Synthesis of Poly(vinyl acetate) by Degenerative Transfer Polymerization in the Presence of Iodine

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ABSTRACT: Polymerization of vinyl acetate initiated by 2,2'-azobis(isobutyronitrile) at 75°C in the presence of iodine has been investigated. The process efficiently controls the number-average molecular weight and low polydispersities ($M_w/M_n \leq 1.52$). Poly(vinyl acetate) with predetermined molecular weight and relatively low polydispersity was successfully synthesized. The polymerization was followed by online ^{1}H-NMR spectra to investigate the evolution of several compounds in the reaction medium, especially the adduct of α-iodoisobutyronitrile (($CH_3)_2$(CN)C—I) between primary radicals and iodine. The structure of the end groups of poly(vinyl acetate) also was investigated using ^{1}H-NMR spectra. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: living polymerization; degree of polymerization (DP); gel-permeation chromatography (GPC); molecular weight distribution; synthesis

INTRODUCTION

Controlled/living radical polymerization (CRP) results in polymers with well-defined molecular weights and narrow molecular weight distributions. All of the currently successful CRP processes are based upon establishing a dynamic equilibrium between propagating radicals and dormant polymer chains. The most efficient CRP methods are nitroxide-mediated polymerization (NMP),[1–4] atom transfer radical polymerization (ATRP),[5–7] reversible addition-fragmentation transfer polymerization (RAFT),[8] and degenerative transfer (DT) polymerization.[9–12] The CRP of vinyl acetate is more difficult than the conjugated monomers, such as (meth)acrylates and styrenes. This is partially due to the high reactivity of the vinyl acetate propagating radical. In recent years, CRP of vinyl acetate was achieved using the RAFT,[13–15] degenerative iodine transfer,[16–18] and cobalt-mediated.[19] Most of them are based on the degenerative chain transfer process, which accomplishes the molecular weight control via a fast interconversion between the growing radical and the covalent dormant species in the presence of a radical initiator.

The DT process was first described in the patent literature in 1990 for the polymerization of fluorinated monomers in the presence of alkyl iodides as transfer agents.[20] In 1995, DT polymerization with alkyl iodides was reported for styrene and butyl acrylate using 1-phenylethyl iodide as transfer agent and 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator.[21] Molecular weights increased linearly with conversion, indicating a CRP, and block copolymers of styrene and butyl acrylate were successfully synthesized.[21] The effect of structure of the transfer agent was investigated for the DT polymerization of styrene.[9] On the basis of the experimental results, it was concluded that for an efficient DT process the C—I bond from iodinated transfer agents [i.e., ethyl iodoacetate (EtIAc)] should be sufficiently labile to allow a facile transfer of the iodine atom from the transfer agent to the propagating radical, and the R group (R stands for else groups except iodine of iodinated transfer agents) should stabilize the resulting radical through inductive or resonance effects.

Due to the weak C—I bond, iodinated transfer agents are not very stable under storage.[22] Iodinated transfer agents are light-sensitive, temperature-sensitive, and prone to decomposition to give free iodine or hydriodic acid (HI) by elimination reaction. To overcome these limitations, a technique of DT polymerization in the presence of iodine was used in the polymerization of vinyl acetate. The technique is based on the *in situ* synthesis of the iodinated transfer agent and was used by Boutevin and coworkers on the polymerization of methyl acrylate and *n*-butyl acrylate.[11] However, the DT polymerization of vinyl

acetate using such a technique has not been reported. In this article, the iodine-end-capped structure of poly(vinyl acetate) with controlled molecular weights and narrow molecular weight distributions by this method are reported.

EXPERIMENTAL

Materials

Vinyl acetate was distilled under reduced pressure to remove the inhibitors. AIBN was purified by recrystallization from ethanol at 50°C. Iodine, ethanol (99.5%), and dichloromethane were used as received. All the reagents and solvents were purchased from Shanghai Chemical Reagent Co. Ltd.

