Synthesis of Block Copolymers Containing Pendant Carbazole Groups via Living Ring-Opening Metathesis Polymerization

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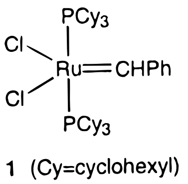
ABSTRACT: A new carbazole-functionalized norbornene derivative, 5-[methylbis(*N*-carbazolyl)silyl]-2-norbornene, was polymerized via living ring-opening metathesis polymerization (ROMP) with $RuCl_2(=CHPh)(PCy_3)_2$. The resulting polymer was of high molecular weight and had a reasonably narrow molecular weight distribution (M_n = 57 000, M_w/M_n = 1.26). Block copolymers of the carbazole-functionalized monomer and a TMS-protected alcohol-functionalized norbornene derivative were also prepared using ROMP techniques. Microphase separation and selective reaction of the alcohol-functionalized domains with $CdMe_2$ were observed by TEM. The UV−visible absorption spectra and fluorescence emission spectra of the polymers were similar to those of poly(*N*-vinylcarbazole).

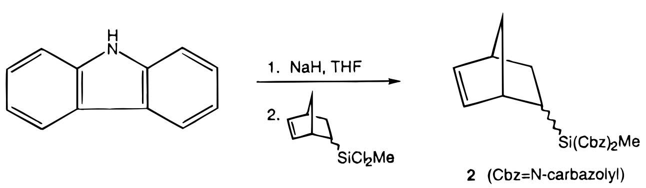
Introduction

Polymers that contain pendant carbazole groups exhibit many interesting properties, such as photoconductivity and photorefractivity.[1,2] They also serve as efficient hole-transport materials when injected with externally generated charge carriers and thus have potential applications in certain optoelectronic devices such as organic light-emitting diodes.[3,4] Recently, carbazole-functionalized norbornene derivatives were polymerized by at least two research groups using classical, nonliving olefin metathesis catalysts such as $RuCl_3$ and $RuCl_2(PPh_3)_3$.[5,6] The resulting homopolymers were reported to exhibit interesting properties, but control over the molecular weight and molecular weight distribution was poor, and block copolymers could not be obtained. In the present study, a well-defined ruthenium complex (**1**) recently described by Grubbs *et al.*[7] was used to prepare low-polydispersity homopolymers of a new carbazole-functionalized norbornene derivative (**2**), which can be conveniently synthesized in one step from commercially available starting materials (Scheme 1). The polymerization proceeds in a living fashion, and the molecular weight can be regulated easily by changing the ratio of catalyst to monomer. Block copolymers of **2** with the protected alcohol **3** were also prepared (Scheme 2), and the polymers were hydrolyzed to remove the protecting group. These latter materials are of special interest since it has already been shown that microphase-separated block copolymers with protic functional groups are useful templates in the synthesis of semiconducting metal sulfide nanoclusters.[8−10] Thus, with the development of a carbazole-functionalized block copolymer, it should now be possible to form such clusters within a charge-transporting polymer matrix. The resulting materials are expected to exhibit novel optoelectronic properties that should be of use in a variety of practical applications.

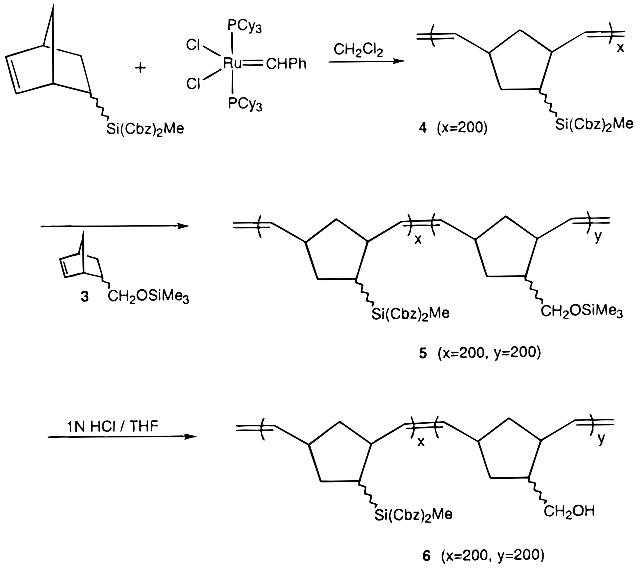

$RuCl_2(=CHPh)(PCy_3)_2$

1 (Cy=cyclohexyl)

