## Step-Growth Polymerization

Polyaddition and Polycondensation Reactions of (2-Furyl)carbenoid as Step-Growth Polymerization Strategies: Synthesis of Furylcyclopropane- and Furfurylidene-Containing Polymers\*\*

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Polymerizations catalyzed by a transition-metal–carbene complex, such as ring-opening-metathesis polymerization (ROMP, Figure  $1 a)^{[1]}$  and acyclic-diene-metathesis polymer-

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[\*\*] We would like to thank Professor Yoshiki Chujo, Dr. Kensuke Naka, and Mr. Tomokazu Umeyama for their assistance with the gel permeation chromatographic and fluorescence spectroscopic analysis, as well as their helpful discussions. This work was supported by a Grant-in-Aid from a 21st Century COE program of a United Approach to New Materials Science from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. Financial support by Scientific Research from the Japan Society for the Promotion of Science is gratefully acknowledged.

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

Angew. Chem. Int. Ed. 2004, 43, 1857-1860

DOI: 10.1002/anie.200352949

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*Figure 1.* Schematic representation of transition-metal-catalyzed metathesis polymerization.

ization (ADMET, Figure 1b),<sup>[2]</sup> have generated great excitement in recent years because of their wide applicability to the synthesis of various alkene-containing polymers. The mechanisms of these chain-growth and step-growth metathesis reactions of these polymerizations require the involvement of a carbenoid species in the catalytic cycle. Herein, we report on transition-metal-catalyzed polyaddition (Figure 2 a) and poly-



*Figure 2.* Schematic representation of transition-metal-catalyzed polyadditions and polycondensations using carbenoid intermediates.

condensation reactions (Figure 2b) as new step-growth polymerization strategies that do not involve metathesis catalysts. Instead the intermediate is a metal carbenoid generated from a carbenoid trigger embedded in the monomer. This method uses a new class of monomer that contains both a carbenoid donor and acceptor and yields alternating copolymers containing cyclopropanes or alkenes.

We previously reported the formation of (2-furyl)carbenoid **2** from enyne ketone **1a** with Group 6 transition-metal complexes,<sup>[3]</sup> and its application to the catalytic cyclopropanation of various alkenes leading to (2-furyl)cyclopropanes (Scheme 1).<sup>[4]</sup> Our studies focused on catalytic reactions



**Scheme 1.** Catalytic cyclopropanation using an in situ generated (2-furyl)carbenoid.

involving (2-furyl)carbenoids, which led us to discover new carbene-transfer polymerizations of enyne ketones that had suitable functionalities to act as carbenoid acceptors.

We examined the synthesis of polymers containing furyl and cyclopropane groups using a catalytic cyclopropanation reaction. When an enyne ketone **1b** with a vinyl group at the *ortho* position of the phenyl ring was treated in  $CH_2Cl_2$  in the presence of a catalytic amount of [{Rh(OAc)\_2}] at room temperature, the reaction immediately afforded the (2furyl)cyclopropane-containing polymer **3b** as a yellow powder (Scheme 2). The yield was 85% after purification by gel permeation chromatography (GPC) with CHCl<sub>3</sub> as the eluent. *Meta-* and *para-*substituted enyne ketones **1c** and **1d** 



Scheme 2. A rhodium-catalyzed polyaddition reaction.

also gave the corresponding polymers **3c** and **3d** in yields of 78 and 92 %, respectively. The molecular weights of polymers **3b–d** were determined by GPC with CHCl<sub>3</sub> employed as the eluent and a calibration curve of polystyrene standards (Table 1). The number-average molecular weight  $(\bar{M}_n)$  of

Table 1: Properties of 3 a and polymers 3 b-3 d.<sup>[a]</sup>

1	3	Yield [%] <sup>[b]</sup>	$ar{M}_{\sf n}[{\sf Da}]^{[{\sf c}]}$	$ar{M}_{ m w}[{ m Da}]^{[ m c]}$	$ar{M}_{ m w}/ar{M}_{ m n}^{ m [c]}$	$\lambda_{\max}$ (UV) [nm] <sup>[d]</sup>
1a	3 a	-	-	-	-	316
1Ь	3 b	85	6400	6800	1.1:1	317
1c	3 c	78	6300	6800	1.1:1	323
1 d	3 d	92	6900	7600	1.1:1	327

