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Novel W(II) complexes for reversible addition-fragmentation chain transfer (RAFT) polymerizations

Chuan-Lin Chen [a], Yih-Hsing Lo [b,*], Chia-Yi Lee [c], Yih-Hsuan Fong [b], Kuo-Chen Shih [d], Chiung-Cheng Huang [c,*]

[a] Department of Biomedical Imaging and Radiological Sciences, National Yang-Ming university, Taipei, Taiwan 112, Republic of China
[b] Department of Natural Science, Taipei Municipal University of Education, Taipei, Taiwan 100, Republic of China
[c] Department of Chemical Engineering, Tatung University, Taipei, Taiwan 104, Republic of China
[d] Department of Optical-Grade Organic Materials, Nanopowder and Thin Film Technologycenter, ITRI, Tainan, Taiwan, Republic of China

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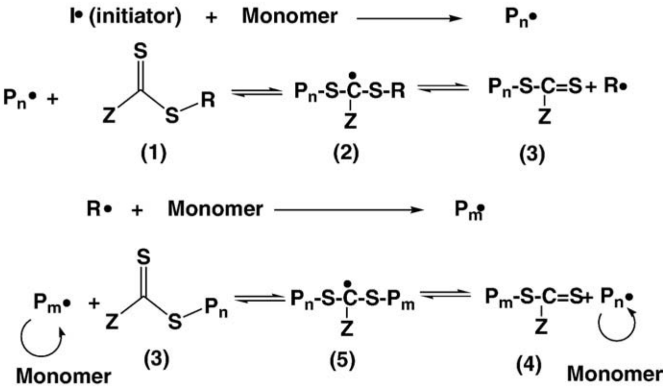
ABSTRACT

Alkylation of the phosphorus coordination of the diphenyl(dithioformato)phosphine ligand in $[W(CO)_5(PPh_2CS_2)]NEt_4$ (**1**) at the S atom results in the formation of the novel RAFT agent $S C[W(CO)_5PPh_2]S–R$ (**2a**, $R = CH_2Ph$; **2b**, $R = CH_2CH CH_2$). These compounds have been shown to be highly effective in reversible addition-fragmentation chain transfer (RAFT) polymerization to produce polymers (homopolymer and diblock copolymer) of predetermined molecular weight and narrow polydispersity (<1.3). Electron-withdrawing organometallic substituents can increase the activity of RAFT agents. To the best of our knowledge, this is the first report of their use as RAFT agents in polymerization.

Most recently, with increased ripeness of polymer technologies, polymer applications are concerned not only in synthetic resin industries and traditional plastics but also in high technology industries such as electronics [1], electroluminescent materials [2], optoelectronics [3] and biotechnologies [4]. Some relative polymer materials with particular properties are critical for the related industries. In 1998, CSIRO [5] disclosed an active free radical polymerization method called reversible addition-fragmentation chain transfer process (RAFT process) to prepare polymer products with narrow molecular weight distribution and further control the polymer chain length. In general, RAFT process controls most free radical polymerizations for alkene monomers. The proposed mechanism for styrene polymerization in the presence of the RAFT agent ($S C(Z)S–R$) is shown in Scheme 1.

Furthermore, demands and significance of polymer materials having terminal organometallic functional groups are steadily on the increase due to application thereof to dispersants, hybrid materials, optoelectrical materials and nanotechnologies. However, polymer materials having terminal organometallic functional groups are unable to be prepared through conventional RAFT reagents. Therefore, it is necessary to develop a novel RAFT reagent for preparing polymer materials having terminal organometallic functional groups with controllable polymerization degree. In this paper, we demonstrated that organometallic RAFT agents $S [W(CO)_5PPh_2]S–R$ (2a, $R = CH_2Ph$; **2b**, $R = CH_2CH CH_2$) could be used to confer living character to radical polymerization.

The complex $[W(CO)_5(PPh_2CS_2)]NEt_4$ (**1**) [6] and $PhCH_2Br$ reacted in CH_2Cl_2 at room temperature for 24 h, red powder was generated and confirmed with elementary analysis and FAB mass spectrometry as the neutral complex $S C[W(CO)_5PPh_2]S–CH_2Ph$ (**2a**) (Scheme 2). Extraction with *n*-hexane followed by removal of the solvent gave the analytically pure product **2a**. This red powder was isolated in 21% yield. Complex **2a** is soluble in polar solvents such as CH_2Cl_2, $CHCl_3$, and acetone, moderately soluble in *n*-hexane, and stable in solution and in air. The FAB mass spectrum of **2a** shows a base peak in



Scheme 1. The mechanism of RAFT.

