Non-equilibrium glassy properties and their relevance in Case II transport kinetics

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Some relevant non-equilibrium properties, frozen into the glassy matrix, have been considered, and related expressions for the excess chemical potential have been proposed. Both isotropic and anisotropic cases have been analysed. In the isotropic case, the out-of-equilibrium has been related to the excess volume over the value of the equilibrium liquid; the calculation of the energy related with the excess volume has been performed by using a liquid lattice constitutive equation. In the anisotropic case, use has been made of the entropy decrease due to the existing orientations. It is shown that, in both cases, the driving force for swelling is heavily influenced by the out-of-equilibrium which is frozen in the glass under the usual operating conditions; in particular, the out-of-equilibrium term becomes the dominant term in the anisotropic case at high orientations. In the isotropic case, the introduction of the excess over-equilibrium results in an improvement of a recently proposed kinetic model.

INTRODUCTION

In a previous paper[1], a quantitative interpretation was proposed for Case II transport kinetics of solvent molecules in glassy polymers. The basic ideas developed[1] were: (i) The solvent action is concentrate into a solvent osmotic stress π, and the corresponding quantitative expression is given; (ii) The kinetic law for craze propagation under mechanical stress is used, with the solvent osmotic stress π properly substituted for the external mechanical stress. In this substitution, it has been taken into account that the usual mechanical tests for craze analysis consider a uniaxial loading, whereas the solvent stress is an isotropic tension. Therefore, the solvent stress has been reduced to an equivalent uniaxial tension, σ_E, which was then substituted into the kinetic law for mechanical craze propagation.

Simple mechanical considerations on yielding lead to the equivalence relationship

$$\sigma_E = \alpha\, \pi \tag{1}$$

where the equivalence factor α is essentially a geometric factor, independent of the solvent and of the order of unity.

The comparison between the above model and kinetic data for *PS-n*-alkane systems shows that the equivalence factor is actually independent of the solvent, and is of the order of unity but, unexpectedly, it proves to be temperature dependent. More precisely, it increases appreciably with decreasing temperatures. This suggests that some significant property of the polymer matrix has not been taken into account.

Actually, the model previously proposed[1] was very simple and necessarily crude. Several approximations were used, e.g. neglect of time-effects, the moving boundary considered as a geometric surface, no plasticization effect, concentration independent properties and, finally, both the glassy matrix and the swollen polymer were dealt with as equilibrium phases.

In this paper, the glassy matrix is no longer considered an equilibrium phase, and the out-of-equilibrium effect on the solvent osmotic stress is evaluated under both isotropic and non-isotropic conditions. The hyptothesis of instantaneous response and localized swelling will be kept.

THEORY

Equilibrium and non-equilibrium contributions to the solvent osmotic stress

As shown in reference (1), for localized swelling the solvent stress π can be calculated as

$$\pi = \frac{\mu_2^0 - \mu_2}{V_2} \tag{2}$$

where μ_2^0 is the pure polymer chemical potential in the glassy phase, μ is the polymer chemical potential in the swollen phase, and V_2 is the polymer molar volume.

The term due to the non-equilibrium frozen in the glassy phase is separated by introducing the chemical potential $\mu_{2,eq}^0$ of the equilibrium liquid at the same temperature and pressure of the glassy phase, so that equation (2) is re-written as

$$\pi = \pi^E + \pi_{eq} \tag{3}$$

where the excess term π^E and the equilibrium term π_{eq} are defined by the following relationships

$$\pi^E = \frac{\mu_2^0 - \mu_{2eq}^0}{V_2} \tag{4}$$

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$$\pi_{eq}=\frac{\mu_{2eq}^{0}-\mu_{2}}{V_{2}} \tag{5}$$

From equations (4) and (5) it is apparent that the terms in equation (3) have the same sign, i.e. the effect of the out-of-equilibrium frozen in the glassy phase results into an increase of the solvent stress. In other words, the non-equilibrium of the pure glass can be regarded as an isotropic tension π^{E} acting on the polymer, which adds to the tension caused by the solvent presence.

