Conductivities of poly (*N*-vinyl carbazoles) containing cation-radicals

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Partial oxidation of poly(*N*-vinyl carbazole) (PNVC) to produce crosslinked PNVC containing dimeric carbazylium cation radicals is shown to produce material with significant semiconductivity (σ) up to $\sim 10^{-5}$ ohm^{-1} cm^{-1} at 293K. The synthesis of these materials (including partly ring-chlorinated analogues) is described and their semiconductivities and activation energies for conductance (E_a) examined as a function of cation-radical content. It is demonstrated that the extent of reaction essentially determines the semiconduction of these materials, provided homogeneous conditions are maintained. The starting molecular weight of the PNVC, and whether or not it is partly chlorinated, have minimal effect on σ.

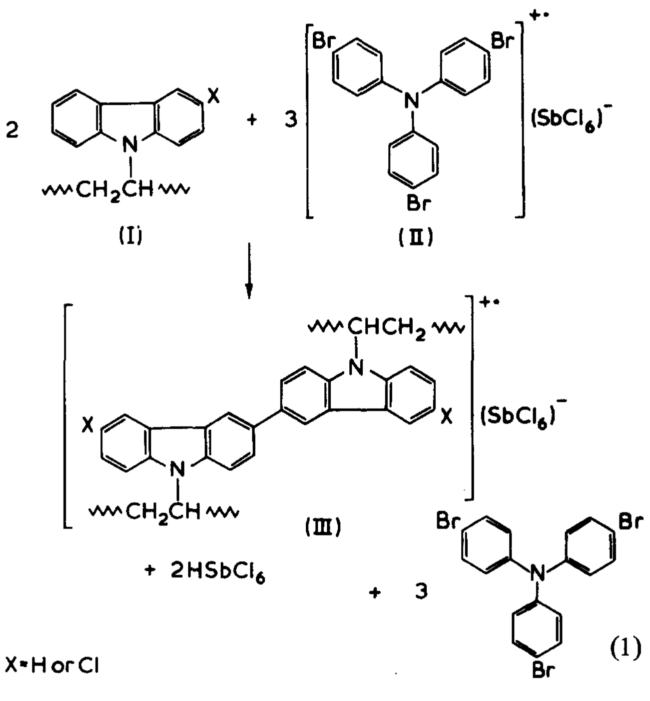
INTRODUCTION

Poly(*N*-vinylcarbazole) (PNVC) has been extensively investigated as a thermal and photoconducting polymer[1–22]. This is particularly so since the presence of selective additives enhances its intrinsic semiconductivity ($\sim 10^{-14}$ ohm^{-1} cm^{-1}) and influences its photoconductivity by shifting the action spectrum into the visible. As an illustration of these effects, iodine increases the semiconductivity (σ) of PNVC to 10^{-5} ohm^{-1} cm^{-1} when present at 77% w/w. At the same time there is a reduction of activation energy (E_a) from $\geqslant 1.3$ to 0.39 eV[10]. Increased photoconductance, and particularly the generation of significant conductance under visible radiation, is achieved by the formation of charge transfer complexes between pendant carbazole residues acting as donor groups, and acceptor additives. A number of acceptor molecules have been shown to be effective in this way, but currently most studies have used 2,4,7-trinitrofluorenone (TNF) as dopant[11–14].

Interest in the electrical properties of PNVC, PNVC/TNF and other polymers containing carbazole rings is particularly motivated by their potential as films to replace selenium in the electro-imaging technique used in photocopying machines[15–17]. For this purpose resistivities high enough to maintain surface charge plus photoconductance under visible illumination for the discharge of surface charge are the requirements. Significant semiconductivity ($\sigma \gtrsim 10^{-13}$ ohm^{-1}cm^{-1}) would not be a desirable feature in electro-imaging. Nevertheless, semiconducting polymers are of value, particularly if they retain the plastic characteristics of most polymers.

