



Structural and Mechanistic Studies of Telomerization of Vinyl Acetate by CDCl_3 via ^1H NMR

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ABSTRACT

Kinetics of radical telomerization of vinyl acetate (VAc) with CDCl_3 as a telogen in the presence of AIBN initiator was studied by ^1H NMR. Structure of the chains was analyzed in detail by ^1H NMR spectroscopy technique. It was observed that two telomers with different α -ends including trichloromethyl- and dichloromethyl-terminated VAc telomers were formed during the telomerization reaction. Therefore, two different mechanisms of the transfer reaction to CDCl_3 telogen have been proposed which were supported in details by the abstraction of either deuterium or chlorine radicals from CDCl_3 molecules. ^1H NMR analysis also allowed us to calculate the conversion of VAc (X_{VAc}), number-average degree of polymerization ($\overline{\text{DP}}_n$), telomer percentage (%), and the ratio of the abstractions of deuterium radicals to chlorine radicals ($R_{\text{D/Cl}}$) from CDCl_3 molecules. These results showed that at the same conversion, at first, $\overline{\text{DP}}_n$ decreases with increase of the initial concentration of AIBN but then increases. Also, $\overline{\text{DP}}_n$ at the same conversion decreases by increasing of the R_0 and decreasing of the reaction temperature. Moreover, at the same conversion, telomer percentage increased by decreasing $[\text{AIBN}]_0$ and reaction temperature while decreased by decreasing of the R_0 (or equivalently $[\text{CDCl}_3]$). The highest yield of telomer was about 60%. There was not any significant difference between the $R_{\text{D/Cl}}$ at various conditions used in VAc telomerization by CDCl_3 . ^1H NMR analysis showed that the rate of the abstraction of deuterium radical from CDCl_3 molecule is favoured relative to its rate of chlorine radical abstraction.

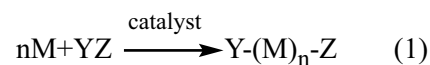
Key Words:

vinyl acetate;
free radical telomerization;
chloroform-d;
 ^1H NMR spectroscopy;
telomerization mechanism.

INTRODUCTION

In contrast to polymerization reactions, telomerization is a reaction that forms oligomers with low molecular weights. Telomerization is defined as the reaction between molecule YZ, called a telogen, with one or several molecules of a polymerizable compound M, called a taxogen, under the polymerization conditions. The product is called

telomer of the formula $\text{Y}(\text{M})_n\text{Z}$ (eqn 1) where n is the number of taxogen molecules incorporated into the reaction.



There are some main differences between telomerization and polymerization. Initially, in telomeriza

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tion, fragments of the initiator mainly induce the rupture of the telogen, whereas in polymerization, they add onto the monomer. Secondly, the number of M units (n) in the final compound obtained by telomerization is low ($n < 100$) though, it is not equal to 1 ($n \neq 1$). The groups formed at the chains' terminals in telomerization are significant because the molecular weights in telomers are always low.

Our interest in the polymerization of vinyl acetate (VAc) for years leads to the solution polymerization of VAc in the presence of an amine chelating compound in an amine mediated controlled reaction where a high yield of polymer with a low polydispersity was formed [1]. The microstructure of PVAc and poly(vinyl alcohol) has been studied with ^1H NMR and ^{13}C NMR [2-5]. We have already reported the increase in the conversion of VAc and a substantial reduction in the reaction time of polymerization with an amine chelating agent in acetic acid and ethyl acetate solutions [1]. This work was then extended in the polymerization of styrene and methyl methacrylate by adopting atom transfer radical polymerization (ATRP) [6,7] where copper(I) halide was added as active catalyst of diamines and its chelating complex with free radicals.

It was not until 2000 that the free-radical telomerization of VAc with CHCl_3 telogen and formation of low molecular weight VAc telomer was reported [8]. This is appeared following a review on telomerization kinetics and mechanism of redox reaction and the synthesis of monofunctional and difunctional (telechelic) telomers [9]. The use of telomer as a potential block incorporated into the diblock or triblock copolymers of styrene, methyl methacrylate, and methyl acrylate reached its importance after the discovery of ATRP and its use in macromolecular engineering. In 2000 vinyl acetate telomer as a macroinitiator was reported in the ATRP reactions and synthesis of block copolymers of VAc and styrene [8].

In 2003, the results on the synthesis of block copolymers by ATRP of methyl methacrylate and methyl acrylate by VAc telomer as a macroinitiator were reported [10,11]. Since the macromolecular architecture of the block copolymers is critical in the macromolecular design and engineering, we published our new results on the effect of molecular weight and its distribution of VAc macroinitiators on

the kinetics of acrylates incorporated into diblock copolymers [12]. The research on the microstructure of macroinitiator seemed exceedingly important in the first step of ATRP reaction. The presence of dormant species and persistent radicals in the first step of reaction and the complex formation with organic halides or trichloromethyl-terminated VAc telomers with CuCl -tetraamine complex required an intensive research. This led to the investigation of the specific effect of chain geometry, length, molecular weight and its distribution, conformation and chemical compositions of vinyl acetate, and the structural activities of telomers in formation of more specific block copolymers which is called "chemical selectivity" [12].

In 2006, Semsarzadeh et al. have reported the effect of molecular weight and its distribution of VAc telomers in the ATRP of methyl acrylate and methyl methacrylate [12]. It was shown that at low conversion, there are major differences in the compositions and tacticities of triblock copolymers of VAc with methyl acrylate and methyl methacrylate [13]. In another report the copolymer composition data obtained from ^1H NMR was used to calculate monomer reactivity ratios for the atom transfer radical copolymerization of methyl acrylate and methyl methacrylate in the presence of trichloromethyl-terminated PVAc macroinitiator [14].

In the present paper, the studies are continued on the macroinitiators of vinyl acetate by considering the instantaneous formation of trichloromethyl-terminated VAc telomers by real time ^1H NMR spectroscopy technique. The identification of structure of telomers formed during the telomerization of VAc with CDCl_3 as a telogen was also important in this research, where the active components involved in telomerization should be identified. To our knowledge, there is no report on the telomerization of VAc with chloroform-d (CDCl_3) as a telogen and using the obtained telomers as macroinitiator in ATRP. Moreover, a new mechanism of transfer reaction to CDCl_3 is given in the present study which is completely different from its transfer reactions to CHCl_3 and CCl_4 in the VAc telomerization.

