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Poly(vinyl ester) Block Copolymers Synthesized by Reversible Addition−Fragmentation Chain Transfer Polymerizations

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ABSTRACT: Homopolymerizations and block copolymerizations of vinyl acetate (VAc), vinyl pivalate (VPv), and vinyl benzoate (VBz) by reversible addition−fragmentation chain transfer (RAFT) polymerization have been studied. Polymerizations of VAc initiated with 2,2′-azobis(isobutyronitrile) (AIBN) at 60 °C using two different xanthate RAFT agents $C_2H_5OC(=S)SR$ (R = $-CH(CH_3)CO_2C_2H_5$ (**1**) and $-CH(CH_3)O_2CC(CH_3)_3$ (**2**)) were examined to elucidate the dependence of the polydispersities of the resulting polymers on the RAFT agent leaving group R. RAFT agent **2**, in which the leaving R-group mimics a growing vinyl ester polymer chain, consistently yields poly(vinyl acetates) having broader polydispersities than those synthesized using **1** ($M_n = 3.6-14$ kg/mol and $M_w/M_n = 1.15-1.33$). While VPv exhibits similar controlled polymerization behavior to VAc, RAFT homopolymerizations of VBz mediated by **1** indicate this electron-deficient vinyl ester requires higher temperatures to effect controlled polymerizations to yield polymers having $M_n = 4-14$ kg/mol and $M_w/M_n = 1.29-1.53$. Chain extension reactions from xanthate-terminated vinyl ester homopolymers with VAc, VPv, and VBz proceed with variable efficiencies to furnish block copolymers that microphase separate in the melt state as determined by small-angle X-ray scattering.

Introduction

The development of inexpensive, degradable polymeric materials with tunable physical properties that retain the versatile attributes of well-known commodity polyolefins is a major challenge in modern polymer science.[1] One motivation for this goal stems from recent government mandates specifying that a minimum weight fraction of both packaging materials and durable goods be comprised of (bio)degradable materials in order to mitigate long-term landfill waste.[2,3] Well-known biodegradable polymers, such as poly(lactide) and poly(3-hydroxyalkanoates), exhibit limited thermal stability under melt processing conditions[4] (e.g., injection molding and extrusion), and their mechanical toughness is limited.[5] These limitations have hampered their widespread used beyond packaging and food containers applications.[6,7] The dearth of robust, economically produced, degradable polymers amenable to widespread applications mandates the continued development of new materials with improved physical properties that degrade in the environment.

Vinyl ester polymers, exemplified by poly(vinyl acetate), are well-known materials used in commodity applications as adhesives, paper coatings, chewing gum bases, and biomedical materials.[8] By virtue of their economical production by palladium-catalyzed oxidative coupling of ethylene with carboxylic acids or transesterification of carboxylic acids with vinyl acetate, a wide variety of vinyl ester monomers are available on commodity scales.[9] Polymers derived from these monomers exhibit a variety of physical and chemical properties, including their known degradability through ester side chain hydrolysis to yield carboxylic acids and poly(vinyl alcohol);[10] the latter polymer degrades by a variety of mechanisms in the environment.[11,12] In spite of this accessible degradation pathway, the all-carbon backbone of these polymers renders them thermally stable and amenable to melt processing for potentially broad applications.

Derived from conventional free radical polymerizations, known poly(vinyl esters) are structurally heterogeneous materials exhibiting broad molecular weight distributions, variably branched macromolecular architectures, and physical properties that depend sensitively upon their exact structures.[8,13] Access to new degradable vinyl ester homopolymers and block copolymers with tunable properties requires the development and optimization of controlled polymerization methodologies for this class of monomers. Advances in this arena may enable the generation of new, degradable pressure-sensitive adhesives and thermoplastic elastomers, based on design principles discovered in the development of traditional styrenic and diene derived thermoplastic elastomers.[14]

Recent progress in controlled free radical polymerizations has afforded access to new classes of well-defined macromolecules having precise architectures, compositions, and chain-end functionalities from a wide variety of monomers.[15] Controlled reversible addition−fragmentation chain transfer (RAFT) polymerizations[16−18] of vinyl acetate mediated by xanthates[19−21] and dithiocarbamates[22] and cobalt-mediated radical polymerizations (CMRP)[23−26] were recently reported to furnish well-defined homopolymers with relatively narrow polydispersities (M_w/M_n = 1.14−1.6). The accepted degenerate transfer mechanism of RAFT polymerization mediated by xanthates (Scheme 1) has been the subject of numerous theoretical[27−31] and experimental studies.[19,29,32,33] Only a few extensions of this convenient synthetic methodology to other vinyl esters are known,[16,34,35] and vinyl ester block copolymers are unknown.

In order to explore the vinyl ester monomer palette as a new platform for the synthesis of polymers having tunable physical properties that are also degradable, we have studied the RAFT homopolymerization and block copolymerization of a subset of vinyl ester monomers. Herein, we report the results of RAFT

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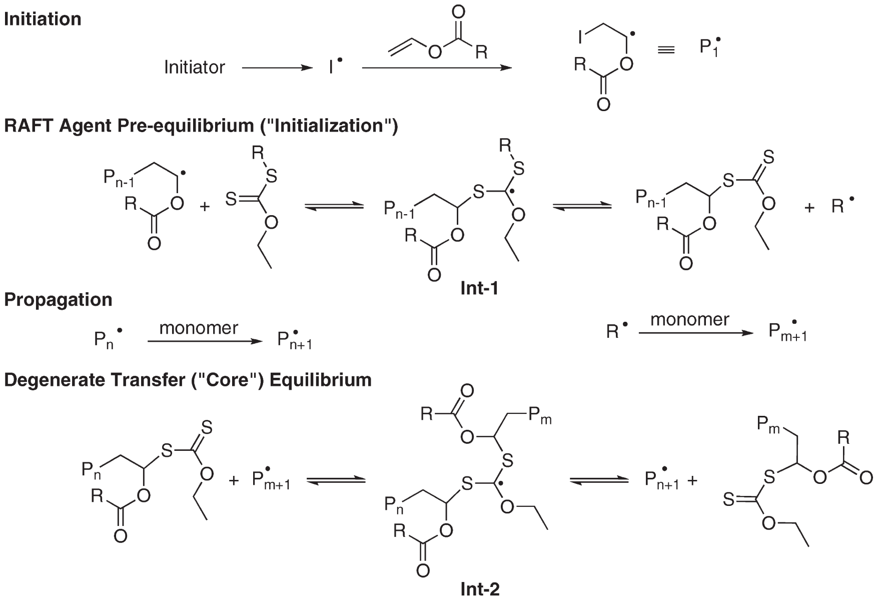
Scheme 1. Initiation, Initialization, Propagation, and Degenerate Transfer Steps of RAFT Polymerizations Mediated by Xanthates



homopolymerizations and block copolymerizations of vinyl acetate (VAc), vinyl pivalate (VPv), and vinyl benzoate (VBz) in the presence of two different RAFT agents, in order to assess potential pitfalls associated with the syntheses of their block copolymers. We report the synthesis of the first relatively monodisperse vinyl ester block copolymers, along with details of the efficiencies of these block copolymerization reactions as a function of the sequence of monomer addition. Finally, preliminary data demonstrate that these poly(vinyl ester) block copolymers microphase separate in the melt to yield well-ordered morphologies at modest molecular weights.