The mechanism of semi- and photoconductance occurring in PNVC-based materials has received some attention. It appears that in most cases hole migration is dominant, although with iodine as additive, electron mobility is also present[10]. The conduction process requires activation, either thermally (σ having a positive temperature coefficient) or by photostimulation. Most recent investigations[18–22] conclude that both in their semi- and photoconductance behaviour, charge migration in PNVC-based materials is controlled by a hopping mechanism between traps, and that such migration is field and thermally stimulated. These various studies suggest that PNVC and doped PNVC provide a matrix for hole and/or electron migration which is very efficient – more efficient than many other readily accessible polymers.

The possibility of introducing unpaired electrons by the formation of free radicals in PNVC could on this basis provide effective semiconductors. Synthetically such a possibility exists since it is known that stable cation radicals can be generated by an oxidative dimerization of carbazoles[23,24]. It is also known that this oxidation occurs with PNVC [equation (1) I] using tris-(*p*-bromophenyl) ammoniumyl hexachloroantimonate (V) [equation (1) II] as oxidant[25], as illustrated in equation (1).



(1)

We report below the semiconductivities and activation energies for conductance of a variety of cation-radical PNVCs and partly chlorinated PNVCs together with details of their syntheses. A study of their photoconductive properties will be described in a subsequent publication.

SYNTHESIS OF CATION-RADICAL CONTAINING PNVCs

Careful attention was given to the purity of all solvents and reagents used in the synthesis so as to remove all extraneous impurities, particularly reducing agents, and moisture. Dichloromethane was refluxed with calcium hydride for 48 h and then fractionated (b.p. 39.3°C). Acetonitrile after drying (phosphorus pentoxide, 48 h) was decanted from the desiccant and fractionated (b.p. 81.8°C). Chloroform (1 litre) was rendered free of ethanol by triple washing with water (3 x 500 cm^3), dried over anhydrous calcium chloride for two days and finally refluxed with calcium hydride (18 h). It was then fractionated (b.p. 61°C). At all stages after washing, light was excluded and the purified chloroform, when not used directly, was stored in the dark for a period not exceeding one week. Benzene and n-heptane were dried (sodium and calcium hydride respectively) and distilled. A.R. quality n-pentane was used as supplied.

Tris-*p*-bromophenylamine was synthesized from recrystallized (ethyl acetate) triphenylamine by bromination in purified chloroform using the method of Walter[26]. Dry n-heptane was used as solvent in the Soxhlet extraction employed for purification. This amine (12.3 g) was converted to tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate(V) by a slightly modified method to that described in the literature[27]. Freshly distilled antimony(V) chloride (7.7 cm^3) was added to the amine dissolved in the minimum quantity of dry benzene. Upon cooling in ice, crystals of tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate(V) separated in high purity and yield (95%), and after filtration and washing with cold benzene these were dried under vacuum for two days prior to use.

