

Supporting Information

A Biodegradable, Polymer-Supported Oxygen Atom Transfer Reagent

Erin E. Ramey¹, Elizabeth L. Whitman², Cole E. Buller¹, James R. Tucker², Charles S. Jolly², Kjersti G. Oberle¹, Austin J. Becksvoot¹, Mark Turlington² and Christopher R. Turlington^{1,}*

¹ Department of Chemistry and Biochemistry, Hope College, Holland, MI 49422, USA

² Department of Chemistry and Biochemistry, Berry College, Mount Berry, GA 30149, USA

* Correspondence: turlington@hope.edu

Contents

I. NMR, GPC, and XPS Spectra	2
A. ArI-TMC monomer	2
B. ArI-TMC homopolymer	3
C. Copolymer of 40% ArI-TMC and 60% Bn-TMC	5
D. Iodosyl copolymer	7
II. Relative Polymerization Rates (50% ArI-TMC and 50% Bn-TMC)	9
III. Triphenylphosphine Oxidation	13

I. NMR, GPC, and XPS Spectra **A. ArI-TMC monomer**

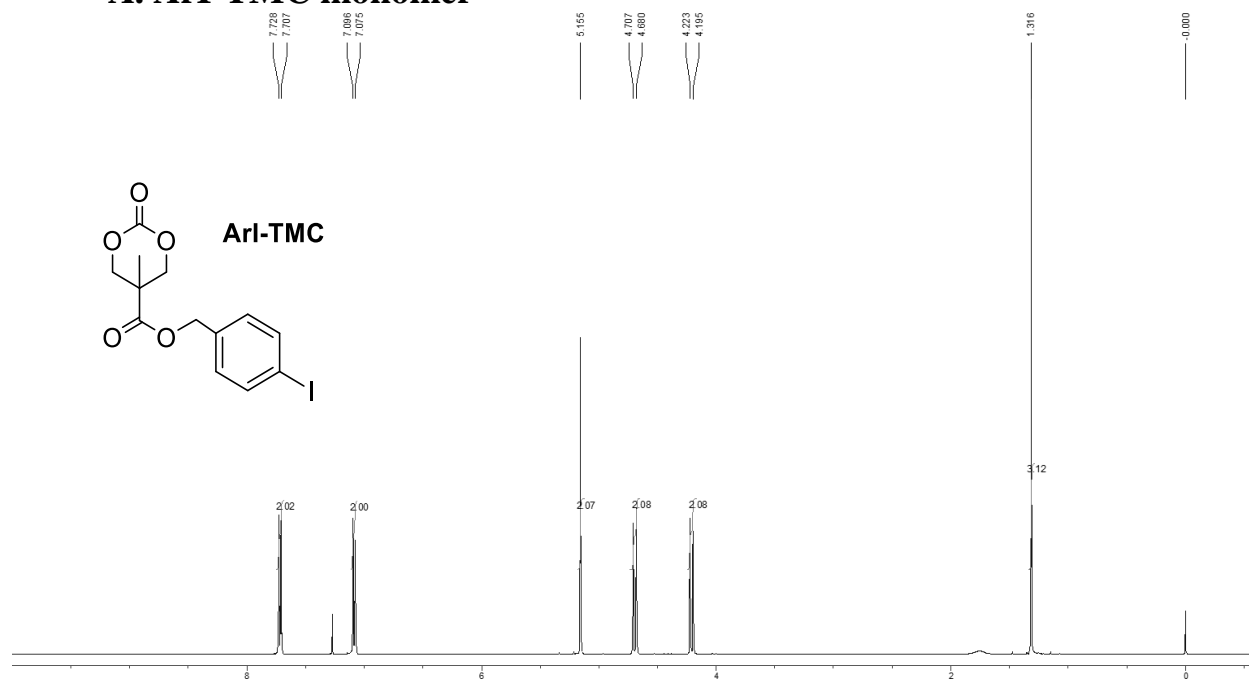


Figure S1. The ¹H NMR spectrum (CDCl₃) of ArI-TMC (4-iodobenzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate).

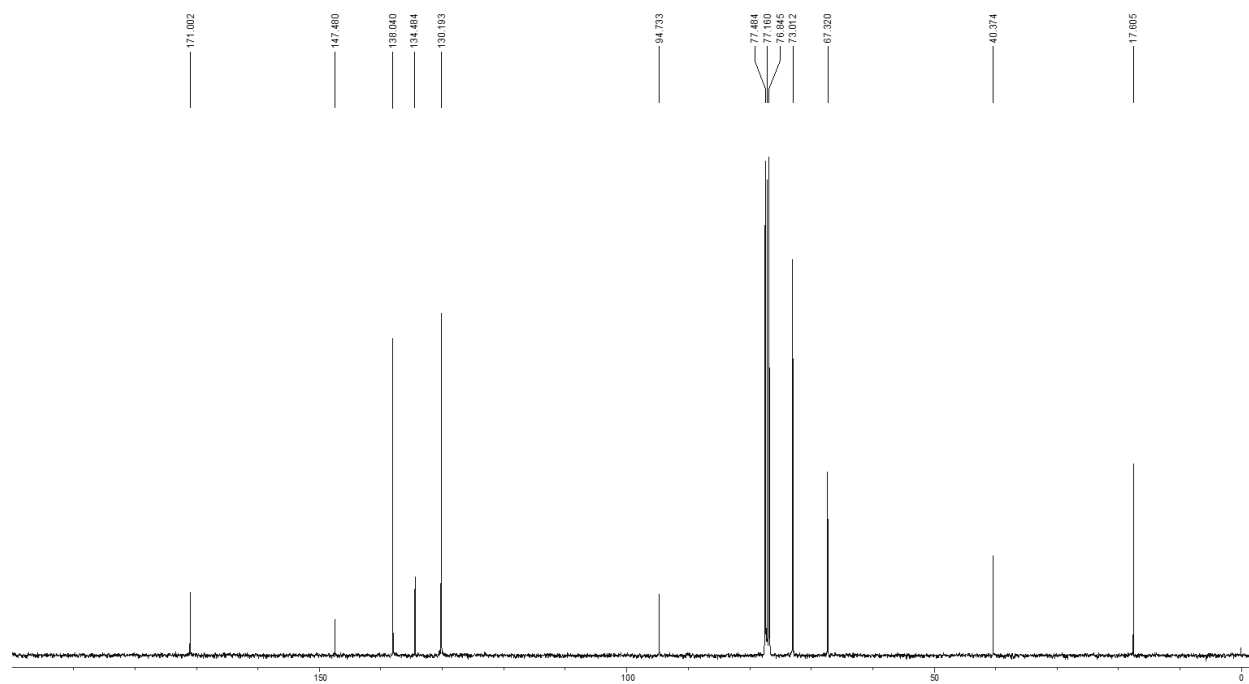


Figure S2. The ¹³C NMR spectrum (CDCl₃) of ArI-TMC.

