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Layered Dendritic Block Copolymers**

Mikael Trollsås, Hans Claesson, Björn Atthoff, and James L. Hedrick*

Macromolecular engineering of complex molecular architectures through block copolymerization or the introduction of controlled branching has become a common theme of research in polymer science. The interest in these synthetic mesoscopic systems and nanostructures is driven by the possible unique mechanical, rheological, and solution properties. Block copolymers are simply two distinct homopolymers covalently bound at one point, and the molecular architecture, block lengths, and composition can be designed to produce materials with a wide range of properties and morphologies.[1] Furthermore, since the two dissimilar materials are covalently bound, miscibility is enhanced and phase separation is restricted to dimensions of 100 to 400 Å. Dendrimers provide the ultimate standard of a well-defined branched macromolecule, while hyperbranched polymers are less perfect elaborations of such three-dimensional structures.[2, 3] The combination of controlled branching with block copolymerization provides additional opportunities to devise new molecular architectures. For instance, dendrimers have often been used as cores for the preparation of star polymers with a well-defined number of arms.[4] Conversely, Fréchet et al.[5] terminated star polymers with dendrons at their focal point, and layered and segmented dendrimers have been reported by other groups.[6] In addition, Tomalia et al.,[7a] Möller and co-workers,[7b–d] and others have reported successive grafting of polymeric building blocks.[7] These "comb-burst" polymers, or arborescent graft polymers, utilize linear building blocks with narrow polydispersity in the construction of highly and randomly branched polymers. A new type of molecular architecture, denoted dendrimer-like star polymers, based on poly(ε-caprolactone) has been recently reported.[8] These highly branched dendrimer-like star polymers are different from comb-burst polymers because the branching is controlled and resembles that of traditional dendrimers. The use of living polymerization methods in combination with selective and quantitative organic transformations allows the design and preparation of classical polymers with molecular architectures similar to the most advanced dendrimers with layered and segmented block structures.

Here layered dendrimer-like star copolymers are reported. These novel polymers, characterized by a radial architecture, are constructed by alternating layers of high molecular weight polymer and dendrons emanating from a central core (Scheme 1). There are many possible routes to these novel geometries but this paper focuses on the possibility of using living polymerization techniques. These polymers contain multiple hydroxyl groups and are of interest in areas of surgery and medicinal chemistry as well as in nanotechnology. In addition, it is of interest to investigate whether these molecular structures display microphase-separated morphologies. The general synthetic strategy is shown in Scheme 1. A multifunctional core molecule is used as an initiator for the controlled ring opening polymerization of ε-caprolactone. The polymer obtained, G1(6OH), is the first generation of the final triblock copolymer. The chain ends of the six-arm star polymer are capped with functional dendrons of different sizes to produce diblock polymers with 12, 24, or 48 functional end groups. These macromolecules will serve as "macroinitiators" for the growth of an additional layer of poly(ε-caprolactone) or the third layer of the dendrimer-like triblock copolymers (Scheme 1).

The six-arm star polymer G1(6OH) was synthesized by the reaction of one equivalent of a hexafunctional "initiator" and 120 equivalents of caprolactone in the presence of 1/400 equivalents of $Sn(Oct)_2$ under bulk conditions at 110 °C. The initiator is a first-generation hydroxyl-substituted dendrimer based on 2,2-bis(hydroxymethyl)proprionic acid (DMPA).[9] The target degree of polymerization (DP) was 20, and the DP obtained was calculated to be 20.6 by ^{1}H NMR spectroscopy. Protected DMPA or second- and third-generation dendrons derived from it were used to construct the second layer in the triblock dendrimer-like copolymer. The benzylidene-protected DMPA was synthesized in one step according to a procedure reported elsewhere,[10] while the

[*] Dr. J. L. Hedrick, M. Trollsås, H. Claesson, B. Atthoff
Center for Polymeric Interfaces and Macromolecular Assemblies (CPIMA)
IBM Research Division, Almaden Research Center
650 Harry Road, San Jose, CA 95120-6099 (USA)
Fax: (+1) 408-927-3310
E-mail: hedrick@almaden.ibm.com

