

Fig. 6. Représentation graphique de η_{sp}/c par rapport à c pour la polyisoprène *cis*-1,4 70%, dans divers solvants.

à l'effet de la concentration critique sous laquelle les molécules de soluté subissent certaines modifications, qui sont influencées aussi par le système polymère-solvant utilisée.

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A Polyvinyl Chloride Electret

Surprisingly few studies of plastic electrets have been reported, although plastics with polar groups seem to be very suitable materials for the purpose. The dipoles are attached to long-chain molecules and their orientation in an electric field depends on cooperative motions of adjacent chain segments, especially when the polar groups are small and rigidly attached. It is known that the mobility of chain segments is very much reduced in the glassy state. This leads one to expect that plastics with polar groups, which have been cooled in a strong electric field from the rubbery state to well below the transition temperature T_g , should be stable electrets. This was indeed confirmed for nylon¹ and for polymethyl methacrylate (PMMA) thus far the most systematically studied plastic for this purpose.^{1,2} However, the effective surface charge density was unexpectedly small, of the order of 5×10^{-9} coul./cm.² In order to obtain data on a plastic with short sidegroups we prepared and studied polyvinyl chloride (PVC) electrets. PVC (Breon 101, Brit. Geon Ltd., prepared by the suspension method) was milled to sheets and molded to transparent plates (0.13 cm. thick) from which samples (3.5 cm. in diam.) were cut. The preparation of the electret

was similar to that described by Wieder and Kaufman.¹ The sample was placed in a thermoregulated sample holder which was connected to a d.c. current source of 1020 v., giving a field strength of 8 kv./cm. The temperature was raised at a heating rate of 4 deg./min. until a constant value of 120°C. was reached. The current during formation of the electret was recorded on a microammeter (Hewlett-Packard) in series with the sample holder. The thermal treatment and the current during formation are shown in Figure 1.

It has become customary to characterize electrets by two quantities. The first is the total charge displaced during formation, $Q = \int_0^\infty i_t dt$, where i_t is the transient current obtained after correction for the steady-state conduction current. For PMMA, Q was found¹ to be 4×10^{-2} . For PVC we find, from integration of the curve in Figure 1, that $Q = 10^{-2}$ coul., which is in the same order of magnitude.

The second quantity is the effective surface charge σ which is determined by the method of electrostatic induction.¹ The electret is placed in a condenser (without any applied field) of which one electrode is earthed. A second known condenser (0.022 μ f) is connected in parallel to the sample holder. An electrometer (Keithly, Model 610 A) in parallel and a shorting switch complete the circuit. After opening the switch the nonearthed electrode is raised by means of an insulated screw. Since the other electrode is earthed, equal charges will be induced in the raised electrode and will develop over the known condenser. By measuring the voltage, the effective charge density is found from $\sigma = 0.022 \times 10^{-4} V/A$ coul./cm.² where A is the surface area of the electret. For PMMA a value $\sigma = 5.5 \times 10^{-9}$ coul./cm.² was reported.¹ For PVC we found $\sigma = 5 \times 10^{-10}$ coul./cm.² This was a heterocharge, which remained constant for 40 days and showed no indications of sign reversal.

Before discussing these values we shall try to evaluate the significance of the two quantities Q and σ . The dielectric displacement is given by the expression $D = \epsilon E = \epsilon_0 E + P$, where E is field strength, P is the polarization, ϵ is dielectric constant, and ϵ_0 is dielectric constant of vacuum. Combining this with the well-known relation $Q = CV = A\epsilon V/d$, we find for the total displaced charge in the electret during formation:

$$Q = (AV\epsilon_0/d) + AP \quad (1)$$

The first term on the right-hand side of eq. (1) results from the charging current of the empty condenser (this charging current is not shown in the figure). The second term results from the polarization of the medium.