B. ArI-TMC homopolymer

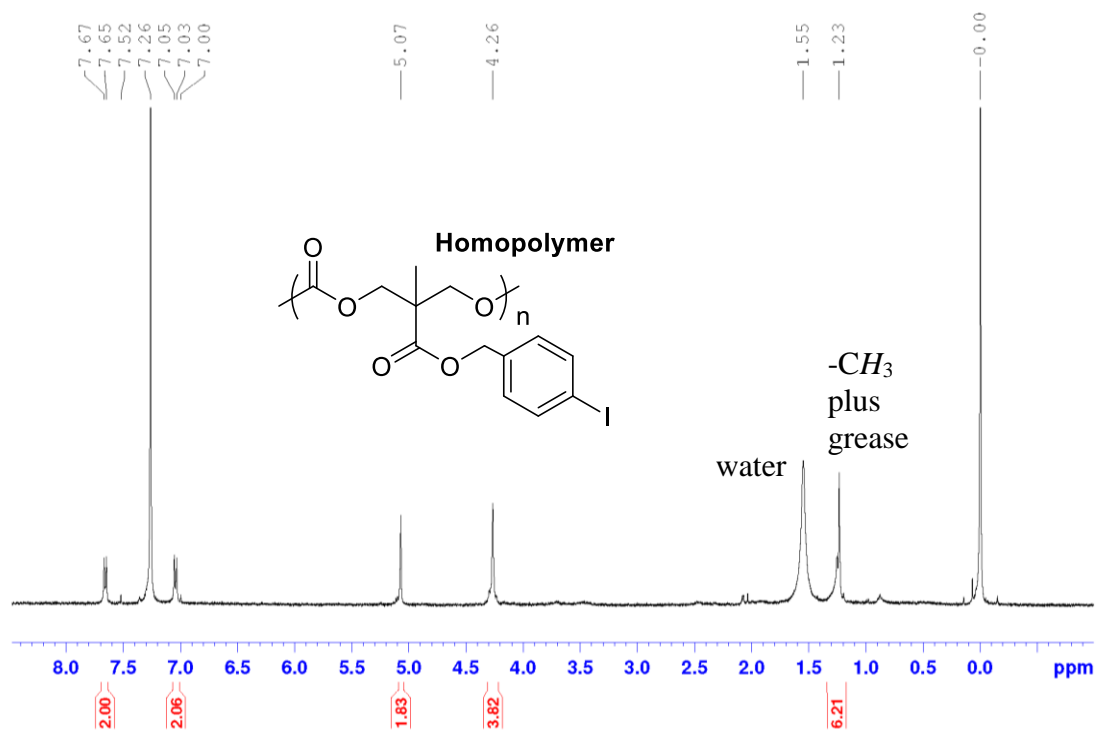


Figure S3. The ^1H NMR spectrum (CDCl_3) of the ArI-TMC homopolymer.

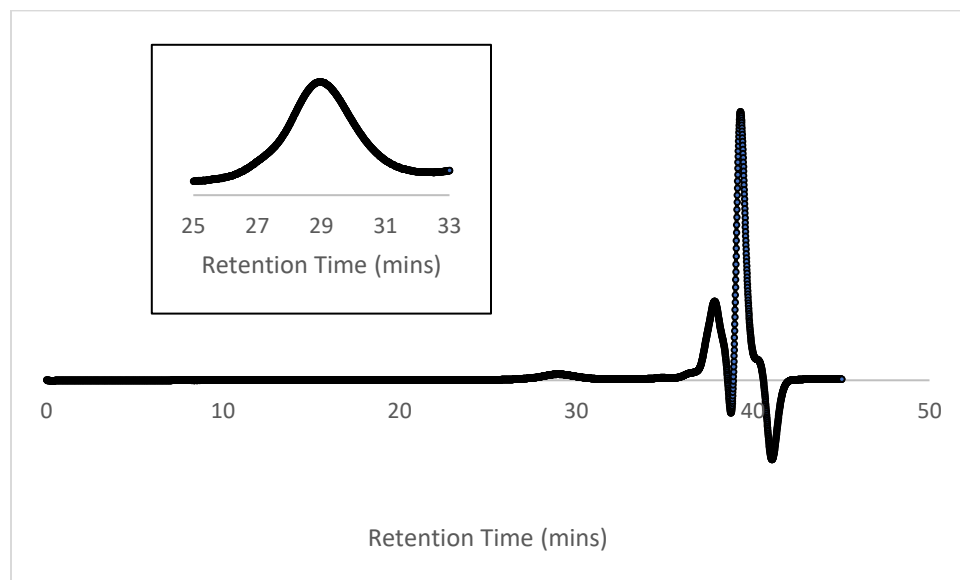


Figure S4. The GPC-RI spectrum (THF) of the ArI-TMC homopolymer. The inset shows an expanded view of the polymer peak. A refractive index detector (RI) was used, and the molecular weight was calculated by comparison to known polystyrene standards. GPC-RI (expected $M_n=37,600$): $M_n=9,900$, $M_w=11,074$, $D=1.12$.

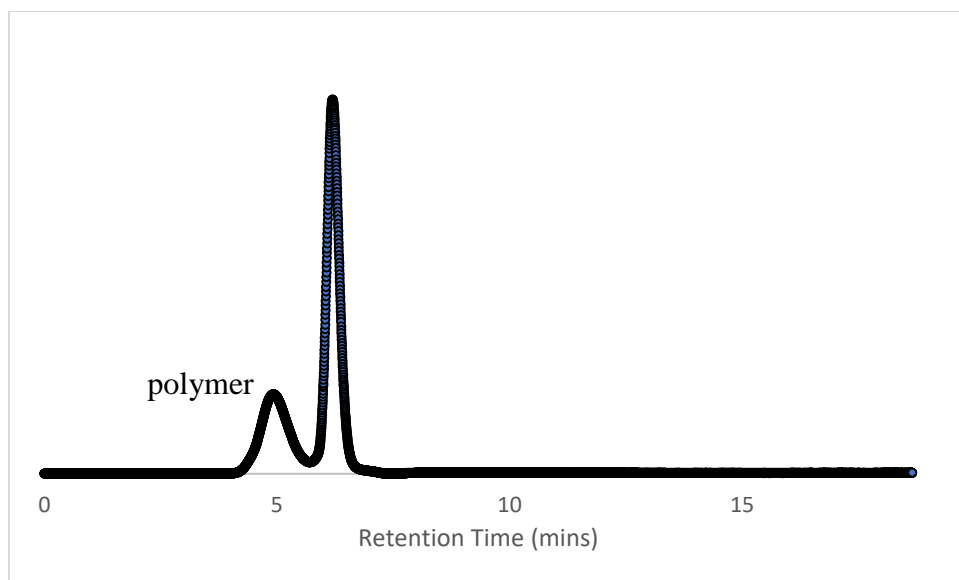


Figure S5. The GPC-UC (UC = Universal Calibration) spectrum in THF of the ArI-TMC homopolymer. A UV-visible detector (UV) was used, and the molecular weight was calculated by a Universal Calibration method using UV and Viscometer detectors with known polystyrene standards. GPC-UC (expected $M_n=37,600$): $M_n=40,300$, $M_w=49,000$, $\bar{D}=1.22$.

