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Study on the Polymer Adsorption/Desorption Behavior Using Continuous Elution Method

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In this paper, a new method for studing the polymer adsorption/desorption behavior, "Continuous Elution Method", has been developed. In the continuous elution method, the target of study is concentrated onto the pre-adsorped powders packed into a small column after the usual adsorption process, solvent eluted and the concentration of polymer desorbed from the adsorbent surface is measured by a UV detector. By this method, the adsorption and desorption behavior of polystyrene and end-functionalized polystyrene by iminium ion on/from the surface of controlled-pore glass (CPG-10), has been investigated.

The adsorption/desorption of polymer on/from solid surface is not only of academic interest, but also of fundamental importance in numerous applications. The studies of polymer adsorption/desorption at the liquid-solid interface are still a developing field, since it is very complex and restricted by the equipment and methods available to study the problems. A lot of work on polymer adsorption has been done and a clear understanding of the mechanisms involved has emerged. However, there are a lot of problems remaining. For example,(ir)reversibility of polymer adsorption, the conformational structural of the adsorbing state, and the kinetics and thermodynamics of the adsorption/desorption process, etc.

Many studies of polymer adsorption on the solid surface from the liquid solution have been carried out. For example, the adsorption amounts are usually determined by measuring the concentrations of polymer remaining in the supernatant after the adsorption period. Also in some recent studies,surface properties of the adsorbent surface after adsorption have been measured by using special techniques, i.e., FT-IR,[1] electrokinetic,[2] microbalance,[3] radio-tracer technique (isotope labeled),[4] etc.

In this study, a new technique to study the adsorption/desorption process of polymer has been introduced. It is called a "Continuous Elution Method". The basic process is pictured in Fig.1.

The main equipment is similar to the usual liquid chromatograph. The difference is that the equipment does not behave as a chromatograph for the sample injected, but acts as a detector for the polymer sample desorbed from the adsorbent. i.e., in the continuous elution method, the target of study is concentrated on the pre-adsorbed powders packed into the column. Adsorbent powders are first pre-adsorbed by a polymer sample in the usual adsorption tube, and then packed into a column, solvent eluted, and the concentration of polymer desorbed from the adsorbent surface measured using an UV detector. This is reason we called this method the "continuous elution method", not chromatograph.

According to our preliminary experimental results, it is thought that this new technique will give some new information on the adsorption/desorption process of polymer on/from the liquid/solid interface.

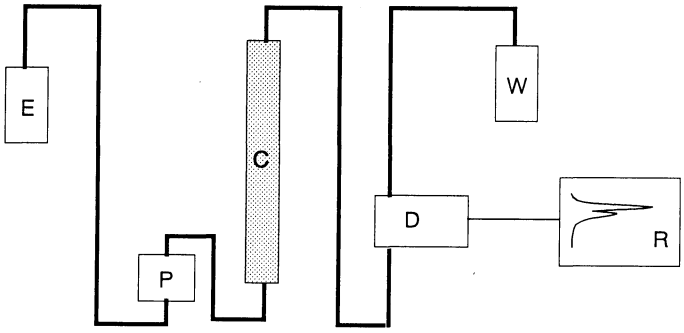

Fig. 1. Continuous elution method processing.
E--Eluent; P--Pump; C--Column;
D--Detector; R--Recorder; W--Waste.

The typical experimental procedure is as follows: First, a polymer coated powder was prepared under defined conditions (a fixed conc. of polymer, adsorption time, adsorpion temperiture, etc.), then packed into a column by a slurry method. After connecting the column to the elution system, eluent was pumped through the column. The concentration of the polymer desorbed from the adsorbent was monitored by a UV detector, and recorded as a concentration-time curve. The resultant curve was intergrated and the area was compared to a standard one. The amount of adsorbent was calculated by the difference between the weights of the packed column filled by the powders and empty.

