

Full Paper

Phosphorus-Containing Gradient (Block)copolymers via RAFT Polymerization and Post-Polymerization Modification^a

Kyle J. Sykes, Simon Harrisson, Daniel J. Keddie*

K. J. Sykes, Dr. D. J. Keddie

Chemistry, School of Science and Technology, University of New England, Armidale, NSW, 2351, Australia.

Dr. S. Harrisson

Laboratoire Interactions Moléculaires et Réactivité Chimique et Photochimique, UMR 5623 CNRS-UPS Toulouse, Université Paul Sabatier Toulouse, 118 route de Narbonne, 31062 Toulouse Cedex 9, France

Dr. D. J. Keddie

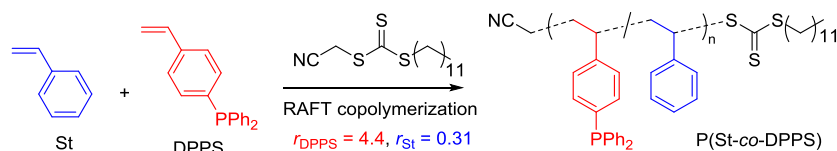
School of School of Biology, Chemistry & Forensic Science, Faculty of Science & Engineering, University of Wolverhampton, Wulfruna Street, Wolverhampton, WV1 1LY, United Kingdom

Email: d.keddie@wlv.ac.uk

Reversible addition-fragmentation chain transfer (RAFT) copolymerization of styrene (St) and 4-(diphenylphosphino)styrene (DPPS) is explored to establish the statistical distribution of the phosphine-functional monomer within the copolymer. RAFT copolymerization of St and DPPS at a variety of feed ratios provides phosphine-functional copolymers of low dispersity at moderate monomer conversion ($D < 1.2$ at conv. $> 60\%$). In all cases the fraction of DPPS in the resulting polymers is greater than that in the monomer feed. Estimation of copolymerization reactivity ratios indicates DPPS has a strong tendency to homopolymerize whilst St preferentially copolymerizes with DPPS ($r_{\text{DPPS}} = 4.4$; $r_{\text{St}} = 0.31$). The utility of the copolymers as macro-RAFT agents in block copolymer synthesis is demonstrated via chain extension with hydrophilic acrylamide (*N,N*-dimethylacrylamide (DMAm)) and acrylate

^a **Supporting Information** is available online from the Wiley Online Library or from the corresponding author.

(poly(ethylene glycol) methyl ether acrylate (mPEGA); di(ethylene glycol) ethyl ether acrylate (EDEGA)) monomers. Finally access to polymers containing phosphine oxide and phosphonium salt functionalities is shown through post-polymerization modification of the phosphine-containing copolymers.



1. Introduction

Phosphines and other phosphorus-containing compounds are used in a wide range of applications, including as ionic liquids,^[1, 2] flame retardants,^[3, 4] surfactants^[5-7] and biocides.^[8] ^{9]} Our interest in the design and synthesis of phosphine-functional polymers stems from the utility of phosphorus-based functional groups in organic synthesis, for example as stereoselective organocatalysts^[10] or as ligands in transition metal catalysis (e.g. Pd, Ru).^[11-15] Functional polymeric catalysts offer distinct advantages over small molecule catalysts including: improved selectivity due to functional group cooperativity and steric strain;^[16] enhanced reaction rates resulting from differing polarity to the bulk solvent phase;^[17] and ease of recovery and reuse.^[18]

Reversible addition-fragmentation chain transfer (RAFT) polymerization is a powerful tool for tailoring polymer properties, such as molar mass, functionality and architecture, with a high level of precision.^[19-27] RAFT offers unparalleled functional group tolerance^[28] compared to other reversible deactivation radical polymerization techniques,^[19, 29-32] allowing for control over the polymerization of a wide range of functional monomers,^[19, 21, 22] including less activated monomers (LAMs.)^[33] such as vinyl esters^[34-36] vinylamides,^[35, 37-40] *N*-vinyl

heteroaromatics^[36, 41-45] and vinyl phosphonates^[46-48] which are typically difficult to control. Importantly RAFT is compatible with phosphine functionality as illustrated through the use of RAFT agents containing either free^[49] or complexed^[49-51] phosphines and the polymerization of phosphine-containing monomers.^[52-57] Furthermore RAFT is relatively simple to implement, with reaction conditions often differing from a conventional radical polymerization only by the addition of a RAFT agent.

Herein we report the synthesis of phosphine-containing gradient copolymers through the RAFT copolymerization of styrene (St) and 4-(diphenylphosphino)styrene (DPPS). We also investigate the efficiency of preparation of block copolymers through chain extension with hydrophilic monomers, *N,N*-dimethylacrylamide, poly(ethylene glycol) methyl ether acrylate and diethylene glycol ethyl ether acrylate. Subsequent elaboration of the phosphine-containing gradient copolymers allows the introduction of phosphine oxide or phosphonium salt functionalities.

2. Experimental Section

2.1. Materials

All solvents were of analytical grade unless otherwise stated. 4-(Diphenylphosphino)styrene (DPPS), Styrene (St), *N,N*-dimethylacrylamide (DMAm), poly(ethylene glycol) methyl ether acrylate (mPEGA, $M_n = 480 \text{ g mol}^{-1}$), di(ethylene glycol) ethyl ether acrylate (EDEGA), chloroacetonitrile, carbon disulfide (CS₂) and potassium *tert*-butoxide (KO^tBu), 1-ethylpiperidine hypophosphate (EPHP), 1,1-azobis(cyclohexanecarbonitrile) (ACHN) were purchased from Sigma-Aldrich. 2,2'-Azobis(2-methyl propionitrile) (AIBN) was purchased from Acros and purified via recrystallization from methanol before use. St, DMAm, MPEGA and EDEGA were filtered through neutral alumina Brockmann activity I (70–230 mesh) to

remove inhibitor prior to use. DPPS was used as received. Tetrahydrofuran (THF) was distilled from sodium-benzophenone immediately prior to use. All deuterated solvents were obtained from Cambridge Isotope Laboratories. Cyanomethyl dodecyltrithiocarbonate **1** was prepared as per the procedure reported by Gupta *et al.*^[58]

2.2. Characterization

Nuclear magnetic resonance (NMR) spectra for structural assignments and monomer conversion were obtained on a Bruker Avance 300 MHz spectrometer. ¹H and ¹³C NMR spectra were internally referenced to residual solvent.^[59] ³¹P NMR spectra were externally referenced to 85% aqueous phosphoric acid (H₃PO₄).^[60] Gel Permeation Chromatography (GPC) was performed on a system comprising a Waters 590 HPLC pump and a Waters 410 refractive index detector and Waters 2998 photodiode array detector equipped with 3 × Waters Styragel columns (HT2, HT3, HT4, each 300 mm × 7.8 mm providing an effective molar mass range of 100-600000). The eluent was *N,N*-dimethylformamide (DMF) containing 2.1 g L⁻¹ of LiCl at 80 °C (flow rate: 1 mL min⁻¹). Number-average (*M_n*) and weight-average (*M_w*) molar masses were evaluated using Waters Empower software. The GPC columns were calibrated with low dispersity polystyrene standards (Polymer Laboratories) ranging from 3100 to 650000 g mol⁻¹ and molar masses are reported as polystyrene equivalents. A third order polynomial was used to fit the log *M_p* vs. time calibration curve, which was linear across the molar mass ranges.

