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Segmental Adsorption Energies for Polymers on Silica and Alumina

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ABSTRACT: Segmental adsorption energies for polymers on inorganic solids can be determined from adsorption/desorption transitions in binary solvent mixtures. These transitions were measured for various polymer/solvent/substrate systems by thin-layer chromatography. Polymers with either phenyl, ether, or ester groups were classified according to their adsorption strength on both silica and alumina. A consistent trend with respect to the adsorption energy for the different polymers was observed for both substrates. Polymer chains with larger alkyl side groups or more $-CH_2-$ groups between ether groups in the backbone have a lower adsorption energy. The adsorption energy for each individual polymer is higher on the silica surface than on the alumina surface. For the polymers studied, the main contribution to the work of adhesion on silica with respect to vacuum is due to dispersive interactions.

Introduction

During the last few decades interest in polymers at interfaces has been steadily growing. Polymers may be considered as tools to manipulate the properties of interfaces, and such modified interfaces are very important in many industrial products and technological processes. The strength of polymer/interface bonds may be of great relevance for the efficiency of processes and the quality of products. For instance, in the case of polymer composites, the adhesion strength between the matrix polymer and the reinforcing filler affects the toughness and flexibility of the composites.[1]

Generally, the adhesion strength of polymers on a substrate can be determined in two ways. The first method involves mechanical removal of polymer from a substrate. This macroscopic disruption process is always irreversible. For such processes the measured adhesion strength (work of adhesion) depends on experimental conditions, such as crack speed and temperature. The reversible (intrinsic) adhesion strength is always smaller because of energy dissipation in the irreversible process. During the detachment of a polymer film from a substrate, energy may be absorbed by the deformation of the polymer film. This viscoelastic component may even be (much) larger than reversible adhesion strength.

The second way to determine the adhesion strength of polymers is microscopic and reversible. Now, chemical energy instead of mechanical work is used to displace polymers from a substrate. Chemical energy is added to the system in the form of a certain chemical compound, a so-called *displacer*. The method gives the segmental adsorption energy which can be related to the thermodynamic work of adhesion. In principle, the thermodynamic work does not depend on experimental conditions and is therefore an intrinsic quantity for the particular system.

The latter method has been proposed and developed by Cohen Stuart et al.[2,3] The experiments are carried out in solution. The amount of displacer which has to be added to the solution for complete desorption of the polymer is called the *critical displacer concentration* or, for short, the *critical point*. This critical concentration can be related to the segmental adsorption energy of the polymer. The thermodynamic work of adhesion can be calculated from this energy provided the number of segments bound per unit surface area is known.

In this study we measured critical points by thin-layer chromatography (TLC). In a previous paper[4] we showed that this technique is sensitive and works very well for polystyrene on silica. The adsorption energies of polystyrene on silica calculated from critical points using different displacers agree very satisfactorily.

In the present paper, the determination of the segmental adsorption energies of five different polymers with basic (proton-accepting) functional groups (phenyl, ester, ether) on both alumina and silica is described. Besides the effect of a particular functional group, the influence of the chain structure on the adsorption energy is studied. The polymers are classified according to their adsorption energy. Not only can adsorption energies of polymers be obtained from critical points but also the adsorption energies of displacers. Therefore, the adsorption energies of displacers on both silica and alumina are also given.

The last part of this paper deals with the work of adhesion of various polymers on silica and involves an attempt for a molecular interpretation. Discrimination is made between the contributions of dispersive interactions and of specific interactions to the work of adhesion of the polymers on the substrate.

Methods

Adsorption Energy. Two interaction parameters control polymer adsorption from solution onto an adsorbent, one for polymer/surface contacts and one for polymer/solvent contacts.

For the interaction free energy of polymer/surface contacts we use Silberberg's[5] χ_s parameter, which is defined as the adsorption energy (in units of kT) of a polymer segment with respect to that of a solvent molecule. The χ_s parameter is by definition positive if the polymer adsorbs preferentially from the solvent. Polymers adsorb only if χ_s exceeds a critical value χ_{sc} which corresponds to the adsorption/desorption transition.[2] The χ_{sc} parameter is related to the conformational entropy loss per segment upon adsorption.

Contact (free) energies between polymer segments and solvent molecules are usually represented by the familiar Flory–Huggins χ parameter.

Values for the χ parameter can be obtained from various observable properties, such as intrinsic viscosity, light scattering, and osmotic pressure.[40] The χ_s parameter can only be determined by a method proposed by Cohen Stu-

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art et al.[2,3] This method is based upon polymer desorption in binary solvent mixtures. Polymers which are adsorbed from solution on an adsorbent may be desorbed by increasing the concentration of a more strongly adsorbing solvent component (displacer). The displacer concentration needed to entirely desorb the polymer is the *critical point* referred to in the Introduction.

In a three-component system (polymer, solvent, displacer), two χ_s and three χ parameters are needed to describe all the interactions. The different χ parameters in such a system are indicated by the superscripts po, pd, and do, which correspond to polymer/solvent, polymer/displacer, and displacer/solvent contacts, respectively. The same superscripts can be used for the χ_s parameters. Now, the superscripts indicate the adsorption of polymer from solvent, polymer from displacer, and displacer from solvent, respectively. These three χ_s parameters are interrelated because of their exchange character: $\chi_s^{po} = \chi_s^{pd} + \chi_s^{do}$. Therefore, only two independent χ_s parameters occur.

Cohen Stuart et al.[2] have derived an equation which relates the volume fraction ϕ_{cr} of displacer at the critical point to the segmental adsorption energy parameters χ_s^{po} and χ_s^{do}:

$$\phi_{cr} = \frac{\exp(\chi_s^{po} - \chi_{sc} + \{(1-\lambda_1)(1-\phi_{cr})(\chi^{po} + \chi^{do} - \chi^{pd}) - \lambda_1(\chi^{do} - \chi^{pd})\}) - 1}{\exp(\chi_s^{do} + \{2(1-\lambda_1)(1-\phi_{cr})\chi^{do} - \lambda_1\chi^{do}\}) - 1} \tag{1}$$

The parameter λ_1 comes from the lattice which is used to describe the solution and represents the fraction of contacts that a site has with sites in one of the adjacent lattice layers. For a hexagonal lattice λ_1 is equal to $3/12 = 0.25$. In this model, it is assumed that one lattice site is occupied by either one solvent molecule, one displacer molecule, or one polymer segment.

The terms −1 in eq 1 may be ignored if the exponentials are much larger than unity, i.e., for strong anchoring of the polymer segments. In this case, eq 1 simplifies to

$$\chi_s^{po} = \chi_s^{do} + \ln\phi_{cr} + \chi_{sc} - \{\lambda_1\chi^{pd} - (1-\phi_{cr})(1-\lambda_1)\Delta\chi^{dop}\} \tag{2}$$

showing that in this limit ϕ_{cr} depends exponentially on $\chi_s^{po} - \chi_s^{do}$. All terms of eqs 1 and 2 within braces refer to solute/solvent interactions. For athermal behavior of the solution these terms are equal to zero. The parameter $\Delta\chi^{dop}$ is an abbreviation for $\chi^{pd} + \chi^{do} - \chi^{po}$.

The critical adsorption energy parameter χ_{sc} can, in principle, be determined from desorption experiments with the monomer unit of the polymer as the displacer. For such displacers χ_s^{do} may be taken to be equal to χ_s^{po}. The χ_{sc} value can then be calculated directly from ϕ_{cr} by using eq 2 if the χ_s parameter for monomer adsorption from solvent is not too small (i.e., >2). For small values of this parameter, χ_{sc} has to be calculated from ϕ_{cr} using the full eq 1 with $\chi_s^{po} = \chi_s^{do}$. However, in that case the value of χ_s^{do} is needed explicitly.

When a polymer is desorbed by its monomeric equivalent, the critical displacer volume fraction is usually found to be close to unity. For such systems, the solute/solvent interaction term with the prefactor $(1-\lambda_1)(1-\phi_{cr})$ is very small and can therefore be ignored. The terms $\lambda_1\chi^{pd}$ (in eqs 1 and 2) and $\lambda_1\chi^{do}$ (in eq 1) may both be significant and have to be taken into account. However, just as in the case of high adsorption energies, the $\lambda_1\chi^{do}$ terms of eq 1 also cancel if ϕ_{cr} is close to unity.

The critical adsorption energy parameter can also be estimated theoretically from the reduction of possible orientations of a segment upon adsorption. Within the restriction of a lattice and ignoring rotational entropy, χ_{sc} calculated in this way equals $-\ln(1-\lambda_1)$, which, for a hexagonal lattice, is 0.288.

