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Surface properties of polyamidines investigated by inverse gas chromatography

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Abstract

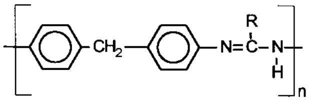
Polymers containing amidine groups –NH–CR=N– (R: –H, $-CH_3$, $-C_6H_5$) in the main chain were characterised by inverse gas chromatography. In dependence on the residue R the dispersive contributions of the surface free energy were determined. From interactions with polar probe molecules the Lewis acid–base properties of the polymer surfaces were concluded. Semiquantitative K_A- and K_B-parameters describing the possibility of the stationary phase to act as electron donor or acceptor showed that polyamidines are Lewis bases. The results were discussed with respect to the conformation of the amidine group and interactions between the polymer chains. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamidines; Inverse gas chromatography; Surface properties

1. Introduction

Chemistry of low molecular weight amidines has been intensively investigated [1]. Due to their basic behaviour amidines are able to interact with several substances. Salt formation [2] and complexation [3] as well as biological [4] and catalytical activity [5] were described.

It is expected that polymers containing amidine groups possess properties similar to that of low molecular weight amidines. Polymers with amidine groups laterally bonded [6,7] or directly incorporated with one [8–10] or two nitrogens in the polymer backbone [11–15] are known. Recently, we reported the synthesis and properties of aromatic polyamidines with both nitrogens in the polymer backbone (–Ar–NH–CR=N–) [16–18]. These polymers were obtained by polycondensation of aromatic diamines with respective orthoesters. ^{1}H, ^{13}C and ^{15}N NMR spectroscopic investigations in solution and in solid state showed that the configuration of the amidine group is strongly dependent on the residue R. In polyformamidines (R=H), strong interactions caused by hydrogen bonds could be evidenced [19–21]. This paper describes the influence of residue R on the surface properties of the polyamidines **1a–1c** based on 4,4′-diaminodiphenyl methane. The surface properties were investigated by inverse gas chromatography (IGC).



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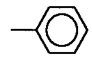
	1a	**1b**	**1c**
R:	H	CH_3	

The IGC is based on interactions of known probe molecules (solutes) with an unknown sample which serves as stationary phase of a chromatographic column. From these interactions, sample properties can be concluded. In recent years, numerous parameters such as degree of crystallinity, glass transition and melting temperatures, degree of crosslinking, partition coefficients, activity coefficients, solution parameters, enthalpy of mixing, enthalpy of adsorption and interaction parameters of polymer–polymer systems were determined by IGC [22–24]. IGC also provides information about the surface free energy and Lewis acid–base interactions on surfaces. Polymer surface properties determined by IGC were described for liquid crystalline polyesters (Vectra® and PET/PHB) [25], poly(dimethacrylate)s [26–29], poly(vinyl chloride) [30], poly(2-ethyl hexyl methacrylate) [31], a styrene–butadiene-copolymer [32] and polymers containing 4-vinylpyridine [33–35].

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Recently, we proved by IGC that aromatic polyesters containing pyridine units in the main chain [36] behave like Lewis-bases.

2. Inverse gas chromatography

The IGC is called 'inverse‘ because it is an inversion of conventional gas chromatography with the stationary phase being under investigation.

Depending on the amount of probe molecules injected, measurements may be carried out either at finite concentration or at infinite dilution. In case of finite concentration non-linear isotherms are obtained and adsorption isotherms can be constructed. When IGC takes place at infinite dilution (zero surface coverage) lateral interactions of probe molecules are negligible, so that only interactions between solute and active sites at the surface of the stationary phase can be assumed. In that case the adsorption isotherms are in a region where Henry's law is valid. Our measurements were carried out at infinite dilution.

In order to calculate dispersive contributions of surface free energy of the stationary phase γ_S^d two different variants were chosen. The first method has its origin in Fowkes [37]. Assuming that in IGC measurement with *n*-alkanes as probe molecules only dispersive interactions are taken into account, the relation between the work of adhesion W_A and the dispersive contribution of the surface free energy of the solute γ_L^d and the stationary phase γ_S^d can be described by Eq. (1)

$$\mathrm{N}aW_A = \mathrm{R}T \ln V_g + C = \mathrm{N}a2(\gamma_S^d)^{1/2}(\gamma_L^d)^{1/2} \tag{1}$$

where N is the Avogadro number, R the gas constant, T the temperature of the column, V_g the specific retention volume, C is a constant depending on the specific area of stationary phase and the choice of a reference state [38,39] and a the surface area of the adsorbed probe molecule [40]. The plot of $\mathrm{R}T \ln V_g$ vs. $a(\gamma_L^d)^{1/2}$ results in a straight line, from the slope of which γ_S^d can be calculated. The γ_L^d values of the *n*-alkanes are available from the literature [40].

