Dipartimento di Ingegneria Chimica Mineraria e Tecnologie Ambientali - DICMA

Alma Mater Studiorum Università di Bologna – Bologna, Italy

Fickian and non-Fickian Diffusion in Solid Polymers

Giulio C. Sarti

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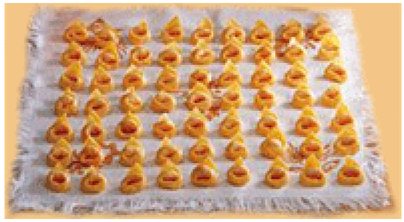
From Bologna: **diffusion** of tortellini



diffusion of mortadella

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Bologna, ITALY

Diffusion of the university system

UniBO is proud of being the oldest University in western world:

In operation since 1088

In 1988 has celebrated the 9th Centennial of its life

Copernicus, Galilei, Galvani, Malpighi were among Bologna's Scholars

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OUTLINE

- ***Fickian diffusion***
  - *non swelling penetrants* ⇒ *no relevant deformations and no stresses*
  - *swelling penetrants* ⇒ *deformations and stresses are induced*
    - *a) how to measure stress effects*
    - *b) how to calculate the stress field*

- ***Non-Fickian Transport***
  - *Effects of swelling and of stresses*
  - *Structural changes and relaxation*
    - *Effects of temperature*
    - *Effects of activity difference*
    - *Effects of pre-history*
    - *Effects of sample dimensions*

⇒

a) Anomalous diffusion
b) Two stage sorption
c) Case II Transport
d) Super-Case II transport

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OUTLINE

- ***Modeling Fickian Transport***
  - *non swelling penetrants* $\Rightarrow$ *nothing special*
  - *swelling penetrants* $\Rightarrow$ *deformations and stresses must be calculated*
    - *Elastic (and viscoelastic) case*

- ***Modeling Non-Fickian Transport***
  - *Lumped models*
    - *Localized swelling (with & without differential swelling stresses)*
    - *Viscoelastic diffusive flux*
  - *General models*
    - *Based on Mixture theory*
    - *Based on a proper expression of the chemical potential in glasses*
      - *Calculate time dependent BC*
      - *Calculate fluxes depending on concentration and deformation/stress gradients*

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Acknowledgements

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Maria-Chiara Ferrari
Jacopo Catalano
and to the group

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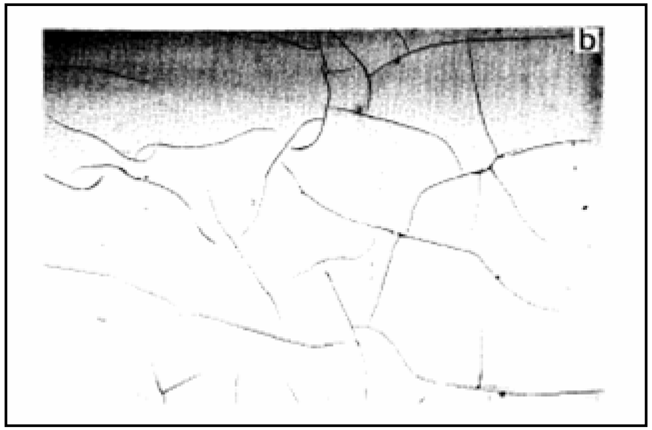
Penetrants can generate swelling and stresses

In gases and in liquids diffusion does not build up a stress field
In solids in general and in polymeric solids in particular stresses are generated by swelling penetrants

- Crazes and even cracks can be produced
- Morphological changes are induced



Methanol in PMMA

After Tomas & Windle, *Polymer* 1982

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Effects of swelling and stresses

Swelling and stress fields may affect diffusion

- through morphological changes
- through solubility changes
    - BC
    - Final solubility
- diffusivity dependence on stress
- through stress dependence of the flux

The viscoelastic nature of the polymer introduces relaxation times in the response , which affects the transport process

Qualitative interpretation is based on diffusion **Deborah number**, (DEB)D:

$$(\mathrm{DEB})_{\mathrm{D}} = \tau D_{12}/l^2$$

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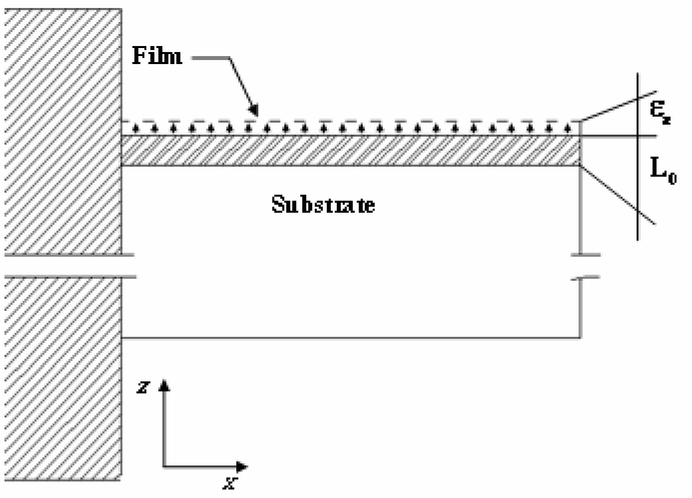
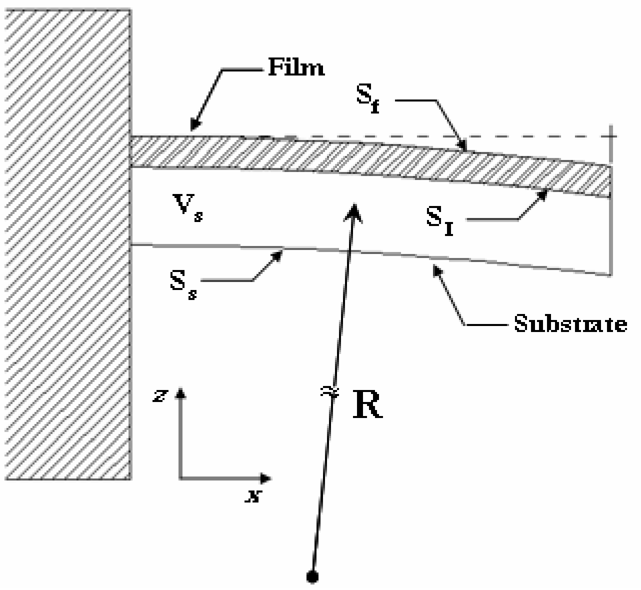
How can stresses be measured

- birefringence
- bending cantilever





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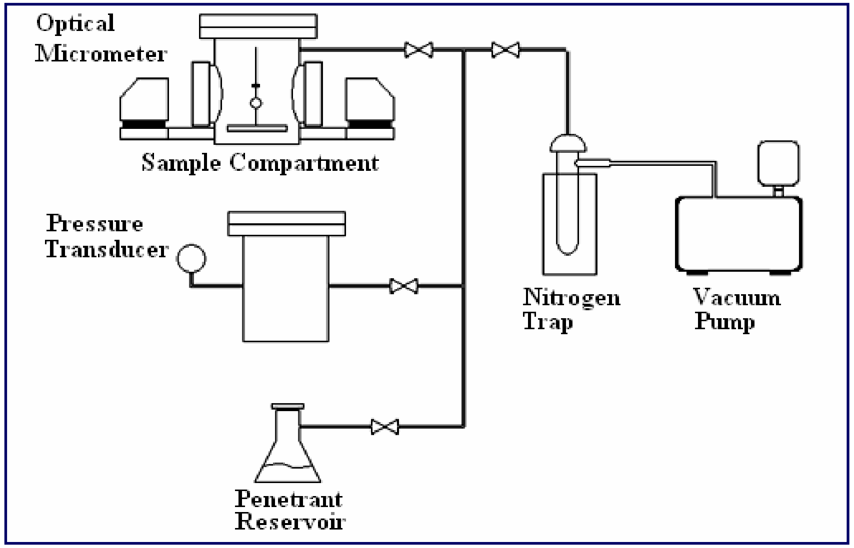
How can stresses be measured

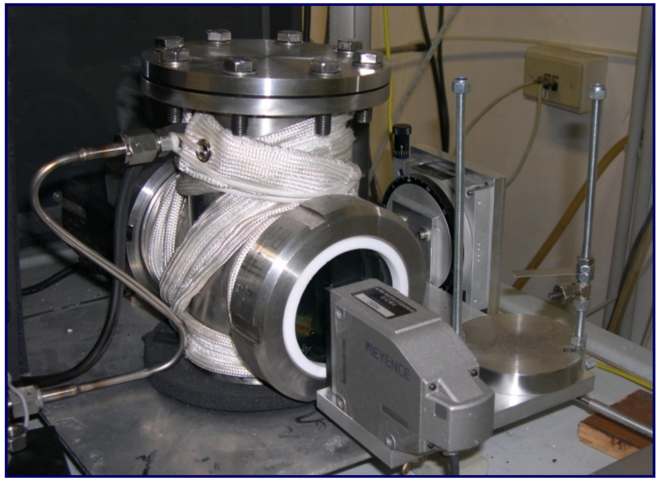


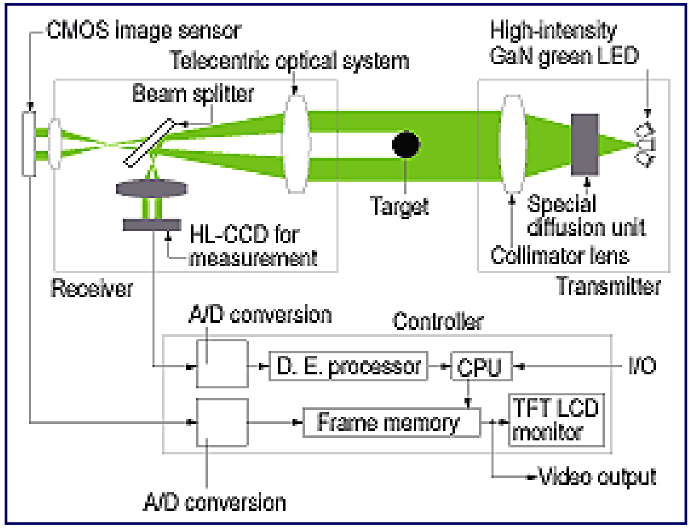
P_{max}= 8 bar
T_{max}= 200°C

Deflection measured through an optical micrometer (Keyence LS7030M)

Precision = ±1 μm

Reproducibility=0.15 μm





How can they be described

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}$$

$$c = c_{eq} \qquad \forall P(x,y,z) \in S_f, \quad \forall t$$

$$\nabla c \cdot n = 0 \qquad \forall P(x,y,z) \in S_I, \quad \forall t$$

$$c = 0 \qquad \forall P(x,y,z) \in V_f, \quad t = 0$$

Swelling condition

$$\varepsilon_i^c = \beta(c)c$$

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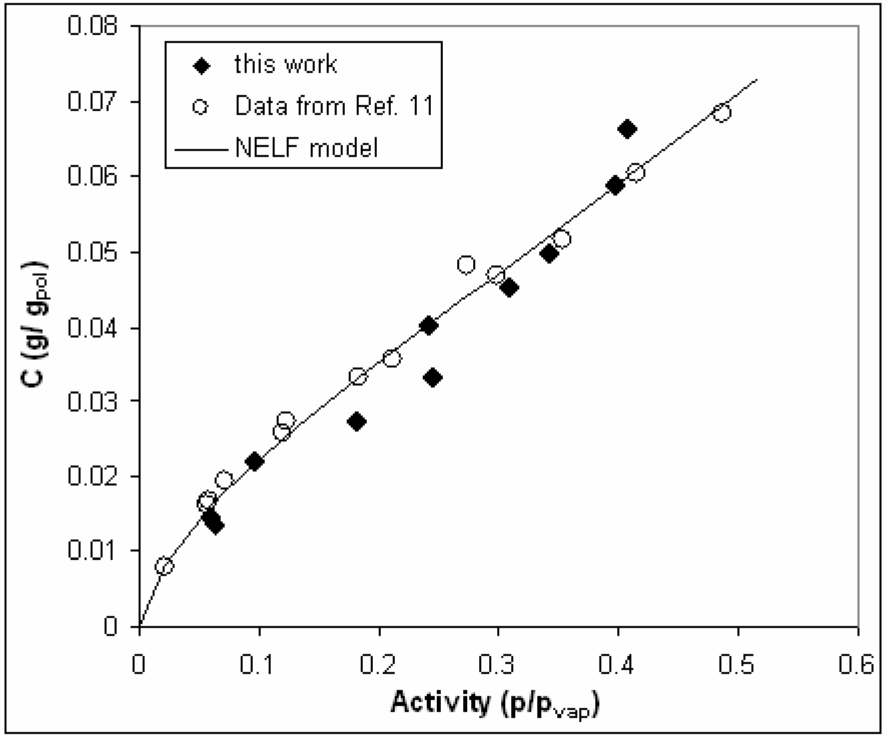

