# Synthesis of Phosphorescent Iridium-Containing Acrylic Monomers and Their Room-Temperature Polymerization by Cu(0)-RDRP

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Received 16 July 2018; Revised 13 August 2018; Accepted 22 August 2018
**DOI: 10.1002/pola.29233**

**ABSTRACT:** A series of acrylic monomers based on cyclometalated iridium(III) complexes have been synthesized based on common phosphorescent emitters for organic light-emitting diodes. A simple room-temperature polymerization procedure for these materials was developed using Cu(0) reversible deactivation radical polymerization, providing polymers with low dispersities of 1.08–1.14 at conversions from 81 to 93% when the Ir complexes are copolymerized with a carbazole-based acrylic host. These methods were also found to be suitable for the preparation of high-molecular-weight polymers with $M_n$ approaching 40,000 Da, as well as block copolymers formed in one pot from the chain extension of methyl acrylate. This scalable room-temperature synthesis of iridium-containing copolymers and block copolymers provides a useful route to optoelectronic materials, which we anticipate can be readily adapted to a broad range of acrylic metallopolymers. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**

**KEYWORDS**: block copolymer; carbazole host; copolymerization; Cu(0)-RDRP; iridium copolymer; living polymerization; metallopolymer

**INTRODUCTION** Cu(0) reversible deactivation radical polymerization (RDRP) has recently attracted considerable attention as a low-cost and scalable route to polymers prepared from a diverse array of vinyl monomers.[1–7] Now widely explored for the polymerization of (meth)acrylates,[3,8,9] styrenes,[5] and acrylamides[10] among others,[11,12] this technique affords polymers with low dispersity while retaining near-quantitative end-group fidelity at conversions >90%. Though some debate persists regarding the mechanistic details of Cu(0)-RDRP,[13–15] the technique offers many advantages with respect to scalability and cost. For example, many Cu(0)-RDRP processes proceed efficiently at room temperature or with only mild heating, and use simple Cu(0) powder or wire as catalyst. The method is also suitable for the preparation of multiblock copolymers in one pot,[16] and can be carried out without explicit degassing of the reaction mixture in some cases.[9,17]

These same advantages also lend themselves well to the polymerization of high-value monomers, as low dispersities can be obtained at high conversions with minimal monomer waste. We recently demonstrated that Cu(0)-RDRP provided a simple and low-cost route to polyacrylates based on p-type and n-type organic semiconductors, giving polymers with dispersities as low as 1.12 with conversions up to 97%.[18,19] The high conversions afforded by these reactions was of additional benefit as it can be difficult to remove large amounts of residual monomer from the product by reprecipitation, owing to the similarity in solubility characteristics between the semiconducting polymer and its large, π-conjugated building blocks. These methods were also used to prepare polyacrylates from organic semiconductors with molecular weights approaching 50,000 Da.

We then reasoned that Cu(0)-RDRP would be ideal for the polymerization of acrylic monomers based on phosphorescent transition-metal complexes. Such complexes, particularly those based on Os, Ir, or Pt, have found widespread use as emitters for organic light-emitting diode (OLED) displays,[20–24] light-emitting electrochemical cells,[25–27] and chemosensors,[28–31] with quantum yields often approaching 100%. Due to the high cost of these materials, a polymerization method that minimizes waste, maximizes yield, and simplifies purification would be highly desirable. Though a recent report describes the photopolymerization of iridium methacrylates,[32] the polymerization of such monomers via Cu(0)-RDRP has not yet been explored. Cu(0)-RDRP offers many advantages, such as the ability to prepare high-molecular-weight polymers with low dispersity. In addition, the versatility of this method has been shown recently through the synthesis of polymers in both aqueous and organic solvents,[33] and through the fact that the catalyst can be recovered after the polymerization.[34] In addition, this

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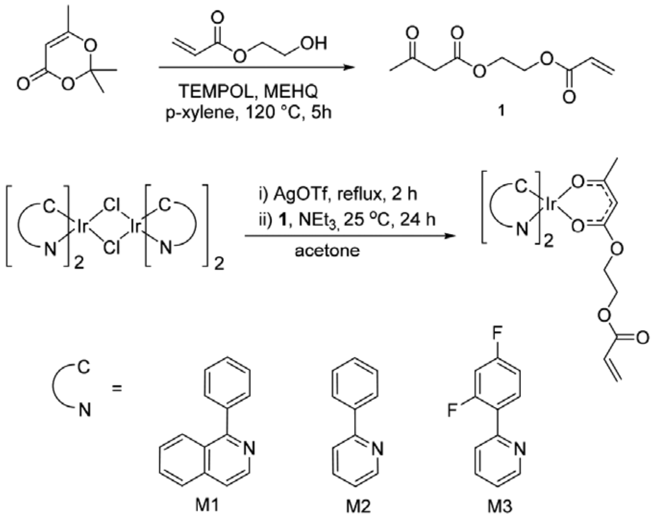

