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Sulfonation of Polyethersulfone by Chlorosulfonic Acid

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Summary

Modification of polyethersulfone (PES) by sulfonation with chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent was carried out. Factors affecting the sulfonation reaction were studied, and reaction conditions for the preparation of sulfonated PES (SPES) with different degrees of sulfonation were determined. The presence of sulfonic acid groups in SPES was confirmed by FTIR and NMR spectroscopy. Thermal analysis of the SPES samples revealed higher glass transition temperatures and lower decomposition temperatures with respect to the PES.

Introduction

Polyethersulfone (PES) is a high-performance engineering thermoplastic consisting of repeated phenyl groups, and ether and sulfone groups with good transparency, flame resistance and low smoke-emittance. The structure of the polymer is shown in Figure1. Broad chemical resistance, hydrolysis resistance, constant use temperature of 180°C and high mechanical strength are the key properties due to the diaryl sulfone group present in the polymer with ether linkages providing chain flexibility and the whole aromatic structure. Its applications span the electronics, automotive, consumer goods, medical and membrane industries.

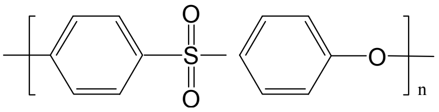


Figure 1. The structure of PES

Although PES has excellent physical performance characteristic, the hydrophobicity of this material has limited its application sometimes. Sulfonation is a frequently used means for polymer modification in order to improve their expected membrane properties such as better hydrophilicity, higher water flux, improved permeability and proton conductivity [1-4].

Sulfonation is an electrophilic reaction affected by both the electrophilicity of the sulfonating agent and the electron-donating characteristic of the polymer. However, polyethersulfone is notoriously difficult to sulfonate due to the electron withdrawing effect of the sulfone linkages that deactivate the adjacent aromatic rings for electrophilic substitution [5,6]. The sulfonation of PES has been described in literature with different sulfonating agents and solvents: SO_3/CH_2Cl_2 [5,7], $ClSO_3H/CH_2Cl_2$ [8], SO_3-triethylphosphate (TEP) /CH_2Cl_2 [9], oleum /concentrated sulfuric acid [10].

Every method for sulfonation of PES has its advantages and disadvantages [11]. In this study, the chosen sulfonating agent was chlorosulfonic acid. The choice of chlorosulfonic acid was due to its simplicity and adaptability. For instance, SO_3 and SO_3 complexes require special handling and/or preparation. The sulfonation of pre-dissolved polymers by chlorosulfonic acid allows for a homogeneous electrophilic substitution. Furthermore, no additional preparation is required for chlorosulfonic acid use [12]. Several researchers have investigated the use of chlorosulfonic acid as a sulfonating agent for some aromatic polymers [1,4,12-16]. As discussed earlier, using chlorosulfonic acid readily causes side reactions occurring, including chain cleavage, branching and/or cross-linking [6]. But, if the reaction is carried out under controlled condition, side reactions could be suppressed to a large extent [1].

In this work, PES was sulfonated with chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent, which few studies were previously conducted in detail [17]. The present paper deals with the influence of the conditions of sulfonation on the degree of sulfonation (DS). A series of SPES samples with different DSs were obtained. Thermal properties and solubilities of SPES samples were also determined.

Experimental

Materials

PES (Ultrason E6020P, M_w=58,000Da) was kindly provided by BASF. All other chemicals obtained commercially were reagent-grade and used as received.

Sulfonation Reaction

The following procedure was used to prepare the sulfonated polyethersulfone (SPES) samples. 20g PES were added to 100ml concentrated sulfuric acid (98%) in a three-neck reaction flask, and dissolved by stirring at room temperature to form homogeneous solution. Chlorosulfonic acid was transferred into a dropper, and then gradually and slowly added to the PES solution while stirring the solution at 800rpm at a fixed temperature. The resulting reaction mixture was stirred for some additional hours. After a determined reaction time, the mixture was gradually precipitated into ice-cold deionized water under agitation, and the resulting precipitate was recovered by filtration and washed with deionized water until the pH value was approximately 6~7.

Characterization and Measurements

FTIR spectra were recorded with a Perkin-Elmer Spectrum One FTIR spectrometer in the wavenumber range 600-4000cm^{-1}. Both ^1H NMR and ^{13}C NMR spectra were obtained using an Oxford 600 MHz spectrometer with DMSO-d_6 as solvent and TMS as the internal standard. The inherent viscosities ($[\eta]_{inh}$) were determined with an Ubbelohde viscometer in 0.5g/dL N-methyl-2-pyrrolidone (NMP) solutions of polymers at 30.0±0.1°C.

