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# Acyclic Diene Metathesis (ADMET) Polymerization: The Synthesis of Unsaturated Polyamines

**Keywords:** metathesis • polymerization • amines

## INTRODUCTION

Metathesis of amine-containing olefins with classical metathesis catalyst systems has been limited<sup>1</sup> because of the highly coordinating ability of the amine functionality with high oxidation state transition metals. With the advent of Schrock's well-defined Lewis-acid-free (cocatalyst) metathesis catalysts, amine-functionalized heterocycles have been synthesized by Fu and Grubbs,<sup>2</sup> and amino-diacetylenes have been cyclopolymerized by Wudl.<sup>3</sup> We now report the ADMET polymerization of amino-functionalized diolefins which produce unsaturated polymers with the amine functionality in the polymer main chain.

Acyclic diene metathesis polymerization (ADMET) represents an equilibrium step condensation reaction where the continuous production and removal of a small alkene, typically ethylene, provides the necessary driving force to obtain high polymer (Fig. 1). ADMET polymerization has become a viable method for producing linear unsaturated polyalkenylenes, as a result of the synthesis of highly active Schrock alkylidenes, and the variety of monomer systems which are accessible.<sup>4–10</sup> To date, unsaturated hydrocarbon polymers<sup>4,5</sup> as well as polymers and oligomers containing ether,<sup>6</sup> carbonyl,<sup>7</sup> silyl,<sup>8</sup> sulfur,<sup>9</sup> and ferrocenyl<sup>10</sup> moieties have been synthesized. Further, unsaturated polymers of this class can be depolymerized, yielding well-defined olefin-terminated<sup>11</sup> and functionalized telechelic oligomers.<sup>12</sup>

A fundamental rule of monomer reactivity has been established to accommodate this broad range of functionalities. Typically, a functional group with catalyst poisoning potential must be separated from the metal center by two or more methylene spacers for the reaction to proceed cleanly to polymer. This monomer structure phenomenon has been reported elsewhere and has been termed the "negative neighboring group effect."<sup>7</sup> The desire to completely understand this phenomenon provided the impetus for continued investigation into more highly coordinating functionalized olefins. Thus, a series of  $\alpha$ ,  $\omega$ -(*N*-phenyl)aminodienes were synthesized to test their polymerizability with Schrock's molybdenum alkylidene, Mo(CHCMe<sub>2</sub>Ph)(N-2,6-C<sub>6</sub>H<sub>3</sub>-*i*-Pr<sub>2</sub>)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (**1**).

## EXPERIMENTAL

### Characterization

<sup>1</sup>H-NMR (300 MHz) and <sup>13</sup>C-NMR (75 MHz) spectra were recorded on a Gemini-Series NMR Superconducting Spectrometer system. All NMR spectra were recorded in CDCl<sub>3</sub> with 0.03% TMS as an internal reference. Resonances are reported in  $\delta$  units downfield from TMS at 0.00 ppm. HRMS data was recorded on a Finnigan 4500 Gas Chromatograph/Mass Spectrometer using electron ionization conditions. Gel permeation chromatography (GPC) data were recorded using a Waters Solvent Delivery System equipped with an UV/RI detector and are relative to polystyrene standards. Samples were prepared in HPLC grade tetrahydrofuran (THF) as eluent and passed successively through  $5 \times 10^3$  Å and  $5 \times 10^4$  Å Phenogel columns at a flow rate of 1 mL/min. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). All polymers were fully characterized from unpurified samples directly from the reaction mixture.

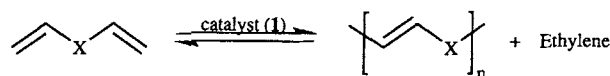
### Monomer Synthesis

*N*, *N*-diallylaniline (**2**) was prepared by the simultaneous dropwise addition of allyl bromide (Aldrich, 16.13 g, 0.1333 mol) and 10M NaOH (70 mL) to stirred aniline (Fisher, 6.20 g, 0.0667 mol) over a period of 3 h. The stirred solution was then refluxed at 110°C for 40 h. The reaction mixture was allowed to cool to room temperature. The organic layer was separated from the reaction mixture and purified by fractional distillation (122°C, 16 mm Hg), yielding 9.48 g (83%) of clear liquid **2**.

