It is noteworthy that the phase inversion time, whatever this phase is, does not seem to be dependent on the CTBN content, at least in the range studied. This means that the thermodynamic conditions for the phase separation are essentially dependent on the degree of advancement of the chemical reaction of the epoxy and its hardener. The perfect independence of the gel point and the CTBN content accounting also for that.

Besides, phase separation is never complete; hundreds of small inclusions stay apart from the larger ones.

As there is no continuous change from these microscopic particles to the larger ones, we conclude that there are two types of particles occurring at different times. We suggest that even after the phase separation some elastomer stays dissolved in the continuous matrix and that this elastomer only separates later at a stage where the overall viscosity is much too large to allow association into spherical particles.

Morphological Changes During a Static Deformation. Simultaneous measurements of tensile stress and light scattering could be easily performed by placing the sample between the jaws of an Instron tester and having the sample illuminated by the laser beam. Figure 6 shows typical V_v patterns obtained for a sample containing 28% CTBN.

An H_v light scattering pattern could not be detected from any specimen at any degree of elongation.

The observed changes of the scattering patterns as a function of deformation are similar for all levels of CTBN. They show: a small deformation of the circular halo that changes into an ellipsoidal one, a sharp drop of intensity on the halo along the stretching direction. The Fourier transform of an ellipsoid with the major axis horizontal is an elliptical halo with its main axis vertical and of constant intensity. It would seem therefore that the particles change from spheres to ellipsoids on stretching. However this explains only partially the evolution of the scattering pattern, the variations of the intensity around the elliptical halo being an additional effect whose explanation probably rests in a correlated orientation of the particles in the direction of stretch. Thus one could propose rows of short rods made up of the ellipsoids, aligned in the direction of tension.

Conclusions and Perspectives

Heterogeneous spherical domains of ABE composites have been investigated by the light scattering technique under several experimental conditions. The results can be summarized as follows: (1) the variation in size and shape of the spherical particles (if any) with the CTBN content can easily be followed; besides, some additional parameters can characterize the heterogeneities at a much smaller level; (2) the phase separation has been studied in a continuous manner during the polymerization by means of a technique that could be applied to most gel-forming materials; (3) a preliminary investigation of the deformation mechanism is reported; the results are promising for relating the variation of intensity due to a sinusoidal stress to the value of tan δ.

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Surface Chemical Properties of Highly Fluorinated Ethylenic Polymers[1]

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ABSTRACT: Wetting properties of seven new, well-characterized, highly fluorinated linear polymers were investigated. Fluorination in the polyethylene backbone was varied by degree of fluorine atom substitution; *n*-alkyl side chains of increasing number were fully fluorinated, whereas phenyl side groups were either fully fluorinated or nonfluorinated. Critical surface tensions of wetting obtained on thin cast films of these fluoropolymers were compared to those of polymers with related structures and surface constitutions. Because of the pressure of the bulky fluorine atoms and aromatic side groups, some of these molecules are extremely sterically blocked, which makes the prediction of an equilibrium surface conformation very difficult. The results are discussed in terms of solid surface constitution, steric hindrance, and electrostatic dipole contribution.

Highly fluorinated linear polymers are characterized by a low free surface energy and concomitant low wettability, as evidenced by the large contact angles of drops of organic and aqueous liquids. A comprehensive set of workable principles had been built up by Zisman and coworkers relating the chemical and spatial constitution in the outermost surface of a polymer with its surface energy.[2] During the last few years Wall, Brown, and Lowry of the National Bureau

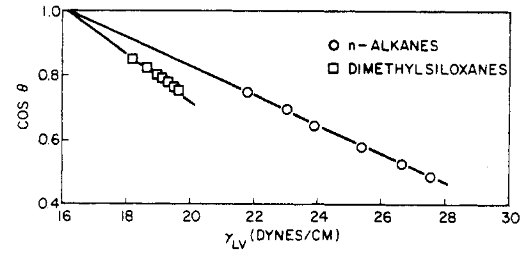

Figure 1. Wettability of polymer $[\text{-CH}_2\text{CH(C}_2\text{F}_5\text{)-}]_n$.

of Standards synthesized several new highly fluorinated ethylene polymers[3-6] and established[3] that according to Wunderlich's "bead" theory and "rule of constant heat increment,"[7,8] the ethylenic polymers with fluorinated side groups generally contribute two carbon atoms to the backbone chain. This two-carbon moiety plus the substituent constitute the smallest unit whose oscillations affect surface lattice equilibrium in a polymeric material, which represents the lowest free energy configuration.

