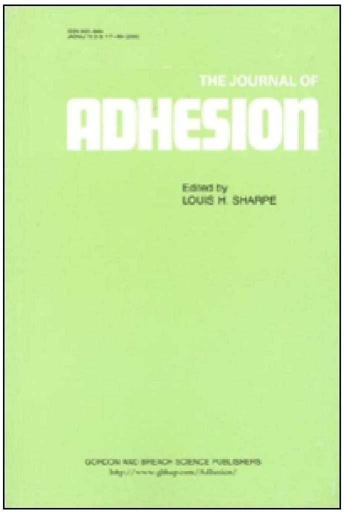

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On Origins of Time-Dependence in Contact Angle Measurements

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Time-dependent variations have been observed in the contact angles of wetting fluids on surfaces of homopolymers poly(styrene) (PS) and poly(methyl methacrylate) (PMMA), and copolymers of styrene and 4-vinyl pyridine (P(S-4VP)) and styrene and methacrylic acid (P(S-MAA)). Variations in the case of PS were unimportant, but significant variations occurred with the other polymers, allowing for the definition of both initial and equilibrium contact angle values. The total change in contact angles was strongly dependent on the acid-base contribution to the free energy of adsorption of the wetting fluids on the respective polymer surfaces, as determined from inverse gas chromatography experiments. A tentative correlation also linked the total change in contact angle with the ability of the polymer surfaces to reorganize when in contact with the polar wetting fluids of this study. Careful consideration must be given to the possibility of polymer surface reorganization when selecting fluids for use in the collection of reliable contact angle data.

Keywords: Homopolymers; Copolymers; Contact angles; Time dependence; Acid/base interaction; Surface reorganization

INTRODUCTION

In earlier papers [1,2], we have commented on the apparent time-dependence of contact angles measured for combinations of polar

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polymers and fluids. Acid-base interaction at the polymer/fluid interface was assumed to be the cause of the time-dependent variations. In certain cases, these were found to be sufficiently large to compromise the validity of experimental values measured at other than strictly controlled times of contact between substrate and wetting fluid. The matter is one of considerable importance, contact angle (θ) data being the source of surface energy measurements for macromolecules, as described in detail in standard treatises [3]. In turn, surface energy (γ) data are requisites in the development of adhesion, wetting and dewetting theories, including the important contributions to these considerations made by deGennes, to whom this paper is dedicated, and his coworkers [4, 5]. A more detailed consideration of the time-dependence problem was indicated and the results of work undertaken with this objective in mind are presented here.

We have selected a matrix of four polymers and five wetting fluids for the present study. Two of the polymers were commodity materials, the others were specialty diblock copolymers, combining moieties capable of acidic as well as basic functionality. The wetting fluids were chosen so as to represent variations in acid-base functionality. Thus, a more detailed picture could be expected of the interdependence between θ and acid/base interaction data. In order to go beyond empirical relationships, the tendency of the polymers to undergo surface reorganization when in contact with the wetting fluids was also investigated. The reorganization phenomenon, the subject of many recent publications [6–9], arises from the thermodynamic demand to minimize interfacial tensions between polymer and fluid. Depending on the polymer structure, and the interaction forces acting at the interface, this may result in a plurality of surface compositions or configurations. Implied is a link between local surface restructuring, a time-dependent process, and the posited time variation in θ.

EXPERIMENTAL SECTION

Materials

Polystyrene (PS) and polymethyl methacrylate (PMMA) were chosen to represent the commodity polymer category. PS was obtained from the Dow Chemical Co. Size exclusion chromatography (SEC) measurements (Varian 4000 LC apparatus) showed this to have Mn = 44,200 and Mw = 67,000. PMMA was obtained from DuPont Chemical Co, and SEC measurements showed it to have Mn = 27,700 with Mw = 45,500. Specialty polymers were represented by two diblock polymers, the synthesis and characterization of which was described in earlier publications [10, 11]. One was a diblock polymer of styrene and 4-vinyl pyridine P(S-4VP); the other a combination of styrene and methacrylic acid P(S-MAA). The block lengths were S/4VP = 180/73, and S/MAA = 416/79.

