Kinetic Study of the Free-Radical Polymerization of Vinyl Acetate in the Presence of Deuterated Chloroform by ^{1}H-NMR Spectroscopy

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ABSTRACT: The free-radical polymerization of vinyl acetate was performed in the presence of deuterated chloroform ($CDCl_3$) as a chain-transfer agent (telogen) and 2,2′-azobisisobutyronitrile as an initiator. The effects of the initiator and solvent concentrations (or equivalent monomer concentration) and the reaction temperature on the reaction kinetics were studied by real-time ^{1}H-NMR spectroscopy. Data obtained from analysis of the ^{1}H-NMR spectra were used to calculate some kinetic parameters, such as the initiator decomposition rate constant (k_d), $k_p(f/k_t)^{1/2}$ ratio (where k_p is the average rate constant for propagation, f is the initiator efficiency, and k_t is the average rate constant for termination), and transfer constant to $CDCl_3$ (C_{CDCl_3}). The results show that k_d and $k_p(f/k_t)^{1/2}$ changed significantly with the solvent concentration and reaction temperature, whereas they remained almost constant with the initiator concentration. C_{CDCl_3} changed only with the reaction temperature. Attempts were made to explain the dependence of $k_p(f/k_t)^{1/2}$ on the solvent concentration. We concluded from the solvent-independent C_{CDCl_3} values that the solvent did not have any significant effect on the k_p values. As a result, changes in the $k_p(f/k_t)^{1/2}$ values with solvent concentration were attributed to the solvent effect on the f and/or k_t values. Individual values of f and k_t were estimated, and we observed that both the f and k_t values were dependent on the solvent (or equivalent monomer) concentration. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1784–1796, 2008

Key words: degree of polymerization (DP); kinetics (polym.); NMR; radical polymerization

INTRODUCTION

Despite extensive attempts and an increasing the number of controlled/living radical polymerization systems, several classes of monomers remain uncontrolled to date. Among them, vinyl acetate (VAc) and vinylidene fluoride remain important challenges. Therefore, examples of poly(vinyl acetate) (PVAc) and poly(vinylidene fluoride) based block copolymers are scarce in the literature.[1–4] However, cobalt-mediated radical polymerization (one of the controlled radical polymerization techniques) has been used recently for the controlled synthesis of PVAc with respect to molecular weight and its distribution as well as to the chain-end functionality.[5] Now, PVAc-based block copolymers are readily obtained by a combination of cobalt-mediated radical polymerization with a second type of controlled/living radical polymerization [e.g., atom transfer radical polymerization (ATRP)].[6–8]

Telomerization reactions are reactions that produce oligomers with low molecular weights. *Telomerization* was defined by Handford[9] for the first time as the reaction between a molecule YZ, which is called a *telogen*, with one or several molecules of a polymerizable compound M, called a *taxogen*, under polymerization conditions to form products called *telomers* with formula Y(M)$_n$Z [eq. (1)], where n is the number of taxogen molecules incorporated into the telomer:

$$n\mathrm{M} + \mathrm{YZ} \xrightarrow{\text{catalyst}} \mathrm{Y} - (\mathrm{M})n - \mathrm{Z} \qquad (1)$$
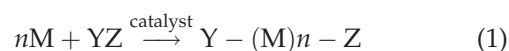
Conventional free-radical polymerization, which produces monofunctional or difunctional polymers, can be suitably combined with some controlled/living radical polymerizations to give novel block copolymers. For example, PVAc-based block copolymers have been prepared by a combination of free-radical telomerization (conventional free-radical polymerization in the presence of telogen) and ATRP (which is one controlled/living radical polymerization system).[10–18] CHCl$_3$ and CCl$_4$ have been used as telogens in the telomerization of VAc to synthesize trichloromethyl (CCl$_3$)-terminated VAc telomers.

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CCl$_3$-terminated VAc telomers were then used as macroinitiators in the ATRP of various monomers, such as styrene[11,12] and (meth)acrylates,[13–18] to prepare PVAc-based block copolymers.

Online ^{1}H-NMR spectroscopy has been used frequently for homopolymerization and copolymerization systems to investigate the kinetics of polymerization reactions with respect to, for example, the overall polymerization rate coefficient and the monomer reactivity ratios, copolymer composition, and stereoregularity (in the case of copolymerization).[19–21] In this study, possibility of using ^{1}H-NMR kinetic experiments for the investigation of the kinetics of the free-radical telomerization of VAc with deuterated chloroform (CDCl$_3$) as a telogen in the presence of 2,2′-azobisisobutyronitrile (AIBN) initiator was examined. To our knowledge, there has been no report on the free-radical telomerization of VAc with CDCl$_3$ as a telogen. Some kinetic parameters, such as the initiator decomposition rate constant (k_d), overall polymerization rate constant (k_{ov}), lumped parameter ($k_p/k_t^{1/2}$, where k_p is the average rate constant for propagation), and transfer constant to CDCl$_3$(C_{CDCl_3}), were calculated with data obtained from ^{1}H-NMR spectra recorded at various time intervals for each experiment. Attempts are made to explain the dependence of $k_p/k_t^{1/2}$ on the solvent (or equivalent monomer) concentration. We believe that synthesized telomers may be used as a macroinitiator in ATRP reactions to synthesize the PVAc-based block copolymers, which will be reported in the near future.

EXPERIMENTAL

Materials

VAc (Merck, >99%) [Tehran, Iran] was distilled under a nitrogen (99.99%) atmosphere before use. AIBN (Fluka, ≥98%) and CDCl$_3$ (99.95%, ARMAR Chemicals, Switzerland) were used without further purification.

Sample preparation

Solution samples with different ratios of the initial concentration of CDCl$_3$ to the initial concentration of VAc ([VAc]$_0$) and different AIBN concentrations were prepared. First, the initiator solution in CDCl$_3$ was prepared. The defined amount of this solution was then added to a given amount of monomer (VAc), and thus, samples with the desired concentrations were obtained (Table I). Various molar ratios of CDCl$_3$ to VAc were chosen, and therefore, solutions with various concentrations of VAc and CDCl$_3$ were made (Table I). The total volume of each sample was adjusted to be about 1 mL. The final reaction mixture was then conducted to the NMR tube

TABLE I
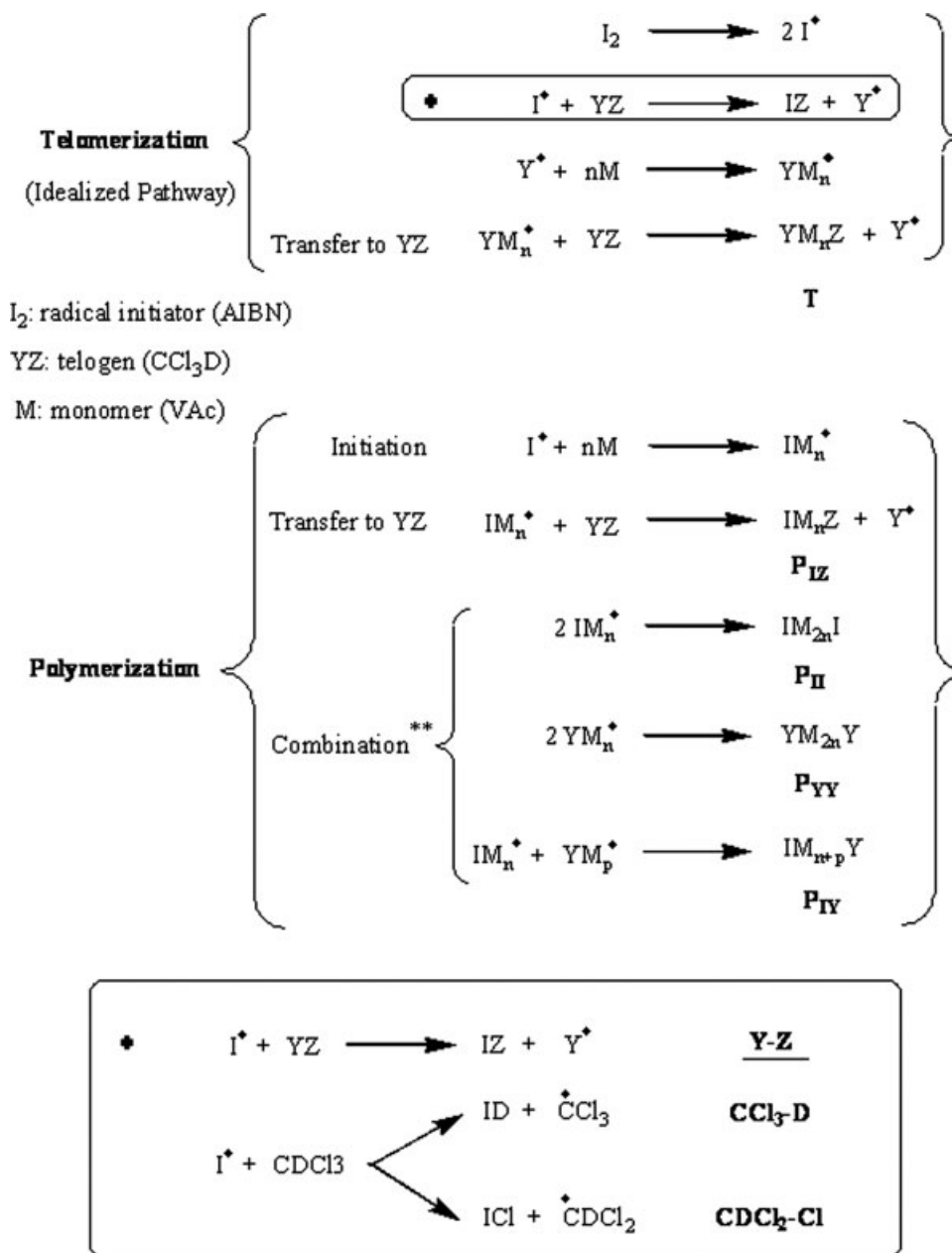**Recipes for the Telomerization of VAc with CDCl$_3$ in the Presence of AIBN**

