Glass Transition Behavior of Dendritic Polymers Containing Mobile Aliphatic Polyether Cores and Glassy Peripheral Polystyrenes

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We investigated the glass transition temperatures (T_g) of dendrons consisting of conformationally mobile aliphatic polyether dendritic cores plus glassy peripheral polystyrenes (PSs), and linear PSs in the molecular weight range of 1000-8500 g/mol. We compared their T_g behavior depending on their polymeric architecture. The linear PSs show a typical growth of T_g up to 92.5 °C as the molecular weight increases to 8300 g/mol, while the dendrons display nearly constant T_g values of 58-61 °C, despite the increase of molecular weight with each generation. The striking contrast of T_g behavior would be mainly attributed to the fact that the dendrons keep the ratio of N_e/M (N_e: number of peripheral chain ends, M: molecular weight) over all the generations. Additionally, for the influence of dendritic spacers on glass transition temperature we prepared dimeric PSs with different linkage groups such as aliphatic ether, ester and amide bonds. We found that the dimer with the ether spacer exhibited the lowest glass transition at 55.4 °C, while the amide linked dimer showed the highest glass transition temperature at 74.2 °C. This indicates that the peripheral PS chains are effectively decoupled by the conformationally flexible ether spacer. The results from this study demonstrated that polymeric architecture and dendritic core structures play a crucial role in the determination of glass transition behavior, providing a strategy for the systematic engineering of polymer chain mobility.

Key Words : Dendrons, Polystyrene, Glass transition temperature

Introduction

Glass transition is a fundamental characteristic of amorphous polymers. As this transition temperature (T_g) is reached, the polymer chains undergo greater segmental movement, accompanied by long-range molecular motion. At glass transition temperature, the motional variation in the molecular level leads to dramatic changes of the polymer's mechanical and thermal properties. Thus, T_g is an important parameter for polymer processing. Many variables, such as chemical composition, stereochemistry, molecular weight etc. have been known to influence the T_g of polymers.

Meanwhile, variation of macromolecular chain architecture has been a versatile tool to modify polymer properties. Particularly, branched polymers have been studied as a counterpart to linear polymers to identify significantly distinct physical behavior.[1,2] As representative branched examples, dendrimers and dendrons (sections of dendrimers)[3] have well-defined chain structures with low molecular weight distributions, and therefore can be ideal models to study the correlation between chain architecture and physical properties.

To date, various types of dendrimers and dendrons have been reported. They have benzyl ether,[4,5] aryl ester,[6] phenylene,[7] and ether ketone[8] etc. as their branching units. As peripheral end groups, most dendrimers/dendrons consist of either small functional groups such as benzyl, cyanide and bromide, or crystalline alkyl groups.[9,10] It is well-known that the end groups make relatively little contribution to the glass transition in comparison to the dendritic backbone, although the more polar units somewhat increase glass transition. On the other hand, their glass transitions are strongly dependent upon the type of branching units and their generation number. This was experimentally demonstrated in previous publications.[9,11] It is important to note that the T_gs increase with each generation.

Meanwhile, we have recently prepared a different type of dendron molecules from 1st to 3rd generation.[12] The dendrons consist of "flexible aliphatic polyether dendritic cores" and "glassy polystyrene peripheries" that have not been employed before. The unique structural features different from the above mentioned dendritic polymers are: i). a more flexible branching unit, and ii). less flexible peripheral end groups. The structural unit of the aliphatic dendritic core is $CH_2CH(CH_2O)_2$ which is almost identical to a doubled poly(ethylene oxide) structural unit: $2\times(CH_2CH_2O)$.[10,13] Since poly(ethylene oxide) (PEO) is one of the most flexible polymers, the homologous PEO-like dendritic core should have comparable flexibility. Indeed, a dendron with the identical core structure and hydroxyl peripheral groups was reported to be liquid at ambient temperature in a previous publication.[14] In contrast to the flexible dendritic core, the peripheral ends consist of a glassy polystyrene with the oligomeric molecular weight of 1000 g/mol, whose T_g was detected to be 41.4 °C. Due to this particular composition, the glass transition temperature of our dendron system is mainly dominated by the peripheral glassy PS chains, which is its key differentiator to the aforementioned dendritic systems.

In this context, the goal of this paper is to investigate the glass transition behavior in the aliphatic polyether dendrons with glassy peripheral chains. First of all, we investigate the dependence of glass transition upon molecular weight (here, equally regarded as generation number), and compare this to that of linear homo PS chains. Through the investigation we verify the correlation between T_g and chain architecture. In addition, we survey the role of the dendritic core (*i.e.* spacers) in the determination of T_g.

