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Adsorption behavior of end-functionalized polymers modified by iminium ion

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Abstract: In order to clarify the end-functionalization effect of polymers modified by iminium ion, a model compound with a modified chain end was prepared by directly reacting *n*-butyllithium with *N*-methyl-2-pyrrolidone and then quenching by the addition of methanol. It is shown that the model compound includes the iminium ion group and that the adsorption bands in the IR-spectra of the chemically modified polymer were similar to those of model compound.

The adsorption behavior of end-functionalized polystyrene(PS-X) and diblock copolymer of PS and polybutadiene(PB) which were modified by iminium ion(PS-PB-X), were examined over a wide range of molecular weights of these polymers. It is evident that the amount of adsorption increased significantly by the end-functionalization and this trend was especially strong in the low molecular weight polymers ($M_w \leq 10^5$). The preference for the end-functionalized polymer was also examined by competitive and sequential adsorption experiments between different molecular weight species. It is shown that a prefered adsorption of PS-X with low molecular mass is pronounced over the adsorption of PS or PS-X with high molecular weight and in the combination of high and low molecular weight species of PS-X, a special enhancement of total adsorption can be observed. This enhancement is based on a combination of different adsorption layers formed by these two molecular weight species.

Key words: Polymer adsorption – end-functionalized polymer – iminium ion group – competitive adsorption – displacement adsorption

1. Introduction

The use of synthetic and natural polymers for controlling the stability of colloidal dispersion is of considerable importance for various industrial applications (1). Recent studies in this field have concentrated on defining the relation between molecular structure and its utility as a stabilizer (2). Homopolymer usually tends to dissolve in a good solvent rather than adsorb on a solid surface although this solvent condition is of great interest for colloid stabilization using the polymer stabilizer (3). In connection with this, an interesting situation is the selective adsorption from two parts of amphiphilic block polymer, where one block of a segment strongly adsorbs with a flattened conformation, and the other is strongly solvated without any adsorption. The polymer in which one block becomes very small is called an "end-functionalized polymer" [4].

In the present study, in order to clarify the specific effects on adsorption of iminium ion, first, some model compounds with a chain end modified by iminium ion were synthesized and the exact chemistry of the iminium ion end was examined. Thereafter, for several types of polymer with chain ends modified by iminium ion, critical experimental data were produced related to adsorption in a single polymer system, and simultaneous and sequential competitive adsorptions under various conditions.

2. Experimental

2.1. Preparation of model compound

To analyze the molecular structure of the chain end of the iminium ion, a model compound was

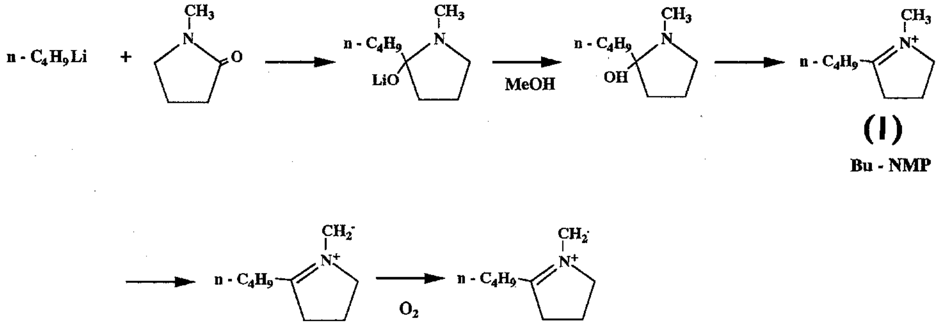

Fig. 1. Synthesis of model compound Bu-NMP and schematic formation of iminium ion group

prepared by reacting a modifier, *N*-methyl-2-pyrrolidone (NMP) with *n*-butyllithium at 40 °C for 30 min. and then quenching the compound with methanol. Figure 1 shows the scheme indicating the formation of the model compound, Bu-NMP, which includes an iminium ion group at one molecular end.

2.2 Preparation of end-functionalized polymer

To synthesize an end-functionalized polystyrene by iminium ion, a living anionic polymerization technique was employed and then modified by NMP in the same way as the case of the model compound using NMP (Fig. 2).

