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Sorption and Swelling in Ultra-Thin Polymer Films

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Summary: Different polymers were investigated with respect to the sorption of solvents and gases. Depending on the chemical nature of the polymers this sorption leads to polymer swelling. The degree of swelling D/D_0 was measured utilizing Small angle X-ray scattering (SAXS) as well as Surface plasmon resonance (SPR). From the change in film thickness after swelling in different solvents Hildebrand parameters of the polymers were determined. By crosslinking of the polymer films the degree of swelling can be controlled. In the case of ultra-thin polyimide films a higher degree of crosslinking led to a decreased selectivity of the transport of gases through the membrane. Reptation of macromolecules was also investigated and the influence of polymer swelling in different solvents has a great influence on the selectivity and diffusion coefficient .

Introduction

Many applications of ultrathin films require a good knowledge of the transport mechanism of polymers in this films. Therefore it is necessary to obtain an appropriate supramolecular structure, where the properties are well known. Transport phenomena through ultra-thin polymer membranes with respect to swelling in different media, the dimension of the molecules transported, reptation effects and application to gas separation have been investigated in relation to the polymer composition and the degree of crosslinking.

Transport through membranes is mainly influenced by the physico-chemical properties of the molecules transported as well as their interactions with the membrane network. The properties of the polymer network of the membrane itself are dependent on parameters like the constitution of the adjacent phases, the membrane dimension, the density of crosslinking and the degree of swelling (see fig.1). Among the parameters discussed, polymer swelling significantly influences the transport within the membrane and is often encountered in technical applications. Therefore our work presented here also focuses on the control of swelling.

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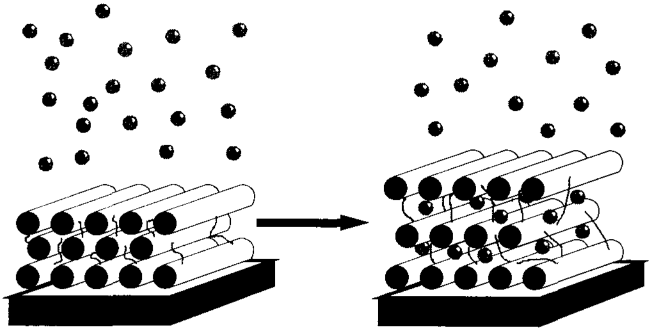

Fig.1: Phenomenon of polymer swelling.

Experiments

Langmuir-Blodgett-Films of variable thickness were formed from cellulose derivatives (isopentyl cellulose,. butyl cellulose), poly(*tert.*-butylmethacrylates) (P*t*BMA) and poly(methylmethacrylates), (PMMA). The film thickness is determined by the number of monolayers. The polymers were crosslinked either chemically or by irradiation with UV-light. The latter was used to obtain the cellulose membranes. These membranes were exposed to different liquid or gaseous organic compounds, such as toluene, methylene chloride and methanol for swelling.

For the investigation of the gas separation efficiency, several 6FDA-based polyimides were synthesized and membranes were formed by spin coating. The gas sorption was measured in a closed apparatus using non linked as well as chemically crosslinked polyimides.

Characterization methods

In order to characterize the thickness as well as the density of the ultra-thin films fabricated by us the following methods were used:

Small angle X ray-scattering (SAXS) of the films previous and after solvent vapour contact was used to measure changes in film thickness due to swelling. Figure 2 shows schematically the set-up of the measurement.

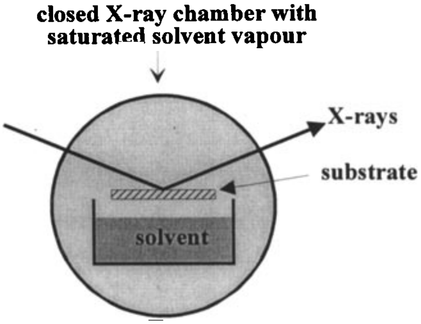

Fig.2: Set-up of SAXS measurement.

As an alternative method surface plasmon resonance (SPR) was utilized to measure the polymer film thickness (see figure 3). With this method swelling of polymer films in direct contact to liquid solvents can be measured. The result is a change in optical thickness (product of layer thickness and refractive index) of the polymer film coated on top of a gold substrate that affects the resonance angle of the coupled light beam. The refractive index of the film changes during swelling according to the solvent polarity and the film thickness as well as the refractive index changes that results in an increase in optical thickness.

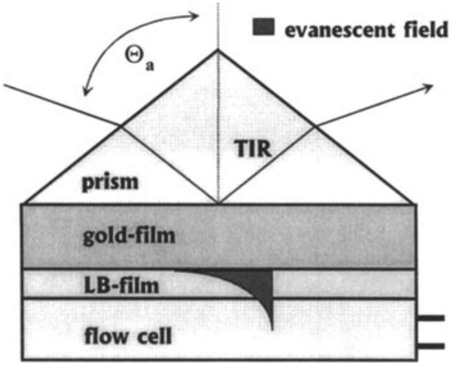

Fig.3: SPR measurement of polymer film thickness.

