tography (SiO$_2$, MeOH/CH$_2$Cl$_2$ 1/9) to afford **15** (3.7 mg, 62%). $R_f = 0.14$ (MeOH/CH$_2$Cl$_2$ 1/9); $[\alpha]_D^{25} = -219.1^\circ$ ($c = 0.14$, MeOH); IR (film): $\tilde{\nu} =$ 3278, 3062, 2962, 2928, 2873, 1652, 1492, 1462, 1342, 1248, 1066, 954, 904, 746 cm^{-1}; ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): $\delta = 7.88-7.84$ (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 C$_{40}$H$_{36}$Cl$_2$N$_6$O$_6$ $[M+H]^+$: 767.22, found: 767.34; calcd for C$_{40}$H$_{36}$Cl$_2$N$_6$O$_6$ $[M-H]^-$: 765.20, found: 765.30; HR-MS (FAB) calcd for C$_{40}$H$_{36}$Cl$_2$N$_6$O$_6$ $[M+\mathrm{Li}]$: 773.2233, found: 773.2248.

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[1] a) N. Lindquist, W. Fenical, G. D. Van Duyne, J. Clardy, *J. Am. Chem. Soc.* **1991**, *113*, 2303–2304; b) N. Lindquist, PhD thesis, University of California, San Diego, CA, **1989**; c) C. Petit, *San Francisco Chronicle*, January 31, **1997**, p. A4; d) COMPARE analysis of **1** was completed at the National Cancer Institute (Developmental Therapeutics Program) on December 1, 1997; NSC: D-700089-Y/1. Exp. ID:9712SR87-64; e) W. Fenical, personal communication.

[2] a) J. D. Kreisberg, P. Magnus, E. G. McIver, *Tetrahedron Lett.* **2001**, *42*, 627–629; b) P. Wipf, J. L. Methot, *Org. Lett.* **2001**, *3*, 1261–1264; c) K. C. Nicolaou, S. A. Snyder, K. B. Simonsen, A. E. Koumbis, *Angew. Chem.* **2000**, *112*, 3615–3620; *Angew. Chem. Int. Ed.* **2000**, *39*, 3473–3478; d) D. E. Fuerst, B. M. Stoltz, J. L. Wood, *Org. Lett.* **2000**, *2*, 3521–3523; e) M. C. Bagley, C. J. Moody, A. G. Pepper, *Tetrahedron Lett.* **2000**, *41*, 6901–6904; f) M. C. Bagley, S. L. Hind, C. J. Moody, *Tetrahedron Lett.* **2000**, *41*, 6897–6900; g) F. Lach, C. J. Moody, *Tetrahedron Lett.* **2000**, *41*, 6893–6896; h) E. Vedejs, D. A. Barda, *Org. Lett.* **2000**, *2*, 1033–1035; i) E. Vedejs, J. Wang, *Org. Lett.* **2000**, *2*, 1031–1032; j) P. Magnus, E. G. McIver, *Tetrahedron Lett.* **2000**, *41*, 831–834; k) F. Chan, P. Magnus, E. G. McIver, *Tetrahedron Lett.* **2000**, *41*, 835–838; l) H. C. Hang, E. Drotleff, G. I. Elliott, T. A. Ritsema, J. P. Konopelski, *Synthesis* **1999**, 398–400; m) P. Magnus, J. D. Kreisberg, *Tetrahedron Lett.* **1999**, *40*, 451–454; n) A. Boto, M. Ling, G. Meek, G. Pattenden, *Tetrahedron Lett.* **1998**, *39*, 8167–8170; o) P. Wipf, F. Yokokawa, *Tetrahedron Lett.* **1998**, *39*, 2223–2226; p) T. F. Jamison, PhD thesis, Harvard University, Cambridge, MA, **1997**; q) C. J. Moody, K. J. Doyle, M. C. Elliott, T. J. Mowlem, *J. Chem. Soc. Perkin Trans. 1* **1997**, *16*, 2413–2419; r) J. P. Konopelski, J. M. Hottenroth, H. M. Oltra, E. A. Véliz, Z. C. Yang, *Synlett* **1996**, 609–611; s) C. J. Moody, K. J. Doyle, M. C. Elliott, T. J. Mowlem, *Pure Appl. Chem.* **1994**, *66*, 2107–2110.

[3] a) X. Chen, L. Esser, P. G. Harran, *Angew. Chem.* **2000**, *112*, 967–970; *Angew. Chem. Int. Ed.* **2000**, *39*, 937–940; b) S. Jeong, X. Chen, P. G. Harran, *J. Org. Chem.* **1998**, *63*, 8640–8641.