C. Copolymer of 40% ArI-TMC and 60% Bn-TMC

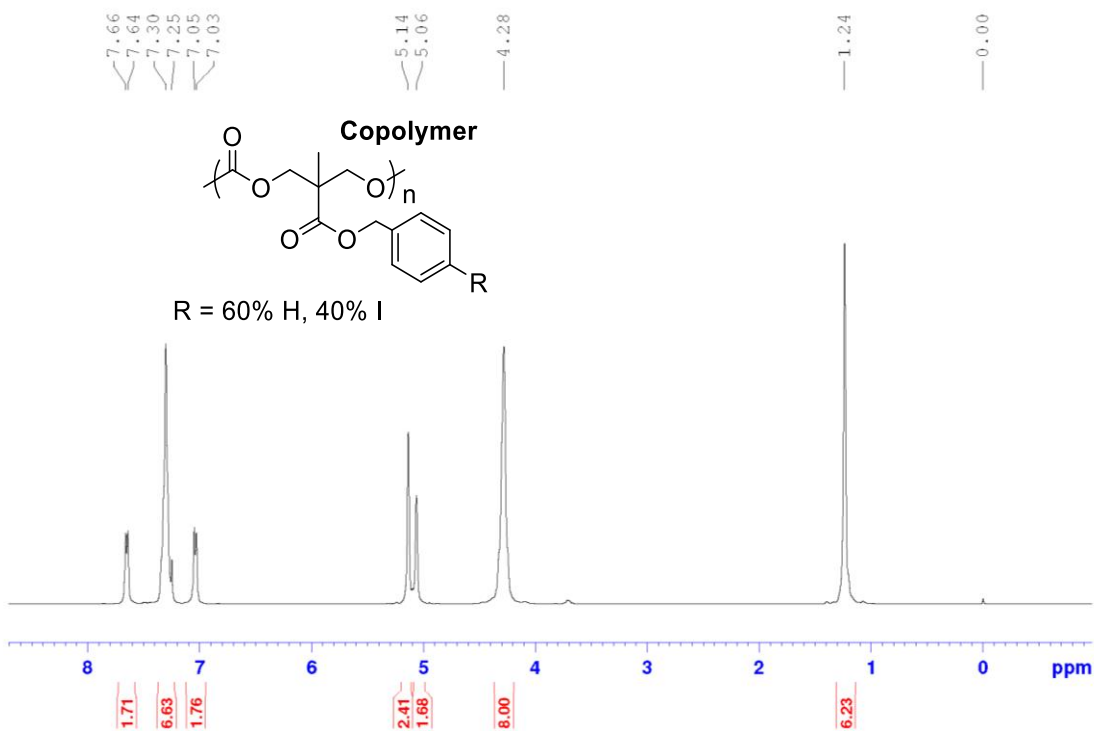


Figure S6. The ¹H NMR spectrum (CDCl₃) of the copolymer from polymerization of 40% ArI-TMC and 60% Bn-TMC.

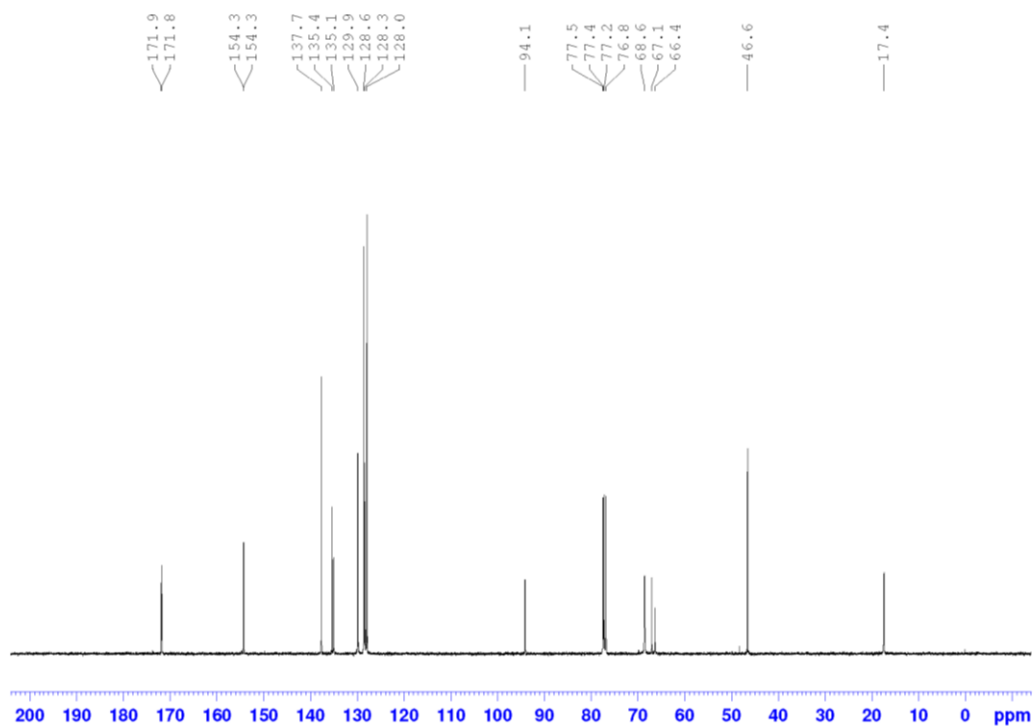


Figure S7. The ¹³C NMR spectrum (CDCl₃) of the copolymer from polymerization of 40% ArI-TMC and 60% Bn-TMC.

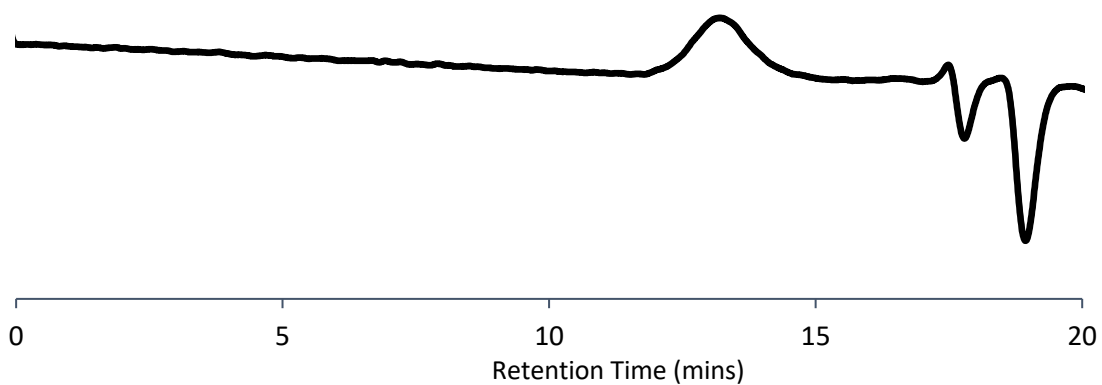


Figure S8. The GPC-LS spectrum (THF) of the copolymerization of 40% ArI-TMC and 60% Bn-TMC. GPC-LS (expected $M_n=30,200$): $M_n= 22,600$, $M_w= 26,900$, $D= 1.19$.

