Polymer Bulletin 61, 157–163 (2008)
DOI 10.1007/s00289-008-0942-6

Polymer Bulletin

Synthesis of poly(ether ether ketone) assisted by microwave irradiation and its characterization

Jun Yin, Aiqing Zhang (✉), Kong Yong Liew, Lihua Wu

Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission
& Ministry of Education, Hubei Province, South-Central University for Nationalities,
Wuhan 430074, P.R. China

E-mail: aiqingzhang_2000@sina.com; Fax: +86 027 67843009

Received: 4 November 2007 / Revised version: 12 March 2008 / Accepted: 25 April 2008

Summary

Poly(ether ether ketone) (PEEK) was synthesized with a good yield, by nucleophilic substitution reaction of 4,4'-difluorobenzophenone (DFBP) with hydroquinone (HQ) in the presence of anhydrous potassium carbonate (K_2CO_3) under microwave (MW) irradiation. The highest yield of 96.1% was obtained using sulfolane as the solvent and with a reaction time of only 55 min. The reaction time was reduced greatly compared with conventional heating. The product was characterised by infrared spectroscopy (IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymer, having inherent viscosities of 0.71 dlg^{-1}, has excellent thermal stability as shown by 10% weight loss in nitrogen at about 563°C. The XRD pattern confirmed the semicrystalline character of PEEK synthesized.

Introduction

PEEK is a semicrystalline polymer first marketed by ICI in 1977. It has a glass-transition temperature (T_g) of 145°C and a melting temperature (T_m) of 345°C. It has become one of the most attractive polymer materials widely used in aerospace, electronics and nuclear industries because of its excellent resistance to heat, wear and chemical as well as friction reduction and good mechanical properties [1-7]. Recently, a number of novel PEEKs have been synthesized via electrophilic or nucleophilic polycondensation in an effort to improve their overall properties. However, the PEEKs synthesis requires rather rigorous reaction conditions because of the polymer's insolubility. PEEK with high molecular weight is generally prepared in diphenylsulfone at elevated temperatures very close to its boiling point [8-11]. The operation is quite inconvenient and the reaction time is long under conventional thermal conditions.

The application of microwave (MW) energy for the synthesis of organic compounds has been reported since 1986. Mallakpour and co-workers [12-15] reported the synthesis of poly(amide-imide)s by the microwave-assisted polycondensation reaction. Microwave is a nonionizing electromagnetic energy and it directly heats up the reactive centers of the reagents. Solvents for the reaction must have a high dielectric constant as it is necessary to have a polar media to absorb the energy from radiation and transfer to the reacting system. In this way the most effective energy transfer is provided. Microwave activation, as a non-conventional energy source, has been proven to be very effective in accelerating organic reactions and attracted much attention in the past decade [16,17]. Almost all types of organic reactions have been performed using the efficiency of microwave (MW) flash heating [18,19]. MW irradiation can be considered selective for synthesis of monomers and polymeric materials.

The application of microwave technique in the synthesis of PEEK has received little attention until now. In the present study, we introduced the microwave heating method to obtain PEEK and the effect of reaction time and solvent on the product yield have also been studied.

Experimental

Materials

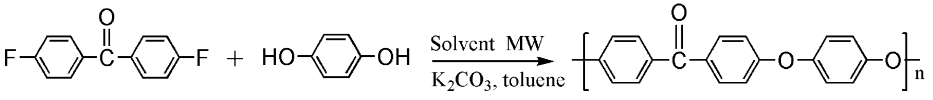
Toluene was dried via refluxing over sodium and distilled before use, stored over molecular sieves (4Å). 4,4'-Difluorobenzophenone and hydroquinone were recrystallized from ethanol. Sulfolane and dimethyl sulfoxide (DMSO) were dried with molecular sieves (4Å) and distilled under reduced pressure. K_2CO_3 was dried at 150°C for 12 h under vacuum. *N*-Methyl-2-pyrrolidone (NMP) was dried via refluxing over calcium hydride and distilled. *N, N*-Dimethylacetamide (DMAc) was dried with molecule sieves (4Å). Other reagents were commercial materials and used without further purification.

