Acknowledgment. The technical assistance of M. A. Grossman is gratefully acknowledged.

References and Notes

(1) Cerfontain, H. "Mechanistic Aspects in Aromatic Sulfonation and Desulfonation"; Wiley: New York, 1968.

(2) Turbak, A. F. *Ind. Eng. Chem. Prod. Res. Dev.* **1962**, *1*, 275.

(3) Turbak, A. F. U.S. Patents 3072618, 3072619, and 3072703.

(4) Knudsen, C. A., Jr. U.S. Patent 3859264.

(5) Vink, H. *Makromol. Chem.* **1981**, *182*, 279.

(6) Thaler, W. A. *J. Polym. Sci.* **1982**, *20*, 875.

(7) Makowski, H. S., unpublished results.

Preparation of (*p*-Vinylbenzyl)polystyrene Macromer

Ryuzo Asami,* Mikio Takaki, and Hiroyuki Hanahata

Department of Synthetic Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan. *Received July 14, 1982*

ABSTRACT: In order to prepare a polystyrene macromer composed of only hydrocarbon, (*p*-vinylbenzyl)polystyrene macromer, the direct coupling reaction of polystyryllithium with an excess of *p*-vinylbenzyl chloride was carried out under various reaction conditions. The effect of solvent on the reaction was pronounced. When a solution of PSt-Li in a mixed solvent of benzene and THF (THF, ca. 20 vol %) was added dropwise to a solution of *p*-vinylbenzyl chloride in THF at 0 °C, the yield of the macromer was approximately 100% whereas when a smaller amount of THF was present in a polystyryllithium solution, the dimeric-terminated polystyryllithium formed to some extent as a byproduct. The characterization of the macromer obtained showed it to have one *p*-vinylbenzyl group per (*p*-vinylbenzyl)polystyrene molecule and an M_w/M_n of 1.0_5.

Introduction

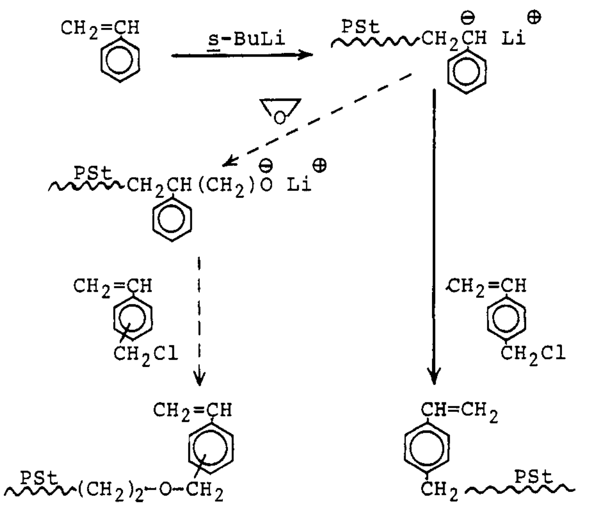
Since 1974, when Milkovich and Chiang[1] demonstrated the syntheses and applications of a variety of macromolecular monomers, which they called macromers, many reports have been published concerning the synthesis and/or application of this chemistry. Their concept has become a subject of growing importance.

Two methods have been used so far for the synthesis of polystyrene macromers. Milkovich and Chiang[1] prepared various vinyl types of polystyrene macromers by means of living polystyrene. On the other hand, recently Yamashita et al.[2] obtained polystyrene having a methacrylic group at a chain end by using the chain-transfer reaction in the radical polymerization of styrene.

In Milkovich's method for the synthesis of the polystyrene macromer, the living end of polystyrene prepared by anionic polymerization was first converted to an alcoholate end by reaction with ethylene oxide and then the intermediate was reacted with vinylbenzyl chloride, in order to exclude the reaction of the vinyl group of vinylbenzyl chloride with an original polystyryl living end. Therefore, the polystyrene macromer obtained by this method has an ether linkage between the vinylbenzyl and polystyrylethyl groups.