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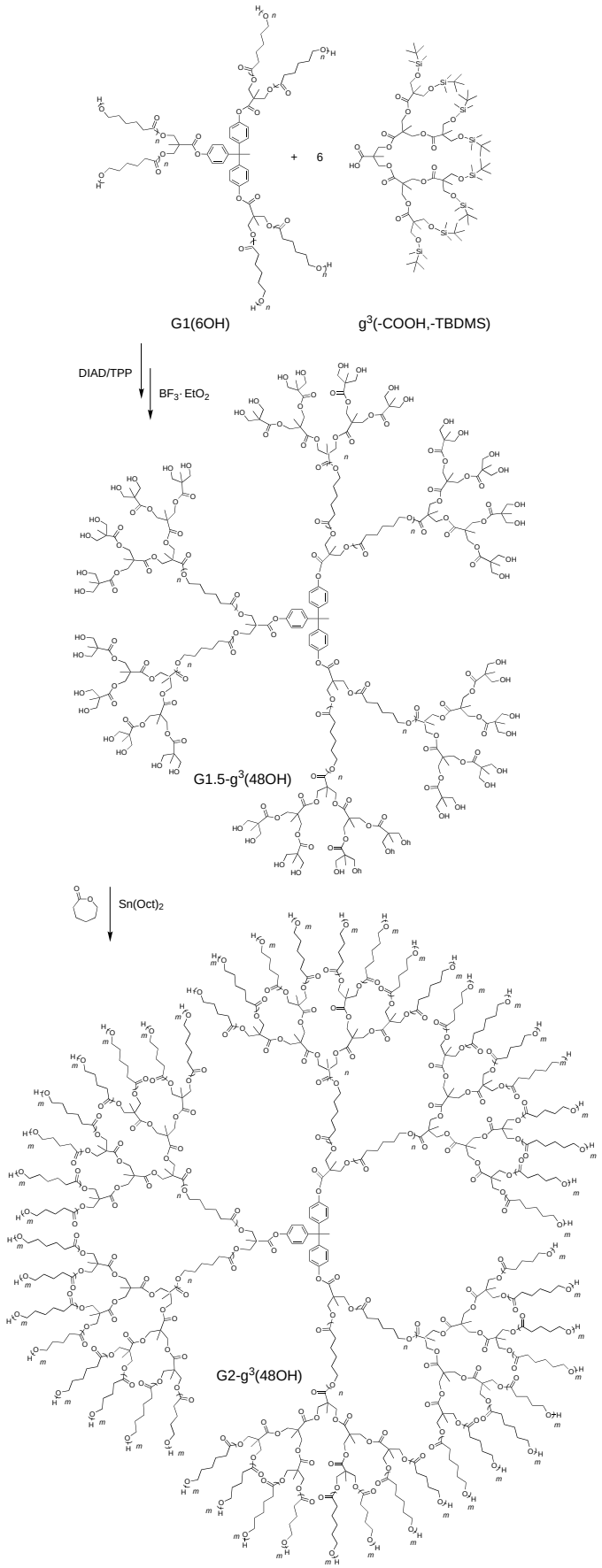
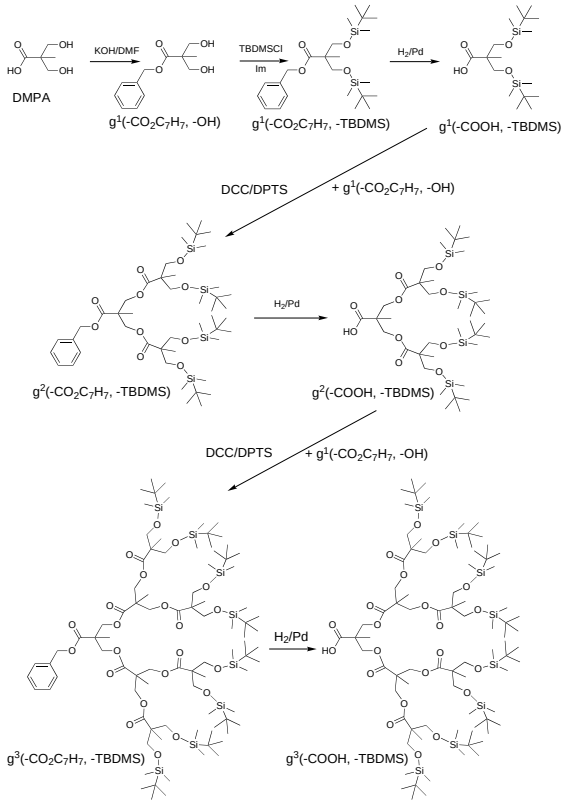


