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Communication

Organometallic-Mediated Alternating Radical Copolymerization of *tert*-Butyl-2-trifluoromethacrylate with Vinyl Acetate and Synthesis of Block Copolymers Thereof^a

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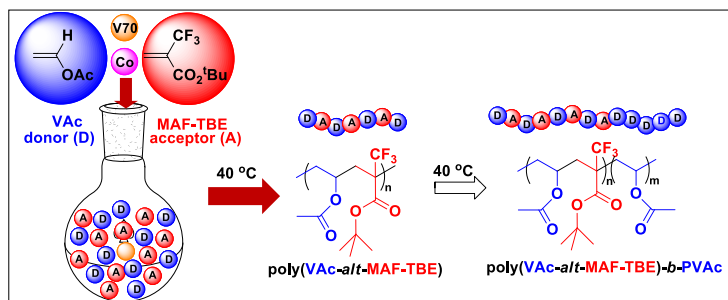
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Organometallic-mediated radical polymerization (OMRP) has given access to well-defined poly(vinyl acetate-*alt*-*tert*-butyl-2-trifluoromethacrylate)-*b*-poly(vinyl acetate) and poly(VAc-*alt*-MAF-TBE) copolymers composed of two electronically distinct monomers: vinyl acetate (VAc, donor, D) and *tert*-butyl-2-trifluoromethacrylate (MAF-TBE, acceptor, A), with low dispersity (≤ 1.24) and molar masses up to 57,000 g/mol. These copolymers have a precise 1:1 alternating structure over a wide range of comonomer feed compositions. The reactivity ratios are determined as $r_{VAc} = 0.01 \pm 0.01$ and $r_{MAF-TBE} = 0$ at 40 °C. Remarkably, from a feed containing >50% molar VAc content, poly(VAc-*alt*-MAF-TBE)-*b*-PVAc block copolymers are produced *via* a one pot synthesis. Such diblock copolymers exhibit two glass transition temperatures attributed to the alternating and homopolymer sequences. The OMRP of this

^a **Supporting Information** is available online from the Wiley Online Library or from the author.

fluorine-containing alternating monomer system may provide access to a wide range of new polymer materials.

FIGURE FOR T₀C_ABSTRACT



1. Introduction

Fluorinated homopolymers are unique materials with outstanding properties for high value added applications. The incorporation of sequences of these polymers into a di- or multiblock^[1] structure is expected to lead to materials of even greater value. To this end, the use of reversible deactivation radical polymerization (RDRP) synthetic techniques should be ideal in most cases. Indeed, Daikin was the first company to develop such materials over 35 years ago,^[2] leading to the industrial scale production of segmented thermoplastic elastomers.^[3] Since these pioneering works, interest in fluorinated block copolymers^[4] has surged in the last decade. This led to the synthesis of a variety of fluorinated block copolymers prepared using telomerization,^[5-8] conventional radical polymerization from functionalized initiators,^[9-12] click chemistry^[13] and using different RDRP techniques^[4, 14]: iodine transfer polymerization (ITP),^[15-17] photoinitiated ITP,^[18] reversible addition fragmentation chain transfer (RAFT) polymerization,^[9, 19-22] and atom transfer radical polymerization (ATRP).^[5, 7, 8] However, for all their merits, telomerization only affords oligomers, and functional initiators lead to broad dispersity.

Alternating copolymers have been reported to constitute a valuable tool to build copolymers with some degree of sequence control.^[23] To date, only a few comonomer pairs have been reported to undergo alternating radical copolymerization such as styrene/maleic anhydride,^[24] styrene/maleimide derivatives,^[25] styrene/methacrylates (in the presence of Lewis acids),^[26] *N*-substituted maleimides/1-methylenebenzo-cycloalkanes,^[27] chlorotrifluoroethylene/vinyl ether^[28] and vinyl ethers/methacrylates.^[29] For other monomer pairs, highly ordered monomer sequence control is still challenging.^[30] Regarding fluorinated polymers, recently, Studer and coworkers^[31] and the Scherf's team^[32] attempted the synthesis of predominantly alternating copolymers composed of hexafluoroisopropyl acrylate with 7-octenyl vinyl ether and *N*-dialkylated benzothiadiazolodithienopyrrole with a dibrominated terephthalophenone derivative, respectively. Recently, Jordan's group reported (phosphinoarenesulfonate)Pd

fluoride complex catalyst reactivation following β -F elimination in ethylene/vinyl fluoride copolymerization.^[33]

