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ARTICLE

Direct One-pot Synthesis of Poly(ionic liquid) Nanogels by Cobalt-Mediated Radical Cross-linking Copolymerization in organic or aqueous media

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Nanogels of controlled kinetic chain length were synthesized by cobalt-mediated radical cross-linking copolymerization (CMRccP) involving a vinyl monomer and a divinyl cross-linker. This strategy was first validated to achieve neutral poly(vinyl acetate) nanogels by CMRccP of vinyl acetate and divinyl adipate as cross-linker, at 40 °C, in presence of an alkyl-cobalt(III) serving both as initiator and controlling agent, using ethyl acetate as solvent. Poly(ionic liquid) nanogels were then directly obtained by CMRccP of *N*-vinyl-3-ethyl imidazolium bromide, in presence of 1,13-divinyl-3-decyl diimidazolium bromide as cross-linker. CMRccP experiments could be conducted either in organic solvent using dimethyl formamide or, more interestingly, in aqueous solution, demonstrating the robustness and the versatility of this one-step process. Chain extensions of PILs nanogels were also carried out in water, forming core-shell structures, thus opening new avenues in the design of functional nanogels.

Introduction.

IUPAC defines nanogels as soluble polymer networks with a dimension lower than 100 nm[1]. Their three-dimensional internal structure results from both intra- and intermolecular cross-linking reactions. Owing to their low viscosity in comparison to linear homologues of same molar mass, nanogels find applications in coatings at high solid content[2], or as additives for organic binders[3]. Specifically, hydrophilic nanogels have emerged, mainly as novel carriers for drug delivery applications[4-6]. Common synthetic methods to obtain nanogels include: i) the post-cross-linking of pre-formed linear polymers, e.g. by chemical post-modification of polymer precursors possessing pendant reactive groups, or by radiation with a high energy source[7, 8], and ii) the free-radical cross-linking copolymerization (RCC) in dispersed media or in highly dilute solution[9-12]. As predicted by Flory[13] and Stockmayer[14, 15], RCC conducted under rather high concentrated solution, or in presence of high content of cross-linker, rapidly leads to macrogels, which eventually correspond to interconnected nano- and microgel particles. Furthermore, RCC provides little control over the internal network structure: both the kinetic chain length and the distribution of cross-link points within the final network are highly heterogeneous. This is attributed to both a very fast chain growth and extensive intramolecular cross-linking (cyclization) forming nano/microgels.

Controlled radical polymerization (CRP) methods have been anticipated to allow access to nano-, micro- and macrogels with a higher structural homogeneity[9, 16-19]. In specific applications such as drug delivery for which structural homogeneity is momentous for controlling the kinetic of drug release, resorting to CRP is thought to be beneficial over conventional free-radical polymerization (FRP). In a RCC operating by CRP, indeed, much more primary chains start growing simultaneously from the early stage of the process, and chain growth is much slower favoring chain relaxation and translational diffusion[20]. Hence intermolecular cross-linking reactions are more likely to occur, compared to a RCC by FRP. Differences between FRP and CRP methods, in a context of RCC, have been supported by experimental findings both at the macroscopic level (e.g. *via* elastic or swelling analyses)[18, 21] and microscopically through light scattering measurements. For instance, CRP-made networks exhibit higher swelling ratios and seem to be softer than those obtained by FRP. These differences have been often interpreted as being due to the formation of a more homogeneous network structure by CRP, compared to FRP. This, however, has been recently questioned by Oppermann *et al*[22]. Indeed, according to these authors, gels obtained by CRP appear to be more homogeneous only because they are much less densely cross-linked (reduced cross-linking efficiency) as compared to FRP[22]. Eventually, a CRP gel would not be more homogeneous than an FRP gel, if both compared gels had the same effective network density.

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In other words, CRP-derived gels do not necessarily exhibit a more even distribution of cross-link points.

Yet, the use of a controlling agent in RCC not only provides a better control of the kinetic chain length, but also enables the gel point to be postponed and to introduce larger amounts of cross-linker[23-26]. Last but not least, dormant chain-ends can be reactivated in gels prepared by CRP, allowing for chain extension and synthesis of core-shell structures[9, 27]. "Controlled" RCC process can be implemented by nitroxide-mediated polymerization (NMP) [28, 29], reversible addition–fragmentation chain transfer (RAFT) [30-32] and atom transfer radical polymerization (ATRP)[8, 26, 33, 34]. Here we wish to describe nanogel synthesis induced by a particular CRP method, referred to as the cobalt-mediated radical polymerization (CMRP) using $Co(acac)_2$ as controlling agent[35, 36]. This technique is particularly suited to control the polymerization of nonconjugated vinyl monomers -also called less activated monomers (LAM) in the context of the RAFT process[35] - such as vinyl esters (vinyl acetate (VAc)[37], vinyl levulinate (VLV)[38] or vinyl ester 1,2,3 triazolium[39]), vinyl chloride (VC)[40], *N*-vinylpyrrolidone (NVP)[41], or *N*-vinyl-3-alkyl-imidazolium bromide (VRImBr)[42, 43] or bis(trifluoromethylsulfonyl)imide ($VRImTf_2N$)[44] monomers. VAc has been here tested first so as to validate the possibility to achieve nanogels by cobalt-mediated radical cross-linking copolymerization (CMRccP). This method has then been applied to VRImBr. Polymerization of the latter monomers leads to cationically charged polymers entering in the category of so-called poly(ionic liquid)s (PILs)[45-48]. PILs are polymeric versions of ILs, representing a new class of polyelectrolytes of tunable solubility, showing an anhydrous ionic conductivity up to 10^{-5} S/cm at room temperature[49], and a broad range of glass transition temperatures. Owing to their combined properties emanating from IL units and their polymeric nature, PILs find potential applications in areas, such as analytical chemistry[50], biotechnology, gas separation[51], dispersants, solid ionic conductors for energy, catalysis[52], etc[53]. Exchange of the counterion (= metathesis reaction) provides an additional method for the variation of PIL properties[54].

In this contribution, synthesis of both PVAc and PIL nanogels of controlled chain length is described. CMRccP of VAc (or VRImBr) using divinyladipate (or an IL-type) cross-linker is performed in solution, in presence of a pre-synthesized alkyl–cobalt(III) complex ($R–Co(acac)_2$, **1**) as a single-component initiator/mediating agent. The capacity to further extend these nanogels is also explored. The synthesis of nanogels composed of a neutral poly(vinyl acetate-*co*-divinyl adipate) central core and a cationic poly(vinyl imidazolium-*co*-divinyl imidazolium) outer shell is also described.