[4] The phenolic oxidation of **2** shown in Scheme 1 is the most efficient identified. Ether **3** is also produced on treatment with di-μ-hydroxo-bis[(*N*,*N*,*N'*,*N'*-tetramethyl-ethylenediamine)copper(II)] chloride (TCI America) under an O$_2$ atmosphere and with various peroxidase isoforms in buffered media. Other oxidants examined (for example, Fe^{III}, V^{V}, Pb^{IV}, Tl^{III}) provide dimers and/or intractibles. Among the possible two-electron oxidation products of **2**, two are regioisomeric (single atropisomers) D/E biaryls (namely, *ortho–ortho* and/or *ortho–para* coupling). Neither has been convincingly detected in an oxidation of **2**.

[5] L. Zhu, R. M. Wehmeyer, R. D. Rieke, *J. Org. Chem.* **1991**, *56*, 1445–1453.

[6] Models of a macrolactam conformer paralleling that observed in the X-ray structure of a relative (ref. [3a]) indicate destabilizing nonbonded interactions between the benzyl ether of the F-ring and the C11 acetoxy substituent in (11*R*)-**6**.

[7] Chlorination of **7** causes a downfield shift of C25-H which, in the ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **8**, remains coupled ($\delta = 7.66$, $J = 2.8$ Hz) to an exchangeable (D$_2$O) signal at $\delta = 8.41$ (indole NH). The chlorine content of **8** and **9** was ascertained by mass spectrometry.

[8] Similar observations have been made in a model study by Magnus and McIver (ref. [2j]).

[9] For an early synthetic application of related methodology, see: S. L. Schreiber, H. V. Meyers, *J. Am. Chem. Soc.* **1988**, *110*, 5198–5200.

[10] Passage of **14** through silica generates trace (5–10%) by-products tentatively assigned as C10 epimers of **14c** (by mass spectrometry). This problem is magnified with hydrogenolyzed samples of crude **14**. By reducing the benzyl carbamate of **14** net deformylation is avoided only under conditions of transfer hydrogenation in neutral phosphate buffer containing excess Mg^{2+} ions. The crude product cannot be purified or adequately characterized.

[11] Crude samples of **14** also perform in this assay (GI$_{50} \approx 5$ μM). 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 (λ_{max}^{ex} 348 nm, λ_{max}^{em} 438 nm, $\varepsilon = 7960$ 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 (λ_{max}^{ex} 359 nm, λ_{max}^{em} 461 nm).

[14] For a seminal demonstration of ML$_n$ (M = Ti, Zr, V)/alkyl hydroperoxide oxidations of phenols and naphthols, see: K. Krohn, H. Rieger, K. Khanbabaee, *Chem. Ber.* **1989**, *122*, 2323–2330.

[15] Preliminary results for treatment of **17** with lanthanide triflates are encouraging. We are now working through issues of product autooxidation, handling, and stability of both **17** and "**18**", as well as conclusive structural assignments. Details will be provided in a forthcoming full article.

[16] W. S. McIntire, D. E. Wemmer, A. Chistoserdov, M. E. Lidstrom, *Science* **1991**, *252*, 817–823.

Ring-Opening Polymerization of 1-Methylene-2-phenylcyclopropane Catalyzed by a Pd Complex To Afford Regioregulated Polymers[**]

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Kohtaro Osakada[*]

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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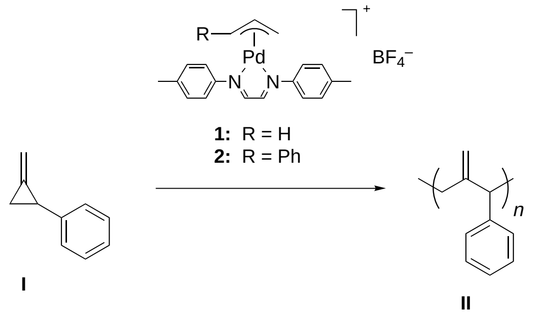
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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

[Pd(η^3-CH$_2$CHCH$_2$)(ArN=CH–CH=NAr)]BF$_4$ (**1**: Ar = 4-MeC$_6$H$_4$) and [Pd(η^3-PhCHCHCH$_2$)(ArN=CH–CH=NAr)]-BF$_4$ (**2**: Ar = 4-MeC$_6$H$_4$) 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 characterized by means of the ^{1}H and ^{13}C{^{1}H} NMR spectra shown in Figure 1 a and b. The ^{1}H NMR signals at $\delta = 4.3-5.0$ and the ^{13}C{^{1}H} NMR signals at $\delta = 110.6$ and 111.2 correspond to the hydrogen and the carbon atoms of the =CH$_2$ 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 $\delta = 5.5-6.5$ and $\delta = 1.5-0.0$, respectively, are entirely absent in the ^{1}H NMR spectrum. The ^{13}C{^{1}H} NMR signal of the *ipso* carbon atom of the phenyl group appears as four resonances in the range $\delta = 148.3-150.0$. 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 ^{13}C{^{1}H} NMR peaks at $\delta = 134.8-136.5$ 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 –CH$_2$–C(=CH$_2$)–CH(Ph)–.



