JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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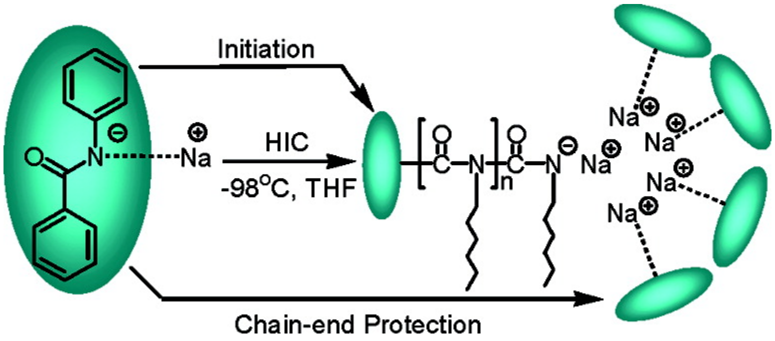
J. Am. Chem. Soc., **2005**, 127 (12), 4132-4133• DOI: 10.1021/ja0427000 • Publication Date (Web): 02 March 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Published on Web 03/02/2005

Unprecedented Control over Polymerization of *n*-Hexyl Isocyanate using an Anionic Initiator Having Synchronized Function of Chain-End Protection

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Polyisocyanates are of considerable interest due to their applications in various fields, such as optical switches, liquid crystals, degradable materials, composites, and chiral recognition.[1] For many of these applications, it is desirable that the molecular weight (MW) and the molecular weight distribution (MWD) of the polymers be controlled and defined. The commonly used initiators for anionic polymerization of the isocyanates, such as NaCN,[2] alkali metal alkyl derivatives and metal naphthalenides,[2,3] amides,[4] and alkoxides,[4,5] are too fast in their initiation and propagation rates and result in polymers of unpredictable MW and broad MWD[2,3] due to side reactions and trimerization from back-biting. Besides, in a number of cases, the living character of the polyisocyanates is absent.[5] Coordination polymerization of alkyl isocyanates using organotitanium(IV) compounds as catalysts[6] is a convenient route to polymers with controlled MW and narrow MWD. However, the reaction is reversible, and hence, even with a long reaction time of 24 h, the yield was restricted to 74−95%.[6c]

We recently succeeded in ensuring the living character of *n*-hexyl isocyanate (HIC) polymerization with sodium naphthalenide (Na−Naph) as the initiator using additives, such as 15-crown-5[7] and sodium tetraphenylborate.[8] The formation of trimers or side reactions as a result of the high reactivity of the naphthalenide carbanion was successfully prevented. To find newer and more effective initiators, we carried out the polymerization of HIC using Na−Naph, sodium diphenylmethane (Na−DPM), and sodium benzanilide (Na−BA). Interestingly, we find that Na−BA is a unique initiator for the polymerization of isocyanates since it serves the dual function of controlled initiation and efficient protection of the living chain-ends (Scheme 1).

The polymerization of HIC using Na−DPM resulted in a drop in the polymer yield due to trimerization when the reaction time exceeded 2 min. It was difficult to control the MW and yield since the rate of polymerization was very fast. Polymerization using Na−Naph as the initiator gave a quantitative yield of the polymer with broad MWD until 10 min, beyond which the yield of the PHIC decreased with the formation of the trimer.[8] The alkali metal benzanilides have an ionic composition that is akin to the ion of the growing polymer chain. We observed that Li−BA failed to initiate the polymerization of HIC, which is ascribed to the formation of tight ion-pairs.[9] K−BA did not polymerize HIC either because it was precipitated in THF at −98 °C. Na−BA, on the other hand, is soluble in THF, and the polymerization of HIC using this initiator turned out to be extremely effective. The yield of PHIC was quantitative, increasing steadily with reaction time until 60 min and beyond. As long as the monomer existed in the reaction mixture, the active chain-ends reacted with the monomer in preference to attacking the carbonyl carbon in the backbone[7,8] (Table 1; see Table S1 of the Supporting Information for detailed data).

