Fr.) 1985, *46*, 156) and for copolymers by Cantor (Cantor, R. *Macromolecules* 1981, *14*, 1186).
(20) de Gennes, P.-G., unpublished results.
(21) de Gennes, P.-G. *J. Phys. Lett.* 1975, *36*, L.55; *J. Phys. Lett.* 1978, *49*, L.299.
(22) de Gennes, P.-G. Collège de France lectures, 1984.
(23) Pincus, P.; Witten, T. A. *Macromolecules* 1986, *19*, 2609. Pincus, P.; Witten, T. A.; Cates, M. *Europhys. Lett.* 1986, *2*, 137.
(24) Goldstein, R. *J. Chem. Phys.* 1986, *84*, 3367.
(25) Semenov, A. N. *Sov. Phys.—JETP (Engl. Transl.)* 1985, *61*, 733; *Zh. Eksp. Teor. Fiz.* 1985, *88*, 1242.

Adsorption of Polybutadienes with Polar Group Terminations on the Solid Surface. 1. Infrared Study at the Silica Surface

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ABSTRACT: Adsorption of polybutadiene terminated with a very polar functional group (T-PBR) on a silica surface from carbon tetrachloride solution has been investigated by using IR spectroscopy and compared with normal polybutadienes (PBR). Carbon tetrachloride is a good solvent for polybutadiene. The adsorbed amount, A, the surface coverage θ of the silanol groups, and the bound fraction of a polymer chain p were measured. A marked difference in adsorption behavior between T-PBR and PBR polymers was observed. T-PBR has an A and θ twice as large as those for PBR, while the p value was approximately the same for both polymers. From the chemical structure of the terminal group we can qualitatively interpret the difference in the adsorption behavior by taking into account the preferential adsorption of the terminal polar functional groups over the double-bond groups in polybutadiene chains onto the silanol groups of silica surface.

Introduction

The loop–train–tail conformation is generally accepted as a structure of flexible polymer chains adsorbed on flat, cylindrical, and spherical surfaces if there is no specific interaction between polymer and surface.[1-4] Tail portions of adsorbed polymer chain are considered to be random-flight chains attached on a surface with one end, and they play an important role in understanding the behavior of flexible polymer chains at surfaces and interfaces. In particular, the large layer thickness of the adsorbed polymer chains is believed to be mainly governed by the tail portions in both theoretical and experimental sides. Moreover, the tail portions of adsorbed chains not only act as a steric stabilization moiety for colloidal particles but also can serve as bridges between different particles in flocculation of colloidal dispersions.[5]

Tail formation on the solid surface in adsorption experiments is available by use of (1) a polymer terminated with a single specific functional group, which strongly interacts with surface sites of the adsorbing surface, or (2) a block copolymer in which one block adsorbs in train conformation and the other block adsorbs negligibly. The two methods described above contain some demerits: (1) A polymer chain adsorbed with one anchored terminal group may desorb from the surface under good solvent conditions as the result of repulsive interaction of dangling tails caused by the excluded volume effect if the bond strength between the terminal group and a surface site is not very strong. (2) One adsorbed block may not behave as one long train part without loop formation.

However, there are a few successful examples. Hadziioannou et al.[6] recently have measured surface forces between 2-vinylpyridine–styrene block copolymers adsorbed on mica surfaces; the 2-vinylpyridine block adsorbs strongly on a mica surface with a flattened conformation, while the styrene block is not adsorbed directly to a mica surface at all. Some block copolymers were used as polymer monolayers at the air-water interface where one block (uncharged block) lays flat on the interface and the other block (charged block) is extended into water.[7,8]