Scheme 1. TBDMS = *tert*-butyldimethylsilyl, DIAD = diisopropyl azodicarboxylate, TPP = triphenylphosphane.

dendrons g^2(-COOH,-TBDMS) and g^3(-COOH,-TBDMS) were obtained by a convergent growth approach (Scheme 2). The hydroxyl groups of the benzyl ester g^1(-$CO_2C_7H_7$,-OH) were protected with *tert*-butyldimethylsilyl chloride (TBDMSCl) to give g^1(-$CO_2C_7H_7$,-TBDMS). The benzyl group could then be selectively removed by catalytic hydrogenolysis to give the free acid g^1(-COOH,-TBDMS), which



Scheme 2. Im = imidazole, DCC = dicyclohexylcarbodiimide, DPTS = 4-(dimethylamino)pyridinium *p*-toluenesulfonate.

was then coupled with g^1(-$CO_2C_7H_7$,-OH) to afford the second-generation dendron g^2(-$CO_2C_7H_7$,-TBDMS). This in turn could be readily hydrogenolysed to give g^2(-COOH,-TBDMS). The third-generation dendron g^3(-$CO_2C_7H_7$,-TBDMS) was synthesized by coupling of g^1(-$CO_2C_7H_7$,-OH) with g^2(-COOH,-TBDMS). Deprotection by hydrogenolysis gave the requisite dendron g^3(-COOH,-TBDMS). The structure of the dendrons was confirmed by ^{1}H and ^{13}C NMR spectroscopy. ^{13}C NMR spectroscopy was used to determine whether the DMPA derivatives were completely substituted or not.[8, 11] Figure 1 reveals that the synthesized dendrons only contain quaternary carbon atoms which originate from disubstituted DMPA, as shown in Scheme 2, without traces of contamination from mono substitution.

The acid-functional dendrons were coupled with the hydroxyl-substituted six-arm star poly(ε-caprolactone) under Mitsunobu conditions to produce diblock copolymers with 12, 24, or 48 hydroxyl groups.[8, 10] The extent of coupling was followed by ^{1}H and ^{13}C NMR spectroscopy and size-exclusion chromatography (SEC). Sections of the ^{13}C NMR spectra for the six-arm star and the copolymers with the third-generation

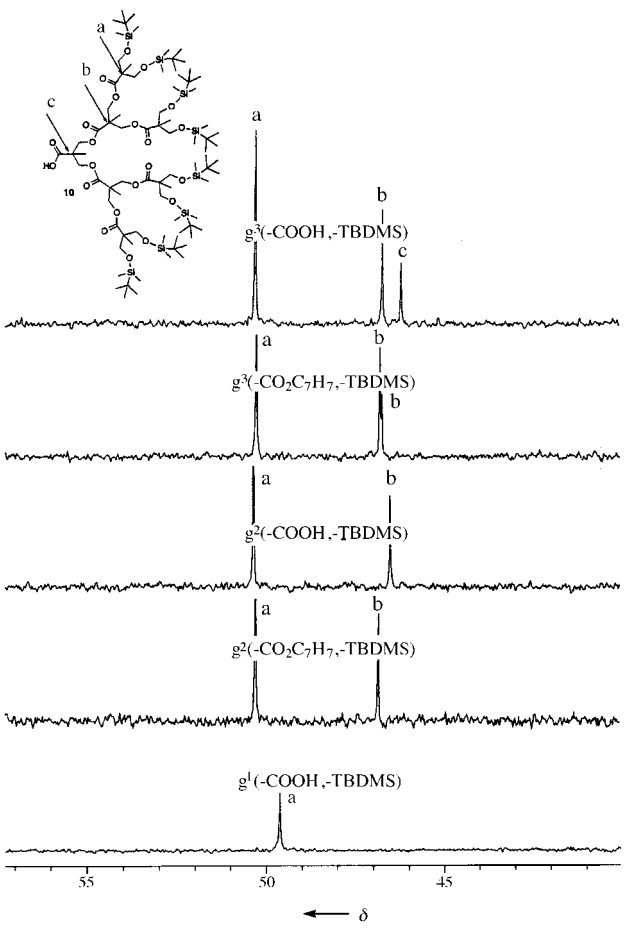


Figure 1. The quaternary carbon atom region in the ^{13}C NMR spectra of the dendrons.

dendron are shown in Figure 2. Quantitative functionalization is confirmed by the complete shift of the CH_2OH signal from $\delta = 62$ to 65 upon esterification of the hydroxyl groups.

