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Wettability of Highly Fluorinated Polymer Coatings[†]

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Wettability of a linear polymer is a function of backbone structure, side-chain substitution, and fluorination. For a polymer to be suitable as a thin coating, a convenient method of application is mandatory to insure continuity and adherence to the respective substrate. Wetting properties of highly fluorinated ethylenic and methacrylic polymers are examined. The latter have proven to be effective barrier films for the prevention of liquid spreading in certain applications, and the effect of solvents on the wetting and adhesion of such films and on their stability with a variety of liquids are discussed.

INTRODUCTION

Highly fluorinated solid linear polymers are characterized by a low surface free energy and concomitant low wettability, as evidenced by the large contact angles of drops of organic and aqueous liquids. A comprehensive set of basic principles has been built up by Zisman and coworkers relating the chemical and spatial constitution in the outermost surface of a polymer with its surface energy.^{1, 2}

This paper discusses specifically (1) the ethylenic polymers and the effect on wettability by replacement of hydrogen in the backbone chain with fluorine and/or pendant group, and (2) a methacrylic polymer containing a fully fluorinated 8-carbon ester group which, because of its low wettability and ease of film preparation, finds successful application as "barrier coating" for the prevention of liquid spreading.

Wettability, as discussed here, is defined quantitatively by γ_c , the critical surface tension of wetting, which is obtained by the "Zisman plot". When

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the contact angle θ of each member of a homologous series of liquids, such as the *n*-alkanes, on the respective clean and smooth surface is plotted against the surface tension γ_{LV} for each of these liquids, a straight line results; the intercept at $\cos \theta = 1$ ($\theta = 0$) is referred to as γ_c .³ Liquids whose $\gamma_{LV} > \gamma_c$ have measurable θ on that surface, whereas liquids whose $\gamma_{LV} \leq \gamma_c$ spread, i.e., they wet the surface.

FLUORINATED ETHYLENIC POLYMERS

Wettability for low-energy solid surfaces is essentially a function of the nature and packing of the exposed surface atoms of the solid and is otherwise independent of the nature and arrangement of the underlying atoms and molecules.^{1, 2} The arrangement of surface atoms, of course, must represent

TABLE I

Effect on critical surface tensions of wetting by replacement of hydrogen with fluorine and/or pendant group

Code	Polymer	γ_c (dyn/cm)	Ref.
I	$[-\text{CH}_2-\text{CH}_2-]_n$	31	6
II	$[-\text{CH}_2-\text{CH}(\text{CF}_3)-]_n$	21.5	7
III	$[-\text{CH}_2-\text{CH}(\text{CF}_2-\text{CF}_3)-]_n$	16.3	8
IV	$[-\text{CH}_2-\text{CH}(\text{CF}_2-\text{CF}_2-\text{CF}_3)-]_n$	15.5	7
V	$[-\text{CH}_2-\text{CFH}-]_n$	28	9
VI	$[-\text{CH}_2-\text{CF}(\text{CF}_3)-]_n$	18.8	8
VII	$[-\text{CH}(\text{CF}_3)-\text{CFH}-]_n$	17.5	8
VIII	$[-\text{CF}_2-\text{CFH}-]_n$	22	9
IX	$[-\text{CF}_2-\text{CF}_2-]_n$	18.5	3
X	$[-\text{CF}_2-\text{CF}(\text{CF}_3)-]_n$	17	10
XI	$[-\text{CF}_2-\text{CF}(\text{nC}_4\text{F}_{11})-]_n$	14.1	8
XII	$[-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-]_n$	33-35	11, 12
XIII	$[-\text{CH}_2-\text{CH}(\text{C}_6\text{F}_5)-]_n$	22.5	8
XIV	$[-\text{CF}_2-\text{CF}(\text{C}_6\text{H}_5)-]_n$	25.4	8
XV	$[-\text{CF}_2-\text{CF}(\text{C}_6\text{F}_5)-]_n$	17.8	8

the lowest free energy configuration for a given set of restraining conditions such as the nature and size of the underlying atoms, length of the chain, etc. For polymeric materials in particular, it depends on the definition of the smallest unit, which for ethylenic polymers consists of two carbons in the backbone^{4, 5} and the substituent. Table I lists γ_c values of fluorine-containing ethylenic homopolymers; the formulae shown are the repeating units in the polymer structure as they would appear if all constituents were present in

the surface. The order of structures is arranged to show progressive substitutions of either a hydrogen or a fluorine atom in the backbone chain by either a fluorine atom or a perfluoro group.