It is simple to apply the same technique to prepare the di-block polystyrene(PS)-polybutadyene(PB) and end-functionalized polymer (PS-PB-X). Here, the composition of PS/PB is fixed at 9/1 moles. In Table 1, the end-functionalized polymers (PS-X) and the end-functionalized block copolymers (PS-PB-X) used in this study are given.

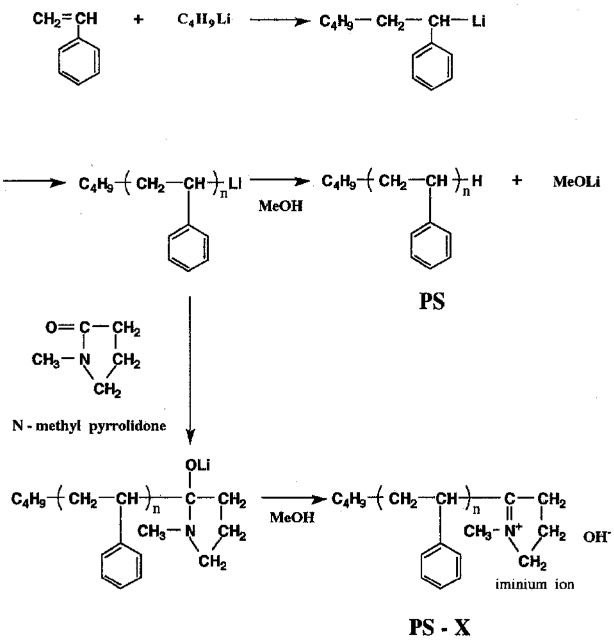

Fig. 2. Synthesis of end-functionalized polymer

2.3. Analysis of the molecular structure of the chain end

The molecular structure of the model compound(Bu-NMP) was determined by IR spectroscopic analysis(IR-810, JASCO) and ESR analysis (RE2X, JEOL). The measurement of each spectrum was carried out according to the common procedure.

2.4. Measurements of the adsorbed amount and competitive adsorbability

Determination of the amount of polymer adsorbed was carried out as follows. 5 ml of the polymer solution containing a known concentration were introduced into an adsorption tube (10 ml volume) which contained 0.2 g adsorbent. After being rotated (10 rpm) end-over-end for various times, the polymer concentration that remained in the supernatant was measured using a digital precision density meter (Anton Paar K.G. PHA02C). The temperature of the adsorption tube was maintained within 0.05 °C. As an adsorbent, commercial porous glass beads with a particle size of 180–280 μm, designated as CPG-10 (Electron Nucleonics Ins.), were used. The average pore radius is

Table 1. Molecular Weight of Polymer Samples

Sample	M_W	Sample	M_W	Sample	M_W
PS-5	5700	PS-X-5	5700	PS-PB-X-5	5000
PS-40	40 000	PS-X-40	40 000	PS-PB-X-50	50 000
PS-125	125 000	PS-X-125	125 000		
PS-200	200 000	PS-X-200	200 000		
PS-285	285 000	PS-X-285	285 000		

about 20–50 times larger than the radius of gyration of the dissolved polymers in cyclohexane at 35 °C.

In order to determine the competitive (or preferential) adsorbability between different molecular weight species, the adsorption amounts of each component in the equiweight mixture were evaluated by GPC analysis. The details concerning the adsorption process and the analysis of these data have been reported previously [5, 6].