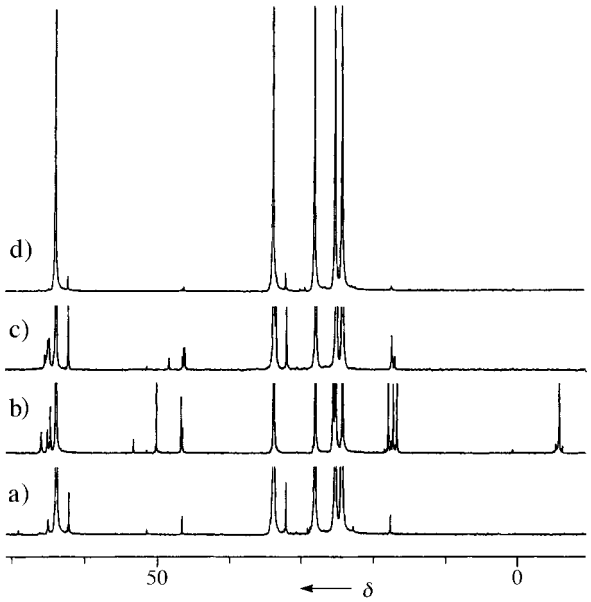


Figure 2. Part of the ^{13}C NMR spectra of a) G1(6OH), b) G1.5-g^3(TBDMS), c) G1.5-g^3(48OH), and d) G2-g^3(48OH).

Figure 3 shows an enlargement of the quaternary carbon atom region of the spectra. The diblock copolymer G1.5-g^3(TBDMS) displays five peaks in this region that are combined signals from the six-arm core and the third-generation dendron. The peak denoted c can be assigned to the outer generation of the dendron.

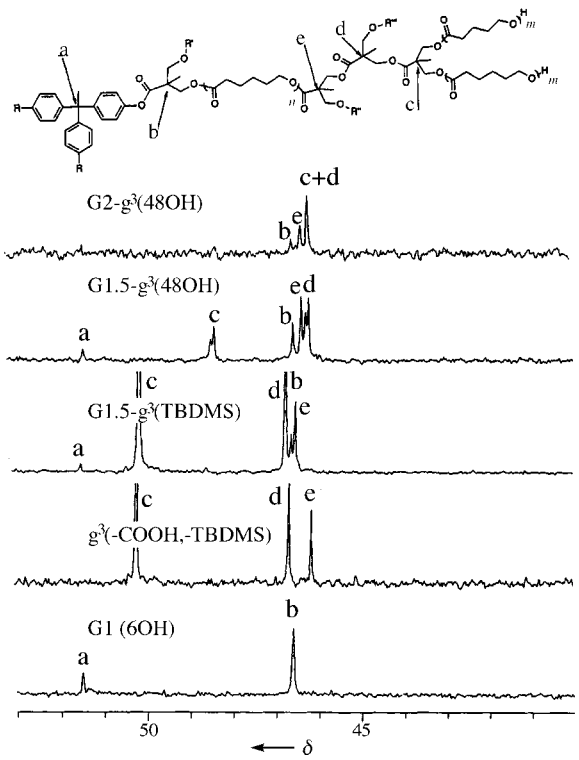


Figure 3. The quaternary carbon atom region in the ^{13}C NMR spectra of G2-g^3(48OH) and intermediates.

The benzylidene groups and the *tert*-butyldimethylsilyl protecting groups were then removed by hydrogenolysis and treatment of $BF_3 \cdot EtO_2$, respectively, to give the requisite 12, 24, and 48 hydroxyl groups along the periphery of the layered diblock polymers G1.5-g^1(12OH), G1.5-g^2(24OH), and G1.5-g^3(48OH) (Scheme 1). The ^{13}C NMR spectrum of G1.5-g^3(48OH) is free from peaks from the protecting group, which is consistent with quantitative deprotection (Figure 2). The transformation is also observed in the quantitative shift of the peak c derived from the quaternary carbon atom in the outer layer of the dendron (Figure 3).

