

## 전자빔 조사에 의하여 가교된 폴리비닐알릴이미다졸륨의 열적 물성

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## Thermal Properties of Crosslinked Poly(1-vinyl-3-allylimidazolium) by Electron Beam Irradiation

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**초록:** 최근에 이온성 액체의 뛰어난 특성으로 인해 관심이 증가하고 있다. 자유 라디칼 중합공정과 친핵성 치환 반응을 이용하여 poly(1-vinyl-3-allylimidazolium)(PVAm)을 제조하였으며, 이를 전자빔을 이용하여 가교하였다(C-PVAm). 고분자의 물성을 향상시키기 위해 가교 가능한 알릴 그룹을 공유 결합으로 도입하였다. 전자빔 조사에 의해 가교된 PVAm의 화학적 구조를 적외선 분광분석과 핵자기 공명 분석을 통하여 확인하였으며, 시차 주사 열량 분석(DSC)을 통하여 가교된 PVAm의 열적 안정성이 향상됨을 확인하였다.

**Abstract:** Ionic liquids (ILs) have attracted widespread interest in recent years because of their favorable characteristics. A highly crosslinked poly(1-vinyl-3-allylimidazolium) (C-PVAm) was synthesized by free radical polymerization and quaternization followed by radiation processing. An allyl group was covalently incorporated into the polymer matrix to enhance the properties of the PVAm. The chemical structures of the synthesized pristine and crosslinked PVAm containing a C=C bond were confirmed by <sup>1</sup>H NMR and FTIR spectra. The thermal properties of the C-PVAm analyzed by differential scanning calorimetry (DSC) were significantly improved because of the thermal stability of the crosslinked networks.

**Keywords:** ionic liquid, crosslinking, thermal property, electron beam, energy device.

### Introduction

Electrochemical energy storage and conversion devices, such as batteries, fuel cells, supercapacitors, dye-sensitized solar cells, etc., have been the focus of recent studies due to their important role in the utilization of renewable energy.<sup>1</sup> Expansion of energy storage systems for next generation devices, such as electric transportation and large scale energy storage systems, however, relies on further developments towards a superior energy density, and a longer durability.<sup>2</sup> To date, most studies have focused on the design of new electrode materials and stable electrolytes in the hard environments of

energy storage systems, and only few groups have reported on the polymeric binder so far.<sup>3</sup>

Besides other key components in energy storage systems, such as electrodes and the electrolyte, an efficient binder is important to sustain both the electronic and mechanical properties of the electrodes. The effect of polymeric binders on the overall behavior of the whole electrode system is highly relevant for the cycling stability of energy storage systems.

Ionic liquids (ILs) have attracted widespread interest in recent years because of their favorable characteristics, such as being chemically inert and having electrochemical stability, non-volatility, and high ionic conductivity, for use as electrolytes.<sup>4-9</sup> In the last few years, polymers prepared with ionic liquid moieties (PILs) have also been studied as solid polymer electrolytes for various applications.<sup>10-12</sup>

To improve the properties of polymers, many innovative

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techniques have been developed such as crosslinking,<sup>13-15</sup> fabricating composite with inorganic materials, and blending with other polymers.<sup>16-18</sup> Among these techniques, crosslinking has been preferred because it is a simple and efficient method, which can improve the thermal and mechanical stability.

A polymer can be crosslinked either by conventional thermal treatment or by exposure to radiation from either radioactive sources or highly accelerated electrons. Radiation-induced crosslinking is a well-known and established technique that does not need any additives. The advantages of radiation induced crosslinking are (1) homogenous and temperature-independent; (2) the gel contents can be easily modified by controlling the irradiation conditions; (3) more polymers can be crosslinked by radiation than by any chemical method; and (4) the chemistry of the reaction system is free from contamination.<sup>19</sup>

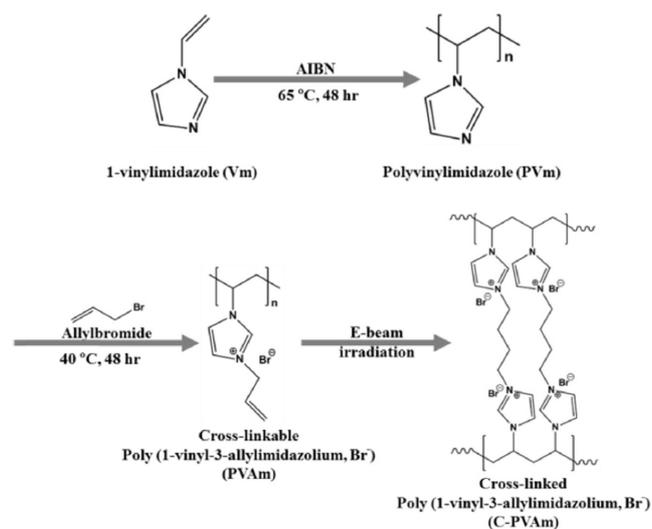
In this paper, we describe a direct route to fabricate a highly C-PVAm. For this, PVAm was crosslinked by electron beam irradiation to obtain a high thermal stability under various conditions.

