Photoiniferter Synthesis of Cyclic Polymers from Vinyl Monomers

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ABSTRACT

Cyclic polymers synthesized from vinyl monomers are somewhat rare in the chemical literature. Examples published to date often involve harsh reaction conditions and lack versatility toward vinyl monomer type. Reported here is a photoiniferter approach to synthesize cyclic polymers from vinyl monomers using mild reaction conditions and high reaction concentrations. The synthetic process is simple, scalable, and will enable the study of cyclic polymer properties on substantial amounts of material in the future. Evidence that the cyclic topology was achieved with little to no linear polymer contaminants includes enhanced glass transition temperatures compared to linear polymers of similar molar mass as well as matrix-assisted laser desorption/ionization time-of-flight mass spectrometry results confirming the target macromolecular structure.

MAIN TEXT

Cyclic polymers, unique for their lack of chain ends, have recently seen a resurgence in interest.[1–4] The first report of a synthetic cyclic polymer by Ruggli in 1912 did not generate much interest outside pure academic curiosity.[5] Early synthetic work in this area involved tedious preparations and purifications that could generate only modest amounts of material to

study. Interest in cyclic macromolecules was renewed when Jacob and Wollmen discovered the existence of circular DNA in *Escherichia coli* in 1958.[6] The importance of cyclic macromolecular topology in nature was underscored by the discovery of the cyclic kalata B1 polypeptide[7] and the protective effects a cyclic topology has against thermal degradation and enzymatic activity.[8] Evidence that the cyclic topology could enhance physical and chemical properties of certain biomacromolecules rejuvenated interest in preparing synthetic cyclic analogues.

Two main strategies exist for preparing synthetic cyclic polymers; ring-closure and ring-expansion. A benefit of ring-closing strategies is that precursor molar mass and chemical composition can be easily controlled by selecting appropriate polymerization chemistry. However, ring-closing strategies are generally beleaguered by the presence of linear or cyclic "oligomers" which form when undesired intermolecular reactions occur. Performing the cyclization step at high dilution avoids (but does not eliminate) oligomerization, but such dilution inherently limits the amount of material produced. Bimolecular and unimolecular ring-closing each have an entropic penalty for coupling two ends of the same macromolecule; the Jacobsen-Stockmayer theory states the probability that a polymer chain will cyclize decreases proportionally to $n^{-5/2}$, where n is the number of repeating units.[9] As a result, macromolecules approximately 20,000 Da or less can be effectively cyclized without clever chemistry to keep the chain ends in close proximity.[10–13]

The inherent opportunity of a ring-expansion approach is that there is no entropically expensive ring-closing step. However, the main limitation of ring-expansion techniques used to date is that each initiator or catalyst has a narrow scope of compatible monomers. Preparation of cyclic polymers with no intermolecular "oligomerization" and few linear "impurities" is possible

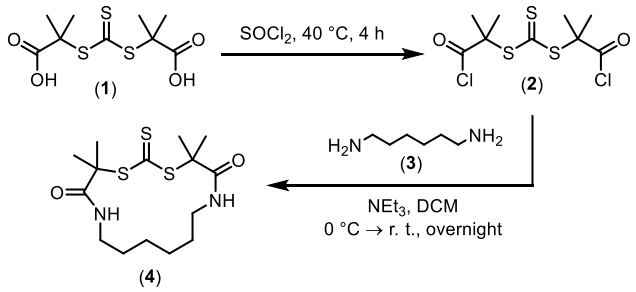
at moderate to high concentrations in these systems. Therefore, these techniques are amenable to preparation of a substantial amount of material to study. Prominent examples of ring-expansion polymerizations include ring-expansion metathesis polymerization (REMP) of cyclic olefins (e.g. cyclooctene) using a ruthenium (Grubbs) catalyst,[14,15] zwitterionic ring-expansion polymerization (ZREP) of lactones to form cyclic polyesters,[16] and polyhomologation of boracyclanes to prepare macrocyclic organoboranes.[17] These examples require carefully matched monomer/initiator combinations.

