Cobalt-Mediated Radical Polymerization Routes to Poly(vinyl ester) Block Copolymers

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ABSTRACT: Cobalt-mediated radical polymerizations (CMRPs) utilizing redox initiation are demonstrated to produce poly(vinyl ester) homopolymers derived from vinyl pivalate (VPv) and vinyl benzoate (VBz), and their block copolymers with vinyl acetate (VAc). Combining anhydrous $Co(acac)_2$, lauroyl peroxide, citric acid trisodium salt, and VPv at 30 °C results in controlled polymerizations that yield homopolymers with $M_n = 2.5$–27 kg/mol with $M_w/M_n = 1.20$–1.30. Homopolymerizations of scrupulously purified VBz proceed with lower levels of control as evidenced by broader polydispersities over a range of molecular weights ($M_n = 4$–16 kg/mol; $M_w/M_n = 1.34$–1.65), which may be interpreted in terms of the decreased nucleophilicity of these less electron donating propagating polymer chain ends. Based on these results, we demonstrate that sequential CMRP reactions present a viable route to microphase separated poly(vinyl ester) block copolymers as shown by small-angle X-ray scattering analyses. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 242–249, 2011

KEYWORDS: biodegradable; block copolymers; cobalt-mediated radical polymerization (CMRP); degenerate transfer polymerization; radical polymerization; self-assembly; vinyl acetate; vinyl ester

INTRODUCTION Controlled/living polymerizations furnish access to macromolecular materials with well-defined molecular architectures, molecular weights, and molecular weight distributions.[1] Each controlled polymerization technique is well suited for the (co)polymerization of monomers of a given structural type. Anionic[2] and cationic[3,4] polymerizations are commercially practiced for the synthesis of polymers derived from styrene, dienes, isobutylene, and vinyl ether monomers. Controlled free radical processes such as atom transfer radical polymerization,[5,6] nitroxide-mediated radical polymerization,[7] and reversible-addition fragmentation chain transfer (RAFT)[8,9] polymerizations facilitate controlled enchainment of styrenic and acrylic monomers, with limited applications to conjugated dienes. Vinyl ester monomers have remained conspicuously absent from the list of monomers amenable to controlled polymerizations until relatively recently.[10–15]

The quest for new, environmentally benign materials motivates the search for families of economically produced monomers and polymers with widely tunable properties, processabilities, and inherent degradability.[16] Many efforts thus far have focused on polymers containing cleavable linkages in the main chain (e.g., poly(esters) and poly(amides)), which degrade by hydrolysis into small molecules.[17] In spite of their all carbon backbone, poly(vinyl esters) degrade by ester side chain hydrolysis to yield carboxylic acids and biodegradable poly(vinyl alcohol).[18,19] As a commodity polymer, PVAc is commonly used in settings ranging from biomedical devices[20] to paper-coating and adhesive applications.[21] The properties of other vinyl ester homopolymers are, however, quite limited and have prevented their widespread use. Surprisingly, the sequential block copolymerization of vinyl esters has only recently been reported[12,13] and the properties of poly(vinyl ester) block copolymers remain unknown. Poly(vinyl ester) block copolymers are expected to possess a subset of the desirable properties of poly(acrylates) and polyolefins, with the added benefit of chemical and biochemical degradability.[20]

Degenerate chain transfer polymerizations have recently emerged as a useful tool for controlled polymerizations of vinyl esters and other highly reactive, nonconjugated monomers such as *N*-vinyl pyrrolidone. Iodine transfer polymerization enables the synthesis of poly(vinyl acetate) (PVAc) with well-defined molecular weights, relatively narrow molecular weight distributions ($M_w/M_n = 1.30$–1.40), and controlled tacticities.[22–24] More recent reports have established the broad utility of RAFT/MADIX processes in mediating the controlled homopolymerizations of VAc, vinyl pivalate (VPv), vinyl benzoate (VBz), and vinyl neodecanoate (VNd) to produce narrow molecular weight distribution poly(vinyl esters) with variable architectures.[10–13] Yamago[25] has demonstrated the utility of organo-tellurium, -stibine, and -bismuthine degenerate transfer reactions for the polymerization of styrenic, acrylic, and vinyl ester monomers, as well as *N*-vinyl

