Macromol. Symp. ***126,*** *203–214 (1997)*

A NEW TECHNIQUE FOR DETERMINING THE ADSORPTION ENERGY OF TERMINALLY ADSORBED POLYMER

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Abstract: Using a new experimental technique, "Continuous Elution Method", the desorption behavior of polystyrene(PS) and polystyrene (PS-X) functionalized by a terminal iminium ion (-X) from α-Al_2O_3 and γ-Al_2O_3 surface were investigated, and found that PS-X is forming a terminally adsorbed polymer layer on α-Al_2O_3 surface. Furthermore, it was found that the adsorption force of terminally adsorbed polymer is balanced with the desorption force which is contributed from the osmotic pressure in the adsorption layer. Based on this concept, the adsorption energy of the end-functionalized polystyrene terminally adsorbed on the α-Al_20_3 surface was evaluated to be 4.2 ~4.3 kT.

INTRODUCTION

Polymers may be considered as tools to manipulate the interfaces. Such modified interfaces are very important in many industrial products and technologies. Adhesives, composites, dispersants or flocculants are just few examples.

Theoretical and experimental studies on polymer adsorption have been carried out extensively (Refs. 1-4), but the desorption behavior have not been studied in detail, even though it is considered that polymer adsorption is generally an irreversible process. Recently, we have developed a new experimental technique, "Continuous Elution Method", to explore precisely the desorption behavior of polymer from the adsorbent particles (Ref. 5). 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 (Refs. 5, 6).

The terminally adsorbed polymers have essential effects on dispersion stability of colloid, and this study is a prominent research area in colloid science (Refs. 7-10). The structure stability of polymer layer on the surfaces, plays an important role in stabilization or flocculation of colloid dispersion. The evaluation of the adsorption energy is important in 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

CCC 1022-1360/98/$ 10.00

published a displacement method to estimate the segmental adsorption energies (Ref. 11). 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 from alumina surfaces has been investigated. After polystyrene functionalized by a terminal iminium ion was confirmed forming a terminally adsorbed polymer layer on α-Al_2O_3 surface, the adsorption energy was evaluated with respect to the osmotic pressure which is considered as a desorption force. Furthermore, the effect of osmotic pressure will be expected to play an important role also in usual polymer adsorption and desorption process.

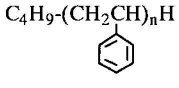
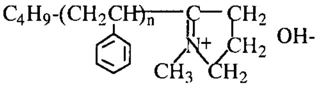
EXPERIMENTAL

Materials

The monodispersed polystyrenes(PS) and their terminal-functionalized materials(PS-X) were supplied from Nihon Zeon Co. Ltd. Japan. The PS-X was synthesized by the anionic polymerization technique and one end of the chain was terminated by an iminium cation (Ref. 12). The characterization data of the polymer samples are shown in Tab. 1.

Two kinds of alumina powders, α-Al_2O_3 and γ-Al_2O_3, were used as adsorbents. These were supplied from Sumitomo Chemical Co. Ltd. Japan and were used without any additional treatments. Some properties of these adsorbents are listed in Tab. 2. γ-Al_2O_3 has porous nature and highly specific surface areas which were considered to be covered with hydroxyl groups and has both Lewis acid and base properties. On the other hand, the surface hydroxyl groups of α-Al_2O_3 were decreased by dehydrolysis and their surface has only Lewis base properties.

Tab. 1. The properties of polymer samples

Samples	M_w*10^{-3} (g/mol)	M_w/M_n	chemical structure
PS0.9	0.9	~1.05	 $C_4H_9\text{-}(CH_2CH)_nH$ **PS**
PS5.7	5.7		
PS40	40		
PS200	200		
PS498	498		
PS1800	1800		
PSX5.7	5.7	~1.05	 **PS-X** iminium ion
PSX40	40		
PSX200	200		

Tab. 2. The properties of alumina particles

Samples	$\bar{D}$, μm	A, m^2/g	pore size, nm
α-alumina	~50	5.8	167
γ-alumina	~50	157	17

