

Expanding the Scope of Controlled Radical Polymerization via Cobalt–Tellurium Radical Exchange Reaction

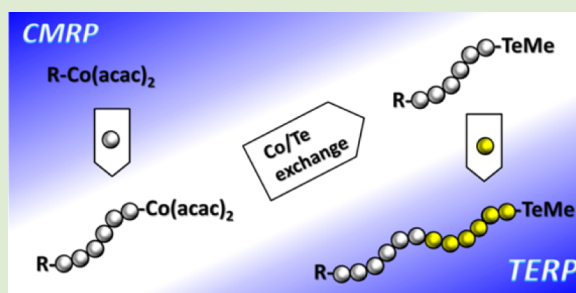
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S Supporting Information

ABSTRACT: Cobalt-mediated radical polymerization (CMRP) and tellurium-mediated radical polymerization (TERP) were combined for the first time, offering new perspectives in the precision design of macromolecular structures. In particular, the present work highlights the benefits of this strategy for the synthesis of novel poly(vinyl acetate)-based block copolymers. A range of well-defined poly(vinyl acetate)s (PVAc) were first produced via CMRP using the bis(acetylacetonato)cobalt(II) complex ($\text{Co}(\text{acac})_2$) as a regulating agent. Substitution of a methyltellanyl moiety for $\text{Co}(\text{acac})_2$ at the ω -chain end of the precursor was then achieved upon treatment with dimethylditelluride. In contrast to the PVAc prepared by TERP, the ones produced by sequential CMRP and Co/Te exchange reaction almost exclusively consist of regular head-to-tail-TeMe chain-end species that can be activated by TERP. Ultimately, a series of monomers problematic in $\text{Co}(\text{acac})_2$ -mediated radical polymerization including *N*-isopropylacrylamide (NIPAM), 2-(dimethylamino)ethyl acrylate (ADAME), *n*-butyl acrylate (BA), isoprene (IP), and vinylimidazole (NVIIm) were polymerized by TERP from the PVAc–TeMe macroinitiators leading to novel diblock copolymers that cannot be made by each technique used separately.



Today, controlled radical polymerization (CRP) is a major tool in the polymer chemists' arsenal to build complex and precise macromolecular architectures.^{1–11} The range of monomers whose radical polymerization can be properly mediated has been considerably enlarged over the last years. Nevertheless, the quest for a universal system appears illusory and a combination of CRP techniques remains a valuable and attractive strategy for the precision synthesis of novel (co)polymer structures. Switchable RAFT agents have been reported to synthesize block copolymers made from monomers having different reactivity, such as conjugated and unconjugated monomers,^{12,13} but its synthetic efficiency has not been fully validated yet. Therefore, development of a new method has been awaited. In this respect, combining cobalt-mediated radical polymerization (CMRP)^{8,14} and tellurium-mediated radical polymerization (TERP)⁶ is particularly appealing. These two systems share a lot of mechanistic similarities, and both can follow a reversible termination (RT) or a degenerative chain transfer (DT) pathway^{15–20} but are complementary regarding the monomers they can deal with.

TERP is characterized by high monomer versatility and good compatibility with polar functional groups and solvents and remains efficient even at elevated monomer conversion.⁶ Among other, well-defined poly(meth)acrylates, polyacrylamides, polystyrene (PS), polyisoprene (PIP), poly(*N*-vinylamide), or poly(vinylimidazole) (PNVIIm) were synthesized by

TERP.^{19,21–24} Numerous block copolymers and end-functionalized polymers have also been prepared by sequential organotellurium-mediated polymerization of these monomers^{22,25–31} and by selective end-group transformation.^{21,32–35}

Nevertheless, TERP suffers from severe limitations regarding the synthesis of poly(vinyl ester)s,³⁶ more particularly for poly(vinyl acetate) (PVAc) which is a large-scale market polymer (>1 million tons/year) with numerous applications as an adhesive emulsifier and precursor of other important polymers including poly(vinyl alcohol).³⁷ During the VAc polymerization, the head-to-head monomer addition mode (H–H) is significant (~1.5 mol % at 70 °C)³⁸ and leads to the extensive buildup of inactive primary alkyl tellurium chain-end (–CHOAc–CH₂–TeMe) adducts along the TERP.³⁶ This inhibits the polymerization and yields poorly defined PVAc with low degree of polymerization (DP ~ 35).³⁶