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* Corresponding authors.
E-mail address: yhlo@mail.tmue.edu.tw (Y.-H. Lo).

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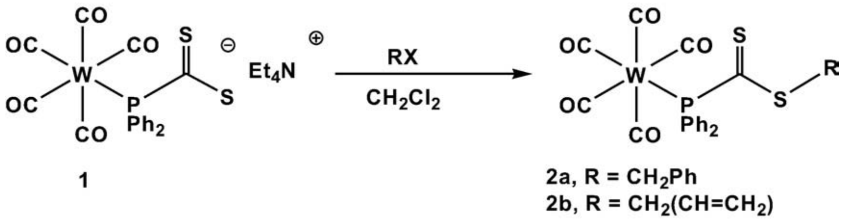


Scheme 2. Synthesis of organometallic RAFT agents.

agreement with the [M$^+$] ion fragment. In the IR spectrum of **2a**, three terminal carbonyl stretchings appear at 2076 (m), 1985 (s), 1921 (vs), a typical pattern for an LM(CO)$_5$ unit in distorted octahedral geometry [6]. In the ^{31}P{^{1}H} NMR spectrum of **2a**, a resonance at δ 59.6 with a pair of tungsten satellites ($^1J_{W–P} = 237.0$ Hz) indicates the P-coordination of the S C(PPh$_2$)S–CH$_2$Ph ligand. The ^{1}H NMR spectrum of **2a** exhibits one resonance at δ 4.54 attributed to the CH$_2$Ph and the corresponding resonances in the ^{13}C NMR spectrum appear at δ 42.3. On the basis of these spectroscopic data, it is probable that the alkylation takes place at one of the sulfur atom. Similarly, the reaction of **1** with ICH$_2$(CH$=$CH$_2$) in CH$_2$Cl$_2$ affords S C[W(CO)$_5$PPh$_2$]S–CH$_2$ (CH CH$_2$) (**2b**) in 76% yield. The ^{31}P{^{1}H} NMR resonance of **2b** (δ 61.5 with $^1J_{W–P} = 252.0$ Hz) is close to that of **2a** [7].

Table 1
Mn, PDI, and conversion data for the polymerization of ^{t}BA at 60 °C.

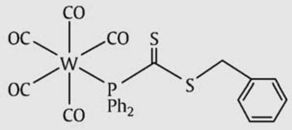
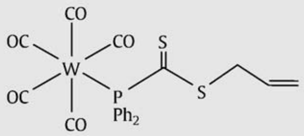
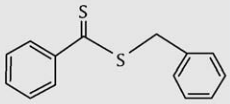
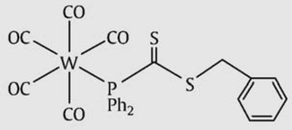
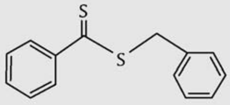
RAFT agent	Time (h)	Conversion (%)	*Mn* (g mol^{-1})	PDI
 2a	1	44.1	43,894	1.19
	3	75.4	64,416	1.21
	6	80.5	76,705	1.26
 2b	1	19.3	10,350	1.19
	3	46.7	23,263	1.19
	6	77.7	40,297	1.18
 3	1	1.76	1041	1.12
	3	6.2	3434	1.15
	6	12	6345	1.18
No RAFT agent	1	82.6	208,610	1.32

Table 2
Mn, PDI, and conversion data for the polymerization of styrene at 60 °C.

RAFT agent	Time (h)	Conversion (%)	*Mn* (g mol^{-1})	PDI
 2a	8	13	6642	1.16
	15	32.7	13,406	1.19
	25	47	18,685	1.17
 3	8	6	3674	1.21
	15	14	6440	1.21
	25	16.7	7588	1.23
No RAFT agent	8	16.7	102,381	1.65

Styrene and ^{t}BA was polymerized with the complexes **2** as RAFT agent using thermal initiation, respectively [8]. The purity of the RAFT agent was established by spectroscopic methods as well as elemental analysis prior to use. RAFT polymerization was performed at 60 °C. The molar ratio between the RAFT agent and monomer was kept constant at 400, the AIBN and RAFT agent was kept constant at 2 in all the polymerization processes. The molar mass characteristics of the polymers were determined by gel permission chromatography (GPC). In addition, in order to check their effectiveness as RAFT agents, we also obtained the polymerization data using the organic RAFT agent benzyl dithiobenzoate S C(Ph)S–Ph (**3**) [9].

