

Polarity Measurements in Block Copolymers (Polyurethaneimides) and Correlation with Their Pervaporation Features

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SYNOPSIS

EtOH/ETBE azeotropic mixture was separated by pervaporation through films of polyurethaneimides (PUI), i.e., alternating block copolymers varying in their structure only by their oligomeric soft blocks. Pervaporation performances strongly depend on the flexible segments: fluxes on the molecular weight and selectivity towards ethanol on the chemical structure in the decreasing order: PEG, PCL, PCD, PTMG, PPG. In order to correlate selectivity with segment polarity, a new solvatochromic polarity probe that was well soluble in PUI was synthesized. Using 13 solvents covering a wide polarity range, $\text{Vis } \lambda^{\text{max}}$ of the photochromic indicator open form was linearly correlated with the $E_T(30)$ polarity scale. By illumination of the dissolved dye, PUI polarity was investigated in relation to soft segment nature and size. The very high PUI polarity values and their splitting for highest size segments were assigned to preferential probe solvation by interblock urethane junctions combined with phase segregation. Polarity values consistent with the chemical structure of the flexible segments were provided by similar measurements on suitably end-capped precursors of these segments and were then linearly correlated with the related PUI pervaporation selectivity. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In a previous article, the authors have proven that the sorption of a liquid in a polymeric material was dependent on the polarity of the liquid. This property was expressed by linear correlations of polymer molar swellings G_m with empirical solvent polarity parameters $E_T(30)$.¹ This correlation type applies to binary systems (polymer-a single solvent, G_m total) as to ternary systems (polymer mixture of two solvents, partial molar swelling for each solvent).

Obviously, it was attractive to widen this approach on the polymer side, i.e., to express the properties of polymer-liquid systems as a function of the polymer polarity. Apart from the knowledges enhancement concerning the polymers solvation phenomena, the practical interest to investigate how polymer properties

change with its polarity lies in the selectivity effect that usually follows the sorption in the case of ternary systems. This preferential solvation phenomenon is essential for separation methods on dense membranes like pervaporation and vapor permeation. The concentration profile of components inside the polymer film is actually established first from their sorption characteristics, then their diffusion ability and, thus, governs the membrane performances, i.e., flux and selectivity during the transfer.

A part of the purpose of this work was to examine if flux and selectivity could be related to polymer polarity during the pervaporation of a given mixture of two organic liquids. Polarity parameters characterize thermodynamic effects and our approach can be, thus, rigorously justified only in the cases where preferential solvation (i.e., sorption) principally governs the pervaporation process. Without denying importance of the diffusion process, we assume that it exerts an analogous influence, whatever the polymer used for this study. Only a significant correlation between per-

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vaporation features and polymer polarity parameters will *a posteriori* justify the validity of the above assumption. As previously, the studied mixture was composed of a protic liquid, ethanol and of an aprotic one, ETBE (ethyl-*t*-butylether), at the azeotropic composition (20 wt % ethanol). This choice first lies in the fact that the displayed interactions are different in nature for each mixture component. Moreover, the ETBE/EtOH azeotropic mixture provides a sufficiently large range in fluxes and selectivities and also leads to true ternary systems with the polymers investigated.

To carry out such investigations, polymers with evolutive structure are best adapted. However, in the chosen polar mixtures, homopolymers cannot be used because it is not possible to examine whole sets without materials that show either too high fluxes but low selectivity or too low fluxes if polymers lie in a glassy state or are semicrystalline; moreover, these morphologies can change with experimental conditions and so are the origin of complications and of instability in performance data. Chemical crosslinking can often stabilize the properties, but is difficult to achieve in a reproducible way from polymer to polymer.

Therefore, the use of block copolymers has been preferred: in these materials, variable flexible segments alternate with invariant very hard polar urethaneimide blocks that provide a strong cohesion by physical crosslinking. The controlled change in structure of these polyurethane *imides* (PUI) was performed by the flexible oligomeric segments (oligoethers, oligoesters, etc.) intercalated between the hard blocks, and they are responsible for flux and selectivity. The segment polarity and length could be quite widely varied in so far as the segment precursors were available and the pervaporation characteristics of the resulting films could, thus, be modulated.

The purpose of relating transfer properties to the polarity of the used polymers required the definition of a polarity parameter. Several methods, which are further reminded, have been already suggested for synthetic homopolymers and extended to some random copolymers. To our knowledge, similar works have, however, never been performed on block copolymers, and that is the reason why this report deals first with investigations on measurement of block copolymers polarity.

EXPERIMENTAL

Solvents

Ethyltertiobutylether (ETBE, provided by Institut Français du Pétrole), was distilled twice from Na

before use. EtOH was of analytical grade, its water content not exceeding 0.3 wt %.

All the common liquids used for polarity measurements were of analytical grade, their water content not exceeding 0.1 wt % except in the case of the most polar alcohols, i.e., MeOH and EtOH (up to 0.2 wt %), according to GC analysis.

Dimethylformamide DMF (Solvants Documentations Synthèses (i.e., SDS, pure for synthesis) and dimethylacetamide DMAC (Aldrich, HPLC grade) used for polymers preparation were distilled from CaH₂ under reduced pressure just before use or stored on molecular sieves.

Instrumentation

IR spectra were recorded on a Perkin-Elmer 580 spectrometer for transmission measurements and on a Brüker IF5 FTIR for reflection measurements. ¹H and ¹³C NMR spectra were recorded on a Brüker AC-2000P using tetramethylsilane as the internal standard. For ¹³C, assignments COESY ¹H-¹³C sequences, J-modulated sequences, ¹H-coupled spectra, and groups contribution methods have been used. The UV-Vis absorption data were measured with a Hitachi 320 spectrophotometer or a Shimadzu UV-2101 PC device coupled with a Victor microcomputer.

Liquid mixtures compositions were determined by GC analysis with a Shimadzu GC-8A chromatograph equipped either with a Porapaq Q column at 170°C and a thermal conductivity detector or with a chromosorb W-SE30 column at 140°C and a flame ionization detector.

Elementary analysis were made by the Service Central d'Analyses of the Centre National de la Recherche Scientifique (CNRS).

Block Copolymers Synthesis

Starting Reagents

4,4'-Methylenebisphenylisocyanate MDI (T.C.I.) was previously distilled under vacuum. Pyromellitic dianhydride AP (Aldrich 99%) was bisublimed under vacuum before use. The oligomeric diols, which are precursors of flexible segments, are designated by their chemical name followed by their molecular weight value; polyethyleneglycols (PEG 600, PEG1000, Merck) were dried before use on heating under vacuum at 100°C while stirring; polytetramethyleneglycols (PTMG650, PTMG1000, PTMG2000, Polysciences Inc.) were used as received; polycaprolactonedioles (PCL530, PCL1250, PCL2000, Aldrich) were used

without purification as well as polypropyleneglycol (PPG1025, Merck) and polycarbonatediol (PCD850, Polysciences).