Experimental Section

Materials. Ethyl 2-bromopropionate, potassium *O*-ethyl xanthogenate, ethanol, and hexanes were purchased from Aldrich and used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich) and V-40 (Wako Chemicals USA) were both recrystallized from methanol prior to use. Vinyl acetate (VAc), vinyl pivalate (VPv), and vinyl benzoate (VBz) were purchased from Aldrich. VAc and VPv were fractionally distilled at ambient pressure from calcium hydride immediately prior to use. VBz was first purified by fractional high-vacuum distillation, followed by reactive purification in a subsequent step by heating with AIBN (10 mg/100 mL) at 75 °C for 20 min to initiate polymerization, followed by distillation at reduced pressure. Xanthate **1**[19,21] and 1-chloroethyl-2,2-dimethylpropanoate[36] were synthesized according to literature procedures.

^{1}H NMR spectra were recorded on both Varian Unity Inova 500 and Bruker AC+ 300 spectrometers and were referenced relative to the residual protiated solvent peaks in the samples. ^{13}C NMR spectra were obtained at 125 MHz using the Varian Unity Inova 500 spectrometer. Elemental analysis was performed at Columbia Analytics Laboratory (Tuscon, AZ).

Size Exclusion Chromatography (SEC). SEC analyses were performed using a Viscotek GPCMax System equipped with two Polymer Laboratories Resipore columns (250 mm × 4.6 mm) and four Viscotek detectors including a differential refractometer, two angle light scattering module (7° and 90°), a four-capillary differential viscometer, and UV/vis detector. Tetrahydrofuran (THF) was used as the mobile phase at 30 °C with a flow rate of 1.0 mL/min. A conventional calibration curve was constructed based on 10 narrow molecular weight distribution polystyrene standards with M_n = 580−377 400 Da (Polymer Laboratories, Amherst, MA), which was then subjected to Mark−Houwink conversion to generate an equivalent calibration curve for poly(vinyl acetate); Mark−Houwink parameters were obtained from the literature.[21] The refractive index increments dn/dc for poly(vinyl pivalate) and poly(vinyl benzoate) were determined by subjecting a single polymer sample to SEC analysis at several different concentrations and measuring the refractive index response at the peak molecular weight. The refractive index increment was then calculated as the slope of the linear fit of the detector response versus concentration curve assuming that the refractive index of THF at 30 °C is $n_{\mathrm{THF}} = 1.406$. At 30 °C in THF, the refractive index increments are dn/dc = 0.076 L/g for poly(vinyl pivalate) and dn/dc = 0.131 L/g for poly(vinyl benzoate). These values were used to calculate the absolute molecular weights for PVPv and PVBz using SEC-LS, while M_w/M_n were calculated using polystyrene standard calibration.

SAXS. Synchrotron small-angle X-ray scattering (SAXS) measurements were performed at the 5IDD beamline of the DuPont−Northwestern−Dow Collaborative Access Team Synchrotron Research Center at the Advanced Photon Source (Argonne, IL). Experiments employed a beam energy of 16 keV (λ = 0.7293 Å^{-1}) and a 8.002 m sample-to-detector distance. Two-dimensional SAXS patterns were recorded on a MAR-CCD detector (133 mm diameter active circular area) with 1048 × 1048 pixel resolution. Samples were heated to the desired temperature in a Linkam DSC and allowed to equilibrate for 5 min before data collection (typical exposure times ~2 s).

Laboratory SAXS measurements were performed in the Materials Science Center at the University of Wisconsin—Madison. Cu Kα X-rays generated by a Rigaku Micromax 002+ microfocus source were collimated using a Max-Flux multilayer confocal optic (Osmic, Inc.) followed by passage through three collimating pinholes to reduce the final beam diameter to less than 0.5 mm. Samples were mounted in a vacuum chamber and heated using a Linkam hot stage with a 10 min equilibration time (typical exposure times ~ 3−5 min). A Gabriel X-ray detector (150 mm diameter active circular area) was used to record 2D-SAXS patterns at a sample-to-detector distance of 2.015 m. The sample-to-detector distance was calibrated using a silver behenate standard (d = 58.38 Å).

Synthesis of 1-(Ethoxycarbonothioylthio)ethyl 2,2-Dimethylpropanoate (2). Potassium *O*-ethyl xanthogenate (4.05 g, 25.1 mmol) was slurried in 20 mL of ethanol at 22 °C in a 50 mL round-bottom flask equipped with a stirbar. 1-Chloroethyl-2,2-dimethylpropanoate (4.00 g, 24.2 mmol) was added, and the reaction was allowed to stir for 12 h. Removal of the solvent by rotary evaporation yielded a yellow oil with a white precipitate. The resulting residue was redissolved in diethyl ether and passed through a column of basic alumina (15 cm × 5 cm diameter) to yield a clear, yellow oil upon removal of the ethereal solvent. To ensure complete removal of any solid matter from this oil, the purified product was filtered through a 0.20 μm filter. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ (ppm) 6.82 (q, 1H, $J = 6.60$ Hz), 4.23 (q, 2H, $J = 7.16$ Hz), 1.32 (d, 2H, $J = 6.60$ Hz), 1.11 (s, 9H), 0.91 (t, 3 H, $J = 7.16$ Hz). ^{13}C NMR (500 MHz, $CDCl_3$, 22 °C): δ (ppm) 210.47, 176.01, 77.51, 69.66, 38.46, 19.44, 13.06. Anal. Calcd for $C_{10}H_{18}O_3S_2$: C 47.97, H 7.25, S 25.61. Found: C 48.04, H 7.66, S 25.00.

Representative Polymerization Procedure. **1** (102 mg, 0.46 mmol) and AIBN (7.6 mg, 0.046 mmol) were dissolved in freshly distilled vinyl acetate (20 mL, 220 mmol). Aliquots of this solution (5 mL) were placed in 10 mL glass ampules, degassed by three freeze−pump−thaw cycles on a vacuum line, and then sealed under vacuum. The sealed reactions were immersed in a 60 °C oil bath and run for the designated times, followed by removal of the ampules from the oil bath, and cooling under running water to terminate the polymerization. Polymers were isolated by precipitation in stirred hexanes (600 mL) and subsequent vacuum filtration. In order to remove any traces of monomer from the polymers, the solids were freeze-dried in vacuo at room temperature from benzene. Monomer conversion was measured based on isolated polymer yields.

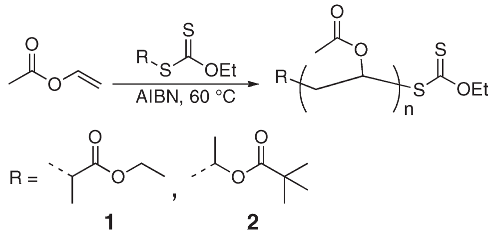
Representative Block Copolymer Synthesis (PVPv-*b*-PVAc-1). **1** (46.1 mg, 0.21 mmol) and AIBN (3.8 mg, 0.023 mmol) were dissolved in freshly distilled vinyl pivalate (21.2 mL, 143 mmol) such that [**1**] = 9.9 mM and [AIBN] = 1.1 mM. The reaction was sealed in a flask, degassed by freeze−pump−thaw cycles (3×), and heated to 60 °C for 3 h. The reaction was removed from the heating bath and cooled under running water to terminate the polymerization. Excess vinyl pivalate monomer was removed under reduced pressure, and the resulting solids were freeze-dried from C_6H_6 in vacuo. PVPv-RAFT agent: M_n = 14.8 kDa (SEC-LS), M_w/M_n = 1.28 (PS Standards).

