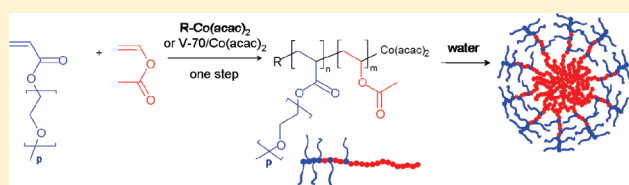# Organometallic-Mediated Radical Polymerization: Unusual Route toward (Quasi-) Diblock Graft Copolymers Starting from a Mixture of Monomers of Opposed Reactivity

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ABSTRACT: Graft copolymers have been prepared by one-step organometallic-mediated radical polymerization (OMRP) for the first time. Poly(ethylene glycol) acrylate (PEGA) was copolymerized with vinyl acetate (VAc) to yield well-defined P(PEGA-*grad*-VAc) gradient graft copolymers using bis(acetylacetonato)-cobalt(II) as the control agent. The influence of experimental parameters such as the PEGA/VAc molar ratio, the nature of the initiator, and the temperature on the control of the copolymerization was discussed. The use of an excess of cobalt complex appeared as a key parameter to maintain a good level of control when higher contents of acrylate were used in the comonomer feed. The reactivity ratios were estimated and revealed that PEGA was added around 30 times faster than VAc, which gave access to a gradient P(PEGA-*grad*-VAc) copolymer or to a P(PEGA-*grad*-VAc)-*b*-PVAc diblock copolymer when the VAc polymerization was pursued after the full consumption of PEGA. The amphiphilic character of the copolymers makes them prone to self-assemble into micelles in water, as evidenced by dynamic light scattering.

INTRODUCTION

Tailor-made and functional polymeric materials for value-added applications find their roots in the development of controlled/living polymerization techniques. Among these, organometallic-mediated radical polymerization (OMRP) is an emerging class of controlled radical polymerization (CRP) processes that is based on the temporary deactivation of the propagating macroradicals by a transition metal complex.[1−3] So far, OMRP involving cobalt complexes, also referred as cobalt-mediated radical polymerization (CMRP),[4] is the most investigated and prolific OMRP system.[5,6] In particular, bis-(acetylacetonato)cobalt(II) (Co(acac)$_2$) was identified as the complex of choice for the controlled polymerization of challenging nonconjugated monomers like vinyl acetate (VAc),[7,8] vinyl chloroacetate (VClAc),[9] vinyl pivalate,[10,11] vinyl benzoate,[10] and N-vinylpyrrolidone.[9,12,13] In addition, the CRP's of conjugated monomers such as acrylonitrile[14,15] and n-butyl acrylate[16] mediated by the same cobalt complex were made possible through the use of additives (coordinating solvents, excess Co-(acac)$_2$) and/or the adjustment of the temperature, since both parameters have an impact on the carbon–cobalt bond strength and therefore on the control imparted to the polymerizations.[8,17]

In addition to the possibility of controlling the polymerization of monomers of different reactivities, another feature of OMRP based on Co(acac)$_2$ is its benefit to macromolecular engineering,[3,5,6] as illustrated by several examples of ω-functionalizations,[18−20] block[11−14,21,22] and statistical copolymerizations.[9,23,24]

CMRP also contributed to the synthesis of graft copolymers. Poly(vinyl acetate)-*graft*-polystyrene (PVAc-*graft*-PS) copolymers were prepared via a two-step strategy: the PVAc backbone was prepared by the statistical copolymerization of VAc with VClAc by CMRP and the PS grafts were initiated from the pendant chloroester groups of the backbone by the atom-transfer radical polymerization (ATRP) of styrene.[25]

Graft copolymers were also prepared by a combination of OMRP using titanium complexes with ATRP. In this case, the backbone was prepared by ATRP while the grafts were polymerized by OMRP.[26] There is however no example of graft copolymers prepared only by OMRP. The development of a more general methodology for the preparation of various kinds of graft copolymers by OMRP would considerably broaden the range of macromolecular architectures available by this technique.

This paper addresses this challenge and reports on the first polymerization of a macromonomer by OMRP. Given its ability to control the polymerization of reluctant unconjugated monomers, Co(acac)$_2$ was selected as control agent for the copolymerization of VAc with a macromonomer, i.e. poly(ethylene glycol) acrylate (PEGA). First, the impact of the experimental conditions (feed composition, initiator, temperature) on the course of the copolymerization was investigated. The reactivity ratios of VAc and

PEGA were also determined and revealed that both radicals add PEGA around 30 times faster than VAc. Such a difference in reactivity induced a strong gradient in the polymer microstructure and yielded P(PEGA-*grad*-VAc) graft copolymers with a brush-like sequence of PEG pendant chains. After PEGA was completely consumed, the polymerization of the remaining VAc led to a diblock graft copolymer P(PEGA-*grad*-VAc)-*b*-PVAc in one step. The amphiphilic nature of these copolymers and their (quasi-)diblock structure led to the formation of well-defined micelles in water. OMRP is therefore a simple way for the preparation of new PEG-based toothbrush copolymers of interest for the biomedical field.[27]

■ EXPERIMENTAL PART

Materials. Vinyl acetate (VAc, >99%, Acros) was dried over calcium hydride, degassed by several freeze−thawing cycles before distillation under reduced pressure and storage under argon. Poly(ethylene glycol) methyl ether acrylate (PEGA, $M_n \sim 454$ g/mol, $DP_{PEG} = 8-9$, Aldrich) was dissolved in dry toluene, dried by vacuum distillation of the water−toluene azeotrope (3 times) and stored at −20 °C under argon. Poly(ethylene glycol) dimethyl ether (Aldrich, $M_n \sim 500$ g/mol) was dissolved in dry toluene, dried by vacuum distillation of the water−toluene azeotrope (3 times) and stored under argon at room temperature. 2,2′-azobis(4-methoxy- 2,4-dimethyl valeronitrile) (V-70) (96%, Wako) was stored at −20 °C and used as received. Bis(acetylacetonato)cobalt(II) (Co(acac)$_2$) (>98%, Acros) was used as received and stored under argon. 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO) (98%, Aldrich) was used as received.