The six-arm star diblock copolymers with 12, 24, and 48 hydroxyl groups at the periphery were used as "macroinitiators" for the growth of an additional layer of poly(ε-caprolactone). The diblock copolymers were soluble in ε-caprolactone, which allowed bulk polymerization. However, approximately 10 % toluene was added to reduce the viscosity of the melt. The polymerization mixtures became extremely viscous after 24 hours at 110 °C, and were then dissolved in THF and the products isolated by precipitation in methanol. It should be pointed out that the only purification needed after polymerization, functionalization, or deprotection was simple precipitation of the polymers into cold methanol. The structure of the 48-arm radial triblock copolymer G2-

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g^3(48OH) was confirmed by NMR spectroscopy. All peaks in the ^{1}H NMR spectra derived from the methylene protons of the outer layer of DMPA were shifted, which indicated that all hydroxyl groups initiated polymerization. This observation was confirmed by ^{13}C NMR spectroscopy (Figure 3). Complete initiation was observed from the quantitative shift of the quaternary carbon atom peak c into the disubstituted region. The experimental DP values, measured by ^{1}H NMR spectroscopy, correspond well with the target value (DP = 20) for G2-g^1(12OH) and for G2-g^2(24OH) (Table 1). However, the signals from the hydroxyl chain ends for G2-g^3(48OH) are much smaller than expected and may be a result of agglomeration.

Table 1. Characteristics of layered dendrimer-like star polymers.

Polymer	M_n[a]	M_n[b]	M_w/M_n[b]	DP[c]	T_m [°C] (ΔH [kJ mol^{-1}])
G1(6OH)	15000	23400	1.16	20.1[d]	53.1 (70.6)
G1.5-g^1(12OH)	15900	24000	1.14	20.1[d]	47.0 (61.5)
G1.5-g^2(24OH)	17000	26900	1.13	20.1[d]	48.8 (49.1)
G1.5-g^3(48OH)	20000	35300	1.09	20.1[d]	44.2 (46.8)
G2-g^1(12OH)	43100	58300	1.16	20.1[d], 21.3[e]	53.5 (60.8)
G2-g^2(24OH)	71800	91000	1.13	20.1[d], 24.7[e]	54.3 (85.6)
G2-g^3(48OH)	129300	221000	1.12	20.1[d, f]	57.1 (66.0)

[a] Theoretical. [b] Determined by SEC. [c] Degree of polymerization as determined by ^{1}H NMR spectroscopy. [d] First generation, [e] Second generation. [f] Second generation could not be measured.

The theoretical and the experimental number average molecular weights as measured by SEC are shown in Table 1. Also shown in Table 1 are the molecular weights and the molecular weight distributions as measured by SEC. The molecular weight distributions, as expected, are lowered when the six-arm stars are esterified with the monodisperse second blocks. The observed increase in molecular weight upon derivatization of the six-arm star with the dendrons, as well as the significant increase in molecular weight after the addition of the outer layer, are in the expected range for all three polymers. Figure 4 shows the size-exclusion chromatograms for each of the steps in the synthesis of the layered copolymers. The three distribution curves are monomodal and all polydispersities are below 1.20. Although these data are relative to a polystyrene standard and branched structures are known to have different hydrodynamic volumes than their linear analogues, the combined results from SEC and ^{13}C and ^{1}H NMR spectroscopy clearly suggest that all the prepared polymers have the requisite complex structures.

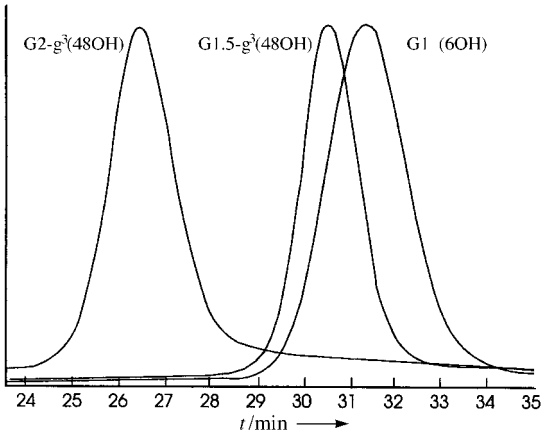

Figure 4. Sections of size-exclusion chromatograms of G2-g^3(48OH), G1.5-g^3(48OH), and G1(6OH).

