Solvent osmotic stresses and the prediction of Case II transport kinetics

Giulio C. Sarti*
Chemical Engineering Department, North Carolina State University, Raleigh, NC 27650, USA
(Received 3 November 1978; revised 12 February 1979)

The rate controlling step in Case II transport kinetics is the swelling which occurs at the internal moving boundary. A physical model describing the swelling kinetics of glassy polymers in liquids is presented here. Using a thermodynamic argument, the stress induced by the penetrant on the glassy matrix is evaluated in terms of the penetrant concentration. The velocity of the swelling front is expressed in terms of the solvent stress, using the same functional relationship which gives the mechanical craze propagation rate, in terms of the mechanical stress. The resulting model permits the prediction of the kinetics of the swelling front from an independent characterization of mechanical properties.

INTRODUCTION

Significant interest has been devoted to the experimental description of diffusion behaviour of small solvent molecules in glassy polymers. The diffusion of n-alkanes in polystyrene[1–4], n-alkyl alcohols in poly(methyl methacrylate)[5–7] and n-alkanes in PS–PPO blends[8–10] has been studied extensively.

The sorption process is non-Fickian over well-defined boundaries of temperature and of solvent activity. More precisely, above a lower limiting value of solvent activities there exists a temperature interval in which the weight gain during sorption is proportional to the first power of time (Case II transport), rather than to its square root (Fickian behaviour). Outside that interval, at lower temperatures, Fickian behaviour is observed while at higher temperatures the weight gain becomes proportional to a power of time with an exponent decreasing from unity to 1/2 with increasing temperature[11]. In addition, the dimensions of the samples are also shown to influence the sorption behaviour[12]. In sufficiently thick samples, the sorption rate decreases significantly after initial penetration (see e.g. refs 4–6), while the sorption rate accelerates in sufficiently thin samples as equilibrium is approached (Super Case II transport).

A sharp moving boundary exists within the sample, separating an outer shell containing an appreciable amount of solvent from an internal core which is essentially unpenetrated and, therefore, remains glassy.

Many previous attempts to provide a satisfactory mathematical description of this anomalous mass transfer behaviour rely on the assumption that the diffusion coefficient varies strongly with penetrant composition[13–15]. According to this viewpoint no special resistance to mass transfer is associated with the swollen–glassy polymer transition.

On the contrary the observed behaviour seems to be explained in terms of 'relaxation-controlled diffusion'. According to this interpretation, the rate controlling process is the transition from the glassy to the swollen state taking place at the moving boundary.

In an early formulation, Peterlin[16] considered a moving boundary diffusion problem; the velocity of the moving boundary was considered a constant given value, and diffusion was considered into the glassy core. In a recent paper, Astarita and Sarti[17] have shown that the introduction of a kinetic expression for the velocity of the glassy–swollen interface is sufficient to explain qualitatively the relevant features of the 'relaxation-controlled' transport. In the simple formulation given by Astarita and Sarti[17], the diffusion coefficient was taken as a constant in the swollen phase and zero in the glassy core; the penetrant equilibrium at the solvent–swelling polymer interface was assumed to occur instantaneously at time $t = 0$ and, finally, the velocity $\dot{\lambda}$ of of the swelling front was assumed to obey a phenomenological power law expression:

$$\dot{\lambda} = K(C - C^*)^n \quad \text{when } C > C^*$$
$$\dot{\lambda} = 0 \quad \text{when } C \leqslant C^* \qquad (1)$$

In spite of the simplicity of these assumptions, the penetration depth, as well as the weight gain, is indeed a linear function of time, until the resistance due to diffusion in the swollen layer is comparable to the mass transport resistance confined to the advancing front. At later times, both weight gain and penetration depth decelerate and tend to the $t^{1/2}$ law because the diffusion resistance becomes the rate-controlling step. The role of temperature in deciding what are the rate-controlling processes can easily be taken into account by using Arrhenius type equations for the kinetic constant and the diffusion coefficient.

The model developed in ref 17 demonstrates that the rate-controlling process is often the phase transition which occurs at the glassy–swollen interface. However, the assumptions used result in an oversimplification of the real phenomena, mainly with respect to the following points:

(i) the kinetics of the advancing front, empirically described by a power law, are given by a first guess expression, with no physical basis.

