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 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 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 %.[1, 2] These numbers are also responsible for the growing problem of plastic waste which has triggered the ongoing 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.[3-5]

Designing recyclable thermosets is particularly challenging as their crosslinked nature prevents processing in solution or melt.[6] 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.[2, 6-8] 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 .[9-13]

However, around 45 % of all polymers are synthesized by free radical polymerization (FRP) of vinyl monomers.[14] Unfortunately, networks prepared by FRP are almost exclusively non-degradable, even if cleavable crosslinkers with labile bonds are employed.[15-17] 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.[18-20]

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.[18, 20] Indeed, copolymerization of vinyl monomers with crosslinkers containing degradable or reversible bonds by RDRP can impart the resulting networks with degradability[16, 17, 21] or vitrimer-like properties.[22, 23] Konkolewicz, Matyjaszewski *et al.* compared polyacrylate gels synthesized using a degradable disulfide diacrylate crosslinker by

RDRP and FRP, and noticed that while the former could be degraded, the latter could not.[17] However, using RDRP is not always feasible, especially in industrial settings, making fully degradable networks synthesized by FRP highly desirable.

Furthermore, Johnson *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.[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.[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.[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,[32-35] as well as vinyl esters,[36] styrene and methacrylates.[37, 38] DOT is compatible with both FRP and RDRP and affords degradation via cleavage of the backbone thioester. Very recently, Guillaneuf *et al.* used DOT in crosslinked systems and reported that a 3D-printed poly(pentaerythritol triacrylate)[39] and a poly(styrene-*co*-divinylbenzene)[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 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.
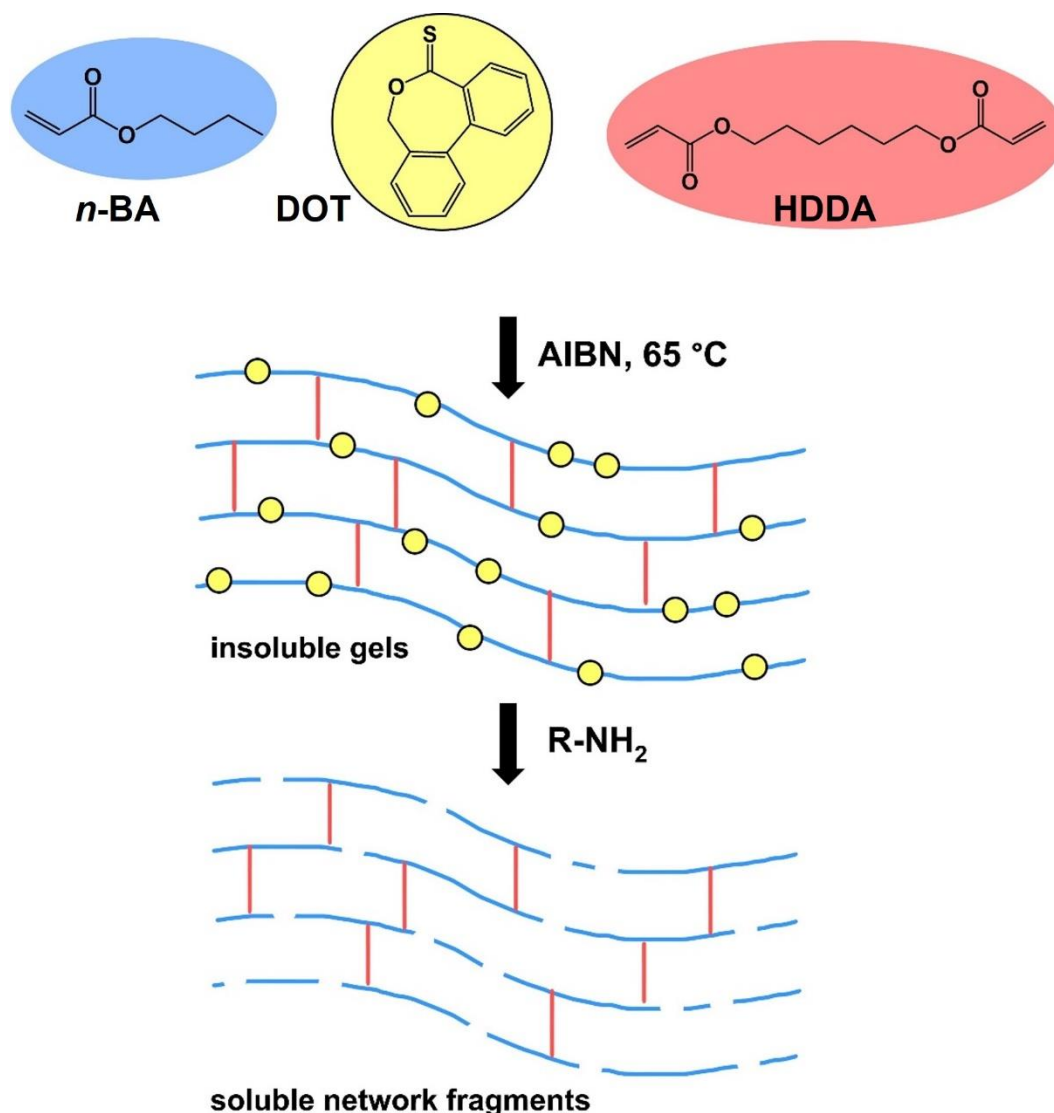
The effect of the DOT addition was immediately evident, with the onset of gelation increasing from c.a. 2 min for polymerization without the DOT (**PBA**) to 135 min for **PBA-DOT8** (**Table 1**). Interestingly, **PBA-DOT10** did not gel in 24 h; such a behavior suggests either retardation, reported before in copolymerizations with DOT,[32] or chain transfer,[40] which could lead to delayed, or even avoided gelation and formation of soluble branched polymers via the so-called 'Strathclyde route'.[41-44] Both of these mechanisms could also occur simultaneously.