In a previous paper,[4] we showed that the chromatographic solvent strength concept of Snyder[6] may be interpreted according to the model of Cohen Stuart et al.[2] However, Snyder considers only athermal solution behavior. Tabulated solvent strengths of various solvents (eluotropic series) in the literature[6,7] serve as a useful source of information for determining adsorption energies. We derived[4] the following relations between our χ_s parameters and Snyder's solvent strengths ϵ:

$$\chi_s^{do} = \alpha' A(\epsilon_d - \epsilon_o) \tag{3}$$

$$\chi_s^{po} = \alpha' A(\epsilon_{cr} - \epsilon_o) + \chi_{sc} \tag{4}$$

Here, the parameters ϵ_o and ϵ_d are the solvent strengths of pure solvent and pure displacer, respectively, and ϵ_{cr} is the solvent strength of the solvent mixture at the critical point. The former two parameters are tabulated by Snyder, and the latter can be calculated by Snyder's equation for the solvent strength of binary solvent mixtures:[6]

$$\epsilon_{cr} = \epsilon_o + \frac{\ln\{\phi_{cr}\exp[\alpha' A(\epsilon_d - \epsilon_o)] + 1 - \phi_{cr}\}}{\alpha' A} \tag{5}$$

The parameter A is the surface area occupied per adsorbate molecule (in nm^2) and α' (which has a dimension of nm^{-1}) is the activity of the adsorbent. We should note here that Snyder originally expressed A in units of 0.085 nm^2, which corresponds to a (dimensionless) surface area of 6 for benzene. In order to equate $\alpha' A\epsilon$ to the molecular adsorption energy in units of kT, we defined[4] an activity α' which is a factor (ln 10)/0.085 = 27.1 greater than Snyder's α. The value of α' depends on such quantities as the amount of physisorbed water, the surface porosity, and the distribution of active sites on the surface.[6] For the determination of α', which is essentially a calibration of the adsorbent, we used the method described by Snyder.[6] This method involves retention factor measurements of several standard (aromatic) compounds on the thin layer, with pentane as the eluent.

The combination of eqs 3–5 can be written as $\phi_{cr}[\exp(\chi_s^{do}) - 1] = \exp(\chi_s^{po} - \chi_{sc}) - 1$, which is the athermal equivalent of eq 1. Extending eq 4 with the solute/solvent interaction term of eq 2 gives

$$\chi_s^{po} = \alpha' A(\epsilon_{cr} - \epsilon_o) + \chi_{sc} - \{\lambda_1\chi^{pd} - (1-\phi_{cr})(1-\lambda_1)\Delta\chi^{dop}\} \tag{6}$$

We note that the solvent/solute interaction term in eq 6 is only valid for the case of high adsorption energies. This means that eq 6 is not suitable for systems that have low adsorption energies and strong solvent/solute interactions at the same time. The advantage of eq 6 for the determination of χ_s^{po} is that tabulated solvent strength data can be used instead of χ_s^{do} parameters which have to be measured separately. In ref 4 we showed that this method works very well for polystyrene (PS) on silica. However, for strongly adsorbing polymers which can only be displaced by very strong displacers another complication arises, namely, that the solvent strength of strong displacers is no longer a constant but depends on the displacer concentration. Snyder explains this phenomenon by *solvent localization*.[7,8] At low displacer concentrations the adsorbed monolayer is undersaturated with displacer. In such cases, all displacer molecules may be *localized* on the surface, i.e., have an optimal orientation with respect to surface sites. The tendency for localization of adsorbate molecules on the substrate increases as the interaction between these molecules with surface sites becomes stronger. At high surface concentrations, molecules become *delocalized* due to sterical hindrance between molecules in the surface layer. The adsorption energy of localized adsorbed molecules is usually more negative than that of delocalized ones.

Instead of using solvent strength data or measuring the adsorption energy of the displacer, one can also use the adsorption energy of a second polymer to determine the χ_s^{po} value for a particular polymer/solvent combination. The difference in adsorption energy for a polymer a and polymer b on the same type of surface sites is by definition

$$\chi_s^{ab} = \chi_s^{ao} - \chi_s^{bo} \tag{7}$$

This difference may be found from the critical points by applying eq 1 for both polymers a and b and the same displacer/solvent/substrate combination. For athermal solution behavior eq 1 may be written as $\exp(\chi_s^{po} - \chi_{sc}) = \phi_{cr}[\exp(\chi_s^{do}) - 1] + 1 \cong \phi_{cr}\exp(\chi_s^{do}) + 1$, where the last approximation is valid for strong displacers (high χ_s^{do}). Hence

$$\chi_s^{ab} = \ln\,[\phi_{cr}^{a}\exp(\chi_s^{do}) + 1] - \ln\,[\phi_{cr}^{b}\exp(\chi_s^{do}) + 1] + \chi_{sc}^{a} - \chi_{sc}^{b} \tag{8}$$

Two more simplifications are possible.

First, in terms of a lattice model (where the rotational entropy is disregarded), χ_{sc} depends only on lattice coordination numbers. Hence, χ_{sc} parameters of different polymers can be taken to be equal so that the critical adsorption energy terms in eq 8 cancel. (In reality differences between the χ_{sc} values for various polymers may arise due to variations in chain stiffness. The lattice model does not account for such an effect.)

Second, for not too small χ_s^{ao} and χ_s^{bo} values the terms $\phi_{cr}^{a}\exp(\chi_s^{do})$ and $\phi_{cr}^{b}\exp(\chi_s^{do})$, respectively, are much larger than unity. In such cases the terms +1 in the logarithmic terms of eq 8 may be omitted. As a result, the expression for χ_s^{ab} becomes very simple:

$$\chi_s^{ab} = \ln\,(\phi_{cr}^{a}/\phi_{cr}^{b}) \tag{9}$$

Hence, χ_s^{ab} may be found from the ratio between critical points, regardless of the displacer used, provided that the individual χ_s values with respect to the solvent are large enough. The effect of the omission of solute/solvent interactions on the determination of χ_s values is usually relatively small. We have already shown this for PS on silica.[4] The above assumptions of athermal solvent behavior and $\chi_{sc}^{a} = \chi_{sc}^{b}$ lead probably to less significant errors than the description of the solution by a lattice in which sites are occupied by either one solvent molecule, one displacer molecule, or one polymer segment. The parameter χ_s^{ab} as given by eq 9 is equal to the difference between the chemical potential of the displacer in the critical solvent mixture for polymer a and for polymer b, under ideal conditions. Hence, for a polymer which is more strongly adsorbed more chemical energy, substantiated by the amount of displacer, has to be added to the system for complete displacement of the polymer.

For PS we have determined the effective segmental adsorption energy χ_s^{po} using the solvent strength concept.[4] The values obtained can be used to transform polymer adsorption energies relative to PS into adsorption energies relative to the solvent, using eqs 7–9.

In the same way as adsorption energies for one polymer can serve as a standard for another, polymer adsorption energies can also be used to determine displacer adsorption energies χ_s^{do}. Adsorption energies of displacers (notably those for which no solvent strength is tabulated) can be calculated from critical points with the help of either eq 1 or 2 provided the χ_s^{po} value for the polymer in question is known. Hence, both polymers and displacers can be classified according to their adsorption strength by the method given above.

Thermodynamic Work of Adhesion. So far, we expressed the adhesion strength of polymers as the segmental adsorption energy relative to that of a solvent molecule, i.e., the interaction energy difference between a polymer/surface and a solvent/surface contact. The segmental adsorption energy is a *reversible* measure for the adhesion strength.

In macroscopic adhesion strength experiments the interaction energy is found as the *work* per unit of surface area needed to disrupt a polymer/substrate joint, i.e., to replace a polymer/substrate interface by an air/substrate plus a polymer/air interface. This work of adhesion is determined in an *irreversible* way because energy dissipation takes place during the disruption process.

In this section we want to convert molecular adsorption energies (χ_s) into the *reversible* work of adhesion with respect to vacuum rather than solvent. The work of adhesion obtained from segmental adsorption energies is a *thermodynamic* (intrinsic) quantity.

Intermolecular surface forces may be decomposed into two categories: dispersive (D) interactions and specific (SP) interactions. Dispersive interactions are always present and may be split up into a long-range term (DL) and a short-range term (DS). The short-range interactions extend only to the first monolayer; the long-range term accounts for forces acting over more than one layer.

The specific interactions, such as hydrogen bonding and polar forces, occur only if the interacting species contain specific groups. These types of interactions may be regarded as short range.

Assuming a simple additivity rule, the intrinsic work of adhesion W_{so} of a liquid (o) on a solid (s) in terms of the interaction types discussed above is given by

$$W_{so} = W_{so}^{DL} + W_{so}^{DS} + W_{so}^{SP} \tag{10}$$

The dispersion contribution $W_{so}^{D}(= W_{so}^{DS} + W_{so}^{DL})$ may be approximated as twice the geometric mean of the dispersion force components of the surface tensions γ^{D} of each of the participating species:[9]

$$W_{so}^{D} = 2(\gamma_s^{D}\gamma_o^{D})^{1/2} \tag{11}$$

Fowkes[1,10] claims that the specific contribution W_{so}^{SP} can be described entirely by acid/base (AB) interactions. Acid/base interaction energies may be predicted by several semiempirical models. Fowkes uses the model of Drago et al.[11] These authors have correlated the enthalpy of acid/base interactions ΔH^{AB} to two constants (C_B, E_B) for the base and two constants (C_A, E_A) for the acid: $-\Delta H^{AB} = C_AC_B + E_AE_B$. This formula is known as the Drago equation. The products C_AC_B and E_AE_B represent the covalent (C) and electrostatic (E) character of the acid/base interaction, respectively. For various compounds the constants E and C are tabulated in the literature.[12] Molar enthalpies of many acid/base pair interactions can then be estimated from the Drago equation.

