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Cite this: *Polym. Chem.*, 2021, **12**, 4253

Polymers from sugars and CS₂: ring opening co-polymerisation of a D-xylose anhydrosugar oxetane†Thomas M. McGuire  and Antoine Buchard  *

A D-xylose anhydro sugar derivative (**1**) has been applied in the ring-opening copolymerisation (ROCOP) with CS₂ to form a polythiocarbonate (poly(CS₂-co-**1**)) with high head-head/tail-tail regioselectivity towards alternating thiono- and trithiocarbonate linkages (up to 95%). Through variation of the reaction parameters (e.g. temperature and CS₂ stoichiometry), some control over the regioselectivity (head-head/tail-tail linkages 57–95%) and the nature of the polymer linkages is possible. Conditions can also be tailored to enable the facile isolation of a polymerisable cyclic xanthate, **2**. Kinetic experiments suggest that across the range of temperatures studied, the formation of poly(CS₂-co-**1**) proceeds at least partially by direct copolymerisation of **1** and CS₂, without necessarily going through the ring-opening polymerisation (ROP) of **2**. Poly(CS₂-co-**1**) exhibits partial chemical recyclability into cyclic monomer **2** (up to 45% after 20 h at 110 °C with [poly(CS₂-co-**1**)]₀ = 1.34 mol L⁻¹). Finally, rapid degradation (<1 h) of poly(CS₂-co-**1**) is possible under UV radiation (λ = 365 nm) and is accelerated in the presence of tris(trimethylsilyl)silane (TTMSS).

Received 4th June 2021,

Accepted 6th July 2021

DOI: 10.1039/d1py00753j

rsc.li/polymers

Introduction

Owing to the environmental issues surrounding plastic use, a societal shift away from traditional petroleum-derived feedstocks is driving innovation in the field of sustainable polymer chemistry. Polymers derived from sugars have huge potential as sustainable alternatives to current commodity plastics.^{1–5} For instance, polymers which incorporate pyranose or furanose motifs typically exhibit remarkably high glass transition temperatures (*T*_g) and the availability of hydroxyl groups of sugar derivatives significantly broadens the scope for prospective material functionalisation.^{6–9}

It is known that the replacement of oxygen atoms with sulfur ones in oxygenated polymers can give the resulting polythioethers, polythiocarbonates and polythioesters enhanced physical and thermal properties,^{10–16} as well as additional advanced optical¹⁷ and electrical characteristics.¹⁸ Moreover, sulfur-containing polymers exhibit biocompatibility and have shown potential in metal and bacterial adhesion.^{19,20} The presence of sulfur atoms in the backbone of polymers may also accelerate degradation under appropriate conditions (e.g. under UV radiation).^{19,21}

The synthesis of polythiocarbonates is possible through polycondensation,^{22–25} the ring-opening polymerisation (ROP) of cyclic thiocarbonates,^{26,27} polyalkylation of trithiocarbonates^{28,29} or the ring-opening copolymerisation (ROCOP) of CS₂^{15,30–33} and COS^{11,34–38} with cyclic ethers (epoxides and oxetane). ROCOP methods are particularly interesting given the array of synthetic possibilities provided by the pool of cyclic ethers usable, coupled with the polymerisation control brought by existing ROCOP catalysts.^{39,40} To date, both heterogeneous (e.g. Zn–Co(III) double-metal cyanide complexes)⁴¹ and homogeneous catalysts/initiators (e.g. metal salen/onium catalysts^{30,34,42} and LiO^tBu³¹) have been reported for CS₂/cyclic ether ROCOP. However, reports of ROCOP between an oxetane and CS₂ remain rare.³²

CS₂ is manufactured by reaction of charcoal or natural gas with sulfur, and despite its known toxicity, incorporating it into polymers has some benefits in terms of waste valorisation. Indeed, sulfur is an abundant by-product of the oil and chemical industry.^{43–45} Our group has previously used CS₂ to synthesise a series of cyclic thiocarbonates for ROP towards sugar-derived polythiocarbonates.²⁷ However, the synthesis of these monomers was challenging, necessitating extensive purification (e.g. successive column chromatography) to be suitable for ROP techniques. For xylose-derived xanthate monomer, **2**, ROP towards poly(**2**) formed a regioregular polymer with up to 87% head-head/tail-tail (HH/TT), trithiocarbonate/thionocarbonate linkages, although no control over the polymer microstructure was demonstrated.

