PART ONE

SYNTHESIS OF AROMATIC POLYKETONES VIA SOLUBLE PRECURSORS DERIVED FROM BIS(α-AMINONITRILE)S

Chapter 1

Literature Overview of Poly(arylene ether ketone) Synthesis

1.1 Introduction

Poly(arylene ether ketone)s (PAEKs), such as PEK, PEKK and PEEK (Scheme 1.1), are an important class of high performance engineering thermoplastics displaying a unique combination of thermal stability, chemical and solvent resistance, good mechanical properties over a wide temperature range, good fire resistance and good electrical performance.[1,2,3] These polymers can be fabricated by conventional techniques, such as extrusion and compression molding, and can be applied as matrix resins for high performance reinforced composites. The T_g and T_m values of some major examples of PAEKs are summarized in Table 1.1.[4,5,6,7] Compared to poly(arylene ether sulfone)s, which are usually amorphous polymers and subject to attack by solvents, PAEKs are semicrystalline polymers and therefore resistant to solvents, which is a critical factor in an aerospace environment. However, because of their crystallinity and the resulting insolubility, together with melting points generally above

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[1] Staniland, P. A. Poly(ether ketone)s in *Comprehensive Polymer Science*; Allen, G.; Bevington, J. C., eds.; Pergamon Press: New York, **1989**, Vol. 5, pp 484-497.

[2] Lakshmana, V. R. *J. Mater. Sci.* **1995**, 35, 661.

[3] Dahl, K. J.; Jansons, V. In *Polymers and Other Advanced Materials: Emerging Technologies and Business Opportunities*, Prasad, P. N. ed., Plenum Press: New York, **1995**, pp 69-81.

[4] Harris, J. E.; Robeson, L. M. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, 25, 311.

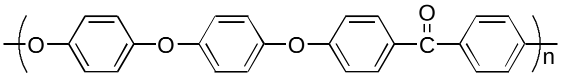
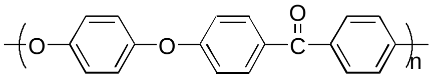
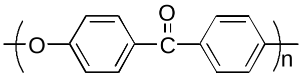
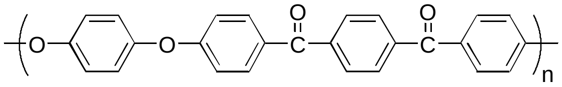
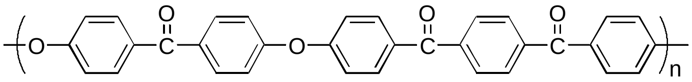
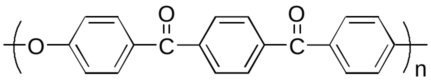
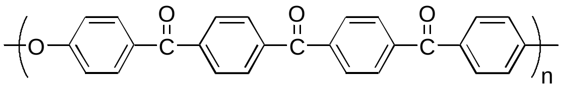
[5] Marks, B. M. US Patent 3,441,538 (**1964**).

[6] Starkweather, H. W. In *Encyclopedia of Polymer Science and Engineering*, John Wiley and Sons: New York, 2nd ed., **1987**, vol. 10, pp 369-373.

[7] Staniland, P. A.; Wilde, C. J.; Bottino, F. A.; Di Pasquale, G.; Pollicino, A.; Recca, A. *Polymer* **1992**, 33, 1976.

300 °C, these polymers are also difficult to prepare with sufficiently high molecular weight unless extreme reaction conditions are used.

Table 1.1 The T_g and T_m values of representative PAEKS

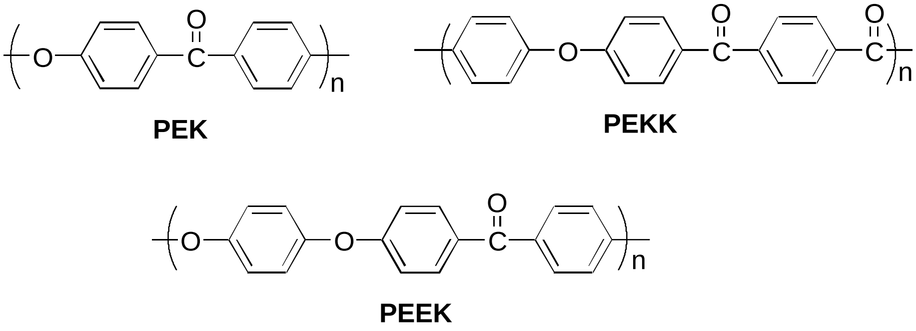
Polymer	Structure	T_g	T_m	Ref
PEEEK		129	324	4
PEEK[a]		144	334	3
PEK[b]		163	361	5
PEEKK		154	358	4
PEKEKK[c]		173	371	3
PEKK		165	391	6
PEKKK		175	439	7

a). “VICTREX PEEK”, ICI

b). “STILAN”, Raychem Corporation

c). “ULTRAPEK”, BASF

Scheme 1.1



PAEKs are generally synthesized by an aromatic nucleophilic substitution reaction of activated aryl dihalides with aromatic diphenolates in a dipolar aprotic solvent, or by electrophilic (Friedel-Crafts) acylation of aryl ethers.