By contrast, CMRP offers excellent control over the VAc polymerization using bis(acetylacetonato)cobalt(II) ($\text{Co}(\text{acac})_2$) as a controlling agent even when a high degree of polymerization is targeted.^{18,39,40} Recently, we demonstrated that H–H addition also occurs in the CMRP of VAc, but no abnormal accumulation of these inverted units was detected at

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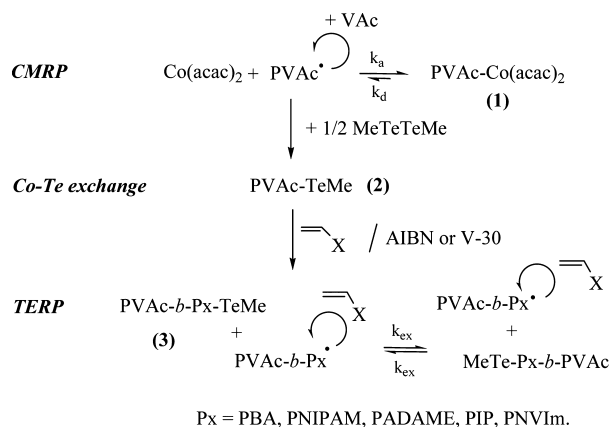
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the chain end (~99% of terminal H–T–Co species), suggesting that the regular head-to-tail (H–T) and inverted H–H cobalt-capped dormant species reactivate at similar rates.⁴⁰ CMRP also proved its efficiency for controlling the polymerization of other nonactivated and challenging monomers including *N*-vinylamides,⁴¹ *N*-vinylimidazolium,⁴² vinyl chloride,⁴³ etc. Nevertheless, the Co(acac)₂-mediated radical polymerization remains ineffective for many monomers. For example, the polymerization of acrylamide in the presence of Co(acac)₂ is out of control due to the weakness of the poly(acrylamide)–metal bond. For similar reasons, a very low efficiency factor was observed for the CMRP of acrylate,⁴⁴ making difficult the Co(acac)₂-mediated synthesis of polyacrylate-containing block copolymer. Isoprene (IP) is also inappropriate for CMRP since addition of IP to organocobalt-terminated chains involves the rapid and almost quantitative bimolecular termination of the chains by coupling.^{45–47} While this reaction, known as cobalt-mediated radical coupling (CMRC),^{45,46} is a powerful tool for the convergent synthesis of block copolymers,⁴⁷ it prevents the controlled polymerization of IP. Finally, CMRP is very sensitive to the complexation of the cobalt center^{17,18,48} by monomers bearing Lewis base groups, like *N*-vinylimidazole (NVI_m), that makes the control of the polymerization more difficult to achieve.

In this work, we explored the possible combination of CMRP and TERP to take benefit of their unique properties to design novel copolymers, more particularly PVAc-based block copolymers **3** (see Scheme 1). This implies the development

Scheme 1. General Strategy for the Synthesis of Block Copolymers by Combination of CMRP and TERP



of a very efficient cobalt–tellurium radical exchange reaction that can be applied at a polymer chain end and allows switching from CMRP to TERP for syntheses of blocks. Given the higher strength reported for the tellurium–carbon bond compared to the Co(acac)₂–carbon one, we prepared well-defined PVAc–Co(acac)₂ species **1** by CMRP and subsequently transformed it into more stable organotellurium functional polymers **2**. Block extension by TERP was then performed with a series of monomers troublesome for CMRP including *N*-isopropylacrylamide (NIPAM), 2-(dimethylamino)ethyl acrylate (ADAME), *n*-butyl acrylate (BA), isoprene (IP), and NVI_m.