PVPv-RAFT agent (0.5 g, 0.034 mmol) was dissolved in VAc (6.3 mL, 68.3 mmol); residual AIBN present in the macro-chain-transfer agent was used as the sole source of initiator. The reaction was degassed by freeze−pump−thaw cycles (3×), sealed, and heated to 60 °C for 3.5 h. The reaction was removed from the heating bath and cooled under running water to terminate the reaction. Excess vinyl acetate monomer was removed by rotary evaporation. The resulting solid polymer was freeze-dried from C_6H_6 in vacuo. $M_{n,NMR}$=24.8 kg/mol (50.4 mol % VAc composition from quantitative ^{1}H NMR integrations of the acetate and pivalate resonances), M_w/M_n = 1.33 (against PS standards in THF at 30 °C).

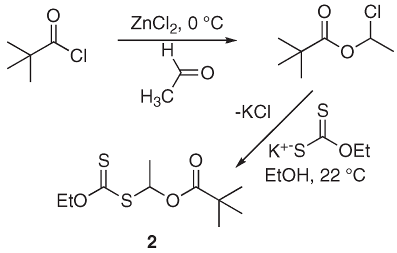
Results

Leaving Group Effects in VAc Polymerizations. Bulk RAFT homopolymerizations of VAc initiated with 10 mol % 2,2′-azobis(isobutyronitrile) (AIBN) at 60 °C were performed in the presence of xanthates **1** and **2** in order to explore the effects of the *S*-alkyl leaving group on the course of the polymerization (Scheme 2). Xanthate **1** bears an α-enoyl *S*-alkyl leaving group and is known to mediate controlled VAc polymerizations.[19] Previously unreported xanthate **2** was designed to have an α-acyloxy leaving group that mimics the poly(vinyl ester) chain, in order to probe RAFT agent initialization effects[37,38] and potential problems associated with chain extension reactions for vinyl ester block copolymerizations. Xanthate **2** was synthesized in two steps from commercially available starting materials as shown in Scheme 3 via chloroethyl pivalate by analogy to previously reported procedures.

Scheme 2. RAFT Polymerization of VAc Mediated by 1 and 2



Scheme 3. Synthesis of Xanthate 2



In accord with previous reports by Stenzel et al., we observed short inhibition periods at the beginning of polymerizations mediated by **1**, during which no polymer is formed.[21] These inhibition periods were quantified using the nonzero intercept of monomer conversion versus time plots (data not shown). The duration of the inhibition period sensitively depends on the purity of *both* the xanthate[19] and the VAc monomer, which we fractionally distilled from CaH_2 prior to use; passage of the VAc monomer through a basic alumina column generally yielded irreproducible inhibition periods. The inhibition periods observed for both **1** and for **2** were both negligible, indicating that the degenerate interchange equilibrium critical to RAFT polymerization is readily established in reactions with both RAFT agents in spite of the different *S*-alkyl leaving groups.

Both **1** and **2** mediate the controlled polymerization of VAc at 60 °C using AIBN initiation ([RAFT] = 21.3 mM and [RAFT]:[AIBN] = 10:1), evidenced by the linearity of the number-average molecular weight (M_n) versus monomer conversion plots (Figure 1). Size exclusion chromatography (SEC) analyses against poly(styrene) standards using Mark−Houwink correction demonstrate that the resulting polymers have polydispersity indices M_w/M_n = 1.20−1.35 and that the polydispersity decreases with increasing monomer conversion as expected based on previous reports (see Supporting Information Figures S1 and S2 for primary SEC data).[21] The close agreement between the theoretical M_n (indicated by the dashed lines in Figure 1a,b) and the experimentally observed M_n indicates that competitive chain transfer to monomer or to polymer is negligible under these reaction conditions. Lower polydispersities are consistently observed for reactions mediated by **1** as compared to **2**. This polydispersity trend results directly from differences in the *S*-alkyl leaving groups that affect the initialization of each RAFT agent in these reactions (Scheme 1).

Vinyl Pivalate (VPv) Homopolymerizations. On the basis of the results of VAc polymerizations mediated by RAFT agents **1** and **2**, we studied the homopolymerization of vinyl pivalate in the presence of **1**/AIBN due to the ease of synthesis and purification of this chain transfer agent. Bernard et al. previously studied the polymerization of vinyl pivalate in the context of star polymer syntheses.[34] Polymerizations of VPv freshly distilled from CaH_2 with [VPv]:[**1**]:[AIBN] = 307:1.0:0.10 ([**1**]) = 22.0 mM) at 60 °C

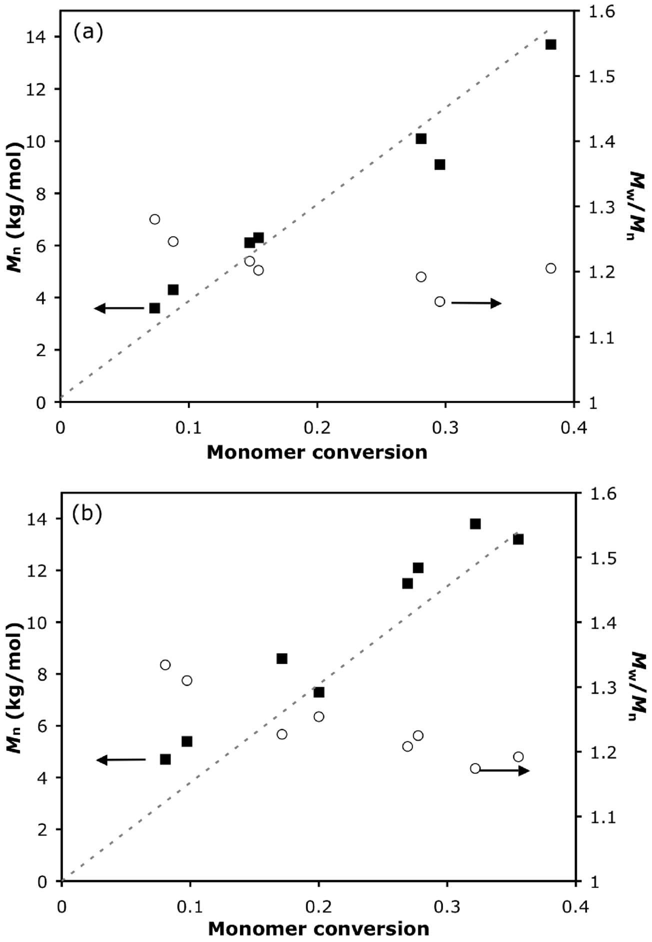


Figure 1. M_n versus monomer conversion plots for bulk RAFT polymerizations of VAc at 60 °C initiated by AIBN: (a) with [VAc]:[**1**]:[AIBN] = 493:1.0:0.10 ([**1**] = 21.3 mM) and (b) **2** with [VAc]:[**2**]:[AIBN] = 493:1.0:0.10 ([**2**]=21.3 mM). The dotted lines indicate the theoretical molecular weight calculated based on isolated polymer yields.

yielded PVPv with absolute M_n=2.6−10.6 kg/mol from light scattering with M_w/M_n = 1.19−1.47 against polystyrene standards (see Supporting Information Figure S3 for primary SEC data). Substantial inhibition periods were observed for this monomer (t_{inh} = 63 ± 37 min), likely a result from impurities present in the monomer and the chain transfer agent. The linear plot of M_n versus monomer conversion and close agreement with the theoretically predicted M_n confirms the controlled nature of these polymerization reactions (with negligible competing chain transfer reactions), for which the molecular weight distribution narrows with increasing monomer conversion (Figure 2).

