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Cobalt-Mediated Radical Coupling (CMRC): An Unusual Route to Midchain-Functionalized Symmetrical Macromolecules

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Abstract: Cobalt-mediated radical coupling (CMRC) is a straightforward approach to the synthesis of symmetrical macromolecules that relies on the addition of 1,3-diene compounds onto polymer precursors preformed by cobalt-mediated radical polymerization (CMRP). Mechanistic features that make this process so efficient for radical polymer coupling are reported here. The mechanism was established on the basis of NMR spectroscopy and MALDI-MS analyses of the coupling product and corroborated by DFT calculations. A key feature of CMRC is the preferential insertion of two diene units in the middle of the chain of the coupling product mainly according to a *trans*-1,4-addition pathway. The large tolerance of CMRC towards the diene structure is demonstrated and the impact of this new coupling method on macromolecular engineering is discussed, especially for midchain functionalization of polymers. It is worth noting that the interest in CMRC goes beyond the field of polymer chemistry, since it constitutes a novel carbon–carbon bond formation method that could be applied to small organic molecules.

Keywords: cobalt · dienes · poly(acrylonitrile)s · polymerization · radical reactions

Introduction

Controlled radical polymerization (CRP) techniques nowadays provide access to a large range of polymeric materials with well-defined molecular parameters, such as low molar mass distributions, predictable molar masses, and precise architectures.[1–11] All these processes are based on the temporary deactivation of the growing radical species, which limits the extent of irreversible termination reactions that occur between radicals by coupling or disproportionation. Indeed, occurrence of termination during CRP is detrimental to the control of the molecular parameters and leads to materials with large and/or multimodal molar mass distributions. A notable exception to this rule is the case in which termination is fast, quantitative, and proceeds specifically by coupling. In that case, a perfect doubling of the polymer molar mass is expected without broadening of the molar mass distribution. Such a quantitative coupling process should be a powerful synthetic tool since α-functional polymers and diblock copolymers should lead to the corresponding telechelic and triblock copolymers, respectively.

The first efficient radical coupling process reported in the literature is atom-transfer radical coupling (ATRC).[12–18] Typically, well-defined polymers formed by atom-transfer radical polymerization (ATRP) have been added with

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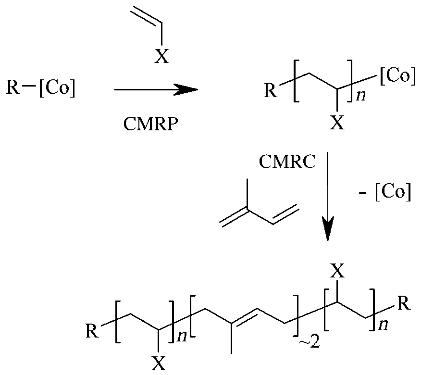
copper catalysts and ligands to generate a large amount of radicals at once and to promote the coupling reaction. When applied to low molar mass precursors ($<5000\,g\,mol^{-1}$), the efficiency of the ATRC is generally above 90%. However, moderate success was achieved when starting from polymers with high molar masses.

Recently, we reported a new radical coupling method, called isoprene-assisted radical coupling (I-ARC),[19] which consists in addition of isoprene to polymer precursors formed by cobalt-mediated radical polymerization (CMRP). As a reminder, CMRP is a CRP process based on the deactivation of the growing polymer species by cobalt complexes.[10] It is efficient for controlling the homopolymerization of acrylates,[20,21] vinyl acetate (VAc),[22–26] *N*-vinyl pyrrolidone (NVP),[27,28] and acrylonitrile (AN)[29,30] and is also a valuable approach for the preparation of block copolymers. However, addition of isoprene onto well-defined poly(acrylonitrile) (PAN) precursors, capped by bis(acetylacetonato)cobalt complexes [$Co(acac)_2$], exclusively leads to the coupling product (PAN-*b*-PAN) instead of forming the poly(acrylonitrile)-*b*-poly(isoprene) (PAN-*b*-PIP) diblock copolymer by chain extension.[19] In this case, the extent of coupling is above 95% even for PAN precursors with a molar mass as high as $25\,000\,g\,mol^{-1}$.[19] Moreover, I-ARC is the first radical coupling method that effectively leads to a symmetrical triblock copolymer when applied to a diblock precursor. For example, well-defined PVAc-*b*-PAN-*b*-PVAc copolymers have been prepared by I-ARC by using PVAc-*b*-PAN-Co($acac)_2$ diblock precursors.[19] Although incorporation of a few isoprene units in the coupling product was suggested in the first communication (Scheme 1), this hypothesis suffered from lack of strong supporting evidence until now.

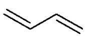


Scheme 1. General scheme for the cobalt-mediated radical coupling (CMRC) method.

Here, we would like to elucidate the mechanistic features that make this process so efficient for radical coupling, to detail the structure of the junction between the two chains, and to illustrate the tolerance of this coupling method towards the structure of the diene coupling agent. A range of dienes, containing different substitution degrees or bearing functional groups, are successfully used for the radical coupling of PAN–Co precursors. NMR spectroscopy and MALDI-MS analyses of the coupling products reveal the insertion of very few diene units in the polymer and their location at the junction of the precursors is unambiguously demonstrated. This observation allows us to progress in the understanding of this unusual coupling process and to go far beyond early elusive mechanistic proposals. Given the versatility of this coupling process towards the structure of the diene, the term I-ARC is clearly too restrictive. Moreover, it does not reflect the crucial role of the cobalt complex in the mechanism. Henceforth, the general term CMRC will be preferred by analogy with ATRC. The impact of this new coupling method on macromolecular engineering, and more particularly for polymer functionalization, will also be highlighted.

Results

Scope of CMRC: As recently communicated,[19] isoprene is a very efficient coupling agent for poly(acrylonitrile) prepared by CMRP and end-capped by a bis(acetylacetonato) cobalt complex. Given the crucial role played by the isoprene in this system, it is worth evaluating the tolerance of CMRC towards various dienes used as coupling agents. In this study, linear and cyclic dienes containing different degrees of substitution and bearing functionalities have been considered.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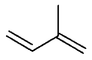
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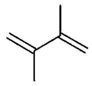
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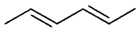
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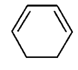
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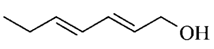

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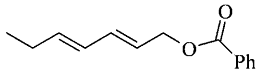

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First, well-defined poly(acrylonitrile) precursors capped by bis(acetylacetonato) cobalt complexes were prepared by following the previously reported procedure.[29] Typically, the controlled radical polymerization of acrylonitrile was initiated with an alkyl–cobalt(III) species [$Co(acac)_2\{CH(OCOCH_3)CH_2\}_{<4}(R_0)$] at 0°C (see Table 1; acac = 2,4-pentanedione). By adjusting the monomer/initiator molar ratio and the monomer conversion, two series of PAN precursors with molar masses of around 4000 and $12\,000\,g\,mol^{-1}$ were synthesized. In all cases, the molar mass distributions were very narrow. It was worth noting that better results were obtained when using a DMF/DMSO mixture as the solvent instead of pure DMSO for the synthesis of PAN with molar masses above $10\,000\,g\,mol^{-1}$.

Table 1. Cobalt-mediated radical coupling (CMRC) reaction of polyacrylonitrile chains capped by $[Co(acac)_2]$.

Diene	PAN–[Co] precursor			Coupling product			x_c[b]
	$M_{n,0}$[a] [g mol^{-1}]	$M_{p,0}$[a] [g mol^{-1}]	M_w/M_n	M_n[a] [g mol^{-1}]	M_p[a] [g mol^{-1}]	M_w/M_n	
1	4080	4320	1.02	7990	8650	1.02	0.98
	11 000	11 000	1.02	21 200	21 600	1.01	0.96
2	4320	4500	1.02	8320	8990	1.02	0.96
	11 800	11 700	1.03	22 100	22 600	1.01	0.93
3	3000	3100	1.01	6000	5800	1.02	1.00
	13 400	13 100	1.01	24 100	24 400	1.01	0.89
4	3100	3250	1.01	6200	6500	1.01	1.00
	11 900	12 200	1.03	22 300	22 700	1.01	0.93
5	3890	4150	1.03	7770	8400	1.02	1.00
	13 900	13 700	1.04	25 100	25 800	1.03	0.90
6	3320	3460	1.01	6450	7060	1.02	0.97
	11 000	10 800	1.02	21 100	22 700	1.03	0.96
7	2800	3300	1.10	4700	5900	1.15	0.81
	11 400	11 200	1.02	21 500[c]	22 800	1.03	0.94