Critical surface tensions of polymers I, V, VIII, IX, X and XII were measured on the respective smooth and flat bulk surface; those of the other polymers were obtained from films adhering to the glass slides on which they have been cast from solution. Figure 1 shows a graph of $\cos \theta$ vs. γ_{LV} for polymer III, $[-CH_2CH(C_2F_5)-]_n$, and is representative of the other polymers with the exception of the perfluorophenyl-substituted polymers XIII and XV. Here the straight line for the n-alkanes displays a marked discontinuity in the region of $\gamma_{LV} = 24-25$ dyn/cm, resulting in two values of γ_c , differing by 1 dyn/cm. Experimental phenomena suggest that the smaller molecules are capable of slipping into the interstices of the poorly adlined structures of polymers XIII and XV, whereas the larger and bulkier molecules are retained on the surface, and are thus more reliable representatives for the true value of γ_c .

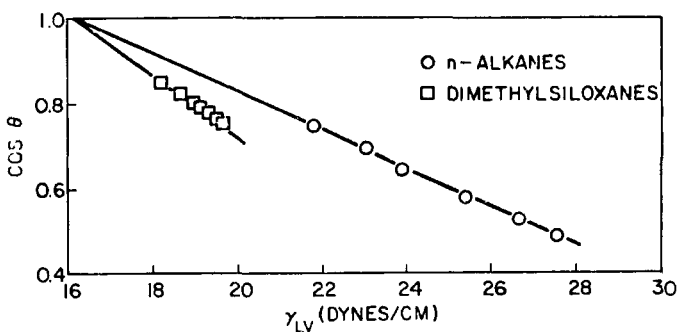


FIGURE 1 Wettability of polymer $[-CH_2-CH(C_2F_5)-]_n$.⁸

Several observations can be made from inspection of γ_c : (a) When the ethylene chain is fully hydrogenated, replacement of one hydrogen by a CF_3 group lowers γ_c approximately 10 dyn/cm (compare I and II, V and VI, and V and VII); (b) When one carbon atom in the two-carbon moiety of the ethylene chain is fully fluorinated, replacement of a hydrogen by a CF_3 group on the other carbon atom lowers γ_c only about 5 dyn/cm (compare VIII and X); (c) Nearly equal γ_c values are observed on several pairs of monomers of unlike molecular constitutions, such as II and VIII, VI and IX, and VII and X. Inspection of Stuart-Briegleb molecular models shows that, in certain steric arrangements, the packing of fluorine atoms at the surface of these pairs could be very similar. In each case the pendant CF_3 groups may be so located as to partially obscure the hydrogen atoms, resulting in a total effect of a balance between the hydrogen and the CF_3 contributions

