

# "Memory" of the Substrate/Solution Interaction in the Properties of Ultrafiltration Membranes Prepared by the Phase-Inversion Method

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## SYNOPSIS

The productivity and some structural properties of membranes made by the casting of aromatic polyamide on various substrates are found to be sensitive to the wetting characteristics of the used substrate. The influence of the interaction substrate/solution expands through the membrane bulk up to the "free" surface which was not in contact with the substrate. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

When preparing membranes by the phase-inversion method, the polymeric solution is cast onto the polished substrate, then it is plunged into the bath where the phase separation occurs and the porous structure of membrane is formed. The adhesion interaction might cause the alteration of the composition, structure, and phase state of the solution adjacent to the substrate microlayer and to propagate into the bulk, thus affecting the character of the structure forming at the stage of phase separation. For example, in some cases, one can observe the formation of a densified layer on that side of the membrane which was forming in contact with the substrate. This effect being unexplainable from the standpoint of polymer deposition kinetics could arise due to increased polymer concentration near the solution/substrate interphase produced by the action of adhesion forces.<sup>1</sup>

This work was aimed at studying the influence of the above-mentioned adhesion interaction on the properties of ultrafiltration membranes made of aromatic polyamide, by considering the functional and structure characteristics of the membranes in connection with the variation of the surface free energy

of the substrate. The surface free energy,  $E_S$ , is one of the most important parameters of such systems as it governs the processes taking place on the solid surface (sorption, wetting, and others). In the present communication, we demonstrate the dependence of the productivity of membranes and some features of their supermolecular organization.

## EXPERIMENTAL

Membranes of 50–70  $\mu\text{m}$  thick were formed from a 15 wt % solution of commercial aromatic polyamide "Fenilon S-2" in dimethyl acetamide (DMAA). The oxypropylene oligomer at a concentration of 20 wt % in solution was used as a nonsolvent pore-forming additivity. The solution was cast onto the polished surface with the help of a narrow slit die. The "upper" (free) surface is proved to be functionally prevailing in membranes of this type.<sup>2</sup> The filter characteristics of membranes were carried out with the help of stirred batch cell FM02-200 at pressure 0.1 MPa and at temperature 25°C.

The structure studies were conducted using IR ATR measurements. The ATR spectra of free and substrate-contacted surfaces were recorded on a grating spectrophotometer Jasco Model DS-403G. To reduce the energy loss due to the air gap arising when the porous sample is adjusted to a solid ATR optical element, the latter one was prepared from

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**Table I** Some Characteristics of the Used Substrates

Substrate	$D_S$ (mJ/m <sup>2</sup> )	$P_S$ (mJ/m <sup>2</sup> )	$E_S$ (mJ/m <sup>2</sup> )
Teflon	20.8	0.6	21.4
Polypropylene	25.4	3.0	28.4
Duralumin	27.8	5.5	33.3
Laminated insulation, <sup>a</sup> type A	27.0	7.4	34.4
Steel	25.5	13.5	39.0
Laminated insulation, <sup>a</sup> type B	32.6	15.1	47.7
Glass	3.8	69.7	73.5

<sup>a</sup> Paper impregnated by resol-cresol formaldehyde resin.

an IR transparent low-melting temperature chalcogenide glass IKS35. This low-melting-temperature material has a refractive index of about 2.4. Being heated together with the tighten specimen to 60–80°C, the chalcogenide optical element softens and the perfect contact element/specimen is provided. This new modification of the ATR technique developed by Zolotarev and co-workers<sup>3</sup> was successfully applied to obtain IR spectra from the very rough polymer surface.<sup>4,5</sup>