2.3. RAFT polymerization.

2.3.1. Copolymerization of Styrene and 4-(Diphenylphosphino)styrene.

Details of the RAFT polymerization conducted via thermally initiated polymerization in bulk using an initial St to DPPS feed ratio of 97.5 to 2.5 ([St]₀: [DPPS]₀ = 97.5:2.5) is given below.

Examples using $[St]_0:[DPPS]_0$ of 95:5, 90:10 and 75:25 are given in the supporting information.

2.3.2. Synthesis of Poly(styrene-*co*-4-(diphenylphosphino))styrene using Cyanomethyl dodecyltrithiocarbonate (**1**) ($[St]_0:[DPPS]_0 = 97.5:2.5$).

The reaction solution was prepared with the dissolution of the RAFT agent **1** (69 mg, 0.22 mmol) and DPPS (126 mg, 0.44 mmol) in St (1.95 mL, 1.77 g, 17.0 mmol). Toluene (100 μ L) was added as an internal standard. The solution was transferred into a Schlenk tube equipped with PTFE stopcock and degassed by three repeated freeze–evacuate–thaw cycles, backfilled with N_2 and sealed. The solution was heated in a thermostatted oil bath at 110 $^{\circ}C$ and sampled at designated intervals (2, 4, 8 and 25 h) using a degassed N_2 flushed syringe.

2.4. Copolymerization Analysis: Determination of reactivity ratios

Point estimates and joint confidence intervals for reactivity ratios were determined using the visualization of the sum of squares method developed by van den Brink et al.^[61] and previously reported by Harrisson et al.^[62, 63] The integrated copolymerization equation was fitted to conversion and monomer feed composition data, assuming non-negligible errors in all variables. Simulated copolymer sequences were calculated as Markov chains according to the method described in Harrisson et al.^[63] The probabilities that a DPPS unit is followed by another DPPS unit or that a St unit is followed by another St unit are given by:

$$P(DPPS|DPPS)_n = r_{DPPS} \cdot f_{DPPS,x} / (f_{St,x} + r_{DPPS} \cdot f_{DPPS,x})$$

$$P(St|St)_n = r_{St} \cdot f_{St,x} / (f_{DPPS,x} + r_{St} \cdot f_{St,x})$$

Where $P(i|j)_n$ is the probability that the unit in the n th position, corresponding to the conversion x ($x = n/DP_{target}$) will be i if the preceding unit is j , $f_{i,x}$ is the mole fraction of i at conversion x and r_i is the reactivity ratio of i .

Analysis was performed on Microsoft Excel software.

2.5. Block Copolymer Synthesis

2.5.1. Synthesis of Poly(styrene-*co*-4-(diphenylphosphino))styrene macro-RAFT agent (P(St-*co*-DPPS) (2))

The reaction solution was prepared with the dissolution of the RAFT agent **1** (690 mg, 2.20 mmol) and DPPS (5.04 g, 17.5 mmol) in St (18.0 mL, 16.30 g, 157 mmol) ([St]₀:[DPPS]₀ = 90:10). Toluene (1 mL) was added as an internal standard. The solution was transferred into a Schlenk tube equipped with PTFE stopcock and degassed by three repeated freeze–evacuate–thaw cycles and sealed. The solution was heated in a thermostatted oil bath at 110°C for 25 h (conv. St = 69 %; conv. DPPS = 88 %; total conv. = 72 %). Following the removal of residual styrene under reduced pressure the resulting sample was purified by precipitation three times into methanol from a minimal volume of DCM and dried under vacuum to constant mass giving the purified macro-RAFT agent P(St-*co*-DPPS) (**2**) (13.63 g, $M_n = 5930$, $D = 1.19$).

2.5.2. Synthesis of Poly(styrene-*co*-4-(diphenylphosphinostyrene))-*block*-poly(*N,N*,*-*dimethylacrylamide).

Into a 25 mL standard volumetric flask were placed macro-RAFT P(St-*co*-DPPS) (**2**) (1.482 g, 0.25 mmol) and DMAm (4.96 g, 50 mmol). AIBN (2.0 mg, 1.25×10^{-2} mmol) was added and the solution was made up to the mark with DMF. The solution was transferred into a Schlenk tube and degassed via sparging with N₂ for 15 min in an ice bath. The solution was heated in a thermostatted oil bath at 60 °C and sampled at designated intervals (3 and 6 h) using a degassed N₂ flushed syringe.

2.5.3. Synthesis of Poly(styrene-*co*-4-(diphenylphosphinostyrene))-*block*-poly(poly(ethylene glycol) methyl ether acrylate).

Into a 25 mL standard volumetric flask were placed macro-RAFT P(St-*co*-DPPS) (**2**) (1.235 g, 0.21 mmol) and PEGA (5.0 g, 10.4 mmol). AIBN (4.8 mg, 2.9×10^{-2} mmol) was added and the solution was made up to the mark with 1,4-dioxane. The solution was transferred into a Schlenk tube and degassed via sparging with N₂ for 15 min in an ice bath. The solution was heated in a thermostatted oil bath at 60 °C and sampled at designated intervals (6 and 14 h) using a degassed N₂ flushed syringe.

2.5.4. Synthesis of Poly(styrene-*co*-4-(diphenylphosphinostyrene))-*block*-poly(di(ethylene glycol) ethyl ether acrylate).

Into a 25 mL standard volumetric flask were placed macro-RAFT P(St-*co*-DPPS) (**2**) (1.482 g, 0.25 mmol) and EDEGA (4.71 g, 25 mmol). AIBN (4.1 mg, 2.5×10^{-2} mmol) was added and the solution was made up to the mark with DMF. The solution was transferred into a Schlenk tube and degassed via sparging with N₂ for 15 min in an ice bath. The solution was heated in a thermostatted oil bath at 60 °C and sampled at designated intervals (3 and 6 h) using a degassed N₂ flushed syringe.

