Physical Properties of Dendritic Macromolecules: A Study of Glass Transition Temperature

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ABSTRACT: The variation of glass transition temperature with molecular weight and chain-end composition for dendritic polyethers and polyesters was studied. A new and modified version of the chain-end free volume theory was derived to account for the large number of chain ends in these unusual structures. For both homopolymers and a variety of novel block copolymers, the experimental variation in T_g with molecular weight was found to correlate well with theoretical predictions, thus demonstrating the wide applicability of the chain-end free volume theory. The glass transition was found to be greatly affected by the nature of the chain ends and internal monomer units.

Introduction

Dendritic macromolecules are a unique class of polymers which are characterized by a highly branched, three-dimensional structure emanating from a central point with a branch juncture at each monomer unit and a large number of chain ends. Dendritic structures have been synthesized by two opposing approaches: a convergent growth approach,[1-3] where growth begins at the chain ends and proceeds inward with the final reaction being attachment of several dendritic fragments to a central polyfunctional core molecule;[4] and a divergent growth approach,[5-8] where growth begins with a central core and proceeds outward with an ever increasing number of reactions required for generation growth. Although syntheses of these novel macromolecules are being well studied, there have been few studies directed toward investigation of the physical properties.

New phenomena and physical properties are expected to result from the unusual architecture of dendritic macromolecules, in comparison to linear polymers. For example, the density of starburst PAMAM dendrimers has been found to go through a minimum on increasing generation number,[5] and the intrinsic viscosity of polyether dendrimers passes through a maximum as a function of generation number while the refractive index increment appears to pass through a minimum.[9]

A large number of studies have reported the effect of molecular weight on the glass transition temperature (T_g) of polymers.[10,11] Entanglements[12] and chain-end composition[11] have also been shown to affect T_g. As dendritic macromolecules synthesized by the convergent growth approach are essentially monodisperse with precise numbers of chain ends, numbers of monomer units, and molecular weights, a unique opportunity exists to correlate their glass transition temperatures with their molecular weight, chain-end composition, and bulk chemical composition.

Experimental Section

The dendritic molecules were prepared as reported in the references which are given for each structure. The glass transition temperature for each sample was measured by differential scanning calorimetry using a Mettler DSC 30 low-temperature cell coupled to a TC10A TA processor. Heating rates were 10 K/min. T_g was taken as the midpoint of the inflection tangent. The lower generation dendrimers (i.e., below molecular weights of ca. 1000 amu) are crystalline materials exhibiting only melting transitions; therefore, quenching experiments were necessary to observe glass transition temperatures. Quenching was achieved within the DSC pans by heating the material to 25 K above the melting point and then quickly transferring the sample from the heated chamber to a Dewar containing liquid nitrogen. This "freezes" the sample in its amorphous state without allowing recrystallization to occur upon cooling. The quenched samples were then transferred from the liquid-nitrogen bath to the DSC cell precooled to 173 K, and the measurement was then conducted as above, giving a T_g endotherm, a crystallization exotherm, and finally a T_m endotherm.

Results and Discussion

Effect of Molecular Weight. For linear polymers, the chain-end free volume theory states the dependency of glass transition temperature on molecular weight by eq 1, where $T_{g\infty}$ is the value of T_g extrapolated to infinite molecular weight, 2 is the number of chain ends, ρ is the density, N is Avogadro's number, θ is the free volume per chain end, and α is the free volume expansion coefficient.[12,13] Equation 1 is often simplified to eq 2, where K is a constant. This allows $T_{g\infty}$ and K to be obtained from

$$T_g = T_{g\infty} - (2\rho N\theta/\alpha)(1/M) \quad (1)$$

$$T_g = T_{g\infty} - K/M \quad (2)$$

a plot of T_g vs $1/M$. However, because K is not constant for dendritic systems since dendritic macromolecules have an ever-increasing number of chain ends, traditional plots of T_g vs $1/M$ have little meaning. In the following derivation, the chain-end free volume theory is applied to dendritic structures to obtain the relationship between molecular weight and glass transition temperature.

