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# Acid–base and surface energy characterization of grafted polyethylene using inverse gas chromatography

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## Abstract

For a specific design of interfaces, i.e. in composites and blends, it is essential to know the surface thermodynamics of the components. Polyethylene grafted with maleic anhydride and maleic anhydride–styrene mixtures, respectively, was the component of interest of our investigations. Inverse gas chromatography (IGC) at infinite dilution was shown to be an appropriate method to evaluate the dispersive and acid–base surface characteristics although there is an influence of bulk absorption and morphology when performing IGC above the glass transition temperature of the polymer.

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## 1. Introduction

Polyalkenes have some excellent properties which are advantageous for their technical application, but normally they have non-polar surface characteristics, a fact which is limiting their field of use. In order to make blends and composites or to improve the adhesion of polyalkenes, it is necessary to introduce polar groups into the interface between the components and the surface, respectively. Grafting is one possibility to do so. Polyethylene of high density (HDPE), the polyalkene we were interested in, was grafted radically with maleic anhydride (MA) and MA–styrene (ST) mixtures in the vapour phase at low temperatures. During this procedure, which is

economically and environmentally advantageous, the consistency of the polymer is not changed [1].

The mechanical properties of such materials with two or more components are strongly influenced by the properties of the components on the one hand and by the properties of the interface or interphase on the other. In cases where there is no chemical bonding between the components, and the surface of the material is smooth, the interaction between the components is of physical nature and the strength of dispersive and acid–base interaction forces is essential for the adhesion between the components and therefore for the properties of the material [2–4].

For a specific design of interfaces (and interphases) it is essential to know the surface thermodynamics of the components. Inverse gas chromatography (IGC) at infinite dilution [5] is a straightforward and very sensitive technique for the characterisation of polymer systems [6–9]. In recent years, IGC was successfully used to evaluate the dispersive and acid–base surface characteristics of polymers [10,11].  $K_A$  and  $K_B$  parameters reflecting the ability

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of the examined surface to act as a electron acceptor and donor, respectively, were calculated using the specific interaction contribution to the adsorption enthalpy of the selected probe molecules [12]. However, when performing IGC with glassy or semicrystalline polymers, such as polyalkenes, the influence of bulk absorption has to be considered [9,13–17]. There are always difficulties to separate the thermodynamic interactions of the injected molecules with the bulk and the surface of the polymer. We tried to solve the problem by taking into account the chemical properties of the polymer bulk and the polymer surface, determined by elemental analysis, differential scanning calorimetry (DSC), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and X-ray photoelectron spectroscopy (XPS); and the morphology of the polymer surface determined by scanning electron spectroscopy (SEM). This knowledge was used for the interpretation of the values of the dispersive component of the free energy of adsorption  $\gamma_s^d$ , as well as of standard adsorption enthalpy and entropy values of a homologous series of *n*-alkanes and of semiquantitative acid–base characteristics  $K_A$  and  $K_B$ . Thus it is possible to discuss the connections between surface chemistry, surface morphology and the thermodynamical values determined by IGC on the one hand and the influence of bulk absorption qualitatively on the other.

IGC at infinite dilution is carried out by injecting minor amounts of gaseous solutes, actually only some molecules, at the limit of detection of the most sensitive detectors. Under these conditions, the retention volume ( $V_g$ ) is independent of the injected amount, i.e. only influenced by the surface properties of the stationary phase under investigation and—when bulk absorption can be neglected—a thermodynamical measure for the affinity of injected probes to the solid surface under investigation.

Normally Fowkes' approach of splitting the energy of adhesion into a disperse (London-type interactions) and specific component is used to evaluate surface thermodynamics by IGC.

In order to determine the London interaction capacity of the investigated surface, nonpolar probes such as *n*-alkanes are used, which are capable of undergoing London-type (or disperse) interactions

only. Injecting a homologous series of *n*-alkanes, the free energy of adsorption  $\Delta G_a^0$  can be calculated from the retention volumes [12]. The problem is now how to correlate surface energetics to the free energy of adsorption. In this respect, it is commonly observed that  $\Delta G_a^0$  of *n*-alkanes varies linearly with their number of carbon atoms. From the slope of the straight line, it is possible to compute an incremental value,  $\Delta G_{CH_2}$ , the free adsorption energy variation corresponding to a  $CH_2$ - group. The London component of the surface energy,  $\gamma_s^d$ , can then be calculated [18].

