Toward Control of Stereochemistry in GTP by a Rational Monomer Design. Cyclopolymerization of 2,2′-Bis((methacryloyloxy)methyl)-1,1′-binaphthyl

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Cyclopolymerization has long been of interest in polymer synthesis. One reason for this is the potential it offers to control stereoregularity of polymers by controlling the mode of ring closure. Recent examples include cyclopolymerization of dienes using Ziegler−Natta catalysts,[1a−c] divinyl ethers by cationic polymerization,[1d,e] diacrylic monomers by free radical[1f−h] and group transfer polymerization (GTP),[1i,j] and diisocyanides by Ni- or Pd-mediated polymerization.[1k] An intriguing possibility is the use of polycyclization reactions in the synthesis of chiral polymers whose chirality is based on main chain stereoregularity rather than side chain chirality.[1c] In this communication, we describe comparative polymerization of a rationally designed chiral monomer, 2,2′-bis((methacryloyloxy)methyl)-1,1′-binaphthyl (**1**) by GTP (Scheme 1), free radical, and anionic methods. The binaphthyl moiety, due to its convergent and rigid structure and demonstrated efficiency in asymmetric inductions,[2] is expected to (1) facilitate faster cyclization (intramolecular) relative to propagation (intermolecular), (2) control both the geometry of the resulting cyclic silyl ketene acetal and the mode of monomer addition, and (3) provide the possibility for inducing a conformationally ordered structure (e.g., helix, as seen in polymethacrylates that contain bulky side groups).[3]

Monomer **1** was synthesized by modification of published procedures[4] and polymerized in dilute solutions (0.026−0.11 M) by standard polymerization techniques. The results and conditions are summarized in Table 1. In all cases, the obtained GTP polymers were soluble in tetrahydrofuran (THF) and $CHCl_3$ and showed no peaks for vinyl groups in the ^1H NMR spectrum (supplementary material). Thus, GTP of **1** occurred exclusively via the cyclization mechanism (Scheme 1). Additional evidence was obtained from field desorption mass spectral (FDMS) analysis of methanol-soluble GTP oligomers (supplementary material). Peaks were observed at 552 and 1002 mass units, corresponding to the cyclic unimer and dimer, respectively, and 522, 536, 972, and 988, corresponding to approximate fragment mass units for loss of CH_3 and OCH_3 from the unimer and dimer. As might be expected, polymerization at a higher monomer concentration (0.3 M) gave polymer that was insoluble in THF, $CHCl_3$, DMF, and DMSO.[5]

Scheme 1. Cyclopolymerization by Group Transfer Polymerization

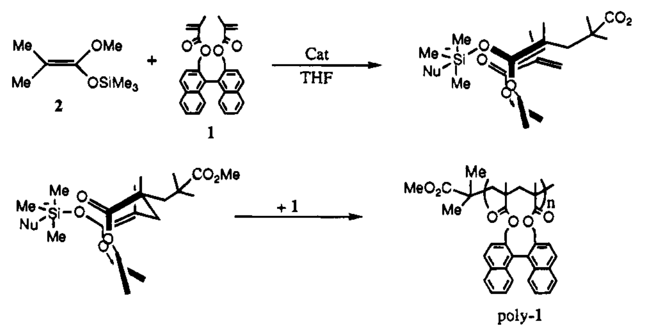

Table 1. Polymerization Conditions and Results for *rac*- and (*S*)-**1**

monomer	catalyst/initiator[a]	method[a]	% yield	$\bar{M}_n$ (GPC)[b] × 10^3	$\bar{M}_w/\bar{M}_n$ (GPC)[b]	% vinyl group
rac	TBA*m*-ClBB/**2**	GTP-batch[d]	>99[c]	10.0	2.05	0
rac	$TASHF_2$/**2**	GTP-batch[d]	>99[c]	18.6	2.93	0
rac	TBA*m*-ClBB/**2**	GTP-feed[d]	>99[c]	10.9	1.84	0
rac	TBAA/**2**	GTP-batch[d]	>99[c]	9	2.25	0
(*S*)	TBAA/**2**	GTP-batch[d]	67[c]	13.6	2.30	0
rac	AIBN	free radical[e,f]	71[c]	5.6	2.36	0
(*S*)	AIBN	free radical[e,f]	52[c]	2.9	2.39	0
rac	FlLi	anionic[g,h,o]	78[i,k]	ND[l]	ND[l]	ND[l]
rac	FlLi	anionic[g,m,o]	98[i]	ND[l]	ND[l]	58[j]
rac	FlLi•PMP	anionic[g,m,p]	91[i]	20	10.6	24[j]
rac	*t*-BuLi/$(t\text{-Bu})_3$Al	anionic[g,m,n,p]	83[i]	75	9.12	36[j]