## RESULTS

### Surface Free Energy

As the direct determination of  $E_S$  is a complicated and laborious task, we used the simplified method developed in Refs. 6 and 7. The procedure is based on the measurements of contact angles ( $Q$ ) of two liquids on the same solid surface with subsequent resolution of the following set of equations:

$$1 + \cos Q_i = 2[(D_{ii} \times D_{ii})^{1/2}]/\sigma_{ii} + 2[(P_{ii} \times P_{ii})^{1/2}]/\sigma_{ii}$$

$$1 + \cos Q_j = 2[(D_S \times D_{ij})^{1/2}]/\sigma_l + 2[(P_S \times P_{ij})^{1/2}]/\sigma_l \quad (1)$$

$$\sigma_l = D_l + P_l \text{ (for every } i, j)$$

$$E_S = D_S + P_S$$

where  $\sigma_l$  is the liquid surface tension:  $D_{ii}$ ,  $D_{ij}$  and  $P_{ii}$ ,  $P_{ij}$ , the dispersive and polar components of the  $i$ -th and  $j$ -th liquids, respectively; and  $D_S$  and  $P_S$ , the dispersive and polar components of the substrate, respectively. The values of the surface tension components were taken from Ref. 6.

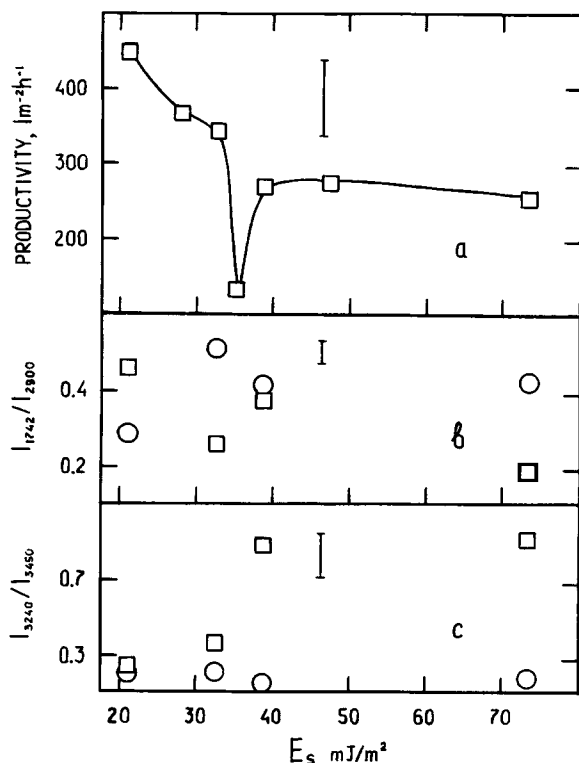
The required parameters were found by the numerical fit carried out for a set of couples of liquids. The results collected in Table I represent the average values obtained from the solution of the system of eqs. (1) for 18 couples of liquids.

### Productivity

The water productivity of the membranes is plotted in Figure 1(a) vs. the calculated surface free energy of the used substrates. The dependence exhibits a sharp minimum at  $E_S = 35\text{--}40$  mJ/m<sup>2</sup>. This value is close to the surface tension of the casting solutions which could vary from 34.2 mJ/m<sup>2</sup> (pure DMMA) to 45.6 mJ/m<sup>2</sup> (20 wt % solution).

### IR Measurements

IR ATR spectra were measured in the vicinity of the 1742 cm<sup>-1</sup> band responding to chain-terminating C=O groups, and in the frequency region of stretching vibrations of NH groups were two intensive bands at 3450 and 3240 cm<sup>-1</sup>, referred to as "free" and hydrogen-bonded groups, respectively. The intensity ( $I$ ) of the 1742 cm<sup>-1</sup> band (which is proportional to the concentration of chain ends) was measured relative to the intensity of the band at 2900 cm<sup>-1</sup> (CH<sub>2</sub> stretching vibrations) which served as the internal intensity standard. The value  $I_{1742}/I_{2900}$  found from the ATR spectra of both sides of the membranes is plotted in dependence on  $E_S$  in Figure 1(b). The positions of the experimental points for substrate-contacted and free surfaces are quite symmetric. The gradual decrease of the C=O groups' concentration on the "lower" side with the increase of  $E_S$  is accompanied by the opposite trend appearing on the "free" side. In both dependencies, there is a singularity in the region of 35–40 mJ/m<sup>2</sup>: The chain-end arrangement formed in most wetting



**Figure 1** (a) Productivity of membranes cast onto various substrates in dependence on the surface free energy of the substrate. (The line is drawn to guide the eyes.) (b,c) Respectively, the relative intensities of the  $1742\text{ cm}^{-1}$  band (chain-terminating groups) and the  $3240\text{ cm}^{-1}$  band (hydrogen-bonded NH groups vs.  $E_S$ ). ( $\square$ ) Substrate-contacted surface; ( $\circ$ ) "free" surface.

solutions demonstrate their preferential localization on the "upper" side of the sample.

