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A New Approach to the Living Anionic Polymerization of 4-Cyanostyrene

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Introduction

Functional polymers are very important materials since they can be converted into novel cost-effective macromolecular devices having nanoscale order, with a wide range of potential applications. Among this group of polymers, poly(4-cyanostyrene), P4CNS, with its electron-withdrawing cyano group can act as electron acceptor and can be used in applications where donor−acceptor interactions are exploited.[1] The cyano group can be transformed, by one-step organic reactions, to other functional groups such as carboxyl, ester, or amino, leading to a plethora of functionalized materials or to complex macromolecular architectures.[2−5] Another attractive functional group transformation is the use of cyano groups in click chemistry with azides.[6]

One of the problems associated with this monomer is its high reactivity which prevents storage of this monomer after purification. In order to take full advantage of the potential of P4CNS-based polymers as macromolecular building blocks, it is desirable to be able to synthesize homopolymers and copolymers having tunable molecular weight, including high molecular weight species, with a high level of structural and compositional homogeneity.[7−9] Anionic polymerization using high-vacuum techniques remains the best method for synthesis of such well-defined macromolecules; but this technique is usually not compatible with polar groups.[7,10−13] However, Ishizone et al. discovered that the anionic polymerization of 4CNS in tetrahydrofuran (THF) at −78 °C is feasible[8,9,14−16] due to the stabilization of carbanions at their active chain ends by electron affinity of the cyano groups, in addition to the usual phenyl resonance stabilization of the anionic chain end. Hirao's group was able to synthesize P4CNS with molecular weights up to 122 000 g/mol and low polydispersity indices (PDI $<$ 1.1), but their synthesis required long reaction times (∼20 h) and cloudiness was observed in the polymerization mixture during the synthesis of the higher molecular weight polymers.[8]

In order to overcome the solubility issues (observed cloudiness) and thus reduce the reaction time, we considered mixing THF (a poor solvent for P4CNS) with *N,N*-dimethylacetamide (DMA), a good solvent for P4CNS, in an appropriate ratio. The use of this mixed solvent in specific ratio resolves the solubility problem of P4CNS in THF and allows the use of DMA at −78 °C, which is far below its freezing point of −20 °C. We report herein our results on the anionic polymerization (using high-vacuum techniques) of 4-CNS in this mixed solvent system.

Experimental Section

Purification of Reagents. *Purification of 4-Cyanostyrene*. The monomer (6 g, 0.046 mol) (97% Acros) was left under stirring overnight in a short path reactor over CaH_2, and the next day the monomer was distilled into an ampule at 40−45 °C (∼5.7 g). The inhibitor-free monomer was then attached to a second reactor and, after treatment with dibutylmagnesium at 0 °C for ∼15 min, was distilled (5.1 g) into a new ampule and diluted with 2 mL of tetrahydrofuran. THF used for dilution of the monomer was distilled from sodium/potassium alloy (K/Na 3:1), followed by treatment with diphenyhexyllithium at room temperature (RT) for an hour. The purified monomer was kept until polymerization at −78 °C, since it easily homopolymerizes, even at temperatures as low as −10 °C, producing an insoluble network.

Purification of N,N-Dimethylacetamide (DMA). A known quantity of DMA (30 mL) ($>$99.5%, Aldrich) was left under stirring with CaH_2 overnight at room temperature and distilled into an ampule under vacuum at 35 °C, since this solvent is known to decompose easily on heating. The ampule of predried DMA was then attached to a reactor, flask B shown in Figure 1. DMA was added into the main flask and treated with a small amount (5−6 mL) of trioctylaluminum (already injected via septum C) at RT for 1 h (until the color of the solution turned to light yellow). It was then distilled into ampule A (Figure 1), again at 35 °C.

As a final purification step, the DMA collected in the ampule was slowly added to a mixture of ∼20 mL of *n*-BuLi and ∼0.5 mL of 1,1-diphenylethylene (DPE) mixed with 100 mL of THF already cooled to −78 °C, in an another reactor similar to that depicted in Figure 2. The THF/DMA mixture was left under stirring for at least 1 h. In the case where the mixture froze, a few additional milliliters of THF were distilled in the reactor until the frozen mixture became liquid again. This procedure was repeated as many times as necessary, until the mixture remained liquid and clear. The final solvent mixture was then distilled into a new ampule at 35 °C, and an aliquot (a few milliliters) was removed for GC-MS characterization, where the THF/DMA 4/1 ratio was established. A ∼15% loss of DMA was observed during distillation at 35 °C due to reaction of its carbonyl groups with DPHLi. For this reason, the ampule of DMA added to THF−DPHLi at −78 °C contained the appropriate excess (30 mL instead of 25 mL).