Instrumental measurements

Inherent viscosity ($\eta_{inh} = \ln\eta r/c$ at polymer concentration $C = 0.5$ gdl^{-1}) was measured with an Ubbelohde suspended-level viscometer at 30°C using conc.H_2SO_4 as solvent. Infrared spectra (IR) were obtained with a Nexus470 FTIR Spectrometer using KBr disks. T_g and T_m were obtained using Diamond DSC TG-DTA 6300 in flowing nitrogen (40 ml min^{-1}) at a heating rate of 10°C min^{-1}. Thermogravimetric analysis data were obtained with TGS-2TG-DTA 6300 under N_2 at a heating rate of 10°C min^{-1} up to 900°C. The temperature of 10% weight loss was taken as the decomposition temperature (T_d). XRD measurement was performed on a Bruker D8 Advance X-ray diffractometer with copper Kα radiation at tube voltage of 40 kV, current of 40 mA and data recorded at room temperature over 2θ range of 10-40°.

Synthesis of PEEK

In a three-necked flask, fitted with a Dean-Stark trap, condenser, mechanical stirrer and nitrogen inlet, 0.66 g (6 mmol) of hydroquinone, 1.31 g (6 mmol) of 4,4'-difluorobenzophenone and 1.24 g (9mmol) of K_2CO_3 were dissolved in a mixture of 15 ml of solvent and 35 ml of toluene. Toluene was used for azeotropic removal of water. The flask was set inside the microwave apparatus (Nanjing, NJL07-5, maximum power 700 W, 2455 MHz). The entire operation was conducted in a nitrogen atmosphere with continuous stirring. During the initial stage of the polymerization, the temperature was maintained at 80–110°C, the reaction mixture was heated under reflux for 20 minutes, and the water generated during the formation of the phenate was essentially removed from the reaction mixture by azeotropic distillation. After the water was removed, the temperature was maintained at 110-130°C for 15 min and toluene was distilled off at the same time. Then, the reaction was maintained at 180-200°C for different lengths of time. The reaction was cooled to room temperature and the polymer was obtained by precipitating from water. The product was refluxed with water and subjected to Soxhlet extraction with methanol. The clean-up of the polymer was carefully done to ensure that the solvent and the inorganic salts were removed fully. The polymer was then dried under vacuum at 100°C for 24 h.



Scheme 1. Synthesis of PEEK

Results and discussion

High efficiency synthesis by microwave radiation

As shown in Scheme 1, PEEK was synthesized in one step and with high yields as shown in Table 1 using microwave radiation. With the same reaction temperature and sulfolane as solvent, the highest yield was 96.1% with a reaction time of only 55 min and its η_{inh} value of the PEEK synthesized was 0.71dlg^{-1}, compared with conventional method for which the yield was only 76.2% for a reaction time of 6 hours and the η_{inh} value was 0.27 dlg^{-1}, which indicated that the molecular weight of PEEK by microwave irradiation was higher than that prepared by conventional heating. Microwave irradiation accelerated the reaction process and increased the yield. The microwave heating is the result of the absorption of microwave energy by a material exposed to the electromagnetic field distributed within a reflective cavity. In the presence of dipole moment, microwave heats up the reactive centers of the reagents directly enhancing energy transfer and accelerates the chemical reactions. Under conventional thermal conditions, the heat comes from the external environment and becomes less effective in the inner zone of the reaction solution.

Effect of irradiation time and solvent on product yield

With sulfolane as solvent, the reaction was maintained at 180-200°C for different irradiation times. As shown in Table 1, the yields of polymer were higher than 80% with irradiation time ≤120 min. The yield of polymer in sulfolane was 96.1% after 20 min microwave irradiation. But the yields of all the other samples are lower than that prepared with 20 min irradiation. The decrease in yield at longer irradiation could be due to the decomposition of the polymer formed [20,21].

Maintaining the reaction at 180-200°C for 20 min, the effect of solvent on the yield was also measured and the yields were higher than 85% (Table 1). The high yield could be attributed to the high polarity of solvents as it has been demonstrated that the greater the polarity of the solvent, the more pronounced the microwave effect [22]. The dielectric constant of these solvent are DMSO (46.7), NMP (32.0), sulfolane (43.0) and DMAc (37.8). The dielectric constants of all these solvents are higher than 30. The use of such an organic medium was necessary to induce effective homogeneous heating of the monomers [14].

The polymer is insoluble in all common organic or inorganic solvents, except conc. H_2SO_4. This could be due to the high crystallinity of PEEK and strong interaction between the chains as a result of their regularity, hence, decreasing the solubility.

