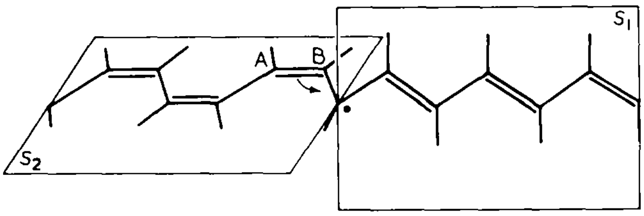

Figure 5 Idealized, schematic illustration of proposed mechanism of *cis–trans* isomerization. The plane of the *cis* segment, S_2 is perpendicular to that of the trans, S_1. In the next step of isomerization due to the marked bond rehybridization, the unpaired electron shifts to the C atom labelled A and the C atom labelled B transfers to plane S_1

In this case the isomerization is related to a rotation of C–C single bonds[24]. The phenomenon is illustrated in *Figure 5*. Rolling maintains the spin concentration but extends the length of the *trans* radicals and thus slightly isomerizes polyacetylene. The observed spins were presumably formed by the heat induced isomerization which took place when the temperature first rose from −78°C to room temperature.

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Electrical conduction in Kapton polyimide film at high electrical fields

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Electrical conduction in Kapton polyimide film was studied under steady-state conditions in the temperature range 100°–200°C and in electric fields of 50–450 kV cm^{-1}. An attempt was made to fit the field dependence of current to one of the several possible mechanisms which have been proposed by different workers. Evidence is presented to suggest that even at high fields ionic conduction may be the operative mechanism of conduction. Values of ionic jump distance of 50–60 Å show good agreement with values reported by other workers.

Keywords Electrical properties; conduction; Kapton polyimide; film; mechanism; ionic jump

Introduction

Kapton, whose chemical name is poly(4,4′-diphenylene pyromellitimide) is a film forming polymer manufactured by EI du Pont de Nemours and Co. Inc., USA. It is known to be strongly heat resistant, is little affected by various kinds of chemicals and has excellent electrical properties as an insulator. It is ideal for use as an insulator under adverse environmental conditions such as those encountered in outer space. However, Kapton is photoconductive[1] which also arouses interest of another kind—its possible use as a photoreceptor in electrophotographic and energy conversion applications. In order to exploit this potential it is essential to understand the mechanism of electrical conduction in the material.

Several workers have reported the results of their investigations in this field. But there is no reasonable agreement among them on the type of conduction mechanism in Kapton, especially at high electric fields. At

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low electric fields the conduction has been shown to be ionic[2], due to protons ionized from polyamic acid in dry samples and due to residual impurity ions in wet samples. Hanscomb *et al.*[3] have studied the electrical conduction at high electric fields in the temperature range 150°–275°C under both transient and steady state conditions. They have suggested, on the basis of this study, that the steady state current is due to a 'thermally assisted tunnelling' of electrons, first presented by Polanco *et al.*[4]. Sawa and his coworkers[5] alternatively, have argued strongly in favour of ionic conduction, even at high fields, on the basis of their study conducted in a temperature range 120°–180°C and electric fields of 4–500 kV cm^{-1}. However, no clear cut and unambiguous picture is available. The fit is very approximate and parameters such as ionic jump distance, apparent activation energy and pre-exponential factor differ widely for the data obtained by different authors.

In this study electrical conduction of Kapton polyimide films at temperatures in the range 100°-200°C is studied as a function of electric field. An attempt is made to examine which hypothesis the data will fit best.

Experimental

2 cm × 2 cm samples of Kapton-H film of 75 μm nominal thickness were vacuum aluminized on one side for use in this study. These samples were heat-treated at 75°C under short circuit conditions for six hours and then cooled slowly to room temperature prior to measurement. Static was removed by irradiating the samples with ultraviolet light for a few minutes with the electric fields on as suggested by Sapieha and Wintle[6]. The front electrode was made of Nesa conducting glass for this purpose.

The sample was kept at a particular temperature for 1 h before commencing measurements. The temperature of the furnace was maintained constant to within ±2°C with the help of a 'Jumo' mercury-contact thermometer and relay. The current was measured using a Keithley model 610C electrometer. After 1 h the lowest value electric field is applied and the current observed after waiting 600 s to allow it to settle down. Thereafter the field is increased in short steps and at each step a time of 300 s is allowed for the dark current to settle down before a reading is taken (*Figure 1*). These settling-down times were chosen following the results of earlier measurements[1]. The slopes and intercepts of the plots were computed using the linear regression technique on a EC-75P programmable desk calculator.