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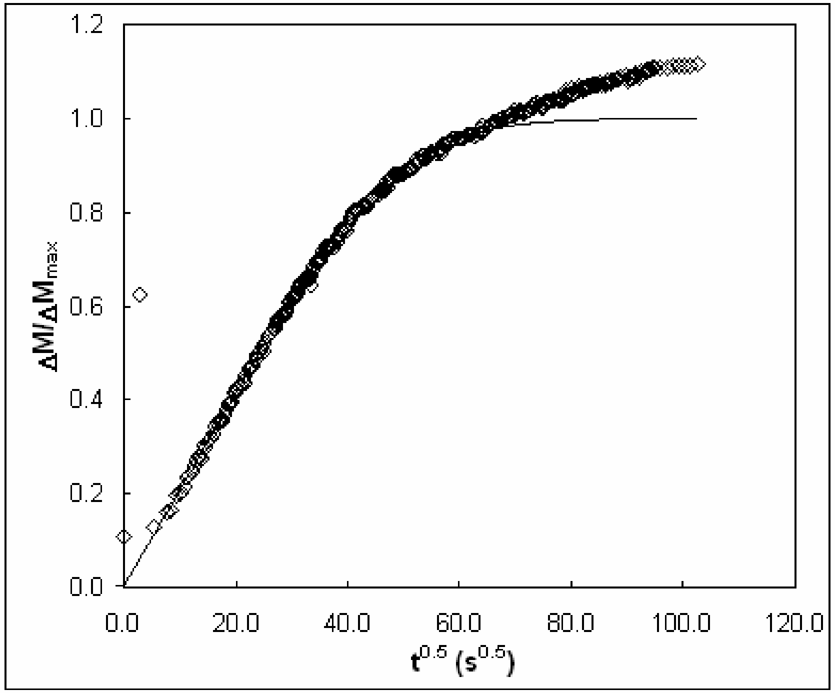
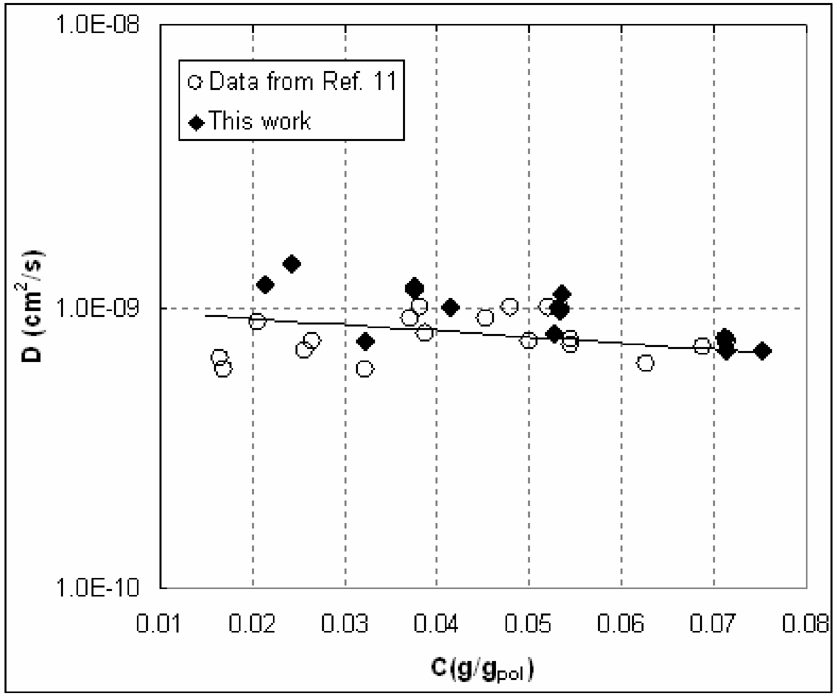
Independent measurements





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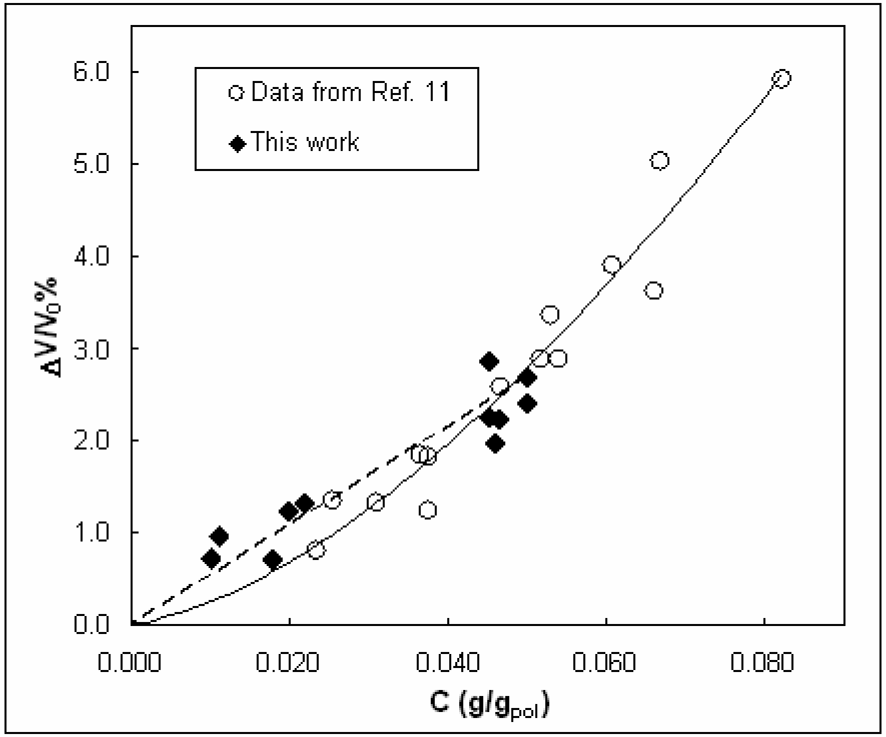
Solubility Isotherms in Glassy Polymers observed behaviors

Swelling condition

$$\varepsilon_i^c = \beta(c)c$$



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How it can be described - mechanics

Elastic constitutive equation

$$\varepsilon_x - \varepsilon_x^c = \frac{1}{E}\left[\sigma_x - \nu\left(\sigma_y + \sigma_z\right)\right]$$

$$\varepsilon_y - \varepsilon_y^c = \frac{1}{E}\left[\sigma_y - \nu\left(\sigma_x + \sigma_z\right)\right]$$

$$\varepsilon_z - \varepsilon_z^c = \frac{1}{E}\left[\sigma_z - \nu\left(\sigma_x + \sigma_{zy}\right)\right]$$

Internal consistency (laminate condition)

$$\begin{Bmatrix} \varepsilon_x \\ \varepsilon_y \end{Bmatrix} = \begin{Bmatrix} \varepsilon_x^0 \\ \varepsilon_y^0 \end{Bmatrix} + z \cdot \begin{Bmatrix} k_x \\ k_y \end{Bmatrix}$$

Mechanical equilibrium with external forces and external moments

$$\sigma_z = 0$$

$$\mathbf{N} = \mathbf{0}$$

$$\mathbf{M} = \mathbf{0}$$

Cantilever deflection:

$$\delta = \frac{1}{2} \cdot k_x \cdot L^2$$

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Data: from independent source

Acetonitrile in PC over Al cantilevers

Film thickness		**0.0155 mm**
Young Modulus	- polymer	2400 MPa
	- substrate	64000 Mpa
Poisson Ratio	- polymer	0.47
	- substrate	0.34
Diffusion kinetic		Fickian diffusion $D = 1.9 \cdot 10^{-9}\, e^{-28c}$ (3)
Linear swelling		$\beta(C) = 0.175 \cdot c$ (3)
(3) This work, c in g/g_{pol} , D in cm^2/s		

Substrate: aluminum cantilever (5 x 1 x 0.275 mm)

Cast film from a solution of PC in CH_2Cl_2

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Layers model: parameters sensitivity

Once we know

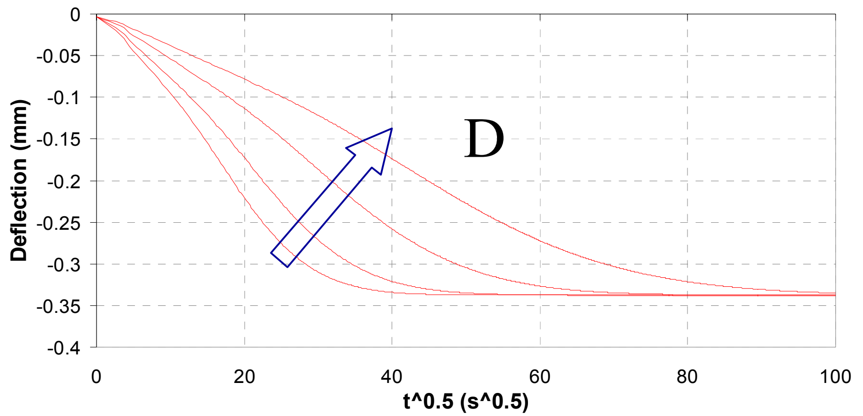
i) the mechanical properties (Young modulus and Poisson ratio),

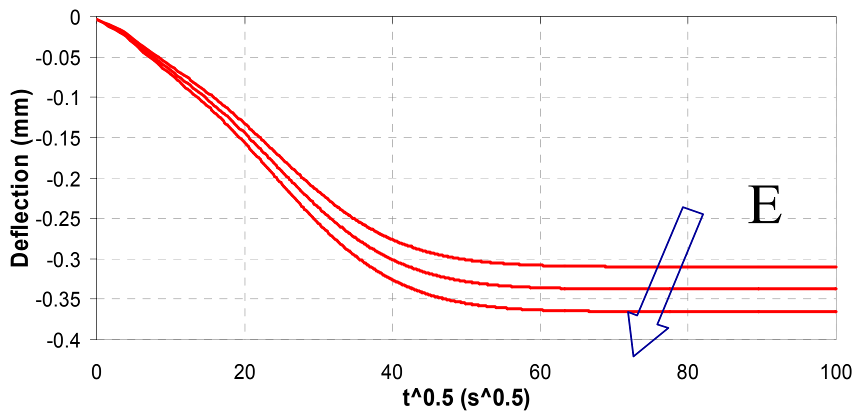
ii) the diffusion coefficient (D),

iii) the concentration profile and the dilation-concentration law

we can calculate:

- **deflection**
- the **stress profile** inside the polymer film.





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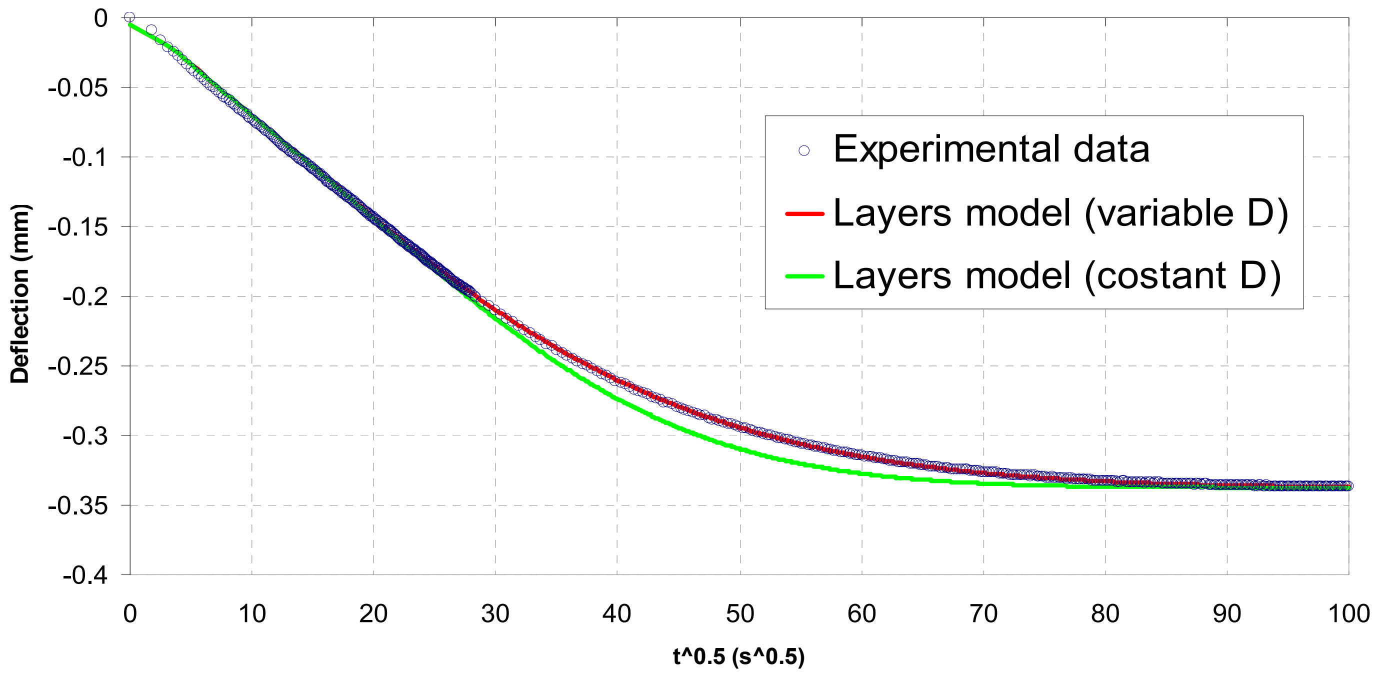
Layers model: variable *D*



$$D = 0.9e^{-9}\,\frac{cm^2}{s}$$

$$D = 1.9e^{-9} \cdot e^{(-C \cdot 28)}$$

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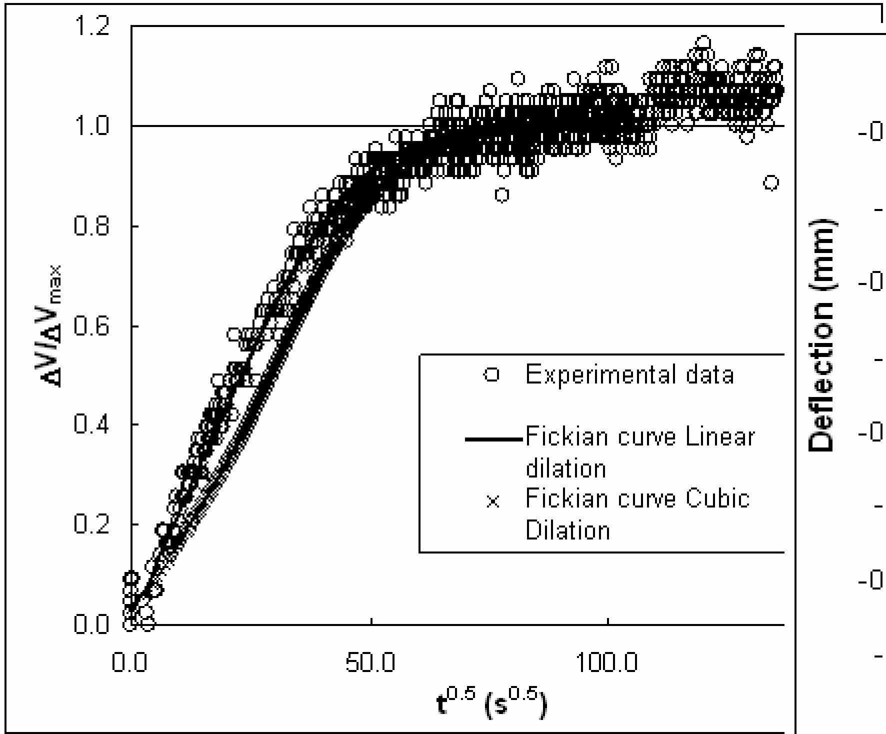
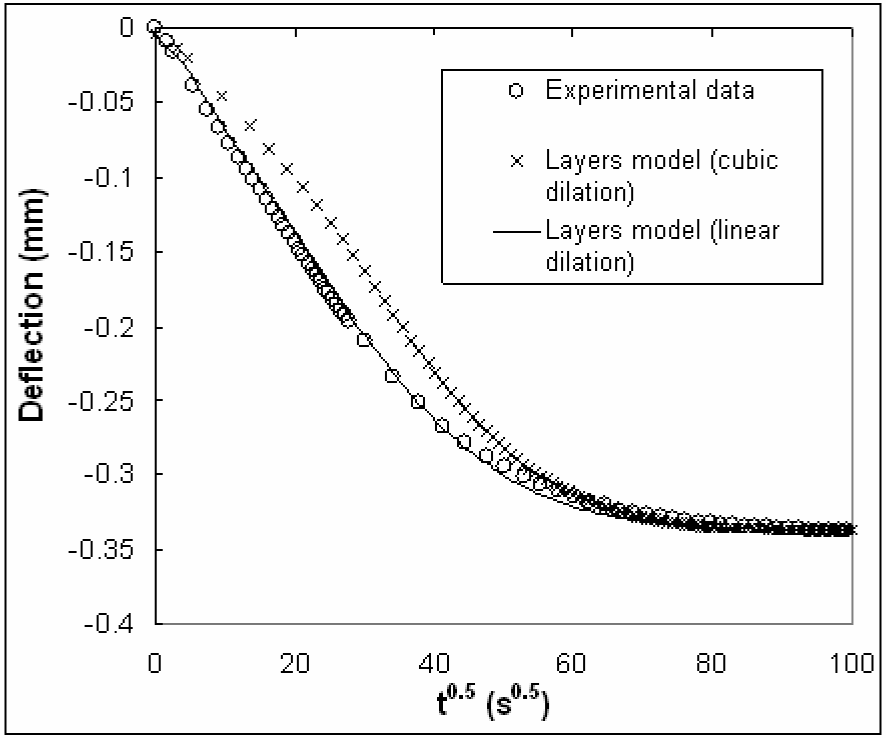
Model predictions vs exp. data



