1,3-Dithiane-Derived Alkoxyamines as One-Carbon Radical Precursors

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Abstract: A new method for the generation of C-2 centered radicals derived from 1,3-dithiane is presented. The radical precursors, 2-dialkylaminoxyl-1,3-dithianes, are readily prepared from 1,3-dithiane and stable nitroxides. Thermal reaction of 2-dialkylaminoxyl-1,3-dithianes with electron-deficient olefins affords carboaminoxylation products or oxidative addition products depending on the nitroxide used. The 2-dialkylaminoxyl-1,3-dithianes can also be used as initiators/regulators for the controlled living free radical polymerization of styrene.

Key words: radical chemistry, nitroxides, 1,3-dithianes, controlled radical polymerization, microwaves

1,3-Dithianes derived from aldehydes and ketones have become highly important in synthetic organic chemistry over the past 50 years.1 Aldehyde derived dithianes are generally used as umpoled carbonyl groups in ionic chemistry.2 The intrinsic electrophilic behavior of an aldehyde carbonyl carbon atom can be altered upon transformation into the corresponding 1,3-dithiane and subsequent lithiation. These lithiated 1,3-dithianes are nucleophilic acyl equivalents, which efficiently react with various electrophiles. Along with the umpolung, dithianes have found widespread application as protecting groups in organic synthesis.3

Acyl radicals are known to undergo fast decarbonylation.4 Slow radical reactions using acyl radicals are therefore not possible. Dithiane chemistry may offer an answer to this problem. To our surprise, only a few reports on the use of 1,3-dithianes as one-carbon radical precursors have appeared in the literature to date. Byers showed that Se-substituted dithiane 1 (Figure 1) can be used in Se-group transfer chemistry.5 Very recently, Zard reported on the use of xanthate 2 (Figure 1) as a C-radical precursor.6 In addition, 1,3-dithiane-derived radicals have also been used in cyclization reactions.7 All these studies showed that these C-radicals are nucleophilic and react efficiently only with activated electron-deficient olefins.

We have recently shown that alkoxyamines derived from persistent nitroxides can be used as C-radical precursors in cyclization and intermolecular addition reactions.8 Thermal reversible C–O bond homolysis delivers efficiently C-radicals. These processes are controlled by the persistent radical effect (PRE).9 Unfortunately, acyl radicals cannot be generated via this approach. For example, the activation energy for the C–O bond homolysis in alkoxyamine 3 (Figure 1) is 150.5 kJ/mol and therefore too high for clean thermal bond homolysis.10 We assumed that 1,3-dithiane-derived alkoxyamines may offer a formal entry into long-lived acyl radicals using our methodology. Herein we present results on the use of alkoxyamines of type 4 (Figure 1) as one-carbon radical precursors in intermolecular addition reactions. Moreover, we show that these alkoxyamines can be applied as initiator/mediators for nitroxide-mediated styrene polymerization.11

TEMPO-derived dithiane 5 was readily prepared from 1,3-dithiane via lithiation and oxidation using TEMPO. In this reaction TEMPO acts as oxidant and as C-radical trapping reagent. Alkoxyamine 5 was isolated in 80% yield (Scheme 1).

Radical additions were first studied using n-butyl acrylate as a radical acceptor. Reaction of 5 in DMF (0.07 M) with 5 equivalents of olefin at 135 °C for 18 hours provided a 1:1 mixture of dithiane 6 and TEMPO-adduct 7 in 16% combined yield (Scheme 2; Table 1, run 1). We found that alkoxyamine 5 is not perfectly stable under the applied conditions. Dithioketeneacetal 6 results from carboaminoxylation of n-butyl acrylate (→ 8) with subsequent

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elimination\textsuperscript{12} of TEMPOH to give 9, which eventually isomerizes to 6. The side product 7 is probably formed via TEMPO-radical addition onto \(n\)-butyl acrylate with subsequent reduction.\textsuperscript{13} Reaction in \(\text{CHCl}_2\text{CH}_2\text{Cl}\) at 120 °C afforded 6 as the sole product in 33% yield (run 2). Addition is even less efficient in toluene (run 3). In order to succeed, reaction in toluene was conducted at higher concentration.

