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ELECTRONIC SUPPORTING INFORMATION

Poly(thioacrylate)s: Expanding the monomer toolbox of functional polymers

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1. Materials

All chemicals were purchased from Sigma-Aldrich (UK) and used as received at the highest purity available. Dichloromethane (DCM, HPLC grade), benzene (HPLC grade), pentane (HPLC grade), methanol (HPLC grade), tetrahydrofuran (THF, HPLC grade) and toluene (HPLC grade), were used as received. Ethyl acrylate (EA, Aldrich, 99%) was destabilized by passing through a short column of basic aluminium oxide prior to polymerization. All other chemicals and solvents were purchased from Sigma-Aldrich (UK) at the highest purity available and used as received unless mentioned otherwise.

2. Characterization

Differential Scanning Calorimetry (DSC)

A PerkinElmer DSC4000 was used to study glass transition (T_g). An indium standard ($T_m = 156.6$ °C and $\Delta H = 28.72$ J/g) was used to calibrate the instrument and ensure accuracy and reliability of the obtained thermograms. Weights of specimen ranged from 5 to 10 mg and were loaded into the calorimeter, using a sealed 50 µL aluminium pan. Instrument was equilibrated at 25 °C, cooled to -40 °C at a rate of 10 °C /min and heated to 100 °C at a rate of 10 °C/min. The cooling and heating scans were repeated twice to erase the effect of previous thermal history of the samples. From DSC curves T_g were determined from the inflection point temperature.

Thermogravimetric Analysis (TGA)

A TGA Q500 thermo thermogravimetric analyzer (TA Instruments, USA) was used to study thermal stability. The samples were heated from 30 °C ton 1000 °C at a ramp rate of 10 °C/min in a nitrogen environment (the balance nitrogen purge flow was 40 mL/min and the sample purge flow was 60 mL/min). Extrapolated onset temperature was calculated, which denotes the temperature at which weight loss begins (T_0). For the next calculation, the

first derivative of the weight loss was determined and indicates the point of greatest rate of change on the weight loss curve (T_p).

Static Contact Angel Measurement to Determine Surface Wettability

Contact angle (θ) measurements were obtained using a goniometer (DSA100, Kruss, Germany) equipped with a digital camera and image analysis software (*DSA1* version 1.80, Kruss, Germany). Static contact angle of a 5-µl drop of deionized water deposited on spincoated solid surface. Sessile drop method was used to analyse contact angles of the water-substrate interface, which results are the average of six measurements.

Gel permeation chromatography (GPC)

GPC was utilized to determine molecular weight averages and polymer dispersity. GPC measurements were performed on an Agilent 390-LC system equipped with a PL-AS RT autosampler, 2PLgel 5 µm mixed-C columns (300×7.5 mm), a PLgel 5 mm guard column (50×7.5 mm), and a differential refractive index (DRI). The system was eluted with THF containing 2% trimethylamine (TEA) at a flow rate of 1 mL min^{-1} and the DRI was calibrated with linear narrow poly(methyl methacrylate) standards.

Nuclear magnetic resonance (NMR)

^1H NMR spectra were recorded on a Bruker AV-400 at 303 K. $CDCl_3$ and the resonance signal at 7.26 ppm (^1H) was used as residual $CDCl_3$ or for $(CD_3)_2CO$ at 2.05 ppm peak for the chemical shift (δ).

Gas Chromatography

Gas chromatography – flame ionisation detection (GC-FID) analysis was performed using Agilent Technologies 7820A. An Agilent J&W HP-5 capillary column of 30 m x 0.320 mm, film thickness 0.25 µm was used. The oven temperature was programmed as

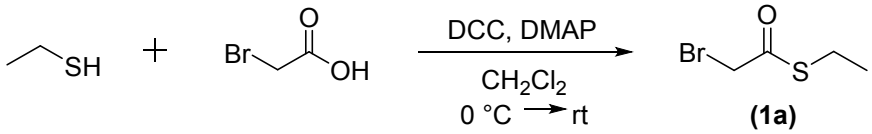
follows: 40 °C (hold for 1 minute) increase at 30 °C min^{-1} to 300 °C (hold for 2.5 minutes). The injector was operated at 250 °C and the FID was operated at 320 °C.

Nitrogen was used as carrier gas at a flow rate of 6.5 mL min^{-1} and a split ratio of 1:1 was applied. Chromatographic data was processed using OpenLab CDS ChemStation Edition, version C.01.05. Conversions were obtained by the comparing the integral of the monomer with the solvent for block copolymers.

3. Preparation of thioacrylate monomers:

3.5 Preparation of ethylthioacrylate (ETA)

Synthesis of S-Ethyl 2-bromoethanethioate (1a)



(1a)

A two-necked 5-L round bottom flask was charged with bromoacetic acid (200 g, 1.439 mol), ethanethiol (140 mL, 1.891 mol) and a catalytic amount of DMAP (17.580 g, 0.144 mol). 1 L of DCM was added and the solution was cooled to 0 °C with stirring under an atmosphere of nitrogen. DCC (17.58 g, 0.144 mol) was diluted in 200 mL of DCM and added dropwise and the solution slowly warmed to room temperature overnight until esterification was complete. The solution was then filtered through Silica and the filtercake was washed several times with DCM. The filtrate was washed with saturated $NaHCO_3$ solution, water and brine and was dried over Na_2SO_4. Evaporation of the solvent in *vacuo* gave (181,68 g, 70%) of a yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.01 (s, Br-C**H**$_2$-), 2.94 (q, J = 7.5 Hz C**H**$_2$-CH_3) and 1.27 (t, J = 7.4 Hz CH_2-C**H**$_3$) ppm.

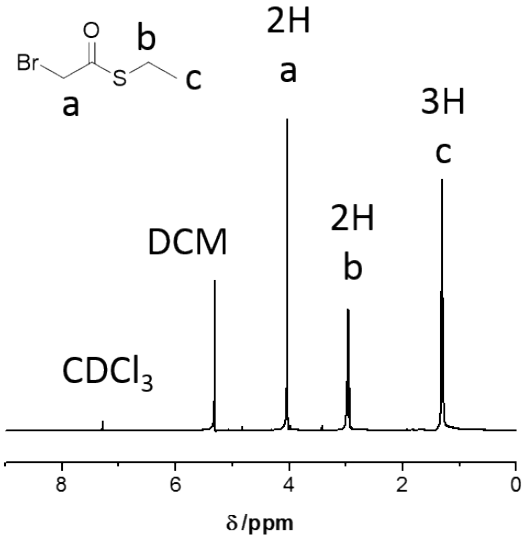
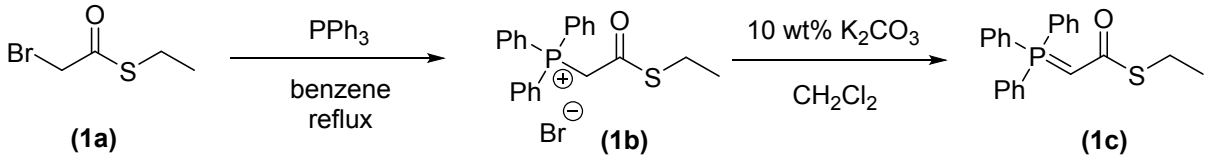