Analysis and measurements

The number-average molecular weight and molecular weight distributions were determined by a Waters 1515 gel-permeation chromatography (GPC), using tetrahydrofuran (THF) as the eluent at 30°C. Calibration based on polystyrene standards was applied for the determination of molecular weights. The ^{1}H-NMR spectra in CDCl$_3$ were recorded on a Varian UNITY INOVA spectrometer, operating at 400 MHz. Monomer conversion was determined by gravimetry [eq. (1)], in which m_p, m_{VAc}, and m_I are the weight of polymer recovered after precipitation, the initial weight of vinyl acetate, and iodine in the reaction medium, respectively.

$$\text{Monomer conversion} = \left(m_p/(m_{\text{Vac}} + m_I) \right) \times 100 \quad (1)$$

Polymerization

Typically, a mixture of vinyl acetate (3.00 g, 34.88 mmol), AIBN (5.72×10^{-2} g, 3.49×10^{-1} mmol), and iodine (2.67×10^{-2} g, 1.05×10^{-2} mmol) was degassed by three cycles of freeze–vacuum–thaw, then the reaction tube was sealed under a nitrogen atmosphere. The tubes were immersed in a thermostatic oil bath at 75°C. All reactions were performed in the dark. In predetermined intervals, the polymerization was terminated by cooling the reaction mixture in a liquid nitrogen bath. The polymer was isolated by precipitation into petroleum ether after dilution with dichloromethane, and then dried under vacuum at room temperature for 24 h.

RESULTS AND DISCUSSION

Polymerization of different molar ratio

Before studying the kinetics, some experiments were performed to check the efficiency of the DT polymerization process with vinyl acetate in the presence of iodine (Table I). Reactions were performed at [VAc] : [AIBN] = 60 : 1, 100 : 1, and 150 : 1, the range of [I$_2$] is 0.2–0.5, respectively. [VAc] represents the concentration of vinyl acetate. The molecular weights obtained by polymerization of vinyl acetate with DT polymerization in the presence of iodine are close to the theoretical values, and the molecular weight distributions (around 1.4) are in good agreement with iodine transfer polymerization (ITP) (i.e., corresponding to a rather low transfer constant as usually reported in ITP of acrylates).[10,21] Iodine concentration effect on reaction speed and relative molecular weight and polydispersity was investigated indicating that the growing rate of molecular weight was more successfully controlled and polydispersity was lower with the increase of iodine concentration (Runs 6–9, Table I). In contrast, in a blank experiment previously reported elsewhere by us in the absence of iodine, the polymerization led to a high molecular weight and a broad molecular weight distribution ($M_n = 89{,}900$, $M_w/M_n = 5.28$).

TABLE I
Polymerization of Vinyl Acetate by DT Polymerization in the Presence of Iodine

