Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Strands *vs* crosslinks: topology-dependent degradation and regelation of polyacrylate networks synthesised by RAFT polymerisation

Frances Dawson,[a] Touseef Kazmi,[b] Peter J. Roth, [b] Maciej Kopeć, [a]*

[a] Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

[b] Department of Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, UK

*e-mail: mk2297@bath.ac.uk

Experimental

Materials

n-Butyl acrylate (*n*-BA, 99%) and anisole (99%) were purchased from Acros Organics. Azobisisobutyronitrile (AIBN, 97%), N,N-dimethylformamide (DMF, ≥99.9%), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, 98%), isopropylamine (≥99.9%), 2,2'-(ethylenedioxy)diethanethiol (EDDET, 95%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), pyridine (>99%), acetic acid (AcOH, 99.9-100%), ethyl acetate (>99.5%) and cysteamine (>98%) were purchased from Sigma-Aldrich. Dithiothreitol (DTT) was purchased from Thermo Scientific. Tetrahydrofuran [THF, gel permeation chromatography (GPC) grade] was purchased from Fisher. Petroleum spirit 40-60 °C was purchased from VWR. 1,6-Hexanediol diacrylate (HDDA, 99%) was purchased from Alfa Aesar. 2,2′-Dithiodiethanol diacrylate (DSDA) was purchased from Specific Polymers. All chemicals purchased from the manufacturers were stored at the recommended temperatures and used as received except DSDA, which was purified by column chromatography using petroleum ether: ethyl acetate as eluent, starting at 50:50 increasing to 10:90 (*v/v*). DOT was synthesized according to the previously published procedure[1] and stored at 5 °C. *n*-BA, DSDA and HDDA were passed basic alumina column to remove inhibitors before use.

Synthesis of PBA gel networks containing disulfide crosslinker by RAFT polymerisation

AIBN (11.5 mg, 0.07 mmol), BA (10 mL, 70.1 mmol), DDMAT (255 mg, 0.7 mmol) and anisole (10 mL, 1:1 *v/v* with BA) were added to a beaker and stirred until homogenous. This mixture was divided equally into 4 push top, neckless vials each containing 5 mL of solution. To each vial an appropriate amount of HDDA or DSDA was added to attain the required crosslinker type/loading (2 mol% or 4 mol% vs BA). Each 5 ml portion was then divided equally into 2 neckless vials to create 2 replicate gel discs for analysis. All 3 vials were sealed and degassed with nitrogen for 30 minutes before heating at 65 °C for 24 hours to ensure high monomer conversions and gel fractions were reached.

For kinetic measurements, a single sample of AIBN (1.4 mg, 0.009 mmol), BA (1.25 mL, 8.8 mmol) and anisole (1.25 mL) was stirred in a vial, then the appropriate amount of DSDA or HDDA was added to reach the desired crosslinking density. Three drops of DMF were added as an NMR internal standard. Molar ratios: [BA]:[DDMAT]:[AIBN]:[XLINKER] = 100:1:0.1:x, where x = 2 or 4.

The vial was heated at 65 °C and samples were taken at time intervals to monitor monomer conversion and polymer molecular weight until sample was too viscous/gelled.

Synthesis of PBA gels containing disulfide crosslinker by FRP

Same procedure as described above for RAFT polymerisation was used to prepare FRP gels, but without the addition of the RAFT agent (DDMAT).

[BA]:[AIBN]:[HDDA or DSDA] =100:0.1:x, where x = 2 or 4.

Synthesis of PBA-DOT gels by RAFT

AIBN (13.8 mg, 0.08 mmol), DDMAT (76.6 mg,0.21 mmol), BA (3 mL, 21.0 mmol), DOT (0-5 mol% vs BA) and anisole (3 mL) were added to vial and stirred until homogenous. 1 mL of this solution was transferred into a separate vial, and 2 drops of DMF were added as an NMR internal standard for kinetic measurements. HDDA (79.5 µL, 0.35 mmol, 2 mol% vs BA) was added to the remaining 5 mL portion and stirred until homogenous. This mixture was split equally between two neckless vials to make duplicate gel discs for analysis. All three vials were degassed with nitrogen for 30 minutes before heating at 65°C for 24 hours to ensure high monomer conversions were reached. Kinetic samples were taken from the non-crosslinked sample to monitor conversion in parallel. Molar ratios: [BA]:[DOT]:[DDMAT]:[AIBN]:[HDDA]=100:x:1:0.4:2 x=0,2,3,4,5.

Polymers with 200 and 500 targeted DP were also made by this procedure, reducing the loading of AIBN, DDMAT and DOT appropriately to give the following molar ratios: [BA]:[DOT]:[DDMAT]:[AIBN]:[HDDA] = 200:4:1:0.4:2, 200:8:1:0.4:2 and 500:4:1:0.4:2.

