β-Radiation Effects on PVC Materials: Methodology for Studying Chemical Modifications

N. YAGOUBI,[1,*] A. BAILLET,[1] B. LEGENDRE,[2] A. RABARON,[3] and D. FERRIER[1]

Centre d'Etudes Pharmaceutiques, [1]Laboratoire de Chimie Analytique and [2]Laboratoire de Chimie Physique, Rue J. B. Clément 92290 Chatenay-Malabry, and [3]Faculté de Pharmacie, Laboratoire de Physique et Mathématiques, 14000 CAEN, France

SYNOPSIS

The radiosterilization of plastic packaging theoretically induces two types of chemical modifications, namely reticulation and cleavage, that depend not only on the chemical structure of the polymer, but also on the kind and dose of radiation. This article proposes a methodology for studying plasticized polyvinylchloride (PVC) behavior submitted to β radiation. Analytical techniques such as thermogravimetric analysis (TGA) and size exclusion chromatography (SEC) coupled with a light scattering detector were used in this study. SEC has informed us directly on the modifications (reticulation, scission) that intervened after a radiotreatment; TGA allowed us to highlight polymer structural changes. In addition, FTIR was employed to demonstrate an intermolecular dehydrochlorination following the radiotreatment. The results of these investigations permitted us to demonstrate both a reticulation and a scission phenomena within the PVC polymer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the last decade, radiosterilization of polymers is a procedure that has undergone a considerable expansion. However, as the effects of radiosterilization on the polymer are not completely predictable, some countries are still reluctant to employ this mode of sterilization. Therefore, there is a crucial need to develop analytical methods allowing the study of the effect of such a treatment, not only for the starting material but also for the finished product.

Previous studies have shown that polymers are affected by ionizing radiations.[1,2] However, radiation doses are well adapted to obtain a total decontamination; little work has been done on the relationships between doses of radiation and effects on polymers. Owing to their high molecular weight, polymers undergo some minor chemical modifications that may produce important modifications of their physical properties. Moreover, polymers contain various amounts of additives that give them some physicochemical or technological particularities. These additives could greatly influence the material behavior during the radiotreatment.[3] On the other hand, those additives could be decomposed, thereby producing complexes that may contaminate the packaged formulation.[4] These studies on the radiochemical behavior of polymers are of interest, not only for the manufacture of plastic packagings and the pharmaceutical, alimentary, or cosmetic industries, but for the consumer as well.

The purpose of our work is to develop a methodology permitting the study of polyvinylchloride (PVC) previously treated by β radiation. This treatment consists of an electronic irradiation procedure in which the energy does not exceed 10 MeV. Size exclusion chromatography (SEC) coupled with a light scattering detector, and thermogravimetric analysis (TGA) were employed as complementary methods for this study. SEC showed some modifications in the molecular weight distribution of the polymer submitted to β rays; TGA was useful in the detection in the polymer structural changes. Finally, the Fourier Transform infrared (FTIR) method was employed to study the eventual formation of a new

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 54, 1043–1048 (1994)
 CCC 0021-8995/94/081043-06

chemical function or a new functional group in polymer chain.

EXPERIMENTAL

Irradiation Method

The ionization of molecules induced by β irradiation leads to the formation of radicals. When applied to plastic materials, the generated energy will in turn be involved in the chemical transformation of radicals. Thus, no release of heat is observed. In addition, the radiotreatment is particularly used for sterilizing of thermosensitive plastic materials. Thus, PVC was irradiated at CARIC (Centre d'Application des Rayonnements Ionisants, France) in granulated form, by β rays with 6 MeV energy, and for which the total penetration is of 3.5 g/cm^2. The effective penetration is of 2 g/cm^2 and the dose heterogeneity is of 40%. Maximal medium intensity of the electronic beam is of 7.5 kW. Consequently, the material was submitted to several runs to reach the dose of 100 kGy, under air, and at ambient temperature. According to the small size of the granulated PVC (3 mm ϕ) and the weak dose of each run, the variation of temperature did not exceed a few degrees during the β sterilization. In order to achieve a nonevoluting state for the treated samples, they were not immediately examined but stored several days at 4°C prior to analysis.

TGA

The thermal decomposition processes were studied by using the TGA on a Netzsch TG 209 instrument (Netzsch Thermal Analysis, France). Conditions of analysis were as follows: sample mass about 17 mg, heating rate 20°C/min, and argon atmosphere.