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.[32, 33]

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

Sample	DOT mol %	Gelation time (min)[a]	Gel Fraction (%)[b]	Equilibrium Swelling Ratio[c]	T_g (°C)	Degradation temperature (°C)[d]	Degradation with R-NH$_2$[e]
PBA	0	2	97 ± 0.4	7.64 ± 0.22	-45.7	333	no
PBA-DOT2	2	30	94 ± 3.1	6.61 ± 0.21	-40.1	349	no
PBA-DOT4	4	50	93 ± 0.7	6.41 ± 0.40	-40.6	345	yes
PBA-DOT6	6	100	90 ± 0.8	8.29 ± 0.21	-37.4	345	yes
PBA-DOT8	8	135	88 ± 2.3	7.05 ± 0.33	-38.1	346	yes
PBA-DOT10	10	no gelation in 24 h	-	-	-	-	yes

[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); %GF = m$_{gel}$/(m$_{gel}$ + m$_{sol}$) × 100 %; [c] average value from three measurements, determined gravimetrically by swelling in excess THF for 48 h; [d] temperature at 5 % mass loss recorded by TGA; [e] degradation in 5.8 M isopropylamine solution in THF for 24 h.

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 ($M_{n,GPC} > 650$ kDa for **PBA** and 50-80 kDa for **PBA-DOT6**) as well as higher dispersities ($Đ = 3.8–5.9$) 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.[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.[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.[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.
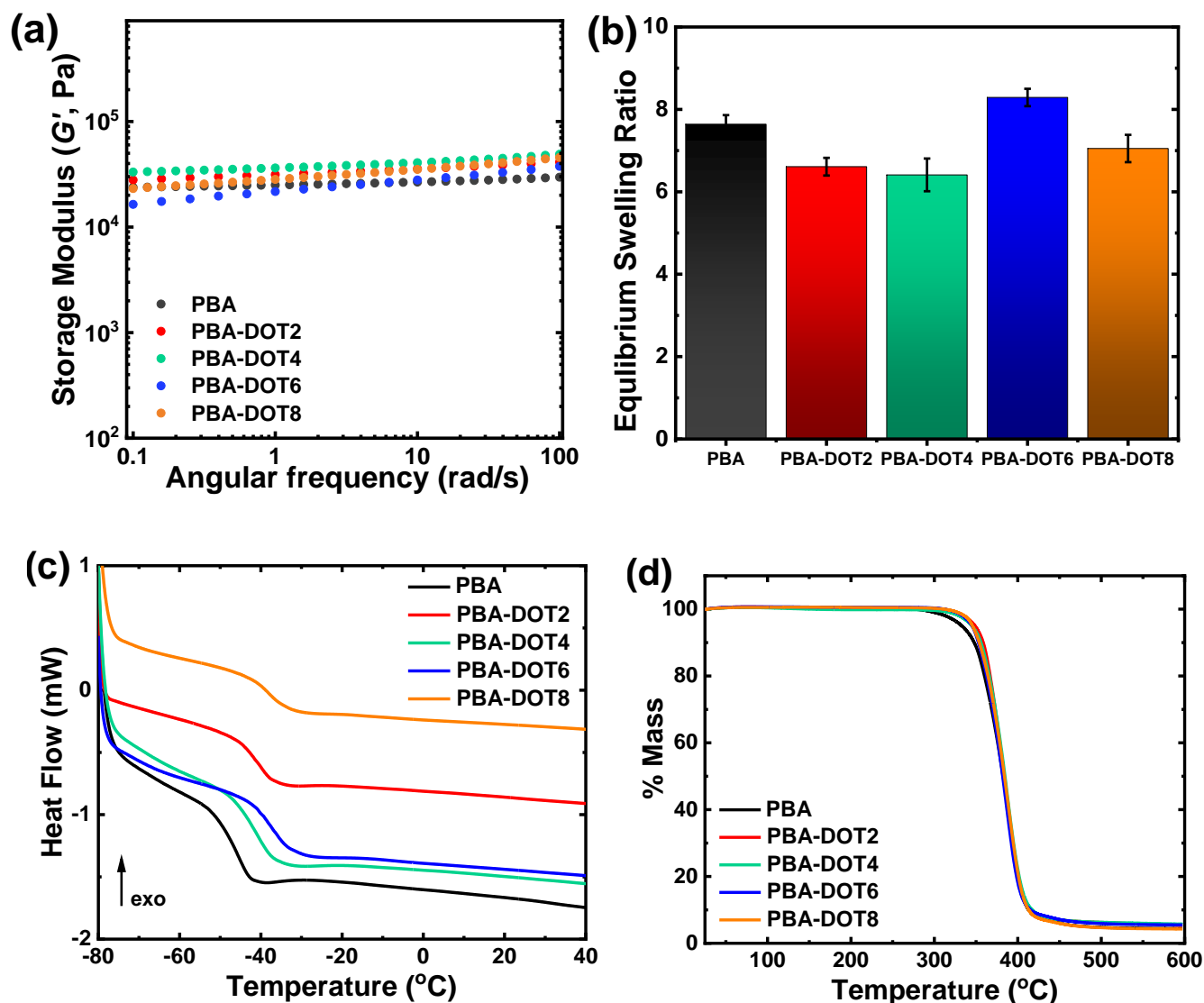
Figure 1. Characterization of the PBA-DOT networks; (a) shear storage moduli of as-synthesized gel disks determined by oscillatory rheology; (b) equilibrium swelling ratio of dried gels in THF; (c) DSC thermograms; (d) thermogravimetric curves.

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.[32, 34] Whereas **PBA** and **PBA-DOT2** gels were still present in the vial (**Figure S6**), samples with 4-8 mol% of DOT fully dissolved. The resulting solutions could pass through a 0.45 µm syringe filter and were analyzed by GPC (**Figure 2**) and ^{1}H NMR (**Figure S7**). While **PBA** showed no sign of degradation, **PBA-DOT2** did partially degrade and a peak with $M_{n, GPC}$ = 4270 Da was

