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Synthesis and inverse gas chromatographic characterization of polyesters containing pyridine units in the main chain*

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Aromatic polyesters with isophthaloyl, pyridine-2,6-dicarbonyl and pyridine,2,5-dicarbonyl units in the main chain were synthesized and were characterized by inverse gas chromatography (i.g.c.). The polyesters containing complex 'triad' monomers and aromatic diols were obtained by high temperature solution polycondensation. In order to investigate whether the surfaces of polycondensates act as Lewis acids or Lewis bases, the donor–acceptor interactions between various probe molecules and polyesters have been studied by means of i.g.c. Because the measurements were carried out at different temperatures, we were able to determine parameters K_A and K_B, which describe the donor–acceptor properties of the stationary phase. One polyester without pyridine units was amphoteric with slight predominance of Lewis-basic behaviour. Polymers containing pyridine units may be considered as Lewis bases. The glass transition temperatures of two polymers have also been determined by i.g.c. © 1997 Elsevier Science Ltd.

(Keywords: aromatic polyesters; inverse gas chromatography; surface properties)

INTRODUCTION

Several aromatic polyesters exhibit liquid crystalline behaviour. They are characterized by outstanding mechanical and thermal properties and have a good processability. One disadvantage, however, are their weak interactions with other compounds[1]. For some applications a higher surface polarity would be desirable. One possibility for increasing the polarity is the incorporation of polar units into the main chain of polyesters. The pyridine unit seems to be a suitable candidate which might possess the required properties.

Aromatic polyethers with pyrazine and pyridine units in the backbone were synthesized and characterized by Kricheldorf and co-workers[2,3]. From the large number of publications considering the properties of polymers containing vinylpyridine and their quaternization the investigations of Navarro-Rodriquez and co-workers should be accented[4–7].

It is the aim of the present publication to investigate the influence of pyridine units on the surface properties of aromatic polyesters. For the surface characterization, inverse gas chromatography (i.g.c.) has been applied.

The advantages of chromatography are the high sensitivity, the possibility of investigation within a wide range of temperatures and the speed of measurements made with standard equipment[8].

The i.g.c. represents a favourable method for quantifying surface properties of such polymers where mainly changes in the high energy sites are expected to be caused by the chemical modifications under investigation. Panzer and Schreiber[1] studied thermotropic liquid-crystal polymers (TLCP) by means of i.g.c. Because of their low polarity, TLCPs showed weak interactions with probe molecules.

Bosse *et al.*[9] and Ruggiero *et al.*[10] carried out i.g.c. investigations on polymers with various contents of vinylpyridine. In the first case, styrene–4-vinylpyridine diblock polymers were adsorbed on two rutile pigments. Because of the greater basicity the 4-vinylpyridine moiety (adsorbate thickness greater than about 60 nm) was preferentially bonded on the acidic rutile surfaces, resulting in an enrichment of the styrene at the surface layer. In the second case the chromatographic columns were filled with cross-linked poly(styrene–vinylpyridine). As probe molecules, hydrocarbons, amines and alcohols were used. With increasing content of pyridine the interactions between probe molecules and polymer decrease, since the solvents as well as the stationary phase act as Lewis bases, so that repulsive interactions occur.

For our investigations a series of polyesters have been synthesized according to Bilibin *et al.*[11]. The procedure and the samples obtained are shown in *Scheme 1*. For comparison purposes, differently substituted pyridine units were used. Additionally, a non-polar polyester with isophthaloyl units has been synthesized.

EXPERIMENTAL

Monomer preparation

Acid chlorides (**1**): 2 mol of the respective dicarboxylic acid was refluxed with thionyl chloride (800 ml) and dry dimethylformamide (DMF, 2 ml)[12]. After 5 h the excess of thionyl chloride was distilled off and the residue was washed with dry hexane.

