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Controlled/Living Radical Polymerization of Vinyl Acetate by Degenerative Transfer with Alkyl Iodides

Mihaela Corina Iovu and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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ABSTRACT: Controlled/living radical polymerization of vinyl acetate was achieved by a degenerative transfer process using alkyl iodides as transfer agents. Poly(vinyl acetate) with predetermined molecular weight and relatively low polydispersity was successfully synthesized. Methyl 2-iodopropionate and ethyl iodoacetate were employed as transfer agents, whereas 2,2′-azobis(isobutyronitrile) and α-cumyl peroxyneodecanoate were used as initiators. Methyl 2-iodopropionate and ethyl iodoacetate are both efficient transfer agents, yielding polymers with good agreement between theoretical and observed molecular weights up to $M_n = 20\,000$ and low polydispersities ($M_w/M_n < 1.5$). In contrast, ethyl iodide was inefficient as a transfer agent, although it retarded polymerization. The influence of temperature and the concentrations of transfer agent and initiator were studied. The structure of poly(vinyl acetate) end groups was investigated using ^{1}H NMR. The iodo-terminated chain ends were unstable and decomposed to aldehyde moieties and subsequently to colored, conjugated structures. The progressive conversion of secondary to primary alkyl iodides chain end groups was observed, which is indicative of head-to-head addition.

Introduction

Controlled/living radical polymerization (CRP) results in polymers with well-defined molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.5$). All of the currently successful CRP processes are based upon establishing a dynamic equilibrium between propagating radicals and dormant polymer chains.[1,2] The most efficient CRP methods are nitroxide-mediated polymerization (NMP),[3] atom transfer radical polymerization (ATRP),[4−7] reversible addition−fragmentation transfer polymerization (RAFT),[8] and degenerative-transfer (DT) polymerization with alkyl iodides.[9,10]

There has been limited success of the CRP of vinyl acetate despite the fact that it can only be polymerized via a radical mechanism. This is partially due to the high reactivity of the vinyl acetate propagating radical. CRP of vinyl acetate was achieved using RAFT/MADIX with xanthates and dithiocarbamates[11−14] as polymerization mediators; however, in the presence of dithioesters, trithiocarbonates, and aromatic dithiocarbamates, the polymerization was strongly inhibited. Metal-mediated CRP of vinyl acetate was previously reported using an initiating system composed of Al(iBu)$_3$/2,2′-bipyridine/TEMPO, but this system was very sensitive to moisture, oxygen, and impurities.[15−17] Poly(vinyl acetate) with the molecular weight predetermined by the ratio of the initial concentration of monomer to initiator, was prepared using CCl_4 as initiator, in the presence of Fe(OAc)$_2$/PMDETA.[18] The process was found to be a redox-initiated radical telomerization in which CCl_4 acted as both initiator and chain-transfer agent (INIFER), resulting in α-chloro and ω-CCl_3 functionalized polymers with $M_w/M_n = 1.8−2.0$. These macroinitiators were successfully used for block copolymerization with *n*-butyl acrylate.[19]

To date, copper-mediated ATRP of vinyl acetate has not been successful. The difficulty in applying the ATRP technique to vinyl acetate polymerization can be attributed to the low equilibrium constant (K_{eq})[20] and to the presence of side reactions, such as decomposition of the dormant species and possible transformation of growing radicals to carbocations through an outer sphere electron-transfer process.[18]

A recent paper by Sawamoto and co-workers reported the CRP of vinyl acetate catalyzed by dicarbonylcyclopentadienyliron dimer with alkyl iodides as initiators and metal alkoxides (aluminum or titanium isopropoxide) as additives.[21] The same system was found to be effective for the CRP of styrene, without additives,[22] and acrylates,[23] using iodine as additive. The proposed mechanism involved metal-catalyzed homolysis of the C−I bond of the initiator and dormant polymer chain end, resulting in polymers with controlled molecular weights. The authors also considered the contribution of iodine degenerative transfer (DT).

In this paper we report the DT polymerization of vinyl acetate with alkyl iodides and conventional radical initiators and without any transition metals. Ethyl iodoacetate and methyl 2-iodopropionate, selected as transfer agents, should easily generate stabilized but sufficiently reactive electrophilic radicals that add rapidly to vinyl acetate.

Experimental Section

Reagents. Vinyl acetate was stirred over CaH_2 for 24 h, distilled under vacuum, and collected over molecular sieves. Ethyl iodoacetate (98%) and ethyl iodide (99%) were used as received. Methyl 2-iodopropionate was synthesized from methyl 2-bromopropionate and sodium iodide in acetone.[24] All the reagents and solvents were purchased from Aldrich and used as received unless otherwise specified. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and α-cumyl peroxyneodecanoate (CPD) (LUPEROX, 75 wt % in odorless mineral spirits, Atofina) was used as received.

Polymerization Procedure. In a typical experiment, a dry Schlenk flask was charged with the 0.05 g

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* Corresponding author. E-mail: km3b@andrew.cmu.edu.

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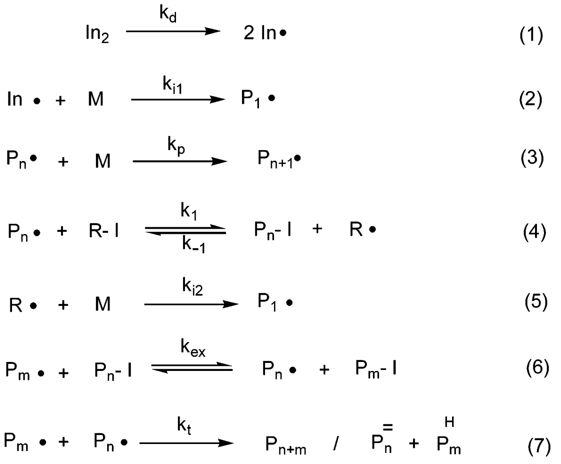
Scheme 1. Elementary Steps in Degenerative-Transfer Polymerization with Alkyl Iodides



$$In_2 \xrightarrow{k_d} 2\,In\bullet \qquad (1)$$

$$In\bullet + M \xrightarrow{k_{i1}} P_1\bullet \qquad (2)$$

$$P_n\bullet + M \xrightarrow{k_p} P_{n+1}\bullet \qquad (3)$$

$$P_n\bullet + R\text{-}I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P_n\text{-}I + R\bullet \qquad (4)$$

$$R\bullet + M \xrightarrow{k_{i2}} P_1\bullet \qquad (5)$$

$$P_m\bullet + P_n\text{-}I \overset{k_{ex}}{\rightleftharpoons} P_n\bullet + P_m\text{-}I \qquad (6)$$

$$P_m\bullet + P_n\bullet \xrightarrow{k_t} P_{n+m} \;/\; P_n^{=} + P_m^{H} \qquad (7)$$

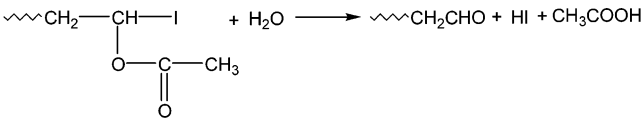
(0.3 mmol) of AIBN, 0.2 g of *p*-dimethoxybenzene (GC internal standard), and 9.3 mL (100 mmol) of deoxygenated vinyl acetate. After 4−5 thaw−freeze cycles, 120 μL (1 mmol) of deoxygenated ethyl iodoacetate (transfer agent) was added using a deoxygenated syringe. An initial sample was removed, and the flask was placed in a thermostated oil bath at the desired temperature. All reactions were performed in the dark. Samples were withdrawn periodically under nitrogen using a deoxygenated syringe to follow conversion and the evolution of molecular weight. The collected samples were diluted with toluene, and *p*-dimethoxybenzene was used as an internal standard.

