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Percentage of Rigid Chain Length, a New Concept for Predicting Glass Transition Temperatures and Melting Points of Poly(aryl ether ketone)s and Poly(aryl ether sulfone)s

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ABSTRACT: Molecular design, microstructure, and physical properties of polymers are strongly related to each other. A better understanding of their interdependence will give the polymer chemist useful ideas for the synthesis of new macromolecules. The present paper aims to compare the thermal behavior of aryl polycondensates based on ether, sulfone, and ketone links. Ultimately the objective is to design a new polymer combining, for example, the glass transition (T_g) of poly(ether sulfone)s and the crystallinity of poly(ether ether ketone)s. By the use of a new concept, the percentage of rigid chain length, it is demonstrated that one can predict T_g and T_m of poly(aryl ether ketone)s and T_g of poly(aryl ether sulfone)s. The feasibility of crystalline poly(aryl ether sulfone)s is also discussed on the basis of the same principle.

Introduction

Poly(aryl ether ketone)s (PEEK, PEK, etc.) and poly(aryl ether sulfone)s (PES, PEES, etc.) exhibit complementary properties which have often been emphasized.[1-6] The former types of polymer are semicrystalline but their fairly low T_g's are often considered to be a limitation. The latter types of polymer are characterized by high T_g's (often above 200 °C), but, since they fail to crystallize, their solvent resistance is often very poor. Many attempts to synthesize polycondensates including both types of linkages (ketone and sulfone) or copolymers have not led to practical solutions. Nevertheless, joining together the best thermal properties of both families in a unique material is a challenge. A better understanding of the factors which give rise to this situation is the objective of this study.

To facilitate this understanding, the glass transition temperatures and melting points of a wide range of poly(aryl ether ketone)s and poly(aryl ether sulfone)s have been examined. A group contribution principle has been deduced from this preliminary study.

I. Glass Transition Study

A. Poly(aryl sulfone)s. It is well known that the T_g of a polymer depends on both chain rigidity and polarity. In Table I, a series of poly(aryl ether sulfone)s is presented which exhibit high T_g due to their chain rigidity (C_6H_4, C_6H_4–C_6H_4, C_6H_4–C_6H_4–C_6H_4 groups) and to the presence of polar links (SO_2). The high polarity of the sulfone link, or its large electronegativity, leads to an electron-withdrawing effect which delocalizes the π-electrons from the aromatic rings. The neighboring links can, therefore, present a double-bond character as shown in Figure 1. Such a delocalization considerably enhances the rotational barrier around the C–S link and consequently the chain rigidity.

Attwood et al.[13] referred to such resonance forms to explain glass transition differences (50–60 °C) between *m*- and *p*-poly(aryl ether sulfone)s. Only one resonance form can be written for the meta polymer (Figure 2) which leads to a lower chain rigidity and a lower T_g.

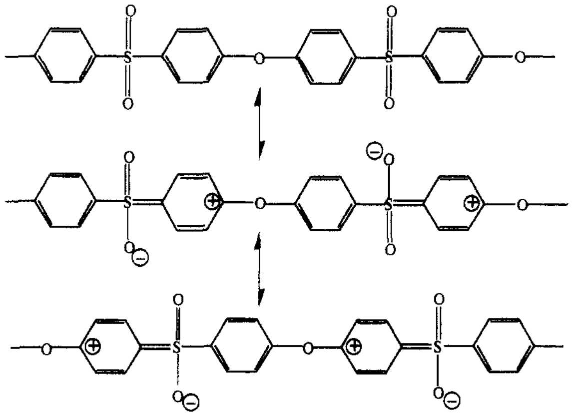

Figure 1. Electron-withdrawing effect in *p*-PES.

