

## Liquid and Solid-State NMR study of the electron irradiated Polystyrene

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### 1. Introduction

Irradiation of polymer widely studied due to improve and control its own properties such as mechanical strength, color and electrical conductivity [1]. Especially, irradiated polystyrene (PS) has shown impressive performance in bioassay and biosensor, for example increase cell adhesion which is important properties for the biochip [2]. However, although several propose has been reported about PS radiolysis [3], exact chemical modification process remains unclear. In this paper, we analyzed the electron irradiated PS using liquid and solid proton nuclear magnetic resonance spectroscopy (NMR) which is a useful to define the chemical configuration.

### 2. Methods and Results

#### 2.1 Experiment methods

Commercialized PS film with 25  $\mu\text{m}$  thickness (GoodFellow, ST311025) was used in the experiments. Before the electron irradiation, the PS film was rinsed with 99.9% pure ethanol and was attached on silicon substrate. And then, the polymers were irradiated with an electron beam, which was generated from a thermionic electron gun with a tantalum filament cathode. The irradiation was carried out in a vacuum chamber under a pressure of less than  $2 \cdot 10^{-5}$  Torr. The energy and the current density of an electron beam were fixed to 50 keV and  $4 \mu\text{Acm}^{-2}$ , respectively. The electron fluence was changed from  $1.0 \times 10^{15} \text{ cm}^{-2}$  to  $7.2 \times 10^{16} \text{ cm}^{-2}$  by varying the irradiation time and the substrate was cooled down to prevent thermal degradation. Liquid  $^1\text{H}$  liquid NMR and COSY spectrum were performed by employing a Bruker Biospin AvanceII 900 model at 305.3 K and 900MHz.  $^{13}\text{C}$  CP-MAS NMR spectroscopy was used by employing Varian 200 MHz model

#### 2.2 $^1\text{H}$ liquid NMR and COSY spectroscopy

Figure 1 shows that NMR spectra of pristine PS and electron irradiated films. All of the films swelled into deuterated chloroform and used tetramethylsilane (TMS) as standard. For pristine PS, there is no chemical shift more down field than the signal for chloroform. However, after electron irradiation ( $1.0 \times 10^{15} \text{ cm}^{-2}$ ), some new chemical shifts has appeared at 7.25-7.35ppm and 7.60ppm which are corresponded to protons of the phenyl unit (-C<sub>6</sub>H<sub>5</sub>) included small molecules [4] and benzene, respectively. The spectrum of the more irradiated sample ( $1.0 \times 10^{16} \text{ cm}^{-2}$ ) showed more new

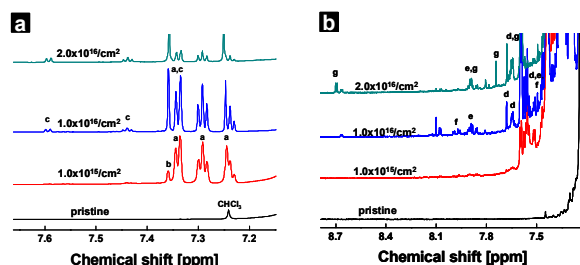


Figure 1. a)  $^1\text{H}$  liquid NMR spectrum of pristine PS and electron irradiated PS. Each character indicate a; phenyl unit included small molecules, b; benzene and c; biphenyl, respectively. b) Magnified  $^1\text{H}$  liquid NMR spectrum in down-field region. Each character indicate d; p-terphenyl, e; 1-phenylnaphthalene, f; 1,4-dimethylnaphthalene and g; phenanthrene, respectively.

