Macromolecules **1994,** *27,* 1968-1971

Notes

Role of End Groups on the Glass Transition of Hyperbranched Polyphenylene and Triphenylbenzene Derivatives

Young H. Kim* and Richard Beckerbauer

DuPont Central Research & Development,[†]
Experimental Station, Wilmington, Delaware 19880-0328

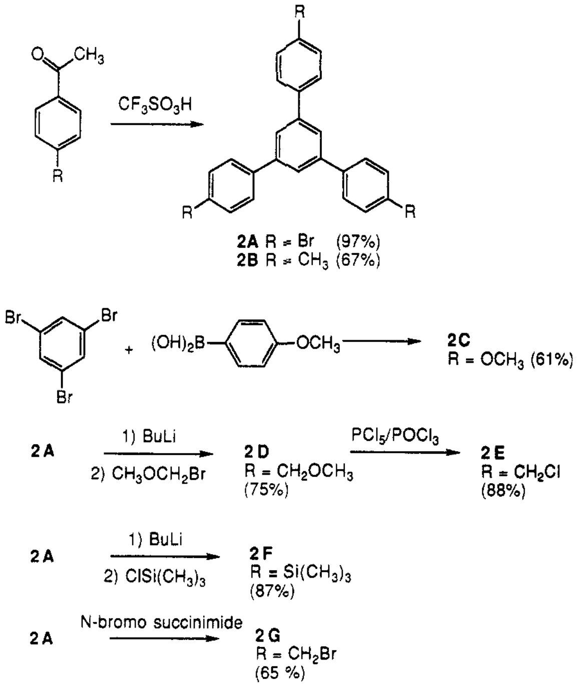
Received October 8, 1993
Revised Manuscript Received January 20, 1994

Introduction

Recent research activities in the area of highly branched polymers have unveiled some intriguing properties of these new types of molecules.[1,2] One of the particularly interesting characteristics of these polymers is their distinct glass transitions. The T_g of a polymer is commonly believed to be associated with long-range, cooperative relaxation phenomena through large segmental motions, and its rheological or thermodynamic origin is well established. For a high molecular weight linear polymer, the chain ends play only a minor role in the glass transition. Since hyperbranched or dendritic polymers are not expected to be extensively engaged in chain entanglement, their glass transitions could originate from a relaxation phenomenon different from that of linear polymers. In particular, the end group contribution becomes significant. For example, a dendritic polymer made from an AB_2 type monomer has as many functional groups as the degree of polymerization. It has been suggested that the unusual behavior of these polymers is based on conformational changes and the degree of association of the polymer at different sizes (generations) of the polymer.[3,4] In the first attempt to understand the thermal relaxation of dendrimers, modified chain-end free volume theory, with consideration of the volume occupied by a large number of chain ends, was proposed to account for the molecular weight dependency of T_g. However, the separate roles of the type of chain ends and of the internal structure in the transition temperature are still not well understood.[5]

We proposed earlier that the main relaxation mode of the glass transition for hyperbranched polyphenylenes, which were polymerized by condensation of (3,5-dibromophenyl)boronic acid, is translational motion of the polymer rather than segmental chain motion as usually assumed for linear polymers.[6] This proposal was based on the fact that the T_gs are highly dependent on the end functional groups of the polymers. Usually, a more polar functional group causes the T_g to be higher, implying a polar end group interaction contribution to the activation energy and the transition temperature. One important factor which distinguishes this polymer is the rigid repeating unit, wherein the dihedral angle between the phenyl rings is expected to be invariant with the size of the polymer, and therefore contraction of the polymer by chain folding with an increase of molecular weight cannot occur. For this reason, the contribution of the chain relaxation at the glass transition, if there is any, would not be dependent on the size of the polymer. On the other hand, the number of end groups increases with an increase of molecular weight and can exert a dominant effect. The hyperbranched polyphenylenes with various end functional groups were prepared by modification of the Br functional gorups and should have essentially the same internal structure.

Scheme 1



In an attempt to gain more insight into the role of end functional groups, we propose to compare the T_gs of these hyperbranched polyphenylenes with those of related small molecules where the contribution from the inner segment relaxation would be minimized. Glassy materials can be obtained with a number of small aromatic molecules by a supercooling from the melt. The glass formation and characterization of *o*-terphenyl,[7] hindered trisubstituted benzenes,[8,9] and a mixture of aromatics[10] are well known. Usually, the slow crystallization kinetics of these molecules allows formation of a glassy state. If the polarity of the end groups of a hyperbranched polymer plays a major role in the T_g, there might be a correlation with the T_g of small molecules of related structure. We have prepared 1,3,5-triphenylbenzene derivatives with *p*′-substitution[11] and compared their T_gs with those of hyperbranched polyphenylenes.