[a] Reaction conditions: A mixture of 1 (0.20 mmol) and [{Rh(OAc)\_2}\_2] (0.0050 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was stirred at room temperature under nitrogen for 1 min. [b] The yield of the isolated product after purification by gel permeation chromatography (CHCl<sub>3</sub>). [c] Determination by gel permeation chromatographic analysis (CHCl<sub>3</sub>) with a polystyrene standard. [d] The absorption spectra were recorded in dilute CHCl<sub>3</sub> solutions at room temperature.

**3b–d** was 6300–6900 Da, which corresponds to a degree of polymerization of 27–29, with a  $\bar{M}_w/\bar{M}_n$  ratio of 1.1:1. The molecular weights ( $\bar{M}_n$  and  $\bar{M}_w$ ) of **3d** obtained without any purification were lowered to 6100 and 6800 Da, respectively, because of the contamination of low-molecular-weight oligomers. Some properties of the model compound **3a** and polymers **3b–3d** are listed in Table 1. The UV/Vis spectra of dilute solutions of **3a–3d** in CHCl<sub>3</sub> at room temperature exhibited absorption maxima near 320 nm. Although there are no clear differences in the absorption maxima between **3a** and polymers **3b–3d**, alternating copolymers with regularly embedded cyclopropane units should attract a great deal of interest in polymer chemistry.

Since introducing a C=C bond rather than a cyclopropane ring in polymers **3b–3d** was anticipated to extend the  $\pi$  conjugation, we investigated the synthesis of a furfurylidene-containing polymer **4** by using a carbene-transfer reaction (Figure 2b). The synthesis of furfurylidene-containing compound **4a** was attempted as a model compound. The reaction of **1a** with 1.2 equivalents of benzaldehyde and 1.2 equivalents of triphenylphosphane in ClCH<sub>2</sub>CH<sub>2</sub>Cl in the presence of 2.5 mol% of [{Rh(OAc)<sub>2</sub>}\_2] at 70 °C for 1 h afforded 2-benzylidenefuran **4a** in a yield of 77% (*cis:trans* = 10:90; Scheme 3). Compound **4a** was not obtained in the absence of triphenylphosphane.<sup>[5]</sup> Therefore, the formation of **4a** can be rationalized by the generation of the (2-furyl)-phosphorus ylide **5** from the (2-furyl)carbenoid **2** and reaction



Scheme 3. A rhodium-catalyzed Wittig-type condensation of 1 a.

of 5 with triphenylphosphane followed by a Wittig-type condensation of the resulting ylide with benzaldehyde.<sup>[6,7]</sup> Thus, we extended this condensation protocol to polymer synthesis. The polycondensation reaction of enyne ketones 1e and 1 f as monomers with a formyl group on the phenyl ring afforded the corresponding polymers 4e and 4f in yields of 51 and 58%. The number-average molecular weights  $(\bar{M}_n)$  of 4e and 4f were 6000 and 6200 Da, which correspond to a degree of polymerization of 27 and 28, respectively. The UV/Vis spectra of model compound **4a** and polymer **4e** (Table 2) exhibited absorption maxima near 380 nm, while the spectra of **4 f** ( $\lambda_{max}$  = 457 nm) showed a red-shift of 85 nm relative to **4a** ( $\lambda_{\text{max}} = 372 \text{ nm}$ ) under identical conditions. This result indicates the effective extension of the  $\pi$  conjugation caused by elongation of the 5-aryl-2-furfurylidene units in 4f. The fluorescence emission spectra of the solutions of 4a, 4e, and **4f** in CHCl<sub>3</sub>  $(2.0 \times 10^{-4} \text{ M})$  measured at room temperature with excitation at 380 nm (4a and 4e) or 440 nm (4f) showed emission peaks centered at 433, 461, and 559 nm, respectively.<sup>[8]</sup>





