JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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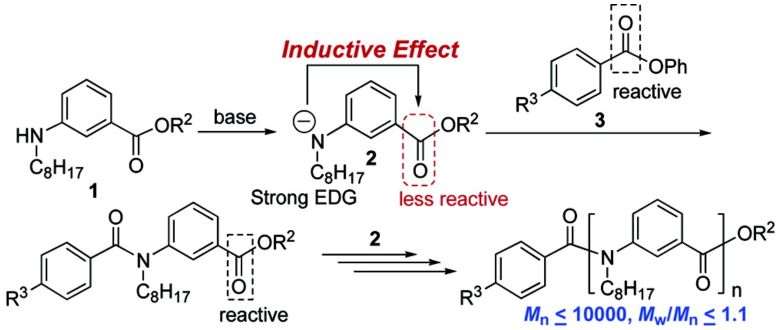
J. Am. Chem. Soc., **2005**, 127 (29), 10172-10173• DOI: 10.1021/ja052566z • Publication Date (Web): 30 June 2005



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Inductive Effect-Assisted Chain-Growth Polycondensation. Synthetic Development from *para*- to *meta*-Substituted Aromatic Polyamides with Low Polydispersities

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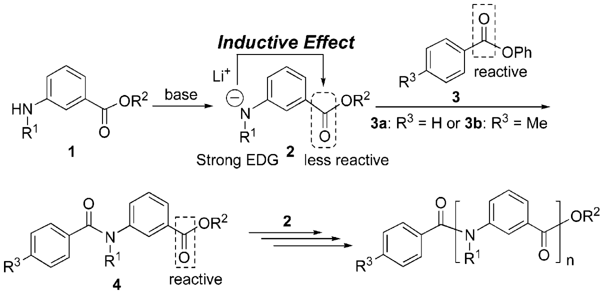
para-Substituted aromatic condensation polymers have high mechanical strength and are useful as tough organic fabrication materials, engineering plastics, and so on. However, these polymers are generally insoluble in organic solvents because of strong intermolecular interaction based on the high symmetry of the polymers. To improve the solubility while maintaining the excellent mechanical properties, long alkyl chains are introduced into the *para*-substituted monomers, or the *para*-substituted monomers are copolymerized with *meta*-substituted ones. We have succeeded in controlling the molecular weight and polydispersity of soluble aromatic condensation polymers, such as polyamides,[1] polyethers,[2a] and polyesters,[2b] by chain-growth polycondensation of *para*-substituted AB-type aromatic monomers having long alkyl chains. In all of these polymerizations, the nucleophilic site of the monomer is the anion formed by deprotonation of an amino or a hydroxyl group, and this strongly electron-donating anion deactivates the electrophilic site at the *para*-position through the resonance effect (+*R* effect). This deactivation results in suppression of self-condensation of the monomer, but selective reaction with an initiator and the propagating end, leading to chain polymerization. Therefore, *para*-substituted monomers are necessary for chain-growth polycondensation.

We now report successful chain-growth polycondensation of *meta*-substituted monomers, 3-(octylamino)benzoic acid esters **1**, which yield poly(*m*-benzamide)s with well-defined molecular weights and low polydispersities ($M_w/M_n \leq 1.1$). This result demonstrates that the inductive effect (+*I* effect) of the nucleophilic site on the reactivity of the electrophilic site at the *meta* position of the monomer is as applicable to chain-growth polycondensation as is the *R* effect of the *para*-substituted monomers.[3] In general, the *I* effect is weaker than the *R* effect, but a functional group with a negative charge is expected to show an *I* effect as strong as the *R* effect. Thus, the aminyl anion of **2** would deactivate the acyl group at the *meta* position through the strong +*I* effect, resulting in suppression of the self-polycondensation of **2**. The anion **2** would then selectively react with an initiator **3** and the polymer chain end, the acyl group of which is more reactive than that of the monomer with the aminyl anion, and growth would continue in a chain-polymerization manner (Scheme 1).