| Run	Ratio [VAc] : [AIBN] : [I$_2$]	Polymerization time (h)	Conversion (%)	$M_{n,\text{theoretical}}$[a] (g mol^{-1})	$M_{n,\text{experimental}}$[b] (g mol^{-1})	M_w/M_n
1	100 : 1 : 0	10 min	66		89,900	5.28
2	60 : 1 : 0.2	4	89	11,700	13,000	1.40
3	60 : 1 : 0.3	7	94	8300	9300	1.27
4	60 : 1 : 0.4	30	59	4000	4400	1.24
5	60 : 1 : 0.5	60	12	800	700	1.20
6	100 : 1 : 0.2	4.5	87	18,900	20,700	1.44
7	100 : 1 : 0.3	8	89	13,000	15,600	1.40
8	100 : 1 : 0.4	30	40	4500	4700	1.32
9	100 : 1 : 0.5	60	7	800	700	1.20
10	150 : 1 : 0.2	4	84	27,300	28,900	1.52
11	150 : 1 : 0.3	11	81	17,600	18,200	1.41
12	150 : 1 : 0.4	30	65	12,200	11,600	1.35
13	150 : 1 : 0.5	60	6	1000	900	1.20
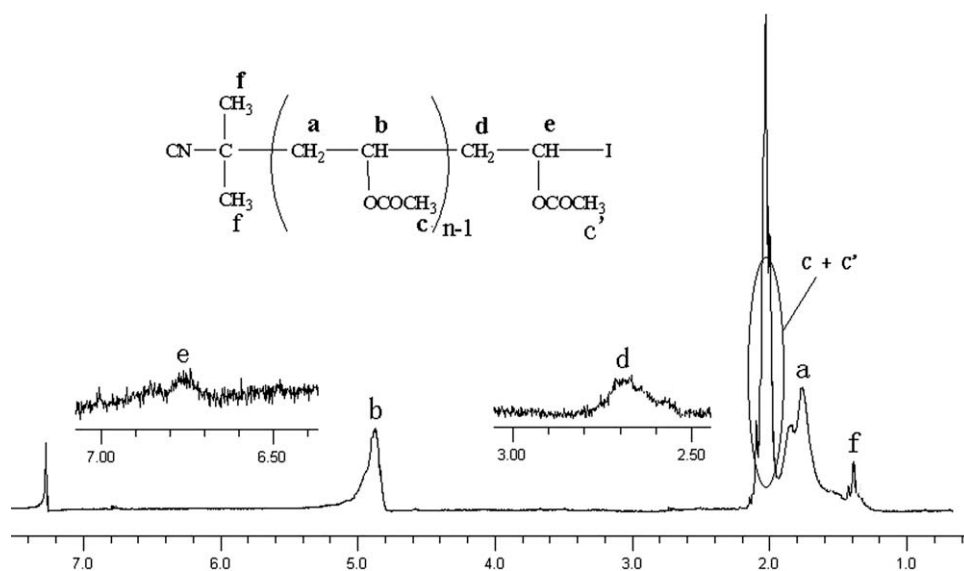
Figure 1 ^{1}H-NMR (400 MHz) spectra of poly(vinyl acetate) in CDCl$_3$ at 30°C, reaction conditions: [VAc] : [AIBN] : [I$_2$] = 100 : 1 : 0.4, at 75°C, 9 h.

Polymerization of vinyl acetate at 75°C in the presence of AIBN as initiator. (a) Calculated by $M_{n,\text{theoretical}} = $ [VAc]$_0$ × M_{VAc} × conversion/(2 × [I$_2$]$_0$) + $M_{\text{A-I}}$, where $M_{\text{VAc}} = 86$ g mol^{-1}, and $M_{\text{A-I}} = M_{\text{chain-ends}} = 195$ g mol^{-1}. (b) Determined by Waters 1515 GPC chromatography overlay using THF as a mobile phase and column temperature 30°C.

The theoretical molecular weight of the polymer by the DT polymerization process with vinyl acetate in the presence of iodine can be calculated by eq. (2), in which $M_{\text{A-I}} = M_{\text{chain-ends}} = 195$ g mol^{-1} ("A" represents (CH$_3$)$_2$(CN)C— from the initiator).

$$M_{n,\text{theoretical}} = (\text{mass of monomer}) \times \text{conversion}/(2 \times \text{moles of I}_2)) + M_{A-I} \quad (2)$$

This equation is simplified assuming a high degenerative chain transfer constant and a low fraction of dead chains. Alternatively, in the case of rather low degenerative chain transfer constant (but still higher than unity), a good approximation of the molecular weight can be given by eq. (2).

End group analysis

The end groups resulting from DT polymerization in the presence of iodine was analyzed using 400 MHz ^{1}H-NMR spectra. The polymerization of vinyl acetate was carried out at 75°C with a molar ratio [VAc] : [AIBN] : [I$_2$] = 100 : 1 : 0.4. The polymerization was terminated after 9 h by cooling the reaction mixture in a liquid nitrogen bath. The polymer was isolated by precipitation into petroleum ether after dilution with dichloromethane, and then dried under vacuum at room temperature for 24 h. The full ^{1}H-NMR spectra are shown in Figure 1.

