Adsorption of Poly(methyl methacrylate) from Dilute Solution by Silica and Silicic Acid

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ABSTRACT: Isotherms were measured for the adsorption of isotactic and conventional poly(methyl methacrylate) fractions from dilute solutions of various solvents by finely divided silica and silicic acid. The adsorbents were characterized by nitrogen adsorption (BET) and electron microscopy. The level of surface coverage in the pseudo-plateau of the silica adsorptions, 0.03 and 0.015 μg/cm^2 for adsorption from toluene and 1,2-dichloroethane, suggested that the chains were adsorbed in flattened configurations with possibly as many as 50% of the segments contacting the surface. Little or no adsorption took place from solvents capable of hydrogen bonding with the surface. Tacticity had little or no effect on adsorption from toluene or 1,2-dichloroethane; however, isotactic polymer was adsorbed by silica from acetonitrile whereas conventional polymer was not. An observed increase in adsorption of conventional polymer from carbon tetrachloride by silicic acid with decreasing molecular weight was interpreted as being due to the known porosity of the adsorbent. Although an observed increase in adsorption level with increasing temperature for the same system is in agreement with theory at the observed level of adsorption, this effect could also have been due to temperature dependence of the rate of diffusion of chain molecules into the pores.

Adsorption of macromolecules is still not adequately understood in spite of numerous experimental and theoretical studies. Progress in this field has been slowed by a lack of experimental data on the adsorption of polymer of sufficiently narrow molecular weight distribution and varying tacticity by well-characterized surfaces. In this paper we present the results of adsorption of fractions of conventional and isotactic poly(methyl methacrylate) by finely divided silica and silicic acid that have been characterized by electron microscopy and nitrogen adsorption.

Experimental Section

Materials. The poly(methyl methacrylate), hereinafter designated as PMMA, used in this study was obtained through the courtesy of the Rohm & Haas Research Laboratories. All the conventional samples were prepared by a special low conversion free radical polymerization. It is appropriate to term these polymers conventional rather than atactic because the polymerization leads to a stereo sequence distribution dominated by short syndiotactic sequencies.[1–3] The sample CI was separated into six fractions by careful temperature controlled precipitation from dilute acetone solution using a 50% acetone–water mixture as a nonsolvent. Sample CII was similarly fractionated into 13 fractions from dilute benzene solution using cyclohexane as a nonsolvent. All of the fractions were dissolved in benzene, passed through a fritted glass filter, and freeze-dried. The viscosity-average molecular weights of the fractions were then determined from intrinsic viscosity measurements in benzene at 25° using the relationship[4]

$$[\eta] = 5.7 \times 10^{-5} M^{0.76}$$

Number-average molecular weights were determined for two of the CII fractions from osmotic pressure measurement; it appears that the fractionations were efficient enough for the purposes of this research, since the number-average molecular weights agreed closely with those determined from intrinsic viscosities.

The isotactic polymer was prepared using 9-fluorenyllithium initiater[1] and was fractionated at room temperature from dilute benzene solution using *n*-hexane as nonsolvent. Viscosity average molecular weights were determined using the same relationship as was used for the conventional fractions, and number-average molecular weights were determined by osmotic pressure. Molecular weights for all of the polymer fractions used in this study are given in Table I.

Fisher reagent grade silica and Merck reagent grade silicic acid were used as adsorbents for all experiments in this study. They were washed repeatedly with fluxing reagent grade acetone, dried in a vacuum oven at 150° for 48 hr, and stored and handled in an atmosphere of dry nitrogen. Electron micrographs were taken of the adsorbent particles at magnifications from 4000 to 45,000. The silica particles were of irregular shapes with an average "diameter" of 6×10^3 Å, and they were nonporous to within the resolution of the microscope (which was ±200 Å in this work). The silicic acid particles were also of irregular shapes, but with an average approximate "diameter" of 1.2×10^5 Å. Unlike the silica, however, the silicic acid was highly porous with pore diameters of 2×10^3 Å and less. Table II shows specific surface areas by the BET method (nitrogen adsorption) and calculated from the electron micrographic determination of particle size (assuming the particles to be spheres). Clearly, most of the surface area of the silicic acid was internal, whereas nearly all of the surface of the silica was external.

