

## Homogeneous Two-Component Polycondensation without Strict Stoichiometric Balance via the Tsuji–Trost Reaction: Remote Control of Two Reaction Sites by Catalysis

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The homogeneous two-component polycondensation reaction holds great historical significance in polymer science.<sup>1</sup> Since many of the desirable physical properties emerge from high molecular weights, obtaining consistently high degree of polymerization (DP) is an important concern in polymer synthesis. About 60 years ago, Carothers and Flory established experimental and theoretical principles by which the extent of reaction ( $p$ ) and the monomer (or functional group) mole ratio ( $r$ ) govern the number-average degree of polymerization ( $DP_n$ ). For an ideal polymerization reaction, the modified Carothers equation<sup>2–4</sup> (eq 1) defines the degree of polymerization. At the completion of the reaction ( $p = 1$ ), eq 1 reduces to eq 2, which indicates that a stoichiometric imbalance of the two monomers should drastically depress  $DP_n$ . For example, a monomer ratio of 1.0/1.1 ( $r = 0.91$ ) would give oligomers of  $DP_n = 21$ , and that of 1.0/1.5 ( $r = 0.67$ ), a  $DP_n$  of 5.0.

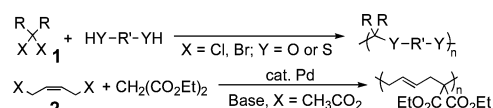
$$DP_n = (1 + r)/(1 + r - 2rp) \quad (1)$$

$$DP_n = (1 + r)/(1 - r) \quad (2)$$

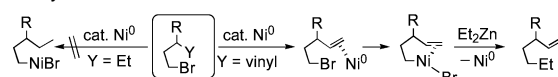
$p$  = extent of reaction;  $r$  = monomer ratio

Equation 2 gives the *maximum attainable*  $DP_n$  at a certain number of  $r$  because two ultimate conditions, the absolute completion of the reaction and lack of side reactions, cannot be met. All textbooks dealing with polymer synthesis prescribe strict adherence to stoichiometric balance of the two monomers (or of the relevant functional groups) to achieve high  $DP_n$ 's. This principle has ruled the *homogeneous* two-component polycondensation for 60 years since the original discoveries, although many notable examples deviating from it had been developed in *heterogeneous* systems.<sup>5,6</sup> The reality is more troublesome because it is difficult to maintain strict stoichiometric balance between the two reagents due to side reactions, chain-transfer processes, and physical loss from the reaction medium by evaporation of monomers or precipitation of polymer segments. Thus, a general strategy for a more robust polycondensation, which is less prone to stoichiometric balance of the two monomers, is highly desirable from both scientific and commercial perspectives. A pattern of such reactions (Scheme 1) is known,<sup>7–10</sup> and those reactions are highly restricted exceptions because of the lack of generality, especially in the electrophiles. In each case, the reactivity of the two electrophilic sites are electronically coupled to each other either by being on the same carbon<sup>7–9</sup> or through a double bond,<sup>10</sup> and the first reaction significantly facilitates the second bond formation. A more general strategy to circumvent the Carothers–Flory stoichiometric restriction would be one in which *two remote reaction sites* are involved and (i) both reaction sites are simultaneously activated or (ii) *the reaction at*

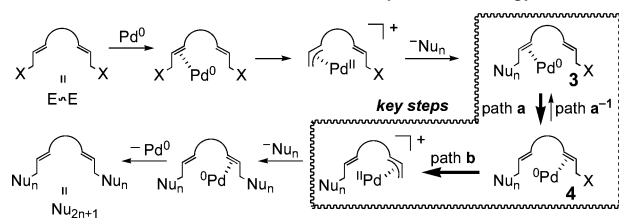
### Scheme 1. Polycondensation without Strict Stoichiometric Balance