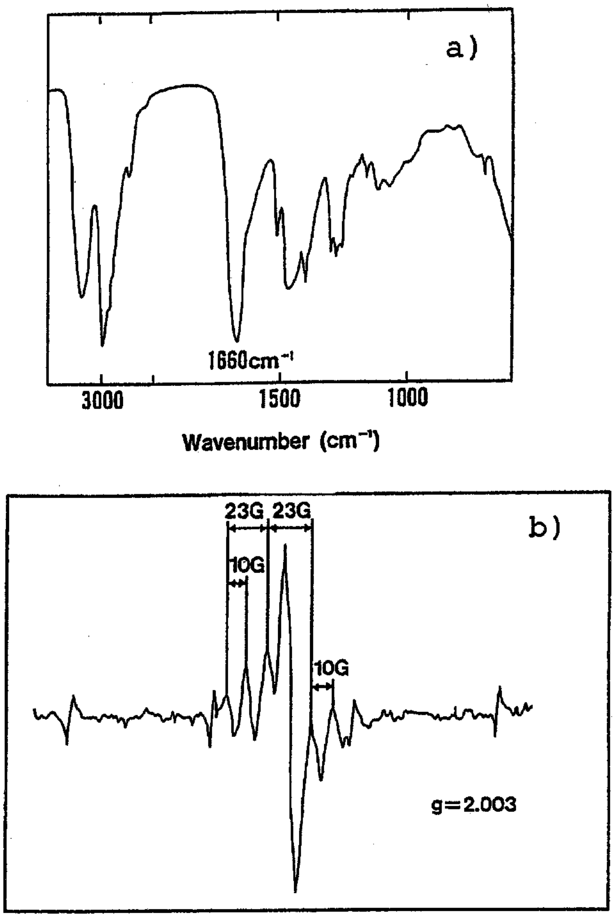

Fig. 3. IR spectrum(a) and ESR spectrum(b) of Bu-NMP

3. Results and discussion

3.1. Determination of the molecular structure of Bu-NMP

Figure 3a shows the IR spectrum of Bu-NMP which was synthesized by directly reacting the NMP with *n*-butyllithium and then quenching by methanol. The spectrum exhibits a strong adsorption band at 1660 cm^{-1} which is a characteristic band of the iminium ion group in the molecule. On the other hand, we could not observe any adsorption at 1660 cm^{-1} on the spectra of the chemical modifier, NMP.

Figure 3b shows an ESR spectrum of a benzene solution of Bu-NMP in an oxygen atmosphere (7). This same solution hardly exhibited any ESR spectra under the no-oxygen atomosphere. From this result, it can be understood that radical formation is closely related to the existence of oxygen molecules. Further, the finding of the super fine structure in the spectra and a *g*-value of 2.00 g, indicates that there is a carbon radical in the present sample. Also, at first, the spectral signal splits into triplet lines, which is based on the interaction between the radical center and two hydrogen atoms (A = 23 gauss). More fine splits of each line into doublet peaks are based on the interaction of the radical center with neighboring nitrogen atom (A = 10 gauss). Furthermore, it is apparent that the reaction product will include an ionic group, because the medium dielectricity increases with increasing reaction times of NMP with BuLi. All these results indicate that the radical producer takes the molecular structure shown by (I) in Fig. 1, and the reaction of NMP with BuLi will progress according to the scheme as shown in Fig. 1. Thus, it is realized that all the polymers synthesized in the same way with the model compound will include an iminium ion group at each polymer end (8).

3.2. Adsorption behavior in a single system

Figure 4 shows the adsorption isotherms for the series of polystyrene (PS) and its end-functionalized polymer (PS-X) on the porous glass (CPG-10) after 48 h. It is evident that the amounts of adsorption in the plateau region were enhanced significantly by the existence of the iminium ion group at each polymer end. The initial isotherm slope was also increased by the end-functionalization of the polymer.

Figure 5 shows the relationship between maximum adsorption after 48 h and the molecular weight of each polymer. It is known that the acceleration effect of iminium ion is observed over the entire range of molecular weights. However, the acceleration tendency of PS-X is gradually faded out and the amount of adsorption for both series (PS and PS-X) approaches the same value respectively.

To estimate the difference in the adsorption rates between PS and PS-X, the quantity of adsorbed polymer was plotted for the various adsorption times at the initial polymer concentration of 5 mg/ml. As shown in Fig. 6, the time required to reach equilibrium depended greatly upon the molecular weight and its structure, i.e., for the PS-X series, a long time is needed to arrive at the real adsorption equilibrium; especially with PS-X with a high molecular weight the adsorption cannot attain real equilibrium even after 1 week. On the other hand, adsorption of the PS series reached equilibrium within a few hours. Therefore, the relation between the maximum adsorption and its molecular weight is greatly dependent on the adsorption time and it is realized that the adsorption enhancement of PS-X with high molecular weight is greatly improved by increasing the adsorption time. The dashed line in Fig. 5 shows the relation between the maximum adsorption and the molecular weight of PS-X series after 96 h.

