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Monte Carlo simulation of free radical telomerization

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Abstract

Free radical telomerization is studied by Monte Carlo method. In telomerization, generalized rate constants for growing radical chain do not reflect accurately because chains less than five monomer units are important for kinetic treatment. Monte Carlo simulation method is applied for characterizing the telomerization such as validity of kinetic constants depending on the size of chain length and chain length distribution according to the ratio of chain transfer agent to monomer. The effect of various chain transfer agents to the chain length distribution is evaluated. The effect of differentiation of chain transfer constant as a function of chain length is studied by comparing the average chain length and broadness of chain length distributions of resulting telomers which C_∞ is used as chain transfer constant.

Keywords: Free radical telomerization; Kinetics; Monte Carlo simulation

1. Introduction

Telomerization is free radical polymerization in the presence of a chain transfer agent to produce low average molecular weight products called oligomers. In 1948, Hanford and Joyce [1] defined telomerization as the process of reacting between a molecule YZ called a telogen (chain transfer agent) with more than one of a polymerizable species M having ethylenic unsaturation called a texogen (monomer) under polymerization conditions. Resulting products, telomers, have the formula Y–(–M–)$_n$–Z, where n is the number of repeating units of monomer, which is any integer greater than one, Y and Z is the fragments of chain transfer agent). Since telomer has a molecular weight of less than 10 units of monomer, the products can be classified as intermediate between organic monomeric and polymeric compounds.

In 1974, Starks [2] reviewed the important aspects of free radical telomerizations. He discussed the general features of telomerization, reactivities and kinetics according to the different chain transfer agents and monomers.

Telomer has two important characteristics for application. One is the low molecular weight which other polymerization processes cannot easily access, the other is the α,ω-difunctionality which can be controlled by fragments of the chain transfer agent. Telomers have been applied for many areas such as modifiers of polyamide and other textiles [3], antiwear agents in lubricant application [4], additives for flexible rubber article [5], protective coatings and laminating application [6], water repellent [7], surfactants for inks for printing [8], amphiphilic telomers for coating application [9], and fuel additives for improving cold flow [10].

In telomerization, generalized rate constants for growing radical chain do not reflect accurately because chains less than five monomer units are important for kinetic treatment. Mayo [11] explained that chain transfer constants were increased approximately 20-fold from the monostyryl to the tetrastyryl radical and not changed radicals containing more than four monomer units in the polymerization of styrene in the presence of carbon tetrachloride as chain transfer agent. Smirnov [12] confirmed that the chain transfer constants change in the sequence: $C_5 \geq C_4 > C_3 > C_2$ (C_5 is chain transfer constant at chain length five, etc) from the analysis of the relative concentrations of each oligomer in the chain transfer catalysis product.

Robb and coworkers [13] have investigated extensively simplified approaches to avoid the complexities of the full treatment of telomerization. In the study of the photochemical telomerization of styrene with bromotrichloromethane, they derived generalized rate equation by assigning average apparent chain transfer constant, chain growth and termination constants from the steady-state assumption.

Walling [14] has expressed the telomer distributions from the rate of chain transfer relative to chain propagation. He

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Table 1
The rate constants used in the simulation. (k_p values are calculated from $k_{pn} = C_n/k_{xn}$. Units of s^{-1} for k_d and units of l/(mol s) for all other rate constants)

Rate constant	Value
k_d	9.0×10^{-5}
k_a	105
k_{p1}	615
k_{p2}	34
k_{p3}	8.7
k_{p4}	3.3
k_{p5} and higher	0.7
$k_{x1} = k_{x2} = k_{x3} \ldots$	320
$k_{td} = k_{tc}$	1.8×10^8

generalized the distribution by using chain transfer constants of different chain lengths and the ratio of chain transfer agent to monomer in the initial feed. In his expression he ignored the termination of telomer radicals and assumed that the concentration of monomer and chain transfer agent remain essentially constant over the telomerization.

Using the simulation technique with telomerization, Tsuchida and Minashi [15] analyzed the telomerization of styrene–carbon tetrachloride system by numerical method. They solved the rates of components reactions expressed by the simultaneous differential equations. They evaluated the chain transfer constants according to different chain length by examining the kinetics of oligomerization. From their studies, simulation technique is the way to calculate a number of reaction characteristics rapidly, some of which are experimentally very difficult to obtain, for example, expected rates of monomer, telogen, and initiator consumption, rate of formation for each individual telomer, the telomer distribution at different stages of reaction.