On the other hand, there are some adsorption studies of polymers terminated by a polar group, which adsorbs preferentially over functional groups in the main polymer chains.[9-11] They used low molecular weight fractions, i.e., $M_n \sim 2 \times 10^3$. The effect of terminal functional groups on adsorption was definitely observed as expected. For high molecular weights of polymers with terminal groups, a definite effect of terminal functional groups on adsorption behavior has not been recognized. In this study we investigate the effect of a terminal functional group with strong adsorbability on polymer adsorption behavior by using well-characterized samples for both adsorbate and adsorbent. Adsorption measurements of high molecular weight ($\sim 10^5$) polybutadienes terminated with bis(p-diethylamino)phenyl)methanol onto the silica surface were performed by using IR spectroscopy in carbon tetrachloride, which is a good solvent for polybutadiene, in comparison with adsorption of normal polybutadiene. The reason why these adsorption experiments are done under good solvent conditions is as follows: under good solvent conditions both the adsorbed amount and surface coverage are usually much smaller than those under poor solvent conditions at the same polymer concentration; thus, it is expected that the differences in adsorbed amount as well as surface coverage between polymers terminated and those not terminated with functional groups will be emphasized by the preferential adsorption of terminal groups.

Experimental Section

Materials. Polybutadiene (PBR) and polybutadiene terminated with bis(p-(diethylamino)phenyl)methanol (T-PBR) were kindly supplied from Nippon Zeon Co., Ltd. The chemical

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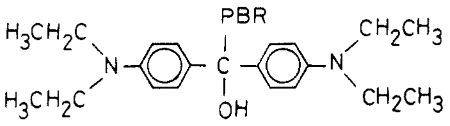

Figure 1. Chemical structure of T-PBR.

Table I
Molecular Characteristics of T-PBR and PBR

sample	$M_n \times 10^{-4}$	M_w/M_n	contents, %: cis-1,4	trans-1,4	1,2 additive
T-PBR-1	36.0	1.8_8	9.3	20.2	70.5
T-PBR-2	26.0	1.4_4	9.9	18.9	71.2
T-PBR-3	13.0	1.2_3	10.7	19.1	70.2
PBR-1	36.0	2.5_6	10.0	19.3	70.7
PBR-2	21.0	1.5_9	10.0	18.7	71.3

structure of T-PBR is shown in Figure 1. PBR was prepared by polymerizing 1,3-butadiene in hexane or benzene with a *n*-butyllithium catalyst in combination with diglyme (diethylene glycol dimethyl ether) at 40 °C. For T-PBR, after the conversion of polymerization reached 100% a modifier such as 4,4′-bis(diethylamino)benzophenone was added to carry out the chemical modification reaction. Supplied polymers were purified by precipitation from their benzene solutions into a large amount of methanol by stepwise addition. GPC measurements of PBR and T-PBR samples prepared in the same batch give similar chromatograms, and this result indicates that T-PBR series make no complex via hydrogen bonding of the polar terminal groups in solution. After the precipitated samples were dried under vacuum they were dissolved again in benzene and fractionated into more than 10 fractions by addition of methanol at 25 °C. The fractionated samples were freeze-dried from benzene solution. The samples so prepared were stored in a brown glass desiccator for protection from light; the desiccator was filled with Ar gas to avoid oxidation.

The number average molecular weights of the fractionated polymers were determined by using a Hewlett-Packard 502 high-speed membrane osmometer in toluene or carbon tetrachloride at 25 °C. A Sartorius SM 67 N 11539 filter was used as a semipermeable membrane. We chose two fractionated PBR samples and three fractionated T-PBR samples for the adsorption studies. The polydispersities of both T-PBR and PBR samples were determined from GPC measurements by using polystyrene samples with narrow molecular weight distributions as a standard. The microstructures such as cis-1,4, trans-1,4, and 1,2 additive of PBR and T-PBR samples were determined from ^{13}C NMR spectra of 7% solution in deuteriochloroform at room temperature by using a Nippon Denshi (Model FX-100) spectrometer.[12] The molecular characteristics of the polymer used in this study are listed in Table I.

The nonporous Aerosil 130 silica (Degussa A. G., West Germany) was used as the adsorbent after being heated at 120 °C. According to the manufacturer, the average particle diameter is 160 Å with a surface area of 141 m^2/g, and the surface concentration of silanol groups on the silica surface is 3 silanol groups/100 $Å^2$.

Carbon tetrachloride used as a solvent for polymer adsorption experiments is purified by a fractional distillation just before use.

