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PolyDODT: a macrocyclic elastomer with unusual properties†

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The effect of reaction conditions on the structure of poly(3,6-dioxa-1,8-octanedithiol) (polyDODT) made by Reversible Radical Recombination Polymerization (R3P) using triethylamine (TEA), H_2O_2 and air was investigated. 800 MHz (1 and 2D) NMR was used to investigate the polymer structures. Sensitivity analysis provided direct evidence for high purity cyclic polyDODT up to $M_n \sim 100\,000$ g mol^{-1}. Comparative analysis by High Resolution Multidetector Size Exclusion Chromatography (SEC) using integrated data showed that the cycles had lower viscosity and were more compact (both for R_g and R_h) than linear samples of similar molecular weight. However, differential data revealed unusual behavior. While lower molecular weight cyclic polymers eluted later and had lower intrinsic viscosity than their linear counterparts at the same molecular weight, at higher molecular weights the polymers showed strange behavior: both the diffusion coefficient measured by Quasielastic Light Scattering (QELS) and Mark–Houwink–Sakurada plots of intrinsic viscosity for linear and cyclic polyDODT were found to converge. R3P, an aqueous based "green" method is capable of producing polymers at the 10–100 g scale in the lab, which will allow more detailed studies of this new class of biodegradable elastomers so further experimentation can be performed to elucidate the reasons for the unusual findings.

Introduction

Polymer macrocycles remain of great fundamental and practical interest, but their synthesis and characterization remain a challenge, especially at high molecular weights. Specifically, small sample size and limits in the detection of linear contaminants in macrocycles hinder the investigation of the dynamics of cyclic polymers, particularly highly entangled ones. Also, most examples in the literature are for polymers with T_g above room temperature, and we found relatively little data for elastomers.[1–3]

In 2012, we reported the synthesis and initial characterization of disulfide polymers obtained by oxidation of 2-[2-(2-sulfanylethoxy)ethoxy]ethanethiol (DODT) using a system comprised of air, dilute hydrogen peroxide and triethylamine (TEA) as a catalyst that can be recycled.[4–6] High molecular weight disulfide polymers (up to M_n = 250 000 g mol^{-1}) with polydispersity indices as low as M_w/M_n = 1.15 were obtained in this two-phase system (with a TEA/monomer organic phase and aqueous reaction mixture). The product is a transparent elastomer (T_g of −50 °C) that can be depolymerized back to the original monomeric units using dithiothreitol (DTT) in 33 h. Up to the highest molecular weights amenable to analysis using MALDI-ToF (up to $M_n \sim 3000$ g mol^{-1}), the products were pure cyclic polymers. Based on these findings, we proposed a mechanism for this unique two-phase system, and coined the term "Reversible Radical Recombination Polymerization" (R3P, Fig. 1).[7,8] The first step is proton abstraction from the dithiol by TEA; then the dianions dissolve into the aqueous phase where H_2O_2 oxidizes them into diradicals, which can recombine into cyclic structures or react with a proton to be end-capped to form linear polymers with thiol end groups. Small cyclic species can reenter the organic phase, as was shown by NMR, where they may be ring-opened by a dithiol monomer. However, we found that the polymerization is extremely fast and high molecular weight polymers rapidly

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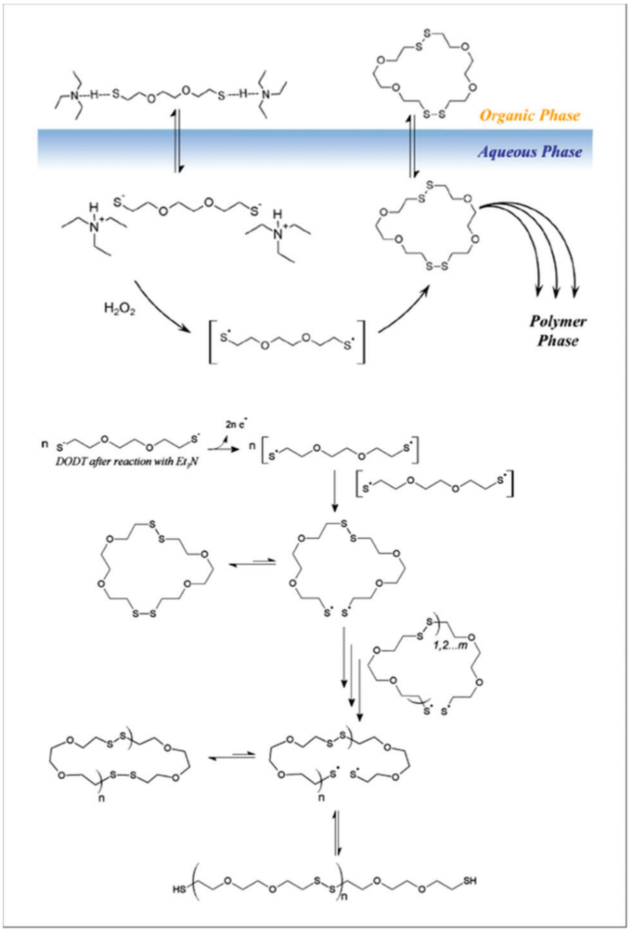

