

Sulfonation of Polyetheretherketone by Chlorosulfuric Acid

FRANCESCO TROTTA,¹ ENRICO DRIOLI,² G. MORAGLIO,¹ E. BAIMA POMA¹

¹ Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali dell'Università, Via Pietro Giuria 7, 10125 Torino, Italy

² Dipartimento di Ingegneria Chimica e Materiali, Università della Calabria, 87030 Arcavacata di Rende (Cosenza), Italy

Received 5 October 1997; accepted 15 February 1998

ABSTRACT: Sulfonated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (PEEK-WC) with various degrees of substitution was obtained by reaction of polyetheretherketone with neat chlorosulfuric acid. Highly sulfonated PEEK-WC was freely soluble in cold water. By working under suitable reaction conditions, no degradation of the polymeric chain was detected. The modified PEEK-WC was able to form asymmetric membranes. The expected chlorosulfonated derivatives were never achieved. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 477–482, 1998

Key words: polyetheretherketone; membrane; sulfonation

INTRODUCTION

Polyetheretherketones [poly(oxa-*p*-phenylene-oxa-*p*-phenylene-oxy-*p*-phenylene) or PEEK] are highly crystalline polymers having very good thermal, chemical, and mechanical stability. These properties are useful in many industrial applications.¹

Due to the strong intermolecular interaction among the polymeric chains, they are practically insoluble in almost all solvents. As a consequence, PEEKs are not easily modified through the common reactions of organic chemistry and they are not able to form membranes by phase inversion.

The sulfonation on these polymers was carried out to increase their hydrophilicity and permeability.² Sulfonation of classical PEEK occurs without detectable degradation by simply dissolving the polymer in concentrated sulfuric acid at room temperature in the presence of a small amount of water to prevent the formation of crosslinking due to the formation of sulfonic

bridges among the chains. We point out that this reaction occurs easily because of the presence of the activated aromatic rings (ether linkage).

However, when activated aromatic rings are not present, such as in polyetherketone (PEK) (which has a highly inactive carbonyl group on all aromatic rings), then aromatic electrophilic substitution does not occur at all and the simple dissolution in concentrated sulfuric acid does not lead to any sulfonation. A longer reaction time, higher reaction temperature, and/or stronger sulfonating agents are needed³ for sulfonation.

Recently, the synthesis of a new kind of PEEK was reported, poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (PEEK-WC), that was obtained by condensation of phenolphthaleine with 4,4'-dichlorobenzophenone. The structure⁴ is shown in Figure 1.

Unlike classical PEEK, PEEK-WC is amorphous. As a consequence, it is soluble in a few aprotic polar solvents and in some chlorohydrocarbon ones; thus, PEEK-WC is able to form membranes that are particularly useful in some applications. It can also be modified to obtain more efficient membranes for special applications.⁵

Correspondence to: F. Trotta (trotta@silver.ch.unito.it).

Journal of Applied Polymer Science, Vol. 70, 477–482 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/030477-06

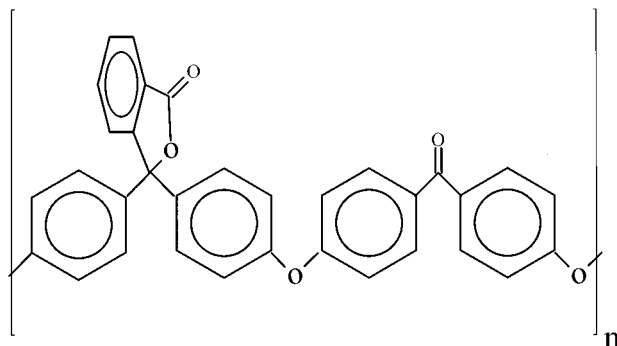


Figure 1 The structure of PEEK-WC.

Lately the synthesis of sulfonated PEEK-WC has been reported by the reaction with 98% sulfuric acid in several experimental conditions. However, the top degree of substitution obtained was always below 0.8 sulfonic groups per repeating unit. Moreover, with this latter degree of substitution, the degradation of the polymeric chain was observed with consequent wear and tear of the obtained membranes.⁶

In this work we used chlorosulfuric acid as a powerful sulfonating agent. Nevertheless, it was possible to obtain a polymer with a high degree of substitution without appreciable degradation. The synthesized hydrophilic polymer was able to form a membrane by the phase inversion technique.

EXPERIMENTAL

PEEK-WC was received from Chan Chung Institute of Applied Chemistry (Academia Sinica, China). It was Soxhlet extracted with methanol to completely remove the unreacted phenolphthaleine and oven dried before use. Chlorosulfuric acid and other solvents and reagents were purchased from Aldrich and used without further purification.

