6th Hellenic Conference on Polymers

Patras, 3-5 November 2006

Book of Abstracts

HELLENIC POLYMER SOCIETY

University of Patras

Foundation for Research and Technology - Hellas,
Institute of Chemical Engineering
and High Temperature Chemical Processes, (FORTH/ICE-HT), Patras

Structure and dynamics of lithium neutralized ionic block copolymers

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In recent years, interest has been focused on solid-state materials that exhibit enhanced ion transport properties. Polymer solid electrolytes constitute a class of materials of high promise for technological applications like in batteries, fuel cells, sensors and other electrochemical devices[1,2]. The advantages of their use include lack of corrosive liquids, wide potential range of electrochemical stability, improved mechanical properties and ability for thin film processing[3].

In the present study, block copolymers of polystyrene-polymethylmethacrylate (SMAA) of various compositions have been prepared by anionic polymerization and have been used as templates for the production of 'single-ion' polymer electrolyte systems. Lithium ions were introduced as the effective component that contributes to ionic conductivity of these hybrid materials. The structure has been studied by infrared spectroscopy (IR), differential scanning calorimetry (DSC), small-angle X-Ray scattering (SAXS), while the dynamics of these systems have been investigated by dielectric spectroscopy (DS).

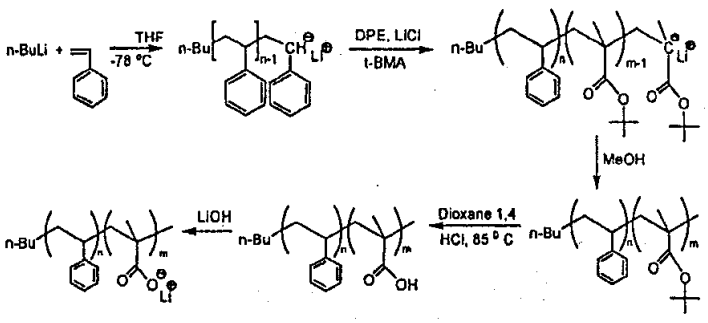

Table 1. Molecular characteristics of the prepared block copolymers

Sample	M_w	I	% wt in PS
SMAA1	44900	1.06	84
SMAA1Li	45500	1.06	82
SMAA2	34500	1.06	72
SMAA2Li	35400	1.06	70
SMAA3	29200	1.06	56.9
SMAA3Li	30300	1.06	54.8

Figure 1 presents the synthesis of block copolymers, while Table 1 gives their molecular characteristics.

The structure of the initial materials and of the ionic block copolymers resulting from the introduction of Li^+ ions was investigated by IR spectroscopy in the mid-IR region. The results depicted in Figure 2 reveal the characteristic bands of each component and their change upon salt concentration. The band at ca. 1699 cm^{-1}, attributed to the asymmetric stretching, $v_{as}(CO_2^-)$, of carboxylic acid[4], disappears upon formation of the Li^+ -polymer salt. In addition, the band at ca. 1548 cm^{-1}, attributed to the v as(CO_2^-) mode with the carboxylate anion being now coordinated to Li^+ ions[4], appears enhanced upon increasing Li^+ concentration and demonstrates clearly the formation of the Li^+ -polymer salt. Thus, the introduction of Li^+ ions within the methylmethacrylate phase is clearly manifested by IR spectroscopy, showing the successful synthesis of these hybrid materials.

Furthermore, the SAXS spectra indicate that introduction of Li^+ ions favors the improvement of structural organization in each system, e.g. SMAA1Li forms cylinders of MAA1Li in a hexagonal lattice while SMAA2 manifests a lamellar morphology upon introduction of Li^+ ions.

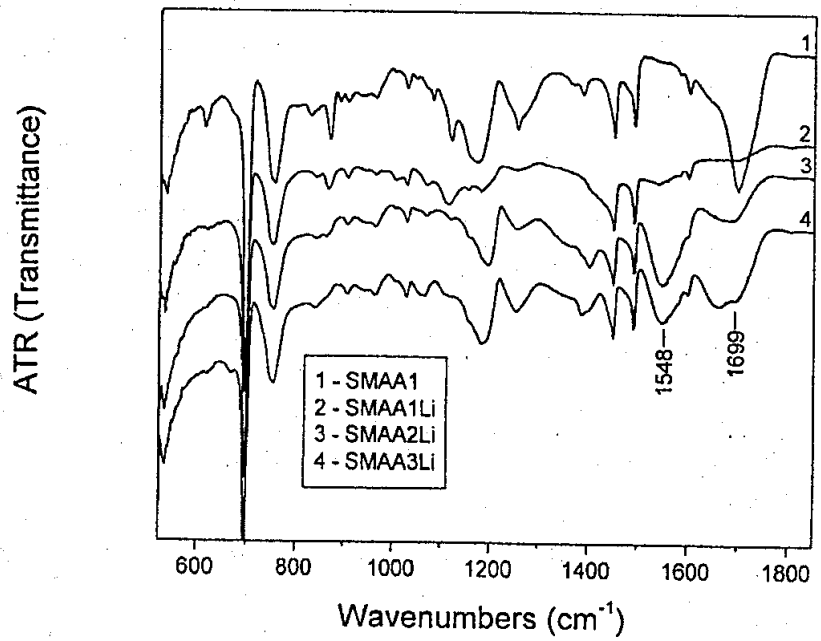

Fig. 2. ATR transmittance spectra of SMAA1 and of ionic block copolymers resulted from Li^+ ion introduction.

The dynamics of each system were investigated by dielectric measurements, which provide information on the type of relaxation mechanisms and the corresponding characteristic relaxation times. The mechanism of conductivity is affected by the concentration of MAALi, while the ionic conductivity of all samples increases by about 3-4 orders of magnitude upon introduction of Li^+ ions (~10^{-10} S/m). Furthermore, for the initial systems (SMAA) a process related to very local movements was observed and it was attributed to formation of hydrogen bonds between carboxylic groups. Finally, another mechanism was observed for the hybrid systems (SMAALi), and this was related to movement of carboxylate groups, which are rearranging to accommodate Li^+ ions.

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