Predicting Glass Transition Temperatures of Polyarylethersulphones Using QSPR Methods

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Abstract

The technique of Quantitative Structure Property Relationships has been applied to the glass transition temperatures of polyarylethersulphones. A general equation is reported that calculates the glass transition temperatures with acceptable accuracy (correlation coefficients of between 90–67%, indicating an error of 10–30% with regard to experimentally determined values) for a series of 42 reported polyarylethersulphones. This method is quite simple in assumption and relies on a relatively small number of parameters associated with the structural unit of the polymer: the number of rotatable bonds, the dipole moment, the heat of formation, the HOMO eigenvalue, the molar mass and molar volume. For smaller subsets of the main group (based on families of derivatives containing different substituents) the model can be simplified further to an equation that uses the volume of the substituents as the principal variable.

Introduction

Poly(arylene ether sulphone)s were originally developed during the 1960s following independent research work by the 3 M Corporation [1], Union Carbide [2] and the Plastics Division of ICI [3] to develop thermally stable thermoplastics suitable for engineering applications. The materials are highly aromatic polymers that comprise phenylene backbones bridged with heteroatoms (O, S) or groups (SO2, CH2, CH2CH3, etc.), to offer thermal stability, good mechanical properties, creep resistance, and chemical resistance. These polymers have now reached a degree of maturity with many variants having been reported in both laboratory and commercial publications, and have been reviewed extensively [4]. Commercial products (e.g. Udel, Radel, and Victrex) are now available in a variety of grades and whether reliable, published empirical data were available for their corresponding Tg values are given in supporting information, Table S1 [3,5,8,10,11,13–47]. They are listed in terms of ID number. The ID numbers are used hereafter in the text.

The Data Set

A series of 66 polyarylene ether sulphones comprising between 1 and 4 phenylene rings in the structural repeat unit (SRU) were selected from a range of sources detailed in supporting information, Table S1. The rationale for selection was based on whether the structures offered a wide variety of different structural types and whether reliable, published empirical data were available for the polymer. The complete set of polyarylene ether sulphones and their corresponding Tg values (shown in order of increasing Tg) are given in supporting information, Table S1 [3,5,8,10,11,13–47]. They are listed in terms of ID number. The ID numbers are used hereafter in the text.

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Computational Details

The program Cerius² (Accelrys, Inc.) using a Dell PC was employed to generate models of the SRUs detailed in supporting information, Table S1 using the amorphous builder module. All structures were fully minimised using conjugate gradients [48] until convergence was achieved. Electronic properties for the SRUs were calculated using MOPAC6 [49] with geometry optimisation, using RHF with the PM3 Hamiltonian. The results from the calculations have been summarised in supporting information, Table S2. The method was to perform multiple linear regression on all the data available to include the eigenvalues for the highest occupied molecular orbitals (HOMOs), lowest unoccupied molecular orbitals (LUMOs), global energy minima, dipole moments, and electrostatic isopotentials (EIPs); the latter were calculated with the QUANTA program [50]. The parameters were chosen carefully on the basis of knowledge of the factors that generally affect the Tg of the polymers. The global energy minimum represents the overall stability of the polymer, and it seems reasonable to conclude that a more stable polymer would have a higher value for its Tg. This is reflected in the negative coefficient for this parameter, as the more negative the energy minimum the more stable the polymer. The EIPs represent the ability of a polymer to form hydrogen bonds. The presence of hydrogen bonds is likely to add stability and hence the larger the magnitude of EIP, the greater the Tg. A similar trend can be seen with the dipole moments. Larger energy differences between the HOMO and LUMO indicate a more stable polymer. Hence, a more negative value for the HOMO and a more positive value for the LUMO would both contribute to a higher value of Tg. The statistical calculations were performed within the SPSS program [51].