The IR spectra were found with a Perkin-Elmer 1710 FTIR spectrophotometer. The viscosity measurements were carried out on an Ubbelohde-type viscosimeter by using freshly distilled DMF, water, or *n*-butanol at 25°C. The thermogravimetric analyses were recorded on a Du Pont 951 apparatus. DSC analyses were carried out on a Du Pont 2100 apparatus. The elemental analyses were recorded on a Carlo Erba model 1106 elemental analyzer, and the microanalysis energy dispersive spectroscopy (EDS) was carried out on an SEM spectrom-

eter with ISIS software. Two different synthesis procedures were followed.

PEEK-WC with High Degree of Sulfonation and Water Solubility

In a typical experiment, 1.0 g of PEEK-WC powder was carefully added to 20 mL of chlorosulfuric acid. The mixture was magnetically stirred for 1.5 h at room temperature. Once the reaction was complete, the mixture was poured into a large excess of crushed ice. The precipitate was recovered by filtration, dissolved in deionized water, and neutralized with NaOH. The solution was ultrafiltered on an Amicon stirred cell by using a membrane having a cutoff of 3000 Da to remove all the inorganic salts. The solution was freeze-dried and the product stored in a desiccator.

The acid form of the sulfonated polymer was obtained by dissolving the product in water and reprecipitating by concentrated HCl. The excess of hydrochloric acid was removed under a vacuum.

PEEK-WC with Low Degree of Sulfonation and Water Insolubility

In a typical experiment, 20 mL of chlorosulfuric acid was placed in a round bottom flask and refrigerated in a crushed ice bath. Then 1.0 g of powdered PEEK-WC was added and the mixture stirred for 0.5–4 h. The mixture was then added to a large excess of crushed ice. The precipitate was recovered and washed with deionized water many times to remove excess acids. Finally the white precipitate was recovered, oven dried, and stored in a desiccator.

RESULTS AND DISCUSSION

Chlorosulfuric acid is a very strong acid, containing a weak sulfur–chlorine bond, that is widely used as a powerful sulfonating agent⁷:



However, it is well known that in the presence of excess acid, sulfochlorination occurs and sulfonyl chlorides are found:



In this work chlorosulfuric acid was always used in a very large excess (up to a 140-fold molar excess) with respect to the PEEK-WC; thus, sulfonyl chloride was the expected derivative. Sulfochlorinated materials generally have poor water solubility, but we found that the product obtained after the reaction of PEEK-WC with an excess of chlorosulfuric acid at room temperature was a highly water soluble polymer. In addition, this polymer was easily precipitated from its water solution simply by lowering the pH (<1.0) with concentrated hydrochloric acid. This fact could be explained by keeping in mind the acid–base equilibrium:



This latter equilibrium is clearly shifted to the right because sulfonic acid is a strong acid and the polymer becomes water soluble. However, at very low pH (<1.0), the molar concentration of H^+ was sufficient to shift the equilibrium to the left and the uncharged polymer became water insoluble. We suppose that the first step of this reaction for this particular polymer should be very fast, as expected. Because chlorosulfuric acid is a poor solvent for sulfonated PEEK-WC, once the sulfonation occurred, the acid environment of the solution forced the polymeric chain to curl up, preventing the second step of the reaction (i.e., the chlorosulfonation).

The reaction between PEEK-WC and chlorosulfuric acid proceeds very fast even at room temperature. Elemental analysis and microanalysis EDS of the product showed a large sulfur content, in accordance with the high degree of substitution (about three sulfuric groups per repeating unit) obtained. Rather surprisingly, trituration of sulfonated PEEK-WC leads to a lower degree of substitution. This fact could be ascribed to the inaccessibility of a part of the SO_3H group of the polymeric chain.

The introduction of several SO_3H groups per repeating unit in the PEEK-WC chain leads to a large modification of its solubility. Table I reports the behavior of PEEK-WC- SO_3H in some common solvents. The very high degree of substitution leads to a particularly hydrophilic macromolecule that was also readily soluble in cold water.

Besides water, PEEK-WC- SO_3H is also soluble in DMF, DMSO, and even in *n*-butanol. On the contrary, it is insoluble in chlorohydrocarbons and in hydrocarbon solvents.