The fluids used for contact angle measurements were n-decane (nC10), dichloromethane (DCM), tetrahydro furan (THF), ethyl acetate (EAc) and acetone (Ac). All were reagent grade chemicals used without additional purification. They were chosen on the basis of their interaction potential, as given by the acid-base theory of Gutmann [12]. The relevant acid and base numbers, AN and DN, for the liquids are reproduced from Gutmann's tabulation [12]:

	AN	DN
nC10	0	0
DCM	20.4	0
THF	8.0	20.0
Eac	9.3	17.1
Ac	12.5	17.0

These show DCM to be a strong, pure acid, THF a pronounced base, and EAc and Ac amphipatic fluids with some prevalence to basicity. The alkane is, of course, a dispersion-force fluid without acid-base interaction capabilities.

Procedures

Contact Angles

Contact angle measurements were made along lines described in Ref. [1]. A Rame-Hart goniometer was used at a temperature controlled at 30.0°C. Polymer samples were compression molded against cleaned Teflon™ sheets at 200°C for 3 min. and immediately quenched in cold water following removal from a Carver press. The molded specimen were vacuum-dried for 5 h at 50°C, then placed in a desiccator and equilibrated at room temperature for 1 week prior to starting measurements. Samples were then placed on the goniometer stage, modified as described by Carre and Schreiber [13]. An open vial of the fluid to be used for θ determination was placed in the enclosed space surrounding the sample, so as to saturate the space with vapor and avoid loss of contact fluid due to evaporation. Droplets of the fluids were contacted with the polymer surface using a 10 μL Hamilton syringe. Contact was maintained for 1 hour. During that time, images were recorded and analyzed with an Oculus 300 image captor.

Contact angle data also were collected on polymer specimens which had been immersed in the fluids of this study at 50°C for various times to a maximum of 7 days, in order to show whether surface reorganization had occurred. The required datum for this purpose was the polar contribution to surface energy, γ^p, as defined by concepts due to Fowkes [14]. The quantity was computed using the quadratic mean equation, given in standard texts [3]. In this portion of the work contact angle determinations used only nC10 and THF and contact times were restricted to 3 min. The characterizing datum was the initial contact angle θ_i, as defined in following sections of this paper.

IGC

Measurements were made with a Varian 3400 gas chromatograph, using both heated wire and flame ionization detectors. The polymers, used as stationary phases in the procedure, were deposited onto Chromosorb 60/80 AW support from solutions in xylene for the homopolymers and THF for the diblock polymers. In all cases, Rotovap apparatus was used to recover the coated support, which was then dried under vacuum for 24 h at 140°C. Conventional ashing procedures [13, 15] showed that the mass of supported polymer was in the range of 8.8 – 10.3%, sufficient to ensure full coverage of the supporting material. Supported polymers were packed into previously washed and dried stainless steel columns, 1.5 mm in diameter and typically 25 cm long. Prior to use, columns were conditioned in a flow of dry He for 24 h at 110°C. He also was the carrier gas for IGC experiments conducted in the range 30 – 50°C., with results at the latter temperature used in the following analyses. Polymer surfaces were probed by vapors of the n-alkanes from nC6 to nC9, and by those of fluids used for contact angle measurements. All vapors were injected at very high dilution from calibrated 1.0 μL Hamilton syringes. In all cases, at least 3 vapor injections were made and retention times, obtained from symmetrical retention peaks, were reproduced to within ±3%.

The characterization of acid-base functionality for the polymers followed well-established principles [6, 15, 16]. In order to obtain reference lines from which to estimate the needed parameters, the retention volumes for the n-alkanes were plotted against their normal boiling points, following the suggestion of Brookman and Sawyer [17]. The retention volumes for the polar probes fell off the linear relationships generated by the alkanes, and the normal distance to the reference line was interpreted as ΔG^{ab}, the acid-base contribution to the free energy of desorption of these vapors. The ΔG^{ab} was used directly as an index of acid-base interaction potential. Values quoted here have an experimental uncertainty not exceeding 7%.