The DS was mainly measured by titration. A sample of precisely weighed SPES was solved in N,N-dimethylformamide (DMF) solution. The released amount of H^+ was then determined by titration with a standard NaOH solution using phenolphthalein as indicator.

Thermogravimetric analysis (TGA) was obtained on a Perkin-Elmer TGA7 instrument under nitrogen at a heating rate of 20°C/min from room temperature to 600°C. Differential scanning calorimetry (DSC) was measured with a Perkin-Elmer DSC7 instrument under nitrogen at a heating rate of 20°C/min from room temperature to 300°C. The DSC curves were taken from the second heating scan after first run to 160°C to eliminate heating history.

Results and Discussion

Sulfonation Reaction

In general, the DS obtained for sulfonation of polymers depends on several factors, including the strength of sulfonating agent, the sulfonating solvent, reaction time, reaction temperature, and concentration of polymer [13,18]. For determined sulfonating agent, and fixed quantity of PES and solvent, sulfonation was carried out by varying in parameters such as the quantity of chlorosulfonic acid (CSA), temperature and time of reaction. We groped the reaction conditions for a long time, then selected suitable parameters. The achieved DSs varied from very low to high enough that can dissolve in the water. The reaction conditions and the DSs determined via both titration and ^1H NMR are presented in Table 1.

Table 1. Dependence of DS on the reaction conditions

PES/CSA (g/ml)	Reaction temperature (°C)	Reaction time (h)	DS by		$[\eta]_{inh}$* (dL/g)
			Titration	^1H NMR	
20/40	10	10	14.14	12.58	0.674
20/45	10	10	16.43	–	0.680
20/50	0	10	10.50	–	0.662
20/50	10	10	26.26	23.75	0.715
20/50	20	10	23.90	–	0.705
20/50	30	10	37.30	–	0.577
20/60	10	7	14.01	12.57	0.669
20/60	10	8	23.73	–	0.699
20/60	10	9	29.47	30.77	0.727
20/60	10	10	41.22	43.72	0.736

*Measured at 30°C in NMP; the value of PES: 0.621

From Table 1, it can be seen that under fixed reaction conditions of 50ml chlorosulfonic acid and 10h, increased temperature led to a higher DS except at

20°C. This was probably due to PES deactivated by concentrated sulfuric acid at about 20°C. Higher temperature (30°C) led higher DS but also readily resulted in chain scission of PES. It's suitable to react at lower temperature such as 10°C. Under the same reaction conditions of fixed temperature (10°C) and fixed reaction time(10h), DS increases with the quantity of chlorosulfonic acid. Also, under the same reaction conditions of fixed temperature (10°C) and fixed chlorosulfonic acid quantity, DS increases with reaction time.

Viscosity measurements were conducted to detect possible chain scission during the electrophilic substitution. As shown in Table 1, at higher reaction temperature, the inherent viscosity of SPES reduces significantly suggesting that the polymer chain is degraded during sulfonation. But at lower reaction temperature, the inherent viscosities of SPES increased with increasing DS. No obvious signs of chain scission or high extents of branching were observed, consistent with increasing inherent viscosity with increasing DS. This was further evident for the readily soluble products. The increase in intrinsic was attributed to the increase in intermolecular H-bonding forces of the sulfonated polymer chain relative to the unmodified polymer chain [12, 18,19].