By this method, the adsorption/desorption behaviour of polystyrene and the end-functionalized polystrene by iminium ion from the surface of porous glass have been analysed. The monodisperse polystyrene (PS) and the end-functionalized polystyrene by iminium ion (PS-X), (Mw=5.7×10^3 and 2.0×10^5), were obtained from Nipon Zeon Co. Ltd in Japan. As an adsorbent, a commercial controlled-pore glass beads, (CPG-10, pore diameter 3000 Å, particle size 120/200 mesh, CPG Inc.), was used after cleaning by the same procedure described previously.[5] PS and PS-X were adsorbed on the surface of CPG-10 from cyclohexane solution (5 mg/ml) at 35 ℃ for various adsorption times. According to our previous work,[5] the concentration of 5 mg/ml was enough to maintain saturated surface coverage. Then, the CPG-10 coated by the PS (or PS-X) was packed into a Teflon tube (ϕ=0.8 mm, l=20 cm) by the slurry method, and connected to the elution systems which are equipped with a UV detector (UVIDECC-100, JASCO) and Chromatocorder-11 (Shimadzu Co.) as a recorder. As the eluent, a pure or a mixed organic solvent was used and eluted at a constant rate of 5 μl/min. All the elution experiments were operated at room temperature.

Typical desorption curves of PS and PS-X from CPG-10 using the different eluents are shown in Fig.2. It is assumed that the non-adsorbing polymer (free polymer) will also be in the column. Therefore as a first step, pure cyclohexane was used as a eluent to wash out the non-adsorbed polymer from the column. Then, a binary mixture solvent (cyclohexane(CH)/chloroform(CF)=3/1 (v/v)) was used as an eluent (step II), where the desorption of the pre-adsorption polymers has taken place and all the polymers adsorbed are removed from the column. Finally, the last step (step III), pure chloroform was used as a stronger eluent. However, in this step, no polymers have been eluted form the column. Therefore the amount of adsorption can be calculated from the elution curve detected at step II , the adsorbed polymers especially PS-X can not be desorbed at step I , even if

they were displaced by a pure cyclohexane for a long time (at lab. scales). This means that pre-adsorbed PS-X from the cyclohexane solution can not be desorbed under the same solvent conditions at least in the macroscopic level, i.e., in the present adsorption conditions, an irrevesible adsorption of polymers has taken place. Similar results are reported in the previous publications.[3] This irreversibility of PS-X is also confirmed by another method, i.e., after adsorption of PS-X under a definite solution condition, the supernatant solution was displaced several times by a pure solvent (cyclohexane). Then, the polymer coated CPG-10 powders were packed into the column by the slurry method. In this case, no peak was detected in step I in Fig.2, and in step II, the same peak area as the peak found in the original step II can be detected. Therefore the washing process will not influence the amount of adsorption even in the column inside. However, the washing process in column inside as the step I, is more convenient and can easily detect whether the washing of free polymer is complete using an UV detector.

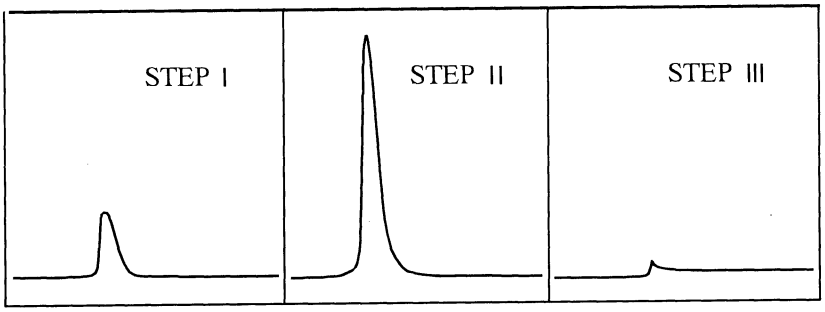

Fig.2. The typical desorption curves of PS and PS-X from CPG-10.
Eluents: step I ,cyclohexane(CH); step II, CH/CF=3/1(v/v); step III, chloroform(CF).

Figure 3 shows the adsorption rate curves for PS and PS-X which was determined by the amount of desorption using the solvent CH/CF=3/1.

