## **Reversible Addition-Fragmentation Chain Transfer Polymerization of Vinyl Acetate Under High Pressure**

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**ABSTRACT:** In this work, high molecular weight polyvinyl acetate (PVAc) ( $M_{n,GPC} = 123,000 \text{ g/mol}, M_w/M_n = 1.28$ ) was synthesized by reversible addition-fragmentation chain transfer polymerization (RAFT) under high pressure (5 kbar), using benzoyl peroxide and *N*,*N*-dimethylaniline as initiator mediated by (*S*)-2-(ethyl propionate)-(*O*-ethyl xanthate) (X1) at 35 °C. Polymerization kinetic study with RAFT agent showed pseudo-first order kinetics. Additionally, the polymerization rate of VAc under high pressure increased greatly than that under atmospheric pressure. The "living" feature of the resultant PVAc was confirmed by <sup>1</sup>H NMR spectroscopy and chain extension experiments. Well-defined PVAc with high molecular weight and narrow molecular weight distribution can be obtained relatively fast by using RAFT polymerization at 5 kbar. © 2015 Wiley Periodicals, Inc. J. Polym. Sci. Part A: Polym. Chem. **2015**, *53*, 1430–1436

**KEYWORDS**: high pressure; kinetics (polym.); living radical polymerization (LRP); reversible addition fragmentation chain transfer polymerization (RAFT); vinyl acetate

**INTRODUCTION** The past decades have witnessed the great development of the controlled/"living" radical polymerization (LRP) with a variety of monomers.<sup>1-9</sup> Among these monomers, vinyl acetate (VAc) has gained extensive attention due to the wide applications of this kind of polymer poly(vinyl acetate) (PVAc) in different areas, such as paints, adhesives, additives to pharmaceuticals, and so on.<sup>10-13</sup> Furthermore, the largest volume water-soluble polymer poly(vinyl alcohol) is also made commercially available by the hydrolysis of PVAc. As an unconjugated monomer, the polymerization of VAc can only follow the radical mechanism. However, the very high reactivity of the propagating radicals makes VAc one of the most challenging monomers for LRP, which usually results in relatively broad molecular weight distributions and limitation of controlled molecular weights for the resultant PVAcs. Up to now, various LRP methods have been applied for the polymerization of VAc, such as atom transfer radical polymerization (ATRP),14,15 degenerative transfer with alkyl iodides,<sup>16-18</sup> iodine transfer radical polymerization,<sup>19</sup> organotellurium-mediated chain transfer polymerization,<sup>20</sup> organostibine-mediated chain transfer polymerization,<sup>21</sup> cobalt-mediated radical polymerization (CMRP),<sup>22–25</sup> and reversible addition-fragmentation chain transfer (RAFT)<sup>26,27</sup> polymerization. Among the above polymerization methods, RAFT/MADIX (macromolecular design via the interchange of xanthates) was explored exten-

The use of high pressure reported in organic chemistry expands our horizons and extends to the synthesis of polymers.<sup>34</sup> Actually, high pressure can facilitate to increase the propagation rate coefficient of the polymerization  $k_{\rm p}$  by several orders of magnitude and to decrease the overall activation volumes of 16-21 cm<sup>3</sup> mol<sup>-1.34</sup> Under high pressure, high molecular weight polymer can be obtained with accessible industrial polymerization process while the propagation of free radicals was enhanced and termination was suppressed.<sup>35</sup> As reported by Penelle et al., poly(methyl methacrylate) (PMMA) has extremely high molecular weight (>1,000,000 g/mol) and narrow molecular weight distribution  $(M_w/M_n = 1.03)$  under high pressure (5 kbar).<sup>36</sup> Later, Fukuda and coworkers<sup>37</sup> synthesized PMMA with a numberaverage molecular weight  $M_{\rm p}$  of 3,600,000 g/mol and a molecular weight distribution of 1.24 via normal ATRP at 5

sively.<sup>26–31</sup> Stenzel et al.<sup>27</sup> first used xanthate as the chain transfer agent for RAFT polymerization of VAc. They found that there should be alkoxy Z-group conjugated with carbon-sulfur double bond to obtain stability and the R-group should be a good leaving group with a comparable reactivity toward the monomer like VAc. RAFT/MADIX showed good controllability on the polymerization of VAc; but to synthesize high molecular weight PVAc still remains as a great challenge.<sup>28–33</sup>



