

Development of quantitative structure property relationships for poly(arylene ether)s

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The technique of quantitative structure–activity relationships (QSAR) is well accepted by the drug design community. The analogous technique of quantitative structure–property relationships (QSPR) has applications in the field of polymer chemistry. A variety of molecular modeling and molecular orbital techniques was used to find molecular descriptors that could be used to derive an empirical equation to describe the glass transition temperature of two related classes of poly(arylene ether)s. The derived equation was then used to predict the thermal characteristics of another polymer of the same type.

Keywords: molecular simulation, poly(arylene ether)s, glass transition temperature, quantitative structure–property relationships.

INTRODUCTION

High-performance thermoplastics are currently receiving considerable attention for potential use as structural materials in aerospace materials.¹ These materials offer an attractive combination of chemical, physical, and mechanical properties: they are thermally stable, show good mechanical properties (particularly the creep resistance), and are resistant to attack by dilute acids and alkalis. Poly(arylene ether sulfone)s form a family of aromatic, thermoplastic polymers, some of which have been accepted for continual use under stress at temperatures in excess of 150°C. The nature of the functional groups linking the aryl portions plays a crucial part in determining properties, for this controls the flexibility of the polymer chain and determines the overall polarity of the macromolecule. Thus, to obtain the properties required these links should be selected such that good

stability is retained and the polymer backbone is sufficiently flexible to show thermoplasticity below the decomposition temperature, but well above 150°C.²

Routes to poly(ether sulfone)s were discovered independently, and almost simultaneously, in the laboratories of 3M Corporation³ and of Union Carbide⁴ in the United States and in the Plastics Division of ICI⁵ in the U.K. The sulfone linkage was a natural choice for investigation as the stability of diaryl sulfones was well known, but it appears that a polymer chain consisting only of phenylene rings linked via sulfone groups, that is, poly(phenylene sulfone) does not display thermoplasticity and tends to be too intractable for easy processing,⁶ and copolymers are more useful. Poly(phenylene sulfone) decomposes before melting² and the introduction of inter-ring linkages other than $-\text{SO}_2-$ is necessary to obtain thermoplasticity. This is achieved in the commercial products predominantly by the introduction of aryl ether linkages, and as the proportion of these linkages is increased there is a progressive reduction in glass transition temperature, T_g , and a corresponding increase in thermoplasticity. Fortunately, the synthetic procedures that were devised^{7,8} for preparing high-performance polymers containing aryl sulfone linkages as the main structural feature led inevitably to the inclusion of other flexible chain bonds, particularly the ether linkage, and attention became concentrated on the poly(arylene ether sulfone)s.

Most poly(arylene ether sulfone)s are amorphous materials and although a few are crystalline “as made” or can be induced to crystallize by solvent treatment, it was noted^{2,9} that it was not possible to find such a material that would crystallize from the melt. Thus, the softening behavior of these polymers is determined by their glass transition temperatures and these vary over a wide range, depending on the polymer repeat unit. Polymers from dichlorodiphenyl sulfone and simple bisphenols have high T_g values, typically in the range of 180 to 220°C, depending on the bulk of the substituents on the central carbon atom, and a T_g can be pushed up a further 10°C by using even more bulky substituents. Whereas sulfone-containing polymers are generally amorphous,^{2,9} those containing, for example, carbonyl linkages are generally semicrystalline.^{10,11} Poly(aryl ether

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ether ketone) (PEEK) was envisaged as the crystalline analog of poly(ether sulfone) (PES), with the high crystallinity and high melting point conferring additional high performance at elevated temperatures and greater solvent resistance.

The prediction of mechanical properties in as yet unsynthesized polymers offers obvious commercial advantages with savings in both material cost and manpower. The glass transition temperature, T_g , is an important factor that largely determines the temperature of use of a polymer, and this parameter was selected to form the basis of this study. A variety of commercially interesting polymers was selected for evaluation using the model.

EXPERIMENTAL

Molecular simulation

The program POLYGRAF (Molecular Simulations, Inc.) using a Stardent Titan 2 graphics minisupercomputer was employed to generate models of the structural repeat units (SRUs) using the organic builder utility (see Table 1 and Color Plates 1–4). All structures were fully minimized using conjugate gradients¹² until convergence was achieved. The formats of the coordinate files were then converted (using the program CONVERT¹³) into a format suitable for use on COSMIC.¹⁴ Molecular orbital calculations were carried out on each SRU using CNDO within the COSMIC program. The results from the calculations have been summarized in Table 2. 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 isopotential. The program MINITAB was used for this purpose. The parameters were chosen carefully on the basis of a knowledge of the factors that generally affect the T_g 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 T_g . This is reflected in the negative coefficient for this parameter, as the more negative the energy minimum the more stable the polymer. The electrostatic isopotentials (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 T_g . 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 T_g .

