Synthesis of Living Cationic Poly(*N*-vinylcarbazole) with Low Molecular Weight

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ABSTRACT: Living cationic polymers of *N*-vinylcarbazole (NVC) with controlled low molecular weight ($M_n = 10^3$ — 10^4) and narrow molecular weight distribution ($M_w/M_n \sim 1.2$) were synthesized with iodine initiator at -78°C in methylene chloride containing a common-ion salt ($n\text{Bu}_4\text{NI}$). The polymerization was carried out at low NVC concentration (20—60 mM; $[\text{I}_2]_0 = 1.0 \text{ mM}$; $[n\text{Bu}_4\text{NI}] = 0.50 \text{ mM}$) by the successive addition of small amounts of the monomer to a completely polymerized solution. At each stage of the monomer addition, the reaction was rapid and quantitative (completed within 5 min), and the number-average molecular weight (M_n) of the polymers was proportional to the total amount of added NVC. In salt-free methylene chloride solvent, on the other hand, such living polymerization did not take place; the M_n of the total polymer decreased with further monomer addition. At higher temperatures (-30 and -15°C), no living polymers were obtained even in the presence of the added salt.

KEY WORDS *N*-Vinylcarbazole / Iodine / Living Polymer / Cationic Polymerization / Molecular Weight Distribution / Common-Ion Salt /

Although the living cationic polymerization of vinyl monomers is difficult because of the instability of the propagating carbocations, our recent studies¹⁻³ have shown that vinyl polymerizations initiated with iodine can be "living" under suitable conditions. For example, the polymerization of *N*-vinylcarbazole (NVC) with iodine leads to living polymers in either CH_2Cl_2 or $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ mixed solvent at -50°C .³ Under these conditions ($[\text{NVC}]_0 = 0.20 \text{ M}$, $[\text{I}_2]_0 = 0.20$ — 1.2 mM), the number-average molecular weight (M_n) of the polymers is in the range of $(0.2$ — $5) \times 10^5$ and increases linearly with increasing monomer conversion, and M_n increases further on addition of a new monomer feed to a completely polymerized solution. The molecular weight distribution (MWD) of the poly(NVC) is narrow ($M_w/M_n \sim 1.3$).

As an extension of our study on living NVC polymerization, this investigation aimed at synthesizing living cationic poly(NVC) having controlled low molecular weight ($M_n = 10^3$ — 10^4) which would be useful for the preparation of end-functionalized polymers, etc. Preliminary experi-

ments showed that under the above-described conditions, simply lowering the monomer concentration cannot give such low-molecular weight living polymers. Thus we polymerized NVC with iodine initiator at -78°C at low monomer concentration (low $[\text{NVC}]_0/[\text{I}_2]_0$ ratio) in CH_2Cl_2 solvent in the presence of a common-ion salt ($n\text{Bu}_4\text{NI}$).

EXPERIMENTAL

Materials

NVC was recrystallized three times from *n*-hexane and stored under vacuum in the dark. Commercial iodine (purity $>99.8\%$) and tetra-*n*-butylammonium iodide ($n\text{Bu}_4\text{NI}$) (polarographic grade) were used as supplied. CH_2Cl_2 as the polymerization solvent was washed with aqueous 10% sodium hydroxide solution and water, and then distilled twice successively over phosphorous pentoxide and calcium hydride before use.

Procedures

Polymerization was carried out at -78 — 15°C

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under dry nitrogen by injecting an iodine solution into a monomer solution, and was terminated by pre-chilled ammoniacal methanol. The initial concentrations of NVC and iodine were $[NVC]_0 = 20\text{--}60\text{ mM}$ and $[I_2]_0 = 1.0\text{ mM}$, respectively; the reaction mixture contained $0.2\text{--}0.3\text{ mM}$ of water as impurity. When a common-ion salt ($n\text{Bu}_4\text{NI}$) was used, it was added to an iodine solution before initiating the reaction. The polymerization mixture after quenching was washed with an aqueous sodium thiosulfate solution to remove residual iodine and evaporated to dryness at *ca.* 40°C to give products that were subsequently vacuum-dried at room temperature overnight. Polymer yields were always quantitative (by gravimetry); no residual NVC monomer was detected by gel permeation chromatography (GPC). The MWD of the polymers was measured by GPC in tetrahydrofuran eluent on a Jasco FLC-700 chromatograph. M_n was calculated from GPC curves using a polystyrene calibration.

