

## 초청강연 III

# LIQUID CRYSTALLINE POLYURETHANES. PHYSICOCHEMICAL CHARACTERISTICS AND PERVAPORATION PROPERTIES

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### 1. Introduction

Although the transport of small molecules through polymer membranes has been extensively studied for a long time, understanding of the transport mechanism is still far from satisfactory. This in turn makes difficult the search for new membrane materials with the desired transport characteristics. Therefore it is of the utmost interest to study the correlations between a polymer's structure and morphology and its transport properties.

Generally, polyurethanes serve as excellent polymer materials for such studies since their physical and chemical properties can be widely and systematically modified by varying the length, composition and chemical structure of the hard and soft segments.

In this paper liquid crystalline polyurethanes are presented as new membrane materials for liquid separation and their transport properties with respect to molecular and supermolecular structure are discussed.

### 2. Experimental

The LC polyurethanes varying in a flexible spacer length and a mesogenic group content were synthesized by the prepolymer two-step technique using poly(oxytetramethylene)diol (PTMO) or poly(butylene adipate)diol (PBA), 2,4-tolylene diisocyanate (TDI), 4,4'-bis(2-hydroxyethoxy) biphenyl (BHBP) and DMF as solvent.

The obtained polymers were characterised by means of FTIR spectroscopy to establish the chemical structure, by GPC (for molecular weight and molecular weights distributions), by DSC and DMTA to study the thermal behaviour and by SEM, SAXS, WAXD and polarising microscope to study the morphology of these polymers.

Homogeneous dense films were prepared by casting the 15% polymer solution in DMF onto glass plates after which the solvent was evaporated.

The sorption and diffusion of solvents into polyurethanes were investigated using conventional weight-gain experiments.

Pervaporation experiments were performed at 25°C for a 45% wt benzene/cyclohexane feed solution and different organic/water mixtures using a standard pervaporation cell. The composition of the feed and permeate were determined by means of refractometry or gas chromatography.

### 3 Results and discussion

Polyurethane elastomers are segmented block copolymers composed of alternating soft (polyether or polyester segments) and hard blocks (diisocyanate and diol segments).

Due to their thermodynamic incompatibility, the blocks undergo microphase separation resulting in a dispersion of soft and hard segment domains.

Although transport of small molecules was shown to occur through the soft segment domains, the soft segments volume fraction, their structure and mobility seem not to be the only factors influencing transport of liquids through LC polyurethanes. It has been found that the hard segment domains contribute to the overall process by suppressing membrane swelling, by influencing tortuosity of a diffusion path as well as by altering the properties of the soft segment matrix in case uncompleted microphase separation takes place.

It was documented by the DSC and DMTA data that by varying the soft segment molecular weight and/or the initial composition of the diols, it was possible to influence the degree of microphase separation. Fairly pure soft segment matrix is assumed to be present for LC polyurethanes with the soft segment molecular weight  $M_n=2000$  (polymers 1 and 1a), whereas LC polyurethanes with hard mesogenic blocks mixed into the soft domains were formed when  $M_n$  of the soft block was lower than 2000 (polymer 2: 49% phase separation degree, polymer 3: 71% phase separation degree).

On the other hand, the expected differences in soft segment domains structure caused by partial phase mixing were confirmed by the results obtained by a positron annihilation method.

Moreover, a strong correlation was found to exist between the values of the  $T_g$ , the average size of the free volume  $V_{av}$  and diffusion coefficient  $D$  of organic liquids, i.e. the lower value of  $T_g$  the greater values of both the  $V_{av}$  and  $D$ .

Table 1.

	Composition	Benzene/Cyclohexane		Benzene/Water		Chloroform/Water	
		45% Benzene		0.065% Benzene		0.065% Chloroform	
		F	$\alpha$	F	$\alpha$	F	$\alpha$
1	BHBP/PTMO 3:1, PTMO 2000	-	-	1.35	782	1.22	525
1a	BHBP/PBA 3:1, PBA 2000	6.4	7.3	-	-	-	-
2	BHBP/PTMO 3:1, PTMO 1000	20	4.2	0.63	628	0.32	280
3	BHBP/PTMO 1:1, PTMO 650	4	11	0.67	447	-	-

F-flux in  $\text{kg}\mu\text{m}/\text{m}^2\text{h}$ ,  $\alpha$  - separation factor  $Y(1-X)/X(1-X)$ , where X and Y - mass fraction of benzene (chloroform) in feed and permeate, respectively.

As can be seen from Table 1, the applied structural and morphological modifications of LC polyurethanes can dramatically alter the membrane performance. The use of LC polyurethanes for which incomplete microphase separation occurs enables separation of mixtures with higher benzene content to be carried out, however, the increase in a membrane's selectivity is accompanied by a decrease in flow rate. Alternatively, the similar effect can be achieved by changing the soft block from polyether to polyester one. For the organic/water separations, it appears that the most effective polyurethane membrane is this which contain the permeable soft domains composed mainly of the PTMO blocks.

Although the structure-transport properties relationships obtained so far are not fully established yet, the results discussed show that it is possible to "tailor" the structure of the polymer to have specific performance.

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