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Effective Cobalt-Mediated Radical Coupling (CMRC) of Poly(vinyl acetate) and Poly(*N*-vinylpyrrolidone) (Co)polymer Precursors

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ABSTRACT: Cobalt-mediated radical coupling (CMRC) is successfully applied to poly(vinyl acetate) (PVAc) and poly(*N*-vinylpyrrolidone) (PNVP) precursors for the first time. The coupling process is based on addition of isoprene onto polymer chains preformed by controlled radical polymerization with cobalt complexes (CMRP). The extents of coupling were high (> 90%) to moderate (75−80%) for PVAc and P*N*VP precursors, respectively. Effects of the length of the polymer precursors and conditions used in the polymerization step on the coupling efficiency are discussed. Mass spectrometry (MS) and nuclear magnetic resonance (NMR) analyses conducted on the coupling products demonstrate the preferential insertion of two isoprene units in the final polymers. The CMRC mechanistic proposal, supported by DFT calculations, is based on this microstructure feature. Finally, illustration of the macromolecular engineering potential of this technique is given by the preparation of symmetrical PVAc-*b*-P*N*VP-*b*-PVAc triblock copolymers starting from the corresponding PVAc-*b*-PNVP-[Co] diblock copolymer.

Introduction

Nowadays, controlled radical polymerization (CRP) techniques enable the preparation of novel polymer materials with complex and precise architectures that cannot be achieved by free radical polymerization (FRP).[1−10] As can be seen through the literature, CRP largely sustains the developments in many fields, e.g., medicine or electronics, which require materials with more and more specific properties. An efficient CRP method consists in conducting the radical polymerization in the presence of a cobalt(II) complex.[10] In this case, the metallic species temporarily deactivates the "active" radical chains by forming a "dormant" organocobalt(III) complex (Figure 1). The main asset of this so-called cobalt-mediated radical polymerization (CMRP)[10] is the possibility to deal with both conjugated monomers, such as acrylates[11−17] and acrylonitrile (AN),[18,19] and nonconjugated ones, such as vinyl acetate (VAc)[20−27] and *N*-vinyl-2-pyrrolidone (NVP).[28,29] In contrast to acrylates, VAc does not exhibit a conjugation between the carbonyl group of the ester and the double bond. Similarly, the amide group of NVP is linked to the double bond by the nitrogen atom contrary to acrylamides. As a result of this lack of conjugation, PVAc and PNVP radical species are very reactive and thus difficult to control. Nevertheless, CMRP succeeded in mediating the radical polymerization of VAc and NVP.[20−29] The sequential CMRP of the above-mentioned monomers also led to novel block copolymers. For example, the synthesis of well-defined PVAc-*b*-PNVP[29] and PVAc-*b*-PAN diblocks[19] was achieved using bis(acetylaceto-nato)cobalt(II) complex (Co(acac)₂), whereas cobalt porphyrin

complexes opened the way to poly(vinyl acetate)-*b*-poly(acrylate) block copolymers.[25]

In the perspective to enlarge the range of novel copolymers achievable by CMRP, isoprene polymerization was tentatively initiated from a PAN-Co(acac)₂ precursor preformed by CMRP.[30] In this case, an almost perfect doubling of the molar mass of the poly(acrylonitrile) was observed instead of formation of the expected PAN-*b*-PIP diblock copolymer. A novel radical coupling method, called cobalt-mediated radical coupling (CMRC), was born (Figure 1).[30,31] Major advantages of CMRC over other existing radical coupling techniques, such as atom transfer radical coupling (ATRC),[32−38] are its efficiency for high molar mass polymer precursors[30,31] and the specific incorporation of two diene units at the center of the coupled product, which makes CMRC a promising tool for midchain polymer functionalization.[31] Recent investigations on CMRC of PAN revealed the high tolerance of the process toward the nature of the diene.[31] Successful coupling experiments were conducted with differently substituted, linear or cyclic, 1,4-dienes but also with derivatives containing an alcohol or an ester function.[31] Another remarkable contribution of CMRC to macromolecular engineering is the preparation of novel PVAc-*b*-PAN-*b*-PVAc symmetrical triblock copolymers starting from the corresponding PVAc-*b*-PAN-[Co] diblocks prepared by CMRP.[30]

In this report, the efficiency of the CMRC process is evaluated for the first time for well-defined PVAc and PNVP precursors prepared by CMRP with bis(acetylacetonato)cobalt(II). In case of success, the synthetic possibilities of this coupling method, which has so far been described only for PAN-Co precursors, would considerably be enlarged. Special care was devoted to the microstructure analyses of the coupling products in order to determine whether specific insertion of two diene units in the

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Figure 1. General scheme for cobalt-mediated radical polymerization (CMRP) and coupling (CMRC) reaction.

backbone of the polymer is a constant feature of CMRC whatever the nature of the precursor. Nuclear magnetic resonance (NMR) and mass spectrometry (MS) techniques were used accordingly. Mechanistic considerations on the CMRC of PVAc and PNVP are presented and supported by DFT calculations. Finally, symmetrical PVAc and PNVP-based symmetrical triblock copolymers were prepared by subsequent CMRP block copolymerization and CMRC.

Experimental Section

Materials. Vinyl acetate (>99%, Aldrich), isoprene (99%, Aldrich), and dimethyl sulfoxide (DMSO) were dried over calcium hydride, degassed by several freeze−pump−thaw cycles before being distilled under reduced pressure, and stored under argon. *N*-Vinyl-2-pyrrolidone (Aldrich) was degassed by several freeze−pump−thaw cycles before being distilled under reduced pressure and stored under argon. 2,2′-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) (Wako), cobalt(II) acetylacetonate (>98%, Acros), and 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO) (98%, Aldrich) were used as received. Two stock solutions in dichloromethane of the alkyl cobalt(III) adduct initiator, i.e., $[Co(acac)_2(-CH(OCOCH_3)CH_2)_{<4}-R_0]$ with R_0 being the primary radical generated by V-70, were prepared according to a previously reported procedure.[23] The cobalt content of these solutions was evaluated by inductively coupled plasma mass spectrometry (ICP-MS) ([Co] = 0.122 and 0.183 M). All polymerizations and coupling reactions were carried out under a protective argon atmosphere using distilled and degassed monomers and solvents.

Characterization. Molecular parameters (M_n, M_p, M_w/M_n) of PVAc were determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF) (flow rate: 1 mL min^{-1}) at 40 °C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (four HP PL gel 5 μm columns: 10^5, 10^4, 10^3, and 10^2 Å). Polystyrene standards were used for calibration. Molecular parameters of PNVP (co)polymers were determined by SEC in dimethylformamide (DMF) containing some LiBr (0.025 M) at 55 °C (flow rate: 1 mL min^{-1}), with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (HR1, 100−5000; HR3, 500−30000; HR4, 5000−500000; HR5, 2000−4000000). Depending on the molar mass of the sample, either poly(methyl methacrylate) calibration or a multiangle light scattering (MALLS) detector, with dn/dc values determined for each sample by refractometry analysis, were used for the molar mass determination. For SEC-MALLS analysis a Wyatt detector (120 mW solid-state laser, λ = 658 nm, Dawn Heleos S/N 342-H) was used, and specific refractive index

increments (dn/dc) were determined using a Wyatt Optilab rEX refractive index detector ($\lambda = 658$ nm). Data were processed with the Astra V software (Wyatt Technology). ^{1}H NMR spectra of PVAc and PNVP containing copolymers were recorded at 353 K in DMSO-d_6 with a 400 MHz Bruker spectrometer. The same equipment was used to monitor the consumption of NVP during the polymerization step by ^{1}H NMR at 298 K in DMSO-d_6. Heteronuclear single quantum coherence (HSQC) spectra were recorded at 298 K at 600 MHz (^{1}H) and 150 MHz (^{13}C) with a Varian instrument and are reported in ppm from internal TMS on the δ scale. Typically, 256 scans, D1 of 50 μs, and a relaxation delay of 1 s were used. HSQC of the PVAc and PNVP coupling products were carried out in CDCl$_3$ and DMSO-d_6, respectively.

Mass spectrometry analyses on the PVAc coupling product were performed on a Waters QToF2 mass spectrometer. The analyte solutions (1 mg/mL) were delivered to the ESI source by a Harvard Apparatus syringe pump at a flow rate of 5 μL/min. Typical ESI conditions were capillary voltage, 3.1 kV; cone voltage, 30 V; source temperature, 80 °C; and desolvation temperature, 120 °C. Dry nitrogen was used as the ESI gas. For the recording of the single-stage ESI-MS spectra, the quadrupole (rf-only mode) was set to pass ions from 500 to 1500 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained.

Mass spectrometry analyses on the PNVP coupling product were carried out by MALDI-ToF. MALDI mass spectra were recorded using our Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J/m^2 delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analysis were performed in the reflectron mode at a resolution of about 10 000. The matrix, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), was prepared as 20 mg/mL solution in chloroform. The matrix solution (1 μL) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in THF to obtain 1 mg/mL solutions. 1 μL aliquots of these solutions were applied onto the target area already bearing the matrix crystals and then air-dried. For the recording of the single-stage MALDI-MS spectra, the quadrupole (rf-only mode) was set to pass ions from 750 to 7000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained.

