Preparation and Characterization of Functional Poly (ether ether ketone)

Containing Nitryl Pendant

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ABSTRACT

The novel functional poly (ether ether ketone) containing nitryl pendant was prepared using concentrated nitric acid under different reaction conditions. The reaction time was varied from 20 to 500 h, and the concentration of nitric acid was varied from 40 to 75%. Structural characterization of the nitrified polymers was carried out by FT-IR and ^{1}H-NMR techniques. FT-IR spectroscopic, elemental analyses and ^{1}H-NMR techniques were performed to determine the structural characterization of the nitrified polymers; thermal analyses determined the dependence of the glass transition temperature measured by DSC, and the degradation behavior on the level of nitration was measured by TGA, combined with other analyses. The DSC experiments showed that with the increase of nitric acid concentration, the temperatures of melting and crystallization of the polymers decreased. No crystallization peak was observed when the concentration of nitric acid was above 60%. Two-step mass loss was observed in thermogravimetric traces (recorded in N_2 atmosphere). The first one (300-450 °C) was attributed to volatilization of NO_2 from the nitryl group. The backbone degradation took place above 450 °C. The novel polymer exhibited excellent solubility at room temperature.

Keywords: Poly (ether ether ketone); nitrated; thermal behavior; structure analysis

Introduction

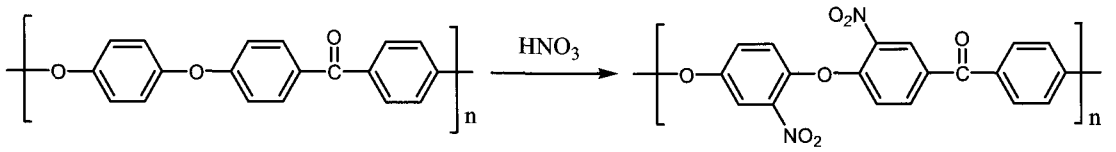
Poly(ether ether ketone) (PEEK), as a member of poly(aryl ether ketone)s, is a semi-crystalline polymer with a glass-transition temperature (Tg) of 144°C and a melting temperature (Tm) of 342 °C. These excellent characteristics make it ideal for a variety of applications from the aerospace to the medical field, as insulation and matrix resins for composite materials, as well as in electronics. (1-10)

In the present work, a new class of functional PEEK containing nitryl pendant are prepared through nitration of PEEK at the presence of nitric acid. It can be easily prepared in a single step reaction in suspension, without any competition reactions.The effect of nitric acid concentration on the nitration of PEEK as well as the chemical structure, solubility and thermal behavior of the obtained nitrated PEEK were studied. The purpose of this note is to describe the nitration process and present the solubility and thermal behavior of the obtained nitrated PEEK in details.

Experimental

The nitration of PEEK powder was carried out in a three-necked round bottom flask and conducted in atmosphere circumstance at room temperature, unless otherwise specified. Given amount of PEEK and

nitric acid were added to the flask and stirred mechanically for a stated period. To disclose the effects of nitric acid concentration on the extent of nitration, 3.33% (w/v) PEEK solution in nitric acid with concentration ranging from 40% to 75% were used. The reaction times were set in the range of 20-500h.



Scheme 1. Preparation of the NPEEK

Results and discussion

Synthesis and structural characterization of NPEEKs

The nitration of PEEK was carried out at room temperature. It is found that the nitration reaction depends strongly on the concentration of nitric acid. If high concentration nitric acid, i. e. >70%, was used, the nitration reaction accomplished within 24h and the products were completely dissolved in the nitric acid.

TABLE I. The nitration conditions for preparing NPEEKs

Samples	Conc. of nitric acid (%)	Reaction time (h)
NPEEK-1	40	500
NPEEK-2	50	500
NPEEK-3	60	500
NPEEK-4	65	500
NPEEK-5	70	500
NPEEK-6	75	20

To confirm the formation of nitrated PEEK, detailed structural analysis of the obtained products has been performed. Figure 1 shows the infrared spectra for PEEK and nitrated PEEK with different nitration degrees. The presence of nitryl groups in the backbone of nitrated PEEK samples was confirmed by a strong absorption peek at 1532 cm^{-1} and a medium intensity absorption peek at 1349 cm^{-1}, which were assigned to nitrogen-oxygen bonds of the nitryl group symmetric stretching vibration and asymmetric stretching vibration, respectively. The intensity of the new band appeared at 1532 and 1349 cm^{-1} increased with increasing the concentration of nitric acid. So, the changes observed in the IR spectra indicate the presence of nitryl groups and the relative extent of nitration.