The results of styrene and ^{t}BA polymerizations for **2** and **3** are summarized in Tables 1 and 2, respectively. The evolution of molecular weight and polydispersity vs conversion for three of the more active RAFT agents are also summarized in Figs. 1–4 The RAFT agent **2** and **3** are demonstrated to be an effective control on free radical polymerization and the reaction behaves like living free radical polymerization with a number-average molecular weight proportional to conversion. We found that by varying the electronic properties of the Z or R group (Scheme 1), the efficiency of polymerization is affected. The increasing trends with complexes **2** were similar to those of organic RAFT agent **3**. However, the polymerization performed in the presence of the organic RAFT agent **3** was slower than that performed with **2a**. In ^{t}BA and styrene polymerization, the organic RAFT agent **3** afforded a conversion yield 12% and 16.7%, compared to over 80% and 47% for the RAFT **2a**, respectively. The relative effectiveness of the RAFT agents is

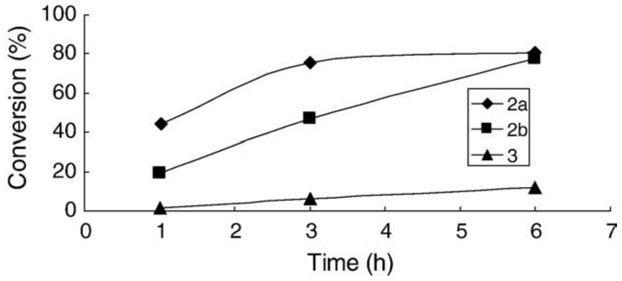


Fig. 1. Trend of the conversion of thermally initiated RAFT P^{t}BA as a function of time.

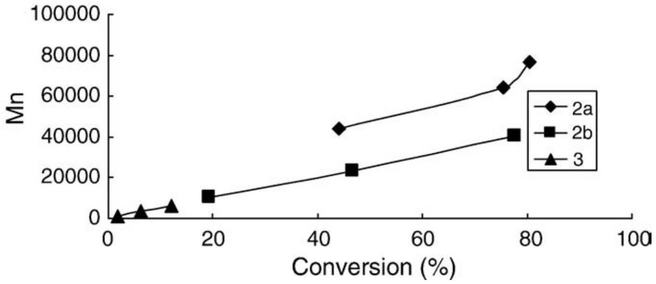


Fig. 2. Trend of the number-average molar mass of thermally initiated RAFT P^{t}BA as a function of conversion rate.

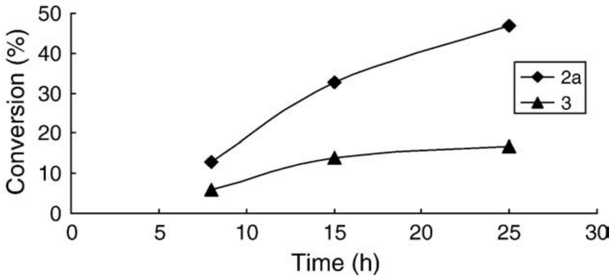


Fig. 3. Trend of the conversion of thermally initiated RAFT polystyrenes as a function of time.

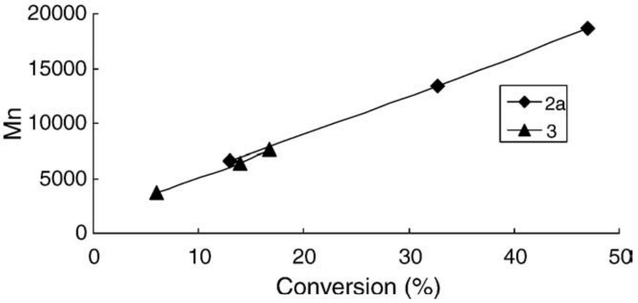


Fig. 4. Trend of the number-average molar mass of thermally initiated RAFT polystyrenes as a function of conversion rate.

rationalized in terms of interaction of the electron-withdrawing organometallic substituents (Z W(CO)$_5$(PPh$_2$)) with the C S double bond to activate that group toward free radical addition (Scheme 1). On the other hand, the ^{t}BA polymerization rate using the allyl derivative (R = CH$_2$CH CH$_2$) **2b** was lower than **2a** with the benzyl derivative (R = CH$_2$Ph), which may be attributed to the more stable benzyl radical group. The partitioning of R radical group between adding to polymeric RAFT agent and monomer (to reinitiate) can also have a significant effect on the rate of consumption of RAFT agent (Scheme 1).