1.2 Synthesis of Poly(arylene ether ketone)s

1.2.1 Electrophilic Routes

In 1962, Bonner[8] at DuPont was the first one who reported the synthesis of wholly aromatic poly(ether ketone ketone)s (PEKK) by Friedel-Crafts acylation. Isophthaloyl chloride or terephthaloyl chloride was condensed with diphenyl ether using nitrobenzene as solvent and aluminum trichloride as a catalyst (Scheme 1.2). However, only low molecular weight polymers (inherent viscosity, IV ~ 0.18 dL/g) were obtained. In 1964, Goodman[9] at ICI reported the successful synthesis of poly(ether ketone) (reduced viscosity, RV ~ 0.5 dL/g) by the self-condensation of *p*-phenoxybenzoyl chloride under similar conditions using methylene chloride as solvent.

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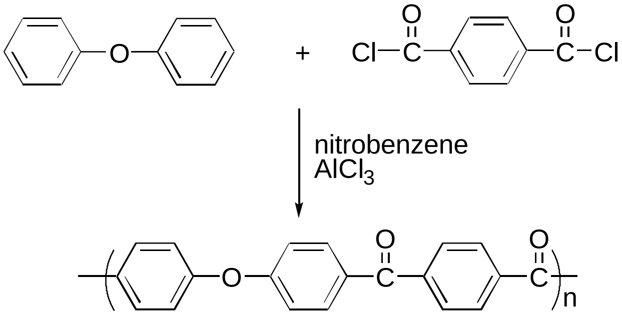
[8] Bonner, W. H. US Patent 3,065,205 (**1962**).

[9] Goodman, I.; McIntyre J. E.; Russell, W. Brit. Patent 971, 227 (**1964**); *Chem. Abstr.* **1964**, 61, 14805b.

Scheme 1.2



PEKK

Aluminum chloride catalyzed polycondensation of diphenyl ether with mixtures of terephthaloyl chloride and isophthaloyl chloride is a low cost route to poly(ether ketone ketone)s. The reactions are carried out in the presence of an excess of aluminum chloride in non-basic solvents such as 1,2-dichloroethane, dichloromethene, or *o*-chlorobenzene.[10] The insolubility of the polymers in these solvents limits the formation of high molecular weight polymers. Special treatment is usually required to improve the melt stability. In some cases, *ortho*-acylation and alkylation of aromatic polymer chains also occur.[11]

The low cost acid chlorides, such as terephthaloyl chloride and isophthaloyl chloride, are weaker base than 4,4'-oxybisbenzoyl chloride and more difficult to activate by $AlCl_3$. The resulting carbocationic intermediates are more reactive and less selective to aromatic sites, which leads to increased *ortho*-acylation during polymerization.

Polymerizations in the presence of a large excess of $AlCl_3$ complexed with a Lewis base, such as DMF, LiCl, dimethyl sulfone, pyridine or *N*-methylpyridinium chloride, were

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[10] Brugel, E. (to DuPont), US Patent 4,987,171 (**1991**).
[11] Clendinning, R.; Kelsey, D.; Botkin, J.; Winslow, P.; Yousefi, M.; Cotter, R.; Matzner, R.; Kwiatowski, G. *Macromolecules* **1993**, 26, 2361.

reported by Jansons *et al*. to produce cleaner and higher molecular weight polymers at or below room temperature.[12,13] The Lewis base can complex with $AlCl_3$ to keep excess $AlCl_3$ in the solution. The complex adducts can be dissolved in a non-basic solvent, such as CH_2Cl_2 or 1,2-dichloroethane. The polar complex solutions also increase the solubility of polymer complexes that lead to high molecular weight polymers. Most of the work in this area was submitted for patents. One of the examples in literature publications was reported by Fukawa and Tanabe.[14] *p*-Phenoxybenzoyl chloride was polymerized in the presence of excess $AlCl_3$ and phenyl ether capping agent in a solution of DMF in methylene chloride to give PEK with 1.37 dL/g inherent viscosity.

Alternatively, PEKK can be obtained by condensation of isophthaloyl chloride and/or terephthaloyl chloride with isolated intermediates such as 4,4'-diphenoxyterephthaloylphenone and 4,4'-diphenoxyisophthoylphenone. These polymerizations yield cleaner polymers, especially in the presence of $AlCl_3$ complexed with a basic co-agent. The copolymer was prepared by Gay and Brunette[15] at DuPont from the isolated intermediates, 1,3-bis(*p*-phenoxybenzoyl)benzene with terephthaloyl chloride, and 1,4-bis(*p*-phenoxybenzoyl)benzene with isophthaloyl chloride (Scheme 1.3). This perfectly alternating copolymer of *meta* and *ortho* phenylene group has high T_g (166 °C) and low T_m (332 °C), which is desirable for facile processing and high heat deformation resistance.