Consider a dendritic structure with n_e end groups and a molecular weight M, where n_e and M are functions of the generation number of the dendrimer. The number of molecules per unit volume will be

$$\rho N/M \quad (3)$$

where ρ is the density and N is Avogadro's number. The number of chain ends per unit volume will then be

$$(\rho N/M)n_e \quad (4)$$

If θ is the free volume per chain end, the total free volume

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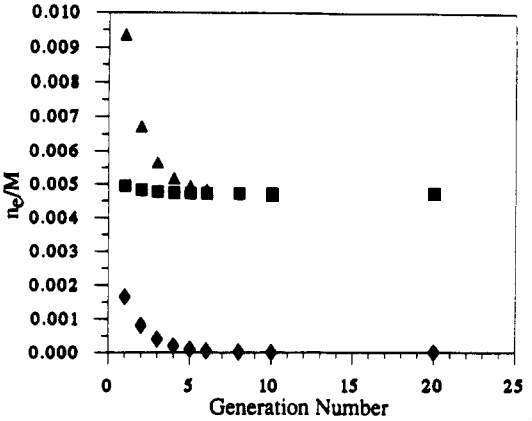
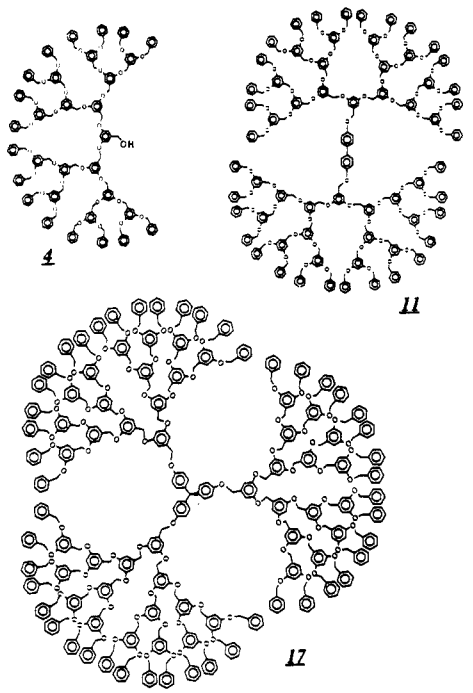


Figure 1. n_e/M vs generation number for benzyl ether dendritic macromolecules (■), dendritic fragments (▲), and linear polymers (♦). n_e/M approaches 0.004 717 for the dendrimers, while for linear polymers, n_e/M approaches zero.

Chart I
Dendritic Poly(benzyl ethers), [G-4]-OH (4), $[G\text{-}4]_2$-[C] (11), and $[G\text{-}4]_3$-[C] (17)



per unit volume is

$$(\rho N/M)n_e\theta \tag{5}$$

where n_e is the number of chain ends per molecule. If this free volume is equated to the free volume created by expanding the polymer above its glass transition, which is expressed as $\alpha(T_{g\infty} - T_g)$, then

$$(\rho N/M)n_e\theta = \alpha(T_{g\infty} - T_g) \tag{6}$$

and

$$T_g = T_{g\infty} - (\rho N\theta/\alpha)(n_e/M) \tag{7}$$

this may be simplified to

$$T_g = T_{g\infty} - K'(n_e/M) \tag{8}$$

Equation 8 predicts a linear relation between the measured T_g and the ratio of n_e/M. The constant K' includes several terms which may not be constant. The fact that a linear relationship is observed experimentally suggests that, if terms such as the density or chain-end free volume vary with molecular weight, this variation either is insignificant or is negated by changes in other terms. Indeed, this derivation is an extension of the traditional chain-end free volume theory for linear polymers, in which the factor "2" in eq 2 is replaced with the number of end groups. However, eq 8 is unlike eq 2, since the term Kn_e/M does not approach zero at high molecular weight. It can be readily shown that n_e/M approaches a constant value at high molecular weight (the value of the constant depends on the molecular weight of the monomer unit, core, and chain end groups, and the branch juncture multiplicity of the monomer unit), and, as shown in Figure 1, $(n_e/M)_\infty$ for the dendritic poly(benzyl ethers)[1] is 0.004 717. Therefore, unlike linear systems, $T_{g\infty}$ is not the y-intercept on extrapolation of T_g vs n_e/M to zero, but it may be found by the following two methods:

1. From eq 8, linear regression of T_g vs n_e/M allows the x value of n_e/M at infinite molecular weight ($(n_e/M)_\infty$) to be entered and the corresponding y value of T_g at infinite molecular weight ($T_{g\infty}$) to then be calculated.