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* Dedicated to Professor Hans-Jörg Jacobasch, Institut für Polymerforschung Dresden, on the occasion of his 60th birthday

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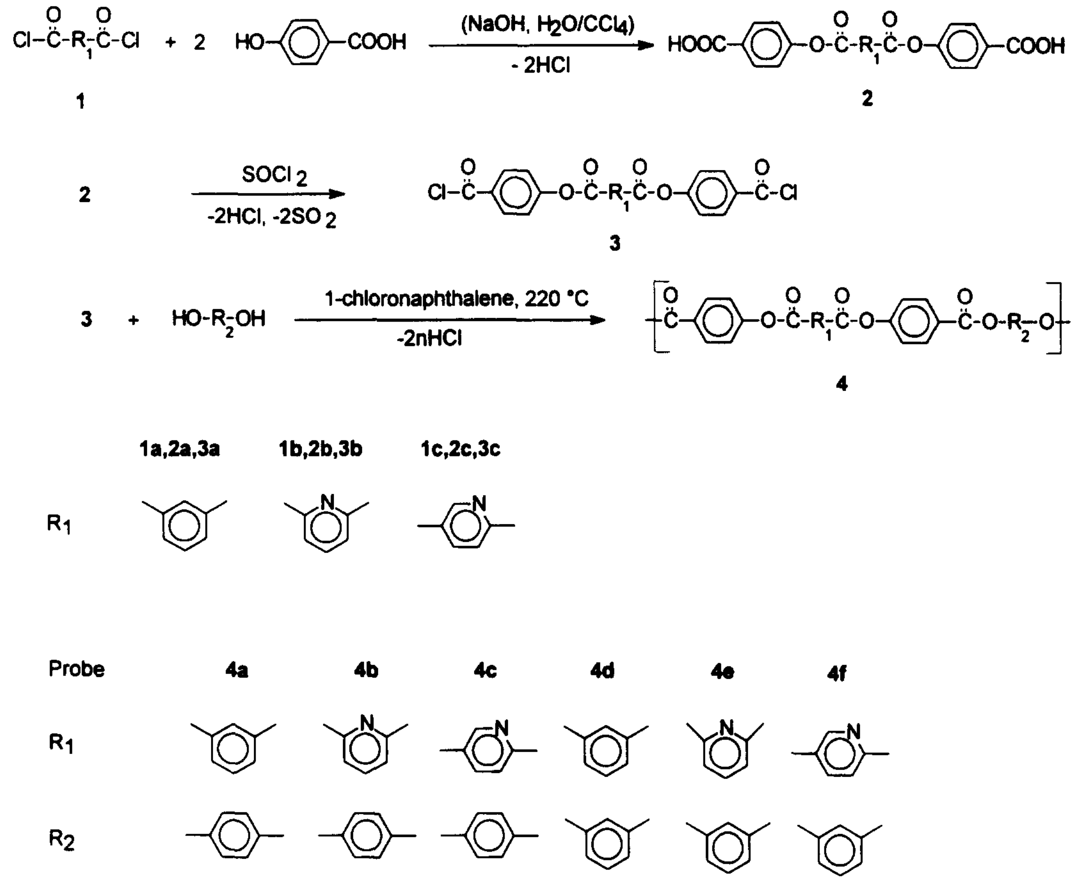

Scheme 1

Isophthaloyl chloride (**1a**): yield: 80%, m.p.: 42–43°C; infra-red (i.r.): 1765, 1745 (C=O), 690 cm^{-1} (C–Cl).

Pyridine-2,6-dicarbonyl dichloride (**1b**): yield 83%; m.p.: 56–58°C; i.r.: 1755 (C=O), 640 cm^{-1} (C–Cl).

Pyridine-2,5-dicarbonyl dichloride (**1c**): yield: 78%, m.p.: 58–59°C, i.r.: 1780, 1745 (C=O), 665 cm^{-1} (C–Cl).

Complex dicarboxylic acids (**2**): *p*-hydroxybenzoic acid (1.2 mol) was dissolved in 2.5 l of 0.5 N NaOH by stirring for 15 min[12]. The respective acid dichloride (0.5 mol) was dissolved in 1 l of dry tetrachloromethane and was added dropwise to the first solution by vigorously stirring, then 1 l of 1 N NaOH was added to the mixture, followed by stirring for 5 h. The precipitate was filtered off, washed with 0.5 N HCl, water and acetone and dried *in vacuo*.

4,4′-(Isophthaloyldioxy)dibenzoic acid (**2a**): yield: 80%; i.r.: 3400 (OH), 1740, 1700 (C=O), 1605 cm^{-1} (C=C); calc. C: 65.02, H: 3.45; found C: 63.96, H: 3.34.

4,4′-(Pyridine-2,6-dicarbonyldioxy)dibenzoic acid (**2b**): yield: 58%, i.r.: 3400 (OH), 1760, 1690, (C=O), 1605 cm^{-1} (C=C); calc. C: 61.92, H: 3.19, N: 3.44; found: C: 60.53, H: 3.08, N: 3.34.