Experiment no.	VAc/CDCl$_3$/AIBN molar ratio	[VAc]$_0$ (mol/L)	Temperature (°C)
1	1/4/0.01	2.42	60
2	1/8/0.01	1.36	60
3	1/8/0.03	1.36	60
4	1/2/0.01	3.95	60
5	1/2/0.01	3.95	52.5

(5 mm in diameter). The solutions in the NMR tubes were degassed with nitrogen gas (99.99% purity) to exclude oxygen from the reaction mixture. During sample preparation and especially during the degassing with nitrogen, the reaction mixture was maintained in an ice/water mixture to prevent the evaporation of CDCl$_3$ (bp ≅ 60.9°C) and progress of the reaction.

Online ^{1}H-NMR kinetic experiments

All NMR kinetic experiments reported in this study were carried out on a Bruker Avance 400-MHz NMR spectrometer [Karlsruhe, Germany]. The sample cavity was equilibrated at a given temperature (i.e., the temperature at which the kinetic experiment was carried out) by a BVT 3000 (±0.1°C) temperature control unit [Karlsruhe, Germany]. The boiling temperature of CDCl$_3$ is about 60.9°C, and therefore, the maximum temperature of the reaction was chosen to be 60°C. To obtain a reasonable polymerization rate, 52.5°C was also chosen as the minimum temperature of reaction.[22] A typical ^{1}H-NMR kinetic experiment consisted of the following sequence of steps.[19]

First, the cavity was set to the desired reaction temperature, and a sample containing only CDCl$_3$ (telogen/solvent) was introduced into the sample cavity and allowed to equilibrate for approximately 10 min. The magnet was then thoroughly shimmed with the CDCl$_3$ sample. Second, the sample tube containing the reaction mixture was inserted into the sample chamber, and the start time was recorded. The sample containing the reaction mixture was allowed to equilibrate for 5 min. The first recorded spectrum at this time (5 min after the sample tube was inserted into the cavity) was regarded as a spectrum representing zero monomer conversion. Although approximately 5 min passed from insertion of the sample into the cavity to the first scan, no conversion of VAc occurred because of the low rate of reaction. An experiment was performed at 45°C, but the progress of the reaction was very slow (the final conversion after 4 h was about 25%). Therefore, the data collected for this experiment was not enough to calculate the corresponding kinetic

$$I_2 \longrightarrow 2\,I^{\bullet}$$

Telomerization

(Idealized Pathway)

$$\boxed{\bullet \quad I^{\bullet} + YZ \longrightarrow IZ + Y^{\bullet}}$$

$$Y^{\bullet} + nM \longrightarrow YM_n^{\bullet}$$

Transfer to YZ $\quad YM_n^{\bullet} + YZ \longrightarrow YM_nZ + Y^{\bullet}$

T

I_2: radical initiator (AIBN)

YZ: telogen (CCl_3D)

M: monomer (VAc)

Polymerization

Initiation $\quad I^{\bullet} + nM \longrightarrow IM_n^{\bullet}$

Transfer to YZ $\quad IM_n^{\bullet} + YZ \longrightarrow IM_nZ + Y^{\bullet}$

$\mathbf{P_{IZ}}$

Combination**

$$2\,IM_n^{\bullet} \longrightarrow IM_{2n}I$$

$\mathbf{P_{II}}$

$$2\,YM_n^{\bullet} \longrightarrow YM_{2n}Y$$

$\mathbf{P_{YY}}$

$$IM_n^{\bullet} + YM_p^{\bullet} \longrightarrow IM_{n+p}Y$$

$\mathbf{P_{IY}}$

$$\bullet \quad I^{\bullet} + YZ \longrightarrow IZ + Y^{\bullet} \qquad \underline{\mathbf{Y\text{-}Z}}$$

$$I^{\bullet} + CDCl3 \left\langle \begin{array}{l} ID + \overset{\bullet}{C}Cl_3 \qquad \mathbf{CCl_3\text{-}D} \\[1em] ICl + \overset{\bullet}{C}DCl_2 \qquad \mathbf{CDCl_2\text{-}Cl} \end{array} \right.$$

** Predominant mode of termination in VAc polymerization [11]

Scheme 1 "l2" has been defined inside the Scheme 1 as radical initiator (AIBN). "l(superscript) star" indicates initiator-derived radical. "P(subscript) ij" indicates polymer chain initiated with i fragment and finally terminated wiht j fragment. T indicate telomer chain.

parameters (see the next section), and as a result, this experiment was omitted from this article. However, this experiment and its corresponding data were given in a previous article.[22]

RESULTS AND DISCUSSION

^{1}H-NMR analysis

In a previous study,[22] the structures of telomers prepared by the telomerization of VAc with $CDCl_3$ as a