Ring-expansion systems developed for synthesis of cyclic polymers derived from vinyl monomers are notably scarce in the literature despite the rich variety of readily available vinyl monomers. A few examples of ring-expansion systems compatible with common vinyl monomers include γ-ray-induced reversible addition/fragmentation chain transfer (RAFT) polymerization of methyl acrylate and N-isopropylacrylamide,[18] ring-expansion RAFT polymerization of N-vinylcarbazoles,[19] nitroxide-mediated polymerization (NMP) of styrenic monomers,[20] living cationic polymerizations of vinyl ethers,[21] and poly(γ-methyl-α-methylene-γ-butyrolactone) synthesized via a B-P-B trifunctional intramolecular frustrated Lewis pair catalyst.[22] Control of molar mass and low dispersities were demonstrated in some cases, but in each study there was a lack of versatility toward monomer type (i.e. cyclic xanthates or nitroxides are compatible with narrow vinyl monomer classes) or undesirable reaction conditions (e.g. γ-irradiation, low temperature, etc.). Vinyl monomers are used ubiquitously and many controlled radical polymerization (CRP) chemistries have been developed to prepare well-defined polymers with excellent control of molar mass, low dispersity, and controlled chemical composition/ architecture under mild reaction conditions.[23–25]

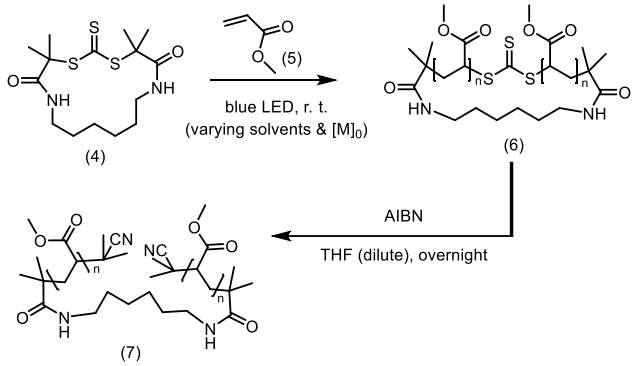
Reported here is an approach to create cyclic polymers via photoiniferter polymerization beginning with an easily-synthesized cyclic photoiniferter molecule. This method generated cyclic polymers with no observed linear contaminants when polymerized at high reaction concentrations in a relatively viscous solvent. This method is compatible with major classes of vinyl monomers including acrylates, acrylamides, styrenics, and acrylonitriles by virtue of the structure of the thiocarbonylthio group employed. The polymerizations were conducted under mild reaction conditions (room temperature, visible light irradiation, and no additives such as exogenous initiator or photocatalysts) at initial monomer concentrations up to 2 M.

RESULTS & DISCUSSION

The hypothesis driving the work presented here was that synthesizing a cyclic small molecule capable of photoiniferter polymerization would, under the right conditions, lead to a polymerization process consisting of reversible homolysis of the small molecule ring, insertion of a vinyl monomer, and reversible ring closing. A photoiniferter approach was favored because a lack of exogenous initiator minimizes irreversible termination events with low molar mass species that would lead to linear "impurities." Synthesis of a cyclic trithiocarbonate capable of photoiniferter polymerization is detailed in Scheme 1. First, trithiocarbonate **1** was treated with thionyl chloride to form the bis(acid chloride) **2**, which was then treated with 1,6-hexanediamine (**3**) to form cyclic photoiniferter **4**. Photoiniferter polymerization experiments irradiated with commercially-available blue LEDs (λ_{max}= 450 nm) were conducted with **4** and methyl acrylate (**5**) under a variety of solvent and concentration conditions. Blue light irradiation excites the n→π* transition of the thiocarbonylthio group of **4** leading to the formation of a thiyl radical and carbon-centered radical. Structure **6** shows the expected structure of the polymer. This chemistry is summarized in Scheme 2.



Scheme 1. Synthesis of cyclic trithiocarbonate **4**. ($SOCl_2$ = thionyl chloride, NEt_3 = triethylamine, DCM = dichloromethane)



Scheme 2. Ring-expansion polymerization of methyl acrylate (**5**) with cyclic trithiocarbonate **4** and subsequent cleavage of thiocarbonylthio group with azobis(isobutyronitrile) (AIBN) (LED = light emitting diode)

Table 1. Polymerization reaction conditions and GPC characterization of as-synthesized and cleaved polymers