Scheme 1



Scheme 2



Experimental Section

Materials. All chemicals were used as received without purification unless otherwise noted. Sodium hydride (dry), carbazole, trimethylchlorosilane, and 5-norbornene-2-methanol (mixture of *endo* and *exo*) were purchased from Aldrich. Bicyclohepten-5-ylmethyldichlorosilane (mixture of *endo* and *exo*) was purchased from Gelest. Bis(tricyclohexylphosphine)-

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benzylideneruthenium dichloride (**1**) and dimethylcadmium were purchased from Strem. All solvents were commercial reagent or anhydrous grade products and were used without degassing or drying.

Synthesis of 5-[Methylbis(*N*-carbazolyl)silyl]-2-norbornene (2). Carbazole (16.2 g, 97 mmol, recrystallized from toluene) was dissolved in anhydrous tetrahydrofuran (THF, 200 mL) and added dropwise under nitrogen to a stirred suspension of dry sodium hydride (2.32 g, 97 mmol), also in anhydrous THF (50 mL). A moderately vigorous evolution of hydrogen gas ensued, and the mixture was refluxed for 2 h to ensure complete deprotonation. The resulting dark blue-green solution was allowed to cool, and bicyclohepten-5-ylmethyldichlorosilane (10.0 g, 48 mmol) was added neat over the course of a few minutes. A mildly exothermic reaction immediately took place, and the mixture turned a creamy off-white in color. The mixture was refluxed for an additional 2 h, stirred overnight at room temperature, and quenched by the cautious addition of methanol (5 mL). THF was then removed under vacuum, and the residue was taken up in 200 mL of CH_2Cl_2. The mixture was filtered to remove insoluble byproducts (mainly NaCl and unreacted carbazole), the CH_2Cl_2 was removed under vacuum, and the crude product was recrystallized from acetone (approximately 150 mL; product is slow to dissolve) to yield 12.4 g (55%) of **2** as a white solid, mp 192−194 °C. This material was sufficiently pure for polymerization. ^{1}H NMR (CD_2Cl_2) (Figure 1): δ 0.0−3.6 (Si−CH_3 and nonolefin norbornene protons, 10 H), 5.5−6.5 (olefin norbornene protons, 2 H), 6.8−8.3 (carbazole protons, 16 H). Anal. Calcd for $C_{32}H_{28}N_2Si$: C, 82.0; H, 6.0; N, 6.0; Si, 6.0. Found: C, 81.0; H, 5.9; N, 5.9; Si, 6.6.

Synthesis of 5-[(Trimethylsiloxy)methyl]-2-norbornene (3). Compound **3** was prepared by R. T. Clay via the reaction of 5-norbornene-2-methanol with trimethylchlorosilane and pyridine in diethyl ether, according to a previously published procedure.[11] The product was obtained as a slightly viscous light yellow oil.

Polymerization Procedure. A stock solution of **1** was prepared by dissolving 15 mg of catalyst in 5 mL of anhydrous CH_2Cl_2 inside a nitrogen-filled drybox. The resulting dark purple solution was stored in the drybox freezer at −35 °C until further use. Nonanhydrous solvent could also be used, with essentially identical results. In a typical polymerization, monomer **2** (170 mg, 200 equiv) was dissolved in 4.5 mL of CH_2Cl_2, and 0.5 mL of catalyst solution was added. The light pink solution was then stirred inside the drybox for 2 h at room temperature. For homopolymers, the reaction was terminated by the addition of a small amount of ethyl vinyl ether (100 μL). For block copolymers, monomer **3** (72 mg, 200 equiv) was added neat to the still-living reaction mixture and the solution was stirred for an additional 1 h before terminating as described above. The color of the solution changed from pink to yellow when either the terminating agent or monomer **3** was added. After termination, the solution was stirred for an additional 5 min and taken out of the drybox, and the polymer was precipitated in excess methanol (50 mL) and dried overnight in a vacuum oven at room temperature. The polymers were obtained as powdery or fluffy white solids in 80−85% yield. Block copolymer **5** was hydrolyzed by adding 0.95 mL of THF and 0.05 mL of 1 N HCl (aq) to 30 mg of polymer and allowing the mixture to stand at room temperature for 2 h, by which time nearly complete solution had been achieved. The polymer was then precipitated in excess methanol (10 mL) and dried overnight in a vacuum oven at room temperature to give a flaky white solid in essentially quantitative yield. The polymers were characterized by ^{1}H NMR (Figures 1 and 3).