Method

The used copolymers were prepared by extending and improving the procedure of A. C. de Visser,² which allows the obtaining of segmented polyurethaneimides (PUI) by reaction of a cyclic dianhydride with a macrodiisocyanate. Synthesis were carried out under continuous stirring and dry nitrogen or argon atmosphere. In the first step, an α,ω -isocyanate terminated segment was prepared by reacting, below 60°C, MDI (2 eq.) with an oligomeric diol (1 eq.) preferably without solvent or in anhydrous DMF if necessary due to the viscosity of the mixture. The reaction progress, especially at the end, was followed by IR spectroscopy (disappearance of the OH absorption band at 3300 cm⁻¹) from a droplet of the reaction mixture, which was spreaded as a thin film on a KBr pellet. Reaction completion was catalyzed by adding a small amount of dry triethylamine TEA.

In the second step, the resulting macrodiisocyanate was chain extended by reaction, at a temperature below 80°C, with AP (1 eq.) in anhydrous DMF (disappearance of isocyanate groups followed by IR at 2250 cm⁻¹) to give a solution of block copolymer that was precipitated by pouring in cold water. The recovered white-yellow polymer was washed in water, then dried under vacuum at 60°C and, at last, thermal cured under reduced pressure (2 to 3 mbar) at 130–140°C for 15 h (while progressive rising in temperature of 10°C/h from 60 to 100°C) to complete the formation of imide rings. This procedure leads with good yields (70–90%) to high molecular weight linear copolymers that are soluble in aprotic dipolar solvents such as DMF or dimethylacetamide DMAC. They are built from the same hard block designated as MDI-AP from the name of the starting reagents, and their full name also includes the initials of the precursor diols so that a copolymer made by reacting PEG600 with MDI and then chain extended by AP is called PEG600-MDI-AP. In most cases, characterization of the chain length has been made by the determination of the reduced viscosity of a 1 g/L solution at 25°C in very anhydrous DMF (to avoid partial hydrolysis during the dissolution on heating); values lay between 1 and 1.6 dL/g.

Table I illustrates the hard segment and soft segment molecular compositions of the polyurethaneimides investigated.

A mixture of PCL 530 (1 eq.), MDI (1 eq.), and 15 mL DMF was allowed to react at 60°C for 6 h and then precipitated by pouring in water. The

recovered polyurethane was dried under vacuum at 70°C.

All the synthesized PUI exhibit the imide characteristic absorption bands at (in cm⁻¹): 1780, 1720, 1380, 720.

Pervaporation Experiments

Films for pervaporation were obtained by casting on a PTFE plate polymer solutions in anhydrous DMF (2 to 3 wt %) prepared under dry atmosphere at a temperature that does not exceed 100°C and filtered on glass-wool. Solvent was then evaporated in a convection oven at 40–50°C at least for 24 h, and the resulting film removed from his backing, dried under vacuum with progressive rising in temperature (10°C/h) from 40 to 100°C, and heat treated at 130°C for 15 h to restore imide rings that might have been opened during dissolution. In any cases, thickness of films was roughly constant (30 to 40 μm) and for a mean value of 35 μm difference of thickness between two different points did not exceed 5–6 μm .

Pervaporation experiments were performed at constant temperature and under reduced pressure (less than 0.5 mmHg) in an apparatus similar to one described elsewhere.³ It consisted of a flat pervaporation cell (membrane surface area, depending on the extent of the flux), and a glass apparatus equipped with traps to condense the pervaporate removed from the membrane by a vacuum pump.

Permeation flux and pervaporate composition were determined by weighing amount of the permeated vapor trapped by liquid nitrogen and analyzing using gas chromatography.

Spiropyran Indicator Synthesis

The requisite quaternary ammonium salt, 1-hexyl-2,3,3-trimethylindolenium iodide (TMII) was prepared by adapting the procedure of C. Damas:⁴ a mixture of 2,3,3-trimethylindolenine (T.C.I) (0.03 mol.), 1-iodohexane (Aldrich) (0.03 mol), 70 mL acetonitrile (Aldrich, HPLC grade), and 30 mL ethylacetate (Aldrich, HPLC grade) was stirred at 50°C for 48 h and then refluxed for 24 h. Solvents were removed by rotary evaporation and the remaining crystalline product treated with boiling THF (SDS anhydrous) for 15 min. The mixture was then cooled to 0°C, the solid collected in a Büchner and washed in 350 mL boiling toluene for 1 h to give a pale yellow product in 48% yield, m.p. = 142°C. ¹³C NMR spectrum is in accordance with the sup-

posed structure and with an elsewhere reported homologous salt.¹³

The spiroopyran, 1-hexyl-3,3-dimethyl-6'-nitrospiro(indoline-2,2'-2H-benzopyran), was synthesized according to a method⁵ that produces the C₆ "Fischer base" *in situ*: in a mixture of 0.016 mol of TMII in 35 mL butanone (Aldrich, HPLC grade), 1.6 mL of piperidine (Aldrich, 99%) was introduced at room temperature, the resulting "Fischer base" dissolving. 5-Nitrosalicylaldehyde (0.018 mol) (Aldrich) was then introduced and the reaction mixture was refluxed for 30 min, then cooled to room temperature, and allowed to stand for 48 h. Piperidine salts were removed by precipitation in 300 mL of dry diethylether then filtrated, and the crude product was recovered by removing the solvent under reduced pressure. To eliminate colored impurities, purification was performed by LC on a silica gel column with alcohol-free chloroform as eluant; caution: spiroopyran in chloroform is in the blue color open form. At last, the solvent of the different elution fractions was removed by rotary evaporation and the product crystallized in petroleum ether to give in 83% yield a straw yellow (when dried) crystalline-pure spiroopyran of m.p. = 114°C.

Characterization (Fig. 1)

Elemental analysis calcd % for C₂₄H₂₈N₂O₃: C: 73.47, H: 7.14, N: 7.14, O: 12.24. Found %: C: 73.56, H: 7.15, N: 7.16, O: 12.14.