Experimental

Materials.

Dimethylformamide (DMF, Aldrich, 99.8%) and methanol (MeOH, HPLC grade) were dried over molecular sieves and degassed by bubbling Argon during 15 minutes. Milli-Q water and acetone were degassed by bubbling Argon during 30 minutes. 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO) (98%, Aldrich) was used as received. The alkyl-cobalt(III) ($R–Co(acac)_2$) was synthesized as already reported[55]. *N*-Vinyl-3-ethyl imidazolium bromide (VEtImBr) was synthesized as reported in the literature[54]. 1,13-Divinyl-3-decyl diimidazolium bromide (DVI) was synthesized following the same strategy. Vinyl acetate (VAc) was dried on calcium hydride to eliminate water, and cryo-distilled prior to use. Divinyl adipate (DVA, Aldrich, >99%) was employed as received.

Characterization.

Molar masses and dispersities of PVAc-type samples were determined by SEC in THF eluent, Jasco pump equipped with a set of 3 TSK gel HXL (4 000, 3 000, and 2 000) 7.5_300 mmSEC columns, a RI Jasco detector and a UV Jasco detector at 290 nm connected in series (flow rate $1mL.min^{-1}$). Molar masses and dispersities of hydrophilic polymers (*i.e.* of poly(*N*-Vinyl-3-ethyl imidazolium bromide) (PVEtImBr) and of poly(vinyl alcohol) (PVA) obtained after methanolysis of poly(vinyl acetate) (PVAc)-based samples) were determined by aqueous size exclusion chromatography (SEC), in an eluent containing NaCl (0.1M) and trifluoroacetic acid (TFA, 0.1%vol), at 30 °C (pressure: 540 PSI; flow rate: $1mL.min^{-1}$), with a SEC equipped with a pre-column (PSS NOVEMA Max analytical 10 micron, 8.0Í50 mm) and a linear column (PSS NOVEMA Max analytical linear S micron 8.0Í300 mm). Molar masses and dispersities of PVEtImBr were also evaluated, after anion exchange of bromide anions by bis(trifluoromethylsulfonyl)imide anions, by SEC in THF in an eluent containing 10 mM LiTFSI, according to the procedure reported by Matyjaszewski *et al*.[50]. ^{1}H NMR spectra of the reaction medium and final product were recorded at 25 °C with a Bruker spectrometer (400 MHz), in DMSO-d_6. Weight loss during SEC experiments, and in particular after filtration step on 0.2 µm filter prior to injection, was evaluated by column-free SEC equipped with an Optilab rex detector, in THF containing 10 mM LiTFSI at 25 °C. Nanogel solutions at 1 mg/mL in THF containing 10 mM LiTFSI were injected with and without filtration step. Peak area of each run corresponds to the concentration of the sample. Comparison of the peak areas with and without filtration determines the possible weight loss of nanogels during filtration (results are summarized in Figure S4).

Transmission electron microscopy (TEM) images were recorded on a Hitachi H7650 microscope working at 80 kV equipped with a GATAN Orius 11 Megapixel camera. Samples were prepared via deposition of a drop of polymeric solution on a TEM grid, and subsequent absorption of solution excess.

Syntheses.

Typical copolymerization of vinyl acetate (VAc) with divinyl adipate (DVA) via CMRccP in ethyl acetate. In a typical experiment, DVA (0.12 g , 6 mol.%, 6.10^{-4}mol.) was introduced in a Schlenk tube and degassed by at least three successive vacuum-Argon cycles, followed by 20 minutes under vacuum. To this initial

mixture, 10 mL of dried degassed ethyl acetate were added under Argon. Vinyl acetate (1mL, 10^{-2} mol.) was then added under Argon. The flask was thermostated at 40 °C and a solution of alkyl-cobalt(III) initiator (1.1 mL, 1.6 10^{-4} mol., solution at 1.5 M) in CH_2Cl_2 was then added. The reaction medium was stirred. Aliquots were taken out regularly, to monitor the monomer conversion by ^{1}H NMR. Samples for THF SEC were quenched by adding TEMPO in the vials and ethyl acetate was removed by dialysis against MeOH before SEC analysis. The results of these syntheses are shown in Table 1 and Figures 2 and S1.

Synthesis of PVAc nanogel (with 4 mol.% DVA) and resumption by 3-ethyl imidazolium bis(trifluoromethylsulfonyl)imide. DVA (0.08 g, 4 mol.%, 4.10^{-4} mol.) was introduced in a Schlenk tube and degassed by at least three successive vacuum-Argon cycles, followed by 20 minutes under vacuum. To this initial mixture, 10 mL of dried degassed ethyl acetate were added under Argon. Vinyl acetate (1 mL, 10^{-2} mol.) was then added under Argon. The flask was thermostated at 40° C and a solution of alkyl-cobalt(III) initiator (1.1 mL, 1.6 10^{-4} mol., solution at 1.5M) in CH_2Cl_2 was then added. The reaction medium was stirred. An aliquot was removed after 120h to check the conversion and molecular parameters. The reaction medium was then rapidly transferred to a flask containing degassed $VEtImNTf_2$ (2 g, 5.10^{-3} mol.) and the mixture was stirred for 48h at 30°C. Results are summarized in Figure S3 (ESI).

Typical procedure for the methanolysis of PVAc nanogels. In a typical experiment, a solution of NaOH in MeOH at 10 $g.L^{-1}$ (volume V) was added under strong stirring into the same volume V of the polymeric solution in MeOH at 100 $g.L^{-1}$. During hydrolysis, poly(vinyl alcohol) precipitates and, after several hours of reaction, the polymer was recovered by decantation followed by purification by several cycles of decantation/ supernatant removal/ addition of a minimal amount of water to solubilize the polymer.