**SCHEME 1** Synthesis of iridium monomers **M1**–**M3**.

polymerization method can be combined with different methods including plasma polymerization to create novel classes of materials.[35]

Herein we report the preparation of three iridium-based acrylic monomers with red, green, and sky-blue phosphorescence, and their copolymerization with a carbazole-based host via Cu(0)-RDRP. These methods are further shown to be applicable to the preparation of doped polymers with molecular weights approaching 40,000 Da, as well as iridium-containing block copolymers prepared using a one-pot protocol. Kinetic data for these polymerizations are also described, alongside the optical, electrochemical, and thermal properties of the iridium-containing products.

## EXPERIMENTAL

### General Experimental Details

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk or glovebox techniques unless otherwise stated. Dry solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves unless otherwise stated. Dry $CH_2Cl_2$ was obtained from Sigma-Aldrich and freshly distilled over $P_2O_5$ before use. All reagents were obtained from Sigma-Aldrich or Alfa Aesar and used as received unless otherwise stated. $NEt_3$ was dried by distillation on $CaH_2$ onto 4 Å molecular sieves, then degassed by three freeze-pump-thaw cycles, and stored under $N_2$ atmosphere. All $^1H$, $^{13}C$, and $^{19}F$ NMR spectra were obtained on Bruker Avance 300 or 400 MHz spectrometers. Absorbance measurements were made on a Cary 60 spectrometer and fluorescence measurements were made on an Edinburgh Instruments FS5 spectrofluorometer. Absolute photoluminescence quantum yields were determined using an Edinburgh Instruments SC-30 Integrating Sphere Module. Toluene was used as solvent for all photophysical experiments. Mass spectra were recorded on a Kratos MS-50 instrument using electron impact ionization. Cyclic voltammograms were recorded using a BASi Epsilon Eclipse potentiostat at room temperature using a standard three-electrode configuration (working electrode: 2 mm diameter Pt disc; reference electrode: Ag/AgCl electrode in saturated KCl; counter electrode: Pt wire). 1-Phenylisoquinoline,[36] 2-(2,4-difluorophenyl)pyridine,[37] and **M4**[18] were prepared according to literature procedures.

### Size Exclusion Chromatography (SEC)

SEC experiments were conducted in chromatography-grade THF at concentrations of 0.5–2 mg $mL^{-1}$ using a Malvern OMNISEC GPC instrument equipped with a Viscotek TGuard guard column (CLM3008), and Viscotek T3000 (CLM3003) and T6000 (CLM3006) GPC columns packed with porous poly(styrene-co-divinylbenzene) particles regulated at a temperature of 35 °C. Signal response was measured using differential viscometer, differential refractive index, photodiode array, and light scattering (90° and 7°) detectors. Interdetector volume was calibrated using a single polystyrene (PS) standard with $M_n$ = 101,000 and PDI = 1.04. Molecular weights for all iridium-containing copolymers were determined by conventional calibration using (a) PS standards and (b) a series of poly(**M4**) standards[18] with molecular weights

