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Anomalous swelling of poly(vinyl alcohol) film in mixed solvents of dimethylsulfoxide and water

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The swelling behaviour of dried and annealed poly(vinyl alcohol) (PVA) films was investigated in several mixed solvents of dimethylsulfoxide (DMSO) and water with different solvent compositions. The swelling ratio *versus* time curves obtained in DMSO-rich solvents were shown to be of anomalous swelling type: the swelling ratio first increased in proportion to time for a while and then catastrophically expanded on approaching the equilibrium ratio. Further, crazing of the films occurred before the catastrophic expansion. These results indicated that the swelling obeyed case II diffusion of solvent through glassy PVA. It was shown that the relaxation rate of the glassy PVA molecules was the key factor that dominated the nature of swelling. The relaxation rate was sufficiently low in the DMSO-rich solvents and too high in the water-rich solvents for the anomalous swelling to be detected. The crystallinity of PVA was also a factor by which the relaxation rate and thus the swelling rate could be controlled over a wide range.

(Keywords: poly(vinyl alcohol); swelling; case II diffusion)

INTRODUCTION

Mixed solvents of dimethylsulfoxide (DMSO) and water with various mixing ratios are very useful as solvents for poly(vinyl alcohol) (PVA), since the solubility of PVA in them can be drastically changed by changing the mixing ratio of the two solvent components. Solid PVA materials are soluble in pure DMSO at room temperature, whereas they swell slightly in a mixed solvent of DMSO/water = 60/40 (vol/vol)[1]. For PVA solutions in DMSO/water prepared at high temperature, cooling to low temperature (below 0°C) causes gelation similar to the swelling nature described above: no gelation occurs from the solution in pure DMSO while a strong gel can be formed from the 60/40 solution[2]. Further, during ageing, the latter gel very gradually excludes as much as 70% of the solvent originally contained. The mixed solvent of DMSO/water has been used for an *N*-isopropylacrylamide gel as a solvent that induces volume phase separation[3]. There is an analogous situation between the above two gels in view of the solubility of polymers in the solvent. However, there is also a big difference between the two: the PVA gel is composed of a network whose junction points are physically linked by crystallites, while the *N*-isopropylacrylamide gel is a chemically crosslinked network. Thus only the latter gel can cause abrupt volumetric expansion when its surrounding solvent is changed from a poor solvent to a good solvent of DMSO. In the case of the physical gel, such a large extent of volume change on solvent exchange is difficult to observe, because the physically crosslinked network is usually dissolved by solvent exchange. However, a slight change in volume of physical gels can be seen if the composition of solvents is changed in a limited region. It is noted here that Hirai has already found a reversible volumetric change on a chemically crosslinked PVA gel by changing solvent between DMSO and water[4].

Our aim in this work is to analyse the swelling of PVA films in DMSO/water mixed solvents as a function of solvent composition, the degree of crystallinity of PVA and swelling temperature. Anomalous swelling has been found when the film was immersed in DMSO-rich solvents. Here, 'anomalous swelling' means swelling that does not obey Fickian diffusion. Most of the cases of anomalous swelling that have been observed in glassy polymers obey the so-called case II diffusion[5]. The glass transition temperature of PVA, ranging from 60 to 90°C depending on crystallinity and water content of the sample, is higher than room temperature, but it is decreased close to room temperature by swelling of solvents. This is one of the necessary conditions for anomalous swelling to be observed. Anomalous swelling has hardly been observed in semicrystalline polymers such as PVA. The presence of the crystal phase in the film would have the same kind of effect on swelling as chemical crosslinking in amorphous polymers, if the crystal phase were not seriously dissolved in the solvent. In the films with higher degree of crystallinity, lower degree of swelling ratio, lower diffusion coefficient of penetrant and lower relaxation rate of the amorphous chains are the expected results on swelling. The variation

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of solvent composition is another factor by which the swelling behaviour can be controlled, since the affinity of PVA with the solvent and the diffusibility of solvent can be changed by it. These two factors, the crystallinity and the solvent composition, which are able to be changed widely and finely in our system, have motivated us to study the anomalous swelling in this system.

