STUDIA UBB CHEMIA, LVI, 3, 2011 (p. 129 - 134)

^{13}C NMR STUDY OF GAMMA IRRADIATED POLYSTYRENE

MIHAELA POP[a], STEFAN TRAIAN[a], LIVIU DARABAN[a],
RADU FECHETE[b]

ABSTRACT. The ^{13}C CP/MAS NMR spectra of *polystyrene* were recorded for un-irradiated samples and for samples exposed to a 8989 Gy dose of gamma radiation. The most intense peaks of unirradiated sample appear at 145 and 127 ppm and are assigned to non-protonated and protonated aromatic carbons, respectively. The gamma irradiation leads to an important decay of $T_{1\rho}$ relaxation time corresponding to aromatic and methylene-methine functional groups.

Keywords: *Polystyrene, ^{13}C CP/MAS NMR, $T_{1\rho}$*

INTRODUCTION

Polymeric materials are strongly affected by ionizing radiation. Based on different values of the absorbed dose, radiation effects on polymers may be classified as follows: i) scission and/or cross-linking of the polymer chains with a consequent molecular weight decrease and/or increase; ii) occurrence of chemical reactions leading to small volatile products and, eventually, organic radicals and iii) occurrence of structural modifications of polymer chains, such as changes in the number of unsaturations, presence of charged units. Such modification can be observed by the use of methods and techniques sensitive to the physical phenomena occurring an atomic and molecular scale, as NMR. This method provides information concening the chemical shift, relaxation process of the magnetization of molecular spins, interaction between neighboring atoms [1]. Using cross-polarization magic angle spinning experiments improved signals can be obtained for nuclei with low gyromagnetic ratio or poor natural abundance sach as ^{13}C nuclei [2]. Other information, such the existence of crystalline and amorphous phase, can be used in NMR experiment special pulse sequence excitation.

Such methods were used to investigate posible modifications induced by gamma irradiation on the structure of polystyrene.

---

[a] *"Babes-Bolyai" University, Faculty of Physics, M. Kogalniceanu No 1, 400084 Cluj-Napoca, Romania, profmihaelapop@yahoo.com*

[b] *"Technical University" of Cluj-Napoca, Physics Department, Str. Memorandumului nr. 28, 400114, Cluj-Napoca, Romania*

RESULTS AND DISCUSSION

In chemical terms, polystyrene is a long chain hydrocarbon wherein alternating carbon centers are attached to phenyl groups (Figure 1).

Some properties of such materials are determined by short range van der Waals attractions between polymers chains. Since the molecules are long hydrocarbon chains, that consist of thousands of atoms, the total attractive force between the molecules is large. Polystyrene results when styrene monomers interconnect. In the polymerization one carbon-carbon double bond (in the vinyl group) is replaced by a much stronger carbon-carbon single bond, hence it is very difficult to depolymerize polystyrene. Typically about a few thousand monomers comprise a chain of polystyrene, giving a molecular weight of 100,000-400,000.

A 3-D model would show that each of the chiral backbone carbons lies at the center of a tetrahedron, with its 4 bonds pointing toward the vertices. Say the -C-C- bonds are rotated so that the backbone chain lies entirely in the plane of the diagram. From this flat schematic, it is not evident which of the phenyl groups are angled toward us from the plane of the diagram, and which ones are angled away. Following the alternation of styrene groups, the polystyrene can adopt sindiotactic or atactic conformations. The isomer where all of them are on the same side is called *isotactic* polystyrene, which is not produced commercially. Sindiotactic arrangement of atoms corresponds to more local order and is characteristic for crystaline phase of the samples. Atactic conformation means less local order and it characteristic for amorphous phase.

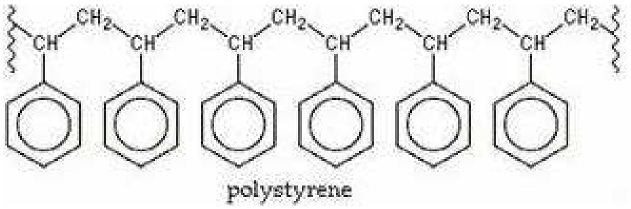

Figure. 1 Chemical structure of polystyrene

Such bonds can be affected by external physical excitations like gamma radiation, resulting in breaking of the chains with corresponding reducing of molecular mass, or modification of local conformation. On the molecular scale the modification of the conformation can affect the vecinity of the nuclear spins attached to the polymeric chain. Two mechanisms can be taken into account: the chemical shift and the relaxation of the magnetization of the nuclear spins. Our interest was to observe such modifications on polystyrene samples irradiated at different doses with gamma photons. For this aim, the high resolution spectra of non-irradiated sample were compared with the spectrum of the irradiated one.

