The Effect of Nonpolymeric Adsorbates on Polymer Adsorption at Solid–Liquid Interfaces

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Received December 1, 1967

ABSTRACT: The influence that low concentrations ($\leq 10\%$ wt/v) of several nonpolymeric additives have on poly(vinyl acetate) (PVAc) and poly(ethylene–vinyl acetate) (EVA) (28.8% vinyl acetate) adsorption has been examined. Experiments were carried out at 24° in trichloroethylene (C_2HCl_3) and cyclohexane (C_6H_{12}) using finely divided silica as the adsorbent. Although methanol, acetonitrile (CH_3CN), cyclohexanol ($C_6H_{11}OH$), 1,8,9-anthracenetriol, and dioxane reduce PVAc adsorbance, significant amounts of PVAc still were adsorbed from C_2HCl_3 in every case examined. This included CH_3CN and $C_6H_{11}OH$ concentrations as high as 5–10%. Infrared bound fraction determinations establish that these additives often reduce the fraction of PVAc carbonyl ester groups bound directly to silica (p), but numerous PVAc surface contacts still exist. For example, 5–10% CH_3CN and $C_6H_{11}OH$ cause p to drop from 0.43 to 0.27–0.32. Unlike PVAc, EVA adsorption is markedly reduced by low concentrations of the above additives in C_2HCl_3 and C_6H_{12}. The effect that several additives have on polymer adsorption tends to parallel their effect on the carbonyl extinction coefficient of both polymers. In such cases this may indicate that polymer–additive interactions in solution influence the interactions at the solid–liquid interface responsible for polymer adsorption. Based on spectroscopic analyses, it has been established that a significant fraction of EVA carbonyl ester groups complex with methanol and $C_6H_{11}OH$ in C_6H_{12}.

The adsorption of polymers from dilute solution at solid–liquid interfaces has been studied extensively in recent years.[1] One factor found to influence such adsorption is the solvent used. For a given polymer, higher adsorbances generally are observed as one goes from good to poor solvents. However, exceptions exist, especially in cases where strong solvent–surface interactions seem to occur and thereby influence polymer–surface interactions. Koral, Ullman, and Eirich[2] found that acetonitrile (CH_3CN) completely inhibits poly(vinyl acetate) (PVAc) adsorption on iron and tin powders having an oxide surface. They postulated that this reflects a specific interaction between the nitrile groups of CH_3CN and the oxide surfaces. Perkel and Ullman[3] observed that water inhibited poly(dimethylsiloxane) (PDS) adsorption onto glass and iron powder having an oxide surface. A 10% CH_3CN and 90% benzene (v/v) mixture reduced PDS adsorption on glass and completely prevented adsorption on iron oxide. Poly(methyl methacrylate) adsorption on iron powder (oxide coated) decreases as the concentration of CH_3CN in benzene increases.[4] Howard and McConnell[5] reported that addition of 1.5% (by volume) dimethylformamide to a solution of poly(ethylene oxide) ($\bar{M}_n$ = 4700) in benzene decreased the latter's specific adsorption on silica approximately 35%. Thus, there is ample evidence that various polar additives can grossly alter the adsorption behavior of a given polymer. Most of the reported observations represent cases where the additive inhibiting polymer adsorption is present in concentrations above 10% (w/v or v/v). Often it is the primary or even sole component of the solvent. How low concentrations of polar additives affect polymer adsorption has not been examined extensively. Accordingly, the present study focused attention on the effect that low (<10% w/v) additive concentrations have on polymer adsorbance and adsorbed structure. The polymers used were PVAc and a poly(ethylene–vinyl acetate) (EVA) copolymer.

Experimental Section

PVAc-1 was prepared by bulk polymerization of freshly distilled vinyl acetate at 25° using azobisisobutyronitrile as initiator. The degree of conversion was low (2.0%) in order to avoid chain branching. The EVA sample (EVA-3) was an experimental polymer obtained through the courtesy of U.S.I. Chemicals Co. (Cincinnati, Ohio) and had a vinyl acetate content of 28.8% as determined by infrared analysis.[6a] Its melt index before reprecipitation (ASTM D 1238) was 2.7 g/10 min.[6b] Both polymers were reprecipitated from benzene into methanol and freeze dried from benzene before use. Number average molecular weights ($\bar{M}_n$) were determined at 37° in toluene using an F & M Model 502 membrane osmometer (F & M Division, Hewlett-Packard Corp., Avondale, Pa.). PVAc-1 had a $\bar{M}_n$ value of 465,000; $\bar{M}_n$ = 37,200 for EVA-3. Both polymers were unfractionated and, hence, polydisperse with regard to molecular weight. Based on the findings of Koral, Ullman, and Eirich,[2] and the high $\bar{M}_n$ value of PVAc-1, such polydispersity is believed to have little effect on its adsorption behavior. This may not be true for EVA-3 due to its lower $\bar{M}_n$, but the lack of prolonged time effects observed for EVA-3 samples suggests that slow adsorption phenomena due to polydispersity effects are not occurring.