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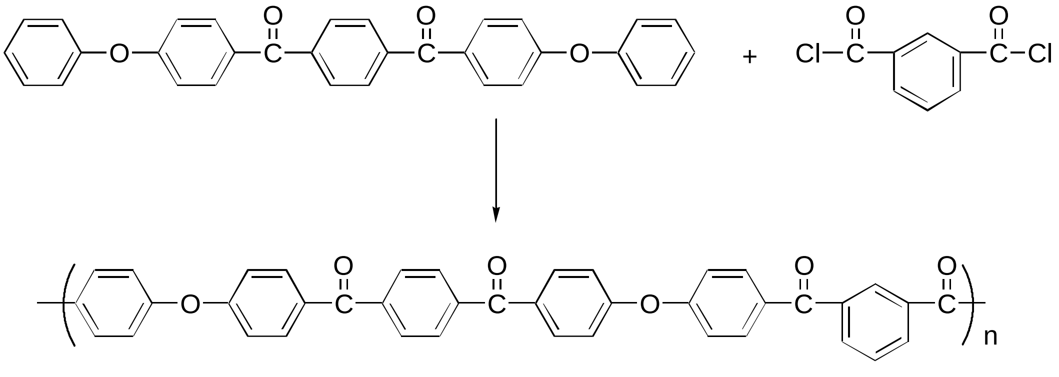
[12] Jansons, V.; Gors, H. C. PCT Int. Appl. WO 84 03, 891 (**1984**).

[13] Jansons, V.; Gors, H. C.; Moore, S.; Reamey, R. H.; Becker, P. (Raychem Corp.) US Patent 4,698,393 (**1987**).

[14] Fukawa, I.; Tanabe, T. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, 31, 535.

[15] Gay, F.; Brunette, C. US Patent 4,816,556 (**1989**).

Scheme 1.3


Alternating PEKK copolymer

Polyphosphoric acid can be used as a solvent to produce high molecular weight poly(ether ketone ketone)s. Previously, Iwakura[16] reported the synthesis of PEK with inherent viscosity of 0.5 dL/g by self-condensation of *p*-phenoxybenzoic acid using polyphosphoric acid as the solvent and catalyst. Later, diphenyl ether was also used to condense with diacids or diacid chlorides in the presence of $AlCl_3$ or $SnCl_4$ to produce high molecular weight poly(ether ketone)s.[17] One of the reasons for the formation of high molecular weight polymers is polyphosphoric acid dissolves the polymers probably by protonation of the carbonyl groups.

Mark[5] developed a more effective solvent/catalyst (HF/BF_3) system to synthesize high molecular weight PEK. Under well-controlled reaction conditions, high molecular weight PEK with an inherent viscosity of 1.33 dL/g was prepared in HF/BF_3 solvent system. Large excesses of solvent and catalyst have to be used to obtain high molecular weight polymers.

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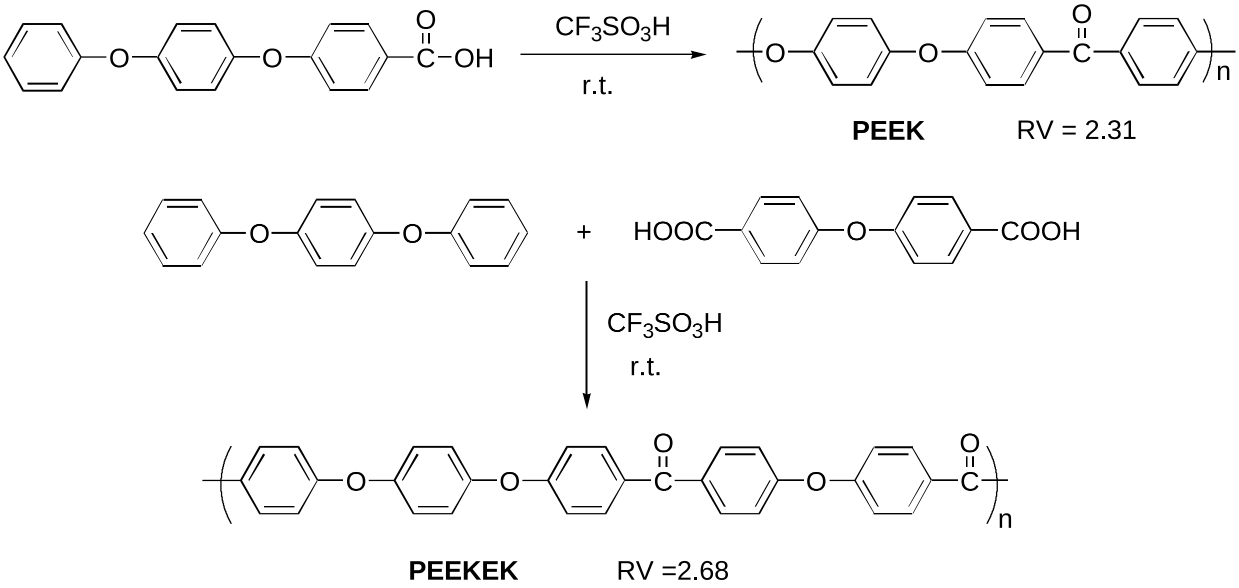
[16] Iwakura, Y.; Uno, K.; Takiguchi, T. *J. Polymer Sci.*, Part A-1 **1968**, 6, 3345.
[17] Devaux, J.; Delimoy, D.; Daost, D.; Legras, R.; Mercier, J. P.; Straszielle, C.; Nield, E. *Polymer* **1985**, 26, 1994.