It was envisioned that the ROCOP of CS₂ with oxetane-functionalised xylofuranose derivative, **1**, may expediate the polymer synthesis given its ease of preparation in purities suit-

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†Electronic supplementary information (ESI) available: Experimental procedures, NMR spectra of polymers and degradation products. SEC, TGA-MS, WAXS and DSC traces. *M*_n plots and mechanistic considerations. See DOI: 10.1039/d1py00753j

Herein we describe the ROCOP of **1** with CS₂ to form sugar-based sulfur-containing polymers with very high regioselectivity towards HH/TT, trithiocarbonate/thionocarbonate linkages (up to 95%), marking an improvement on the similar polymer synthesised through the ROP of **2**. The head/tail configuration of poly(CS₂-*co*-**1**) can be varied through modulation of the reaction temperature and CS₂ stoichiometry. Mechanistic investigations show that ROCOP proceeds at least partially directly. Lastly, poly(CS₂-*co*-**1**) exhibits partial chemical recyclability into **2**, as well as full degradation under UV light.

Possible linkages:

S2 **detected** **S1**

not detected

Figure 1 displays the ^{13}C NMR spectra of poly(1,3-bis(2-mercaptoethyl)oxetane) (PMBE) and its thiol-ene adducts. The spectra are labeled (a) through (e). The x-axis represents the chemical shift in ppm, ranging from 0 to 230.

- (a) PMBE spectrum:** Shows peaks labeled a, b, c, d, e, e'xanthate, and e'trithio. The chemical structure of PMBE is shown above the spectrum.
- (b) PMBE-1,2-bis(2-mercaptoethyl) adduct spectrum:** Shows peaks labeled a, b, c, d, and e. The chemical structure of the adduct is shown above the spectrum.
- (c) PMBE-1,3-bis(2-mercaptoethyl) adduct spectrum:** Shows peaks labeled a, b, c, d, and e. The chemical structure of the adduct is shown above the spectrum.
- (d) PMBE-1,4-bis(2-mercaptoethyl) adduct spectrum:** Shows peaks labeled a, b, c, d, and e. The chemical structure of the adduct is shown above the spectrum.
- (e) PMBE-1,4-bis(2-mercaptoethyl) adduct spectrum:** Shows peaks labeled a, b, c, d, e, f, and g. The chemical structure of the adduct is shown above the spectrum.

Minor resonances associated with the *e* environment were also observed between $\delta = 2.65\text{--}3.13$ ppm and $\delta =$