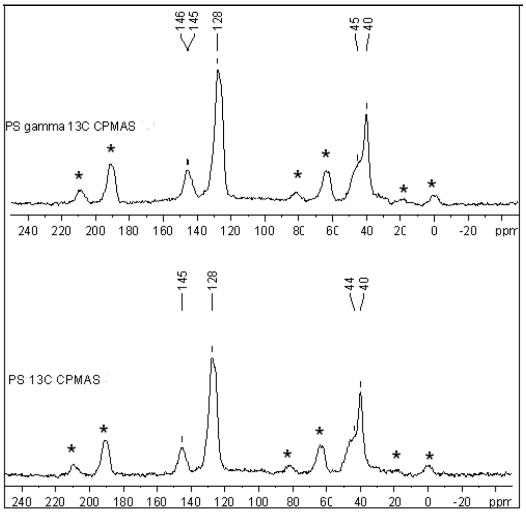

Figure. 2 The CP/MAS ^{13}C NMR spectra of un-irradiated and gamma irradiated polystyrene

Figure 2 shows the CP/MAS ^{13}C NMR spectra of commercial PS recorded at room temperature. A control measurement was performed on un-irradiated polystyrene samples. To correctly assign the signals of PS we used the data described in the literature [2, 3]. Resonances at 145 and 128 ppm were assigned to non-protonated and protonated aromatic carbons, respectively. Methylene and methyne carbon resonances were ascribed signals at 46 and 40 ppm, respectively [4]. All observed resonance lines were very broad, as the material is an amorphous polymer. The remaining of CP MAS ^{13}C NMR spectra signals are sppining side bands.[2]

Next, we studied the polystyrene gamma irradiated sample. Gamma radiation can excite the electrons from theirs initial state higher energy level and can even break chemical bonds. We expect that the radiation may produce some structural changes, with corresponding chemical shift of the resonance lines. Gamma irradiated sample shows the same peaks but with smaller amplitude. In the table I we can see the chemical shifts peaks of CP/MAS ^{13}C NMR spectra of polystyrene before and after gamma irradiated.

Table 1. NMR parameters for PS

un-irradiated PS (ppm)	gamma irradiated PS (ppm)
40	40
44	45
128	128
145	145

Note that basedon the NMR spectra there was no change in the chemical bonds induced by such doses.

In order to quantify the effects of irradiation on the polystyrene chain dynamics the longitudinal relaxation times in rotating frame, $T_{1\rho}$ for different functional groups (aromatic, aliphatic), were measured. The evolution of the spin system magnetization function of spin-lock time τ, for different functional groups in un-irradiated and gamma irradiated polystyrene, shows multi- or mono-exponential dependences (see Figure 3). Therefore, the values of $T_{1\rho}$ can be determined by fitting the decays corresponding to the aromatic component (filled symbols in Figure 3) with a bi-exponential decay given by,

$$M(\tau) = M_0^{(f)} \exp\left\{-\frac{\tau}{T_{1\rho}^{(f)}}\right\} + M_0^{(s)} \exp\left\{-\frac{\tau}{T_{1\rho}^{(s)}}\right\}, \tag{1}$$

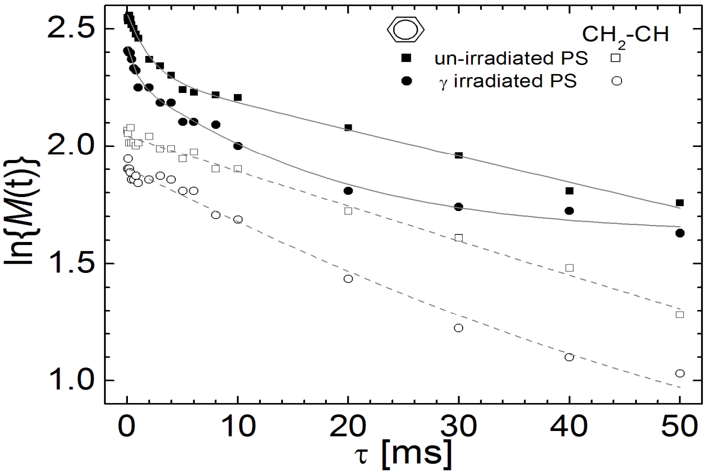

Figure. 3 Logarithmic plots of ^{13}C resonance intensities corresponding to aromatic (filled symbols) and methylene-methine (open symbols) functional groups function of spin-lock time τ for un-irradiated (squares) and gamma irradiated polystyrene (circles).

where $M_0^{(f)}$ is the equilibrium magnetization and $T_{1\rho}^{(f)}$ the relaxation time in rotating reference frame of the fast decaying component and $M_0^{(s)}$ is the equilibrium magnetization and $T_{1\rho}^{(s)}$ the relaxation time in rotating reference frame of the slow decaying component. The values of $T_{1\rho}$ corresponding to the methylene-methine component can be found by fitting the decays (open symbols in Figure 3) with a mono-exponential decay given by [5].

