Notes

Conformational Properties of Poly(ether sulfone) and Poly(ether ketone)

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Analyses offered for the conformational statistics of the two polymers poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene), or poly(ether sulfone), PES,[1] and poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene), or poly(ether ketone), PEK,[2] have arrived at rather different interpretations of the properties of these chains in dilute solution, despite their similar structure. In both cases, the dependence of the intrinsic viscosity $[\eta]$ on the weight-average molecular weight M_w gives a large Mark−Houwink−Sakurada exponent $\nu = \partial \ln[\eta]/\partial \ln(M_w)$, with ν equal to 0.73 and 0.78 for PEK and PES, respectively, but the interpretation of this feature differs in the two works. The study on dilute solutions of PEK in 96.4% sulfuric acid, SA, concluded that the excluded volume effects on chain dimensions could be neglected on the basis of light scattering data on the weight-average molecular weight M_w, the light-scattering averaged mean square radius of gyration $(R_G^2)_{LS}$, and second virial coefficients $(A_2)_{LS}$ from static light scattering and hydrodynamic radius $(R_H)_{LS}$ from dynamic light scattering. Data on the dependence of $[\eta]$ on M_w were then analyzed with a wormlike chain model with negligible excluded volume effect on $[\eta]$ to determine the persistence length $\hat{a}$ for PEK, to give $\hat{a} \approx 2$ nm. By comparison, in the analysis of data on solutions of PES in *N*-methyl-2-pyrrolidone, NMP, with 0.1 M LiBr, it was assumed that the limiting value A_0 of $[\eta]/M_w^{1/2}$ determined by extrapolation of $[\eta]/M_w^{1/2}$ vs $M_w^{1/2}$ to zero $M_w^{1/2}$ to eliminate the effects of excluded volume on $[\eta]$ could be interpreted in terms of the unperturbed chain dimensions, to deduce $\hat{a} \approx 0.52$ nm. It is the objective here to reexamine the data on PES in the frame used to analyze the data on PEK, to determine whether the same treatment could be applied and, if so, whether it results in a substantial change in the estimate for $\hat{a}$.

Inspection of the data shows that, for a given M_w/M_L, both $M_L[\eta]$ and $(R_G^2)_{LS}$ are smaller for PES than for PEK. Here, M_L is the mass per unit contour length, equal to m_0/l, with m_0 the molar mass of a chain element with length l projected on the chain contour. Note that l so defined is not the bond length but involves a projection of that length on the chain contour axis. Following the method described in detail elsewhere,[2−4] $[\eta]M_L/L^2$ and $R_G^2/\hat{a}^2$ are each expected to be essentially universal functions of $L/\hat{a}$ and $d_T/\hat{a}$, with d_T a thermodynamic diameter, neglecting any normally weak dependence of $[\eta]$ on $d/\hat{a}$, with d the diameter of a chain element:

$$M_L[\eta] = \pi N_A K R_G^2 R_H/L \quad (1)$$

$$M_L[\eta]/L^2 = (\pi N_A/6)(\hat{a}/L)S(L/\hat{a},d_T/\hat{a}) \times H(L/\hat{a},d_T/\hat{a},d/\hat{a})\, K(L/\hat{a},d/\hat{a}) \quad (2)$$

$$R_G^2/\hat{a}^2 = (L/3\hat{a})S(L/\hat{a},d_T/\hat{a}) \approx (L/3\hat{a})\{\alpha^{-2} + 4\hat{a}/L\}^{-1} \quad (3)$$

$$R_H/\hat{a} = (L/2\hat{a})H(L/\hat{a},d_T/\hat{a},d/\hat{a}) \approx (L/2\hat{a})\{(27L/16\hat{a}\alpha^2) + \ln^2(3L/2d)\}^{-1/2} \quad (4)$$

