

Inverse gas chromatographic study of some polyethers

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Abstract

Surface properties of two polyethers containing pyridine and pyrazine units, respectively, were compared with polysulfone. The polymers were investigated by inverse gas chromatography. The dispersive contributions of the surface free energy and the K_A and K_B parameters expressing the ability of the stationary phase to act as Lewis acid or Lewis base were calculated. It was shown that the polymer with pyridine units possessed extraordinarily high K_B values whereas the polysulfone showed amphoteric behaviour with predominant Lewis basicity. © 1998 Elsevier Science Ltd. All rights reserved.

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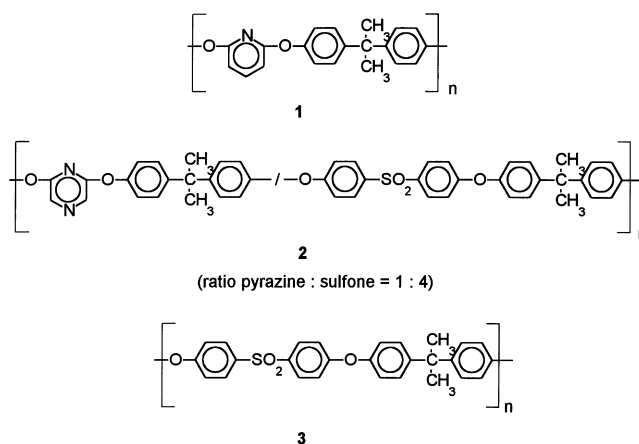
1. Introduction

Polymers with polar groups are required for many applications, for example polymer blending, surface modification, bioactive materials and membranes. We recently published new results about the synthesis and properties of amidine and pyridine group containing polymers [1,2]. It was shown by inverse gas chromatography (i.g.c.) that the surface properties of these polymers are strongly determined by the basic nature of the polar groups [2].

Another application is the utilization of pyridine and pyrazine group containing polyethers and polyether sulfones for membranes [3,4]. For example, methylated poly(pyridine ether sulfones) exhibit excellent gas separation properties which are comparable with the best poly(ether imide) membranes. High selectivities are found for CO₂/CH₄ and He/N₂ separation. Additionally, the reactivities of various alkylating agents such as methyl triflate, dimethyl sulfate, methyl methanesulfonate, methyl iodide and γ -propanesulfone have been investigated and it was found that the alkylation of poly(pyridine ether)s is sterically hindered by substitution in the 2,6-position [3,4].

This paper reports investigations of the surface properties of three different polyethers by i.g.c. In two of them, pyridine and pyrazine groups were incorporated into the polymer chain in order to increase the surface polarity. The two nitrogen-containing polymers **1** and **2** were

compared with the conventional polysulfone **3**, which is known to be one of the most suitable materials for membranes. The behaviour of the polymers was compared by means of dispersive contributions of the surface free energy, which is a measure for dispersive interactions, as well as the K_A and K_B values which describe the ability of a polymer surface to act as electron acceptor or donor.



2. Inverse gas chromatography

Inverse gas chromatography involves the adsorption of known, volatile probe molecules onto the surface of an unknown stationary phase. From the interactions of the

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probe molecules with the solid a variety of parameters and magnitudes may be calculated.

Depending on the amount of injected probe molecules, i.g.c. measurements can be carried out in two different concentration ranges: (i) at finite concentration and (ii) at infinite dilution. We performed measurements at infinite dilution. Here, lateral interactions of probe molecules are negligible and the retention times only depend on the active sites of the investigated surface.

The values which were directly measured were the retention time of a non-interacting marker (methane), t_M , the retention times of solutes, t_R , the mass of the stationary phase, i.e. of the polymers, m_{Poly} , the temperature of the column, T , the flow rate, F , the column inlet pressure, p_i and the column outlet pressure, p_o . The net retention volume, V_N , can be computed from:

$$V_N = F_{\text{CORR}} \cdot t_R' \quad (1)$$

where F_{CORR} is the corrected flow rate depending on F , T , p_i and p_o . t_R' is the effective retention time, i.e. the difference between t_R and t_M . From the net retention volume the specific retention volume, V_g , standardized to 0°C and 1 g mass of stationary phase (polymer) is found from [5]:

$$V_g = \frac{273.15K \cdot V_N}{T \cdot m_{\text{Poly}}} \quad (2)$$

For the evaluation of the dispersive interactions between the mobile and the solid phase two different variants have been described [6,7]. In this paper we have only applied the approach described by Dorris and Gray [6].