Fisher Certified Reagent carbon tetrachloride was used for PMMA adsorption onto silicic acid. It was dried over Drierite and then over phosphorus pentoxide and distilled through a 3-ft column of 1-mm glass beads. The center cut, about two-thirds of the total, was collected and stored over dry nitrogen. Solvents for the series of adsorption measurements using silica were Fisher purified grade 1,2-dichloroethane and Baker reagent grade toluene, acetone, and acetonitrile. The 1,2-dichloroethane and acetonitrile were dried over $CaCl_2$ and distilled through a 50-cm column packed with glass helices. Center cuts (70%) were treated with P_2O_5 and redistilled through a Stedman column rated at about 125 theoretical plates. The same column was used in a single distillation of toluene over sodium. The acetone was used without any further purification.

Adsorption Measurements. Between 2 and 6 g of silica or silicic acid were weighed to the nearest milligram into carefully cleaned and dried 20-cm test tubes which had constricted necks for subsequent sealing. In the experiments using silica, these operations were performed inside a glove box in a dry nitrogen atmosphere. Immediately before each experiment the adsorbent in the glass tubes was heated at 150° under vacuum for 4 hr and then cooled in a dry nitrogen atmosphere. Polymer solutions of known concentra-

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Table I
Polymer Molecular Weights

Polymer fraction	$M_v \times 10^{-3}$	$M_n \times 10^{-3}$
CI-2	520	
CI-4	230	
CI-5	110	
CII-2	638	
CII-8	231	
CII-10	115	113
CII-11	77.2	70.0
CII-12	31.2	
I-2	2960	510
I-11	50.7	26.0
I-12	40.6	20.0
I-13	31.8	15.0

Table II
Adsorbent Characterization

	Silica	Silicic acid
Average diameter, Å	6×10^3	1.2×10^6
Specific surface area by electron microscopy, m²/g	2	0.1
Specific surface area by nitrogen adsorption, m²/g	3	190

tion were then added to the tubes. To establish the quantities of solutions added, the tubes were weighed to the nearest milligram before and after each addition. The loaded tubes were quickly frozen in liquid nitrogen and were sealed off under vacuum. Following a warm-up period of 30 min at 25°, the tubes were shaken vigorously and placed on a tumbler which rotated them coaxially at about 20 rpm for 48 hr in a water bath. The temperature of the bath was controlled to within ±0.03°. All measurements were made at 25°, except when indicated otherwise. Sonntag and Jenckel[5] reported that vigorous agitation in the presence of adsorbents could lead to the degradation of PMMA. But in these present studies the agitation rates and the amounts of adsorbents used were significantly lower than those used by Sonntag and Jenckel. Since Felter and Ray[6] report no degradation under conditions similar to those used in this work we expected no problem with degradation. After completion of the adsorption period, the adsorbents were separated from the solutions by overnight sedimentation in the bath; the small amount of adsorbent that possibly remained suspended was removed by pressure filtration in the silicic acid experiments and by centrifuging in the silica experiments. Polymer concentrations were determined by evaporating aliquot weights of the solutions in aluminum pans and weighing the residues to a precision of ±0.02 mg. The polymer films in the dishes were vacuum dried at 95° for 15 hr before weighing. Experiments with solutions of known concentrations, treated the same way as the adsorbate solution, indicated that the accuracy of this concentration determination technique was better than ±1% of the reported concentration for the higher, and ±2–6% of the reported concentration for the lower concentration regions (*i.e.*, below 0.1 mg/g). From these measurements, the amount of polymer present in solution before and after adsorption was determined and the specific adsorptions, q, in milligrams of adsorbed polymer per gram of adsorbent, were calculated. For one very low equilibrium concentration experiment an alternate method was used that made it possible to measure concentrations down to 10^{-4} mg/g with an average accuracy of ±10%. In this technique, several (10–16) adsorption tubes were loaded for each fixed concentration at a constant ratio of adsorbant weight to solution volume. After the usual equilibration and separation procedures (discussed above), the adsorbate solutions were collected from all the tubes at the same initial polymer concentration and evaporated in small increments in a single aluminum pan. To eliminate errors due to the large volume of solvent evaporated (up to 400 ml), the dry residue of the solvent was separately determined and used as a correction factor. The total weights of the recovered polymers in these experiments ranged from 0.1 to 10 mg.