4,4′-(Pyridine-2,5-dicarbonyldioxy)dibenzoic acid (**2c**): yield: 57%; i.r.: 3400 (OH), 1735, 1700 (C=O), 1605 cm^{-1} (C=C); calc. C: 61.92, H: 3.19, N: 3.44; found: C: 59.27, H: 2.95, N: 3.30.

Complex acid dichlorides (**3**): 0.2 mol of the respective dicarboxylic acid **2** was refluxed with 1.2 l of thionyl chloride and dry DMF (2 ml) for 2 h[12]. After cooling, the precipitate was filtered off, washed with dry hexane and dried *in vacuo*.

4,4′-(Isophthaloyldioxy)dibenzoyl dichloride (**3a**): yield: 86%; m.p.: 190°C; i.r. 1780, 1745 (C=O); 1600 (C=C), 715 cm^{-1} (C–Cl); ^{13}C nuclear magnetic resonance (n.m.r.): 167.3 ppm ($\mathrm{C_{ar}{-}\underline{C}O{-}Cl}$), 163.2 ppm ($\mathrm{C_{ar}{-}\underline{C}O{-}O}$), 156.1 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}O}$), 135.5, 133.2, 129.7, 129.5, 122.3 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}C_{ar}}$), 132.0, 131.1 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}CO}$).

4,4′-(Pyridine-2,6-dicarbonyldioxy)dibenzoyl dichloride (**3b**): yield: 75%; m.p. 214°C; i.r.: 1775, 1740 (C=O), 1600 (C=C), 745 cm^{-1} (C–Cl); ^{13}C n.m.r.: 167.3 ppm, $\mathrm{C_{ar}{-}\underline{C}O{-}Cl}$), 162.2 ppm ($\mathrm{C_{ar}{-}\underline{C}O{-}O}$), 156.1 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}O}$), 139.0, 133.2, 129.5, 122.4 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}C_{ar}}$), 147.5 ppm ($\mathrm{CO{-}\underline{C}_{ar}{-}N}$), 131.2 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}CO}$).

4,4′-(Pyridine-2,5-dicarbonyldioxy)dibenzoyl dichloride (**3c**): yield 87%; m.p. 200°C (**1c**); i.r. 1775, 1740 (C=O), 1600 (C=C), 730 cm^{-1} (C–Cl); ^{13}C n.m.r.: 167.28, 167.24 ppm ($\mathrm{C_{ar}{-}\underline{C}O{-}Cl}$), 162.09, 161.98 ppm ($\mathrm{C_{ar}{-}\underline{C}O{-}O}$), 156.03, 155.56 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}O}$), 151.6, 133.28, 133.25, 125.8, 122.3, 122.17 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}C_{ar}}$, 150.6 ppm ($\mathrm{CO{-}\underline{C}_{ar}{-}N}$), 139.3 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}N}$), 131.49, 131.39, 128.2 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}CO}$).

Polymer (4) preparation

The complex acid dichloride **3** (20 mmol) and the respective dihydroxy compound (20 mmol) were placed, together with 1-chloronaphthalene (40 ml), in a three-necked flask[11,12]. The flask was equipped with a stirrer, N_2 inlet and distilling head. The high temperature solution polycondensation was carried out at 220°C for 2 h. After cooling, the condensation polymer was precipitated in ethanol (200 ml), filtered off and extracted for 12 h with ethanol using a Soxhlet apparatus and vacuum-dried at 60°C for 18 h.

Polyester **4a**: i.r.: 3400 (OH), 1740 (C=O), 1605, 1505 cm^{-1} (C=C); ^{13}C n.m.r.: 166.4, 165.6 ppm ($\mathrm{C_{ar}{-}\underline{C}O{-}O}$), 155.2, 148.5 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}O}$), 132.2, 129.9, 122.8, 122.1 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}C_{ar}}$), 129.5, 127.0 ppm ($\mathrm{C_{ar}{-}\underline{C}_{ar}{-}CO}$).

