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End Group Characterization of Poly(phthalaldehyde): Surprising Discovery of a Reversible, Cationic Macrocyclization Mechanism

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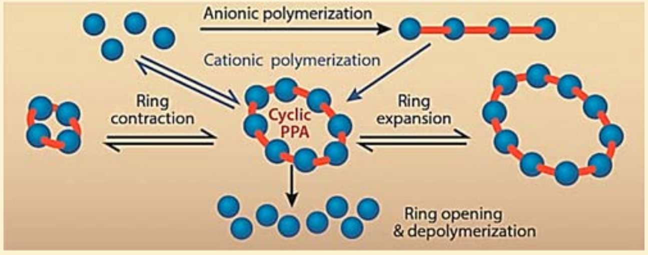
S *Supporting Information*

ABSTRACT: End-capped poly(phthalaldehyde) (PPA) synthesized by anionic polymerization has garnered significant interest due to its ease of synthesis and rapid depolymerization. However, alternative ionic polymerizations to produce PPA have been largely unexplored. In this report, we demonstrate that a cationic polymerization of *o*-phthalaldehyde initiated by boron trifluoride results in cyclic PPA in high yield, with high molecular weight, and with extremely high cyclic purity. The cyclic structure is confirmed by NMR spectroscopy, MALDI-TOF mass spectrometry, and triple-detection GPC. The cyclic polymers are reversibly opened and closed under the polymerization conditions. Owing to PPA's low ceiling temperature, cyclic PPA is capable of chain extension to larger molecular weights, controlled depolymerization to smaller molecular weights, or dynamic intermixing with other polymer chains, both cyclics and end-capped linears. These unusual properties endow the system with great flexibility in the synthesis and isolation of pure cyclic polymers of high molecular weight. Further, we speculate that the absence of end groups enhances the stability of cyclic PPA and makes it an attractive candidate for lithographic applications.



INTRODUCTION

Poly(phthalaldehyde) (PPA) is a stimuli-responsive polymer that has garnered significant interest in recent years.[1−3] PPA has been shown to have a ceiling temperature around −40 °C;[4] i.e., at room temperature without a kinetically stabilizing end cap, it spontaneously depolymerizes to monomer. Since its first syntheses in the 1960s, PPA has been widely used as an acid-sensitive, radiation-sensitive, or heat-sensitive degradable film for lithography.[5] Recently, Philips et al. demonstrated that end-capped PPA prepared via anionic polymerization is activated to depolymerize with specific triggering moieties that remove the end cap.[2] Relative to other depolymerizable polymer classes, PPA benefits from its ease of synthesis[3] and rapid and complete depolymerization.

Interestingly, the cationic polymerization of *o*-phthalaldehyde (*o*-PA) has been studied to a far lesser extent than its anionic counterpart.[4,6] PPA prepared with a boron trifluoride initiator is reportedly isolated without end capping,[6] prompting the authors to speculate that chain entanglement at high molecular weights affords polymer stability above its ceiling temperature. A rigorous assessment of the end group structure of PPA prepared by cationic polymerization is lacking in the literature, and as a result, the polymer prepared by the cationic route has not found wide use in stimuli-responsive applications. We therefore initiated a rigorous study of PPA prepared under cationic conditions, with the intent to attain control over the final molecular weight of the chains, as well as to understand the end capping of the polymers, with the aim to eventually use these polymers for stimuli-responsive applications.

RESULTS AND DISCUSSION

Anionic and Cationic Polymerization of *o*-Phthalaldehyde. The polymerization of *o*-phthalaldehyde was conducted with both anionic and cationic initiators following reported procedures (see Tables 1 and 2).[1,3,4] The cationic polymerization is very fast, yielding PPA within minutes, while the anionic polymerization requires several hours to reach full conversion (see the Supporting Information for full synthetic procedures). PPAs generated under cationic conditions have molecular weights ranging from M_n ca. 3 kDa to greater than ca. 100 kDa, with polydispersities ranging from ca. 1.5 to 4.5 (Table 1). The molecular weights of the cationic polymers do not conform to predictions based on monomer conversion and initial monomer to initiator ratios, a known issue with the cationic polymerization of *o*-phthalaldehyde which will be discussed in subsequent sections.[4,6] Consistent with prior observation, PPA was collected without quenching by addition of a neutralizing base (entry 10).[6] Stable PPA was also isolated without a methanol washing step (entry 11), suggesting that neither pyridine nor methanol is involved in end-capping the polymer chains. Instead, pyridine's role is to neutralize the Lewis acidic initiator, but this step is not essential to