RESULTS AND DISCUSSION

QSAR and QSPR

In a study using quantitative structure–activity relationships (QSARs) 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. Use of quantitative structure–property relationships (QSPRs) is the analogous method used for polymer modeling. 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 temperature, T_g) to the parameters from the set of test data.

The method used was based on work described by Hopfinger.¹⁶ Successful polymer modeling requires the accurate prediction of bulk polymer properties and three computational techniques are available: (1) additive properties, (2) static energy calculations, and (3) molecular dynamics simulation. Previously work has concentrated on the group additive approach, in which empirical relationships are derived between physical properties of interest and group contributions. Group contributions are basically numbers that, when summed, give the property of interest. These relationships can be accurate as they reproduce what they have been designed to reproduce (e.g., see the work of van Krevelen).¹⁷ There are a number of commercial applications using this approach (e.g., the EXPOD system).¹⁸ A disadvantage of this approach is that the parameters used provide no chemical information about the monomers composing the polymer other than that it contains a CH_2 group, and so on.

An alternative approach is to derive parameters based on molecular models of the polymers, which can then be di-

Table 1. Structure repeat units and their sources

SRU number	SRU	T_g (°C)	Ref.
1	–[Ar–C(CH ₃) ₂ –Ar–O–Ar–SO–Ar–O]–	165	7
2	–[Ar–CO–Ar–O–Ar–SO ₂ –Ar]–	205	7
3	–[Ar–CH ₂ –Ar–O–Ar–SO ₂ –Ar]–	180	8
4	–[O–Ar–C(CH ₃) ₂ –Ar–O–Ar–SO ₂ –Ar]–	190	9
5	–[O–Ar–O–Ar–CO–Ar]–	160	7
6	–[O–Ar–O–Ar–CO–Ar–CO–Ar]–	155	10
7	–[O–Ar–O–Ar–O–Ar–CO–Ar]–	150	7
8	–[O–Ar–O–Ar–SO ₂ –Ar]–	210	7
9	–[Ar–C(Ph) ₂ –Ar–O–Ar–SO ₂ –Ar]–	230	7
10	–[Ar–S–Ar–O–Ar–SO ₂ –Ar]–	175	7
11	–[Ar–SO ₂ –Ar–O–Ar–SO ₂ –Ar]–	245	7

Table 2. Results from the molecular orbital calculations

SRU number	HOMV (eV)	LUMO (eV)	Dipole moment (Debyes)	Global energy minimum (kcal/mol)
1	-11.5	1.8	4.48	-173 245
2	-12.0	1.3	5.96	-172 792
3	-11.4	1.2	5.11	-138 890
4	-11.4	1.4	7.35	-184 768
5	-11.4	1.9	4.60	-125 863
6	-11.5	1.2	4.41	-170 557
7	-11.3	1.9	0.97	-166 063
8	-11.7	1.3	5.73	-139 801
9	-11.0	1.4	7.66	-219 512
10	-11.1	1.3	7.51	-163 695

rectly related to the chemical structure of the monomers. Hopfinger's approach gives rise to the torsion angle unit (TAU) theory, which involves the decomposition of a polymer into subunits called structure repeat units (SRUs). These may in turn be further subdivided into the torsion angle units and any bulk property of the system can then be described as a sum of the properties of the TAUs (which can be obtained through energy calculations and molecular simulation). The polymer can be described in terms of its SRU, which specifies its molecular properties and, as a result, only one SRU needs to be modeled. The properties studied here were the HOMO and LUMO eigenvalues, global minimum conformational energies, and electrostatic isopotentials.

The two classes of polymers investigated were poly(aryl ether sulfone)s and poly(aryl ether ketone)s. The initial step was to select the set of test data for which the various parameters could be calculated. Because the final equation was to be derived using MLR, it was essential to maintain some degree of similarity between the samples chosen and it was decided for the sake of simplicity to consider only systems consisting of a linear arrangement of phenyl rings linked by one functional group between the rings. Furthermore, only para linkages have been included and no biphenyl linkages are contained within the SRU, although two SRUs may be joined by a biphenyl linkage within a polymer. The literature was then searched for SRUs fulfilling the above criteria, so that a selection could be obtained where no two polymers had the same value of T_g (in order to reduce the possible complications arising from the regression). Ten polymer repeat units were selected, and photographs of four (2, 4, 6, and 9) have been included (references for the sources of the data can be found in Table 1).