2-(Trifluoromethyl)acrylic acid (MAF) and alkyl 2-trifluoromethacrylate (MAF-esters) are very interesting monomers. Although homopolymers can be produced anionically,^[34] these monomers do not homopolymerize under radical conditions,^[35-37] but can be copolymerized together with electron-donating monomers such as vinyl ethers.^[35] MAF- and MAF-esters-containing fluorinated copolymers led to suitable materials for molecularly imprinted polymers, microlithography, polymer electrolyte membranes for fuel cells and for Li-ion batteries.^[35] Recently, a nitroxide-mediated alternating copolymerization of VAc and MAF-TBE has been achieved.^[38] However, the polymerization control was not entirely satisfactory and attempts to synthesize block copolymers failed even with styrene, probably because the C-ON bond at the chain-ends cannot be cleaved at a reasonably low temperature.^[39]

This contribution aims at developing a well-controlled radical copolymerization of VAc and MAF-TBE by organometallic mediated radical polymerization (OMRP) using cobalt(II) acetylacetonate, [Co(acac)₂] as a controlling agent.^[40, 41] It is focused on this particular RDRP technique due to its ability to efficiently control the polymerization of several non-conjugated monomers,^[42, 43] in particular VAc.^[42, 43] Notably, RDRP of VAc was only achieved using a few techniques: reversible addition fragmentation chain transfer (RAFT) polymerization,^[44] iodine transfer polymerization (ITP),^[45] and organometallic-mediated radical polymerization (OMRP).^[42] Following a straightforward “one-pot” approach, a series of well-defined fluorinated copolymers was prepared including 1:1 alternating VAc-MAF-TBE copolymers as well as block copolymers where this poly(VAc-*alt*-MAF-TBE) alternating sequence is followed by a PVAc homopolymer block (Scheme 1). Although the “one-pot” strategy to prepare copolymer-*b*-polymer architectures was reported previously,^[46-48] its implementation in combination with OMRP to synthesize a novel block copolymer (containing a fluorinated alternating block) is unprecedented.

2. Results and Discussion

The homopolymerization of VAc initiated by 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) (V-70) in the presence of [Co(acac)₂] at 40 °C produced PVAc with controlled molar mass ($M_n = 28,200$ g/mol) and low dispersity ($D = 1.16$), as previously described^[49] (entry 1 in Table S1 and **Figure S1**). In contrast, attempts to obtain a MAF-TBE homopolymer under the same conditions failed (entry 2, Table S1), as expected, since MAF-TBE does not homopolymerize under radical conditions.^[35-37]

