# Notes

## Chiral Polymer Materials: Asymmetric Cyclopolymerization of a Divinyl Functional Monomer Using Protective Group Chemistry[†,‡]

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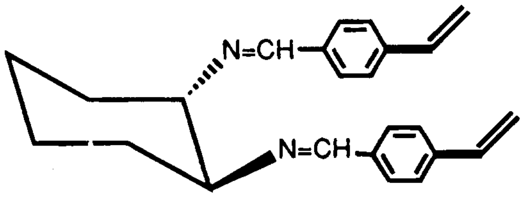
Development of synthetic procedures to obtain polymers exhibiting optical activity due to macromolecular configuration and conformation has attracted a great deal of research interest in recent years.[1−3] Optically active polymer chains with single-handed helical conformations have been synthesized by asymmetric polymerization of sterically demanding monomers that leads to conformationally immobile polymer chains.[4,5] Macromolecular asymmetry originating from main-chain configurations of vinyl polymers requires addressing the complicated symmetry properties that are unique to polymeric systems. The primary requirement for realizing chiral configurations in polymer chains is to circumvent the symmetry properties (e.g., mirror plane, glide reflection plane, *etc.*) at the molecular and macromolecular level.[6] Wulff et al.[7] have offered an ingenuine solution to the problem of circumventing reflection and mirror symmetry of polymer chains. By rigorous stereochemical structure analysis they proposed that, if the (co)polymer chains consist of a specific arrangement of monomer units at the triad, tetrad, hexad, *etc.*, level as the repeat units, the resulting polymers will be chiral. Utilizing the template-mediated (although Wulff et al. have termed the chirality-inducing agent as template, we prefer to address it as chiral auxiliary, which is a more standard stereochemical nomenclature) approach, they demonstrated enantioselective generation of such stereoregular vinyl polymer structures exhibiting optical activity.[8,9] Followed by the work of Wulff et al., other groups have attempted to utilize this concept to synthesize newer types of optically active vinyl polymer structures. For example, Yokota et al.[10] have reported the synthesis of optically active methacrylate polymers using ester-linked L-threitol as the chiral auxiliary. A novel strategy to obtain such optically active vinyl polymers from achiral bifunctional olefins by asymmetric catalytic cyclopolymerization has been developed by Waymouth et al.[11] In all these cases, the polymerization reactions proceed through a cyclopolymerization mechanism of the bifunctional monomers, as has been originally proposed by Wulff et al.[8]

We have been pursuing a research program on the use of the principle of *protective group chemistry* to synthesize various functional polymers.[12,13] One of our research goals has been to use this methodology to precisely ascertain asymmetric inductions in previously reported copolymer systems based on 1,2-disubstituted olefins.[14,15] This study[13] led us to explore further and expand the scope of the aforementioned asymmetric cyclopolymerization of divinyl monomers. Toward this end, we designed a divinyl-type functional monomer where the polymerizable vinyl moieties are connected to the chiral auxiliary through an easily cleavable linker (protecting group). The appropriate monomer designed for this purpose is (*R*,*R*)-*N*,*N*′-bis(4-vinylbenzylidene)-1,2-diaminocyclohexane (**1**). This bifunctional compound is anticipated to undergo cyclopolymerization. Copolymerization of this monomer with another vinyl monomer is anticipated to generate the appropriate asymmetric triad structures in the polymer backbone which are responsible for manifesting optical activity in the resulting copolymers. The azomethine linkage of 1, that connects the polymerizable groups with the chiral auxiliary, is known[12,13] to be cleaved quantitatively under milder conditions. Thus functional polymers completely free from chiral auxiliaries can be obtained.



**1**

Monomer **1** was synthesized by reacting 1 mol equiv of *trans*-(1*R*,2*R*)-(−)-1,2-diaminocyclohexane with 2 mol equiv of 4-vinylbenzaldehyde, and it was obtained as a pure crystalline product.[16] Copolymerization of this monomer with different achiral vinyl monomers, viz., styrene and methyl methacrylate, was carried out at 60 °C in a toluene medium using AIBN (1% w/w with respect to a monomer mixture) as a free-radical polymerization initiator. The concentration of monomer **1** in the polymerization media was typically 0.5 mol/L. In order to achieve homogeneous composition of the copolymers, conversion of monomers to copolymers was restricted to 15−20%. The copolymers were isolated by precipitating the polymerization mixture into methanol to remove unpolymerized monomers. The copolymers thus formed were soluble in the reaction media at all compositions of the monomer mixtures. This suggests the occurrence of intramolecular cyclization of **1** during chain propagation, instead of chain cross-linking that is often encountered during polymerization of divinyl compounds. These polymers, which were completely soluble in the reaction media, became sparingly soluble after precipitation in methanol. Although surprising and the reasons are unknown at the present time, we