SEC

A Hewlett—Packard series 1050 pump and a Rheodyne injection valve equipped with a 20-μL loop were used. Liquid chromatographic separations were achieved on a Ultra-styragel 10^5 Å 10-μm and PLgel 102 Å 10-μm columns (Waters, France) in an isocratic elution mode using tetrahydrofuran (THF) as mobile phase. The flow rate was 1 mL/min. A chromatograph was used in connection with a light scattering detector type DDL11 (Cunow, France), thermostated at 37°C and 2 bars of nitrogen pressure. Data were recorded on a Chromjet integrator (Spectraphysics, France) coupled with a microcomputer type Epson PCe, equipped with software for data analysis in SEC.

FTIR

Both control and irradiated PVC samples were dissolved in THF. Five hundred microliters of these solutions were evaporated on a watch glass to obtain thin films. IR spectra were monitored between 4600 and 400 cm^{-1} using a JASCO 5300 FTIR spectrometer (Prolabo, France).

RESULTS AND DISCUSSION

SEC performed on the PVC shows that radiosterilization leads to an increase of its average molecular weight, M_w (Table I). This rise is more pronounced for z or z + 1 average molecular weights (M_z) or (M_{z+1}). These two parameters are sensitive to the presence of even low quantities of species having a high molecular weight. These results clearly make the evidence that a reticulation process occurred. Simultaneously, the number average molecular weight (M_n), which is sensitive to the presence of species of low molecular weight, decreased. This result suggests that a scission phenomenon occurred

Table I Influence of β Radiation (100 kGy) on Average Molecular Weights and Asymmetric Coefficients

Average Molecular Weight	Variation after β Radiation (%)
$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i}$	−5
$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$	+26
$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$	+50
$\overline{M_{z+1}} = \frac{\sum N_i M_i^4}{\sum N_i M_i^3}$	+65
$I_1 = \frac{M_w}{M_n}$	+32
$I_2 = \frac{M_z}{M_w}$	+21
$g = \frac{(M_n \cdot M_w \cdot M_z) - 3(M_n^2 \cdot M_w) + 2M_n^3}{(M_n M_w - M_n^2)^{3/2}}$	+35

See Experimental Section for experimental conditions of size exclusion chromatography.

in addition to the reticulation discussed above. On the other hand, positive values of the asymmetric coefficient g indicate that the chromatographic peak is skewed to high elution volumes.[5] In addition, a 35% increase of g is observed on the radiotreated PVC. Both M_n and g values confirm that the scission process of macromolecular chains occurred. These two modifications (reticulation and scission) lead to a heterogeneity within the polymer noted by the increase of the polydispersity indexes (I_1 and I_2) and the broadening of the chromatographic peaks (Fig. 1).

Thermal analysis was then investigated to confirm these previous results. The PVC is an amorphous polymer; nevertheless its stiffness at ambient temperature is due to the attraction between electronegative chloride atoms of the macromolecular chain and electropositive hydrogen atoms of the neighboring chains. So, it is obvious that both the amorphous character and the presence of a relative amount of additives in plastized PVC will lead to a softening of the PVC instead of a fusion upon increase of temperature. Indeed, we usually mention "gelling" to define the progressive softening of the material that is observed for temperatures above the glass temperature, T_g. The determination of this latter transition compared with the one obtained for a nonirradiated reference material could be useful to detect whether or not a polymer has undergone a β-ray treatment.