The adsorbent was Cab-O-Sil M-5, a finely divided nonporous silica with a reported surface area of approximately 200 m²/g (Cabot Corp., Boston, Mass.). It was dried at 105° for 72 hr and stored in a desiccator until used. The

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(1) J. J. Kipling, "Adsorption from Solutions of Non-electrolytes," Academic Press Inc., London, 1965, Chapter 8.

(2) J. Koral, R. Ullman, and F. R. Eirich, *J. Phys. Chem.*, **62**, 541 (1958).

(3) R. Perkel and R. Ullman, *J. Polym. Sci.*, **54**, 127 (1961).

(4) S. Ellerstein and R. Ullman, *ibid.*, **55**, 123 (1961).

(5) G. J. Howard and P. McConnell, *J. Phys. Chem.*, **71**, 2974 (1967).

(6) (a) F. M. Trent, C. L. Key, M. Lewis, and R. A. Vordenberg, 3rd National Meeting of the Society for Applied Spectroscopy, Sept 1964. (b) These data were generously supplied by Dr. J. F. Woldering, U.S.I. Chemicals Co., Cincinnati, Ohio.

Table I
Tabulation of Carbonyl Stretching Frequency Shifts Used to Determine Infrared Bound Fraction Values

Polymer	Solvent	Carbonyl frequency,[a] cm^{-1} Free	Shifted	$-\Delta\nu$, cm^{-1}
	Adsorbed Polymers			
PVAc-1	C_2HCl_3	1745	1715	30
EVA-3	C_2HCl_3	1737	1705	32
EVA-3	C_6H_{12}	1746	1709	37
	Polymers in Solution			
EVA-3	$C_6H_{12} + CH_3OH$	1742	1722	20
EVA-3	$C_6H_{12} + C_6H_{11}OH$	1742	1727	15

[a] Frequency of the absorption band maximum.

Table II
Influence of Several Additives on Water Content of C_6H_{12} Polymer Solutions

Sample	Water content,[a] mg/g
Pure C_6H_{12}	0.12
0.29 g of EVA-3 + 1.07 g of $C_4H_8O_2$/100 ml	0.13
1.36 g of $C_4H_8O_2$/100 ml	0.11
1.0 g of CH_3OH/100 ml	0.13
0.2792 g of EVA-3 + 0.25 g of CH_3OH/100 ml	0.12
5.59 g of $C_6H_{11}OH$/100 ml	0.12

[a] Determined by Karl Fisher analysis.

solvents for adsorption experiments were Spectroquality trichloroethylene (C_2HCl_3) and cyclohexane (C_6H_{12}). The polar additives employed included methanol (CH_3OH) (ACS Analytical Reagent grade), Spectroquality[7] acetonitrile (CH_3CN), cyclohexanol ($C_6H_{11}OH$), and *p*-dioxane ($C_4H_8O_2$). 1,8,9-Anthracenetriol ($C_{14}H_7(OH)_3$) (Aldrich Chemical Co., Milwaukee, Wis.) was recrystallized from ethanol before use.

Adsorption isotherms for both polymers were constructed at 24 ± 1° and are reported as plots of adsorbance (x/m, milligrams per gram of silica) *vs.* equilibrium concentration of polymer in solution (c_s, grams per 100 ml). PVAc-1 and EVA-3 concentrations were determined by infrared spectroscopy (Perkin-Elmer 337) using their carbonyl ester bands at 1740 and 1742 cm^{-1}, respectively. Infrared spectroscopy also was used for analysis of all polar additives. The infrared bands involved are as follows: CH_3CN, 2257 cm^{-1}; CH_3OH, 3660 cm^{-1}; $C_6H_{11}OH$, 3663 cm^{-1}; $C_{14}H_7(OH)_3$, 1445 cm^{-1}. All experiments showing the influence of various additives on PVAc-1 and EVA-3 adsorbance were carried out at constant initial polymer concentration (0.30 g/100 ml) and weight of adsorbent (0.155 ± 0.005 g). The absence of significant amounts of silica in supernatant solutions was established spectroscopically using the 1110 cm^{-1} band characteristc of silica. Centrifugation was carried out at approximately 5400 *g* to ensure complete silica removal.