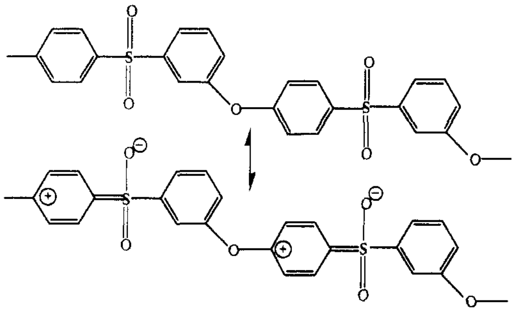

Figure 2. Electron-withdrawing effect in *m*-PES.

It can be deduced from the above considerations that the polarity of sulfone links influences the glass transition of poly(aryl ether sulfone) chains through an enhancement of chain rigidity. Therefore, it would be attractive to find a relationship between this one parameter and the T_g value.

As it is difficult to correctly evaluate the rigidness induced by resonance around the sulfone group, it is proposed, as a first approximation, to consider that the two S–C links on both sides of the SO_2 group are fully (100%) rigid (i.e., rotation around the links is impossible) while the two O–C links on both sides of the ether group

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Table I
Thermal Transitions of Synthesized Poly(aryl ether sulfone)s and Their PRCL

	T_g (°C)	T_m (°C)	PRCL (%)	ref
$(C_6H_4O)_n$	110	285	50	7
$(C_6H_4SO_2)_n$	350	>520, >580	100	5, 8
$(C_6H_4OC_6H_4OC_6H_4OC_6H_4SO_2)_n$	180		64	9
$(C_6H_4OC_6H_4OC_6H_4SO_2)_n$	217		68	10
$(C_6H_4OC_6H_4SO_2)_n$	223–230		76	11, 12
$(OC_6H_4C_6H_4OC_6H_4SO_2C_6H_4)_n$	232		74	10
$(\underline{OC_6H_4C_6H_4SO_2C_6H_4})_n$	265		83	12
$(C_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4O)_n$	280–290	395	87	11, 12, 13
$(C_6H_4SO_2C_6H_4C_6H_4C_6H_4SO_2C_6H_4OC_6H_4SO_2C_6H_4O)_n$	281–290		85	6, 12, 13
$(\underline{C_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4OC_6H_4SO_2C_6H_4O})_n$	258		83	13
$(C_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4OC_6H_4SO_2C_6H_4O)_n$	284–289		87	13
$(C_6H_4SO_2C_6H_4C_6H_4C_6H_4SO_2C_6H_4OC_6H_4C_6H_4O)_n$	264	383	84	6
$(\underline{C_6H_4SO_2C_6H_4C_6H_4C_6H_4SO_2C_6H_4OC_6H_4O})_n$	259	393	82	6
$(C_6H_4SO_2C_6H_4C_6H_4C_6H_4SO_2C_6H_4O)_n$	311	398	89	6
$(OC_6H_4C_6H_4C_6H_4OC_6H_4SO_2C_6H_4)_n$	251	389	79	6
$(OC_6H_4C_6H_4C_6H_4OC_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4)_n$	263	408	85	6

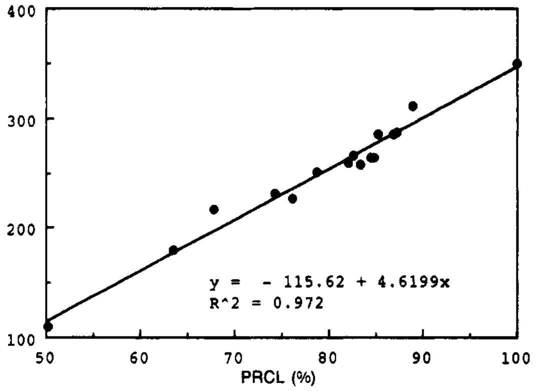


Figure 3. Linear relationship between PRCL and T_g of poly(aryl ether sulfone)s.