In 1971 Hu and Zisman[9] reported on the surface chemical properties of two of these new polymers, $[\text{-CH}_2\text{CH(CF}_3\text{)-}]_n$ and $[\text{-CH}_2\text{CH(}n\text{-C}_3\text{F}_7\text{)-}]_n$, and copolymers prepared from them. The present investigation extends the study to seven additional polymers characterized by either various fluorinated substituents and/or various degrees of fluorination in the backbone chain.

Experimental Section

The seven experimental fluoropolymers had generously been made available by the late Dr. Leo Wall for our investigation. Table I shows the data obtained from Wall on the structural formulas, intrinsic viscosities $[\eta]$ in hexafluorobenzene, and glass transition temperatures T_g, along with the code numbers used for this report. With the exception of polymer III, the polymers were in the form of small agglomerated solid chunks. A solution of 0.05 g of solids in 20 ml of freshly Florisil-percolated hexafluorobenzene (Whittaker Corp.) was prepared for each polymer (benzene was used for polymer XIV) and was cast on acid-cleaned microscope slides. The solvent was permitted to evaporate first under controlled conditions for 20 hr at ambient temperatures and then under vacuum for 6 hr at 40°. The resulting films were transparent and glossy and adhered well to the glass substrate. Fluoropolymer III, received as a smooth film, was used without further treatment other than thorough washing with Tide solution and rinsing with distilled water.

Freshly percolated liquids of two homologous series, *n*-alkanes and dimethylsiloxanes, along with water and methylene iodide, were used for the wetting studies. Advancing contact angles (θ) were measured on sessile drops with the contact angle goniometer;[10] reproducibility was ±0.5°. All measurements were carried out at 23° and 50% RH.

Results and Discussion

Critical Surface Tensions of Wetting. When the cos θ of each member of a homologous series of liquids on a smooth, clean, solid, low-energy surface is plotted against the surface tension (γ_{LV}) for each of those liquids, a straight line results; the intercept at cos $\theta = 1$ ($\theta = 0°$) is referred to as the critical surface tension of wetting (γ_c) for that particular surface.[10] Figure 1 shows such a graph for polymer III, $[\text{-CH}_2\text{CH(C}_2\text{F}_5\text{)-}]_n$, and is representative of the graphs for the other polymers with the exception of XIII and XV. Values of γ_c thus obtained for each polymer film are given in Table I. Except for the perfluorophenyl substituted polymers (as will be discussed later), γ_c resulting from the two homologous series was never separated by more than 0.2 dyn/cm; most often the γ_c values coincided.

Table I
Physical Properties of Ethylenic Fluoropolymers

Code	Polymer	$[\eta]$, dl/g	T_g, °C	γ_c, dyn/cm
XIII	$[\text{-CH}_2\text{CH(C}_6\text{F}_5\text{)-}]_n$	4.0[a]	105	22.5
XV	$[\text{-CF}_2\text{CF(C}_6\text{F}_5\text{)-}]_n$	0.27[a]	194	17.8
XIV	$[\text{-CF}_2\text{CF(C}_6\text{H}_5\text{)-}]_n$	1.0[b]	202	25.4
VI	$[\text{-CH}_2\text{CF(CF}_3\text{)-}]_n$	4.65[c]	49	18.8
VII	$[\text{-CHFCH(CF}_3\text{)-}]_n$	0.23[a]	87	17.5
III	$[\text{-CH}_2\text{CH(C}_2\text{F}_5\text{)-}]_n$	0.33[a]	41	16.3
XI	$[\text{-CF}_2\text{CF(}n\text{-C}_5\text{F}_{11}\text{)-}]_n$	$\bar{M}_n \approx$ 25,000[a]	235	14.1

[a] In hexafluorobenzene. [b] In benzene. [c] In acetone.

Table II
Effect on Critical Surface Tensions of Wetting by Replacement of Hydrogen with Fluorine and/or Pendant Group

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

[a] New polymer.

Since the seven new polymers could not be classed in any particular order within themselves, we thought to compare their wetting properties with those of previously studied polymers. Table II thus lists both currently obtained and previously established γ_c values of fluorine-containing ethylenic polymers. The formulas shown are the repeating units in the polymer structure, as they would appear if all constituents were present in the surface and 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 $\text{-(CF}_2\text{)}_x\text{F}$ group, where $1 < x < 5$.