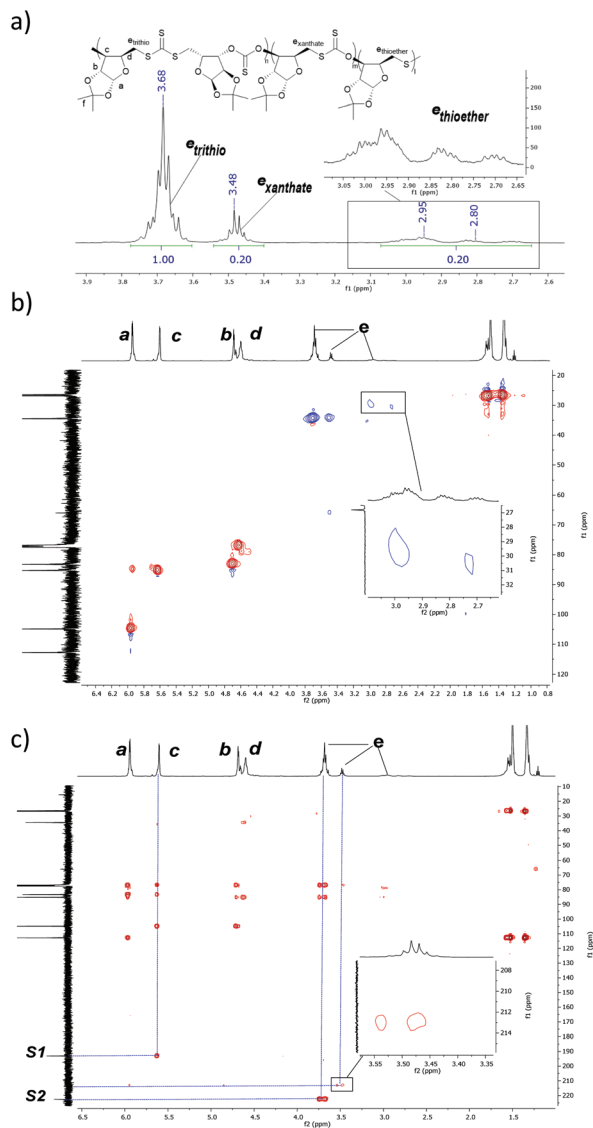


Fig. 2 (a) ^1H NMR (500 MHz, CDCl_3) and (b) ^1H - ^{13}C HSQC (500 MHz, CDCl_3) spectra of isolated poly(CS_2 -co-**1**) formed neat at 80 °C with $[\mathbf{1}]_0 : [\text{CS}_2]_0 : [\text{CrSalen}]_0 : [\text{PPNCl}]_0$ loadings of 100 : 200 : 1 : 1. (c) ^1H - ^{13}C HMBC spectrum (500 MHz, CDCl_3) of crude poly(CS_2 -co-**1**). Reaction performed neat at 80 °C with $[\mathbf{1}]_0 : [\text{CS}_2]_0 : [\text{CrSalen}]_0 : [\text{PPNCl}]_0$ loadings of 100 : 200 : 1 : 1.

3.42–3.56 ppm, suggesting the occurrence of other polymer linkages (Fig. 2). While only resonances **S1** and **S2** were observed in the thiocarbonyl region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated poly(CS_2 -co-**1**) (Fig. 1e), a weak correlation between a xanthate-like ($\delta = 212.8$ ppm) and an **e** ($\delta = 3.42$ – 3.56 ppm) proton environment was detected by ^1H - ^{13}C $\{^1\text{H}\}$ NMR HMBC spectroscopy (Fig. 2c), revealing the presence of xanthate polymer linkages (**e**_{xanthate}). Conversely, no ^1H - ^{13}C $\{^1\text{H}\}$ NMR HMBC correlation was observed for the **e** proton environment detected at $\delta = 2.65$ – 3.13 ppm. Comparison with literature data³² revealed that the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR shift values of this resonance was comparable to known polythioethers (Fig. 2b),³⁶ corroborating the absence of a nearby

quaternary carbon. This resonance was therefore attributed to a thioether polymer linkage (**e**_{thioether}). The complexity of the signals seen may stem from random position of the thioether linkages in the polymer sequence. Regardless of the origins of those various linkages, the **e** environments in the ^1H NMR spectra were thus identified as an easy way to assess the selectivity of the ROCOP process.

Encouraged by this preliminary data, further catalytic ROCOP experiments were performed to study the effect of concentration, temperature, CS_2 stoichiometry and nature of the catalyst and of co-catalyst on the products of the ROCOP reaction (Table 1).