Analysis and Measurements. Monomer conversion was determined on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector, using a Chrom Expert CEC-Wax capillary column (30 m × 0.53 mm × 1.0μm), against an internal standard (*p*-dimethoxybenzene). Conditions: injector and detector temperature 250 °C; initial column temperature 40 °C; isotherm 1 min; heating rate 20 °C/min; final column temperature 180 °C; isotherm 1 min. Size exclusion chromatography (SEC) measurements were performed on a Waters SEC system with refractive index detector, using THF as the eluent (flow rate 1 mL/min, 30 °C), with a series of three Styragel columns (10^5, 10^3, 100 Å; Polymer Standard Services). Toluene was used as an internal standard, and calibration based on poly(methyl methacrylate) standards was applied for the determination of molecular weights. The ^{1}H NMR spectra in C_6D_6 were recorded on a Bruker spectrometer operating at 600 MHz.

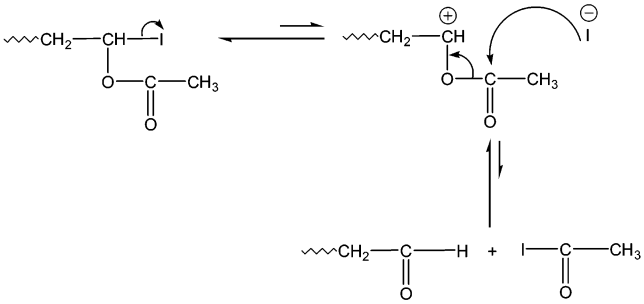
Results and Discussion

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.[25] In 1995, DT polymerization with alkyl iodides was reported for styrene and butyl acrylate using 1-phenylethyl iodide as the transfer agent and AIBN as the initiator.[26] Molecular weights increased linearly with conversion, indicating a controlled/living radical polymerization, and block copolymers of styrene and butyl acrylate were successfully synthesized.[26] 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 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 should stabilize the resulting radical through inductive or resonance effects.

Scheme 2. Hydrolysis of C−I End Groups



Scheme 3. Decomposition of Iodo-Terminated Poly(vinyl acetate)



The mechanism of degenerative-transfer polymerization with alkyl iodides is shown in Scheme 1.[9]

The initiating radical, $In^\bullet$, is generated by thermal decomposition of a conventional initiator, such as AIBN, in step 1. $In^\bullet$ adds to monomer in step 2, and the resulting radical propagates as shown in step 3. The exchange of iodine from the alkyl iodide, R−I, to the propagating radical, $P_n^\bullet$, results in the formation of the polymeric alkyl iodide, P_n−I, and a new initiating radical, $R^\bullet$ (step 4). Large differences in the stability of the reactants and products involved in step 4 could result in shifting the equilibrium overwhelmingly to the right or to the left. Therefore, the ideal case is when the structure of R closely resembles the structure of the propagating radical, resulting in a thermodynamically neutral transfer step. In the step 5, $R^\bullet$, generated from the alkyl iodide, adds to monomer. The exchange process described in step 6 is thermodynamically neutral, because the propagating chains $P_n^\bullet$ and $P_m^\bullet$ are identical. As in any radical process, termination occurs in DT polymerization with alkyl iodides (step 7). Steps 4 and 6 may proceed through the $[R/P\text{- - -}I\text{- - -}P]^\bullet$ intermediate, which may have a relatively long lifetime and lead to retardation, like in a RAFT process.[27] To obtain polymers with narrow molecular weight distributions in a DT process, the rate of exchange should be comparable with the rate of propagation.[9,28]

Such a DT process was applied to vinyl acetate using alkyl iodides as transfer agents and a thermally labile initiator such as AIBN or CPD. High reaction temperatures are undesirable for DT polymerization with alkyl iodides due to the possibility of decomposition of the chain end of iodo-terminated polymers. The polydispersity index for degenerative-transfer polymerization of styrene was $M_w/M_n = 1.28$ at 80 °C but was lowered by decreasing the reaction temperature.[28] Because CPD has a low decomposition temperature ($t_{1/2} = 1$ h at 56 °C), polymerization of vinyl acetate can be performed at 50 °C, which should also result in the reduced decomposition rate of the iodo-terminated poly(vinyl acetate).

The system is sensitive to moisture, because traces of water could result in the hydrolysis of C−I end

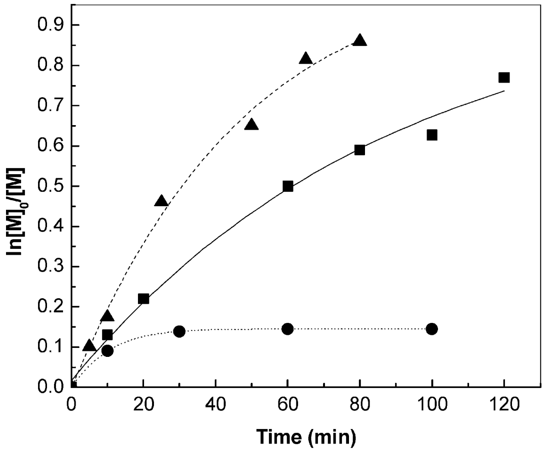


Figure 1. Semilogarithmic kinetic plots for bulk polymerization of vinyl acetate with EtIAc as transfer agent at different concentrations of CPD (50 °C): (●) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:1.0:0.15; (■) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:1.0:0.3; (▲) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:1.0:0.5.