---

* Permanent address: Istituto di Principi di Ingegneria Chimica, Universita di Napoli, Naples, Italy

0032–386/79/070827–06$02.00

(ii) the diffusion coefficient in the swollen phase is taken as a constant;

(iii) the equilibrium at the solvent–swollen polymer interface is assumed to be reached instantaneously while the polymer matrix undoubtedly requires a certain time to achieve the equilibrium swelling demanded by the solvent activity;

(iv) no convective term is considered in spite of the swelling phenomenon.

(v) the diffusion coefficient is taken as zero in the glassy core.

Of course, not all the points above are of the same importance. For instance, improvement of the points (iii) and (v) result in a better interpretation of the initial behaviour of the diffusion process but has very little effect on the subsequent behaviour. On the contrary, the kinetics of the advancing front are of crucial importance in most cases and further detailed analysis of its mechanism seems appropriate. So far, the existence of an advancing boundary is just accepted as an experimental fact, but it is not well understood how to relate it to the physical properties of both penetrant and polymer. A better understanding of this step is needed. Useful indications can come from it in the prediction of the behaviour of solvent–polymer pairs different from those directly investigated.

The primary objective of this work is to formulate a kinetic model for the swelling rate, in which the velocity of the advancing front is expressed in terms of independently measurable quantities.

A preliminary thermodynamic analysis is first considered, to establish some relevant relationships among the phases of the typical system showing Case II sorption behaviour. An evaluation of the solvent-induced stresses is then found. The latter is used, together with some mechanical properties of the glassy polymer, to formulate a kinetic equation which predicts the sorption rate when the glassy–swollen transition takes place.

THERMODYNAMIC ANALYSIS AND THE SOLVENT-INDUCED STRESS

Consider a typical system in which a moving boundary process takes place. The penetrant has a finite solubility in the polymer matrix while the polymer is almost insoluble in the low molecular weight liquid. At equilibrium, therefore, the system presents a miscibility gap, the boundaries of which are almost pure solvent and equilibrium swollen polymer. The latter is typically above its glass transition temperature.

During the sorption process three phases are present: pure solvent, swollen polymer and glassy polymer. An expression for the chemical potentials is needed to provide for a mathematical description of the phases present. It is known that this can be obtained by using either Prigogine's corresponding state theory[18,19] or the Flory–Huggins theory[20,21]. Since it was proved by Biros *et al.*[22] that remarkably similar results are found using either approach, the commonly used Flory–Huggins treatment will be followed in the analysis presented here.

With reference to a single molecular weight polymer, the following well-known expression for the Gibbs free energy of mixing is assumed:

$$\frac{\Delta G_M}{RT} = n_1 \ln \nu_1 + n_2 \ln \nu_2 + \chi_1 n_1 \nu_2 \qquad (2)$$

In equation (2) subscripts 1 and 2 refer to solvent and polymer respectively, n_1 and n_2 are numbers of moles, ν_1 and ν_2 represent volume fractions. If the ratio $1/X$ between solvent and polymer molar volumes is negligible with respect to unity, the following expressions for the chemical potentials hold true:

$$\frac{\mu_1 - \mu_1^0}{RT} = \ln \nu_1 + (1 - \nu_1) + \chi_1 (1 - \nu_1)^2 \qquad (3)$$

$$\frac{\mu_2 - \mu_2^0}{XRT} = -\nu_1 + \chi_1 \nu_1^2 + \frac{1}{X} \ln(1 - \nu_1) \qquad (4)$$

The symbols μ_1^0 and μ_2^0 have been used for the chemical potentials of the pure substances. The above description is sufficient to provide for an evaluation of the driving force for swelling. Here, only the effects due to the solvent presence are considered, irrespective of the sample dimensions and geometry. Therefore a sufficiently large slab will be considered so that only local effects will be relevant. Moreover, in such a case we can neglect the thickness of the region in which the glassy–swollen transition occurs, and consider it to take place at a plane surface. The effects related to sample dimensions are briefly discussed in the Conclusions.

The driving force for swelling is related to the non-equilibrium conditions encountered at the moving boundary. On both sides of it, polymer molecules are present with different chemical potentials. In the pure polymer side the chemical potential is μ_2^0, while in the swollen polymer side the chemical potential has been lowered by the solvent to the value μ_2.

