

Nitro Derivatives of PEEK-WC

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ABSTRACT: Nitrated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (PEEK-WC) with various average degrees of substitution was obtained by reaction with several nitrating agents. By working under controlled reaction conditions, little degradation of the parent polymer is observed. The nitro derivatives of PEEK-WC show a high thermal stability, and are able to form membranes by means of phase inversion technique. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1037–1045, 2001

Key words: polyetheretherketones; membrane; nitration

INTRODUCTION

Polyetherketones (PEK)^{1,2} and polyetheretherketones (PEEK)³ are polymers with a high degree of crystallinity, and have a very high thermal stability as well as mechanical and resistance to chemical agents, and they have found uses in several technological and industrial applications.

Because they are insoluble in water and in almost all common organic solvents, they are not able to form membranes by means of phase inversion technique,^{4,5} the most interesting technique for thin and asymmetric industrial membrane production.

On the other hand, the membranes show additional new applications every day, and there is a great request for new polymers suitable to form membranes that have more adequate properties for special uses.

Recently, the insolubility of the PEEK was overcome by synthesizing a different kind of PEEK named PEEK-WC (poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxy-phenylene)),⁶ characterized by the presence of the cumbersome lactonic group that reduces the degree of crystallinity, thus making it more soluble in some chlorohydrocarbon solvents and also in DMF and DMSO. As a consequence, it is then possible to obtain PEEK-WC membranes that are now studied for many applications.

It is well known, however, that the properties of the membranes in the applications where they separate molecules that have very close molecular dimensions (i.e., gas separation) are widely influenced by the choice of the polymer. Moreover, the insertion of side groups on the polymeric chain can modify the selectivity and the permeability of the membrane. For example, it is known that an electron-withdrawing group like COOH and bromine have a positive effect on the gas separations.^{7,8}

PEEK-WC is already reported to be sulfonated, thus increasing its selectivity towards

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CO₂/CH₄ gas separation,⁹ and also water-soluble sulphonated PEEK-WC derivatives were obtained.¹⁰

To our knowledge, no other detailed modifications are reported in the literature. On the contrary, the simple insertion of the nitro group on the polymeric chain allows us to obtain a new material with possible positive properties, and also to have at our disposal a reactive group suitable for further modifications through a previous reduction to the amino group.

In this work we wish to report a simple synthetic route to produce nitro derivatives of PEEK-WC. The reaction is carried out at room temperature, and leads to a polymer soluble in several organic solvents and suitable for forming membranes by means of a phase inversion technique, which itself has interesting and peculiar features.

MATERIALS AND METHODS

PEEK-WC was received from Chan-Chung Institute (Academia Sinica, Shanghai, China). Before use, the PEEK-WC was purified by Soxhlet extraction with methanol to remove low molecular weight by-products.

Ammonium Nitrate, Chloroform, Tetrabutyl ammonium nitrate, Trifluoroacetic anhydride, methanol, anhydrous sodium sulphate, and hexane were ACS grade, and were bought from Fluka (Switzerland) and used in the exact form in which they were consigned.

The reactions were thermostated by using a Lauda RC6 thermostat. Infrared spectra were recorded by Perkin-Elmer FTIR model 1710 spectrophotometer, making a film of the polymer on a KBr pellet. The thermogravimetric analyses were carried out on a Du Pont 951 apparatus under nitrogen flow. Scanning Electron Microscopy (SEM) analyses were performed on a LEO 420 apparatus. Atomic Force Microscopy (AFM) analysis was executed on a Autoprobe CP-100 device from Park Scientific Instruments. High magnification images of the membrane surfaces were obtained by using microfabricated cantilevers. Measurements were made directly in air operating in a noncontact mode. The analysis of surface pore characteristics and single pore region profiles was obtained by means of the AFM images processing program, which gives image representation in a top view and in perspective.

The membranes were prepared following the process of traditional phase-inversion technique

(evaporation or precipitation method), which permits the production of membranes with both symmetric or asymmetric pore structure, respectively. The solvent used was *N,N*-dimethylformamide (DMF), and the nonsolvent was distilled water.