RESULTS AND DISCUSSION

Polymerization in CH_2Cl_2 at -78°C

Because at this low temperature NVC and its polymer are both insoluble in nonpolar solvents (*e.g.*, toluene), polymerization was carried out in a polar medium (CH_2Cl_2) at low monomer concentrations ($[NVC]_0 = 20\text{--}60\text{ mM}$; $[I_2]_0 = 1.0\text{ mM}$). Under these conditions (at low monomer to initiator ratios), the reaction was rapid enough to be completed within five min; the change in polymer molecular weight (M_n) with NVC conversion could not be followed. To see whether living polymerization actually proceeded, we applied a "successive monomer addition" technique by which a small amount of a fresh monomer solution was repeatedly added to a completely polymerized solution (usually in every five min). At each stage of the monomer addition, the polymerization was quantitative.

Figure 1 plots the M_n of poly(NVC) recovered after each monomer addition (up to five times) as a function of the total amount of added NVC ($[NVC]_{\text{total}}$). The polymer molecular weight monotonously decreased with increasing $[NVC]_{\text{total}}$, and the MWD of the polymers became broader with successive monomer addition. Therefore, no living propagating species formed in the polymerization in CH_2Cl_2 at low monomer concentrations. This fact

Figure 1. M_n of poly(NVC) obtained after successive monomer addition in salt-free CH_2Cl_2 solvent at -78°C : $[I_2]_0 = 1.0\text{ mM}$.

Figure 2. M_n and MWD of poly(NVC) obtained after successive monomer addition in CH_2Cl_2 containing $n\text{Bu}_4\text{NI}$ (0.50 mM) at -78°C : $[I_2]_0 = 1.0\text{ mM}$.

is in contrast to the results obtained at a higher $[NVC]_0$ (0.20 M) at -50°C in the same solvent where M_n increases linearly with monomer conversion (see below).³

Polymerization in CH_2Cl_2 Containing a Common-Ion Salt

The non-living polymerization in CH_2Cl_2 , described above, may be due to the involvement of a reactive, highly dissociated propagating species that tends to undergo frequent chain transfer reactions.^{1,2} According to our previous studies,^{1,2} it is necessary to suppress the ionic dissociation of the propagating species to obtain living (long-lived) polymers.

Thus, we carried out NVC polymerization in

CH_2Cl_2 containing a common-ion salt, $n\text{Bu}_4\text{NI}$, that would lead to a less reactive, "nondissociated"²⁴ propagating species. As in the salt-free CH_2Cl_2 solvent, the successive monomer addition technique was employed. The reactions in the presence of the salt were rapid and quantitative (completed within five min) at each stage of monomer addition. Figure 2 shows the M_n and MWD of poly(NVC) obtained in a typical experiment in the presence of $n\text{Bu}_4\text{NI}$ half molar equivalent to the iodine.

The polymers showed a very narrow MWD ($M_w/M_n \sim 1.2$) which shifted clearly toward high molecular weight with increasing $[\text{NVC}]_{\text{total}}$; no broadening of the MWD was observed. More importantly, the M_n of these polymers increased linearly with $[\text{NVC}]_{\text{total}}$ and the linear M_n versus $[\text{NVC}]_{\text{total}}$ plot passed through the origin. These results show that living (long-lived) propagating species form in the polymerization at -78°C in the presence of the added common-ion salt.

Figure 3 compares the number of poly(NVC) chains, N , produced per unit iodine in the presence and absence of the salt. N can be calculated by eq 1:

$$N = \frac{193 \cdot [\text{NVC}]_{\text{total}}}{M_n \cdot [\text{I}_2]_0} \quad (1)$$

The N values for the salt-containing CH_2Cl_2 solvent were independent of $[\text{NVC}]_{\text{total}}$ ($N \sim 0.5$); i.e., chain transfer and termination are absent in this solvent and one living chain is formed from two iodine molecules. In contrast, the N values obtained with salt-free CH_2Cl_2 steadily and considerably increased with increasing $[\text{NVC}]_{\text{total}}$. The progressive increase in N is due to chain transfer reactions and/or formation of new propagating chains from the residual iodine with successive monomer addition.

The linear relationship between M_n and $[\text{NVC}]_{\text{total}}$ means that one can control the polymer molecular weight by simply regulating the $[\text{NVC}]_{\text{total}}/[\text{I}_2]_0$ ratio. Figure 4 demonstrates such control of the M_n of poly(NVC). In these experiments, a number of polymer samples were prepared in the presence of $n\text{Bu}_4\text{NI}$ by successive monomer addition, starting from different $[\text{NVC}]_0$ (20–60 mM). Regardless of the initial NVC concentration and number of monomer additions the M_n 's were nearly proportional to $[\text{NVC}]_{\text{total}}$ and, when plotted against $[\text{NVC}]_{\text{total}}$, gave a single straight line through the origin.