When the assumption is made that the swollen phase is, contrary to the glassy one, at equilibrium, the π_{eq} term can be easily calculated by using the Flory–Huggins equation (see reference (1)). One obtains

$$\pi_{eq}=\frac{RT}{V_{1}}\left[v_{1}-\chi_{1}v_{1}^{2}-\frac{1}{x}\ln(1-v_{1})\right] \tag{6}$$

where V_1 is the solvent molar volume, v_1 is the solvent volume fraction χ_1 is the Flory–Huggins interaction parameter and x represents the ratio between polymer and solvent molar volumes

In order to estimate the excess term π^{E}, some further considerations follow.

The excess term. Isotropic case.

It is well known that, at temperatures below T_g, a non-equilibrium structure is obtained even in the absence of anisotropy. This shows up in the well-known phenomena of physical aging in glassy materials. Particularly significant are the effects of volume relaxation analysed after Kovacs[2,3] and those enthalpy relaxation[4,5]. For the case of volume relaxation, it is well known that by decreasing the temperature below T_g the specific volume does not follow the equilibrium liquid line (extrapolated from temperatures above T_g). The volume in the glassy state then remains larger than an equilibrium. The excess volume over the equilibrium value is, of course, history-dependent in so far as it changes with the cooling rate, annealing conditions, dwelling time, etc. In a similar way, an excess entropy and an excess internal energy above equilibrium have to be accounted for.

For isotropic samples, we shall make the assumption that all excess terms depend only upon the excess volume. This represents a considerable simplification in so far as all material properties are thus uniquely related to the present value of the density. The effect of the thermomechanical history is incorporated into that parameter.

In view of the dense packing of the glassy phase, the main contribution to the excess Gibbs free energy over the equilibrium value is taken to be the internal energy term associated to the excess free volume. In the isotropic case considered here, the entropic contribution is taken to be negligible.

We thus have

$$\mu_{2iso}^{0}-\mu_{2eq}^{0}=u_{2iso}^{0}-u_{2eq}^{0} \tag{7}$$

where u indicates molar internal energy and the subscript iso indicates that the isotropic case is considered. The approximation is now made that the out-of-equilibrium internal energy, u_{2iso}^{0}, corresponding to the actual volume v, is well represented by the equilibrium value which would be achieved when the same volume v is obtained at the same temperature by applying the appropriate value of the pressure (which may well be negative i.e. a tension). The following well-known relationship will thus be used

$$u_{2iso}^{0}-u_{2eq}^{0}=\int_{V_{eq}}^{V}\left(\frac{\delta u_{2}^{0}}{\delta V}\right)dV= \tag{8}$$

$$=\int_{v_{eq}}^{v}\left[-p+T\left(\frac{\delta p}{\delta T}\right)_{v}\right]dV$$

From equation (8), an explicit expression for the excess internal energy is obtained once a constitutive equation for$p$ is introduced. It has been shown[6] that an Ising-type equation is often appropriate to describe the behaviour of a polymeric substance. According to reference (6), the following liquid lattice equation will be assumed

$$\tilde{\rho}^{2}+\tilde{P}+\tilde{T}\left[\ln(1-\tilde{\rho})+\tilde{\rho}\left(1-\frac{1}{r}\right)\right]=0 \tag{9}$$

where $\tilde{\rho}$, $\tilde{P}$ and $\tilde{T}$ represent dimentsionless density ρ/ρ^{*}, pressure P/P^{*} and temperature T/T^{*} respectively, and the quantities ρ^{*}, P^{*} and T^{*} are constant values. The symbol r indicates the number of lattice cells occupied by the polymer chain. By neglecting $1/r$ with respect to unity, substitution of equation (9) into equation (8) leads to

$$\mu_{2iso}^{0}-\mu_{2eq}^{0}=u_{2iso}^{0}-u_{2eq}^{0}=M_{2}\frac{P^{*}}{\rho^{*2}}(\rho_{eq}-\rho) \tag{10}$$

In equation (10), M_2 indicates the polymer molecular weight, ρ is the density and $\rho_{eq}=1/V_{eq}$ is the equilibrium density.

By using equations (4) and (7), finally one obtains for the excess stress under isotropic conditions, π_{iso}^{E}

$$\pi_{iso}^{E}=\frac{P^{*}}{\rho^{*2}}\rho(\rho_{eq}-\rho) \tag{11}$$

Equation (11) represents the main result so far and will be discussed later. As noted previously, in spite of the instantaneous relationship established by equation (11), the extra stress π_{iso}^{E} is history-dependent through the history-dependence of density.