$$\alpha = \{1 + 7.542\hat{z} + 11.06\hat{z}^2\}^{0.0886} \quad (5)$$

$$z = (3/\pi)^{1/2}(3d_T/16\hat{a})(L/\hat{a}) \quad (6)$$

where $\alpha = (3R_G^2/\hat{a}LS(L/\hat{a},d_T/\hat{a}))^{1/2}$ is the expansion factor of the root-mean-square radius of gyration, and $\hat{z} = A(L/\hat{a})z$, with $A(L/\hat{a})$ a known function;[5−7] $A(L/\hat{a})$ is unity for large $L/\hat{a}$ (coil), decreasing to zero for small $L/\hat{a}$ (an approximate analytical form is available[3]). The definition for K is given elsewhere;[2−4] $K \approx 10/3$ for $L/\hat{a} \gg 1$, and $K = 1$ for $L/\hat{a} \ll 1$ and $d/a \ll 1$. These expressions are based on approximations to theoretical relations given by a number of authors, as discussed in the references cited. Certain nuances are suppressed in this representation, and alternative forms for some of the functions given are available. For example, as discussed in the references cited, the functions given for $S(L/\hat{a},d_T/\hat{a})$ and $H(L/\hat{a},d_T/\hat{a},d/\hat{a})$ are numerically acceptable approximations to more complex, analytically known functions, and an alternative definition for α based on the hydrodynamic radius might be used in the expression for $R_H/\hat{a}$ to account for some effects.[8,9] Alternative forms for the functions $A(L/\hat{a})$ and α have also found use in interpreting data on semiflexible chains,[6] e.g., see ref 10. However, these alternatives will not have a significant effect on the conclusions reached below.

These expressions simplify if $\alpha \approx 1$, either because $d_T = 0$ or because $L/\hat{a}$ is small enough that $A(L/\hat{a}) \approx 0$. It is anticipated that the latter feature will have an influence, given the long effective bonds in the polymer (see below). In that case, assuming identical d/l for the hydrodynamic units of PES and PEK, the ratio of $\hat{a}/l$ for the two polymers can be approximated as the factor q required to superpose plots of $M_L[\eta]/L^2$ vs L/q or plots of $(R_G^2)^{1/2}/q$ vs L/q, with $q = (\hat{a}/l)/(\hat{a}/l)_{REF}$ equal to unity for the polymer taken as the reference. Assuming identical l for the two polymers, this amounts to the value of $\log(q)$ that will superpose plots of $\log[m_0[\eta]/(M/m_0)^2]$ vs $\log(M/m_0)$ by a "horizontal shift" $\log(q)$ along $\log(M/m_0)$ or plots of $\log[(R_G^2)^{1/2}]$ vs $\log(M/m_0)$ by "vertical and horizontal shifts" $\log(q)$ along $\log[(R_G^2)^{1/2}]$ and $\log(M/m_0)$, respectively. A difference in l for the two

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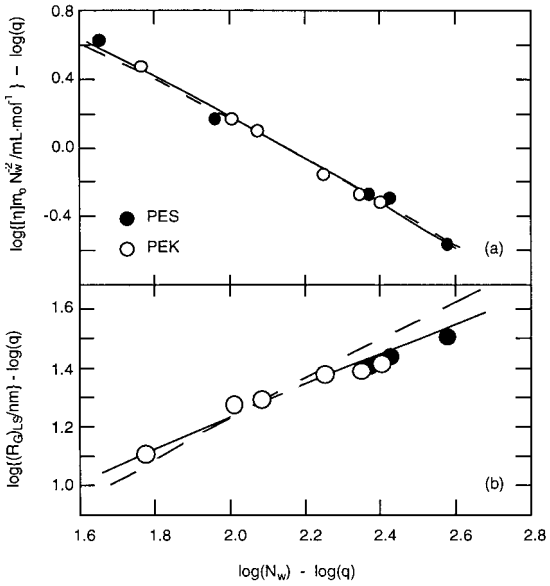

Figure 1. Log$[m_0[\eta]/N_w^{1/2}]$ and log$[(R_G)_{LS}] - \log(q)$ vs $\log(N_w) - \log(q)$ for solutions of PEK and PES, in parts a and b, respectively, with $N_w = M_w/m_0$ and $(R_G)_{LS} = (R_G^2)_{LS}^{1/2}$. As discussed in the text, q is chosen to superpose the data on the two polymers. The full and dashed curves were calculated with $\hat{a}/l$ equal to 2.2 and 1.0, respectively, including a factor $[M_{(\mu+1)}/M_w]^{\mu+1}$ to account for the effects of molecular weight polydispersity on $(R_G)_{LS}$ as described in the text.