Figure S1. ^{1}H NMR (A) showing successful synthesis of thioester **1a.**

S-Ethyl 2-(triphenyl-λ^{5}-phosphanylidene)ethanethioate (1c)



(1a) **(1b)** **(1c)**

Product 1c (181.0 g, 0.99 mol) and triphenylphosphine (337 g, 1.28 mol) in 750 mL of benzene was heated to reflux under nitrogen for one hour. The solvent was evaporated under reduced pressure to yield white crystals after filtering and washing with toluene. The crystals were then dissolved in 500 mL of DCM and vigorously stirred with 200 mL of 10% aqueous K_2CO_3 solution for 30 min. The organic layer was separated and the aqueous layer was extracted twice with DCM. The combined organic phases were dried over magnesium sulfate and partially concentrated in *vacuo* and diluted in pentane which afforded 4 (259.77 g, 72% yield) of light-brown crystals after 24h.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.70-7.40 (m, P**Ph**$_3$), 3.66 (d, J = 22.7 Hz, -C**H**-), 2.84 (q, J = 7.4 Hz, C**H**$_2$-CH_3) and 1.25 (t, J = 7.4 Hz CH_2-C**H**$_3$) ppm.

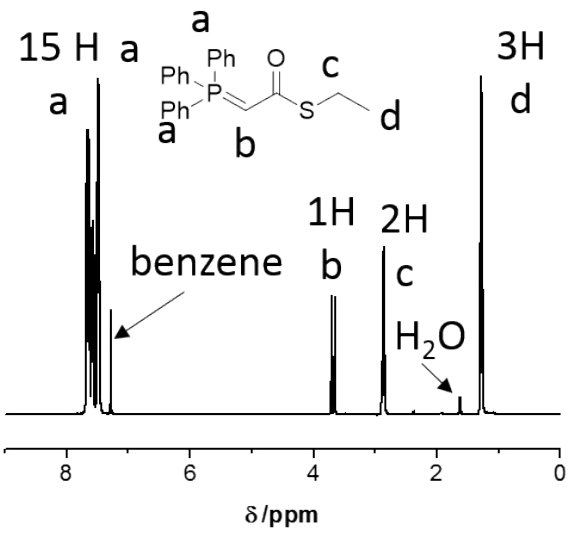
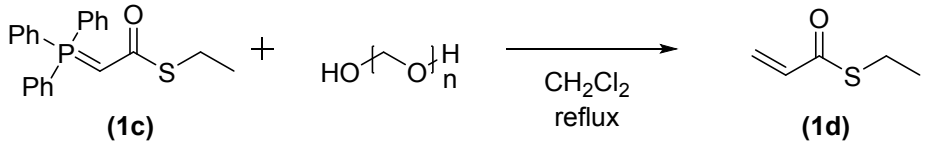


Figure S2. ^{1}H NMR (A) showing successful synthesis of phosphorane **1c.**

Synthesis of S-Ethyl prop-2-enethioate (1d)



(1c) **(1d)**

In a 1-L two-necked flask equipped with a cooling system and magnetic stirrer, (100 g, 0.27 mol) of Wittig reagent 1c were introduced into 700 mL of DCM. Then, (41,7 g, 1.37 mol) of paraformaldehyde was poured into the solution. The mixture was heated for 1 hour under then concentrated in *vacuo* and the residue was suspended in cold pentane (250 mL) and filtered over silica. The filtercake was washed with cold (10:90 Et_2o/pentane). Hydrochinone was added to the solution to prevent polymerization. The solution was distilled over CaH_2 (2 g/L) at reduced pressure (11 mbar/80°C) to yield (17,96 g, 57% yield) of a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz), $CDCl_3$ δ = 6.32 (dd, J = 17.2, 9.7 Hz, C**H**$_2$-CH), 6.28 (dd, J = 17.2, 1.6 Hz, C**H**$_2$-CH), 5.59 (dd, J = 9.8, 1.6 Hz, CH_2-C**H**), 2.89 (q, J = 7.4 Hz, C**H**$_2$-CH_3), 1.21 (t, J = 7.4 Hz, CH_2-CH_3**)**.

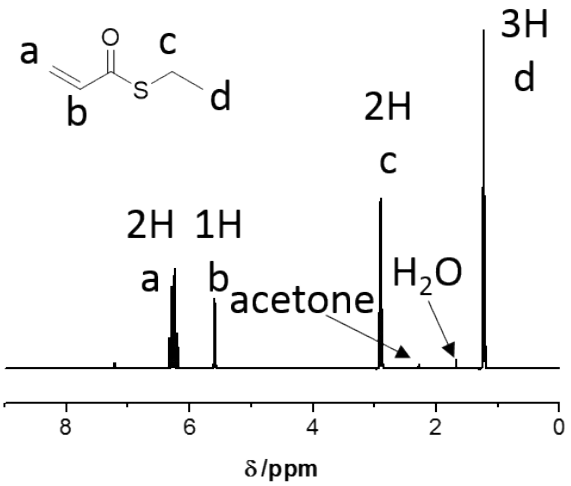
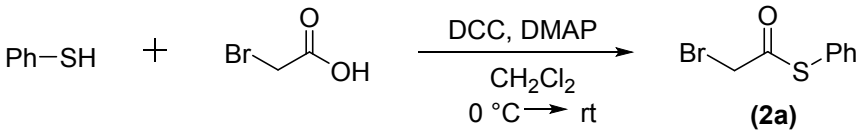


Figure S3. ^{1}H NMR (A) showing successful synthesis of thioacrylate **1d.**

3.2 Preparation of thiophenolacrylate (TPA)

Synthesis of S-Phenyl 2-bromoethanethioate (2d)



A two-necked 2-L round bottom flask was charged with bromoacetic acid (14.08 g, 0.10 mol), thiophenol (13.42 mL, 0.13 mol) and a catalytic amount of DMAP (1.257 g, 10 mmol). 300 mL of DCM was added and the solution was cooled to 0 C with stirring under an atmosphere of nitrogen. DCC (22.02 g, 0.11 mol) was diluted in 200 mL of DCM and added dropwise and the solution slowly warmed to room temperature overnight until esterification was complete. The solution was then filtered through Silica and the filtercake was washed several times with DCM. The filtrate was washed with saturated $NaHCO_3$ solution, water and brine and was dried over $Na2SO_4$. Evaporation of the solvent in *vacuo* gave (14.09 g, 42%) of a yellowish oil.

^{1}H NMR (CDCl3, 400 MHz) δ = 7.30-7.01 (br-m, **Ph**-S-) and 3.94 (s, Br-C**H**$_2$-) ppm.

