Critical Surface Tensions of Radiation-Induced Polymers and Copolymers of Tetrafluoroethylene with Fluorinated Propenes or Pentenes

William K. H. Hu[1a] and W. A. Zisman*[1b]

Department of Chemistry, Eastern Carolina University, Greenville, North Carolina 27834, and Laboratory for Chemical Physics, Naval Research Laboratory, Washington, D. C. 20390. *Received July 12, 1971*

ABSTRACT: The wetting properties of seven new, well-characterized, linear polymers and copolymers of 3,3,3-trifluoropropene, 3,3,4,4,5,5,5-heptafluoropentene, and tetrafluoroethylene have been investigated. Using homologous series of the pure *n*-alkane liquids and the open-chain polydimethylsiloxanes, well-defined reproducible contact angles (θ) were measured. From plots of cos θ *vs.* the mole per cent of tetrafluoroethylene in each polymer or copolymer, highly indicative results were obtained. These plots are also in interesting contrast with the related but simpler plots of the behavior of analogous copolymers of ethylene with tetrafluoroethylene. The full interpretations of all these results will require solving for very hindered polymers the general problem of computing, by a minimum-energy principle, the correct equilibrium solid surface conformation of the polymer, the dipolar contributions of each monomer, and their relation to the observed critical surface tension of wetting.

The first publications demonstrating the reproducible, reversible, and orderly changes in the contact angles of liquids with solid surface constitution were by Zisman and coworkers.[2-6] These concerned smooth, clean, high-energy solid surfaces coated with any one of a variety of organic polar-nonpolar monolayers; the results have been summarized.[4-6] Subsequent investigations[7-9] concerned the wetting of planar, smooth, clean, glossy surfaces of structurally analogous linear, unbranched, organic polymers. The overall experimental results were interpreted in terms of a critical surface tension of wetting (γ_c). That the values of γ_c of these low-energy solids were determined only by the surface molecular constitution and molecular packing and that these were in good agreement with the conclusions derived from the prior work on the wettability of adsorbed monolayers were shown by Zisman in 1957.[6] Later investigations concerned (a) the mechanisms determining the contact angles and spreading of a large variety of pure liquids on high-energy surfaces,[10,11] (b) the relation of wetting by freshly purified methylene iodide to adsorbed monolayer constitution,[12] (c) wetting (and γ_c) of solid polymers by aqueous solutions of pure surface-active agents,[13] and (d) the effect on wetting and γ_c of the progressive fluorination of adsorbed monolayers of fatty acids.[14,15] The values of γ_c obtained from these and other investigations were systematically related to surface constitution by Shafrin and Zisman.[16] Results of the entire program and their relation to past research on wetting were given by Zisman in the Kendall Award review[17] of 1963.

More recent investigations by Bernett and Zisman concerned the contact angles and γ_c of solid copolymers of tetrafluoroethylene and hexafluoropropene,[18] polyhexafluoropropylene,[19] and several acrylic and methacrylic polymers containing fluorinated side chains[20] which had been synthesized earlier by Husted, *et al.*[21] Subsequent valuable publications by Pittman and coworkers[22-24] concerned the synthesis and values of γ_c of a group of highly fluorinated polymers derived from the fluoroketones.

Recently a new group of interesting, highly fluorinated polymers and copolymers have been synthesized by Wall, Brown, and Lowry[25-29] using different proportions of tetrafluoroethylene and either 3,3,3-trifluoropropene or 3,3,4,4,5,5,5-heptafluoropentene-1. As pure specimens of these polymers were kindly made available to us by Dr. Wall, we report here their wettability properties, critical surface tensions, and their relation to polymer constitution.

