pect that appreciable distortion of C* in the quenching complex would be necessary to facilitate the transition. By the Franck–Condon Principle, formation of the ionic complex could well lead to the necessary strong oscillations, rapidly carrying the system to a crossing point with the ground state, and final internal conversion.[20] The electronic energy would not be primarily transformed into relative translational motion of C and M, as indicated in the two-dimensional figure, but into the internal modes of both M (the complexed metal ion) and C. It is not likely that the idealized ionic form would be merely a strongly polarized complex, in which nuclear distortion is sufficient to permit internal conversion, in view of the several cases of weak quenching observed here.

Such a mechanism affords, in particular, some explanation of the effects of changing solvation (hydration) on the probability of quenching, although a quantitative discussion is difficult. The possibility of formation of the complex evidently depends on the relative free energies of C^*-M and C^--M^+, which is to say, on the respective oxidation–reduction potentials, whose values will depend on solvation. In the particular case of Mn^{++}, the relatively low rate may be associated with the special stability of the half-filled shell.[21] Franck–Condon restrictions on the charge-transfer process will also influence the rate,[22] and, by involving participation of ion-solvent vibrations in the configuration necessary for transition, will lead to entropy as well as energy of activation barriers. Finally, the charge-transfer process may involve movement of heavy particles (H atoms) belonging to molecules in the complexing envelope of the quenching ion.[20]

This mechanism suggests the possible existence of charge-transfer absorption bands in solutions containing quencher and substrate at high concentrations. A search for such bands in the systems studied here has given negative results thus far. A modification of this picture frequently has been discussed, in which the complex decomposes to a pair of one-electron oxidation–reduction products, which then return to the initial state via relatively slow back-reactions. Such a process evidently permits spin-conservation in the fast step, with either diamagnetic or paramagnetic quenchers.

Further work is in progress on the quenching of both singlet and triplet states in mixed solvents.

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[20] J. Franck and R. Livingston, *J. Chem. Phys.*, **9**, 184 (1941).

[21] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 1505 (1956).

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WALTHAM, MASS.

[CONTRIBUTION NO. 92 FROM E. I. DU PONT DE NEMOURS & CO., INC., ELASTOMER CHEMICALS DEPARTMENT, WILMINGTON, DEL.]

Structural and Compositional Analysis of Vinylidene Fluoride–Hexafluoropropylene Copolymers by Nuclear Magnetic Resonance Spectroscopy

BY RAYMOND C. FERGUSON

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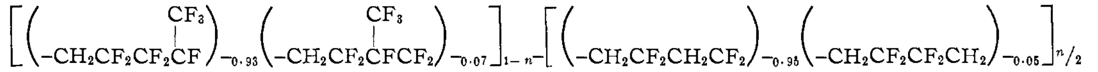
Nuclear magnetic resonance spectra of solutions of vinylidene fluoride–hexafluoropropylene copolymers have been measured and interpreted. The gross structure of the linear copolymer deduced from the fluorine spectra is



$$\left[\left(-CH_2CF_2CF_2\overset{CF_3}{\overset{|}{C}}F\right)_{-0.93}\left(-CH_2CF_2\overset{CF_3}{\overset{|}{C}}FCF_2\right)_{-0.07}\right]_{1-n}-\left[\left(-CH_2CF_2CH_2CF_2\right)_{-0.95}\left(-CH_2CF_2CF_2CH_2\right)_{-0.05}\right]_{n/2}$$

where n is a function of the mole fraction of vinylidene fluoride. The mole ratio of monomers in the copolymer can be determined from line intensity relationships.

Introduction

Copolymers of vinylidene fluoride and hexafluoropropylene have been reported by Dixon, *et al.*[1] High resolution nuclear magnetic resonance spectra of copolymers covering a range of monomer composition have been analyzed to determine the structure. The spectra also provide a means of determining the monomer ratio.

Experimental

Four copolymers of known composition were prepared by a persulfate initiated emulsion polymerization. Elemental analyses of the products agreed with the expected compositions, which were 61, 70, 78 and 85 mole % vinylidene fluoride.