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 dyne/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 which approximates the surface constitution of the linear unbranched configuration. An example that an equal degree of fluorination does not necessarily result in the same value of surface energy is shown in polymers VI and VII; despite the identical fluorine content, the molecular structures differ sufficiently to restrict free rotation of the CF_3 groups in polymer VII with the net result of closer surface packing of the fluorine

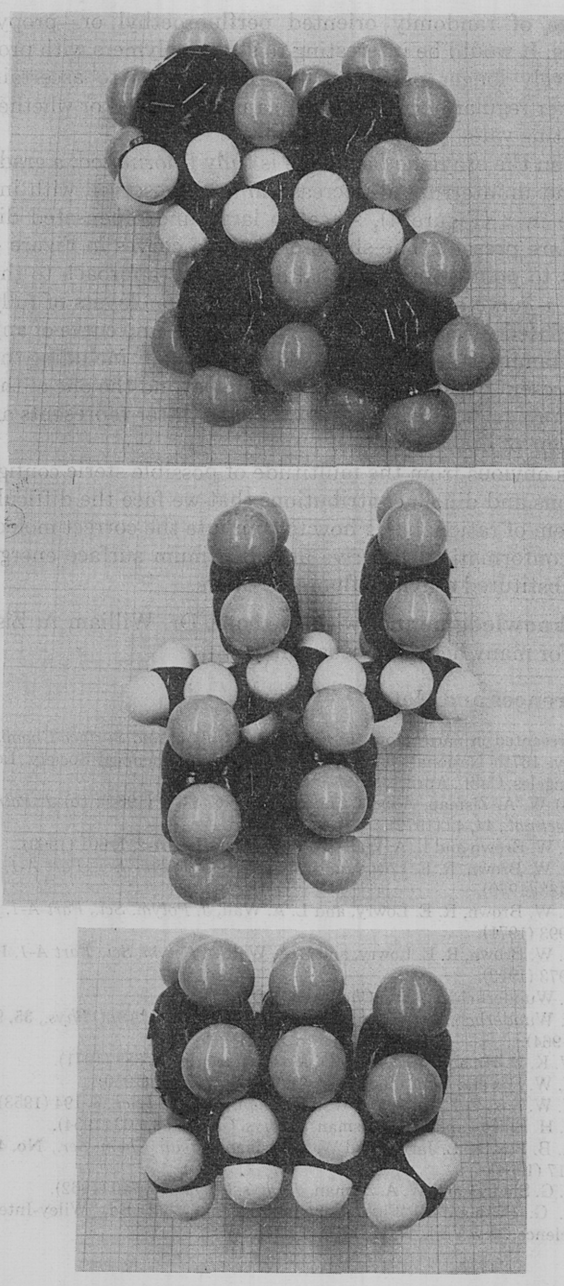

Figure 2. Various configurations of polymer $[-CH_2CH(C_6F_5)-]_n$: (top) syndiotactic, exposure of flat side; (middle) syndiotactic, exposure of edge; (bottom) isotactic.

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. Possibly, a further increase in chain length will continue to decrease γ_c as yet better adlineation will occur. (e) Aromatic substitutions are not as neatly categorized as those of aliphatic side chains. γ_c values of surfaces exhibiting phenyl groups vary from 25 dyn/cm for single crystals of anthracene or naphthalene,[11] where the phenyl group is situated edge on in the surface, to 33–35 dyn/cm for adsorbed monolayers of φ-stearic acid; γ_c for polystyrene, XII, also is in that vicinity.[12,13] 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 33–35 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 2). Total fluorination, as in polymer XV, of course results in even lower γ_c, since only fluorine atoms are exposed in the surface.

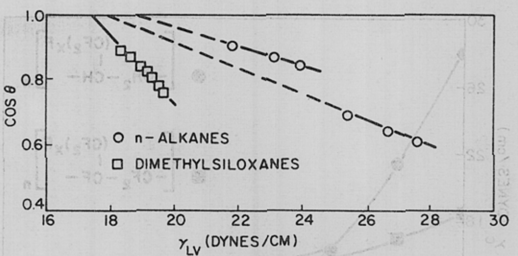

Figure 3. Wettability of polymer $[-CF_2CF(C_6F_5)-]_n$.

An interesting parallel can be observed; 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 CF_3 or the aromatic C_6F_5 (II and X; XIII and XV). When, on the other hand, the alkyl CF_3 group is replaced by the aromatic C_6F_5 group, whether on a fully hydrogenated or fully fluorinated backbone, γ_c is raised by approximately 1 dyn/cm (II and XIII; X and XV). Although the direction of the γ_c changes gratify generally established trends, the observation of such exact and parallel differences undoubtedly is fortuitous.