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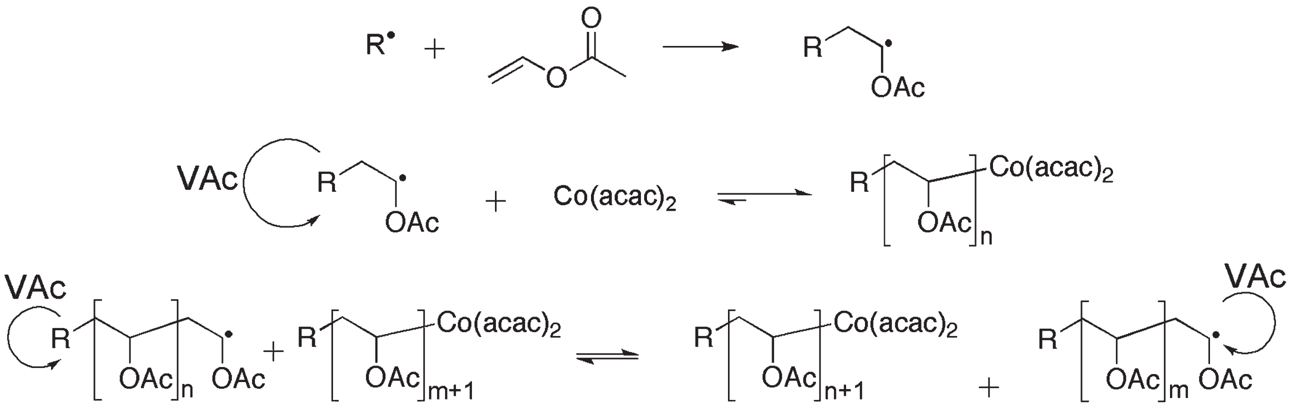


SCHEME 1 Mechanism of cobalt-mediated radical polymerization of vinyl acetate (VAc).

pyrrolidone and other nonconjugated monomers. Cobalt-mediated radical polymerization (CMRP) has emerged as another convenient degenerate transfer polymerization methodology for the controlled enchainment of VAc and acrylic monomers (Scheme 1).[26–30] In these procedurally simple polymerizations, a combination of a Co(II) complex, a free radical initiator, and VAc generates alkyl-Co(III) species *in situ* that mediate the controlled polymerization of VAc to PVAc (M_w/M_n = 1.15–1.3).[31] Debuigne et al.[26] have extensively explored the scope and utility of CMRP for the synthesis of block copolymers of VAc with acrylates and acrylonitrile, styrene, and olefin monomers through sequential chain extension reactions and various chain-end transformations that enable tandem copolymerizations of “mechanistically incompatible monomers.” It is worth noting that CMRP reactions conducted in the absence of strongly coordinating axial ligands for cobalt typically operate by a combination of a reversible trapping and a degenerate chain transfer mechanism involving a transient dialkyl-Co(IV) intermediate,[32] whereas the addition of coordinating ligands to the polymerization reaction (e.g., DMSO) typically biases the polymerization mechanism toward an organometallic radical polymerization reaction manifold.[33–36] Additionally, the polymerization behavior of cobalt complexes depends sensitively on the ancillary ligation at the metal center and may thus be tuned to control the reactivity of any given monomer.[30,37,38]

Toward the goal of developing vinyl esters as a monomer platform for the generation of new biodegradable polymeric materials with widely tunable properties, we demonstrate the viability of CMRP using redox initiation[39] for the homopolymerization of VPv and VBz and for vinyl ester block copolymerization to yield well-defined microphase separated poly(vinyl ester) block copolymers with VAc.

RESULTS AND DISCUSSION

Bulk VAc homopolymerizations mediated by $Co(acac)_2$ at 30 °C using lauroyl peroxide (LPO) as an initiator and citric acid (CA) or citric acid tribasic sodium salt (Na_3CA) as a reducing agent in a ratio [VAc]:[Co]:[LPO]:[Na_3CA] = 339:1.77:1.36:1.00 provide PVAc with M_n = 2.5–37.5 kg/mol and narrow molecular weight distributions (M_w/M_n = 1.17–1.29), in accordance with prior work by Bryaskova et al.[39] This previously reported redox initiation scheme was chosen to obviate the use of expensive, low temperature azo-initiators for CMRP and the byproducts of CA oxidation were not found to have deleterious effects on the course of the polymerization. We found that both Na_3CA and CA both furnish a high level of control in bulk CMRP of VAc, even though these reagents are not particularly soluble in the monomer used for these reactions. PVAc molecular weights linearly increase with monomer conversion at low conversions ($\leq$ 5%), consistent with a controlled polymerization process and the aforementioned report by Bryaskova et al.[39] In this low conversion limit, we consequently observe that M_n monotonically increases with time in a linear fashion as illustrated in a plot of M_n versus reaction time t (Fig. 1). Extrapolation of the latter plot to the low molecular weight limit provides an estimate of the induction period during which no polymer is formed, which is ascribed to the time required for all of the Co(II) precursor to be converted into alkyl-Co(III) species that mediate the degenerate transfer polymerization.[32] Our observed polymerization induction periods are substantially shorter (t_{ind} = 1.5 h) than those previously reported (t_{ind} = 3–4 h),[38] which we attribute to differences in monomer

