Highly Branched Block Copolymers: Design, Synthesis, and Morphology

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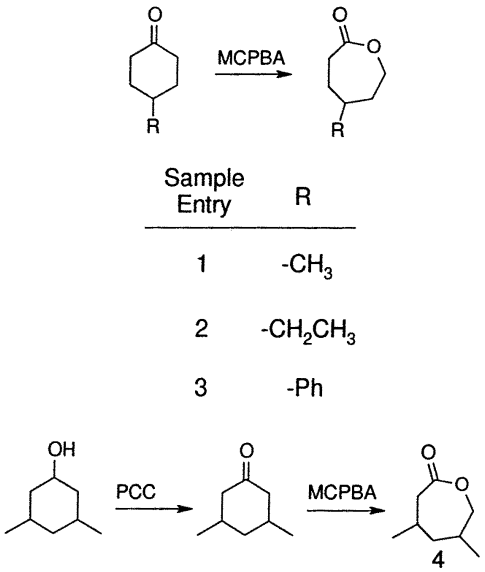
ABSTRACT: Several new approaches to biodegradable dendritic aliphatic block copolymers are described, including hyperbranched and dendrimer-like star structures. The hyperbranched polymers were obtained by the co-condensation of different AB_2 macromonomers. The macromonomers were prepared by ring-opening polymerization (ROP) of either ϵ-caprolactone, L-lactide, or various substituted lactones using the benzyl ester of 2,2′-bis(hydroxymethyl)propionic acid as initiator. Catalytic hydrogenation of the benzyl ester generated the requisite acid functional AB_2 macromonomer. The second route utilizes a new type of molecular architecture, denoted as dendrimer-like star polymers. These block copolymers are described by a radial geometry where the different layers or generations are comprised of high molecular weight polymer emanating from a central core. With this architecture, more control in the placement of the different blocks is afforded over the hyperbranched analogue. As a means of imparting desirable mechanical properties to the dendritic copolymers, a series of new substituted lactones were prepared. The use of such monomers prevents crystallization of the poly(lactone), allowing dendritic polyesters with a range of mechanical properties from thermoplastic elastomers to rubber toughened systems, depending on the relative composition of the two components. The synthesis, characterization, and morphology of these new copolymers are discussed.

Introduction

The macromolecular engineering of complex molecular architectures through the introduction of controlled branching or block copolymerization has continued to assume an increasingly important theme in polymer science.[1] Accordingly, the synthesis of star, starburst, hyperbranched, graft, block, dendri-graft, dendrimers, and related architectures has been the goal of many research groups.[1−3] For instance, hyperbranched polymers are prepared in a single-step polymerization from an AB_x monomer producing polymers with irregular branching, while dendrimers are the perfect elaboration of a well-defined branched macromolecule.[2] Considerable flexibility has been demonstrated in these architectures by the incorporation of building blocks that are monodispersed linear polymers. For instance, the successive grafting of linear chains has led to dendri-graft and comburst molecular architectures.[3] Most dendritic-linear hybrids reported have been based on reactive dendrons, where the focal point is capable of subsequent transformations such as the initiation or termination of linear chains.[2i,4] Alternatively, the functional periphery groups on the surface of both dendrimers and hyperbranched polymers have been used to initiate living polymerizations to prepare star structures.[5] Another means of nanoscopically tailoring materials is by the preparation of block copolymers. Block copolymers are examples of amphiphiles that are capable of self-assembly into periodic geometries with long-range order. Block copolymers contain at least two distinct polymer chains covalently bound at one point, which promotes the miscibility of the two intrinsically dissimilar materials, and phase separation is limited to dimensions on the order of 100−400 Å.[6] Depending on the relative volume fractions of the blocks, block copolymers can self-assemble into a variety of morphologies including lamellar, hexagonal-packed cylindrical, and body-centered cubic micellar structures. Such compositional variations provide another way of controlling polymer properties including thermoplastic elastomers, rubber toughened polymers, micelles, etc.

Scheme 1



The variation of block copolymer morphology as a function of composition described above has primarily emerged from the investigation of diblock copolymers. However, the molecular architecture of the polymer chain also has a pronounced effect on the morphology and interfacial activity, and this is of concern in property control in branched copolymers.[6] For instance, larger values of χn, where χ is the Flory interaction parameter and n is the degree of polymerization, have been predicted for phase separation in branched polymers including graft and star architectures than those for the corresponding diblock polymers.[7a] In addition, phase diagrams for star block polymers were shifted (i.e.,

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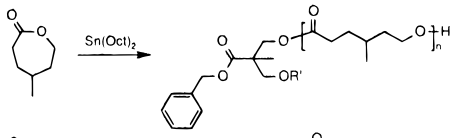
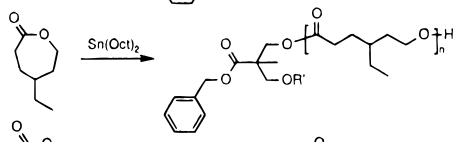
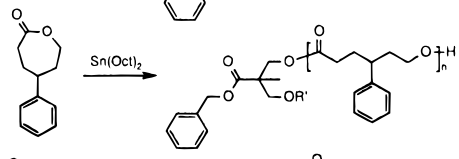
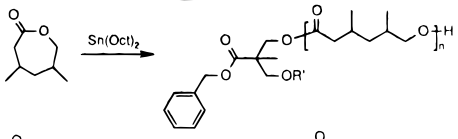
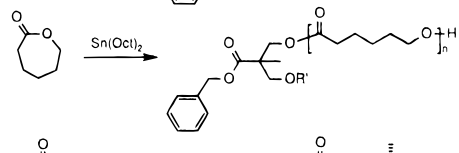
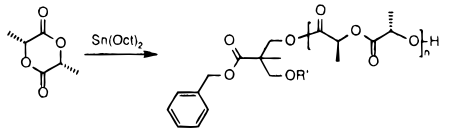
Table 1. Characteristics of AB_2 Macromonomers

