Gradient Polymers

DOI: 10.1002/anie.201101853

Zwitterionic Copolymerization: Synthesis of Cyclic Gradient Copolymers[**]

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Gradient copolymers are intriguing because their comonomer composition varies continually from the beginning to the end of the linear chain (Figure 1).[1] Experimental and theoretical studies indicate that linear gradient copolymers exhibit distinct physical properties from random and block copolymers as a consequence of their sequence distribution.[1a,2] Because cyclic polymers have no ends, we were intrigued by the challenge of devising an expedient synthesis of cyclic gradient copolymers as these materials would contain both a sharp comonomer interface and a gradient interface in the same molecule.

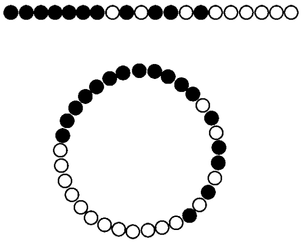

Figure 1. Schematic diagrams of linear and cyclic gradient copolymers.

The topological differences between cyclic and linear macromolecules influence their behavior in ways that remain poorly understood.[3] Cyclic polymers are more compact and entangle differently as a consequence of the chemical bond that connects the chain ends.[3a,d,e,4] Cyclic block copolymers exhibit smaller microdomains and, in some cases, different morphologies than linear diblocks as a consequence of topological constraints on phase separation.[3c,5] These studies highlight the need for synthetic strategies to prepare cyclic polymers[6] with defined sequences to enable studies on the influence of topology and sequence distribution on the self-organization and properties of macromolecules.

We have previously described a synthetic strategy for generating cyclic polyesters by the zwitterionic ring-opening of lactones with nucleophilic N-heterocyclic carbenes.[7] Kinetic studies revealed that the active zwitterions exhibit lifetimes commensurate with that of the growing chains, but attempts to generate block-copolymers were frustrated by reinitiation from unactivated carbenes upon addition of a second batch of monomer.[7c,8] We report here that a one-step gradient batch copolymerization[1] provides a facile method for generating cyclic gradient block copolymers.

The synthesis of gradient copolymers in a batch copolymerization requires that all chains grow under similar conditions and the composition of the monomers in the polymerization medium must change continually as the chains grow.[1a] The first criterion is generally met by living polymerization methods, but it was our hypothesis that the kinetic lifetime of the growing zwitterions might be sufficient to satisfy this first criterion for a gradient copolymerization.

The second criterion requires that the reactivity of the two monomers be sufficiently different such that one monomer is consumed more rapidly than the other.[1] The reactivity of different lactone monomers in ring-opening polymerization of lactones with metal alkoxides is typically not very different,[9] limiting the gradients that could be generated. As previous studies had suggested that the copolymerization selectivities for organic catalysts are different than those of metal alkoxides,[10] the reactivity ratios for the copolymerization of ε-caprolactone (CL) and δ-valerolactone (VL) were determined using benzyl alcohol and 1,3,4,5-tetramethylimidazol-2-ylidene (IMe_4) carbene in THF to generate linear copolymers. The reactivity ratios for VL and for CL were determined to be: $r_{VL} = 9.0$ and $r_{CL} = 0.24$, by the Fineman–Ross method (see Supporting Information). The large difference in reactivity ratios between VL and CL suggested that this system would be competent for a gradient copolymerization.[1] In addition, these data illustrate the significant influence of the organocatalysts on the comonomer reactivities, as the copolymerization of CL and VL with the carbene IMe_4 at 25 °C exhibits a very different copolymerization behavior than $Sn(Oct)_2$ catalysts at 160 °C, for which $r_{VL} = 0.49$ and $r_{CL} = 0.25$.[9]

As the IMe_4 catalyst was fast and difficult to control, we investigated the less active carbene 1,3-diethyl-4,5-dimethylimidiazol-2-ylidene (Me_2IEt) for the generation of cyclic VL/CL copolymers in toluene solution (Figure 2). Copolymerizations of ε-caprolactone (CL) and δ-valerolactone (VL) ($[M_{tot}]_0 = 1.0$ M, $M_{tot}/I = 100$) (M_{tot} = total monomer; I = ini-

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[**] We gratefully acknowledge support from the NSF (NSF-DMR 1001903 and GOALI NSF-CHE-0645891). We thank the Samsung Foundation of Culture for a Samsung Scholarship for E.J.S. and Stanford University for a Stanford Graduate Fellowship for H.A.B.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201101853.