CMRC of PVAc-Co(acac)$_2$ Precursors. A solution of alkyl−cobalt(III) initiator, i.e., $[Co(acac)_2(-CH(OCOCH_3)CH_2)_{<4}-R_0]$,

in CH_2Cl_2 (1.0 mL of a 0.122 M stock solution, 0.12 mmol) was introduced under argon in a Schlenk tube and evaporated to dryness under reduced pressure at room temperature (rt). The residue was dissolved under argon in VAc (5.0 mL, 4.7 g, 54 mmol) at the same temperature. The Schlenk tube was stirred and immersed in an oil bath at 40 °C. After 5 h, an aliquot was withdraw in order to evaluate the VAc conversion by gravimetry (37%) and to measure the molecular parameters of the PVAc by SEC with a PS calibration ($M_n = 12\,200$ g/mol, $M_p = 13\,000$ g/mol, $M_w/M_n = 1.05$). After removal of the unreacted VAc under reduced pressure at rt, the PVAc precursor was dissolved in degassed DMSO (5.0 mL) and treated with isoprene (10 mmol, 0.68 g, 1.0 mL). After 2 h stirring at rt, residual monomer was removed under reduced pressure, and a second aliquot was withdrawn from the reaction medium in order to characterize the final polymer PVAc by SEC with a PS calibration ($M_n = 22\,800$ g/mol, $M_p = 26\,900$ g/mol, $M_w/M_n = 1.12$). The extent of coupling ($x_c = 2[1 - (M_{n,0}/M_n)]$) reached 0.93 (Table 1, entry 4). The final polymer was purified by subsequent precipitation in H_2O and heptane.

The same procedure was used for the coupling of PVAc-Co(acac)$_2$ precursors with different molar masses prepared by adjusting the $[VAc]/[Co(acac)_2(-CH(OCOCH_3)CH_2)_{<4}-R_0]$ molar ratio in the polymerization step. As a rule, the [isoprene]/[Co] molar ratio, used in the coupling step, was kept constant (Table 1, entries 5 and 6). A similar procedure was used for the CMRC of PVAc-Co(acac)$_2$ precursors prepared by CMRP initiated at 30 °C by V-70 in the presence of Co(acac)$_2$ (Table 1, entries 1–3).

CMRC of PNVP-Co(acac)$_2$ Precursors. A solution of $[Co(acac)_2(-CH(OCOCH_3)CH_2)_{<4}-R_0]$ in CH_2Cl_2 (1.0 mL of a 0.183 M stock solution, 0.18 mmol) was introduced under argon in a Schlenk tube and evaporated to dryness under reduced pressure at room temperature. The residue was dissolved under argon in dry and degassed anisole (5.0 mL) and NVP (23 mmol, 2.6 g, 2.5 mL) at room temperature. The Schlenk tube was immersed in an oil bath and stirred at rt. After 1 h, an aliquot was withdrawn. Part of the sample was used to evaluate the NVP conversion (20%) by ^1H NMR in DMSO-d_6. The rest of the aliquot was precipitated in diethyl ether, and the polymer was filtered and dried under vacuum at 70 °C, before being analyzed by SEC-MALLS in order to measure molecular parameters of PNVP ($M_n = 16\,600$ g/mol, $M_p = 20\,900$ g/mol, $M_w/M_n = 1.12$, dn/d$c = 0.064$ mL/g). In parallel, the polymerization medium was treated with isoprene (10 mmol, 0.68 g, 1.0 mL) without removing the unreacted NVP and stirred for 2 h at rt. The crude mixture was then poured into diethyl ether. The final PNVP was filtered and dried under vacuum at 70 °C, before SEC-MALLS analysis ($M_n = 28\,000$ g/mol, $M_p = 33\,700$ g/mol, $M_w/M_n = 1.11$, dn/d$c = 0.064$ mL/g). The extent of coupling ($x_c = 2[1 - (M_{n,0}/M_n)]$) reached 0.81 (Table 2, entry 1).

Similar procedures were used for the CMRC of PNVP-Co precursors having different molar masses, prepared by adjusting [NVP]/[Co] molar ratio in the polymerization step. As a rule, the [isoprene]/[Co] molar ratio was kept constant in the coupling reaction (Table 2, entry 1).

CMRC of Co(acac)$_2$($-CH(OAc)CH_2$)$_{\sim4}-R_0$ Oligomers for NMR and MS Studies. A solution of the alkyl-cobalt(III) initiator, i.e., $[Co(acac)_2(-CH(OCOCH_3)CH_2)_{<4}-R_0]$, in CH_2Cl_2 (1.0 mL of a 0.183 M stock solution, 0.18 mmol) was introduced under argon in a Schlenk tube and evaporated to dryness under reduced pressure at room temperature. The residue was then subsequently treated with isoprene (1.0 mL, 0.68 g, 10 mmol) and degassed DMSO (0.2 mL). After 1 h stirring at rt, the mixture was diluted with THF and filtered on silica in order to remove the cobalt. The slightly yellow residue was then extracted with a dichloromethane/water mixture. The final product was recovered by evaporation of the organic layer, dried at 80 °C under vacuum, and analyzed by ^1H NMR, HSQC, and ESI-MS (see Figures 4 and 6).

CMRC of PNVP–Co Precursors for NMR and MS Studies. Co(acac)$_2$ (0.600 g, 2.34 mmol) and V-70 (0.720 g, 2.34 mmol) were placed under argon in a round-bottom flask and dissolved in degassed anisole (8.0 mL) and freshly distilled NVP (8.0 mL). The reaction vessel was immersed in an oil bath and stirred at 30 °C for 40 min. The reaction was stopped very early in order to recover polymer chains as short as possible. At this stage, monomer conversion reached a few percent but could not be determined with precision. An aliquot was withdrawn and poured into diethyl ether, and the precipitated polymer was filtered and dried under vacuum at 70 °C. Polymer chains were too short to allow a good detection by MALLS in DMF and molecular parameters were thus measured by SEC in DMF using a PMMA calibration ($M_n = 3300$ g/mol, $M_w/M_n = 1.09$). In parallel, the polymerization medium was treated with isoprene (2.0 mL, 1.36 g, 20 mmol) without removing the unreacted NVP and stirred for 2 h at rt. The crude mixture was then poured into diethyl ether. The final PNVP was filtered and dried under vacuum at 70 °C, before being analyzed by SEC ($M_n = 4600$ g/mol, $M_w/M_n = 1.12$), ^1H NMR, HSQC, and MALDI-TOF (see Figures 5 and 7).

Synthesis of PVAc-b-PNVP-b-PVAc Triblock by CMRC. Co(acac)$_2$ (0.20 mmol, 52 mg) and V-70 (0.60 mmol, 184 mg) were placed in a round-bottom flask under argon and dissolved in distilled and degassed VAc (54 mmol, 4.7 g, 5.0 mL). The reaction medium was stirred at 30 °C for 40 h. A sample was picked out in order to measure the monomer conversion by gravimetry (conversion = 27%) and molecular parameters of the PVAc by SEC using THF as eluent and a PS calibration ($M_n = 6700$ g/mol, $M_w/M_n = 1.08$). After evaporation of residual VAc, dry and degassed anisole (5.0 mL) and NVP (28 mmol, 3.1 g, 3.0 mL) were subsequently added to the reaction mixture at rt. After stirring for 1 h at rt, NVP conversion reached 30% according to NMR analyses carried out in DMSO-d_6. An aliquot was then picked out and poured in diethyl ether. The collected copolymer was characterized by SEC-MALLS (dn/d$c_{PVAc-b-PNVP} = 0.059$ mL/g, $M_{n,MALLS,PVAc-b-PNVP} = 29\,000$ g/mol, $M_w/M_n = 1.2$) and ^1H NMR in DMSO-d_6 (PNVP/PVAc ratio = 1.2, PVAc$_{78}$–PNVP$_{93}$). Without removal of the residual NVP, isoprene (1.0 mL, 0.68 g, 10 mmol) was added to the medium at rt which was stirred for an additional 2 h. The final product was recovered by precipitation in diethyl ether before SEC-MALLS characterization (dn/d$c_{PVAc-b-PNVP-b-PVAc} = 0.060$ mL/g, $M_{n,MALLS,PVAc-b-PNVP-b-PVAc} = 45\,000$ g/mol, $M_w/M_n = 1.2$) and ^1H NMR analysis in DMSO-d_6 (PNVP/PVAc molar ratio = 1.1) (PVAc$_{78}$-b-PNVP$_{186}$-b-PVAc$_{78}$). The extent of coupling (x_c) of the copolymer was 0.71.

Computational Details. For consistency, the computational work was carried out at the same theoretical level as previous contributions dealing with different applications of the same metal complex[18,23] using the Gaussian03 suite of programs.[39] The geometry optimizations were performed without any symmetry constraint using the B3LYP density functional method with the 6-31G** basis functions for all light atoms (H, C, N, O) and the LANL2DZ function augmented by an f polarization function ($\alpha = 0.8$) for Co. The unrestricted formulation was used for open-shell molecules, yielding only minor spin contamination ($\langle S^2 \rangle$ at convergence was very close to the expected value of 0.75 for the radical species and 3.75 for the spin quartet species). All final geometries were characterized as local minima by verifying that all second derivatives of the energy were positive. Thermochemical corrections were obtained at 298.15 K on the basis of frequency calculations, using the standard approximations (ideal gas, rigid rotor, and harmonic oscillator). The B3LYP-optimized geometries were then used for single point energy calculations using the B3PW91* functional, a modified version of the B3PW91 functional, in which the c_3 coefficient in Becke's original three-parameter fit to thermochemical data was changed to 0.15. The reported thermochemical data result from

Table 1. Cobalt-Mediated Radical Coupling (CMRC) of PVAc Precursors Prepared by CMRP[a]