Anomalies for Perfluorophenyl Pendant Group. On polymer XV, $[-CF_2CF(C_6F_5)-]_n$ (Figure 3), as well as on polymer XIII, $[-CH_2CH(C_6F_5)-]_n$, the cos θ *vs.* γ_{LV} straight line for the *n*-alkanes displayed a marked discontinuity in the region of γ_{LV} = 24–25 dyn/cm, between the *n*-decane and *n*-dodecane. On extrapolation of the two straight lines formed by either the higher molecular or the lower molecular *n*-alkanes, two values of γ_c, differing by 1 dyn/cm, were obtained. During the measurement of contact angles it was noted that the angles decreased rapidly for the *n*-octane, *n*-nonane, and *n*-decane, while those for the longer chain *n*-alkanes, as well as those for the bulky dimethylsiloxanes and CH_2I_2, remained unaltered. On polymer XV water contact angles dropped quickly from 108 to 40°, while tailing at the periphery. These phenomena suggested that the smaller molecules are capable of slipping into the interstices of the poorly adlineated structures of polymers XIII and XV; the larger and bulkier molecules were retained on the surface and are thus more reliable representatives for the true value of γ_c.

Steric Configurations. For simple unsubstituted polymers such as $(-CF_2CF_2-)_n$ or $(-CH_2CH_2-)_n$, Stuart–Briegleb molecular models can be arranged in possible conformations on a flat surface. However, the introduction of side chains into the model also serves as introduction of steric hindrances. It would be simplistic to theorize the values of surface energy from the probable configurations of such models. 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. This, in turn, makes any prediction of surface packing even more hazardous. 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.

Electrostatic Dipoles. The effect on the contact angle of an uncompensated electrostatic dipole at the juncture of

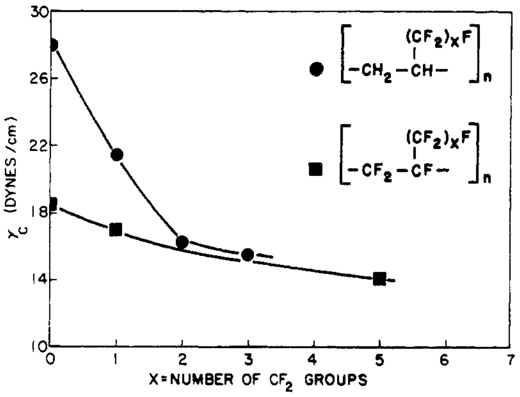

Figure 4. Effect of substituent chain length on γ_c.

the $-CH_2CH<$ backbone and the $(CF_2)_xF$ side group was discussed by Hu and Zisman.[9] 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 in their report and in the present study 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 $2 < x < 3$. Shafrin and Zisman,[14] in their study of adsorbed monolayers of progressively fluorinated fatty acids of the general formula $F(CF_2)_x(CH_2)_{16}COOH$ and $F(CF_2)_x(CH_2)_{10}COOH$, showed that the uncompensated dipole has a large effect on wetting when $x \leq 7$ but becomes less significant when $x \geq 7$. They also noticed an abrupt reversal of the effect of homology at $2 < x < 3$ where the difference in γ_c was only 0.8 dyn/cm because of random tilting of the fluorocarbon group. The similar abrupt discontinuity at $2 < x < 3$ in the present study can be explained by restriction of rotation of the substituent and the 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 -propyl 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. The shape of the two curves in Figure 4 seems to point to an eventual asymptotic approach to the γ_c *vs.* x curve obtained from adsorbed monolayers of fully fluorinated carboxylic acids.[14] Since to date no curve of any other family or series of related compounds,[15] including the two present ones, has crossed or gone beyond the one of the perfluoro acids, it is suggested that the latter represents an envelope of limiting values.

It is obvious from the multitude of possible steric configurations and dipole contributions that we face the difficult problem of rationalizing how to compute the correct molecular conformation to arrive at a minimum surface energy for substituted ethylene fluoropolymers.

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Critical Surface Tensions of Tetrafluoroethylene–Perfluoro(propyl vinyl ether) Copolymers

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ABSTRACT: An investigation of the wetting characteristics of random copolymers of tetrafluoroethylene with 1.5, 2.1, and 2.6 mol % perfluoro(propyl vinyl ether) has shown a rectilinear decrease in the critical surface tensions of wetting (γ_c) at 20° from 18.7 to 17.7 dyn/cm. Heat aging these thermoplastic resins, *e.g.*, at 260°, depresses γ_c by an additional 1.5 dyn/cm, so that an overall decrease in γ_c below that of the homopolymer of 1 dyn/cm for each mol % comonomer is achieved. The depression in γ_c resulting from heat treatment (8 to 8.5% of an already low-energy surface) is larger by an order of magnitude than what has been observed heretofore with other polymers.

Low-energy solid surfaces are characteristic of highly fluorinated polymers. Polytetrafluoroethylene (PTFE) was the first of such highly fluorinated polymers to have its hydrophobic and oleophobic properties carefully studied and defined.[1] Through the years PTFE has retained its appeal to the scientific, industrial, and military market by virtue of its many outstanding properties, such as very low-energy surface, low coefficient of friction, nearly total chemical in-