The driving force for the process can thus be expressed in terms of Gibbs free energy difference per mol, as $\mu_2^0 - \mu_2$. In other words it is given by the chemical potential decrease due to the solvent concentration on the swollen side.

It is convenient to evaluate the mechanical stress which is equivalent to that driving force. In the present problem, this can be done easily by calculating what stress must be exerted on the pure polymer, in order to obtain a chemical potential decrease equal to that caused by the penetrant volume fraction. To this end, a pressure decrease π is needed on the glassy matrix, such that:

$$\mu_2 = \mu_2^0 - \pi V_2 \qquad (5)$$

In equation (5) the polymer molar volume V_2 has been considered to be a constant. Applying equation (4) the following result is obtained

$$\pi = \frac{RT}{V_1} \left[\nu_1 - \chi_1 \nu_1^2 - \frac{1}{X} \ln(1 - \nu_1)\right] \qquad (6)$$

The solvent molar volume V_1 has been substituted for the ratio V_2/X.

Equation (6) represents an important result and will be crucial in the following. Clearly π is positive; thus an isotropic *tension* must be exerted on the pure glassy polymer in order to obtain the same decrease in the chemical potential as that induced by the solvent presence. Equivalently, π can be regarded as the overpressure which should be imposed on the swollen phase in order to compensate for the change in chemical potential due to the solvent. In other words, π can be considered as the pressure which equilibrates the stresses due to the solvent presence. It is assumed that equation (6) gives the stresses induced by the solvent on the pure polymer at the glassy–swollen interface.

The same result can equivalently be found by considering the following isothermal equilibrium:

$$\text{Pure polymer} \rightleftharpoons \text{Polymer in the swollen phase} \qquad (7)$$

Equilibrium (7) can be considered 'osmotic' insofar as the following characteristics are obeyed:

(a) phase equilibrium is reached only for one component and not for the other;

(b) such equilibrium can be obtained only by applying a suitable pressure difference.

This observation allows us to refer to the solvent-induced stress as to an osmotic stress[†], as is sometimes done in the existing qualitative descriptions.

Focussing attention on the swollen–penetrant interface, we can evaluate the solvent concentration using straightforward equilibrium considerations. Since the polymer is insoluble in the low molecular weight liquid, in that phase the equilibrium solvent activity remains at a constant value a_1^0 chosen before sorption. The equilibrium composition in the swollen phase is thus given by:

$$\ln a_1^0 = \ln \nu_1 + (1 - \nu_1) + \chi_1(1 - \nu_1)^2 \qquad (8)$$

In view of the particular miscibility gap which is to be encountered, the Flory interaction parameter must have a sufficiently high value. Roughly, it can be said that the immiscibility condition is fulfilled for all molecular weights of practical interest, when

$$\chi_1 > 0.62 \qquad (9)$$

KINETICS OF PENETRATION: A COMPREHENSIVE MODEL

In order to make suggestions for a kinetic equation of the advancing front it is convenient at this stage to analyse some mechanical properties of the pure polymer. In particular, we shall consider the crazing-under-stress behaviour of the glassy matrix, which seems to be strictly related to the phenomena here examined.

Above a critical value of the tensile stress, crazes are formed in a glassy polymer. The propagation of crazes occurs in the direction perpendicular to the tensile stress, starting from existing microvoids often located at the sample surface.

Depending on experimental conditions, a sharp front separating crazed and uncrazed material can be observed because of the different optical properties of the two regions. The propagation rate of that front usually increases by increasing the applied tensile stress.

The crazing behaviour of a glass is commonly analysed by applying a uniaxial tensile stress, σ. By measuring the craze penetration depth, λ, with time, the functional dependence of the crazing rate upon the stress is experimentally determined. Formally we have:

$$\dot{\lambda} = f(\sigma) \qquad \sigma \geqslant \sigma_c$$

$$\dot{\lambda} = 0 \qquad \sigma < \sigma_c \qquad (10)$$

In equation (10), σ_c indicates the threshold value of the stress above which crazing takes place. Many similarities exist between mechanical crazing and Case II sorption behaviour. Indeed, the elementary physical steps occurring in both cases appear similar. Both phenomena require that the highly packed glassy state move towards a structure in which a high free volume is present. The difference between the processes is confined to the driving force, which is the applied stress in one case, and the effect of the solvent in the other.