Polyester **4b**: i.r.: 3400 (OH), 1760, 1735 (C=O), 1605, 1505 cm^{-1} (C=C); ^{13}C n.m.r.: 166.2, 163.1 ppm (C_{ar}–$\underline{C}$O–O), 154.9, 148.4 ppm (C_{ar}–$\underline{C}_{ar}$–O), 147.3 ppm (CO–$\underline{C}_{ar}$–N), 140.4, 132.3, 130.4, 122.7, 121.8, 116.3 ppm (C_{ar}–$\underline{C}_{ar}$–C_{ar}), 127.2 ppm (C_{ar}–$\underline{C}_{ar}$–CO).

Polyester **4c**: i.r. 3400 (OH), 1735 (C=O), 1605, 1505 cm^{-1} (C=C); ^{13}C n.m.r.: 166.2 ppm (**2**), 163.1, 162.1 ppm (C_{ar}–$\underline{C}$O–O), 154.8 ppm (**2**), 149.5 ppm (C_{ar}–$\underline{C}_{ar}$–O), 150.7 ppm (C_{ar}–$\underline{C}_{ar}$–N), 148.5 ppm (CO–$\underline{C}_{ar}$–N), 141.1, 132.4, 126.7, 122.7, 122, 121.7 ppm (C_{ar}–$\underline{C}_{ar}$–C_{ar}), 129.5, 127.4 ppm (C_{ar}–$\underline{C}_{ar}$–CO).

Polyester **4d**: i.r. 3400 (OH), 1740 (C=O), 1600, 1505 cm^{-1} (C=C); ^{13}C n.m.r.: 166.0, 165.3 ppm (C_{ar}–$\underline{C}$O–O), 155.3, 151.1 ppm (C_{ar}–$\underline{C}_{ar}$–O), 132.2, 130.4, 129.8, 122.1, 119.7, 115.6 ppm (C_{ar}–$\underline{C}_{ar}$–C_{ar}), 129.5, 127.0 ppm (C_{ar}–$\underline{C}_{ar}$–CO).

Polyester **4e**: i.r.: 3400 (OH), 1735 (C=O), 1600, 1505 cm^{-1} (C=C); ^{13}C n.m.r.: 165.7, 162.9 ppm (C_{ar}–$\underline{C}$O–O), 154.9, 151.5 ppm (C_{ar}–$\underline{C}_{ar}$–O), 147.3 ppm (CO–$\underline{C}_{ar}$–N), 140.3, 132.2, 130.3, 130.2, 121.8, 119.7, 115.5 ppm (C_{ar}–$\underline{C}_{ar}$–C_{ar}), 127.2 ppm (C_{ar}–$\underline{C}_{ar}$–CO).

Polyester **4f**: i.r. 3400 (OH), 1735 (C=O), 1600, 1505 cm^{-1} (C=C); ^{13}C n.m.r.: 165.84, 165.79, 162.9, 162.2 ppm (C_{ar}–$\underline{C}$O–O), 154.81, 154.77, 151.1 ppm (C_{ar}–$\underline{C}_{ar}$–O), 150.7 ppm (C_{ar}–$\underline{C}_{ar}$–N), 149.5 ppm (CO–$\underline{C}_{ar}$–N), 141.0, 132.34, 132.32, 130.4, 126.7, 122, 121.7, 119.7, 115.7 ppm (C_{ar}–$\underline{C}_{ar}$–C_{ar}), 129.5, 127.3 ppm (C_{ar}–$\underline{C}_{ar}$–CO).

Polymer characterization

The solution viscosities of the polyesters were measured with an automated Ubbelohde viscometer (capillary Ic) at 25°C (polymer concentration 0.5 g dl^{-1}) in a chloroform/2,3,4,5,6-pentafluorophenol mixture (1/1 v/v).

The i.r. spectra were recorded on a Bio-Rad FTS 155. Melting points were determined on a hot-stage polarizing microscope (Cambridge Instruments). Thermal analysis was carried out with a Perkin-Elmer DSC 7 and a Perkin-Elmer TGA 7 at a heating (cooling) rate of 10 K min^{-1}.

For gel permeation chromatography (g.p.c.) polyesters were dissolved in a chloroform/2,3,4,5,6-pentafluorophenol mixture (1/1 v/v) and diluted with a *m*-cresol/chloroform mixture (1/3 v/v). A Knauer g.p.c. system, with Waters Styragel HT 3/HT 6 E columns (flow rate 0.8 ml min^{-1}) was used.

