

# Block Copolymerization of Vinyl Acetate and Vinyl *neo*-Decanoate Mediated by Dithionodisulfide

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ABSTRACT: Block copolymerization of vinyl acetate (VAc) and vinyl *neo*-decanoate (VNDc) is carried out in the presence of a disulfide, isopropylxanthic disulfide (DIP), using 2,2'-azoisobutyronitrile (AIBN) as the radical initiator. The polymerization proceeds in a controlled/"living" style, as illustrated by stepwise increase in molecular weight and relatively narrow molecular weight distribution of the final product. The reaction mechanism is investigated in detail for the system of VAc homopolymerization in the presence of DIP. The results of chromatography, NMR, and mass spectra reveal that there exists two kinds of RAFT agents, that is, *S*-(cyano)isopropyl *O*-isopropyl xanthate and diisopropyl dithiocarbonate, the former coming from the reaction of 2-cyano-isopropyl radical with DIP and the latter being formed in situ during a series of radical process participated by the monomer. High efficiency of the cross initiation is achieved for the sequential polymerization. The block lengths are well controlled by the ratio of monomer to RAFT agents. The resulting block copolymer, PVAc-*b*-PVNDc, is hydrolyzed to prepare PVOH-*b*-PVNDc. These block copolymers, before and after hydrolysis, undergo self-assembly in solution and phase separation in bulk state.

#### Introduction

Controlled/"living" radical polymerizations based on the RAFT (reversible addition-fragmentation chain transfer) process have been extensively studied in the past 10 years.<sup>1,2</sup> The living feature of the RAFT-based polymerization is achieved through the reversible chain transfer of propagating radicals toward thiocarbonylthio compounds such as dithioesters and trithiocarbonates.<sup>2</sup> When xanthates are used as chain transfer agent, the reaction is independently nominated as macromolecular design via the interchange of xanthates (MADIX) processes,<sup>3-</sup> which is a very efficient approach in the synthesis of narrow disperse vinyl alkanoate polymers.<sup>6-13</sup> Usually, the studies of the RAFT and MADIX polymerizations require the synthesis of thiocarbonylthio compounds on a laboratory scale. The synthesis of dithioesters and xanthates is generally done using Grignard reagent,<sup>1</sup> whereas the latter can also be synthesized from corresponding salts.<sup>5</sup> Some of these compounds are already commer-cially available.<sup>14,15</sup> An alternative way is to form RAFT agent in situ by the reaction of radical initiator and disulfide. Sanderson and coworkers have reported RAFT polymerization initiated by AIBN in the presence of bis(dithiobenzoyl) disulfide,<sup>16</sup> in which dithioester derived from fragments of AIBN and disulfide<sup>17,18</sup> seems to play the role of RAFT agent. Nevertheless, the reports on the in situ formation of dithioesters or xanthates are quite seldom up to date.19,20

In the present work, we use isopropylxanthic disulfide (DIP, Scheme 1), a conventional rubber vulcanization accelerator, to mediate the RAFT/MADIX polymerization of vinyl acetate (VAc) and vinyl *neo*-decanoate (VNDc). DIP is a bifunctional xanthogenic derivative and has been reported as a photo or thermal iniferter in radical polymerizations of styrene, (meth)acrylates, acrylonitrile, and VAc.<sup>21–24</sup> The present work demonstrates,

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however, that DIP is rather a precursor of RAFT agent than an iniferter during the polymerization of vinyl alkanoates, thereby resulting in narrower disperse polymer products.

VNDc is a functional monomer with bulky branched alkyl group (Scheme 1). It is usually used to copolymerize with VAc to endow the product with higher water and alkaline resistance due to the hydrophobicity of VNDc units.<sup>25,26</sup> VNDc has also been homopolymerized through MADIX process.<sup>9,27</sup> Nevertheless, the synthesis of block copolymer of VNDc and VAc has never been reported. In addition, the block copolymer prepared in the present work has been selectively hydrolyzed on PVAc segments, taking advantage of alkaline resistance of VNDc units.<sup>28,29</sup> Amphiphilic diblock copolymer possessing semicrystalline poly-(vinyl alcohol) segments, PVOH-*b*-PVNDc, is therefore obtained.

## **Experimental Section**

**Materials.** DIP (XiaWei,  $\geq 98\%$ ) was recrystallized from ethanol. VAc (Sinopharm Chemicals,  $\geq 99\%$ ) and VNDc (Helixon Chemicals,  $\geq 99\%$ ) were distilled after being stirred over CaH<sub>2</sub> for 24 h. Benzene (ShenXiang Chemicals,  $\geq 99\%$ ) and tetrahydrofuran (Sinopharm, 99%) were refluxed over sodium and distilled. 2,2-Azobis-(isobutyronitrile) (AIBN, Shanghai fourth Factory of Chemicals, 99%) was recrystallized from methanol. Methanol (99.5%), dimethylsulfoxide (99%) (both LingFeng Chemicals), petroleum ether (ShenXiang Chemicals, 99%), acetone (Dahe Chemicals,  $\geq 99.5\%$ ), and *N*-methyl-2-pyrrolidone (Sinopharm Chemicals,  $\geq 98\%$ ) were used as received.