2. Alternatively, an additional term, $(n_e/M)_\infty$, may be subtracted from n_e/M to essentially shift the plot to the left, with the y-intercept then occurring at $x = 0$. This gives eq 9, from which $T_{g\infty}$ may be obtained as the y-intercept from a plot of T_g vs $[n_e/M - (n_e/M)_\infty]$

Table I
Data for Dendritic Poly(benzyl ethers) (Entries 1–18) and Phenolic Terminated Dendritic Polyesters (Entries 19–22)

entry	compound	T_g (K)	M	n_e	n_e/M	$[n_e/M - (n_e/M)_\infty]$
1	[G-1]-OH	255	320	3	0.009 375	0.004 658
2	[G-2]-OH	285	744	5	0.006 720	0.002 003
3	[G-3]-OH	305	1592	9	0.005 653	0.000 936
4	[G-4]-OH	312	3288	17	0.005 170	0.000 453
5	[G-5]-OH	315	6680	33	0.004 940	0.000 223
6	[G-6]-OH	316	13464	65	0.004 828	0.000 111
7	$[G\text{-}0]_2$-[C]	270	366	2	0.005 464	0.000 747
8	$[G\text{-}1]_2$-[C]	287	790	4	0.005 063	0.000 346
9	$[G\text{-}2]_2$-[C]	306	1656	8	0.004 831	0.000 114
10	$[G\text{-}3]_2$-[C]	311	3354	16	0.004 770	0.000 053
11	$[G\text{-}4]_2$-[C]	311	6750	32	0.004 741	0.000 024
12	$[G\text{-}5]_2$-[C]	312	13542	64	0.004 726	0.000 009
13	$[G\text{-}0]_3$-[C]	282	576	3	0.005 208	0.000 491
14	$[G\text{-}1]_3$-[C]	298	1212	6	0.004 950	0.000 233
15	$[G\text{-}2]_3$-[C]	309	2484	12	0.004 831	0.000 114
16	$[G\text{-}3]_3$-[C]	312	5026	24	0.004 775	0.000 058
17	$[G\text{-}4]_3$-[C]	314	10126	48	0.004 740	0.000 023
18	$[G\text{-}5]_3$-[C]	315	20292	96	0.004 731	0.000 014
19	$[C]\text{-}(OH)_6$	446	714	6	0.008 403	0.001 050
20	$[C]\text{-}(OH)_{12}$	458	1530	12	0.007 843	0.000 490
21	$[C]\text{-}(OH)_{24}$	467	3162	24	0.007 590	0.000 237
22	$[C]\text{-}(OH)_{48}$	474	6426	48	0.007 470	0.000 117

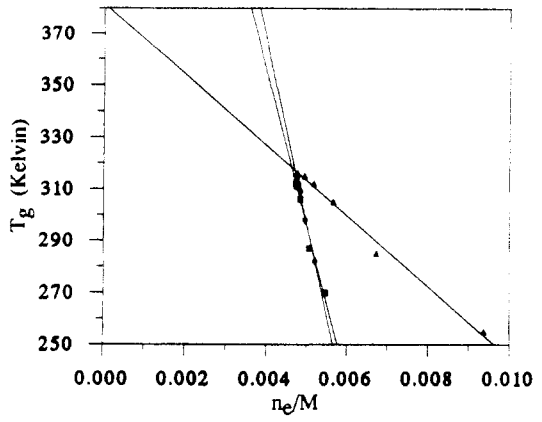


Figure 2. Overlay of plots of T_g vs n_e/M for dendritic poly(benzyl ethers), [G-x]-OH (▲), [G-x]$_2$-[C] (■), and [G-x]$_3$-[C] (♦).

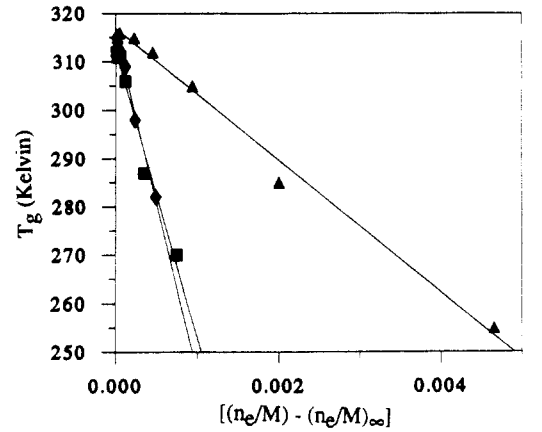


Figure 3. Overlay of plots of T_g vs $[n_e/M - (n_e/M)_\infty]$ for poly(benzyl ether) dendrimers, [G-x]-OH (▲), [G-x]$_2$-[C] (■), and [G-X]$_3$-[C] (♦).