Equilibrium swelling ratio and gel fraction determination

30-100 mg of a gel sample was placed into a pre-weighed vial and 4 mL THF added. This was left for 3-6 hours to wash and then the THF was transferred to another pre weighed vial to measure the polymer sol. This process was repeated 3 times so that the sample was immersed in THF for a total of at least 24 hours. The final THF wash was removed, and the mass of the swollen gel was recorded ($m_{swollen}$). Any excess surface solvent was removed before recording the mass of the swollen gel. The swollen gel and the THF washings were allowed to dry overnight, followed by 24 hours under vacuum. The mass of the dry gel (m_{dry}) and the mass of the remaining solids from the washings (m_{sol}) were recorded. The equilibrium swelling ratio (ESR) was calculated as ESR = $m_{swollen}/m_{dry}$. The gel fraction was calculated as % GF= $m_{dry}/(m_{dry}+m_{sol}) \times 100\%$. All measurements were performed in triplicate.

Degradation of PBA-DSDA gels with DTT

30-100 mg of dry gel sample was placed in a pre-weighed vial and 3 mL of DTT solution in DMF (25 mg/mL) was added. The vial was sealed and degassed with nitrogen gas for 30 minutes before heating at 65 °C for 24 hours. If the gel sample macroscopically degraded, the solution was analysed by GPC. If solid gel remained, the sample was washed with 2 ×3 ml portions of DMF, leaving the sample immersed in DMF for 24 hours to remove the DTT. This was then repeated with 3 × 3 mL washings of THF. The swollen gel sample was weighed ($m_{swollen,deg}$) and allowed to dry overnight in air, followed by 24 hours under vacuum. The mass of the dry gel after degradation was recorded ($m_{dry,deg}$). The mass loss through degradation was calculated as % mass loss= $(m_{dry}-m_{dry,deg})/m_{dry}$ ×100%. The ESR after degradation was calculated as $ESR_{deg}=m_{swollen,deg}/m_{dry,deg}$. All measurements were performed in triplicate.

Degradation of PBA-DOT gels by isopropylamine

30-100 mg of dry gel sample was placed in a pre-weighed vial. 2 ml of 5.8 M isopropylamine in THF was then added to the vial. The vial was sealed and kept at room temperature for 24 hours. If gel remained in the vial it was removed, then the degraded fragments were concentrated by evaporating the solution using nitrogen gas. 1 mL of THF was added to the remaining solution before filtration though a 0.45 μm PTFE filter, and the filtrate was analysed by GPC. Any remaining gel was washed in THF then dried to quantify the mass loss through degradations.

Degradation and regelation of PBA-DSDA gel networks

Between 0.3 and 0.6 g (1 equiv. disulfide units) of dried PBA-DSDA gel was placed into a large vial. 3 mL of DMF was added with an appropriate amount of 2,2′-(Ethylenedioxy)diethanethiol (1.5 equiv.). The vial was sealed and degassed with nitrogen for 30 minutes, before heating at 65 °C for 24 hours. AcOH (1.2 equiv.) was then added to preserve thiol functionality and the mixture was left for 20 minutes before opening the vial. The degraded fragments were precipitated in 25 mL cold methanol/water (90:10, *v/v*), adding the solution using a pipette close to the bottom of the vial. The precipitate was left in the solution for 90 minutes. The excess methanol/water was removed using a pipette and the fragments solution was transferred to a small 7mL vial. Pyridine (1.2 equiv.) was then added to promote disulfide formation, and the solution was heated at 30 °C for 24 hours with the vial open to air. The ESR was remeasured to quantify crosslink density after regelation.

Degradation and regelation of PBA-DOT gel networks

Between 0.4-0.9 g (1 equiv. thioester units) of dried PBA-DOT gel was placed into a large vial. 10 ml DMF was added with an appropriate amount of cysteamine (1.5 equiv.) and DBU (1.8 equiv.). The vial was sealed and degassed with nitrogen for 30 minutes and left at room temperature for 24 hours AcOH (1.2 equiv.) was then added to preserve thiol functionality and the mixture was left for 20 minutes before opening the vial. The degraded fragments were precipitated in 25 mL cold methanol/water (90:10), adding the solution using a pipette close to the bottom of the vial. The precipitate was left in the solution for 90 minutes. The excess methanol/water was removed using a pipette and the fragments solution was transferred to a small 7mL vial. Pyridine (1.2 equiv.) was then added to promote disulfide formation, and the solution was heated at 30 °C for 24 hours with the vial open to air. The ESR was remeasured to quantify crosslink density after regelation.