Entry	Reaction Time (h)	[M]:[I][a]	Polymerization Solvent[b]	Reaction Temp. (°C)	$[M]_0$	% conv.[c]	Theo. M_n (kDa)[d]	Exp. M_n (kDa)	Đ[e]
A	24	100:1	DMSO	25	2.0	>99	8.51	8.20	1.10
						Sample A cleaved:		4.20	1.11
B	24	1165:1	DMSO	25	2.0	98	98.2	83.9	1.16
						Sample B cleaved:		40.9	1.16
C	24	2330:1	DMSO	25	2.0	95	190.	184.	1.74
						Sample C cleaved:		92.7	1.62
D	24	100:1	DMSO	25	0.75	64	5.50	232.	1.33
						Sample D cleaved:		195.	1.21
E	24	100:1	DMSO	25	1.0	95	8.17	114.	1.75
						Sample E cleaved:		-[f]	-[f]
F	24	100:1	DMSO	25	1.5	93	7.99	58.7	1.63
						Sample F cleaved:		19.7	1.90
G	24	100:1	DMSO	25	2.0	>99	8.51	126.	2.19
						Sample G cleaved:		12.3	1.53
H	24	100:1	DMSO	25	2.5	>99	8.51	193.	3.42
						Sample H cleaved:		18.6	1.55
I	24	100:1	THF	25	0.75	55	4.73	3.85	1.45
						Sample I cleaved:		5.29	1.58
J	24	150:1	THF	25	1.0	68	5.85	4.61	1.41
						Sample J cleaved:		4.37	1.46
K	24	200:1	THF	25	1.5	84	7.22	6.69	1.42
						Sample K cleaved:		7.95	1.42
L	24	100:1	THF	25	2.0	86	7.40	7.35	1.34
						Sample L cleaved:		5.97	1.30

[a] [M]:[I] is the monomer to initiator ratio where [I] refers to compound **4** with the exception of entries A-C in which compound **1** was used to synthesize linear PMA at varying molar mass to use as known linear samples for comparison. [b] THF = tetrahydrofuran, DMSO = dimethyl sulfoxide [c] Determined by integrating the residual vinyl ^{1}H NMR peaks between 6.5-5.7 ppm relative to the -CH_3 singlet at ~3.6 ppm in polymerization solution [d] Calculated by multiplying the % conversion by the molar mass of methyl acrylate (86 g/mol) [e] M_w/M_n [f] Bi-modal GPC trace observed

Table 1 details the characteristics of poly(methyl acrylate) (PMA) samples prepared with photoiniferter **4** in DMSO (entries D-H) and THF (entries I-L). Entries A-C were linear PMA samples prepared for comparison (using **1** as the photoiniferter species). DMSO and THF are both common solvents for polymerizations with a radical propagating species. They were selected in this case to probe the effect of solution viscosity in obtaining the desired cyclic topology. Prior work shows that increased viscosity in photoiniferter systems limits chain diffusion, promoting a reversible deactivation mechanism.[26,27] Table 1 also includes the molar

mass and dispersity characteristics of each sample cleaved with AIBN (see Scheme 2). Figure 1 shows the GPC traces for each sample as-synthesized (solid) and cleaved (dashed) along with a qualitative UV-Vis measurement for each sample prior to cleavage and after cleavage (plots inset). Note that the $\pi \rightarrow \pi^*$ UV-Vis absorbance at ~310 nm disappears after cleavage, indicating that thiocarbonylthio groups were successfully removed, and any cyclic polymers present in the samples as-synthesized were linear after cleavage.

Examining entries A-C in Table 1 (linear PMA samples), it was expected that the molar mass would be reduced by a factor of 2 since the thiocarbonylthio group was located roughly in the center of each linear chain. As expected, the intentionally prepared linear polymers showed a decrease in molar mass by about a factor of 2 and the dispersity changed very little between the as-synthesized and cleaved polymers (Table 1 and Figure 1, A-C). Cyclic polymers have a smaller hydrodynamic volume compared to a linear polymer of the same molar mass and chemical composition.[28] It was expected that by cleaving samples D-L, a small decrease in the GPC retention time would be observed because of the change in topology (assuming one thiocarbonylthio group per polymer chain in the final product). The expected decrease in retention time after cleavage was not observed for any of the samples synthesized.

For the samples polymerized in DMSO (D-H), the experimental molar masses far exceeded the theoretical molar masses and the dispersities were larger than expected for this iniferter/monomer combination. After cleavage with AIBN, the measured molar mass decreased, and the observed trend was that the larger $[M]_0$ was the smaller the average molar mass of the cleaved species (see Figure 1, D-H). For samples polymerized in THF (I-L), the cleaved samples showed a slight increase in retention time and very little change in dispersity (see Figure 1, I-L).