The analogue of eq 10 for the reversible work of adhesion between a polymer (p) and a solid (s) is

$$W_{\mathrm{sp}} = W_{\mathrm{sp}}^{\mathrm{DL}} + W_{\mathrm{sp}}^{\mathrm{DS}} + W_{\mathrm{sp}}^{\mathrm{SP}} \qquad (12)$$

Subtracting eq 10 from eq 12 gives

$$W_{\mathrm{sp}} - W_{\mathrm{so}} = W_{\mathrm{sp}}^{\mathrm{DL}} - W_{\mathrm{so}}^{\mathrm{DL}} + (W_{\mathrm{sp}}^{\mathrm{DS}} + W_{\mathrm{sp}}^{\mathrm{SP}}) - (W_{\mathrm{so}}^{\mathrm{DS}} + W_{\mathrm{so}}^{\mathrm{SP}}) \qquad (13)$$

The short-range interaction energy of a polymer with a substrate minus that of a solvent with the same substrate (i.e., the terms in between the brackets in eq 13) can directly be related to $\chi_{\mathrm{s}}^{\mathrm{po}}$ because this parameter accounts precisely for the short-range interactions with the substrate. The value of $\chi_{\mathrm{s}}^{\mathrm{po}}$ divided by the surface area A of one monomer unit gives the difference in the free energy of interaction per unit of surface area. Hence, the last four terms in the right-hand side of eq 13 may be replaced by $\chi_{\mathrm{s}}^{\mathrm{po}}kT/A$.

Assuming the long-range dispersive interaction energy difference between a polymer/surface and a solvent/surface contact is not significant, the term $W_{\mathrm{sp}}^{\mathrm{DL}} - W_{\mathrm{so}}^{\mathrm{DL}}$ in eq 13 may be neglected.

For solvents with no specific groups, the term W_{so} in the left-hand side of eq 13 is equal to $W_{\mathrm{so}}^{\mathrm{D}}$ and may then be substituted by $2(\gamma_{\mathrm{s}}^{\mathrm{D}}\gamma_{\mathrm{o}}^{\mathrm{D}})^{1/2}$ (eq 11). Equation 13 can now be rewritten as

$$W_{\mathrm{sp}} = 2(\gamma_{\mathrm{s}}^{\mathrm{D}}\gamma_{\mathrm{o}}^{\mathrm{D}})^{1/2} + \chi_{\mathrm{s}}^{\mathrm{po}}kT/A \qquad (14)$$

Hence, the reversible work of adhesion of a polymer on a substrate may be estimated if an apolar solvent ($\gamma_{\mathrm{o}} \approx \gamma_{\mathrm{o}}^{\mathrm{D}}$) is used which does not have specific interactions with the surface ($W_{\mathrm{so}} \approx W_{\mathrm{so}}^{\mathrm{D}}$). This work is then obtained from $\chi_{\mathrm{s}}^{\mathrm{po}}$ as measured by displacement, the solvent surface tension γ_{o}, and the dispersion contribution $\gamma_{\mathrm{s}}^{\mathrm{D}}$ of the surface free energy of the substrate.

In solution, the dispersive interaction energy (long range plus short range) difference between polymer segments with the substrate and solvent molecules with the substrate is in most cases very small. Hence, the energy difference between a polymer/surface and a solvent/surface contact, represented by $\chi_{\mathrm{s}}^{\mathrm{po}}$, is mainly determined by the difference in specific interaction energy. For solvents with no specific interactions, $\chi_{\mathrm{s}}^{\mathrm{po}}$ may be approximated as the specific interaction energy of a polymer segment with the surface.

The procedure given above is of course approximate. For instance, all functional groups which have contact with the surface are assumed to have the same adsorption energy. In practice, there may be different types of surface sites. Moreover, it is likely that on a fully covered surface not all segments can assume an optimal orientation toward the surface sites.

Experimental Section

The polymers used in this study were polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(butyl methacrylate) (PBMA), polytetrahydrofuran (PTHF), and poly(ethylene oxide) (PEO). Three different functional groups occur in these polymers, i.e., a phenyl (PS), an ester (PBMA, PMMA), and an ether group (PTHF, PEO). The particular samples and the chemical structure of the polymers are given in Table I. We have chosen polymers with a molecular weight of about 100 000 for the following reasons. The retention behavior of polymers with M_{w} > 10 000 on thin-layer plates is known to depend little on the molecular weight.[13] However, for very high molecular weight polymers (M_{w} > 1 000 000) the kinetics for polymer exchange between the stationary and the mobile phase may become too slow. The obtained retention factor is then not only a function of thermodynamic quantities. Another consequence of slow exchange kinetics between the different phases is that in the case of desorption the size of the final spot becomes larger. As an illustration, Figure 1 shows final spots of different molecular weight PS samples eluted on alumina with pure toluene (which is a displacer for PS). The elution time for all samples was about $^1/_2$ h. As can be seen in this figure, the polymer moves up with the eluent front. The final spot size for the samples with a molecular weight of 9000 and 120 000 is relatively small, whereas the size of the spot for M_{w} = 3 000 000 is rather big. For the highest molecular weight sample the exchange kinetics of the polymer between the mobile and stationary phase becomes too slow, so that part of the polymer lags behind. The polymer is then distributed over a considerable area.

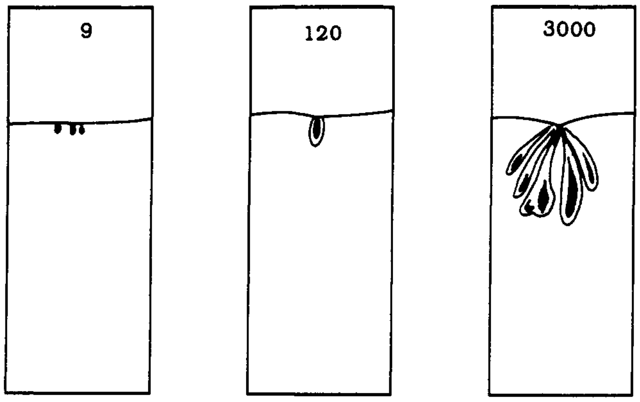
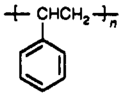
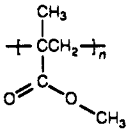
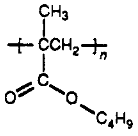


Figure 1. Final spots of monodisperse polystyrene on an alumina thin layer developed by the displacer toluene, for polymer samples of three different molecular weights. The molecular weights (×10^{-3}) are indicated in the chromatograms.

Table I
Polymer Samples

sample	structure	$M_{\mathrm{w}} \times 10^{-3}$	$M_{\mathrm{w}}/M_{\mathrm{n}}$
polystyrene (Polymer Laboratories)		120	1.03
poly(methyl methacrylate) (Aldrich)		90	2.0
poly(butyl methacrylate) (Aldrich)		240	2.5
polytetrahydrofuran (Polymer Laboratories)	$-\!\!\!+ CH_2CH_2CH_2CH_2O -\!\!\!+_n$	258	1.13
poly(ethylene oxide) (Polymer Laboratories)	$-\!\!\!+ CH_2CH_2O -\!\!\!+_n$	246	1.09

The retention behavior of different polymers on a thin-layer plate was recorded as a function of binary eluent (*displacer/solvent*) composition. For all experiments we used carbon tetrachloride as the *solvent*. The displacers have to be chosen carefully because the polymer in question must be soluble in each of the eluent mixtures and the displacer has to be strong enough to desorb this polymer. In total we used 16 displacers with different displacement strengths. All displacers and the solvent carbon tetrachloride were of analytical grade. Some displacers contain stabilizing agents. Such additives have to be removed if the displacer is weak and the additive adsorbs strongly (e.g., ethanol in chloroform). Although the concentration of such an additive is usually very low, it may be responsible for polymer desorption instead of the displacer itself.[4]

The thin-layer chromatoplates used were plastic sheets with either a silica layer (Kieselgel 60 F_{254}; Merck) or an aluminum oxide layer (type 60 F_{254}; Merck) of 0.2 mm thickness. Before

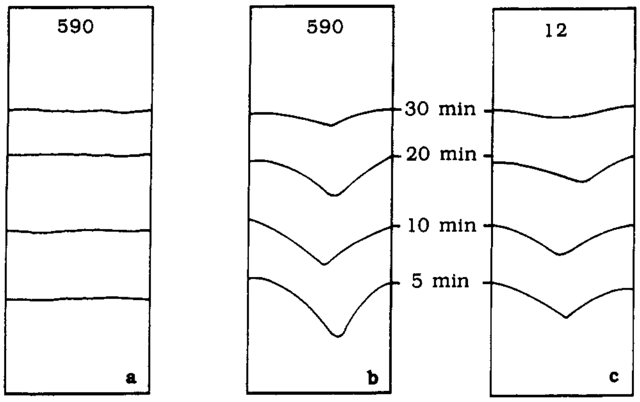


Figure 2. Shapes of eluent fronts on alumina thin layers with monodisperse PMMA for different elution times, eluents, and molecular weights of PMMA. The molecular weights ($\times 10^{-3}$) and elution times are indicated in the figure. The eluents used are toluene, in which PMMA on the thin layer is immobile (a), and dioxane (where it is mobile) (b and c).