EXPERIMENTAL

Films

PVA powder used was a commercial product (Gosenol NH-26) of Japan Synthetic Chemical Inc. The degrees of polymerization and saponification were 2600 and 99.5 mol%, respectively. The tacticity measured by ^{1}H n.m.r. revealed the atactic nature of this polymer (0.191 (*mm*), 0.510 (*mr*) and 0.299 (*rr*)). PVA films were prepared by casting on a glass plate from aqueous solution. The PVA solution with a polymer concentration of 10 wt% was prepared in a sealed test tube at 120°C. The thickness of the dried films used was 0.20 ± 0.03 mm. The films were allowed to recrystallize to various degrees of crystallinity by annealing *in vacuo*: 28–35 wt% of crystallinity by annealing at 50°C for 48 h, 34–40 wt% at 100°C for 24 h, 44–46 wt% at 150°C for 30 min, and 45–60 wt% at 180°C for 10 min.

Swelling of films

The films (2 cm × 5 cm) were immersed in mixed solvents of DMSO and water with various mixing ratios. The solvent composition was expressed as the mixing ratio of DMSO/water (vol/vol or mol/mol) or the content of DMSO (vol% or mol%) in the mixed solvents. The weight of the film, W, was measured periodically to determine the swelling ratio, W/W_0, where W_0 was the weight of the film before swelling. The swelling temperatures were 30, 40 and 50°C.

Estimation of the degree of crystallinity

The degree of crystallinity (X_c) of dried films was estimated from their density by using the following equation:

$$1/d = X_c/d_c + (1 - X_c)/d_a \qquad (1)$$

where d is the measured film density, and d_c and d_a are the densities of the crystal phase and the amorphous one, respectively. The following reported density values were used[6]: $d_c = 1.345\,\mathrm{g\,cm^{-3}}$ and $d_a = 1.269\,\mathrm{g\,cm^{-3}}$. The film density was measured by a flotation method using methanol and carbon tetrachloride as the floating solvents.

RESULTS AND DISCUSSION

Films with similar crystallinity

Both the swelling ratio and the swelling rate depended on the degree of crystallinity of the original film, as will be discussed later in this paper. The swelling is discussed first on the films with similar degrees of crystallinity before swelling.

Figure 1 shows the swelling ratio at 40°C as a function of swelling time and solvent composition. The crystallinity of the film is 45.7 wt%. The most striking feature is that the time evolution of the ratio is quite different above and below a solvent composition of 50 vol% DMSO. The swelling in the solvents with DMSO contents less than 50 vol% (DMSO/water (vol/vol) = 0/100, 20/80 and 40/60) seems to be apparently normal, whereas swelling in the other solvents (60/40, 80/20 and 90/10) is anomalous. Each of the swelling processes in the latter solvents is composed of two parts: the gradually increasing part in the first half of swelling and the following abruptly increasing part up to their equilibrium states. The abrupt increase of swelling ratio in the second part is a catastrophic expansion of the swollen film.

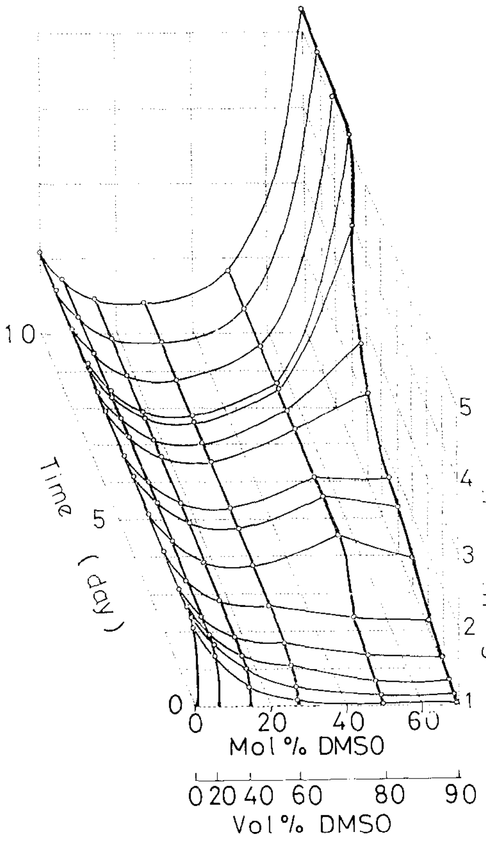

Figure 1 Three-dimensional swelling curves at 40°C: swelling ratio is represented as a function of time and composition of swelling solvent. The crystallinity of PVA film samples used was 45.7 wt%