Characterization. Monomer conversions were determined by ^{1}H NMR spectroscopy at 298 K with a Bruker spectrometer operating at 400 MHz in CDCl$_3$. The relative molecular weights (M_n) and polydispersity indices (M_w/M_n) of the polymers were determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) (flow rate: 1 mL/min) at 40 °C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (four columns HP PL gel 5 μm, 10^5 Å, 10^4 Å, 10^3 Å, and 10^2 Å). Polystyrene (PS) standards were used to determine the relative molecular weights of the P(PEGA-*grad*-VAc) samples. The molecular weight of the final copolymers was also determined by SEC/MALLS in dimethylformamide (DMF) with lithium bromide LiBr (0.025 M) using a Wyatt multiangle laser light scattering (MALLS) detector (120 mW solid-state laser, $\lambda = 658$ nm, DawnHeleos S/N342−H). The specific refractive index increment (dn/dc) of the copolymers was determined by using a Wyatt Optilab rEXrefractive index detector ($\lambda = 658$ nm). Data were processed with the Astra V software (Wyatt Technology).

The concentration of the alkylcobalt(III) adduct stock solution in CH$_2$Cl$_2$ was determined by inductively coupled plasma-mass spectrometry (ICP-MS) with an Elan DRC-e Perkin-Elmer SCIEX instrument. Samples were prepared by evaporating 1 mL of the cobalt adduct stock solution and reacting with 0.5 mL of HNO$_3$ (65%) at 60 °C for 2 h. The solution was then diluted to 250 mL with bidistilled water prior to ICP-MS analysis.

Dynamic Light Scattering (DLS) experiments were performed on a Malvern CGS-3 apparatus equipped with a He−Ne laser with a wavelength of 633 nm. The measurements were performed in water at 90° angle at a concentration of 0.1 g/L (sample 8) or 5 g/L for the weakly diffusing sample 7c. Data were analyzed using the CONTIN method which is based on an inverse-Laplace transformation of the data and gives access to a size distribution histogram for the analyzed micellar solutions.

Copolymerization of Poly(ethylene glycol) Methyl Ether Acrylate with Vinyl Acetate Initiated by V-70 in the Presence of Co(acac)$_2$. All
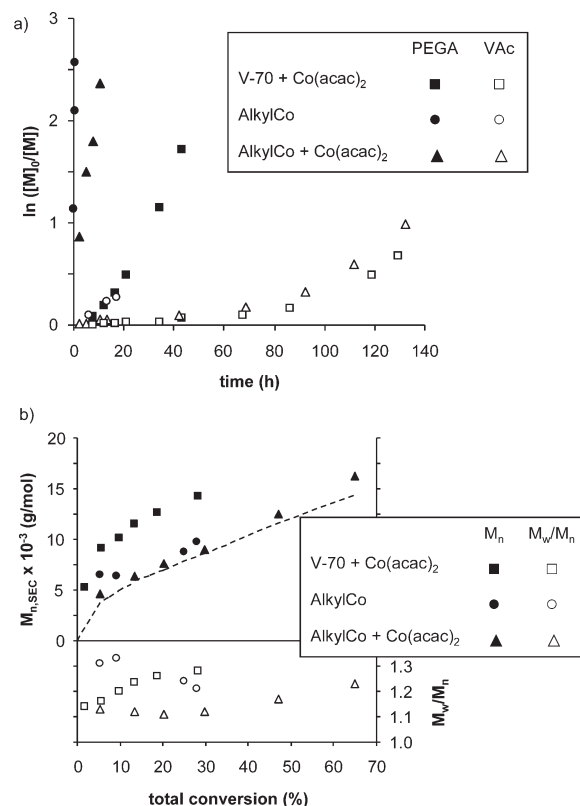

Figure 1. Bulk copolymerization of PEGA with VAc ([PEGA]$_0$/[VAc]$_0$ = 5/95) at 30 °C initiated by V-70 (Table 1, entry 3), the alkylcobalt(III) adduct without additional Co(acac)$_2$ (entry 4) or the alkylcobalt(III) adduct with additional Co(acac)$_2$ (entry 5). (a) Semilogarithmic kinetic plot. (b) Evolution of M_n and M_w/M_n vs total conversion. The theoretical molecular weight is represented by the dotted line and is calculated according to the [monomer]$_0$/[initiator]$_0$ ratio and conversion.

polymerizations were performed by classical Schlenk techniques under argon. A typical example for the copolymerization of PEGA with VAc ([PEGA]$_0$/[VAc]$_0$ = 5/95) in presence of Co(acac)$_2$ is given below. Co(acac)$_2$ (0.220 g, 0.855 mmol) and V-70 (0.264 g, 0.855 mmol) were added into a round-bottom flask capped by a three-way stopcock and purged by three vacuum-argon cycles. After addition of VAc (14.4 mL, 0.156 mol) and PEGA (3.42 mL, 8.211 mmol), the reaction mixture was heated at 30 °C under stirring. Samples were periodically taken from the medium via a syringe during the polymerization and a few milligrams of TEMPO were added in order to quench the polymerization. The monomer conversion of each sample was determined by ^{1}H NMR spectroscopy, and macromolecular parameters (M_n, M_w/M_n) were measured by SEC after evaporation of the residual VAc under reduced pressure. The final polymer was quenched with a solution of TEMPO in toluene (3 equiv of TEMPO relative to the cobalt complex) and precipitated twice in cold heptane before drying under vacuum. Results are shown in Table 1 (entry 3) and Figure 1 (squares).

General Procedure for Polymerizations Initiated by the Alkylcobalt-(III) Adduct. The synthesis and the complete characterization of the low molecular weight alkylcobalt(III) adduct have been described elsewhere.[8] The cobalt complex was stored as a CH$_2$Cl$_2$ solution at −20 °C under argon. The cobalt concentration of the stock solution was determined by ICP-MS ([alkylcobalt(III)] = 0.1669 M). A typical example for the copolymerization of PEGA with VAc ([PEGA]$_0$/[VAc]$_0$ = 5/95) in presence of Co(acac)$_2$ at 30 °C is given below. Co(acac)$_2$ (0.037 g, 0.0144 mmol) was added in a round-bottomed flask capped by a three-way stopcock and purged by three vacuum-argon cycles. The