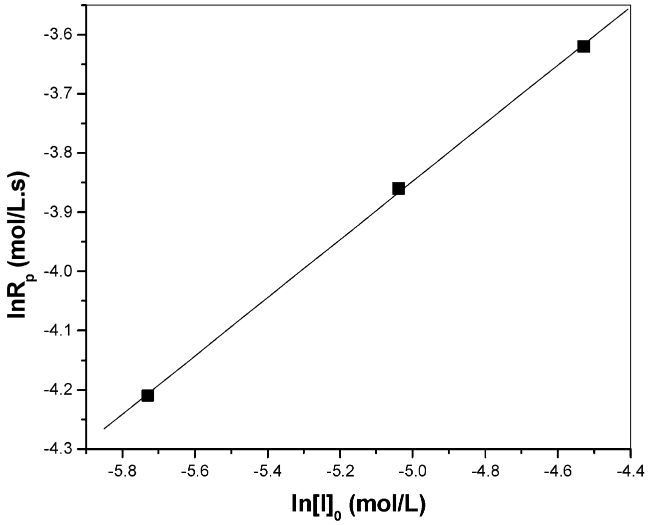


Figure 2. Plot of the logarithm of the initial rate of polymerization vs the logarithm of the initiator concentration (reaction conditions listed in Figure 1).

groups,[29,30] leading to poly(vinyl acetate) with aldehyde end groups (Scheme 2). The hydrolysis may proceed either by the nucleophilic attack of water molecule at the $C^{+\delta}-I^{-\delta}$ (S_N 2) or via S_N 1 process and hydrolysis of C−I bond.

Another potential side reaction is the decomposition of the iodo-terminated polymer with the formation of aldehyde end groups and acetyl iodide[31,32] (Scheme 3). Increased polarity of the reaction medium may accelerate this decomposition reaction, which is essentially opposite to the formation of α-haloacetates.

Because alkyl iodides are UV and light sensitive, all the polymerization reactions were performed in the dark.

Influence of Initiator Concentration

The effect of initiator concentration was studied for CPD-initiated DT polymerization of vinyl acetate using ethyl iodoacetate (EtIAc) as the transfer agent. Reactions were performed at a constant molar ratio of $[VA]_0$:$[EtIAc]_0$ = 500:1 and three different concentrations of CPD.

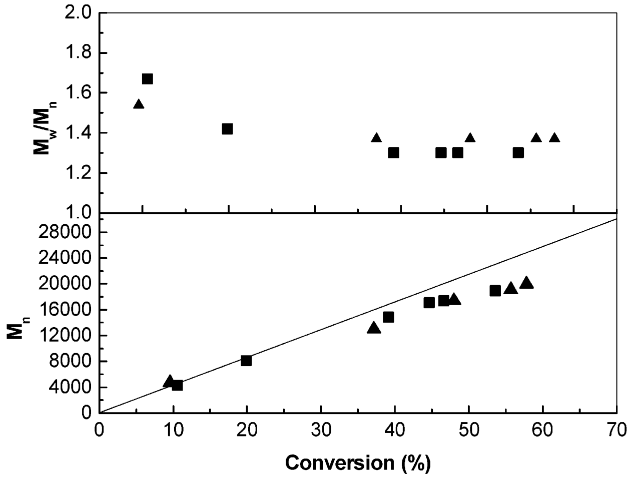


Figure 3. Dependence of molecular weights and polydispersities on conversion for bulk polymerization of vinyl acetate with EtIAc as transfer agent at different concentrations of CPD (50 °C): (▲) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:1.0:0.5; (■) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:1.0:0.3. The line shows the theoretical molecular weight.

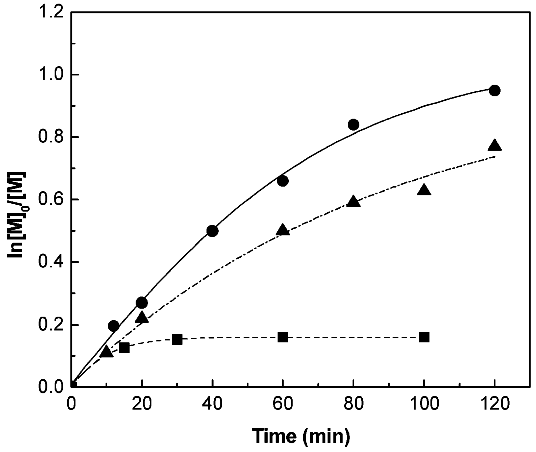


Figure 4. Semilogarithmic kinetic plots for bulk polymerization of vinyl acetate initiated with CPD at different concentrations of ethyl iodoacetate (50 °C): (●) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:0.5:0.3; (▲) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:1.0:0.3; (■) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:2.0:0.3.

The reaction rate increased with increasing concentration of CPD initiator, as shown in Figure 1.

A value of 0.5 for the reaction order with respect to initiator was obtained from the slope of the plot of the logarithm of the initial rate of polymerization vs the logarithm of the initiator concentration (Figure 2). However, the polymerization with the lowest initial concentration of CPD resulted in limited conversion.

A linear increase of molecular weight with conversion was observed for experiments performed at $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:1.0:0.3 and 500:1:0.5 (Figure 3). The theoretical molecular weights could be reasonably well predicted by the ratio $\Delta[M]/[R-I]_0$. The slightly lower experimental values may be due to additional chains generated by the decomposed initiator (CPD).

Polymers with narrower molecular weight distributions ($M_w/M_n \sim 1.35$) were obtained in the reactions performed at lower concentration of CPD.

Influence of Transfer Agent Concentration

The effect of transfer agent concentration was studied for both CPD- and AIBN-initiated polymerization of

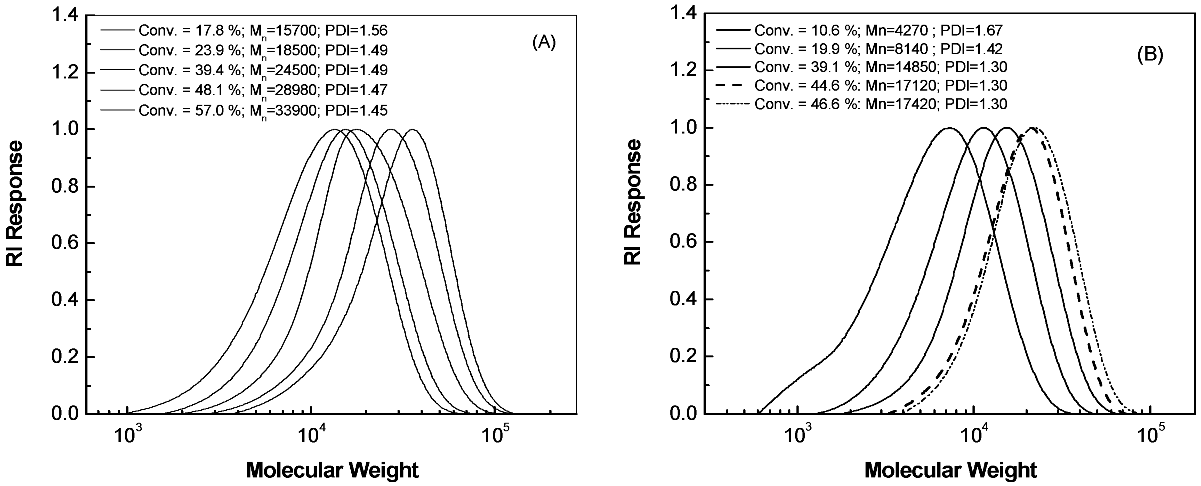


Figure 5. SEC traces for bulk polymerization of vinyl acetate initiated with CPD (50 °C): (A) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:0.5:0.3; (B) $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:1.0:0.3.