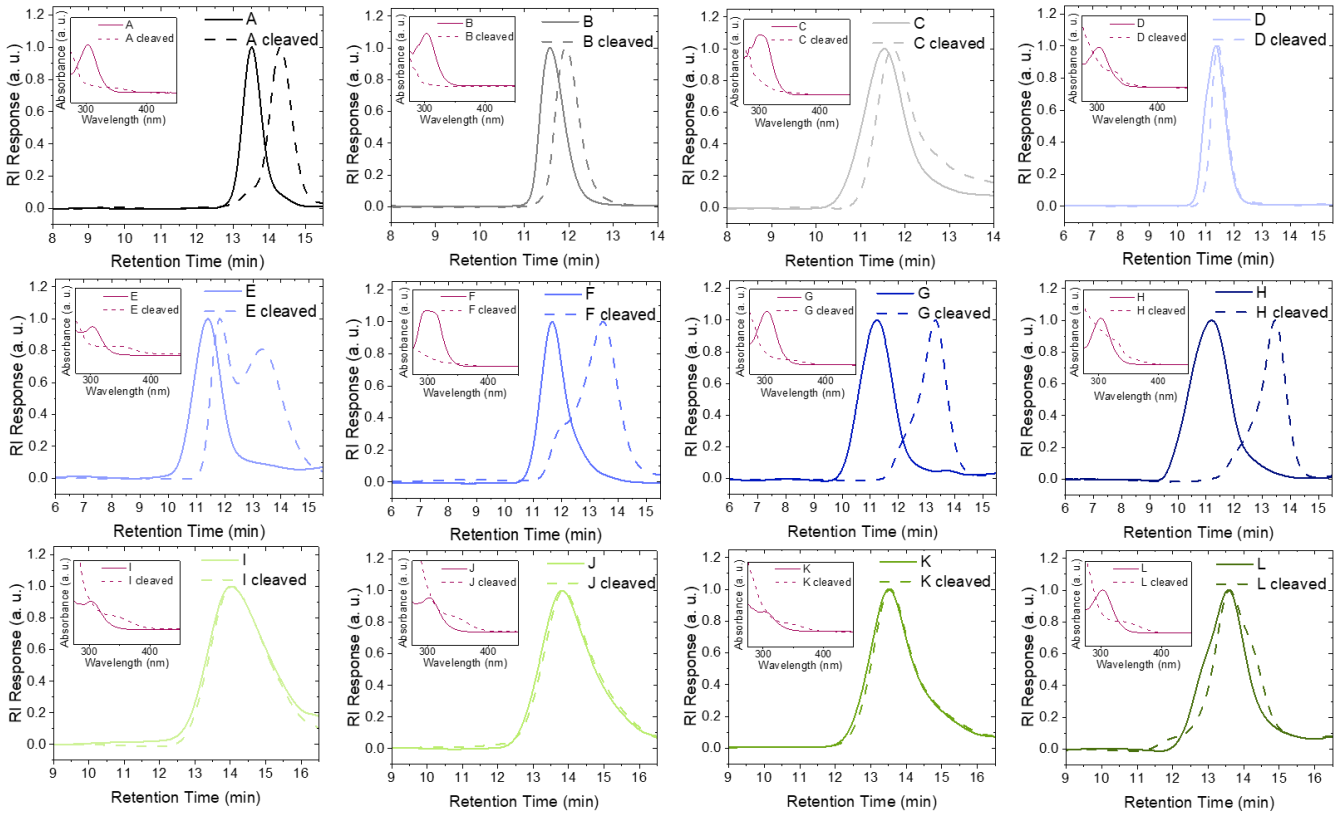


Figure 1. GPC Traces of Entries A-L (Table 1) as-synthesized polymer (solid) and cleaved polymer (dashed). Inset in each GPC plot are the UV-Vis curves (in fuchsia) of as-synthesized polymer (solid) and cleaved (dashed). Grey GPC traces indicate linear PMA, blue GPC traces are samples polymerized in DMSO at increasing $[M]_0$, and green GPC traces are samples polymerized in THF at increasing $[M]_0$.

