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Studies on electrical conductivity of gamma irradiated polyaniline

Qi Yao*, Limin Liu, and Changjiang Li

Department of Applied Mathematics and Physics, Beijing Institute of Chemical Technology, Beijing 100029, People's Republic of China

Summary

dc electrical conductivity at surface of γ–irradiated polyaniline (PAn) has been studied. EPR spectroscopic results indicate that the variation of spin concentration is consistent with the increase of σ_{dc}.Electrical conductivity (σ_{dc}) versus temperature (T) characteristics of unirradiated and irradiated PAn were performed, which demonstrate that the unirradiated curve can fit to $\ln\sigma_{dc} \propto T^{-1}$, while the irradiated curve fit to $\ln\sigma_{dc} \propto T^{-1/4}$.

Introduction

Polyaniline is one of the most intensely investigated conducting polymers [1–3]. Due to its high chemical and thermal stability and the ease of polymerization, together with the relative low cost of production, it has also the potential of many technological applications. But the studies of PAn subjected to ionizing radiation has not yet attracted enough interest. Recently, high energy proton beam bombardment of PAn has been performed [4]. This article will present the studies on dc electrical conductivity of γ–irradiated PAn.

Experimental

PAn was synthesized using the standard chemical oxidation procedure [5], An aqueous solution of $(NH_4)_2S_2O_8$ was added with HCl until its pH value exceeds one,then aniline $C_6H_5NH_2$ was slowly dripped into the mixture, stirred at temperature 5℃ , polymerized to a precipitate, and the precipitate was washed subsequently by distilled water, methanol, and ether. The material was heated in an evacuated chamber, and dark blue powder was prduced. The powder was compressed into round pellets of 13mm in diameter, and 1mm thick. PAn samples were irradiated by ^{60}CO source of 3.45×10^5Curie intensity, with dose rate 2.04KGy / min. σ_{dc} at surface was measured by standard four–probe method. EPR results were obtained at room temperature using a Bruker ER–200D spectrometer, with resolution 10mG, operating at 9.5 GHz. Samples were introduced into the cavity of a cylindrical glass tube, diameter 2mm. Spectra were recorded using the following instrumental parameters; scan range, 20G; microwave power, 63μW; modulation frequency, 100KHz; magnetic field intensity H, 3368.8G; time constant, 200ms; scan time, 200sec. σ_{dc} vs T characteristics were performed by recording the resistance using four–probe method, of which resistivity precision is $10^{-4}\Omega\cdot$cm, and the curves plotted by a X–Y recorder.

*Corresponding author

Results and Discussion

σ_{dc}.

σ_{dc} values at surface of unirradiated and irradiated PAn were carefully measured, the results are sure and reproduced, listed in Table 1, change of conductivity is reversible.

Table 1: σ_{dc} of PAn irradiated by various dose

σ_{dc}(S / cm)	Radiation Dose(MRad)
2.2	0
2.2	5
2.2	20
2.7	30
2.7	40

By inspection of preceding results, one can observe that σ_{dc} sustained no variation when the radiation dose is less than 30 MRad, and σ_{dc} increased from 2.2 to 2.7 S / cm when the dose exceeds 30MRad, later σ_{dc} kept constant in the range 30–40MRad. Thus it can be shown that PAn revealed low resistance (10^6–10^7Rad) in concern of electrical conductivity.

Although conductivity sustained no significant variations when radiation dose exceeds 30MRad, comparison between gamma and proton irradiation on PAn is meaningful. Irradiations on PAn have been performed for proton energy ranging from 30kev to 30Mev [4,6], both resulted in decrease of electrical conductivity σ_{dc} at surface, [e.g. σ_{dc} of PAn subjected to 30kev proton irradiation(for ion fluence 2.25×10^{16} ions / cm^2) varied from 2.6 S / cm to 0.77S / cm]. Preceding results show that, although both proton and gamma radiations are ionizing, their σ_{dc} variations are contrary, which means that mechanisms of gamma and proton irradiations on PAn are distinctly different, thus investigation on these aspects should be proceeded further.

EPR spectroscopic results

EPR spectra were shown in Figure 1. g factor might be obtained by the formula

$$g = \frac{h\nu}{H\beta}$$

Calculation on unirradiated and irradiated (30MRad) PAn gave g = 2.0030 and 2.0031), i.e, g remained constant on exposure to γ–radiation. The lineshapes of EPR spectra are both Lorentzian determined by their asymmetric ratios, which fits the preceding results [7]. The only significant change comes from spin concentration determined by numerical calculation of the area under the curves within $\Delta H_{PP} = 0.6G$.

The height of the peak of irradiated PAn is about twice that of the unirradiated sample, but the weight of irradiated PAn was 6mg, while that of unirradiated PAn was 4mg.

We can obtain the ratio of spin concentration $I_2 / I_1 = 202 / 171$, which is consistent with the ratio of σ_{dc} 2.7 / 2.2, as shown in Table 1.

