Fully degradable polymer networks from conventional radical polymerization of vinyl monomers enabled by thionolactone addition

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Abstract: We report the preparation of degradable polymer networks by conventional free radical copolymerization of n-butyl acrylate with a crosslinker (1 mol%) and dibenzo[c,e]oxepane-5-thione (DOT) as a strand-cleaving comonomer. Addition of only 4 mol% of DOT imparts the synthesized networks with full degradability by aminolysis, whereas gels with less DOT (2-3 mol%) cannot be degraded, in excellent agreement with the recently proposed reverse gel-point model. Importantly, even though DOT significantly slows down the polymerization and delays gelation, it has a minimal effect on physical properties of the networks such as shear storage modulus, equilibrium swelling ratio, glass transition temperature or thermal stability.
Annual global production of polymers approaches 400 Mt, of which crosslinked networks such as thermosets, rubbers or (hydro)gels constitute around 18%. These numbers are also responsible for the growing problem of plastic waste which has triggered the search for more sustainable alternatives. Ideally, such polymers could preserve their unique physical properties, such as elasticity, mechanical strength, or thermal and chemical resistance while being able to degrade or depolymerize on demand.

Designing recyclable thermosets is particularly challenging as their crosslinked nature prevents processing in solution or melt. The main strategy to degradable networks involves introduction of labile bonds, e.g. esters or disulfides, that can be selectively cleaved by physical or chemical stimuli. In the last decade, further advances in this field led to the development of vitrimers or covalent adaptive networks, which can be reshaped and reprocessed by reversible, dynamic covalent bonds.

However, around 45% of all polymers are synthesized by free radical polymerization (FRP) of vinyl monomers. Unfortunately, networks prepared by FRP are almost exclusively non-degradable, even if cleavable crosslinkers with labile bonds are employed. This is due to the mechanism of gelation in FRP which involves rapid formation of polymers with very high molecular weights, leading to microgelation and a highly clustered, heterogeneous internal structure of the network.

Reversible deactivation radical polymerization (RDRP) techniques can overcome this problem as they afford more homogeneous networks thanks to the linear growth of well-defined, uniform chains. Indeed, copolymerization of vinyl monomers with crosslinkers containing degradable or reversible bonds by RDRP can impart the resulting networks with degradability or vitrimer-like properties. Konkolewicz, Matyjaszewski et al. compared polyacrylate gels synthesized using a degradable disulfide diacylate crosslinker by
RDRP and FRP, and noticed that while the former could be degraded, the latter could not.\textsuperscript{17} However, using RDRP is not always feasible, especially in industrial settings, making fully degradable networks synthesized by FRP highly desirable.

Furthermore, Johnson \textit{et al.} recently proposed a reverse gel-point model, which suggests that cleavable moieties should be installed in the backbone of the network primary chains (strands) rather than in the crosslinks, in order to render it degradable at low co-monomer loadings.\textsuperscript{24} They demonstrated that crosslinked polydicyclopentadiene synthesized by ring-opening metathesis polymerization underwent a complete degradation after addition of only 10 mol\% of a silyl ether-based, cleavable comonomer.\textsuperscript{24-26}

In the case of vinyl polymers, degradable bonds can be installed in the backbone by radical ring-opening polymerization (RROP) of cyclic monomers such as cyclic ketene acetals or allyl sulfide lactones.\textsuperscript{27-31} Thionolactones, such as dibenzo[c,e]oxepane-5-thione (DOT) have been recently presented as a degradable comonomer which undergo RROP with acrylates, acrylamides, acrylonitrile,\textsuperscript{32-35} as well as vinyl esters,\textsuperscript{36} styrene and methacrylates.\textsuperscript{37, 38} DOT is compatible with both FRP and RDRP and affords degradation via cleavage of the backbone thioester by e.g. primary amines, strong bases or thiols. Very recently, Guillaneuf \textit{et al.} used DOT in crosslinked systems and reported that a 3D-printed poly(pentaerythritol triacrylate)\textsuperscript{39} and a poly(styrene-co-divinylbenzene)\textsuperscript{38} both underwent degradation with 2 wt\% and 5 mol\% of DOT, respectively.

Herein we investigate the effect of the DOT loading on the properties and degradability of model networks/gels based on crosslinked poly($n$-butyl acrylate). We copolymerized $n$-butyl acrylate ($n$-BA) with 1 mol\% of a crosslinker (1,6-hexanediol diacrylate, HDDA) in anisole (1:1 v/v), with the addition of 0-10 mol\% of DOT (referred to as PBA-DOTx). The reaction
was initiated by azobisisobutyronitrile (AIBN) and conducted under nitrogen at 65 °C for 24 h (Scheme 1).