polymers would require division of $(R_G^2)^{1/2}$ by l and $[\eta]$ by l^3 in the analyses, but that is unnecessary here as $l \approx 1.0$ nm for both polymers using bond angles and lengths given for benzophenone, diphenyl ether, and diphenyl sulfone.[11] Since the polymers are heterodisperse in M in both studies, $N_w = M_w/m_0$ is used in the analysis of the viscometric data, with the results shown in Figure 1a if it is assumed that $\alpha \approx 1$, so that excluded volume effects maybe neglected. The use of M_w is expected to be a very good approximation to account for molecular weight dispersion for the analysis of $[\eta]$, especially as ν approaches unity, in which case $[\eta] \propto M_w$. The result from the analysis of $[\eta]$ gives $(\hat{a}/l)_{PES}/(\hat{a}/l)_{PEK} \approx 0.57$ using the data on PEK as the reference. The solid curve shown in Figure 1a is calculated with $(\hat{a}/l)_{PEK} \approx 2.2$, using the expressions given above.

Removal of the constraint that $\alpha \approx 1$ requires increasing values of d_T as $\hat{a}/l$ decreases to fit the viscometric data, with d_T specific to each polymer. This is most conveniently estimated by determining the parameter $w = z/(L/\hat{a})^{1/2} \approx (3/16)(3/\pi)^{1/2} d_T/\hat{a}$ required to fit $[\eta]$ as a function of M_w given a choice of $\hat{a}/l$. The results for $\hat{a}/l$ with d_T/l are given in Table 1 for both PEK and PES, along with the value of α for $\log(L/\hat{a}) = 2.2$. For example, the fit to the data with $(\hat{a}/l)_{PEK} \approx 1$, shown in Figure 1a as the dashed curve, requires the extremely large estimate $d_T \approx 56$ nm and correspondingly large values of α (see Table 1); similarly, $d_T \approx 16$ nm for $(\hat{a}/l)_{PES} \approx 0.57$. Using the analysis applied to estimate $\hat{a}$ from A_0, as applied with PES, A_0 is found to be 0.087 and 0.313 (with $[\eta]$ in mL/g) for PES and PEK, respectively. With A_0 interpreted as $A_0 = \Phi'(\hat{a}l/3m_0)^{3/2}$, $(\hat{a}l)_{PES}/(\hat{a}l)_{PEK} \approx 0.50$, assuming Φ' is the same for both polymers, by comparison with $(\hat{a}/l)_{PES}/(\hat{a}/l)_{PEK} \approx 0.57$ obtained above. Use of the estimate $\Phi' \approx (20/9)\pi N_A$ expected for $L/\hat{a} \gg 1$ gives $(\hat{a}l)_{PEK} \approx 1.04$ nm^2 and $(\hat{a}l)_{PES} \approx 0.52$ nm^2, similar to the values reported above for a large excluded volume effect if $l \approx 1$ nm, as estimated from the polymer structure. It may be seen that there

Table 1. Characterization Parameters for PEK and PES

polymer	w^a	$\hat{a}/l^b$	d_T/l^c	α^d	$[M_{(\mu+1)}/M_w]^{\mu+1\,e}$
PEK	0.00	2.2	0	1	6.76
	0.04	2.0	0.22	1.14	6.25
	0.11	1.8	0.59	1.28	5.76
	0.45	1.5	2.46	1.61	4.41
	2.40	1.2	13.1	2.18	3.24
	4.40	1.1	24	2.45	2.89
	10.0	1.0	54.6	2.86	2.25
PES	0.00	1.2	0	1	3.42
	0.10	1.0	0.55	1.32	2.40
	0.40	0.8	2.18	1.67	1.82
	1.20	0.7	4.58	2.04	1.44
	3.60	0.6	19.65	2.51	1.00

[a] $w = z/(L/\hat{a})^{1/2} = (3/\pi)^{1/2}(3/16)(d_T/\hat{a})$. [b] $\hat{a}/l$ computed for listed w from the dependence of $[\eta]$ on M_w. [c] d_T/l corresponding to the listed w and $\hat{a}/l$. [d] Value of α corresponding to the listed w and $\hat{a}/l$ and $\log(L/\hat{a}) = 2.2$. [e] $[M_{(\mu+1)}/M_w]^{\mu+1}$ needed to fit the $(R_G^2)_{LS}$ on N_w corresponding to the listed w and $\hat{a}/l$.