2.6. Post-polymerization Modification of Phosphine Functional Polymers

2.6.1. Radical induced end-group removal from poly(styrene-*co*-4-(diphenylphosphinostyrene))

Adapted from the method reported by Chong *et al.*^[64] A Schenk flask was charged with P(St-*co*-DPPS) **2** (2.0 g), ACHN (37 mg) and EPHP (640 mg). The solid reagents were dissolved in a minimal volume of toluene (~2 mL) and the resulting solution degassed via sparging with N₂ for 15 min in an ice bath. The solution was then heated in a thermostatted oil bath at

100 °C for 16 h. The toluene was removed under reduced pressure. The polymer residue was precipitated into MeOH from a minimum volume of DCM and the solid washed with 1 M aq. HCl and MeOH to give the end-group reduced polymer P(St-*co*-DPPS) **6** (1.84 g, $M_n = 6000$, $\bar{D} = 1.17$).

2.6.2. Oxidation of Poly(styrene-*co*-4-(diphenylphosphinostyrene)) to Poly(styrene-*co*-4-(diphenylphosphorylstyrene))

Adapted from the method reported by Li *et al.*^[65] The reduced polymer P(St-*co*-DPPS) **6** (375 mg) was dissolved in DCM (6.25 mL) and H₂O₂ (30 wt% in H₂O; 6.25 mL) was added. The resulting mixture was stirred vigorously at RT for 24 h. Subsequently the DCM layer was separated, washed with water (2 × 10 mL) and dried (Na₂SO₄). The resulting solution was purified by precipitation into MeOH and dried under vacuum to constant mass to give the polymeric phosphine oxide P(St-*co*-DPPOS) **8** (362 mg, $M_n = 6220$, $\bar{D} = 1.19$).

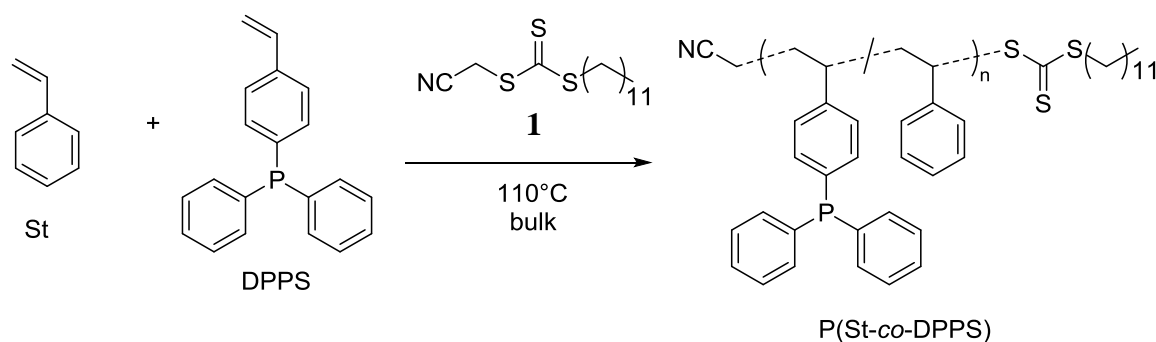
2.6.3. Quaternization of Poly(styrene-*co*-4-(diphenylphosphinostyrene)) with Methyl α -Bromoacetate

Adapted from the method reported by Hon *et al.*^[66] The end-group reduced polymer P(St-*co*-DPPS) **6** (375 mg) was dissolved in toluene (2 mL) and methyl α -bromoacetate (100 μ L) was added. The resulting mixture was stirred at RT for 24 h. Subsequently the toluene was removed under reduced pressure and the residue taken up in a minimum volume of acetone. The resulting solution was purified by precipitation into *n*-heptane and dried under vacuum to constant mass to giving the polymeric phosphonium salt **7** (294 mg, $M_n = 2890$, $\bar{D} = 1.85$).^[67]

3. Results and Discussion

3.1. Copolymerization of Styrene and 4-(Diphenylphosphino)styrene

RAFT-based synthesis of single-chain nanoparticles,^[55] core cross-linked micelles,^[54, 56, 57, 68] porous networks^[52] and soluble polymers^[53] bearing phosphine functionalities as polymeric supports for transition metal catalyzed organic transformations has received recent attention within the scientific community. A common monomer used in this context has been the commercially available phosphine-functional styrenic 4-(diphenylphosphino)styrene (DPPS), with several reports focusing on its copolymerization with other styrenic monomers.^[52, 54, 57, 68] Surprisingly little focus has been given to the distribution of phosphine functionality along the polymer with these copolymers; the copolymerization behavior, including the reactivity ratios, of DPPS and styrene (St) has not yet been reported.



Scheme 1: Statistical RAFT Copolymerization of St and DDPS.

The thermally initiated RAFT copolymerization of St and DPPS was undertaken in bulk at 110 °C, using cyanomethyl dodecyltrithiocarbonate **1** as the RAFT agent (**Scheme 1**). The degree of polymerization (DP) was targeted as 80. To ascertain the incorporation of the phosphine functionality, with a view towards potential catalysis application, the feed ratio of DPPS was varied (2.5%, 5%, 10% and 25% DPPS) (**Table 1**, for GPC chromatograms see **Figure 1**). In all cases the fraction of DPPS (F_{DPPS}) incorporated into the polymer is greater than the concentration in the initial monomer feed ($f_{\text{DPPS},0}$). This indicates a propensity for the copolymerization of St and DPPS to form gradient copolymers, with DPPS consumed preferentially to St (*vide infra*). From the pseudo-first order kinetics plots the rate of

polymerization was seen to decrease with increasing proportion of DPPS in the monomer feed (k_p^{app} 2.5% = 0.049 h⁻¹, 5% = 0.044 h⁻¹, 10% = 0.038 h⁻¹, 25% = 0.033 h⁻¹, see **Figure S2**).^[69] In each case the increase in M_n with monomer conversion was reasonably linear (see **Figure S1**), bearing in mind the difference in molar mass of the two monomers and the drift in composition of the monomer feed with conversion. The evolution of M_n with conversion is apparent from the GPC chromatograms (**Figure 1**). The molar mass dispersity decreased from relatively high for moderate conversion ($\mathcal{D} = \sim 1.40\text{-}1.50$ at $\sim 30\%$ total conv.) to low at higher conversion ($\mathcal{D} = \sim 1.15\text{-}1.20$ at $\sim 60\text{-}80\%$ conv.), suggesting a relatively low chain transfer coefficient of RAFT agent **1** in the St/DPPS copolymerization (see **Table 1**). This is attributed to inefficient partitioning^[26, 27] of the RAFT intermediate formed upon radical addition towards products (i.e. cyanomethyl radical, $\bullet\text{CH}_2\text{CN}$, and polystyryl-functional macro-RAFT agent) during the RAFT pre-equilibrium. The feed ratio of St and DPPS did not have a major influence on the molar mass dispersity of the polymers.

Table 1: Synthesis of P(St-co-DPPS) in bulk at 110°C^{a)}.