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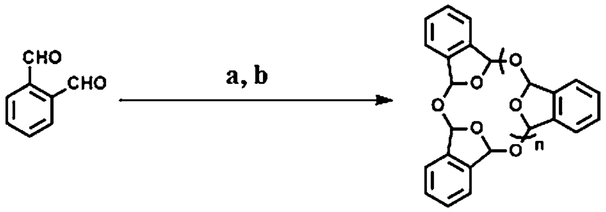
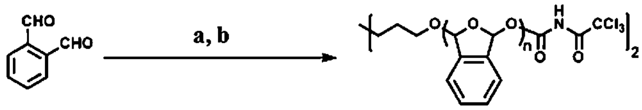
Table 1. Cationic Polymerization Reaction[a]



entry	[*o*-PA] (M)[b]	$[M]_0/[I]_0$	yield (%)	M_n (kDa)[c]	M_p (kDa)[c]	PDI[c]
1	1.0	10/1	86	36.1	158	4.5
2	0.7	7/1	99	109	199	2.5
3	0.7	11/1	73	13.2	31.5	2.5
4	0.5	10/1	77	6.7	10.1	2.4
5	0.1	10/1	48	14.9	54.1	3.5
6	0.1	5/1	52	7.9	9.1	1.7
7	0.4	5/1	60	5.9	17.2	3.0
8[d]	0.1	1/2	17	2.7	2.5	1.6
9[e]	0.2	10/1	63	10.5	22.0	2.2
10[f]	0.7	6/1	76	15.4	73.7	4.4
11[g]	0.7	8/1	99	51.5	107	2.0
12[h]	0.2	6/1	68	25.0	71.4	2.8
13	0.9	20/1	94	104	218	2.3
14[i]	0.9	20/1	92	88.6	158	2.2
15[j]	0.9	20/1	86	89.4	181	2.3
16[k]	0.8	20/1	92	26.2	57.2	2.3

[a] Legend: (a) $BF_3 \cdot OEt_2$, CH_2Cl_2, −78 °C; (b) pyridine, −78 °C. Polymer collected after precipitation into methanol and washing with methanol and diethyl ether. [b] Monomer purified before use according to a literature procedure.[1a] [c] Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards. [d] Polymer made by inverse addition of monomer to 2 equiv of initiator. Low yield attributed to low monomer concentration and use of excess initiator (see the Supporting Information for synthetic details). [e] 3-Fluoropyridine substituted in place of pyridine. [f] No pyridine added. Polymer precipitated directly at −78 °C in diethyl ether and washed in diethyl ether and methanol. [g] Precipitation and washing conducted in hexanes and diethyl ether only. [h] Addition of 1-pyrene methanol following reaction and precipitation into diethyl ether. [i] Triethyloxonium tetrafluoroborate initiator. [j] Tin(IV) chloride initiator. [k] Triphenylcarbenium tetrafluoroborate initiator.

Table 2. Anionic Polymerization Reaction[a]



entry	[*o*-PA] (M)[b]	$[M]_0/[I]_0/[P_2]_0$[c]	yield (%)	M_n (kDa)[d]	M_p (kDa)[d]	PDI[d]
1	0.7	125/1/2	83	4.4	5.4	1.8
2	0.7	250/1/2	92	6.3	8.1	3.0
3	0.7	625/1/2	92	9.0	11.5	2.1
4	0.7	2500/1/3	36	16.1	26.5	2.7
5	0.7	5000/1/3	34	20.4	40.9	2.0

[a] Legend: (a) P_2-*t*-Bu, 1,6-hexanediol, THF, −78 °C; (b) trichloroacetyl isocyanate, −78 °C. Polymer collected by precipitation into methanol and washed in methanol and diethyl ether. [b] Monomer purified before use according to a literature procedure.[1a] [c] Initial monomer to initiator to catalyst ratio.[3] [d] Average molecular weights and polydispersity determined by gel permeation chromatography (GPC), calibrated with monodisperse polystyrene standards.

successfully isolate polymer. Polymerizations were also performed with the alternative cationic initiators triethyloxonium tetrafluoroborate (entry 14), tin(IV) chloride (entry 15), and triphenylcarbenium tetrafluoroborate (entry 16). Regardless of the cationic initiator, PPA was produced with yields and molecular weights similar to those with boron trifluoride initiation.

