Electrical conductivity and electron spin resonance studies of pyrolysed polyimide

C. Z. Hu, K. L. DeVries and J. D. Andrade
Department of Material Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA

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Recent studies of polymer-based pyrolytic amorphous carbon for use in organic electrolyte-lithium batteries and as metal-doped carbon electrodes show considerable promise. Polyimide can be thermally converted to amorphous carbon films. The irreversible evolution of polyimide under progressive heat treatment is characterized by three successive structural changes: pyrolysis, carbonization and graphitization. Four-point contact conductivity and electron spin resonance (e.s.r.) measurements were used to study and correlate electrical conductivity changes with unpaired electrons. From these studies it is concluded that at low pyrolysis temperature (<650°C) the pyrolysed polyimide is a nonmetallic amorphous carbon incorporating residual oxygen and nitrogen. At higher pyrolysis temperatures (>700°C) a microcrystalline graphite-like metallic domain starts to appear in the amorphous matrix. The development of this 'metallic domain' causes the conductivity of the pyrolysed polyimide to increase sharply.

(Keywords: conductivity; electron spin resonance; pyrolysed polyimide)

INTRODUCTION

The major means of making conducting polymers has been by various treatments which change the insulating nature of the polymer to a semiconductor or conductor. Conducting polymers have been achieved in three distinct ways. The first method for increasing the conductivity of polymers is through incorporation of macroscopic pieces of conducting materials, such as metal flakes or carbon black particulates, into host polymers to form conducting composites[1]. The second method of producing conducting polymers is by means of chemical doping, electrochemical treatment, etc. The two polymers of this type that have been studied most extensively in the past several years are polyacetylene and polydiacetylene[2-4]. The third method of making a conducting polymer is by modifying the intrinsic bulk properties of polymers by pyrolysis. Recently studies have shown drastic changes in electronic properties of some aromatic base polymers after pyrolysis[5,6].

The main reasons for selecting polyimide for the pyrolysis work are: (a) Polyimide is available in plastic sheet, fibre and solution forms. Almost any desired shape of polyimide can be achieved by these three forms. For example very thin polyimide can be obtained by the spin-casting technique and patterned polyimide can be obtained by photolithographic techniques. (b) The pyrolysis process of making polyimide conductive is simple and inexpensive, unlike most other methods of producing conducting polymers which require complex laboratory equipment and skill. (c) By controlling the pyrolysis conditions, the polyimide conductivity can be made to range from 10^{-5} to 10^{3} S cm^{-1}. This wide range of conductivities warrants further study of pyrolysed polyimide as a light weight material for unique conductor or semiconductor application. (d) Polyimide makes an interesting model compound for studying amorphous carbon. Pyrolysed polyimide is an amorphous carbon ($>90\%$ carbon content) and since it can be prepared by a variety of experimental methods it is a good candidate for studying the properties of amorphous carbon. (e) Pyrolysed polyimide has great potential for applications in carbon electrodes, biomedical devices, low temperature heating elements, patternable conductor circuitry, electromagnetic shielding, radiation and gas detectors[7,8].

EXPERIMENTAL

Materials

The material investigated in this study was Kapton^{R} film, supplied by DuPont, in sheet form (0.13 mm thickness). Pre-cut Kapton films were sandwiched between to quartz plates to prevent the Kapton film from curling during pyrolysis. The Kapton films were pyrolysed in an argon atmosphere at various temperatures and times. The resulting pyrolysed polyimide was a flat black film with reduced flexibility and a metallic lustre.

Conductivity measurements

The electrical conductivity of pyrolysed Kapton was measured by a four-point contact method[9], and the measurement of temperature dependence of the conductivity was achieved with a DISPLEX compressor system.

E.s.r. absorption measurements

Pyrolysed Kapton films produced by various pyrolysis conditions were ground under a nitrogen atmosphere, and the resulting powder was loaded into e.s.r. sample tubes. The tubes were then held under vacuum for 24 hours prior to e.s.r. measurement. The e.s.r. measurements were made with a Varian Model E-3 ESR spectrometer in which the resulting spectra were first

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derivatives of absorption vs. applied magnetic field. The free radical concentration of each pyrolysed Kapton sample was obtained by double integration of these spectra and comparison with a standard pitch sample (supplied by Varian) as described in ref. 10.