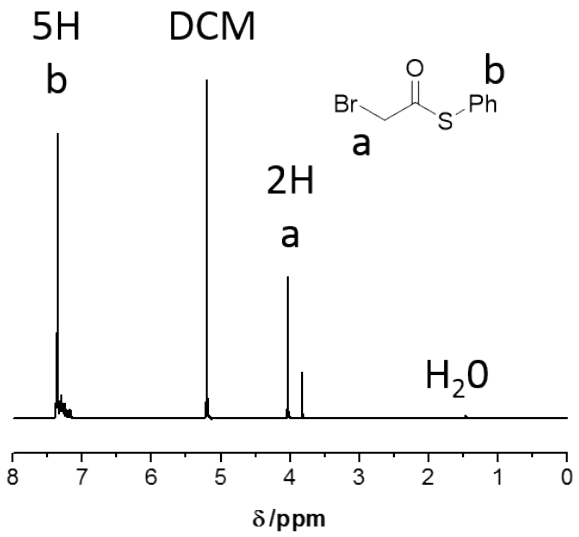
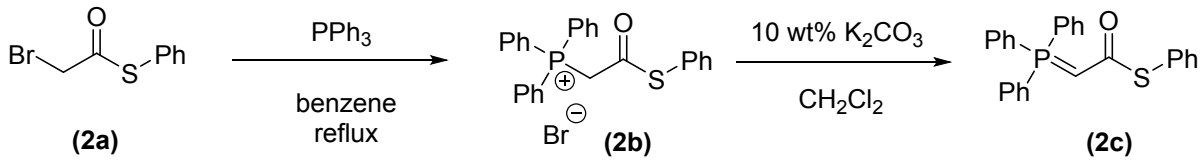


Figure S4. ^{1}H NMR (A) showing successful synthesis of thioester **1a.**

Synthesis of S-Phenyl 2-(triphenyl-λ^5-phosphanylidene)ethanethioate (2c)



The obtained oil (13.93 g, 0.10 mol) and triphenylphosphine (5.134 g, 0.17 mol) in 75 mL of benzene was heated to reflux under nitrogen for one hour. The solvent was evaporated under reduced pressure to yield white crystals after filtering and washing with toluene. The crystals were then dissolved in 75 mL of DCM and vigorously stirred with 50 mL of 10% aqueous K_2CO_3 solution for 30 min. The organic layer was separated and the aqueous layer was extracted twice with DCM. The combined organic phases were dried over magnesium sulfate and partially concentrated in *vacuo* and diluted in pentane which afforded (16.14 g, 44% yield) of light-brown crystals after 24h.

^{1}H NMR (DMSO-d_6, 400 MHz) δ = 7.80-7.45 (m, P**Ph**$_3$), 7.45-7.24 (br-m, **Ph**-S-) and 3.52 (d, J = 22.1 Hz, PPh_3-C**H**) ppm.

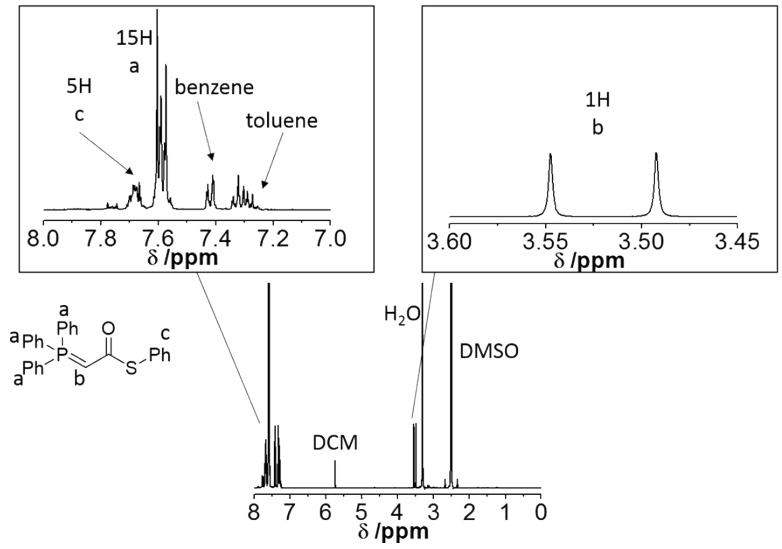
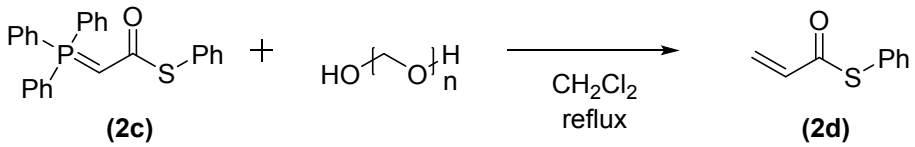


Figure S5. [1]H NMR (A) showing successful synthesis of phosphorane **2c.**

Synthesis of S-Phenyl prop-2-enethioate (2d)



(2c) **(2d)**

In a 1-L two-necked flask equipped with a cooling system and magnetic stirrer, of Wittig reagent 2d were introduced into 700 mL of DCM. Then, (4.59 g, 152 mmol) paraformaldehyde were poured into the solution. The mixture was heated for 1 hour under an atmosphere of argon then concentrated in *vauo* and the residue was suspended in cold pentane (50 mL) and filtered over silica. The filtercake was washed with cold (10:90 Et_2o/pentane). Hydrochinone was added to the solution to prevent polymerization. The solution was distilled over CaH_2 (2 g/L) at reduced pressure to yield (3.20 g, 62% yield) of a colorless oil.

^{1}H NMR (DMSO-d_6, 400 MHz) δ = 7.26 (m, **Ph**-S-), 6.37 (dd, J = 10.4, 6.7 Hz, C**H**$_2$-CH-S-), 6.13 (d, J = 17.2 Hz, C**ha**$_1$-CH-S-) and 5.72 (d, J = 10.4 Hz C**Ha$_2$**-CH-S-) ppm.

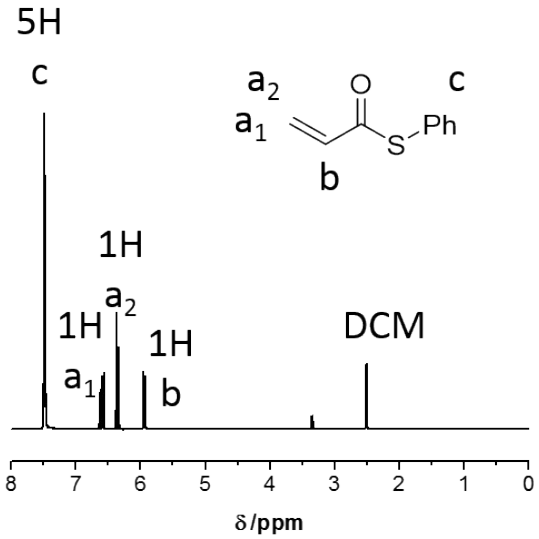
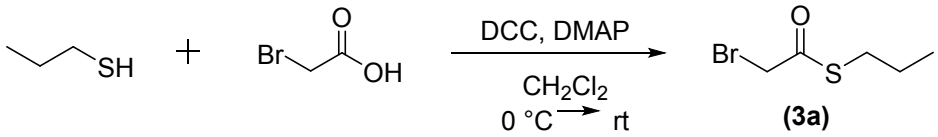


Figure S6. ^{1}H NMR (A) showing successful synthesis of thioacrylate **2d.**

3.3 Preparation of propylthioacrylate

Synthesis of S-Propyl 2-bromoethanethioate (3a)



A two-necked 5-L round bottom flask was charged with bromoacetic acid (54 g, 0.39 mol), 1-propanethiol (50 mL, 0.50 mol) and a catalytic amount of DMAP (5.05 g, 0.04 mmol). 200 mL of DCM was added and the solution was cooled to 0°C with stirring under an atmosphere of nitrogen. DCC (89.50 g, 0.43 mol) was diluted in 100 mL of DCM and added dropwise and the solution slowly warmed to room temperature overnight until esterification was complete. The solution was then filtered through Silica and the filtercake was washed several times with DCM. The filtrate was washed with saturated $NaHCO_3$ solution, water and brine and was dried over $Na2SO_4$. Evaporation of the solvent in *vacuo* gave (60 g, 74%) of a yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.01 (s, Br-C**H**$_2$-), 2.94 (t, J = 7.5 Hz, C**H**$_2$-CH$_2$-CH3), 1.63 (sxt, J = 7.3 Hz, -CH$_2$-C**H**$_2$-CH$_3$) and 1.27 (t, J = 7.4 Hz, -CH$_2$-C**H**$_3$) ppm.