are fully nonrigid (0%) (i.e., free rotation around these links). A percentage of rigid chain length (PRCL) of the repeat unit can be defined as the ratio between the total rigid length of this unit (including the phenyl length, the biphenyl and terphenyl lengths, which are rigid by π-conjugation, and the S–C lengths) and the full length of the unit. The use of a percentage in the latter definition somewhat counterbalances the absoluteness of the rigidity evaluation. The practical method for calculation of PRCL is given in the last section. The PRCL values have been calculated and are reported for all the poly(aryl ether sulfone)s listed in Table I. The value of the PRCL parameter is demonstrated in Figure 3, which shows the T_g's taken from Table I as a function of PRCL. All the T_g's lie on a straight line. This simple relationship is, therefore, very easy to use to estimate with accuracy the T_g of any poly(aryl ether sulfone) (before its synthesis). Moreover, this relationship shows that PRCL rather than the global rigid chain length effectively governs the T_g of the polymer. As an example, for the polymers underlined in Table I, $(OC_6H_4C_6H_4SO_2C_6H_4)_n$ exhibits PRCL and T_g close to those of the polymers $(C_6H_4SO_2C_6H_4C_6H_4C_6H_4SO_2C_6H_4OC_6H_4O)_n$ and $(C_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4OC_6H_4SO_2C_6H_4O)_n$.

B. Poly(aryl ether ketone)s. In Table II the values of T_g and T_m for different poly(aryl ether ketone)s found in the literature are reported. Due to the analogy between the chemical structure of poly(aryl ether sulfone)s and poly(aryl ether ketone)s, an extension of the linear relationship between T_g and PRCL was attempted. The ketone linkage also induces an electron-withdrawing effect leading to a chain rigidification by electron delocalization (Figure 4). However, because of its lower electronegativity, its efficiency will certainly be less than that of the sulfone group.

Again, the rigidification induced by a ketone group is difficult to quantify accurately. Therefore, the hypothesis was made that the glass transition temperatures of the poly(aryl ether ketone)s have to follow the same T_g–PRCL linear relationship as the poly(aryl ether sulfone)s. This hypothesis leads to the assignment to the C–C links on both sides of a ketone group a rigidity of 33%. On this basis the calculations lead to the PRCL values of poly(ether ketone)s reported in Table II. Figure 5 shows the linear relationship between PRCL and T_g for all the poly(aryl ether sulfone)s and poly(aryl ether ketone)s cited in Tables I and II. The slopes coincide when 33% of the rigidity is assigned to ketone.

C. Discussion. It is important to note the large number of literature references in Tables I and II. All the cited T_g's have not necessarily been measured under the same conditions. Scan frequency differences give rise to discrepancies, and in some cases too low degrees of polymerization lead to T_g misestimation.

Nevertheless, the new PRCL concept allows predictions of the glass transition temperatures of aromatic polymers containing only ether, ketone, or sulfone links in para positions to be made clearly, easily, and with a fairly good degree of accuracy. The calculation of PRCL is based on the assumptions that the percentages of rigidity of ether, ketone, and sulfone are respectively, 0%, 33%, and 100%.

However, the attribution of these percentages is not purely arbitrary since they aim to take into account the increase of the rotational energy barrier due to the electronic delocalization which leads to increasing double-bond character of the $C–C_6H_4$ or $S–C_6H_4$ links. From a kind of mesomeric effect, sometimes called the "bridge effect", the ketone unit $OC_6H_4COC_6H_4O$ and the sulfone unit $OC_6H_4SO_2C_6H_4O$ can be compared to a carbonate unit and a sulfate unit, respectively.[28] For the carbonate and sulfate ions, in which all the C–O and S–O links must have the same length, it can be deduced from experimental length measurements that the bond number must lie between 1 and 2 (1.33 and 1.83, respectively);[22,23] the above hypotheses for the rigidity percentages seem, therefore, at least reasonable.

Of course, for each polymer, a more detailed evaluation of each rotational energy barrier by orbital overlapping is necessary to refine the PRCL concept. Thermal molecular modeling can also be a good choice. A better accuracy is expected and an extension to other links (C_6H_4–S, C_6H_4–SO, esters, $C_6H_4–C(CH_3)_2$, etc.) can perhaps be deduced.

