Communications to the Editor

The First Report of Cyclopolymerization of Bis(oxazolines) To Give Optically Active Polymacrocycles

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As part of our overall goal to control polymer architecture, we report the first example of *cyclopolymerization* of chiral bis(oxazolines) to give high molecular weight polymers of high optical rotation. Although cyclopolymerization of divinyl monomers has been used in the synthesis of polymers with well-defined architectures,[1−4] application of the method to non-vinyl monomers is rare.[5] In general, the extent of cyclization varies considerably, depending upon the particular reaction, concentration of reactants, the type of monomer, and ring size.[1] Yokota and co-workers prepared binaphthyl-containing polymacrocycles using cationic polymerization of divinyl ethers.[2] We have recently demonstrated that polymerization of 2,2′-bis[(methacryloyloxy)methyl]-1,1′-binaphthyl (**1**; Scheme 1), using group transfer polymerization and free-radical methods, gave polymers whose main-chain chirality and tacticity are controlled by the rigid binaphthyl group.[4] A major obstacle in cyclopolymerization is cross-linking, which results from the competing intermolecular propagation. The fraction, X_c, of cyclization relative to intermolecular propagation is given by the relation

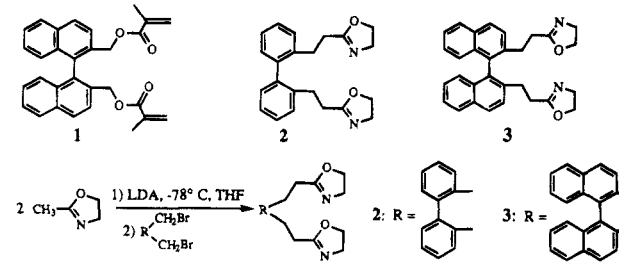
$$X_c = \frac{R_c}{R_c + R_p} \tag{1}$$

where $R_p = 2k_p[P^*][M]$ and $R_c = k_c[P^*]$ and M, P*, R_c and R_p denote monomer and propagating species and rates of intramolecular cyclization and intermolecular propagation, respectively. Hence,

$$X_c^{-1} = 1 + 2k_p[M]/k_c \tag{2}$$

from which it follows that low monomer concentrations and high k_c/k_p should favor cyclization and, conversely, intermolecular propagation should be favored by high monomer concentration. Furthermore, cyclization is accompanied by a smaller decrease in the entropy of activation compared with a corresponding intermolecular reaction and, hence, favored by increasing temperature. The rigid, bulky binaphthyl group is chosen to accomplish the following: (1) provide the convergence necessary for favoring intramolecular cyclization over intermolecular propagation, so that the polymer is devoid of pendent unreacted oxazoline groups that may lead to cross-linking and (2) enhance the helix-forming propensity of poly(oxazolines).[6,7] Appropriately substituted polyoxazolines have been shown to form helices. For example, Goodman and co-workers recently reported that the minimum-energy conformation of poly[(*S*)-2,4-dimethyl-2-oxazoline]is a helix.[7] Additionally, the amphiphilic nature of poly(oxazolines) will permit the study of how chirality affects air/water interfacial behavior.[8a,b] The binaphthyl derivatives are also expected to give optically stable polymers since solutions of 2,2′-disubstituted 1,1′-binaphthyls are known to remain optically stable up to temperatures of 290 °C for many hours.[9]

Scheme 1. Monomers and Their Synthesis



Current synthetic methods for 2-oxazolines usually involve the use of high temperatures in high boiling polar solvents and, sometimes, acidic and basic conditions,[8] making them inappropriate for the synthesis of optically active oxazolines. Hence, we recently developed an efficient method that employs alkylation of the relatively inexpensive 2-methyl-2-oxazoline in excellent yields.[10] Monomers **2** and **3** were, thus, synthesized in high yields as outlined in Scheme 1. Optimum polymerization conditions were first established for monomer **2** and then applied to the polymerization of **3**.[11] The results are summarized in Table 1. To maintain favorable X_c, the polymerizations were carried out in dilute (10−50 mM) *o*-dichlorobenzene (ODCB) at 100 °C. At 100 mM monomer concentration broader and/or bimodal molecular weight distributions were observed, often accompanied by formation of some insoluble polymer. Perusal of the results in Table 1 reveals the following: (1) Polymers of high molecular weight (MWs) are obtained in high isolated yields. (2) The MWs increase as monomer to initiator ratios are increased. (3) Methyl tosylate (MeOTs), triflate (MeOTf), and iodide (MeI) and *N*-methyl-2-phenyl-2-oxazolinium triflate (PhOXA) are suitable initiators for the polymerization. (4) Number-average molecular weights, $\bar{M}_n$, measured by gel permeation chromatography (GPC, polystyrene standards), agree with calculated MWs below 15 000 (runs 1, 2, 4, and 10) but are lower at higher MWs. (5) At the higher monomer to initiator ratios, MWs at peak maximum, $\bar{M}_p$, agree better with calculated MWs above 20 000 (runs 5−8 and 11), within experimental error. (6) The polydispersity index, PDI, calculated from $\bar{M}_w/\bar{M}_n$, is high, especially for the highest monomer to initiator ratios. The differences in observed and calculated MWs may be due to the unavailability of appropriate MW standards and/or chain transfer reactions.[8d]