**Measurements.** <sup>1</sup>H and <sup>13</sup>C NMR and HSQC measurements were carried out on a Bruker (500 MHz) NMR instrument, using tetramethylsilane (TMS) as the interior reference. Gel permeation chromatography (GPC) was performed on a Waters 410 system equipped with three TSK columns (TSK Gel H-type, pore size 15, 30, and 200 Å) in series, a Waters 410 RI detector, and a Waters 486 UV detector (300 and 254 nm), using THF as the eluent at a flow rate of 1 mL/min at 40 °C. The columns were calibrated by narrow polystyrene standard with molecular



weight ranging from  $2.2 \times 10^3$  to  $5.2 \times 10^5$  g/mol. Highperformance liquid chromatography (HPLC) was performed on an instrument composed of a Waters 515 pump, a C-18 column, and a UV detector with the wavelength set at 254 and 300 nm. Acetonitrile/water (v/v 85/15) was used as eluent (1.0 mL/min) at 40 °C. For VAc polymerization, monomer conversion was measured by TGA performed on a Perkin-Elmer Pyris 1 instrument under a nitrogen atmosphere (40 mL/min). The temperature was elevated from 20 to 700 °C at a rate of 20 °C/min. The solvent and monomer evaporated rapidly up to 150 °C, whereas polymer degradation starts at 300 °C. Polymer content was calculated using weight loss above 300 °C.

Gas chromatography-mass spectrometry (GC-MS) was performed on a Thermo Focus DSQ system, equipped with a massselective detector using electron impact ionization. Analytes were separated by an HP-5MS capillary column of 30 m (0.25 i.d. and  $0.25 \,\mu$ m film thickness), which was inserted directly into the ion source of the MS system. Helium (99.999%) was the carrier gas maintained at a flow-rate of 1 mL/min. The injector was kept at 250 °C, and samples were split injected (1  $\mu$ L, split ratio 30:1). The column oven temperature was programmed to start at 60 °C for 2 min, ramp at 20 °C/min for 12 min, and held at 300 °C for 5 min. EI spectra were scanned between 41 and 350 Da in the full-scan acquisition mode. The transferline and EI source temperature were both 250 °C. The electron multiplier voltage was set on 70 eV.

Matrix-assisted laser desorption ionization-time-of-flight mass spectroscopy (MALDI-TOF MS) measurements were performed using a Voyager DE-STR instrument (Applied Biosystems) equipped with a 337 nm nitrogen laser. Data were acquired in the reflector mode. Sodium trifluoroacetate and 2,5-dihydroxybenzoic acid (DHB) were used as the cationization agent (10 mg/mL in THF) and the matrix (20 mg/mL in THF), respectively. The polymer sample was dissolved in THF at a concentration of 10 mg/mL. The matrix, cationization agent, and sample solutions were premixed at a 10:1:2 (v/v) ratio. Approximately 0.5  $\mu$ L of the obtained mixture was dropped on the target plate. After the solvent was evaporated, the target was inserted into the mass spectrometer. For each spectrum, 1000 laser shots were accumulated.

Dynamic light scattering (DLS) was performed on a modified commercial light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multidigital time correlator and ADLAS DPY425II solid-state laser (output power = 22 mW at  $\lambda_0$  = 632.8 nm, angle = 90°). The scattering cell was surrounded by a bath of filtered toluene at a temperature of 298.13 K. Thermal properties of block copolymers were determined by a Mettler DSC-1 apparatus using indium ( $T_m$  = 156.60 °C and  $\Delta H_f^0$  = 28.45 J/g) as standard and nitrogen as flow gas. The samples were heated to 300 °C (20 °C/min), kept for 5 min, cooled to -20 °C (20 °C/min), and then heated to 300 °C at a rate of 20 °C/min. For the annealing, the sample was heated to 200 °C (10 °C/min), kept for 90 min, cooled to -40 °C (10 °C/min), and then heated to 300 °C at a rate of 10 °C/min. IR spectra were obtained on a Magna-550 FTIR instrument.

Kinetic Study of RAFT Homopolymerizations of VAc and VNDc Mediated by DIP. VAc (31.70 g, 0.37 mol), DIP (0.50 g, 1.85 mmol), and AIBN (0.45 g, 2.74 mmol) were dissolved in benzene (22 mL) in a 100 mL flask. The solution was deaerated through three cycles of freezing-pumping-thawing. The reaction mixture was warmed to 60 °C under argon. An aliquot of

the reaction mixture was taken from the flask at predetermined periods and analyzed by GPC. The final product was obtained after three times of dissolving in THF and precipitating from cool petroleum ether (bp 60–90 °C).  $M_{n,GPC} = 22\,000$  g/mol (24 h), PDI = 1.48.