Two of the samples of PNVC were synthesized by cationic polymerization. To this end a commercial sample of *N*-vinyl carbazole was recrystallized twice from A.R. methanol, ensuring that at no time did the temperature exceed 44°C (to avoid thermal polymerization). Before use, the monomer was freed of excess methanol by extensive (4 days) vacuum drying. Cycloheptatrienyl salts were used as initiators for the polymerizations. The perchlorate, synthesized by the method of Reid *et al.*[28] was used to prepare the low molecular weight polymer. For the high molecular weight polymer preparation by cationic initiation, recourse was made to the hexachloroantimonate(V) salt prepared by the method of Dauben *et al.*[29]. PNVC sample A was prepared by initiating 40 g of monomer in 2 dm^3 dichloromethane with 20 cm^3 of 2 % w/v cycloheptatrienylperchlorate in acetonitrile for 1 h at ambient temperature. PNVC sample B was prepared by adding dropwise a solution of 0.02 g of cycloheptatrienyl hexachloroantimonate(V) in 300 cm^3 of dichloromethane, to 60 g of monomer in 300 cm^3 of dichloromethane. Before and during the addition, the reaction mixture was cooled (–5° to 0°C) and well stirred and these conditions were maintained for a further period of 2 h after all the initiator has been added. Both samples A and B were isolated by precipitation into excess A.R. methanol. These materials and a commercial sample (C; courtesy of Xerox Corporation, New York) were purified by two cycles of dissolution (dichloromethane), precipitation and washing (A.R. methanol) followed by drying under vacuum until free of methanol. Molecular weights were: sample A, $\bar{M}_n = 1.6 \times 10^3$ (vapour pressure osmometry in benzene at 303K); sample B, $\bar{M}_w = 10^6$, $\bar{M}_n = 1.6 \times 10^5$ (gel permeation chromatography in toluene at 303K); sample C, $\bar{M}_w = 1.25 \times 10^6$ (quoted by Xerox Corporation). Two partly chlorinated (3- and to a minor extent 3,6-dihalogenated) PNVCs were also investigated. One of these (D) was supplied by the courtesy of Professor A. Ledwith at the University of Liverpool; it was 75% substituted (based on monosubstitution) and had a $\bar{M}_n = 9.5 \times 10^3$. The other sample (E, ~90% substituted) was synthesized from sample B by chlorination with 1-chlorobenzotriazole[30], the method also used for sample D. To this end, sample B (7.97 g) dissolved in dichloromethane (60 cm^3) was mixed with 1-chlorobenzotriazole (5.71 g)[31], dissolved in dichloromethane (30 cm^3) and left to react for 12 h at ambient temperature. At the completion of reaction benzotriazole was removed by extraction with four 100 cm^3 aliquots of 3% w/v aqueous sodium hydroxide, the organic phase well washed with water and dried over anhydrous sodium sulphate. Following some concentration, the polymer was isolated by precipitation into A.R. methanol and purified as for samples A–C. The synthetic procedure used for D and E is known[25] to lead to nearly stoichiometric substitution at the expense of some chain degradation (for sample D a 15% reduction in the number average degree of polymerization).

Cation radical sites were generated in polymers A–E by reaction (1) using tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate(V) as oxidizing agent. In the majority of cases dichloromethane acted as solvent for both substrate and oxidant, the latter being added dropwise to a well stirred solution of the former at ambient temperature. In all cases the addition of oxidant resulted in the immediate formation of the characteristic intense green colour of the dicarbazolyl-cation radical III (equation 1). This observation is consistent with the high reactivity of carbazole rings to such oxidation[23,24] and indicates that the three electron-transfer processes applicable to simple monomeric carbazoles occur here also. After the addition of oxidant was complete, the reaction was left for 2 h before the oxidized polymers were isolated. This was achieved in most cases by precipitation into excess n-pentane, in some cases (A, B2 and B3) after some prior evaporation of solvent. Products were then well washed with n-pentane and vacuum dried. Details for individual preparations are shown in *Table 1.*

Since the oxidation [reaction (1)] is a crosslinking reaction it will, if sufficient oxidant is present, result in gelation. This was found to occur with samples prepared from polymer B, even at the low extent of oxidation used. Thus, samples B2 and B3 gelled on concentration while sample B4 gelled during reaction and had to be isolated by solvent evaporation and subsequently well washed with n-pentane. Sample B1, although apparently remaining soluble during reaction, was found to have become insoluble in dichloromethane after precipitation. This propensity for sample B to gel is undoubtedly the result of its broad molecular weight distribution and contrasts with sample C of similar molecular weight. In order to study higher concentrations of radical cations in polymer B, heterogeneous conditions were used to synthesize samples B5 and B6. To this end polymer B was swollen in acetonitrile and reacted with oxidant in this solvent for 12 h. The oxidized forms were then isolated by filtration, washed with n-pentane and vacuum dried. Visual examination did indicate that samples B5 and 6 were heterogeneous having some larger particles with white non-oxidized centres. The oxidation of sample E was accomplished without gelation. This may be due to a reduction in its molecular weight during chlorination, or to a lower