The cobalt–tellurium exchange reaction was first studied on well-defined Co(acac)₂-terminated PVAc chains **1** with moderate molar mass ($M_n = 5900 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D} = 1.05$). The latter were prepared by CMRP of VAc in bulk at 40 °C according to a well-established procedure involving a

preformed alkyl–Co(acac)₂ initiator.¹⁸ The substitution of the terminal organocobalt by an organotellurium derivative consists of the homolytic cleavage of the terminal carbon–cobalt bond followed by the reaction of the radical polymer chains with a radical tellurium scavenger.^{49,50} Some reported postfunctionalizations of polymers prepared by CMRP follow a similar radical pathway.⁵¹ Here, we tried to exchange Co(acac)₂ by a methyltellanyl moiety (–TeMe). The latter is characterized by a high exchange constant,^{36,52} which could facilitate the resumption and the control of the polymerization of a large range of monomers. Inspired by a synthetic procedure of low molecular weight TERP initiators,⁴⁹ we reacted the PVAc–Co(acac)₂ **1** with dimethylditelluride (MeTeTeMe) to form PVAc–TeMe **2**. A preliminary experiment demonstrated that injection of one equivalent of ditelluride during the CMRP of VAc inhibits the polymerization, thus highlighting the ability of MeTeTeMe to trap PVAc macroradicals (Figure 1). The

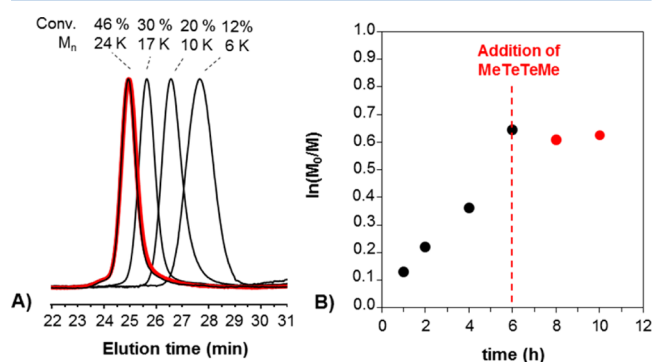


Figure 1. Addition of dimethylditelluride (MeTeTeMe) during the course of the CMRP of VAc performed in bulk at 40 °C (after 6 h). (A) Overlay of the SEC chromatograms before (black curves) and after (red curves) addition of the ditelluride compound. (B) Evolution of $\ln(M_0/M)$ vs time. Conditions: $[\text{VAc}]/[\text{R-Co}(\text{acac})_2] = 630$, 40 °C, 6 h. Addition of MeTeTeMe in the polymerization medium at 40 °C, $[\text{MeTeTeMe}]/[\text{PVAc-Co}(\text{acac})_2] = 1.2$.

Co(acac)₂/TeMe exchange reaction conditions were carefully chosen to promote the PVAc–cobalt bond cleavage and preserve the final PVAc–tellurium. First, we used an excess of MeTeTeMe compared to the PVAc–Co(acac)₂ (1.2 equiv). Second, the reaction was performed at 40 °C, which is sufficient to activate the PVAc–Co(acac)₂ bond but too low to promote the homolytic cleavage of the targeted PVAc–TeMe bond. Indeed, the rate constant of thermal dissociation (k_d) of PVAc–TeMe is known to be negligible at 60 °C.³⁶ Third, dimethylformamide (DMF) was used as solvent because it is known to activate the cleavage of the Co–C bond by complexation of the metallic species⁴⁸ and is inert toward the targeted tellanyl-functional polymers.