Impact of temperature on polymer linkages

Polymerisations were carried out at 25 °C, 60 °C, 80 °C, 100 °C and 140 °C at $[\mathbf{1}]_0 : [\text{CS}_2]_0 : [\text{CrSalen}]_0 : [\text{PPNCl}]_0$ loadings of 200 : 400 : 1 : 1 (Table 1, entries 1–5). **CrSalen** was found to be active for $\mathbf{1}/\text{CS}_2$ ROCOP at all temperatures tested, including at 25 °C (Table 1, entry 1). The room temperature reactivity of the $\text{CS}_2/\mathbf{1}$ ROCOP contrasts strongly with analogous reactions with cyclic anhydrides which necessitate high temperatures and long reaction times (100 °C, 2–6 days) to give similar oxetane conversions. Overall, the reactivity of **1** with CS_2 seems comparable with that of cyclohexene oxide,³⁰ cyclopentene oxide⁴² and oxetane,³² although direct comparisons of TOFs are not appropriate due to substantial differences in the reaction conditions used. The enhanced activity of **CrSalen** in the ROCOP of $\text{CS}_2/\mathbf{1}$ as compared with cyclic anhydrides may be a result of two effects. Firstly, CS_2 is a stronger electrophile than cyclic anhydrides owing to the lower enthalpy of the $\text{C}=\text{S}$ bond vs. the $\text{C}=\text{O}$ bond (573 and 799 kJ mol^{-1} , respectively).^{50,51} Secondly, following CS_2 insertion, the resulting thiocarbonate species are more nucleophilic than a carboxylate and the Cr-S bond is likely less strong than a Cr-O bond, which promotes propagation.

Within the limits of ^1H NMR spectroscopy, in all the experiments performed, all resonances seen could be assigned to poly(CS_2 -co-**1**) (as described above), cyclic xanthate **2** or oxetane monomer **1** (Fig. 1). However, varying the reaction temperature caused significant divergences in product distributions. Increasing the temperature resulted in a loss of regioselectivity (Table 1, entries 1–5 and Fig. S6†). At 25 °C, 60 °C and 80 °C, high HH/TT regioselectivity was observed (92, 85 and 89%, respectively, Table 1, entries 1–3). Conversely, for reactions performed at 100 °C and 140 °C, lower percentages of trithiocarbonates linkages were observed (73 and 57%, respectively, Table 1, entries 4 and 5) with an increase in thioether linkages detected (16% and 31%, respectively). The increased occurrence of thioether linkages at elevated temperatures likely arises from the elimination of COS from propagation intermediates, favoured by entropy (Scheme S2†) and as noted in previous studies.^{30,32,42} The ratio of xanthate links also increased with temperature, but to a lesser extent than for the thioethers (6% at 25 °C up to 12% at 140 °C, Table 1 entries 1–5). The formation of xanthate linkages may be a result of several mechanisms: the ‘expected’ $\text{CS}_2/\mathbf{1}$ ROCOP, but



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Polym. Chem., 2021, **12**, 4253–4261 | 4257

Table 2 ROP of **2** and depolymerisation of poly(**CS₂-co-1**)

Entry	T (°C)	Reagent	% ^a Conv	% ^b Polym	<i>n</i> : <i>m</i> : <i>l</i> ^c	<i>M_{n,SEC}</i> [<i>D_M</i>] ^d
1 ^e (ref. 27)	25	2	86	86	87 : 10 : 3	10 600 [1.5]
2	80	2	75	75	85 : 12 : 3	12 700 [2.05]
3 ^f	80	Poly(CS₂-co-1)	0	100	76 : 8 : 16	8200 [1.70]
4 ^f	110	Poly(CS₂-co-1)	45	55	65 : 10 : 25	3600 [1.62]
5 ^f	140	Poly(CS₂-co-1)	— ^g	—	—	—