**Table 1. Effect of Initiator and Comonomer Ratio on the Copolymerization of PEGA with VAc Mediated by Co(acac)$_2$[a]**

entry	initiator	initiator/ Co(acac)$_2$	PEGA/VAc (mol %)	time (h)	PEGA convn (%)	VAc convn (%)	total convn (%)	$M_{n,th}$ (g/mol)	$M_{n,SEC}$ (g/mol)	PDI
1	V-70	1/1	25/75	8	27	1	7	5900	36000	1.6
				30	97	10	29	22300	53300	3.5
				46	100	12	31	23300	53300	5.3
2	V-70	1/1	15/85	12	44	5	11	6400	23000	1.1
				30	100	11	25	14700	27000	1.6
				89	100	21	40	16100	29000	1.9
3	V-70	1/1	5/95	34	68	3	6	3500	9200	1.2
				67	100	9	13	5900	11500	1.2
				99	100	25	28	8500	14300	1.3
4	AlkylCo	1/0	5/95	0.2	68	2	5	3400	6500	1.3
				3	100	10	15	6200	6700	1.3
				17	100	24	28	8200	9800	1.2
5	AlkylCo	1/0.3	5/95	5	78	2	5	3800	4600	1.1
				28	100	9	13	5900	6000	1.1
				132	100	63	65	14400	16300	1.2
6	AlkylCo	1/0.3	15/85	2	75	7	17	10900	9200	1.2
				7.5	96	11	24	14200	11400	1.2
				50	100	56	63	21000	16500	1.3
7	AlkylCo	1/0.3	25/75	2	88	14	30	20800	15300	1.4
				7.5	99	19	36	23800	17600	1.4
7c				50	100	60	70	29300	22800	1.5

[a] Conditions: [monomers]$_0$/[initiator]$_0$ = 192/1 at 30 °C.

alkylcobalt(III) adduct (3.5 mL of the CH$_2$Cl$_2$ stock solution, 0.481 mmol) was introduced under argon and evaporated to dryness under reduced pressure at room temperature. VAc (8.08 mL, 87.6 mmol) and PEGA (1.92 mL, 4.61 mmol) were then added under argon. The reaction mixture was stirred at 30 °C and samples were regularly withdrawn with a syringe prior to quenching by TEMPO. Monomer conversions and macromolecular parameters were determined by ^{1}H NMR spectroscopy and SEC, respectively. The molecular weight of the final copolymer was determined by SEC/MALLS. The final polymer was quenched with a solution of TEMPO in toluene (3 equiv of TEMPO relative to the cobalt complex) and precipitated twice in cold heptane before drying under vacuum. Results are shown in Table 1 (entry 5), Figure 1 (triangles) and Figure 2. The same experiment was also performed with an increase of the temperature from 30 to 40 °C or 50 °C after the total consumption of PEGA (Figure 4).

Effect of Poly(ethylene glycol) on the Course of the Cobalt-Mediated Radical Polymerization of Vinyl Acetate. The alkylcobalt(III) adduct (1 mL of the CH$_2$Cl$_2$ stock solution, 0.167 mmol) was introduced under argon and evaporated to dryness under reduced pressure at room temperature. VAc (5 mL, 54.3 mmol) and poly-(ethylene glycol) dimethyl ether (1.08 mL, 2.36 mmol) were added under argon and the reaction mixture was stirred at 40 °C. Samples were taken from the medium to evaluate the conversion and macromolecular parameters. As a blank experiment, the polymerization of VAc initiated by the alkylcobalt(III) adduct was carried out without poly(ethylene glycol) methyl ether at 40 °C. Results are shown in Figure 5.

Determination of the Reactivity Ratios. Reactivity ratios were determined using the terminal model for copolymerization.[28] The latter assumes that the reactivity of the propagating species is independent of the number or kind of attached units. The ratio of the consumption of each monomer at time t (d[M$_1$]/d[M$_2$]) is equal to the ratio of the instantaneous molar concentrations of the two monomers incorporated in the copolymer (d(m_1)/d(m_2)) and is given by the copolymer
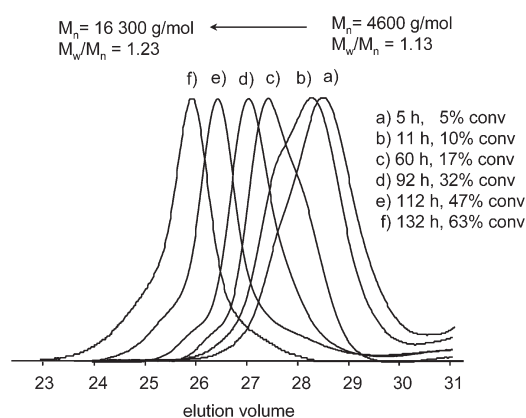
Figure 2. SEC chromatograms for the bulk copolymerization of PEGA with VAc ([PEGA]$_0$/[VAc]$_0$ = 5/95) at 30 °C initiated by the alkylcobalt(III) adduct with additional Co(acac)$_2$ (Table 1, entry 5).

composition equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{d(m_1)}{d(m_2)} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1 \cdot [M_1] + [M_2]}{r_2 \cdot [M_2] + [M_1]} \quad (1)$$

where r_1 and r_2 are the reactivity ratios which relate the preference of a monomer to react with itself or with the second monomer. Equation 1 can be rewritten as a linear dependence between r_1 and r_2, according to the Fineman–Ross linearization method:[29]

$$y = r_1 x - r_2, \quad \text{with } y = \frac{[M_2]}{[M_1]} \cdot \left(1 - \frac{d[M_1]}{d[M_2]}\right) \text{ and } x = \frac{d[M_1]}{d[M_2]} \cdot \frac{[M_2]^2}{[M_1]^2}$$

Plots of y as a function of x gave r_1 as a slope and $-r_2$ as an intercept. [M$_1$] and [M$_2$] were monitored by ^{1}H NMR over time and d[M$_1$]/dt

Scheme 1. Synthesis of P(PEGA-*grad*-VAc) (Quasi-) Diblock Graft Copolymers by OMRP with Co(acac)$_2$

R = –(CH(OAc)CH$_2$)$_{<4}$-C(CH$_3$)(CN)–CH$_2$–C(OCH$_3$)(CH$_3$)$_2$.
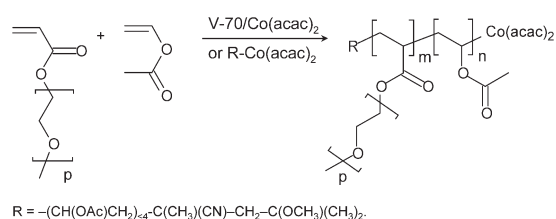
and d[M$_2$]/dt were determined from the plots of ln([M]$_0$/[M]) vs time for both comonomers, in which experimental points were fitted with a first-order regression law. The slope of this line equals the apparent constant of propagation (k_p), which allows us to calculate d[M]/dt = k_p[M] for each comonomer at different reaction times. Reactivity ratios were estimated as r_{PEGA} = 30 and r_{VAc} = 0.03 for experiment 7 in Table 1.