For the investigation of the specific interaction potential (specific means non-disperse), polar probes with known electron acceptor (AN) and donor numbers (DN) (according Gutmann's semiempirical acid–base scale [19]) are injected. We used the corrected parameter AN\*, as proposed by Riddle and Fowkes [20], to analyse IGC results. AN\* is taking into account the Lifshitz–van der Waals contribution to AN and has the same unit as DN (kcal/mol; 1 cal=4.184 J), which overcomes the asymmetry between the units of parameters of Gutmann's scale. Most acid–base evaluations on chromatographic supports are based on the application of the relation:

$$-\Delta H^{sp} = AN^*K_B + DN^*K_A \quad (1)$$

where  $\Delta H^{sp}$  is the specific enthalpy of interaction, due to sole specific interactions between the probe and the solid surface. For the separation of specific and disperse interactions, both of which an injected probe exchanges with the support, a descriptor of the properties of the solutes is needed. We used the approach of Sawyer and Brookman [21,22], i.e. the boiling temperature of the solute as a descriptor.

The determination of the specific interaction parameter ( $ISP = \Delta G^{sp}$ ) is based on the comparison of the retention of polar probes and *n*-alkanes. One supposes that both types of molecules will have access to the same area of adsorption, i.e. size exclusion and bulk absorption effects have to be excluded. By measuring at several temperatures  $\Delta H^{sp}$  is accessible and  $K_A$  and  $K_B$ , which are semiquantitative acid–base parameters of the surface, can be calculated by plotting  $\Delta H^{sp}/AN$  versus  $DN/AN$  [11].

## 2. Experimental

### 2.1. Materials

Powders of HDPE were modified by radical grafting [1] in the vapour phase (Buna, Schkopau, Germany). Polar monomers as MA or MA–ST mixtures were introduced into the polymer matrix this way. The particle size of the powders was not changed during this procedure.

Additionally unplasticized poly(vinyl chloride) (UPVC) and polyether ether ketone (PEEK) (both by Goodfellow, Cambridge, UK) were used for the purpose of comparison because it was possible to carry out IGC below the glass transition temperature of both polymers and because of their known Lewis acidity (UPVC) [23] and basicity (PEEK) [24]. The sample parameters are summarised in Table 1.

### 2.2. Methods

#### 2.2.1. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT)

For the investigation of 1–3 mg of the polymer powder (with a constant particle distribution), a IFS-28 FT-IR spectrometer (Bruker Optics, Billerica, MA, USA) was used. The interpretation was made by averaging of 200 scans.

#### 2.2.2. X-Ray photoelectron spectroscopy

XPS was carried out using an ESCALab 220i spectrometer (Vacuum Generators, East Grenstead, UK) equipped with a non-monochromatized Mg K $\alpha$  X-ray source. The kinetic energy of the photoelectrons was determined using a hemispherical analyzer with a constant pass energy of 80 eV for survey spectra and 25 eV for high resolution spectra. All