Fig. 1 Proposed mechanism of R3P of DODT. The organic phase is TEA/monomer, a clear oily liquid. Reproduced with permission from ref. 8.

precipitate in the water phase. Despite its exothermic character, the process easily scales to 10–100 g batches of polyDODT in the lab. The recovered precipitates were shown to be either cyclic or a mixture of cyclic and linear polymers, depending on the reaction conditions (see Fig. 1).[7,8] Recovered polymers could be chain-extended readily with ethylene-dithiol (ED) or could be further oxidized into larger polymers, to $M_n \sim 400\,000$ g mol^{-1}. According to the proposed mechanism, a minimum of two molar equivalent of TEA is needed to form the dianion, and excess H_2O_2 is needed for effective oxidation. Scouting experiments showed that less than 2/1 TEA/DODT and H_2O_2/DODT yielded low molecular weight, predominantly linear oligomers ($M_n < 3000$ g mol^{-1}) with traces (<1%) of cyclic structures.[9]

We extended R3P to thiol-functionalized polyisobutylene (HS-PIB-SH) to produce PIB-disulfide elastomers up to $M_n \sim 100\,000$ g mol^{-1}.[10] 750 MHz correlation NMR demonstrated the formation of a high purity macrocycle with $M_n = 25\,000$ g mol^{-1}. A sample with $M_n \sim 125\,000$ g mol^{-1}, believed to be cyclic, was analyzed by five-detector SEC and compared to linear PIB standards. The putative cyclic polymer had lower intrinsic viscosity but, surprisingly, larger R_g and R_h than linear PIBs at the same molecular weight. This PIB-disulfide had higher T_g than a linear PIB standard (−63 *vs.* −73 °C), an additional evidence for cyclic structure based on some reports,[11–13] but others reported similar T_g.[14] However, end group quantification by NMR at this molecular weight may be challenged.

The cationic macrocyclization of polypthalaldehyde (PPA) reported in 2013,[15] which also provides chain extension or contraction and produces cyclic structures such as our DODT- and PIB-based R3P systems, uses a backbone for which depolymerization is favored at room temperature (PPA ceiling temperature −40 °C) and is prevented by either cyclization or "end capping". Since residual linear PPA is expected to spontaneously depolymerize, very pure cycles could be obtained. Using triple-detection SEC, a cyclic PPA with $M_n = 11\,700$ g mol^{-1} was compared to a linear counterpart made by anionic polymerization and end-capped to prevent depolymerization. The cyclic PPA eluted later than the linear PPA and had lower intrinsic viscosity. Elution time and viscosity plots were not shown for higher molecular weight samples. The highest M_n reported for the cationic PPA system was 100 000 g mol^{-1}, claimed to have cyclic structure based on the chemistry of the system, but no direct evidence was provided. Cyclic structures with higher molecular weights (up to 600 000 g mol^{-1}) have been reported for PS,[16] polyoctanomers[17] and DNA[18,19] but comparative physico-chemical analyses have only been provided for much lower molecular weights.

Purification of cyclic polymers, mostly PS, by Liquid Chromatography at the Critical Condition (LCCC) has been reported, claiming less than 1% linear contaminants.[20–22] However, when applied to polyDODT, we have shown that this method was not able to detect up to 6 wt% linear contaminants that were deliberately added.[23] Literature suggested that rheological investigations of high molecular weight cyclic PS purified by LCCC have yielded contradictory results because of the presence of undetected linear contaminants.[14,24] For polyDODT, an additional challenge is that linear samples with $M_n > 3000$ g mol^{-1} have not been available for comparative studies until now. This paper will discuss the effect of reaction conditions on the structure of polyDODTs, and a comparative analysis of cyclic and linear polyDODTs using Five-detector High Resolution Size Exclusion Chromatography.

Experimental

Materials

3,6-Dioxa-1,8-octanedithiol (DODT) 95% (Aldrich), triethylamine (TEA) (TCI), H_2O_2 30 wt% (Sigma-Aldrich), acetone technical grade (Sigma), tetrahydrofuran (THF) HPLC grade non-stabilized (Fischer Scientific), methanol (MeOH) HPLC grade (Fischer Scientific), mercaptoethanol (SH-Et-OH, Sigma), deuterated chloroform ($CDCl_3$, 99.8%, Chemical Isotope Laboratories) were used as received.

Synthesis of polyDODTs

End-capping with mercaptoethanol. DODT, TEA and SH-Et-OH were mixed for 30 minutes in a 100 mL beaker with a magnetic stir bar at 200 rpm. Five samples were prepared as shown in Table 1. The TEA : –SH ratio was kept at 1 : 1. 6.5 mL 30 wt% (57.35 mmol). H_2O_2 was added to the mixture using a KD Scientific K100 syringe pump at a rate of 8.4 mL h^{-1}, with mixing increased to 400 rpm and compressed air bubbled into the mixture. After all the peroxide was added, the mixture was stirred for 2 h at a rate of 200 rpm. A photo of the setup can be seen in Fig. S1† A. The supernatant was decanted, and the product was washed 3 times for 30 minutes with distilled water and 3 times for 30 minutes with methanol. Then the polymer was dried under vacuum until constant weight. Samples are denoted M*X* where *X* is the DODT/SH-Et-OH molar ratio.