By taking into account the differences in the bulk monomer concentrations associated with VPv and VAc, comparison of the slopes of monomer conversion versus time plots for VPv and VAc under comparable RAFT agent and AIBN concentrations allows quantitative comparison of the polymerization behavior of these related vinyl alkanoate monomers. On the basis of a second-order rate law for chain propagation in bulk monomer at low monomer conversions, the rates of RAFT polymerization of VPv and VAc are comparable (within 10%) in spite of the substantially different steric demands for these two monomers.

Vinyl Benzoate (VBz) Hompolymerizations. Successful RAFT homopolymerization of VBz in the presence of **1**/AIBN sensitively depends on monomer purity and reaction temperature. In order to achieve reproducible polymerization kinetics, VBz monomer was fractionally distilled under vacuum from CaH_2 followed by reactive distillation from AIBN above 60 °C; the monomer was distilled from a polymerization reaction to minimize potential impurities that could affect the reaction kinetics. The polymerization is severely retarded by **1** at 60 °C, as evidenced by small increases in the absolute M_n and polydispersities with increasing reaction times (Table 1). Furthermore, the observed absolute molecular weights were much higher than the theoretical molecular weights $M_{n,thy}$ calculated from the expression

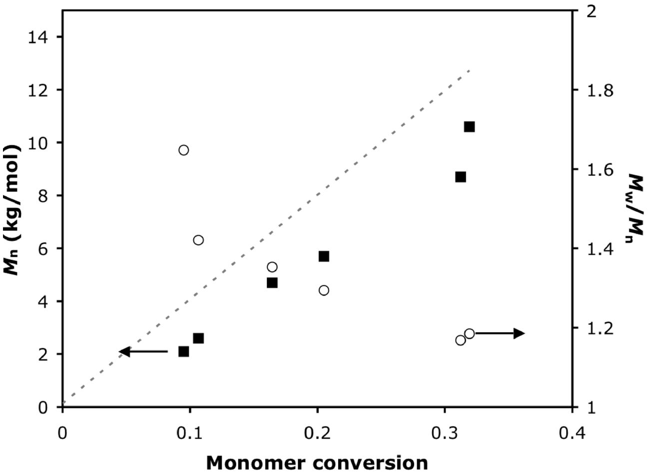


Figure 2. Absolute M_n versus monomer conversion plot for RAFT polymerization of VPv at 60 °C with [VPv]:[**1**]:AIBN] = 307:1.0:0.10 ([**1**] = 22.0 mM). The dotted line indicates the theoretical molecular weight based on isolated polymer yields.

$$M_{n,thy} = \frac{p[\mathrm{VBz}]}{[\mathbf{1}]}\mathrm{MW}_{\mathrm{VBz}} + \mathrm{MW}_{\mathbf{1}}$$

where p is the percent monomer conversion, [VBz] is the monomer concentration, MW_{VBz} is the monomer molecular weight, and $MW_{\mathbf{1}}$ is the molecular weight of RAFT agent **1**. On the basis of the hypothesis that polymerization retardation stems from slow fragmentation of the tertiary carbon-centered radical **Int-1** (Scheme 1) resulting from polymeryl radical addition to **1** and thus slow rates of radical interchange,[38,39] we explored the temperature dependence of the polymerization of VBz with **1**/AIBN. Using **1**/AIBN at 70 °C resulted in slightly faster polymerization rates with broader polydispersities that increased with increased reaction time; again, discrepancies between the theoretical and observed molecular weights were pronounced. Increasing the temperature further to 75 °C results in controlled polymerization of VBz confirmed by linear M_n versus time plots in the range M_n = 7.2−9.7 kg/mol and decreasing polydispersities M_w/M_n = 1.29−1.38 (Figure 3a); however, the observed molecular weights deviate substantially from those expected theoretically.

Polymerizations of VBz mediated by **1** were also conducted at elevated temperatures using 1,1′-azobis(cyclohexane-1-carbonitrile) (V-40) as the initiator in order to optimize the reaction conditions. Given that xanthate chain end fidelity in RAFT polymerizations depends critically on having only a small concentration of initiating radicals in the polymerization reaction,[16] we opted to use V-40 since it has a longer half-life at higher temperatures ($t_{1/2}$ = 10 h at 88 °C) compared to AIBN. Bulk VBz polymerizations initiated with V-40 at 80 °C yielded polymers exhibiting time-dependent increases in M_n and M_w/M_n = 1.41−1.45 (Table 1). Increasing the polymerization temperature to 88 °C resulted in fast,

Table 1. Vinyl Benzoate RAFT Bulk Homopolymerizations Mediated by 1 at Various Temperatures

initiator[a]	T_{rxn} (°C)	t_{rxn} (h)	% conv[b]	$M_{\text{n,thy}}$ (kg/mol)[c]	$M_{\text{n,SEC-LS}}$ (kg/mol)[d]	M_w/M_n[e]
AIBN	60	1	0.66	0.50	2.7	1.19
AIBN	60	2	1.8	1.0	2.9	1.28
AIBN	70	1	4.3	2.0	3.4	1.39
AIBN	70	2	7.0	3.1	4.5	1.45
V40	80	1	6.1	3.1	3.7	1.46
V40	80	2	18.1	8.7	8.6	1.42
V40	88	1	11.4	6.0	5.8	1.53
V40	88	2	25.3	13.0	11.3[f]	1.39

[a] Reaction conditions: [**1**] = 22.0 mM and [**1**]:[initiator] = 10:1. [b] Percent monomer conversion was measured based on isolated polymer. [c] $M_{\text{n,thy}} = \text{MW}_{\text{VBz}}p[\text{VBz}]/[\mathbf{1}] + \text{MW}_{\mathbf{1}}$, where MW_{VBz} and $\text{MW}_{\mathbf{1}}$ are the molecular weights of VBz and **1**, respectively, p is the percent monomer conversion, and [VBz] is the monomer concentration. [d] Absolute M_n determined from SEC with light scattering detection. [e] Determined using SEC with polystyrene standard calibration. [f] End-group analysis by ^{1}H NMR gives $M_{\text{n,NMR}} = 12.3$ kg/mol.