Table 2. Relaxation times for PS

Sample	C protonated aromatic		C methylene-methine
	$T_{1\rho}^{(f)}$ (ms)	$T_{1\rho}^{(s)}$ (ms)	$T_{1\rho}$ (ms)
PS un-irradiated	1.9	81.3	63.8
PS gamma irradiated	0.7	14.3	32.7

$$M(\tau) = M_0 \exp\left\{-\frac{\tau}{T_{1\rho}}\right\}, \qquad (2)$$

The experimental data were fitted with equation (1), continuous lines in figure 3, or eq. (2), dashed line in figure 3, and the corresponding $T_{1\rho}$ values are summarized in Table II. One can observe a general decrease of $T_{1\rho}$ after irradiation. The $T_{1\rho}^{(f)}$ corresponding to aromatic groups is reduced at half for the gamma irradiated polystyrene sample, while a dramatically effect off irradiation can be observed for the slow decaying components since the $T_{1\rho}^{(s)}$ decays with approximately 5.7 time after irradiation. The $T_{1\rho}$ relaxation time in rotating reference frame corresponding to methylene-methine functional group decays also approximately two times. All these results can be associated with a low effect of crystallization induced by irradiation.

Analyzing the $T_{1\rho}$ values we observed that the carbons showed different values depending on the gamma doses. They can be attributed to the fact that the microstructure has different molecular mobility and consequently belongs to different domains [6].

CONCLUSIONS

The effect of gamma radiation on the properties of polystyrene was investigated by CP/MAS ^{13}C NMR spectroscopy. The $T_{1\rho}$ of the protonated carbon located in different functional groups were measured by combining the solid state CP/MAS with the spin-lock experiments. The $T_{1\rho}$ values obtained for PS gamma irradiated samples were several times smaller than those for un-irradiated PS. These results make it possible to obtain information on the polymer microstructure, showing that the radiation gamma led to a decrease of PS molecular mobility. Changes in the microstructure of polystyrene are due to rupture of molecular bonds. After irradiation the shrinkages and collapse of PS chains take place.

EXPERIMENTAL SECTION

Polystyrene was received as a gift sample from SC Napochim SA (Cluj Napoca). The samples were exposed to gamma radiations using a source of ^{60}Co, which offers a high and compact density of radiation, [4]. The doze of radiation was D = 5,3Gy/h and samples were exposed until 8989 Gy Solid state ^{13}C NMR spectra were recorded at 500 MHz ^{13}C Larmor frequency with a Bruker Avance 500-spectrometer. All NMR experiments were performed at room temperature and the sample was centred- packed in zirconium rotors. In the modified CP/MAS experiment, the proton field was turned off after cross-polarization. After a delay ranging from 10 µs to 100 ms, the acquisition was performed under high-power decoupling.

For proton relaxation time in the rotating frame ($T_{1\rho}$) measurements, we used the normal cross-polarization pulse sequence. The magnetization initially builds up to a maximum due to de carbon-proton dipolar interactions, and the signal decays exponentially to equilibrium with time constant $T_{1\rho}$ [7]. Thus $T_{1\rho}$ can be obtained from a semi-log plot of the intensity as a function of spin-locking time (t) after the signals have reached their maximum intensity [8].

ACKNOWLEDGMENTS

Mihaela Pop acknowledges financial support from a program co-financed by The SECTORAL OPERATIONAL PROGRAMME HUMAN RESOURCES DEVELOPMENT, Contract POSDRU 6/1.5/S/3 – „Doctoral studies: through science towards society**".**

REFERENCES

1. M.Todica, *“ Metode Aplicative de Rezonanță Magnetică Nucleară “*, *Presa Universitara Clujeana*, **2001,** 5.
2. C. R. Martins,F. Hallwass**,** *Annals of Magnetic Resonance* **2007**, *6*,46.
3. R.R. Wu, H.M. Kao, J.C. Chiang, E.M. Woo, *Polymer* **2002,** *43*, 171.
4. M. Li, C. Li, B. Zhang, W. Huang, A. Men, B. He, *European Polymer Journal* **1998,** 34, 515.
5. T. Nakaoki, M. Kobayashi, *Journal of Molecular Structure* **2003,** 343.
6. S.G.Bond,J.R.Ebdon,M.N.Hussin, *Polymer* **1998**, *39*, 6875.
7. E.O. Stejskal, J.D. Memory, *High Resolution NMR in the Solid State,***1994,** *35*, 48.
8. N.Carretta,V.Tricoli, F.Picchioni, *Journal of Membrane Science ,* **2000,** *166*, 189