Cyclic polymers are known to have enhanced thermal properties compared to linear analogues of similar molar mass and chemical composition.[29] Glass transition temperatures (T_g) were measured to gain further insight into the topological characteristics of samples D-L. T_g scales proportionally to molar mass for linear polymers, so the linear samples as-prepared and cleaved are helpful for comparison. The T_g characteristics measured via differential scanning calorimetry (DSC) for each sample are presented in Figure 2. The linear PMA samples (and their cleaved counterparts) behaved as expected, with the non-cleaved linear polymers having T_g values between -8.44 °C and +5.04 °C depending on the molar mass. The T_g values of each cleaved linear sample decreased as expected.

The samples polymerized in DMSO (with photoiniferter **4**) each showed a decrease in T_g after cleavage with AIBN. The samples polymerized at higher $[M]_0$ had T_g values significantly higher than the T_g value of the largest molar mass linear PMA sample (M_n = 184 kDa, T_g = +5.04 °C) despite having similar molar masses to the known linear polymer (sample C). This effect was most pronounced for sample H which had M_n = 193 kDa, and T_g = +24.03 °C. This large enhancement in T_g despite a similar number average molar mass to linear PMA sample C is compelling evidence of a cyclic topology. However, no claim about the cyclic "purity" (i.e. lack of linear PMA "contaminants") of the sample can be made from this measurement alone.

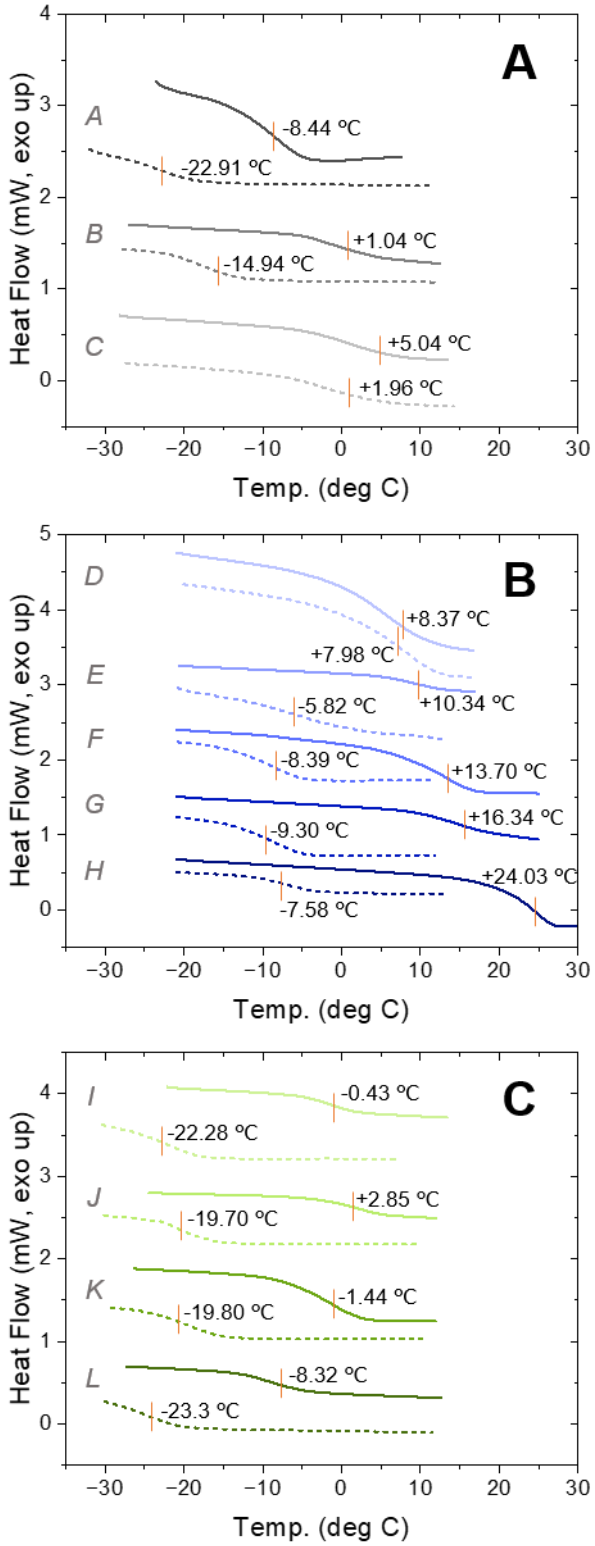


Figure 2. DSC traces of as-synthesized samples (solid curves) and cleaved samples (dashed curves) of linear PMA (A), PMA synthesized with cyclic photoiniferter **4** in DMSO (B), and PMA synthesized with cyclic photoiniferter **4** in THF (C). Letter labels on each set of curves correspond to the entries in Table 1.