The originally flat film first became wavy in the first part and subsequently crazed at the very beginning of the second part of swelling. The crazing and the wavy appearance disappeared when the second part of swelling was completed. These peculiar changes have not been observed in our cases of swelling in water-rich solvents. Crazing is one of the characteristic properties for the anomalous diffusion of solvents through glassy polymers[7]. It is well known that the penetration of solvents through glassy films often makes two clearly separated parts, the swollen gel layer and the glassy core. The relaxation of the polymers from the glassy state to the rubbery state is caused slowly by the sorbed solvent molecules through the expansion of PVA chain, forming the swollen gel layer. The diffusion of the penetrant also occurs so slowly that the glassy core coexists with the gel layer. Such a situation is usually a necessary condition for the anomalous swelling to be detected. The crazing results from the shear stress caused between the two layers. The appearance of the crazing may accelerate the swelling of the glassy core, because the solvent can be introduced to the core region through the crazing region. The completion of swelling means formation of a homogeneous structure so that the crazing becomes unobserved.

The equilibrium swelling ratio (*ESR*) vs. solvent composition curve after swelling for 10 days, in *Figure 1*, has a *U* shape with a minimum at around 25 mol% DMSO. This 25 mol%, corresponding to 57 vol%, has been reported to be a particular composition in the system of DMSO and water at which a DMSO molecule forms a stable hydrate with three water molecules in certain conditions[8,9]. The presence of this kind of particular composition of the solvent for PVA has already been mentioned by Watase and Nishinari when they described the structure and properties of PVA gels prepared from solutions in DMSO/water mixed solvents[10,11]: PVA molecules in the solvent of 25 mol% DMSO have the weakest affinity with the solvent among all the solvent compositions. This situation produced the minimum swelling ratio of the film in *Figure 1* and the maximum exclusion of solvent from the aged gel[2], both at around a DMSO content of 25 mol%. The deviation of solvent composition from 25 mol% DMSO induces the increase of equilibrium swelling ratio. This means that the solubility of solvent with PVA is increased the further the DMSO content is from 25 mol%. This supports the possibility of the control of gel volume by changing solvent composition. The steep increase of the equilibrium swelling ratio at 90 vol% DMSO indicates that the solubility of a given PVA film is drastically changed at this point. Here, it should be noted that, although the special solvent composition at which the particular structure between DMSO and water was observed without PVA corresponded to the composition at which the swelling ratio became the minimum in our system, the complex structure of the two solvents in the PVA matrix is thought to be different from that in the system of two solvents alone, over the whole range of solvent composition. Unfortunately, there have been few studies on the structure of DMSO and water in PVA.

The solvent uptake:

$$M_t/M_\infty = (W_t - W_0)/(W_\infty - W_0)$$

is obtained from the data in *Figure 1* and is plotted against swelling time on a log–log graph in *Figure 2*. M_t is the mass of penetrant sorbed at time t and M_∞ is the mass sorbed at the equilibrium state. The solvent uptake in the first swelling part can normally be expressed by the following equation[5]:

$$M_t/M_\infty = kt^n \qquad (2)$$

where k is a constant indicative of the system. The observed n values were 0.54 for 60/40 and 1.0 for 80/20 and 90/10 solvents. For a slab, a value of $n = 0.5$ means Fickian diffusion, a value of $n = 1.0$ indicates case II diffusion, and a value between $n = 1.0$ and 0.5 indicates anomalous diffusion. According to this definition, the swelling behaviour observed here obeys anomalous diffusion in the 60/40 solvent and case II diffusion in the 80/20 and 90/10 solvents. The relation for the solvents of 0/100, 20/80, 40/60 and 60/40 cannot be analysed exactly from only these data, because of the lack of data in the region of the first swelling for 1 h.