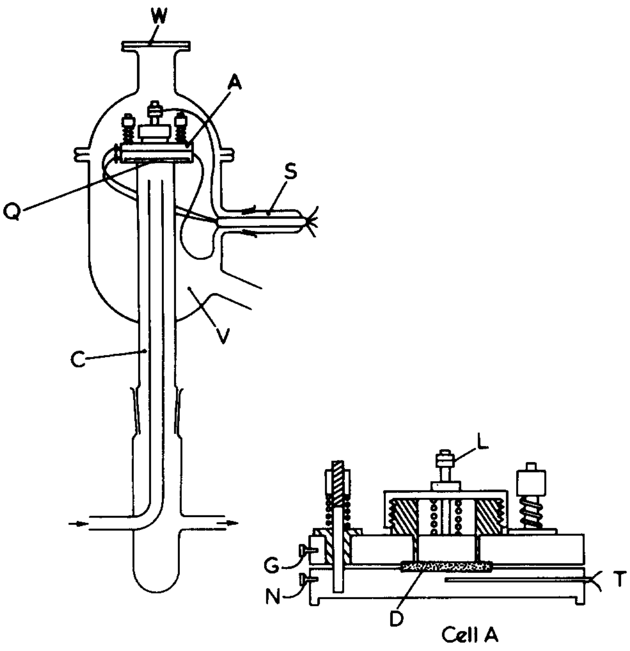


Figure 1 Cell assembly for semiconductance measurement. For description see text

crosslink density per chain (because the 3-mono or 3,6-dichlorinated groups cannot readily dimerize) or both.

METHOD OF ELECTRICAL MEASUREMENTS

Electrical measurements were made using 1.5 cm diameter discs of the various oxidized PNVCs. Such discs were readily obtained by compression moulding in a Beckman 'KBr disc' die at pressures of 10^8–10^9 N/m^2. They ranged from very pale to deep green in colour (depending on the radical concentration), were translucent or transparent, and mechanically moderately strong. During several months storage *in vacuo* the majority of samples showed little visible change. An exception was sample A6 which exhibited surface deterioration from a glassy green to a matt grey.

The resistance of such discs (D) was measured either directly or after the provision of tin-foil or gold surface electrodes (see below) with the equipment illustrated in *Figure 1*. This consisted of the three-electrode cell assembly (A) made of brass with Teflon insulation (hatched), mounted on a quartz plate (Q) located at the top of the chimney (C). This chimney was part of the evacuable glass vessel (V) which also contained a quartz cone joint (S) carrying the live (L), neutral (N), guard (G) and thermocouple (T) leads. (Facility for illumination was also provided in the form of a quartz window (W), but this was not used in the present study.) During electrical measurements, vessel V was evacuated ($< 10^{-3}$ mmHg) and the temperature of the sample varied by streaming preheated or cooled nitrogen onto the underside of Q via the chimney C. The sample temperature was monitored by means of a chromel–alumel thermocouple embedded in A.

Resistances of discs were determined by connecting a Wareham SO7 variable-voltage source, the cell and an appropriate ammeter (milli-, micro- or electrometer as picoammeter) in series using screened electrical connections, except internal to the vessel (V). The vessel (V) and ammeter were also enclosed in an earthed aluminium box.

A number of preliminary experiments were undertaken to find the most satisfactory system of surface contact to the discs. Direct contact between the brass electrodes of the cell and sample surface was found to result in non-ohmic behaviour at low voltages, with ohmic response only occurring at higher field strengths (20–60 kV/m). This behaviour is shown in *Figure 2*. However, the pressing of polymer discs between tin foil, directly in the die, did result in ohmic behaviour over the entire voltage range (*Figure 2*) and optimized the conductance. Evaporation of gold–palladium electrodes on to the surface was briefly investigated, but it was found that at least five evaporations were required to provide a continuous film, and even then the conductances were still somewhat less than for the sample between tin foil. On occasion (samples C1-3) tin-foil electrodes were dispensed with; under these conditions higher field strengths ($\geqslant$ 60 kV/m) were used to ensure ohmic behaviour. The presence of tin-foil electrodes also negated the operation of the guard-ring and thus made measurements of any surface conductance impossible. However, independent measurements with plain discs indicated the absence of any measurable surface contribution to conductance. The use of tin-foil electrodes also limited the upper temperature of measurement to 318K since above this temperature separation of tin-foil from the surface often occurred.