Equilibrium Time Studies. The following experiment was carried out to estimate the time required to reach adsorption equilibrium in the experiments with silica. Several test tubes were loaded with equal amounts of adsorbent and with equal weights of polymer solutions of equal concentration. The quantity of adsorbed polymer was determined after agitating the tubes for various times from 0.5 to 240 hr. The amount of polymer adsorbed in each case was the same, indicating that equilibrium had been attained in less than 0.5 hr. The short equilibration time appears to be in agreement with adsorption studies reported in the literature when noncarbonaceous and nonporous adsorbents were used.[7–14] Adsorption by silicic acid appeared complete after 48 hr of agitation.

Adsorption Reversibility. Conventional PMMA (fraction CII-10) was adsorbed from 1,2-dichloroethane solution onto silica under conditions very similar to those used in the isotherm studies. After centrifuging and separating the solution, the adsorbent was extracted five times, with 12 hr of agitation per extraction, with 1,2-dichloroethane. Analysis of the solutions withdrawn after each extraction indicated that only very small amounts of polymer had been removed. One subsequent extraction with acetonitrile, however, removed all the adsorbed polymer. Thus there had been no irreversible attachments formed between PMMA and silica, and thermodynamic equilibrium could, at least in principle, be established in this system. The ineffectiveness of the extraction is easily explained on the basis of an isotherm with an incredibly steep initial slope. Just such isotherms have been recently predicted by theory;[15–17] indeed with sufficiently strong segment–surface interaction, theory predicts the initial portion of the isotherm to be experimentally inaccessible.

Results and Discussion

Isotherms. As can be seen in Figures 1–6, the initial portions of all the isotherms reported here were experimentally inaccessible. This is predicted[15–17] theoretically for even modest segment–surface interactions—say greater than 0.2 kcal/mol. So considering the polymer–surface interactions expected in these experiments, this experimental observation is not surprising.

Except for Figure 5, the only other interesting feature of the isotherms are the pseudo-plateau adsorption levels (we prefer the term pseudo-plateau, since for most of the results reported here, adsorption continued to increase very slowly with concentration in those regions of the isotherms which at first inspection would be considered as plateaus). Since the silica particles presented effectively flat surfaces for polymer adsorption, we can estimate the specific surface coverage in this region. Using the BET surface area (which is essentially the same as that determined by electron microscopy), we

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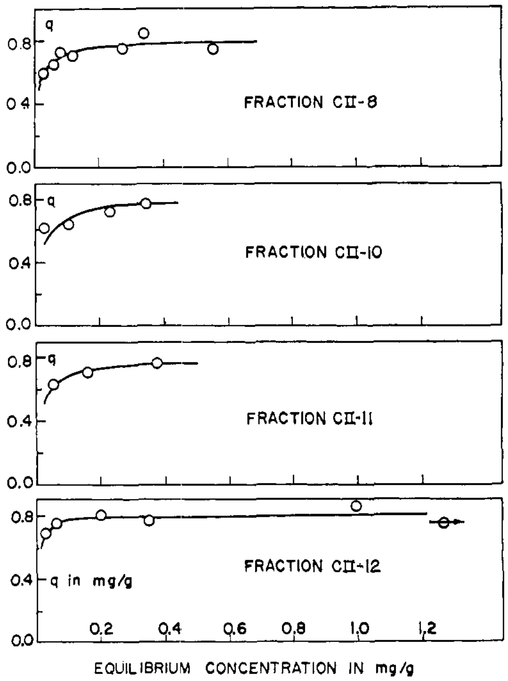

Figure 1. Adsorption of conventional fractions from toluene by silica at 25°.