After 3 h of reaction under these conditions, the resulting PVAc was purified from the released cobalt complex and from the excess of MeTeTeMe by precipitation under inert atmosphere. The yield of the Co/Te exchange reaction and the ratio between the regular H–T–TeMe and the inactive H–H–TeMe species were evaluated by ¹H NMR (Figure 2). Besides the peaks corresponding to the main chain, i.e., methine a, methylene b, and methyl c, smaller signals could be assigned to the methoxy group characteristic of the V-70 initiating fragment d ($\delta_{\text{H}} 3.17$) present at the α -end of the polymer. On the basis of assignments previously reported in TERP studies of VAc,³⁶ the signal at 6.3 ppm could be

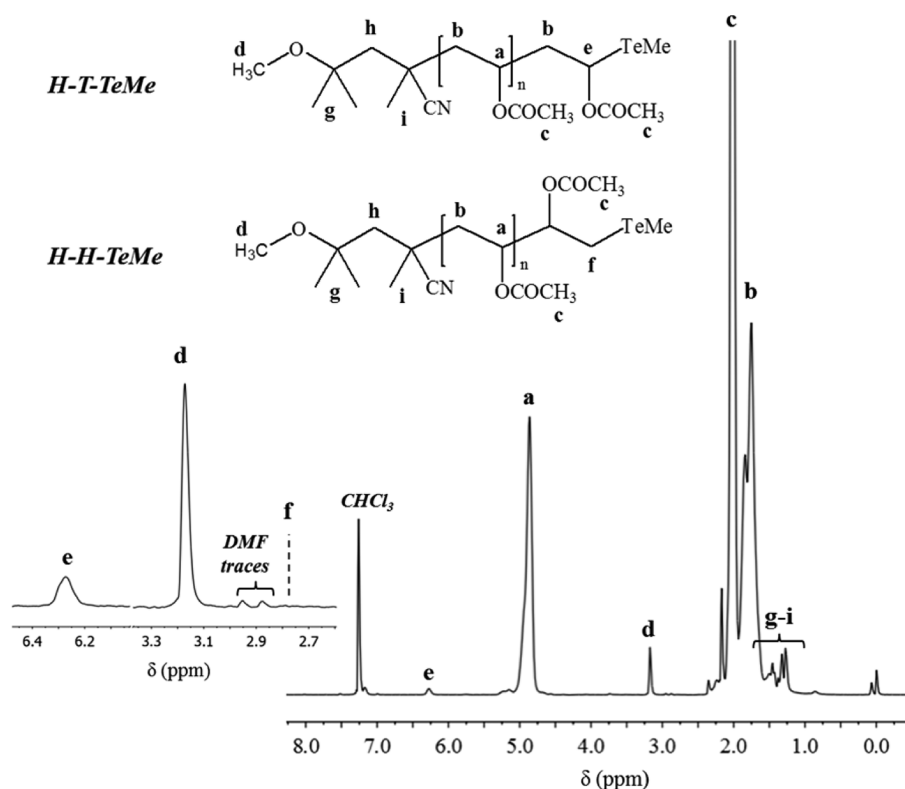


Figure 2. ^1H NMR spectrum of the PVAc–TeMe **2** produced by treatment of a PVAc–Co(acac) $_2$ **1** with 1.2 equiv of MeTeTeMe in DMF at 40 °C. Spectra were recorded under inert atmosphere at 298 K in CDCl_3 . The expanded ^1H spectrum shows typical signals from the α - and ω -chain ends. The peaks were assigned based on previous studies by Debuigne et al.⁴⁰ and Yamago et al.³⁶

Table 1. Block Copolymerization by Sequential CMRP and TERP

run	PVAc–[Co]		conditions (°C/h)	yield ^b (%)	PVAc- <i>b</i> -Px	
	M_n^a , Đ	monomer			M_n , Đ	composition (DP) ^c
1	19300, 1.05	BA	60/5.5 ^f	68	41000 ^a , 1.17	PVAc ₂₂₄ –PBA ₂₁₅
2	20000, 1.09	NIPAM	60/24 ^g	99	52700 ^c , 1.22	PVAc ₂₃₂ –PNIPAM ₁₆₁
3	11000, 1.08	ADAME	60/24 ^g	63	23200 ^c , 1.29	PVAc ₁₂₇ –PADAME ₁₃₇
4	10400, 1.08	IP	120/16 ^f	43	35600 ^c , 2.08	PVAc ₁₂₁ –PIP ₂₈₂
5	14300, 1.06	NVIm	55/29 ^g	41	43400 ^c , 1.47	PVAc ₁₆₅ –PNVIm ₅₂₂