Entry	$f_{\text{St},0}$	$f_{\text{DPPS},0}$	Time (h)	St conv. %.	DPPS conv. %.	Total conv. %.	F_{St}	F_{DPPS}	M_n calc. ^{c)}	M_n ^{b)}	\bar{D} ^{b)}
1	0.975	0.025	2	7	19	7	0.935	0.065	970	— ^{d)}	— ^{d)}
			4	14	40	15	0.932	0.068	1720	— ^{d)}	— ^{d)}
			8	33	65	34	0.952	0.048	3390	1480	1.47
			25	60	81	61	0.967	0.033	5700	4880	1.14
2	0.95	0.05	2	12	17	12	0.931	0.069	1440	— ^{d)}	— ^{d)}
			4	14	52	16	0.836	0.164	2040	— ^{d)}	— ^{d)}
			8	26	79	29	0.862	0.138	3320	1770	1.38
			25	57	86	58	0.926	0.074	5780	5130	1.18
3	0.90	0.10	2	8	8	8	0.900	0.100	1100	— ^{d)}	— ^{d)}
			4	15	18	15	0.882	0.118	1830	— ^{d)}	— ^{d)}
			8	25	36	26	0.862	0.138	3010	1940	1.42
			25	71	82	72	0.886	0.114	7520	5790	1.16
4	0.75	0.25	2	7	6	7	0.778	0.222	1130	— ^{d)}	— ^{d)}
			4	9	16	11	0.628	0.372	1840	2050	1.43
			8	21	34	24	0.649	0.351	3560	4040	1.26
			25	75	91	79	0.712	0.288	10300	8590	1.17

^{a)}[St + DPPS]:[**1**] = 80:1; ^{b)}GPC DMF eluent, T = 80°C, LiCl = [50 mM]; ^{c)} $M_n(\text{calc}) = ([\text{St}]_0 + [\text{DPPS}]_0)/[\mathbf{1}]_0 \times ((M_{r,\text{St}} \times F_{\text{St}}) + (M_{r,\text{DPPS}} \times F_{\text{DPPS}})) \times \text{total \% conv.} + M_{r,\text{RAFT}}$ (where F is the mole fraction of monomer in the polymer); ^{d)}a significant portion of the polymer peak eluted outside of the GPC calibration window as such accurate analysis was not possible.

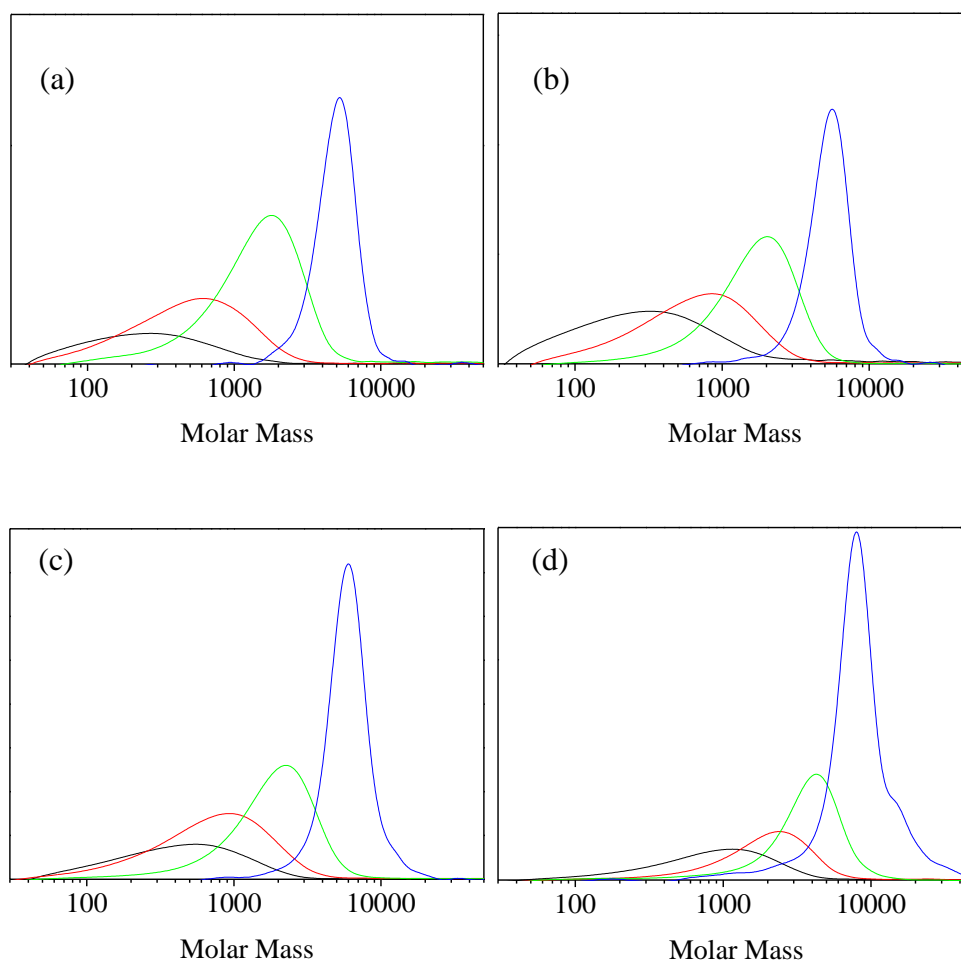


Figure 1: Evolution of molar mass distributions for bulk copolymerization of St and DPPS at 110 °C from GPC at 2 (—), 4 (—), 8 (—) and 25 h (—) for feed ratios of (a) 97.5 % St/2.5 % DPPS, (b) 95 % St/5 % DPPS, (c) 90 % St/10 % DPPS and (d) 75 % St/25 % DPPS. All chromatograms normalized with respect to total monomer conversion.

To further investigate the statistical distribution of the phosphine functionality along the polymer backbone the copolymerization reactivity ratios of St and DPPS were estimated using non-linear least squares fit of copolymerization data.^[61-63]

The evolution of the DPPS monomer fraction (f_{DPPS}) with conversion is shown in Figure 2a, with the best fit to the integrated copolymer composition equation, corresponding to reactivity ratios of 4.4 (r_{DPPS}) and 0.31 (r_{St}). The uncertainty in these values is indicated by the 95% joint confidence region, shown in Figure 2b, which covers the range 2-10 for r_{DPPS} and 0.20-

0.55 for r_{St} . DPPS shows a strong tendency to homopolymerize, while St preferentially copolymerizes with DPPS. This tendency is probably due to the electron-withdrawing character of the diphenylphosphine substituent,^[70] and is in line with the reactivity of other p -substituted styrenes with electron-withdrawing substituents, such as p -cyanostyrene ($r_{StCN} = 1.2$, $r_{St} = 0.19$)^[71] or p -chlorostyrene ($r_{StCl} = 1.1$, $r_{St} = 0.55$)^[72].