use, the plates were dried in a oven at 120 °C for about 16 h. Spots of polymer were placed upon the thin layer, about 2 cm from the bottom line of the plate, by evaporating a few droplets of polymer solution with a concentration of 4000 ppm. The size of the spot depends on the solvent used for this deposition. When the solvent has a weaker interaction with the substrate than the polymer, the distribution of polymer within the circular spot has a Gaussian form.[14] When the solvent is a *displacer*, the deposited polymer will mostly be found at the periphery of the spot. Because a Gaussian distribution of the polymer is the most favorable one for determining the retention factor, we used solvents from which the polymer adsorbs on the thin layer. Prior to development, the plate was suspended just above the eluent with the appropriate composition in a closed thermostated cylindrical vessel for 45 min. This ensures equilibrium between the liquid phase, the vapor phase, and the adsorbed phase and prevents solvent demixing on the thin layer during the development. The upward elution is then started by lowering the plate just into the eluent. All experiments were carried out at 35 °C. After elution the eluent front on the thin layer was marked before the plate was dried. The shape of this front already gives an indication of whether the polymer is displaced or not. Figure 2 shows examples of eluent fronts for PMMA eluted on alumina with either pure dioxane (displacer, middle, and right) or toluene (solvent, left). For toluene, in which the polymer is immobile, the boundary is a straight line. In the case of dioxane, this front shows a dip at the position of the polymer spot. This dip becomes smaller for lower molecular weight polymers and longer elution times. The appearance of this dip signals a reduction of the elution rate and can be explained by an increase in viscosity due to polymer dissolved in the mobile phase. Besides this indirect indication for complete polymer desorption we used the following methods to visualize polymer spots: fluorescence quenching, iodine vapor, and wetting.

The fluorescence quenching method is especially suitable for localizing polystyrene spots. This method can only be used for polymers which absorb ultraviolet light.

Exposure of thin-layer plates to iodine vapor is a more general staining method. Almost all polymers except those which have a very low polarity form complexes with iodine, giving dark brown spots.

The wetting method can be applied to hydrophobic polymers on hydrophobic thin layers like silica and alumina. Spraying the thin-layer plate with water wets the whole plate except the polymer spot, which then shows up as a bright patch because it scatters more light than the wet parts.

Adsorption Mechanisms

Silica Surface. The silica surface has an acidic character ($pH^0 = 2-3$).[15] This character may vary somewhat due to variations in the number of silanol groups on the surface, the surface regularity, and crystallinity. Basic functional groups adsorb onto the hydroxyl groups of silica by acid/base interaction. The π electrons of aromatic molecules and the lone electron pairs of basic molecules interact with the protons of the silanol groups (hydrogen bonding). Infrared studies show that the frequency of silanol vibrations changes upon adsorption of basic molecules on silica.[16] Kawaguchi et al.[17] and several other investigators[18-20] were able to determine the fraction of occupied silanol groups by PS or other polymer chains from the intensity ratio of perturbed and unperturbed OH vibrations.

The *activity* of silica surfaces shows a maximum as a function of the activation temperature (from 25 to 1000 °C), which also proves that the hydroxyls are the active surface sites.[6] The adsorbent activity is first increased due to a reduction of physically adsorbed water, which liberates hydroxyl groups on the surface. For high temperatures the activity decreases because the number of surface hydroxyl groups reduces due to condensation reactions.

We have to note that there are different types of silanol groups present on a silica surface (isolated, vicinal, and geminal hydroxyls) with different adsorption strengths. Not only does the total amount of silanol groups diminish upon heating but also the relative proportions of the different groups change.[21,22]

Alumina Surface. Alumina exists in many different crystal forms. The alumina surface has both acidic and basic groups. We consider only the acidic sites because the polymers we used have basic functional groups. The hydroxyls on the alumina surface are not the only active sites for the adsorption of basic molecules as in the case of silica. Aluminum ions, which act as Lewis acid sites, may also bind basic molecules. The aluminum ions are not found in the top layer but may be exposed by vacancies in the surface layer consisting of oxygen and hydroxyl ions.[23,24] There are different Lewis acid sites with varying acidity due to the existence of different kinds of vacancies. Vacancies may differ with respect to size and nearest-neighbor configuration. Vacancies in the top layer are formed as the temperature is increased due to surface dehydroxylation. Hence, the amount of hydroxyl groups decreases and the number of Lewis acid sites increases with increasing activation temperature. Not only the number but also the strength of the Lewis acid sites may be increased by heating. Snyder[6] has measured the activity of alumina as a function of temperature with aromatic probe molecules. The activity appears to increase continuously with increasing temperature, indicating that the Lewis acid sites are the most active binding sites for basic molecules. The relative binding strength and concentration of different adsorption sites on solids are usually probed by infrared spectroscopy.[25,26] Acidic surface sites are frequently characterized by pyridine adsorption because this substance is a very strong base.[24,27,28] Infrared spectra of adsorbed pyridine give a clear distinction between molecules bound on hydroxyls and on Lewis acid sites. Healy et al.[29] have studied the adsorption of pyridine and other strong bases on different kinds of alumina. The following results of this study indicate that the Lewis acid sites are indeed the most strongly binding sites for basic molecules:

(i) The shift of a particular absorption band of pyridine upon adsorption on Lewis acid sites is larger than on hydroxyls.

(ii) The adsorption of pyridine on Lewis acid sites has a more pronounced high-affinity character than that of pyridine which binds only via hydrogen bonding.

(iii) The ratio of Lewis acid coordination to hydrogen-bonded complexes increases with decreasing pyridine vapor pressure.

(iv) The percentage of pyridine molecules left on the surface upon increasing temperature is much larger for molecules adsorbed on aluminum ions than on hydroxyls.

Adsorption of Phenyl Groups on Inorganic Solids. Aromatic molecules tend to adsorb in a flat conformation on active surface sites of inorganic solids.[30] The solvent strength concept of Snyder predicts retention values of many aromatic compounds on alumina and silica only correctly if a value for the surface area of the adsorbate is used which corresponds to flat adsorption.[6,31] Aromatic molecules with strongly adsorbing substituents, such as phenols, may, however, adsorb in a vertical orientation.[32-34] Nagao et al.[35] have studied the adsorption of benzene, toluene, and chlorobenzene on hydroxylated and dehydroxylated titanium oxide (rutile). From IR measurements they concluded that on a dehydroxylated surface these aromatic molecules were adsorbed as Lewis acid/base complexes with the titanium ions, whereas on a hydroxylated surface adsorption was due to interaction with hydroxyl groups. The occupied area for a benzene molecule on a dehydroxylated surface obtained from the monolayer capacity was 0.55 nm^2. This value is somewhat higher than the cross-sectional area of benzene (0.43 nm^2) which supports the idea that the molecules have a flat orientation on the surface. The fraction of covered surface area as calculated from the adsorbed amount and the cross-sectional area per molecule is about 0.78. For a fully hydroxylated surface this fraction appears to be about 0.95. Hence, benzene covers a hydroxylated rutile surface more effectively than a dehydroxylated one. The same conclusion can be drawn for the adsorbates toluene and chlorobenzene. The observed difference in adsorption onto hydroxylated and dehydroxylated rutile surfaces can be explained by different active-site densities. However, the fact that Lewis acid sites have more rigidly fixed positions on the surface than protons taking part in hydrogen bonding may also explain this observation. Steric hindrance between adsorbate molecules in the surface layer becomes more important as the adsorbed amount increases. This increased hindrance will lead to less optimal orientations for adsorbate molecules on Lewis acid sites, which reduces the affinity for adsorption. Hydroxyl groups, however, have the ability to rotate and may therefore adjust their direction to the adsorbing groups for optimal interactions. Hence, the adsorption energy is less affected by steric hindrance between adsorbate molecules than in the case of adsorption onto Lewis acid sites. The surface layer can now be packed more densely without losing much adsorption energy per molecule. Phenyl groups may even adsorb in a moderately tilted orientation on hydroxyls and still have efficient interaction. Several orientations of adsorbed benzene molecules on hydroxyl groups with equal interaction energy are schematically shown in Figure 3a. Figure 3b shows the only favorable conformation of a benzene molecule on a Lewis acid site. Parts a and b of Figure 3 also show that for the same distribution of active sites more benzene molecules may be adsorbed on the hydroxylated than on the dehydroxylated titanium oxide surface.

Adsorption of basic functional groups on silica only takes place onto hydroxyl groups. Hence, the silica surface may, in this respect, be compared to a hydroxylated titanium oxide surface.

For an alumina surface with both alanol groups and exposed aluminum ions on the surface, adsorption of basic functional groups takes place on both types of active sites. In this case, the surface takes an intermediate position between a fully hydroxylated and dehydroxylated rutile surface.