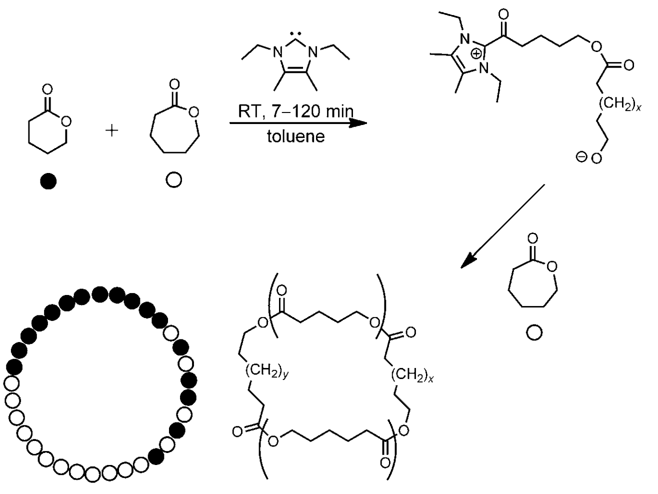

Figure 2. Zwitterionic ring-opening copolymerization of VL and CL.

tiating carbene) were carried out using Me_2IEt in toluene at room temperature for reaction times ranging from 7 min to 2 h to produce a range of copolymer compositions (Table 1).

The resulting copolymers were characterized by NMR spectroscopy, GPC, and DSC. The copolymers obtained exhibited polydispersities (M_w/M_n) ranging from 1.7 to 2.4.[11] Evidence that the copolymers were cyclic were obtained by comparing the intrinsic viscosity[7a,c] of the copolymers produced at each molecular weight by the zwitterionic polymerization versus that of linear VL/CL copolymers prepared with Me_2IEt in the presence of an alcohol initiator. The lower intrinsic viscosities observed for the copolymers obtained in the absence of the alcohol compared to their linear analogs prepared in the presence of alcohol initiators, is indicative of a cyclic structure for the former copolymers (see Supporting Information). The ratio of the intrinsic viscosities are calculated to be around 0.6–0.78, which is in good agreement with theoretical predictions and other experimental findings.[3d]