If, for sake of simplicity, volume relaxations are neglected, the density difference in the right hand side of equation (11) can be represented by using the thermal expansion coefficients α_{eq} and α of the equilibrium liquid and of the glass, according to

$$\rho_{eq}-\rho=\rho_{g}(\alpha_{eq}-\alpha)(T_{g}-T) \tag{12}$$

where ρ_g is the density at the glass transition.

Substitution of equation (12) into equation (11) leads to the following simplified expression for the excess stress under isotropic conditions

$$\pi_{iso}^{E}=P^{*}\frac{\rho\rho_{g}}{\rho^{*2}}(\alpha_{eq}-\alpha)(T_{g}-T) \tag{13}$$

According to equation (13), the excess stress is linearly increasing with decreasing temperature below T_g, and vanishes at the glass transition.

Table 1 Values of equilibrium stress π_{eq}, of the excess stress π^E, of the total stress π, and of the equivalence parameter α needed to fit experimental data of penetration rate

	T (°C)	$\lambda\ 10^6$ (cm/sec)	π_{eq} (atm)	π^E (atm)	π (atm)	$E = 40$ kcal min^{-1} *a*	$E = 45$ kcal min^{-1} *a*
nC_5	30	0.39	35.5	81.3	116.8	2.15	1.99
nC_6	35	0.89	38.0	75.4	113.4	1.86	1.62
	40	2.08	39.2	69.6	108.8	1.69	1.41
	45	3.56	40.4	63.7	104.1	1.36	1.13
	50	5.33	41.6	57.9	99.5	1.09	0.93
	55	7.55	42.8	52.1	94.9	0.91	0.81
nC_7	45	1.84	37.0	63.7	100.7	1.12	1.00
	50	3.50	38.4	57.9	96.3	1.01	0.90
	55	5.33	39.5	52.1	91.6	0.88	0.81
	60	7.11	40.6	46.3	86.9	0.77	0.73
	70	10.2	42.9	34.7	77.6	0.61	0.59
nC_8	55	2.78	40.3	52.1	92.4	0.81	0.67
	60	4.28	41.7	46.3	88.0	0.74	0.71
	65	5.00	42.7	40.5	83.2	0.66	0.65
	70	7.17	43.8	34.7	78.5	0.59	0.58
	75	9.44	45.0	28.9	73.9	0.52	0.52

The total osmotic stress π is now given by the sum of the excess term, equation (11), and of the equilibrium term, equation (6)

$$\pi = \frac{P^*}{\rho^{*2}}\rho(\rho_{eq} - \rho) + \frac{RT}{V_1}\left[v_1 - \chi_1 v_1^2 - \frac{1}{x}\ln(1 - v_1)\right] \quad (14)$$

In order to estimate the relevance of the excess term, we refer to the case of polystyrene for which, as reported by Sanchez and Lacombe[6], the following values must be used for the critical constants

$$P^* = 3530 \text{ atm}$$
$$\rho^* 1.105 \text{ g cm}^{-3} \quad (15)$$

The thermal dilation difference is given, according to reference (7), by

$$\alpha_{eq} - \alpha = 3.7\ 10^{-4}\ K^{-1} \quad (16)$$

while $\rho_g = 1.037$ g cm^{-3} and $\rho(23°\text{C}) = 1.048$ g cm^{-3}.

The results of the calculations of the excess term are reported in the *Table*. In the same table, the values of the equilibrium term, π_{eq}, are also reported from reference (1). One may notice that the two contributions are of the same order of magnitued in all cases.

Swelling kinetics. According to the kinetic model analysed in reference (1), the swelling kinetics can be obtained from the stress crazing rate $\dot{\lambda}$ in which the applied mechanical stress is substituted by the equivalent solvent stress given by equation (1).