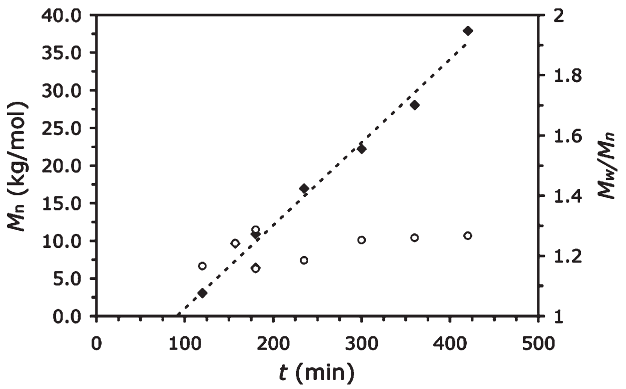


FIGURE 1 M_n versus time (filled symbols) and M_w/M_n versus time plots (open circles) for CMRP of VAc with [VAc]:[Co]:[LPO]:[Na_3CA] = 339:1.77:1.36:1.00. The dotted line is a linear regression of the M_n versus time data indicating an induction period t_{ind} = 1.5 h.

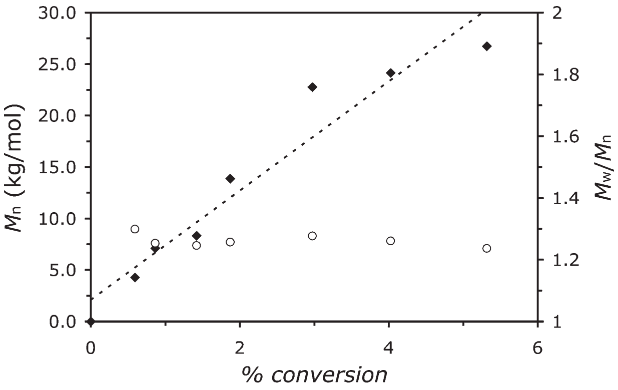


FIGURE 2 M_n versus monomer conversion (filled symbols) and M_w/M_n versus monomer conversion plots (open circles) for CMRP of VPv with [VPv]:[Co]:[LPO]:[Na_3CA] = 340:1.76:1.36:1.00. The dotted line reflects a best fit that is intended as a guide to the eye; see text for details.

purification protocols and batch-wise variability in VAc monomer purity. Due to the facile hydrolysis of VAc to acetaldehyde and acetic acid, VAc is inherently contaminated with a potent aldehyde chain termination agent.[21] Careful purification of the VAc monomer results in removal of the acetaldehyde and reduced induction periods. Consistent with our earlier studies of RAFT polymerizations of vinyl esters, this finding underscores the need to rigorously purify vinyl ester monomers to achieve controlled and reproducible polymerization behavior.[12]

Bulk CMRP of freshly distilled VPv at 30 °C proceeds in a manner similar to that of VAc. Using [VPv]:[Co]:[LPO]:[Na_3CA] = 340:1.76:1.36:1.00, VPv homopolymerizations yield polymers with $M_n = 2.5$–27 kg/mol having narrow polydispersities ($M_w/M_n = 1.20$–1.30), the latter of which appear to be independent of monomer conversion. Linearity of the M_n versus monomer conversion plot indicates that this polymerization is well controlled (Fig. 2). In spite of the linearity of this plot, we note that the observed molecular weights are much higher than those theoretically predicted from the equation

$$M_{n,thy} = p[M]_0/[Co(acac)_2]_0,$$

where p is the monomer conversion, $[M]_0$ is the initial monomer concentration, and $[Co(acac)_2]_0$ is the initial cobalt complex concentration, which assumes that every cobalt complex regulates the growth of one polymer chain. By examining the ratio $M_{n,thy}/M_{n,expt} = 0.030$–0.050, we observed that the initiation efficiency in this system is low; this indicates that a substantial amount of the cobalt complex may participate in oxidative side reactions, such as trapping of the carboxy radicals resulting from LPO decomposition to generate inactive Co(III) species as previously suggested by Bryaskova et al.[39] Extrapolation of the corresponding M_n versus reaction time plot for this polymerization reaction indicates an induction period $t_{inh} = 2.5$ h (data not shown). These polymerizations proceed with a comparable level of control to bulk VAc polymerizations, reflecting the comparable reactivities of the propagating chain ends in these reactions and the ability of the Co(III) species to form and to mediate reactions of nucleophilic α-acyloxy carbon-centered radicals. The near independence of the polydispersity with increasing conversion further suggests that polymeryl-Co(III) species are easily generated and that a rapid degenerate chain transfer equilibrium is readily established, thus resulting in controlled polymerizations.