The average fraction of PVAc-1 and EVA-3 ester carbonyl groups attached directly to silica, *p*, was calculated from a shift in each polymer's infrared spectrum which occurred upon adsorption.[8-10] Calculations of *p* assumed negligible overlap between free and shifted bands, and did not involve extinction coefficients of the shifted bands.[9] Frequencies of the free and shifted carbonyl stretching bands used are shown in Table I. Included are shifts in the carbonyl band of EVA-3 caused by addition of CH_3OH and $C_6H_{11}OH$ to C_6H_{12} solutions of this polymer (*i.e.*, no silica adsorbent present). The average fraction of EVA-3 carbonyl ester groups bound to these alcohols in C_6H_{12} was calculated by resolving such free and shifted bands. The procedure used is identical with that employed to determine values of *p* for adsorbed polymers. Infrared analyses carried out in this study consistently involved solutions containing various amounts of polar additives. Thus, sample and reference cells of the spectrophotometer contained exactly the same solvent–additive mixture during all determinations of polymer adsorbance values and infrared bound fractions. Extinction coefficients (*k*) of the PVAc-1 and EVA-3 carbonyl ester bands were determined over a range of polymer concentrations in each solvent–additive mixture studied. In all cases, values of *k* obeyed Beer's law over the polymer concentration range examined.

Water contents of several solutions containing polar additives were determined by Karl Fisher analyses. Such analyses utilized 10-ml samples rather than the usual 1 ml, because of the low water concentrations involved. Results given in Table II establish that the additives examined caused no measurable increase in water content of C_6H_{12} solutions containing EVA-3. Thus, the effects that these additives have on the adsorbance of either polymer in C_6H_{12} are not due to significantly increased water contents of the solutions involved. All analyses were limited to C_6H_{12} solutions because chlorinated solvents interfere with Karl Fisher analyses.

Results and Discussion

Adsorption isotherms (24°) for PVAc-1 and EVA-3 are shown in Figures 1 and 2, respectively. Numbers on the graphs represent the infrared bound fraction (*p*) values at that point. For PVAc-1, *p* is the average fraction of segments of adsorbed polymer bound directly to the silica. Values of *p* for EVA-3 differ somewhat, since they represent the average fraction of vinyl acetate segments bound directly to silica and not the fraction of segments bound based on the total number of segments in the EVA-3 chain. The average fraction of ethylene units bound to silica was not determined and is not involved in calculations of reported *p* values for EVA-3.

The high PVA-1 *p* values shown in Figure 1 indicate a compressed and firmly bound adsorbed PVAc-1 layer. There is no strong dependence of *p* on PVAc-1 adsorbance, except for an increase from 0.30–0.38 to 0.40–0.46 as the PVAc-1 adsorbance increases from 8.0 mg/g of silica to 27.0 mg/g of silica. A similar increase has been observed for a high molecular weight PMMA sample adsorbed on silica.[10] The lack of other substantial changes in *p* with increasing PVAc-1 adsorbance has been reported for several polymers which experience strong affinities for silica surfaces.[8,10,11] In contrast, Figure 2 shows that values of *p* for EVA-3 decrease uniformly with increasing polymer adsorbance. The high values of *p* for EVA-3 indicate that the vinyl acetate units are concentrated in the interfacial region and act as the primary units responsible for adsorption. At low EVA-3 adsorbances, nearly all the vinyl acetate units are bound to silica whether C_2HCl_3 or C_6H_{12} is the solvent. However, values of *p* are somewhat higher at

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[7] Registered trademark, Matheson Coleman and Bell, Division of The Matheson Co., Inc., Norwood, Ohio.

[8] B. J. Fontana and J. R. Thomas, *J. Phys. Chem.*, **65**, 480 (1961).

[9] C. Thies, P. Peyser, and R. Ullman, Proceedings of the 4th International Congress on Surface Active Substances, Vol. II, Gordon and Breach, Science Publishers, New York, N. Y., 1967, p 1041.

[10] C. Thies, *J. Phys. Chem.*, **70**, 3783 (1966).

[11] P. Peyser, D. J. Tutas, and R. R. Stromberg, *J. Polym. Sci., Part A-1*, **5**, 651 (1967).