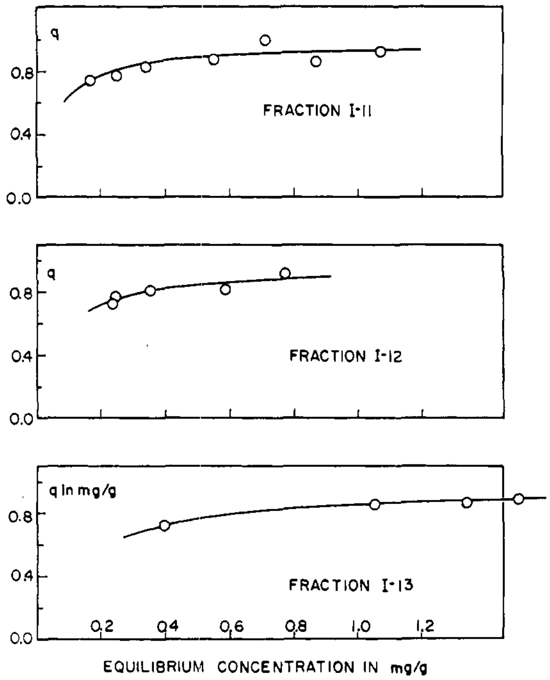

Figure 2. Adsorption of isotactic fractions from toluene by silica at 26°.

estimated surface coverages of 0.03 μg/cm^2 for adsorption from toluene and 0.015 μg/cm^2 from 1,2-dichloroethane. These values are in good agreement with recent infrared measurements by Thies[18] of the adsorption of PMMA by Cab-O-Sil M-5, a very high specific surface area (but nonporous) adsorbent. Based on a reported BET surface area of 175–200 m^2/g, he determined an adsorption level of about 0.08 μg/cm^2 and estimated that 35% of the segments were interacting with the surface. The above results are surprisingly similar to those observed in the adsorption of

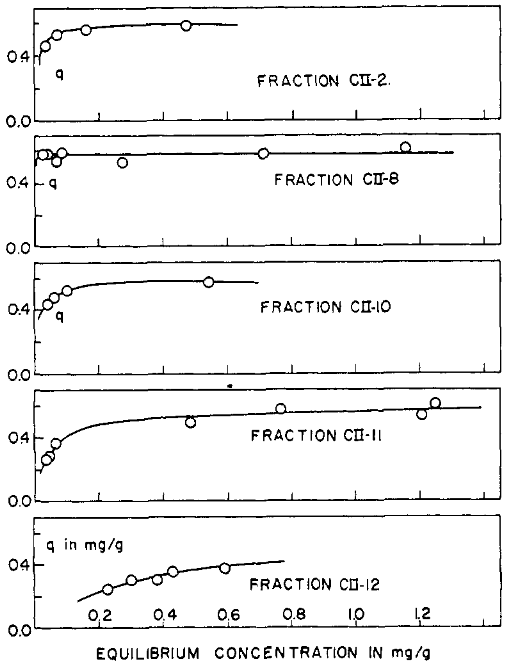

Figure 3. Adsorption of conventional fractions from 1,2-dichloroethane by silica at 25°.

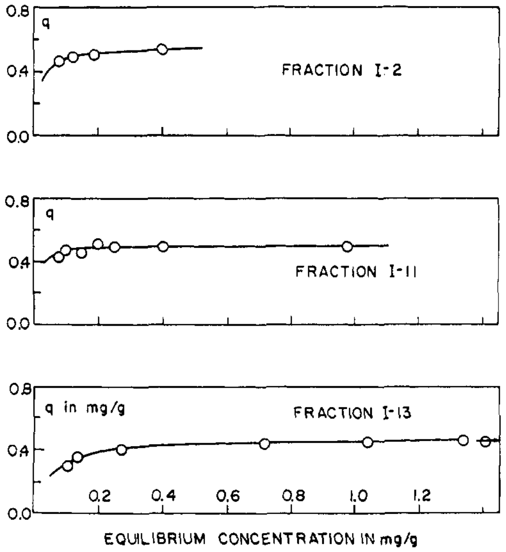

Figure 4. Adsorption of isotactic fractions from 1,2-dichloroethane by silica at 25°.

poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) (PDMVPMS) from water solutions onto finely divided silica and aluminum foils. Shyluk[19] determined a coverage of 0.05 μg/cm^2 in the water–silica system and estimated (by ion exchanged methods) that about 60% of the pyridinium groups were absorbed at the surface. Grills[20] found a coverage of about 0.03 μg/cm^2 in the adsorption of the same polymer by aluminum foils over the entire equilibrium concentration range between 0.1 and 100 ppm polymer. We know that the ionic polymer–surface interactions are strong in the PDMVPMS–silica system;[19] since the levels of adsorption are about the same, we can conclude that the PDMVPMS–aluminum interactions are equally as effective. If we can extend our argument to the PMMA–silica system, we conclude that the

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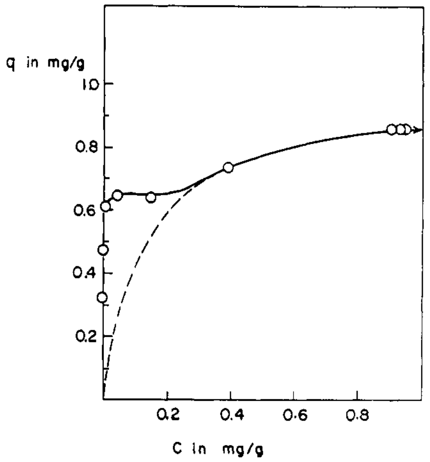

Figure 5. Adsorption of fraction I-13 from extremely dilute toluene solutions by silica. The dashed line represents extrapolation of the Langmuir isotherm predicted by the data for $C > 0.2$ mg/g.

hydrogen bonds between the silica hydroxyls and the polymer carbonyls, which could be several kilocalories per mole, are also strong enough to effect a collapse of the polymer coils onto the surface, yielding a nearly equivalent coverage.

We should also add that similar levels of adsorption have been reported by Felter and Ray[6] (0.05 μg/cm^2) in their study of the adsorption of poly(vinyl chloride) by calcium carbonate from monochlorobenzene. This result is somewhat suprising since one might expect polymer–surface interaction energies to be substantially lower in this system.

The level of adsorption in the systems described above are in agreement with the following theoretical expression[21] which was derived for sufficiently strong segment–surface interactions.

$$\text{pseudo-plateau coverage} = \pi\delta/2\bar{v}$$

The parameter δ is the mean interaction distance (potential well) for segment–surface interaction and $\bar{v}$ is the specific volume of the polymer. The above expression was found to be associated with a volume fraction of polymer near unity at the surface, but which falls off rapidly in the direction normal to the surface, and with about 50% of the segments interacting with the surface. If we let $\delta = 2 \times 10^{-8}$ cm and $\bar{v} = 1.0$ cm^3/g, theory predicts a coverage of about 0.03 μg/cm^2, which is in good agreement with the experimental values reported above. We conclude that the adsorption of PMMA by silica from dilute toluene solutions is consistent with a picture of considerably flattened polymer chains with the order of 50% of the segments interacting with the surface.

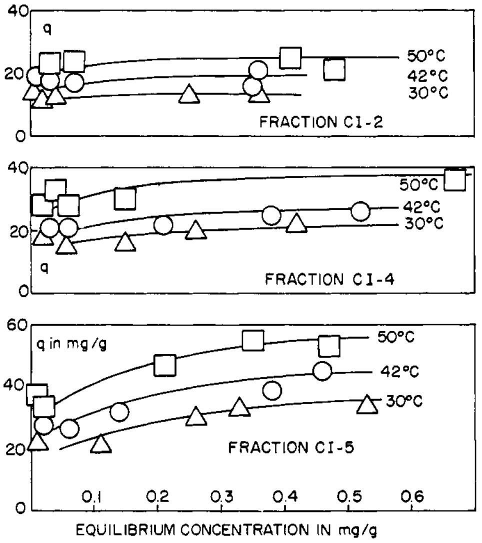

Figure 6. Adsorption of conventional fractions from carbon tetrachloride by silicic acid at various temperatures.

