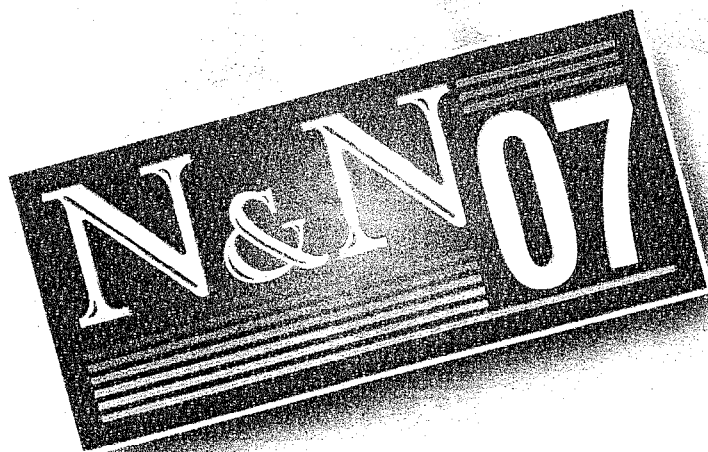




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ABSTRACT BOOK



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Induced Nanophase Ordering in Lithium Neutralized Ionic Block Copolymers

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Abstract: In recent years, interest has been focused on solid-state materials that exhibit enhanced ion transport properties. Solid polymer electrolytes constitute a class of materials of high promise for technological applications like in batteries, fuel cells, sensors and other electrochemical devices. 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.

In the present study, diblock 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 alters the phase state and contributes to ionic conductivity of these hybrid nanomaterials. The structure has been studied by small-angle X-Ray scattering (SAXS), differential scanning calorimetry (DSC) and infrared spectroscopy (IR), while the dynamics have been investigated by dielectric spectroscopy (DS).

Table 1 summarizes the molecular and morphological characteristics of the initial diblock copolymers and the resulting hybrid nanomaterials.

Table 1: Molecular and morphological characteristics of the block copolymers.

Sample	M_w	I	wt% in PS	f_{MMA} , f_{MAALI}	T_g (K)	Δc_p (J/gK)	Structure (SAXS)	d_{SAXS} (nm)	d_{MAALI} , R_{MAALI} (nm)
SMAA1	49900	1.06	84	0.13	373	0.30	spheres	30.5	8.8
SMAA1Li	45500	1.06	82	0.14	366	0.39	cylinders	31.7	6.3
SMAA2	34500	1.06	72	0.23	357	0.25	DIS	27.3	6.3
SMAA2Li	35400	1.06	70	0.25	362	0.25	lamellar	35.3	8.8
SMAA3	29200	1.06	57	0.35	361	0.20	DIS	30.5	11.3
SMAA3Li	30300	1.06	55	0.37	-	-	DIS	-	-

The copolymers' phase state was investigated by small-angle X-ray scattering (SAXS) and infrared (IR) spectroscopy. SAXS spectra indicate that introduction of Li^+ ions in the MMA phase results in an increased interaction parameter that favours the self-assembly by inducing a disorder-to-lamellar transition for SMAA2 and a cubic-to-cylinder transition for SMAA1. In addition, the ATR transmittance spectra of SMAA1 and of the ionic block copolymers resulting from the introduction of Li^+ ions reveal that the band at ca. 1699 cm^{-1} attributed to the asymmetric stretching, $\nu_{as}(CO_2^-)$, of carboxylic acid disappears upon formation of the Li^+ -polymer salt. The band at ca. 1548 cm^{-1} , attributed to the $\nu_{as}(CO_2^-)$ mode with the carboxylate anion being now coordinated to Li^+ ions, appears enhanced upon increasing Li^+ ion concentration and this demonstrates the formation of a Li^+ -polymer salt.

The dynamics of each system was investigated with dielectric measurements, which provide information on the kind of relaxation mechanisms and the characteristic relaxation times of each. The dc conductivity is in the range of 10^{-13} S/m . The Arrhenius plots for the relaxation times of the primary diblock copolymers and the ionic block copolymers resulted from Li^+ ion introduction revealed that: (i) the ionic conductivity increases by about 3 orders of magnitude ($\sim 10^{-10}\text{ S/m}$) and (ii) a new dynamic process with an Arrhenius temperature dependence related to motion of Li^+ ions coupled to the MMA segments.

The above results indicate that introduction of Li^+ ions in the MAA phase increases the interaction parameter and results in a stronger segregation. SMAA1 forms spheres but SMAA1Li forms cylinders of MAA1Li in a hexagonal lattice. SMAA2 is in the disordered phase while introduction of Li^+ ions produces a lamellar morphology. Both domain spacings increase by Li^+ ion introduction implying polymer chain stretching. As with the SMAA1, the dynamic investigation, apart from the increased ionic conductivity, revealed a new dielectrically active process associated with relaxation of Li^+ ions coupled to MMA segments.