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Gamma-ray-induced modifications of the chemical structure of an ion exchange resin

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Gamma-ray irradiation of ion exchange resins used for processing nuclear effluent may lead to considerable modifications of the molecular structure and macroscopic properties. In the present study, crosslinked poly(4-vinylpyridine) (P4VP), irradiated by a ¹³⁷Cs γ -source up to an integrated dose of 14 400 kGy, has been investigated. The particle-induced desorption-mass spectrometry (PDMS) technique is able to detect the radiation-induced structural degradation of such an infusible and insoluble material. From the results of PDMS, a coherent description of the production of specific radical fragments and modified chains is proposed. Both the nature of these fragments as well as their formation, as a function of the dose of irradiation, correlate with results of electron paramagnetic resonance spectrometry and Fourier transform infrared spectroscopy, and with thermogravimetric and dynamical mechanical analysis. In addition, analysis of the soluble and insoluble fractions helps to discriminate between different possible processes. In particular, it is shown that the loss of pyridine fragments correlates well with chemical measurements like the loss of protonatable sites.

1 INTRODUCTION

The acid–base and loading properties of its pyridine group have stimulated the use of poly(4-vinylpyridine) (P4VP) resin in various applications such as a chemical reagent,¹ a catalyst² or catalyst support,³ an extractant for organic pollutants⁴ and for the selective isolation of a host of dissolved metals.⁵ Among these applications, there is particular interest in its adsorbing properties towards radionuclides from liquid wastes of low or medium activity.^{6,7} The on-going effects of radiation-induced ageing on the properties and performances of such materials have been a topic of considerable interest. It has been shown that, among the synthetic resins, those of the vinylpyridine type are more resistant towards ionizing radiation.⁸ A chemical evaluation of the stability of such crosslinked materials has already been under-

taken,^{9,10} but a detailed investigation of the structural modifications induced by gamma radiation has still to be performed before any industrial technique aimed at nuclear waste reprocessing can be considered.

As part of such a programme is the study of the radiochemical stability of P4VP irradiated with a dose of up to 14 400 kGy, and this work is aimed at obtaining an insight into the modification of both molecular structure and macroscopic properties. For such an infusible and insoluble material most of the commonly used techniques for polymer characterization [infrared spectroscopy (IR), ultraviolet spectrophotometry (UV), nuclear magnetic resonance spectroscopy (NMR), electron paramagnetic resonance spectrometry (EPR), electron spectroscopy for chemical analysis (ESCA), etc.] give limited or uncorrelated results. In a forthcoming paper¹¹ we demonstrate that negative ion emission under ion beam impact can be sensitive to the chemical modifications induced in such a material by

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γ -irradiation, provided that the primary ions are used in the MeV instead of the keV regime. Thus particle-induced desorption-mass spectrometry (PDMS)—or, adopting the terminology proposed by Sundqvist,¹² HSF-SIMS—has been widely used in this study to give a coherent description of these modifications that is in agreement with results of other techniques such as EPR, IR, thermogravimetric analysis (TGA) and dynamical mechanical analysis (DMA).

2 EXPERIMENTAL

2.1 Materials

The crosslinked (2% with divinylbenzene) P4VP resin used in this study was supplied by Reilly Industries Inc., Indianapolis, IN, USA. The material was a fine, white, insoluble and infusible powder, with a specific area of $\sim 0.5 \text{ m}^2 \text{ g}^{-1}$. It has the chemical structure sketched in Fig. 1.

2.2 Gamma irradiation

Plugged glass containers filled with 1.8 g of P4VP were exposed to various irradiation doses of a ^{137}Cs γ -source. The doses absorbed were determined by calibration to be 148, 480, 3360, 7200 and 14 400 kGy at a dose rate of 20 kGy h^{-1} .

2.3 Sample preparation

2.3.1 General procedure

Pellets of thickness 1 mm were made by compressing (at 2 tonne cm^{-2}) 0.1 g of the powder into a stainless steel cylinder of 8 mm internal diameter.