As a comparison, we also prepared PPA by an anionic polymerization of *o*-phthalaldehyde. In conjunction with an alcohol initiator, the phosphazene base P_2-t-Bu (1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-$2\Lambda^5,4\Lambda^5$-catenadi(phosphazene)) is a known potent catalyst for anionic *o*-phthalaldehyde polymerization.[1a,3] The polymerization reaction is terminated by addition of an electrophile; both trichloroacetyl isocyanate and acetic anhydride effectively end-cap the polymer chains. The PPA chains generated under anionic conditions have molecular weights ranging from M_n ca. 4 kDa to ca. 20 kDa, with polydispersities ranging from ca. 2 to 3 (Table 2). The molecular weights obtained under anionic conditions are lower than the theoretically calculated values from conversion and monomer to initiator ratios, but this was attributed to impurities in the monomer causing side reactions or providing additional initiation sites.[1a]

Spectroscopic Characterization of PPAs. PPAs prepared by cationic and anionic polymerization were examined by a combination of spectroscopic techniques, including nuclear magnetic resonance (NMR) spectroscopy and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry, in an attempt to definitively identify the end groups produced by the different polymerization mechanisms.

End groups are clearly observed by ^1H NMR in PPA prepared by anionic polymerization of *o*-phthalaldehyde. When trichloroacetyl isocyanate was used for end capping, only the 1,6-hexanediol initiator was observed (Figure 1a); moreover, we have previously demonstrated the presence of various anhydride end-capping reagents in the *n*-butyllithium initiated anionic polymerization of *o*-phthalaldehyde.[1b] On the other hand, end groups are not observed in the ^1H NMR of a PPA of similar molecular weight prepared by cationic polymerization when comparable signal to noise is attained (Figure 1b). Fluorinated end groups are also not detected by ^{19}F NMR on quenching a cationically initiated polymerization with 3-fluoropyridine (Table 1, entry 9), and only trace solvent peaks are observed on addition of various nucleophilic end-capping reagents (see Figures S9−S13 in the Supporting Information). Alternative cationic initiators also fail to show the presence of an end group (see Figures S14−S16 in the Supporting Information). In an attempt to incorporate a chromophore end cap, 1-pyrene methanol was added to the polymerization reaction prior to precipitation (Table 1, entry 12; see Figure S18 in the Supporting Information), but the UV detector on the GPC confirmed that pyrene was not incorporated into the polymer.[7]

All analytical techniques failed to identify end groups in PPA samples polymerized by cationic initiation. Without end caps, PPA is expected to rapidly depolymerize to monomer due to its known ceiling temperature of −40 °C.[4] This depolymerization reaction has been shown to occur rapidly and completely on end-cap removal by specific deprotecting reagents for PPA samples produced by anionic polymerization.[2] We therefore hypothesized that a cyclic polymer is the sole product of the boron trifluoride initiated polymerization. We envisioned the possibility of a back-biting mechanism leading to cyclic

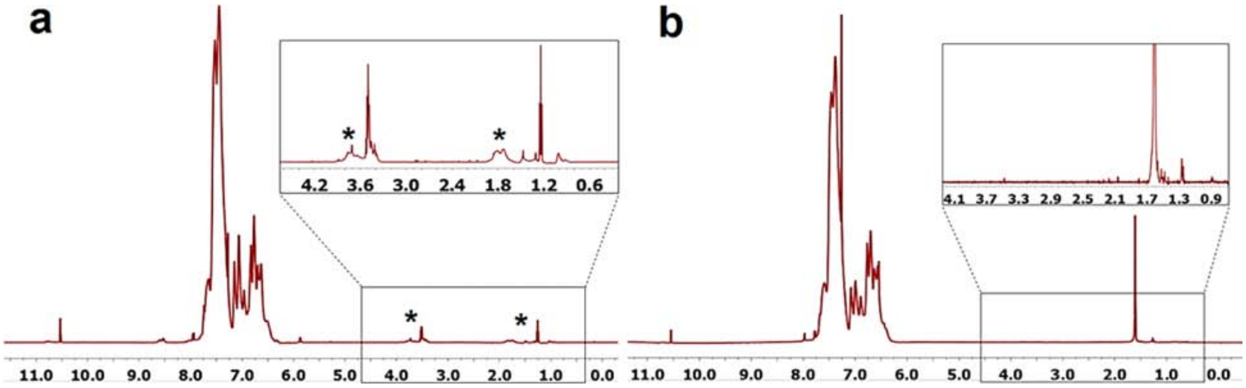
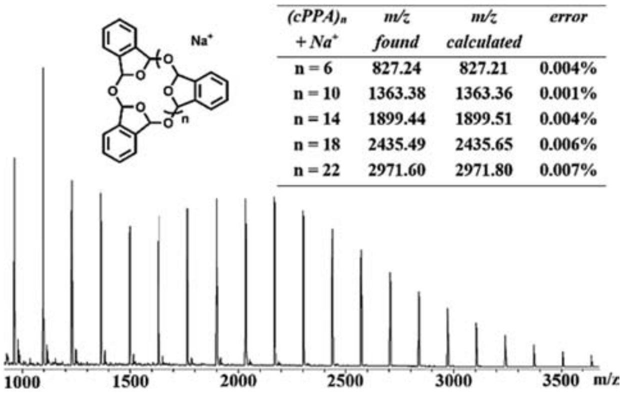