Desorption experiments

Each polymer was adsorbed on the alumina powders by the usual depletion technique in cyclohexane solution (Ref.12). Alumina powder and a cyclohexane solution of polymer were poured in a glass tube (10 ml in volume) and the tube was agitated slowly in a water bath maintained at 35℃ (the θ condition of polystyrene in cyclohexane). After some adsorption period (0 ~ 120 h), the adsorbent particles covered by the polymer layers were packed into a Teflon tube (i.d.=0.8 mm, length=20 cm) by a slurry method. In this process, some quantity of polymer solution was also transferred into the Teflon column. The schematic diagram of the "continuous elution method" is shown in Fig. 1. After setting the column into the elution system, an eluent was pumped through the column, where a micro pump with a stable flow rate (~6 μl/min) was used. The concentration of polymer components in the liquid flowed out from the column was analyzed by a UV-detector (λ=260 nm) and recorded as a absorbance-time curve.

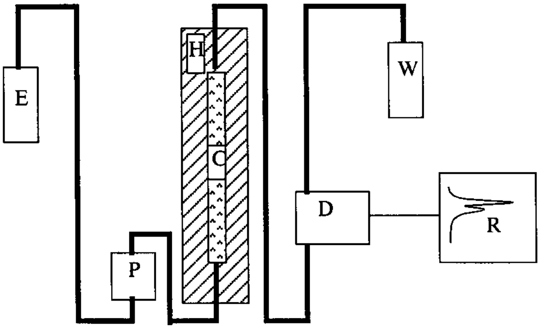


Fig. 1. Schematic diagram of continuous elution method. E-Eluent, P-Pump, H-Heater (controlled at 35 °C), C-Column D-Detector(UV), W-Waste, R-Recorder.

Elution procedure

As a first step (step-I), elution with the pure solvent (cyclohexane) was conducted at 35℃, because in the column both the pre-adsorbed polymers on adsorbent and the free polymer in the solution were contained. Only the free polymers in the column were drained out by flowing cyclohexane for a few hours.

As a second step (step-II), a desorption process of pre-adsorbed polymer was conducted using a mixed solvent of cyclohexane and chloroform (good solvent). From the peak area of this elution curve resulted in step-II, the adsorbed amounts of pre-adsorbed polymer were calculated using a calibration curve. As an eluent in step-II, a mixed solvent of $\phi_{cf}=0.25$ was usually employed. Here, ϕ_{cf} is the volume fraction of chloroform in the mixture, i.e., ϕ_{cf}=chloroform/(chloroform + cyclohexane). In some cases, step-II was further divided into sub-steps, i.e., step-II-a, II-b, etc.,where the ϕcf was increased step by step, for detail examination of the effect of solvent power on desorption behavior.

As the third step (step-III), the elution was conducted by using pure chloroform ($\phi_{cf}=1.0$) for checking whether the desorption was complete or not.

After all these processes, the column was dried at 70℃ and the amounts of adsorbent was weighed to calculate the amount of desorbed polymer.

RESULTS AND DISCUSSION

Elution Behavior from α-Al_2O_3

Fig. 2 shows some typical elution curves of PS-X from the α-Al_2O_3 surface. After the process of step-I, the polymer remaining in the column was the pre-adsorbed polymer. So the peak that appears at step-II is attributed to the desorption of the polymer. At step-III, which used a better solvent than that at step-II, no peak appeared, meaning that all the preadsorbed polymer had desorbed at step-II. From the form and the area of the peak at step-II, some desorption kinetics behavior and (pre)-adsorbed amount can be obtained.

As mentioned above, Fig. 2 clearly shows that the adsorbed polymer PS-X cannot be desorbed at step-I, even if they were displaced by a pure cyclohexane for a long time. This means that preadsorbed PS-X from the cyclohexane solution cannot be desorbed under the same solvent conditions at least at the macroscopic level; i.e., in the present adsorption conditions, an irreversible adsorption of polymers has taken place. Similar results are reported in previous publications (Refs. 13, 14).