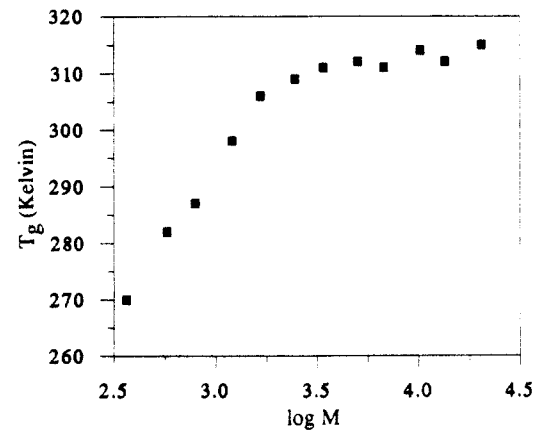


Figure 4. Variation of T_g as a function of log M for the benzyl ether dendritic macromolecules (entries 7–18).

$$T_g = T_{g\infty} - K'[n_e/M - (n_e/M)_\infty] \quad (9)$$

extrapolated to zero.

Both of these treatments of the data are equivalent and give the same values for $T_{g\infty}$ and K'.

A series of monodisperse dendritic benzyl ether macromolecules of varying generation numbers (sizes) have been synthesized from the monomer unit, 3,5-dihydroxybenzyl alcohol.[1] A study of the dependency of the glass transition temperature on molecular weight is possible due to the wide range of molecular weights that have been synthesized. The polyether dendrimers studied can be divided into three classes. Representative examples of these three classes shown in Chart I are the fourth-generation dendritic fragment [G-4]-OH, **4**, the macromolecule [G-4]$_2$-[C], **11**, obtained from attachment of two fourth-generation fragments to a difunctional core, and the macromolecule [G-4]$_3$-[C], **17**, obtained from attachment of three fourth-generation fragments to a trifunctional core. The glass transition temperatures, molecular weights, and number of chain ends for the different benzyl ether dendrimers are given in Table I.

An overlay of plots of T_g as a function of n_e/M for the dendritic fragments (entries 1–6) and macromolecules (entries 7–12 and 13–18) is shown in Figure 2. From this graph, it is obvious that extrapolation to $n_e/M = 0$ is incorrect. The experimental data fits eq 8 with correlation coefficients in the range of 0.98–0.995, and application of method 1 gives $T_{g\infty}$ values of 317, 312, and 316 K and K' values of 13 700 ± 673, 59 600 ± 4290, and 69 900 ± 2450, for [G-x]-OH, [G-x]$_2$-[C], and [G-x]$_3$-[C], respectively, at $n_e/M = (n_e/M)_\infty = 0.004\,717$. Since each of the dendritic structures contain the same monomer units with only slightly dissimilar cores or focal points,[1] the result of equal $T_{g\infty}$'s, within experimental error, is expected. However, the slopes of the lines are dramatically different. It would be expected that the slope of the T_g vs n_e/M correlation would be identical for the structures **11** and **17** which have identical end groups with no end group added by the core and only slightly different for **4** for which the total free volume is modified by a hydroxy end group in the core. Therefore, the equation relating T_g to the structure of **4** is

$$T_g = T_{g\infty} - \left(\frac{\rho N \theta_e}{\alpha}\right)\left(\frac{n_e}{M}\right) - \left(\frac{\rho N \theta_e}{\alpha}\right)\left(\frac{N_c \theta_c}{\theta_e}\right) \quad (10)$$

where n_c is the number of chain ends on the core, and θ_c represents the free volume of the hydroxy unit on the dendrimer core. Equation 10 predicts a nonlinear relationship between T_g and n_e/M. The fact that a linear relationship between T_g and n_e (Figure 2) indicates that the free volume of the hydroxyl group is similar to that of benzyl ($\theta_c = \theta_e$ gives the additional term as a constant) or that the additional term including θ_c in eq 10 is insignificant. It should be noted that the dendritic polyether fragments with a bromomethyl group as the focal point have glass transition temperatures equal to the corresponding fragments containing a hydroxymethyl functionality at the focal point, which supports the effect observed from θ_c being insignificant. If, in the calculation of n_e/M, the core chain end is not included, a K' value of 41 700 is obtained. This value is still significantly different from the other systems. The observed differences between all three classes may be due to different densities or effective free volumes of chain ends caused by the change in structural buildup or geometry of the molecules of the different classes. Alternatively, the differences in slopes could be due to the nature and functionality of the core.