In particular, symmetric membranes were obtained by dissolving the polymer in DMF (15 wt %) and magnetically stirring overnight to allow the complete dissolution at room temperature. The solution was cast with a knife on to a glass plate. The knife was supplied from Brane Instruments. The knife height was set at 250 μm , and the evaporation occurred at room temperature.

Asymmetric membranes were obtained from the same above-mentioned solution of the polymer in DMF and cast with a knife on a glass plate at the same thickness (250 μm), and after an initial evaporation time of 45 s at room temperature, it was immersed in a coagulation bath containing distilled water. The cast film was kept in water for 10 min and then transferred to fresh distilled water.

Solubility tests were performed at room temperature by weighing 50 mg of the polymer and then adding 1 mL of the selected solvent.

Synthesis of the Nitro Derivative of PEEK-WC: Method a

In a three-necked round-bottom flask with a condenser 20 mL of alcohol-free chloroform was put, and then 1.0 g of PEEK-WC was slowly added under magnetic stirring until a homogeneous solution was obtained. Once the complete polymer dissolution was reached, 0.16 (2.0 mmol) of lyophilized ammonium nitrate was added. Then 0.55 mL (4.0 mmol) of trifluoroacetic anhydride was added drop by drop to the mixture, and the mixture was allowed to react at 30°C for 3 h under constant stirring.

Once the reaction was over, unreacted ammonium nitrate was removed by centrifugation, and the clear organic solution put into 100 mL of methanol. The obtained precipitate was recovered by filtration under vacuum and washed several times with water until neutrality was reached. Then the polymer was dissolved in the minimum possible amount of chloroform, and the organic solution was extracted many times with distilled water. The organic phase was anhydriified with anhydrous sodium sulphate, filtered under vacuum, and the solution added to 100 mL of hexane.

The precipitate was recovered by filtration under vacuum, dried, and stored in a desiccator.

Synthesis of the Nitro Derivative of PEEK-WC:

Method b

One gram (2.0 mmol) of purified PEEK-WC was dissolved in 20 mL of alcohol-free chloroform. After complete dissolution of the polymer, 0.625 g (2 mmol) of tetrabutyl ammonium nitrate was added and then 0.55 mL (4.0 mmol) of trifluoroacetic anhydride. After a few minutes the solution becomes homogeneous, and was allowed to react for 30 min at 25°C. Once the reaction was over, the solution was put in 100 mL of hexane. The precipitate was recovered by filtration under vacuum and dissolved again in the minimum amount of chloroform. The organic phase was extracted many times with distilled water and then anhydried with anhydrous sodium sulphate and added to 100 mL of hexane. The polymer was recovered by filtration under vacuum, dried, and stored in a desiccator.

Synthesis of the Nitro Derivative of PEEK-WC:

Method c

In a three-necked round-bottom flask with a condenser 100 mL of nitrobenzene and 10 g of purified PEEK-WC were put. The temperature was increased to 85°C by using an oil bath, and the sulphonitric mixture (0.92 mL of HNO₃ and 2.16 mL of H₂SO₄) was added. The red mixture was allowed to react for 2 h at 85°C. Once the reaction was over, the mixture was cold at room temperature and then put in to 300 mL of methanol. The dark precipitate was recovered by filtration, washed with methanol, and then with water until neutrality was obtained, and finally with methanol. The precipitate was recovered and dissolved in CH₂Cl₂ and precipitated again in methanol. This latter operation was repeated twice. Then the precipitate was recovered by filtration and dried under vacuum. Traces of nitrobenzene were removed by prolonged Soxhlet extraction with methanol. The solid was recovered and stored in a desiccator.

RESULTS AND DISCUSSION

The nitration reaction of aromatic compounds is a classic example of electrophilic aromatic substitution. The availability of π electrons and the

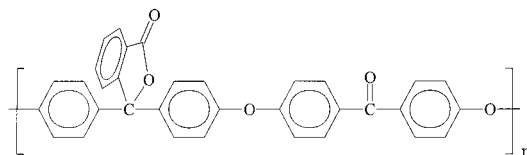


Figure 1 Molecular structure of PEEK-WC.

aromatic ring stability leads to the introduction of an electrophilic group and to a release of a H⁺ cation from the aromatic ring. Obviously, this reaction is influenced by the presence of different groups on the aromatic ring. It is well known that withdrawing groups, as they delocalize the π electrons, make the aromatic ring towards the electrophilic groups less reactive.