Monomer	Polymer	Sample Entry	M_n (SEC)	M_w/M_n	T_g (°C)
		**5a**	3,200	1.23	-64
		5b	8,600	1.24	-64
		**6a**	3,000	1.47	-64
		6b	5,200	1.30	-65
		**7a**	8,800	1.19	-41
		7b	13,500	1.25	-42
		**8a**	5,600	1.41	3
		8b	8,100	1.46	6
		**9**	3,200	1.18	-60
		**10**	4,000	1.56	50

spherical morphologies were observed where cylindrical structures were expected) due to steric crowding near the branch point, leading to high curvature at the interface of the microphase separated domains.[7b]

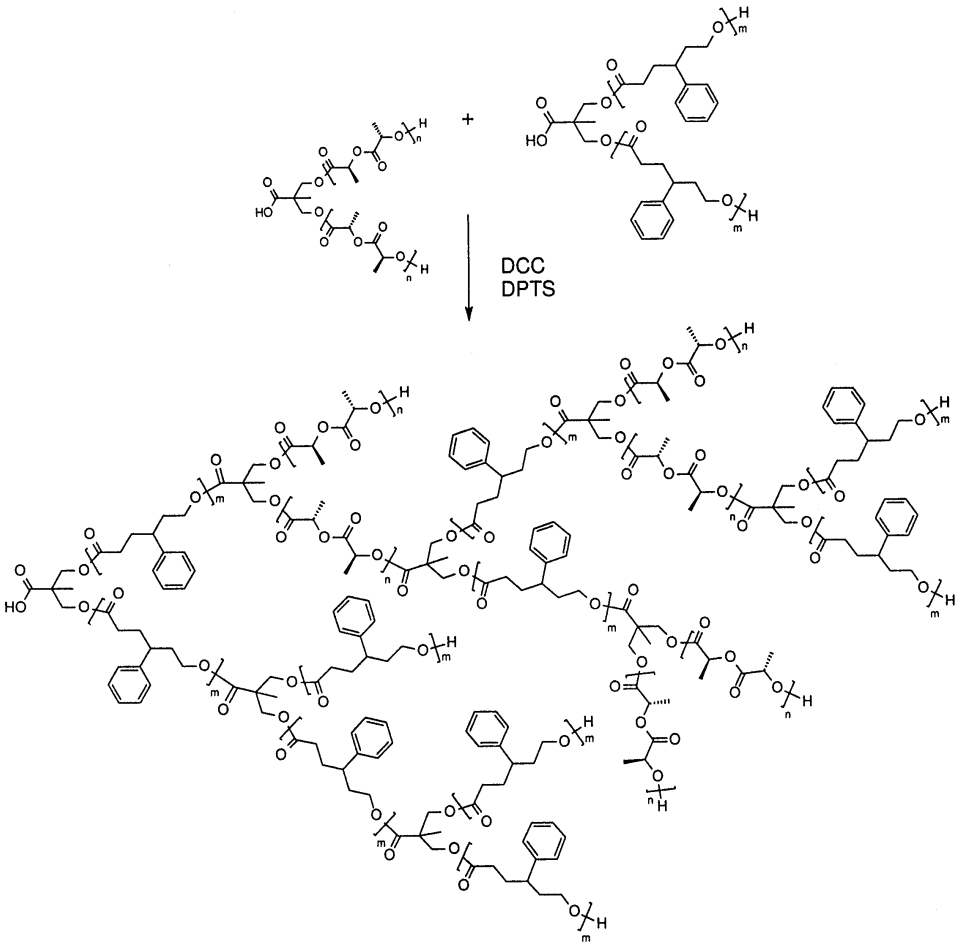
Recently, a new type of molecular architecture has been reported, denoted as dendrimer-like star polymers, that combines aspects of dendrimer synthesis with that of star polymers.[8] For instance, three generations of dendrimer-like star poly(ϵ-caprolactone)s have been prepared by the divergent growth approach using repetitive ring-opening polymerization (ROP) coupled with functionalization and deprotection of an AB_2 branching juncture formed at the chain ends between generations.[8b−d] Similarly, block copolymers can be prepared simply by using different monomer sets or different polymerization chemistry between generations.[8bc] For example, microphase separated morphologies were observed for dendrimer-like star polymers, having different generations comprised of poly(ϵ-caprolactone) with poly(methyl methacrylate). Likewise, it is of interest to survey morphology variations from copolymers with an irregularly branched system. Hyperbranched aliphatic polyesters comprising linear segments have been demonstrated from AB_x macromonomers.[9] The macromonomers were prepared from the ROP of ϵ-caprolactone initiated from 2,2′-bis(hydroxymethyl)propionic acid (bis-MPA) in the presence of stannous 2-ethylhexanoate ($Sn(Oct)_2$). These intrinsically branched macromonomers were self-polymerized by a simple esterification procedure.[9,10] As a means of imparting morphology variations and desirable mechanical properties, hyperbranched block copolymers have been prepared along with a new series of substituted lactone monomers.[11] The substituents of these monomers prevent crystallization of the poly(lactone), allowing hyperbranched block copolymers with properties ranging from thermoplastic elastomers to rubber toughened polyesters depending on the relative composition of the two components. In this article, the synthesis of the new substituted lactone monomers will be reported. Moreover, the first examples of hyperbranched block copolymers will be discussed, and to facilitate comparison, the synthesis and characterization of dendrimer-like star polymer analogues will also be presented.