Polymer Adsorption. A 20-mL polymer solution with known concentration was mixed with 0.16 g of silica in a stoppered glass tube for centrifugation. After equilibration by sitrring with a magnetic stirrer chip at 25 °C the supernatant solution was separated to sediment the silica particles by using a Kubota KB-200 B centrifuge. The equilibrium concentration C_p in the supernatant solution was determined by using a JASCO FT/IR-3 IR spectrometer at a characteristic wavenumber of 2920 cm^{-1}, which corresponds to the streching vibration of CH groups.

The sedimented silica gel was placed in an IR cell made from 4 × 4 cm^2 KBr plates, and it was subjected to the IR spectrometer with the reference cell containing carbon tetrachloride or the supernatant solution. To confirm the reproducibility of adsorption measurements we performed at least two measurements for the same concentration. The errors in the adsorbed amount are less than 5% whereas those in both θ and p are less than 10%.

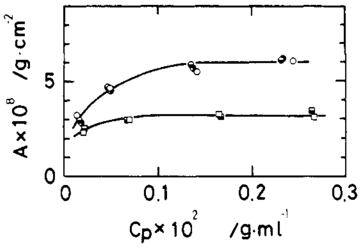

Figure 2. Adsorption isotherms of T-PBR and PBR polymers: (○) T-PBR-1; (◓) T-PBR-2; (◑) T-PBR-3; (□) PBR-1; (⊟) PBR-2.

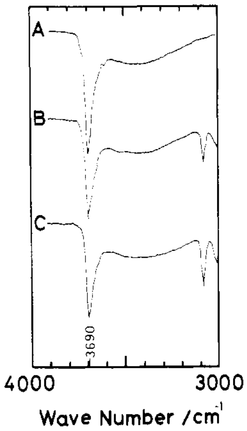

Figure 3. IR spectra of Aerosil 130 silica in carbon tetrachloride: A, silica; B, silica on which PBR-1 adsorbs at a dosing concentration C_0 of 0.2 g/100 mL (equilibrium concentration in the supernatant solution C_p = 0.164 g/100 mL); C, silica on which T-PBR-2 adsorbs at C_0 of 0.1 g/100 mL (C_p = 0.046 g/100 mL).

Table II
Adsorption Data at the Plateau Region of T-PBR and PBR

sample	$A \times 10^8$, g cm^{-2}	θ	p
T-PBR-1	6.1	0.31	0.14
T-PBR-2	6.2	0.34	0.15
T-PBR-3	6.3	0.25	0.11
PBR-1	3.2	0.18	0.15
PBR-2	3.3	0.13	0.11

Results

The cis-1,4, trans-1,4, and 1,2 additive contents of all polymer samples used here are almost the same, as seen from Table I. In Figure 2 all adsorption isotherms of PBR and T-PBR are illustrated. The adsorbed amount A, expressed in g/cm^2, increases with the equilibrium concentration C_p and reaches a plateau value at higher C_p. The shape of all adsorption isotherms is the rounded curve, reflecting the somewhat wide molecular weight distribution of T-PBR and PBR samples and not their high-affinity character. Adsorption isotherm curves are independent of molecular weight for the respective series. We notice that the plateau adsorbed amount of T-PBR is twice as large as that of PBR, as seen in Table II.

Figure 3 shows IR spectra of the silica gel: A, the silica suspended in carbon tetrachloride; B, the silica equilibrated with the plateau adsorbed amount of PBR; and C, the silica equilibrated with the adsorbed amount of T-PBR one lower than the plateau value. The absorption peak of silanol groups in carbon tetrachloride was observed at 3690 cm^{-1}. There are two characteristic peaks in the IR spectra of B and C: one peak at 3690 cm^{-1} corresponds to the absorbance of free silanol groups and another peak at ~3100 cm^{-1} is due to the absorbance of CH streching vibration of adsorbed polymer chains. The absorbance at ~3100 cm^{-1} in Figure 3C is stronger than that in Figure 3B since the magnitude of adsorbed amount of T-PBR (C)

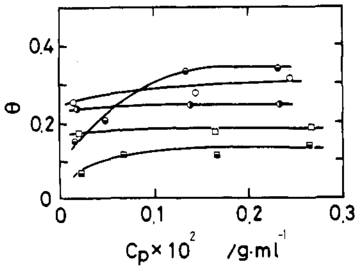

Figure 4. Plots of θ vs the equilibrium concentration C_p in the supernatant solution. Symbols are the same as in Figure 2.

is larger than that of PBR (B).