2.3.2 Extraction of the soluble part

The soluble part of the irradiated samples was obtained by shaking 0.15 g of the P4VP powder

Fig. 1. Molecular structure of the P4VP resin crosslinked with 2% divinylbenzene.

with 2 cm^{-3} ethanol for 15 min. After filtration, the resin in the filter was dried and weighed. The value obtained was then compared with that resulting from evaporation to dryness of the organic phase. For the most soluble samples (high irradiation doses) good agreement was found from such a comparison. The percentage of soluble part was expressed according to the following expression:

$$\% = \frac{M_i - M_f}{M_i} \times 100$$

where M_i and M_f are the weights of the dried resin before and after extraction.

2.3.3 Spin-coating deposition

In order to determine the polymer amount of these solutions of different concentrations, thin films were prepared by spin-coating deposition on aluminized Mylar backings. However, as explained later in the text, such solutions have to be subjected to a given number of dilutions. Thus the films were made from assays of $10 \mu\text{l}$. For a typical area of deposit around 2.5 cm^2 the largest thickness value never exceeded $5 \mu\text{g cm}^{-2}$.

2.4 Instrumentation

2.4.1 FTIR spectra

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 1720X spectrometer from P4VP pellets (1% in KBr).

2.4.2 EPR spectra

The EPR spectra were recorded, at room temperature, on a Varian E Line electron paramagnetic resonance spectrometer, at a magnetic modulation frequency of 100 kHz. The quartz EPR cells contained 30 mg of resin powder. The spin concentrations were obtained by comparison of the experimental spectra with a calibrated Varian pitch sample EPR spectrum containing a definite number of spins.

2.4.3 Thermal analysis

Thermogravimetric (TG) measurements were performed on a DuPont Instruments TGA 2950 apparatus, under helium atmosphere. Amounts

of 10–15 mg of P4VP were weighed into the thermobalance and the weight loss was determined as a function of temperature from 30 to 600°C with a heating rate of 10°C min⁻¹.

The dynamical mechanical (DMA) experiments were carried out with a DMA 7 analysis system from Perkin–Elmer, on samples in pellet form (diameter = 0.8 cm) between two parallel plates, using the compression mode (surface area submitted to the forces = surface area of the analysed pellet). The frequency was 3.00 Hz and the dynamic and static forces applied were 900 and 1200 mN, respectively. The scanned temperature range was between 230 and 40°C at a rate of 1°C min⁻¹.

2.4.4 HSF-SIMS measurements

Since HSF-SIMS analysis provides information from the surface layer, great care must be taken to ensure that this information can be correlated with the bulk results of the preceding techniques. Among the possible sources of artefacts are, of course, accidental contamination and analysis-induced damage. In both cases, there are some decisive advantages in using argon ions accelerated up to 9 MeV by the 4 MV Van de Graaff machine of the Institut de Physique Nucléaire, instead of the more conventional ²⁵²Cf source. First, the special configuration of our set-up uses a sharp and well-aligned primary beam¹³ which offers the possibility of lateral homogeneity probing, even at the micrometre level of resolution.¹⁴ As for the second point, since the intensity of the continuous beam is around 1000 ions s⁻¹, the analysis is essentially non-destructive and no charge compensation is required. This does not mean that the detection is always free from secondary effects (background or peak broadening) but, with a typical integrated dose of the order of 5 × 10⁹ ions cm⁻², no surface evolution can be observed for reasonable counting statistics and secondary ion experimental yields are still high (as determined from reference materials such as alkali halides).¹³ This has been made possible because of the optics of our time-of-flight (TOF) system: with a flight path of 125 mm only the transmission is around 85%. However, the mass resolution is poor (typically 190 FWHM at mass 133).