Due to their high crystallinity and consequent low solubility in almost all solvents, modifying the chain of polyetherketones and polyetheretherketones is particularly difficult. Functionalized derivatives of PEK or PEEK are normally obtained by means of a suitable change of the parent monomers.

Unlike other polyetheretherketones, PEEK-WC is more amorphous, and it is soluble in few aprotic polar solvents; it is also soluble in some chlorohydrocarbons. Thus, generally speaking, further modifications on the polymeric chain are possible by means of normal organic reactions.

PEEK-WC (Fig. 1) has a repeating unit of five benzene rings, each of which have very different reactivity levels from one other. In particular, the presence of a strong deactivating group such as carbonyl greatly slow down or even prevent the reaction on the benzene rings directly bonded to the carbonyl group. Similar behavior could be ascribed to the other carbonyl groups of the latic part of the molecule. Due to steric hindrance, the reaction at the ortho position of the rings, which are directly bonded to the latic group, is unlikely.

As a consequence, aromatic electrophilic substitution could be easily performed only on the two benzene rings not directly bonded to the carbonyl group, especially by working with a limited amount of the selected electrophile and under controlled reaction conditions.

In the literature many nitrating agents are mentioned,¹¹ among these the sulphonitric mixture is the cheaper and more easily prepared, and it is the most-used nitrating system in the laboratory and in the industry.

The reaction mechanism is well understood, and it requires the formation of the nitronium

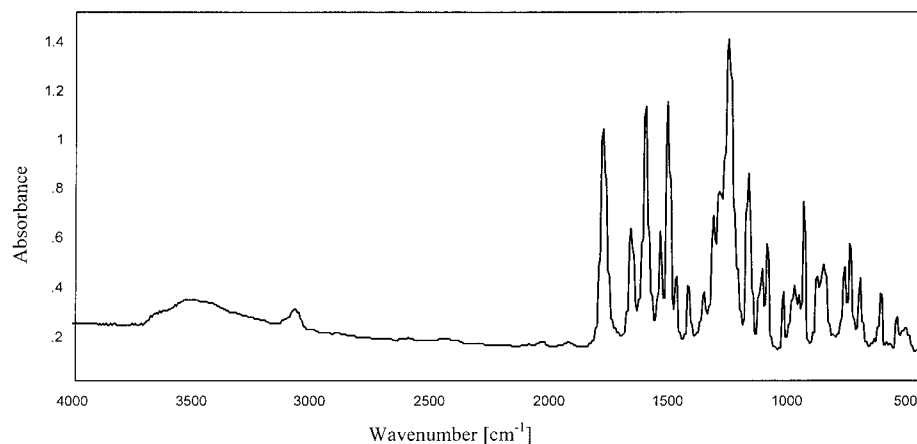
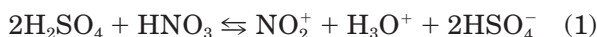


Figure 2 FTIR spectrum of the nitrated PEEK-WC. Film from CHCl_3 on the KBr pellet.

cation by means of acid-base equilibrium from sulphuric acid and nitric acid:



The presence of solvents able to donate electron pairs shifts unfavorably to the left side of the equilibrium position.

For these reasons the nitration reaction of PEEK-WC with classic sulphonitric mixture was carried out in nitrobenzene, practically the only solvent able to solubilize both PEEK-WC and a small amount of sulphonitric mixture, thus allowing the reaction to occur.