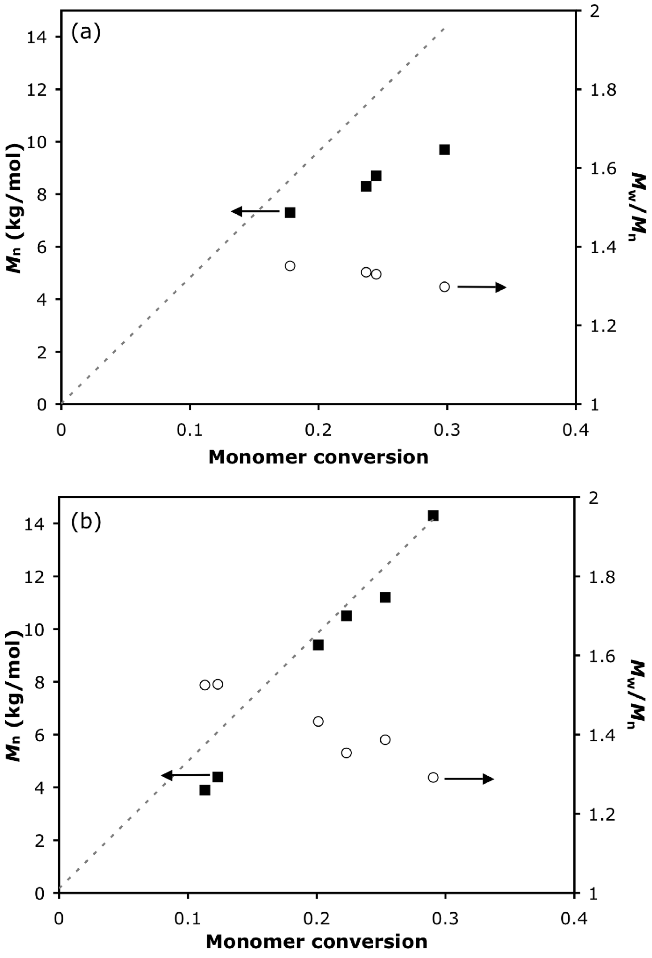
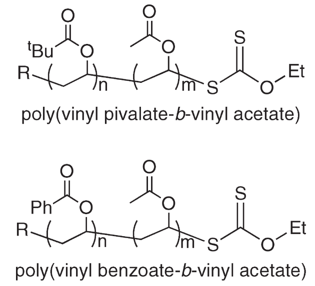


Figure 3. (a) M_n (against PS Stds) for VBz RAFT polymerization at 75 °C initiated with AIBN with [VBz]:[**1**]:[AIBN] = 327:1.0:0.10 ([**1**] = 22.0 mM) and (b) absolute M_n versus conversion plot for VBz RAFT polymerization at 88 °C initiated with V-40 with [VBz]:[**2**]:[V-40] = 309:1.0:0.10 ([**1**] = 23.4 mM). The dotted lines indicate the theoretical molecular weight calculated based on isolated polymer yields.

controlled polymerizations exhibiting linear M_n vs monomer conversion dependences in the range $M_n = 4.0-14.3$ kg/mol and decreasing polydispersities as a function of monomer conversion ($M_w/M_n = 1.29-1.55$; see Supporting Information Figure S4 for primary SEC data). The theoretical M_n values calculated from the monomer conversion agree quite well with those obtained from SEC-LS analyses (Table 1 and Figure 3b), demonstrating that the polymerization proceeds with no appreciable barriers to RAFT agent initialization and negligible competitive chain transfer to monomer or to polymer.

Scheme 4. Block Copolymers Synthesized by RAFT Polymerization Using 1



Vinyl Ester Block Copolymers. Sequential RAFT polymerization of different vinyl esters provides rapid access to well-defined and previously unknown vinyl ester block copolymers with relatively narrow molecular weight distributions (Scheme 4). Pairwise block copolymerizations of VAc, VPv, and VBz were explored in order to probe the efficiency of various macro-RAFT agents in mediating controlled chain extension reactions of different monomers (Table 2).

Poly(vinyl pivalate-*block*-vinyl acetate) (PVPv-*b*-PVAc) copolymers were synthesized by sequential block copolymerization reactions starting with either VAc or VPv monomers. For example, bulk homopolymerization of VPv at 60 °C mediated by **1**/AIBN ([VPv]:[**1**]:[AIBN]=618:1.0:0.10) yielded a xanthate-terminated PVPv with an absolute molecular weight $M_n = 14.8$ kg/mol and $M_w/M_n = 1.28$ (22.5% conversion) as determined by SEC with light scattering detection. Employing this xanthate-terminated PVPv as a macro-RAFT agent for chain extension with VAc at 60 °C ([VAc]:[PVPv] = 2026:1) using AIBN furnished PVPv-*b*-PVAc-1 diblock copolymer with 50.4 mol % VAc incorporation (6.8% monomer conversion) as assessed by quantitative ^{1}H NMR analysis of the isolated polymer (Table 2). SEC analysis of PVPv-*b*-PVAc-1 (Figure 4a) demonstrates the quantitative conversion of the parent PVPv to a unimodal block copolymer (with calculated $M_{\text{n,NMR}} = 24.8$ kg/mol and $M_w/M_n = 1.33$ from SEC against polystyrene standards). Chain extension of the same PVPv macro-RAFT agent with [VAc]:[PVPv] = 2794:1 at 60 °C with AIBN yielded PVPv-*b*-PVAc-2 with 52.6 mol % VAc incorporation (1.8% VAc conversion), total $M_{\text{n,NMR}} = 23.7$ kg/mol, and $M_w/M_n = 1.43$ from SEC against polystyrene standards. These two experiments demonstrate that variation of the monomer to macro-RAFT agent ratio and control over monomer conversion enables the systematic synthesis of block copolymers of comparable compositions with variable polydispersities. Results of the sequential RAFT polymerization of VAc followed by VPv are also shown in Table 2,

Table 2. Poly(vinyl ester) Block Copolymers Synthesized by Sequential RAFT Polymerizations

	initial block		block copolymer			
entry	M_n (kg/mol)[a]	M_w/M_n[b]	$M_{n,total}$ (kg/mol)[c]	M_w/M_n[b]	mol fraction[c]	morphology[d]
PVAc-*b*-PVBz	5.0 (60 °C, AIBN)	1.25	24.9 (80 °C, AIBN)	1.33	0.704	dis
PVBz-*b*-PVAc	11.3 (75 °C, AIBN)	1.39	17.1 (60 °C, AIBN)	1.34	0.471	dis
PVPv-*b*-PVAc-1	14.8 (60 °C, AIBN)	1.28	24.8 (60 °C, AIBN)	1.33	0.504	Hex
PVAc-*b*-PVPv	5.6 (60 °C, AIBN)	1.24	14.9 (60 °C, AIBN)	1.23	0.538	dis
PVBz-*b*-PVPv	7.1 (75 °C, AIBN)	1.42	14.8[e] (60 °C, AIBN)	1.85	0.565	Lam
PVPv-*b*-PVBz	14.8 (60 °C, AIBN)	1.28	35.0[b] (75 °C, AIBN)	2.93[f]	n.d.[g]	n.d.[g]
PVPv-*b*-PVBz	17.1[b] (80 °C, V-40)	1.25	49.8[b] (88 °C, V-40)	2.24[f]	n.d.[g]	n.d.[g]

[a] Absolute M_n from SEC analysis with light scattering detection, with reaction temperature and initiator listed in parentheses. [b] Determined using SEC calibrated using polystyrene standards. [c] $M_{n,total}$ was calculated using the molar composition the block copolymer determined by quantitative ^{1}H NMR in conjunction with the M_n of the initial block; the reaction temperature and initiator are listed in parentheses, and [macro-RAFT] = 2−19 mM in bulk monomer. [d] Determined by SAXS at 160 °C. [e] Benzene cosolvent was added so that $[VBz]_0$ = 3.3 M. [f] Multimodal according to SEC analysis. [g] Not determined.

