Volume 60
Number 74
21 September 2024
Pages 10035–10218

ChemComm

Chemical Communications

rsc.li/chemcomm

ISSN 1359-7345

ROYAL SOCIETY
OF **CHEMISTRY**

COMMUNICATION
Steve P. Rannard *et al.*
Employing transfer-dominated branching radical telomerisation (TBRT) and atom transfer radical polymerisation (ATRP) to form complex polyester-polymethacrylate branched-linear star copolymer hybrids *via* orthogonal initiation

60 YEARS
ANNIVERSARY

ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Commun.*, 2024, **60**, 10116

Received 3rd May 2024,
Accepted 29th July 2024

DOI: 10.1039/d4cc02142h

rsc.li/chemcomm

Open Access Article. Published on 31 July 2024. Downloaded on 2/7/2026 4:06:29 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Employing transfer-dominated branching radical telomerisation (TBRT) and atom transfer radical polymerisation (ATRP) to form complex polyester-polymethacrylate branched-linear star copolymer hybrids *via* orthogonal initiation†

Andrew B. Dwyer,[ab] William Sandy,[ab] Faye Y. Hern,[ab] Oliver B. Penrhyn-Lowe,[ab]
Samuel McKeating,[ab] Sean Flynn,[ab] Stephen Wright,[ab] Sophie Pate,[ab]
Pierre Chambon[ab] and Steve P. Rannard *[ab]

TBRT and ATRP are orthogonal initiation chemistries used in vinyl polymerisations. Here, we present the first combination of these techniques to readily create high molecular weight branched polyester macroinitiators capable of forming star copolymers from a range of methacrylate monomers.

Combinations of different polymer architectures have been of significant academic interest, generating highly interesting complex macromolecular structures using varied strategies. For example, linear-dendritic hybrids, and dendronized polymers have utilised approaches such as: (1) iterative or one pot dendron synthesis from preformed polymers;[1,2] (2) dendron focal point propagation of linear polymers using step growth[3] or chain growth[4,5] mechanisms; (3) light branching[6,7] or cross-linking;[8] (4) propagation of dendritic macromonomers;[9] and (5) click chemistry strategies.[1,2]

Highly branched polymers have been utilised as macroinitiators for extended hyperbranched polymerisation,[10] and the formation of linear polymer arms to form core–shell structures.[11–13] The use of self-condensing vinyl polymerisation[14,15] to form hyperbranched macroinitiators has been a popular theme in such research, and utilises the polymerisation, or copolymerisation, of a vinyl monomer that is also able to undergo initiation of new chains; an inimer.[16] The formation of macroinitiators using non-vinyl inimers[17,18] has also been achieved, with the incorporation of ATRP initiator or reversible addition fragmentation chain-transfer (RAFT) agent functionality into lactone or alcohol structures, allowing the ring-opening copolymerisation of mono/bis-lactones. The resulting polyester "cores" contained numerous initiators/RAFT agents to mediate the controlled radical polymerisation of vinyl monomers.[19] Here, we demonstrate the first use of the new polymerisation technique TBRT,[20–26] to form branched polyester macroinitiators containing ATRP initiating functionality using conventional free radical chemistry techniques. Subsequent Cu-catalysed ATRP polymerisation yields complex star copolymer structures with poly(methacrylate) arms emanating from the branched polyester core. The versatility of the approach is demonstrated using five methacrylate monomers and the physical properties of the resulting polymers are studied.