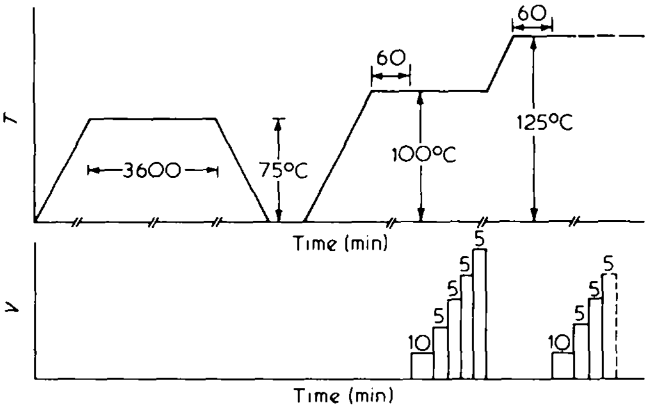

Figure 1 Experimental procedure

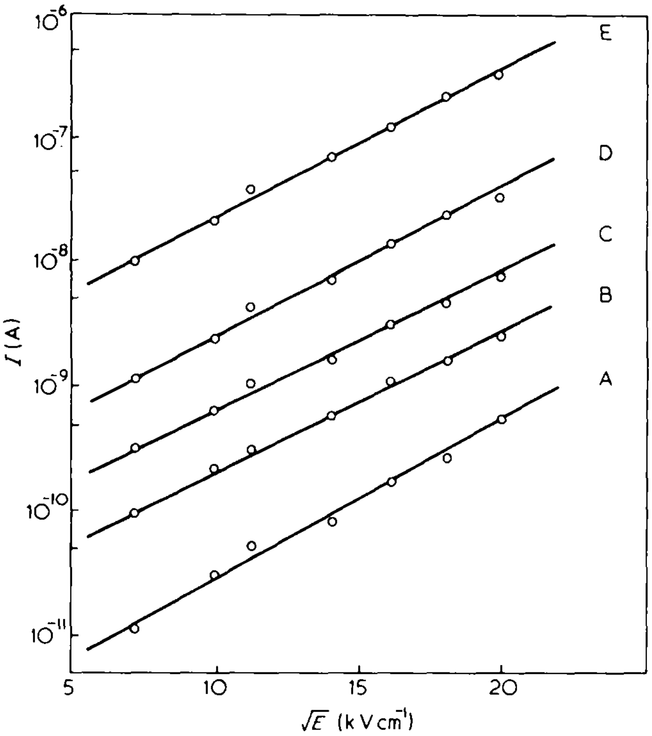

Figure 2 Log *I* vs. *E* curves (A) 100°C, (B) 125°, (C) 150°C, (D) 175°C, (E) 200°C

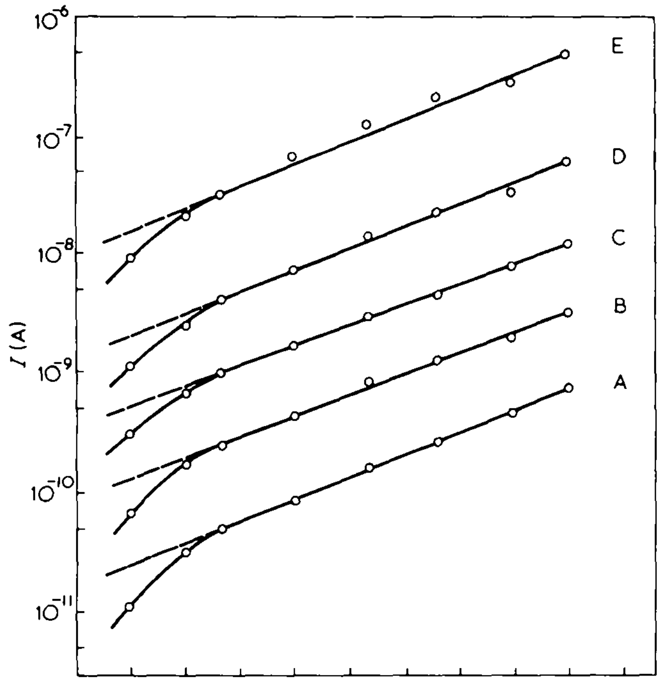

Figure 3 Log *I* vs. $\sqrt{E}$ plots (A) 100°C, (B) 125°C, (C) 150°C, (D) 175°, (E) 200°C

Results

The dependence of steady-state d.c. current on the electric field in Kapton is well known[1,5]. In the range below 100 kV cm^{-1} the log *I* vs. log *E* plot shows an ohmic behaviour consistent with the results of other workers[2,4]. Above this value, however, it clearly deviates from the linear plot and becomes superlinear. Plots of log *I* vs. *E* and log *I* vs. $E^{1/2}$ at various temperatures are shown in *Figures 2* and *3*. The latter give straight lines whereas the former may only be approximated to straight lines for fields above 100–150 kV cm^{-1}. The slopes and intercepts of these curves and the values of parameters like the ionic jump distance, high frequency dielectric constant, etc., calculated from these are summarized in *Table 1*.