Characterization. ^{1}H NMR spectra were recorded on a Bruker WM-250 nuclear magnetic resonance spectrometer. Gel permeation chromatography (GPC) was carried out on a series of three Waters Styragel HR4 columns equipped with a Waters 510 HPLC pump and a Waters 410 differential refractometer, using polystyrene calibration standards and THF as the eluent at a flow rate of 1.0 mL/min. Transmission electron microscopy (TEM) was performed on a JEOL 200CX instrument operating at 200 kV. UV−visible absorption spectra and fluorescence emission spectra were recorded on a Cary 5E spectrophotometer and a SPEX Fluorolog spectrophotometer, respectively. Elemental analyses were performed by Galbraith Laboratories of Knoxville, TN.

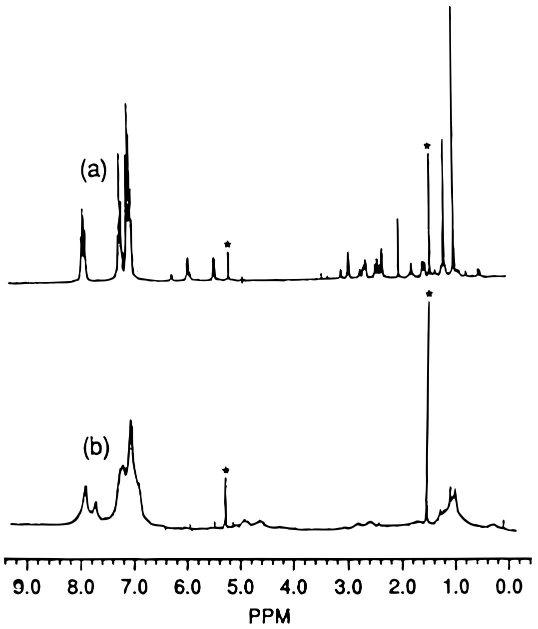

Figure 1. 250 MHz ^{1}H NMR spectra taken in CD_2Cl_2 at 25 °C: (a) monomer **2**; (b) homopolymer **4**. Starred peaks are due to solvent or dissolved water.

Results and Discussion

The synthesis of monomer **2** proceeded smoothly despite the seemingly high degree of steric crowding in the product, lending credence to an earlier report that two or even three carbazole groups can comfortably fit around a central silicon atom.[12] The Si−N bonds showed no tendency to hydrolyze under ambient conditions, also in accord with earlier observations.[12] This is probably due in part to steric factors and in part to the low basicity of the carbazole nitrogen, which forms part of a Hückel-stabilized aromatic system and hence is not easily protonated.[13]

The polymerization of **2** was also observed to proceed smoothly, affording homopolymer **4** in high yield. The ^{1}H NMR spectra of both the monomer and the polymer are shown for comparison in Figure 1. The broadening of the resonances in the latter is due mainly to the decreased conformational mobility of the bulky polymer chains, while the upfield shift of the olefin resonances is due to the opening of the highly strained norbornene ring. Integration of the aromatic and olefin regions of the spectrum gives the expected 8:1 ratio, providing further confirmation of the polymer structure.