Investigation of the kinetics and mechanisms involved in the formation of different telomers of VAc produced by CDCl_3 telogen can be of further assis-

tance in controlling the ATRP reactions. It also allows the proper selection of the tacticity needed for any particular macromolecular design and engineering of the diblock or triblock copolymers of styrene, methyl acrylate and methyl methacrylate. The free-radical telomerization study of VAc in CDCl_3 with real time ^1H NMR spectroscopy technique enables us to follow the course of this reaction, specifically and identify all the structures formed under different conditions. We believe that the sequential arrangements of active groups in VAc telomers in diblock or triblock copolymers may have a strong effect on the selectivity of monomers in the ATRP of methacrylates and styrene.

EXPERIMENTAL

Materials

Vinyl acetate (VAc, Merck-Schuchardt, > 99%) was distilled under nitrogen (99.99%) atmosphere. 2,2'-Azobisisobutyronitrile (AIBN, Fluka, $\geq 98\%$) and chloroform-d (CDCl_3 , ARMAR Chemicals, Switzerland, 99.95%) were used without further purification.

Sample Preparation

Solution samples with different $[\text{CDCl}_3]_0/[\text{VAc}]_0$ ratios as well as different AIBN concentrations were prepared (Table 1). First, initiator solution in CDCl_3 was prepared. The defined amount of this solution was then added to a given amount of monomer (VAc) thus samples with the desired concentrations were obtained. Total volume of each sample was adjusted to be about 1 mL. The final reaction mixture was then conducted in the NMR tube (5 mm in diameter). The solutions in the NMR tubes were degassed with nitro-

gen gas (99.99% purity) to exclude oxygen from the reaction mixture. It should be noted that during sample preparation and especially degassing by nitrogen, the reaction mixture was maintained in the ice/water mixture to prevent the evaporation of CDCl_3 (b.p. $\cong 60.9^\circ\text{C}$).

Kinetic Study of Telomerization by ^1H NMR

All ^1H NMR kinetic experiments reported in this study were carried out on a Bruker Avance 400 MHz NMR spectrometer. The sample cavity was equilibrated at a given temperature (i.e., a temperature at which the kinetic experiment was carried out) by a BVT 3000 (with precision of $\pm 0.1^\circ\text{C}$) temperature control unit. A typical ^1H NMR kinetic experiment consists of the following steps sequence.

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 using 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, as there was no conversion of VAc taken place because of the low rate of reaction.

RESULTS AND DISCUSSION

^1H NMR Analysis

^1H NMR technique has been used frequently for

Table 1. Recipes for telomerizations of VAc by CDCl_3 in presence of AIBN.

Experiments No.	$[\text{VAc}]_0/[\text{CDCl}_3]_0/[\text{AIBN}]_0^a$	$[\text{VAc}]_0$ (mol/L)	Temperature ($^\circ\text{C}$)
Exp.1	1/4/0.01	2.42	60
Exp.2	1/8/0.01	1.36	60
Exp.3	1/8/0.02	1.36	60
Exp.4	1/8/0.03	1.36	60
Exp.5	1/2/0.01	3.95	60
Exp.6	1/2/0.01	3.95	52.5
Exp.7	1/2/0.01	3.95	45

(a) Molar ratio of components in the initial reaction mixture.

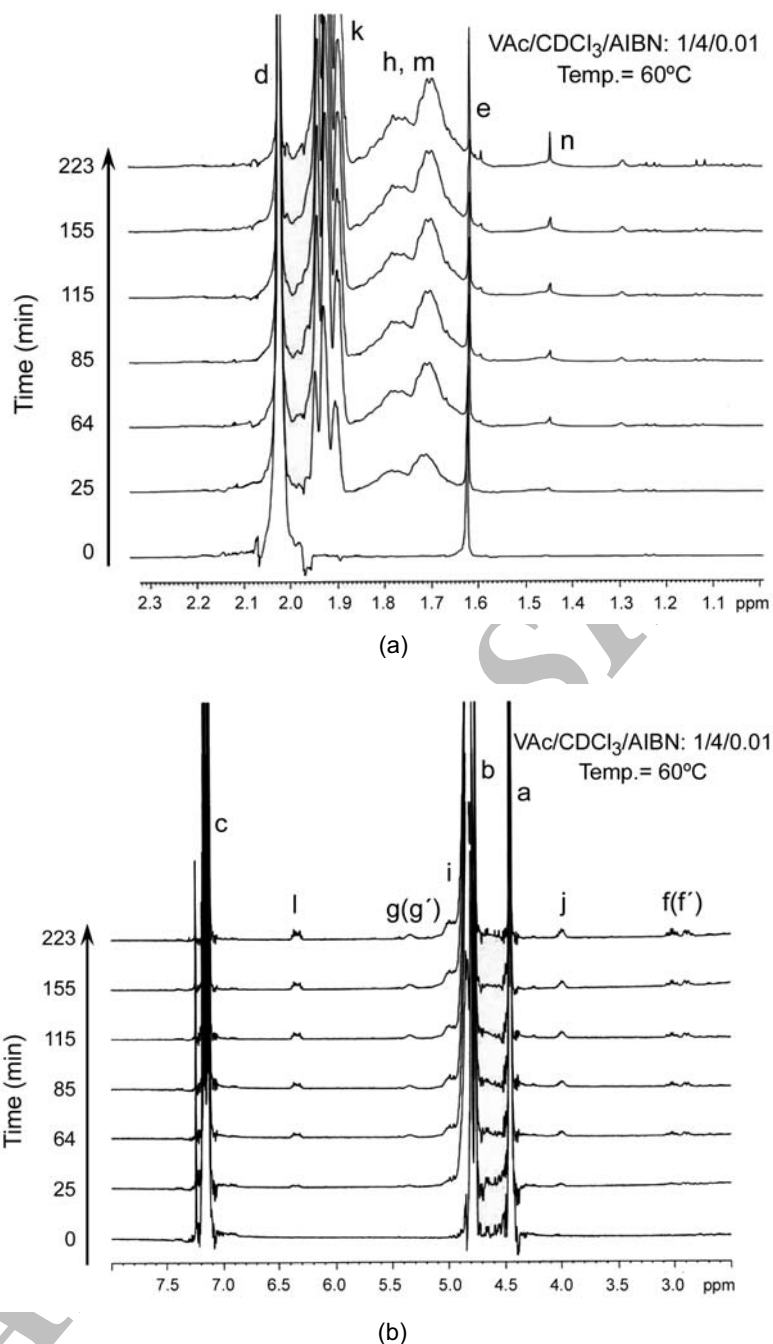


Figure 1. Progress of VAc telomerization as a function of reaction time in Exp.1 (Table 1) along with the assignments of protons signal (Scheme II and Table 2) in the chemical shift ranges of: (a) 1-2.3 ppm and (b) 2.5-8 ppm.

homo- and co-polymerization of various vinyl monomers in order to investigate the kinetics of polymerization reactions with respect to the overall polymerization rate coefficient and monomer reactivity ratios (in the case of copolymerization). In this work, the possibility of using ^1H NMR kinetic experiment for investigation of the radical telomerization of VAc by CDCl_3 as a telogen in the presence of AIBN initia-

tor is discussed.