Table I Solubility of Sulfonated PEEK-WC in Several Solvents at Room Temperature

| Solvent | Solubility |
|------------------------|------------|
| H_2O | + |
| DMF | + |
| DMSO | + |
| THF | – |
| CH_3OH | + |
| Diethyl ether | – |
| Ethanol | + |
| CHCl_3 | – |
| <i>n</i> -Pentane | – |
| <i>n</i> -Butanol | + |

The degree of substitution was 2.7.

Moreover, the elemental analysis and microanalysis EDS performed on the products showed no chlorine content. This fact obviously agrees with the sulfonation reaction, but it is incompatible with chlorosulfonation.

Further confirmations were derived from viscosity measurements. These were accomplished in three different solvents: water, DMF, and *n*-butanol. The data obtained from the three sets of experiments and treated with the Huggins equation are reported in Figure 2(a). As was expected from the structure of sulfonated PEEK-WC, a typical polyelectrolyte trend was shown.⁸ In fact, because polyelectrolytes have great charge density that lowers the polymer concentration, an increasing in the reduced viscosity was observed. This is due to the negative charges located along the polymeric chains that repulsed each other in solution, inducing the chain extension. The higher the charge density and degree of ionization, the more marked the phenomenon.

The viscosity data reported in Figure 2(a) show that water is the best solvent for sulfonated PEEK-WC because, as predicted, it is the solvent that favors the deprotonation to a great extent. However, *n*-butanol is a bad solvent that produces the formation of an aggregate.

By processing the reported data with the Fuoss–Strauss relation⁸ and plotting the reciprocal of the reduced viscosity versus the square root of the concentration, the value of the intrinsic viscosity was readily obtained. In any case, a degradation of the polymer was never observed. In fact, as reported in Figure 2(b), the viscosity of sulfonated PEEK-WC is even greater than the parent polymer in accordance with the reaction. In actuality, the SO_3H groups grafted on the chain were

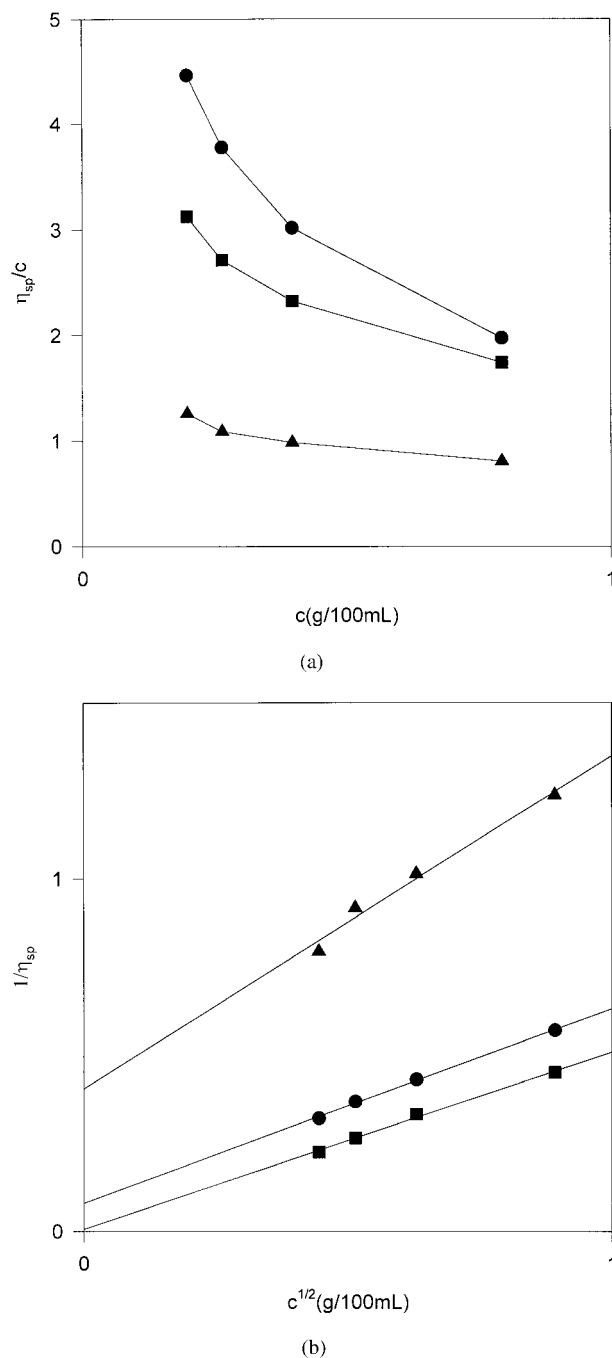


Figure 2 (a) The viscosity measures of PEEK-WC in (●) *n*-butanol, (■) DMF, and (▲) water at 25°C. (b) Fuoss–Strauss plot for PEEK-WC solution in (▲) *n*-butanol, (●) DMF, and (■) water at 25°C.

highly polar and in interacting with each other were able to stretch the polymeric chain in the solvents tested, leading to an enhancement of the viscosity.