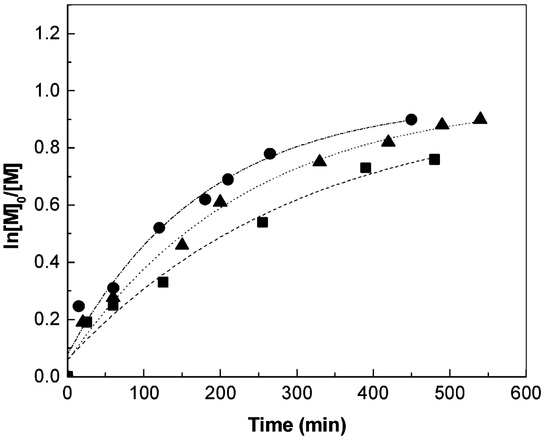


Figure 6. Semilogarithmic kinetic plots for bulk polymerization of vinyl acetate initiated with AIBN at different concentrations of ethyl iodoacetate (75 °C): (●) $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 500:2.5:1.5; (▲) $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 500:5.0:1.5; (■) $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 500:10:1.5.

vinyl acetate. The transfer agent employed in this study was ethyl iodoacetate (EtIAc).

The influence of transfer agent concentration was evaluated for CPD-initiated polymerization of vinyl acetate at 50 °C, in bulk, using a constant molar ratio $[VA]_0$:$[CPD]_0$ = 500:0.3. Reactions were performed at three different concentrations of EtIAc. Comparing the rates of polymerization of vinyl acetate at a molar ratio $[VA]_0$:$[CPD]_0$ = 500:0.3 in the absence of EtIAc (70% conversion was reached in 20 min) with the polymerizations performed with EtIAc as transfer agent, retardation was observed (Figure 4). The reaction rate decreased with increasing EtIAc concentration. The reaction performed at the highest concentration of EtIAc resulted in a limited conversion.

The molecular weight increased with monomer conversion for both experiments performed at molar ratios $[VA]_0$:$[EtIAc]_0$:$[CPD]_0$ = 500:0.5:0.3 and 500:1.0:0.3, as shown in Figure 5.

AIBN-initiated polymerization of vinyl acetate was performed at 75 °C, in bulk, using a constant molar ratio $[VA]_0$:$[AIBN]_0$ = 500:1.5. Reactions were conducted at three different concentrations of EtIAc. Rates of vinyl acetate polymerization progressively decreased with increasing concentration of EtIAc and were slower than polymerizations in the absence of EtIAc ($[VA]_0$:$[AIBN]_0$ = 500:1.5, 60% conversion was reached in 30 min), as shown in Figure 6 Although good agreement between theoretical and predicted molecular weights and low polydispersities ($M_w/M_n \sim 1.2$) was observed for the reaction performed at molar ratio $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 500:10:1.5 (Figure 7), polymers with lower molecular weights than defined by the ratio $\Delta[M]/[RI]_0$ were observed for the reactions performed at $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 500:5:1.5 and 500:2.5:1.5, as shown in Figure 7.

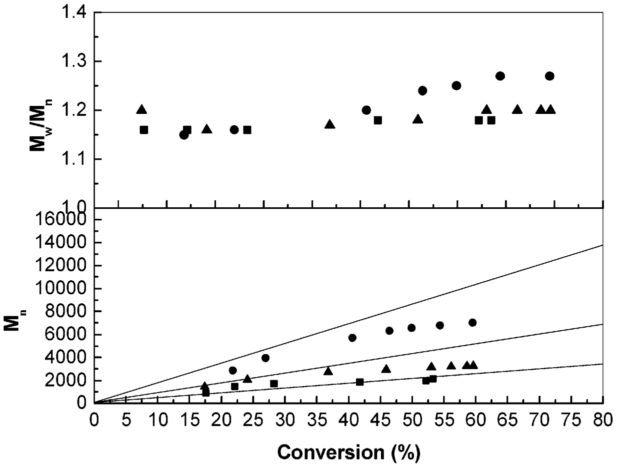
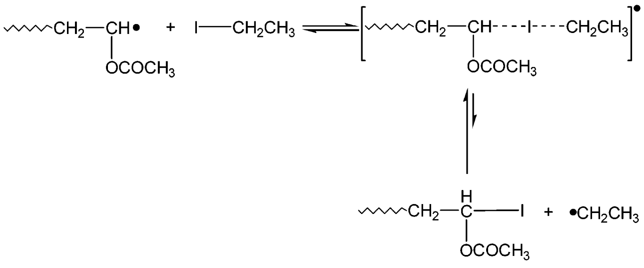
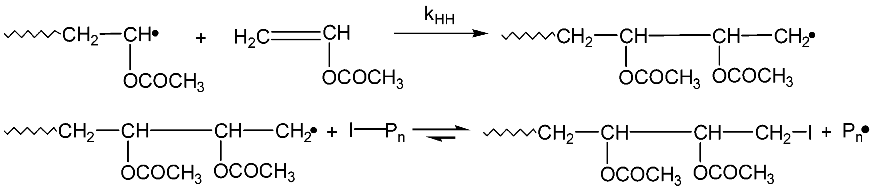


Figure 7. Dependence of molecular weights and polydispersities on conversion for bulk polymerization of vinyl acetate initiated with AIBN at different concentrations of ethyl iodoacetate (75 °C): (●) $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 500:2.5:1.5; (▲) $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 500:5.0:1.5; (■) $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 500:10:1.5. The lines show the theoretical molecular weights.

Scheme 4. Formation of Long-Lived Intermediates in DT Polymerization of Vinyl Acetate



Scheme 5. Head-to-Head Addition Followed by Iodine Transfer



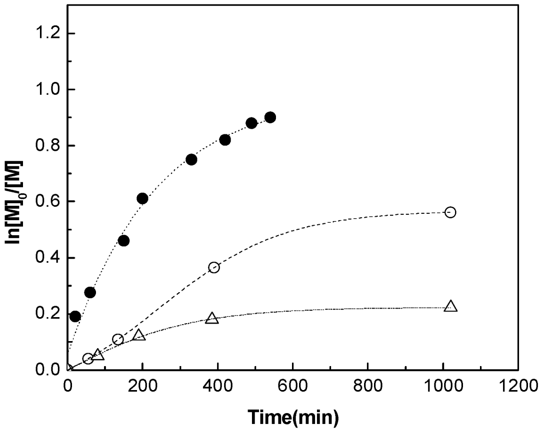


Figure 8. Semilogarithmic kinetic plots for bulk polymerizations of vinyl acetate performed with ethyl iodoacetate and ethyl iodide as transfer agents (75 °C): (●) [VA]$_0$:[EtIAc]$_0$:[AIBN]$_0$ = 100:1:0.3; (○) [VA]$_0$:[EtI]$_0$:[AIBN]$_0$ = 100:1:0.3; (△) [VA]$_0$:[EtI]$_0$:[AIBN]$_0$ = 100:3:0.3.

