

Xanthate-Mediated Controlled Radical Polymerizations of *N*-Vinylcarbazole and Synthesis of Star Polymers

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Introduction

Poly(*N*-vinylcarbazole), poly(NVC), is the first and the most widely studied polymeric photoconductor. Since the first success of poly(NVC) in electrophotographic applications, numerous studies have been devoted to carbazole-containing polymers [1]. Recent developments in this field are mostly connected to the applications in polymeric light emitting diodes, organic photorefractive materials, and photovoltaic devices.

Controlled/living radical polymerization has allowed to synthesize various functional polymers with predetermined molecular weights, narrow polydispersity, and controlled architectures by a facile approach. Although several attempts to synthesize poly(NVC) using controlled/living radical polymerization systems have appeared in the literature, the convincing proof for the controlled character of the homopolymerization of NVC was not provided. The difficulties in adapting the controlled radical polymerization to NVC may rely on the fact that the NVC propagating radical is relatively unstable and thus highly reactive, which is mainly due to the electron-donating carbazolyl pendant.

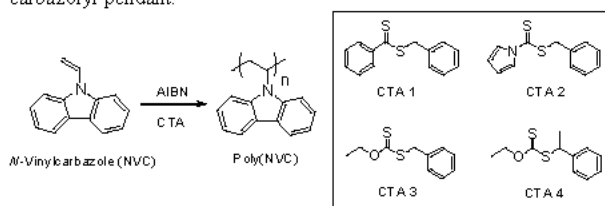


Figure 1. Controlled radical polymerization of NVC in the presence of chain transfer agent (CTA) and the structures of CTAs.

We now report the controlled synthesis of poly(NVC) with predetermined molecular weights and a narrow polydispersity by the xanthate-mediated controlled radical polymerization (Figure 1) [2]. In this study, we employed the xanthate-type CTA, because it increases the electron density at the radical center, which may lead to the destabilization of the intermediate RAFT-adduct radicals and the increase in the fragmentation rate.

Results and discussion

In this study, four different CTAs, a dithioester-type (CTA 1), a dithiocarbamate-type (CTA 2), and two xanthate-type (CTA 3 and CTA 4) mediating agents were selected (Figure 1). The polymerization of NVC was conducted at 60 °C using four different CTAs and AIBN as an initiator in various solvents. Our preliminary experiments indicated that the xanthate-type mediating agent (*O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate, CTA 4) was efficient for the preparation of poly(NVC)s with controlled molecular weights and low polydispersities. For example, a high conversion (> 99%) was reached after 24 h and the resulting polymer showed a sharp symmetrical SEC peak ($M_w/M_n < 1.2$) with reasonable molecular weights, when NVC was polymerized with the xanthate-type CTA 4.

The controlled/living character of this process was investigated by performing kinetic investigations in 1,4-dioxane at 60 °C. The linear first-order kinetic plots were seen in the polymerizations of NVC with AIBN in the presence of CTA 4. The polymerization rate apparently decreased with the increasing the $[CTA\ 4]_0/[AIBN]_0$ ratio. As shown in Figure 2a, a linear increase in the M_n with conversion reveals a constant number of propagating chains throughout the polymerization and the absence of a nondegenerative chain transfer reaction. The SEC traces of the poly(NVC)s obtained at different reaction times are shown in Figure 2b. A progressive increase in the molar mass with

the conversion with the narrow unimodal peaks is clearly seen, as normally evidenced for a controlled/living polymerization.

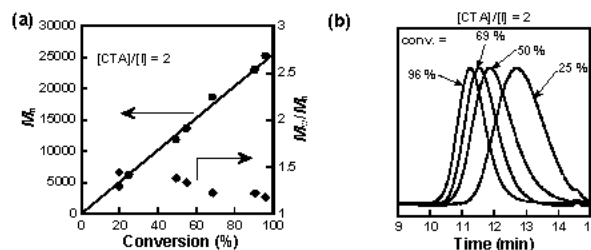


Figure 2. (a) M_n (circles) and M_w/M_n (squares) as a function of conversion, and (b) evolution of SEC traces with conversion for the polymerization of NVC with AIBN in the presence of CTA 4 at the ratio $[NVC]_0/[CTA\ 4]_0 = 200$ and $[CTA\ 4]_0/[AIBN]_0 = 2$.

Under suitable conditions using the xanthate-type CTA 4, the controlled/living character of the polymerization was also confirmed by the formation of the narrow polydispersity products, feasibility to control molecular weight based on the ratio of monomer consumed to the amount of CTA used (Figure 3), and the ability to extend the chains by the second addition of the monomer.

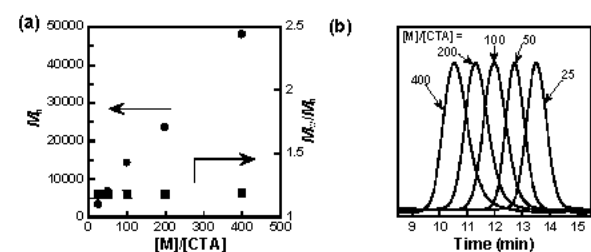


Figure 3. (a) Dependence of M_n and M_w/M_n on $[NVC]_0/[CTA\ 4]_0$ ratio for polymerization of NVC using AIBN and CTA 4 in 1,4-dioxane at 60 °C for 24 h. (b) SEC traces of the corresponding poly(NVC)s obtained at different $[NVC]_0/[CTA\ 4]_0$ ratios.

The xanthate-mediated controlled radical polymerization was also applied for the synthesis of novel polymeric architectures having poly(NVC) segments. An example is the synthesis of star polymers using a tetrafunctional xanthate as the RAFT agent, in which the stabilizing groups are linked to the core (Figure 4). The poly(NVC) stars with relatively narrow polydispersities ($M_w/M_n < 1.3$) were obtained with reasonable conversion.

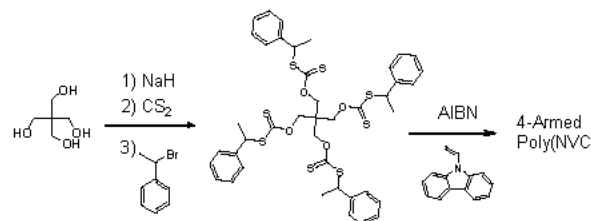


Figure 4. Synthesis of tetrafunctional RAFT agent and poly(NVC) star.

Conclusions

This work substantially broadens and extends the scope of carbazole-containing polymers, in which precise control of the molecular weight, polydispersity, topology, composition, and functions can be achieved using controlled radical polymerization technique.

References

- Grazulevicius, J. V.; Strohriegel, P.; Pieliowski, J.; Pieliowski, K. *Progress in Polymer Science* 2003, 28, 1297-1401.
- Mori, H.; Ookuma, H.; Nakano, S.; Endo, T. *Macromolecular Chemistry and Physics* 2006, 207, 1005-1017.