RESULTS AND DISCUSSION

Contact Angle Measurements

As was the case in earlier work [1], considerable time-dependence in values of θ was documented in the present research. The effect was not uniform, however, as illustrated in Figure 1 by the sequence of θ values for PMMA in contact with nC10, THF and DCM. The contact angle for decane, a liquid able to interact with the polymer through dispersion forces only, was constant within experimental error for the entire contact time. Significant time variation was found with THF and, as shown, the effect was more pronounced when DCM was the contacting fluid. Previous studies have shown PMMA to be basic, a finding confirmed by our ΔG^{ab} results, to be discussed shortly. The strong time dependence of θ for the acidic DCM, and the weaker one for the base THF suggests the involvement, in the time dependence of θ, of acid-base interaction at the fluid/solid interface. Further with regard to Figure 1, it is convenient to define two limiting values of the contact angle. An initial value, θ_i, already introduced above, may be obtained by extrapolating the experimental data to zero contact time. This value may be assumed to characterize the polymer surface as

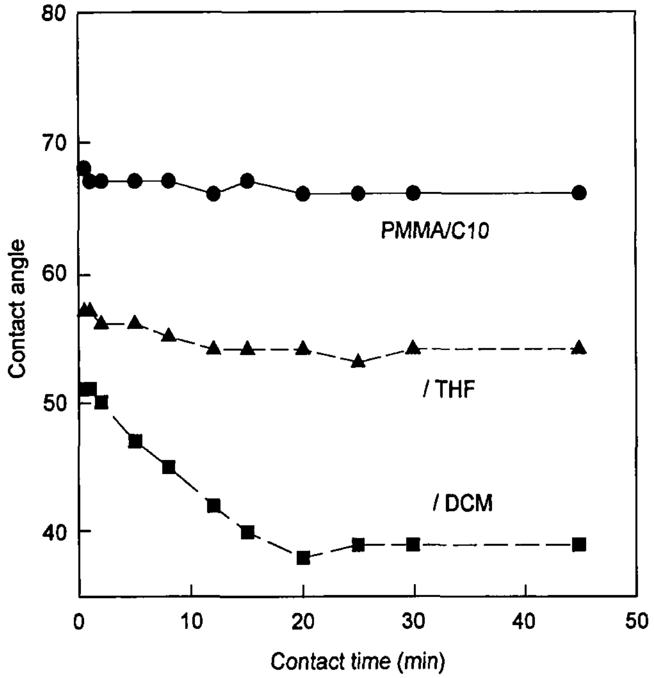

FIGURE 1 Illustrating the time dependence of contact angles; the polymer is PMMA at 30°C.

prepared for the θ measurement. The attainment of steady-state values of θ following prolonged contact with the measuring fluid allows for the definition of an equilibrium value, θ_{eq}. This datum may be assumed to characterize the region of the polymer surface in contact with the fluid after its response to the interfacial forces in play. The difference $\theta_{eq} - \theta_i$ may be used as a convenient parameter describing the total time dependence of contact angles for the polymer-fluid pairs of this work. The data are given in Table I. Several points are noteworthy:

The contact angles for nC10 on all of the polymers are constant over the entire contact period of some 50–60 min. It is reasonable to conclude that dispersion forces alone are ineffective in producing significant time variations in the datum. Obviously, however, this statement must be restricted to cases where the alkane is not a strong solvent for the polymer. The θ for PMMA and the two copolymers in contact with fluids other than nC10 are significantly time-dependent.