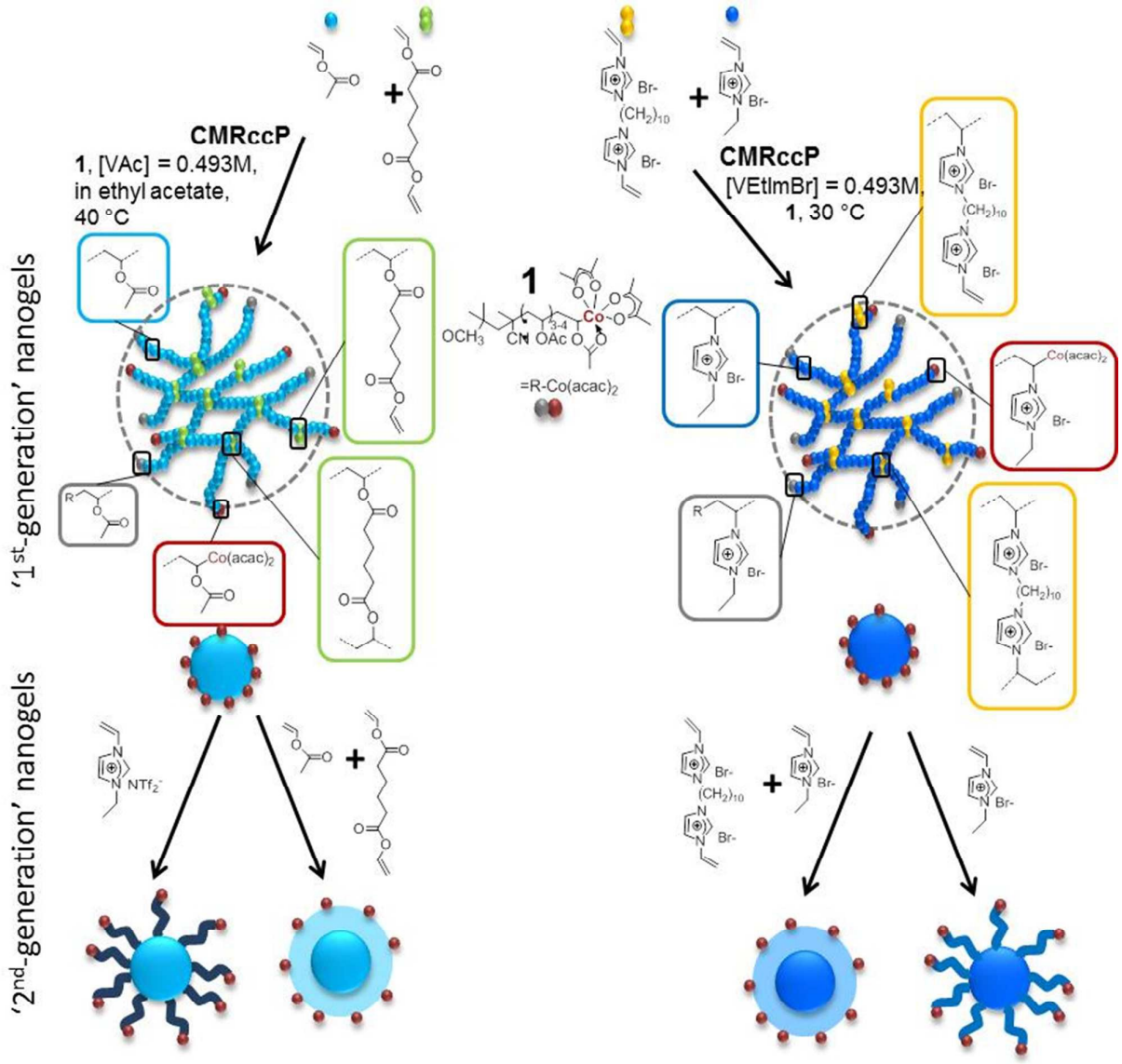
Typical copolymerization of 1-vinyl-3-ethyl imidazolium bromide (VEtImBr) with 1,13-divinyl-3-decyl diimidazolium bromide (DVI) via CMRccP in organic solvent. VEtImBr (1 g, 6.2 10^{-3} mol.), and divinylimidazolium DVI (0.1 g, 4.8 mol.%) were introduced in a Schlenk tube and degassed by 3 vacuum-argon cycles, and 12 mL of dry, degassed solvent were added. The solvent was either dimethylformamide (DMF) or a mixture of DMF and methanol (MeOH) (8/4) (v/v). The flask was thermostated at 30 °C and a solution of alkyl-cobalt(III) initiator (0.40 mL, 7.4 10^{-5} mol., solution at 1.18M) in CH_2Cl_2 was then added. The reaction medium was stirred. Aliquots were regularly removed for determining the conversion by ^{1}H NMR. Samples for SEC H_2O were quenched by TEMPO and DMF is removed by dialysis before SEC H_2O (results are summarized in Table S4, and in Figure S5). Samples for SEC in THF undergo an anion exchange before SEC THF. The results of these syntheses are shown in Table 2, entries 1 to 6 and Figure 4.

Aqueous copolymerization of 1-vinyl-3-ethyl imidazolium bromide (VEtImBr) and 1,13-divinyl-3-decyl diimidazolium bromide (DVIBr) via CMRccP. A solution of alkyl-cobalt(III) initiator (0.40 mL, 7.4 10^{-5} mol., solution at 1.18 M) in CH_2Cl_2 was introduced in a Schlenk tube already degassed by 3 vacuum-argon cycles. The CH_2Cl_2 was then evaporated under vacuum. The Schlenk tube was put under argon again, and the alkyl-cobalt(III) adduct was solubilized in 0.5 mL of previously degassed acetone. VEtImBr (1g, 6.2 10^{-3} mol.), and divinylimidazolium DVI (0.1 g, 4.8 mol.%) were introduced in another Schlenk tube and degassed by 3 vacuum-Argon cycles, and 12 mL of milli-Q water were added. The second Schlenk tube was degassed by bubbling Argon during 30 minutes, and the solution of ionic liquid monomer in water was added to the first Schlenk tube, containing the solution of alkyl-cobalt(III) adduct. The reaction medium was stirred at 30 °C. Aliquots were regularly withdrawn for determining the conversion by ^{1}H NMR. Samples for SECs were quenched by TEMPO, and samples for THF SEC were submitted to an anion exchange before injection. The results of these syntheses are shown in Table 2, entries 7 to 9 and Figure 4 (reaction monitoring on Table S3, entries 7-9).
For nanogels of second-generation (chain extensions), the copolymerization was not quenched, but a fresh feed of VEtImBr (respectively a mix of VEtImBr with 5 mol.% of DVI) was added to the copolymerization medium. No new Cobalt(III)-adduct **1** is added. Results are summarized Figure 6.