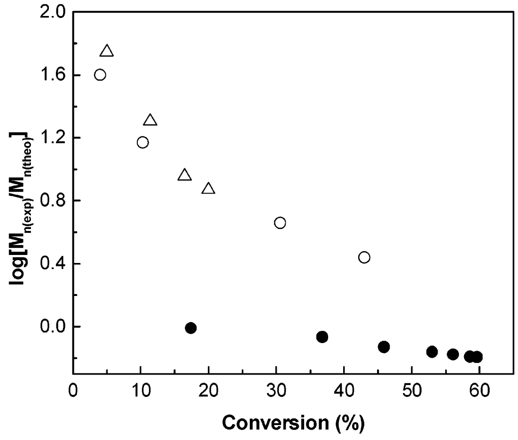


Figure 9. Plot of log[$M_{n(exp)}/M_{n(theo)}$] vs conversion for bulk polymerization of vinyl acetate performed with ethyl iodoacetate and ethyl iodide as transfer agents (75 °C): (●) [VA]$_0$:[EtIAc]$_0$:[AIBN]$_0$ = 100:1:0.3; (○) [VA]$_0$:[EtI]$_0$:[AIBN]$_0$ = 100:1:0.3; (△) [VA]$_0$:[EtI]$_0$:[AIBN]$_0$ = 100:3:0.3.

On the basis of the results, a higher concentration of transfer agent is beneficial for the control of the molecular weights and lower polydispersities. However, higher concentrations of alkyl iodide lead to slower polymerization and to polymers with lower molecular weights. When higher molecular weights are targeted, lower concentrations of alkyl iodides are necessary, leading to polymers with higher polydispersities.

Similar concentration-dependent retardation has been observed in RAFT polymerization, which is another degenerative-transfer process.[1]

Potential reasons for the retardation observed for the DT polymerization of vinyl acetate with alkyl iodides include

- The initiating radical generated in step 4 (Scheme 1) could add slowly to the monomer.

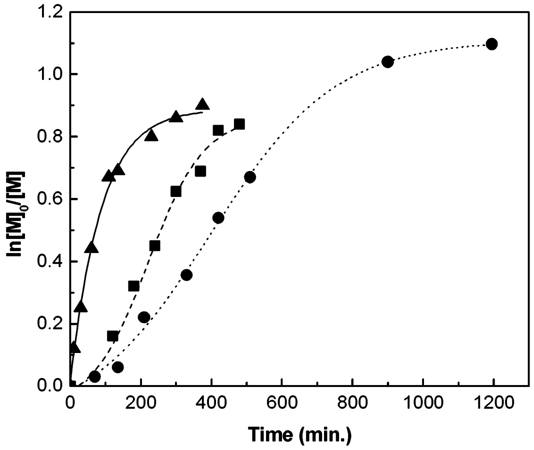


Figure 10. Semilogarithmic kinetic plots for bulk polymerizations of vinyl acetate performed at different temperatures ([VA]$_0$:[MIP]$_0$:[AIBN]$_0$ = 100:1:0.3): (●) 60 °C; (■) 70 °C; (▲) 80 °C.

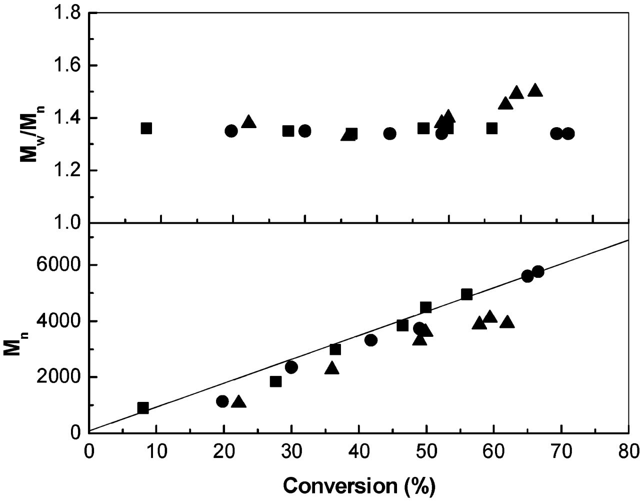


Figure 11. Dependence of molecular weights and polydispersities on conversion for bulk polymerizations of vinyl acetate performed at different temperatures ([VA]$_0$:[MIP]$_0$:[AIBN]$_0$ = 100:1:0.3): (●) 60 °C; (■) 70 °C; (▲) 80 °C. The line shows the theoretical molecular weight.

- Transfer of the iodine from the iodo-terminated dormant polymer to the radical in step 6 (Scheme 1) may involve long-lived intermediate with hypervalent iodine species ([C- - -I- - -C]$^{\bullet}$) (cf. e.g. Scheme 4).
- The alkyl iodide may decompose and generate iodine, which can inhibit/retard polymerization, especially at higher concentrations of alkyl iodides.
- Head-to-head monomer addition may be followed by fast end-capping with iodine, leading to primary alkyl iodides, which cannot be successfully reactivated (vide infra and Scheme 5).

To explain the retardation observed for DT polymerization of vinyl acetate, ethyl iodide was used as transfer agent and the results were compared with those obtained with ethyl iodoacetate.

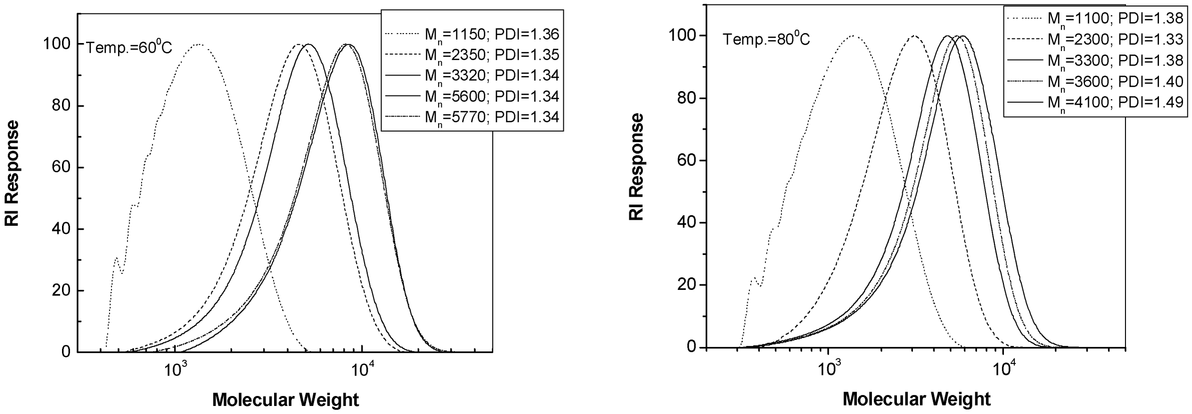


Figure 12. SEC traces for bulk polymerization of vinyl acetate performed at 60 and 80 °C ($[VA]_0$:$[MIP]_0$:$[AIBN]_0$ = 100:1:0.3).