Figure 1. ^1H NMR spectra of PPA prepared by anionic and cationic polymerization. (a) NMR spectra of M_n = 6.3 kDa PPA prepared by anionic polymerization (Table 2, entry 2) in $CDCl_3$. Asterisks indicate peaks corresponding to 1,6-hexandiol initiator. Residual *o*-phthalaldehyde monomer is also observed. The inset gives a magnification of the region δ 0−5 ppm. (b) NMR spectra of M_n = 5.9 kDa PPA prepared by cationic polymerization (Table 1, entry 7) in $CDCl_3$. No end groups are observed. Additional peaks correspond to water and residual *o*-phthalaldehyde monomer. The inset gives a magnification of the region δ 0−5 ppm (see the Supporting Information for magnifications and additional NMR spectra).

poly(phthalaldehyde) (cPPA) in a process analogous to the zwitterionic ring-opening polymerization of lactides established by Waymouth.[8a−c] The Aso group has previously demonstrated the formation of small cyclic oligomers in the cationic polymerization of *o*-formylphenylacetadehyde by boron trifluoride.[9]

Cyclic polymers have interested chemists in recent decades due to the unique structural and physical properties imbued into the large macrocycles through the topological constraint of connected chain ends.[10] Several synthetic strategies exist for the preparation of cyclic polymers, including the use of solid supports,[11] the coupling of reactive chain ends of linear precursors at high dilution,[12] and ring-expansion strategies utilizing cyclic initiators.[8,13,14] Ring-expansion strategies are advantageous in that they produce cyclic polymer in high purity and circumvent additional synthetic steps in high dilutions to generate cyclic macromolecules in high yields. However, the synthetic methods currently available are still limited by the inability to effectively separate residual linear contaminants.[10] The Waymouth and Zhang groups have recently demonstrated a zwitterionic ring-opening polymerization strategy toward the synthesis of cyclic polyesters and polyamides.[8] Cyclic polymers were obtained in high yields with good control over molecular weight and polydispersity, and the cyclic structure was confirmed by several analytical methods.[8]

The proposed cyclic structure of PPA prepared by cationic polymerization was further elucidated by MALDI-TOF mass spectrometry and comparisons of the solution properties to analogs of similar molecular weight PPAs prepared by anionic polymerization. The MALDI-TOF mass spectrum clearly shows molecular ions for the sodium-complexed cPPA (Figure 2). The signals are spaced by 134 mass units and correspond perfectly to *o*-phthalaldehyde monomer units plus a sodium ion. A series of minor peaks separated by +18 mass units from the major peak series is also occasionally observed. This presumably corresponds to PPA with hemiacetal groups produced by hydrolysis on reacting with the acidic MALDI matrix (2,5-dihydroxybenzoic acid, DHB; see Figure S25 in the Supporting Information). Importantly, since uncapped linear PPA rapidly degrades to monomer, cPPA is solely obtained in high yield without residual linear contaminants, as confirmed by the presence of a single distribution of cyclic polymer species in the MALDI-TOF mass spectra (Figure 2 and Figures S24−S30 (Supporting Information)).



