Surface Characteristics of Solvent-Cast Polymers

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Synopsis

Films of poly(methyl methacrylate) (PMMA), polystyrene, and a styrene/acrylic terpolymer have been cast from solutions of varying thermodynamic quality and the film properties studied by inverse gas chromatography and by critical surface tension measurements. Surface properties of the non-polar polystyrene were independent of solvent medium, but significant variations in these properties were observed in the case of PMMA and the terpolymer. Solvent balance also appeared to affect the bulk properties of the latter films, as judged by the penetration rates of interacting liquids. The observations indicate the feasibility of controlling film properties of the solid by the appropriate selection of solution media; a time-dependent variation in solid properties is to be expected, however, as the film structure attains an equilibrium state.

INTRODUCTION

The ever rising demand for polymeric materials to deliver optimum performance in their varied fields of application is nowhere more pronounced than in the area of protective coatings. Here the technology associated with the application and use of coatings is further complicated by the rules of environmental conservation, which are narrowing and redefining the range of acceptable solvents and thereby focusing new attention on the response of polymer film properties to the solvent balance from which these films are formed. It is widely recognized that solvent quality determines the chain configuration of macromolecules in solution.[1] Consequently, it might be expected that this polymer–solvent balance would also affect the manner in which polymer chains pack together in the coating and therefore influence its bulk and surface characteristics. Earlier, we have shown[2] that the surface properties of poly(methyl methacrylate) (PMMA), deposited onto inert reference substrates from solvents of varying thermodynamic quality varied significantly, as judged by their retention capacities for selected vapor probes in a gas chromatographic investigation. This lent credence to the suggested relationship between the polymer state in solution and its properties in the solid state, and motivated an extension of research, the results of which are reported here.

In this article we report surface properties for three polymers cast into film form from solutions in which the polymers had very different configurations as judged from intrinsic viscosity data. As in the earlier work,[2] gas chromatography was used to obtain retention volume data (V_g^0) and here we also present critical surface tension values (γ_0). The critical surface tension data though less precise than chromatographic results, were used as an independent check of apparent differences in surface states, indicated by the chromatographic results. In certain

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surface tension experiments, interacting liquids were contacted with the polymer films and the penetration rates of these liquids into the films were followed as a means of detecting possible variations in bulk, as well as surface properties, arising from variations in the balance between solvent and polymer solute.

EXPERIMENTAL

Materials

Three polymers, all of potential interest as film-formers, were used. One of these was the PMMA sample employed earlier[2]; its M_v (toluene) = 130,000 and T_g = 105°C (by differential scanning calorimetry). Also involved was a polystyrene (PS) sample with narrow molecular weight distribution, M_w = 82,000, and T_g = 94°C, and a styrene/butyl acrylate/methacrylic acid terpolymer (S/BA/MAA), with a wt % composition ratio of S/BA/MAA = 80/15/5. The latter commercially produced sample had been used in earlier rheological studies,[3] and had an apparent M_w = 170,000 and T_g = 55°C.

The solvents chosen for the deposition of polymer films reflected common industrial usage. They are given in Table I along with the pertinent intrinsic viscosities at 30°C. In the case of PMMA, systems P_2 and P_4, though involving respectively a nonpolar and polar modifier to the base solvent toluene, are very near the θ point.[1] The polymer is therefore assumed to be in a tightly coiled configuration. The relatively high $[\eta]$ in chloroform (system P_5) indicates that the polymer is in a significantly extended state in this case. The $[\eta]$ values for PS and S/BA/MAA vary appreciably though the solvents brought neither of these materials near a corresponding θ point. Further descriptions of materials are included in the following sections.