To verify the "livingness" of the process, we investigated the ability to chain-extend the PS (Table 2, *Mn* = 18,685, PDI = *Mw*/*Mn* = 1.17) to yield diblock copolymers consisting of PS and P^{t}BA. The polymer PS was used as a RAFT agent for the growth of the P^{t}BA second block (PS-*block*-P^{t}BA, *Mn* = 36,138, PDI = 1.21). Intriguingly, treatment of P^{t}BA (Table 2, *Mn* = 76,705, PDI = 1.26) in CH$_3$CN at room temperature in a 5-mm NMR tube causes cleavage of the W–P bond and affords W(CO)$_5$(CH$_3$CN) and organic polymer P^{t}BA. The terminal organometallic functional group may be removed by subjecting the obtained polymer to elimination to provide the corresponding organic polymer.

We synthesized W(II) complexes at high yields from [W(CO)$_5$(PPh$_2$CS$_2$)]NEt$_4$ (**1**). They were very stable towards air and moisture. To the best of our knowledge, this is the first report of their use as RAFT agents in polymerization. In addition, the terminal organometallic functional group may be removed by subjecting the obtained polymer to elimination to provide the corresponding organic polymer.

Acknowledgment

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[7] Dichloromethane (40 mL) was added to a round-bottomed flask charged with [Et$_4$N] [W(CO)$_5$(PPh$_2$CS$_2$)] (3.0 g, 4.2 mmol) and C$_6$H$_5$CH$_2$Br (0.5 mL, 4.2 mmol) and the mixture was stirred at room temperature for 24 h. The solvent was removed and the residue was extracted with hexane (2 × 10 mL), and the extracts were filtered through Celite. The filtrate was concentrated to ca. 5 mL and cooled to − 18 °C for 12 h to give the analytically pure product S C[W(CO)$_5$PPh$_2$]S–CH$_2$Ph (**2a**, 21% yield). Spectroscopic data for **2a**: IR (KBr, νco): 2076 (m), 1985 (s), 1921 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.63–7.47 (m, Ph), 4.54 (s, 2H, C*H*$_2$). ^{13}C NMR (CDCl$_3$): δ 237.4 (d, *trans*-CO, $^2J_{pc}$ = 7.5 Hz), 199.1 (d, CS$_2$, J_{pc} = 25.1).

[8] Styrene polymerizations: Styrene (28.0 mmol) were degassed via four freeze pump–thaw cycles, transferred along with 5.5 mg (0.028 mmol) AIBN and **2a** (0.048 mmol) into a nitrogen-filled glovebox where stock solutions of monomer, AIBN, and RAFT agent were prepared. A few drops of toluene (ca. 1.5 mL) were added in the case of polymerization to guarantee the dissolving of the RAFT agent. The stock solution were filled into individual glass vials and sealed with Teflon/rubber septa. The vials were subsequently inserted into a block heater thermostated at 60 °C for 25 h. The reactions were stopped by cooling the solutions in an ice bath and quenched in CH$_3$OH, then diluted with CH$_2$Cl$_2$. The **PS** (*Mn* = 18685, PDI = 1.17) was purified by precipitation from CH$_2$Cl$_2$ solution into CH$_3$OH. The **P^{t}BA** (*Mn* = 76705, PDI = 1.26) was prepared by using a similar procedure as that of **PS**. Synthesis of Diblock Copolymer (PS-*block*-P^{t}BA): **PS** (0.016 mmol), 2.6 mg (0.017 mmol) AIBN and ^{t}BA (0.064 mmol) were added in a Schlenk flask. The reaction mixture was degassed by four freeze and thaw cycles and sealed under nitrogen. Bulk thermally initiated polymerization was conducted at 60 °C for 9 h. The reactions were stopped by cooling the solutions in an ice bath and quenched in CH$_3$OH, then diluted with CH$_2$Cl$_2$. The diblock copolymer (*Mn* = 36138, PDI = 1.21) was purified by precipitation from CH$_2$Cl$_2$ solution into CH$_3$OH. Synthesis of organic polymers from organometallic RAFT agent: the polymer **P^{t}BA** (10 mg) in CH$_3$CN prepared under N$_2$ in NMR tube was heated to reflux for 24 h. The solvent was removed under vacuum and washed with 1 mL of CH$_3$OH. After filtration, the white precipitate was washed with 1 mL of *n*-hexane and dried under vacuum to give the organic polymer. The filtrate was dried and extracted with 2 mL of CH$_2$Cl$_2$. The extract was filtered, and the filtrate was dried under vacuum to give the product W(CO)$_5$(CH$_3$CN).

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