In general, when the polymer chains adsorb on the silanol groups *via* an interaction such as hydrogen bonding the frequency of silanol groups should shift lower; that is, the frequency shift of vibrations of silanol groups is observed to be due to the perturbed silanol groups. In this study the particular frequency shift of silanol groups was not apparent in IR spectra of the silica on which the polymers adsorb. However, the presence of the peak at ~ 3100 cm^{-1} in the IR spectra of B and C indicates that both T-PBR and PBR molecules adsorb on the silica surfaces. Moreover, the concentration of free silanol groups was actually changed to decrease after adsorption of T-PBR or PBR. These facts mean that both polymers interact with the silanol groups.

The previous works showed that the double bonds in polybutadiene[13,14] and some organic compounds[15-17] containing the CH=CH group induce an IR frequency shift of the perturbed silanol groups when they adsorb on the silica surface. The reason for the weak interaction between double bonds and silanol groups in this study is not clear, but it may be due to the much higher content of the 1,2 additive, i.e., the vinyl bond, in T-PBR and PBR samples in comparison with polybutadienes used in our previous study.[13]

The fraction θ of the silanol groups occupied by adsorbed polymer chains can be calculated from

$$\theta = (C_s - C_{OH})/C_s \tag{1}$$

where C_s and C_{OH} are the numbers of silanol groups before and after adsorption, respectively. Plots of θ vs the equilibrium concentration C_p in the supernatant solution are displayed for all polymers in Figure 4. The θ value increases with C_p and reaches a constant value above C_p = 0.1 g/100 mL. The plateau value θ shows a slight molecular weight dependence; that is, high molecular weight samples have a somewhat larger θ than low molecular weight ones for the respective polymers. For PBR series the higher molecular weight species tend to have higher θ; however, for T-PBR series the similar tendency was not observed. The difference in θ between T-PBR-1 and T-PBR-2 exceeds experimental errors. In this stage we have no explanation for this difference. The plateau values of θ tabulated in Table II show that their magnitudes for T-PBR are almost twice as large as those for PBR.

We can calculate the fraction p of monomer units attached directly to the silanol groups by the following equation, assuming that a double bond in butadiene chains should interact with one silanol group:

$$p = (\text{weight of monomer units directly attached to silanol groups per unit area})/(\text{weight of adsorbed amount per unit area}) \tag{2}$$

The p values so determined are plotted against C_p in Figure 5. These curves are almost independent of molecular weight as well as polymer species because of the twice larger adsorbed amount and θ of T-PBR than of PBR. The plateau value of p listed in Table II is taken as ~ 0.1.

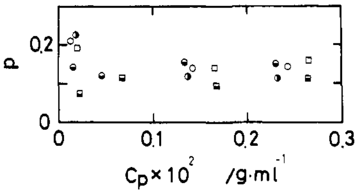

Figure 5. Plots of p vs the equilibrium concentration C_p in the supernatant solution. Symbols are the same as in Figure 2.

Discussion

We can notice some features from the plateau values of adsorption data listed in Table II. The plateau values of adsorbed amount as well as p for PBR are lower in comparison with most data reported previously.[3,17] This fact is understandable since polybutadiene is a less polar polymer and has complicated structures involving three different microstructures and also since carbon tetrachloride is a very good solvent for polybutadiene, showing a large second virial coefficient of $\sim 2.0 \times 10^{-3}$ mol/g^2. Consequently, the relative strength of the bond between double bonds of butadiene and silanol group in comparison with the bond between solvent and silanol groups is weaker than for the other polymer–solvent–silica combinations, and thus no evident frequency shift of the occupied silanol groups is observed.