The porosity of the silicic acid makes it impossible to determine the surface coverage in this case. But if a formal coverage were calculated based on BET surface area, it would be anomalously low, such as the results reported by Frisch, *et al.*[22] (0.003 μg/cm^2), in their study of the adsorption of polystyrene from toluene solutions by high-surface-area carbon. Nevertheless, since the surface–segment interactions would be even greater than with silica, undoubtedly the PMMA chains are at least as flattened when adsorbed by silicic acid as when adsorbed by silica.

Adsorption levels reported here are far smaller than those for polystyrene reported by Sparks,[23] who studied adsorption by aluminum foils from dilute benzene solutions (2.0 μg/cm^2), by Stromberg, *et al.*,[24] who studied adsorption by metal oxide surfaces from dilute cyclohexane solutions (about 0.8 μg/cm^3), and by Rowland,[25] who studied adsorption by finely divided silica from benzene solutions (0.8 μg/cm^3). We conclude that the relatively nonpolar polystyrene demonstrates far weaker segment–substrate interactions than the systems discussed previously. Each polymer molecule would thus be adsorbed at only a few segments with the rest of the chain distributed in an interface phase of dimensions normal to the surface approximately equal to that of the unperturbed chains in solution. Indeed these levels of adsorption are associated with film thicknesses found experimentally by Stromberg, *et al.*,[25–27] and Rowland,[25] and also predicted theoretically.[15–17]

Surface coverage reported here is also substantially lower than that reported by Ellerstein and Ullman[10] in their studies of the dilute solution adsorption of atactic PMMA by finely divided glass and iron. Using their reported surface areas, we estimate pseudo-plateau levels of 0.2 and 0.6 μg/cm^2 for iron and glass, respectively. These values are more nearly like those reported for the polystyrene experiments described above, and are apparently associated with considerably weaker segment–surface interactions than in adsorption of PMMA by silica.

Figure 5 shows an interesting effect. Although we were still not able to resolve the initial portion of the isotherm by extending measurements to extremely dilute solutions (as is described in the Experimental Section), the results yielded an isotherm that is indicative of two-layer adsorption. It nevertheless seems premature to suggest that two-layer adsorption is the final explanation until more very careful adsorption studies have been made in extremely dilute solution.

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Effects of Solvent and Stereoregularity. The solvents used in adsorption of PMMA by silica can be ranked according to decreasing solvent power as follows:[17] (1) 1,2-dichloroethane, (2) toluene, (3) acetone, (4) acetonitrile.

Examination of the isotherms in Figures 1–4 indicates that more of both isotactic and conventional polymer is adsorbed from toluene than 1,2-dichloroethane. This would be expected in the case of constant (or nearly constant) surface–solvent interactions. But the trend is not consistent, however, since conventional PMMA demonstrated "negative" adsorption[28] from both acetonitrile and acetone. This same effect was observed in attempts to measure adsorption of conventional PMMA by silicic acid from 2-butanone solutions. Clearly, as is predicted by theory,[21] it is the combined effect of polymer–surface, surface–solvent, and polymer–solvent interactions that is effective in determining polymer adsorption, and solvent power alone gives no reliable criterion of level of adsorption. Studies by Fontana and Thomas[29] indicate that hydrogen bonding plays an important role in adsorption of poly(*n*-lauryl acrylate) by silica. They suggest that the hydroxyl groups at the silica surface bonded to the carbonyl groups of polymer. One must simply conclude, in the studies reported here, that the silica forms stronger hydrogen bonds with both acetone and acetonitrile than with PMMA.

Figures 1, 2, 3, and 4 indicate that tacticity has little or no effect on adsorption from toluene and 1,2-dichloroethane. Although the results suggest that isotactic polymer adsorbs slightly more from the first solvent, and atactic more from the second, these conclusions are wholly speculative since the difference could be accounted for by experimental error.

