NOTES

Comments on Paper by Nemoto *et al.* Concerning Self Diffusion Coefficient, D_s, and Zero Shear Viscosity, η_0 of Polystyrene in Dibutylphthalate

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Nemoto *et al.*[1] obtained data on two narrow distribution at-polystyrenes, $\bar{M}_n = 43300$ and $\bar{M}_n = 335000$ at concentration of 40 and 50% by weight in dibutylphthalate at temperatures from 0 to 120°C. Data were presented in both tabular and graphical form. They concluded correctly that these data did not follow a simple Arrhenius plot for either $\log D_s - T^{-1}$ or $\log \eta_0 - T^{-1}$. Then they fitted these data by the WLF procedure.[2] They concluded that this free volume approach yielded a correct description of their results.

Visual inspection of their plotted data, their Figures 3a and 3b specifically, with assistance from a straight edge, suggested to us an opposite conclusion, namely, that all experimental data for D_s and η_0 followed a double or possibly a triple Arrhenius plot whose intersections implied liquid state transitions, one of which is T_{ll} lowered from its bulk state value by diluent. T_{ll} is the intramolecular liquid–liquid transition normally found in atactic polymers and copolymers at $(1.20 \pm 0.05) T_g(K)$; the other is an intramolecular event designated $T_{l\phi}$.[6]

As we have noted on several occasions,[3,5-7] Frenkel and his colleagues postulate that T_{ll} arises from intermolecular segment–segment associations which are thermally reversible and shear reversible. The source of these associations is the same intermolecular attraction that holds simple liquids together. These associations lead to a three dimensional physical network which inhibits but does not prevent flow. We suggest[6] that the sharp decrease in enthalpy of activation for η_0 across T_{ll} results from the disappearance of these physical networks.

Figure 1 is a plot of $\log D_s$ and $\log \eta_0$ against $1000/T(K)$ for 40% by weight of at-PS, 43900 in dibutylphthalate. Slope changes are indicated by vertical lines which occur at about the same values of $1000/T$ by both methods. A similar plot was prepared for at-PS, 335000 at 50% concentration, using D_s data, with one sharp slope change at 362 K (not shown).

EXPERIMENTAL BACKGROUND

Since 1966, when it was first suggested that $\log \eta_0 - T^{-1}$ plots followed a double Arrhenius pattern with a slope change at T_{ll},[8] we have examined various bodies of such published data as a function of molecular weight for a given polymer[9,10]; polymer types[6,7]; and more rarely polymer concentrations in polymer–diluent system.[11]

The number of intersections found in η_0
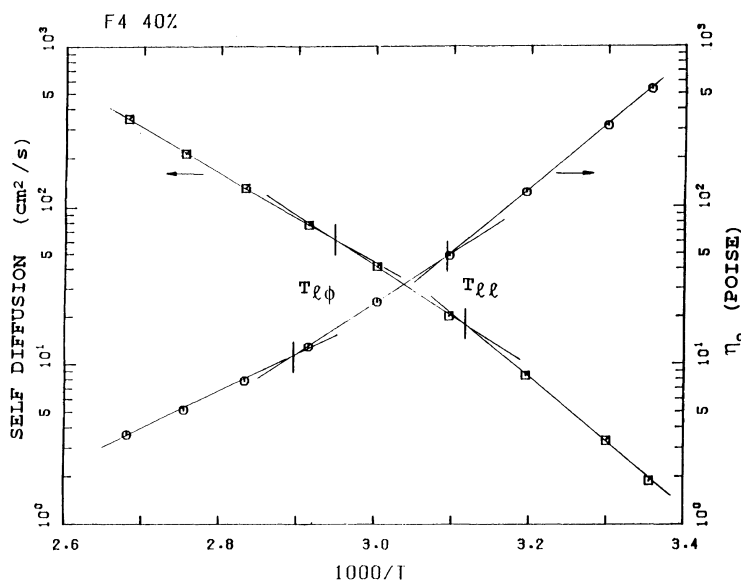
Figure 1. Self diffusion, D_s, and melt viscosity, η_0, triple Arrhenius plots for 40% by weight at -PS, $\bar{M}_n =$ 43,300 in dibutylphthalate from data of Nemoto *et al.*[1] We have added the T_{ll} and $T_{l\phi}$ designations.