Table II
Thermal Transitions and Calculated PRCL of All Poly(aryl ether ketone)s Found in the Literature

	T_g (°C)	T_m (°C)	PRCL (%)	ref
$(C_6H_4OC_6H_4OC_6H_4OC_6H_4CO)_n$	129	324	54	7
$(C_6H_4OC_6H_4OC_6H_4CO)_n$	141–145	335	55	7, 14, 17
$(C_6H_4OC_6H_4OC_6H_4COC_6H_4OC_6H_4CO)_n$	148	345	56	7
$(C_6H_4OC_6H_4CO)_n$	152–155	365–367	58	7, 15, 17
$(C_6H_4OC_6H_4OC_6H_4COC_6H_4CO)_n$	150	365	58	7
$(C_6H_4OC_6H_4COC_6H_4OC_6H_4COC_6H_4CO)_n$	160	384	59	7
$(C_6H_4OC_6H_4COC_6H_4CO)_n$	165	384–391	60	7
$(C_6H_4OC_6H_4C_6H_4CO)_n$	216	478	69	16
$(C_6H_4COC_6H_4OC_6H_4C_6H_4O)_n$	167	416	64	17, 18
$(OC_6H_4OC_6H_4COC_6H_4C_6H_4COC_6H_4)_n$	192	428	64	16
$(OC_6H_4C_6H_4OC_6H_4COC_6H_4C_6H_4COC_6H_4)_n$	209	469	69	16
$(C_6H_4SO_2C_6H_4OC_6H_4COC_6H_4O)_n$	205		67	9

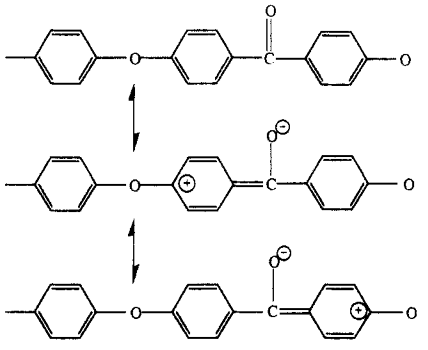


Figure 4. Electron-withdrawing effect in PEK.

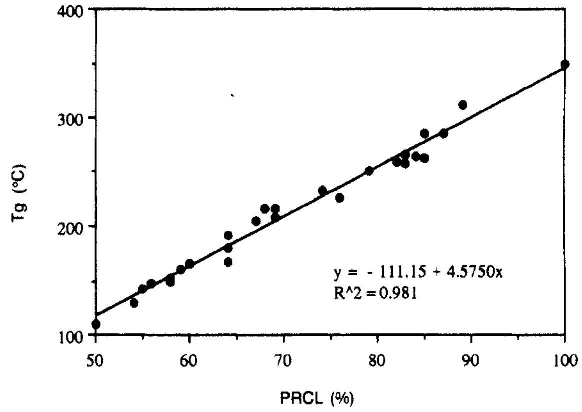


Figure 5. Linear relationship between PRCL and T_g for all poly(aryl ether sulfone)s and poly(aryl ether ketone)s reported in Tables I and II.

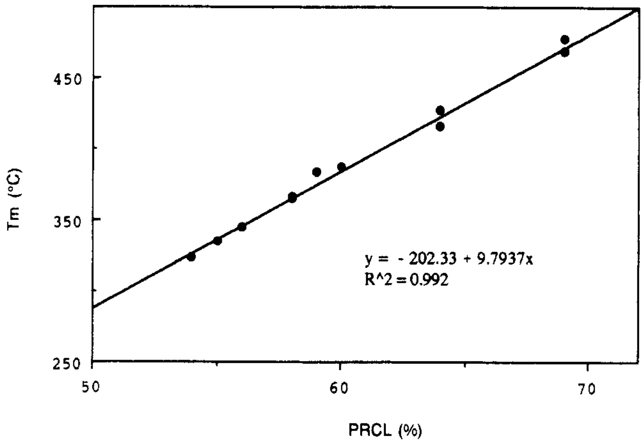


Figure 6. Linear relationship between PRCL in T_m for poly(aryl ether ketone)s.