Polymerizations under varying reaction conditions. Polymerizations were carried out by varying reaction conditions as described in Table 2.

In general, DODT and TEA were mixed for 30 minutes in a 100 mL beaker with a magnetic stir bar at 200 rpm.

In **Method 1**, 3% aqueous H_2O_2 was added to the DODT/TEA mixture by a KD Scientific K100 syringe pump at a rate of 8.4 mL h^{-1}, while mixing was set to 400 rpm. Three reactions were carried out. After all the peroxide was added, the mixtures were stirred for 2 h at a rate of 200 rpm. The supernatant layers were decanted, and the products were washed 3 times for 30 minutes with distilled water and 3 times for 30 minutes with methanol. Then the polymers were dried under vacuum until constant weight.

In **Method 2**, DODT/TEA mixtures were dumped into 30% aqueous H_2O_2. Three reactions were performed for 1, 2 and 5 minutes and stopped by pouring the mixtures into 400 mL chilled methanol. The resulting milky samples were centrifuged for 30 minutes (4000 rpm with 7 minutes ramping up and 5 minutes ramping down) then the supernatant layers were decanted. The polymers were washed with methanol and centrifuged 2 more times. Then the polymers were dissolved in 15 mL chloroform to separate water residues and dried under the hood under vacuum until constant weight.

In **Method 3**, the DODT/TEA mixture was added into 30 wt% aqueous H_2O_2 by a KD Scientific K100 syringe pump at a rate of 20 mL h^{-1}. After the addition of the DODT/TEA mixture, the supernatant was decanted, and the white creamy product was washed 3 times for 30 minutes with 50 mL acetone and dried under vacuum until constant weight.

In **Method 4**, 30 wt% peroxide was dripped into the DODT/TEA mixture manually for 45 minutes, with compressed air bubbled through a glass pipette submerged into the reaction mixture. The volume rate of compressed air was several bubbles per second without foaming up the reaction. After all the peroxide was added, the reaction flask was closed, and the mixture was stirred for 2 h. Then supernatant was decanted, and the product was washed 2 times for 30 minutes with distilled water and 3 times for 30 minutes with acetone. Then the polymer was dried under vacuum until constant weight.

Table 1 R3P polymerization of 27.5 mmol DODT in the presence of SH-Et-OH

Sample ID	TEA (mmol)	Mercaptoethanol (mmol)
M1	123.4	54.96
M10	86.2	5.50
M25	83.9	2.20
M50	83.3	1.10
M100	82.8	0.55

Synthesis of high molecular weight PolyDODTs

The synthesis method was very similar to Method 4 but after completion of the peroxide addition the mixtures were stirred for 2 h in an open flask, and the polymers were washed with methanol instead of acetone before drying under vacuum to constant weight.

Proton and carbon nuclear magnetic resonance spectroscopy (^{1}H and ^{13}C NMR)

^{1}H NMR spectra were recorded on Bruker 400, 700 or 800 MHz NMRs using deuterated chloroform ($CDCl_3$) as solvent. The resonance of non-deuterated chloroform at $\delta = 7.27$ ppm was used as internal reference. The number of scans was 128, with a relaxation time of 10 seconds. Data was collected at 298 K. For the sensitivity analysis, a linear polyDODT was mixed with a cyclic polyDODT and data was collected at 288 K using the 800 MHz NMR equipped with a 5 mm Triple-resonance Inverse (TXI) cryoprobe with Z-Gradients. ^{13}C NMR was collected with 2048 scans and 10 s relaxation at 298 K on the Bruker 700 MHz NMR (more sensitive for carbon than the 800 MHz instrument) using a 5 mm Triple-resonance Observe (TXO) cryoprobe with Z-Gradients. 2D multiplicity-edited HSQC measurement with sensitivity enhancement was carried out on the Bruker 800 MHz NMR: spectral width ^{1}H (16 ppm) and ^{13}C (240 ppm); data matrix 2048 × 128; number of scans:

Table 2 Polymerization conditions

Method	Sample ID	Peroxide (%)	Reaction	Air bubbling
1	1.1.; 1.2.; 1.3.	3	Pump H_2O_2 into DODT/TEA	No
2	2.1.; 2.2.; 2.3.	30	Dump DODT/TEA into H_2O_2	No
3[a]	3.1.[a]	30	Pump DODT/TEA into H_2O_2	No
4	4.1.	30	Drip H_2O_2 into DODT/TEA	Yes

DODT : TEA : H_2O_2 = 27.5 : 82.2 : 57.3. [a] DODT : TEA : H_2O_2 = 32 : 73 : 64.

16; relaxation delay: 1 s. NMR data were processed and analyzed using TopSpin 3.6.2, and chemical shifts (^1H and ^{13}C) were referenced internally against the solvent peak.

