

# IGC Study of Surface Properties of Adsorbed Styrene/Methacrylic Acid Diblock Polymers

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## SYNOPSIS

An inverse gas chromatographic study has been carried out on a styrene/methacrylic acid diblock polymer adsorbed on particulates of varying acid/base interaction potential. Acid/base interactions between polymer and substrate were shown to result in the selective adsorption of copolymer moieties, leading to interphase surface compositions that varied with thickness. At higher interphase thicknesses, bulk and surface compositions became similar; however, depending on the interaction potential of the adsorbent, the interphase thicknesses at this point varied from 100 to 1000 Å. Adsorbed diblock interphases are to be considered nonisotropic in local composition and molecular conformation. These properties may make possible designing diblock interphases to meet specific compatibilization requirements in polymer composites. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Continuing efforts are underway in these laboratories to further an understanding of the part played by interactions at contacts between constituents of complex polymer systems and the properties of those systems. As part of the research program, we have investigated the capability of certain macromolecules to act as bridging agents at interfaces between matrix and inclusions, such as pigments or fillers. Particular attention was given to diblock copolymers, notably a series of styrene/4-vinyl pyridine (S/VP) diblocks.<sup>1,2</sup> It was noted that when adsorbed on various particulates, the copolymers formed interphases whose surface compositions varied with the strength of specific interactions at the solid/copolymer interface. By applying Fowkes' acid/base concepts,<sup>3,4</sup> the specific interactions at contacts between substrates and adsorbing copolymers could be expressed as acid/base interactions. These pointed to differences in the configuration of adsorbed species as the cause of different surface compositions in the adsorbed interphases.

The reported work<sup>1,2</sup> raised questions about the generality of the observed surface structure effects. An extension to other diblock copolymers was therefore indicated. Further, the S/VP family combined moieties (S and 4VP) both of which were identified as bases. More pronounced differences in the surface composition of adsorbed polymers might be attainable in a diblock combining acidic and basic moieties. Thus the present selection for study of a styrene/methacrylic acid diblock (S/MAA).

Emphasis on the importance of component interactions has been related directly to the evolution of methods offering quantitative measurements of these. Notable among the methods is inverse gas chromatography (IGC). The principles and applications of IGC have been reviewed frequently<sup>5-7</sup> and need not be reconsidered here. The most relevant facet of IGC to this work is its ability to provide indexes of surface acidity and basicity for stationary phases used in the experiments. The required indexes are obtained by probing the surfaces of stationary phases with dispersion-force vapors, such as *n*-alkanes, and with vapors defined as electron donors (bases) and acceptors (acids). The definitions call into play (Lewis) acid/base theories, that of Gutmann<sup>8</sup> having been used in our work to define reference acid and base vapor probes. The strengths

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and limitations inherent to the use of the Gutmann approach have been considered elsewhere.<sup>9,10</sup> The methods used in this work result in acid and base indexes (AN and DN) that are not consistent as to units.<sup>1,2,10</sup> They retain full usefulness, however, as indicators of *relative* acid/base tendencies in stationary phases of the IGC procedure.

The purpose of this article is to study the surface interactions of a S/MAA diblock when adsorbed on substrates that include an acid, a base, and a chromatographic support solid known to be only weakly interactive. An indication is sought of the potential usefulness of the diblock as a bridging agent in multi-component polymer systems.

## EXPERIMENTAL

### Materials

S/MAA specimens were prepared by anionic polymerization, a favored method for the synthesis of block copolymers with well-defined architecture and molecular weight parameters.<sup>11</sup> Rigorously followed procedures are required if these desirable polymer properties are to be attained, as described in the literature.<sup>12-15</sup> The diblocks were synthesized in previously described apparatus,<sup>16</sup> by sequential anionic polymerization of styrene monomer, followed by *t*-butylmethacrylate monomer (*t*-BuMA). The initiator was *n*-butyllithium. Polymerization occurred in tetrahydrofuran (THF) at  $-78^{\circ}\text{C}$  under nitrogen. In order to avoid high molecular weight contamination, the polystyrellithium chains were capped with diphenylethylene before introducing *t*-BuMA monomer.