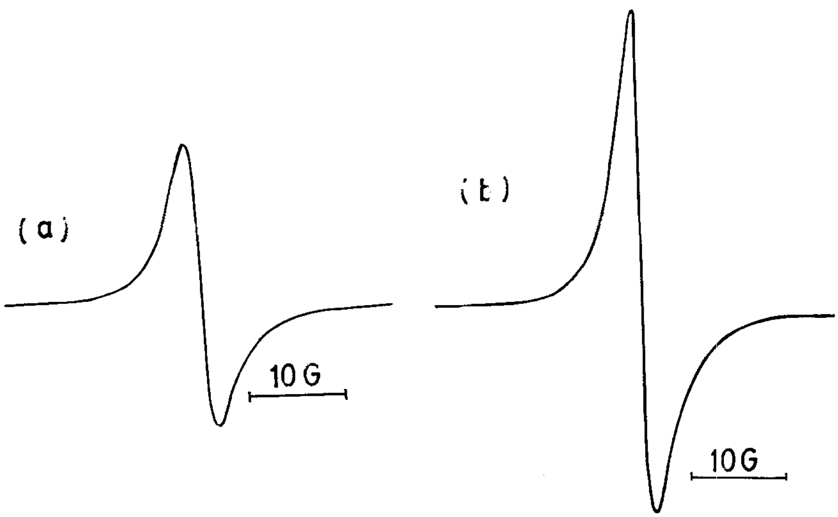

Fig.1 EPR spectra unirradiated (a) and irradiated (b) PAn. operated at 9.5 GHz, instrumental parameters, scan range, 20G; microware power, 63μW; modulation frequency, 100KHz; H, 3368.8G; time constant, 200ms; scan time, 200sec.

σ_{dc} vs T Characteristics

σ_{dc} vs T characteristics are shown in Figures 2 and 3.

The curve in Fig 2(a) is characterized for unirradiated PAn, it can be fit to the curve [Fig.2(b)] determined by the relation

$$\ln\sigma_{dc} \propto T^{-1}$$

which might be explained with the semiconducting property [8], using the granular polymeric metal system [9], i.e, percolation transprt via charging energy limited tunneling between metallic islands.

The curve in Fig 3(a) is characterized for irradiated PAn, it can be fit to the curve [Fig.3(b)] given by relation

$$\ln\sigma_{dc} \propto T^{-1/4}$$

consistent with the variable–range hopping model [10], i.e, charge hopping among fixed polaron sites.

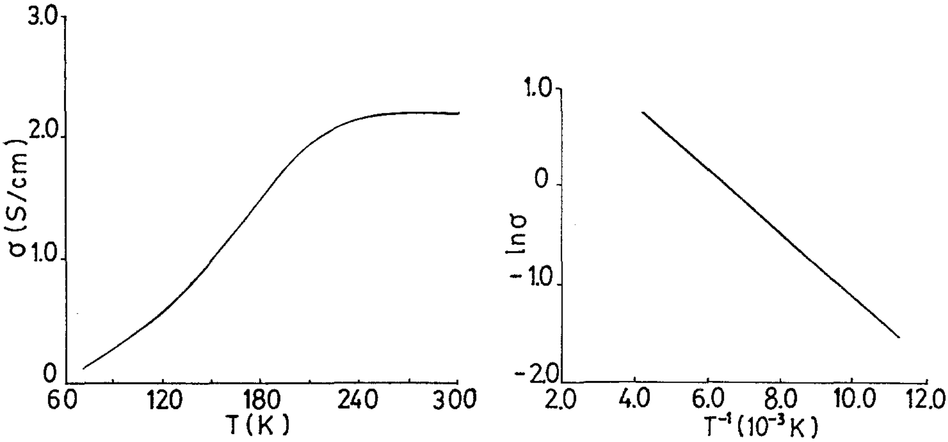

Fig.2 σ_{dc} vs T (a) and lnσ_{dc}∝vs T^{-1}(b) characteristics of unirradiated PAn.

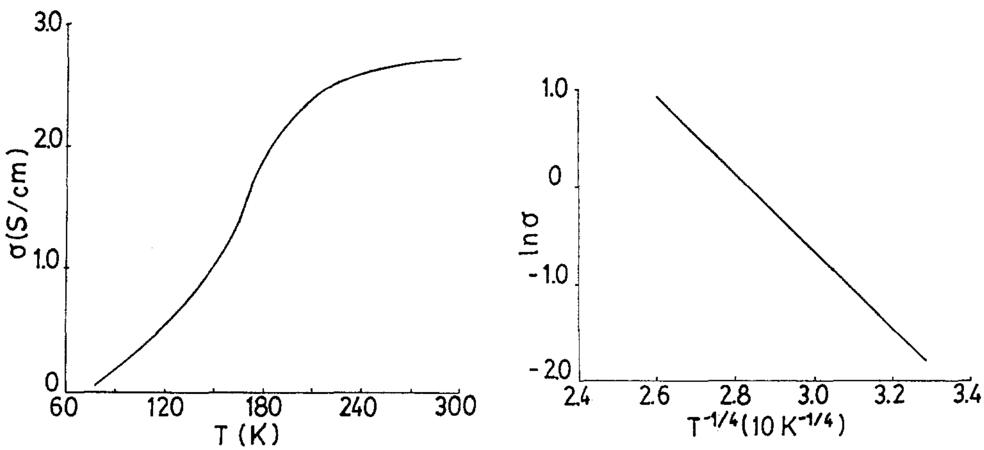

Fig.3 σ_{dc} vs T (a) and lnσ_{dc}∝vs $T^{-1/4}$(b) characteristics of irradiated PAn.

Size of pellet

The size of pellet is not changed after γ–irradiation.

Conclusion

Preceding results show that σ_{dc} of PAn increased after γ–irradiation, but the radiation resistance (dose 10^6–10^7Rad) in concern of electrical conductivity is low. The increase of σ_{dc} is consistent with the increase of spin (or radical) concentration, which shows that the variation of σ_{dc} is originated from the increase of charge carriers (assuming that the spin carriers are also charge carriers [11]). Variation of σ_{dc} vs T characteristics suggest that the electrical conduction changed from granular polymeric metallic system to variable–range hopping mechanism.

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