A third method was utilized that is easy to perform and allows to measure the gain of weight of a polymer film in contact to gases and vapours using a micro balance. This is a very accurate method to measure the sorption respective desorption of gases in polymer films. Nevertheless no information about the change in film structure can be obtained from these measurements.

Results

SAXS experiments show clearly the change in film thickness during polymer swelling in solvent vapours. According to the chemical nature of the polymer the sorption of polar or unpolar solvents is favoured. For instance P*t*BMA swells is at most in $CHCl_3$ and PMAA in Ethanol. On the basis of Hildebrand's theory /1/ the maximum change of film thickness D/D_0 in various solvents gives the Hildebrand parameter of the polymer (see figure 4).

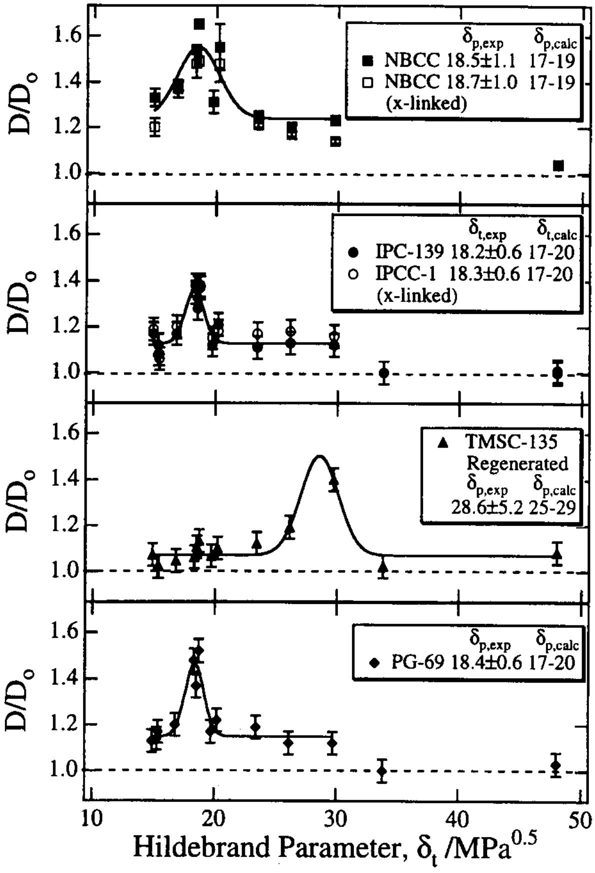

Fig.4: Determination of the Hildebrand parameter of a polymer in form of ultrathin films. IPC: Isopentylcellulose; NBCC: n-Butylcellulose; TMSC: Trimethylsilylcellulose; PG-69: α-helical poly(methyl-co-octadecyl-γ-glutamate)

For crosslinked isopentyl cellulose and polymethacrylate almost the same Hildebrand parameters were found allowing the conclusion that the van-der-Waals interactions of the alkyl chains substantially determine the solubility behaviour. Maximum swelling was found in CH_2Cl_2 and $CHCl_3$, respectively /2/. Analogous results were obtained from SPR measurements of isopentyl cellulose in direct contact to liquid solvents (figure 5).

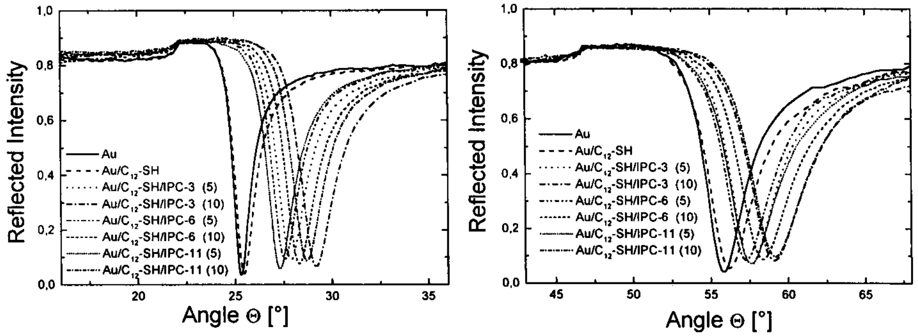

Fig. 5: Surface plasmon resonance as a function of resonance angle for different cellulose derivatives in contact with air (left) and Methanol (right).

The figure shows the change of the resonance angle of different cellulose derivatives after contact with the solvent. It has to be noted that strongly swelling solvents induce the biggest change of the refractive index. Hence, the shift in the resonance angle is no absolute measure of swelling. Nevertheless, the change of the resonance angle is proportional to the number of layers of the cellulose film. The proportionality constant, i.e. the increment per layer depends on the degree of swelling and increases in strongly swelling solvents.

Furthermore the SPR experiments show that LB-films of 5 and 10 monolayers swell uniformly, thus revealing "block swelling".

Solvent saturated crosslinked cellulose membranes were used for the separation of macromolecules by transport through the membrane under variation of their chain lengths /3/. Macromolecules move through a membrane network composed of hairy-rod macromolecule by reptation (see figure 6).