telogen in the presence of AIBN initiator were characterized by ^{1}H-NMR spectra. It was observed that the telomerization of VAc with the $CDCl_3$ telogen proceeded via two different mechanisms of the transfer reactions to telogen, that is, the abstraction of either deuterium or chlorine from $CDCl_3$ (Schemes 1 and 2). As a result, telomers with two different α-end groups (CCl_3 or CCl_2D) were formed during the telomerization reaction. A portion of the chains could initiate by initiator radicals to produce polymers with a P_{IZ}-type structure (P_{ID} or P_{ICl},
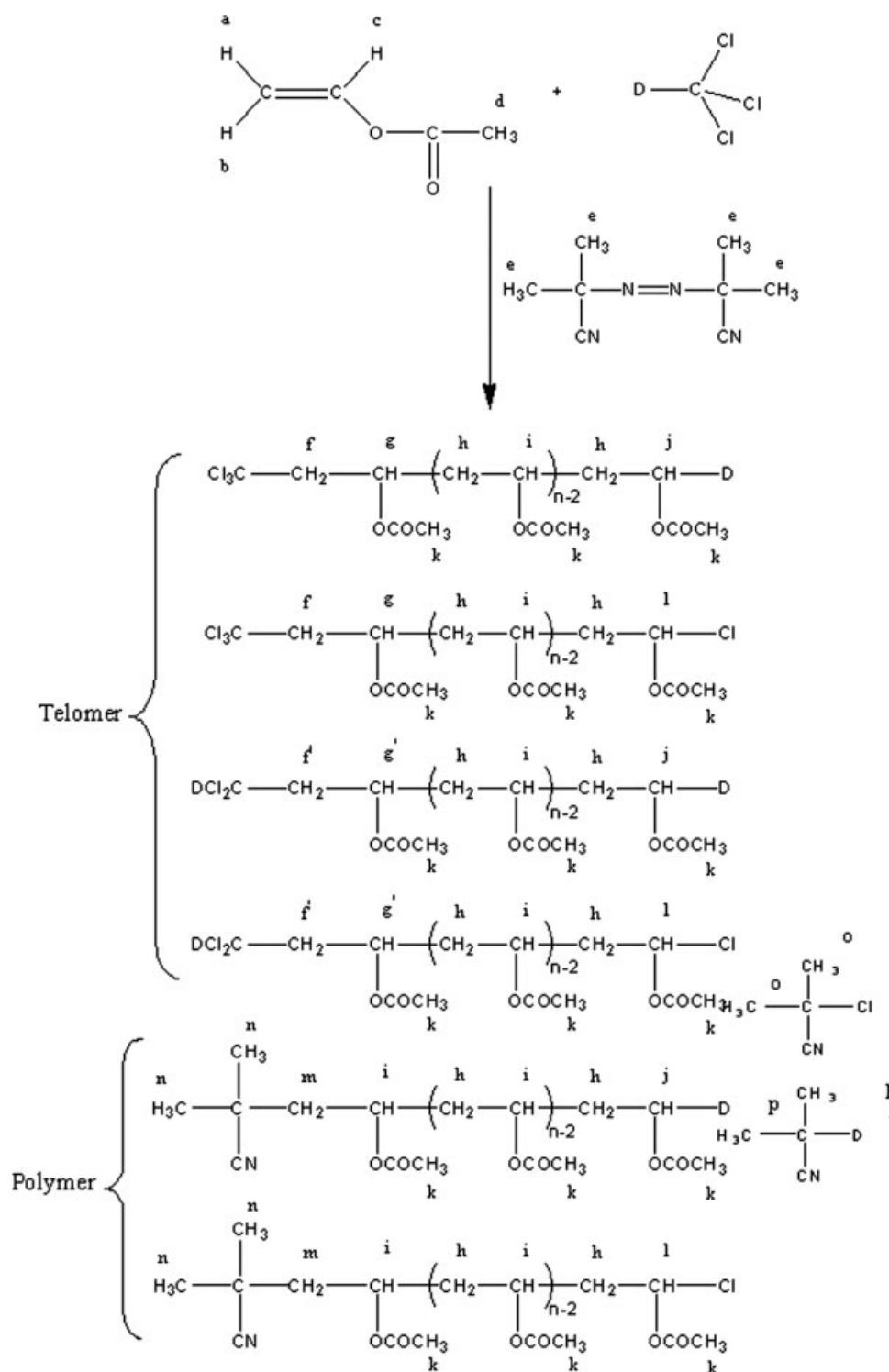
Scheme 2 "p" indicates the methyl protons in (CH3)2C(CN)D compound. Thus, it should be given in the vicinity of methyl group.

depending on the type of transfer reaction to telogen) as shown in Scheme 2.[22]

Figure 1 shows a typical ^{1}H-NMR spectra recorded for a reaction mixture containing an initial VAc/CDCl$_3$/AIBN molar ratio equal to 1/4/0.01 (experiment 1, Table I) as a function of the reaction time. Signal assignments for this telomerization system were carried out in the previous study[22] by consideration of the ^{1}H-NMR spectra reported in the literature for VAc telomers synthesized with CHCl$_3$[11,14] and CCl$_4$[23] and their comparison with the spectra recorded here for VAc telomers obtained
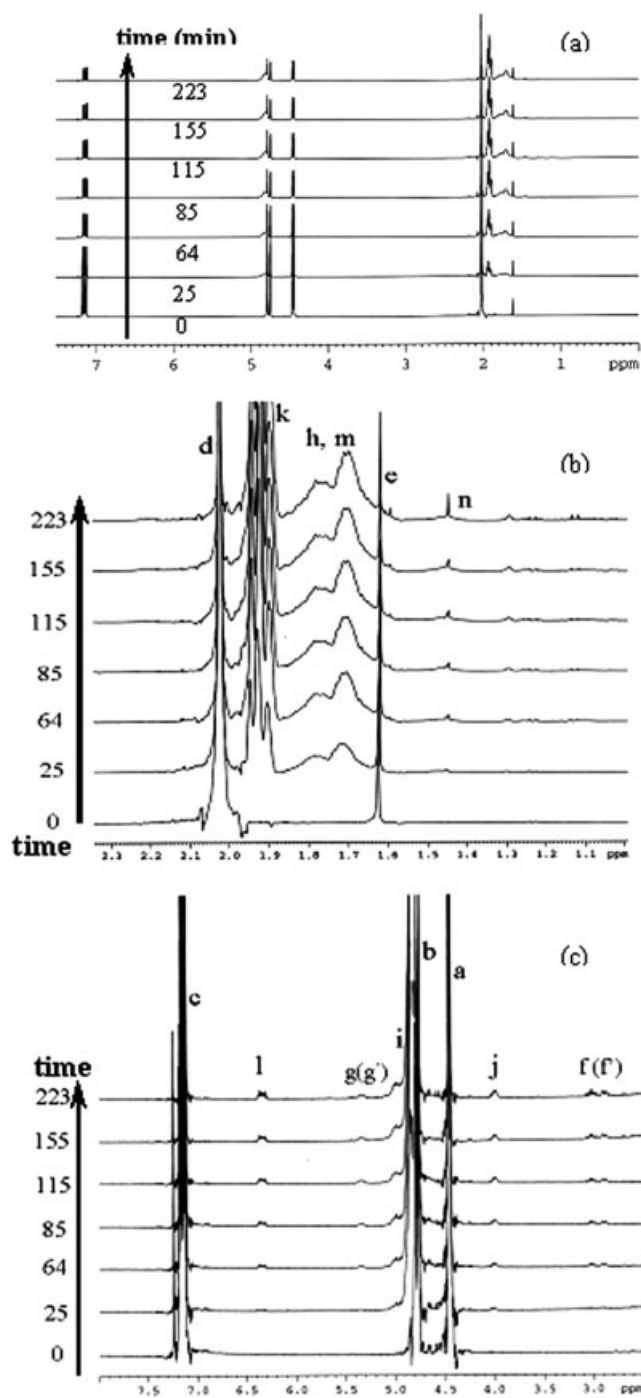
Figure 1 (a) Original and (b,c) expanded typical ^{1}H-NMR spectra recorded at various time intervals for the VAc telomerization with CDCl$_3$ (experiment 1, Table I) along with the assignments of the proton signals (Scheme 2).

with CDCl$_3$. According to the signals observed during the progress of VAc telomerization with CDCl$_3$, the mechanism of the reaction was considered to be that shown in Scheme 1. It is clear from Figure 1 that with the progress of the telomerization reaction, the intensities of the signals related to the protons of the monomer (VAc) incorporated into the telomer and polymer chains increased. So, the progress of

the reaction could be followed with time. Consequently, it was possible to investigate the kinetics of the VAc telomerization reaction. Isothermal conditions were established during the course of the reaction because of the low rate of the telomerization reaction and the relatively high amount of the solvent (telogen).