An overlay of plots of T_g vs $[n_e/M - (n_e/M)_\infty]$ for the dendritic benzyl ether fragments and macromolecules is shown in Figure 3. By application of method 2, the data fits eq 9 to give exactly the same results as were obtained from eq 8 with $n_e/M = (n_e/M)_\infty$ (method 1).

Also included in Table I are data for dendritic polyester macromolecules[14] (entries **19–22**). These macromolecules have phenolic chain ends, and $(n_e/M)_\infty$ is calculated to be 0.007 353. Linear regression of T_g vs $[n_e/M - (n_e/M)_\infty]$ and application of eq 9 give $T_{g\infty}$ and K' values of 475 K and 28 600, respectively, with a correlation coefficient of 0.98. An interesting comparison can be made with the hyperbranched polyester macromolecules prepared by a

Table II
Data for Dendritic Fragments Constructed from 3,5-Dihydroxybenzyl Alcohol as the Monomer Unit and Containing H, Br, or CN at the Chain Ends

entry	X	compound	M	n_e/M	$(n_e/M)_\infty$	T_g (K)	$T_{g\infty}$ (K)	K'
23	H	[G-1]-OH	320	0.009 375	0.004 717	255	317	13 600
24	H	[G-2]-OH	744	0.006 720	0.004 717	285	317	13 600
25	H	[G-3]-OH	1592	0.005 653	0.004 717	305	317	13 600
26	H	[G-4]-OH	3288	0.005 170	0.004 717	312	317	13 600
27	H	[G-5]-OH	6680	0.004 940	0.004 717	315	317	13 600
28	H	[G-6]-OH	13464	0.004 828	0.004 717	316	317	13 600
29	Br	Br_2-[G-1]-OH	478	0.006 276	0.003 436	271	331	20 800
30	Br	Br_4-[G-2]-OH	1060	0.004 717	0.003 436	309	331	20 800
31	Br	Br_8-[G-3]-OH	2224	0.004 047	0.003 436	316	331	20 800
32	Br	Br_{16}-[G-4]-OH	4552	0.003 735	0.003 436	325	331	20 800
33	CN	CN_2-[G-1]-OH	370	0.008 108	0.004 219	287	353	16 800
34	CN	CN_4-[G-2]-OH	844	0.005 924	0.004 219	327	353	16 800
35	CN	CN_8-[G-3]-OH	1792	0.005 022	0.004 219	334	353	16 800
36	CN	CN_{16}-[G-4]-OH	3688	0.004 610	0.004 219	349	353	16 800

one-step process.[15,16] These macromolecules have the same number of chain ends but are less regularly branched than the corresponding "perfect" dendritic macromolecules prepared by the convergent growth approach. Glass transition temperatures of 473 K were observed for these macromolecules with molecular weights up to 200 000, which correlates well with the $T_{g\infty}$ calculated for the "perfect" dendritic polyesters.

Variations of the glass transition temperature with molecular weight can also be represented by plotting T_g as a function of log M.[10,11] This is demonstrated in Figure 4 for the dendritic benzyl ether macromolecules (entries 7–18). The trend of T_g "leveling-off" with increasing molecular weight is characteristic of all of the dendritic systems studied; this trend is similar to that observed for linear polymers.[10,11] For linear polymers, the entanglement molecular weight is a significant transition, with entanglements contributing to the physical properties of the polymers. The entanglement molecular weight may be obtained from T_g data by plotting[12] T_g vs $1/M$ or by plotting[10,11] T_g vs log M. However, although plots of T_g vs log M for dendritic systems resemble those of linear systems, we do not believe that the dendritic structures studied exhibit the same entanglement behavior as linear polymers. This is supported by intrinsic viscosity data. It has been shown[9] that the intrinsic viscosity passes through a maximum at ca. generation 4 ([G-4]-OH) for the dendritic fragments and ca. generation 3 ($[G\text{-}3]_3$-[C]) for the dendritic macromolecules. Entanglements may occur in lower generations resulting in the increasing viscosity, but the decreasing viscosity with increasing generation number beyond ca. 3500 molecular weight suggests that entanglement is not a factor for the larger dendrimers. It is interesting to note that the points where T_g levels off and where intrinsic viscosity reaches a maximum both occur at approximately $[G\text{-}3]_3$-[C] for the dendritic macromolecules. This suggests that some transition in macromolecular shape is taking place, perhaps a transition from a loose, flexible, extended, and somewhat entangled structure to a more globular structure.