data for the liquid state depends on the polymer, the range in temperature, the number of data points, and the accuracy of the data. At-PS under ideal conditions indicates three transitions: T_{ll}, $T_{l\rho}$, and $T_{l\phi}$ in order of ascending temperature. T_{ll} increases with $\bar{M}_n$, finally leveling off at $T_{ll}(\infty)$. $T_{l\rho}$ is independent of $\bar{M}_n$ at a constant value $= T_{ll}(\infty)$. $T_{l\phi}$ is also independent of $\bar{M}_n$ with a value of 190 ± 5 K in PS, but more generally at $T_{ll} + 30$—50 K. $T_{l\rho}$ is most easily found at $\bar{M}_n < 2000$ and hence should not be located in any data discussed in the present study. All three of these loci are found in Figure 1 of ref 6. An earlier plot[5] designated $T_{l\phi}$ as $T_{l\rho}$.

Data were of 3 types: tabulated, graphical and both as in the present case.[1] Tabulated data have been examined by regression analysis with residuals,[9,10] by point to point first derivatives[9]; and by the Solc automatic intersection method which determines the number of linear segments and their coordinates in a given body of data which will minimize the standard deviation.[12] In the present instance, the number of data point -9 for three lines

with FA-40 and FA-50 is borderline for use of computerized intersection method discussed in ref 12.

Actually, visual inspection of plotted data can be quite accurate, especially with high T_{ll} polymers. The change in enthalpy of activation across T_{ll} in bulk at-PS drops from *ca.* 75 kcal mol^{-1} at $T < T_{ll}$ to *ca.* 43 kcal mol^{-1} just above T_{ll} with no marked dependence on molecular weight.[9] This same study covering values of $\bar{M}_n$ from 3500 to 390000 showed no evidence for a change in the behavior of T_{ll} based on intersections on going through the entanglement molecular weight, M_c (Figure 11 of ref 9). This is consistent with the findings for D_s and η_0 in dibutylphthalate solutions.[1]

SELF-DIFFUSION DATA FOR PS

Later, with the advent of self-diffusion data in the polymer literature, such as that of Bachus and Kimmich,[13] we followed this type of work as a possible source of T_{ll} and other liquid state events. The cited work[13] represented their $\log D_0 - T^{-1}$ data on PS as a

double Arrhenius plot, with an intersection at $T_{l\phi}$. Later we examined in considerable detail the published data of Sillescu *et al.*[14] on self-diffusion of end tagged PS for a range of molecular weights present in high dilution in a host PS of constant molecular weight. By replotting their data we located two mol. wt. independent transitions, one at 162°C which we assigned as T_{ll} of the host polymer; the second at 180°C which we ascribed to $T_{l\phi}$ of the host or the tagged polymer. This analysis is found in Figure 8 of ref 8.

We had concluded from our various studies of $\log \eta_0 - T^{-1}$ and $\log D_s - T^{-1}$ data that, depending on the temperature range covered, any given data set was correctly represented by a double or triple Arrhenius plot with the intersection(s) indicating liquid state transitions: T_{ll} alone; T_{ll} and $T_{l\phi}$; or $T_{l\phi}$ alone. While any data set could be fitted by a WLF equation with values of C_1 and C_2 in the usual range, WLF was only a convenient approximation to a real situation.[10] Limited experience with self-diffusion data suggested a similar conclusion. Hence we automatically subjected the data under study[1] to similar scrutiny.

We recognize that multiple Arrhenius lines require a slope and intercept for each line and a set of coordinates defining each intersection. The WLF representation is mathematically much simpler. Our concern, however, is with the physical nature of the liquid state. We believe that the intersections under discussion are caused by liquid state transitions and indicate (or locate) transition temperatures, as already stated.