Procedures analogous to those described earlier<sup>1,2</sup> were employed to isolate copolymers at constant polystyrene (PS) block length and with poly(*t*-BuMA) segments varying in length between  $\sim 10$  and  $\sim 200$  units. Polymers were recovered and purified by repeated precipitation in methanol, methanol/water mixtures, or water, depending on the diblock composition. The *p*(S-MAA) copolymers were obtained by acid catalyzed hydrolysis of the *t*-BuMA segments in toluene, using *p*-toluenesulfonic acid as catalyst.<sup>15</sup> Molecular weight characterization was by size exclusion chromatography using a Varian 5000 LC at  $50^{\circ}\text{C}$ . The solvent was THF, and standardization was by monodisperse PS references (Varian TSK kit). The present article reports on a diblock with a PS content of 420 units and a MAA segment length of 80 units. The polydispersity index was found to be 1.12 for the PS block and 1.15 for

the acrylic block. In addition, monodisperse PS[500] was used as received from Polysciences Inc., and a specimen of pure MAA[100] was supplied courtesy of Dr. Sunil Varshney of the McGill laboratory.

Substrates for the adsorption of diblock were the chromatographic support Chromosorb W<sup>TM</sup>,<sup>1</sup> the acidic rutile R-1,<sup>2</sup> and a CaCO<sub>3</sub>, representative of fillers with basic surface interactions.<sup>17</sup> The rutile was known to be surface coated by the supplier (Tioxide Canada), and to have a surface area of 9 m<sup>2</sup>/g. The CaCO<sub>3</sub>, from ICI Plc, had a surface area of 3.3 m<sup>2</sup>/g, and Chromosorb near 1.0 m<sup>2</sup>/g.

### IGC

The stationary phases of this work were prepared by depositing diblock on Chromosorb, rutile or CaCO<sub>3</sub> from solutions in THF. An associated objective of this work was to establish variations in the properties of the adsorbed polymer as a function of the polymer/substrate mass ratio. Consequently, starting concentrations of dissolved polymer were varied to produce coating weights that varied from 0 to nearly 20 wt %. Detailed compositions of chromatographic columns are given in Table I. Standard ashing procedures<sup>18</sup> were employed to obtain quantitative measurements of adsorbed polymer.

Retention data were obtained with a Perkin-Elmer Sigma-2 apparatus, equipped with a hot wire detector. Retention volumes,  $V_n$ , were computed for *n*-alkanes from C<sub>6</sub> to C<sub>9</sub>, acting as dispersion-force surface probes. Chloroform (CHL) and diethyl ether (DEE) were selected as reference acid and base probes, as in the earlier reports,<sup>1,2</sup> based on the Gutmann convention.<sup>8</sup> Acetone was used as a vapor typical of amphoteric materials. Probe molecules were injected at least in triplicate. Elution peaks were symmetrical, and retention times calculated

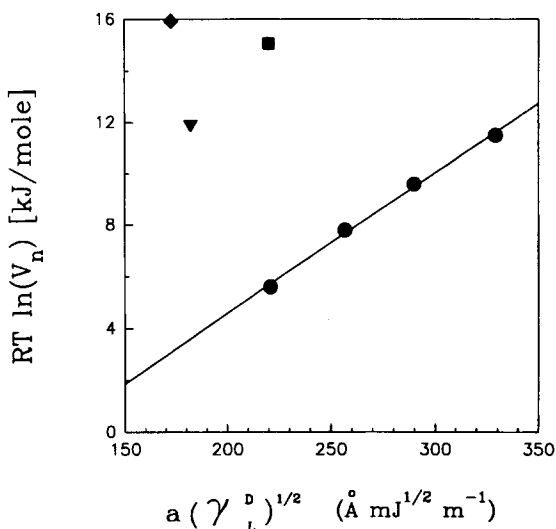
**Table I** Composition of Stationary Phases