Several analogies are also found from a phenomenological viewpoint: (i) in both cases the phenomenon starts when the driving force (tensile stress or solvent activity) exceeds a certain threshold value; (ii) the higher the driving force, the higher is the front propagation rate; (iii) a sharp moving boundary separating the two regions is clearly visible. Moreover, it must be observed that in many cases in which Case II sorption exists, visible crazes are also found which are usually referred to as solvent crazes. The kinetics of the two phenomena are, presumably, strictly related to each other.

However, while in solvent crazing one refers to an isotropic tension, π, given by equation (6), in the usual mechanical tests a uniaxial tension, σ, is considered. The question then arises of the value of the uniaxial stress which can be considered equivalent to an isotropic tension, as far as crazing is concerned. In yielding mechanics, a uniaxial stress, σ_E, can be found which is equivalent to the applied triaxial stress according to a suitable yield criterion (Tresca, Beltrami, von Vises, etc.). In particular, when the applied stress is an isotropic tension π, the uniaxial equivalent stress σ_E is given by:

$$\sigma_E = a\pi \qquad (11)$$

The proportionality constant a has a precise value depending upon the yield criterion chosen. In all cases, however, the order of magnitude of 'a' is unity. Although crazing and yielding are not the same physical phenomenon, they occur at nearly the same stress levels, and therefore the equivalence relationships used in the case of yielding are considered to hold true for crazing phenomena as well.

Due to the uncertainty about the yield criterion to be chosen, however, and since the yield criterion changes with temperature (especially close to T_g) it is convenient to consider a as an adjustable parameter with the only requirement that it be of order unity.

The kinetic equation of Case II transport can then be summarized as follows:

(1) the solvent presence at the inner interface induces an isotropic tension given by equation (6) on the glassy matrix, which is then transformed to an equivalent uniaxial tension σ_E by means of equation (11);

(2) the velocity of the advancing front, separating the swollen region from the glassy matrix, is given by the rate equation for mechanical crazing, equation (10), in which the applied stress has been substituted by the equivalent stress σ_E.

Comparison with experiments

A significant comparison of the proposed kinetic model with experimental data can be made only for polymers which have been sufficiently analysed both for mechanical proper-

---

[†] Possible confusion must be avoided about this point. The osmotic pressure usually considered for dilute polymer solutions is a completely different quantity. It derives from a different osmotic equilibrium, i.e. that between solution and pure solvent. This latter osmotic pressure clearly cannot be used here as a measure of the solvent-induced stress. It would be sufficient to observe that it decreases with increasing solvent concentration

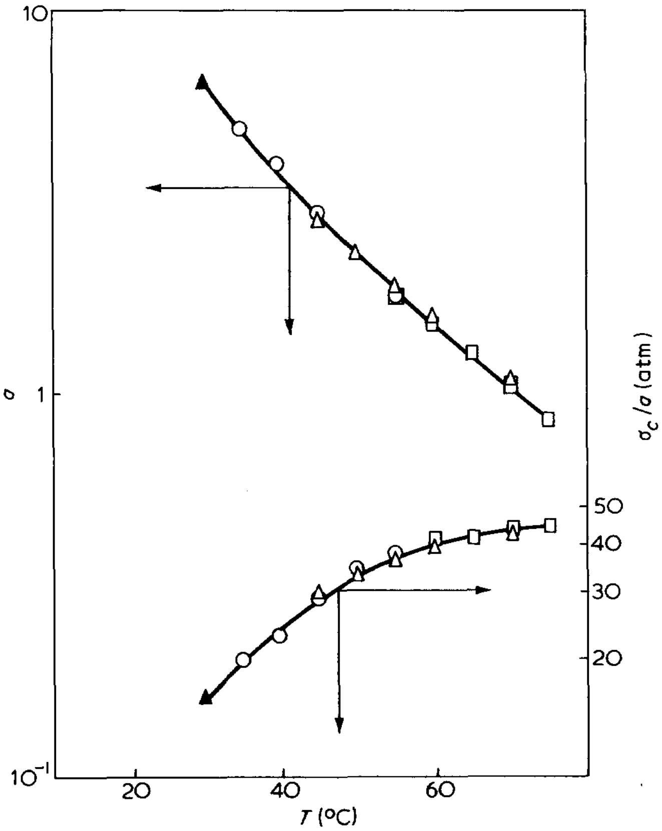

Figure 1 Temperature dependence of the parameter *a* and of the critical stress σ_c/a: ▲, n-pentane; ○, n-hexane; △, n-heptane; □, n-octane. Activation energy used: ΔE = 40 (kcal mol^{-1})