Experimental Materials and Techniques

The seven fluoropolymers investigated containing various proportions of -CH, -CH_2, and CF_3 groups had been prepared under

---

(1) (a) Eastern Carolina University; (b) Naval Research Laboratory.
(2) (a) D. L. Pickett and W. A. Zisman, U. S. Patent 3,015,580 (1962); (b) W. C. Bigelow, D. L. Pickett, and W. A. Zisman, *J. Colloid Sci*, **1**, 513 (1946).
(3) W. C. Bigelow, E. Glass, and W. A. Zisman, *ibid.*, **2**, 563 (1947).
(4) E. G. Shafrin and W. A. Zisman in "Monomolecular Layers," H. Sobotka, Ed., American Association for the Advancement of Science, Washington, D. C., 1954, p 129.
(5) H. W. Fox, E. F. Hare, and W. A. Zisman, *J. Colloid Sci.*, **8**, 194 (1953).
(6) W. A. Zisman in "A Decade of Basic and Applied Science in the Navy," Office of Naval Research Symposium, U. S. Government Printing Office, Washington, D. C., 1957, p 30.
(7) H. W. Fox and W. A. Zisman, *J. Colloid Sci.*, **5**, 514 (1950).
(8) H. W. Fox and W. A. Zisman, *ibid.*, **7**, 109, 4280 (1952).
(9) A. H. Ellison and W. A. Zisman, *J. Phys. Chem.*, **58**, 260 (1954).
(10) E. F. Hare and W. A. Zisman, *ibid.*, **59**, 335 (1955).
(11) H. W. Fox, E. F. Hare, and W. A. Zisman, *ibid.*, **59**, 1097 (1955).
(12) O. Levine and W. A. Zisman, *ibid.*, **61**, 1068, 1188 (1957).
(13) M. K. Bernett and W. A. Zisman, *ibid.*, **63**, 1241, 1911 (1959).
(14) E. G. Shafrin and W. A. Zisman, *ibid.*, **61**, 1046 (1957).
(15) E. G. Shafrin and W. A. Zisman, *ibid.*, **66**, 740 (1962).
(16) E. G. Shafrin and W. A. Zisman, *ibid.*, **64**, 519 (1960).
(17) W. A. Zisman, *Advan. Chem. Ser.*, **No. 43**, 1 (1964).
(18) M. K. Bernett and W. A. Zisman, *J. Phys. Chem.*, **64**, 1292 (1960).
(19) M. K. Bernett and W. A. Zisman, *ibid.*, **65**, 2266 (1961).
(20) M. K. Bernett and W. A. Zisman, *ibid.*, **66**, 1207 (1962).
(21) D. W. Codding, T. S. Reid, A. H. Ahlbrecht, G. H. Smith, Jr., and D. R. Husted, *J. Polym. Sci.*, **15**, 515 (1955).
(22) A. G. Pittman, D. L. Sharp, and R. E. Lundin, *ibid.*, *Part A-1*, **4**, 2637 (1966).
(23) A. G. Pittman, D. L. Sharp, and B. A. Ludwig, *ibid.*, *Part A-1*, **6**, 1729 (1968).
(24) A. G. Pittman, B. Ludwig, and D. L. Sharp, *ibid.*, *Part A-1*, **6**, 1744 (1968).
(25) D. W. Brown and L. A. Wall, *ibid.*, *Part A-1*, **6**, 1367 (1968).
(26) D. W. Brown and L. A. Wall, *ibid.*, *Part A-2*, **7**, 601 (1969).
(27) D. W. Brown, R. E. Lowry, and L. A. Wall, *ibid.*, *Part A-1*, **8**, 2441 (1970).
(28) D. W. Brown, R. E. Lowry, and L. A. Wall, *ibid.*, *Part A-1*, **8**, 348 (1970).
(29) D. W. Brown, R. E. Lowry, and L. A. Wall, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **11**, 1042 (1970).