However, T_g determination studies showed spread curves without inflection point, and this observation was markedly pronounced for the irradiated PVC. This curve shape was attributed to the presence of a high proportion of plastizer [30% of bis(2-ethylhexyl phthalate] whose effects on the electrical and mechanical properties of a polymer have been extensively studied.[6] We concluded that, in the present study, the thermal behavior could not be the only criterion to be taken into account for a comparison between a treated and nonirradiated PVC. Therefore, the PVC radiochemical behavior study was carried out by TGA to obtain new information on the thermal degradation of this material. During the analysis of the PVC reference, we observed a release of hydrogen chloride and the material turned deep brown as the reaction proceeded. In this step of thermolysis, two types of reaction are envisaged: first, an intramolecular dehydrochlorination with the formation of conjugated polyene sequences, a reaction was previously reported by Allan et al.[7] Another possibility is an intermolecular dehydrochlorination that induces a reticulation of chains. The degradation phenomenon involving these possible theoretical reactions have been examined for the PVC sample submitted to radiosterilization. The TGA curve of PVC control [unirradiated, Fig. 2(a)] shows a loss of mass near 70%. This must not be attributed only to the degradation of the bis(2-ethylhexyl phthalate) because its content has already been determined not to exceed 30%. In fact, several inflection points observed on the derivative curve [Fig. 2(b)] were attributed to the presence of some entities formed during the material aging as these inflection points were also observed for the reference polymer. In contrast, the TGA curve obtained for the same PVC but irradiated at 100 kGy [Fig. 2(c,d)] exhibits a 2% higher loss of mass and the shoulder intensities on the derivative curve are relatively more important. These differences proved that the radiotreatment of the polymer induces an increase of its heterogeneity. Moreover, a 20% loss of hydrochloric acid occurs for temperatures higher than 400°C. In fact, the release of gas is observed as soon as the first step of the thermolysis is initiated and should correspond to the dehydrochlorination of entities of low molecular weight. Compared with the PVC control, the loss of hydrochloric acid is 1% lower for irradiated PVC. This confirms that a dehydrochlorination process has already occurred during the radiotreatment.

All these observations have suggested that three mechanisms are likely to occur after radiotreatment: scission, reticulation, and formation of double bonds in polymer chains. The decrease of M_n, which confirms the scission phenomenon, could be also a consequence of the intramolecular dehydrohalogenation that leads to the formation of ethylenic groups going with a loss of hydrochloric acid. Moreover the yellow color observed was an additional evidence of this loss of HCl. In order to verify if this color change was related to the formation of conjugated double bonds in the polymer, we employed UV spectroscopy for a comparison between irradiated and nonirradiated polymer. Although this latter method is useful for sequences longer than about 10 conjugated units, we failed to disclose any differences between the spectrum obtained for nonirradiated PVC and that obtained for the irradiated PVC sample. One possible explanation is that the irradiation dose (100 kGy) employed in this investigation is too low to induce the formation of conjugated double bonds. This was readily confirmed by FTIR analysis as the characteristic $=C-H$ vibration band at 3010 cm^{-1}, the $=C-H$ out of plane deformation band at 740 cm^{-1}, and the $C=C$ stretching band at about 1650 cm^{-1} were not observed in the irradiated PVC (Fig. 3). Because of its highly specific nature, a bet-