Kinetics of polymer dilation for the system acetonitrile–PC at 40°C experimental data and comparisons with different swelling models



Kinetics of deflection of an aluminum cantilever for an integral sorption run of acetonitrile in PC for an activity jump from 0 to 0.3 at 40°C, sample thickness 16 mm.

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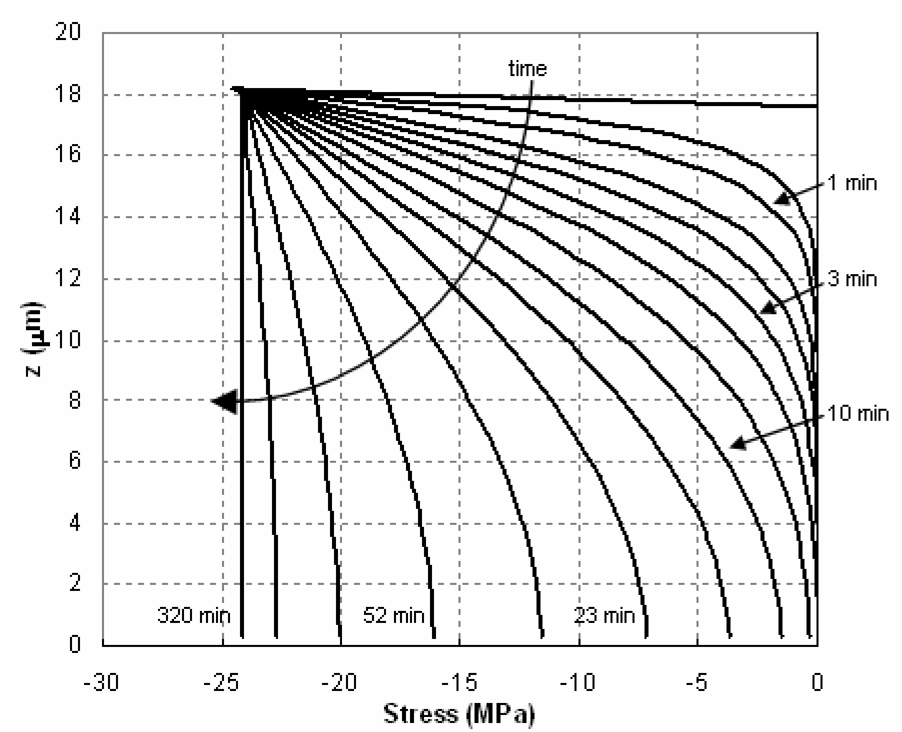
Evolution of stress profiles during sorption



Time evolution of the stress profile inside a PC film of d=18 mm, during an integral sorption run of acetonitrile up to an activity of 0.20 at 40°C.

The stress is:

- compressive
- ≅ 20 ÷ 40 MPa

Yield ≅ 62 MPa

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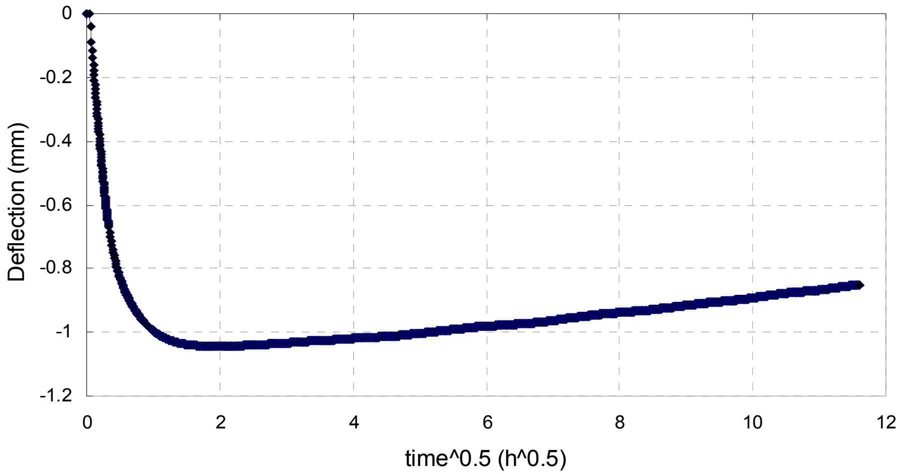
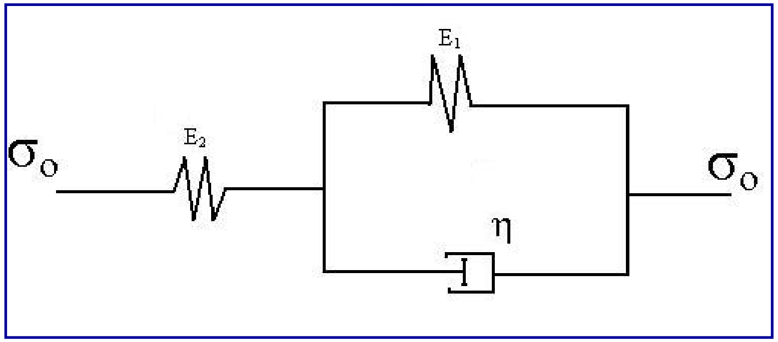
Deflection relaxation dynamics

Long time experiments reveal a decrease of deflection after a maximum is reached



The phenomena is likely related to a stress relaxation due to the viscoelastic behavior of the polymer.

The constitutive equation of viscoelastic materials is being implemented in the mechanical problem



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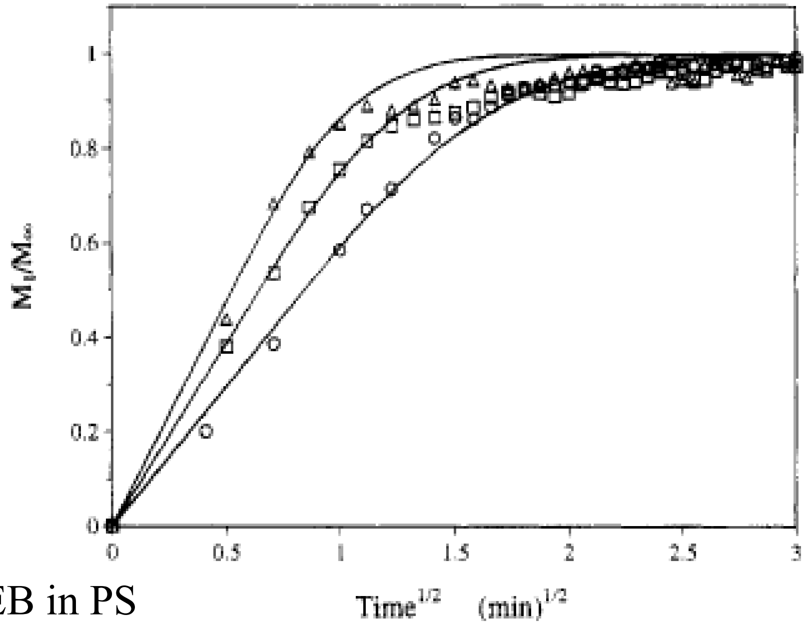
Different behaviors observed



EB in PS

Plot of *M,/M, vs t for* ***(ω1*** **=0.1181), circles,** ***(ω1 = 0.1308 squares), and (ω1 = 0.1425 triangles);*** all three uptake curves show Fickian characteristics (Billovitis et al Macromol 1994)

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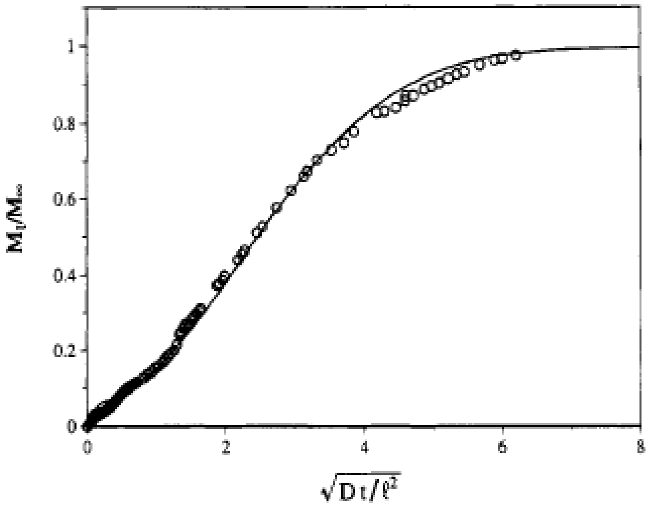
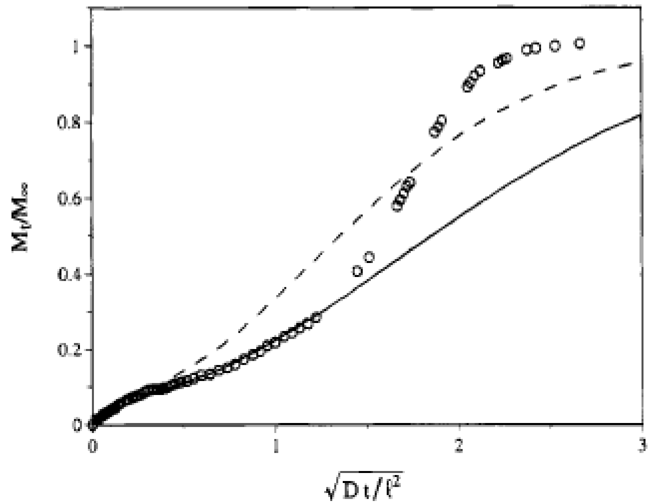
Different behaviors observed





EB in PS
Plot of *M,/M, vs t for* (*ω1* = 0.0276), Fickian characteristics (Billovitis et al Macromol 1994)

ω1 **=** 0.0600 delta P (torr): 4.0-4.9
glass ; two-stage

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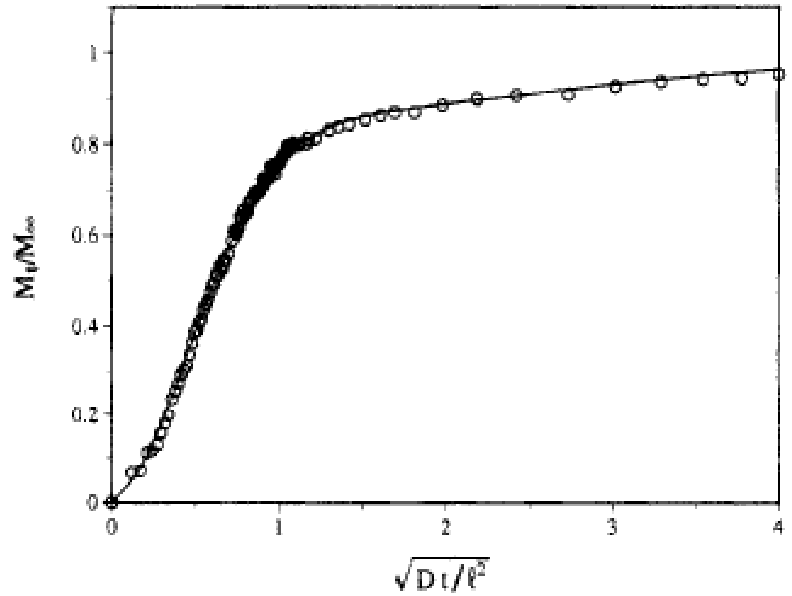
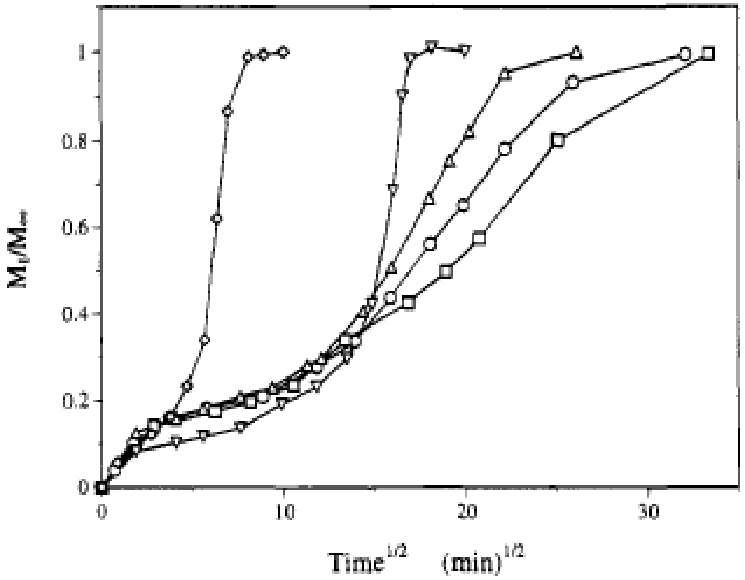
Different behaviors observed





Plot of *Mt/M- vs (t*) for* ***ω1*** =0.1068, P from 7.0- to 7.1 torr *showing the* data and the predictions for two Maxwell elements
After Billovitis et al 1994

Differential sorption data33 for polystyrene/ benzene at 25 “C where the initial pressure is at **47.5 Torr** and the final pressures are
53 (□), **55** (O), **56** (Δ), **59** (V), and **62** Torr (◊).