Following Hsiao and Sauer[8], the mechanical crazing rate $\dot{\lambda}$ for *PS* is given by

$$\dot{\lambda} = K(\sigma - \sigma_c) \quad (17)$$

The threshold value for craze front propagation σ_c and the kinetic constant K at 25°C have the values

$$\sigma_c = 1670 \text{ psi}$$
$$K = 0.85\ 10^{-7} \text{ in/h psi} \quad (18)$$

For σ_c and K, the same temperature dependence will be used as the one considered in reference (1), i.e.

$$\sigma_c = A(T_g - T) \quad (19)$$

$$K = K_0 \exp(-E/RT) \quad (20)$$

The activation energy for K lies between 40 and 45(kcal gmol^{-1}). In order to obtain the value reported in equation (18) at 25°C, the preexponential factor k_0 is given by

$$k_0 = 1.918\ 10^{20} \text{ cm (s atm)}^{-1} \text{ when } E = 40 \text{ kcal gmol}^{-1} \quad (21)$$

or

$$k_0 = 8.917\ 10^{23} \text{ cm (s atm)}^{-1} \text{ when } E = 45 \text{ kcal gmol}^{-1} \quad (22)$$

when in equation (17) the equivalent solvent stress σ_E, given by equation (1), is substituted for the external mechanical stress σ, the following kinetic law for the swelling rate $\dot{\lambda}$ is obtained

$$\dot{\lambda} = K(\alpha\pi - \sigma_c) \quad (23)$$

In equation (23), π represents the total solvent stress, given by equation (14). It is worthwhile to recall that the equivalence parameter α should be independent of the solvent as well as of temperature, and of the order unity.

The validity of equation (23) is checked by comparing it with the kinetic data reported by Nicolais *et al.*[9]. Only the initial values of the velocity $\dot{\lambda}$ of the advancing front have been considered, so that the solvent volume fraction to be used in equation (6) is equal to its equilibrium value. The comparison has been made by calculating the value of α, which is needed in order to match the experimental value of $\dot{\lambda}$ with that given by equation (23). The calculations have been made for both activation energies $E = 40$ kcal gmol^{-1} and $E = 45$ kcal gmol^{-1}. The results are reported in

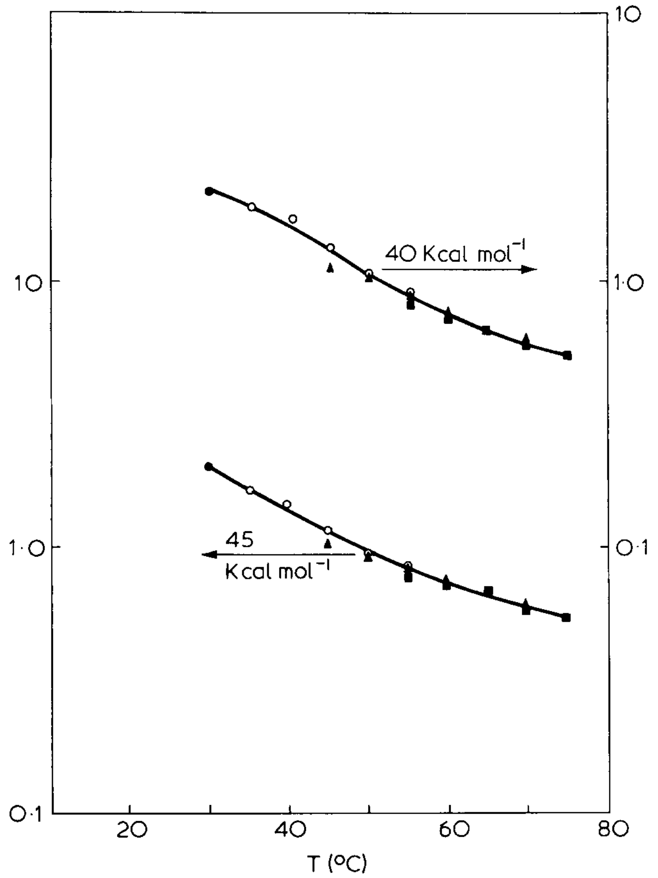

Figure 1 Equivalence parameter α vs temperature, for both activation energies 40 (lower) and 45 kcal mol^{-1} (upper)

the *Table*. *Figure* 1 shows a plot of the equivalence parameter *vs* temperature.

It is apparent that the equivalence factor α, is solvent independent to within 13% for $E=40$ kcal gmol^{-1} and to within 10% for $E=45$ kcal gmol^{-1}. In the temperature range inspected, the equivalence factor α is temperature-dependent and changes by a factor of about 4, going from 1.99 at 30°C to 0.515 at 75°C. It must be noted that, in the previous work[1], a much higher temperature-dependence was obtained than in the present case. This is due to the fact that the out-of-equilibrium effect, which is temperature-dependent, was not considered; therefore, at lower temperatures an important term was neglected in the driving force, thus obtaining higher values for the equivalence parameter α.