Results and Discussion

Development of Quantitative Structure Property Relationships

The method used was based on QSPR theory, in which an attempt is made to describe the activity or reactivity within a set of compounds by means of a mathematical formalism that incorporates structure-dependent parameters. In QSPR it is assumed that the effects of the various parameters included are additive, and that they vary in a linear manner. Multiple linear regression (MLR) can be performed on the data to obtain an equation relating the property under investigation (in this case the glass transition, Tg) to the parameters from the set of test data. In this study, the method used was based on the work of Hopfinger and Koehler [52], who assumed that bulk properties of polymers can be described as a sum of the properties (e.g. HOMO and LUMO eigenvalues, global energy minimum, etc.) of the repeat unit. Thus, only the SRU needs to be modelled (1).

\[ \text{Polymer Property} = \text{constant} + \sum B_i \times \text{repeat-unit property}_i \]  

(1)

where \( B_i \) = coefficient in the equation and \( i \) = the name of the SRU.

A series of selected SRU properties were determined to represent the parameters that might influence the magnitude of Tg:

- heat of formation (\( \Delta H_f \)),
- dipole moment (DM),
- total energy (\( E_{\text{total}} \)),
- HOMO eigenvalue (HOMO),
- LUMO eigenvalue (LUMO),
- electrostatic isopotential maximum (EIP\(_{\text{max}}\)),
- electrostatic isopotential minimum (EIP\(_{\text{min}}\)).

The statistical calculations were performed within the SPSS program [51].

Table 2. Variables in equation (2) for 42 SRUs, \( F = 35.299 \).

| Variables | Coefficient (B) | \( \sigma_B \) |
|-----------|----------------|----------------|
| DF        | -45.557        | 5.129          |
| DM        | 2.844          | 2.137          |
| \( E_{\text{total}} \) | -0.029        | 0.005          |
| \( \Delta H_f \) | 0.099         | 0.043          |
| HOMO    | 17.709         | 6.995          |
| Mass    | -0.176         | 0.064          |
| \( V_{\text{chain}} \) | 1.301         | 0.272          |
| constant | 428.799        | 75.132         |

Multiple correlation coefficient \( R = 0.932 \).
Coefficient of the multiple determination \( R^2 = 0.869 \).
Adjusted \( R^2 = 0.842 \).
Standard error = 35.248.
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Table 3. Tg values (°C) for different backbone motifs with the same number of bonds.

| X            | Motif 1 (3 ring sulphone with \times bridging group) | Motif 2(4 ring sulphone with \times bridging group) |
|--------------|----------------------------------------------------|---------------------------------------------------|
| \(-\)        | 180                                                | 145                                               |
| \(-\)        | 180                                                | 146                                               |
| \(-\)        | 245                                                | -                                                 |
| \(-\)        | 205                                                | 176                                               |
| \(-\)        | 180                                                | 146                                               |
| \(-\)        | 205                                                | 176                                               |
| \(-\)        | 245                                                | -                                                 |

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molar mass of SRU (Mass),
sum of the cubes of the van der Waals' radii of all atoms in the SRU [53] (proportional to volume) \( V_{\text{tot}} \),
sum of the cubes of the van der Waals' radii of atoms in the substituents of the SRU \( V_{\text{sub}} \),
sum of the cubes of the van der Waals' radii of atoms in the backbone of the SRU \( V_{\text{chain}} = V_{\text{tot}} - V_{\text{sub}} \),
degree of freedom: number of bonds in the backbone of the SRU around which any rotation is possible (DF).

In all regressions vchain only was used instead of vtot and vsub because absolute values of the B coefficients of these parameters were very similar. The first seven properties represent electronic and polar properties associated with the SRU, and the remainder describe its volume, mass and relative flexibility. The complete set of calculated parameters for each SRU (along with the reported empirical Tg) is given in supporting information, Table S2. Initially a multiple regression was performed on all the parameters (supporting information, Table S2) for the entire data set (of 57 SRUs) and yielded the following regression data (Table 1):

