Controlled Synthesis of Optoelectronic Polymers by RAFT Polymerization

Hideharu Mori

Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, 992-8510, Japan
h.mori@yz.yamagata-u.ac.jp

Introduction

Nitrogen-containing heterocyclic compounds are important components of many natural and synthetic products with wide range of properties. In recent years, there has been renewed interest in the synthetic polymers having nitrogen-containing heterocyclic moieties. For example, poly(N-vinylcarbazole), poly(NVC), is the first and the most widely studied polymeric photoconductor.[1] Recent developments in this field are mostly connected to the applications in polymeric light emitting diodes, organic photorefractive materials, and photovoltaic devices. To manipulate unique electronic and photonic functions of these polymers, it is desirable to establish precise synthetic methods to control molecular weight, polydispersity, topology, composition, and functions.

Here, we present controlled synthesis of optoelectronic polymers with complex architectures by reversible addition-fragmentation chain transfer (RAFT) polymerization[2-6] of functional monomers, such as NVC, N-vinylindole derivatives (NVIn, 2MNVIn, 3MNVIn), and N-vinylphtalimide (NVPI), as shown in Figure 1. Controlled/living radical polymerization has allowed to synthesize various functional polymers with predetermined molecular weights, narrow molecular weight distribution, and controlled architectures, such as graft and block copolymers, by a facile approach. Among various controlled radical polymerizations, in this study, we selected RAFT polymerization, because of versatility with respect to monomer type and reaction conditions.

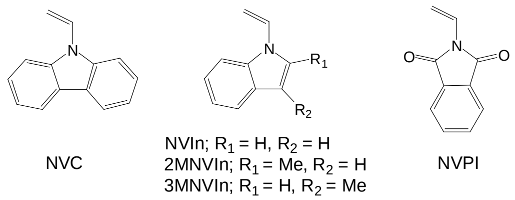

Figure 1. Structures of N-Vinyl Monomers

Experimental

Monomers

N-Vinylcarbazole (NVC, Tokyo Kasei, 98%) was recrystallized two times from methanol. 2-Methyl-N-vinylindole (2MNVIn) was obtained by the N-alkylation of 2-methylindole, followed by the elimination reaction.[7] N-Vinylindole (NVIn) and 3-methy-N-vinylindole (3MNVIn) were synthesized from indole and 3-methylindole, in a manner similar to 2MNVIn, respectively. N-Vinylphthalimide (NVPI, Tokyo Kasei Kogyo, 98%) was purified twice by recrystallization from diethyl ether/hexane (5/1 vol %).

Synthesis of Chain Transfer Agents (CTAs)

Seven different CTAs were employed in this study, as shown in Figure 2. CTA 1 and CTA 2 were synthesized by the reaction of potassium ethyl xanthogenate and corresponding bromide (benzyl bromide for CTA 1 and 1-bromoethyl benzene for CTA 2).[8, 9] Similarly, the synthesis of CTA 4[10] was conducted by the reaction of potassium ethyl xanthogenate with ethyl 2-bromopropanoate. The same method was employed for the syntheses of CTA 3 and CTA 5 using ethyl bromoacetate and ethyl 2-bromo-2-methylpropanoate, respectively. CTA 6[11, 12] and CTA 7[13, 14] were synthesized according to the procedures reported previously.

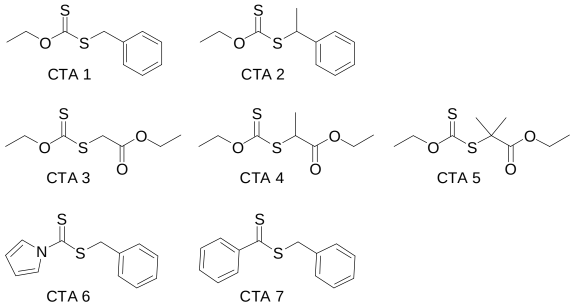

Figure 2. Structures of Chain Transfer Agents (CTAs)

General Polymerization Procedure

All polymerizations were carried out with AIBN as an initiator in the presence of CTA in a degassed sealed tube.

Results and Discussion

Synthesis of Poly(NVC) Stars by RAFT Polymerization

Controlled radical polymerization of N-vinyl and O-vinyl monomers had been difficult, since the generated radical species are highly reactive due to their non-conjugated nature and strong electron donating pendant groups. In a previous study, we found that xanthate-type CTA having a -CH(CH$_3$)Ph moiety as a leaving group (CTA 2) was effective as an RAFT agent for the homopolymerization of NVC.[8] Our recent investigations with various CTAs suggested the effectiveness of the structures of the leaving groups (R = CH(CH$_3$)Ph and CH(CH$_3$)COOCH$_3$ in S=C(OEt)S-R, CTA 2 and CTA 4) in the xanthate derivatives for the controlled polymerization of NVC.