Table 1  
Investigated polymers and experimental parameters of IGC

Polymer	$A_{sp}$ (m <sup>2</sup> /g)	Particle size ( $\mu$ m)	Column (mm)	$m$ (mg)	$T_c$ (°C)	$p_E$ (kPa)	$p_A$ (kPa)	$F \times j$ (ml/min)
Polyethylene (Buna)								
PE unmodified (PEA75ZA)	1.19	36–100	$d=4$ $l=150$	488.3	35 40 55	95 98 100	101.3	8.66 8.72 9.59
PE modified: MA/PE=0.025 (TPPE 9078)	0.45	36–100	$d=4$ $l=150$	578.4	35 45 55	91 98 101	101.2	7.25 7.29 7.44
PE modified: MA/PE=0.05 (TPPE 9082)	0.45	36–100	$d=4$ $l=150$	582.4	35 45 55	92 98 100	100.2	6.57 6.67 6.96
PE modified: MA/PE=0.05; ST/MA=0.5 (TPPE 9083)	0.45	36–100	$d=4$ $l=150$	581.1	35 45 55	95 99 100	101.3	7.90 8.13 8.37
PE modified: MA/PE=0.05; ST/MA=1 (TPPE 9084)	0.45	36–100	$d=4$ $l=150$	544.6	35 45 55	90 98 100	101.3	8.19 8.81 9.43
PE modified: MA/PE=0.05; ST/MA=2 (TPPE 9085)	0.45	36–100	$d=4$ $l=150$	575.6	35 45 55	97 99 101	99.7	8.59 8.87 9.05
Unplasticised PVC UPVC Good Fellow	0.50	100–200	$d=4$ $l=300$	1804.1	35 45 55	48 51 50	101.3	9.16 9.38 9.74
Polyether ether ketone (PEEK) Good Fellow	0.55	100–200	$d=4$ $l=300$	1835.5	45 55 65	100 101 102	101.1	14.43 15.08 15.22

$A_{sp}$ , specific surface area;  $d$ , diameter;  $l$ , length;  $m$ , mass;  $T_c$ , temperature of the column;  $p_E$ , inlet pressure;  $p_A$ , outlet pressure;  $F \times j$ , corrected flow ( $j$ , James-Martin factor).

spectra were referenced to the hydrocarbon reference peak C 1s at a binding energy BE=285.00 eV. Quantitative elemental compositions were determined from peak areas after using Wagner's sensitivity factors and the spectrometer transmission function. The high resolved spectra were decomposed by means of the VG ECLIPSE routines. Free parameters of component peaks were their binding energy, height, full width at half maximum and the Gaussian–Lorentzian ratio. Every sample was extracted by cyclohexane for 6 h and evacuated at  $10^{-6}$  mbar for at least 24 h before measurement to remove impurities and monomers. The used powders were fixed by Scotch adhesive on a slide (see also Ref. [25]).

SEM was carried out using a LEO Gemini DSM 982 microscope (Carl Zeiss, Oberkochen, Germany) with magnifications of 10 000 and 30 000.

### 2.2.3. Elemental analysis

This was carried out using an elemental analyser EA 1108 (Carlo Erba, Milan, Italy).

### 2.2.4. Differential scanning calorimetry (DSC)

For DSC experiments, a DSC7 system (Perkin-Elmer Instruments, Shelton, CT, USA) was used.

### 2.2.5. Inverse gas chromatography

A commercial gas chromatograph (HP 5890A, Series II, Hewlett-Packard, Palo Alto, CA, USA) equipped with flame ionisation detector and the ChemStation software (version 03.34) was used. Dried helium 5.0 was used as carrier gas with a flow-rate of about 10 ml/min. The polymer powders were filled into glass columns and conditioned overnight at 65 °C prior to measurement. The experimental parameters are listed in Table 1. A homologous series of *n*-alkanes (*n*-pentane to *n*-decane, Fluka, Taufkirchen, Germany) was used to investigate dispersive interactions of the polymer surfaces, and chloroform, dichloromethane, benzene, acetonitrile, acetone, ethyl acetate, diethyl ether and tetrahydrofuran (THF) (analytical grade, Fluka, Taufkirchen, Germany) were used as polar probes.

## 3. Results and discussion

### 3.1. DRIFT

The investigations of the HDPE powders grafted with MA and ST/MA gave the following results (see also Fig. 1):

- (i) The samples grafted with 2.5 and 5% MA in PE, respectively, contained no anhydride but maleic acid.
- (ii) Addition of ST causes an increase in the amount of anhydride and a decrease in the amount of maleic acid in the polymer matrix by protection of the anhydride from hydrolysis.
- (iii) A content of ST/MA > 1 had no further influence on the ratio of maleic anhydride to maleic acid on the powder surface.