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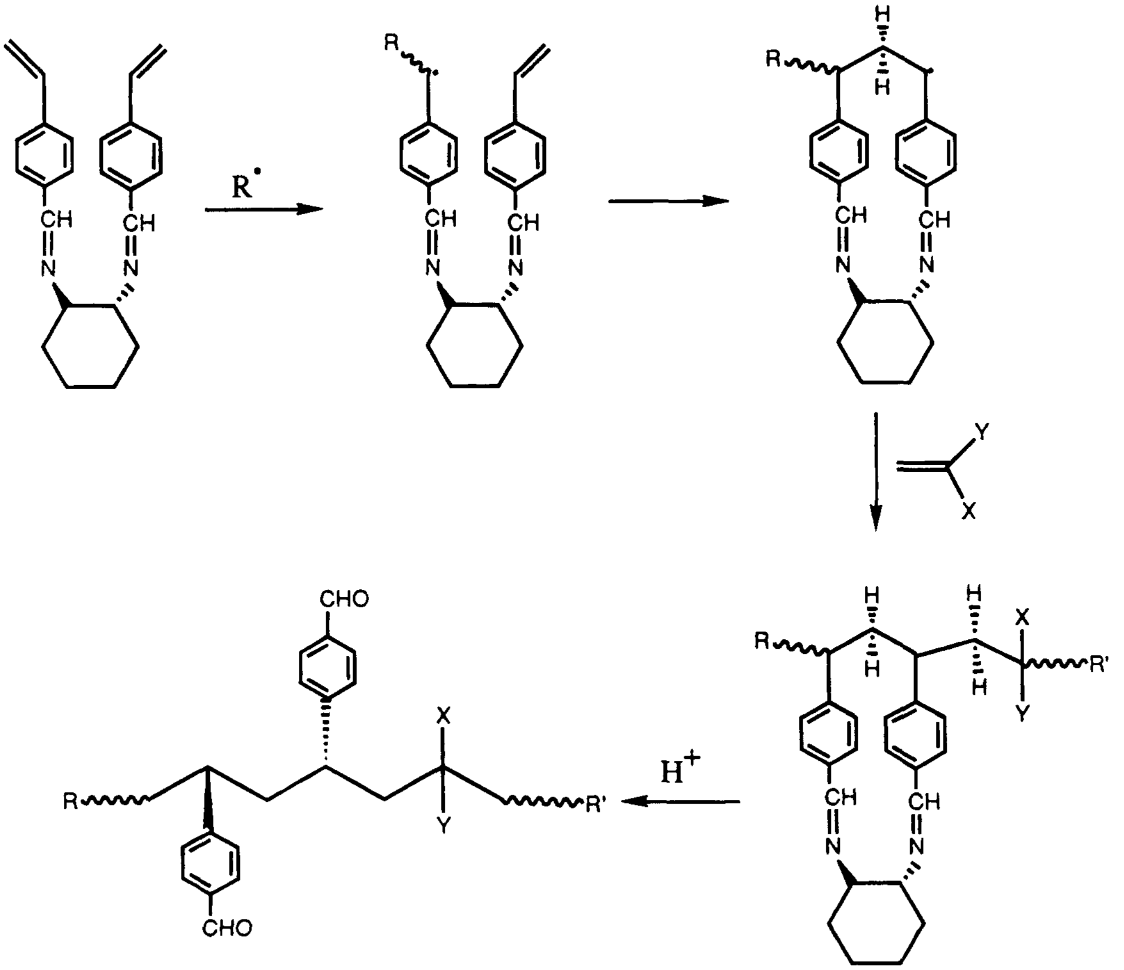
Scheme 1



presume that during the isolation procedure contaminated moisture might have brought about some amount of interchain *trans*-imination, leading to cross-linking. The composition and structures of these copolymers were determined by elemental analysis as well as by infrared (IR) and NMR spectroscopy. IR spectra of these copolymers showed the presence of a 1644 cm$^{-1}$ peak corresponding to the stretching vibration band of the azomethine group. The absence of any peak at 1700 cm$^{-1}$ due to aldehyde carbonyl stretching suggests that the azomethine linkage between the chiral auxiliary and the functional monomer (incorporated in the polymer) remained intact during polymerization. Furthermore, $^1$H NMR spectra of the polymers did not reveal the presence of any residual double bonds.

The key to generation of the chiral motifs in the polymer chains is the cyclopolymerization of the bifunctional monomer bearing the chiral auxiliaries. In order to acertain asymmetric inductions (if any) in these copolymer systems due to the main-chain chiral triad configuration, it is necessary to remove the chiral auxiliaries quantitatively from the polymers. As has been evident from our previous studies,[13] the azomethine linkages can be cleaved quantitatively under milder reaction conditions. The sparingly soluble cyclopolymers were taken in mildly acidified (with HCl) THF, and the mixtures were stirred at room temperature under nitrogen. The polymers, which were sparingly soluble initially, became soluble after some time, thus indicating cleavage of the azomethane linkages. The reaction mixtures were allowed to stir for 24 h and were subsequently precipitated into methanol. The polymers were isolated by filtration, and the above hydrolysis and precipitation cycle was repeated thrice to ensure complete cleavage of the chiral diaminocyclohexane moieties from the polymer. In this manner we obtained a series of aldehyde groups bearing optically active functional copolymers. IR spectroscopy was employed to assess the completeness of this cleavage process. The characteristic peak in the IR spectra of the copolymers bearing the chiral amine moieties is the azomethine stretching band at 1644 cm$^{-1}$. In the case of hydrolyzed copolymers, this peak has completely disappeared. On the contrary, a new peak at 1698 cm$^{-1}$ corresponding to the aldehyde carbonyl stretching has appeared. Furthermore, the characteristic features of the $^1$H NMR spectra of the hydrolyzed copolymers include the complete disappearance of the azomethine proton resonance at 8.4 ppm and the presence of a new peak at 9.6 ppm due to the aldehyde proton. These spectral evidences attest to complete cleavage of the azomethine linkage and hence removal of the chiral diamine. The number-average molecular weights of these hydrolyzed copolymers, as determined by GPC, were found to be in the range of 20 000–25 000. The reaction pathway leading to formation of the optically active aldehyde functional copolymers is illustrated in Scheme 1.