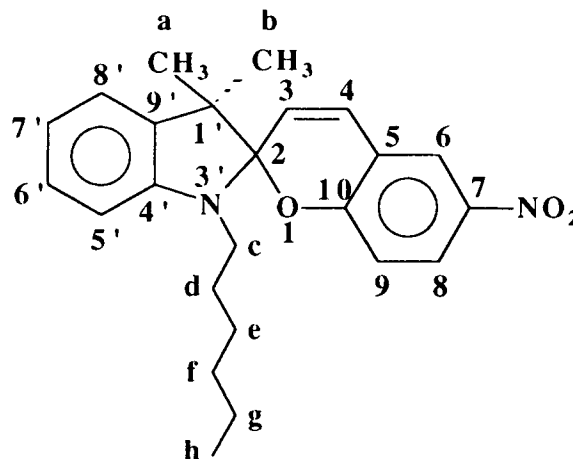


Figure 1 Spiroopyran probe structure. H and C numbering for NMR characterization.

¹H NMR (CDCl₃), δ ppm and J Hz, s (singlet), d (doublet), t (triplet), dd (split doublet), etc.: 8.0 (ABX, H₈, J_{8,9}: 8.25, J_{8,6}: 2.79); 8 (ABX, H₆); 7.19 (td, H₆, J_{6,5}, J_{6,7}: 7.59, J_{6,8}: 1.38); 7.09 (dd, H₈, J_{8,7}: 7.29, J_{8,5}: 0.6); 6.9 (d, H₄, J_{4,3}: 10.4, J_{4,9}: 0.8); 6.87 (td, H₇, J_{7,5}: 1); 6.75 (dt, H₅); 6.58 (d, H₉); 5.86 (d, H₃); 3.14 (m, H_c); 1.57 (m, H_d); 1.28 (s, H_b); 1.26 (m, H_{g,f,e}); 1.18 (s, H_a); 0.86 (t, H_h, J_{h,g}: 6.34).
¹³C NMR (CDCl₃), δppm: 160 (C₁₀), 147.5 (C_{4'}), 141.2 (C₇), 136.3 (C_{9'}), 128.4 (C₄), 128.1 (C_{6'}), 126 (C₆ or C₈), 123 (C₈ or C₆), 122.4 (C₃), 122 (C_{8'}), 119.5 (C_{7'}), 118.8 (C₅), 115.8 (C_{5'}), 107.1 (C_{2'} and

Table I Soft Segment and Hard Segment Molecular Compositions of the Polyurethaneimides Investigated

Abbreviation	Name	Molecular Composition
Soft Segments Precursors		
PCD	polycarbonate diol	HO—((CH ₂) ₆ —O—COO—) _n —CH ₂ OH
PCL	polycaprolactone diol	HO—((CH ₂) ₅ —COO—) _n —(O—CH ₂ —CH ₂) ₂ —OH
PEG	polyoxyethyleneglycol	HO—(CH ₂ —CH ₂ —O) _n —H
PPG	polypropyleneglycol	HO—(CH ₂ —CH(CH ₃)—O) _n —H
PTMG	polytetramethyleneglycol	HO—((CH ₂) ₄ —O) _n —H
Hard Block		
MDI-AP	pyromellitimide	

C_9), 53 (C_1), 44.1 (C_c), 31.9 (C_e), 29.2 (C_d), 27.3 (C_f), 26.4 (C_a), 22.9 (C_g), 20.2 (C_b), 14.4 (C_h).

End-Capped Diols Synthesis

Commercial products (Fluka): dimethylPEG500 and dimethylPEG1000, were purified by liquid chromatography ($Al_2O_3/2$ -propanol) to remove polar impurities. Purity was tested by TLC, and lack of hydroxyl groups was checked by derivatization with trichloroacetylisocyanate (Aldrich).^{6,7}

DimethylPTMG650 and dimethylPPG725 were prepared from PTMG650 (Polysciences) and PPG725 (Aldrich) by adapting the sodium naphthalene metallation method.⁸ The synthesis was performed under inert atmosphere: 1.45 g Na (8.2 eq.) in small pieces were added to a mixture of 8.9 g naphthalene (Aldrich 99%) and 150 mL of dry tetrahydrofuran THF (Solvents Documentation Synthèses, distilled from $LiAlH_4$ just before use) and stirred for 3 h at room temperature to give a naphthalene radical anion solution. This solution was then introduced dropwise under stirring in a mixture of the diol (1 eq.) and 100 mL of dry THF until the persisting green color of a slight excess of radical anion appeared. Then 6.55 g (6 eq.) of iodomethane (Aldrich, 99%) was added over 1 h at room temperature and the mixture was allowed to react for 15 additional hours to give a clear solution.

After solvent removing and dissolution in a 150 mL mixture of alcohol-free chloroform and toluene (1 : 1 vol), sodium salts were washed out three times with distilled water and then aqueous fractions once extracted with chloroform. The combined organic fractions were dried with anhydrous sodium sulfate, filtered, and then the solvent was removed.

DimethylPTMG650 was purified by LC, the different steps being followed by TLC (silicagel/distilled chloroform). Aluminium oxide (Merck, neutral activity I) was used first with toluene to eliminate remaining naphthalene and dihydronaphthalene, then with a THF-toluene mixture (1 : 1 vol) to recover the product. A second chromatography was carried out on silica gel (Chromagel 60–200 μm , SDS) with alcohol-free chloroform as first eluent to separate less polar impurities and then dry THF to recover the pure product. At last, solvents were removed to the last traces by evaporation under vacuum on a cold condensing surface (liquid nitrogen): yield 75%.

DimethylPPG725 was purified by LC on a column comprising a silica gel part surmounted by an equal amount of aluminium oxide (30 mL for 2.5 g product). Aromatics were first eliminated by toluene and then the dimethylPPG recovered in 83% yield with

a mixture of dry THF-toluene (3 : 1 vol), which was removed by the trapping technique. A conversion ratio more than 99.5% was observed from the analysis method used for dimethylPEG.

α,ω -DiacetylPCL530 was prepared by adding dropwise acetylchloride (4 eq.) (Aldrich 98% distilled) under stirring and dry atmosphere to a mixture of 5 g PCL 530 (1 eq.) (Aldrich), dry triethylamine (2 eq.) (Fluka), and 100 mL anhydrous THF (distilled from CaH_2) cooled to 0°C. Stirring was continued for 2 h, then the mixture was allowed to warm to 20°C and reaction completed for 20 additional hours. Ammonium salts were then filtered and the crude product recovered by removing the solvent. Purification was made first by decolorizing a toluene solution with charcoal at 40°C followed by filtration on Celite. The pure product was obtained in 74% yield by LC on silicagel with a mixture of toluene-dry THF (1 : 1 vol) as eluent, solvents then being removed to the last traces as before. Complete conversion was checked by 1H NMR spectroscopy from the peak area of terminal methyl groups (2.03 and 2.08 ppm in $CDCl_3$).