RESULTS AND DISCUSSION

The room temperature conductivity of pyrolysed Kapton as a function of pyrolysis temperature is given in *Figure 1*. For pyrolysis temperatures above 700°C, conductivity gradually increased to $10^{-2}\,\mathrm{S\,cm^{-1}}$ up to a temperature of approximately 800°C. This was followed by a rather abrupt increase in conductivity as the pyrolysis temperature was increased from 800 to 850°C, from approximately 3.5 to $20\,\mathrm{S\,cm^{-1}}$. For temperatures greater than 850°C, conductivity again slowly increased with increasing pyrolysis temperature. Samples held at a pyrolysis temperature for 1 hour (line B in *Figure 1*) exhibited similar behaviour for conductivity vs. pyrolysis temperature with a similar step increase in conductivity from 24 to $83\,\mathrm{S\,cm^{-1}}$ as the pyrolysis temperature was increased from 800 to 850°C. These conductivity experiments indicate that the polyimide changes from an insulator to a semiconductor at pyrolysis temperatures of the order of 700°C ($>10^{-2}\,\mathrm{S\,cm^{-1}}$) and to a 'metallic' conductor at pyrolysis temperatures higher than 900°C ($\sim 10^{2}\,\mathrm{S\,cm^{-1}}$). The step change in conductivity between 800°C and 850°C suggests the presence of a thermally activated process which results in the formation of dense heterocyclic carbon ring networks in the polymer.

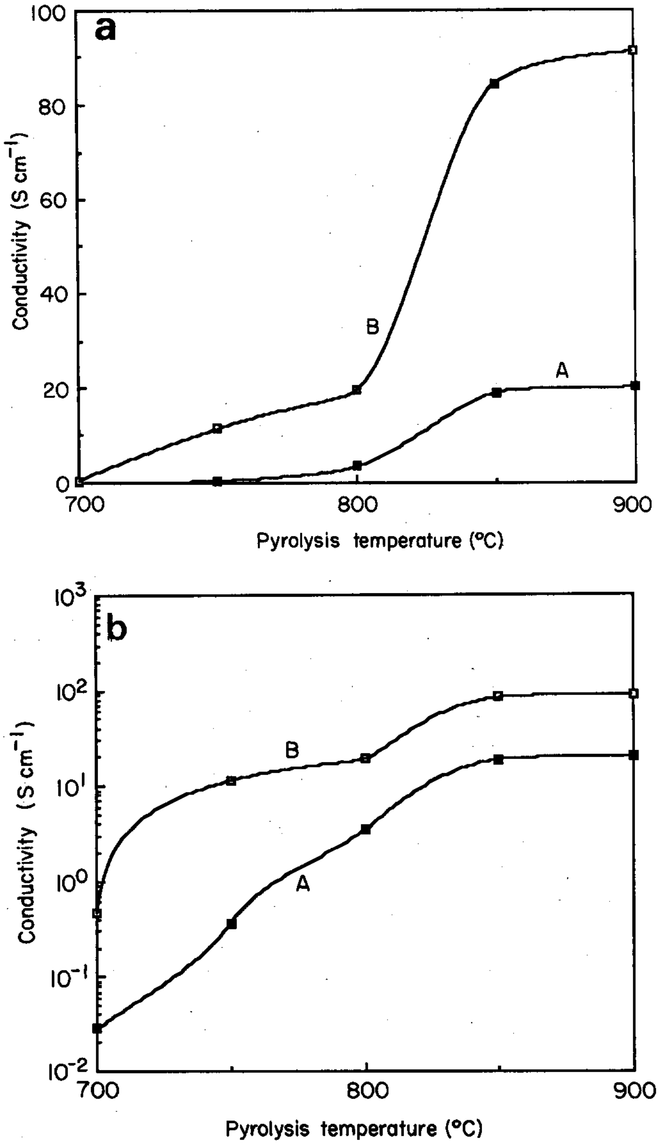

Figure 1 (a) Conductivity *versus* pyrolysis temperature for Kapton. Line A: sample cooled immediately after reaching the desired temperature and line B: sample held at desired temperature for 1 h. (b) Conductivity *versus* pyrolysis temperature for Kapton. Line A: a sample cooled immediately after reaching the desired temperature and line B: sample held at desired temperature for 1 h

