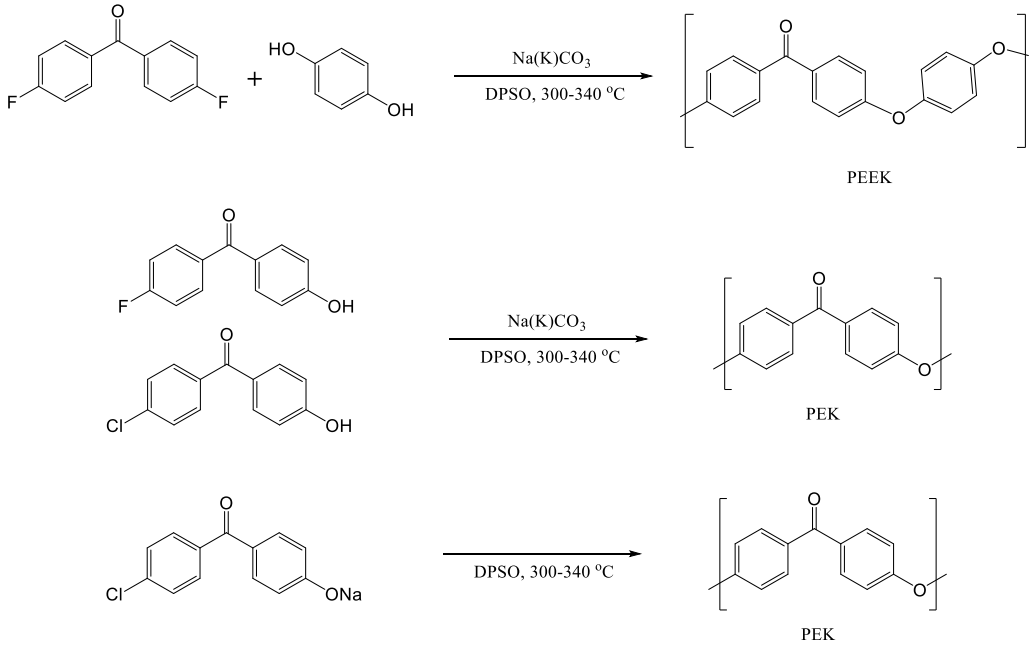
A method of synthesis of poly (arylene ether ketone)s

PAEKs, such as poly(ether ketone) (PEK), poly(ether ether ketone) (PEEK), poly(ether ether ether ketone) (PEEEK), and poly(ether ketone ether ketone ketone) (PEKEKK), are generally semi-crystalline and insoluble materials that exhibit a unique combination of physical and thermal stability, chemical and solvent resistance, good mechanical properties, good fire resistance, and good electrical performance. It is these properties that make these materials important for applications in the aerospace, automobile, nuclear, electronics, and many other high technology fields. They can be fabricated by conventional techniques and can also be applied as a matrix resin for high performance reinforced composites. The most widely used PAEKs are PEEK and PEK. In spite of its superior properties, commercial use PAEKs has been limited due to the high price, which is mainly restricted by the complex synthesis process. Hence the improvement of current synthetic routes for PAEKs production remains a necessity.

PAEKs are synthesized by polycondensation via Nucleophilic Aromatic Substitution (NAS) reactions. NAS reaction is done by first reacting a phenol with a base where upon the resulting anion then acts as the nucleophile. The nucleophile attacks the other monomer, usually an aryl halide activated by a strong electron-withdrawing group (such as ketone) in the ortho or para positions, leading to an anionic intermediate known as a Meisenhiemer complex. Loss of the halide, with a concurrent re-aromatization, affords the aryl ether bond. To get high molecular weight polymers, current processes for PAEKs production are using diphenyl sulfone solvent and the reaction is carried out at high temperature of 310 to 340 ^{o}C. This solvent system has been commercially used in PEEK and PEK production with different monomers, as shown below.



Scheme 1. Typical PAEKs (PEEK and PEK) synthesis route.

Most of the efforts in the literature on the synthesis of PAEKs are focused on the selection of monomers, bases and other reaction conditions such as temperature and protection gases. Diphenyl sulfone is a common solvent used in these processes. Although there are several other approaches by using lower boiling point solvents have been studied for the PAEKs production, these methods are not suitable for large scale production ether due to the presence of extra non-reactants/catalysts which are difficult to remove during the subsequent workup, or due to the lower reactivity under lower reaction temperature which result lower molecular weight polymers.