The main absorption signals of poly(vinyl acetate) were assigned as shown. The methylene protons (a) in the polymer backbone absorbs at 1.72 ppm, the methine (b) group at 4.89 ppm, methyl (c) group at 2.03 ppm, respectively. The two end protons in the polymer can also be identified from Figure 1. The methyl protons (f) from AIBN absorb at 1.36 ppm. The ω-terminal methine protons (e), methylene protons (d), and methyl protons (c') CH$_2$(d)—CH(e)—(OCOCH$_3$(c'))I in the poly(vinyl acetate) appeared at 6.85, 2.69, and 2.08 ppm, respectively.

The average degree of polymerization[DP$_n$ (NMR, α-end)] was calculated by comparing the intensity of the α-end protons (f) that originated from AIBN to the methine protons (b) of the poly(vinyl acetate) (DP$_{n,\ \alpha\text{-end}} = 6b/f$). In the same way, the DP$_n$ (NMR, ω-end) was calculated by comparing the intensity of the ω-terminal methine protons (e) CH$_2$—CH—(OCOCH$_3$)I in the poly(vinyl acetate) to the methine protons (b) of the poly(vinyl acetate) (DP$_{n,\ \omega\text{-end}} = b/e$). The theoretical mean number degree of polymerization (DP$_{n,\ \text{theoretical}}$) is given by eq. (3), where [I$_2$]$_0$ is the initial concentration of iodine in the reaction medium, [VAc]$_0$ is the initial concentration of vinyl acetate.

$$\text{DP}_{n,\text{theoretical}} = [\text{VAc}]_0 \times \text{monomer conversion}/(2 \times [\text{I}_2]_0) \quad (3)$$

The value of DP$_{n,\ \text{GPC}}$ from GPC is calculated by eq. (4), in which $M_{n,\ \text{GPC}}$ is the experimental molecular weights determined by Waters 1515 GPC chromatography overlay with THF as a mobile phase at

TABLE II
The Comparison of Various DP_n at 75°C, [VAc] : [AIBN] : [I_2] = 100 : 1 : 0.4, 9 h

Reaction time (h)	Conversion vinyl acetate (%)	DP_n (Theoretical)	DP_n (ω-end)	DP_n (α-end)	DP_n (GPC)	M_w/M_n
9	44.3	55	49	47	54	1.33

column temperature 30°C, M_{VAc} is molecular weight of vinyl acetate (M_{VAc} = 86 g mol^{-1}), and M_{A-I} = $M_{chain-ends}$ = 195 g mol^{-1}. The calculated results are shown in Table II.

$$DP_{nGPC} = (M_{nGPC} - M_{A-I})/M_{VAc} \qquad (4)$$

The value of $DP_{n, \alpha\text{-end}}$ is nearly consistent with the value of $DP_{n, \omega\text{-end}}$, and the theoretical value ($DP_{n, theoretical}$) from monomer conversion is nearly consistent with the value of $DP_{n, GPC}$ obtained by GPC, and the four values is also nearly consistent with each other (Table II), suggesting that one molecular of the iodine compound generates one polymer chain.