Experimental Section

Characterization. ^1H NMR spectra were recorded from $CDCl_3$ solutions on a Varian 200 spectrometer. The purity of the products was checked by thin-layer chromatography (TLC; Merck, silica gel 60). A Perkin Elmer DSC-7 differential scanning calorimeter equipped with a 1020 thermal analysis controller was used to determine the glass transition temperatures, which were reported as the half-way position of the transition heat flow. In all cases, the heating rate was 10 °C/min. Gel permeation chromatography (GPC) measurements were carried out in THF and Waters R401 instruments equipped with Stragel HR 2, 3 and 4 columns at a flow rate of 1.0 mL/min.

Materials. 1,4-Dibromobutane (99%), sodium azide (≥99.5%), 4-dimethylaminopyridine (DMAP, 99%), *N,N'*-diisopropylcarbodiimide (DIPC, 99%), and succinic anhydride (97%) were purchased from Sigma-Aldrich Chemical Co. 4-Toluenesulfonyl chloride (98%) was purchased from JunseiChemical Co. Ltd. Sodium hydride (min. 55%) was purchased from Kanto Chemical Co., Inc. Dimethylformamide (DMF), dichloromethane (DCM), and NEt_3 were distilled from CaH_2. Tetrahydrofuran (THF) was distilled from sodium metal.

Synthesis. The synthesis of dendrons (**Generation-n**) was carried out *via* a convergent synthetic method consisting of a Williamson etherification and hydroboration/oxidation reactions as chain growth and activation steps, respectively.[15] The synthetic details of **Generation-n** and linear polymers (**PS-n**) were already described in a previous publication.[12] The synthetic route of dimeric polystyrenes with various spacer groups is outlined in Scheme 2.

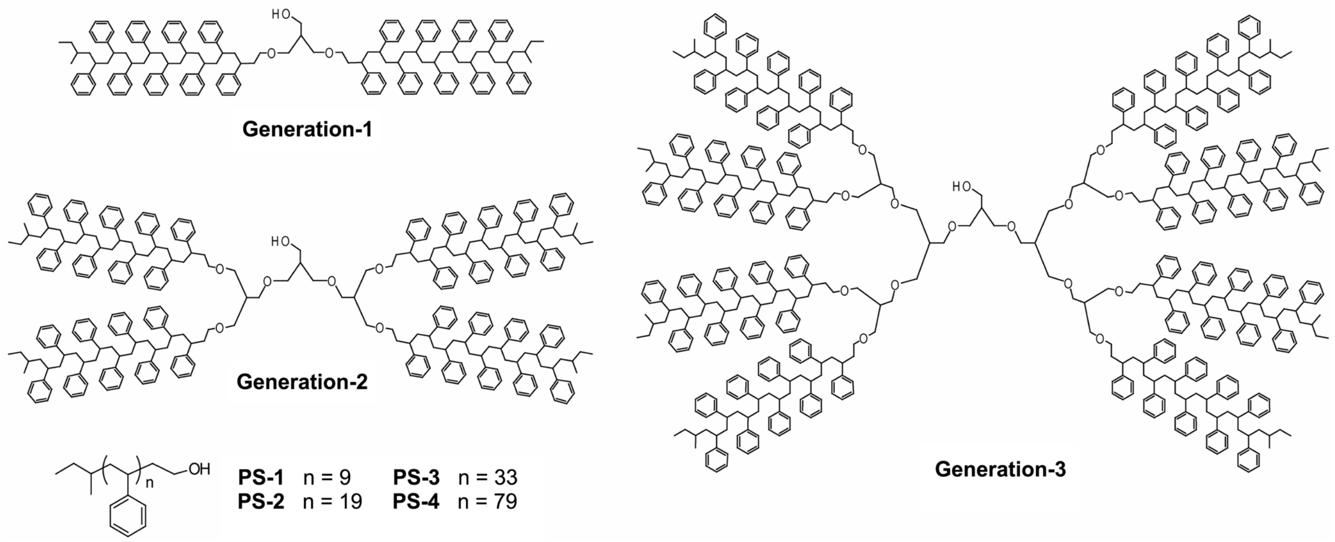
Synthesis of PS-ether-PS. PS-1 (1.1 g, 1.157 mmol, 2.5 eq.), NaH (500 mg, 4.63 mmol, 10 eq.), and 1,4-dibromobutane (100 mg, 0.463 mmol, 1.0 eq.) were dissolved in 10 mL of THF/DMF (1:1 volume ratio) solvent mixture. The mixture was heated at reflux for 48 hours under an N_2 atmosphere. After cooling to room temperature, the solution was concentrated and dissolved with dichloromethane (100 mL), then washed with deionized water (3×150 mL), and dried over $MgSO_4$. The resulting solid was purified by column chromatography (from hexane:CH_2Cl_2 = 3 : 7, silica) to yield 0.1 g (11%) of a light yellow glassy solid. ^1H NMR (200 MHz, $CDCl_3$) δ 7.38-6.36 (br, Ar-H), 3.23-2.86 (br, $\text{-}CH_2CH_2OCH_2CH_2\text{-}$), 2.53-1.90 (br, C$H$ of the polystyrene backbone; $\text{-}CH_2CH_2OCH_2CH_2\text{-}$), 1.90-1.31 (br, C$H_2$ of the polystyrene backbone), 1.30-0.53 (br, -CH(phenyl)$CH_2CH(CH_2CH_3)CH_3$); TLC (eluent; Hexane/CH_2Cl_2 = 3:7) R_f 0.36.