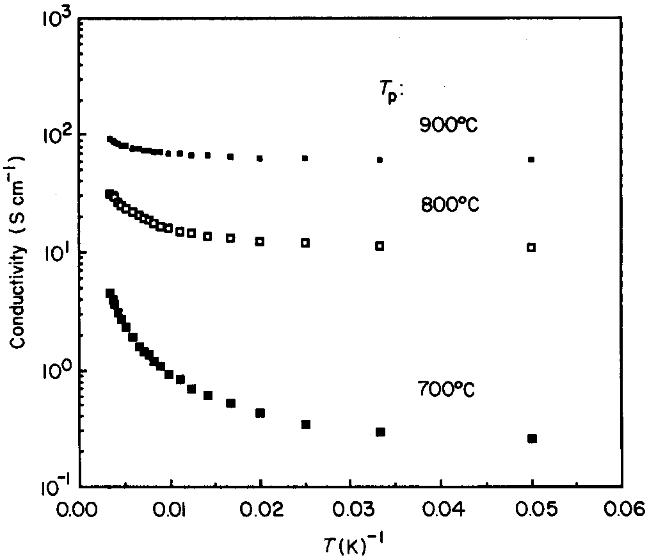

Figure 2 Temperature dependence of conductivity *versus* T^{-1} for Kapton pyrolysed 1 h at 700, 800 and 900°C

Table 1 Temperature-independent conductivity of pyrolysed Kapton

Pyrolysed Kapton	^{a}T ($\mathrm{S\,cm^{-1}}$)	$^{b}T.I.C.$ ($\mathrm{S\,cm^{-1}}$)
700°C, 1 h	4.48	0.25
800°C, 1 h	31.8	10.5
900°C, 1 h	91.7	59.0

[a] T = Total conductivity
[b] $T.I.C.$ = Temperature-independent conductivity

The inverse temperature dependence of the electrical conductivity ($\log\beta$ vs. $1/T$) of the polyimide pyrolysed at T_p (pyrolysis temperature) = 700°C, 800°C, 900°C is shown in *Figure 2*. The plots of conductivity vs. temperature in *Figure 2* exhibit temperature-independent conductivity at low temperatures. The amplitude of this temperature-independent conductivity is dependent on the pyrolysis temperature is shown in *Table 1*. The temperature-independent conductivity was subtracted from the original temperature dependent conductivity data for each pyrolysed Kapton sample. Plots of log conductivity vs. $T^{-0.25}$, after subtracting the temperature-independent conductivity, are shown in *Figure 3*. The total conductivity of the pyrolysed polyimide at various pyrolysis temperatures can be closely approximated by an equation of the form

$$\beta=\beta(m)+\beta(T)=\beta(m)+\beta_1\exp[-(T_0/T)^{1/4}]$$

where $\beta(m)$ is the temperature-independent conductivity and $\beta_1\exp[-(T_0/T)^{1/4}]$ is the temperature-dependent conductivity. This is consistent with Mott's variable-range hopping mechanism[11].

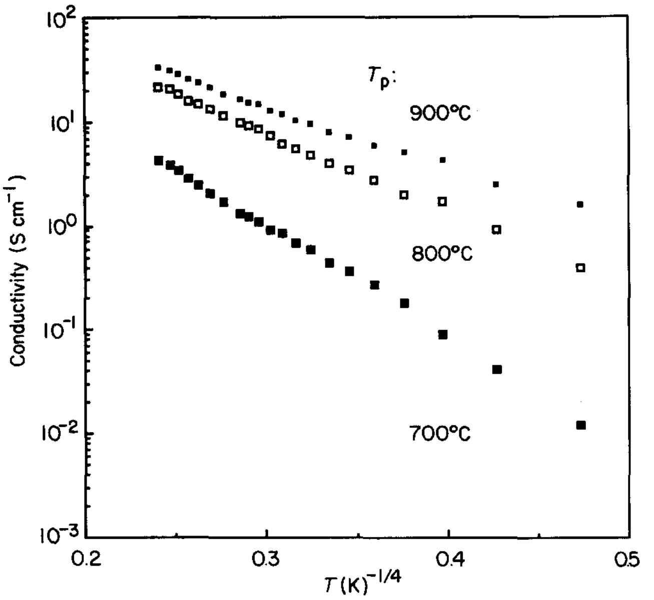

Figure 3 Temperature-dependent part of the conductivity *versus* $T^{-1/4}$ for Kapton pyrolysed at 700, 800 and 900°C

