Letter

Dependence of the glass transition on molecular weight*

A widely used equation for relating the glass transition temperature to molecular weight was developed by Fox and Flory[1] and is given by:

$$T_g = T_{g,\infty} - \frac{K}{M} \quad (1)$$

where T_g is the glass transition temperature for a liquid with a molecular weight M, $T_{g,\infty}$ is the corresponding glass transition temperature for a liquid with infinite molecular weight and K is a constant.

Subsequent work has shown that the parameter K is not constant when data for liquids covering an extended range of molecular weight are compared to equation (1)[2]. For example, in order to fit the polystyrene data of Ueberreiter and Kanig[3] (M varied from 208 to 94 000 and T_g varied from −78°C to 98°C) Boyer[2] was forced to use 3 different values of K which ranged from 2×10^4 for M less than 10^3 to 20×10^4 for $M > 10^4$.

We have found that a simple equation similar in form to equation (1) can be used to represent T_g, M data over the entire range of M. The equation, expressed in terms of M, is given by:

$$T_g = T_{g,\infty} - \frac{A}{M + B} \quad (2)$$

and expressed equivalently in terms of P, the degree of polymerization, by:

$$T_g = T_{g,\infty} - \frac{A'}{P + B'}$$

where A and B are parameters, $A' = A/M_0$, $B' = BM_0$ and M_0 is the molecular weight of the repeating unit. Equation (2) has been tested using data for a very wide range of liquids. There are no T_g, M data known to us which do not conform to equation (2).

Some representative experimental data and the corresponding behaviour of equation (2) are shown in the accompanying Figures. *Figure 1* shows the dependence of T_g on the reciprocal of the degree of polymerization for poly(methyl methacrylate)[4] as the circles while the full curve represents the prediction of equation (2). The values of the parameters required for this fit are shown in *Table 1*. It may be noted that equation (1) would predict that the data be linear with a negative slope; as may be seen this is decidedly not true.

Figure 2 shows the data for a series of poly(vinyl chloride) polymers reported by Pezzin *et al.*[5]. The full curve is the prediction of equation (2). *Figure 3* shows the corresponding data for polystyrene taken from both Ueberreiter and Kanig[3,6] and of Fox and Flory[7]. Again, the full curve is the prediction of equation (2).

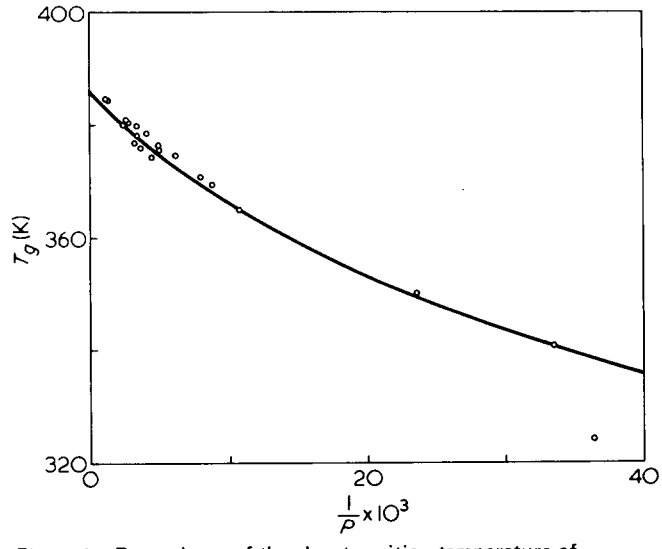

Figure 1 Dependence of the glass transition temperature of poly(methyl methacrylate) on the reciprocal of the degree of polymerization. Points from ref 4, full curve is prediction of equation 2

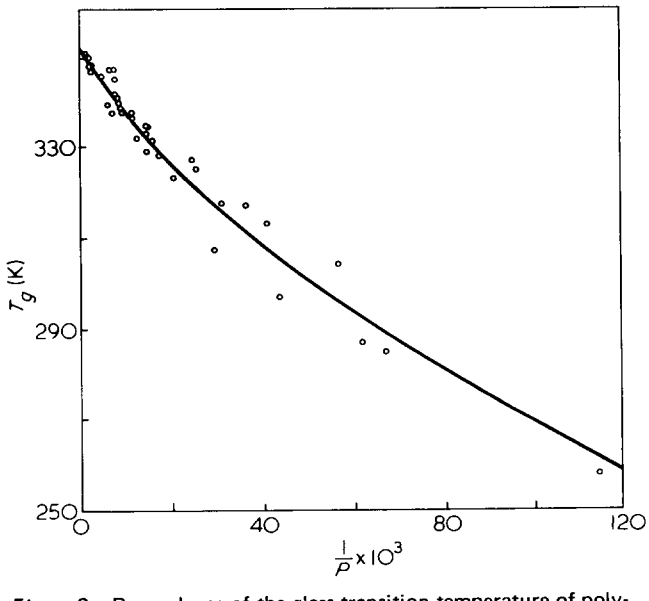

Figure 2 Dependence of the glass transition temperature of polyvinyl chloride on the reciprocal of the degree of polymerization. Points are experimental data taken from ref 5 and full curve is the prediction of equation 2