Synthesis of PS-ester-acid. PS-1 (192 mg, 0.202 mmol, 1.0 eq.), succinic anhydride (61 mg, 0.606 mmol, 3.0 eq.) and DMAP (99 mg, 0.808 mmol, 4.0 eq.) were dissolved in 2 mL of THF. The mixture was stirred at ambient temperature for 20 hours under an N_2 atmosphere. The solution was concentrated and dissolved with dichloromethane (10 mL), then washed with deionized water (3×10 mL), and dried over $MgSO_4$. The resulting solid was purified by column chromatography (from CH_2Cl_2:ether = 7:3, silica) to yield 140 mg (66%) of a colorless glassy solid. ^1H NMR (200 MHz, $CDCl_3$) δ 7.38-6.36 (br, Ar-H), 3.87-3.54 (br, $\text{-}CH_2CH_2OCOCH_2CH_2COOH$), 2.53-1.90 (br, C$H$ of the polystyrene backbone; $\text{-}CH_2CH_2OCOCH_2CH_2COOH$), 1.90-1.31 (br, C$H_2$ of the polystyrene backbone), 1.30-0.53 (br, CH(phenyl)$CH_2CH(CH_2CH_3)CH_3$); TLC (eluent; CH_2Cl_2/ether = 7 : 3) R_f 0.70.

Synthesis of PS-ester-PS. PS-ester-acid (140 mg, 0.133 mmol, 1.1 eq.), **PS-1** (115 mg, 0.121 mmol, 1.0 eq.), DIPC (61 mg, 0.484 mmol, 4.0 eq.) and DMAP (30 mg, 0.242 mmol, 2.0 eq) were dissolved in 2 mL of dichloromethane. The mixture was stirred at ambient temperature for 15 hours under an N_2 atmosphere, then the solution was diluted with dichloromethane and washed with deionized water (3×10 mL), and dried over $MgSO_4$. The resulting solid was purified by column chromatography (from hexane:CH_2Cl_2 = 2:8, silica) to yield 120 mg (50%) of a colorless glassy solid. ^1H NMR (200 MHz, $CDCl_3$) δ 7.38-6.36 (br, Ar-H), 3.87-3.54 (br, $\text{-}CH_2CH_2OCOCH_2CH_2COOCH_2CH_2\text{-}$), 2.53-1.90 (br, C$H$ of the polystyrene backbone; $\text{-}CH_2CH_2OCOCH_2CH_2COOCH_2CH_2\text{-}$),), 1.90-1.31 (br, C$H_2$ of the polystyrene backbone; $\text{-}CH_2CH_2OCOCH_2CH_2COOCH_2CH_2\text{-}$), 1.30-0.53 (br, CH(phenyl)$CH_2CH(CH_2CH_3)CH_3$); TLC (eluent; hexane: CH_2Cl_2 = 4 : 6) R_f 0.34.

Synthesis of PS-OTs. PS-1 (0.97 g, 1.02 mmol, 1.0 eq.), 4-toluene sulfonyl chloride (1.0 g, 5.1 mmol, 5 eq.), and pyridine (40 mg, 5.1 mmol, 5.0 eq.) were dissolved in 7 mL of dichloromethane. The mixture was stirred at ambient temperature for 24 hours under an N_2 atmosphere. The solution was diluted with dichloromethane and then washed with deionized water (3×30 mL), and dried over $MgSO_4$. The resulting solid was purified by column chromatography (from hexane : CH_2Cl_2 = 6 : 4 to 5 : 5, silica) to yield 0.9 g (80%) of a colorless glassy solid. ^1H NMR (200 MHz, $CDCl_3$) δ 7.38-6.36 (br, Ar-H), 3.83-3.45 (br, $\text{-}CH_2CH_2OTs$), 2.61-1.90 (br, CH of the polystyrene backbone; $\text{-}CH_2CH_2O$-Ts), 1.90-1.31 (br, CH_2 of the polystyrene backbone), 1.30-0.53 (br, -CH(phenyl)$CH_2CH(CH_2CH_3)CH_3$); TLC (eluent; Hexane/CH_2Cl_2 = 1 : 1) R_f 0.53.