Instrumentation

^{1}H NMR measurements were performed on a 400 MHz Bruker Neo in $CDCl_3$. DMF (δH = 8.0 ppm) was used as an internal reference in kinetic experiments. GPC analysis was conducted using a 1260 Infinity Multi-Detector GPC/SEC System manufactured by Agilent. The system uses three columns, two identical PLgel 5 μm Mixed-D columns (300 × 7.5 mm) and a guard column, PLgel 5 μm Mixed Guard (50 × 7.5 mm). All GPC analyses were conducted at 35 °C using THF as the mobile phase; each sample injection was 100 μL, with a run time of 40 min and 1 mL/min flow rate. Data acquisition was performed using linear polystyrene calibration standards. Oscillatory rheology measurements were carried out using a TA Instruments Discovery HR-30 rheometer fitted with a 20 mm crosshatched parallel plate geometry and a crosshatched base plate. As-synthesized disc-shaped gel samples with a thickness of 2.5-4 mm were assessed under a constant axial force of 0.35N. Frequency sweeps were carried out at 25 °C over a range of 0.01–100 rad s^{-1} at a constant strain of 0.1%. Amplitude sweeps were carried out at 25 °C over a range of 0.01%-1% strain at 0.1 rad s^{-1} angular frequency. Rheology measurements were performed in duplicate.

Synthesis and characterisation of PBA-DSDA gels by FRP

Table S1: Summary of synthesis and properties of PBA networks synthesised by conventional free radical polymerisation with DSDA or HDDA crosslinker. [BA]:[AIBN][x-linker] = 100:0.1:2 or 4.

Polymerisation method	Mol % crosslinker	Gel time /mins	Estimated conversion at gel point /%	ESR	Gel fraction /%
FRP	2% DSDA	26	-	6.0 ± 0.1	98 ± 0.5
FRP	2% HDDA	3	-	5.8 ± 0.1	95 ± 5.3
FRP	4% DSDA	36	-	3.9 ± 0.1	99 ± 0.7
FRP	4% HDDA	2	-	4.2 ± 0.2	99 ± 0.1

