

ON THE RELAXATION MECHANISMS OF SOME RADIATION INDUCED FREE RADICALS IN POLYMERS

M. Velter-Stefanescu^{*}, O. G. Dului^a, N. Preda

National Institute of Materials Physics, Magurele, P.O. Box MG-7,
RO-077125 Bucharest, Romania

^aUniversity of Bucharest, Department of Atomic and Nuclear Physics, Magurele,
P.O. Box MG-11, RO-077125 Bucharest, Romania

Electronic spin-lattice relaxation measurements performed in X and Q bands on electrons irradiated polyethylene, polycarbonate and polymethylmethacrylate have shown that at liquid helium temperatures and higher, up to 12K, the spin-lattice relaxation time of radiation induced free radicals does not depend on the magnetic field but varies inverse proportionally with the square of absolute temperature and free radicals concentration. These peculiarities have been well explained by admitting that below 77 K there is a considerable amount of stable free radicals coupled in pairs that mediate the spin-lattice relaxation process of single radicals. Consequently, we have proposed an analytical equation that, within this hypothesis, quantitatively describes all these particularities.

(Received December 20, 2004; accepted March 23, 2005)

Keywords: Relaxation mechanism, Free radicals, Polymers, Irradiated polyethylene, PMMA

1. Introduction

Polymers are long chain molecules called also macromolecules (from Greek makro – long) that are composed by addition of a great number of simpler units called monomers. Polymers are extremely wide spread in nature both in organic and inorganic world. Cellulose, lignite, proteins or nucleic acids are typical examples of organic polymers while diamond, quartz, feldspar represent some examples of inorganic polymers. An impressive number of synthetic polymers such as polyethylene, polyurethane, polycarbonate, etc. should be added to these substances. As the number and varieties of synthetic polymers continues to grow, their investigation by various techniques never ceased.

One of these methods frequently used to investigate the polymers structure is Electron Paramagnetic Resonance (EPR). Due to its capacity to evidence only the paramagnetic centers, EPR represents an adequate method for such studies. Paramagnetic free radicals are generated by breaking of the two electrons chemical bonds of the macromolecules by various factors such as mechanical grinding, action of various chemical agents or irradiation with ionizing radiation. In this way, the investigation of free radicals in polymers is very useful in understanding different processes linked with the breaking of molecule chains such as aging, action of irradiation or other chemical agents, etc.

As a rule, the free radicals, due to a weak spin-orbit interaction, are characterized by g-factors closed to free electron ones. At the same time, frequently, the EPR spectra of free radicals present well resolved hyperfine or superhyperfine splittings that reflect their chemical structure allowing for a better identification of the investigated radicals [1]. On the other hand, polymers, even the highly ordered ones, are not typical crystalline solids, but present some properties similar to glassy state [2].

* Corresponding author: velter@infim.ro

EPR investigation can be performed by using continuous wave or pulse techniques. In the last case, it is possible to investigate in a more direct manner the electronic spin-lattice relaxation, which could provide significant information concerning polymers lattice.

Bowman and Kevan [3] have shown that at low temperatures the spin-lattice relaxation of the free radicals formed by irradiation in ethanol glasses consists of the modulation of the Electron Nuclear Dipolar (END) interaction with the units (free radicals), which tunnelate between the minima of a double-well asymmetrical potential. Within this mechanism, considered to be dominant in the glassy material, the spin-lattice relaxation time T_1 depends on magnetic field B and absolute temperature T by a simple law:

$$T_1^{-1} \sim B^{-2}T \quad (1)$$

In order to understand the nature of spin-lattice relaxation mechanism in polymers, we have determined the experimental dependence of the spin-lattice relaxation time T_1 on magnetic field and absolute temperature of the radiation induced free radicals in three different types of high amorphous polymers, *i.e.* high pressure polyethylene (PE), polycarbonate (PC) and poly(methylmethacrylate) (PMMA).

2. Materials and methods

The investigated samples were irradiated at 77 K with 3 MeV and 10 MeV electrons, at integral doses ranging between 30 kGy and 3 MGy, respectively at the Linear Accelerator Irradiation Facilities of the Institute of Atomic Physics, Bucharest. For the same doses, no significant differences in the ESR spectra of the samples irradiated with 3 MeV and 10 MeV electrons were noticed.

The relaxation measurements were carried-out in the Q and X bands, in the temperature ranges: (1.2-4.2) K and respectively, (2-12) K, using an original pulsed-saturation method [4]. This method consists of a long microwave pulse that saturates the spins, followed by a train of short equidistant microwave pulses, which monitor the recovery of the magnetization towards the thermal equilibrium value. It must be pointed out that, for all samples, the relaxation curves have shown the presence of a cross-relaxation process (biexponential curves). Consequently, in order to avoid the complications introduced by the cross-relaxation, the most probable between the singular free radicals and those coupled in pairs, the calculations of T_1 from the recovery curves were done only when the spin systems were close to thermal equilibrium. The concentration of free radicals has been determined from 77 K EPR spectra by using an organic carbon reference sample containing 1.6×10^{16} centres cm^{-3} .