Effect of activity jump

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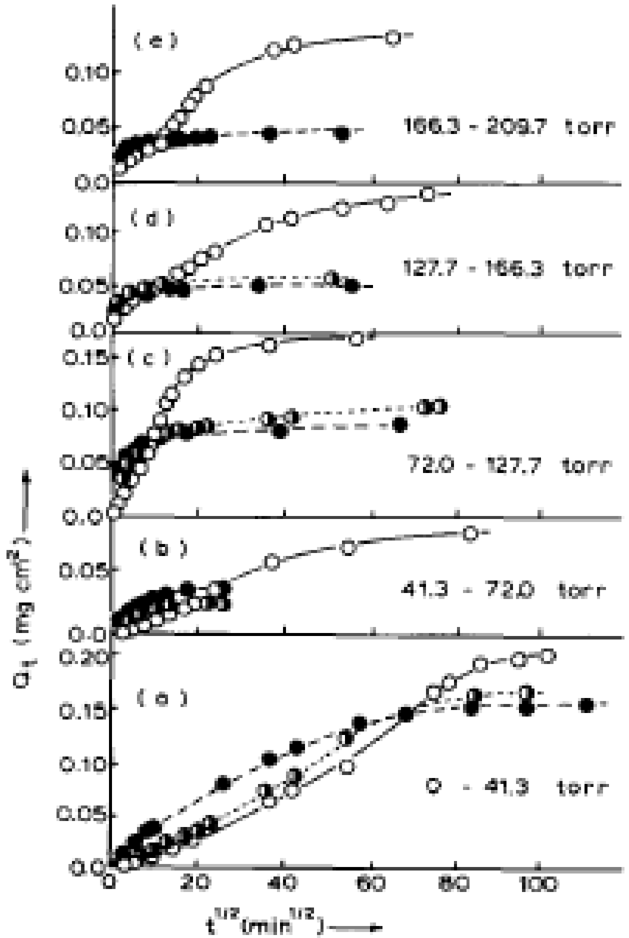
Different behaviors observed



Series of successive sorption kinetic runs on membrane M-59. Absorption: ○*;* desorption: ●*; resorption:* @. An absorption-desorption-resorption cycle was performed at each step. After Sanopoulou and Petropoulos, J. Plym. Sci. B 1995

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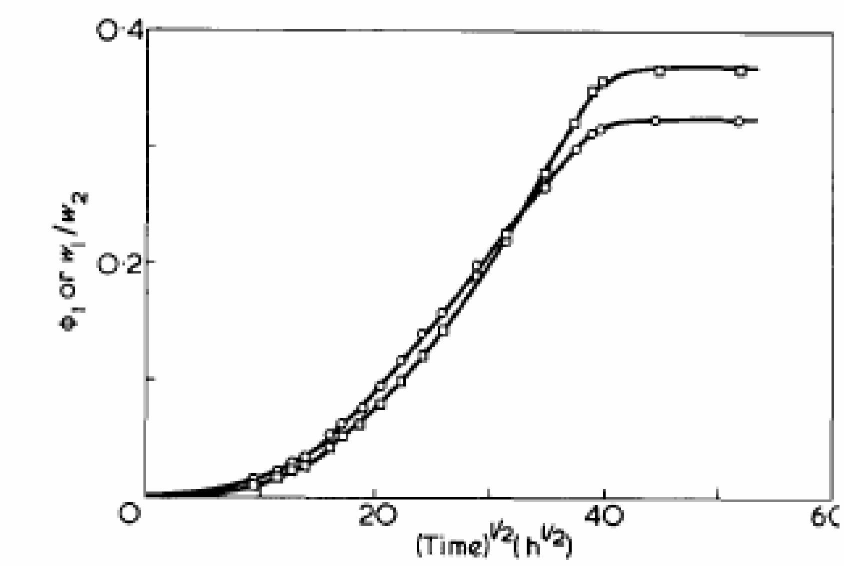
Different behaviors observed



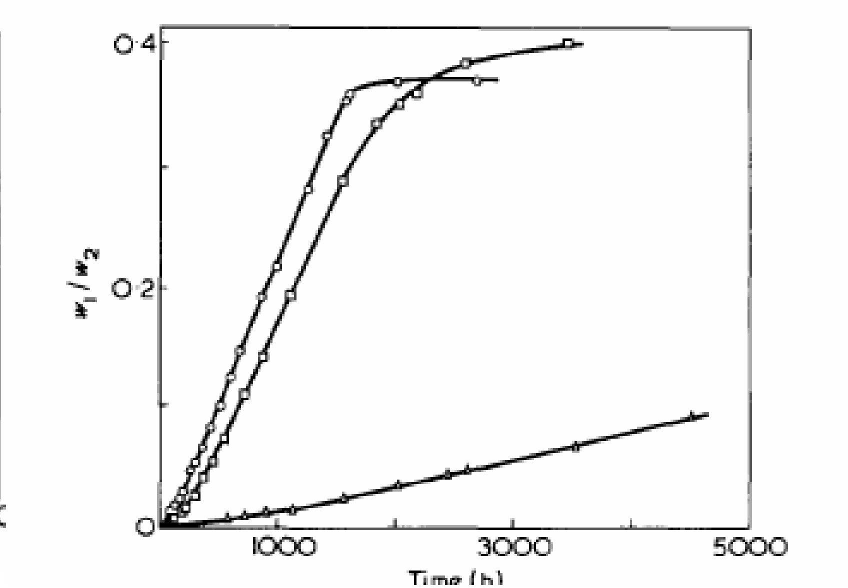


Figure 1 Anomalous Fickian kinetics of n-propyl alcohol absorption in poly(methyl methacrylate) sheets. [Volume fraction or weight ratio, w_1/w_2, as a function of $t^{1/2}$ (T = 318 K)]. Volume fraction ϕ_1, ○; weight ratio w_1/w_2, □

Figure 2 Case II kinetics of n-propyl, i-propyl and n-butyl alcohol absorption in poly(methyl methacrylate) sheets. [Weight of alcohol per original dry sheet weight, w_1/w_2, *versus* t (T = 318 K)] ○, n-propyl alcohol; □, isopropyl alcohol; △, n-butyl alcohol

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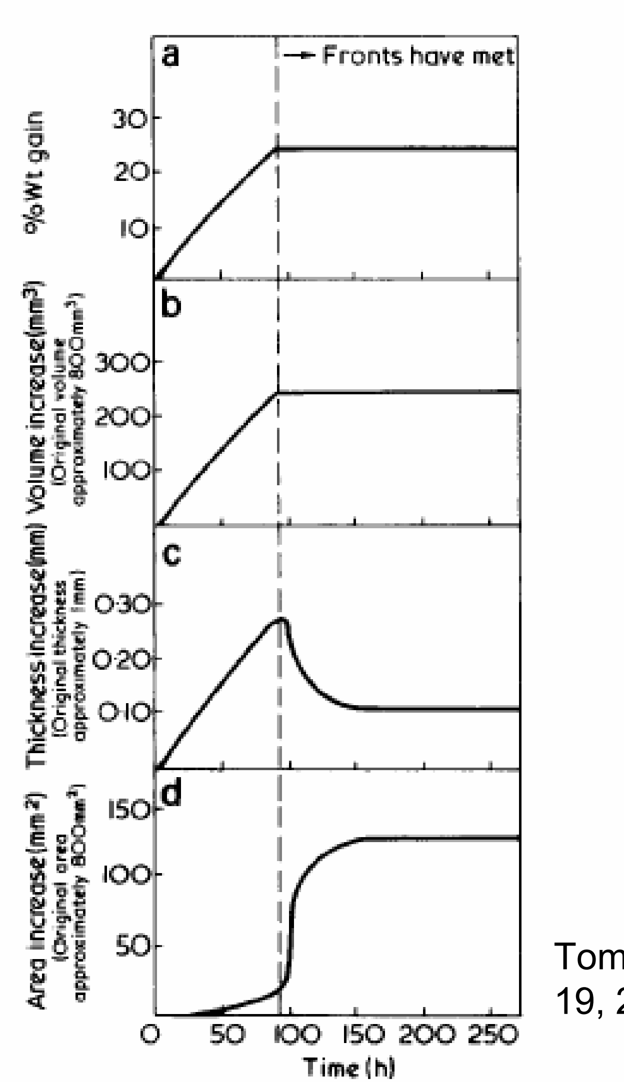
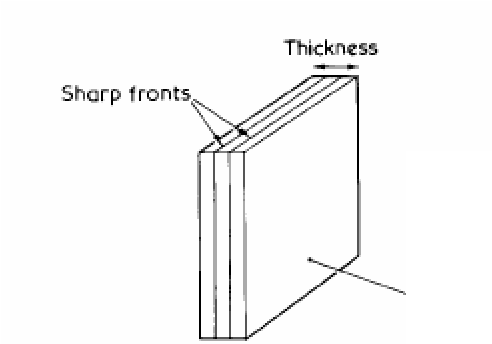
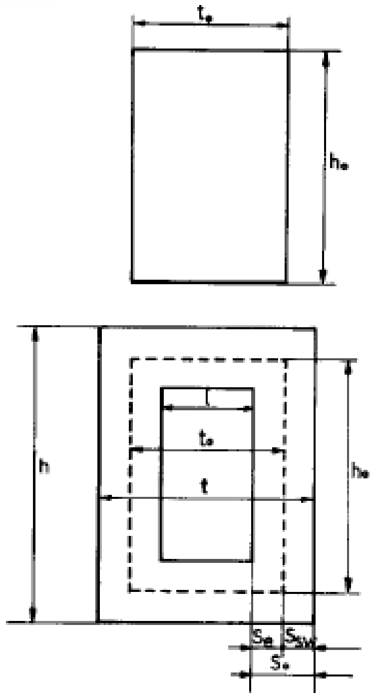
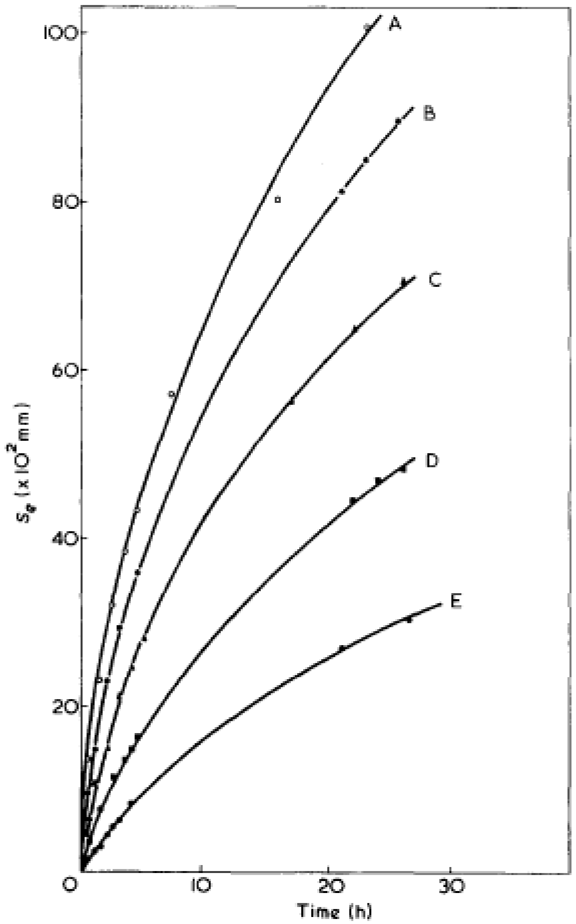


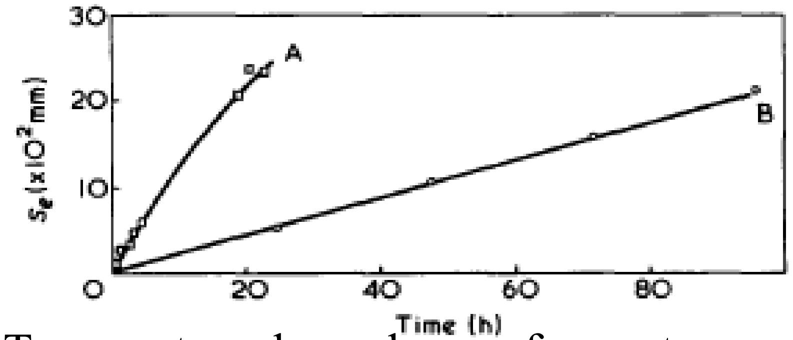




Tomas & Windle Polymer 1978, 19, 255

Effect of temperature





Temperature dependence of n-pentane penetration of polystyrene sheets. A, T = 30°C; B, T = 25°C

Temperature dependence of n-hexane penetration of polystyrene sheets. A, T = 55°C; B, T = 50°C; C, T = 45°C; D, T =40 °C; E, T= 35 °C, *after Tidone et al., Polymer 1977*

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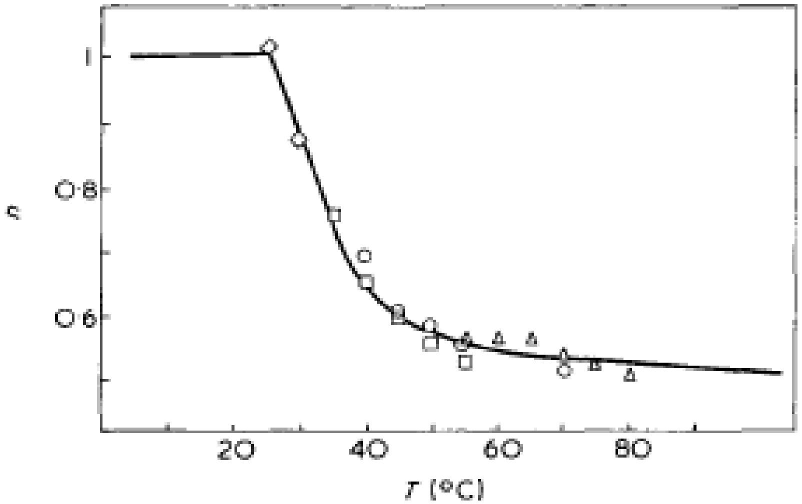
Effect of temperature



$$S_e = at^n$$

Relationship between exponent, *n,* in equation and temperature, describing penetration of the n-alkane series from pentane through octane in polystyrene sheets. (after Tidone et al. Polymer 1977)