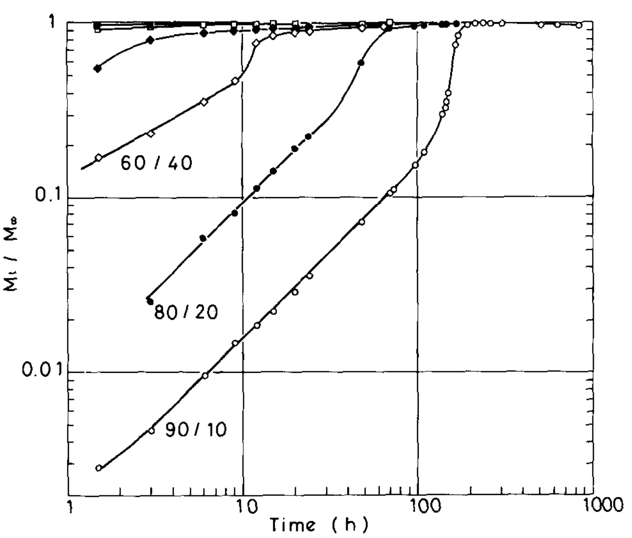

Figure 2 Solvent uptake M_t/M_∞ (g/g) vs. time curves from the data in *Figure 1*. The symbols represent DMSO/water (vol/vol) ratios of the swelling solvents: (○) 90/10; (●) 80/20; (◇) 60/40; (◆) 40/60; (□) 20/80; (■) 0/100

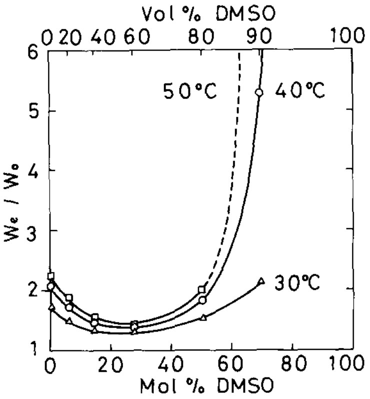

Figure 3 Equilibrium swelling ratio (W_e/W_0) vs. solvent composition curves at the three swelling temperatures indicated

The swelling ratio vs. time curves were obtained also at 30 and 50°C. The degree of crystallinity of the films used for measurements at these temperatures were at almost the same level: 45.3% (30°C), 45.7% (40°C) and 44.3% (50°C). Similar swelling behaviour to that observed at 40°C could be found at 30°C. The time required for the film to reach the equilibrium ratio was about 20 times longer at 30°C than at 40°C. The value of n was 1.0 for swelling at 30°C in the 90/10 and 80/20 solvents. Contrary to swelling at 30°C, too much acceleration of swelling rate at 50°C made it difficult to detect the anomalous swelling as described above. However, the anomalous nature of swelling appeared faintly on the curve for the 80/20 solvent. The curve for the swelling in the 0/100 solvent (pure water) slightly overshot at the early stage of swelling. This is due to the retardation of the molecular relaxation compared with solvent diffusion[12]. This behaviour could be observed on all curves obtained in this work on variable timescales depending on the relaxation rate.

The three *ESR* vs. composition curves shown in *Figure 3* have the same shape. The *ESR* increases with increasing temperature at all compositions and its variation with temperature is more remarkable at higher

DMSO compositions. The film dissolved in the 90/10 solvent at 50°C. However, the change in *ESR* with temperature at low DMSO contents is quite small. The observed temperature dependence is mainly due to the increase of the solubility with increasing temperature. The partial dissolution of the crystallites that must have occurred on swelling is also an important factor that determines the dependence of the swelling ratio on solvent composition and temperature, and will be discussed in a later section.

Figure 4 shows the swelling rate as a function of solvent composition, the swelling rate being calculated as the inverse of the time required for the film to reach its equilibrium swelling ratio. The dependence of swelling rate on solvent composition or swelling temperature is completely different from that of *ESR*. The total rate of swelling depends on the rate of the first part of swelling. The second part of swelling starts when the solvent uptake reaches a value of ca. 0.2 in the two solvents (80/20 and 90/10), as shown in *Figure 2*, and the time period required for completion of the second swelling process is quite short compared with that of the first process. Thus the total swelling rate is dominated by the rate of the first part of swelling. The swelling rate decreases exponentially with increasing DMSO content and decreasing temperature.