The magnitude of the various coefficients reflects the importance of each parameter in the regression equation. It can clearly be seen that this is not a robust regression as the standard deviations of the coefficients are in some cases greater than the coefficients themselves. This is further reflected in the poor value of the correlation coefficient which shows that these parameters...
only model 68% of the data and the high value of the proportionality constant which is large at 170 and acts to provide most of the variation in $T_g$. From these data, it was apparent that not all of the parameters in the regression were making a significant contribution. Indeed in the case of four variables ($DF$, $E_{total}$, $E_{IP_{max}}$ and $V_{chain}$) a correlation coefficient of $R = 0.671$ was obtained (only 0.017 less than for all the variables). At the same time, the value of $F$ for this regression was 10.62, which was only three times greater than $F$ calculated for 4 degrees of freedom, for the 52 SRUs at the 0.01 probability level, which was 3.7 (at the 0.99 confidence limit). This assumes that all of the variables are independent which may not be the case with e.g. $E_{total}$ and $E_{IP_{max}}$ but nevertheless provides some confidence in the reliability of the regression to yield equation (2):

$$T_g = 312.2 - 32.898 \times DF - 0.02139 \times E_{total} + 0.28295 \times E_{IP_{min}} - 0.5828 \times V$$

Therefore the $DM$, $E_{IP_{max}}$, $AH_f$, $HOMO$, $LUMO$ and $Mass$ parameters were all removed before a second multiple regression was performed for the entire data set (of 57 SRUs) to yield the following regression data:

- Multiple correlation coefficient $R = 0.671$
- Coefficient of the multiple determination $R^2 = 0.450$
- Adjusted $R^2 = 0.407$
- Standard error $= 33.906$

Figure 3. Plot of $T_g$ versus $V_{sub}$ for Victrex PES (repeat unit ID 5) and its derivatives.
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Figure 4. Plot of $T_g$ versus $V_{sub}$ for repeat unit ID 22 and its derivatives.
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Figure 5. Plot of $T_g$ versus $V_{sub}$ for Radel™ R (repeat unit ID 26) and its derivatives.
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Figure 6. Plot of $T_g$ versus $V_{sub}$ for Udel™ polysulphone (repeat unit ID 12) and its derivatives.
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Figure 7. Plot of $T_g$ versus $V_{sub}$ for repeat unit ID 10 and its derivatives.
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After rejecting 15 SRUs, ID numbers 1, 4, 5, 6, 7, 13, 24, 25, 29, 33, 47, 50, 53, 54 and 56 from the original data set (on the basis that their predicted \( T_g \) values deviated by more than 10% from the empirical data), the multiple regression was repeated using the same seven parameters but for a set of 42 SRUs. This second regression yielded the following statistics (Table 2):

The marked improvement in the correlation coefficient (from 67% to 93.2%) indicates that the \( T_g \) is well replicated using the following equation, although not all the factors are taken into account as 7% of the data are still unaccounted for.

\[
T_g = 428.8 - 45.557 \times DF + 2.844 \times DM - 0.02873 \times E_{total} + 0.09938 \times \Delta H_f + 17.71 \times HOMO - 0.1757 \times mass + 1.3006 \times V_{chain}
\]  

The small standard deviations of most of the coefficients and the value of \( F \) at 32.9, compared to the tabulated value of \( F \) at the 0.01 probability level for 7 degrees of freedom and 34 SRUs at 3.3 indicate that the equation is reasonably well determined with a probability greater than 99.5%. Addition of the remaining variables gave only very small improvements in the correlation coefficient. The smallest deviations are for the \( T_g \) values in the range 190–220°C, presumably due to the population being greatest in this temperature range.