Another feature point is the twice larger adsorbed amount and θ for T-PBR than for PBR. The terminal group of T-PBR contains some specific functional groups such as hydroxyl, amine, and phenyl as seen from its chemical structure (see Figure 1). Adsorption experiments of organic compounds containing such functional groups on the silica surface in carbon tetrachloride by using IR spectrometer showed that amines and alcohols form tight hydrogen bonds with silanol groups, respectively, and thus shift the perturbed silanol groups to a lower frequency as compared with the frequency of unperturbed silanol groups.[16,18-20]

In this experiment the absence of an evident frequency shift of silanol groups perturbed by the terminal groups of T-PBR is due to the extremely lower number of the terminal groups compared to butadiene monomeric units. The evidence for the stronger interaction between the terminal group of T-PBR and silanol groups is proved by the displacement adsorption of T-PBR and PBR from the silica surface by addition of displacers such as benzene, dioxane, and acetone.[21] The displacement adsorption by adding 1 mL of benzene showed that T-PBR chains are not desorbed from the silica surface, while PBR chains are completely exchanged with displacer molecules. However, the addition of 1 mL of dioxane or acetone leads to a complete desorption of both T-PBR and PBR chains from the silica surface. Therefore, three functional groups in the terminal group of T-PBR chain more strongly interact with the silanol groups than double bonds in polybutadiene chains.

We now propose a rather speculative model with which we wish to explain at least qualitatively our observations. The terminal groups preferentially adsorb on the silanol group over the double bonds in polybutadiene chains at an earlier adsorption time. In this stage the terminal group only interacts with the silica surface, while the remaining part, i.e., a polybutadiene chain, behaves as a long tail. However, this preferential adsorption of the terminal groups of T-PBR chains will be reduced with increasing

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adsorption time because of blocking of the unoccupied silanol groups by earlier arrivals, in which the overall chain conformation of one end-attached T-PBR chain is not much different from the free chain conformation suggested by Hesselink[22] and Tanaka.[23] Subsequently, the double bonds in butadiene parts of T-PBR chains adsorb on the silanol groups in order to attain an equilibrium state, and finally an adsorbed amount twice as large as that of PBR chains is established for T-PBR chains.

The bound fraction p is sometimes useful to infer the conformation of adsorbed polymer chain. Since the plateau value of p is nearly constant irrespective of polymers, one can imagine that the conformation of adsorbed T-PBR chains is not different from that of adsorbed PBR chains. However, for T-PBR chains their one end is undoubtedly attached to the silica surface due to the high adsorbability of the terminal group. The polymer segments located close to the anchored end adsorb easily on the silica surface since their mobility should be restrained in comparison with that of unadsorbed segments located far from the adsorbed end segment. Therefore, in the equilibrium state T-PBR chains take a conformation consisting of one relative long tail and some short loops as well as trains. On the other hand, the adsorbed PBR chains will take the generally accepted loop–train–tail conformation, where both ends are dangling. The difference between both adsorbed conformations may be explored by the measurement of adsorbed layer thickness. A preliminary ellipsometric study[24] of adsorption of T-PBR and PBR onto a platinum plate from carbon tetrachloride solution showed that the thickness of T-PBR is thicker than that of PBR and the adsorbance of T-PBR is ~1.5 times that of PBR. These ellipsometric data seem to be convenient for more adsorbed polymer on the surface for the T-PBR chains.

The plateau data on p and θ for T-PBR imply on the order of 300 covered adsorbed segments per chain ($p \sim 0.1$) and on the order of 600 silanol groups per particle; i.e., two molecules are adsorbed on the silica surface if no bridging between different silica particles is assumed. T-PBR chains whose radii of gyration is on the order of 200 Å will be able to wrap around the silica particle well by taking the suggested structure of adsorbed chains.

Conclusions

High molecular weight polybutadienes terminated with a single very polar group show a different adsorption behavior at the silica surface in carbon tetrachloride as compared with normal polybutadiene. The former has an adsorbed amount and a surface coverage of the silanol groups that are twice as large as the same features in the latter, but the bond fraction p (i.e., the fraction of monomers of adsorbed chains being in contact with the surface) is almost equal for both polymers. This difference is rather speculatively interpreted by taking into account the preferential adsorption of terminal polar groups to the silanol groups over the double bonds in butadiene chains. We wish to emphasize that a chain end terminated with polar groups is very important for the determination of adsorption behavior of polymer chains.

