End unit effect on the glass transition temperature of low-molecular-weight polymers and copolymers

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Experimental results for five series of linear oligomers of different molecular weights, having a common perfluorinated molecular body and five different pairs of equal foreign end units, generally demonstrate the substantial influence of the chemical nature of the end units on the T_g–x relation of polymers and copolymers, with progressive evidence when the molecular weight is lowered. Positive or negative deviations from the body T_g asymptotic value are observed with different types of end units. Previous experimental results and theoretical expectations for the T_g at low x values are reviewed briefly. As a first approximation, the applicability of the simplest two-parameter T_g–x equations to the new results is discussed, as well as the situation when x is translated in terms of end copolymeric composition.

(Keywords: fluorinated polymers; oligomers; glass transition; end groups; copolymers)

INTRODUCTION

The relation between properties and degree of polymerization of low-molecular-weight polymers or copolymers has received considerable attention in the last few years. These compounds have become of interest not only as macromonomers for the synthesis of macromer segmented copolymers, but also directly as chemicals or materials for an increasing variety of applications.

It is common knowledge that when the molecular weight of a polymeric system is lowered, changes in properties are, in general, to be expected as a consequence of the related structural modifications, which can be described in terms of increasing end-group concentration.

In particular, when considering the glass transition temperature T_g, it is a common view that its value must decrease on decreasing the molecular weight; this is because of the progressive loosening of the cohesive state of the system due to the greater mobility of the end units compared to those of the molecular body (frequently referred to as the 'plasticizing effect' of the end groups).

This view is certainly correct when the end units or groups have chemical similarity to the body units. However, many polymeric or copolymeric systems have end units or groups which are chemically dissimilar to those of the molecular body, either in their intrinsic constitution, or structurally, as a consequence of the method used in their synthesis (polycondensation polymers or copolymers, segmented or graft copolymers, star polymers, telomers, telechelic oligomers, etc.). Hence, some contribution from this chemical dissimilarity to a complete 'end-group effect' is reasonably to be expected.

The aim of this paper is to review, to demonstrate and to stress the general presence of this type of chemical dissimilarity effect of the end units or groups on the T_g (and plausibly on other properties), to determine to what extent it can become a prevailing factor, and yield experimental results which, considering the present state of knowledge, may seem quite unexpected (as it will be illustrated by the brief review that follows).

Alternatively, this contribution to the end effect, specifically due to a difference in the chemical nature of the constituent units, may also be seen as a 'copolymer end effect', which, especially for the lowest molecular weights, tends to become closely related to that typical of triblock copolymeric structures.

T_g–x FOR POLYMER AND COPOLYMER SYSTEMS

The T_g–x relation of a polymer system, including low-molecular-weight oligomers, is frequently studied by estimating the asymptotic T_g value at high molecular weights and taking into consideration the T_g deviations from that value at lower molecular weights. Experimental results are sometimes compared with those suggested by theoretical, tractable models, whose development manages to qualitatively or quantitatively account for such deviations.

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In this brief review, we shall consider, first, systems which are by themselves devoid of an end effect (true homopolymers), namely cyclic polymers; second, systems so far studied disregarding any chemical dissimilarity end effect (linear and star polymers); and finally, systems intentionally studied with chemical dissimilarity end effects (with linear polymeric or copolymeric molecular body), including our new experimental results.

Cyclic polymers

The molecular structure of a cyclic polymer system may be seen, at an infinite molecular weight, as that of a single, infinite linear chain. By decreasing the molecular weight, only minor cohesion energy changes may be forseen, whereas every molecule, being cyclic, intrinsically loses conformational degrees of freedom, increasingly as the length of the cyclic chain diminishes. If the molecular rings happen to be catenated, additional losses of degrees of freedom take place. However, the number of molecules increases in the system, which thus gains degrees of freedom.

For these systems, the first reliable experimental results for the T_g appear to be those of Clarson *et al.*[1] for cyclic poly(dimethylsiloxane); by decreasing x, moderate positive deviations of T_g from the asymptotic value were found, which became noticeable, in a monotonic rise from the asymptote, with x going below about 20.

Positive deviations are also described by Hogen-Esch and Toreki[2] for cyclic poly(2-vinylpyridine), and again by Clarson *et al.*[3] for cyclic poly(phenylemethylsiloxane).

