A Novel Evaluation Method for the Adsorption Energy of Terminally Adsorbed Polymer

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Using a new experimental technique, "continuous elution method", polystyrene (PS-X) functionalized by a terminal iminium ion(X) was found forming a terminally adsorbed polymer layer on α-Al_2O_3 surface. Based on the balance between adsorption and desorption, the adsorption energy of the terminally adsorbed polymer was evaluated to be 4.2~4.3 kT with regarding to the osmotic pressure as a desorption force.

Recently, we have developed a new technique, "continuous elution method", to explore precisely the desorption behavior of polymer from the adsorbent particle.[1] This method has already been used for clarifying the (ir)reversibility of the adsorption process of polymer, molecular weight dependence of adsorption and desorption amounts, the structure and conformation of adsorbed polymer layer, and the effect of the porosity of adsorbent on the adsorption and desorption processes.[1,2]

The terminally adsorbed polymers have essential effects on dispersion stability of colloid, and this study is a prominent research area in colloid science. The structure stability of polymer layer on the surfaces, plays an important role in stabilization or flocculation of colloidal dispersion. The evaluation of the adsorption energy is important in the understanding of the interactions between polymer and adsorbent in liquid. However, no general method has yet been developed for the measurement of polymer adsorption energy. Cohen Stuart et al., have published a displacement method to estimate the segmental adsorption energies.[3] However, this method is applicable effectively only to the weak and multi-point-segment adsorption, not to the strong and the one point (terminal group) adsorption process.

In this work, the desorption process of an end-functionalized polystyrene desorbed from α-Al_2O_3 surface has been investigated. The adsorption energy was evaluated with respect the osmotic pressure which is considered as a desorption force.

The mono-dispersed polystyrenes (PS) and the end-functionalized polystyrenes (PS-X, X is an iminium cation: $-\underline{C{=}\overset{\oplus}{N}(CH_3)CH_2CH_2CH_2}$), were synthesized by the anionic polymerization technique.[4] The molecular weight of the polymer samples are 5700, 40000 and 200000 respectively. The adsorbent, α-Al_2O_3 powder, was supplied by Sumitomo Chemical Co. Ltd., Japan. The specific surface area is 5.7 m^2/g.

The polystyrenes adsorbed on the adsorbent in cyclohexane solution (5 mg/ml) at 35 °C (θ condition) for about 100 h, then the resulting particles with pre-adsorbed polymer were packed into a column. The eluents were pumped through the column (35 °C), and the amount of the polymer flow out of the column was monitored by a UV detector and recorded as a concentration vs. time curve. A binary mixture solvent of cyclohexane(CH) and chloroform(CF) with a volume fraction of CF, ϕ_{cf}, was used as the eluent, and solvent was eluted at a constant rate of 6 μl/min. After a pure cyclohexane was eluted through the column to wash out the non-adsorbed polymer completely, as the desorption process, a pure chloroform was used as a good solvent to desorb all the pre-adsorbed polymer, or a serial mixture solvents with ϕ_{cf}-value increasing step by step conducted as the eluents, hence the respective desorption curves were made for one column. From the peak areas of these elution curves, the desorbed amounts of pre-adsorbed polymer, according to the previous method,[1] can be measured with a calibration curve.

Figure 1 shows the desorption amounts (Γ) of PS and PS-X from the surface of α-Al_2O_3, against the elapsed time of adsorption. The normal polystyrene has nearly zero adsorption on α-Al_2O_3. On the contrary, the end-functionalized polystyrene has an obvious adsorption. This result clearly indicated that the end-functional group is the key element in the adsorption process. Thus, PS-X was adsorbed terminally on α-Al_2O_3 surface by the end-functional group. That the molecular weight has no significant effect on adsorption amount (Γ) suggests that the adsorbed polymer coils are packed closely on the surface.[1]

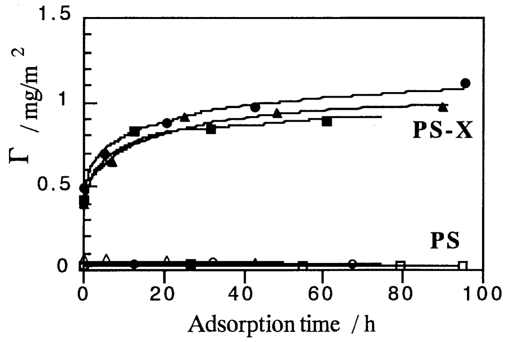

Figure 1. Desorbed amounts of PS and PS-X from α-Al_2O_3 at different adsorption time. Mw: circle-200000; triangle-40000; square-5700.

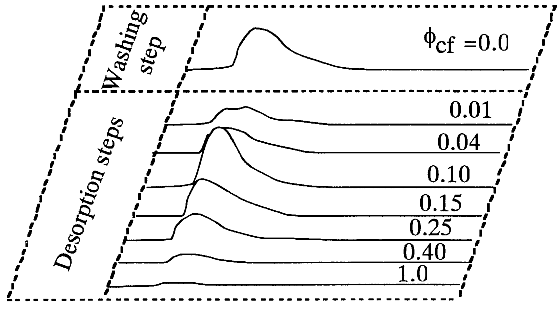

Figure 2. Typical elution curves. After washing step, the pre-adsorbed polymer desorbed stepwise with increasing the volume fraction of chloroform in the eluent(ϕ_{cf}).