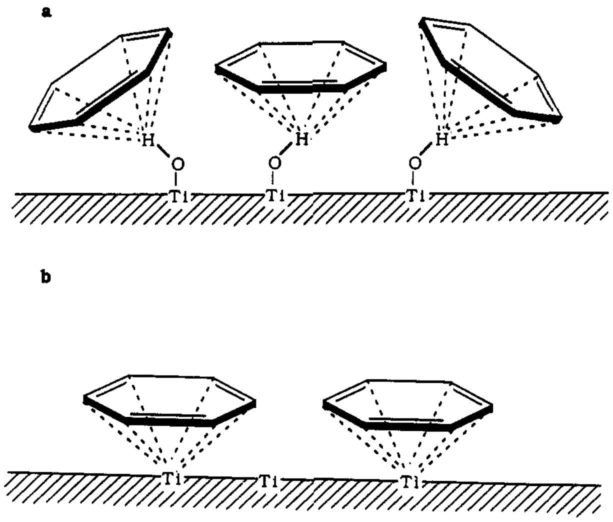


Figure 3. Possible conformations of benzene molecules adsorbed on hydroxyl groups (a) and on a Lewis acid sites (b) of titanium oxide.

Table II
Critical Points ϕ_{cr} for PS on Silica and Alumina in Carbon Tetrachloride

displacer	silica	alumina
ethylbenzene	0.92	0.48
toluene	0.68	0.33
chloroform	0.68	0.22
benzene	0.55	0.28
methylene chloride	0.35	0.18
1,2-dichloroethane	0.33	0.13
isopropyl ether	0.026	0.027
ethyl ether	0.019	0.021
dioxane	0.028	0.014
isopropyl acetate	0.027	0.012
tetrahydrofuran	0.015	0.011
ethyl acetate	0.017	0.009
acetonitrile	0.012	0.008
acetone	0.008	0.005

Results and Discussion

Segmental Adsorption Energy for PS. In ref 4 we already discussed the adsorption energy of PS on silica relative to cyclohexane and carbon tetrachloride, respectively, measured at a temperature of 25 °C. The data for PS in carbon tetrachloride from this study are included in Table II. This table gives critical points for the displacement of PS from both silica and alumina in carbon tetrachloride by various displacers. We checked that a temperature difference of 10 °C did not affect the critical displacer concentration. By way of example, retention curves of PS on alumina and silica are shown in Figure 4, for the aromatic displacers benzene, toluene, and ethylbenzene. The transition between complete retention ($1 - R_f = 1$) and no retention ($1 - R_f = 0$) of the polymer on the thin layer is in all cases very sharp. Small changes in the molecular structure of the displacer give a distinctly different retention curve. Hence, TLC is a very sensitive method to determine critical points.

Table II and Figure 4 show that PS is displaced more easily from alumina than from silica by nearly all displacers used in this study. Only ethyl ether and isopropyl ether have about the same critical points on both substrates. The order of displacement strengths (as measured

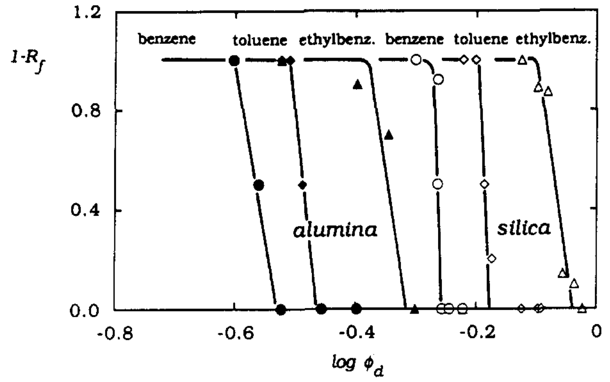


Figure 4. Retention ($1 - R_f$) of PS on silica (open symbols) and alumina (filled symbols) in carbon tetrachloride/displacer mixtures as a function of the logarithm of the volume fraction of three displacers: ethylbenzene (triangles), toluene (squares), and benzene (circles).

Table III
Solvent Strengths ϵ and Molecular Areas A of Solvents and Displacers[7]

solvent (o) or displacer (d)	ϵ_o or ϵ_d		A_o or A_d (nm^2)
	silica	alumina	
carbon tetrachloride (o)	0.11	0.17	0.43
toluene (d)	0.22	0.30	0.58
benzene (d)	0.25	0.32	0.51
chloroform (d)	0.26	0.36	0.43
methylene chloride (d)	0.30	0.40	0.35

by the critical volume fraction) is the same on both substrates, for all displacers used.

Ethylbenzene, which is the weakest displacer, may be considered as the monomer unit of PS. In this case we may, as a first approximation, assume that PS and ethylbenzene interact equally strongly with a given substrate; i.e., $\chi_s^{do} = \chi_s^{po}$. Then we can estimate χ_{sc}. The simplest way to do this is to use eq 2; the precise value of χ_s^{do} is then irrelevant. However, eq 2 applies only for sufficiently strong adsorption. If χ_s^{do} is small, the full eq 1 has to be used, for which the value for χ_s^{do} is needed.

An estimate for χ_s^{do} can be obtained by using eq 3. Solvent strengths and areas per molecule of various displacers and carbon tetrachloride on both silica and alumina are given in Table III. Because of the assumption made in the model of Cohen Stuart et al.[2] that the size of a displacer molecule, a solvent molecule, and a polymer segment are equal, we use a value for A which is the average of A_o, A_d, and A_p for the calculation of χ_s^{po}, χ_s^{pd}, and χ_s^{do}. The contact area A_p of a PS segment is, according to Glöckner,[36] equal to 0.57 nm^2. The activity α' of the adsorbent, which is also needed for the calculation of the adsorption energy, was determined according to Snyder's method. This quantity appeared to be 11.1 nm^{-2} for the alumina we used. For silica we determined this parameter previously[4] and found 17.6 nm^{-2}. Average A values and the calculated χ_s^{do} for various displacers in PS/carbon tetrachloride systems are given in Table IV.

The value of χ_s^{do} for ethylbenzene with respect to carbon tetrachloride on silica and alumina cannot be calculated directly from eq 3 because Snyder does not give solvent strengths for ethylbenzene. However, we expect that the χ_s^{do} values of ethylbenzene are certainly not higher than those of toluene, which are 1.0 and 0.76 on silica and alumina, respectively. Such values are too small to justify the use of eq 2. Hence, we need an estimate χ_s^{do} for ethylbenzene.

Table IV
Average Molecular Areas $\bar{A}$ and χ_s^{do} Values of Various Displacers in PS/Carbon Tetrachloride Systems with either Silica or Alumina

displacer	$\bar{A}$ (nm^2)	χ_s^{do}	
		silica	alumina
methylene chloride	0.45	1.50	1.15
benzene	0.50	1.23	0.83
toluene	0.53	1.03	0.76
chloroform	0.47	1.24	0.99

Table V
Flory-Huggins Interaction Parameters

component a	component b	χ^{ab}	ref
carbon tetrachloride	toluene	-0.05	37
	benzene	0.19	38
	PS	0.396	39
polystyrene	toluene	0.432	39
	benzene	0.438	39
	ethylbenzene	0.45	40, 41

A reasonable estimate is obtained using χ_s^{do} values found for toluene and benzene and assuming that each additional methylene group gives the same increment to χ_s^{do}. Using χ_s^{do} for toluene and benzene as given in Table IV, we find values of χ_s^{do} for ethylbenzene of 0.8 and 0.7 on silica and alumina, respectively.

In order to calculate χ_{sc} from the full eq 1, we need the solvency parameters χ^{pd}, χ^{po}, and χ^{do}. The χ values for PS/ethylbenzene and PS/carbon tetrachloride interactions are given in Table V. For the interaction between ethylbenzene and carbon tetrachloride we have taken the same χ^{do} as for toluene and carbon tetrachloride (i.e., -0.05). This latter assumption certainly does not lead to serious errors because a change of less than 0.2 in χ^{do} has no significant effect on the calculated χ_{sc}. The term $\lambda_1\chi^{pd}$ constitutes the most important correction. The critical adsorption energies are found as 0.2 and 0.4 for silica and alumina, respectively. The athermal version of eq 1, neglecting all solvency effects, would have given χ_{sc} as 0.05 for silica and 0.3 for alumina. Apparently, the solvency correction increases χ_{sc} by about 0.1.

The obtained χ_{sc} values for PS are comparable to the theoretical prediction of 0.288 for a hexagonal lattice. It is remarkable that χ_{sc} for PS on alumina is somewhat different from that on silica. Theoretically, χ_{sc} does not depend on the type of substrate, because rotational entropy effects are neglected in the lattice model. The reason for the difference in the experimental χ_{sc} may perhaps be found in the adsorption mechanism. Polystyrene adsorbs on alumina by interaction of the phenyl groups with both hydroxyl groups and Lewis acid sites. The phenyl groups attached to the polymer chain may have less possibilities for optimal orientation toward the Lewis acid sites than adsorbed ethylbenzene molecules. Polystyrene segments may therefore have a lower adsorption energy on these sites than the detached monomers. Hence, the assumption of equal interaction strength ($\chi_s^{po} = \chi_s^{do}$) which was made for the determination of χ_{sc} is perhaps not valid in this case. When χ_s^{po} is smaller than χ_s^{do}, the value for χ_{sc} calculated in the way described above is too high. For PS adsorption on hydroxyls of an alumina or silica surface the effect of the internal sterical hindrance of the polymer chain is partly compensated by the rotational mobility of the active hydroxyl groups. Because the silanols are the only active sites on a silica surface, the determination of χ_{sc} based on the assumption that $\chi_s^{po} = \chi_s^{do}$ is still tenable for this substrate, and $\chi_{sc} = 0.2$ is a reasonable estimate for this case.