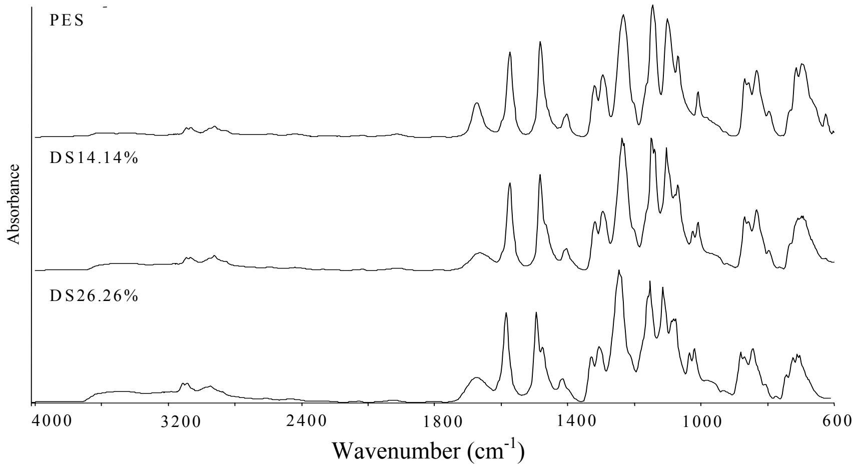


Figure 2. The FTIR spectra of PES and SPES

FTIR

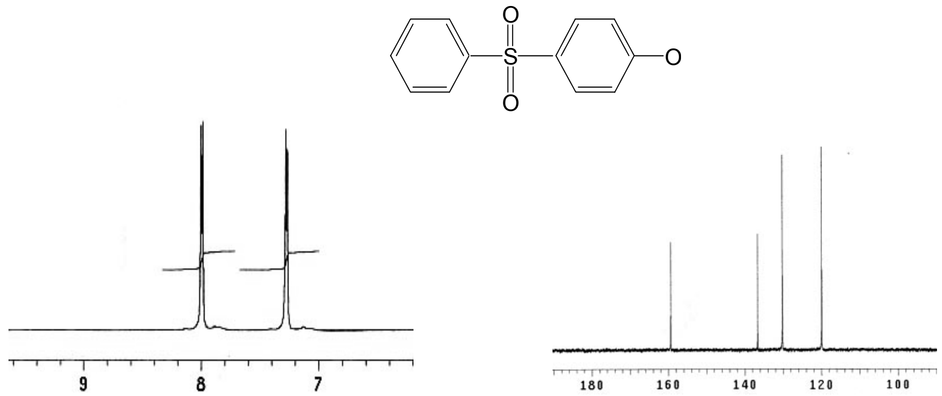
Successful introduction of the sulfonate groups was confirmed by the FTIR spectra (Figure 2). The major difference in the figure is the presence of an absorbance at about 1025 cm^{-1} in the SPES, which is attributed to the symmetrical stretch of the sulfonate groups [7,8,20,21]. The characteristic absorption bands increased with DS. The asymmetric stretch is believed to be near 1180 cm^{-1} but not readily observable due to the presence of other overlapping absorbances in that area [8,21].

In fact, the regular changes in the characteristic absorption peak at ~1025 cm^{-1} compared with an internal standard could be used to quantitatively study the DS [20,22], as shown in Table 2, where A_{1025} and A_{1580} are the absorbance values at ~1025 and ~1580 cm^{-1} respectively.

Table 2. FTIR wavenumber and absorbance value at ~1025cm^{-1}

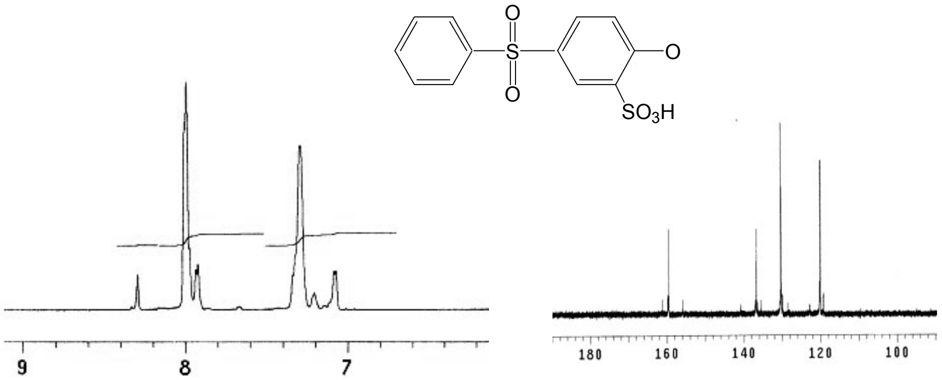
DS (%)	Wavenumber at ~1025cm^{1}	A_{1025}	A_{1580}	A_{1025}/A_{1580}
14.01	1025.65	0.48	1.02	0.47
23.73	1024.80	0.65	0.97	0.63
29.47	1024.10	0.71	0.93	0.76
41.22	1023.63	0.77	0.95	0.81

Moreover, the absorption peak at ~1025cm^{-1} might be used to match interactions that involve the SO_3H^- group. In general, all absorption bands, either sulfone or sulfonate groups, might be considered as sensitive to interactions with their environment. To get an inside on these specfic interactions, we have focused on the absorption peak at ~1025 cm^{-1}. In table 2, a slight red shift of the sulfonate symmetric stretch takes place at a high sulfonation degree. This indicates that sulfonate groups most probably interact with the main chain sulfone groups [23,24].



Chemical Shift (ppm)

Figure 3. ^{1}H (left) and ^{13}C (right) NMR spectra of PES



Chemical Shift (ppm)

Figure 4. ^{1}H (left) and ^{13}C(right) NMR spectra of SPES

NMR

In order to determine the sulfonation site, PES and SPES were characterized by both ^{1}H NMR and ^{13}C NMR spectroscopy (Figure 3 and 4). The ^{1}H NMR spectra of PES and SPES resembled those of PES and SPES published. The presence of a sulfonic acid group caused a significant down-field shift from 7.27 to 8.30 ppm of the hydrogen located in the *o*-position to sulfonate group which could attribute to two electron-withdrawing groups of sulfone and sulfonate. By ^{1}H NMR, DS can also be derived with a method described in an article by Noshay and Robeson for sulfonated polysulfone, as shown in Table 1 [7,8].