Polarity Parameter Measurements

A very small quantity of the spiropyran probe was dissolved in liquids, including end blocked oligomeric diols, to obtain 1 to 1.5 OD values, and the solutions were then poured into 0.5 cm thermostated quartz UV cells. The determination of the Vis absorption maximum wavelength of the merocyanine open form was made after illumination carried with two 15 W UV lamps ($\lambda = 365$ nm). The merocyanine quickly comes back to the spiropyran form and spectra have had to be recorded over a short range on either side of the peak maximum.

In the case of polymers in the solid state, a very small amount of spiropyran was added to a solution of 45 mg of polymer in 2 mL of the suitable solvent (anhydrous DMF for PUI). The mixture was then casted in an UV cell closed at the top but a face of which was missing. Solvent was evaporated at 70°C in a convection oven for 18 h then at 50°C under vacuum for 5 h. The film ($e \#150 \mu m$) was then illuminated as before and the spectrum was quickly recorded.

RESULTS AND DISCUSSION

Pervaporation Results

All the pervaporation results (Table II) were obtained at 30°C with EtOH/ETBE feed mixtures

Table II Pervaporation at 30°C of ETOH/ETBE Mixtures Closed to the Azeotropic Composition Through Polyurethaneimide X-MDI-AP Films

X: Soft Segment Molecular Weight	<i>C</i>	<i>C'</i>	<i>J</i> _{ETOH}	<i>J</i> _{ETBE}	$\ln \frac{J_{\text{ETOH}}}{J_{\text{ETBE}}}$	<i>E_T</i> (30)
PEG 600	0.221	0.901	0.103	0.011	2.24	40.6
PCL 530	0.200	0.85	0.085	0.015	1.74	39.6
PTMG 650	0.213	0.625	0.850	0.500	0.53	37.0
PCD 850	0.194	0.747	0.230	0.080	1.056	
PEG 1000	0.192	0.815	1.054	0.239	1.484	40.6
PCL 1250	0.208	0.594	1.100	0.750	0.383	39.6
PTMG 1000	0.205	0.477	2.660	2.914	-0.091	37.0
PPG 1025	0.200	0.460	4.650	5.460	-0.160	36.5

C, *C'* ethanol weight fractions of the feed mixture and pervaporate. *J*: mass flux in kg/h · m² for 5 μm film thickness. *E_T*(30): polarity parameter of the blocked soft segment X.

close to the azeotropic composition (ethanol weight ratio *C* = 0.20). Films, whose thickness was generally in the range of 30–40 μm, were prepared from various polyurethaneimide block copolymers (PUI), which differ from each other only by the nature and/or the molecular weight of the oligomeric soft segment (PEG, PTMG, etc.). The hard block composition, i.e., MDI-AP (pyromellitimide from methylenediphenylisocyanate and pyromellitic dianhydride), was kept the same in order to isolate the influence of the chemical structure of the flexible segments as well as the number of their functional groups on the pervaporation features, mainly the selectivity.

Selectivity towards ethanol (as *C'*, pervaporate ethanol weight ratio) is already high for PEG and decreases, whatever the molecular weight of the soft segment, in the order: PEG, PCL, PCD, PTMG, PPG. Selectivity and flux strongly depend on the soft segment molecular weight, and when two sets of roughly equal size segments are compared, selectivity increases with decreasing soft segment length, whereas fluxes are normally varying in the opposite way. Selectivity effects can be interpreted as an evidence for specific interactions between the protic permeant (ethanol) and the basic groups of the polymer chains (ethers, esters, etc.) through hydrogen bondings. Our aim was to describe the effects of these interactions in terms of general polarity.

Determination of Polymer Polarity

Except for the numerous investigations concerning problems of local polarity in the case of proteins in presence of solvents, the importance of polarity determination for a synthetic polymer, regarded as a

solvating medium, was rarely mentioned. Among the more outstanding results, D. Walter was one of the first who was interested in determination of polarity of polymer films from the solvatochromic behavior of a molybden complex. The *E_K* parameter (*K* = Komplex) was defined in this intention and a semi-empirical scale of solvent polarity was established (over 40 solvents), which was linearly related to the *E_T*(30) scale of Dimroth and Reichardt only by class of components (protic solvents, haloalkanes, substituted aromatics).⁹

An *S* parameter, which correlates linearly with the *E_T*(30) scale, was determined by H. Langhals from an aminophthalimide fluorescent probe.¹⁰ It was used to define the polarity of glassy polymethacrylates and to describe the polar feature of binary liquid mixtures, that of solid polymers as well as the composition of copolymers.

Other authors^{11,12} introduced by copolymerization a solvatochromic monomer in the main chain of various polymers. However, that original approach concerning synthetic polymers requests the synthesis of modified polymers, which is not always feasible. In spite of this drawback, the technique allowed the study of the probe microenvironment polarity in the case of linear synthetic polymers dissolved either in pure solvents or in binary mixtures.

At last, M. Yoshikawa and T. Shimidzu made investigations to correlate the pervaporation selectivity to the polarity of the polymers used. They characterized the solvatochromic behavior of a photochromic spiropyran probe¹³ and established, from measurements in solvents, a relationship between the wavelength of the Vis absorption maximum of the previous illuminated dye and the *E_T*(30) scale.

The results were then systematically applied to the determination of polarity of polymers used for pervaporation tests¹⁴⁻¹⁷ and, thus, allowed the correlation of pervaporation selectivity in the case of several polymers used for the separation of water-ethanol mixtures.

To achieve the present objective and after having made a range of unfruitful tests with the liposoluble-modified Reichardt dye¹⁸ (systematic degradation of the probe), we preferred to use the above spiro-*pyran* probe technique. In order to well adapt the method to the polar PUI and to preserve a sufficient solubility in apolar media, the following spiro-*pyran* S (Fig. 2) was synthesized. It differs from the Shimidzu and Yoshikawa indicator in the length of the side alkyl chain (6 carbons instead of 18).

Spiro-*pyran* S is a photochromic molecule that can be converted in an open form merocyanine M by UV light illumination. The M form can be converted back to S form by leaving it in the dark. The highly conjugated zwitterion is blue in CHCl_3 and pink in MeOH, i.e., the Vis absorption maximum, is shifted to shorter wavelength as the polarity of solvent increases (negative solvatochromism) and the position of the maximum determines the polarity measurement. Systematic measurements were made in 13 pure solvents at the reference temperature 25°C (Table III) to express the polarity, in an homogeneous way, in the $E_T(30)$ scale. The following linear correlation (1) was established

$$E_T(30) = \frac{1}{3.797} (737.7 - \lambda^{\max})$$

$$(r = 0.9971, 13 \text{ values}) \quad (1)$$

It should be underlined that this relationship is somewhat closely related to those established (from six solvents) with the spiro-*pyrans* bearing either a 18 or 1 carbon side chains.^{13,14} However, the slope and the intercept have not halfway values between the corresponding extreme ones, and the slope is especially noticeably higher.