The OMRP of VAc with MAF-TBE was initiated by V-70/Co(acac)₂ in bulk at 40 °C (Scheme 1) using various MAF-TBE feed contents ($f_{MAF-TBE}$) ranging from 0.1 to 0.9) (entries 3-8, Table S1). The reaction progress (conversions of VAc and MAF-TBE) was monitored by ¹H (equation S1) and ¹⁹F (equation S2) NMR spectroscopies. **Figures S2-S3** show representative stack plots of two such ¹H NMR kinetic experiments using different VAc/MAF-TBE comonomer feed ratios, $f_{MAF-TBE} = 0.5$ and 0.1, respectively. **Figure S4** exhibits a corresponding time evolution of the ¹⁹F NMR spectra for $f_{MAF-TBE} = 0.5$. In all cases, equimolar conversions of VAc and MAF-TBE were recorded, until the depletion of MAF-TBE (**Figure 1** and **Figures S5-S10**), suggesting highly alternating copolymerizations (entries 3-8, Table S1). The ¹H NMR spectra (Figure S2) corresponding to the copolymerization with $f_{MAF-TBE} = 0.5$, display a complex signal around 5.20 ppm, assigned to the -CH group of VAc in the VAc-MAF-TBE alternating dyads. This complex shape probably results from the adjacent stereocenters in VAc and MAF-TBE units. In contrast, copolymerizations using higher VAc feed contents ($f_{MAF-TBE} = 0.1, 0.2$ and 0.3) and continued beyond the complete MAF-TBE consumption, led to poly(VAc-*alt*-MAF-TBE)-*b*-PVAc block copolymers, as evidenced by the appearance of an additional NMR signal centered at 4.80 ppm characteristic of the -CH group of VAc in the PVAc block^[50] (Figure S3).

The semilogarithmic kinetic plots of these copolymerizations (carried out at $f_{MAF-TBE} = 0.1$, 0.2 and 0.3, **Figures S11-S13**) displayed three distinct regimes: a short (30-45 min) induction period (such induction period was already observed for the CMRP of VAc), a relatively fast copolymerization reaction (until complete MAF-TBE consumption), and a slower homopolymerization of VAc, as confirmed by entry 1, Table S1 ($f_{VAc} = 1.0$). Both segments of the plots are linear indicating that both the copolymerization and the homopolymerization followed first order kinetics. As expected, for copolymerizations using 1:1 VAc:MAF-TBE and an excess of MAF-TBE ($f_{MAF-TBE} = 0.7$ and 0.9), the semilogarithmic plots (**Figures S14-S16**) exhibited only one regime corresponding to the alternating copolymerization. When there is no more VAc in the comonomer feed, the polymerization stops. The apparent propagation rate constant of the copolymerization ($k_{p(app)}$) was determined from the slope of the first order kinetic plots ($\ln([M]_0/[M])$ vs. t , **Figure S17a**).^[51] The $k_{p(app)}$ vs. $f_{MAF-TBE}$ plot (**Figure S17b**) reveals a bell-shaped curve with a maximum at $f_{MAF-TBE} = 0.5$ ($k_{p(app)} = 3.9 \times 10^{-4} \text{ s}^{-1}$) that is in further agreement with an alternating copolymerization. The SEC traces (**Figure 2a** and **Figures S18a-S22a**) remained monomodal throughout the polymerization and the M_n vs. conversion plots (**Figure 2b** and **Figures S18b-S22b**) show a regular increase of M_n with monomer conversion, maintaining narrow D . These features are consistent with RDRP.

To gain further insight on the controlling mechanism, we have compared the bond dissociation free energy (BDFE) for the putative $(acac)_2Co$ -VAc-coP and $(acac)_2Co$ -MAF-TBE-coP dormant species (coP = copolymer) by DFT calculations, using model systems where the coP chain beyond the Co-bonded monomer was replaced by an H atom (details are in SI, Pages S7-S8 and Table S2). These new calculations integrated thermal and dispersion corrections, relative to those previously published for $(acac)_2Co$ -VAc-H.^[52] The resulting BDFE for the Co-VAc bond is 31.4 kJ/mol, whereas that of the Co-MAF-TBE is only 8.4 kJ/mol, suggesting a much higher lability of the latter.