(cPPA)$_n$ + Na$^+$	*m/z found*	*m/z calculated*	*error*
n = 6	827.24	827.21	0.004%
n = 10	1363.38	1363.36	0.001%
n = 14	1899.44	1899.51	0.004%
n = 18	2435.49	2435.65	0.006%
n = 22	2971.60	2971.80	0.007%

Figure 2. MALDI-TOF mass spectrum of cPPA. Peaks match the sodium adduct of cyclic PPA. DHB (2,5-dihydroxybenzoic acid) was used as the matrix and sodium iodide as the cationization agent.

Size−Molecular Weight Correlations by Triple Detection GPC. Additional evidence for the cyclic structure of the cationic PPA was provided by GPC coupled with a refractometer, light-scattering detector, and viscometer. PPAs of comparable molecular weight distributions were synthesized by cationic and anionic polymerizations (Table S7 in the Supporting Information) and analyzed. Cationic PPA elutes later than anionic counterparts of the same molecular weight (Figure 3a; molecular weights calculated by Zimm plot), indicative of the compact cyclic structure. Furthermore, Mark−Houwink−Sakurada plots demonstrate that PPA prepared by cationic polymerization has a lower intrinsic viscosity than its anionic analogue (Figure 3b). Both polymers presented a Mark−Houwink coefficient of ca. 0.6, and the calculated $[\eta]_{\text{cationic}}/[\eta]_{\text{anionic}}$ ratio was found to be 0.7, consistent with the cyclic/linear ratio on the basis of theoretical predictions and experimental findings on other cyclic polymers.[8,12−15] These results, in conjunction with MALDI-TOF measurements and ^1H NMR spectroscopy, were taken as ample evidence for the cyclic structure of PPA synthesized by cationic polymerization.

Reversible Macrocyclization Polymerization. Upon confirming the cyclic structure of PPA prepared by cationic polymerization, we questioned the reversibility of ring closure under the polymerization conditions. In the case of anionic

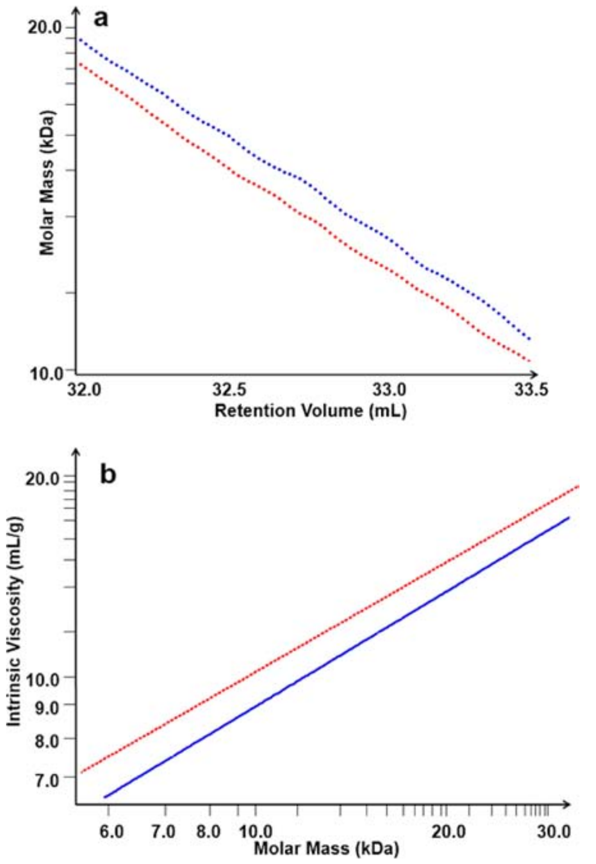


Figure 3. Comparison of the physical properties of PPA prepared by cationic and anionic polymerization. (a) Plot of molecular weight (logarithmic axis) versus retention volume. PPA prepared by cationic polymerization (blue trace) exhibits greater retention volume than PPA prepared by anionic polymerization (red trace). (b) Mark−Houwink−Sakurada double log plot of intrinsic viscosity versus molecular weight. PPA prepared by cationic polymerization (blue trace) exhibits lower intrinsic viscosity than PPA prepared by anionic polymerization (red trace).

PPA, end capping terminates the reaction (and this stabilizes the resulting chains from depolymerization); the obtained chains are unreactive. In the cationic polymerization, stabilization is achieved by an intramolecular ring closure rather than end capping. Similarly, ring closure could represent an irreversible termination step that inactivates the polymer from further growth or contraction. We hypothesized, however, that the cPPA acetal backbone is reopened under the Lewis acidic polymerization conditions. To test this hypothesis, the isolated macrocycles were subjected to boron trifluoride at temperatures below the ceiling temperature in an attempt to carry out further propagation on the stable, linear chains produced.