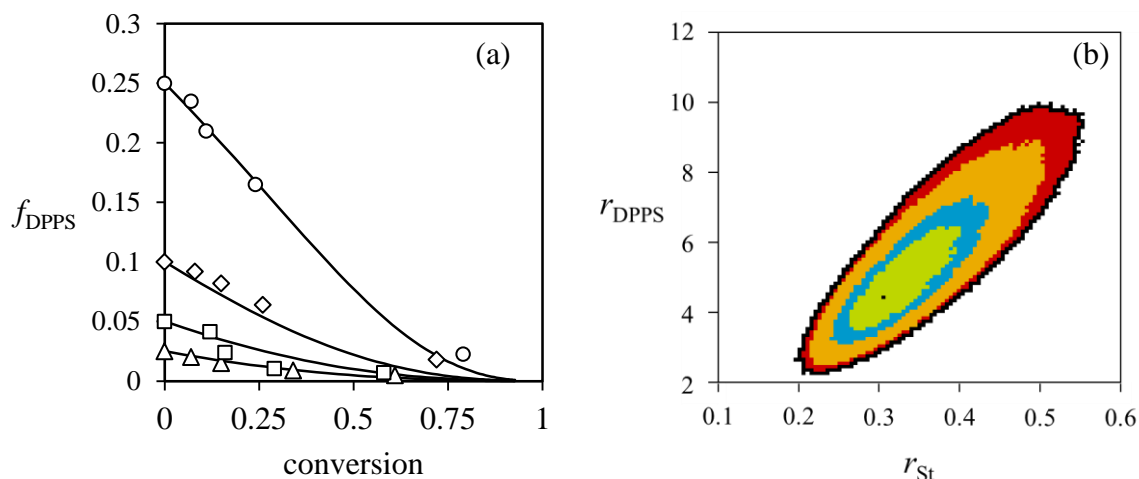


Figure 2: (a) Modeled (lines) and measured (symbols) monomer compositions for $f_{DPPS,0} = 2.5\%$ (triangles), 5% (squares), 10% (diamonds) and 25% (circles). Model parameters: $r_{DPPS} = 4.4$ and $r_{St} = 0.31$. (b) 95% joint confidence region for r_{DPPS} and r_{St} . Internal contours represent 50%, 70% and 90% joint confidence regions.

The resulting instantaneous copolymer composition profiles are shown in Figure 3, with simulated polymer chains illustrating typical distributions of phosphine functionality.

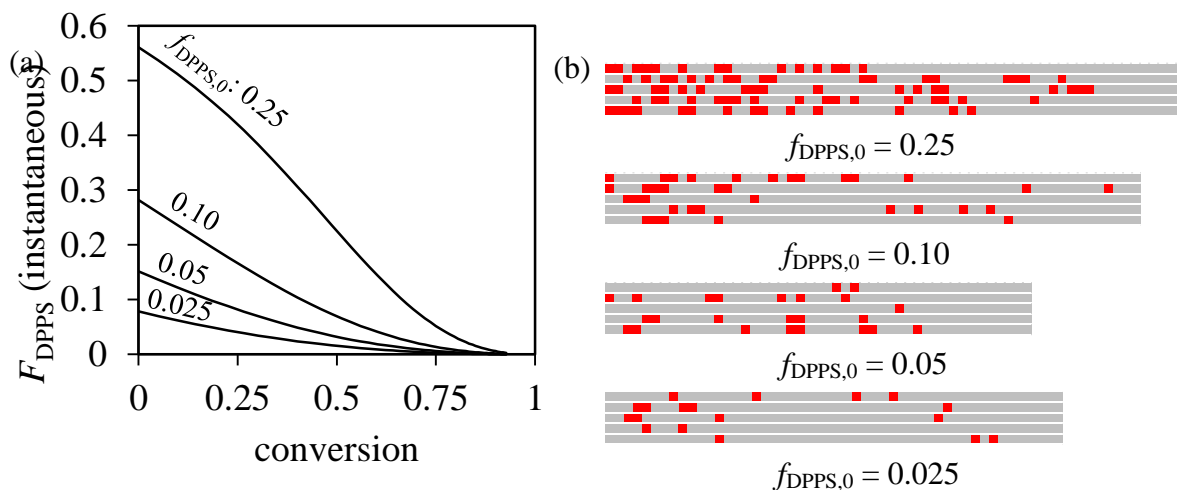


Figure 3: (a) Modeled instantaneous copolymer compositions for $f_{\text{DPPS},0} = 2.5\%$, 5% , 10% and 25% as a function of total monomer conversion, using $r_{\text{DPPS}} = 4.4$, $r_{\text{St}} = 0.31$. (b) simulated polymer sequences (5 each) for each polymer. DPPS units are colored red. The direction of polymerization is from left to right, and the number of units in each simulated chain is equal to the number-average degree of polymerization.

In all chains, the probability of DPPS incorporation decreases along the length of the chain. The composition gradient is most pronounced in the polymers with higher initial DPPS concentration (25% and 10%), while the 5% and 2.5% DPPS polymers show a more uniform distribution of DPPS.

The gradient structure of the polymer has two potentially beneficial effects. It is often desirable to stop a polymerization before reaching complete conversion in order to maintain a high level of active chain ends. As DPPS is incorporated more rapidly than styrene, the fraction of unconsumed DPPS which must be discarded at the end of the polymerization is smaller than it would be in a truly random copolymerization. Secondly, the strong tendency of DPPS to homopolymerize ($r_{\text{DPPS}} = 4.4$) facilitates the formation of DPPS-DPPS dyads. The presence of phosphines in neighbouring units of the polymer may encourage cooperative effects in catalytic applications through chelation and enhanced sterics.^[73-76]

From examination of the ^{31}P NMR of the high conversion polymer samples (25 h samples) following purification by precipitation the presence of phosphine oxide functionality is evident ($\delta \sim 30$ ppm), presumably formed through aerobic oxidation (see **Figure 3**, see **Figure S4** for corresponding ^1H NMR). The relative ratio of phosphine ($\delta \sim -5$ ppm) to phosphine oxide is affected by the relative concentration of phosphine monomer, with complete oxidation of phosphine to phosphine oxide observed for the polymer formed from 2.5 % feed ratio of DPPS. The ratio of phosphine oxide to phosphine decreases appreciably as the significance of exposure to discrete levels of oxygen during manipulation decreases with increasing phosphine content (see **Figure 3**).