Another strong acid system, trifluoromethanesulfonic acid, was reported by Rose[18] to catalyze the condensation of carboxylic acid with activated phenyl ether (Scheme 1.4). High molecular weight polymers were synthesized using this solvent system. For semi-crystalline PAEKs, replacement of CF_3SO_3H with the less expensive CH_3SO_3H failed to yield high molecular weight polymers. These two strong acid systems are not very attractive for industrial applications due to the harsh reaction conditions and cost factors.

Scheme 1.4



1.2.2 Nucleophilic Routes

The nucleophilic aromatic substitution reaction involves use of activated aromatic dihalides and aromatic diphenolates. The general reaction is shown in Scheme 1.5. In general, a strong electron withdrawing group such as carbonyl, sulfone or phosphine oxide is

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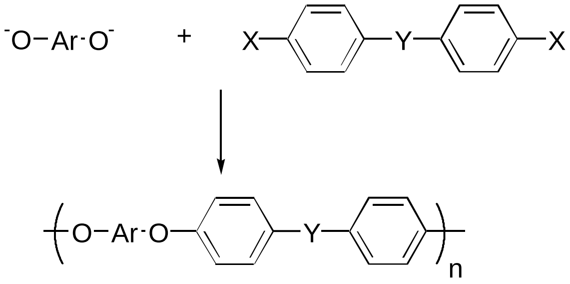
[18] Rose, J. B. European Patent 63, 874 (**1983**); *Chem. Abstr.* **1983**, 98, 180081.

necessary to activate the aromatic dihalides. The reactivity of the halogens are in the order of F>>Cl>Br. Typically potassium carbonate is used as base to avoid the side reaction of alkali metal hydroxides[19] and dipolar aprotic solvents such as DMSO, DMAc and NMP are utilized.

Scheme 1.5



X = F, Cl; Y = SO_2, CO, etc.

Johnson *et al*.[20] reported the first attempt to synthesize PEEK by polycondensation of bisphenolate with activated dihalides using DMSO as a solvent and NaOH as a base. High molecular weight polymers were difficult to obtain due to the crystallinity and the resulting insolubility of polymers in DMSO. To circumvent the solubility problem, Attwood[21] and Rose[22] used diphenyl sulfone as a solvent to obtain high molecular PEEK (Scheme 1.6). The polymerization was carried out near the melting point of the polymer to maintain solubility. Victrex PEEK was commercialized by ICI in 1982 using this method. At high temperatures, side reactions such as ether exchange and cleavage became important. Under careful optimization, high molecular weight poly(ether ketone)s can be obtained.

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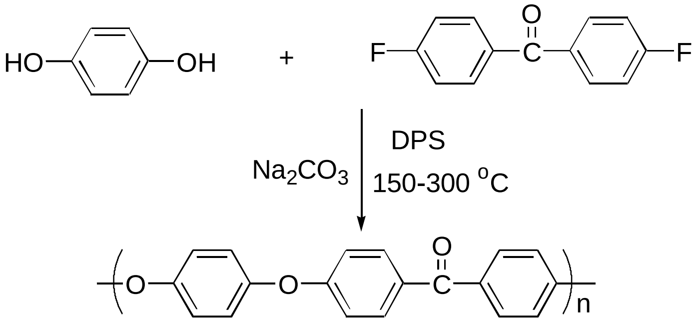
[19] Mohanty, D. K.; Sachdeva, Y.; Hedrick, J. L.; Wolfe, J. F.; McGrath, J. E. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1984**, 25, 19.

[20] Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci.*, Part A-1, **1967**, 5, 2375.

[21] Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, 20, 1204.

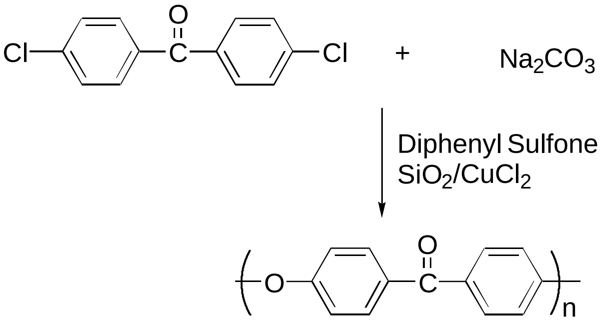
Scheme 1.6



PEEK

One of the major drawbacks for this synthetic route is the expense of fluoro monomers. For dihalides activated with carbonyl groups, less reactive chloro monomers fail to produce high molecular weight polymers. Side reactions such as single electron transfer reaction were observed during polymerization of dichlorides.[23-24]

Scheme 1.7



PEK

To develop a low cost route to PAEKs, expensive fluoro monomers are being replaced with activated chloro monomers. Fukawa[25] successfully prepared high molecular weight PEK

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[22] Rose, J. B.; Staniland, P. A. US Patent 4,320,224 (**1982**).