The second method was introduced by Dorris and Gray [41]. Considering that each methylene group of the *n*-alkanes has its own contribution to the free energy of adsorption, γ_S^d can be calculated according to Eq. (2).

$$\gamma_S^d = \frac{(\Delta G_{\mathrm{CH_2}})^2}{4\mathrm{N}^2 a_{\mathrm{CH_2}}^2 \gamma_{\mathrm{CH_2}}} \tag{2}$$

$a_{\mathrm{CH_2}}$ and $\gamma_{\mathrm{CH_2}}$ are the surface area (6 Å^2) and the surface free energy of a methylene group, respectively. $\Delta G_{\mathrm{CH_2}}$ is the contribution of one methylene group to the free energy of adsorption. This increment results from the slope of the plot of $\mathrm{R}T \ln V_g$ vs. the number of C atoms of the respective *n*-alkanes.

In order to investigate the acid–base characteristics of the polymer surfaces, solutes with gradual polarity were used. Besides dispersive interaction these solutes are able to interact in a specific manner by electron donor–acceptor interactions. Therefore the variation of the free energy of adsorption may be considered as a sum of dispersive and specific contributions [42,43]. The latter (ΔG_a^{sp}) is available by the procedure described by Sawyer et al. [44,45] and from its temperature dependence one can conclude the enthalpy of specific interactions ΔH_a^{sp}. The ΔH_a^{sp}-values are the basis for the estimation of the semiquantitative K_A- and K_B-parameters which characterise the Lewis acid–base properties of a surface [46]:

$$-\Delta H_a^{sp} = K_A \mathrm{DN} + K_B \mathrm{AN}^* \tag{3}$$

DN and AN* are donor and acceptor numbers introduced by Gutmann [47]. The original acceptor numbers were corrected for van der Waals contributions by Riddle and Fowkes [48]. DN and AN* give information as to whether a solvent is able to act as electron donor or electron acceptor. When $-\Delta H_a^{sp}/\mathrm{AN}^*$ is plotted vs. $\mathrm{DN}/\mathrm{AN}^*$ a straight line should be obtained. The slope of the line gives K_A and the intercept K_B.

3. Experimental

3.1. Materials

The synthesis of polyamidines **1a**–**1c** by melt polycondensation of 4,4′-diaminodiphenyl methane with triethylorthoformate (**1a**), triethylorthoacetate (**1b**) and triethylorthobenzoate (**1c**), respectively, was described in a previous paper [18].

3.2. IGC measurements

A HP 5890 Series II gas chromatograph equipped with a flame ionisation detector was used for IGC measurements. The carrier gas was helium. The flow rate of 10 ml/min was measured and controlled by an electronic flow meter. The flow rates were corrected for the pressure drop along the column and also for the temperature differences between the column and the electronic flow meter. The optimal flow rate was determined by means of the number of theoretical plates which were calculated from the retention time and the half width of a symmetrical peak [49]. For this flow rates were usually varied between 5 and 30 ml/min. The measurements were carried out in a temperature range of 40–60°C, distinctly below the glass transition temperature of the polymer. In order to prevent lateral interactions of the probe molecules, measurements were carried out at infinite dilution. For this, probes were taken from the vapour phase of the solvents with a Hamilton syringe which was than flushed several times with air prior to injection. Under these conditions it is assumed that retention of the probe molecules is only caused by surface adsorption and diffusion can be neglected. This assumption is supported by the symmetry of the retention peaks and their independence on the amount of probe molecules injected into the column. Net retention

Table 1
γ_S^d-values of polyamidines

Sample	Method	γ_S^d (mJ/m^2)			Extrapolation on 25°C
		40°C	50°C	60°C	
1a	Ref. [37]	45.3	41.8	38.8	50.1
	Ref. [41]	43.3	40.6	38.4	46.9
1b	Ref. [37]	31.9	29.4	27.5	35.1
	Ref. [41]	32.8	30.8	29.3	35.3
1c	Ref. [37]	31.9	30.1	27.7	35.2
	Ref. [41]	32.8	31.5	29.5	35.4

times were determined as the difference between the retention times of the solutes and a non-interacting marker (methane) using peak maxima.

Since the solubility of some polyamidines in common solvents was restricted, coating of all samples onto a porous support failed. Due to the excellent free-flowing behaviour of the polymers, columns could be packed properly with powders. For this polyamidines were crushed and sieved with an electromagnetic jig. Particle sizes in a range of 100–150 μm were obtained. The pure polyamidines were packed into glass columns of 0.25 m length and an inner diameter of 4 mm. The use of a glass column allowed the checking of homogeneous packing of all samples. As probe molecules (solutes) *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, chloroform, dichlormethane, tetrahydrofuran, diethyl ether, acetone and ethylacetate were used. The solvents of analytic grade purity (p.a.), were dried with molecular sieves and used without further purification.

4. Results and discussion

The dispersive contributions of the surface free energies γ_S^d determined according to the procedures of Fowkes [37] and Dorris and Gray [41] are summarised in Table 1. For the measurements a series of *n*-alkanes were used as probe molecules. The γ_S^d-values were determined at different temperatures and extrapolated to 25°C. Both methods yielded comparable results. As expected, the γ_S^d-values decrease steadily with increasing temperature. It can be seen that the γ_S^d-values of the polyformamidine **1a** are significantly higher than those of **1b** and **1c**.

