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Electronic Supplementary Information for:

Dispersity Control in Atom Transfer Radical Polymerizations through Addition of Phenylhydrazine

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Scheme S1. Polymerization of tert-butyl acrylate using ATRP

Calculation of Molecular Weight with NMR Analysis

We calculated M_n from the ¹H NMR data using end-group analysis and the theoretical M_n using the reaction conversion ($M_{n,NMR}$).

End-group analysis: The degree of polymerization (DP) was calculated from the areas of the $-(CH_3)_2C$ - peak of the initiator (peak c, area A_c, labeled in Figures S1, S4, S7) and of the $-(CH_3)_3C$ peak of the polymer (peak f, area A_f, labeled in Figures S1, S4, S7), as DP = (6A_f /9A_c). Subsequently, DP was used to calculate the $M_{n,NMR}$.

Theoretical: From the conversion obtained from the ¹H-NMR data obtained prior to purification (for example, shown in Figure S2), we calculated the theoretical M_n as $M_{n,th}$ = (Conversion × [Monomer]₀/ [Initiator]₀) + MW_{EBiB}).



Figure S1. ¹H NMR spectrum for PtBA synthesized without PH addition ([PH] : [EBiB] = 0:1). For this polymer, M_n = 13.2 kg mol-1 and \mathcal{D} = 1.08. The ratio of (peak f + peak d) / (peak e) was 11.05 (theoretical value = 11) and the ratio of (peak c) /(peak b + peak g) was 2.03 (theoretical value = 2). ¹H-NMR peak assignments (CDCl₃, δ , ppm): 2.08 – 2.32 (br, methine CH of the polymer backbone), 1.72 – 1.90 (br, meso methylene CH₂ of the polymer backbone), 1.28 – 1.69 (br, meso, and racemo CH₂ of the polymer backbone), 1.20 – 1.67 (br, (CH₃)₃C), 1.18 – 1.25 ppm (methyl resonance of CH₃CH₂O group from EBiB), 1.06 – 1.13 ppm (methyl resonance from (CH₃)₂C group from EBiB) and 4.02 – 4.12 ppm (methine resonance of CHBr and methylene resonance from CH₃CH₂O group from EBiB)In the range of 1.20 – 1.70 ppm, peaks were deconvoluted using the mixed Gaussian and Lorentzian functions in the JEOL software.



Figure S2. ¹H NMR spectra for PtBA synthesized without phenylhydrazine (PH) addition ([PH]:[EBiB] = 0:1) at different reaction times. Spectra were taken directly after removing the aliquot from the reaction flask without purification to determine the monomer conversion. Respective peaks are marked on the spectra.



Figure S3. GPC refractometer data for PtBA synthesized without PH ([PH]:[EBiB] = 0:1) at different reaction times. Molecular weight and dispersity for each polymer are given in Table S1.



Figure S4. ¹H NMR spectrum for PtBA synthesized with PH addition ([PH] : [EBiB] = 1:1). For this polymer, $M_n = 10.2$ kg mol⁻¹ and D = 1.78. The ratio of (peak f + peak d) / (peak e) was 11.08 (theoretical value = 11) and the ratio of (peak c) /(peak b + peak g) was 2.52 (theoretical value = 2). In the range of 1.20 - 1.70 ppm, peaks were deconvoluted using the mixed Gaussian and Lorentzian function in the Jeol software. Peaks in region of 7.08 – 7.25 ppm are attributed to chain ends terminated with PH (details in main text), which are absent in Figure S1.



Figure S5. ¹H NMR spectra for PtBA with [PH]:[EBiB] = 1:1 at different reaction times. Spectra were taken directly after removing the aliquot from the reaction flask without purification to determine the monomer conversion.



Figure S6. GPC refractometer data for PtBA synthesized using [PH]:[EBiB] = 1:1 at different reaction times. Molecular weight and dispersity for each polymer are given in Table S1.