TABLE I Variation of contact angles for polymer-fluid pairs

	θ_i	$\theta_{eq.}$	$\Delta(= -[\theta_{eq.} - \theta_i])$
System			
PS/nC10	72	73	0
/THF	55	53	2
/DCM	46	42	4
/Acetone	51	51	0
/ET.Ac.	48	46	2
PMMA/nC10	68	66	2
/THF	57	51	6
/DCM	50	40	10
/Acetone	56	51	5
/ET.Ac.	56	50	6
P(S-4VP)/nC10	71	70	0
/THF	60	53	7
/DCM	52	39	13
/Acetone	52	42	10
/ET.Ac.	56	48	8
P(S-MAA)/nC10	69	70	0
/THF	49	39	10
/DCM	54	48	6
/Acetone	50	42	8
/ET.Ac.	50	44	6

The basicity of PMMA has already been alluded to and the appreciable acid-base characteristics of the copolymers were a subject of previous study [10, 11]. Thus, a general association may be made between the time dependence of θ and the presence of acid-base interactions between polymer and wetting fluid. The case of PS, however, appears at first glance to be an anomaly; PS behaves as a mild base [1, 2], yet the θ values for all fluids are essentially constant. Closer scrutiny of this case is warranted. IGC and surface reorganization data are called on to clarify the issue.

IGC Measurements

Figure 2 illustrates the IGC data with the relationship for PMMA and the volatile probes injected at very high dilution; the temperature is 50°C. The expectation of a linear plot of RT ln Vn *vs.* T_b is fully met when n-alkanes are the vapor probes. Similar excellent linearity was obtained for each of the stationary phases. The placement of the polar

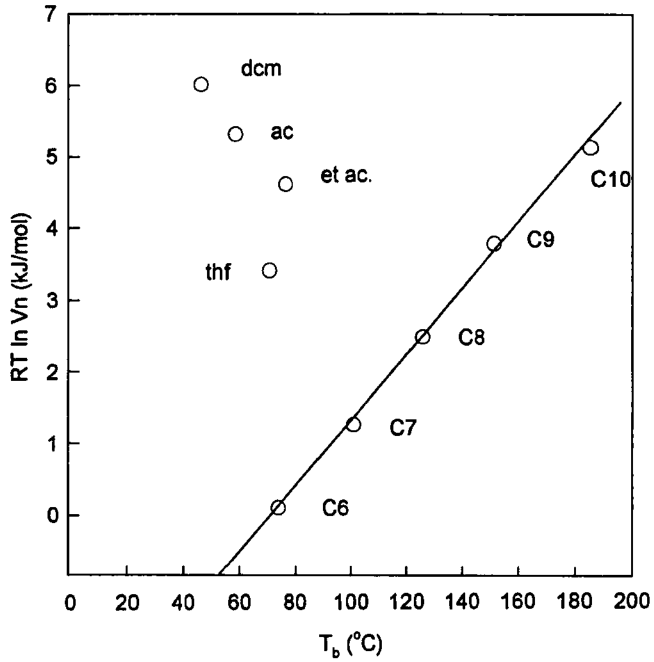

FIGURE 2 Inverse chromatographic data for PMMA at 50°C. Retention volumes for volatile probes are plotted against their normal boiling temperatures, T_b.

probes then permits the evaluation of ΔG^{ab}, as specified earlier. The basicity of the polymer is evident, the distance from the reference line of the acidic DCM being substantially greater than that for the basic THF probe. The amphipatic Ac and EAc probes generate ΔG^{ab} values intermediate between THF and DCM. Table II lists the entire set of free energy parameters. This substantiates the predominantly basic interaction of PMMA and PS surfaces and that of the P(S-4VP) copolymer. The result is expected, both moieties of this macromolecule being significantly basic [10, 11]. The S-MAA copolymer, on the other hand, is somewhat acidic, judging by the relative values of ΔG^{ab} for THF and DCM. Clearly, the procedure of depositing the polymer from solution for chromatographic study leads to a surface composition in which the acidic MAA moiety makes a sizeable contribution to the balance of interactions.