To compare measurements on polymers already reported in the literature, λ^{\max} of two homopolymers

Table III Wavelengths of the Vis Absorption Maximum of the Spiro-*pyran* Probe Dissolved in 13 Liquids at 25°C

Liquid	$E_T(30)$ (kcal/mol)	λ^{\max} (nm)	$C_{\text{H}_2\text{O}}$
Cyclohexane	30.9	622	0.000
<i>n</i> -hexane	31.0	622	0.022
Tetrachloromethane	32.4	614	0.008
Benzene	34.3	611	0.021
Ethylacetate	38.1	591	0.045
Chloroforme	39.1	585	0.030
Dichloromethane	40.7	581	0.046
1,2-Dichloroethane	41.3	582	0.132
Acetonitrile	45.6	562	0.097
2-Propanol	48.4	552	0.060
1-Propanol	50.7	548	0.070
Ethanol	51.9	542	0.091
Methanol	55.4	529	0.181

$C_{\text{H}_2\text{O}}$: water content in wt %. $E_T(30)$: liquid polarity parameter.

in solid state was determined and the corresponding $E_T(30)$ was calculated from eq. (1). The same polarity value as that previously measured with the C_{18} spiro-*pyran*¹⁴ was found for PVC (solvent DMF, λ^{\max} : 576 nm, E_T : 41 kcal/mol), but PVAC, after it was purified because of a smell of VAC monomer, gave a lower value (solvent acetone, λ^{\max} : 570 nm, E_T : 44.2 kcal/mol, lit.:¹⁴ 45.5). Indeed, the great influence of contamination of polymers by monomer or polar compounds was already mentioned in the case of PMMA.¹⁰

Influence of the PUI Soft Segment Nature

The semi-empirical polarity parameter $E_T(30)$ of various PUI block copolymers was determined with the spiro-*pyran* indicator S and the values obtained at 25°C are given in Table IV within an experimental error domain of ± 0.15 kcal/mol. According to these results, the influence of the soft segment nature does not appear and, except the case of oligoesters (PCL), which present a rather higher polarity, the probe microenvironment is roughly the same for PUI hav-

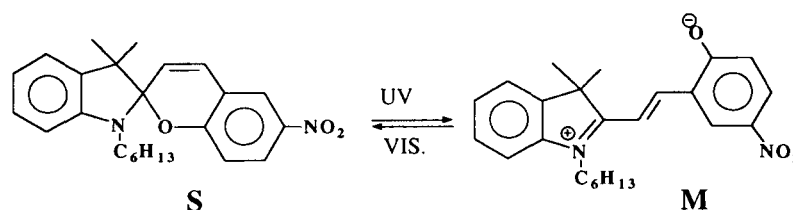


Figure 2 Spiro-*pyran* photoconversion.

Table IV Influence of the Soft Segment Nature on the $E_T(30)$ Polarity Parameter of the Corresponding PUI Determined from the Vis Absorption Maximum of the Photochromic Probe

Polyurethaneimide	λ^{\max} (nm)	$E_T(30)$ (kcal/mol)
PCL 530-MDI-AP	543	51.3
PEG 600-MDI-AP	558	47.3
PTMG 650-MDI-AP	558	47.3
PCL 1250-MDI-AP	550	49.4
PPG 1025-MDI-AP	561	46.5
PTMG 1000-MDI-AP	560	46.8
PEG 1000-MDI-AP	558	47.3
PCD 850-MDI-AP	557	47.6

ing soft segments of different natures. Furthermore, the averaged value of polarity ($E_T = 47$ kcal/mol) and even more distinctly for PCL segments ($E_T > 50$ kcal/mol) is quite greater than the averaged polarity of the most polar functional groups (esters, ethers, carbonates) of the oligomeric segment structure.

Until now, and to our knowledge, no measurement of polarity was reported in the literature concerning block copolymers like PU (i.e., polyurethanes), PUI, etc. In regard to these first results, we will limit us to advance a few assumptions to interpret the high and apparent consistency of polarity of PUI, differing only by the nature of their soft segment.

The PUI are block copolymers and, like PU, they can yield to more or less phase separation and, thus, to the formation of microdomains of different polarities within the material. Numerous studies on PU have already revealed that phase separation in these materials leads to microdomains by more or less important aggregation of the hard blocks. In the case of polyurethanes synthesized from polyethers like PTMG, PEG, and PPG, phase separation is already important even for low length of the soft polyether segment, and increases with the molecular weight of the polyether precursor.¹⁹⁻²²

In our experiments, the Vis spectrum of the illuminated probe (M form) introduced in PUI synthesized from low molecular weight polyethers (Fig. 3) shows a shoulder on the short wavelength side of the absorption band, thus giving evidence for probe solvation by two sites of different polarity: a site of moderate polarity and a site of strong polarity close to the hard blocks. Indeed, the shoulder cannot be assigned to a vibronic structure that rather arises in weakly polar medium. An evidence was the absorption band of the illuminated spiroopyran intro-

duced in an α,ω -dimethylPEG500, which corresponds to the less polar part of PUI copolymers: only one peak was observed, which was not the case for the probe dissolved in an apolar solvent like *n*-hexane (Fig. 4).

Moreover, probe amounts introduced were not sufficient (owing to the absorption coefficient of the merocyanine) to saturate all the differentiated sites, and the zwitterionic merocyanine, a highly polar compound, was preferentially solvated by functional groups that are the most polar while remaining accessible. Such groups could come from junctions between hard and soft blocks and, according to their protic-like polarity (i.e., in the $E_T(30)$ scale: 47 kcal/mol for the maximum, 56 kcal/mol for the shoulder), are likely urethane functions. This assumption is supported by the following measurements or observations:

1. The $E_T(30)$ value for a simple polyurethane (PCL 530/MDI), i.e., without imide groups and phase separation, is about 47.3 kcal/mol.
2. Usual $E_T(30)$ values of ether functional groups are much lower than those determined in PUI: 34.5 for diethylether, 38.6 for dimethoxyethane, and the value measured for

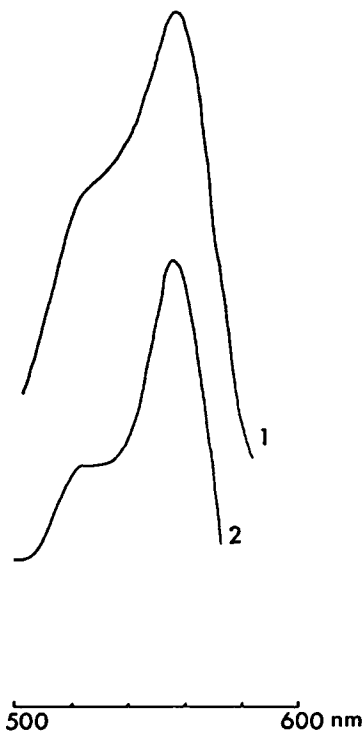


Figure 3 Vis spectra of the illuminated spiroopyran dissolved in polyetherurethaneimides X-MDI-AP: (1) X = PTMG 650, (2) X = PEG 600.