The existence of a temperature-independent conductivity at low temperature is thought to involve an irreversible disorder-induced nonmetal–metal transition. The Cohen–Jortner Transition model (CJT) for such a transition has been proposed for amorphous carbon[12]. In contrast to the Anderson–Mott Transition[13], the CJT model explains inhomogeneous material conductivity. Pyrolysed polyimide is considered to be a type of amorphous carbon. According to this model different structure changes of pyrolysed polyimide are considered to occur during three pyrolysis temperature dependent regions: pyrolysation at temperatures less than 700°C, carbonization at temperatures between 700°C and 1800°C, and graphitization at temperatures greater than 1800°C[14]. The microscopic inhomogeneities of pyrolysed polyimide are caused by growing heterocyclic carbon rings within the amorphous carbon matrix at pyrolysis temperatures higher than 700°C. These structural inhomogeneities also cause inhomogeneities in the electronic structure. From an electric conduction point of view, the pyrolysed polyimide has metallic domains in a nonmetallic amorphous carbon medium. These metallic domains are the result of local development of heterocyclic carbon rings which form graphite-like dense heterocyclic carbon ring networks with strong π-orbital overlap.

The conductivity experiments clearly demonstrate that the pyrolysed polyimide is converted to a high electrical conductor by pyrolysis. At low pyrolysis temperatures the pyrolysed polyimide is in an amorphous state and electric conduction is due to variable-range hopping. At temperatures higher than 700°C, the pyrolysed polyimide is in a heterogeneous state with two conducting paths: one is a metallic channel with extended electronic states for which the conductivity has no temperature dependence, and the other is a disordered system where the electron conduction is by a variable-range hopping mechanism.

Electron spin resonance spectroscopy was used to probe the 'break up' of the polymer structure through thermal degradation (scission) of covalent bonds. The resulting spectra had no fine structure to identify the location of the unpaired electrons. It is not certain if these unpaired spins (hereafter referred to as free radicals or spins) are associated with specific organic free radicals or perhaps on isolated very small clusters of amorphous carbon. The g value of the spectra was very near the 'free electron' value of 2 consistent with organic free radicals.

The time dependence of the e.s.r. spin concentration for Kapton pyrolysed at 550°C is shown in *Figure 4*. The corresponding weight loss is also shown in *Figure 4*. The initial e.s.r. spin concentration was about 6×10^{18} spins/gram. The maximum spin concentration reached 9.8×10^{18} spins/gram after 50 min pyrolysis, after which it started to decrease and became flat at a spin concentration near 6×10^{18} spins/gram after three hours pyrolysis. The sample heat treated at 550°C shows that the e.p.r. spin concentration increases with pyrolysis time and reaches a maximum after 50 min of heating. Most polyimide weight loss also occurs during the first 40 min of the heating period, with only a slight change in weight observed beyond 40 min. During this time hydrogen, carbon monoxide and carbon dioxide are given off as the result of cleavage of polyimide functional groups and C–H bonds, simultaneously creating reactive β-radicals. Once reactive β-radicals are created, followed by a limited polycondensation of the aromatic rings through the reactive β-radical, stable π-radicals are formed[14]. The process of forming stable π-radicals is described by Lewis[15]. After the spin concentration reaches a maximum, at about 50 min pyrolysis, a drastic decrease of spin concentration is observed which finally levels off after about 120 min. This diminishing of the spin concentration is thought to arise from a pairing of the free radicals during the pyrolysis process. At 550°C the reorganization of scissioned aromatic rings through free radical pairing is limited by this low temperature with the result that only isolated or semi-isolated condensed aromatic rings are formed. The material in this stage is still an insulator ($> 10^{-6}$ S cm^{-1}) and no conductivity can be detected at this pyrolysis temperature.