Scheme 1. Synthesis of PBA-DOT networks by FRP and their degradation by aminolysis of the thioester bonds located in the primary chains.

The effect of the DOT addition was immediately evident, with the onset of gelation increasing from c.a. 2 min for polymerization without the DOT (PBA) to 135 min for PBA-DOT8 (Table 1). Interestingly, PBA-DOT10 did not gel in 24 h; such a behavior suggests either retardation, reported before in copolymerizations with DOT,\textsuperscript{32} or chain transfer.\textsuperscript{40}
which could lead to delayed, or even avoided gelation and formation of soluble branched polymers in a so-called ‘Strathclyde route’.

To gain more insight into this observation we analyzed copolymerization kinetics of \( n\)-BA with 0, 2 and 6 mol\% of DOT without the addition of the crosslinker (Figure S1a in Supporting Information). PBA reached 22 \% conversion in 10 minutes, compared to 11 \% for PBA-DOT2 and 5 \% for PBA-DOT6. After 90 minutes, both PBA and PBA-DOT2 reached similar conversions (64 \% and 62 \%, respectively). By that time DOT was no longer visible in the NMR spectrum of PBA-DOT2 (Figure S2). In the case of PBA-DOT6, conversion of \( n\)-BA increased to only 10 \% in 90 min and reached 23 \% in 180 min, whereas DOT was consumed at roughly double that rate. This confirms retardation of \( n\)-BA polymerization in the presence of DOT as well as faster incorporation of DOT than the acrylate in the polymer, in line with previous reports.

Table 1. Summary of properties and degradation ability of the PBA-DOT networks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOT mol %</th>
<th>Gelation time (min)(^{a})</th>
<th>Gel Fraction (%)(^{b})</th>
<th>Equilibrium Swelling Ratio(^{c})</th>
<th>( T_g ) (°C)</th>
<th>Degradation temperature (°C)(^{d})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA</td>
<td>0</td>
<td>2</td>
<td>97 ± 0.4</td>
<td>7.64 ± 0.22</td>
<td>-45.7</td>
<td>333</td>
</tr>
<tr>
<td>PBA-DOT2</td>
<td>2</td>
<td>30</td>
<td>94 ± 3.1</td>
<td>6.61 ± 0.21</td>
<td>-40.1</td>
<td>349</td>
</tr>
<tr>
<td>PBA-DOT4</td>
<td>4</td>
<td>50</td>
<td>93 ± 0.7</td>
<td>6.41 ± 0.40</td>
<td>-40.6</td>
<td>345</td>
</tr>
<tr>
<td>PBA-DOT6</td>
<td>6</td>
<td>100</td>
<td>90 ± 0.8</td>
<td>8.29 ± 0.21</td>
<td>-37.4</td>
<td>345</td>
</tr>
<tr>
<td>PBA-DOT8</td>
<td>8</td>
<td>135</td>
<td>88 ± 2.3</td>
<td>7.05 ± 0.33</td>
<td>-38.1</td>
<td>346</td>
</tr>
<tr>
<td>PBA-DOT10</td>
<td>10</td>
<td>no gelation in 24 h</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{a}\) defined as the moment when reaction mixture lost mobility upon vial inversion; all reactions were conducted for 24 h; \(^{b}\) average value from three measurements for different parts of a gel, determined by weighing a dried gel and solids extracted from the gel upon washing in THF (sol); \(^{c}\) %GF = \( \frac{m_{gel}}{m_{gel} + m_{sol}} \) × 100 \%; \(^{d}\) temperature at 5 \% mass loss recorded by TGA.

Additionally, gel permeation chromatography (GPC) showed little variation of the molecular weight (MW) with time for each polymerization, as expected in FRP, but a clear shift
towards much lower MWs ($M_n$,$\text{GPC} > 650$ kDa for PBA and 50-80 kDa for PBA-DOT6) as well as higher dispersities ($D = 3.8–5.9$) with increased DOT content (Figure S1b). A similar broad peak was also observed in the non-gelled PBA-DOT10 (Figure S3), which does include some branching due to the presence of HDDA. Overall, the addition of DOT leads to both slower reaction and lower MW resulting in delayed gelation, which can be caused either by retardation alone or by simultaneous retardation and chain transfer.\textsuperscript{45} The detailed mechanism of this phenomenon is beyond the scope of the current communication and will be investigated separately.