chemical shift at the region 7.3-8.2ppm. These signals assigned to several multi ring aromatic units such as biphenyl;  $\delta=7.34(2\text{H}, t)$ ,  $7.44(4\text{H}, t)$ ,  $7.60(4\text{H}, d)$ , p-terphenyl;  $\delta=7.36(2\text{H}, t)$ ,  $7.46(4\text{H}, t)$ ,  $7.64(4\text{H}, d)$ ,  $7.68(4\text{H}, s)$ , 1,4-dimethylnaphthalene;  $\delta=7.19(2\text{H}, s)$ ,  $7.51(2\text{H}, dd)$ ,  $8.0(2\text{H}, dd)$  and 1-phenylnaphthalene;  $\delta=7.40-7.52(9\text{H}, m)$ ,  $7.85-7.91(3\text{H}, m)$ . In addition, large irradiated sample ( $2.0 \times 10^{16} \text{ cm}^{-2}$ ) shows additional signals at 7.64-7.68, 7.76, 7.91 and 8.70ppm which are corresponded to phenanthrene [5].

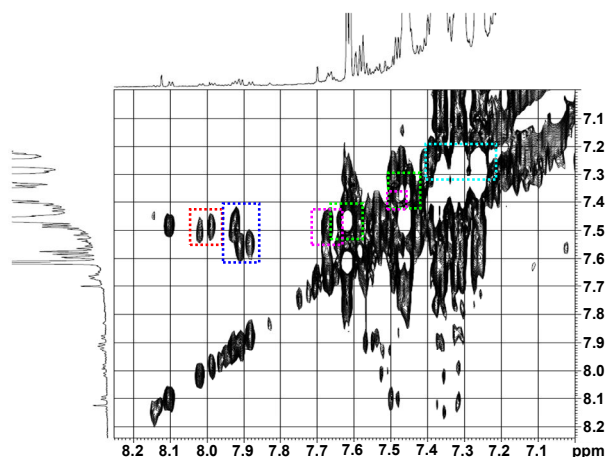


Figure 2. Section of the corresponding  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of electron irradiated sample with fluence of  $1.0 \times 10^{16} \text{ cm}^{-2}$ . Each color correspond to correlation of protons in phenyl unit included small molecules (sky-blue), biphenyl (green), p-terphenyl (violet), 1-phenylnaphthalene (blue) and 1,4-dimethylnaphthalene (red).

Figure 2 shows the two-dimensional H-H correlation spectroscopy (H-H COSY) of the electron irradiated PS film with fluence of  $1.0 \times 10^{16}/\text{cm}^2$ . These spectra give the more clear evidence of the existence of multi ring aromatic units in the irradiated PS film by defining the correlation of protons attached on each unit.

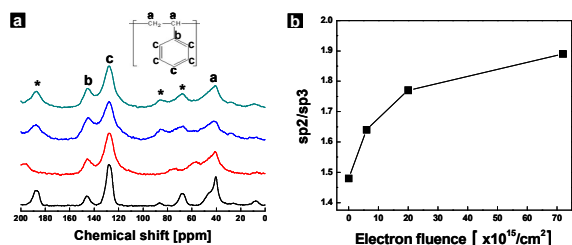


Figure 3. a) CP-MAS spectrum of pristine and electron irradiated PS. The peak assignments are noted on the figure, where asterisks denote spinning sidebands. b) The  $\text{sp}^2/\text{sp}^3$  ratio in the irradiated PS as a function of fluence.

## 2.2 $^{13}\text{C}$ CP-MAS NMR spectroscopy

Although NMR analysis can support chemical modification in irradiated PS film, liquid NMR has a restriction for the sample condition that sample should be swelled into non-polar solvent. Actually, we can not obtain any significant signal from large irradiated sample because PS film becomes more insoluble as increase of irradiation. Thus, large irradiated samples are analyzed solid state  $^{13}\text{C}$  CP-MAS NMR spectroscopy (Fig. 3a). According to the spectrum, it could not find new peak appearance from the all samples, where relative peak intensity for the each component was changed. Figure 3b shows that  $\text{sp}^2/\text{sp}^3$  ratio in the PS film was increased with the electron irradiation. Therefore, from both of liquid and solid NMR results, it can be supposed that electron irradiation induce breakage of chemical bonding and clusterization of  $\text{sp}^2$  carbon via formation of non-fused or fused polycyclic structure.

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