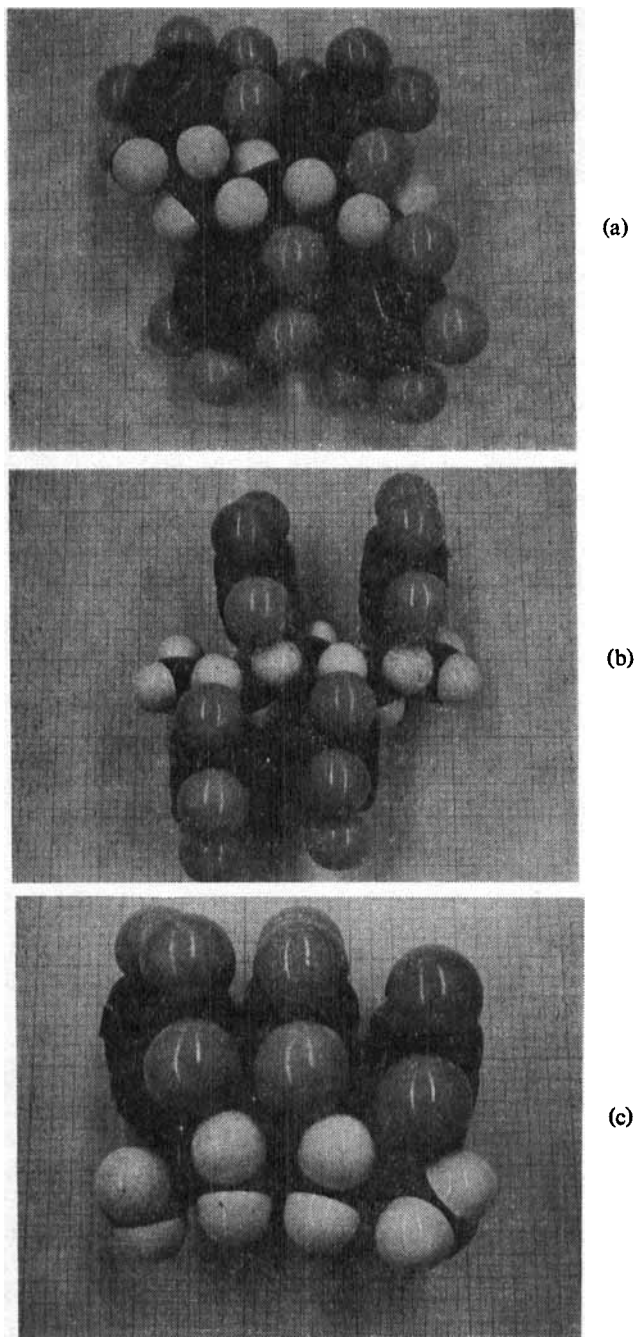


FIGURE 2 Various configurations of polymer $[-\text{CH}_2-\text{CH}(\text{C}_6\text{F}_5)-]_n$: (a) syndiotactic exposure of flat side; (b) syndiotactic, exposure of edge; (c) isotactic.

which approximates the surface constitution of the linear unbranched configuration. That an equal degree of fluorination does not necessarily result in the same value of surface energy ¹³ is shown in polymers VI and VII; despite the identical fluorine content, the molecular structure differs sufficiently to restrict free rotation of the CF₃ groups in polymer VII with the net result of closer surface packing of the fluorine atoms; (d) The lowest γ_c , 14.1 dyn/cm, was obtained for the fully fluorinated polymer XI. The increase in length of the pendant perfluorinated group from one carbon to five carbons decreased γ_c about 3 dyn/cm (X and XI) because of better adlineation and less restriction in the longer chain; (e) Aromatic substitutions are not as neatly categorized as those of aliphatic side chains. Replacement of the hydrogen with fluorine in either the phenyl group, XIII, or the backbone chain, XIV, lowers γ_c about 10 dyn/cm from the 33–34 dyn/cm of polystyrene. Variations or spread of γ_c values for a given polymer can be explained by the various orientations of the phenyl group in the surface, such as exposure of the flat side, or the edge, or the tacticity of the arrangement (Figure 2a,b,c). Total fluorination, as in polymer XV, of course results in even a lower γ_c , since only fluorine atoms are exposed in the surface.

An interesting parallel can be observed (see Figure 3): γ_c is lowered about 4.5 dyn/cm when the hydrogen atoms in the ethylenic backbone are replaced by fluorine atoms, regardless of whether the pendant group is the alkyl CF₃ or the aromatic C₆F₅. When, on the other hand, the alkyl CF₃ group is replaced by the aromatic C₆F₅ group, whether on a fully hydrogenated or fully fluorinated backbone, γ_c is raised approximately 1 dyn/cm.

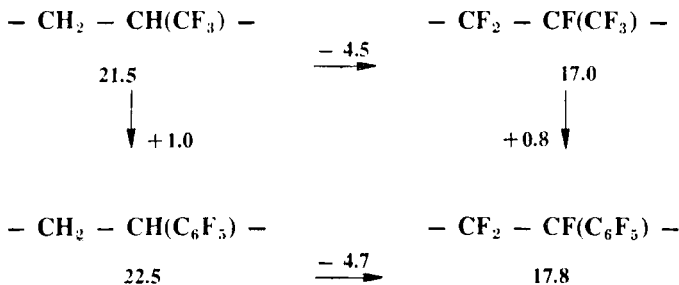


FIGURE 3 Effect of fluorine or substituent replacement on γ_c (dyn/cm).