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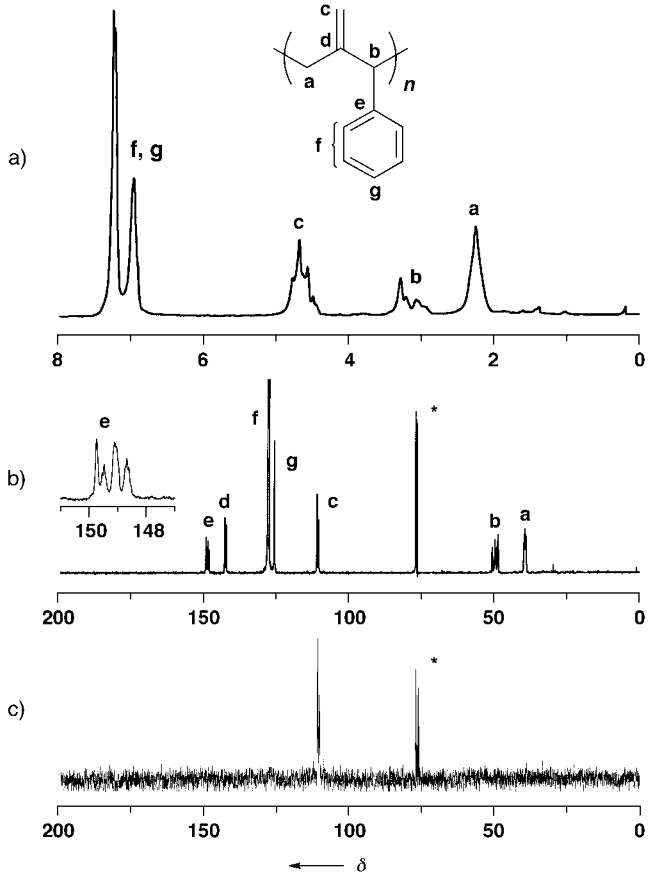


Figure 1. a) ^{1}H and b) ^{13}C{^{1}H} NMR spectra of **II** in CDCl$_3$ at 25 °C. The polymerization of 1-methylene-2-phenylcyclopropane (**I**) was carried out in the presence of **1** ([**1**] = 25 mM, [**I**]/[**1**] = 70/1) in CH$_3$CN at 80 °C (entry 1 in Table 1). c) ^{13}C{^{1}H} NMR spectrum of **II**-^{13}C in CDCl$_3$ at 25 °C. The polymerization conditions are the same as above. Peaks with asterisks in (b) and (c) correspond to the solvent.

The ring-opening polymerization of **I** is also promoted by [PdCl(Me)(ArN=CH–CH=NAr)] (**3**: Ar = 4-MeOC$_6$H$_4$, **4**: Ar = 4-MeC$_6$H$_4$, **5**: Ar = 2,6-(iPr)$_2$C$_6$H$_3$) and by a mixture of [PdCl$_2$(ArN=CH–CH=NAr)] (**6**: Ar = 4-MeC$_6$H$_4$) and AgBF$_4$, whereas [(η^3-CH$_2$CHCH$_2$)Pd(PPh$_3$)$_2$]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 AgPF$_6$ with a [**I**]/[**6**] ratio of 200/1 gives a product having an M_n value as high as 11000 ($M_w/M_n = 1.59$). 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}.