For the isolation of small molecular species formed during induction period ( $P_{254}$  and  $P_{300}$ , see the Results and Discussion), the reaction was stopped after heating the polymerization mixture for 8 h. Solvent and monomer were removed by rotary evaporation. The residual viscous mixture was subsequently fractionated by column chromatography, employing gradient eluent of chloroform/hexane (from 1/1 to 9/1 v/v). The purification of each fraction was repeated three times by column chromatography. The obtained liquid substances were analyzed by NMR and GC-MS.  $P_{300}$ : <sup>1</sup>H NMR:  $\delta$  1.37 (6H, d, SCH-(CH<sub>3</sub>)<sub>2</sub>), 1.39 (6H, d, OCH(CH<sub>3</sub>)<sub>2</sub>), 3.75–3.83 (1H, m, SCH-(CH<sub>3</sub>)<sub>2</sub>), 5.75-5.83 (1H, m, OCH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR: δ 21.3 (SCH(CH<sub>3</sub>)<sub>2</sub>), 22.3 (OCH(CH<sub>3</sub>)<sub>2</sub>), 29.7 (SCH(CH<sub>3</sub>)<sub>2</sub>), 40.5 (OCH(CH<sub>3</sub>)<sub>2</sub>), 213.8 (C=S). GC (Figure 6): 100%, MS (70 eV) m/ *z*: 178 [M<sup>+</sup>], 136 [C<sub>4</sub>H<sub>8</sub>S<sub>2</sub>O<sup>+</sup>], 120 [C<sub>4</sub>H<sub>8</sub>S<sub>2</sub><sup>+</sup>], 103 [C<sub>4</sub>H<sub>7</sub>SO<sup>+</sup>], 94  $[CH_2S_2O^+]$ , 75  $[C_3H_7S^+]$ , 59  $[C_3H_7O^+]$ , 43  $[C_3H_7^+]$ .  $P_{254}$ : <sup>4</sup>H NMR:  $\delta$  2.15 (3H, s, O=CCH<sub>3</sub>), 3.72-3.76 and 4.08-4.13 (1H, q, SCH<sub>2</sub>CH), 6.63–6.66 (1H, q, SCH(CH<sub>2</sub>)O). <sup>13</sup>C NMR: δ 20.8 (O=CCH<sub>3</sub>), 41.0 (SCH<sub>2</sub>CH), 81.0 (SCH(CH<sub>2</sub>)O), 169.6 (CH<sub>3</sub>C=O), 195.1 (S-C=O). GC (Figure 8): 96.3%, MS (70 eV) m/z: 179 [M-H<sup>+</sup>], 118 [C<sub>4</sub>H<sub>6</sub>SO<sub>2</sub><sup>+</sup>], 90 [C<sub>2</sub>H<sub>2</sub>S<sub>2</sub><sup>+</sup>], 76  $[C_2H_4SO^+]$ , 59  $[C_2H_3O_2^+]$ , 43  $[C_2H_3O^+]$ .

The polymerization of VNDc was carried out using the same procedure as that in VAc system, with feeds of monomer (28.40 g, 0.14 mol), DIP (0.20 g, 0.74 mmol), and AIBN (0.12 g, 0.73 mmol) in 32 mL of benzene. The final product was obtained after three times of dissolving in THF and precipitating from methanol.  $M_{n,GPC} = 21900 \text{ g/mol} (30 \text{ h})$ , PDI = 1.48.

A model reaction between AIBN (1.02 g, 6.22 mmol) and DIP (1.55 g, 5.74 mmol) was carried out in benzene (50 mL) in the absence of monomer. The solution was deaerated through three cycles of freezing-pumping-thawing and warmed to 60 °C under argon for 20 h. The resulting reaction product was analyzed by GC-MS.

Synthesis of PVAc-*b*-PVNDc Block Copolymers. The synthesis of the first block, PVAc, is carried out using same process as that in the above kinetic study except the feeding amount: VAc (30.50 g, 0.35 mol), DIP (0.50 g, 1.85 mmol), and AIBN (0.30 g, 1.83 mmol) in benzene (22 mL). The reaction mixture was heated for 16 h. A viscose liquid was obtained after three times of dissolving in THF and precipitating from cool petroleum ether. The viscose liquid became solid after being dried in vacuum at room temperature for 3 days. The solid was redissolved in acetone and dialyzed for 3 days to eliminate the small molecular impurities completely. The final product was PVAc with xanthate terminus. Conversion = 32%,  $M_{n,GPC} = 5600$  g/mol, PDI = 1.35.  $M_{n,NMR} = 9600$  g/mol (in acetone- $d_6$ ). VNDc (19.36 g, 0.10 mol), PVAc with xanthate terminus

VNDc (19.36 g, 0.10 mol), PVAc with xanthate terminus  $(M_{n,NMR} = 9600 \text{ g/mol})$  (3.00 g, 0.32 mmol), and AIBN (0.04 g, 0.24 mmol) were dissolved in benzene (20 mL) in a 100 mL flask. The solution was deaerated through three cycles of freezing-pumping-thawing. The reaction mixture was warmed to 60 °C under argon. For kinetic study, an aliquot of the reaction mixture was taken out from the flask at predetermined periods and analyzed by GPC.

To obtain block copolymer, the reaction was conducted using the same mixture for a period of 24 h, followed by three times of dissolving in THF and precipitating from methanol/water (v/v 1:1), and dried in vacuum for 1 week at 50 °C. Conversion = 12%,  $M_{n,GPC} = 12200$  g/mol, PDI = 1.36.  $M_{n,NMR} = 13200$ g/mol (in THF- $d_8$ ).

**Hydrolysis of PVAc-***b***-PVNDc Block Copolymers.** A solution of PVAc(11200)-*b*-PVNDc(38300) (0.70 g) in 5 mL of THF was mixed with a solution of potassium carbonate (1.20 g) in 40 mL of methanol. The mixture was stirred at 50 °C for 15 h. After the



removal of methanol by distillation, the reaction mixture was dispersed in water and transferred to a dialysis package. After dialysis for 4 days in water, the aqueous solution was lyophilized for 2 days to get a cotton-like copolymer. GPC analysis was not done because of poor solubility of the hydrolyzed product in THF. Yield = 65.6%.