Studies of bulk VBz homopolymerizations yielded notably different results from those of the alkyl vinyl esters. Using [VBz]:[Co]:[LPO]:[Na_3CA] = 340:1.77:1.36:1.00, bulk VBz polymerizations at 30 °C proceed with lower levels of control to produce polymers having $M_n = 4$–16 kg/mol and $M_w/M_n = 1.35$–1.64 with much shorter induction periods ($t_{ind} = 0.25$ h); reproducible polymerization kinetics were obtained only after scrupulously purifying the VBz monomer by sequential vacuum distillation from CaH_2 and reactive distillation from AIBN. While M_n increases linearly with monomer conversion (Fig. 3), we note that the observed molecular weights are much larger than those that are theoretically anticipated based on the level of monomer conversion, initial monomer concentration, and the $Co(acac)_2$ concentration. Examination of the ratio $M_{n,thy}/M_{n,expt} = 0.016$–0.024 demonstrates that the initiation efficiency of this system is quite low and that side reactions shunt a majority of the cobalt(II) complex into some inactive form as previously observed by Bryaskova et al.[39] The relatively higher values of M_w/M_n indicate that propagating PVBz chains are less effectively captured by $Co(acac)_2$ and less well controlled by alkyl-Co(III) species generated *in situ* when compared with PVAc and PVPv chain ends. The observed effects may stem from the presence of the less electron donating α-benzoyloxy substituent adjacent to the propagating carbon radical center in PVBz that: (i) diminishes the efficiency with which polymeryl-Co(III) species are produced and (ii) decreases the propensity of the propagating chain end to undergo nucleophilic degenerate transfer reactions with polymeryl-Co(III)

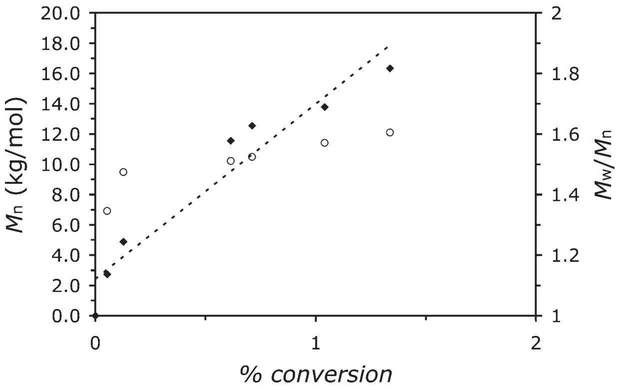
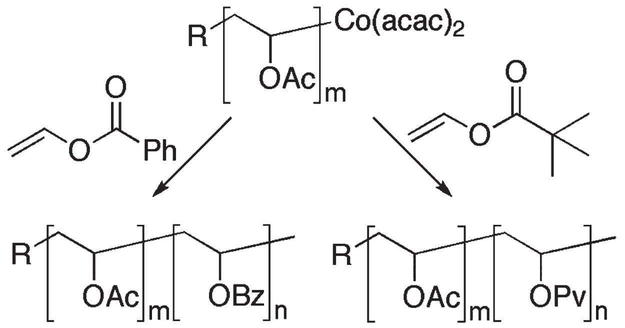


FIGURE 3 M_n versus conversion (filled symbols) and M_w/M_n versus monomer conversion plots (open circles) for CMRP of VBz with [VBz]:[Co]:[LPO]:[Na_3CA] = 340:1.77:1.36:1.00. The dotted line is reflects a best linear fit that is intended as a guide to the eye; see text for details.



SCHEME 2 CMRP block copolymerization of VAc with VBz and VPv.

chain transfer agents via a putative dialkyl-Co(IV) species.[26] The confluence of these effects reduces the observed induction times and gives rise to uneven initiation and propagation of the polymer chains, leading to broader polydispersities. The lower degree of control observed in the CMRP of the less electron donating VBz monomer is consistent with previous reports of difficulties associated with the polymerization of vinyl chloroacetate.[40] In view of mechanistic studies of CMRP,[32] these findings suggest that these relatively electron poor vinyl ester monomers do not effectively undergo controlled CMRP in the absence of coordinating ligands for cobalt. Similar effects in RAFT homopolymerizations of VBz and VClAc have been observed and were attributed to the reduced electron donating character of the propagating PVBz chain end that reduces the rate of chain transfer by a combination of slow addition to the RAFT agent and slow fragmentation of the tertiary carbon-centered radical intermediate.[12,41] This type of behavior has also been previously termed "hybrid behavior" in the RAFT literature as observed by Barner-Kowollik et al.[42] in the dithiobenzoate-mediated RAFT polymerization of methyl methacrylate and by Klumperman and coworkers[43] in xanthate-mediated *N*-vinyl pyrrolidone RAFT polymerizations.