Reactions carried out for 20 h in σ -dichlorobenzene with $[2/1_{\text{monomer unit}}]_0 : [\text{CrSalen}]_0 : [\text{PPNCl}]_0$ loadings of 200 : 1 : 1, and $[2/1_{\text{monomer unit}}]_0 = 1.34 \text{ mol L}^{-1}$ unless otherwise stated. ^a Conversion of substrate determined by ^1H NMR spectroscopy in CDCl_3 using relative integration of anomeric protons (1H) in substrates and products (**1**: $\delta = 6.26 \text{ ppm}$ (d, $J = 3.7 \text{ Hz}$)); poly(**CS₂-co-1**): $\delta = 5.88\text{--}5.99 \text{ ppm}$; **2**: $\delta = 6.03 \text{ ppm}$ (d, $J = 3.7 \text{ Hz}$). ^b Calculated by ^1H NMR spectroscopy using relative integration of anomeric protons in poly(**CS₂-co-1**) and **2**. ^c Calculated by ^1H NMR spectroscopy in CDCl_3 using relative integration of *e* environments (CH_2) assigned to HH/TT trithiocarbonate linkages *n* ($\delta = 3.68 \text{ ppm}$ (h, $J = 6.9 \text{ Hz}$, 4H)), HT xanthate linkages *m* ($\delta = 3.51 \text{ ppm}$ (t, $J = 6.6 \text{ Hz}$, 2H)) and thioether linkages *l* ($\delta = 3.04\text{--}2.74 \text{ ppm}$ (m, 2H)). ^d Calculated by SEC relative to polystyrene standards in THF eluent; $D_M = M_w/M_n$. ^e Reaction performed with $[2]_0 : [\text{TBD}]_0 : [4\text{-MeBnOH}]_0$ loadings of 100 : 1 : 1 in DCM with $[2]_0 = 1.0 \text{ mol L}^{-1}$, time = 15 minutes. ^f Substrate polymer data: *n* : *m* : *l* ratio = 82 : 6 : 12; $M_{n,SEC} = 8500 \text{ g mol}^{-1}$. ^g Insoluble black residue formed during 20 h reaction.

200 : 1 : 1 gave 75% conversion of **2** into a polymer with similar microstructure, molar mass and D_M values to those obtained previously *via* reaction of **1** with CS_2 (Table 2, entry 1 vs. Table 1, entry 3). In addition, the final product distribution matched well that observed in 1/ CS_2 ROCOP (around 75 : 25 polymer : cyclic monomer ratio). This demonstrates that ROP of xanthate **2** is accessible at 80 °C with the CrSalen/PPNCl catalyst system.

In order to probe whether the copolymerisation of CS_2 /**1** occurred *via* ROP of **2**, reaction monitoring by ^1H NMR spec-

troscopy was performed at 25 °C, 80 °C and 110 °C with $[1]_0 : [\text{CS}_2]_0 : [\text{CrSalen}]_0 : [\text{PPNCl}]_0$ loadings of 200 : 400 : 1 : 1 (Fig. 4). At 80 °C, inspection of the early stages (<1 h) of the reaction revealed that polymer and **2** formed at approximately the same rate (Fig. 4a). After 1–2 h, the concentration of **2** plateaued as the polymer concentration increased.

At 110 °C, simultaneous rapid formation of both the polymer and cyclic xanthate was also observed (Fig. 4c), whereas at 25 °C, minimal xanthate was detected across several days (Fig. 4d). An experiment to monitor the ROP of **2**