Results and Discussion

1,3,5-Tris(*p*-bromophenyl)- and 1,3,5-tris(*p*-methylphenyl)benzene (**2A** and **2B**) were prepared by acid-catalyzed condensation of the corresponding acetophenones; they were modified to give other derivatives as shown in Scheme 1. The methoxy derivative (**2C**) was obtained via a Suzuki coupling reaction[12] of the corresponding boronic acid with 1,3,5-tribromobenzene. The derivatives prepared and investigated are also shown in Table 1. Hyperbranched

---

* Author to whom correspondence should be addressed.

[†] Contribution No. 6703.

0024-9297/94/2227-1968$04.50/0

Table 1. Thermal Properties of Hyperbranched Polyphenylene and Triphenylbenzene Derivatives[a]

		hyperbranched polyphenylenes			1,3,5-triphenylbenzenes						
compd	R	T_g (°C)	transition range[b]	ΔC_p (J/mol)	T_m (°C)	ΔH_f (cal/mol)	ΔS_f (eu)	T_g (°C)	transition range	ΔC_p (J/mol)	T_g/T_m
1,2	H	121	117–129	19.9	168	5.6	12.7	no T_g			
1,2A	Br	221	210–230	20.2	261	9.3	17.4	no T_g			
1,2B	CH_3	177	166–185	18.0	179	6.9	15.3	39.2[c]	37–41	116	0.69
1,2C	OCH_3	223	214–230	15.3	242	6.2	12.0	65.2	30–34	105	0.65
1,2D	CH_2OCH_3	121	109–134	50.3	90	8.2		2.6	−1.4 to +5.1	161	0.76
					115						0.71
1,2E	CH_2Cl	182	173–193	19.3				43.3	39–47	173	
1,2F	$Si(CH_3)_3$	141	134–150	28.2	146	7.5	17.9	33.0	61–66	123	0.73
1,2G	CH_2Br				179	4.8	10.6	54.5	50–55	140	0.72

[a] The sample size for all DSC measurements range between 8 and 12 mg. [b] The transition range indicates the extrapolated temperatures of the starting and end of the T_g region. [c] Heating rate 40 and 50 °C. At the slower heating rate, the T_g was obscured by crystallization.

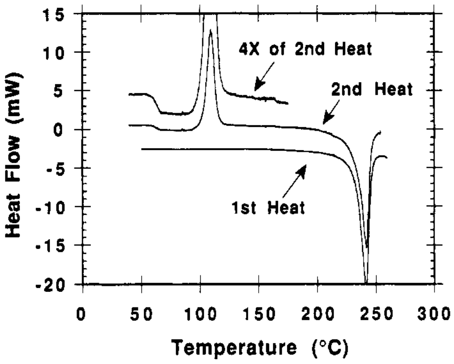


Figure 1. DSC experiment of tris(*p*-(trimethylsilyl)phenyl)benzene (**2F**).

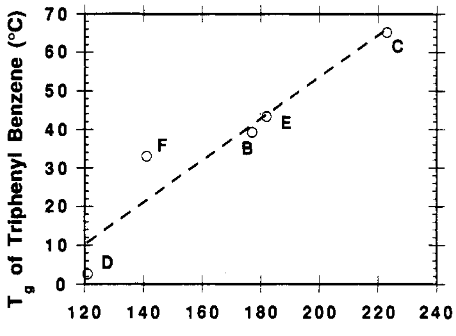


Figure 2. Correlation of T_gs of hyperbranched polyphenylene and 1,3,5-triphenylbenzene derivatives. The letters in the graphs correspond to the functional groups in Table 1.

