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### Nonuniformity in Thin Polymer Films

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## **Nonuniformity in Thin Polymer Films**

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### **ABSTRACT**

Thin polymer films solidified from solutions can display a broad range of barrier and mechanical properties, depending on the quality of the solvent and the initial polymer concentration. These findings apply specifically to polymers containing polar groups,

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exemplified in this work by polymethyl methacrylate and a styrene-butyl acrylate copolymer, but not to polymers like polystyrene. In the former two cases it has also been shown that very different surface tensions exist at the air and the substrate interface, provided the films were solidified against high surface energy solids. These observations have been attributed to the ability of polar-group-containing polymers to adopt various chain conformations at and near interfaces, these conformations reflecting interactions between polymer and solvents and between polymer and substrate. An additional contribution is attributed to the degree of chain entanglement persisting in solutions. The measured properties often pertain to metastable states of the films, and the findings thus indicate the existence of a thermodynamic driving force for the time-dependent change (aging) in properties of protective films.

## INTRODUCTION

It is increasingly apparent that the conformational properties of certain polymers cast as thin films can vary considerably, depending on the precise condition of film preparation. Thus, the helix-coil characteristics of biological polymers are determined by the solvents from which these polymers are cast [1], and a more general dependence of polymer surface properties on the solvent media from which they are formed has been reported by Prest [2]. The detailed configuration of chain molecules at interfaces, particularly of those macromolecules containing polar groups, is also a current focal point of theoretical consideration [3]. The importance of the problem is therefore discernible at both theoretical and experimental levels.

Work in our laboratories focusing on surface and interfacial properties of film-forming polymers has clearly indicated the complexity of this issue. Inverse gas chromatography has shown [4, 5] that in such polymers as PMMA the retention of vapors was strongly dependent on the solvent from which the polymer was cast, although little difference could be detected in the critical surface tension ( $\gamma_c$ ) of these polymers.

In contrast, with nonpolar polystyrene, the retention properties of films were not dependent on the casting solvent medium.

In more recent work [6] a broader impact of film formation conditions on properties was noted. Films of PMMA were deposited onto metal and polymer substrates, again using solvents with varying thermodynamic interaction with the polymer. Though  $\gamma_c$  at the air interface was again essentially independent of solvent medium, the barrier properties of films to polar and nonpolar liquids varied broadly [6], suggesting that polymer chain conformation as well as the packing density in the bulk films was solvent-dependent. An observation of particular interest concerned the  $\gamma_c$  of the PMMA surfaces removed from substrate

interfaces: when cast onto a low energy solid (PTFE), the  $\gamma_c$  at the substrate interface was found to be equal to that at the air interface. However, films removed from Hg had higher  $\gamma_c$  values at the substrate than at the air interface [6]. These films were therefore nonisotropic and could be considered subject to time-dependent (aging) property changes as thermodynamic demands for equilibrium isotropic states were met.

The above subject is further considered in the present report, which extends the data base to films cast onto a wider range of solid substrates, and involves copolymeric film-formers in addition to PMMA and PS. The aging or relaxation phenomena alluded to above have been studied more explicitly, as have the variations in transport and in mechanical properties of selected films, arising from differences in film formation procedures. The paper therefore touches on aspects of nonuniformity in both surface and bulk properties of thin films.

## EXPERIMENTAL

### 1. Materials

The commercial PMMA sample used was that already described [6]; its  $T_g = 105^\circ\text{C}$  and the  $M_v$  was found to be  $1.1 \times 10^5$ . An isotactic, commercial PS (Dow Chemical Co.) used in this work had an intrinsic viscosity showing that  $M_v = 8.2 \times 10^4$ . The styrene (S)-butylacrylate (BA) copolymer was kindly supplied by C-I-L Paints Inc. of Toronto, Canada. The copolymer composition was S/BA = 85/15 (mol%), and the material displayed a  $T_g$  near  $63^\circ\text{C}$ . Solvents involved were chloroform (c), toluene (t), mixtures of toluene-butanol (t/b) and, in a few instances, toluene-heptane (t/h) and cyclohexane (cx). Intrinsic viscosities  $[\eta]$  of the polymers in these solvents were determined using Ubbelohde-type viscometers. Solutions of PMMA and S/BA in toluene were titrated with n-butanol to cloud points in order to define solvent compositions and  $[\eta]_0$ .