Solutions of the copolymers in acetone, trifluoroacetic acid or trifluoroacetic anhydride were used for the nuclear magnetic resonance measurements. The preferred solvent for fluorine spectra was acetone, concentrations of 10 to 50% giving well resolved spectra.

A Varian Associates V-4300B spectrometer employing a 12-inch magnet system with a V-K3506 superstabilizer was employed. All measurements were made at 40 mc. The spectra were run at room temperature in 5 mm. and 8 mm. outside diameter sample tubes. The line widths were relaxation time controlled, and 50% solutions in 8-mm. sample tubes could be employed for increased sensitivity without sacrificing resolution. Intensities obtained by numerical integration of the areas under the lines were estimated to have probable relative errors of less than 10%.

Results

Spectra.—The proton spectra consisted of a broadened methylene resonance line at −89 c./s. from the water reference line. The line could not be resolved further to provide structural information. The fluorine spectra of two copolymers at the extremes of the composition range are shown in Fig. 1. The line frequencies were measured relative to

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[1] S. Dixon, D. R. Rexford and J. S. Rugg, *Ind. Eng. Chem.*, **49**, 1687 (1957).

TABLE I

ASSIGNMENTS OF THE FLUORINE RESONANCE LINES

Line	$\Delta\nu^a$		Group	Rel. intensity Obsd.	Calcd.
		Unit U	$-CH_2CF_2CF_2CF(CF_3)-$		
b	$+70$		$C-\underline{CF_3}$	3.0	3.0
e f	-1320 -1430		$CH_2\underline{CF_2}CF_2$	1.9	2.0
h	-1650		$CF_2\underline{CF_2}CF$	1.8	2.0
i	-4290		$CF_2\underline{CF}(CF_3)CH_2$	1.0	1.0
		Unit V	$-CH_2CF_2CF(CF_3)CF_2-$		
a	$+250$		$C-\underline{CF_3}$	3.0	3.0
d	-1040		$CH_2\underline{CF_2}CF$	3.5	4.0
c	-570	Unit W	$-CH_2\underline{CF_2}CH_2\underline{CF_2}-$		
g	-1535	Unit X	$-CH_2\underline{CF_2CF_2}CH_2-$		

[a] $\Delta\nu = \nu_{line} - \nu_{ref}$ in c./s., where ν_{ref} = the frequency of the trifluoroacetic acid line; measurements at 40 mc.

the trifluoroacetic acid line, negative values indicating absorption at higher magnetic field strengths (Table I).

Line Assignments.—The fluorine resonance line assignments were based on structure–chemical shift correlation data obtained in the laboratories of this Company. Not all of the model structures desired were available; therefore the assignments were based in part on generalizations about the effect of electronegative substituents on fluorine chemical shifts[2,3]: (1) Replacing hydrogens on the same carbon atom as a fluorine with electronegative substituents shifts the fluorine resonance to lower magnetic field, the magnitude of the shift being roughly proportional to the sum of the electronegativities of the substituents. (2) Shifts of smaller magnitude to higher field, also obeying a sum of electronegativities rule, are produced by replacing hydrogens on carbon atoms *alpha* to the group. (3) Smaller but measurable shifts may be produced by replacing hydrogens on carbon atoms *beta* to the group. These rules appear to be reliable for restricted classes of aliphatic compounds, particularly in cases where only hydrogen, carbon and fluorine atoms are involved.

The first rule led to the assignment of the $C-CF_3$ (a and b), the $C-CF_2-C$ (c through h), and $C-\overset{\overset{\textstyle C}{|}}{C}F-C$ (i) lines. The second rule led to $C-CF_2-C$ assignments in the order c through h: $-CH_2\underline{CF_2}CH_2-$, $-CH_2\underline{CF_2}\overset{\overset{\textstyle CF_3}{|}}{C}F-$, $-CH_2\underline{CF_2}CF_2-$, $-CF_2\underline{CF_2}\overset{\overset{\textstyle CF_3}{|}}{C}F-$. Mole ratio dependent line shapes, particularly of lines c, e, and the weak line f, were attributed to β-carbon substituent effects.