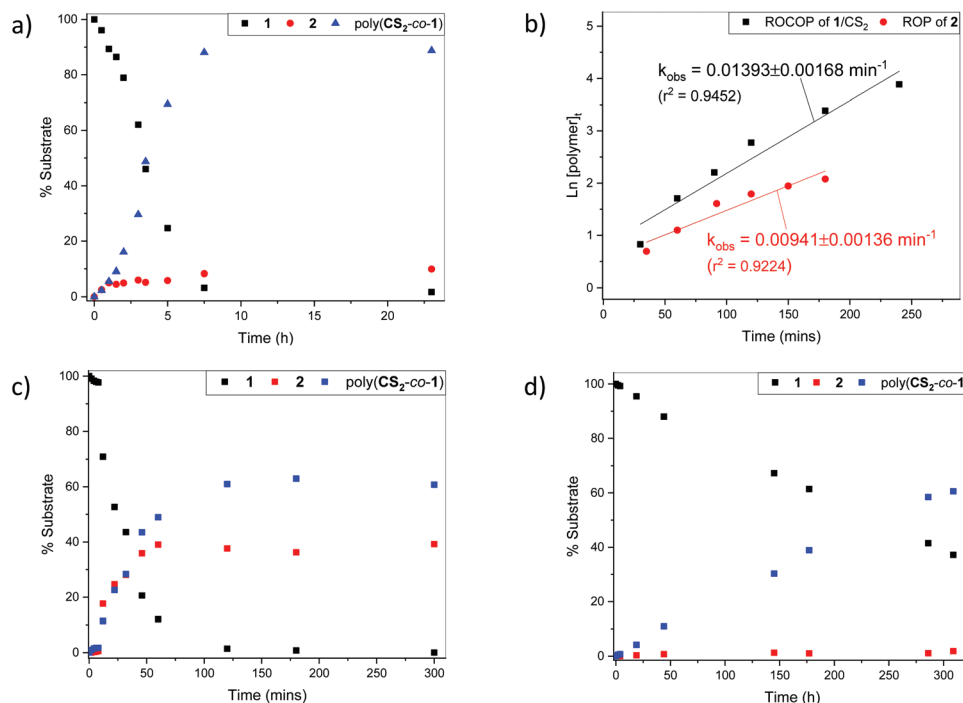


Fig. 4 Time vs. conversion of **1** (black, square) and formation of xanthate **2** (red, circle) and poly(**CS₂-co-1**) (blue, triangle) determined by ^1H NMR spectroscopy for reactions performed in σ -dichlorobenzene with $[1]_0 : [\text{CS}_2]_0 : [\text{CrSalen}]_0 : [\text{PPNCl}]_0$ loadings of 200 : 400 : 1 : 1 with $[1]_0 = 1.34 \text{ mol L}^{-1}$ at (a) 80 °C; (c) 110 °C and (d) 25 °C. (b) Relative rates of poly(**CS₂-co-1**) formation (determined by ^1H NMR spectroscopy) at 80 °C in the ROCOP of **1** and CS_2 (red, circle, $[1]_0 : [\text{CS}_2]_0 : [\text{CrSalen}]_0 : [\text{PPNCl}]_0$ loadings of 200 : 400 : 1 : 1 with $[1]_0 = 1.34 \text{ mol L}^{-1}$) and in the ROP of **2** (black, square, with $[2]_0 : [\text{CS}_2]_0 : [\text{CrSalen}]_0 : [\text{PPNCl}]_0$ loadings of 200 : 200 : 1 : 1 with $[2]_0 = 1.34 \text{ mol L}^{-1}$).



was also performed at 80 °C, with $[2]_0:[CS_2]_0:[CrSalen]_0:[PPNCl]_0$ loadings of 200:200:1:1 in the presence of a alcohol initiator, 4-MeBnOH. CS_2 and 4-MeBnOH were added to the reaction mixture in attempt to simulate ROCOP conditions, in which excess CS_2 and polymer growing chains are present in solution. Assuming first order kinetics in monomer, the rate of polymer formation was slower in the ROP of **2** than in the $1/CS_2$ ROCOP (Fig. 4b). With no build-up of **2** seen during ROCOP, this data therefore suggest that polymer is formed at least partially *via* direct ROCOP.

2 could also be formed *via* back-biting of the polymer chains (Fig. 3). A reaction performed at 80 °C with isolated polymer as substrate, at $[poly(CS_2-co-1)]_0:[CrSalen]_0:[PPNCl]_0$ loadings of 200:1:1, gave no formation of cyclic xanthate after 20 h (Table 2, entry 3). This suggests that at 80 °C, cycloaddition of **1** and CS_2 is the dominant mechanism for formation **2**. However, at 110 °C, back-biting was observed, with approximately 45% xanthate formed after 20 h. No other cyclic species were detected in solution (Table 2, entry 4). The polymer molar mass also decreased from 8500 g mol⁻¹ to 3600 g mol⁻¹, corroborating the loss of **2** from polymer chains. Increasing the temperature further to 140 °C led to formation of a black, insoluble residue (Table 2, entry 5). SEC analysis of the THF-soluble fraction indicated the presence of oligomers only. These data suggest that at elevated temperatures, alternative depolymerisation mechanisms are operative leading to significant, uncontrolled, polymer degradation.