Anion exchange. The aliquot undergoing anion exchange - from bromide to bis(trifluromethanesulfonyl)imide NTf_2^-, was first solubilized in deionized water[43]. Then, under stirring, 2 equivalents of $LiNTf_2$ were added to the aqueous solution. The solutions became turbid almost instantly, since the polymer $PVEtImNTf_2$ precipitates in aqueous medium. However, to complete the anion exchange on branched imidazolium-type nanogels, the medium had to be stirred several days (a complete exchange is observed after 6 days of stirring). Then, the polymers were washed several times with deionized water, to eliminate the LiBr salt formed during the anion exchange.

Results and discussion

A. Poly(vinyl acetate) nanogels as validation of the concept.



Scheme 1. Cobalt-mediated radical cross-linking copolymerization of a vinyl monomer and divinyl cross-linker mediated by **1** in solution, and chain extension reactions. The 'second-generation' nanogels is synthesized using a new feed of monomer. In the case of poly(VAc-*co*-DVA), the extensions are realized with a mixture of VAc and DVA or with *N*-vinyl-3-ethyl imidazolium bis(trifluoromethylsulfonyl)imide (VEtImNTf$_2$); in the case of poly(VEtImBr-*co*-DVI), the extensions are realized with VEtImBr or with a mixture of VEtImBr and DVI.

PVAc nanogels were first considered in order to validate the principle of CMRccP. VAc, indeed, is the benchmark of the LAM family, the polymerization of which can be controlled by xanthates or dithiocarbamates as RAFT agents[56, 57], or by CMRP[58-60]. Here CMRccP of VAc was carried out using divinyl adipate (DVA) as the cross-linker, owing to the structural analogy of DVA with VAc. Synthesis of PVAc nanogels by xanthate-mediated RAFT polymerization was previously reported[56]. CMRccP was carried out in presence of the preformed alkyl-cobalt(III) adduct (R-Co(acac)$_2$ denoted as **1**) as mediating agent, using various VAc/DVA/**1** ratios (Scheme 1). As mentioned above, CMRP mediated by Co(acac)$_2$ is a method of choice to achieve linear PVAc samples with a narrow molar mass distribution and controlled molar masses. This was confirmed here as shown in Table 1, entry 1. On the other hand, it has been established in a previous report that the two double bonds of DVA are of equal reactivity[56]. Initial experiments were performed in bulk at 40 °C. In such conditions, however, soluble

Table 1. Cobalt-mediated radical polymerization of vinyl acetate and its copolymerization with divinyl adipate in ethyl acetate at 40 °C.

Entry	DVA (mol.%)	[VAc]/[1]	Conv.[a] (%)	M_n (g/mol)[b]	M_p (g/mol)[b]	M_w/ M_n[b]
1	0	60	100	11700	13400	1.4
2	2	60	100	5500	10700	2.4
3	4	60	100	4300	11900	2.6
4	6	60	100	16600	39400	2.8
5	6	120	90	17100	87200	3.4
6	6	180	73	18500	97500	4.4

Conditions: 40 °C, [VAc] = 10 wt% in ethyl acetate. [a] Determined by ^{1}H NMR in $CDCl_3$. [b] Determined by SEC in THF.

PVAc samples were achieved only for low monomer conversions (conversion of 40% of vinyl groups only, after 8 hours of reaction), before macrogelation occurred, whatever the DVA content (see Table S1). In the absence of DVA, the SEC traces were monomodal and narrow (M_w/M_n ~1.1), while they became rapidly multimodal in the presence of DVA with an important increase of the dispersity with the monomer conversion or the content of DVA, in line with expectations for nanogels prepared by RCC. The shift of the SEC traces towards the higher molar mass side confirmed the incorporation of DVA units (Table S1).

Copolymerizations leading to 1st-generation nanogels of PVAc

Better results, *i.e.* higher monomer conversion (up to 90%, as determined by ^{1}H NMR) with no evidence of macrogel formation, were obtained when carrying out CMRccP in ethyl acetate as solvent (at a VAc concentration of 10 wt%). Increasing the DVA concentration from 2 to 6 mol.% led to higher molar masses and dispersities, for a given concentration of R-Co(acac)$_2$ **1** (Table 1, entries 1-4; Fig. S1a and Table S2). Likewise, lower amounts in **1** gave higher molar masses for a fixed amount of DVA (Table 1, entries 4-6). Figure 1 shows the final copolymer, denoted as poly(VAc-6 mol.% DVA) (Table 1, entry 4) after precipitation and subsequent solubilization in THF at 1%w/v, imaged by transmission electron microscopy (TEM). The formation of spherical nanostructures was clearly evidenced, with a statistical analysis of images giving an average value of 12 ± 2 nm, in agreement with the definition of nanogels[1].

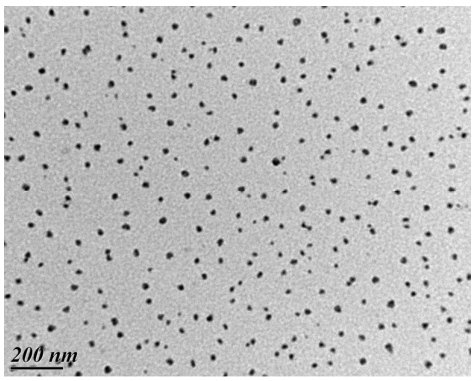
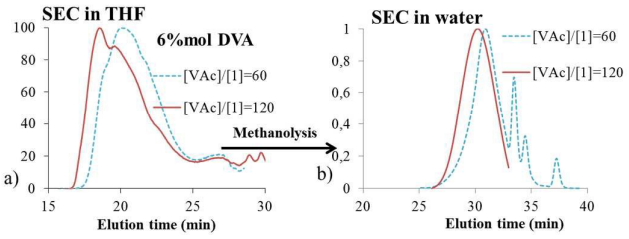


Figure 1. TEM imaging of the precipitated poly(VAc-DVA) nanogel (Table 1, Entry 4). After purification, the compound is re-dissolved in THF at a concentration of 1%w/v, and a drop is deposited on the TEM grid.