The problem of determining the arrangement of the atoms and substituents of the first layer of the solid surface of a polymer or copolymer needs to be solved before we can relate the observed value of γ_c to the most probable surface composition of the polymeric solid. For simple unsubstituted polymers such as $[-\text{CF}_2-\text{CF}_2-]_n$ or $[-\text{CH}_2-\text{CH}_2-]_n$, the surface conformation can be rationalized by molecular models arranged in possible conformations on a flat table. However, where side chains are introduced into the

model, steric hindrances are also introduced. It is obvious that in a three-dimensional array a multitude of alternate conformations are possible, limited only by steric considerations. Although tacticity is an important factor of concern, no information is available on the particular configuration of these polymers, which probably means that they are atactic, i.e., randomly oriented. Any prediction of surface packing is thus problematic. In addition to the spatial arrangements, polymers such as VII also exhibit cis and trans isomerism with respect to the orientation of the F and CF_3 substituents on the backbone, further complicating and expanding the number of possible configurations.

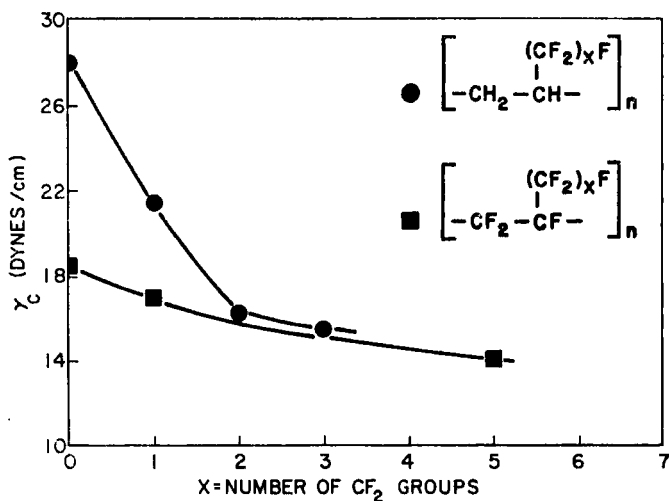


FIGURE 4 Effect of substituent chain length on γ_c .⁸

The effect on the contact angle of an uncompensated electrostatic dipole at the juncture of $-\text{CH}_2\text{CH}-$ backbone and the $(\text{CF}_2)_x\text{F}$ side group has been discussed by Hu and Zisman.⁷ If one assumes that the side group is directed away from the polymer solid surface into the wetting liquid, the dipole is closer to the interface the lower the value of x . Results of their work and those reported here show that θ is lower with lower values of x . Thus, when x changes from 1 to 3, γ_c is lowered from 21.5 to 15.5 dyn/cm (Figure 4), with the larger decrease of 5.2 dyn/cm when $1 < x < 2$ and the smaller decrease of 0.8 dyn/cm when $2 < x < 3$. The abrupt discontinuity at $2 < x < 3$ can be explained by restriction of rotation of the substituent and subsequent shielding of the electrostatic dipole. The latter is accentuated by the fact that the ethylenic hydrocarbon, to which the perfluoroalkyl side groups are connected, imposes restrictions on the packing of these substituent groups, necessitating progressively larger intramolecular rotations

and bending within the chain. This results in exposure of the CF_2 atomic grouping in an outermost surface of randomly oriented perfluoroethyl or perfluoropropyl groups. It would be interesting to study polymers with progressively longer perfluoroalkyl side groups to ascertain whether regular decreases in γ_c can be observed or whether a limiting value has been approached. When the ethylene backbone is fully fluorinated, a gradual and uninterrupted decrease in γ_c is observed with increase in x (Figure 4), since no large uncompensated dipoles are present.

