Hyperbranched Copolymers versus Linear Copolymers: A Comparative Study of Thermal Properties

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ABSTRACT: Copolymerization of two AB_2-type monomers that incorporate spacer segments of similar lengths but different flexibility permitted, for the first time, the preparation of a range of hyperbranched copolymers, wherein the backbone rigidity was varied while maintaining similar branching densities. The copolymers were prepared via a recently developed melt transetherification methodology to yield moderately high molecular weight polymers, with molecular weights ranging from 20 000 to 50 000. ^{1}H NMR spectroscopic studies revealed that the composition of the copolymers varied linearly with monomer composition, confirming the formation of truly random copolymers. Analogous linear copolymers based on suitably designed AB-type monomers, containing the same two spacers, were also prepared for comparison. Thermal analysis of these copolymers using DSC indicated that the T_g's of both linear copolymers and hyperbranched copolymers varied with composition in a manner that was in complete accordance with the Fox equation, although all the linear copolymers exhibited significantly higher T_g values than their hyperbranched counterparts. It is interesting that, despite their very different topology and the presence of large number of chain ends, hyperbranched copolymers exhibit a similar T_g variation as their linear analogues. The generality of this observation in the broader context of hyperbranched copolymers, such as those possessing different branching densities and terminal functionalities, remains to be tested.

Introduction

Hyperbranched polymers represent an interesting class of highly branched soluble macromolecules, which has witnessed growing attention during the past decade.[1] Typically, they are prepared in a single step by polycondensation of AB_x-type monomers (where $x \geq 2$), in contrast to the stepwise approach for the preparation of dendrimers. Despite the presence of structural imperfections, hyperbranched polymers have attracted a great deal of attention primarily due to their potential applications, such as in coatings, modifiers, additives, nanomaterials, biomaterials, etc.[2] Many of these applications exploit the unique properties of these polymers, such as their very low viscosities and/or the presence of a very large number of peripheral functional end groups. Several types of hyperbranched polymers, such as polyphenylenes,[3] polyesters,[4] polyurethanes,[5] polyamides,[6] polyethers,[7] polyacrylates,[8] etc., have been synthesized using different approaches, like polycondensation of AB_n-type monomers, self-condensing vinyl polymerization (SCVP),[9] self-condensing ring-opening polymerization (SCROP),[10] proton-transfer polymerization (PTP),[11] etc. Although a large number of hyperbranched polymers have been synthesized and well documented in the literature, understanding of the fundamental structure−property correlations has lagged behind. The molecular structural variables associated with hyperbranched structures are many more than in their linear counterparts, which make them more interesting at the same time complex. The typical structural variables are molecular weight, molecular weight distribution, degree of branching, nature and length of the spacer segments, nature of the end groups, etc. Several attempts have been made to systematically vary these structural features, such as the degree of branching, molecular weights, end groups and spacer segments. For instance, it has been shown that the nature of the end groups have a very strong influence on the glass transition temperatures of hyperbranched polymers.[12] Copolymerizations using AB + AB_2 type monomers,[13−16] and self-condensing vinyl copolymerization (SCVCP) methodologies,[17] have helped reveal several interesting property variations of hyperbranched polymers as a function of branching density. In a very recent study,[18] we showed that the length of the spacer segment that links the branch points greatly influences the compactness of the conformation of hyperbranched polymers. Furthermore, we also showed that, just as in the case of dendrimers, in hyperbranched structures too compact conformations are adopted only beyond a certain molecular weight.

It is evident from the published literature that copolymerization in the context of hyperbranched structures primarily refers to systems wherein branching monomers of the AB_n type are copolymerized with simple linear AB-type ones. Several others have examined the use of A_3 + B_2,[19] ABB′ + A_2,[20] etc., most of which have focused on improving the preparation methodologies, primarily to enhance the branching densities and preclude the formation of cross-linked species. Copolymerizations using two different AB_2-type monomers are very rare, and more importantly, attempts to understand copolymer properties as a function of composition have never been made. It is in this context that we have undertaken the present investigation wherein two types of AB_2 monomers, which have spacer segments of similar lengths but different flexibility, have been copolymerized. This approach ensures that while one molecular feature, namely flexibility of the spacer, is varied the other features, specifically the branching density, remain invariant. The variation of the T_g's of the hyperbranched copolymers with composition has been compared with an analogous linear counterpart.