[a] Determined by SEC-MALLS in DMF $((dn/dc)_{PAN}=0.076\ mL\,g)^{-1}$, with the exception of the last sample but one that was determined by SEC with a PMMA calibration corrected by the Mark–Houwink equation. [b] Extent of coupling $= x_c = 2.[1-(M_{n,0}/M_n)]$.[14] Conditions for polymer precursors below 5000 g mol^{-1}; polymerization: $[Co(acac)_2\{CH(OCOCH_3)CH_2\}_{<4}(R_0)]$ as initiator (0.12 mmol), AN (38 mmol) and DMSO as the solvent (DMSO/AN 1:1 v/v), 0 °C, 4 h, monomer conv. = 17–21 %. Coupling: diene (5.0 mmol), RT, 2 h. Conditions for polymer precursors above 10 000 g mol^{-1}; polymerization $[Co(acac)_2\{CH(OCOCH_3)CH_2\}_{<4}(R_0)]$ as initiator (0.09 mmol), AN (38 mmol)DMSO/DMF mixture as the solvent (DMSO/DMF/AN 0.5:0.5:1 v/v/v), 0 °C, 24 h, monomer conv. = 33–38 %. Coupling: dilution with DMF ($V_{DMSO}/V_{DMF} = 0.4$, addition of diene (5.0 mmol) at RT, 2 h. [c] 2.5 mmol of **7** was used.

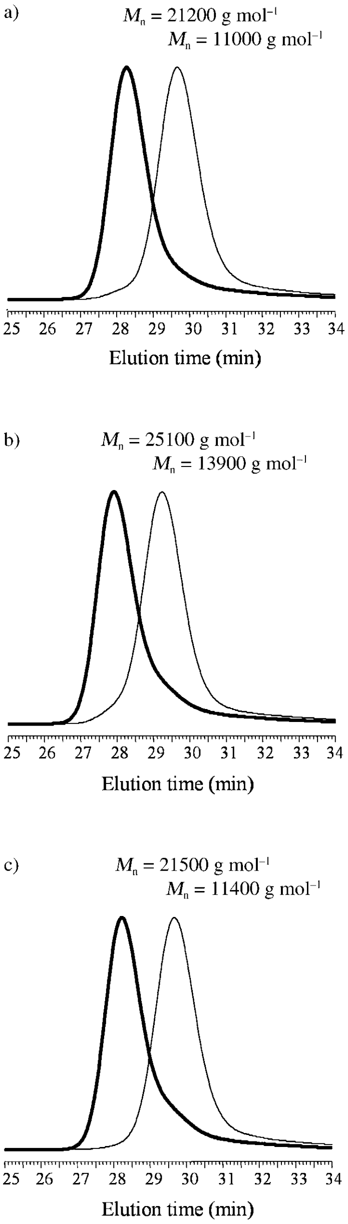


Figure 1. Size-exclusion chromatograms (RI) of the PAN–[Co] precursors prepared from a CMRP initiator (——) and the resulting coupling product (——) upon treatment with butadiene (**1**) (a), 1,3-cyclohexadiene (**5**) (b), and 2,4-heptadienyl benzoate (**7**) (c).

After polymerization, the residual monomer was evaporated under reduced pressure and the PAN–$[Co(acac)_2]$ chains were treated with the diene. For each experiment, the extent of coupling (x_c) was calculated as $x_c = 2[1-(M_{n,0}/M_n)]$ in which $M_{n,0}$ and M_n are the molar masses of the precursor and the coupling product, respectively.[14] After repeating the previously described coupling reaction of the PAN chains with isoprene (**2**),[19] butadiene (**1**) was the most obvious candidate as the coupling agent in the CMRC. The coupling process appeared to be nearly quantitative (extents of coupling close to unity) for both short and long polymer chains. The overlay of the size-exclusion chromatograms (SEC) of the reaction mixture before and after addition of butadiene exhibits a clear shift towards lower elution volume, thus higher molar masses (Figure 1a). The monomodal SEC profile for the final reaction mixture and the absence of tailing due to unreacted chains reflect the completeness of the coupling process. Next, we examined the effect of alkyl substituents (e.g., by using dienes **3** and **4**) on the coupling efficiency. An almost perfect doubling of the molar mass was again observed with both dienes. Thus, substitution at the diene 1,3- or 2,4-positions does not appear detrimental to the CMRC process. Good results were also obtained with cyclohexadiene (**5**). For example, a PAN with a molar mass of 7770 g mol^{-1} was recovered after treatment of a precursor of 3890 g mol^{-1}. However, when the molar mass of the precursor was above 10 000 g mol^{-1}, the calculated extent of coupling was slightly lower (90 %). Although the overlay of the SEC chromatograms, before and after coupling, appears very good at first sight, a discreet low molar mass population is observed at the base of the main peak (Figure 1b). It most probably corresponds to some unreacted PAN chains. Finally, experiments were conducted by using functional dienes, such as 2,4-heptadien-1-ol (**6**) and the corresponding esterified product, 2,4-heptadienyl benzoate (**7**). The presence of an alcohol or an ester function on the coupling agent does not drastically alter the efficiency of the CMRC process (Figure 1c). Extents of coupling around 95 % were obtained. In addition to widening the range of the useful coupling agents for the CMRC, these last two experiments are of prime importance for macromolecular engineering because they demonstrate the possibility of specific midchain functionalization. This point will be further discussed below.

1D NMR spectroscopic studies: To dispel any doubt about the insertion of diene during the coupling process and to address the CMRC mechanism, 1D ^{1}H NMR spectroscopic analyses were carried out on the coupling product obtained with each diene. The lower molar mass poly(acrylonitrile) samples were preferred to facilitate the detection of the significant protons at the junction of the PAN precursor chains. In all cases, very intense signals were detected at $\delta = 3.2$ and 2.1 ppm, corresponding to the methyne and methylene protons of the PAN main chain, respectively. Smaller signals also appeared in all spectra at $\delta = 5.3$–4.2 and 1.4–1.1 ppm (see Figure 2), corresponding to the methyne and methyl protons, respectively, issued from the cobalt(III) initiating species $[\mathrm{Co(acac)_2\{C}\mathit{H}\mathrm{(OAc)CH_2\}_{<4}\{C(CH_3)(CN)\}(CH_2)\{C(OCH_3)(C}\mathit{H}_3)_2\}]$. Integration of these signals confirmed that the initiator contains an average number of four vinyl acetate units.

In addition to the above signals, assigned to the PAN precursors, other small diene-specific signals were detected, which proved that a tiny amount of diene had been incorporated in the polymer (see Figure 2). For example, small signals were detected in the vinylic region of the PAN sample recovered after coupling with butadiene. Similarly, signals typical of poly(isoprene) were detected in the vinylic and allylic regions when isoprene was used. Based on typical signals in the aliphatic, allylic, vinylic, and aromatic region, it is possible to conclude that incorporation of diene occurred in each case. Note that only the 1,4-*trans*-addition products are represented in Figure 2. The question of the regio- and stereochemistry of the midchain unsaturations has been addressed by 2D NMR spectroscopic analyses (see later). The relative intensities of the olefinic and/or allylic protons assigned to the inserted diene units and those of the poly(acrylonitrile) protons gave access to the average number of diene units per chain in the coupling product, which is generally close to two (Figure 2). The use of functionalized dienes in the CMRC process thus appears as an interesting approach to introduce functions selectively in the middle of a polymer backbone.