ties and sorption behaviour. In order not to introduce other assumptions, concerning for example the diffusion coefficient, the density, etc., a proper test for the kinetic model must be made by considering the initial front velocity data. In such a case, the solvent volume fraction at the interface is the equilibrium volume fraction, which is known or at least easily predictable.

We have thus chosen a single polymer, polystyrene and various n-alkanes as diffusing species. In this case experimental data exist both for the mechanical crazing kinetics[23,24] and for the swelling behaviour[1–4].

The experiments by Sauer and Hsiao, ref 24, have shown that the crazing penetration rate is a linear function of the applied uniaxial tensile stress, given by:

$$\dot{\lambda} = K(\sigma - \sigma_c) \qquad \sigma > \sigma_c \tag{12}$$

At room temperature the values reported for K and σ_c are the following

$$K = 0.85 \times 10^{-7} \frac{\text{in}}{\text{h psi}}\ ; \quad \sigma_c = 1670\,\text{p.s.i.} \tag{13}$$

When use is made of the data of ref 23, at 3500 psia, it can be shown that the kinetic constant K changes with temperature following an Arrhenius law:

$$K = K_0\, e^{-\Delta E/RT} \tag{14}$$

The evaluated activation energy ΔE is about 40 kcal mol^{-1} the corresponding K_0 value is 1.918 × 10^{20} cm (sec atm)$^{-1}$

The critical stress, σ_c, varies with temperature and vanishes at the glass transition; experimental evidence shows that σ_c decreases linearly with increasing temperature towards T_g[25,26]:

$$\sigma_c = A(T_g - T) \tag{15}$$

According to the kinetic model formulated, the swelling rate into the polystyrene matrix is given by:

$$\dot{\lambda} = K(a\pi - \sigma_c) \tag{16}$$

where the constants K and σ_c are given by equations (14) and (15), respectively. More explicitly, the values of K and σ_c are independent of the nature of the penetrant and are only related to the properties of the polymer matrix. With changing the chemical nature of the solvent, Flory's parameter changes and a different solvent stress is obtained.

The comparison with the initial front velocity data reported in ref 4 can be done provided the equilibrium composition is known. Equilibrium data are not reported at all temperatures examined in ref 4. Therefore the equilibrium volume fractions were here evaluated using the equilibrium equation (8). The Flory interaction parameter was evaluated using the regular solution theory by Hildebrand and Scatchard[27]. Since non-polar components are considerd, according to Blank and Prausnitz[28], the following expression was used:

$$\chi_1 = 0.34 + \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \tag{17}$$

The value 0.34 stands for the average value of the entropic contribution χ_s. The values used for the solubility parameters, reported in ref 28.

The solvent-induced stress was evaluated using equation (6), with χ_1 given by equation (17) and ν_1 given by the corresponding equilibrium composition in the swollen phase.

Equation (16) was then used to calculate the value of parameter *a*, which is needed to obtain the experimental front velocity value. The results of these calculations are reported in *Figure 1*.

It can be seen that parameter *a* ranges from 7.0 at 30°C (n-pentane), to 0.86 at 75°C (n-octane). At a given temperature, *a* has the same value for all the solvents considered, to within 12%. This property is in full agreement with the predictions of the model, in which *a* enters as a factor depending upon the yield behaviour of the pure matrix alone. The value of *a* is of the order of magnitude predicted by the theory, although it is not a constant value. It is found to be a function of temperature, decreasing with increasing *T*. The latter property was not expected and is accepted here on a phenomenological basis.