The data in Tables I and II have been used to substantiate the putative correlation between acid-base interaction and the

TABLE II Acid-base contribution to free energy of probe desorption ΔG^{ab} (kJ/mol) for

Polymer	*PS*	*PMMA*	*P(S-4VP)*	*P(S-MAA)*
Probe				
nC10	0	0	0	0
THF	3.7	3.2	3.3	6.4
DCM	6.8	7.6	6.7	4.4
Acetone	5.7	5.2	5.8	5.3
Et. Acetate	5.0	4.4	4.9	5.0

time-dependence of θ. The results are shown in Figures 3 and 4, the former reporting data for the two block copolymers, the latter for the homopolymers. The linear plots in Figure 3 have correlation coefficients of 0.944 and 0.939 for P(S-MAA) and P(S-4VP), respectively. An even better degree of linearity is shown for PMMA in Figure 4, with a correlation coefficient of 0.965. Clearly, for these

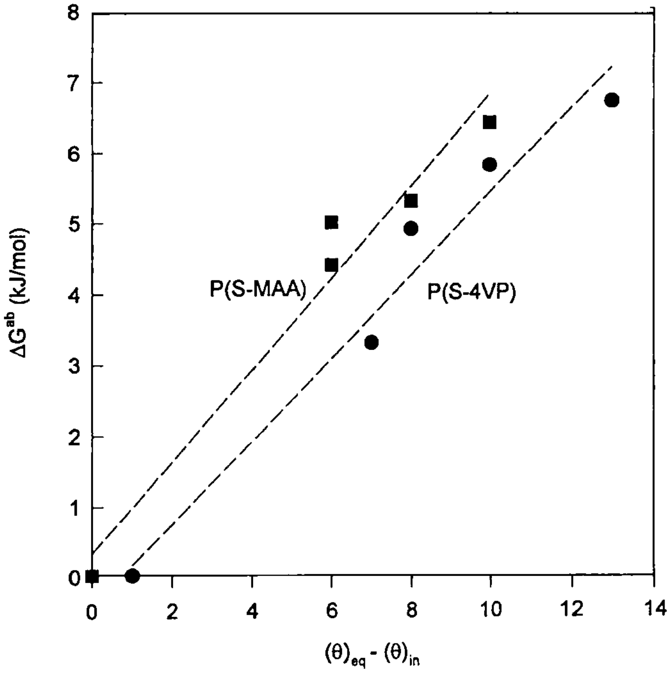

FIGURE 3 Correlation between the acid/base contribution to the adsorption on block copolymers of IGC probes and the time dependence of contact angle measurements for the same fluids.

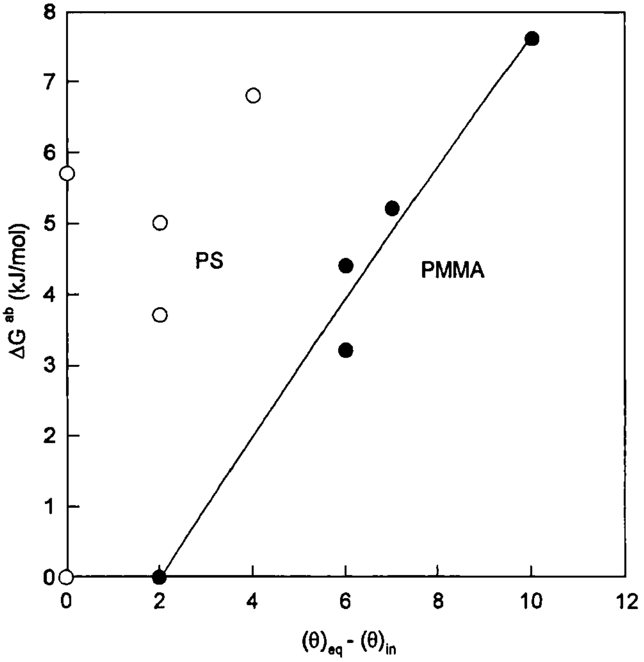

FIGURE 4 Correlation between the acid/base contribution to the adsorption on PMMA, but not on PS, of IGC probes and the time dependence of contact angle measurements for the same fluid.

polymers a quantitative link has been established between acid-base interaction at the solid/liquid interface and the time-dependent variation of the contact angle. The PS case, however, remains anomalous. Although ΔG^{ab} varies appreciably, the variation in contact angle values is slight enough to raise questions about its significance. The relationship between interaction and time-dependence phenomena, in this case, remains in doubt. Thus, acid-base interaction may be termed a necessary but insufficient condition for time-variant contact angles. Further insight into the cause of the apparent anomaly is provided by the surface reorganization results.