Now, from the complete assignment of the entire signals (see Scheme 2), it was possible to calculate the molar conversion of VAc (x_{VAc}), the cumulative number-average degree of polymerization [$(\overline{DP}_n)_{cum}$], the fraction of CCl$_3$- and CDCl$_2$-terminated chains relative to the initiator-fragment-terminated chains [telomer percent (Telomer%)], and the ratio of deuterium abstraction to chlorine abstraction from CDCl$_3$ ($R_{D/Cl}$; equivalently, the ratio of chains with deuterium ω ends to those with chlorine ω ends) with eqs. (2)–(5), respectively:

$$x_{VAc} = \frac{I_{4.7-5.0} - I_{4.5} + I_{3.9-4.1} + I_{5.2-5.4} + I_{6.3-6.4}}{I_{4.7-5.0} + I_{3.9-4.1} + I_{5.2-5.4} + I_{6.3-6.4}} \quad (2)$$

$$\left(\overline{DP}_n\right)_{cum} = \frac{I_{4.7-5.0} - I_{4.5} + I_{3.9-4.1} + I_{5.2-5.4} + I_{6.3-6.4}}{I_{3.9-4.1} + I_{6.3-6.4}}$$

$$(3)$$

$$\text{Telomer\%} = \frac{\frac{I_{2.8-3.2}}{2}}{I_{3.9-4.1} + I_{6.3-6.4}} \quad (4)$$

$$R_{D/Cl} = \frac{I_{3.9-4.1}}{I_{6.3-6.4}} \quad (5)$$

where I_{i-j} indicates the intensity of the proton(s) signal appearing at chemical shifts of i up to j. It was observed in the previous study[22] that $(\overline{DP}_n)_{cum}$ values calculated by eq. (3) were in good agreement with those measured by gel permeation chromatography.

As is clear from Figure 1, the intensities of the proton signals of VAc units incorporated into the chains at two α and ω ends were very low at the initial stage of the reaction (typically, at conversions below 20%). So, it was impossible to calculate the number-average degree of polymerization ($\overline{DP}_n$), Telomer%, and $R_{D/Cl}$ at conversions below 20%. With increasing conversion of VAc, the intensities of the aforementioned signals became significant, and thus, the aforementioned parameters could be calculated according to eqs. (2)–(4) as a function of the reaction time.[22] Table II shows a summary of the data calculated from the online ^{1}H-NMR kinetic experiments.

Determination of k_d

The determination of the rate constants for the individual steps in a radical polymerization is an important task because it provides information about the better understanding of the polymerization reaction

TABLE II
Summary of the Kinetic Parameter Values Obtained for the Telomerization of VAc with CDCl$_3$ in the Presence of AIBN Under Various Conditions

Experiment no.	[VAc]$_0$ (mol/L)	R_0[a]	Temperature (°C)	$V_0 \times 10^2$ [min^{-1}; eqs. (11) and (12)[b]]	$k_d \times 10^4$ [s^{-1}; eq. (11)]	$2V_0/k_d$ [eq. (8)]	$k_p(f/k_t)^{0.5} \times 10^2$ [L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$; eqs. (8) and (12)[b]]	$C_{CDCl_3} \times 10^3$ [eq. (19)]
1	2.42	4	60	1.71 (1.57[b])	2.82	1.94	10.49 (10.02[b])	1.74
2	1.36	8	60	0.655 (0.573[b])	0.900	2.31	6.65 (6.10[b])	1.75
3	1.36	8	60	0.766 (0.739[b])	1.16	2.10	6.11 (5.66[b])	1.65
4	3.95	2	60	2.28 (2.24[b])	3.23	2.48	11.33 (10.90[b])	1.79
5	3.95	2	52.5	0.937 (0.830[b])	1.12	2.76	7.34 (6.78[b])	2.18

[a] See Table I.
[b] The values inside the parentheses were determined with eq. (12).

mechanism and the molecular weight distribution of the polymer. k_d is one of the rate constant involved in free-radical polymerization or telomerization. Ng and Chee[24] reported a method by which k_d is determined under actual polymerization conditions. This method is described briefly in the following section.

The rate of classic radical polymerization, which can also be used for radical telomerization, is expressed by Tobolsky's equation[25] [eq. (6)]:

$$R_p = -\frac{d[M]}{dt} = k_{ov}[I]^{1/2}[M] \quad \text{where} \quad k_{ov} = k_p\left(\frac{fk_d}{k_t}\right)^{1/2} \tag{6}$$

in which t = reaction time, R_p is the polymerization rate, k_t is the average rate constant for termination, f is the initiator efficiency, and [I] and [M] are the instantaneous concentrations of the initiator and monomer, respectively, at any time.

This basic equation is derived from classic polymerization kinetics on the basis of the steady-state condition of the radical concentration and an assumption that the reactivity of propagating (macro)radicals is independent of the chain length. Because the decomposition of the initiator follows first-order kinetics, [I] is given by eq. (7):

$$[I] = [I]_0 \exp(-k_d t) \tag{7}$$

where [I]$_0$ is the initial concentration of the initiator. The introduction of eq. (7) into eq. (6) and then integration results in eq. (8):

$$\ln\left(\frac{1}{1-x}\right) = \frac{2V_0}{k_d}\left[1 - \exp\left(-\frac{k_d t}{2}\right)\right] \tag{8}$$

where x is the molar conversion of the monomer and the parameter V_0 is defined as

$$V_0 = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I]_0^{1/2} = k_{ov}[I]_0^{1/2} \tag{9}$$

A unique feature of eq. (8) is that k_d is mathematically separable from the other rate constants because

the exponential function contains one kinetic parameter, that is, k_d, only. Consequently, this equation, which was first developed by Tobolsky in 1958,[25] forms the dead-end polymerization method for the evaluation of k_d. The use of the dead-end polymerization technique depends critically on a precise knowledge of the limiting value of [M] at long reaction times ($t \to \infty$). Moreover, it also requires the absence of an autoacceleration effect at high conversion.[26] The method of Ng and Chee[24] overcomes these difficulties. They derived a mathematical relationship [eq. (10)] by expanding the exponential function in eq. (8) in a power series and simplifying the resulting expression as follows:

$$\frac{\ln\left(\frac{1}{1-x}\right)}{t} = V_0\left[1 - \frac{1}{2!}\left(\frac{k_d}{2}\right)t + \frac{1}{3!}\left(\frac{k_d}{2}\right)^2 t^2 \cdots\right] \tag{10}$$

At the initial reaction times, the t term is much larger than the t^2 term on the right side, and the equation can be truncated to eq. (11):

$$\frac{\ln\left(\frac{1}{1-x}\right)}{t} = V_0 - V_0\left(\frac{k_d}{4}\right)t \tag{11}$$

A plot of the left side of eq. (11) versus time should give a straight line with an intercept of V_0 and slope of $-V_0(k_d/4)$. Then, k_d can be computed from the values obtained from the intercept and the slope of the straight line. This graphical method is applicable over the appropriate ranges of conversion, in which the relationship between $\ln[1/(1 - x)/t]$ and t is linear. This method can be applied to virtual and conventional initiators with k_d on the order of 10^{-4} to 10^{-6} s^{-1} for chain polymerization.[24]

$\ln[1/(1 - x)]/t$ as a function of time for the all experiments (Table I) is plotted in Figure 2. Linear relationships were obtained for all of the experiments, which indicated that k_d could be calculated under actual polymerization conditions by the aforementioned graphical method. The results of the k_d of
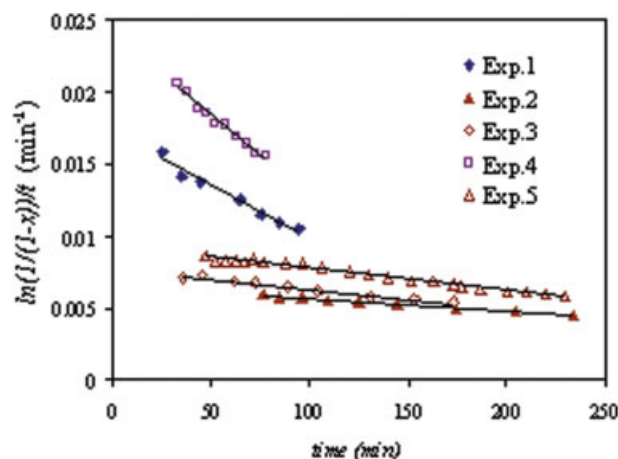
Figure 2 Plots of $\ln[1/(1 - x)]/t$ as a function of time for the VAc telomerization with $CDCl_3$ under various reaction conditions (see Table I). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

AIBN under various conditions are given in Table II. It is clear that the k_d values of AIBN at 60°C were dependent on the initial reaction mixture composition (i.e., on the initial molar ratio of VAc to $CDCl_3$). This dependence was not a linear function from the VAc molar fraction. The same results have been reported for the k_d of AIBN in various solvent/monomer mixtures, such as N,N-dimethylformamide (DMF)/ methyl methacrylate (MMA),[27] DMF/acrylonitrile (AN),[28,29] and DMF/MMA/AN[30] at 60°C. The dependence of the k_d of AIBN on the solvent concentration (or equivalent [M]) has been interpreted on the bases of the hypothesis of initiator solvation by the monomer and solvent alone and by the mixed monomer/solvent.[29,31]

Determination of the ratio of $k_p(f/k_t)^{1/2}$

To calculate the precise value of V_0 by eq. (8), it is necessary to obtain a precise k_d value for the given reaction mixture. For this reason, k_d values were calculated individually for each experiment, and then, the corresponding k_d value obtained for each experiment was used in eq. (8) to estimate the values of V_0 and then $k_p(f/k_t)^{1/2}$. When $\ln[1/(1 - x)]$ versus $[1 - \exp(k_d t/2)]$ was plotted, a straight line with a slope of $2V_0/k_d$ was obtained. As values of k_d and $[I]_0$ were known, the ratio $k_p(f/k_t)^{1/2}$ was then calculated.