Encouraged by our recent results on microwave induced alkoxyamine additions we decided to repeat the experiments under microwave conditions.\textsuperscript{14,15} Reaction of 5 with \(n\)-butyl acrylate in DMF at 170 °C for 9 min provided 6 and 7 in 47% combined yield (run 4). Interestingly, running the experiment in the presence of \(\text{Et}_3\text{N}\) (1.5 equiv) under otherwise identical conditions yielded 6 as the sole product in 72% yield (run 5). Microwave experiments in \(-\text{Cl}_2\text{C}_6\text{H}_4\) and in DMSO were less efficient (runs 6 and 7). Therefore, the following experiments were conducted in DMF.

\[ \text{5} \rightarrow \text{6} \rightarrow \text{7} \]

\[ \text{8} \rightarrow \text{9} \]

Scheme 2 Oxidative addition of 5 onto \(n\)-butyl acrylate

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>(c) [M]</th>
<th>Solvent</th>
<th>6 (%)</th>
<th>7 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130</td>
<td>18</td>
<td>0.07</td>
<td>DMF</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>38</td>
<td>0.07</td>
<td>(\text{CHCl}_2\text{CH}_2\text{Cl})</td>
<td>33</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>21</td>
<td>1.00</td>
<td>toluene</td>
<td>12</td>
<td>21</td>
</tr>
<tr>
<td>4\textsuperscript{a}</td>
<td>170</td>
<td>9</td>
<td>0.07</td>
<td>DMF</td>
<td>34</td>
<td>13</td>
</tr>
<tr>
<td>5\textsuperscript{a}</td>
<td>170</td>
<td>8</td>
<td>0.07</td>
<td>DMF\textsuperscript{b}</td>
<td>72</td>
<td>–</td>
</tr>
<tr>
<td>6\textsuperscript{a}</td>
<td>180</td>
<td>8</td>
<td>0.07</td>
<td>DMSO\textsuperscript{b}</td>
<td>39</td>
<td>10</td>
</tr>
<tr>
<td>7\textsuperscript{a}</td>
<td>170</td>
<td>14</td>
<td>0.07</td>
<td>(-\text{Cl}_2\text{C}_6\text{H}_4)</td>
<td>33</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Microwave-induced heating.
\textsuperscript{b} \(\text{Et}_3\text{N}\) (1.5 equiv) was added.

Microwave-induced addition of 5 onto acrylonitrile provided the oxidative addition isomerization product 10 in a high yield (82%, Scheme 3). In the presence of \(\text{Et}_3\text{N}\) under otherwise identical conditions 10 was isolated in 64% along with 12% of carboaminoxylation product 11. TEMPO-acrylonitrile adduct was formed in 12% yield. Obviously, \(\text{Et}_3\text{N}\) retards TEMPOH-elimination. Similar results were obtained for the reaction of 5 with \(N,N\)-dimethylacrylamide. In the amine-free experiment, 12 was obtained in 70% yield along with carboaminoxylation compound 13. As above, the experiment conducted in the presence of \(\text{Et}_3\text{N}\) delivered more of the carboaminoxylation compound. Reaction of 5 with methyl methacrylate gave oxidative addition product 15 in moderate yield as the only regioisomer. In the presence of \(\text{Et}_3\text{N}\), compound 15 was obtained in 49% yield. In addition, olefin 14 was formed in 19% yield. Hence, \(\text{Et}_3\text{N}\) influences the regioselectivity of the TEMPOH-elimination. Reaction with \(\alpha\)-methyl styrene showed no amine effect. The regioisomers 16 and 17 were isolated in 53% or 56% combined yield (without or with \(\text{Et}_3\text{N}\), respectively). Regioselective elimination was obtained for the carboaminoxylation/elimination reaction using styrene. Isomerization of the double bond was not observed. Styrene derivative 18 was isolated in 49% yield using \(\text{Et}_3\text{N}\) as an additive. The amine-free process provided 18 in lower yield (22%).

As expected,\textsuperscript{5,6} addition of 5 to electron rich olefins such as butyl vinyl ether or 1-octene did not work. Zard showed that oxidation of dithiane 2 to the corresponding mono sulfoxide can readily be accomplished. Moreover the oxidized xanthate delivers far more reactive one-carbon-
centered radicals than the parent dithiane. Therefore we prepared alkoxyamine \( \text{19} \) (Scheme 3). \( m \)-Chloroperbenzoic acid treatment of dithiane \( \text{5} \) afforded monosulfoxide \( \text{19} \) as a 5.8:1 mixture of diastereoisomers. The isomers were separated by chromatography. The relative configuration was not assigned. Unfortunately, both isomers of alkoxyamine \( \text{19} \) turned out to be highly unstable under the applied conditions. Attempted carboaminoxylation of \( n \)-butyl acrylate and 1-octene using \( \text{19} \) failed (both isomers were tested).