Surface Reorganization

The ability of polymers to undergo surface reorganization when in contact with orienting media has been demonstrated on numerous occasions [6–9]. The driving force is thermodynamic. In contact with a non-polar medium, such as air, n-alkane, *etc.*, a polymer capable of surface reorganization will tend to orient non-polar moieties into the surface region in order to minimize the surface free energy. When in contact with a polar medium, in the present work represented by DCM, THF, Ac and EAc, the polymer must orient so as to minimize the interfacial tension. The reorganization has been shown to be a diffusion-dependent process [6–9], its kinetics a function of temperature and molecular structure. The polar component of the surface tension, γ^p, obtained by the procedure stated earlier in this article, is a convenient parameter for following the reorganization process. Figure 5 presents the results for PMMA and PS. In its initial state of equilibrium in air, the PMMA reports a γ^p of 2.9 mJ/m^2. In contact with DCM, the value rises over a period of some 100 h to a steady state value of 4.0 mJ/m^2. Cause for the effect may be attributed to a greater

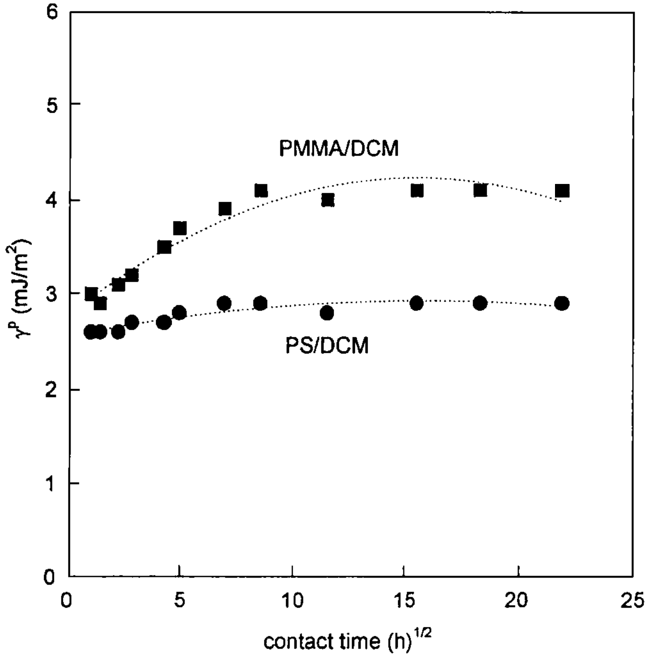

FIGURE 5 Response of the polar contribution to surface energy of PMMA and of PS to extended contact with DCM at 50°C.

concentration of pendent methacrylate groups in the surface region when the polymer is contacted with the orienting DCM fluid. In contrast, the γ^p of PS is non-responsive; no reorganization takes place when the polymer is taken from a non-orienting to an orienting medium.