D. Iodosyl Copolymer

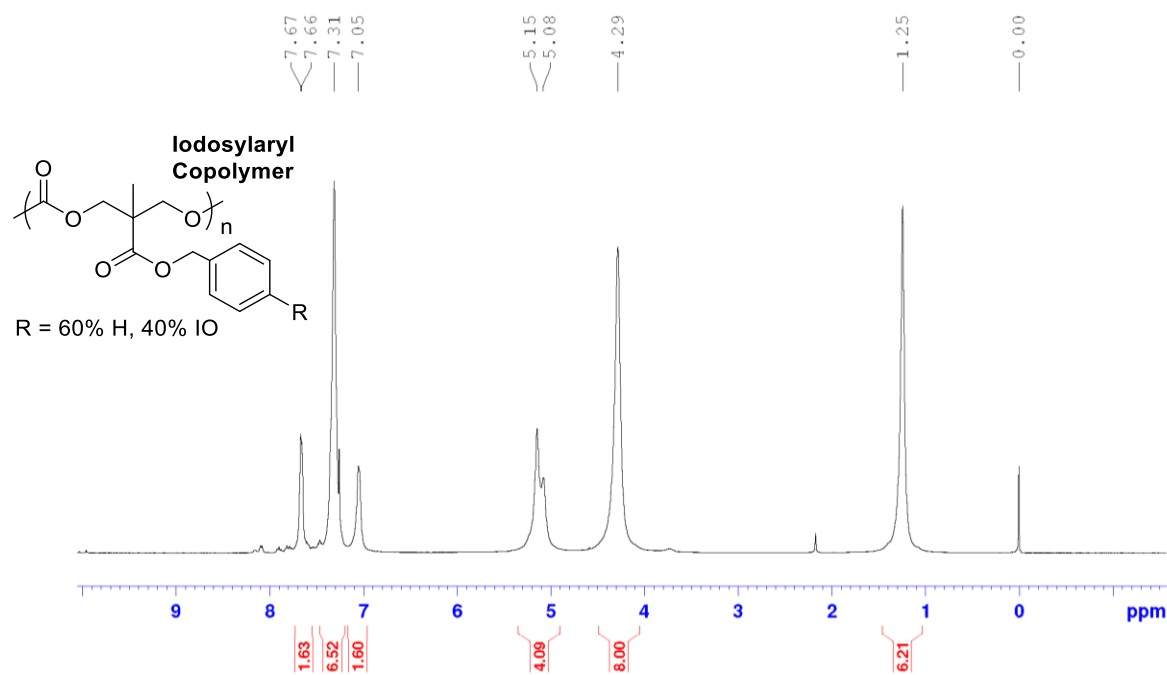


Figure S9. The ^1H NMR spectrum (CDCl_3) of the oxidation of poly(40% [ArI-TMC]-co-60% [Bn-TMC]) to the iodosyl copolymer.

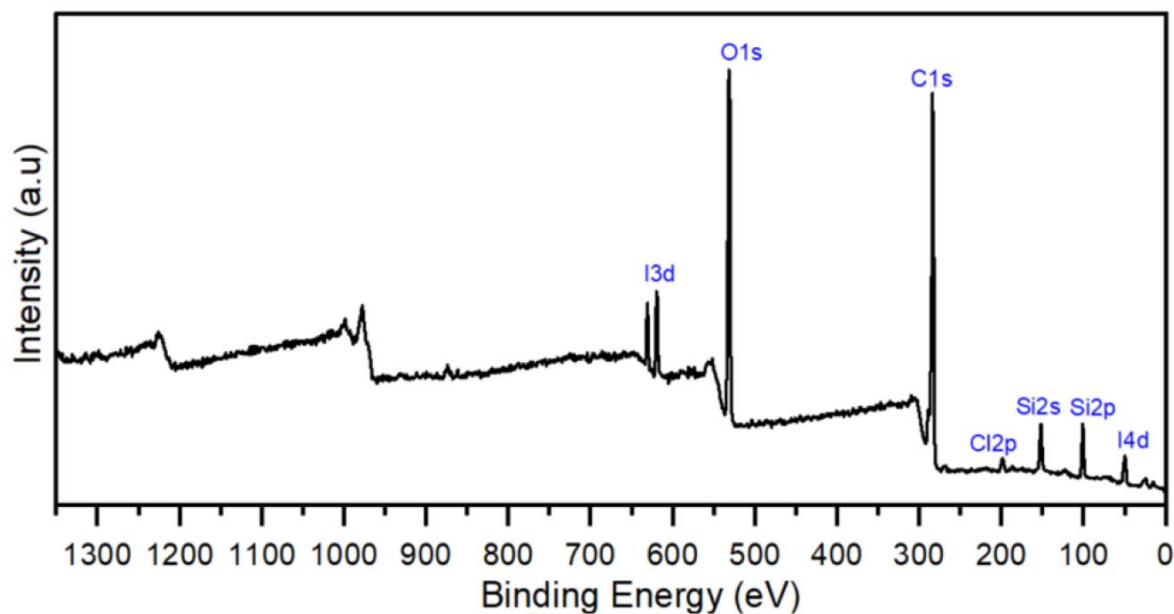


Figure S10. A survey XPS scan of the Iodosyl copolymer. Iodine, oxygen, and carbon are detected. Chlorine is detected, but it is residual from the chloroform solvent used to prep the sample. Silicon is detected, but silicon is a common contaminant when storing samples in glass vials.