First, the structure of the synthesized telomers (and polymers) was characterized by ^1H NMR spectroscopy technique. Then, some kinetic parameters were calculated by data obtained from ^1H NMR spectra of each sample at various time intervals, further to what we had suggested for the mechanism of transfer reaction to telogen.

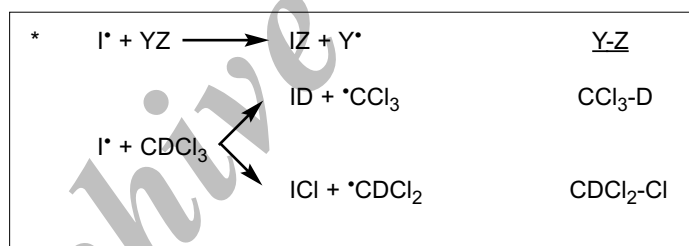
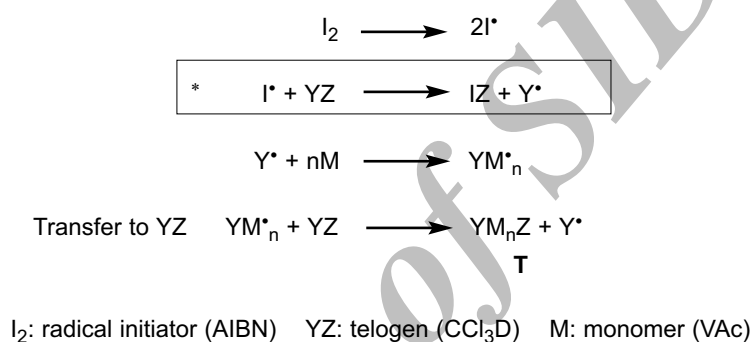
Typical ^1H NMR spectra were recorded for the reaction mixture containing the initial molar ratios of VAc/ CDCl_3 /AIBN equal to 1/4/0.01 (Experiment No. 1 in Table 1, reaction temperature = 60°C) which are shown in Figure 1 as a function of the reaction time. Signals assignments for the telomerization system were carried out by considering the off-line ^1H NMR spectra reported in the literature for VAc telomers synthesized by CHCl_3 [8,10] and CCl_4 [15] and were compared with the spectra recorded for VAc telomers obtained by CDCl_3 .

According to the signals observed during VAc

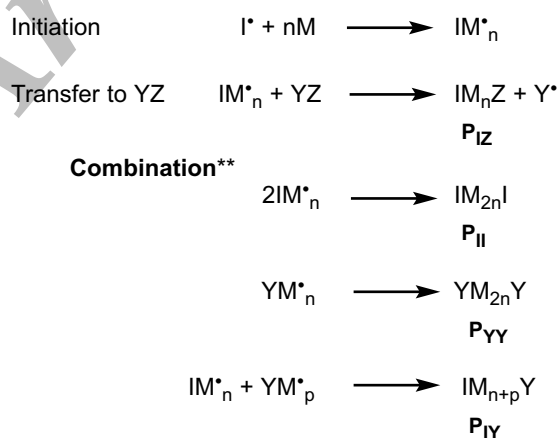
telomerization with CDCl_3 , the mechanism of the reaction was considered to be as Scheme I. In turn, this mechanism has resulted in various structures of telomers ($\text{Y}-(\text{M})_n-\text{Z}$) where, Y-Z can be $\text{CCl}_3\text{-D}$ or $\text{CDCl}_2\text{-Cl}$ and M is the VAc with n units incorporated into the telomers) and polymers (P: any other chain structure but not that of the telomers, P_{IZ} : polymer chains initiated by the radical initiator and terminated by transfer to the telogen).

In radical telomerization, the termination reactions can be considered to be negligible providing that the initial molar ratio of telogen to monomer (i.e.,

Telomerization (Idealized Pathway)