We have previously shown that the nitroxide structure heavily influences the outcome of nitroxide-mediated radical additions. Based on these results we prepared alkoxyamine \( \text{22} \) from dithiane \( \text{5} \) and nitroxide \( \text{21} \) (Scheme 4). Sterically highly hindered nitroxide \( \text{21} \) was readily prepared from known nitroxide \( \text{20} \).

Alkoxyamine \( \text{22} \) underwent highly efficient thermal addition onto acrylonitrile under conventional heating at 110 °C (Scheme 5). Product \( \text{23} \) was isolated in 92% yield. A lower yield was obtained for the addition of \( \text{22} \) to \( n \)-butyl acrylate (44%). Along with the desired carboaminoxylation product, telomers resulting from renewed addition of \( \text{24} \) onto \( n \)-butyl acrylate were observed (mainly containing 2 or 3 acrylate units). In order to decrease the propensity of telomer formation, reaction was repeated with 1.1 equivalent of acrylate (115 °C). Unfortunately, formation of telomers could not be completely suppressed. Carboaminoxylation product \( \text{24} \) was formed in 57% yield.

Guided by this unwanted side reaction we decided to study controlled carboaminoxylations using adducts \( \text{23} \) and \( \text{24} \). To this end, alkoxyamines \( \text{23} \) and \( \text{24} \) were reacted with \( 1 \)-octene to provide alkoxyamines \( \text{25} \) and \( \text{26} \) in good yields (\( \text{25} \): 40%; \( \text{26} \): 56%).

Moreover, we tested whether alkoxyamine \( \text{5} \) can be used as initiator/regulator for the controlled living radical polymerization of styrene. Polymerization was conducted in a sealed tube using 1% of alkoxyamine initiator \( \text{5} \) at 125 °C and was stopped after 24 hours (neat styrene). The conversion (61%) was determined gravimetrically. The polydispersity index (PDI) and the molecular weight of the polymer were analyzed using SEC (\( \text{Mn} = 6600 \text{ g/mol} \), Scheme 6). The narrow PDI (1.12) obtained indicates that controlled polymerization of styrene occurred. Importantly, the 1,3-dithiane-modified polystyrene should readily be deprotonated using alkyl lithium bases. The corresponding polymeric Li-derivative can then be used to initiate an anionic polymerization. Hence, \( \text{5} \) can be regarded as radical and ionic polymerization initiator. Experiments along this line are under way.

Finally, we studied the kinetics of the C–O bond homolysis for alkoxyamines \( \text{5} \) and \( \text{22} \). The kinetic experiments were conducted in the EPR cavity in \( \text{tert} \)-butylbenzene in the presence of oxygen at 403 K and 373 K for alkoxyamines \( \text{5} \) and \( \text{22} \), respectively. Oxygen was used to scavenge the 3-dithianyl radical and the concentration of the released nitroxide was measured by EPR spectroscopy, as previously described. The activation energies \( E_a \) were estimated from the experimentally determined rate
As expected, the sterically highly hindered alkoxyamine 22 shows a lower activation energy for C–O bond homolysis than TEMPO-derivative 5 ($E_a[5] = 136.9 \text{ kJmol}^{-1}$, $E_a[22] = 127.5 \text{ kJmol}^{-1}$). This is in agreement with the addition experiments where carboximinoxylation could be performed at 90 °C using the efficient alkoxyamine 22 (acylonitrile, 10 h, 58%). For TEMPO-alkoxyamine 5, however, reaction was successful only at higher temperatures (120 °C, see Table 1, runs 2 and 3). At 90 °C no addition product was observed using 5.

In conclusion, we have show that readily prepared 1,3-dithiane derived alkoxyamines can be used as one-carbon radical precursors in radical addition reactions. The nucleophilic 1,3-dithiane-2-yl radical reacts efficiently only with electron-deficient olefins. Depending on the nitroxide used, carboximinoxylation or oxidative addition of the alkoxyamine is obtained. Microwave induced heating can be applied to conduct these reactions in a short time. In addition, dithiane modified polystyrene with a narrow PDI can be prepared using 5 as alkoxyamine initiator/regulator.