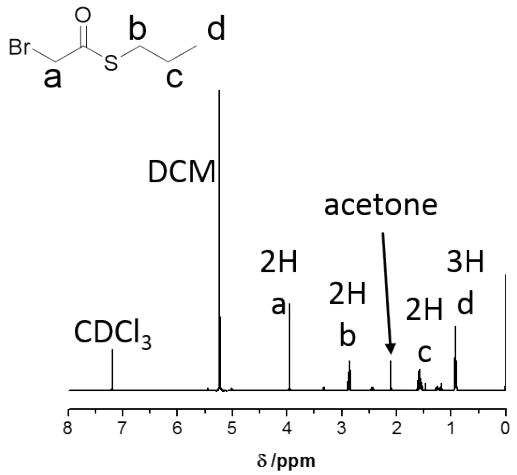
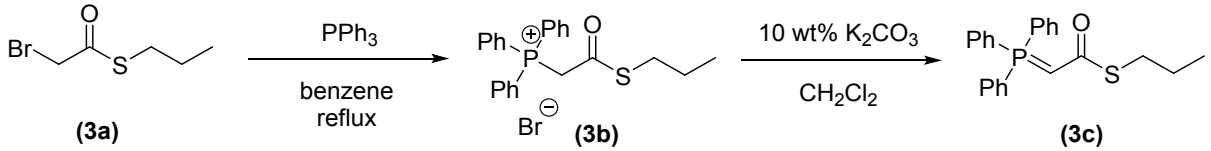


Figure S7. ^{1}H NMR (A) showing successful synthesis of thioester **3a.**

Synthesis of S-Propyl 2-(triphenyl-λ^5-phosphanylidene)ethanethioate (3c)



The obtained oil (60 g, 0.304 mol) and triphenylphosphine (103.7 g, 0.396 mol) in 200 mL of benzene was heated to reflux under nitrogen for one hour. The solvent was evaporated under reduced pressure to yield white crystals after filtering and washing with toluene. The crystals were then dissolved in 200 mL of DCM and vigorously stirred with 200 mL of 10% aqueous K_2CO_3 solution for 30 min. The organic layer was separated and the aqueous layer was extracted twice with DCM. The combined organic phases were dried over magnesium sulfate and partially concentrated in *vacuo* and diluted in pentane which afforded 4 (58.9 g, 50%) of light-brown crystals after 24h.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.70-7.43 (m, **Ph**$_3$P), 3.66 (d, J = 20.6 Hz, Ph_3P-C**H**-), 2.82 (t, J = 7.2 Hz, C**H**$_2$-CH_2-CH_3), 1.61 (sxt, J = 7.3 Hz, -CH_2-C**H**$_2$-CH_3) and 0.96 (t, J = 7.4 Hz, -CH_2-C**H**$_3$) ppm.

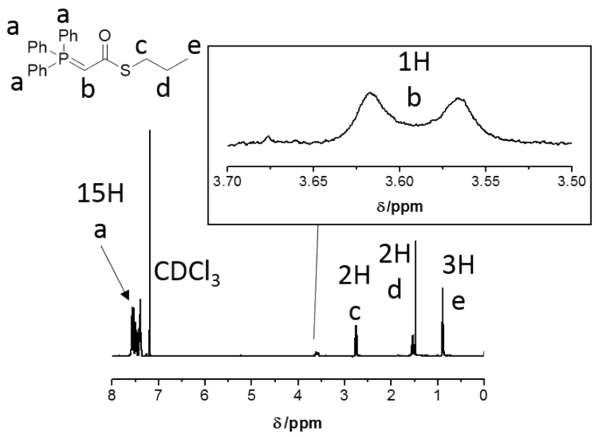
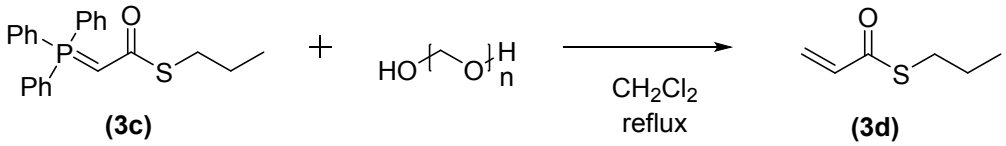


Figure S8. ^{1}H NMR (A) showing successful synthesis of phosphorane **3c.**

Synthesis of S-Propyl prop-2-enethioate (3d)



Phosphorane (35 g, 0.085 mol) and paraformaldehyde (12.77 g, 0.358 mol) were poured into a nitrogen flushed round botton flask. The mixture was heated for 1 hour under an atmosphere of argon at reflux temperature, then concentrated in *vauo* and the residue was suspended in cold pentane (100 mL) and filtered over silica. The filtercake was washed with cold (10:90 Et_2o/pentane). Hydrochinone was added to the solution to prevent polymerization. The solution was distilled over CaH_2 (2 g/L) at reduced pressure to yield a yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.39-6.15 (m, C**H**$_2$-CH-), 5.59 (dd, J = 9.9, 1.25 Hz, CH_2-C**H**), 2.89 (t, J = 8.3 Hz, C**H**$_2$-CH_2-CH_3), 1.58 (sxt, J = 8.4 Hz, -CH_2-C**H**$_2$-CH_3) and 0.93 (t, J = 7.4 Hz, -CH_2-C**H**$_3$) ppm.

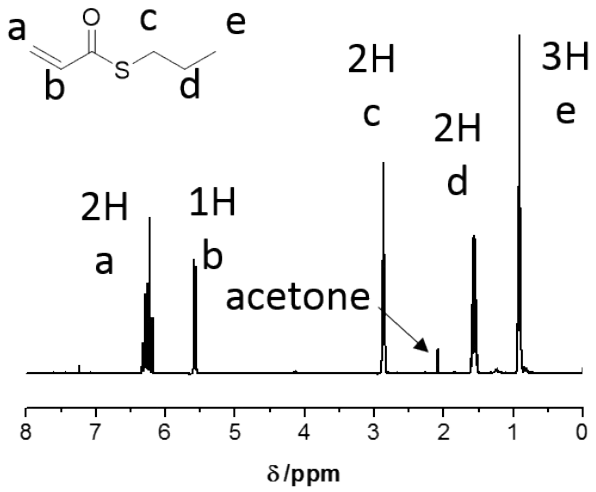
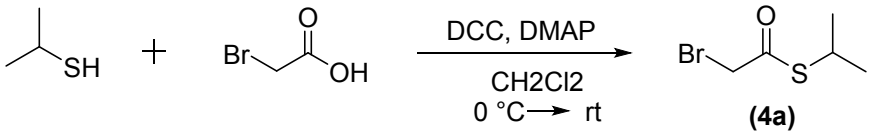