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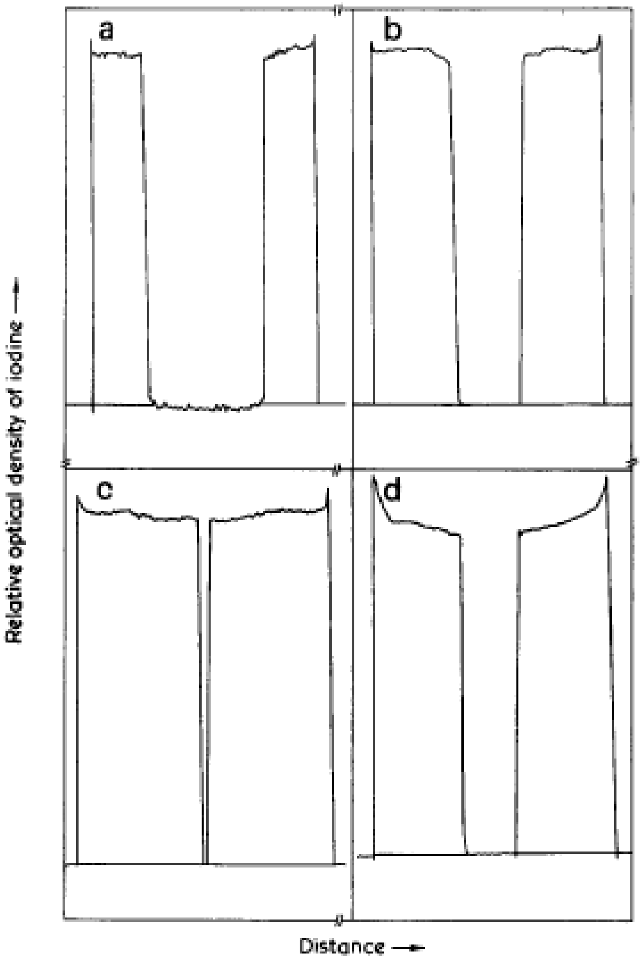
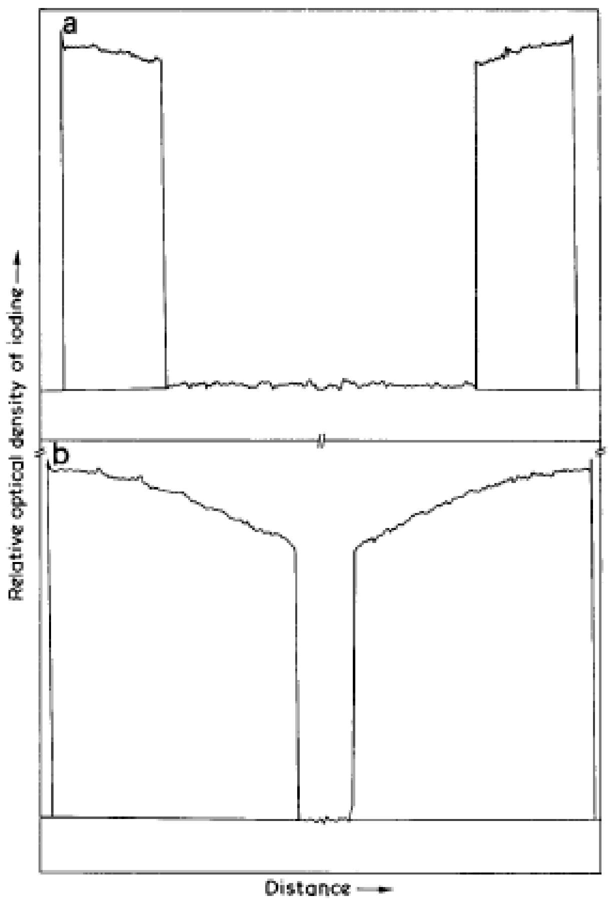
Different behaviors observed





Me-OH in PMMA

Tomas & Windle Polymer 1980

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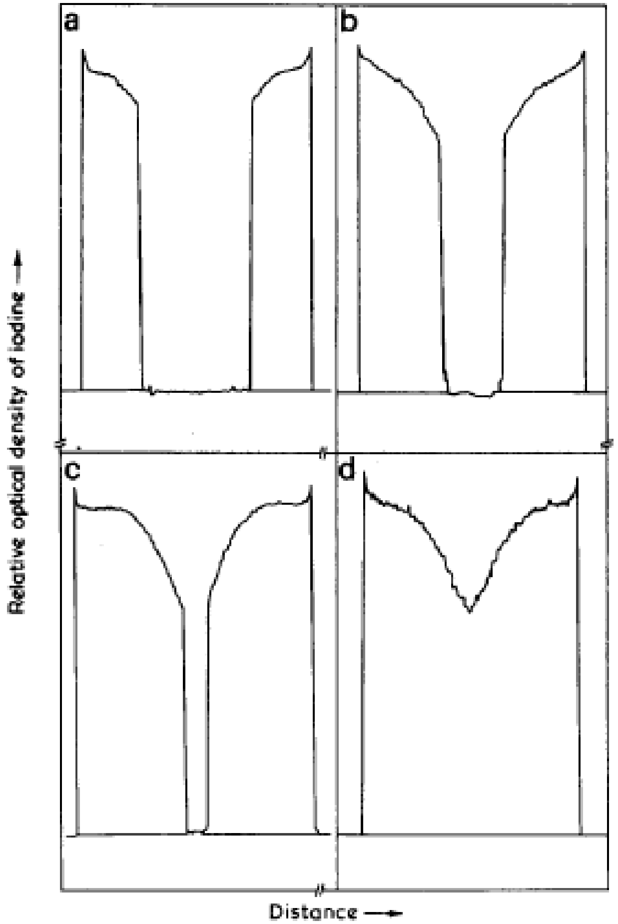
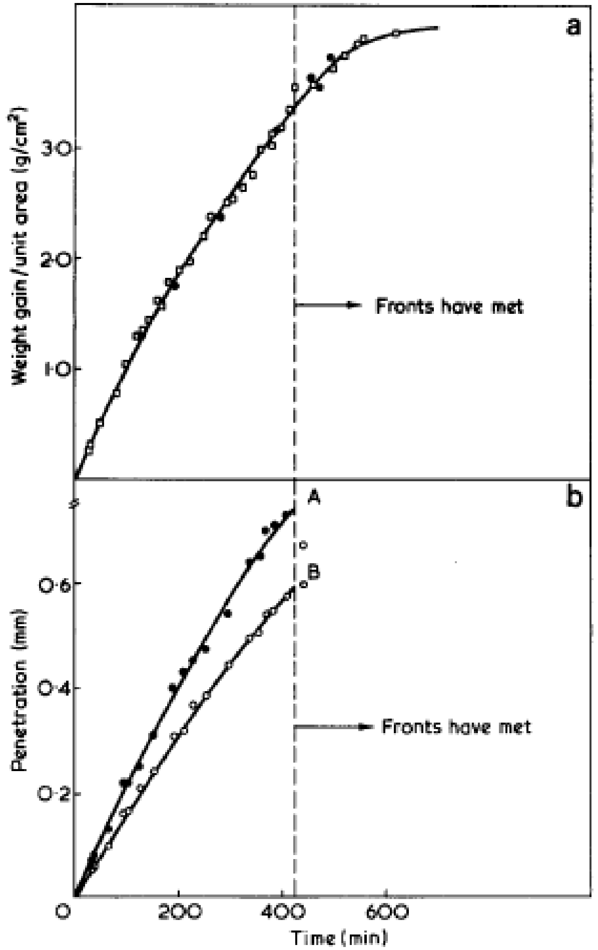
Different behaviors observed





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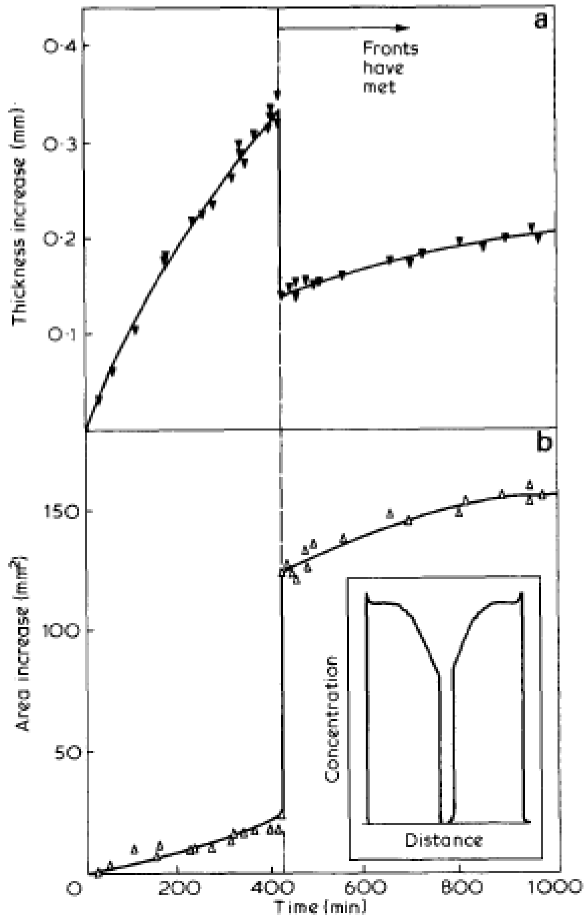

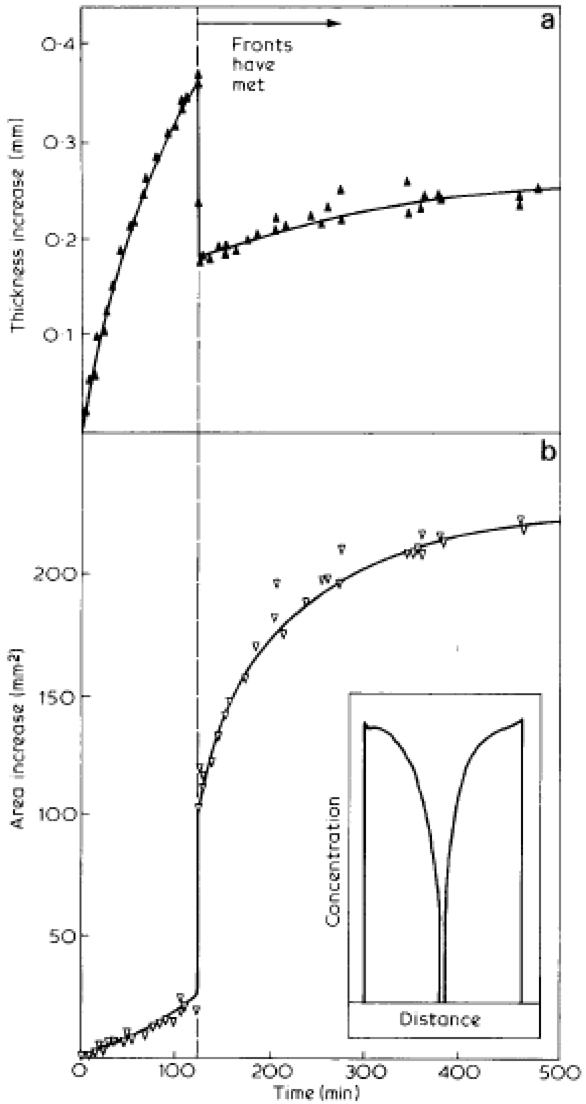

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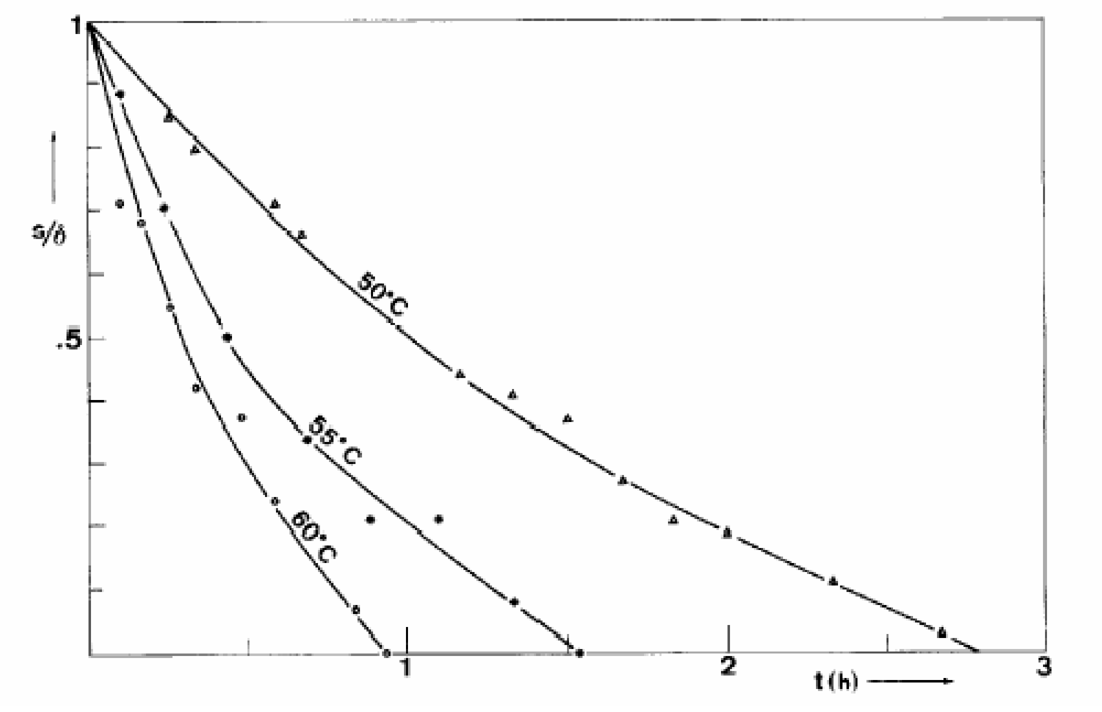
Different behaviors observed