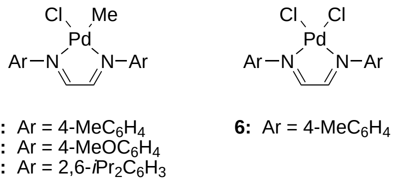
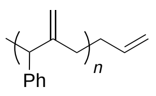


Table 1. Polymerization of 1-methylene-2-phenylcyclopropane when catalyzed by Pd complexes.[a]

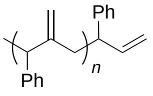
Entry	Catalyst	Time [h]	Conv [%][b]	M_n[c]	M_w/M_n[c]
1	**1**	3	82	4000	1.47
2	**2**	10	95	5900	1.48
3[d]	**3**	21	75	4800	1.48
4	**4**	24	93	5700	1.44
5	**5**	24	85	4000	1.54
6[e]	**6** + AgBF$_4$	6	94	5700	1.46
7[e,f]	**6** + AgPF$_6$	15	89	11000	1.59
8[e]	[g]	48	trace	–	–

[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] [(η^3-CH$_2$CHCH$_2$)Pd(PPh$_3$)$_2$]BF$_4$.

The polymerization of **I** by **1** and **2** in a low monomer-to-catalyst molar ratio ($[\mathbf{I}]/[\mathbf{Pd}] = 20/1$) 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]

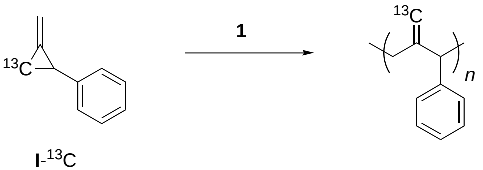


II'



II"

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 1c) 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 1a 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 1b), 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.



I-^{13}C **II**-^{13}C (**2**)

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 °C.

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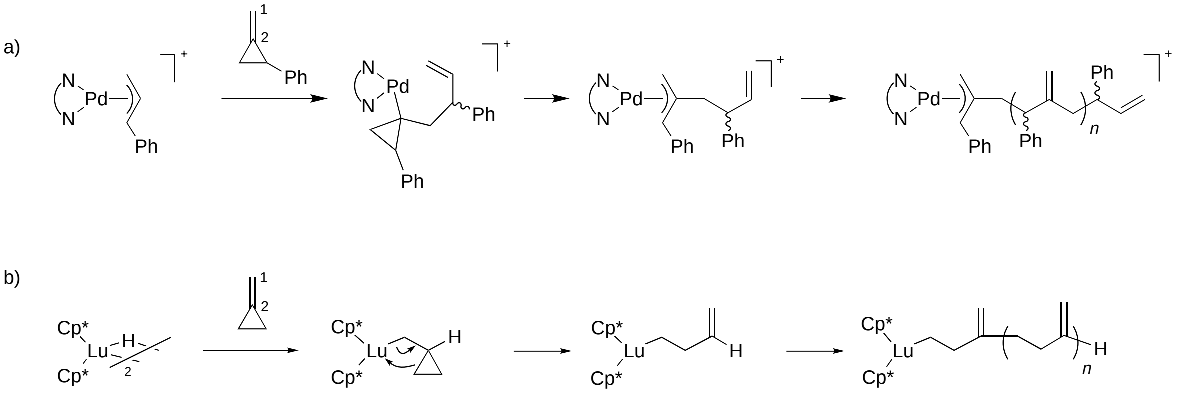

Scheme 1. Plausible mechanism of the polymerization of methylenecyclopropanes by a) palladium complexes and b) lutenocene complexes.

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[1] a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1203; b) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; c) S. Mecking, *Coord. Chem. Rev.* **2000**, *203*, 325–351; d) A. C. Gottfried, M. Brookhart, *Macromolecules* **2001**, *34*, 1140–1142; e) D. J. Tempel, L. K. Johnson, R. L. Huff, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* **2000**, *122*, 6686–6700.

[2] a) S. Rush, A. Reinmuth, W. Risse, J. O'Brien, D. R. Ferro, I. Tritto, *J. Am. Chem. Soc.* **1996**, *118*, 12230–12231; b) C. Mehler, W. Risse, *Macromolecules* **1992**, *25*, 4226–4228.

[3] Electrophilic metallocene cations of Zr and Lu were found to promote the ring-opening polymerization of unsubstituted methylenecyclopropane, where the produced polymer was furnished with vinylidene groups or polyspiropyrane depending on the catalyst: a) X. Yang, A. L. Jia, T. J. Marks, *J. Am. Chem. Soc.* **1993**, *115*, 3392–3393; b) L. Jia, X. Yang, A. M. Seyam, I. D. L. Albert, P.-F. Fu, S. Yang, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 7900–7913.

[4] Details of synthesis and physical data of the polymers are available in the Supporting Information.