Further evidence that samples prepared in DMSO were overwhelmingly comprised of cyclic polymer is presented in Figure 3A. Analysis by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) shows one population of m/z peaks which correlate with the proposed cyclic polymer structure **6**. Another minor population of peaks shows the expected cyclic product, but oxidation of the trithiocarbonate group was observed, likely from trace water present in the DMSO (see Figure S13). Overall, this data supports the idea that the sample was comprised of nearly all cyclic products since any linear contaminants would create additional peak populations offset from those observed due to the presence of end groups. Considering the GPC data for these samples, it appears that the majority of the chains are likely "oligomerized" via radical ring cross over reactions, a phenomenon which has been observed in other radically polymerized cyclic polymer systems (see Figure 4, top).[20] The larger than anticipated dispersity for samples G & H as-synthesized can be explained by uneven oligomerization via radical ring crossover (step-growth crossover of 3, 4, 5, etc. chain segments containing a thiocarbonylthio group). The growth of the individual segments via the chain growth photoiniferter process was still relatively well controlled, so smaller dispersities were observed for the cleaved segments. The large cyclic "oligomers" that resulted from radical ring crossover were too large to be observed via MALDI-TOF MS. The combination of DSC results and MALDI-TOF MS results suggests that at high $[M]_0$ in DMSO, the polymerization mixture became quite viscous early in the reaction, a reversible deactivation/ radical ring cross-over mechanism was indeed favored versus degenerative chain transfer or irreversible termination.

It should be noted that sample D showed little decrease in molar mass after cleavage, and little change in T_g between the as-synthesized and cleaved sample. Perhaps the samples polymerized in more dilute DMSO solutions contain some cyclic chains, since all samples had

measured T_g values above the linear samples PMA samples, but they may contain high molar mass linear "impurities" resulting from unexpected chain transfer events. A mixture of cyclic and linear polymers in the lower $[M]_0$ samples polymerized in DMSO is also supported by the GPC data. Sample D showed little decrease in molar mass after cleavage, and Sample E showed a bimodal distribution of cleaved products compared to the other DMSO samples. As the $[M]_0$ in DMSO increased, the bimodal cleaved trace gave way to cleaved traces with a higher molar mass shoulder that diminished as $[M]_0$ increased. Each sample prepared in DMSO showed a decrease in T_g after cleavage. The T_g values scale proportionally with molar mass for the cleaved samples, signifying the cleaved polymers are likely linear.