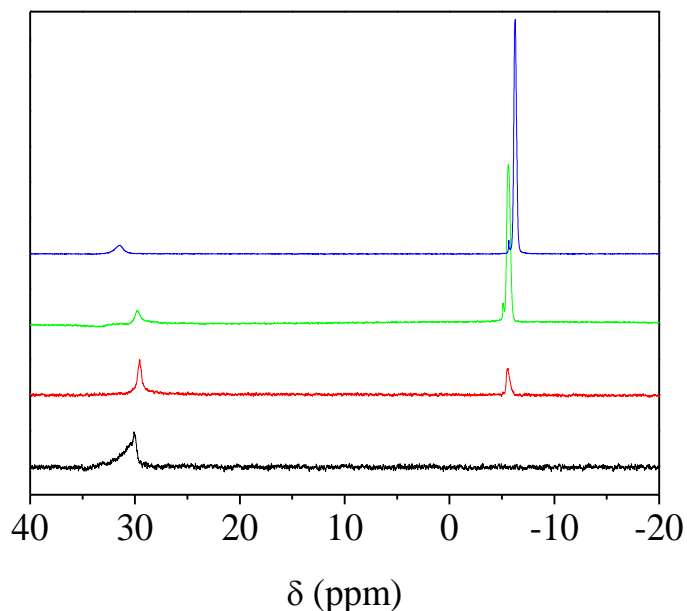
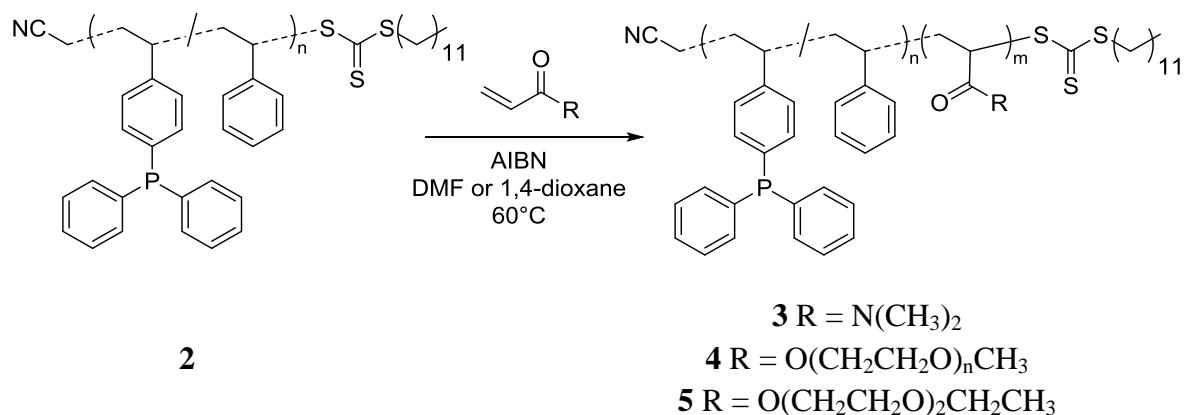


Figure 3: ^{31}P NMR of samples isolated after copolymerization of St and DPPS at feed ratios of 97.5 % St/2.5 % DPPS (—), 95 % St/5 % DPPS (—), 90 % St/10 % DPPS (—) and 75 % St/25 % DPPS (—) at 110 °C for 25 h and purified by precipitation into methanol. Spectral intensity normalized to phosphorus feed concentration. .

3.2. Block Copolymer Synthesis

Block copolymers were prepared from hydrophilic acrylamide (DMAm) and acrylate (mPEGA) monomers to probe the utility of P(St-*co*-DPPS) copolymers towards block extension (see **Scheme 2**). Incorporation of hydrophilic blocks alongside the hydrophobic phosphine functional block is expected to promote polymer self-assembly and facilitate subsequent catalysis application.^[17, 77-80] The P(St-*co*-DPPS) macro-RAFT agent **2** used in block copolymer synthesis was prepared by scaling up the copolymerization using 10% DPPS monomer feed using the same methodology as discussed above (see Entry 1 **Table 2**). This ratio was seen as the best compromise between retention of phosphine functionality in the final polymer whilst keeping the feed ratio of DPPS relatively low.^[81]



Scheme 2: Synthesis of phosphine-containing block copolymers by chain extension of P(St-*co*-DPPS) **2** with DMAm, mPEGA, and EDEGA to give P(St-*co*-DPPS)-*b*-PDMAm **3**, P(St-*co*-DPPS)-*b*-mPEGA **4** and P(St-*co*-DPPS)-*b*-PEDEGA **5** respectively.

Block extension with DMAm delivered block copolymers of relatively low dispersity (see Entries 2a and 2b, **Table 2**). The efficiency of block extension was high with low amounts of tailing to low molar mass seen in the GPC chromatograms (see **Figure 4a**). From the UV trace detected at 310 nm^[82, 83] it is evident that the low molar mass tail still bears the trithiocarbonate chain end. This indicates that the tailing is due to inefficient reinitiation of DMAm polymerization by the functional-polystyryl macro-radical rather than formation of

dead chains. Note that the contribution of the phosphine-containing main chain towards the UV absorbance at 310 nm was found to be negligible following radical-induced end-group removal (*vide infra*; see Figure S4 and S5).^[64, 84] Polymerization of mPEGA in the presence of the macro-RAFT agent **2** also furnished block copolymers of low dispersity (Entries 3a and 3b, **Table 2**), however due to poor peak resolution between the macro-RAFT agent and the block copolymers (see **Figure 4b**), qualitative analysis of the reinitiation efficiency of mPEGA with the macro-radical derived from **2** was not possible. Targeting higher DP for the poly(mPEGA) block to improve GPC resolution was deemed impractical due to the self-diluting nature of this macromonomer; increased volume fraction of mPEGA in the polymerization mixture was found to prevent complete dissolution of **2**. Instead EDEGA was used as a low molar mass analogue of mPEGA to probe the efficiency of block extension using acrylate-based monomers. The low dispersity of the macro-RAFT agent **2** was reflected in block copolymers formed upon chain extension with EDEGA at lower conversion (Entry 4a, **Table 2**), however at moderate conversion polymers were found to have relatively high dispersity (Entry 4b, **Table 2**) and a significant shoulder at low molar mass (see **Figure 4c**). The corresponding UV trace detected at 310 nm illustrates conservation of the trithiocarbonate functionality on the polymer chains that comprise this shoulder, indicating poor reinitiation efficiency of EDEGA polymerization with polystyryl-based macro-radicals. This hypothesis agrees with other reports within the literature where tailing has been attributed the poor reinitiation of monomer polymerization by the RAFT agent-derived macro-radical during block copolymer synthesis.^[85, 86] The same poor reinitiation efficiency seen in EDEGA polymerization is expected to occur during mPEGA polymerization with the same macro-RAFT agent, it is simply not observed in the GPC trace.

From these observations it is concluded that chain extension of the phosphine functional polystyryl macro-RAFT agent **2** is more effective with acrylamides than acrylates.

Table 2: Synthesis of P(St-co-DPPS) containing block copolymers by chain extension with DMAm, mPEGA and EDEGA at 60°C.