Reproducibility in the measured semiconductivities (σ) depended significantly on its magnitude. Thus, for samples with $10^{-5} \geqslant \sigma \geqslant 10^{-7}$ ohm^{-1} cm^{-1} errors were generally within ± 5% (including duplicate pressed discs); for lower conductivities ($<10^{-11}$ ohm^{-1} cm^{-1}) errors rose progressively to ~10%; while for very low conductivities ($<10^{-12}$ ohm^{-1} cm^{-1}) measurements became significant only to an order of magnitude. Errors in the derived activation energies E_a were ~ ± 0.1 eV.

CONDUCTIVITIES OF THE CATION-RADICAL POLYMERS

Measured semiconductivities at 293K (σ_{293}) and E_a values obtained from temperature dependence measurements (see *Figure 3*) are given in *Table 1*. Also quoted therein are the mole fractions (x) of cation-radicals [species III in equation (1)] calculated from the stoichiometry of the reaction for

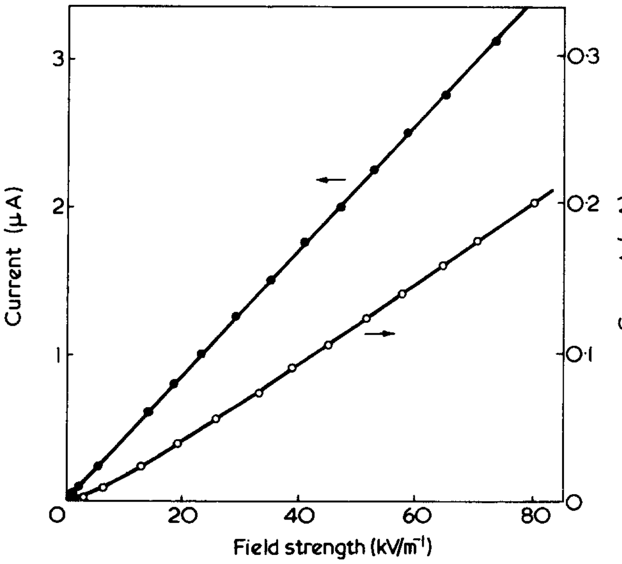


Figure 2 The influence of tin-foil on the current–voltage dependence of sample A2. ○, no electrodes; ●, with tin foil electrodes

the materials studied. The time-independent behaviour of the conductance which was observed with all samples, together with the rapid response to application and removal of e.m.f., strongly support that these oxidized PNVCs, as PNVC itself, conduct by an electronic rather than ionic mechanism. Qualitatively it can be seen from *Table 1* that increasing x enhances σ_{293} and reduces E_a. The increasing conductivity is considerable, rising to $\sim 10^{-5}$ ohm^{-1} cm^{-1} at the quite moderate extents of oxidation achievable before the crosslinking of the low molecular weight PNVC-A occurs. Quantitatively there is a good correlation between σ_{293} values and x, provided that series B samples are excluded, as illustrated in *Figure 4*. For series A, C, D and E the double logarithmic plot shown in *Figure 4* indicates that neither the molecular weight of the starting polymer, nor the substitution of chlorine into some of the carbazole rings, influences the conductivity. Also, the manner in which the radicals are introduced, for example by mixing PNVC with PNVC containing moiety III (sample AC1) rather than by direct oxidation, does not greatly affect the trend shown in *Figure 4*. What does influence the behaviour in *Figure 4* is any heterogeneity introduced during preparation. We believe that we are then dealing with composite materials which have regions of high conductivity interspersed into bulk polymer of low conductivity.