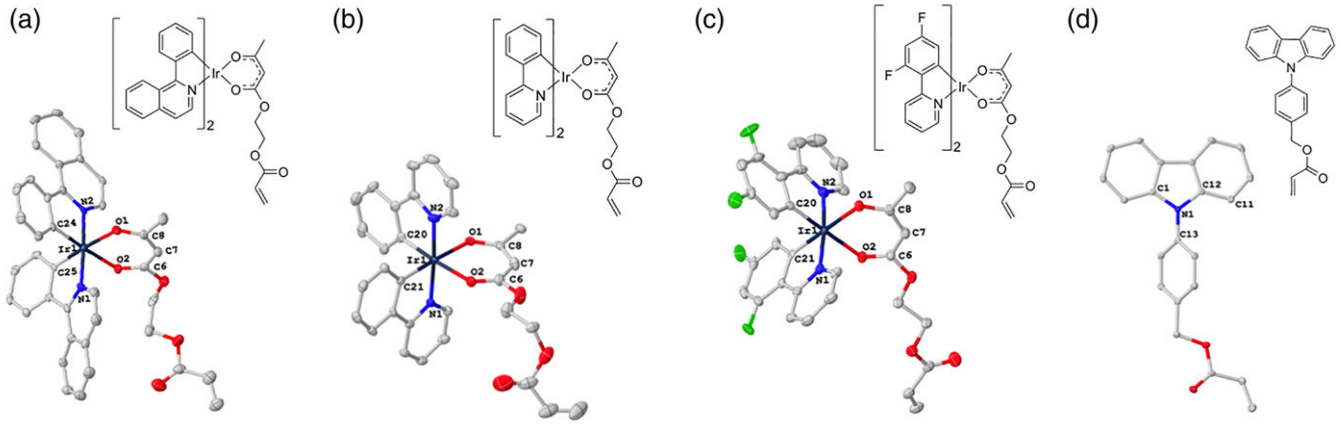

**FIGURE 1** Crystal structures of (a) **M1**, (b) **M2**, (c) **M3**, and (d) **M4** obtained from X-ray diffraction analysis, depicted with 50% thermal ellipsoids. [Color figure can be viewed at wileyonlinelibrary.com]

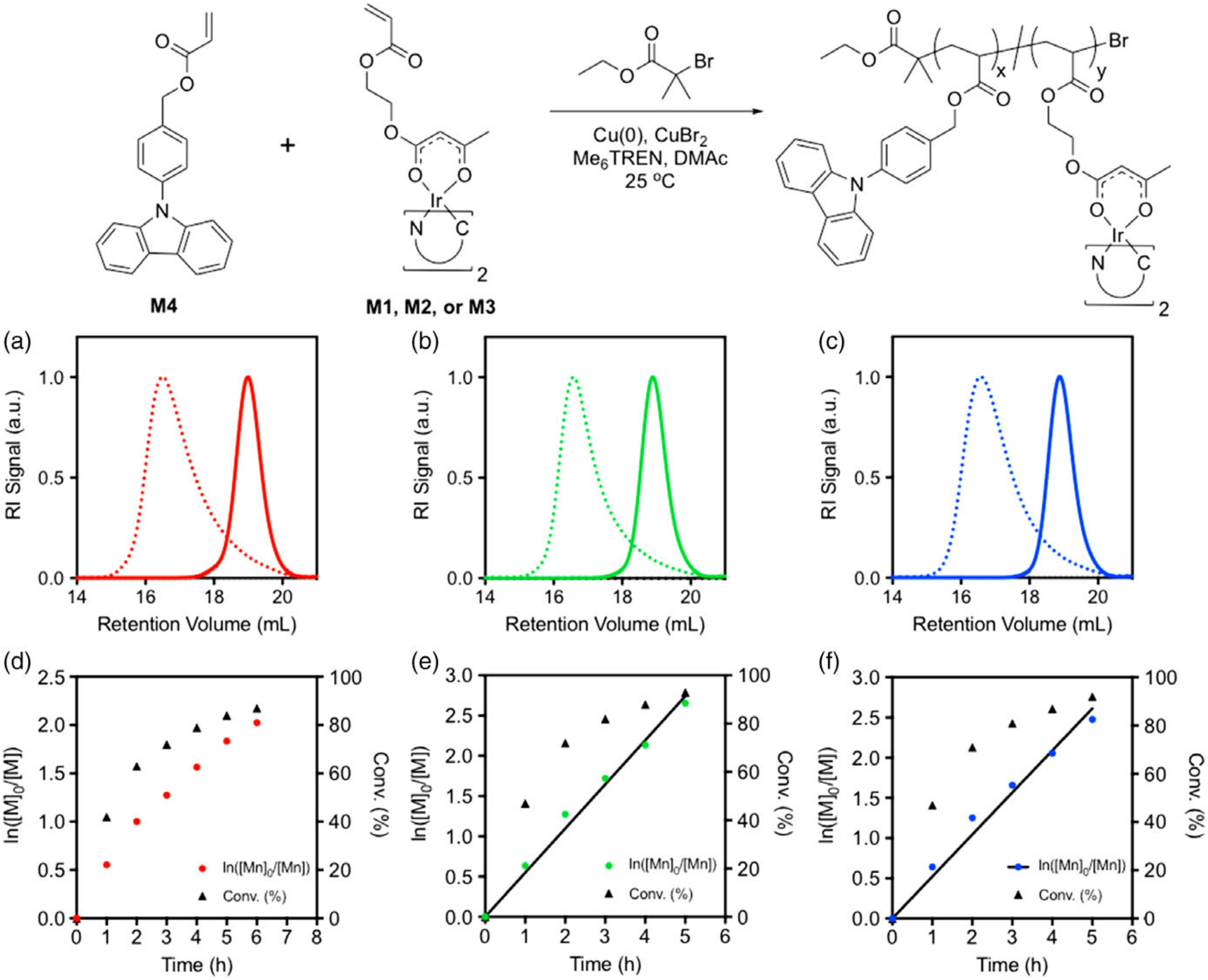

**FIGURE 2** SEC RI traces (a–c) and kinetic data (d–f) for poly(**M4**) doped with 5 mol % of **M1** (a,d), **M2** (b,e), and **M3** (c,f). Target molecular weights = 10 kDa (a–c solid lines; d–f) or 50 kDa (a–c dashed lines). [Color figure can be viewed at wileyonlinelibrary.com]

between 3000 and 50,000 Da. Molecular weights for poly(**M4**) standards were determined using triple detection and the refractive index increment (d*n*/d*c* = 0.195 in THF) of the polymer.