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, pointing out to uneven distribution of the DOT due to its faster incorporation in the copolymer; however, this was already enough to make the degraded network fully soluble. **PBA-DOT6** and **PBA-DOT8** showed better defined GPC peaks, with decreasing MW ($M_{n, GPC}$ = 3160→2280 Da) and dispersities ($Đ$ = 5.48→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.
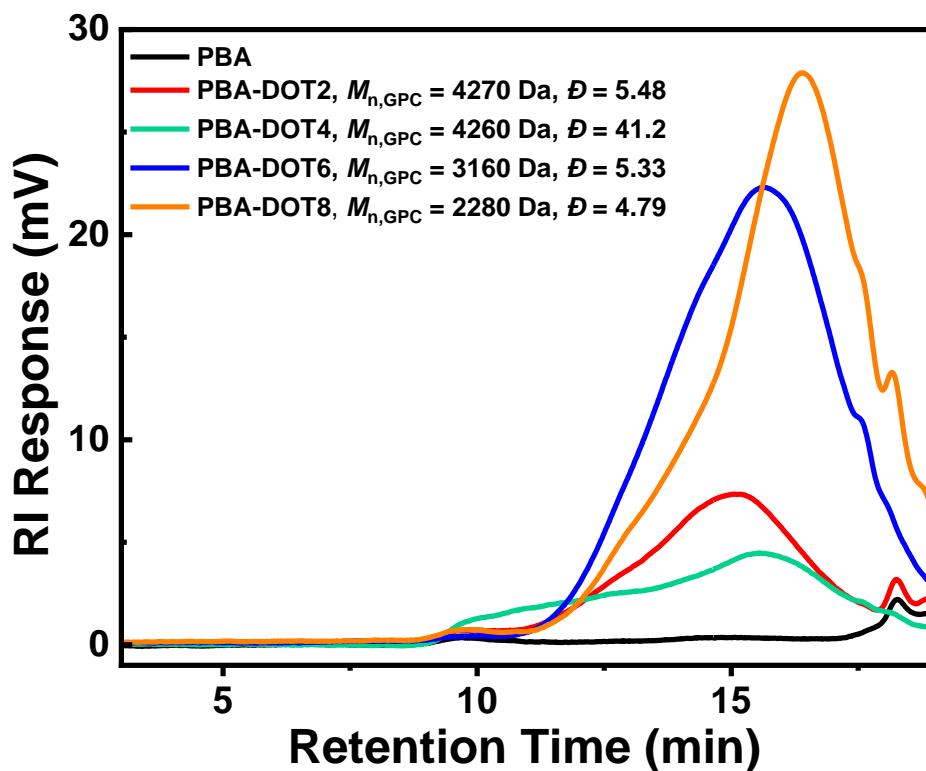
Figure 2. GPC traces of PBA-DOT network fragments after degradation in 5.8 M isopropylamine in THF for 24 h. **PBA** and **PBA-DOT2** did not macroscopically degrade.

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:

$$x > \frac{c(2f-1)-f}{c+f} \qquad (1)$$

Where c is the number of crosslinks and f is the number of repeating units in the primary chain. If $f \gg c$ as is typical for radical polymerization (for our conditions $f = 100c$, i.e., 1 mol% of crosslinker), equation 1 can be simplified to $x > 2c$. Remarkably, our experimental results are in excellent agreement with the theory; namely, network containing 2 mol% of DOT ($x = 2c$) could not be fully degraded but increasing the DOT content to 4 mol% ($x = 4c$) lead to full dissolution. This is 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] 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 the most probable distribution of the primary chains ($Đ = 2$), and completely random distribution of the cleavable comonomers in the strands. Our kinetic data suggest higher $Đ$ in the presence of DOT and 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. However, despite the deviation from

ideal copolymerization, 4 mol% of DOT allows for complete degradation of the 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