## Experimental

**Materials.** 1-Vinylimidazole (Alfa Aesar, 98%) (Vm), allyl bromide (Sigma-Aldrich, 99%), 4,4'-azo-bis(4-cyanovaleric acid) (Sigma-Aldrich, 98%), diethyl ether (Duksan, Extra pure grade), tetrahydrofuran (THF) (Duksan, extra pure grade) were used without any further purification.

**Synthesis of Polyvinylimidazole (PVm).** PVm was synthesized by free radical polymerization. First, 1-vinylimidazole (8 g, 0.085 mol) and D.I. water (110 mL) were added to a round bottom flask. Then, 4,4'-azobis(4-cyanovaleric acid) was added as an initiator. Afterward, the flask was de-gassed and the inside was filled with nitrogen. Then, it was reacted at 65 °C for 48 hr with magnetic stirring. After termination of the reaction, the mixed solution was precipitated in THF (1 L). Finally, the collected PVm was dried in a vacuum oven overnight at 40 °C.

**Synthesis of PVAm.** PVAm was synthesized by a nucleophilic substitution reaction of PVm and allyl bromide. This synthesis was done using a mole ratio of 0.05:0.057. First, PVm (5 g, 0.05 mol), Allyl bromide (7.3267 g, 0.06 mol) and methanol (100 mL) were added to a round bottom flask and reacted at 40 °C for 48 hr with magnetic stirring. After 48 hr, the mixed solution was precipitated in the diethyl ether (1 L). Finally, the collected PVAm was dried in a vacuum oven over-



**Figure 1.** Reaction scheme for the synthesis of C-PVAm.

night at 40 °C as shown in Figure 1.

**Electron Beam Irradiation.** The PVAm films were put into an aluminum bag filled with nitrogen gas. Electron beam irradiation was performed using an E-beam accelerator installed at the KAERI (Daejeon, Korea). The voltage and current density of the electron beams were 1 MeV and 1 mA/cm<sup>2</sup>, respectively. Each sealed sample was E-beam irradiated under various conditions (10, 20, 50, 100, 200, 500 kGy).

**Characterization.** The gel content of the crosslinked PVAm was determined by a solvent extraction and evaluated from the following eq. (1):<sup>20</sup>

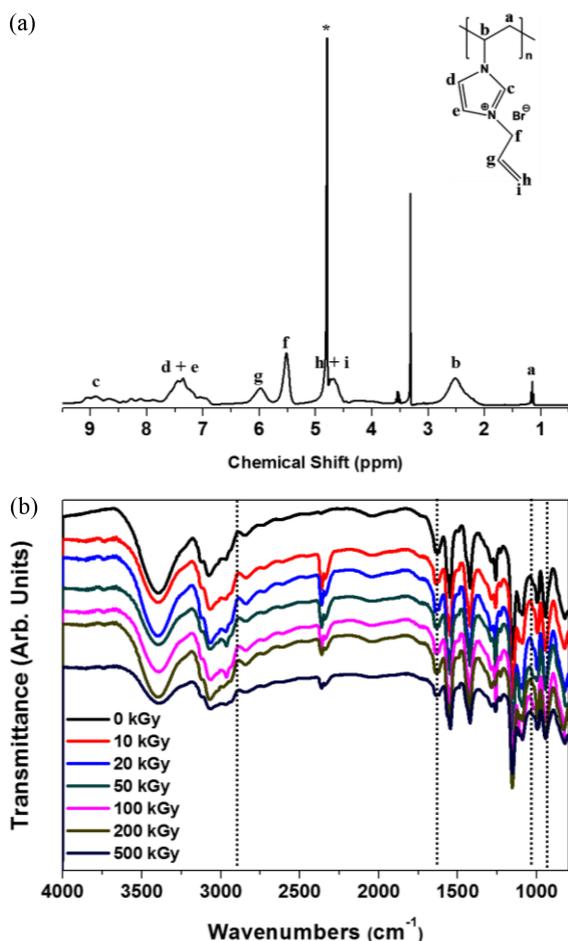
$$\text{Gel content (\%)} = M_2/M_1 \times 100 \quad (1)$$

where  $M_1$  and  $M_2$  are the weights of the irradiated PVAm before and after the solvent extraction, respectively.

The total absorption dose ranged from 10 up to 500 kGy. The thermal properties and chemical structures of the pristine and crosslinked PVAm were characterized using DSC, FTIR, and <sup>1</sup>H NMR spectroscopy.