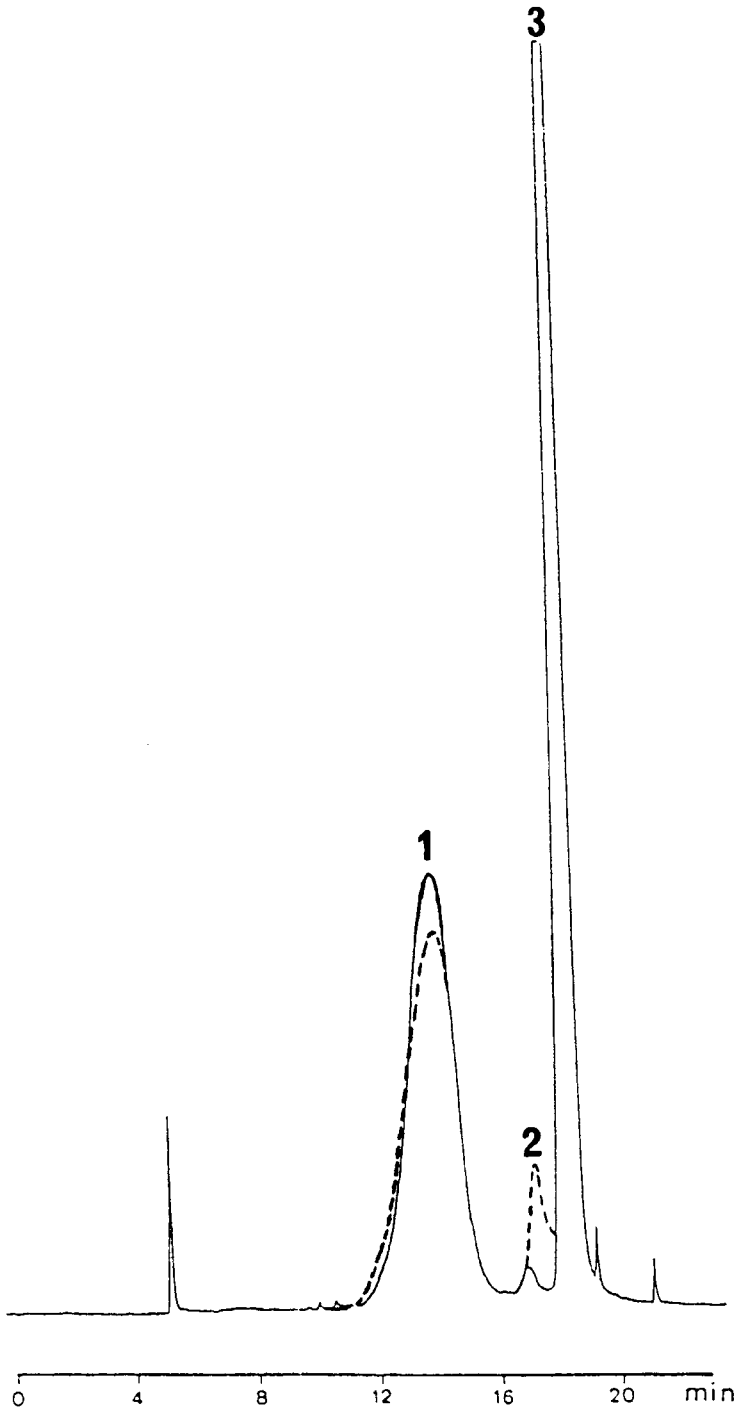

Figure 1 Size exclusion chromatography of PVC: (—) unirradiated PVC; (---) PVC irradiated at 100 kGy; chromatographic peaks: 1 = PVC, 2 = entities of low molecular weight, 3 = 2-ethylhexylphthalate. See Experimental Section for experimental conditions.

ter technique to characterize this latter band when nonconjugated would be resonance raman.[8,9] Using this method it would be possible to determine also the degree of dehydrochlorination. Therefore, the reticulation probably occurs between the original macromolecular chain and some fragments of molecule formed by scission. Indeed, the increase of average molecular masses, which is less than 65%, supports this assumption. Moreover, the irradiated PVC solubility in THF was not modified although it should be insoluble after intermolecular reticulation.

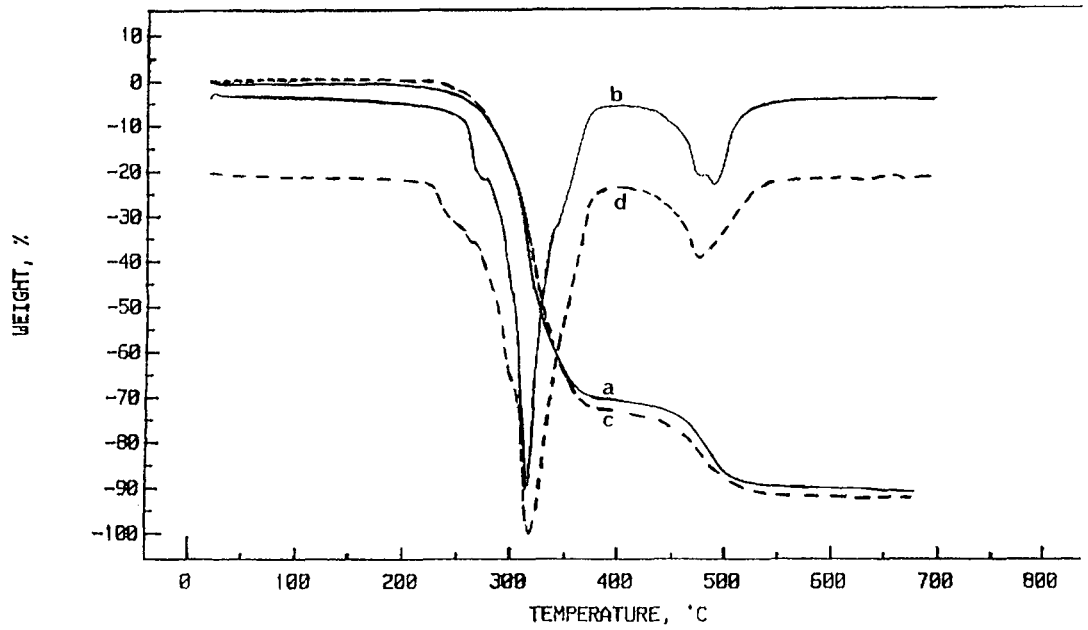

Figure 2 Thermogravimetric analysis of PVC: thermogram of (a) PVC unirradiated and (b) its first derivative curve; thermogram of PVC irradiated (c) at 100 kGy and (d) its first derivative curve; (—) unirradiated PVC; (---) PVC irradiated at 100 kGy. See Experimental Section for experimental conditions.