The methyl ester monomer **1a** was first polymerized with 1.1 equiv of LDA, the basicity of which is higher than that of the base (*N*-octyl-*N*-triethylsilylaniline/CsF) that we used for the polymerization of the *para*-counterpart,[1a] in the presence of initiator **3a**[4] at −78 °C to yield a polymer with a rather narrow molecular weight distribution, implying that the polymerization had proceeded in a chain-polymerization manner (Table 1, entry 1). However, LDA seemed to gradually react with the propagating chain end to terminate the polymerization because the ^1H NMR spectra of the obtained polymer showed a weaker signal of the terminal methyl ester moiety. Thus, the polymerization was performed with lithium amides having bulkier alkyl substituents to give polymers with narrower molecular weight distributions (entries 2−4). When lithium hexamethyldisilazide (LiHMDS) was used, the conversion of **1a** was almost 100%, although the M_n values of the polymers were lower than the calculated values (entries 4, 5). When the polymerization of **1a** was carried out at higher temperature than −78 °C, the M_n values of the polymers were close to the calculated values (entries 6, 7). However, prolongation of the polymerization time at 0 °C after consumption of **1a** resulted in a broad molecular weight distribution due to a small shoulder of the GPC chromatogram in the higher molecular weight region (entry 7). This implies that there was a small amount of self-polycondensation polymer, which might react with the chain end of the chain-growth polymer after **1a** was consumed.[5]

Scheme 1



1a: $R^1 = C_8H_{17}$, R^2 = Me, **1b**: $R^1 = C_8H_{17}$, R^2 = Et, **1c**: R^1 = Me, R^2 = Me

Table 1. Polymerization of **1** with **3**[a]

entry	1	3	base	*T* (°C)	$[\mathbf{1}]_0/[\mathbf{3}]_0$	time	conv.[d] (%)	M_n calcd	M_n [e]	M_w/M_n [e]
1	**1a**	**3a**	LDA	−78	19.6	8 h	85	3990	3940	1.24
2			LiTMP[b]		19.3	5 h	74	3540	2820	1.11
3			LiN(*i*-Pr)^{t}Bu		18.9	5 h	87	3780	3250	1.09
4			LiHMDS[c]		19.1	5 h	98	4100	3700	1.08
5			LiHMDS		34.5	6 h	96	7750	4560	1.10
6			LiHMDS	−30	39.8	1 h	96	8930	7210	1.12
7			LiHMDS	0	47.3	5 min	98	10800	9690	1.18
						1 h	98		9790	1.25
8	**1b**	**3b**	LiHMDS	0	47.1	5 min	100	10800	10000	1.05
						2 h	100		10000	1.05

[a] Polymerization of **1** with **3** in the presence of 1.1 equiv of base in THF ($[\mathbf{1}]_0 = 0.40$ M). [b] Lithium 2,2,6,6-tetramethylpiperidide. [c] Lithium hexamethyldisilazide. [d] Determined by GC. [e] Determined by GPC based on polystyrene standards (eluent: THF).

To prevent self-polycondensation, the ethyl ester monomer **1b** was used because lower reactivity of the ethyl ester moiety is

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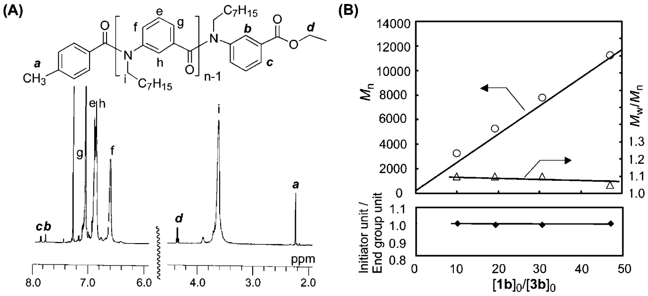

Figure 1. (A) ^{1}H NMR spectrum of poly**1b** obtained by the polymerization of **1b** with **3b** in the presence of 1.1 equiv of LiHMDS in THF at 0 °C. (B) M_n and M_w/M_n values of poly**1b**, obtained with 1.1 equiv of LiHMDS in the presence of **3b** in THF ($[\mathbf{1b}]_0 = 0.40$ M) at 0 °C, as a function of the feed ratio of **1b** to **3b**. The lines indicate the calculated M_n values assuming that one polymer chain forms per unit of **3b**.

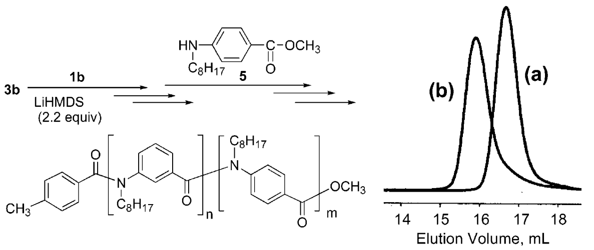

Figure 2. GPC profiles of block copolymerization of **1b** and **5** by the monomer addition method: (a) poly**1b** as a prepolymer ($[\mathbf{1b}]_0/[\mathbf{3b}]_0 = 20$, 100% monomer conversion), $M_n = 4600$, $M_n/M_n = 1.09$; (b) poly**1b**-*b*-poly**5** as a postpolymer ([added $\mathbf{5}]_0/[\mathbf{3b}]_0 = 23$, 94% monomer conversion), $M_n = 11\,000$, $M_w/M_n = 1.12$.

