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Chain-Length Dependence of the Glass Transition Temperature

Introduction. It is well-known that the glass transition temperature, T_g, of a given polymer is a function of its chain length.[1,2] However, a detailed model of T_g that is generally accepted has yet to be produced, and therefore the chain length dependence of T_g has yet to be modeled in detail. Perhaps the most commonly used description of the chain-length dependence of T_g is that of Flory and Fox[1]

$$T_{g,n} = T_{g,\infty} - K/X_n \qquad (1)$$

where X_n is the number-average chain length, K is a polymer-specific constant, and $T_{g,\infty}$ is the asymptotic value twoard which T_g tends as molecular weight increases. Equation 1, though empirical, is usually justified on the ground that chain ends introduce incremental amounts of free volume over that of segments. Although many data show that T_g does vary linearly with $1/X_n$ at high molecular weights, departures from linearity have been noted by several investigators[3-6] for a variety of polymers at molecular weights (M_n) less than about 5000.

Other, theoretical descriptions of T_g have been given that contain a chain-length dependence. A thermodynamic approach to a description of T_g put forward by Gibbs and DiMarzio[7] has been used by Beevers and White[2] to develop the following relationship between T_g and X_n

$$\frac{X_n}{X_n-2}\left[\frac{V_0 \ln V_0}{V_0-1}+\frac{\ln 2X_n}{X_n}-\frac{X_n-1}{X_n}\right]= \frac{2\beta \exp(\beta)}{1+2\exp(\beta)}+\ln\,[1+2\exp(\beta)] \qquad (2)$$

where V_0 is the fraction of free volume existing at T_g and β is a measure of the flex energy of the segments.

In a more recent model Dibenedetto has described T_g based on the principle of corresponding states.[8] There can also be found a function relating T_g to chain length

$$\frac{T_{g,\infty}}{T_{g,n}} = \frac{[X_n + (C_e/C_m)][X_n + (S_e/S_m)]}{[X_n + (S_e/S_m)(\epsilon_{ee}/\epsilon_{mm})^{1/2}]^2} \qquad (3)$$

where the subscripts e and m refer to end groups and middle segments, respectively, and the terms ϵ, S, and C refer to interactions, contact areas, and mobilities, respectively.

In the course of work involving the preparation of low molecular weight polymers using a catalytic chain-transfer agent,[9] we have had occasion to measure the T_g of poly(methyl methacrylates) (PMMA) varying in molecular weight from as low as several hundred to as high as 14 000. We have found empirically that nonlinear regression with our results gives an inverse dependence on T_g on the number-average chain length raised to the 0.66 power; i.e., our results can best expressed by an equation of the form

$$T_g = T_{g,\infty} - K/X_n^{2/3} \qquad (4)$$

We have also found that eq 4 represents literature data for several other polymers as well or better than does eq 1. In this paper we present our results and discuss eqs 1-4.

Experimental Section. PMMA was prepared in the presence of the catalytic chain-transfer agent Cobaloxime boron fluoride (COBF) as previously described.[9] These were bulk polymerizations using an azo initiator at 60 °C, with amounts of COBF ranging from 0.1 to 20 ppm based on a monomer. The resultant polymer was analyzed by both GPC and NMR to determine its molecular weight. The samples had a rather narrow polydispersity; typically the ratio of weight to number-average molecular weights, M_w/M_n, ranged from 1.4 to 1.9. T_g was determined on 5-10 mg of annealed polymer samples using a Perkin-Elmer DSC-4 with a heating rate of 25 °C/min. From thermogravimetry of a sample with M_n = 316 it was determined that the dimer boiled at 176 °C, much higher than any of the T_g measurements made.