In order to study the nature of the chain ends, the controlled copolymerization of VAc/MAF-TBE (80/20) was initiated from a $\text{PVAc}_{<4}\text{-Co(acac)}_2$ initiator and monitored by spin trapping electron paramagnetic resonance (EPR) experiments (**Figures 3 and S23-S24**). Along the polymerization, the dormant species were isolated from aliquots of the reaction mixture and reacted with the *tert*-butyl nitroso ($^t\text{BuNO}$) spin trap. *ESR-a* and *ESR-c* spectra corresponding to $\text{PVAc}_{<4}\text{-}^t\text{BuNO}\cdot$ and to the final poly(VAc-*alt*-MAF-TBE)-*b*-PVAc- $\text{NO}\cdot$, respectively, appear interpretable as the overlap of two different triplets of doublets (*dt*), with similar hyperfine splittings for the doublets but slightly different ones for the triplets. Each of these *dt* envelopes results from the coupling of the radical with N (1:1:1 triplet) and H of CHOAc (doublet) and probably derives from a different stereochemistry (*m* and *r*) of the last dyad (components A and B). Simulation of *ESR-a* (Figure S23) using this model and isotropic parameters gave a satisfactory fit, with component A (64.5%) having $a_{\text{N}} = 36.1$ MHz and $a_{\text{H}} = 4.38$ MHz, and component B (45.5%) having $a_{\text{N}} = 41.2$ MHz and $a_{\text{H}} = 3.81$ MHz. In contrast, the intermediate *ESR-b* spectrum corresponding to the trapping of the intermediate poly(VAc-*alt*-MAFTBE)- Co(acac)_2 species that is present during the alternating copolymerization regime appears as a mixture of two signals: a major 1:1:1 triplet assigned to PMAF-TBE(^tBu) $\text{NO}\cdot$, in which only the coupling of the unpaired electron with the N nucleus is visible, and a smaller feature corresponding to PVAc- $\text{NO}\cdot$. Although no quantitative information can be deduced, this observation suggests that both types of chain ends (P-MAF-TBE \cdot and P-VAc \cdot) might be reversibly trapped by Co(acac)_2 in the alternating copolymerization regime.

Confirmation of the alternating structure was obtained by ^1H , ^{19}F , ^{13}C and 2D NMR characterizations. The detailed NMR assignments are available in the supporting information (**Figures S25-S32**). MALDI-TOF spectrometry of both poly(VAc-*alt*-MAF-TBE) alternating copolymer and poly(VAc-*alt*-MAF-TBE)-*b*-PVAc block copolymer was also attempted to confirm and determine the monomer sequences but these analyses gave inconclusive results.

Actually, NMR spectroscopy evidences and the determination of the reactivity ratios (see below) constitute sufficiently solid proofs to claim alternating microstructures of these polymers.

The OMRP kinetics enabled us to determine the reactivity ratios of these monomers (details are in SI, Page S7). The copolymer-monomer composition curve (**Figure 4**) reveals that the copolymer composition is always 1:1, independent of the feed composition. These data points, fitted with the Mayo-Lewis copolymerization equation^[53] (S3) provide the following reactivity ratios: $r_{VAc} = 0.01 \pm 0.01$ and $r_{MAF-TBE} = 0$ at 40 °C. These values are close to zero, which illustrates exclusive cross-propagation leading to alternating copolymerization, independent of the comonomer feed.

The thermal properties of these copolymers were studied by thermogravimetric analysis and differential scanning calorimetry (DSC). The 21% weight loss of the poly(VAc-*alt*-MAF-TBE) copolymer just above 150 °C (*vs.* a reduced weight loss for the block copolymer and no loss for PVAc, **Figure S33**) matches the value calculated for the loss of the carbo-*tert*-butoxy groups of the MAF-TBE monomers. It is likely due to the *tert*-butyl ester group decomposition into a carboxylic acid function with release of isobutene, followed by the decarboxylation of the carboxylic acid group (Scheme S1).^[54] The polymers exhibited glass transition temperatures (T_g 's) depending on both the monomer compositions and sequences (**Figure 5**). PVAc ($T_g = 40$ °C) and poly(VAc-*alt*-MAF-TBE) alternating copolymer ($T_g = 72$ °C) displayed a single T_g . The poly(VAc-*alt*-MAF-TBE)-*b*-PVAc copolymer exhibited two T_g 's at 43 °C and 67 °C, which correspond to those of the PVAc homopolymer and of the poly(VAc-*alt*-MAF-TBE) alternating copolymer, respectively.