An analysis of the reaction mixture by GPC revealed the presence of both unreacted monomer and polymer after 1 h. The polymerization was essentially complete by 2 h, with the polymer peak shifting to higher molecular weight and the monomer peak diminishing in area to about 10% of its initial value. The apparent value of the molecular weight (M_n = 57 000) was somewhat lower than the stoichiometrically calculated value due to the use of a polystyrene calibration, while the molecular weight distribution was relatively narrow (M_w/M_n = 1.26), as expected for a living polymerization (Table 1). The molecular weight distribution would have been even narrower were it not for the presence of a small amount (~15%) of exceptionally high molec-

Table 1. Molecular Weight Data for Carbazole-Containing ROMP Polymers and Block Copolymers[a]

polymer	M_n (calculated)	M_n (observed)	M_w/M_n	$(M_w/M_n)^b$
4	94 000	57 000	1.26	(1.05, 1.09)
5	133 000	134 000	1.22	(1.13, 1.07)
6	118 000	104 000	1.46	(1.08, 1.25)

[a] Determined by GPC using polystyrene calibration standards. [b] Individual PDI's of main polymer peak and double-MW peak.

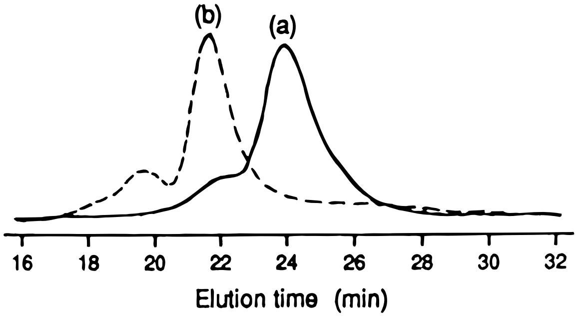

Figure 2. GPC elution profiles (taken in THF at a flow rate of 1.0 mL/min): (a) homopolymer **4**; (b) block copolymer **5**.

ular weight material, which occurred at exactly twice the molecular weight of the main polymer peak (Figure 2). High molecular weight material of this sort has been observed previously[14] in polymerizations catalyzed by an analog of **1** and may possibly be due to some sort of polymer coupling reaction.

The living nature of the polymerization was demonstrated by adding a small amount of monomer **3** to the unterminated reaction mixture to form a block copolymer, which showed a clear increase in molecular weight relative to the homopolymer and also possessed a narrow molecular weight distribution ($M_n = 134\ 000$, $M_w/M_n = 1.22$). ^{1}H NMR analysis of the block copolymer showed a number of additional peaks in the olefin and aliphatic regions of the spectrum due to the presence of the second block, including a relatively sharp, intense peak at 0.1 ppm arising from the nine equivalent protons of the trimethylsilyl group (Figure 3). Integration of the olefin region of the block copolymer spectrum showed that the two blocks had approximately equal degrees of polymerization, in accord with the employed reaction stoichiometry.

The hydrolysis of block copolymer **5** was carried out under acidic conditions to remove the trimethylsilyl protecting groups from the polymer and unmask the alcohol functionalities. Analysis of the hydrolyzed product **6** by ^{1}H NMR showed that removal of the trimethylsilyl group was nearly quantitative, while the Si−N bonds remained intact. The GPC trace showed a clear decrease in polymer molecular weight, consistent with loss of the bulky trimethylsilyl group. The molecular weight distribution also appeared to broaden somewhat ($M_w/M_n = 1.46$), possibly as a result of some sort of aggregation phenomenon caused by hydrogen bonding interactions between the free hydroxyl groups of the polymer chains. Attempts to prepare block copolymer **6** in a more direct fashion by polymerization of the unprotected alcohol were unsuccessful, apparently as a result of catalyst deactivation. This was somewhat surprising, as catalyst **1** is known to be exceptionally tolerant of alcohols and carbonyl-containing compounds, but it has also been reported that at least some of these functional groups are less well-tolerated when present as *endo*-norbornenyl substituents, perhaps as the result of an intramolecular geometry favorable to chelation.[14]