TABLE I
CHARACTERISTICS OF NBS POLYMERS INVESTIGATED

NBS no.	Polymer and composition, mol %	Intrinsic viscosity, dl/g
I	$\text{-CH}_2\text{-CH(CF}_3\text{)-}$	1.10
II	$[\text{-CH}_2\text{-CH(CF}_3\text{)-}]_{58} + [\text{-CF}_2\text{-CF}_2\text{-}]_{42}$	5.00
III	$[\text{-CH}_2\text{-CH(CF}_3\text{)-}]_{39} + [\text{-CF}_2\text{-CF}_2\text{-}]_{61}$	2.10
IV	$\text{-CH}_2\text{-CH(CF}_2\text{CF}_2\text{CF}_3\text{)-}$	0.63
V	$[\text{-CH}_2\text{-CH(CF}_2\text{CF}_2\text{CF}_3\text{)-}]_{79} + [\text{-CF}_2\text{-CF}_2\text{-}]_{21}$	0.74
VI	$[\text{-CH}_2\text{-CH(CF}_2\text{CF}_2\text{CF}_3\text{)-}]_{52} + [\text{-CF}_2\text{-CF}_2\text{-}]_{48}$	1.63
VII	$[\text{-CH}_2\text{-CH(CF}_2\text{CF}_2\text{CF}_3\text{)-}]_{25} + [\text{-CF}_2\text{-CF}_2\text{-}]_{75}$	1.30

pressure using a^{60}Co radiation source as initiator, and each had been characterized by Wall and coworkers[25–29] at the National Bureau of Standards. Table I lists data obtained from Wall on the structural formulas, compositions, and intrinsic viscosities of these polymers.

About 0.05 g of each of these fluoropolymers was dissolved in 25 ml of purified hexafluorobenzene obtained from the Whittaker Corp., San Diego, Calif. The supplier's data on this liquid listed a mp of 3.7–4.1° and a bp of 80.2–80.3°. After we had percolated this solvent through a long adsorption column packed with activated Florisil to remove any traces of adsorbable impurities, the melting point was 4.7–5.5°. The polymer films used in our work were cast by pouring on a smooth flat plate measured quantities of the polymer dissolved in this solvent. A hot nitric acid solution was used to clean Fischer soda-lime microscope slides which then were soaked with grease-free distilled water and finally dried in a clean oven at 105°. Subsequently, slow and controlled evaporation of the solvent occurred at room temperature followed by a final exposure for 12 hr in a clean vacuum oven at 40°. The resulting polymer films were glossy and nonporous, transparent and essentially planar. Each specimen adhered well to its glass substrate.

All traces of polar impurities in each of the many liquids used for sessile drops in the contact angle measurements were removed just prior to each experiment by slow percolation through an adsorbent column packed with activated Florisil. Surface tensions at 25° and 50% relative humidity of the resulting liquid specimens were measured by means of a National Instrument Co. Cassel surface tensiometer which is a convenient maximum bubble pressure type of device. It was calibrated as described by Jarvis and Zisman.[30] Agreement with the previously reported values was within 0.2 dyn/cm. The Dow-Corning DC 200 fluids (polydimethylsiloxanes) used had viscosities at 25° of approximately 3.0, 2.0, and 1.5 cSt at 25°. The slowly advancing contact angle observed on each fluoropolymer was determined with a previously described goniometer telescope.[2,7] Each contact angle reported in Table II was the result of at least three measurements on different sessile drops. Receding contact angles were, as usual with such smooth surfaces, equal to the advancing angles[17] and so are not recorded here. All contact angle observations were made at 25° and 50% relative humidity. Table II lists the resulting 25° surface tension (γ_{LV}) and observed average contact angle (θ) for each liquid on the polymeric sheets.