High resolution five-detector size exclusion chromatography (SEC)

The SEC instrument consisted of an Agilent 1260 infinity isocratic pump, a Wyatt Eclipse DUALTEC separation system, an Agilent 1260 infinity variable wavelength detector (UV set at 254 nm), a Wyatt OPTILAB T-rEX interferometric refractometer (DRI), a Wyatt DAWN HELOS-II 18-angle static light scattering detector (MALS) with a built-in dynamic light scattering (QELS) module, a Wyatt Viscostar online differential viscometer and an Agilent 1260 infinity standard autosampler. 6 StyragelVR columns (HR6, HR5, HR4, HR3, HR1, and H0.5) were thermostated at 35 °C. THF was the mobile phase at a flow rate of 1 mL min^{-1}, continuously distilled from CaH_2. In each case 100 μL of 2 mg mL^{-1} polymer solution was injected. The results were analyzed using the ASTRA 6 software (Wyatt Technology). Two concentration detectors were used: DRI with $dn/dc = 0.132$ for polyDODT[6] and UV with absorption coefficients obtained assuming 100% mass recovery. The traces overlapped exactly. Two close to monodisperse PS standards (M_n = 30 000 and 100 000 g mol^{-1}) were injected with each new series of measurements to doublecheck accuracy of the instrument.

Results and discussion

Synthesis of linear PolyDODT by end-capping with mercaptoethanol (SH-Et-OH)

As mentioned in the Introduction, until recently we had been able to produce only low molecular weight linear polyDODT oligomers (M_n ~ 1000–3000 g mol^{-1}).[23] End-capping with SH-Et-OH provided molecular weight control with M_n directly proportional to the DODT/SH-Et-OH ratio – Fig. 2 displays the excellent correlation, and Table 3 summarizes the data.

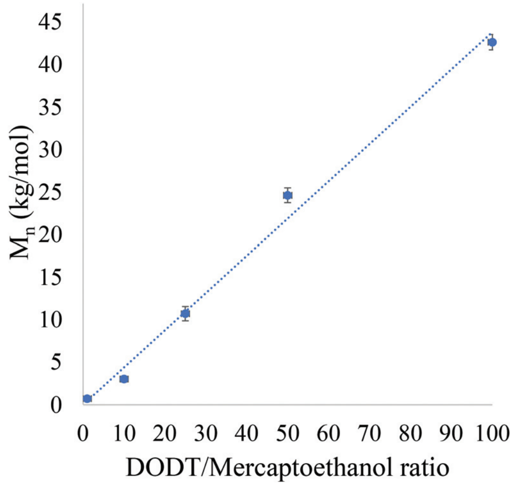

Fig. 2 M_n *vs.* DODT/SH-Et-OH ratio, R^2 = 0.9958. Error bars represent 95% confidence level calculated by Astra (SEC).

Table 3 Molecular weight and conversion data for the reactions in the presence of SH-Et-OH

ID	M_n (g mol^{-1})	M_w (g mol^{-1})	Đ	Conversion (%)
M1	700	830	1.27	62
M10	3000	7000	2.34	82
M25	10 700	18 600	1.74	95
M50	24 400	33 400	1.36	99
M100	42 500	59 500	1.40	84

The end groups in this case were $–CH_2–CH_2–OH$, as shown by ^1H NMR of sample M10 (Fig. 3). The main chain proton signals appear at δ_H(400 MHz; $CDCl_3$) 2.98 (4 H_d, t, $\mathbf{CH_2}S S\mathbf{CH_2}$); 3.65 (4 H_f, s, $O\mathbf{CH_2}\mathbf{CH_2}O$); 3.75 (4$H_{c,e}$, t, $O\mathbf{CH_2}CH_2SSCH_2\mathbf{CH_2}O$) ppm, while signals related to the end groups appear at 2.35 (2 H_a, br s, $CH_2\mathbf{OH}$) and 3.81–3.83 (4 H_b, t, $\mathbf{CH_2}OH$) ppm. This method yielded linear polyDODTs with up to M_n ~ 40 000 g mol^{-1}, but the NMR of the last sample had signals assigned to –SH end groups so not all chain ends were capped with –OH groups.

Effect of reaction conditions on polymer structure

Polymers were produced by four different methods – the results are summarized in Table 4. Method 1 and the first two samples of Method 2 yielded polymers with thiol end groups (see a picture of L1.1 in Fig. S1B† and the proton NMR of L2.2 in Fig. S2†). The M_n of the samples was calculated based on the ratio of the end group protons (**SH**, 1.6 ppm and $\mathbf{CH_2}SH$, 2.75 ppm) relative to the main chain protons (2.98–3.75 ppm). Table 4 compares M_n values from SEC and NMR. There is very good agreement up to M_n ~ 80 000 g mol^{-1}. In case of the third sample from Method 2, the M_n calculated from NMR is higher than that from SEC, indicating that a fraction of the sample does not have thiol end groups, so this sample is a mixture of linear (~40%) and cyclic (60%) polyDODTs. A representative ^{13}C NMR is shown in Fig. S3.†

The 800 MHz NMR of the polymers from Methods 3 and 4 did not show any end group signals (see the NMR of C3.1 in Fig. S4†). This may be an indication of cyclic structures. NMR and MALDI-MS of low molecular weight polyDODT (M_n < 3000 g mol^{-1}) also demonstrated cyclic structures.[6,23] At ~30 nM theoretical detection limit,[25] 800 MHz NMR would be able to detect 0.4 and 1.7% linear polyDODT with -SH end groups in 45 mg cyclic samples of M_n = 35 800 and 84 700 g mol^{-1} (C3.1 and C4.1 in Table 4) in the NMR tube. Thus, NMR data may be interpreted as indicating very pure cycles for C3.1 and C4.1.