Monte Carlo simulations have been used to investigate the kinetics and molecular weight distribution during polymerization. This method is the master equation approach in which a chemical reaction can be considered as a stochastic process defined by a master equation. Gillespie [16] has developed a numerical method, which simulates the stochastic evolution of any given chemical system in time by setting up the master equation. The concentrations of each species of the chemical process are estimated as expectation values of the stochastic process.

Recently, stochastic method is applied to simulate the chain length distribution in the free radical polymerization [17,18]. They concluded that the Monte Carlo method is useful tool for characterizing the behavior of free radical polymerization.

In this article, Monte Carlo simulation method is applied for characterizing the free radical telomerization such as validity of kinetic constants depending on the size of chain length and chain length distribution according to the ratio of chain transfer agent to monomer. The effect of various chain transfer agents to the chain length distribution also is studied. Finally the effect of differentiation of chain transfer constant as a function of chain length is studied by comparing the average chain length and broadness of chain length distributions of resulting telomers which C_∞ is used as chain transfer constant.

2. Simulation technique

The basic theory for the stochastic approach to reaction kinetics is described elsewhere [19]. Stochastic approach provides a theoretical basis for the use of differential equations to model complex reaction systems. In this study, telomerization of styrene in bromotrichloromethane is used as a model for studying the validity of kinetic constants depending on the size of chain length. Telomerization of ethylene with various chain transfer agents is evaluated for studying the effect of chain transfer constant to the chain length distribution and the effect of differentiation of chain transfer constant as a function of chain length.

Telomerization of vinyl monomer in bromotrichloromethane, as example, by chain transfer mechanisms can be divided into the component reactions. Representing the monomer by M, the scheme is as follows [13]:

- *Initiation*:

$$\mathrm{CCl_3Br(Y\text{–}Z)} \xrightarrow{h\nu} \mathrm{CCl_3 \cdot (Y\cdot) + Br \cdot (Z\cdot)} \qquad k_d \tag{1}$$

- *Propagation*

$$\mathrm{Y\cdot + M \rightarrow YM_1\cdot} \qquad k_a \tag{2}$$

$$\mathrm{YM_1\cdot + M \rightarrow YM_2\cdot} \qquad k_{p1} \tag{3}$$

$$\mathrm{YM_2\cdot + M \rightarrow YM_3\cdot} \qquad k_{p2} \tag{4}$$

$$\mathrm{YM_3\cdot + M \rightarrow YM_4\cdot} \qquad k_{p3} \tag{5}$$

$$\mathrm{YM_4\cdot + M \rightarrow YM_5\cdot} \qquad k_{p4} \tag{6}$$

$$\vdots$$

$$\mathrm{YM_{\mathit{n}-1}\cdot + M \rightarrow YM_n\cdot} \qquad k_{pn} \tag{7}$$