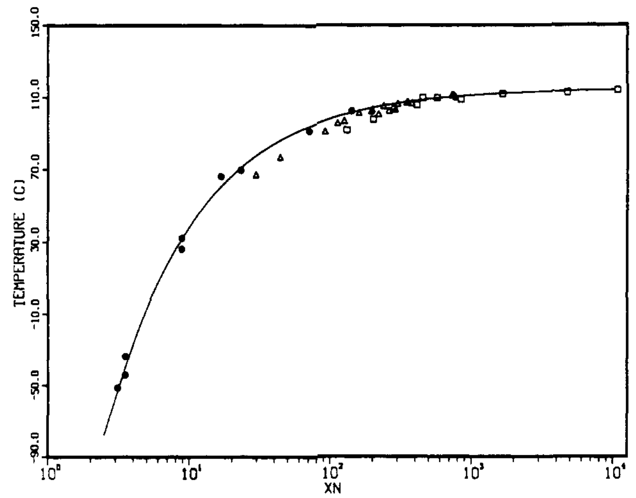

Figure 1. T_g as a function of X_n for PMMA: (△) ref 12, (■) ref 13, (●) this work, Table I. Solid line fitted to eq 4 with $T_{g,\infty}$ = 386 and K = 353.

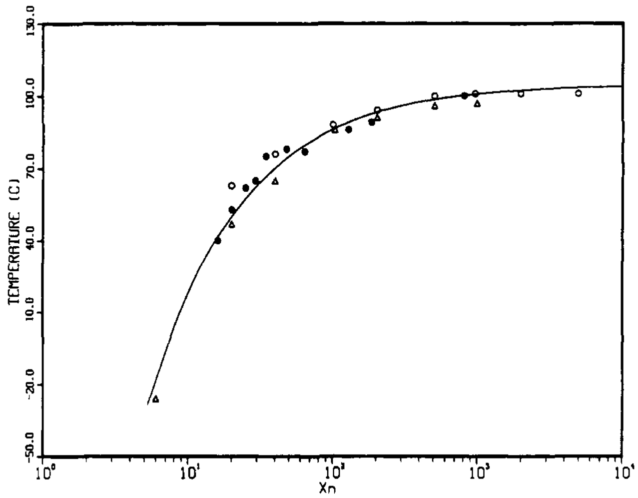

Figure 2. T_g as a function of X_n for PSTY: (●) ref 1, (○) ref 5, (△) ref 14. Solid line fitted to eq 4 with $T_{g,\infty}$ = 378 and K = 404.

Results and Discussion. Table I presents the DSC results on the T_g of PMMA samples whose molecular weight was determined by GPC and, where feasible, checked by NMR. These data were fitted to eqs 1, 3, and 4 by using a nonlinear regression analysis (a modified Gauss-Newton algorithm from a statistical analysis system). We also tried fitting eq 2, but, as pointed out by Kusy and Greenberg,[10] it does not lead to a unique solution in regression analysis because of its many parameters. Therefore, eq 2 is not discussed any further. Equation 3 was used in a modified form as suggested by Dibenedetto, where the term $\epsilon_{ee}/\epsilon_{mm}$ is set equal to unity. This approach led to wide 95% confidence intervals and also gave S_e/S_m values much less than the value of 1-2 expected by Dibenedetto.[11] For these reasons, we do not consider eq 3 any

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Table I
T_g of PMMA as a Function of Chain Length

X_n	140.80	70.51	23.14	16.75	8.83	8.83	3.51	3.52	3.16	3.10
T_g	102.73	91.58	69.91	66.33	32.46	26.41	−34.31	−44.02	−52.37	−51.33

Table II
Comparison of Estimates of Parameters in Equations 1 and 4

polymer and X_n range	eq	$T_{g,\infty}$	K	residual sum sqs
PSTY[5]	1	374 ± 2	1005 ± 187	13.8
38–4790	4	376 ± 1	313 ± 36	5.5
PSTY[1]	1	369 ± 4	873 ± 130	93
16–817	4	376 ± 6	370 ± 60	110.2
PSTY[14]	1	365 ± 8	704 ± 413	232.1
6–960	4	376 ± 2	404 ± 22	14.3
PSTY	1	368 ± 3	756 ± 65	676.3
all 3 data sets above	4	378 ± 2	404 ± 22	280.2
PMMA[13]	1	387 ± 2	2902 ± 539	12.9
130–4730	4	390 ± 3	618 ± 155	22.8
PMMA[12]	1	384 ± 1	1607 ± 170	48.4
44–776	4	390 ± 1	500 ± 36	23.1
PMMA (this work)	1	366 ± 10	467 ± 49	545.2
3–140	4	388 ± 5	357 ± 18	124.2
PMMA	1	378 ± 3	511 ± 27	1957.9
all 3 data sets above	4	386 ± 1	353 ± 8	352.5

