



Study on synthesis and physical properties of charged surface modifying macromolecules with different end-capping materials for membrane applications

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ABSTRACT

Polyol and end-capping agent were changed systematically when charged surface modifying macromolecules (cSMMs) were synthesized and characterized. Fourier transform infrared spectroscopy detected different degrees of hydrogen bonding interactions for different polyols and end-capping agents via shifting of absorption bands characteristic to the urethane group. Polyol of the lower molecular weight showed the stronger interaction and thus increased the cSMM's structural rigidity. The cSMM's rigidity increased from hydroxyl benzene sulfonate to hydroxyl propane sulfonate when poly(propylene glycol) was used as polyol. The effects of polyol and end-capping agent on the contact angle and water uptake were studied.

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1. Introduction

There have been many initiatives to modify membrane surfaces at the laboratory scale for various membrane applications. Most of the work has attempted to change the hydro-philicity/-phobicity of the membrane surface. The addition of a compatible modifier into the casting solution is an excellent option that can modify membrane surfaces using a single casting step. The Surface Modifying Macromolecules (SMMs) are polymers tailor-made to be compatible with the host polymer and end-grouped with either hydrophobic or hydrophilic tails [1]. During casting, SMMs preferably migrate to the membrane surface in order to minimize the total free energy of the system [2]. This migration then modifies the membrane surface to be either more hydrophilic or hydrophobic depending on hydro-philicity/-phobicity of SMMs added [3].

There are three types of SMMs that have been reported in the membrane literature: hydrophobic [4], hydrophilic [5], and charged SMM. Among those SMMs, the charged SMM (cSMM) was synthesized to be incorporated in membranes for fuel cell applications [6,7]. The SMM synthesis consists of the following two steps: (I) reacting diisocyanate with polyol to form polyurethane prepolymer, and (II) end-capping of prepolymer with chemicals

with appropriate functional groups to endow hydrophobic, hydrophilic or charged properties to the SMMs. Until now, the main diisocyanates used for SMM preparation were methylene bis-*p*-phenyl isocyanate (methylene diphenyl diisocyanate, MDI) and hexamethylene diisocyanate (HDI) [8–12]. The polyols employed were polypropylene diol (PPO) [8–11], polycaprolactone diol (PCL) [9], di-ethylene glycol (DEG) and hydroxyl diphenyl sulfone (DPS) [10,11], and polytetramethylene oxide (PTMO) [11]. As for the end group, hydrophobic, hydrophilic and charged SMM were made by end-capping with fluoro-alcohol, poly(ethylene glycol) (PEG) and hydroxyl benzene sulfonate (HBS), respectively.

When SMMs were blended with a base polymer in the casting dope, changes in several surface characteristics of prepared membranes were recognized [13,14]. When a hydrophobic SMM was blended into the polyethersulfone (PES) film, the surface contact angle (CA) was significantly increased [15]. On the other hand, when a hydrophilic SMM was incorporated into the PES ultrafiltration membrane, Rana et al. observed a decrease in the static CA with increasing SMM concentration [5]. In addition, the use of charged SMM also reduced the surface CA [7]. Hence, the change in CA is an early indication of the migration of SMM to the membrane surface. Membrane evaporation time prior to gelation had a strong effect on SMM migration. Using newly synthesized hydrophobic SMMs, Suk et al. showed that the CA increased with an increase in solvent evaporation time. They also found that at least 3 min were necessary to cause a significant increase in the CA [15]. However, in some cases, the membrane CA did not

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significantly increase even when a measurable increase in the fluorine content was noticed at the surface of the membrane.

The reported average molecular weight of SMM was primarily determined by the size of the prepolymer generated in the first step, and not by the size of the fluorine-containing [15] or other end-capping groups. However, a general trend of decreasing fluorine content with increasing molecular weight was observed possibly due to the reaction of unreacted hydroxyl groups from the polyol with the diisocyanate end-capped prepolymer during the fluoro-alcohol capping procedure [16].

Differential scanning calorimetry (DSC) monitoring the change in enthalpy of SMM film was used to study thermal characterization of SMMs. It is reported by Tang et al. that glass transition temperature (T_g) was highly dependent on the polyol used [12]. For example, Tang et al. reported that the SMM containing a PPO segment showed a higher T_g value than those containing PTMO, which was further supported by our experiments [7]. Moreover, Qtaishat et al. showed that the reactant mole ratio, the reactant concentration, and the type of fluoro-alcohol did not show any correlation with the variation in T_g [8].