Table VI
Critical Solvent Strengths ϵ_{cr} and χ_s^{po} Values for PS on Silica and Alumina

	silica			alumina		
		χ_s^{po}			χ_s^{po}	
displacer	ϵ_{cr}	*a*	*b*	ϵ_{cr}	*a*	*b*
methylene chloride	0.23		1.1	0.23		0.49
benzene	0.21	1.0	1.1	0.23	0.53	0.51
toluene	0.20	0.9	1.0	0.23	0.41	0.53
chloroform	0.23		1.2	0.23		0.51

[a] Calculated by eq 6; χ values taken into account. [b] Calculated by eq 4; athermal solvent behavior assumed.

Since the value 0.4 obtained for alumina is less reliable, we assume $\chi_{sc} = 0.2$ also for PS on alumina. Anyhow, in the determination of χ_s^{po} the χ_{sc} term usually constitutes only a small correction.

We are now in the position to calculate χ_s^{po} from critical points. To that end, we used eqs 5 and 6 and the solvent strengths given in Table III, for the displacers methylene chloride, benzene, toluene, and chloroform. Chloroform is a relatively acidic displacer which can have specific interactions with PS. This implies that the formation of PS–surface bonds may also be blocked by the formation of stronger PS–chloroform bonds, i.e., a strong surface/displacer interaction need not be involved. Such a desorption mechanism may affect or even determine polymer displacement. Fortunately, chloroform gave the same χ_s^{po} for PS on silica as the other displacers, indicating that specific interactions between chloroform and PS do not significantly affect the results.

For each displacer we calculated ϵ_{cr} from eq 5 and the athermal χ_s^{po} value from eq 4, for PS adsorbing from carbon tetrachloride on alumina. Results are given in Table VI. For benzene and toluene, for which the solvency parameters are known, we calculated also the nonathermal χ_s^{po} value from eq 6. The Flory–Huggins parameters needed for this calculation are given in Table V. For comparison, we also inserted in Table VI the corresponding energy parameters for silica from our previous work.[4]

The χ_s^{po} values for PS on silica and alumina, determined with the different displacers, agree very well with each other, which supports the consistency of the procedure. For alumina, the average nonathermal and athermal χ_s^{po} values for PS from carbon tetrachloride are 0.47 and 0.51, respectively. The difference is very small and certainly not significant, just as in the case of silica. Apparently, the solvency correction is relatively unimportant in these cases. Comparison between the data for silica and alumina leads to the conclusion that the segmental adsorption energy of PS on silica is higher by an amount of about 0.5 *kT*.

In Table IV it can be seen that the (athermal) adsorption energies of small aromatic molecules are also higher on silica than on alumina. For benzene and toluene we find differences of 0.40 and 0.27 *kT*, respectively, between silica and alumina. These differences are, however, smaller than those obtained for PS. The adsorption energy for PS on alumina is lower than that on silica for two reasons: a smaller interaction energy with the active surface sites and a less effective contact between the phenyl groups and the surface due to their restricted orientational freedom. For the small molecules, only the former effect plays a role.

Kawaguchi et al.[42,43] have also published data for PS displacement from silica into carbon tetrachloride. The critical adsorption energy χ_{sc} for PS obtained by these authors is 0.5, which differs significantly from our value. We note that the value for χ_{sc} from Kawaguchi et al. is questionable for several reasons. First, they assumed benzene to behave as the monomer unit of PS. As can be seen from our results, the critical points of benzene and ethylbenzene which we take as the monomer unit of PS differ significantly. Second, they used eq 2 for the calculation of χ_{sc}. As discussed above, this equation is not valid for weak segment/surface interaction and can therefore not be used for PS/carbon tetrachloride systems. Finally, their solvency correction term $\lambda_1\chi^{pd}$ has the wrong sign. Apart from the erroneous χ_{sc}, Kawaguchi et al.[42,43] report several χ_s values which are also incorrect because of their using eq 2 where it is not allowed.

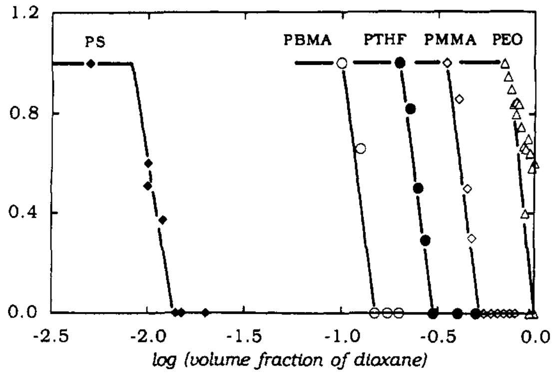


Figure 5. Retention ($1 - R_f$) of five polymers on an alumina thin layer in carbon tetrachloride/dioxane mixtures, as a function of the logarithm of the volume fraction of dioxane.

Adsorption Energies for Other Polymers and Displacers. Figure 5 shows the displacement of PS, PBMA, PTHF, PMMA, and PEO from alumina by dioxane in a carbon tetrachloride/dioxane solvent mixture. This figure already gives an indication of the adsorption energies of the different polymers. For instance, PBMA can be entirely displaced at a much lower dioxane concentration than needed for PEO. Hence, PBMA on alumina has a smaller adsorption energy than PEO. Table VII gives the critical points of the given polymers on both silica and alumina for various displacers. The dashes in the table represent systems where either the polymer cannot be desorbed by the particular displacer or the polymer does not dissolve in the displacer/solvent mixture with the critical composition. The descending order of the displacers in this table corresponds to an increasing displacement strength for most polymers. This order agrees very well for the two substrates.

A remarkable finding is that we were not able to displace PTHF from silica by acetonitrile whereas this could be done at low volume fractions of acetonitrile from alumina. Acetonitrile is a nonsolvent for PTHF. Higher concentrations of acetonitrile reduce the solubility of this polymer in the solvent mixture. Polytetrahydrofuran does not dissolve any more in the solvent mixture with that acetonitrile concentration which would be needed for total displacement of PTHF from silica. This is the reason why PTHF is easily displaced by acetonitrile from alumina but not at all from silica. The opposite is the case for the other displacers in Table VII. The critical points for these displacers are smaller for PTHF on silica than for PTHF on alumina.

Most of the displacers given in Table VII have only basic characteristics, just as the polymers. Only acetone and acetonitrile are exceptions. According to Fowkes[10] these displacers also have some acidic properties. Acetonitrile is, however, much more acidic than acetone. For

Table VII
Critical Points ϕ_{cr} for Several Polymer/Displacer Combinations on Silica and Alumina in Carbon Tetrachloride

	silica					alumina				
displacer	PS	PBMA	PTHF	PMMA	PEO	PS	PBMA	PTHF	PMMA	PEO
ethyl ether	0.019	0.35	-	-	-	0.021	-	-	-	-
isopropyl acetate	0.027	0.24	-	-	-	0.012	0.34	0.57	-	-
ethyl acetate	0.017	0.18	-	0.85	-	0.009	0.22	0.37	-	-
tetrahydrofuran	0.015	0.11	0.35	0.53	-	0.011	0.19	0.38	0.75	-
acetone	0.008	0.10	0.28	0.39	-	0.005	0.12	0.33	0.58	-
dioxane	0.028	0.11	0.28	0.39	-	0.014	0.14	0.29	0.49	1.0
acetonitrile	0.012	0.12	-	0.32	-	0.008	0.09	0.12	0.34	-
pyridine		0.06	0.14	0.26	0.52		0.08	0.20	0.35	0.50

Table VIII
Values for χ_s^{ab} of Several Polymers Relative to PBMA, on both Silica and Alumina

	silica				alumina			
displacer	PS	PTHF	PMMA	PEO	PS	PTHF	PMMA	PEO
ethyl ether	-2.4							
isopropyl acetate	-1.7				-2.1	0.6		
ethyl acetate	-1.9		1.6		-2.0	0.5		
tetrahydrofuran	-1.6	1.2	1.6		-1.7	0.7	1.4	
acetone	-2.1	1.0	1.4		-2.0	1.0	1.6	
dioxane	-1.0	0.9	1.3		-1.3	0.7	1.3	2.0
acetonitrile	-1.8		1.0		-1.3	0.3	1.3	
pyridine		0.9	1.5	2.2		0.9	1.5	1.8
average	-1.8	1.0	1.4	2.2	-1.7	0.7	1.4	1.9

displacers which are both acidic and basic, care has to be taken in the interpretation of the results for the following reasons.

