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Surface characterization of polyethersulfone by inverse gas chromatography

Hongfeng Zhang, Qianru Zhang, Baoli Shi (✉), Caiying Sun

College of Science, Northeast Forestry University, Harbin, Heilongjiang 150040, PR China
E-mail: shi_baoli@yahoo.com; Fax: +86 451 82192327

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Summary

In this work, the surface properties of polyethersulfone (PES) were analyzed by inverse gas chromatography (IGC). Five *n*-alkanes (*n*-C_6, *n*-C_7, *n*-C_8, *n*-C_9, and *n*-C_{10}) were chosen as apolar probes to characterize the surface dispersive free energy at different temperatures. Acetone (Acet), dichloromethane (DCM) and tetrahydrofuran (THF) were chosen as polar probes to detect the Lewis acid-base parameters, i.e. the Lewis acidic number K_a and Lewis basic number K_b. It was found that the surface dispersive free energy was 32.09, 30.41, 28.52, and 27.21mJ/m^2 at 60, 70, 80, and 90°C, respectively. The Lewis acidic number K_a is 0.086 and Lewis basic number K_b is 1.523. Compared with other polymers characterized by IGC, the PES belongs to a strong basic polymer material.

Introduction

Polyethersulfone (PES) is a special engineering plastic. It was first manufactured by ICI Company (U.K.) in 1972. Nowadays, the main trade names and manufacturers of PES are Victrex ^{TM} (ICI company, U.K.), ultrason ^{TM} (BASF company, Germany) and Astyel ^{TM} (3M company, U.S.) [1]. PES is a versatile thermoplastic. It belongs to high T_g polymers. Figure 1 shows the chemical structure of PES. Generally, PES possesses high mechanical intensities, thermal stabilities and chemical resistances. In addition, it has low creep properties, flame retardancies, excellent insulation properties and high dielectric strengths. Therefore, PES is widely used in aviation, microelectronics, automobile, membrane separation etc [2]. In membrane separation fields, PES has been prepared to ultrafiltration, reverse osmosis and nanofiltration membranes [3-5]. Furthermore, it is made into hemodialysis membranes due to its perfect biocompatibilities [6]. Many PES composite materials were researched in order to enhance its performances further, such as carbon fiber reinforced PES, glass fiber reinforced PES, PES/PA and PES/PEEK alloy [7-9].

For polymer composites, alloys and blends, the miscibilities of the species have great effects on their performances. The most important method of improving the miscibility is decreasing the differences in the facial or interfacial energies of the species. Therefore, it is very significant to research the surface properties of polymer

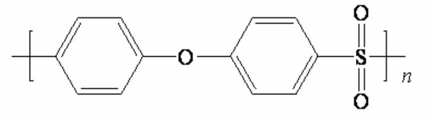

Figure 1. Chemical structure of polyethersulfone

matrix. Generally, surface forces or energies come from two categories, i.e. the dispersive forces and special forces (e.g. hydrogen bonds). Recently, the Lewis acid-base concept for describing surface forces has been widely accepted. According to the Lewis acid-base theories, surface interactions can be classified into two categories: Lifshitz-van der Waals interactions and Lewis acid-base interactions. Hydrogen bond can be taken as a Lewis acid-base interaction [10]. Santos *et al.* has used the Lewis acid-base theories to explain the miscibility and mechanical properties of PC/PBT blends [11,12].

The usual techniques for measuring surface acid-base properties are isoelectric point, indicator dye adsorption, X-ray photoelectron, calorimetry and inverse gas chromatography (IGC) [13]. Nowadays, IGC has been developed as a universal technique of surface characterization for solid materials, especially for polymer materials [14-17]. The mechanisms, experimental processes and data reduction methods of IGC had been discussed by Santos *et al.* in detail [12].

To our knowledge, the surface dispersive free energies and acid-base properties of PES are not measured until now. In this study, IGC was used to characterize quantificationally the Lewis acid-base properties and surface dispersive free energies of PES. The results will be significant to the works relating to PES, especially to PES composite materials.

Experimental

Materials

PES Ultrason® 6020P (M_w 5800, T_g 225°C) was purchase from BASF, Germany. It was dried at 120°C for 12h before use. Chromosorb 101 (80-100 mesh) was purchased from Shanghai Chemical Plant, China. For the IGC analysis, the apolar *n*-alkanes probes were *n*-hexane (*n*-C_6), *n*-heptane (*n*-C_7), *n*-octane (*n*-C_8), *n*-nonane (*n*-C_9), and *n*-decane (*n*-C_{10}). The polar probes were dichloromethane (DCM), acetone (Acet) and tetrahydrofuran (THF). They were analytical grade solvents purchased from Tianjin Kermel chemical reagents development center, China. Ethine was used as the non-interacting probe, which was prepared in our laboratory. The characteristics of the probe solvents are listed in Table 1 [18,19].