HRMS: 173.1219, calcd for C<sub>12</sub>H<sub>15</sub>N (173.1204). ANAL. Calcd: C, 83.24%; H, 8.67%; N, 8.09%. Found: C, 83.05%; H, 8.71%; N, 8.04%.

Further details and complete characterization of monomer **2** is given elsewhere.<sup>13</sup>

*N*, *N*-dibutenylaniline (**3**) was prepared by a similar procedure to that used for **2** using 4-bromobutene (Aldrich). After repeated fractional vacuum distillations (116°C, 1 mm Hg), 5.20 g (74%) of clear liquid **3** was recovered.



**Figure 1.** Acyclic diene metathesis (ADMET) polymerization.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.27 (m, 2H), 3.28 (t, 2H), 5.02 (m, 2H), 5.76 (m, 1H), 6.50–7.30 (ArH, 5H).  $^{13}\text{C-NMR}$ :  $\delta$  31.80, 50.12, 112.05, 115.96, 116.20, 129.10, 135.34, 147.42; HRMS: 201.1539, calcd for  $\text{C}_{12}\text{H}_{15}\text{N}$  (201.1517). ANAL. Calcd: C, 83.24%; H, 8.67%; N, 8.09%. Found: C, 83.05%; H, 8.71%; N, 8.04%.

**N, N-dipentenylaniline (4)** was prepared by a similar procedure to that used for **2** using 5-bromopentene (Aldrich). After multiple fractional vacuum distillations (135°C, 1 mm Hg), 7.60 g (62%) of clear liquid **4** was recovered.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.63 (m, 2H), 2.03 (m, 2H), 3.21 (t, 2H), 5.22 (m, 2H), 5.75 (m, 1H), 6.50–7.30 (ArH, 5H).  $^{13}\text{C-NMR}$ :  $\delta$  26.11, 31.05, 50.21, 111.71, 114.76, 115.28, 129.00, 137.86, 147.77 HRMS: 229.1827, calcd for  $\text{C}_{16}\text{H}_{23}\text{N}$  (229.1832). ANAL. Calcd: C, 83.84%; H, 10.04%; N, 6.12%. Found: C, 83.79%; H, 10.08%; N, 6.13%.

### Metathesis Conditions

All glassware was thoroughly cleaned and oven-dried 24 h before use. All monomers were fractionally distilled and dried prior to polymerization by stirring over calcium hydride for several days and subjected to several freeze–pump–thaw cycles under high vacuum ( $<10^{-4}$  torr). The monomers were also checked by GC to determine purity of  $>99.5\%$ . The molybdenum analog of Schrock's catalyst (**1**) was synthesized as reported in the literature.<sup>14</sup>

All metathesis reactions were initiated in the bulk, under argon glove box conditions. Monomers were introduced into a 50 mL round-bottomed flask equipped with a high vacuum teflon valve and magnetic stir bar. After addition of catalyst the charged reaction vessels were removed from the dry box and placed under high vacuum to remove the continuously generated ethylene. All reactions were initiated at room temperature, but the elevated viscosity generated during polymerization required the reactions to be gradually heated, over several days, to maintain stirring. Metathesis reactions were run on a 1.0–2.0 g scale, with monomer to catalyst ratios ranging from 500 : 1–1000 : 1.

The absence of impurities is paramount for successful metathesis to be realized. This is primarily due to the highly sensitive nature of the catalyst system and the strict stoichiometric balance required for step polymerization. All reactions were quenched by exposure to air.

### Metathesis Reactions

**1-Phenyl-3-pyrroline (5).** Molar ratio of **2** : **1** @ 500 : 1; rt, 24 h. The product was recrystallized in methanol in an 85% yield.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.12 (s, 4H), 5.97 (s, 2H), 6.62–7.28 (Ar-H, 5H);  $^{13}\text{C-NMR}$ :  $\delta$  54.38, 111.12, 115.57, 126.37, 129.29; HRMS: 145.0999, calcd for  $\text{C}_{10}\text{H}_{11}\text{N}$  145.0892.