Figure 3 shows the plots of $\ln[1/(1 - x)]$ as a function of $[1 - \exp(k_d t/2)]$ for the various polymerization conditions. Decreasing the molar fraction of VAc in the initial reaction mixture had a remarkable influence on the slope (slope $= 2V_0/k_d$) of the curves. Because k_d and $[I]_0$ were known for each experiment, $k_p(f/k_t)^{1/2}$ was then calculated by eq. (9)

and the $2V_0/k_d$ values (Table II). The results in Table II indicate that $k_p(f/k_t)^{1/2}$ values increased with $[VAc]_0$ (see experiments 1, 2, and 4, Table II). This means that the chain propagation and/or termination rate constants and f may have been dependent on the solvent concentration (see the next section). The same results have been reported for the solution homopolymerization of VAc and butyl acrylate (BuA) in toluene and ethyl acetate solvents.[32–34] Moreover, there are numerous reports on the effect of solvents on the polymerization rate constant.[35,36] Because f, k_p, and k_t were not individually available for this system, it is hard to discuss the effect of the solvent on the individual constants. However, this effect may be clarified when the transfer constant to telogen (C_T) is known, which will be discussed in the next section.

In the initial stage of free-radical polymerization (or equivalent telomerization), [I] can be assumed to be constant and equal to $[I]_0$. Then, the integration of eq. (6) results in eq. (12):

$$\ln\left(\frac{1}{1 - x}\right) = k_{ov}[I]_0^{1/2}t = V_0t \qquad (12)$$

The conversion data for the short time in the initial stage of telomerization was used to plot $\ln[1/(1 - x)]$ versus t (Fig. 4), from which a straight line with a slope of $V_0 = k_{ov}[I]_0^{1/2}$ was obtained (Table II). The results in Table II show that the V_0 values obtained by eq. (12) were in good agreement with those obtained by eq. (11). Again, because $[I]_0$ and k_d were known, $k_p(f/k_t)^{1/2}$ could be calculated with eq. (9) and the V_0 values (Table II) obtained from the curves of eq. (12) in Figure 4. The corresponding results are given in Table II, which indicate that there was good agreement between these values and those obtained from eq. (8).
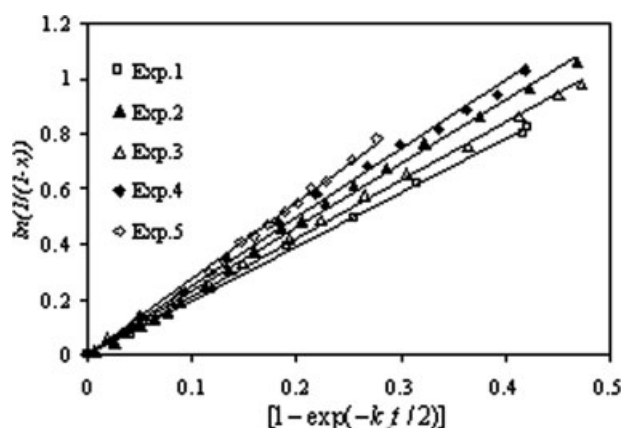

Figure 3 Plots of $\ln[1/(1 - x)]$ as a function of $[1 - \exp(-k_d t/2)]$ for the VAc telomerization with $CDCl_3$ under various reaction conditions (see Table I).
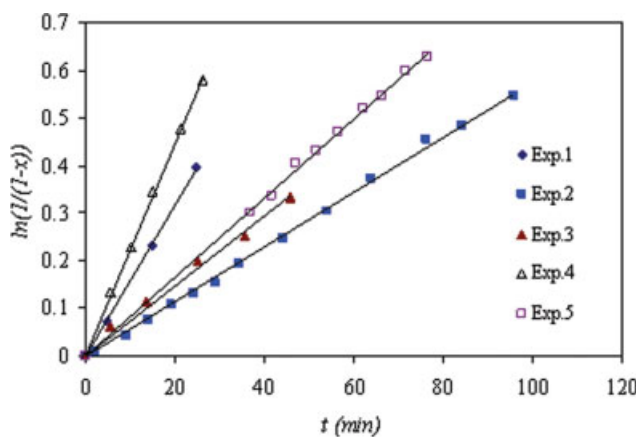
Figure 4 Plots of $\ln[1/(1-x)]$ as a function of reaction time for the VAc telomerization with CDCl$_3$ under various reaction conditions (see Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Now, a theoretical evaluation of x_{VAc} as a function of reaction time was possible with eq. (8) and the rate constants [k_d and $k_p(f/k_t)^{1/2}$] obtained here. Both theoretical and experimental values of x_{VAc} versus time are shown in Figure 5. There was good agreement between the model and experimental results, which indicated the accuracy of the calculated rate constants. As a result, online ^{1}H-NMR kinetic experiments could be used to reasonably evaluate the kinetics of the free-radical reactions in the whole range of conversion.[19–21]

Determination of C_{CDCl_3}

$(\overline{DP}_n)_{cum}$ in the case of the ideal telomerization reaction (see Scheme 1) could be obtained with the following equation.[37]

$$(\overline{DP}_n)_{cum} = \frac{[M]_0 - [M]}{[T]_0 - [T]} \qquad (13)$$

in which [T] is the instantaneous concentration the telogen at any time and [T]$_0$ and [M]$_0$ are the initial concentrations of the monomer and telogen, respectively.

Variations in [T] and [M] with conversion are given by eqs. (14)[38] and (15), respectively:

$$[T] = [T]_0(1-x)^{C_T} \qquad (14)$$

$$[M] = [M]_0(1-x) \qquad (15)$$

in which C_T is the transfer constant to telogen (C_{CDCl_3} in this case) and is defined as the ratio of the chain-transfer rate constant ($k_{tr,CDCl_3}$ in this study) to the chain-propagation rate constant (i.e., k_p).

With the substitution of eqs. (14) and (15) into eq. (13) and with some manipulation, the following equation is obtained:

$$(\overline{DP}_n)_{cum} = \frac{x}{R_0[1-(1-x)^{C_T}]} \qquad (16)$$

where R_0 is the molar ratio of telogen to solvent or [T]$_0$/[M]$_0$.