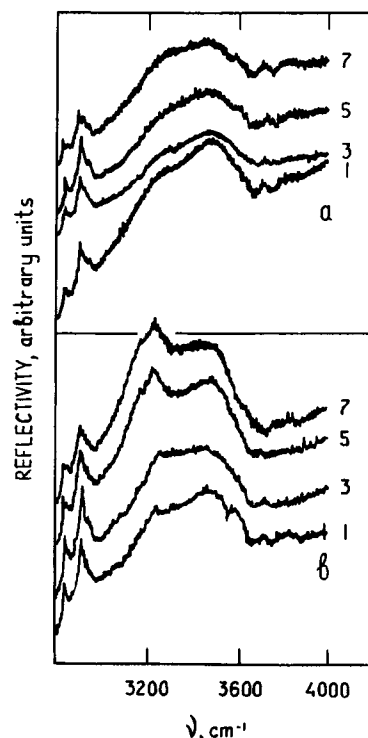
Figure 2 represents the ATR spectra recorded around the hydrogen-bond sensitive bands. The intensity of the band at  $3240\text{ cm}^{-1}$  grows gradually with the increase of  $E_S$  in the spectra of the "lower" side of the membranes and remains almost the same in the spectra of the free surface. To characterize numerically the change in intermolecular interactions, we calculated the relation of the band intensity of the hydrogen-bonded NH groups to that of "free" groups and plotted  $I_{3240}/I_{3450}$  vs.  $E_S$ . Although the relation  $I_{3240}/I_{3450}$  is of semiquantitative character only (due to strong alteration of the  $3450\text{ cm}^{-1}$  band's absorptivity coefficient with the change of the strength of the hydrogen bonding in polyamides<sup>8</sup>), it is clearly seen in Figure 1(c) that there are no peculiar features in the region of  $E_S = 35\text{--}40\text{ mJ/m}^2$ , where the monotonic dependence for the membrane productivity as well as for the chain-end band intensity is disturbed.

The data obtained with the help of the ATR technique are referred to the surface layer whose thickness is determined by the IR light penetration depth. In our case, the penetration depth was about  $1\text{--}2\text{ }\mu\text{m}$  in the NH groups' stretching region and reached  $3\text{--}4\text{ }\mu\text{m}$  in vicinity of the C=O groups' absorption.

## DISCUSSION

The coincidence of the surface free energy of the substrate with the surface tension of the casting solution gives the best wetting of the substrate. The membrane prepared on the respective substrate demonstrates the maximal productivity which, we remind, is defined by the permeability of the "free" surface layer of the membrane. Thus, the thin film of the solution conserves the memory of the initial contact with the substrate.

The mechanism of formation of the long-range order of this kind is of practical interest as it governs, to a certain degree, the membrane functional properties. The infrared data give the possibility to evaluate roughly the energy of interaction which realizes the memory mechanism.



**Figure 2** IR ATR spectra of membranes cast on various substrates. See Table I for notation of the samples.

The chain-end concentration in both surface layers, as well as the membrane productivity, appeared to be in correlation with the variation of the surface wetting. The maximal wetting is related to that chain arrangement when the ends of molecules penetrate lesser into the "lower" surface layer, but on the "free" surface, the chain concentration is increased. Thus, the influence of the substrate on the structure of the membrane is expanded through its whole thickness at both supermolecular and microscopic levels.

At the same time, the hydrogen-bond-involved NH groups do not feel the point of the maximal wetting. The energy of hydrogen bonding is approximately 20 kJ/mol while the energy of the van der Waals interaction which regulates the macromolecular chains arrangement is not more than 5 kJ/mol. One can conclude that the energy of the influence of the substrate on the polymer which leads to specific structural ordering lies between these two values.

## CONCLUSION

To summarize, the functional and structural properties of polymeric membranes are sensitive to the

chemical nature of the used substrate. The memory of the interaction substrate/solution manifests itself not only in the interface region but also involves the "upper" surface layer which formed without direct contact with the substrate.

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