poly(bromophenylene) (**1A**) as polymerized has ca. one Br functional group per repeating unit and has an $\bar{M}_n$ of ca. 5000. In this molecular weight range the T_g is virtually invariant with molecular weight.[6] Other functionalized hyperbranched polyphenylenes were prepared by replacement of the Br in **1A**. The number of end groups per phenyl for triphenylbenzene derivatives is 0.75, whereas that for hyperbranched polyphenylene is 1.0. However, since only 70–80% of the original Br functional group of the polymer was found to be converted to the respective functional groups through a lithiated intermediate, we believe *p*′-substituted triphenylbenzenes adequately serve as model compounds. The thermal transitions of these compounds were studied by DSC. The glassy state was obtained by supercooling the substances from the melt in the DSC aluminum pan by placing it on a cold surface or in liquid nitrogen. The T_g was determined as the midpoint of the step change in heat capacity when heated at 20 °C/min unless stated otherwise. The ability to form the glassy state varies with the structure. The parent 1,3,5-triphenylbenzene (**2**) and **2A** did not give glassy material under various quenching conditions. All other derivatives could be completely quenched to the glassy state by rapid cooling to below the T_g from the melt. Most recrystallize completely when heated above the T_g with a heat of crystallization of similar magnitude as the subsequent heat of fusion. A typical example of these heating profiles with the T_g is shown in Figure 1. **2C** and **2D** were found never to melt crystallize, even though both readily crystallized from a solution. As summarized in Table 1, the T_g/T_m ratios are in the range 0.65–0.76. Typically, this ratio for small molecules is ~0.75, regardless of the relaxation mechanism of the glassy state.[13]

In general, for both the hyperbranched polymer and the triphenylbenzenes, T_g increases with end group polarity. However, no direct correlation between the transition temperatures and the inductive or resonance effect of these functional groups could be found; attempts to correlate the T_gs with any empirical σ values were not successful.

On the other hand, in comparing the T_gs of triphenylbenzene derivatives and hyperbranched polyphenylenes, we found an excellent correlation for the same functionality as shown in Figure 2. Only the trimethylsilyl derivative shows a slight deviation from the linear fit. That could be due to a higher entropic contribution of the trimethylsilyl group, as exemplified by the large fusion entropy of **2F**. The linear correlation indicates that the T_g of the hyperbranched polymer may be strongly dependent on the interassociation of these functional groups with the neighboring molecule as well as the volume fraction occupied by the terminal group. It may also suggest that the relaxation mechanism of these two classes of molecules is similar but different from that in linear polymers. In a typical linear molecule, extrapolation of the relaxation mechanism from a small molecule to a polymer is not conceivable. However, the nature of the interaction and relaxation mechanism associated with the glass transition is not yet clear, and more investigation is needed.

The large shift of the T_gs for the polymers compared to those of the triphenylbenzene derivatives could be a manifestation of the inner phenyl unit contribution to the thermal relaxation or due to a higher relaxation activation energy for translational movement of the larger mass. The range of shift in T_g for the polymers associated with changes in end groups is roughly equivalent to the increase associated with moving from the small molecule to the higher molecular weight core. These two factors are difficult to separate at this point.

In the analysis of the T_gs of polyether dendrimers, Wooley et al. found that the experimental data are fit well by a modified Flory equation (eq 1), suggesting the T_g of the highly branched polymer is not different from that of a linear polymer as long as the volume expansion of the end group is accounted for. In eq 1, $T_{g\infty}$ is the T_g of infinite

$$T_g = T_{g\infty} - K'(n_e/M) \qquad (1)$$

molecular weight polymer, K' is a constant related to the density and thermal expansion coefficient of the terminal group, n_e is the number of chain ends per molecule, and M is the molecular weight.

In the case of dendritic or hyperbranched polymer, it seems to us that $T_{g\infty}$ is the T_g without the chain end contribution rather than the T_g of infinite molecular weight polymer. However, this value is difficult to fathom at this time, conceptually or experimentally.

Comparing the different types of inner units illustrates the complexity and might be helpful in understanding the situation. Higher homologues made of 1,3,5-triphenylbenzene repeating units were found to be increasingly more difficult to crystallize due to steric reasons; thus symmetric dendritic polyphenylenes with 46 rings could not be crystallized completely.[14] These symmetrically constructed polyphenylene dendrimers exhibit higher T_gs than hyperbranched polyphenylenes of comparable molecular weights. This might be related to the propensity of phenylenes to have a high packing order, for which molecules with higher symmetry would have an advantage. In the solid state, 1,3,5-triphenylbenzene exists as an orthorhombic crystal, and the torsion angle between the phenyl rings is in the range 34–39°.[15] Such a twist torsional angle is responsible for an ~11 kcal/mol stabilization compared to the flat conformation for steric reasons.[16] However, one of the phenyl rings was found to be twisted in the opposite direction (causing nonsymmetry and loss of 0.8 kcal/mol) in order to gain a maximum crystalline packing energy. In a higher molecular weight polymer, whether it is a dendrimer or a hyperbranched polymer, molecular packing is less likely, though packing through inner branches cannot be ruled out. A large number of geometric and symmetric isomers in a hyperbranched polymer could reduce the chance of such internal order, thus lowering the relaxation energy barrier.