Entry	Polymer	Time (h)	M_n^d	Mn (calc.) ^{e)}	D^d	Conv. %
1	P(St-co-DPPS) (2)	—	6540	5930 ^{f)}	1.12	—
2a	P(St-co-DPPS)- <i>b</i> -PDMAm (3) ^{a)}	3	8070	8520	1.10	10
2b		6	17900	18800	1.24	62
3a	P(St-co-DPPS)- <i>b</i> -mPEGA (4) ^{b)}	6	10100	9930	1.14	18
3b		14	10600	18200	1.28	62
4a	P(St-co-DPPS)- <i>b</i> -PEDEGA (5) ^{c)}	3	10100	10100	1.17	15
4b		6	12800	19300	1.44	53

^{a)}[DMAm]:[**2**]:[AIBN]=200:1:0.05, [DMAm]=2 M in DMF; ^{b)}[PEGA]:[**2**]:[AIBN]=50:1:0.14, [mPEGA]=0.416 M in 1,4-dioxane; ^{c)}[EDEGA]:[**2**]:[AIBN]=200:1:0.25, [EDEGA]=1M in DMF; ^{d)}GPC DMF eluent, T = 80 °C, LiCl = [50 mM]; ^{e)} $M_n(\text{calc}) = ([M]_0 - [M]_t) / ([\mathbf{2}]_0 \times M_{r,M} + M_{n,2}(\text{NMR}))$; ^{f)} M_n from ¹H NMR

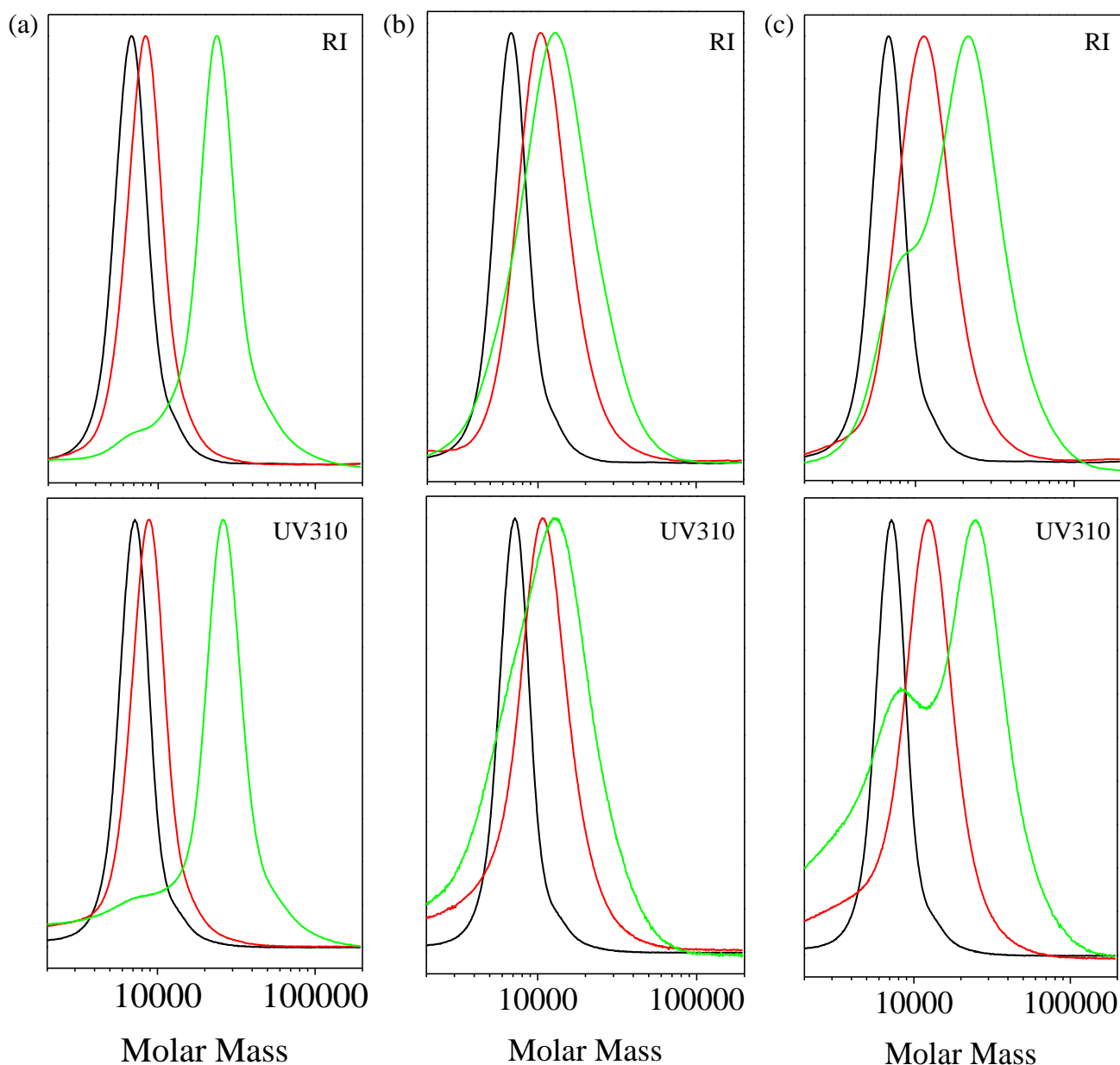


Figure 4: Evolution of normalized molar mass distributions with conversion for (a) P(St-*co*-DPPS)-*bl*-PDMAm at 0 h (—), 3 h (—), and 6 h (—), (b) P(St-*co*-DPPS)-*b*-PPEGA at 0 h (—), 6 h (—), and 14 h (—) and (c) P(St-*co*-DPPS)-*b*-PEDEGA at 0 h (—), 3 h (—), and 6 h (—) from GPC with refractive index (RI) and UV detection at 310 nm (UV310).