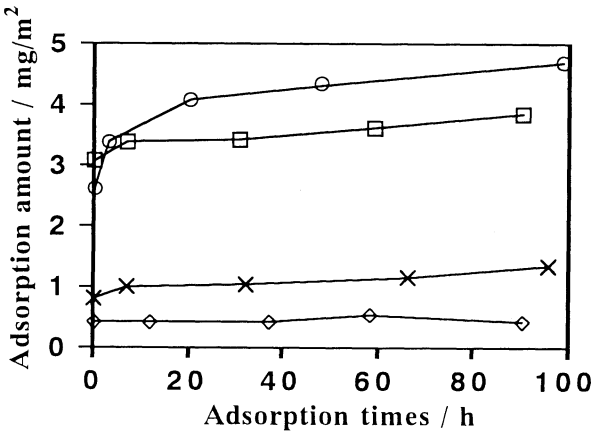

Fig. 3. Adsorption rates of PS and PS-X at the surfaces of CPG-10 in cyclohexane at 35 ℃. Adsorption amount was measured by the elution method.
○: PS-X(2.0×10^5); □: PS(2.0×10^5)
×: PS-X(5.7×10^3); ◇: PS(5.7×10^3)

By comparing Fig.3 with the previous data obtained by the usual depletion technique using the same polymer/ adsorbent system, it is found that the amount of adsorption for high molecular weight polymers, shows the same behavior, except for low molecular weight species, the result obtained from the present work is some lower than the usual data.[5] This may be expained by the following, in the values obtained from the above mentioned technique there will be included weakly adsorbed polymer and some component washed out at the stage of the cyclohexane elution (step I). So, this component will not be included in step II . It is also reported

that low molecular weight polymers adsorb more weakly than is the case for the high molecular weight polymers. However, Fig.3 shows that adsorbed amounts increase with increasing molecular weight of polymer, and values are significantly enhanced by end-functionalization of the polymer. This tendency is coincident with the result obtained by the usual method and indicates that this new technique is useful for investigating the adsorbed polymer layer.

Further, it is known that the continuous elution method can give other critical information about the adsorbed polymer layer using the various mixture of the solvent CH/CF as the eluent. For example, step II in Fig.2 was divided into two (or more) steps, i.e.,step II -a and step II -b by changing the component ratio of CH/CF to CH(40)/CF(1): II -a and CH(3)/CF(1): II -b. The elution curves obtained are shown in Fig.4 and indicate that there are two or three different types in adsorbed polymer layers, which are adsorbed by the different energetic state on the adsorbent surface,as a very broad elution curves have been obtained in step II -a. Especially, the curve for PS-X which shows a characteristic branched shape, suggesting that this technique can be used as an analytical method for quantifying the component ratio of adsorbed polymer layers with different energetic states.

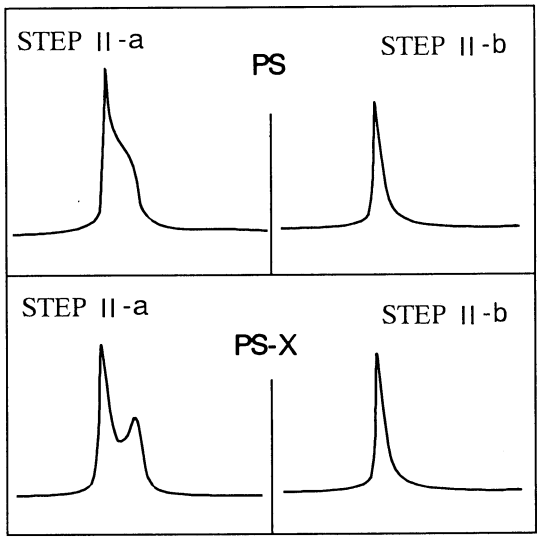

Fig. 4. The typical curves of step II in Fig.2 changed by various eluents. Eluents: cyclohexane/chloroform a=40/1, and b=3/1 (v/v) (PS, PS-X: Mw=200000).

These results indicate that the continuous elution method can be very useful for the study of polymer adsorption and can give us new imformation on the mechanism of polymer adsorption/desorption, especially of the end-functionalized polymer.

References

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