The price to pay for processing samples in the simple pellet form for time-of-flight spectrometry is to set a reproducible electric field between the sample surface and the extraction electrode,

Fig. 2. TOF spectrometer experimental set-up using the 'start electron' technique. Constant fraction discriminators (CFD) are used for digitization of the time signals.

which are 2 mm apart.¹³ Once correctly applied and controlled, the 5 kV biasing applied to the target allows the secondary ions to be accelerated over the flight distance of 125 mm towards the microchannel plates assembly (MCP). Based on ion-by-ion detection conditions, such spectrometry implies that the time of arrival of each primary ion must be recorded (start signal). This is easily done for the thin films, which can transmit fast projectiles and let them start at a surface barrier detector (SBD). For analysis of the thick samples and since we are only interested in negative ion emission,¹¹ we take full advantage of the so-called 'start electron' technique.¹³ As sketched in Fig. 2, each primary ion impact will give rise to an electron shower preceding the emitted ions, if any. Then, once split, the same MCP signal can be used for generation of the start signal from the electron pulse and, after an appropriate delay, for the stop signals (the same electron pulse plus ion pulses, if any). The analysis is performed in conventional vacuum conditions (10⁻⁷ mbar).

3 RESULTS AND DISCUSSION

3.1 Bulk sample characterization

The consequences of the γ -irradiation of P4VP are visible in the negative ion spectra of Fig. 3. Under the present experimental and material preparation conditions, C_nH⁻ fragments are emitted with quite high intensity. For odd values of *n* (49, 73, 97, 121) surface contamination resulting from the vacuum conditions is observed along with inorganics,¹⁵ while C_nH⁻ fragments

Fig. 3. Negative ion mass spectra: (a) from an unirradiated P4VP pellet sample; (b) from an irradiated sample with an integrated dose of 148 kGy. Characteristic ions are underlined, new ions following γ -ray irradiation are circled, contaminants or C_nH^- fragments bear a * label.

with even values of n come from multifragmentation of the polymer backbone and also do not reflect its chemical structure. Four peaks have been selected and will be considered as characteristic of the material. From the unirradiated material they correspond to masses at 41, 78, 146 and 158 Da. Of course, the ion emission itself is just a consequence of a localized energy deposition inducing scissions along the chains, as-formed or modified fragments being susceptible to escape in a more or less stable charged form. Thus the increase in intensity of the characteristic peaks observed for the smallest γ dose [148 kGy, Fig. 3(b)] is a strong indication that the pre-formation of some fragments facilitates ion emission. Finally, the emission of new peaks at higher masses (183–184, 197 and 211 Da) has to be explained by the production under γ -irradiation of fragments not formed under ion bombardment. As sketched in Fig. 4, the randomly distributed scissions induced by the interaction with γ -rays could lead to fragments or modified chains from which the ion emission under primary ion interaction is easier, since one of the simultaneous processes needed is no

longer required. As an extreme example, mass 158, which is produced from two pyridinic scissions (A + A) plus a benzylic scission (B), is more easily emitted from A + B or A + A scissions from a modified chain or a fragment. As for the ions appearing only after γ -irradiation, as sketched in Fig. 5, their production from a modified chain only requires a B scission instead of the B + B scissions that are never observed on the unirradiated material. On the other hand, the fragment of mass 211 when formed under ion bombardment is preferentially ionised and leads to $[M + H]^+$ ion emission.¹¹ Formed under γ -irradiation, it can be responsible for production of the associated ions. More details on these processes are given in Ref. 11.

All these tentative interpretations require the formation of stable free radicals as well as the formation of double bonds, single or conjugated. In addition, this production should correlate with yield variation of the associated ions as a function of the integrated dose. For the characteristic ions, such a variation is shown in Fig. 6.

Concerning the radicals, EPR spectrometry gives unambiguous results concerning the existence of paramagnetic centres. Since we are dealing with an amorphous polymer, the absence of hyperfine structure cannot be attributed to the delocalized single electrons of ethylenic and/or aromatic free radicals.¹⁶ Quantitatively, the variation of the number of spins per g of resin as a function of the integrated dose is shown in Fig. 7. Such a curve, which averages the contribution of the different free radicals, is comparable to the variation of the related individual ions (Fig. 6). This is a first support of our interpretation of the formation of various entities.