All the diblock and triblock polymers are semicrystalline, as observed by differential scanning calorimetry (DSC) measurements (Table 1). In addition to the melting transition temperatures (T_m), glass-transition temperatures (T_g) of around $-50\,^\circ$C were observed for all polymers commensurate with the T_g observed for linear poly(ε-caprolactone). A second glass transition corresponding to the DMPA dendrons could not be detected by DSC since it was probably hidden beneath the melting endotherm of the ε-caprolactone block. Hult and co-workers have reported T_g values between -4 and $+57\,^\circ$C for dendrimers and hyperbranched polymers based on DMPA.[12] However, since the glass-transition temperatures are similar for the copolymers and the linear homopolymer, these data suggest that the different layers are partially phase-separated. If the layers were completely phase-mixed, a shift in T_g in accordance with the Fox equation would have been observed. Dielectric spectroscopy measurements indicate similar behavior. Films of the layered dendritic block copolymers were tough and ductile. A more thorough discussion of these results will be reported separately.

Experimental Section

The synthesis of the six-armed star poly(ε-caprolactone) and the benzylidene protected DMPA have been published elsewhere.[10, 11b] The synthesis of the second- and third-generation dendrons are available in the supporting information.

Synthesis of G1.5-g^2(TBDMS); a general procedure for esterification with DIAD: DIAD (1.30 g, 6.46 mmol) was slowly added to a stirred solution of G1(6OH) (8.00 g, 0.538 mmol), g^2(-COOH,-TBDMS) (3.98 g, 4.84 mmol), and TPP (1.69 g, 6.46 mmol) in THF (5 mL). After 12 h the mixture was poured into cold MeOH, and the precipitated product was filtered off to yield 10.56 g (99%) of a white crystalline powder. ^{1}H NMR ($CDCl_3$): $\delta =$ 0.00 (s, 144H; $Si(CH_3)_2$), 0.84 (s, 216H; $C(CH_3)_3$), 1.05 (s, 36H; CH_3), 1.20 (s, 18H; CH_3), 1.30–1.42 (m, poly; CH_2), 1.57–1.69 (m, poly; CH_2), 2.26–2.32 (t, poly; CH_2O), 3.57–3.72 (q, 48H; CH_2O), 4.01–4.07 (t, poly; CH_2CO), 4.10–4.26 (m, 24H; CH_2O), 4.33 (s, 12H; CH_2O), 6.91–7.09 (q, 12H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = -5.59$, 17.00, 17.59, 18.18, 24.55, 25.50, 25.81, 28.33, 34.09, 46.77, 50.38, 64.11, 64.89, 65.27, 120.72, 129.70, 146.26, 148.65, 171.40, 172.61, 172.83, 173.50, 174.15.

Synthesis of G1.5-g^2(24OH); a general procedure for the removal of the TBDMS group: G1.5-g^2(TBDMS) (10.03 g, 0.52 mmol) was placed in a sealed flask. The flask was evacuated and flushed with nitrogen (3 ×). Dry dichloromethane (30 mL) and then $BF_3 \cdot Et_2O$ (0.37 g, 2.6 mmol) were added. The mixture was stirred for 12 h at 40 °C and then poured into cold MeOH. The precipitated product was filtered and dried to give 7.1 g (80%) of a white crystalline powder. ^{1}H NMR ($CDCl_3$): $\delta = 1.04$ (s, 36H; CH_3), 1.20 (s, 18H; CH_3), 1.32–1.42 (m, poly; CH_2), 1.57–1.69 (m, poly; CH_2CH_2), 2.26–2.32 (t, poly; CH_2O), 3.63–3.84 (m, 48H; CH_2O), 4.01–4.06 (t, poly; CH_2CO), 4.13–4.24 (t, 48H; CH_2OCO), 4.29–4.44 (m, 36H; CH_2CO), 6.91–7.09 (q, 12H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 17.03$, 17.71, 18.00, 24.47, 25.43, 28.24, 34.01, 46.29, 46.68, 49.82, 64.04, 64.79, 65.13, 66.84, 120.66, 129.62, 146.21, 148.59, 171.36, 172.77, 172.94, 173.45, 174.89.