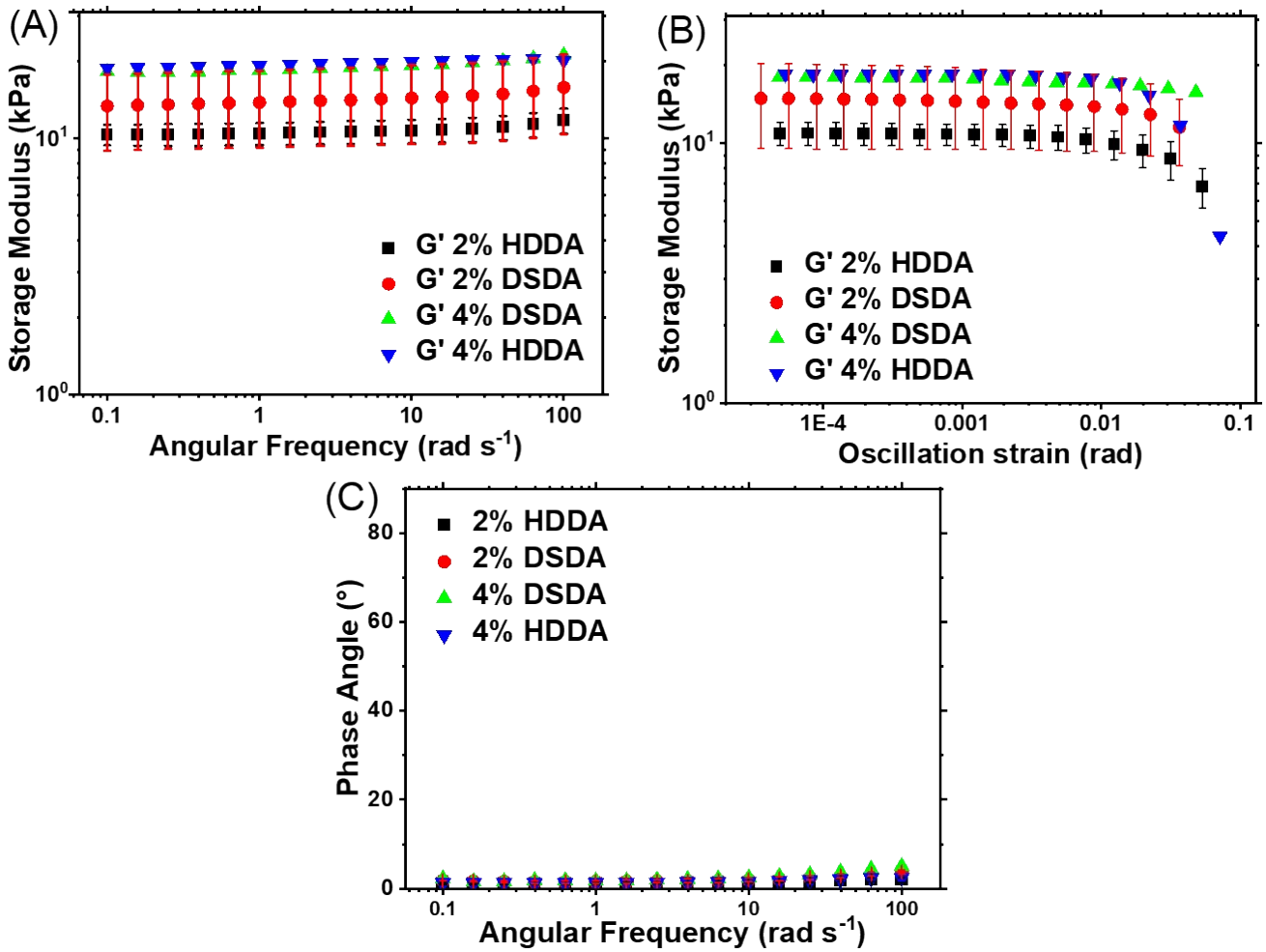

Figure S1: Oscillatory rheology data for PBA-DSDA and PBA-HDDA gels synthesised by FRP. (A) Storage modulus measurement for frequency sweep at 0.1% strain. (B) Amplitude sweep at 0.1 rad s^{-1}. (C) Phase angle measurement for frequency sweep at 0.1% strain.

Rheology of PBA-DSDA and PBA-HDDA RAFT gels

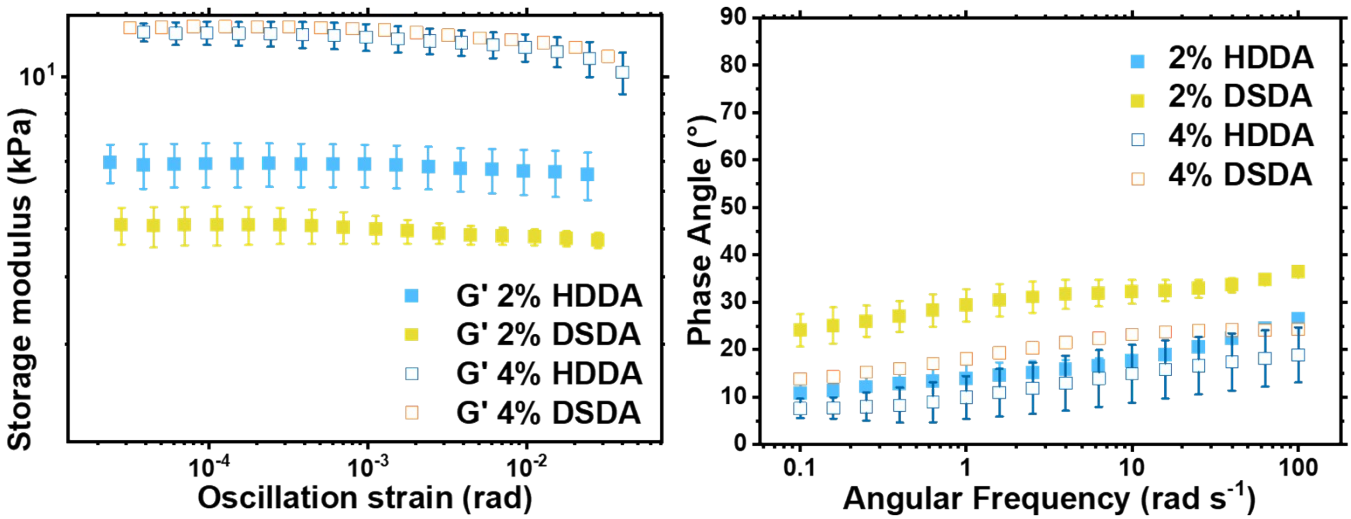

Figure S2: Oscillatory rheology data for PBA-DSDA and PBA-HDDA gels synthesised by RAFT. Left: Storage modulus measurement for amplitude sweep at 0.1 rad s^{-1}. Right: Phase angle measurement for frequency sweep at 0.1% strain.