3. Conclusions

A simple approach for the preparation of well-defined 1:1 alternating VAc (electron-donating): MAF-TBE (electron-accepting) copolymers and a novel diblock copolymer

(composed of one alternating block and one PVAc homopolymer sequence) by OMRP has been described. This is the first report on the synthesis of a fluorinated copolymer using OMRP. The relative length of the two blocks can be varied by simply tuning the comonomer feed ratio. The very low reactivity ratios account for the nearly perfect alternating copolymer structure over the whole tested range of comonomer feeds. Due to the remarkable properties of the fluorinated groups (low refractive index/dielectric constant, and interesting surface properties), the resulting copolymers are of interests for potential applications in high value added materials (e.g., coatings for optics, lithography, to prepare graft copolymer surfactants and fluorinated hydrophilic copolymer for membranes for water purification. This one-pot synthetic strategy will further contribute to the development of high-performance sequence-specific copolymers, a step toward advanced materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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Scheme & Figure Captions

Scheme 1. Synthesis of either poly(VAc-*alt*-MAF-TBE) alternating copolymers or poly(VAc-*alt*-MAF-TBE)-*b*-PVAc block copolymers by “one-pot” OMRP.

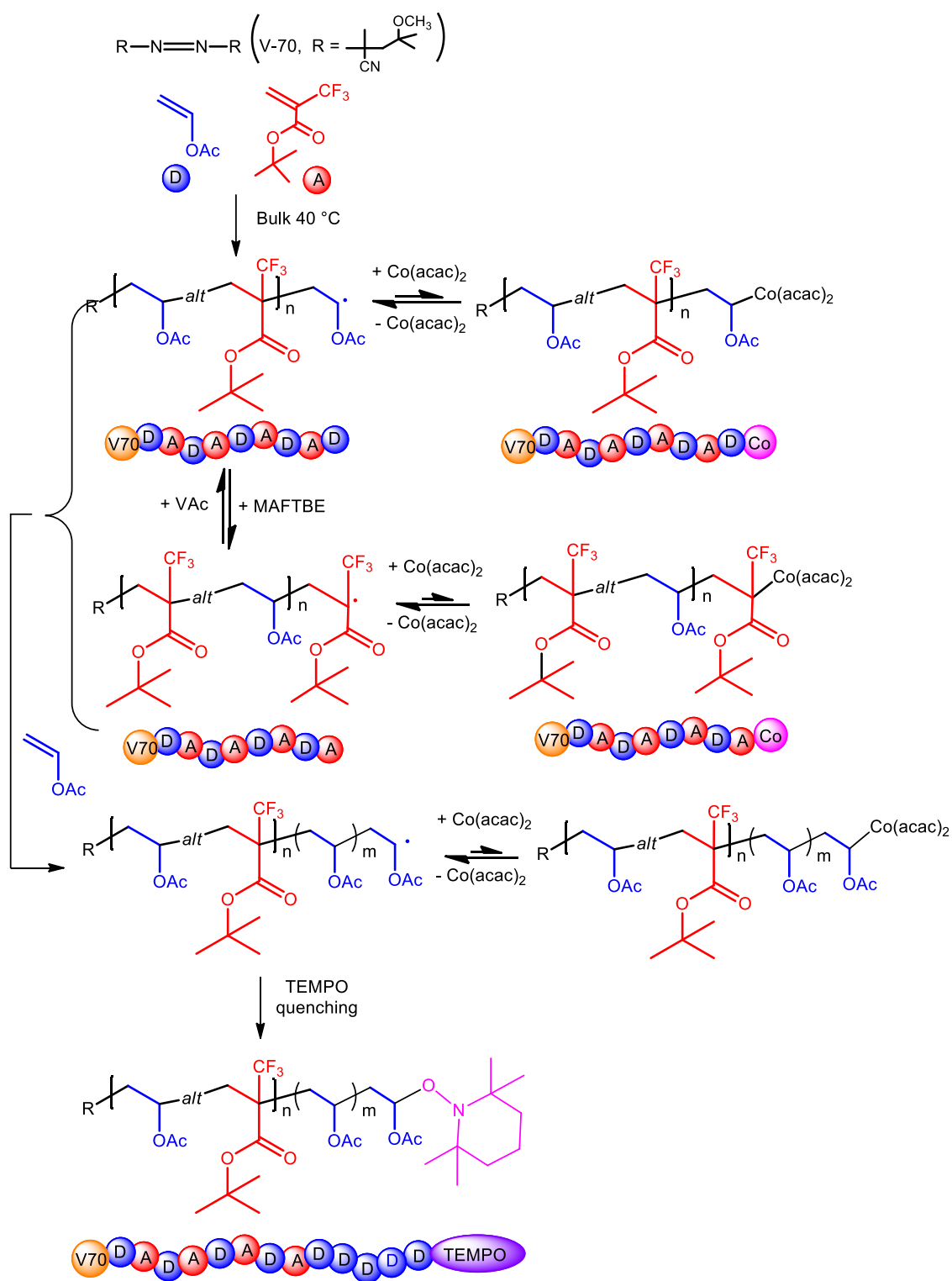
Figure 1: No. of mmol monomer conversion vs. time plot of VAc and MAF-TBE during the OMRP of VAc and MAF-TBE ($f_{MAF-TBE} = 0.1$) mediated by V-70/Co(acac)₂ at 40 °C in bulk (entry 3, Table S1).