Influence of iodine concentration

The effect of iodine was investigated for the DT polymerization of vinyl acetate in the presence of iodine at 75°C, using a constant molar ratio [VAc] : [AIBN] = 100 : 1. Reactions were carried out at two different concentrations of iodine. The reaction rate decreased with increasing iodine concentration (Fig. 2). The polymerization of vinyl acetate by DT polymerization in the presence of iodine can be divided into two main stages, including inhibition period and polymerization period, as shown in Figure 2. During the inhibi-
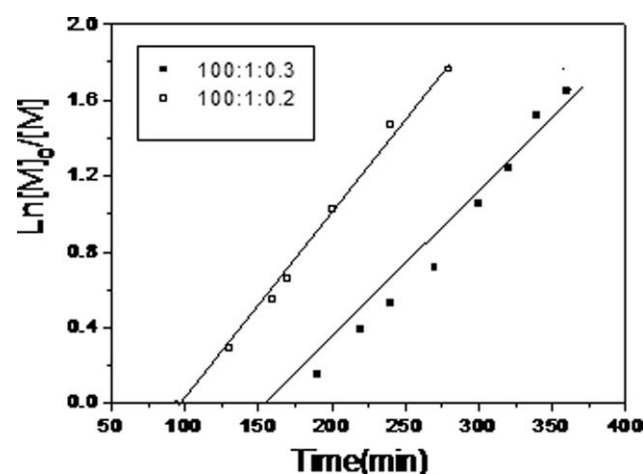
tion period, the free radicals predominantly react with iodine to form *in situ* the reversible chain transfer agent. With the color of iodine fading at the end of the inhibition period, the polymerization occurs. In this way, the ratio [initiator] : [I_2] is a very important parameter because it will determine both the duration of the inhibition period and the subsequent kinetics of the polymerization. Thus, taking into account the efficiency of the initiator f and its rate constant of dissociation k_d, the inhibition time $t_{inhibition, theoretical}$ can be calculated by eq. (5), in which [I_2]$_0$ is the initial concentration of iodine, k_d = 6.17 × 10^{-5} s^{-1} at 75°C, and f = 0.7 for AIBN.

$$t_{inhibition,theoretical} = -\ln\left(1 - [I_2]_0/\left(f[initiator]_0\right)\right)/k_d$$
$$(5)$$

The inhibition times of the experiment agree well with that of theory for DT polymerization of vinyl acetate in the presence of iodine at 75°C (Fig. 2).

A linear increase of molecular weight with conversion was observed for experiments performed at [VAc] : [AIBN] : [I_2] = 100 : 1 : 0.2, and 100 : 1 : 0.3 (Fig. 3). The theoretical molecular weights could be reasonably predicted by eq. (2). Experimental

Figure 2 Evolution of ln([M]$_0$/[M]) vs. time for DT radical polymerization of vinyl acetate in the presence of iodine at 75°C performed with different iodine concentrations:■[I_2] = 3.18 × 10^{-2}M ([VAc] : [AIBN] : [I_2] = 100 : 1 : 0.3), □[I_2] = 2.12 × 10^{-2}M ([VAc] : [AIBN] : [I_2] = 100 : 1 : 0.2). Experimental conditions: 3.00 g (3.49 × 10^{-2} mol) of VAc, 5.72 × 10^{-2} g (3.49 × 10^{-4} mol) of AIBN.
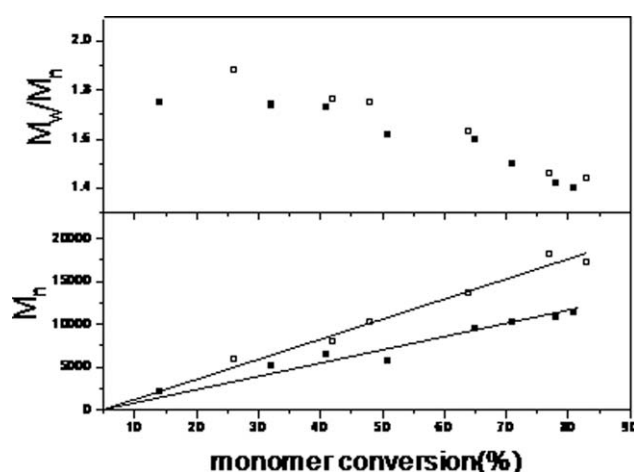

Figure 3 Dependence of molecular weights (M_n) and polydispersities (M_w/M_n) on monomer conversion for polymerization of vinyl acetate by DT radical polymerization in the presence of iodine at different iodine concentrations (75°C): ■[I_2] = 3.18 × 10^{-2}M ([VAc] : [AIBN] : [I_2] = 100 : 1 : 0.3), □[I_2] = 2.12 × 10^{-2}M ([VAc] : [AIBN] : [I_2] = 100 : 1 : 0.2). Experimental conditions: 3.00 g (3.49 × 10^{-2} mol) of vinyl acetate, 5.72 × 10^{-2} g (3.49 × 10^{-4} mol) of AIBN. The line shows the theoretical molecular weight.