TBRT utilises the chain-transfer controlled telomerisation of divinyl monomers to yield highly branched polymers with complete vinyl group consumption whilst avoiding gelation. The number average degree of polymerisation (DP_n) derived from vinyl group propagation is maintained at <2 vinyl groups, and the extended macromolecular structure is derived from the linking chemistry between the unsaturated double bonds. Essentially, the ester functionality of a dimethacrylate becomes the dominant chemistry within the backbone of the resulting branched polymer and a polyester structure is formed. Within telomerisation nomenclature the vinyl functional monomers are termed taxogens, and chain transfer agents are known as telogens. The introduction of low concentrations of vinyl taxogens (VTs) relative to multi-vinyl taxogens (MVTs) allows new copolymer structures to be synthesised.[27]

The definition of "orthogonality" within synthetic chemistry has varied over the years and was initially used to describe mixed protecting group chemistries that could be selectively removed using different mechanisms.[28] The ability to mix functional groups that react independently under defined but inherently different reaction conditions has since been exploited in numerous contexts across diverse chemical fields.[29] We use the term "orthogonal" within the context previously presented for dendrimer synthesis and glycosylation reactions, namely "two sets of chemically distinct (orthogonal) [groups] and activation conditions"[30] and "functional groups …inert to the [reaction]