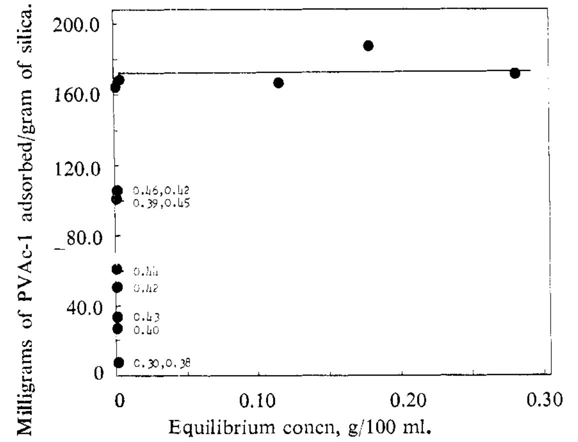

Figure 1. Equilibrium adsorption isotherm of PVAc-1 on silica from C_2HCl_3 at 24°. Numbers on the graph represent infrared-bound fraction values at that point.

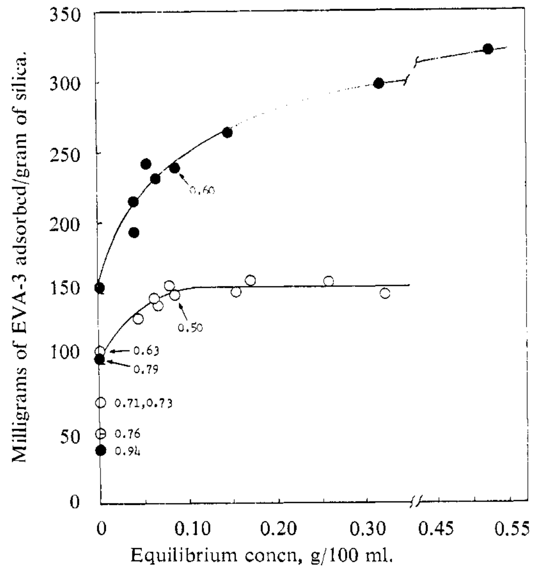

Figure 2. Equilibrium EVA-3 adsorption isotherms on silica at 24°. Numbers on the graph represent infrared-bound fraction values at that point based only on the vinyl acetate units of EVA-3: ○, C_2HCl_3 as solvent; ●, C_6H_{12} as solvent.

equivalent EVA-3 adsorbances when C_6H_{12} is the solvent indicating that the solvent influences its adsorbed structure somewhat. This differs slightly from the observations of Fontana and Thomas[8] and Fontana[12] that the solvent had no effect on adsorbed structures of their polymers. Such a difference in behavior may be due to a more firmly bound adsorbed layer in the latter cases, as suggested by Kipling.[1] Figure 2 also shows that silica adsorbs more than twice as much EVA-3 from C_6H_{12} than C_2HCl_3. This reflects stronger solvent–surface and/or solvent–polymer interactions occurring in C_2HCl_3 relative to those in C_6H_{12}

Since this study was designed to characterize the effect of various additives on polymer adsorption, it was necessary to establish that they were adsorbed on silica from the solvents used. Results in Table III show that this is the case. Complete isotherms for each additive were not obtained, but these data suffice to demonstrate that adsorption always occurs. Adsorbances reported here are much lower than observed for polymers. They also scatter considerably due to the relatively weak infrared bands being used for analysis in most cases and the lower adsorbances involved. Absorbance data for CH_3OH are not given, since CH_3OH undergoes such extensive self-association in C_2HCl_3 and C_6H_{12} that reliable quantitative analyses based on its hydroxyl band are difficult to make. Nevertheless, the experimental data for CH_3OH firmly demonstrated that it is adsorbed by silica from both solvents.

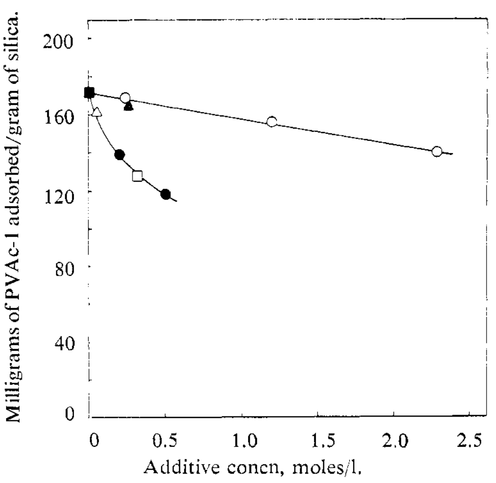

Figure 3. The effect of several additives on PVAc-1 adsorption from C_2HCl_3 on silica (24°): ■, no additives; ○, CH_3CN; ●, $C_6H_{11}OH$; △, $C_{14}H_7(OH)_3$; ▲, $C_4H_8O_2$; □, CH_3OH.