References

1.   Geyer, R.; Jambeck Jenna, R.; Law Kara, L., Production, use, and fate of all plastics ever made. *Sci. Adv.* **2017,** *3* (7), e1700782.
2.   Ma, S.; Webster, D. C., Degradable thermosets based on labile bonds or linkages: A review. *Prog. Polym. Sci.* **2018,** *76*, 65-110.
3.   Coates, G. W.; Getzler, Y. D. Y. L., Chemical recycling to monomer for an ideal, circular polymer economy. *Nat. Rev. Mater.* **2020,** *5* (7), 501-516.
4.   Fagnani, D. E.; Tami, J. L.; Copley, G.; Clemons, M. N.; Getzler, Y. D. Y. L.; McNeil, A. J., 100th Anniversary of Macromolecular Science Viewpoint: Redefining Sustainable Polymers. *ACS Macro Lett.* **2020,** *10* (1), 41-53.
5.   Haque, F. M.; Ishibashi, J. S. A.; Lidston, C. A. L.; Shao, H.; Bates, F. S.; Chang, A. B.; Coates, G. W.; Cramer, C. J.; Dauenhauer, P. J.; Dichtel, W. R.; Ellison, C. J.; Gormong, E. A.; Hamachi, L. S.; Hoye, T. R.; Jin, M.; Kalow, J. A.; Kim, H. J.; Kumar, G.; LaSalle, C. J.; Liffland, S.; Lipinski, B. M.; Pang, Y.; Parveen, R.; Peng, X.; Popowski, Y.; Prebihalo, E. A.; Reddi, Y.; Reineke, T. M.; Sheppard, D. T.; Swartz, J. L.; Tolman, W. B.; Vlaisavljevich, B.; Wissinger, J.; Xu, S.; Hillmyer, M. A., Defining the Macromolecules of Tomorrow through Synergistic Sustainable Polymer Research. *Chem. Rev.* **2022**.
6.   Post, W.; Susa, A.; Blaauw, R.; Molenveld, K.; Knoop, R. J. I., A Review on the Potential and Limitations of Recyclable Thermosets for Structural Applications. *Polym. Rev.* **2020,** *60* (2), 359-388.
7.   Fortman, D. J.; Brutman, J. P.; De Hoe, G. X.; Snyder, R. L.; Dichtel, W. R.; Hillmyer, M. A., Approaches to Sustainable and Continually Recyclable Cross-Linked Polymers. *ACS Sustain. Chem. Eng.* **2018,** *6* (9), 11145-11159.
8.   Shieh, P.; Hill, M. R.; Zhang, W.; Kristufek, S. L.; Johnson, J. A., Clip Chemistry: Diverse (Bio)(macro)molecular and Material Function through Breaking Covalent Bonds. *Chem. Rev.* **2021,** *121* (12), 7059-7121.
9.   Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L., Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011,** *334* (6058), 965-968.
10.   Denissen, W.; Winne, J. M.; Du Prez, F. E., Vitrimers: permanent organic networks with glass-like fluidity. *Chem. Sci.* **2016,** *7* (1), 30-38.
11.   Chakma, P.; Konkolewicz, D., Dynamic Covalent Bonds in Polymeric Materials. *Angew. Chem. Int. Ed.* **2019,** *58* (29), 9682-9695.
12.   Christensen, P. R.; Scheuermann, A. M.; Loeffler, K. E.; Helms, B. A., Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds. *Nat. Chem.* **2019,** *11* (5), 442-448.
13.   Scheutz, G. M.; Lessard, J. J.; Sims, M. B.; Sumerlin, B. S., Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets. *J. Am. Chem. Soc.* **2019,** *141* (41), 16181-16196.
14.   Nesvadba, P., Radical Polymerization in Industry. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*, 2012.
15.   Lee, H.; Park, T. G., Reduction/Oxidation Induced Cleavable/Crosslinkable Temperature-Sensitive Hydrogel Network Containing Disulfide Linkages. *Polym. J.* **1998,** *30* (12), 976-980.
16.   Oh, J. K.; Tang, C.; Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K., Inverse Miniemulsion ATRP: A New Method for Synthesis and Functionalization of Well-Defined Water-Soluble/Cross-Linked Polymeric Particles. *J. Am. Chem. Soc.* **2006,** *128* (16), 5578-5584.

17.   Cuthbert, J.; Wanasinghe, S. V.; Matyjaszewski, K.; Konkolewicz, D., Are RAFT and ATRP Universally Interchangeable Polymerization Methods in Network Formation? *Macromolecules* **2021,** *54* (18), 8331-8340.

18.   Gao, H.; Matyjaszewski, K., Synthesis of functional polymers with controlled architecture by CRP of monomers in the presence of cross-linkers: From stars to gels. *Prog. Polym. Sci.* **2009,** *34* (4), 317-350.

19.   Gao, Y.; Zhou, D.; Lyu, J.; A, S.; Xu, Q.; Newland, B.; Matyjaszewski, K.; Tai, H.; Wang, W., Complex polymer architectures through free-radical polymerization of multivinyl monomers. *Nat. Rev. Chem.* **2020,** *4* (4), 194-212.