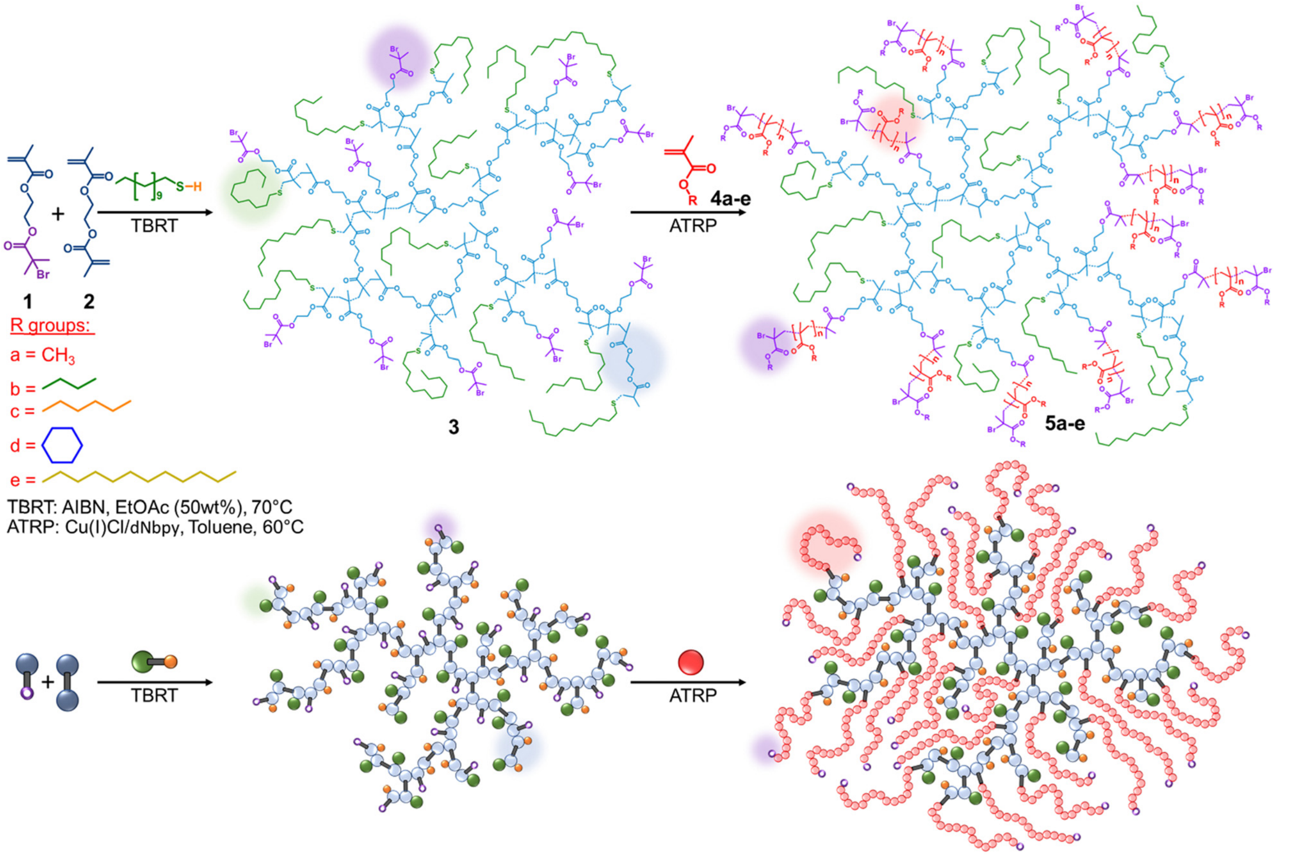
---

[a] *Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD, UK. E-mail: srannard@liv.ac.uk*
[b] *Materials Innovation Factory, University of Liverpool, Crown Street, L69 7ZD, UK*

† Electronic supplementary information (ESI) available: Materials, full experimental details and characterisation. See DOI: https://doi.org/10.1039/d4cc02142h

This journal is © The Royal Society of Chemistry 2024

Open Access Article. Published on 31 July 2024. Downloaded on 2/7/2026 4:06:29 AM. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.



Scheme 1 Synthesis of polyester-polymethacrylate star copolymer hybrids: initial TBRT copolymerisation of the ATRP inimer (**1**) with ethylene glycol dimethacrylate (**2**) yields a branched polyester with highly conserved pendant ATRP initiating functionality (**3**). Subsequent ATRP of various methacrylates (**4a–e**) yields a star copolymer with large numbers of pendant methacrylate chains (**5a–e**).

conditions of the other…allow[ing them] to be employed consecutively''.[31]

TBRT utilises conventional free radical initiation chemistry, therefore incorporation of an ATRP-functional vinyl inimer within a dimethacrylate TBRT reaction was considered a valid strategy in the creation of branched polyester macroinitiators, as ATRP requires organometallic catalysis to create the redox conditions for controlled radical polymerisation, Scheme 1. Thio-bromo "click" reactions have been widely reported under basic conditions,[32] therefore, to confirm the stability of ATRP initiation groups under standard telomerisation conditions, 2-hydroxyethyl methacrylate was reacted with α-bromoisobutyryl bromide to form an inimer containing the α-bromoisobutyrate ATRP initiating functionality, **1** (2-(α-bromoisobutyryloxy)ethylmethacrylate; BBEMA)[33] [ESI,† Fig. S1–S6]. The inimer was incorporated into a linear telomerisation of methyl methacrylate (MMA), using 1-dodecanethiol (DDT) as telogen and azobisisobutyronitrile (AIBN) in ethyl acetate (EtoAc; 50 wt% solids) at 70 °C (DDT : MMA : **1** molar ratio = 1.00 : 1.70 : 0.85). The linear telomerisation was monitored by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy and matrix-assisted laser desorption/ionisation time of flight (MALDI-TOF) mass spectrometry. The resulting liquid product showed complete consumption of the vinyl functionality of MMA and **1**, with no detectable vinyl resonances within the ^{1}H NMR spectrum [ESI,† Fig. S7–S11]. Within TBRT, and branched polymers generated from the reaction of vinyl functional feedstocks, it is important to differentiate between conversion of monomer to polymer (associated with conventional chain polymerisation concepts and usually equated to the loss of vinyl groups), and vinyl group consumption. The consumption of vinyl functionality in TBRT is a direct indication of the extent of reaction as the complete conversion of MVT to polymer may nevertheless result in many unreacted pendant vinyl groups.