		CMRP of VAc				CMRC of PVAc−[Co]			
entry	initiator	[VAc]/[Co]	$M_{n,0}$ [g/mol]	$M_{p,0}$ [g/mol]	M_w/M_n	M_n [g/mol]	M_p [g/mol]	M_w/M_n	x_c
1	V-70	270	4 700	5 200	1.07	9 100	10 500	1.09	0.97
2	V-70	540	17 500	19 000	1.07	30 600	37 800	1.13	0.86
3	V-70	1080	25 600	27 400	1.08	41 800	58 200	1.19	0.78
4	R-Co	450	12 200	13 000	1.05	22 800	26 900	1.12	0.93
5	R-Co	890	24 200	25 800	1.06	42 000	52 500	1.17	0.85
6	R-Co	1330	36 600	39 700	1.08	61 600	86 700	1.18	0.81

[a] (1−3) *Polymerization*: [V-70]$_0$/[Co(acac)$_2$]$_0$ = 3, 30 °C (entry 1: 32 h, 20%; entry 2: 22 h, 29%; entry 3: 17 h, 25%). *Coupling*: [isoprene]/[PVAc-Co] = 100, 2 h at rt, [PVAc-Co]$_0$ in DMSO = 0.040, 0.020, and 0.010 M (in entries 1−3, respectively). (4−6) *Polymerization*: [Co(acac)$_2$-(−CH(OCOCH$_3$)CH$_2$)$_{<4}$−R$_0$] was used as initiator at 40 °C (entry 4: 5 h, 37%; entry 5: 7 h, 32%; entry 6: 10 h, 33%). (entry 1: 32 h, 20%; entry 2: 22 h, 29%; entry 3: 17 h, 25%). *Coupling*: [isoprene]/[PVAc-Co] = 90, 2 h at rt, [PVAc-Co]$_0$ in DMSO = 0.024, 0.012, and 0.008 M (in entries 4−6, respectively). All molecular parameters were determined by SEC in THF using PS as calibration. Extents of coupling (x_c) were calculated as follows: $x_c = 2[1 − (M_{n,0}/M_n)]$.

Table 2. Cobalt-Mediated Radical Coupling (CMRC) of PNVP-[Co] Precursors Prepared by CMRP[a]

	CMRP of NVP				CMRC of PNVP-[Co]			
entry	[NVP]$_0$/[R-Co]$_0$	$M_{n,0}$ [g/mol]	$M_{p,0}$ [g/mol]	M_w/M_n	M_n [g/mol]	M_p [g/mol]	M_w/M_n	x_c
1	128	16 600	20 900	1.12	28 000	33 700	1.11	0.81
2	256	25 000	32 000	1.13	39 000	48 900	1.12	0.72
3	384	32 500	42 600	1.13	51 500	63 300	1.13	0.74

[a] *Polymerization*: [Co(acac)$_2$(−CH(OCOCH$_3$)CH$_2$)$_{<4}$−R$_0$] was used as initiator at rt, $V_{NVP}/V_{anisole}$ = 0.5 (v/v), 1 h, conversion = 15−20%. *Coupling*: [isoprene]/[Co] = 55, rt, 2 h. Determined by SEC-MALLS (dn/dc_{PNVP} = 0.064 mL/g). All molecular parameters were determined by SEC-MALLS (dn/dc_{PNVP} = 0.064 mL/g). The extents of coupling (x_c) were calculated as $x_c = 2[1 − (M_{n,0}/M_n)]$.

the B3PW91* electronic energy, with the thermal corrections from the B3LYP calculations.

Results and Discussion

Cobalt-Mediated Radical Coupling of PVAc−[Co] Precursors. As previously reported, radical polymerization of VAc presents all the characteristics of a controlled process when conducted in the presence of bis(acetylacetonato)cobalt(II) (Co(acac)$_2$).[20,23] Depending on the experimental conditions, the CMRP of VAc either follows a reversible-termination (RT) pathway or a degenerative chain transfer (DT) mechanism.[22,23] As a rule, the DT regime is established when the polymerization is initiated with an excess of V-70 compared to Co(acac)$_2$, and no external ligand is necessary under these conditions. Conversely, RT is the predominant mechanism when an alkylcobalt(III) compound which mimics the "dormant species", i.e., [Co(acac)$_2$(−CH(OCOCH$_3$)CH$_2$)$_{<4}$−R$_0$] where R$_0$ corresponds to V-70 initiating fragment, is used as initiator and when external ligands such as DMSO, DMF, or water are present.[27] Whatever the initiating system used, well-defined PVAc capped by the cobalt complex were collected even when high molar masses were targeted. As illustrated by several examples of block copolymerization, the carbon−metal bond at the end of the PVAc chain can be reactivated which makes it a potential candidate for CMRC.[30] In agreement with the above expectation, a range of PVAc samples with different lengths were prepared by CMRP and treated with isoprene in order to evaluate the efficiency of CMRC coupling process. Both initiating systems, i.e., the V-70/Co(acac)$_2$ pair and the alkylcobalt(III) initiator (R-Co), were considered for the preparation of the PVAc precursors. The results are summarized in Table 1.

As expected, Co(acac)$_2$-capped PVAc precursors with low polydispersities (M_w/M_n < 1.1) and molar masses in close agreement with theoretical predictions were obtained whatever the CMRP initiating system. After removal of the unreacted VAc, these cobalt-functionalized PVAc precursors were dissolved in degassed DMSO before addition of a large excess of isoprene compare to the cobalt concentration (90−100-fold excess). Such a treatment induced the doubling

of the polymer molar masses, suggesting the occurrence of the coupling reaction. ^{1}H NMR of the final products allowed us dismissing the formation of the PVAc-*b*-PIP diblock copolymer (see Supporting Information Figure A). The CMRC efficiency was then evaluated following the previously reported equation: x_c (extent of coupling) = 2[1 − $(M_{n,0}/M_n)$], where $M_{n,0}$ and M_n are the molar masses of the precursor and the coupling product, respectively.[33] As can be seen in the three first entries of Table 1, CMRC occurred for all PVAc precursors prepared in the DT mode and appeared quantitative when conducted on short PVAc precursors (~5000 g/mol, x_c = 0.97, entry 1). The completeness of the coupling reaction is clear when considering the overlay of the SEC chromatograms before and after addition of isoprene (Figure 2A). Noteworthy, the coupling efficiency tends to decrease for precursors with higher molar masses (compare entries 1−3). Indeed, x_c is limited to 0.86 and 0.78 when precursors of 17 500 and 25 000 g/mol were used. Nevertheless, these results remain satisfactory since other radical coupling processes have only proved efficient for very short polymer chains (<3000 g/mol). At a first sight, similar extents of coupling were measured when an alkylcobalt(III) derivative was used as initiator in the polymerization step (entries 4−6). After close examination, CMRC appeared slightly more efficient when the precursor was prepared with the alkylcobalt(III) compared to the V-70/cobalt pair (compare entries 3 and 5 where the precursors have similar lengths). This discrepancy is probably related to the variation of the level of control in the polymerization step, and thus the percentage of end-functionalized chains, which is certainly slightly higher when using a preformed organocobalt(III) initiator. The impact of the molar mass of the precursor on the coupling efficiency was also evidenced when using the alkylcobalt(III) initiator in the polymerization step (entries 4−6). This trend is very clear considering the overlays of the SEC chromatograms before and after coupling reaction (Figure 2). Indeed, unreacted precursor could hardly be detected in the coupling product of the reaction involving a 12 000 g/mol PVAc-Co sample and isoprene (Figure 2B), whereas a significant amount of precursor was
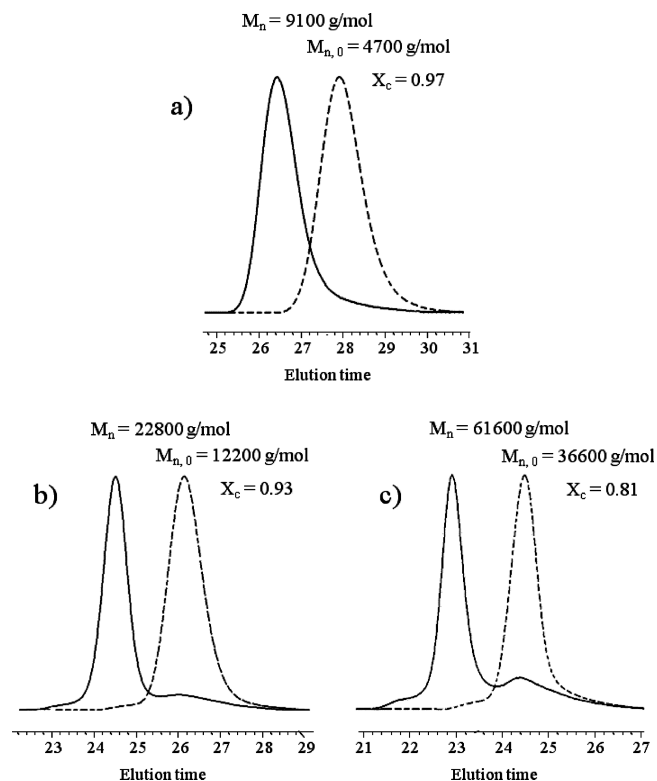
a)

$M_n = 9100$ g/mol
$M_{n,0} = 4700$ g/mol
$X_c = 0.97$

b)

$M_n = 22800$ g/mol
$M_{n,0} = 12200$ g/mol
$X_c = 0.93$
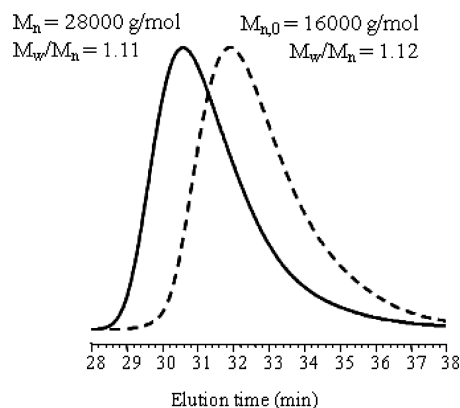
c)

$M_n = 61600$ g/mol
$M_{n,0} = 36600$ g/mol
$X_c = 0.81$

Figure 2. Size-exclusion chromatograms (RI) of the coupling products (full line) and the corresponding PVAc-[Co] precursors (dotted line). For detailed conditions of experiments corresponding to overlays (a), (b) and (c), see Table 1, entries 1, 4, and 6, respectively.

left after CMRC conducted on a 36 000 g/mol PVAc-Co sample (Figure 2C). Nevertheless, a coupling extent of 80% for polymer precursors having molar masses as high as 36 000 g/mol (entry 6) is far beyond what could be obtained by ATRC,[32,38] which is restricted to polymers with molar masses below 5000 g/mol.

