

tography (SiO₂, MeOH/CH₂Cl₂ 1/9) to afford **15** (3.7 mg, 62 %). R_f = 0.14 (MeOH/CH₂Cl₂ 1/9); $[\alpha]_D^{25}$ = -219.1° (c = 0.14, MeOH); IR (film): $\tilde{\nu}$ = 3278, 3062, 2962, 2928, 2873, 1652, 1492, 1462, 1342, 1248, 1066, 954, 904, 746 cm⁻¹; ¹H NMR (400 MHz, [D₈]THF, 25 °C): δ = 7.88–7.84 (m, 2H), 7.49–7.46 (m, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.35–7.32 (m, 2H), 7.27–7.00 (m, 6H), 6.85 (d, J = 8.2 Hz, 1H), 6.79 (td, J = 7.5, 0.9 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 4.95 (dd, J = 7.3, 1.3 Hz, 1H), 4.37–4.31 (m, 1H), 3.25 (t, J = 12.0 Hz, 1H), 3.03 (d, J = 4.4 Hz, 1H), 2.69 (dd, J = 12.4, 3.4 Hz, 1H), 2.21–2.16 (m, 2H), 2.02–2.00 (m, 2H), 1.09 (d, J = 6.8 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 7.0 Hz, 3H); ES-MS: calcd for C₄₀H₃₆Cl₂N₆O₆ [M+H]⁺: 767.22, found: 767.34; calcd for C₄₀H₃₆Cl₂N₆O₆ [M–H][–]: 765.20, found: 765.30; HR-MS (FAB) calcd for C₄₀H₃₆Cl₂N₆O₆ [M+Li]: 773.2233, found: 773.2248.

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- [11] Crude samples of **14** also perform in this assay (GI₅₀ ≈ 5 μ M). No significant difference in potency is observed in the *epi*-C37 series (derived from D-valine).
- [12] Compound **13** has a fluorescence quantum yield (QY) of 0.45, as estimated by emission at 350–550 nm relative to an equal optical density of 1-aminoanthracene (QY = 0.61) in MeOH. Nonchlorinated congener **12** is more intensely luminescent ($\lambda_{\text{max}}^{\text{ex}}$ 348 nm, $\lambda_{\text{max}}^{\text{em}}$ 438 nm, ϵ = 7960 L mol⁻¹ cm⁻¹ at 348 nm, QY = 0.62) but less active against OVCAR-3.
- [13] Fluorescence micrographs were obtained on a Zeiss Axiovert 100M microscope using the OpenLab Imaging System and a Chroma Tech filter set optimized for 4',6-diamidino-2-phenylindole, dihydrochloride (DAPI) imaging ($\lambda_{\text{max}}^{\text{ex}}$ 359 nm, $\lambda_{\text{max}}^{\text{em}}$ 461 nm).
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Ring-Opening Polymerization of 1-Methylene-2-phenylcyclopropane Catalyzed by a Pd Complex To Afford Regioregulated Polymers**

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Palladium(II) complexes with N-donor ligands have recently attracted significant interest as a result of their utility as alkene polymerization catalysis.^[1] Strained cyclic olefins such as cyclopropenes and norbornadiene also undergo addition polymerization catalyzed by palladium(II) complexes.^[2] On the other hand, much less effort has been devoted to applying Pd catalysis to polymer synthesis that involves ring opening of the monomer. Herein we report a ring-opening polymerization of 1-methylene-2-phenylcyclopropane that is catalyzed by a Pd complex to give a polymer with a highly

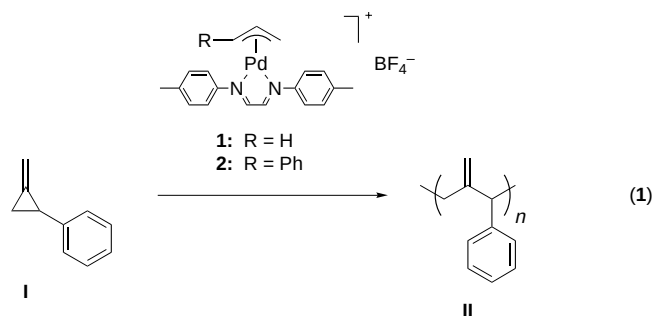
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regulated structure. We also propose a unique mechanism for the polymer chain growth on the basis of detailed studies on the polymerization.^[3]