20.   Bagheri, A.; Fellows, C. M.; Boyer, C., Reversible Deactivation Radical Polymerization: From Polymer Network Synthesis to 3D Printing. *Adv. Sci.* **2021,** *8* (5), 2003701.

21.   Yoon, J. A.; Kamada, J.; Koynov, K.; Mohin, J.; Nicolaÿ, R.; Zhang, Y.; Balazs, A. C.; Kowalewski, T.; Matyjaszewski, K., Self-Healing Polymer Films Based on Thiol–Disulfide Exchange Reactions and Self-Healing Kinetics Measured Using Atomic Force Microscopy. *Macromolecules* **2012,** *45* (1), 142-149.

22.   Röttger, M.; Domenech, T.; Weegen, R. v. d.; Breuillac, A.; Nicolaÿ, R.; Leibler, L., High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **2017,** *356* (6333), 62-65.

23.   Lessard, J. J.; Garcia, L. F.; Easterling, C. P.; Sims, M. B.; Bentz, K. C.; Arencibia, S.; Savin, D. A.; Sumerlin, B. S., Catalyst-Free Vitrimers from Vinyl Polymers. *Macromolecules* **2019,** *52* (5), 2105-2111.

24.   Shieh, P.; Zhang, W.; Husted, K. E. L.; Kristufek, S. L.; Xiong, B.; Lundberg, D. J.; Lem, J.; Veysset, D.; Sun, Y.; Nelson, K. A.; Plata, D. L.; Johnson, J. A., Cleavable comonomers enable degradable, recyclable thermoset plastics. *Nature* **2020,** *583* (7817), 542-547.

25.   Husted, K. E. L.; Shieh, P.; Lundberg, D. J.; Kristufek, S. L.; Johnson, J. A., Molecularly Designed Additives for Chemically Deconstructable Thermosets without Compromised Thermomechanical Properties. *ACS Macro Lett.* **2021**, 805-810.

26.   Shieh, P.; Nguyen, H. V.; Johnson, J. A., Tailored silyl ether monomers enable backbone-degradable polynorbornene-based linear, bottlebrush and star copolymers through ROMP. *Nat. Chem.* **2019,** *11* (12), 1124-1132.

27.   Agarwal, S., Chemistry, chances and limitations of the radical ring-opening polymerization of cyclic ketene acetals for the synthesis of degradable polyesters. *Polym. Chem.* **2010,** *1* (7), 953-964.

28.   Evans, R. A.; Moad, G.; Rizzardo, E.; Thang, S. H., New Free-Radical Ring-Opening Acrylate Monomers. *Macromolecules* **1994,** *27* (26), 7935-7937.

29.   Phelan, M.; Aldabbagh, F.; Zetterlund, P. B.; Yamada, B., Mechanism and kinetics of the free radical ring-opening polymerization of cyclic allylic sulfide lactones. *Polymer* **2005,** *46* (26), 12046-12056.

30.   Paulusse, J. M. J.; Amir, R. J.; Evans, R. A.; Hawker, C. J., Free Radical Polymers with Tunable and Selective Bio- and Chemical Degradability. *J. Am. Chem. Soc.* **2009,** *131* (28), 9805-9812.

31.   Pesenti, T.; Nicolas, J., 100th Anniversary of Macromolecular Science Viewpoint: Degradable Polymers from Radical Ring-Opening Polymerization: Latest Advances, New Directions, and Ongoing Challenges. *ACS Macro Lett.* **2020,** *9* (12), 1812-1835.

32.   Bingham, N. M.; Roth, P. J., Degradable vinyl copolymers through thiocarbonyl addition-ring-opening (TARO) polymerization. *Chem. Commun.* **2018,** *55* (1), 55-58.

33.   Smith, R. A.; Fu, G.; McAteer, O.; Xu, M.; Gutekunst, W. R., Radical Approach to Thioester-Containing Polymers. *J. Am. Chem. Soc.* **2019,** *141* (4), 1446-1451.