[a] Reaction conditions: A mixture of 1 (0.20 mmol), triphenylphosphane (0.48 mmol) and [{Rh(OAc)\_2}\_2] (0.0050 mmol) in ClCH\_2CH\_2Cl (2 mL) was stirred at room temperature under nitrogen for 1 h. [b] The yield of the isolated product after purification by gel permeation chromatography (CHCl\_3). [c] Determination by gel permeation chromatographic analysis (CHCl\_3) with a polystyrene standard. [d] Absorption and emission spectra were recorded in dilute CHCl\_3 solutions at room temperature. [e] Solutions ( $2.0 \times 10^{-4}$  M) were excited at 380 nm (4a and 4e) or 440 nm (4f).

Angew. Chem. Int. Ed. 2004, 43, 1857–1860

In conclusion, we have developed a polymerization of enyne ketones to give furylcyclopropane-containing polymers **3** and furfurylidene-containing polymers **4** by the in situ generation of (2-furyl)carbene complexes with a  $[Rh(OAc)_2]_2$ catalyst. The two systems could be widely applicable to polymer synthesis and may find some applications in other polymerizations using catalytic 2-furfurylidene-transfer reactions.

## **Experimental Section**

Typical procedure: **3b**:  $[{Rh(OAc)_2}_2]$  (2.2 mg, 0.0050 mmol) was added at room temperature under nitrogen to a solution of 1b (47 mg, 0.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL). After stirring the mixture for 1 min, the rhodium catalyst was removed by centrifugal separation. The solvent was removed under reduced pressure to afford the cyclopropanecontaining polymer **3b** as a yellow powder (40 mg, 0.17 mmol, 85%) yield); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.12 - 1.86$  (brm, 6H), 1.86– 2.89 (brm, 6H), 6.57-7.85 ppm (brm, 4H) [the following peaks are attributed to terminal or internal alkene functionalities in this polymer, the values of protons being relative ratios compared with the above intensity;  $\delta = 4.94-5.39$  (m, 0.2 H), 5.39-5.75 (br m, 0.2 H), 6.28–6.57 ppm (m, 0.2 H)]; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 11.0, 14.1,$ 20.3-20.7 (br), 22.0-23.0 (br), 28.9, 29.7, 30.4, 34.1, 38.7, 68.1, 113.7, 119.2-119.4 (br), 120.7, 125.1-130.9 (br), 132.4, 135.4, 136.2, 137.2, 137.3, 145.4–145.5 ppm (br), 167.8; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  $(\varepsilon \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1})$ , 317 nm (3845).

**4e**: [{Rh(OAc)<sub>2</sub>]<sub>2</sub>] (2.2 mg, 0.0050 mmol) was added at room temperature under nitrogen to a solution of enyne ketone **1e** (48 mg, 0.20 mmol) and triphenylphosphane (0.13 g, 0.50 mmol) in 1,2-dichloroethane (2 mL). After stirring the mixture at 70 °C for 1 h, the solvent was removed under reduced pressure to give crude polymer **4e** containing phosphane compounds, which could be removed by a gel permeation chromatography with CHCl<sub>3</sub> as the eluent to give **4e** as an orange powder (22 mg, 0.10 mmol, 51 % yield); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31-2.00$  (brm, 4H), 2.20–2.97 (brm, 4H), 6.81–7.24 (brm, 1H), 7.20–8.25 (brm, 5H) [δ 10.00 (brs, 0.3H) assigned as terminal formyl hydrogen]; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 14.0$ , 21.0, 21.1, 22.3–23.2 (br), 29.7, 34.1, 115.1, 121.0–137.9 (br), 144.9–147.0 (br), 192.3 ppm; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (ε mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>), 380 nm (17665).

Received: September 25, 2003 [Z52949]

**Keywords:** carbenoids · homogeneous catalysis · metathesis · polymerization · rhodium

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## Communications

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