However, all these improvements are beyond the scope of the present paper.

Wunderlich[24,25] had a similar approach to the PRCL concept when he defined the "bead" as the smallest section of a molecule that can move as a unit in internal rotation. On the basis of the hole theory of liquids he concluded that ΔC_p per structural bead at T_g should be constant. He observed also that the stiffest chains (with the largest end-to-end distance) have the highest energy requirement for hole creation. Van Krevelen[25] used additive group contributions and obtained good predictions of T_g for a large number of polymers.

II. Melting Point Study

The melting point is related to the melting enthalpy and entropy by the relationship

$$T_m = \Delta H_m / \Delta S_m$$

where $\Delta H_m = H_{melt} - H_{cryst}$ and $\Delta S_m = S_{melt} - S_{cryst}$ with m, melt, and cryst indices standing for melting, melt phase, and crystalline phase, respectively. As S_{melt} is directly related to the rigidity of a polymer chain, it has been attempted to apply the PRCL concept to a melting temperature study.

A. Poly(aryl ether ketone)s. The melting enthalpy ΔH_m is fairly constant for the full range of poly(aryl ether ketone)s studied due to the isomorphism of the diphenyl ether and diphenyl ketone groups leading to a good compaction of the crystal unit, whatever the chemical structure;[15] therefore, the melting temperature differences arise mainly from variation in the melting entropy. This is probably the main reason for the observed linear relationship (Figure 6) between the melting temperature and the PRCL for these polymers.

This is an important observation since, for poly(aryl ether ketone)s, the PRCL value appears to govern both T_g and T_m through linear relationships. The slope of the straight line is, significantly, higher for T_m than for T_g (Figures 5 and 6).

When sufficient data become available, the equilibrium melting temperature instead of melting temperature may be correlated to PRCL to avoid any crystallization dependence of T_m. However, the accuracy already seems good even if in some cases a low degree of polymerization leads to a misestimation of T_m values.

B. Poly(aryl ether sulfone)s. While many poly(aryl ether sulfone)s exhibit a symmetrical chain structure, it is generally recognized that polysulfones are noncrystallizable polymers. The most common explanation of that behavior is the steric hindrance of the sulfone group and the difference between the valence angles of the chain links. For instance, the valence angle of the diphenyl ether link is about 124°, while the valence angle of the diphenyl sulfone link is only 105°.[1] Table III confirms, via selected structures, that both steric hindrance and large valence angle differences (>11°) are needed to hinder the crystallization.

Table III
Crystallizability Study on Polymers Containing C–S Links

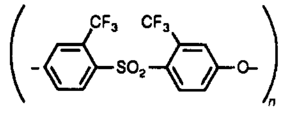
	T_g (°C)	T_m (°C)	steric hindrance due to SO_2	valence angle difference (deg)	ref
$(C_6H_4SO_2)_n$	350	>580	yes	0	5, 9
$(C_6H_4SC_6H_4SO_2)_n$		285–305	yes	±0	20
$(C_6H_4OC_6H_4SO_2)_n$	245		yes	±20	1, 12, 13
$(C_6H_4OC_6H_4S)_n$		340	no	±20	21
$(C_6H_4SC_6H_4OC_6H_4SC_6H_4SO_2)_n$	210–230		yes	±20	20
$(C_6H_4SC_6H_4SC_6H_4SC_6H_4CO)_n$		220–230	no	±20	20
		380	yes	±11	29