Equation (16) can be rewritten as the following equation:

$$\ln\left(1 - \frac{x}{R_0(\overline{DP}_n)_{cum}}\right) = C_T \ln(1-x) \qquad (17)$$

Equation (17) is established by the assumption that the contribution of the radical initiator is negligible (i.e., telomerization is ideal). However, the results of Telomer% in the previous study indicated that telomerization is not ideal (Telomer% was less that 100% so that the maximum Telomer% was obtained to be close to 65%),[22] and some polymer chains also formed during the telomerization reaction. Consequently, it is necessary to correct eq. (13) by the introduction of Telomer% into the equation as follows:

$$(\overline{DP}_n)_{cum} = \frac{[M]_0 - [M]}{([T]_0 - [T]) + \left(1 - \frac{Telomer\%}{100}\right)([T]_0 - [T])} \qquad (18)$$

where $\left(1 - \frac{Telomer\%}{100}\right)([T]_0 - [T])$ is related to the contribution of initiator radicals in the initiation of chains, whereas ([T]$_0$ − [T]) is related to the chains initiated by the telogen radicals. With the introduction of
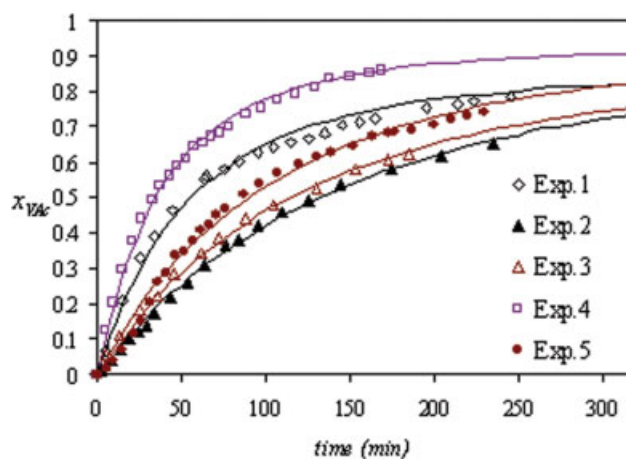

Figure 5 Theoretical (solid lines) and experimental (points) data of x_{VAc} versus time for the VAc telomerization with CDCl$_3$ under various reaction conditions (see Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
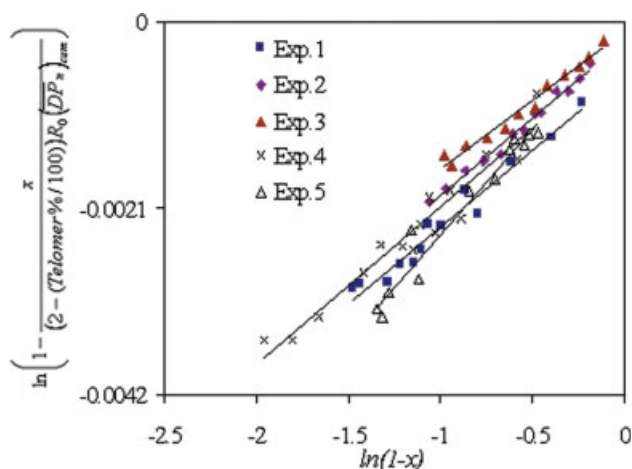
Figure 6 Plots of $\ln\left(1 - \frac{x}{(2-(\text{Telomer}\%/100))R_0\left(\overline{\text{DP}}_n\right)_{\text{cum}}}\right)$ as a function of $\ln(1 - x)$ for the VAc telomerization with CDCl$_3$ under various reaction conditions (see Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

eqs. (14) and (15) into eq. (18) and with some manipulation, eq. (19) is obtained:

$$\ln\left(1 - \frac{x}{\left(2 - \frac{\text{Telomer}\%}{100}\right)R_0\left(\overline{\text{DP}}_n\right)_{\text{cum}}}\right) = C_T \ln(1 - x)$$

(19)

It is clear from eq. (19) that C_T (C_{CDCl_3} in this system) can be directly obtained from the slope of the plots of $\ln\left(1 - \frac{x}{(2-(\text{Telomer}\%/100))R_0\left(\overline{\text{DP}}_n\right)_{\text{cum}}}\right)$ versus $\ln(1 - x)$. The corresponding plots and C_{CDCl_3} values are given in Figure 6 and Table II, respectively. As the transfer constant to CHCl$_3$ (C_{CHCl_3}) in the free-radical telomerization of VAc with chloroform was reported to be close to 0.01,[11] the results in Table II indicate that the C_{CDCl_3} value was lower than the C_{CHCl_3} value. The maximum value of Telomer% in this study was obtained to be about 60%,[22] whereas the minimum value of Telomer% in the free-radical telomerization of VAc with CHCl$_3$ was reported to be 72% (when $R_0 = 0.5$ in the presence of benzene solvent).[11] This could be attributed to the lower value of C_{CDCl_3} in comparison to the C_{CHCl_3} value. The lower the value of C_T is, the lower the rate constant of chain transfer will be. Therefore, the initiation of chains by the initiator (AIBN) radicals will compete with the initiation of chains by the telogen (CDCl$_3$ in this study) radicals (see Scheme 2). As a result, Telomer% decreases with decreasing the C_T value. The results in Table II also show that at a constant temperature, C_{CDCl_3} values did not change with [M] (or equivalent solvent concentration). This suggested that k_p and k_{tr,CDCl_3} values may not have

changed with solvent concentration because, as mentioned previously, C_{CDCl_3} is defined as the ratio of the k_{tr,CDCl_3} to k_p. As a result, the variation in the value of $k_p(f/k_t)^{1/2}$ as a function of [M] (or equivalent solvent concentration) at a constant reaction temperature could be attributed to the effect of the solvent on the f and/or k_t values; this is discussed in the next section.

Estimation of the f and k_t values

The instantaneous degree of polymerization $[(\overline{\text{DP}}_n)_i]$ is related to [M], [T], and [I] and to the appropriate rate constants [eq. (20)]:[39]

$$\frac{1}{\left[(\overline{\text{DP}}_n)_i\right]} = \frac{(2fk_dk_t)^{1/2}}{(1+a)k_p}\frac{[I]^{1/2}}{[M]} + C_T\frac{[T]}{[M]}$$

(20)

where the value of a depends on the termination reactions ($a = 0$ for disproportionation termination and $a = 1$ for bimolecular termination). In an ideal telomerization without bimolecular termination of macroradicals, a is considered to be zero. The concentration of the solvent ([T]) does not change substantially during the reaction. The relationship between [I] and conversion can be obtained by the substitution of eq. (8) into eq. (7) (which results in $[I]^{1/2} = [I]_0^{1/2}\left(1 + \frac{k_d\ln(1-x)}{2V_0}\right)$). Therefore, the substitution of this relationship and eq. (15) into eq. (20) and some manipulation results in eq. (21):

$$\frac{1}{(\overline{\text{DP}}_n)_i} = \frac{(2fk_dk_t)^{1/2}}{(1+a)k_p}\frac{[I]_0^{1/2}}{[M]_0}\frac{1 + \frac{k_d\ln(1-x)}{2V_0}}{(1-x)} + C_T\frac{R_0}{(1-x)}$$

(21)

The method for the calculation of $(\overline{\text{DP}}_n)_{\text{cum}}$ consists of a divided conversion of the reaction into several intervals i (where i is an integer number) equal to b (b is a constant), with the assumption that in each interval $(i - 1)b$ to ib, the reaction is isomolecular.[40] The $(\overline{\text{DP}}_n)_{\text{cum}}$ value is then given by the various $(\overline{\text{DP}}_n)_i$ values of each interval according to eq. (22):

$$\left(\overline{\text{DP}}_n\right)_{\text{cum}} = \frac{i}{\sum_0^i \frac{1}{(\overline{\text{DP}}_n)_i}}$$

(22)