DT polymerization of vinyl acetate was performed with ethyl iodide (EtI) as transfer agent at molar ratios $[VA]_0$:$[EtI]_0$:$[AIBN]_0$ = 100:1.0:0.3 and 100:3.0:0.3, at 75 °C. A higher reaction rate was observed with EtIAc as the transfer agent when compared with the rate for EtI. The reaction rate decreased with increasing concentration of EtI, as shown in Figure 8.

This behavior can be explained by formation of long-lived intermediate with hypervalent iodine species $[P_n$- - -I- - -$CH_2CH_3]^\bullet$, as shown in Scheme 4. The long-lived intermediate generated from ethyl iodide apparently does not dissociate efficiently to form iodo-terminated vinyl acetate and the initiating ethyl radical.

This is confirmed by much higher experimental molecular weights than theoretical ($DP_{n,theo} = \Delta[M]/[R-I]_0$), when EtI was used as transfer agent (Figure 9). At low conversion the ratio $M_{n(exp)}/M_{n(theo)} \approx 100$ was found for EtI, in contrast to EtIAc ($M_{n(exp)}/M_{n(theo)} \approx 1$).

Influence of Temperature

The influence of temperature was studied for AIBN-initiated polymerization of vinyl acetate in the presence of methyl 2-iodopropionate (MIP) as the transfer agent. Reactions were performed at three different temperatures (60, 70, and 80 °C) and the molar ratio of reagents was $[VA]_0$:$[MIP]_0$:$[AIBN]_0$ = 100:1:0.3. As expected, the reaction rate increased with temperature (Figure 10).

Good agreement between theoretical and experimental molecular weights was observed for both reactions performed at 60 and 70 °C and polymers with polydispersities less than 1.4 were obtained (Figure 11). Polymers with lower molecular weights than defined by the ratio $\Delta[M]/[RI]_0$ were obtained at 80 °C, which was probably due to a more significant chain transfer or even more likely to a larger proportion of the decomposed initiator.

The SEC traces shown in Figure 12 indicate some low molecular weight tailing for the reaction performed at 60 °C. The maximum of the SEC traces shifted toward higher molecular weights, whereas the low molecular weight tail remained for the polymer synthesized at 80 °C. This may imply the loss of the iodo end groups; this process was intensified at higher reaction temperatures. All the polymerizations reported in this study showed incomplete consumption of the monomer.

End Group Analysis

To better understand the DT process and analyze the end groups resulting from transfer agent and side reactions, a detailed 600 MHz ^1H NMR study was performed. The polymerization of vinyl acetate was carried out at 70 °C with a molar ratio $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 100:1:0.3. The reaction was performed in solution using 30 vol % deuterated benzene as solvent, in sealed NMR tubes. The reaction was stopped by cooling the NMR tubes in ice at different time intervals. The spectra obtained after 3 and 24 h are analyzed here.

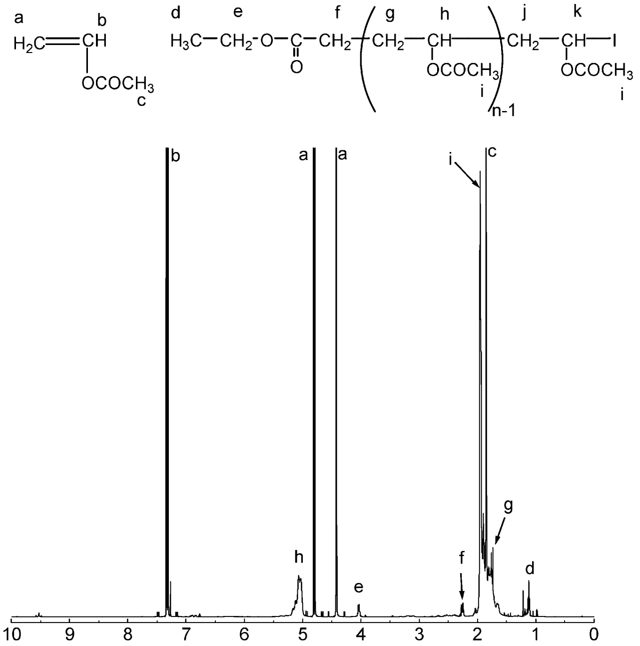


Figure 13. ^1H NMR (600 MHz) spectrum of the reaction mixture (after 24 h at 70 °C). Conditions: $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 100:1:0.3; $[VA]_0/[C_6D_6]$ = 70/30 (v/v); 70 °C.

The full ^1H NMR spectrum of the reaction mixture (spectrum recorded after 24 h at 70 °C) is shown in Figure 13.

The main absorption signals of poly(vinyl acetate) and vinyl acetate were assigned as shown. The methine proton (b) in vinyl acetate absorbs at 7.3 ppm, and the two vinyl protons (a) absorb at 4.4 and 4.8 ppm. The methine proton (h) in the polymer backbone absorbs at ~5 ppm, and the methylene (g) group, at 1.8 ppm. Methyl groups in monomer (c) and polymer (i) absorb at 1.85 and 1.95 ppm, respectively.