SCHEME 1 The synthetic routes of xanthates with different Z- or R- groups, (a) X1, (b) X2, and (c) X3.

kbar. Recently, Matyjaszewski and coworkers<sup>38</sup> applied activators generated by electron transfer for ATRP to high polymerization system and obtained high molecular weight polystyrene with  $M_n$  more than 1,000,000 g/mol and molecular weight distribution less than 1.25 at 6 kbar at room temperature. However, to the best of our knowledge, there have been no reports on the polymerization of unconjugated monomers (e.g., VAc) under high pressure.

Whether can we realize the controlled polymerization of VAc under high pressure to obtain high molecular weight and low molecular weight distribution PVAc? To investigate the possibility, in this contribution, we combine the advantages of high pressure polymerization and controlled polymerization of VAc with MADIX to demonstrate the RAFT polymerization of VAc under high pressure at lower temperature (35 °C) for the first time, using benzoyl peroxide (BPO) and *N*,*N*-dimethylaniline (DMA) as the redox initiators and (*S*)-2-(ethyl propionate)-(*O*-ethyl xanthate) (X1) as the model RAFT agent.

### **EXPERIMENTAL**

## **Materials**

VAc (>99%, Aldrich) was dried over calcium hydride and then stored in the refrigerator. BPO (Chemical pure, Sinopharm Chemical Reagent) was purified by recrystallization. DMA (>99%, Sinopharm Chemical Reagent) was used as received. Ethyl 2-bromoisobutyrate (>98%) and ethyl 2bromopropionate (>98%) were purchased from Acros and used as received. Benzyl bromide (>99%) was purchased from Sinopharm Chemical Reagent. *p*-Cresol (Chemical pure, Sinopharm Chemical Reagent) was purified twice by recrystallization. Ethanol (analytical reagent), tetrahydrofuran (THF, analytical reagent), *n*-heptane (analytical reagent), ethyl acetate (EA, analytical reagent), and all other chemicals were obtained from Shanghai Chemical Reagents (Shanghai, China) and used as received unless mentioned.

## Synthesis of (S)-2-(Ethyl propionate)-(O-ethyl xanthate) (X1)

X1 was synthesized according to the method reported by literature.<sup>30,39</sup> First, the intermediate potassium *O*-ethyl xanthate was prepared by the reaction of KOH (5.63 g, 0.1 mol),

ethanol (40 mL, 0.645 mol), and CS<sub>2</sub> (20 mL, 0.332 mol). Finally, X1 (Scheme 1) was obtained by the reaction of potassium *O*-ethyl xanthate (9.50 g, 59.3 mmol) and ethyl-2-bromo-propionate (9.48 g, 52.4 mmol) in ethanol (30 mL) under stirring at room temperature and purified by column chromatography using hexane/ethyl acetate (95:5 v/v) as the eluent. The yellow colored oily product X1 (7.83 g, 67.3% yield) was characterized by <sup>1</sup>H NMR: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 4.66 (q, 1H; CH), 4.40 (q, 2H; C(O)OCH<sub>2</sub>), 4.23 (q, 2H;C(S)OCH<sub>2</sub>), 1.59 (d, 3H;CH<sub>3</sub>CH), 1.44 (t, 3H; C(S)OCH<sub>2</sub>CH<sub>3</sub>), and 1.31 (t, 3H; C(O)OCH<sub>2</sub>CH<sub>3</sub>).

## Synthesis of (S)-2-(Benzyl)-(O-methxypheny xanthate) (X2)

X2 was synthesized according to the method reported by the literature.<sup>40</sup> Briefly, the product X2 (Scheme 1) was prepared by the mixture of potassium *O*-methxypheny xanthate (12.88 g, 57.9 mmol) and benzyl bromide (9.01 g, 52.7 mmol) in ethanol (30 mL) under stirring for 16 h at room temperature. The resultant white precipitate was filtered off, washed with diethyl ether and deionized water. Finally, a yellow colored powdered product (X2) (5.92 g, 41.0% yield) was obtained. The product X2 was characterized by <sup>1</sup>H NMR: <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ ) 7.44 (m, 5H; Ar H), 6.96 (m, 4H; CH<sub>3</sub>—Ar H), 5.10 (s, 2H; CH<sub>2</sub>), 3.76 (s, 3H; CH<sub>3</sub>).