Experimental Section

Materials. 1,4-Cyclohexanediol, 4-methylcyclohexanone, 4-ethylcyclohexanone, 4-phenylcyclohexanone, 1-pyrenebutyric acid, pyridinium chlorochromate (PCC), *m*-chloroperoxybenzoic acid, benzyl bromide, trimethylsilyl iodide, Pd/C (10 wt %), 1,3-dicyclohexylcarbodiimide (DCC), and sodium hydride (70% dispersion in mineral oil) were all purchased from Aldrich and used as delivered. Stannous(II) 2-ethylhexanoate ($Sn(Oct)_2$) and ammonium hydroxide (EM Science) were used as delivered. 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) and 2,2-bis(hydroxymethyl)benzyl propionate were prepared according to literature procedures.[10,2k] Toluene was dried over Na, distilled, and stored under N_2(g).

Measurements. Size-exclusion chromatography (SEC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. Four 5 μm Waters columns (300 × 7.7 mm) connected in a series in order of increasing pore size (100, 1000, 10^5, 10^6 Å) were used with THF as solvent. The SEC was calibrated with polystyrene. The thermophysical properties were recorded on a Perkin-Elmer DSC-7. ^{1}H NMR spectra were recorded in a solution with a Bruker AM 250 (250

Scheme 2



MHz) spectrometer. ^{13}C NMR spectra were recorded at 62.9 MHz on a Bruker AM 250 spectrometer with the solvent carbon signal as an internal standard. GC analysis was performed with a Hewlett-Packard 5890 series II gas chromatograph.

Synthesis. *4-Methyl-ϵ-caprolactone (**1**) and a General Procedure for Lactone Formation.* A solution of 4-methylcyclohexanone (30 g, 268.0 mmol) in $CHCl_3$ (30 mL) was added to a stirring solution of *m*-chloroperbenzoic acid (MCPBA) (64.9 g, 0.375 mol) in $CHCl_3$ (100 mL). After 10 h, the mixture was filtered through Celite and washed twice with saturated $NaHCO_3$ and once with brine. The solution was then dried with $MgSO_4$, filtered, and concentrated in vacuo. The lactone was isolated by distillation under vacuum to yield 10.8 g (31.6%) of a clear liquid. ^1H NMR ($CDCl_3$) δ 0.94 (d, 3H, $-CH_3$), 1.17−1.53 (m, 2H, $-CHCH_3CH_2-$), 1.63−1.97 (m, 3H, $-CH_2CHCH_3-CH_2-$ and $-CH_2CHCH_3CH_2-$), 2.49−2.69 (m, 2H, $-CH_2COO-$), 4.07−4.28 (m, 2H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$) δ 22.0, 30.7, 33.0, 35.0, 37.1, 67.9.

*4-Ethyl-ϵ-caprolactone (**2**).* 4-Ethylcyclohexanone (25.0 g, 198 mmol) and MCPBA (44.6 g, 258 mmol) were reacted according to the general procedure for lactone formation. The lactone was isolated by distillation under vacuum to yield 15.2 g (54.1%) of a clear liquid. ^1H NMR ($CDCl_3$) δ 0.79−0.92 (t, 3H, $-CH_3$), 1.17−1.35 (q, 2H, $-CH_2CH_3$), 1.35−1.52 (m, 1H, $-CH-$), 1.82−2.00 (q, 2H, $-CH_2CH_3$), 2.50−2.69 (m, 2H, $-CH_2COO-$), 4.06−4.33 (m, 2H, $-COOCH_2-$).

*4-Phenyl-ϵ-caprolactone (**3**).* 4-Phenylcyclohexanone (10.0 g, 57.0 mmol) and MCPBA (11.9 g, 0.068 mol) were reacted according to the general procedure for lactone formation. The lactone was isolated by flash chromatography on silica gel (20% EtOAc in hexane) to yield 5.2 g of a white powder (47.7%). ^1H NMR ($CDCl_3$) δ 1.72−2.00 (m, 1H, $-CH_3$), 2.00−2.20 and 2.65−2.91 (m, 6H, $-CH_2CHCH_2CH_2COO-$), 4.24−4.44 (m, 2H, $COOCH_2-$), 7.11−7.36 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ 30.3, 33.7, 36.7, 47.1, 68.3, 76.8, 77.3, 77.8, 126.5, 127.6, 128.8, 145.0, 175.8.