MALDI-TOF mass spectrometric analysis: Before discussing the mechanism of the polymerization reaction, it is obviously of prime importance to establish the distribution of diene units inserted during the CMRC process. This piece of information is likely to be derived from MALDI-TOF measurements on the polymer coupling product. To facilitate the spectral interpretation and clearly evidence the number of inserted diene units, the coupling agent and initiator were carefully selected to inter alia avoid isobaric interferences. First of all, the alkyl–cobalt(III) reagent $[\mathrm{Co(acac)_2\{CH(OCOCH_3)CH_2\}_{\sim 4}(R_0)}]$ was excluded because it consists of a distribution of PVAc oligomers. Indeed, the simultaneous presence of two molecular mass distributions (VAc and AN) would probably render the determination of the amount of inserted diene units extremely complex since the mass spectrum would definitively be more crowded. Secondly, the use of butadiene as the coupling agent is not appropriate since its molecular mass (54 u) is too close to that of the acrylonitrile repeating unit (53 u). As a direct consequence, populations with a different numbers of diene units would overlap, complicating the determination of the number of incorporated butadiene residues. Taking these considerations into account, the poly(acrylonitrile) specifically prepared for the MALDI analysis was obtained by using 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) as the initiator. This reagent provides an initiating fragment with a nonin-

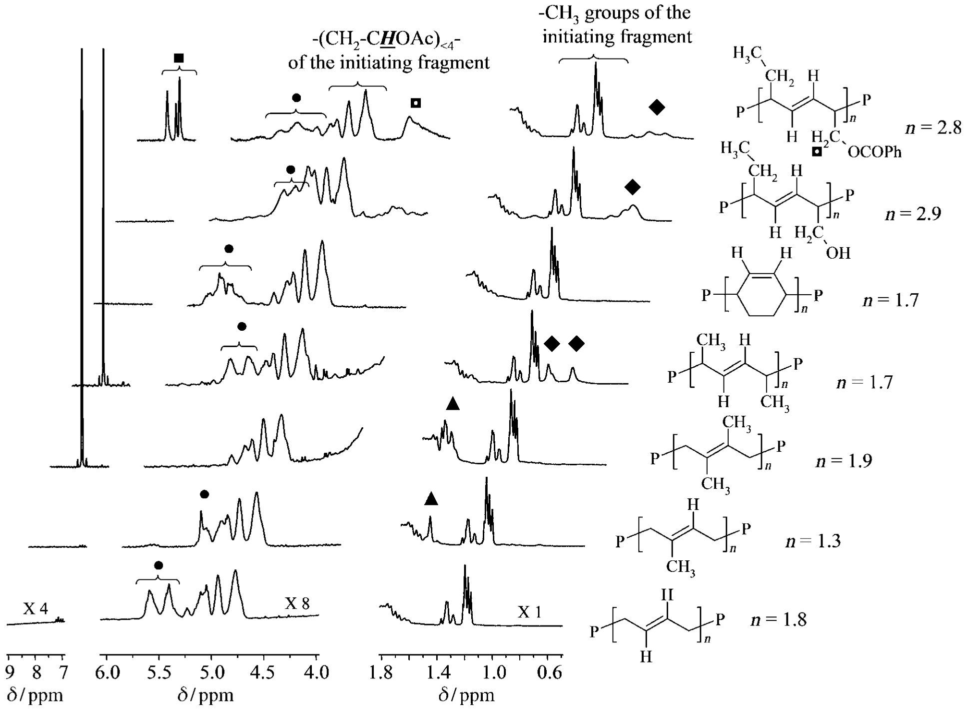


Figure 2. Overlay of the 1D ^{1}H NMR spectra of the PAN coupling products. The number of diene units incorporated in the coupling products (*n*) is determined by comparison of intensities of signals typical of the PAN main chain (the molar mass of which is determined by MALLS) and olefinic or allylic protons of the coupling species (for a typical example of a full NMR spectrum of PAN see the Supporting Information, Figure A). ■ = H arom., ● = H olefinic, ▲ = CH allylic, ◆ = CH, aliphatic, □ = other.

terfering molecular mass (140 u). Finally, isoprene (68 u) was selected as the coupling agent. Although the molecular mass distribution of the so-obtained PAN polymer was larger (M_w/M_n~1.2) than that of the polymer obtained by starting with the alkyl–cobalt(III) species, the mass spectrometry data were by far easier to analyze. For the sake of information, a clear shift of the SEC chromatograms was also observed towards higher molecular masses upon treatment with isoprene (Figure 3). This observation is consistent with data here above presented.

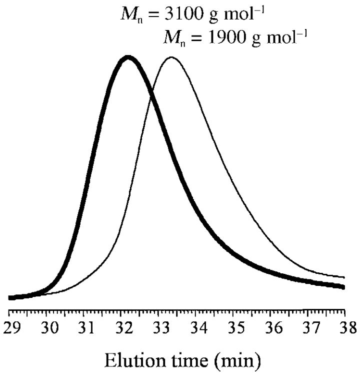


Figure 3. Size-exclusion chromatograms (RI) of the PAN–[Co] precursor prepared from [Co(acac)$_2$] and V-70 (——) and the resulting coupling product upon treatment with isoprene (——).

Several experimental conditions were tested to optimize the MALDI analysis of the PAN sample. Various matrices (cyano-4-hydroxycinnamic acid (CHCA), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), dithranol, *trans*-3-(3-indolyl)acrylic acid, and 4-hydroxybenzylidene malononitrile) and different cationizing agents (sodium, copper, or silver salts) were tested. In general, the sensitivity was poor, except when 4-hydroxybenzylidene malononitrile was associated with NaI, in agreement with a previous report.[31] Figure 4a shows a typical MALDI spectrum acquired under those conditions for the PAN coupling product. At a first glance, one ion series clearly emerges and presents a 53 u interval that undoubtedly corresponds to the residual mass of AN. The fast decreasing profile of the distribution and the lower value of M_n measured by MALDI-MS relative to the SEC-MALLS (MALLS = multi-angle laser light scattering) determined value is ascribed to easier desorption/ionization of shorter polyacrylonitrile chains. In the enlargement of the MALDI spectrum (Figure 4b), the most intense detected population corresponds to a sodium-cationized PAN coupling product constituted by two isoprene units (X_2) in its backbone. As an example, the peak detected at *m/z* 1183 was attributed to a sodium-cationized oligomer constituted by fourteen acrylonitrile (Y) units together with two isoprene (X) units ($Y_{14}X_2$). Nevertheless, a 2 u mass difference is observed between the experimental data and the theoretical isotope model (*m/z* 1181 for $Y_{14}X_2Na^+$) as revealed in Figure 4c. It is reasonable to assume that this discrepancy of 2 u arises from a hydrogenation reaction of the coupling product during the ionization process in the presence of 4-hydroxybenzylidene malononitrile. On the basis of this putative reduction reaction, a novel isotope model was generated for $Y_{14}X_2H_2Na^+$ and, as presented in Figure 4c, this experimental isotope pattern is now perfectly in agreement with the theoretical one.

Hydrogenation/reduction processes upon MALDI were recently observed and studied and were generally detected when using the so-called reductive matrices. For instance, the use of 2,5-dihydroxybenzoic acid (DHB)[32] and 1,5-diaminonaphtalene (DAN)[33] as MALDI matrices were shown to induce hydrogenation reactions. In the case of DHB, the reduction process was proposed to occur through hydrogen-atom transfer from one of the hydroxylic groups of the matrix molecule to the analyte.[32] The presence of such a phenolic hydrogen atom on the matrix used in our measurement, namely 4-hydroxybenzylidene malononitrile, is then consistent with the observation of the proposed hydrogenation process. To test this hypothesis, we measured the MALDI-TOF mass spectrum of the same polymer with DCTB as the matrix, by using NaI as the cationization agent. Even if the recorded mass spectrum is characterized by a poor signal-to-noise S/N ratio, this spectrum definitively confirms that the hydrogenation process is matrix dependent (Figure 4c). All these results clearly point to the importance of the experimental conditions (matrix and cationization agent) upon the nature of the observed ions starting with a given analyte.

Figure 4a and b also present some minor populations barely emerging from the noise of the spectrum. These ion series could correspond to PAN containing three, four, and five isoprene units. However, the really poor signal-to-noise ratio represents an obstacle to a totally certain identification. To improve the S/N ratio of the MALDI spectrum, we replaced sodium iodide by copper chloride as the cationization agent, given the fact that copper ions are known to be excellent cationization agents for poly(isoprene).[31] However, under these conditions, the S/N ratio remains weak and the ion series constituted by ionized oligomers containing two isoprene units remains the dominant population in the MALDI spectrum (see Figures B and C in the Supporting Information).

On the other hand, species containing only one or no isoprene units were never detected whatever the choice of matrix/cationization agent. For example, coupling products containing no isoprene ($Y_{18}X_0Na^+$ at *m/z* 1257) or only one unit ($Y_{16}X_1Na^+$ at *m/z* 1219 or $Y_{16}X_1(H_2)Na^+$ at *m/z* 1221) were definitively absent in the MALDI spectrum (Figure 4b). In this respect, CMRC is completely different from ATRC, which relies on the direct coupling of the polymer precursors without insertion of any compound at the junction of the chains.[12–14]

The high tendency of the CMRC to promote specific insertion of two diene units in the polymer is unique and makes it a promising tool for precise midchain functionalization. Moreover, this characteristic constitutes a serious clue for the mechanistic investigations developed below.