Fractional residual core thickness for methanol sorption in PUMA sheets; 1 mm nominal thickness; as-received samples.
After Masoni Sarti J. Membr Sci 1983

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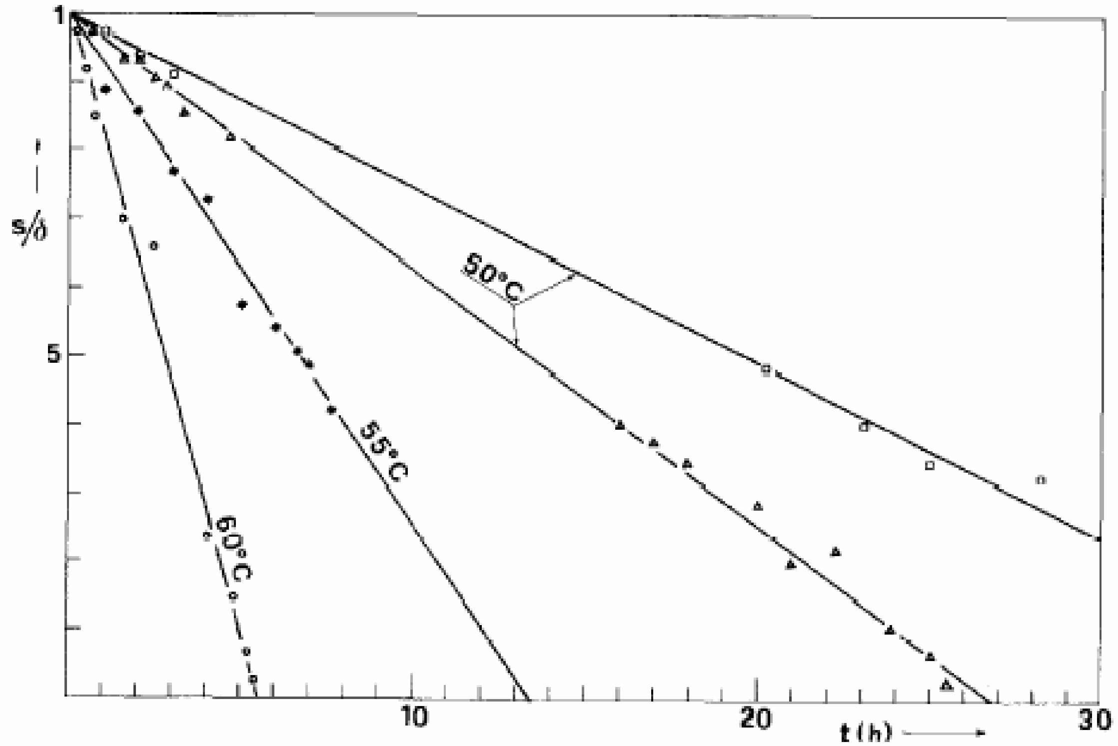
Different behaviors observed



Fractional residual core thickness for ethanol sorption in PMMA sheets; 1 mm nominal thickness; as-received samples: 50, 55, 60 °C; and samples annealed 24 hr at lOO °C, penetrated at 50°C.

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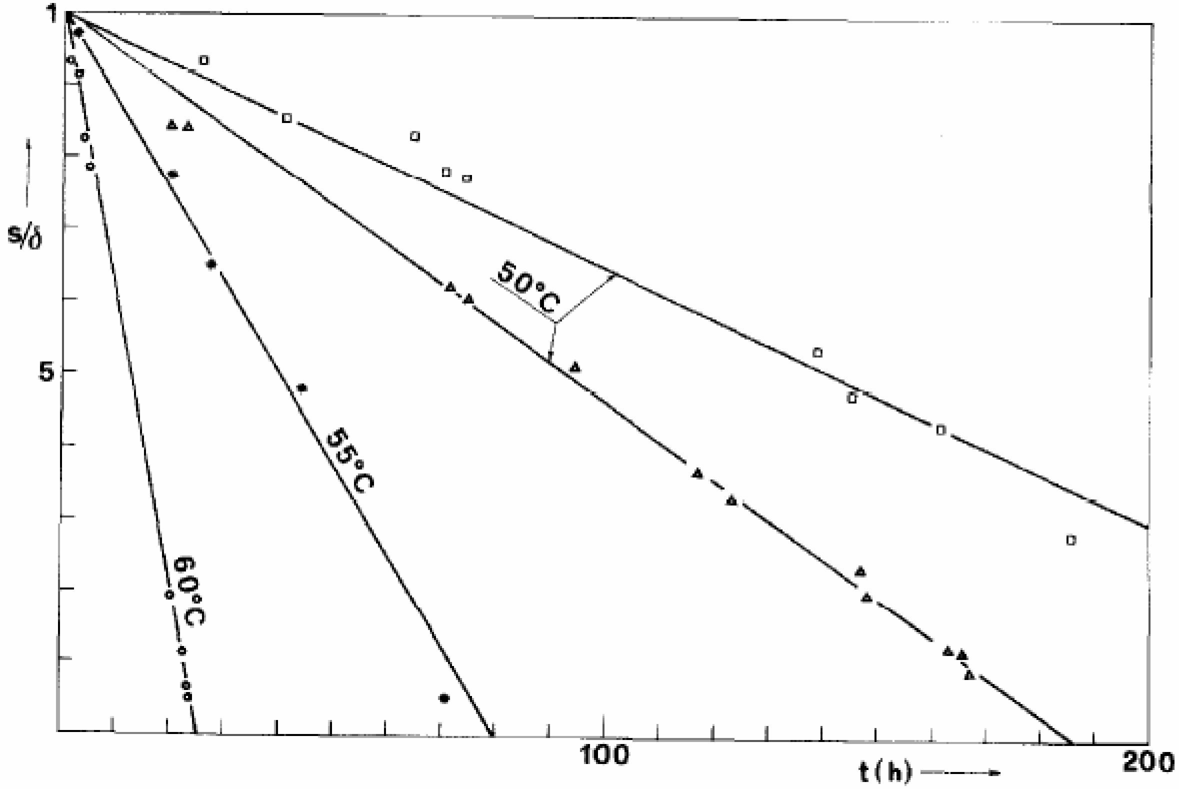
Different behaviors observed



Fractional residual core thickness for n-propanol sorption in Fractional residual core thickness for ethanol sorption in PMMA sheets; 1 mm nominal thickness; as-received samples: 50, 55, 60 °C; and samples annealed 24 hr at lOO °C, penetrated at 50°C.

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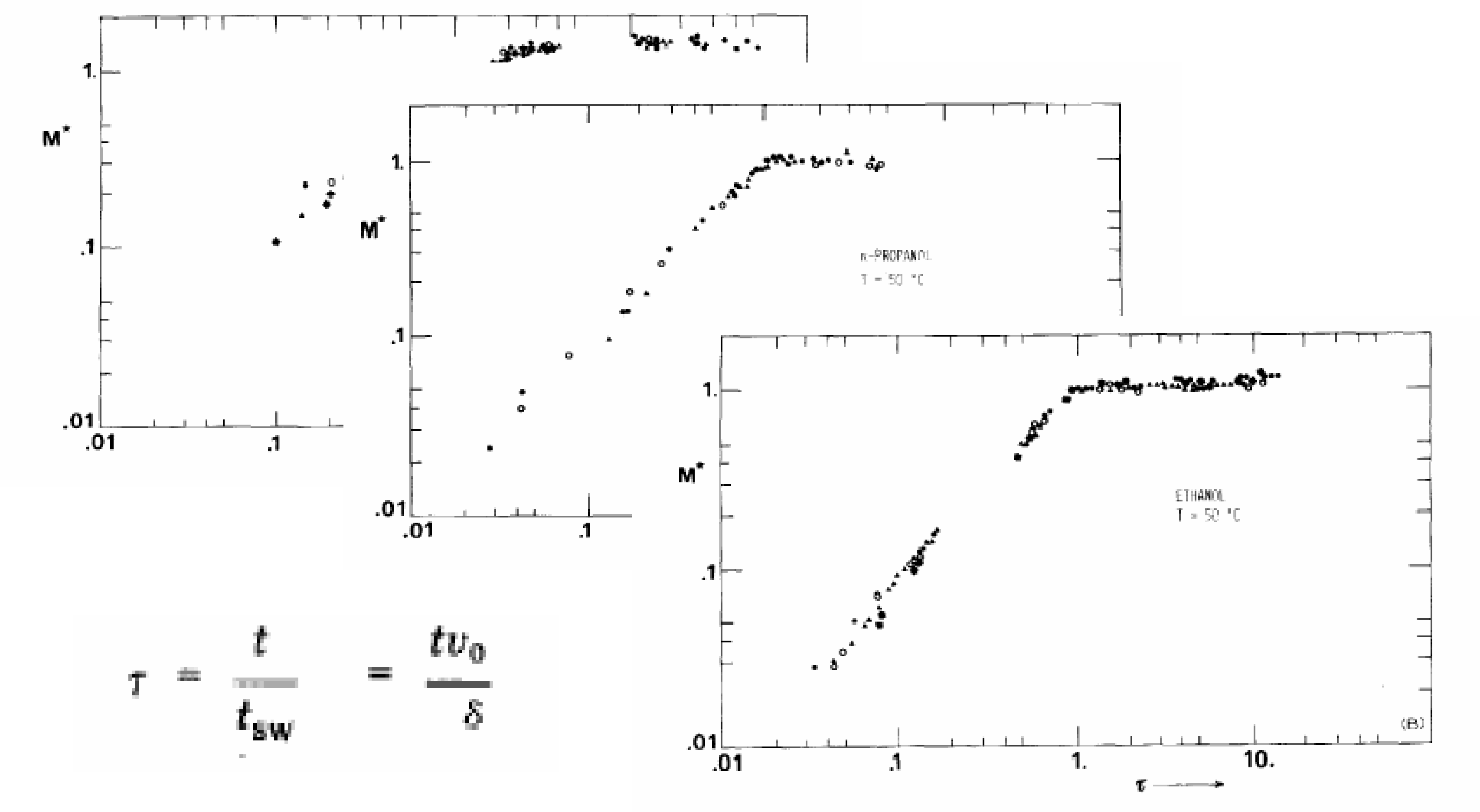
Different behaviors observed



$$\tau = \frac{t}{t_{sw}} = \frac{t v_0}{\delta}$$

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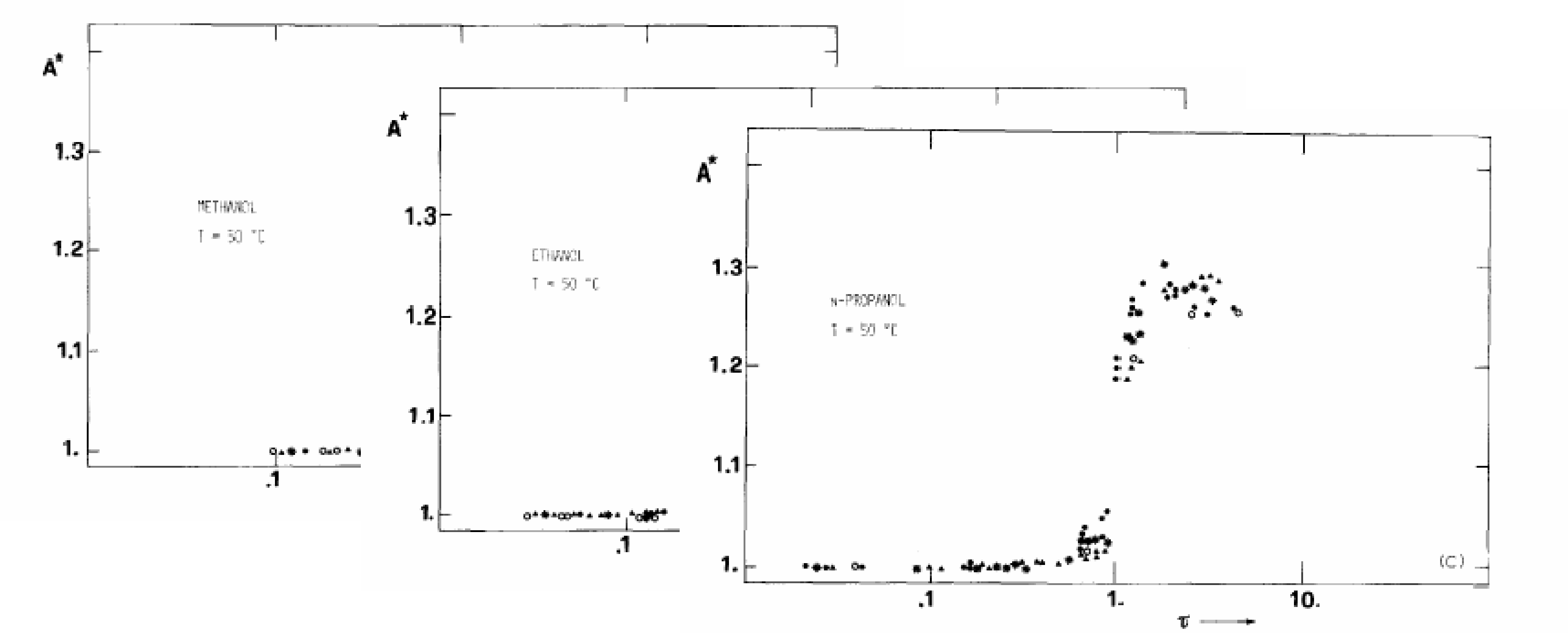
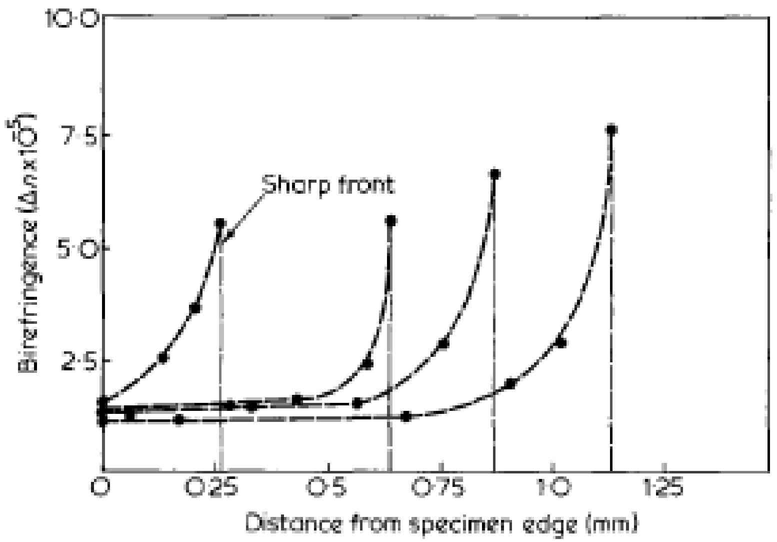
Different behaviors observed