As far as double bond formation is concerned, some lack of sensitivity (already evoked for such type of samples) has prevented the detection of any significant modification of IR spectra below the irradiation dose of 3360 kGy. As shown in Fig. 8, the presence of well-defined peaks at 1690 and 1654 cm^{-1} can be attributed to the stretching vibration mode of aliphatic, double and conjugated double bonds, respectively.¹⁷ The increase in intensity of these two bands with integrated dose is qualitatively observed, also in agreement with our interpretation. Particularly interesting is the seemingly steeper increase of intensity of the band corresponding to conjugated C=C bonds, when increasing the integrated dose. This is in agreement with the yield variation of fragments

Fig. 4. Proposed mechanisms for emission of the characteristic negative fragments from A and B scissions induced by γ -irradiation.

of mass 158 and 146 (Fig. 6) and would favour, among their mechanisms of formation proposed in Fig. 5, the one involving A scissions from γ -irradiation.¹¹ Finally, although the samples were not irradiated in vacuum, no oxidation has been detected from these spectra (absence of CO, RCO₂H and RCO₂R₁ bands). It must be

noted, however, that the containers were closed during irradiation, and that the pyridine groups of the crosslinked P4VP are highly resistant to oxidizing and reducing agents.¹⁸

The evolution of these γ -induced modifications, either observed from the yield of specific ions or from the concentration of paramagnetic

Fig. 5. Proposed mechanisms for emission of new negative fragments resulting from modifications to B scissions induced by γ -irradiation.

Fig. 6. Evolution, as a function of the integrated dose, of the yield of fragments observed on the unirradiated sample (m/z 41, 78, 146 and 158).

Fig. 7. Evolution, as a function of the integrated dose, of the number of spins per g of P4VP resin.

centres, is characterized by an almost linear increase in the low-dose region (<500 kGy), followed by a more or less marked saturation regime. The occurrence of recombination processes taking place once a given concentration of fragments or modified chains is reached, is suspected. This would explain why the emission of new ions following low-dose irradiation

Fig. 8. FTIR spectra of the P4VP resin: (a) unirradiated; (b) irradiated with 3360 kGy integrated dose; (c) irradiated with 14 400 kGy integrated dose.

Fig. 9. Evolution, as a function of the integrated dose, of the yield of fragments resulting from modifications induced by γ -irradiation (m/z 183–184, 197 and 211).

exhibits a marked decrease and then disappears (Fig. 9) while the specific ion emission tends to slow down. A good approach to investigating such bulk modifications is to perform TGA in an inert atmosphere. The variation of weight loss as a function of temperature is shown for various integrated doses in Fig. 10. No significant deviation from the unirradiated case is found until the 3360 kGy integrated dose, when a noticeable amount of dry tar and a decrease of the degradation temperature are observed. Since this last parameter is related to early desorption of the fragments formed under irradiation, it is not surprising to observe a further evolution

Fig. 10. Relative residual weight as a function of temperature for P4VP samples at different integrated doses.

limited to some change of the slope. Moreover, it is particularly interesting to note that the amount of dry tar reaches a value of 50% for a 25% crosslinked unirradiated resin. Thus its continuous increase up to a value of 18% is typical of a continuous increase of crosslinking processes as a function of integrated dose.

Another powerful technique for assessing the existence of crosslinking under γ -irradiation and its evolution as a function of integrated dose is dynamical mechanical analysis, by which the glass transition temperature (T_g) can be deduced from the variation of $\tan \delta$, δ being the loss angle. As can be seen from Fig. 11, the data have been obtained with decreasing temperatures; this removes the possibility of artefacts due the initial presence of a significant amount of water in the samples, as observed in the low-temperature region of the previous thermograms (Fig. 10). The main result is an important (around 40°C) increase in T_g for the largest dose together with a significant decrease of the chain mobility from the decrease of $\tan \delta$. For the lowest dose (148 kGy) the observed decrease is not as significant because of the reproducibility of the measurements for such a sintered material, and one has to be cautious when observing an increase of T_g since undesirable crosslinking processes can develop when starting at such a high temperature (230°C).