Theoretical support for these findings is given by Di Marzio and Guttman[4], based on equilibrium thermodynamics arguments and the evaluation of conformational entropic differences between cyclic (non-catenated) and corresponding linear polymers. Their treatment predicts that, whereas 'linear chains always show a decrease of T_g', as the molecular weight is lowered (see below), cyclic polymers either show a smaller decrease or, more usually, an increase in T_g.

Linear polymers

The T_g–x relation of linear polymer systems has been studied by many authors either experimentally or theoretically. The nature of the end units, although not always known precisely, has in general been conceptually considered as not substantially different from that of the body units, except for their inherent greater mobility. For such a model of a polymeric system which may be seen as 'scissor-made' from an infinite chain, on lowering the molecular weight, a kind of 'discohesion' progressively takes place, with a gain of degrees of freedom and a loss of cohesion energy. Hence, a progressive lowering of T_g from its asymptotic value is clearly to be expected, with *negative* T_g deviations. This has, as a rule, been confirmed for the systems studied, both by experimental data and theoretical considerations.

The first fully theoretical treatment is that of Gibbs and Di Marzio[5]. By assuming that the glass transition can be dealt with as an equilibrium thermodynamic transition of the Ehrenfest[6] second-order type, and that the configurational entropy, calculated on a Flory–Huggins lattice model, should be zero along the transition line, an equilibrium value of T_g can be predicted (because of relaxation, at about 50 K below the experimental value). From this treatment, a rather complex T_g–x relation could also be obtained, which proved successful for high to rather low molecular weights with some linear polymer systems[7–11], but unsuccessful with others (see for example ref. 12).

More successful for several systems are simple statements which can be derived as a first approximation from the view of a hole contribution of the chain ends to an 'iso-free-volume state' at T_g, first put forward by Fox and Flory[13] from experimental data of a polystyrene system, leading to an equation of the type:

$$T_g = T_g(\infty) - \frac{K}{x} \tag{1}$$

where $T_g(\infty)$ is the T_g asymptotic value at $x \to \infty$, and K is a positive constant.

Ueberreiter and Kanig[14], with arguments based on their dilatometric results with polystyrene fractions (x from 2 to 928)[15] and mixtures of fractions[14], found as more adequate, on an essentially empirical ground, an equation of the type:

$$\frac{1}{T_g} = \frac{1}{T_g(\infty)} + \frac{H}{x} \tag{2}$$

where H is a positive constant. Its validity was reconsidered by Schulz *et al.*[16] and Fox and Loshaek[17].

Equation (1) is frequently used to represent or discuss experimental data of various systems (see for example refs. 1, 3, 12, 18–21).

Fox and Loshaek[17], further developing volumetric considerations, obtained a more general relation of the type:

$$T_g = T_g(\infty)\frac{x-A}{x+B} \tag{3}$$

which can be rewritten in the following two ways:

$$T_g = T_g(\infty)\left(1 - \frac{A+B}{x+B}\right) = T_g(\infty) - T_g(\infty)\frac{A+B}{1+(B/x)}\frac{1}{x} \tag{4}$$

$$\frac{1}{T_g} = \frac{1}{T_g(\infty)}\left(1 + \frac{A+B}{x-A}\right) = \frac{1}{T_g(\infty)} + \frac{1}{T_g(\infty)}\frac{A+B}{1-(A/x)}\frac{1}{x} \tag{5}$$

where A and B are essentially volumetric and dilatometric parameters.

For sufficiently high values of x, equations (4) and (5) reduce to the form of equations (1) and (2) respectively. Considering the possible values of the parameters which express the constants of equations (4) and (5), it may be argued[17] that equation (2) should provide a better approximation than equation (1) for a wider range of x. Rigorously, equations (1) and (2) would be directly derivable from equation (3) if $B=0$ or $A=0$ respectively (in the treatment of Fox and Loshaek[17], where A and B are volumetric parameters, this appears to be physically unrealizable).

Kelley and Bueche[22] suggested a simple calculation of the K constant of equation (1) from volumetric quantities and a parametric average hole volume.

Somcynsky and Patterson[23], by considering polymers of different x as being in corresponding states at T_g, on the lines of a Prigogine thermodynamic theory of liquids, could obtain directly an equation like equation (2), whose H constant is expressed in terms of molecular flexibility parameters and of a cohesion energy factor accounted for through the $T_g(\infty)$ parametric value (formally, their equation corresponds to equation (3) with $A=0$, and therefore to equation (2)).