A 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 20 ml min^{-1} 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 and the electronic flow meter. The measurements were carried out in the temperature range 40–170°C. Hamilton syringes were used for injection of 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. Retention peaks obtained were almost symmetrical and independent on the amounts of probe molecules injected into the column.

Polymers were crushed and sieved with an electromagnetic jig. Particle sizes were in the range 71–125 μm. The pure polyesters were packed into glass columns (0.2 m length; 4 mm inner diameter). As probe molecules (solutes), n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, chloroform (CHL), dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether (DEE), acetone (ACE) and ethyl acetate (ETAC) were used. The solvents, which were of analytical grade purity (p.a.), were dried with molecular sieves and used without further purification.

INVERSE GAS CHROMATOGRAPHY

Inverse gas chromatography is similar to conventional gas chromatography as far as equipment and techniques are concerned, but is called 'inverse' because it is the properties of the solid stationary phase which are to be investigated.

From intermolecular interactions of the solid phase with 'probe' molecules, which act as chromatographic solutes, the thermodynamic properties of surfaces can be concluded. We considered the adsorption processes as reversible, because diffusion into the polymer bulk was negligible at the measuring temperature which was far below the T_g of the polymer. Depending on the amount of the injected solute there are two possible concentration ranges of i.g.c.: finite concentration and infinite dilution. In this work we only performed i.g.c. at infinite dilution (zero surface coverage). In this region of the adsorption isotherm of the solute, lateral interactions between probe molecules are negligible. The retention volume, as a measured value, is only dependent on the properties of the investigated solid surface.

In order to determine thermodynamic surface properties i.g.c. represents a relatively simple method. A conventional instrument serves as the gas chromatograph. The chromatographic columns are filled with pure solid or support (often Chromosorb) coated with the compound to be studied. Coating of a capillary column is an additional possibility. The difficulties and problems of coating of polymers on to Chromosorb and a capillary column were described in detail by Al-Saigh and Munk[13] and Bonifaci *et al.*[14]. In this work we preferred the pure polyesters to be packed into columns, because the only solvent (2,3,4,5,6-pentafluorophenol) in which the polymers were soluble could not be removed completely after coating the polymer on the support.

In i.g.c. the measured value is the retention time t_R. The net retention volume V_N is related to the corrected flow rate F_{CORR} and the effective retention time t'_R, calculated as the difference between t_R and the retention time of a non-interacting marker:

$$V_N = F_{CORR} \cdot t'_R \tag{1}$$

and forms the basis for determination of specific retention volume V_g standardized for 0°C and 1 g mass of the adsorbent[15]:

$$V_g = \frac{273.15K \cdot V_N}{T_S \cdot m_{Poly}} \tag{2}$$

where T_S represents the temperature of column, m_{Poly} is the mass of the stationary phase (polymer).

The specific retention volume is related to the variation of free energy of adsorption ΔG_a by

$$\Delta G_a = -RT \ln V_g + C \tag{3}$$

where R is the gas constant, T is the temperature of the column, and C is a constant depending on the specific area of the stationary phase and the choice of a reference state[16,17].

Using Fowkes' approach[18], introduced for the work of adhesion W_A between a non-polar liquid and a solid surface which only involves a dispersion interaction, the expression can be written:

$$RT \ln V_g + C = NaW_A = Na2(\gamma_S^d)^{1/2}(\gamma_L^d)^{1/2} \qquad (4)$$

where N is the Avogadro number, γ_L^d is the dispersive contribution of the surface free energy of the solute, and a is the surface area of the adsorbed probe molecule[19]. From the plot of $RT \ln V_g$ *versus* $a(\gamma_L^d)^{1/2}$ a straight line results, from which γ_S^d can be calculated from the slope, when n-alkanes, exerting only a dispersive interaction, are used as probe molecules.

Another goal of surface characterization by i.g.c. is to gain information about the specific interaction exerted by the investigated surface. For that, polar probes, i.e. organic solvents, will be injected into the column. Because only one peak per injected probe is obtained, polar or specific and dispersive interactions have to be separated afterwards. Here again the idea of Fowkes and Mostafa[20] as well as of Owens and Wendt[21] is used to express the variation of the free energy of adsorption as the sum of a dispersive (d) and a specific component (sp):

$$\Delta G_a = \Delta G_a^d + \Delta G_a^{sp} \qquad (5)$$

For interpreting i.g.c. results it was shown to be very useful to consider the retention volumes of the n-alkanes as a measure of the dispersive interaction exerted by the solid surface and to use this reference for the separation of dispersive and specific interactions exerted by the solid surface. The calculation of the specific contribution to the free surface energy change is then possible using the following equation:

$$\Delta G_a^{sp} = -RT\left(\ln V_g - \ln V_g^{ref}\right) \qquad (6)$$

where V_g^{ref} is the specific retention volume of a reference solute, i.e. a hypothetical n-alkane.