Ring opening and ring expansion of cPPA to larger molecular weights was achieved under the polymerization conditions in the presence of boron trifluoride and additional monomer (Figure 4a). Interestingly, the polymer was also made to controllably depolymerize to smaller cyclic polymers or even remain at an identical molecular weight after monomer addition, depending on the monomer concentration (Figure 4b). This unique property is a result of polymerization occurring close to the polymer ceiling temperature, rendering propagation and depropagation dependent on monomer concentration.[4a] The cyclic polymer molecular weight is therefore under thermodynamic control and is tuned by both the polymerization temperature[4a] and the monomer concentration (defined as the amount of *o*-phthalaldehyde added plus the amount of phthalaldehyde repeat units in the cPPA).[16] Attempts to make low-molecular-weight polymer by inverse addition of monomer to excess initiator confirmed that the molecular weight does not strongly correlate with percent initiator (see Table S3 in the Supporting Information). Significantly, this property enables the reversible ring expansion and ring contraction of cPPA to form cyclic polymer of various sizes with reasonable control.

To conclusively illustrate the dynamic reversibility of cPPA polymerization and demonstrate the unique features of the system, we designed two control experiments. In the first, polymerization reactions were carried out at monomer concentrations of 1.0 and 0.1 M. A third reaction was run in parallel in which the monomer concentration began at 1.0 M, and then a second batch of monomer was added such that the overall concentration dropped to 0.1 M. In analogous experiments investigating the zwitterionic macrocyclic polymerization of lactones, researchers identified two outcomes: either chain extension to larger cyclic polymer was observed or reinitiation occurred to generate a second distribution of cyclic polymer.[8a] In this case, though, the molecular weight distribution mirrors that of the polymerization at 0.1 M after the addition of the second batch of monomer (Figure 5a),

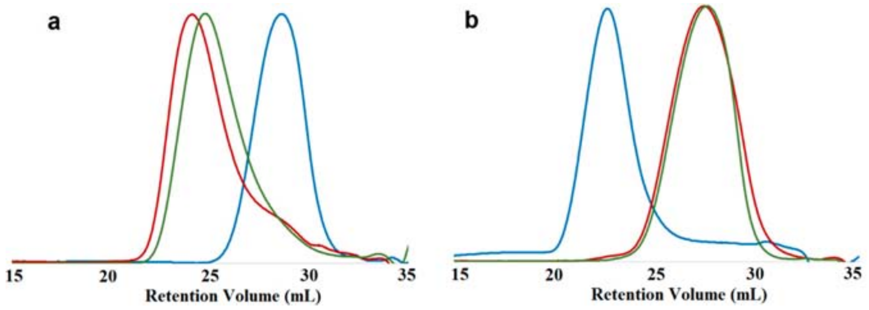


Figure 4. cPPA ring-opening testing. (a) Normalized GPC chromatogram of cPPA (blue, M_p = 5.1 kDa) repolymerized to higher molecular weight at a total monomer concentration of 0.6 M (red, M_p = 67 kDa) and the resulting product repolymerized again at 0.6 M (green, M_p = 46 kDa). All polymerizations were conducted at −78 °C. (b) Normalized GPC chromatogram of cPPA (blue, M_p = 199 kDa) repolymerized to lower molecular weight at a total monomer concentration of 0.5 M (red, M_p = 10 kDa) and the resulting product repolymerized again at 0.5 M (green, M_p = 9.1 kDa). All polymerizations were conducted at −78 °C.