Equation (2) was then systematically interpreted by Kanig[24] through a detailed classical thermodynamic treatment of an attractive physical model: the liquid polymer is assumed to be a saturated 'solution' of holes, which becomes oversaturated, because frozen, when, by lowering the temperature, T_g is reached. The corresponding (free) volume is conceived to be due not only to frozen holes, but also to non-freezable thermal vibrations, with a characteristic ratio of the two-component free-volume fractions at T_g (about 2:1). This is seen as a universal feature determining T_g, in addition to a factor bound to the energy for creating a hole, which, on the contrary, depends on the nature of the polymer system considered. From generally formulated relations, equation (2) could be interpreted by assuming a similarity in the nature of the end units and the body.

More recently, Lee and Williams[25], on the basis of a non-equilibrium thermodynamic theory previously formulated[26] and of a generalized definition of thermomechanical transitions, expressed the T_g–x relation in the following terms:

$$\ln x = B_0 - \frac{B_1}{T_g} \quad \text{or} \quad T_g = \frac{B_1}{B_0 - \ln x} \tag{6}$$

where B_0 and B_1 are intrinsically positive constants, the latter being proportional to the activation enthalpy of the transition process. They observed good agreement with the experimental data of Fox and Flory[27], Rudin and Burgin[28], and Gillham and Boyer[18,19] for polystyrene, of Beevers and White[7] for poly(methyl methacrylate), and of Pezzin *et al.*[9] for poly(vinyl chloride). Marchionni *et al.*[29] then found agreement of equation (6) with their experimental results for copolymeric perfluoropolyethers.

However, Di Benedetto[30], by assuming that the principle of corresponding states is valid and that a single universal value for the reduced glass transition temperature can be considered, used some additional simplifying assumptions in the calculation of a total lattice energy, and derived an equation of the type:

$$T_g = T_g(\infty)\frac{(a+x)^2}{(b+x)(c+x)} \tag{7}$$

in which a, b and c are constants expressed as ratios between parameters referring to end groups and chain units, respectively bound to interaction energies, segmental mobilities and number of contacts between segments or groups. His treatment explicitly takes into consideration the role of the end groups; however, it could not be checked by adequate experimental data from the point of view of a proper copolymer end effect. In addition, difficulties arise in determining univocal triads of reliable values for the structural parameters from the four-parameter equation (7)[31].

Finally, it should be noted that discussion is still in progress about a possible piecewise or segmented form of the T_g–x relation from experimental data represented by equation (6)[25,29] or otherwise[18,20,32-37].

Star polymers

An interesting case of non-linear polymers is that of star polystyrenes, studied by Roovers and Toporowski[21] with the aim of clarifying the relation between T_g and 'end-group concentration'. The structure of the end units of their star samples (styryl) was very close to that of the chain units. Thus, strictly speaking on the lines of the present work, this is a particular case of copolymers (the central unit of the body greatly different from the chain units) practically devoid of a chemical dissimilarity end effect (end units very similar to the chain units). These authors[21], by analysing their results in terms of equation (1), found that the (positive) K values for their four- and six-branched star polymers are respectively about two and three times those for linear polystyrenes. The influence of the end groups was, therefore, investigated on the basis of their number per molecule, and not from the point of view of a (practically absent) chemical dissimilarity.

T_g–x OF POLYMERS AND COPOLYMERS WITH FOREIGN END UNITS

Previous results

A definite end effect of a chemical dissimilarity of end units was studied and reported by Ueberreiter and Rohde-Liebenau[38] in 1961. Using a particular radical initiator, they synthesized polystyrenes rich in decidedly foreign end groups (trichloro-triphenyl-methyl groups) and found some *slightly positive* T_g deviations from the asymptotic value with decreasing x, instead of *marked negative* deviations, as expected for 'normal' polystyrenes. As far as we know, this is the only example in the literature of observed positive T_g deviations, surprisingly ignored in subsequent literature (apart from the recent different case, examined above, of cyclic polymers[1-3]).