In the present study we prepared (*p*-vinylbenzyl)polystyrene containing no ether linkage by the direct reaction of living polystyrene with *p*-vinylbenzyl chloride. That is, polystyryllithium prepared by the polymerization of styrene with *sec*-butyllithium was reacted with an excess of *p*-vinylbenzyl chloride, thus skipping the reaction with ethylene oxide that Milkovich employed. The whole reaction is shown in Scheme I. Although it was considered that carbanions of the living polymer could react with both the double bond and the chloromethyl group of *p*-vinylbenzyl chloride, a model reaction[3] of *sec*-butyllithium with *p*-vinylbenzyl chloride suggested that the S_N reaction of carbanions with chloromethyl groups was much faster than the addition reaction of carbanions to the vinyl groups. The present paper describes that in this direct reaction of polystyryllithium with *p*-vinylbenzyl chloride, a polystyryl anion exclusively attacks the chloromethyl group and leaves the vinyl group of *p*-vinylbenzyl chloride unreacted, thus giving the polystyrene macromer quantitatively. The macromer thus obtained is composed of only hydrocarbon and is named as (*p*-vinylbenzyl)polystyrene. This is in contrast to the polystyrene macromer prepared by Milkovich, which would be termed as vinylbenzyl polystyrylethyl ether.

Scheme I



VB-PSt

Experimental Section

Materials. Polystyryllithium (PSt-Li) was prepared by polymerization of styrene with *sec*-butyllithium in benzene or THF. *p*-Vinylbenzyl chloride (*p*-VBC) was synthesized according to one[4] of the known methods. *p*-VBC was stirred with calcium hydride for 30 h and distilled over the drying agent in a high-vacuum system. Reagent grade *p*-methylstyrene was rectified just before its use. Benzene and tetrahydrofuran (THF) used as solvents of PSt-Li and *p*-VBC were purified by the usual methods and distilled in the presence of the sodium–benzophenone complex under high vacuum.

Coupling Reaction. The coupling reaction was performed by the following methods using three types of apparatus as shown in Figure 1. Method A: With apparatus A, a solution of PSt-Li in benzene (at ambient temperature) was added dropwise to a

0024-9297/83/2216-0628$01.50/0 © 1983 American Chemical Society

Table I
Coupling Reaction of PSt-Li with *p*-VBC under Various Reaction Conditions

	PSt-Li soln			*p*-VBC soln			reaction[b]		products		
expt	[LE][a] × 10, mol/L	vol, mL	solvent	[*p*-VBC], mol/L	vol, mL	solvent	[*p*-VBC]/[LE]	meth-od[c] of addition	yield, g	dim[d] PSt, %	VB-PSt, %
1	1.39	107.7	Bz	0.839	16.5	THF	9.25	A	8.64	50	50
2	2.17	5.53	Bz	0.992	1.72	THF	14.3	A	0.64	38	62
3	1.84	94.1	Bz	0.208	125	THF	15.0	A	6.52	23	77
4	2.17	6.26	Bz	0.992	1.93	THF	14.0	B	0.72	13	87
5	2.17	5.10	Bz	0.469	3.35	THF	14.2	B	0.58	7	93
6	1.75	7.90	THF/Bz[e]	0.992	1.94	THF	13.9	C	0.73	0	100
7	1.81	93.4	THF/Bz[f]	0.992	22.1	THF	13.0	C	8.93	0	100
8	4.86	60.6	THF[g]	0.839	22.0	THF	6.27	C'	6.10	0	100

[a] Concentration of living ends. [b] Reaction temperature, 0 °C; time, ca. 10 min. [c] Method of adding a PSt-Li solution to a *p*-VBC solution. [d] Dimeric-terminated PSt-Li. [e] THF = 19.4 vol %. [f] THF = 16.8 vol %. [g] THF = 96 vol %.

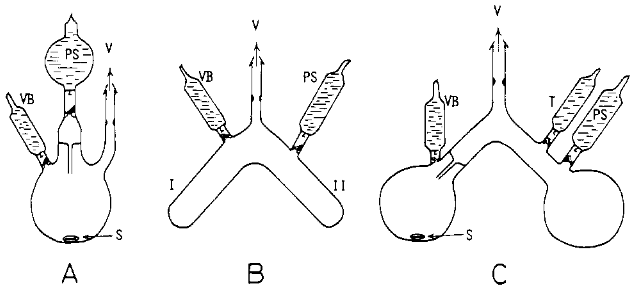


Figure 1. Apparatus for the coupling reaction. A, B, and C, reactors; VB, *p*-VBC solution; PS, PSt-Li solution; T, THF solvent; S, stirrer; V, to vacuum line.