Synthesis of PS-N_3. PS-OTs (0.84 g, 0.76 mmol, 1.0 eq.) and sodium azide (0.5 g, 7.6 mmol, 10 eq.) were dissolved in 4 mL of DMF. The mixture was heated at 110 °C for 48 hours under an N_2 atmosphere. After cooling to room temperature, the solution was concentrated and dissolved with dichloromethane (20 mL), then washed with deionized water (1×40 mL), and dried over $MgSO_4$. The resulting solid was purified by column chromatography (from hexane: CH_2Cl_2 = 1 : 1, silica) to yield 0.7 g (94.6%) of a light yellow



Scheme 1. Molecular structures of **Generation-n** and **PS-n**.

glassy solid. ^{1}H NMR (200 MHz, CDCl_3) δ 7.38-6.36 (br, Ar-*H*), 3.12-2.69 (br, $\text{-CH}_2\text{C}\mathit{H}_2\text{N}_3$), 2.61-1.90 (br, C*H* of the polystyrene backbone; $\text{-C}\mathit{H}_2\text{CH}_2\text{N}_3$), 1.90-1.31 (br, $\text{C}\mathit{H}_2$ of the polystyrene backbone), 1.30-0.53 (br, -CH(phenyl)-$\text{C}\mathit{H}_2\text{C}\mathit{H}(\text{C}\mathit{H}_2\text{C}\mathit{H}_3)\text{C}\mathit{H}_3$); TLC (eluent; Hexane/$\text{CH}_2\text{Cl}_2$ = 1 : 1) R_f 0.73.

Synthesis of PS-NH$_2$. PS-N$_3$ (0.68 g, 0.69 mmol, 1.0 eq.) and LiAlH_4 (432 mg, 10.5 mmol, 15 eq.) were dissolved in 4 mL of THF. The mixture was stirred at ambient temperature for 2 days. The solution was diluted with dichloromethane (15 mL) then quenched with deionized water (10 mL), and then extracted. The solution was concentrated to yield 0.63 g (95.5%) of a colorless solid. ^{1}H NMR (200 MHz, CDCl_3) δ 7.38-6.36 (br, Ar-*H*), 2.61-1.90 (br, C*H* of the polystyrene backbone; $\text{-C}\mathit{H}_2\text{C}\mathit{H}_2\text{N}_3$), 1.90-1.31 (br, $\text{C}\mathit{H}_2$ of the polystyrene backbone), 1.30-0.53 (br, -CH(phenyl)$\text{C}\mathit{H}_2\text{C}\mathit{H}$-($\text{C}\mathit{H}_2\text{C}\mathit{H}_3)\text{C}\mathit{H}_3$); TLC (eluent; CH_2Cl_2 / ether = 1 : 1) R_f 0.73.

Synthesis of PS-amide-acid. PS-NH$_2$ (247 mg, 0.26 mmol, 1.0 eq) and succinic anhydride (90 mg, 0.78 mmol, 3.0 eq) were dissolved in 2 mL of THF. The mixture was stirred at ambient temperature for 24 hours under an N_2 atmosphere. The solution was diluted with dichloromethane and then washed with deionized water (3 × 10 mL), and dried over MgSO_4. The resulting solid was purified by column chromatography (from CH_2Cl_2 : ether = 1 : 1, silica) to yield 102 mg (36.6%) of a colorless glassy solid. ^{1}H NMR (200 MHz, CDCl_3) δ 7.38-6.36 (br, Ar-*H*), 5.19-4.95 (br, $\text{-CH}_2\text{CH}_2\text{N}\mathit{H}\text{COCH}_2\text{CH}_2\text{COOH}$), 3.12-2.74 ($\text{-CH}_2\text{C}\mathit{H}_2\text{NH-COCH}_2\text{CH}_2\text{COOH}$), 2.61-1.90 (br, C*H* of the polystyrene backbone; $\text{-CH}_2\text{CH}_2\text{NHCOC}\mathit{H}_2\text{C}\mathit{H}_2\text{COOH}$), 1.90-1.31 (br, $\text{C}\mathit{H}_2$ of the polystyrene backbone), 1.30-0.53 (br, -CH(phenyl)-$\text{C}\mathit{H}_2\text{C}\mathit{H}(\text{C}\mathit{H}_2\text{C}\mathit{H}_3)\text{C}\mathit{H}_3$); TLC (eluent; CH_2Cl_2/ether = 1 : 1) R_f 0.56.