2D NMR of L1.1 (Fig. 4) highlights the signal correlating the carbon (24.6 ppm, ^{13}C) with the protons (2.75 ppm, ^1H) in the $–CH_2$ group next to the thiol ($–\mathbf{C}–\mathbf{H_2}–S–H$). No signal was found at 24.6 ppm in the ^{13}C NMR spectrum of C3.1, indicating that there were no end groups in the polymer.

To test the sensitivity (the amount of linear chains that need to be added to be detectable) of 800 MHz NMR, 1.3 – to 17 wt% L1.1 was mixed with C3.1 and tested with the 800 MHz NMR which has the highest sensitivity for ^1H NMR measure-

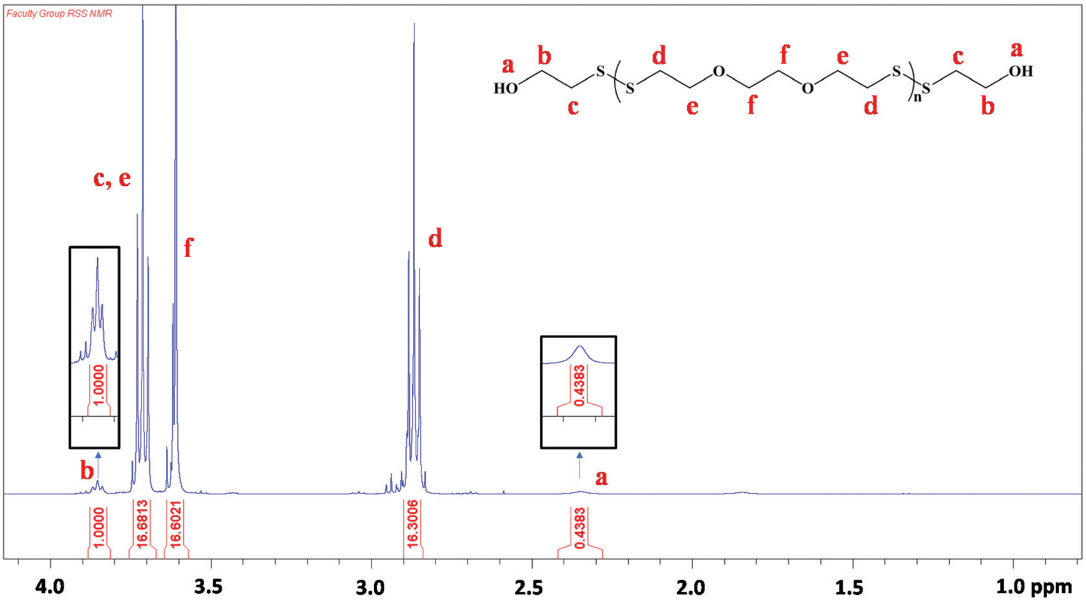

Fig. 3 400 MHz ^{1}H NMR spectrum of M10 (OH end) (M_n (SEC) = 3000 g mol^{-1}, Table 2, M_n (NMR) = 2900 g mol^{-1}) scaling factor is 2 and for the insets it is 16.

Table 4 Effect of reaction conditions on the R3P of DODT

ID	M_n (SEC) (g mol^{-1})	M_n (NMR) (g mol^{-1})	$Đ$	DODT conversion (%)
Method 1				
L1.1	27 800	33 800	1.95	73
L1.2	27 900	28 700[a]	2.18	90
L1.3	37 800	31 300[a]	2.21	85
Method 2				
L2.1	15 100	17 500	1.61	32
L2.2	78 000	82 900	2.05	55
L/C2.3				
40/60	94 300	146 000	2.16	75
Method 3				
C3.1	35 800		2.74	54
Method 4				
C4.1	84 700		1.26	

800 MHz, except. [a] 400 MHz.

ment (S/N = 7400 for 0.1% ethylbenzene standard). Measurements were carried out at 288 K to shift the broad water peak from the solvent downfield to not overlap with the –SH resonance at 1.6 ppm. Since the **HS**– triplet was very clean while the –$\mathbf{CH_2}$–SH seemed to overlap with a satellite, this integral was used to calculate M_n = 33 800 g mol^{-1} for L1.1 (see Table 4). Fig. 5 and Table 5 summarize the data. At 29 nmol linear content, no HS-end group signals were detected. At 37 nmol a small signal appeared, and the integral indicated 1.8 wt% L1.1, in comparison with the nominal 1.3 wt% due to the linear chains that were added.

As the concentration of the linear polymer increases the –SH signal intensity increases, giving good agreement between the nominal and measured end group concentrations. C3.1 had M_n = 35 800 g mol^{-1} measured by SEC, which is similar to that of L1.1 (see Table 4). Therefore, based on our NMR investigation, C3.1 contains less than 1.3 wt% linear contamination, if any. This agrees well with the calculated sensitivity data.[25] The lack of any other signals that may be associated with end groups suggest that C3.1 is a cyclic polyDODT.