Diphenyl sulfone is a solid at room temperature. It's melting point is about 126 ^{o}C and boiling point is of 379 ^{o}C. Limitations for using diphenyl sulfone as solvent in PAEKs production including:

1. High melting point (126 ^{o}C) makes polymer product separation process very complex. After polymerization at high temperature, the PAEK polymers are always co-solidified together with diphenyl sulfone. Very intensive solvent extraction step is needed and yet it is very difficult to remove all diphenyl solvent from the product.
2. High viscosity of the reaction system with diphenyl sulfone solvent will affect the reaction rate and molecular weight of the polymer products.
3. Diphenyl sulfone will be slowly oxidized at the temperature over 300 ^{o}C. This property will require the high temperature polymerization reaction to be protected under high purity inner gas, such as N_2 or Ar. Even under protection, diphenyl sulfone will still be consumed significantly during the entire PAEKs production process.

To overcome the problem of diphenyl sulfone solvent in the process of PAEKs production, we proposed a mixture solvent system for this process. Ideally, the second solvent should be in liquid form at room temperature, boiling point should be high than 360 ^{o}C. And importantly, this solvent should be very stable at high temperature of 340 ^{o}C and basic condition (co-existed with carbonate base). Eventually, we identified poly-toluene, specifically dibenzyltoluene as the second solvent in the PAEKs production. Dibenzyltoluene, melting point is of -35 ^{o}C and boiling point is of 397 ^{o}C, viscosity is of 16 mm^2/s at 40 ^{o}C. Advantages of using mixture solvents include:

1. Lower viscosity of reaction mixture as comparing to diphenyl sulfone sole solvent system which will benefit the condensation reaction.
2. Simply the work up process, polymer product can be separated by filtration at relatively low temperature, such 50 ^{o}C-100 ^{o}C.
3. Mixture solvent could stabilize diphenyl sulfone. Dibenzyltoluene is stable under reaction condition which will also protect diphenyl sulfone from being oxidized.

The ratio of mixture solvent with dibenzyltoluene : diphenyl sulfone could be (0 : 100 to 90 : 10). The mixture solvent could potentially decrease the solubility of staring materials and other reactants, such as inorganic bases. This issue can be solved by introducing small amount of phase transfer catalyst, such as phosphonium or ammoniums. Typically, molar ratio of phase transfer catalyst to monomer is about 0.01% to 10%. The phase transfer catalyst can increase the reaction rate and improve the molecular weight of resulted polymer products.

Experimental section

Example 1: In a three-necked flask, fitted with condenser, mechanical stirrer and nitrogen inlet, 11.6 g of the 4-chloro,4'-hydroxy benzophenone (CHBP) was mixed with 20 g of diphenyl sulfone and 10 g of dibenzyl toluene. The reactor was protected with nitrogen gas flow. A thermo couple temperature indicator was present in the reactor to measure the reaction mixture temperature. To the reaction mixture, 26.2 mmoles of K_2CO_3/Na_2CO_3 (1:10) and 1 mmol of tetraphenyl phosphonium chloride (0.374 g) were added. The mixture was heated to 200 °C and maintained for one hour under nitrogen flow. The temperature was then increased to 250 °C and maintained at this temperature for 1 hour. The temperature was then increased to 310 °C to 320 °C and maintained at this temperature for 3 hours. The polymer was end capped by adding 1 mole% of 4-fluoro benzophenone and maintaining for 0.5 hrs. The reaction mixture was cooled to 150 °C and was filtered at 150 °C. The solid part was further extracted with toluene and washed with water. The extraction process was repeated until all the mixture solvent was leached out and mineral salts were fully removed. The final product was dried to give 9.5 g of white grey solids—a yield of 96% PEK polymer. The solids had an inherent viscosity of 1.03 dll/g.

Example 2: In a three-necked flask, fitted with condenser, mechanical stirrer and argon inlet, 4-chloro,4'-NaO-benzophenone (NaCHBP, 0.04 mol, 10.2 g) were added with 20 ml of DPSO and 5 ml of dibenzyl toluene. The reactor was protected under argon gas flow. Then the reaction mass was heated to 200 °C and maintained at this temperature for 1 hour and 250 °C and maintained at this temperature for 2 hrs. The reaction mixture was eventually heated to 315-320°C and maintained at this temperature for 5 hours. The polymer was end capped by adding 1 mol% of 4-fluoro benzophenone and maintaining for 0.5 hrs. The reaction mixture was cooled to 150 °C and discharged into 30 ml of toluene under stirring. The mixture was filtered and the solid part was further washed with toluene and water to remove DPSO/dibenzyl toluene and mineral salts. The final product was dried to give 9.2 g of white grey solids—a yield of 97% PEK polymer. The solids had an inherent viscosity of 0.95 dll/g.