The purification of THF (Aldrich, 99.9%), the terminating agent (methanol, 99.9%, Aldrich), trioctylaluminum (25 wt % in hexanes, Aldrich), dibutylmagnesium (1 M in heptane, Aldrich), and 1,1-diphenylethylene (Aldrich, 99%) was performed to the standards required for anionic polymerization, using well-established high-vacuum techniques.[17,18] *sec*-Butyllithium (*sec*-BuLi), prepared from *sec*-butyl chloride (99.9% Aldrich) and lithium dispersion (99% high sodium, Aldrich) end-capped with one monomeric unit of DPE (diphenylhexyllithium, DPHLi), served as the initiator for all polymerizations.

Homopolymerization of 4-Cyanostyrene. All polymerizations were carried out in evacuated, *n*-BuLi-washed, and solvent-rinsed

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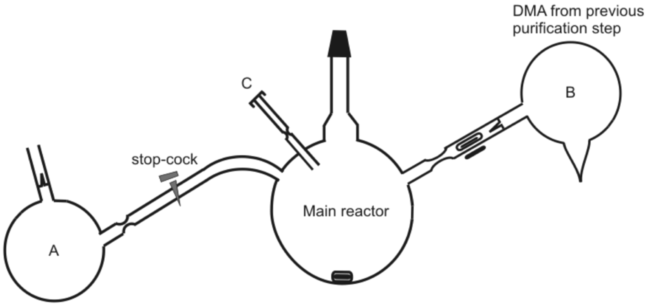


Figure 1. Reactor for the purification of DMA with trioctylaluminum and DPHLi under high vacuum.

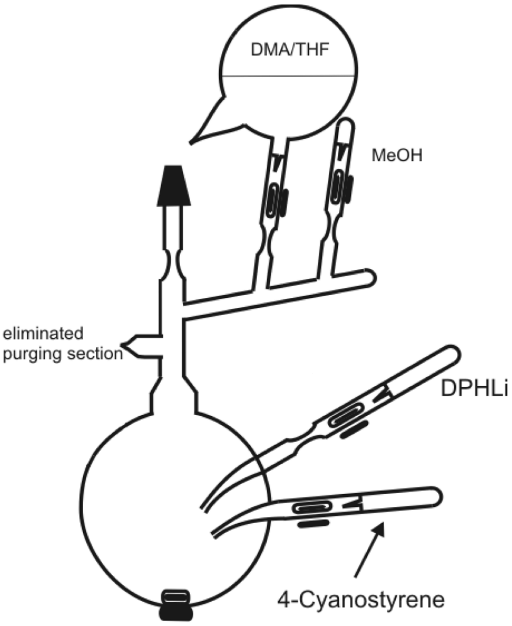


Figure 2. Polymerization reactor used for the polymerization 4-cyanostyrene in THF:DMF (4:1, v/v) at −78 °C.

glass reactors. Reagents were introduced via break-seals, and aliquots for characterization were removed by heat-sealing of constrictions. Full details of the high-vacuum techniques are given elsewhere.[17,18] The apparatus in Figure 2 was used for the synthesis of the poly(4-CNS) homopolymers.

The mixture of THF−DMA (125 mL, 4/1 v/v) was added in the main reactor (Figure 2) after breaking the corresponding break-seal and was left at −78 °C for 20 min. The initiator DPHLi (*sec*-BuLi end-capped with one monomeric unit of DPE, 9.6×10^{-5} mol) was introduced, and the dark orange color of the initiator immediately turned into dark red. The monomer ampule was then opened, and 4-CNS (5.1 g, 0.040 mol) was added (slowly poured) into the main reactor under stirring. The color of the solution turned dark rose red and remained stable until termination of the polymerization.

After complete addition of the monomer, the polymerization was left to proceed for an additional 20 min; the reaction was terminated by addition of a small amount of degassed MeOH, and the polymer was precipitated in MeOH. The white polymer was filtered and dried in vacuum (4.75 g, yield 93%).