Degradation of PBA-DSDA and PBA-HDDA gels

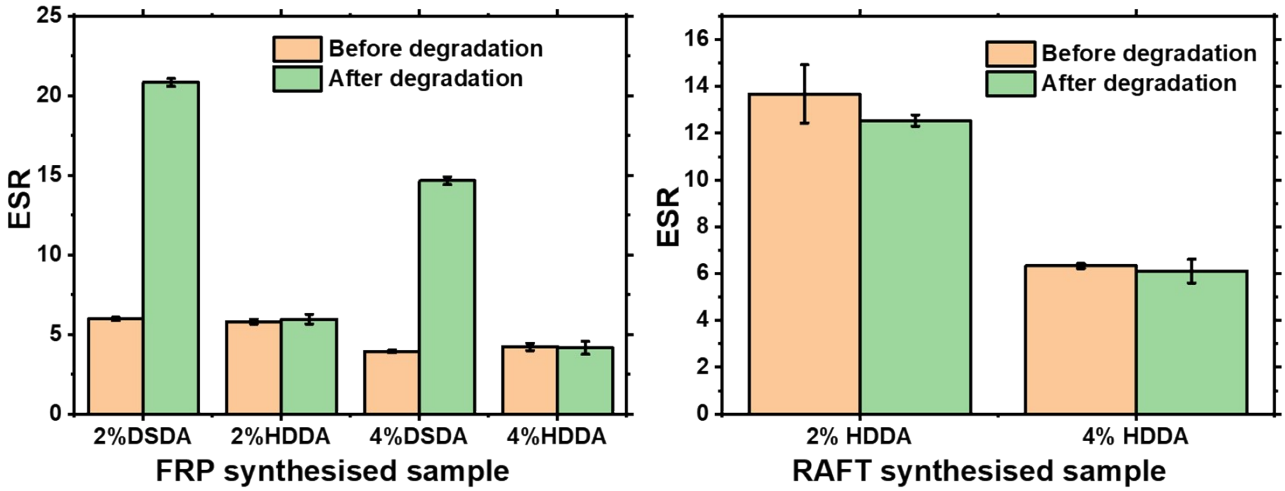

Figure S3: Equilibrium swelling ratio measurements before and after degradation with 25 mg/mL DTT solution in DMF. Left: ESR for gels synthesised by FRP. Right: ESR for gels synthesised by RAFT. 2% DSDA and 4% DSDA networks synthesised by RAFT macroscopically degraded, so no ESR was measured after degradation.

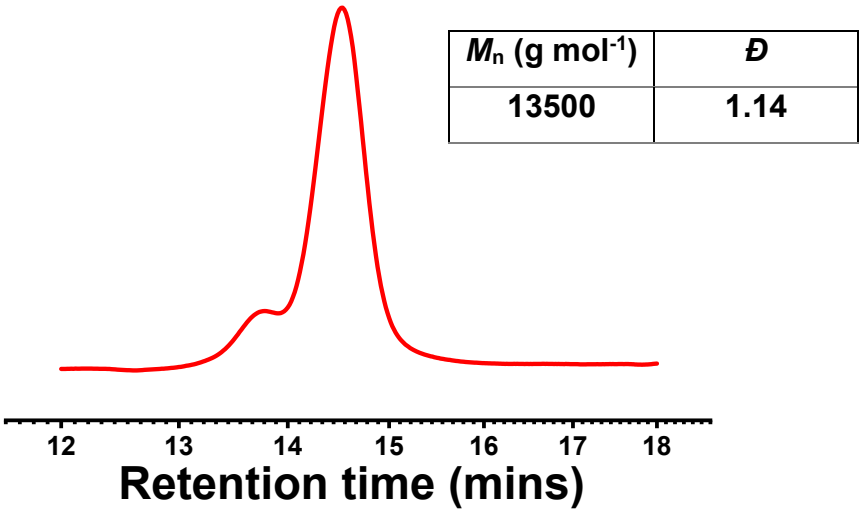

Figure S4: GPC trace for linear PBA synthesised by RAFT after 24 hours reaction time at 65 °C. [BA][DDMAT]:[AIBN]=100:1:0.4, BA:anisole 1:1 v/v.

Degradation of PBA-DOT networks and linear polymers

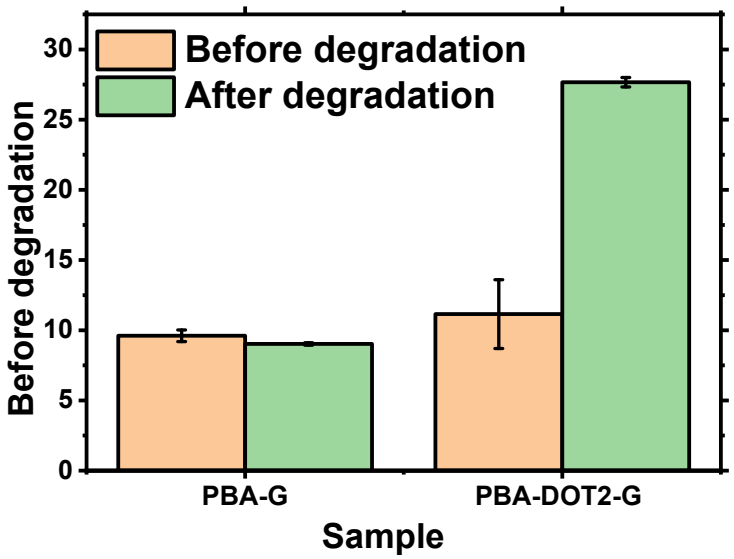

Figure S5: Equilibrium swelling ratios for PBA-DOT gel networks before and after degradation by aminolysis. Gels with DOT loadings greater than 2 mol% fully degraded so ESR could not be measured after degradation.