Synthesis of PS-amide-PS. PS-amide-acid (95 mg, 0.09 mmol, 1.0 eq.), **PS-NH$_2$** (112 mg, 0.117 mmol, 1.3 eq.), DIPC (45.4 mg, 0.36 mmol, 4.0 eq.) and DMAP (22 mg, 0.18 mmol, 2.0 eq.) were dissolved in 2 mL of dichloromethane. The mixture was stirred at ambient temperature for 24 hours under an N_2 atmosphere, then the solution was diluted with dichloromethane and washed with deionized water (3 × 10 mL), and dried over MgSO_4. The resulting solid was purified by column chromatography (from CH_2Cl_2 : ether = 19 : 1, silica) to yield 80 mg (45%) of a colorless glassy solid. ^{1}H NMR (200 MHz, CDCl_3) δ 7.38-6.36 (br, Ar-*H*), 5.45-5.24 (br, $\text{-CH}_2\text{CH}_2\text{N}\mathit{H}\text{COCH}_2\text{CH}_2\text{CON}\mathit{H}\text{CH}_2\text{-CH}_2\text{-}$), 3.05-2.58 (br, $\text{-CH}_2\text{C}\mathit{H}_2\text{NHCOCH}_2\text{CH}_2\text{CONHC}\mathit{H}_2\text{-CH}_2\text{-}$), 2.61-1.90 (br, C*H* of the polystyrene backbone; $\text{-CH}_2\text{CH}_2\text{NHCOC}\mathit{H}_2\text{C}\mathit{H}_2\text{CONH CH}_2\text{CH}_2\text{-}$), 1.90-1.31 (br, $\text{C}\mathit{H}_2$ of the polystyrene backbone), 1.30-0.53 (br, -CH-(phenyl)$\text{C}\mathit{H}_2\text{C}\mathit{H}(\text{C}\mathit{H}_2\text{C}\mathit{H}_3)\text{C}\mathit{H}_3$); TLC (eluent; CH_2Cl_2/ether = 1 : 1) R_f 0.56.

Results and Discussion

The design of the dendrons (**Generation-n**) in this study focused on the construction of an aliphatic polyether dendritic core surrounded by glassy polystyrene peripheries (Scheme 1). In contrast to other dendritic polymers having either small end groups or crystalline alkyl chains, the unique structural feature of this dendron system is that the peripheral ends are composed of glassy PS chains. With respect to the conformational freedom, the PS chains are less flexible than the PEO-like dendritic core structure. To this end, the glass transition behavior of the dendrons would be expected to be mainly dominated by the peripheral PS chains. This is in great contrast to the conventional dendritic polymers whose glass transitions are mainly influenced by their dendritic core backbones.

The synthesis of the dendron molecules was performed *via* a convergent route consisting of a Williamson etherification and hydroboration/oxidation reactions as chain growth and activation steps, respectively. The synthetic details and characterization have been described elsewhere.[12] The reason for adopting the PS chain with an oligomeric molecular weight of 1000 g/mol as peripheral ends was for the ease of monitoring of the T_g dependent upon the generation variation. If a high molecular weight PS whose T_g levels off had been chosen, it would have been difficult to observe the T_g change.

In addition, in order to understand the dependence of T_g upon chain architecture and dendritic core spacers, we have prepared linear PS chains by a conventional anionic polymerization method. The linear PS chains (**PS-n**) have molecular weights of 2100, 3500 and 8300 g/mol. These values are approximately comparable to the molecular weights of the dendron molecules, and are thus suitable for comparative study of T_g upon chain architecture. The glass transition temperatures of the dendrons and linear PS chains were investigated by differential scanning calorimetry (DSC) experiments. The heating and cooling rates were at 10 °C/min, and glass transitions were defined as the half-way position of the transition heat flow. The obtained glass transition temperatures are summarized in Table 1.