A comparison between the time dependence of the e.s.r. spin concentration and four-point contact conductivity for Kapton pyrolysed at 650°C is shown in *Figure 5*. The e.s.r. spin concentration vs. time curve exhibits an initial spin concentration of about 5.3×10^{18} spins/gram, with a distinct drop of spin concentration to nearly 1.6×10^{18}

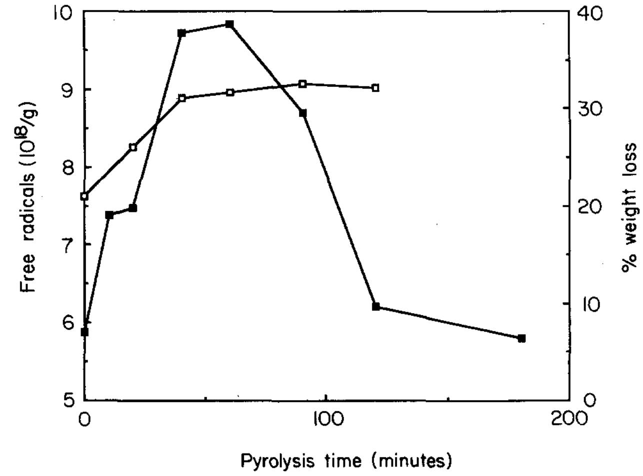

Figure 4 Time dependence of e.s.r. spin concentration (■) and percent weight loss (□) for Kapton pyrolysed at 550°C for different periods of heating time

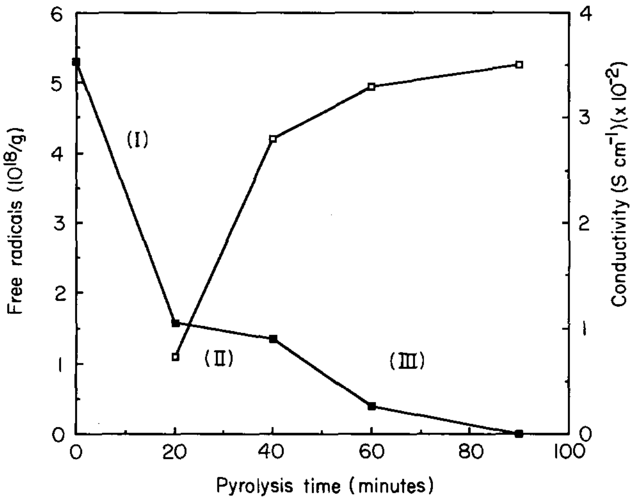

Figure 5 Time dependence of e.s.r. spin concentration and conductivity for Kapton pyrolysed at 650°C for different periods of heating time

spins/gram after 20 min (region I), followed by a gradual decrease to 1.3×10^{18} spins/gram after 40 min heating (region II), and subsequently decreasing to 2.3×10^{15} spins/gram (region III). The conductivity of the pyrolysed Kapton sample was $9\times10^{-3}\,\mathrm{S\,cm^{-1}}$ after 20 min heating and reached a plateau value of $3.2\times10^{-2}\,\mathrm{S\,cm^{-1}}$ for heating periods greater than 60 min. For polyimide pyrolysed at 650°C the spin concentration did not increase nor was significant weight loss detected. The samples for the 650°C e.s.r. time dependent measurements were prepared by heating the polyimide from room temperature to 650°C at a constant heating rate of 10°C/min. After the polyimide sample reached the desired temperature it was maintained at that temperature for the desired time, and then cooled to room temperature. During this heating process when the temperature only exceeded 550°C slightly, the polyimide started to dissociate reaching near completion at temperatures above 600°C. At this time the free radicals had already been created and then paired during the heating stage from 550°C to 650°C of the pyrolysation treatment. The spin concentration vs. time curve of Kapton pyrolysed at 650°C can be divided into three regions as follows: (I) A step decrease of spin concentration within 20 min pyrolysis time associated with the radical pairing process. (II) A very gradual decrease in spin concentration observed in the 20 to 40 min heating period. The flat region corresponds to the change in conductivity of pyrolysed Kapton from insulator to semiconductor (conductivity greater than $10^{-4}\,\mathrm{S\,cm^{-1}}$). It is hypothesized that this is the result of the semi-isolated or isolated heterocyclic carbon rings gradually merging into a continuous network of dense heterocyclic carbon rings with the development of increasingly effective π-orbital overlap[16]. In order to initiate the development of dense and continuously heterocyclic carbon ring networks, the pyrolysis temperature of polyimide should be no less than 600°C. This is a thermally activated process. (III) A step decrease of spin concentration is observed after a 40 min heating period. The diminishing of the free radical concentration in this stage is caused by the growth of heterocyclic carbon rings, followed by sufficient development of π-orbital overlap to induce a change in the electronic structure of the material from insulator to semi-metallic.