Nonetheless, polymerization conditions with 0-8 mol% DOT produced well-developed gels (Figure S4). Reactions with DOT changed color from deep to pale yellow, indicative of incorporation of DOT via RROP.\textsuperscript{33} This color remained in the final gels, but disappeared after extensive washing with THF, suggesting little unreacted DOT (Figure S5). To confirm efficient incorporation of copolymer chains in the network, the gel fraction of each sample was determined by multiple washings in THF and weighing the remaining extracted solids. As shown in Table 1, gel fractions for all samples were very high, between 88-97 %, with minimally lower values recorded for samples with more DOT.

The internal structure of the PBA-DOT networks was investigated by means of swelling analysis and rheological measurements. Both methods can be used to estimate the average molecular weight between crosslinks (i.e., the crosslinking density) based on the affine network elasticity model.\textsuperscript{46} Figure 1a shows shear storage moduli (G’) measured by oscillatory rheology for 2.5 mm thick gel disks directly after synthesis. All networks showed a constant modulus within the frequency range of 0.1 to 100 rad/s, typical for covalently crosslinked polymers. Virtually no difference in modulus between samples with various DOT loadings was observed suggesting a similar crosslinking density. This was further corroborated by measuring the equilibrium swelling ratios (ESR) of the dried networks in
THF. All samples swelled by c.a. 6-7 times in 48 h, with only **PBA-DOT6** showing a slightly higher ESR of 8.29 (Figure 1b).

The increased DOT content in the networks also had a minor effect on their thermal properties. Glass transition temperature ($T_g$) determined by differential scanning calorimetry (DSC) increased only slightly from −45.7 °C for PBA to −37.4 °C for **PBA-DOT6** (Figure 1c). Moreover, incorporation of DOT increased the onset of thermal decomposition measured by thermogravimetry (TGA) from 333 to 345-349 °C (Figure 1d). Both are consistent with introduction of rigid phenyl rings in the polymer backbone. Overall, these measurements confirm that despite different polymerization kinetics in the presence of DOT, all networks have a similar structure. Importantly, PBA-DOT networks do not exhibit deteriorated mechanical properties or thermal stability and behave nearly identically as the standard, non-degradable PBA gels.
Figure 1. Characterization of the PBA-DOT networks; (a) shear storage moduli of as-synthesized gel disks determined by oscillatory rheology; (b) equilibrium swelling ratio of dried gels in THF; (c) DSC thermograms; (d) thermogravimetric curves.

Degradation of the PBA-DOT networks was then studied by stirring a fragment of a dried gel (5-50 mg) in a 5.8 M solution of isopropylamine in THF for 24 h based on our previous work.\textsuperscript{32, 34} Whereas PBA, PBA-DOT2 and PBA-DOT3 gels were still present in the vial (Figure S6), samples with 4-8 mol% of DOT fully dissolved, suggesting 4 mol% DOT as a threshold for full degradation. The remaining solids were weighed and revealed that while essentially no mass loss was recorded for PBA, PBA-DOT2 lost 27% ± 8.7 and PBA-DOT3
34% ± 23.5 of their weight, consistent with more cleavable sites in the chains (Table 2). The large error in PBA-DOT3 resulted from some sections of the gels undergoing almost complete dissolution, while others remaining largely intact, pointing to uneven distribution of the DOT due to its faster incorporation in the copolymer as earlier confirmed by the kinetic analysis (Fig. S1). The resulting post-degradation solutions could pass through a 0.45 μm syringe filter and were analyzed by GPC (Figure 2) and 1H NMR (Figure S7). While no dissolved polymer was observed for PBA, partial degradation PBA-DOT2 and PBA-DOT3 did occur and peaks with $M_n,_{GPC} = 4270$ Da and 5100 Da, respectively, were recorded by GPC. Interestingly, PBA-DOT4 showed a similar peak ($M_n,_{GPC} = 4260$), but with an extensive tailing in the high MW region characteristic of branched structures, suggesting that long, non-degraded fragments were still present in the network; however, this was already enough to make the degraded gel fully soluble. PBA-DOT6 and PBA-DOT8 showed better defined GPC peaks, with decreasing MW ($M_n,_{GPC} = 3160 \rightarrow 2280$ Da) and dispersities ($D = 5.48 \rightarrow 4.79$). This suggests that a more regular distribution of the DOT units at higher loadings results in more uniform degradation products. In a control experiment, all samples remained intact after stirring in pure THF for 24 h.