### 2. Filming Procedures and Property Evaluations

Solutions of the polymers at initial concentrations of 5, 10, 15 and 20 wt% were used in film-forming operations. The substrates were freshly milled and acetone-washed PTFE, doubly-distilled Hg maintained in a dust-free chamber, and freshly degreased and dried panels and foils of steel, copper, and gold. Solutions placed on the substrates were drawn down to uniform wet thickness and dried to give solid films about  $30 \mu\text{m}$  thick. Drying was in vacuum at  $50^\circ\text{C}$  for up to 72 h. These

conditions were set by exploratory work in which infrared spectra were used to ensure the disappearance of all features associated with retained solvent. Dried films supported on steel were used for property characterizations as noted below; in the case of PTFE and Hg substrates, the dried films were carefully lifted to permit study of both air and substrate interfaces. Films were also recovered from Cu and Au by contacting with Hg until the amalgamated metals could be easily removed from the polymer. Polymers so recovered were again exposed to vacuum at room temperature for 1 h before further use.

Surface characterization and barrier property evaluation followed the precedent of earlier reported work [6]. Critical surface tensions were obtained by following the Zisman approach [7]; constant volumes of nominally noninteracting fluids were placed on polymer surfaces for contact angle determinations. These fluids included water (W,  $\gamma_L = 72.6 \text{ mJ/m}^2$ ), formamide (F,  $\gamma_L = 58.2 \text{ mJ/m}^2$ ), di-iodomethane (DM,  $\gamma_L = 50.8 \text{ mJ/m}^2$ ), and bromonaphthalene (BN,  $\gamma_L = 44.6 \text{ mJ/m}^2$ ). Contact angles were measured on photographs taken of liquid droplets over contact times of up to 10 min. For purposes of procedure normalization, extrapolations of contact angles to zero contact time were used for  $\gamma_c$  estimates, thus also avoiding errors due to possible polymer-liquid interactions. The photographic method was also well suited for evaluating barrier properties of films, as detailed in Ref. 6.

Mechanical properties of supported films were measured using the Microindentation Hardness Tester (MIHT), developed by ICI Paints Division and illustrated in Fig. 1. In this procedure, supported film specimens were maintained on a thermostated stage ( $22^\circ\text{C}$ ) and deformed by applying to the surface a spherical needle ( $r = 1.58 \text{ mm}$ ) under a load of 1 g for 2 min. Penetration of the needle triggers a response in a pneumatic sensing system, giving a measure of the penetration depth. On removal of the load, relaxation of the film can be traced, so that a deformation-relaxation record is obtained (lower portion of Fig. 1). In the example given in Fig. 1,  $X_m$  is the maximum deformation and  $X$  the equilibrium (permanent) deformation level. The MIHT assembly is operated in a dust-free dry box (not shown) to avoid random errors arising from changes in relative humidity or from the intrusion of dust particles in the vicinity of the needle probe.

## RESULTS AND DISCUSSION

### 1. Intrinsic Viscosities

Intrinsic viscosity data are summarized in Table 1. Evidently, the polymers are substantially chain-extended in chloroform [8]. In  $t/b =$

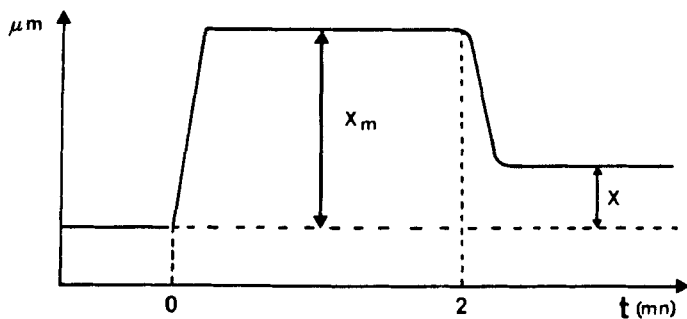
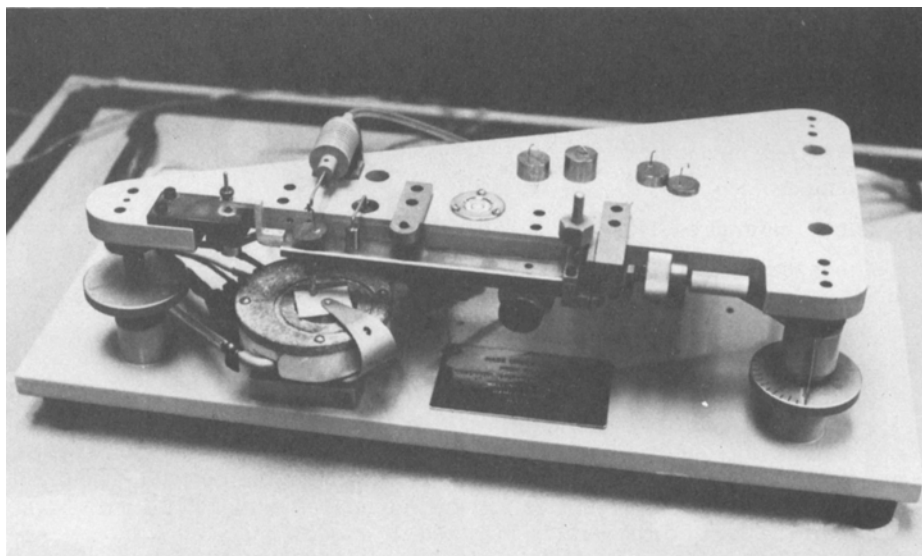


FIG. 1. Top: Microindentation Hardness Tester; spherical needle in contact with specimen on thermostated stage. Bottom: Typical indentation trace, showing maximum deformation,  $X_m$ , and steady-state value,  $X$ . Load applied at point 0, removed at 2.