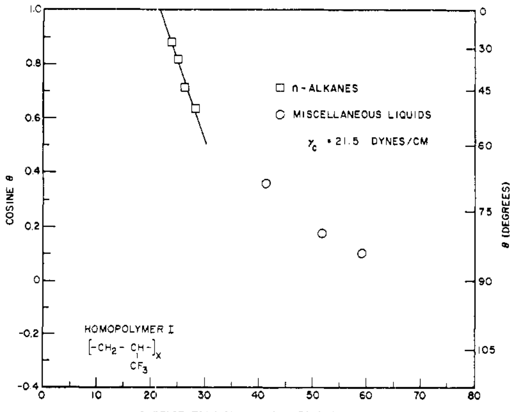

Figure 1. Cos θ *vs.* γ_{LV} for homopolymer I.

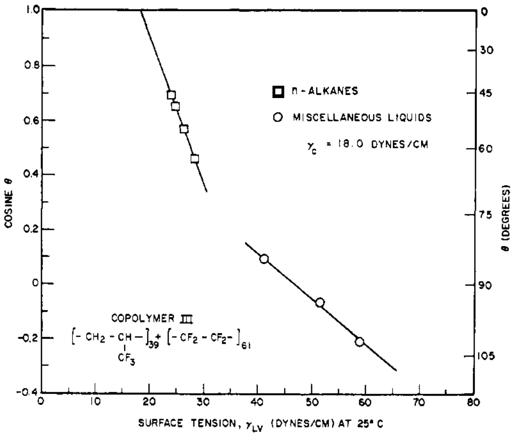

Figure 2. Cos θ *vs.* γ_{LV} for copólymer III.

Results

Plots of cos θ *vs.* γ_{LV} for these liquids on each polymer surface studied are exemplified in Figures 1–5. Note that the homologous family of open-chain polydimethylsiloxane fluids produced the same γ_c values as did the family of *n*-alkanes. Deviations from straight lines, however, were observed with the hydrogen-bonding or polar liquids tricresyl phosphate, methylene iodide, and formamide, whose surface tensions ranged from 40.8 to 58 dyn/cm at 25°. This is in agreement with the results exemplified in publications by Ellison and Zisman[9] and Bernett and Zisman[20] in their studies of halogenated organic solid surfaces. Table III lists the values of γ_c obtained for all seven polymers and copolymers investigated and listed in Table I by extrapolating graphically to the value of γ_{LV} at which cos θ = 1 in the cos θ *vs.* γ_{LV} charts. An interesting chart to be discussed later is a graph of γ_c for each polymer plotted against the mole per cent of tetrafluoroethylene in the copolymer. This is shown in Figure 6. Also included are data from an early paper by Fox and Zisman[31] on an investigation of the wettability of copolymers of tetrafluoroethylene and ethylene.

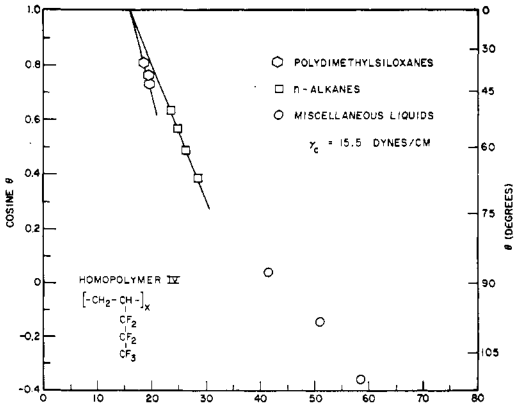

Figure 3. Cos θ *vs.* γ_{LV} for homopolymer IV.

---

(30) N. L. Jarvis and W. A. Zisman, "The Stability and Surface Tension of Teflon Dispersions in Water," NRL Report No. 5306, Naval Research Laboratory, Washington, D. C., May 6, 1959.

(31) H. W. Fox and W. A. Zisman, *J. Colloid Sci.*, 7 (2), 109 (1952).