[23] Percec, V.; Clough, R. S. *Macromolecules* **1994**, 27, 1535.

[24] Percec, V.; Clough, R. S.; Grigors, M.; Rinaldi, P. L.; Litman, V. E. *Macromolecules* **1993**, 26, 3650.

[25] Fukawa, I.; Tanabe, T.; Dozono, T. *Macromolecules* **1991**, 24, 3838.

with 1.15 dL/g inherent viscosity using 4,4'-dichlorobenzophenone (Scheme 1.7). The polymerization was carried out in diphenyl sulfone at high temperature (2 hours at 280°C, 1 hour at 300 °C, and then 1 hour at 320°C) using 4,4'-dichlorobenzophone to react with sodium carbonate in the presence of $SiO_2/CuCl_2$ catalyst. SiO_2 was removed by washing with 4% aqueous NaOH solution at 60 °C.

Dichloro monomers were also polymerized with bisphenols in the presence of fluorides as promoting agents.[26] The fluoride ions promote the displacement of the chloride sites to form more reactive fluoride sites, which react with phenoxide anion to form high molecular weight polymers. The nucleophilicity and solubility of phenoxide anion increased by adding 5-10 mol % phase transfer catalysts such as *N*-alkyl-4-(dialkylamino)pyridium chlorides.[27] The reaction time to obtain the same molecular weight was reduced up to 5 fold compared to the uncatalyzed reaction.

Kricheldorf and coworkers[28,29] used trimethylsilylated phenols to react with activated difluoro monomers, such as 4,4'-difluorobenzophenone, in the presence of CsF to prepare poly(ether ketone)s. The polymers were prepared in the melt without the use of base and solvent. The volatile side product, trimethylsilyl fluoride, can be removed at high temperature.

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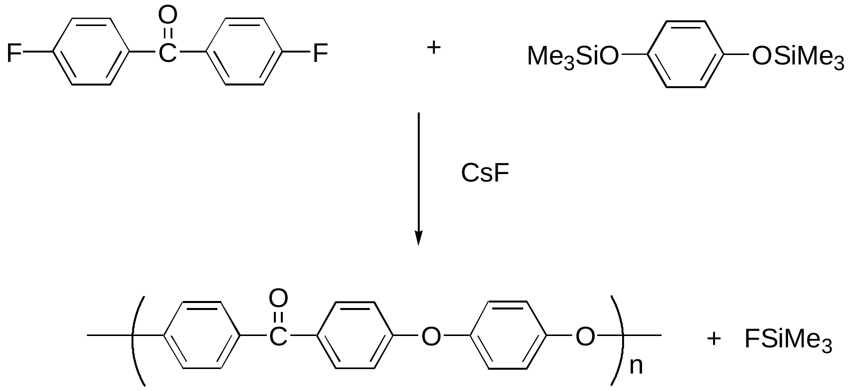
[26] Ebata, S.; Higuchi, Y. (to Mitsuhishi Gas Chem. Co.) Eur. Pat. Appli. EP 88 11407 (**1988**).

[27] Hoffmann, U.; Helmer-Metzmann, F.; Klapper, M.; Mullen, K. *Macromolecules* **1994**, 27, 3575.

[28] Kricheldrof, H. R.; Bier, B. *Polymer* **1984**, 25, 1151.

[29] Kricheldrof, H. R.; Delius, U. *Macromolecules* **1989**, 22, 517.

Scheme 1.8



1.2.3 Soluble Precursor Approaches

Despite the success of electrophilic and nucleophilic routes, harsh reaction conditions are usually required to obtain high molecular weight poly(ether ketone)s. To address the solubility problems, several soluble precursor approaches were reported to initially produce high molecular weight, soluble precursors, which could then be chemically modified to remove the solubilizing groups.

McGrath[30] and later Sogah[31] independently reported the synthesis of soluble high molecular weight PEEK containing pendent t-butyl groups in the polymer backbone (Scheme 1.9). *t*-Butylhydroquinone was polymerized with 4,4'-difluorobenzophone in DMSO at relatively low temperature (170 °C). Polymers with inherent viscosity up to 2.7 dL/g(in H_2SO_4) were obtained. Retro Friedel-Crafts alkylation in the presence of Lewis acid catalysts such as CF_3SO_3H removed the *t*-butyl substituents to produce high molecular PEEK.