TABLE 1. Intrinsic Viscosities (30°C) of Polymers Studied

Solvent	PMMA	$[\eta]$ , dL/g, S/BA	S
Chloroform	0.420	0.611	-
Toluene	0.260	0.437	0.56
Toluene/butanol (1:1)	0.230	0.350	0.27
Toluene/butanol <sub><math>\theta</math></sub> <sup>a</sup>			

<sup>a</sup>23/47 for PMMA, 42/58 for S/BA.

1:1, the chains are in significantly coiled states, being close to the corresponding  $\theta$ -solvent compositions. The copolymer is less tolerant to the presence of butanol, presumably because the concentration of polar (interactive) groups is reduced compared with PMMA. Because of the rapid drying rates involved, it may be postulated that the chain conformation in solution is carried over into the solid state [2, 4, 5]. Morphological effects (e.g., different chain orientations and packing densities) may then be expected in the thin films arising from these solutions. These expectations have already been cited in accounting for the various gas chromatographic and barrier property results reported earlier [6].

## 2. Barrier and Mechanical Properties

Barrier properties were characterized by rates of droplet penetration, using the photographic method described in Ref. 6. This required plotting the ratio of droplet volumes supported on the film surface at some finite contact time to the initial droplet volume,  $V/V_0$ , vs the square root of contact time, basing this on the assumption that changes in droplet volumes arise due to diffusion dependent processes. Thus,

$$V/V_0 = 1 - Kt^{1/2}, \quad (1)$$

where  $K$  is an overall transport coefficient characteristic of the interaction between polymer-droplet pairs. The results shown in Fig. 2 are typical examples of data obtained. Each datum is the average of at least three separate experiments. The data show, inter alia, that the assumption of diffusion-dependent processes is justifiable and, as is further noted below, that the barrier characteristics of the PMMA and S/BA films are notably dependent both on the solvent from which the films were formed and on the initial polymer concentration. The

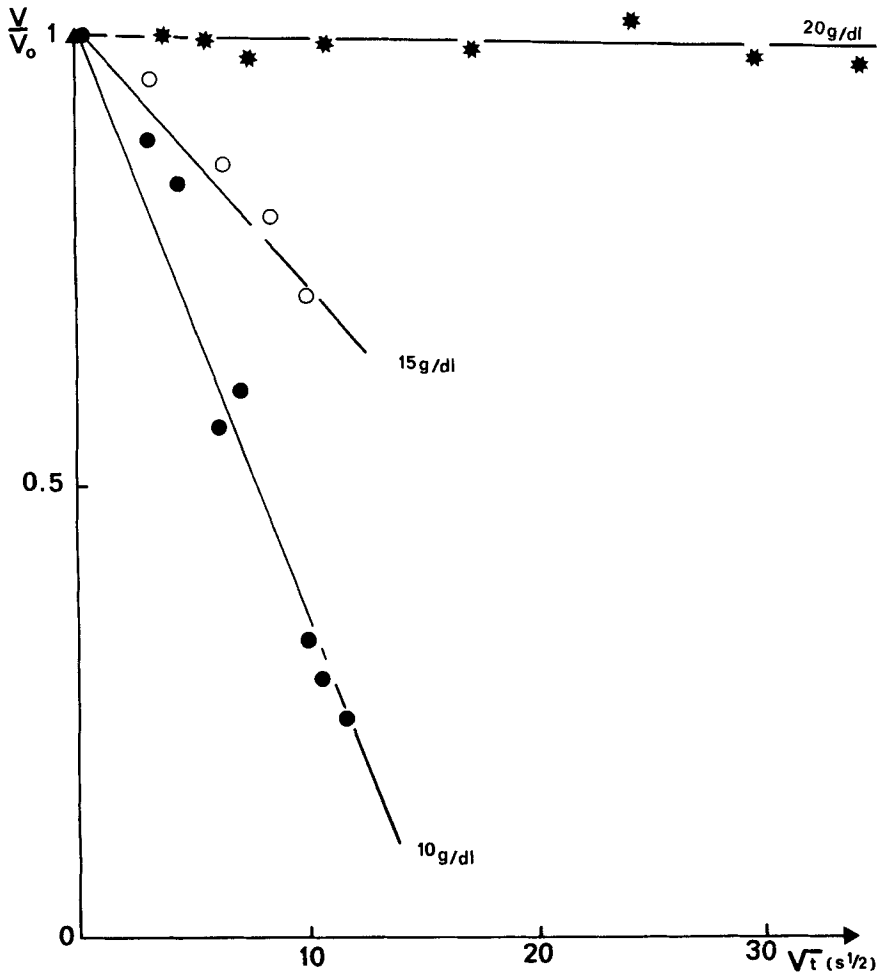


FIG. 2. Spreading (penetration) of BN through PMMA cast from toluene-butanol (1:1).