1H NMR and 13C NMR spectra were recorded on Bruker AMX-400, ARX-300 or Varian inova-500 spectrometers. TLC as performed by using Merck silica gel coated aluminium 60 F 254 plates; detection with UV or dipping into a solution of KMnO4 (1.5 g in 400 mL H2O, 5 g NaHCO3) or a solution of Ce(SO4)2·H2O (10 g), phosphomolybdic acid hydrate (25 g), concd H2SO4 (60 mL) and H2O (940 mL). Flash column chromatography was performed using Merck silica gel 60 (40–63 um). IR spectra were obtained as a thin film smeared onto NaCl plates on a Bruker IFS-28 spectrometer. Melting points were determined with a hot-stage apparatus. Mass spectra were recorded as ESI–MS on a waters-micromass Quattro LC or a Bruker MicroTof instrument. Elemental analyses were performed on an Elementar vario ELIII Laboratories (pentaene-MTBE, 100:1) afforded 6 (100 mg, 0.406, 72%). Butyl 3-[(2,2,6,6-tetramethyl-1-piperidinyl)oxy]propanoate (7) was obtained as a side product if other conditions were applied (see text). Oxidative Addition Reaction ; General Procedure (GP 1) A solution of 5, olefin and Et3N (in some cases) in degassed DMF (0.07 M) was sealed off under Ar. The mixture was flash heated at 170 °C in a microwave oven for 8–25 min. DMF and excess of olefin were removed in vacuo. The crude product was purified by flash chromatography on silica gel.

**Butyl 3-(1,3-Dithian-2-ylidene)propanoate (6)**

According to GP1, compound 5 (156 mg, 0.567 mmol), n-butyl acrylate (363 mg, 2.836 mmol), Et3N (86 mg, 0.85 mmol) in DMF (8 mL) were employed for 8 min. Flash chromatography (pentane–MTBE, 100:1) afforded 6 (100 mg, 0.406, 72%). Butyl 3-[(2,2,6,6-tetramethyl-1-piperidinyl)oxy]propanoate (7) was obtained as a side product if other conditions were applied (see text).

**Compound 7**

A solution of 5, olefin and Et3N (in some cases) in degassed DMF (0.07 M) was sealed off under Ar. The mixture was flash heated at 170 °C in a microwave oven for 8–25 min. DMF and excess of olefin were removed in vacuo. The crude product was purified by flash chromatography on silica gel.

**Oxidative Addition Reaction ; General Procedure (GP 2)**

A solution of 5, olefin and Et3N (in some cases) in degassed DMF (0.07 M) was sealed off under Ar. The mixture was flash heated at 170 °C in a microwave oven for 8–25 min. DMF and excess of olefin were removed in vacuo. The crude product was purified by flash chromatography on silica gel.

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**Compound 7**

A solution of 5, olefin and Et3N (in some cases) in degassed DMF (0.07 M) was sealed off under Ar. The mixture was flash heated at 170 °C in a microwave oven for 8–25 min. DMF and excess of olefin were removed in vacuo. The crude product was purified by flash chromatography on silica gel.
According to GP 2, compound (13) afforded a non-separable mixture (92 mg) of 3-
{(1,3-Dithian-2-ylidene)propanenitrile (10) and 3-
{(1,3-Dithian-2-ylidene)propanamide (12) as determined by 1H NMR spectroscopy:

**Compound 10**

IR (film): 2975, 2916, 2248, 1678, 1580, 1420, 959 cm⁻¹.

1H NMR (400 MHz, CDCl3): δ = 5.76 (t, J = 7.1 Hz, 1 H, Hvinyl), 3.27 (d, J = 7.1 Hz, 2 H, SCH2), 2.91 (m, 4 H, SCH2), 2.10 (m, 2 H, SCHCH2).

13C NMR (100 MHz, CDCl3): δ = 135.6 (C), 117.1 (C), 116.6 (CH), 29.3 (CH3), 29.0 (CH2), 17.4 (CH3).


Anal. Calcd for C16H28N2OS2: C, 58.49; H, 8.59; N, 8.53. Found: C, 58.12; H, 8.66; N, 8.76.

3-(1,3-Dithian-2-ylidene)propanenitrile (10)

**Compound 11**

IR (film): 2973, 2934, 2873, 1467, 1423, 1259, 1132 cm⁻¹.