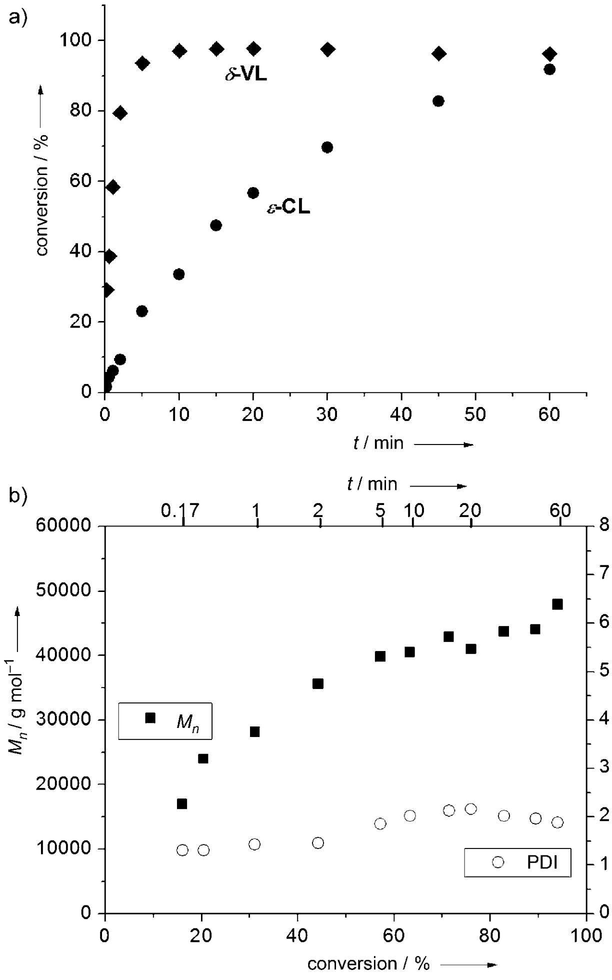

Figure 3. a) Conversion of each monomer with time and b) molecular weight with conversion for M_{VL}:M_{CL} = 1:1, $[M_{tot}]_0$ = 1 M, M_{tot}/I = 100.

The copolymerization behavior was characterized by studying the conversion of each monomer with time and molecular weight with conversion. As seen in Figure 3, the molecular weight increases steadily with conversion, indicative of a continuous incorporation of both monomers into the growing polymer chain. As shown in Figure 3a, VL converts rapidly to reach 94% conversion within 5 min, while the conversion of CL is more gradual over the 1 h period. These results reveal that the composition of the monomers in the polymerization medium changes continually as the chains grow,[1a] implicating the growth of a block consisting predominantly of VL followed by a block consisting predominantly of CL. The cumulative and instantaneous fraction of VL in the copolymer as a function of conversion (see Supporting Information) are also consistent with the formation of a gradient copolymer.

Table 1: Polymerization and characterization data for cyclic gradient copolymers generated by using Me_2IEt.

Entry	VL:CL[a]	t [min]	Conv. [%][b]	% CL[c]	M_w [kg mol^{-1}][d]	M_n [kg mol^{-1}][e]	PDI[e]	T_m [°C][f]	ΔH_m [J g^{-1}][g]
1	100:0	7	92	0	94	85	2.1	57	52
2	70:30	60	94	33	102	46	2.1	44[h]	35
3	50:50	120	91	46	98	56	2.4	38/44	30
4	30:70	120	97	68	110	77	1.9	40/46	41
5	0:100	50	61	100	82	76	1.7	56	55

[a] Feed ratio of δ-valerolactone and ε-caprolactone. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] Percentage of caprolactone; determined by ^{13}C NMR spectroscopy. [d] Absolute molecular weight (M_w) measured by GPC using light scattering. [e] Number average molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography (GPC) with polystyrene calibration. [f] Melting temperature; determined by differential scanning calorimetry (DSC). [g] Heat of melting; determined by DSC.

The microstructure, melting behavior, and solid-state structure of the cyclic copolymers were compared to those of a series of linear VL/CL copolymers prepared by different techniques. The ^{13}C NMR specra revealed that both cyclic and linear copolymers generated by the Me_2IEt carbene, (entries 1 and 2 of Table 2), contain a larger fraction of

Table 2: Selected samples for microstructure analysis.

Entry	Type	CL[a] [%]	M_w[b]	M_n[c]	PDI[c]	T_m[d] [°C]	ΔH_m[e]
1	cyclic NHC	46	98	56	2.4	38/44	30
2	linear NHC	48	43	41	2.1	32/40	40
3	linear $SnOct_2$	47	32	21	1.7	21	54
4	linear diblock	49	20	19	1.2	51/55	69

[a] Percentage of caprolactone; determined by ^{13}C NMR spectroscopy. [b] Absolute molecular weight (M_w, $kg\,mol^{-1}$) measured by GPC using light scattering. [c] Number average molecular weight ($kg\,mol^{-1}$) and polydispersity index; determined by GPC with polystyrene calibration. [d] Melting temperature; determined by DSC. [e] Heat of melting ($J\,g^{-1}$); determined by DSC.