[a] Abbreviations: TBA*m*-ClBB, tetrabutylammonium *m*-chlorobenzoate; TBAA, tetrabutylammonium acetate; $TASHF_2$, tris(dimethylamino)sulfonium bifluoride; AIBN, azobis(isobutyronitrile); FlLi, 9-fluorenyllithium; FlLi•PMP, fluorenyllithium/(+)-1-(2-pyrrolidinylmethyl)pyrrolidine complex; For GTP: [mon]/[init] = 10; THF, 25 °C. [b] Universal calibration. [c] Polymer precipitated from hexane. [d] [Mon] = 0.052 M. [e] [Mon] = 0.026 M. [f] Solvent = THF; [mon]/[init] = 8; temperature = 60 °C. [g] [Mon]/[init] = 10; temperature = −78 °C; weight (mon) = 0.5 g. [h] [Mon] = 0.11 M. [i] Methanol insoluble. [j] Determined by NMR. [k] Mostly insoluble in $CHCl_3$ and THF. [l] ND = not determined. [m] [Mon] = 0.028 M. Weight (mon) = 0.25 g. [n] Stirred at −78 °C for 23 h and then at 0 °C for 19 h. [o] In THF. [p] In toluene.

Free radical polymerization also gave soluble polymer with no vinyl groups. However, anionic polymerization gave polymer that either was completely insoluble or was soluble but possessed pendant vinyl groups. At a monomer concentration of 0.028 M, the anionic polymer was soluble in $CHCl_3$ and THF, but the ^1H NMR spectrum (supplementary material) showed the presence of unreacted vinyl groups. At a higher concentration (0.11 M), the polymer was mostly insoluble in $CHCl_3$ and THF. The soluble portion gave a very broad molecular weight distribution (MWD), which may partly be due to the fact that intramolecular and intermolecular reactions require opposing conditions. Conditions that normally favor

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(4) (a) Magriot, N.; Mazaleyrat, J.-P. *Synthesis* **1984**, 317. (b) Treatment of racemic 2,2′-bis(bromomethyl)-1,1′-binaphthyl (10 g, 27.7 mmol) with potassium methacrylate (56 mmol) in DMF in the presence of Bu_4NBr (1.46 g, 4.54 mmol) and phenothiazine (35 mg) gave 11.34 g (91%) of **1**, which was purified by crystallization from ether/benzene followed by column chromatography (SiO_2: hexane/ethyl acetate, 8/2, v/v). Mp 141.5−142.5 °C. Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 80.10; H, 5.84. HRMS: calcd 450.18311, found 450.18250. ^1H NMR (400 MHz, $CDCl_3$): δ 1.81 (3H, *s*, CH_3), 4.91 (4H, *s*, $ArCH_2$), 5.46 (1H, *m*, vinyl-H), 5.92 (1H, *m*, vinyl-H), 7.08−8.01 (12H, *m*, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.19 (CH_3), 64.68 (MeC=), 126.22 (H_2C=), 125.71, 126.25, 126.28, 126.60, 128.01, 128.72, 132.40, 132.74, 133.21, 134.42 (Ar). (c) Following the same procedure, (*S*)-2,2′-bis(bromomethyl)-1,1′-binaphthyl (1.97 g, 4.50 mmol) was converted to the corresponding optically active monomer, (*S*)-**1**: $[\alpha]_D^{25}$ −43° (c = 1.00, benzene).

(5) The polydispersities of the polymers are higher than expected. Since there is no indication of bisinitiation in GTP, the origin of the broad MWD is not immediately known. It may be partly due to differences in reactivity of diastereomeric "living" ends and partly to inappropriateness of polystyrene as a MW standard for these unusual polymers. PMMA obtained from esterification of the hydrolyzed polymer gave $\bar{M}_w/\bar{M}_n$ = 1.80 compared with 2.36 for the original polymer.

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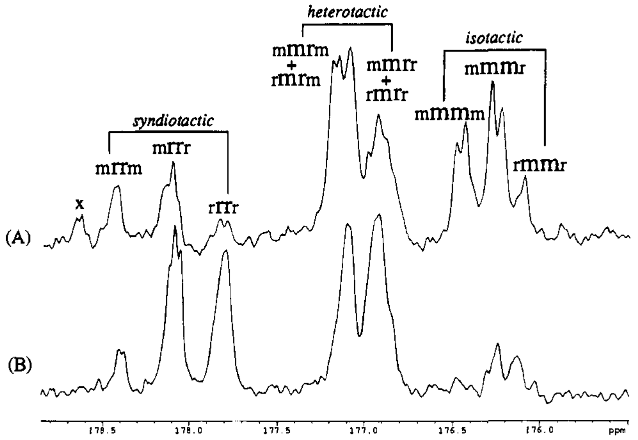