Prior to the investigation of **Generation-n**, for the chain architectural comparison we determined values for T_g for **PS-n**. In Figures 1 and 3, the glass transitions of **PS-n** increase gradually from 41.4 up to 92.3 °C when moving from **PS-1** to **PS-4**. This is the typical T_g trend upon molecular weight in conventional amorphous linear polymers.[17] On the other hand, the dendrons show a significantly different T_g behavior. The glass transitions of all the dendrons fall within the narrow temperature range of 58-61 °C, although the overall mass of polystyrenes increases with each generation (Figures 2 and 3). Consequently, the glass transition temperature in our dendron system remains constant regardless of generation number. Here, we may consider several factors which influence T_g. For linear polystyrenes, the minimum molecular weight where chain entanglement occurs is known to be 18,700 g/mol. Therefore, this effect can be ruled out in the interpretation.[18]

Meanwhile, a chain end free volume theory can be applied.[9] The related equation is shown in (Eq. 1).

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

where K is a constant related to density, free volume expansion coefficient, the nature of the end group, and T_g is the glass transition temperature at infinite molecular weight.

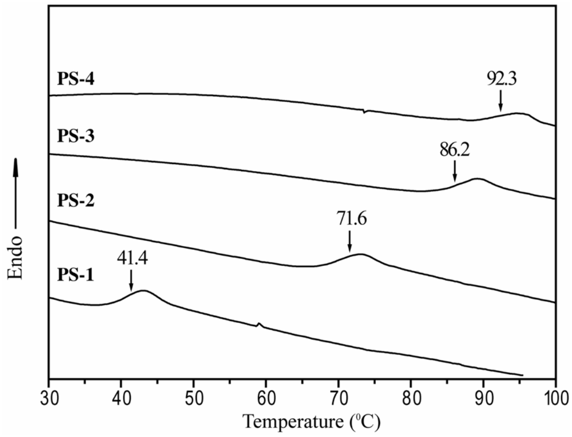


Figure 1. DSC thermograms of **PS-n**.

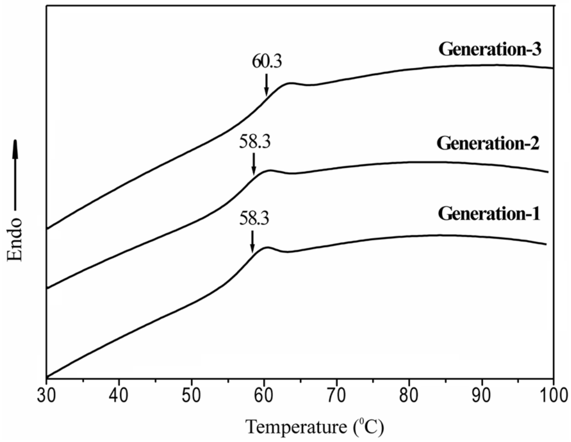


Figure 2. DSC thermograms of **Generation-n**.

In the above equation, N_e and M are designated as the number of chain ends and molecular weight, respectively. Since a chain end has a certain degree of extra mobility, the free volume assigned to the chain end is greater than that of the chain middle. Therefore, T_g would be lowered as the number of chain ends increases. In this regard, the ratio of N_e/M becomes an important parameter to determine the overall chain mobility associated with T_g. In the linear PS chains, N_e is a value of two over all the **PS-n**, thus T_g is increasing proportional to the molecular weight (M). On the other hand, in the dendron series both number of chain ends and molecular weight increase equivalently by a factor of 2 from generation to generation. Therefore, the ratio of N_e/M remains constant over all the generations. As a consequence, the glass temperature is hardly changed.

To better fit the observed T_g data to the above approach, we excluded the hydroxyl focal end when counting the number of chain ends. On the basis of the observed T_g data, we could assume that the peripheral PS chains are conformationally decoupled *via* the aliphatic polyether dendritic core (considered as a "spacer"). To satisfy this interpretation, the peripheral end groups must make a dominant contribution to the overall T_g, in other words the peripheral chains

Table 1. Characterization of linear PSs (PS-n), dendrons (Generation-n) and dimeric PSs with various spacer groups

Compound	M_n g/mol	M_w/M_n^a	T_g (°C)
PS-1	1000^a	1.12	41.4
PS-2	2100^a	1.05	71.6
PS-3	3500^a	1.05	86.2
PS-4	8300^a	1.05	92.3
Generation-1	2100^b	1.05	58.3
Generation-2	4200^b	1.03	58.3
Generation-3	8500^b	1.03	60.3
PS-ether-PS	2050^b	1.04	55.4
PS-ether-PS	2080^b	1.03	59.7
PS-amide-PS	2080^b	1.02	74.2

[a]Calculated by a GPC based on PS standards. [b]Theoretical number average molecular weight calculated based on the of M_n^{GPC} **PS-1**.