Assuming that in i.g.c. measurements with n-alkanes as probe molecules only dispersive interactions are to be taken into account and that each methylene group of the n-alkanes has its own contribution to the free energy of adsorption, the dispersive contribution of the surface free energy of the stationary phase, γ_s^d , can be calculated according to:

$$\gamma_s^d = \frac{(\Delta G_{\text{CH}_2})^2}{4N^2 a_{\text{CH}_2}^2 \gamma_{\text{CH}_2}} \quad (3)$$

N is Avogadro's number, a_{CH_2} and γ_{CH_2} are the surface area (6 \AA^2) and the surface free energy of one methylene group, respectively. ΔG_{CH_2} is the contribution of one methylene group to the free energy of adsorption. This increment results from the slope of the plot of $RT \ln V_g$ vs. the number of C atoms of the respective n-alkanes.

In addition to dispersive interactions, electron donor–acceptor interactions take place when polar (specific) solutes are injected into the chromatographic column. Consequently, the variation of the free energy of adsorption, ΔG_a , may be written as a sum of dispersive (d) and specific (sp) contributions [8,9]:

$$\Delta G_a = \Delta G_a^d + \Delta G_a^{\text{sp}} \quad (4)$$

In this work, the ΔG_a^{sp} values were obtained by Sawyer's method [10,11]. Sawyer and Brookman plotted $RT \ln V_g$ vs.

the boiling temperatures of solvents. ΔG_a^{sp} resulted from the distance between the $RT \ln V_g$ values of polar solutes and the straight n-alkane line. From its temperature dependence the enthalpy of specific interactions, ΔH_a^{sp} , can be calculated

$$\Delta G_a^{\text{sp}} = \Delta H_a^{\text{sp}} - T \Delta S_a^{\text{sp}} \quad (5)$$

where ΔS_a^{sp} is the specific entropy of adsorption. ΔH_a^{sp} results from the slope of the $\Delta G_a^{\text{sp}}/T$ vs. $1/T$ plot.

There are various concepts to quantify electron donor–acceptor interactions. The acid–base concepts introduced by Drago [12,13] and Gutmann [14] are the most widely used in i.g.c. The 4-parameter equation described by Drago et al. allows prediction of the enthalpies of adduct formation in gas-phase or poorly solvating media for several Lewis acid–base systems. These parameters represent covalent and electrostatic contributions.

Gutmann attributed donor (DN) and acceptor (AN) numbers to Lewis bases (electron donors) and Lewis acids (electron acceptors). Later, the acceptor numbers were corrected for van der Waals contributions (AN^*) by Riddle and Fowkes [15]. The advantages and disadvantages of both methods were compared by Schreiber et al. [16,17]. In this paper we have chosen Gutmann's approach [14].

Using ΔH_a^{sp} values, K_A and K_B parameters can be calculated according to Eq. (6) [18]. The validity of this method was proven by Schreiber et al. [17]:

$$-\Delta H_a^{\text{sp}} = K_A DN + K_B AN^* \quad (6)$$

K_A and K_B describe the Lewis acid–base character of investigated surfaces. K_A results from the slope of the $-\Delta H_a^{\text{sp}}/AN^*$ vs. DN/AN^* plot. The intercept of the straight line represents K_B .

3. Experimental

3.1. Materials

Polyethers containing heterocycles (**1**, **2**) were synthesized as described previously [19]. Polysulfone (**3**) was obtained by nucleophilic aromatic reaction of bisphenol-A with 4,4'-dichlorodiphenyl sulfone according to Lezzi and Huang [20]. An excess of bisphenol-A was added to the reaction mixture in order to obtain OH group terminated oligomers. Details about their synthesis and use for preparation of multiblock copolymers were described in ref. [21]. Properties of polymers **1–3** are summarized in Table 1.

3.2. I.g.c. measurements

An HP 5890 Series II gas chromatograph equipped with a flame ionization detector was used for i.g.c. measurements. The carrier gas was helium. The flow rate of 10–15 ml/min was measured and controlled by an electronic flow meter. The flow rates were corrected for the pressure drop along the column and the temperature differences between the column

Table 1
Sample characteristics

Sample	Colour	η_{inh}^a (dl/g)	M_n^b (g/mol)	Mass loss ^c	
				1% at	10% at
1	white	0.075	8300	406°C	479°C
2	light brown	0.076	7150	184°C	490°C
3	white	0.255	7500	380°C	492°C

^a In chloroform; $c = 0.2$ g/dl.

^b GPC in chloroform using polystyrene standards.

^c Investigated by TGA.

Table 2
 γ_S^d values of investigated polymers

Polymer	γ_S^d (mJ/m ²)					
	32°C	40°C	50°C	110°C	130°C	150°C
1	37.2	36.6	33.6	–	–	–
2	44.6	45.0	46.1	–	–	–
3	–	–	–	34.9	34.9	33.9

and the electronic flow meter. The measurements were carried out in a temperature range from 32°C to 150°C. Hamilton syringes were used for injection of very small amounts of probe molecules. Net retention times were determined as the difference between the retention times of the solutes and a non-interacting marker (methane) using peak maxima. The retention peaks obtained were almost symmetrical and independent of the amounts of probe molecules injected into the column.