Cobalt-Mediated Radical Coupling of PNVP-[Co] Precursors. A previous study revealed that the use of the V-70/Co(acac)$_2$ pair only leads to moderate control of NVP polymerization unless VAc is used as comonomer.[28] In the latter case, well-defined PNVP-*co*-PVAc copolymers with high NVP content were prepared. However, because of the uncertainty about the nature of the chain end of the copolymer (VAc or NVP as last unit), we considered that applying CMRC[30,31] on this type of copolymer would not be representative of the real ability of the PNVP-[Co] species to undergo the coupling reaction.

On the other hand, we have found that the control of pure NVP polymerization is satisfactory when initiated by a PVAc-Co(acac)$_2$ macroinitiator.[29] In spite of a low amount of unreacted PVAc chains, PVAc-*b*-PNVP block copolymers with relatively low polydispersities ($M_w/M_n \sim 1.3$) were prepared accordingly. Consequently, for the sake of the CMRC study, we synthesized well-defined homo-PNVP-Co(acac)$_2$ precursors in degassed anisole at room temperature starting from a low molecular weight alkylcobalt(III) species ([Co(acac)$_2$(−CH(OCOCH$_3$)CH$_2$)$_{<4}$−R$_0$]), which mimics the PVAc macroinitiator. Well-defined PNVP precursors with different lengths were prepared by adjusting the [NVP]/[initiator] molar ratio (see Table 2). In this case, the calculated CMRP efficiency factors were low ($f = M_{n,theoretical}/M_{n,experimental} \sim 0.2-0.25$) most probably due to the partial passivation of the initiating species at the early stage of the polymerization. This hypothesis is in line

$M_n = 28000$ g/mol
$M_w/M_n = 1.11$
$M_{n,0} = 16000$ g/mol
$M_w/M_n = 1.12$

Figure 3. Size-exclusion chromatograms (RI) of the coupling products (full line) and the corresponding PNVP-[Co] precursors (dotted line) prepared with an alkylcobalt(III) adduct initiator ([Co(acac)$_2$(−CH-(OCOCH$_3$)CH$_2$)$_{<4}$−R$_0$]), R$_0$ being the primary radical generated by V-70; see Table 2, entry 1).

with the partial deactivation of the PVAc macroinitiator observed in the above-mentioned block copolymerization. Nevertheless, these well-defined PNVP-Co(acac)$_2$ precursors with various length were suitable to probe the efficiency of the CMRC process (see Table 2).

Because of the low volatility of NVP, removal of the residual monomer under reduced pressure prior to the coupling reaction was not possible. Therefore, isoprene was directly injected in the crude NVP polymerization medium. Such a procedure was already successfully tested for the CMRC of PAN.[30] A few minutes after isoprene addition the color of the medium changed from dark green to purple, the characteristic color of Co(acac)$_2$. This observation was a very a good omen with regard to CMRC, and the reactions were allowed to proceed for another 2 h at room temperature. Again, ^{1}H NMR analysis of the crude mixture did not reveal any signal supporting the formation of polyisoprene-based diblock copolymer (see ^{1}H NMR section below). Comparison of the absolute molar masses (M_n MALLS) of the polymers before and after treatment with isoprene, reported in Table 2, clearly suggests that CMRC is also active for P*N*VP. In all cases, a strong increase of the molar mass was observed as illustrated for the case of entry 1 in Figure 3. Noteworthy, both chromatograms present a tailing on the low molecular weight side, which suggests a moderate control during the polymerization step. As can be seen in Table 2, the extents of coupling (x_c) were between 0.80 and 0.75 for precursors with molar masses ranging between 15 000 and 35 000 g/mol (Table 2).

In general, these experiments illustrate that CMRC is not restricted to PAN-based precursors. Moreover, it can be concluded that the efficiency of the coupling reaction varies in the order PAN > PVAc > PNVP. This tendency could be connected to the intrinsic reactivity of each cobalt−carbon bond but must also be related to the quality of the control in the polymerization step which determines the proportion of chains likely to be activated in the CMRC process.

NMR Analyses. As reported in a previous study, a typical feature of CMRC applied to poly(acrylonitrile) precursor is the incorporation of isoprene units in the middle of the coupling product backbone, at the junction of the precursors.[31] An average number of 2 isoprene units per chain was measured by NMR.[31] From the mechanistic point of view, it is important to know whether insertion of the diene in the coupling product is a special feature of the coupling reaction of PAN-Co chains or a general characteristic of CMRC
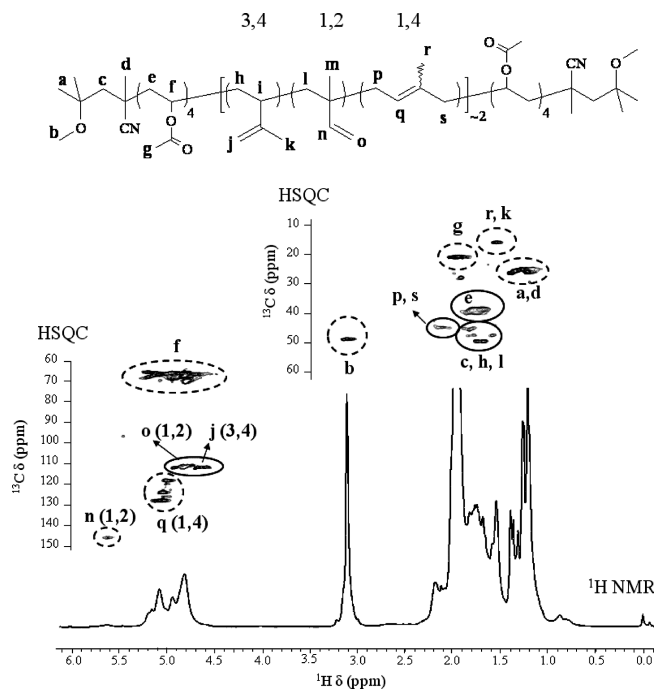
Figure 4. ^{1}H NMR and HSQC spectra (CDCl$_3$, 298 K) of the PVAc coupling product obtained by treatment of alkylcobalt(III) species ([Co(acac)$_2$(−CH(OCOCH$_3$)CH$_2$)$_{<4}$−R$_0$]) upon addition of isoprene.

whatever the nature of the polymer precursor. NMR analyses were carried out on PVAc and P*N*VP coupling products in order to address this question.

For the ease of interpretation of the NMR spectra, CMRC was carried out on short chains capped by Co(acac)$_2$, i.e., Co(acac)$_2$(−CH(OCOCH$_3$)CH$_2$)$_{<4}$−R$_0$, using isoprene as coupling agent. Proton (^{1}H) and heteronuclear ([1]H−[13]C) single quantum coherence (HSQC) NMR of the low molar mass PVAc coupling product are provided in Figure 4. Typical signals of PVAc and V-70 initiating fragment were easily identified, i.e., PVAc methine protons **f** (4.6−5.2(δ_H)−68(δ_C)), PVAc methylene protons **e** (1.7(δ_H)−40(δ_C)), PVAc methyl protons **g** (1.9(δ_H)−22(δ_C)), and V-70 methoxy protons **b** (3.1(δ_H)−49(δ_C)). The HSQC analysis also revealed the presence of olefinic protons, in the 4.8−5.5 ppm (δ_H) region, proving the insertion of isoprene in the PVAc coupling product. The abundance of signals in this region is due to the different addition modes of isoprene. For example, cross-peaks for olefinic protons **q** at 5.0−5.1(δ_H) and 118−130(δ_C) correspond to the 1,4-*cis/trans*-addition products. Although less intense, peaks corresponding to the other addition modes were also observed, i.e., methine proton of 1,2-addition **n** (5.6(δ_H)−146(δ_C)), methylene protons of 1,2-addition **o** (4.8(δ_H)−111(δ_C)), and methylene protons of 3,4-addition **j** (4.6(δ_H)−112(δ_C)). These data evidence the isoprene insertion during the CMRC process of PVAc, mainly according to the 1,4-addition pathway. This conclusion is perfectly in line with previous observations made on the PAN coupling product. Moreover, while direct proof of the insertion of isoprene units in the polymer backbone is provided by the mass spectrometry (MS) analyses in the next section, this conclusion is also corroborated by heteronuclear multiple bond correlation (HMBC) analyses. Most noteworthy were the correlations between olefinic protons at δ5.01 and carbons **f** (−CH(OAc)−) at δ69.80 but also between protons **f** (−C*H*(OAc)−) at δ4.80 and δ4.95 with olefinic carbons at δ118.40 and δ130.80, respectively (see Supporting Information Figure B).
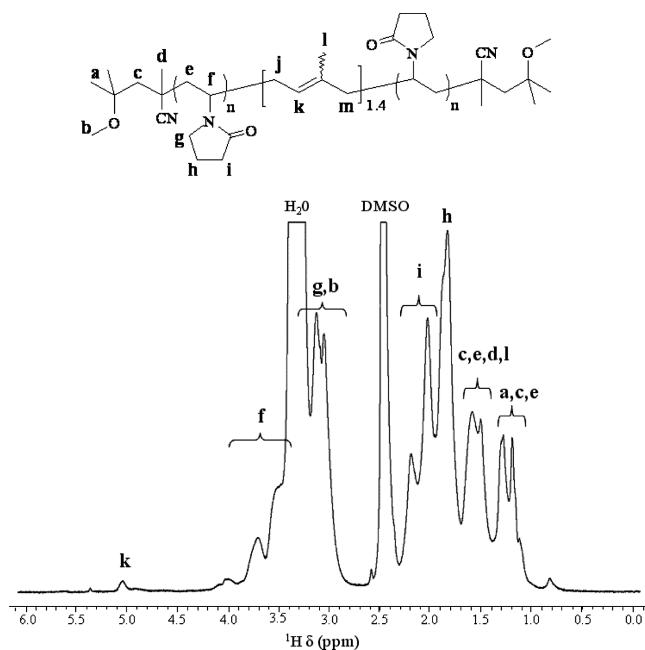
Figure 5. ^{1}H NMR spectrum (DMSO-d_6, 298 K) of the PNVP coupling product prepared by addition of isoprene onto PNVP-Co(acac)$_2$ precursor formed by CMRP using V-70 as initiator.