(i) Displacers with both acidic and basic groups can display significant self-association which may reduce their displacement strength. This effect may have a greater influence on the critical point for one polymer than for another because self-association is concentration dependent. A measure for self-association is the acid/base contribution to the surface tension of a liquid. For acetonitrile 28% of the surface tension is considered to be due to acid/base interactions. In the case of acetone the acid/base contribution is only 4%.[10]

(ii) Displacers with acidic characteristics may also change the desorption mechanism. Desorption caused by strong specific interactions of the displacer with the basic groups of the polymer may significantly contribute to the displacement of the polymer. The model used in this study does not apply for displacement due to specific interactions between polymer and displacer, since, at best, average interactions in solution are taken into account through the χ parameters.

(iii) In the case of alumina and displacers with acidic properties, strong interaction between the basic surface sites and the acidic group of the displacer may be possible. Because of steric hindrance, displacer molecules on basic surface sites may reduce the accessibility of basic polymer groups to the acidic sites of the substrate.

Adsorption energy differences between polymers can be calculated from the critical points given in Table VII by using either eq 8 or eq 9. The results are collected in Table VIII. All the χ_s^{ab} values were calculated relative to PBMA adsorption. For the strongly adsorbing polymers PTHF, PMMA, and PEO the simple eq 9 could be used. The adsorption energy of PS relative to PBMA has to be calculated from eq 8 because the χ_s^{po} values for PS on both silica and alumina are too low to use eq 9. This implies that for this calculation χ_s^{do} values of the relevant displacers have to be known. Adsorption energies of displacers can be obtained from the critical points for PS and the adsorption energy of PS (Table VI) using the athermal version of eq 1. We did not correct for solvency effects because not all relevant χ values are known and the corrections are usually small. The χ_s^{do} values calculated in this way are given in the columns designated "PS" in Table X. The remainder of Table X will be discussed below.

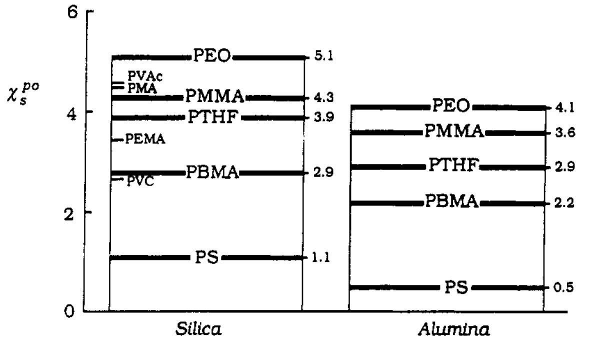


Figure 6. Adsorption energies (χ_s^{po}) of polymers relative to carbon tetrachloride on both silica and alumina. The χ_s^{po} values of polymers indicated in small print were calculated from results reported by Inagaki et al.[14,44] The adsorption energies indicated by bold lines were determined in this work.

Table VIII gives the χ_s^{ab} values calculated as described above for various polymer/displacer combinations on both silica and alumina. The variation in the values for the adsorption energy of a particular polymer calculated for the different displacers is very reasonable, in view of the assumptions made in the model applied here. The largest scatter is obtained for PS, which is because of the very small values for the critical concentrations and the dependence of the results on the adsorption energy of displacers. In the last line of Table VIII we give the average adsorption energy determined for each polymer. These average values (and χ_s^{po} for PS, see Table VI) were used to construct Figure 6, which is a diagram of the adsorption energies relative to carbon tetrachloride for the various polymers on both silica and alumina. Differences between polymer adsorption energies on silica and alumina can be clearly seen in this diagram. The difference in adsorption energies for polymers with the same functional group but with a different chain structure can be relatively large. The ether groups in the main chain of PEO and PTHF

Table IX
Critical 2-Butanone Volume Fractions, Taken from Inagaki,[14] for Several Polymers, and χ_s^{ab} Values Relative to PBMA

polymer	ϕ'_{cr}[a]	χ_s^{ab} [b]
polybutene (PB)	0.00	
poly(α-methylstyrene) (PMS)	0.02	
poly(p-chlorostyrene) (PCS)	0.03	
polystyrene (PS)	0.07	
poly(vinyl chloride) (PVC)	0.19	−0.1
poly(butyl methacrylate) (PBMA)	0.21 (0.14)	0.0
poly(ethyl methacrylate) (PEMA)	0.38	0.6
poly(methyl methacrylate) (PMMA)	0.62 (0.58)	1.1 (1.4)
poly(methyl acrylate) (PMA)	0.77	1.3
poly(vinyl acetate) (PVAc)	0.86	1.4

[a] Volume fraction of displacer where polymer starts to migrate.
[b] Calculated from the first column with the help of eq 9.

are separated by two and four methylene groups, respectively. Due to this difference in the chain, the χ_s^{po} value for PEO is 1.2 higher than that for PTHF on both silica and alumina. The adsorption energy difference between the polymers with ester groups (PBMA and PMMA) is for both substrates equal to 1.4 kT. In the latter case, the main chains of the polymers are the same but the side groups are different. The butyl group linked to the ester group of PBMA is for PMMA replaced by a methyl group.

Hence, the functional (active) group of a polymer is not the only property to determine the adsorption energy, but the rest of the chain is also important in this respect. The results of Inagaki et al.[14,44] confirm this conclusion. These authors studied the separation and fractionation of polymeric substances and report the chromatographic behavior of 10 different polymers, including five polymers with an ester group, on a silica thin layer using binary developers of 2-butanone and carbon tetrachloride with different compositions. In this study, not the critical volume fractions for 2-butanone but the volume fractions at which polymer samples just start to migrate are given. The latter volume fractions are probably not much different from the critical points because transitions between complete polymer retention and no retention are very sharp (see Figures 4 and 5). The volume fraction data of Inagaki et al.[14,44] and the adsorption energies calculated from these values (using eq 9) are given in Table IX. We could not give χ_s^{ab} values for polybutene, poly(α-methylstyrene), and poly(p-chlorostyrene) because the χ_s^{po} values for these polymers are too low to use eq 9. Calculation of χ_s^{ab} by eq 8 is hampered by the fact that we do not know χ_s^{do} for 2-butanone on the silica sample used by Inagaki et al. For comparison, we have also determined the critical volume fraction of 2-butanone for PBMA and PMMA. These volume fractions and our average adsorption energy are given within brackets in Table IX. Qualitatively, the results of Inagaki agree with our data, i.e., polyesters with larger aliphatic groups have lower adsorption energies.

The segmental adsorption energies for the polymers poly(vinyl chloride) (PVC), poly(ethyl methacrylate) (PEMA), poly(methyl acrylate) (PMA), and poly(vinyl acetate) (PVAc) on silica, which were calculated from Inagaki's results (Table IX) with the help of eq 7, are incorporated in Figure 6 (indicated in small print). The χ_s^{po} values of PMA and PVAc, as given in this figure, are not based on the segmental adsorption energy of PBMA but on that of PMMA. PMA and PVAc have adsorption energies quite different from that of PBMA but close to that of PMMA. Using χ_s^{po} of PMMA for the calculation of the adsorption energy for PMA and PVAc reduces the absolute error in the calculated values. We have to note that the experimental conditions, such as temperature, molecular weights of the polymers, type of silica, and pretreatment of the thin layer before development, are not mentioned by Inagaki et al.[14,44] and were probably different from ours. Because Inagaki et al. carried out their displacement experiments with only one displacer under unknown experimental conditions, the polymer adsorption energies calculated from these data are only indicative.

In Figure 6 it can be seen that the polymer adsorption energies on silica are all larger than those on alumina. The order of increasing adsorption strength is the same for both substrates. The adsorption energies of the polyesters (PBMA, PMMA) is 0.7 kT larger on silica than on alumina. For the polyethers (PTHF, PEO) this energy difference is equal to 1 kT, which is the largest energy difference between adsorption on silica and alumina we have found. This relatively large interaction energy difference of ethers is confirmed by the displacement experiments of PS. The critical points for isopropyl ether and ethyl ether, respectively, were about the same for both substrates while we found for the other displacers a much lower critical volume fraction on alumina than on silica. The weaker a displacer is, the more of it has to be added to obtain the same displacement strength.

The large energy difference between ether groups on silica and alumina may reflect that OH groups are more accessible for ether groups than Lewis acid sites. Ether groups in the main chain of adsorbate molecules are less exposed than functional end groups and are therefore more sterically hindered to find optimal orientations on the substrate. This sterical hindrance will be more effective for Lewis acid sites than for hydroxyl groups, as explained earlier.

The diagram of Figure 6 can predict which polymers will and which will not adsorb on a substrate from a particular solvent when the adsorption energy of this solvent is inserted into the diagram. For instance, the adsorption energy of benzene calculated by eq 3 lies above the level of PS and below the levels of the other polymers. Hence, benzene is only a displacer for PS and not for the other polymers. On the other hand, the diagram may be indicative for the adsorption energy of a solvent when it is known which polymers can and which cannot be displaced by this solvent. Poly(ethylene oxide) adsorbs on silica from pure water.[45,46] Hence, the adsorption energy of water is probably smaller than that of PEO.