expected to suppress the reaction between the deprotonated **1b** monomers (self-condensation). Thus, monomer **1b** polymerized with LiHMDS at 0 °C to yield a polymer with a defined molecular weight and a very low polydispersity (entry 8). Furthermore, the M_n value and the M_w/M_n ratio were not changed even 2 h after **1b** was consumed. The ^{1}H NMR spectrum of the poly**1b** obtained shows the signal ***a*** of the methyl group of the initiator **3b** unit and the signals of the terminal monomer units ***b***, ***c***, and ***d***. The integral ratio of ***a***:***b***:***c***:***d*** is 3:1:1:2, indicating that one initiator molecule formed one polymer chain (Figure 1A). When the polymerization of **1b** was carried out with various feed ratios of **1b** to initiator **3b** ($[\mathbf{1b}]_0/[\mathbf{3b}]_0$), the observed M_n values of the polymers increased linearly in proportion to the $[\mathbf{1b}]_0/[\mathbf{3b}]_0$ ratio, and the polydispersity was quite narrow, maintaining an M_w/M_n ratio of less than 1.1 over the entire range of the $[\mathbf{1b}]_0/[\mathbf{3b}]_0$ ratio. Moreover, the ratio of the initiator unit to the end group was consistently 1.0, irrespective of the $[\mathbf{1b}]_0/[\mathbf{3b}]_0$ ratio (Figure 1B). This polymerization behavior is consistent with the features of living polymerization and is consistent with the chain-growth polycondensation of the *para*-substituted counterpart.[1a]

With this established polymerization method, we tried to synthesize a well-defined diblock copolymer of *meta*- and *para*-substituted poly(benzamide).[6] Thus, **1b** was polymerized in the presence of **3b** ($[\mathbf{1b}]_0/[\mathbf{3b}]_0 = 20$) and 2.2 equiv of LiHMDS to give a prepolymer (Figure 2 (a), $M_n = 4600$ (M_n(calcd) = 4790), $M_w/M_n = 1.09$). A fresh feed of methyl 4-(octylamino)benzoate **5** was added to the prepolymer in the reaction mixture.[7] The added **5** feed was smoothly polymerized. The GPC chromatogram of the product (Figure 2 (b)) was clearly shifted toward the high molecular weight region, while retaining a narrow molecular weight distribution ($M_n = 11\,000$ (M_n(calcd) = 9700), $M_w/M_n = 1.12$), indicating successful production of the block copolymer of **1b** and **5**. It should be noted that excess LiHMDS in the polymerization of **1b** as the first step did not react at all with the terminal ester moiety of poly**1b**, which was able to initiate the polymerization of **5** as the second step.

Finally, density functional theory (DFT) calculations were performed to understand the present polymerization. The results indicate that successful chain-growth polycondensation of the *meta*-substituted monomers is based on the different reactivity of the ester moieties between the polymer end group and monomer **2b**, as we expected; the polymer end group is much more reactive than **2b**, which is deactivated by the $+I$ effect of the aminyl anion at the *meta* position. To address the different reactivity (electrophilicity) in question, we examined the propagation reaction of **4c** (R^3 = H) with **2c** and the self-condensation of **2c** as model reactions using the DFT (B3LYP/6-31G*)[8] method. The activation energies for the propagation and self-condensation are 21.6 and 27.0 kcal/mol, respectively. On the basis of the geometries, energies, and vibrational frequencies obtained, the theoretical rate constants were then evaluated at 298.15 K and 1 atm. The reaction rate constant (1.1×10^{-3} s^{-1}) for the propagation is 8.6×10^3-fold greater than that for the self-condensation (1.3×10^{-7} s^{-1}) and, hence, is consistent with the experimental finding that propagation was observed exclusively over self-condensation; that is, successful chain-growth polycondensation of *meta*-substituted aminobenzoic ester monomers proceeded.

In conclusion, our present results demonstrate that not only *para*-substituted AB-type aromatic monomers but also *meta*-substituted ones undergo chain-growth polycondensation by virtue of different inductive effects between monomer and polymer. This *I* effect-assisted polycondensation should enable us to extend the synthesis of well-defined condensation polymers from *para*-substituted aromatic polymers to a variety of *meta*-substituted ones, which possess higher solubility. Furthermore, this polymerization method should be applicable to chain-growth polycondensation of even aliphatic monomers, such as amino acid and lactic acid derivatives, and so on. Experiments along these lines are in progress.

Supporting Information Available: Synthesis of monomer **1a** and **1b**, polymerization procedure, the synthesis of diblock copolymer of **1b** and **5**, and computational methods (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA052566Z