To determine if polymers have any "living" character, a sequential, "three batch−one pot" polymerization of **2** was carried out. The first batch of monomer was polymerized to 88% conversion (run 6), after which half of the reaction mixture was removed and quenched. An

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Table 1. Polymerization of 2 and 3 in *o*-Dichlorobenzene at 100 °C

run no.	monomer type	[Mon] (mM)	initiator type	Mon:Init mol ratio	time (h)	yield (%)	M_n[a] calcd	M_p[b] GPC	M_n[b] GPC	PDI
1	**2**	10	MeOTs	41	440	92	13 100	23 600	12 700	2.4
2	**2**	50	MeI	51	118	47	8 300	7 100	6 300	1.5
3	**2**	50	MeOTf	52	118	93	16 800	20 800	8 800	2.1
4	**2**	50	PhOXA[d]	38	118	91	12 000	24 900	14 100	1.7
5	**2**	50	MeOTs	158	408	89	48 900	43 700	28 900	2.2
6[c]	**2**	50	MeOTs	50	132	88	15 400	20 500	8 300	2.1
7[c]	**2**	50	MeOTs	100	312	94	32 700	31 500	11 800	2.4
8[c]	**2**	50	MeOTs	150	408	90	47 000	52 700	34 200	2.4
9	*rac*-**3**	10	MeOTs	41	440	90	16 500	23 700	11 000	1.8
10	*rac*-**3**	50	MeOTs	13	24	91	5 300	9 000	3 700	1.3
11	*rac*-**3**	50	MeOTs	48	118	94	20 200	19 300	7 900	2.1
12	(*S*)-**3**	50	MeOTs	55	120	97	23 900	26 700	17 800	1.5

[a] Calculated M_n (corrected for conversion). [b] Determined by gel permeation chromatography in THF with respect to polystyrene standards. [c] Runs 6–8 done in the same reactor: Half the reaction mixture of run 6 was removed and quenched, and an appropriate amount of monomer was added to give the mole ratio for run 7. This was repeated starting from run 7 to give data for run 8. [d] *N*-Methyl-2-phenyl-2-oxazolinium triflate.

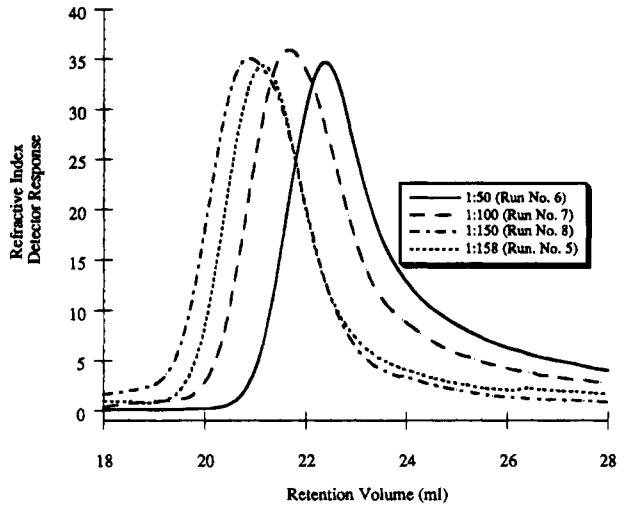
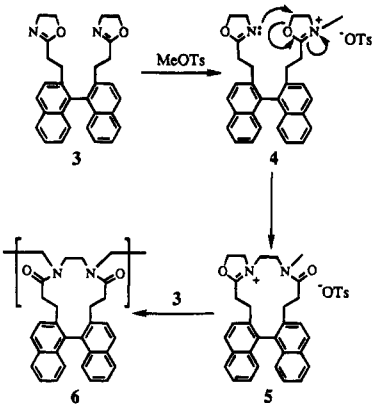