Asymmetric induction in the backbone of these functional copolymers was investigated by the measurement of optical rotational values of the hydrolyzed copolymers. The results on the specific optical rotations and the compositions of these copolymers are summarized in Table 1. All the copolymers exhibit negative optical rotations. Optical activity exhibited by these copoly-

**Table 1. Optical Activities of the Copolymers Based on 1 after Removal of Chiral Auxiliary**

| entry | mol fractn of **1** in the polymn mixt | mol fractn of **1** in the copolymer | $[\alpha]^{25}_{435}$ [a] after hydrolysis |
|---|---|---|---|
| | | Styrene as the Comonomer | |
| 1 | 0.30 | 0.25 | −3.84 |
| 2 | 0.40 | 0.32 | −2.69 |
| 3 | 0.60 | 0.52 | −2.85 |
| 4 | 0.70 | 0.63 | −3.66 |
| | | Methyl Methacrylate as the Comonomer | |
| 5 | 0.30 | 0.27 | −5.04 |
| 6 | 0.40 | 0.36 | −7.30 |
| 7 | 0.50 | 0.47 | −18.07 |

[a] Optical rotational measurements of the polymers were carried out in a 1,4-dioxane medium at a concentration of ~5 mg/mL.

mers suggests generation of the configurationally chiral structures in the polymer backbone with one of the antipodes formed in excess during polymerization. While the specific optical rotational values of the copolymers based on styrene are less sensitive to copolymer composition, those based on methyl methacrylate show an increase in the rotational values with increasing concentration of **1** in the copolymer. Previous studies of Wulff et al.[8] revealed that specific optical rotational values of this class of copolymers were dependent on the nature of the comonomer used. Furthermore, since the chiral contributions of the copolymers stem from the presence of the asymmetric diad units in the chain separated from one another by the comonomer units,[7] higher values of specific optical rotation will be exhibited by those copolymers which possess a larger number of such chiral moieties in the chain. This trend is conceivably dependent on the copolymer composition which was observed in our study (Table 1, entries 5–7).

With regard to the mechanism of chain propagation in this asymmetric copolymerization, it is proposed that the bifunctional monomer **1** undergoes cyclization prior to its copolymerization with the accompanying achiral vinyl monomer in the medium. The energy-minimized structure of this chiral bifuncational monomer is shown Figure 1, which reveals that this compound has the propensity to undergo macrocyclization. Cyclopolymerization of nonconjugated diene derivatives to yield soluble polymers bearing cyclic structures is documented in the literature.[17] Although it may appear that cyclopolymerization would involve some entropic constraint to form a 17-membered ring, a close analysis of its structure reveals the presence of a few flexible points in this molecule. As a result the monomer is locked in a particular conformation with minimal rotational freedom and would favor cyclization of the divinyl compound prior to its addition to another monomer. This cyclopolymerization behavior and mechanism of asymmetric induction parallels the observation made by Wulff et al. and others.[8,11] Further detailed studies involving the role of different comonomers on the chirooptical behavior of the copolymers based on this new monomer as well as the absolute configuration of the resulting copolymers need to be undertaken to answer many of the issues concerning this asymmetric polymerization system.

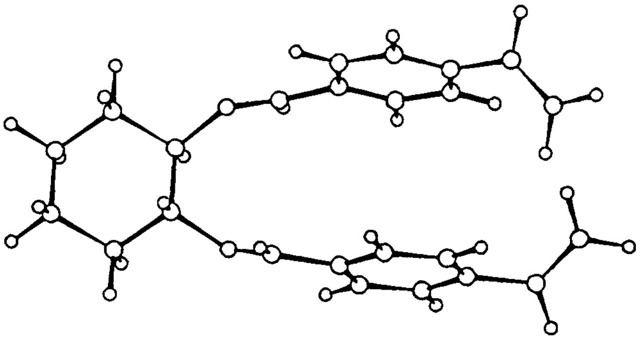


**Figure 1.** PM3-optimized minimum energy conformation of **1**.

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(16) The compound **1** was characterized thoroughly. Some representative analytical data are as follows: mp 112.0 °C. Anal. Calcd for $C_{24}H_{26}N_2$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.43; H, 7.34; N, 5.82. $[\alpha]^{25}_D = -97.0°$ ($c$ = 0.9, THF).
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