### Density Functional Theory

Calculations were performed using the Gaussian 09 software package. Ground state geometries and energies were calculated using the hybrid functional B3LYP and the 6-31 + G(d) basis set for all atoms except for iridium, for which the LANL2DZ ECP basis was used. To simulate electronic properties of our polymeric materials, analogous versions of each monomer were calculated in which the alkene group in the acrylate moiety is replaced with a *sec*-butyl group, similar to the structure found in the corresponding polymer.

### General Procedure for Cu(0)-RDRP

**M4** (0.46 mmol, 24 eq.) and iridium monomer (0.12 mmol, 6 eq., 20 mol % of total monomer content) were weighed into a 4 mL vial capped with a Teflon-lined lid equipped with a magnetic stir bar and brought into a nitrogen atmosphere glovebox. In the glovebox, 75 μL of ethyl α-bromoisobutyrate (EBiB) solution in DMAc ($C_{\mathrm{EBiB}}$ = 50 mg/mL; EBiB: 3.7 mg, $1.9 \times 10^{-2}$ mmol, 1 eq.), 82 μL of CuBr$_2$/Me$_6$TREN solution in DMAc ($C_{\mathrm{Cu}}$ = 3.4 mg/mL; CuBr$_2$: 2.8 mg, $1.2 \times 10^{-3}$ mmol, 0.065 eq.; Me$_6$TREN: mg, $1.3 \times 10^{-3}$ mmol, 0.068 eq.), and 1,3,5-trimethoxybenzene (3 eq.) as an internal standard were added to the vial containing monomers. DMAc was added to make the total polymerization volume 1.15 mL. The mixture was stirred at room temperature for several minutes until all reagents were dissolved. Concurrently, a 0.96 cm piece of 18 gauge copper (0) wire was stirred in concentrated HCl for 15 minutes to remove surface impurities, then washed sequentially with deionized water and acetone and dried for 10 minutes in an oven at 120 °C. The wire was added to the reaction vial to initiate the polymerization and the reaction was allowed to stir at room temperature until complete by $^1$H

NMR. The polymerization was quenched by the addition of water, followed by centrifugation to isolate the polymer. The polymer was dissolved in $CH_2Cl_2$, dried over $MgSO_4$, and concentrated *in vacuo.* The residue was purified by size exclusion chromatography on a reusable Bio-Rad Bio-Beads S-X1 support in THF, and fractions containing polymer were collected and dried *in vacuo* overnight. The polymers may also be purified by reprecipitation of polymer from $CH_2Cl_2$ into hexanes, providing a more convenient purification method as the reaction scale increases.

### Chain Extension of Methyl Acrylate with Iridium-Doped M4

Methyl acrylate (MA, 190.0 mg, 100 eq.) was weighed into a 4 mL vial equipped with magnetic stir bar and capped with a Teflon-lined lid and brought into a nitrogen atmosphere glovebox. In a glovebox, 17 μL of EBiB solution in DMAc ($C_{\mathrm{EBiB}}$ = 250 mg/mL; EBiB: 4.3 mg, $2.2 \times 10^{-2}$ mmol, 1 eq.), 41 μL of $CuBr_2$ and $Me_6TREN$ solution in DMAc ($C_{\mathrm{Cu}}$ = 7.9 mg/mL; $CuBr_2$: 0.32 mg, $1.4 \times 10^{-3}$ mmol, 0.065 eq.; $Me_6TREN$: 0.44 mg, $1.5 \times 10^{-3}$ mmol, 0.068 eq.) and 1,3,5-trimethoxybenzene (1 eq.) were added to the vial containing MA. DMAc was added to make the total volume 200 μL, and the vial was stirred at room temperature for several minutes until all reagents were dissolved. Concurrently, a 1.1 cm piece of 18 gauge copper (0) wire was cleaned as per the procedure listed above. The wire was added to the reaction vial to initiate polymerization and the reaction was allowed to stir at room temperature until a conversion of 98% was reached by NMR. Once complete, **M4** (0.63 mmol, 28.5 eq.), and **M1**, **M2**, or **M3** (0.033 mmol, 1.5 eq.), 74 μL of $CuBr_2$ solution in DMAc ($C_{\mathrm{Cu}}$ = 4.3 mg/mL; $CuBr_2$: 0.32 mg, $1.4 \times 10^{-3}$ mmol, 0.065 eq.; $Me_6TREN$: 0.34 mg, $1.5 \times 10^{-3}$ mmol, 0.068 eq.), and 1.1 cm of freshly cleaned copper (0) wire was added to the reaction vial. DMAc was added to bring the total reaction volume up to 1.35 mL. The reaction was stirred at room temperature until the polymerization was complete by $^1H$ NMR spectroscopy.