Thermal properties of the polymers

Thermal analysis of the polymers with a range of $n:m:l$ ratios was undertaken to understand the impact of varying polymer linkage on properties (Table 3, Fig. S7–15†). All polymers analysed were found to have temperatures of onset of degradation ($T_{d,onset}$) of between 167–208 °C. Glass transition temperatures (T_g) were between 108–137 °C, higher than those reported previously,²⁷ but mostly lower than those reported for the analogous, fully oxygenated polycarbonate developed by Gross and

co-workers ($T_g = 128$ °C).⁵⁸ Contrasting with earlier studies which showed a clear impact of sulfur content on polymer properties,^{30,42} no general trend between the polymer microstructure and thermal properties was observed. However, as samples of similar molar masses could not be obtained and compared, any existing relationship may be overshadowed by the effect of chain length variations. No crystallinity was detected by differential scanning calorimetry (DSC) or wide-angle X-ray scattering (WAXS) analysis (Fig. S16†).

Degradability of the polymers

A potential advantage of sulfur-containing analogues of polycarbonates is that their degradation into small molecules may be possible under UV light. For example, a catalyst-free method for removal of trithiocarbonate RAFT chain transfer agents from poly(vinylpyridine)s has recently been developed

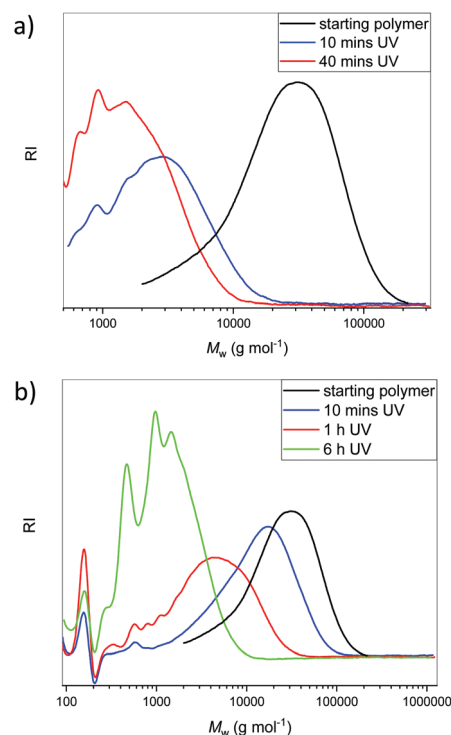
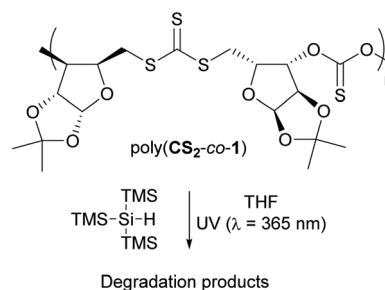


Fig. 5 SEC traces following exposure of poly(CS_2-co-1) ($M_{n,SEC} = 8400$, $D_M = 1.67$) to UV ($\lambda = 365$ nm) in the presence of (a) TTMSS (7.5 monomer equiv.) and (b) with no silane present. The reactions were performed at room temperature with $[poly(CS_2-co-1)]_0 = 0.0267$ mol L⁻¹.

Table 3 Impact of poly(CS_2-co-1) linkage ratio ($n:m:l$) on polymer thermal properties

Entry	$n:m:l^a$	$M_{n,SEC} [D_M]$ (g mol ⁻¹) ^b	$T_{d,onset}$ (°C)	T_{d5} (°C)	T_g (°C)
1	95:5:0	14 000 [1.78]	188	216	114
2	89:9:2	15 400 [2.13]	167	190	110
3	87:10:3	9100 [1.78]	191	216	108
4	69:17:14	14 400 [1.27]	208	257	137
5	61:5:34	14 000 [1.19]	172	186	117
6	57:12:31	8400 [1.67]	178	209	120

^a Calculated by ¹H NMR spectroscopy in CDCl₃ using relative integration of e environments (CH₂) assigned to HH/TT trithiocarbonate linkages n ($\delta = 3.68$ ppm (h, $J = 6.9$ Hz, 4H)), HT xanthate linkages m ($\delta = 3.51$ ppm (t, $J = 6.6$ Hz, 2H)) and thioether linkages l ($\delta = 3.04$ – 2.74 ppm (m, 2H)). ^b Calculated by SEC relative to polystyrene standards in THF eluent; $D_M = M_w/M_n$.





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