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Experimental Section

2,4,6-Trimethylphenol (Mesitol), 1,6-hexanediol, 1,4-cyclohexanedimethanol, and camphorsulfonic acid were purchased from Aldrich Chemical Co. Structures of all intermediates, monomers, and polymers were confirmed by ^{1}H NMR spectroscopy. NMR spectra were recorded on a Bruker AV400 MHz spectrometer, using CDCl$_3$ and TMS as the solvent and reference, respectively. GPC measurements were carried out using Viscotek TDA model 300 system, coupled to a refractive index (RI) and a differential viscometer (DV) in series. The separation was achieved using a series of two PLgel mixed bed columns (300 × 7.5 mm) operated at 30 °C using THF as the eluent. Molecular weights were determined using a universal calibration curve based on the data from the refractive index (RI) and differential viscometeric (DV) detectors using narrow polystyrene standards. The glass transition temperature of the samples was determined using a Rheometric Scientific DSC PLUS instrument at a heating rate of 10 °C/min under a dry N$_2$ atmosphere. The samples were first heated to about 180 °C (to ensure that the sample flows and makes adequate contact with the pan) and quenched prior to recording their T_g. The glass transition temperature was taken as the midpoint of the inflection tangent.

3,5-Bisbromomethyl-2,4,6-trimethylphenol (2). 50 mL of HBr in acetic acid (33 wt %) was added to the mixture of 4.0 g (29.4 mmol) of mesitol and 2.6 g (29.0 mmol) of trioxane. The mixture was refluxed for 2 h, cooled to RT, and poured into 1.0 L of cold water. The residue was filtered, washed thoroughly with water (4−5 L) to ensure it is acid-free, and then dried under vacuum (yield = 90.0%, mp = 145 °C; lit.[21]-139 °C).

^{1}H NMR (δ, ppm, CDCl$_3$): 2.31 (s, 6H, Ar (**CH$_3$**)$_2$); 2.40 (s, 3H, Ar (**CH$_3$**); 4.57 (s, 4H, Ar**CH$_2$**Br).

3,5-Bismethoxymethyl-2,4,6-trimethylphenol (3). Sodium metal (3.2 g, 139.1 mmol) was added to 50 mL of dry methanol in portions. The solution of **2** (7.5 g, 23.3 mmol) in dry methanol (170 mL) was added dropwise to the degassed sodium methoxide solution. The reaction mixture was refluxed for 18 h under a N$_2$ atmosphere and cooled to room temperature, and the methanol was removed using a rotary evaporator. 80 mL of cold water was added to the residue, and it was acidified with 50% HCl (v/v). The white precipitate formed was extracted with CHCl$_3$ (120 mL), dried over anhydrous Na$_2$SO$_4$, and passed through a silica bed to remove some colored impurities. The chloroform was then removed by a rotary evaporator, and the residue was recrystallized from hot petroleum ether to yield the desired product (yield = 76%, mp = 79 °C; lit.[7a] 77−79 °C).

^{1}H NMR (δ, ppm, CDCl$_3$): 2.25 (s, 6H, Ar(**CH$_3$**)$_2$); 2.35 (s, 3H, Ar(**CH$_3$**)); 3.40 (s, 6H, ArCH$_2$O**CH$_3$**); 4.47 (s, 4H, Ar**CH$_2$**OCH$_3$); 4.72 (s, 1H, ArO**H**).

1-(6-Hydroxyhexyloxy)-3,5-bis(methoxymethyl)-2,4,6-trimethylbenzene (A). A mixture of K$_2$CO$_3$ (5.5 g, 39.8 mmol), a catalytic amount of KI, and 1-bromohexanol (3.6 g, 20.0 mmol) were taken in 40 mL of dry CH$_3$CN. The mixture was degassed for 20 min, after which 1.5 g (6.7 mmol) of **3** was added to it. The reaction mixture was degassed for an additional 20 min and then refluxed for 72 h under a N$_2$ atmosphere. The solvent was then removed with a rotary evaporator, and 50−60 mL of cold water was added to it. The product was extracted with 100 mL (2 × 50 mL) of ether, and the ether layer was washed with 10% (w/v) aqueous NaOH solution (4 × 30 mL) followed by water. The ether layer was dried over anhydrous Na$_2$SO$_4$ and concentrated, and the residue was recrystallized from hot petroleum ether to give the product (yield = 73%, mp = 73 °C).

^{1}H NMR (δ, ppm, CDCl$_3$): 1.40−1.85 (m, 8H, ArOCH$_2$(**CH$_2$**)$_4$CH$_2$OH); 2.30 (s, 6H, Ar(**CH$_3$**)$_2$); 2.36 (s, 3H, Ar(**CH$_3$**); 3.38 (s, 6H, ArCH$_2$O**CH$_3$**); 3.61−3.63 (m, 4H ArO**CH$_2$**(CH$_2$)$_4$**CH$_2$**OH); 4.45 (s, 4H, Ar**CH$_2$**OCH$_3$).

1-(4-Hydroxymethylcyclohexylmethoxy)-3,5-bis(methoxymethyl)-2,4,6-trimethyl-benzene (B). **3** was coupled with 4-bromomethylcyclohexylmethanol using the same procedure as **A**, and the product was purified by recrystallization from hot petroleum ether (yield = 52%, mp = 110−111 °C).