## RESULTS AND DISCUSSION

Three iridium-containing monomers were designed and synthesized based on the N^C chelate ligands 1-phenylisoquinoline (piq, **M1**), 2-phenylpyridine (ppy, **M2**), or 2(2,4-difluorophenyl) pyridine (dfppy, **M3**). These ligands are commonly used to give red, green, or sky-blue emission in complexes of Ir and Pt, generally exhibiting mixtures of ligand-centered ($^3$LC) or metal-to-ligand charge-transfer ($^3$MLCT) phosphorescence.[23,37–39] A polymerizable group was then prepared using an acrylate-functionalized β-ketoester, structurally analogous to the acetylacetonate ligands commonly used in high-performance OLED emitters.[40,41] This ligand is conveniently prepared by heating commercially available 2-hydroxyethyl acrylate to 120 °C, which can react with 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one in the presence of radical inhibitors to cleanly afford compound **1** with the elimination of acetone (Scheme 1).

μ-dichloro-bridged dimers of Ir(III) and each cyclometalating ligand was then prepared by Nonoyama reaction of $IrCl_3{\cdot}H_2O$, which were then treated with AgOTf to abstract the chloride ligands. Addition of **1** to this mixture in the presence of $NEt_3$ then gave complexes **M1–M3**, which were isolated as analytically pure compounds following precipitation from $CH_2Cl_2$ into hexanes.

Single crystals of **M1–M3** suitable for X-ray diffraction analysis were then obtained by slow evaporation from $CH_2Cl_2$/hexanes. All complexes crystallize with the N atoms from the cyclometalating ligands in a *trans* configuration (see Figure 1), placing the ketoester ancillary ligand *trans* to both carbon atoms. Space groups of $P2_1/c$, $I2/a$, and $C2/c$ are observed for **M1–M3**, respectively. A crystal structure was also obtained for carbazole-based monomer **M4**, which would form the host

**TABLE 1** Synthesis of Iridium-Doped Polymers by Cu(0)-RDRP.[a]

| | $M_n$ (Da, **M4** Calibration) | | $M_n$ (Da, PS Calibration) | | | | | |
|---|---|---|---|---|---|---|---|---|
| Ir Dopant mol % | $M_n$ | Đ[b] | $M_n$ | Đ[b] | $M_{n,\mathrm{theory}}$ | Conv. (%) | $t$ (h) | $k_p^{\mathrm{app}}$ ($\times 10^{-5}$ s$^{-1}$) |
| 20% **M1** | 10,600 | 1.13 | 4900 | 1.11 | 9100 | 72 | 7.5 | – |
| 20% **M2** | 11,100 | 1.09 | 5100 | 1.08 | 10,700 | 89 | 4.5 | 13.9 |
| 20% **M3** | 12,100 | 1.11 | 5500 | 1.10 | 11,200 | 90 | 6.5 | 10.6 |
| 10% **M1** | 12,300 | 1.14 | 5600 | 1.11 | 9500 | 84 | 7 | – |
| 10% **M2** | 11,300 | 1.09 | 5100 | 1.08 | 9900 | 90 | 5 | 13.6 |
| 10% **M3** | 11,700 | 1.10 | 5300 | 1.09 | 10,200 | 91 | 5 | 13.9 |
| 5% **M1** | 10,600 | 1.09 | 4800 | 1.08 | 8600 | 81 | 6.5 | – |
| 5% **M2** | 11,100 | 1.09 | 5100 | 1.08 | 9700 | 93 | 5 | 15.3 |
| 5% **M3** | 11,100 | 1.09 | 5100 | 1.08 | 9600 | 92 | 5 | 14.4 |
| 0%[18] | 10,100[c] | 1.11 | 4800 | 1.07 | 9600 | 96 | 8 | 14.7 |

[a] Reaction conditions: [Monomer[/][EBiB]/[$CuBr_2$]/[$Me_6TREN$] = 30/1/0.065/0.068; DMAc = 1.15 mL; 18 gauge Cu(0) wire = 0.96 cm. Monomer = **M4** + **M1**, **M2** or **M3**.