TABLE III

ADSORPTION OF NONPOLYMERIC ADDITIVES ON SILICA

Additive	Solvent	Range of c_s, g/100 ml	Range of x/m, mg/g	No. of runs
CH_3CN	C_2HCl_3	0.347–0.864	20–39	5
$C_6H_{11}OH$	C_2HCl_3	0.883–0.967	24–37	2
$C_{14}H_7(OH)_3$	C_2HCl_3	0.292–0.314	13–14	2
$C_6H_{11}OH$	C_6H_{12}	0.527–1.140	45.7–59.4	5

Figure 3 illustrates how CH_3OH, $C_{14}H_7(OH)_3$, $C_6H_{11}OH$, CH_3CN, and $C_4H_8O_2$ influence PVAc-1 adsorption on silica from C_2HCl_3 (24°). Since molecular weights of the additives varied, their concentrations are expressed on a molar basis rather than in terms of grams per 100 ml. Initial polymer concentrations and weights of adsorbent were held constant, and all data were obtained after 48–96 hr of agitation. Such variations in agitation time had no effect on reported results, since equilibrium adsorbances were reached within 48 hr.

As shown in Figure 3, all additives reduce the adsorbance of PVAc-1. The effect of CH_3OH, $C_{14}H_7(OH)_3$, and $C_6H_{11}OH$ is described well by one curve which suggests that these compounds have equivalent effects on PVAc-1 adsorbance. This probably is due to the hydroxyl function common to all of them. Such additives also cause greater reductions in PVAc-1 adsorbance at a given molar concentration than do CH_3CN or $C_4H_8O_2$. The multifunctionality of $C_{14}H_7$-

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[12] B. J. Fontana, *J. Phys. Chem.*, 67, 2360 (1963).

TABLE IV
EFFECT OF NONPOLYMERIC ADDITIVES ON PVAc-1 INFRARED-BOUND FRACTION VALUES[a]

Initial PVAc-1 concn, g/100 ml	Additive	Additive concn, *M*	PVAc-1 x/m, mg/g	p
0.31	None	0	103.2	0.43
0.31	CH_3CN	1.23	103.3	0.31
0.31	CH_3CN	2.44	106.9	0.32
0.31	$C_6H_{11}OH$	0.216	101.5	0.35
0.31	$C_6H_{11}OH$	0.511	105.4	0.28
0.31	$C_6H_{11}OH$	1.01	91.9	0.27
0.31	$C_{14}H_7(OH)_3$	0.044	105.8	0.41
0.19	None	0	61.5	0.44
0.18	$C_6H_{11}OH$	0.129	62.7	0.42

[a] Weight of adsorbent = 0.43 ± 0.01 g; c_s for PVAc-1 = 0 g/100 ml in most cases.

TABLE V
EFFECT OF ADDITIVES ON EVA-3 ADSORPTION ON SILICA AT 24°

Solvent	C_0, g/100 ml	Additive	Additive concn, *M*	EVA-3 C_s, g/100 ml	x/m, mg/g
C_2HCl_3	0.3060	None	0	0.157	144.0
C_2HCl_3	0.3050	CH_3OH	0.376	0.387	0
C_2HCl_3	0.3097	$C_6H_{11}OH$	0.485	0.314	0
C_6H_{12}	0.3110	None	0	0.0556	242.8
C_6H_{12}	0.3022	$C_4H_8O_2$	0.228	0.1665	159.7
C_6H_{12}	0.3038	$C_6H_{11}OH$	0.0990	0.141	114.8
C_6H_{12}	0.3012	$C_6H_{11}OH$	0.486	0.253	45.5
C_6H_{12}	0.3122	CH_3OH	0.340	0.285	27.5

$(OH)_3$ was expected to make it the most effective additive as far as blocking polymer adsorption is concerned. The three hydroxyl groups per $C_{14}H_7(OH)_3$ molecule conceivably could enable it to compete more effectively with PVAc-1 for surface sites and also cause $C_{14}H_7(OH)_3$ to have an adsorption isotherm approaching that observed for several simple polyfunctional esters.[13] No such effects were observed, perhaps due to the rigid structure of $C_{14}H_7(OH)_3$ which may make simultaneous attachment of all three hydroxyls to silica unlikely. Significantly, although all additives studied reduce PVAc-1 adsorbance, none of them completely inhibits or blocks PVAc-1 adsorption over the additive concentration range studied. A substantial amount of PVAc-1 is adsorbed at CH_3CN and $C_6H_{11}OH$ concentrations as high as 10 g/100 ml (2.4 and 1.0 *M*, respectively). PVAc-1 successfully competes for silica surface sites and is able to retain to a great degree its affinity for such sites under the conditions examined. This behavior is attributed to the high affinity of PVAc-1 for silica, but may be related to its high molecular weight and the resulting large number of surface attachments per polymer molecule.