Figure S7. ¹H NMR spectrum for PtBA synthesized with PH addition ([PH] : [EBiB] = 3:1). For this polymer, $M_n = 6.46$ kg mol⁻¹ and D = 1.71. The ratio of (peak f + peak d) / (peak e) was 11.07 (theoretical value = 11) and the ratio of (peak c) /(peak b + peak g) was 2.56 (theoretical value = 2). Ratio of (peak x) /(peak y) was 1.52 (theoretical value = 1.5). In the range of 1.20 – 1.70 ppm, peaks were deconvoluted using the mixed Gaussian and Lorentzian function in the Jeol software. Peaks in region of 7.08 – 7.25 ppm are attributed to chain ends terminated with PH (details in main text), which are absent in Figure S1.



Figure S8. ¹H NMR spectra for PtBA with [PH]:[EBiB] = 3:1 at different reaction times. Spectra were taken directly after removing the aliquot from the reaction flask without purification to determine the monomer conversion.



Figure S9. GPC refractometer data for PtBA synthesized using [PH]:[EBiB] = 3:1 at different reaction times. Molecular weight and dispersity for each polymer are given in Table S1.

[PH]:[EBiB]	Time	Conversion	<i>M</i> n,NMR	<i>M</i> n,GPC	<i>M</i> n,th	Dispersity ^c
	(min)	(%) ^b	(kg mol⁻¹) ^b	(kg mol⁻¹) ^c	(kg mol⁻¹) ^b	
0:1	10	16	2.6	3.5	2.5	1.11
	25	33	4.8	5.6	5.1	1.08
	40	43	6.2	7.2	6.6	1.07
	60	56	8.4	8.5	8.6	1.07
	90	69	10	10	11	1.08
	120	77	11	11	12	1.08
	150	81	12	12	12	1.08
	180	85	13	12	13	1.08
	210	85	13	12	13	1.08
1:1	4	25	4.4	4.3	3.8	1.47
	8	33	5.8	5.2	5.0	1.47
	15	43	7.6	6.0	6.5	1.53
	25	51	8.3	6.9	7.8	1.57
	40	56	9.4	7.4	8.6	1.65
	60	62	10	7.8	9.5	1.77
	90	65	11	8.6	10	1.83
	120	67	11	9.1	10	1.78
	150	67	11	9.4	10	1.76
	180	68	11	9.6	10	1.80
3:1	5	23	4.6	3.1	3.6	1.79
	10	28	5.1	3.8	4.4	1.80
	15	31	5.8	3.9	4.8	1.82
	20	31	6.1	4.0	4.9	1.86
	25	33	6.1	4.1	5.2	1.83
	30	34	5.9	4.0	5.3	1.89
	60	35	6.1	4.0	5.5	1.84
	90	35	6.3	4.1	5.5	1.82
	120	36	6.5	4.8	5.7	1.71

Table S1. Characterization of PtBA synthesized using various ratios of [PH]:[EBiB] at different reaction times^a

^a [tBA]:[EBiB]:[CuBr]:[PMDETA] = 120:1:1:1 was used in all reactions.

^b Characterized with ¹H NMR: $M_{n,NMR}$ was determined through end-group analysis while $M_{n,th}$ was calculated from the NMR monomer conversion.

^c Characterized with GPC (polystyrene standards).



Figure S10. ¹H NMR spectra for PtBA synthesized in the presence of tin (II) 2ethylhexanoate. Spectra were obtained under the following conditions: tin (II) 2ethylhexanoate : EBiB = 3:1 after 30 and 120 min. of reaction time, and tin (II) 2ethylhexanoate : EBiB = 10:1 after 300 min. of reaction time. Spectra were obtained directly after removing the aliquot from the reaction flask without purification to determine the monomer conversion.

Analysis to Verify Presence of PH End-Groups

Nomenclature: Subscript 1 indicates reaction product in absence of chain termination and subscript 2 indicates product in presence of chain termination

In the following analysis, the area of peak b+g was set to 1. All peak areas reported below are referenced to this value.