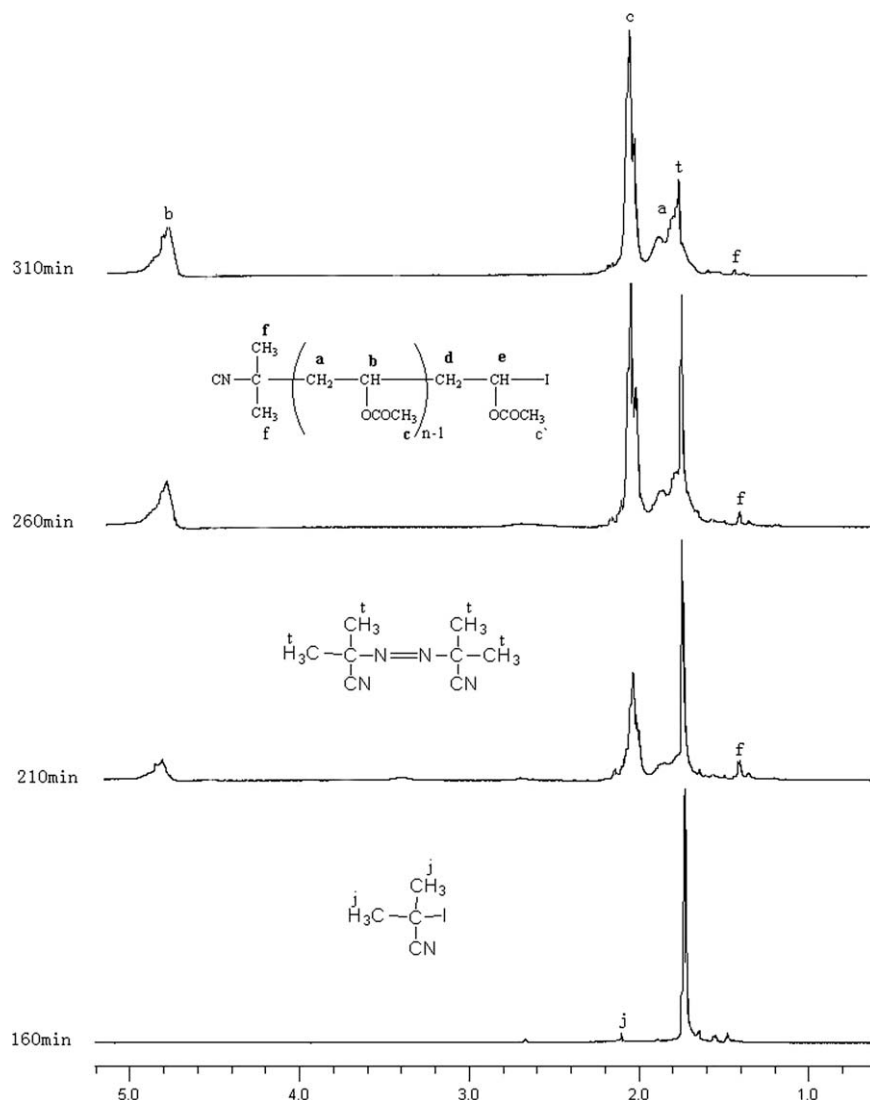**Figure 4** ^{1}H-NMR (400 MHz) spectra of poly(vinyl acetate) in CDCl$_3$ at 30°C, reaction conditions: [VAc] : [AIBN] : [I$_2$] = 100 : 1 : 0.3, at 75°C.

molecular weights observed well agreed with the corresponding theoretical molecular weights. Molecular polydispersities gradually decrease with the improvement of monomer conversion of vinyl acetate, and polymers with a relatively narrow molecular polydispersities ($M_w/M_n \leq 1.41$) are obtained when the monomer conversion of vinyl acetate reaches approximately 80%.