The data reported in *Figure 1* are obtained using an activation energy for K of 40 kcal mol^{-1}. In *Figure 2*, it is shown that the change in *a* values with changing solvent can be maintained to within 6% by simply using a slightly different activation energy and the corresponding K_0 value, i.e. ΔE = 45 kcal mol^{-1} and K_0 = 8.917 × 10^{23} cm (sec atm)$^{-1}$. Some relevant data used in the above calculations are reported in *Table 1*.

DISCUSSION AND CONCLUSIONS

A schematic analysis was considered of systems in which Case II sorption behaviour is encountered. Some essential features have been pointed out, which lead to the formulation of a kinetic equation for the swelling front velocity. An important result concerns the evaluation of the solvent-induced stresses, obtained through equations (5) and (6).

We then assumed the kinetics of the swelling front to be exactly the same kinetics encountered in pure mechanical crazing. This hypothesis enables us to construct a model in which only one adjustable parameter is present, the order of magnitude of which is unity. That parameter, *a*, is strictly related to the yield behaviour of the pure glassy matrix and is independent of the particular solvent considered. These predictions are completely in agreement with the experimental behaviour presented by PS–n-alkane systems for which the maximum deviation presented by *a* with changing solvent is around 10%. A comparison with existing experimental data for PS, shows that *a* is a temperature-dependent property of the polymer matrix, ranging from 7.0 at 30°C to 0.86 at 75°C.

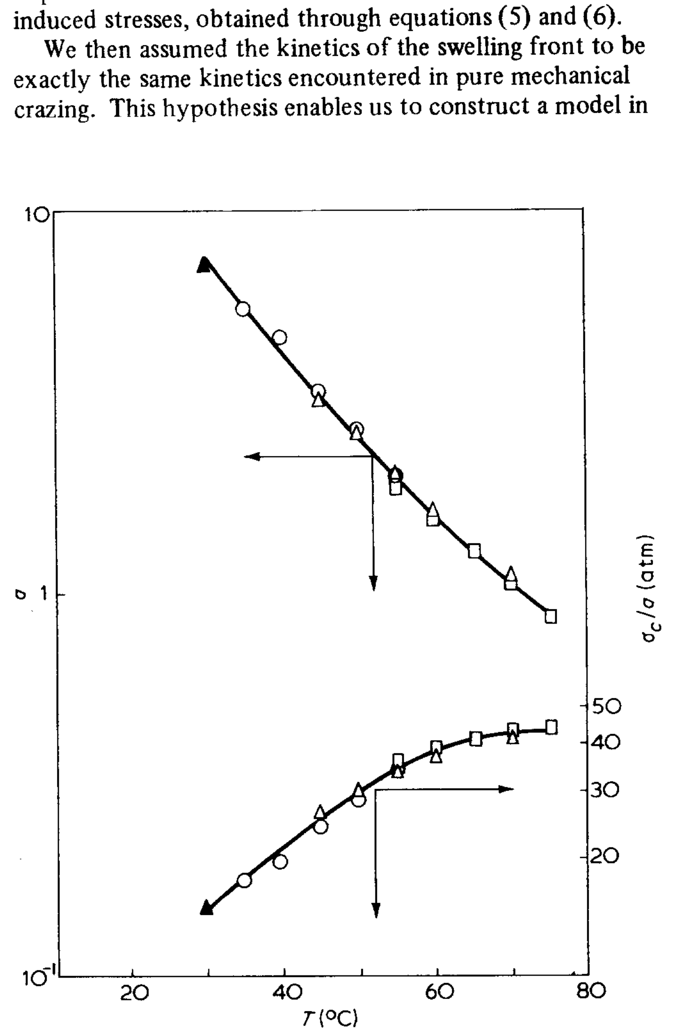

Figure 2 Temperature dependence of the parameter *a* and the critical stress σ_c/a: ▲, n-pentane; ○, n-hexane; △, n-heptane; □, n-octane. Activation energy used: ΔE = 45 (kcal mol^{-1})

The predictive ability of the proposed model must be stressed. On the basis of the experimental behaviour encountered in tests different from sorption, i.e. pure mechanical experiments and equilibrium thermodynamics, the order of magnitude is evaluated for the velocity of the advancing front, without doing any preliminary sorption experiments (*a* ranges between 0.86 and 7.0). If, in addition, the sorption behaviour of only one solvent has been previously analysed, the parameter *a* can be found as a function of temperature and can be used to obtain better predictions for the sorption of all other solvents. In the latter case, the maximum deviation between predictions and experiments is less than 12% in the cases examined. These results seem very encouraging; at least, they allow us to believe that in the present model the most relevant effects which determine Case II sorption behaviour have been taken into account quantitatively.