Figure S9. ^{1}H NMR (A) showing successful synthesis of thioester **3d.**

3.4 Preparation of Isopropylthioacrylate (IPTA)

Synthesis of S-Isopropyl 2-bromoethanethioate (4a)



A two-necked 5-L round bottom flask was charged with bromoacetic acid (70 g, 0.51 mol), 2-propanethiol (60 mL, 0.66 mol) and a catalytic amount of DMAP (6.06 g, 0.05 mmol). 200 mL of DCM was added and the solution was cooled to 0°C with stirring under an atmosphere of nitrogen. DCC (107 g, 0.52 mol) was diluted in 100 mL of DCM and added dropwise and the solution slowly warmed to room temperature overnight until esterification was complete. The solution was then filtered through Silica and the filtercake was washed several times with DCM. The filtrate was washed with saturated $NaHCO_3$ solution, water and brine and was dried over Na_2SO_4. Evaporation of the solvent in *vacuo* gave (76 g, 77%) of a yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.99 (s, Br-CH_2-), 2.94 (quint, J = 6.9 Hz, CH-$(CH_3)_2$) and 1.33 (d, J = 6.9 Hz, -CH-$(CH_3)_2$) ppm.

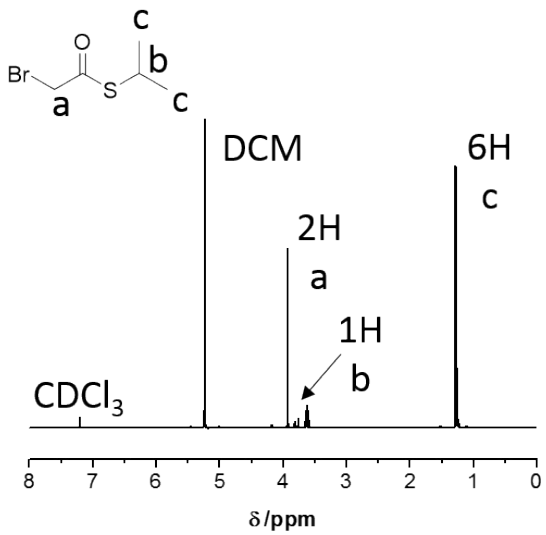
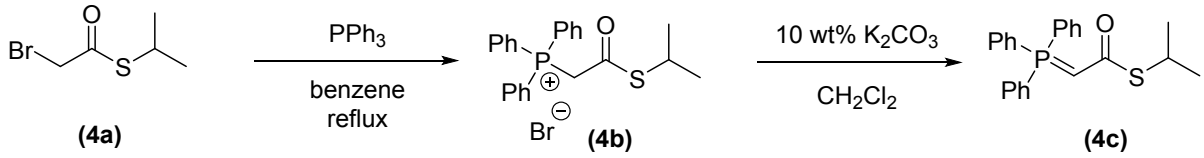


Figure S10. ^{1}H NMR (A) showing successful synthesis of thioester **4a.**

Synthesis of S-Isopropyl 2-(triphenyl-λ^5-phosphanylidene)ethanethioate (4c)



The obtained oil (30 g, 0.152 mol) and triphenylphosphine (51.5 g, 0.198 mol) in 120 mL of benzene was heated to reflux under nitrogen for one hour. The solvent was evaporated under reduced pressure to yield white crystals after filtering and washing with toluene. The crystals were then dissolved in 150 mL of DCM and vigorously stirred with 150 mL of 10% aqueous K_2CO_3 solution for 30 min. The organic layer was separated and the aqueous layer was extracted twice with DCM. The combined organic phases were dried over magnesium sulfate and partially concentrated in *vacuo* and diluted in pentane which afforded 4c (30 g, 49%) of lightbrown crystals after 24h.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.89-7.39 (m, **Ph**$_3$P), 5.64 (dd, J = 9.41, 1.88 Hz, Ph_3P-C**H**), 3.74 (quint, J = 6.9 Hz, -C**H**-$(CH_3)_2$) and 1.34 (d, J = 6.9 Hz, -CH-(C**H**$_3)_2$) ppm.

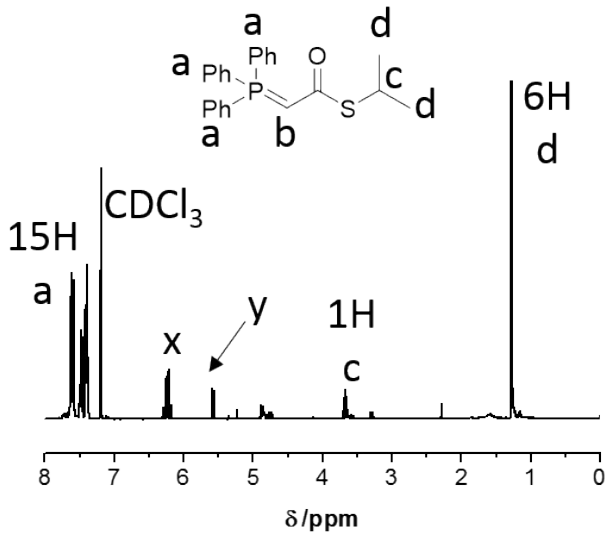
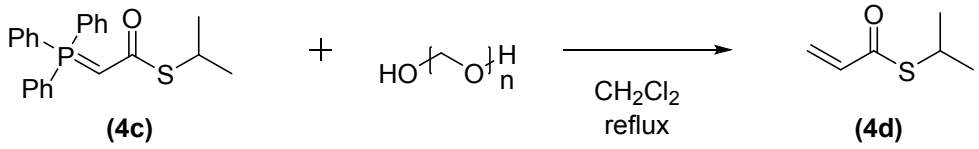


Figure S11. ^{1}H NMR (A) showing successful synthesis of phosphorane **4c.**

Synthesis of S-Isopropyl prop-2-enethioate (4d)



Then, phosphorane (30 g, 0.073 mol) and paraformaldehyde (11 g, 0.36 mol) were poured into a nitrogen flushed round botton flask. The mixture was heated for 1 hour under an atmosphere of argon at reflux temperature, then concentrated in *vacuo* and the residue was suspended in cold pentane (100 mL) and filtered over silica. The filtercake was washed with cold (10:90 Et_2o/pentane). Hydrochinone was added to the solution to prevent polymerization. The solution was distilled over CaH_2 (2 g/L) at reduced pressure to yield yellowish crystals.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.38-6.20 (m, C**H**$_2$-CH-), 5.62 (dd, J = 9.54, 1.88 Hz, CH_2-C**H**-), 3.72 (quint, J = 6.9 Hz, -C**H**-$(CH_3)_2$) and 1.33 (d, J = 7.0 Hz, -CH-(C**H**$_3)_2$) ppm.

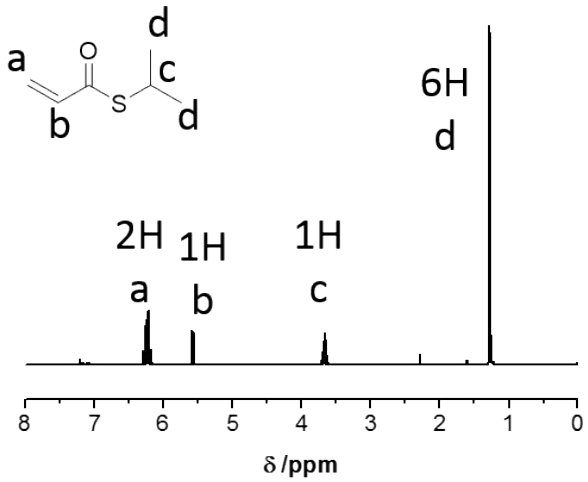


Figure S12. [1]H NMR (A) showing successful synthesis of thioacrylate **4d.**

Figure S13. Different Wittig reagents that have been prepared and have been used/can be used for Wittig reaction to yield respective thioacrylate via Wittig reaction with paraformaldehyde.