Some evidence of a chemical dissimilarity end effect on T_g was recently pointed out by Tadlaoui *et al.*[37]. Using mercaptan chain transfer reagents, they radically synthesized methyl methacrylate telomers with different end groups (C_6H_5S– or $C_8F_{17}C_2H_4S$–) and found marked negative T_g deviations, however claimed as different from those 'of a standard' poly(methyl methacrylate).

Our results

Our T_g measurements were made on five series of oligomers of different molecular weights, having the same perfluorinated body (PFB) and two equal foreign end groups E of five different types.

The system has the general constitution E–$CF_2O[(CF_2CF_2O)_p(CF_2O)_q]CF_2$–E, abbreviated to E(PFB)E, with degree of polymerization $x=x_M+2$ (i.e. $x=x_M$ monomeric units + 2 end units), where $x_M=p+q+1$, substantially consisting of a non-crystallizable, random copolymeric body (a perfluoro poly(oxymethylene-oxyethylene) chain, having a ratio p/q between 0.91 and 1.11) with two equal end groups or units of one of the following types: $-CH_2OCH_3$; $-CH_2OSi(CH_3)_3$; $-CH_2OCOCF_3$; $-CH_2OH$; $-CH_2OK$.

The diolic $HOCH_2(PFB)CH_2OH$ series was first investigated with several samples of different x_M. Four were samples of Fomblin-ZDOL^R (Ausimont SpA, Montedison Specialty Chemicals, Milan), having $M_n = 700$–3700, and M_w/M_n in the range 1.19–1.50. From these base samples, others were obtained by fractional separation using distilled Delifrene-LS^R (Ausimont) as solvent, and methanol or CH_2Cl_2 as non-solvent. The data relating to this diolic series are collected in *Table 1*. In *Figure 1a* the T_g values are plotted against x_M.

Table 1 Characterization of the fractions of the diolic series $HOCH_2(PFB)CH_2OH$

Fraction	p/q	M_w/M_n	M_n	x_M	f_M	T_g (°C)	T_g (K)
F12	0.96	1.07	350	2.90	0.592	−81.0	192.1
F11[a]	0.96	1.29	700	6.77	0.772	−97.5	175.6
F10[a]	0.91	1.19	1150	11.82	0.855	−107.0	166.1
F9	0.93	1.37	1950	20.67	0.912	−113.2	159.9
F8[a]	1.02	1.50	2100	22.06	0.917	−113.9	159.2
F7	1.04	1.21	3250	34.58	0.945	−117.0	156.1
F6	1.10	1.10	3500	37.03	0.949	−117.2	155.9
F5[a]	1.03	1.40	3700	39.55	0.952	−117.9	155.2
F4	1.11	1.05	3900	41.32	0.954	−117.3	155.8
F3	1.09	1.16	4300	45.77	0.958	−117.9	155.2
F2	1.01	1.16	8000	86.84	0.977	−120.8	152.3
F1	0.99	1.23	10600	115.69	0.983	−121.1	152.0

[a] Base samples of Fomblin-ZDOL

Portions of the four base samples were then derivatized by reaction with dimethylsulfate, hexamethyldisilazane, trifluoroacetic anhydride and potassium *t*-butoxide, respectively, (all Aldrich reagents), in order to investigate diversified end-capped series. The data relating to these series are reported in *Table 2*, and the T_g values graphically represented in *Figure 1b* as a function of x_M.

In *Tables 1* and *2*, all the M_n data were calculated from ^{19}F n.m.r. spectra (Varian 200 MHz), in good agreement with results obtained from v.p.o. measurements (Hitachi–Perkin-Elmer-115). The M_w/M_n ratio was determined by g.p.c. (Waters-5900). The T_g data were recorded by d.s.c. (Mettler TA 3000) in a cooling run from 35 to −170°C, at $10°C\,min^{-1}$.

From our results it immediately appears that the T_g–x relation for a given polymeric system (with a common molecular body) can be heavily modified by changing the chemical nature of the end groups or units. Qualitatively, the experimental data are by themselves expressive from a phenomenological point of view; both positive and negative T_g deviations can take place. Quantitatively, the data do not encompass x values below that of a body trimer, and for four series the data are relatively few, so that it is convenient at present to limit our discussion to the possible validity of the simplest, two-parameter equations (1) and (2).