Lines c and g were assigned, respectively, to the head-to-tail and head-to-head poly-(vinylidene fluoride) chain segments because of a close match with the spectrum of poly-(vinylidene fluoride).[2]

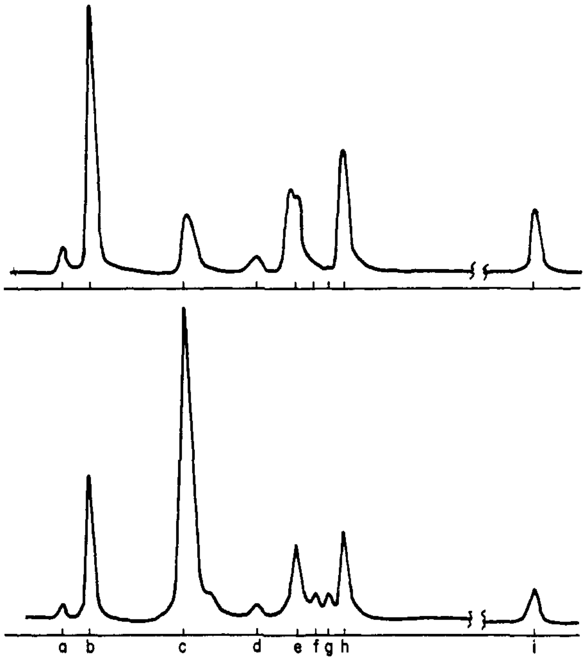

Fig. 1.—Fluorine resonance spectra (at 40 mc.) of vinylidene fluoride–hexafluoropropylene copolymer: upper, 61 mole % vinylidene fluoride; lower, 85% vinylidene fluoride; 50% solutions in acetone.

Structure.—The gross structure of the copolymer was deduced from the line assignments on the assumption that it was a random linear copolymer, except that no hexafluoropropylene–hexafluoropropylene repeat units were present. The assumption was justified by the lack of spectral evidence for branched and/or unsaturated structures, and on chemical grounds. Randomness in the incorporation of the two monomers was expected from the method of polymerization. However, polymerization of hexafluoropropylene under these or similar conditions has not been reported, and indeed it appeared to be impossible to incorporate more than 50 mole % hexafluoropropylene into the copolymer.

Four repeat units U, V, W and X satisfactorily accounted for the main features of the fluorine spectra. The line frequencies and assignments are summarized in Table I.

Comparison of the observed and calculated relative intensities of the CF_3, CF_2 and CF lines of unit U, and of the CF_3 and CF_2 lines of unit V confirmed the consistency of the assignments. These relationships were independent of the monomer ratio, the average values for the four copolymer compositions being given. The apparent discrepancy for line d of unit V was not outside experimental error, which was relatively large because of the low line intensities. The CF line of unit V, which would have one-third of the intensity of line a, was not observed, probably because of unfavorable signal-to-noise ratios.

Two other intensity relationships were independent of the monomer ratio. The relative concentrations of units U and V, from the intensity ratios of CF_3 lines a and b and CF_2 lines d and e + f + h were constant. Similarly, the ratios of units W and X, from lines c and g, were constant.

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(2) R. E. Naylor, Jr., and S. W. Lasoski, Jr., "Nuclear Magnetic Resonance Spectra of Some Fluorine-containing Polymers," to be published.

(3) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 321.

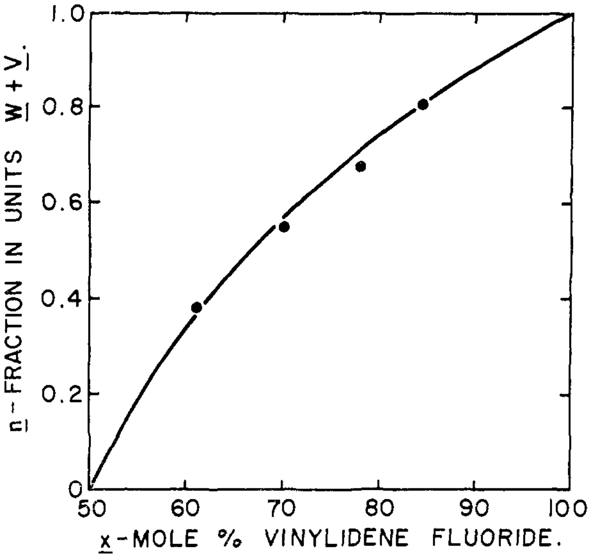

Fig. 2.—Fraction of vinylidene fluoride in units W + V *vs.* mole %: —, calculated; •, observed.