Conclusions

Chain end groups are found to have a large effect on the thermal relaxation of hyperbranched polyphenylenes. A good correlation of the effect of the functional groups between small molecules and polymers implies similarities in the relaxation mechanism. However, to further understand the thermal relaxation phenomena of highly branched polymers, more data on the rheology and the free volume contribution of the inner unit and the chain end are necessary. We are planning pressure–volume measurement experiments of some of these substances to address those needs. Comparison with similarly substituted polymers would provide further insight.

Experimental Section

THF was dried by refluxing with sodium ketyl anion under nitrogen and distilled just prior to use. All reagents and solvents were purchased from various vendors and used as received. Syntheses of hyperbranched polyphenylenes were published elsewhere.[6] Thermal properties were obtained from a DuPont 9600 thermal analyzer with a heating rate of 20 °C/min unless stated otherwise.

Synthesis of 1,3,5-Tris(*p*-bromophenyl)benzene (2A). A mixture of 143.88 g (0.723 mol) of 4-bromoacetophenone and 1.0 mL of triflic acid in 700 mL of toluene was heated to reflux, while water was removed through a Dean–Stark trap. About 12.0 mL of water was collected in 6 h, and a total of 12.5 mL of water was removed in 30 h. As the reaction mixture was cooled to room temperature, 113.42 g of orange needles crystallized (mp 259–261 °C). As the solvent was concentrated, an additional 15.89 g of product having a melting point of 255–256 °C was obtained. The analytical sample was recrystallized from toluene. ^{1}H NMR ($CDCl_3$, ppm) 7.61, 7.70 (AB quartet, J = 9 Hz, 12 H), 7.86 (s, 3H).

Synthesis of 1,3,5-Tris(*p*-tolyl)benzene (2B). A mixture of 134.2 g (1.0 mol) of 4-methylacetophenone and 0.5 mL of triflic acid in 700 mL of toluene was refluxed with removal of water through a Dean–Stark trap. About 13.0 mL of water was collected in 22 h. An additional 0.5 mL of triflic acid was added, and then reflux was continued for 60 h to collect a total of 16 mL of water. The solution was concentrated to 150 mL and then cooled to room temperature to crystallize the crude reaction product. Recrystallization from toluene gave 81.0 g of orange needles (yield 67%). The analytical sample was recrystallized from CH_2Cl_2/MeOH (2:1). ^{1}H NMR ($CDCl_3$, ppm) 2.1 (s, 9H), 7.29, 7.59 (AB quartet, J = 7 Hz, 12H), 7.74 (s, 3H).

Synthesis of 1,3,5-Tris(*p*-methoxyphenyl)benzene (2C). To 23.40 g (100 mmol) of *p*-iodoanisole in 200 mL of THF was added 71 mL of 1.55 M *n*-BuLi (110 mmol), while keeping the internal temperature below −70 °C. The mixture was stirred for 30 min, followed by addition of a solution containing 43 mL of trimethyl borate in 100 mL of THF at −78 °C. After warming to room temperature, 100 mL of 3 N HCl was added for hydrolysis, and the organic layer was then extracted three times with 3 N NaOH. The NaOH solution layer was neutralized with 6 N HCl to give 14.35 g of white (*p*-methoxyphenyl)boronic acid. The boronic acid was reacted with 6.30 g (20 mmol) of 1,3,5-tribromobenzene and 200 mg of $Pd(PPh_3)_3$ in 150 mL of toluene, 50 mL of EtOH, and 80 mL of 1 M K_2CO_3 under reflux for 6 h. The product was extracted with toluene and recrystallized from EtOH/CH_2Cl_2 to give 4.87 g of the product. ^{1}H NMR ($CDCl_3$, ppm) 3.86 (s, 9H), 7.02, 7.62 (AB quartet, J = 10 Hz, 12 H), 7.66 (s, 3H).

Synthesis of 1,3,5-Tris(*p*-(methoxymethyl)phenyl)benzene (2D). To 5.43 g (10 mmol) of **2A** in 300 mL of THF was added 31.2 mL (50 mmol) of 1.6 M *n*-BuLi in 8 min. After ~20 mL of *n*-BuLi had been added, a greenish gummy solid started to appear. The mixture was stirred for 2 h, and then 4.1 mL (50 mmol) of bromomethyl methyl ether was added at that temperature, which caused dissolution of all the precipitate. This solution was concentrated and chromatographed on a silica gel column with CH_2Cl_2/petroleum ether. A total of 3.3 g of product was obtained. ^{1}H NMR ($CDCl_3$, ppm) 3.43 (s, 9H), 4.52 (s, 6H), 7.45, 7.68 (AB quartet, J = 7 Hz, 12 H), 7.77 (s, 3H).