Hydrolysis of both homopolymers was conducted under otherwise identical conditions except for the reaction time. In the case of PVNDc, no reaction occurred after 24 h, whereas a period of 2 h is enough for completely hydrolysis of PVAc.

Self-Assembly of the Diblock Copolymers. In typical, a sample of block copolymer, PVAc(11200)-*b*-PVNDc (10200) (60 mg,  $2.6 \times 10^{-3}$  mmol) in 10 mL acetone was stirred overnight. The dispersion (6 mg/mL) was filtered by passing through a PTFE syringe filter (pore size 0.45  $\mu$ m) before being analyzed by DLS.

#### **Results and Discussion**

**RAFT** Polymerizations of VAc and VNDc Mediated by DIP. The general synthetic route is outlined in Scheme 2. As the first step, we study the homopolymerizations of VAc and VNDc, both of which are carried out in benzene solution at 60 °C, using AIBN as the initiator and DIP as the MADIX agent precursor. It is reported that a trace amount of impurity in chain transfer agents such as xanthate<sup>8</sup> and dithioesters<sup>30</sup> would cause inhibition and retardation. The compound DIP, with a purity of >98% as received, has been recrystallized to reach a purity of as high as 99.4% (by HPLC). As the polymerization proceeds, the reaction solution becomes more and more viscous. An aliquot of the reaction mixture is taken at a predetermined period and analyzed directly by GPC equipped with a set of special columns capable of resolving both polymeric and small molecular species.<sup>31</sup> Therefore, the molecular weight of the product and the monomer conversion are obtained simultaneously.

Figure 1 displays the GPC traces monitoring the RAFT homopolymerizations of VAc and VNDc mediated by DIP. There is a clear shift of  $M_n$  to larger molecular weight along with a decrease in monomer peak intensities. Note that VAc



**Figure 1.** Evolution of molecular weight with increasing conversion in (a) VAc and (b) VNDc solution polymerization mediated by DIP.

gives inverse peaks and partially overlaps with unknown species (inset in Figure 1a); therefore, monomer conversion is measured by TGA. The polydispersity is close to 1.5, the lowest theoretical value of radical polymerization, although larger than that of typical living polymerization due to the quasi-living feature of MADIX system.

An induction period of up to 5 h is observed for both systems, as shown in Figure 2. At the end of the induction period, molecular weight starts to increase linearly with monomer conversion. Nevertheless, the molecular weight increases abruptly when it starts to grow, as shown in Figure 2b, exhibiting a "hybrid" behavior of conventional and controlled radical polymerization in the initial stage. In the system of VNDc, the deviation of molecular weight from a linear dependence on monomer conversion is more obvious in which the extrapolation does not pass the origin of the coordinates (dashed line in Figure 2d). This is in sharp contrast with the polymerization behavior of styrene in the presence of dithioesters, in which a stepwise increase in molecular weight is observed from the start of the polymerization.<sup>31,32</sup> The "hybrid" behavior has been observed in RAFT polymerization of MMA and VAc mediated by either xanthates<sup>7</sup> or dithioester<sup>33</sup> and has been ascribed to larger propagation rate in relative to the rate of RAFT process.

GPC is used to monitor the reaction in the induction period, setting UV detector at double wavelengths, 254 and 300 nm, which are close to the two peak absorptions in UV spectrum of DIP. Figure 3 shows the elution diagram of VAc polymerization mixture at various reaction times in the initial stage. For both working wavelengths a new peak appears at the right side of DIP, thereafter denoted as peaks  $P_{254}$  and  $P_{300}$ , respectively. As the reaction proceeds, the intensity of DIP peak decreases as those of  $P_{254}$  and  $P_{300}$  increase. After complete consumption of DIP, the intensity of  $P_{254}$  stays constant, whereas that of  $P_{300}$ decreases when the polymer peak appears (insets in Figure 3), indicating participation of  $P_{300}$  species in the polymerization. However, remarkable amount of  $P_{300}$  remains unreacted up to high conversion of monomer, as shown by GPC trace for 24 h in the inset in Figure 3b.

The peaks of  $P_{254}$  and  $P_{300}$  may be ascribed to possible xanthate species formed in the reaction of DIP- and AIBNderived radical. It has been reported that bis(dithiobenzoyl) disulfide,<sup>16</sup> in reaction with AIBN, formed dithioester, which acted in situ as a RAFT agent. However, the resulting dithioester has not been identified in ref 16. In the present work, species of  $P_{254}$  and  $P_{300}$  are isolated by column chromatography using the reaction mixtures in the induction period, that is, before the beginning of polymerization.

Figure 4 shows an HPLC diagram in which species of  $P_{254}$  and  $P_{300}$  are observed at elution time of 3.2 and 6.0 min, respectively, as detected under 254 and 300 nm. The correlation



Figure 2. (a,c) Reaction kinetics and (b,d) the increase in molecular weight along with monomer conversion during homopolymerizations of VAc and VNDc in the presence of DIP. Feeding molar ratio: VAc/DIP/AIBN 200/1/1.5; VNDc/DIP/AIBN 200/1/1. The molecular weights are reported in relative to polystyrene standards.