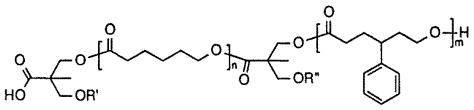
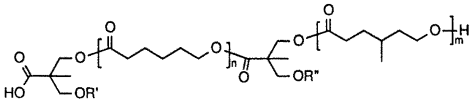
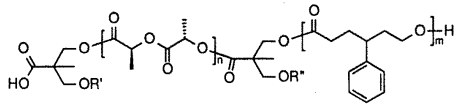
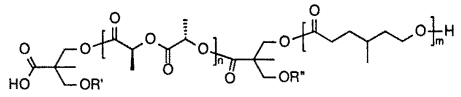
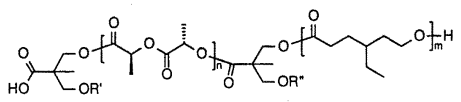
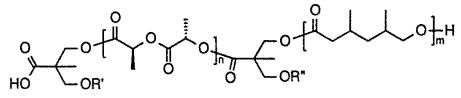
*3,5-Dimethyl-ϵ-caprolactone (**4**).* Pyridinium chlorochromate (PCC) (70.7 g, 328 mmol) was added to a solution of 3,5-dimethylcyclohexanol (35.0 g, 273 mmol) in CH_2Cl_2 (300 mL). After 17 h the solution was diluted with Et_2O (500 mL) and filtered through silica and concentrated in vacuo. The ketone, a clear liquid, was isolated by distillation. Yield: 14.2 g (41%). ^1H NMR ($CDCl_3$) δ 0.99−1.02 (d, 6H, $-CH_3$), 1.71−2.04 (m, 6H, $-COCH_2-$, $-CH_2-$, and $-CH-$), 2.30−2.34 (d, 2H, $-CH_2-$). The ketone (12.0 g, 95 mmol) and MCPBA (21.4 g, 124 mmol) were then reacted according to the general procedure for lactone formation. The lactone was isolated by flash chromatography on silica gel (10% EtOAc in hexane) to yield 7.8 g of a clear liquid (60%). ^1H NMR ($CDCl_3$) δ 0.87 (d, 3H, $-CH_3$), 0.95−1.02 (m, 1H, $-CH-$), 1.01 (d, 3H, $-CH_3$), 1.78−2.00 (m, 3H, $-CH-$ and $-CH_2-$), 2.40−2.55 (q, 2H, $-COCH_2-$), 3.86−4.01 (q, 2H, $-COOCH_2-$).

Polymerizations. The macromonomers as well as the hyperbranched and dendrimer-like star block copolymers were prepared according to literature procedures.[5c,8a,9a,b]

Results and Discussion

Four monomers were prepared containing methyl, dimethyl, ethyl, and phenyl substituents (Scheme 1). The two methyl-substituted monomers have previously been reported while the ethyl- and phenyl-substituted monomers are new.[11] The monomers were prepared by the oxidation of the corresponding substituted cyclohexanol or cyclohexanone (**1**−**4**). Polymerization of the new monomers was accomplished using the benzyl ester of bis-MPA as an initiator in the presence of a catalytic

Table 2. Characteristics of Hyperbranched Block Copolymers

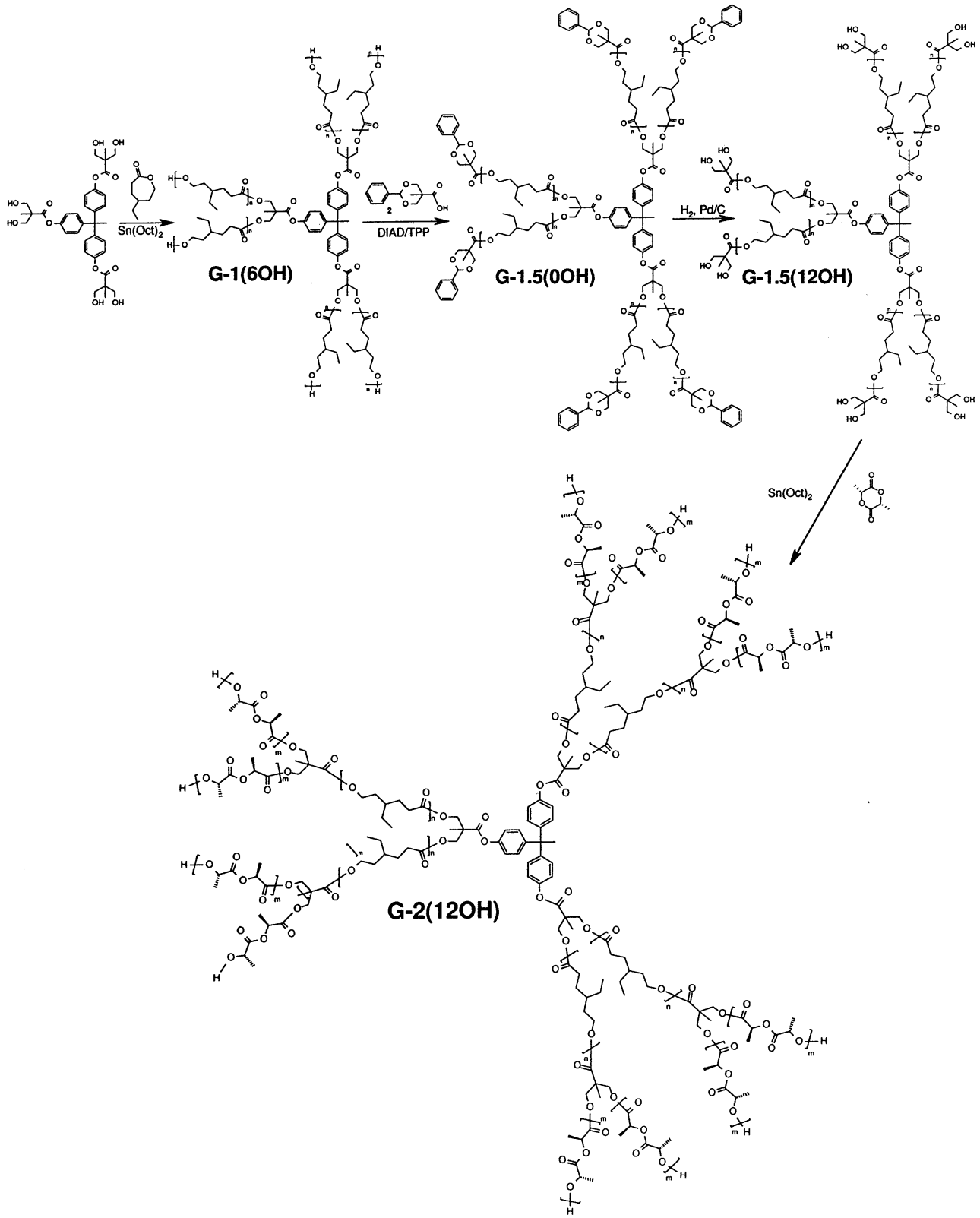
Block Copolymer	Sample Entry	M_n (SEC)	M_w/M_n	T_g (°C)	T_m (°C)
	**11**	24,300	1.56	-28	33
	**12**	24,000	1.76	-62	2, 46
	**13**	27,000	1.58	1	125
	**14**	23,700	1.71	-49	48, 122
	**15**	19,000	1.69	-37, 45	33
	**16**	26,000	1.56	-32, 54	154

