Synthesis & Electrical Properties of Organic Semiconducting Polymers: Polythioacridine & Sulphur Bridged Polyacrylonitrile

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Received 13 February 1984; revised and accepted 1 June 1984

Two crosslined polymers have been obtained by the reaction of (a) acridine and (b) polyacrylonitrile with sulphur in an inert atmosphere at elevated temperatures. Both the polymers are amorphous in nature and behave as n-type semiconductors. Transport process at low temperatures (up to about 100°C) for polythioacridine obtained from the reaction (a) follows hopping conduction mechanism. The polymer obtained from the reaction (b) shows an abnormal photoelectric effect, namely, photoelectric fatigue.

Organic semiconducting polymers constitute one of the most fascinating, recent research topics, deeply involving both chemists and solid state physicists. Considerable interest has been shown in the synthesis and study of organic polymers which may behave like metals or at least show high conductivities. In this context, polyyacetylene\(^1,2\) and polypyrrole\(^3\) deserve special mention. The former can be reversibly doped to make it behave either as a \(p\)-type or as an \(n\)-type material and both can be combined to construct rechargeable electric cells. Also, it has been shown that films of polypyrrole prepared under controlled electrochemical conditions are highly conducting in nature, have strong adhesion to the metal surface and have appreciable thermal stabilities making them attractive electrode material.

Akamatu and Inokuchi\(^4,5\) were the first to observe a very high conductivity in crosslinked sulphur polymers. The conductivity of these materials increases with sulphur content and reaches a maximum value. This suggests that carrier transport between crosslinked molecules is favoured by sulphur bridges rather than by \(C-C\) bonds. Highly conducting polytetrafluorophenylthioether is also of interest. This infusible black polymer acts as a rectifier when placed between silver and platinum electrodes\(^6\).

With the above perspective in view, we have attempted to synthesize similar polymers involving heterocyclic aromatic compounds in order to study the effect of hetero atoms on electrical properties of the materials.

Materials and Methods

(a) Reaction of acridine with sulphur

Acridine and excess sulphur were mixed thoroughly and poured into a glass tube. The tube was flushed several time with nitrogen and placed in a furnace in a nearly horizontal position. The issuing hydrogen sulphide gas was trapped in lead acetate solution. After several hours, the tube was removed and allowed to cool. The material was washed with concentrated sulphuric acid, followed by concentrated alkali solution to remove low molecular weight products and finally with hot carbon disulphide solution to remove excess sulphur. The yield was about 72%.

(b) Reaction of polyacrylonitrile with sulphur

Polyacrylonitrile, obtained following the standard procedure\(^7\), was mixed with sulphur as before and the experiment repeated. The issuing gases in this case were trapped in lead acetate solution and Nessler’s reagent respectively. The same experimental procedure was applied to purify and work up the polymer. The yield of this sulphur bridged polyacrylonitrile polymer was about 70%. Several runs were carried out to optimize the conditions for the synthesis of the polymers. In both cases the optimum temperature was found to be about 400°C and the time required for the polymerization was nearly four hours.

Results and Discussion

The characteristic properties of the polymers are shown in Table 1. That the polymers are (a) polythioacridine and (b) sulphur bridged polyacrylonitrile is revealed from the following facts. The structures of the repeating units were indicated by IR spectra and elemental analyses. For polythioacridine, hydrogen could not be analysed accurately due to its very low content. The reaction for the formation of polythioacridine may be written as (Eq. 1). A higher relative ratio of sulphur to nitrogen content in the
Table 1—Characterisation Data of the Polymers

<table>
<thead>
<tr>
<th>Polymer*</th>
<th>Elemental analysis (Found, %)</th>
<th>Activation energy† (E₀) (eV)</th>
<th>Carrier concentration (n) (cm⁻³)</th>
<th>Thermoelectric power‡ (mV/deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Polythioacridine</td>
<td>C, 57.7</td>
<td>H, 1.6</td>
<td>N, 5.2</td>
<td>S, 35.5</td>
</tr>
<tr>
<td>(b) Sulphur bridged polyacrylonitrile</td>
<td>C, 63.2</td>
<td>H, 5.3</td>
<td>N, 12.2</td>
<td>S, 19.3</td>
</tr>
</tbody>
</table>

*Dark conductivity (τ) measured at room temperature was of the order of 10⁻¹⁰ ohm⁻¹ cm⁻¹ for both the polymers; majority carriers were electrons.
†measured from conductivity variation with temperature.
‡measured at room temperature.

polymer (b) indicates partial elimination of the latter. A more direct evidence of this was obtained from the fact that during fusion reaction the evolution of ammonia was confirmed by Nessler’s test after removal of hydrogen sulphide with alkali. The polymers were found to be insoluble in most of the polar and non-polar solvents including alkalies and several oxidizing and non-oxidizing acids.

After removal of excess sulphur, the polymers were refluxed with lithium aluminium hydride¹ in ether under nitrogen atmosphere for about two days. The excess of the reducing agent was decomposed with ice cold water-alcohol mixture, the products treated with excess barium hydroxide solution and filtered. The filtrates showed the absence of sulphide ions. The compounds would have been expected to release sulphide ions according to the reaction (2), if they contained −Sₓ linkages where x ≥ 3.

R − Sₓ − R → 2RSH + (x − 2) H₂S .... (2)

The absence of sulphide ions confirmed the absence of −Sₓ −(x ≥ 3) linkages. The reduced acidified products retained Hg²⁺ on treatment with HgCl₂ solution which is presumably due to the presence of −SH groups. However, the crosslinking by disulphide linkages in the acridine moiety was supposed to be random in nature as thin layer chromatography of the reduced product produced several spots. The reduced acidified product from polymer (b) is a black insoluble residue.