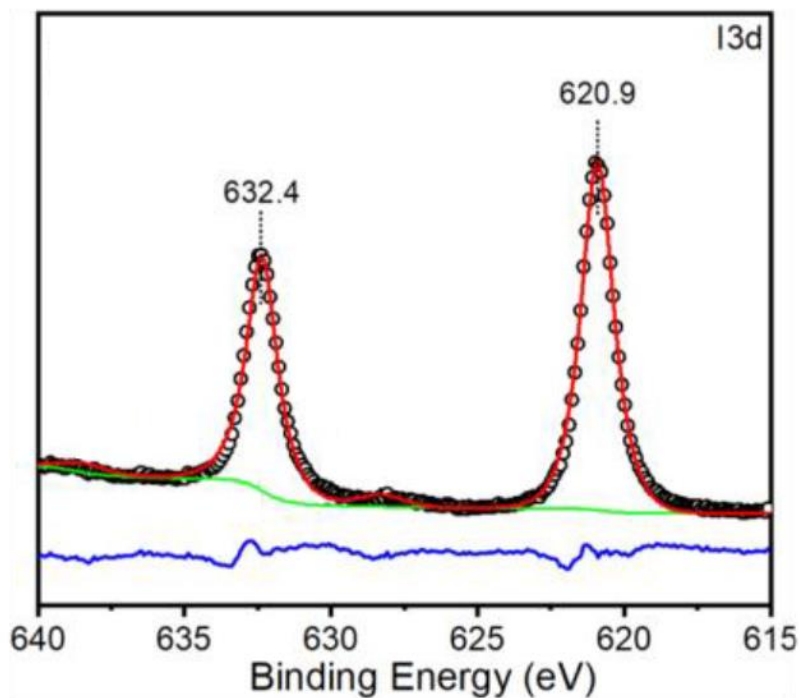


Figure S11. A high resolution XPS scan of the I3d_{5/2} band (620.9 eV) and the I3d_{3/2} band (632.4 eV), showing only a single iodine species was present. The I3d_{5/2} band was closer to the +3 oxidation state reported for ICl₃ (621.5 eV) than the 0 oxidation state reported for I₂ (619.9 eV), suggesting that iodine was closest to the +3 oxidation state and was coordinated to a highly electronegative atom, such as oxygen.

II. Relative Polymerization Rates (50% ArI-TMC and 50% Bn-TMC)

15 minutes

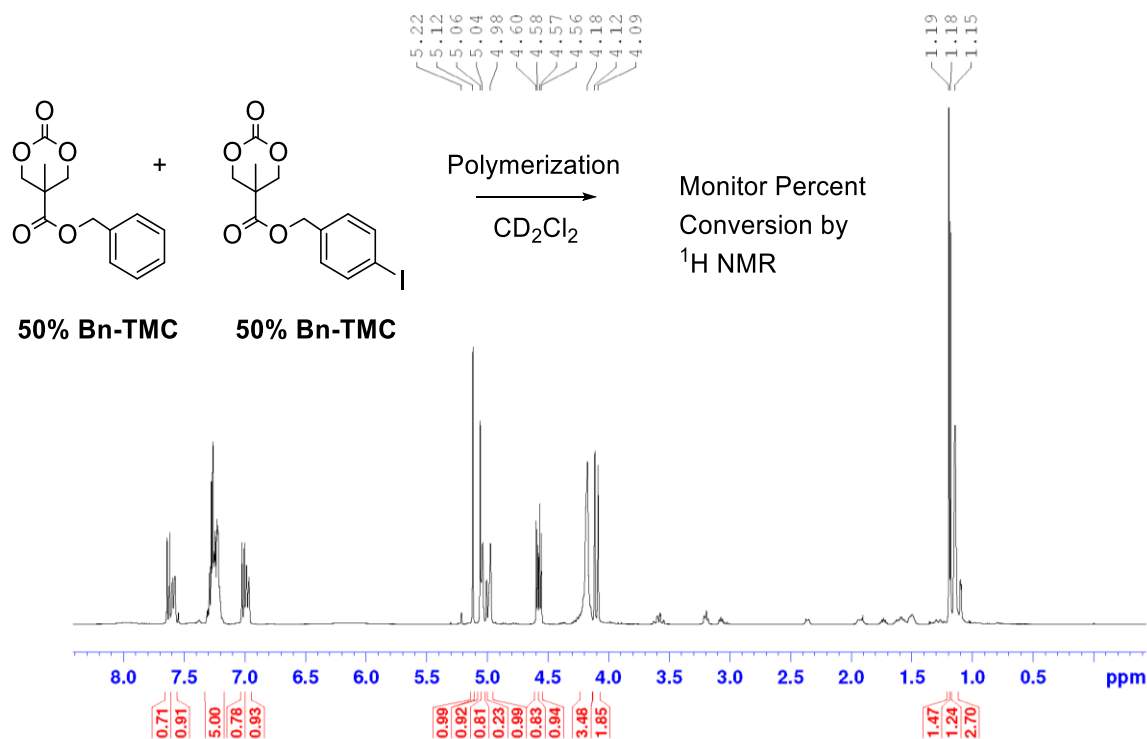


Figure S12a. The ^1H NMR spectrum (CD₂Cl₂) of the polymerization of 50% ArI-TMC and 50% Bn-TMC at 15 minutes of reaction time.

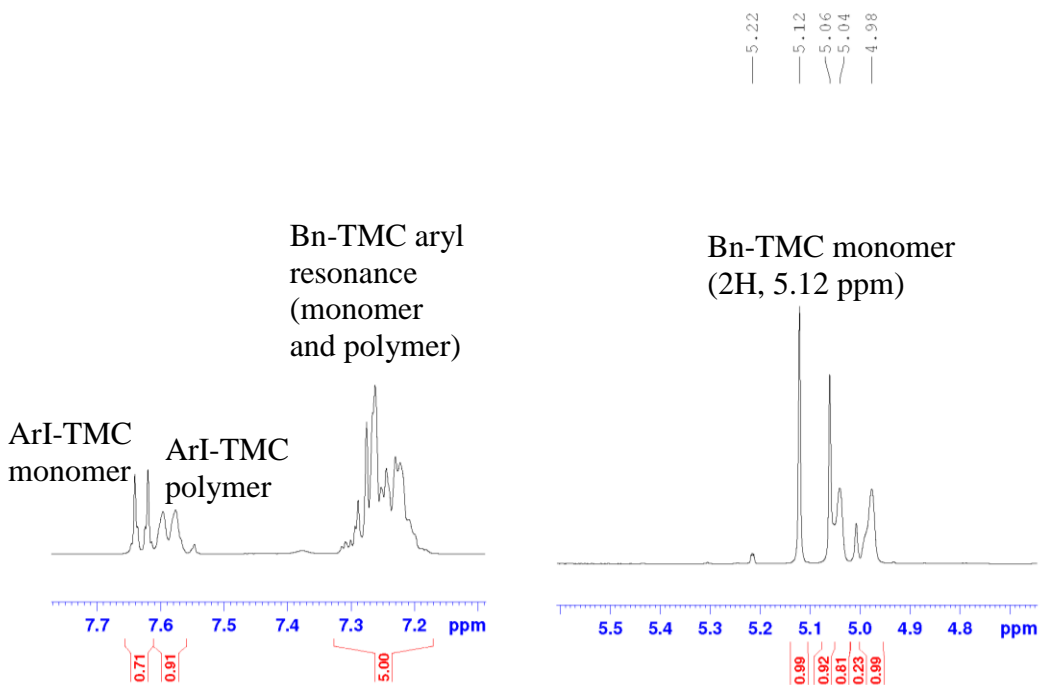


Figure S12b. Expansions of the ^1H NMR spectrum (CD₂Cl₂) at 15 minutes of reaction time. The percent conversion of ArI-TMC was 56% and the percent conversion of Bn-TMC was 51%.