Figure 5 shows the dependence of E_a on x. Here again, if series B is excluded, a general trend can be seen of decreasing E_a with increasing radical concentration. The re-

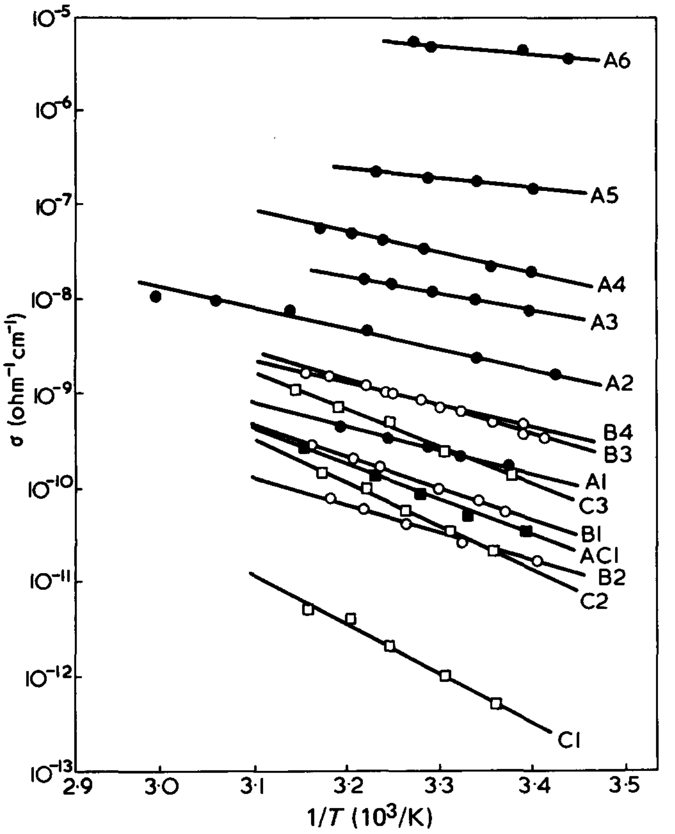


Figure 3 The temperature dependence of cation-radical containing PNVCs. For listing of sample codes see *Table 1*

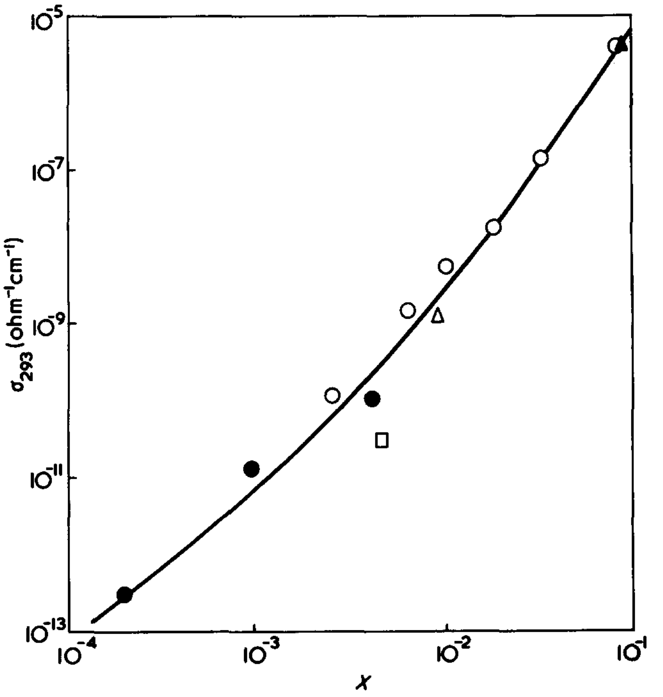


Figure 4 The dependence of σ_{293} on x for cation-radical containing PNVCs. ○, series A; ●, series C; ▲, series D; △, series E; □, AC1

Table 1 Synthetic and conductivity data for the carbazylium cation radical containing polymers