**Figure 3.** GPC diagrams detected at (a) 254 and (b) 300 nm for solution polymerization of VAc initiated with AIBN and mediated by DIP at 60 °C. Feed: VAc/DIP/AIBN 200/1/1.5 (molar ratio).

between GPC and HPLC results is done using the authentic samples isolated by column chromatography employing gradient eluent of chloroform/hexane (from 1/1 to 9/1 v/v). It is obvious that  $P_{254}$  and  $P_{300}$  are different fractions in the HPLC profile, although they are very close in GPC diagram. These species are characterized in the following section. A small peak, partially overlapped with benzene signal, appears at elution time of 4.2 min in Figure 4b ( $S_{300}$ ) and turns out to be *S*-(cyano)isopropyl xanthate (**3** in Scheme 3) (Supporting Information). Compound **3** is generated by the reaction of 2-cyano-isopropyl radical and DIP. In addition, broad multimodal peaks appear in the range of 6.0 to 7.3 min under both wavelengths, of which the analytical data is unavailable because of low content and difficulty in separation.

The isolated species of  $P_{254}$  and  $P_{300}$  are analyzed by NMR and GC-MS. As shown in Figure 5, a xanthate structure, diisopropyl dithiocarbonate, is assignable from both <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $P_{300}$ . In the <sup>1</sup>H spectrum, four groups of protons are observed at chemical shift of 5.78, 3.79, 1.39, and



**Figure 4.** HPLC diagrams of reaction mixture of VAc, AIBN, and DIP at 60 °C in benzene during the induction period. Feed: VAc/DIP/AIBN 200/1/1.5 (molar ratio). The elution is detected under (a) 254 and (b) 300 nm.

Scheme 3. Reaction Mechanism between AIBN and DIP in the Presence of Vinyl Acetate





Figure 5. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of P<sub>300</sub> (diisopropyl dithiocarbonate) in CDCl<sub>3</sub>.



Figure 6. GC-MS (EI) spectra of species  $P_{300}$  (diisopropyl dithiocarbonate).

1.37 ppm, which are assigned to methines and methyls of isopropyloxy and isopropylthio groups, respectively. In addition, the integration and the splitting constants correlate very well with the proposed structure. GC shows a single peak at retention time of 6.63 min (Figure 6a); the EI-MS is given in Figure 6b. The molecular ion at m/z = 178 agrees with the formula mass of isopropyl xanthate; the base peak is the isopropyl cation (m/z = 43). Proposed complete fragmentation schemes for fractions of  $P_{254}$  and  $P_{300}$  are given in the Supporting Information.

Figure 7 shows the <sup>1</sup>H and <sup>13</sup>C NMR and HSQC spectra of  $P_{254}$ . In the former, the signal at chemical shift of 2.15 ppm comes from acetoxy group, and those at 6.65, 4.10, and 3.75 ppm are assignable to cyclic -CH-CH<sub>2</sub>- system in which the geminal splitting of methylene is -12.95 Hz. <sup>13</sup>C NMR shows carbonyl group at 195 ppm in addition to that at 170 ppm for carbonyl in acetoxy. These lead to the assignment of a cyclic 1,3-dithiol-2-one structure. The integration and the 2D NMR, HSQC, and the splitting constants correlate very well with the proposed structure. GC shows two peaks, the smaller one at 5.27 min is residual AIBN, and the main peak at 8.57 min gives the mass spectrum shown in Figure 8b. The molecular ion is not observed at m/z = 178, possibly because of the instability of the cyclic structure. A small peak appears at m/z = 179, which is assigned to protonated molecules of the cyclic compound. The base peak at m/z = 43 is acetyl cation.

Therefore, it seems that in the polymerization of VAc, the main products formed during the induction time are diisopropyl dithiocarbonate and the cyclic 1,3-dithiol-2-one compound. These are quite unexpected because the anticipated product in the reaction of AIBN and DIP is S-(cyano)isopropyl xanthate according to the work by Zard<sup>17</sup> and Thang.<sup>18</sup> Sanderson and coworkers performed RAFT polymerization initiated by AIBN in the presence of bis(dithiobenzoyl) disulfide.<sup>16</sup> They observed that dithioester derived from fragment of AIBN and disulfide had formed in situ in the reaction system. Beckman and coworkers prepared xanthate with functional groups from the reaction of azo compound and O,O-diethyl bisxanthate.<sup>34</sup> In the present work, a model reaction between AIBN and DIP in the absence of monomer indeed gives similar results as those in refs 16–20. GC-MS spectrum shows high content of *S*-(cyano)isopropyl xanthate (RT = 8.13 min with m/z = 203) in the reaction mixture (Supporting Information).

We propose that the formation of diisopropyl dithiocarbonate and the cyclic 1,3-dithiol-2-one compound is through a series of radical processes, as shown in Scheme 3. The process is triggered by 2-cyano-isopropyl radical, 1, derived from AIBN. The attack of 1 to DIP results in the formation of 2, a thio-centered radical, and a xanthate 3. The thio-centered radical can either recouple to 1 to give 3 or, more possibly, add to monomer to give 4 as normal initiation. However, there is no further chain growth because 4 tends to cyclize through an intromolecular radical transfer process, yielding 6  $(P_{254})$  and releasing an isopropyl radical. The isopropyl radical can either recombine with 2 to form diisopropyl xanthate  $\mathbf{8}(P_{300})$  or react with DIP to result in  $\mathbf{2}$  and  $\mathbf{8}$ . The overall consequence of the process is the formation of 3, 6, and 8 by the consumption of AIBN, DIP, and monomer. The cyclic compound 6 will not take part in further reaction, reaching a stationary concentration after the radical process, as described above. Xanthates 3 and 8 will act as RAFT agents in the subsequent polymerization.