The greatest problems with the dataset were associated with estimating the flexibility of the chain, the parameter representing the degrees of freedom and the volume of the chain. The methods used were quite simplistic and insufficient to tackle the wider range of SRUs. Consequently, a smaller set of compounds was derived from the full dataset in order to find a correlation between the flexibility and \( T_g \) (Table 3) and between the volumes of the polymer chains. An attempt was made to discern any relationships between the various calculated parameters and the magnitude of \( T_g \). Figure 1 shows the scatter chart for the values of \( T_g \) versus dipole moment for the smaller subset of sulphone derivatives identified above. It is clear that no discernible relationship was evident, and this was the case for all of the parameters, save the volume of the substituent \( (V_{sub},) \), which is displayed in Figure 2. In this case, although there is some scatter evident at lower values of substituent volume, there does appear to be a trend of increasing \( T_g \) with increasing volume. Polyarylethersulphones in common with many synthetic polymers contain areas of amorphous chains and areas of crystallinity, the relative proportion of these regions can differ with the material and its method of preparation. This in turn would affect the glass transition values determined for the materials. Hence there is expected to be a scatter in the degree of correlation of the materials chosen and we have chosen to concentrate on those that give the best correlations. On this basis a series of graphs (Figures 3, 4, 5, 6, 7) were plotted for \( V_{sub} \) versus \( T_g \) for each of the individual derivatives. In addition to the original dataset, a series of 9 poly(arylether sulphone)s (originally published in reference 10), were also incorporated into the later plots and were examined in more detail. The introduction of a stiffening group into the backbone is known to raise \( T_g \) and the data in Table 3 demonstrate how \( T_g \) is enhanced by the incorporation of more rigid bridges having lower rotational freedom or the potential for dipole-dipole interactions between adjacent polymer chains. An attempt was made to discern any relationships between the various calculated parameters and the magnitude of \( T_g \). Figure 1 shows the scatter chart for the values of \( T_g \) versus dipole moment for the smaller subset of sulphone derivatives identified above. It is clear that no discernible relationship was evident, and this was the case for all of the parameters, save the volume of the substituent \( (V_{sub},) \), which is displayed in Figure 2. In this case, although there is some scatter evident at lower values of substituent volume, there does appear to be a trend of increasing \( T_g \) with increasing volume. 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### Table 4. \( T_g \) and \( V_{sub} \) values for the derivatives of the commercial polymer Victrex™ PES (shown below), repeat unit ID 5.

| ID | \( T_g \) (°C) | \( V_{sub} \) (Å³) |
|----|--------------|-----------------|
| 5  | 165          | 0               |
| 38 | 234          | 8.86            |
| 40 | 238          | 25.56           |

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### Table 5. \( T_g \) and \( V_{sub} \) values for the derivatives of the repeat unit ID 22.

| ID | \( T_g \) (°C) | \( V_{sub} \) (Å³) |
|----|--------------|-----------------|
| 22 | 210          | 0               |
| 31 | 225          | 65.5            |
| 34 | 227          | 76.2            |
| 39 | 235          | 86.3            |
| 43 | 240          | 114.3           |
| 51 | 265          | 152.5           |

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### Table 6. \( T_g \) and \( V_{sub} \) values for the derivatives of the commercial polymer Radel™ R, repeat unit ID 26.

| ID | \( T_g \) (°C) | \( V_{sub} \) (Å³) |
|----|--------------|-----------------|
| 26 | 220          | 0               |
| 48 | 262          | 40.4            |
| 52 | 270          | 152.5           |
| H  | 280          | 158.3           |
| 55 | 281          | 53.1            |
| I  | 285          | 172.7           |
| G  | 265          | 228.7           |

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### Table 7. \( T_g \) and \( V_{sub} \) values for the derivatives of the commercial polymer Udel™ polysulphone, repeat unit ID 12.

| ID | \( T_g \) (°C) | \( V_{sub} \) (Å³) |
|----|--------------|-----------------|
| 12 | 186          | 0               |
| D  | 205          | 11.7            |
| 1  | 138          | 37.9            |
| C  | 192          | 42.0            |
| 23 | 210          | 32.3            |
| 9  | 178          | 20.2            |
| 27 | 220          | 24.1            |
| 7  | 171          | 57.3            |
| F  | 235          | 40.4            |
| G  | 175          | 107.3           |
| B  | 191          | 76.2            |

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Table 8. \( T_g \) and \( V_{\text{sub}} \) values for the derivatives of the repeat unit ID 10.