^aDetermined by SEC in THF using PS as calibration. ^bDetermined by ^1H NMR of the crude mixture in CDCl_3 or $\text{DMSO}-d_6$. ^cMeasured by SEC in DMF using PS as calibration. ^dDetermined by ^1H NMR in CDCl_3 or $\text{DMSO}-d_6$ after purification. ^ePolymerization in bulk. ^fPolymerization in DMF. AIBN was used in all TERP chain extensions, except for the TERP of IP performed with V-30.

attributed to the methine proton **e** geminal to the methyltellanyl group in the regular H–T–TeMe adduct (–CH₂–CH(OAc)–TeMe). However, we did not detect any signal corresponding to the inverted H–H–TeMe adduct (–CH(OAc)–CH₂–TeMe) **f**, reported at 2.8 ppm. The integration ratio of peaks **e** and **d** indicates that at least 90% of the PVAc chains are functionalized by a –TeMe group in the H–T mode. This result is in sharp contrast with the abnormal accumulation of inactive H–H–TeMe units (58%) observed at the ω -chain-end of PVAc synthesized by TERP.³⁶ The extreme predominance of secondary H–T–TeMe adduct at the ω -chain of the PVAc produced by sequential CMRP and Co/Te exchange reaction will allow efficient block extension by TERP due to its hundred times higher C_{ex} compared to the H–H–TeMe derivatives.⁶

A range of methyltellanyl-terminated PVAc **2** (10000–20000 $\text{g}\cdot\text{mol}^{-1}$, Đ \sim 1.1) were prepared following the approach outlined above. They were then used as macroinitiators for the TERP of challenging monomers for CMRP, i.e., NIPAM,

ADAME, BA, IP, and NVIm. While TERP can be performed under purely thermal conditions, we privileged ternary systems in which an azo-initiator is added to the macroinitiator **2** and the monomer.¹⁷ In this case, the polymerization proceeds under milder conditions compared to the thermal system and exclusively via a DT mechanism. In some cases, the azo-initiator was introduced in larger amounts (1–3 equiv) to shorten the inhibition period due to residual traces of MeTeTeMe in **2**. Compared to other CRP techniques, TERP exhibits a much lower dependence on the order of monomer addition in the block copolymerization,²² which is an advantage when considering chain extension experiments. The TERP polymerization conditions were adapted for each comonomer in light of the previous studies. The copolymerization experiments are presented in Table 1 and discussed below.

The chain extension of the PVAc–TeMe (19 300 $\text{g}\cdot\text{mol}^{-1}$, Đ = 1.05) was first considered with BA (Table 1, run 1). The polymerization was performed in bulk at 60 °C in the presence of AIBN. After 5.5 h, the conversion reached 68% conversion.

The overlay of the SEC chromatograms evidenced the successful chain extension and the formation of a well-defined PVAc-*b*-PBA block copolymer (Figure 3). The SEC peak of the

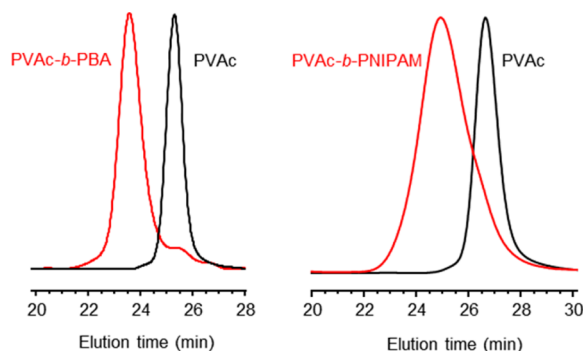


Figure 3. Overlay of SEC chromatograms of PVAc macroinitiators obtained by CMRP (black lines) and corresponding to the block copolymers (red lines) produced by subsequent Co/Te exchange reaction and TERP of BA (left, SEC in THF) and NIPAM (right, SEC in DMF). For the detailed conditions, see runs 1 and 2 in Table 1 and the experimental details.