**Poly(N-phenylamino-3-hexene-1, 6-diyl) (6).** Molar ratio of **3** : **1** @ 1000 : 1; rt, 36 h, then increased 10°C/day to 65°C. Yield: 92%

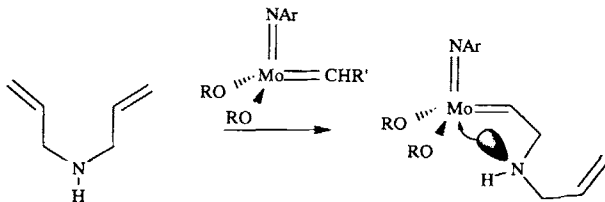
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.26, 3.25, 5.47, 6.62, 7.19.  $^{13}\text{C-NMR}$ :  $\delta$  25.43 (*cis* allyl, 20%), 30.52 (*trans* allyl, 80%), 50.75, 111.72, 115.52, 128.22 (*cis* C=C), 129.13, 129.21 (*trans* C=C), 147.48. UV:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) = 261 nm,  $\epsilon$  = 16,900 (@  $10^{-4}\text{M}$ ); ANAL. Calcd: C, 83.17%; H, 8.73%; N, 8.06%. Found: C, 83.18%; H, 8.68%; N, 8.06%.

**Poly(N-phenylamino-4-octene-1, 8-diyl) (7).** Molar ratio of **4** : **1** @ 1000 : 1; rt, 36 h, then increased 10°C/day to 65°C. Yield: 94%.

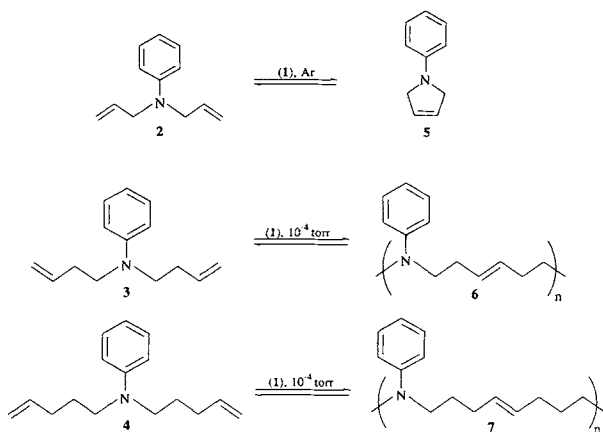
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.61, 2.01, 3.22, 5.43, 6.61, 7.16.  $^{13}\text{C-NMR}$ :  $\delta$  24.64 (*cis* allyl, 26%), 26.87, 30.52 (*trans* allyl, 74%), 50.36, 111.74, 115.22, 129.04 (*cis* C=C), 129.53, 129.97 (*trans* C=C), 147.83. UV:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) = 261 nm,  $\epsilon$  = 15,350 (@  $10^{-4}\text{M}$ ). ANAL. Calcd: C, 83.58%; H, 9.49%; N, 6.9%. Found: C, 83.56%; H, 9.46%; N, 6.95%.

### RESULTS AND DISCUSSION

The objective of this study was to determine the polymerizability, with Schrock's catalyst, of diolefin monomers which possess the nucleophilic amine functionality. The primary obstacle in this investigation was the ability of the Lewis basic nitrogen lone pair to coordinate to the metal complex, thereby slowing or preventing metathesis. Lewis base binding interactions with Schrock type alkylidenes have been reported in the literature.<sup>15</sup> This fundamental concern was supported by the fact that our initial investigations with diallylamine showed only limited metathesis reactivity with a very low monomer to catalyst ratio of 10 : 1. The slowed or greatly inhibited reactivity of diallylamine with Schrock's catalyst has been attributed to the previously mentioned "negative neighbor" phenomenon (Fig. 2). To circumvent this competitive interaction, a monomer was prepared in which a phenyl substituent was placed on the amine group. The phenyl sub-



**Figure 2.** Negative neighboring group effect for diallylamine.



**Figure 3.** Bulk ADMET reactions of  $\alpha$ ,  $\omega$ -(*N*-phenyl)aminodienes with **1**.

stituent should play a key role in decreasing the nucleophilicity, via delocalization, of the nitrogen lone pair as well as providing a small degree of steric hinderance to decrease the possibility of intramolecular coordination. This synthetic strategy proved to be successful for a series of  $\alpha$ ,  $\omega$ -(*N*-phenyl)aminodienes which were reacted with Schrock's molybdenum alkylidene (**1**) to generate their corresponding metathesis products (Fig. 3).