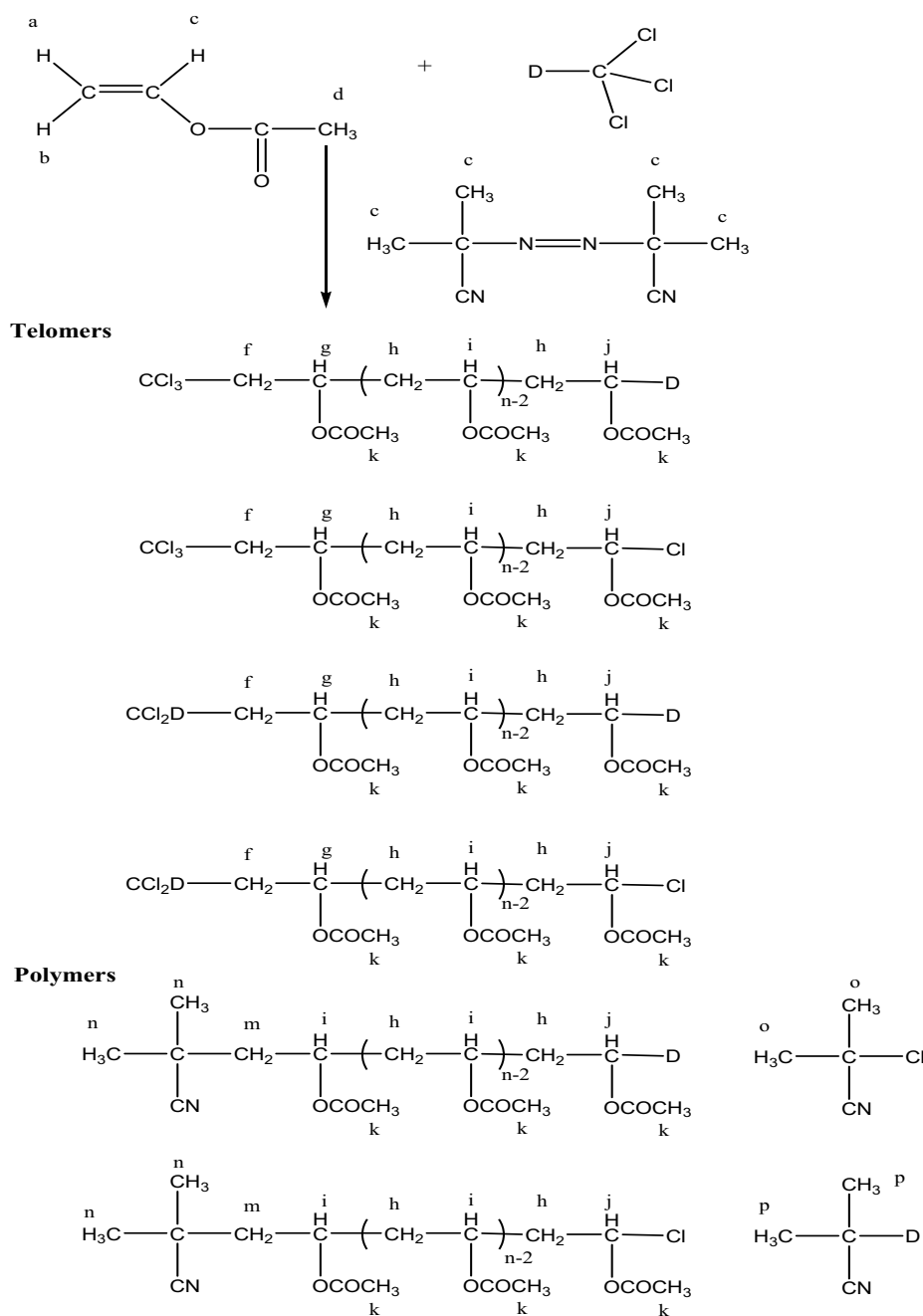


Polymerization



** Predominant mode of termination in VAc polymerization.

Scheme I



Scheme II

$R_0 = [\text{CCl}_4]_0 / [\text{VAc}]_0$ is high enough. As a result, only P_{IZ} -type polymer structure can be formed. At this time, it is possible to report that only six species can be formed during the VAc telomerization with CDCl_3 : four species are telomers with CCl_3 and CCl_2D α -end groups and others are polymers with P_{IZ} -type structure (P_{ID} and P_{ICl}) as shown in Scheme II.

Assignments of the entire characteristic signals of

all the structures described in Scheme II along with the chemical shifts of the corresponding protons are given in Table 2. In the structural analysis of telomers and polymers by ^1H NMR spectroscopy technique, one additional signal at 6.3-6.4 ppm was observed in comparison to those obtained by telomerization of VAc with CHCl_3 . No signal at the range 6.3-6.4 ppm has been reported for the products of VAc telomerization with CHCl_3 [8,10]. However, ^1H NMR spectra of

Table 2. Assignments and corresponding chemical shifts of the protons of unreacted VAc monomer and AIBN initiator, telomers, and polymers of the VAc telomerization by CDCl_3 in presence of AIBN initiator.

Protons	VAc monomer	AIBN initiator	CCl_3 terminated telomers	CDCl_2 terminated telomers	Polymers
a	4.5 (d.d.) ^a	-	-	-	-
b	4.8 (d.d.)	-	-	-	-
c	7.15 (d.d.)	-	-	-	-
d	2.0 (singlet)	-	-	-	-
e	-	1.62 (singlet)	-	2.8-3.2	-
f or f'	-	-	2.8-3.2	5.0-5.1	-
g or g'	-	-	5.3-5.4	1.5-2	-
h	-	-	1.5-2	4.7-5	1.5-2
i	-	-	4.7-5	3.9-4.1	4.7-5
j	-	-	3.9-4.1	1.8-1.9	3.9-4.1
k	-	-	1.8-1.9	6.3-6.4	1.8-1.9
l	-	-	6.3-6.4	-	6.3-6.4
m	-	-	-	-	1.8-1.9
n	-	-	-	-	1.45 (singlet)
o	-	-	-	-	2.0 (singlet)
p	-	-	-	-	1.3 (singlet)

(a) doublet of doublet

telomers and polymers synthesized in the present work (Figure 1) showed a signal at about 6.3-6.4 ppm. On the other hand, a similar signal has been observed for the telomers of VAc with two functional end groups (i.e., trichloromethyl and chlorine groups at the α - and ω -ends, respectively) synthesized by the redox telomerization of VAc by CCl_4 in the presence of $\text{Fe}(\text{OAc})_2/\text{PMDETA}$ [15].

It has been reported that the signal at about 6.35 ppm corresponds to the methine proton adjacent to terminal chlorine at the ω -end [15]. Therefore, it was concluded that telomerization of VAc by CDCl_3 is initiated by either deuterium or chlorine radicals abstractions from CDCl_3 as a result of chain transfer reaction. Hence, deuterium or chlorine atoms can be abstracted radically from CDCl_3 during the telomerization reaction. Therefore, transfer reaction between the initiator radical (I^\cdot) and telogen (CDCl_3) forms either the ID or the ICl inactive species as shown in Scheme II, leaving either $\cdot\text{CCl}_3$ or $\cdot\text{CDCl}_2$ radicals, respectively. The telogen radicals can then initiate telomerization of VAc. Chains can propagate up to a certain $\overline{\text{DP}}_n$ depending on the transfer constant to telogen (C_T) and $[\text{CDCl}_3]_0/[\text{VAc}]_0$ ratio.

Finally, the obtained macro-radicals with certain $\overline{\text{DP}}_n$ terminate by transfer to the telogen via abstraction of either the deuterium or the chlorine from CDCl_3 . Consequently, four telomer chains with different α - and ω -ends (Scheme II) can be formed during the telomerization reaction. Moreover, as initiator radicals (I^\cdot) can also initiate the polymerization of VAc, two polymer chains with different ω -ends may be formed by transfer to the telogen as shown in Scheme II. When the $[\text{CDCl}_3]_0/[\text{VAc}]_0$ ratio is high enough and the initiator concentration is relatively low, then the bimolecular termination of macro-radicals will be negligible.

The analysis of ^1H NMR spectra has confirmed the formation of all above mentioned six species during the telomerization of VAc with CDCl_3 . It should be noted that signals of methylene protons in the neighbours of $\cdot\text{CCl}_3$ (f) and $\cdot\text{CDCl}_2$ (f') have appeared at 2.8-3.2 ppm [8,10] while, those in the neighbours of initiator fragment (m) have appeared at 1.8-1.9 ppm [16]. Signals appeared at 3.9-4.1 ppm and 6.3-6.4 ppm correspond to the methine protons adjacent to the D (j) and Cl (l) atoms at the ω -end, respectively [16]. Protons of the $(\text{CH}^\circ_3)_2(\text{CN})\text{C}-\text{Cl}$ and $(\text{CHP}_3)_2(\text{CN})\text{C}-\text{D}$

molecules which are formed by the transfer reaction between the initiator radical and telogen (Schemes I and II) are appeared at about 2.0 (overlapped with the other high intensive signals) and 1.3 ppm, respectively.