PVAc macroinitiator clearly shifted toward higher molar masses ($41\,000\text{ g}\cdot\text{mol}^{-1}$, $\bar{M}_w = 1.17$), and only a few percent of unreacted PVAc was detected in the final product. The low \bar{M}_w value of the PVAc-*b*-PBA copolymer as well as the increase of the molar mass with BA conversion (Figure S1A, Supporting Information) confirmed the controlled character of the TERP polymerization. The degree of polymerization of the PBA ($DP = 218$) was evaluated based on the relative intensities of ^1H NMR signals characteristic of PVAc ($-\text{CHOAc}-$ at 4.8 ppm) and PBA ($-\text{CO}_2-\text{CH}_2-$ at 3.9 ppm) (Figure S2A, Supporting Information). This result contrasts with the ill-defined and multimodal copolymer obtained within a few seconds upon addition of BA to a PVAc-Co(acac) $_2$ precursor in the bulk at 25 °C.⁵³ Similar block copolymers were previously prepared by Wayland et al. using cobalt porphyrin complexes, but the monomer conversions were rather low in this case.⁵⁴

A similar procedure was applied to the TERP of NIPAM and ADAME, which was initiated from **2** at 60 °C in DMF solution (Table 1, runs 2 and 3). After 24 h, full consumption of NIPAM was observed with formation of a PVAc-*b*-PNIPAM copolymer with rather low dispersity ($\bar{M}_w = 1.22$) (Figure 3), although a small tailing corresponding to few unreacted PVAc chains appears on the final SEC chromatogram. Despite this imperfection, it should be underlined that such a diblock could not be formed by CMRP only due to the excessively weak poly(acrylamide)-Co(acac) $_2$ bond. The desired PVAc-*b*-PADAME block copolymers also formed although the \bar{M}_w value was slightly higher (1.29) (Figure S1C and S2C, Supporting Information, for SEC and ^1H NMR).

As discussed above, the synthesis of PVAc-*b*-PIP copolymer by CMRP is impossible because addition of IP to PVAc-Co(acac) $_2$ promotes fast and massive coupling of the starting block with few IP units (about 2) inserted in the middle of the coupling product.^{45,46} However, this block copolymerization becomes possible when realized from a PVAc-TeMe prepared by Co/Te exchange reaction. The IP polymerization was performed in bulk at 120 °C in a sealed tube using a high-temperature azo-initiator (V-30). Although the molar mass distribution was broad, the starting block **2** was largely consumed; the expected PVAc-*b*-PIP was monomodal; and

only a small amount of PVAc remained unreacted (Figure S1D, Supporting Information).

Finally, the TERP polymerization of NVIm was initiated with success from **2** at 55 °C in DMF in the presence of AIBN (Table 1, run 5, and Figures S1E and S2E, Supporting Information). In spite of the rather high \bar{M}_w value of the final material (1.47), a PVAc-*b*-PNVIm copolymer was successfully prepared by the CMRP/TERP combination, while the controlled polymerization of monomers containing the imidazole group by CMRP is uncertain due to the cobalt complexation by the electron-donating functions. In this case, some unreacted PVAc chains were detected and easily removed from the desired copolymer by precipitation in diethyl ether.

In conclusion, an efficient transformation of organocobalt complexes into the corresponding organotellurium derivatives is reported for the first time and used to combine CMRP and TERP. This original Co/Te radical exchange reaction was successfully applied to substitute the methyltellanyl moiety for Co(acac) $_2$ at the ω -chain end of the PVAc formed by CMRP. In sharp contrast to the PVAc samples prepared by TERP, the PVAc produced by Co/Te exchange almost exclusively consists of regular H-T-TeMe chain-end species that can be activated by TERP. These TERP macroinitiators were then successfully used in chain extension experiments with a series of monomers which are problematic in CMRP. This approach afforded the synthesis of novel block copolymers that cannot be made by each technique used separately. In other words, the Co/Te exchange reaction enables the combination of CMRP and TERP and offers new macromolecular engineering opportunities.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental section detailing the polymer preparation and analysis, the instrumentations, the SEC chromatograms of all chain extension experiments, and the NMR spectra of all the block copolymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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