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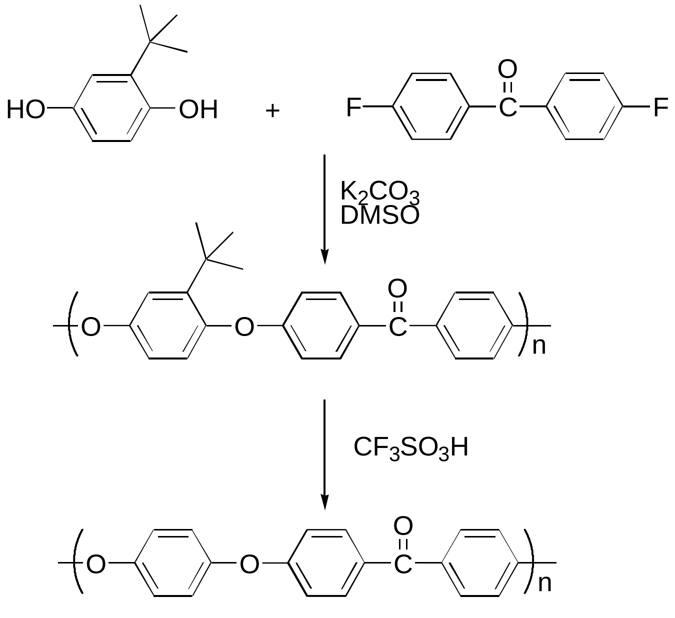
[30] Mohanty, D. K.; Lin, T. S.; Ward, T. C.; McGrath, J. E. *Int. SAMPE Symp. Exp.* **1986**, 31, 945.
[31] Risse, W.; Sogah, D. Y. *Macromolecules* **1990**, 23, 4029.

Scheme 1.9



PEEK

Kelsey *et al.*[32] used the cyclic ketal of 4,4’-dihydroxybenzophenone to polymerize with 4,4’-difluorobenzophenone in DMAc at 150 °C (Scheme 1.10). The polymerization produced soluble amorphous polyketal, which was quantitatively converted to PEK by acid catalyzed hydrolysis. Since the polymerization is carried out at lower temperatures, PEK with minimal defect structures can be obtained by this process. Compared to PEEK prepared under the usual high temperature conditions (diphenyl sulfone as solvent), PEK produced by this approach displayed excellent physical properties, especially the high degree of crystallinity and higher T_g, which indicate a uniform linear backbone structure.

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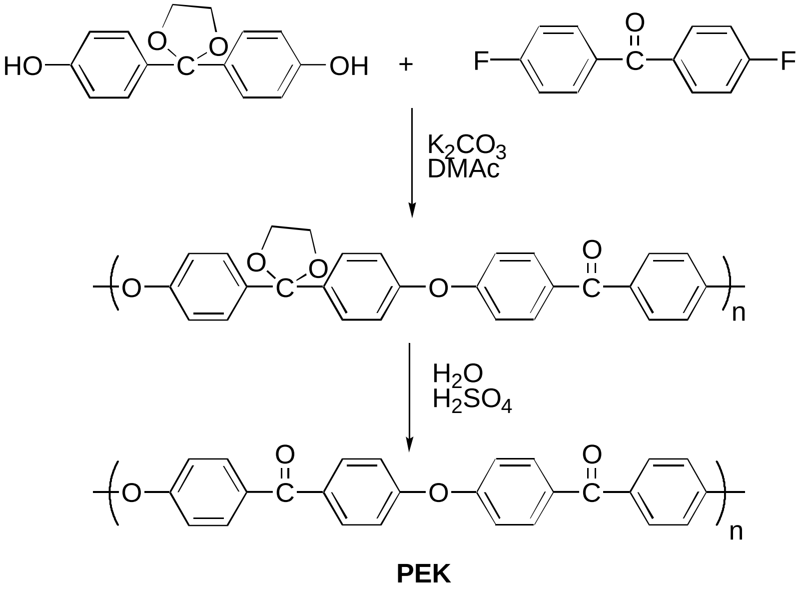
[32] Kelsey, D. R.; Robeson, L. M.; Clendinning, R. A. *Macromolecules* **1987**, 20, 1204.

Scheme 1.10



McGrath and coworkers[33] developed another method to produce soluble precursor for PEEK using the Schiff base (ketimine) of 4,4'-difluorobenzophenone to polymerize with hydroquinone in NMP at lower temperature (Scheme 1.11). The amorphous polyketimines were synthesized in high molecular weight and converted to poly(ether ketone)s by acid catalyzed hydrolysis. Later, the Schiff base of 4,4'-dichlorobenzophenone was polymerized in the presence of zinc dust and complexes of $NiCl_2$ with triphenylphosphine and 2,2'-bipyridine in NMP at 80 °C to form a soluble polyketimine of 0.36 dL/g inherent viscosity in NMP.[34] This polyketimine was hydrolyzed with dilute HCl to give crystalline polyketone.