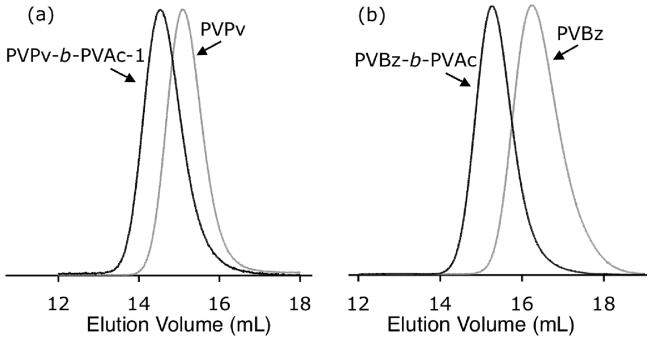


Figure 4. Overlays of SEC traces of poly(vinyl ester) diblock copolymers synthesized by sequential xanthate-mediated block copolymerizations initiated with AIBN: (a) PVPv macro-RAFT agent derived from **1** and the resulting diblock copolymer PVPv-*b*-PVAc-1 and (b) PVBz macro-RAFT agent derived from **1** and the resulting PVBz-*b*-PVAc. (See Table 2 for molecular parameters.)

indicating that the polydispersities of the resulting copolymers do not depend on the monomer addition sequence for VPv and VAc.

On the basis of the optimized results for VBz RAFT homopolymerizations, we examined the block copolymerization of VBz with VAc and VPv, respectively. Successful block copolymerization of VBz and VAc can be achieved by synthesizing either block first with only modest differences in the polydispersities of the resulting copolymers under optimized conditions (Table 2 and Figure 4b). Consistent with our optimized conditions for VBz homopolymerizations, the block copolymerization of VBz from a xanthate-terminated PVAc requires a higher reaction temperature to facilitate efficient, quantitative, and controlled chain extension to produce a diblock copolymer; similar reactions carried out at 60 °C were slow and yielded copolymers with very broad molecular weight distributions. Contrary to these results, the block copolymerization of VBz and VPv proved problematic due to the limited solubility of the initial homopolymer blocks in the bulk monomer used for chain extension. Attempts to grow PVBz blocks from a PVPv macro-RAFT agent using either AIBN or V-40 initiation resulted in multimodal polymers, and SEC analyses show substantial amounts of the unreacted macroinitiator (Table 2). Reversing the direction of copolymer synthesis by growing VPv from a xanthate-terminated PVBz was hampered by the lack of solubility of PVBz in VPv monomer. Chain extension of a PVBz macro-RAFT agent having an initial M_w/M_n = 1.42 with VPv using benzene as a cosolvent (49% VPv v/v) at 60 °C using AIBN yielded a PVBz-*b*-PVPv diblock copolymer with a polydispersity much broader than that of the parent homopolymer (M_w/M_n = 1.85). Attempts to further optimize block copolymerizations of VBz and VPv failed to yield materials with narrow molecular weight distributions.

Morphological Studies. Diblock copolymers self-assemble into various microphase-separated morphologies at the nanometer length scale that balance the interfacial tension between the chemically dissimilar homopolymer blocks and the entropic elasticity of the polymer chains.[40,41] While the phase behavior of monodisperse diblock copolymers with $M_w/M_n < 1.15$ is well-understood both theoretically[42] and experimentally,[43] studies of the effects of broadening the molecular weight distribution on block copolymer phase behavior are relatively new.[44−46] Vinyl ester block copolymers were characterized by small-angle X-ray scattering (SAXS) in order to assess their potential to microphase separate in the melt state. Synchrotron SAXS analysis of the monodisperse diblock copolymer PVPv-*b*-PVAc-1 establishes that this polymer melt microphase separates at 160 °C into a hexagonal morphology with a high degree of long-range order, evidenced by the appearance of six reflections at q^*, $2q^*$, $q^*\surd 7$, $3q^*$, $q^*\surd 12$, and $q^*\surd 13$ in the azimuthally integrated SAXS pattern with a structure factor extinction at $q^*\surd 3$ (Figure 5a). PVPv-*b*-PVAc-2 also melt microphase separates at 150 °C into a hexagonal morphology with a high degree of long-range order according to lab source SAXS measurements, in spite of a slightly broader overall copolymer polydispersity (data not shown). On the basis of the near symmetric molar composition of the polymers and the expected high degree of chain stiffness of the PVPv associated with the steric bulk of the pivalate side chains, we assign these microphase-separated block copolymer morphologies as cylinders of PVAc in a matrix of PVPv. Temperature-dependent SAXS analyses of quiescent melts did not reveal any order−order or order−disorder transitions at temperatures up to 240 °C. We also investigated the melt morphology of the unimodal and relatively polydisperse PVBz-*b*-PVPv listed in Table 2 and found that it microphase separates into a lamellar morphology at 150 °C evidenced by observed scattering maxima at q^*, $2q^*$, and $3q^*$ (Figure 6); the order−disorder transition temperature

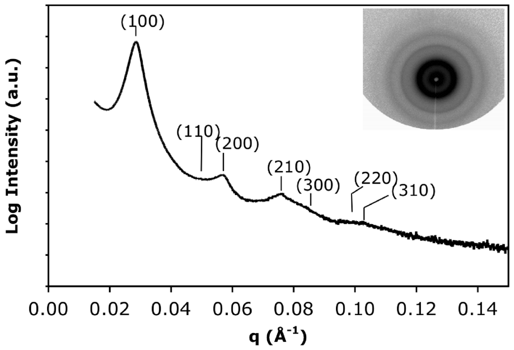


Figure 5. Two-dimensional synchrotron SAXS pattern of PVPv-*b*-PVAc-1 (Table 2) at 160 °C (inset) and the azimuthally integrated intensity profile as a function of the magnitude of the scattering wavevector q (Å^{-1}). Peak labels indicate the expected positions for reflections associated with a hexagonal morphology with $q^* = 0.0291$ Å^{-1}.

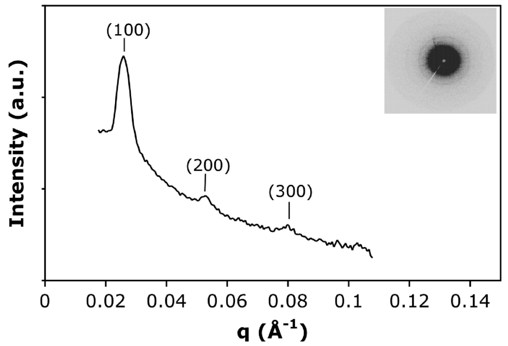


Figure 6. Azimuthally integrated intensity profile and two-dimensional lab source SAXS pattern (inset) for a polydisperse PVBz-*b*-PVPv (Table 2). Peak labels indicate the expected positions for reflections associated with a lamellar morphology having $q^* = 0.0268$ Å^{-1}.

for this material is also in excess of 240 °C according to temperature-dependent SAXS analyses. The remainder of the block copolymers listed in Table 2 exhibited only low-intensity correlation-hole scattering[47] indicative of melt disorder at 150 °C.