In an attempt to gain further insights into the problems encountered in the CMRP of VBz, we studied the homopolymerization of vinyl 4-methoxybenzoate (MeOVBz) with [MeOVBz]:[Co]:[LPO]:[Na_3CA] = 341:1.78:1.37:1.00 with [MeOVBz] = 1.6 M in C_6H_6. Based on the electron donating character of the methoxy substitutent of the aromatic vinyl ester, we hypothesized that the reactivity of the propagating radical toward the cobalt complex would increase to provide better polymerization control and narrower polydispersities. These polymerizations instead proceeded sluggishly at 30 °C and yielded only small amounts of polymer after 77.5 h with M_n = 2.3 kg/mol and M_w/M_n = 2.11. We attribute the observed reactivity to the previously observed slow homopolymerization of MeOVBz at 30 °C and the dilution of the reaction medium with C_6H_6 required for solution polymerization.[44]

Sequential CMRP block copolymerizations of VAc with acrylic,[27,33] styrene,[45] and olefin[45] monomers have been previously reported without chain end transformations, whereby an air-sensitive PVAc-Co(acac)$_2$ macroinitiator was isolated by removal of excess monomer *in vacuo*, followed by introduction of a second monomer to initiate polymerization of a second block. Building on this foundation, we explored the sequential block copolymerization of VAc with VPv and VBz by CMRP as an alternative to RAFT polymerization syntheses of reported poly(vinyl ester) block copolymers. Due to their higher volatilities, either VAc or VPv may be used to synthesize an initial homopolymer block; however, the low volatility of VBz limits its ability to be removed *in vacuo* for chain extension reactions. Consequently, VBz was typically incorporated into block copolymers by CMRP as the final block.

PVAc-*b*-PVBz diblock copolymers may be synthesized by a two-step sequential monomer addition polymerization procedure (Scheme 2 and Table 1). Bulk homopolymerization of VAc with [VAc]:[Co]:[LPO]:[Na_3CA] = 339:1.77:1.36:1.00 at 30 °C for 4.2 h followed by removal of the monomer *in vacuo* yielded a PVAc-Co(acac)$_2$ macromolecular chain transfer agent with M_n = 8.79 kg/mol and M_w/M_n = 1.22. Redissolution of the cobalt end-capped macromolecular chain transfer agent in bulk VBz and warming to 30 °C resulted in the formation of a PVAc-*b*-PVBz diblock copolymer, which was quenched by addition of a solution of TEMPO radical after 5.75 h to mitigate oxidative chain coupling reactions upon exposure to air. Quantitative ^{1}H NMR spectroscopy of this PVAc-*b*-PVBz-**1** using the PVBz methine (δ 5.20 ppm) and the PVAc methine (δ 4.85 ppm) resonances indicates that the polymer composition is 48.9 mol % VAc (Fig. 4). SEC analyses [Fig. 5(a)] demonstrate that this protocol yields a unimodal diblock copolymer with $M_{n,NMR}$ = 24.6 kg/mol and M_w/M_n = 1.74, based on the absolute

TABLE 1 Poly(vinyl ester) Block Copolymers Synthesized by Sequential CMRP

	Initial Block		Diblock Copolymer			
Entry	M_n (kg/mol)[a]	M_w/M_n[b]	$M_{n,total}$ (kg/mol)[c]	M_w/M_n[b]	Composition (mol % VAc)[c]	Morphology[d]
PVAc-*b*-PVBz-**1**	8.79	1.22	24.4	1.74	0.49	dis
PVAc-*b*-PVBz-**2**	15.6	1.42	36.9	1.61	0.56	dis
PVAc-*b*-PVPv-**1**	19.3	1.35	141	1.32	0.19	unknown

[a] M_n from SEC analysis with Mark-Houwink corrected polystyrene standards.

[b] Obtained from SEC analysis relative to polystyrene standards.

[c] $M_{n,total}$ was obtained using the degree of polymerization of the PVAc block from SEC analysis and the polymer composition determined from quantitative ^{1}H NMR.

[d] From SAXS measurements at 150 °C; dis = disordered.