#### Attempted Polymerization of *N*, *N*-diallylaniline (**2**)

The immediate evolution of ethylene was observed upon addition of catalyst **1** to pure monomer **2**. The reaction rapidly generated a brown solid product which halted stirring within 1 min. The reaction continued under vacuum for an additional 24 h prior to analysis, but only yielded cyclic **5**. It was determined by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR and GC/HRMS that the product generated, as a result of metathesis, was 1-phenyl-3-pyrroline (**5**). This result was consistent with previous investigations by Fu and Grubbs,<sup>2</sup> and with other diallyl cases previously studied.<sup>6,8,9,16</sup> The marked difference in reactivity between monomer **2** and diallylamine remains mechanistically unclear, but it appears obvious that the *N*-phenyl substituent is playing a vital role.

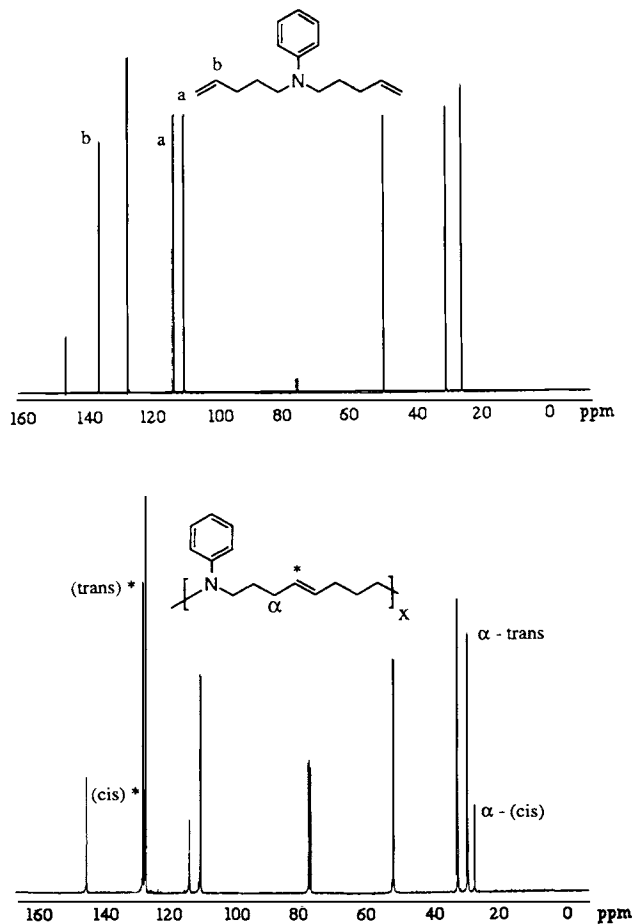
#### Synthesis of Unsaturated Poly(*N*-phenyl)amines (**6**–**7**)

When a catalytic amount (see Experimental) of **1** was added to monomers **3** and **4**, where the number of methylene spacers between the terminal olefin and the nitrogen lone pair are two and three respectively, an immediate evolution of ethylene was observed and the viscosity of the reaction steadily increased. Elevated temperatures (up to 65°C) and high vacuum was applied to drive the equilibrium to high polymer. When the evolution of ethylene

stopped, the polymerizations were quenched by exposure to air.

Polymers **6** and **7** were characterized by NMR, GPC, and elemental analyses, and were found to be consistent with their assigned structure and typical for ADMET polymers.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy showed the polymer structure to be completely linear with unsaturated units consistent with the repeat structure. The internal C=C bonds generated as a result of metathesis polymerization possessed a trans/cis ratio approaching 4 : 1 in each case, which is consistent with several other ADMET systems. In addition, the terminal C=C end groups were not detectable from quantitative  $^{13}\text{C}$ -NMR ( $T_1 = 15$  s) analysis (Fig. 4). This was due to their low concentration relative to the internal olefin, which indicated a relatively large degree of polymerization. This was further supported by the GPC analysis which showed  $M_n$  values of 8200 and 14,000 for polymers **6** and **7**, respectively, with polydispersities approaching 2.0. Elemental analysis, based upon GPC-determined molecular weights, provided additional evidence to support the assigned structure of these very pure polymer systems (Table I).

Polymers **6** and **7** are soluble in several common organic solvents and exist as very viscous materials at room



**Figure 4.**  $^{13}\text{C}$ -NMR of monomer **4** and polymer **7**.

temperature. These polymers have also been solubilized in 0.5M H<sub>2</sub>SO<sub>4</sub> as a protonated ionomer. This may prove to be important due to the various ionomer structures which can be derived from the neutral amine parent polymer or from a specifically designed ionic monomer.