- *Chain transfer*

$$\mathrm{YM_1\cdot + YZ \rightarrow YM_1Z + Y\cdot} \qquad k_{x1} \tag{8}$$

$$\mathrm{YM_2\cdot + YZ \rightarrow YM_2Z + Y\cdot} \qquad k_{x2} \tag{9}$$

$$\mathrm{YM_3\cdot + YZ \rightarrow YM_3Z + Y\cdot} \qquad k_{x3} \tag{10}$$

$$\mathrm{YM_4\cdot + YZ \rightarrow YM_4Z + Y\cdot} \qquad k_{x4} \tag{11}$$

$$\mathrm{YM_5\cdot + YZ \rightarrow YM_5Z + Y\cdot} \qquad k_{x5} \tag{12}$$

$$\vdots$$

$$\mathrm{YM_n\cdot + YZ \rightarrow YM_nZ + Y\cdot} \qquad k_{xn} \tag{13}$$

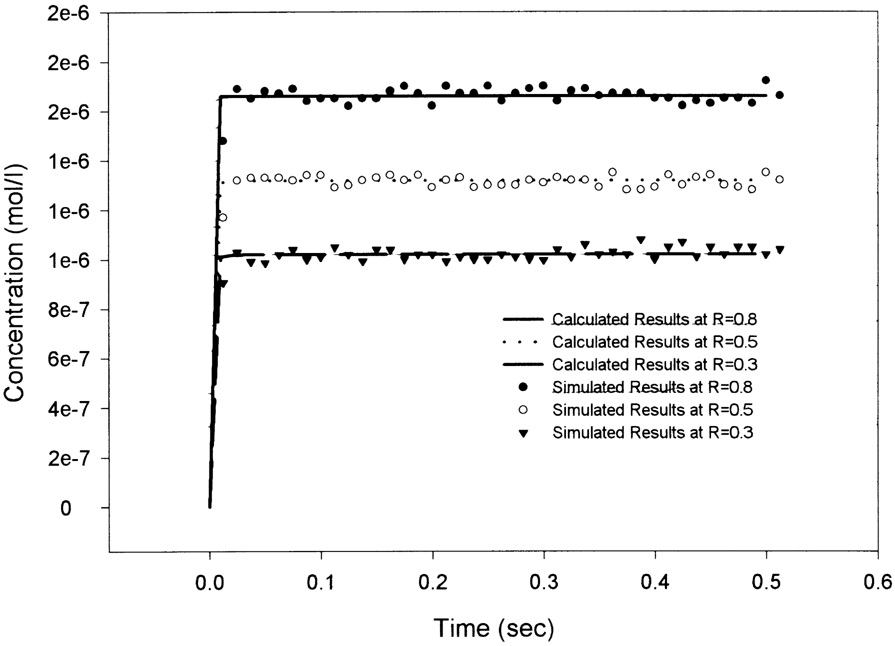

Fig. 1. Time dependent concentration of propagating radical as a function of ratio of chain transfer agent to monomer at initial feed (R = [YZ]/[M], the values of [YZ] used in this simulation are 3, 5 and 8 mol/l when the value of R are 0.3, 0.5, and 0.8, respectively, solid lines are calculated according to Eq. (25). Symbols are simulated results).

- *Termination*

$$YM_n\cdot + YM_m \rightarrow YM_{n+m}Y \qquad k_{tc} \tag{14}$$

$$Y\cdot + YM_n\cdot \rightarrow YM_nY \qquad k_{td} \tag{15}$$

In this simulation, for the chain transfer constants for different chain lengths of propagating radicals the readers are referred to Robb's study [13]. The rate constants for the simulation are listed in Table 1.

In this simulation, propagation rate constants are estimated as a function of chain length from the value of chain transfer constants. Gridnev and Ittel [19] mentioned that the values of propagation rate constants decreases as chain length increases at low degrees of polymerization but remains constant after reaching certain length of the chain. They showed that the propagation rate constants for the primary monomer radicals are approximately 20 times greater than those for polymeric radicals.

For the Monte Carlo simulation, deterministic rate constants, k^{de}, which measured by experiment should be changed to stochastic one, k^{st}, according to the following relations:

$$k^{st} = k^{de} \qquad (\textit{for first order reactions}) \tag{16}$$

$$k^{st} = \frac{k^{de}}{VN_A} \qquad (\textit{for second order reactions}) \tag{17}$$

where N_A is the Avogadro constant and V is the total volume of the system range from 10^{-13}–10^{-15} in this simulation.

For calculating the stochastic time evolution of a chemically reacting system, two random numbers, τ and μ, must be generated. Time interval for reaction τ be calculated from the random number r_1 from the uniform distribution in the unit interval:

$$\tau = (1/a_0)\ln(1/r_1) \tag{18}$$

a_0 is the sum of rates of reactions, $a_0 = \sum_{\mu=1}^{M} a_\mu$, where a_μ is the rate of the μth reaction, M is the number of kinds of reaction.

The certain kind of reaction μ during time interval τ can be determined from the random number r_2 by uniform distribution in the unit interval by following relations:

$$\sum_{\nu=1}^{\mu-1} a_\nu < r_1 \cdot a_0 \le \sum_{\nu=1}^{\mu} a_\nu \tag{19}$$

where μ is the number of the possible kinds of reaction and a_ν is the rate of reaction ν.