amount of $Sn(Oct)_2$ according to a literature procedure.[5c,d] The polymerizations were conducted in bulk conditions at 110 °C. Near quantitative monomer consumption was observed after 48 h, according to ^1H NMR spectroscopy. It is important to note that the substituted lactones polymerize significantly slower than ϵ-caprolactone. Nonetheless, accurate control of molecular weight, as predicted from the monomer-to-initiator ratio, and narrow polydispersities were demonstrated (Table 1). These polydispersities are somewhat broader than those previously reported, which probably stems from some transesterification as a result of the extended polymerization times.[5d,9b] Also shown in Table 1 is the thermal analysis for the substituted poly(lactone)s (**5**−**8**). Each of the polymers, isolated as viscous oils, displayed a low-temperature T_g with no evidence of crystallization. The T_g's of the methyl-substituted polymers (**5** and **8**) correspond well with previously reported values.[11] The benzyl groups on the initiator were removed from the polymers by catalytic hydrogenation as previously reported.[9] This simple and mild transformation generated the requisite α-carboxylic-ω-dihydroxy macromonomers. SEC measurements show no change in the molecular weights or molecular weight distributions before and after deprotection. The synthesis of the poly(ϵ-caprolactone) and poly(L-lactide) AB_2 macromonomers was accomplished according to literature procedures, and the characteristics of the macromonomers are shown in Table 1 (**9** and **10**).[5d,f,9b]

The copolymerization of the intrinsically branched AB_2 macromonomers was performed in CH_2Cl_2 using dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)-pyridinum 4-toluenesulfonate (DPTS) as reagents (Scheme 2).[9,10] For the most part, the compositions of the mixed AB_2 macromonomers in the copolymerizations were designed in such a way as to have the low-T_g, amorphous component as the continuous phase and the poly(ϵ-caprolactone) or poly(L-lactide) as the dispersed phase. The characteristics of the hyperbranched copolyesters are shown in Table 2. Clearly, an increase in molecular weight is observed, and the molecular weight distribution broadens, as expected with a condensation polymerization. The yields were approximately 90%, suggesting that unreacted macromonomer may exist. To this end, the macromonomers were designed to be of moderate to low molecular weight with the anticipation that unreacted material after copolymerization may be readily removed during the copolymer precipitation in methanol. The SEC chromatograms show minimal amount of, if any, macromonomer in the hyperbranched copolymers. The branching characteristics of this type of polymers have previously been discussed.[9b]

The second synthetic route surveyed to block copolymers with controlled branching utilizes a new type of molecular architecture, denoted as dendrimer-like star polymers.[8] These block copolymers are described by a radial geometry where the different generations or layers are comprised of high molecular weight polymer emanating from a central core. For optimal mechanical properties, the copolymer should be designed such that the interior of the radial copolymer be comprised of the low-T_g, amorphous component and the outer block(s) be comprised of the high-T_g or semicrystalline component. The polymerization was initiated by the first-generation hexahydroxyl functional bis-MPA dendrimer in the presence of a catalytic amount of $Sn(Oct)_2$ using bulk conditions according to a literature procedure (Scheme 3).[8] The initiator was synthesized by a method, developed by Ihre et al.[2m] Ethyl-substituted ϵ-caprolactone was employed as the monomer for this first-generation star polymer containing six hydroxyl end groups and designated as **G-1(6OH)**. The target degree of polym-

Scheme 3



erization (DP) for each arm of the star polymer was 30, and the average DP measured by ^{1}H NMR spectroscopy was 27. This translates into a total molecular weight of 23 000 g/mol. The polydispersity was found to be 1.27 by SEC. This value is somewhat higher than for the analogous poly(ϵ-caprolactone) and may be a result of the longer reaction time (48 h). Nonetheless, the SEC chromatogram showed a monomodal distribution, and ^{13}C NMR spectroscopy showed a quantitative initiation from all hydroxyl groups.[8a] **G-1(6OH)** was then functionalized with benzylidene protected bis-MPA, using diisopropyl azodicarboxylate (DIAD) and triphenylphosphine (TPP) in dry THF to generate **G-1.5(0OH)**. The benzylidene was removed by catalytic hydrogenolysis to generate **G-1.5(12OH)**, which contains 12 hydroxyl end groups. Figure 1 shows the ^{1}H NMR spectra of the two