barrier properties of PS films are more uniform, their dependence on initial polymer concentration being slight and little if any effect due to choice of solvent is evident. The pertinent results may be summarized conveniently by values of the liquid transport coefficient,  $K$ . These are entered in Table 2 and again are averaged from at least three separate determinations, with an error in  $K$  of less than 10%.

As will be noted later on, the surface tensions of these polymers at the air interface again are essentially independent of film-formation



TABLE 2. Transport Coefficient K for Various Liquid-Polymer Pairs,  $K \times 10^4 \text{ min}^{1/2}$

Polymer and coatings detail	Contact liquid			
	BN	DM	F	W
PMMA from:				
c 5 g/dL	19.0	8.5	6.2	3.2
c 10 g/dL	12.6	5.8	3.7	1.1
c 15 g/dL	10.1	5.0	3.0	0.9
c 20 g/dL	5.6	3.4	1.9	0.7
t 10 g/dL	94	52	23.6	17.5
t 15 g/dL	45	33	21.5	8.3
t 20 g/dL	10.5	9.7	4.4	2.5
t/b (1:1) 10 g/dL	660	456	207	57.5
t/b (1:1) 15 g/dL	133	90	59	20.5
t/b (1:1) 20 g/dL	15.5	18.5	11.0	6.3
S/BA from:				
c 5 g/dL	22.5	-	-	8.8
c 10 g/dL	20.0	-	-	5.5
c 15 g/dL	17.7	-	-	3.0
c 20 g/dL	8.5	-	-	3.2
t/b (1:1) 10 g/dL	245	-	-	37.5
t/b (1:1) 15 g/dL	91	-	-	16.0
t/b (1:1) 20 g/dL	11.7	-	-	4.8
S from:				
c 10 g/dL	21.2	30.4	27.0	18.6
c 15 g/dL	19.9	21.7	25.5	17.5
c 20 g/dL	17.0	18.8	20.7	15.8
t 5 g/dL	23.5	30.0	29.5	10.0
t 10 g/dL	18.8	26.5	24.5	6.5
t 20 g/dL	16.5	20.5	21.0	6.0
t/b (1:1) 10 g/dL	23.0	27.5	25.5	13.5
t/b (1:1) 15 g/dL	21.5	24.0	20.8	9.2
t/b (1:1) 20 g/dL	19.2	24.0	20.0	4.5

details. The barrier properties evaluated in Fig. 2 and Table 2, however, indicate that very substantial differences in chain morphology are created by these filming procedures. This shows once again that chain morphology in solution is carried over into the solid, the polymer relaxation times being too large to permit the attainment of equilibrium states as the films dry and, consequently, as polymer viscosities increase. Thus, we suppose that films formed from the thermodynamically preferred solvent, chloroform, consist of more densely packed polymer chains in relatively extended states, while in films formed from poorer solvents, chains in more highly coiled states are more loosely packed, giving rise to more porous, penetrable barriers.

Two other property features are notable for their implications as to the micromorphology in these thin films. One is the evident dependence of barrier properties on the initial polymer concentration in solution. The second is the equally evident selectivity of barrier properties in PMMA and S/BA films, and the near constancy of the properties of PS (see K information in Table 2). The concentration dependence reasonably may be connected with the residual entanglement density [9, 10] of the solvated macromolecules. Thus, in the case of PMMA, better barrier properties are obtained when films are cast from solutions in which an increased degree of chain entanglement may be postulated. The effect is particularly noted in films formed from *t/b* mixtures where, judging from  $[\eta]$  data, polymer-polymer contacts should be strongly favored. In films dried from chloroform we assume a prevalence of extended chains. The macromolecule in this state would be less subject to form physical crosslinks; the concentration effect on barrier properties would then be less important, as observed. Chain extension and rigidity presumably also determine the entanglement density of which SBA and PS chains are capable. In the case of PS, the limited response to shear and solution treatments of the melt viscoelasticity in this polymer, reported elsewhere [11], confirms the relatively restricted entanglement network structure which this polymer is capable of forming. Accordingly, PS films display much lower dependence on initial concentration. It is apparent that the measured barrier properties report on transient states in the respective film micromorphologies. Regardless of the starting concentration, the final polymer concentration in dried films is, effectively, 100%. Again, however, the rapid drying processes involved do not permit full relaxations in chain morphology, hence creating the temporary but practically very important artifacts exemplified in Fig. 2 and Table 2.