The isoprene incorporation during the CMRC of PNVP was also probed by NMR. Figure 5 shows the ^{1}H NMR spectrum for a P*N*VP coupling product with moderate molar mass ($M_{n,MALLS}$ = 4600 g/mol, M_w/M_n = 1.12). The latter was obtained after addition of isoprene on a precursor prepared by NVP polymerization initiated by V-70 at 30 °C in the presence of Co(acac)$_2$ ($M_{n,MALLS}$ = 3300 g/mol, M_w/M_n = 1.09) (see Supporting Information Figure C). In this particular case, V-70 was preferred to Co(acac)$_2$(−CH-(OCOCH$_3$)CH$_2$)$_{~4}$−R$_0$ as initiator in the polymerization step in order to avoid the overlap between isoprene and VAc signals in the coupling product spectrum. Again, besides the peaks assigned to the V-70 fragment (**a**−**d**) and PNVP main chain (**e**−**i**), a signal characteristic of the olefinic proton **k** of the isoprene units was detected at 5.05 ppm (Figure 5). Because of low isoprene content in the PNVP sample, only the 1,4-addition product could clearly be identified. The comparison of the intensity of the signal for proton **k** and the cumulative intensities of protons **i** and **h** of PNVP gave access to the average number of isoprene units per chain which is equal to 1.4. It is noteworthy that the number of isoprene units per chain in the coupling product is certainly slightly underestimated due to the incompleteness of the CMRC process.

Mass Spectrometry Analyses. Electrospray ionization (ESI) mass spectrometry analyses were also carried out on the low molecular weight PVAc coupling product used in the above-mentioned NMR study. A major advantage of this technique is the possibility to determine the exact number of inserted isoprene units per chains whereas NMR could only provide an average value (~2). ESI spectra of the PVAc oligomer precursor, i.e., [Co(acac)$_2$(−CH(OCOCH$_3$)-CH$_2$)$_{<4}$−R$_0$], and the corresponding coupling product are presented in parts A and B of Figure 6, respectively.

Given the weakness of Co−C bond in the [Co(acac)$_2$-(−CH(OCOCH$_3$)CH$_2$)$_{<4}$−R$_0$] complex and its sensitivity to air, acquisition of the ESI spectrum before decomposition was quite challenging. Nevertheless, measurements were made possible by dissolution of the cobalt complex in a
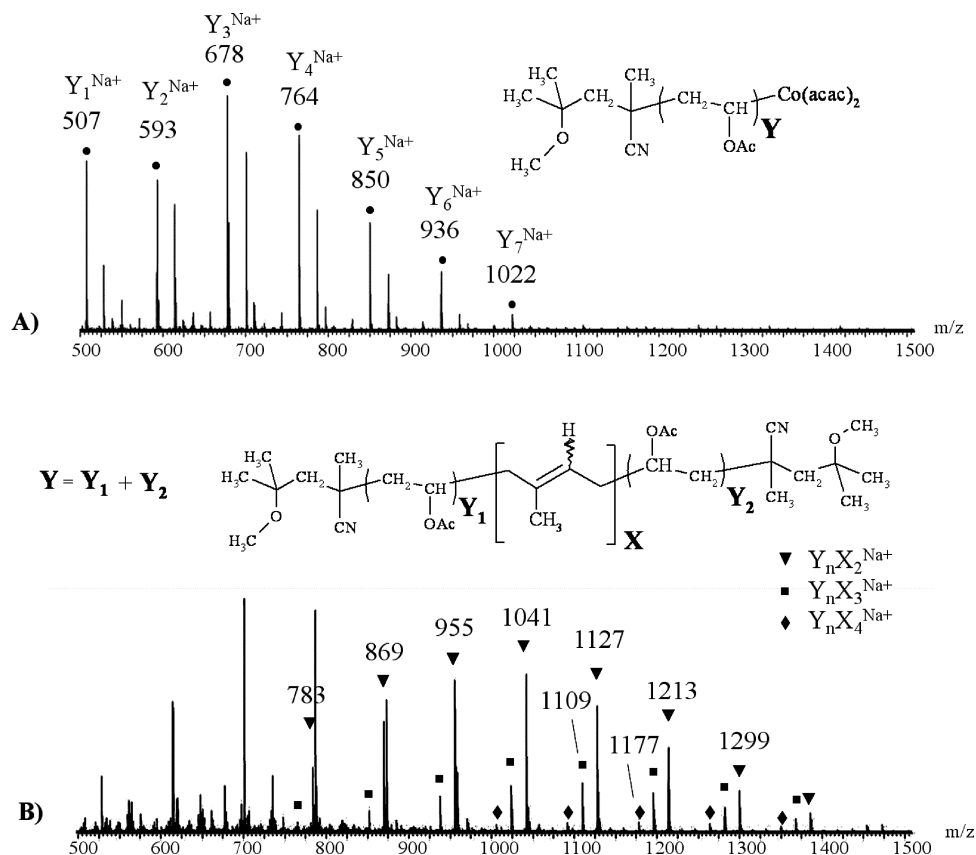
$Y_1{}^{Na+}$
507

$Y_2{}^{Na+}$
593

$Y_3{}^{Na+}$
678

$Y_4{}^{Na+}$
764

$Y_5{}^{Na+}$
850

$Y_6{}^{Na+}$
936

$Y_7{}^{Na+}$
1022

A)

500 600 700 800 900 1000 1100 1200 1300 1400 1500   m/z

$Y = Y_1 + Y_2$

$\blacktriangledown\ Y_nX_2{}^{Na+}$
$\blacksquare\ Y_nX_3{}^{Na+}$
$\blacklozenge\ Y_nX_4{}^{Na+}$

783   869   955   1041   1127   1109   1177   1213   1299

B)

500 600 700 800 900 1000 1100 1200 1300 1400 1500   m/z

Figure 6. ESI-MS spectra of the PVAc oligomer precursor ([Co(acac)$_2$($-$CH(OCOCH$_3$)CH$_2$)$_{<4}$$-R_0$]) (A) and of the corresponding coupling product obtained upon isoprene addition (B). See the Experimental Section for the analysis conditions.

degassed sodium iodide/acetonitrile solution followed by quick transfer in the spectrometer (Figure 6A). The main ion series presents an 86 u interval corresponding to the VAc repeating unit. A minute analysis of the measured m/z ratios allowed the unambiguous assignment of this ion series to the sodium-cationized precursor ions, remarkably still capped by the Co(acac)$_2$ group. As for an example, the base peak of the dominant population was detected at m/z 678 ($Y_3{}^{Na+}$) and can be attributed to the sodium-cationized PVAc oligomer containing three VAc units, with the V-70 initiating residue ($-$C(CN)(CH$_3$)$-$CH$_2$$-$C(OCH$_3$)(CH$_3$)$_2$) and the bis(acetylacetonato)cobalt complex (Co(acac)$_2$) at the α and ω chain ends, respectively.

In the ESI spectrum of the crude CMRC mixture (Figure 6B), the ions corresponding to the [Co(acac)$_2$-($-$CH(OCOCH$_3$)CH$_2$)$_{<4}$$-R_0$] precursor completely disappeared at the benefit of a new ion series characterized by higher m/z values. This significant increase of the position of the maximum of the ion series (m/z 678 in Figure 6A to m/z 1041 in Figure 6B) reveals that the coupling reaction is definitively efficient. Moreover, the measured m/z ratios unambiguously demonstrate that the PVAc coupling product incorporates two isoprene units (X$_2$) inserted in the backbone. For instance, the most intense signal ($Y_7X_2{}^{Na+}$) is observed at m/z 1041 and can be attributed to sodium-cationized oligomers incorporating seven vinyl acetate units, two isoprene units, and two V-70 initiating residues, one at each both chain ends. Minor populations were nevertheless detected and correspond to insertion of 3 and 4 isoprene units in the polymer backbone during the CMRC process. Species $Y_7X_3{}^{Na+}$ and $Y_7X_4{}^{Na+}$ were observed at m/z 1109 and m/z 1177, respectively. Noteworthy, no signal corresponding to PVAc containing one or no isoprene unit

(i.e., $Y_7X_1{}^{Na+}$, m/z 973 and $Y_7X_0{}^{Na+}$, m/z 905) could be detected. This latter information allows us to dismiss the hypothesis that the PVAc precursors undergo a direct coupling by combination.