Synthesis of 1,3,5-Tris(*p*-(chloromethyl)phenyl)benzene (2E). To 34.42 g (78 mmol) in 350 mL of $POCl_3$ was added 81.21 g (390 mmol) of PCl_5, and then the clear orange solution was refluxed for 10 h. About 100 mL of solvent was distilled off, and the remainder was poured into ice water. The precipitate was washed with water, $NaHCO_3$ solution, and water again. The light tan powder weighed 44.02 g. A 42.97-g portion of this crude product was passed through a short silica gel solumn with CH_2Cl_2 as eluent to give 34.73 g of product, which was recrystallized from 50:50 CH_2Cl_2/MeOH. The resulting freely flowing crystals turned waxy when they were exposed to air, but repeated MeOH washing gave nonsticky crystals. The first crop was 14.10 g (mp 162 °C), the second crop was 5.45 g (mp 164 °C), and the third crop was 10.60 g (mp 145–155 °C). Yield 88%. ^{1}H NMR ($CDCl_3$, ppm) 4.66 (s, 6H), 7.51, 7.65 (AB quartet, J = 9 Hz, 12H), 7.75 (s, 3H).

Synthesis of 1,3,5-Tris(*p*-(trimethylsilyl)phenyl)benzene (2F). To 5.49 g (10 mmol) of **2A** in 250 mL of THF was added 30 mL of 1.5 M *n*-BuLi (45 mmol), and the mixture was stirred for 1 h at −78 °C. To this was added 5.0 mL of neat chlorotrimethylsilane. After removal of solvent under reduced pressure, the toluene-soluble fraction was purified by chromatography on a silica gel column to give 4.61 g of product, which was recrystallized from CH_2Cl_2/MeOH. ^{1}H NMR ($CDCl_3$, ppm) 0.31 (s, 9H), 7.64, 7.67 (AB quartet, J = 7 Hz, 12H), 7.78 (s, 3H).

Synthesis of 1,3,5-Tris(*p*-(bromomethyl)phenyl)benzene (2G). A mixture of 30.0 g (86.1 mmol) of **2B**, 450 mL of CCl_4, 53.63 g (301 mmol) of *N*-bromosuccinimide, and 200 mg of benzoyl peroxide was refluxed for 4 h. After cooling to room temperature, the precipitate was filtered off and recrystallized from CCl_4/MeOH to give 23.77 g of product (65%). ^{1}H NMR ($CDCl_3$, ppm) 4.58 (s, 6H), 7.51, 7.65 (AB quartet, J = 9 Hz, 12H), 7.75 (s, 3H).

References and Notes

(1) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(2) Kim, Y. H. *Adv. Mater.* **1992**, *4*, 764.

(3) Moreno-Bondi, M. C.; Orellana, G.; Turro, N. J.; Tomalia, D. A. *Macromolecules* **1990**, *23*, 910.

(4) Hawker, C. J.; Wooley, K. L.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1993**, *115*, 4375.

(5) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Frechet, J. M. J. *Macromolecules* **1993**, *26*, 1514.

(6) Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561.

(7) Chang, S. S.; Bestul, A. B. *J. Chem. Phys.* **1972**, *56*, 325.

(8) Ishikawa, W.; Inada, H.; Nakano, H.; Shirota, Y. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1992**, *211*, 431.

(9) Shirota, Y.; Kobata, T.; Noma, N. *Chem. Lett.* **1989**, 1145.

(10) Molaire, M. F.; Johnson, R. W. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2569.

(11) Elmorsy, S. S.; Pelter, A.; Smith, K. *Tetrahedron Lett.* **1991**, *32*, 4175.

(12) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.

(13) Brawer, S. *Relaxation in Viscous Liquids and Glasses: Review of Phenomenology, Molecular Dynamics Simulations, and Theoretical Treatment*; The American Ceramic Society, Inc.: Columbus, OH, 1985; Chapter 1.

(14) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.

(15) Lin, Y. C.; Williams, D. E. *Acta Crystallogr., Sect. B* **1975**, *B31*, 318.

(16) Busing, W. R. *J. Am. Chem. Soc.* **1982**, *104*, 4829.