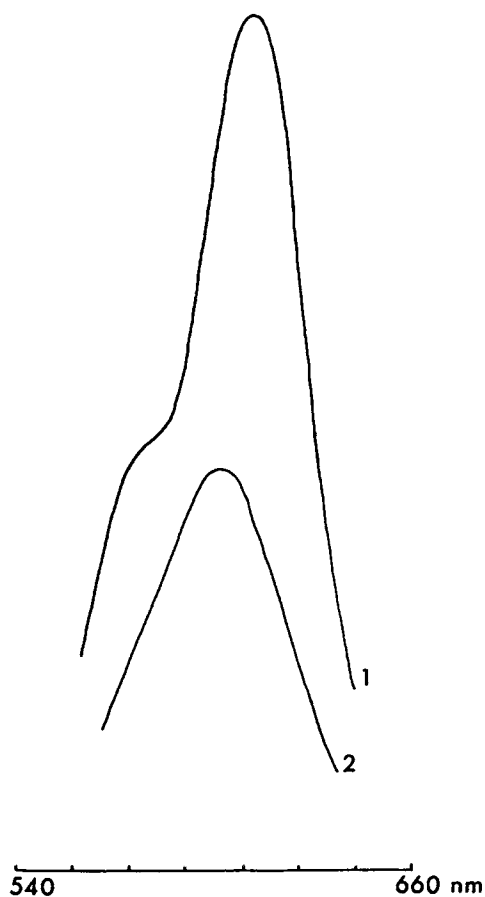


Figure 4 Vis spectra of the illuminated spiropyran probe dissolved in: 1) *n*-hexane, 2) α,ω -diMePEG 500.

α,ω -dimethylPEG 500 raises to only 40.6 kcal/mol (see below).

3. $E_T(30)$ measurement of a commercial aromatic polyetherimide (ULTEM[®]) with the same indicator gave the value of 39.2 kcal/mol.

Unfortunately, $E_T(30)$ values of low molecular weight carbamates are not available to allow a straightforward comparison, but it can be pointed out that the polarity parameter of the very protic *N*-methylformamide reaches 54.1 kcal/mol, value that has to be compared with 42.8 kcal/mol corresponding to the highly polar but aprotic DMF.

So it is clear that the two solvation sites in PUI can be due to urethane links in a partial phase separation similar to what was observed in PU leading to the formation of separate microdomains on short distances. These protic interblock junctions can be located either on greatly polar but not very accessible microdomains, which result from phase separation (shoulder) or in an interphase mixing with ether

groups where they are more accessible but have taken an averaged polarity (main peak). Probe molecules in PUI are then divided proportionally to urethane group ratio and their accessibility.

In the case of polyesterurethaneimide (PCL-MDI-AP) with polyester soft segments of low molecular weights ($M \leq 1250$), a single peak appears in the spectrum of the irradiated spiropyran (Fig. 5): here, the probe detects only one type of urethane group. This result is in agreement with structural investigations made on low molecular weight ($M \leq 1000$) polyester segment-based PU, which afford only very weak phase separation²³⁻²⁵ compared with polyetherurethanes. Urethane groups then only lie in a mixed phase and in a higher content than in the case of a segregated phase. The averaged polarity (E_T #50 kcal/mol) is then higher but is not representative of the flexible segment polarity.

Influence of the Soft Segment Length

Molecular weight increase of PUI flexible segments (not exceeding $M = 2000$, above polymer becomes too fragile) reduces two to three times carbamate function number and, thus, might allow decreases in their influence and to determine a polarity parameter that better reflects the flexible segment nature.

In relation to the behavior differences observed between polyetherurethaneimides and polyesterurethaneimides, the influence of the soft segment length was studied on two representative sets of PUI (Table V): PTMG-MDI-AP (PUI polyether) and PCL-MDI-AP (PUI polyester). The variation of the absorption maximum and, thus, of the related polarity (ΔE_T #1 kcal/mol) is very small in the case of the PTMG set. Shoulder intensity (Fig. 5) is decreasing while the segment length increases and, at last, overlaps with the main band due to the decrease in the content in urethane groups. As it was already reported in the case of related block copolymers, i.e., polyetherurethanes,^{21,24} we assume that phase separation increases with the PUI soft segment molecular weight. Under the above assumption and in good agreement with the UV spectra of the spiropyran probe embedded in the PTMG/MDI/AP, it can be concluded that interphasic groups are no more accessible in the polyetherurethaneimides built from the soft segment of highest molecular weights. In these materials, the probe is, thus, mainly solvated by the urethane functions in the residual mixed phase.

A much more important decrease of polarity was observed when soft segment length increases in PUI