Table IV contains representative infrared bound fraction values (p) which show how several additives influence the adsorbed structure of PVAc-1. In most cases, PVAc-1 absorbances are less than or equal to those required for saturation of the silica surface. Under these conditions, low $C_{14}H_7(OH)_3$ and $C_6H_{11}OH$ concentrations (0.044 and 0.13 *M*, respectively) have essentially no effect on p, even though PVAc-1 adsorbance at surface saturation is reduced slightly (Figure 3). Higher $C_6H_{11}OH$ and CH_3CN concentrations reduce p to 0.27–0.32. This decrease implies that both additives cause the PVAc-1 adsorbed layer to be more extended. However, in no case did these additives greatly extend the thickness of this layer as would be inferred from a gross reduction in the average fraction of PVAc-1 segments directly attached to silica. PVAc-1 molecules adsorbed from C_2HCl_3 solutions containing substantial amounts of CH_3CN or $C_6H_{11}OH$ still form numerous polymer–surface attachments. Perhaps the observed decrease in p is partially due to reduced polymer adsorbances at surface saturation caused by higher concentrations of CH_3CN or $C_6H_{11}OH$. The actual PVAc-1 absorbance in most systems was held constant. However, as the additive concentrations increased, this adsorbance began to more closely approach that required for surface saturation and under such conditions it is possible that lower p values would result.

Unlike PVAc-1, EVA-3 adsorption is markedly affected by low concentrations of polar additives. Table V shows that EVA-3 is not adsorbed on silica from several C_2HCl_3 solutions containing CH_3OH and $C_6H_{11}OH$. Addition of CH_3OH or $C_6H_{11}OH$ to C_6H_{12} solutions of EVA-3 also causes a marked reduction in polymer adsorbance, although some EVA-3 still is adsorbed. Both EVA-3 and PVAc-1 have the same interface active vinyl acetate group, with only the frequency of this group along the chain being varied. That is, an average of 28.8% of the segments in an EVA-3 chain are vinyl acetate units. The much more pronounced effect of CH_3OH and $C_6H_{11}OH$ on EVA-3 adsorption reflects how the presence of ethylene units in the EVA-3 chain alters its adsorption tendency relative to that of PVAc-1. The much higher $\bar{M}_n$ values for PVAc-1 may contribute to the observed differences, but the fact that EVA copolymers are attached less firmly to silica than PVAc has been demonstrated by the ability of PVAc to displace an EVA copolymer from silica.[14]

An explanation for the effect of various additives on polymer adsorption lies in characterizing the relative importance of the intermolecular interactions that occur in the systems examined. As others have stressed,[4] the adsorption behavior of a given system reflects the sum of all molecular interactions in solution, as well as at the adsorbent–solution interface. Since the systems in this study contained polymer, solvent, polar additive, and silica surface sites, four components potentially capable of interacting with each other were always available. The specific interactions believed to control the various adsorption effects observed are those causing hydrogen bond formation. All additives and polymers used possess functional groups known to form such bonds. Furthermore, the polar silica surface sites are capable of hydrogen bonding with the polymers and additives used. Even the polarized hydrogen in C_2HCl_3 can participate in hydrogen bonding. Although C_6H_{12} has little hydrogen bonding capability, it is able to interact with other species by dispersion forces.

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(13) B. J. Fontana, *J. Phys. Chem.*, 70, 1801 (1966).

(14) C. Thies, to be submitted for publication.

Thus, ample opportunities for complex bonding phenomena exist in all adsorption systems used.

Hydrogen bonding between various molecular species can be detected using infrared spectroscopy.[15] Infrared bands of the groups involved broaden and experience a frequency shift relative to the same groups not involved in hydrogen bonding. Such a frequency shift occurs when PVAc-1 and EVA-3 adsorb on silica and enables one to determine the infrared p values shown in Figures 1 and 2, and Table III. Gallopoulos[16] used such shifts to study the interaction of a poly(alkyl methacrylate–N-vinyl-2-pyrrolidone) copolymer with several alcohols in carbon tetrachloride and a white mineral oil. Blanks and Prausnitz[17] likewise used infrared spectroscopy to study the binding of isopropyl alcohol to two polymers in carbon tetrachloride. Noninteracting molecular groups yield infrared bands having absorbance values (A) which obey Beer's law: $A = klc$, where k represents the extinction coefficient, l, cell path length, and c, concentration of the absorbing species. Variation with additive concentration of k values for the carbonyl ester group of EVA-3 and PVAc-1 provides a measure of polymer–additive interactions in solution. Magnitudes of the deviation observed are related to the extent and possibly intensity of such interaction. That deviations occur is shown in Figure 4, where carbonyl ester k values of PVAc-1 in C_2HCl_3 and EVA-3 in C_6H_{12} are seen to vary with additive concentration. Measureable changes are not limited to higher additive concentrations since even 0.30 M CH_3OH (or 0.96 g/100 ml) causes a substantial variation. The magnitude of the effect on k observed in a specific case appears to depend on two factors: additive concentration and nature of the additive. Variations in k induced by these additives tend to parallel the additives' effect on polymer adsorbance. The alcohols tend to have the greatest effect on k, as well as the greatest effect on PVAc-1 adsorbance. CH_3CN and $C_4H_8O_2$ have the least effect on k and PVAc-1 (or EVA-3) adsorbance. Increasing additive concentrations always tend to decrease polymer adsorbance and polymer k values.