Table 1. The effect of irradiation time and solvent on yield

Irradiation time ^{a} (min)	Solvent	Yield (%)	$\eta_{inh}{}^b$ (dLg^{-1})
20	Sulfolane	96.1	0.71
60	Sulfolane	80.2	0.24
80	Sulfolane	81.1	0.20
100	Sulfolane	85.2	0.26
120	Sulfolane	87.7	0.20
20	NMP	89.8	0.20
20	DMSO	86.2	0.16
20	DMAc	85.4	0.13

^{a} The irradiation time at 180-200 °C; ^{b} Measured at a concentration of 0.5 gdl^{-1} in concentrated sulfuric acid at 30 °C

Characterization of PEEK

The IR spectra of the PEEK was shown in Fig. 1, the band at 1649 cm^{-1} due to C=O stretching, 1596 cm^{-1} and 1490 cm^{-1} due to aromatic skeletal vibration, and the band at 1226 cm^{-1} attributable to the asymmetric stretching of the C-O-C bond. The p-substituents on the aromatic ring appear at 841 cm^{-1}. Thus, the functional groups in the main chain structure can be ascertained.

As shown in Fig. 2, XRD pattern of PEEK synthesized shows that it has an orthorhombic uniform structure, with four distinct peaks observed at $2\theta = 18.76°$, 20.70°, 22.84° and 28.77°, corresponding to the interplanar distances of 4.72, 4.28, 3.88 and 3.09 Å, respectively. This is in agreement with what has been reported for the PEEK crystal unit cells [1,11]. The sharp and diffuse patterns for PEEK were characteristic of semicrystalline polymers.

Thermogravimetric analysis was performed in the range 30~900°C in N_2 atmosphere. Fig. 3 shows the TGA/DTG curves of the PEEKs resulted from classical heating and MW. All of the polymers have a relatively high T_d at about 563°C. When the temperature was raised to 900°C, the residues weight % was about 45%. Only one weight loss step was observed, shown by one broad peak in the DTG curve. The weight loss, in the range 420~750°C corresponding to a minimum at about 586 and 607°C in the DTG curve, is due to the pyrolysis of the polymer. The results indicate that the product has good heat stability.

The PEEK powder exhibited no obvious glass transition temperature in the DSC measurements, but a crystallite melting point was detected at about 345°C.