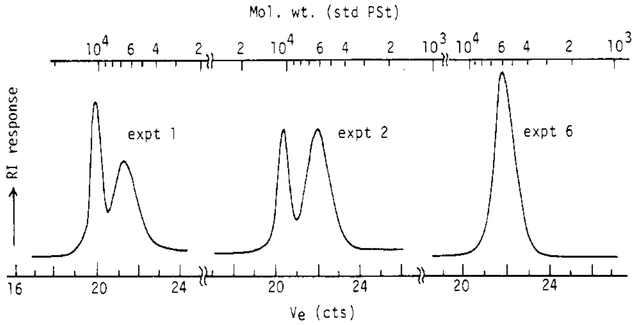


Figure 2. GPC curves of the polymers obtained in experiments 1, 2, and 6.

solution of *p*-VBC in THF (at 0 °C) with stirring. Method B: With apparatus B, the solutions of the reactants were mixed completely in a few seconds by inverting sides I and II of the reactor alternately at 0 °C. Method C: With apparatus C, a solution of PSt-Li in a mixed solvent of benzene and THF was added dropwise to a solution of *p*-VBC in THF with stirring at 0 °C. Also, with apparatus C, a solution of PSt-Li in THF, which was prepared by polymerization of styrene with *sec*-butyllithium in THF (THF/benzene, 96/4 (v/v)), was added dropwise to a solution of *p*-VBC in THF with stirring at 0 °C (method C').

All operations were carried out in a high-vacuum system. Further details of the procedure were the same as described previously.[5]

Measurement and Characterization. Number-average molecular weights were measured with a vapor pressure osmometer (VPO; Hitach Perkin-Elmer 115) in benzene at 40 °C. Gel permeation chromatograms (GPC) were obtained on a Toyo Soda HLC-802UR equipped with two columns (G2000H$_8$ and G3000H$_8$, Toyo Soda), with THF as eluent (1.0 mL/min at 40 °C). Ultraviolet spectra (UV) were recorded on a Hitachi Model 200-20 spectrophotometer by using a quartz cell (path length 0.2 cm) and THF (specially prepared for UV measurement, UVS-82, Nakarai Chemicals Ltd.) as a solvent.

Quantitative analyses of *p*-vinylbenzyl groups of the macromers, i.e., end-group analyses, were carried out by taking advantage of the large difference between the molar extinction coefficient of the model compound *p*-methylstyrene ($\epsilon = 1.64 \times 10^4$ L/(mol·cm) at $\lambda = 250$ nm) and that of polystyrene ($\epsilon = 1.33 \times 10^2$ L/(mol·cm) at $\lambda = 250$ nm). The molecular weight distributions (M_w/M_n) of the polymers were calculated from their GPC traces by using a calibration curve constructed from standard polystyrenes. The yields of VB-PSt and dimeric-terminated PSt-Li were determined from their GPC peak areas (RI detector).

Results and Discussion

Preparation of VB-PSt. We have already reported[6-9] reactions of living polystyrene with pendant chloromethyl groups of polymers to prepare graft polymers and concluded that the extent of coupling reaction of living polystyrene with benzylic halides is dependent upon solvent. When the reaction was carried out in the mixed solvent of hydrocarbon solvent with enough aprotic polar solvent such as THF, the coupling reaction was almost quantitative, whereas when this reaction was carried out in benzene, the coupling reaction involved to some extent the side reaction which formed dimeric-terminated living polystyrene by a one-electron-transfer mechanism.

In this study, therefore, the effect of solvent on the yield of VB-PSt was investigated. Also, since the termination reaction of PSt-Li with chloromethyl groups proceeded instantaneously, it was believed that the method of adding a PSt-Li solution to a *p*-VBC solution affected the yield of VB-PSt. Thus several modes of adding were compared using the apparatus shown in Figure 1.