As pointed out in section Adsorption Energy, adsorption energies of displacers can be determined from critical points and polymer adsorption energies with the help of either eq 1 or eq 2. The results for PS have already been discussed. For the other polymer/displacer systems eq 2 can be used to calculate these adsorption energies. We have neglected the solute/solvent interaction term of eq 2 for these calculations. Table X gives the χ_s^{do} values for all our displacer/substrate/polymer combinations. We have to note that the given values include, in principle, only the adsorption on acidic surface sites because we have only considered the displacement of basic polymers. The agreement between displacer adsorption energies determined using different polymers is very good except for some values obtained for PS. Most critical points for PS are very small and therefore less accurate.

We do not observe *localization effects* such as found by Snyder.[7,8] He claims that the solvent strength of a displacer may decrease as the concentration increases because more molecules become *delocalized* on the surface as the adsorbed amount increases. Our adsorption energies

Table X
Values for χ_s^{do} of Various Displacers on both Silica and Alumina Relative to Carbon Tetrachloride

	silica						alumina					
displacer	PS	PBMA	PTHF	PMMA	PEO	ave	PS	PBMA	PTHF	PMMA	PEO	ave
toluene	1.1					1.1	0.7					0.7
chloroform	1.1					1.1	1.0					1.0
benzene	1.3					1.3	0.8					0.8
methylene chloride	1.6					1.6	1.1					1.1
1,2-dichloroethane	1.7					1.7	1.3					1.3
isopropyl ether	4.0					4.0	2.6					2.6
ethyl ether	4.4	3.7				4.1	2.9					2.9
isopropyl acetate	4.0	4.1				4.1	3.4	3.1	3.3			3.2
ethyl acetate	4.5	4.4		4.3		4.4	3.7	3.5	3.7			3.6
tetrahydrofuran	4.6	4.9	4.7	4.7		4.8	3.5	3.7	3.7	3.7		3.7
acetone	5.2	5.0	5.0	5.0		5.0	4.3	4.1	3.8	3.9		3.9
dioxane	4.0	4.9	5.0	5.0		5.0	3.3	4.0	3.9	4.1	3.9	4.0
acetonitrile	4.8	4.8		5.2		5.0	3.8	4.4	4.8	4.5		4.6
pyridine		5.5	5.7	5.4	5.6	5.6		4.5	4.3	4.5	4.6	4.5

(solvent strengths in Snyder's terminology) of displacers become not consistently lower as the concentration of the displacer needed to fully desorb a particular polymer becomes higher (going from PS to PEO). Hence, solvent localization effects do not play a significant role for the given polymer displacement experiments. We also give in Table X the adsorption energies averaged over the values for the different polymers. We excluded for this averaging the χ_s^{do} values obtained with PS and strong displacers (i.e., from ethyl acetate to pyridine) because these values are less accurate.

For the calculation of the adsorption energy difference between PS and PBMA we used only the χ_s^{do} values obtained with PS. This energy difference remains the same when the average (more accurate) χ_s^{do} values are used. Hence, the χ_s^{po} values of the polymers PTHF, PMMA, and PEO, which are based on the χ_s^{po} of PBMA, do not need to be corrected.

It is remarkable that the trends between the different displacer adsorption energies are the same as those found for the polymers. All the displacers have a lower adsorption energy on alumina than on silica. The largest energy difference between adsorption on silica and alumina is again obtained for the ethers. Displacers with larger alkyl groups have smaller adsorption energies.

The displacers acetonitrile and chloroform have the smallest adsorption energy difference between silica and alumina. Acetonitrile is an even stronger displacer than pyridine on alumina, whereas the reverse is the case on silica. The same phenomenon is found for chloroform and benzene. It may be noted that chloroform and acetonitrile are the displacers with the most acidic character. Probably, the interaction between these displacers and basic surface sites on alumina indirectly increases their displacement strengths for polymers on acidic surface sites. This may be explained by the steric hindrance of displacer molecules on basic surface sites for polymer adsorption on acidic surface sites.

Work of Adhesion. For the calculation of the work of adhesion in vacuum the dispersion force component of the surface tension of the substrate has to be known (see eq 14). The determination of γ_s^D for inorganic hydrophilic surfaces is experimentally difficult. For instance, the amount of physically adsorbed water and the contamination by impurities may drastically change the value of γ_s^D.[47] The value obtained for γ_s^D may also depend on the method used. Fowkes[48] reports for silica a γ_s^D of 78 mJ/m^2. Other values for this parameter from the literature are 44,[49] 75.5,[50] 89.7,[50] and 71.3 mJ/m^2.[51] We have chosen the value reported by Fowkes to calculate the dispersive work of adhesion of a solvent on silica, using eq 11.

Table XI
Work of Adhesion of Several Polymers on Silica

polymer	χ_s^{po} [a]	$(1/A)^b$ (nm^{-2})	$\chi_s^{po}kT/A$ (mJ/m^2)	W_{sp} (mJ/m^2)	% specific interaction
PS	2.0	1.4	11	100	11
PBMA	3.8	1.4	21	110	19
PMMA	5.2	2.0	43	132	33
PTHF	4.8	2.5	48	137	35
PEO	6.0	3.9	97	186	52

[a] Relative to cyclohexane. [b] Calculated on the basis of the molecular dimension.[6]

In this study, we consider the work of adhesion of polymers only with silica as the substrate. Due to the uncertainty in γ_s^D for inorganic substrates, it is not very useful to compare the dispersive work of adhesion between a polymer on silica and on alumina. We just mention that Janczuk et al.[50] found γ_s^D for alumina to be about 10 mJ/m^2 larger than that for silica.

We use cyclohexane as the reference solvent for the calculation of W_{sp} for the different polymers on silica. This hydrocarbon has no specific interactions with the silica surface. Since γ_o^D for cyclohexane is equal to 25.5 mJ/m^2,[10] we find, with γ_s^D = 78 mJ/m^2, from eq 11 W_{so}^D = 89 mJ/m^2.

The χ_s^{po} values from carbon tetrachloride (Figure 6) are 0.9 higher than those from cyclohexane.[4] The adsorption energies of the polymers used relative to cyclohexane are given in the second column of Table XI. The term $\chi_s^{po}kT/A$ in eq 14, which is mainly determined by specific interactions, can be calculated if the surface area per polymer segment A is known. This surface area can be estimated from the molecular dimension of the polymer segment. We used the procedure described by Snyder,[6] in which molecular areas of common chemical groups, occurring in many relevant compounds, are calculated on the basis of covalent bond lengths and van der Waals' radii. The molecular area of an arbitrary organic compound is then obtained by the summation of areas of the chemical groups in that compound.

The reciprocal molecular area is equal to the number of bound polymer segments per unit area. Values of $1/A$ are given in the third column of Table XI and range from 1.4 nm^{-2} for PS to 3.9 nm^{-2} for PEO. The hydroxyl density for most silicas is between 4 and 8 silanols/nm^2.[21,52] This implies that, in principle, all functional groups may be in contact with an active surface site. The specific work of adhesion $\chi_s^{po}kT/A$ for several polymers on silica is given in the fourth column of Table XI.

The last two columns of this table give the total work of adhesion for the polymers on silica and the percentage of this work due to specific interactions. The data should be interpreted carefully because of the assumptions made and the uncertainties in the various input parameters. The percentage of the work of adhesion due to specific interactions increases by 3–7% when γ_s^D as reported by Van Pelt et al.[49] (i.e., 44 mJ/m^2) instead of Fowkes[48] value of 78 mJ/m^2 is used.

The order of the polymers according to increasing work of adhesion is not the same as for the segmental adsorption energies. PTHF has a higher work of adhesion than PMMA whereas the reverse is the case for the segmental adsorption energies. This effect is due to the size of the polymer segments. When the segments are small the number of specific interactions per surface area increases and so does the work of adhesion.

About half of the work of adhesion for PEO on silica is due to specific interactions. This contribution is even less for the other polymers. Hence, dispersive interactions are very important for the work of adhesion of polymers on silica.

Conclusions

The segmental adsorption energies relative to carbon tetrachloride for the polymers PS, PBMA, PTHF, PMMA, and PEO increase in the given order on both silica and alumina. Each individual polymer has a lower adsorption energy on alumina as compared to silica. Polymers with more methylene groups per segment in the main chain or with larger alkyl groups attached to the functional groups have a lower adsorption energy.

Polymers can serve as standards for the adsorption energy of solvents and displacers. Unlike the results reported by Snyder,[7,8] the adsorption energies of strongly adsorbing solvents do not depend on the concentration in our experiments.

The work of adhesion of pure polymers on silica is on the order of 100–200 mJ/m^2. The contribution of specific interactions to the total work of adhesion relative to vacuum range from about 10% for PS to about 50% for PEO. The contribution of the specific interactions to the total work of adhesion is determined not only by the segmental adsorption energy but also by the area of a segment.

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Registry No. PS (homopolymer), 9003-53-6; PMMA (homopolymer), 9011-14-7; PBMA (homopolymer), 9003-63-8; PTHF (homopolymer), 24979-97-3; PEO, 25322-68-3; SiO_2, 7631-86-9; Al_2O_3, 1344-28-1.