Contrary to the research for sulfonation carried out with sulfuric acid at relatively high tem-

perature, we never found a lowering of the reduced viscosity of PEEK-WC-SO₃H; this is evidence of the substantial stability of the polymeric chain under our reaction conditions.⁶

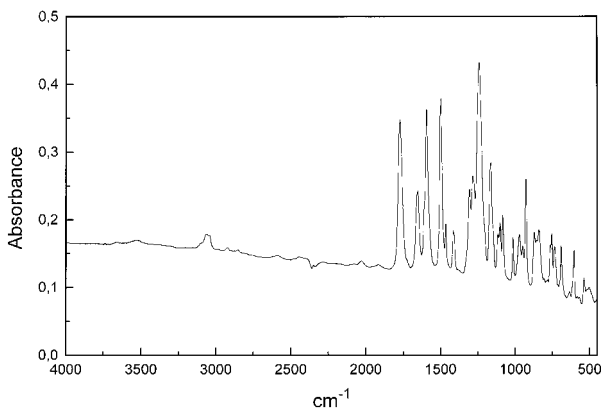
On the other hand, the high reactivity of chlorosulfuric acid makes it difficult to control the degree of substitution. Indeed, at room temperature the simple reduction of the reaction time did not give any appreciable lowering of the degree of substitution and the product obtained was still water soluble. Better results are achieved by working at a lower temperature.

Working at 0°C for 30 min, PEEK-WC with a low degree of sulfonation was obtained (about 0.3 sulfonic groups per repeating unit). These derivatives are insoluble in water and in chlorinated solvents, but they are easily dissolved in polar aprotic solvents such as DMF and DMSO. The higher the reaction temperature, the higher the degree of substitution. At 70°C highly substituted polymers were obtained. These showed bad mechanical properties and were unable to form stable membranes; thus, they were not studied and characterized any further.

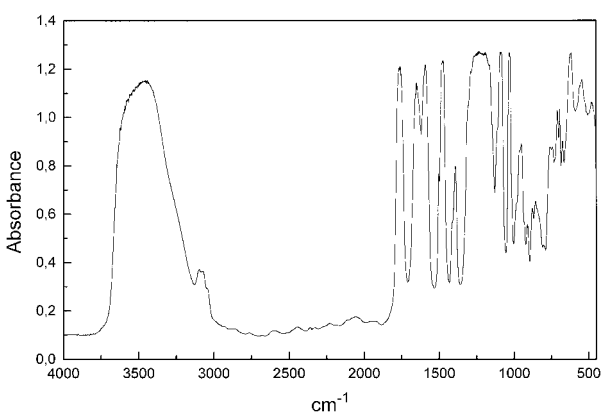
The sulfonation reaction can be easily followed by IR spectroscopy. Figure 3 shows a typical FTIR spectrum of the parent PEEK-WC and its highly sulfonated derivative. In addition to the predictable signals due to the stretching of the hydroxyls of the SO₃H group⁹ at 3400 cm⁻¹, the reaction is better following the behavior of the signal at 1500 cm⁻¹ related to the aromatic ring substituted in the 1,4 position. Grafting the aromatic ring with a further substitution induces the formation of a new absorption³ at 1475 cm⁻¹. Obviously, by increasing the degree of sulfonation, the latter will trend to almost completely supersede the former. At the moment we are trying to produce calibration curves by simultaneously performing the corresponding elemental analysis and FTIR spectra.

Thermogravimetric analysis (TGA) and DSC were performed. It is well known that the parent PEEK-WC is a highly thermostable polymer. Figure 4 shows the TGA of the sulfonated PEEK-WC. As can be easily noted, the first loss in weight occurs at about 100°C, which is due to the loss of the adsorbed water. A second loss in weight only occurs at about 400°C and could be ascribed to the decomposition of the SO₃H group. The flex point at about 450°C is probably due to the progressive breakage of the C—C bond.

From the DSC analysis reported in Figure 5, it is easy to see that the sulfonated PEEK-WC does



(a)



(b)

Figure 3 (a) The FTIR spectrum of PEEK-WC of a cast film from CH_2Cl_2 . (b) The FTIR spectrum of sulfonated PEEK-WC of a cast film from water.

not reach the glass transition temperature before its decomposition.