### Scheme 2. A Remote Olefin as a Labile Ligand Affecting Reactivity



### Scheme 3. Remote Cascade Double Allylation Strategy



*one site remotely enhances the reactivity of the other.*<sup>11</sup> Neither an example nor a mechanistically credible conceptualization of these ideas has been proposed in the homogeneous polycondensation. We propose here a strategy for achieving high  $DP_n$ 's without strict stoichiometric balance and provide experimental support to validate the latter mechanistic concept. Quite recently, an alternative unique polycondensation under imbalanced stoichiometry was introduced.<sup>12</sup>

Under many circumstances, coordination of transition metals to double bonds is very labile. This interaction is an initiating process of many transition metal-catalyzed reactions.<sup>13,14</sup> A remotely placed olefin is known to assist an oxidative addition of an alkyl bromide to Ni(0), and subsequently stabilizes the Ni(II)–Csp<sup>3</sup> intermediate<sup>15,16</sup> (Scheme 2). Keeping such a mechanistic construct in mind, we investigated a two-component polycondensation reaction via the palladium-catalyzed allylic substitution reaction<sup>17</sup> (Tsuji–Trost reaction<sup>13,14,18</sup>) without strict stoichiometric balance. The strategy which involves a remote cascade double allylation is illustrated in Scheme 3. After the first allylic substitution, **3** is formed, in which Pd(0) holds in coordination to a double bond. Ligand exchange with the remote double bond of the allylic-X gives **4**. The olefin–Pd(0) complex **3** should be sufficiently stable so as to prevent from dissociation to a free olefin and Pd(0), but labile enough to consistently undergo ligand exchange with the substrate to give **4**. If the oxidative addition of the substrate to Pd(0) in **4** (path **b**) is much faster than dissociation of Pd(0) from this complex, subsequent C–C bond formations will ensue. Path **a**<sup>–1</sup> should also be suppressed to facilitate the propagation step. Thus *if the exclusive remote cascade double substitution can be achieved, an excess of the electrophile will not have an influence on the  $DP_n$  values because the deficient nucleophile will keep existing at the polymer*

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**Table 1.** Polycondensation without Strict Stoichiometric Balance via the Tsuji–Trost Reaction<sup>a</sup>

Entry	Electrophile (X = OCOPh)	Nucleophile (E = CO <sub>2</sub> Et)	E/N <sup>b</sup> (DP <sub>n</sub> by eq 2)	Polymer (E = CO <sub>2</sub> Et)	Isolated yield, %	M <sub>n</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	DP <sub>n</sub> <sup>d</sup>
1		CH <sub>2</sub> E <sub>2</sub> (6)	1.0/1.0 (–)		97	16,000	1.5 <sub>3</sub>	110
2	<b>5</b>		1.5/1.0 (5)		98	14,000	1.6 <sub>2</sub>	99
3			1.0/1.5 (5)		– <sup>e</sup>	800	1.7 <sub>6</sub>	6 <sup>f</sup>
4		CH <sub>2</sub> (COMe) <sub>2</sub>	1.5/1.0 (5)		82 <sup>g</sup>	13,000	1.3 <sub>9</sub>	120
5		= CH <sub>2</sub> E <sub>2</sub>	1.5/1.0 (5)		99	14,000	1.5 <sub>2</sub>	100
6			1.5/1.0 (5)		99	16,000	1.4 <sub>7</sub>	65
7		<b>6</b>	1.0/1.0 (–)		95	32,000	1.5 <sub>4</sub>	270
8	<b>7</b>		1.5/1.0 (5)		94	41,000	1.5 <sub>7</sub>	340
9			2.0/1.0 (3)		96	41,000	1.5 <sub>7</sub>	340
10			1.0/1.5 (5)		– <sup>e</sup>	800	1.5 <sub>9</sub>	6 <sup>f</sup>
11	X-CH=CH-N(Ph)-CH=CH-X <b>8</b>	<b>6</b>	1.5/1.0 (5)		97	13,000	1.4 <sub>7</sub>	73
12	X-CH=CH-Ph-CH=CH-X <b>9</b>	<b>6</b>	1.5/1.0 (5)		92	10,000	1.7 <sub>5</sub>	64