Synthesis of a P(PEGA-*grad*-VAc) Copolymer with a High VAc Content. Co(acac)$_2$ (0.037 g, 0.0144 mmol) was added into a round-bottomed flask capped by a three-way stopcock and purged by three vacuum—argon cycles. The alkylcobalt(III) adduct (3.5 mL of the CH$_2$Cl$_2$ stock solution, 0.481 mmol) was introduced under argon and evaporated to dryness under reduced pressure at room temperature. VAc (8.08 mL, 87.6 mmol) and PEGA (1.92 mL, 4.61 mmol) were then added under argon. The reaction mixture was stirred at 30 °C for 67 h (20% total conversion). Another portion of VAc (50 mL, 46.7 g) was then added and the mixture was heated at 40 °C to reach 30% conversion of VAc. The polymer was quenched with a solution of TEMPO in toluene (3 equiv of TEMPO relative to the cobalt complex) and precipitated twice in cold heptane before drying under vacuum. The molecular weight and the composition of the copolymer were determined by SEC and NMR, respectively (sample 8 in Table 2).

Preparation of P(PEGA-*grad*-VAc) Micelles in Water. Polymeric micelles consisting of a hydrophobic PVAc core and hydrophilic PPEGA shell were prepared as follows. Typically, 10 mg of a P(PEGA-*grad*-VAc) copolymer were dissolved in 10 mL of methanol, followed by the dropwise addition of 100 mL of bidistilled water. The solution was stirred at room temperature for 24 h in order to evaporate the methanol and passed through 1.2 μm filter before analysis by dynamic light scattering.

■ RESULTS AND DISCUSSION

With the aim of preparing novel graft copolymers of interest, the copolymerization of a PEG macromonomer (PEGA) with VAc mediated by bis(acetylacetonato)cobalt(II) was investigated (Scheme 1). In order to achieve an optimal control on the copolymerization, the influence of various experimental parameters was examined.

Effect of the Comonomers and Cobalt Concentrations on the Copolymerization of PEGA with VAc. In previous studies on the *n*BA/VAc statistical copolymerization,[23] it was reported that increasing the proportion of VAc in the comonomer feed had a beneficial effect on the polymerization control at 30 °C. Indeed, the higher ability of Co(acac)$_2$ to deactivate VAc than acrylate radicals resulted in the shift of the control equilibrium between active and dormant species toward the dormant species. The bulk copolymerization of PEGA with VAc was therefore carried out with a relatively high amount of VAc (75 mol %) in the feed to ensure a sufficient level of control. When an azo compound (V-70) was used as initiator and Co(acac)$_2$ as control agent (Table 1, entry 1), the copolymerization became uncontrolled at conversions beyond 7%, as assessed by the stagnation of

M_n and conversion over time, as well as by the high polydispersity indices (PDIs). The lack of control is due to the inefficient trapping of PEGA radicals by Co(acac)$_2$ in these conditions. Therefore, the amount of VAc in the initial feed was increased from 75 mol % to 85 mol % in order to shift the control equilibrium toward the dormant species and impart some control to the copolymerization (Table 1, entry 2). Although the molar mass of the copolymer slightly increased with conversion, termination reactions caused the broadening of the molecular weight distributions above 20% conversion. The amount of VAc was then further increased to 95 mol % (Table 1, entry 3) and the copolymerization fell under control in these conditions, as shown by the linear increase of the molecular weight vs conversion and the rather low PDIs (1.2−1.3). Noticeably, the acrylate comonomer was converted much faster than VAc in all experiments, as assessed by their respective conversions determined by NMR.

Nevertheless, there is still some room for improvement since it was demonstrated that the replacement of the bimolecular V-70/Co(acac)$_2$ system by a preformed alkylcobalt(III) adduct, capable of both initiation and control upon thermal dissociation, could help improve the control of the radical polymerization of various monomers.[8,15,16] Therefore, we used the single-component alkylcobalt(III) adduct (R$_0$—(CH$_2$—CHOAc)$_{<4}$—Co(acac)$_2$; R$_0$ = primary radical from the decomposition of V-70) to initiate the copolymerization of PEGA with VAc in place of V-70, with other parameters kept constant (Table 1, entry 4). In line with the previous reports, the initiation by the alkylcobalt(III) adduct rather than by V-70 resulted in a much faster polymerization and also allowed a better control. Further improvement of this system was achieved by adding an excess of control agent (0.3 equiv of Co(acac)$_2$ relative to the alkylcobalt(III) adduct, Table 1, entry 5), which resulted in a shift of the control equilibrium toward the dormant species (*vide infra*). This phenomenon was also observed in the case of the *n*BA/VAc copolymerization.[16]

Figure 1a shows the semilogarithmic kinetic plot for the bulk copolymerization of PEGA with VAc ([PEGA]$_0$/[VAc]$_0$ = 5/95) initiated either by V-70 (Table 1, entry 3) or by the alkylcobalt-(III) adduct without (entry 4) or with additional Co(acac)$_2$ (entry 5). In all cases, PEGA was consumed much faster than VAc, as expected for a copolymerization of VAc with an acrylate (*vide infra* for reactivity ratios). The comparison of the three systems showed that the copolymerization was faster when initiated by the alkylcobalt(III) adduct rather than with V-70. As already observed for the CMRP of acrylonitrile initiated by V-70/Co(acac)$_2$,[15] the initial curvature of the first-order kinetics plot may result from the slow decomposition of V-70, producing an increasing concentration of radicals with time. The presence of additional Co(acac)$_2$ contributed to slow down the copolymerization initiated by the alkylcobalt(III) adduct. Indeed, the apparent propagation rate constant of PEGA (k_{obs}), corresponding to the slopes of the semilogarithmic kinetics plots, decreased from 2.16 to 0.17 h^{-1} when Co(acac)$_2$ was added in the case of the initiation with the alkylcobalt(III) adduct, which is consistent with the shift of the active/dormant species equilibrium toward the dormant species. Figure 1b displays the evolution of M_n and M_w/M_n vs total conversion. In all cases, the molecular weight increased regularly with conversion, but the initiation efficiency was higher for the experiments initiated with the preformed initiator rather than with V-70, as usually observed. Noticeably, the change in the evolution of the theoretical molecular weight at around 5% conversion is related to the disappearance of the PEGA macromonomer from the

comonomer feed. The lowest PDIs (1.1−1.2) were obtained for the copolymerization initiated by the alkylcobalt(III) adduct in the presence of additional $Co(acac)_2$.