The ^{13}C NMR resonance associated with the tertiary bromide was readily observed within the spectrum of **1** at 55.4 ppm and was clearly preserved within the linear *p*([DDT-MMA]-*stat*-BBEMA) telomer sample. The MALDI-TOF spectrum of the linear telomer showed mass ions separated by the molecular weights of MMA and **1**, strongly implying the robustness of the tertiary bromide under TBRT conditions. For example, a species with an $M[\mathrm{H}]^{+}$ = 305.52 Da was associated with a telomer comprising a degree of polymerisation (DP) of one MMA taxogen residue (added to one DDT telogen; note: S isotopes); subsequent peaks at $M[\mathrm{Na}]^{+}$ = 608.66 Da was indicative of a DP_2 species containing one MMA and one **1** residue, within $M[\mathrm{Na}]^{+}$ ions ranging from 708.78–1009.10 Da representing DP_{3-5} telomers containing a single inimer with its preserved tertiary bromide functionality [ESI,† Fig. S11].

The TBRT of ethylene glycol dimethacrylate (EGDMA, **2**) with **1** (polymer target **1** : **2** ratio = 1 : 1) was undertaken using DDT

Open Access Article. Published on 31 July 2024. Downloaded on 2/7/2026 4:06:29 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Table 1 ^{1}H NMR spectroscopic and TD-SEC analyses of branched polyester macroinitiators generated *via* TBRT and star copolymer hybrids synthesised using ATRP

	^{1}H NMR (CDCl$_3$)			TD-SEC^c				DSC^d
Polymer	[EGDMA]$_F$/[DDT]$_F$^{a}	[BBEMA]$_F$/[DDT]$_F$^{a}	Vinyl cons^b (%)	M_n (g mol^{-1})	M_w (g mol^{-1})	$Đ$	α	T_g (°C)
Branched								
p(DDT-EGDMA)	1.07	—	>99	174 490	2 499 000	14.3	0.416	−44
p([DDT-EGDMA]-*stat*-BBEMA) **3**	0.95	1.04	>99	12 290	205 330	16.7	0.225	−6
Branched star								
p([DDT-EGDMA]-*star*-MMA) **5a**	—	—	97	892 050	3 473 000	3.9	0.206	95
p([DDT-EGDMA]-*star*-*n*-BuMA) **5b**	—	—	98	1 301 000	5 952 000	4.6	0.232	23
p([DDT-EGDMA]-*star*-HMA) **5c**	—	—	>99	3 012 000	17 560 000	5.8	0.250	−5
p([DDT-EGDMA]-*star*-cHMA) **5d**	—	—	>99	504 390	7 645 000	15.2	0.171	97
p([DDT-EGDMA]-*star*-LMA) **5e**	—	—	97	572 350	6 070 000	10.6	0.103	−48

[a] Calculated by ^{1}H NMR of purified and dried material. [b] Determined by ^{1}H NMR of crude sample. [c] Triple-detection size exclusion chromatography using THF eluent. [d] Differential scanning calorimetry at a heating rate of 20 °C min^{-1}.

and AIBN under identical conditions to the MMA linear telomerisation. The crude reaction showed no vinyl proton resonances (^{1}H NMR) and the purified material confirmed the statistical copolymer/macroinitiator *p*([DDT-EGDMA]-*stat*-BBEMA), **3**, with a DDT : **2** : **1** ratio of 1 : 1 : 1 [ESI,† Fig. S12–S20].

For comparison, an inimer-free EGDMA/DDT TBRT was conducted; subsequent triple-detection size exclusion chromatography (TD-SEC) yielded a number average molecular weight (M_n) of 174 490 g mol^{-1} and a weight average molecular weight (M_w) of 2 499 000 g mol^{-1}, Table 1 [ESI,† Fig. S16]. VT incorporation in TBRT is known to yield lower molecular weight branched polymers due to the presence of non-branching units in the telomer sub-unit distribution and vinyl functionality dilution when working at constant solids content. This was also seen when using **1** (purified **3**: M_n = 12 290 g mol^{-1}; M_w = 205 330 g mol^{-1}), Table 1. Differential scanning calorimetry studies of the *p*(DDT-EGDMA) and *p*([DDT-EGDMA]-*stat*-BBEMA), **3**, showed a the influence of the pendant tertiary bromide groups; the glass transition temperature (T_g) increased by 38 °C [ESI,† Fig. S19 and S20]. The effect of VTs on TBRT copolymer T_g has been reported previously.[27] The 1 : 1 : 1 molar ratio of DDT : **2** : **1** in **3** allowed the nominal repeat unit, Fig. 1A, or tertiary bromide equivalent weight, to be readily calculated as 681 g mol^{-1}, thus enabling molar calculations of initiator (**3** has a number average of 18, and weight average of 302