The selectivity in transport properties evident from K values in Table 2 is of comparably high interest. A variation in barrier properties should, of course, be observed for any polymer film depending on the solvating strength of the contacting fluid. Indeed, in the case of PS, this factor may account for the slight variations of K among the four contact fluids. An additional factor (or factors), however, is (are) involved in PMMA and (to a lesser degree) in SBA copolymer films.

We believe this type of macromolecule to be capable of adopting various chain conformations at, and near, interfaces. This contention already has been used to account for the very large differences in inverse-chromatography data [4, 5] obtained for PMMA deposited from a range of solutions. It is further confirmed and elaborated by surface analyses of polyethylene-acrylic acid graft polymers, which will be the subject of forthcoming publications [12]. Well-established theoretical concepts [13] and the very recent developments of Flory and co-workers [3] also recognize the potential for conformational variations in polar chain molecules at interfaces. In the present cases, we suggest, the PMMA and copolymer molecules can so orient as to enrich the surface and the interface region either in polar or nonpolar chain components, depending on the nature of the environment (fluid) in contact with the film. This type of conformational plurality is not possible in PS however, since the alkyl and phenyl group components of this polymer differ only sterically, but not to any marked extent in polar contribution ( $\gamma_s^{\text{ND}}$ ) to the overall surface energy ( $\gamma_s$ ).

Film mechanical properties are consistent with the above concepts, thereby broadening the importance of relationships between polymer film properties and the conformational and micromorphological states of the polymer in solutions from which the solid is formed. These determinations were performed primarily on PMMA films, and typical results are shown in Fig. 3 for films cast from t/b, at varying initial concentrations,  $C_1$ . Films prepared from  $C_1 = 20$  g/dL are essentially

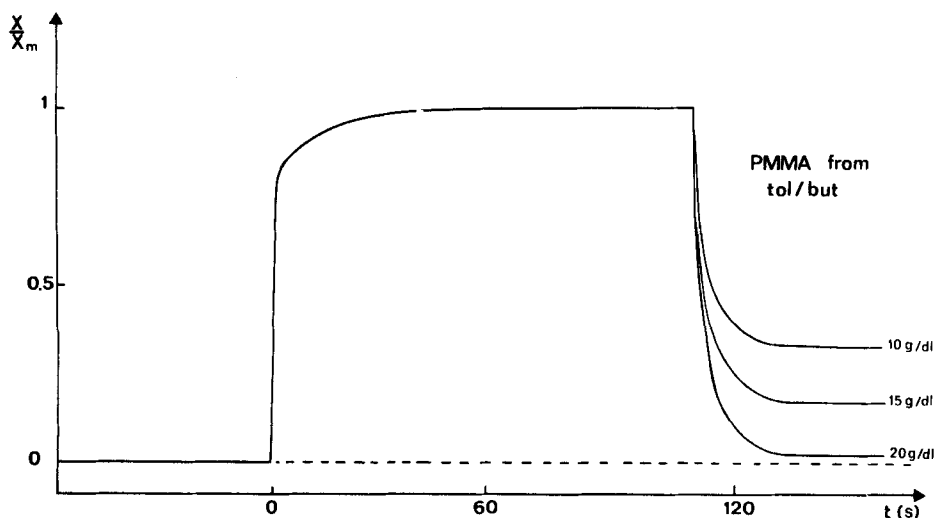


FIG. 3. Microindentation thermograms for PMMA cast from toluene-butanol (1:1). Effect of initial polymer concentration.

TABLE 3. Maximum and Equilibrium Deformation of Polymer Films Cast from Various Solvents

Solvent	g/dL	$X_m$ , $\mu\text{m}$	$X/X_m$
<u>A. PMMA</u>			
Chloroform, $C_1$	5	0.33	0.36
	10	0.31	0.31
	15	0.27	0.05
	20	0.21	0.01
Toluene/butanol (1:1), $C_1$	5	0.71	0.50
	10	0.51	0.33
	15	0.44	0.17
	20	0.36	0.02
<u>B. PS</u>			
Toluene, $C_1$	5	0.42	0.41
	10	0.41	0.33
	15	0.35	0.11
	20	0.29	0.12
Toluene/butanol (1:1), $C_1$	10	0.50	0.28
	15	0.47	0.12
	20	0.45	0.08

elastic, there being nearly total recovery from the maximum deformation. Films prepared from 15 and 10 g/dL solutions are progressively "lossier." In keeping with the postulates introduced above, we attribute this to varying degrees of chain entanglement in starting solutions. More contiguous solid films with greater capacities for elastic recovery from deformation are created when, in this thermodynamically poor solvent, entanglements among the solvated polymer chains are favored.