### Table 2. Summary of degradation analysis of PBA-DOT networks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOT mol%</th>
<th>Macroscopic degradation</th>
<th>Mass loss upon degradation (%)</th>
<th>$M_n$ of degraded fragments (Da)</th>
<th>$D$ of degraded fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA</td>
<td>0</td>
<td>No</td>
<td>2.4 ± 2.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PBA-DOT2</td>
<td>2</td>
<td>No</td>
<td>27.0 ± 8.7</td>
<td>4270</td>
<td>5.48</td>
</tr>
<tr>
<td>PBA-DOT3</td>
<td>3</td>
<td>No</td>
<td>34.2 ± 23.5</td>
<td>5100</td>
<td>8.11</td>
</tr>
<tr>
<td>PBA-DOT4</td>
<td>4</td>
<td>Yes</td>
<td>100</td>
<td>4260</td>
<td>41.2</td>
</tr>
<tr>
<td>PBA-DOT6</td>
<td>6</td>
<td>Yes</td>
<td>100</td>
<td>3160</td>
<td>5.33</td>
</tr>
<tr>
<td>PBA-DOT8</td>
<td>8</td>
<td>Yes</td>
<td>100</td>
<td>2280</td>
<td>4.79</td>
</tr>
</tbody>
</table>
*degradation in 5.8 M isopropylamine solution in THF for 24 h followed visually;  ‖ measured gravimetrically after drying the remaining solids post-degradation, an average value from at least five measurements; when full macroscopic degradation was observed, the mass loss was assumed to be 100%; ‖ measured by GPC.

Figure 2. GPC traces of PBA-DOT network fragments after degradation in 5.8 M isopropylamine in THF for 24 h. PBA, PBA-DOT2 and PBA-DOT3 did not macroscopically degrade.

Furthermore, according to the reverse gel-point model proposed by Johnson et al., 24 degradation of a network should occur if the average number of degradable units $x$ in the primary chain is:

$$x > \frac{c(Df - 1) - f}{c + f} \quad (1)$$
Where \( c \) is the number of crosslinks, \( f \) is the number of repeating units in the primary chain and \( D \) is the dispersity of the degradation fragments. If \( f >> c \) as is typical for radical polymerization (for our conditions \( f = 100c \), i.e., 1 mol\% of crosslinker), equation 1 can be simplified to \( x > Dc \). For the most probable distribution (\( D = 2 \)), this condition is then \( x > 2c \). However, based on the GPC data, \( D \) of fully degraded fragments in the PBA-DOT system is between 4 and 5, and thus the degradation would occur at \( x > 4-5c \). This is remarkably close to what we observe; namely, networks containing 2 and 3 mol\% of DOT (\( x = 2c \) and \( 3c \)) could not be fully degraded but increasing the DOT content to 4 mol\% (\( x = 4c \)) lead to complete dissolution. Indeed, the significant tailing in the PBA-DOT4 chromatogram suggests that this sample is very near the degradation threshold, whereas higher DOT loadings allow facile degradation to smaller soluble fragments.

These results seem to be also in line with the very recent reports of Guillaneuf et al. who showed degradation of a crosslinked polystyrene with 5 mol\% DOT and 1 mol\% of crosslinker,\(^{38}\) as well as a 3D-printed poly(pentaerythritol triacrylate)-based resin at even lower DOT loading, i.e., 2 wt\% (corresponding to 3.1 mol\%),\(^{39}\) although detailed comparison is not possible as these works only used one DOT loading. We note however, that homopolymerization of a multivinyl monomer will inevitably lead to a large extent of intramolecular cyclization reactions.\(^{18,19}\) This reduces the number of effective crosslinks and allows degradation at a lower \( x \) than predicted by the theory, which assumes no intramolecular cyclization.\(^{24}\) In our system, given the relatively low crosslinker content and high initial monomer concentration (3.47 M), intramolecular cyclization should not significantly influence degradability of the PBA-DOT networks. However, the reverse gel-model also assumes a completely random distribution of the cleavable comonomers in the strands while our kinetic data suggest faster consumption of the DOT than the acrylate. Thus, the exact correlation between the DOT loading and degradability is likely more complex and
will require further investigation. Nevertheless, despite the deviation from ideal copolymerization, a 4:1 molar ratio of DOT to crosslinker allows for complete degradation of the PBA-DOT networks. These results demonstrate a straightforward path to fully degradable polymer networks using commodity monomers and industry-relevant conditions, without compromising their physical properties.

**Supporting Information**

Experimental details, kinetic measurements, additional GPC traces, $^1$H NMR spectra and digital images of the gels.

**Acknowledgments**

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**References**


For Table of Contents Only