The relative concentrations of 1:1 copolymer and poly-(vinylidene fluoride) units were strongly dependent on the monomer ratio. Several intensity relationships could be used to calculate the ratios, with good consistency. The ratio of CF_3 line b *vs.* CF_2 line c appeared to give the greatest probable accuracy. However, the more general relationship $n = (c + g)/[c + g + {}^1/_2(d + e + f + h)]$ was preferred, since it required no assumption in regard to the relative concentration head-to-tail and head-to-head repeat units; n is defined as the fraction of vinylidene fluoride in units W + X.

Assuming no hexafluoropropylene–hexafluoropropylene repeat units occur, $n = (x - 50)/x$, where x is the mole % vinylidene fluoride. The calculated and observed relationships between n and x are shown in Fig. 2. The agreement was within experimental error. As a result of this analysis the structure of the copolymer can be expressed as $(U_{0.93}V_{0.07})_{1-n}(W_{0.95}X_{0.05})_{n/2}$.

Discussion

Analysis of the spectra of the vinylidene fluoride-hexafluoropropylene copolymers has shown (1) that certain modes of addition of the monomers to the propagating chain are highly preferred, (2) that little or no homopolymerization of hexafluoropropylene occurs, (3) that little or no chain branching occurs, and (4) that the four basic repeat units are randomly distributed. The second and third conclusions must be qualified, since the sensitivity of the nuclear resonance method was inadequate to detect homopolymer units, branches or unsaturation spaced at intervals greater than 10 to 20 mononer units.

A highly random arrangement of the four basic repeat units is required to account for the mole ratio-dependent line shapes of the CF_2 lines. These effects have been attributed to small chemical shifts due to β-carbon substituents, which can arise only at junctions between different repeat units. A block polymer of the type UUU...WWW..., etc., would have too few junctions to affect the line shapes measurably.

Two methods of analysis for the monomer ratios of the copolymers have been employed. The most general method uses the integrated CF_3 and CF_2 line intensities, and the relationship, mole % vinylidene fluoride = $(3\Sigma CF_2 - 2\Sigma CF_3)/3\Sigma CF_2$. This is an absolute method, provided that appropriate precautions against systematic intensity errors are taken.[4] A second method, used more routinely because of its simplicity, employs empirical calibration of the peak height ratios of lines b and c or h and c. With appropriate care, the mole % vinylidene fluoride can be obtained with a standard deviation of about 1%.

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(4) H. S. Gutowsky in W. G. Berl's "Physical Methods in Chemical Analysis," Academic Press, Inc., New York, N. Y., 1956, p. 370.

[Contribution No. 1588 from the Sterling Chemistry Laboratory, Yale University, New Haven, Conn.]

Ion-pairing in Aqueous Ethanolic Solutions of Sulfonium Salts

By Ada L. Jacobson[1] and James B. Hyne[2]

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The ionic association constants of trimethylsulfonium iodide in ethanol–water mixtures have been measured from 0 to 0.94 mole fraction ethanol by the static conductance method of Fuoss, *et al.* The degree of association to ion-pairs changes from slight ($K_A = 5$) in water-rich solvents to appreciable ($K_A = 120$) to ethanol-rich solvents. The results indicate that in ethanol-rich media the ion-pair equilibrium may be of importance in formulating the mechanism of sulfonium salt solvolysis.

Introduction

Interest in the kinetics of the neutral solvolysis of sulfonium salts has derived largely from the fact that such systems represent the case where the formal charge of the initial state is presumably dispersed on moving to the transition state of the rate determining step. Consequently it would be

$$R_2\text{-}S^+\text{-}R \longrightarrow (R_2\text{-}\overset{\delta_+}{S}\ldots\overset{\delta_+}{R}) \longrightarrow R_2S + R^+$$

expected that the transition state would be more favored as the solvent dielectric constant decreased and an increase in reaction rate observed. Behavior of this type was observed by Ingold and

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