1H NMR (400 MHz, CDCl3): δ = 4.91 (t, J = 7.12 Hz, 1 H, OCH), 4.16 (t, J = 6.3 Hz, 1 H, SCH), 2.86 (m, 4 H, SCH2), 2.33 (m, 2 H, SCHCH2), 2.11 (m, 1 H, SCHCH2), 1.90 (m, 1 H, SCHCH2), 1.48 (m, 6 H, NCH2CH2CH3), 1.31 (s, 3 H, CH3), 1.20 (s, 3 H, CH3), 1.10 (s, 3 H, CH3), 1.07 (s, 3 H, CH3).

13C NMR (100 MHz, CDCl3): δ = 113.5 (C), 65.9 (CH), 55.6 (C), 54.5 (C), 36.8 (CH), 34.7 (CH), 34.5 (CH), 33.0 (CH2), 28.6 (CH3), 28.5 (CH2), 24.6 (CH2), 24.5 (CH2), 20.5 (CH3), 15.2 (CH2), 15.1 (CH), 11.7 (CH3).

MS (ESI): m/z 351 [M + Na]⁺.

Anal. Calcd for C10H12N2O2S: C, 56.26; H, 6.63; N, 7.76. Found: C, 56.21; H, 6.61; N, 7.76.

3-(2,2,6,6-Tetramethyl-1-piperidinyl)oxy]propanenitrile

1H NMR (400 MHz, CDCl3): δ = 3.93 (t, J = 6.3 Hz, 2 H, OCH), 2.52 (t, J = 6.3 Hz, 2 H, NCCH2), 1.43 (m, 6 H, CH2CH2CH3), 1.16 (s, 6 H, 2 × CH3), 1.11 (s, 6 H, 2 × CH3).

13C NMR (75 MHz, CDCl3): δ = 37.3 (CH3), 35.5 (CH3), 34.4 (CH2), 30.0 (CH3), 29.5 (CH2), 24.9 (CH).

**Compound 13**

IR (film): 2931, 1651, 1466, 1183, 1120, 909 cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 171.5 (C), 77.2 (CH), 60.6 (C), 59.3 (C), 43.0 (CH), 40.4 (CH2), 37.8 (CH), 36.8 (CH2), 35.8 (CH2), 33.6 (CH2), 32.4 (CH3), 30.0 (CH3), 29.7 (CH2), 25.8 (CH2), 20.2 (CH2), 19.9 (CH), 16.9 (CH3).

MS (ESI): m/z 397 [M + Na]⁺.

Anal. Calcd for C16H28N2O4S2: C, 57.71; H, 9.15; N, 7.48. Found: C, 57.24; H, 8.98; N, 7.27.

Methyl 3-(1,3-Dithian-2-ylidene)-2-methylpropanoate (14)

**Compound 14**

IR (film): 2974, 2933, 1735, 1453, 1433, 1168, 1143 cm⁻¹.

1H NMR (400 MHz, CDCl3): δ = 5.92 (d, J = 9.2 Hz, 1 H, Hvinyl), 3.67 (s, 3 H, OCH3), 2.89 (m, 5 H, CH2CH2CH2S), 2.15 (m, 2 H, SCHCH2), 1.24 (d, J = 7.1 Hz, 3 H, CH3).

13C NMR (75 MHz, CDCl3): δ = 174.2 (C), 130.6 (CH), 129.3 (C), 51.8 (CH3), 39.9 (CH3), 29.8 (CH2), 29.1 (CH3), 24.8 (CH2), 17.4 (CH3).


13Dithiane-Derived Alkoxyamines as One-Carbon Radical Precursors
Compounds 16 and 17

IR (film): 3055, 3027, 2932, 2898, 2827, 1494, 1444, 763 cm⁻¹.

Compounds 16 and 17

IR (film): 3002, 2971, 2931, 2871, 1469, 1426, 1365, 1065, 879 cm⁻¹.

IR (film): 2966, 2881, 2819, 1463, 1382, 1099, 808 cm⁻¹.

IR (film): 2962, 2880, 2818, 1463, 1382, 1099, 808 cm⁻¹.


Anal. Calcd for C₁₉H₂₃NO₂S₂: C, 53.57; H, 6.85; N, 4.81. Found: C, 53.21; H, 8.47; N, 4.60.