30 minutes

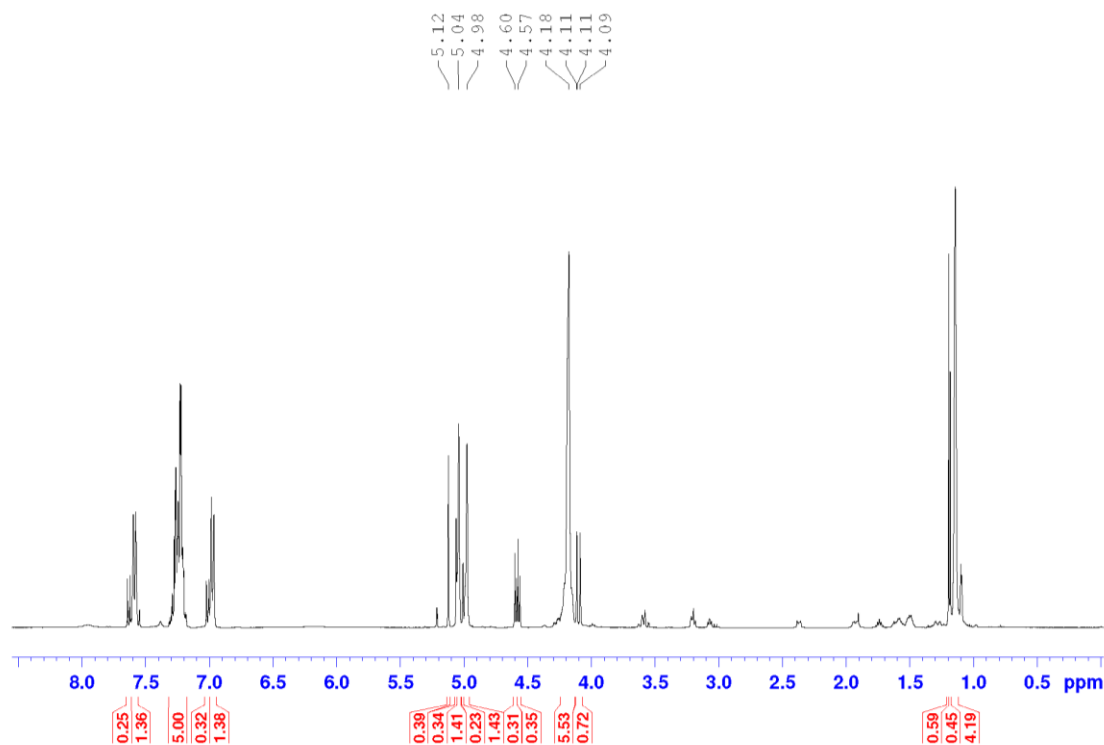


Figure S13a. The ^1H NMR spectrum (CD_2Cl_2) of the polymerization of 50% ArI-TMC and 50% Bn-TMC at 30 minutes of reaction time.

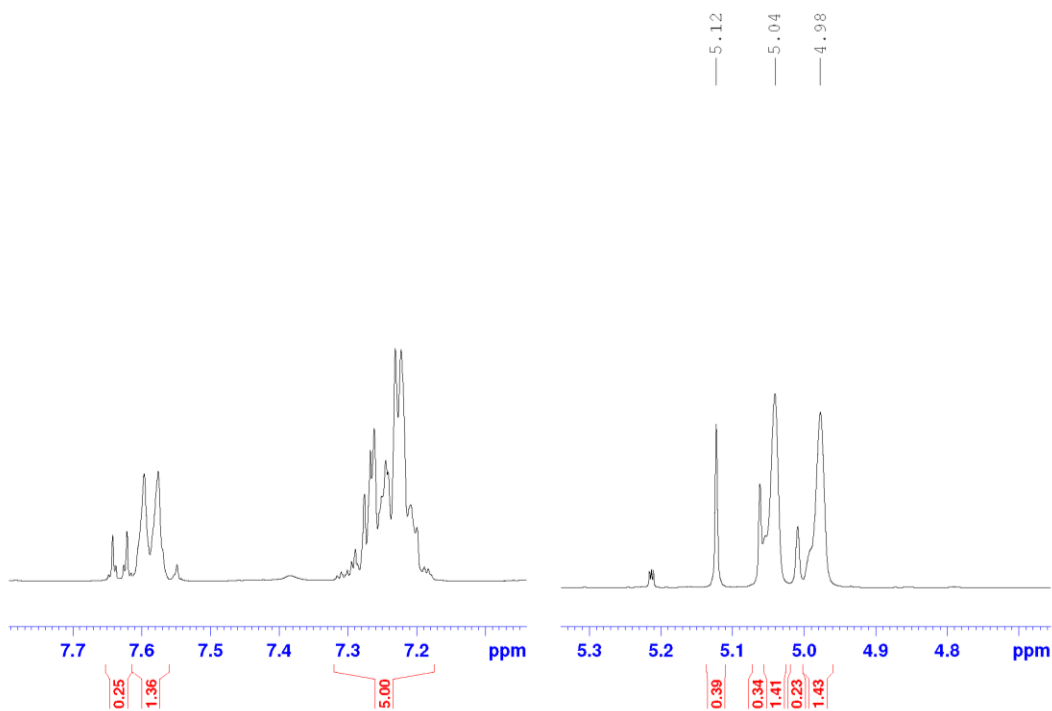


Figure S13b. Expansions of the ^1H NMR spectrum (CD_2Cl_2) at 30 minutes of reaction time. The percent conversion of ArI-TMC was 85% and the percent conversion of Bn-TMC was 80%.