Now, by having the complete assignment of the entire signals (Scheme II and Table 2) it is possible to calculate the kinetic parameters such as the molar conversion of VAc (X_{VAc}), number-average degree of polymerization (\overline{DP}_n), fraction of CCl_3 or $CDCl_2$ terminated chains (telomer percentage) and the ratio of the abstractions of deuterium radical to chlorine radical from $CDCl_3$ ($R_{D/Cl}$, or equivalently the ratio of chains with deuterium ω -ends to those with chlorine ω -ends) by the following eqns (2)-(5).

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

$$\overline{DP}_n = \frac{I_{4.7-5.0} - I_{4.5} + I_{3.9-4.1} + I_{5.2-5.4} + I_{6.3-6.4}}{I_{3.9-4.1} + I_{6.3-6.4}} \quad (3)$$

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

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

Where, I_j indicates the intensity of proton(s) signal appeared at chemical shift of j th.

1H NMR spectra recorded for Exp. 1 (Table 1) as a function of the reaction time are shown in Figure 1. It can be found that by progress of the reaction, intensities of the signals related to the protons of VAc monomers incorporated into the telomer and polymer chains are increasing. Thus, the progress of reaction can be followed as a function of time. It is also clear from Figure 1 that the intensities of the proton signals of VAc units incorporated into the chains at two α - and ω -ends are very low at the initial stage of reaction (typically conversions below 20%). Therefore, it is impossible to calculate \overline{DP}_n , telomer percentage and $R_{D/Cl}$ at the conversions below 20%.

By increasing the conversion of VAc, the intensities of the above-mentioned signals become significant and thus the above parameters can be calculated as functions of the reaction time according to eqns (2)-(4). Table 3 shows the summary of data calculated from the 1H NMR kinetic experiments.

Table 3. Summary of data obtained from the 1H NMR kinetic experiments for VAc telomerization with $CDCl_3$ in presence of AIBN initiator.

Experiments No.	\overline{DP}_n (X_{VAc})	Telomer percentage (X_{VAc})	$R_{D/Cl}$ ^a
Exp.1	43.7 (0.55)	56.8 (0.46)	0.86
	44.3 (0.77)	55.1 (0.77)	
Exp.2 ^b	30.8 (0.23)	47.1 (0.23)	0.88
	26.8 (0.27)	45.5 (0.27)	
Exp.3	29.4 (0.17)	39.4 (0.38)	0.75
	25.2 (0.65)	38.5 (0.62)	
Exp.4	32.7 (0.22)	38.7 (0.42)	0.79
	31.1 (0.60)	39.7 (0.58)	
Exp.5	110.8 (0.53)	38.5 (0.67)	0.79
	90.4 (0.73)	36.4 (0.86)	
Exp.6	117.6 (0.40)	50.8 (0.40)	0.86
	87.7 (0.68)	44.7 (0.72)	
Exp.7 ^c	-	-	-

(^a) This value was obtained at the final conversion for each experiment. (^b) Due to the low rate of telomerization, only two data for \overline{DP}_n and telomer percentage could be obtained for Exp.2. For other Experiments, more data obtained; however, only two data are given in Table 3. (^c) Conversion in Exp.7 was not high enough to calculate \overline{DP}_n , etc.

Table 4. Conversion rate (dx/dt) and polymerization rate (R_p) data obtained for VAc telomerization by CDCl_3 at the various reaction conditions.

Experiments No.	$[\text{VAc}]_0$ (mol/L)	Temperature ($^{\circ}\text{C}$)	dx/dt (min^{-1})	$R_p \times 10^4$ (mol/L.s)
Exp.1	2.42	60	0.0133	5.40
Exp.2	1.36	60	0.00156	0.35
Exp.3	1.36	60	0.00504	1.10
Exp.4	1.36	60	0.00757	1.70
Exp.5	3.95	60	0.0198	13.0
Exp.6	3.95	52.5	0.00709	4.70
Exp.7	3.95	45	0.00144	0.95

Effects of R_0 , $[\text{AIBN}]_0$, and Reaction Temperature on X_{VAc}

Figures 2-4 show the dependence of X_{VAc} versus time data on the R_0 ($[\text{CDCl}_3]_0/[\text{VAc}]_0$ ratio), initiator concentration, and reaction temperature, respectively. The rate of classical radical polymerization which can also be used for the radical telomerization is expressed by the Tobolsky's equation [17] (eqn 6).

$$R_p = -\frac{d[\text{M}]}{dt} = [\text{M}]_0 \frac{dx}{dt} = k_p[\text{R}^*][\text{M}] = k_{\text{ov}}[\text{I}]^{\frac{1}{2}}[\text{M}] \quad (6)$$

$$k_{\text{ov}} = k_p \left(\frac{fk_d}{k_t} \right)^{\frac{1}{2}} \quad (7)$$

Where, R_p , x , k_d , k_{ov} , f , $[\text{M}]_0$, $[\text{R}^*]$, $[\text{I}]$, $[\text{M}]$, k_p , and k_t are polymerization rate, molar conversion of monomer, decomposition rate constant for initiator, overall polymerization rate constant, initiator efficiency, initial concentration of monomer, free-radical

concentration, initiator concentration, monomer concentration, propagation average rate constant, and termination average rate constant at the any time, respectively.

The effect of $[\text{CDCl}_3]_0/[\text{VAc}]_0$ ratios on X_{VAc} versus time has been given in Figure 2. It is clear that by decreasing the R_0 or equally, by increasing the monomer concentration, the conversion rate (dx/dt which was obtained from the slope of the linear part of conversion-time graphs) is increased. Thereby, R_p (which is calculated by multiplying the conversion rate by the initial monomer concentration as in eqn (6)) increased as well (Table 4). This is reasonable as the propagation of macro-radicals (living chains) accelerates by increasing the monomer concentration.