3.2 Analysis of the soluble fraction

The previous results obtained from the different techniques clearly establish the formation of stable free radicals within the irradiated material,

Fig. 11. Dynamical mechanical analysis: variation of $\tan \delta$ as a function of annealing temperature.

as well as the development of crosslinking processes, as a function of the integrated dose. Starting with such a resin initially crosslinked with divinylbenzene (DVB) implies the formation of two types of radical. Summarized in Fig. 12 are the most illustrative cases. While the radicals incorporating one DVB bridge are denoted R_c , the others can be intact oligomers resulting from a benzylic scission (denoted R_1), or modified by the loss of a pyridine and the creation of double bonds (denoted R_2) or of simple fragments like the pyridine unit (denoted R_3). Then, recombinations leading to R_c-R_c or R_c-R_1 fragments will be responsible for a higher density of crosslinking, while R_1-R_1 fragments lead to intact or modified oligomers of longer chains. The free radicals, as well as this last category of fragments, must be soluble in organic polar solvents.

Indeed, the variation of the quantity of soluble material extracted by ethanol is remarkably comparable to the EPR data variation, as shown in Fig. 13. From such solutions where the concentration increases as a function of integrated dose, HSF-SIMS analysis can help in discriminating the relative abundance of the individual fragments. This requires the preparation of spin-coating targets for which the amount of deposited material is proportional to the concentration. Then, if the thickness of the samples is maintained below the depth of origin of the secondary ion emission and if a linear correspondence between ion yield and sample thickness can be established, the variation of the amount of a given species can be obtained. Such a procedure has been described in detail in Ref. 11. As observed in Fig. 14, from the yield variation of the ions of mass 41 and 78, the corresponding fragments are extracted in the same proportions as free radicals are formed. The difference with what is observed from the bulk, is that the ion yield of the mass 41 is proportionally smaller. This gives some credit to the various origins (free radicals or modified chains) of these smallest fragments. Moreover, from the HSF-SIMS analysis of the insoluble residue one can determine what has been lost. For the highest dose (14 400 kGy), where the effect is expected to be the most important, the yield is reduced by a factor of 5.0 and 2.6 for masses 78 and 41, respectively. By comparison, the emission of ions of mass 146 and 158 is only reduced by a factor of 1.6 and 1.2, respectively.

Fig. 12. Summary of fragment formation under γ -irradiation and subsequent ion emission under primary beam impact.

From this result it can be concluded that the negative ions are a direct signature of the pyridinic scissions and that the double bond formation is associated with the crosslinked material.

Conversely, the positive ion emission is unambiguously a consequence of benzylic scissions¹¹ and analysis of the same spin-coating targets indicates that production of the related fragments (Fig. 12) follows the same previous trend. The dimer of mass 211 is not the only one leading to the $[M + H]^+$ ion of the highest yield,

but the detection in solutions of the negative ions of mass 197 and 211 also validates their formation from it, as proposed in Fig. 5. Moreover, as the yield of these ions remains almost constant with dose, the cessation of their emission from the bulk shown in Fig. 9 is related to some kind of ion trapping, instead of recombination processes, of these larger fragments.

As a final comparison, we present in Fig. 15 the evolution of the number of spins g^{-1} , the

Fig. 13. Variation of the weight fraction of the P4VP material soluble in ethanol, as a function of integrated dose.

evolution of the yield of the pyridine ion ($m/z = 78$) from the soluble fraction and the evolution of the relative loss of protonatable sites (% , as obtained from acid–base titration¹⁰). It can be observed that the largest discrepancies are observed at the lowest doses. However, in terms of palladium efficiency of extraction (in which two pyridine sites are required for the extraction of one atom of palladium), no significant loss is observed before 3360 kGy.¹⁰ Then, for the low-dose region where the recombination processes are not yet observed, the production of free pyridine radicals does not seriously affect the extraction efficiency because free pyridines can still participate in the extraction process. From

Fig. 14. Evolution, as a function of the integrated dose, of the yield of ions of mass 41 and 78 from thin films corresponding to the resulting concentration of soluble material.

Fig. 15. Comparative evolution of number of spins g^{-1} , yield of pyridine ion from the soluble fraction and loss of protonatable pyridine sites (%), as a function of the integrated dose. Data have been normalized on the value at 14 400 kGy.

the 3360 kGy irradiation dose, the recombinations are responsible for a decrease in the amount of free pyridine radicals and new crosslinks make the extraction sites less accessible, resulting in a decrease in the efficiency of palladium extraction.