Data consistency

Various physical factors affect the T_g of polymers including molecular weight, the diluent, the degree of cross-linking, the effect of random polymerization for copolymers, and the effect of structural isomerism.⁶ Of these, only the molecular weight was appropriate for consideration for this class of linear thermoplastics. In the literature⁷⁻¹⁰ from

which the 10 sample structures were selected, few explicit references have been made to the average molecular weights of the polymers. Generally, the molecular weights quoted are around 25 000 to 30 000, with others quoted at much higher values (of the order of 10^5). For the present work, it has been assumed that only the variation in SRU molecular weights and their chemical nature have an effect on T_g .

Elsewhere¹⁹ we have discussed the nature of the bridging groups in these thermoplastics, and those findings suggested that the presence of sulfone groups yields polymers with a high degree of flexibility. However, the polymers in the current data set that include sulfone groups show higher T_g values (Table 1), which generally implies more rigidity within the polymer. The presence of hydrogen bonding to the sulfone groups may be a possible reason for this phenomenon, as sulfone groups are of a highly polar nature. To investigate this theory, a useful parameter to consider was the tensile strength of poly(aryl ether sulfone)s and poly(aryl ether ketone)s. If hydrogen bonding does occur, which can be regarded as constituting weak cross-links, greater force would be required to stretch the chain. Values of Young's modulus from the literature were 5×10^9 for poly(aryl ether ketone)s and 4×10^9 for the corresponding poly(aryl ether sulfone). These, along with values for the tensile modulus and tensile yield strength, suggest that, if anything, the hydrogen bonding in the ketones is stronger than in the sulfones. A search of the Cambridge Crystallographic Database V.3²⁰ was conducted for the fragment $R-Ar-SO_2-Ar-R$ which resulted in several entries²¹⁻²³ suggesting the presence of hydrogen bonding between the sulfone groups in polymers or general compounds of this type.

Multiple linear regression on the dipole moments, energy minimum, electrostatic isopotential minimum, and LUMO and HOMO gave a correlation coefficient of 79.3%, indicating that some fundamental parameter has been overlooked.

The problem seemed to lie with the molecular mass of the TAUs; hence adding the molecular mass of each SRU and the combined number of degrees of freedom of the TAUs as two further parameters gave the following equation with a correlation coefficient of 98.4%:

$$T_g = -189 - 3.03*(\text{DIPOLES}) \\ - 0.0006*(\text{energy minimum}) \\ - 0.973*(\text{EIP}) \\ - 8.1*(\text{LUMO}) \\ - 35.2*(\text{HOMO}) \\ + 0.79*(\text{mass of TAU}) \\ - 7.95*(\text{degrees of freedom of TAU})$$

The rationale for the addition of these two extra parameters was that the mass represents the opportunity for more van der Waals contact in the larger units and the degrees of freedom mitigate against the increasing mass by reducing the rigidity and decreasing the T_g . The magnitude of the various coefficients reflects the importance of each parameter. Hence, in the case of polymer SRU number 1, the major contributors to the T_g are the HOMO (404.8) and the energy minimum (103.95). The effect of the other parameters is to decrease these values to achieve the observed T_g . The magnitudes of the coefficients are those obtained from the MINITAB correlation. The derived equation was then tested on polymer SRU number 11 (Color Plate 5) and gave the results tabulated below:

True:	$T_g = 245^\circ\text{C}$
Predicted:	$T_g = 252.66^\circ\text{C}$
Deviation:	$= 3.13\%$

As can be seen from these results, the calculated value is clearly in close agreement with the observed value of T_g . The program "TG" has also been written in QuickBASIC to allow the calculation of the T_g of poly(aryl ether ketone)s and poly(aryl ether sulfone)s, when the relevant parameters have been input. The program is available on request from the authors.

CONCLUSIONS

This article presents an equation (derived using multiple linear regression) relating the glass transition temperature of poly(aryl ether ketone)s and poly(aryl ether sulfone)s to various atomistic parameters. Several molecular modeling techniques were used for building and minimization of the structures and the 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 sulfone)s (i.e., the equation points to the importance of charge interactions and chain flexibility in determining the T_g). A further study of the importance of charge interactions in poly(aryl ether sulfone)s derived from this work is presented elsewhere.¹⁹ A program has also been written to predict the T_g of new polymers of this general type. We appreciate that a limited data set has been used for the derivation of these parameters, but the approach is useful in providing a molecular insight into the polymers studied. Further correlations with a more diverse data set of polymers are proceeding.

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