Registry No. SiO_2, 7631-86-9.

References and Notes

(1) Vincent, B.; Whittington, S. In *Surface and Colloid Science*; Matijevic, E., Ed.; Plenum: New York, 1981; p 1.
(2) Tadros, Th. F. In *The Effect of Polymers on Dispersion Properties*; Tadros, Th. F., Ed.; Academic: London, 1982; p 1.
(3) Takahashi, A.; Kawaguchi, M. *Adv. Polym. Sci.* **1982**, *46*, 1.
(4) Fleer, G. J.; Lyklema, J. In *Adsorption from Solution at the Solid/Liquid Interface*; Parfitt, G. D., Rochester, C. H., Eds.; Academic: London, 1983; p 153.
(5) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic: London, 1983.
(6) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.
(7) Kawaguchi, M.; Oohira, M.; Tajima, M.; Takahashi, A. *Polym. J.* **1980**, *12*, 849.
(8) Bringuier, E.; Vilanove, R.; Gattot, Y.; Selb, J.; Rondelez, F. *J. Colloid Interface Sci.* **1985**, *104*, 95.
(9) Crowl, V. T.; Matati, M. A. *Discuss. Faraday Soc.* **1966**, *42*, 301.
(10) Crowl, V. T. *J. Oil Colour Chem. Assoc.* **1967** *50*, 1023.
(11) Sakai, I.; Nakamae, K.; Ohkawa, T.; Inubushi, H.; Mastumoto, T. *Kobunshi Ronbunshu* **1977**, *34*, 661.
(12) Yoshioka, A.; Komuro, K.; Ueda, A.; Watanabe, H.; Akita, S.; Masuda, T.; Nakajima, A. *Pure Appl. Chem.* **1986**, *53*, 1697.
(13) Kawaguchi, M.; Sano, T.; Takahashi, A. *Polym. J.* **1981**, *13*, 1019.
(14) Kawaguchi, M.; Aoki, M.; Takahashi, A. *Macromolecules* **1983**, *16*, 635.
(15) Little, L. H.; Mathieu, M. V. *Actes Congr. Int. Catal., 2nd* **1960**, 771.
(16) Marshall, K.; Rochester, C. H. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1754.
(17) Howard, G. J. In *Interfacial Phenomena in Apolar Media*; Eicke, H. F., Parfitt, G. D., Eds.; Dekker: New York, 1987; p 281.
(18) Griffiths, D. M.; Marshall, K.; Rochester, C. H. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 400.
(19) Curthoys, G.; Davydov, V. Ya.; Kiselev, A. V.; Kiselev, S. A.; Kuznetsov, B. V. *J. Colloid Interface Sci.* **1974**, *48*, 58.
(20) Rochester, C. H. *Adv. Colloid Interface Sci.* **1980**, *12*, 43.
(21) Kawaguchi, M.; Kawarabayashi, M.; Takahashi, A., unpublished data.
(22) Hesselink, F. Th. *J. Colloid Interface Sci.* **1975**, *50*, 606.
(23) Tanaka, T. *Macromolecules* **1977**, *10*, 51.
(24) Kawaguchi, M.; Kawarabayashi, M.; Takahashi, A., unpublished data.

Molecular Rheology of H-Polymers

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ABSTRACT: The rheological behavior of branched polymer melts contrasted with that of linear melts motivates a discussion of a molecular model of a melt of H-polymers. Concentrating on the dynamics of the "backbone", we derive and discuss the linear viscoelastic properties in the light of experiments by Roovers.[23] The model is extended to treat nonlinear deformations, with path-length extension treated in a self-consistent way, and compared with rheological behavior of branched LDPE.

Introduction

The primitive path or tube model of polymer melts as developed by Doi and Edwards[1–4] has met with considerable success when applied to the dynamics of linear polymers.[5–7] The extension of the theory to star polymers has been made[8,9,20] and is in accord with both numerical[10]

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