For the sake of completion, in both A and B of Figure 6, an additional ion series is detected, but we were not able to identify the corresponding oligomers. However, the presence of this side population in the spectrum of the coupling product suggests that this inactive species contaminates the alkylcobalt(III) precursor species prior CMRC and MS analysis. Partial passivation of the precursor might be at the origin of this product. As a confirmation, the cobalt-terminated species was modified according to a previously reported procedure prior MS analysis, i.e., replacement of the cobalt by a hydrogen atom upon treatment with propanethiol.[40] Besides intense signals corresponding to the cobalt-free PVAc oligomers terminated by a hydrogen atom, the above-mentioned side population was still detected (see Supporting Information Figure D), which is in favor of the partial organocobalt precursor degradation hypothesis. Nevertheless, the relative intensities of the ESI MS peaks do not reflect the extent of the contamination which must be relatively low given the reported high efficiency factors obtained when using the alkyl cobalt(III) species as polymerization initiator.[23]

For the mass spectrometry analyses of the PNVP samples, MALDI-ToF was preferred over ESI-ToF which generates multicharged species making interpretation of spectra definitively less straightforward. Typically, *trans*-2-[3-{4-*tert*-butylphenyl}-2-methyl-2-propenylidene]malononitrile (DCTB) and sodium iodide were used as matrix and cationization agent, respectively. Figure 7A presents the spectrum obtained when analyzing the PNVP precursor formed by
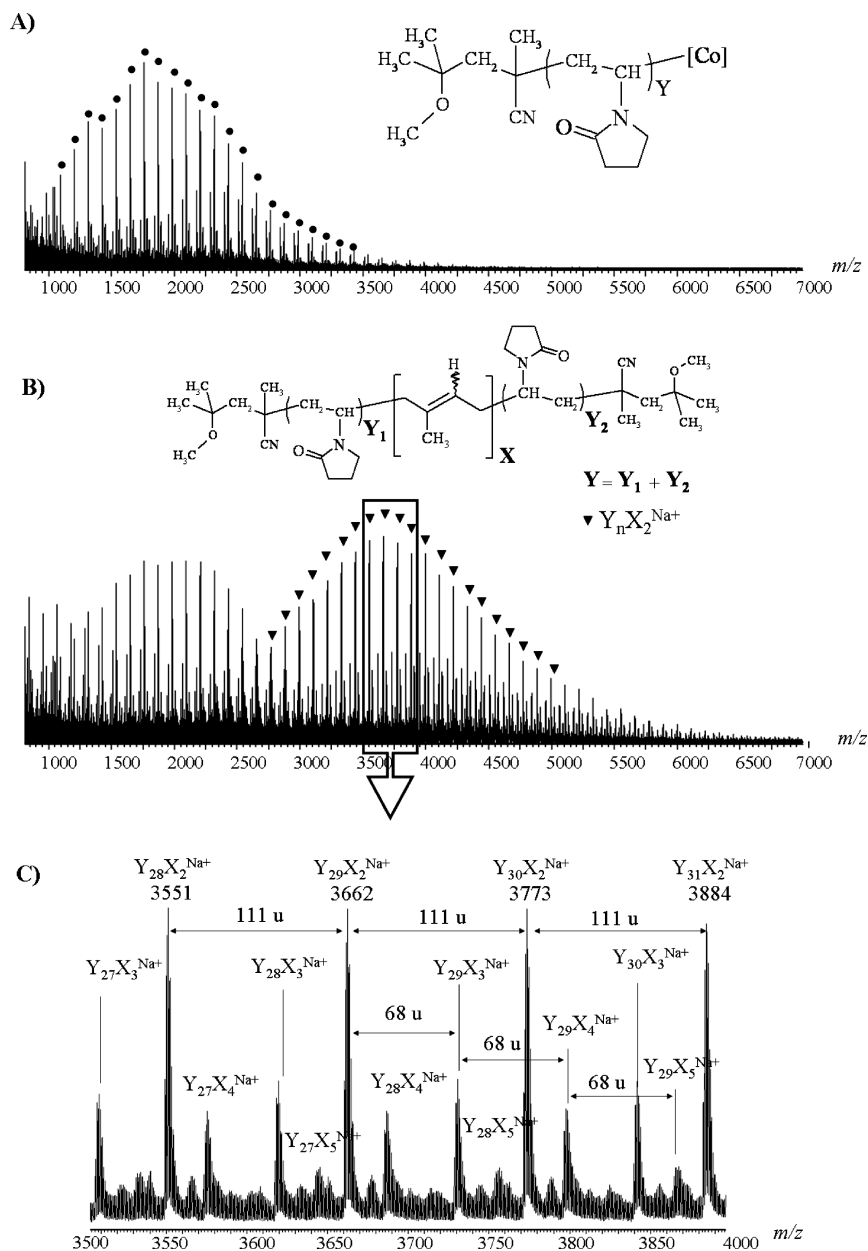
Figure 7. MALDI-ToF spectra of the PNVP precursor (A) and of the coupling product obtained after treatment with isoprene (B). An enlargement of the coupling product spectrum is provided in (C). See the Experimental Section for the analysis conditions.

CMRP. As expected, the measured m/z 111 peak-to-peak interval corresponding to a NVP unit was observed, but the end group of the PNVP precursor could not be determined. Again, alteration of the sample upon exposure to air during the preparation of the sample prior to the MALDI measurement probably affords the unidentified end group. The MALDI-ToF spectrum recorded when measuring the PNVP coupling product (Figure 7B) presents several new populations at higher molar masses. As can be seen in the enlargement of the MALDI spectrum (see Figure 7C), the main population corresponds to insertion of two diene units in the PNVP ($Y_nX_2^{Na+}$), whereas other minor populations contain more isoprene moiety in their backbone ($Y_nX_3^{Na+}$, $Y_nX_4^{Na+}$, $Y_nX_5^{Na+}$). Noteworthy, signals corresponding to the precursor still have significant intensities after the coupling reaction (Figure 7B). This might be due to the incompleteness of CMRC applied to PNVP ($x_c \sim 0.75$ see section above) but also to an easier desorption/ionization of the low molecular weight PNVP precursors. Once again, as a general

rule, it must be emphasized that the relative intensities of different ionized species in a given mass spectrum cannot be considered representative of the solution compositions, especially for molecules presenting different functions.

In conclusion, preferential insertion of two isoprene units in the middle of the polymer backbone of the coupling product is a general characteristic of CMRC whatever the nature of the precursor. This feature could be exploited for specific midchain functionalization of PAN, PVAc, and PNVP containing polymers by using functionalized dienes as coupling agents. For example, pendant hydroxyl groups were specifically introduced in the middle of PAN chains when CMRC was conducted with a hydroxyl-substituted diene.[31] Unique star-shaped copolymers could be prepared by using these pendant groups to reinitiate polymerizations or to graft polymer segments. Such synthetic approaches are under current investigation.

Importantly, CMRC has always been conducted with a large excess of diene compared to the polymer precursor
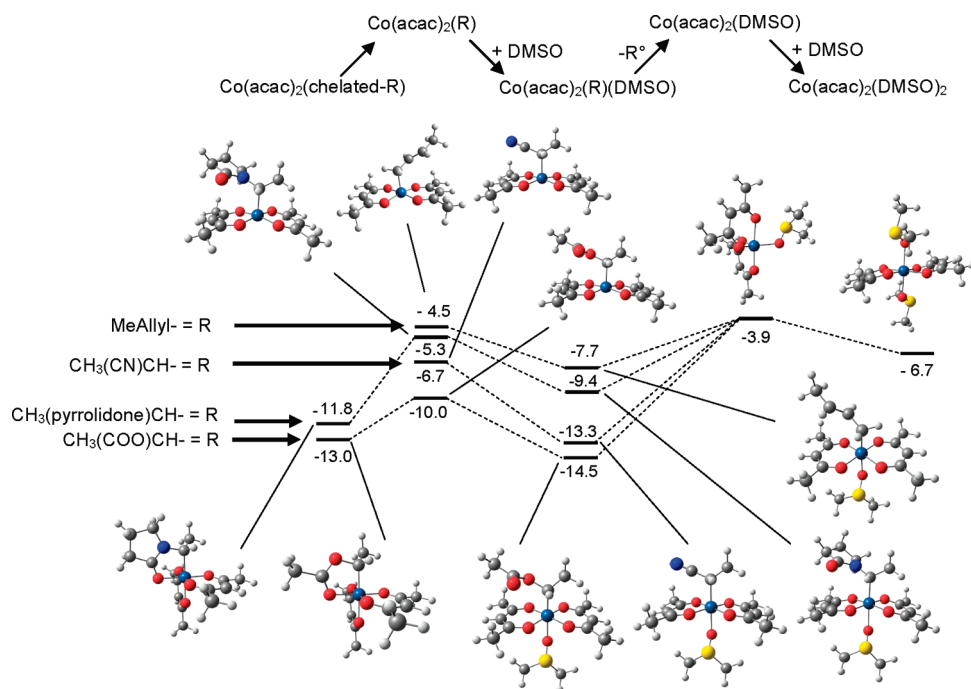
Figure 8. Calculated enthalpy diagram (at 298.15 K) and views of optimized geometries for all species relevant to the CMRC of PAN, PVAc, and PNVP in DMSO. The zero energy level corresponds to the separated $Co(acac)_2$, radical and solvent molecules. Table of the Cartesian coordinates of all new optimized geometries is provided as Supporting Information (see Table C).

(100-fold excess) until now, which could be a sever limitation when precious functional dienes are used. Fortunately, good coupling efficiency ($x_c = 0.94$) was also observed when CMRC was conducted with a [isoprene]/[PVAc-Co] molar ratio equal to 10. However, using 2 equiv of isoprene only led to partial coupling ($x_c = 0.74$) (see Supporting Information Table A). In summary, using a 10-fold excess of diene with respect to the polymer precursor appears as a good compromise between the CMRC efficiency and the amount of coupling agent involved.