Example 3: In a three-necked flask, fitted with condenser, mechanical stirrer and argon inlet, 3.3 g (30 mmol) of hydroquinone, 6.56 g (30 mmol) of 4,4'difluorobenzophenone were added in a mixture of 20 ml of DPSO and 20 ml of dibenzyl toluene. To the reaction mixture, 60.5 mmol of K_2CO_3/Na_2CO_3 (1:10) and 2 mmol of tetraphenyl phosphonium chloride (0.75 g) were added. The mixture was heated to 200 °C and maintained for two hours under argon flow. The temperature was then increased to 250 °C and maintained at this temperature for 1 hour. The temperature was then increased to 310 °C to 320 °C and maintained at this temperature for 4 hours. The polymer was end capped by adding 1 mole% of 4-fluoro benzophenone and maintaining for 0.5 hrs. The reaction mixture was cooled to 150 °C and was filtered at 150 °C. The solid part was further extracted with acetone and washed with water. The extraction process was repeated until all the mixture solvent was leached out and mineral salts were fully removed. The final product was dried to give 8.2 g of white grey solids—a yield of 95% PEK polymer. The solids had an inherent viscosity of 1.02 dll/g.

Example 4: In a three-necked flask, fitted with condenser, mechanical stirrer and argon inlet, 4-chloro,4'-NaO-benzophenone (NaCHBP, 0.04 mol, 10.2 g) and 1 mmol of tetraphenyl phosphonium chloride (0.374 g) were added with 20 ml of DPSO. The reactor was protected under argon gas flow. Then the reaction mass was heated to 200 °C and maintained at this temperature for 1 hour and 250 °C and maintained at this temperature for 1 hrs. The reaction mixture was eventually heated to 315-320°C and maintained at this temperature for 3 hours.

The polymer was end capped by adding 1 mol% of 4-fluoro benzophenone and maintaining for 0.5 hrs. The reaction mixture was cooled to 150 °C and discharged into 30 ml of toluene under stirring. The mixture was filtered and the solid part was further washed with toluene and water to remove DPSO and mineral salts. The final product was dried to give 9.3 g of white grey solids—a yield of 98% PEK polymer. The solids had an inherent viscosity of 1.12 dll/g.

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Summary

In a first aspect, the present disclosure relates to a method for preparing the poly (arylene ether ketone)s polymer materials as described herein, compromising the steps of mixing of organic monomers and bases with or without of phase transfer catalysts in a solvent system at elevated temperature for a time duration.

The method may further comprise the steps of collection of products by filtration at elevated temperature and washing.

The solvent can be diphenyl sulfone (DPS), dibenzyl toluene or their mixture.

The temperature for reaction may be from 150 ^{o}C to 340 ^{o}C. The temperature for filtration/collection may be from 50 ^{o}C to 170 ^{o}C. The time duration may be from 5 to 25 hours.

The phase transfer catalyst may be phosphoniums, ammoniums or crown ethers. The catalyst molar ratio may be from 0 to 10%.

Claims:

1. A process for the production of the poly (arylene ether ketone)s polymer materials (PEK, PEEK) compromising the steps of mixing of organic monomers and bases with or without of phase transfer catalysts in a solvent system at elevated temperature for a time duration.
2. A process as claimed in claim 1, wherein the compatible solvent is diphenyl sulfone (DPS), dibenzyl toluene or their mixture.
3. A process as claimed in claim 1 wherein the compatible reaction temperature for reaction may be from 150 ^{o}C to 340 ^{o}C.
4. A process as claimed in claim 1 wherein the compatible the reaction time duration may be from 5 to 25 hours.
5. A process as claimed in claim 1 wherein the method may further comprise the steps of collection of products by filtration at elevated temperature and washing.
6. A process as claimed in claim 5 wherein the compatible processing temperature for filtration/collection may be from 50 ^{o}C to 170 ^{o}C.
7. A process as claimed in claim 5 wherein the compatible washing solvent may be toluene.
8. A process as claimed in claim 1 wherein the compatible phase transfer catalyst may be phosphoniums, ammoniums or crown ethers.
9. A process as claimed in claim 8 wherein the compatible phase transfer catalyst molar ratio may be from 0 to 10%.