### 3.2. XPS

[O]/[C] and [C–O]/[C=O] ratios calculated from C 1s and O 1s peaks of the obtained spectra are summarised in Table 2.

The most important results of XPS (compare Refs. [25] and [26]) can be summarised as follows:

- (i) The [O]/[C] ratios on the surface of the grafted PE are about five times higher than that in the bulk polymer (determined by elemental analysis), see Fig. 2.
- (ii) A maximum of the [O]/[C] ratio was found for the sample ST/MA = 0.5. On the one hand, the

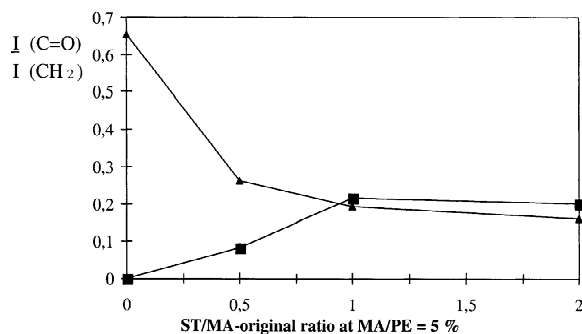


Fig. 1. DRIFT measurements: Intensity ratio of the carbonyl bands and of the  $\delta(\text{CH}_2)$ -vibration bands ( $1490\text{--}1450\text{ cm}^{-1}$ ) against the styrene–MSA original ratio at MSA/PE = 5% (▲, acid:  $1760\text{--}1670\text{ cm}^{-1}$ ; ■, anhydride:  $1800\text{--}1760\text{ cm}^{-1}$ ).

Table 2  
Oxygen carbon ratios of MA and ST/MA grafted PE determined by XPS

MA/PE	0.025	0.05	0.05	0.05	0.05
ST/MA	0	0	0.5	1	2
[O]/[C]	0.0119	0.0211	0.1162	0.0784	0.0533
[C–O]/[C=O]	–	0.497	0.853	0.610	0.650

grafting yield is increasing with increasing amount of ST (causing an increasing amount of [O]) and on the other hand, hydrolysis of MA is decreased by adding ST (causing a decreasing amount of [O]). These two opposite tendencies cause a maximum of the [O]/[C] ratio at ST/MA=0.5.

The SEM images show that the PEEK particles were relatively smooth, while UPVC had homogeneously distributed pores, but no nanopores. Untreated PE consists of clusters (diameter of 20–40  $\mu\text{m}$ ) of smaller particles (ca. 1–5  $\mu\text{m}$ ). The primary particles are connected with a porous sponge-like lamellae containing polymeric structure (Fig. 3A). While grafting with MA only had no great influence, grafting with ST–MA mixtures has a considerable influence on the morphology of the PE powder. It leads to closing of the pores and levelling of the surface dependent on the amount of ST. Grafting with a ST/MA ratio of 0.5 causes a closing of the small pores in the primary particles and a partly closing of the sponge-like structures between the primary particles. An increase in the amount of ST