Scheme 1

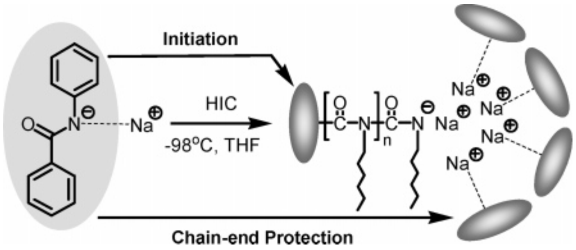

Table 1. Anionic Polymerization of HIC using Na−BA as the Initiator

Na–BA (mmol)	HIC (mmol)	time (min)	$M_n \times 10^{-3}$ calcd[a]	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n[b]	polymer yield (%)
0.390	8.24	60	2.7	13.6	1.09	100
0.340	8.64	60	3.2	16.8	1.11	100
0.350	13.3	60	4.8	22.1	1.12	99
0.380	18.0	70	5.9	30.5	1.08	98
0.265	17.6	70	8.2	40.8	1.16	97

[a] M_n is calculated using the relation {([HIC]/[Na−BA]) × molecular weight of HIC + molecular weight of BA} × yield of polymer/100. [b] M_n and M_w/M_n were measured by SEC−LS in THF at 40 °C.

The three initiators, Na−Naph, Na−DPM, and Na−BA, differ in their reactivity and stability. The carbanion from Na−Naph is the most unstable species, and hence, it led to rapid polymerization with side reactions in the initial stages.[8c] The pK_a values of diphenylmethane and benzanilide in water are 32.2 and 20, respectively,[9] which means that the DPM$^-$ anion is more reactive than the amidate anion, BA$^-$.[10] Thus, with Na−DPM, the control of MW was difficult due to fast initiation rates. The amidate anion from Na−BA acts as a relatively weak nucleophile due to efficient charge delocalization by the phenyl ring as well as the carbonyl group. Hence, the initiation of polymerization using Na−BA occurred more slowly compared to Na−DPM. The MWD of the resulting polymer (**1**, Figure 1) was narrow due to low probability of side reactions. The BA$^-$ anion mimics the amidate ion of the polymer, establishing a perfect harmony between initiation and propagation rates, leading to PHIC in ∼100% yield.

The reason Na−BA is most effective in furnishing polymers with controlled MW and narrow MWD is not clear from the above argument since the propagating species is the same for all three initiators. In the case of polymerization by Na−BA, the observed MW is about 5 times the calculated MW. In the expression used to calculate the molecular weight (see footnote of Table 1), the concentration of the initiator appears in the denominator. An observed 5-fold higher MW evidently indicates that the effective concentration of the initiator for polymerization of HIC is ∼20% of its actual concentration. A rationale for this typical behavior of Na−BA is proposed (Supporting Information). It is suggested that

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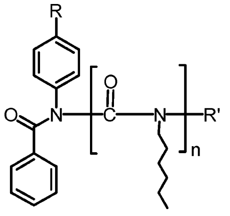

1 R: H, R': H
2 R: $CH=CH_2$, R': H
3 R: H, R': $COCH_3$
4 R: H, R': $COCH(X)CH_3$ (X=Cl, Br)
5 R: H, R': $COC(CH_3)=CH_2$
6 R: H, R': $COC^{*}H(CH_3)OCOCH_3$
7 R: $CH=CH_2$, R': $COC^{*}H(CH_3)OCOCH_3$

Figure 1. Structure of the synthesized PHICs with ∼100% yield.

five Na−BA molecules could form a cluster of which only one covalently binds with the HIC.