Figure 7. (a) <sup>1</sup>H NMR, (b) <sup>13</sup>C NMR, and (c) HSQC spectra of  $P_{254}$  in CDCl<sub>3</sub>.



Figure 8. GC-MS spectra of  $P_{254}$ . (a) GC and (b) EI-MS.

The above mechanism is very similar to that proposed by Gareau et al.<sup>35</sup> In their work, they prepared unsaturated cyclic 1,3-dithiol-2-ones from the reaction between alkynes and DIP. However, they observed that most of alkenes were unreactive and do not yield cyclic 1,3-dithiol-2-ones. Instead, some vinyl compounds gave double-addition products of disulfide toward the vinyl group. We indeed do not observe any peaks analogous to  $P_{254}$  and  $P_{300}$  in the reaction of DIP with AIBN in the presence of other vinyl monomer such as styrene or methyl methacrylate. Therefore, the formation of **6** and **8** is quite specific for the monomer of VAc.

The end-group analysis by NMR and MALDI-TOF MS may provide more information about the reaction mechanism. Figure 9 shows the <sup>1</sup>H NMR of the polymerization

product purified by dialysis and freeze-drying. For PVAc (A), the methine and methylene protons of the main chain show broad complex signals at 4.82-5.05 and 1.72-1.93 ppm, respectively, resulting from stereoisomers, with integration ratio of 1:2. The acetoxy appears as three peaks due to different configuration sequences of the triad, *mm*, *mr*, and *rr*. The methine of *O*-isopropyl end group shows a weak but clear heptet around 5.75 ppm. The heptet seems to be further split or overlapped with another heptet, which cannot be currently explained. Theoretically, there are three kinds of methyl termini derived from isopropyl radical, 2-cyano-isopropyl radical (both at  $\alpha$ -end) and *O*-isopropyl fragment of xanthate ( $\omega$ -end), respectively. Unfortunately, it is difficult to assign these methyl signals in the range of



**Figure 9.** <sup>1</sup>HNMR spectra of (A) PVAc with xanthate terminus  $(M_{n,NMR} = 9600 \text{ g/mol}, \text{PDI} = 1.35)$  in acetone- $d_6$  and (B) PVNDc with xanthate terminus  $(M_{n,NMR} = 8500 \text{ g/mol}, \text{PDI} = 1.45)$  in THF- $d_8$ .

0.70 to 1.72 ppm because the signals in this region are quite complex. Similarly, the methine signal of *O*-isopropyl terminus in PVNDc appears as a broad complex at  $\sim$ 5.75 ppm (Figure 9B). The signal broadening may be due to mediate solubility of PVNDc in THF. PVNDc is insoluble in most organic solvents such as acetone, DMF, *N*-methylpyrolidone, chloroform, dichloromethane, cyclohexane, toluene, and benzene and is partially soluble in DMSO at 80 °C. In fact, THF is the most soluble solvent we have ever found for homo PVNDc. Therefore, NMR spectroscopy confirms the presence of xanthate terminus but does not distinguish the structures of the other end, either isopropyl from **8** or cyanoisopropyl from **3**.

To analyze the structure of end group, MALDI-TOF MS is carried out on a PVAc sample with low molecular weight, 2400 g/mol (by NMR, Supporting Information). In fact, this is the lowest molecular weight we have ever obtained because of the abrupt and uncontrolled polymerization in the initial stage. According to previous reports, <sup>36,37</sup> we have tried the following substances as the matrix: 2[(2E)-3-(4-tert-butyl-phenyl-2-methylprop-2-enylidene) malononitrile (DCTB), 2,5-di-hydroxy-benzoic acid (DHB),  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA), and  $3-\beta$ -indole acrylic acid (IAA). DHB gives a clearly better resolved spectrum, as shown in Figure 10. There are five series of signals, all of which show an interval of 86 mass units corresponding to VAc repeating



**Figure 10.** Matrix-assisted laser desorption ionization time-of-flight mass spectrum of PVAc with xanthate terminus ( $M_{n,GPC} = 2100 \text{ g/mol}$ ,  $M_{n,NMR} = 2400 \text{ g/mol}$ ); matrix: DHB; cationization agent: sodium trifluoroacetate.

unit. The main series is assignable to polymer chains with  $\alpha$ -cyanoisopropyl and  $\omega$ -xanthate termini, which results from 3 and new initiation of AIBN. Polymer with  $\alpha$ -isopropyl and  $\omega$ -xanthate termini, derived from 8, shows a signal at 1663.9 with relatively low intensity. In addition, some terminated species are observed at m/z = 1641.0, 1658.0, and 1683.0, which are assigned to H-terminated chains (by disproportionation), recombination terminated chains with  $\alpha$ - and  $\omega$ -isopropyl termini, and recombination terminated chains with  $\alpha$ -cyanoisopropyl and  $\omega$ -isopropyl termini, respectively. The origins of these species are quite complex. Whereas chains with unsaturated terminus, the counterparts of H-terminated ones in disproportionation, are observed at m/z = 1639.0, these species, saturated and unsaturated, can also be formed by disproportionation between propagating chains and primary radicals such as isopropyl and 2-cyano-isopropyl radicals. In a similar way, recombination termination may occur between homologous propagating chains or between propagating chain and primary radicals. The former pathway would result in the formation of telechelic species with cyanoisopropyl termini. However, these species are not observed in the spectrum. Therefore, we propose that the recombination terminated chains form by cross termination between propagating chains and isopropyl radical, the latter being generated as the leaving group in the chain transfer process of 8.