P(S-MAA) [420-80] on Substrates		
TiO <sub>2</sub> (Acid) Ratio Wt/Wt (g/g)	CaCO <sub>3</sub> Ratio Wt/Wt (g/g)	Chromosorb W Ratio Wt/Wt (g/g)
0.011	0.011	0.010
0.029	0.030	0.030
0.050	0.051	0.050
0.075	0.075	0.075
0.096	0.101	0.096
0.200	0.201	0.199

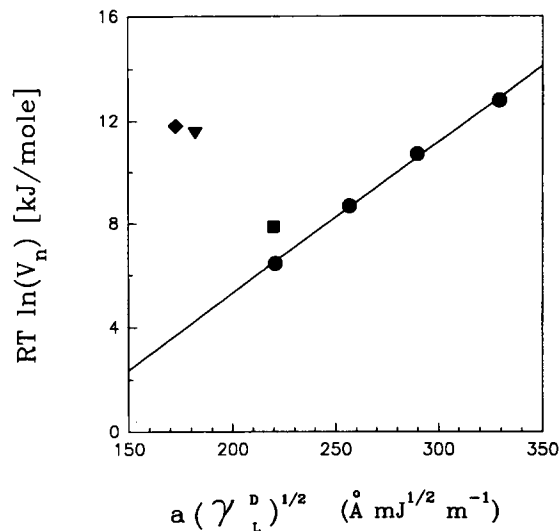
from them were repeatable to better than 4%. All measurements were at 70°C. The parameters to be used in this work were obtained from data representations using the equation:

$$RT \ln V_n = 2Na[(\gamma_l^d)]^{1/2}[(\gamma_s^d)]^{1/2} + \text{const} \quad (1)$$

where  $a$  is the diameter of cross section of the vapor phase molecules,  $\gamma$  are the surface energies of vapor and solid phases,  $N$  is the Avogadro number, and all other terms retain their usual meaning. The use of this expression has been justified previously in the literature.<sup>7,10,19</sup> Linear sections in plots of  $RT \ln V_n$  versus the product  $a[(\gamma_l^d)]^{1/2}$ , generated by alkane probes can be used for evaluations of the stationary phase  $(\gamma_s^d)$ . The application should be viewed with the realization that the surface energies obtained do not invariably agree with those from "classical" procedures, for example, contact angle determinations. Reasons for this include possible uncertainties in contact angle data caused by local plasticization of the solid surface by the contacting liquid,<sup>20</sup> and the tendency of IGC at infinite dilution to interact with surface sites in the higher energy end of the distribution.<sup>21</sup> Deviations from the straight line for the nondispersion probes are the contributions to the free energy of adsorption due to acid/base forces,  $\Delta G_{ab}$ , or, empirically, the acceptor/donor numbers, AN and DN of the stationary phase. Clearly, the AN of the solid is given by the position of the basic probe (DEE), DN by that of the reference acid (CHL).



**Figure 1** Representation of IGC results for vapors retained by PS-MAA [420-80] adsorbed on Chromosorb. Polymer weight ratio is 0.096. Vapor probes: (●) alkanes; (■) CHL; (▼) DEE; (◆) acetone.



**Figure 2** Representation of IGC results for vapors retained by MAA homopolymer adsorbed on rutile. Polymer weight ratio is 0.10. Vapor probes: (●) alkanes; (■) CHL; (▼) DEE; (◆) acetone.

## RESULTS AND DISCUSSION

An example of applying eq. (1) to the experimental results is given in Figures 1 and 2. Figure 1 presents data for the diblock polymer on Chromosorb at a weight ratio of 0.096. The excellent linearity of alkane points leads to an evaluation of  $(\gamma_s^d) = 20.4$  mJ/m<sup>2</sup>. The surface of the adsorbed diblock is amphoteric at this level of coverage, the positions of the CHL and DEE points being well removed from the alkane line. The skew however is to basicity because the acidic probe falls somewhat further off the line than does the datum for the basic DEE. As a result the ratio AN/DN = 0.9. Figure 2 shows analogous results for the pure MAA polymer on TiO<sub>2</sub>. The pronounced acidity of the polymer is in clear evidence, with the basic probe significantly further from the alkane reference line than the acidic vapor. The corresponding AN/DN is 5.3. This result indicates that the surface of the adsorbed phase in the diblock (Fig. 1) contains appreciable amounts of the basic PS component. The finding is consistent with the requirement to minimize surface energy, that of the MAA component, at about 24 mJ/m<sup>2</sup>, being some 15% greater than that of the PS moiety.