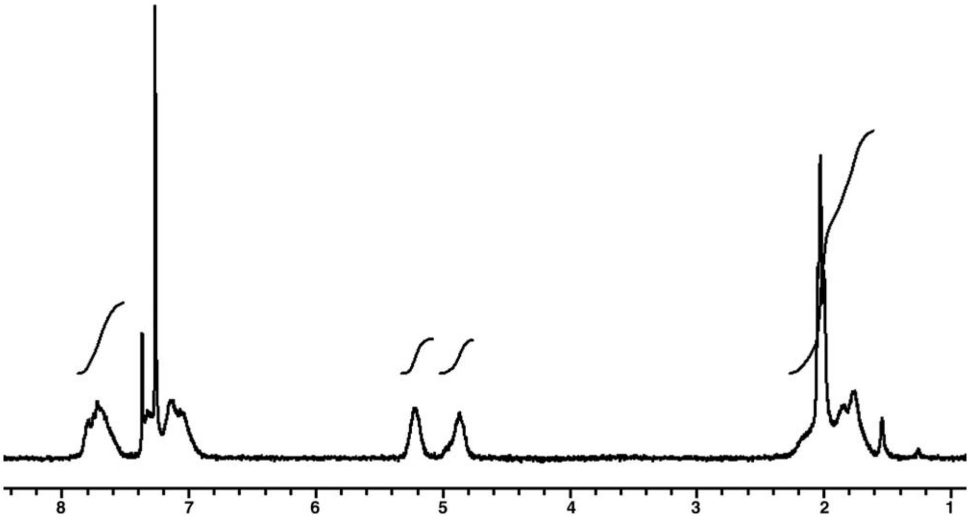


FIGURE 4 ^{1}H NMR spectrum of PVAc-*b*-PVBz-**1** with [VAc] $=$ 48.9 mol % synthesized by sequential CMRP.

molecular weight of the PVAc starting block and the polymer composition. The somewhat broad polydispersity of this block copolymer likely originates in the low propensity of the PVBz chain end to undergo degenerate transfer as observed in VBz homopolymerizations (*vide supra*).

Sequential block copolymerizations of VAc and VPv similarly furnish unimodal PVAc-*b*-PVPv diblock copolymers [Table 1 and Fig. 5(b)]. Molecular parameters for a representative diblock copolymer produced by sequential CMRP are listed in Table 1. Notably, very high molecular weight alkyl vinyl ester block copolymers may be produced with relatively narrow polydispersities. Note that we have recently reported the CMRP block copolymerization of PVPv-*b*-PVAc, in which the PVPv block is synthesized first with subsequent VAc chain extension to produce a diblock copolymer with narrow polydispersity (M_w/M_n = 1.35).[46] These data taken together demonstrate a high degree of blocking efficiency irrespective of the order of monomer addition for these alkyl vinyl ester CMRP block copolymerizations.

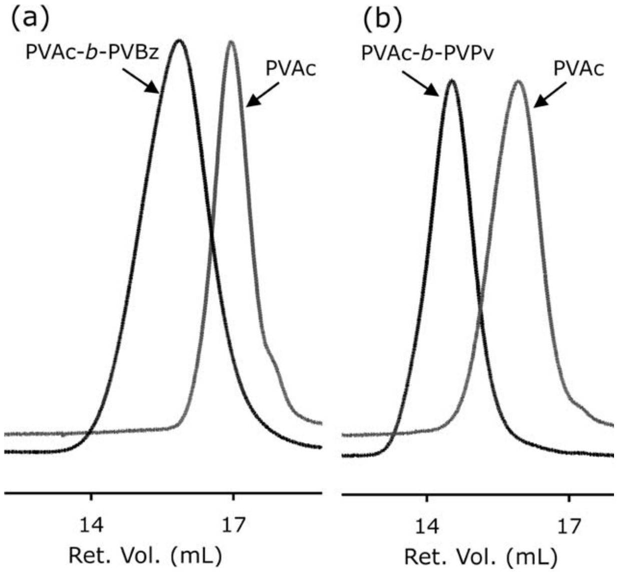


FIGURE 5 SEC trace overlays for poly(vinyl ester) diblock copolymers synthesized by sequential CMRP reactions under redox initiation conditions: (a) PVAc-Co(acac)$_2$ macromolecular chain transfer agent and the resulting diblock copolymer PVAc-*b*-PVBz-**1**, and (b) PVAc-Co(acac)$_2$ macromolecular chain transfer agent and the resulting diblock copolymer PVPv-*b*-PVAc-**1**.

Block copolymers comprised of chemically incompatible homopolymer segments microphase separate into ordered nanostructures that balance polymer chain stretching entropy against unfavorable interblock repulsions, the morphologies of which may be readily assigned by small-angle X-ray scattering (SAXS).[47,48] Results of SAXS analyses of diblock copolymers produced by sequential CMRP block copolymerizations are listed in Table 1. PVAc-*b*-PVPv-**1** clearly microphase separates with a modest degree of long range order at 150 °C as discerned from the broad scattering maxima (Fig. 6), which likely originate from a combination of sample polydispersity and poor ordering due to the high molecular