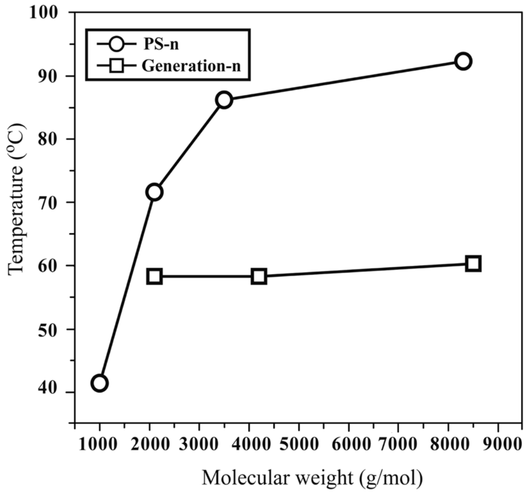


Figure 3. Trends of glass transition temperature as a function of molecular weight; circle: PS-n, square: **Generation-n**.

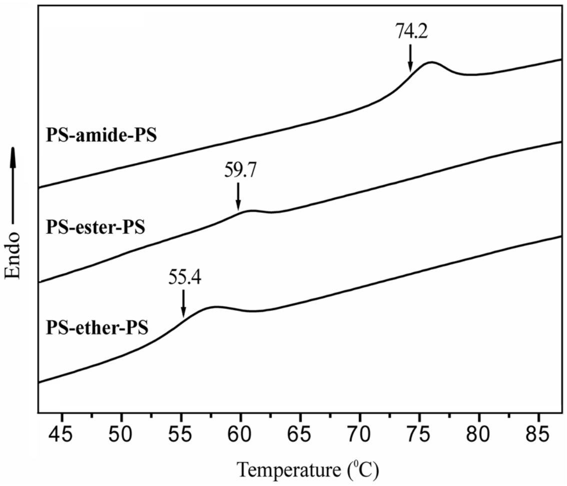
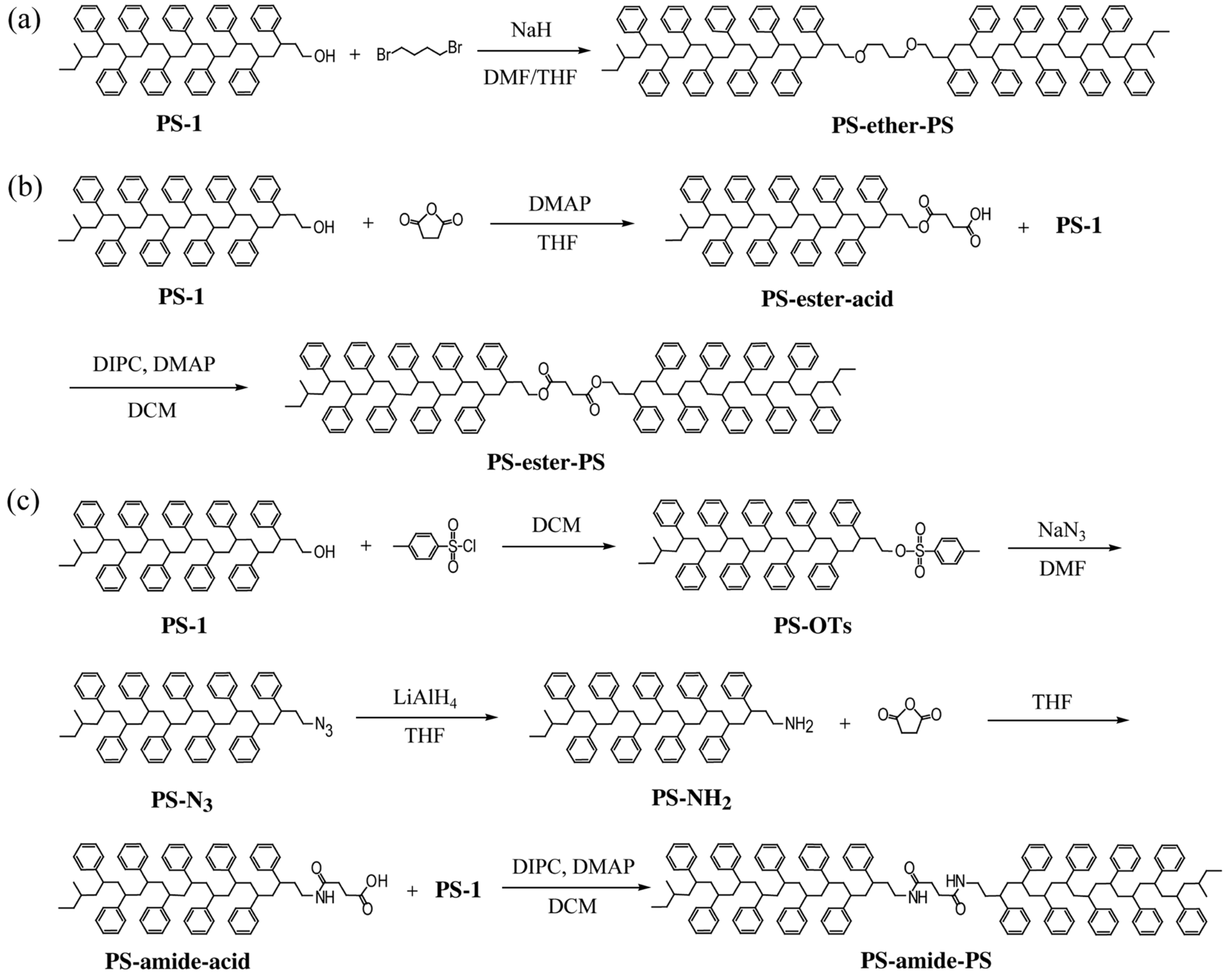