# Synthesis of (S)-2-(Ethyl isobutyrate)-(0-ethyl xanthate) (X3)

X3 was prepared according to the method reported by literature.<sup>30</sup> Similarly, X3 (Scheme 1) was obtained by the reaction of potassium *O*-ethyl xanthate (9.50 g, 59.3 mmol) and ethyl 2-bromoisobutyrate (10.26 g, 52.6 mmol) in ethanol (30 mL) under stirring at room temperature and purified by column chromatography using hexane/ethyl acetate (40:1 v/v) as the eluent. A yellow colored oily product (X3) (7.10 g, 57.1% yield) was obtained. The product X3 was characterized by <sup>1</sup>H NMR: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ) 4.56 (q, 2H; C(O)OCH<sub>2</sub>), 4.13 (q, 2H; C(S)OCH<sub>2</sub>), 1.55 (s, 6H; C(CH<sub>3</sub>)<sub>2</sub>), 1.31 (t, 6H;CH<sub>2</sub>CH<sub>3</sub>,CH<sub>2</sub>CH<sub>3</sub>).

## **General Procedures for the Polymerization of VAc**

A typical solution RAFT polymerization with a molar ratio of  $[VAc]_0/[CTA]_0/[DMA]_0/[BPO]_0 = 20,000/2/1/1$  was as



TABLE 1 RAFT	<sup>•</sup> Polymerization	of VAc at 1	bar and 5 kbar
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Entry	R	Time (h)	Conv. [%]	M <sub>n,th</sub> <sup>a</sup> (g/mol)	M <sub>n,GPC</sub> <sup>b</sup> (g/mol)	$M_{\rm w}/M_{\rm n}$
1	10,000/2/1/1	24	10.8	46,700	35,800	1.46
2	20,000/2/1/1	6	NA	NA	NA	NA
3	20,000/2/1/1	24	6.6	56,700	49,400	1.52
4	20,000/2/1/1	48	33.8	290,500	101,900	1.73
5	10,000/2/1/1	3	35.9	154,400	92,800	1.48
6	20,000/2/1/1	3	NA	NA	NA	NA
7	20000/2/1/1	5.5	37.4	322,200	123,000	1.28
8	20,000/4/1/1	5.5	22.6	97,300	67,200	1.32
9	20,000/8/1/1	5.5	18.6	40,300	47,000	1.27
10 <sup>c</sup>	10,000/4/1/1	6	20.5	45,000	30,500	1.40
11 <sup>d</sup>	10,000/4/1/1	6	12.2	27,200	32,500	1.53

Polymerization conditions: R = [VAc]<sub>0</sub>/[CTA]<sub>0</sub>/[DMA]<sub>0</sub>/[BPO]<sub>0</sub>,  $V_{VAc} = V_{EA} = 2.5$  mL; X1 was used as the CTA except entries 10 and 11, T = 35 °C. Entries 1–4 polymerized at 1 bar, and entries 5–11 polymerized at 5 kbar.

follows: A mixture was obtained by adding DMA (0.17 mg,  $1.36 \times 10^{-3}$  mmol), BPO (0.33 mg,  $1.36 \times 10^{-3}$  mmol), X1 (0.60 mg, 2.72  $\times$   $10^{-3}$  mmol), EA (2.5 mL), and VAc (2.5 mL, 27.2 mmol) to a dried ampoule (10 mL) (under atmospheric pressure) or a bag made by polyperfluorinated ethylene propylene film (under high pressure). The solution was bubbled with argon for about 20 min to eliminate the dissolved oxygen. Then, the ampoule was flame-sealed and placed in an oil bath at 35 °C. The bag was sealed by plasticenvelop machine and placed in a water bath with high pressure (5 kbar). The high pressure reaction system (HPP L2–600/0.6, Tianjin, China) was purchased from Tianjin Huatai Sen Miao Biological Engineering Technology. The reactor includes a hydraulic piston-cylinder unit with pressure reaction vessel equipped with a temperature controller and a pressure sensor using water as the medium of pressure conductivity. The ampoule or a bag was opened after the desired polymerization time under atmospheric pressure and high pressure, respectively. The mixture was dissolved in 2 mL of THF and precipitated into 250 mL of hexane. The polymers were isolated by filtration and dried under vacuum at room temperature until a constant weight was achieved. The conversion of the monomer was determined gravimetrically.