4. Polymerization

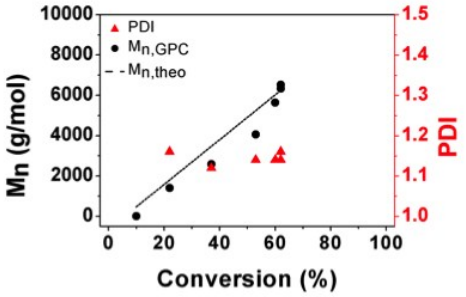
4.1 Poly(thiophenol acrylate), DP = 60

In a typical polymerization, (0.4092 g, 2.492 mmol) thiophenol acrylate, BDTMP (14.7 mg, 0.041 mmol), V-601 (1.00 mg, 4.34 mmol), 0.04 mL of mesitylene and 50% 0.4 mL toluene were charged into a schlenk tube and degassed by gentle bubbling of N_2 gas for 30 minutes. Schlenk tube was submerged into an oil bath at 70°C or 100°C. Samples were taken *via* degassed syringe at desired time points and analyzed. The samples were then analyzed by GPC, GC and ^{1}H NMR.

A

Time (min)	$M_{n,theo}$ (g·mol)	$M_{n,GPC}$ (g·mol) [a]	PDI [a]	Conversion [b]
15	1410	2130	1.16	10
30	2590	4000	1.12	22
45	4070	5100	1.14	37
60	5640	5700	1.14	53
120	6530	6430	1.16	62

B



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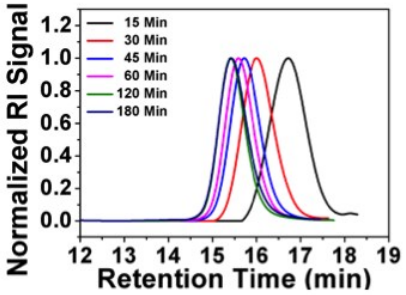

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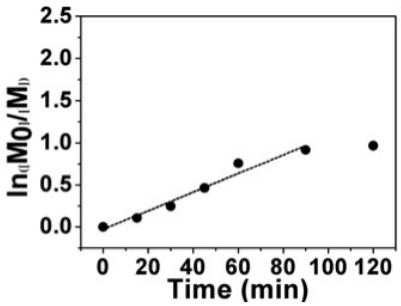


Figure S14. (A) Macromolecular parameters for P(TPA), [a] THF eluent, linear PMMA standard, [b] measured by ^{1}H NMR. (B) M_n vs. conversion plot for P(TPA).Black symbols represent $M_{n,GPC}$, dashed lines represents respective $M_{n,theo}$ and red symbols represents their $Đ$. (C) GPC traces of the obtained poly(thiophenol acrylate)s with DP = 60 in toluene at 70°C. (D) Ln($[M]_0$/[M]) *vs*. time plot for P(TPA).

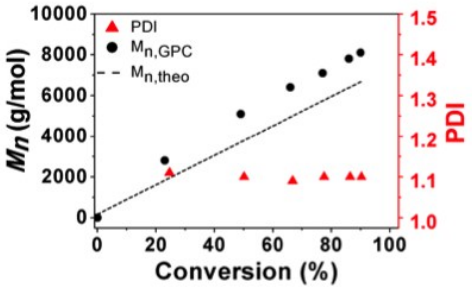
4.2 Poly(ethylthio acrylate), DP = 60

In a typical polymerization, (0.629 g, 5.414 mmol) ethylthioacrylate, BDTMP (33.9 mg, 0.081 mmol), V-601 (1.92 mg, 0.008 mmol), 5% v/v mesitylene and 50% v/v toluene were charged into a schlenk tube and degassed by gentle bubbling of N_2 gas for 30 minutes. Schlenk tube was submerged into an oil bath at 70°C or 100°C. Samples were taken *via* degassed syringe at desired time points and analyzed. The samples were then analyzed by GPC, GC and ^{1}H NMR.

A

Time (min)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol) [a]	PDI [a]	Conversion [b]
15	2020	2790	1.11	23
30	3840	5130	1.10	49
45	5010	6370	1.09	66
60	5790	7060	1.10	77
90	6200	7820	1.10	86
120	6690	8130	1.10	90

B



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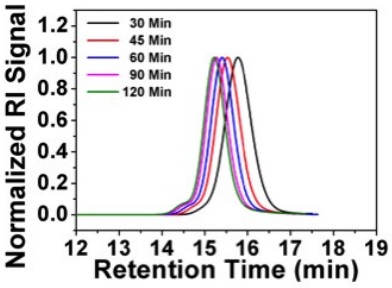

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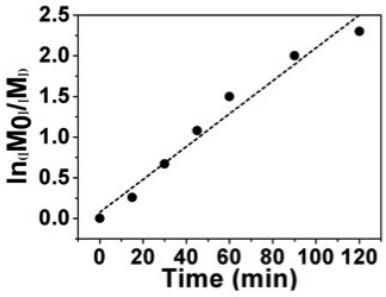


Figure S15. (A) Macromolecular parameters for P(ETA), [a] THF eluent, linear PMMA standard, [b] measured by ^{1}H NMR. (B) M_n vs. conversion plot for P(TPA). Black symbols represent $M_{n,GPC}$, dashed lines represents respective $M_{n,theo}$ and red symbols represents their *Đ*. (C) GPC traces of the obtained poly(ethylthio acrylate)s with DP = 60 in toluene at 70°C. (D) Ln([M]$_0$/[M]) *vs*. time plot for P(ETA).

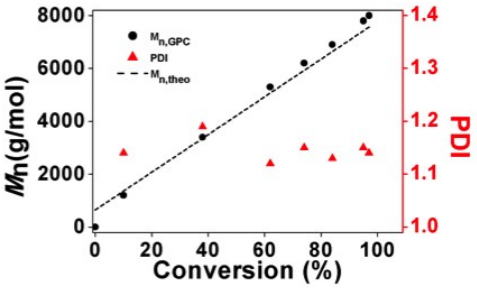
4.3 Poly(isopropylthio acrylate), DP = 60

In a typical polymerization, (0.40 g, 3.077 mmol) isopropylthioacrylate, BDTMP (21.5 mg, 0.051 mmol), V-601 (1.18 mg, 0.005 mmol), 0.04 mL mesitylene and 0.4 mL of toluene were charged into a schlenk tube and degassed by gentle bubbling of N_2 gas for 30 minutes. Schlenk tube was submerged into an oil bath at 70°C or 100°C. Samples were taken *via* degassed syringe at desired time points and analyzed. The samples were then analyzed by GPC, GC and ^{1}H NMR.