[b] Determined after purification by preparative SEC.

[c] Determined using triple detection SEC.

**TABLE 2** Molecular Weights for 50 kDa Polymers of **M4** Doped with **M1–M3**.

| | **M4** Calibration | | PS Calibration | | | |
|---|---|---|---|---|---|---|
| Ir Dopant % | $M_n$ | Đ[b] | $M_n$ | Đ[b] | $M_{n,\text{theory}}$ | Conv.[a] (%) |
| 5% **M1** | 37,400 | 1.47 | 15,800 | 1.46 | 41,500 | 79 |
| 5% **M2** | 37,900 | 1.40 | 15,900 | 1.37 | 43,400 | 84 |
| 5% **M3** | 38,100 | 1.42 | 16,000 | 1.40 | 41,900 | 71 |

[a] Reaction conditions: [Monomer]/[EBiB]/[$CuBr_2$]/[$Me_6$TREN] = 150/1/0.065/0.068; DMAc = 1.15 mL; 18 gauge Cu(0) wire = 0.22 cm. Monomer = **M4** + **M1**, **M2**, or **M3**. Reaction time = 24 h.

[b] Determined after purification by preparative SEC.

material in subsequent Cu(0)-RDRP reactions. For all Ir complexes, the Ir-O bond lengths ranged from 2.13 to 2.17 Å, with little to no difference observed between the ester and ketone-based carbonyl groups. These distances are consistent with reported structures of the common OLED emitter $Ir(ppy)_2$(acac),[42] indicating similar bond strengths for the acetylacetonate and the ketoester.

## Polymer Synthesis

Polymers of **M4** doped with 5, 10, or 20 mol % of either **M1**, **M2**, or **M3** were then prepared via Cu(0)-RDRP in DMAc, which we previously found to provide a balance of catalyst activity and monomer solubility for common small-molecule organic semiconductors.[18,19] Polymerizations were carried out in a nitrogen atmosphere glovebox to rigorously exclude oxygen while aliquots were taken throughout the reaction, but can also be conveniently conducted on a Schlenk line under $N_2$. Polymerizations were conducted using 0.96 cm of 18-gauge Cu(0) wire, freshly cleaned prior for 15 minutes to remove impurities and the CuO surface layer. Using EBiB as initiator and *tris*[2-(dimethylamino)ethyl]amine ($Me_6$TREN) as ligand, polymerizations were carried out with [EBiB]/[$CuBr_2$]/[$Me_6$TREN] = 1/0.065/0.068 targeting molecular weights of 10 and 50 kDa. Doping of the iridium compound into a carbazole matrix is designed to give highly phosphorescent polymer products with minimal quenching from triplet–triplet annihilation upon excitation, which reduces quantum yields of materials with high concentrations of triplet emitters.

The results of the polymerizations using 5 mol % of **M1**, **M2**, or **M3** are shown in Figure 2 and summarized for all doping concentrations in Table 1. Targeting molecular weights of 10 kDa gave dispersities of 1.09–1.14 in all cases, with very slight increases observable as the iridium content of the polymers increased. Molecular weights measured by SEC were in good agreement with theory at 10,600, 11,100, and 11,100 for the 5 mol % **M1**, **M2**, and **M3** polymers, respectively.

Special care had to be taken to obtain accurate molecular weights by SEC for these materials, as the phosphorescence spectra of **M1–M3** were sufficiently broad as to interfere with detection by light scattering at 640 nm. Molecular weight determination was first attempted by conventional calibration against PS standards, but the poor structural analogy between PS and the large organic semiconductors employed here gave measured molecular weights approximately 50% below the theoretical expected value (Table 1). All $^1$H NMR signals from the polymer end groups were also obscured by signals from the iridium dopants, making estimation of molecular weight by NMR spectroscopy impractical.

To circumvent this, we synthesized a series of standards of **M4** alone using previously reported methods,[18] with $M_n$ ranging from 3 to 50 kDa. Absolute molecular weights for these polymers could then be determined using triple detection and the d$n$/d$c$ value for poly(**M4**) (0.195 in THF), giving a calibration which more accurately reflects the elution times of poly(**M4**) doped with iridium phosphors. Using these methods, agreement of the molecular weights obtained by SEC and theory are improved substantially (Table 1).