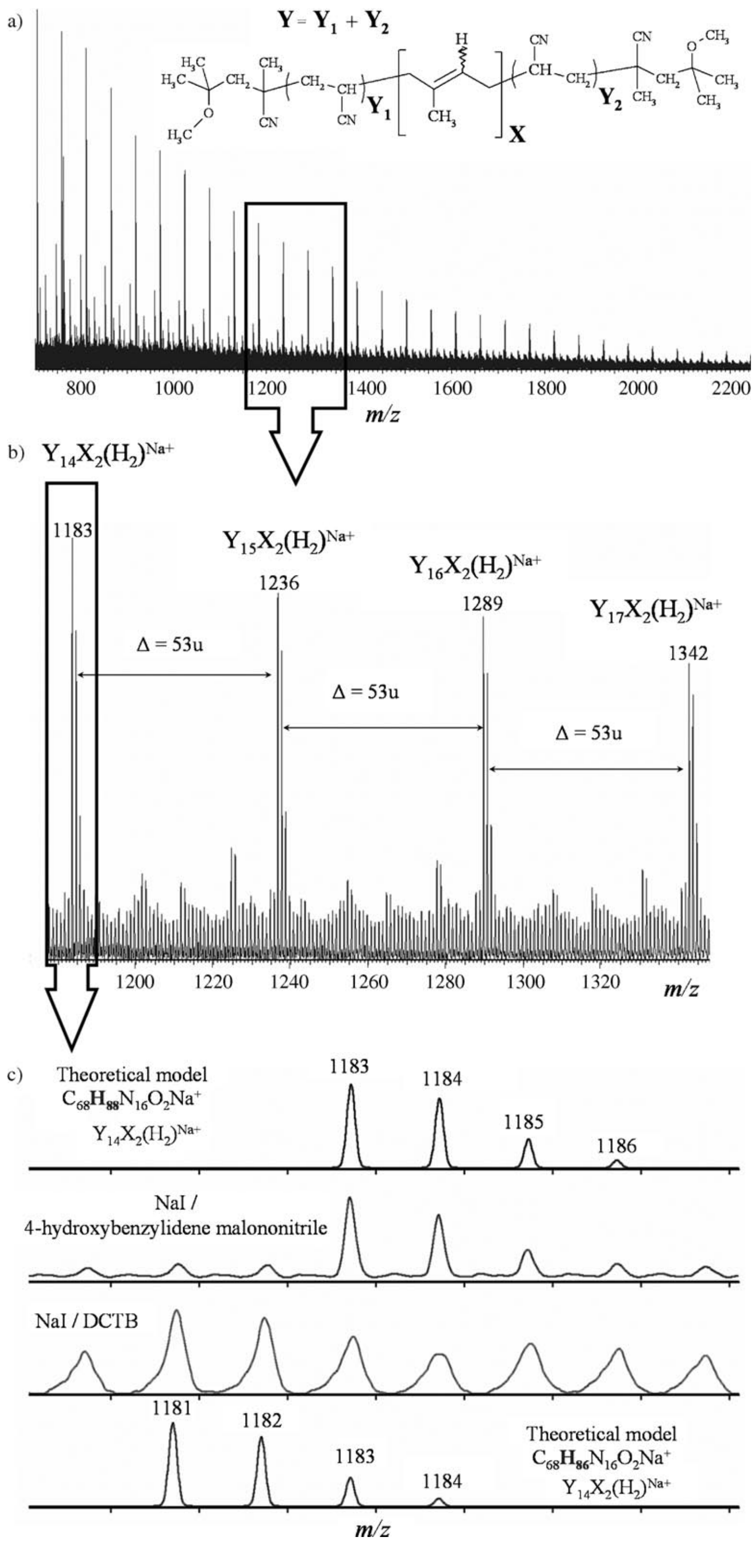


Figure 4. a) MALDI-TOF mass spectrum (matrix: 4-hydroxybenzylidene malononitrile; cationization agent = NaI) of a poly(acrylonitrile) sample prepared by CMRP from V-70 and bis(acetylateconato)cobalt(II) followed by coupling with isoprene. b) Enlarged region (*m/z* 1280–1340) of the mass spectrum. c) Comparison between experimental data and theoretical isotope patterns for $C_{68}H_{88}N_{16}O_2Na^+$ and $C_{68}H_{86}N_{16}O_2Na^+$.

2D NMR spectroscopic studies: In the approach to the CMRC mechanism, it is essential to define the addition modes (1,4 vs. 1,2) of the diene and the stereochemistry of the resulting unsaturations. This information was provided by 2D heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) NMR spectroscopic experiments carried out on the product recovered after coupling with butadiene (see Table 1, entry 1).

A section of the HSQC spectrum (Figure 5a) reveals cross peaks for H_a ($\delta = 5.2$–4.6 ppm) and C_1 ($\delta = 69$ ppm), which can be unambiguously assigned to the signal corresponding to −*CH*(OAc)− groups of the initiating fragment. Other evident correlations, designated by HSQC as CH groups, are observed between H_c ($\delta = 5.40$ ppm) and C_4 ($\delta = 124$ ppm) and between H_d ($\delta = 5.55$ ppm), and C_5 ($\delta = 133$ ppm). These chemical shifts are typical of an alkene proton and carbon nuclei and correspond to −CH= groups resulting from the polymer inserted with butadiene. Based on the chemical shifts, the C_4 and C_5 signals can also be clearly assigned to the 1,4-addition product.[34–36] Smaller correlations were also observed between $\delta = 5.05$ (δ_H) and 117 ppm (δ_C) and between $\delta = 5.5$–5.6 (δ_H) and 140 ppm (δ_C). According to the HSQC spectrum, they correspond to CH_2 and CH groups, respectively, of pendant vinyl groups resulting from the 1,2-addition mode (−CH=CH$_2$). Considering the intensities of these signals, insertion of diene by the 1,2-addition mode appears to be very limited in the CMRC process relative to the 1,4-addition pathway.

Furthermore, an HMBC experiment was carried out not only to confirm the assignments of HSQC, but also to determine the double-bond stereochemistry in the major 1,4-addition product (Figure 5b). Indeed, HMBC shows the long-range

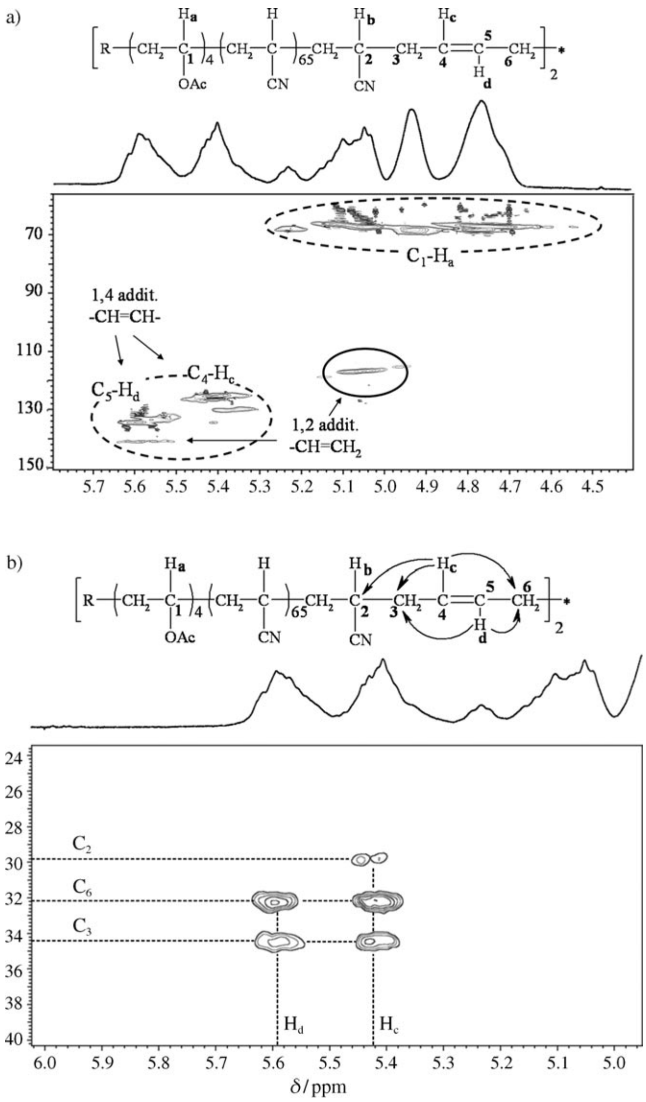


Figure 5. Enlarged regions of HSQC (a) and HMBC (b) spectra of a poly(acrylonitrile) sample after the coupling reaction with butadiene (for preparation, see Table 1, entry 1). In spectrum (a), cross-coupling signals circled by —— and – – – correspond to CH_2 and CH groups, respectively.