The nitration reaction is followed along the way simply by FTIR analysis of a thin film on KBr pellet. In fact, the NO_2 group shows an infrared characteristic absorption at 1535 cm^{-1} in a zone free of other signals of the parent PEEK-WC (Fig. 2). By evaluating the ratio between the signal of the NO_2 group at 1535 cm^{-1} and the carbonyl group at 1650 cm^{-1} , it is possible to roughly estimate the relative average degree of substitution reached. In particular, the reported values were determined by means of previous execution of the calibration curve. To this goal infrared absorption of two defined molecular compounds was undertaken, i.e., nitrobenzene and acetophenone in DMSO solution. The latter two molecules are arbitrarily assumed to have the same infrared absorption behavior of the nitrated polymer and the parent PEEK-WC, respectively. Considering the fact that the Lambert-Beer law is completely obeyed, the average degree of substitution (D.S.)

could be determined by the following empirical relation:

$$C_{\text{NO}_2}/C_{\text{CO}} = 0.41 \times A_{\text{NO}_2}/A_{\text{CO}} \quad (2)$$

Although this procedure requires many arbitrary hypotheses, some elemental analyses performed on the nitrated polymer nevertheless lead to very close D.S values, thus supporting the simple FTIR determination.

The nitration reaction is carried out in nitrobenzene with a stoichiometric amount of sulphonitric mixture. However, this process presents some disadvantages. First of all, the procedure is time consuming and tedious. A toxic solvent is used, and, due to its high boiling point, is hard to remove completely. But, above all, a low molecular weight polymer is obtained compared to the parent one. In fact, by comparing the viscosity measurements at 30°C in DMF solution, it was noted that the parent PEEK-WC shows an intrinsic viscosity of $0.8 \text{ dm}^3/\text{g}$, while the corresponding nitro derivative leads to a viscosity of only $0.25 \text{ dm}^3/\text{g}$, which is probably evidence of a partial polymer chain degradation under the reported reaction conditions.

In the literature, the sulphonitric mixture was reported to be successfully employed in the nitration of polysulfone polymer.¹² However, the authors did not report any viscosity data for the obtained derivatives, and thus we are not able to ascribe the observed partial PEEK-WC degradation to the particular nitrated polymer or to the nitrating agent and/or reaction conditions. Never-

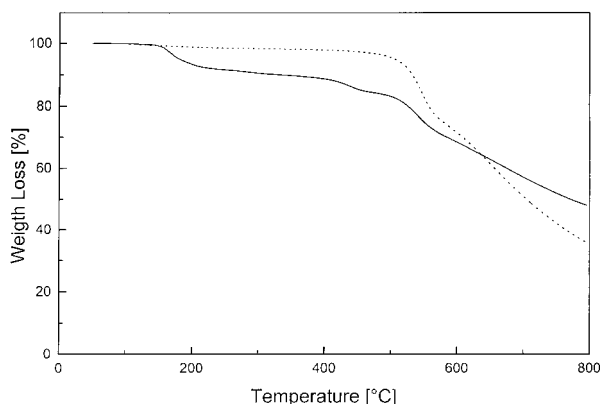


Figure 3 Thermogravimetric analysis of the parent PEEK-WC (••••) and nitrated PEEK-WC (—) under nitrogen flow.

theless, the obtained nitrated PEEK-WC is still able to form membranes by means of the phase inversion technique.

To find milder reaction conditions, a simpler workup procedure, shorter reaction time, and to reduce the degradation of the polymeric chain, other nitrating systems were studied.

In particular, NH_4NO_3 was used as a nitrating agent in the presence of trifluoroacetic anhydride in chloroform by following the synthetic procedure reported by Crivello.¹³

Under the latter reported reaction conditions, the trifluoroacetic anhydride reacts with NH_4NO_3 to give the nitronium cation, the true nitrating agent towards the aromatic rings:

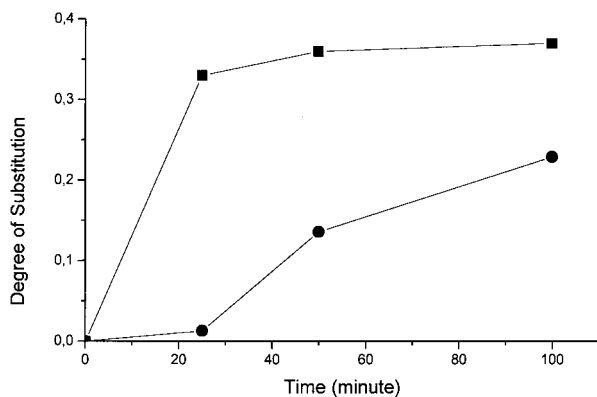
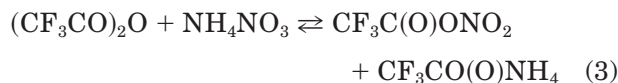


Figure 4 Influence of the amount of NH_4NO_3 on the degree of substitution (●) 2 mmol (■) 10 mmol respect to the parent PEEK-WC. Room temperature. Constant stirring.