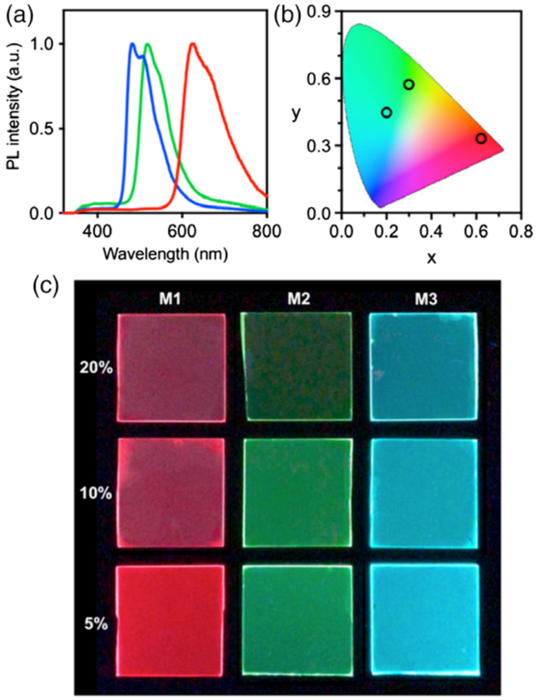

**FIGURE 3** (a) Solid-state emission spectra for poly(**M4**)$_{10k}$ doped with 5 mol % **M1** (red), **M2** (green), or **M3** (blue) ($\lambda_{ex}$ = 300 nm). (b) CIE 1931 diagram showing the corresponding emission colors of these polymers. (c) Photograph of thin films of poly(**M4**)$_{10k}$ doped with **M1–M3** under UV irradiation ($\lambda_{ex}$ = 365 nm). [Color figure can be viewed at wileyonlinelibrary.com]

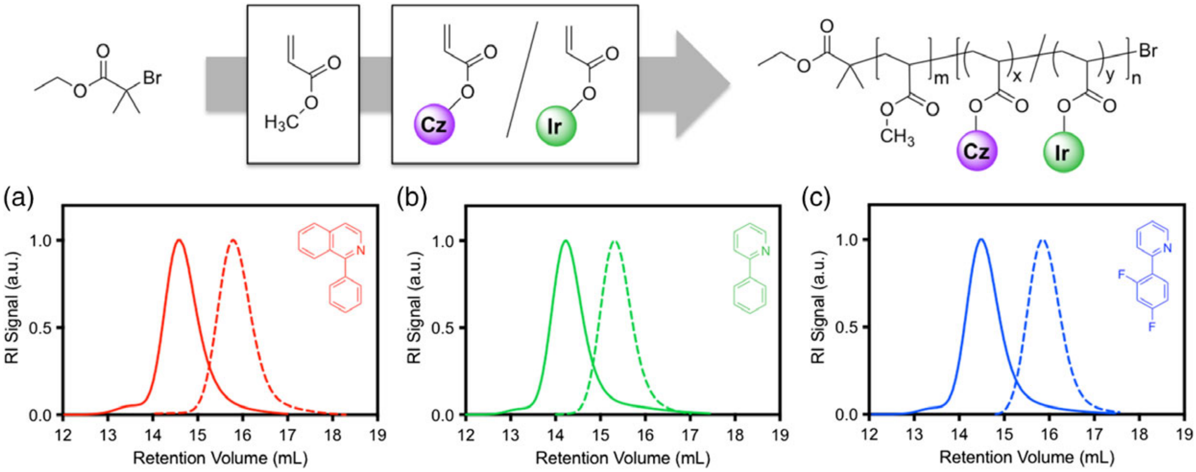

**FIGURE 4** SEC traces showing the chain extension of PMA$_{100}$ (dashed lines) with (a) **M4**-co-**M1**, (b) **M4**-co-**M2**, (c) **M4**-co-**M3** (solid lines). Cz and Ir represent the structures of **M4** and iridium-containing monomers **M1**–**M3**. $x$ = 0.95, $y$ = 0.05. [Color figure can be viewed at wileyonlinelibrary.com]

Compared to undoped polymers of **M4**, the relative rates of the copolymerization reactions described in Table 1 were largely unchanged, with a small reduction in apparent rate constant ($k_p^{app}$) observable as the doping concentration of iridium monomer increased. In the case of the bulkier red monomer, the kinetic data showed some deviation from linearity at higher conversions, implying that steric effects may be reducing chain-end livingness. This was particularly apparent in the case of the polymer doped with 20% of **M1**, which reached the lowest conversion of the series at 72% in 7.5 h.

In all cases, the conversion of the polymerizations (10 kDa target MW) was monitored by $^1$H NMR spectroscopy. Once a change in conversion with respect to time was no longer observed, each polymerization was stopped. For this reason, reaction times and final conversions for each polymerization differ.

