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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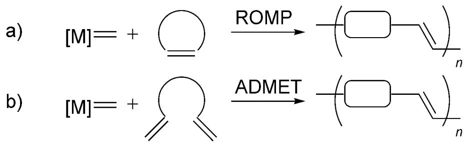


Figure 1. Schematic representation of transition-metal-catalyzed metathesis polymerization.

ization (ADMET, Figure 1b),[2] 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 2a) and polycondensation 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.

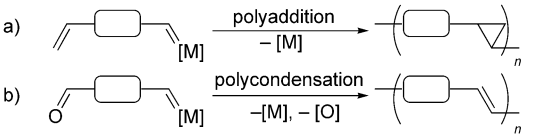
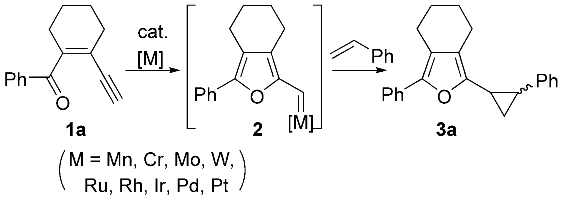


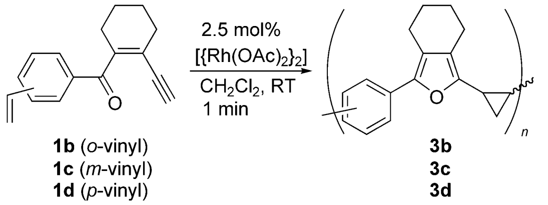
Figure 2. Schematic representation of transition-metal-catalyzed polyadditions and polycondensations using carbenoid intermediates.

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



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

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)$_2$}$_2$] at room temperature, the reaction immediately afforded the (2-furyl)cyclopropane-containing polymer **3b** as a yellow powder (Scheme 2). The yield was 85% after purification by gel permeation chromatography (GPC) with $CHCl_3$ as the eluent. *Meta*- and *para*-substituted enyne ketones **1c** and **1d** 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 $CHCl_3$ employed as the eluent and a calibration curve of polystyrene standards (Table 1). The number-average molecular weight ($\bar{M}_n$) of **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 $CHCl_3$ 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.



Scheme 2. A rhodium-catalyzed polyaddition reaction.

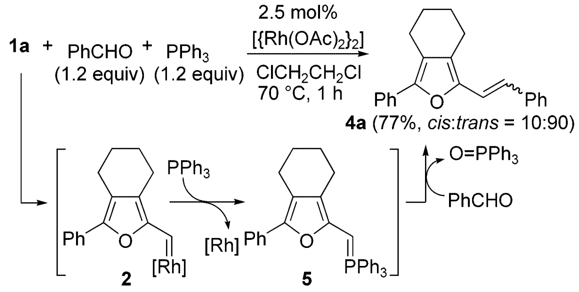
Table 1: Properties of **3a** and polymers **3b–3d**.[a]

1	3	Yield [%][b]	$\bar{M}_n$ [Da][c]	$\bar{M}_w$ [Da][c]	$\bar{M}_w/\bar{M}_n$[c]	λ_{max} (UV) [nm][d]
1a	**3a**	–	–	–	–	316
1b	**3b**	85	6400	6800	1.1:1	317
1c	**3c**	78	6300	6800	1.1:1	323
1d	**3d**	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_2Cl_2 (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 ($CHCl_3$). [c] Determination by gel permeation chromatographic analysis ($CHCl_3$) with a polystyrene standard. [d] The absorption spectra were recorded in dilute $CHCl_3$ solutions at room temperature.

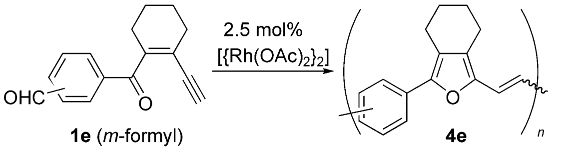
Since introducing a C=C bond rather than a cyclopropane ring in polymers **3b–3d** was anticipated to extend the π conjugation, we investigated the synthesis of a furfurylidene-containing polymer **4** by using a carbene-transfer reaction (Figure 2b). The synthesis of furfurylidene-containing compound **4a** was attempted as a model compound. The reaction of **1a** with 1.2 equivalents of benzaldehyde and 1.2 equivalents of triphenylphosphane in $ClCH_2CH_2Cl$ in the presence of 2.5 mol% of [{Rh(OAc)$_2$}$_2$] 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.[5] 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 of **5** with triphenylphosphane followed by a Wittig-type condensation of the resulting ylide with benzaldehyde.[6,7] Thus, we extended this condensation protocol to polymer synthesis. The polycondensation reaction of enyne ketones **1e** and **1f** 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 **4f** ($\lambda_{max} = 457$ nm) showed a red-shift of 85 nm relative to **4a** ($\lambda_{max} = 372$ nm) under identical conditions. This result indicates the effective extension of the π 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 $CHCl_3$ (2.0×10^{-4} 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.[8]



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

Table 2: Properties of **4a** and polymers **4e** and **4f**.[a]



1e (*m*-formyl)
1f (*p*-formyl)

4e
4f

1	**4**	Yield [%][b]	$\bar{M}_n$ [Da][c]	$\bar{M}_w$ [Da][c]	$\bar{M}_w/\bar{M}_n$[c]	λ_{max} (UV) [nm][d]	λ_{max} (PL) [nm][d,e]
1a	**4a**	77	–	–	–	372	433
1e	**4e**	51	6000	6500	1.1:1	380	461
1f	**4f**	58	6200	6900	1.1:1	457	559

[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 (2.0×10^{-4} M) were excited at 380 nm (**4a** and **4e**) or 440 nm (**4f**).

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_2Cl_2 (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 cyclopropane-containing polymer **3b** as a yellow powder (40 mg, 0.17 mmol, 85% yield); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.12–1.86$ (br m, 6H), 1.86–2.89 (br m, 6H), 6.57–7.85 ppm (br m, 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, 0.2H), 5.39–5.75 (br m, 0.2H), 6.28–6.57 ppm (m, 0.2H)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.0$, 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 ($CHCl_3$): λ_{max} (ε $mol^{-1} dm^3 cm^{-1}$), 317 nm (3845).

4e: $[\{Rh(OAc)_2\}_2]$ (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 $CHCl_3$ as the eluent to give **4e** as an orange powder (22 mg, 0.10 mmol, 51% yield); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.31–2.00$ (br m, 4H), 2.20–2.97 (br m, 4H), 6.81–7.24 (br m, 1H), 7.20–8.25 (br m, 5H) [δ 10.00 (br s, 0.3H) assigned as terminal formyl hydrogen]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.0$, 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 ($CHCl_3$): λ_{max} (ε $mol^{-1} dm^3 cm^{-1}$), 380 nm (17665).

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