The amounts of desorption(Γ^D) for the samples of PS and PS-X with different molecular weights were calculated from the peak areas (step-II), under considering the elapsed time of adsorption. These results are shown in Fig. 3. If we regard the amounts of desorption(Γ^D) to be equal to the amounts of adsorption at the respective elapsed time, Fig. 3 can be viewed as the usual adsorption rate curves.

It is evident from Fig. 3 that when α-Al_2O_3 powders are used as the adsorbent, the amount of adsorbed polymer is significantly enhanced by the existence of the end-functional group on the polymer chain. In fact, there is nearly zero adsorption in the PS-α-Al_20_3 system. This result indicates that the end-functional group(iminium ion) on the polymer chain-end plays a dominating role in the adsorption of PS-X on the α-Al_20_3 surface. Furthermore, it is seen from the figure that the desorbed amount (Γ^D) is not significantly influenced by the molecular weight of the polymer. This reveals that the adsorption layer has a monolayer structure where the polymer coils are packed closely with each other.

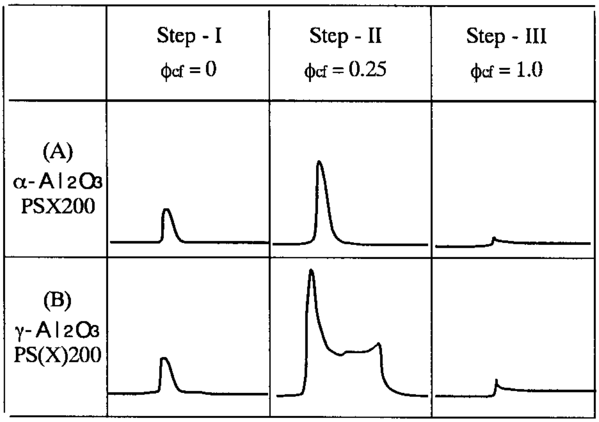


Fig. 2. The typical elution curves of three-steps elution process. Abscissa-elution time (correspond to elution volume); Ordinate-absorbance (UV, correspond to concentration of polymer), arbitrary unit. ϕ_{cf}-volume fraction of chloroform in eluent.

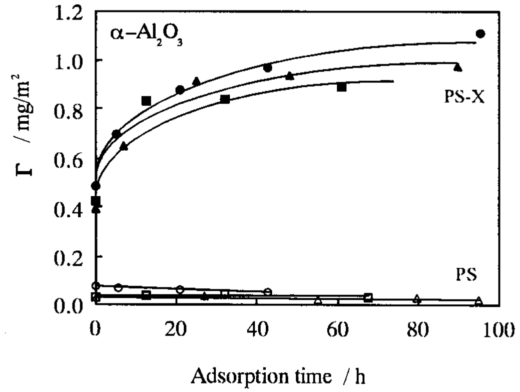


Fig. 3. The adsorbed amounts of PS and PS-X from α-Al_2O_3 at various adsorption times.
Γ : adsorption amount. ●: PSX200; ▲: PSX40; ■: PSX5.7; ○: PS200; △: PS40; □: PS5.7.

Elution Behavior from γ-Al_2O_3

As can be seen from Fig. 2, the elution curves of polymer (both PS and PS-X) desorbed from γ-Al_2O_3 show usually a complicated form, consisting of a narrow initial peak followed by a broad plateau. Presumably, this differs with the case of α-Al_2O_3, due to the porous nature of γ-Al_2O_3. The pore diameter of γ-Al_2O_3 is ~17 nm and roughly has the same order of the diameter of the PS200 coil (~27 nm) in cyclohexane at 35℃.