It is most intriguing, however, that while negative adsorption is demonstrated by conventional PMMA in the acetonitrile–silica system, isotactic polymer is slightly adsorbed ($q = 0.01$ mg/g at $C = 1.0$ mg/g). Apparently the additional energy effects due to the ability of isotactic chains to take on low-energy configurations in the interface phase is sufficient to reverse the equilibrium in favor of adsorption. This tactic selectivity suggests that appropriate adsorption systems could be designed to effect fractionation by tacticity.

Substrate Morphology and Temperature Effect. In the previous discussion, we argued that the adsorption isotherms presented here are typical of those associated with high segment–surface interactions. Theoretical work by two of us[21] and others[30] indicates that for such adsorption conditions there would be little or no molecular weight dependence of the pseudo-plateau of the isotherms. Figures 1–4 which show adsorption of both types of polymer by silica do indeed show no molecular weight dependence. Figure 6, on the other hand, shows an increasing level of adsorption with decreasing molecular weight. This is as would be expected. The silicic acid, in contrast to the silica, was shown to have a tremendous internal surface area with an associated distribution of pore sizes. The amount of available adsorption surface would thus decrease with increasing molecular weight. Similar results have been reported in polymer adsorption studies using porous adsorbents.[31–35] Indeed these results suggest that polymer absorption could be used as a probe in studying distribution of pore sizes.

Figure 6 shows that adsorption in the PMMA–toluene–silicic acid system increases with increasing temperature. This effect is predicted by theory[21] for systems with segment–surface interactions that are strong enough to affect adsorption of a significant fraction (say at least 25%) of the polymer segments. Theory predicts that increasing the temperature weakens segment–surface interactions and allows the polymer chains to expand in the direction normal to the adsorbing surface. This chain expansion would then free adsorption sights and allow additional polymer molecules to be accommodated at the surface. Ellerstein and Ullman[11] observed a slight decrease in adsorption of PMMA by powdered glass and iron with increasing temperature. But theory[21] also indicates that with continued increase in temperature the effect would be reversed and that adsorption would decrease with increasing temperature. Gajnos[36] did indeed observe such a maximum in the pseudo-plateau adsorption level in measurements of the adsorption of poly(isopropyl acrylate) by silica from dilute 1,2-dichloroethane solutions.

We must exercise caution, however, in drawing conclusions from our observed temperature effects. There is always the question of whether or not the adsorbing systems were at thermodynamic equilibrium. It is also possible that the effect reported here was due to temperature dependence of the rate of diffusion of the chain molecules into the pores of the silicic acid particles. Indeed, although both positive and negative temperature coefficients of adsorption have been reported, we can safely conclude that most of the systems were not well enough characterized to allow one to draw any universally valid conclusions about the effect of temperature on polymer adsorption.

Conclusions

We should like to conclude with some suggestions concerning the nature of polymer adsorption. There is experimental and theoretical evidence that two extremes in behavior can be identified. With sufficiently high polymer–segment interaction polymer chains are adsorbed in considerably flattened configurations with, for example, between one-half and one-quarter of their segments interacting with the surface. This level of surface–segment interaction is associated with a specific surface coverage in the pseudo-plateau in the general range of 0.02–0.08 μg/cm.^{2}

At lower surface–segment interaction energies, the energy effects are insufficient to overcome unfavorable polymer–polymer interactions and the loss in configurational entropy that accompanies flattening of the chains. Under these conditions, adsorbed polymer molecules will be only slightly flattened. Since they are in highly extended configurations, far more polymer is accommodated at the surface and specific coverages are in the general range of 0.5–2.0 μg/cm^2 and higher. This apparent paradox—that higher surface coverage is associated with lower polymer–surface interaction energies—is thus resolved when all energy and entropy effects are considered.

Nevertheless, it is still true that somewhere at the low-

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(28) By "negative" adsorption, we imply an observed increase in polymer concentration when the solution is contacted with adsorbent. This is thermodynamically equivalent to preferential solvent adsorption. But since unfavorable segment–surface interactions prevent the centers of mass of polymer molecules from approaching the surface closer than about their root-mean-square radius of gyration, the effect is far more noticeable than in small molecule systems.