Figure 2: a) Evolutions of the SEC traces vs. time and b) plot of M_n and D vs. the total monomer conversion for the OMRP of VAc and MAF-TBE ($f_{MAF-TBE} = 0.5$) mediated by V-70/Co(acac)₂ at 40 °C in bulk (entry 6, Table S1).

Figure 3: EPR spectra of the spin trapped PVAc-Co(acac)₂, poly(VAc-*alt*-MAFTBE)-Co(acac)₂ and poly(VAc-*alt*-MAFTBE)-*b*-PVAc-Co(acac)₂ (see Experimental Section in the SI for the detailed experimental conditions).

Figure 4: Evolution of copolymer-monomer composition curve for the OMRP of VAc with MAF-TBE mediated by V-70/Co(acac)₂ in bulk at 40 °C.

Figure 5: DSC thermograms of pure PVAc, poly(VAc-*alt*-MAF-TBE) and poly(VAc-*alt*-MAF-TBE)-*b*-PVAc copolymers (entries 1, 6 and 3, respectively, Table S1).



Scheme 1. Synthesis of either poly(VAc-*alt*-MAF-TBE) alternating copolymers or poly(VAc-*alt*-MAF-TBE)-*b*-PVAc block copolymers by “one-pot” OMRP.

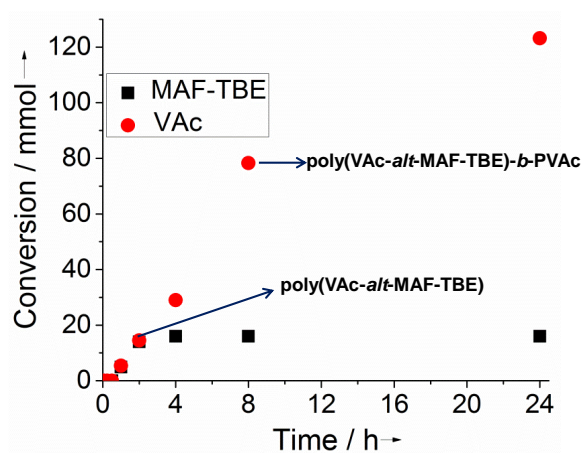


Figure 1. No. of mmol monomer conversion vs. time plot of VAc and MAF-TBE during the OMRP of VAc and MAF-TBE ($f_{MAF-TBE} = 0.1$) mediated by V-70/Co(acac)₂ at 40 °C in bulk (entry 3, Table S1).

