

Moisture Sorption of Polyelectrolyte Complex between Poly(acrylic Acid) and Poly(4-vinylpyridine)

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Synopsis

Successive differential sorptions have been measured for the system polyelectrolyte complex of poly(acrylic acid)/poly(4-vinylpyridine) + water vapor. The sorption data revealed that the sorption process of water vapor in the complex is controlled not only by diffusion mechanism but also by relaxation mechanism of polymer chains. It has been considered that the complex is composed of a loosely crosslinked, slightly ionized, and relatively homogeneous network structure. The sorption-desorption kinetics have also been investigated for the region of intermediate and high vapor pressures. The interval sorption-desorption curves demonstrated that the complex has the nature of the hysteresis effect in sorptions. It has been concluded that the appearance of sorption hysteresis is due to the depression of mobility of polymer chains resulting from crosslinks between carboxyl groups and pyridine rings.

INTRODUCTION

Polyelectrolyte complexes are ionically bonded hydrogels. The gels are usually employed in the moisture-swollen state. Their properties in this condition have been noted and investigated extensively.¹⁻⁵

On the contrary, the sorption behavior of water in the gels and the structural change caused by moisture sorption have been investigated to a lesser extent; no paper dealing with sorption process of water in the gels has been published, and morphological structure associating with sorption has not been discussed. A knowledge of the sorption behavior and the structure of the gels will be of great value for a clear understanding of this new class of polymer materials.

Meanwhile, the measurements of sorption process are very effective in order to research the morphological structure and the chain mobility of polymer materials in the moisture-swollen state.⁶ The technique brings about the information which is hard to obtain from other experimental means, such as X-ray diffractometry or measurements of viscoelasticity.

We try to examine the complex between weak polymeric acid and weak polymeric base, in the beginning of an investigation on sorption properties of polyelectrolyte complexes. In the present paper, the detailed data on sorption process and on sorption-desorption kinetics for the complex of poly(acrylic acid)/poly(4-vinylpyridine) are presented, and the morphological structure of the complex and the mobility of polymer chains are discussed.

EXPERIMENTAL

Poly(acrylic acid) ($\overline{Mw} = 2.0 \times 10^5$) was commercially obtained from Aldrich Chemical Co., and poly(4-vinylpyridine) ($\overline{Mw} = 9.6 \times 10^4$) was supplied from Koei Chemical Co.

The films of stoichiometric complex were prepared by solvent casting. The equimolar mixture of poly(acrylic acid) and poly(4-vinylpyridine) was dissolved in the 50% aqueous solution of formic acid, and the solution was poured onto the surface of mercury in reaction flasks. The solvent was allowed to evaporate slowly under reduced pressures at 40°C, and films of 1.59×10^{-2} and 4.27×10^{-2} cm thickness were prepared. Sample films cut rectangular were then suspended from quartz springs in a sorption apparatus, and final traces of solvent were removed by drying in vacuum at 30°C for more than 30 days.

The sorption apparatus is constituted by sorption chambers, wide-bore mercury manometers, large vapor reservoirs, tubes connecting them, and various stopcocks. The calibrated quartz helical springs were hung from the top of the chambers; the spring constants of these spirals were 13.9 and 23.5 mg/cm. The entire system was located in an air thermostat, and the chambers were immersed in water baths regulated to $\pm 0.05^\circ\text{C}$. In the system, water vapor can be admitted to, or evacuated from, the sorption chambers as required.

A travelling microscope, capable of detecting displacements as small as 0.002 cm, was used to observe the spring-length reflecting water contents in the sample films. Thus, displacements as small as 0.028 and 0.047 mg in terms of mass for each spring were detectable.

The behavior of sorption or of sorption-desorption was investigated at 30°C.

RESULTS

Family of Differential Sorption

Figure 1 shows a family of successive differential sorption curves for the complex of poly(acrylic acid)/poly(4-vinylpyridine). The increments of the water concentration in successive steps were approximately the same, about 1×10^{-2} g water/g dry complex.

For the first step the sorption is of a sigmoid type. When the initial concentration is increased, a two-stage process appears on the step followed by a pseudo-Fickian type. The second-stage portion of the two-stage curve shifts to the short time region as the initial concentration of each step increases. With further increase of the initial concentration the curve changes to the Fickian type through the pseudo-Fickian step.

Such sorption curves comprise the valuable information on the morphological structure of the complex and on the change of structure caused by sorption of water.