From the results of chromatography, NMR, and MALDI-TOF MS, it is clear that the reaction of AIBN, DIP, and VAc results in the formation of **3**, **6**, and **8** in the induction period,

			PVAc wit	h xanthate terr	minus					PVAc-b-PVN	Dc			PVOH-b- PVNDc
un	[VAc] <sub>0</sub> /[DIP]/ [AIBN] <sup>a</sup>	time (h)	$\operatorname{conv.}(\%)^b$	$M_{ m n,theor}$ (g/mol) <sup>c</sup>	$M_{ m n,GPC}$ (g/mol) <sup>d</sup>	$M_{ m n,NMR} \ ( m g/mol)^e$	IDI	[VNDc] <sub>0</sub> / [CTA]/[AIBN] <sup>′</sup>	time (h)	Conv. (%) <sup>g</sup>	$M_{ m n,GPC} ({ m g/mol})^d$	$M_{\mathrm{n,NMR}} \over (\mathrm{g/mol})^h$	IQI	ratio of repeating units
-	200/1/1	16	32	2750	5600	9600	1.35	400/1.3/1	24	12	12 200	13 200	1.36	6:1
2	300/1/1	25	75	9680	15600	18000	1.36	320/1.6/1	38	32	23 500	30200	1.41	10:3
б	200/1/1.5	12	41	3256	8000	11 200	1.35	200/1/1	36	38	18600	21400	1.42	5:2
								600/1/1	24	30	41000	49 500	1.54	2:3
4	200/1/2	6.5	40	3200	8000	11 900	1.45							
$^{a}\mathrm{F}$	eed molar ratio. <sup>b</sup> ]	Measured	1 by TGA. <sup>c</sup> Calc	ulated accordir	ng to $M_{\rm n,theor} =$	$([VAc]_0 \times cor$	iversion)/	$([DIP]_0 \times 2) \times MW_1$	$_{\rm Ac} + {\rm MW}_{\rm C1}$	rA. <sup>d</sup> In relative to	o PS standards.	. <sup>e</sup> Analyzed by	<sup>1</sup> H NMR	using the intensity
"atio	of h to d in Figure	- 9a / CT	A refers to PVA.	c with xanthat	e terminus <sup>g</sup> Mu	easured by GI	PC <sup>h</sup> Ana.	lvzed hv <sup>1</sup> H NMR	using the rat	tio of the inteors	tion 4 / 4	in Figure 12		



**Figure 11.** GPC diagrams of samples taken at various conversions (indicated in the Figure) in VNDc polymerization mediated by PVAc with xanthate terminus (9600 g/mol).



Figure 12. <sup>1</sup>HNMR spectrum of PVAc(11200)-*b*-PVNDc(38300) in THF- $d_8$ .

whereas **3** and **8** mediate further RAFT polymerization of VAc. Although **8** is a main product, as indicated by chromatography, chain species derived from **8** constitute only a minor fraction of the polymer products. Instead, the major part of living chains is initiated by 2-cyano-isopropyl radical, either from **3** or from continuous initiation of AIBN. This may be a consequence of poor leaving and reinitiating abilities of isopropyl in relative to cyanoisopropyl group. Indeed, Klumperman and coworkers have found that cyanoisopropyl is a better leaving and reinitiating group than *tert*-butyl,<sup>38</sup> a group similar to isopropyl, in RAFT polymerization of VAc.

Synthesis and Hydrolysis of Block Copolymers of VAc and VNDc. After the induction period, the reaction is transformed into a typical MADIX system in which 3 and 8 play the role of chain transfer agents. A number of block copolymers are prepared by chain extension polymerization of VNDc using the first segment as the macro chain transfer agent. For the first block, the molecular weight is controlled by the molar ratio of VAc to DIP, whereas the ratio of DIP to AIBN determines the polymerization rate and the inhibition time. The results are listed in Table 1. The molecular weight measured by GPC is reported in relative to polystyrene standards, giving lower  $M_{n,GPC}$  in relative to that measured by NMR,  $M_{n,NMR}$ , which is more close to the real value. Polydispersity is reasonably low in all cases.

The first block is purified by repeated precipitation in iced petroleum ether. (For the measurement, the sample is dialyzed in acetone for 3 days and freeze-dried overnight.) The first block is dissolved in benzene and mixed with a

Table 1. Synthesis and Characterization of PVAc and Block Copolymers, PVAc-b-PVNDc

predetermined amount of AIBN and VNDc. The mixture is heated to 60 °C to start the block copolymerization. GPC traces of a typical polymerization, shown in Figure 11, illustrate a stepwise increase in molecular weight and high efficiency of the transformation to the second block.

The ratio of repeating units (m/n in the block copolymer) is measured by <sup>1</sup>H NMR using samples dried in vacuum for 1 week at 50 °C after precipitation. As shown in Figure 12, the methine signals of the main chain (a and c) from different monomer units overlap in the range of 4.8 to 5.0 ppm. The



**Figure 13.** <sup>1</sup>H NMR spectrum of hydrolyzed product PVOH(5730)-*b*-PVNDc(38300) measured in DMSO-*d*<sub>6</sub> at 80 °C.

percentage of the VNDc units is estimated by the ratio of the integration,  $A_c/A_{a+c}$ , in which the area of  $A_c$  equals to 1/9 of that of peak e. The results are listed in Table 1.