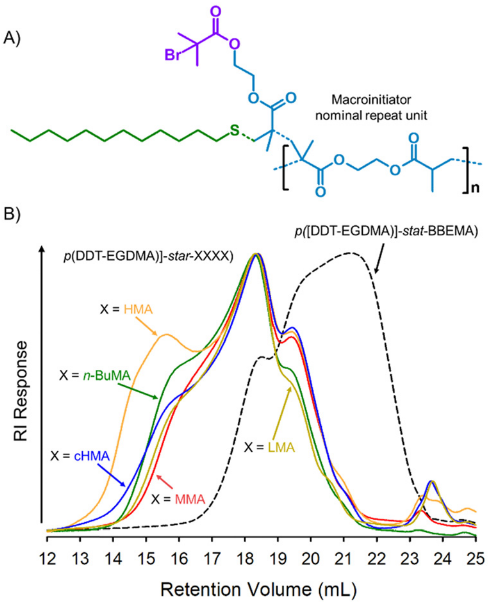


Fig. 1 (A) Nominal repeat unit within *p*([DDT-EGDMA]-*stat*-BBEMA) branched polyester macroinitiator and (B) comparative refractive index (TD-SEC) chromatograms of the TBRT macroinitiator (black dashed line) and various star copolymer hybrids *p*([DDT-EGDMA]-*star*-XXXX) with arms derived from the ATRP of MMA (red), *n*-BuMA (green), HMA (orange), cHMA (blue) and LMA (mustard).

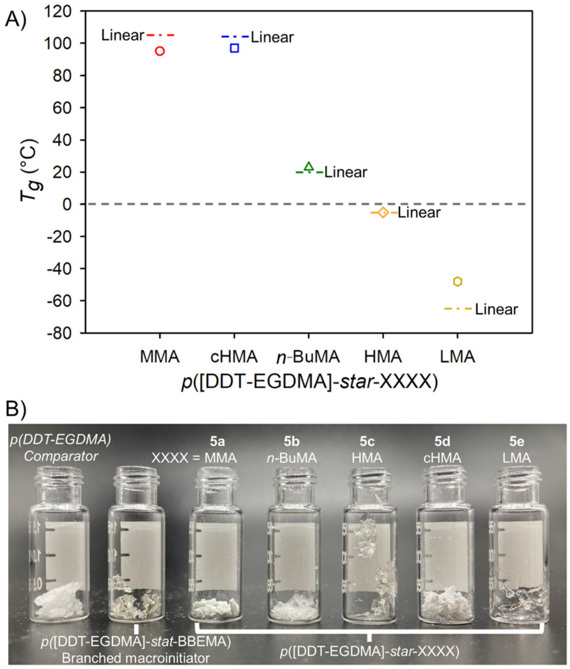


Fig. 2 Star copolymer hybrids: (A) glass transition temperature (T_g) analysis of star copolymer hybrids with arms derived from MMA (red circle), *n*-BuMA (green triangle), HMA (orange diamond), cHMA (blue square) and LMA (mustard hexagon), compared with literature values for linear polymer analogues (dash-dot-dash lines); (B) visual representation of each star copolymer sample, compared to TBRT synthesised *p*(DDT-EGDMA) and the branched polyester macroinitiator.