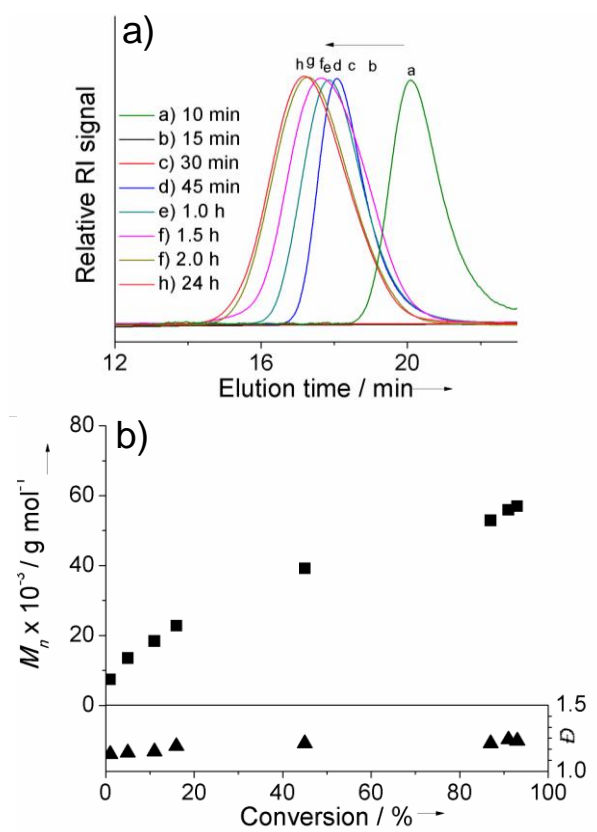


Figure 2. a) Evolutions of the SEC traces vs. time and b) plot of M_n and D vs. the total monomer conversion for the OMRP of VAc and MAF-TBE ($f_{\text{MAF-TBE}} = 0.5$) mediated by V-70/Co(acac)₂ at 40 °C in bulk (entry 6, Table S1).