For our purposes equation (1) can be rewritten as follows:

$$T_g = T_g(\infty) + \frac{2D}{x_M + 2} \qquad (0 \leqslant x_M \leqslant \infty) \tag{8}$$

or alternatively:

$$\Delta T_g = T_g - T_g(\infty) = \frac{2D}{x_M + 2} \tag{8'}$$

where D is a parameter expressing, for any given pair of end groups, the sign and extent of the T_g deviations from the (parametric) $T_g(\infty)$ asymptotic value of the chosen polymeric body.

Figure 2 shows the T_g data relating to the diolic $HOCH_2(PFB)CH_2OH$ series when linearly plotted according to equation (8).

A corresponding result can be obtained starting with equation (2), evidently because the experimental accuracy in the investigated x interval lies in the purely mathematical differences between the T_g values predicted by equations (1) and (2) (as already apparent from previous literature on other systems). Thus, for the diolic series (with *positive* T_g deviations), in the x range examined ($x \geqslant 5$), equations (1) and (2) can be considered as valid (as previously observed for several other systems with *negative* T_g deviations, at 'sufficiently high' x values).

Figure 3 shows the ΔT_g experimental results of *Table 2* linearly plotted according to equation (8′). By

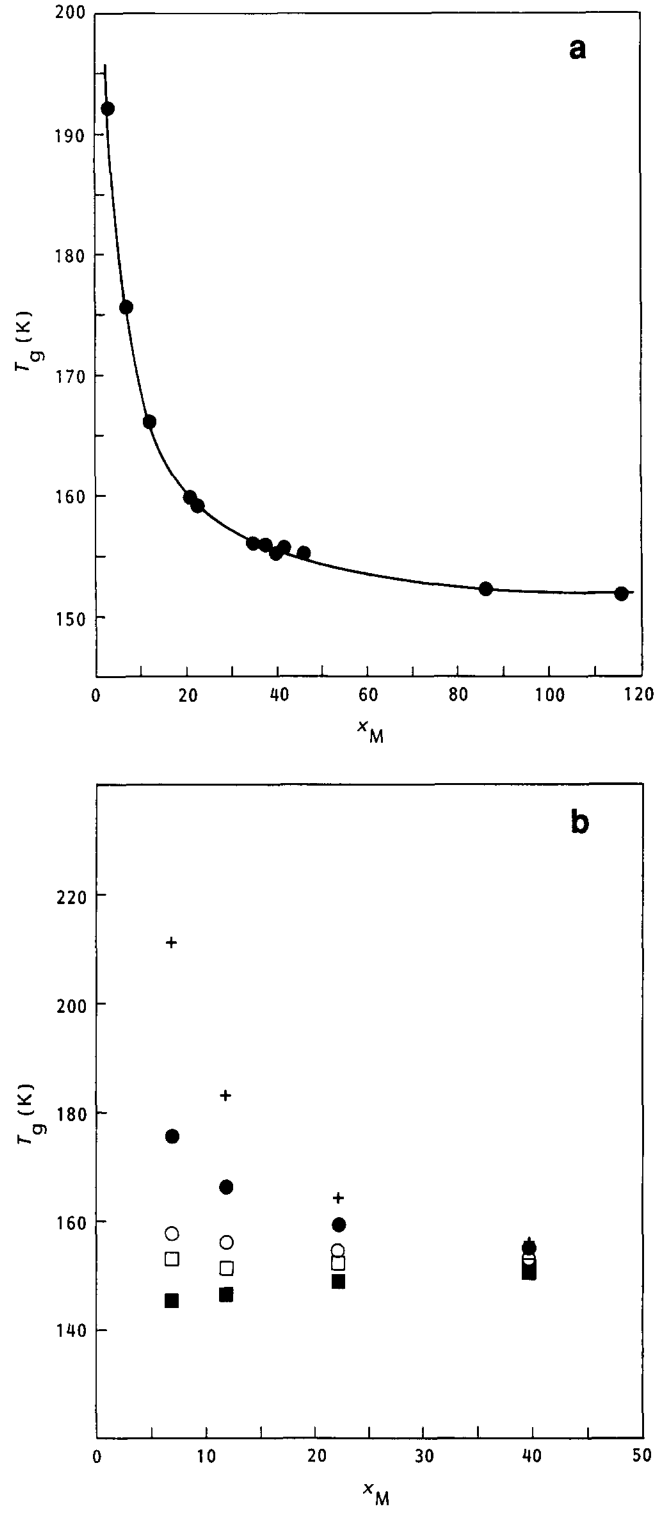

Figure 1 Relation between T_g and body degree of polymerization x_M of: (a) the diolic series of fractions $HOCH_2(PFB)CH_2OH$ (data of *Table 1*); (b) the five end oligomeric series examined (data of *Table 2*): ■, met; □, sil; ○, acf; ●, dol; +, ok; end group abbreviations as in *Table 2*