Effect of Chain-End Composition. Some fundamental characteristics of the convergent growth approach are that the number of chain ends increase with increasing generation number (degree of polymerization) and that the nature of these chain ends may be accurately controlled.[17,18] A recent report on methyl methacrylate telomers[11] concludes that the chemical nature of the chain termination affects the entanglement behavior and, therefore, the critical or entanglement molecular weight, M_c. As stated above, dendritic macromolecules do not exhibit a characteristic entanglement molecular weight. However,

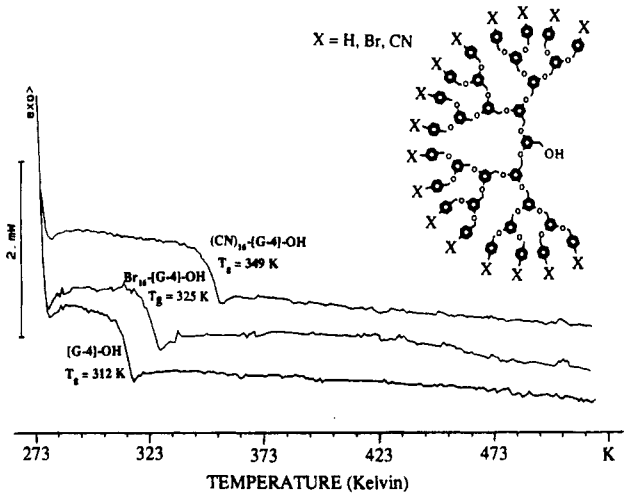


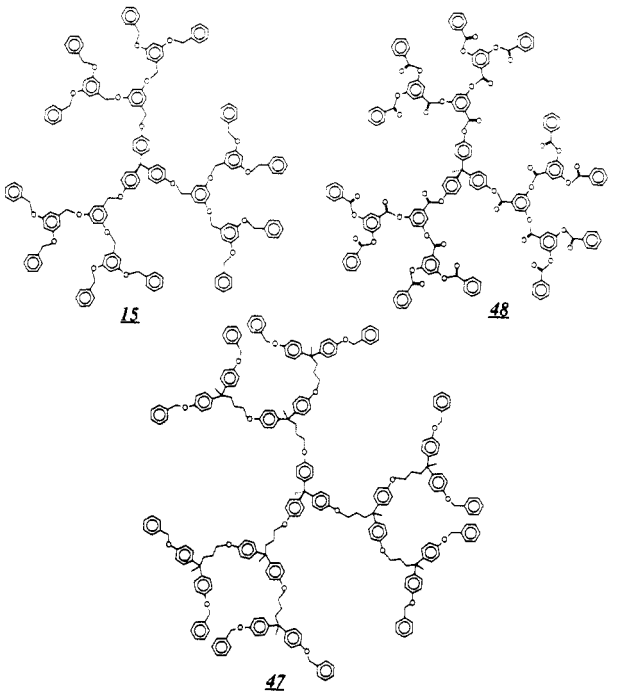
Figure 5. Differential scanning calorimetry plots for substituted dendritic fragments, X_{16}-[G-4]-OH.

because each molecule has a large number of chain ends, the chemical composition of the chain ends has a drastic effect on T_g (Table II). This is demonstrated in Figure 5, which shows a composite of DSC traces for the various fourth-generation dendritic polyether fragments with hydrogen, bromo, or cyano groups at the 16 chain ends and a hydroxymethyl group at the focal point. On increasing end-group polarity from hydrogen to bromo to cyano, the T_g increases from 315 to 325 to 349 K, even though the molecules differ only in the chain-end functional groups. A larger effect is seen in dendritic polyesters,[14] where T_g increases by 128 K, from 346 to 474 K, as one proceeds from a benzyl ether terminated dendrimer to an analogous phenolic terminated dendrimer. This dramatic increase may be due to the hydrogen-bonding capability of the phenolic chain ends.