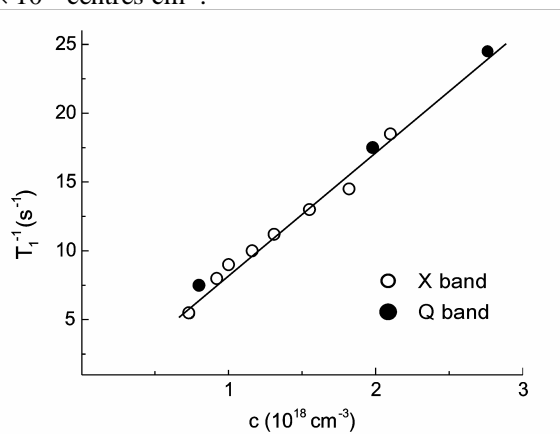


Fig. 1. Dependence of the electronic spin-lattice relaxation rate on the free radicals concentration for irradiated PMMA samples. Similar dependence has been noticed for the other two irradiated polymers.

3. Results and discussion

By analyzing all experimental data concerning the dependence of the free radical spin-lattice relaxation times T_1 by temperature, as well as radical concentration for all samples, we have found the following particularities:

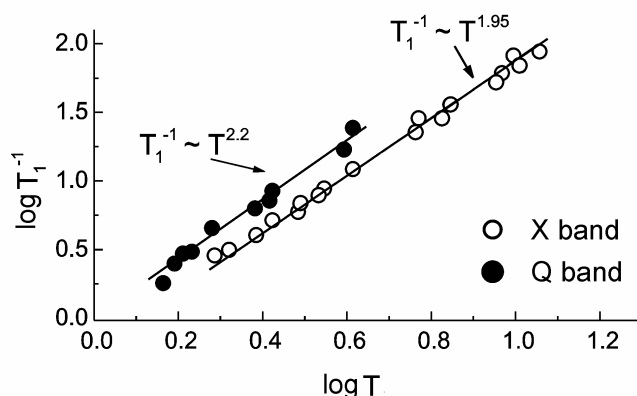


Fig. 2. Temperature dependence of T_1 spin-lattice relaxation time for irradiated PMMA, Analogous tendencies were observed for the other two polymers.

i. - in the region where there is a positive correlation between free radical concentration and irradiation time, the experimental data exhibit a linear dependence of the relaxation rate on the radical concentration: $T_1^{-1} \sim c$ (Figure 1). As for each kind of polymers the experimental points corresponding both to X and Q bands are disposed on the same line, it results that T_1 is magnetic-field independent, too.

ii. - the temperature dependence of the reciprocal of relaxation time T_1^{-1} obeys to a power type law: $T_1^{-1} \sim T^{2\pm 0.2}$ (Figure 2).

All these data allow us to state the existence of the same relaxation mechanism for the all free radicals, regardless of host lattice. Accordingly, the following expression of the T_1^{-1} better describes the experimentally observed peculiarities:

$$T_1^{-1} \sim c B^0 T^{2\pm 0.2} \quad (2)$$

completely different of eq. (1), what excludes the relaxation mechanism proposed by Bowman and Kevan. Here the term B^0 (i.e. B at power "zero") has been introduced to emphasizes the fact that the T_1^{-1} does not depends on magnetic field.

On the other hand, it must be pointed out that the free radicals formed in all investigated polymers differ by the number of CH_3 groups. In PMMA all free radicals contain CH_3 groups, in PC their number is much lower, while in PE are practically absent. The CH_3 groups exhibit rotational motion by tunneling even at liquid helium temperatures, which can modulate the END-interaction (or another interaction) generating relaxation transitions [5]. Considering such a mechanism as a dominant one, the relaxation rate values of the three types of polymers under study would be very different, in contrast with experimental results. At liquid helium temperatures, the electron spin-lattice relaxation times in all three polymers have the order of magnitude of about one second.

By supposing that the spin-lattice relaxation process can take place also via paired radicals found on the triplet state, it results that between the relaxation rate T_1^{-1} of the single radicals and that of the paired radicals T_{1p}^{-1} there is the following relation [6]:

$$T_1^{-1} \sim \frac{c_p}{c} T_{1p}^{-1} \quad (3)$$

where c and c_p represent the concentration of single and, respectively, paired radicals.

This affirmation is well sustained by the existence of a significant cross-relaxation process between single and paired radicals resulting from a substantial overlapping of the EPR resonance lines of both categories of radicals (Fig. 3).

At the same time, the relaxation of the paired radicals is determined, the most probable, by an "inverse" Orbach-Aminov process [7]. By taking into account the fact that the structure of the polymer macromolecules is linear, and thus, by considering a one- dimension lattice, it follows that [8]:

$$T_{1p}^{-1} \sim J \left(\exp \frac{J}{kT} - 1 \right)^{-1} \quad (4)$$

where J stands for the exchange integral.