Figure 2 shows some typical elution curves of PS-X from α-Al_2O_3 where the eluents are changed step-by-step by increasing ϕ_{cf}-value of mixture solvent. The pre-adsorbed polymer was intact during washing process, even though the column was washed with cyclohexane for a very long times(>48 h). The adsorbed polymer can be desorbed stepwise by changing the eluent to a good solvent step-by-step. Figure 3 shows the accumulated fraction of desorbed polymer (Σf) calculated at each elution step, plotted against the component ϕ_{cf} of the eluent employed in the respective step.

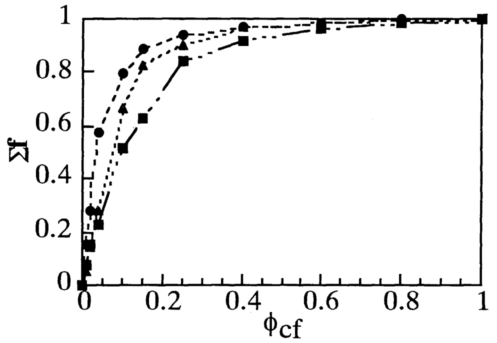

Figure 3. The relation between the fraction of accumulated desorbed amounts (Σf) and the fraction of chloroform in mixed eluent (ϕ_{cf}). (Mw symbol as same in Figure 1).

The behavior in Figure 3 may be included some insight with the desorption mechanism, and this is worthy of further investigation. Here we only pay attention to the stage after the washing step and before the desorption step where the pre-adsorbed polymer is coexisting only with the θ-solvent. This state is shown in Figure 4 schematically where the pre-adsorbed polymer chains (P-zone) were anchored on the solid surface, and out side of the P-zone, there is a solvent phase which is called O-zone. In this state, the adsorbed polymer seems to lay some mechanical balance, since if the solvent is changed even a little to good, some polymer molecules desorption will be induced (as showing in Figure 3). Thus, the polymer adsorption energy here should almost equal to the desorption energy. Based on this assumption, we analyze the force of the adsorbed polymer molecules gained. As showing in Figure 4, it is clearly that the adsorption energy is contributed by the interaction between the end-functional group and surface site, and the desorption energy should be contributed by the osmotic pressure, since the chemical potential energy of the solvent in the O zone is higher than that in the P zone, thus the solvent in the O zone tends to enter the P zone to displace the polymer.

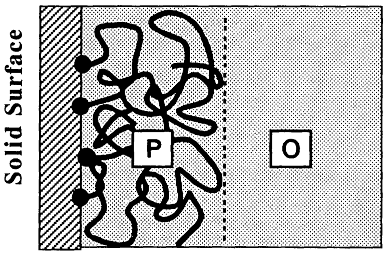

Figure 4. Schematic picture of polymer adsorbed terminally on the surface. P-polymer; O-solvent.

As we discussed before, the monodispersed PS-X molecules adsorbed terminally on the surface of α-Al_2O_3. Considering the terminally adsorbed polymer chain formed a semi-sphere conformation on the surface,[5] therefore, in the θ-condition the thickness of adsorption layer (h) is equal to the radius of gyration (Rg) of the polymer coil in solution (h=Rg). Assuming that the polymer segments are distributed uniformly in the adsorbed layer, we get the volume fraction (ϕ_2) of polymer segment in the adsorption layer as the following,

$$\phi_2=\Gamma/\rho_2/Rg \qquad (1)$$

Here, ρ_2 is the polymer density in the solid state. Γ is the pre-adsorbed amount per unit area.

According to the Flory-Huggins' solution theory, from the chemical potential difference between the solvent phase (O zone) and polymer layer (P zone) in Figure 4, the osmotic pressure, π, in the adsorbed layer is

$$\pi=\Delta\mu_1/v_1=-(kT/v_1)[\ln(1-\phi_2)+(1-1/x)\phi_2+\chi_1\phi_2^2] \qquad (2)$$

Here, χ_1 is the Flory-Huggins interaction parameter in the present polymer-solvent system, and x is the number of repeated units of a polymer molecule, v_1 is the volume of a solvent molecule. Therefore, the interaction energy of osmotic pressure worked on an unit area of adsorbed surface, is expressed as follows,

$$\Delta G_{os}=\pi Rg \qquad (3)$$

On the other hand, the adsorption energy of anchored polymer on the surface can be expressed as the following,

$$\Delta G_{ad}=N_a(\Gamma/M)\chi_s kT \qquad (4)$$

Here, $N_a(\Gamma/M)$ is the number density of adsorbed polymer, N_a is the Avgadro constant, and $-\chi_s kT$ is the adsorption energy of one chain-end.

In the equilibrium conditions, the adsorption energy is in balance with the desorption energy.

$$\Delta G_{ad}=\Delta G_{os}$$

$$\chi_s=-RgM/(N_a\Gamma v_1)[\ln(1-\phi_2)+(1-1/x)\phi_2+\chi_1\phi_2^2] \qquad (6)$$

With the three PS-X/α-Al_2O_3 systems, the adsorption energy parameter(χ_s) was calculated using the experimental data from Figure 1 (the saturated adsorbed amounts are 0.88, 0.97 and 1.02 mg/m^2 for Mw=5700, 40000 and 200000 respectively), and these are: χ_s=4.2 for Mw= 5700, χ_s=4.2 for Mw=40000, and χ_s=4.3 for Mw=200000.

A constant and reliable value of χ_s(4.2~4.3 kT) was evaluated from the analysis using a wide range of molecular weight of polymer, this suggests that the osmotic pressure plays an important role on their desorption process of polymers.

References

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