Several methods have been established to construct the straight reference line of the n-alkanes by plotting $RT \ln V_g$ against several values as the x axis.

Sawyer and Brookman[22,23] made use of boiling temperatures, plotting $RT \ln V_g$ against T_b. Instead of T_b the logarithm of vapour pressure of the solvents was applied by Papirer[24,25]. An additional method is given by equation (4). It was shown that all methods gave the same results when a and γ_L^d were determined accurately[26].

In order to be able to determine the specific adsorption enthalpy ΔH_a^{sp} the measurements have to be carried out at various temperatures. According to the relation:

$$\Delta G_a^{sp} = \Delta H_a^{sp} - T\Delta S_a^{sp} \qquad (7)$$

ΔH_a^{sp} can be calculated from the slope of the $-\Delta G_a^{sp}/T$ *versus* $1/T$ plot. The intercept of the ordinate is the specific entropy of adsorption.

The acid–base character of the solid may be expressed by the semi-quantitative parameters K_A and K_B, as proposed by Papirer[25]:

$$-\Delta H_a^{sp} = K_A DN + K_B AN^* \qquad (8)$$

where DN is the donor number according to Gutmann[27] and AN^* the acceptor number of Gutmann corrected for van der Waals' contributions by Riddle and Fowkes[28]. DN and AN^* give information on whether a solvent is able to act as electron donor or electron acceptor.

Linearizing equation (8), i.e. $-\Delta H_a^{sp}/AN^*$ is plotted against DN/AN^*, K_A and K_B are obtained as slope (K_A) and intercept (K_B) of the straight line.

RESULTS AND DISCUSSION

Some common properties of the polymers synthesized are summarized in *Table 1*. It can be seen that the thermal stability of the polyesters decreases with introduction of pyridine units. Additionally, the polymers containing heterocycles exhibit molecular weights lower than those of polyesters with isophthaloyl units. The copolyester **4a** was the only one having liquid-crystalline properties. Because of their molecular structure polymers **4b** and **4c** were expected to show liquid-crystalline

Table 1 Results of polymer characterization

Polyester	Yield (%)	η_{inh}[a] (dl g^{-1})	M_n (g.p.c.) M_w (g.p.c.) (g mol^{-1})[b]	Mass loss[c] (%)	T_m (microscope) (°C)	T_g (d.s.c.) (°C)	T_m (d.s.c.) (°C)
4a	71	0.68	18 150	1 : 138°C	385 lc 425	283	400
			49 300	10 : 490°C			
4b	87	0.45	5 200	1 : 115°C	$T_m > T_{dec}$[e]	Not detectable	—
			10 200	10 : 362°C			
4c	83	0.62	Not sol.[d]	1 : 270°C	$T_m > T_{dec}$	Not detectable	—
				10 : 417°C			
4d	86	0.96	29 150	1 : 310°C	275	156	286
			88 500	10 : 490°C			
4e	69	0.43	8 250	1 : 136°C	200	Not detectable	202
			23 400	10 : 327°C			
4f	75	0.27	3 100	1 : 219°C	245	Not detectable	245
			8 400	10 : 302°C			

[a] $T = 25$°C; conc.: 0.5 g dl^{-1}; chloroform/2,3,4,5,6-pentafluorophenol mixture (1/1 v/v)
[b] *m*-Cresol/chloroform (1/3 v/v) mixture using PS standards
[c] Thermogravimetry
[d] Not soluble in *m*-cresol/chloroform
[e] dec = decomposition

behaviour as well; however, in both cases the polyesters decomposed below their melting points.

For i.g.c. investigations, polymers with a suitable particle size (>50 μm) are necessary. From the polymers under discussion only the samples **4d**, **4e** and **4f** fulfilled this requirement. The particle sizes of samples **4a**, **4b** and **4c** were too small (<10 μm). Additionally, residues of 1-chloronaphthalene were found in **4c**, which would have influenced the measurements. For these reasons only the polymers **4d**, **4e** and **4f** were investigated by i.g.c.