Figure 4. DSC thermograms of dimeric polystyrenes with various linkage groups.

should have a much higher T_g than the dendritic core. With respect to the molecular composition, we expect that the PS chain is conformationally more rigid than the PEO-like dendritic core. To verify the dependence of T_g upon the spacer group, we prepared a series of dimeric polystyrenes with different spacer groups such as ether, ester and amide linkages (Scheme 2). The synthetic details are described in the Experimental section, and the obtained DSC data are summarized in Table 1. In Figure 4, the glass transition temperatures of the dimeric polystyrenes are strongly dependent upon the spacer group. The T_gs were found to be



Scheme 2. Synthetic routes of (a) **PS-ether-PS**, (b) **PS-ester-PS**, and (c) **PS-amide-PS**.

55.4, 59.7 and 74.2 °C for **PS-ether-PS, PS-ester-PS** and **PS-amide-PS**, respectively. With respect to torsional strain and polarity, the molecular conformational freedom would be the highest in the **PS-ether-PS**, while the ester and amide spacers have more polar bonding character to hinder free rotation. Particularly, the amide spacer provides the lowest freedom due to its partial resonance character and hydrogen bonding. Of course, relative to the **PS-ether-PS**, the higher T_g (71.6 °C) of **PS-2** with the almost identical PS mass can be understood *via* an identical concept, because the styryl group can be considered as a bulky spacer connecting two **PS-1** chains. Therefore, it can be concluded that a more flexible spacer leads to more effective decoupling of the peripheral polymeric chains.

As compared to conventional dendritic molecules mentioned in the introduction, it is worth noting that the glass transition temperatures for **Generation-n** do not change significantly, but persist within a narrow temperature range. In other words, T_g can be kept constant by: i). the dendritic architectural effect, and ii) the decoupling of the peripheral chain mobility from the dendritic core structure; although the overall peripheral PS chain mass reaches the molecular weight of the corresponding linear polymer showing "leveling off" of the T_g. Consequently, this molecular concept provides a versatile route for precisely engineering peripheral chain mobility. Since the extent of microphase-separation in block copolymers is proportional to the overall degree of polymerization (DP) of blocks,[19] and by extension to self-assembling block macromolecules, the suggested dendritic block may be a promising building block with well-defined peripheral chain mobility.

Conclusions

In this study, we surveyed the glass transition behavior of the dendrons (**Generation-n**) from 1st to 3rd generation, which are composed of conformationally flexible aliphatic polyether dendritic cores and glassy polystyrene peripheries. From the molecular composition, the overall glass transition temperatures are mainly determined by the glassy PS peripheries. Interestingly, all the generations show approximately constant T_g values around 60 °C. On the other hand, linear PS chains with various molecular weights exhibited a typical T_g growth with increasing generation. The remarkable T_g contrast between the dendrons and linear PS chains appears to be dominantly attributed to the chain architecture. In the dendritic architecture, the number of mobile chain ends and the molecular weight increase equally by a factor of 2 from generation to generation. In addition to the chain architecture, the composition of the dendritic spacer plays another important role in the T_g. Among the three dimeric PS chains with different spacers, the ether linked PS dimer displays the lowest T_g value, suggesting that the peripheral PS chains are effectively decoupled *via* the conformationally flexible ether spacer. Consequently, the molecular concept with the presented dendritic architecture provides a way to precisely control polymer chain mobility at the peripheral sites.

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