Clearly, the proposed kinetics can be used when the solvent stress exceeds the lower limiting value necessary for craze propagation. This observation, together with the thermodynamic properties of the system, allows us to predict whether or not in a given polymer–solvent pair Case II transport will be encountered. In fact, the parameter χ_1 can be estimated for many systems, according to existing procedures (see ref 28). If χ_1 is sufficiently large, say larger than 0.62, the insolubility condition for the polymer is obeyed, and the proper miscibility gap will be present. After the evaluation of the equilibrium composition in the swollen phase, through equation (8), the value of the solvent osmotic stress can be calculated. Case II behaviour is expected when

Table 1 Values of Flory's interaction parameter, solvent osmotic stress, critical stress used to evaluate the model parameter *a*. The values of $\dot{\lambda}$ are experimental (see ref 4)

						E = 40 kcal mol^{-1}		ΔE = 45 kcal mol^{-1}	
	T (°C)	χ_1	π (atm)	σ_c (atm)	$\dot{\lambda} \times 10^6$ (cm sec^{-1})	a	σ_c/a (atm)	a	σ_c/a (atm)
nC_5	30	1.183	35.5	106.1	0.39	7.0	15.0	6.5	16.2
nC_6	35	1.047	38.0	98.5	0.89	5.6	17.7	4.8	20.5
	40	1.035	39.2	91.0	2.08	4.7	19.4	3.9	23.2
	45	1.024	40.4	83.4	3.56	3.5	23.9	2.9	28.7
	50	1.014	41.6	75.8	5.33	2.6	29.1	2.2	34.3
	55	1.004	42.8	68.2	7.55	2.0	34.1	1.8	37.8
nC_7	45	1.016	37.0	83.4	1.84	3.1	27.2	2.7	30.8
	50	1.005	38.4	75.8	3.50	2.5	30.1	2.3	32.8
	55	0.995	39.5	68.2	5.33	2.0	34.1	1.9	35.8
	60	0.985	40.6	60.6	7.11	1.7	36.6	1.6	37.8
	70	0.966	42.9	45.5	10.2	1.1	41.4	1.1	42.4
nC_8	55	0.907	40.3	68.2	2.78	1.9	36.8	1.8	38.3
	60	0.898	41.7	60.6	4.28	1.6	39.1	1.5	40.4
	65	0.890	42.7	53.1	5.00	1.3	41.2	1.3	42.1
	70	0.882	43.8	45.5	7.17	1.1	42.7	1.0	43.5
	75	0.874	45.0	37.9	9.44	0.86	44.2	0.85	44.5

the solvent stress is larger than the critical stress for craze propagation. In the water–PS system, for instance, the solubility of water in the polymer is too low to obtain an appreciable solvent stress, and Case II sorption is not encountered.

One further observation is worthwhile. In the present work, attention has been restricted to the local stress effects due to the solvent. These are always present, irrespective of the sample dimensions; the latter however are sometimes responsible for significant changes in sorption behaviour. Such effects can easily be taken into account within the theory presented here. To this end, it is sufficient to add to the solvent osmotic stress (equation 6), another term which accounts for the 'overall effects' due to sample geometry and shape. This term can be calculated following just the same procedure shown by Alfrey *et al.*[30], and recently used, in a more elaborate context by Petropoulos and Roussis[31]. It is easy to show that this last term satisfactorily explains the Super Case II effects presented by thin samples. The detailed analysis of this effect will be examined in future work.

ACKNOWLEDGEMENTS

The author wishes to thank Professor G. Marrucci for encouraging and stimulating discussions. Access to original experimental results by Professor L. Nicolais and his comments are gratefully acknowledged. Also gratefully acknowledged are the interesting and stimulating discussions with Professors H. B. Hopfenberg and J. H. Petropoulos during a workday on 'Diffusion in Glassy Polymers', Naples, June 8, where a first version of this work was presented. Fruitful discussions with Professor A. Peterlin are also acknowledged. This work was supported by CNR Grant No 75.00720.03/115.1729. The final version of the manuscript was prepared while the author was Visiting Associate Professor at the Chemical Engineering Department, North Carolina State University, Raleigh, NC, USA.