· Chromatography

The use of inverse gas chromatography in studies of interactions between polymer stationary phases and selected mobile vapor phases near infinite dilution has become a popular investigative tool.[4,5] The apparatus and procedures used in the present case have been discussed in an earlier article.[2] Details of column composition are given in Table I. Compositions were determined by ashing to constant weight, and a correction was applied for weight loss incurred in ashing the uncoated chromosorb W support.[6] All columns were aged at 50°C for 12 hr

TABLE I
Polymer/Solvent Systems

| Polymer: | | PMMA | | | | PS | | S/BA/MAA | |
Code	P_1	P_2	P_3	P_4	P_5	S_1	S_2	TP_1	TP_2
Solvent[a]	t	t/h 80/20	t/b 80/20	t/b 40/60	c	t	t/b 60/40	t	ed/e 95/5
$[\eta]$(dl g^{-1})	0.298	0.165	0.350	0.165	0.534	0.372	0.225	0.308	0.491
wt % polym. in chromato. column	6.90	7.01	7.70	7.53	5.91	8.15	7.40	6.33	7.12

[a] Solvent code: t = toluene; h = n-heptane; b = n-butanol; c = chloroform; ed = ethylene dichloride; e = ethanol.

under vacuum before performing measurements at 30°C. In PMMA, measurements at 30°C were repeated after the columns had been baked for 48 hr at 150°C, under a flow of N_2. Samples of coated chromosorb involving all of the systems indicated in Table I were also exposed at 50°C in near vacuum and weighed after selected exposure periods to ensure that no significant retention of solvents was incurred by this preparation procedure. In general, small weight losses were observed in the first 2 hr of conditioning but thereafter only minor and random drifts in sample weight (net variation ±3%) occurred. We conclude that solvent retention by the solidified polymers is not a significant issue. A total of five vapor probes were selected and these are listed with the experimental data in Table II. For ease of comparison this tabulation reproduces certain of the PMMA data reported in our earlier study.[2] The probes were chosen so as to reflect a range of intermolecular forces. As noted already,[2] present experiments were performed under nonideal equilibrium conditions, hence no attempt was made to compute thermodynamic interaction parameters[1,7] for the polymer–probe pairs. Instead, specific retention volumes V_g^0 were calculated using the expression of Littlewood and co-workers,[8] and these were used to characterize the interaction between probe and polymer surface. Since all chromatographic experiments were conducted well below the T_g values for the polymers, we expect bulk sorption to have been negligible and consequently the V_g^0 was a precise measure of surface characteristics for the polymers.

Surface Tension

The experimental procedure for measuring γ_c has been described in detail elsewhere.[9,10] Briefly the method involves depositing constant-volume droplets of reference liquids with known surface tension (γ_{LV}) onto a polymer film supported on a metal substrate and in good thermal contact with a temperature-controlled metal bar. Photographs of the droplets, taken from a position exactly normal to the plane of the polymer specimen, are used to produce prints of the image on standard paper, and the weights of the image are then recorded. Plots of the image weight versus γ_{LV} produce generally linear segments which may then be used, in the manner of ref. 10, to estimate γ_c. The γ_c is, of course, not a precise thermodynamic quantity.[11] It is a pragmatic measure of the surface state in low surface energy solids however, and hence useful in the present context of comparison.

In this work, polymer films 0.004 ± .0005 cm thick were cast onto freshly de-

TABLE II
Specific Retention Volumes for Polymer/Vapor Pairs at 30°C[a]

System Probe	P_1	P_2	P_3	P_4	P_5	S_1	S_2	TP_1	TP_2
n-octane	95.0	88.0	81.0	76.0	53.0	311.0	308.0	263.5	240.0
2,2,5-trimethyl hexene	111.0	106.0	91.0	79.0	58.0	277.0	279.5	281.0	247.0
toluene	67.0	70.0	116.0	89.0	46.0	355.0	360.0	306.0	512.0
p-dioxane	63.0	70.0	135.0	150.0	56.0	208.0	200.0	129.0	173.0
propyl acetate	82.0	90.0	185.0	210.0	56.0	167.0	171.0	145.0	191.0

[a] Specific retention volumes (V_g^0) in ml g^{-1}.

greased "Bonderite" steel panels, and these were conditioned under reduced pressure of N_2 for 12–24 hr at 60°C prior to use. All γ_c measurements were at 30°C. For this purpose, hypodermic microsyringes were used to deposit 10 μl droplets of reference liquids onto the film surface. The reference liquids were solutions of reagent grade propionic acid in distilled water. Their compositions and γ_{LV} measured using a du Nuoy ring tensiometer were as follows:

　(1)　1.91% acid, $\gamma_{LV} = 60.2$ dyn cm^{-1}
　(2)　5.84% acid, $\gamma_{LV} = 49.2$ dyn cm^{-1}
　(3)　9.80% acid, $\gamma_{LV} = 44.0$ dyn cm^{-1}
　(4)　13.00% acid, $\gamma_{LV} = 40.9$ dyn cm^{-1}
　(5)　21.78% acid, $\gamma_{LV} = 35.8$ dyn cm^{-1}

The liquids were shown, in preliminary experiments, to interact slowly with PMMA and the terpolymer. Accordingly, droplet shapes were photographed at 1-min intervals for the first 5 min of contact, and the weights of shapes so generated were extrapolated to zero contact time. This defined an effective droplet weight $\overline{W}$ free of errors because of the possible interaction between film and fluid. The γ_c values obtained from representations of $\overline{W}$ against γ_{LV} (ref. 10) were reproducible to within ±0.6 dyn cm^{-1}.

RESULTS AND DISCUSSION

The chromatographic data and the surface tension results are presented in Tables II and III, respectively. Because of the high precision of V_g^0 data, in the present case reproducible to ±1% or better, Table II may be considered to show important differences in the surface character of PMMA films deposited from the various solvent media.[2] Particularly noteworthy is the uniformly low set of V_g^0 values for system P_5. Chloroform is an excellent solvent for PMMA (see $[\eta]$ in Table I) and the polymer therefore exists in a relatively extended chain configuration in this solution. We assume that the polymer will deposit in a similar configuration onto the substrate,[12] and will tend to form into tightly packed void-free films into which vapor penetration is restricted, resulting in low retention times. In thermodynamically less efficient solvents, such as toluene, chains are more tightly coiled, intramolecular interactions will be favored over intermolecular linkages, and a more porous film structure may be postulated, along the lines of Boberski.[13] Retention of vapors by such films will tend to be greater than in the above case. Also of interest are the distinct V_g^0 values of films from systems P_2 and P_4; though in each case the polymer solution is near the θ condition, the solid properties clearly reflect the fact that the two solvent mod-

TABLE III
Critical Surface Tension of Polymer Films at 30°C

System:	PMMA	γ_c[a]	PS	γ_c[a]	Terpolymer	γ_c[a]
	P_1	41.5	S_1	34.6	TP_1	34.1
	P_2	42.0	S_2	35.0	TP_2	35.3
	P_3	40.5				
	P_4	41.8				
	P_5	39.2				

[a] Units are dyn cm^{-1}.

ifiers in these cases are of very different polar character. It seems possible that the relative concentrations of polar and nonpolar polymer moieties in the film surface vary with solvent balance, thereby at least partially accounting for the chromatographic results. As already noted, however,[2] no simple correlation between V_g^0 and the thermodynamic quality of solutions from which the films are cast can as yet be started, and a fuller discussion of this subject must therefore be deferred.

The importance of polar groupings in the polymer to the dependence of surface properties on solvent balance seems to be confirmed by the PS and S/BA/MAA data in Table II. In spite of distinct differences in the configuration of PS chains in the two solutions, no detectable change in V_g^0 is noted. The surface properties of PS appear to be independent of the solution history. The range of V_g^0 is narrow, the exception being data for the polar propyl acetate probe, which is much less "compatible" with the polymer than the remaining vapors.

The absolute values of V_g^0 for the terpolymer resemble those for PS, but the solvent-balance effect is observed here, consistent with the presence of polar constituents in this polymer. The general similarity in numerical V_g^0 values between PS and terpolymer indicate the dominance of PS moieties in the surface structure of the terpolymer—a tendency consistent with the thermodynamic requirement for minimizing the surface free energy of the solid. The TP_2 system, however, involving films produced from the thermodynamically stronger solvent (see $[\eta]$ values) has lower V_g^0 values for the aliphatic probes, but higher V_g^0 for the more polar groups. Arguably in this case, a relatively higher proportion of polar groups is present in the surface. The observation relates to other aspects of the polar/nonpolar constituent balance in the surface of this terpolymer,[10] as discussed previously.