Polymers were crushed and sieved with an electromagnetic jig. Particle sizes were in the range 80–150 μ m. The sieved polymers were packed into glass columns (0.5 m length, 4 mm inner diameter) without further treatment. n-Hexane, n-heptane, n-octane, n-nonane, n-decane,

n-undecane, chloroform, dichloromethane, tetrahydrofuran, diethyl ether, acetone, ethylacetate and acetic acid were used as probe molecules (solutes). The solvents of analytical grade purity (p.a.) were dried with molecular sieves and used without further purification.

4. Results and discussion

In order to determine the dispersive contributions of the surface free energies, γ_S^d , of the polymers 1–3, the retention behaviour of different n-alkanes was investigated. Analysis of the resulting retention volumes according to the procedure of Dorris and Gray [6] yielded the γ_S^d values shown in

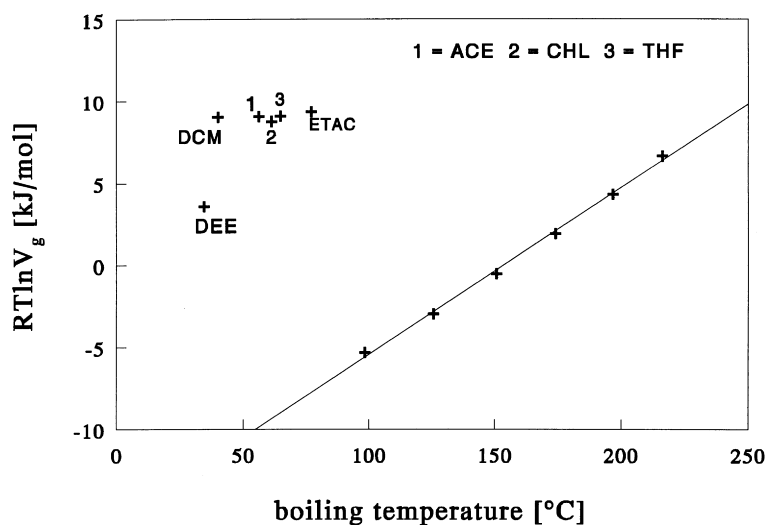


Fig. 1. Determination of the specific contribution of the free energy of adsorption, $-\Delta G_a^{sp}$ (Sawyer method, 110°C, sample 3). DEE: diethyl ether, DCM: dichloromethane, CHL: chloroform, ACE: acetone, THF: tetrahydrofuran, ETAC: ethyl acetate.

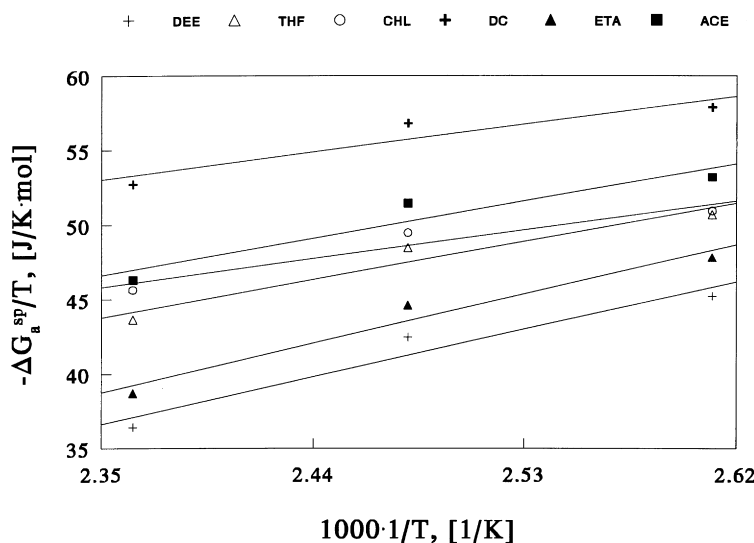


Fig. 2. Determination of the specific adsorption enthalpy (sample 3). DEE: diethyl ether, THF: tetrahydrofuran, CHL: chloroform, DCM: dichloromethane, ETAC: ethyl acetate, ACE: acetone.

Table 2. Any significant influence of the pyridine or pyrazine group on the dispersive surface interactions of the polyethers under investigation could not be concluded. The values obtained are comparable to those of aromatic polyesters [22].

Measurements with solvents of different polarity allowed evaluation of the Lewis acid–base properties of the sample surfaces. The procedure is demonstrated for polymer 3. According to Sawyer et al. [10,11], $RT \ln V_g$ values vs. boiling temperatures of the respective solvents were plotted. The plots are shown in Fig. 1.