REFERENCES

1 Michaels, A. S., Bixler, H. J. and Hopfenberg, H. B. *J. Appl. Polym. Sci.* 1968, **12**, 991

2 Hopfenberg, H. B., Holley, R. H. and Stannett, V. T. *Polym. Eng. Sci.* 1969, **9**, 242

3 Baird, B. R., Hopfenberg, H. B. and Stannett, V. T. *Polym. Eng. Sci.* 1971, **11**, 274

4 Nicolais, L., Drioli, E., Hopfenberg, H. B. and Tidone, D. *Polymer* 1977, **18**, 1137

5 Hopfenberg, H. B., Nicolais, L. and Drioli, E. *Polymer* 1976, **17**, 195

6 Thomas, N. and Windle, A. H. *J. Membrane Sci.* 1978, **3**, 337

7 Nicolais, L., Drioli, E., Hopfenberg, H. B. and Caricati, G. *J. Membrane Sci.* 1978, **3**, 231

8 Jacques, C. H. M., Hopfenberg, H. B. and Stannett, V. T. *Polym. Eng. Sci.* 1973, **13**, 81

9 Jacques, C. H. M. and Hopfenberg, H. B. *Polym. Eng. Sci.* 1974, **14**, 449

10 Hopfenberg, H. B., Stannett, V. T. and Folk, G. M. *Polym. Eng. Sci.* 1975, **15**, 261

11 Hopfenberg, H. B. 'Membrane Science and Technology' (Ed. J. Flinn), Plenum, NY, 1970, p 16

12 Baird, B. R., Hopfenberg, H. B. and Stannett, V. T. *Polym. Eng. Sci.* 1970, **10**, 274

13 Crank, J. 'The Mathematics of Diffusion', Clarendon Press, Oxford, 1972

14 Duda, J. L. and Vrentas, J. S. *J. Polym. Sci. (A-2)* 1968, **6**, 675

15 Yih-O Tu, *Quart. Appl. Math. XXXV* 1977, 269

16 Peterlin, A. *Makromol. Chem.* 1969, **124**, 136

17 Astarita, G. and Sarti, G. C. *Polym. Eng. Sci.* 1978, **18**, 388

18 Prigogine, I., Trappeniers, N. and Mathot, V. *J. Chem. Phys.* 1953, **21**, 559

19 Prigogine, I., 'The Molecular Theory of Solutions', North Holland, Amsterdam, 1957

20 Flory, P. J. *J. Chem. Phys.* 1941, **9**, 660; 1942, **10**, 51

21 Huggins, M. L. *J. Phys. Chem.* 1941, **9**, 440

22 Biros, J., Zeman, L. and Patterson, D. *Macromolecules* 1971, **4**, 30

23 Maxwell, B. and Rahm, L. F. *IEC* 1949, **41**, 1988

24 Sauer, J. A. and Hsiao, C. C. *Trans. ASME* 1953, **75**, 895

25 Haward, R. N. 'Critical Stages in the Fracture of an Organic Glass' in 'Amorphous Materials', (Eds. R. W. Douglas and B. Ellis) Wiley, London, 1972

26 Kambour, R. P. and Robertson, R. E. 'Mechanical Properties of Plastics' in 'Polymer Science', (Ed. A. D. Jenkins) North Holland, 1972

27 Hildebrand, J. H., Scott, R. L. 'Solubility of Nonelectrolytes', Reinhold, New York, 1950

28 Blanks, R. F. and Prausnitz, J. M. *IEC Fund* 1964, **3**, 1

29 (Eds. J. Brandrup and Immergut, E. H.) 'Polymer Handbook' Interscience, New York, 1966

30 Alfrey, Jr, T., Gurnee, E. F. and Lloyd, W. O. *J. Polym. Sci. (C)* 1966, **12**, 249

31 Petropoulos, J. H. and Roussis, P. P. *J. Membrane Sci.* 1978, **3**, 343