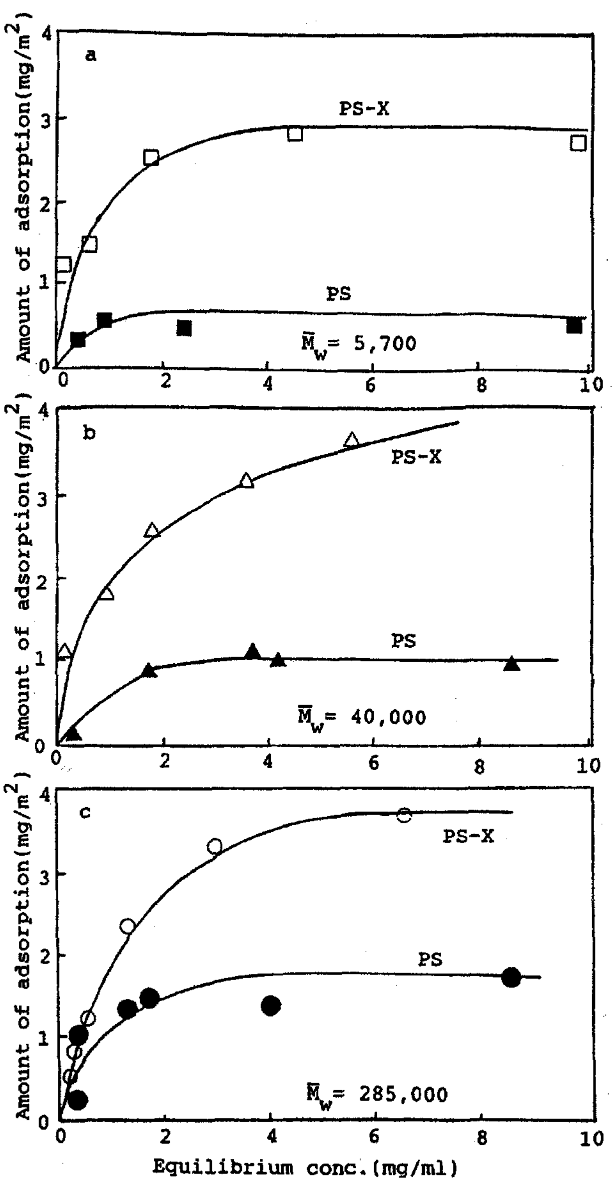

Fig. 4. Comparison of adsorption isotherms between end-functionalized polystyrene(PS-X) and polystyrene(PS) in cyclohexane at 35 °C

3.3. Competitive adsorption from mixtures

The end-effect of iminium ion on the adsorption of polymer has been measured by the competitive adsorption experiments from mixtures of PS-X and PS with different molecular weights. Figure 7 shows some typical examples of adsorption isotherms for the equiweight mixtures of PS samples with different molecular weights.

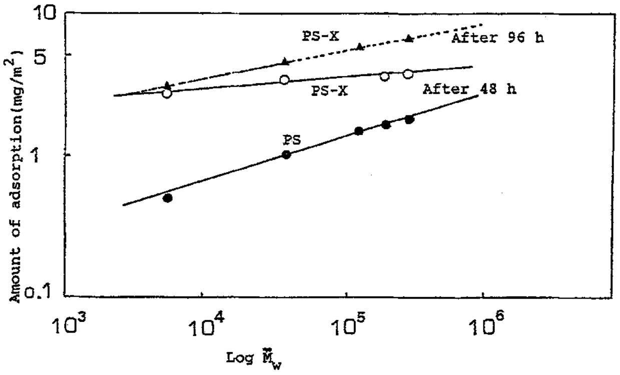

Fig. 5. Relations between maximum adsorption and molecular weight of PS and PS-X after 48 h. The dotted line shows the same relation of PS-X after 96 h