Figure 3 indicates the dependence of X_{VAc} on the initial concentration of initiator (AIBN). Based on eqn (6), it is expected, that the conversion rate and therefore polymerization rate increase with the initial

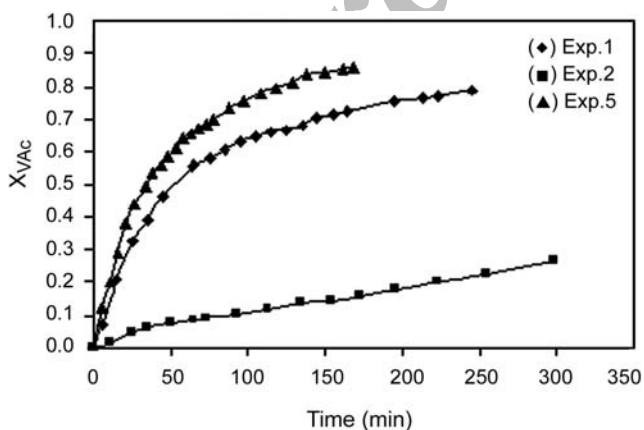


Figure 2. Effect of R_0 on X_{VAc} vs. time for the VAc telomerization by CDCl_3 in the presence of AIBN.

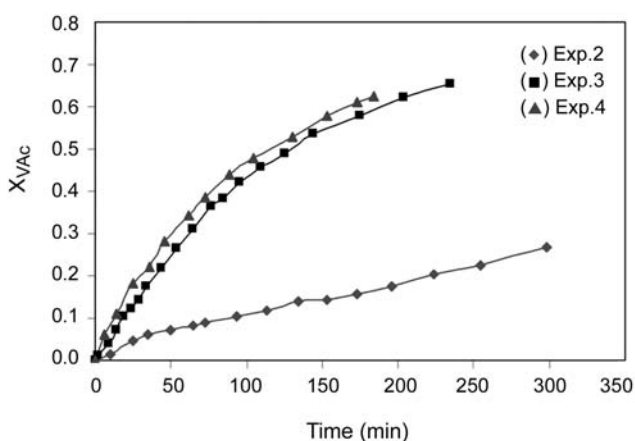


Figure 3. Effect of AIBN concentration on the X_{VAc} vs. time for the VAc telomerization by CDCl_3 in the presence of AIBN.

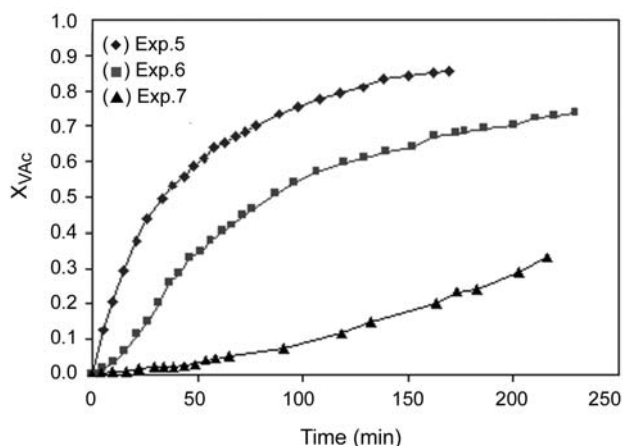


Figure 4. Effect of the reaction temperature on the X_{VAc} vs. time for the VAc telomerization by $CDCl_3$ in the presence of AIBN.

AIBN concentration (Table 4). Increasing the initial concentration of AIBN increases the concentration of free-radicals at constant temperature which in turn increases the propagation reactions. Also, the inhibition time decreases by increasing initial AIBN and VAc concentrations.

Figure 4 shows the dependence of X_{VAc} on the reaction temperature. It is clear from Figure 4 and Table 4 that conversion rate and therefore polymerization rate increase by raising the reaction temperature. If we consider the Arrhenius equation for the overall polymerization rate constant (k_{ov}), based on eqn (7) then, according to eqn (6) the dependence of R_p on temperature is known and raising the reaction temperature would also increase the value of k_{ov} which in turn accelerates the polymerization rate. Moreover, the inhibition time decreases by raising the reaction temperature because the rate of initiator decomposition increases by temperature elevation.

Effects of the R_0 , $[AIBN]_0$ and Reaction Temperature on \overline{DP}_n

Formula established by Mayo [18] for radical polymerization can be used for the radical telomerization as well. Hence, when we consider only transfer to the solvent (telogen in our case) which is the most important step in the radical telomerization, the instantaneous degree of polymerization, $(\overline{DP}_n)_i$ as in eqn (8), will be dependent on the concentrations of monomer ($[M]$), telogen ($[T]$), and initiator ($[I]$) and the

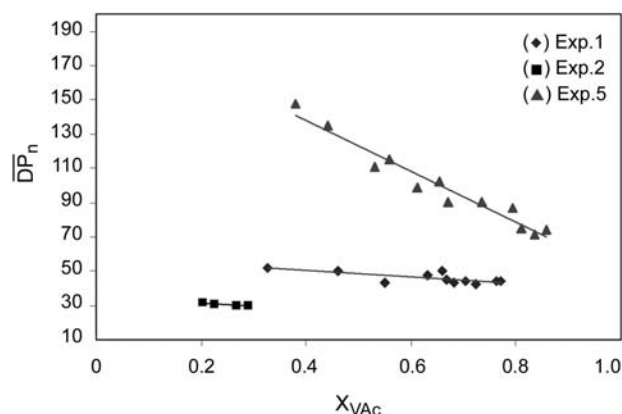


Figure 5. Effect of R_0 on the \overline{DP}_n vs. time for the VAc telomerization by $CDCl_3$ in presence of AIBN.

appropriate rate constants.

$$\frac{1}{(\overline{DP}_n)_i} = \frac{1}{1-x} \left(\frac{(2fk_d k_t)^{1/2} [I]^{1/2}}{k_p [M]_0} + C_T \frac{[T]_0}{[M]_0} \right) \quad (8)$$

and

$$C_T = \frac{k_{tr}}{k_p} \quad (9)$$

in which C_T is the transfer constant to telogen and k_{tr} is the rate constant of transfer to telogen.

