Radical Coupling

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Isoprene-Assisted Radical Coupling of (Co)polymers Prepared by Cobalt-Mediated Radical Polymerization[**]

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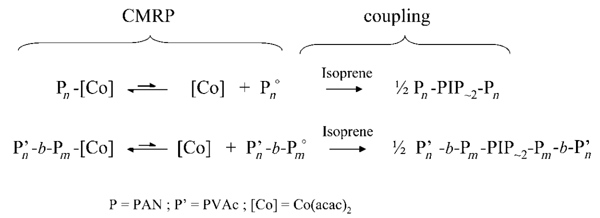
Controlled radical polymerization (CRP) techniques are tools of choice to prepare well-defined macromolecules with predictable molar masses (M_n) and low polydispersity (M_w/M_n).[1] These methods are based on the temporary deactivation of the propagating centers to preserve them from irreversible termination. Reactivation of the protected radicals can be used to end-functionalize macromolecules or polymerize other monomers leading to multiblock copolymers. Although radical coupling reactions must be minimized along the CRP process, the development of innovative methods able to promote on demand the selective self-coupling of two radical polymer chains would open novel synthetic perspectives. Indeed, self-coupling of α-functionalized polymers and AB diblock copolymers, preformed by CRP, should give access to telechelic polymers and symmetrical ABA triblock copolymers, respectively. For the latter, the coupling or "convergent" approach should have advantages over the reported "sequential" and "divergent" strategies. Indeed, ABA triblocks obtained by sequential polymerization of different monomers from a monofunctional initiator suffer from a lack of symmetry and are often contaminated by homopolymer and/or diblock copolymer.[2,3] In this respect, the divergent polymerization of two monomers by using a bisfunctional initiator[2–4] is more reliable, but a higher level of control of the chain ends is expected following the coupling technique. However, such a radical convergent strategy has been disregarded until now because of the rareness of quantitative and selective radical coupling methods. Atom-transfer radical coupling (ATRC)[5–12] has proved efficiency to couple short polymer chains preformed by atom-transfer radical polymerization or by reverse iodine transfer polymerization[12] and to provide telechelic polymers. Recently, silane radical atom abstraction was introduced as a metal-free alternative coupling method.[13] In theory, ATRC applied to halogenated diblocks should lead to the ABA triblock copolymer but only modest results have been reported.[14]

Herein, we report an efficient radical coupling method called isoprene-assisted radical coupling (I-ARC), which involves the addition of isoprene to polymer chains preformed by cobalt-mediated radical polymerization (CMRP)[15–26] (Scheme 1). The latter CRP technique notably allows control of the polymerization of vinyl acetate (VAc) and acrylonitrile (AN) by temporary deactivation of the propagating radical with the bis(acetylacetonato)cobalt(II) complex [Co(acac)$_2$].[19–26] By following this procedure, a range of well-defined PAN chains capped by [Co(acac)$_2$] ($M_w/M_n \approx 1.1$, $M_n \approx 10\,000$–$25\,000$ g mol^{-1}) were prepared with an alkylcobalt(III) compound [R$_0$-(CH$_2$CHOAc)$_{<4}$-Co(acac)$_2$] as initiator[24] (Table 1, entries 1–3). After removal of the unreacted monomer, the PAN-[Co] samples were treated with a large amount of isoprene at room temperature for 2 h.



Scheme 1. General strategy for the coupling reaction of (co)polymers preformed by CMRP with isoprene. PAN = polyacrylonitrile, PVAc = poly(vinyl acetate), acac = acetylacetonato.