The γ_c data in Table III, though less precise than the V_g^0 values, present independent confirmation of the trends established by the chromatographic results. The γ_c for PS is independent of the solvent balance in the two cases, as was V_g^0, but the surface tensions for both terpolymer and particularly PMMA again vary significantly with the solvent balance. The very complex surface properties of the terpolymer will require further study for their adequate understanding. We suggest in the more fully investigated case of PMMA, however, that the low γ_c value for films P_5 indicates that the surface structure of these films is closer to equilibrium than are those in systems P_1–P_4. A time-dependent change in the latter's surface properties toward those of system P_5 may therefore be expected. This suggestion is confirmed by comparing V_g^0 data of PMMA columns before and after these have been exposed to a 48 hr/150°C bake. The pertinent data were previously published,[2] and for completeness are reproduced in Table IV. The very slight decrease of some 4% in the V_g^0 for system P_5 is consistent with the equilibrium nature of the surface structure in this system. In contrast, V_g^0 values in columns P_1–P_4 were strongly influenced by the baking process. The effect of high temperature exposure is complex, the interaction between polymer and probe becoming more selective. Thus, systems P_3, P_4 become strongly interactive with nonpolar probes but correspondingly less strongly interacting with the more polar vapor molecules following baking. P_1–P_2 become uniformly less interacting with the vapor phase, regardless of the nature of the probe molecule. While the specific changes induced in the polymer surface by heating clearly are complex and cannot be further explained at this time, they contrast strongly with

TABLE IV
Comparison of V_g^0 Values in PMMA/Probe Pairs for Polymer Baked 48 hr/150°C and
Polymer in Initial State[a]

$(V_g^0)_t/(V_g^0)_{ref}$ Probe	P_1	P_2	P_3	P_4	P_5
n-octane	0.884	0.931	1.148	1.461	0.981
2,2,5-trimethyl hexane	0.856	0.792	1.056	1.493	0.931
toluene	0.910	0.871	0.939	1.000	0.956
p-dioxane	0.968	0.743	0.874	0.700	1.000
propyl acetate	0.939	0.811	—	0.848	1.000

[a] All V_g^0 data are at 30°C.

the stability of system P_5 and thus support the suggestions of a thermodynamic origin for these observations. The long exposure at 150°C is tantamount to an accelerated aging step, and it is therefore evident that in spite of their metastability, the surface properties of films P_1–P_4 will persist for very long times under normal use conditions.

In all of the above, emphasis has been placed on film surface properties. Assuming the films to be essentially isotropic, the previously noted tendency for droplets of propionic acid solution to penetrate into the PMMA and terpolymer films, however, suggests that it may be feasible to seek variations in polymer bulk properties from measurements of solvent penetration rates. The existence of practical consequences arising from the indicated dependence of film surface structure on the solvent medium would also thereby be inferred. Accordingly, the penetration (spreading) rate of droplets into the various films was measured at 30°C, by evaluating the parameter $\overline{W}$ as a function of contact time, up to contact periods of 60 min. Droplets of test solution 4 (13% propionic acid) were used for the polar polymers; for convenience of testing, toluene was contacted with PS films. The gradual increase in droplet size for a PMMA film cast from toluene (system P_1) is demonstrated in Figure 1. The parameter $\overline{W}/\overline{W}_0$, where $\overline{W}_0$ is now the weight of trace made by the contacting liquid at zero contact time, is plotted versus contact time for the three polymers, in the pertinent parts of Figure 2.

The behavior of the nonpolar PS is uncomplicated: penetration of the film by toluene droplets is appreciable, but the rate of solvent attack is not affected by the solvent history of this polymer. The barrier properties of PMMA and
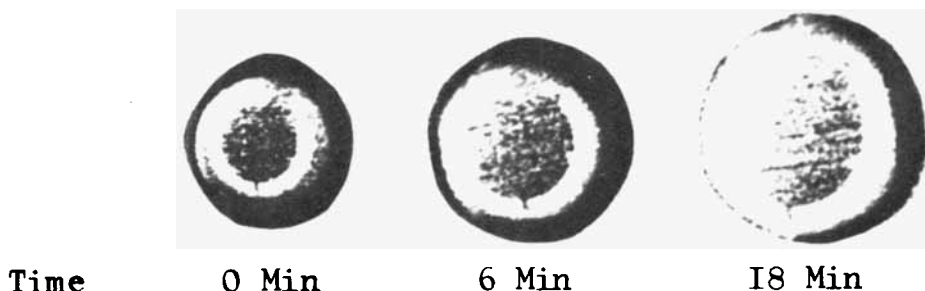