Based only on the data reported in this paper, one can construct a consistent correlation between changes in k caused by an additive and the additive's influence on PVAc-1 or EVA-3 adsorbance. Additives which cause greatest reductions in k also cause greatest reductions in adsorbances of these polymers. However, more recent observations establish that such a relationship cannot be generalized, because it does not hold for all additives. Phenol interacts extensively with PVAc-1 and EVA-3 in solution as determined spectroscopically, but has proportionately little effect on polymer adsorbance.[18] Although the extent and intensity of polymer–additive interactions in solution can be established spectroscopically, the occurrence of such interactions does not necessarily mean that they control polymer adsorption. Additive–surface interactions also must be considered. For example, the lack of substantial reduction in polymer adsorbance caused by phenol may be due to the ability of the silica surface to adsorb simultaneously both phenol and polymer in substantial amounts.[18]

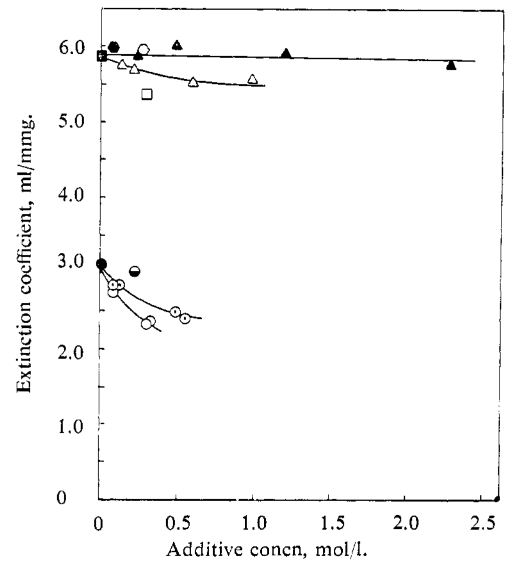

Figure 4. The effect of several additives on the carbonyl ester extinction coefficient of PVAc-1 and EVA-3: ●, EVA-3 in C_6H_{12}; ○, EVA-3 in C_6H_{12} + CH_3OH; ⊙, EVA-3 in C_6H_{12} + $C_6H_{11}OH$; ◒, EVA-3 in C_6H_{12} + $C_4H_8O_2$; ■, PVAc-1 in C_2HCl_3; ▲, PVAc-1 in C_2HCl_3 + CH_3CN; △, PVAc-1 in C_2HCl_3 + $C_6H_{11}OH$; □, PVAc-1 in C_2HCl_3 + CH_3OH; , PVAc-1 in C_2HCl_3 + $C_{14}H_7(OH)_3$; ⬡, PVAc-1 in C_2HCl_3 + $C_4H_8O_2$.

Before concluding, it is significant to mention that several additives have a particularly interesting effect on the carbonyl ester band of EVA-3 when C_6H_{12} is the solvent. The decrease in values of k caused by these additives is due to formation of a distinct shoulder (or even distinct peak) adjoining the free carbonyl ester band at 1742 cm^{-1}. Phenol causes formation of a shifted band at 1717 cm^{-1} ($\Delta\nu$ = 25 cm^{-1}),[18] CH_3OH forms a shoulder located at 1722 cm^{-1} ($\Delta\nu$ = 20 cm^{-1}), and $C_6H_{11}OH$ forms a shoulder at 1727 cm^{-1} ($\Delta\nu$ = 15 cm^{-1}). Using the same double beam compensation method employed to obtain values of p for adsorbed polymers,[8,9] one can calculate the fraction of EVA-3 carbonyl ester groups complexed in solution with these additives. Initial results in Table VI establish that a substantial fraction of the vinyl acetate units are bound to CH_3OH and $C_6H_{11}OH$ in C_6H_{12}. Equilibrium constants for the above complexing reaction can be determined as a function of temperature and thereby enable one to examine in more detail the nature of the complex. Blanks and Prausnitz[17] have done this for binding of