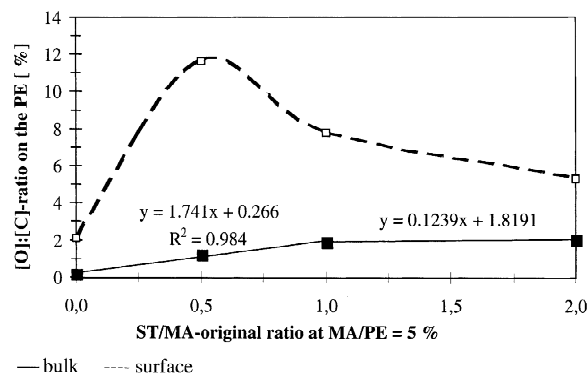
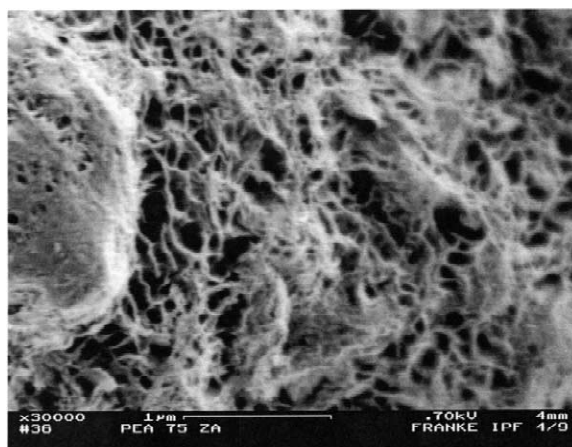
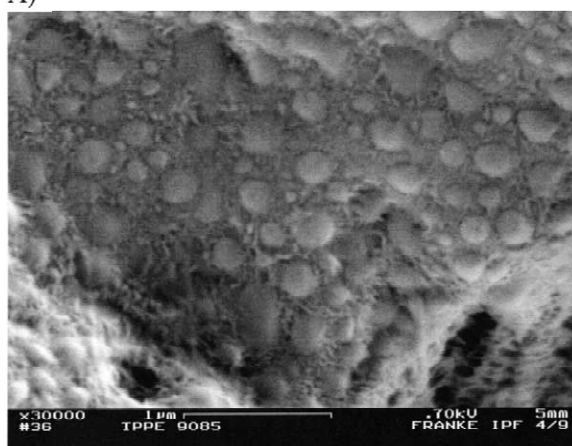


Fig. 2. XPS: [O]/[C] ratios calculated from C 1s and O 1s peaks of the obtained spectra.



A)



B)

Fig. 3. SEM images: (A) untreated PE; (B) grafted PE: MSA/PE=0.05, ST/MSA=2.

causes a more homogeneous closing of those pores. When grafting with a ST/MA ratio of 2, the pores are closed and small blister-like structures appear on the surface (Fig. 3B). An explanation for this may be that alternating MA–ST copolymers are grafted firstly and then remaining ST forms as blister-like islands on the surface.

IGC at infinite dilution had to be carried out above the glass transition temperature of the PE samples, therefore influences of bulk absorption had to be considered. The calculated  $\gamma_s^d$  values (according to Dorris and Gray [18]) of the PE samples were higher compared to values found in earlier studies [27,28]

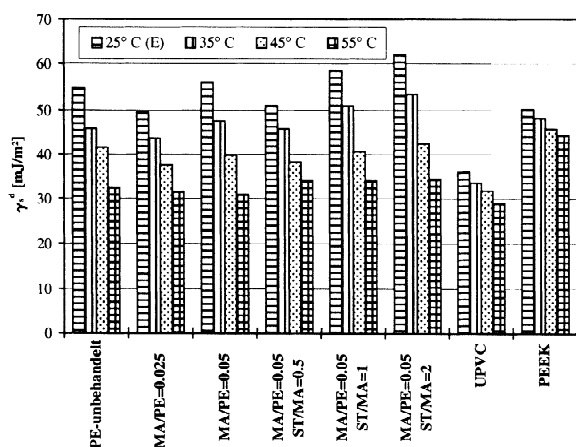


Fig. 4. Comparison of the dispersive components of the surface energy  $\gamma_s^d$  of modified PE, UPVC and PEEK at 25, 35, 45 and 55 °C (calculated according to Dorris and Gray [18]).

and more dependent on temperature than the values of UPVC and PEEK where IGC could be carried out below the glass transition temperature (Fig. 4).

This indicates an influence of bulk absorption and nanomorphology. Fig. 5 shows the crystallinity of several PE samples determined by means of DSC measurements. Comparing Figs. 4 and 5, it can be seen that the samples showing the highest  $\gamma_s^d$  values have the lowest crystallinity (ST/MA=1 and 2). This is due to the fact that bulk absorption in amorphous polymers is much more likely. The relatively high-temperature dependence also points to an influence of absorption and morphology.