## Chain extension of PVAc Macro-RAFT agent

A predetermined quantity of DMA/BPO, PVAc, and VAc was dissolved in predetermined quantity of EA, and the polymerization temperature was kept at 35 °C. The rest procedure was the same as described above, except for the chain transfer agent (CTA) which was replaced by the macro-RAFT agent PVAc.

### Characterization

The number-average molecular weight ( $M_{n,GPC}$ ) and molecular weight distribution ( $M_w/M_n$ ) results of the resultant polymers were determined using a TOSOH HLC-8320 gel permeation chromatograph (GPC) equipped with a

<sup>a</sup>  $M_{n,th} = [VAc]_0/[CTA]_0 \times M_{VAc} \times Conv. + M_{CTA}.$ 

<sup>b</sup> Determined by GPC with poly(methyl methacrylate) calibration.

<sup>c</sup> RAFT polymerization of VAc using X2 as the CTA.

<sup>d</sup> RAFT polymerization of VAc using X3 as the CTA.

refractive-index detector (TOSOH), using TSKgel guardcolumn SuperMP-N (4.6 mm  $\times$  20 mm) and two TSKgel SupermultiporeHZ-N (4.6 mm  $\times$  150 mm) with measurable molecular weight ranging from 5  $\times$  10<sup>2</sup> to 1  $\times$  10<sup>6</sup> g/mol. THF was used as the eluent at a flow rate of 0.35 mL/min and 40 °C. GPC samples were injected using a TOSOH plus autosampler and calibrated with linear poly(methyl methacrylate) standards purchased from TOSOH. The <sup>1</sup>H NMR spectra were recorded on an Inova 300 MHz nuclear magnetic resonance (NMR) instrument using CDCl<sub>3</sub> or dimethyl sulfoxide (DMSO) as the solvent and tetramethylsilane as the internal standard at the ambient temperature.

## **RESULTS AND DISCUSSION**

## Polymerization of VAc at 1 bar and 5 kbar

To investigate the effect of pressure on the polymerization of VAc in the presence of different structures of xanthates X1, X2, and X3, the polymerization was conducted at a lower temperature (35  $^{\circ}$ C) using EA as the solvent under atmospheric and high pressure, respectively, and the results are summarized in Table 1.

It is found from Table 1 that the polymerization of VAc under high pressure was successful, and the polymerization rate increased with the decrease of molar ratio of monomer to initiator, both under atmospheric pressure (1 bar) (entry 1, 10.8% of monomer conversion for  $[VAc]_0/[DMA]_0/[BPO]_0 = 1000/1/1$  versus entry 3, 6.6% of conversion for  $[VAc]_0/[DMA]_0/[BPO]_0 = 2000/1/1)$  and high pressure (5 kbar) (entry 5, 35.9% of monomer conversion for  $[VAc]_0/[BPO]_0 = 1000/1/1$  versus entry 6, no polymer obtained for  $[VAc]_0/[DMA]_0/[BPO]_0 = 2000/1/1)$ . It results from the decrease of initiator concentration in the case of higher molar ratio of monomer to initiator as expected. At the same time, the polymerization rate decreased with increasing of the amount of CTA (entries 7–9), demonstrated