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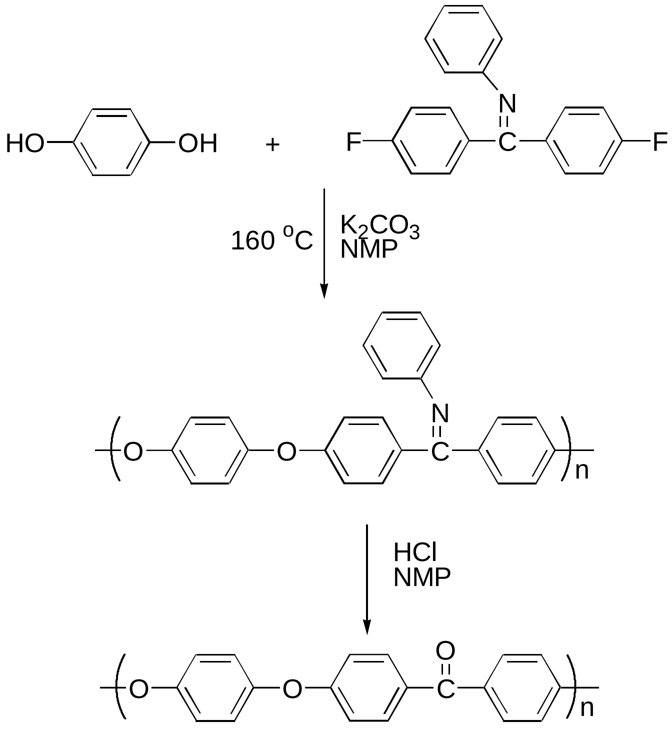
[33] Mohanty, D. K.; Lowery, R. C.; Lyle, G. D.; McGrath, J. E. *Int. SAMPE Symp. Exp.* **1987**, 32, 408.

[34] Phillips, R. W.; Sheares, V. V.; Samulski, E. T.; DeSimone, J. M. *Macromolecules* **1994**, 27, 2354.

Scheme 1.11



PEEK

In 1993, Pandya, Yang and Gibson[35] developed a new polyketone synthesis based on the nucleophilic substitution of bis(α-aminonitrile) derivatives with activated aromatic dihalides. Bis(α-aminonitrile)s were prepared from aromatic dialdehydes in high yield by Strecker synthesis. The conjugate bases of the α-aminonitriles are powerful and selective nucleophiles, which can react with activated aromatic dihalides to form a carbon-carbon bond. Polymerization of isophthalaminonitrile with 4,4'-difluorophenyl sulfone in anhydrous DMF at room temperature using NaH as base gives a soluble high molecular weight polyaminonitrile

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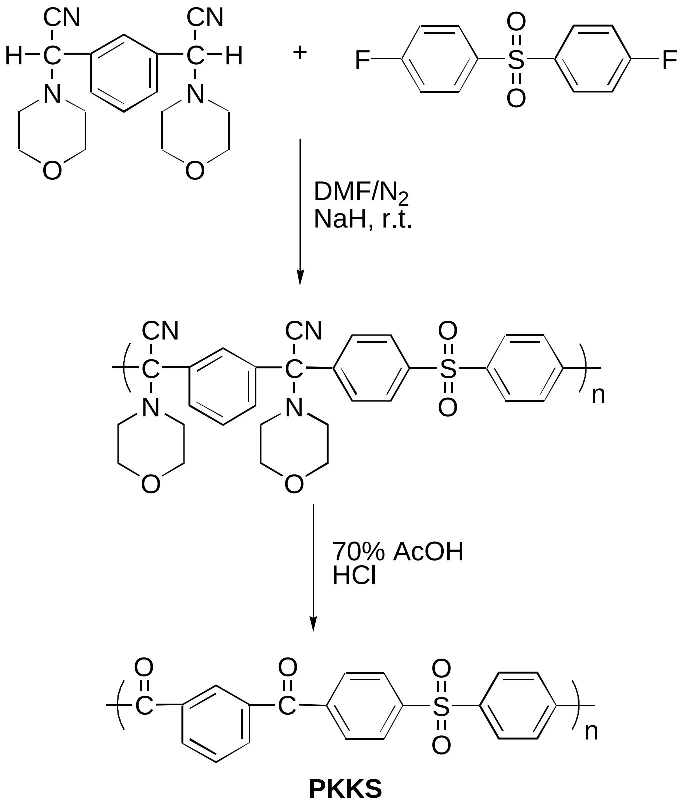
[35] Pandya, A.; Yang, J.; Gibson, H. W. *Macromolecules* **1994**, 27, 1367.

(Scheme1.12). Acid hydrolysis of this polyaminonitrile yielded the corresponding poly(ketone ketone sulfone).

Scheme 1.12



1.2.4 Other Routes

A. Carbon-Carbon Coupling Routes

Nickel-catalyzed coupling of chlorophenyl groups in a dipolar aprotic solvent such as DMAc was reported to produce poly(ether ketone)s.[36] Dichlorides containing ether and ketone linkages polymerized in the presence of Zn/$NiCl_2$ complexes with triphenylphosphine

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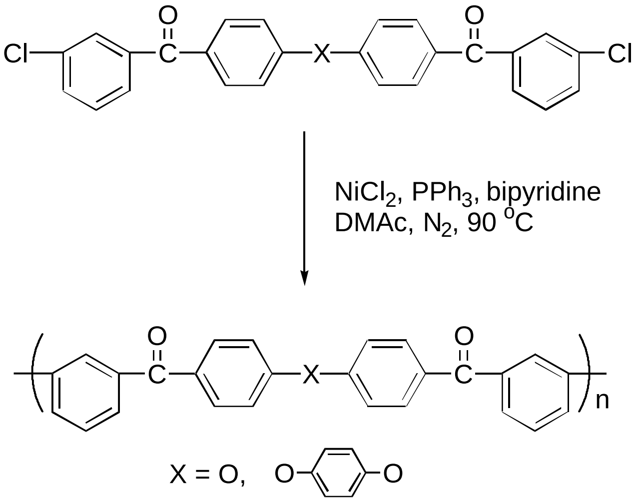
[36] Ueda, M.; Ichikawa, F. *Macromolecules* **1990**, 23, 926.