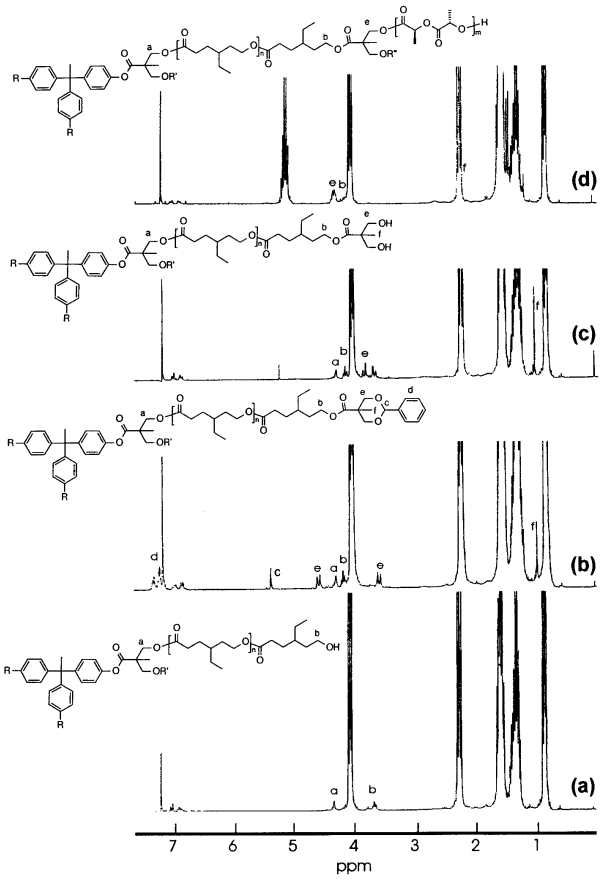


Figure 1. ^{1}H NMR spectra of **G1(6OH)** (a), **G1.5(0OH)** (b), **G1.5(12OH)** (c), and **G2(12OH)** (d).

polymers and their intermediates. All the spectra show the major peaks that can be assigned to the repeating units of the monomer(s). The spectrum of **G-1(6OH)** shows one peak assigned to the chain ends (**b**) and a small peak from the initiator (**a**) (Figure 1a). Upon transformation of the chain ends from alcohols into esters, the **b** peak shifts, and five new peaks appear (**c**, **d**, 2 times **e**, and **f**) from the protected bis-MPA. Deprotection erases the **c** and the **d** peaks derived from the benzylidene part of the protected bis-MPA and shifts the **e** ($-CH_2$ in bis-MPA) and **f** ($-CH_3$ in bis-MPA) resonances. This deprotected polymer was then used as the macroinitiator for the ROP of L-lactide to give the dendrimer-like star polymer **G-2(12OH)**. The ^{1}H NMR spectrum of **G-2(12OH)** shows a shift of the **e** peaks into a singlet (Figure 1d). In addition, the peaks originating from the repeating lactide units are clearly observed. ^{1}H NMR spectroscopy also shows that the DP was 13 per arm (target 15), which translates to a total molecular weight of approximately 46 500 g/mol. The polydispersity was found to be 1.30 by SEC.

The thermal characteristics for selected hyperbranched copolymers are shown in Table 2. The most pronounced difference in the morphology of the copolymers stems from the use of either poly(ϵ-caprolactone) or poly(L-lactide) as co-macromonomers. Shown in Figure 2 are selected dynamic mechanical spectra plotted with the calorimetry data for the hyperbranched block copolymers comprising ϵ-caprolactone (**11** and **12**). The ϵ-caprolactone-based block copolymers showed a single-phase morphology, as manifested by a single T_g, and depending on the co-macromonomer, the T_g falls between that of poly(ϵ-caprolactone) and the substituted

