
ATTI ACCADEMIA NAZIONALE DEI LINCEI
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI
RENDICONTI

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**Electrical conductivity of biological and organic
compounds. - Part IV. Electrical conductivity in
polycaprolactam of different molecular weight before
and after gamma irradiation**

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche,
Matematiche e Naturali. Rendiconti, Serie 8, Vol. 48 (1970), n.6, p. 630-635.*
Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1970_8_48_6_630_0>

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Chimica. — *Electrical conductivity of biological and organic compounds.* — Part IV. *Electrical conductivity in polycaprolactam of different molecular weight before and after gamma irradiation* (*). Nota di ALBERTO BRECCIA, SERGIO DELLONTE e GIUSEPPINA NUCIFORA, presentata (**) dal Socio G. SEMERANO.

RIASSUNTO. — Vengono riportati i dati relativi a misure di conducibilità elettrica prima e dopo irradiazione gamma di campioni di policaprolattame, aventi $\bar{M}_n = 16,600, 40,000$ e $60,000$.

Lo scopo è di studiare il meccanismo di conduzione per temperature inferiori a 70°C e la funzione del peso molecolare sulla conducibilità elettrica.

INTRODUCTION.

Studies on electrical properties of polyamides have been developed during the years, especially a.c. conductivity [1, 2] and d.c. conductivity [3, 8].

It was found that the factors influencing electrical conductivity, in these kinds of polymers, are: crystallinity [1, 7]; amide group concentration [9] and water adsorption [5].

Generally two mechanisms of electrical conduction in polyamides are today considered: a ionic mechanism, with protons involved as charge carriers [1, 2, 5, 7] and an electronic one [10, 11].

Seanor [4] suggested that below 90°C the mechanism of conduction in polyamides is primarily electronic and above 120°C it is ionic.

The purpose of this work is to investigate the conduction mechanism of polycaprolactam for temperatures below 70°C and the function of molecular weight in the electrical conductivity, before and after gamma irradiation.

EXPERIMENTAL PROCEDURE.

Three samples of polycaprolactam of $\bar{M}_n = 16,600; 40,000$ and $60,000$ kindly provided by the Montecatini Edison Soc. (Milano) in purified form were used.

Conductivity measurements in d.c. electrical field were carried out: the electrical system was the same as that of a previous work [12].

Extruded samples had a thickness in the range of $0.210\text{--}0.215\text{ cm}$ and a cross-section in the range of $0.031\text{--}0.036\text{ cm}^2$.

Contacts were made by coating both sides with aquadag.

(*) Work carried out by C.N.R. in the Laboratorio di Fotochimica e Radiazioni d'Alta Energia - Bologna (Via dei Castagnoli, 1).

(**) Nella seduta del 13 giugno 1970.

Before measurements, samples were left at 70° C under vacuum (10^{-4} mm Hg) for 24 hours. Measurements were carried out in nitrogen atmosphere at 760 mm Hg.

For current-voltage measurements the same system for the bulk conductivity was used and an interval of 45 minutes allowed after each voltage change.

A Co-60 source (dose-rate: 10 rad/min) was used for the irradiation of the samples. The total dose given to each sample was of 3 Mrad.

After irradiation, radical presence was registered by a Varian mod. 4502, 12 inch magnet, spectrometer with a frequency of 9000 Mc/S and a field modulation of 100 Kc/S.

RESULTS AND DISCUSSION.

1) *Conduction mechanism.*

Activation energy and resistivity values versus molecular weight are shown in fig. 1.

Successive cooling and heating cycles of the irradiated and not irradiated samples gave lines with the same graphs but with higher resistivity values. The data obtained for each sample are referred to the first cycle of heating.