is little reason to differentiate between the estimates for $(\hat{a}/l)_{PEK}$ equal to 1 and 2.2 on the basis of the fits to the data in Figure 1b; a similar situation applies to the data on $(\hat{a}/l)_{PES}$ over the range $0.57-1.2_5$. However, consideration of the corresponding values of d_T does provide some insight. In the absence of electrostatic interactions, d_T might be expected to be no larger than about twice the geometric diameter d_G of the chain. As discussed elsewhere, consideration of the data on the reduced parameter $(A_2)_{LS} M_w^2/N_A(R_G^2)_{LS}^{3/2}$, in the range $0.3-0.5$ solutions of PEK in SA, gave $d_T \approx 0.08$ nm, corresponding to a rather weak excluded volume effect on the chain dimensions and supporting the use of the analysis with $\alpha \approx 1$ for PEK. Electrostatic effects in the PEK/SA system were estimated to give a contribution $d_{elec} \approx 0.6$ nm to d_T, with this offset by negative contributions to d_T for the bare chain, to give the estimate $d_T \approx 0.08$ nm quoted above. Consequently, on this basis, it appears that excluded volume effects are essentially unimportant, giving an estimate of $\hat{a} \approx 2.2$ nm for PEK on the basis of the viscometric data. The parameter $(A_2)_{LS}M_w^2/N_A(R_G^2)_{LS}^{3/2}$ reported for solutions of PES in NMP:0.1 M LiBr are close to unity, suggesting a larger d_T might be appropriate for this system than for the PEK/SA system, but in any case, a result with $\hat{a}$ less than the value for a freely rotating chain (see below) should be rejected as physically unreasonable.

An alternative estimate for q, and $\hat{a}$, may be determined in principle from the dependence of $(R_G^2)_{LS}$ on N_w, but since $(R_G^2)_{LS}$ is very sensitive to molecular weight dispersion and the polymers are heterodisperse in M in both studies, the vertical and horizontal shifts required for superposition of $\log[(R_G^2)_{LS}^{3/2}]$ vs $\log(M_w/m_0)$ for the two polymers could differ unless this effect is taken into account. If it is assumed that $R_G^2/\hat{a}^2 \approx r(L/\hat{a})^{\mu}$ with constant r and μ for a monodisperse sample, then $(R_G^2)_{LS}/\hat{a}^2 \approx r(M_w/\hat{a}M_L)^{\mu}(M_{(\mu+1)}/M_w)^{\mu+1}$, where $M_{(s)} = \{\Sigma w_i M_i^s\}^{1/s}$ for a polydisperse polymer with weight fraction w_i of chains with molecular weight M_i.[12] Since $\mu \approx 1$ for the data on PEK and PES, $[M_{(\mu+1)}/M_w]^{\mu+1} \approx M_z/M_w$ for these polymers. Accordingly, $(R_G^2)_{LS}^{1/2}/D$ is used in the analysis of the experimental data, with the results shown in Figure 1b, where $D^2 = \{[M_{(\mu+1)}/M_w]/[M_{(\mu+1)}/M_w]_{REF}\}^{\mu+1}$ is intended to account for the difference in the effects of molecular weight dispersion between the two polymers, with $D = 1$ for PEK. Use of the result $q \approx 0.57$ from the analysis of $[\eta]$ for the case with $\alpha \approx 1$ gives $D \approx 0.75$ for PES or a narrower distribution of molecular weight for the PES samples

than for the PEK polymers. The curves drawn in Figure 1b are calculated for PEK with $l \approx 1$ nm, $\hat{a} \approx 2.2$ or 1.0 nm, and the d_T given above associated with these values. In addition, values of $[M_{(\mu+1)}/M_w]^{\mu+1}$ equal to 6.76 and 2.25 were used with PEK to superpose the computed curves on the experimental data for $\hat{a}$ equal to 2.2 and 1.0 nm, respectively. It is seen that the fit of the calculated curves to the data is significantly better for the larger $\hat{a}$, even though the corresponding estimates for $[M_{(\mu+1)}/M_w]^{\mu+1}$ is unexpectedly large for both values; the data on PES are too sparse to permit a similar differentiation. Estimates of $[M_{(\mu+1)}/M_w]^{\mu+1}$ for intermediate $\hat{a}/l$ are shown in Table 1 for both PEK and PES. The extreme values shown for PES range from $[M_{(\mu+1)}/M_w]^{\mu+1}$ equal to 2.51 and 1.0 for $\hat{a}$ equal to 1.2 and 0.6 nm, respectively. The unexpectedly large $[M_{(\mu+1)}/M_w]^{\mu+1} \approx M_z/M_w$ corresponding to the larger $\hat{a}/l$ (and $\alpha \approx 1$) could be caused by otherwise undetected components with large M, including either a weakly populated high molecular weight tail or, more likely, possible intermolecular aggregates. Either would have a far greater effect on the dependence of $(R_G^2)_{LS}$ on M_w than that of $[\eta]$ on M_w.