Differential Sorptions of Two-Stage Type

The sorption curve of two-stage type is one of the characteristic curves reflecting the morphological structure of polymers. A typical two-stage sorp-

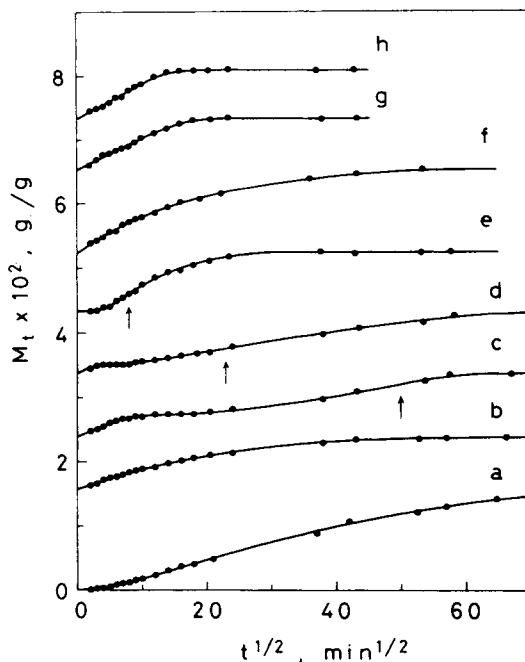


Fig. 1. Successive differential sorptions of the system poly(acrylic acid)/poly(4-vinylpyridine) complex + water at 30°C. Pressure intervals of each step (mm Hg \rightarrow mm Hg): (a) 0 \rightarrow 2.2; (b) 2.2 \rightarrow 4.3; (c) 4.3 \rightarrow 6.9; (d) 6.9 \rightarrow 9.9; (e) 9.9 \rightarrow 12.9; (f) 12.9 \rightarrow 15.7; (g) 15.7 \rightarrow 17.9; (h) 17.9 \rightarrow 19.9. Arrow signs indicate the inflection point for second-stage portion.

tion satisfies two conditions⁷⁻⁹: (a) the first-stage portion is of Fickian type; (b) the rate of second-stage portion is almost independent of film thickness. This is because the two-stage sorption corresponds to the following sorption mechanism. When polymer solids have sorbed a certain amount of solvent vapor, the solid structure becomes able to initially respond rapidly to an increased external vapor pressure. The rapid structure change results from sorption of solvent vapor by the Fickian process; this appears as the first-stage portion. The sorption mechanism for the residual fraction differs appreciably from that sorbed because of the released structure. The sorption of this residual fraction is coupled to the slow relaxation of polymer chains under the swelling stress. The rate of relaxation should be independent of film thickness; this corresponds to the second-stage portion.

Figure 2 shows the reduced water vapor uptake plots for the complex films of differing thickness. The first stage portion seems to meet a criteria for Fickian type diffusion. Figure 3 represents the amount of water vapor sorbed during the second-stage plotted against the square root of the time; the beginning of the second stage is fixed to zero on the abscissa in the figure. The slope of the curves in such a plot indicates the rate of sorption for the second-stage portion. The observations demonstrate that the second-stage rate is almost independent of film thickness. That is to say, the two-stage sorption curves for this complex satisfy entirely two conditions denoted above.

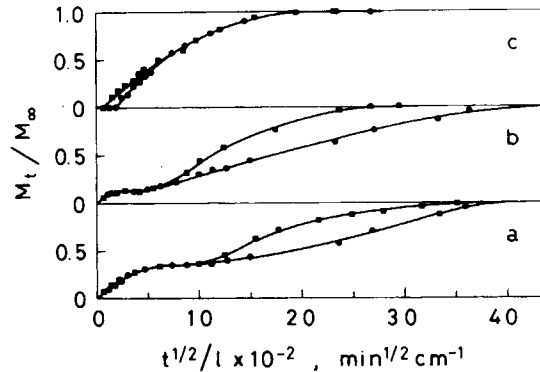


Fig. 2. Reduced sorption curves for two-stage type. Pressure intervals (mm Hg \rightarrow mm Hg): (a) 4.3 \rightarrow 6.9; (b) 6.9 \rightarrow 9.9; (c) 9.9 \rightarrow 12.9. Film thicknesses (cm): (●) 1.59×10^{-2} ; (■) 4.27×10^{-2} .