Time   0 Min   6 Min   I8 Min

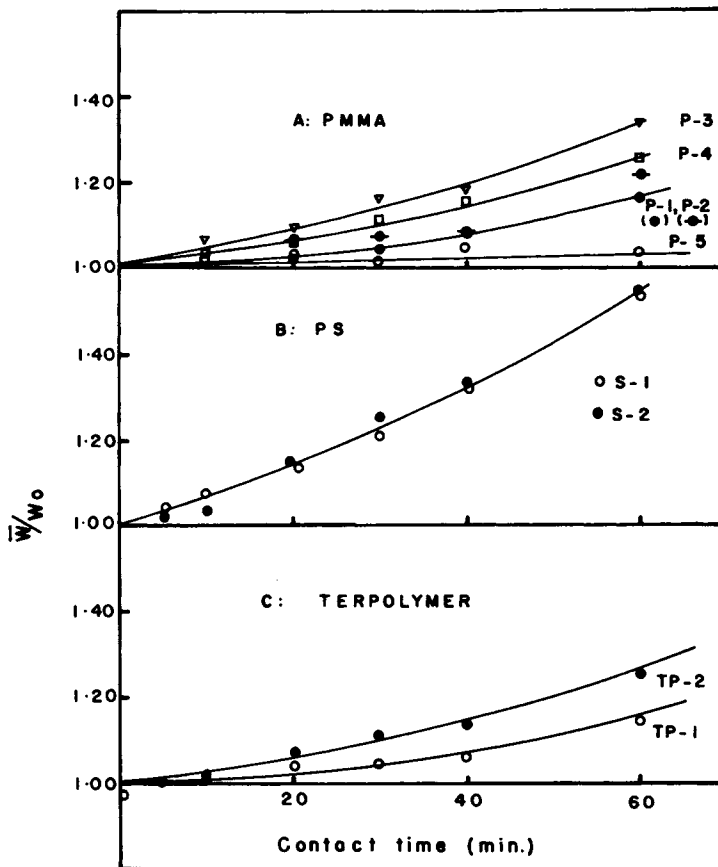Fig. 1. Time-dependent increase in droplet size for propionic acid solution on PMMA film cast from toluene; $T = 30$°C.

Fig. 2. Penetration rates of liquids in polymers cast from solution. (Propionic acid solution on PMMA and TP; toluene on PS films); $T = 30°C$.

terpolymer to acid solutions, however, are by no means single-valued characteristics. The most highly resistant PMMA film is again P_5, for which we had previously deduced a close-packed structure of extended chains. As before, P_2 and P_4 have dissimilar barrier properties in spite of the polymer having been near θ condition in both cases. Presumably this is in keeping with the different polar character of the modifying solvent in the pertinent solution. The high penetration of acid solution into P_3 is of particular interest. Evidently, polymer swollen in solution by the polar butanol deposits in a much looser structure than when chloroform is the solvent. Butanol is a relatively high-boiling liquid, and one possible result may be an increase in the fraction of surface-oriented polar groups in the film with a consequent higher tendency of the film to interact with polar liquids. The similar behavior of terpolymer film TP_2 tends to reinforce the possibility of there being varying proportions of polar and nonpolar constituents in the surface layer of films formed from these complex materials.

CONCLUSIONS

The combination of retention volume, critical surface tension, and liquid penetration rate data for polymer films has shown that surface interaction and, apparently, bulk properties of such films may be complex functions of the solvent

balance in solution from which the films were formed. The apparent dependence of surface and bulk polymer properties on solvent history applies to chemically complex macromolecules combining polar and nonpolar constituents. In a chemically simple material such as polystyrene, however, surface and bulk properties were found to be independent of the solvent balance variable. These results indicate that a potentially valuable performance control parameter is available to the coatings technologist. It is noted, however, that for any polymer only a single equilibrium surface structure can obtain; when a nonequilibrium surface condition is produced, slow but significant time-dependent variations in film properties are to be expected as the equilibrium condition is sought and attained.

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