^{1}H NMR (δ, ppm, CDCl$_3$): 0.9−2.0 (m, 10H, cyclohexane); 2.30 (s, 6H, Ar(**CH$_3$**)$_2$); 2.37 (s, 3H, Ar(**CH$_3$**)); 3.39 (s, 6H, ArCH$_2$O**CH$_3$**); 3.44−3.49 (m, 4H, **CH$_2$**-cyclohexyl); 4.46 (s, 4H, Ar**CH$_2$**OCH$_3$).

3-Bromomethyl-2,4,6-trimethylphenol (4). 30 mL of glacial acetic acid was added to the mixture of 4.0 g (29.4 mmol) of mesitol (**1**), 1.7 g (18.8 mmol) of trioxane, and 16.0 g (155.0 mmol) of NaBr followed by dropwise addition 5 mL of concentrated H$_2$SO$_4$. The mixture was stirred for 1 h at RT, and the contents were poured into 1.0 L of cold water. The precipitate formed was filtered, washed thoroughly with water, and dried under reduced pressure (yield = 92%, mp = 130 °C).

^{1}H NMR (δ, ppm, CDCl$_3$): 2.18−2.29 (m, 9H, Ar(**CH$_3$**)$_3$); 4.55 (s, 2H, Ar**CH$_2$**Br); 6.79 (s, 1H, Ar−**H**).

2,3,4,6-Tetramethylphenol (5). 1.0 g (4.3 mmol) of the compound **4** in 25 mL of dry ether was added dropwise to the mixture of 1.0 g (26.3 mmol) of LiAlH$_4$ in 50 mL of dry ether under a dry nitrogen atmosphere. The reaction mixture was stirred for 0.5 h at RT, and then the excess LiAlH$_4$ was destroyed with 10% (v/v) aqueous HCl. The ethereal layer was separated, washed with water, and dried over anhydrous Na$_2$SO$_4$. It was then concentrated and passed through silica gel column to obtain the product (yield = 77%, mp = 72−73 °C).

^{1}H NMR (δ, ppm, CDCl$_3$): 2.15−2.19 (m, 12H, Ar(**CH$_3$**)$_4$); 6.78 (s, 1H, Ar−**H**).

5-Methoxymethyl-2,3,4,6-tetramethylphenol (6). 60 mL of glacial acetic acid was taken along with 4.0 g (26.6 mmol) of **5**, 6.0 g (66.6 mmol) of trioxane, and 17.0 g (165.0 mmol) of NaBr in a round-bottom flask, and 10 mL of concentrated H$_2$SO$_4$ was added to it dropwise. The mixture was stirred for 12 h at RT, and the contents were poured into 1.0 L of cold water and filtered. The precipitate formed was washed thoroughly with water and dried under reduced pressure. 4.4 g (18.1 mmol) of the above bromomethylated product was dissolved in 60 mL of dry methanol and added dropwise to sodium methoxide solution (2.0 g, 86.9 mmol of sodium metal in 50 mL of dry methanol) under a N$_2$ atmosphere. The reaction mixture was refluxed for 13 h under a N$_2$ atmosphere and cooled to room temperature, and the methanol was removed using a rotary evaporator. 70 mL of cold water was added to the residue, and it was acidified with 50% HCl (v/v). The white precipitate formed was extracted with ether (100 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated. The crude product was distilled in a Kugelrohr at 150 °C/0.5 mm of Hg to yield the desired product (yield = 57%, mp = 62 °C).

^{1}H NMR (δ, ppm, CDCl$_3$): 2.23 (s, 6H, Ar(**CH$_3$**)$_2$); 2.29−2.30 (s, 6H, Ar(**CH$_3$**)$_2$); 3.45 (s, 3H, ArCH$_2$O**CH$_3$**); 4.51 (s, 2H, Ar**CH$_2$**OCH$_3$); 4.59 (s, 1H, ArO**H**).

1-(6-Hydroxyhexyloxy)-5-methoxymethyl-2,3,4,6-tetramethylbenzene (C). **6** was coupled with ω-bromohexanol using same procedure as **A**, and the product was purified by distillation using a Kugelrohr at 210 °C/0.5 mmHg (yield = 79%, mp = 48−49 °C).