Table S2: Molecular weight and dispersity values of linear PBA-DOTX-L polymers before and after degradation by aminolysis, measured by GPC.

Sample	Before degradation		After degradation	
	M_n (g/mol)	$Đ$	M_n (g/mol)	$Đ$
PBA-L	13000	1.14	11900	1.22
PBA-DOT2-L	12000	1.17	5300	1.74
PBA-DOT3-L	11200	1.16	3900	1.82
PBA-DOT4-L	11100	1.17	2600	2.03
PBA-DOT5-L	9500	1.25	3500	1.84

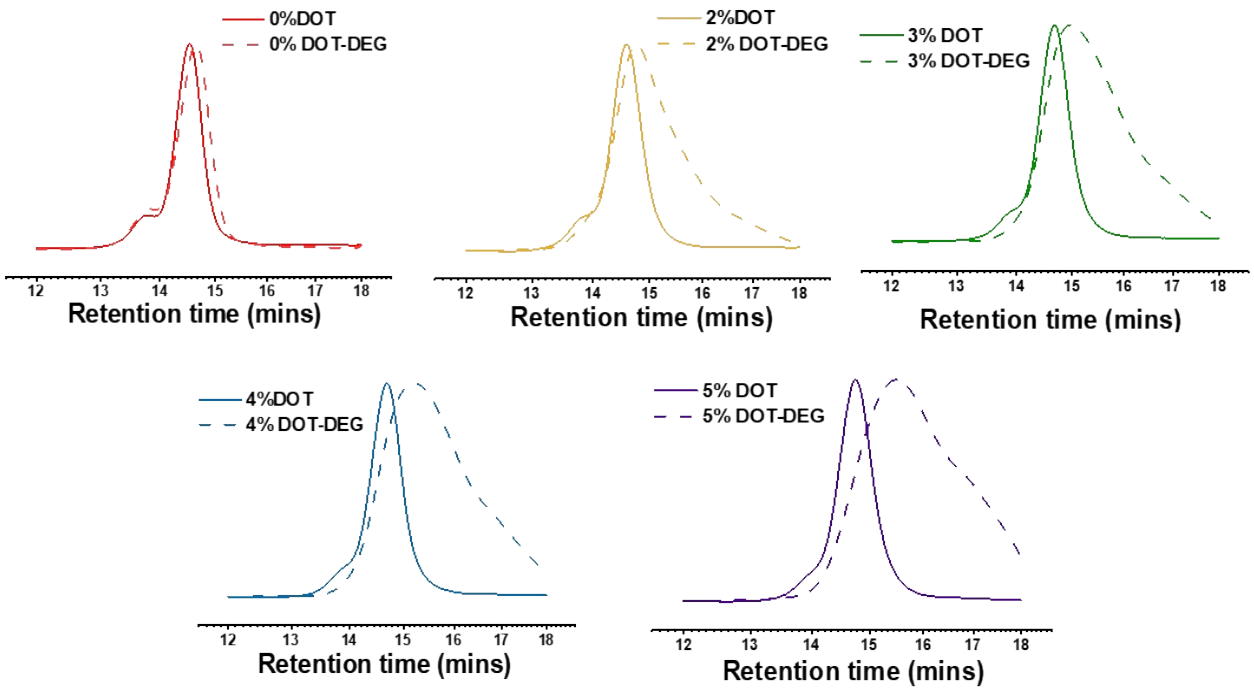

Figure S6: GPC traces for linear PBA-DOTx-L polymers before and after degradation.

Synthesis and degradation of higher DP PBA-DOT networks

[BA]:[DDMAT]:[DOT]:[HDDA]	Acrylate conversion at 100% DOT conversion[a]	$M_{n,\,theory}$ (g/mol)	$M_{n,\,GPC}$[b] (g/mol)	$Đ^{b}$
100:1:4:2	76%	12300	11100	1.17
200:1:4:2	59%	25700	25900	1.24

500:1:4:2	52%	59800	54400	1.34

Table S3: Synthesis of PBA-DOT-G networks with higher targeted DPs.

a- estimated from parallel linear PBA-DOT kinetics. b- measured by GPC.