High-molecular-weight polymers with molecular weights of 50 kDa were then targeted via polymerization of **M4** containing 5 mol % of **M1**, **M2**, or **M3**. Though dispersities broadened significantly (1.40–1.47), polymers with $M_n$ = 37,400–38,100 were successfully obtained with conversions of 71–84% (Table 2).

### Photophysical Characterization

All iridium-doped polymers show strong luminescence under UV irradiation at 365 nm, with emission bands originating from both **M4** and the iridium dopants in dilute toluene solution. As anticipated, the relative amount of dopant-based emission increases with doping concentration, with the polymers containing 20 mol % of the iridium complexes showing the greatest proportion of phosphorescence in all cases. While the polymers doped with **M1** show impressive quantum yields ranging from 51% (5 mol % **M1**) to 81% (20 mol % **M1**), the quantum yields of the polymers doped with **M2** and **M3** decrease substantially with increased iridium content, falling from 42% and 32% with 5 mol % iridium, respectively, to 11% and 2.7% at 20 mol % (Supporting Information Fig. S11). Interestingly, the emission from **M4** vanishes almost entirely when thin films of these materials are examined in the solid state, consistent with an improvement in energy transfer from host to emitter (Figs. 3 and S12). This effect improves the emission color purity of the samples substantially, giving CIE 1931 coordinates of (0.62, 0.33), (0.30, 0.57), and (0.20, 0.44) for poly(**M4**) doped with 5 mol % of **M1**, **M2**, and **M3**, respectively. As selecting an ideal host for phosphorescent materials is critical for achieving efficient energy transfer,[43,44] further study on the relationship between these dopants and a variety of acrylic monomer hosts is required to optimize quantum yields further.

Finally, we examined the synthesis of iridium-containing block copolymers by chain-extension of MA prepared by Cu(0)-RDRP (see Figure 4). Polymerization of MA in DMAc with [MA]/[EBiB]/[CuBr$_2$]/[Me$_6$TREN] = 100/1/0.065/0.068 gave

**TABLE 3** Molecular Weight and Dispersities for MA-*b*-(**M4**-*co*-Ir) Polymers.

| | MA Block | | | Ir-Doped Block | | Block Copolymer | |
|---|---|---|---|---|---|---|---|
| Monomer | $M_n$[a] | Đ | DP$_n$ | $M_n$[b] | DP$_n$ | $M_n$[b] | Đ |
| **M1** | 9200 | 1.03 | 104 | 11,200 | 32 | 20,400 | 1.04 |
| **M2** | 8000 | 1.05 | 91 | 9300 | 27 | 17,300 | 1.06 |
| **M3** | 8500 | 1.01 | 97 | 12,200 | 35 | 20,800 | 1.04 |

[a] Determined by SEC in THF.

[b] Determined by $^1$H NMR.

well-defined polymers with dispersities of 1.00–1.03 reaching 98% conversion after 8.5 hours. Without workup or quenching the reaction, a mixture of **M4** and one of **M1**–**M3** was then added to this reaction to extend the polymer chain. Consistent with our earlier results and those of Bates and Hawker,[45] high chain-end livingness is preserved when additional catalyst is added with the second batch of monomer. The resulting $\text{PMA}_{100}$-*b*-poly(**M4**-*co*-Ir) block copolymers showed monomodal molecular weight distributions with dispersities of 1.04, 1.07, and 1.04 for the **M1**, **M2**, and **M3**-containing diblock copolymers, respectively, indicating minimal termination before the addition of the luminescent block (Table 3). These results indicate that Cu(0)-RDRP provides a facile route for the incorporation of phosphorescent metal complexes into block copolymers, which may have applications as self-assembled materials, luminescent polymer dots, or lithographic resists.

## CONCLUSIONS

Here we have demonstrated a facile method for the synthesis of iridium-containing acrylic polymers using Cu(0)-RDRP. The β-ketoester acrylate ligand was shown to effectively provide a polymerizable handle to red, green, and sky-blue iridium complexes, which could be copolymerized with a carbazole-based host material to give good color purity in the solid state. Resulting polymers showed dispersities as low as 1.08 with conversions reaching 93%, providing a low-cost route to phosphorescent metallopolymers with minimal waste. High-molecular-weight polymers with $M_n$ approaching 40 kDa were also successfully prepared, as well as block copolymers by chain extension of MA in one pot. We anticipate that this strategy can be readily applied to the polymerization of other organometallic acrylates via Cu(0)-RDRP, providing an inexpensive and scalable route to well-defined metallopolymers.

## ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC). **C. J. Christopherson** and **D. M. Mayder** thank the University of British Columbia for 4-year fellowships, **N. R. Paisley** and **E. R. Sauvé** thank NSERC for Postgraduate Scholarships, and ZMH is grateful for support from the Canada Research Chairs program.

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