Penetrants can generate swelling and stresses



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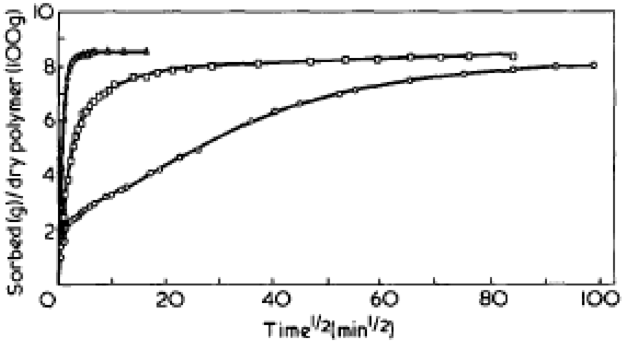
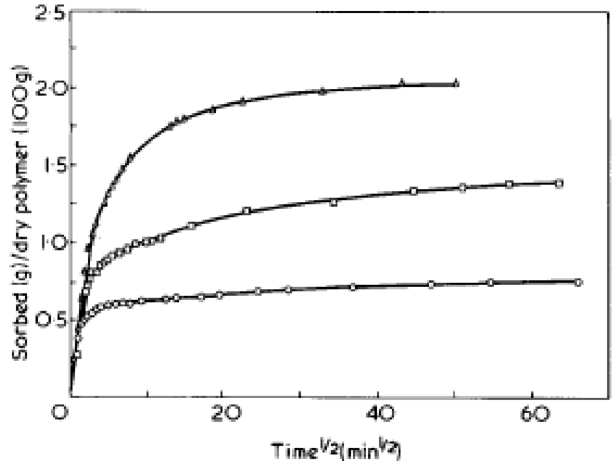
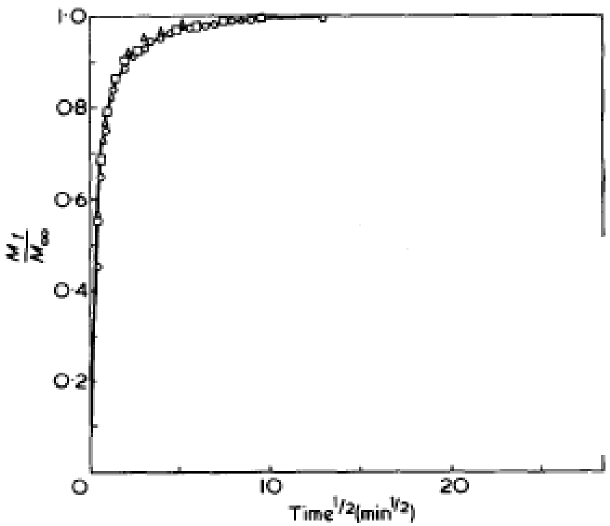
Effects of prehistory



Comparison of n-hexane sorption in preswollen (△), 'as-received' (□), and annealed samples (○) at p/p^0 = 0.75 and 30°C. Sorption-cycle 1, polystyrene, d = 0.534 μm



Comparison of n-hexane sorption in preswollen (△), 'as-received' (□), and annealed samples (○) at p/p^0 = 0.10 and 30°C. Sorption-cycle 1, polystyrene, d = 0.534 μm



Comparison of n-hexane desorption from preswollen (△), 'as-received' (□), and annealed samples (○) previously equilibrated at p/p^0 = 0.75 and 30°C. Desorption-cycle 1, polystyrene, d = 0.534 μm

After Hopfenberg et al Polymer 1980

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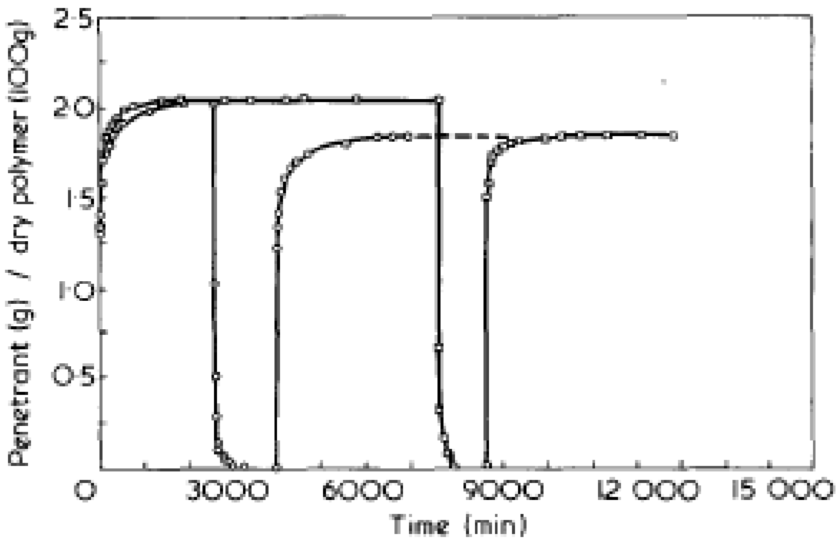
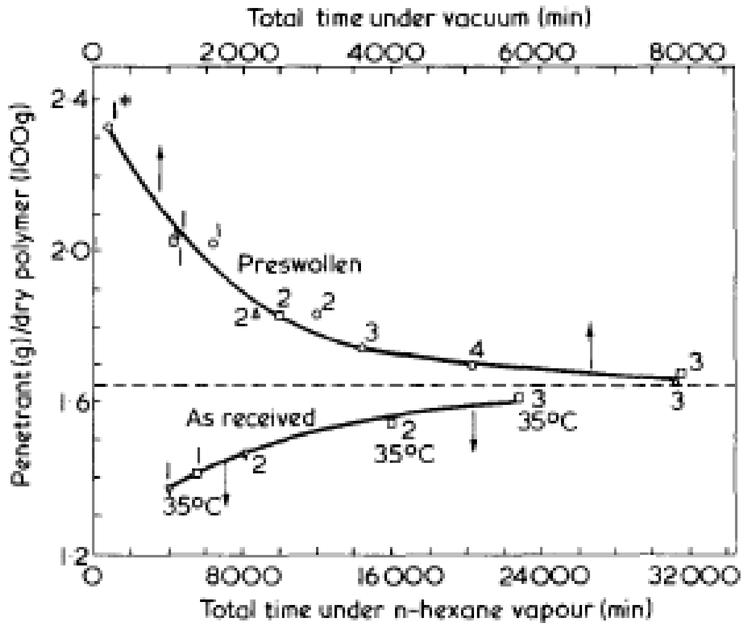
Effects of prehistory



Comparison of n-hexane resorption in preswollen samples, contacted with n-hexane for various time intervals during the preceding sorption cycle. Resorption was carried out at p/p^0 = 0.10 and 30°C. ○, sample 1; □, sample 2. Sorption-cycling, polystyrene preswollen d = 0.534 μm



Effect of cycling on the apparent equilibrium sorption of n-hexane at p/p^0 = 0.75 and 30°C in preswollen and 'as-received' samples. Sorption-equilibria, polystyrene, d = 0.534 μm. * Cycle number

Enscore et al Polymer 1980

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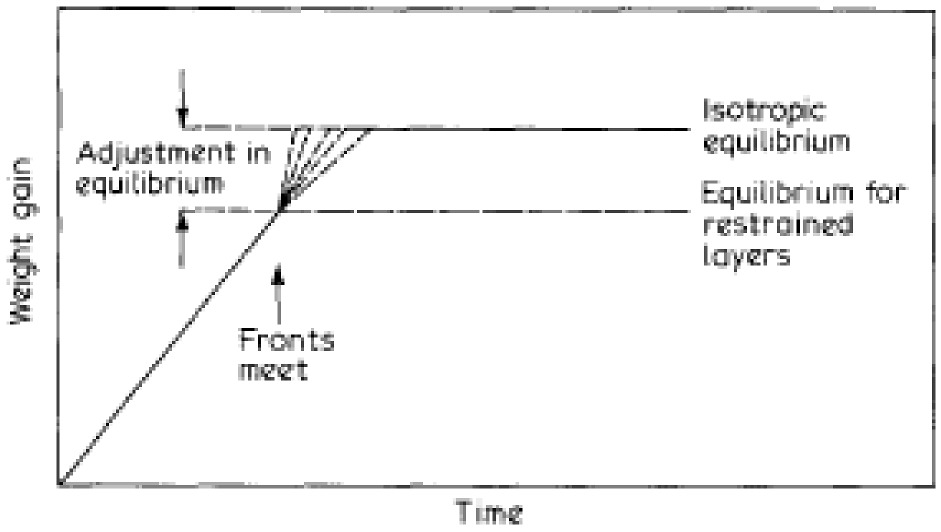
accelerations

Effects of film thickness !:

Higher δ: no accel
Lower δ: larger acceleration



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Modeling

Boundary conditions (solubility and its relaxation)
Localized swelling
Flux dependence on stress and history
- lumped models
- General models

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Solubility (BC): from NET-GP

NET GP *General Results*

- ***The Helmholtz and Gibbs free energies under asymptotic pseudo-equilibrium conditions are uniquely related to the equilibrium Helmholtz free energy at the same T, V and composition (T, ρ_1, ρ_2) as :***

$$\hat{A} \equiv \hat{A}_{NEq}\left(T, p, \rho_1, \rho_2\right) = \hat{A}_{Eq}\left(T, \rho_1, \rho_2\right)$$

- ***polymer density ρ_2 is the non equilibrium value measured in the glass***
- ***Pressure is not the equilibrium value at the given T, V and composition***

$$\mu_1^{(GP)} = \left(\frac{\partial m\hat{G}}{\partial m_1}\right)_{T,p,m_2,\rho_2} \equiv \left(\frac{\partial \rho \hat{A}_{Eq}}{\partial \rho_1}\right)_{T,\rho_2}$$

Doghieri & Sarti JMS 1996, Chem. Eng. Sci 1998

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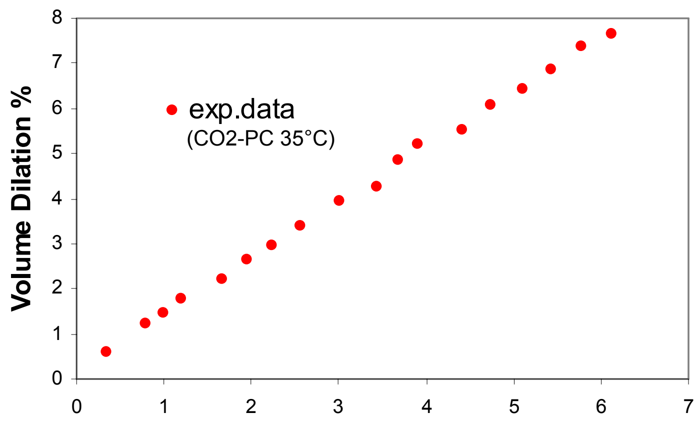
Solubility Isotherm from Dilation Data ……

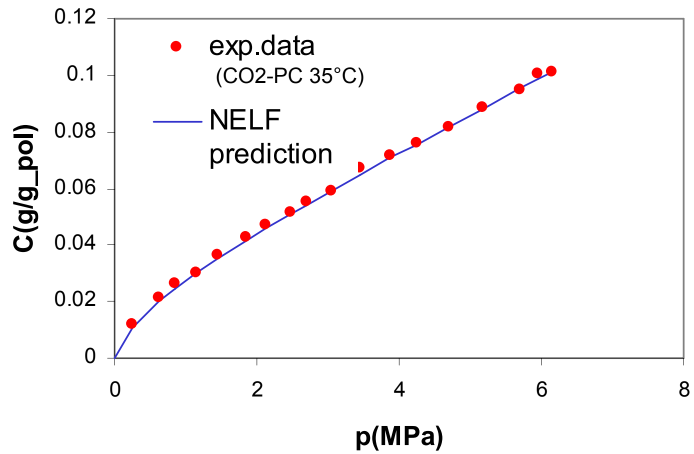
Assume lattice fluid model (SL):

- *The **SL** Parameters (**P*,T*,ρ***) for both penetrant and polymer*
- *The density of the polymer during the Sorption (e.g Dilation data)*

The NELF gives the Sorption Isotherm



(data from Fleming and Koros, 1990)



(data from Fleming and Koros, 1990)

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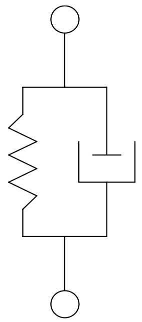
Effect of relaxation processes on gas/vapor solubility in glassy polymers: volume swelling model (VS)

Swelling kinetics of polymeric elements induced by sorption processes

Volume dilation modeled through simple Kelvin-Voigt model for bulk rheology:

$$\frac{1}{\rho_{pol}}\frac{\partial \rho_{pol}}{\partial t} = \frac{p^{EXT} - p^{EQ}\left(\Omega, \rho_{pol}\right)}{\eta}$$



solubility data in sorption processes **driven by volume relaxation** phenomena:

n-hexane in PS @ 40°C

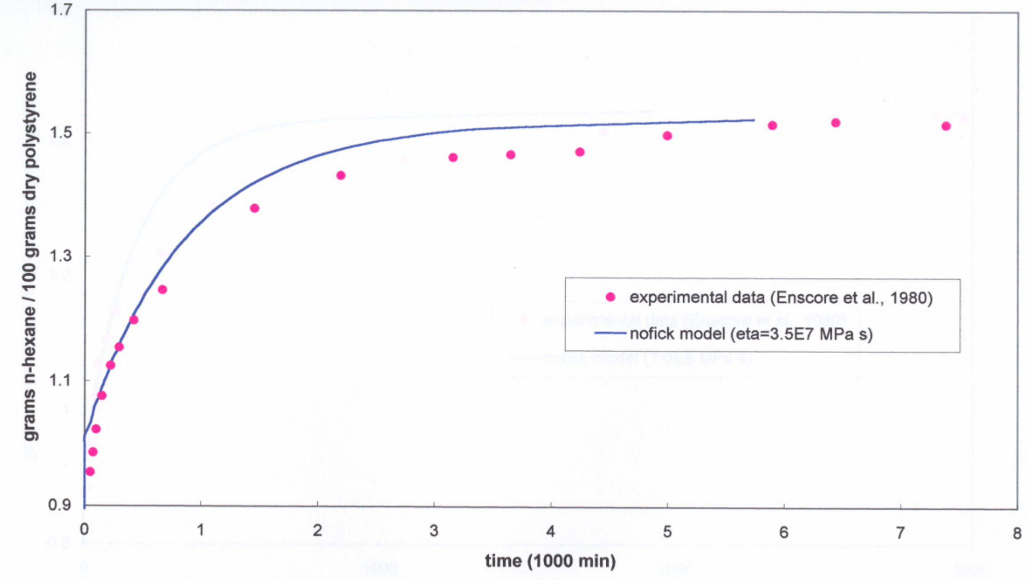
sorption process in microspheres

(d ≈ 0.5 μm)