To clarify the effect of pore size of γ-Al_2O_3 on the elution profile of polymer, systematic experiments using the various PS samples with different molecular weights have been conducted. As seen from Fig. 4, the profiles of elution curves in step-II do depend strongly on the molecular weight of PS, showing the strong effect of porosity geometry of γ-Al_2O_3, i.e., when polymer size is appreciably smaller than the pore size (Fig. 4-a,b), one single peak without the following plateau appeared. When the polymer size is roughly equal to the pore size of adsorbent (Fig. 4-c,d), the curves show an initial narrow peak followed by a plateau similar to that see in in Fig. 1B. Further, when the polymer size becomes appreciably larger than the pore diameter (Fig. 4-e,f), the elution curve has a single broad peak without an initial narrow peak. All these results indicate that the different elution profile in γ-Al_2O_3-PS series can be related to the size ratio of the diameter of PS coils to the pore diameter of adsorbent particles. The geometric effect between them plays an important role on the elution process of adsorbed polymer.

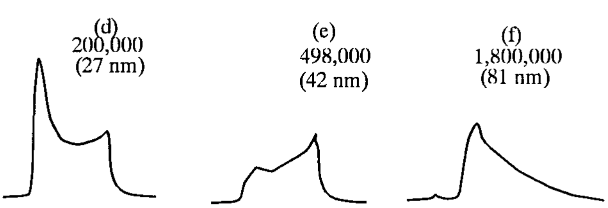


Fig.4. The profiles of desorption curve affected with molecular weight of polymers in PS/γ-Al_2O_3 adsorption systems. Abscissa-elution time; Ordinate- absorbance (UV), arbitrary unit.

The reader is reminded that our method differs from GPC, in which the polymer is added to a pre-packed column, rather than preadsorbed. Fig. 4 suggests the existence of a specific γ-Al_20_3 -polymer interaction, whose strength might be influenced strongly from the geometrical effect between the pore size of adsorbent and the radius of polymer coil in solvent. Some polymers having radii of gyration roughly equal or larger than the pore size of γ-Al_20_3 will be introduced with some degree into the empty pores by their strong entropic reason. It is assumed that the polymer chains introduced into the narrow pore have taken an elongated and flat conformation on the pore surface. Therefore, the elution curve in such a system becomes a complicated profile and the longer elution times will be necessary for these polymer molecules. The detailed effect of porosity of adsorbent was investigated by using a well-defined porosity adsorbent (controlled pore glass beads, CPG-10) (Ref. 6).

The desorption amounts from γ-Al_20_3, which were calculated from the peak area (step-II) of respective elution curves, are plotted in Fig. 5. It is found that the amount of adsorption/desorption (Γ^D) at the long-time saturation level increased gradually with the increasing molecule weight of the polymer. The existence of the end-functional group hardly influences the amount of adsorption, indicating that the polymer adsorption progresses by the usual loop-train model.

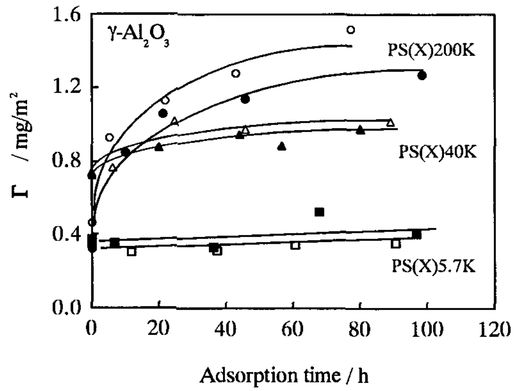


Fig. 5. The adsorbed amounts of PS and PS-X from γ-Al_2O_3 at various adsorption times. Γ : adsorption amount. ●: PSX200; ▲: PSX40; ■: PSX5.7; ○: PS200; △: PS40; □: PS5.7.