Table IV
PRCL$_{ns}$ for the Poly(aryl ether sulfone)s Listed in Table I

	T_m (°C)	$(PRCL)_{ns}$
$(C_6H_4OC_6H_4OC_6H_4OC_6H_4SO_2)_n$		50
$(C_6H_4OC_6H_4OC_6H_4SO_2)_n$		50
$(C_6H_4OC_6H_4SO_2)_n$		49
$(OC_6H_4C_6H_4OC_6H_4SO_2C_6H_4)_n$		60
$(OC_6H_4C_6H_4SO_2C_6H_4)_n$		63
$C_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4O)_n$	395	56
$(C_6H_4SO_2C_6H_4C_6H_4C_6H_4SO_2C_6H_4OC_6H_4SO_2C_6H_4O)_n$		59
$(C_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4OC_6H_4SO_2C_6H_4O)_n$		54
$(C_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4OC_6H_4SO_2C_6H_4O)_n$		56
$(C_6H_4SO_2C_6H_4C_6H_4C_6H_4SO_2C_6H_4OC_6H_4C_6H_4O)_n$	383	66
$(C_6H_4SO_2C_6H_4C_6H_4C_6H_4SO_2C_6H_4OC_6H_4O)_n$	393	61
$(C_6H_4SO_2C_6H_4C_6H_4C_6H_4SO_2C_6H_4O)_n$	398	63
$(OC_6H_4C_6H_4C_6H_4OC_6H_4SO_2C_6H_4)_n$	389	67
$(OC_6H_4C_6H_4C_6H_4OC_6H_4SO_2C_6H_4C_6H_4SO_2C_6H_4)_n$	408	67
$(OC_6H_4COC_6H_4OC_6H_4SO_2C_6H_4)_n$		49

Table V
Calculation Data

sequence	length (Å)	% rigidity	valence angle (deg)
C_6H_4	2.79	100	
C_6H_4–C_6H_4	7.08	100	
C_6H_4–C_6H_4–C_6H_4	11.37	100	
C–CO–C	1.5–1.5	33	124
C–O–C	1.36–1.36	0	124
C–SO_2–C	1.73–1.73	100	105

Thermodynamically, these two conditions correspond, through a lower compaction within the crystalline unit cell, to a lower ΔH_m, leading to a lowering of T_m. As simultaneously the sulfone link strongly rigidifies the polymer chain, the glass transition temperature is increased. Therefore, the $T_m - T_g$ difference decreases and the crystallization rate is very low. This observation is confirmed by the crystallizability of PEES when a lowering of T_g is induced by a solvent.[21]

A solution to the problem of the crystallization of poly(aryl ether sulfone)s from the melt can be found by increasing rigidification of the chain by a means other than the sulfone link. This will lead to a large decrease of the entropy of the melt without any corresponding decrease of the enthalpy (no increase of steric hindrance nor in valence angle difference). The melting point will remain fairly high.

This solution has been realized by Staniland[6] through the use of biphenyl and terphenyl groups, which can be considered as rigid due to the π-conjugation. Five poly(aryl ether sulfone)s of that structure are presented in Table I.

It is possible to calculate PRCL$_{ns}$, the contribution to the PRCL of all the rigid groups except the sulfone link (C_6H_4, C_6H_4–C_6H_4, and C_6H_4–C_6H_4–C_6H_4), for all the polysulfones in Table I. From Table IV it can be seen that the lower limit of this contribution lies around 61% in order to get a melt-crystallizable chain structure. The only exception is $(OC_6H_4C_6H_4SO_2C_6H_4)_n$, which requires reexamination. That limit of 61% of PRCL$_{ns}$ contribution seems to constitute a necessary condition to synthesize a crystallizable poly(aryl ether sulfone).

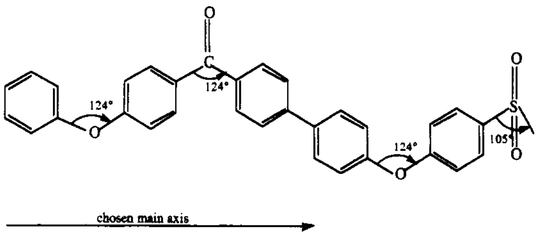


Figure 7. Repeat unit of a model poly(ether ketone-*co*-sulfone).