OTHER LITERATURE DATA

We have considered two other literature studies in relation to the present paper: the older one covers η_0 measurements on poly(*n*-butylmethacrylate), PnBMA, in diethylphthalate over the entire composition range and for a tempeature span from 273—393 K. These

Table I. T_{ll}, K for at-PS–diluent systems

Composition	From $\log \eta_0 - T^{-1}$ [a]	From $\log D_s - T^{-1}$ [a]	TBA[b,a]
40 wt% PS	323	320	319
50 wt% PS	330, 328	338	332

[a] PS MW 43906. Diluent dibutyl phthalate.[1]
[b] PS, $\bar{M}_n = 37000$ plus diluent.[19,20]
[c] Torsional braid apparatus.[19]

NOTES: Brief remarks are in order concerning differences in $\bar{M}_n$, diluent and effective frequency of the several methods as they affect the determined values of T_{ll}.

F4 has a slightly higher $\bar{M}_n$ which should increase T_{ll} at a given W_2 value. The $\bar{M}_n$ effect is further illustrated by the T_{ll} value of F40—50, namely 362 K by D_s, with $\bar{M}_n = 335000$, 50% concentration.

TBA has a frequency of about 0.3 Hz as compared to estimated effective frequencies of 10^{-2}—10^{-4} for D_s and η_0 so that TBA should give higher T_{ll}'s at fixed W_2.

Lacking detailed studies, it is difficult to predict the relative effectiveness of the two diluents in lowering T_{ll} since they differ both in molecular weight and presumably in solubility parameters.

data are available in graphical form only.[16] The second involves at-PS of $\bar{M}_n = 37000$ in a diphenylether type diluent measured by torsional braid analysis to locate T_{ll} and $T_{l\phi}$. Graphical and tabulated data are available.

PS DILUENT SYSTEMS BY DYNAMIC MECHANICAL LOSS

Since the work under study involves at-PS in dibutylphthalate, the most pertinent comparable work known to us is a study of Gillham *et al.*[17] of at-PS, $\bar{M}_n = 37000$ in an aromatic-ether diluent $(C_6H_5OC_6H_4O)_2C_6H_4$, MW 447, using the torsional braid analysis technique to detect T_g and two $T > T_g$ transitions, T_{ll} and $T_{l\phi}$, over the entire composition range. The original study shows graphical data only.[17] A review paper contains both graphical and tabulated results.[18]

Table I lists intersection temperatures estimated by us from ref 1 D_s and η_0 data and values of T_{ll} from ref 18. It seems likely that these former intersections represent T_{ll}. The same conclusion holds for the 50% PS data.

The higher temperature intersections at 343 and 348 K in Figure 1 may be $T_{l\phi}$ but clearly lower than that shown for TBA data in ref 18, namely 370 K at 0.19 Hz.

SUMMARY AND CONCLUSIONS

1. The D_s and η_0 data of Nemoto et al.[1] can be and should be represented by multiple Arrhenius plots with the low temperature intersection corresponding to the T_{ll} transition temperature for PS of $\bar{M}_n \sim 40000$.

2. A 1:1 correspondence in T_{ll} values obtained from D_s, η_0, and TBA was shown for at-PS with $\bar{M}_n \sim 40000$.

3. All results in (1) and (2) above are consistent with the Frenkel view of T_{ll} as caused by intermolecular segment–segment associations which "melt out" on heating and are forced to lower temperature by diluents.

4. $D_0 - T^{-1}$ data in solution (1) and in bulk[13,14] provide an absolute method for obtaining T_{ll} and $T_{l\phi}$ at very low frequencies, just as $\eta_0 - T^{-1}$ data do.

5. Even if the existence of the T_{ll} and/or $T_{l\phi}$ transitions is rejected, the fact remains that double or triple Arrhenious plots are superior to WLF, leading to the need for an explanation of the slope change(s).

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18. See Figure 9 and Table 2 of ref 4 for both plotted and tabulated data, respectively.