Table II

Contact Angles (Deg) of Liquids on Fluoropolymers

Liquids	γ_{LV}, dyn/cm (25°)	Polymer no.[a] I	II	III	IV	V	VI	VII
n-Alkanes								
Hexadecane	27.8	50.7	51.3	62.9	67.1	64.5	61.2	59.3
Tridecane	26.0	45.1	42.4	55.8	60.9	59.3	55.1	53.0
Undecane	24.6	35.9	34.9	49.5	55.5	54.4	48.1	48.2
Decane	23.6	28.8	29.3	47.0	50.9	50.9	45.1	44.2
Dow-Corning 200 fluids (polydimethylsiloxanes)								
3.0[b]	19.4				43.3	43.8	37.5	37.3
2.0[b]	18.9				40.6	39.7	32.6	32.6
1.5[b]	18.1				36.5	35.9	28.2	29.3
Others								
Tricresyl phosphate	40.8	68.8	71.6	84.6	87.0	84.3	32.2	81.3
Methylene iodide	51.1	79.2	79.5	93.7	98.2	96.6	93.3	93.9
Formamide	58.1	84.0	87.0	102.5	110.5	102.7	99.9	98.0

[a] Polymer structures corresponding to these numbers are given in Table I. [b] cSt at 25°.

Table III

γ_c Values of the Fluoropolymer Films Investigated

NBS no.	T_g, °C	γ_c (25°)
I	27	21.5
II	19	21.1
III	9	18.0
IV	58	15.5
V	45	16.2
VI	29	16.5
VII	21	16.5

Discussion

Comparison of γ_c Values of Homopolymers. Table III indicates that insertion of two $-CF_2-$ groups to a side chain of trifluoropropene forming polyheptafluoropentene lowered γ_c from 21.5 to 15.5 dyn/cm. If this side chain is directed away from the solid into the liquid, the presence of an uncompensated electrostatic dipole in the $>CH(CF_2)_xF$ group, which is closer to the interface when $x = 1$ than when $x = 3$, will lower the contact angle with the wetting liquid. On this basis, Shafrin and Zisman[14,15] had explained the greater wettability of trifluorinated ω carbon atoms of vertically oriented, close packed, long-chain fatty acids than was evidenced by perfluorinated fatty acids. Measurements of electrical and mechanical properties of insoluble monolayers on water by Bernett and Zisman[32] supported their view also.

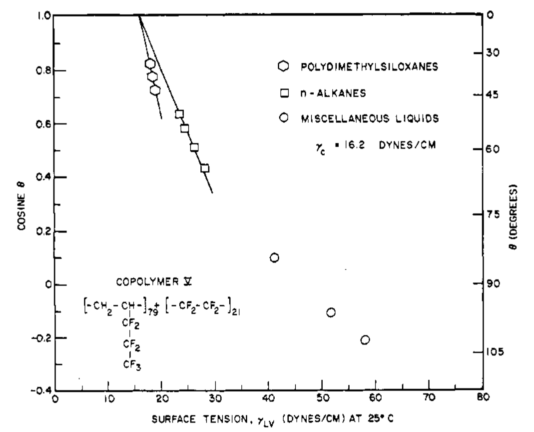

Figure 4. Cos θ *vs.* γ_{LV} for copolymer V.

The magnitude of this lowering of γ_c corresponds to about 3.0 dyn/cm as each $-CF_2-$ unit is introduced into the side chain. Shafrin and Zisman,[15] in their study of the effect of progressive fluorination of adsorbed homologous fatty acid monolayers on the critical surface tension, obtained a regular decrease of 2.2 dyn/cm per $-CF_2-$ unit when $3 \leq x < 7$, indicating an extrapolated γ_c value of 22.4 dyn/cm when $x = 0$, in good agreement with published values of 22–24 dyn/cm for stearic acid. This is much smaller than our value reported here. There are two reasons for this result. First, Shafrin and Zisman had shown that the effect on wetting of an uncompensated dipole becomes insignificant only when $x \geq 7$. Also, the $>CH(CF_2)_xF$ unit being a stronger dipolar linkage their $-CH_2(CF_2)_xF$ unit is therefore more compensated as x increases. Secondly, the perfluoromethyl side chain in our case is connected to an ethylenic hydrocarbon backbone. Apparently, the perfluoroalkyl groups do not pack as effectively for perfluoroalkylalkenes as do perfluoroalkylheptadecanoic acids owing to restriction by the ethylenic backbone. As more monomer units of the ethylenic type group together, progressively larger intramolecular rotations and bending are required to accommodate the end groups. This results in exposure of the $-CF_2-$ atomic grouping in an outermost surface of randomly oriented perfluoroethyl groups. Such a