| ID | \( T_g \) (°C) | \( V_{\text{sub}} \) (Å³) |
|----|---------------|-----------------|
| 10 | 180           | 0               |
| 12 | 186           | 20.2            |
| 19 | 200           | 48.2            |
| 18 | 200           | 28.6            |
| 21 | 205           | 2.7             |
| E  | 205           | 24.6            |
| 20 | 205           | 41.8            |
| 37 | 230           | 76.2            |
| 54 | 280           | 74.5            |

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Table 9. A and B coefficients and correlation coefficient (R) produced from equation (4).

| ID | A     | B        | R     |
|----|-------|----------|-------|
| 5  | 230.57| 0.2905   | 0.982 |
| 22 | 204.99| 0.3477   | 0.963 |
| 25 | 251.34| 0.1345   | 0.548 |
| 12 | -     | -        | 0.091 |
| 10 | 181.24| 0.2857   | 0.764 |

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The coefficients are given in Table 9 and these demonstrate the strength of the correlations for the top two SRUs, where a correlation greater than 90% is obtained, but this clearly only works for relatively simple structures. This indicates that \( T_g \) can be correlated with the volumes of the substituents using a very simple equation but only for a small set of repeat units, excluding for example biphenylene or methylene bridges in the SRU. In this paper an equation (derived from multiple linear regression) is presented relating the glass transition temperatures of poly(aryl ether sulphone)s to various atomistic parameters. Several molecular modelling techniques were used for building and minimization of the structures and subsequent molecular orbital calculations on these structures. The equation is useful in providing molecular insight into the observed \( T_g \) values of poly(aryl ether sulphone)s (i.e. the equation points to the importance of chain stiffness and substituent volume in determining the \( T_g \)).

Supporting Information

Table S1 Poly(arylene ether sulphone)s examined in this work (shown in order of increasing \( T_g \)).

(DOC)

Table S2 The complete set of parameters from the molecular orbital calculations for each SRU (for ID refer to Table S1).

(DOC)

Author Contributions

Conceived and designed the experiments: IH BJH GK. Performed the experiments: GK. Analyzed the data: IH BJH. Contributed reagents/materials/analysis tools: IH BJH GK. Wrote the paper: IH BJH.

References

1. Vogel HA (1963) Polysulphone Polymers. British Patent: 1,060,546.
2. Farnham AG, Johnston KN (1973) Polysulphone Polymers. British Patent: 1,078,234.
3. Jones MEB (1962) Manufacture of Polysulphones. British Patent: 1,016,245.
4. Cotter RJ (1995) Engineering Plastics. A Handbook of Polyarylethers, Basel: Gordon and Breach Publishers. 357 p.
5. Brostow W, Chiu R, Kalogeras IM, Vassilikou-Dova A (2008) Prediction of Glass transition Temperatures: Binary Blends and Copolymers. Materials Letters 62: 3152–3155.
6. Howlin BJ, Hall SA, Hamerton I, Billault C, Baidak A, et al. (2012) Improvement of molecular simulation techniques to predict properties of crosslinked epoxy resins. PLOS1: in press.
7. Howlin BJ, Hamerton I, Klesapatinand P, Shortley H, Takada S (2006), Developing predictive models for polycyanurates using a comparative study of molecular simulation and empirical thermo-mechanical data. Polymer 47: 690–698.
8. Hamerton I, Howlin BJ, Mitchell AL, Hall SA, McNamara LT (2011) Using molecular simulation to predict the physical and mechanical properties of polybenzoxazines. In: Ishida H, Aag T, editors. Handbook of Benzoxazine Resins. Amsterdam: Elsevier. 127–142.
9. Hamerton I, Heald CR, Howlin BJ (1996) Molecular simulation of the comparative flexibility of bridging linkages in poly(aryl ether sulfone)s and poly(aryl ether ketone)s from a study of isolated oligomers. Die Macromol Chemie Theor Simul 5: 303–320.
10. Hamerton I, Heald CR, Howlin BJ (1996) Molecular modelling of a Polyarylethersulfone under bulk conditions. Modell Simul Mater Sci Eng 4: 151–159.
11. Van Krevelen DW, Nijenhuis TK (2009) Properties of Polymers. Their Correlation with Chemical Structure, Their Numerical Estimation and Prediction from Additive Group Contribution. Amsterdam: Elsevier. 1000 p.
12. Hamerton I, Howlin RJ, Larwood V (1995) Development of Quantitative Structure-Property Relationships for Poly(arylene Ether)s. J Mol Graphics 13: 14–17.