45 minutes

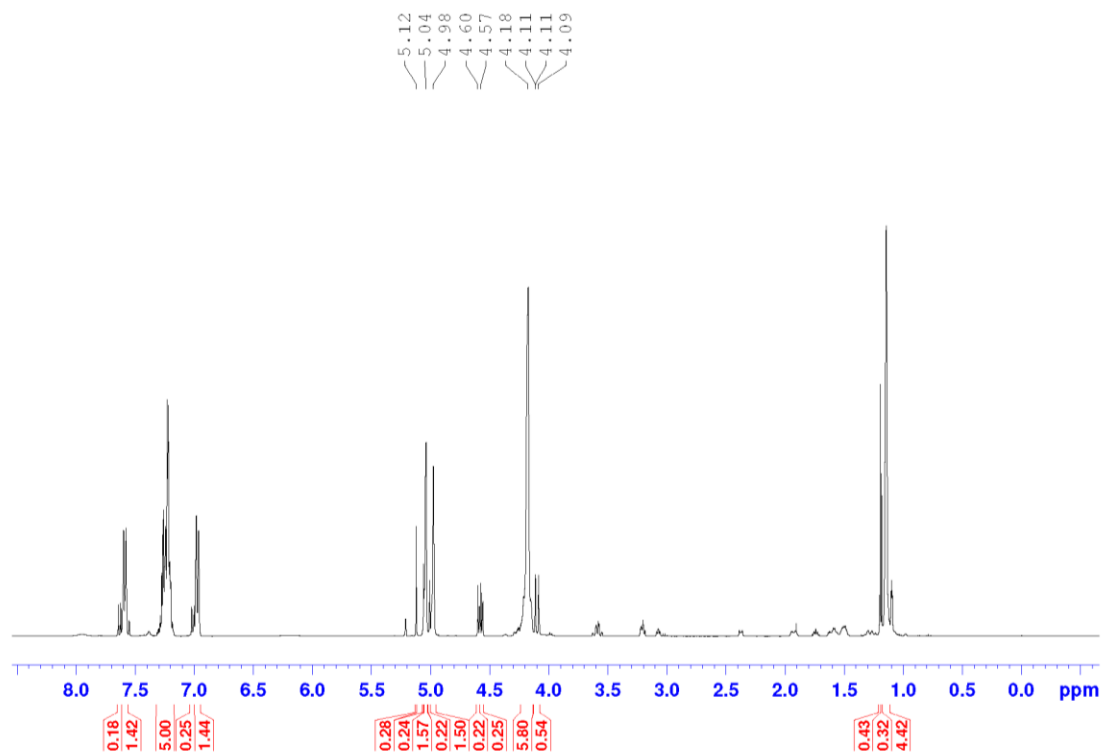


Figure S14a. The ^1H NMR spectrum (CD_2Cl_2) of the polymerization of 50% ArI-TMC and 50% Bn-TMC at 45 minutes of reaction time.

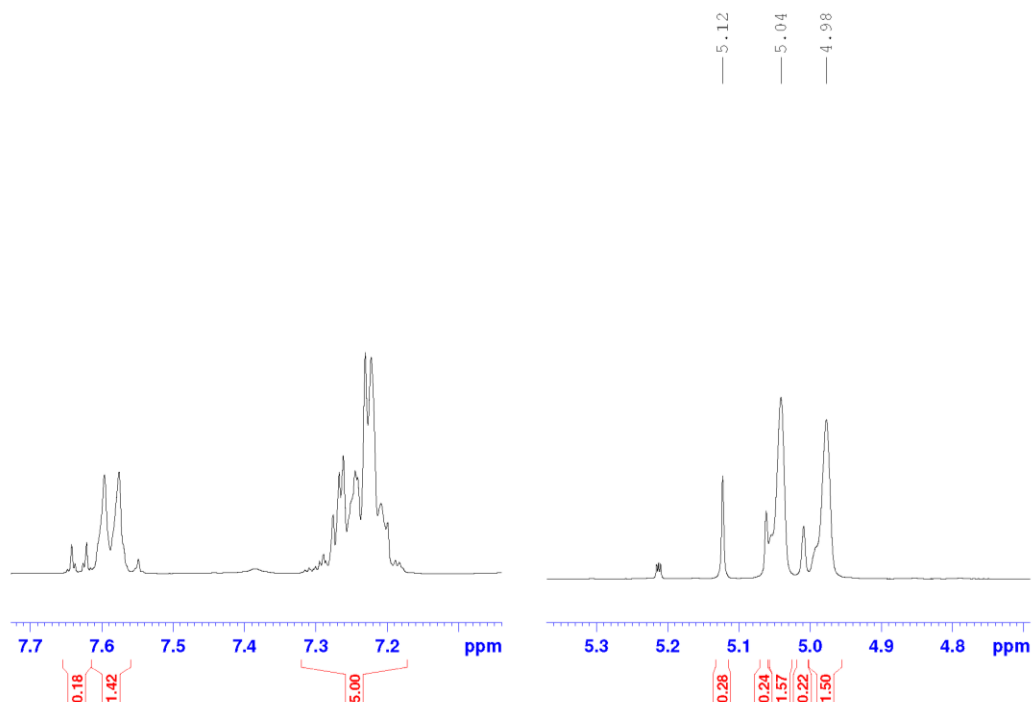


Figure S14b. Expansions of the ^1H NMR spectrum (CD_2Cl_2) at 45 minutes of reaction time. The percent conversion of ArI-TMC was 89% and the percent conversion of Bn-TMC was 86%.

60 minutes

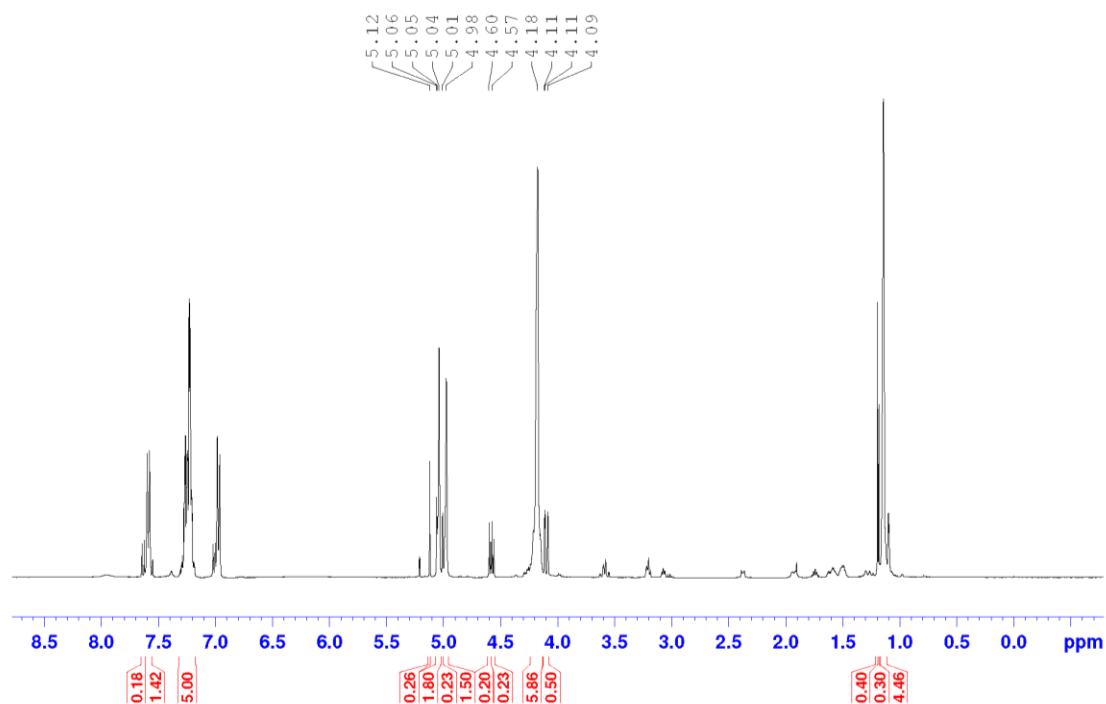


Figure S15a. The ^1H NMR spectrum (CD_2Cl_2) of the polymerization of 50% ArI-TMC and 50% Bn-TMC at 60 minutes of reaction time.