Experimentally, electron spin resonance of conduction electrons has been observed in only a small number of metals[17,18]. This is very likely due to the fact that in many metals the electronic resonance line width (which is inversely proportional to the spin-lattice relaxation time T_1) is so large that the signal is unobservable. Therefore a possible reason for the observed decrease in spin concentration, in the present study, may be that the mobility of those free radicals, which exist in the heterocyclic carbon ring networks, gradually increases and becomes more and more like conducting electrons in metals. If this hypothesis can be accepted, the increase of mobility of those free radicals will cause the spin-lattice relaxation time T_1 to decrease. The result of this structural change is that the e.s.r. absorption intensity and the measurable free radical concentration decreases. Because the pyrolysis temperature is insignificantly high, only a portion of the isolated heterocyclic carbon rings in the sample can further recombine into dense heterocyclic carbon ring networks and only those regions will be converted from insulator to semi-metallic. Free radicals in those semi-metallic regions are undetected by e.s.r. spectroscopy. By comparing the degree of decreasing free radical concentration and the increase of conductivity between the 550°C and 650°C samples, it is concluded that the size of this heterocyclic carbon ring network is determined by the pyrolysis temperature and time. The rule of thumb is the higher the pyrolysis temperature and longer the time the larger the heterocyclic carbon ring network.

The pyrolysis temperature dependence of the e.s.r. absorption measurement is shown in *Figure 6*. A plot of full width half maximum (*FWHM*) of the e.s.r. peak vs. pyrolysis temperature is shown in *Figure 7* (in arbitrary units). The *FWHM* was increased from 8.5 to 11.9 Gauss with a pyrolysis temperature change from 550°C to 650°C. *Figure 6* illustrates the e.s.r. absorption measurement of Kapton as a function of different pyrolysis temperatures along with the corresponding weight loss. The spin concentration initially increased from 5.8×10^{18} to a maximum of 9.4×10^{18} spins/gram (corresponding to pyrolysis temperature increase from 550°C to 600°C) followed by a rapid decrease to

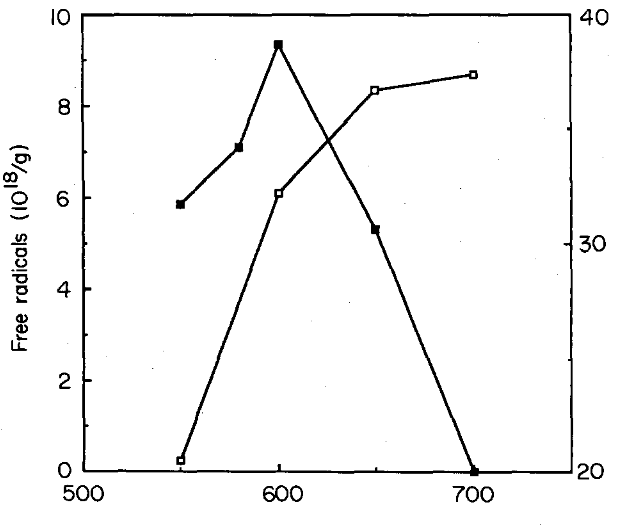

Figure 6 E.s.r. spin concentration (■) and percent weight loss (□) as a function of pyrolysis temperature for Kapton