High-resolution size exclusion chromatography (SEC)

Table 6 summarizes integrated SEC data for the linear and cyclic polymers with similar molecular weights from Table 4, and Fig. 6 compares the SEC traces. Cyclic samples eluted later than the linear counterparts, but the difference is smaller at higher molecular weight. This difference in time is due to the smaller hydrodynamic volumes that physically more compact cyclic polymers possess, which is consistently reported for cyclic polymers.[26,27] The R_g and R_h values and intrinsic viscosities of the cycles are also smaller than those of the linear samples of similar molecular weight and close to the theoretical expectation of $g \approx 0.66$.[16,28–32]

Cyclic polymers are expected to have lower intrinsic viscosities than linear counterparts: theory suggests a ratio of g' = $[\eta_{\text{cyclic}}]/[\eta_{\text{linear}}]$ = 0.4–0.5.[28–31] However, this ratio has been reported experimentally to range from 0.3–0.9. Jeong *et al.* carried out a thorough study on cyclic and linear PSs focusing on the dilute solution properties and measured g' = to be 0.57–0.63.[33] We found g' values of 0.74 and 0.65, respectively (see Table 6).

To take out the influence of polydispersity, plots from individual SEC runs were constructed. Fig. 7(A and B) compares M_i – retention time plots for the linear-cyclic pairs in Table 6 (L1.1 – C3.1 and L2.2 – C4.1). Cyclic samples eluted later than

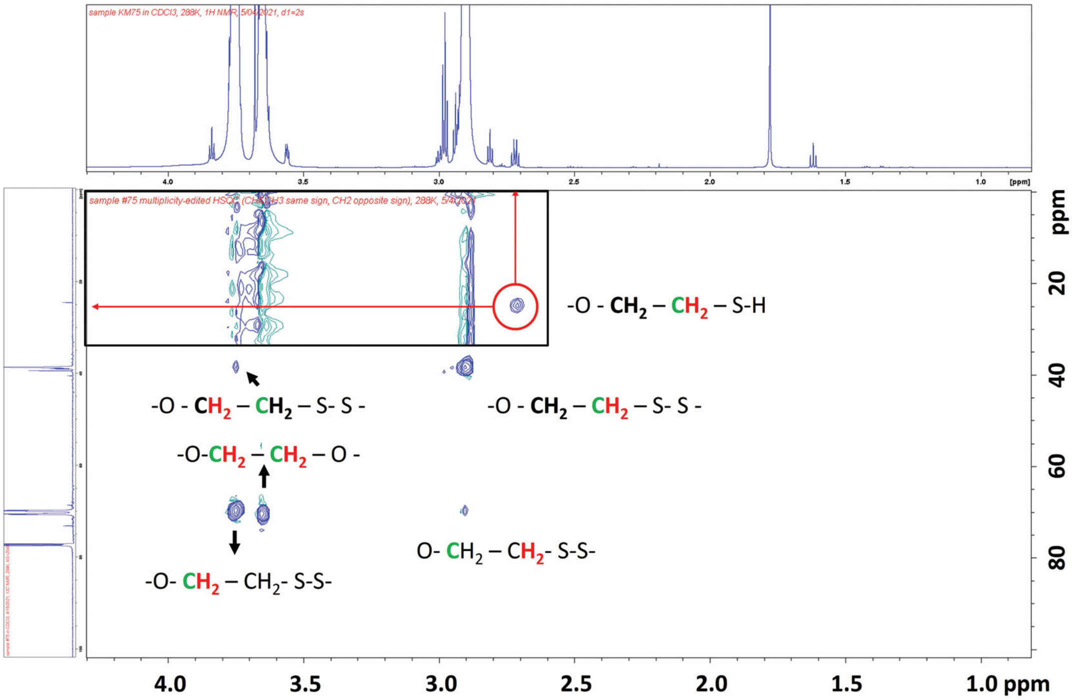

Fig. 4 2D multiplicity edited ^{1}H–^{13}C HSQC spectrum of L1.1. Inset: enlargement for the $-CH_2-S-H$ correlation. Red color highlights ^{1}H and green the ^{13}C correlations of either one or two bonds.

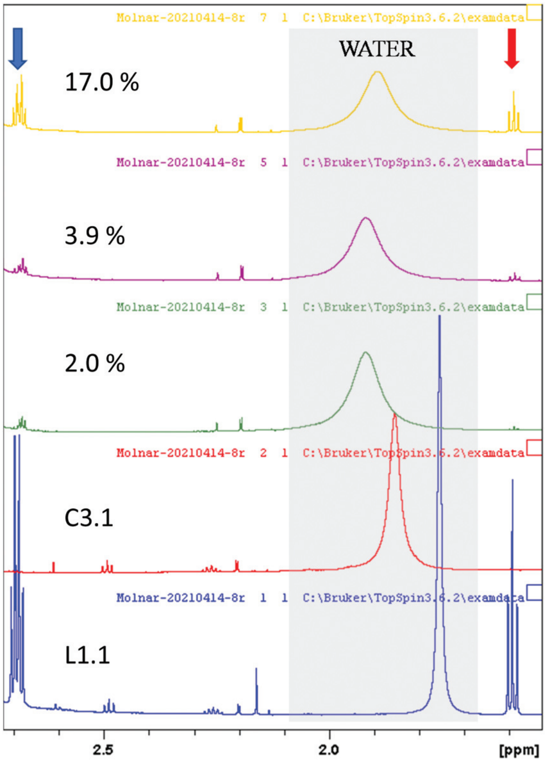

Fig. 5 Sensitivity analysis for ^{1}H NMR (800 MHz). Broad peak to the left to the $-SH$ 1.6 is water. Pure L1.1 (blue), pure C3.1 (red), Mix 2 (green), Mix 5 (purple), Mix 7 (yellow). Blue arrow indicates the $-CH_2-SH$ at 2.71 ppm and the red arrow indicates the $-SH$ triplet at 1.6 ppm. Numbers indicate linear content in wt%.