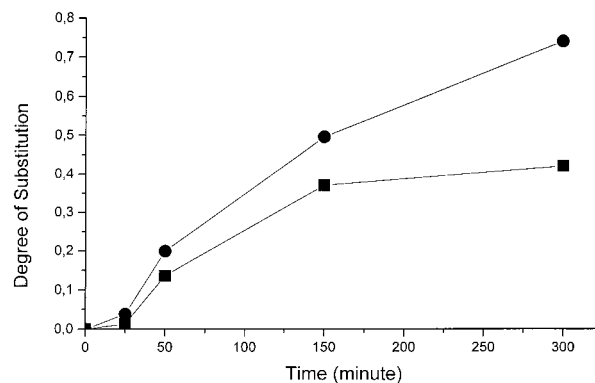


Figure 5 Influence of the amount of TFAA on the degree of substitution (■) 4 mmol (●) 8 mmol respect to the parent PEEK-WC. Room temperature. Constant stirring.



The reaction has a wide applicability, and proceeds to room temperature in a few hours. The system is typically heterogeneous, and the reaction rate is reported to be largely influenced by the solubility of NH_4NO_3 in the selected solvent. Although the reaction can also occur by using other metallic nitrates, it is preferable to employ the ammonium nitrate because the latter shows a moderate solubility in many organic solvents. Nevertheless, the use of more polar solvents such as acetonitrile, that leads to a higher reaction rate, is not recommended for the nitration of the PEEK-WC because the latter polymer is not soluble enough in these solvents.

It was reported that the nitration of some polymers occurs without significant degradation under the above-mentioned reaction conditions. Only with particularly sensitive polymers such as polycarbonate was partial degradation observed.¹³

Some viscosity data determined for the nitrated PEEK-WC polymer (D.S. = 0.42) shows an intrinsic viscosity of about $0.32 \text{ dm}^3/\text{g}$, thus showing a minor degradation compared to that observed with the sulphonitric mixture. It is important to point out that by working at lower temperature and reduced reaction time it is possible to obtain a polymer with high viscosity, although it has a low D.S. This aspect is not a disadvantage, because in several applications i.e., gas separation, important effects could be seen even with a very small amount of functional groups on the polymeric chain.

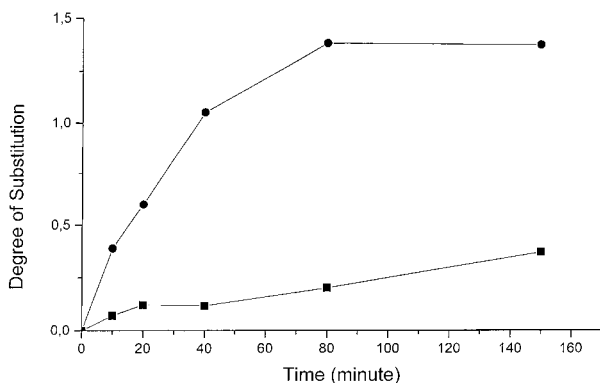


Figure 6 Effect of the amount of NH_4NO_3 and TFAA on the degree of substitution. (■) 2 mmol of NH_4NO_3 and 4 mmol of TFAA. (●) 10 mmol of NH_4NO_3 and 8 mmol of TFAA respect the parent PEEK-WC. Room temperature. Constant stirring.

The deactivating effect of the nitro group towards the aromatic electrophilic substitution reaction makes the second substitution on the same aromatic ring unlikely. In this respect we remember that nitrobenzene does not react under the described reaction conditions.