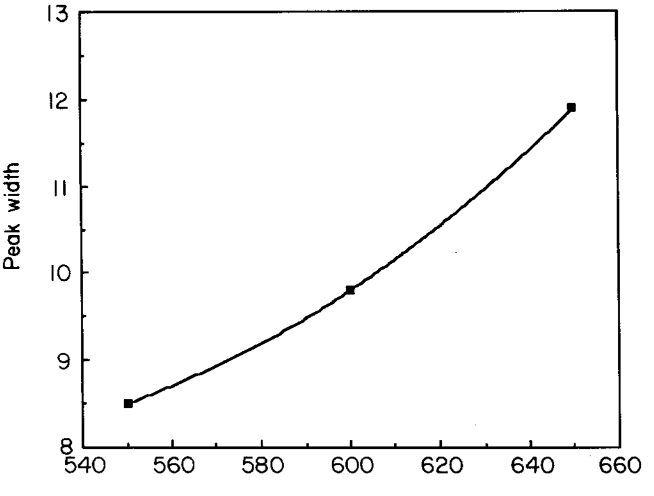

Figure 7 E.s.r. peak width as a function of pyrolysis temperature for Kapton

9.5×10^{15} spins/gram at a pyrolysis temperature of 700°C. The corresponding weight loss slowly increased from 20 to 37.4%. Most polyimide weight loss also occurs during the temperature change from 550°C to 650°C with only a small change in weight observed beyond 40 min. The e.s.r. absorption curve of Kapton at temperatures below 700°C shows a Curie doublet type spectrum. A gradual increase of spin concentration at temperatures between 550°C and 600°C is matched by the strong dissociation of the polyimide. The free radicals generated during this period of strong dissociation are still limited to isolated individual aromatic carbon rings. At pyrolysis temperatures between 600°C and 700°C, the Kapton sample is in transition between the two different processes. At temperatures just higher than 600°C, continuous thermal dissociation (which creates the free radical) and limited heterocyclic carbon ring condensation (with free radical pairing) are possible. Apparently, in this temperature range the latter process dominates and the spin concentration of the pyrolysed Kapton gradually decreases as the pyrolysis temperature increases. As the pyrolysis temperature is further increased, the thermal degradation and free radical pairing process continuously decreases. Eventually, both processes will become insignificant at temperatures higher than some critical temperature T_c (T_c is between 600°C and 700°C). With temperatures above this critical temperature, the carbonization process becomes dominant. Pyrolysed polyimide at this stage starts to form a continuous dense heterocyclic carbon ring network and sufficient π-orbital overlap is developed to form semi-metallic regions. Conductivity at 700°C approaches 10^{-2} S cm^{-1} indicating the pyrolysed polyimide has become a semiconducting material. As pyrolysis temperatures exceed 700°C, there is an abrupt disappearance of the e.s.r. absorption spectra and an increase in conductivity indicating the formation of metallic-like conduction electrons. As mentioned earlier, the conduction electron has a very short spin-lattice relaxation time T_1 and a corresponding e.s.r. peak width inversely proportional to T_1, resulting in a significantly broadened e.s.r. peak width resulting in a disappearance of the e.s.r. signal. The increasing e.s.r. peak width *versus* pyrolysis temperature probably implies a gradual increase in semi-metallic regions.

CONCLUSIONS

The temperature dependent conductivity experiments suggest that pyrolysed polyimide from low temperature pyrolysis (less than 700°C) contains homogeneous amorphous carbon consistent with the Mott variable-range hopping mechanism. At temperatures higher than 700°C, metallic conductivity arises (temperature-independent conductivity), due to the inhomogeneity of the pyrolysed polyimide. It is proposed that this metallic conductivity is due to the formation of graphite-like metallic domains with extended electronic states that increase with pyrolysis temperature. The total conductivity of pyrolysed polyimide is equal to the conductivity contributed by metallic conduction, which is independent of temperature, $\beta(m)$, plus the temperature-dependent conductivity contributed by the non-metallic amorphous carbon medium, $\beta(T)$, which obeys the Mott variable-range hopping conduction mechanism.

The free radicals created during polymer scission can be investigated by e.s.r. There are three major processes occurring during high temperature heat treatment. At low pyrolysis temperature (less than 600°C), stable π-radicals are created by thermal degradation of polymer chains. At pyrolysis temperatures higher than 600°C, but less than 700°C, free radicals created by thermal scission of polyimide chains are paired with each other and form larger heterocyclic carbon rings. Finally, at pyrolysis temperatures higher than 650°C, a decrease in e.s.r. signals observed associated with a corresponding increase in conductivity suggesting that the formation of conduction electrons during carbonization leads to formation of continuous dense heterocyclic carbon ring networks with sufficient π-orbital overlap to result in a disappearance of the e.s.r. signal.

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