Discussion

Successful RAFT polymerization and block copolymerization of vinyl esters depends heavily on the purity of the monomer. While previous work established that chain transfer agent purity greatly influences the kinetics of RAFT polymerizations,[19] the present studies reveal that monomer purification is another important parameter that must be controlled in order to achieve reproducible and predictable polymerization kinetics. In previous reports of vinyl ester RAFT homopolymerizations, monomers were purified by passage through basic alumina to remove hydroquinone that was added as a free radical polymerization inhibitor. The known batchwise variability of the inhibition periods associated with conventional free radical vinyl acetate polymerizations[8] in the absence of *exogenously added* inhibitors suggests that vinyl ester feed streams are inherently contaminated with impurities that quench free radical polymerizations.[48] This is not surprising in view of the hydrolytic instability of these monomers that produces a carboxylic acid and acetaldehyde, the latter of which is known to be a potent chain transfer agent in these polymerizations.[49] This inherent impurity necessitates stringent monomer purification by fractional distillation or reactive purifications in order to achieve predictable vinyl ester polymerization results.[48,49] The level of impurities present in the vinyl ester feedstocks employed in the present work were below the limits of detection of gas chromatography and other available analytical methods.

Xanthates **1** and **2** both mediate RAFT homopolymerizations of VAc with quantitatively different results that provide critical insights into potential problems in the synthesis of poly(vinyl ester) block copolymers. AIBN-initiated RAFT polymerization of VAc in the presence of chain transfer agent **1**, bearing an electrophilic α-enoyl *S*-alkyl leaving group, provides PVAc homopolymers with narrower polydispersities than those obtained with **2**, which bears an *S*-alkyl leaving group that mimics a growing poly(vinyl ester) chain end. After RAFT agent initialization, i.e., replacement of the initial *S*-alkyl leaving group with a growing polymer chain end, the electronic structures of the resulting xanthate-terminated chains are similar and the polymerizations proceed analogously. Therefore, the observed differences in the polydispersities in polymerizations mediated by **1** and **2** likely originate from the different leaving groups in these chain transfer agents and their initialization behaviors (Scheme 1). The lower polydispersity values associated with **1** are consistent with a combination of faster polymeryl radical addition to the xanthate to yield **Int-1** and faster RAFT agent initialization by productive fragmentation of **Int-1**. Comparison of the ^{13}C NMR chemical shifts in C_6D_6 of the xanthate carbons indicates that **1** (δ 212.4 ppm) is slightly more electrophilic than **2** (δ 210.5 ppm), which may facilitate more efficient trapping of the vinyl acetate chain ends to afford lower polydispersities at early reaction times. Computational studies by Matyjaszewski and Poli support the notion that fragmentation of the α-enoyl radical leaving group is more thermodynamically favorable than the fragmentation of the α-acyloxy carbon-centered radical required for initialization of **2**.[25] Therefore, we conclude that the observed polydispersities of vinyl ester block copolymers synthesized by sequential RAFT polymerizations may be inherently limited by the structure of the resulting macro-RAFT chain transfer agent that resembles **2**.

Vinyl ester monomers exhibit variable reactivities that correlate with the structure of the parent carboxylic acid from which they derive. Both VAc and VPv polymerize readily with a high degree of control at 60 °C when initiated with AIBN, consistent with the similar electronic structures of the propagating free radical chain ends in both reactions. Polymerizations of VBz at 60 °C proceeded sluggishly and resulted in low levels of monomer conversion, although VBz homopolymerizes at these temperatures in the absence of **1**. Additionally, there were large discrepancies between the theoretical and experimentally observed molecular weights of the isolated polymers. Performing these reactions at elevated temperatures resulted in faster VBz polymerizations, better agreement between the theoretical and observed molecular weights, and relatively narrow polydispersities ($M_w/M_n \sim 1.3-1.6$). These observations taken together suggest that retardation observed at low temperatures derives from slow fragmentation of tertiary carbon-centered radicals **Int-1** and **Int-2** formed by addition of a propagating vinyl benzoate chain to the RAFT agent (Scheme 1). Previously reported theoretical and experimental studies of RAFT polymerization have provided substantial evidence that these intermediate radicals may exhibit long lifetimes and may serve as radical sinks by virtue of their kinetic stability toward termination reactions.[50] Furthermore, RAFT agent capture of the propagating chains is imperfect, thus allowing some high molecular weight polymer chains to be produced; a similar type of "hybrid behavior" was previously observed in cumyl dithiobenzoate-mediated RAFT polymerizations of methyl methacrylate.[51] At higher temperatures, the rate of fragmentation increases to enable productive degenerate interchange and fast chain propagation evidenced by close agreement between the experimentally observed and theoretical M_n values. This observation is consistent with previous work demonstrating that higher reaction temperatures tend to increase the rates of radical interchange relative to the rate of monomer propagation resulting in improved polymerization kinetics.[39] The broader polydispersity indices observed at elevated temperatures are consistent with a lower chain transfer rate constant associated with **1** for VBz relative to that for VAc. The decreased efficiency of VBz radical chain interchange likely stems from two effects: (i) decreased rate of radical addition to the xanthate to form **Int-1** and **Int-2** due to the more electron deficient character of the α-benzoyloxy radical chain end in VBz polymerizations relative to the more nucleophilic α-acetoxy radical chain ends in VAc polymerizations and (ii) slow fragmentation of stabilized carbon-centered radicals **Int-1** and **Int-2** due to the presence of two electron withdrawing α-benzoyloxy substituents bound to the sulfur atoms.

Chain extension reactions of xanthate-terminated vinyl ester homopolymers with different vinyl ester monomers proceed with variable efficiencies, establishing the viability of block copolymer syntheses by sequential monomer addition reactions to yield melt microphase-separated materials. Block copolymerizations of VAc with either VPv or VBz produce diblock copolymers with narrow molecular weight distributions independent of the order of block synthesis, indicating that monomer crossover reactions are highly efficient. On the other hand, attempts to produce diblock copolymers of VBz and VPv using either PVPv or PVBz macro-RAFT agents yielded multimodal and polydisperse block copolymers, respectively. We attribute these results to the low macro-RAFT agent concentrations employed in these reactions due to the limited solubilities of the macro-RAFT agents in the bulk monomers. These vinyl ester block copolymers melt microphase separate at modest molecular weights, as indicated by preliminary temperature-dependent SAXS measurements. Our initial studies indicate that PVPv-*b*-PVAc diblocks are relatively strongly segregated, since these materials remain microphase separated at temperatures up to 240 °C. The observed microphase separation of PVPv-*b*-PVAc-1, PVPv-*b*-PVAc-2, and PVPv-*b*-PVBz indicate that block polydispersity does not inhibit long-range ordering of these copolymer melts, consistent with previous reports on the phase behavior of polydisperse diblock copolymers.[44]

Conclusion

We have described the syntheses of a new class of microphase separated block copolymers derived from vinyl ester monomers using xanthate-mediated RAFT polymerizations. Our studies have demonstrated that a high level of monomer purity is essential for predictable and reproducible controlled polymerizations of these monomers to yield relatively monodisperse homopolymers bearing xanthate termini. Comparisons of vinyl acetate homopolymerizations in the presence of a RAFT chain transfer agent bearing an α-enoyl leaving group against one bearing an α-acyloxy leaving group, similar to a growing vinyl ester polymer chain end, demonstrated the inherent limits of controlled block copolymerization achievable using poly(vinyl ester) macro-RAFT agents. Optimization of the RAFT polymerization of vinyl benzoate showed that propagating radical chain ends bearing electron withdrawing substituents require elevated temperatures in order for the rates of degenerate interchange to be fast enough for efficient and controlled polymerization reactions. Xanthate-terminated vinyl ester homopolymers can act as macromolecular RAFT agents for the block copolymerization of vinyl esters such as vinyl acetate, vinyl pivalate, and vinyl benzoate with varying efficiencies. Temperature-dependent SAXS analyses demonstrate that these block copolymers melt microphase separate with high degrees of long-range order. Studies of the melt-phase behavior and mechanical properties of these new degradable polymers are currently in progress.