Table 2 Characterization of the four fractions of the five different end oligomeric series examined

Fraction[a]	p/q	M_w/M_n	x_M	T_g (°C)	T_g (K)	ΔT_g
met 1				−127.8	145.3	−5.9
sil 1				−120.0	153.1	1.9
acf 1	0.96	1.29	6.77	−115.4	157.7	6.5
dol 1				−97.5	175.6	24.4
ok 1				−62.2	211.0	59.75
met 2				−126.6	146.5	−4.7
sil 2				−121.6	151.5	0.3
acf 2	0.91	1.19	11.82	−117.0	156.1	4.9
dol 2				−107.0	166.1	14.9
ok 2				−90.0	183.1	31.9
met 3				−124.2	148.9	−2.3
sil 3				−120.7	152.4	1.2
acf 3	1.02	1.50	22.06	−118.5	154.6	3.4
dol 3				−113.9	159.2	8.0
ok 3				−109.0	164.1	12.9
met 4				−122.5	150.6	−0.6
sil 4				−121.3	151.8	0.6
acf 4	1.03	1.40	39.55	−120.1	153.0	1.8
dol 4				−117.9	155.2	4.0
ok 4				−117.4	155.7	4.5

[a] End groups: met = CH_2OCH_3; dol = CH_2OH; sil = $CH_2OSi(CH_3)_3$; ok = CH_2OK; acf = CH_2OCOCF_3

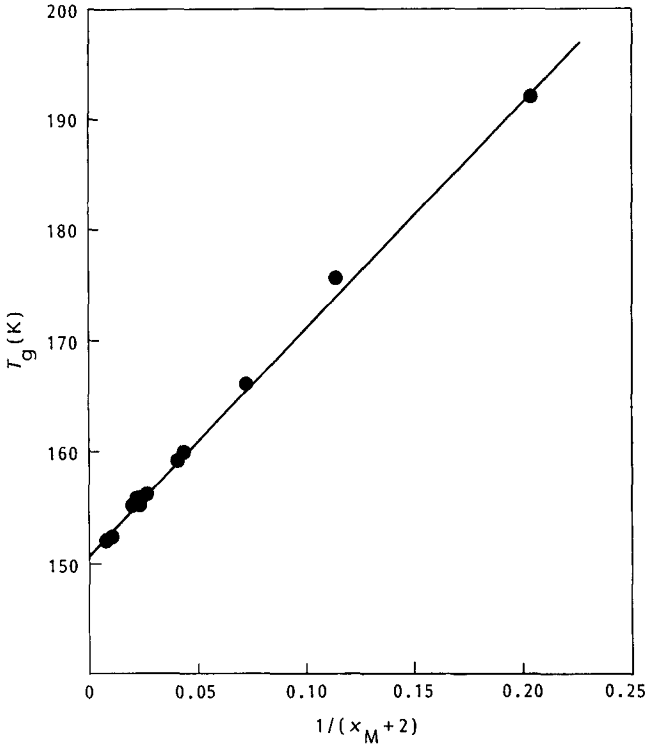

Figure 2 Plot of T_g against $1/(x_M+2)$, according to equation (8), of the diolic series $HOCH_2(PFB)CH_2OH$ (data from *Table 1*)

assuming, as a first approximation, strictly linear behaviour, from a least-squares fitting one obtains $T_g(\infty) = 151$ K and the following most probable values for the deviation parameter D for each specified end group: $-CH_2OCH_3$, −26; $-CH_2OSi(CH_3)_3$, +9; $-CH_2OCOCF_3$, +32; $-CH_2OH$, +102.

With the fifth end-group type, giving the largest positive deviations, a linear interpolation is clearly unacceptable, so that for $-CH_2OK$, D is largely positive, increasing with decreasing x. This behaviour might indicate that for all the series a curved T_g–$1/x$ trend could be more realistic, in fact experimentally detectable only when the T_g deviations are comparatively large.