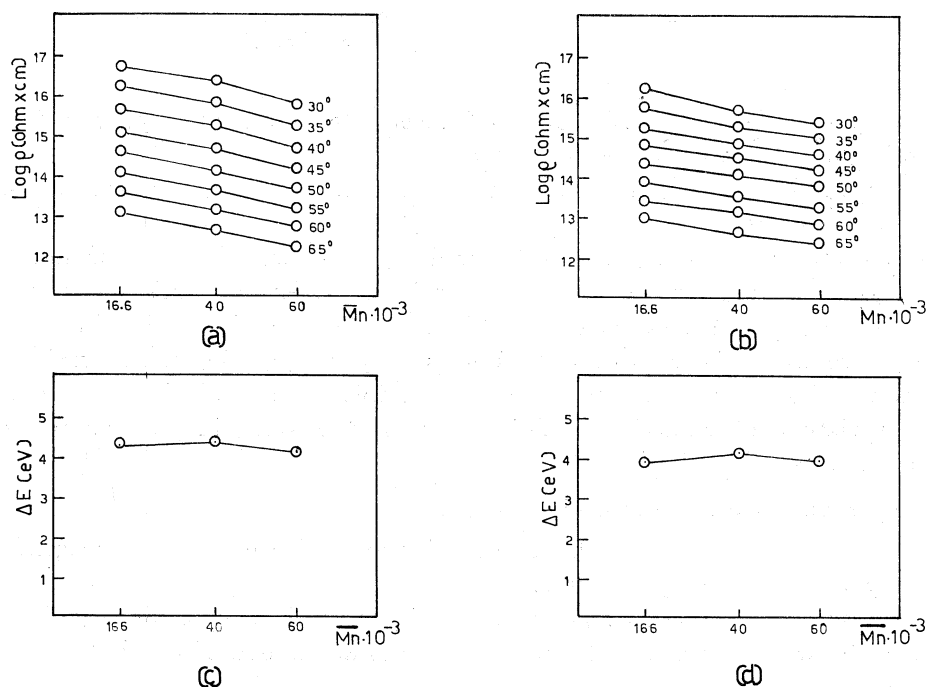


Fig. 1. - (a) Resistivity ρ vs $\overline{M}_n$ of not irradiated samples. (b) Resistivity ρ vs $\overline{M}_n$ of irradiated samples. (c) ΔE vs $\overline{M}_n$ on non-irradiated samples. (d) ΔE vs $\overline{M}_n$ of irradiated samples.

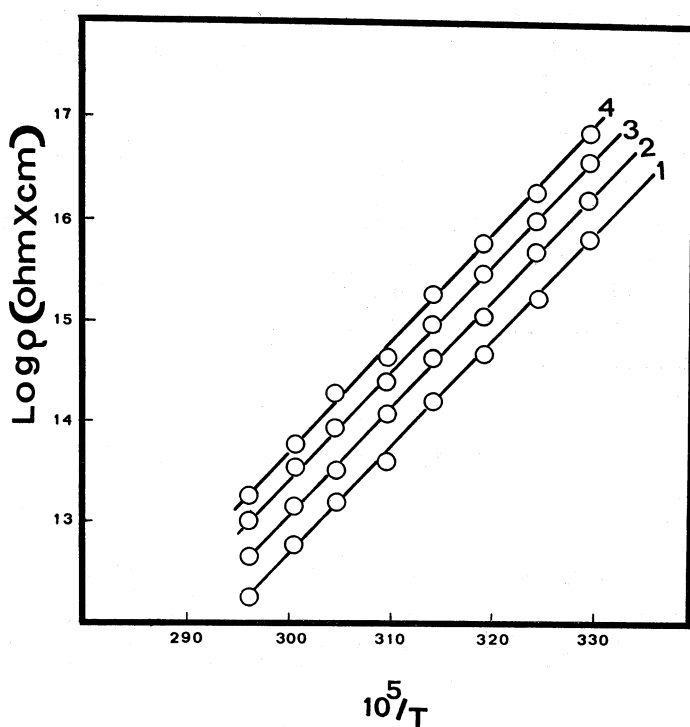


Fig. 2. - Resistivity ρ vs reciprocal temperature of the $\bar{M}_n = 60,000$.

1 - first heating cycle; 3 - third heating cycle;
2 - second heating cycle; 4 - fourth heating cycle.

Fig. 2 shows the resistivity variations after successive cycles for the non-irradiated sample of $\bar{M}_n = 60,000$.

Current-voltage characteristics for the non-irradiated sample of $\bar{M}_n = 40,000$ are presented in fig. 3.

Also the samples of $\bar{M}_n = 16,600$ and $60,000$ showed the same behaviour.

E.P.R. spectra were registered 5 minutes after irradiation and after intervals of time the samples were placed under the electrical field. This procedure was followed to see if radicals were responsible for the variation of conductivity shown by the irradiated samples. In fig. 4 it is presented the variation of radical population versus the time in the sample of $\bar{M}_n = 40,000$.

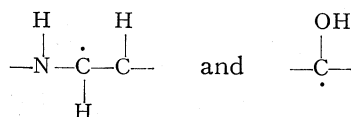
Our data show the following effects:

a) An increase of the bulk resistivity for each sample after successive cooling and heating cycles without the activation energy varying.

b) After gamma irradiation, resistivity of each sample decreased but it reached the value of the non-irradiated ones at the end of the first heating cycle.

c) Radical population appeared after irradiation and varied slowly with the applied electrical field.

d) A first interpretation of free radicals formed by irradiation were mostly of the type:



as suggested by Ulbert [13]. This kind of radicals should support a proton motion inside the molecules.