The SEC chromatograms for experiment 5 in Table 1 (Figure 2) are narrow and regularly shifted toward lower elution volumes, although small shoulders at higher molecular weights indicate the occurrence of coupling reactions. These coupling reactions are indeed observed when withdrawing samples from the reaction medium for SEC analysis. Although most of the chains are deactivated by TEMPO after sampling, a tiny amount of them are coupled when exposed to air before reaction with TEMPO. This observation was already made in a previous report for VAc polymerization.[30]

As the copolymerization was controlled by the alkylcobalt(III) adduct in the presence of added $Co(acac)_2$, we progressively increased the PEGA/VAc molar ratio in order to probe the maximum concentration of PEGA tolerated by the system. The proportion of PEGA was thus increased from 5 to 15 and 25 mol % in the comonomer feed (Table 1, entries 6 and 7). The copolymerizations displayed the characteristics of controlled processes, although PDI's increased with the PEGA initial content. The kinetics and M_n plots for the copolymerizations with 25 mol % of PEGA are displayed in Figure 3 and illustrate the emergence of control when V-70 (Table 1, entry 1) was replaced by the alkylcobalt(III) adduct with additional $Co(acac)_2$ (entry 7). Although $M_{n,th}$ appear higher than $M_{n,SEC}$, the latter are relative values determined with linear polystyrene standards. Absolute molecular weights ($M_{n,MALLS}$) were determined for selected samples by SEC coupled to a multiangle laser light scattering (MALLS) detector and are closed to the theoretical values (see later in Table 2). Therefore, copolymerizations with a higher PEGA content (15 and 25 mol %) could be controlled only in the presence of a sufficient amount of Co^{II} deactivator. A further increase of the PEGA content to 50 mol % led to an uncontrolled process, which sets the maximum acceptable amount of PEGA in these copolymerizations to around 25 mol %.

Effect of the Temperature. Although the best level of control for the copolymerization with $[PEGA]_0/[VAc]_0$ = 5/95 was obtained at 30 °C with some added $Co(acac)_2$, the copolymerization proceeded extremely slowly. Indeed, the complete consumption of PEGA beyond 9% total conversion leaves a monomer feed made up of ∼100% VAc with an excess of Co^{II}. The polymerization in these conditions is expected to be very slow.[8] In order to decrease the reaction time and make this copolymerization more practical, we considered increasing the temperature after the complete consumption of PEGA. Indeed, it was reported that the polymerization of VAc initiated by the alkylcobalt(III) adduct could be accelerated by raising the temperature from 30 to 40 °C or 50 °C without detrimental effect on the control.[17] Therefore, the PEGA/VAc copolymerization with 5 mol % of PEGA was carried out at 30 °C until the complete consumption of PEGA monomer (monitored by ^{1}H NMR). The temperature was then increased to 40 or 50 °C to polymerize VAc. As expected, the polymerization was much faster when the temperature was increased to 40 or 50 °C, although the control of the molecular weights was slightly reduced at 50 °C (Figure 4). The best compromise between kinetics and control for this copolymerization is therefore achieved when the temperature is increased from 30 to 40 °C after the complete consumption of PEGA, i.e. when the monomer feed only consists of VAc.
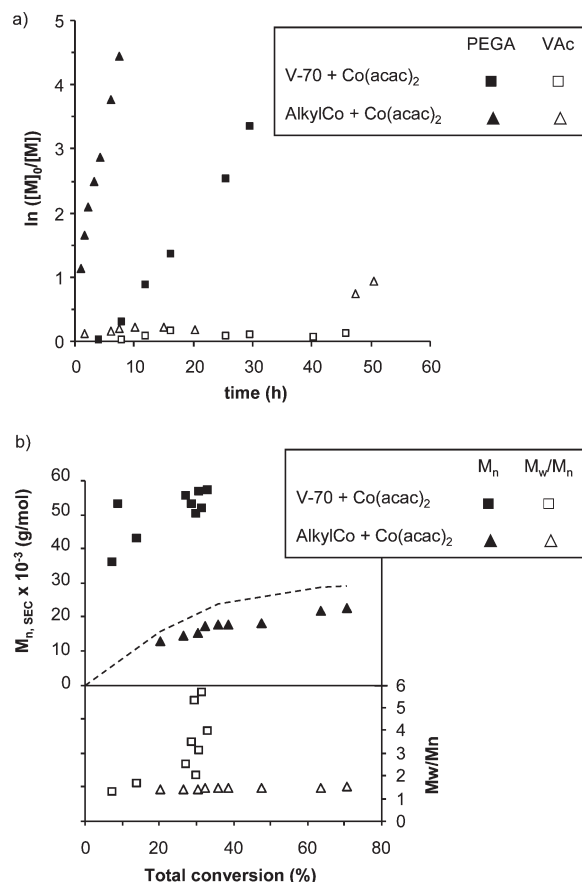
Figure 3. Bulk copolymerization of PEGA with VAc ($[PEGA]_0/[VAc]_0$ = 25/75) at 30 °C initiated by V-70 (Table 1, entry 1) or the alkylcobalt-(III) adduct with additional $Co(acac)_2$ (entry 7). (a) Semilogarithmic kinetic plot. (b) Evolution of M_n and M_w/M_n vs total conversion. The theoretical molecular weight is represented by the dotted line and is calculated according to the $[monomer]_0/[initiator]_0$ ratio and conversion.