$[\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{ArN}=\text{CH}-\text{CH}=\text{NAr})]\text{BF}_4$ (**1**: Ar = 4-MeC₆H₄) and $[\text{Pd}(\eta^3\text{-PhCHCHCH}_2)(\text{ArN}=\text{CH}-\text{CH}=\text{NAr})]\text{BF}_4$ (**2**: Ar = 4-MeC₆H₄) catalyze the ring-opening polymerization of 1-methylene-2-phenylcyclopropane (**I**) at 80 °C in acetonitrile to give polymer **II** with the *exo*-methylene group in the repeating unit [Eq. (1)].^[4] The polymer was charac-



terized by means of the ¹H and ¹³C{¹H} NMR spectra shown in Figure 1 a and b. The ¹H NMR signals at δ = 4.3–5.0 and the ¹³C{¹H} NMR signals at δ = 110.6 and 111.2 correspond to the

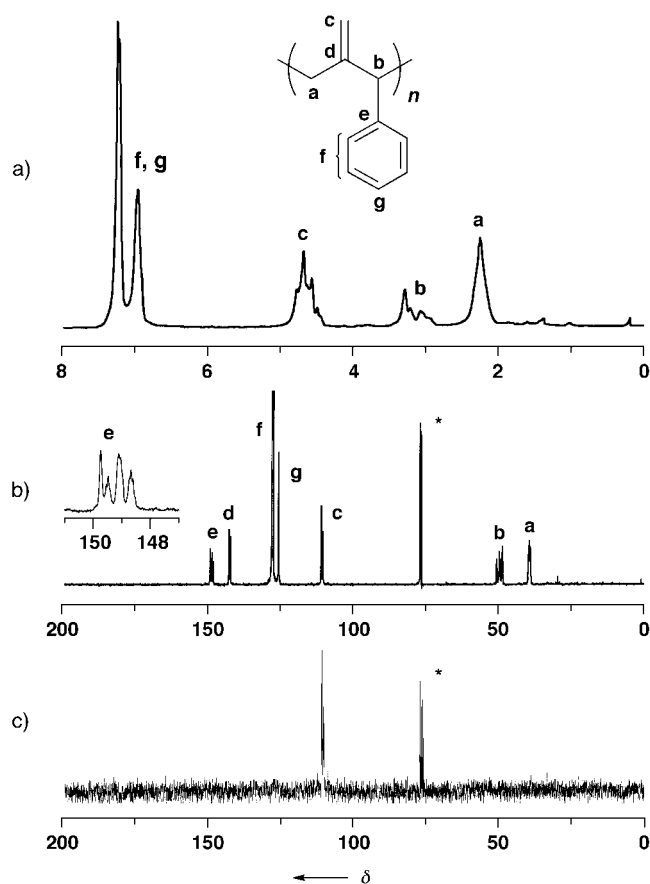
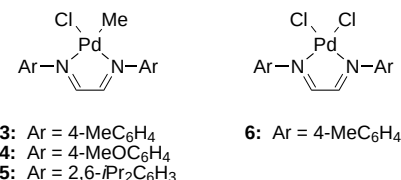


Figure 1. a) ¹H and b) ¹³C{¹H} NMR spectra of **II** in CDCl₃ at 25 °C. The polymerization of 1-methylene-2-phenylcyclopropane (**I**) was carried out in the presence of **1** ([**1**] = 25 mM, [**I**]/[**1**] = 70/1) in CH₃CN at 80 °C (entry 1 in Table 1). c) ¹³C{¹H} NMR spectrum of **II**-¹³C in CDCl₃ at 25 °C. The polymerization conditions are the same as above. Peaks with asterisks in (b) and (c) correspond to the solvent.