The reported thermoanalysis for the sulfonated PEEK-WC shows almost the same stability observed for the parent PEEK-WC.

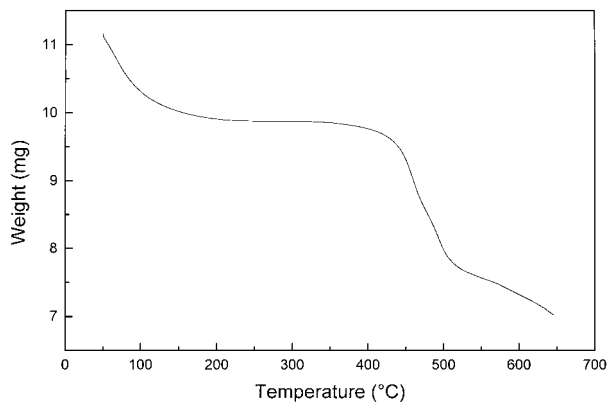


Figure 4 The TGA of sulfonated PEEK-WC under nitrogen flow.

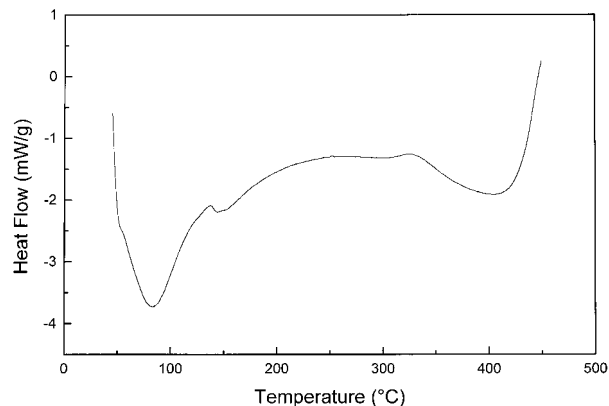


Figure 5 DSC of sulfonated PEEK-WC under nitrogen flow.

Moreover, hydrosoluble sulfonated PEEK-WC can interact with several cations of inorganic salts to give the corresponding sulfonate. The modified polymer is completely precipitated with aqueous solutions of FeCl_3 and CaCl_2 . The other salts seem to be less suitable. The PEEK-WC- SO_3H precipitated by adding the CuCl_2 solution is still water soluble and could be suitable to form asymmetrical membranes containing Cu^{++} cations with potential catalytic applications.

The ease with which PEEK-WC- SO_3H bonds to many metallic cations also allows the easy removal of these cations from wastewater.

We postulate that the precipitation of salted polymers could be due to the formation of ionic bonds that are intra- and intermolecular among SO_3H groups and cations that lead to a cross-linked structure.

CONCLUSIONS

It was proved that sulfonation of PEEK-WC occurred in neat chlorosulfuric acid at room temperature: a high degree of sulfonation was reached and the obtained polymer was water soluble and acted as a polyelectrolyte. Despite the drastic pH of the reaction environment, detectable degradation of the polymeric chain was never observed. The hydrophilic polymer synthesized was absolutely soluble in water at room temperature.

By choosing suitable reaction conditions, it was possible to obtain polymers with a lower degree of substitution that were soluble in polar aprotic

solvents but insoluble in water and in chlorated ones. The predictable chlorosulfonated product was never observed.

Moreover, the thermal stability of the sulfonated PEEK-WC was also comparable with the parent PEEK-WC. The product obtained formed membranes that could be used in gas separation applications.

REFERENCES

1. E. Drioli and Z. H. Chun, *Chim. Oggi*, **November**, 59 (1989).
2. C. Bailly, D. J. Willians, F. E. Karasz, and W. J. Macknight, *Polymer*, **28**, 1009 (1987).
3. J. Devaux, D. Delinoy, D. Daoust, R. Legras, J. P. Mercier, C. Strazielle, and E. Nield, *Polymer*, **26**, 1994 (1985).
4. H. Zhang, T. Chen, and Y. Yuan, *Chin. Pat.* 85,108,751 (1985).
5. W. Y. Liu, Z. G. Wang, T. L. Chen, and J. P. Xu, *Proceedings ICOM 90*, Vol. II, p. 836.
6. L. Jia, X. Xu, I. Zhang, and J. Xu, *J. Appl. Polym. Sci.*, **60**, 1237 (1996).
7. J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, 1992, p. 529.
8. R. M. Fuoss and U. P. Strauss, *J. Polym. Sci.*, **3**, 246 (1948).
9. D. Lin-Vien, N. B. Colthup, W. G. Fateley, and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic, New York, 1991.