The persistence length $\hat{a}_{FR}$ for the chain with free rotation about fixed effective bond lengths with fixed bond angles provides a convenient norm for comparison of the chain conformations. The PEK and PES structures involve one (equivalent) bond length b and two bond angles, giving[13]

$$\hat{a}_{FR} = \frac{b^2}{2l}\frac{(1 - \cos(\vartheta_1))(1 - \cos(\vartheta_2))}{(1 - \cos(\vartheta_1)\cos(\vartheta_2))} \qquad (7)$$

Thus, based on the optimal structures for benzophenone, diphenyl ether, and diphenyl sulfone,[11] b is 0.565 and 0.597 nm for the O−Ph−(CO) and O−Ph−(SO_2) segments, respectively, and the bond angles are 123.3°, 120.1°, and 104.2° for C−O−C (ether), C−(CO)−C (ketone) and C−(SO_2)−C (sulfone), respectively, and l is 0.987 and 0.996 nm for PEK and PES, respectively. With these parameters, $(\hat{a}_{FR})_{PES} \approx 0.80$ nm and $(\hat{a}_{FR})_{PEK} \approx 1.04$ nm (note that different values would obtain if the bond length and not its projected value were to be used in the definition of M_L). Using the estimates for $\hat{a}$ given above obtained in the absence of excluded volume effects, $(\hat{a}/\hat{a}_{FR})_{PES} \approx 1.5$ and $(\hat{a}/\hat{a}_{FR})_{PEK} \approx 2.1$; the estimate for PES could drop to unity if excluded volume effects are included with $d_T = 2.2$ nm (and $[M_{(\mu+1)}/M_w]^{\mu+1} \approx 1.82$). Rotation about the ether−phenyl bonds is only slightly hindered in diphenyl ether, compared with the corresponding rotation about the carbonyl−phenyl or sulfone−phenyl bonds in benzophenone or diphenyl sulfone, respectively.[11] The planes of the phenyls tend to lie in the molecular plane for benzophenone or orthogonal to that plane for diphenyl sulfone.[11] The relatively free rotation about the ether−phenyl bonds tends to negate the effects of any hindrance to rotation at the ketone or sulfone functionalities with respect to the chain conformation and to reduce $\hat{a}/\hat{a}_{FR}$ toward unity for both polymers. Although PEK is protonated in solution in SA, an estimate of the electrostatic contribution to $\hat{a}$ showed it to be small, about 0.2 nm, owing to electrostatic screening due to the high ionic strength of SA.[2] The difference between $\hat{a}$ for the two polymers may reflect a somewhat enhanced ability to form resonance structures for PEK, with concomitant increase in $\hat{a}$.[14]

Though a definitive evaluation of $\hat{a}$ and d_T from data on $[\eta]$ as functions of M_w is not possible for the data on PEK and PES, is concluded that $\hat{a}/\hat{a}_{FR}$ is closer to unity for PES than PEK and does not exceed about 2 for either polymer, regardless of the treatment of excluded volume effects, with $\hat{a}$ larger for PEK than PES. It appears that for PEK the larger values of $\hat{a}$ are best consistent with the anticipated d_T from analysis of the second virial coefficient, with further support from the analysis of dependence of $(R_G^2)_{LS}$ on M_w as providing the best fit to the data, even though that analysis leads to a rather large estimates for $[M_{(\mu+1)}/M_w]^{\mu+1}$, possibly owing to the effects of intermolecular association. With this interpretation, the overall conformation is that of a semiflexible coil, in a range of $L/\hat{a}$ for which $S(L/\hat{a},d_T/\hat{a}) \approx 1$. The range of the estimates for $\hat{a}$ for PES from $\hat{a} \approx \hat{a}_{FR} \approx 0.8$ nm, with $d_T \approx 2.2$ nm, to $\hat{a} \approx 1.25$ nm for $d_T = 0$ is relatively narrow, indicating a chain with nearly free rotation about the O−Ph−(SO_2) effective bond.

References and Notes

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