Initiation of the isoprene polymerization was anticipated from the PAN macroradical formed by homolytic cleavage of the Co−C bond, but no polyisoprene (PIP) was detected by NMR spectroscopy in the final material. Nevertheless, the M_n of the precursors systematically doubled (Figure 1 a), which suggests a radical coupling reaction between two PAN chains (Scheme 1). Based on the accurate molar masses for the precursor ($M_{n,0}$) and the final product (M_n), provided by a size-exclusion chromatography (SEC) column equipped with a multiangle light-scattering (MALLS) detector, the extent of coupling (x_c) was estimated from the following equation: $x_c = 2[1-(M_{n,0}/M_n)]$. In all cases the x_c was close to unity, which confirms the efficiency of this coupling process.[7] The SEC-MALLS profiles of the coupled products were monomodal and narrow ($M_w/M_n < 1.1$), even for PAN with higher M_n (for example, $\approx 25\,000$ g mol^{-1}; Table 1, entry 3). The I-ARC technique is thus not restricted to short homopolymeric chains, as was the case for previously reported convergent radical systems.[5–12] Additional experiments showed that the

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Table 1: Coupling reaction of PAN-[Co] prepared by CMRP.

	Preparation of P_n-[Co] precursors					P_{2n} by coupling		
Entry	$[M]_0/[Co]_0$	t [h]	Conversion[c] [%]	$M_{n,0}$[d] [g mol^{-1}]	M_w/M_n	M_n[d] [g mol^{-1}]	M_w/M_n	x_c[e]
1[a]	664	6	12	9400	1.01	19100	1.02	1.02
2[a]	1328	6	10	12500	1.02	25800	1.01	1.03
3[a]	1328	12	21	24900	1.02	51200	1.04	1.02
4[b]	96	4	27	6900	1.07	12300	1.07	0.88

[a] Polymerization: $[Co(acac)_2(\text{-}CH(OCOCH_3)CH_2)_{<4}\text{-}R_0)]$ as initiator, $V_{DMSO}/V_{AN} = 1$, 0°C. DMSO = dimethyl sulfoxide. Coupling: removal of the unreacted AN prior to isoprene addition, [isoprene]/[Co] = 88, room temperature, 2 h. [b] Polymerization: $[AN]/[Co(acac)_2]_0/[V\text{-}70]_0 = 97{:}1{:}1$, $V_{DMSO}/V_{AN} = 1$, 30°C. Coupling: [isoprene]/[Co] = 8.3, room temperature, 2 h. [c] ^1H NMR spectroscopy. [d] SEC-MALLS (specific refractive index increment, $(dn/dc)_{PAN} = 0.076$ mL g^{-1}). [e] $x_c = 2[1-(M_{n,0}/M_n)]$.

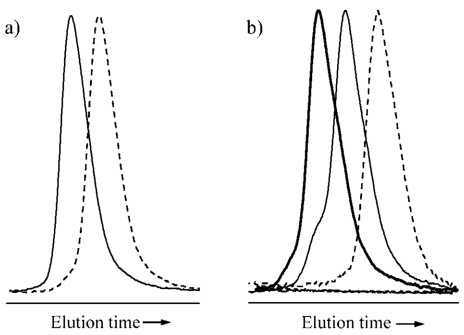

Figure 1. SEC-MALLS chromatograms for a) PAN-[Co] precursor (-----) and the coupling product upon treatment with isoprene (——) (Table 1, entry 1), and b) PVAc-[Co] macroinitiator (-----), PVAc-*b*-PAN-[Co] diblock (——), and the final PVAc-*b*-PAN-*b*-PVAc triblock copolymer (bold line; Table 2, entry 2).

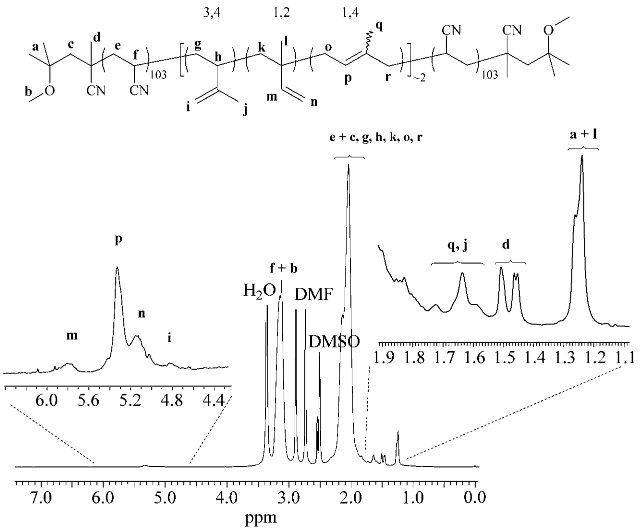

Figure 2. ^1H NMR analysis of a PAN sample recovered after the coupling reaction with isoprene (Table 1, entry 4).

coupling reaction is complete within 5 min, but also that removal of the unreacted AN prior to injection of isoprene is not essential (see the Supporting Information).