Activity jump 0 → 0.1

Exp. data from Enscore et al., Polymer 1980

Fitting parameter = bulk viscosity



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Mass transport model for gas sorption in glassy polymeric systems with both diffusion and volume relaxation

$$\frac{\partial \rho_{sol}}{\partial t} = -\underline{\nabla} \bullet \underline{J}$$

$$\underline{J} = -\mathcal{D}\, \rho_{sol}\, \underline{\nabla} \mu$$

$$\frac{1}{\rho_{pol}} \frac{\partial \rho_{pol}}{\partial t} = \frac{p^{EXT} - p^{EQ}\left(\Omega, \rho_{pol}\right)}{\eta}$$

Example of simulation results for n-hexane sorption in PS films

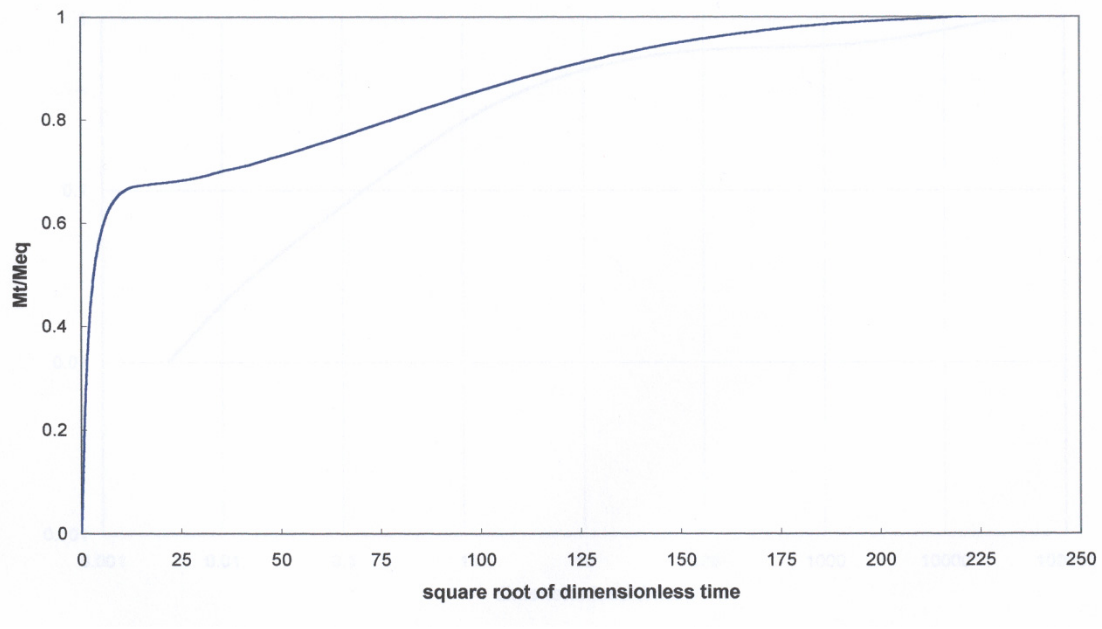
T= 40°C

Film thickness = 1 μm

activity jump 0 → 0.1

Diffusion coefficient from Vrentas and Duda Free Volume Theory

Bulk viscosity from analysis of relaxation data



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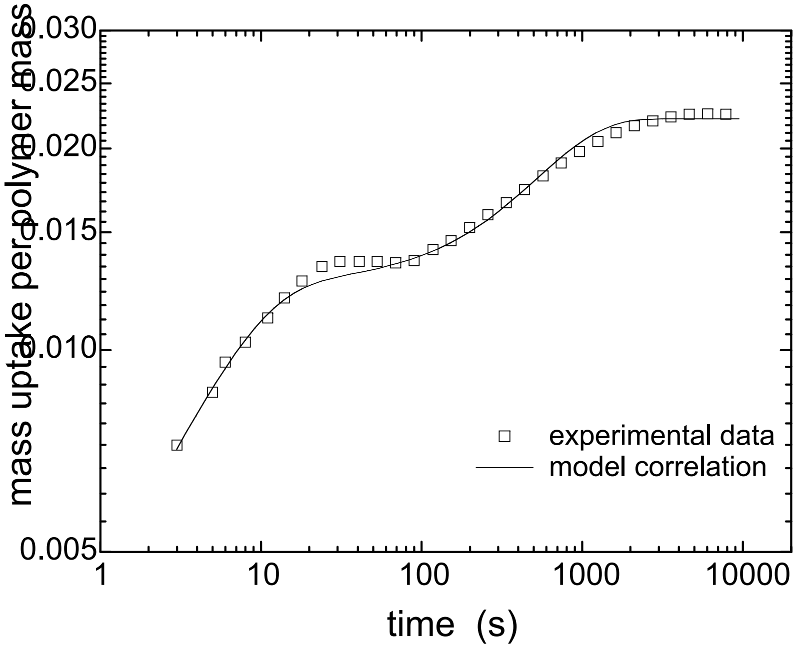
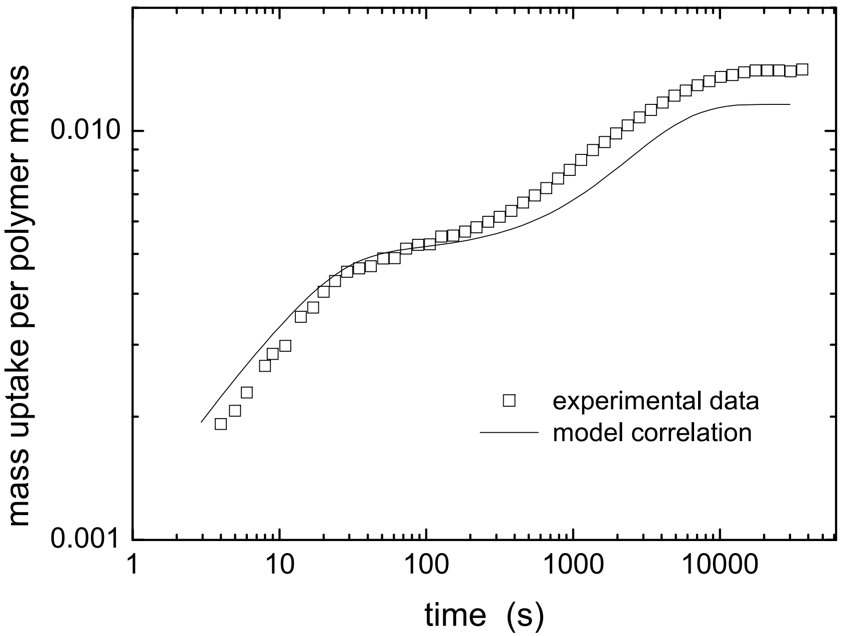


Kinetics of CO_2 sorption in PMMA film for sorption step from 12.4 *bar* to 23.4 *bar*. Comparison of experimental values with model results.



Kinetics of CO_2 sorption in PMMA film for sorption step from 25.4 *bar* to 33.1 *bar*. Comparison of experimental values with model results.

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Rate-Type (RT) lumped models for viscoelatic diffusion

$$\frac{\partial \rho_{sol}}{\partial t} = -\underline{\nabla} \bullet \underline{J}$$

$$\tau \frac{\partial \underline{J}}{\partial t} + \underline{J} + \mathcal{D} \rho_{sol} \underline{\nabla} \mu = 0$$

$$\frac{1}{\rho_{pol}} \frac{\partial \rho_{pol}}{\partial t} = \frac{p^{EXT} - p^{EQ}\left(\Omega, \rho_{pol}\right)}{\eta}$$

Hyperbolic problem accounting for

- a relaxation time τ in the flux
- relaxation phenomena in volume swelling and in relax in BC

Thermodynamic Analysis for the development of shock concentration waves in the system

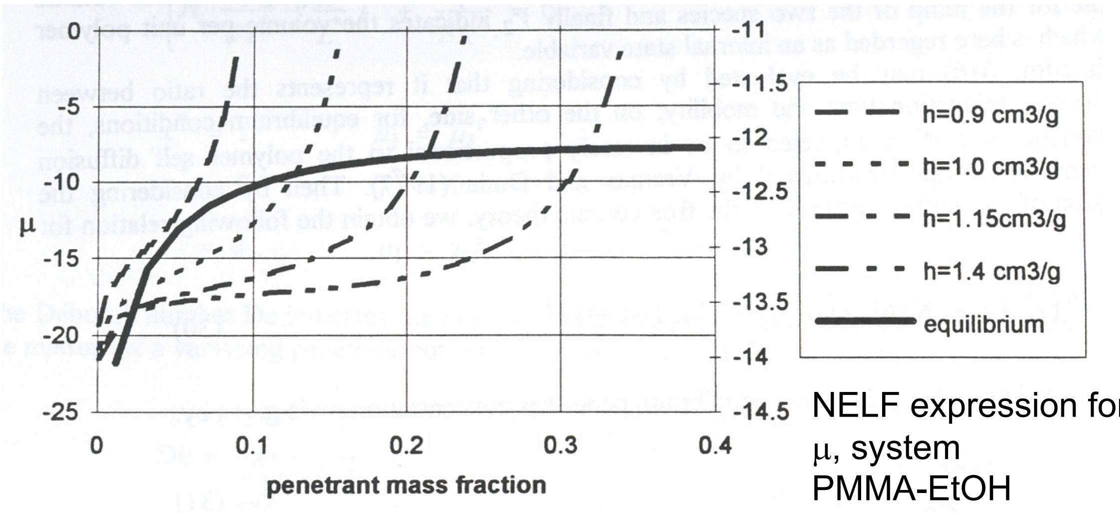
Results from the application

of 2nd law:

Necessary condition for the formation of shock concentration waves is that:

$$\left(\frac{\partial^2 \mu}{\partial \rho_{sol}^{\ 2}}\right)_{\rho_{pol}} > 0$$

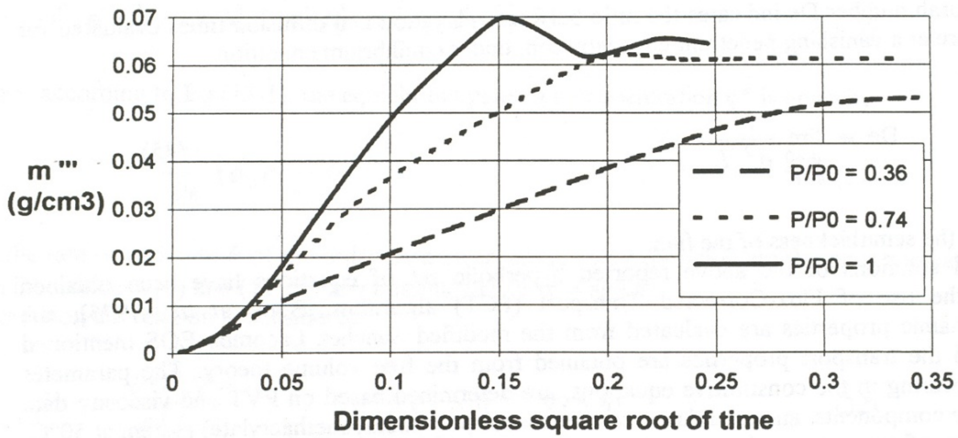
at least in a concentration range

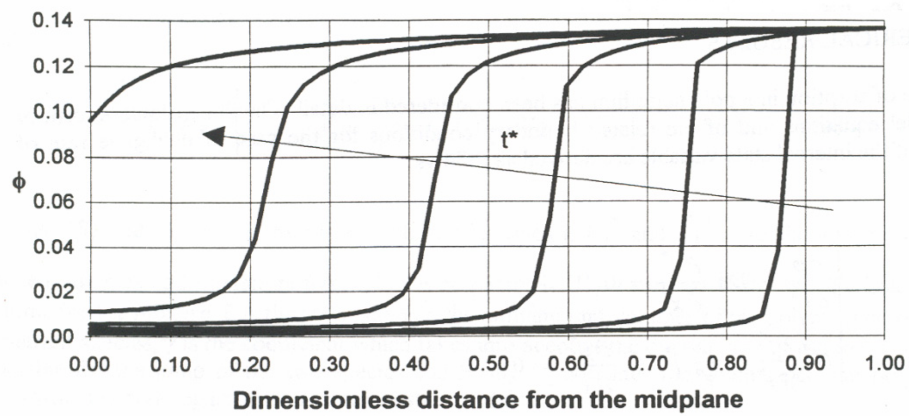


NELF expression for μ, system PMMA-EtOH

Example of simulation results for RT sorption model: case of negligible volume swelling

Sorption kinetics for the case of ethanol-PMMA system at 30°C ρ_{pol} =1.10 g/cm^3 e diffusivity exponentially increasing function of concentration:
Effect of external solute fugacity





Examples of concentration profiles from simulation of sorption process for ethanol in PMMA (De = 30)

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More general models

$$\mathbf{j}_2^1 \equiv \varrho_1(\mathbf{v}_1 - \mathbf{v}_2) = \frac{\varrho_1\varrho_2}{\varrho m_{12}}\left(\frac{1}{\varrho_1}\nabla\cdot\mathbf{T}_1 - \frac{1}{\varrho_2}\nabla\cdot\mathbf{T}_2\right);$$

Mass balance

+

Mechanical problem
with viscoelastic response

e.g. Billovitis, Macromol. 1994

Caruthers & Peppas Chem Eng Sci 1992, 1996

Petropolulos et al Macromol 2002

Doghieri et al. 2004, 2005

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