3.3. Post Polymerization Functionalization of Phosphine-Containing Polymers

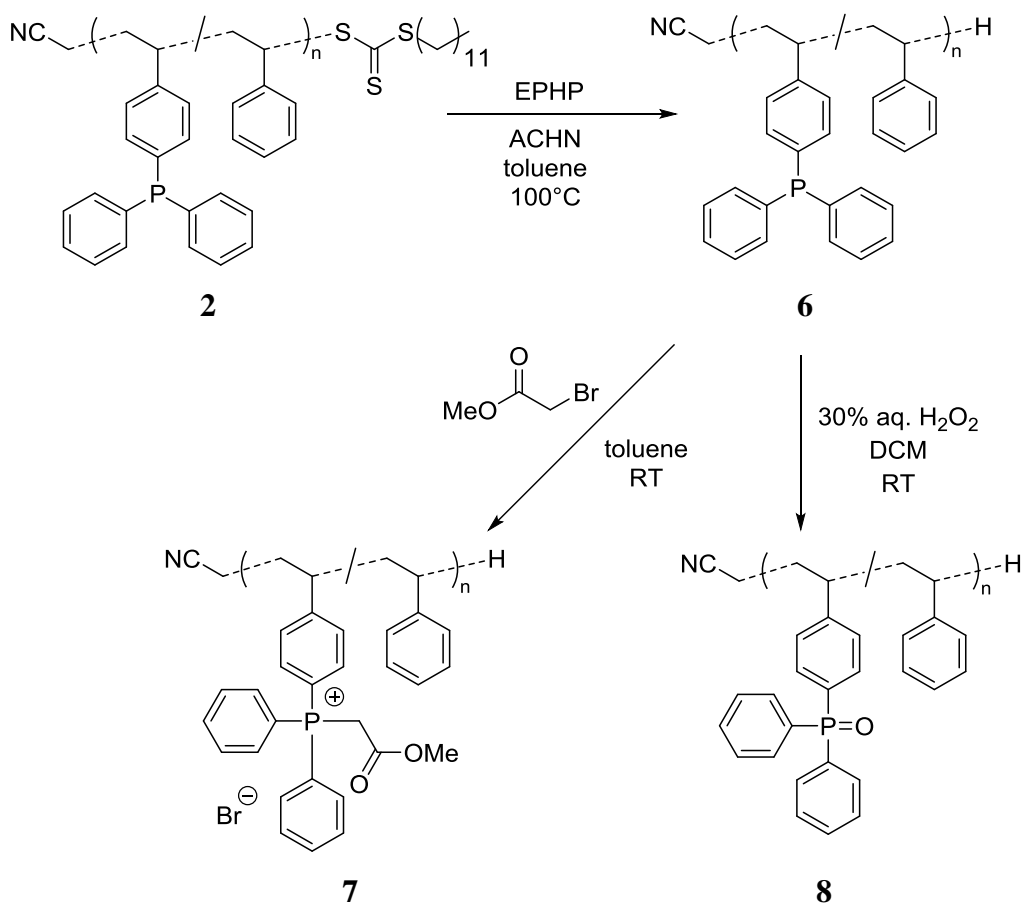
Following on from syntheses of phosphine-containing gradient and block copolymers, we sought to examine the scope for elaboration of the polymeric phosphine functional groups to

phosphine oxides and phosphonium salts. Materials containing these functionalities act as catalysts or reagents in a range of organic transformations and find application more broadly.

To prevent complications associated with the RAFT chain end, post polymerization modification of phosphine functional groups within the synthesized P(St-*co*-DPPS) copolymers was undertaken following radical-induced reduction of the trithiocarbonate chain end from the macro-RAFT agent **2** to give the reduced polymer **6**. This was achieved by adapting a literature procedure,^[64, 84] whereby the polymer bearing trithiocarbonate end-group functionality was heated in toluene at 100 °C, in the presence of ACHN as a radical source and EPHP as hydrogen donor (see **Scheme 3**). Complete end-group removal was confirmed via GPC using UV detection at 310 nm (see Figure S3b and S4) and resulted in negligible changes in the molar mass distribution of the copolymer (see Figure S3a). ³¹P NMR of **6** showed no significant changes in the ratio between phosphine and phosphine oxide from that of the starting material (see **Figure S8**).

Oxidation of the phosphine-functional polymer **6** to the phosphine oxide polymer **8** was achieved stirring a biphasic solution in 30% aqueous H₂O₂ and DCM. This method was adapted from that reported by Li *et al.*^[65] The oxidation to **8** resulted in a slight shift to higher mass in the GPC from that of phosphine starting material **6** (see **Figure S6**), indicating the incorporation of oxygen, providing **8** as a low dispersity polymer. The quantitative conversion of phosphine to phosphine oxide was confirmed by ¹H and ³¹P NMR (see **Figure S7 and S8**).

Additionally the polymeric phosphonium salt **7** was prepared via simple quaternization of **6** with methyl α -bromoacetate in toluene (see **Scheme 3**). Again the successful reaction was confirmed by ¹H and ³¹P NMR (see **Figure S7 and S8**), indicating the presence of the phosphonium group. The M_n and \mathcal{D} obtained for **7** from GPC was dramatically altered from that of the phosphine starting material **6**; this is attributed to interaction between the charged polymer and the chromatographic stationary phase detrimentally affecting the separation.



Scheme 3: Radical induced thiocarbonylthio end-group removal from P(St-co-DPPS) **2** and subsequent synthesis of phosphonium bromide **7** and phosphine oxide **8** containing copolymers by post polymerization modification.

4. Conclusions

The RAFT copolymerization of St and DPPS was investigated to examine the statistical distribution of phosphine-functionality within the copolymers obtained. Thermally initiated RAFT copolymerization of St and DPPS at a variety of feed ratios resulted in a linear increase of molar mass with monomer conversion, providing phosphine-functional copolymers of low dispersity at moderate monomer conversion ($D < 1.2$ at conv. $> 60\%$). In all cases the fraction of DPPS in the resulting copolymer was greater than that in the initial monomer feed (i.e. $F_{\text{DPPS}} > f_{\text{DPPS},0}$). Interestingly the reactivity ratios, estimated from non-linear least squares fit of the copolymerization data, indicate DPPS has a strong tendency to homopolymerize whilst St preferentially copolymerizes with DPPS ($r_{\text{DPPS}} = 4.4$; $r_{\text{St}} = 0.31$). Regardless of DPPS feed

ratio the probability of incorporation of a DPPS unit decreases along the length of the copolymer chain. Simulation of the copolymer sequence distribution indicates the compositional gradient is most pronounced at higher DPPS feeds (i.e. 10 and 25 %). Additionally due to the relative reactivity of the monomers there is a propensity to form DPPS-DPPS dyads.

Phosphine-containing block copolymers of DMAM, mPEGA and EDEGA were synthesized through block extension from a P(St-*co*-DPPS) macro-RAFT agent. The efficiency of block copolymer formation was best with the acrylamide monomer, DMAM. Block copolymers prepared from mPEGA were of low dispersity; however overlap of the molar mass distributions with that of the macro-RAFT agent limited analysis of block extension efficiency via GPC analysis. Use of EDEGA as a model acrylate resulted in a bimodal molar mass distribution indicating poor reinitiation efficiency of the polystyryl-based propagating radical in acrylate polymerization.

Finally access to polymers containing phosphine oxide and phosphonium salt functionalities was illustrated via facile oxidation and quaternization processes respectively following thiocarbonylthio end-group removal. These results further demonstrate the utility RAFT polymerization as a tool for the synthesis of polymers bearing a variety of phosphorus-containing functional groups. Application of these polymers as macromolecular catalysts for a range of organic transformations is of current focus within our laboratory.

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5. Supporting Information

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