A more detailed view of the reorganization potential of the polymers used here is given in Table III. The PS may be taken as incapable of surface reorganization. PMMA reorganizes in strongly acidic and amphipatic media with a significant acid component. The copolymers respond more dramatically. Since the surface energy of the S component is lower than that of either 4VP or MAA, it must be the S moiety which is preferentially oriented into the surface region when the polymer is in equilibrium with air or other non-orienting media. This contention has been confirmed in previously published work [10, 11]. In P(S-4VP) both constituents are basic. Thus, contact with basic media (THF) may produce a slight increase in the relative surface preponderance of S with minor effects on the surface energy, but major reorganization should occur when acidic media motivate a larger surface concentration of 4VP linkages. The response of γ^p values strongly supports this suggestion. In P(S-MAA) basic media (THF) should be prime sources of surface reorganization, as is the case. Acidic fluids (DCM) merely reinforce the tendency for surface preponderance of S groups, already characteristic of this polymer when in contact with air. The surface reorganization of polymers, caused by changes in the strength of acid-base interactions, then may be postulated as a principal source for time-dependence in contact angle measurements. The contention predicts the existence of a correlation between $\Delta\gamma^p$ and $\Delta\theta$, and is tested by the data in Figure 6.

The relationship shown in Figure 6 is sufficient to confirm the hypothesis, but the scatter of data indicates that time-dependence of θ

TABLE III Polar surface energy increment – evidence of surface restructuring

$\Delta\gamma^{ab}$ (mJ/m^2) *for*	*PS*	*PMMA*	*P(S-4VP)*	*P(S-MAA)*
nC10	0	0	0	0
THF	0	0.5	1.8	5.6
DCM	0.3	1.1	6.6	2.5
Acetone	0.2	0.9	4.9	4.5
Et. Ac.	0	0.7	5.0	4.2

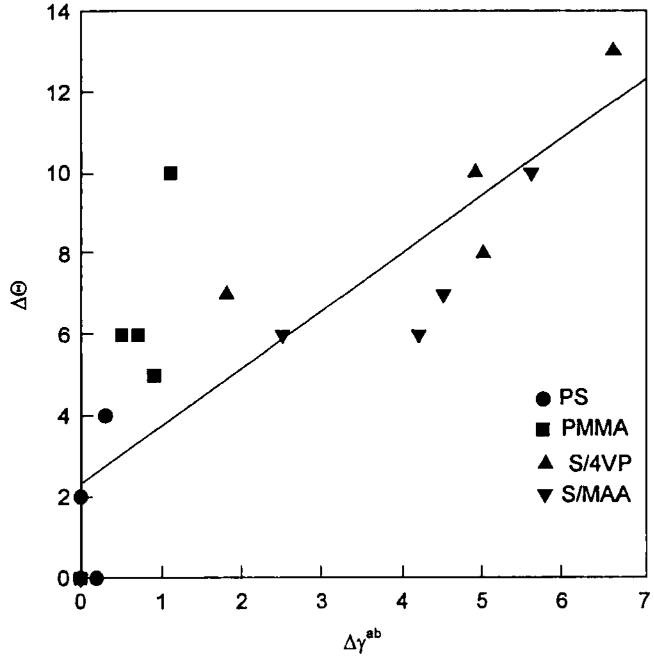

FIGURE 6 View of apparent relationship between surface reorganization tendencies of polymers and their time-dependent contact angle measurements.

is more complex. Several reasons are put forth to account for the less-than-expected quality of the correlation. First, the effect of polymer swelling during prolonged contact with the liquids of this work cannot be ruled out. Visual, and in some instances gravimetric, observation showed no evidence of this, but slight perturbations of the polymer surface by imbibed liquid may escape these observations, yet affect the θ datum. Second, it is possible that θ and γ^p are sensitive to surface reorganization to different degrees. Thus, a steady-state indication signaled by one parameter may not necessarily mandate time independence in the other. Finally, different degrees of surface reorganization may be produced by immersion of the polymer in fluid and by a droplet of the fluid localized on a small section of the surface. The latter case, typified by the θ measurement, may produce local surface stresses and, thus, changes in the surface energy, not totally simulated by the procedure used here to monitor $\Delta\gamma^p$. Nevertheless, the results of this study fully confirm the earlier preliminary work [1,2] and show that careful attention is to be paid to possible time-dependent phenomena in the collection of contact angle data, if these are to have more than anecdotal significance. The strong contribution of polymer surface reorganization to time-dependence effects is evident and is to be attributed to the strength of acid-base interactions at polymer-test liquid contacts.

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