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Kinetic modeling of anhydrous proton conduction in side chain liquid crystal polyacrylates

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ABSTRACT

Mesomorphic polyacrylates with different degree of sulfonation (DS) in side chains were synthesized by post polymerization functionalization. The sulfonated polymer exhibited thermotropic smectic A (S_A) and/or nematic (N) phases when DS was 0.2–0.4. The temperature-dependent anhydrous proton conductivities of the polymers depended on both ion exchange capacity (IEC) and phase type. A modified Arrhenius equation containing IEC and phase coefficient M simultaneously was proposed to model the conduction behavior. Least-squares regression analysis on the kinetic parameters quantitatively revealed proton conduction characteristics in different liquid crystal phases. The activation energies for proton transportation in the S_A , N, and isotropic states were 106, 95 and 44 kJ mol⁻¹, respectively. The inherent conductivities per unit IEC in the S_A , N, and isotropic states were 8.5×10^8 , 5.3×10^7 and 77 S cm⁻¹, respectively. The enhancement of anhydrous proton conduction in liquid crystal phases was ascribed to the increased conducting pathways induced by ordered molecular arrangements.

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Introduction

Materials exhibiting acceptable proton conductivities at moderate temperatures (100–200 °C) have attracted widespread interests due to the advantage in improving performance of electrochemical devices [1–4]. Great efforts have been made to develop conductors transporting protons through the vehicle or the hopping mechanism under anhydrous conditions [5–8]. The vehicle strategy is to employ ionic liquids instead of water as proton carriers in polymeric matrixes [9–12]. For example, perfluorinated sulfonic acid Nafion[®] membranes doped with 1,2,4-triazole exhibited proton conductivity of 0.1 S cm⁻¹ at 180 °C [9]. The hopping strategy makes use of protogenic groups to construct

continuous pathways for proton conduction [13]. Molecular self-assemblies including acid-base composites [14,15], comb-polymers [16], and supramolecular dimer [17] have been employed to induce regular arrangements of protogenic groups. For instance, benzotriazole or imidazole groups in amphiphilic styrenic comb-polymers formed lamellar or linear pathways by virtue of self-assembly. Anhydrous proton conductivity of the imidazole self-assembly reached 1×10^{-3} S cm⁻¹ at 200 °C, which was several orders of magnitude higher than that of the random architectures formed by similar imidazole molecules [16].

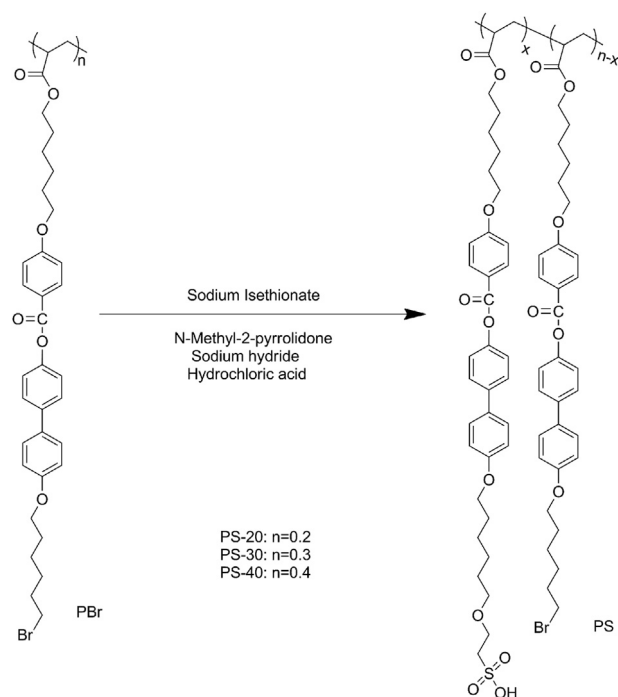
Thermotropic liquid crystals are promising candidates for anhydrous proton conductors due to the dynamic order. We confirmed that biphenyl-based sulfonic molecules exhibited proton conductivity of 1.24×10^{-2} S cm⁻¹ at 219 °C in the