1. [PH]:[EBiB] = <u>3:1</u>

Total peak area associated with methyl group on initiator: $c = 2.56 = c_1 + c_2$ Area of peak associated with aromatic end groups of PH: x = 0.67

- \Rightarrow Area of c₂ = 2x (from stoichiometry) = 1.34
- \Rightarrow Area of c₁ = 2.56 1.34 = 1.22
- \Rightarrow Area of b₂ = 2x/3 (from stoichiometry) = 0.44
- \Rightarrow Area of b₁+g₁ = c₁/2 (from stoichiometry) = 0.61

Therefore, we can calculate the expected peak area of $b_1+g_1+b_2 = 0.61+0.44 = 1.05$

The measured value of peak (b+g) from the NMR spectrum was 1, which is very close to this value obtained using stoichiometry.

2. [PH]:[EBiB] = <u>1:1</u>

Total peak area associated with methyl group on initiator: $c = 2.52 = c_1 + c_2$ Area of peak associated with aromatic end groups of PH: x = 0.48

- \Rightarrow Area of c₂ = 2x (from stoichiometry) = 0.96
- \Rightarrow Area of c₁ = 2.52 0.92 = 1.56
- \Rightarrow Area of b₂ = 2x/3 (from stoichiometry) = 0.32
- \Rightarrow Area of b₁+g₁ = c₁/2 (from stoichiometry) = 0.78

Therefore, we can calculate the expected peak area of $b_1+g_1+b_2 = 0.78+0.32 = 1.10$

The measured value of peak (b+g) from the NMR spectrum was 1, which is very close to this value obtained using stoichiometry.

The slight variation in the calculated and measured peak areas for (b+g) could be attributed to the error in peak area calculation for the convoluted peaks of the aromatic protons in PH.

Confirmation of Presence of Phenylhydrazine End-Groups with Matrix-Assisted Laser Desorption/Ionization–Time of Flight (MALDI-TOF) Spectroscopy

MALDI-TOF Instrumental Details

MALDI-TOF spectra were collected using a Bruker Daltonics Autoflex Speed mass spectrometer in reflection mode, equipped with a Smartbeam-II UV laser (λ = 355 nm), operating at a frequency of 2000 Hz, and calibrated with a set of peptide standards covering the mass range of m/z from 700 – 3500.

Sample Preparation

The matrix was prepared by dissolving dihydroxyacetophenone in acetonitrile/H₂O (ratio = 7:3), with the addition of 0.5% trifluoroacetic acid. The polymer samples were dissolved in tetrahydrofuran at a concentration of 50 mg/mL. The final samples were made by combining 9 μ L of the matrix solution and 1 μ L of the polymer solution, along with 0.5 μ L of a 1 mg/mL sodium acetate solution. The sodium acetate solution was prepared in acetonitrile/H₂O (ratio = 3:7). A volume of 1 μ L of the polymer/matrix solution was applied to the target and dried.

MALDI-TOF Spectrum



Figure S11. MALDI-TOF spectrum obtained from PtBA synthesized by ATRP with [PH] : [EBiB] = 3:1 (synthetic details provided in main text).



Figure S12. A closer view of the MALDI-TOF spectrum obtained from PtBA synthesized by ATRP with [PH] : [EBiB] = 3:1. The PtBA repeat unit (128.17 g/mol) is clearly observed.

Proposed Chemical Structures

The main text describes the proposed reaction mechanism of chain termination in the presence of PH (Figure 5 in the main text). Thus, three potential end-groups structures are anticipated after the ATRP of *tert*-butyl acrylate in the presence of PH:



Figure S13. Chemical structures of PtBA anticipated following ATRP of *tert*-butyl acrylate in the presence of PH: a) structure containing a traditional Br end-group, b) structure containing a PH end-group, and c) structure resulting from radical coupling of polymer chains.

During the MALDI sample preparation, the polymer was cationized and accelerated with counter ions. Thus, when the m/z values of peaks in the MALDI spectra are analyzed, the molecular weight of adsorbed cations (i.e. sodium or hydrogen in our experiment) are included. Additionally, it is anticipated that the bromine end-groups may undergo various transformations during the MALDI sample preparation due to the presence of trifluoroacetic acid, tetrahydrofuran and water, as well as during ionization, which were previously described in ref 1-3. We have considered the various end-group structures outlined in ref 1-3.