In this simulation the rate of the reactions are as follows:

$$a_1 = k_d^{st}[YZ] \tag{20}$$

$$a_2 = k_a^{st}[Y\cdot][M] \tag{21}$$

$$a_{i+2} = k_{pi}^{st}[YM_i\cdot][M] \qquad (i = 1–5) \tag{22}$$

$$a_8 = k_x^{st}[YM\cdot][YZ] \tag{23}$$

$$a_9 = k_t^{st}[YM\cdot][YM\cdot] \tag{24}$$

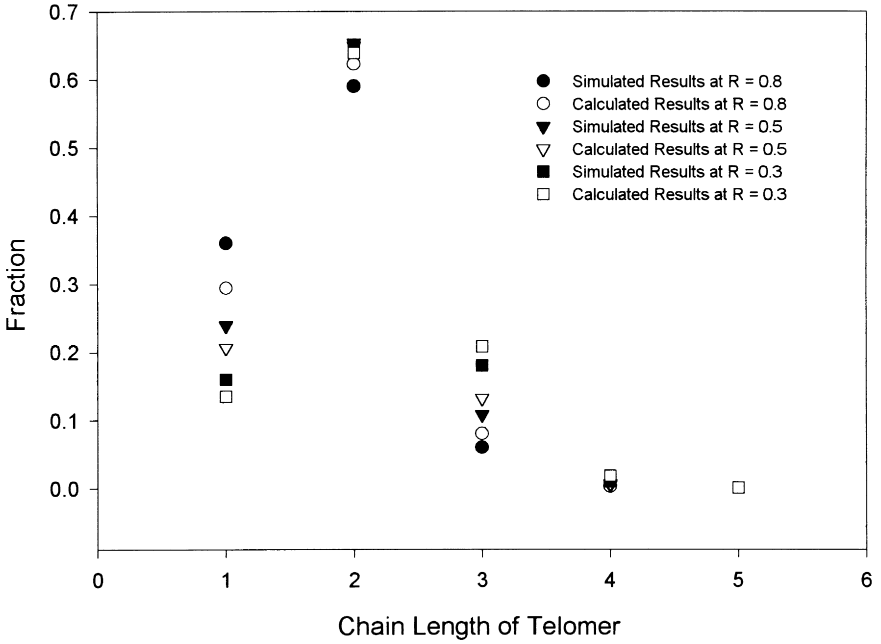

Fig. 2. Chain length distribution as a function of ratio of chain transfer agent to monomer (terminated by disproportionation, solid lines are calculated according to Eq. (26), symbols are simulated results).

From the stochastic values transferred from the deterministic values, we can simulate by following algorithm:

Initialization: input the values for reaction rate constants, initial number of monomer, ratio of chain transfer agent to monomer.
Step 1: calculate stochastic value of rate constants from the deterministic rate constants.
Step 2: calculate and store the quantities of the rate of reactions a_1, a_2, …, a_9 for the current molecular populations.
Step 3: calculate and store as a_0 the sum of the M a_μ values.
Step 4: generate two independent random numbers r_1 and r_2 uniformly between 0 and 1, and calculate τ and μ according to Eqs. (18) and (19).
Step 5: advance t by $\tau t = t + \tau$ by using the τ and μ values obtained in step 4.
Step 7: adjust the molecular population levels to reflect the occurrence of reactions:

7.1. initiation (Eq. (1)): decrease [YZ] by 1 and increase [Y·] by 1;
7.2. propagation (Eq. (2)): decrease [Y·] and [M] by 1, increase $[YM_1\cdot]$ by 1
7.3. propagation (Eqs. 3–7): decrease $[YM_i\cdot]$ and [M] by 1, increase $[YM_{i+1}\cdot]$ by 1 ($i = 1$–n);
7.4. chain transfer (Eqs. 8–13): decrease $[YM_i\cdot]$ and [YZ] by 1, increase $[YM_iZ]$ and [Y·] by 1 ($i = 1$–n);
7.5. termination (Eqs. (14) and (15)): if combination decrease $[YM_n\cdot]$ and $[YM_m\cdot]$ by 1, increase $[YM_{n+m}Y]$ by 1, if disproportionation decrease [Y·] and $[YM_n\cdot]$ by 1, increase $[YM_nY]$ by 1.

Step 8: recalculate the quantities a_ν corresponding to reactions, increase the reaction counter by 1 and return to step 2.

3. Results and discussion

The time-dependent concentration of propagating radicals during the polymerization can be calculated by following equations:

$$[R\cdot] = \sqrt{\frac{k_d \cdot [YZ]_0}{k_t}} \tanh(2\sqrt{k_d \cdot k_t \cdot [YZ]_0 \cdot t}) \tag{25}$$

Fig. 1 illustrates the comparison between the simulated results and calculated results by Eq. (25) for several ratio of concentration of chain transfer agent to monomer. As shown in this figure, simulated results have good agreement with calculated results. All the curves in Fig. 1 show that the steady-state can be reached within a few seconds. It is considered that the assumption of steady-state works well for the theoretical study of radical polymerizations.