The excess term. Anisotropic case.

The non-isotropic case represents a more complex situation than the isotropic one. In fact, the non-equilibrium properties frozen in the glass will be related both to the excess volume and to the existing orientations. On an ituitive physical basis, the more oriented are the polymer chains the lower is the resistance encountered by the penetrant, and a faster penetration rate is expected. Recent experimental results confirm this expectation[10].

The excess chemical potential over the equilibrium value is given in the present case by two contributions. One is related to the existing excess volume while the other takes into account the effect due to anisotropy alone. The first contribution is clearly exactly the same as that analysed above. The anisotropic term is to be related essentially to the entropy changes due to orientations, the energetic term being negligible. For the anisotropic term, the following assumption is made

$$\mu_2^0-\mu_{2iso}^0=-T(S_2^0-S_{2iso}^0) \tag{24}$$

In order to calculate the excess entropy associated with the orientations frozen in the glass, the following simplifying considerations will be made

(i) the conformational entropy remains unchanged when temperature goes from above to below the glass transition.

(ii) above the glass transition, the rubber elasticity theory well represents the polymer behaviour.

If α_x, α_y and α_z are the extension ratios with respect to the unstretched conformation, along the x, y and z directions, the above assumptions lead to the following expression for the excess entropy due to orientations[11]

$$\begin{aligned} S_2^0-S_{2iso}^0&=(S_2^0-S_{2iso}^0)_{rubber}=\\ &=-\frac{1}{2}Rv_e[\alpha_x^2+\alpha_y^2+\alpha_z^2-3-\ln(\alpha_x\alpha_y\alpha_z)] \end{aligned} \tag{25}$$

In equation (25), v_e represents the effective number of chains and R is the ideal gas constant. After substitution of equation (25) into equation (24), the anisotropic contribution to the excess chemical potential takes the following form

$$\mu_2^0-\mu_{2iso}^0=\frac{1}{2}GV_2[\alpha_x^2+\alpha_y^2+\alpha_z^2-3-\ln(\alpha_x\alpha_y\alpha_z)] \tag{26}$$

In equation (26), use has been made of the relationship which relates the shear modulus G of the rubbery state, to v_e, i.e.

$$G=\frac{RTv_e}{V_2} \tag{27}$$

In the particular case of uniaxial stretching α and of constant volume deformations, equation (26) becomes

$$\mu_2^0-\mu_{2iso}^0=\frac{1}{2}GV_2\left(\alpha^2+\frac{2}{\alpha}-3\right) \tag{28}$$

Equations (26) and (28) represent, in terms of chemical potential changes, the increase in the driving force for swelling, due to the orientations existing in the glassy matrix.

The additional contribution due to anisotropy can be considered equivalent to an additional average isotropic tension given, according to equation (28), by

$$\pi_{aniso}^E=\frac{1}{2}G\left(\alpha^2+\frac{2}{\alpha}-3\right) \tag{29}$$

In view of equation (29), the excess stresses are rapidly increasing with draw ratio α. Since the shear modulus of the rubbery state is of the order of 10 kgf cm^{-2}, for $\alpha=2$ the additional stress is of the order of 10 atm, which is of the same order of the solvent stress of the isotropic case (see *Table*). For $\alpha=5$, the additional stress becomes 112 atm which is higher than almost all the encountered solvent stress of the isotropic case. Finally, for $\alpha=10$, one

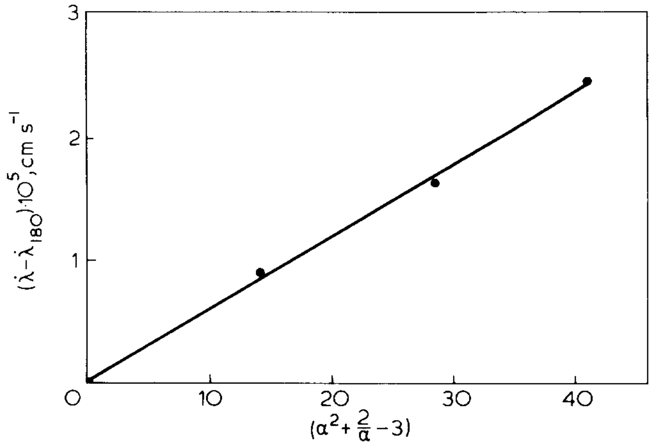

Figure 2 Increase in the initial penetration rate due to orientations, *vs* $(\alpha^2 + 2/\alpha - 3)$