The influence of nanomorphology on the inter-

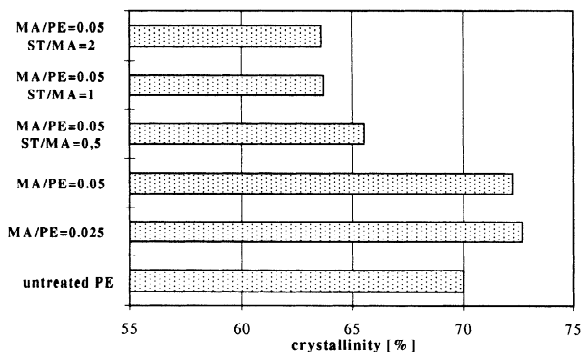


Fig. 5. Influence of the treatment of PE on its crystallinity.

action of the PE surface with a homologous series of *n*-alkanes was described by means of standard adsorption enthalpy ( $\Delta H_A^\circ$ ) and standard adsorption entropy ( $\Delta S_A^\circ$ ) values. These values were calculated using the standard state of de Boer [29] and showed a linear dependence on the number of carbon atoms of the *n*-alkane, i.e. the interaction potential of one methylene group of the *n*-alkanes with *one* of the sample surfaces was independent of its chain length.

Comparing the adsorption of *n*-alkanes on the *different* sample surfaces, it was found that the differences of  $\Delta H_A^\circ$  values were increasing with decreasing chain length. The fact that the alkanes with a smaller chain length were able to gain access to pores with larger differences in their dispersive interaction potential was regarded as a reason for this. Regarding the  $\Delta H_A^\circ$  values of pentane or hexane, a decrease in  $\Delta H_A^\circ$  is observed when grafting with an increasing amount of MA and MA–ST. This goes along with a closing of the accessible pores which could also be seen at the SEM images. From the  $\Delta H_A^\circ$  values of decane, which were only negligibly influenced by nanomorphology, it may be concluded that the dispersive interaction potential of the PE samples was increasing with increasing amounts of MA and MA–ST ratios. No correlation with the crystallinity of the polymer samples was found (Fig. 6).

The influence of morphology is seen even more clearly when regarding the  $\Delta S_A^\circ$  values of the *n*-alkanes, calculated by means of the Gibbs-Helmholtz equation. It can be seen that  $\Delta S_A^\circ$  was decreasing with increasing amounts of MA and MA–ST. This decrease was stronger the shorter the chain length of the *n*-alkane. However, the  $\Delta S_A^\circ$  values of decane show an increase with increasing MA and MA–ST ratios, which again confirmed the idea of closing the pores by grafting (Fig. 7).

For the determination of the acid–base properties of the polymers, the retention behaviour of several polar probes of approximately the same size was used.  $K_A$  and  $K_B$  values, calculated as described above, are listed in Table 3. It can be seen that grafting with MA caused amphoteric behaviour of the PE samples with predominant donor properties. An increasing amount of MA causes an increasing acceptor character of the surface, but has only a small influence on  $K_B$ .

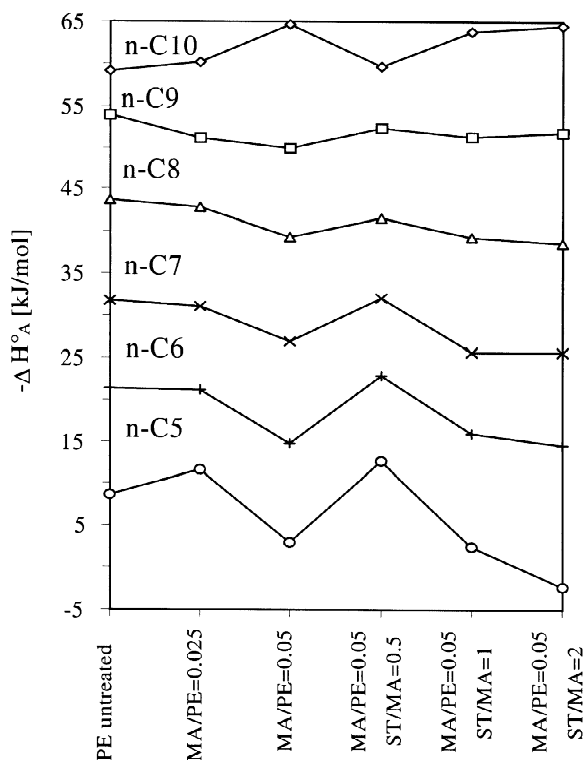


Fig. 6. Influence of nanomorphology on the interaction of the PE surface with a homologous series of *n*-alkanes: variation of  $\Delta H_A^0$ .