^1H–^{13}C correlations of the vinyl proton H_d ($\delta = 5.59$ ppm) with allylic carbon atoms C_3 ($\delta = 34$ ppm) and C_6 ($\delta = 32$ ppm), whereas H_c exhibits an extra correlation with a carbon atom at $\delta = 30$ ppm that corresponds to the carbon C_2 of the last AN unit of the precursor. Finally, chemical shifts of the allylic carbon atoms are typical of the *E* isomer (above $\delta = 30$ ppm), whereas the *Z* isomer generally yields resonances around $\delta = 27$ ppm.[34–36]

Based on the NMR and MALDI analyses of the coupling products, it is possible to conclude that most polymer chains recovered after the CMRC process contain two diene units inserted preferentially by the 1,4-*trans*-addition pathway. This information is a keystone in the mechanistic discussion below.

Mechanistic considerations: In the absence of diene monomer, the $[Co(acac)_2(PAN)]$ dormant chains are in rapid equilibrium with $[Co(acac)_2]$ and free PAN radical chains. The latter can either 1) recombine with $[Co(acac)_2]$ leading again to the dormant state or 2) undergo bimolecular terminations (suppressed by the persistent radical effect) or 3) add a new AN molecule to propagate the chain, followed again by trapping, by the improbable termination, or by further growth.

The addition of the diene monomer changes the picture because monomer addition transforms a cyanocarbyl-type radical to an allyl-type radical. This addition reaction should be quite favorable considering the reactivity ratios of the radical polymerization of AN and butadiene (B) ($r_1 = 0.03$ and $r_2 = 0.2$),[37] which shows a great propensity of cross-propagation from the cyanocarbyl to the allyl radical. The new radical is now faced with the same three possibilities: 1) combine with $[Co(acac)_2]$ to yield a new dormant organometallic species, 2) undergo bimolecular terminations, or 3) further add diene monomer molecules. Addition of acrylonitrile to come back to a $PAN^{\bullet}$-type radical is not an option, because the diene was added after removal of the residual AN monomer.

The experimental evidence of a strong preponderance of coupled polymer chains containing two diene units suggests that further monomer addition is slow relative to the other two processes. The question then concerns whether the allyl-terminated radical chains, obtained after the first diene addition (for instance, $PAN{-}CH_2{-}CH{\cdots}CH{\cdots}CH_2^{\bullet}$ in case of butadiene), can be transformed into a sufficiently stable $[Co(acac)_2]$-capped dormant chain or not. This question has been addressed at the computational level.

DFT calculations: Previous work has demonstrated the value of DFT calculations for the rationalization of various phenomena in CMRP.[26,29,38] Specifically, the homolytic bond dissociation enthalpy (BDE) of the Co^{III} bond in the dormant organometallic species of both vinyl acetate and acrylonitrile CMRP was found to be located in a suitable intermediate range, not too high, allowing a sufficiently rapid generation of free radicals, and not too low, insuring a low free-radical concentration, and consequently, negligible bimolecular terminations, under the persistent radical effect. The effect of donor solvent molecules L on the effective polymerization rate could also be rationalized.[24,29,38] These molecules affect the rate by shifting the activation/deactivation equilibrium through coordination of both the Co^{III} center in the dormant state, yielding $[Co^{III}(acac)_2(L)]$ polymer, and the Co^{II} deactivator, yielding $[Co(acac)_2(L)_2]$.

The nature of the dormant chains in the present system, prior to diene addition to induce the coupling process, is $[Co^{III}(acac)_2(L)(PAN)]$ in which L is either DMF or DMSO. Calculations on this system have been reported previously[29] with PAN being modeled by the short alkyl chain $-CH(CN)CH_3$ (the polymer chain beyond the first monomer unit is replaced by a H atom for computational efficiency). It was found that DMSO is slightly better than DMF as a ligand for $[Co^{II}(acac)_2]$, whereas the opposite is true for $[Co^{III}(acac)_2(PAN)]$.[29] The most important result of the previous study was the need to use the ad hoc functional B3PW91* with a reduced Hartree–Fock exchange contribution to obtain reasonable values for the enthalpy of the activation equilibrium (from $[Co^{III}(acac)_2(L)\{CH(CN)CH_3\}] + L \rightleftarrows [Co^{II}(acac)_2(L)_2] + CH_3CH(CN)^{\bullet}$: 9.2 kcal mol^{-1} for L = DMF, 6.6 kcal mol^{-1} for L = DMSO). When using the more popular B3LYP, the calculated bond strengths were too low to be in agreement with the experimentally observed efficient reversible trapping of the PAN radical chains.

We focused initially on the Co^{III}–R BDE in the absence of solvent. By using the same computational level of the previous study, we have calculated the BDE between the $[Co(acac)_2]$ complex and the allyl radical $CH_3CH{=}CH{=}CH_2^{\bullet}$, taken as a model of the PAN–$CH_2CH{=}CH{=}CH_2^{\bullet}$ radical chain. The results are compared with those of the corresponding PAN$^{\bullet}$ model in Figure 6. η^1 coordination of the allyl radical can occur in two different ways, binding either the terminal (primary) carbon atom or the internal (secondary) one, in both cases leading to a five-coordinate square-pyramidal configuration with the alkyl group in the axial position. Binding the terminal carbon atom leads, as expected, to the more stable product, stabilized by only 4.5 kcal mol^{-1} relative to the separate $[Co(acac)_2]$ and allyl radical. This stabilization is approximately 2 kcal mol^{-1} weaker than that associated to the $CH_3CH(CN)^{\bullet}$ radical, model of the PAN$^{\bullet}$ chain (6.7 kcal mol^{-1}). Binding the internal carbon atom is endothermic. In principle, one way to stabilize the system would be to rearrange the allyl ligand from η^1 to η^3 coordination, leading to an electronically saturated system. However, unexpectedly, the $[Co^{III}(acac)_2(\eta^3\text{-}C_4H_7)]$ derivative has in fact higher enthalpy than the 16-electron $[Co^{III}(acac)_2(\eta^1\text{-}CH_2CH{=}CHCH_3)]$. Each system was computed on the expected most stable stereoisomer (*syn* isomer for the η^3 coordination, *E* isomer for the η^1 coordination). Indeed, optimization of the η^3 *anti* isomer (CH_3 substituent *anti* relative to the central allyl H atom) leads to a local minimum approximately 5 kcal mol^{-1} higher in enthalpy relative to the *syn* isomer. The reason for this unexpected result is attributed to the less favorable *cis* arrangement of the two acetylacetonate ligands, required to accommodate the η^3-allyl ligand, relative to the *trans* arrangement adopted in the square-pyramidal five-coordinate geometry. The weak energetic gain associated to the coordination of the soft C=C π electrons to the hard Co^{III} center is apparently insufficient to compensate for the cost of this structural rearrangement.

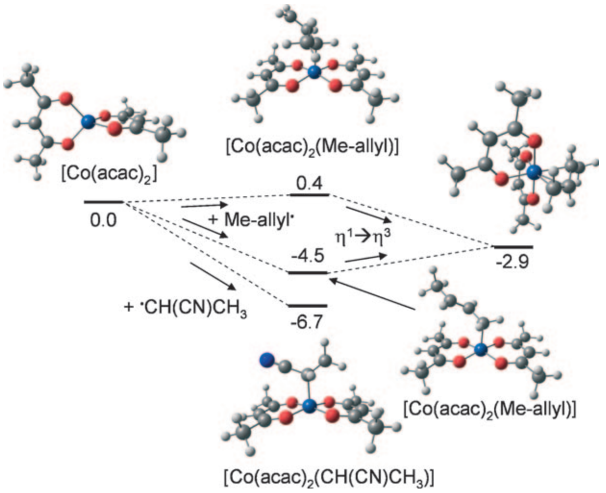


Figure 6. Calculated relative enthalpies [kcal mol^{-1}] and optimized geometries of $[Co(acac)_2]$ and its addition products with $CH_3CH(CN)^{\bullet}$ and $CH_3CH{=}CH{=}CH_2^{\bullet}$.

The above results already suggest that the allyl radicals are less tightly held by binding to cobalt than the cyanocarbyl radicals. However, the Co^{III}–C BDE can be modulated by the solvent coordination, as demonstrated in our previous contributions.[24,29,38] In the present study, we have restricted our consideration to DMSO as a ligand. Addition of DMSO to the five-coordinate $[Co^{III}(acac)_2(\eta^1\text{-}CH_2CH{=}CHCH_3)]$ species leads to 18-electron $[Co^{III}(acac)_2(dmso)(\eta^1\text{-}CH_2CH{=}CHCH_3)]$, with a gain of only 3.2 kcal mol^{-1}, whereas addition to $[Co^{III}(acac)_2\{CH(CN)CH_3\}]$ yields $[Co^{III}(acac)_2(dmso)\{CH(CN)CH_3\}]$ with a gain of 6.6 kcal mol^{-1} (see Figure 7). Subsequent homolytic cleavage of the Co^{III}–C bonds leads to the common $[Co(acac)_2(dmso)]$ intermediate, which is, however, further stabilized by coordination of a second DMSO molecule.