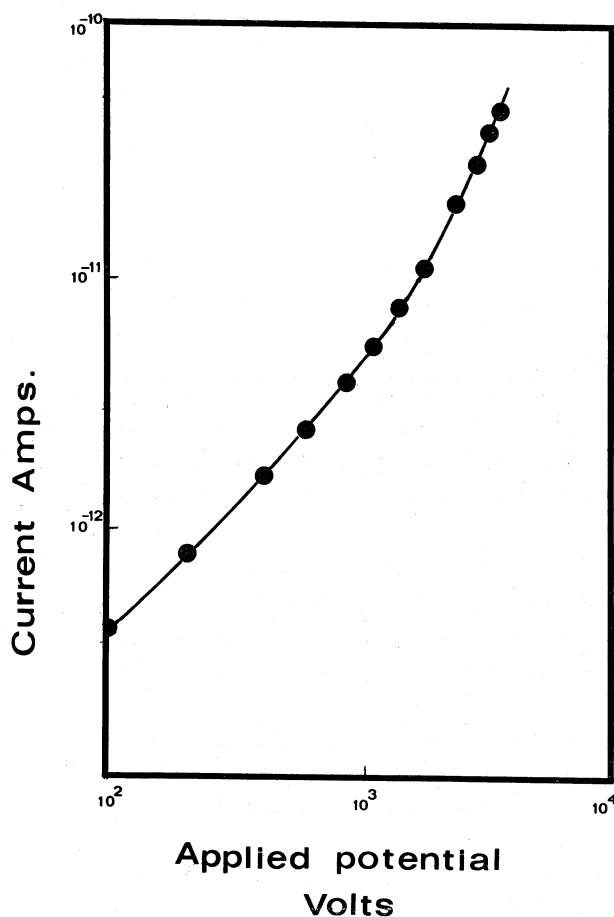


Fig. 3. - Characteristic current-voltage for the sample of $\overline{\text{Mn}} = 40,000$.
Sample thickness: 0.01 cm, electrode area 0.7 cm².

High activation energy values, current-voltage characteristics, obeying a law of the kind $I = AV^n$ and the range of temperature used [4], would let suppose an electronic conduction mechanism. In the other case, protonic conduction, the current-voltage characteristics should obey the law $I = A \sinh bV$ [14].

However, resistivity variations after successive heating and cooling cycles, the decreases in the irradiated samples, likely due to a higher contribution of protons produced by irradiation and the slight decrease of activation energy showed by irradiated samples would also confirm the presence of an ionic conduction mechanism.

Water acting as impurity or as plasticizer is always present in polyamides, giving polar groups. Adsorbed water remains in the amorphous regions of polymer because crystalline regions show higher formation of dipolar bonds through the chains, therefore a bond with water molecules is highly unlikely.

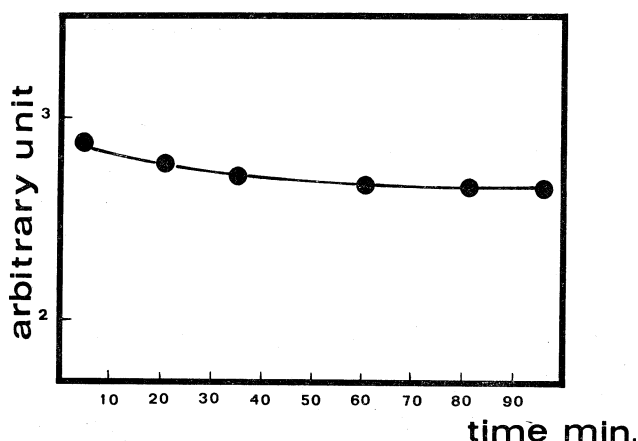


Fig. 4. - Variation of the radical population in the sample $\overline{M}_n = 40,000$ with the electric field applied.

Riehl [15] reported in his experiments on ice, that proton transitions between two neutral water molecules are always possible and that the displacement of the charge over great distances can take place in a very short time. This charge transfer mechanism indifferently occurs in ice and in all the substances containing hydrogen bridges.

Therefore ionic contribution to the conductivity of polyamides can be explained by the mechanism proposed by Riehl: that is, proton transitions between neutral and neighbouring molecules of water, and amide groups ionization by water.

On the contrary, electron charge carrier sources are probably the carbonyl groups of the amide linkage as suggested for proteins [16, 18].

2) Conductivity as function of molecular weight.

In a previous work on polycaprolactam [19] we have seen by X-ray cristallography that the percentage of crystalline regions slightly decreased at increasing molecular weight. Because adsorbed water remains in the amorphous regions of polymer giving high possibility to form dipolar bonds, as has been said before, and since all the samples have been treated in the

same experimental condition to dehydrate, we can suppose that adsorbed and uneliminated water was in a higher quantity in $\bar{M}_n = 60,000$ than in $\bar{M}_n = 40,000$ and 16,000.

Therefore the decrease of resistivity at the molecular weight increasing is probably due to the different quantity of adsorbed water in the samples.

This is a further support that water and consequently protonic contribution has an important role in the conductivity of polyamides also for temperatures below 70°C.

In conclusion, the values obtained at various molecular weights such as activation energy values, water presence and current-voltage characteristics, support the hypothesis of a conduction mechanism both protonic and electronic in polycaprolactam in the range of temperature 25°–70°C.

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