Evolution of the molecular weights and several compounds

To disclose the DT polymerization mechanism of poly(vinyl acetate) in the presence of iodine, the kinetics of the polymerization was followed by online ^{1}H-NMR spectra in order to determine the monomer conversion and to follow the evolution of several compounds in the reaction media. The polymerization of vinyl acetate was performed with a molar ratio [VAc] : [AIBN] : [I$_2$] = 100 : 1 : 0.3 at 75°C. In predetermined intervals (after 160, 210, 260, and 310 min, respectively), the polymerization was terminated by cooling the reaction mixture in a liquid nitrogen bath. The monomer of vinyl acetate was isolated by vacuum pump at below 40°C, the compounds in the tube was analyzed by ^{1}H-NMR spectra. The ^{1}H-NMR spectra data, ranging from 0.6 to 5.2 ppm, are shown in Figure 4.

The main absorption signals of poly(vinyl acetate), α-iodoisobutyronitrile, and AIBN were assigned. The signals of 1.36 (f), 2.03 (c), and 4.89 (b) ppm attribute to the repeat units of poly(vinyl acetate), 1.72 ppm attribute to the methylene protons (a) of poly(vinyl acetate) and the methyl protons(t) of AIBN (pure compound of AIBN absorbs at 1.72 ppm at same condition). The methyl protons (j) of α-iodoisobutyronitrile from the reaction of AIBN with iodine absorbs at 2.16 ppm (160min ^{1}H-NMR spectra).

Reaction time (min)	160	210	260	310
$DP_{n,\alpha\text{-end}}$	0	35	62	94

The predicted inhibition period of the polymerization of vinyl acetate with a molar ratio [VAc] : [AIBN] : [I$_2$] = 100 : 1 : 0.3 at 75°C is 155 min calculated by eq. (5). The average degree of polymerization [DP_n (NMR, α-end)] was calculated by comparing the intensity of the α-end protons (f) that originated from AIBN to the methine protons (b) of the poly(vinyl acetate) ($DP_{n, \alpha\text{-end}} = 6b/f$). $DP_{n, \alpha\text{-end}}$ are given in Table III. The evolution of several compounds in the polymerization process of vinyl acetate by DT polymerization in the presence of iodine is shown in Figure 4. A little of α-iodoisobutyronitrile was synthesized by the direct reaction of radicals from AIBN with iodine in the mixture after 155 min (160 min ^{1}H-NMR spectra), at the same time, no polymer was synthesized (Table III). The peak of methyl protons (t) of AIBN lowered while the peak of methine (b), methyl (c), and methylene (a) protons of poly(vinyl acetate) increased with the reaction time, indicating clearly that the molecular weights increase with time (Table III) and α-iodoisobutyronitrile, as a transfer agent, efficiently controls the molecular weights, as agree with the conclusion of the kinetic of the vinyl acetate polymerization by DT polymerization in the presence of iodine.

CONCLUSION

The iodine-end-capped structure of poly(vinyl acetate) with controlled molecular weights and relatively narrow molecular weight distributions ($M_w/M_n \leq 1.52$) was synthesized using DT polymerization in the presence of iodine. The evolution of several compounds in the reaction medium, especially the adduct of α-iodoisobutyronitrile have been observed by online ^{1}H-NMR spectra. The transfer agent of α-iodoisobutyronitrile ((CH_3)$_2$(CN)C—I) is *in situ* synthesized based on the direct reaction of AIBN and iodine in the DT polymerization in the presence of iodine, which causes an inhibition period at the earlier stage, avoiding the presynthesis and storage of the unstable alkyl iodide. The adduct of α-iodoisobutyronitrile ((CH_3)$_2$(CN)C—I) efficiently controls the DT polymerization of vinyl acetate in the presence of iodine as transfer agent.

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