The observed dependence of the swelling rate on solvent composition is difficult to explain only by the dependence of the diffusion coefficient of the penetrant on solvent composition. The size of the penetrant is thought not to be a monotonically decreasing function with increasing solvent composition. The size becomes a maximum at a composition around 25 mol% of DMSO, because of the formation of the complex. If the diffusion coefficient of penetrant was controlled by the penetrant size and further the swelling rate was dominated only by the diffusion coefficient, the swelling rate vs. composition curve would also be a U-shaped curve similar to the swelling ratio curve. Therefore, it is speculated that the swelling rate in our case must be dominated by the relaxation rate of the PVA chain in the partly sorbed glassy phase. The relaxation rate must be much smaller in DMSO-rich solvents than in water-rich solvents, though the solubility estimated from the equilibrium swelling ratio is much larger in DMSO-rich solvents than in water-rich solvents. In the case of swelling in water-rich solvents, the relaxation rate might be so much larger than the diffusion rate of the penetrant that the swelling rate must be increased, and that the anomalous swelling could not be detected. The observed decrease of the swelling rate with the decrease of swelling temperature can also be explained by the relaxation rate. The decrease of the temperature means an increase of the temperature difference from the glass transition temperature. Thus, the relaxation rate was decreased at low swelling temperatures.

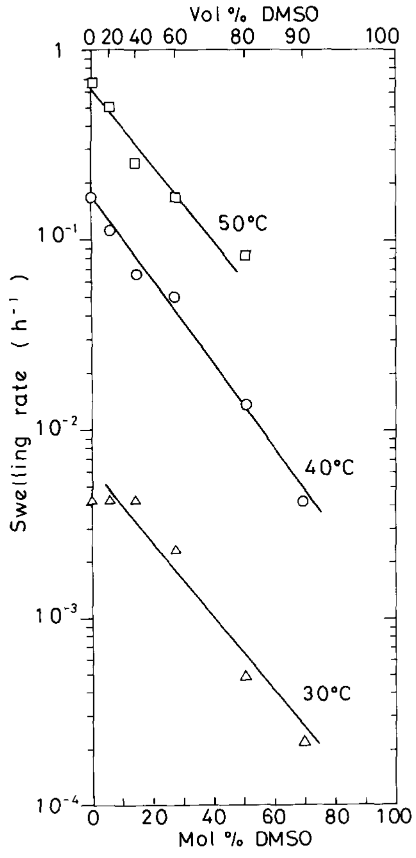

Figure 4 Swelling rate vs. solvent composition curves at the three swelling temperatures indicated

An unsolved problem is why the relaxation rate of the glassy PVA chain on swelling is much lower in DMSO-rich solvents compared with that in water-rich solvents. This problem can be solved if the heterogeneity of the solvent is more clearly analysed. The PVA chain may relax faster when it is sorbed by free water than by a free DMSO molecule. This is thought to be due to the difference of the local affinity with some portion of the PVA molecule, between the free water in the water-rich solvents and free DMSO in the DMSO-rich solvents. The conclusion cannot be induced from our data.

The dissolution rate in the 90/10 solvent at 50°C of the same film as used in *Figure 4*, measured as the inverse of the induction time for dissolution, was larger than the imaginary swelling rate, which was obtained by extrapolation of the straight line in *Figure 4* to 90 vol% DMSO. This means that the swollen surface layer successively dissolves into the solvent, leaving the partially swollen region of the film, so that the thickness of the film is successively reduced during swelling. In other words, the swelling rate was apparently accelerated. However, a big change in the affinity of the solvent with PVA, from swelling to dissolution, occurred at this swelling condition, resulting in the successive reduction of the film thickness during dissolution.

Films with different degrees of crystallinity

Swelling will now be discussed for films that have different degrees of crystallinity before swelling.