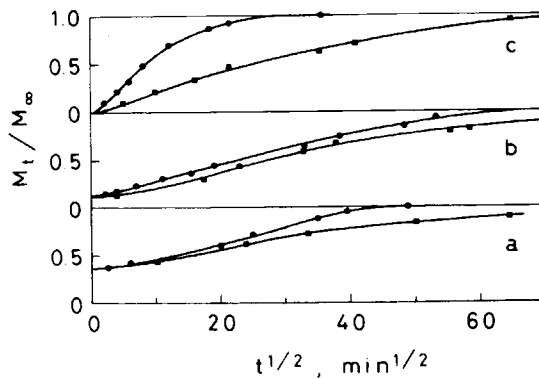


Fig. 3. The second-stage sorptions of two-stage type; the beginning of the second-stage for each curve is fixed to zero on abscissa. Pressure intervals (mm Hg \rightarrow mm Hg): (a) 4.3 \rightarrow 6.9; (b) 6.9 \rightarrow 9.9; (c) 9.9 \rightarrow 12.9. Film thicknesses (cm): (●) 1.59×10^{-2} ; (■) 4.27×10^{-2} .

Differential Sorptions of Fickian Type

As can be seen from Figure 1, sorption curves change their type from the pseudo-Fickian to the Fickian at the concentration of water 0.065 g/g. It is known that polymer-vapor mixture changes from glassy to rubbery state at this critical concentration^{10,11}; the temperature of the experiment is the glass transition temperature for the mixture.

Figure 4 shows the reduced plots of successive sorption for films of differing thickness started from the initial concentration above such a critical point. The sorption curves are initially linear, and beyond the linear region they have an upward convex tail; the linearity holds over 70% of total concentration. If the effect of film thickness was not examined, each sorption will be considered to be of Fickian type. Evidently, the data exhibit thickness anomaly; the thicker film gives the curve which is located to the left of the curve obtained for the thinner film. This describes that the sorption process of water in the complex-water mixture is not governed by purely Fickian diffusion mechanism even in the region of such a concentration; the sorption

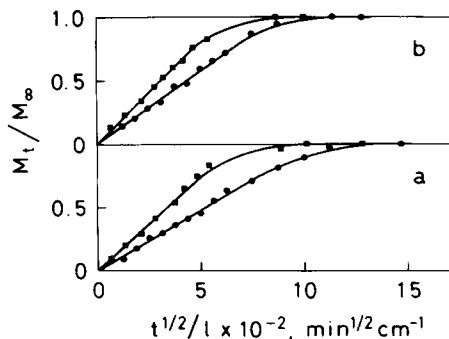


Fig. 4. Reduced sorption curves for Fickian type. Pressure intervals (mm Hg \rightarrow mm Hg): (a) 15.7 \rightarrow 17.9; (b) 17.9 \rightarrow 19.9. Film thicknesses (cm): (●) 1.59×10^{-2} ; (■) 4.27×10^{-2} .

process is controlled not only by the diffusion mechanism but also by the relaxation mechanism of polymer chains.

Sorption-Desorption Kinetics

The results of an examination in the region of the vapor pressure producing the two-stage sorption are presented in Figure 5. Curve (a) represents a typical sorption step after equilibration at an intermediate vapor pressure. Curve (b) represents the change of the amount sorbed when the vapor pressure was reduced to the initial value. The change of water content with time becomes negligible without returning to its initial value. Similar behavior was also observed in the region of the vapor pressure at which a curve of Fickian type appeared; this is shown in Figure 6.

This behavior means the irreversibility of the sorption isotherm, in other words, this complex exhibits sorption hysteresis. The sorption hysteresis is well known for the sorption of water vapor by natural polymers such as cellulose or proteins.^{12,13} This phenomenon, however, has rarely been observed for synthetic polymers. As an almost unique example, it is known that polyester fibers exhibit a permanent hysteresis.¹⁴

In order to interpret the sorption hysteresis, various concepts have been presented. One of them assumed the existence of some active site available.¹⁵ However, there is the fact that poly(vinyl alcohol)¹⁶ and nylon 66¹⁷ do not

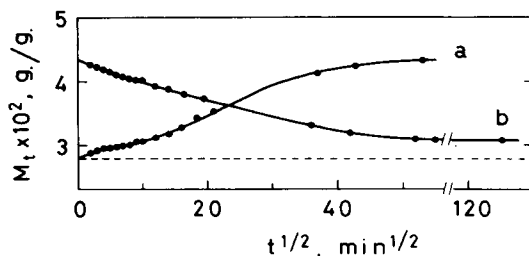


Fig. 5. Sorption and desorption in the region of intermediate vapor pressures: (a) two-stage sorption following a vapor pressure increment from 4.9 to 9.2 mm Hg; (b) desorption from the equilibrium following a return to the initial vapor pressure.