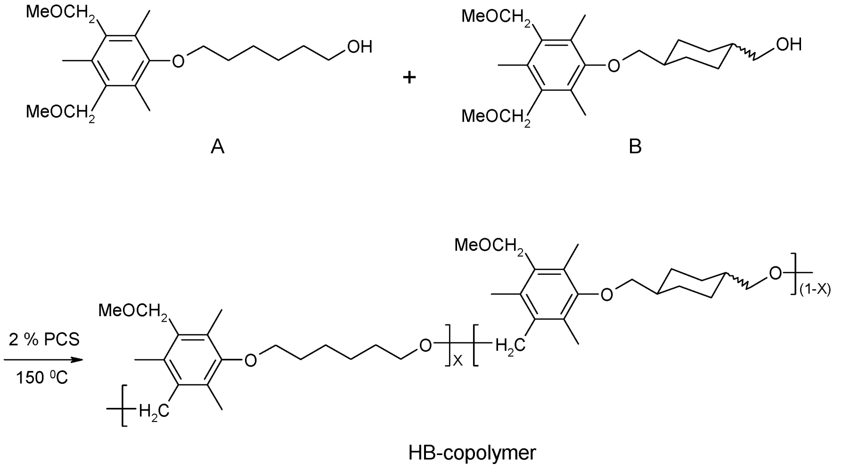
^{1}H NMR (δ, ppm, CDCl$_3$): 1.42−1.83 (m, 8H, ArOCH$_2$(**CH$_2$**)$_4$CH$_2$OH); 2.16−2.30 (m, 12H, Ar(**CH$_3$**)$_4$); 3.41 (s, 3H, ArCH$_2$O**CH$_3$**); 3.62−3.68 (m, 4H ArO**CH$_2$**(CH$_2$)$_4$**CH$_2$**OH); 4.46 (s, 2H, Ar**CH$_2$**OCH$_3$).

1-(4-Hydroxymethylcyclohexylmethoxy)-5-methoxymethyl-2,3,4,6-tetramethylbenzene (D). **6** was coupled with 4-bromomethylcyclohexylmethanol using the same procedure as for the alkylene series **A**, and the product was purified by recrystallization from hot petroleum ether (yield = 91%, mp = 62−64 °C).

^{1}H NMR (δ, ppm, CDCl$_3$): 0.9−2.03 (m, 10H, cyclohexane); 2.16−2.29 (m, 12H, Ar(**CH$_3$**)$_4$); 3.40 (s, 3H, ArCH$_2$O**CH$_3$**); 3.44−3.57 (m, 4H, **CH$_2$**-cyclohexyl); 4.46 (s, 2H, Ar**CH$_2$**OCH$_3$).

Typical Polymerization Procedure. Monomer **A** (600 mg, 1.8 mmol) along with 2 mol % of pyridinium camphorsulfonate (PCS) was placed in the test tube-shaped polymerization tube. It was degassed for 10 min and dipped into an oil bath at 110 °C under continuous N$_2$ purge to ensure homogeneous mixing of catalyst with monomer. The temperature of the oil bath was raised to 150 °C, and polymerization was carried out

Scheme 1. Synthesis of Hyperbranched Copolymers



under N$_2$ for 2 h with constant stirring. The polymerization tube was cooled to room temperature and connected to a Kugelrohr apparatus, in which the polymerization was continued for an additional 1 h at 150 °C under reduced pressure (0.1 Torr), with continuous mixing of the melt by rotation. The polymer was dissolved in THF, and the solution was neutralized with solid NaHCO$_3$ and filtered. The filtrate was concentrated and poured into methanol to obtain the polymer. Typical yields of the purified polymer ranged from 50 to 60%. All the copolymers, both linear and hyperbranched, were prepared using a similar procedure by taking the required mole fraction of the appropriate monomers. In the case of the linear copolymers, a slightly longer polymerization time (2 h under N$_2$ flow and 4−5 h under vacuum) was used to ensure formation of high molecular weight polymers. The copolymers were all purified by two dissolution−reprecipitation steps using THF−methanol.

Results and Discussion

Synthesis and Structural Characterization. The two AB$_2$ monomers, **A** and **B** (Scheme 1), were synthesized in good yields and purity by previously reported procedures starting from mesitol.[18] The spacer segments in these monomers, namely hexamethylene and 1,4-cyclohexyldimethylene, were chosen because their lengths are roughly the same. Also, the reactivities of the condensing functionalities during the polymerizations are expected to be nearly the same, and therefore the copolymers formed should be of a truly random nature. Additionally, the hyperbranched hompolymers prepared from these two monomers were reported to have T_g's of 1 and 77 °C, respectively,[18] thereby providing a large enough window to examine the variation in copolymer systems.