Figure 5 shows the *ESR* vs. DMSO content plots for swelling at 30°C. Films with various degrees of crystallinity were used. It is clearly understood from this figure that the crystallinity has almost the same or a higher level of influence on *ESR* compared with swelling temperature. As the region of the film in which solvent can be taken up is only the amorphous phase of PVA, the swelling ratio is actually proportional to the crystallinity. However, the *ESR* is not a linear function of the crystallinity, as shown in *Figure 6*. One of the reasons

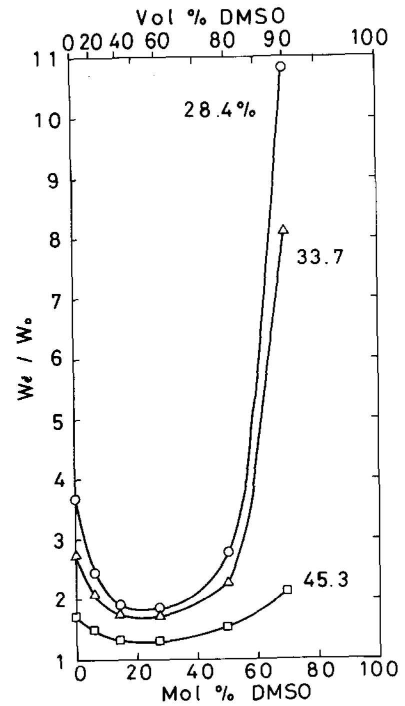

Figure 5 Equilibrium swelling ratio (W_e/W_0) vs. solvent composition curves. The swelling temperature was 30°C. The numbers on the figure show crystallinity (wt%)

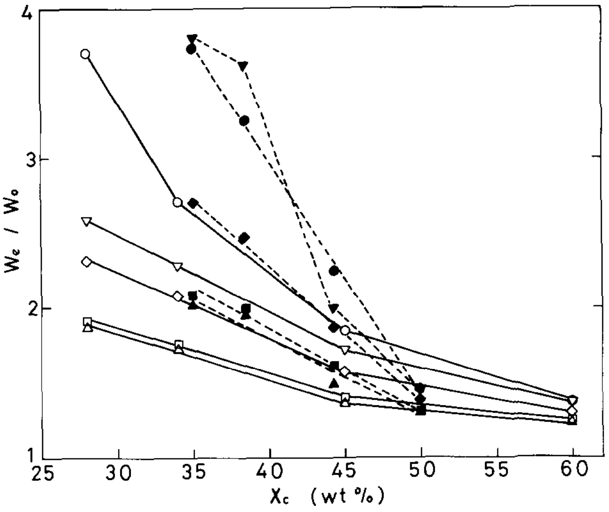

Figure 6 Equilibrium swelling ratio (W_e/W_0) vs. crystallinity (X_c) curves. The symbols show DMSO/water (vol/vol) ratios of the swelling solvents: (○, ●) 0/100; (◇, ◆) 20/80; (□, ■) 40/60; (△, ▲) 60/40; (▽, ▼) 80/20. The open and full symbols represent the swelling temperatures 30 and 50°C, respectively

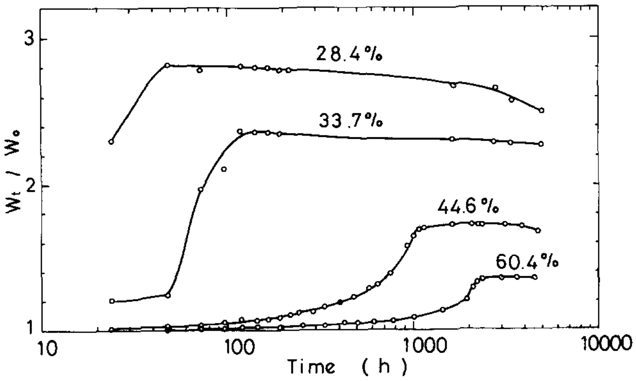

Figure 7 Swelling curves in the DMSO/water = 80/20 (vol/vol) solvent at 30°C for films with different degrees of crystallinity. The numbers on the curves show crystallinity (wt%)