A

Time (min)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol) [a]	PDI [a]	Conversion [b]
15	1200	1570	1.14	10
30	3390	3840	1.19	38
45	5300	5490	1.12	62
60	6200	5990	1.15	74
90	6900	6710	1.13	84
120	7840	7050	1.15	95
180	8000	7330	1.14	97

B



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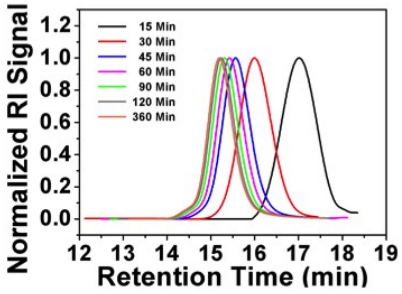

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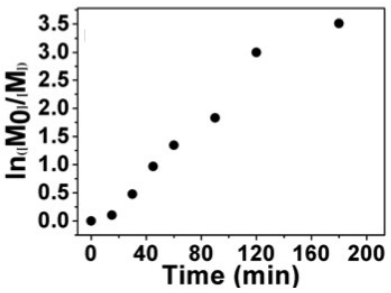


Figure S16. (A) Macromolecular parameters for P(*i*-PTA), [a] THF eluent, linear PMMA standard, [b] measured by ^{1}H NMR. (B) M_n vs. conversion plot for P(*i*-PTA), Black symbols represent $M_{n,GPC}$, dashed lines represents respective $M_{n,theo}$ and red symbols represents their *Đ*. (C) GPC traces of the obtained poly(isopropylthio acrylate)s with DP = 60 in toluene at 70°C with [I] = 0.1 mol%. (D) Ln([M]$_0$/[M]) *vs*. time plot for P(*i*-PTA).

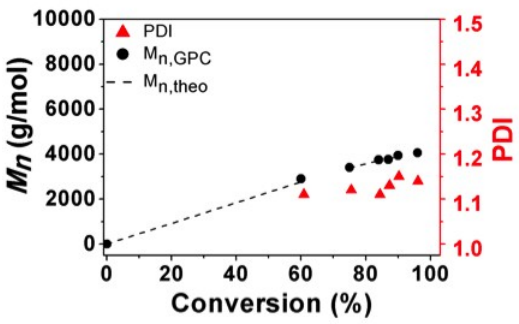
4.4 Poly(propylthio acrylate), DP = 60

In a typical polymerization, (0.65 g, 4.99 mmol) propylhioacrylate, BDTMP (34.05 mg, 0.081 mmol), V-601 (1.88 mg, 0.008 mmol), 0.04 mL mesitylene and 0.4 mL of toluene were charged into a schlenk tube and degassed by gentle bubbling of N_2 gas for 30 minutes. Schlenk tube was submerged into an oil bath at 70°C or 100°C. Samples were taken *via* degassed syringe at desired time points and analyzed. The samples were then analyzed by GPC, GC and ^{1}H NMR.

A

Time (min)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol) [a]	PDI [a]	Conversion [b]
15	2760	2880	1.11	60
30	3400	3400	1.11	75
45	5700	3750	1.11	84
60	3800	3770	1.13	87
90	3930	3950	1.15	90
120	4200	4060	1.14	96

B



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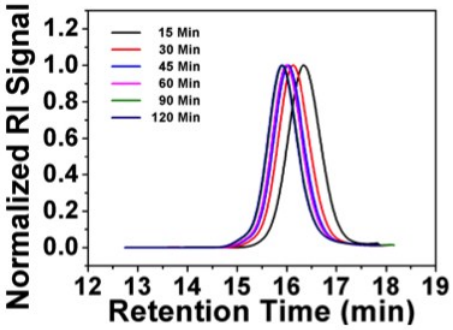

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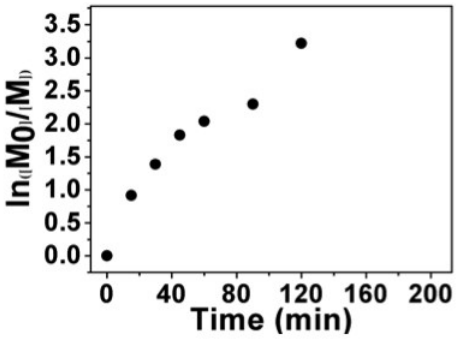


Figure S17. (A) Macromolecular parameters for P(*n* -PTA), [a] THF eluent, linear PMMA standard, [b] measured by ^{1}H NMR. (B) M_n vs. conversion plot for P(*n*-PTA), Black symbols represent $M_{n,GPC}$, dashed lines represents respective $M_{n,theo}$ and red symbols represents their

Đ. (C) GPC traces of the obtained poly(isopropylthio acrylate)s with DP = 60 in toluene at 70°C with [I] = 0.1 mol%. (D) Ln($[M]_0/[M]$) *vs*. time plot for P(*n*-PTA).

4.5 Poly(ethylthio acrylate), DP = 120

In a typical polymerization, (0.58 g, 5.00 mmol) ethylthioacrylate, BDTMP (17 mg, 0.04 mmol), V-601 (0.9 mg, 0.004 mmol), 0.06 mesitylene and 0.6 mL toluene were charged into a schlenk tube and degassed by gentle bubbling of N_2 gas for 30 minutes. Schlenk tube was submerged into an oil bath at 70°C or 100°C. Samples were taken *via* degassed syringe at desired time points and analyzed. The samples were then analyzed by GPC, GC and ^{1}H NMR.

Table S1. Macromolecular parameters for homopolymerization of ETA with DP = 120

Time (min)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol) [a]	PDI [a]	Conversion [b]
15	1320	7100	1.11	13
30	3900	10600	1.11	50
45	4940	12310	1.12	65
60	5850	12700	1.12	78
90	6470	13600	1.14	87
120	6750	13800	1.16	91
180	6960	13500	1.19	94

[a] THF eluent, linear PMMA standard, [b] measured by ^{1}H NMR.

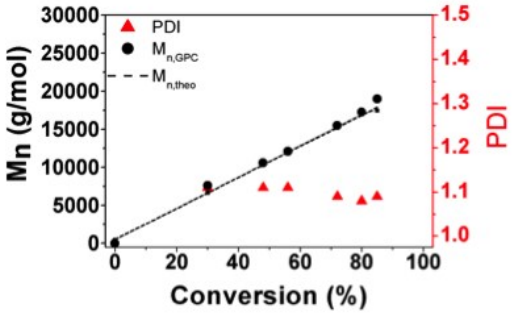
4.6 Homopolymerization of ethylthio acrylate with DP = 180

In a typical polymerization, (1.14 g, 9.83 mmol) ethylthioacrylate, BDTMP (23.00 mg, 0.05 mmol), V-601 (1.26 mg, 0.005 mmol), 0.11 mL mesitylene and 1.14 mL of toluene were charged into a schlenk tube and degassed by gentle bubbling of N_2 gas for 30 minutes. Schlenk tube was submerged into an oil bath at 70°C or 100°C. Samples were taken *via* degassed syringe at desired time points and analyzed. The samples were then analyzed by GPC, GC and ^{1}H NMR.