CONCLUSIONS

The combined SEC and TGA constitutes a simple, sensitive, and rapid method for studying the modifications that could occur following a radiotreatment of a PVC material. Moreover the methodology developed in this work can be easily applied to studies on the radiochemical behavior of other polymeric materials. In particular, these techniques show the presence of oligomers, a parameter of great interest in contain–container compatibility studies. However the irradiation dose used in this study in order to enhance the various phenomena described, is markedly high in comparison to the dose level prescribed

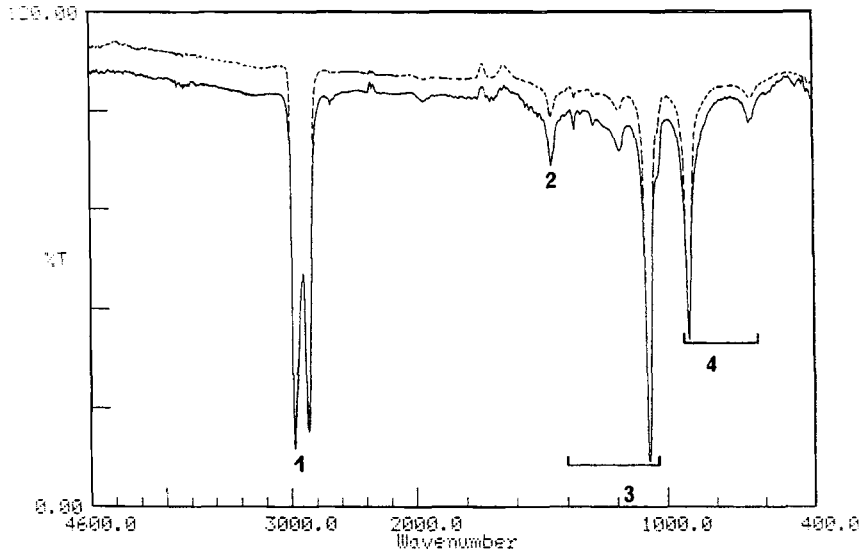

Figure 3 IRFT spectra of PVC (—) before and (---) after radiotreatment. See Experimental Section for experimental conditions. 1: Aliphatic CH stretching; 2: CH_2 bending; 3: CH stretching and CH—Cl deformation; 4: CH_2 rocking, and C—Cl stretching.

by the French Pharmacopeia (25 kGy). The migration of some low molecular entities from PVC container to content is likely to occur. Further research will focus on the study of polymer radiated at the legal dose, and on the identification and determination of the percent of migration of these low molecular entities.

REFERENCES

1. H. L. McMurry and V. Thornton, *Anal. Chem.*, **24,** (1952).
2. T. Ooi, M. Schiotsubo, Y. Hama, and K. Shinokara, *Polymer,* **16**(7), 510 (1975).
3. A. G. Taylor and J. P. Harmon, *Polym. Degrad. Stabil.*, **41,** 1 (1993).
4. D. W. Allen, D. A. Leathard, C. Smith, and J. D. McGuinness, *Chem. Ind.*, **6,** 198 (1987).
5. T. Provder and E. M. Rosen, in *Gel Permeation Chromatography,* K. H. Altgelt and L. Segal, Eds., Marcel Dekker Inc., New York, 1971, p. 251.
6. L. Audoin, B. Dalle, G. Metzger, and J. Verdu, *Appl. Polym. Sci.*, **45,** 2097 (1992).
7. J. Allan, G. Baillie, D. Gerard, and J. Birnie, *Vib. Spectrosc.*, **1**(1), 97 (1990).
8. A. Baruya, D. L. Gerrard, and W. F. Maddams, *Macromolecules,* **16,** 578 (1983).
9. M. Bowden, P. Donaldson, D. J. Gardiner, J. Birnie, and D. L. Gerrard, *Anal. Chem.*, **63,** 2915 (1991).

Received January 24, 1994
Accepted April 25, 1994