Walling [14] has derived an expression relating the fraction of telomer with different units of monomer as a function of the ratio of chain transfer agent to monomer in the initial feed.

General equation of the mole fraction of *n*th telomer is

$$F_n = \frac{C_n R}{\prod_1^n (1 + C_i R)} \tag{26}$$

Here C_n represents the ratio of rate constant kx_n/kp_n, which is a constant characteristic of the reaction system, n

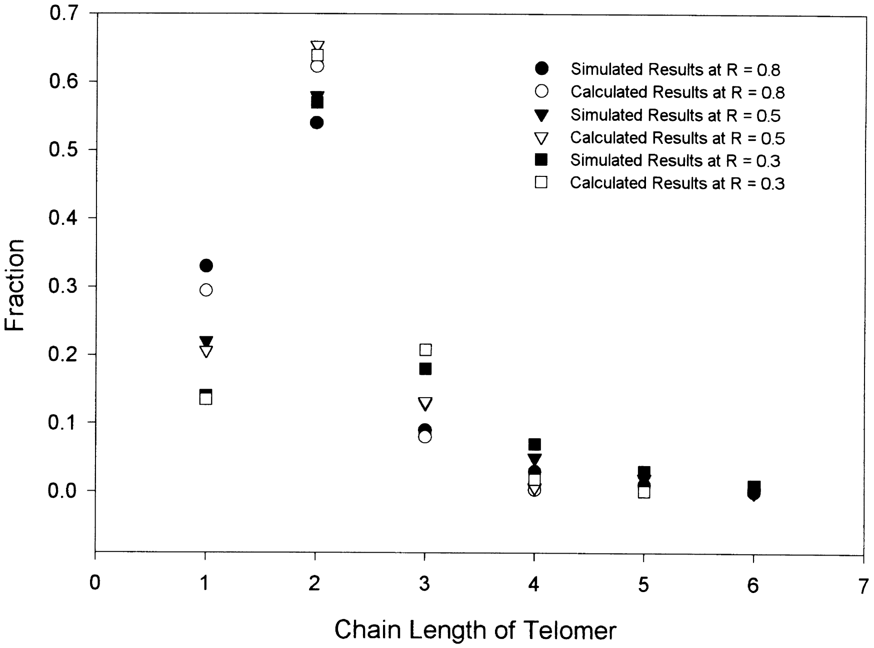

Fig. 3. Chain length distribution as a function of ratio of chain transfer agent to monomer (terminated by combination, solid lines are calculated according to Eq. (26), symbols are simulated results).

is the number of repeating units of monomer. The ratio of chain transfer agent to monomer, [YZ]/[M], represented by R for simplification; is an experimentally controllable variable and has appreciable effect on product distributions.

The results of the simulation are shown in Figs. 2 and 3 which are simulated results based on the terminations by disproportionation and combination, respectively. As shown in Fig. 2, the calculated results of the chain length distribution from Eq. (26) are in quite good agreement with results simulated by assuming disproportionation termination.

But in Fig. 3, simulated results show a little deviation at high chain length because Walling's equation does not consider the combination termination.