According to this calculation, assuming that the results can be extrapolated to the real radical chains and dormant organometallic complexes, the PAN$^{\bullet}$ chain can be trapped leading to a relatively favored dormant species, stabilized by 6.6 kcal mol^{-1} relative to the $[Co(acac)_2(dmso)_2]$ trapping complex, whereas trapping after the addition of a butadiene molecule is essentially thermoneutral (Co^{III} complex stabilized by only 1.0 kcal mol^{-1}), thus leaving a large free-radical concentration at equilibrium. The entropic contribution to these equilibria, which is neglected in the above considerations, is probably not too large because the process involves the same number of species on the two sides of the equilibrium. We prefer, however, to avoid the considerations of the free energy in the condensed phase, because of the uncertainties in the handling of the translational and rotational entropy.[39] A correction to the enthalpy values, which derive from gas-phase calculations, for solvation effects is also not expected to change significantly the results because of the low polarity of the compounds.

Discussion

The present contribution has shown that addition of dienes to a $[Co^{III}(acac)_2]$-capped PAN leads to efficient radical coupling, for a variety of different diene molecules, yielding polymers that are dominated by PAN–(diene)$_2$–PAN chains. An important experimental result, from the NMR spectroscopic analysis, is the mode of diene insertion, mostly of 1,4-*trans* type but with a visible small contribution of the 1,2 type. Coming back to the mechanistic issue, the inclusion of

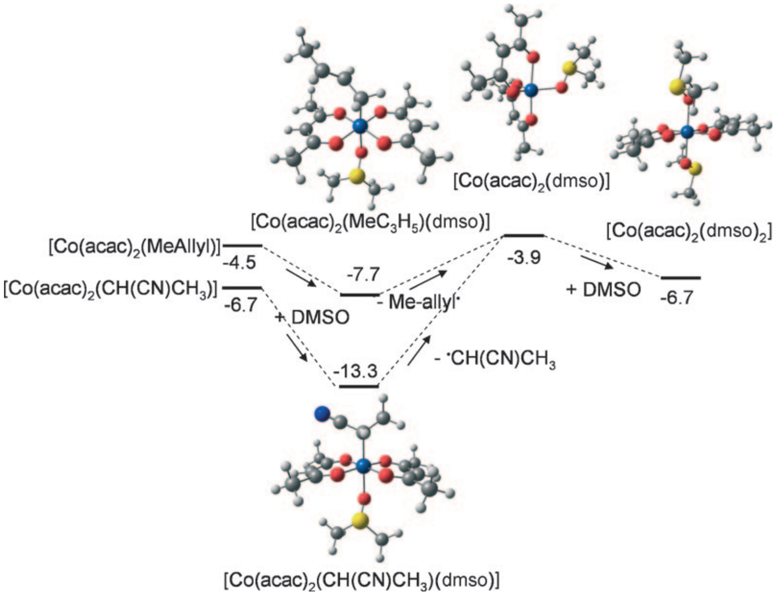
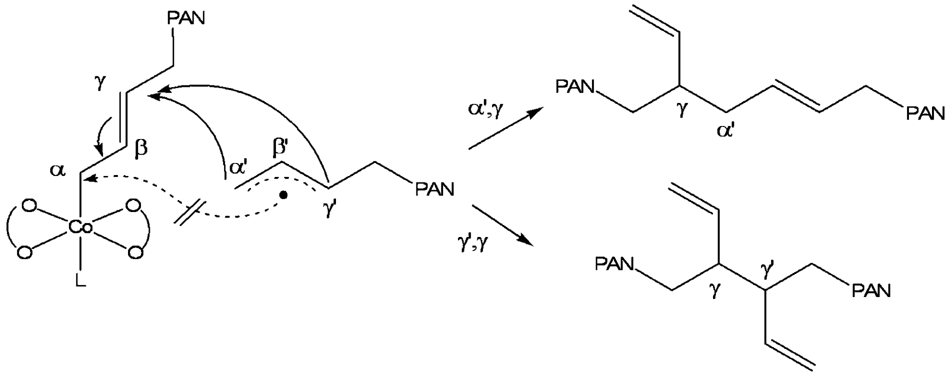


Figure 7. Calculated relative enthalpies [kcal mol^{-1}] and optimized geometries of DMSO adducts for Co^{III} and Co^{II} compounds of relevance to CMRP and CMRC. Enthalpies shown are relative to the separate [Co(acac)$_2$], DMSO, and corresponding free radicals.

only two diene molecules in the dominant portion of the chains indicates that chain propagation is disfavored relative to either trapping by [Co(acac)$_2$] or binuclear coupling. Noteworthy was that the initiation of isoprene polymerization at 30 °C by V-70 in the presence of a catalytic or an equimolar amount of [Co(acac)$_2$] did not produce specifically the isoprene dimer. Moreover, the molar mass distributions of PIP oligomers collected in the above-mentioned experiments were strictly identical to the one produced for the same isoprene polymerization conducted in absence of cobalt (see Figure D in the Supporting Information). This experiment suggests that only preformed alkyl–cobalt(III) species can undergo the coupling process. In case trapping to an organometallic [Co(acac)$_2$]-capped dormant species would be favored, the dominant formation of coupled product could be understood under the assumption that the metal-bonded allyl unit is activated toward radical addition. However, two considerations are against this assumption.



Scheme 2. Modes of allyl coupling for a [Co(acac)$_2$]-capped PAN–allyl chain.

The first one is that, according to the DFT calculations, trapping of the allyl radicals is not greatly favored from the energetic standpoint. The uncertainties and approximations associated to the computations of bond strengths, especially for systems, such as this one in which the spin state changes on going from reagents to products, certainly do not make this a very solid consideration. We expect, however, that the calculations give credible results in terms of trends for systems of the same type and within the same spin state. Thus, even though the absolute BDE values may not be precise, the relative stability of isomers and the relative strength of the $Co^{III}-CH_2CH=CHCH_3$ and $Co^{III}-CH(CN)CH_3$ bonds is to be considered reliable.

The second consideration comes from the observed regiochemistry. Under the assumption that a cobalt(III) dormant species indeed forms, and thus its structure for the butadiene addition product should be $[Co(acac)_2(dmso)(CH_2CH=CHCH_2-PAN)]$ as shown for its model system in Figure 7, then the most favorable addition of a second $PAN-CH_2-CH\cdots CH\cdots CH_2^{\bullet}$ radical should take place at the less-hindered γ-carbon atom, as shown in Scheme 2, leading to coupled chains with at least one diene monomer inserted in the 1,2-mode. The free radical would probably add predominantly through its less-hindered (and more reactive) terminal C atom (α′). The fact that the dominant diene insertion mode is the 1,4-*trans*, therefore, casts serious doubts on the cobalt-trapping hypothesis.

If cobalt trapping is excluded, then how can diene addition lead to efficient coupling instead of further propagation and to a dominant 1,4-*trans* stereochemistry for the two diene units in the coupled chains? Efficient coupling requires that a large concentration of the free-radical chains is generated very rapidly, as in the ATRC processes from halogen-terminated dormant chains in the presence of very active copper catalysts. In fact, we can easily rationalize the fast free-radical generation from the [Co(acac)$_2$(L)(PAN)] dormant chains. Under controlled radical PAN growth, we can estimate the rates of activation and deactivation on the basis of the data in Figure 7. The transition state is not necessarily fully dissociative, consisting of the five-coordinate [Co^{II}(acac)$_2$(L)] complex plus the free radical, because solvent molecules are present at large concentrations and Co^{II}–L bond formation is probably concerted with Co^{III}–PAN bond breaking, in a sort of “interchange” mechanism similar to those established for ligand exchange in Co^{III}-coordination compounds,[40,41] except that in this case a one-electron ligand (the PAN chain) is replaced by a two-electron ligand (L), whereas Co^{III} becomes Co^{II}. If this is the case, the barrier corresponding to the Co^{III}–PAN BDE (9.4 kcal mol^{-1}) is a higher estimate for the activation enthalpy, and the activation entropy is expected to be relatively small. Considering this value as a rough estimate for the activation free energy at 298 K, the Eyring equation yields an activation rate constant of approximately 8×10^5 s^{-1}. Trapping, however, is even faster ($>4\times10^{10}$ s^{-1} if $\Delta G^{\neq}<3$ kcal mol^{-1}), and the equilibrium constant heavily favors the dormant state ($K=1.5\times10^{-5}$ for the activation process, based on $\Delta G=6.6$ kcal mol^{-1} at 298 K).