Detailed comparisons of the characteristics of adsorbed diblocks are given in Tables II-IV. These report the AN and DN values and estimates of  $(\gamma_s^d)$  as a function of surface coverage on the three selected adsorbents. Rutile is the substrate in Table II, CaCO<sub>3</sub> in Table III, and the Chromosorb in Table IV. The first lines in each of these tables may be

**Table II Parameters From IGC Investigation of 420/80 Diblock on Rutile**

Ratio Wt/Wt (g/g)	$\Delta G_{\text{SP}}^{\text{DEE}}$ (AN kJ/mol)	$\Delta G_{\text{SP}}^{\text{CHL}}$ (DN kJ/mol)	$\Delta G_{\text{SP}}^{\text{AC}}$ (kJ/mol)	AN/DN	$\gamma_{\text{S}}^{\text{D}}$ (mJ/mol)
0	10.0	3.6	11	2.7	25.2
0.011	7.9	2.4	9.7	3.3	28.8
0.029	5.8	2.4	10	2.5	27.6
0.050	7.4	4.0	11	1.9	23.6
0.075	7.0	4.6	10	1.5	24.1
0.096	5.5	4.6	9.9	1.2	17.8
0.200	6.5	6.0	10	1.1	18.8

used to characterize the adsorbents. The rutile (Table II) has acidic tendencies, as indicated by the relatively larger AN parameter, and as conveniently quantified by the AN/DN ratio. In contrast, the  $\text{CaCO}_3$  has a somewhat basic surface, with AN/DN < 1 (Table III). The dispersion surface energies of these solids are lower than would be expected for pure specimens, but are reasonable for surface-modified versions of the particulates as supplied by their manufacturers. The chromatographic support displays relatively smaller deviations from dispersion-force behavior, its AN and DN numbers being lower than for the rutile and chalk samples. Unlike the other solids however, Chromosorb W is an almost pure acid, the DN value being barely significant. Clearly, the force fields at surfaces of these solids are sufficiently different to impose different adsorption and orientation tendencies on the diblock adsorbate.

Further consideration of Tables II–IV elaborates on the above expectation. Primary emphasis is placed on the results at low coverages, that is, below polymer/support ratios of about 0.075 g/g. It is here that the different force fields exerted by the adsorbents may affect the conformation of the adsorbed polymer. In principle, the acidic rutile surface should

promote the preferential orientation to the surface of the basic PS moiety leaving the acidic MAA chains directed toward the air interface. The trend in AN and DN values is consistent with the hypothesis: there is an initial increase in the parameter ratio, followed by a decrease toward a steady-state value near 1.1 at high polymer coverages (>0.075 g/g). Given the somewhat higher ( $\gamma_{\text{S}}^{\text{D}}$ )<sup>d</sup> of MAA as compared with S groups, the inferred composition of surface layers at low diblock concentrations presents a thermodynamic curiosity because minimization of surface free energy would call for the presence of PS groups in the surface region. This expectation seems to be met at the higher adsorbate concentrations. The steady-state structure of the surface layer at this point, and thus the surface structure of the unadsorbed diblock polymer itself, as represented by the observed value of AN/DN, may be assumed to reflect a surface composition enriched in PS.