Figure 13 also allows the identification of protons from the end group generated by the EtIAc transfer agent. The methyl protons (d) originated from EtIAc (α-end group in polymer) absorb at 1.12 ppm (*t*). The C(O)-OCH_2 protons (e) and $O(O)CCH_2$ protons (f) originated

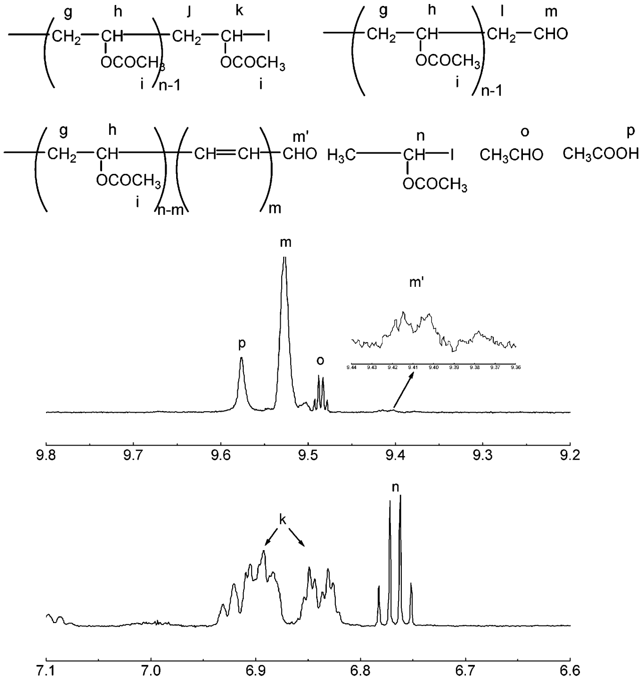


Figure 14. Expansions of ^{1}H NMR (600 MHz) spectra of the regions 6.6−7.1 ppm and 9.2−9.8 ppm. Conditions: $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 100:1:0.3; $[VA]_0/[C_6D_6]$ = 70/30 (v/v); 70 °C.

from EtIAc (α-end group in polymer) appeared at 4.04 ppm (q) and 2.27 ppm (m), respectively. The end groups originating from AIBN could not be clearly identified in the NMR spectra.

The expansion of the ^{1}H NMR spectrum, region 6.6−7.1 ppm, where the methine protons from the dormant chain end absorb is presented in Figure 14. Figure 14 also includes region 9.2−9.8 ppm, where the aldehyde and acidic protons resulting from decomposition reactions absorb.

The ω-terminal methine protons (k) $CH_2-C\mathbf{H}(OCOCH_3)I$ in poly(vinyl acetate) absorb in the region 6.8−6.95 ppm. This assignment was further confirmed by the two-dimensional COSY experiment, which determines the connectivity of a molecule by showing spin−spin coupled protons. In addition to signals from the chain end $CH_2-C\mathbf{H}(OCOCH_3)I$, broadened by the tacticity of the penultimate units, a sharp quartet at 6.77 ppm appears at later stages (when almost all the initiator was consumed). This was assigned to the vinyl acetate−HI adduct that is formed by the addition of HI to the double bond of vinyl acetate (Figure 14, bottom spectrum). HI can be formed by the hydrolysis of the iodo-terminated poly(vinyl acetate), as shown in Scheme 2, or by the decomposition of the chain ends due to elimination of HI. This reaction can continue in the absence of a radical initiator.

The poly(vinyl acetate) synthesized by DT with EtIAc also contains aldehyde end groups, as can be seen in Figure 14 (top spectrum). The formation of aldehyde end groups in the polymer is due to the decomposition of iodo-terminated poly(vinyl acetate), as shown in Schemes 2 and 3. The decomposition of the vinyl acetate−HI adduct according to the reaction shown in Scheme 3, should generate acetaldehyde (a sharp quartet at 9.48 ppm is shown in Figure 14, top spectrum) and acetyl iodide.

The reaction mixture became progressively brown after 24 h at 70 °C, whereas it was colorless at the beginning of the reaction. The polymer precipitated from the reaction mixture after 24 h was also brown. The initial decomposition of the iodo-terminated poly(vinyl acetate) should result in the formation of an aldehyde-terminated polymer, which could further decompose (CH_3COOH elimination), leading to conjugated unsaturated structures (polyene) (broad signals at 6−6.4 ppm in Figure 15, top spectrum) that are responsible for the brown color of the polymer. It is possible that both the higher temperature and the presence of HI (formed by elimination) could accelerate the decomposition of chain ends, leading to conjugated unsaturated structures. The polarity of the reaction medium should accelerate the decomposition of the chain ends (Scheme 3). It was noticed that the polymers synthesized in benzene showed less color and better agreement of the observed and theoretical molecular weights, whereas the polymers synthesized in bulk were more colored and had lower molecular weights than predicted. Similar chain end decomposition with the formation of polyene structures was reported in vinyl ether polymerizations.[33,34]

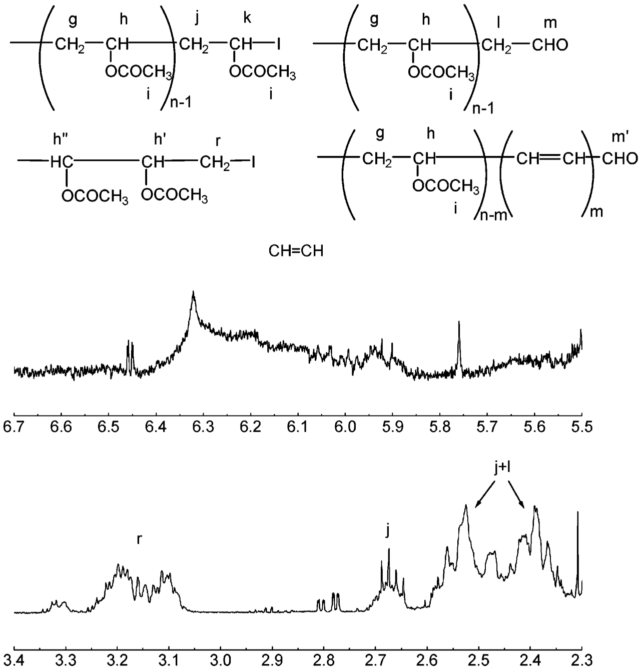


Figure 15. Expansions of the ^{1}H NMR (600 MHz) spectra of the regions 2.3−3.4 ppm and 5.5−6.7 ppm. Conditions: $[VA]_0$:$[EtIAc]_0$:$[AIBN]_0$ = 100:1:0.3; $[VA]_0/[C_6D_6]$ = 70/30 (v/v); 70 °C.

The signals (r) in the region 3.05−3.3 ppm (Figure 15, bottom spectrum) were difficult to assign in the ^{1}H NMR spectrum. Inspection of the ^{1}H−^{1}H COSY NMR spectrum in the region 3−5.4 ppm (Figure 16) indicates the internal connectivity of the r protons at 3.1 ppm with protons at 5.07 and 5.17 ppm. The protons at 5.07 and 5.17 ppm were assigned to the $C\mathbf{H}(OCOCH_3)$ protons (h′) in the polymer backbone. Because the $C\mathbf{H}(OCOCH_3)$ protons h′ at 5.07 and 5.17 ppm were coupled to another set of $C\mathbf{H}(OCOCH_3)$ protons (h″) at 5.27 and 5.29 ppm, the r protons were assigned to $CH(OCOCH_3)C\mathbf{H_2}I$. Two sets h′ and h″ signals should be due to meso and racemic structures. The $CH(OCOCH_3)$-$CH(OCOCH_3)CH_2I$ end groups can be formed by head-to-head radical addition followed by the transfer of iodine from the polymeric alkyl iodide, P_n−I (Scheme 5). These primary alkyl iodides are much less efficient transfer agents than secondary alkyl iodide end groups (cf. earlier experi-