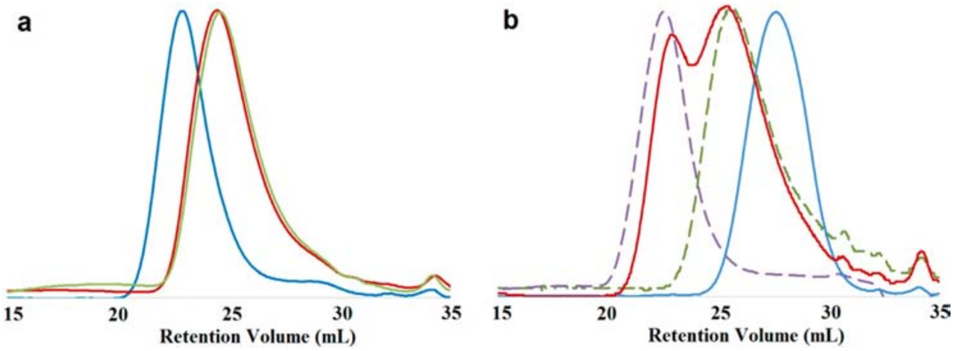
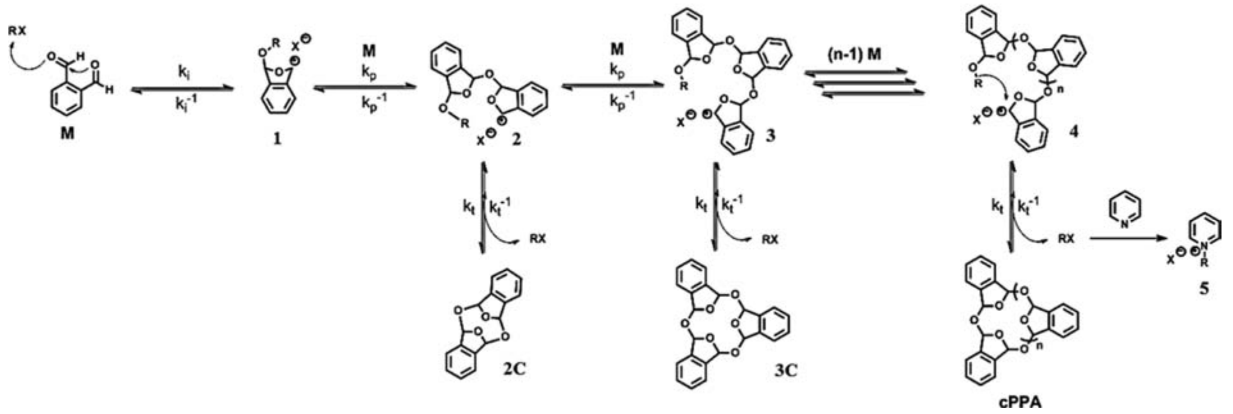


Figure 5. Cycloreversible polymerization studies. (a) Normalized GPC chromatogram of cPPA polymerized at monomer concentrations of 1.0 M (blue) and 0.1 M (red) and an initial [*o*-PA] of 1.0 M followed by addition of a second batch of *o*-PA to final concentration of 0.1 M (green). The monomodal peak at lower molecular weight is indicative of reversible polymerization. (b) Normalized GPC chromatogram of two cPPA polymers (green and purple, dashed lines) and blends of the two polymers in the presence (blue, 0.5 M monomer) and absence (red, 0.5 M monomer) of initiator. Mixing of polymers to a monomodal peak at lower molecular weight is again indicative of dynamic, reversible polymerization.

Scheme 1. Proposed Mechanism of Reversible, Cationic Macrocyclization PPA Polymerization



demonstrating the dynamic equilibrium nature of the polymerization.

As a second control experiment, two cPPA polymers of different molecular weights were mixed together and subjected to the cationic polymerization conditions. In one reaction, boron trifluoride etherate was added, while no initiator was added to the second. GPC analysis of the molecular weight distributions clearly reveal the dynamic intermixing of polymers in the presence of boron trifluoride, whereas the polymer blend remained unchanged in the absence of initiator (Figure 5b). Interestingly, linear PPA prepared by anionic polymerization can be converted to cPPA using cationic polymerization conditions. By subjecting linear PPA as well as mixtures of linear PPA and cPPA to cationic polymerization conditions, the dynamic polymer intermixing to a single distribution of macrocyclic product is observed (see Figures S23 and S32 in the Supporting Information). Polymer recoveries of 90% and higher corroborate the incorporation of linear polymer into cyclic polymer products, with remaining uncapped PPA presumably depolymerized and removed in the workup.