To rule out the possibility that the initiator sample could contain unreacted benzanilide, and hence a possible source of error in calculated MW, we first estimated the benzanilide anion content in Na−BA from a reaction between Na−BA and CH_3COCl and found it to be quantitative with at least 90% yield of *N*-acetyl benzanilide (Supporting Information). Hence, the low initiating efficiency of ∼20% could mean that about 80% Na−BA molecules are probably protecting the growing chain-end and, hence, preventing a back-biting reaction, as illustrated in Scheme 1. To confirm that this indeed is happening, we carried out a set of experiments in which a mixture of Na−Naph and Na−BA (2−3-fold excess) was used. In the case of Na−Naph, and in the absence of an additive, back-biting reaction is usually observed specifically at longer reaction time,[7b] leading to low yields of the polymer. Interestingly, in the presence of Na−BA, the yield of PHIC was ∼100% (Table S1), which clearly indicates that Na−BA is able to efficiently protect the growing chain-end as an additive.

In the above experiment, again, it is likely that Na−BA can initiate the polymerization instead of Na−Naph, though such a possibility is faint considering the high reactivity of the naphthalenide anion. We compared the ^{1}H NMR spectra of PHIC obtained from initiation of polymerization of HIC by Na−Naph, Na−BA, and a mixture of Na−Naph and Na−BA. In the case of polymerization by Na−Naph, the naphthalene moiety does not bind covalently to the polymer, and hence no aromatic protons are seen in the NMR spectra.[7,8] In the ^{1}H NMR of PHIC obtained using Na−BA as the initiator, the aromatic protons were clearly seen. On the other hand, the ^{1}H NMR of the PHIC sample obtained using a Na−Naph and Na−BA mixture had no aromatic proton peaks. The spectral features are similar to that of PHIC obtained by Na−Naph initiator only. This confirms that Na−BA used in the presence of Na−Naph acts as the protector of the anion chain-end.

The living nature of PHIC was established from (1) a good linear plot between [monomer]/[initiator] and MW (Figure S4), (2) block copolymerization with another isocyanate monomer, (3-triethoxysilyl)propyl isocyanate, and (3) a first-order rate dependence of HIC polymerization on both HIC and Na−BA concentration.

Polymerization of HIC using sodium 4-vinyl benzanilide (Na−4VBA led to macromonomer **2** (Figure 1). The vinyl group on the initiator did not polymerize in the reaction conditions because the initiator is weakly reactive. With Na−BA-initiated polymerization, the long reaction time provided scope to introduce a number of functionalities to the chain-end. Terminating the reaction with aliphatic acid chlorides, such as CH_3COCl, $CH_3CH(X)COCl$ (X = Cl, Br), and $CH_2{=}C(CH_3)COCl$, in the presence of pyridine led to the corresponding polymers **3** (reactive end-group), **4** (suitable for atom transfer radical polymerization), and **5** (macromonomer), respectively. Terminating the polymer chain by $CH_3COOCH(CH_3)$-COCl afforded the polyisocyanate **6** (chiral polymer). With Na−4VBA as the initiator for HIC polymerization and employing the chiral terminating agent, **7** (chiral macromonomer) was afforded. All of these polymers (**1**−**7**) were isolated in ∼100% yields. Thus, it is possible to introduce the desired functionality at the termini of the polymer and still exercise a perfect control over polymerization of the isocyanates.

In summary, for the polymerization of a highly reactive monomer HIC, we have identified Na−BA as a very efficient initiator. It has a slow initiation rate with the additive function of chain-end protection eliminating the need for another additive, offering in the process a perfect control over MW and MWD. Using this initiator and its derivatives, it is possible to introduce a number of functionalities at the termini of the polymer with 100% yields. Easy access to such functionalized polymers has prompted us to investigate further to expand the application scope of these novel materials.

Acknowledgment. This work was supported by a grant from the National R&D Project for Nano Science and Technology (M10214000169-02B1500-02710), and the Korea Science and Engineering Foundation (Contract No. R01-2004-000-10143-0). The authors thank Hyung Jin and Chan Hee for technical assistance.

Supporting Information Available: Experimental details and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0427000