The aim of i.g.c. measurements was the quantitative evaluation of acid–base interactions and the determination of glass transition temperatures. Firstly, the retention volumes of the n-alkanes were evaluated in order to obtain the reference lines and to calculate the dispersive contribution of surface free energy γ_S^d. *Figure 1* shows the $RT \ln V_g$ *versus* T_b plot (Sawyer method) of n-alkanes at various temperatures. With increasing temperature the slopes are decreasing. The γ_S^d values were calculated by plotting $RT \ln V_g$ *versus* $a(\gamma_L^d)^{1/2}$ using equation (4). The results are listed in *Table 2*. In particular, γ_S^d values of polymers containing pyridine units strongly decrease at higher temperatures.

After that the retention behaviour of polar probes DCM and CHL (acidic) and DEE and THF (basic), as well as ACE and ETAC (amphoteric), according to Gutmann's scale, was investigated in order to obtain $-\Delta G_a^{sp}$ values. In *Figure 2* the Sawyer plot is given; the vertical distance of a polar probe from the corresponding point on the n-alkane line at the same x value is $-\Delta G_a^{sp}$. Because of their dependence on the temperature the determined ΔG_a^{sp} values only possess a quite low information value. Therefore, we have computed the specific enthalpy of adsorption based on equation (7). The respective plots for the adsorption of DCM, ACE and ETAC on polyester **4e** are shown in *Figure 3*.

Now we were able to evaluate K_A and K_B parameters from the representation of $-\Delta H_a^{sp}/AN^*$ *versus* DN/AN^* according to equation (8). The K_A and K_B values obtained are listed in *Table 2*. These parameters having semi-quantitative character give some information on whether the polymer surface acts as a Lewis acid or Lewis base. As expected, the polyester **4d** can be considered as an amphoteric polymer with a slight predominance of basicity. Polymers **4e** and **4f** show lower K_A values, but higher K_B values. This is most probably caused by the substitution of phenylene units (slight acidic) by pyridine units (basic). However, it is somewhat surprising that the K_B value for **4e** is distinctly increased compared to the value for **4f**. It was expected that the K_B values of polyesters containing heterocycles are similar. There are two possible explanations: the position of the N atom in the pyridyl unit differs from **4e** to **4f**, i.e. in polymer **4f** the pyridyl units are *para*-substituted whereas in **4e** a *meta*-substitution occurs. The *para*-substituted pyridyl unit is assumed to be able to

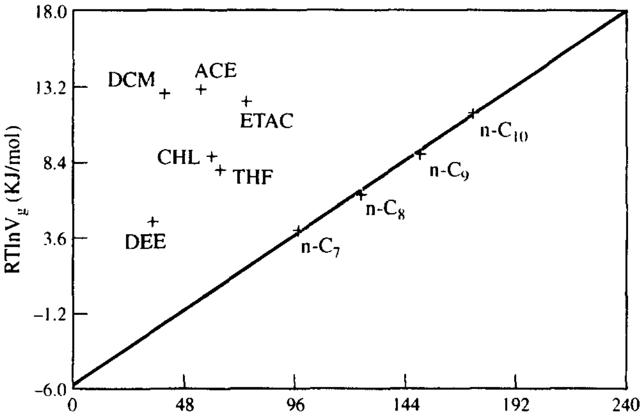

Figure 2 Determination of $-\Delta G_a^{sp}$ (Sawyer method. 60°C, sample **4e**) (DEE: diethyl ether; DCM: dichloromethane; CHL: chloroform; ACE: acetone; THF: tetrahydrofuran; ETAC: ethyl acetate)

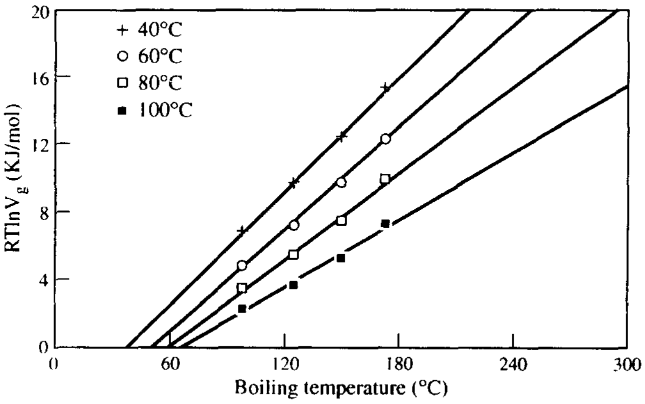

Figure 1 Reference line of n-alkanes (C_7–C_{10}) at various temperatures (sample **4f**)