Figure 5 shows the dependence of \overline{DP}_n versus X_{VAc} values. It is clear from Figure 5 that at the same conversion, the cumulative number-average degree of polymerization (\overline{DP}_n) decreases by increasing in the R_0 . This can be attributed to the inverse relationship between the R_0 and $(\overline{DP}_n)_i$. It should be noted that \overline{DP}_n can be calculated from $(\overline{DP}_n)_i$ data by the following equation [19].

$$\overline{DP}_n = \frac{i}{\sum_{j=0}^{i-1} \frac{1}{(\overline{DP}_n)_j}} \quad (10)$$

Eqn 10 consists of the divided conversion of a reaction into several intervals i (i : integer number) equal to b (b is a constant number). The \overline{DP}_n values are given by several $(\overline{DP}_n)_i$ of each interval. \overline{DP}_n values decrease with the progress of reaction as shown in Figure 5. It is reasonable because the concentration of monomer decreases with the progress of reaction and thereby, \overline{DP}_n decreases according to eqn (11) (since $[M] = (1-x) [M]_0$ and concentration of telogen does

not change significantly with conversion. Therefore, eqn (8) can be expressed as eqn (11).

$$\frac{1}{(\overline{DP}_n)_i} = \frac{(2fk_d k_t)^{1/2} [I]^{1/2}}{k_p [M]} + C_T \frac{[T]}{[M]} \quad (11)$$

The effect of the initial AIBN concentration on \overline{DP}_n values as a function of X_{VAc} has been shown in Figure 6. According to eqn (8) it is expected that \overline{DP}_n decreases by an increase in AIBN concentration. The expected trend was observed when the $[AIBN]_0/[VAc]_0$ ratio increased from 0.01 in Exp. 2 to 0.02 in Exp. 3 (Table 1 and Figure 6). However, by further increasing the $[AIBN]_0/[VAc]_0$ ratio to 0.03 (Exp. 4) \overline{DP}_n value increases slightly. This increase in \overline{DP}_n value may be attributed to the occurrence of termination reaction by combination in high concentration of initiator. There are no termination reactions in the ideal telomerization reactions and the living chains terminate by the transfer reaction to telogen.

However, when the concentration of initiator and thereby the concentration of macro-radical increases, bimolecular termination of macro-radicals may happen in addition to the transfer reaction to telogen. As the dominant mode of bimolecular termination of macroradicals in the VAc polymerization has been reported to be the combination of macro-radicals [20] hence, the increase of the \overline{DP}_n value with further increase in AIBN concentration in the telomerization reactions are explained by the occurrence of the termination reactions in addition to the transfer reactions to telogen.

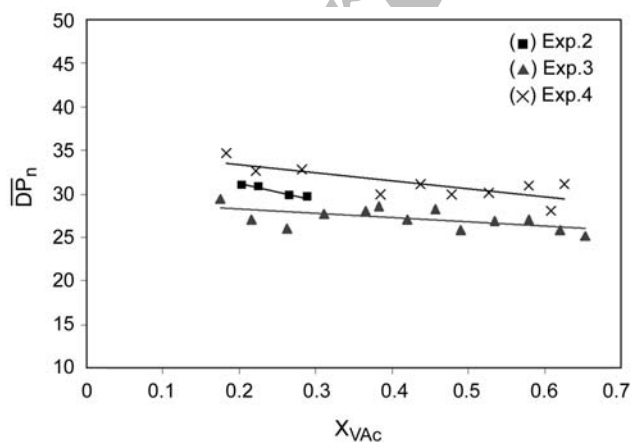


Figure 6. Effect of AIBN concentration on \overline{DP}_n vs. time for VAc telomerization by $CDCl_3$ in presence of AIBN.

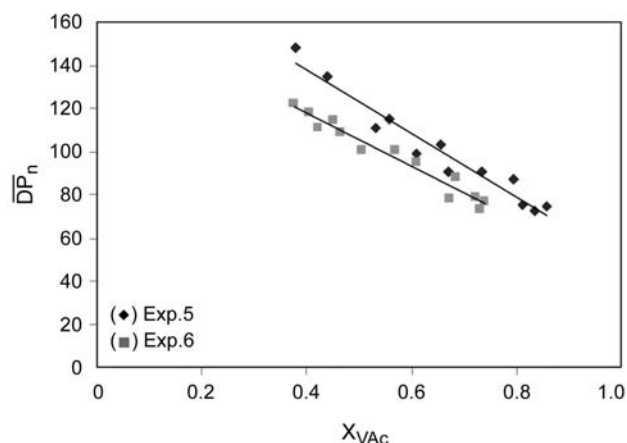


Figure 7. Effect of reaction temperature on \overline{DP}_n vs. time for VAc telomerization by $CDCl_3$ in presence of AIBN.

Figure 7 shows the effect of reaction temperature on \overline{DP}_n versus X_{VAc} . There is not any significant difference among values of \overline{DP}_n observed at various reaction temperatures. However, \overline{DP}_n values decreased slightly with decreasing the temperature. Based on eqn (8), the dependence of \overline{DP}_n on the reaction temperature may be attributed to the dependence of k_p on temperature. When k_p increases with temperature \overline{DP}_n increases accordingly. It should be noted that the \overline{DP}_n decreases with the increase in conversion (Figure 7) due to the reduction of monomer concentration (eqn 8).

Effects of the R_0 , $[AIBN]_0$, and Reaction Temperature on Telomer Percentage

The dependence of telomer percentage versus time on the R_0 has been shown in Figure 8. It is clear from this

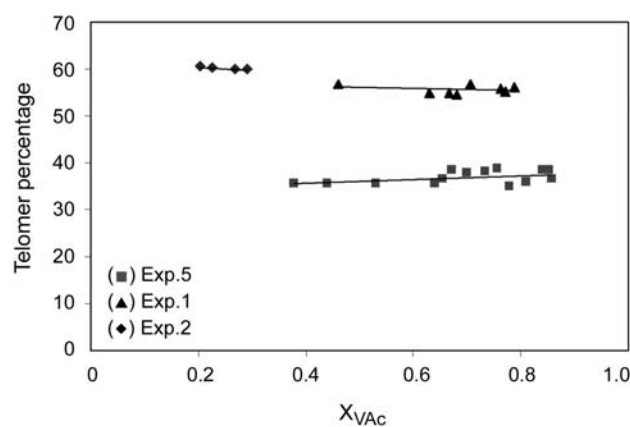


Figure 8. Effect of R_0 on telomer percentage vs. time for VAc telomerization with $CDCl_3$ in presence of AIBN.