IGC Instrument and Experimental Conditions

The chromatographic measurements were carried out on a GC-900A gas chromotograph equipped with a flame ionization detection (FID) system, which was

Table 1. Characteristics of the probe solvents

Probe	a ($\times 10^{20}$m^2)$^{(1)}$	γ_l^d (mJ/m^2)$^{(2)}$	$a(\gamma_l^d)^{0.5}$ ($\times 10^{20}$m^2(mJ/m^2)$^{0.5}$)	AN^* (kJ/mol)$^{(3)}$	DN (kJ/mol)$^{(3)}$
n-C_6	51.5	18.4	221	–	–
n-C_7	57.0	20.3	257	–	–
n-C_8	63.0	21.3	291	–	–
n-C_9	69.0	22.6	329	–	–
n-C_{10}	75.0	23.4	363	–	–
DCM	31.5	27.6	165	16.3	0.0
Acet	42.5	16.5	173	10.5	71.4
THF	45.0	22.5	213	2.1	84.4

(1) *a*: Molecular area of probe;
(2) γ_l^d: Surface free energy of probe;
(3) AN^* and *DN*: Gutmann's modified Acceptor number and Donor number of probe.

purchased from Shanghai TianPu Analytical Instrument Ltd., China. Nitrogen was used as the carrier gas. The flow rate was measured at the end of column by using a soap bubble flow meter. The column was prepared from a stainless steel tube (column length 60cm, internal diameter 2.56mm, external diameter 3.00mm). It was washed with acetone before use. The PES inert stationary phase was prepared by the following procedure. First, PES was dissolved in N-methyl-pyrrolidine, then the chromosorb was added. The solvent was volatilized at certain temperature to make PES deposit onto the chromosorb, and then the chromosorb covered with PES was packed in the column. The column was aged at 120°C under fast nitrogen flow rate (25ml/min) for 8 hours before measurement. The probe solvents were injected manually, using a 1.0μl Hamilton syringe. The injection volumes were from 0.05 to 0.1μl to accord with infinite dilution conditions [20]. For each measurement, the probe solvents were injected at least three times. The IGC experiments were performed at 60, 70, 80, and 90°C.

Results and discussion

The data were manipulated by the same procedures as described in Ref. [12]. Figure 2 shows the plots of $RT\ln(V_n)$ versus $a(\gamma_l^d)^{0.5}$ of *n*-alkanes at the four temperatures. From the slope of these lines, the surface dispersive free energy γ_s^d of PES at each temperature was calculated. The results are listed in Table 2. It shows that the surface dispersive free energies increase with the increasing of temperatures. Table 3 lists the surface free energies of some polymers measured by IGC. It shows clearly that PANI and $PPyNO_3$ are high-energy materials [21,22]. Compared with the polymers in Table 3, PES belongs to a low surface energy polymer.

Figure 3 shows the plots of the adsorption free energy by Lewis acid-base interactions ΔG_a^s of the polar probes at 60°C. Table 4 lists the enthalpy of specific interaction ΔH_a^s of the polar probes. The negative data mean that the adsorptions of polar probes on PES are all exothermic processes.

Figure 4 shows the plot of $-\Delta H_a^s / AN^*$ versus DN / AN^* for the polar probes. The linear correlation for the three polar probes is fine. The Lewis acidic number K_a is 0.086, which is obtained from the slope, and the basic number K_b is 1.523, which is obtained from the intercept. Meanwhile, the numbers of K_a, K_b and K_b/K_a for other materials are listed in Table 5.

The results of K_b/K_a listed in Table 5 show that PES is a strong Lewis basic polymer, the acidity is very weak. This can be elucidated from its molecular structure as shown in Figure 1. The repeated segment of PES consists of two benzene rings, an ether bond and sulfuryl groups. The delocalized π-electrons on the benzene rings and the lone electron pairs of oxygen atoms of the sulfuryl groups must endow PES with strong Lewis basic property. Because no groups of strongly accepting electrons existing in the molecular chains, such as methylene group(-CH_2-), the acidity of PES is weak.

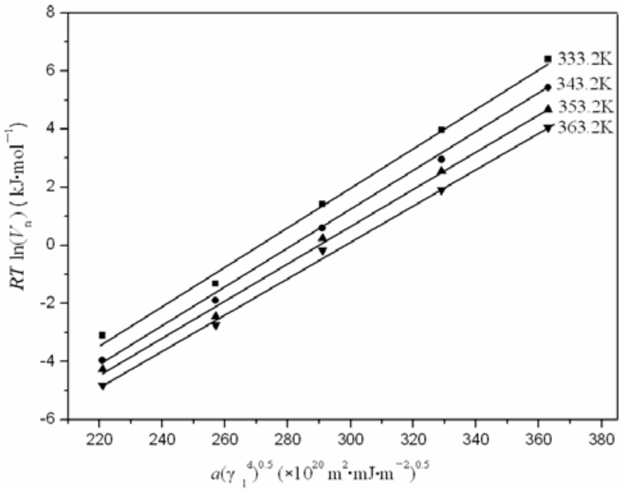

Figure 2. $RT\ln(V_n)$ vs. $a(\gamma_l^d)^{0.5}$ for n-alkanes at different temperatures