Equation (1) allows one to estimate the maximum of Q , which should be recorded if all the dipoles were to become aligned in the field: $Q_{\max} = AP = AN\mu$. The dipole moment of a C—Cl group equals about 2 debyes, or 6.66×10^{-28} coul.-cm. With the assumptions that the specific gravity is 1 g./cm.³ and that per dipole there is one C₂H₃Cl group, $N = 10^{22}$ dipoles/cm.³. In our experiments $A = 9.6$ cm.². Making use of these data we find $Q_{\max} = 6.4 \times 10^{-6}$ coul. This value is much lower than the experimental one of $Q = 10^{-2}$ coul. In other words, dipole orientation could be responsible for at most about one hundredth of the

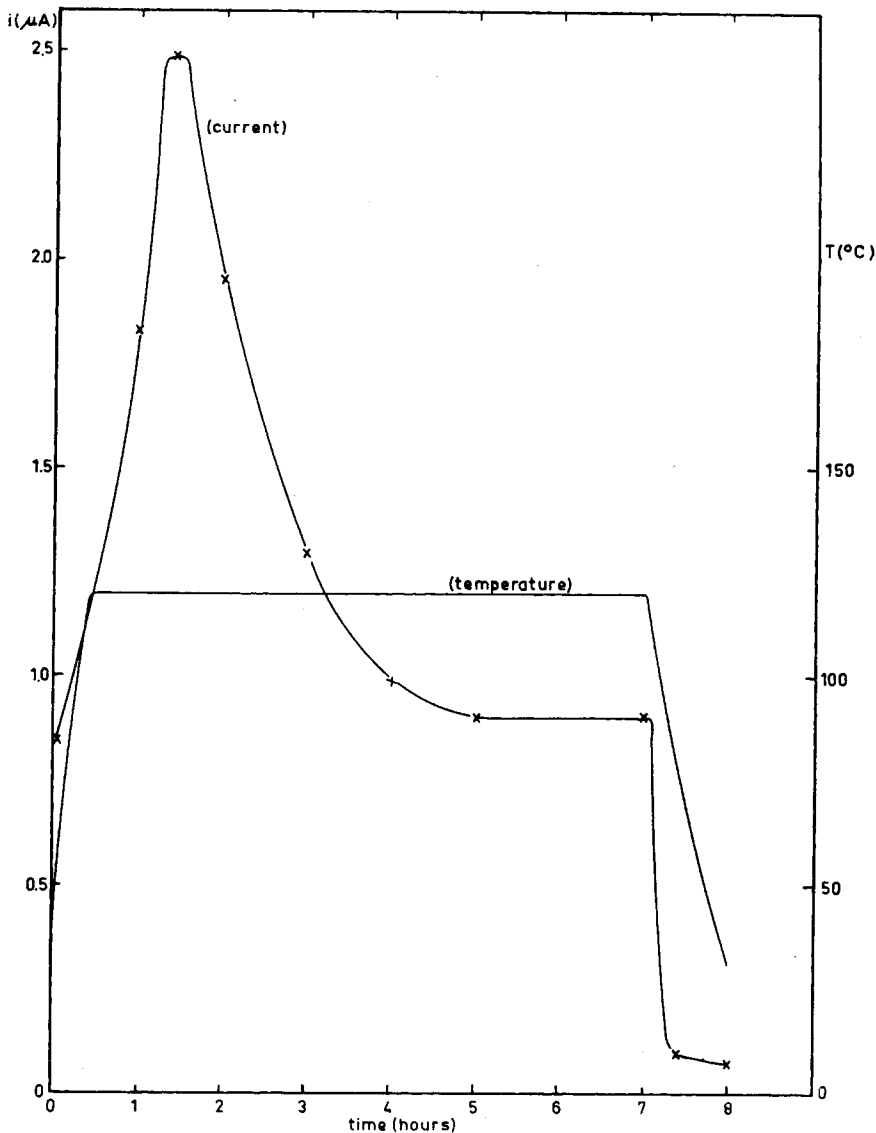


Fig. 1. Current and temperature during formation of PVC electret.

total charge displaced. Obviously Q is not determined by dipole orientation, but by disturbing effects such as ionic conductance. Therefore, there is no need to follow other authors in attempts to explain the observed discrepancy between the Q and σ values found.

From eq. (1) also the maximum effective surface charge can be calculated as $\sigma_{\max} = Q_{\max}/A = N\mu$. With the same assumptions as before we find $\sigma_{\max} = 6.66 \times 10^{-9}$ coul./cm.². If not all the dipoles, but only one in every 10^4 , remain oriented, then $\sigma = 7 \times 10^{-10}$ coul./cm.², in agreement with experiment. This seems to be a reasonable result; Debye calculated that the experimentally determined dielectric constants can be accounted for when only one dipole in every 10^6 is aligned in the field. It would anyway be a very improbable situation if all the dipoles were orientated simultaneously because of the resultant strains in the con-

necting chain segments. There seems, therefore, to be no reason for assuming breakdown of surrounding air¹ or partial compensation by homocharge⁸ in order to explain σ values of 10^{-9} to 10^{-10} coul./cm.². It also seems doubtful whether much higher charge densities could be obtained through the action of stronger fields alone.