## Results and Discussion

The chemical structure of the PVAm were confirmed by <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR spectrum of the PVAm had four peaks at 9, 7.5, 2.5 and 1.2 ppm related to the polymer backbone and three peaks at 6, 5.5 and 4.8 ppm for a functionalized allyl bromide (Figure 2(a)).<sup>21,22</sup> These kinds of peaks are the specific spectrum for the PVAm, which indicate

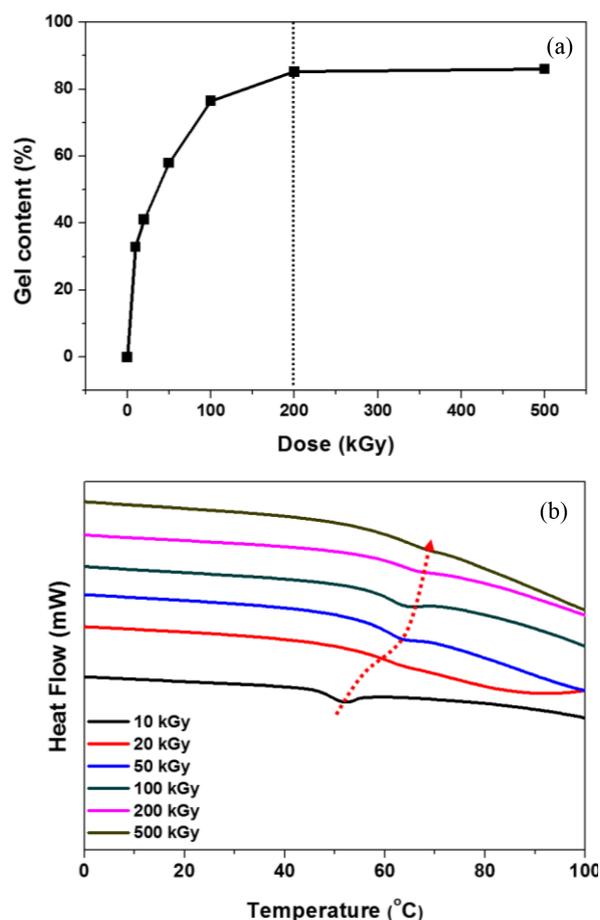


**Figure 2.** (a) <sup>1</sup>H NMR spectrum of the PVAm; (b) FTIR analysis of the C-PVAm as a function of the absorption dose.

that the synthesis of the PVAm was successfully carried out.

The chemical changes in the PVAm were confirmed by FTIR spectroscopy, and the results are shown in Figure 2(b). The characteristic bands of the original PVAm were observed at 3066 cm<sup>-1</sup> (C-H stretch in the imidazole ring), 2942 cm<sup>-1</sup> (C-H stretch in the CH<sub>3</sub>) and 1643 cm<sup>-1</sup> (C=C stretch), 1550 cm<sup>-1</sup> (C-C and C-N stretch in imidazole ring), 1423 cm<sup>-1</sup> (C-H bending in the back bone), and 1178 cm<sup>-1</sup> (C-H bending in the imidazole ring).<sup>23-25</sup> After irradiation, the band intensity of the CH<sub>3</sub> groups at 2942 cm<sup>-1</sup> was increased by the electron beam irradiation.<sup>26</sup> This increase in the intensity of the CH<sub>3</sub> band implies that the C=C in the allyl group was broken by the electron beam irradiation and the resultant radicals participated in the crosslinking reaction with the neighboring PVAm chains shown in Figure 1.

C-PVAm was prepared by radiation-induced crosslinking. It is well known that high-energy irradiation of the C=C bond



**Figure 3.** (a) Gel content; (b) DSC analysis of the irradiated PVAm as a function of the absorption dose.

leads to the formation of insoluble crosslinked networks in a polymer matrix. The gel content as a function of the absorption dose is shown in Figure 3(a). The results confirmed that the gel content was significantly increased with increase in absorption dose up to 200 kGy, above which it was saturated.<sup>20</sup> To check the irradiation effect on the thermal properties, C-PVAm was analyzed by DSC as shown in Figure 3(b). As expected, the glass transition temperature ( $T_g$ ) of the C-PVAm increased with increase in the absorption dose because the  $T_g$  of the C-PVAm increased with increase in the absorption dose due to the generation of crosslinked networks in the PVAm, which hindered the rotation of the PVAm chains.<sup>27</sup>

## Conclusions

In summary, a highly crosslinked PVAm was prepared by free radical polymerization and quaternization followed by

electron beam irradiation. The chemical structures of the PVAm were confirmed by  $^1\text{H}$  NMR and FTIR. The thermal properties of the C-PVAm analyzed by DSC were considerably improved. The fabricated C-PVAm has potential use as electrolytes and electrode binders for energy devices with improved properties.

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