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Supporting Information Available: SEC data and SAXS data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ober, C. K.; Cheng, S. Z. D.; Hammond, P. T.; Muthukumar, M.; Reichmanis, E.; Wooley, K. L.; Lodge, T. P. *Macromolecules* **2009**, *42*, 465.

(2) Avella, M.; De Vlieger, J. J.; Errico, M. E.; Fischer, S.; Vacca, P.; Volpe, M. G. *Food Chem.* **2005**, *93*, 467.

(3) Lenz, R. W. *Biodegradable Polymers and Plastics in Japan: Research, Development, and Applications*; Internationl Tehcnology Research Institute, Loyola College in Maryland: Baltimore, MD, 1995.

(4) Schreck, K. M.; Hillmyer, M. A. *J. Biotechnol.* **2007**, *132*, 287.

(5) Anderson, K. S.; Schreck, K. M.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 85.

(6) Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841.

(7) Gruber, P.; O'Brien, M. In *Biopolymers: Polyesters III-Applications and Commerical Products*; Doi, Y., Steinbuchel, A., Eds.; Wiley-VCH: New York, 2002; Vol. 4, p 410.

(8) Daniels, W. E. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Ed.; Wiley: New York, 1985; Vol. 17, p 393.

(9) Barry, D. ICIS News & Pricing, **2007**.

(10) Marten, F. L. In *Encyclopedia of Polymer Science & Engineering*, 2nd ed.; Mark, H. F., Ed.; Wiley: New York, 1985; Vol. 17, p 167.

(11) Chiellini, E.; Corti, A.; D'Antone, S.; Solaro, R. *Prog. Polym. Sci.* **2003**, *28*, 963.

(12) Matsumura, S. *Biopolymers* **2003**, *9*, 329.

(13) Pinto, M. A.; Li, R.; Immanuel, C. D.; Lovell, P. A.; Schork, F. J. *Ind. Eng. Chem. Res.* **2008**, *47*, 509.

(14) Holden, G.; Legge, N. R. In *Thermoplastic Elastomers*; Holden, G., Legge, N. R., Quirk, P. R., Schroeder, H. E., Eds.; Hanser: Munich, 1996; p 47.

(15) Frontiers in Polymer Chemistry; Percec, V., Ed.; *Chem. Rev.* **2001**, *101* (12).

(16) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.

(17) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379.

(18) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 669.

(19) Favier, A.; Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Macromol. Chem. Phys.* **2004**, *205*, 925.

(20) Stenzel, M. H. In *Handbook of RAFT Polymerization*; Barner-Kowollik, C., Ed.; Wiley-VCH: Weinheim, 2008; p 315.

(21) Stenzel, M. H.; Cummins, L.; Roberts, G. E.; Davis, T. P.; Vana, P.; Barner-Kowollik, C. *Macromol. Chem. Phys.* **2003**, *204*, 1160.

(22) Destarac, M.; Charmot, D.; Franck, X.; Zard, S. Z. *Macromol. Rapid Commun.* **2000**, *21*, 1035.

(23) Debuigne, A.; Poli, R.; Jerome, C.; Jerome, R.; Detrembleur, C. *Prog. Polym. Sci.* **2009**, *34*, 211.

(24) Li, S.; Bruin, B. d.; Peng, C.-H.; Fryd, M.; Wayland, B. B. *J. Am. Chem. Soc.* **2008**, *130*, 13373.

(25) Poli, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 5058.

(26) Maria, S.; Kaneyoshi, H.; Matyjaszewski, K.; Poli, R. *Chem.—Eur. J.* **2007**, *13*, 2480.

(27) Coote, M. L. *Macromolecules* **2004**, *37*, 5023.

(28) Coote, M. L. *J. Phys. Chem. A* **2005**, *109*, 1230.

(29) Coote, M. L.; Henry, D. J. *Macromolecules* **2005**, *38*, 5774.

(30) Coote, M. L.; Henry, D. J. *Macromolecules* **2005**, *38*, 1415.

(31) Matyjaszewski, K.; Poli, R. *Macromolecules* **2005**, *38*, 8093.

(32) Barner-Kowollik, C.; Coote, M. L.; Davis, T. P.; Radom, L.; Vana, P. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2828.

(33) Theis, A.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Polymer* **2006**, *47*, 999.

(34) Bernard, J.; Favier, A.; Zhang, L.; Nilasaroya, A.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *Macromolecules* **2005**, *38*, 5475.

(35) Lee, H.; Terry, E.; Zong, M.; Arrowsmith, N.; Perrier, S.; Thurecht, K. J.; Howdle, S. M. *J. Am. Chem. Soc.* **2008**, 130 12242.

(36) Saari, W. S.; Freedman, M. B.; Hartman, R. D.; King, S. W.; Raab, A. W.; Randall, W. C.; Engelhardt, E. L.; Hirschmann, R.; Rosegay, A.; et al. *J. Med. Chem.* **1978**, *21*, 746.

(37) Perrier, S.; Takolpuckdee, P. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5347.

(38) Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49*, 1079.

(39) Chiefari, J.; Rizzardo, E. In *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley-Interscience: Hoboken, 2002; p 920.

(40) Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, *52*, 32.

(41) Abetz, V.; Simon, P. F. W. *Adv. Polym. Sci.* **2005**, *190*, 125.

(42) Cochran, E. W.; Garcia-Cervera, C. J.; Fredrickson, G. H. *Macromolecules* **2006**, *39*, 2449.

(43) Khandpur, A. K.; Foerster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796.

(44) Lynd, N. A.; Meuler, A. J.; Hillmyer, M. A. *Prog. Polym. Sci.* **2008**, *33*, 875.

(45) Ruzette, A.-V.; Tence-Girault, S.; Leibler, L.; Chauvin, F.; Bertin, D.; Guerret, O.; Gerard, P. *Macromolecules* **2006**, *39*, 5804.

(46) Bendejacq, D.; Ponsinet, V.; Joanicot, M.; Loo, Y. L.; Register, R. A. *Macromolecules* **2002**, *35*, 6645.

(47) Bates, F. S. *Macromolecules* **1985**, *18*, 525.

(48) Matsumoto, M.; Ukida, J.; Takayama, G.; Mukumoto, K.; Imai, K.; Kazusa, Y.; Maeda, M. *Makromol. Chem.* **1959**, *32*, 13.

(49) Clarke, J. T.; Howard, R. O.; Stockmayer, W. H. *Makromol. Chem* **1961**, *46*, 427.

(50) Feldermann, A.; Coote, M. L.; Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *J. Am. Chem. Soc.* **2004**, *126*, 15915.

(51) Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 7849.