Mechanistic Considerations. The essential mechanistic considerations leading to the efficient coupling of the Co-$(acac)_2$-terminated polymer chains upon introduction of diene have been discussed in our previous contribution, which dealt with the CMRC of PAN in DMSO.[31] As a brief reminder, the activation/deactivation equilibrium for the PAN-$Co(acac)_2$(DMSO) dormant chains (leading to PAN$^•$ and $Co(acac)_2$(DMSO)$_2$) is favorable for a controlled polymerization process, but upon diene addition and formation of the first allyl radical, PAN$-CH_2-$allyl$^•$, trapping by $Co(acac)_2$ is not sufficiently favorable, resulting in an accumulation of radicals in solution and coupling. Computation of bond dissociation energies, using $CH_3(CN)CH^•$ as a model for PAN$^•$ and $CH_3CH=CHCH_2^•$ for PAN$-CH_2-$allyl$^•$, fully backed up this analysis.[31]

We have now extended the computational work to the new coupling processes reported here, namely the CMRC of PVAc in DMSO and of PNVP in NVP/anisole and in DMSO, in order to rationalize the observed trends and the solvent effect. Before analyzing the results, it is necessary to remind the limited quantitative significance of the calculated enthalpy changes for describing the solution equilibria because of the neglect of solvation and entropic effects, as amply discussed in our previous contributions.[18,23] The results of the computational work are useful, however, to interpret relative changes for similar systems. The energy values were obtained by use of the B3PW91* functional featuring a reduced coefficient for the exact Hartree−Fock

exchange term, which appears to provide more adequate results relative to the more popular B3LYP functional.[18]

The energetics relevant to the coupling processes in the DMSO solvent are summarized in Figure 8, which also shows the previously analyzed PAN coupling for comparison. The PVAc$^•$ and PNVP$^•$ chains are modeled by the corresponding H-terminated unimer radical and isoprene is modeled by butadiene; thus, both PVAc$-CH_2-$allyl$^•$ and PNVP$-CH_2-$allyl$^•$ radical chains are modeled by $CH_3CH=CHCH_2^•$.

As previously discussed,[22] the dormant chain is stabilized by coordination of a solvent molecule (L), if this has sufficiently strong coordinating properties, to yield 6-coordinate $Co(acac)_2$(R)(L), which is closed-shell and diamagnetic. For PVAc in DMSO, solvent coordination is exothermic by 4.5 kcal mol^{-1} and is therefore more favorable than chelation, which yields the 6-coordinate $[Co(acac)_2\{\kappa^2:C,O-CH-(CH_3)OCOCH_3\}]$ stabilized by only 3.0 kcal mol^{-1}(see Figure 8).[27] For PAN, DMSO coordination is even more favorable (6.6 kcal mol^{-1}) because PAN is less sterically encumbering than PVAc, while no chelation is possible.[18] Thus, the dormant species for both polymer chains is Co-$(acac)_2$(R)(DMSO). Concerning the NVP polymerization, the calculations indicate a weaker Co$-$CH(pyrrolidone)CH$_3$ bond (5.3 kcal mol^{-1}) relative to the Co$-$PAN and Co$-$P-VAc models (6.7 and 10.0 kcal mol^{-1}, respectively). In this case, chelation provides greater enthalpic stabilization (6.5 kcal mol^{-1}) than DMSO coordination (4.1 kcal mol^{-1}). However, the resulting chelated species is still higher in enthalpy than the PVAc and PAN dormant species. Furthermore, the trapping process occurs on DMSO-coordinated Co^{II} complexes and thus leads directly to the 6-coordinate solvent adduct $Co(acac)_2$(PNVP)(DMSO). While d^7 Co^{II} is labile with respect to ligand dissociation and exchange, d^6 Co^{III} is inert. Hence, DMSO loss and chelation of the polymer chain might be slower than the chain reactivation, in which case the higher energy solvent adduct is the actual dormant species. One way or the other, the calculations
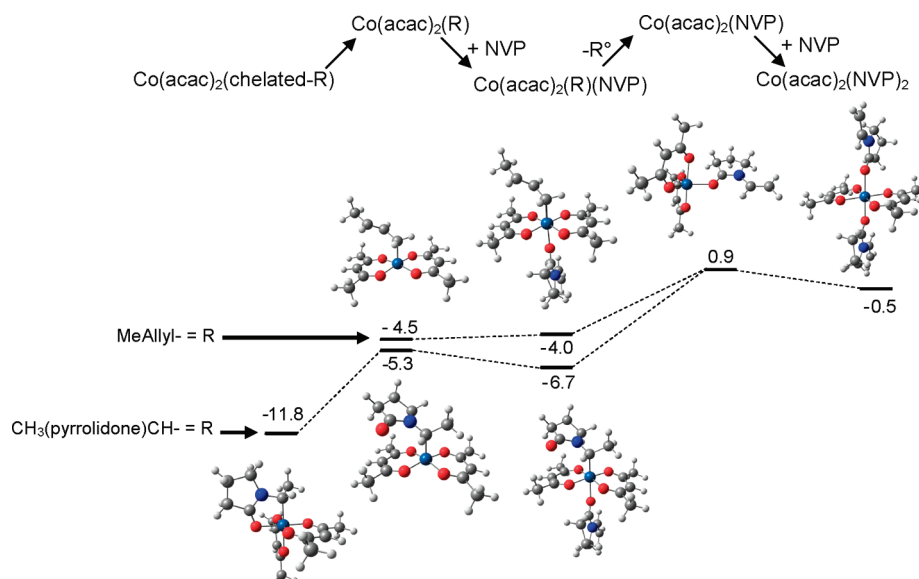
Figure 9. Calculated enthalpy diagram (at 298.15 K) and views of optimized geometries for all species relevant to the CMRC of PNVP in anisole. The zero energy level corresponds to the separated Co(acac)$_2$, radical, and solvent molecules. Table of the Cartesian coordinates of all new optimized geometries is provided as Supporting Information (see Table C).

predict a greater latent radical concentration for NVP relative to VAc or AN. The polymerization rate is also proportional to k_p, but the k_p values for these three monomers are very similar ($\sim 10^3$ M^{-1} s^{-1}).[41] Hence, the effective polymerization rate by CMRP in DMSO should vary in the order NVP > AN > VAc, in agreement with the experimental observation. Indeed, polymerization of NVP initiated at room temperature in DMSO reached a 50% conversion in 20 min while 1 h was necessary to observe the same conversion for AN and only 20% of VAc was consumed after 1 h under the same conditions (see Supporting Information Table B). As expected, this fast NVP polymerization in DMSO suffered from drastic lack of control.

When diene is added to the mixture, it adds to the active chain to yield an allyl-type radical. This addition must be very favorable because no coupled chains containing only one diene molecule could be observed for any of the polymers. Following conversion to the allyl-type radical, three possible processes can occur: (i) trapping by cobalt to yield a new dormant chain; (ii) addition of a second diene molecule; (iii) coupling with another radical chain to give a dead chain with double molecular mass. However, process i is not favored as already discussed[31] because the Co(acac)$_2$(allyl)-(DMSO) dormant chain is not sufficiently stabilized relative to the free radical and Co(acac)$_2$(DMSO)$_2$ (only -1.0 kcal mol^{-1} according to the calculations). The relative importance of processes ii and iii depends on the radical and diene concentrations, since the coupling rate is second order in radicals and the diene addition rate is first order in both radical and diene. Coupling should be more favored for faster radical generations (greater radical concentration). Note, however, that insertion of one (or more) additional diene molecule continues to yield allyl-type radicals that are not efficiently trapped, and thus coupling of all chains must ultimately occur. Faster dormant chain activation should just ensure the predominance of coupled chains with only two diene units, whereas slower activation should yield chains containing more diene monomers, with a progressively smaller probability for longer polydiene sequences. According to this argument, the coupling efficiency should not be affected by the cobalt−carbon bond reactivity (bond

strength) and should be equally efficient for all polymers. Hence, any difference in coupling efficiency must result from the presence of inactive chains (not terminated by the cobalt complex) prior to diene addition.

The calculations predict that the PVAc dormant species should yield free radicals at a slightly slower rate than the PAN dormant species, yielding a slower coupling process. If one assumes that the calculated dissociation enthalpy is a good estimate of the activation free energy, rates of radical generation from the dormant species of 1.1×10^5 and 5.7×10^5 s^{-1} are obtained from the Eyring equation for the PVAc and PAN radicals, respectively. On the other hand, coupling should be faster for the cobalt-terminated PNVP chains. This result predicts equally efficient coupling for all three polymers but with slightly higher incidence of longer polydiene sequences for PVAc than for PAN. Such differences could not be experimentally highlighted, however, because of the very low incidence of polydiene sequences with a length greater than two units. The experimentally different coupling efficiencies can be related to the controlling abilities in CMRP as argued above.

It is now interesting to compare the P*N*VP coupling in DMSO and in anisole. For the polymerization process run in anisole, which offers the best control of the CMRP of NVP, the solvent is not sufficiently coordinating to afford adducts with cobalt. However, the monomer itself has donating properties through the carbonyl oxygen atom and represents the strongest potential donor available in the reaction mixture. Thus, a potential dormant species is Co(acac)$_2$(PNVP)-(NVP), whereas the Co^{II} complex released during the activation process could be transformed into Co(acac)$_2$-(NVP)$_2$. The energetic diagram for the PNVP equilibria under these conditions is reported in Figure 9.