In telomerization, termination by combination may not be

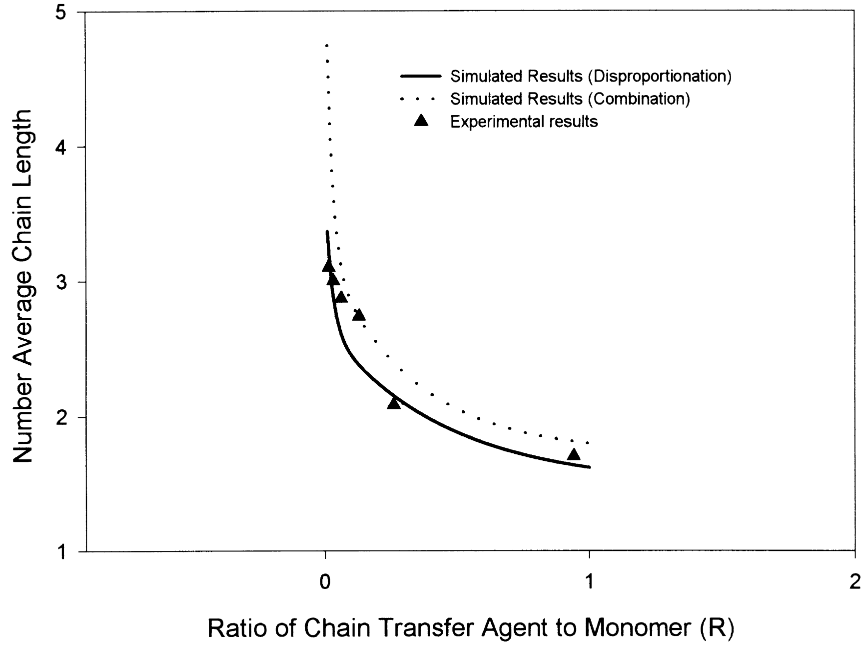

Fig. 4. Comparison between the simulated results of number average chain length and experimental results of telomerization of styrene with bromotrichloromethane as a function of chain transfer agent to monomer. (solid lines are simulated results based on the terminations by disproportionation and combination).

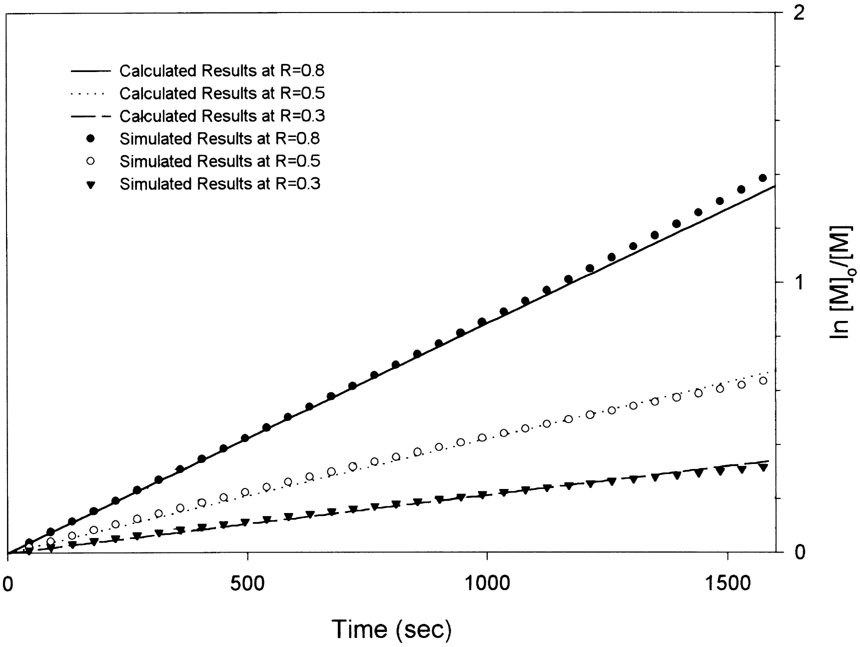

Fig. 5. Comparison between simulated results of time dependent monomer consumption and calculated results according to Eq. (27) (solid lines are calculated results, symbols are simulated results).

predominant due to the high reactivity of propagating radical and chain transfer agent.

Fig. 4 shows the comparison between the simulated results of number average chain length and experimental results [13] of telomerization of styrene with bromotrichloromethane as a function of the ratio of chain transfer agent to monomer.

As shown in Fig. 4, the simulated results of the number average chain length are in quite good agreement with experimental results. The experimental results show that the number average chain length increases from 1.6 to 3.4 as the ratio of chain transfer agent to monomer decreases from 1 to 0.01.

Time-dependent monomer consumption during the polymerization can be calculated by following equations:

$$\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]} = k_\mathrm{p}\sqrt{\frac{k_\mathrm{d}[\mathrm{YZ}]_0}{k_\mathrm{t}}}\,t \tag{27}$$

The comparison between simulated results of time dependent monomer consumption and calculated results according to Eq. (27) is shown in Fig. 5.

As shown in the figure, simulated results fit well to the equation. As mole ratio of chain transfer agent to monomer decreases, monomer consumption decreases sharply.