$T_{g\infty}$ and K' are also affected by the chain-end functionalization; the values for the three systems are included in Table II. It is observed that $T_{g\infty}$, like T_g, increases with increasing polarity of the chain ends. However, K' seems to be dependent on the size of the chain-end functional group and increases from 13 600 for H to 16 800 for CN and then to 20 800 for Br. This observation may be explained by an increase in density (ρ) of the material and/or the larger chain ends having greater free volume per chain end (θ).

Effect of Macromolecular Composition. For this comparison, three different systems, based on 3,5-dihydroxybenzyl alcohol,[1] 4,4-bis(4'-hydroxyphenyl)pentanol,[4] and 3,5-dihydroxybenzoic acid[14] as the monomer units, were studied. For each of these systems, the second-

Chart II
Dendrimers Based on 3,5-Dihydroxybenzyl Alcohol (15), 3,5-Dihydroxybenzoic Acid (48), and 4,4-Bis(4′-hydroxyphenyl)pentanol (47) as the Monomer Units



generation dendrimers attached to a trifunctional core are shown in Chart II. These dendrimers give T_g's of 309, 326, and 340 K for **15**, **47**, and **48**, respectively. $T_{g\infty}$ and K' for the benzyl ether terminated valeryl polyethers (constructed from 4,4-bis(4′-hydroxyphenyl)pentanol) are 340 K and 41 100 with $(n_e/M)_\infty = 0.002\,907$. It may seem surprising that these macromolecules with the flexible spacer groups have larger values for T_g and $T_{g\infty}$ than do the macromolecules constructed from 3,5-dihydroxybenzyl alcohol ($T_{g\infty}$ = 316 K, K' = 69 900, $(n_e/M)_\infty = 0.004\,717$). However, the presence of the quaternary carbon between the two phenyl rings in the 4,4-bis(4′-hydroxyphenyl)-pentanol monomer unit is expected to cause a large amount of local rigidity, which would account for the larger glass transition temperatures.

Recently, we reported the synthesis of dendritic block copolymers based on blocks composed of different monomer units (i.e., ester and ether)[17] or the same monomer units with the blocks having different surface functional groups.[18,19] The synthetic strategy employed was the convergent growth approach which allowed the macromolecules to be prepared with an accurately known number of each type of monomer units and blocks. Chart III shows an ether/ester segment block copolymer (**37**), a layer block copolymer, $[G\text{-}4]_6$-[val.C] (**39**), and a chain-end block copolymer, CN_8-[G-3]-[C]-[G-4] (**45**). The glass transition temperature, molecular weight, and weight fraction of each different monomer unit are given in Table III.

There are a large number of equations relating the T_g of a copolymer to the percent composition and T_g of the pure components, ranging from logarithmic to linear correlations.[20]

$$\ln T_g = m_1 \ln T_{g1} + m_2 \ln T_{g2} \qquad (11)$$

Application of eq 11 to the dendritic ether/ester block copolymers affords a good correlation with the experimentally determined copolymer glass transitions. For the ether/ester segment block copolymer which is essentially a copolymer of a [G-3]-OH dendritic benzyl ether fragment

Chart III
Ether/Ester Segment Block Copolymer 37 Constructed from 3,5-Dihydroxybenzyl Alcohol and 3,5-Dihydroxybenzoic Acid, a Benzyloxy/Cyano Chain End Block Copolymer 45, and a Layer Block Copolymer 39 Constructed from 3,5-Dihydroxybenzyl Alcohol and 4,4-Bis(4′-hydroxyphenyl)pentanol as Monomer Units