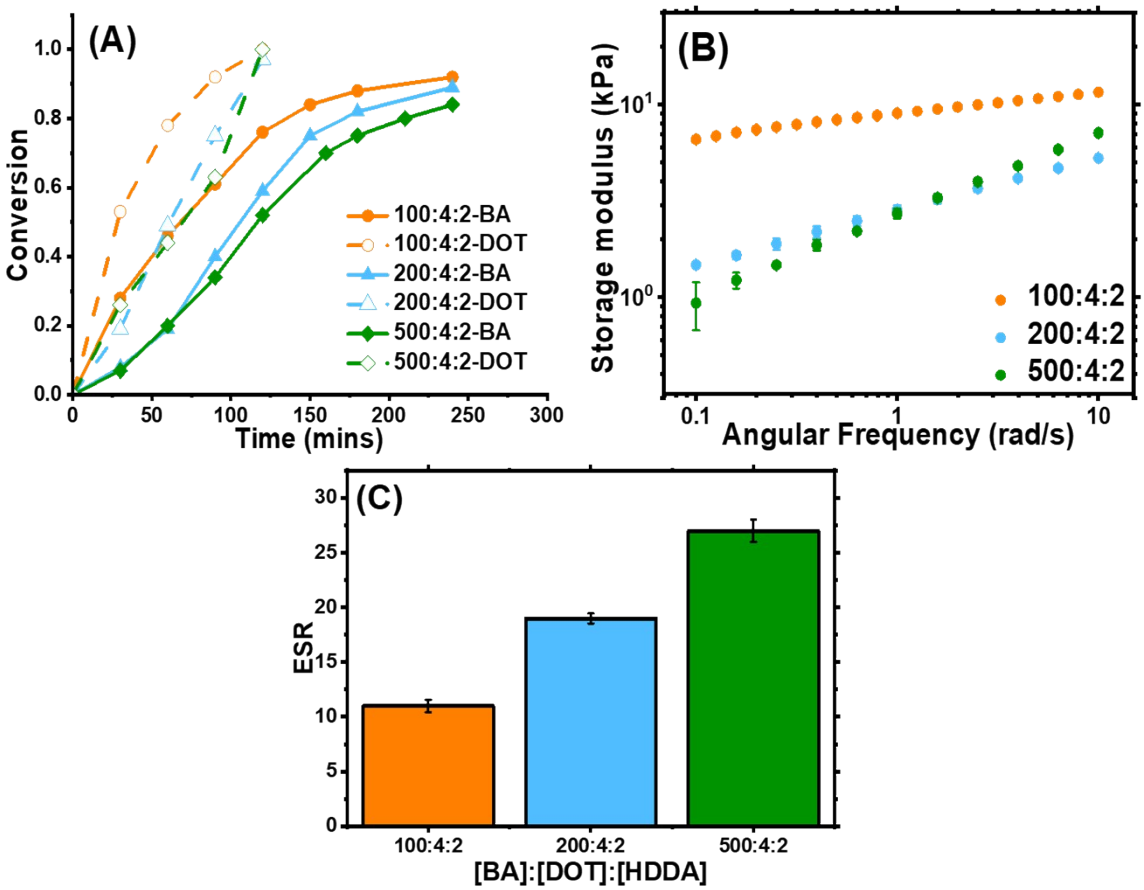

Figure S7: Polymerisation kinetics and physical properties of PBA-DOT networks with higher targeted DPs. [BA]:[DDMAT]:[DOT]:[HDDA] of 100:1:4:2,200:1:4:2,200:1:8:2 and 500:1:4:2. (A) Conversion plots for PBA-DOT linear polymers with higher DP. Closed markers show BA conversion, open markers show DOT conversion. (B) Storage modulus measured by oscillatory rheology, frequency sweep at 0.1% strain. (C) ESRs in THF.

Table S4: Degradation of PBA-DOT-G networks with higher targeted DPs by aminolysis.

[BA]:[DDMAT]:[DOT]:[HDDA]	**Macroscopic degradation[a]**	**M_n of degraded fragments (g mol^{-1})[b]**	**$Đ$ of degraded fragments[b]**

100:1:4:2	yes	5500	7.26
200:1:4:2	yes	9000	13.69
500:1:4:2	yes	-	-

[a] determined visually- macroscopic degradation successful when no solids remain after degradation. [b] measured by GPC.

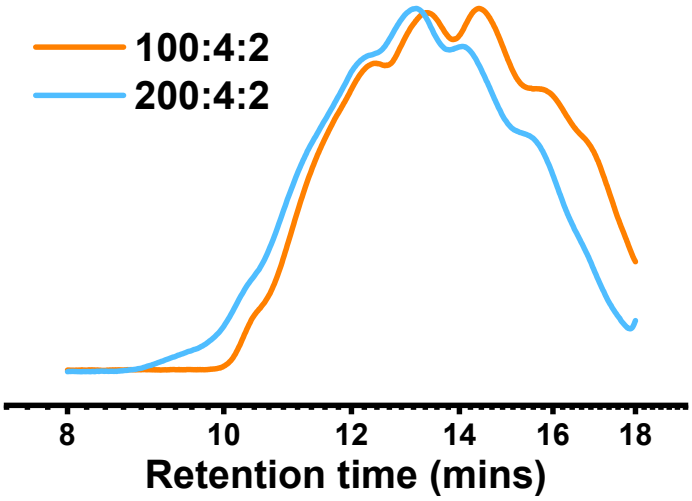

Figure S8: GPC traces of fragments produced from degradation of PBA-DOT networks with [BA]:[DDMAT]:[DOT]:[HDDA] of 100:1:4:2 and 200:1:4:2. The 500:1:4:2 network fully degraded but the fragments could not be filtered for GPC analysis.