The tabulation of  $X_m$  and  $X/X_m$  values in Table 3 completes the overview of mechanical property data. Tabled values are averages of at least 10 determinations made on a random selection of points on each film sample; the error estimate is  $\pm 10\text{-}12\%$ . The performance of PMMA films in terms of both parameters is quite sensitive to details of film formation; that of PS films much less so. Of particular interest is the

$X_m$  of PMMA films formed from chloroform. The penetrability is uniformly low, even in films formed from the most dilute solutions. This result again is reasonable if we assume the formation of solids from randomly oriented, closely packed, extended chains. Such deformation as does occur when entanglement densities are reduced, however, tends to be inelastic, as seen from relatively high  $X/X_m$  for films produced at  $C_1 = 5$  and  $10$  g/dL. The more uniform performance of PS films again is consistent with the stated hypotheses. The polymer is limited as to conformational changes (thus low sensitivity to type of solvent), and limited as to the degree of chain entanglement possible (thus relatively insensitive to concentration effects).

We conclude therefore that in polymers, such as PMMA, consisting of polar and nonpolar moieties, chain conformation and chain packing density in solid films reflect chain conformations and entanglement states in solutions from which the films were formed. Highly significant consequences arise in barrier and certain mechanical properties as a result. These phenomena must therefore be considered when film property optimization is attempted.

### 3. Critical Surface Tensions and Components of Surface Energies

While the preceding section demonstrated the sensitivity of bulk properties on details of film formation, the focus of interest here is on surface and interfacial properties. The procedures described in the Experimental section permitted an evaluation of  $\gamma_c$  on polymer surfaces formed both against air and against the selected substrate. For convenience, in one part of this work segment each of the polymers was cast from only one solvent and from a constant initial solution concentration (10 g/dL). Results are given in Table 4.

Of the polymers studied, only PS appears to form isotropic solid films, regardless of the substrate's surface energetics. In PMMA and S/BA, however, the situation is far more complex. The thermodynamic requirement to minimize the surface energy at the air as well as the substrate interface brings into play the conformational potential which has been attributed to these polymers. Thus, only when cast against PTFE ( $\gamma_c < 20$  mJ/m<sup>2</sup>) do these polymers form isotropic films. In those cases involving substrates with high surface energies, the stated thermodynamic requirements apparently produce different polymer chain conformations at the air and the substrate interfaces.

The differences in chain conformation can be related to the existence in these polymers of finite contributions from dispersive and non-dispersive origins to the overall surface energy,  $\gamma_s$ . Using the notation and concepts of Fowkes [15], and the procedures developed by Schultz and Gent [16], it is possible to calculate the dispersive ( $\gamma_s^D$ )

TABLE 4. Critical Surface tensions of Polymers at Air and Substrate Interfaces

PMMA films cast from chloroform, 10 g/dL

$$(\gamma_c)_{\text{air}} = 41.5 \pm 0.5 \text{ mJ/m}^2$$

S/BA films formed from toluene, 10 g/dL

$$(\gamma_c)_{\text{air}} = 37.3 \pm 0.5 \text{ mJ/m}^2$$

EPS films formed from cyclohexane, 10 g/dL

$$(\gamma_c)_{\text{air}} = 34.0 \pm 0.5 \text{ mJ/m}^2$$

Substrate	PMMA		S/BA		PS	
	$(\gamma_c)_{\text{sub}}$	$\Delta\gamma_c$	$(\gamma_c)_{\text{sub}}$	$\Delta\gamma_c$	$(\gamma_c)_{\text{sub}}$	$\Delta\gamma_c$
PTFE	41.0	-0.5	38.0	0.7	33.0	-1.0
Hg	47.5	6.0	39.5	2.2	35.0	1.0
Cu	48.5	7.0	40.5	3.2	33.5	-0.5
Au	49.0	7.5	40.5	3.2	34.5	0.5

and nondispersive ( $\gamma_s^{\text{nD}}$ ) portions of  $\gamma_s$  of PMMA. The data are given in Table 5. They are once again consistent with the concept that the surface energy of this polar-group-containing macromolecule depends on the force field of the substrate in contact with it.  $\gamma_s$  is shown to be a thermodynamic potential quantity. Depending on the nature of the environment in contact with the polymer, the polymer is capable of orienting so as to enrich the interface either with polar or nonpolar moieties.