Open Access Article. Published on 31 July 2024. Downloaded on 2/7/2026 4:06:29 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

initiating sites). The ability of **3** to act as a macroinitiator was studied using five monomers, namely methyl, *n*-butyl (*n*-BuMA), hexyl (HMA), cyclohexyl (cHMA) and lauryl (LMA) methacrylate. All reactions were conducted in toluene, targeting arms of DP_n = 50 monomer units, using a Cu(I)Cl/4,4′-dinonyl-2,2′-dipyridyl catalyst system, Scheme 1 [ESI,† Fig. S21–S30], and reaching very high/near complete, conversion. TD-SEC analysis showed a considerable increase in molecular weight for each *p*([DDT-EGDMA]-*star*-XXXX) copolymer, **5a–e**, Table 1 and Fig. 1B [ESI,† Fig. S21–S25 and S31–S34]. *p*([DDT-EGDMA]-*star*-LMA), **5e**, formation was examined in detail, displaying first order kinetics of ATRP, indicating steady radical concentration during arm growth [ESI,† Fig. S35]. After purification, the five star copolymers were visually different to **3** displaying T_g values that strongly correlate to literature $T_g\infty$ values of the corresponding linear methacrylate homopolymers, Table 1 and Fig. 2A, B [ESI,† Fig. S36].

In conclusion, we demonstrate the first orthogonal synthesis of star copolymers using TBRT and ATRP leading to complex polyester-polymethacrylate branched-linear hybrids. The scope for further study is considerable and is underway to vary the number of initiating sites in the core macroinitiator, arm chemistry, and their chain length.

ABD – overseeing the investigation, supervision, conceptualisation, manuscript review, editing; WMS – investigation, data curation; FYH – methodology; OBP-L, SM, SF, SW, SP – analysis, methodology; PC – conceptualisation, manuscript review; SPR – conceptualisation, interpretation, funding, investigation, administration, resources, supervision, writing (original draft, review & editing).

The authors acknowledge the Engineering & Physical Sciences Research Council for funding (EPSRC; EP/R010544/1). WMS, OBPL and SM thank the University of Liverpool, EPSRC and Unilever for funding. Dr Megan Carr of the Materials Innovation Factory is thanked for analytical support (MALDI-TOF).

Data availability

The data supporting this article have been included within the ESI.†

Conflicts of interest

SPR and PC are co-inventors on licenced patents that form the basis of Polymer Mimetics Ltd (Company number 12598928).