For the determination of the specific contribution of the surface free energy, polar solvents like chloroform, dichlormethane, tetrahydrofuran, diethyl ether, acetone and ethylacetate were used as probe molecules. Measurements carried out at different temperatures allowed us to obtain the enthalpies of specific interactions ΔH_a^{sp}. With the use of Gutmann's donor and acceptor numbers of the solute molecules the K_A- and K_B-parameters could be determined according to Eq. (3). The values are summarised in Table 2.

Table 2
K_A- and K_B-parameters

Sample	K_A	K_B	K_B/K_A
1a	0.1	0.4	4.0
1b	0.1	0.9	9.0
1c	0.1	1.0	10.0

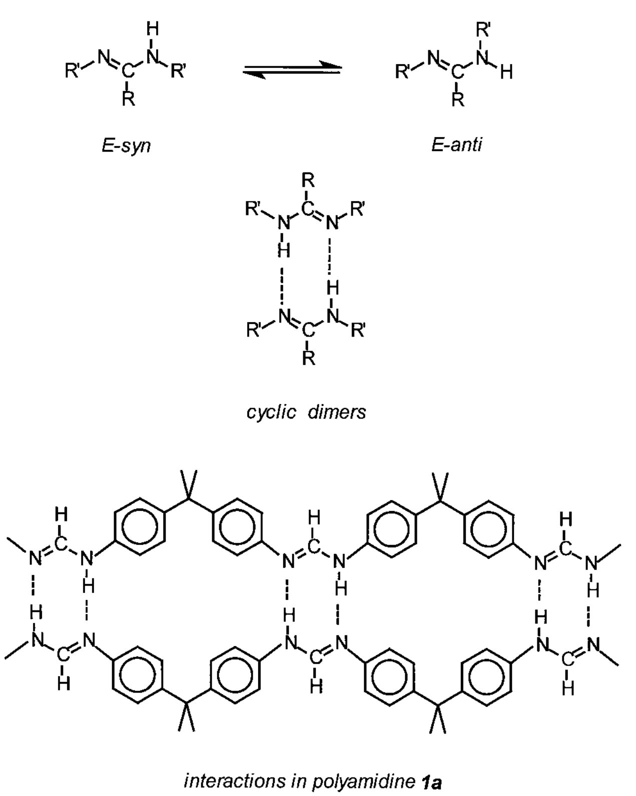

Fig. 1. Configuration of amidine groups and their interactions in polyamidines.

Considering that the K_A- and K_B-parameters express the ability of a surface to act as Lewis-acid or Lewis-base, one can conclude that the polyamidines exhibit rather a Lewis-basic character than a Lewis-acidic character.

Both the parameters for specific (K_A, K_B) and dispersive interactions (γ_S^d) reveal the exceptional position of the polyformamidine **1a**. This polymer exhibits the highest dispersive contributions of surface free energy and the lowest sum of K_A- and K_B. The Lewis-basicity of **1a** is relatively small whereas **1b** and **1c** are substances with distinct Lewis-basic surfaces.

The behaviour of **1a** can be explained by its solid phase structure. It was shown earlier [18–21] that the amidine groups in **1a** adopt *E-syn* configuration preferably, resulting in the formation of cyclic dimers (see Fig. 1). These cyclic dimers promote fast proton exchange in solution and also in the solid phase as evidenced by NMR spectroscopy [20–21]. Due to the strong interactions polyformamidine **1a** is highly crystalline. In contrast with this, *E-anti* configuration is predominant in polyamidines **1b** and **1c**. In this configuration, formation of hydrogen bonds and prototropic tautomerism is retarded. These polymers are amorphous.

It is assumed that the interactions of **1a** and the resulting delocalisation of the π-electrons over the two nitrogens of the amidine group are responsible for the increased γ_S^d-values. On the other hand these interactions leads to a mutual shielding of the amidine groups so that specific surface interactions with other polar molecules are decreased. Therefore lower K_A and K_B values were obtained.

Similar results concerning the influence of delocalised π-electron systems on the dispersive contributions of the surface free energies γ_S^d were found by Jacobasch et al. [50] on modified carbon fibres. The authors evidenced that untreated carbon fibres with a high degree of π-electron delocalisation exhibit distinctly higher dispersive forces than fibres with oxidised surfaces.

The IGC measurement allows one to conclude the Lewis acid–base properties of the high energy side of the polyamidine surfaces. It could be shown that amidine groups behave distinctly basic. This is in good accordance with their Brønsted base properties that were investigated by Oszczapowicz et al. [51,52]. The authors determined the pK_a-values of the respective low molecular weight amidines diphenylformamidine (7.17), diphenylacetamidine (8.35) and diphenylbenzamidine (7.43) by titration. The pK_a-values show that aromatic amidines are moderately weak bases and it is assumed that polyamidines possess similar Brønsted base properties. Due to their multifarious interactions as Lewis and Brønsted bases polyamidines are expected to be promising candidates for supramolecular chemistry and surface modification. This will be the subject of further investigations.

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