Structure and Self-Assembly of the PEGA/VAc Copolymers. Although the copolymerization of PEGA with VAc was controlled under certain conditions, it is worth noting that the system only tolerates 25 mol % of PEGA in the initial feed to fall under control, vs at least 50 mol % of nBA in the nBA/VAc copolymerization.[16,23] Such a decrease of control following the replacement of an n-butyl group by a PEG side-chain needs rationalization. It is known that Lewis bases (L) such as water, DMSO, DMF and pyridine coordinate $Co(acac)_2$ and lead to coordinately saturated $Co(acac)_2L_2$,[31] which shifts the equilibrium toward the active species by consumption of the control agent.[8] The hypothetical complexation of the cobalt complex by PEG might lead to a decrease of concentration of available control agent and affect the control. In order to probe the influence of PEG side-chains on the CMRP, the homopolymerization of VAc was carried out in the presence or absence of added PEG dimethyl ether. Figure 5 shows that the polymerization is somewhat faster and that M_n and M_w/M_n are slightly bigger in the presence of PEG. However, such a small effect can reasonably not account for the discrepancy observed between nBA/VAc and PEGA/VAc copolymerizations.

Therefore, the lesser extent of control observed in the PEGA/VAc than in the nBA/VAc copolymerization is probably not due to the cobalt complexation by PEG. Most likely, it might be
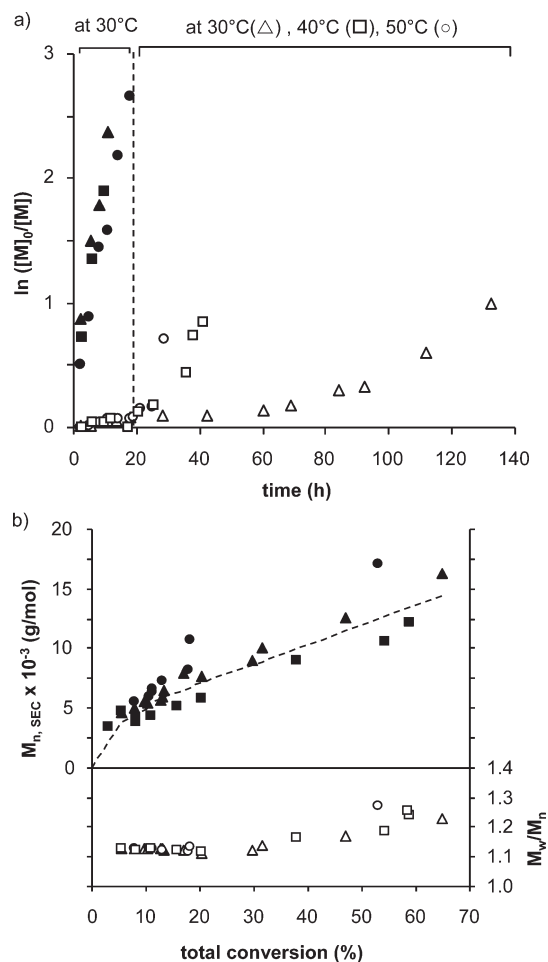
Figure 4. Bulk copolymerization of PEGA with VAc ($[PEGA]_0/[VAc]_0 = 5/95$) initiated by the alkylcobalt(III) adduct with additional $Co(acac)_2$, at 30 °C ($\blacktriangle$, $\triangle$) or with an increase of the temperature to 40 °C ($\blacksquare$, $\square$) or 50 °C ($\bullet$, $\circ$) after the consumption of PEGA. (a) Semilogarithmic kinetic plot for PEGA (full symbols) and VAc (empty symbols). (b) Evolution of M_n (full symbols) and M_w/M_n (empty symbols) vs total conversion. The theoretical molecular weight is represented by the dotted line and is calculated according to the $[monomer]_0/[initiator]_0$ ratio and conversion.

related to (i) a slower deactivation of the PEGA radical by $Co(acac)_2$ due to more pronounced steric effects compared to *n*BA and/or (ii) to the differential incorporation of PEGA vs *n*BA in their respective copolymers with VAc. The latter hypothesis would account for different concentrations of acrylate-terminated propagating chains and different levels of control in PEGA/VAc or *n*BA/VAc copolymerizations, since $Co(acac)_2$ does not deactivate acrylate radicals efficiently.[16,23] This hypothesis was studied by evaluating the reactivity ratios with the Fineman−Ross linearization method,[29] which is based on the Mayo−Lewis terminal model.[28] Reactivity ratios determined accordingly were $r_{PEGA} = 30$ and $r_{VAc} = 0.03$, which means that PEGA is added around 30 times more rapidly than VAc by both radicals. This contrasts with $r_{nBA} = 15$ and $r_{VAc} = 0.02$ for the *n*BA/VAc copolymerization determined elsewhere.[23] The increase of $r_{acrylate}$ when going from *n*BA to PEGA might result from a preferential distribution of PEGA around the PEGA-rich propagating chains, leading to an increased effective acrylate concentration near the chain-end radical. Known as the "bootstrap
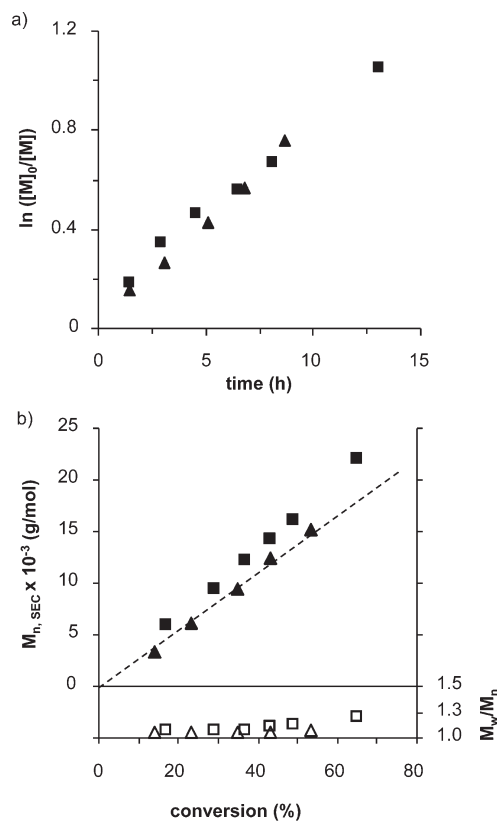

Figure 5. Bulk polymerization of VAc initiated by the alkylcobalt(III) adduct at 40 °C with ($\blacksquare$) or without ($\blacktriangle$) added PEG dimethyl ether. (a) Semilogarithmic kinetic plot. (b) Evolution of M_n (full symbols) and M_w/M_n (empty symbols) as a function of conversion. The theoretical molecular weight is represented by the dotted line and is calculated according to the $[monomer]_0/[initiator]_0$ ratio and conversion.