Table 5 Sample compositions and results of sensitivity analysis for ^{1}H NMR (800 MHz)

	Linear content		
	Nominal		
ID	(nmol)	(%)	–SH integral (%)
L1.1	2381	100.0	100.0
Mix 1	29	1.5	NA
Mix 2	37	1.3	1.8
Mix 3	63	2.0	2.0
Mix 4	124	3.9	3.8
Mix 5	250	7.7	8.6
Mix 6	473	17.0	17.9

Table 6 Integrated SEC data

				R_h (nm)			
ID	M_n (SEC) (g mol^{-1})	$Đ$	R_g (nm)	Visc	QELS	Visc (mL g^{-1})	g'
Lower MW							
L1.1	27 800	1.95	12.2	8.5	8.4	36.3	
C3.1	35 800	2.74	9.5*	5.8		26.7	0.74
Higher MW							
L2.2	78 000	2.05	21.9	15.5	15.7	86.8	
C4.1	84 700	1.26	16.1	10.9	—	56.7	0.65

* R_g measurements below 10 nm are not reliable.

the linear counterparts at the same molecular weight but the difference decreased with increasing molecular weight, similarly to that shown in the SEC traces in Fig. 6.

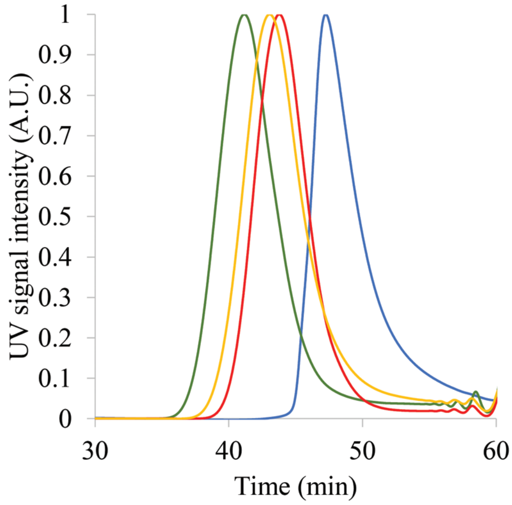

Fig. 6 UV traces (A) of L1.1 (red); C3.1 (blue); L2.2 (green); C4.1 (orange) from Table 6.

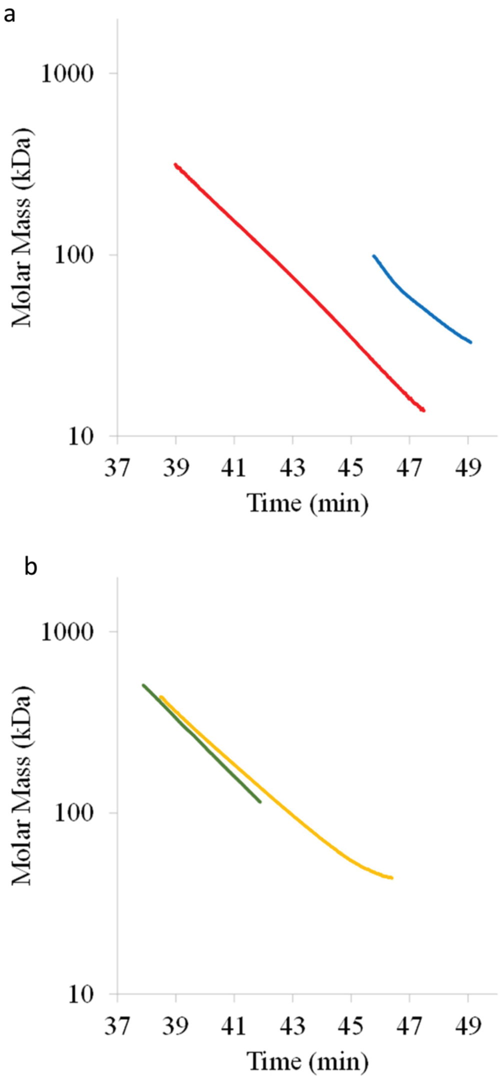

Fig. 7 M_i – retention time plots for linear and cyclic polyDODTs: C3.1 – L1.1 (a) and C4.1 – L2.2 (b) from Table 6.