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A New Method for Determining Effective Tensile Gage Length

It has been shown by a photographic method that cross-head displacement can be used to calculate the elongation for a dumbbell specimen in tensile extension by using an effective gage length.¹ We wish to report here a convenient method for determining this effective gage length from tensile data at different crosshead speeds *without actually measuring the gage length* and to show that this method can be applied to dumbbell specimens as well as specimens of film strips.

It has been shown¹ that at constant temperature the true stress αS , measured at different strain rates R , is related to experiment time t in the following manner

$$\alpha S/R = f(t) \quad (1)$$

where α is the extension, S the stress based on the original cross-sectional area of the specimen, and $f(t)$ a function of t . By definition

$$\alpha = 1 + \gamma = (L_e + D)/L_e \quad (2)$$

$$R = V/L_e \quad (3)$$

where γ is the elongation, L_e the effective gage length, and V and D are the speed and displacement of the crosshead respectively. Substitution of (2) and (3) into (1) and transposing gives

$$D = f(t)V/S - L_e \quad (4)$$

When the crosshead displacements at constant value of time t are plotted against the ratios of crosshead speed V to apparent stress, the result will be a straight line, since $f(t)$ is a function of t only. The intercept of this line with the ordinate will give the value of $-L_e$. Since L_e does not change with t , all lines of constant t should converge to the same $-L_e$ on the ordinate.

An example of this kind of D vs. V/S plot is reproduced in Figure 1. Figure 1 is based on tensile data obtained from specimens of rectangular strips of a commercial polyisobutylene (Vistanex 120) at 24°C. and using crosshead speeds of 5 to 50 in./min. with an initial jaw separation of 1 in. The actual isochronic lines do not intercept the D axis at the same point of $-L_e$. However, the variation is within experimental error. The isochronic lines shown in Figure 1 were drawn through the average of $-L_e$ which is 0.93 in. for 1 in. jaw separation to compare with the experimental points which are shown as dots. The excellent agreement shows that this method is adequate for the determination of effective gage length. Another experiment on the same

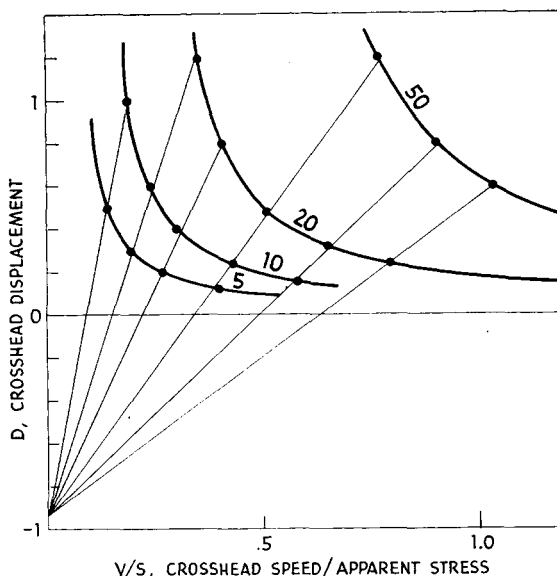


Fig. 1. The D vs. V/S curves for a polyisobutylene. The numerals indicate the crosshead speeds in in./min.

material but with a jaw separation of 2 in. gives an effective gage length of 1.85 in.

This method was applied to the stress-strain data on NBS polyisobutylene obtained¹ with dumbbell specimens, to which an effective gage length correction had been already applied. For this case eq. (4) can be modified to

$$\gamma = f(t)R/S - 1$$

The intercept of isochronic lines should, therefore, be -1 , instead of $-L_e$. This was the actual result. Therefore, this method is applicable to dumbbell specimens as well.

In the region of small crosshead displacement where the hyperbolic D vs. V/S curve is almost flat, a small experimental error would cause a considerable error in L_e . At the other end of the curve, i.e., at large displacement, eq. (1) may not hold. The application of this method for determining effective gage length is probably, therefore, limited to a region from 20 to 120% nominal elongation.

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Reactions of Primary Amines with Epoxides

The advent of epoxy resin technology has created considerable interest in the reactions of amines with epoxides.¹ The reactions of ammonia and primary amines with epoxides are competitive consecutive processes and present con-