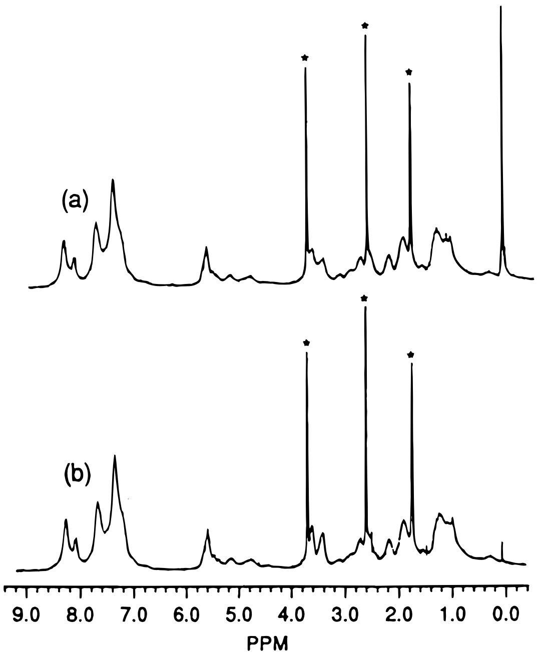

Figure 3. 250 MHz ^{1}H NMR spectra taken in THF-d_8 at 25 °C: (a) TMS-protected block copolymer **5**; (b) deprotected block copolymer **6**. Starred peaks are due to solvent or dissolved water.

Polymers **4**−**6** were all highly soluble in common organic solvents such as THF and pyridine, with complete dissolution generally being achieved in a matter of minutes for solution concentrations of a few weight percent. Polymer **4** was also soluble in chlorobenzene and chloroform, although the block copolymers merely swelled in these solvents. The polymers could be spin-coated onto glass slides from chlorobenzene solution (or a 1:1 mixture of THF and chlorobenzene in the case of **5** and **6**) to yield tough, adherent, optically clear films approximately 1000 Å thick. Free-standing bulk films (approximately 0.1 mm thick) could also be prepared by slow static casting from THF in a Teflon-lined cup; the films were either tough and slightly flexible (polymer **5**) or rigid and somewhat brittle (polymers **4** and **6**). Visual observation of a small piece of bulk film under an optical microscope equipped with a hot stage revealed that polymer **4** underwent a distinct transition to a liquid-like state in the vicinity of 175−225 °C when heated at a rate of 10−20 °C/min. This event is presumably a glass transition but is somewhat difficult to study, as a thermally initiated cross-linking reaction of the double bonds in the polymer backbone appears to take place simultaneously over the same temperature range. The cross-linked material is insoluble in THF and other solvents and does not exhibit an obvious transition when heated a second time. A saturated analog of polymer **4** (prepared by stoichiometric hydrogenation of the polymer backbone with diimide, using a general method[15] which has been previously described) did not display any evidence of cross-linking and remained soluble even after heating to 300 °C.

The UV−visible absorption spectra and fluorescence emission spectra of the spin-coated polymer films were recorded and were similar in appearance to the spectra of other carbazole-containing polymers such as poly(*N*-vinylcarbazole) (PVK). Block copolymer **5** showed four distinct UV absorption maxima characteristic of the

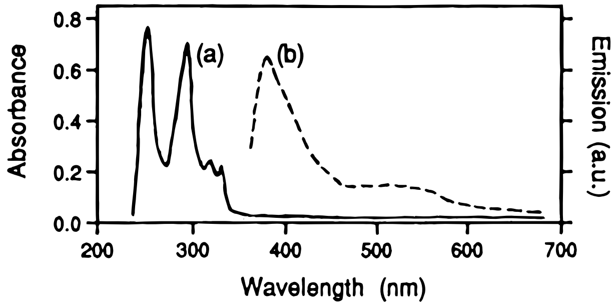

Figure 4. Optical properties of a spin-coated thin film of block copolymer **5**: (a) UV−visible absorption spectrum; (b) fluorescence emission spectrum (330 nm excitation).

carbazole group at 254, 294, 316, and 328 nm, and also exhibited a strong carbazole fluorescence, with peak emission occurring in the near-UV at approximately 385 nm and extending into the blue−violet region of the spectrum (Figure 4). A low-level emission observed at higher wavelengths is probably due to excimer formation. The spectra of polymers **4** and **6** (not shown) were nearly identical to those of **5**, indicating that the electronic structure of the carbazole group is not greatly perturbed by the presence or absence of the second block. The general similarity of the observed spectra to those of PVK suggests also that neither (1) variation in the chemical structure of the polymer backbone nor (2) substitution of silicon for carbon at the carbazole nitrogen has much of an effect upon the electronic structure of the carbazole group. These results are encouraging, insofar as they suggest that the optoelectronic and charge transport properties of the polymers reported here may not be too different from those of better-studied polymers such as PVK.