According to eq. (21), the only problem for calculation of $(\overline{\text{DP}}_n)_i$ is the unknown value of f because, if it was known, the value of $k_p/k_t^{1/2}$ could be calculated from the known $k_p(f/k_t)^{1/2}$ value. $(\overline{\text{DP}}_n)_{\text{cum}}$ values as a function of x_{VAc} were calculated theoretically and then fitted with experimental values (Fig. 7). Best fitting between the theoretical and
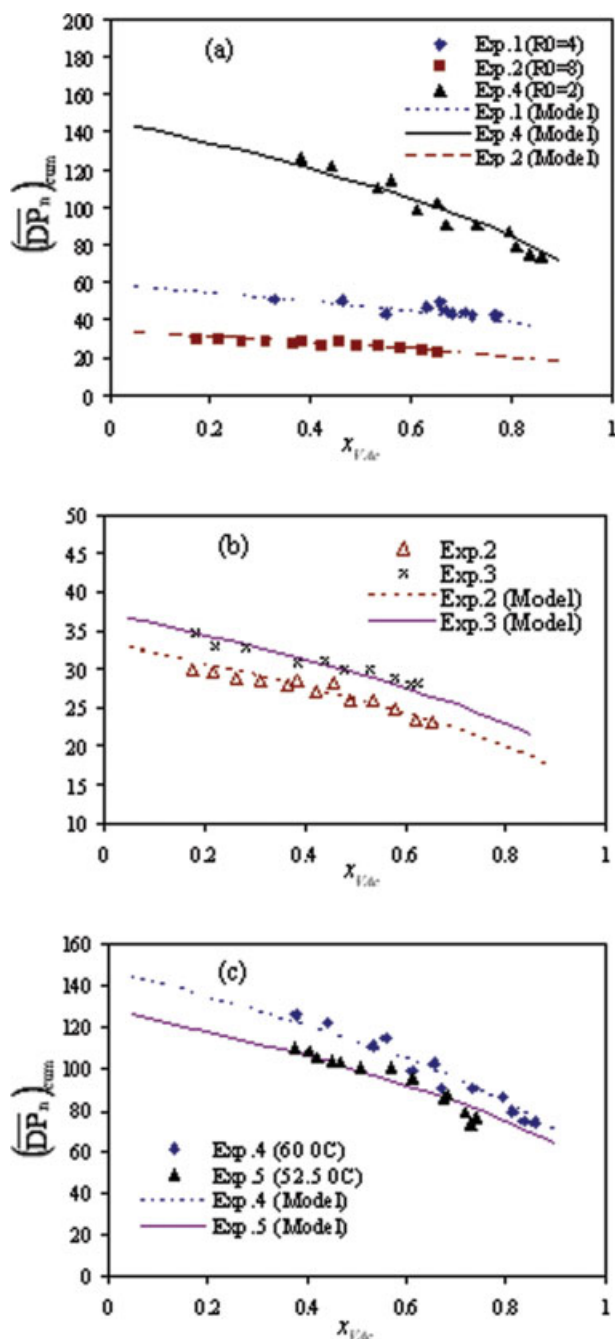
Figure 7 Theoretical (solid lines) and experimental (points) data of $(\overline{DP}_n)_{cum}$ versus x_{VAc} for the VAc telomerization with $CDCl_3$ under various reaction conditions: (a) R_0, (b) $[I]_0$, and (c) temperature (see Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

experimental values of $(\overline{DP}_n)_{cum}$ were observed when the variable f value was used for the various reaction conditions. The f values used in each experiment are given in Table III. It was observed in the previous study[22] that the bimolecular termination of macroradicals also occurred when $[I]_0$ and, thereby, the concentration of macroradicals were relatively

high (experiment 3, Table I). For this reason, the best fitting between the theoretical and experimental values of $(\overline{DP}_n)_{cum}$ for experiment 3 was obtained with a nonzero a value ($a = 0.5$; see Table III). For other experiments, $a = 0$ was used in the calculation of the theoretical $(\overline{DP}_n)_{cum}$.

It is clear from Table III that the f values were dependent only on the solvent concentration/[T]. The effect of $[I]_0$ and reaction temperature on the f value was considered to be negligible. The solvent concentration dependence of the f value of AIBN has been reported for the homopolymerization of MMA and AN in DMF at $60°C$.[41,42] This dependence has been interpreted on the basis of a model of initiator solvation by the monomer and solvent alone as well as by the mixed monomer/solvent.[29,31]

By using $k_p(f/k_t)^{1/2}$ and the corresponding f values for each experiment, we calculated $k_p/k_t^{1/2}$ (Table III). The results show that the ratio $k_p/k_t^{1/2}$ was strongly dependent on [T] (solvent concentration) and the reaction temperature. The effect of $[I]_0$ on the $k_p/k_t^{1/2}$ value was negligible. An increase in the $k_p/k_t^{1/2}$ value with temperature suggested that the temperature dependence of k_p was more than that of k_t, which was reasonable. As mentioned before, constant C_T values with a constant reaction temperature (Table II) suggested that the k_p values did not change with solvent concentration. As a result, variation in the $k_p/k_t^{1/2}$ value with solvent concentration were attributed to the effect of the solvent on the k_t value. Therefore, it is possible that the termination rate of the VAc telomerization was chain-length controlled, even at low concentrations/conversions. The effect of the solvent on the rate constants in the solution polymerization of VAc has been investigated,[33,34] and according to the results, the variation in the value of $k_p/k_t^{1/2}$ as a function of [M] was probably due to the solvent effect on k_t. This possibility has also been discussed, for example, for MMA[43–47] and BuA[32,34] homopolymerizations.

Diffusion theory,[48–51] the theory of radical charge-transfer complexes,[52–55] and the theory of hot radicals[56] are theories explaining the solvent effect on $k_p/k_t^{1/2}$. The solvent effect is attributed to a single elementary reaction by all three theories. Diffusion theory is concerned with the termination step, and the latter two theories are concerned with the propagation step.[35] In this study, a change in the $k_p/k_t^{1/2}$ value with solvent concentration was attributed to the solvent-dependent k_t. As a result, diffusion theory could be used to explain the solvent effect on $k_p/k_t^{1/2}$.

Diffusion theory relates the rate constant of termination to the initial viscosity of the polymerization system (η). The rate-determining step of termination is, accordingly, the segmental diffusion of chain ends,[49] which is inversely proportional to the

TABLE III
Results of the Estimation of Some Kinetic Parameters for the Telomerization of VAc with CDCl₃ in the Presence of AIBN Under Various Conditions

Experiment no.	[VAc]$_0$ (mol/L)	R_0	Temperature (°C)	a	f	$k_p/k_t^{1/2} \times 10^2$ [L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$; eq. (8)]	$k_{tr,CDCl_3}$ (L mol^{-1} s^{-1})	$k_t \times 10^{-9}$ (L mol^{-1} s^{-1})
1	2.42	4	60	0	0.50	14.83	16.46	4.07
2	1.36	8	60	0	0.65	8.25	16.56	13.15
3	1.36	8	60	0.5	0.65	7.58	15.61	15.58
4	3.95	2	60	0	0.25	25.33	16.93	1.39
5	3.95	2	52.5	0	0.30	13.40	17.42[a]	3.56[a]

[a] These values were calculated with $k_p = 7990$ L mol^{-1} s^{-1} at 52.5°C.[60]

microviscosity of the solution. These considerations implied a modification of eq. (6) as follows:[35,57]

$$R_p = -\frac{d[M]}{dt} = k_{ov}^0 [I]^{1/2}[M]$$

$$\text{where} \quad k_{ov}^0 = k_p \left(\frac{fk_d}{k_t^0}\right)^{1/2} \eta^{1/2} \quad (23)$$

where k(ov)(0) is the overall polymerization rate constant if the viscosity of the solution is unity and k_t^0 is the termination rate constant if the viscosity of the solution is unity. According to eq. (23), the overall rate constant of polymerization should be proportional to the square root of η.

A common way to express the overall rate constant of termination in terms of diffusion coefficients is via the following equation:[32,33,58]

$$k_t = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} k_t^{i,j} \phi_i^* \phi_j^* \quad \text{where} \quad k_t^{i,j}$$
$$= 2\pi\sigma p_{spin}(D_i + D_j)N_A \quad (24)$$

where "phi (subscript)j (superscript) star" is the concentration of radical of length j, D(subscript)j is the rate coefficient of a polymeric radical with chain length and N(subscript)A is the Avogadro's number, ϕ_i^* is the concentration of radicals of length i, D_i is the rate coefficient of a polymeric radical with chain length i, and p_{spin} and σ are the spin probability that forbids a certain fraction of radical–radical encounters and the capture radius of the termination reaction, respectively. From the C_{CDCl_3} values obtained here, it seemed unlikely that the k_p of VAc was significantly affected by the solvent concentration. Consequently, the variation in $k_p/k_t^{1/2}$ with [M] (or equivalent solvent concentration) was attributed to the dependence of k_t on [M] (or equivalent solvent concentration). This means that if the individual rate constants of the terminating macroradicals were a function of the diffusion rate constants, they were a function of chain length as well.[32,33] This, in turn, implies that the kinetic rate constant for termination was diffusion controlled, even in dilute solutions where the Tromsdorff effect played no role at all.[33]