Compounds 19a, 19b


Anal. Calcd for C₁₉H₂₃NO₂S₂: C, 53.57; H, 6.85; N, 4.81. Found: C, 53.21; H, 8.47; N, 4.60.

Compounds 20, 21

EPR: g = 2.006; aₓᵧ = 14.25 G.

IR (film): 2966, 2881, 2819, 1463, 1382, 1099, 808 cm⁻¹.

MS (ESI): m/z = 265 [M + Na]+.
A solution of vinyl]oxy]propanenitrile (23) (484 mg, 2.0 mmol) in anhyd dimethoxyethane was added at –35 °C under Ar. After 45 min of stirring, a solution of nitroxide 22 (197 mg, 0.545 mmol) and 1-octene (27 mg, 0.242 mmol) in degassed dichloroethane (48 μL, 1 M) was sealed off under Ar. The mixture was heated at 135 °C in an oil bath for 24 h and was then allowed to cool to r.t. The solvent and excess of 1-octene were removed in vacuo. The residue was purified by flash chromatography (pentane–MTBE, 98:2) to afford 24 (20 mg, 0.041 mmol, 57%).

Compound 24

IR (film): 2959, 2878, 2816, 1738, 1464, 1167, 1098, 990 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 4.42 (dd, J₁ = 10.0 Hz, J₂ = 4.3 Hz, 1 H, COCH), 4.11 (m, 2 H, OCH₂), 3.84 (dd, J₁ = 4.1 Hz, J₂ = 10.2 Hz, 1 H, SCH), 3.35 (m, 1 H, MeOCH₃), 3.31 (s, 3 H, OCH₃), 2.82 (m, 4 H, SCH₂), 2.29 (m, 1 H), 2.19–1.97 (m, 2 H), 1.91–1.20 (m, 17 H), 1.00 (t, J = 7.3 Hz, 3 H, CH₃), 0.94 (t, J = 7.4 Hz, 3 H, CH₃), 0.90–0.82 (m, 9 H, CH₃).

13C NMR (75 MHz, CDCl₃): δ = 172.6 (C), 80.8 (CH), 71.1 (CH), 66.1 (CH), 66.5 (C), 64.6 (CH), 55.7 (CH), 42.3 (CH), 38.9 (CH), 36.2 (CH), 36.1 (CH), 30.6 (CH), 30.4 (CH), 30.3 (CH), 30.0 (CH), 29.9 (CH), 27.5 (CH), 27.2 (CH), 25.6 (CH), 19.2 (CH), 13.7 (2 × CH₂), 10.0 (CH₃), 8.1 (2 × CH₂).


2-(1,3-Dithian-2-ylmethyl)-4-[(2,2,6,6-tetraethyl-4-methoxy-1-piperidinyl]oxy]decanenitrile (25)

A solution of 23 (20 mg, 0.048 mmol) and 1-octene (27 mg, 0.242 mmol) in degassed dichloroethane (48 μL, 1 M) was sealed off under Ar. The mixture was heated at 135 °C in an oil bath for 24 h and was then allowed to cool to r.t. The solvent and excess of 1-octene were removed in vacuo. The residue was purified by flash chromatography (pentane–MTBE, 98:2) to afford 25 (10 mg, 0.019 mmol, 40%).

Compound 25 (Both Isomers)

IR (film): 2963, 2878, 2817, 2239, 1462, 1378, 1098 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 4.19 (m, 1 H, NOCH), 3.80 (m, 1 H, SCH), 3.37 (m, 1 H, MeOCH₃), 3.32 (s, 3 H, OCH₃), 2.92 (m, 1 H, CHC₆H₄), 2.86 (m, 4 H, SCH₂), 2.17–1.18 (m, 28 H), 0.97–0.78 (m, 15 H, 4 × CH₂, OCH₃).

13C NMR (500 MHz, CDCl₃): δ = 121.4 (C), 121.1 (C), 78.6 (CH), 78.4 (CH), 71.3 (CH), 65.8 (C), 65.7 (C), 55.5 (CH), 55.3 (CH), 44.4 (CH), 44.3 (CH), 38.3 (CH), 38.3 (CH), 37.2 (CH), 37.0 (CH), 36.8 (CH), 36.7 (CH), 35.4 (CH), 33.1 (CH), 32.3 (CH), 31.8 (CH), 31.7 (CH), 30.9 (CH), 30.9 (CH), 30.7 (CH), 30.6 (CH), 30.4 (CH), 30.2 (CH), 30.1 (CH), 29.8 (CH), 29.7 (CH), 29.6 (CH), 29.5 (CH), 29.3 (CH), 29.2 (CH), 26.2 (CH), 25.8 (CH), 25.8 (CH), 25.7 (CH), 25.3 (CH), 25.0 (CH), 22.6 (CH), 14.0 (CH), 10.2 (CH), 8.9 (CH), 8.7 (CH), 8.2 (CH), 7.6 (CH).