A small proportion (<1%) of cyclic compounds was isolated at elevated temperatures, in addition to the obtained polymers. These cyclics are a result of postcondensation metathesis chemistry where the chain end cleaves off a cyclic structure from its own main chain (Fig. 5). This back-biting mechanism occurs when the terminal olefin concentration has decreased to a level where transmetathesis (chain-chain interchange) and cyclization become more favorable. These cyclic structures were confirmed by GC/HRMS to be composed of either a single or two repeat units in each case. Polymer **6** generated only a seven-membered cyclic, whereas polymer **7** produced not only a nine-membered product but also an 18-membered unsaturated heterocycle as a result of postcondensation cyclization. This back-biting phenomenon has also been observed for several unsaturated ADMET silyl-type polymer systems.<sup>8</sup>

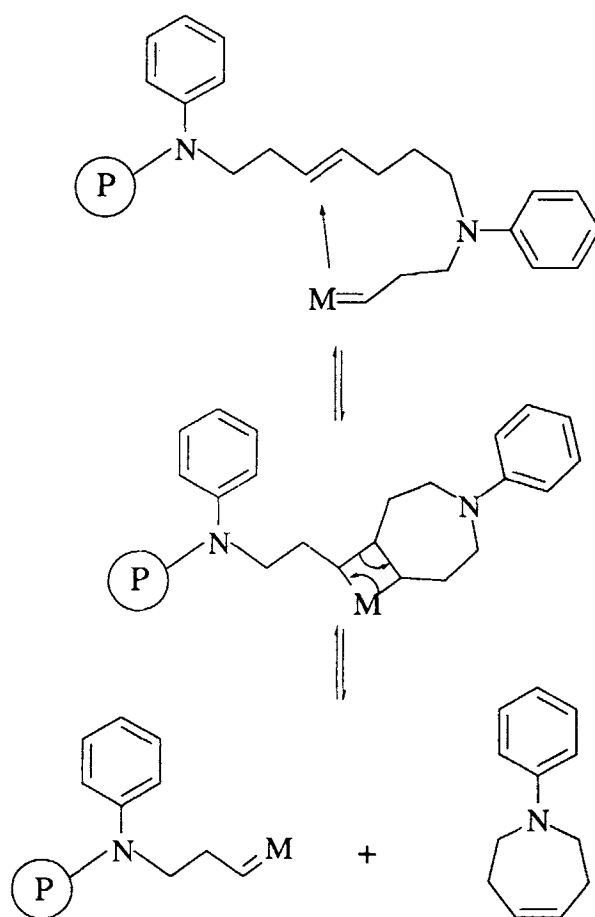
## CONCLUSIONS

Based on these results, a new class of linear unsaturated amine containing polymers may be accessible through ADMET chemistry, providing the vehicle for new and technologically important materials containing the amine functionality. A series of  $\alpha, \omega$ -(*N*-phenyl)aminodienes have been metathesized under standard ADMET conditions. In addition to spacing requirements, which helped to satisfy the negative neighboring group effect, delocalization of the nitrogen lone pair via an aromatic ring, appeared to enhance the metathetic reactivity of these compounds when compared to diallylamine. When one methylene spacer separates the lone pair from the reactive olefin, cyclization occurs under bulk conditions, and polymerization immediately ensues when greater than two spacer units are present. The true mechanistic role of the *N*-phenyl substituent has provided some interesting funda-

**Table I.** Characterization Data for Unsaturated Polyamines **6** and **7**

Polymer	$M_n^a$	$M_w/M_n^a$	Elemental Analysis
			(%)
<b>6</b>	8200	1.86	C: 83.18 (83.17)
			H: 8.68 (8.73)
			N: 8.06 (8.06)
<b>7</b>	14,100	2.06	C: 83.56 (83.58)
			H: 9.46 (9.49)
			N: 6.95 (6.91)

<sup>a</sup> Determined by gel permeation chromatography relative to polystyrene standards.



**Figure 5.** Back-biting mechanism for production of cyclic dimer.

mental questions which are being currently investigated. The ability of this polymer system to be solubilized in acidic aqueous solution may also provide a route to a new class of ionomers. Continued investigations in this area are currently underway with attention focused on phosphorous and nitrogen ionomers.

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