hydrogen and the carbon atoms of the =CH₂ group, respectively; the other signals were assigned to the other hydrogen and carbon atoms in the structure.^[5] Signals corresponding to –CH=CR– (R = H, Ph) and the cyclopropyl group, which should exhibit the corresponding signals at δ = 5.5–6.5 and δ = 1.5–0.0, respectively, are entirely absent in the ¹H NMR spectrum. The ¹³C{¹H} NMR signal of the *ipso* carbon atom of the phenyl group appears as four resonances in the range δ = 148.3–150.0. They are assigned to four possible triads (*rr*, *rm*, *mr*, and *mm*) with regard to the chiral benzyl carbon atom in the repeating unit.^[6] A similar poly(styrene-*co*-CO) with a regulated head-to-tail linkage of the monomer units also exhibits four distinct ¹³C{¹H} NMR peaks at δ = 134.8–136.5 for the *ipso* phenyl carbon atom, whereas the polymer with a disordered linkage shows a significantly broadened peak in the same region.^[7] All these NMR data indicate that the produced polymer **II** has a well-regulated head-to-tail sequence of the single repeating unit –CH₂–C(=CH₂)–CH(Ph)–.

The ring-opening polymerization of **I** is also promoted by $[\text{PdCl}(\text{Me})(\text{ArN}=\text{CH}-\text{CH}=\text{NAr})]$ (**3**: Ar = 4-MeOC₆H₄, **4**: Ar = 4-MeC₆H₄, **5**: Ar = 2,6-*i*Pr₂C₆H₃) and by a mixture of



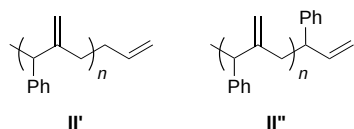
$[\text{PdCl}_2(\text{ArN}=\text{CH}-\text{CH}=\text{NAr})]$ (**6**: Ar = 4-MeC₆H₄) and AgBF₄, whereas $[(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Pd}(\text{PPh}_3)_2]\text{BF}_4$ does not bring about the polymerization. Table 1 summarizes the results of the polymerization of **I**. The produced polymers have molecular weights *M_n* of approximately 5000 with an *M_w*/*M_n* ratio of 1.44–1.54 (gel-permeation chromatography (GPC), polystyrene standards). The polymerization of **I** when catalyzed by a mixture of **6** and AgPF₆ with a [**I**]/[**6**] ratio of 200/1 gives a product having an *M_n* value as high as 11 000 (*M_w*/*M_n* = 1.59). The polymerization of **I** by **3** displays first-order kinetics with respect to the monomer, and has an activation energy *E_a* of 67.6 kJ mol^{–1}.

Table 1. Polymerization of 1-methylene-2-phenylcyclopropane when catalyzed by Pd complexes.^[a]

Entry	Catalyst	Time [h]	Conv [%] ^[b]	<i>M_n</i> ^[c]	<i>M_w</i> / <i>M_n</i> ^[c]
1	1	3	82	4000	1.47
2	2	10	95	5900	1.48
3 ^[d]	3	21	75	4800	1.48
4	4	24	93	5700	1.44
5	5	24	85	4000	1.54
6 ^[e]	6 + AgBF ₄	6	94	5700	1.46
7 ^[e,f]	6 + AgPF ₆	15	89	11 000	1.59
8 ^[e]	^[g]	48	trace	–	–

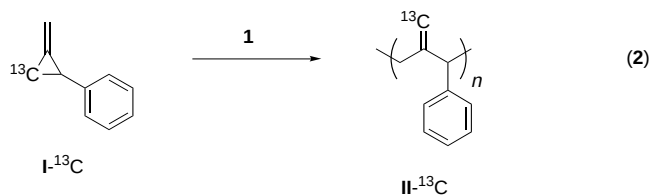
[a] Reaction conditions: [Pd] = 25 mM, [**I**] = 1.8 M, at 80 °C in MeCN unless otherwise stated. [b] Ratio of the consumed monomer to the originally charged monomer. [c] Determined by GPC in THF with polystyrene standards. [d] In *N*-methylpyrrolidinone. [e] [Pd]/[Ag] = 1/3. [f] [Pd] = 25 mM, [**I**] = 5.0 M. [g] $[(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Pd}(\text{PPh}_3)_2]\text{BF}_4$.