Synthesis of G2-g^2(24OH); a general procedure for polymerization of ε-caprolactone: G1.5-g^2(24OH) (0.90 g, 0.05 mmol) was dried over $MgSO_4$ in warm THF, and filtered into a dried reaction flask, which was then sealed. The solvent was then evaporated under vacuum at 90 °C. Dry toluene

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(2 mL) was added and evaporated to remove residual H_2O. This process was repeated three times. The reaction flask was then filled with nitrogen and dry toluene (2 mL) to dissolve the initiator. ε-Caprolactone (2.89 g, 25.3 mmol) was added, and the temperature was increased to 110 °C before a catalytic amount of $Sn(Oct)_2$ was added. The catalyst/initiator ratio was 1/400. The polymerization mixture was stirred for 24 h, diluted with THF, and poured into cold MeOH to precipitate a white crystalline powder. Yield: 3.7 g (98 %). ^{1}H NMR ($CDCl_3$): $\delta = 1.30-1.42$ (m, poly; CH_2), 1.55–1.69 (m, poly; CH_2), 2.26–2.32 (t, poly; CH_2O), 3.60–3.65 (t, 18H; CH_2OH), 4.01–4.07 (t, poly; CH_2CO), 4.33 (s, 12H; $CCH_3(CH_2O)_2$), 6.88–7.24 (m, 12H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 17.74$, 24.50, 25.45, 28.27, 32.20, 34.03, 46.69, 51.58, 62.38, 64.05, 65.07, 120.67, 129.64, 146.22, 148.60, 171.37, 172.78, 173.65.

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A Novel Domino Reaction: Cyclization of Alkynyl Sulfides by Reaction with IPy_2BF_4**

José Barluenga,* Gustavo P. Romanelli, Lorenzo J. Alvarez-García, Isidro Llorente, José M. González, Esther García-Rodríguez, and Santiago García-Granda

Synthetic methodologies relying on transition metal chemistry have opened unusual approaches to polycyclic structures.[1, 2] Intramolecular cyclizations of diynes mediated by organometallic complexes[3] often take place according to an *exo-exo* coupling mode,[4] whereas *endo-endo*[3] and *exo-endo*[5, 6] cyclizations have rarely been observed (Figure 1). Described here is a novel approach to accomplish the *exo-endo* cyclization of α,ω-diynes, and preliminary studies on a related intermolecular process.

Figure 1. Possible intramolecular cyclizations. The arrow shows the carbon–carbon bond formed in the metal-promoted intramolecular cyclization as a function of the diyne coupling mode.

Bis(pyridyl)iodonium(I) tetrafluoroborate (IPy_2BF_4) can be efficiently used as a catalyst or a stoichiometric reagent for unconventional coupling reactions of 1-iodoalkynes[7] and 1-*t*BuMe_2Si-substituted alkynes.[8] These two processes were restricted to aryl-substituted alkynes. Now, we have found for the first time that upon activation by sulfur substituents aliphatic alkynes can enter in a carbocyclization process mediated by IPy_2BF_4. This provides a new entry to unusual *exo-endo* intramolecular cyclizations of α,ω-diynes, as depicted in Scheme 1 for the conversion of the acetylenic sulfide **1a**[9] derived from 1,6-heptadiyne.[10] The overall process comprises two different carbon–carbon bond forming reactions—namely, an alkyne–alkyne coupling and a novel Friedel–Crafts-like ring closure—and is thus a new domino reaction.[11] The process is very fast at low temperature and is completed within a few minutes; increasing the reaction time results in lower yields owing to significant side processes. The reaction takes place upon addition of the starting diynyl

[*] Prof. Dr. J. Barluenga, Dr. G. P. Romanelli, L. J. Alvarez-García, Dr. I. Llorente, Dr. J. M. González
Instituto Universitario de Química Organometálica "Enrique Moles"
Unidad Asociada al C.S.I.C, Universidad de Oviedo
E-33071 Oviedo (Spain)
Fax: (+34) 98-510-3450
E-mail: barluenga@sauron.quimica.uniovi.es
E. García-Rodríguez, Dr. S. García-Granda
Departamento de Química Física y Analítica
Universidad de Oviedo
E-33071 Oviedo (Spain)

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