Another interest in using DVA as cross-linker is that the crosslinks can be cleaved by a simple basic treatment in methanol (= methanolysis), yielding individual poly(vinyl alcohol) (PVA) chains having the same chain length than that of the constitutive (primary) chains of the parent poly(VAc-DVA) nanogels[9]. Methanolysis was thus carried out using a catalytic amount of NaOH (see experimental section). Molar masses of resulting linear PVA's, as determined by aqueous SEC (Fig. S1b), proved nearly the same for a fixed VAc/**1** ratio, and were close to the value of a PVA sample obtained after methanolysis of a linear PVAc sample prepared using the same ratio. On the other hand, lower amounts in **1** increased the length of the primary chains, as illustrated in Figure 2b. This supported that the constitutive chain length of parent poly(VAc-DVA) nanogels directly depended on the initial concentration of the mediating agent (**1**) during CMRccP, and was independent of the amount of cross-linker for a fixed amount of **1**.



c)

[VAc]/[1]	Before methanolysis			After methanolysis		
	M_n (g/mol.)	M_p (g/mol.)	M_w/ M_n	M_n (g/mol.)	M_p (g/mol.)	M_w/ M_n
60	16600	39400	2.8	6500	5100	1.6
120	17100	87200	3.4	7200	7800	1.3

Figure 2. a) SEC traces in THF of poly(VAc-6 mol.% DVA) nanogels before methanolysis for two different [VAc]/[**1**] ratios (Table 1, entry 4 for [VAc]/[**1**] = 60 and entry 5 for [VAc]/[**1**] = 120); b) SEC traces (in water) of PVA after methanolysis (primary chain length); c) molecular characteristics of the different polymers.

Chain extension reactions leading to 2nd-generation nanogels of PVAc

As already emphasized, dormant C-Co(III) chain-ends are expectedly

preserved in (nano)gels prepared by CMRccP, in contrast to 'conventional' RCC by FRP, hence further modifications as well as chain extensions can be implemented. Introduction of a fresh feed of degassed VAc containing 5 mol.% DVA to a "first-generation" poly(VAc-4 mol.% DVA) nanogel solution ([VAc]/[**1**] = 60) indeed resumed the copolymerization, with no need for adding **1** further. Note here that DVA was added during the chain extension reaction in order to facilitate the observation of the chain extension as noted elsewhere[56]. This 2nd-generation synthesis resulted in core-shell-type nanogels, following a core-first approach. This is exemplified in Figure S2 showing a chain extension of a parent poly(VAc-DVA) nanogel with a new load of VAc/DVA. One can note a clear shift toward higher molar masses after chain extension, witnessing that C-Co(III) chain ends were accessible to grow a "second-generation" nanogel based on PVAc. Comparison of the aqueous SEC trace of the methanolyzed product highlights the chain-extension of the primary chains.

Even more interestingly, synthesis of nanogels with a PVAc-based inner core and a PIL-based outer shell was attempted (Scheme 1). For this purpose, PIL chains featuring hydrophobic bis(trifluoromethylsulfonyl)imide (Tf_2N^-) anions were grown from a "first-generation" poly(VAc-4 mol.% DVA) nanogel. This strategy is based on our recent investigations demonstrating that CMRP of ionic liquid monomers (ILMs) with Tf_2N^- counter-anions can be controlled[44]. *N*-Vinyl-3-ethyl imidazolium bis(trifluoromethylsulfonyl)imide, denoted as $VEtImNTf_2$, was thus added to a solution of a poly(VAc-DVA) nanogel precursor formed at complete monomer conversion (copolymerization similar to Scheme 1, Table 1, entry 3). SEC analysis evidenced the chain extension of the poly(VAc-DVA) nanogel with the shift of the elugram towards the higher molar mass side (Figure S3a). Figure 3 shows the ^{1}H NMR spectrum of the resulting nanogel with characteristic signals of the two monomer units in the polymer chain. By comparison of the integration of the signal of $–CH_2$-*CH*-O- (proton **b**) of VAc at 4.8 ppm and of the signal of aromatic protons **h** of imidazolium ring at 7.8 ppm, the composition of the nanogel can be determined : VAc/$VEtImNTf_2$ = 19.

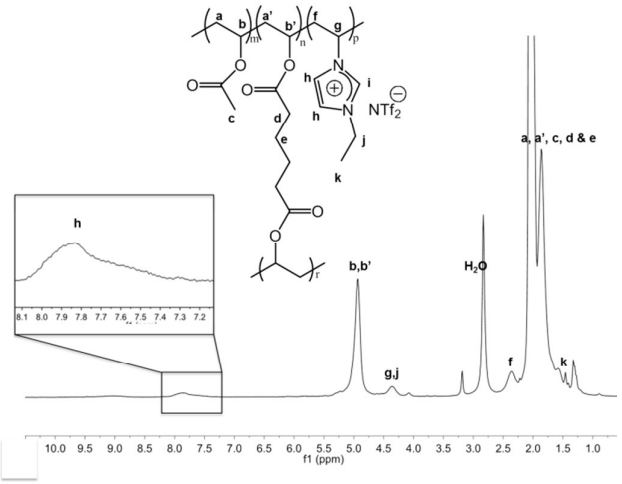


Figure 3. ^{1}H NMR spectrum of the poly(VAc-DVA 4 mol.%) after chain extension reaction with $VEtImNTf_2$, in acetone-d6.

B. PIL nanogels.

Of particular interest, ILMs of *N*-vinyl-3-alkylimidazolium-type with bromide (Br^-) counter-anions can not only be polymerized in organic media *via* CMRP, for instance, in DMF or in DMF/MeOH mixture[42, 61], but also directly in water under mild conditions[43]. On this basis, and having established the proof of concept of CMRccP through the synthesis of neutral PVAc nanogels, we examined the possibility to directly achieve hydrophilic PIL nanogels by this method. Previous works have very recently reported on the synthesis of branched PILs by RCC.[62-64]. To the best of our knowledge, however, there is only one example that has described the synthesis of PIL nanogels by RCC, using RAFT polymerization in this case[65]. Shape-persistent PIL nanogels could be of practical interest, for instance, as additives in coatings or as membranes for CO_2 capture or in highly added value applications, *e.g.* in medical diagnostic tests, antibody purifications, or drug delivery systems[66].

We selected hydrophilic ILMs, namely, *N*-vinyl-3-ethyl imidazolium bromide, denoted as VEtImBr, and 1,13-divinyl-3-decyl diimidazolium bromide (DVI) as cross-linker, again due to the structural similarity of DVI with VEtImBr. CMRccP experiments were conducted at 30 °C, in presence of the same R-Co(acac)$_2$ **1**, either in DMF, or in a mixture of methanol and DMF (1/2 vol.), or directly in aqueous solution. Scheme 1 illustrates theses syntheses (with A and B being VEtImBr and DVI). Both the effect of a variation in the concentration of DVI (2.9 mol % and 4.8 mol % relatively to VEtImBr) and the solvent nature at a given amount of DVI were examined.