Molecular Characterization. Size exclusion chromatography (SEC) analysis of PCNS was carried out at 25 °C using a PL-GPC 50 Plus (Polymer Laboratories, Inc.) with a differential refractive index detector, one PSS GRAL guard column (50 × 8 mm, 10 μm particles, Polymer Standards Service-USA, Inc.), and two PSS GRAL linear columns (each 300 × 8 mm, 10 μm, molecular weight range from 500 to 1 000 000 according to Polymer Standards Service-USA, Inc.). Calibration was performed with polystyrene samples at 25 °C, and DMF was used as the mobile phase at a flow rate of 1 mL/min.

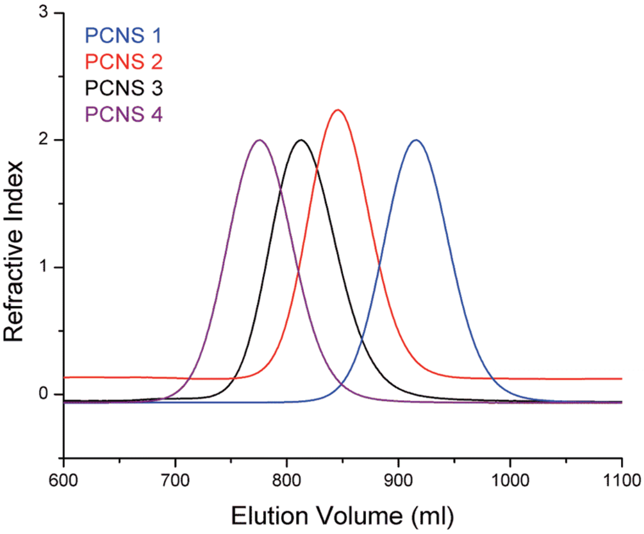


Figure 3. SEC traces of poly(4-cyanostyrene)s synthesized using DPHLi initiator in THF:DMA (4:1, v/v) mixture solvent at −78 °C.

Results and Discussion

The very high reactivity of cyanostyrenes is attributed to the strong electron-withdrawing ability of the cyano group on the aromatic ring, which delocalizes the π-electron of the vinyl bond. The electron-withdrawing ability of the cyano group also severely affects the stability of propagating anions. Hirao and co-workers showed that during the anionic polymerization of 4-cyanostyrene using various anionic initiators and with target molecular weights above 30 000 g/mol the polymer precipitated from the solution. As the reaction was performed in THF, the polymerization of substituted styrene, especially 4CNS, would propagate rapidly through solvent-separated contact ion-pair intermediates. In order to obtain quantitative monomer conversion, the polymerization was performed for 20 h.

High dielectric solvents such as dimethylformamide (DMF), dimethylacetamide (DMA), and hexamethylphosphoric triamide (HMPT) can be used along with THF to improve the solubility of 4CNS during the polymerization. Jerome and Varshney and co-workers used these solvents to alleviate the poor solubility of poly(4-vinylpyridine) in THF during anionic homo and block copolymerization.[19,20] In order to overcome the lack of solubility of P4CNS in THF and thus to reduce the reaction time to less than 30 min, we used a THF/DMA solvent mixture in 4/1 (v/v) ratio. The cosolvent DMA was selected as it is a good solvent for P4CNS, and in the presence of a large excess of THF (75%), the THF/DMA mixture does not freeze at −78 °C. This ratio resolves the problem of the P4CNS limited solubility in THF and significantly minimizes the polymerization time to less than 30 min, regardless of the target molecular weight.

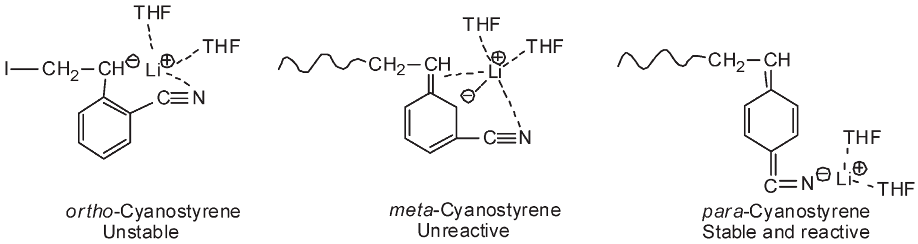
DMA is not generally a solvent of choice for anionic polymerization due to its high reactivity with alkyllithium compounds as well as purification difficulties. For this reason, a less reactive resonance stabilized adduct of *sec*-BuLi with 1,1-diphenylethylene (DPHLi) was used as initiator, and the polymerization was conducted at −78 °C. Several different methods[20] were used for the purification of DMA, and finally the following procedure was found to be the most appropriate for our system. Treatment with trioctylaluminum to remove unwanted amines, the most common impurity, was followed by exposure to the THF/DPHLi mixture, already cooled to −78 °C. At this low temperature