FLUORINATED METHACRYLIC POLYMERS

Acrylic or methacrylic polymers with highly fluorinated side chains exhibit very low surface energies provided these chains are sufficiently adlined to present a surface constitution of closely packed trifluoromethyl groups.^{14, 15}

The critical surface tension of 10.6 dyn/cm for a substituted methacrylate with the repeating unit $[-\text{CH}_2-\text{C}(\text{CH}_3)(\text{COOCH}_2\text{C}_7\text{F}_{15})-]_n$ ¹⁴ remains the lowest reported value for a bulk material.¹⁶ Because this polymer not only can easily be applied from solution by casting or painting with a brush directly onto the substrate, but also adheres well after evaporation of the solvent, it has proved extremely useful as stain and soil repellent on fabrics, adhesive agent, nonstick releaser, and especially as barrier film for prevention of liquid spreading,^{17, 18} where the coating is applied to the surface surrounding the liquid. Such barrier films have become particularly useful for confining lubricants in miniature ball bearings.¹⁹ More recent applications are coatings on mechanical, electrical, and electronic equipment to provide water-, oil-, or fuel resistance, or to reduce electrical leakage.

The polymer is a 3M Co product and was originally made available in hexafluoroxylene solvent (HFX) which assured the formation of uniform, smooth, and well-adherent films. The polymer is now available in a mixed solvent system (a perfluorocyclic ether, PCE, and Freon TF). To compare the fluoropolymer films prepared from these solvents with films prepared from HFX solution as to wettability and stability after exposure to elevated temperatures in air or in contact with organic liquids, films cast on glass from several formulations, including mixed solvents, were investigated. A representative sampling of these formulations is listed in Table II. Wettability and adhesion of the various films were essentially the same for all specimens. The cast films were exposed to 210°C in a clean oven and were examined after intervals of 5 and 11 hr. Adhesion and transparency of all films remained excellent, although C films became somewhat pitted. No adverse effect on the wettability on A, B and C was noted as shown by the minimal decrease in contact angles of hexadecane and water before and after exposure

to 210°C (Table III). Some deleterious effects on the wettability of films D and E were indicated by the decrease in θ with exposure time.

Cast films were also immersed for 18 hr at 105°C in one of the following liquids: dimethylsiloxane DC200 (50 cSt), bis(2-ethylhexyl)sebacate, Versilube F-50 (chlorinated polysiloxane from General Electric Co.), and NRL MB-20B (mixture of a polyolester, diester, and additives). The specimens were then drained free of liquid, washed with Tide solution, rinsed with

TABLE II
Barrier film formulations

Code	Polymer, Wt %	Solvent
A	2.0	HFX
B	2.0	Freon TF
C	2.0	PCE
D	0.5	PCE: 75% Freon TF: 25%
E	0.5	HFX: 75% Freon TF: 25%

TABLE III
Effect of 210°C exposure in air on wettability of films cast from different solvents

Film	Time (hrs)	θ (degree)	
		C ₁₆ H ₃₄	H ₂ O
A	0	75	112
	5	73	112
B	0	74	112
	11	73	111
C	0	74	112
	11	73	110
D	0	74	113
	11	73	108
E	0	74	116
	11	73	100-113

distilled water, and dried. Selected data in Table IV show some deleterious effects on wettability for films cast from Freon TF, especially E; such films did not remain coherent or evenly wettable.^{20, 21}

While there is no ready explanation for the differences in the quality of films from the individual solvents or mixtures, ongoing work at our Laboratory indicates that their variation in solvent evaporation rates and/or the influence of their solubility parameters and polarities are involved.²²

TABLE IV

Effect of 19-hour immersion at 105°C on wettability of films cast from different solvents

Film	Oil	θ (degree)	
		$C_{16}H_{34}$	H_2O
A	Air	75	112
	Diester	75	110
	MB 20B	72	110
B	Air	75	112
	Diester	69	107
	MB 20B	70	107
C	Air	75	112
	Diester	70	109
	MB 20B	70	109
D	Air	75	112
	Diester	69	109
	MB 20B	70	109
E	Air	75	112
	Diester	67-58	109-92
	MB 20B	70	109-90

CONCLUSIONS

The wettability of fluorinated linear polymers can be predicted from their surface constitution, but the effects of steric configuration must be taken into account.

Substituted methacrylic polymers with highly fluorinated side chains have a lower surface energy than substituted ethylenic polymers possibly because of the length of the side chain.

Films cast from solutions of the former are being employed as barrier coatings to prevent the spreading of liquids. The efficacy of these films is affected by the solvent properties including volatilities, solubility parameters, and polarities.

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