All these results suggest that in our case the end effect is prevalently determined by (probably polar) surcohesion phenomena, and less by the geometric features of the end groups.

On this basis we can interpret the T_g data of Marchionni *et al.*[29] for a series of samples (Fomblin-Z^R) having a perfluorinated body similar to that of our system, and end groups $-OCF_3$. Although in a range of somewhat higher x, they show a trend of marked negative deviations, comparatively greater than the negative ones observed in our system (with $E = -CH_2OCH_3$). The $-OCF_3$ end groups are very similar in chemical nature to the body, so that this case may be seen as very close to a reference, from an infinite chain 'scissor-made' molecular model, with the minimal foreign-end-unit effect, and an easier theoretical interpretation. At present, this comparison may generally be assumed as a criterion for a quantitative evaluation of the chemical dissimilarity end effect.

An interesting physical meaning of the parameter D can be suggested by the copolymeric view of the end effect. Every oligomeric or polymeric compound may be seen as belonging to an 'end copolymeric system', in our case: $EM_{x_M}E$ (generally $E'M_{x_M}E''$), whose extreme pure components are M_∞ on one side, and E_2 on the other, having T_g values: $T_g(\infty)$ and $T_g(E)$ respectively. Its composition can be expressed by the molar fraction of the different M and E units:

$$f_M = \frac{x_M}{x_M + 2} \qquad f_E = \frac{2}{x_M + 2}$$

By assuming (to a first approximation) equation (8) as

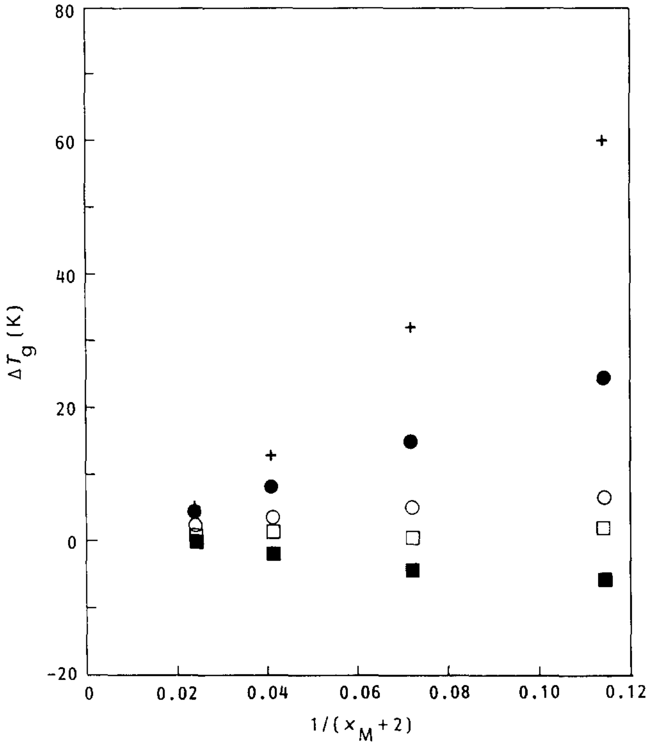

Figure 3 T_g deviations (ΔT_g) of the five end copolymeric series examined as a function of $1/(x_M+2)$, according to equation (8'): ■, met; □, sil; ○, acf; ●, dol; +, ok; end group abbreviations as in *Table 2*