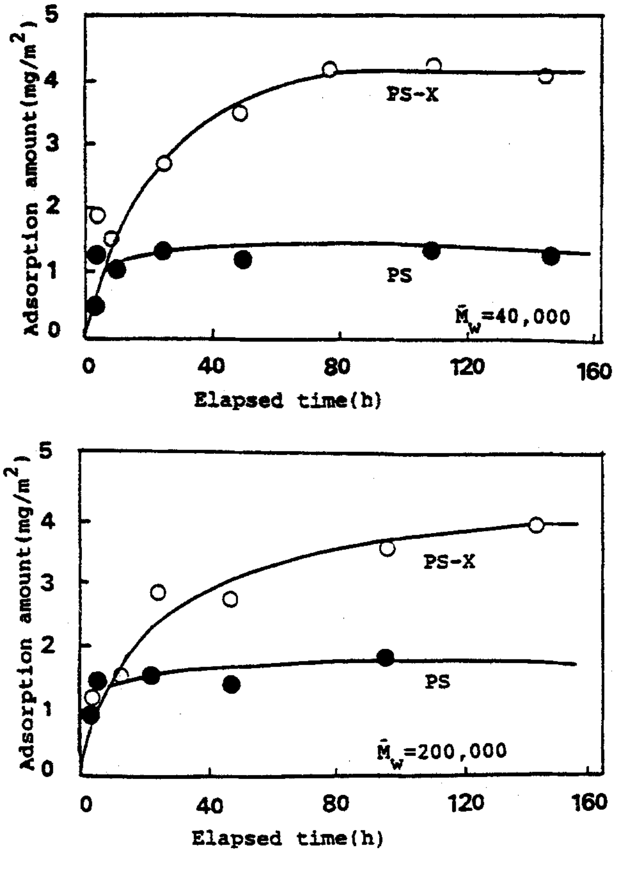

Fig. 6. Comparison of adsorption rates between PS-X and PS in cyclohexane at 35 °C

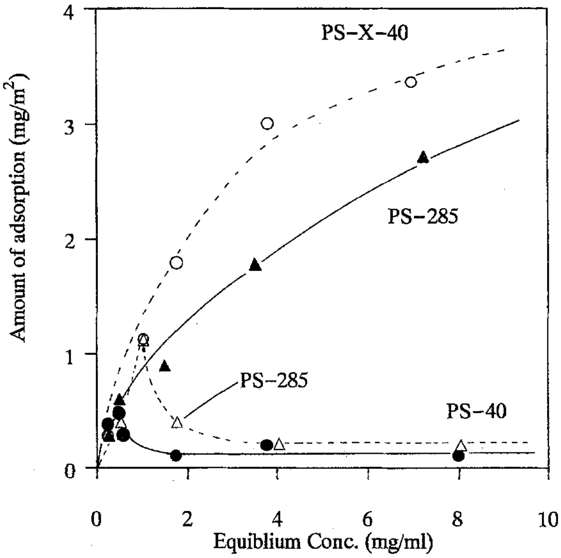

Fig. 7. Adsorption isotherms for a mixture containing two components of different molecular weights after 24 h (in cyclohexane, 35 °C). (●), PS-40 in equiweight mixture (PS-40 + PS-285); (▲), PS-285 in equiweight mixture (PS-40 + PS-285); (○), PS-X-40 in equiweight mixture (PS-X-40 + PS-285); (△), PS-285 in equiweight mixture (PS-X-40 + PS-285)

The determination of the amount of adsorption for each species was carried out using the GPC technique (6). It was found that preferential adsorption of high molecular weight species over lower ones is pronounced and, especially in a concentration range higher than 2 mg/ml, the low molecular weight species are completely eliminated from their adsorption layer. The same preferential adsorption of a large molecular weight species over a small one was also observed for other combinations of PS samples with different molecular weights (9). However, by using PS-X sample as one of the components, the preferential behavior showed a completely different tendency. The typical result is shown by the dashed line in Fig. 7. As can be seen from the figure, a preferred adsorption of PS-X with low molecular mass is pronounced over the adsorption of PS with high molecular weight and the preferential behavior is enhanced in a medium of concentrated polymer solutions.