**FIGURE 1** In([M]<sub>0</sub>/[M]) as a function of time (a) and numberaverage molecular weight ( $M_{n,GPC}$ ) and molecular weight distribution ( $M_w/M_n$ ) versus monomer conversion (b) for the RAFT polymerization of VAc at 1 bar and 5 kbar. Polymerization conditions: [VAc]<sub>0</sub>/[X1]<sub>0</sub>/[DMA]<sub>0</sub>/[BPO]<sub>0</sub> = 20,000/4/1/1,  $V_{VAc} = V_{EA} =$ 2.5 mL, T = 35 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

by monomer conversion decreasing from 37.4%, 22.6% to 18.6% when the molar ratio of  $[VAc]_0/[CTA]_0$  increases from 2000/2, 2000/4 to 2000/8. This contributed to retardation phenomena of RAFT polymerization.<sup>41-50</sup> In addition, by comparison of entry 1 and entry 5, it is discernible that the polymerization rate under high pressure (35.9% of monomer conversion after 3 h) was much faster than that under atmospheric pressure (10.8% of monomer conversion after 24 h). To the best of our knowledge, till now, the reported high molecular weight PVAc ( $M_{n,GPC} = 119,400$  g/mol,  $M_{\rm w}/M_{\rm n} = 1.37$ ) could be obtained by photoinduced CMRP<sup>51</sup> and photoinduced electron transfer-RAFT polymerization (PVAc,  $M_{n,GPC} = 101,400$  g/mol,  $M_w/M_n = 1.24$ ),<sup>52</sup> respectively. From entry 7 in Table 1, high molecular weight PVAc up to 123,000 g/mol with narrow molecular weight distribution  $(M_w/M_n = 1.28)$  could be obtained at 5 kbar in this work. Besides X1, from entries 10 and 11, other two kinds of xanthates with different Z- and R-groups can also be used as the CTAs under high pressure.

**Polymerization Kinetics of VAc** 

To further investigate the polymerization behaviors under atmospheric and high pressure, the polymerization kinetics was carried out under both pressures with molar ratio of  $[VAc]_0/[CTA]_0/[DMA]_0/[BPO]_0 = 20,000/4/1/1$  at 35 °C. From Figure 1(a), it can be seen that an induction period was observed both under atmospheric and high pressures. This suggests that it needed a certain time to generate initiator species and establish a dynamic equilibrium between the CTA and propagating radicals during the polymerization. In addition, a much longer induction period (~21.5 h) was observed under atmospheric pressure than that (~4.2 h) under high pressure. After the induction period, a linear relationship between  $ln([M]_0/[M])$  and polymerization time was observed in Figure 1(a), which demonstrated that constant propagating radicals maintained in both cases.



**FIGURE 2** In([M]<sub>0</sub>/[M]) as a function of time (a) and numberaverage molecular weight ( $M_{n,GPC}$ ) and molecular weight distribution ( $M_w/M_n$ ) versus monomer conversion (b) for the RAFT polymerization of VAc with different molar ratios of [VAc]<sub>0</sub>/ [X1]<sub>0</sub>/[DMA]<sub>0</sub>/[BPO]<sub>0</sub> at 5 kbar. Polymerization conditions: [VAc]<sub>0</sub>/[X1]<sub>0</sub>/[DMA]<sub>0</sub>/[BPO]<sub>0</sub> = 20,000/x/1/1 (x = 2, 4, 8),  $V_{VAc} =$  $V_{EA} = 2.5$  mL, T = 35 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 3** <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>) of PVAc prepared in the solution polymerization of VAc at 5 kbar. Polymerization condition:  $[VAc]_0:[X1]_0:[AIBN]_0 = 20,000:4:1:1, V_{VAc} = V_{EA}$ = 2.5 mL, T = 35 °C, time = 4 h, conversion = 6.6%.

Furthermore, an extraordinary increase of the polymerization rate under high pressure was discernable from Figure 1(a). It was further quantitatively calculated by the apparent rate constant  $k_p^{app}(R_p = -d[M]/dt = k_p[P_n, M] = k_p^{app}[M])$  from the slopes of the kinetic plots, which was 0.243  $h^{-1}$  in the case of 5 kbar and 0.0164  $h^{-1}$  in the case of 1 bar, respectively. The former is 15.2 times of the latter. The reason for these differences should be attributed to the fact that the propagation of free radicals was enhanced, and termination was suppressed under high pressure.<sup>35</sup> High pressure may make the formation of the stable carbon centered radicals easily and enhance their reactivity.<sup>38</sup> The evaluation of the molecular weight and molecular weight distribution with conversion is shown in Figure 1(b). Both the polymer molecular weights linearly increased with the monomer conversion. At the same time, it can be seen that narrower molecular weight distributions were obtained in the case of high pressure.