The introduction of the nitro group on the PEEK-WC chain does not significantly affect the thermal stability of the polymer. In fact, as shown in Figure 3, the thermogravimetric analysis of the nitro derivative of PEEK-WC shows an initial weight loss from 100°C and then demonstrates substantial stability up to 400°C. Above this a first degradation step occurs, followed by the principal thermal degradation process above 500°C. In comparison to the thermal behavior of the parent PEEK-WC, it is possible to see a marked influence of the nitro group on the thermal stabil-

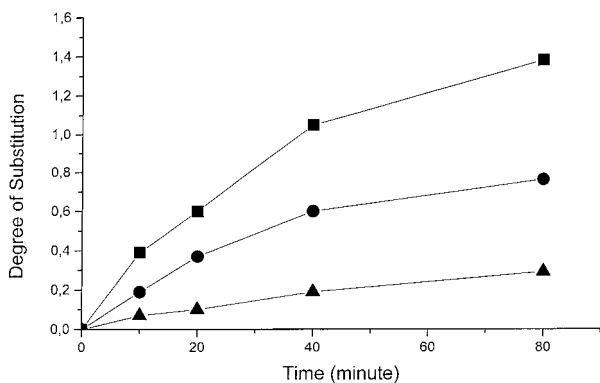


Figure 7 Influence of the reaction temperature on the degree of substitution. (▲) 10°C. (●) 20°C. (■) 30°C. Constant stirring.

Table I Solubility of Nitro Derivative of PEEK-WC in Several Solvents

H_2O	—
Ethanol	—
Methanol	—
DMSO	+
DMF	+
THF	+
Pyridine	+
Petroleum ether	—
Chloroform	+
Acetone	+/-

Room temperature: 50 mg/mL.

ity of the polymer that is seen to be higher than the parent PEEK-WC above 600°C. Because polyetheretherketones find applications in many fields thanks to their exceptional thermal stability, this behavior is a relevant point.

The nitration of PEEK-WC by ammonium nitrate and trifluoroacetic anhydride is, however, highly influenced by the amount of NH_4NO_3 and TFAA used and by the reaction temperature. Figure 4 reports the D.S. obtained as a function of the reaction time by using two different amounts of liophylized NH_4NO_3 . It can be easily noted that by using a five times greater amount of NH_4NO_3 , higher D.S. are quickly reached (<30'), while at the same time, a lower amount of NH_4NO_3 leads to a very moderate conversion. However, because in both cases the amount of ammonium nitrate is superior to its solubility in CHCl_3 this result, obviously, does not depend on the concentration of NH_4NO_3 in solution, but could probably be ascribed to the higher surface area at the reaction's disposal, as is predictable for a heterogeneous reaction.

The reaction is also influenced by the concentration of trifluoroacetic anhydride. Figure 5 re-

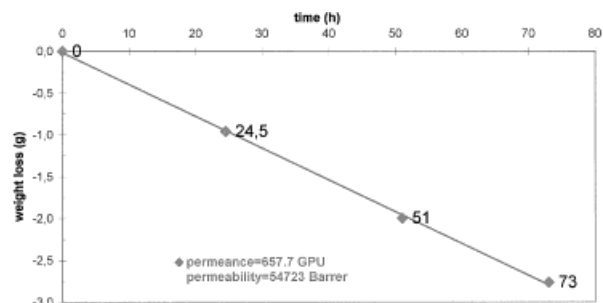


Figure 8 Water vapor flow through symmetric PEEK-WC- NO_2 membranes.