Main results are summarized in Table 2 and include the homo-CMRP of VEtImBr and its copolymerization with DVI. For the sake of clarity, SEC traces of soluble samples synthesized in the three different solvents, and obtained after anion exchange, are compared in Figure 4. Control of VEtImBr was first verified, through the increase of molar masses and the production of low dispersities, under the same conditions used for copolymerization experiments (10 wt%, 30 °C, [VEtImBr]/[**1**] = 60).

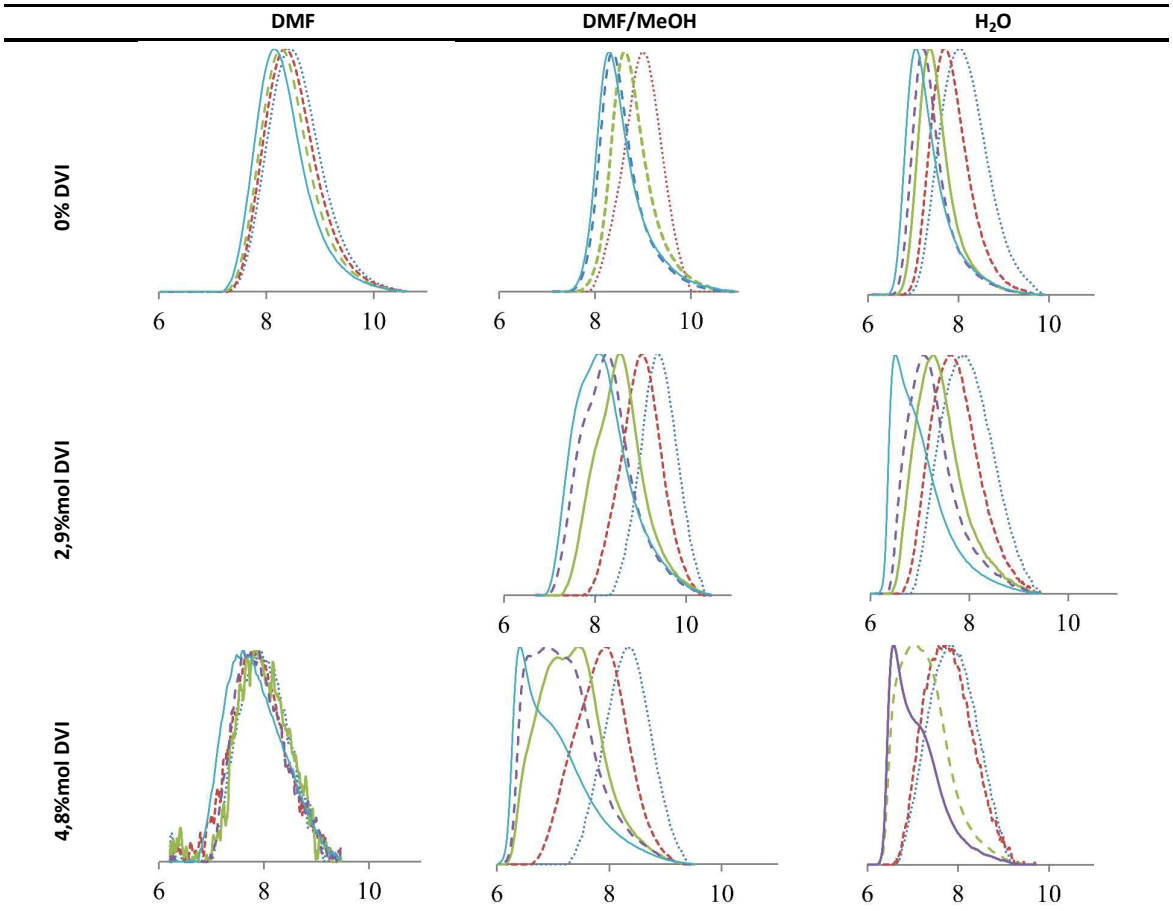


Figure 4. SEC traces (in THF with 10mM $LiTf_2N$ after anion exchange) for the homopolymerizations of *N*-vinyl-3-ethyl imidazolium bromide (VEtImBr) and its copolymerizations with different amounts of 1,13-divinyl-3-decyl diimidazolium bromide (DVI) in various solvents. SEC traces are ordered by solvent nature (per column) and by amount of cross-linker (DVI) (per row). Complete data on reaction monitoring are given on ESI (Table S3).

1st-generation nanogels of PIL in organic media

CMRccP's carried out in solution in DMF gave lower polymerization rates as the amount of DVI increased (polymerization monitoring is provided in Table S3, ESI): conversion was almost complete after 4 hours for CMRccP with 2.9 mol.% of DVI, while a conversion of 77% was reached after the same period of time using 4.8 mol.% DVI (near quantitative conversion was noted for CMRP of VEtImBr, *i.e.* in absence of DVI, after 4h). Transmission electron microscopy (TEM) analysis of the purified poly(VEtImBr-4.8 mol.% DVI) nanogel showed spherical objects with a diameter around 35 nm ± 6 nm (Figure 5a). For TEM analysis, residual monomer was removed by precipitation in diethyl ether, followed by redissolution of the nanogel in water (1wt%) and deposition onto the TEM grid. Importantly, no filtration of the samples was carried out prior to TEM analyses, confirming the absence of aggregates.

As reported elsewhere[50], SEC analysis of poly(vinyl *N*-alkylimidazolium bromide)s is not straightforward and requires an anion-exchange, from Br^- to Tf_2N^-, prior to injection in THF containing 10 mM $LiTf_2N$. Nevertheless, when the anion exchange was applied to our Br-containing PIL nanogels, the resulting Tf_2N-containing products proved hardly soluble in this eluent. SEC analyses were therefore not always reliable because part of the polymer was eliminated when filtering the sample on a 0.2 μm filter prior to analysis; only a signal of low intensity was observed (Figure 4). The linear PILs prepared without DVI were however totally soluble and SEC analysis could be performed (Figure 4 first row).

Table 2. Cobalt-mediated polymerization of *N*-vinyl-3-ethyl imidazolium bromide and its copolymerization with different amounts of 1,13-divinyl-3-decyl diimidazolium bromide in various solvents (polymerization monitoring are detailed in Table S3).