The characteristic IR absorption bands were found at 3300, 3030, 1600, 1200 cm⁻¹ for polymer (a) and at 3500, 1450, 1200, 500 cm⁻¹ for polymer (b) respectively. For (a) the peak appearing at 3300 cm⁻¹ is probably due to absorbed moisture. A very weak peak at 3030 cm⁻¹ seems to be due to aromatic C − H stretch. The peak at 1600 cm⁻¹ may either be due to >C = C < or due to >C = N − (delocalized). The peak at 1200 cm⁻¹ may be due to >C − N< stretch. For (b) the peaks may be due to >N − H (secondary), >C = C < , >C − N< and >C − S< stretch respectively.

Thermogravimetry showed that the polymer (a) is stable upto 300°C and polymer (b) upto 400°C in air. From Fig. 1a, degradation of the polymer (a) appears to take place in two distinct stages. The melting point, Tₘ, and glass transition temperature, Tₜ, are found to be around 260° and 160° for polymer (a). The overall mass loss upto 300°C is only about 15%. No residue is left at 900°C. The rate of mass loss is, however, maximum in the temperature range 400-560°C. Degradation of polymer (b) (Fig. 1b) appears to be a single stage process, maximum mass loss occurring in the temperature range 500-800°C.

X-ray powder diffractions of the samples were taken using Mo Kα radiation. The diffraction pattern is depicted in Fig. 2 showing the maxima only. Both the polymers are found to be amorphous in nature. Interchain separation, R, was calculated using the relation², R =\[ \frac{\lambda}{8 \sin \theta} \] and was found to be 4.99 Å and 4.32 Å for polymers (a) and (b) respectively. Radial distribution function analysis is being carried out with a view to obtaining structural information.

Before performing the electrical measurements, the samples were thoroughly dried in vacuo over P₂O₅. Compacted powders of the polymers were used to measure variation of electrical conductivity with temperature. Graphite paint was found to be ohmic in
both the cases. In the low temperature region (upto about 100°C), for both the samples, conductivity increases very slowly as shown in Fig. 3. From the slope of the upper portion of the graph, the activation energy values were calculated using the relation $\sigma = \sigma_0 e^{-E_a/kT}$. The upper portions of the graphs may be intrinsic region for both the samples. The slope in the low temperature portion of the graph for polymer (a) is found to vary continuously. This indicates that transport process for (a) in this region follows hopping conduction mechanism. The carrier concentration, $n$, was calculated using the relation\(^{10}\), $n = 2\left(\frac{2nm*e^2}{\hbar^2}\right)^{3/2} e^{-E_a/kT}$ assuming that the effective mass is equal to the rest mass of the electron. The low mobility (0.19 cm\(^2/\)V. sec) upto about 100°C calculated
for the polymer (a) using the relation $\sigma = ne^\beta$, is consistent with the hopping transport.

Thermoelectric power measurements for both the polymers show that they are of $n$-type in nature. Variation of thermoelectric power for polymer (a) with temperature up to about 250°C in the intrinsic region in vacuum is shown in Fig. 4. As the temperature increases, the contributions of holes and electrons cancel each other, hence the thermoelectric power decreases. The validity of Johnson and Lark-Horovitz equation\textsuperscript{11} is proved. From the slope of the plot in Fig. 4, individual mobilities of electrons and holes, $\mu_e$ and $\mu_h$, were calculated and were found to be 0.11 and 0.08 cm\textsuperscript{2}/V sec respectively. It is observed that electrons are slightly more mobile than holes.

Sheinkman and Ya. Shik\textsuperscript{12} discussed the characteristic features and mechanism of abnormal photoconductivity, particularly long term relaxation and residual conductivity in inhomogeneous semiconductors. Experiments on steady state photoconductivity of polymer (b) were performed by illumination with tungsten halogen lamp (Philips 600 W). Graphite contact was found to be ohmic. The following characteristics are observed (Fig. 5):

(a) On illumination (↑) the photoconductivity increased initially and then decreased slowly below the
dark value. After switching off (\( \downarrow \)) the light it took several hours or even days to reach the dark value.

(b) The photoresponse was independent of the wave length of radiation.

c) The magnitude of photoconductance peak was dependent on the intensity of light.

(d) On heating the sample after illumination ended, the photoconductivity reached the dark value instantaneously.

Regarding the plausible mechanisms for this type of phenomena, Sheinkman and Ya. Shik\(^{12}\) pointed out the significance of the following two points:

(i) The density of the recombining carriers may be sufficiently low.

(ii) Photochemical reactions may occur under certain conditions.

This anomalous photoelectric effect has also been observed in pure and doped CdS crystals\(^{13-15}\) and GaSb\(^{16}\) doped with sulphur.

It is very likely that point (ii) is the cause of the photoelectric fatigue in this newly synthesized polymer. This view is corroborated by the fact that the simple pyrolyzed polyacrylonitrile does not show the photoelectric fatigue. The \(-S-S-\) linkage is highly susceptible to photolytic decomposition. Elementary observations show that when the surface of the sulphur bridged polymer is reduced by lithium aluminium hydride and then methylated, the photoresponse of the product so obtained is very poor, which is in conformity with point (ii). This polymer may be a promising material for photomemory devices due to its very slow recovery of the initial dark conductance. Further investigations on such anomalous photoelectric effect are in progress.

Acknowledgement

One of the authors (D. Mukherjee) is indebted to the CSIR, New Delhi for financial assistance.

References

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