Figure 1. GPC chromatograms of runs 6–8 showing an increase in molecular weight as the monomer to initiator mole ratio increases. The numbers in the inset refer to the monomer to initiator ratios for runs 6–8 in the table of results.

appropriate amount of monomer was then added to give the monomer to initiator mole ratio for run 7. The procedure was repeated to give the data for run 8. The GPC chromatograms of the three batch–one pot polymers (Figure 1) clearly reveal that the MW increases as the monomer to initiator ratio increases. Figure 1 further shows that the MW characteristics of the final polymer (run 8) approximate those of the polymer obtained in a continuous single batch polymerization at approximately the same monomer to initiator ratio (run 5). Since the reaction went to almost complete conversion of monomer at each stage, these results indicate that the polymerization is "living". However, the extent of "livingness" could not be quantitatively determined due to lack of an appropriate MW standard. Efforts to use universal calibration with an on-line viscometer proved futile.

The polymers of **2** and *rac*-**3** possess glass transition temperatures, T_g, of 200 and 278 °C, respectively, as determined by differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) reveals that the polymers are highly thermally stable with a decomposition onset temperature of 400 °C and a maximum decomposition temperature (inflection point in TGA) of 450 °C. All the polymers are extremely soluble in solvents such as chloroform, dichloromethane, tetrahydrofuran, dimethylformamide, *o*-dichlorobenzene, and benzonitrile. The progress of the reaction was monitored by ^{1}H NMR spectroscopy and GPC until signals due to the monomer completely disappeared and MW remained constant. No monomer signals were detected in ^{1}H NMR, ^{13}C NMR, and FTIR spectra of the final polymer. The high isolated yields, the high solubility of the products, and the complete absence of oxazoline characteristic peaks in the NMR confirm that the reaction occurs by the cyclopolymerization mechanism outlined in Scheme 2. The similarity between the polymerization results of **2** and **3** implies that both 1,1′-diaryl monomers provide the convergence necessary for the cyclopolymerization.

Scheme 2. Proposed Mechanism for Cyclopolymerization of 3



The reaction was applied to the optically active monomer (*S*)-(+)-**3** to give the corresponding optically active polymer (run 12). This polymer has a high *mean residue molar optical rotation*, $[\Phi^{27°C}_D$ −1157° (THF, c = 0.9). In contrast, the monomer has an extremely low rotation of opposite sign, $[\Phi^{27°C}_D$ +4° (THF, c = 0.8), and an oligomer ($\bar{M}_n$ = 1200) isolated from 1:1 monomer: initiator reaction has a rotation $[\Phi^{27°C}_D$ = −721° (THF, c = 0.3). Surprisingly, the optically active polymer has a higher T_g (301 °C) and higher decomposition onset temperature (420 °C) than the racemic polymer. Whether or not these results are indications that the high molecular weight optically active polymer adopts an ordered conformation will have to be determined by further studies.

In conclusion, we have demonstrated for the first time the feasibility of cyclopolymerization of bis(oxazolines) to give polymers of very high molecular weights in high yields despite long reaction times (necessitated by the use of very dilute solutions) and high temperatures. Efficient cyclization with almost total exclusion of

acyclic propagation has been realized through a rational monomer design and judicious balance of reaction conditions. The polymers possess high glass transition temperatures and high thermal stability and may, therefore, find use in high-temperature applications. The optically active polymer has an unusually high molar rotation and possesses higher T_g and thermal stability than the racemic one.

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References and Notes

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(11) A typical polymerization procedure is as follows: Inside a drybox, a 50-mL round-bottomed flask, equipped with a wide-bore Rotaflo stopcock and magnetic stirring bar, was charged with 0.22 g of *rac*-**3** and 9 mL of *o*-dichlorobenzene (ODCB) previously distilled twice from CaH_2. To this solution was added 0.25 mL of a MeOTs solution (100 mg/15 mL of ODCB). [MeOTs was distilled twice under nitrogen.] The flask was stoppered, removed from the drybox, and heated in an oil bath at 100 °C for 5 days. The reaction was quenched with t-BuOH and evaporated in vacuo. The crude polymer was dissolved in 4 mL of $CHCl_3$, added dropwise to 200 mL of CH_3CN, vigorously stirred, and then filtered through a 4–8-μm sintered glass filter to give 208 mg (95%) of the desired polymer.

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