Table 2. Surface dispersive free energy γ_s^d (mJ/m^2) of PES

Temperature (K)	333.2	343.2	353.2	363.2
PES	32.09	30.41	28.52	27.21

Table 3. Surface dispersive free energy γ_s^d (mJ/m^2) of some polymer materials

Polymer materials *	γ_s^d	Temperature (K)	Reference
PC	37.3-29.3	353-393	[11]
PBT	44.7-40.7	295-318	[11]
$PPyNO_3$	113	321	[21]
PMMA	40	321	[21]
PANI	87.3-89	331-341	[22]
POT	34.2	331	[22]

* PC: Polycarbonate; PBT: Poly(butylene terephthalate); $PPyNO_3$: Polypyrrole (nitrate-doped); PMMA: Poly(methyl methacrylate); PANI: Polyaniline; POT: Poly(3-octyl thiophene).

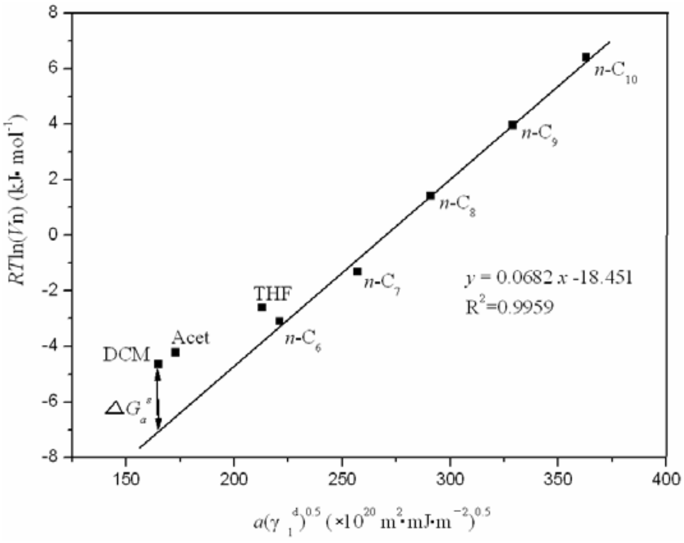

Figure 3. Surface free energy of adsorption vs. $a(\gamma_l^d)^{0.5}$ for *n*-alkanes and polar probes on PES at 333.2K.

Table 4. Enthalpy of specific interactions ΔH_a^s (kJ/mol) of DCM, Acet and THF adsorbed on PES

Probes	DCM	Acet	THF
$-\Delta H_a^s$	24.049	22.840	10.431

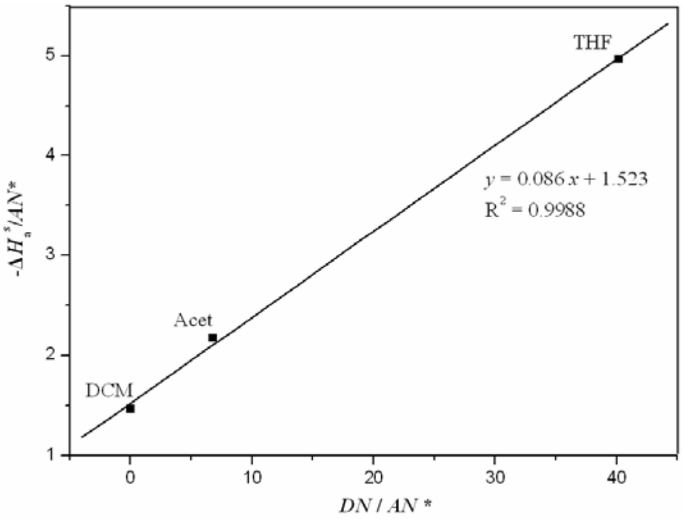

Figure 4. Determination of Lewis acid-base numbers K_a and K_b of PES.

Table 5. The Lewis acidic and basic numbers of some polymers

Polymer materials	K_a	K_b	K_b/K_a	Reference
PC	0.09	0.48	5.33	[11]
PBT	0.49	0.96	1.96	[11]
PVC *	0.149	0.218	1.46	[20]
$PPyNO_3$	0.115	0.192	1.67	[20]
PMMA	0.076	0.354	4.66	[21]
PANI	0.071	0.255	3.59	[21]
POT	0.08	0.091	1.14	[21]
PES(Ultrason E 6020P)	0.086	1.523	17.71	this work

* PVC: Poly(vinyl chloride)

Conclusions

In this work, the surface dispersive free energies and Lewis acid-base properties of PES (Ultrason® 6020P) were characterized by inverse gas chromatography. The surface dispersive free energy was 32.09, 30.41, 28.52, and 27.21mJ/m^2 at 60, 70, 80, and 90°C, respectively. The surface dispersive free energies decrease when the temperature increases. Compared with other polymers characterized by IGC, PES is a low surface energy and strong Lewis basic polymer material.

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