and bipyridine in DMAc at 90 °C (Scheme 1.13). For soluble *meta* isomers, poly(ether ketone)s with inherent viscosity up to 0.87 dL/g (in NMP) could be obtained. The reaction must be performed under an inert atmosphere and in the absence of water. The zinc dust used must have a low level of oxide and a high surface area. The optimum reaction temperature in DMAc was about 80°C. Higher reaction temperatures gave lower molecular weight. Because of their crystallinity and the resulting insolubility in DMAc, poly(ether ketone)s with all *para*-linkages could not be obtained in high molecular weight.

Scheme 1.13



Colon *et al.*[37] prepared poly(ether sulfone ketone) copolymers by copolymerizing 4,4'-bis(p-chlorophenoxy)diphenyl sulfone and aryl dichlorides such as 4,4'dichloro-benzophenone (RV = 0.58 dL/g). The key for a successful preparation of high molecular weight polymer is the solubility of the monomer and the obtained polymer in the reaction medium. For low solubility semicrystalline poly(ether ketone)s, high molecular weight polymers are difficult to

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[37] Kwiatkowski, G. T.; Colon, I. In *Contemporary Topics in Polymer Science*, vol. 7, Salamone, J. C. and Riffle, J. S. Ed., Plenum Press: New York, **1992**, pp 57-74

synthesize by this carbon-carbon coupling route unless a better solvent is found or monomers with solubilizing groups are used.

Deeter and Moore[38] reported an aromatic polyketone synthesis based on palladium catalyzed cross-coupling of aromatic diacid chlorides and bis(trimethylstannane) monomers. The polymerization can be carried out under mild conditions (70 °C) and polymers without ether linkages can be synthesized from this method. One of the major drawbacks is that high molecular weight polyketones can not be obtained in the absence of alkyl substituents.

B. Ring Opening Polymerization

Recently nucleophilic ring opening polymerization of macrocyclic arylene ether ketone oligomers has been reported as a means of direct conversion of low viscosity cyclic species to form high performance poly(ether ketone)s. Colquhoun[39] at ICI reported the first synthesis of macrocyclic monomers containing ether and ketone linkages through nickel catalyzed coupling of aryl dihalides under pseudo high dilution conditions. Gibson and Chen[40,41,42] synthesized poly(ether ether ketone) single size macrocycles and macrocyclic oligomer mixtures by both nucleophilic aromatic substitution and Friedel-Crafts acylation. The ring opening polymerization is initiated by a catalytic amount of nucleophiles, such as CsF or potassium salts of phenoxides. Control of ring opening polymerization is difficult. Complete

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[38] Deeter, G. A.; Moore, J. S. *Macromolecules* **1993**, 26, 2535.

[39] Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; O’Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 336.

[40] Chen, M.; Fronczek, F.; Gibson, H. W. *Macromol. Chem. Phys*., **1996**, 197, 4069.

[41] Chen, M.; Gibson, H. W. *Macromolecules*, **1996**, *29*, 5502.

[42] Chen, M.; Gibson, H. W. *Macromolecule*, **1997** 30, 2516.

conversion of the monomers is very difficult to achieve. In some cases, melting points of the cyclics or cyclic mixtures are too high for practical ring opening polymerization.

1.3 Summary and Conclusions

Poly(arylene ether ketone)s are commercially available under different trade names. These polymers are suitable for harsh environments or premium applications justifying the relatively high cost. PAEKs are generally synthesized by electrophilic or nucleophilic routes. Each route has its own problems and limitations. For electrophilic routes, large amounts of Lewis acid catalysts or harsh reaction conditions are usually required to achieve solubilization and high molecular weight. For nucleophilic routes, high reaction temperatures and expensive fluoro monomers are required to produce high molecular weight polymers. Attempts to develop low cost routes to PAEKs often lead to low molecular weight polymers, or difficult to remove impurities, or polymers containing structural defects. $AlCl_3$ complexed with basic co-agent systems allow effective and cleaner polymerization at low temperatures for electrophilic routes. Expensive fluoro monomers used in nucleophilic routes are being replaced by activated chloro monomers. To address the solubility problem, several approaches utilizing soluble precursors were reported to produce high molecular weight PAEKs. However, an extra step is required to remove the solubilizing groups.

Despite the large amount of work in this area, there are very few reports of polymers with backbones consisting of arylene and carbonyl groups only. These polyketones can not be synthesized by nucleophilic routes that would require the use of phenoxide anion. Polyketones without ether linkages synthesized by Friedel-Crafts acylation are often of low molecular weight due to insolubility. Wholly aromatic polyketones without ether linkages and alkyl substituents in the polymer backbone can be synthesized using soluble precursors derived from bis(α-aminonitrile)s under mild reaction conditions. The details are described in later chapters.