A

Time (min)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol) [a]	PDI [a]	Conversion [b]
30	10400	10600	1.11	30
45	12100	12100	1.11	48
60	15400	15500	1.11	56
90	17100	17300	1.09	72
120	17500	19000	1.09	80

B



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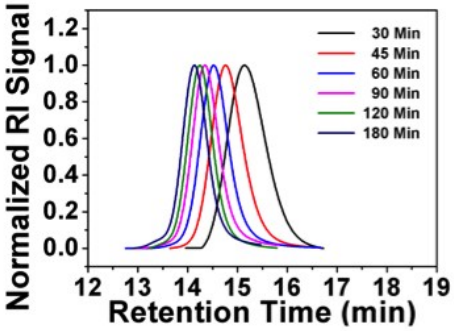

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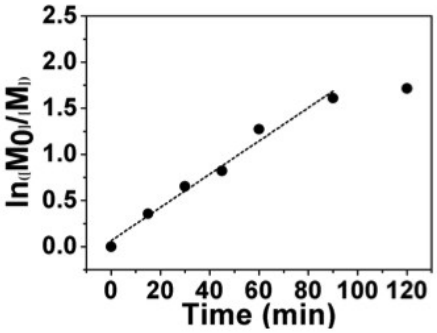


Figure S18. (A) Macromolecular parameters for P(ETA) with DP = 180, [a] THF eluent, linear PMMA standard, [b] measured by ^{1}H NMR. (B) M_n vs. conversion plot for P(TPA). Black symbols represent $M_{n,GPC}$, dashed lines represents respective $M_{n,theo}$ and red symbols represents their $Đ$. (C) GPC traces of the obtained poly(ethylthio acrylate)s with DP = 60 in toluene at 70°C. (D) Ln($[M]_0$/[M]) *vs*. time plot for P(ETA).

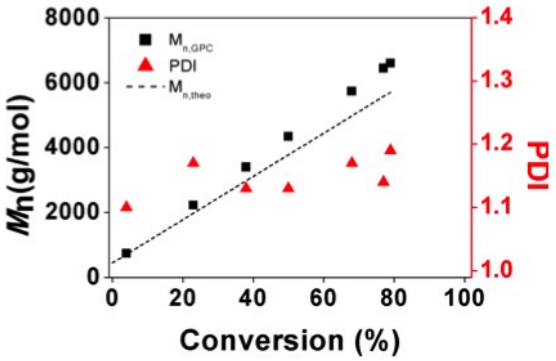
4.7 Homopolymerization of isopropylthio acrylate with DP = 60 and [I] = 0.01 mol%

In a typical polymerization, (0.408 g, 3.52 mmol) ethylthioacrylate, BDTMP (23.6 mg, 0.056 mmol), V-601 (0.117 mg, 0.0005 mmol), 0.11 mL mesitylene and 1.14 mL of toluene were charged into a schlenk tube and degassed by gentle bubbling of N_2 gas for 30 minutes. Schlenk tube was submerged into an oil bath at 70°C. Samples were taken *via* degassed syringe at desired time points and analyzed. The samples were then analyzed by GPC, GC and ^{1}H NMR.

A

Time (min)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol) [a]	PDI [a]	Conversion [b]
15	730	800	1.10	4
30	2220	2090	1.17	23
45	3390	3170	1.13	38
60	4330	4130	1.13	50
90	5730	5010	1.17	68
120	6440	5340	1.14	77
180	6590	5520	1.19	79

B



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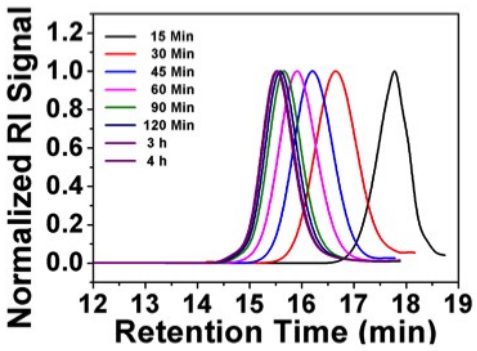

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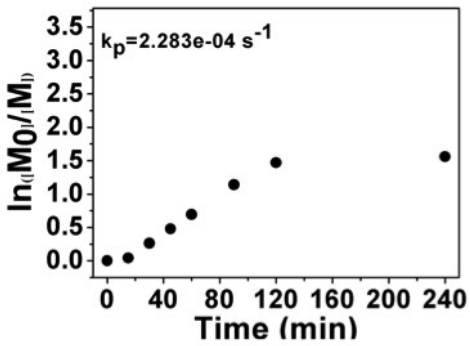

Figure S19. (A) Macromolecular parameters for P(*i*-PTA), [a] THF eluent, linear PMMA standard, [b] measured by ^{1}H NMR. (B) M_n vs. conversion plot for P(*i*-PTA), Black symbols represent $M_{n,GPC}$, dashed lines represents respective $M_{n,theo}$ and red symbols represents their *Đ*. (C) GPC traces of the obtained poly(isopropylthio acrylate)s with DP = 60 in toluene at 70°C with [I] = 0.01 mol%. (D) Ln([M]$_0$/[M]) *vs*. time plot for P(*i*-PTA).

4.8 Block copolymerization of ETA with EA, DP = 60

In a typical chain extension experiment, (0.59 g, 5.08 mmol) ethylthioacrylate, BDTMP (34.4 mg, 0.082 mmol), V-601 (2 mg, 0.0087 mmol), 0.06 mL mesitylene and 0.6 mL of toluene were charged into a schlenk tube and degassed by gentle bubbling of N_2 gas for 30 minutes. Schlenk tube was submerged into an oil bath at 70°C. Sample was taken *via*

degassed syringe after 4.5 h and block was chain extended with 0.4924 g (4.924 mmol) ethylacrylate in 0.49 mL of toluene and samples were measured at desired time intervals.

Table S2. Macromolecular parameters for P(ETA-*b*-EA).

Time (min)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol) [a]	PDI [a]	Conversion [b]
1st Block				
4.5 h	6960	7070	1.12	94
2nd Block				
15	7640	8280	1.13	11
30	8220	8900	1.13	21
45	9120	10150	1.17	36
60	9780	10800	1.13	47
90	10500	11800	1.14	59
120	10980	12400	1.14	67
150	11580	13300	1.14	77
240	12060	13800	1.14	85

[a] THF eluent, linear PMMA standard, [b] measured by ^{1}H NMR.

4.8 Block copolymerization of EA with ETA, DP = 60

In a typical chain extension experiment, (0.4946 g, 4.94 mmol) ethylacrylate, BDTMP (36.0 mg, 0.086 mmol), V-601 (2 mg, 0.0087 mmol), 0.05 mL mesitylene and 0.5 mL of toluene were charged into a schlenk tube and degassed by gentle bubbling of N_2 gas for 30

minutes. Schlenk tube was submerged into an oil bath at 70°C. Sample was taken *via* degassed syringe after 4.5 h and block was chain extended with 0.58 g (5.00 mmol) ethylthioacrylate in 0.49 mL of toluene and samples were measured at desired time intervals.

Table S3. Macromolecular parameters for P(EA-*b*-ETA).

Time (min)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol) [a]	PDI [a]	Conversion [b]
1st Block				
4.5 h	5940	6910	1.17	92
2nd Block				
15	6850	8400	1.19	13
30	8240	9500	1.20	33
45	9072	10660	1.20	45
60	9700	10950	1.22	54
90	10600	11700	1.23	66
120	10900	12400	1.21	71
150	11400	12600	1.22	79
240	11800	12900	1.23	84

[a] THF eluent, linear PMMA standard, [b] measured by ^{1}H NMR.