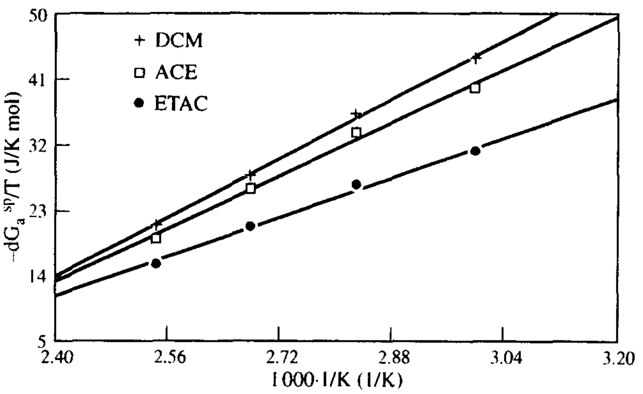

Figure 3 Determination of the specific adsorption enthalpy (sample **4e**)

Table 2 Dispersive contributions of surface free energy and K parameters

Polyester	γ_S^d (mJ m^{-2}) 40°C	60°C	80°C	100°C	120°C	K_A	K_B
4d	—	—	44.7	37.0	31.0	0.21	0.51
4e	—	28.4	18.4	8.9	3.0	0.13	2.70
4f	40.9	32.9	22.3	11.4	—	0.12	0.89

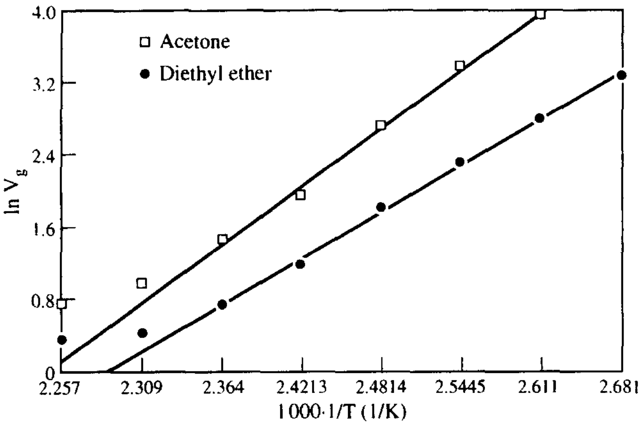

Figure 4 Determination of the glass transition temperature (sample **4d**)

undergo ring flips around the molecular axis. On principle, these ring flips may cause changes in the surface polarity. Depending on the surroundings of the surface it is possible that the N atom of the pyridyl unit turns to the surface or to the bulk. Those structural rearrangements play an important role during the precipitation of the polymer from the reaction mixture. In the case of the polymers with the *meta*-substituted pyridyl unit structural changes are less likely. Another reason could be that the copolyester containing pyridine-2,6-dicarbonyl units was precipitated in ethanol, whereas the polycondensate with the pyridine-2,5-dicarbonyl units precipitated during the synthesis in 1-chloronaphthalene. The different polarity of the solvents could have influenced the surface properties. Remarkable also is the difference in the degree of crystallinity, from 0.08 (**4e**) and 0.35 (**4f**).

Additionally, we have tried to determine the glass transition temperatures T_g of copolyesters **4d** and **4f**. Braun and Guillet[29] have found that the first deviation from linearity of the straight line obtained at lower temperatures is in good agreement with T_g. This deviation is caused by a change from surface sorption (below T_g) to bulk sorption (above T_g). The respective plot for **4d** is shown in *Figure 4*. The resulting glass transition temperature for **4d** is obtained in the temperature range 155–160°C. This is in good agreement with the 156°C measured by differential scanning calorimetry (d.s.c.) (*Table 1*). The T_g of copolyester **4f** was 110°C (±5°C). With d.s.c. measurement the T_g of this copolyester was not detectable. This shows the high sensitivity of i.g.c. measurements. In further i.g.c. studies we want to clarify the influence of the position of the N atom on the surface polarity. For this reason investigations on ethyl esters of dicarboxylic acids (**2**) are intended.

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