13. Ueda M, Toyota H, Ochi T, Sugiyma J, Yonetak K, et al. (1993) Synthesis and Characterization of Aromatic poly(ether sulphone)s containing pendant sodium-sulfonate groups. J Polym Sci A 31: 853–858.

14. Ueda M, Ito T. (1991) Synthesis of Aromatic Poly(ether sulphone)s by Nickel-catalyzed Coupling Polymerization of Aromatic Dichlorides. Polym J 23: 297–303.

15. Podkoscielew W, Dethloff J, Dethloff M, Brunn J. (1991) Aliphatic-aromatic Polyethersulfones.2. Polycondensation Products of bis(4-hydroxyphenyl)sulfone and bis(4-chloromethylphenyl) compounds - Synthesis and Structure. Angew Makromol Chemie 189: 143–153.

16. Attwood TE, Barr DA; King T, Newton AB, Rose JB. (1981) (Poly(arylene ether sulfone)s by Polyetherification.2. Polycondensations. Polymer, 18: 35–364.

17. Vogel HA (1970) Polyarylsulfones, Synthesis and Properties. J Polym Sci A-1 8: 2053.

18. Hsiao BS, Gardner KH, Matheson RR, Jr. (1991) Structure, crystallisation and melting of poly(aryl ether ketone) (PEKK). Part II: Crystallisation and melting. ACS Polym Prep 32: 256–260.

19. Robeson LM, Farnham AG, McGrath JE. (1973) Polym. Prep 16: 476.

20. Johnson RN, Farnham AG, Clendinning RA, Hale WF, Merriam, CN (1967) Poly(aryl ethers) by Nucleophilic Aromatic Substitution.1. Synthesis and Properties. J Polym Sci A-1 5: 2373. DOI: 10.1002/pol.1967.15005.050.

21. Robeson LM, Crisafi ST (1983) Microcavitation Formation in Engineering Polymers Exposed to Hot Water. J Applied Polym Sci 28: 2925–2936.

22. O’Shea FX, Cornell RJ (1974) Aromatic polyether-polyetherether-polysulfone thermoplastics. Can Patent 946,091.

23. Ghosal K, Chem RT (1992) Arylation of Poly(phenylene oxide) and Polysulfone - Structural Characterization and Gas-permeability. J Membr Sci 72: 91–97.

24. Kamps KMP, Teunis HA, Wesling M, Smolders CA (1992) Gas-transport and Sub-critical Relaxations in Unmodified and Nitrate Polyarylethersulfones. J Membr Sci 74: 193–201.

25. Lee JA, Hogen-Esch TE (1993) Polym Prep 34: 570.

26. McHattie JS, Koros WJ, Paul DR (1991) Gas-transport Properties of Polysulfone.1. Role of Symmetry of Methyl-group Placement on Bisphenol rings. Polymer 32: 840–850.

27. Goh SH, Lau WW, Lee CS(1992) Miscibility of Poly(4-vinyl pyridine) with Polysulfone and Carboxylated Polysulfone. Polym Bull 29: 521–525.

28. Schmidt M, Maurer FHJ (1987) Pressure–volume–temperature properties and free volume parameters of PEO/PMAA blends. J Polym Sci B Polym Phys 31: 1061–1080.

29. Artwood TE, Davson PG, Freeman JL, Hoy LRJ, Rose JB, et al. (1983) Synthesis and Properties of Polyaryletherketones. Polymer, 22: 106–1105.