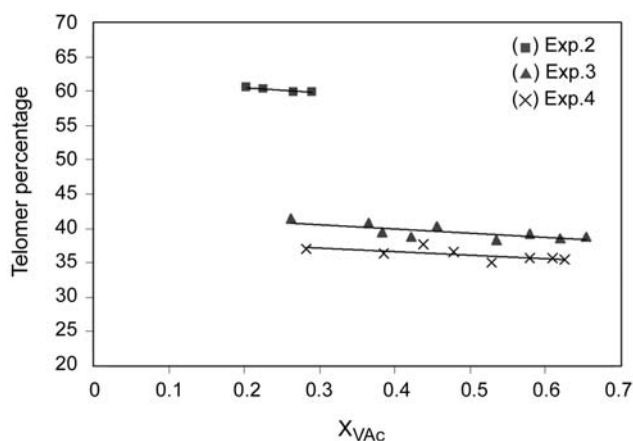


Figure 9. Effect of AIBN concentration on telomer percentage vs. time for VAc telomerization by CDCl_3 in the presence of AIBN.

figure that at the same conversion, telomer percentage increases with the increase of R_0 . It is reasonable because portion of the termination of initiator radicals by transfer to telogen increases telogen concentration (or equally R_0) in comparison with the propagation of initiator radicals by monomer. Therefore, telogen radicals obtained from the transfer reaction initiate most of the chains. As a result, the ratio of the chains initiated by telogen radicals to the chains initiated by the initiator radicals (telomer percentage) increases with the increase of R_0 .

Figure 9 shows the effect of initial AIBN concentration on the telomer percentage versus X_{VAc} . It is clear from this figure that the higher initial concentration of AIBN results in lower telomer percentage. Transfer reaction between the macro-radical and telogen results in the dead end chain (telomer or polymer) and a telogen radical (CCl_3 or CDCl_2 radical). Then, telogen radical can initiate a new telomer chain. On the other hand, bimolecular termination of macro-radicals (which exists in the case of higher initiator concentration) results in the dead end chains without generation of telogen radicals. As a result, telogen radicals and thereby growing telomer chains decrease by increasing the initiator concentration due to the termination of macro-radicals. However, the main reason for decrease in telomer percentage by increasing AIBN concentration is the increased concentration of initiator radicals which in turn increases the portion of the chains initiated by the initiator radicals.

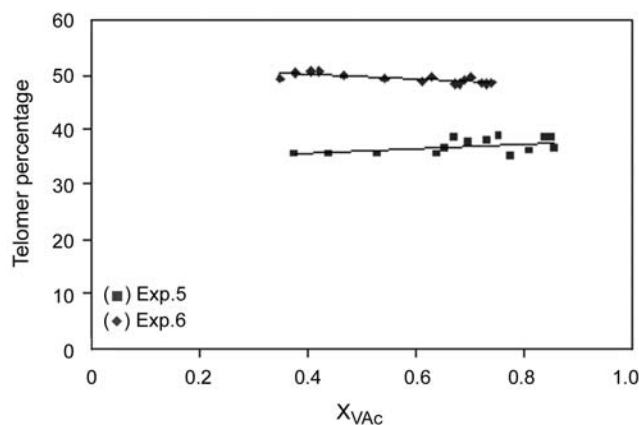


Figure 10. Effect of reaction temperature on telomer percentage for VAc telomerization by CDCl_3 in the presence of AIBN.

At the same conversion, telomer percentage decreases by raising the temperature (Figure 10). Raising the temperature increases the concentration of initiator radicals which in turn increases the portion of chains initiated by the initiator radicals.

Effects of the R_0 , $[\text{AIBN}]_0$ and Reaction Temperature on $R_{\text{D/C1}}$

Effect of various variables on the $R_{\text{D/C1}}$ has been given in Table 2. It should be noted that the values of $R_{\text{D/C1}}$ reported in Table 2 are those obtained at the final conversion of each experiments. However, $R_{\text{D/C1}}$ values at the various time intervals were observed to be almost constant. There is no significant difference between the $R_{\text{D/C1}}$ values obtained at the various conditions of VAc telomerization reaction by CDCl_3 . $R_{\text{D/C1}}$ value for all experiments was obtained to be close to 0.8. In other words, it means that the ratio of (both telomer and polymer) the chains with the deuterium ω -end to the chains with the chlorine ω -end is close to 0.8. Moreover, as the ratio of deuterium atom to the chlorine atoms in CDCl_3 is 1/3, the value of 0.8 for $R_{\text{D/C1}}$ means that the abstraction of deuterium radical from CDCl_3 is almost 2.4 (0.8×3) times greater than the abstraction of its chlorine radical.

This can be explained by considering the stability of resulting radicals from two different mechanisms of transfer reaction to telogen, i.e., abstractions of either deuterium radical or chlorine radical from CDCl_3 . While the former would produce $\cdot\text{CCl}_3$ radicals the latter results in $\cdot\text{CDCl}_2$ ones. It is obvious that $\cdot\text{CCl}_3$

radicals are more stable than $\cdot\text{CDCl}_2$ radicals due to the radical delocalization among the three large chlorine atoms. Consequently, the abstraction of deuterium radical from CDCl_3 which results in more stable $\cdot\text{CCl}_3$ radical is more favorable than the other abstraction reaction.

CONCLUSION

^1H NMR kinetic experiments were used to investigate the radical telomerization of VAc with CDCl_3 as a telogen in the presence of AIBN initiator. Effects of R_0 ($[\text{CDCl}_3]_0/[\text{VAc}]_0$), $[\text{AIBN}]_0$, and reaction temperature were studied. Analysis of the ^1H NMR spectra allowed us to calculate X_{VAc} , $\overline{\text{DP}}_n$, telomer percentage, and $R_{\text{D/Cl}}$. Moreover, it was observed that there are two different mechanisms for the transfer reaction to telogen (CDCl_3), i.e., abstraction of either of deuterium or chlorine radicals from CDCl_3 . As a result, two telomers with different α -ends, i.e., trichloromethyl- or dichloromethyl-terminated VAc telomers were obtained. Both telomers are expected to be efficient macroinitiators in the ATRP of various monomers such as styrene(s) and (meth)acrylates.

The results showed that with the same conversion, X_{VAc} is increased with the increase of $[\text{AIBN}]_0$, reaction temperature, and monomer concentration (or equally with decreasing of telogen concentration). It was observed that, at the same conversion, by increasing the initiator concentration, $\overline{\text{DP}}_n$ decreases first and then increases with further increase in the initiator concentration. Also, $\overline{\text{DP}}_n$ at the same conversion, increases with the increase of monomer concentration and reaction temperature.

The effect of various variables on the telomer percentage was investigated and it was observed that at the same conversion, it increases by increasing the R_0 and decreasing the $[\text{AIBN}]_0$ and temperature. High telomer percentage is preferred when the synthesized telomers are used as a macroinitiator in the ATRP. The highest telomer percentage obtained in this study was about 60%. No significant difference between $R_{\text{D/Cl}}$ at various conditions of VAc telomerization by CDCl_3 was observed. Results indicated that the deuterium radical abstraction from CDCl_3 is more favourable than the chlorine radical abstraction.

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