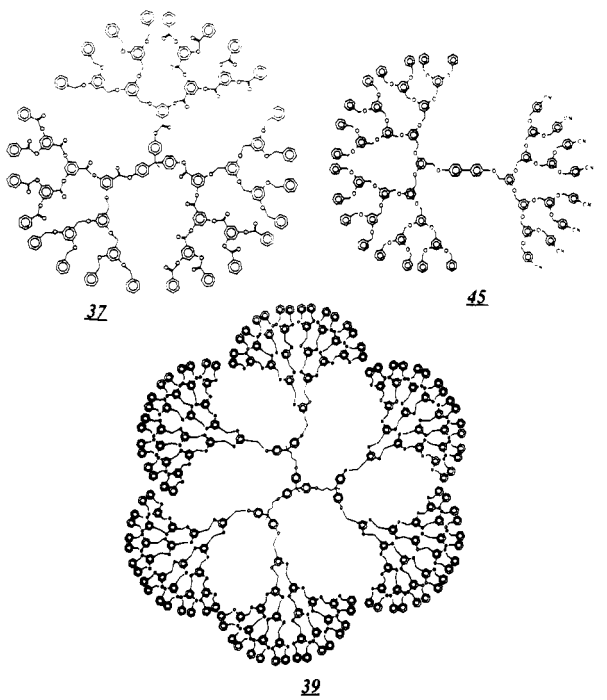


Table III
Data for Dendritic Segment, Layer, and Chain-End Block Copolymers

entry	compound	M	w	$(T_g)_{calc}$	$(T_g)_{obs}$
37	ether/ester segment	5 364	47:53	352	351
38	ether/ester layer	10 242	90:10	319	319
39	$[G\text{-}4]_6$-[val.C]	20 712	95:5	315	322
40	$[G\text{-}4]_{12}$-[val.C]	41 881	94:6	318	320
41	$[G\text{-}4]_{24}$-[val.C]	84 219	93:7	318	321
42	$(Br_{16}\text{-}[G\text{-}4])_2$-[C]-[G-4]	12 644	73:27	323	330
43	CN_2-[G-1]-[C]-[G-2]	1 264	35:65	286	311
44	CN_4-[G-2]-[C]-[G-3]	2 586	35:65	313	325
45	CN_8-[G-3]-[C]-[G-4]	5 230	35:65	320	327
46	CN_{16}-[G-4]-[C]-[G-5]	10 530	35:65	327	329

(T_g = 305 K, entry 3) and a $[G\text{-}3]_3$-[C] dendritic polyester macromolecule (T_g = 399 K), the calculated T_g is 352 K; this agrees with the experimentally determined value of 351 K. The ether/ester layer block copolymer is composed of a $[G\text{-}3]_3$-[C] dendritic polyether macromolecule (T_g = 312 K, entry **16**) and a $[G\text{-}1]_3$-[C] dendritic polyester macromolecule (T_g = 385 K), and both the calculated and experimental values of T_g are 319 K.

For the other block copolymers included in Table III, the observed T_g's are intermediate between the two pure components, but eq 10 does not accurately predict the glass transition temperature. Slight variations between the theoretical and experimental glass transition temperatures may arise due to the difficulty in choosing accurate models for the respective blocks which are then used as references for the calculations. It is possible that the structures available for comparison are not accurate models for the final block copolymers. Of more importance is the observation of single glass transitions in all of the copolymer systems cited. This finding indicates that, even in the segmented block copolymers, intimate mixing on a molecular level occurs in these dendritic systems. However, for dendritic block copolymers containing very different and incompatible chain ends, two glass transition

temperatures have been recently observed.[21] This may be due to phase separation by aggregation of like segments of chain-end blocks.

Conclusion

The glass transition temperature has been measured for a number of dendritic molecules, based on 3,5-dihydroxybenzyl alcohol, 3,5-dihydroxybenzoic acid, or 4,4-bis(4'-hydroxyphenyl)pentanol as the monomer units. The variation of glass transition temperature with molecular weight was shown to correlate to n_e/M. The traditional relationship between T_g, $T_{g\infty}$, and M for linear polymers was modified to account for the unusual macromolecular architecture of dendritic structures.

It was also observed that the nature of the chain ends dramatically affects the glass transition temperature of dendritic macromolecules, with increases in T_g following increases in chain-end polarities. When groups capable of hydrogen bonding (for example, phenol or carboxylic acid) were placed at the chain ends, an even larger increase in T_g was observed. Comparison of dendritic block copolymers with their parent dendritic homopolymers demonstrated that the internal composition of dendrimers also affects the glass transition temperature. Therefore, by varying chain-end functionalization and internal monomer units, a variety of dendritic macromolecules may be prepared covering a wide range of glass transition temperatures.

Future studies will be directed toward further understanding of the physical properties of these novel dendritic macromolecules and hybrid dendritic/linear copolymers.

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