The objective of this work is to elucidate the relationship between the chemical structure and the physicochemical properties of charged surface modifying macromolecules (cSMMs). For this purpose, cSMMs are systematically synthesized and subjected to characterization by FTIR, DSC, and thermo-gravimetric analysis (TGA). Moreover, cSMMs are blended into sulfonated poly(ether ether ketone) (SPEEK) to prepare SPEEK/cSMM blend membranes and CA and water uptake of the latter blend membranes are measured. Since it was revealed in our earlier work that CA and water uptake values are closely related to conductivity and methanol diffusivity of the cSMM blended membranes, the information acquired by this work will contribute significantly to the rational design of cSMMs for membrane performance enhancement in direct methanol fuel cell applications.

2. Experimental

2.1. Materials

The chemicals used in the study are presented in Table 1. In this study, methylene diisocyanate (MDI) was first reacted with four types of polyols (soft segment): diethylene glycol (DEG),

Table 2
Name of the various cSMMs.

cSMM	Structural units	End capping groups
DEG-HBS	MDI-DEG-HBS	Aromatic sulfonate
PEG200-HBS	MDI-PEG200-HBS	Aromatic sulfonate
PEG400-HBS	MDI-PEG400-HBS	Aromatic sulfonate
PPG-HBS	MDI-PPG-HBS	Aromatic sulfonate
DEG-HPS	MDI-DEG-HPS	Aliphatic sulfonate
PPG-HPS	MDI-PPG-HPS	Aliphatic sulfonate

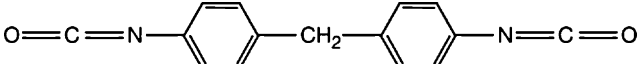
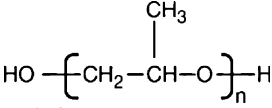
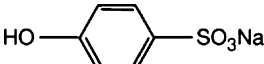
poly(ethylene glycol) (PEG) of typical number average molecular weight (M_n) 200 Da (PEG200), and PEG of M_n 400 Da (PEG400), and poly(propylene glycol) (PPG) of M_n 425 Da. The pre-polymers were then terminated with the addition of sodium salt of hydroxybenzene sulfonate (HBS) and sodium salt of hydroxypropane sulfonate (HPS), except for PEG200 and PEG400 which were terminated only with HBS. All formulations were based on stoichiometry molar ratio 3:2:2. The charged SMMs so synthesized are summarized in Table 2 with the codes given to the SMMs. The details of the synthesis are as follows.

2.2. Synthesis of charged surface modifying macromolecules

The charged surface modifying macromolecule, cSMM, end-capped with HBS or HPS, was synthesized using a two-step solution polymerization method. The initial step involved the reaction of MDI with di-ol (DEG, PEG or PPG) in a common solvent of N,N-dimethyl acetamide (DMAC), which resulted in a urethane prepolymer solution. The prepolymer is a segment-blocked urethane oligomer having both ends capped with isocyanate. The reaction was then terminated by the addition of HBS or HPS, resulting in a solution of sulfonated surface modifying macromolecules. The scheme of the chemical reaction for the synthesis of cSMMs is shown in Fig. 1(A).

The effect of moisture was eliminated by drying all glassware overnight at 100 °C, and the polymerization reaction and end-capping were performed in a controlled atmosphere of purified nitrogen inside a reaction vessel. A detailed procedure is given for an example of DEG-HBS synthesis: a solution of 0.03 mol (7.5 g) MDI in 50 mL of degassed DMAC was loaded in a 1 L Pyrex round bottom flask. Then, a solution of 0.02 mol (2.122 g) degassed DEG

Table 1
Chemicals used for the synthesis of cSMMs.

Abbreviation	Chemical name	Chemical structure
MDI	Methylene diisocyanate	 Molecular weight 250 Da
<i>Soft segment, HO-R-OH</i> DEG	Diethylene glycol	$\text{HO}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{OH}$ Molecular weight 106 Da
PEG200	Poly(ethylene glycol)	$\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$ Typical M_n 200 and 400 Da
PEG400		
PPG	Poly(propylene glycol)	 Typical M_n 425 Da
<i>Ends capping, HO-R'</i> HBS	Hydroxybenzene sulfonate, sodium salt	 Molecular weight 196.16 Da
HPS	Hydroxypropane sulfonate, sodium salt	$\text{HO}-(\text{CH}_2)_3-\text{SO}_3\text{Na}$ Molecular weight 162.14 Da

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