Notes and references

1 B. Helms, J. L. Mynar, C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**(46), 15020.
2 A. Carlmark, C. Hawker, A. Hult and M. Malkoch, *Chem. Soc. Rev.*, 2009, **38**, 352.
3 I. Chandrasiri, D. G. Abebe, S. Gupta, J. S. D. Williams, W. D. Rieger, B. L. Simms, M. L. Yaddehige, Y. Noh, M. E. Payne, A. W. Fortenberry, A. E. Smith, J. Ilavsky, S. M. Grayson, G. J. Schneider and D. L. Watkins, *J. Polym. Sci., Part A: Polym. Chem.*, 2019, **57**, 1448.
4 D. L. Patton, P. Taranekar, T. Fulghum and R. Advincula, *Macromolecules*, 2008, **41**, 6703.
5 S. E. R. Auty, O. C. J. Andrén, F. Y. Hern, M. Malkoch and S. P. Rannard, *Polym. Chem.*, 2015, **6**, 573.
6 F. L. Hatton, P. Chambon, T. O. McDonald, A. Owen and S. P. Rannard, *Chem. Sci.*, 2014, **5**, 1844.
7 F. L. Hatton, L. M. Tatham, L. R. Tidbury, P. Chambon, T. He, A. Owen and S. Rannard, *Chem. Sci.*, 2015, **6**, 326.
8 L. A. Connal, R. Vestberg, C. J. Hawker and G. G. Qiao, *Macromolecules*, 2007, **40**, 7855.
9 A. D. Schlüter, A. Halperin, M. Kröger, D. Vlassopoulos, G. Wegner and B. Zhang, *ACS Macro Lett.*, 2014, **3**, 991.
10 D. Wilms, F. Wurm, J. Nieberle, P. Böhm, U. Kemmer-Jonas and H. Frey, *Macromolecules*, 2009, **42**, 3230.
11 C. Porsch, Y. Zhang, C. Ducani, F. Vilaplana, L. Nordstierna, A. M. Nyström and E. Malmström, *Biomacromolecules*, 2014, **15**, 2235.
12 W. Li, X. Zhao and H. Liu, *Polym. Chem.*, 2014, **5**, 1905.
13 R. M. England, J. I. Moss, A. Gunnarsson, J. S. Parker and M. B. Ashford, *Biomacromolecules*, 2020, **21**(8), 3332.
14 J. M. J. Fréchet, M. Henmi, I. Gitsov, S. Aoshima, M. R. Leduc and R. B. Grubbs, *Science*, 1995, **269**, 1080.
15 R. W. Graff, X. Wang and H. Gao, *Macromolecules*, 2015, **48**(7), 2118.
16 X. Wang and H. Gao, *Polymers*, 2017, **9**, 188.
17 J. Kim, C. Waldron, B. Cattoz and C. R. Becer, *Polym. Chem.*, 2020, **11**, 6847.
18 S. E. Wright, A. Clarkson, J. M. Korns, E. Haljun, L. Lofving, M. Ourgessa and Y. D. Y. L. Getzler, *Green Chem. Lett. Rev.*, 2022, **15**, 683.
19 Y. Zheng, W. Turner, M. Zong, D. J. Irvine, S. M. Howdle and K. J. Thurecht, *Macromolecules*, 2011, **44**, 1347.
20 S. R. Cassin, P. Chambon and S. P. Rannard, *Polym. Chem.*, 2020, **11**, 7637.
21 S. R. Cassin, S. Flynn, P. Chambon and S. P. Rannard, *RSC Adv.*, 2021, **11**, 24374.
22 O. B. Penrhyn-Lowe, S. Flynn, S. R. Cassin, S. Mckeating, S. Lomas, S. Wright, P. Chambon and S. P. Rannard, *Polym. Chem.*, 2021, **12**, 6472.
23 O. B. Penrhyn-Lowe, S. R. Cassin, P. Chambon and S. P. Rannard, *Nanoscale Adv.*, 2022, **4**, 4051.
24 S. Flynn, O. B. Penrhyn-Lowe, S. Mckeating, S. Wright, S. Lomas, S. R. Cassin, P. Chambon and S. P. Rannard, *RSC Adv.*, 2022, **12**, 31424.
25 S. R. Cassin, S. Wright, S. Mckeating, O. B. Penrhyn-Lowe, S. Flynn, S. Lomas, P. Chambon and S. P. Rannard, *Polym. Chem.*, 2023, **14**, 1905.
26 S. Flynn, B. Linthwaite, O. B. Penrhyn-Lowe, S. Mckeating, S. Wright, S. R. Cassin, P. Chambon and S. P. Rannard, *Polym. Chem.*, 2023, **14**, 5102.
27 S. R. Cassin, S. Flynn., P. Chambon and S. P. Rannard, *Polym. Chem.*, 2022, **13**, 2295.
28 G. Barany and R. B. Merrifield, *J. Am. Chem. Soc.*, 1977, **99**, 7363.
29 C.-H. Wong and S. C. Zimmerman, *Chem. Commun.*, 2013, **49**, 1679.
30 O. Kanie, Y. Ito and T. Ogawa, *J. Am. Chem. Soc.*, 1994, **116**, 12073.
31 F. Zeng and S. C. Zimmerman, *J. Am. Chem. Soc.*, 1996, **118**, 5326.
32 A. Moreno, G. Lligadas, J. Adamson, D. S. Maurya and V. Percec, *Polymers*, 2023, **15**, 1075.
33 M. Zhang, J. Wu, Z. Li, W. Hou, Y. Li, Y. Shi and Y. Chen, *Polym. Chem.*, 2022, **13**, 4895.