The exchange integral J covers a wide range of values, as the inter-radical distance is not precisely defined (r_{ij} varies between 5 and 10 Å). In this case, for a uniform distribution of J -the exchange interaction within a pair, the relaxation rate of the paired radicals becomes:

$$T_{1p}^{-1} \sim \int_0^{k\theta} J \left(\exp \frac{J}{kT} - 1 \right)^{-1} P(J) dJ \approx B^0 T^2 \quad (5)$$

where: θ represents the Debye temperature; also, the B^0 factor was introduced to emphasize that the Orbach-Aminov process is magnetic-field independent.

As the pairs are formed by the random overlapping single radicals, it follows that between pair-radicals concentration c_p and single radicals concentration c there is the relation [6]:

$$c_p \sim c^2 \quad (6)$$

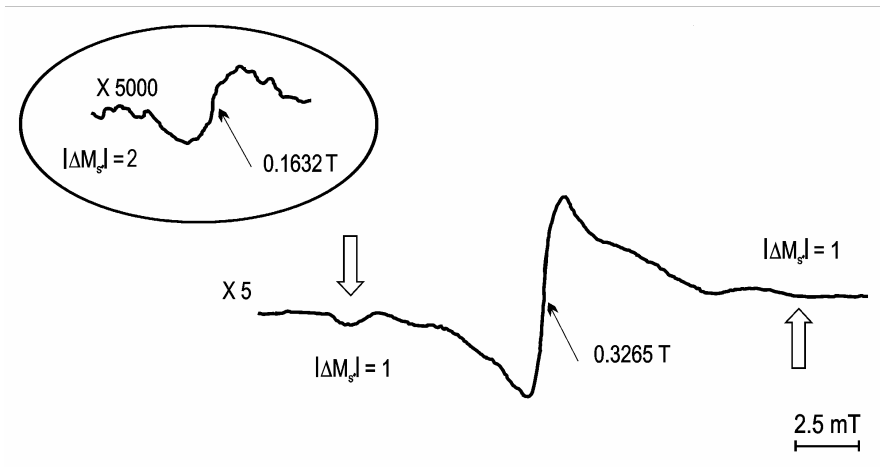


Fig. 3. The experimental EPR spectra of electron irradiated PMMA. The central line is due to single free radicals while the lateral ones are due to radical pairs ($\Delta M_s = 1$). The inset shows the low field ($\Delta M_s = 2$) EPR line of radical pairs. Free radicals concentration was of 1.3×10^{18} centers cm^{-3} . Measurements were performed at 77 K in X band (9.209 GHz) for 10 mW microwave power. Similar spectra have been observed for the other irradiated polymers.

Finally, by combining equations (3-6) it results:

$$T_1^{-1} \sim cB^0T^2 \quad (7)$$

in excellent agreement with the experimental data.

4. Concluding remarks

The electronic spin-lattice relaxation time has been measured at liquid helium temperatures and higher, up to 12 K, both in X and Q bands on electrons irradiated polyethylene, polycarbonate and polymethylmethacrylate. The experimental dependencies on temperature, concentration as well magnetic field have shown that the spin-lattice relaxation times of radiation generated free radicals in these materials vary inverse proportionally with the square of absolute temperature and free radicals concentration but does not depend on the magnetic field. All these peculiarities could be very well explained by taking into account that below 77 K there is a considerable amount of stable paired radicals that mediate the spin-lattice relaxation process of the single radicals. Accordingly, an analytical equation that quantitatively describes all these particularities has been deduced by following this model. It must be pointed up that similar results concerning the temperature dependence of T_1^{-1} were reported in some vitreous samples for which it was assumed the existence of a coupling between single and paired paramagnetic centres [9,10].

References

- [1] Y.-S. Lin, S. Lee, S. Lin, C.P. Cheng, *Mat. Chem. Phys.* **78**, 847, (2003).
- [2] W. A. Phillips (ed) "Amorphous Solids-Low temperature Properties, Springer-Verlag, Berlin (1981).
- [3] M. K. Bowman, L. Kevan, *J. Chem. Phys.* **81**, 456 (1977).
- [4] M. Velter-Stefanescu, B. Ianculovici, *Rev. Roum. Phys.* **19**, 431, (1974).
- [5] M. K. Bowman, L. Kevan, in "Time Domain Electron Spin Resonance" L. Kevan and R. N. Schwartz Eds., John Wiley and Sons (1979), pg. 67.
- [6] J.C. Gill, *Prog. Rep. Phys.* **30**, 91, (1975).
- [7] A. A. Manenkov, R. Orbach, "Spin-lattice Relaxation in Ionic Solids", Harper and Row, New York, 1996.
- [8] M. Velter-Stefanescu, R. Grosescu, *Rev. Roum. Phys.* **23**, 369, (1978).
- [9] S. K. Mishra, *Spectrochim. Acta, A* **54**, 2257 (1998).
- [10] J. Pescia, S. K. Misra, M. Zaripov, Y. Servant, *Phys. Rev. B* **59**, 9442 (1999).