effect",[32] the ability of a growing chain to control its environment has already been reported[33−36] and may explain the effect of the acrylate side-chain on the reactivity ratios. A comparatively preferential incorporation of PEGA compared to *n*BA in their respective copolymerizations with VAc might account for the lesser extent of control in the former case since $Co(acac)_2$ does not deactivate acrylate radicals efficiently.[16,23]

Reactivity ratios are decisive parameters for the microstructure of the copolymer. Figure 6 shows the dependence of the instantaneous composition of the copolymer on the composition of the comonomer feed, as calculated by the copolymer composition equation in which the aforementioned reactivity ratios have been introduced. The curve is characteristic of a copolymerization in which one monomer (PEGA) is preferentially added to the growing radical, whatever the terminal unit. Regarding the structure, the growing chain is mainly composed of PEGA at the first stages of the copolymerization and progressively incorporates VAc. When the copolymerization is pursued after the complete consumption of PEGA, a block copolymer composed of a P(PEGA-*grad*-VAc) and a pure PVAc segment, i.e. P(PEGA-*grad*-VAc)-*block*-PVAc, is obtained. This achievement is of particular relevance to macromolecular engineering. Indeed, one of the state-of-the-art methodologies for the synthesis of well-defined graft copolymers is the macromonomer or grafting-through method, which consists in copolymerizing a macromonomer with a small monomer[37−40] by a controlled/living
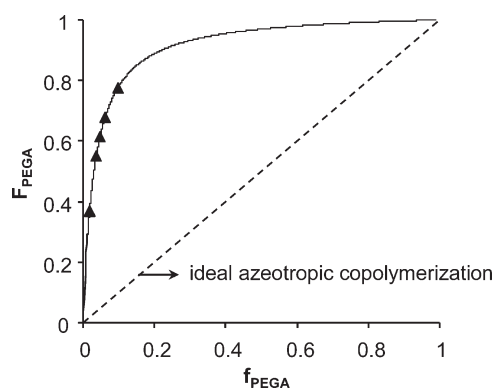
Figure 6. Dependence of the instantaneous copolymer composition (F_{PEGA} = mole fraction of PEGA in the copolymer) on the comonomer feed composition (f_{PEGA} = mole fraction of PEGA in the comonomer feed). Triangles correspond to data obtained from experiment 7 in Table 1.

Scheme 2. Strategies for the Synthesis of Graft Copolymers with Different Branching Distributions by Combination of the Macromonomer Method with Controlled Radical Polymerization
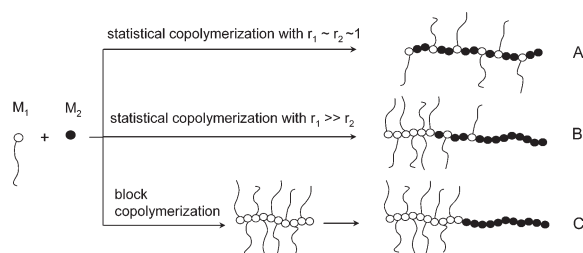
technique. The number of grafts and their distribution along the backbone are determined by the molar ratio of macromonomer to comonomer in the feed and their reactivity ratios. If the comonomers have similar polymerizable groups and reactivities ($r_1 \sim r_2 \sim 1$), their statistical copolymerization leads to a homogeneous distribution of the branches along the main chain (Scheme 2, species A). If one comonomer (M_1) is preferentially added whatever the propagating radical ($r_1 > 1$, $r_2 < 1$) the copolymerization leads to a gradient graft copolymer with heterogeneously distributed grafts. For comonomers of tremendously different reactivities ($r_1 \gg 1$ and $r_2 \ll 1$) there is a tendency toward block copolymerization, provided that the copolymerization is controlled (Scheme 2, species B). As this prerequisite is scarcely ever met, block graft copolymers that cumulate the properties of block and graft copolymers, are usually prepared by block copolymerization, i.e. by sequential addition of the two monomers (Scheme 2, species C).[41−44]

By contrast to these works, the PEGA/VAc statistical copolymerization by CMRP affords (quasi-) diblock graft structures in one step (Scheme 2, species B). This achievement relies on the ability of Co(acac)$_2$ to control the statistical copolymerization of a macro- and a small monomer having tremendously different reactivity ratios. The difference in reactivity between conjugated (acrylate) and unconjugated (VAc) monomers itself induces a spontaneous strong gradient and a heterogeneous distribution of the PEG side-chains along the backbone, yielding an amphiphilic (quasi-) diblock structure with a hydrophilic brush of PEG grafts
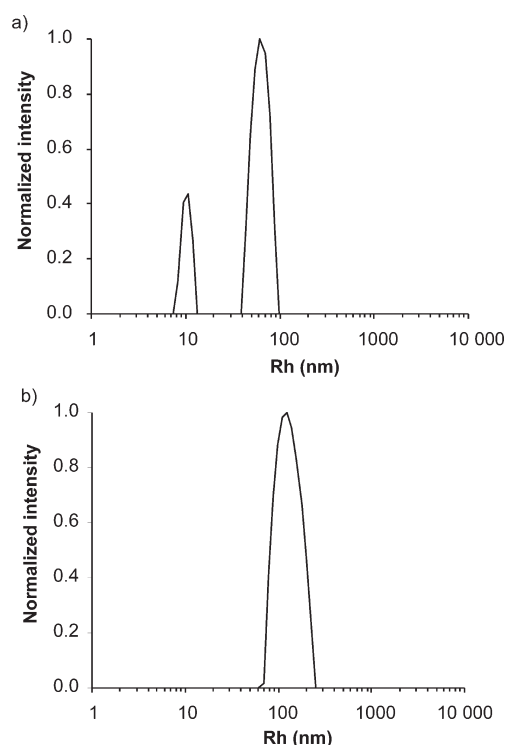

Figure 7. CONTIN size distribution histograms obtained on the solutions containing P(PEGA-*grad*-VAc)-*b*-PVAc: (a) sample **7c**; (b) sample **8**.