Polymerization of the AB$_2$ monomers proceeded under acid-catalyzed melt transetherification conditions,[22] with the exclusion of methanol. The underlying mechanism for the transetherification process relies on the facile generation of the benzylic carbocationic intermediate under the acid-catalyzed conditions. Therefore, the three methyl groups on the benzene ring of the monomer are essential to prevent cross-linking that can occur via an electrophilc aromatic substitution.[22a] The ^{1}H NMR spectra of the two monomers are shown in Figure 1, along with that of one representative copolymer. Upon polymerization the relative intensity of methoxy protons

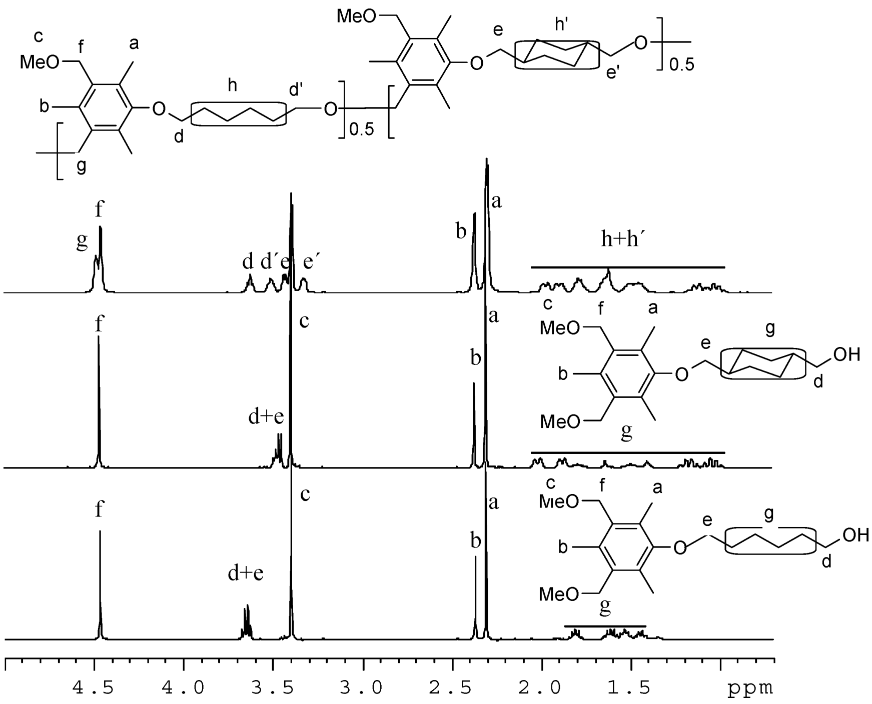


Figure 1. ^{1}H NMR spectra of the two monomers, **A** and **B**, along with that of a representative copolymer.

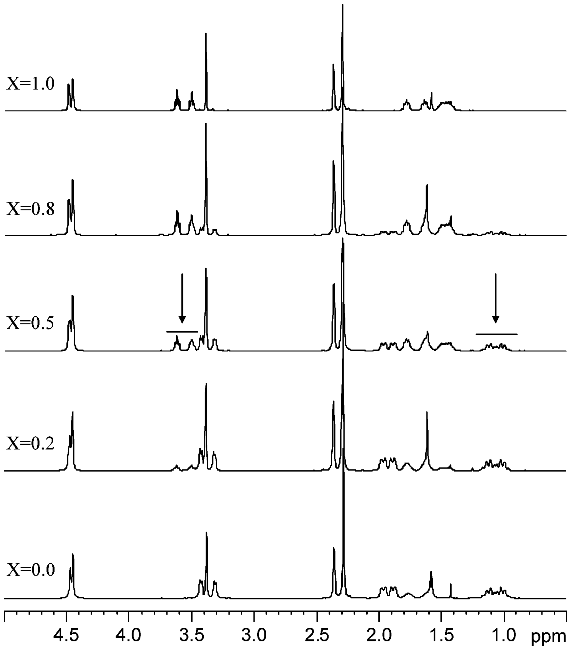


Figure 2. ^{1}H NMR spectra of all the hyperbranched copolymers (**HP1** to **HP5**). The weight fraction of the comonomer with hexylene spacer (A) systematically varied from 0.0 to 1.0. The regions indicated arrows were used for the determination of copolymer composition.

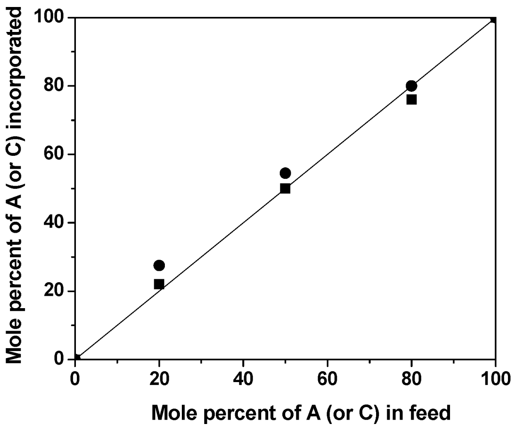
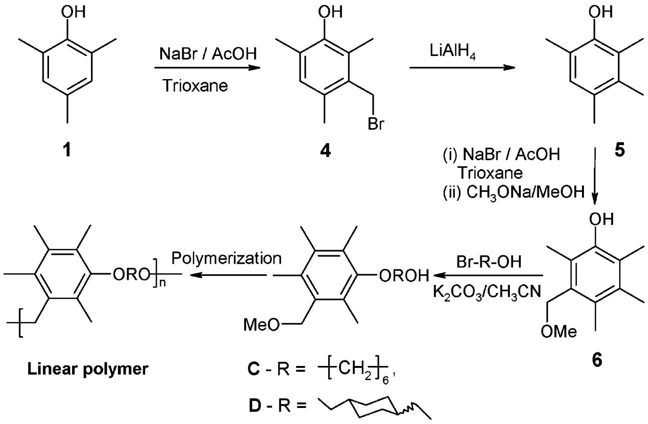