The calculations indicate that NVP coordinates much less strongly than DMSO (cf. Figures 8 and 9). For the dormant PNVP species, NVP coordination stabilizes the system by only 1.4 kcal mol^{-1} (vs 4.1 kcal mol^{-1} for DMSO), whereas NVP coordination is not at all favored (slightly endothermic) for the model of the allyl-terminated dormant chain. Concerning the Co^{II} complexes, the differential is even greater, the stabilization decreasing from 3.9 to -0.9 kcal mol^{-1} on going from DMSO to NVP for the addition of one L

molecule to $Co(acac)_2$ and from 6.7 to 0.5 kcal mol^{-1} for the addition of two molecules. It is questionable, therefore, whether the radical trapping species under these conditions is $Co(acac)_2(NVP)_2$ or simply the tetrahedral complex $Co(acac)_2$. Indeed, whereas a bis-adduct of $Co(acac)_2$ with DMSO has been structurally characterized,[18] other known $Co(acac)_2(L)_2$ structures are limited to the adducts with H_2O, MeOH, substituted pyridines, and diamines, and no related adducts with amide-type donors are known according to the Cambridge Structural Database.

Comparison of Figures 8 and 9 shows that activation of the PNVP−Co dormant chain should be slower in anisole than in DMSO (this is true whether the dormant species is $[Co(acac)_2(\kappa^2:C,O\text{-}PNVP)]$ or, in case chelation is slow, $[Co(acac)_2(PNVP)(L)]$). This is in agreement with the observed slower rate of polymer growth in anisole (see Supporting Information Table B). Furthermore, the comparison of the energy changes related to the PNVP• activation in anisole and the PVAc• and PAN• activations in DMSO leads to the expectation of a slower polymerization for NVP in anisole relative to those of VAc and AN in DMSO. This is also in agreement with the experimental evidence (see Supporting Information Table B).

When diene is added to the $Co(acac)_2$-terminated PNVP dormant chain in anisole, the new allyl-type radical seems to have a greater tendency to be weakly trapped (the dormant 5-coordinate $Co(acac)_2$(allyl) chain is stabilized by 4.0 kcal mol^{-1} relative to the free radical and the 6-coordinate Co^{II} trapping species) relative to the same system in the DMSO solvent (stabilization by only 1.0 kcal mol^{-1} for the dormant 6-coordinate DMSO adduct). However, this trapping is obviously not sufficient to turn the system toward controlled polymer growth since a relatively efficient coupling is still observed. However, this trapping may contributed to some degree to the multiple diene insertion process. Indeed, although the family of coupled chains with two inserted diene molecules is still predominant, visible amounts (by MS) of families with multiple diene additions (up to five) can be observed in this case (see Figure 7). In the light of these considerations, the CMRC of PNVP-[Co] should be more effective, leading to the incorporation of closer to two diene units per chain, when carried out in DMSO on a precursor prepared by CMRP in anisole. Nevertheless, the coupling efficiency remained limited to 74% under these conditions, again suggesting that the coupling efficiency is determined by the degree of control in the NVP polymerization (see Supporting Information Figure E).

Synthesis of Symmetrical PVAc- and PNVP-Based Triblock Copolymers by CMRC. As an illustration of the potential of CMRC for macromolecular engineering, CMRC was tentatively applied to a PVAc and PNVP containing diblock in order to prepare the corresponding symmetrical triblock copolymers. Synthesis of well-defined PVAc-*b*-PAN-*b*-PVAc triblock copolymers is already reported according to this strategy.[30] Given the higher coupling efficiency of PVAc−Co compared to PNVP−Co, the PNVP-*b*-PVAc-Co(acac)_2 diblock is a more promising candidate for CMRC than the PVAc-*b*-PNVP-Co(acac)_2 counterpart. However, only the sequential CMRP of VAc followed by NVP gives access to diblocks in a controlled manner. A PVAc(6.7K)-*b*-PNVP(10.5K)-Co(acac)_2 diblock was thus prepared following a previously reported procedure and further used in a CMRC process involving isoprene. Again, the residual NVP could not be removed prior to the coupling reaction; hence, isoprene was added onto the PVAc-*b*-PNVP-Co(acac)_2 diblock dissolved in an NVP/
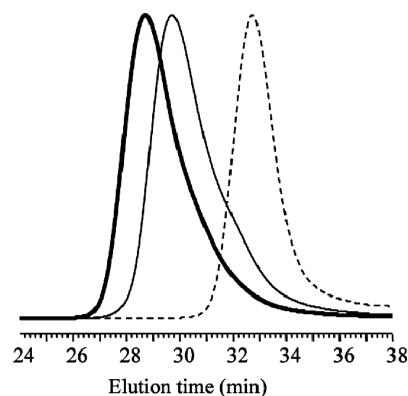
Figure 10. Overlay of RI signals of SEC-RI chromatograms for PVAc-[Co] (dotted line, $M_{n,MALLS}=6700$ g/mol, $M_w/M_n=1.1$), PVAc-*b*-PNVP-[Co] (plain line, $dn/dc=0.059$ mL/g, $M_{n,MALLS}=29\,000$ g/mol, $M_w/M_n=1.2$), PVAc-*b*-PNVP-*b*-PVAc (bold line, $dn/dc=0.060$ mL/g, $M_{n,MALLS}=45\,000$ g/mol, $M_w/M_n=1.2$), extent of coupling $=x_c=2[1-(M_{n,PVAc\text{-}b\text{-}PNVP}/M_{n,PVAc\text{-}b\text{-}PNVP\text{-}b\text{-}PVAc})]=0.71$.
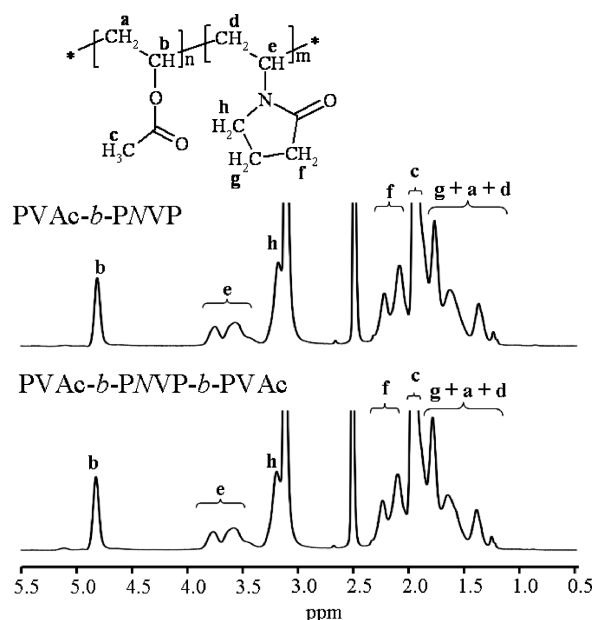
Figure 11. Overlay of the ^{1}H NMR spectra of a PVAc(6.7K)-*b*-PNVP-(10.5K)-[Co] diblock copolymer prepared by CMRP and of the corresponding PVAc(6.7K)-*b*-PNVP(19.2K)-*b*-PVAc(6.7K) triblock copolymer obtained by CMRC.

anisole mixture. The medium was allowed to react for 2 h. As can be seen from the overlay of the SEC chromatograms presented in Figure 10, the diblock (plain line) is contaminated by a small amount of PVAc macroinitiator (dotted line), in agreement with previously reported results. Moreover, a clear shift of SEC chromatograms toward higher molar masses (M_n from 29 000 to 45 000 g/mol) is observed upon treatment of the diblock with isoprene, suggesting the successful formation of the symmetrical PVAc-*b*-PNVP-*b*-PVAc triblock copolymer.

One could argue that this shift may be caused by further polymerization of the residual NVP present in the medium during the coupling assay. However, this hypothesis must be rejected since the PNVP/PVAc molar composition of the copolymer before and after treatment with isoprene remains constant (1.1), as illustrated by the overlay of the ^{1}H NMR spectra presented in Figure 11. The ^{1}H NMR of the final product also confirmed the absence of a formation of poly-(isoprene).

As expected, the extent of coupling of this reaction, calculated considering the absolute molar masses of the diblock and the triblock, was in the range of those observed for the CMRC of homo-PNVP, i.e., x_c equal to 0.7. To our knowledge, this is the first example of the synthesis of this type of triblock copolymer, which emphasizes the specific potential of CMRC for polymer design.

Conclusion

The cobalt-mediated radical coupling (CMRC), previously developed on poly(acrylonitrile) precursors, was successfully applied for the first time to poly(vinyl acetate) and poly(*N*-vinylpyrrolidone). This achievement is all the more important since it is first example of a radical coupling reaction for this type of polymer. The extents of coupling (x_c) were very high (>97%) to moderate (70%), depending on the nature and the length of the precursors. As a rule, the shorter are the precursor chains, the more efficient is the coupling reaction. Moreover, the efficiency of CMRC varies in the order PAN > PVAc > PNVP. These features seem related to the degree of control of the polymerization process before the diene-induced coupling, as suggested by the mechanistic arguments supported by the DFT calculations. Importantly, we demonstrated by NMR and by MS spectrometry that preferential insertion of two isoprene units, mainly according to the 1,4-addition pathway, is a general feature of CMRC which does not depend on the nature of the precursor. This characteristic allows generalizing the previously reported mechanism established for the CMRC of PAN. Therefore, CMRC could also be used for the mid-chain functionalization of PVAc- and PNVP-based materials. The DFT calculations also suggest that the incorporation of more than two diene units may occur under conditions where the allyl-type chain is more favorably trapped, as experimentally observed for the coupling of PNVP in anisole. Finally, the synthesis of novel well-defined PVAc-*b*-PNVP-*b*-PVAc triblock was achieved by CMRC starting from the corresponding diblock, illustrating the potential of this technique for macromolecular engineering.

Supporting Information Available: Table of the Cartesian coordinates of all new optimized geometries, additional CMRP and CMRC experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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