Adsorption on  $\text{CaCO}_3$  produces a somewhat different pattern of results. At high surface coverages, the AN/DN values are essentially equal to those in Table II, albeit the actual AN and DN numbers are slightly higher than in the case of adsorption on rutile. However, here the AN index varies only

**Table III Parameters From IGC Investigation of 420/80 Diblock on  $\text{CaCO}_3$** 

Ratio Wt/Wt (g/g)	$\Delta G_{\text{SP}}^{\text{DEE}}$ (AN kJ/mol)	$\Delta G_{\text{SP}}^{\text{CHL}}$ (DN kJ/mol)	$\Delta G_{\text{SP}}^{\text{AC}}$ (kJ/mol)	AN/DN	$\gamma_{\text{S}}^{\text{D}}$ (mJ/mol)
0	7.1	8.7	13	0.8	23.2
0.011	6.3	2.8	9.8	2.3	29.4
0.030	6.7	3.2	9.9	2.1	23.9
0.051	7.0	5.2	12	1.3	24.1
0.075	7.9	6.0	11	1.3	18.8
0.100	6.3	6.7	11	0.9	20.8
0.200	8.6	7.8	14	1.1	23.3

**Table IV Parameters From IGC Investigation of 420/80 Diblock on Chromosorb W**

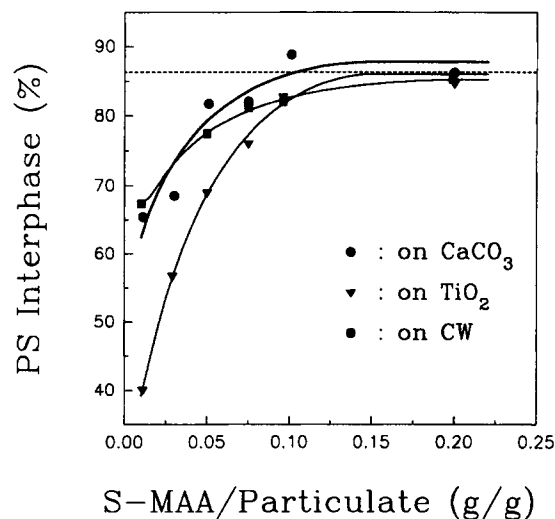
Ratio Wt/Wt (g/g)	$\Delta G_{SP}^{DEE}$ (AN kJ/mol)	$\Delta G_{SP}^{CHL}$ (DN kJ/mol)	$\Delta G_{SP}^{AC}$ (kJ/mol)	AN/DN	$\gamma_S^D$ (mJ/mol)
0	2.1	0.3	3.8	7.0	27.0
0.010	6.2	4.8	10	1.3	33.3
0.051	6.6	6.6	11	1.0	30.3
0.075	7.5	8.8	13	0.9	21.1
0.100	8.3	9.4	13	0.9	20.4
0.200	8.6	7.8	13	0.8	23.4

slightly as compared with the sensitivity of DN to the presence of the diblock. Seemingly, on initial adsorption of the diblock, the quantity of PS sensed by the vapor probe is now greater than was the case with the acidic R-1 as the adsorbent. The Chromosorb, though acidic, has lower AN and DN indexes and may therefore be considered a less powerful orienting medium than the other adsorbents. Steady-state values of the interaction parameters appear to be established at lower surface coverages than is the case with the more strongly "interactive" solids in Tables II and III. Nevertheless, here also the influence of the substrate on the composition of the surface layer of the adsorbed phase appears to extend to appreciable thicknesses of the adsorbate.

It is possible to make an estimate of the surface composition of the adsorbed layer if the acid/base characteristics of the pure diblock components are taken into account. The PMAA sample, shown in Figure 2 is used to represent the MAA moiety of the diblock. At 10 wt % loading on the rutile,  $\text{CaCO}_3$ , and Chromosorb, it was assumed that the surface structure of the adsorbed polymer was unaffected by the substrate. Under these conditions, the averaged values of AN and DN were, respectively, 7.6 and 1.7, with AN/DN = 4.5. As stated in connection with Figure 2, the MAA homopolymer behaves as an acid. Corresponding values for the S homopolymer,<sup>1</sup> show AN = 2.4, DN = 7.3, and AN/DN = 0.33. These AN/DN values may be used to compute the *relative* proportions of the two polymers to be found in the surface layer of adsorbed diblocks. The stoichiometry of the diblock polymer calls for a PS concentration equivalent to 86 wt % of the total. The apparent PS concentration in the interphase on the three support solids has been calculated for the various quantities of adsorbed polymer, with results given in Figure 3.