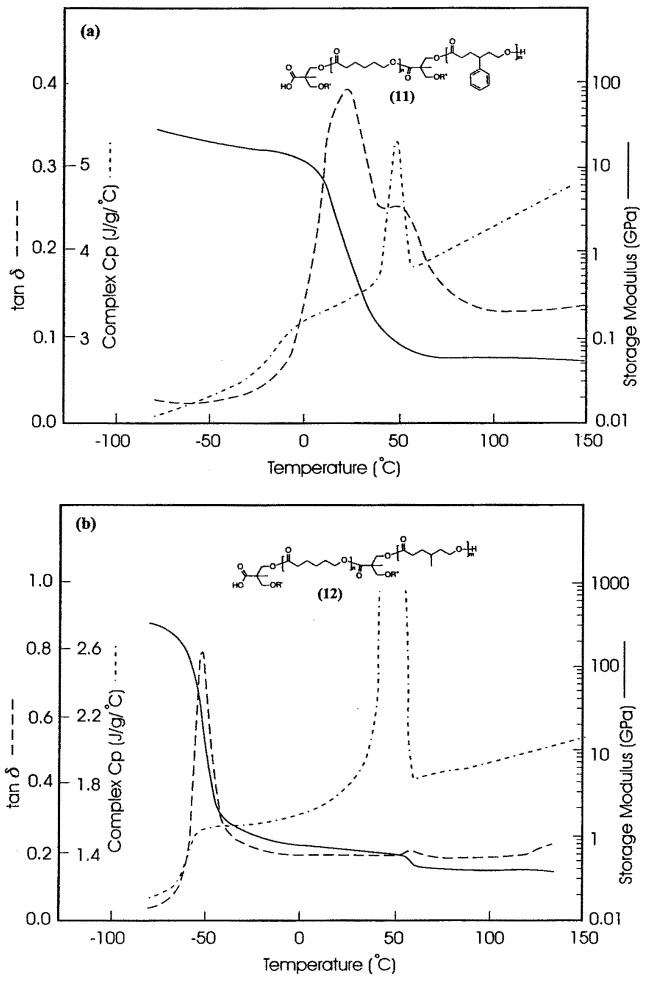


Figure 2. Dynamic mechanical and thermal spectra of copolymer **11** (a) and **12** (b).

poly(lactone) (Table 2). For instance, the copolymer (**11**) (Figure 2a) derived from the phenyl-substituted macromonomer has a higher mixed T_g than the copolymer (**12**) (Figure 2b) derived from the methyl-substituted macromonomers, as evident from the dynamic mechanical spectra. The miscibility of the two components is not surprising considering the similarities in the structures and the low block lengths, required to facilitate polymerization. The copolymers derived from the methyl-substituted lactone show a second melting endotherm. The origin of this endotherm (clearly seen in Figure 3 (**14**)) is not understood but presumably stems from the crystallization of the mixed amorphous phase, facilitated by copolymerization. What is interesting about these hyperbranched copolymers is that the mixed amorphous phase does not prevent the poly(ϵ-caprolactone) block from crystallizing. In each case, a crystalline melting point is observed, although somewhat depressed from the ϵ-caprolactone homopolymers of comparable molecular weight. The retention of the crystallinity in these copolymers may provide a means to tailor the mechanical properties. Examination of the dynamic mechanical spectra shows two decreases in the modulus with temperature. The first reduction corresponds to the softening associated with the mixed T_g's, while the second is associated with the melting of the semicrystalline poly(ϵ-caprolactone) component. Above the last transition, the polymer flows. However, between the transitions there is sufficient modulus retention to prevent flow and provide elastomeric mechanical prop-

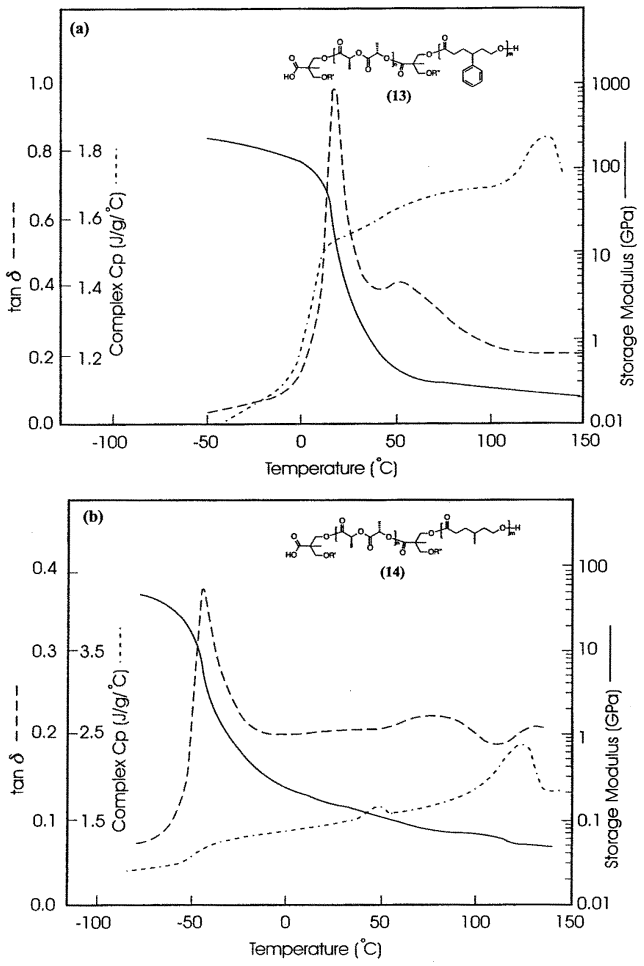


Figure 3. Dynamic mechanical and thermal spectra of copolymer **13** (a) and **14** (b).

erties. Many of the targeted applications for aliphatic polyesters require elastomeric mechanical properties. This has been accomplished by preparing triblock copolymers of for example ϵ-caprolactone and 1,5-dioxepan-2-one (DXO) or by using multifunctional cyclic esters such as 2,2′-bis(ϵ-caprolactone-4-yl)propane or bis(ϵ-caprolactone-4-yl) to cross-link low-T_g aliphatic polyesters and impart elastomeric character.[12,13] Alternatively, Storey et al.[14] have prepared thermosetting poly(ester−urethane) copolymers comprising soft segments derived from poly(ϵ-caprolactone-*co*-γ-valerolactone) oligomers. Although the two polyesters are highly crystalline, the crystallinity in the random copolymer was found to be significantly diminished. However, the polyester segments in these poly(ester−urethane) copolymers tended to undergo stress-induced crystallization, causing permanent set. Among these strategies to prepare elastomeric aliphatic polyesters, few have focused on thermally reversible systems. In our system, the substituted poly(lactone) prevents crystallization of this component while the crystallinity of the poly(ϵ-caprolactone) affords the requisite modulus retention for elastomeric mechanical properties and serves as a thermally reversible cross-link juncture. Furthermore, it is unlikely that such a highly branched system would undergo stress-induced crystallization at high deformations.