Figure 3. Feed vs incorporation of **A** or **C** (from ^{1}H NMR) plot of hyperbranched (■) and linear (●) copolymers. Solid line represents the variation for ideal copolymerization.

Scheme 2. Synthesis of Analogous Linear AB-Type Monomer and Copolymers



(CH_3OCH_2− ~3.4 ppm) decreases to nearly half its original value, confirming that the condensation has proceeded to high conversion. In further confirmation of this, the benzylic proton peaks (~4.5 ppm) split into two peaks of equal intensity upon polymer formation: one belonging to CH_3OCH_2− and the other to the −R−OCH_2− unit along the polymer backbone. The degree of branching in this homopolymer was calculated to be about 0.54,[23] in near accordance with the theoretically expected value of 0.5. Furthermore, the alkoxymethylene units of the spacer segment (−OCH_2− and −CH_2-OH), which are not well-resolved in both the monomers, separate into two sets of peaks each (in the region 3.3−3.7 ppm) upon polymerization, giving rise to four clusters of peaks of roughly equal intensity in the 1:1 copolymer.

The stack plot of the ^{1}H NMR spectra of the hyperbranched copolymers with varying composition along with those of the two homopolymers is shown in Figure 2. It is evident from this figure that the compositional variation is clearly reflected by the increase in the relative intensities of the peaks corresponding to the two kinds of repeat units. The most uncluttered and comonomer-specific regions in the spectra are the region between 0.9 and 1.2 ppm due to the four axial protons of the cyclohexyl ring of monomer **B**[24] and the two sets of oxymethylene proton peaks of the spacer of monomer **A** in the region 3.5−3.7 ppm, each representing two protons (see Figure 1). The composition of the copolymers was thus readily calculated using the relative intensities of the peaks in these two regions, and a plot of the copolymer vs feed composition is shown in Figure 3. The excellent straight-line fit with a slope of nearly one confirms the equal reactivity of the two monomers toward the condensation process. This in turn also ensures that the copolymers formed are statistically random in nature. As mentioned earlier, one important feature of these hyperbranched copolymers is the near identical lengths of the spacer segment in the two repeat units; in both cases they are six carbon atoms long with the exception that in monomer **B** four of the carbons are an integral part of a cyclohexane ring.

To compare the variation of properties of hyperbranched copolymers, it is essential to ensure that while one structural parameter is varied the others must remain constant. Thus, in this case, while the flexibility of the spacer in the two repeat units are different, the branching density (defined as the number of branch points per unit volume) remains roughly constant. In our earlier paper, we had shown that the conformational compactness, as reflected by the Mark−Howink exponent, is roughly the same for the homopolymers prepared from both these monomers.[18]

To compare the variation of properties in hyperbranched copolymers with those in analogous linear systems, a series of linear copolymers were also prepared (Scheme 2). The AB-type monomers[25] **C** and **D** were prepared from the same starting material—mesitol—but by carrying out a selective mono-bromomethylation followed by reduction to yield the tetramethylphenol. A second bromomethylation step followed by conversion to the corresponding methoxymethyl derivative was carried out as described previously to yield the premonomer intermediate. Coupling this intermediate with the appropriate bromoalcohol resulted in the two desired monomers (Scheme 2).

The homopolymers and the various copolymers, using monomers **C** and **D**, were prepared using the same acid-catalyzed melt-transetherification methodology to yield polymers of moderate molecular weights (see Table 1).

Table 1. Molecular Weights of the Hyperbranched and Linear Copolymers along with Their Corresponding Glass Transition Temperatures (T_g)

copolymers	content of **A** or **C** (mol %)	M_w[a]	PDI	T_g (°C)
HP-1	0	28 300	2.1	77
HP-2	20	22 600	2.5	57
HP-3	50	40 200	2.2	35
HP-4	80	32 300	2.1	15
HP-5	100	51 100	2.5	1
P-1	0	16 000	3.0	95
P-2	20	10 100	2.4	70
P-3	50	13 200	2.4	45
P-4	80	18 600	2.4	23
P-5	100	39 600	5.1[b]	9

[a] Determined using universal calibration plot constructed from refractive index (RI) and viscometry (DV) detector signals. [b] The unusually high value in this case could be due to the inadvertent formation of cyclics and/or due to physical inhomogeneities during the polymerization.