TABLE VI
INFRARED-BOUND FRACTION VALUES FOR EVA-3 INTERACTING WITH POLAR ADDITIVES IN C_6H_{12} AT 24°

Polar additive	Additive concn, M	EVA-3 concn, g/100 ml	p
CH_3OH	0.325	0.1830	0.24
$C_6H_{11}OH$	0.506	0.3140	0.22

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isopropyl alcohol to *p*-(*n*-butyl methacrylate) and poly(propylene oxide) in carbon tetrachloride. They concluded that at the low polymer concentrations used, hydrogen bonding between isoproyl alcohol and these polymers occurs to about the same extent as it would in solutions of corresponding monomer molecules. Higher polymer concentrations might reduce the number of hydrogen bonds formed due to coiling effects. Further quantitative spectrosopic studies of hydrogen bonding between polar additives and polymers in solution should provide considerable insight into the nature of interactions between these species. If coupled with adsorption experiments, such data may be a particularly fruitful means of establishing the influence of various additives on polymer adsorption.

Acknowledgment. The support and encouragement of this work by J. A. Herbig and H. F. Huber is gratefully acknowledged.

Thermal Expansivities of Polymers at Cryogenic Temperatures[1]

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Received April 24, 1968

ABSTRACT: In an extension of earlier work the linear expansion coefficients between about 20 and 120°K have been measured for ten poly(alkyl methacrylates) (PAMA), poly-4-methylpentene-1 (P4MP1), and a 49:51 ethylene–propylene (E–P) copolymer. The methacrylates exhibit an increasing expansion coefficient up to $\sim$40°K, except for PMMA, followed by a plateau and a relaxation region located between 80 and 110°K. The magnitude of this transition increases with flexibility in the alkyl side group. The existence of this region is consistent with both dynamic mechanical and proton spin lattice relaxation data for the higher members of the series. P4MP1 behaves similarly to the methacrylates, but with larger expansion coefficients. The E–P copolymer exhibits a relaxation around 56°K, lower than that ascribed to supposedly similar molecular motions in alkyl side chains. There are indications of possible further transitions in the higher methacrylates and P4MP1 below the temperature range studied.

We have recently carried out thermal expansion measurements for polyalkyl methacrylates between approximately 90°K and the glass transition temperature which show the existence of multiple transitions or relaxations in the glass.[4] With increasing length of the side chain, these could not be resolved by means of mechanical low frequency measurements. The results moreover suggested the presence of a transition around the lower limit of this temperature range for polymers with a fairly flexible side group. Such a relaxation would be consistent with audiofrequency dynamic measurements for poly(*n*-alkyl methacrylates)[5,6] in which a transition is observed at about 120°K, and also for similar systems such as poly(alkyl acrylates),[7] poly(alkyl vinyl ethers),[7] and poly-α-olefins,[8] all possessing flexible side chains.

In the present work, the temperature range has been extended to liquid helium temperatures for a series of poly(*n*-alkyl methacrylates), the isomers of poly(butyl methacrylate), poly-4-methylpentene-1, and a random copolymer of ethylene and propylene.

Experimental Section

Materials. The ten poly(alkyl methacrylates) (PAMA) studied are the same samples used in ref 4. Poly-4-methylpentene-1 (P4MP1) was kindly supplied by ICI Plastics Division. It had a melt flow index of 2 (260°/5 kg), representing a fairly high molecular weight. The ethylene–propylene copolymer (E–P) was kindly furnished by Drs. Kontos and Nudenberg of the U. S. Rubber Co. It contains 49% ethylene with 2.6% ethylene and 1.6% propylene crystallinity and intrinsic viscosity of 3.34 at 135° in tetralin. The latter two polymers were molded to shape at room temperature and a pressure of 5000 psi. Neither polymer appeared altered on this treatment as evidenced by differential scanning calorimetry.

Procedures. The linear expansion coefficients were measured in a recording quartz dilatometer similar to that previously described.[4] For the present temperature range, however, it was necessary to keep the sample under vacuum during a run. The sensitivity of the dilatometer was about 2×10^{-4} in. of sample expansion per inch of recorder deflection and the recorder chart could be read to ±0.01 in. corresponding to a length change of 2×10^{-6} in. Temperature was measured with a copper–constantan thermocouple which could be read to $\pm 10^{-3}$ mV. The thermocouple was found to be very close at both liquid nitrogen and liquid helium temperatures to values given by Powell, Bunch, and Corruccini[9] and intermediate values were taken from their

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(1) Supported by the National Aeronautics and Space Administration under Grant NsG-343 to the University of Southern California.

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