Driving Force for PS and PS-X Adsorption on Alumina

It is known that as a driving force for polymer adsorption, Lewis acid-base (electron acceptor-donor) interaction plays an important role. This concept was introduced originally by Fowkes (Ref. 15), and our present data on polymer adsorption/desorption (in Fig. 3 and Fig. 5) have been analyzed using this concept. There are Lewis base sites (B) on the α-Al_20_3 surface, and on the γ-Al_20_3 surface there are both the Lewis acid and base sites (A+B). Meanwhile, the phenyl group in PS and PS-X and the iminium cation in PS-X are the base and acid sites, respectively. Therefore, PS has n base sites (nb) and PS-X has n base sites and one acid site (nb+a) in a single polymer molecule, where n means the number of repeating units in a single polymer. Fig. 6 shows the acid-base interaction models schematically. The binding interaction operates predominantly between X in PS-X and base sites on α-Al_20_3(a/B) and between phenyl groups in PS (or PS-X) and acid sites on γ-Al_20_3 surfaces (A/nb). On the basis of these considerations, we can understand that the α-Al_20_3 cannot adsorb PS but can adsorb PS-X through the anchored action of the end-functional group (X) on the solid surface. On the γ-Al_20_3 surfaces, however, both the PS and PS-X molecules can be adsorbed by the interaction between the phenyl groups included in the respective molecule and the solid surface. Here it should be noted that cyclohexane used as the solvent does not compete as an adsorption component.

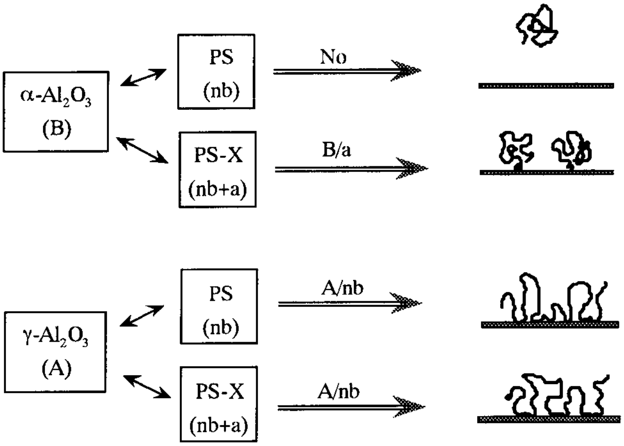


Fig. 6. Schematic picture showing the Lewis acid-base interaction between polymer and adsorbent, and the structure model of adsorbed polymer layers. B/a: interaction between basic site of surface (B) and terminal-functional group (a); A/nb: interaction between acidic sites of surface (A) and phenyl groups in polymer (nb).

Effect of Solvency of Eluent

In above studies, we selected the eluent ϕ_{cf}=0.25 as a good solvent which is good enough to desorb the pre-adsorbed polymers as showing in Fig. 2. If the solvent power of the eluent is strengthened gradually from ϕ_{cf}=0 to ϕ_{cf}=1.0 step by step to elute the same column, the elution curves obtained will give us other information on the adsorption energy of polymer layer.

Fig. 7 shows the accumulated fraction of desorbed polymer (Σf) at each step plotted against the component fraction ϕ_{cf} of eluent employed at respective step. It is well known that, for polystyrene polymer, the solvent power of eluent of the present binary mixture solvent (chloroform + cyclohexane) increases linearly with increasing the ϕ_{cf}-value. Fig. 7 shows firstly that the Σf increases about linearly with increasing ϕ_{cf}, the solvent power of eluent used. It indicates that in a polymer adsorption/desorption process, adsorbed amount is inverse proportion to the solvent power of the solvent used. Secondly, Fig. 7 shows that the slope (dotted line) of Σf vs. ϕ_{cf} plot in the PS-X-α-Al_2O_3 system is smaller than that in PS- and PS-X-γ-Al_2O_3 systems. In order to get mainly desorption (>90%), the solvent power of eluent needs to be about ϕ_{cf}=0.25 and 0.12, respectively. These indicate that the polymers adsorbed with different energetic states, i.e., the PS-X on α-Al_2O_3 is adsorbed more strongly than the PS (X) on γ-Al_2O_3, due to the strong acid-base interaction between the end group of PS-X molecule and the surface of α-Al_2O_3. Fig. 7 also shows that on the γ-Al_2O_3, surface, the end-functional group has no clear effect on the plot of Σf vs. ϕ_{cf}. It agrees with the result of Fig. 5.