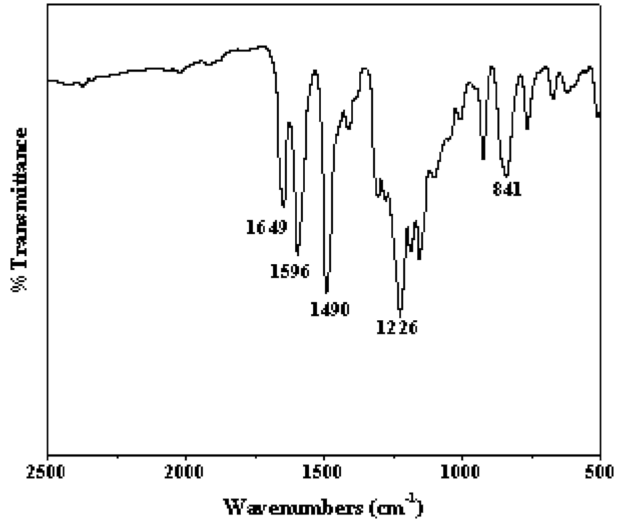


Fig 1. FTIR spectra of PEEK

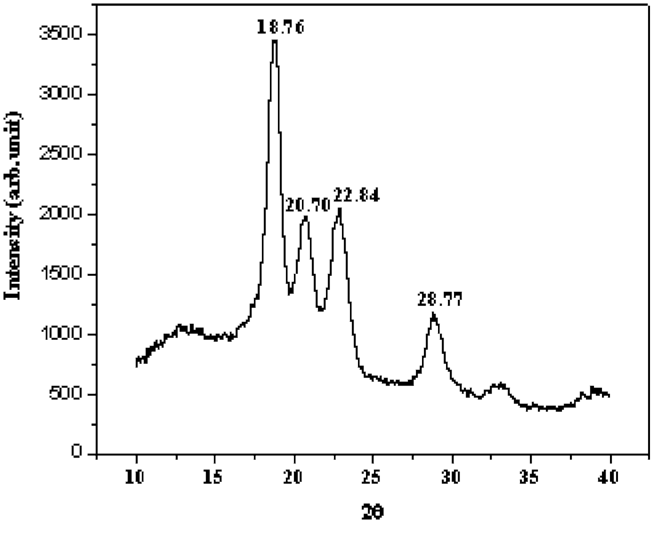


Fig 2. X-ray diffraction of PEEK

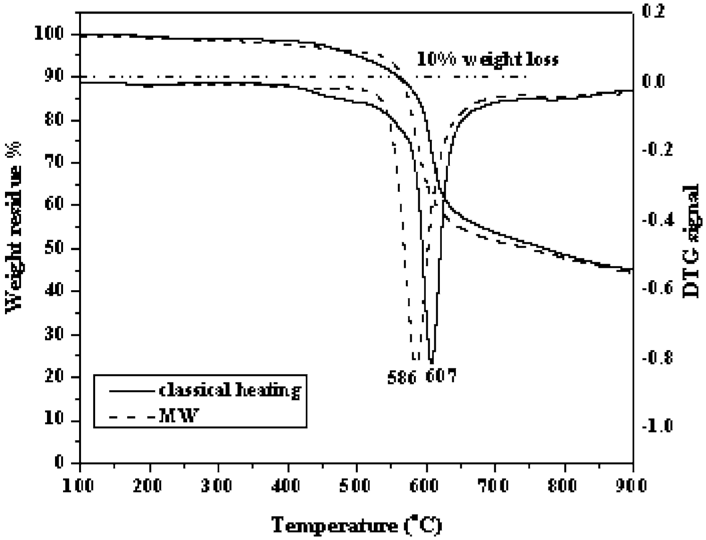


Fig 3. TGA and DTG curves of PEEK resulted from classical heating and MW

Conclusions

PEEK was successfully synthesized with a good yield under microwave irradiation which also accelerated considerably the process of nucleophilic polycondensation. Compared to classical thermal heating, it is an effective and novel alternative approach to prepare PEEK. The advantages of microwave-assisted production of PEEK are the shorter reaction time and an easier work-up.

Acknowledgements. This work is supported by the National Natural Science Foundation of China (Grant No. 50373052).

References

1. Woo EM, Tseng YC (1999) J Polym Sci Part B: Polym Phys 37:1485
2. Gao Y, Jian XG, Dai Y, Xue JM, Peng SM, Liu SJ (2000) J Appl Polym Sci 78:20
3. Meng YZ, Hlil AR, Hay AS (1999) J Polym Sci Part A: Polym Chem 37:1781
4. Gao Y, Jian XG, Xuan YN, Xiang S, Liang P, Guiver MD (2002) J Polym Sci Part A: Polym Chem 40:3449
5. Harrison WL, Wang F, Mecham JB, Bhanu VA, Hill M, Kim YS, Mcgrath JE (2003) J Polym Sci Part A: Polym Chem 41:2264
6. Zhang G, Liao H, Yu H, Ji V, Huang W, Mhaisalkar SG (2006) Coddet C. Surf Coat Technol 200:6690
7. Giants TW (1994) IEEE Trans Electr Insul 1:991
8. Salunke AK, Sharma M, Kute V, Banerjee S (2005) J Appl Polym Sci 96:1292
9. Gao X, Wang R, Zhang AQ (2007) Mater Lett 61:3647
10. Bottino FA, Pasquale GD, Leonardi N, Pollicino A (1998) Polym 39:3199
11. Goyal RK, Negi YS, Tiwari AN (2006) J Appl Polym Sci 100:4623
12. Mallakpour S, Kowsari E (2003) J Polym Sci Part A: Polym Chem 41:3974
13. Mallakpour S, Kowsari E (2004) J Appl Polym Sci 91: 2992

14. Mallakpour S, Zamanlou MR (2004) J Appl Polym Sci 91: 3281
15. Mallakpour SE, Hajipour AR, Zamanlou MR (2001) J Polym Sci Part A: Polym Chem 39: 177
16. Peng Y, Song G (2007) Catalysis Communications 8:111
17. Koopmans C, Iannelli M, Kerep P, Klink M, Schmitz S, Sinnwell S, Ritter H (2006) Tetrahedron 62:4709
18. Pal SK, Bisoyi HK, Kumar S (2007) Tetrahedron 63: 6874
19. Pimentel LCF, Andréa Luzia FDS, Fernández TL, Wardell JL, Antunes OAC (2007) Tetrahedron Letters 48:831
20. Mallakpour S, Rafiemanzelat F (2004) J Appl Polym Sci 93:1647
21. Mallakpour S, Rafiemanzelat F (2005) J Appl Polym Sci 98:1781
22. Loupy A (2004) C R Chimie 7:103