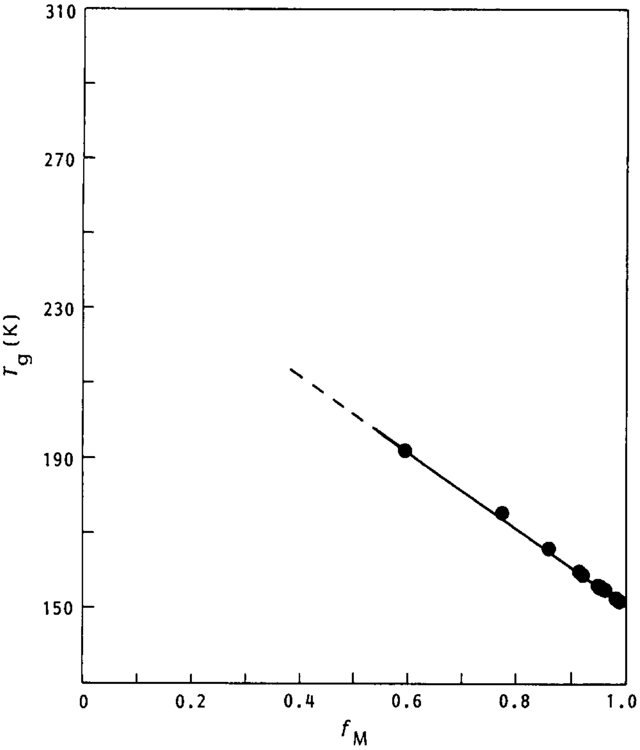

Figure 4 End copolymer composition diagram representing T_g (according to equation (10)) of the diolic series $HOCH_2(PFB)CH_2OH$

valid over the whole range of x_M, when $x_M = 0$, $T_g = T_g(E)$; it follows that:

$$D = T_g(E) - T_g(\infty) \qquad (9)$$

i.e. D represents the difference between the T_g of the component E_2 and that of the component M_∞ (D being positive when $T_g(E) > T_g(\infty)$). Equation (8) can thus be rewritten as:

$$T_g = T_g(\infty) + \frac{2[T_g(E) - T_g(\infty)]}{x_M + 2} \qquad (8'')$$

Hence, by expressing x_M in terms of composition, the following 'end copolymer composition equation' can be derived:

$$T_g = T_g(E) + (T_g(\infty) - T_g(E))f_M \qquad (10)$$

or, in a distributive form:

$$T_g = T_g(\infty)f_M + T_g(E)f_E \qquad (10')$$

In *Figure 4* the T_g data of the diolic series are plotted according to equation (10) as a function of f_M; they are indeed well represented by a straight line.

With the present knowledge it is of course hardly possible to predict the limits of reliability of such a relation, because of lack of experimental data at the lowest x, i.e. f_M values, largely expanded for a few oligomers on the left of *Figure 4*.

An attempt to evaluate equation (10) may be made by calculating $T_g(E)$ from D using equations (8) and (9), and comparing this value to that of the T_g of the pure E_2 component. For the diolic series, for example, equation (9) gives $T_g(E) = 253$ K, but the T_g of ethylene glycol (estimated with the Tammann rule: $T_g = 2/3T_m$) should be about 170 K, i.e. much smaller than that calculated. However, for the series with end groups $-CH_2OCH_3$, the calculated value is 125 K, relatively close to 143 K, which can be estimated for $CH_3OCH_2CH_2OCH_3$. No better agreement can be obtained starting with equation (2) instead of equation (1).

CONCLUSIONS

The effect definitely demonstrated of the molecular end groups or units having chemical structures different from that of the body units on the T_g of a polymeric system, reliably measurable in the x range of oligomeric values, appears to be substantial and must be taken into full consideration. Various theoretical treatments of the T_g–x relation, briefly reviewed in this paper, clearly should be either revised or better specified in order to explicitly take into account this 'copolymer end effect'.

From an intuitive, physical point of view, the glass transition temperature has to be related to a whole cohesion state of the system, and not uniquely to a cohesive energy[39,40] or to (intrinsic or consequent) degrees of freedom[20]. Thus, as a quite general remark, it might be said that, in principle, a lowering of the molecular weight of a polymeric system should result by itself in important structural changes generally implying a kind of discohesion of the matter constituting the system itself. Major structural changes can, however, be brought about by the chemical nature and size of the progressively ensuing end groups or units by decreasing x. Good compatibility, for example, between end groups and body can improve cohesion, whereas poor compatibility can enhance discohesion, but, at the limit, can give rise to end molecular associations. These may result either in a surcohesion, or in further discohesion, depending on the relative intensities of body/body and end/end affinities. Furthermore, incompatibility leads to substantial morphological changes, such as sub-phase or phase separations of different order, degree or size scale in the originally homogeneous systems or sub-systems, with an outstanding variety of possible ensuing structures, and consequent effects on their properties, increasing as the molecular weight decreases.

Clearly, such a variety of phenomenological possibilities can make the form of the T_g–x relation particularly complex, and complicate its theoretical interpretation in the delicate range of the lowest x values, in which the copolymer end effect becomes dominant, in addition to possible abrupt changes of structural regime which are still under discussion.

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