Compared to PES spectrum, some additional signals were found in ^{13}C NMR spectrum of SPES, this was due to sulfonic acid groups bonded to the benzene rings affecting the chemical shifts of the neighbor carbon atoms.

Thermal Properties

The thermal stabilities of the PES and SPES were studied by TGA. In Figure 5,TG analysis results are reported for SPES samples and compared with PES. The parent PES is a highly thermostable polymer, of which the 5wt% loss temperature is above 500°C and there is only one weight loss step that is ascribed to the decomposition of polymer main chain. For the SPESs, three transitions of loss in weight in three separate temperature ranges can be distinguished in the figure. Similar observation was made for other sulfonated high performance polymers [25-28]. The first step around 100°C is related to the loss of the absorbed water. The second, between 350°C to 450°C, can be attributed to the decomposition of the $-SO_3H$ groups. The third thermal degradation of SPES at about 490°C is assigned to the degradation of the polymer main chain. Figure 5 also shows that SPESs with higher DS lose weight more quickly than those with lower DS in the second step.

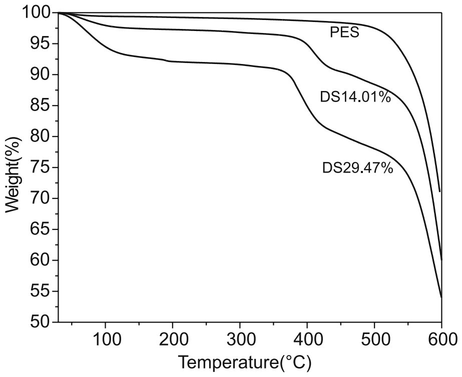


Figure 5. TGA traces of PES and SPES

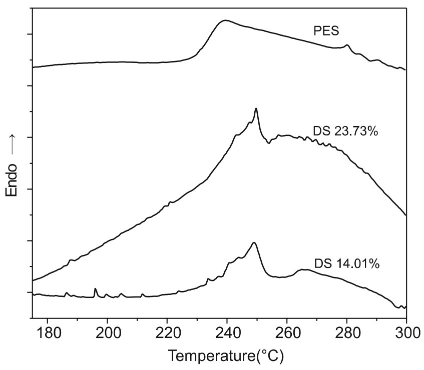


Figure 6. DSC traces of PES and SPES

As shown in Figure 6, DSC analysis reveals higher glass transition temperature (T_g) for SPES samples with respect to PES sample, although T_g values change with DS. The introduction of $-SO_3H$ groups into polymer chains led to increasing in T_g values because of the increased intermolecular ionic interactions [26].

Solubility of SPES

Solubilities of PES and SPES were tested and the results are listed in Table 3. It shows that the solubilities of polymers are different before and after sulfonation. PES is soluble in selected polar aprotic solvents and in chlorinated solvents such as chloroform and dichloromethane. However, SPES with higher DS can dissolve in the water, methanol and ethanol, reflecting the more ionic nature of the polymer. Introduction of -SO_3H groups into PES causes an increase of solubility for high polarity solvents and a reduction of solubility for chlorinated solvents [1,18,25].

Table 3. Solubilities of PES and SPES

Solvent	PES	DS14.01%	DS23.73%	DS29.47%	DS41.22%
N,N-Dimethylformamide	+	+	+	+	+
N,N-Dimethylacetamide	+	+	+	+	+
N-methyl-2-pyrrolidone	+	+	+	+	+
Dimethyl sulfoxide	+	+	+	+	+
Chloroform	+	△	−	−	−
Dichloromethane	+	△	−	−	−
1,2-Dichloroethane	△	−	−	−	−
Water	−	−	−	−	±
Methanol	−	−	−	−	+
Ethanol	−	−	△	+	+
Acetone	−	−	−	△	△
Tetrahydrofuran	−	−	−	−	△
Diethylether	−	−	−	−	−
Hexane	−	−	−	−	−

Solubility: (+) soluble at room temperature, (−) insoluble, (±) soluble at high temperature, (Δ) swollen.

Conclusions

In this study, sulfonated PES was successfully prepared using chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent. Under suitable reaction conditions, it was possible to obtain polymers without evident chain scission. The degree of sulfonation was controlled, to some extent, by varying the quantity of chlorosulfonic acid to the quantity of polymer or reaction time at lower reaction temperature. The structure of SPES was confirmed by FTIR and NMR spectroscopy. As the DS of SPES increased, glass transition temperatures increased and decomposition temperatures decreased. Introduction of -SO_3H groups into PES causes an increase of solubility for high polarity solvents and a reduction of solubility for chlorinated solvents.

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