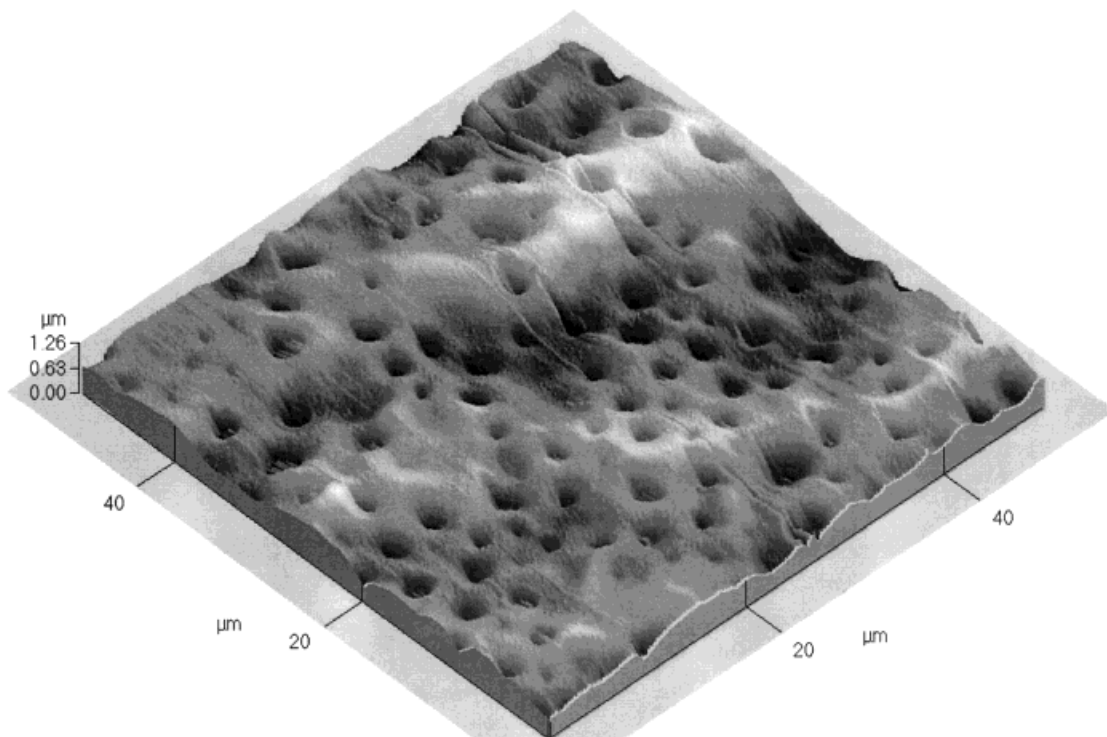


Figure 9 AFM image of nitrated PEEK-WC.

ports the D.S. as a function of the reaction time for two different amounts of TFAA, with all other reaction conditions being the same. These results are highly predictable, considering the shift of the equilibrium to the right side in reaction (3) that leads to the formation of a higher amount of $\text{CF}_3\text{COONO}_2$, i.e., the intermediate that generates the reactive nitronium cation.

Obviously, when the amount of both reagents are enhanced simultaneously, the effect on the reaction rate is magnified. Figure 6 shows that it is possible to reach very high D.S., that is, polymers that have more than one NO_2 group per repeating unit. As the double substitution is highly unfavorable, the nitration probably occurs on two different aromatic rings.

The reaction proceeds under mild temperature conditions and it is effective already at 10°C . Figure 7 shows that by increasing the reaction temperature to 30°C , it is possible to obtain poly substituted derivatives after about 40 min. However, by working at a lower temperature, low D.S. compounds are obtained. By using NH_4NO_3 under the above-mentioned reaction conditions, it is possible to obtain nitro derivatives of PEEK-WC that have different D.S. even working under mild reaction conditions. However, the presence of two

layers can give reaction low reproducibility. To avoid this problem the nitration reaction was carried out by using a completely soluble nitrate in the organic phase, i.e., tetrabutyl ammonium nitrate, a typical onium salt widely used in Phase Transfer Catalysis. In these conditions of shortened reaction time, less degraded polymers are obtained, although the procedure is more expensive.

Polymers that have different solubility compared to the parent PEEK-WC were obtained. Table I reports the solubility at room temperature of nitrated PEEK-WC. The latter is rather soluble in many common organic solvents and not soluble only in very polar protic solvents (water and low alcohols) or completely apolar ones such as petroleum ether.

The nitro PEEK-WC derivatives are useful for the preparation of membranes by means of the phase inversion technique. In particular, it is possible to obtain symmetric membranes by solubilizing the polymer in DMF and then carrying out slow evaporation of the solvent at room temperature.