The values for the n-alkanes lie on a straight line, reflecting the reference state for the dispersive interactions. Deviations of the other measuring points from this reference line point to additional interactions caused by the polar nature of the solvents. The distances from the reference line correspond to the specific contributions of the free

Table 3
Semi-quantitative K_A and K_B parameters

Polymer	K_A	K_B	K_B/K_A
1	0.13	2.24	17.2
3	0.31	1.28	4.1

energy of adsorption, ΔG_a^{sp} . From their temperature dependences, shown in Fig. 2, enthalpies of specific interactions, ΔH_a^{sp} , could be obtained.

In order to obtain the characteristic surface parameters K_A and K_B , the ΔH_a^{sp} values were related to the donor and acceptor numbers of the solvents using Eq. (6). The respective plot for polymer 3 is shown in Fig. 3 and the resulting K_A and K_B values are summarized in Table 3.

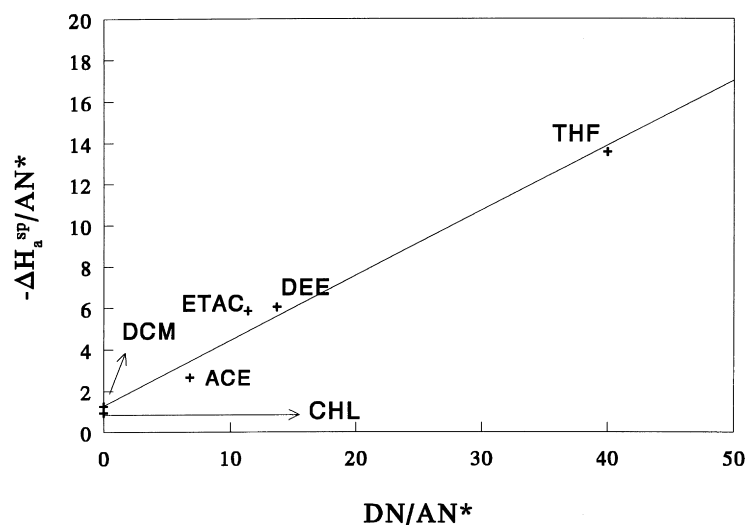


Fig. 3. Determination of K_A and K_B (sample 3).

Table 4
 K_A and K_B parameters of different polymers

Compound	K_A	K_B	K_B/K_A	Reference
Vectra®	0.20	0.13	0.65	[22]
Vectra® (modified with NH ₃)	0.16	0.73	4.57	[22]
Vectra® (modified with Cl ₂ /CO ₂)	0.57	0.19	0.33	[22]
PET/PHB ^a	0.18	0.14	0.78	[22]
PET/PHB (with amide groups)	0.44	0.44	1.0	[22]
Polycarbonate	0.55	1.93	3.51	[22]
Polystyrene	0.06	0.35	5.83	[24]
Chlorinated polyethylene	0.35	0.06	0.17	[24]
Nylon-6,6	0.08	0.40	5.0	[23]
Glass fibre	0.34	0.40	1.18	[23]
Aromatic polyester	0.21	0.51	2.43	[2]
Polyester (with pyridine groups)	0.13	2.70	20.7	[2]
Polyamides	0.10	0.4–1.0	4–10	[25]

^a Poly(ethylene terephthalate-co-oxybenzoate)

It should be mentioned that for polymer **2** no reproducible conditions were found, so that with respect to polar interactions only polymer **1** and **3** could be compared.

Based on earlier results obtained for polyamides and polyesters with pyridine units in the main chain [1,2], it was expected that the poly(pyridine ether) **1** is a Lewis base. Polysulfone **3** was also assumed to be an electron donor. The evaluation of the retention behaviour of specific solutes and the resulting K_A and K_B values proved these expectations. Both polymers showed distinct donor properties which are, however, more pronounced for polymer **1**. Compared to other main chain polymers the K_B value of **1** is extraordinarily high. Only polycarbonate with $K_B = 1.93$ and a polyester with pyridine-2,6-dicarboxy units [2] with $K_B = 2.70$ possess similarly high values. Polysulfone **3** also exhibits a relatively high K_B value compared to several aromatic polyesters [2,22], or even compared to nylon-6,6 [23]. Some K values from the literature are summarized in Table 4

In contrast to polymer **1**, polysulfone **3** was found to be amphoteric, i.e. it is able to act as a Lewis acid and a Lewis base, but the Lewis basicity predominates. The K_B/K_A ratio is similar to that of polycarbonate, whose sum of K_A and K_B values is, however, higher.

Comparing our results, it can be concluded, that pyridine units have the greatest influence on surface properties. The nucleophilic character is distinctly improved when pyridine units are introduced into polymer chains. Sulfone and ester group containing polymers were amphoteric with a predominance of nucleophilic behaviour.

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