Butyl 2-(1,3-Dithian-2-ylmethyl)-4-[(2,2,6,6-tetraethyl-4-methoxy-1-piperidinyl]oxy]propanoate (24)

A solution of 24 (13 mg, 0.0266 mmol) and 1-octene (15 mg, 0.133 mmol) in degassed dichloroethane (27 μL, 1 M) was sealed off under Ar. The mixture was heated at 115 °C in an oil bath for 9.5 h and was then allowed to cool to r.t. The solvent and excess of n-butyl acrylate were removed in vacuo. The residue was purified by flash chromatography (pentane–MTBE, 98:2) to afford 26 (9 mg, 0.015 mmol, 56%).

Compound 26 (Both Isomers)

IR (film): 2958, 2926, 2877, 1731, 1464, 1378, 1158, 1066 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 4.07 (m, 2 H, OCH₂, NOCH), 3.96 (dd, J₁ = 8.4, 6.2 Hz, 2 H, OCH₂), 3.62 (m, 1 H, SCH), 3.36 (m, 1 H, MeOCH₃), 3.32 (s, 3 H, OCH₃), 2.86 (m, 1 H, COCH), 2.81 (m, 4 H, SCH₂), 2.16–1.17 (m, 32 H, 0.96–0.85 (m, 18 H, CH₃).

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$^{13}$C NMR (500 MHz, CDCl$_3$): δ = 175.4 (C), 175.2 (C), 79.2 (CH), 78.8 (CH), 71.1 (CH), 65.9 (C), 65.7 (C), 65.3 (C), 64.4 (CH), 64.4 (CH), 55.7 (C), 45.1 (CH), 45.0 (CH), 39.8 (CH), 39.6 (CH), 38.3 (CH), 36.9 (CH), 36.8 (CH), 36.5 (CH), 36.0 (CH), 33.0 (CH), 32.2 (CH), 31.9 (CH), 31.8 (CH), 30.9 (CH), 30.7 (CH), 30.5 (CH), 30.3 (CH), 30.0 (CH), 30.0 (CH), 29.9 (CH), 29.7 (CH), 29.6 (CH), 25.9 (CH), 25.9 (CH), 24.5 (CH), 22.6 (CH), 19.2 (CH), 14.1 (CH), 13.7 (CH), 10.5 (CH), 10.2 (CH), 8.8 (CH), 8.6 (CH), 8.2 (CH), 8.0 (CH).

HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{33}$H$_{64}$NO$_4$S$_2$: 602.4277; found: 602.4273.

Polymerization of Styrene with Alkoxyamine (5)

A Schlenk tube was charged with alkoxyamine initiator 5 (72 mg, 0.262 mmol) and styrene (3 mL, 26.21 mmol). The tube was subjected to three freeze-thaw cycles and sealed off under Ar. The polymerization was carried out under Ar at 125 °C for 24 h. The resulting mixture was cooled to r.t., dissolved in CH$_2$Cl$_2$, and poured into a glass dish, and the residual monomer was removed in a vacuum-drying cabinet at 60 °C for 12 h. The conversion was evaluated gravimetrically (1.667 g, 61%), the experimental number-average molecular weight ($M_n$,exp) = 6600 gmol$^{-1}$, and PDI = 1.12 were determined by SEC.

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References

(2) Gröbel, B. T.; Seebach, D. Synthesis 1977, 357.
(15) The microwave experiments were conducted using professional laboratory microwave equipment. A MLS-Ethos 1600 Mikrowellen System (Milestone) was used for the present studies. The reactions were run in 40 mL MLS-reaction high-pressure vessels (up to 15 bars), which contain pressure control valves. An advanced temperature control system from MLS allowing direct contactless temperature monitoring was used. The microwave power is continuously and dynamically adjusted to follow the defined temperature profile.
(20) This compound decomposes in the absence of solvents, upon exposure to air.