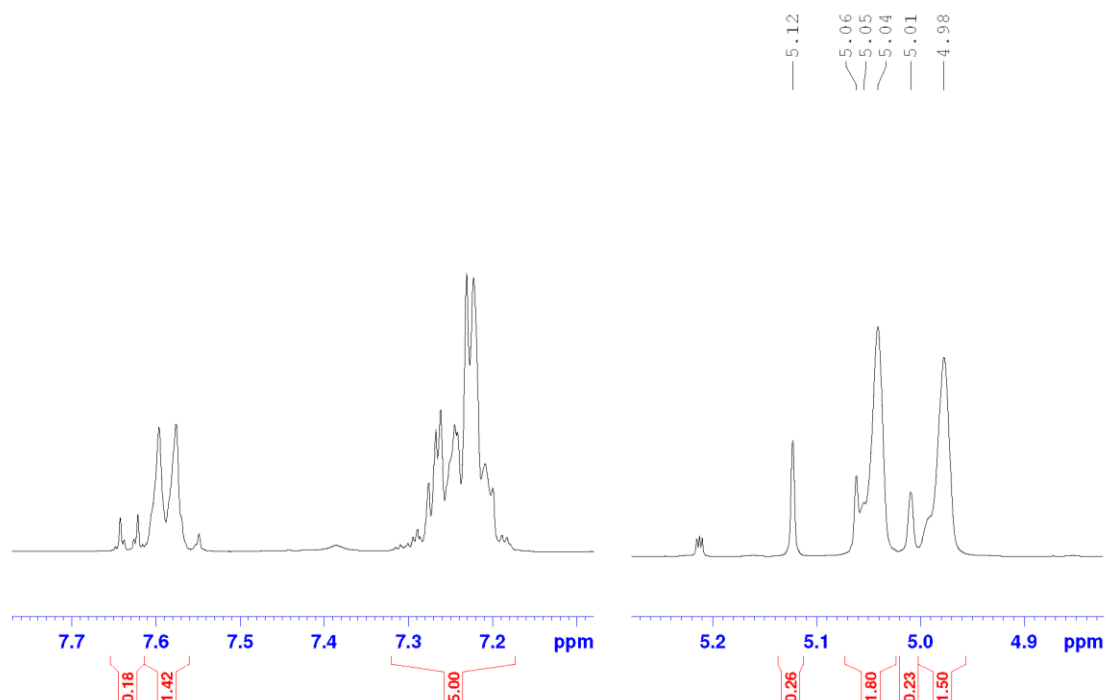


Figure S15b. Expansions of the ^1H NMR spectrum (CD_2Cl_2) at 60 minutes of reaction time. The percent conversion of ArI-TMC was 89% and the percent conversion of Bn-TMC was 87%.

III. Triphenylphosphine oxidation

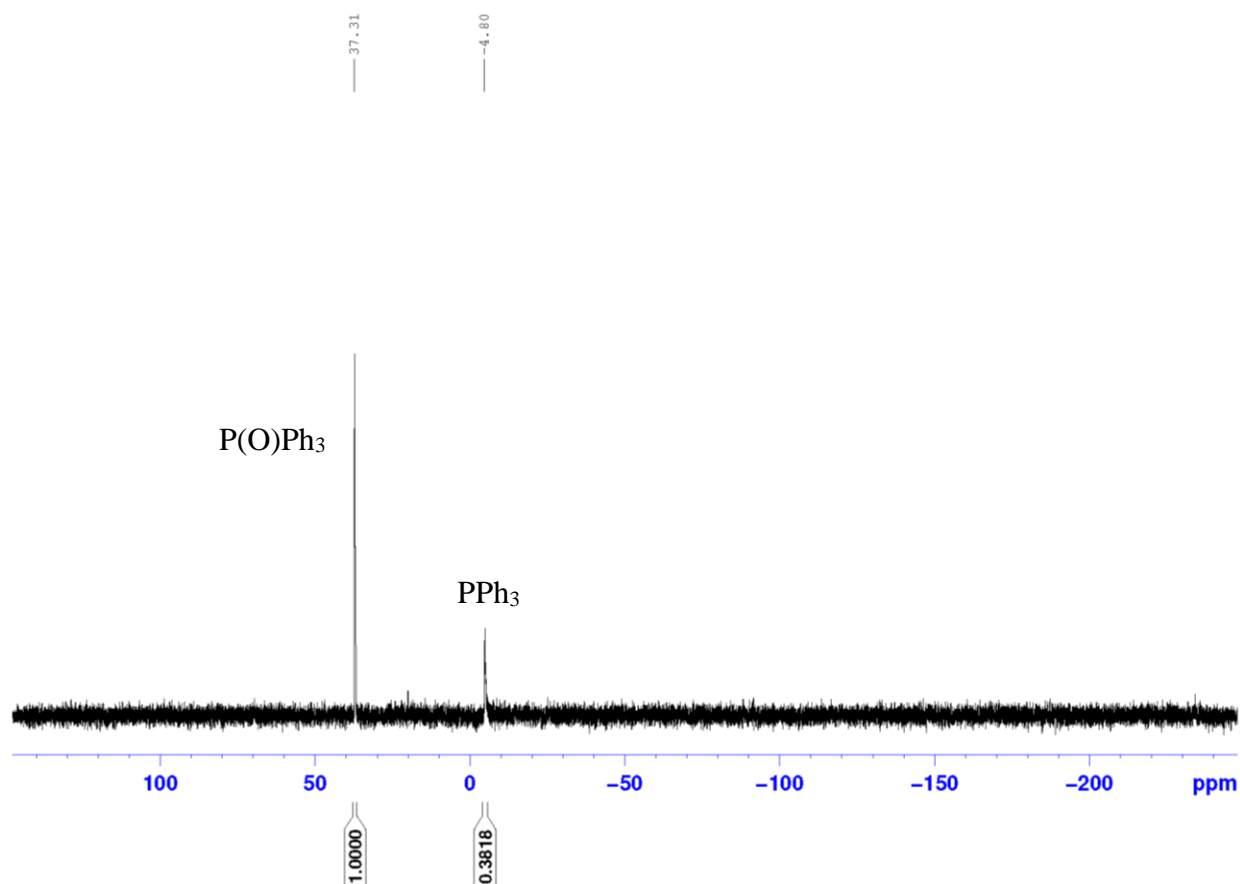


Figure S16. The ^{31}P NMR spectrum (CDCl_3) of the oxidation of triphenylphosphine to triphenylphosphine oxide using the iodosyl copolymer. The two species were verified by known standards of triphenylphosphine and triphenylphosphine oxide.