30. Clendinning RA, El-Hibri MJ, Matzner M, Kwiakowski GT (1988) Polym Prep 32: 166.

31. Rose JB (1974) Preparation and Properties of Poly(arylene ether sulfones). Polymer 15: 456–465.

32. Matsuo S, Murakami T, Takasawa R (1993) Synthesis and Properties of New Crystalline Poly(arylene ether nitride)s. J Polym Sci A Polym Chem 31:3439–3446.

33. Mohanty DK, Hedrick JL, Gobetz K, Johnson BC, Villor I, et al. (1982) Poly(arylene ether sulfones) and related materials via a potassium carbonate, m-methyl pyridolone process. Polym Prep 23: 204.

34. Cotter RJ (1989) Novel Poly (arylethers).US Patent 4,449,503.

35. Baron L, Blank DR (1970) Synthesis and Properties of Some Aromatic Polyetherthiols. Makromol Chem 140: 83.

36. Kim WJ, Hay AS (1992) Soluble Poly(ether ketone)s and Poly(ether sulfone)s From Phenyl-substituted Hydroquinones. J Macromolecular Science Pure Appl Chem A29: 1141–1154.

37. Hartmann LA (1979) High Molecular Weight Polyesulfones. US Patent 4,156,068.

38. Tam CM, Dal-Cia M, Guiwer MD (1995) Polysulfone Membranes. Performance Evaluation of Radel-a/pvp Membranes. J Membr Sci 78: 123–134.

39. Attwood TE, Barr DA, King T, Newton AB, Rose JB (1977) Poly(arylene ether sulfones) by Polyetherification.2. Polycondensations. Polymer, 18: 358–364.

40. Rose JB (1968) Poly(arylene sulfones) and Poly(arylene ketones). Chem Ind 1061–1080.

41. Robeson M, Farnham AG, McGrath JE. (1973) Effect of Structure on Dynamic Mechanical-Behavior of Poly(aryl ethers). Abstr Papers ACS 169: 90–91.

42. Marasco LM, Chaos HS (1984) Poly (arylether)s. US Patent number 4,473,604.

43. Wham GK, Hay AS (1991) Soluble homopoly(aryl ether ketone) (HPAE) from 2,2',3,3',6,6'-hexaphenyl-4,4'-diphenol (HPDP) and 4,4'-difluorobenzophenone (DFPK). Polym Prep 32: 389–390.

44. Andrews SM (1992) Synthesis, characterization, and blends of high temperature poly(aryl ether sulfone)s. J Polym Sci Polym Chem A 30: 221.

45. Perece V, Wang JH, Oishi Y, Feiring AE (1991) Synthesis of Aromatic Polymers by Scholl Reaction.1. Homopolymerization and Copolymerization of Alpha, Omega-bis [4-(naphthyl)] phenylsulfonyletherfluorovolkanes. J Polym Sci, Polym Chem A29: 965–976.

46. Rose JB (1974) Synthetic Routes to Polyesulfophales. Chimaia 28: 561–567.

47. Ivin KJ, Rose JB (1966) in Adv Macromol Chem W Pauskar (Ed.) 1: 335.

48. Fletcher R, Reeves CM (1964) Function Minimization by Conjugate Gradients. J Comput 7: 149.

49. Stewart JJP (1990) Special Issue - MOPAC - A Semiempirical Molecular-Orbital Program. J Comput-Aided Mol Des 4: 1–45.

50. QUANTA, Accelrys Inc. (http://lms.chem.tamu.edu/quanta.html), accessed 22 May 2012.

51. SPSS for Windows 6.1.3 (http://www-01.ibm.com/software/analytics/spss/), accessed 22 May 2012.

52. Kochler MG, Hopfinger AJ (1989) Molecular Modeling of Polymers.5. Inclusion of Intramolecular Energies in Estimating Glass and Crystal-enthal Transition- Temperatures. Polymers 30: 116–126.

53. Pauling L (1960) The Nature of the Chemical Bond, Cornell University Press: Ithaca, 664 p.