Table 1. Anionic Polymerization of 4-Cyanostyrene (4CNS) Using Diphenylhexyllithium (DPHLi) as Initiator in THF:DMA (4:1, v/v) Mixture Solvent at −78 °C

sample	[4CNS] (mol/L)	[DPHLi] (10^{-4} mol/L)	t (min)	target M_n[a] (kg/mol)	M_n observed[b] (kg/mol)	PDI[b] (M_w/M_n)
P4CNS 1	0.069	2.976	20	30	32.2	1.06
P4CNS 2	0.316	7.846	20	52	58.6	1.05
P4CNS 3	0.139	2.272	25	79	75.6	1.06
P4CNS 4	0.071	0.080	25	110	98.5	1.09

[a] $M_{n,th}$ = grams of 4CNS/[DPHLi]. [b] Determined using SEC in DMF at 25 °C and $M_{n,obs} = (0.459\ M_{n,SEC\text{-}PS}) = 3820$.

Scheme 1. Effect of −CN in Stabilization of Solvated Propagating Anion of Poly(cyanostyrene) in THF at −78 °C



DPHLi reacts only with the remaining impurities in DMA and not with its carbonyl groups. The constant dark red color of the solution, typical of DPHLi in THF, is a proof of the high purity of the solvent mixture. The THF/DMA ratio is critical for the successful polymerization since deviations lead to either DMA freezing or polymer insolubility.

Another significant issue is the storage of pure 4CNS, which undergoes rapid self-polymerization at room temperature due to its high reactivity and thus was diluted with THF and kept at −78 °C. Several polymerizations of 4CNS were conducted using DPHLi as initiator. Upon addition of the monomer solution, the dark orange color of the initiator solution changed to red and the polymerization proceeded for about 20−30 min. The polymerization solution was homogeneous in all the reactions, and the precipitation of growing P4CNS was not observed in THF/DMA (4:1, v/v) solvent mixture at −78 °C. In all cases, the recovered yield was >90% due to loss of polymer from the reactor.

The SEC chromatograms of all the P4CNS synthesized are given in Figure 3, and the molecular weight characterization data are summarized in Table 1. The number-average molecular weights ($M_{n,obs}$) of the samples were calculated using the following equation,[6] which was established by Ishizone et al.[8] via end-group analysis using ^{1}H NMR spectroscopy to estimate the molecular weights of P4CNS samples bearing a trimethylsilyl end-group:

$$M_{n,\,obs} = 0.459 M_{n,\,SEC\text{-}PS} - 3820$$

Here, $M_{n,SEC\text{-}PS}$ is the molecular weight determined by SEC based on polystyrene calibration.

Previous results obtained by Hirao et al.[8,9] indicated that the problem associated with the controlled anionic polymerization of various substituted cyanostyrenes in THF at −78 °C can be attributed to (a) intramolecular attack of propagating anions on the cyano group in the case of ortho-cyanostyrene and (b) formation of stable resonance stabilized propagating anion coordination with lithium counterion and cyano group in the case of *m*-cyanostyrene. However, this side reaction and resonance stabilization, which render unstable and nonreactive propagating species, do not occur in the anionic polymerization of *p*- or 4-cyanostyrene (Scheme 1). Only the insolubility of poly(4-cyanostyrene) at high degree of polymerization in THF at low temperature needed to be taken into consideration.

The presence of high dielectric solvent such as DMA in THF substantially improves the solubility of P4CNS (Table 1). In spite of the fact that the observed molecular weights of P4CNS were higher than 30 000 g/mol (32 200 < $M_{n,obs}$ < 98 500), these polymers are soluble in the THF/DMA (4:1, v/v) solvent mixture during the polymerization. From the data in Table 1 and Figure 3, it is clear that our method leads to well-defined P4CNS with predictable molecular weights and low polydispersity indices.

Conclusions

The successful anionic living polymerization of 4-CNS was achieved by employing a 4/1 THF/DMA solvent mixture. Under our polymerization conditions, previously reported solubility problems are overcome, and well-defined polymers are obtained in under 30 min, without any observed molecular weight limitations. The difficulty in the purification of the two (polar) solvents is a small price to pay in light of the significant reduction in polymerization time. Finally, our method can be applied to the synthesis of P4CNS-based homopolymers and copolymers of various molecular architectures.

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