For the synthesis of well-defined poly(NVC) stars, a suitable selection of multifunctional CTA having effective R and Z groups is crucial. Four arm poly(NVC) stars were synthesized by RAFT/macromolecular design via interchange of xanthate (MADIX) polymerization using three different xanthate-type tetrafunctional CTAs. Two Z-designed CTAs having different R (leaving) groups, in which the Z (stabilizing) groups are linked to the core, and one R-designed CTA were compared, as shown in Scheme 3. Four-arm poly(NVC) stars with relatively narrow polydispersity (M_w/M_n = 1.3-1.5) were obtained by using a Z-designed tetrafunctional xanthate (Z-CTA 1).[15] In contrast, R-group approach was found to be the most efficient for the controlled synthesis of four-arm poly(NVC) stars having low polydispersity. The comparison of the polymerization behaviors using two Z-designed tetrafunctional xanthates suggested that the structure of the leaving group (R-group) has a clear effect on the polymerization kinetics, but has no significant influence on the controlled character of the polymerization. The induction period and the retardation were found to be affected by the structure of the R-group, while these behaviors were independent of the R-group or Z-group approach. Amphiphilic star block copolymers were synthesized by the polymerization of NVC using poly(acrylic acid) star, which were prepared from R-designed tetrafunctional CTA. Characteristic assembled structures in selective solvents and optical properties of the amphiphilic star block copolymers were investigated by DLS, UV-vis, and fluorescence spectroscopic methods.

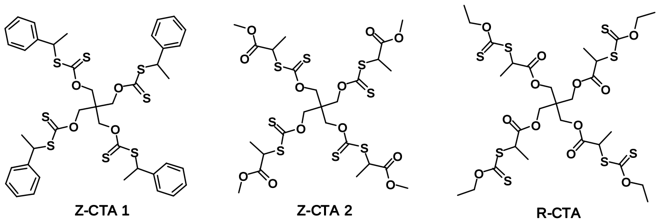

Figure 3. Structures of Z- and R-designed xanthate-type tetrafunctional CTAs

RAFT Polymerization of N-Vinylindole (NVIn) Derivatives

The polymerization of three N-vinylindole derivatives, NVIn, 2MNVIn, and 3MNVIn (Figure 1), were carried out by RAFT/MADIX process.[7] Various CTAs were compared for these polymerizations with AIBN as an initiator. The xanthate-type RAFT agent (CTA 2) was the most efficient for obtaining poly(2MNVIn) with controlled molecular weights (M_n = 1,700-19,400) and narrow molecular weight distributions (M_w/M_n = 1.20-1.40). The effects of several parameters, such as solvent, temperature, monomer concentration, and CTA-to-initiator molar ratio, were examined in order to determine the conditions leading to optimal control of the polymerization. The resulting polymers gave clear spectroscopic evidence of the formation of charge-transfer complexes with efficient sensitizers, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for photoconductivity. The UV-vis spectra of the polymers showed additional absorptions due to the formation of charge-transfer complexes with acceptors. It was found that the structure and properties of the complexes with poly(2MNVIn) are different from those with poly(NVIn) and that the ability to form the complexes is in the order of DDQ > TCNE > TCNQ. In particular, strong CT absorption bands were obtained at longer wavelength (448-860 nm) without any microscopic precipitation, when TCNE was used as an acceptor. The poly(2MNVIn)s obtained by RAFT polymerization showed molecular weight dependence on the glass transition temperature (T_g = 150-190 °C) and thermal stability (T_d[10] = 300-430 °C).

RAFT Polymerization of N-Vinylphthalimide (NVPI)

The polymerization of N-vinylphthalimide (NVPI) was carried out by RAFT process using seven different CTAs.[16] Five xanthate-type CTAs, a dithiocarbamate-type CTA, and a dithioester-type CTA were compared for these polymerizations. Poly(NVPI)s with controlled molecular weights (M_n = 4,100-13,000) and narrow molecular weight (M_w/M_n = 1.29-1.38) distributions were obtained using the xanthate-type RAFT agents (CTA 4 and CTA 5) and carbamate-type one (CTA 6). Good control of the polymerization was confirmed by the molecular weight controlled by the monomer/CTA molar ratio, linear increase in the molecular weight with the polymer yield, and the ability to extend the chain by the second addition of the monomer. Hydrazinolysis of the poly(NVPI) proceeded quantitatively to give water-soluble poly(vinyl amine).

Conclusions

This work presents the controlled radical polymerization of various N-vinyl monomers involving NVC, 2MNVIn, and NVPI using suitable xanthate-type CTAs. This methodology was successfully applied for the synthesis of well-defined optoelectronic polymers with complex architectures, such as block copolymers, star polymers, and amphiphilic star block copolymers. This work substantially broadens and extends the scope of the polymers having nitrogen-containing heterocyclic moieties, in which precise control of the molecular weight, polydispersity, topology, composition, and functions can be achieved using controlled radical polymerization technique.

Acknowledgments

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