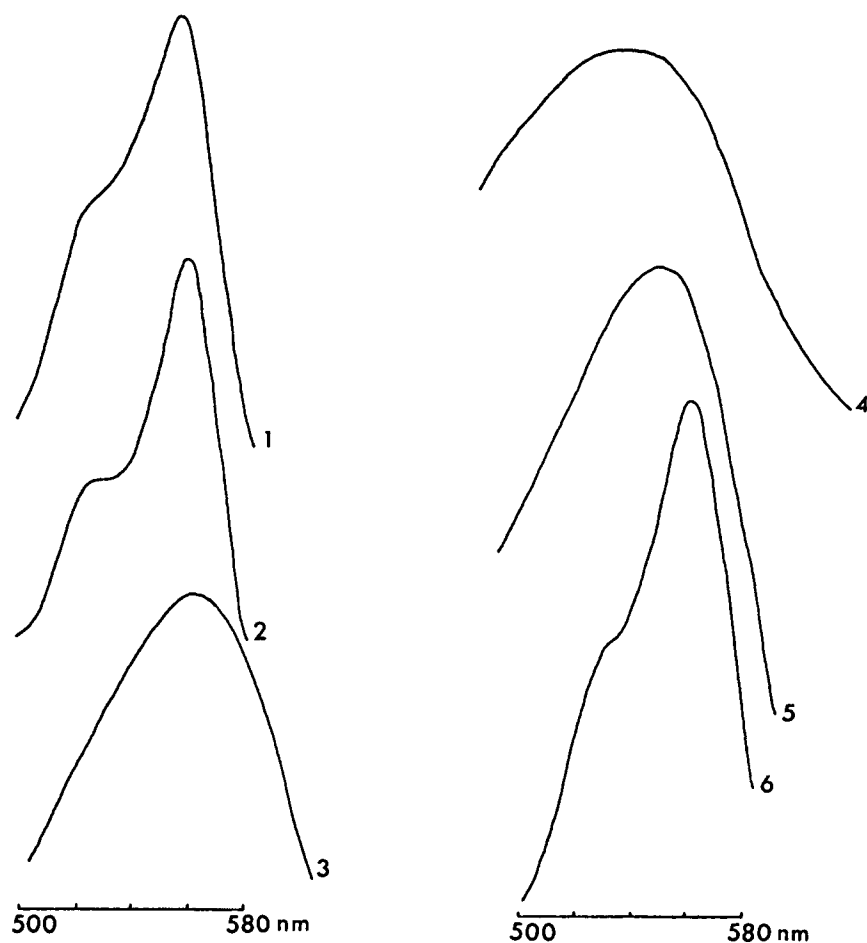


Figure 5 Vis spectra of the illuminated spiropyran probe dissolved in polyether or polyesterurethaneimides X-MDI-AP varying in flexible segment molecular weight: 1) X = PTMG 650, 2) X = PTMG 1,000, 3) X = PTMG 2,000, 4) X = PCL 530, 5) X = PCL 1,250, 6) X = PCL 2,000.

of the PCL set (ΔE_T #5 kcal/mol). Due to a lesser extent of phase separation, a single peak was first observed (Fig. 5) whose bathochromic shift by increasing molecular weight can then be related to the

Table V Influence of the Soft Segment Molecular Weight on the $E_T(30)$ Polarity Parameter of the Corresponding PUI Determined from the Vis Absorption Maximum of the Photochromic Probe

Polyurethaneimide	λ^{\max} (nm)	$E_T(30)$ (kcal/mol)
PTMG 2000-MDI-AP	562	46.3
PTMG 100-MDI-AP	560	46.8
PTM 650-MDI-AP	558	47.3
PCL 2000-MDI-AP	562	46.3
PCL 1250-MDI-AP	550	49.4
PCL 530-MDI-AP	543	51.3

decrease of the number of urethane functions. For PCL2000, a shoulder appeared at the same wavelength than previously in the case of phase separation, and its rather great intensity can be related to a better accessibility of the interphasic urethane groups.

But one of the most important result following from the examination of the highest molecular weight flexible segments was that the measured polarity parameters tended towards the same value, whatever the soft segment nature.

Conclusion about Block Copolymers Polarity Determination

As previously explained, our aim was to define a polarity parameter characterizing the soft segment microenvironment in complex materials (polyurethaneimides). Even if the dye could detect phase

Table VI Influence of the Molecular Weight of Various diMe-PEG (Glymes) on Their $E_T(30)$ Values Calculated from the Vis Absorption λ^{\max} of the Photochromic Probe

Me—(O—CH ₂ —CH ₂) _n —O—Me	Molecular Weight (g/mol)	$E_T(30)$ kcal/mol
Monoglyme $n: 1$	90	38.2 (26)
diDiglyme $n: 2$	134	38.6 (26)
Triglyme $n: 3$	178	38.9 (26)
DiMe-PEG 500 $n: 10.3$	500	40.6
DiMe-PEG-1000 $n: 21.7$	1000	40.4 (50°C)

separation in these block copolymers, which was *a priori* rather unexpected, the study of phase separation in PUI or related polymers, i.e., polyurethanes, was far beyond our scope. Nevertheless, the above results clearly show that, whatever the extent of phase separation in these block copolymers (i.e., even for the soft segment of highest molecular weights), the spiropyran probe is preferentially solvated by the most polar sites, i.e., urethane groups at the ends of the PUI hard blocks. This specific phenomenon leads to a quasiconstancy of the polarity detected by the dye, irrespective of the PUI soft segment nature and, thus, could not depict the PUI pervaporation performances that evidently are strongly dependent on polymer soft blocks (Table II).

Polarity Parameters of Soft Segments Analogs

The introduction of a polarity indicator into PUI did not allow definition of a parameter that was characteristic of the flexible segment influence and of its variation inside the PUI. To solve this problem with the same probe method, isolated soft segments were used: such models are analogs of the flexible segments but were not inserted in the PUI matrix. Assumption was then made that the polarity of the analogs was following the same order as the related segments in the macromolecular structure.

First measurements made on different oligomeric diol precursors have led to very high polarity values, which are fairly sensitive to the molecular weight of the diol: E_T value of PEG600 is 47.6 kcal/mol but 49.5 for PEG300, whereas the E_T value of the dimethylated PEG500 is only 40.6 kcal/mol. These results showed the very strong influence of the polar terminal hydroxyl groups. To greatly reduce the amount of these end groups, homopolymers of molecular weight as great as possible might be used. Unfortunately, such homopolymers, which would

correspond to the different soft segments at an “infinite” length, are not all available and are often contaminated by highly polar impurities (catalyst, etc.): by way of example, commercial polyoxyethylene 3 10^5 , whose high polarity ($E_T(30)$: 45.7 kcal/mol) compared to that of dimethylPEG500, shows this type of contamination.

The end blocking of the diol oligomers by functions similar to those of the main chain (e.g., ether for oligoethers) was, thus, the best way to eliminate the polarity effect of terminal hydroxyl groups. Before syntheses were undertaken, the influence of the oligomer molecular weight on its polarity was investigated from the already known dimethylPEG (glymes). Polarity parameters of the first terms (mono, di, and triglyme) being reported in the literature,²⁶ the two other commercially available polyglymes were analyzed with the spiropyran probe after they were carefully purified by liquid chromatography; measurements were made at 25°C for dimethylPEG500, whereas, in the case of the crystalline solid dimethylPEG1000, a temperature of 50°C was necessary; however, and as already reported,²⁷ the influence of temperature on E_T values is rather low and for ethers, like dibutylether, the variation does not exceed 0.2 kcal/mol between 25 and 50°C.

