An ESR Study of γ-Irradiated P4VP Polymers : Dose-Effect Relationships

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The behavior of poly(vinylpyridine) with a gamma ray source has been studied. In the present work, samples were irradiated in air with a ^{60}Co or ^{137}Cs gamma cell source (absorbed dose 10 Gy to 14400 kGy). All tested samples show well defined ESR signals whose amplitude increases with time. The behavior at room temperature and dose–effect relationships were investigated.

Irradiation has a wide range of applications such as polymerization,[1] grafting of polymers,[2] decontamination or sterilization of goods,[3] or disposable equipment for hospital and medical use.[4] There is needs for methods which could discriminate between irradiated and non-irradiated goods. The method should be accurate, reproducible, quick and easy to perform. In practice, it has been proved difficult to fulfill all these requirements simultaneously.[3]

The methods which have been the most extensively studied and which have the greatest scope of application include thermo luminescence (TL),[5] methods monitoring the formation of long-chain volatile hydrocarbons and 2-alkylcyclobutanones[6] and Electron Spin Resonance (ESR) spectroscopy.[7] However, it appeared from preliminary measurements on foodstuffs and polymers, that the stability of radiation-induced radicals is often low. This low stability is attributed to the high moisture content, or to the fast recombination of small reactive radicals with others, giving rise to a stable low molecular weight product. It means that those methods can not be used for identification of irradiated goods as such.

Because of energy-transfer processes, radiation induced chemistry is not completely random. Energy can migrate over short distances, selectively causing relatively weak chemical bonds to break, or becoming trapped by certain functional groups such as aromatic rings, that undergo efficient non-reactive decay to the ground state. For reasons discussed elsewhere, the presence of an aromatic ring and even more of a hetero aromatic ring[8,9] in the poly(vinylpyridine) exerts a strongly stabilizing influence on the yield of radiation-induced cross-linking or scission.

In the present work, production of stable long-lived radical center in poly(vinylpyridine) generated by gamma ray radiation is studied by ESR. Dose effect relationships and decay are investigated whereas nature of the radicals, produced within the polymer, was studied by time-of-flight particle induced desorption mass spectrometry (TOF-PDMS) in previous papers.[10,11]

In a first set of measurements the cross-linked poly(4-vinylpyridine) (P4VP) samples[12] were irradiated in the 148–14400 kGy absorbed dose range with a ^{137}Cs γ source at a dose rate of 20 kGy h^{-1} and stored in air at room conditions.[13] In a second set of measurements, the P4VP samples[14] were irradiated in the 10–100 Gy absorbed dose range with a ^{60}Co source at a dose rate of 1.06 kGy h^{-1}, and stored in air at room conditions[15]. Figure 1 shows the ESR signal[16] of a cross-linked P4VP sample for a 148 kGy integrated dose. The signal is typical for free radicals, both in the *g* value and in microwave power dependence. But, a unique value of 2.005 for the *g* factor was determined which did not allow to distinguish the kind of radicals in the bulk of the polymer. This signal is also present in the un-irradiated samples at a much lower intensity.

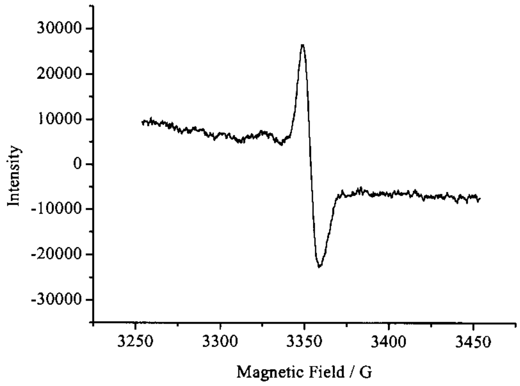

Figure 1. ESR signal of a cross-linked P4VP sample for a 148 kGy integrated dose with a VARIAN E Line spectrometer at a modulation frequency of 100 kHz, microwave frequency 9.3 GHz, mass of polymer = 30 mg.

Figure 2 shows the ESR spectra of a linear P4VP sample for a 100 Gy integrated dose. While the integrated dose is 1500 times lower than previously, the signal remains as intense and well defined.

In both cases, ESR spectroscopy gives unambiguous results concerning the existence of paramagnetic centers. The number of spins can be found by double integration of the derivative curve and comparison with a VARIAN standard sample. By this way, we determined the number of spins per gram of polymer as a function of the integrated dose.