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Table 1 Values of $T_{g,\infty}$, A and B for various liquids

Liquid	T_g (K)	A (g/mol)	B (g/mol)	Reference
Poly(dimethyl siloxane)	149	7580	42.8	8
n-Alkanes	184	30 200	195	9
Polypropylene	270	49 800	267	10
Poly(vinyl chloride)	351	85 800	382	5
Polystyrene	373	100 000	378	3, 6, 7
Poly(methyl methacrylate)	387	270 000	2880	4
Polycarbonate	436	259 000	1270	11
Poly(α-methylstyrene)	446	448 000	2400	12

The values of $T_{g,\infty}$, A and B obtained from fitting data for various polymers are listed in *Table 1*. As may be seen, values for both A and B tend to be larger, the higher the value of $T_{g,\infty}$; however,there does not appear to be any simple correlation among these parameters. Further work on this problem is in progress.

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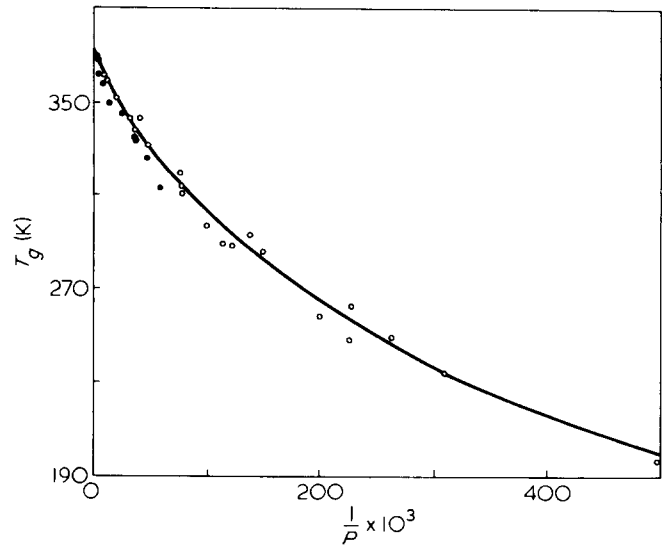

Figure 3 Dependence of the glass transition temperature of polystyrene on the reciprocal of the degree of polymerization. Points are experimental data: ref 7, ●; refs 3 and 6, ○. The full curve is the prediction of eqution 2

References

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Book Review

Encyclopaedia of PVC, Volume 3
Leonard I. Mass
Marcel Dekker, 1978, pp. 610

This is the last volume of PVC Encyclopaedia; it involves ten chapters, involving the main kinds of PVC processing and includes also interesting environmental and disposal considerations, as well as subjects of specifications, health and safety, testing and quality control, operation of plants for production and profit maximization.

The two first chapters treat the main aspects of PVC extrusion and injection moulding: flow behaviour of PVC resin and compounds, single- and twin-screw extrusion, degassing of extruder feed stock, unplasticised and plasticized PVC applications, injection moulding machines, injection moulding technology, economics of PVC moulding, applications for moulded PVC.

The chapter regarding calendering and calendering laminating contains problems concerning principal and auxiliary equipment, equipment–material relations, process control and instrumentation; it ends with a useful comparison of the calender–laminator sequence with other processes.

The following threec hapters (4, 5 and 6), discuss spread coating, coating operations using vinyl powders and liquids, postfabrication, decorating, and finishing.

Chapter 7 approaches some economic aspects such as: effect of rate of processing, profits through quality control, cost of plant labour, amximum use of equipment, material shrinkage and loss, etc.

The eighth chapter is entitled 'Testing rigid PVC products – analysis of test results'; among the aspects treated here are mentioned rigidity, stress–strain measurements, ultimate elongation, toughness, thermal properties, weathering resistance, chemical resistance, environmental considerations in manufacturing, using and disposing of PVC materials and products.

This third volume, with its content, completes harmoniously the former volumes which comprise vinyl chloride production and polymerization, and respective principal aids for PVC modifying and processing.

Like the other volumes, this one has a great number of figures and tables which lightens the understanding of the problems.

The whole work is presented at a high scientific level and it is very useful for researchers, engineers and technologists of the field of synthesis and processing of PVC.

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