

thermodynamic and non-equilibrium (dynamic) factors such as surface fields at the substrate, radius of gyration versus film thickness, solvent properties, as well as parameters of the spinning procedure.

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P02 Polymer gel structure findings resulted from swelling investigations

M. G. TOKMACHEV¹; N. B. FERAPONTOV²

1: Faculty of Physics, Lomonosov Moscow State University, Moscow, Russia

2: Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia

mike_tokm@yahoo.com

Swelling of the hydrophilic polymers in water is known to be greater than in water vapour (Schroeder paradox). However, if a polymer swollen in water is exposed again to the atmosphere of saturated water vapour it loses water. This phenomenon is known as syneresis and has common character for all polymers. Thus, the phase state of water influences on polymer swelling, and their full dissolution is possible only in liquid phase.

Water sorption by polymers is the initial stage of their dissolution. However, if polymer molecules are cross-linked their dissolution is stopped at the stage of swelling. In this case, polymer gels (PG) are formed.

The dependence of polymer swelling on the properties of a solution in which the polymer is immersed is a characteristic feature of polymer gels. It is known that solutes penetrate into the swollen polymer but their concentration in the polymer always differs from that in the external solution. It was shown elsewhere that swollen polymer being immersed in a solution besides the volume occupied by the polymer matrix contains two liquid phases different in their composition. One phase has the composition closely related to that of the external solution and the other phase is pure water. The amount of this water depends on the activity of water in the external solution and changes in agreement with the water vapour sorption isotherm. Thus, it was suggested to distinguish for a polymer swollen in a solution a phase of sorbed or “bound water” and a phase of external solution or “free water” (if the polymer was allowed to swell in pure water, it contained both “bound” and “free water”).

This work is aimed at studying of the polymer swelling in dependence on the properties of an external phase. Swelling of various types of the hydrophilic polymers in the solutions of different composition was studied by optical method (OM). The obtained results were compared with reference data on water vapour sorption obtained earlier for the same polymers by the dynamic desorption porometric (DDP) method.

The analysis of the experimental results made it possible to describe and formulate a new previously unknown property of the studied polymer gels. The volume of the external solution taken up by polymer at swelling in liquid (after it has swollen in vapour) is constant and independent of concentration of the solution. In other words, volumetric polymer network functioning in gel as vessel walls is stretched in liquid for one and the same value independently on concentration of the solution. Observed at that change of gel volume is connected with change of the amount of “bound” water influencing on polymer framework;

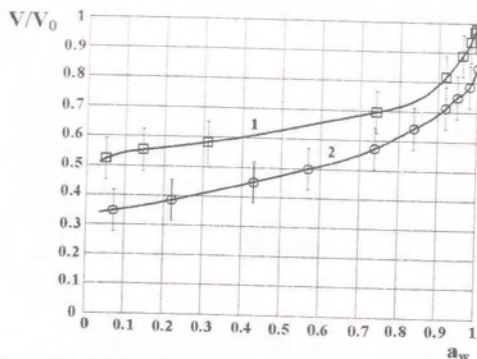


Fig. 1. KU-2x8 (H-form) polymer swelling in H_2SO_4 solution (curve 1) and in vapor (curve 2).

the former is sorbed by polymer in agreement with water vapour sorption isotherm. This result confirms the adequacy of the heterophase model, where the amount of water sorbed by polymer is a function of water activity in the external solution.

The analysis of the mathematical models simulating the structure of polymer gel showed that the model "planes" provides more plausible description of the experimental results. According to this model the polymer gel has a sandwich-type structure, which consists of alternate layers of hydrated polymer and the external solution.

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Contact angle measurements for polymer membranes

Yu. G. BOGDANOVA¹; V. D. DOLZHIKOVA¹; A. A. YUSHKIN²; A. N. FILIPPOV³

1: Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia

2: Topchiyev Institute of Petrochemical Synthesis RAS, Moscow, Russia

3: Gubkin Russian State University of Oil and Gas, Moscow, Russia

yulibogd@yandex.ru

Recently, problem of solvent transport investigation through polymeric membranes is under close attention because of great potential of such membranes in organic solvent nanofiltration (OSN). Permeability of dense polymeric membranes is determined by the free volume fraction of polymers. This work focuses on investigation of polymer surface energy, contact angle measurements and its correlation with free volume fraction. The correlation between the experimentally determined dispersion component of polymer free surface energy γ_{SV} , fractional free volume and gas permeability was found for polymers of different types (metathesis polynorbornenes, poly(1-trimethylsilyl-1-propyne)—PTMSP, Hyflons[®] AD and Teflons[®] AF). The results obtained show the especial sensitivity of dispersion interactions to the coils packing density at the surface and, consequently, in bulk of polymer film.

The new technique permitting to determine the alcohol concentration corresponding to the beginning of its sorption in membrane and polymer free volume is developed. Technique includes complex investigation of wetting of polymer surface with aqueous alcohol solutions, tensiometry of solutions, determination of surface energy characteristics of initial polymer membrane and one after the contact with alcohol solutions.

It is necessary to note that results of surface energy determination of polymer membranes using contact angles point out the heterogeneous character of wetting and, consequently, heterogeneous character of surface of high free volume polymers.

So, the perspectives of contact angle measurements for prediction of polymer membrane efficiency with respect to gas and liquid transport were demonstrated.

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