Entry	Solvent	DVI (%mol)	Conv. [a] (%)	M_n [b] (g.mol^{-1})	M_p [b] (g.mol^{-1})	M_w/M_n [b]
1	DMF	0	100	14800	20000	1.25
2	DMF	2.9	100	- [c]	- [c]	- [c]
3	DMF	4.8	95	- [c]	- [c]	- [c]
4	DMF/MeOH	0	75	11900	17800	1.27
5	DMF/MeOH	2.9	85	15300	20900	1.38
6	DMF/MeOH	4.8	81	24900	37100	1.63
7	H_2O	0	87	21200	35600	1.36
8	H_2O	2.9	82	28500	78300	1.59
9	H_2O	4.8	gel	-	-	-

Conditions: 30 °C; [VEtImBr]/[**1**] = 60; $[VEtImBr]_0$= 0.493M, 30 h of polymerization. [a] Conversion was calculated by ^{1}H NMR in deuterated DMSO. [b] Molar masses were determined by SEC in THF after anion exchange using PS calibration. [c] Most of the polymer was removed after filtration of the solution on a 0.2 µm filter, thus preventing the SEC analysis itself.

We then turned to the use of a mixture of DMF and MeOH (8/4, v/v) as solvent for CMRccP (entries 4-6, Table 2). Such a mixture has previously been reported to decrease the CMRP rate of VEtImBr, as compared to DMF[42]. After 24 h of reaction, conversions were in the range 81-85%, irrespective of the concentration in DVI. After 8 hours, conversions for CMRP of VEtImBr and CMRccP using 2.9 mol.% of DVI reached 75% in both cases (Table S3, ESI). In contrast to nanogels prepared in DMF, those prepared in DMF/methanol were soluble in the SEC eluent after anion exchange. This was evidenced by free-column refractometric measurements before and after filtration of the nanogel samples. No significant loss of mass occurred during the filtration step prior to injection in SEC (Figure S4a).

For a same conversion, higher molar masses and dispersities were obtained in the presence of DVI than for in the case of the homopolymerization of VEtImBr (Table S3, ESI), with SEC shapes characteristic of the formation of branched architectures (Figure 4). The multimodality of SEC traces is characteristic of the formation of nanogels[67]. Both the Br-containing linear and nanogel samples were also analyzed by SEC in aqueous media (using 0.1M NaCl and 0.1 vol% trifluoroacetic acid as eluent, see experimental section). Although some interactions of PILs with the SEC columns could not be totally ruled out in these conditions, Figure S5 (ESI) shows unimodal shapes for PILs prepared in absence of DVI with a rather low dispersity, whereas multimodal chromatograms can be observed for PIL nanogels with a high dispersity (Table S4, ESI).

1st-generation nanogels of PIL in water

Even more interesting, water could be directly employed as solvent for a new series of CMRccP experiments, both DVI and VEtImBr being soluble in aqueous media[43], as well as the resulting branched PILs. However, R-Co(acac)$_2$ **1** being insoluble in water, a low amount of acetone was added to ensure homogeneous conditions. In contrast to CMRccP's performed in DMF, rates in water were not significantly affected by the incorporation of DVI. At 8 hours of reaction, for instance, conversion was 73% for CMRP of VEtImBr, and 72% and 78%, respectively, for the CMRccP using 2.9 mol.% and 4.8 mol.% of DVI (Table S3, ESI). However, while in organic solvents, copolymerizations could be run during 30h without macrogelation, the reaction performed in water with 4.8 mol.% of DVI (Table 2,

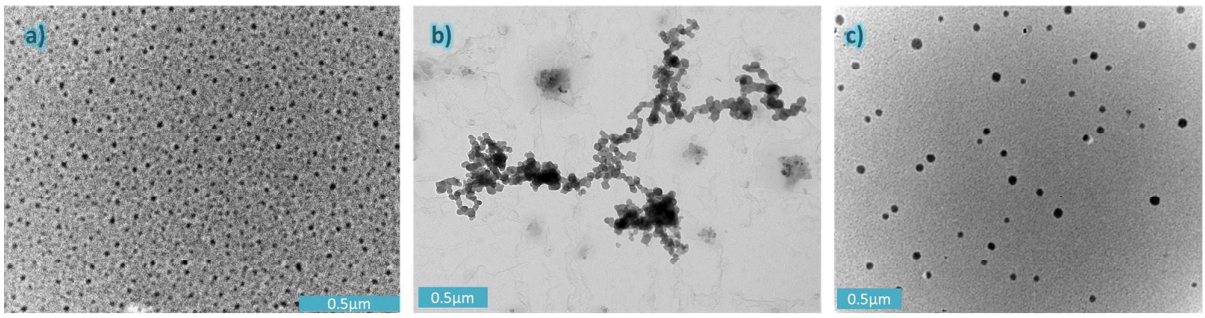


Figure 5. TEM imaging of: a) poly(VEtImBr-4.8 mol.% DVI) synthesized in DMF (scale bar: 500 nm); b) poly(VEtImBr-4.8 mol.% DVI) synthesized in H_2O (scale bar: 500 nm); c) the latter copolymer, after anion exchange and dissolution in THF (scale bar: 500 nm).

entry 9) formed a macrogel overnight.

The PIL nanogel prepared in water with 4.8 mol.% DVI before macrogelation occurs, *i.e.* after 8h of reaction and 78% conversion (Table S3, entry 9, ESI), was imaged by TEM after purification and subsequent re-dissolution in water (Figure 5b). Two major populations were observed: a population was likely due to the aggregation of individual nanogels, while the other seemed to correspond to necklaces of nanogels. Individual nanogels were found in the 20-50 nm size range. Formation of necklaces might be explained either by the development of intermolecular cross-linking occurring at the completion of the CMRccP, or simply to a drying artifact. Hydrophilic nanogels were then subjected to the anion exchange reaction, forming hydrophobic PIL derivatives. The latter materials were dissolved in THF and deposited on a carbon TEM grid (Figure 5c). The above necklaces of nanostructures were not further observed, indicating that these unexpected arrangements were merely due to drying artifacts.