Analysis of Figure 3 amplifies on the discussion presented above. At coverages above about 10 wt %, the diblock appears to be randomly oriented at the

adsorbate surface, with a PS content very close to the expected. At these coverages therefore, little if any effect due to the underlying substrate is detectable. At lower surface coverages (<10 wt % polymer), there is indeed significant dependence of the surface composition of the adsorbed interphase on the nature of the support solid. In all cases the PS content is lower than called for by the diblock composition. The largest deviation is with R-1, where the PS would tend to be strongly oriented to the acidic substrate, leaving the MAA anchor exposed at the surface (see above), and leading to a highly nonisotropic adsorbed interphase. The *relative* quantity of PS in the surface layers is greater when  $\text{CaCO}_3$  and Chromosorb are the adsorbents, but that quantity still falls below expectation and indicates persistence of nonrandom conformation in the adsorbed layers. From the data available at present it is not possible to elaborate on this in detail. Some



**Figure 3** Showing variation in PS content of adsorbed interphase as function of the adsorbate/adsorbent weight ratio.

rationalization may be offered, however. The  $\text{CaCO}_3$ , though basic, contains a considerable quantity of acidic surface sites, as shown by its AN value (Table III). As a consequence both MAA and S moieties would tend to adsorb, the *relative* significance of these tendencies depending on the energies of the relevant surface sites. As a result, the capability of PS "hairs" to orient to the vapor interface would be restricted and, equally, the quantity of MAA segments accommodated by the substrate would be limited. Both of these events would contribute to the observations of Figure 3. The pattern on Chromosorb, rather than following that set by the rutile, is almost identical with the behavior on  $\text{CaCO}_3$ : Chromosorb is acidic but, as noted in connection with Table IV, either the number or the energy of acidic surface sites is low. The preferential adsorption of the PS is therefore limited, and its depletion from the surface is similarly affected.

Finally, attainment of near-stoichiometric compositions at surface coverages near 10 wt %, implies that the thickness of the interphase (in addition to its composition) is affected by the underlying surface. A crude calculation of interphase thickness can be performed if we make the reasonable assumption that the density of the solid polymer in the interphase is near  $1 \text{ g/cm}^3$ . The interphase thickness then follows when the stoichiometric composition is multiplied by the density and divided by the surface area of the underlying particulate. The procedure yields thickness values of 110, 300, and 1000 Å for rutile,  $\text{CaCO}_3$  and Chromosorb, respectively. Clearly, the interaction potential of the underlying surface influences the conformation of the adsorbed polymer layer over very appreciable distances. This adds an element of complexity to the nonisotropy of the interphase layer, whose local composition has already been shown to vary with the acid/base interaction between adsorbate and adsorbent. An alternative approach to analysis of the interphase, based on NMR data,<sup>22</sup> confirms the nonisotropic character of the interphase layer. That study has shown that if one segment of a copolymer diblock is adsorbed selectively by the substrate, then a linear relation is observed between the interphase thickness and the acid/base interaction strength, as given by the IGC indexes introduced above.

## CONCLUSIONS

An IGC study of a PS/PMAA diblock polymer adsorbed on rutile,  $\text{CaCO}_3$ , and on a chromatographic

support has been carried out. In each case it was shown that the adsorbent surface is coated by a nonisotropic polymer interphase, the composition of which varies over dimensions in the range of  $10^3 \text{ Å}$ .

IGS determinations showed that acid/base interactions appeared to be the determinant factor in the composition of the adsorbed interphase. Strong depletion of the basic PS moiety occurred when an acidic rutile was the adsorbent. Lower depletion of PS was observed for the less acidic chromatographic support and when  $\text{CaCO}_3$  was the adsorbent.

At adsorbate coverages exceeding about 10 wt %, the surface composition of the diblock was found to agree with the stoichiometry of the polymer. Apparently the polymer now is randomly oriented at the surface and is no longer affected by the nature of the adsorbent surface. Stoichiometric surface compositions led to computations of interphase thicknesses, which varied in the range 100–1000 Å, depending on the interaction potential of the solid particulates.

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