In the superlinear region the steady-state conduction may be explained by the ionic hopping or Schottky or Pool-Frenkel or thermally assisted tunnelling mechanism of conduction. In case of ionic hopping conduction the current I at high electric fields may be approximately expressed as[5]

$$I = I_0 \exp(qEa/2kT)$$

where a is the ionic jump distance, q the charge of the ion and E the electric field strength.

The slope of the straight portion (where $qEa \gg 2kT$) of the log I vs. E plot would therefore give the ionic jump distance a. The values calculated from the plots of log I vs. E (*Figure 2*) using the same adjustment parameters as those used by Sawa *et al.*[5] are given in *Table 1*. These are in fair agreement with those reported by Tanaka *et al.*[11] based on t.s.c. measurements.

The non-linear behaviour of polymers at high fields may also be due to thermionic emission either from the cathode (Schottky emission) or from the donor-like defect states in the sample (Pool-Frenkel effect). In the latter case the current density is expressed as[8]

$$J = BE \exp\{-(\Phi_F - \beta_F E^{1/2})/kT\}$$

where B is a constant, Φ_F is the zero field ionization energy of the donor and $\beta_F E^{1/2}$ is the reduction in this field due to the applied electric field. By plotting log I against $E^{1/2}$ a straight line is obtained (*Figure 3*). The slope of this line enables one to estimate β_F and K. An agreement with the experimentally measured value of dielectric constant would thus be a reasonable indication of confirmation of the existence of the Pool-Frenkel effect as the operative mechanism. The values of ε_s and ε_{PF} obtained from the slopes of log I vs. $E^{1/2}$ plots are given in *Table 1*. The values of K at different temperatures, as estimated from these plots, are about 40% higher as compared to those quoted in the literature[9].

In thermally assisted tunnelling the d.c. conduction is described by an empirical relation of the form[4]

$$I = G.\exp(-\Phi/kT)\exp\{(b/kT + c).E^{1/2}\}$$

where G, b and c are constants. The form is essentially Pool-Frenkel modified to explain some observed anomalies.

Discussion

A preliminary examination of the present investigation and others[4,5] quoted here shows that the choice is between thermally assisted tunnelling and ionic conduction. We shall now examine the implications of the results in detail.

Table 1 Values of ionic jump distance 'a', dielectric constants ϵ_s and ϵ_{pf} and slope obtained from log I vs. I vs. $\sqrt{E}$ plots

T (°C)	100	125	150	175	200
a (Å)	52	50	54	56	59
ϵ_s	1.27	1.27	1.22	1.17	1.04
ϵ_{pf}	5.1	5.1	4.9	4.68	4.17
Slope of log I – $\sqrt{E}$ plot	0.24	0.24	0.24	0.25	0.27

Values of the ionic jump distance in Kapton have been extimated by Sawa *et al.*[5], Nagao *et al.*[10] and Tanaka *et al.*[11]. Sawa has also estimated these values using the data of Hanscomb *et al.* and reported these in his paper[5]. While Sawa's own values show a strong dependence on temperature, our values and also those of others show only a moderate variation with temperature. Further, the values estimated by other investigators differ widely. While Nagao[10] and his co-workers have reported a value of 75 Å, Tanaka *et al.*[11] have put their estimate at 46 Å. The values obtained by us agree with those of Hanscomb as well as Tanaka in spite of the fact that the heat treatment of our sample is different from these two. In spite of this agreement the magnitude of these values seems to militate against ionic conduction as the operative mechanism. An electron can travel over relatively large distances particularly in a regular lattice but an ion is a relatively massive particle which may hop into an adjacent site but is unlikely to travel freely over distances which are significantly greater than inter atomic distances in polymers. It may however be argued that the ionized vacancies where these ionic carriers may jump to or from are much fewer than one per lattice site. In summary, our data as well as that of Hanscomb and others appear to lend more support to Sawa's hypothesis of conduction being ionic in nature.

Let us now examine the paramaters on the basis of which a fit may be attempted with the Pool-Frankel or the tunnelling mechanism. The values of the dielectric constant estimated by us are higher than those quoted in literature by as much as 40%, although their rate of decrease with temperature is about the same. However, unlike the results of Hanscomb, our data yield values of slope (of log I vs. $E^{1/2}$ curves) which do not show a linear variation with reciprocal temperature. This not only goes against Pool-Frenkel effect but also against thermally assisted tunnelling as being the possible operative mechanisms of conduction at high fields.