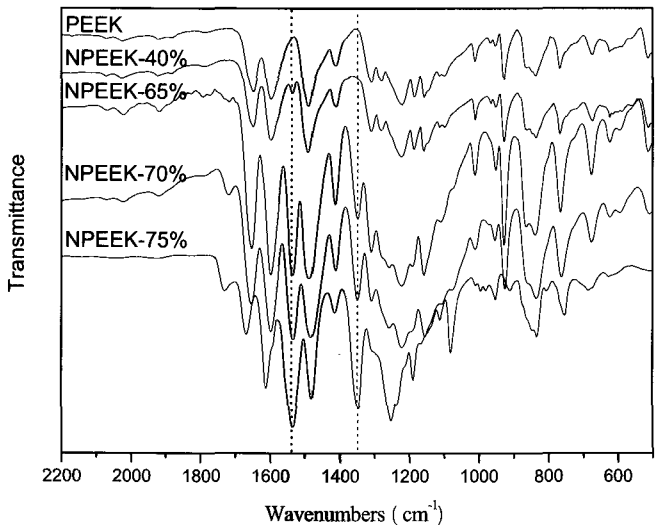


Figure 1. FT-IR spectra of PEEK and NPEEKs

The ^{1}H-NMR spectra of NPEEK samples are shown in Fig. 2. The ^{1}H-NMR spectrum of non-nitrated PEEK does not present here since no suitable organic solvents of it has been found. Therefore, a direct comparison of the ^{1}H-NMR spectra for the nitrated and non-nitrated PEEKs cannot be fulfilled. Nevertheless, the presence of nitryl group in the hydroquinone ring of NPEEK will lead to a downfield chemical shift of H_h protons compared to H_b protons. Therefore the observed signal at 7.82 ppm should correspond to H_h protons and indicate the nitration of PEEK in nitric acid with concentration over 50%. Moreover, elemental analysis further confirms the occurrence of nitration of PEEK in nitric acid with concentration over 50%. For example, the elemental analyses result of NPEEK5 (N, 5.99%; C, 65.78%; H, 3.26%) reveal that there are about two -NO_2 groups per repeat unit of NPEEK5.

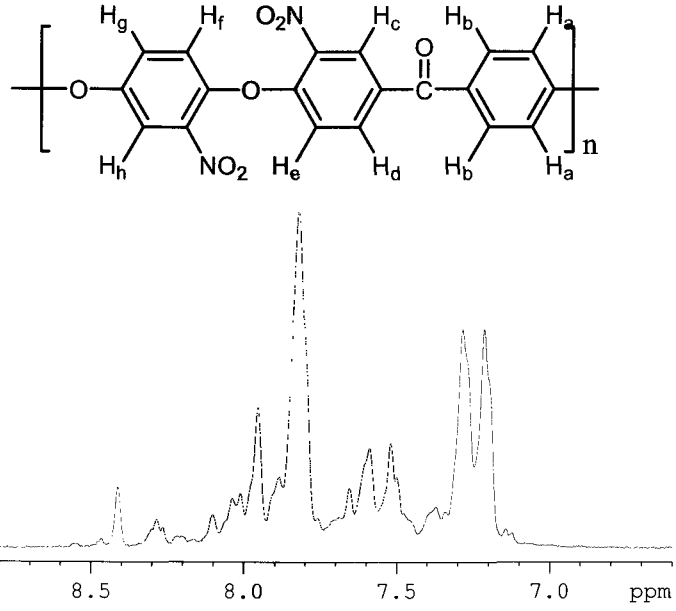


Figure 2. Proton NMR spectrum of poly(ether ether ketone) containing nitryl pendant in DMSO-d6

Solubility and thermal behavior of NPEEKs

Dissolution test indicates that the nitrated PEEKs exhibit indeed excellent solubility in most common organic solvents. As an example, the NPEEK5 can solve in THF, DMSO, DMF, NMP and DMAc easily. DSC measurement shows that the PEEK melts at 342.7°C, see Figure 3. The NPEEK samples treated in nitric acid with concentration lower than 50% melt at temperatures slightly lower than the PEEK. When the nitric acid concentration ranges from 50 to 70%, the obtained NPEEK samples exhibit endothermic transitions at about 310°C. With further increase of the nitric acid concentration, i.e. over 70%, no endothermic transition was observed during DSC heating scan.

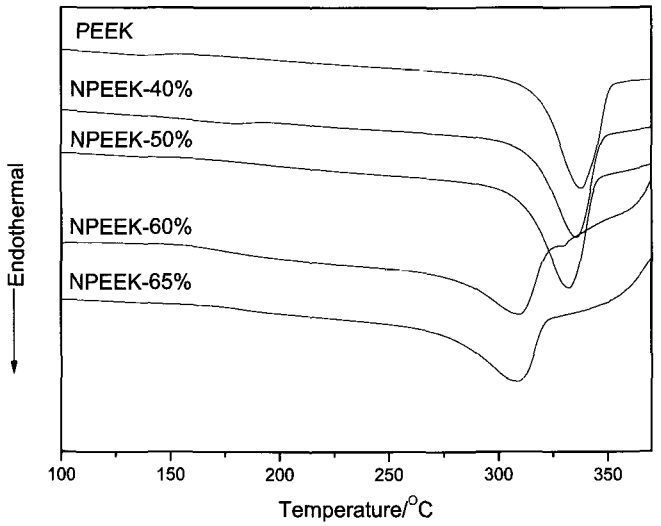


Figure 3. DSC heating curves of PEEK and NPEEK.

The thermal stability of nitrated PEEKs were tested by TGA. PEEK exhibits a single decomposition in the temperature range of 500-600°C, while nitrated samples existed two-step mass loss in the temperature range of 300–450°C (Td1) and 450–800°C (Td2), respectively. The first thermal degradation temperature observed between 300–450°C in NPEEK samples should be attributed to decomposition of the nitryl group, eliminating NO_2. The mass loss in this step increases with the increase of nitration extent further confirms that it represents the decomposition of the nitryl group only. The second step mass loss is related to the decomposition of the main chain of PEEK at about 450°C.

Conclusions

The effect of nitric acid on the nitration of poly (ether ether ketone) was studied in this paper. The results show that nitrated PEEK samples can be obtained by varying the reaction time and concentration of nitric acid. Structure analysis confirms the formation of nitrated PEEK with the nitration extent increases with increasing nitric acid concentration. Dissolution test indicates that the nitrated PEEK can dissolve in most of the organic solvents easily. Thermal test indicates that the melting temperature of the nitrated PEEK is lower than that of PEEK and decrease increasing nitration extent. TGA measurement shows that the decomposition of nitryl group occurs in temperature range of 300–450°C, while the decomposition of the PEEK main chain happens at about 450°C. (Next see p125)