Conformationally nonisotropic films can be stable only as long as molecular contact is maintained at the interface. Given the very high probability that under normal filming conditions such contacts will be interrupted by the presence of impurities, by hydrodynamic perturbances occurring during drying, etc., it follows that these films will generally be in metastable states. Thus relaxation, or aging, effects must arise, driven by the demand to equate  $(\gamma_c)_{\text{sub}}$  with  $(\gamma_c)_{\text{air}}$ . At least two mechanisms may be suggested for such relaxation processes. These are:

1. Mechanical relaxation—e.g., curling, twisting, and cracking.
2. Appropriate changes in chain conformation.

Each of these mechanisms appears feasible and each would, of course, strongly influence the performance and durability of the film as a protective coating.

TABLE 5. Dispersive and Nondispersive Contributions to  $\gamma_s$  of PMMA

PMMA vs	$\gamma_s$ , mJ/m <sup>2</sup>		$\gamma_s^D$ , mJ/m <sup>2</sup>		$\gamma_s^{nD}$ , mJ/m <sup>2</sup>	
	Initial	Final	Initial	Final	Initial	Final
Hg	53	44	47	40.6	6	3.5
PTFE	44.5		41.5		3	
Air	46		43		3	

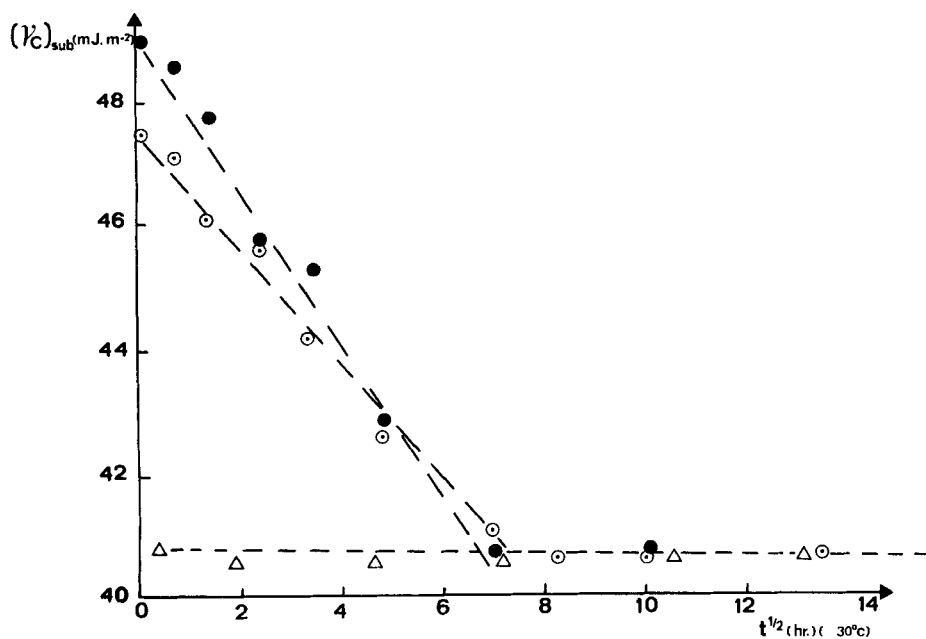


FIG. 4. Relaxation of  $(\gamma_c)_{sub}$  in PMMA cast from chloroform (10 g/dL) onto: (●) Au substrate, (○) Hg substrate, and (△) PTFE substrate.

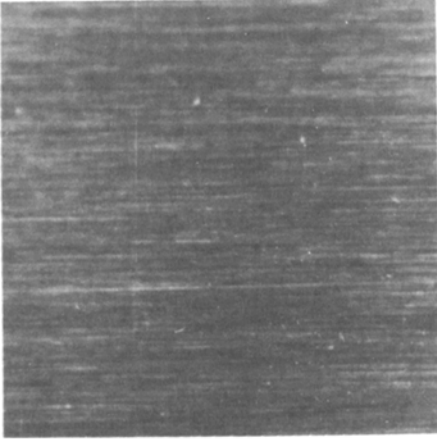
Mechanical relaxation in PMMA and S/BA separated from high energy surfaces was very evident, since the freed films began to curl and generally deform within a few minutes of being lifted from the substrate. In the work reported here, freed films had to be transferred rapidly to glass or steel panels, the surface originally in contact with the substrate now facing out and secured to the support by adhesive tape.

Changes in chain conformation were followed by placing freed supported film specimens into air ovens at 30°C and monitoring the evolution of  $(\gamma_c)_{\text{sub}}$  with time. The result of this procedure is given in Fig. 4 for PMMA films. Evidently, only the films cast against PTFE were isotropic and this presumably because the polymer did not achieve molecular contact with the substrate during drying. When cast against Hg, Au, and Cu (not shown in Fig. 4), the initially high  $(\gamma_c)_{\text{sub}}$  values decreased toward the equilibrium value ( $\approx 40.5 \text{ mJ/m}^2$ ) following what appear to be diffusion-dependent processes. The suggestion that physicochemical driving forces may play an important role in the performance and durability of coatings therefore seems further justified.