To further confirm the retardation phenomena as discussed in Table 1, the polymerization kinetics with the three molar ratios of  $[VAc]_0/[X1]_0 = 20,000/2, 20,000/4, 20,000/8$  was investigated at 5 kbar. As shown in Figure 2(a), all the polymerization kinetics was first order with the monomer concentration, indicating almost constant propagating radicals during the polymerization. Similarly, we can calculate the apparent rate constant  $k_{\rm p}^{\rm app}$  values to directly judge the change of the polymerization rate in three cases. A  $k_n^{app}$  $0.299 h^{-1}$  for the case of 20,000/2, 0.243  $h^{-1}$  for the case 20,000/4, and 0.170 h<sup>-1</sup> for the case of 20,000/8, was obtained, respectively, fully confirming the rate retardation in the presence of larger amount of CTAs even if under high pressure. Philipp Vana explained that the pressure may not only make the addition reaction diffusion-controlled and retard it but also compensated the amount of the stable

intermediate radical by decreasing the termination rate.<sup>53</sup> Both of the two factors could be suppressed to a larger extent than the reaction between two macroradicals just like the situation under atmospheric pressure. From Figure 2(b), the molecular weights of PVAc increased linearly with monomer conversion (below 30%), and the molecular weight distributions remained less than 1.5. However, the molecular weights deviated the linear increase with the monomer conversion when the conversion was more than 40%, and the  $M_w/M_n$  values increased correspondingly. This may due to the active monomer radicals which caused chain transfer and chain termination reactions of PVAc.

### Analysis of Chain End and Chain Extension of PVAc

The end group of the PVAc  $(M_{n,GPC} = 29,800 \text{ g/mol}, M_w/M_n = 1.12)$  obtained at 5 kbar was confirmed by <sup>1</sup>H NMR, as shown in Figure 3. Peaks (e, e", f, f", g, and g") were the characteristic repeating unit of the VAc as assigned in Figure 3. The remaining peaks are from the X1 mediator. All of the 2-ethyl propionate protons (a, b, c, d) were observed at around 1.42, 4.66, 3.89, and 1.16 ppm, respectively. In addition, *O*-ethyl protons (h, i) were observed at 4.11 and 1.25 ppm, respectively. The peak of the methine proton f" of the terminal VAc group close to *O*-ethylxanthate group was observed at around 6.61 ppm.

To further confirm the living feature of PVAc, the chainextension experiments were conducted at 35 °C. When the PVAc prepared at 5 kbar was used as the macro-RAFT agent, from Figure 4, there has been a peak shift from the original PVAc ( $M_{n,GPC} = 22,900$  g/mol,  $M_w/M_n = 1.27$ ) to the chainextended PVAc ( $M_{n,GPC} = 73,500$  g/mol,  $M_w/M_n = 1.41$ ) at 1 bar for 28 h and PVAc ( $M_{n,GPC} = 68,700$  g/mol,  $M_w/M_n = 1.48$ ) at 5 kbar for 5 h, respectively. The GPC traces of the chain-extended PVAc showed unimodal



**FIGURE 4** GPC traces of PVAc before and after chain extension, using PVAc prepared by the RAFT polymerization of VAc at 1 bar (a) and 5 kbar (b) as the macro-RAFT agents. The polymerization condition:  $[VAc]_0/[PVAc]_0/[DMA]_0/[BPO]_0 = 20,000/2/1/1$ ,  $V_{VAc} = V_{EA} = 2.5$  mL, T = 35 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

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distribution. All of these evidences confirmed the features of the controlled/living polymerization under high pressure when using DMA/BPO as the initiator and X1 as the xanthate.

#### CONCLUSIONS

In summary, high pressure can enhance the polymerization rate significantly (15.2 times) in comparison with that under atmospheric pressure. It is more important that PVAc with high molecular weight up to 123,000 g/mol and narrow molecular weight distribution ( $M_w/M_n = 1.28$ ) can be easily obtained via RAFT polymerization under high pressure (5 kbar).

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