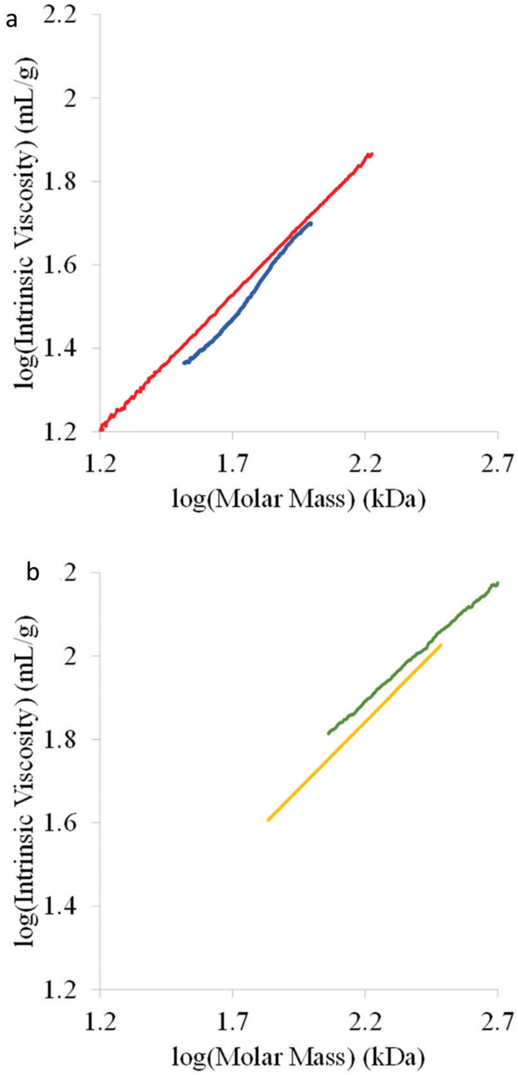

Fig. 8 MHS plots of cyclic and linear polyDODTs: L1.1 (red) – C3.1 (dark blue) (a) and L2.2 (green) – C4.1 (orange) (b).

Fig. 8 compares the Mark–Houwink–Sakurada plots for the linear-cyclic pairs in Table 6 (L1.1 – C3.1 and L2.2 – C4.1). In the lower molecular weight range, the viscosity of C3.1 is lower than that of L1.1, but with increasing molecular weights the plots converge. The 800 MHz NMR sensitivity analysis demonstrated that C3.1 had less than 1.3% linear contaminants if any. The situation is similar for L2.2 and C4.1, with less difference.

The QELS detector measures translational diffusion coefficients (D). The ratio of D of circular and linear species $C = D_C/D_L$ is predicted to be greater than unity and independent of length for long molecules, but the exact value is still debated.[18,34] Calculations based on classical Kirkwood hydrodynamic theory predicted $C \sim 1.18$, while renormalization group calculations predicted $C \sim 1.45$. Some experiments on synthetic polymer solutions reported values of $C \sim 1.11–1.2$, in reasonable agreement with the calculations using Kirkwood theory, but one reported $C \sim 1.36$, in closer agreement with the renormalization group theory calculation. We found that

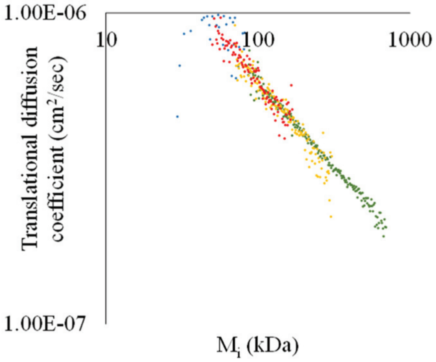

Fig. 9 Diffusion coefficient *vs.* molecular weight (M_i) for: L1.1 (red), L2.2 (green), C3.1 (dark blue) and C.4.1 (orange).

Table 7 High molecular weight polyDODT samples

ID	M_n (g mol^{-1}) SEC	M_w (g mol^{-1}) SEC	$Đ$
X1	175 500	398 500	2.27
X2	206 700	301 900	1.46
X3	280 500	399 900	1.43
X4	300 000	417 000	1.39
X5	325 400	405 900	1.25
X6	366 700	556 000	1.52

the D–M_i plots are identical within experimental error (see Fig. 9) but it must be considered that QELS is less accurate than viscometry.

The NMR investigations indicate pure rings, not mixtures, but the dilute solution properties are contradictory, especially at higher molecular weights. We have no explanation for the strange behavior currently, but detailed investigations of these unique elastomers are in progress. One theory is the flexible nature of these elastomers. The unique capability of R3P is that it can produce high molecular weight polymers at large scale, for rheological and other studies. Table 7 gives some examples and Fig. S1C† shows a picture of a sample. The very high molecular weight, however, prevented detailed structural investigations so they are labeled “X”. Rheological testing of the polymers is in progress and will be published separately.

Conclusions

In summary, we synthesized polyDODTs by R3P and characterized the polymers by NMR and High-resolution Five-detector SEC. Sensitivity analysis by 800 MHz NMR showed a detection limit of ~1.3% linear contaminants in a sample with M_n = 35 800 g mol^{-1}. PolyDODT is capable of chain extension to higher molecular weights, depolymerization to lower molecular weights, or dynamic intermixing with other polymer chains, both cyclics and linears. These properties may give great flexibility in the synthesis and characterization of pure cyclic polymers. The aqueous “green” R3P method yields polymers at the 10–100 g scale in the lab, which will allow more detailed studies into the reasons for the unusual findings at higher molecular weights.

Conflicts of interest

There are no conflicts to declare.

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