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energy end of the domain of weaker surface–segment interactions adsorption must increase with increasing energy. This is obviously true, since for sufficiently weak interactions adsorption will not take place. Experimental evidence therefore indicates that, with all other factors the same, there is a surface–segment interaction energy which willl give a maximum adsorption. Since changing temperature changes the effective surface–segment interaction, the above argument may explain the conflicting reports of the temperature dependence of polymer adsorption. In general, however, it is very nearly impossible to change surface–segment interactions without changing the whole array of parameters that effect polymer adsorption, so it is not surprising that, except for the one case cited,[36] such an adsorption maximum has never been observed.

Acknowledgments. This work was supported in part by the Advanced Research Projects Agency of the Department of Defense. We are indebted to the Rohm and Haas Co. for PMMA samples and for doing the BET measurements on the adsorbents.

X-Ray Diffraction Studies of the Relaxation of Ethylene–Methacrylic Acid Copolymers and Their Salts[1a]

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ABSTRACT: The degrees of crystallinity and crystal orientation of quenched and annealed ethylene–methacrylic acid copolymers and their salts are studied by X-ray diffraction. The degrees of crystallinity of the annealed acid and salt are comparable with those of branched polyethylene but the crystallinity of the quenched acid is reduced by about half. Orientation functions for crystal axes have been determined as a function of the temperature of elongation and are used to calculate the crystalline component of birefringence. It is found that crystalline orientation makes an appreciable contribution to the birefringence. The change in orientation function with elongation varies with temperature in a very different manner for the acid and the salt, suggesting different orientation mechanisms for the two. At a temperature corresponding to the α mechanical dispersion, a marked increase is seen in the amorphous orientability of the salt, whereas no such increase is found for the acid. This suggests that a process occurs within the amorphous phase of the salt at this temperature, permitting greater orientation to occur. This is consistent with the assignment of this loss maximum to a softening temperature of a proposed ionic domain.

In a previous publication,[2] the results of birefringence studies of the relaxation processes of ethylene–methacrylic acid copolymers and their salts were presented. The variation of the strain optical coefficient, K, with temperature was determined for the un-ionized acid and the salt. A maximum in K was found at about 40° for the ionized salt but none was found for the un-ionized acid. This maximum occurs at a temperature corresponding to the α mechanical loss peak which has been associated with a glass temperature of a proposed ionic domain.[3] The birefringence maximum was associated with an increase in orientability of the amorphous part of the polymer as the ionic regions soften.

Since the copolymers are partly crystalline, it is likely that the crystallites may contribute significantly to the birefringence. It was a principal objective of the work described here to determine the temperature variation of this crystalline component of the birefringence in order to establish whether the α orientation maximum was of crystalline or amorphous origin.

Experimental Section

The samples studied were derived from the commercial Du Pont ethylene–methacrylic acid copolymer ("Surlyn") and are identical with those used in previous studies.[2,3b-7] The polymer has a weight-average molecular weight of about 300,000, a methacrylic acid content of 4.1 mol %, and around 25 methyl branches/1000 carbon atoms. The acid groups were ionized by a method described previously.[4] Quenched samples (Q) were prepared by molding in a laboratory press at 125° and rapidly cooling under pressure by transferring to a previously cooled laboratory press. The annealed samples (A) were prepared by holding the quenched samples in an oil bath at 94° for 24 hr and then cooling very slowly to room temperature.

Degrees of crystallinity were determined by the method of Mathews[8] using data obtained with a homemade spectrometer.[9] Data were corrected in the usual manner for polarization, absorption, and incoherent scattering. The diffracted intensity was resolved into a contribution from the amorphous scattering and diffraction from the 110 and 200 peaks by trial and error after making the following assumptions.

1. The form of the variation of the amorphous scattering with 2θ is the same over all temperatures of this study.
2. The diffracted intensity at $2\theta = 16.5°$ entirely results from amorphous scattering.
3. The 110 and 200 diffraction peaks are symmetrical in Bragg angle about their diffraction maxima.

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