Conclusions

Steady-state current in Kapton polyimide film of thickness 75 μm in the temperature range of 100°–200°C has been measured as a function of electric field (50 kV cm^{-1} to 450 kV cm^{-1}). Values of ionic jump distance, high frequency dielectric constant and apparent activation energy have been estimated from this data. Although on the basis of the present data alone, it is not possible to say exclusively whether the conduction at high fields in Kapton is ionic, Pool-Frenkel or due to thermally assisted tunnelling, yet when these results are seen in the background of those reported by other investigators[5] these appear to support ionic conduction. Further, light on this may be thrown by investigations on photoconductivity in Kapton. Results of this are in the process of being compiled and will be the subject of another communication.

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N.m.r. study of copolymer of styrene with methyl methacrylate prepared in presence of zinc chloride

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In the n.m.r. spectrum of a styrene (Sty)-methyl methacrylate (MMA) copolymer prepared in presence of zinc chloride at 60°C the phenyl protons of the styrene unit appeared as one peak at 3τ, the methoxy protons of methyl methacrylate unit appeared as three peaks at 6.4–6.8τ, 7.1–7.3τand 7.5τ. The position of these peaks indicated an alternate copolymer. This was further confirmed by estimation of copolymer composition from n.m.r. spectrum and element analysis. The value of 'σ' which is the probability of alternating MMA and Sty units having same configuration was also determined and found to be 0.865 ±0.006. It was found that the value of 'σ' was a direct function of concentration of zinc chloride.

Keywords Polymerization; nuclear magnetic resonance; styrene; methylmethacrylate; zinc chloride; analysis

Introduction

Nuclear magnetic resonance (n.m.r.) spectroscopy has been widely used for characterization of polymers. Ito[1,2] has determined structure, composition and stereochemistry of styrene methyl methacrylate copolymer prepared in presence of benzoyl peroxide and n-butyl lithium.

In this communication composition and stereochemistry of styrene-methyl methacrylate copolymer prepared in presence of zinc chloride has been determined.

Experimental

The methyl methacrylate, styrene monomers, Lewis acid (zinc chloride), initiator (azobis-isobutyronitrile, AIBN) were purified by standard methods[3]. The copolymerization reaction was carried out in a modified dilatometeric apparatus[3,4] under inert atmosphere of nitrogen gas at 60°C. The copolymer was precipitated with acidic methanol and was washed with acrylonitrile and cyclohexane to remove homopolymer and was dried to a constant weight.

The n.m.r. spectrum of the copolymer was taken on Perkin 100 M.C. spectrometer using CCl_4 as solvent and tetramethylsilane as internal reference.

Results and Discussion

The n.m.r. spectrum of copolymers prepared at 60°C in presence of 2×10^{-4} mol l^{-1} (*Figure 1*), 8×10 mol l^{-1} (*Figure 2*), 9×10^{-4} mol l (*Figure 3*) of zinc chloride showed following the characteristic peaks.

(i) One peak at 3τ due to phenyl protons of styrene unit.

(ii) Three separate peaks appeared at 6.4–6.8τ, 7.1–7.3τ, and at 7.5τ. These peaks are due to methoxy group of methyl methacrylate unit.

(iii) Three split peaks are present in the highest field

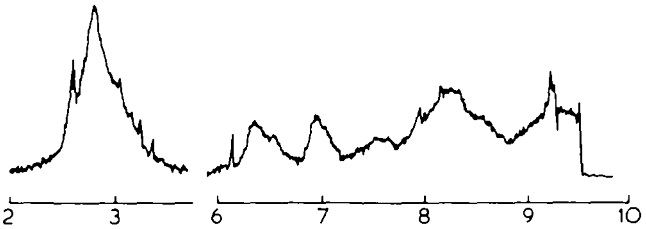

Figure 1 N.m.r. spectra of 1:1 styrene methyl methacrylate copolymer: $ZnCl_2 = 2\times10^{-4}$ mol l^{-1}, time = 2 h, AIBN = 2×10^{-4} mol l^{-1}, temperature = 60°C

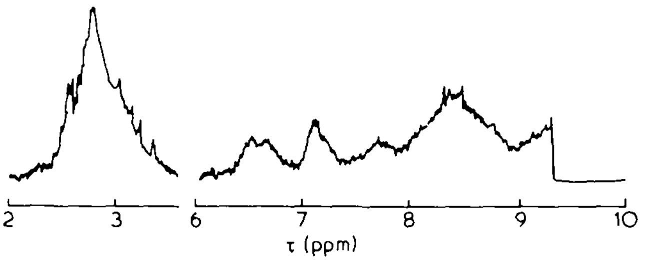

Figure 2 N.m.r. spectra of 1:1 styrene methyl methacrylate copolymer: $ZnCl_2 = 8\times10^{-4}$ mol l^{-1}, time = 2 h, AIBN = 2×10^{-4} mol l^{-1}, temperature = 60°C

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