Table S5: Molecular weights and dispersities of linear PBA-DOT polymers with higher targeted DPs.

[BA]:[DOT]:[HDDA]	Before degradation		After degradation	
	M_n (g/mol)	$Đ$	M_n (g/mol)	$Đ$
100-4-2	11100	1.17	2600	2.03
200-4-2	26000	1.24	6700	2.46
500-4-2	54500	1.34	18600	2.19

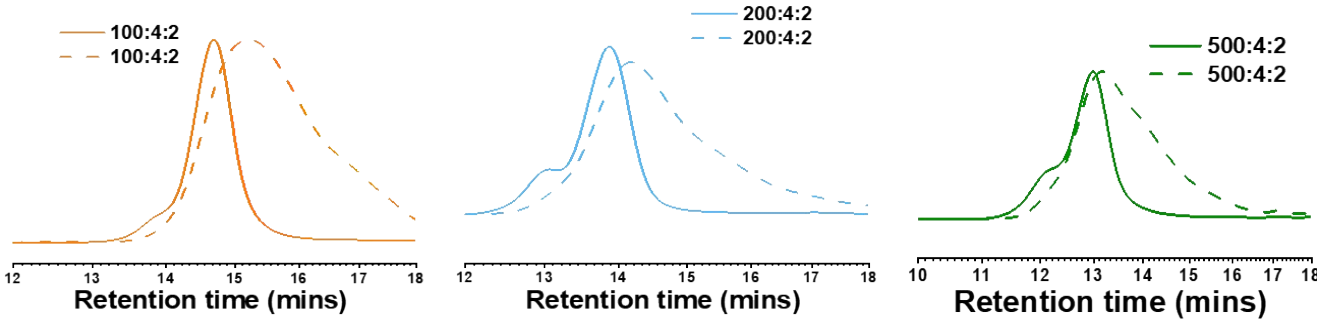

Figure S9: GPC traces for linear PBA-DOT polymers with higher targeted DPs before and after degradation by aminolysis.

Regelation

Table S6: Degradation and regelation results for **PBA-DSDA** and **PBA-DOT** networks.

Sample	ESR before degradation[a]	ESR after 1st degradation/regelation[a]	ESR after 2nd degradation/regelation[b]
PBA-DSDA2	13±0.2	23±0.1*	37*
PBA-DSDA4	6±0.5	20±4.7	42
PBA-DSDA5	5±0.1	17±0.4	17
PBA-DOT3	10±0.8	27±0.3	10
PBA-DOT4	11±0.6	27±0.5	14
PBA-DOT5	13±1	32±1.1	18

[a] average value from triplicate measurements of gel equilibrium swelling ratio (ESR), determined gravimetrically by swelling in excess THF for 24 hours. ESR = $m_{swollen}/m_{dry}$.[b] ESR after 2nd degradation/regelation cycle not performed in triplicate due to small amount of material produced. * Regelation of PBA-DSDA2 was only successfully performed at 65°C, using 2.4 equiv. pyridine, and 48 hours reaction time.

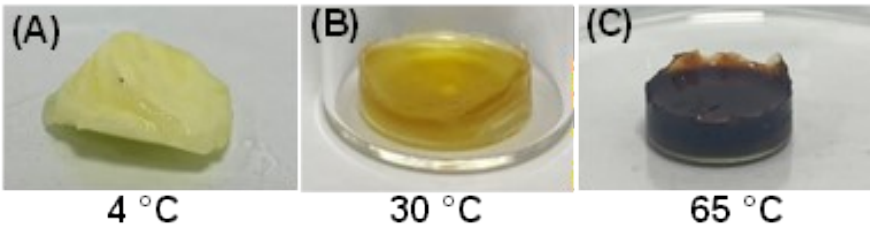

Figure S10: Regelled **PBA-DOT3** sample at different temperatures. (A) Regelation of fragments left in methanol/water precipitation in the fridge for 24 hours with no addition of pyridine. (B) Regelation of precipitated fragments when heated in air at 30 °C with 1.2 equiv. pyridine added. (C) Regelation of precipitated fragments when heated in air at 65 °C with 1.2 equiv. pyridine added. Additional brown colour likely indicates side reactions are present.

References

1. N. M. Bingham and P. J. Roth, *Chem. Commun.*, 2018, **55**, 55–58.