34.   Spick, M. P.; Bingham, N. M.; Li, Y.; de Jesus, J.; Costa, C.; Bailey, M. J.; Roth, P. J., Fully Degradable Thioester-Functional Homo- and Alternating Copolymers Prepared through Thiocarbonyl Addition–Ring-Opening RAFT Radical Polymerization. *Macromolecules* **2020,** *53* (2), 539-547.

35.   Bingham, N. M.; Nisa, Q. u.; Chua, S. H. L.; Fontugne, L.; Spick, M. P.; Roth, P. J., Thioester-Functional Polyacrylamides: Rapid Selective Backbone Degradation Triggers Solubility Switch Based on Aqueous Lower Critical Solution Temperature/Upper Critical Solution Temperature. *ACS Appl. Polym. Mater.* **2020,** *2* (8), 3440-3449.

36.   Ivanchenko, O.; Authesserre, U.; Coste, G.; Mazières, S.; Destarac, M.; Harrisson, S., ε-Thionocaprolactone: an accessible monomer for preparation of degradable poly(vinyl esters) by radical ring-opening polymerization. *Polym. Chem.* **2021,** *12* (13), 1931-1938.

37.   Rix, M. F. I.; Higgs, S. J.; Dodd, E. M.; Coles, S. J.; Bingham, N. M.; Roth, P. J., Insertion of Degradable Thioester Linkages into Styrene and Methacrylate Polymers. *ChemRxiv* **2022**.

38.   Gil, N.; Caron, B.; Siri, D.; Roche, J.; Hadiouch, S.; Khedaioui, D.; Ranque, S.; Cassagne, C.; Montarnal, D.; Gigmes, D.; Lefay, C.; Guillaneuf, Y., Degradable Polystyrene via the Cleavable Comonomer Approach. *ChemRxiv* **2022**.

39.   Gil, N.; Thomas, C.; Mhanna, R.; Mauriello, J.; Maury, R.; Leuschel, B.; Malval, J.-P.; Clément, J.-L.; Gigmes, D.; Lefay, C.; Soppera, O.; Guillaneuf, Y., Thionolactone as Resin Additive to Prepare (bio)degradable 3D Objects via VAT Photopolymerization. *Angew. Chem. Int. Ed.* **2022** (n/a).

40.   Meijs, G. F.; Rizzardo, E.; Le, T. P. T.; Chen, Y.-C., Influence of thionoesters on the degree of polymerization of styrene, methyl acrylate, methyl methacrylate and vinyl acetate. *Makromol. Chem.* **1992,** *193* (2), 369-378.

41.   O'Brien, N.; McKee, A.; Sherrington, D. C.; Slark, A. T.; Titterton, A., Facile, versatile and cost effective route to branched vinyl polymers. *Polymer* **2000,** *41* (15), 6027-6031.

42.   Slark, A. T.; Sherrington, D. C.; Titterton, A.; Martin, I. K., Branched methacrylate copolymers from multifunctional comonomers: the effect of multifunctional monomer functionality on polymer architecture and properties. *J. Mater. Chem.* **2003,** *13* (11), 2711-2720.

43.   Isaure, F.; Cormack, P. A. G.; Sherrington, D. C., Facile synthesis of branched poly(methyl methacrylate)s. *J. Mater. Chem.* **2003,** *13* (11), 2701-2710.

44.   Isaure, F.; Cormack, P. A. G.; Sherrington, D. C., Synthesis of Branched Poly(methyl methacrylate)s: Effect of the Branching Comonomer Structure. *Macromolecules* **2004,** *37* (6), 2096-2105.

45.   Odian, G., *Principles of Polymerization*. Wiley-Interscience: Hoboken, N.J., 2004.

46.   Danielsen, S. P. O.; Beech, H. K.; Wang, S.; El-Zaatari, B. M.; Wang, X.; Sapir, L.; Ouchi, T.; Wang, Z.; Johnson, P. N.; Hu, Y.; Lundberg, D. J.; Stoychev, G.; Craig, S. L.; Johnson, J. A.; Kalow, J. A.; Olsen, B. D.; Rubinstein, M., Molecular Characterization of Polymer Networks. *Chem. Rev.* **2021,** *121* (8), 5042-5092.

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insoluble gels   degraded network fragments

R-NH₂