Figure 3 shows the variation of numbers of spins per gram of resin as a function of the integrated dose in the 0–14400 kGy range. The zero integrated dose signal shows a non negligible concentration of spins, corresponding to the free radicals produced during polymerization. For an integrated dose of 10000 kGy a plateau is reached, indicating some possible intramolecular reactions, such as cross-linking.

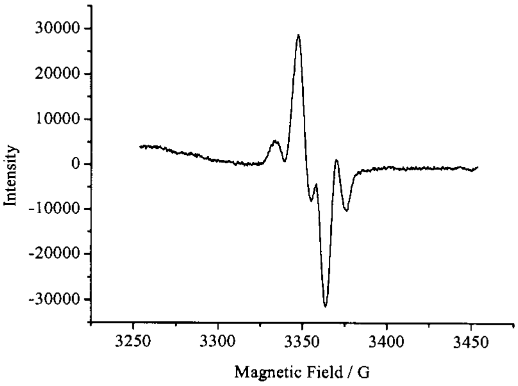

Figure 2. ESR spectra of a linear P4VP sample for a 100 Gy integrated with a BRUKER ESP300E spectrometer at a modulation frequency of 100 kHz, microwave frequency 9.4 GHz, mass of polymer = 50 mg.

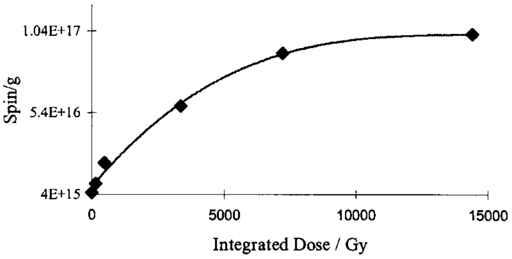

Figure 3. Number of spin per g of cross-linked P4VP as the function of the integrated dose.

The intensity of the ESR signals of cross-linked P4VP was found to be almost constant after several months in air. In addition, the time dependence of the ESR signal amplitude for a 10000 kGy integrated dose sample did not show any appreciable variation.

Although we find a polymer, which shows a stable and strong correlation between integrated dose and ESR signal from 500 to 10000 Gy, we were interested in the potential of such materials with lower integrated dose. Linear P4VP shows well-defined ESR spectrum that could allow us to study lower integrated doses.

Linear P4VP shows a strong dependence of the number of spin per gram of resin as a function of the integrated dose (Figure 4). With such polymer one could determine the integrated doses that are common to various goods.[3]

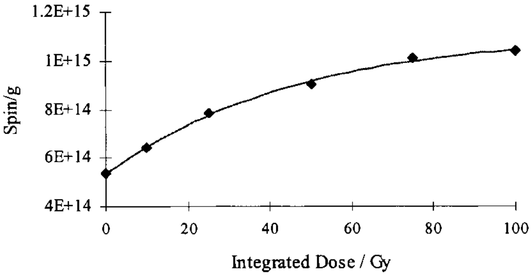

Figure 4. Number of spin/g of the linear P4VP as the function of the integrated dose.

Unlike cross-linked P4VP, the intensity of the ESR spectra of linear P4VP decreases at room temperature. The radical's concentration decreases linearly with the time and after 20 days in air at room temperature, the number of spin per gram is by half decreased while after 40 days the signals fall to the background. The time decrease of the free radicals concentration in the linear P4VP samples makes this material inadequate for its straight out application as a dosimeter.

The results obtained in the present investigation confirm that the ESR technique is a valuable tool for studying the behavior of polymeric materials under irradiation. Moreover, the time evolution in air of radicals produced in the cross-linked samples tested in this work suggests a possible application of this material as a dosimeter. In fact the possibility of keeping information and non destructive readings for a long time should allow the use of cross-linked P4VP samples as a permanent record of delivered dose values.

The search for an improvement to dosimeter has barely begun and cross-linked PVP appears to be at least as good as L-α-alanine in high dose range[17]. Our research efforts are currently focused on the synthesis of poly substituted vinyl pyridine in order to improve the radicals stability.

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13 The absorbed doses were determined after calibration to be 148, 480, 3360, 7200 and 14400 kGy.
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