

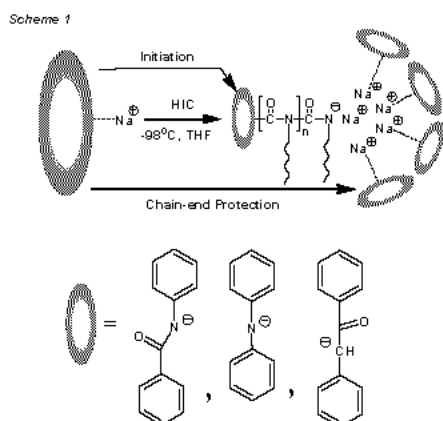
## Living Anionic Polymerization of Isocyanates

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### Introduction

Polyisocyanates and its block copolymers are fascinating materials because of their various applications such as, optical switching, liquid crystals, degradable materials, composites, chiral recognition, and templates for mesoporous inorganic materials[1]. For most basic studies on polyisocyanates it is desirable that the molecular weight (MW) be controlled with narrow molecular weight distribution (MWD). The anionic polymerization of isocyanates carried out using conventional initiators is associated with side reactions due to rapid initiation and propagation rates as well as backbiting by the growing chain resulting in a lack of control over the MW and MWD of the polymers. Recently we achieved control over the polymerization of isocyanate by using additives such as 15-crown-5 and sodium tetraphenylborate that could prevent backbiting[2]. In the present study the polymerization of isocyanate by using various initiators such as sodium benzanilide (Na-BA), sodium diphenyl amine (Na-DPA) and sodium deoxibenzooin (Na-DB) is reported. Interestingly, we find that these initiators are effective for the polymerization of isocyanates since it serves the dual function of controlled initiation and propagation rate with efficient protection of the living chain-ends (Scheme 1)[3]. In addition the controlled synthesis and morphology study of di-, and triblock copolymers of isocyanate with 2-vinylpyridine also discussed



### Experimental

**Anionic Polymerization of HIC.** The polymerization carried out by adding the HIC in THF to the initiator solution at  $-98\text{ }^{\circ}\text{C}$ . At this point, the color of the reaction solution changed into light yellow. The polymerization was terminated (Na-BA:60min, Na-DPA:10min, and Na-DB:10min) by adding a 20-fold to the initiator excess HCl in methanol. The yield of the polymer was 100%.

**Synthesis of P2VP-*b*-PHIC, P2VP-*b*-PHIC-*b*-P2VP, and PHIC-*b*-P2VP-*b*-PHIC.** The homopolymerization of 2VP was carried out at  $-78\text{ }^{\circ}\text{C}$  for 30 min and then copolymerization with HIC was performed in presence of NaBPh<sub>4</sub> at  $-98\text{ }^{\circ}\text{C}$  for 20 min., the Na<sup>+</sup> ion of which substitutes the counter cation K<sup>+</sup>. The resulted living polymer, P2VP-*b*-PHIC, was used for synthesis of P2VP-*b*-PHIC-P2VP by coupling reaction with malonyl chloride. For the synthesis of rod-coil-rod triblock copolymer, PHIC-*b*-P2VP-*b*-PHIC, Na-Naph was used as an initiator. A 5-10 fold excess of NaBPh<sub>4</sub> was used before addition of HIC to protect the backbiting. The optimum condition of polymerization of HIC is 20 minutes at  $-98\text{ }^{\circ}\text{C}$ .

### Results and discussion

**Anionic polymerization with Na-BA, Na-DPA, and Na-DB.** The polymerization of HIC using Na-BA turned out to be extremely effective. The yield of PHIC was quantitative, increasing steadily with reaction time until 60 min and beyond. The MWD of the resulting

polymer was narrow due to low probability of side reactions. The BA<sup>-</sup> anion mimics the amidate ion of the polymer establishing a perfect harmony between initiation and propagation rates, leading to PHIC in  $\sim 100\%$  yield. In case of polymerization by Na-BA the observed MW is about five times the calculated MW. A five times high observed MW evidently indicates that the effective concentration of the initiator for polymerization of HIC is  $\sim 20\%$  of its actual concentration. It is suggested that five Na-BA molecules could form a cluster of which only one covalently binds with the HIC.

Na-DPA and Na-DB also play a role in such polymerization in the foot steps of Na-BA but with different reaction rates. In case of polymerization by Na-DPA the observed MW is about three times the calculated MW. A three times high observed MW evidently indicates that the effective concentration of the initiator for polymerization of HIC is  $\sim 28\%$  of its actual concentration. The results of the polymerization of HIC using Na-DB are nearly similar to that of Na-DPA. We estimated that Na-DB has an initiating efficiency of  $\sim 33\%$  and about 66% Na-DB molecules are protecting the growing chain end, preventing the process of backbiting reaction.

The block copolymers obtained with quantitative yields, narrow MWD, and the clear shift of SEC-LS profile from homo to block copolymer without tailing indicate the living polymerization[4].

**Phase separation and micellization.** The di- and triblock copolymer shows lamellar phase separation as the volume fraction of PHIC increases. The block copolymers composed of two distinct blocks having different solubility in selective solvents were self-assembled and led to micelles and reverse micelles (Figure 1). The rod-coil-rod block copolymer having equimolar rod and coil blocks shows spherical micelles of  $\sim 20\text{ nm}$  in CHCl<sub>3</sub>. Whereas, well-defined hollow spheres with average diameter of  $\sim 200\text{ nm}$  were observed in CH<sub>3</sub>OH.

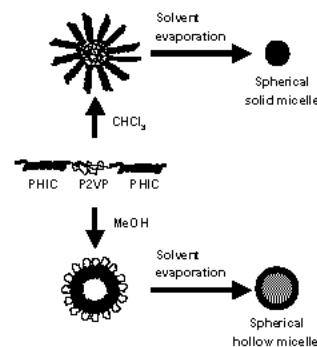


Figure 1. The schematic representation of self-assembly of rod-coil triblock copolymer

### Conclusions

For the polymerization of a highly reactive monomer HIC we have identified Na-BA, Na-DPA and Na-BA as very efficient initiators. It has a slow propagation 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. The well-defined amphiphilic coil-rod, coil-rod-coil, and rod-coil-rod block-copolymers of PHIC and P2VP with controlled architecture has been synthesized for the first time with  $\sim 100\%$  yields. The resulting block copolymers showed lamellar film, donuts, solid and hollow micelles, by simply varying the solvents and the block compositions.

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