	Conditions of preparation				
Code	Polymer (wt mg/vol in cm^3)	Oxidant (wt mg/vol in cm^3)	10^2x	σ_{293} (ohm^{-1} cm^{-1})	E_a (eV)
A1	1.50/100	48.7/200	0.257	1.3×10^{-10}	0.5
A2	3.07/100	257/250	0.665	1.6×10^{-9}	0.43
A3	1.50/100	202/250	1.07	6.3×10^{-9}	0.38
A4	3.04/100	733/400	1.94	1.8×10^{-8}	0.39
A5	1.50/100	602/400	3.27	1.5×10^{-7}	0.18
A6	0.995/100	997/600	8.58	4.1×10^{-6}	0.15
B1	7.35/150	9.9/60	0.011	4.2×10^{-11}	0.67
B2	4.01/150	9.8/60	0.019	1.6×10^{-11}	0.56
B3	4.01/150	35.5/250	0.070	3.5×10^{-10}	0.55
B4	8.00/300	164/250	0.162	4.3×10^{-10}	0.47
B5	1.01/100	55.9/50	0.439	10^{-14}	–
B6	0.500/100	500/150	8.57	7.4×10^{-9}	0.34
C1	0.798/1500	2.0/100	0.020	3×10^{-13}	1.0
C2	1.02/1500	12.4/100	0.096	1.4×10^{-11}	0.87
C3	0.956/1600	50.3/100	0.417	1.1×10^{-10}	0.75
D1	1.07/500	989/600	8.94	4.6×10^{-6}	–
E1	2.04/500	212/250	0.961	1.3×10^{-9}	–
AC1	1.01/500	334/100	0.464	3×10^{-11}	0.75

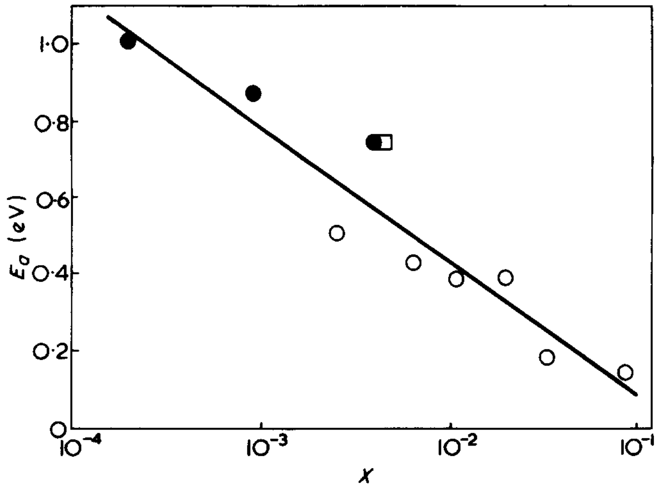


Figure 5 The dependence of E_a on x for cation-radical containing PNVCs. ○, series A; ●, series C; □, AC1

sults shown in *Figures 4* and *5* illustrate not only that the introduction of cation radicals by oxidation of PNVC provides materials of significant semiconductivities, but also that σ_{293} values are synthetically adjustable in the range 10^{-5}–10^{-12} ohm^{-1} cm^{-1}. Further extrapolation of the data in *Figures 4* and *5* to higher values of x suggests that even higher σ_{293} and lower E_a values would result. To achieve such material with the necessary uniformity of radical distribution would require either PNVC of lower molecular weight than sample A, or a carbazole-derived monomer or polymer which would not crosslink or become heterogeneous during oxidation. Particularly, the latter would be of interest since with such material it might be possible to achieve complete conversion to radical cation ($x = 1$). Then, if the trends illustrated in *Figures 4* and *5* were maintained, σ_{293} values of $\sim 10^{-2}$ ohm^{-1} cm^{-1} and very low E_a values would result. The development of alternative cation radical polymers which do not crosslink or which are derived from monomers by oxidative crosslinking is currently being investigated.

The potential usefulness of cation-radical polymers depends not only upon their conductivities but also upon these values being maintained with age. We have examined the stability of samples A2 and A6 on storage in a desiccator and noted that sample A6 had a reduced σ_{293} value (1.27×10^{-7} ohm^{-1} cm^{-1}) after 1 month storage whilst sample A2 had not changed its σ_{293} value after 6 months. Thus, PNVC cation-radical polymers at high cation radical contents do exhibit some loss of conductivity with time. This phenomenon would also have to be overcome in any useful semiconductor based on cation-radical polymers.

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