The coupling reaction was also investigated on PAN-[Co] prepared from azo initiator (V-70) and $[Co(acac)_2]$ instead of the alkylcobalt(III) initiator.[24] Under these conditions the level of control of the AN was lower and thus end-functionalization of the chain by the cobalt was less efficient, which explains the moderate extent of the coupling ($x_c = 0.88$; Table 1, entry 4, and Figure C in the Supporting Information). In this case, it was observed by ^1H NMR spectroscopy that an average of two isoprene units were incorporated in the polymer (mainly 1,4-addition product; Figure 2). Based on this observation, a reasonable mechanistic hypothesis is the following: 1) release of PAN$^\bullet$ radicals from the preformed PAN-Co^{III} species; 2) addition of a few isoprene units; 3) deactivation by Co^{II} of the newly formed PAN-PIP$_{\approx 2}^\bullet$ radical, and 4) addition of a second PAN$^\bullet$ radical chain onto the unreacted double bond of the last isoprene unit of the PAN-PIP-Co^{III} intermediate, with formation of the coupling product (PAN-PIP$_{\approx 2}$-PAN) and release of Co^{II}.

The release of the metal from the polymer during the coupling process was confirmed by inductively coupled plasma analyses. Less than 3% of the initial amounts of cobalt were detected in the final PAN samples after precipitation (see the Supporting Information). Unfortunately, it is not trivial to reveal formation of the PAN-PIP$_{\approx 2}$-Co intermediate in such a complex medium, especially for such a fast reaction. Moreover, although it is tempting to carry out the coupling reaction on small model compounds, such as $[CH_3\text{-}(CN)CH\text{-}Co(acac)_2]$, to simplify the system, the synthesis and isolation of the latter complex does not appear realistic today. Indeed, all attempts to synthesize the parent $[CH_3\text{-}CH(OCOCH_3)\text{-}Co(acac)_2]$ adduct, which is more stable than the above-mentioned one,[22] remained unsuccessful and still represents a real challenge.[27]

As shown in Scheme 1, I-ARC has also been applied to well-defined PVAc-*b*-PAN-[Co] diblock copolymers with different compositions prepared by CMRP as follows: 1) synthesis of PVAc-[Co] with $[R_0\text{-}(CH_2CHOAc)_{<4}\text{-}Co(acac)_2]$ as initiator at 30°C in bulk in the presence of water;[22] and 2) initiation of the AN polymerization from the PVAc-[Co] block in DMF at 0°C[23] (Table 2). After removal of residual AN and the addition of isoprene to the PVAc-*b*-PAN-[Co] samples, the expected PVAc-*b*-PAN-*b*-PVAc triblock copolymers were formed at 0°C. The doubling of the peak molar mass (M_p) was observed in both cases, but the M_n of the final material obtained from diblocks with a longer chain was slightly lower than expected. This result suggests that a small amount of the diblock did not participate in the coupling reaction ($x_c = 87\%$; Table 2, footnote [c]). Nevertheless, the overlay of the SEC-MALLS chromatograms of samples withdrawn from the medium at every reaction step illustrates the efficiency of this convergent synthesis of ABA triblock copolymers (Figure 1b).

Table 2: Synthesis of PVAc-*b*-PAN-*b*-PVAc triblock copolymers.