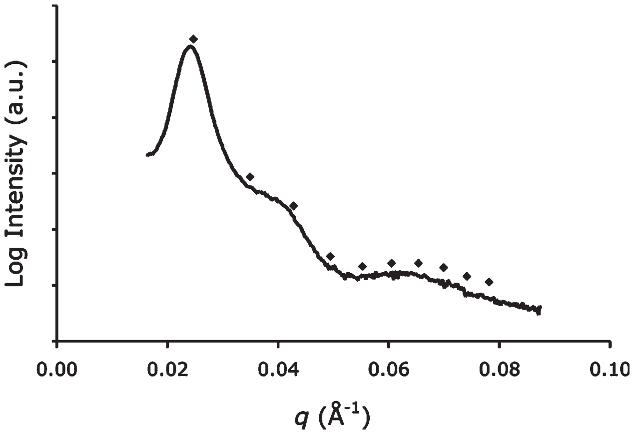


FIGURE 6 Azimuthally integrated intensity profile as a function of scattering wavevector q (Å^{-1}) of an isotropic two-dimensional lab source SAXS pattern of PVAc-b-PVPv-**1** at 150 °C. Filled symbols indicate the expected positions associated with a tentatively assigned body-centered cubic spheres morphology.

weight of the polymer. Based on the position of the principal scattering maxima observed in the azimuthally integrated SAXS pattern, this poorly ordered microphase separated morphology exhibits a principal spacing $d^* = 2\pi/q^* = 36.5$ nm. SAXS patterns for PVAc-*b*-PVBz diblock copolymers with nearly symmetric molar compositions exhibit only low intensity correlation-hole scattering at 150 °C consistent with a homogeneous melt.[49] These observations are consistent with prior work on microphase separated poly(vinyl ester) block copolymers, which indicate that PVAc-*b*-PVBz block copolymers remain homogeneous in the melt at modest molecular weights while PVAc/PVPv block copolymers are quite strongly melt-segregated.[12]

EXPERIMENTAL

Materials

All reagents were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI) and used as received unless otherwise noted. Vinyl acetate (VAc) and VPv were distilled at ambient pressure from CaH_2 to remove inhibitors and other impurities. VBz was purified by the previously described two-step, reactive purification procedure.[12] 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from methanol. LPO was recrystallized from hexanes and dried under vacuum. $Co(acac)_2 \bullet 2H_2O$ (Alfa Aesar) was dehydrated by recrystallization from acetone and subsequent drying *in vacuo*. Citric acid tribasic sodium salt (Na_3CA) and citric acid (CA) were recrystallized from water and dried at 110 °C. 2,2,6,6-Tetramethylpiperidine-*N*-oxyl (TEMPO) was purified by sublimation at reduced pressure. Mercury(II) acetate (Fisher, 99.7%) was used as received. C_6H_6 was vacuum transferred from Na/benzophenone and stored under nitrogen.

All ^{1}H NMR spectra were acquired in $CDCl_3$ on a Bruker AC+ 300 MHz spectrometer and were referenced to the residual protiated solvent peak.

Size Exclusion Chromatography (SEC)

SEC analyses were performed on a Viscotek GPCMax System equipped with two Polymer Labs Resipore columns (300 × 7.5 mm) and a differential refractometer, light scattering module (7°- and 90°-angle detection), and a differential viscometer; tetrahydrofuran was used as a mobile phase at a elution rate of 1.0 mL/min at 30 °C. For PVAc, number average molecular weights (M_n) and polydispersities (M_w/M_n) were obtained using a Mark-Houwink corrected poly(styrene) calibration curve as previously described.[12] Absolute molecular weights for PVPv and PVBz were determined by SEC with light scattering detection using previously reported dn/dc values, while M_w/M_n for these samples are reported relative to PS Standards.[12]

SAXS

Laboratory source SAXS patterns were acquired in the Materials Science Center at the University of Wisconsin–Madison using a Rigaku SMAX-3000 employing Cu K_a X-rays and a Gabriel X-ray detector with a 2.015 m sample-to-detector distance. SAXS patterns acquired at elevated temperatures employed a Linkam temperature stage.

Synthesis of Vinyl 4-methoxybenzoate

This preparation is an optimized version of a previously reported procedure:[44] In a 500 mL three-necked flask fitted with a reflux condenser and a thermometer, 4-methoxybenzoic acid (24.40 g, 0.160 mol), mercury(II) acetate (1.46 g, 4.58 mmol), and VAc (94 mL, 1.02 mol) were suspended in $CHCl_3$ (80 mL) and refluxed at 75 °C for 8 h. The reaction mixture was then diluted with hexanes (80 mL), cooled to room temperature, and washed with a saturated $NaHCO_3(aq)$ (3 × 50 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed *in vacuo*. The resulting white solid was recrystallized from anhydrous EtOH and dried. Yield: 30.1% (8.64 g). ^{1}H NMR: (300 MHz, $CDCl_3$, 22 °C): δ (ppm) 8.07 (dt, $^3J_{\text{H-H}} = 9.0$, 2.8 Hz, 2H, Ar—*H*), 7.51 (dd, $^3J_{\text{H—H}} = 13.9$, 6.3 Hz, 1H, $H_2C{=}CH$—), 6.95 (dt, $^3J_{\text{H—H}} = 9.0$, 2.8 Hz, 2H, Ar—*H*), 5.04 (dd, $^3J_{\text{H—H}} = 14.1$, 1.7 Hz, 1H, $H_2C{=}CH$—), 4.67 (dd, $^3J_{\text{H-H}} = 6.3$, 1.5 Hz, 1H, $H_2C{=}CH$—), 3.88 (s, 3H, —OCH_3).