The ^{1}H NMR spectra of the homopolymers and the copolymers are given in Figure 4. As in the case of the hyperbranched copolymers, here again the peaks in the same two regions (indicated by an arrow) could be used to calculate the copolymer composition. However, in this case a small peak to the left of the two sets of peaks around ca. 3.6 ppm is seen even in the homopolymer prepared from **D**. This is ascribed to the cis isomer in the starting cyclohexane dimethanol, which is present to the tune of about 20 mol %. This peak adds to the intensity of one of the peaks due to the comonomer **C** and hence complicates the calculation of the composition. As an alternate approach, the relative intensities of the peak in the region 0.9−1.2 ppm was compared with the single peak at 4.5 ppm, which is due to the benzylic protons belonging to both the repeat units. A plot of the variation of the copolymer composition, thus obtained, with the feed composition in this case also is seen to follow the expected linear variation with a slope of nearly one (see Figure 3), once again confirming the randomness of the copolymers formed.

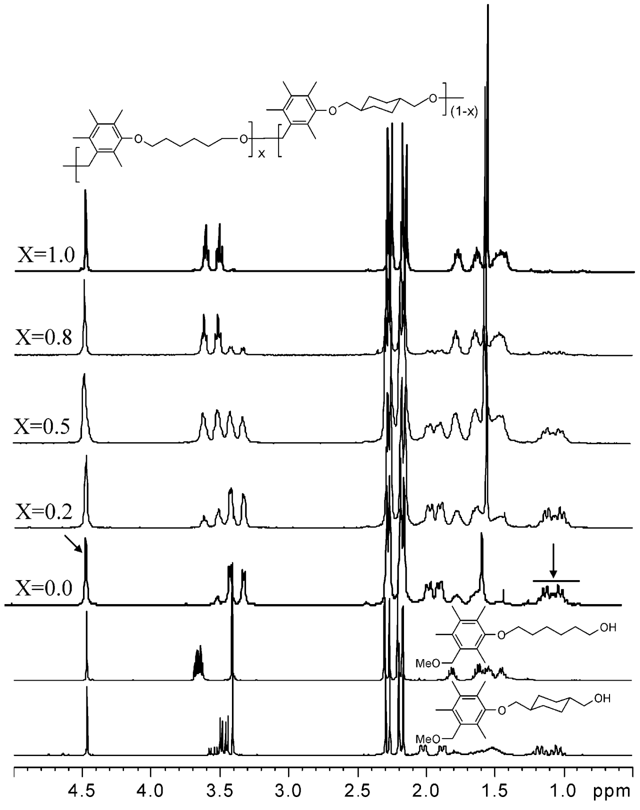


Figure 4. ^{1}H NMR spectra of the two monomers, **C** and **D**, along with that of copolymers (**P1** to **P5**). The region indicated by the arrow was used for determination of copolymer composition.

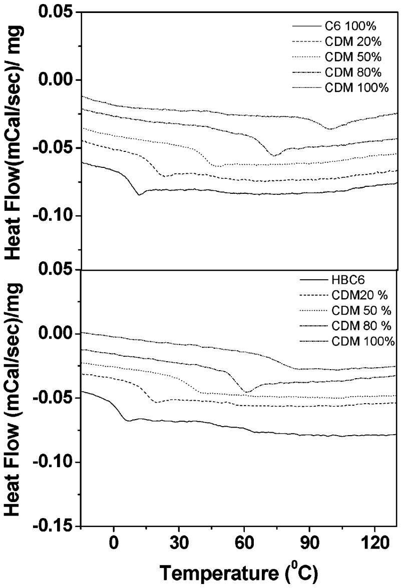


Figure 5. DSC thermograms of hyperbranched copolymer (bottom) and linear (top) copolymers.

Molecular Weights and Thermal Properties. The molecular weights of the polymers were determined by GPC using a dual detector system, consisting of a refractive index (RI) and a differential viscometric (DV) detector connected in series. The absolute molecular weights of all the polymers were determined by the universal calibration curve[26] and were found to be reasonably high, with M_w values ranging from 22 600 to 51 000, as shown in Table 1. These molecular weights are adequately high to ensure that the properties, such as T_g, will have become almost invariant with molecular weight. In a recent study, we showed that the T_g values of hyperbranched polymers begin to level off beyond M_w values of about 9000.[18] Similar observations have also been made in the case of dendrimers.[27]