<sup>a</sup> The polycondensation was catalyzed by 1 mol % of Pd<sub>2</sub>(dba)<sub>3</sub> (5 μmol)–2.0 mol % of 1,4-bis(diphenylphosphino)butane (10 μmol) in the presence of 3.0 mmol of *N,O*-bis(trimethylsilyl)acetamide in CH<sub>2</sub>Cl<sub>2</sub>–DMF (9/1, 1.0 mL). <sup>b</sup> The mole ratio of electrophile/nucleophile. The *E* or *N* value “1.0” stands for 0.50 mmol; for example, *E/N* = 1.5/1.0, 0.75 mmol of the electrophile and 0.50 mmol of the nucleophile were used. <sup>c</sup> Determined by SEC. <sup>d</sup> Each DP<sub>n</sub> value was calculated using M<sub>n</sub> by SEC and the molecular weight of the repeating unit. <sup>e</sup> Not isolated. A crude reaction mixture was analyzed by SEC. <sup>f</sup> The DP<sub>n</sub> value was 5.0 ± 0.5 by <sup>1</sup>H NMR. <sup>g</sup> Some amount of an insoluble material was obtained.

*termini*, while an excess of the nucleophile will dictate the maximum attainable DP<sub>n</sub> by the deficient electrophile. Once Pd(0) happens to dissociate from the olefin, DP<sub>n</sub> of the polymer will follow normal behavior according to eqs 1 and 2. Therefore, to obtain high DP<sub>n</sub> without strict stoichiometric balance, it is critically important that *the reaction follows the highly remote-selective path a followed by path b throughout the polymerization.*

Even under the best of circumstances DP<sub>n</sub> values are never infinite in any polycondensation reaction, and a practical way of examining *polycondensation out of stoichiometric control* is to compare DP<sub>n</sub> values with various stoichiometric ratios of the individual monomers. The results under our optimal conditions<sup>11</sup> are shown in Table 1. Under stoichiometric balance of electrophile **5** and nucleophile **6** (*E/N* = 1.0/1.0), the polycondensation afforded a polymer with DP<sub>n</sub> = 110 (entry 1). When the reaction was conducted at *E/N* = 1.5/1.0 or 1.0/1.5, a DP<sub>n</sub> value of 5.0 was expected according to eq 2. However, with *E/N* = 1.5/1.0 a value of 99 (entry 2), comparable to entry 1, was obtained. In sharp contrast, with *E/N* = 1.0/1.5 a value of 6 (entry 3) was observed. These results are in accordance with the expectations outlined in Scheme 3, and the DP<sub>n</sub> value obtained with *E/N* = 1.0/1.5 was confirmed by <sup>1</sup>H NMR. Other nucleophiles gave DP<sub>n</sub> values even higher than what is observed for **6** (entries 4–6). Electrophile **7** afforded the polymer with a high DP<sub>n</sub> value (entry 7), while a surpassing high DP<sub>n</sub> of 340 is observed with a ratio of **7/6** = 1.5/1.0 and 2.0/1.0 (entries 8 and 9). Reversing the ratio of **7** to **6** (**7/6** = 1.0/1.5) has the expected result (entry 10), and a near normal DP<sub>n</sub> value of 6 is observed. Monomers **8** and **9** are also good electrophiles for the polycondensation less prone to stoichiometric balance (entries 11 and 12). All polycondensations reported here are homogeneous throughout the polymerization reactions. We cannot rule out at present that the propagation reactions were terminated by formation of cyclic polymers during the final stage of polymerization as well as by some side reactions and/or side reaction pathways.

In summary, we have demonstrated that a *homogeneous* two-component polycondensation reaction without strict stoichiometric balance can lead to polymers of high molecular weight by catalysis if certain structural reactivity criteria are met in the monomers. In the current version, it is important to design a dielectrophile in such a fashion that the coordinated Pd(0)-catalyst after the first allylation

is delivered to the remote intramolecular double bond, so that cascade sequence can proceed.<sup>11</sup> Even though the present system has some limitations, the logic of principle and versatility in both electrophiles and nucleophiles have been illustrated.

**Supporting Information Available:** Scheme of the remote double activation, experimental details, and analytical data of the polymers in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0492743