Figure 8 shows the competitive adsorption from mixtures of two end-functionalized polymers with different molecular weights. As can be seen, the pronounced preference of low molecular weight species over the large ones is observed.

All these results indicate that the acceleration effect of the iminium ion group in polymer adsorption suppresses the effect of high molecular mass.

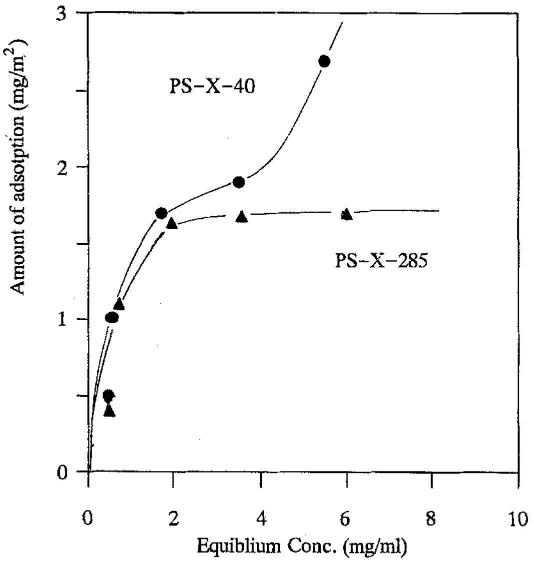

Fig. 8. Adsorption isotherms for a mixture containing two components of different molecular weights (in cyclohexane, 35 °C). (●), PS-X-40 in equiweight mixture (PS-X-40 + PS-X-285) after 24 h; (▲), PS-X-285 in equiweight mixture (PS-X-40 + PS-X-285) after 2n4 h

3.3. *Sequential adsorption*

Sequential adsorption of polymers with different molecular species can be divided into two sub-processes. Adsorption of one polymer species is followed by the addition of a second species to the polymer-adsorbent complex. Additional adsorption of the second species may occur or the second species may displace the pre-adsorbed polymer, all depending on the relative affinities of the two polymer species to the surface. In the present experiments, the time interval between the two additions was fixed at 12 h, and the displacement process of pre-adsorbed polymers and the additional adsorption process of the second polymer was analyzed by the GPC technique.

Figures 9 and 10 show the results obtained here. In Fig. 9a, PS-X-285 was pre-adsorbed and PS-X-5 was added in a later stage. A clear displacement of PS-X-285 by PS-X-5 can be observed. However, in the case of the opposite sequence, no displacement of pre-adsorbed polymer and slight additional adsorption occurred (Fig. 9b). This behavior can be explained as follows. In the first sequence (Fig. 9a), PS-X-285 in the first step includes some loop segments in their adsorption layer, because a very long period is needed for the anchoring of high molecular weight polymers with one end only. This layer featuring easily results in some additional adsorption of second species with low molecular weights among their loops.