The results obtained for the reaction of PSt-Li with *p*-VBC under various conditions are listed in Table I. It is unequivocally said that the polystyrene macromer, VB-PSt, can be obtained by direct reaction of PSt-Li with *p*-VBC with yields of 50–100% as long as an excess of *p*-VBC ([*p*-VBC]:[living ends] > 6) was used. The GPC curves of the polymers recorded after the coupling reactions are shown in Figure 2. The curve of the polymer in experiment 6 is unimodal. However, the curves of the polymers in experiments 1 and 2 are bimodal, and these bimodal curves indicate that two kinds of polymers were formed in the reactions. The first peak at lower elution counts is ascribed to polystyrene with just twice the molecular weight of PSt-Li, viz., the dimeric-terminated PSt-Li, which will be abbreviated as "dimer" below. The second peak is ascribed to VB-PSt, as will be demonstrated in the following section. The fact that no peak except those of VB-PSt and the dimer appeared in GPC traces implies that the reaction of PSt-Li with the chloromethyl groups of *p*-VBC is much faster than the addition of polystyryl anions to the vinyl groups of *p*-VBC and that a polymer with a molecular weight higher than that of the dimer did not form.

The effect of solvent on the yield of VB-PSt was shown to be pronounced. In the presence of ca. 20 vol % THF,

Table II
Characterization of VB-PSt Macromer

	mol wt[b] × 10^{-3}				C=C/molecule[c]	M_w/M_n[d]	
expt[a]	$(M_n)_{GPC}$	$(M_w)_{GPC}$	$(M_n)_{VPO}$	$(M_n)_{UV}$	$(M_n)_{VPO}/(M_n)_{UV}$	PSt-Li	VB-PSt
5	5.7	6.0	5.9	6.2	0.9_5	1.0_5	1.0_5
6	5.7	6.0	5.7	5.6	1.0	1.0_5	1.0_5
7	5.6	6.0	6.0	5.7	1.1	1.0_5	1.0_7
8	3.5	4.1	3.8	3.5	1.1	1.1_5	1.1_7

[a] Experimental numbers are the same as in Table I. [b] Determined by GPC, VPO, and UV methods. [c] The number of *p*-vinylbenzyl groups per VB-PSt molecule. [d] Evaluated from GPC data.

in a solution of PSt-Li in benzene, VB-PSt was obtained almost quantitatively (experiments 6 and 7) whereas in the absence of THF in the PSt-Li solution, a considerable amount of the dimer was formed as a byproduct (experiments 1–5). Since the mechanism of the dimeric termination of PSt-Li with *p*-VBC seems basically similar to that[7,8] of living polystyrene with benzylic chloromethyl groups, the extent of formation of the dimer or VB-PSt would be closely related to the solvation of PSt-Li with THF and the dielectric constant of the solvent used. In other words, the high yields of VB-PSt in experiments 6 and 7 may stem from the highly solvated ion pairs or solvent-separated ion pairs, which would preferably attack α-carbons of benzylic chloromethyl groups rather than donate one electron to the halide as described in a previous paper.[7]

The method of adding a PSt-Li solution to a *p*-VBC solution affected the yield of VB-PSt, varying from 50% (experiment 1, method A) to 87% (experiment 4, method B). This also may be ascribed to the solvation of PSt-Li and the dielectric constant of the solvent. That is, in method A, PSt-Li, which associated in benzene in its dimer form, was added dropwise to a *p*-VBC solution in THF; thus PSt-Li would react with *p*-VBC before significant solvation of PSt-Li with THF. In method B, since the two reactant solutions were mixed instantaneously, it seems that the reaction of PSt-Li with *p*-VBC competes with the solvation of PSt-Li with THF in mixed benzene–THF solvent, and the S_N reaction of well-solvated PSt-Li takes place in the mixed solvent.

When a solution of PSt-Li in benzene was added to a solution of *p*-VBC in THF, the lower the concentration of *p*-VBC, the higher was the yield of VB-PSt in both method A and method B (experiments 1 and 3 and experiments 4 and 5). This minor effect of *p*-VBC concentration also may be explained in terms of the solvation of PSt-Li. In the case of the lower concentration of *p*-VBC, an ion pair of PSt-Li which was added to a solution of *p*-VBC in THF would be solvated with THF molecules before it collided with a *p*-VBC molecule. However, in the case of the addition of a solution of PSt-Li in a mixed solvent of benzene and THF (i.e., a well-solvated PSt-Li solution), the high concentration of *p*-VBC and low concentration of PSt-Li would be favorable for the formation of the macromer, because the undesired addition reaction of PSt-Li to VB-PSt which has already formed in the solution may be likely to take place at a low concentration of *p*-VBC and a high concentration of PSt-Li.

In conclusion, the reaction of PSt-Li with *p*-VBC is profoundly affected by the solvent used, and VB-PSt macromer can be prepared quantitatively by using PSt-Li well solvated with THF and an excess of *p*-VBC.