The polymerization of **1** by **1** and **2** in a low monomer-to-catalyst molar ratio ($[I]/[Pd] = 20/1$) produces polymers with low molecular weights (**II'** and **II''**, respectively) in quantitative yield. The $^{13}C\{^1H\}$ NMR spectra of **II'** and **II''** contain the



signals of the respective terminal groups, $CH_2=CH-CH_2-$ and $CH_2=CH-CH(Ph)-$.^[8] On the basis of these results, the polymerization is initiated by formation of a C–C bond between the monomer and the allyl group bonded to the Pd ion. The existence of the $CH_2=CH-CH(Ph)-$ terminal group of **II''** and its well-regulated head-to-tail sequence of the repeating unit indicate that insertion of the monomer occurs preferentially into the Pd–CHPh bond of the η^3 -1-phenylallylpalladium species both in the initiation step and in the propagation step of the polymerization.^[9, 10]

The polymerization of 1-methylene-2-phenyl-3- ^{13}C -cyclopropane (**I- ^{13}C**) produces polymer **II- ^{13}C** whose NMR spectra provided the essential information to explain the mechanism of polymer growth [Eq. (2)]. The $^{13}C\{^1H\}$ NMR spectrum of



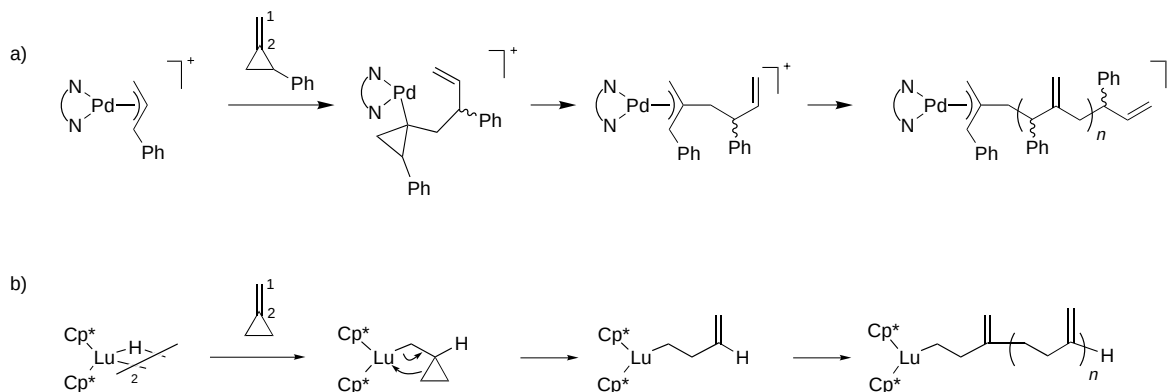
II- ^{13}C (Figure 1 c) shows signals at $\delta = 110.4$ and 110.9 . These signals arise from the ^{13}C -enriched carbon atom and correspond to the $=CH_2$ carbon atom of the polymer. This result indicates selective cleavage of the distal C–C bond of the monomer during the polymerization. Scheme 1 a illustrates a plausible mechanism of the polymerization initiated by **2**. The 2,1-insertion of the monomer into the Pd–CHPh bond of **2** leads to the formation of a cyclopropylpalladium intermediate which undergoes rapid β -alkyl activation,^[11] which leads to

regeneration of a π -allylpalladium complex. Repetition of the above procedure accounts for the smooth polymerization that gives the product in a regulated head-to-tail sequence of monomer units. This polymerization mechanism contrasts that proposed for the metallocene-catalyzed polymerization of methylenecyclopropane (Scheme 1 b), in which polymer growth takes place by repetition of the 1,2-insertion of the monomer into the metal–alkyl bond and subsequent β -alkyl elimination.