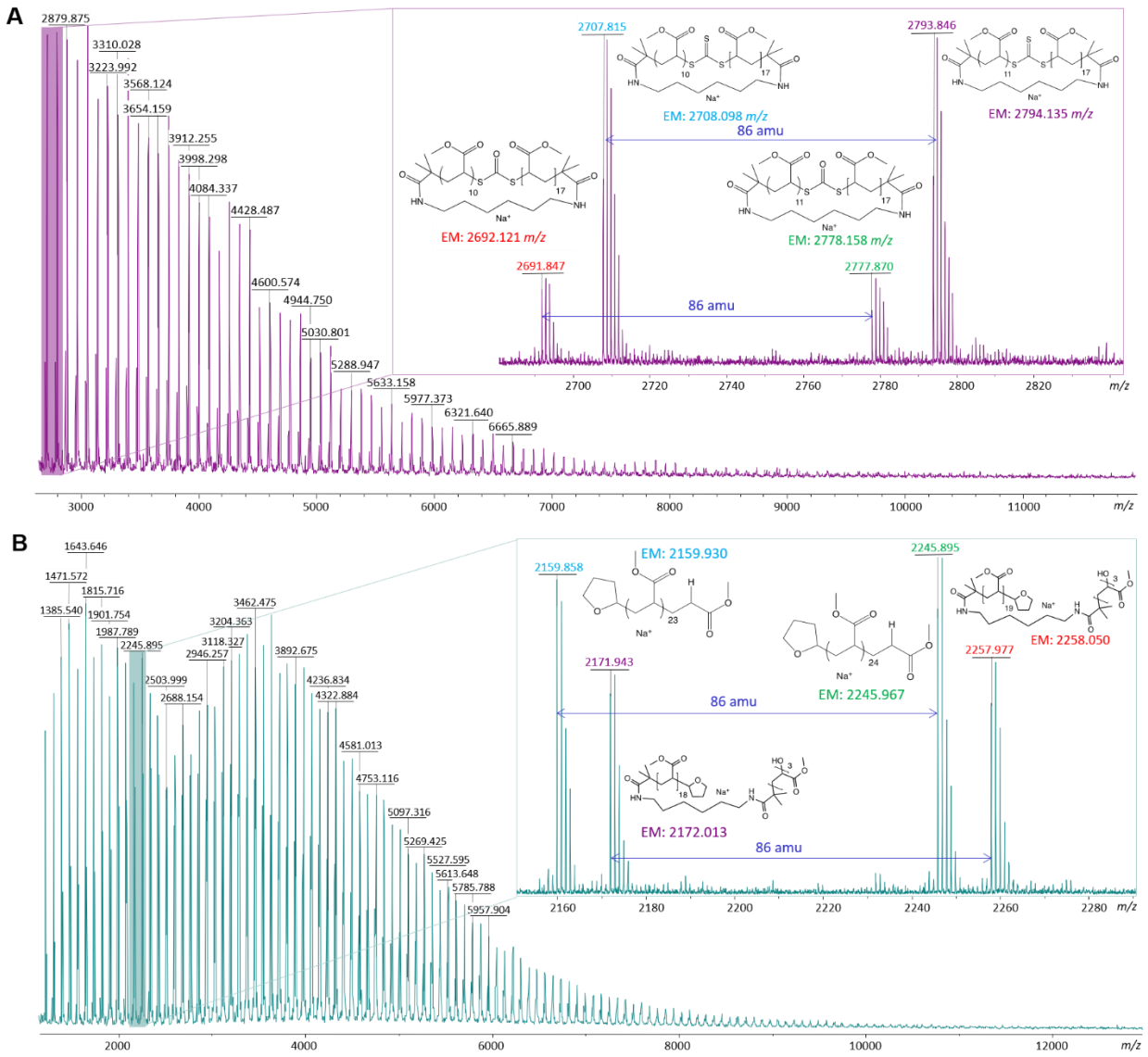


Figure 3. Representative MALDI-TOF mass spectra of polymer samples prepared in DMSO (A, M_n = 362 + (n x 86) + 23 or M_n = 346 + (n x 86) + 23) and THF (B, M_n = 72 + (n x 86) + 23, or M_n = 239 + (n x 86) + 17 + 71 +23) where 362 = mass of thiocarbonylthio iniferter, 86 = mass of methyl acrylate repeat unit, 23 = mass of Na^+, 346 = mass of oxidized iniferter, 72 = mass of THF, 239 = mass of amide linker, 17 = mass of HO•, 71 = mass of THF•. These specific results correspond to sample E (A) and sample I (B). Peak heights represent relative intensities. "EM" under assigned chemical structures refers to expected mass (calculated), peaks are labeled with experimentally found masses.

The samples polymerized in THF (with photoiniferter **4**) showed a general trend of larger T_g values prior to cleavage and lower T_g values after cleavage. This change in T_g despite minimal change in M_n does not suggest a change in topology between pre-/post-cleavage

samples cyclic topology when combined with the GPC observations. Based on the MALDI-TOF MS results (Figure 3B), it appears that chain transfer to solvent (THF) afflicted these polymerizations (also supported by the kinetic data, see Figure S10). A proposed reason for the change in T_g is that samples H-K are fairly low molar mass, so replacement of polar end groups with less polar isobutyronitrile end groups could significantly impact chain-end reptation and local chain mobility leading to decreased T_g without much change in molar mass detected by GPC (see Figure 4, bottom).