This unique property of cPPA is intriguing, because the polymer can be grown, depolymerized, and repolymerized by adjusting the reaction temperature and concentration. The thermodynamic control over the final product allows for precise production of polymers with predefined molecular weights and sizes. Whereas some cyclic polymers cannot be reopened and polymerized to different molecular weights after initiator removal (since cyclization is an irreversible termination process), cPPA is capable of participating in reversible activation−deactivation processes. Furthermore, cPPA can be made to intermingle with and redistribute repeat units of other polymer chains, even linear chains. One could imagine mixing cPPA, or linear PPA, with a second similar polymer such as poly(4-bromophthalaldehyde)[17] to arrive at a completely intermixed, cyclic copolymer where the product composition is completely defined by thermodynamics. Such structural reorganization of distinct polymer blends could facilitate the preparation of complex and novel cyclic copolymers.

Cyclic PPA Mechanism. On the basis of these observations, we propose a cationic propagation mechanism for the cyclopolymerization of *o*-phthalaldehyde, generating cPPA by a back-biting reaction (Scheme 1). While a zwitterionic propagation mechanism with negatively charged boron trifluoride bound at one polymer terminus is possible, polymerizations performed with alternative cationic initiators suggest that the chains grow via cationic propagation. In the proposed mechanism, initiation by an acidic or cationic species (RX) generates the charged monomer **1**. Propagation proceeds by monomer addition to the cationic center, and cyclization to produce cPPA extrudes the acidic species, which is neutralized by addition of a base (**5**). Back-biting can theoretically occur at any position along the chain to produce cPPA and a shortened cationic chain, but ring closure from only the terminal position is shown for simplicity. As discussed previously, the macrocyclization is entirely reversible. The polymers presumably grow by a reversible activation−deactivation (RAD) process, much like controlled radical polymerization[18] mechanisms, except in this case rings equilibrate between closed (cyclic; **2C**, **3C**) and open (cationic; **2**, **3**) forms. This enables cyclic polymers to re-engage in the polymerization, even after their isolation. Cyclic PPA could potentially react with growing cationic chain ends, cationic monomeric intermediate, or initiator itself; only cPPA ring opening by reaction with the acidic "RX" (reverse termination) is shown, again for simplicity. Notably, the equilibrium dramatically shifts to favor monomer (M) under dilute conditions and at temperatures above −40 °C. Therefore, noncyclized PPA rapidly degrades to monomer such that cPPA is obtained in high yield with high purity.

CONCLUSIONS

To conclude, while trying to incorporate specific end caps to cationically polymerized *o*-phthalaldehyde, we unexpectedly discovered an expedient cationic polymerization to generate high-molecular-weight cyclic polymer with high purity via a thermodynamically controlled process. The cyclic structure of the polymer product was confirmed by a variety of techniques, namely NMR spectroscopy, MALDI-TOF mass spectrometry, and triple-detection GPC. Significantly, the cyclic polymers were shown to be reversible; the macrocycles are ring-opened to produce either larger cPPA by propagation or smaller cPPA by depropagation, depending on the reaction conditions. These cyclic polymers scramble with other PPA (cyclic or linear) or similar polymer chains and dynamically intermix to a monomodal distribution of macrocyclic product.

The flexibility in sequence and molecular weight distributions make cPPA an exceptional polymer system that merits further exploration. The dynamic polymer is completely recyclable, given that it is composed entirely of phthalaldehyde repeat units and therefore will undergo re- or depolymerization depending on the conditions. The lack of end groups in cPPA is additionally advantageous in that it could overcome issues from residual nonvolatile end groups in applications that require total material removal. For example, this could improve capabilities in highly sensitive applications such as lithography or packaging of transient electronics.[3,5,19] We also note that cPPA is remarkably stable in comparison to linear PPA. Samples left on the benchtop have been observed to remain a pristine white polymer for several months in air, while linear PPA analogues require meticulous storage or risk depolymerizing within days, likely as a result of end-cap removal.[1a]

Finally, we highlight that polymerization near the ceiling temperature may provide a general route to cyclic polymer synthesis with near-perfect purity. We anticipate that when an avenue is available for cyclization, and when transfer reactions or other side reactions are avoided, cyclic polymer can be obtained as the sole product without resorting to high-dilution conditions.[20] Cyclization would be enforced by the thermodynamic preference to self-correct, i.e., to stabilize by ring closure, and cyclic polymer would be obtained in high purity by concurrent depolymerization of linear, uncapped products. This potentially general route to cyclic polymer synthesis is currently under investigation in further experimental and computational studies.

ASSOCIATED CONTENT

Supporting Information

Text, figures, and tables giving experimental details, synthetic procedures, NMR spectra, GPC data, MALDI-TOF MS data, and TGA and DSC analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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