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Scheme 1 – Synthetic pathway of the sulfonated polyacrylates.

smectic A (S_A) phase [18]. We have also reported proton conduction of partially sulfonated side chain liquid crystal polymers exhibiting S_A or nematic (N) phases [19,20]. The conductivity of the smectic polymer is one order of magnitude higher than that of a non-mesogenic sulfamide acid polymer with similar ion exchange capacity (IEC) [21]. In addition, anisotropic and enhanced conduction could be achieved by shearing the smectic polymer mechanically. These results suggested that the ordered liquid crystal assemblies had positive effect on anhydrous proton conduction. However, there is not a unified model yet to quantitatively describe dependence of proton conductivities on both IEC and liquid crystal phase.

There is a significant difference in molecular arrangements between S_A and N liquid crystal phases. N phase exhibits only long-range orientational order while S_A phase formed layer architectures in addition to orientational order. In order to characterize the effect of liquid crystal phase on anhydrous

proton conduction, we prepared sulfonated polyacrylates exhibiting S_A and/or N phases to evaluate conduction behavior of these mesomorphic polymers. A modified Arrhenius equation was proposed to describe anhydrous proton conduction in liquid crystal phases. Kinetic parameters such as activation energy (E_a) and phase coefficient (M) were derived by regression analysis of the measured proton conductivities. The change in kinetic parameters of the smectic and nematic polymers was attributed to molecular arrangement and mobility. The estimated kinetic parameters quantified the advantage of liquid crystal phase on anhydrous proton conduction for the first time and provided guidance for the developments of ordered proton conductors.

Experimental

Materials

In addition to the previously reported smectic sulfonated polyacrylates [19], we prepared polyacrylates with different degrees of sulfonation ($DS = 0.3$ and 0.4) by the post polymerization functionalization approach [20]. Sulfonic acid group was introduced to the terminal position of side chains by modifying poly [4'-(6-bromohexyloxy)-biphenyl-4-yl 4-((6-(acryloyloxy)hexyl)oxy) benzoate] with sodium isethionate through etherification reaction (Scheme 1). DS was adjusted by molar ratio between reactants (listed in Table 1).

Instrumentation

The ^1H NMR spectra were measured by using a Bruker AV II-400 spectrometer. The FT-IR spectra were obtained with the use of a NEXUS 670 FT-IR spectrometer. DSC measurements were performed by a TA modulated Netzsch DSC 204 F1. Thermogravimetric analyses (TGA) were carried out by a TA instrument Netzsch TGA 209C. The scanning of DSC and TGA were both with a rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen. Cross-polarizing optical microscopies of thin samples were performed using a Weitu XPL-30TF polarizing optical microscope (POM) equipped with a WT-3000 hot-stage. Elemental analyses (EA) were done by using a Euro EA3000 CHNS/O Elemental Analyzer. PH value was determined by using a Youke PHS-3C pH meter. XRD analysis were conducted on a Bruker AXS D8 Discovery diffractometer equipped with a Hi-Star 2D detector, using Cu- $K\alpha$ radiation filtered by cross-

Table 1 – DS and thermal behavior of the sulfonated polyacrylates.

Polymer	Molar ratio		DS	IECs/(meq/g)		Phase transition temperatures/ $^\circ\text{C}$	Decomposition temperature/ $^\circ\text{C}$	Residue In Fr/%
	PBr	Sodium isethionate		By titration	By EA			
PS-20	1	0.8	20	0.31	0.32	H ^b :G ^a 52 K ^a 145 S_A 215 I C ^b :I 199 S_A 139 K	306	88
PS-30	1	1	30	0.47	0.45	H:G 58 K 138 S_A 197 N 215 I C:I 208 N 192 S_A 125 K	273	89
PS-40	1	1.3	40	0.62	0.6	H:K 141 N 225 I C:I 216 N 134 K	276	87

^a G, glassy; K, crystal.

^b H, second heating scan; C, first cooling scan.

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