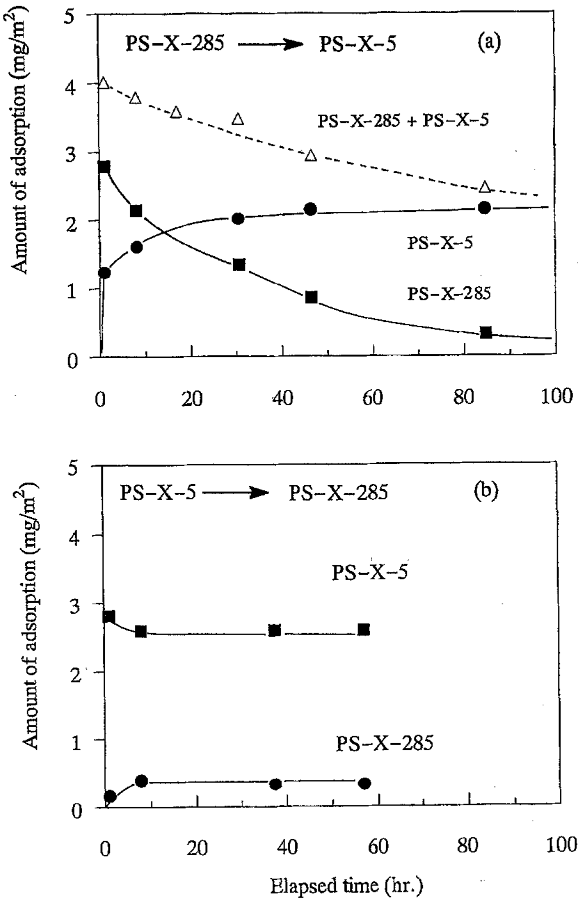

Fig. 9. Displacement amount pre-adsorbed and additionally adsorbed amount as a function of elapsed time after 12 h (polymer conc. = 6 mg/ml in cyclohexane at 35 °C)

Figure 10a shows the results for the combination of PS-PB-X-50 (pre-adsorbed polymer) and PS-PB-X-5 (second species) in a carbon tetrachloride solution at 35 °C. It appears that the same tendency as in the result shown in Fig. 9a can be realized. As carbon tetrachloride is a good solvent for a polystyrene part, PS-PB-X-50 will adsorb mainly by the PB and X parts, and will adopt an extended configuration on the surface [2, 3]. Furthermore, Figs. 9a and 10a illustrate that in the sequential adsorption of end-functionalized polymers with different molecular sizes, a special cooperative effect can be found, i.e., in the

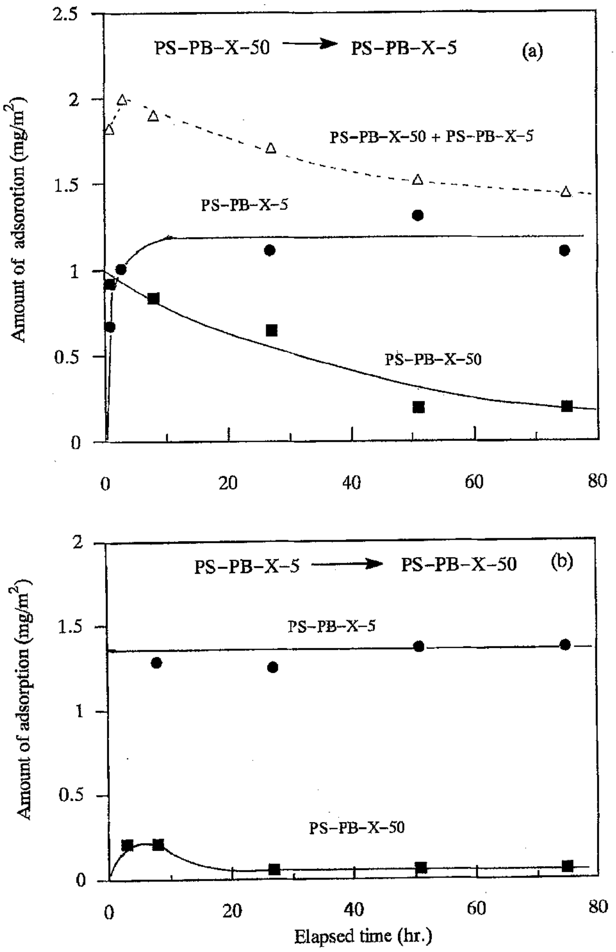

Fig. 10. Displacement amount pre-adsorbed and additionally adsorbed amount as a function of elapsed time after 12 h (polymer conc. = 6 mg/ml in cyclohexane at 35 °C)

combination of high and low molecular weight species of end-functionalized polymers, a special enhancement of total adsorption can be realized. This adsorption enhancement is based on a combination of adsorption layers of a loop-train conformation formed by high molecular weight species and of a special conformation of small molecular weight species adsorbed additionally [2]. It is expected that such a high amount of total adsorption will be useful in many industrial applications [1] where electrostatic stabilization is less successful and stability is needed at high volume fractions of particles as well as under extreme conditions of temperature and flow.

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