Characterization of VB-PSt. The UV spectrum of VB-PSt is shown in Figure 3, together with the UV spectra of polystyrene and *p*-methylstyrene for reference. It is found that the UV spectrum of VB-PSt has a λ_{max} at 259 nm in THF and is similar to a resultant spectrum of those of polystyrene and *p*-methylstyrene.

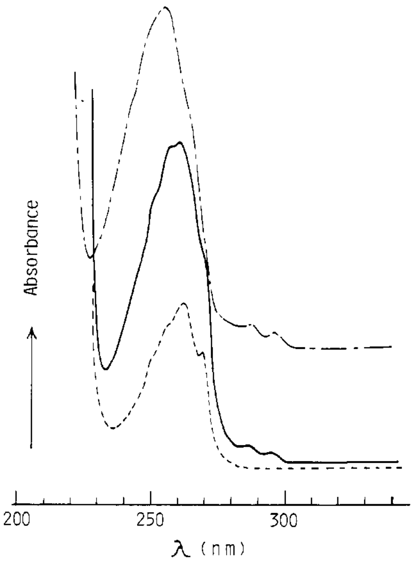


Figure 3. UV spectra of polystyrene (- - -), VB-PSt (—), and *p*-methylstyrene (–·–) as a model compound.

The ratio of number-average molecular weight by VPO to that by UV (end-group analysis), $(M_n)_{VPO}/(M_n)_{UV}$, is taken to indicate the number of *p*-vinylbenzyl groups per VB-PSt molecule. As shown in Table II, the values of $(M_n)_{VPO}/(M_n)_{UV}$ in experiments 5–8 are regarded as unity within experimental error. Thus it can be concluded that VB-PSt obtained by the direct coupling reaction under the conditions described above is highly pure polystyrene macromer.

The molecular weight distributions (M_w/M_n) of the VB-PSt macromers in experiments 5–7 were as low as that of the original PSt-Li. This fact suggests that a side reaction such as polymerization of VB-PSt did not occur in the course of the coupling reaction.

The chlorine contents in VB-PSt macromers (experiments 7 and 8) were determined by a method involving reaction of these samples with sodium–naphthalene and establishing the number of chloride ions released. The results of the chlorine analyses indicated that the number of chloromethyl groups per VB-PSt molecule in experiments 7 and 8 were 0 and 0.02, respectively. This finding confirms the reaction of polystyryl anions with the vinyl groups of *p*-VBC to be negligible.

The radical polymerizability of VB-PSt was tested under the following polymerization conditions: VB-PSt, 161 mg; AIBN, 1.57 mg; benzene, 510 mg; temperature 60 °C; time, 24 h. VB-PSt was converted to poly(VB-PSt) at 53% and the degree of polymerization of poly(VB-PSt) was estimated to be 3.4 from the GPC curve. On the other hand, VB-PSt was copolymerized almost quantitatively with styrene by AIBN at 60 °C (24 h) and was polymerized by *sec*-butyllithium in benzene at a conversion as high as 98%. Details on these radical and anionic homo- and copolymerizations will be published in the near future.

Registry No. PSt-Li, 36345-04-7; *p*-VBC, 1592-20-7.

References and Notes

(1) Milkovich, R.; Chiang, M. T. U.S. Pat. 3 842 050 (1974) and other patents.

(2) Yamashita, Y.; Ito, K.; Mizuno, H.; Okada, K. *Polym. J.* **1982**, *14*, 255.

(3) Asami, R.; Tanaka, Y.; Takaki, M., to be published.

(4) Miyake, T.; Tanimoto, S. *Yuki Gosei Kagaku Kyokai Shi* **1973**, *31*, 1050.

(5) Takaki, M.; Asami, R.; Mizuno, M. *Macromolecules* **1977**, *10*, 845.

(6) Takaki, M.; Asami, R.; Ichikawa, M. *Macromolecules* **1977**, *10*, 850.

(7) Takaki, M.; Asami, R.; Kuwata, Y. *Macromolecules* **1979**, *12*, 378.

(8) Takaki, M.; Asami, R.; Inukai, H.; Inenaga, T. *Macromolecules* **1979**, *12*, 383.

(9) Takaki, M.; Asami, R.; Kuwata, Y. *Polym. J.* **1979**, *11*, 425.