Table 2. P(PEGA-*grad*-VAc)-*b*-PVAc Diblock Copolymers and Hydrodynamic Radii of the Corresponding Micelles in Water

sample[a]	DP_{PEGA}/ DP_{VAc}[b]	$M_{n,MALLS}$	$M_{n,SEC}$	$M_{n,th}$	M_w/ $M_{n,SEC}$	R_h (nm)[c]
7c	50/94	31 000	22 800	29 300	1.5	11
						65
8	10/429	41 500	44 700	37 000	1.2	125

[a] Syntheses: see Table 1 and experimental part for sample **8**. [b] Determined using $M_{n,MALLS}$ and the copolymer composition determined by ^{1}H NMR. [c] Determined by DLS.

and a hydrophobic PVAc segment. For sake of clarity, the term "quasi-diblock" copolymer refers to the gradient P(PEGA-*grad*-VAc) copolymer formed until the full consumption of PEGA, and the term "diblock" copolymer refers to P(PEGA-*grad*-VAc)-*b*-PVAc copolymer obtained when the VAc polymerization is pursued after the full consumption of PEGA.

To illustrate the amphiphilic nature of the P(PEGA-*grad*-VAc)-*b*-PVAc diblock copolymers, the self-assembly in water of two copolymers with opposite composition was studied by dynamic light scattering (DLS) (Table 2).

For the copolymer with the highest PEGA content (**7c**), two populations are observed on the CONTIN size distribution histogram: one corresponding to objects with an average hydrodynamic radius (R_h) of 11 nm and one with an R_h around 65 nm (Figure 7a). The population at 11 nm most probably corresponds to small micelles, and the one at 65 nm to aggregates of micelles. The latter are, however, largely negligible since the intensity distribution as presented in Figure 7 scales as R.[6] To further prove that the small objects are indeed micelles and not
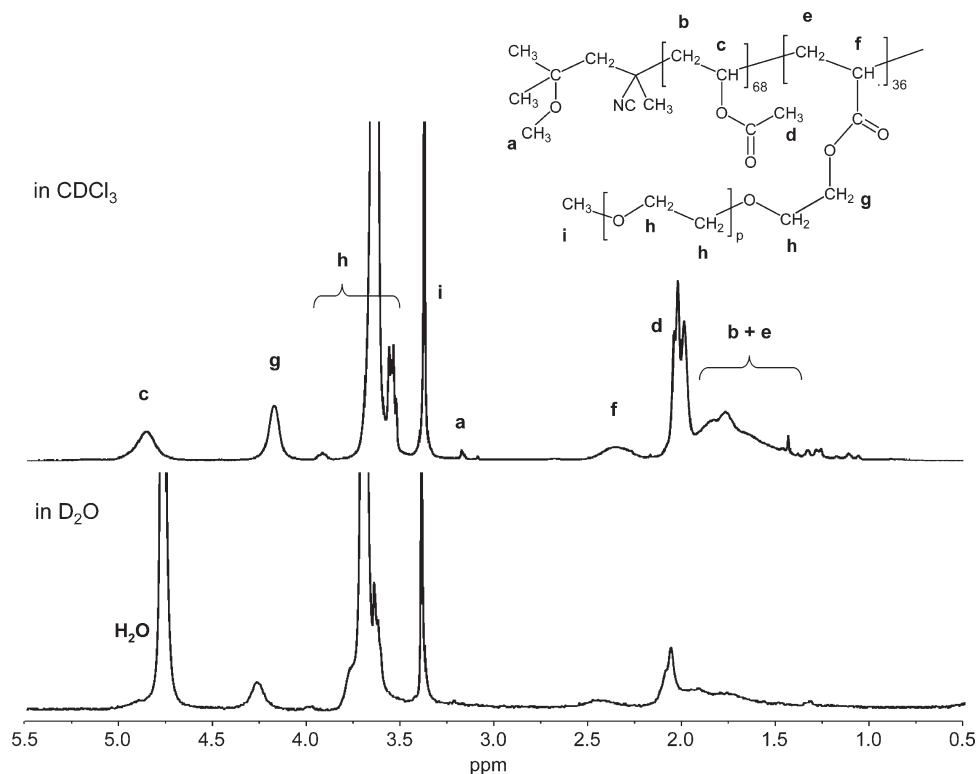
Figure 8. ^{1}H NMR spectrum of a P(PEGA-*grad*-VAc)-*b*-PVAc copolymer (sample **7c** in Table 1) in CDCl$_3$ or D$_2$O.

free chains, the ^{1}H NMR analysis of the copolymer was realized in D$_2$O (Figure 8). The ratio between the intensities of the protons related to hydrophobic (b + d + e + f) and hydrophilic (h) sequences decreased from 46/100 to 11/100 when CDCl$_3$ was replaced by D$_2$O. This observation indeed supports the formation of micelles with a practically desolvated PVAc core, rather than unimers. For the copolymer with the lowest PEGA content (sample 8, see Experimental Part for synthesis), a single population at an R_h of 125 nm is observed (Figure 7b). These well-defined objects (polydispersity = 0.06, as determined by a cumulant analysis) correspond to the so-called crew-cut micelles.[45] This kind of micelles is obtained from highly asymmetric copolymers with a very short hydrophilic block, such as indeed sample **8** here. Considering this strong asymmetry, the micellar characteristics are essentially determined by the length of the hydrophobic block, and they thus follow different scaling laws from the more common star-like micelles.[46]

CONCLUSION

The polymerization of a macromonomer by organometallic-mediated radical polymerization (OMRP) was investigated for the first time. Bis(acetylacetonato)cobalt(II) was selected as control agent for the copolymerization of VAc with a macromonomer of interest, i.e. PEG acrylate. The experimental conditions (comonomers ratio, nature of the initiator, temperature) were adjusted in order to achieve a good level of control. The replacement of the bimolecular V-70/Co(acac)$_2$ system by a preformed alkylcobalt(III) adduct in presence of additional Co(acac)$_2$ allowed to increase the amount of PEGA in the comonomer feed while maintaining the control over the polymerization. The reactivity ratios for PEGA and VAc were determined and indicate that PEGA is converted much faster than

VAc, leading to the formation of P(PEGA-*grad*-VAc) graft copolymers with a strong gradient. The difference in reactivity between PEGA and VAc is such that the gradient tends toward a blocky structure with a hydrophilic brush of PEG grafts and a hydrophobic PVAc segment. As an evidence of their blocky structure, these block-like amphiphilic graft copolymers were shown to form micelles in water. The ability of Co(acac)$_2$ to control the copolymerization of a macromonomer with a monomer of very different reactivity therefore allowed to prepare new PEG-based amphiphilic graft copolymers in one step. This achievement constitutes a significant headway for macromolecular engineering and makes OMRP and in particular, CMRP, a unique synthetic tool for the preparation of quasi-block graft copolymers in one step.

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