The E_T values collected in Table VI show the polarity becomes stable for dimethylPEG of the highest molecular weights ($M \geq 500$) after it increases for small oligomers. It seems as the molecules of oligomers have reached a critical length to begin to take the random coil conformation (first entanglements) they can produce a constant microenvironment. This “polymer effect” allows comparison of various end-capped oligomers with different but sufficiently high molecular weight. According to this principle, three new pure end-capped diol oligomers were synthesized and the related E_T values (in kcal/mol) were measured

with the spiropyran probe, i.e., dimethylPTMG650 (E_T : 37.0 at 25°C), dimethylPPG725 (E_T : 36.5 at 25°C), and diacetylPCL530 (E_T : 39.6 at 30°C). PCD850 diol was blocked by reacting it with ethylchloroformate, but purifications failed due to the presence of many polar impurities in the starting diol.

As expected, polarity values, in agreement with the structure, are shown by blocked oligomer diol precursors of the PUI flexible segments, and their variation was significant towards the related properties in pervaporation.

Linear Correlation of the Pervaporation Selectivity

Separation selectivity with respect to alcohol can be well defined by the partial fluxes ratio

$$\frac{J_{\text{EtOH}}}{J_{\text{ETBE}}} = \frac{C'}{1 - C'}$$

(C' = ethanol weight ratio in permeate): the feed mixture composition being kept constant, the value of this ratio is proportional to the usual pervaporation selectivity parameter α .

From the results given in Table II, two linear relationships can be established (Fig. 6) between $\ln(J_{\text{EtOH}}/J_{\text{ETBE}})$ and the $E_T(30)$ polarity parameter of soft segments analogs. Everyone of the correlations corresponds to a set of PUI composed of soft blocks of roughly the same M_w , and twice the molecular weight is responsible for a large increase in fluxes and a gap in selectivity. It must be pointed out that the selectivity increases quite strongly with the polarity of the soft segment oligomer chain according to the presence and the number of polar functions (ether, ester, carbonate, etc.), and such correlations might help to better optimize polymer film performances.

CONCLUSION

During the pervaporation (PV) of mixtures of two organic liquids through polymer films of various chemical structures, the transfer selectivity can be quite linearly correlated to the polymer polarity. This result confirms *a posteriori* that the sorption effects are mainly governing the PV mass transfer properties variations in the case of the PUI investigated and, thus, justifies the first assumption of this work. Such correlations apply to polar ternary systems (polar polymer and polar mixture), the

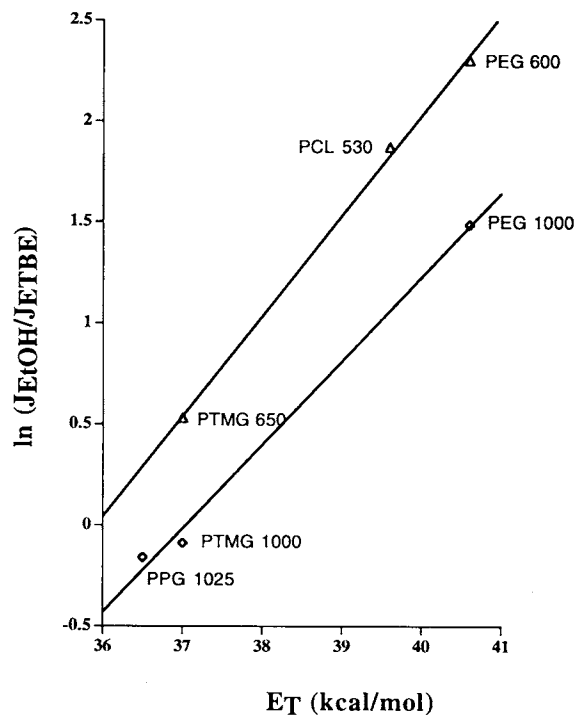


Figure 6 Correlation between pervaporation selectivity and flexible segment (X) polarity during separation of EtOH–ETBE azeotropic mixture at 30°C through films of polyurethaneimides X-MDI-AP.

component preferentially permeated displaying specific interactions with the polymer as it was already observed for the pervaporation of water–ethanol mixtures (water being the preferential permeant) through hydrophilic polymer films.²⁸ In the present work, the above feature was established for wholly organic EtOH–ETBE mixtures (EtOH being the preferential permeant) and polar block copolyurethaneimides (PUI) including soft segments, which are responsible for swelling and transport. Moreover, the selectivity dependence on the oligomeric segment size was also observed, these two parameters varying in an opposite way.

However, in our investigations, the problem encountered was to define, for block copolymers, a polarity by a semiempirical parameter including polar, polarization, and hydrogen bonding effects, as was already done for organic solvents. The solvatochromic dyes generally used for solvent polarity determination were not suitable because of their low polymer solubility associated to their systematic degradation in PUI.

An indolinospiryran derivative whose closed form is soluble in PUI materials proved to be, after UV illumination, a reliable polarity indicator giving values linearly correlated to the E_T scale of Dimroth

and Reichardt, as it was found by Yoshikawa et al. in the case of a parent dye.

The spiropyran probe revealed itself particularly appropriated for the study of high molecular weight homopolymers as well as oligomers, provided that the possible higher polarity of the end groups was eliminated by a suitable functional group blocking. Moreover, by using oligomers of increasing size, a "polymer effect" was observed: polymer polarity increases with the molecular weight up to a limit value corresponding to a \overline{DP} of roughly 10 or 12.

More complicated is the case of block copolymers like PUI, when attempts are made to determine the polarity of flexible segments that are less polar than the hard blocks responsible for the strong material cohesion. Spiropyran probe is, indeed, preferentially solvated by the most polar sites of the polymeric network, i.e., in PUI, the urethane junctions between soft and hard blocks and, thus, cannot indicate soft segments polarity, whatever the extent of phase separation. However, due to partial phase segregation, these protic functional groups are in two types of microenvironments depicted by two different polarity parameters. This probe behavior might then be used to detect phase separation, which usually occurs in block copolymers, but it was far beyond our scope, which was, in fact, only restricted to soft segment polarity measurements in block copolymers. Due to specific solvation of the spiropyran probe by the most polar sites of the materials investigated, our first approach failed to characterize the soft segment polarity parameter straight in the polymer structure.

However, the suggested solution to the problem of PUI soft segment polarity determination, consisting of direct polarity measurements on precursor oligomers after polar end-groups modification, gave reliable results and should be generally applied.

Financial support for the work was provided by Centre National de la Recherche Scientifique (CNRS), Le Carbone Lorraine and the Economic European Communities (EEC).

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Received August 24, 1994

Accepted November 30, 1994