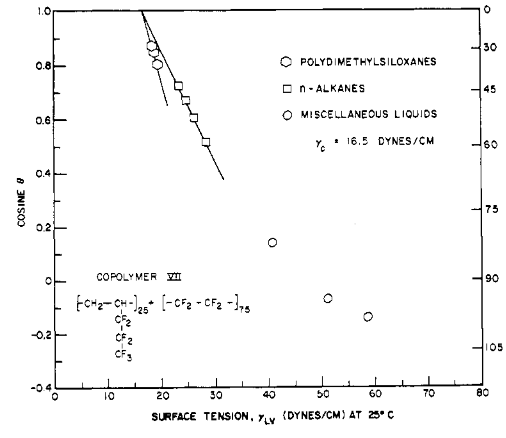

Figure 5. Cos θ *vs.* γ_{LV} for copolymer VII.

---

(32) M. K. Bernett and W. A. Zisman, *J. Phys. Chem.*, **67**, 1534 (1963).

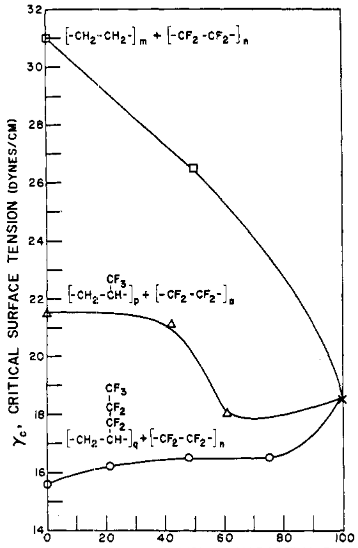

Figure 6. Critical surface tension *vs.* mole per cent tetrafluoroethylene in polymer.

surface should resemble in its wetting characteristics those surfaces which are rich in both $-CF_2-$ and $-CF_3$ groups. An example of this is $-CH_2(CF_2)_2F$, where random tilting of fluorocarbon groups leads to an abrupt reversal of the effect of homology in the series of progressively fluorinated fatty acids. It is interesting to note also that our value reported for polyheptafluoropentene of 15.5 dyn/cm is in closer agreement with their value of 16.0 dyn/cm for $-CH_2(CF_2)_2F$ fatty acids than with their value of 16.8 dyn/cm for $-CH_2(CF_2)_3F$.

Effect of Substitution of Hydrogen and Fluorine on γ_c. Shafrin and Zisman[16] studied the effect of progressive fluorine substitution on wettability of the poly(halogenated ethylene) plastic surfaces and obtained a straight-line relationship in their plot of γ_c against the atom per cent replacement of hydrogen by fluorine in the ethylene monomer. Pittman, Sharp, and Lugwig[23] attributed the lower γ_c value of poly(heptafluoroisopropyl acrylate) than poly(1*H*,1*H*-heptafluorobutyl acrylate) to its higher overall fluorine content. They also mentioned incorporation of more fluorine atoms in the lower energy $-CF_3$ groups as a possible reason. Table III shows that the γ_c value of 15.5 for polyheptafluoropentene is almost identical with the value of 15.2 for poly(heptafluorobutyl acrylate), both having the same side chain $-CF_2CF_2CF_3$ but, of course, having major differences in the overall fluorine content. This is in accord with the conclusion of Pittman, Sharp, and Ludwig that in a particular fluorinated polymer, γ_c is not necessarily dependent on the total fluorine content.