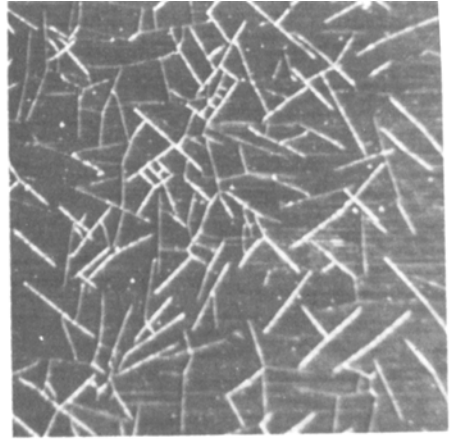
Since polar group-containing polymers (e.g., PMMA, S/BA) can form films with very different air and interfacial surface energies, it follows that such films may be under considerable internal stress. The existence of such stresses may be inferred from the tendency of supported films to form cracks and fissures when contacted by a wetting liquid. An illustration of the phenomenon is given in Fig. 5; PMMA films, some 30  $\mu\text{m}$  thick, cast from various of the solvent media onto steel, were contacted with bromonaphthalene. Fissures developed over a period of several minutes, the number and size of these depending on the casting solvent medium. The least strained films were those cast from chloroform. Thus, to obtain film durability, the extended chain state of PMMA and a reduced network structure appear to be preferred when coating high energy substrates such as steel.

A near quantitative relationship was found between the number of cracks developed per unit area of film and polymer-solvent interaction strength. This can be demonstrated using solubility parameter data [14] ( $\delta$ ) as indexes of interaction. Figure 6 thus presents a plot of crack frequency against the difference in  $\delta$  between polymer and the solvents, the latter including chloroform, toluene, t-b mixtures at 50/50 and 40/60 volume ratios, and t-heptane (90/10). The inference from Fig. 6 is that an "ideal" solvent for PMMA films to be cast onto high energy substrates would have a  $\delta$  equal to that of the polymer (i.e.,  $9.1 (\text{cal/cm}^3)^{1/2}$ ). Of course, this is, at best, a very rough definition of ideality, the overall  $\delta$  value being an imperfect index of the dispersive and associative (polar) contributions to the polymer's interaction potential.

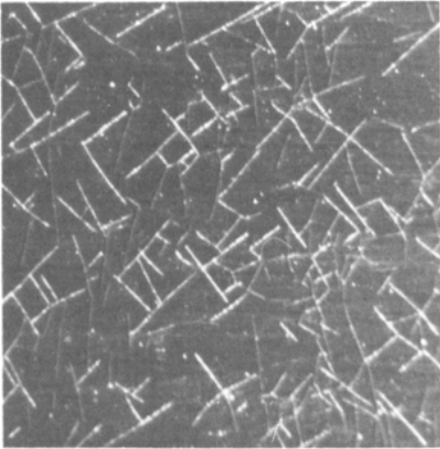




CONTROL



CHLOROFORM



TOLUENE



TOLUENE / BUTANOL  
50/50

FIG. 5. Fissuration in PMMA solidified from various solvents and contacted with bromonaphthalene.

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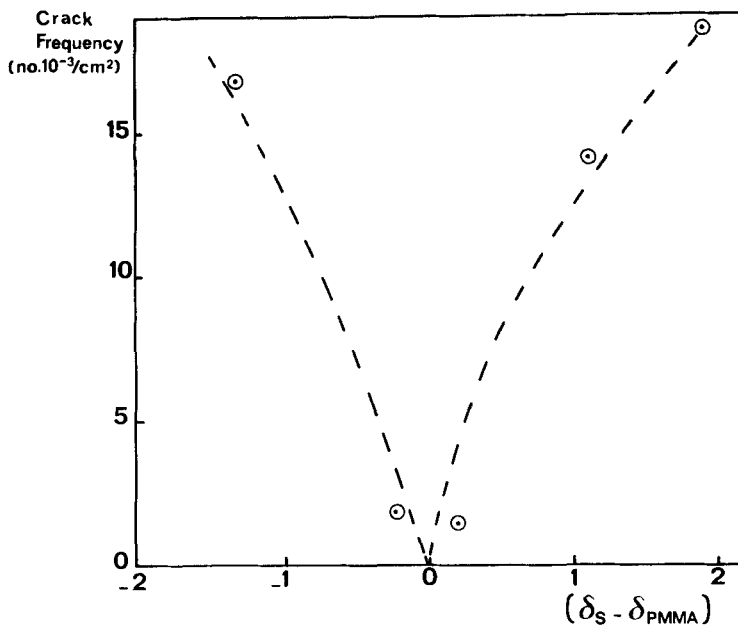


FIG. 6. Stress release in PMMA films: Dependence on polymer-solvent interaction.

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