The DSC thermograms of the copolymers are shown in Figure 5. All the copolymers are completely amorphous and exhibit only a single T_g and no melting transition. It is evident that the T_g varied continuously with composition in both hyperbranched copolymers as well as the linear copolymers. The variation of the T_g of copolymers, in general, has been fitted to a variety of equations, such as the Gordon−Taylor equation,[28] Gibbs−Di Marzio equation,[29] etc., most of which are formulated based on the assumption that the copolymer can be treated as if it were a mixture of small molecules that follows ideal mixing (without contraction or expansion) behavior.[30] The Gordon−Taylor equation can be expressed as follows

$$T_g(\text{copolymer}) = \frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2}$$

where T_g is the glass transition temperature of the copolymer, T_{g1} and T_{g2} are the glass transition temperatures of the two homopolymers, and w_1 and w_2 are the weight fractions of the two repeat units in the copoly-

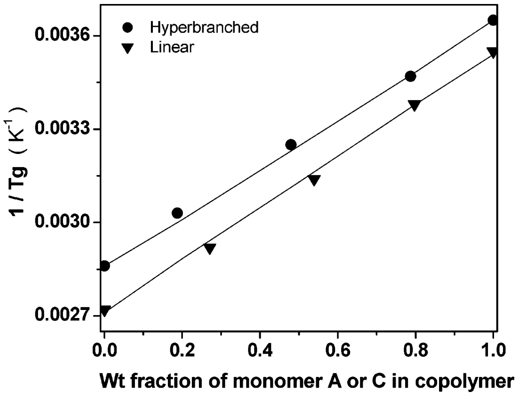


Figure 6. Variation of T_g of hyperbranched (●) and (▼) linear copolymers as a function of composition. The solid line indicates the T_g calculated from the Fox equation.

mer. The constant $K = (\rho_1/\rho_2)(\Delta\alpha_2/\Delta\alpha_1)$, where ρ_i are the densities and $\Delta\alpha_i$ the increment of the expansion coefficient at T_g. Assuming that the densities of both the homopolymers are very similar, i.e., $\rho_1/\rho_2 = 1$, the Gordon−Taylor constant K becomes equal to T_{g1}/T_{g2} under the Simha−Boyer approximation,[31] i.e., $\Delta\alpha T_g = 0.113$. Thus, the above G−T equation transforms to the more popular Fox equation[32]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

A plot of $1/T_g$ vs w_1 for the hyperbranched copolymers is shown in Figure 6. It is clear that the variation closely follows the expected behavior according to the Fox equation, which is represented by the straight line linking the two homopolymer T_g's. A similar behavior is also exhibited by the analogous linear copolymers, although the line is shifted slightly reflecting their consistently higher T_g values when compared to the hyperbranched systems. The consistently lower T_g values of the hyperbranched copolymers is probably a reflection of the absence of chain entanglement and/or due to the large number of end groups in them. The remarkable agreement with the Fox equation demonstrates its robustness and confirms its validity and usefulness even for of highly branched copolymer systems. It may be added here that we have carefully chosen the two monomers, such that they have similar branching densities. However, when two monomers, which generate hyperbranched polymers with different branching densities and/or different types of terminal functionality, are copolymerized, the resulting copolymers may exhibit T_g's that differ from this expected behavior.

Conclusions

The present study primarily attempts to address the question: Do hyperbranched copolymers obey the Fox equation? To do so, representative hyperbranched copolyethers utilizing two different AB_2-type monomers that incorporate spacer segments of different flexibility but of similar lengths were prepared by a melt transetherification strategy. One of the monomers contain a flexible hexamethylene spacer while the other one has a cyclohexyldimethylene spacer: the former yielded a homopolymer with a T_g of 1 °C, while the latter yielded one with a T_g of 77 °C. For comparison, analogous linear copolymers containing the same two spacer segments were also prepared from the appropriate AB-type monomers. The structures of all the copolymers were confirmed by ^{1}H NMR spectroscopy, and their molecular weights were found to be moderately high by GPC measurements. The glass transition temperatures of both the hyperbranched and the linear counterparts were found to vary in complete accordance with the Fox equation, which has generally been applied only to linear copolymers. It was, however, noticed that the hyperbranched copolymers had consistently lower values of T_g compared to their linear analogues. This difference is probably due to the absence of chain entanglements and/or due to the presence of a very large number of end groups in hyperbranched polymers. Importantly, this study also confirms the applicability of Fox equation to very highly branched copolymers, provided that their branching density, as defined by the number of branches per unit volume, is maintained constant. However, under conditions wherein other molecular structural parameters, such as the nature of the end groups or the degree of branching, also vary with copolymer composition, such a correlation may be less straightforward. Further studies are needed to probe the limits of the applicability of the Fox equation to hyperbranched copolymers.

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(24) This was confirmed from the relative intensities of this set of peaks in the homopolymer spectrum.

(25) The meta-linked AB-type monomers were chosen because of their greater molecular similarity to the hyperbranched polymer, with regard to the connectivity along the polymer backbone, except that they are devoid of branching. Furthermore, they were also synthetically easily accessible.

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