The number-average degree of polymerization at zero reaction time [$(\overline{DP}_n)_i^0$] was calculated for all of

the experiments with eq. (21), and the various rate constants were calculated individually for all of the experiments in this study. Figure 8 shows the $(\overline{DP}_n)_i^0$ values of the PVAc samples versus [M]. It is clear from this figure that $\overline{DP}_n$ seemed to vary linearly with [M], which indicated that transfer to solvent/telogen (CDCl₃) was the dominant term in the development of the molecular weight [see eq. (21)]. However, $k_p/k_t^{1/2}$ also seemed to vary more or less linearly with [M]$_0$ as well.[32,33] $k_p/k_t^{1/2}$ as a function of the square root of $(\overline{DP}_n)_i^0$ and [M]$_0$ are shown in Figures 9 and 10, respectively. The relationship between $k_p/k_t^{1/2}$ and $(\overline{DP}_n)_i^0$ was almost linear over the range of values considered in this study. Similar results have been reported for the solution homopolymerization of BuA and VAc.[32,33] Moreover, the chain-length-dependent k_t of VAc was recently proven by the living free-radical polymerization (macromolecular design via the interchange of xanthates) of VAc at 80°C.[59] However, the chain length dependence of k_t was less pronounced in the VAc system than in the corresponding acrylate systems under identical conditions. The chain-length-dependent $k_p/k_t^{1/2}$ (or k_t actually) can be explained as follows.[32–34]

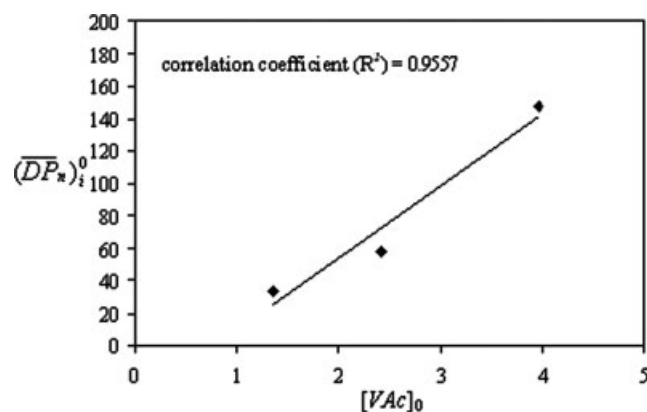If, as Russel[45] suggests, the real value of k_t for a macroradical is controlled by its center of mass

Figure 8 Dependence of $(\overline{DP}_n)_i^0$ on the initial VAc concentration in the VAc telomerizations performed with different concentrations of CDCl₃ (or equivalent VAc; see experiments 1, 2, and 4, Table I) at a constant temperature.

diffusion, longer chains should have a lower value of k_t than shorter chains. Therefore, conditions that favor the growth of long chains should have smaller values of k_t and, thus, higher values of $k_p/k_t^{1/2}$ than those reactions that favor shorter chain growth. If we accept this concept, it would, therefore, be reasonable to expect that in cases where there is a significant amount of chain transfer to small molecules (CDCl$_3$ in this study), transfer of (macro)radicals to solvent/telogen molecules would create significant populations of short, highly mobile radicals and, thus, lead to an increase in the overall value of k_t. This would explain not only the fact that the value of $k_p/k_t^{1/2}$ increased as [M]$_0$ increased (this was equivalent to a decrease in the amount of solvent/telogen and, thus, the fraction of short radicals in the solution) but also why the reactions slowed down at long times (Fig. 5). In the latter case, the ratio of monomer to solvent decreased as the monomer was consumed, which led to a situation similar to a change in [M]$_0$.

The k_p value of VAc homopolymerization has been reported frequently in the literature. However, a more accurate k_p value of VAc homopolymerization was measured with a pulsed laser polymerization technique ($k_p = 9460$ L mol^{-1} s^{-1} at 60°C).[60] $k_p/k_t^{1/2}$ and C_{CDCl_3} values calculated here along with the literature-reported k_p value[60] were used to estimate the k_t and $k_{tr,CDCl_3}$ values (Table III), respectively. Figures 9 and 10 show the $k_t^{1/2}$ as a function of $(\overline{DP}_n)_i^0$ and [VAc]$_0$, respectively. It is clear from these figures that $k_t^{1/2}$ values decreased with increasing [M] (this was equivalent to a decrease in the amount of solvent/telogen) and the square root of $\overline{DP}_n$, which was consistent with the previous explanation. The $k_{tr,CDCl_3}$ values remained constant not only with
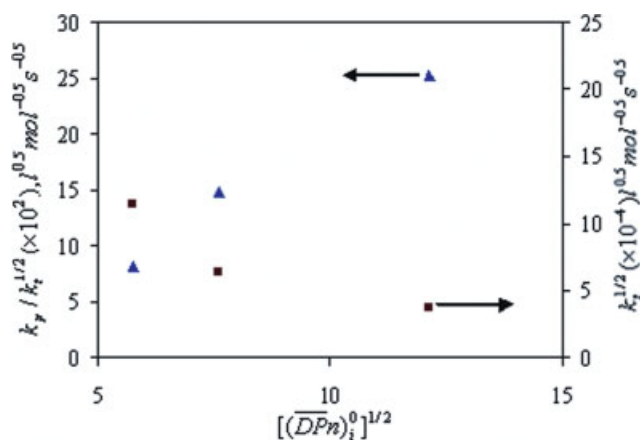

Figure 9 Variations of $k_p/k_t^{1/2}$ and $k_t^{1/2}$ as a function of the square root of $(\overline{DP}_n)_i^0$ for the VAc telomerizations performed with different concentrations of VAc (or equivalent CDCl$_3$; see experiments 1, 2, and 4, Table III) at a constant temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
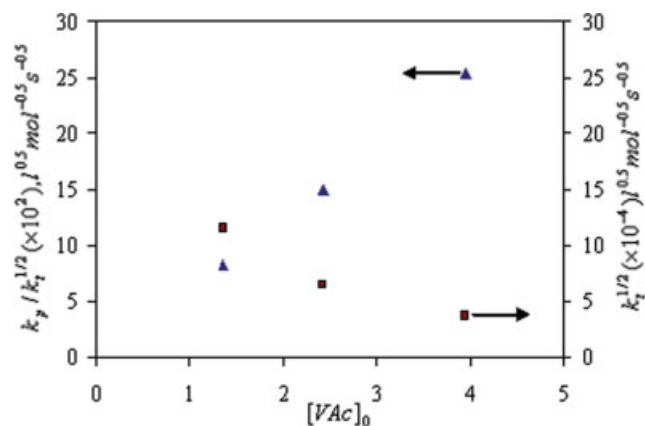

Figure 10 Dependence of $k_p/k_t^{1/2}$ and $k_t^{1/2}$ on [VAc]$_0$ (or equivalent CDCl$_3$ concentration) for the VAc telomerizations performed with different concentrations of VAc (or equivalent CDCl$_3$; see experiments 1, 2, and 4, Table III) at a constant temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the reaction mixture compositions (i.e., [M] and [I]) but also more or less with the reaction temperature.

CONCLUSIONS

Real-time ^{1}H-NMR spectroscopy was used to investigate the kinetics of the free-radical polymerization of VAc in the presence of CDCl$_3$ as a chain-transfer agent (telogen) and AIBN as an initiator. Analysis of the ^{1}H-NMR spectra recorded at the various time intervals for each experiment allowed us to calculate some kinetic parameters of the polymerization/telomerization reaction. The results show that k_d and $k_p(f/k_t)^{1/2}$ changed significantly with the solvent concentration and reaction temperature, whereas they remained almost constant with [I]. C_{CDCl_3} also changed only with the reaction temperature. By considering the constant C_{CDCl_3} values at a constant temperature, we concluded that solvent did not have any significant effect on the k_p value. The dependence of $k_p(f/k_t)^{1/2}$ values on the solvent concentration was attributed to the solvent effect on both the f and k_t values. We estimated f values individually by fitting the theoretical values of $(\overline{DP}_n)_{cum}$ with the experimental ones. k_t values were then calculated by the $k_p/k_t^{1/2}$ values obtained here along with the accurate k_p value reported in the literature. The effect of the solvent on the f and k_t values was explained by the initiator solvation with the monomer/solvent mixture and the chain-length-dependent termination rate constant, respectively.

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