PVAc-*b*-PAN-[Co]				PVAc-*b*-PAN-*b*-PVAc				
$M_{n,0}$[a] [g mol^{-1}]	$M_{p,0}$[a] [g mol^{-1}]	M_w/M_n	Compos. PVAc-*b*-PAN	M_n[a] [g mol^{-1}]	M_p[a] [g mol^{-1}]	M_w/M_n	Compos.	x_c[d]
9400[b]	9900	1.05	5.8 K-*b*-3.6 K	18 200	19 600	1.05	5.8 K-*b*-7.2 K-*b*-5.8 K	0.97
24 800[c]	25 600	1.06	16.3 K-*b*-8.5 K	43 800	49 300	1.07	16.3 K-*b*-17.0 K-*b*-16.3 K	0.87

[a] SEC-MALLS. [b] PVAc-[Co]: $[VAc]_0/[H_20]_0/[Co(acac)_2(\text{-}CH(OCOCH_3)CH_2)_{<4}\text{-}R_0)]_0 = 203{:}18{:}1$, bulk, 30 °C, 6.5 h, conv. = 50%. $M_{n\,PVAc} = 5800$ g mol^{-1}. PVAc-*b*-PAN-[Co]: $[AN]_0/[PVAc\text{-}Co]_0 = 286$, $V_{DMF}/V_{AN} = 1$, 0 °C, 16 h, 25%. PVAc-*b*-PAN-*b*-PVAc: $[isoprene]_0/[PVAc\text{-}b\text{-}PAN\text{-}Co]_0 = 75$, 0 °C, 2 h. ($(dn/dc)_{PVAc} = 0.030$ mL g^{-1}, $(dn/dc)_{PVAc\text{-}b\text{-}PAN} = (dn/dc)_{PVAc\text{-}b\text{-}PAN\text{-}b\text{-}PVAc} = 0.055$ mL g^{-1}). [c] PVAc-[Co]: $[VAc]_0/[H_20]_0/[Co(acac)_2(\text{-}CH(OCOCH_3)CH_2)_{<4}\text{-}R_0)]_0 = 406{:}36{:}1$, bulk, 30 °C, 12 h, conv. = 50%. $M_{n\,PVAc} = 16\,300$ g mol^{-1}. PVAc-*b*-PAN-[Co]: $[AN]_0/[PVAc\text{-}Co]_0 = 572$, $V_{DMF}/V_{AN} = 1$, 0 °C, 16 h, 20%. PVAc-*b*-PAN-*b*-PVAc: $[isoprene]_0/[PVAc\text{-}PAN\text{-}Co]_0 = 150$, 0 °C, 2 h. ($(dn/dc)_{PVAc} = 0.030$ mL g^{-1}, $(dn/dc)_{PVAc\text{-}b\text{-}PAN} = (dn/dc)_{PVAc\text{-}b\text{-}PAN\text{-}b\text{-}PVAc} = 0.052$ mL g^{-1}). [d] $x_c = 2[1-(M_{n,0}/M_n)]$.

Finally, hydrolysis of the ester functions of PVAc-*b*-PAN-*b*-PVAc copolymers led to the novel corresponding amphiphilic PVOH-*b*-PAN-*b*-PVOH triblock (PVOH = poly(vinyl alcohol)), whereas a fully hydrosoluble PVOH-*b*-PAA-*b*-PVOH triblock (PAA = poly(acrylic acid)) was obtained upon specific basic treatment (see the Supporting Information, Figure E).

In conclusion, I-ARC is an efficient radical coupling method for PAN-containing (co)polymers prepared by CMRP. The observed release of cobalt from the polymer chain and tiny incorporation of isoprene allowed us to make a mechanistic proposal. Contrary to the previously reported radical coupling techniques, I-ARC is not restricted to short polymeric chains and homopolymers. Indeed, it has been successfully applied to PAN-[Co] homopolymers with M_n equal to 25 000 g mol^{-1} and to the coupling of PVAc-*b*-PAN-[Co] diblocks leading to PVAc-*b*-PAN-*b*-PVAc triblocks. In addition to being a straightforward approach for the synthesis of symmetrical ABA copolymers, this unique coupling reaction also paves the way towards telechelic polymers by using α-functional precursors. Finally, the extension of this methodology to other monomers, whose polymerization can be controlled by CMRP today, such as VAc,[18–22] *N*-vinyl pyrrolidone,[25,26] and acrylic monomers,[15–17] should give access to a completely novel class of valuable polymeric materials.

The Experimental Section is provided as Supporting Information.

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