Adsorption of Polystyrene onto a Metal Surface in Good Solvent Conditions

Masami Kawaguchi,* Kazuhisa Hayakawa, and Akira Takahashi

Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan.

Received February 9, 1982

ABSTRACT: The adsorption of linear polystyrene from carbon tetrachloride and toluene solutions onto a chrome plate at 35 °C was studied by ellipsometry. The adsorbance is lower than that in the Θ solvent (cyclohexane, 35 °C) and the thickness of the adsorbed layer is larger than that in the Θ solvent. In particular, the dependence of molecular weight on the measured quantities of both adsorbance and thickness of the adsorbed layer in the plateau region was studied. In both solvents, the adsorbance is almost independent of the molecular weight and the thickness is approximately proportional to the square root of the molecular weight. As a result, the average polymer concentration in the adsorbed polymer layer varies in inverse proportion to the square root of the molecular weight. The results are compared with the theories of Silberberg and Scheutjens and Fleer. The molecular weight dependence of the adsorbance is in agreement with both theories but the molecular weight dependence of the thickness of the adsorbed layer is interpreted supposing that the dangling tails in adsorbed chains predominantly determine the thickness of the adsorbed layer as predicted by Scheutjens and Fleer. It is concluded that the thickness of the adsorbed polystyrene layer onto the chrome surface is governed by tails.

Adsorption of polymers on an interface plays an essential role in a diversity of practical problems in industry, technology, and biology, including adhesion, flocculation and stabilization of colloid particles, chromatography, reinforcement, and artificial organs in medicine. In these cases not only the adsorbance but also the conformation of adsorbed polymer on an interface is of considerable importance. Various efforts have been devoted to clarify the conformation of adsorbed polymer chains.[1-24] For the conformation of flexible polymer chain adsorbed on an interface, it is now widely accepted that some portions of the polymer chain come into direct contact with the interface as trains, with remaining portions extending into the bulk solution as loops and/or tails, which lead to a thick adsorbed layer.

In a previous paper,[22] adsorption of polystyrene onto a chrome plate from cyclohexane at the Θ temperature was studied by ellipsometry. It was shown that the conformation of polystyrene is the loop–train–tail, and predominant contribution of tails to the thickness of the adsorbed layer was indicated.

In good solvent conditions, one intuitively expects the thickness of the adsorbed layer to be greater than that in Θ solvents due to interactions between loops or tails caused by the excluded-volume effect. The adsorbance should be smaller than that in Θ solvents since the occupied area per polymer chain on the interface will increase with solvent power.

In another paper,[23] we studied the adsorption of polystyrene on a chrome plate from cyclohexane solution at 40 and 45 °C by ellipsometry and showed that the adsorbance slightly decreases and the thickness of the adsorbed layer slightly increases with increasing temperature. The adsorbance was nearly constant, independent of the molecular weight, and the thickness of the adsorbed layer was approximately proportional to the square root of the molecular weight at both temperatures.

Several theoretical studies of the effect of solvent power on polymer adsorption have been reported.[2,3,10,14,16-20] Although theories predicted that the adsorbance decreases with increasing solvent power, in some theoretical predictions[2,10] particularly based on the loop–train model, it was concluded that the thickness due to loops in good solvents is smaller than that in Θ solvents, since in good solvents more segments are forced to contact the surface.

To clarify the solvent power dependence of the adsorbed polymer layer, we use in this study toluene and carbon tetrachloride as solvents. Since they are better solvents than cyclohexane at 40 and 45 °C for polystyrene, we may expect in these good solvents more pronounced differences in the thickness of the adsorbed layer and the adsorbance compared with the data in cyclohexane.[23] The aim of this paper is to offer experimental results for the adsorption of homodisperse polystyrene onto chrome plates from toluene and carbon tetrachloride since data for such well-defined systems are rare but are needed to compare with theoretical predictions. Measurements of polystyrene adsorption were carried out by ellipsometry at 35 °C. The dependences of molecular weight and solvent power on the thickness of the adsorbed layer, the adsorbance, and the average polymer concentration in the adsorbed layer are examined and discussed in light of relevant theories.

Experimental Section

Materials. Linear polystyrene samples having a narrow molecular weight distribution were supplied from Pressure Chemical

0024-9297/83/2216-0631$01.50/0