Reply to 'Comment on "Dielectric behaviour and morphology on poly(vinylidene fluoride)"'

We are grateful for the comments by Davies and Rushworth [1] and their alternative explanation for the dielectric data on oriented polyvinylidene fluoride (PVDF) published previously [2]. These data were obtained from measurements on specimens parallel and perpendicular to the draw direction and also on isotropic specimens and showed a similar anisotropy for both the α (associated with crystalline regions) and β (associated with amorphous regions) relaxations.

The anisotropy of the α relaxation was interpreted in terms of chain motion within the lamellae [3], and the analysis of Davies and Rushworth supports this conclusion. The anisotropy of the β relaxation was suggested as being due to some "lining up" of the chains in the amorphous regions, but the analysis of Davies and Rushworth, on the basis of a two phase model with an isotropic amorphous phase, gives an alternative explanation.

The samples were drawn at 169° C and, with $T_g \approx -40°$ C, Davies and Rushworth suggest an oriented amorphous phase is not likely. However, similar studies with polychlorotrifluoroethylene (PCTFE) of low crystallinity ($\approx 35\%$) drawn at $\approx 100°$ C with $T_g \approx 50°$ C also exhibit the same anisotropy for the β relaxation [4].

Considerable wide-angle and small angle (both point and slit collimated) X-ray work has been done by us on oriented and isotropic PVDF, but this was not included in the previous paper. However, a non-uniform amorphous halo is not visible in the oriented samples.

It is difficult to distinguish which explanation for the anisotropy of the β relaxation is correct, for this depends on whether or not there is a truly isotropic amorphous component. This problem has not been completely resolved yet, but there seems to be considerable evidence in support of a degree of ordered chain packing in so called amorphous regions (see, for example, [5]).

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Correlation between electric strengths and heats of atomization of gaseous dielectrics

In high-voltage technology, gaseous materials are frequently used as dielectrics and it is of central interest to delineate the fundamental factors which determine the relative electric strengths of various gases. For a given gas, the Paschen's law [1] describes quantitatively the breakdown strength in terms of the gas pressure, electrode separation and related physical parameters; this law does not permit, however, to correlate the breakdown strength of a gas with its basic physico-chemical characteristics. With the success of SF_6 as a gaseous dielectric in high-voltage technology, it was generally felt that the symmetrical bonding (and thence the zero dipole moment) of SF_6 is probably responsible for its high electric strength. With the discovery of several fluoro compounds, especially the fluoronitriles (Table I), it became clear that symmetrical bonding and zero dipole moment are not the primary factors responsible for the high electric strength of gases. We have found that high electric strengths of gases are directly related to their heats of atomization per mole (Fig. 1) for gases for which the appropriate data are available in the literature (Table I). It would thus appear that the physico-chemical event responsible for the electric breakdown of a gas is the complete atomization of its molecules into the constituent atoms. In other words, high electric strengths are associated with gases for which high amounts of energy are

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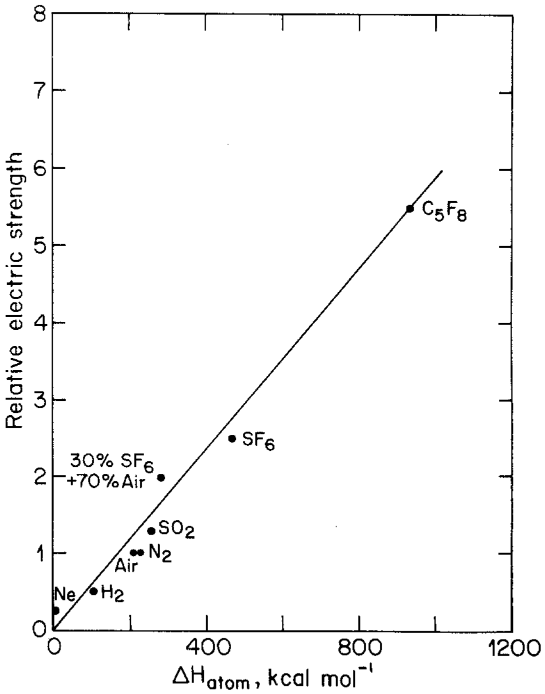

Figure 1 A correlation between relative electric strengths and heats of atomization per mole of several gaseous dielectrics; for data and their source, see Table I.

needed to rupture *all* the inter-atomic covalent bonds of the molecules. This would then be theoretically consistent with the case of highly ionic solid dielectrics, i.e. alkali halides, in which high electrical strengths are directly related to the energies of the electrostatic bonds, that is, their lattice energies [2].

In conclusion, high electric strengths of gases arise from the high energy needed to atomize them. The application of this viewpoint in developing new and improved dielectrics for high-voltage technology and related applications is obvious.

TABLE I Electric strengths and heats of atomization of some gaseous dielectrics

Gas	Relative electric strength	Heat of atomization (k cal mol^{-1})
Ne	0.25	0
H_2	0.50	104.0
N_2	1.0	226.8
Air (20% O_2 + 80% N_2)	1.0	215.2
SO_2	1.3	256.0
30% SF_6 + 70% Air	2.0	291.2
SF_6	2.5	469.0
C_5F_8	5.5	938
C_2F_6	1.4	–
CF_2Cl_2	2.4	–
CF_3CN	3.5	–
C_2F_5CN	4.5	–
C_3F_7CN	5.5	–

Notes: (1) The relative electric strengths have been taken from Alston [1] (pp.49 and 219), except for Ne and SO_2 which were estimated from Fig. 3.15 (p.63) of Harrop [3].

(2) The heats of atomization are from Weast [4] (pp.F-158) and Sanderson [5] (p.65 for Ne, p.227 for SO_2); for C_5F_8, the heat of atomization has been approximated as twice that of CF_4 (Sanderson [5], p.292). All heat of atomization values are per mole; for mixtures of gases they have been estimated as the arithmetic means of constituent gases. No heats of atomization values are apparently available for several fluoro and fluronitrile compounds listed in Table I.

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