Effect of $-CF_2CF_2-$ Groups on γ_c Values of Trifluoropropene and Heptafluoropentene Copolymers. Critical surface tension results obtained on low-energy surfaces in numerous well-controlled experiments[17] led to the generalization that the wettability of low-energy organic surfaces is determined essentially by 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. The arrangement of the surface atoms, of course, must represent the lowest free energy configuration for a given set of restraining conditions such as the nature, size of the underlying atoms, length of the chain, etc.; in particular, for polymeric materials it depends on definition of the smallest unit whose oscillations affect surface lattice equilibrium.

Wunderlich[33,34] considers the molecular unit which fits the "hole theory" of Hirai and Eyring[35,36] as a "bead" of the polymer chain. He deduced the "rule of constant heat capacity increment" and showed that the change in heat capacity at the glass-transition temperature (T_g) per hypothetical backbone bead commonly has a value in the range of 2.7 ± 0.5 cal/(deg mol). Brown and Wall[25] determined $\bar{M}\Delta C_p$ values of 17 fluoropolymers, and only four of them are thought to be significantly outside this range. Values for both of the homopolymers trifluoropropene and heptafluoropentene and for the copolymer of perfluorostyrene and tetrafluoroethylene are within this range. Thus, it appears that heptafluoropentene, trifluoropropene, and tetrafluoroethylene in general contribute two carbon atoms to the backbone chain.

In Figure 6 the three graphs show the comparative case of predicting the effect on γ_c of copolymerization of tetrafluoroethylene with ethylene (upper curve), and the greater difficulty (middle graph) of predicting the effect on γ_c of copolymerization with trifluoropropene and the intermediate effect with heptafluoropentene (bottom curve). It should be evident that we are dealing with several effects of adding fluorinated carbon atoms, (i) those due to London dispersion force changes (upper graph) and (ii) those combining electrostatic effects and steric hindrance effects (lower two graphs).

The General Problem of Relating γ_c to Surface Conformation. The problem of determining the probable 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. In the past the probable surface conformation of the molecules studied could be rationalized through study of the Stuart–Briegleb ball model arranged in possible conformations on a flat table. Often such consideration of the possible arrangements were simple or self-evident, as in the case of PE or PTFE. Such is not the case with polyperfluorpentene, polyperfluorheptene, or the copolymers with variable proportions of tetrafluoroethylene comonomer. Steric hindrances exist to some conformations and must be considered.

As regards the effects of the contributory dipoles present in the molecule, the axial arrangement of dipoles around the principle axis of polyethylene would be such that a net dipolar contribution of zero would result; the effect of distance of contributory dipoles in a surface monolayer would be great enough for some systems to lead to zero contribution, as was shown[14,15] in the work on the adsorbed progressively fluorinated monolayers of fatty acids. But in the system of interest here, it is not obvious that dipolar contributions from the monomers or side chains can be neglected.

Therefore, we must face the more difficult problem of rationalizing how, from the possible molecular conformations and dipolar contributions of the surface layer of molecules, one can compute the correct one by using a minimum-energy principle. The so-determined conformation should then be used to relate chemical constitution, dipolar contributions, and bond angles to the observed value of γ_c and the known polymer composition. We are investigating this problem.

Acknowledgments. We wish to thank Dr. Leo Wall of the National Bureau of Standards for the gift of the well-characterized polymers and copolymers of Table I. Our associate, Elaine G. Shafrin, gave us helpful suggestions and comments.

(33) B. Wunderlich, *J. Phys. Chem.*, **64**, 1052 (1960).

(34) B. Wunderlich, D. M. Bodily, and M. H. Kaplan, *J. Appl. Phys.*, **35**, 95 (1964)).

(35) N. Hirai and H. Eyring, *ibid.*, **29**, 810 (1958).

(36) N. Hirai and H. Eyring, *J. Polym. Sci.*, **37**, 51 (1959).