MALDI-TOF Spectrum Analysis

Figure S14 shows a targeted region of the MALDI spectrum. Table S3 summarizes proposed chemical structures with molecular weights which agree with the m/z values of major peaks observed in Figure S14 (we concluded that the molecules have z = +1 due to the separation of isotope peaks in the spectrum). Peaks 1 and 2 (1292.20 and 1377.25 m/z, respectively) are attributed to PtBA chains with PH end-groups. Peak 3 (1382.26 m/z) is attributed to chains which originally contained Br end-groups, and were subsequently transformed during the MALDI sample preparation and ionization procedures (ref 1).

Table S2: Analysis of MALDI Spectrum



Figure S14. MALDI-TOF spectrum obtained from PtBA synthesized by ATRP with [PH] : [EBiB] = 3:1.

Code	Proposed Chemical Structure	Molecular	Chemical
		weight (g/mol)	Formula
1		1292.65 (n = 7)	C ₆₈ H ₁₁₂ O ₁₈ N ₂ Na ₂ H+
	This structure includes exchange of 2 H atoms with Na (not shown above). Ion: H+ Note: alternatively, the same molecular weight is achieved with a Na+ ion, and exchange of 1 H atom with Na.		
2	lon: H+	1376.86 (n = 8)	C75H126O20N2 H+
3	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	1382.74 (n = 8)	C71H119O22F3 H+
	IUII. Π +		

Model accounting for chain termination with PH to fit experimental kinetic data

$$P_{n} - X + Cu^{I}X/L \xrightarrow{K_{eq}} P_{n} + Cu^{II}X_{2}/L$$

$$P_{n} + M \xrightarrow{k_{p}} P_{n+1} + P_{n-1} + P_{n-1}$$

[PX] indicates concentration of Pn-X

$$K_{eq} = \frac{[P \cdot][Cu(II)]}{[Cu(I)][PX]} = > [P \cdot] = \frac{\kappa_{eq} [Cu(I)][PX]}{[Cu(II)]} = D[PX]$$

$$\frac{dM}{dt} = -k_p [P \cdot][M] = -k_p D[PX][M]$$

$$\frac{d[PX]}{dt} = -k_{PH} [PX][PH]$$
(1)

Assuming [PH] \gg [PX], therefore, reaction is pseudo first order with [PH] considered a constant.

$$\Rightarrow [PX] = [PX]_0 e^{-k_{PH} [PH]t}$$
(2)

Substituting equation 2 into equation 1, we obtain:

$$dM/dt = -k_p D[M][PX]_0 e^{-k_{PH}[PH]t}$$

Solving the differential equation, we obtain:

$$\ln\left(\frac{[M]_{0}}{[M]}\right) = \frac{k_{p}D[PX]_{0}}{k_{PH}[PH]} (1 - e^{-k_{PH}[PH]t})$$
$$\ln\left(\frac{[M]_{0}}{[M]}\right) = \frac{A}{B}(1 - e^{-Bt})$$
$$A = \frac{k_{p}K_{eq} [Cu(I)][PX]_{0}}{[Cu(II)]}, B = k_{PH}[PH]$$

[PH]:[EBiB]	Time	Conversion	<i>M</i> n,GPC	Dispersity ^c
	(h)	(%) ^b	(kg mol⁻¹) ^c	
0:1	6	17	2.8	1.08
	12	25	3.7	1.07
	18	45	6.8	1.07
	30	52	8.1	1.08
	36	54	8.3	1.08
0.2:1	5	20	3.9	1.14
	10	34	9.3	1.19
	16	46	15	1.32
	36	64	21	1.53
1:1	4	15	10	1.74
	8	18	12	2.30
	12	17	10	1.96
3:1	4	11	7.1	1.65
	8	14	9.6	1.60
	12	16	8.2	1.73
	36	17	9.1	1.88

Table S3. Characterization of PS synthesized using various ratios of [PH]:[EBiB] at different reaction times^a

^a [styrene]:[EBiB]:[CuBr]:[PMDETA] = 120:1:1:1 was used in all reactions.

^b Characterized with ¹H NMR

^c Characterized with GPC (triple detection).

References

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