Figure 3. Number of poly(NVC) chains produced per unit initiator in CH_2Cl_2 solvent at -78°C : $[\text{I}_2]_0 = 1.0$ mM. A (○), Salt-free; B (●), $[n\text{Bu}_4\text{NI}] = 0.50$ mM.

Figure 4. M_n as a function of the total amount of added NVC in the polymerization at -78°C in CH_2Cl_2 containing $n\text{Bu}_4\text{NI}$ (0.50 mM): $[\text{I}_2]_0 = 1.0$ mM.

Effects of Common-Ion Salt, Monomer Concentration, and Temperature

The living character of the iodine-initiated NVC polymerization depended strongly on the concentrations of $n\text{Bu}_4\text{NI}$ and the monomer and on reaction temperature.

Experiments at different salt concentrations showed that living NVC polymerization proceeds only in the range of $0.5 \leq [n\text{Bu}_4\text{NI}]/[\text{I}_2]_0 \leq 1.0$. At lower salt concentrations ($[n\text{Bu}_4\text{NI}]/[\text{I}_2]_0 \leq 0.25$), the polymerization was transfer-dominant, as in

Table I. Effect of temperature on the living polymerization of NVC with iodine^a

Temp °C	DP_n	M_w/M_n	Living ^b polymn.
-78	34	1.23	Yes
-50	52	1.33	— ^c
-30	65	1.40	No
-15	69	1.46	No

^a $[NVC]_0 = 20 \text{ mM}$; $[I_2]_0 = 1.0 \text{ mM}$; $[nBu_4NI] = 0.50 \text{ mM}$; conv., ~100%.

^b Judged by an increase in the DP_n (M_n) of polymers on monomer addition.

^c M_n increased slightly with $[NVC]_{\text{total}}$ but was not proportional to $[NVC]_{\text{total}}/[I_2]_0$.

salt-free CH_2Cl_2 solvent. Excess amounts of the salt over iodine ($[nBu_4NI]/[I_2]_0 > 1.0$), in contrast, inhibited the reaction completely, because the excess salt consumes iodine to form an inactive triiodide salt (nBu_4NI_3).

Polymerization at a higher NVC concentration (0.1–0.2 M) was rather slow in the presence of the common-ion salt (less than 10% conversion in 20 min; $[I_2]_0 = 1.0 \text{ mM}$, $[nBu_4NI] = 0.50 \text{ mM}$), and resulted in polymers with broad MWD, probably due to slow initiation by the less reactive nondissociated propagating species. Thus, high monomer concentrations are not suitable for living NVC polymerization.

At the same monomer concentration, the polymer molecular weight was smaller in the presence of the salt than in its absence. In salt-free CH_2Cl_2 solvent, decreasing $[NVC]_0$ from 0.20 M to 0.020 M broadened the MWD of the polymers ($M_w/M_n = 1.2$ –1.3, $[NVC]_0 = 0.20 \text{ M}$;³ $M_w/M_n = 1.69$, $[NVC]_0 = 0.020 \text{ M}$ (Figure 1)), whereas the narrowest MWD was obtained at the lowest $[NVC]_0$ (0.020 M) in CH_2Cl_2 with the added salt (Figure 2). The effect of the monomer concentration is thus complex and depends on the common-ion salt. Perhaps the nature of the propagating species varies with the monomer concentration, and at a low $[NVC]_0$ the stable NVC carbocation, which leads to

living polymers at a high $[NVC]_0$,³ may undergo a chain transfer reaction before reacting with the monomer, since the chance to encounter the monomer is smaller at a lower monomer concentration. Such a transfer reaction will be suppressed when the propagating carbocation is in a strong interaction with the iodide counterion in the presence of the common-ion salt.

The results of polymerizations at temperatures above -78°C are summarized in Table I. No living polymerizations were possible above -30°C even in CH_2Cl_2 containing the common-ion salt; *i.e.*, polymer molecular weight did not increase with $[NVC]_{\text{total}}$ and the polymers showed a broad MWD. At -50°C , the M_n of polymers increased on monomer addition, but the extent to this increase was small and M_n versus $[NVC]_{\text{total}}$ plots showed an intercept.

In conclusion, living cationic poly(NVC) with controlled low molecular weight and narrow MWD can be synthesized by polymerization with iodine initiator at low NVC concentration at -78°C . Suppression of the ionic dissociation of the propagating species plays a critical role in controlling the polymer molecular weight (M_n) which, under living conditions, is simply proportional to the $[NVC]_{\text{total}}/[I_2]_0$ ratio.

Evidently, the stability of the propagating species is another important factor affecting the living character of polymerization. It is the great stability of the propagating NVC carbocation that leads to the nearly perfect living cationic polymerization described in this paper. Extension of our investigation to a variety of monomer/initiator combinations is now under way.

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