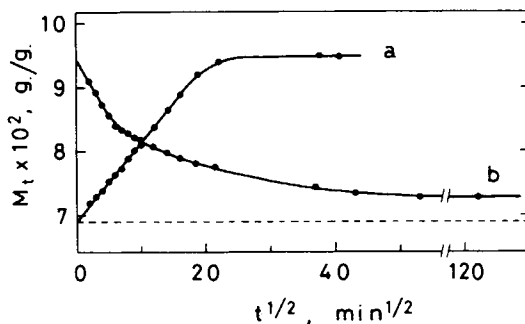


Fig. 6. Sorption and desorption in the region of high vapor pressures: (a) Fickian sorption following a vapor pressure increment from 16.3 to 21.0 mm Hg; (b) desorption from the equilibrium following a return to the initial vapor pressure.

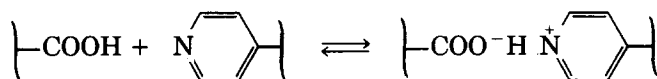
exhibit sorption hysteresis, though they have similar active sites as in cellulose and proteins. Further, recent studies have revealed that chemical modification of chemical groups has little effect on sorption hysteresis.¹⁷ The most reliable interpretation at present is that sorption hysteresis is associated with the segmental mobility of polymer chains. In other words, the hysteresis can be observed when the segmental mobility of polymer chains is limited for some reason.

The present results reflect the immobility of component polymer chains in the complex. Such immobility must result from crosslinks between polymer chains.

DISCUSSION

As described in the preceding section, the successive differential sorptions revealed that the relaxation mechanism of polymer chains plays an important role in the sorption of water in the complex. Further, the examination of sorption-desorption kinetics demonstrated that the complex has the nature of the hysteresis effect in sorptions.

The crosslinking reaction between poly(acrylic acid) and poly(4-vinylpyridine) is considered to follow the scheme¹⁸



The scheme expresses that the degree of dissociation of component polymers themselves is small, and that the crosslinked points are necessarily ionized. Meanwhile, the degrees of conversion of this reaction will not be so high.¹⁸ This refers to low degrees of crosslinks and low charge densities, for the complex. The low degrees of crosslinks may suggest the formation of the domain structure of component polymers in the complex. If the well-defined domain structure is formed, some phenomenon reflecting such a structure would appear in sorptions; for example, two-stage sorptions for block copolymers display clearly the microdomain structure.¹⁹ However, such a phenome-

non was not observed in the present experiments. Therefore, it is reasonable to conclude that this complex is composed of loosely crosslinked, slightly ionized, and relatively homogeneous network structure. This means that the structure of the complex is similar to that of common amorphous polymers. Such a structural model can well interpret the observations in successive differential sorption experiments; the complex sorbs water vapor not only by diffusion mechanism but also by a relaxation mechanism of polymer chains, and changes its morphological structure from glassy state to rubbery state.

The effect of crosslinks was observed as the phenomenon of sorption hysteresis. As mentioned above, the sorption hysteresis originates from the immobility of polymer chains. Such immobility, however, is not correlated to great cohesive force. If the mobility of polymer chains is depressed completely, the sorption hysteresis will not be observed as well as the case in which rearrangements of chains are sufficiently free. The appearance of sorption hysteresis will require that the segmental mobility of polymer chains is limited to some extent; this is just realized for loosely crosslinked chains. The phenomenon of sorption hysteresis supports the structural model derived from successive differential sorptions.

The sorption behavior observed in the present investigation is distinct from that for the complex of sodium poly(styrene-sulfonate)/poly(vinylbenzyltrimethylammonium) chloride, while the properties of this complex have been investigated extensively. For the complex, it was suggested from the sorption isotherm that sorption could be regarded as a process of dissolution of water in polymer.²⁰ The most significant differences between the present material and the complex of sodium poly(styrene-sulfonate)/poly(vinylbenzyltrimethylammonium) chloride, will be the magnitude of the degrees of crosslinks and the charge densities. The dissolution process suggested for the complex may be associated with the densely crosslinked network structure of polyelectrolytes with high degrees of dissociation.

It will be desirable that the accurate charge densities and degrees of crosslinks are evaluated by means of some experimental techniques being complementary to sorption experiments adopted in the present investigation.

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