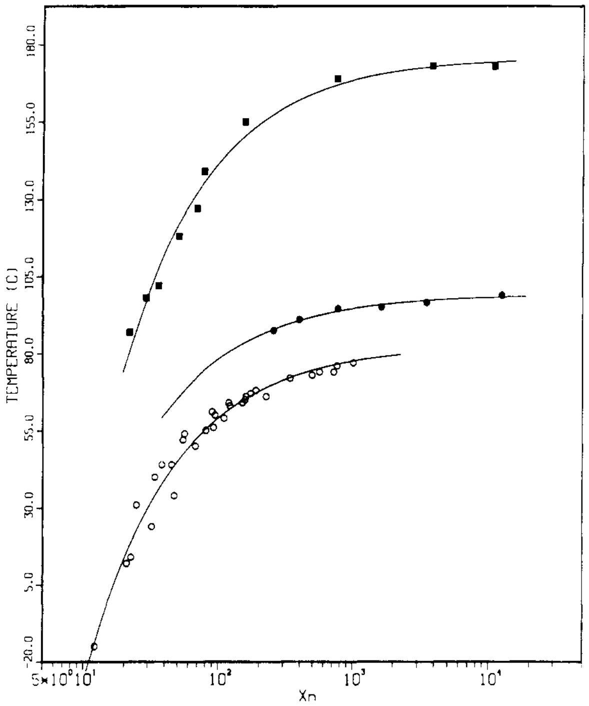

Figure 3. T_g as a function of X_n for various polymers; solid line fitted to eq 4 with indicated parameter values: (a) PVC (○) ref 4; $T_{g,\infty} = 356$, $K = 508$. (b) PACN (●) ref 6; $T_{g,\infty} = 372$, $K = 450$. (c) PAMS (■) ref 3; $T_{g,\infty} = 449$, $K = 739$.

further but restrict our comparisons to eqs 1 and 4.

Table II compares the nonlinear regression results for the data in Table I using eqs 1 and 4; also included are similar comparisons for other PMMA data and for several data sets on polystyrene (PSTY).

Figures 1 and 2 show the fit of eq 4 to the data for PMMA and PSTY. Figure 3 shows the fit of eq 4 to the literature data for three other polymers: poly(vinyl chloride) (PVC), poly(acrylonitrile) (PAN), and poly(α-methylstyrene) (PAMS).

Inspection of the results in Table II shows that eq 4 consistently gives smaller 95% confidence intervals for both $T_{g,\infty}$ and K than does eq 1, especially for those data sets where the molecular weight range extends to low levels. It is also important to note that the residual sum of squares is consistently less for eq 4 than for eq 1, indicating that the former is the better model for these data. The same is true for the data for PVC, PAN, and PAMS. If one analyzes the data, excluding the lowest chain lengths (e.g., $X_n < 40$ being excluded), it is found that the residual sum of the squares still favors the $^2/_3$ dependency over the first power, thus indicating that the inclusion of lower chain lengths alone is not the cause for observation of the $^2/_3$ dependency.

In the absence of a detailed, theoretical model for T_g where the chain-length dependence of T_g can be unambiguously analyzed, we can only regard eq 4 as an empirical expression of that chain-length dependence. It does, however, appear to be a better empirical expression, valid over a wider range than the Flory–Fox eq 1.

It may also be worth noting than an inverse $^2/_3$ dependence on chain length has also been experimentally observed and modeled for both the polymer surface tension[15] and the interfacial tension of immisicible polymers.[16] As is the case with T_g, alternative modeling approaches exist,[17] so there is no simple consensus on the subject. Clearly more experimental and theoretical work is needed.

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