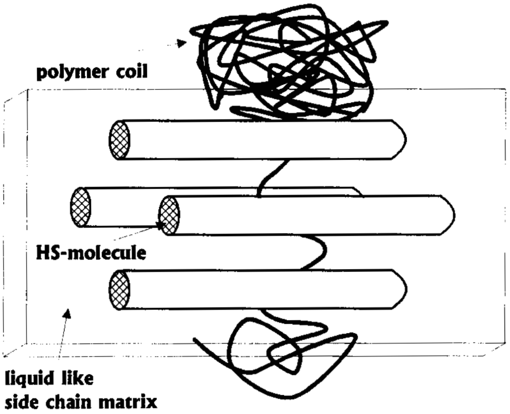

Fig.6: Reptation of macromolecules through dense polymer films.

Experimental results revealed that P*t*BMA of different chain length are able to diffuse through isopentyl cellulose membranes swollen in CH_2Cl_2. The reptation time is a function of the chain length. In contrast to that, isopentyl cellulose swollen in methanol only allows P*t*BMA with shorter chain length to diffuse through the film. Thus, different swelling in different solvents influences the selectivity of reptation.

Another example for transport phenomena through ultra-thin polymer films is the gas separation through polyimide films. Experiments were carried out in order to separate ethylene and ethylene oxid through a 6FDA- polyimide membrane. A good selectivity for nitrogen, oxygen, carbon dioxide, ethylene and ethylene oxide was observed. Ethylene oxide showed a very high solubility in the membrane compared to other gases, followed by CO_2 which solubility is much less. The plasticization effect of CO_2 in glassy polymers is well known /4/.

Micro balance experiments showed that the desorption of ethylene is fast and complete. In contrast to that ethylene oxide doesn't desorb completely even after days under reduced pressure (see figure 7).

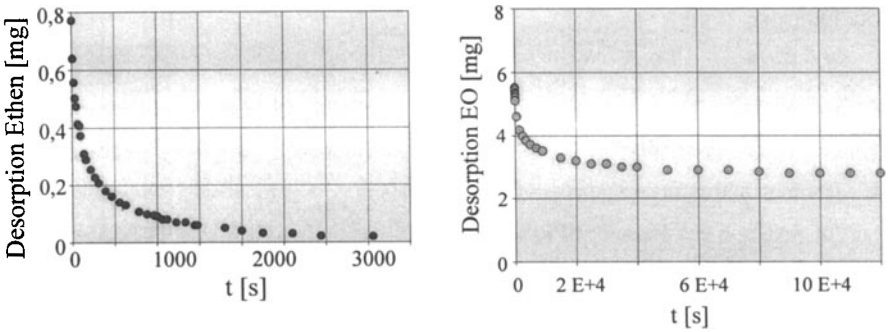

Fig.7: Desorption as a function of time for ethene and ethylene oxide (EO).

The high solubility of ethylene oxide leads to considerable swelling of the dense membrane and hence, dramatically reduces the separation efficiency of a gas mixture. This result was confined by REM images (see Fig. 8).

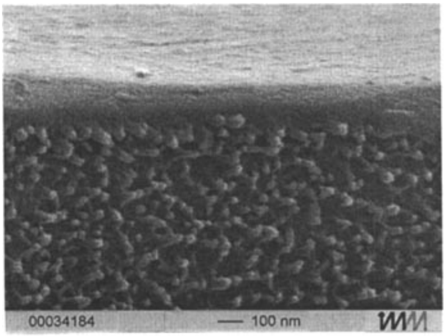

Fig. 8: Scanning electron micrograph of swollen polyimide

Swelling can be controlled by crosslinking of the membrane material with ethylene glycol. In that way stable membranes were obtained for the separation of ethylene and ethylene oxide. Dependent on the degree of crosslinking the polymer swelling decreased and a higher permeation for all gases was measured. Thus, separation of ethylene and ethylene oxid was possible with the selectivity being smaller than before crosslinking, but remaining reasonably high. Usually one expects that the permeation is reduced and the selectivity increases with an increase of the degree of crosslinking. The data measured showed a different trend perhaps originating from the similar molecule size of ethylene and ethylene oxide.

Conclusions

The cases presented here confirm that polyimides or cellulose films obtained from either spin coating or Langmuir-Blodgett (LB)-technique provide a model system for adsorption studies. The adsorption and diffusion process of gases, liquids in a polymer matrix can be followed by means of SAXS in gas phase or SPR using a special set-up in a flow cell. The derivatization with different crosslinking groups is one possibility for changing the chemical properties of the polymer films. Subsequent chemical modifications of the system should be generalizable to convenient methods for introducing desired surface properties and membrane swelling behaviour.

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References

/1/ J.H. Hildebrand, R.L. Scott, Solubility of non-electrolytes, Reinhold, 3rd Ed., New York, 1950
/2/ A.R. Esker, C. Mengel, G. Wegner, Science, 280 (1998), 892-895
/3/ F. Meier, Thesis, University Mainz, 1999
/4/ A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, J. Mem. Science, 155 (1999), 67-78