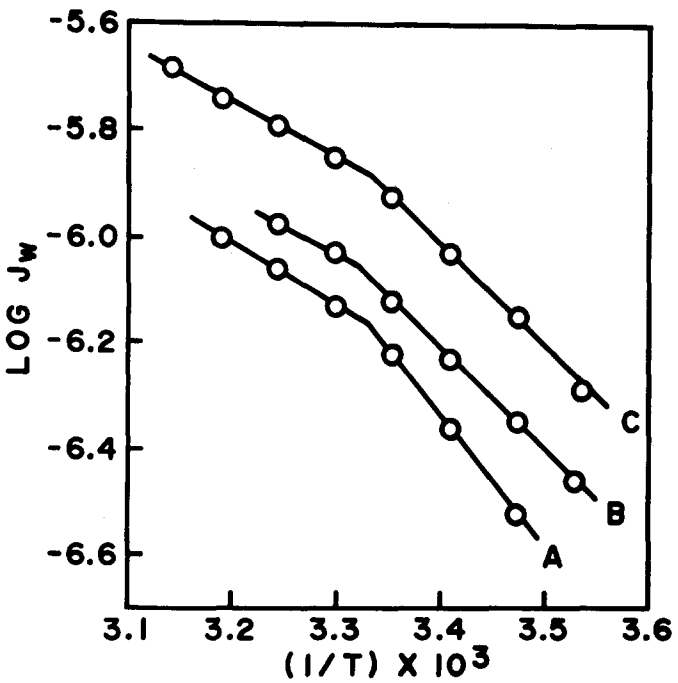

Fig. 1. Temperature dependence of water flux through poly(BOL) membrane (membrane No.5; drying up after casting; thickness, 0.029 mm; degree of hydration, 0.32). A, original membrane; B, after drying up A; C, after drying up B.

ultrafiltration cell, of which effective membrane area was 13.9 cm^2. As shown in Figure 1, the relationship between $log J_w$ and reciprocal absolute temperature apparently refracted at about 27°C although the values of J_w varied with the drying process of the membrane.

Values of the apparent activation energy ΔE for water flux through the poly(BOL) membrane at the temperature ranges of 27-45°C and 10-27°C were 4.6-5.5 and 9.0-12.0 kcal/mole, respectively, which were comparable with those through the crosslinked cellulose (KAWAGUCHI et al. 1975) and the poly(methyl-L-glutamate) membrane (TAKIZAWA et al. 1977), respectively (Table 1).

According to the frictional model (SPIEGLER 1958; KEDEM and KATCHALSKY 1961), the water flux J_w under the pressure gradient $\Delta p/\Delta x$ is expressed as follows:

$$J_w = (S_w/f_{wm})(\Delta p/\Delta x) = K_w(\Delta p/\Delta x) \qquad (2)$$

TABLE 1

Apparent activation energy of water flux, J_w, for poly(BOL) membrane

Membrane No.	Degree of hydration[a]	Thickness,[b] mm	Temp. range, °C	ΔE, kcal/mole
5	0.32	0.029	27-45 10-27	4.6-5.5 9.0-12.0
Cellulose[c]	0.69	0.032	25-50	4.5
Poly(amino acid)[d]	0.11	0.007	25-50	9.2

a Volume fraction of water in membrane.
b In wet state.
c Crosslinked. Data of KAWAGUCHI et al.(1975).
d Poly(methyl-L-glutamate). Data of TAKIZAWA et al.(1977).

where S_w, f_{wm}, and K_w are the partition coefficient of water between membrane and feed, the molar frictional coefficient between water and membrane polymer, and the hydraulic permeability, respectively. As the degree of hydration and the thickness of the used membrane were substantially constant at the temperature range from 10°C to 45°C, the above-mentioned apparent activation energy for water flux must correspond to that for hydraulic permeability, K_w, in other words for the reciprocal frictional coefficient, $1/f_{wm}$. Therefore the marked change in the activation energy at 27°C may be due to the change of the quality of the frictional force at the temperature.

The value of ΔE above 27°C is a little larger than the apparent energy obtained from the viscosity coefficient of water (about 4 kcal/mole), which suggests that the frictional force between water molecules and polymer segments is not so much concerned in the resistance for water permeation at the temperature range. Such an inference is consistent with the conclusion described previously that a large number of relatively weak polar sites for water permeation are present in the poly(BOL) membrane and it has a relaxed structure accompanying the relatively weakened interaction between polar sites above 25°C (MATSUKURA et al. 1978). On the other hand, at lower temperatures, the interaction between the poly(BOL) segments and the permeating water molecules is presumed to participate strongly in the water permeation, from the standpoint

of the large activation energy at the temperature range of 10-27°C. It may be inferred that the temperature of 27°C was an essential transition point of the wet poly(BOL). At such a temperature, some participation mode of water molecules in polar sites, including inter- and intramolecular hydrogen bonds through amide and ether groups, along poly(BOL) chains may vary discontinuously, which may result in the marked change of the permeability and permselectivity of the membrane.

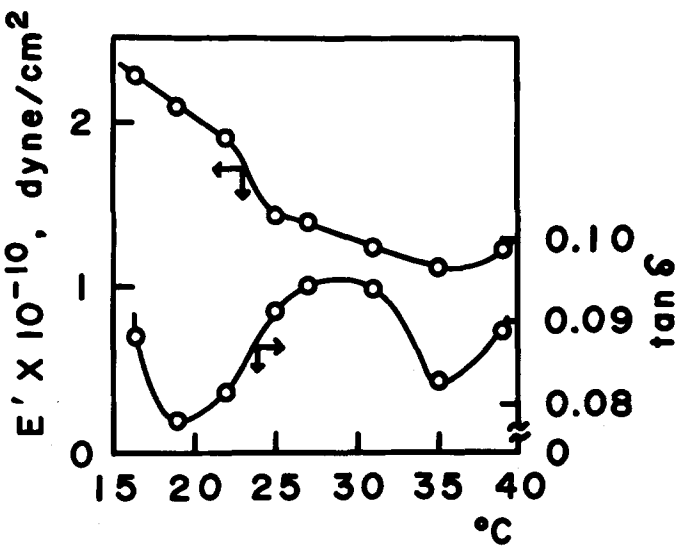

Fig. 2. Temperature dependence of dynamic elastic modulus, E', and loss angle, tan δ, for wet poly(BOL) film.

The dynamic modulus, E', and loss angle, tan δ, of the wet poly(BOL) membrane (thickness, 0.18 mm) were determined by the vibrating reed method in an atmosphere saturated with water vapor at 16-39°C as shown in Figure 2. According to our expectation a maximum of tan δ was observed at about 28°C, which suggests that the mechanical property of the wet poly(BOL) also remakably varies at the above-mentioned transition temperature.

SUMMARY

The relationship between the logarithmic hydraulic permeability and the reciprocal absolute temperature for a novel hydrophilic polyamide membrane peculiarly refracted at about 27°C, which was inferred to be some kind of transition point of the poly(BOL) in water. Some participation mode of water molecules in polar sites, including inter- and intramolecular hydrogen bonds through amide and ether groups, along poly(BOL) chains may vary discontinuously at the temperature.

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