In conclusion, we have demonstrated the ring-opening polymerization of 1-methylene-2-phenylcyclopropane catalyzed by a Pd complex to give structurally regulated polymers, and a new mechanism for polymer growth accompanied by ring opening of the monomer. The stable growing polymer end containing a π -allyl–Pd bond is suitable for smooth and selective insertion of the monomers at temperatures as high as $80^\circ C$.

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Scheme 1. Plausible mechanism of the polymerization of methylenecyclopropanes by a) palladium complexes and b) lutenocene complexes.

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Nematic Dendrimers Based on Carbosilazane Cores**

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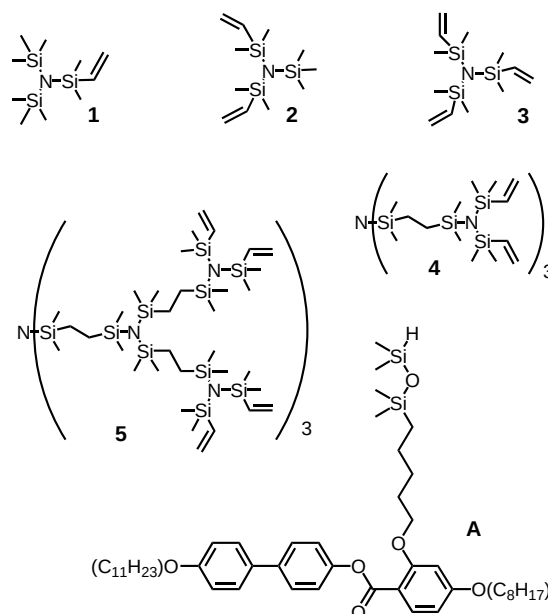
Research on dendritic liquid crystal systems has focused mainly on the investigation of materials that exhibit layered, columnar, cubic-phase structures.^[1, 2] The emphasis has been associated with the chemical structure of these systems, in which a dendritic core and a periphery consisting of functional groups of different chemical composition, which are responsible for self-assembly processes, leads to nanoscopic phase segregation between core and periphery.^[3, 4]

Thus, well-defined dendritic systems that exhibit nematic phase behavior and that are characterized only by orienta-

tional ordering and contain functional groups promoting nanophase separation have attracted considerable interest. The opposing forces of the nematic director field, which are attributed to the peripheral mesogens, and the tendency of the dendritic cores to undergo phase separation should lead to a new class of compounds with interesting properties in the liquid-crystalline (LC) state.^[5]

This structural concept should allow the decoupling of the transition behavior and the ordering of the LC phase from the size of the molecules, which is a long-standing aim of LC polymer research. The materials should additionally be characterized by comparatively low viscosities.

The use of carbosilazane cores **1–5**, which display an overall threefold symmetry and possess a planar central core, allows the synthesis of microphase-separated systems.^[6] The



absence of nucleophilicity in the nitrogen atoms prevents complexation of ionic species in the dendritic core, which is detrimental for most electrooptic applications. Furthermore the use of these comparatively novel compounds, which are closer in structure to synthons applied in nonaqueous sol–gel synthesis of ceramic precursors than to conventional organic materials, is an attractive preparative challenge.

The synthesis of the dendritic and multipodal cores **3** to **5** has been reported earlier and is based on the reaction of the potassium salt of divinyltetramethyldisilazane ($\text{K}[\text{N}(\text{SiMe}_2\text{vinyl})_2]$) with chlorodimethylvinylsilane, which leads to the center of the dendritic system **3** (G_0).^[6] Hydrosilylation of **3** with dimethylchlorosilane and the subsequent reaction with $\text{K}[\text{N}(\text{SiMe}_2\text{vinyl})_2]$ leads to compound **4** (G_1). Repetition of this divergent synthesis allows the preparation of compound **5** (G_2) and higher generation carbosilazane dendrimers, which bear functional vinyl groups at the periphery of the molecules. Compound **2**, which provides access to a dimeric system, was obtained by the reaction $\text{K}[\text{N}(\text{SiMe}_2\text{vinyl})_2]$ with trimethylchlorosilane. The carbosilazane **1**, which was synthesized to complete the homologous series, was obtained by the reaction

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