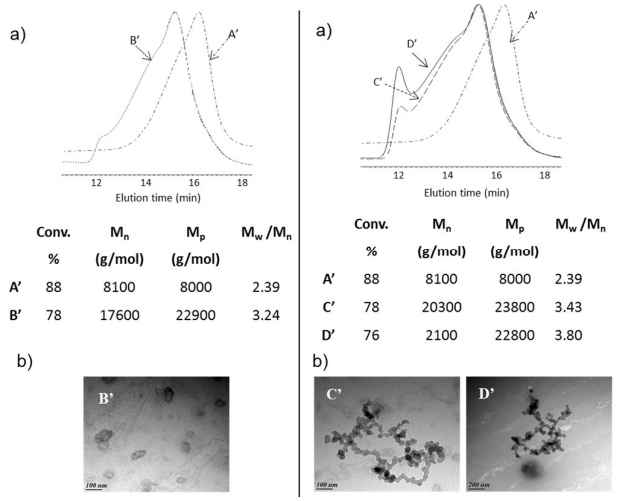
Figure 4 shows the increase of the sample molar mass with the monomer conversion with multimodal SEC traces and an increase in dispersity (Table S3, ESI). Further evidence of intermolecular cross-linking is shown by the kinetics of the CMRccP using 2.9 mol.% of DVI where an increase of the conversion of 2% doubled the peak molar mass (M_p) of the copolymer (from 39700 to 78300 g.mol^{-1}). Refractometric analysis of a typical nanogel sample prepared with 4.8 mol% DVI (sample Table S3, entry 9) evidences that no significant loss of mass occurred during the filtration (on a 0.2 µm filter) of the samples prior to injection in SEC (Figure S4b). Nanogel samples prepared under these conditions after Br^-/Tf_2N^- exchange are therefore soluble in THF and are not forming aggregates higher than 200 nm.

Nanogel formation in the presence of DVI was also evidenced by SEC analysis of Br-containing PILs in aqueous media, *via* the formation of multimodal SEC traces as well and high dispersities (Figure S5, Table S4).

The solvent effect could be accounted by examining, for instance, experiments using 4.8 mol.% of DVI (entries 3, 6 and 9, Table S3; see also CMRP of VEtImBr in Table S3 entries 1, 4 and 7 for comparison). DMF gave rapid reaction kinetics with nanogels that were not totally soluble in the SEC eluent, while both the DMF/MeOH mixture and the aqueous solution induced slower reaction rates. Interestingly, for the same conversion of vinyl group, the copolymerization performed in water with 2.9 mol.% of DVI (Table 2, entry 8) achieved higher molar masses than CMRccP carried out in DMF/MeOH with 4.8 mol.% of DVI (Table 2, entry 6). Furthermore, while M_n values remained close (28800 *vs.* 24900 g/mol), the peak molar mass, M_p, more than doubled (78300 *vs.* 37100 g/mol) indicating a difference in the nanogel structure. In the aqueous solvent, intermolecular cross-linking might be more favored than in organic media, leading to higher M_p values. This is supported by the fact that only the CMRccP conducted in water (with 4.8 mol.% of DVI) led to macrogelation at high conversion.

Chain extension reaction leading to the formation of 2nd-generation nanogels of PIL in water

To demonstrate that PIL nanogels thus prepared in water could be reactivated, a chain extension experiment was performed. To a solution of the 1st-generation poly(VEtImBr-4.8 mol.% DVI) nanogel prepared in water until 88% conversion, an aqueous solution of VEtImBr containing 0, 2.9 or 4.8 mol.% of DVI ([VEtImBr]/[**1**] = 60) was added. Monomer conversions were above 75% in all cases after 24h of polymerization (Figure 6a). SEC traces showed a shift to the higher molar masses, attesting that the C-Co bond could be reactivated (Figure 6a). When DVI was present for chain extension, a very high molar mass peak was observed on the SEC traces (M_p = 329 500 g/mol), which was assigned to inter-nanogels cross-linking. TEM imaging showed well-defined spherical nanostructures for the 2nd-generation, in a range of 40-70 nm diameter (Figure 6b). These experiments thus demonstrated that CMRccP was robust enough to be performed in water with a high chain-end fidelity, enabling the production of second generation PIL nanogels.



	Conv. %	M_n (g/mol)	M_p (g/mol)	M_w/M_n
A'	88	8100	8000	2.39
B'	78	17600	22900	3.24

	Conv. %	M_n (g/mol)	M_p (g/mol)	M_w/M_n
A'	88	8100	8000	2.39
C'	78	20300	23800	3.43
D'	76	2100	22800	3.80

Figure 6. a) aqueous SEC traces and macromolecular parameters of 1st (A') and 2nd generation of PILs nanogels prepared in the absence (B') and presence of 2.9 mol.% (C') or 4.8 mol.% (D') DVI; and b) TEM imaging of the corresponding 2nd generation of nanogels (B' in the absence of DVI; C' in the presence of 2.9 mol.% DVI, and D' in the presence of 4.8 mol.% DVI).

Conclusions

Neutral and positively charged nanogels based on poly(vinyl acetate) (PVAc) and poly(*N*-vinyl-3-ethyl imidazolium bromide), respectively, were prepared by one-step cobalt-mediated radical crosslinking copolymerization (CMRccP) in solution. The pre-synthesized alkyl-cobalt(III) mediating agent enables to introduce rather larger amounts of cross-linker without the occurrence of macrogelation. Use of divinyl adipate as cross-linker allowed cleaving the cross-linked points of PVAc nanogels and accounting that control over the constitutive chain length could be achieved.

The particle size could be fine-tuned by varying the initial monomer/cross-linker/mediating agent ratio. Furthermore, dormant carbon-cobalt(III) chain-ends could be reactivated, enabling the synthesis of core-shell structures, following a divergent approach. Robustness and efficacy of this strategy were demonstrated through its direct implementation in aqueous solution for the production of poly(ionic liquid) (PIL) nanogels. Core-shell nanostructures with a PVAc core and a PIL shell were also accessible by chain extension of a PVAc nanogel by a hydrophobic *N*-vinyl imidazolium salt. Exchange of the counter-ion (not exploited here, except for the purpose of characterization) could provide an additional means to vary the PIL nanogels properties. All these attributes make CMRccP-derived nanogels versatile nano-sized polymeric materials for varied applications, from coatings to catalysis or biomaterials. Work is currently in progress in our groups to exemplify this CMRccP method to other types of ionic liquid monomers and to valorize PIL nanogels in specific applications, including catalysis and as antimicrobial coatings.

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Graphical abstract