III. Calculation Procedure

The repeat unit is written in its extended form. Each sequence length is then calculated from the values reported in Table V[15,26,27] and projected onto the main axis of the molecule, taking into account the valence angles (Table V). The rigid length is then calculated by multiplication of the projected length of each rigid segment by its percentage of rigidity (see Table V). Finally, the percentage of rigid chain length is calculated as the ratio of the rigid length on the full length of the repeat unit. An example of calculation is given below for a model poly(ether ketone-*co*-sulfone) (Figure 7).

Example:

$$L_{rigid} = 3L_{C_6H_4} \cos 28° \times 100\% + L_{C_6H_4\text{-}C_6H_4} \cos 28° \times 100\% + 2L_{C\text{-}C} \times 33\% \times \cos 28° + 4L_{C\text{-}O} \cos 28° \times 0\% + L_{C\text{-}S} \cos 28° \times 100\% + L_{C\text{-}S} \cos 47° \times 100\% = 3 \times 2.79 \times \cos 28° + 7.08 \times \cos 28° + 2 \times 1.5 \times 33\% \times \cos 28° + 1.73 \times \cos 28° + 1.73 \times \cos 47° = 17.2 \text{ Å}$$

$$\begin{aligned} L_{\text{tot}} &= 3L_{C_6H_4}\cos 28° + L_{C_6H_4-C_6H_4}\cos 28° + 2L_{C-C}\cos 28° + 4L_{C-O}\cos 28° + L_{C-S}\cos 28° + L_{C-S}\cos 47° \\ &= 3 \times 2.79 \times \cos 28° + 7.08 \times \cos 28° + 2 \times 1.5 \times \cos 28° + 4 \times 1.36 \times \cos 28° + 1.73 \times \cos 28° + 1.73 \times \cos 47° = 23.8\ \text{Å} \end{aligned}$$

$$L_{\text{rigid (not from sulfone)}} = 3L_{C_6H_4}\cos 28° \times 100\% + L_{C_6H_4-C_6H_4}\cos 28° \times 100\% + 2L_{C-C} \times 33\% \times \cos 28° = 14.5\ \text{Å}$$

$$\text{PRCL} = L_{\text{rigid}}/L_{\text{tot}} = 17.2/23.8 = 72.3\%$$

$$\text{PRCL}_{\text{ns}} = L_{\text{rigid (not from sulfone)}}/L_{\text{tot}} = 14.5/23.8 = 60.9\%$$

Conclusion

The percentage of rigid chain length (PRCL) was defined as the ratio between the rigid length (each projected length weighted by its attributed rigidity: 0% for ether, 33% for ketone, and 100% for phenyl, biphenyl, terphenyl, and sulfone) and the full projected length of the repeat unit. The definition of this new concept leads to the glass transition temperatures of poly(aryl ether ketone)s and poly(aryl ether sulfone)s being univocally defined through a very simple linear relationship. In addition to the new perspectives it opens up for glass transition studies, this new parameter allows melting points of poly(aryl ether ketone)s to be predicted.

Additionally, the noncrystallizability of poly(aryl ether sulfone)s was discussed. A major conclusion of this study is the identification of a crystallization condition for these polymers: they can crystallize by enhancing their chain rigidity by a way other than introducing sulfones.

Through a slight modification (the exclusion of sulfone links from the rigid length calculation, leading to the percentage PRCL_{ns}), the concept allows the lower limit of PRCL_{ns} to be fixed at about 61% to get poly(aryl ether sulfone) crystallizable from the melt.

Predictions of T_g and T_m of a series of homopolymers by defining PRCL and PRCL_{ns}, both concepts related to the chain rigidity, suggest the important role of the chain mobility during these two thermal transitions. This observation is in keeping with the proposition that the mobility of the polymer chain is the same in the amorphous state and the melt phase.[28]

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