Representative Synthesis of Poly(vinyl pivalate)

LPO (135.5 mg, 0.34 mmol) and $Co(acac)_2$ (113.7 mg, 0.442 mmol) were combined in a dry Schlenk flask equipped with a stirbar under nitrogen. A combination of Na_3CA (73.5 mg, 0.25 mmol) and the monomer (12.6 mL, 85 mmol) were degassed by three freeze-pump-thaw cycles in a second dry Schlenk flask equipped with a stirbar. The monomer-citric acid suspension was then cannula transferred to the flask containing the $Co(acac)_2$/LPO to initiate polymerization at 30 °C. Reaction aliquots were withdrawn by gas-tight syringe at regular intervals and diluted with hexanes, followed by rotary evaporation of the solvent and monomer, and freeze-drying the resulting solids from C_6H_6 as previously reported.[12] Typical monomer conversions were less than 5%.

PVBz polymers were precipitated into hexanes at least once to remove residual monomer and were subsequently freeze-dried from C_6H_6. Typical monomer conversion was limited to less than 2%.

Representative Diblock Copolymer Synthesis: PVAc-*b*-PVBz-1

$Co(acac)_2$ (113.8 mg, 0.442 mmol) was combined with LPO (136 mg, 0.341 mmol) in a Schlenk flask under nitrogen. In a separate flask, a suspension of CA (65.3 mg, 0.340 mmol) in freshly distilled VAc (7.9 mL, 85.7 mmol) was prepared and degassed by three freeze-pump-thaw cycles. The CA/VAc slurry was cannula transferred onto the $Co(acac)_2$/LPO mixture, and this reaction mixture was heated to 30 °C to initiate the polymerization. After 5.8 h, the reaction was removed from the heating bath and cooled under nitrogen. The cobalt-end-capped PVAc was isolated by removal of the excess VAc *in vacuo* to yield a solid. Size exclusion chromatography analysis of a reaction aliquot showed $M_n = 8.7$ kg/mol and $M_w/M_n = 1.21$.

The resulting PVAc-$Co(acac)_2$ macromolecular chain transfer agent was redissolved in degassed, freshly distilled VBz (10.3 mL, 74.4 mmol), and the reaction was re-heated to 30 °C for 11.8 h. The polymerization was cooled to room temperature, stirred with TEMPO (181 mg, 1.16 mmol) in THF (17 mL) and exposed to air. The resulting copolymer was then precipitated into cold hexanes (300 mL) to yield a PVAc-PVBz copolymer. Using SEC, the polydispersity of the resultant PVAc-PVBz copolymer was determined to be $M_w/M_n = 1.74$ (against PS Standards). Quantitative ^{1}H NMR analysis shows that this polymer contains 51.1 mol % VBz and the polymer has a calculated $M_{n,total} = 24.4$ kg/mol.

Synthesis of Poly(vinyl 4-methoxybenzoate)

To a Schlenk flask equipped with a stirbar, vinyl 4-methoxybenzoate (2.51 g, 14.0 mmol), Co(acac)$_2$ (18.6 mg, 0.073 mmol), lauoryl peroxide (22.2 mg, 0.056 mmol), and citric acid tribasic sodium salt (10.7 mg, 0.041 mmol) were added. On a vacuum line, anhydrous C_6H_6 (8.8 mL) was added to the reaction mixture under nitrogen and it was stirred at 30 °C. After 77.5 h, the reaction was exposed to air and poured into hexanes to yield a small amount of solid. $M_n =$ 2.3 kg/mol, $M_w/M_n = 2.11$.

CONCLUSIONS

CMRPs of VPv and VBz were explored to extend this useful degenerate chain transfer polymerization methodology to the synthesis of well-defined vinyl ester block copolymers by sequential chain extension reactions. Bulk homopolymerization studies revealed that alkyl vinyl esters such as VAc and VPv have comparable reactivities and their CMRP proceeds with a high degree of control to yield polymers with $M_w/M_n \leq 1.3$, whereas CMRP of VBz resulted in less controlled polymerization with higher polydispersities $M_w/M_n \leq 1.7$. Sequential block copolymerizations of VAc with either VPv or VBz yield unimodal block copolymers with variable molecular weights that may microphase separate in the melt. These findings demonstrate that CMRP is a convenient and complementary synthetic method to RAFT for the (co)polymerization of commercially available vinyl ester monomers. Investigations of the mechanical properties of these new block copolymers are ongoing and will be reported in due course.

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