Upon addition of diene, the rate of allyl radical generation is, therefore, very high because the activation rate of the [Co(acac)$_2$(L)(PAN)] dormant chains is very high and the rate of diene addition to the resulting PAN$^\bullet$ radical chains is also expected to be very high. However, contrary to the PAN$^\bullet$ radicals, the resulting PAN–CH$_2$–CH$\overset{\cdots}{=}$CH$\overset{\cdots}{=}$CH$_2^\bullet$ radicals are not efficiently trapped by Co^{II}, see Scheme 3. These radicals will, therefore, have no other choice than to couple with each other (or to further add diene, but coupling is predominant since the radical concentration is very high). This mechanistic scheme is compatible with the formation of a certain amount of chains containing more than two diene units, which seems to be indicated by the mass spectrometric analysis. On the other hand, it does not predict the formation of chains with less than two diene units, again in harmony with the MS results.

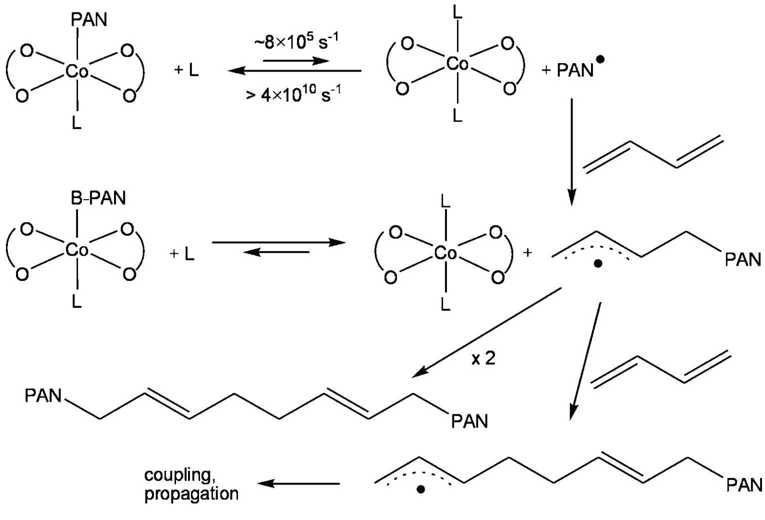
For what concerns the regio- and stereochemistry of diene insertion during the CMRC process, it is quite comparable to that of polybutadiene prepared by free-radical polymerization. Indeed, a typical free-radical polymerization of butadiene mainly follows the 1,4-addition pathway (1,4/1,2 80:20) and the *trans* isomer is much more abundant than the *cis* isomer (*trans*/*cis* 75:25).[42] The similarity of this stereochemistry with that detected in the coupling product corroborates the free-radical character of the CMRC process.

Conclusion

We have described a novel radical polymer chain coupling process based on cobalt complexes. Well-defined poly(acrylonitrile) precursors, prepared by CMRP, undergo a nearly quantitative coupling reaction when treated with a large variety of 1,3-diene compounds. In all cases, insertion of few diene units in the middle of the coupling product was observed, which is of interest for future use in specific mid-chain functionalization. An in-depth examination of the coupling products by NMR spectroscopy and MALDI-TOF, revealed the preferential insertion of two diene units, mainly following a *trans*-1,4-addition pathway.

On the basis of the evidence collected and with the help of DFT calculations, we propose that CMRC proceeds by a radical mechanism. The ease of cross-propagation from the cyanocarbyl to the allyl radical and the weak propensity of [Co(acac)$_2$] to deactivate the allyl radical terminated chains results in the release of a large amount of radical chains in the medium followed by a fast combination reaction instead of diene polymerization.

The efficiency of this radical process, even for poly(acrylonitrile) with quite high molar masses, is unprecedented as well as the precise incorporation of diene units in the middle of the chains, which makes the CMRC process quite unique. The ability of CMRC to deal with polymer precursors other than PAN will be investigated and the full potential of this technique will be explored in the near future. Importantly, the impact of this new coupling reaction goes well beyond the field of polymer chemistry and constitutes a novel C–C bond formation method that could be applied to smaller organic molecules for the synthesis of symmetrical derivatives.



Scheme 3. Mechanism of generation of coupled PAN–B$_n$–PAN. Only the most probable reactivity at the terminal (primary) position for the allyl radical is shown for simplicity.

Experimental Section

Materials: Vinyl acetate (>99 %, Aldrich), acrylonitrile (>99 %, Aldrich), and DMSO were dried over calcium hydride, degassed by several freeze–pump–thaw cycles before being distilled under reduced pressure and stored under argon. Compounds 2,2′-azo-bis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) (Wako), cobalt(II) acetylacetonate (>98 %, Acros), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (98 %, Aldrich), butadiene, isoprene, 2,4-hexadiene (mixture of isomers, 90 %), 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene (97 %, Aldrich), 2,4-heptadien-1-ol (>98 %, Fluka, 95 % *trans,trans*), benzoic acid, *N,N′*-dicyclohexylcarbodiimide (99 %, Aldrich), 4-(dimethylamino)pyridine (99 %, Aldrich), cyano-4-hydroxycinnamic acid (CHCA), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), dithranol, *trans*-3-(3-indolyl)acrylic acid, and 4-hydroxybenzylidene malononitrile were used as received. Two stock solutions in dichloromethane of the alkyl cobalt(III) adduct initiator ($[Co(acac)_2\{CH(OCOCH_3)CH_2\}_{<4}(R_0)]$; R_0 being the primary radical generated by V-70) were prepared as described previously.[26] The cobalt content of these solutions was evaluated by inductively coupled plasma mass spectrometry (ICP-MS) ([Co] = 0.122 and 0.183 M).

Characterization: SEC of poly(acrylonitrile) was carried out in 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, 500–30 000; HR4, 5000–500 000; HR5, 2000–40 000 000). Molecular parameters (M_n, M_p, M_w/M_n) were determined by MALLS, by using (d_n/d_c) values determined for each sample by refractometry analysis. However, molecular parameters of PAN samples with short chains (<3000 g mol^{-1}) were determined by SEC with a PMMA (PMMA = poly(methyl methacrylate) calibration corrected by the Mark–Houwink equation ($[\eta]=K_nM_n^a$, in which $K_n=K(M_w/M_n)^{0.5a(a+1)}$) (in DMF, $K_{PMMA}=1.32\times10^{-4}$, $a_{PMMA}=0.674$; $K_{PAN}=3.17\times10^{-4}$, $a_{PAN}=0.746$).[37,43] Importantly, measurements of M_n and M_w/M_n for the coupled product were always carried out before precipitation to avoid fractionation of the samples. The NMR spectra (^{1}H, ^{13}C, HSQC, and HMBC) were recorded at 298 K in [D$_6$]DMSO at 600 (^{1}H) and 150 MHz (^{13}C) with a Varian instrument and are reported in ppm from internal TMS on the δ scale. For the HSQC spectrum, 256 scans, D1 of 50 μs and a relaxation delay of 1 s were used. For the HMBS spectrum, 200 scans, D1 of 50 μs and a relaxation delay of 1 s were used. The ^{13}C spectrum was recorded at 298 K with a Bruker spectrometer (400 MHz). MALDI mass spectra were recorded by using a 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 a 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10000. The matrix was prepared as a 10 mg mL^{-1} solution in THF. The matrix solutions (1 μL) were applied to a stainless steel target and air-dried. Polymer samples were dissolved in DMSO to obtain 1 mg mL^{-1} solutions. 1 μL aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and then air-dried. Finally, 1 μL of a solution of NaI (2 mg mL^{-1} in acetonitrile/water (1:1)) was applied onto the target plate. For the recording of the single-stage MALDI-TOF spectra, the quadrupole (rf-only mode) was set to pass ions from 700 to 2250 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 the continuum mode until acceptable averaged data were obtained. EI-MS analysis of the diene **7** was carried out in positive mode on a Waters AutoSpec 6F spectrometer. IR spectra were recorded with a Perkin–Elmer FTIR instrument from 4000 to 600 cm^{-1}.