Asymmetric membranes were made by precipitating a thin film of the DMF polymer solution into water.

Water vapor permeability tests by using the "cup method" have been carried out. The latter method measures the amount of water that pass through the membrane surface collected on the cup, containing liquid water by means of the difference of weigh for the cup at a fixed time range. The driving force of the process is the difference of water vapor concentration between the inside of the cup (humidity near to 100%) and the outside (anhydrous environment) at a fixed temperature. Figure 8 accounts for the results obtained. As predicted, a linear dependence of the weigh loss from the time is observed at different permeance, and permeability values in comparison with the parent PEEK-WC membrane were detected.

Further information on the nitro PEEK-WC membranes were obtained from AFM micrographs. Four membranes that had been prepared from the two polymers by following different methods were examined. Figure 9 shows an AFM micrograph of the surface of the symmetric nitro PEEK-WC membrane. The image is given in perspective representation, and it refers to an area of $30 \times 30 \mu\text{m}$. The colors show the vertical profile of the sample, with the light regions being the highest point, and the dark the depressions (the pores). The morphology of the symmetric nitro PEEK-WC membranes is very different compared to the asymmetric one, which is in accordance with the dense top layer morphology of the asymmetric membranes. The image also reveals a clear microporous structure, which is also different from the symmetric PEEK-WC membrane.

These considerations were also confirmed by SEM analyses. For instance, Figure 10 reports a SEM image of the freeze-fractured cross-section of a symmetric nitro derivative of PEEK-WC

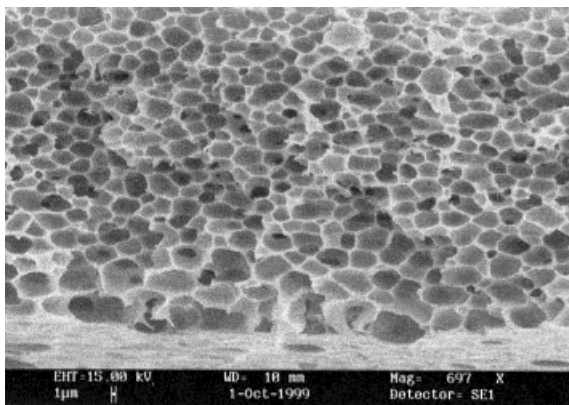


Figure 10 SEM microphotograph of symmetric PEEK-WC-NO₂ membranes.

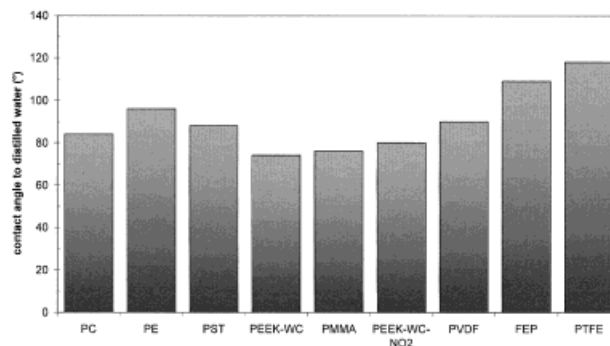


Figure 11 Contact angle values for some polymers.

membrane. The micrograph confirms the porosity observed with the AFM analyses and its evenness through the section of the membrane.

Interestingly, the contact angle values for the membrane of the nitro derivative of PEEK-WC are higher than the parent PEEK-WC (Fig. 11). This property is important in many applications such as membrane contactors, i.e., equipment in which membranes are used to improve mass transfer coefficients in respect to traditional extraction and absorption processes. It is expected that by increasing the NO₂ contents in the polymer chain, higher values of the contact angle could be reached.

CONCLUSIONS

A new polymeric material suitable to form membranes by means of the phase inversion technique was obtained by carrying out the nitration reaction on PEEK-WC under mild reaction conditions and different nitrating agents. Unlike the parent PEEK-WC, nitrated PEEK-WC is soluble in many polar organic solvents and also in THF. Low degrees of substitution lead to a polymer that has high thermal stability. Further modifications are predictable by previous reduction of the nitro group to the amino group.

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