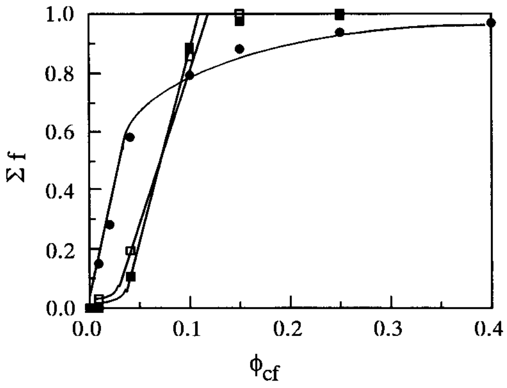


Fig. 7. The accumulated fraction of desorbed polymer (Σf) at each step plotted against the component fraction ϕ_{cf} of eluent employed. straight lines: PS200(□) and PSX200(■) / γ-Al_2O_3 ; bent curve: PSX200/ α-Al_2O_3(●).

Desorption Mechanism and Adsorption Energy of Terminally Adsorbed Polymer

The behavior in Fig. 7 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 Fig. 8 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 Fig. 7). 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 Fig. 8, 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.

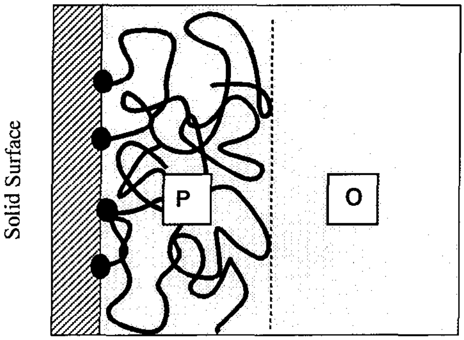


Fig. 8. Schematic picture of polymer adsorbed terminally on the surface. adsorbed polymer layer is co-existing with pure cyclohexane. P-polymer; O-solvent.

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, therefore, in the θ-condition the thickness of adsorption layer (h) is equal to the radius of gyration (R_g) of the polymer coil in solution ($h=R_g$). 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,

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

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 Fig. 8 the osmotic pressure, π, in the adsorbed layer is

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

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 osmosis pressure worked on an unit area of adsorbed surface, is expressed as follows,

$$\Delta G_{os} = \pi R_g \tag{3}$$

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

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

Here, $Na(\Gamma/M)$ 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.

$$\Delta G_{ad}=\Delta G_{os} \tag{5}$$

$$\chi_s= -R_g M/(N_a\Gamma v_1)[\ln(1-\phi_2)+(1-1/x)\phi_2+\chi_1\phi_2^2] \tag{6}$$

With the three PS-X/α-Al_2O_3 systems, the adsorption energy parameter (χ_s) was calculated using the experimental data from Fig. 3 (the saturated adsorbed amounts are 0.88, 0.97 and 1.02 mg/m^2 for M_w=5700, 40000 and 200000 respectively), and these are: χ_s=4.2 for M_w= 5700, χ_s=4.2 for M_w=40000, and χ_s=4.3 for M_w=200000.

A constant and reliable value of χ_s (4.2~4.3kT) 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 (Ref. 16).

CONCLUSION

The "continuous elution method" introduced in this research, is valuable for studying the desorption behavior of pre-adsorbed polymer on the surface of solid particles, and can supply some new information. According to this new method, the irreversibility of polymer adsorption can be clearly observed, the adsorption/desorption amount can be determined, and new information of kinetics of desorption, adsorption energy, and solvency effect, etc. can also be obtained.

The desorption behavior of pre-adsorbed polystyrene (PS) and polystyrene (PS-X) functionalized by a terminal iminium ion(X) from α- and γ-alumina surface was investigated. It was found that, on α-alumina, only the (X)-group is the driven force for adsorption, and the adsorbed layer has a higher energetic state than that on γ-alumina. A complicated desorption kinetics of polymer was observed from γ-alumina, which has a relation to the porosity of adsorbent. The solvency of medium has a strong effect on a adsorption/desorption behavior. Based on the balance between adsorption and desorption, the adsorption energy of the terminally adsorbed polymer layer was evaluated to be 4.2 ~ 4.3 kT with regarding to the osmotic pressure as a desorption force.

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