When adding ST, a maximum of the acceptor character (a minimum donor and a maximum amphoteric character) of the polymer surface was observed at a ST/MA ratio of 0.5 which was in a good accordance with the maximum value of the [O]/[C] and the [C–O]/[C=O] ratio determined by XPS. It can also be seen that with an increasing amount of ST, the donor character of the surface is increasing while the acceptor character is decreasing. This can be explained with the increasing amount of anhydride on the surface determined by DRIFT.

#### 4. Conclusion

The aim of this study was the investigation of surface thermodynamics of real polyalkenes of technological importance. IGC at infinite dilution, as the chosen method, had to be carried out above the glass

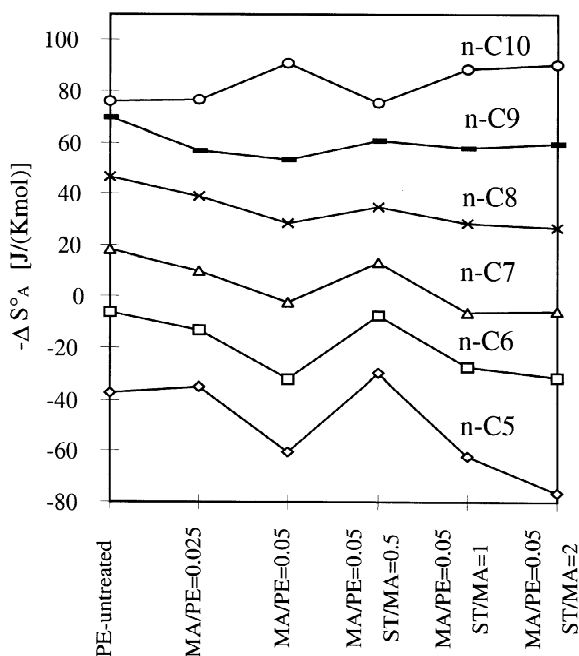


Fig. 7. Influence of nanomorphology on the interaction of the PE surface with a homologous series of *n*-alkanes: variation of  $\Delta S_A^0$ .

transition temperature of the PE samples grafted with different amounts of MA and ST–MA mixtures. Because of bulk absorption, all determined  $\gamma_s^d$  values were too high and dependent on the amorphous proportion of the PE. The influence of morphological retention was shown by means of the change in  $\Delta H_A^0$  and  $\Delta S_A^0$  values that confirmed the idea of closing the pores of the PE by grafting. The change of donor ( $K_B$ ) and acceptor ( $K_A$ ) numbers calculated by means of  $\Delta H^{sp}$  proved the introduction of polar groups onto the surface by grafting. All grafted samples had amphoteric surface properties. The donor and acceptor character was influenced by the amount of MA and the ST/MA ratio and coincided with the surface chemical properties determined by XPS and DRIFT.

Therefore it was shown that IGC gives reasonable information about dispersive and acid–base properties of polymeric surfaces even when it is performed above their glass transition temperature. Some efforts have to be made, however, to relate the results to chemistry and morphology of the polymeric surface to be able to discuss the influence of bulk absorption at least qualitatively.

Table 3  
Donor and acceptor values of the polyethylene samples

Polyethylene powders	$100K_A$ (kcal/mol)	$100K_B$ (kcal/mol)	$K_A/K_B$
PE untreated	0.0	0.0	–
MA/PE=0.025	3.8	31.3	0.12
MA/PE=0.05	8.2	29.3	0.28
MA/PE=0.05, ST/MA=0.5	14.1	16.4	0.86
MA/PE=0.05, ST/MA=1	8.5	28.3	0.30
MA/PE=0.05, ST/MA=2	2.9	34.8	0.08

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