Microphase separation in the block copolymers was observed by TEM, using bulk films which were stained by exposure to $CdMe_2$ vapor overnight, pumped down under vacuum, and microtomed into sections approximately 500 Å thick. Block copolymer **5** displayed a lamellar morphology, while block copolymer **6**, in which the second block constituted a much smaller volume fraction of the sample due to removal of the bulky trimethylsilyl groups, displayed a spherical morphology (Figure 5). The high degree of contrast visible in these micrographs indicates that preferential incorporation of cadmium into the alcohol and silyl ether-containing domains is taking place (presumably by the direct reaction of $CdMe_2$ with these groups to form a bound metal alkoxide and either methane or tetramethylsilane); irreversibly strong dative binding between $CdMe_2$ and the carbazole nitrogen appears not to occur, in accord with the aforementioned low basicity of the carbazole group.[16] The synthesis of CdS nanoclusters spatially confined within the microdomains of these carbazole-containing block copolymers is currently in progress and will be reported elsewhere.

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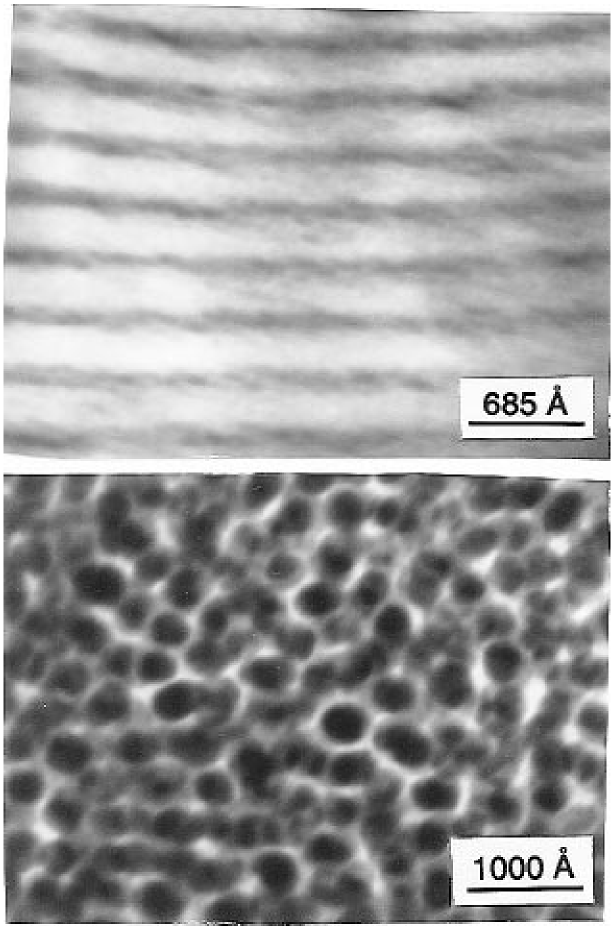

Figure 5. TEM micrographs of $CdMe_2$-stained block copolymers: (a) block copolymer **5**; (b) block copolymer **6**.

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(16) Further evidence of the very low coordinating ability of the carbazole nitrogen comes from solution-state studies. A 3 wt % solution of homopolymer **4** in THF undergoes no change when treated with excess $CdMe_2$, whereas a solution of block copolymer **6** gels completely within 4−6 h, presumably as a result of the formation of oxygen−cadmium−oxygen bridges or cross-links. The lack of gelation in the homopolymer suggests that analogous bridges involving the carbazole nitrogens do not occur.

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