General procedure for the radical coupling of poly(acrylonitrile) with a molar mass below 5000 g mol^{-1}: All polymerization and coupling reactions were carried out under a protective argon atmosphere by using distilled and degassed monomers and solvents. A solution of alkyl–cobalt(III) initiator ($[Co(acac)_2\{CH(OCOCH_3)CH_2\}_{<4}(R_0)]$) in CH_2Cl_2 was introduced under argon in a Schlenk tube (1.0 mL of a 0.122 M stock solution, 0.12 mmol) and evaporated to dryness under reduced pressure at RT. The residue was dissolved under argon in DMSO (2.5 mL) and to the resulting solution was added AN (2.5 mL L, 2.0 g, 38 mmol) ([AN]/[Co] = 310) at RT. The Schlenk tube was then immersed in an ice bath and stirred for 4 h at 0 °C. An aliquot was then withdrawn to evaluate the AN conversion by ^{1}H NMR spectroscopy (18 %) and to measure the molecular parameters of the PAN by SEC-MALLS ($M_{n\ MALLS}=4080$ g mol^{-1}, $M_w/M_n=1.02$). Monomer conversion was maintained sufficiently low to prepare a polymer with low molar mass to facilitate the NMR spectroscopic analysis. After removal of the unreacted AN under reduced pressure at RT, the reaction medium was treated with butadiene (5.0 mmol, 0.27 g, 0.45 mL) and stirred for 1 h at RT. An aliquot was then withdrawn to characterize the resulting PAN by SEC-MALLS ($M_{n\ MALLS}=8650$ g mol^{-1}, $M_w/M_n=1.02$) before purification of the coupling product by repeated precipitation in a MeOH/H$_2$O (20:80) mixture and drying under vacuum at 70 °C.

All coupling experiments were carried out by following the exact same procedure with different dienes. When 2,4-heptadienyl benzoate (**7**) was used as the coupling agent, the PAN was recovered by subsequent precipitation in a MeOH/H$_2$O (20:80) mixture and in pure methanol.

General procedure for the radical coupling of poly(acrylonitrile) with molar mass above 10 000 g mol^{-1}: All polymerization and coupling reactions were carried out under a protective argon atmosphere by using distilled and degassed monomers and solvents. A solution of alkyl–cobalt(III) initiator $[Co(acac)_2\{CH(OCOCH_3)CH_2\}_{<4}(R_0)]$ in CH_2Cl_2 was introduced under argon in a Schlenk tube (0.50 mL of a 0.183 M stock solution, 0.092 mmol) and evaporated to dryness under reduced pressure at RT. The residue was then placed under argon at 0 °C and added with a mixture of DMSO (1.25 mL), DMF (1.25 mL), and AN (2.5 mL, 2.0 g, 38 mmol) previously cooled at 0 °C ([AN]/[Co] = 422). The reaction medium was then stirred for 24 h at 0 °C. An aliquot was withdrawn to evaluate the AN conversion by ^{1}H NMR spectroscopy (37 %) and to measure the molecular parameters of the PAN by SEC-MALLS ($M_{n\ MALLS}=11\,000$ g mol^{-1}, $M_w/M_n=1.02$). After removal of the unreacted AN under reduced pressure at RT, the reaction medium was diluted with DMF (2.0 mL), treated with butadiene (5.0 mmol, 0.27 g, 0.45 mL), and stirred for 2 h at RT. A second aliquot was withdrawn to characterize the PAN by SEC-MALLS ($M_{n\ MALLS}=21\,200$ g mol^{-1}, $M_w/M_n=1.01$) before purification of the coupling product by repeated precipitation in a MeOH/H$_2$O (20:80) mixture and drying under vacuum at 70 °C.

All coupling experiments were carried out by following exactly the same procedure with 5.0 mmol of each diene, with the exception of the coupling experiment carried out with 2,4-heptadienyl benzoate (**7**). In this case, the coupling agent (2.5 mmol) was previously dissolved in degassed DMF (1 mL) before injection.

CMRC of homopoly(acrylonitrile) precursors prepared by CMRP with V-70 as the initiator: $[Co(acac)_2]$ (0.600 g, 2.34 mmol) and V-70 (0.720 g, 2.34 mmol) were introduced into a round-bottomed flask capped by a three-way stopcock and purged by three vacuum-argon cycles. After subsequent addition of distilled and degassed DMSO (15.0 mL) and AN (15.0 mL, 12.1 g, 228 mmol), the reaction medium was heated at 30 °C with stirring ([AN]/[Co] = 97). After 1 h, a sample was withdrawn. A few drops of the sample were diluted in deuterated DMSO containing TEMPO to measure the AN conversion by ^{1}H NMR spectroscopy (298 K, $D_1=2$ s, 16 scans) (AN conv. = 10 %). Monomer conversion was maintained sufficiently low to prepare a low molar mass polymer for the ease of MALDI-TOF MS analysis. Half of the reaction medium was precipitated in methanol. The recovered polymer was dried under vacuum at 70 °C before its molecular parameters were measured by SEC ($M_{n\ SEC}=1900$ g mol^{-1}, $M_w/M_n=1.21$). Then, unreacted AN was removed from the polymerization medium under vacuum at RT before the addition of isoprene (1.0 mL, 0.68 g, 10 mmol). The mixture was then stirred at RT for 1 h. After removing the residual isoprene under vacuum, the polymer was precipitated by addition of methanol. The resulting PAN was characterized by SEC ($M_{n\ SEC}=3100$ g mol^{-1}, $M_w/M_n=1.31$). After purification, the final PAN was analyzed by MALDI-TOF mass spectrometry. Molar masses of the above mentioned PAN samples were determined by SEC with a PMMA calibration corrected by the Mark–Houwink equation.

Synthesis of 2,4-heptadienyl benzoate (7): 2,4-Heptadiene-1-ol (**6**) (2.24 g, 20.0 mmol) was introduced in a round-bottomed flask and subsequently dissolved in dichloromethane (20.0 mL) at RT. Benzoic acid (2.44 g, 20.0 mmol), dicyclohexyl carbodiimide (DCC; 5.00 g, 24.0 mmol), and dimethylaminopyridine (DMAP; 0.25 g, 2.0 mmol) were added to the resulting solution. The reaction mixture was then stirred for 4 h at RT. The white precipitate formed during the reaction was removed by filtration. The reaction medium was then extracted with a dichloromethane/water mixture. The organic layer was recovered, dried over magnesium sulfate, filtered, and evaporated to dryness under reduced pressure. After purification by chromatography on silica by using dichloromethane as the eluent ($R_f=0.8$), a colorless liquid was recovered (2.9 g, yield = 67 %). IR (neat NaCl): $\tilde{\nu}=3090$, 3063, 3027, 2933, 2873, 1719, 1601, 1451, 1269, 710 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.40$–7.76 (m, 2H; arom.), 7.80–7.30 (m, 3H; arom.), 6.35 (dd, $J=15.1$, 10.4 Hz, 1H; vinyl.), 6.07 (dd, $J=15.1$, 10.5 Hz, 1H; vinyl.), 5.79 (m, 2H; vinyl.), 4.84 (d, $J=7.6$ Hz, 2H; $-CH_2-OCOPh$), 2.12 (m, 2H; allyl.), 1.02 ppm (t, $J=7.5$ Hz, 3H; aliph.); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta=166.39$, 138.33, 135.11, 132.90, 130.34, 129.63, 128.33, 128.16, 124.02, 65.44, 25.66, 13.36 ppm. EI-HRMS: calcd for $C_{14}H_{16}O_2$: 216.1150; found: 216.1146; EI-MS: m/z: (%): 216 (10), 105 (100), 77 (30), 69 (18).

Computational details: All geometry optimizations were performed by using the B3LYP three-parameter hybrid density functional method of Becke,[44] as implemented in the Gaussian 03 suite of programs.[45] The basis functions consisted of the standard 6–31G** for all light atoms (H, C, N, O), plus the LANL2DZ function, which included the Hay and Wadt effective core potentials (ECP) and an f polarization function ($\alpha=0.8$), for Co. All geometry optimizations were carried out without any symmetry constraint and all final geometries were characterized as local minima of the potential energy surface (PES) by verifying that all second derivatives of the energy were positive. The unrestricted formulation was used for open-shell molecules. The value of $<S^2>$ at convergence was very close to the expected value of 0.75 for the radical species and 3.75 for the spin quartet species (the greatest deviation was 3.760 for complex $[Co(acac)_2(dmso)_2]$), which indicates minor spin contamination. All energies were corrected for zero-point vibrational energy and for thermal energy to obtain the bond-dissociation enthalpies at 298 K. The standard approximations for estimating these corrections were used (ideal gas, rigid rotor and harmonic oscillator) as implemented into Gaussian 03. Additional calculations were also carried out with the same basis set by use of the B3PW91* functional, at the fixed geometries optimized by B3LYP. The thermal enthalpy correction was carried out by using the B3LYP values. The B3PW91* functional is 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.

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