[5] Selected NMR data of the structurally related compound $PhCH_2C({=}CH_2)CH_2CH_3$: ^1H NMR ($CDCl_3$): $\delta = 1.99$ (q, 2H, CH_2Me), 3.36 (s, 2H, $PhCH_2$), 4.78 (dd, 2H, $C{=}CH_2$), 7.18–7.29 (m, 5H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 28.1$ (CH_2Me), 43.2 ($PhCH_2$), 109.8 ($C{=}CH_2$), 125.3(*p*-Ph), 128.2–128.9 (*o*, *m*-Ph), 139.9 (*C*=CH_2), 150.6 (*ipso*-Ph).

[6] The four $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR signals corresponding to the triads did not show any significant difference in their relative peak intensity, which suggests that the polymerization is not stereoselective.

[7] A. Aeby, A. Gsponer, G. Consiglio, *J. Am. Chem. Soc.* **1998**, *120*, 11000–11001.

[8] $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR data ($\mathrm{CDCl_3}$) of the terminal groups: **II′**: $\delta = 138.4$ ($\mathrm{CH_2{=}}$), 114.4 ($\mathrm{{=}CH{-}}$), 34.1 ($\mathrm{CH_2}$); **II″**: $\delta = 141.7$ ($\mathrm{CH_2{=}}$), 114.3 ($\mathrm{{=}CH{-}}$), 47.8 (CHPh). The signals were assigned by comparison of the positions with those of $\mathrm{CH_2{=}CHCHPhCH_3}$ and *trans*-$\mathrm{PhCH{=}CHCH_2CH_3}$.

[9] The formation of π-allyl–Pd species by the insertion of methylenecyclopropanes into H–Pd bonds has been proposed to account for results of coupling reactions of methylenecyclopropanes with malonates or amines when catalyzed by a Pd complex; see N. Tsukada, A. Shibuya, I. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **1997**, *119*, 8123–8124.

[10] The reaction of a 1,3-diene with π-allyl–Pd complexes was also reported to cause formation of a C–C bond between a vinyl carbon atom of the diene and a sterically hindered π-allyl carbon atom of the complex; see R. P. Hughes, J. Powell, *J. Am. Chem. Soc.* **1972**, *94*, 7723–7732. Their results may be accounted for by assuming a 2,1-insertion of a double bond of butadiene into the more sterically hindered Pd–C bond of the π-allylpalladium complex, although they suggested another kind of mechanism at that time.

[11] a) L. Resconi, F. Piemontesi, G. Franciscono, L. Abis, T. Fiorani, *J. Am. Chem. Soc.* **1992**, *114*, 1025–1032; b) Z. Guo, D. C. Swenson, R. F. Jordan, *Organometallics* **1994**, *13*, 1424–1432; c) B. C. Ankianiec, V. Christou, D. T. Hardy, S. K. Thomson, G. B. Young, *J. Am. Chem. Soc.* **1994**, *116*, 9963–9978; d) T. C. Flood, J. A. Statler, *Organometallics* **1984**, *3*, 1795–1803.

Nematic Dendrimers Based on Carbosilazane Cores[**]

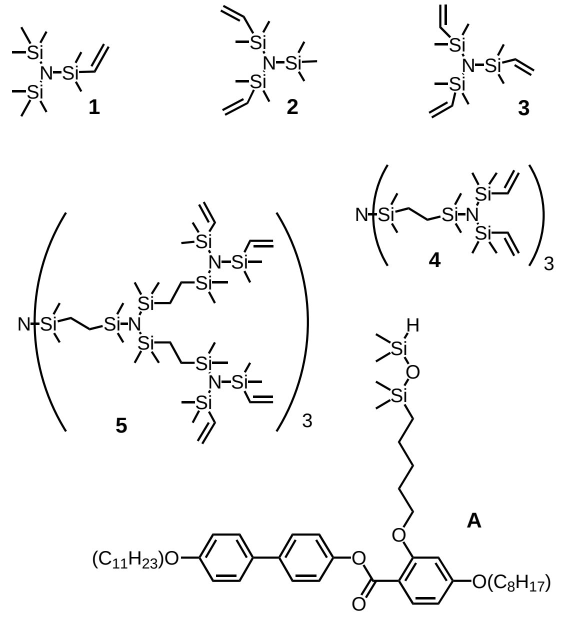
Ralf Elsäßer, Georg H. Mehl,[*] John W. Goodby, and Michael Veith

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 orientational 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 ($\mathrm{K[N\{SiMe_2vinyl\}_2]}$) 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 $\mathrm{K[N\{SiMe_2vinyl\}_2]}$ 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 $\mathrm{K[N\{SiMe_2vinyl\}_2]}$ with trimethylchlorsilane. The carbosilazane **1**, which was synthesized to complete the homologous series, was obtained by the reaction

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