obtains $\pi^E_{aniso}=475$ atm which largely exceeds the value obtained in the isotropic case and becomes the dominant value. This observation leads to the expectation that, at high draw ratios, the penetration rate is the same for all solvents which form a swollen layer; in fact, the dominant term in the driving force, π^E_{aniso}, is independent of the solvent. This indication seems to be confirmed by some unpublished experimental data[12].

Swelling kinetics

The swelling kinetics in the presence of orientations can be reasonably represented by an equation similar to equation (17), although the numerical values of the kinetic parameters are not expected to be the same used in the isotropic case. The presence of anisotropy, in fact, changes the material properties. Some experimental work is in progress about this point.

Some preliminary experimental tests have been performed in order to check whether the increase in the penetration rate due to the anisotropy frozen in the glass is uniquely related to conformational entropy change, equation (25), or equivalently to the anisotropic contribution to the osmotic stress, equation (29).

We have analysed the initial penetration rate for one solvent (*n*-hexane) at the temperature of 55°C, according to experimental procedures[10]. Use has been made of oriented and unoriented polystyrene samples. The former were obtained from an extrudate melt uniaxially oriented at different draw ratios and water-quenched, while the isotropic samples were obtained by compression-moulding followed by a water-quenching[13]. By using a density gradient column with a gradient of 0.0025 gr/(cm^{3}m), their densities were seen to be undistinguishable. In the oriented samples, the actual orientation was related to the reversion ratio, α, measured by analysing the dimensional recovery upon annealing at 135°C, according to reported procedures[13]. Since the oriented and unoriented samples have the same density, the differences in the initial penetration rate, $\lambda-\lambda_{iso}$, is to be attributed to the anisotropy frozen in the glassy matrix. In *Figure* 2, such a difference is plotted *vs* $(\alpha^2+2/\alpha-3)$ which, apart from a proportionality constant, represents the chemical potential increase due to orientation or the anisotropic contribution to the osmotic stress. A linear relationship is obtained.

CONCLUSIONS

With reference to polymer-solvent pairs which present Case II sorption behaviour, the driving force for the localized swelling has been considered. The polymer chemical potential difference between the glassy and swollen phases have been separated into two terms. The first represents the excess free energy of the pure glass, over the hypothetical equilibrium structure; the second term is the chemical potential difference existing between the equilibrium glass and the swollen phase.

In the isotropic case, the excess free energy over equilibrium has been related to the excess volume over the equilibrium structure. In terms of solvent osmotic stress, the out-of-equilibrium frozen in the glass is equivalent to an increase of the solvent stress by a term which increases with decreasing temperature below T_g, and vanishes at the glass transition (see equation (11)). At all the temperatures considered, in this case study of PS-*n*-alkane systems, the out-of-equilibrium term represents an important contribution to the total osmotic stress and cannot be neglected.

The solvent osmotic stress, including the out-of-equilibrium contribution, has been used in a recently proposed kinetic model for Case II transport. The applicability of the model used is improved with respect to the previous formulation. The temperature dependence of the out-of-equilibrium term of the solvent stress results in a much weaker temperature-dependence of the equivalence factor α, (see equation (1)). As it is apparent in *Figure* 1, the equivalence factor now ranges from 0.515 to 1.99 over the entire temperature range considered.

It must be observed that, by means of density measurements alone, the theory presented here allows one to account for the changes in the swelling kinetics caused by the different past histories experienced by the samples. It is expected that the excess term given in equation (11) represents the key to quantitatively understand the cycling effects reported[14].

In the presence of orientations frozen in the glassy matrix, the out-of-equilibrium term has been expressed both in terms of excess chemical potential and of an additional stress. The result obtained shows that, at small draw ratios, the orientations do not affect appreciably the driving force for swelling, whereas, on the contrary at high draw ratios (around 10), the effect of the orientations becomes the dominant one and the swelling kinetics is about the same for all the swelling solvents. The increase in penetration rate caused by the orientation alone is found to be a linear function of the conformational entropy decrease due to the imposed orientations.

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