The second series of hyperbranched block copolyesters (i.e., those derived from poly(L-lactide)) showed markedly different behavior (Table 2). Shown in Figure 3 are

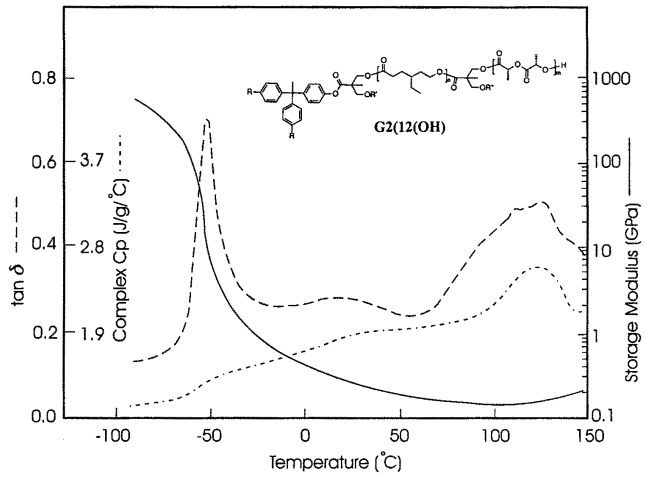


Figure 4. Dynamic mechanical and thermal spectra of copolymer **G2(12OH)**.

the dynamic mechanical spectra with the calorimetry data as a function of temperature for selected samples. Irrespective of the substituted AB_2 macromonomer used, microphase-separated morphologies were observed. The two T_g's are clearly evident, particularly in the dynamic mechanical spectra. Those copolymers (**13**) derived from the phenyl-substituted lactones have T_g's which are nearly identical to those of the initial macromonomers employed. Conversely, the other hyperbranched copolymers (**14**−**16**) have T_g's somewhat higher than that of the substituted lactone macromonomer used, which may be a result of possible phase mixing or from constraint imposed on the end groups due to the short block lengths. In most samples, the T_m of the semicrystalline phase was in the proximity of 125 °C, which is only somewhat depressed from the L-lactide macromonomer. The examples shown in Figure 3 are asymmetric block copolymers (**13**, **14**), where the poly(L-lactide) is the dispersed phase. In these examples, elastomeric mechanical properties are obtained between the two T_g's. However, if a higher composition of the AB_2 lactide macromonomer was used in the copolymer synthesis, the properties of the final hyperbranched copolymer would resemble that of a rubber toughened poly(L-lactide). Clearly, considerable flexibility in the mechanical properties may be realized simply by varying the AB_2 macromonomer compositions.

The thermal analysis for the dendrimer-like star polymer, **G-2(12OH),** also showed a microphase separated morphology. Shown in Figure 4 are the dynamic mechanical spectra and calorimetry measurements as a function of temperature. Two T_g's are clearly observed, and they are nearly identical to those of the respective homopolymers, suggesting phase purity. However, similar to the hyperbranched copolymers, the transitions were broad and diffuse, characteristic of diffuse phase boundaries. This is not surprising considering the short block lengths used. As before, the mechanical properties may be adjusted simply by varying the lengths of the blocks. However, unlike the hyperbranched analogue, the mechanical properties can be controlled to a greater extent since either the outer or inner block can be designed to be the continuous phase simply by adjusting the degree of polymerization of each block. The outer block can be designed to be the high-T_g component or the thermally reversible cross-link junctures, providing optimal mechanical properties. One case where this may be important is in the design of elastomers, since

"dangling chain ends" can be eliminated. This is in sharp contrast to the hyperbranched analogues, where the blocks are arranged randomly. Other examples of possible applications for the dendrimer-like star polymers include the preparation of amphiphilic block copolymers for unimolecular micelles, nanoreactors, and drug delivery systems.

Summary

Several new approaches to dendritic aliphatic polyester block copolymers were demonstrated, including the first example of hyperbranched block copolymers. A series of new substituted ϵ-caprolactones monomers, containing methyl, ethyl, phenyl, and dimethyl groups, were prepared as a means of preventing the crystallization of the subsequent polyester. These new lactones provided a means of imparting desirable mechanical properties to the dendritic polyester copolymers ranging from thermoplastic elastomers to rubber toughened systems, depending on the relative compositions of the two components. The hyperbranched copolymers were prepared by the co-condensation of different intrinsically branched AB_x macromonomers. The second route surveyed as a means to block copolymers with controlled branching utilizes a new type of molecular architecture, denoted as dendrimer-like star polymers. These block copolymers are described by a radial geometry where the different layers or generations are comprised of high molecular weight polymer emanating from a central core. With this architecture, more control in the placement of the different blocks is afforded over the hyperbranched analogue. Irrespective of the molecular architecture, microphase morphologies were observed when poly(L-lactide) was employed as one of the blocks. In addition, the crystallization of the poly(L-lactide) block was largely unaffected by the copolymerization. Conversely, the copolymers comprising poly(ϵ-caprolactone) blocks manifested a homogeneous or single-phase morphology with the blocks derived from the new substituted lactones.

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