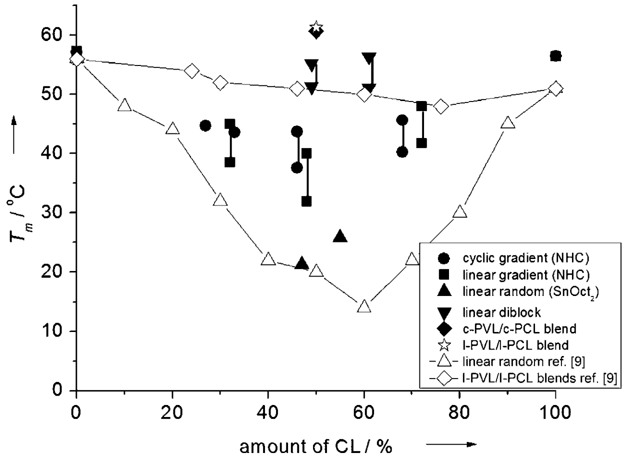

Figure 4. Melting points of various samples compared with literature values (ref. [9]). Two melting peaks from one sample are drawn as two symbols connected with a vertical line.

homo-dyad (CL-*CL* and VL-*VL*) sequences compared to hetero-dyad sequences (CL-*VL* and VL-*CL*) (see Supporting Information). In contrast, the copolymer generated by the tin(II) ethylhexanoate catalyst (entry 3 of Table 2) shows an equal ratio of the homo- and hetero-dyad sequences, consistent with a more random copolymer. For comparison, a linear poly(CL-*b*-VL) diblock copolymer prepared in a stepwise fashion with a 1,5,7-triazabicyclo[4.4.0]dec-5-ene) (TBD) organic catalyst (entry 4 of Table 2)[10a] exhibited only two peaks corresponding to the CL-*CL* and VL-*VL* homo-dyad sequences.

The melting points of the cyclic and linear VL/CL copolymers obtained from the carbene IMe_2Et were compared with those obtained from the copolymerization of VL and CL with $Sn(Oct)_2$ and that of the linear diblock copolymer. The homopolymers of VL and CL are both semicrystalline thermoplastics with melting points of 57 °C ($\Delta H_m = 52\,J\,g^{-1}$) and 56 °C ($\Delta H_m = 55\,J\,g^{-1}$), respectively. Storey[9] and Yoshida[12] have previously shown that random (or slightly alternating) copolymers of VL and CL are semicrystalline across the full composition range but that random copolymers exhibit lower melting points than either of the homopolymers with the lowest melting point (21 °C) being observed for copolymers with approximately 60 mol % CL.

The gradient copolymers exhibit different properties from either the random or block copolymers. For similar compositions (approx. 47 % CL), the gradient copolymers obtained from the carbene catalysts exhibit higher melting points (32–44 °C, solid squares, circles in Figure 4) than those of the random copolymers obtained from $Sn(Oct)_2$,[9] and lower melting points than those of the linear diblock copolymers or blends. The melting exotherms of the gradient copolymers are broader than those of the linear diblock copolymer and have smaller heat of melting compared to the homopolymers, as might be expected if the two comonomers co-crystallize.[9]

In summary, the wide difference in reactivity between VL and CL with NHC catalysts, coupled with sufficiently long lifetimes of the growing zwitterions provides an expedient synthesis of gradient cyclic (or linear) VL-*grad*-CL copolymers comprised of VL-rich sequences that transition to CL-rich sequences in a cyclic macromolecule. The gradient sequences and ability of VL and CL to co-crystallize lead to cyclic copolymers with melting points that are similar to the homopolymers. This synthetic approach provides a strategy for generating unusual topologies and sequences, whose properties are under further investigation.

Received: March 15, 2011
Revised: April 8, 2011

Keywords: block copolymers · copolymerization · lactones · ring-opening polymerization · zwitterions

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