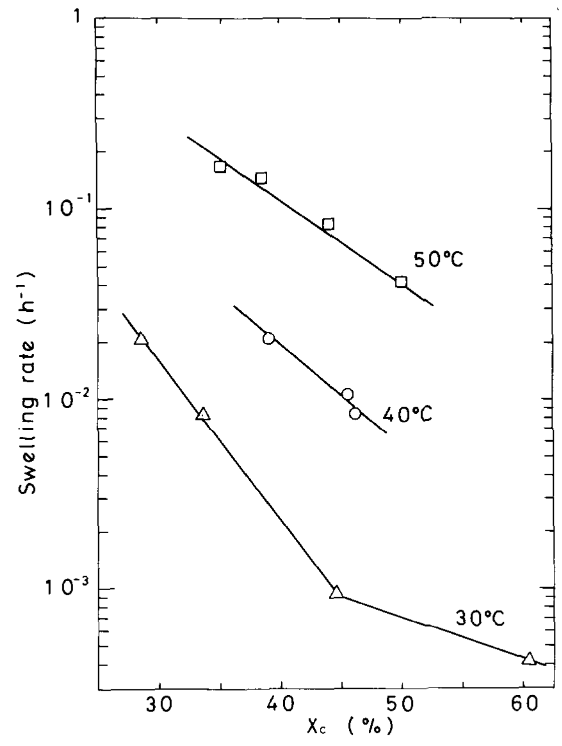

Figure 8 Swelling rate vs. crystallinity (X_c) curves at the swelling temperatures indicated. The solvent composition was DMSO/water = 80/20 (vol/vol)

for this is that the average size of the crystallite, its distribution in size and the packing order of molecules in crystallites are variable factors with the total crystallinity. Some of the crystallites with a smaller size or a lower degree of packing order could be dissolved on swelling, resulting in the increase of *ESR*. Moreover, the relaxation of the amorphous molecules on swelling is also much affected by the structural change of crystallites caused by annealing, since the tension of the amorphous molecules should be enhanced by crystallization on annealing. The extension degree of the amorphous chain after the relaxation is not necessarily inversely proportional to the crystallinity of the unswollen film, even if the crystal phase suffered no damage on swelling.

Here, we focus the discussion on the swelling in the 80/20 solvent, since the swelling rate in this solvent is suitable for measurements. *Figure 7* shows the swelling isotherms at 30°C for the films with different degrees of crystallinity. The swelling rates from *Figure 7* are plotted against X_c in *Figure 8*. The dependent nature of swelling rate on X_c is analogous to that on solvent composition shown in *Figure 4*. As a result, the swelling rate is an exponentially decreasing function of X_c. The degree of crystallinity must have varied during swelling depending on the solvent composition, swelling temperature and initial crystallinity. So the X_c values indicated here are thought to be higher than those of once fully swollen films. The diffusion coefficient of the penetrant through crystalline polymers (D) can be expressed by the following equation[13]:

$$D = D_a/(\tau\beta) \tag{3}$$

where D_a is the coefficient for the polymer in the completely amorphous state, τ is the tortuosity factor ($1/\tau$ represents the fractional reduction in diffusibility arising from the geometric impedance offered by the crystallites) and β is the chain-immobilization factor ($1/\beta$ represents the fractional reduction in diffusibility attributable to restriction of chain movement in the amorphous phase). The increases of τ and β with the increase of crystallinity are the main reasons for the decrease of D. In addition, the rate of the relaxation of the glassy PVA molecule is also restrained by the increase of the crystallinity, as described above. In conclusion, the decreased diffusion coefficient of the penetrant and the decreased relaxation rate of the PVA molecule, both with the increase of the crystallinity, decrease the swelling rate and make the anomalous swelling behaviour easier to detect.

CONCLUSIONS

The anomalous swelling, so-called case II diffusion, has been found in DMSO-rich solvents. The relatively small relaxation rate of the amorphous PVA molecule compared with the diffusion coefficient of the penetrant was the main reason for the detectable anomalous swelling in DMSO-rich solvents. Contrary to this, the disappearance of the anomalous nature in water-rich solvents indicated that the relaxation of the PVA molecule was facilitated by sorbed free water. Besides the solvent composition, the crystallinity of PVA was also a key factor that could control the relaxation rate.

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