The pendent ester groups of PVNDc segment are resistant to alkaline,<sup>25–29</sup> whereas those of PVAc segment can easily be hydrolyzed at room temperature.<sup>39</sup> Indeed, we observe complete hydrolysis of PVAc within 2 h, whereas a homopolymer of VNDc remains stable under similar conditions. Therefore, the block copolymer is selectively hydrolyzed to prepare an amphiphilic block copolymer, PVOH-b-PVNDc, which is then purified by dialysis. The final product is insoluble in organic solvents such as acetone, THF, DMF, N-methylpyrolidone, chloroform, dichloromethane, cyclohexane, toluene, and benzene and is partially soluble in DMSO at 80 °C. <sup>1</sup>H NMR spectrum is measured in DMSO-d<sub>6</sub>, as shown in Figure 13, although not well resolved, which is indicative of low solubility or high viscosity of the solution. The acetoxy signal at 2.0 ppm has disappeared, whereas three singlets appear in the range of 3.95 to 4.50 ppm, which are attributable to pendent hydroxyl group. The methine signal of VAc units shifts to 3.9 ppm. The retention of VNDc units after hydrolysis is demonstrated by the presence of the bulky alkyl protons (e signal in Figure 13). The presence of both hydroxyl and ester groups in the hydrolyzed product is further confirmed by IR. (See the Supporting Information.)

**Properties of the Block Copolymer.** Owing to the hydrophobicity of PVNDc segment,<sup>27–29</sup> the block copolymer



Figure 14. Size distribution of PVAc-b-PVNDc (with different ratio of repeating units) micelles formed in acetone.



Figure 15. (a) DSC curves of PVAc, PVAc(18000)-b-PVNDc(12200), PVAc(11200)-b-PVNDc (38300), and PVNDc (from top to bottom) and (b) DSC spectra of PVOH, PVOH(9200)-b-PVNDc(12200), PVAc(5800)-b-PVNDc(38300), and PVNDc (from top to bottom).

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synthesized in this work displays amphiphilic properties that would result in self-assembly in selective solvents. However, the hydrolyzed block copolymer after drying is difficult to be redissolved or form stable dispersion in many solvents. The only solvent we have found is DMSO, but the dissolving should be performed at a temperature higher than 80 °C. We hereby give only preliminary results on the aggregation of PVAc-*b*-PVNDc in solution and bulk state as a demonstration of successful block copolymer synthesis.

PVAc-*b*-PVNDc is sonicated and then stirred in acetone, a selective solvent for PVAc segment. The gel-like polymer readily forms a more homogeneous dispersion with opalescence, which is indicative of micelle formation. The resulting dispersion is filtered using a PTFE syringe filter (pore size: 0.45  $\mu$ m) before investigation by DLS. As shown in Figure 14, the hydrodynamic radius ( $R_h$ ) of the micelles is 44 and 27 nm, respectively, for PVAc(18000)-*b*-PVNDc(12200) and PVAc(11200)-*b*-PVNDc(10200) with narrow distributions. These values are smaller than the chain lengths of the block copolymers at fully extended conformation. However, the copolymer PVAc(11200)-*b*-PVNDc(38300) does not form any stable dispersion in acetone. It is dissolved in good solvent such as THF but immediately precipitates upon addition of acetone, possibly because of longer block of PVNDc.

The bulk property of the block copolymers is investigated using DSC. The results are shown in Figure 15 together with those of hompolymers PVAc and PVNDc. The block copolymer clearly displays two glass-transition temperatures ( $T_g$ ) at around 0 and 42 °C, corresponding to the segments of PVNDc and PVAc, respectively. This demonstrates that microphase separation occurred in the bulk sample of block copolymer. For the hydrolyzed products, PVOH-*b*-PVNDc, a melting peak can be clearly seen at ~215 °C, which is slightly lower than that of PVOH hompolymer (Figure 15b). It can be concluded that the domain of PVOH after phase separation crystallizes into less perfect morphology.

#### Conclusions

Radical polymerization of VAc in the presence of DIP undergoes a RAFT process mediated by xanthate formed in situ via a series of radical process. Two kinds of xanthates play the role of RAFT/MADIX agents, that is, S-(cyano)isopropyl xanthate (3) and diisopropyl dithiocarbonate (8). The presence of 8 is specific for VAc, formed through intramolecular rearrangement of the intermediate. After the induction period, the polymerization proceeds in a controlled/"living" style because of the presence of 3 and 8, the former being the main RAFT/MADIX agent. Block copolymers are successfully synthesized by sequential polymerization of VAc and VNDc. The length of blocks can be tuned by changing the molar ratio of the second monomer, VNDc, to the first block PVAc. The block copolymer is selectively hydrolyzed to prepare well-defined PVOH-b-PVNDc possessing semicrystalline PVOH segment. The block copolymer before hydrolysis aggregates into micelles in acetone, a selective solvent of PVAc, and undergoes microphase separation in bulk state. For the hydrolyzed block copolymer, the melting temperature is observed at 215 °C for PVOH domain.

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**Supporting Information Available:** GC-MS of compound **3**; the complete fragmentation scheme of **8** ( $P_{300}$ ) and **6** ( $P_{254}$ ); IR

spectra of block copolymer before and after hydrolysis; <sup>1</sup>H NMR of PVAc with low molecular weight (2400 g/mol). This material is available free of charge via the Internet at http:// pubs.acs.org.

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