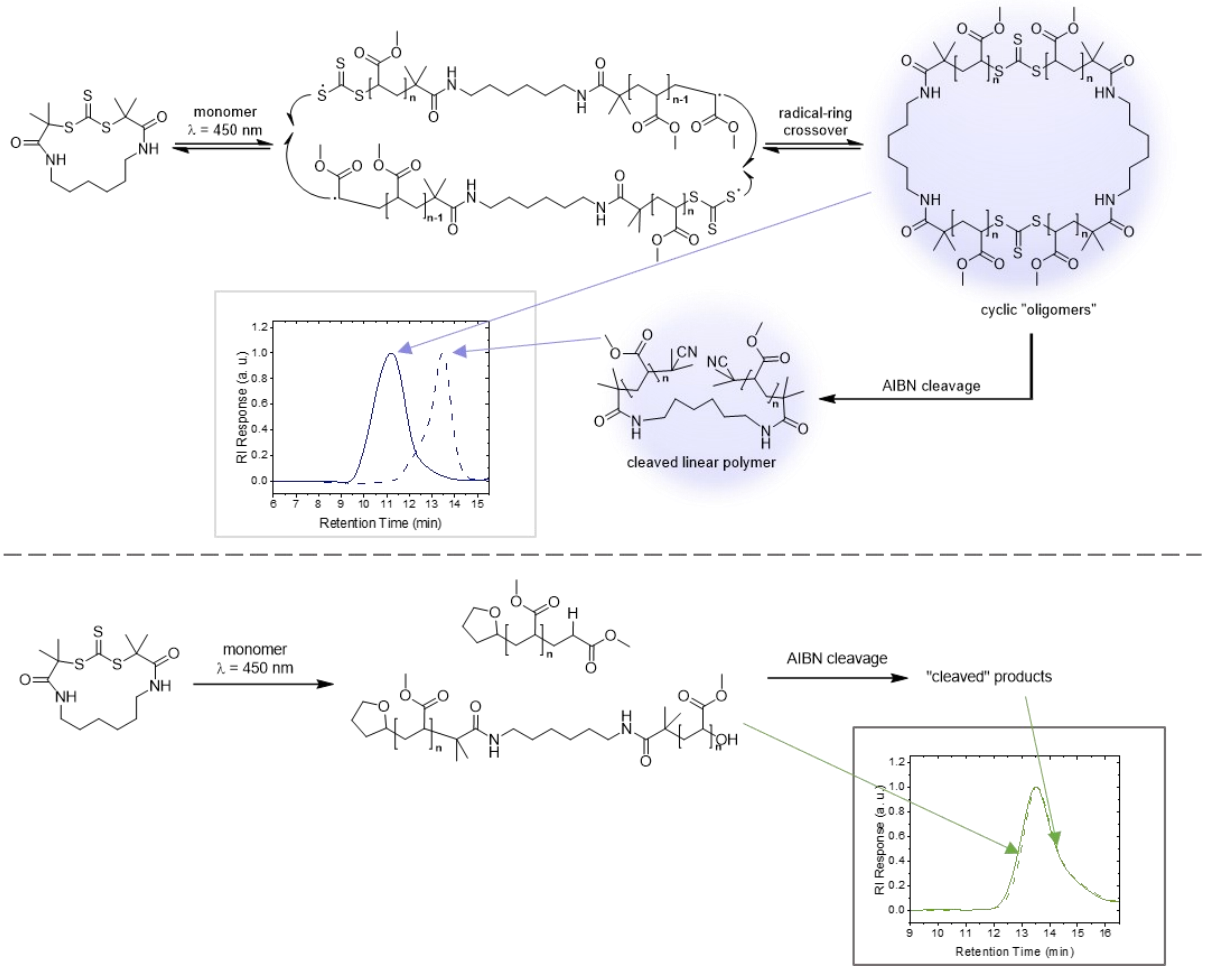


Figure 4. Graphical depiction of how assigned chemical structures relate to GPC traces for samples polymerized in DMSO (top) and THF (bottom).

CONCLUSION

Presented here was a simple and versatile approach to synthesize cyclic polymers from vinyl monomers by leveraging the elegance of photoiniferter chemistry. Polymerization solvent and initial monomer concentration were found to play key roles in obtaining cyclic polymers with few (if any) linear impurities while avoiding photolytic degradation of the photoiniferter species or undesired chain transfer events, though a minor cyclic product containing the oxidized iniferter was found. The cyclic polymers obtained exhibited enhanced T_g values, and the target macromolecular topology was confirmed by MALDI-TOF MS.

ASSOCIATED CONTENT

Supporting Information including experimental methods, characterization data, kinetic studies, and other additional data is available free of charge at (link).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to the donors of the American Chemical Society Petroleum Research Fund Award #62588-UNI7 for support of this research.

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