4 CONCLUSION

From the negative ion emission observed under HSF-SIMS conditions, chemical modifications induced by γ -irradiation of P4VP resin are shown to involve the production of small fragments including the pyridine radical, easily extracted in the soluble fraction. On the other hand, double bonds or conjugated double bonds are essentially formed on insoluble modified chains. Such a picture is in good agreement with EPR and IR data. As a function of absorbed dose, a fast and linear increase of this production is observed in the low-dose range (<150 kGy), followed by a much slower variation. Larger fragments (dimers or trimers) are also found in the soluble fraction but the corresponding ion emission from the bulk disappears above 150 kGy. The recombination processes responsible for these changes are supported by TGA and DMA measurements, where irradiation-induced crosslinking processes are qualitatively shown to increase up to a saturation level. Finally, as the production variation of the pyridine fragments is comparable to that of the loss of protonatable sites, one may

interpret the excellent stability of the extraction efficiency of the material as being due to the presence of pyridine fragments left undestroyed.

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REFERENCES

- Cardillo, G., Orena, M., Sandri, S. & Tomassini, C., *Chem. Ind.*, **16** (1983) 643.
- Hünig, S., Lücke, E. & Brenninger, W., *Org. Syn. Coll.*, **5** (1973) 808.
- Chanda, M., O'Driscoll, K. F. & Rempel, G. L. J., *J. Mol. Catal.*, **7** (1980) 389.
- Kawabara, N., Yoshida, S. & Tanigawa, N., *Ind. Eng. Chem. Prod. Res. Dev.*, **20** (1980) 386.
- Sugii, M., Ogawa, N., Linuma, Y. & Yamamura, H., *Talanta*, **28** (1981) 551.
- Draye, M., Chevillotte, R., Chomel, R., Doutreluingne, P., Guy, A., Foos, J. & Lemaire, M., *Sep. Sci. Technol.*, **307-9** (1995) 1245.
- Lemaire, M., Chevillotte, R., Draye, M., Guy, A., Foos, J. and Chomel, R., French Patent 9 202, 1992.
- Gangwer, T. E., Godstein, M. and Pillay, K. K. S., *Radiation Effects on Ion Exchange Materials*, BNL-50781. Brookhaven National Laboratory, Upton, NY, 1977.
- Marsh, S. F., *The Effects of In Situ Alpha Particle Irradiations on Six Strong-Base Anion Exchange Resins*, LA-12055, UC-731. Los Alamos National Laboratory, Los Alamos, NM, 1991.
- Draye, M., Ph. D. Dissertation (unpublished), Université Lyon I, Villeurbanne, France, 1994.
- Nsouli, B., Draye, M., Allali, H., Lemaire, M. and Thomas, J.-P., *Int. J. Mass Spectr. Ion Proc.*, **154** (1996) 179.
- Sundqvist, B. U. R., *Sputtering by Particle Bombardment III*, ed. P. Behrisch and K. Wittmaack. Springer, Berlin, 1991, p. 257.
- Allali, H., Nsouli, B. & Thomas, J.-P., *Int. J. Mass Spectr. Ion Proc.*, **127** (1993) 111.
- Thomas, J.-P., Oladipo, A. A. & Fallavier, M., *Nucl. Instrum. Meth. Phys. Res.*, **B42** (1989) 127.
- Allali, H., Nsouli, B., Thomas, J.-P., Szymczack, W. & Wittmaack, K., *Nucl. Instrum. Meth. Phys. Res.*, **B90** (1994) 501.
- Chipara, M. I., Ifrim, A., Grecu, V. V., Toscan, M. I., Popescu-Pogrión, N., Ionescu, A., Chipara, M. D. & Reyes Romero, J., *Polym. Degrad. Stab.*, **43** (1989) 165.
- Bellamy, L. J., *The Infrared Spectra of Complex Molecules*, Vol. 1. Chapman and Hall Publishers, London and New York, 1975.
- Reilly Chemicals, *A New Family of Crosslinked Poly(vinylpyridine), Metal Recovery*, Reillex reports 2, 3, 4 and 5. 1990. Bruxelles, Belgium.