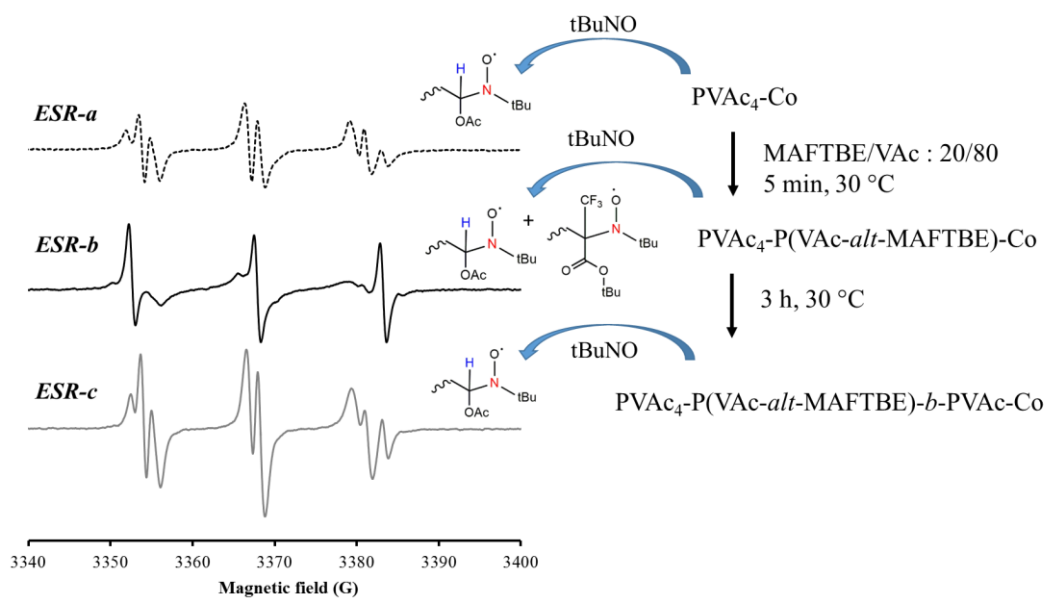


Figure 3. EPR spectra of the spin trapped PVAc-Co(acac)₂, poly(VAc-*alt*-MAFTBE)-Co(acac)₂ and poly(VAc-*alt*-MAFTBE)-*b*-PVAc-Co(acac)₂ (see Experimental Section in the SI for the detailed experimental conditions as well as simulated spectra).

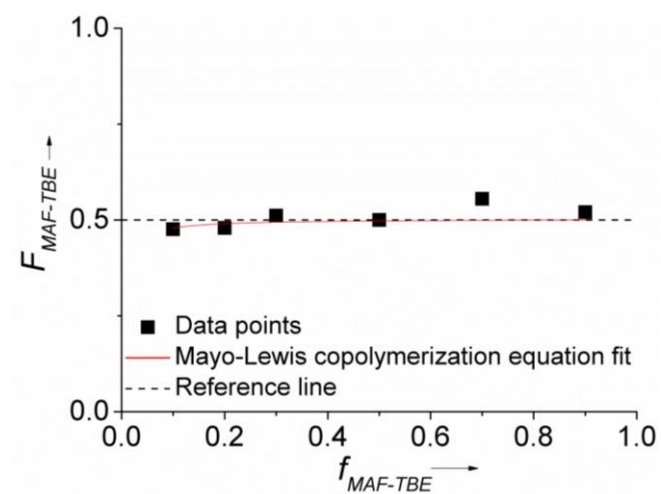


Figure 4. Evolution of copolymer-monomer composition curve for the OMRP of VAc with MAF-TBE mediated by V-70/Co(acac)₂ in bulk at 40 °C.

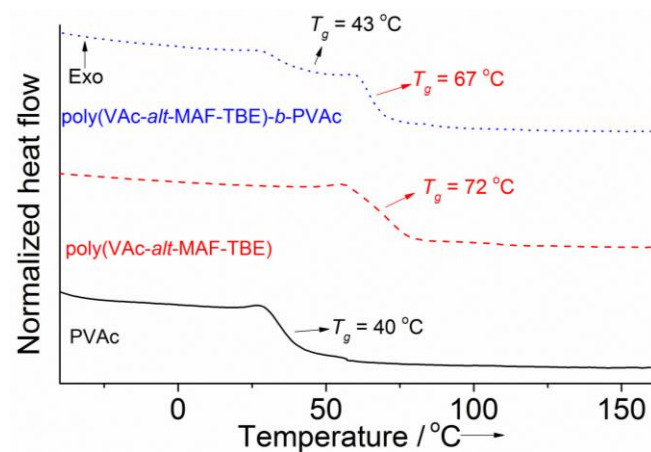


Figure 5. DSC thermograms of pure PVAc (black thermogram), poly(VAc-*alt*-MAF-TBE) (red dotted curve) and poly(VAc-*alt*-MAF-TBE)-*b*-PVAc copolymers (blue dotted curve) (entries 1, 6 and 3, respectively, Table S1).

The table of contents entry

Organometallic-mediated radical copolymerization has been successfully employed for 1:1 alternating controlled copolymerization (independent of the monomer feed) of VAc (electron-donating) and MAF-TBE (electron-accepting). By simply tuning the comonomer feed ratio, well-defined poly(VAc-*alt*-MAF-TBE) alternating copolymers or novel poly(VAc-*alt*-MAF-TBE)-*b*-PVAc diblock copolymers (comprising of one alternating block and one homopolymer block) can be prepared.

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Organometallic-Mediated Alternating Radical Copolymerization of *tert*-Butyl-2-trifluoromethacrylate with Vinyl Acetate and Synthesis of Block Copolymers Thereof

ToC figure