Figure 1. 100 MHz ^{13}C NMR spectra in $CDCl_3$ (carbonyl region) of PMMA derived from poly((*S*)-**1**) (A) and poly(*rac*-**1**) (B); x denotes an impurity peak.

fast initiation, necessary for molecular weight (MW) control in living polymerizations, will likely lead to simultaneous reaction with both monomer sites. Hence, to achieve MW and MWD control in polycyclizations, not only must the relative initiation and propagation rates be controlled but also the intramolecular cyclization rate must be favorable. Obviously, in the case of anionic polymerization, this has not been achieved. Further evidence for this was obtained by FDMS of oligomers obtained in an equimolar reaction (supplementary material). Two sets of peaks were detected at 616.4, 1066.8, 1518.2, 1970.9, and 2302.6, corresponding, respectively, to unimer through pentamer, each of which contained one initiator unit per chain, and at 782.4, 1234.3, 1684.6, and 2136.2, corresponding, respectively, to unimer through tetramer, each with two initiator units per chain. Additional peaks, corresponding to initiator addition to unreacted pendant vinyl groups, were also observed. The results clearly demonstrate the lack of balance among the various rates in the anionic method leading to bisinitiation and inefficient cyclization. It can, therefore, be concluded that, in the case of GTP and free radical methods, the binaphthyl group, indeed, facilitated faster cyclization relative to the intermolecular propagation, thus satisfying the first subgoal.

The stereochemistry of the polymers was determined from the ^{1}H and ^{13}C NMR of PMMA obtained by hydrolysis of poly-**1** using *t*-BuOK/H_2O followed by CH_2N_2 esterification.[3,6] Figure 1 compares the ^{13}C NMR spectra of PMMA derived from poly((*S*)-**1**) (Figure 1A) and poly(*rac*-**1**) (Figure 1B) obtained by GTP. The triad compositions $f_{mm}/f_{mr}/f_{rr}$ are 0.10/0.48/0.42 for poly(*rac*-**1**) and 0.34/0.48/0.18 for poly((*S*)-**1**). Using the expression $f_m = f_{mm} + 0.5f_{mr}$, the dyad composition, f_m, was calculated to be 0.58 and 0.34, respectively. This ($f_m = 0.58$), to our knowledge, is the highest isotacticity obtained for poly(alkyl methacrylate) prepared by GTP. The previously reported high value ($f_m = 0.94$) for poly(trityl methacrylate) (PTrMA) is an exception since the stereochemistry in that case is influenced by helix formation.[3,7] Furthermore, the polymerization of TrMA, unlike standard GTP processes, is non-Bernoullian, which casts doubt on whether or not TrMA polymerizes by a GTP mechanism.[7] Compared with results for PMMA prepared directly under standard GTP conditions ($f_{mm}/f_{mr}/f_{rr} = 0.05/0.39/0.56$ and $f_m = 0.25$),[7,8] the above results amount to a 130% increase in the meso content for poly((*S*)-**1**). The results for poly(*rac*-**1**) compare well with those for GTP of bulky diphenylmethyl methacrylate.[7] The increased meso and heterotactic contents at the expense of syndiotactic content are consistent with our design postulate. Further examination of Figure 1 reveals that the use of the optically active monomer dramatically suppresses the occurrence of the *rrrr* pentad sequence while increasing *mmmm*. Hence, ring closure and monomer addition are controlled by the binaphthyl group, giving preferentially cis geometry. In the case of free radical polymerization, and in contrast to GTP, both *rac*- and (*S*)-**1** monomers gave almost the same stereoregularity: $f_{mm}/f_{mr}/f_{rr} = 0.14/0.50/0.36$ and $f_m = 0.39$ for poly(*rac*-**1**), and $f_{mm}/f_{mr}/f_{rr} = 0.14/0.51/0.33$ and $f_m = 0.40$ for poly((*S*)-**1**). These results are similar to the values reported for PMMA derived from free radical cyclopolymerization of optically active threitol dimethacrylate.[1h] Hence, besides the influence of the convergent binaphthyl group, the presence of Si appears to play a role in the stereochemical control, with impportant implications for the mechanism of the reaction which we are currently studying. Regarding helix formation, there is no evidence that the polymers are highly ordered conformationally, and further studies are required.

In conclusion, we have shown that the judicious choice of properly designed GTP monomers can lead to enhanced macrocyclization and higher meso and heterotactic contents but lower racemic placement. As has been observed by others,[1j] anionic polymerization fails to give cyclic polymers in the cases where GTP succeeds. Efforts are underway to take advantage of these results to design second-generation monomers capable of forming higher order structures.

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Supplementary Material Available: Listings of ^{1}H NMR (400 MHz) spectra of polymer obtained by GTP and anionic methods, field desorption MS spectra of oligomers obtained in both reactions, and ^{1}H NMR (400 MHz) spectrum of monomer **1** with complete assignment of chemical shifts (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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