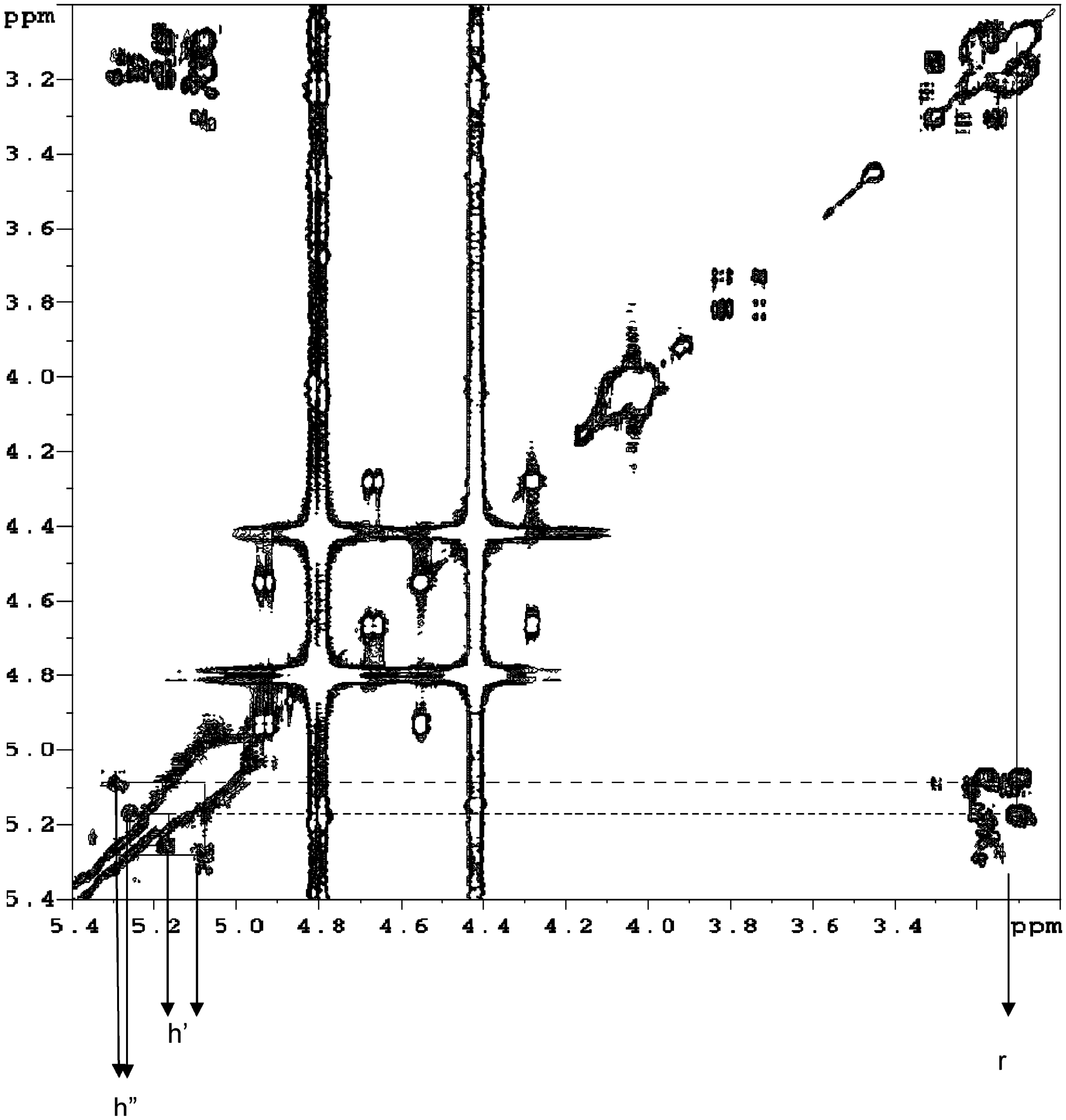


Figure 16. $^1H-^1H$ COSY NMR spectrum (region 3−5.4 ppm). The rectangles show the off-axis peaks establishing the connectivity.

ments with EtI). Therefore, they should accumulate during the reaction and be responsible for the limited conversion and retardation. Higher amounts of transfer agent lead to more efficient trapping and stronger retardation.

Monomer conversion was determined by the integration of the CH signals from vinyl acetate (b) and poly(vinyl acetate) (h). DP_n was calculated by comparing the intensity of the α-end protons (e) that originated from EtIAc to the poly(vinyl acetate) protons (h) ($DP_n = 2h/e$). The ω-end functionality was calculated by comparison of C**H**($OCOCH_3$)I protons (k) vs α-end protons (e) originated from EtIAc. In the same way contents of the aldehyde and $CH(OCOCH_3)CH_2I$ end groups (r protons) were estimated. The values of conversion, DP_n, and degree of functionality of poly(vinyl acetate) obtained after 3 and 24 h are given in Table 1. The value of DP_n(α-end) is lower than predicted from monomer conversion, plausibly due to limited solubility of the polymer with conjugated unsaturated units. The concentration of α-end groups is within ±1% of the sum of concentrations of ω-end groups (secondary and primary alkyl iodides and aldehyde). If reactivation of primary alkyl iodides is insignificant, then the proportion of head-to-head units should be equal to the product of the total fraction of the end groups ($1/DP_n$(α−end)) and a fraction of CH_2-I groups among all ω-end groups. Thus, after 3 h the proportion of head-to-head units was 0.7%; i.e., (1/15 × 0.1) and after 24 h it was 1%, i.e., (1/26 × 0.26). This relatively high proportion of head-to-head units suggests an efficient trapping of primary radicals by fast iodine transfer and low transfer constants for primary alkyl iodides.

Table 1. Monomer Conversion, DP_n, and % of Iodo and Aldehyde End Groups in Poly(vinyl acetate); $[VA]_0:[EtIAc]_0:[Aibn]_0 = 100:1:0.3$; $[VA]_0/[C_6D_6] = 70/30$ (v/v); 70 °C

reaction time (h)	conv VA (%)	DP_n (α-end)	% CH−I end groups	% aldehyde end groups	% CH_2−I end groups
3	16.9	15	81	9.7	10
24	37.0	26	49	26	26

Conclusions

Poly(vinyl acetate) with controlled molecular weights and relatively narrow molecular weight distributions was synthesized using DT polymerization with alkyl iodides. The analysis of chain end functionality of poly(vinyl acetate) synthesized by degenerative-transfer polymerization with ethyl iodoacetate as transfer agent revealed that the iodo end groups were not stable and decomposed during the reaction, leading to aldehyde-terminated polymer. Primary alkyl radicals formed by head-to-head addition are trapped to form primary alkyl iodides, which retard polymerization and are inefficient transfer agents.

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