Starks [2] mentioned when the end group Y of the growing radical, $\mathrm{Y{-}({-}CH_2CH_2)_n}\cdot$, is a polar group then chain transfer constants increase as n increases toward the limiting value. The electronic nature of Y may affect the chain transfer transition state either through space (field effect) or through carbon–carbon σ bonds (inductive effect) or both. If variation of C_n with n is due to field effects between the telomer radical end group,Y, and chain transfer agent, YZ, the C_n can be expressed by following equation [2]:

$$\log(C_n) = \frac{-\alpha}{(2n+1)^2} + \log(C_\infty) \tag{28}$$

where α is a proportionality constant determined by temperature, dielectric constant, and other structural parameter and n is the number of repeating units of monomer. Plots of $\log(C_n)$ vs. $1/(2n+1)^2$ should give straight lines with slope of $-\alpha$ and intercept of $\log(C_\infty)$.

The chain transfer constants of several halo compounds

Table 2
Chain transfer constants of several halo compounds as a function of chain length for the telomerization of ethylene and slope of α calculated from Eq. (28)

Chain transfer agent	C_1	C_2	C_3	C_4	C_5	C_∞	α [a]
$\mathrm{CCl_4}$	0.10	3.0	7.0	10.3	13.3	13	−45.7
$\mathrm{CHCl_2Br}$	7.0	48.5	81.3	87.0	87.0	87.0	−26.2
$\mathrm{CHCl_3}$	0.247	1.55	2.49	3.12	3.84	4.1	−25.8
$\mathrm{CH_2Cl_2}$	0.0067	0.032	0.052	0.052	0.052	0.052	−22.4
$\mathrm{CH_3CH_2I}$	13.6	14.3	14.8	14.8	14.8	14.8	−0.8

[a] Calculation of α refers to Ref. [2].

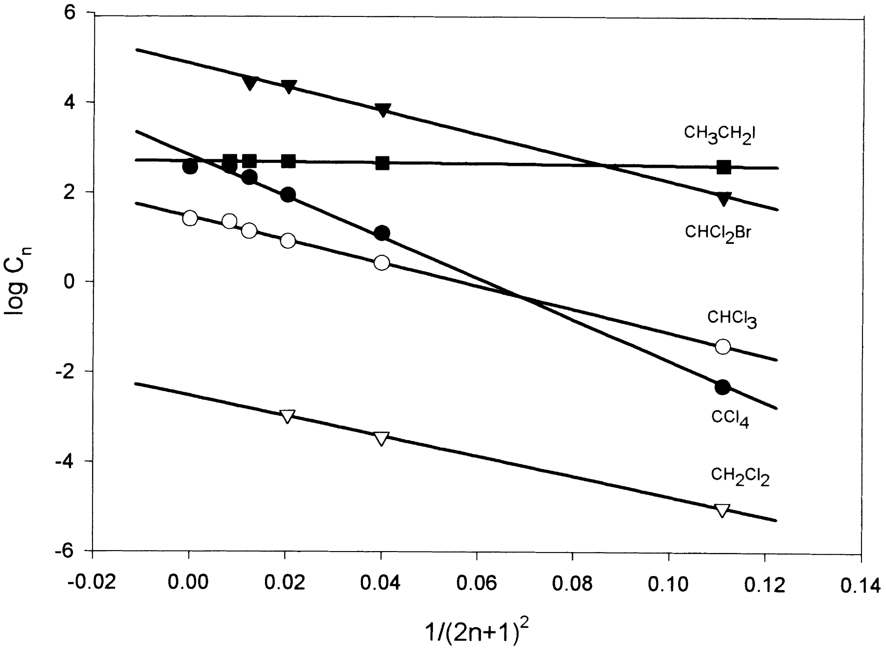

Fig. 6. Straight line relationship of various halo compounds as a function of chain length for the telomerization of ethylene.

as a function of chain length for the telomerization of ethylene and slope of α are listed in Table 2.

As shown in Table 2 absolute value of slope, α, depends on the polarity of Y group. As polarity of Y group increases the absolute value of slope increases.

Fig. 6 shows the straight-line relationship between $\log(C_n)$ and $1/(2n + 1)^2$. For CH_3CH_2I, which Y is an ethyl group, the absolute value of α is small which means that chain transfer constants are approximately equal at all values of n.

The chain length distributions of various chain transfer agents as a function of ratio of chain transfer agent to monomer are tabulated in Table 3. As shown in Table 3, average number and weight chain length are mainly determined by the value of C_1. Broadness of distributions (PI) is mainly affected by the value of α. Comparing the results of CCl_4 and $CHCl_3$ which have approximately equal values of C_1 but have different values of α, average chain length is approximately equal but the PI values are different. As absolute value of α decreases, the broadness increases. As expected, CH_2Cl_2 having the lowest value of C_1 shows the highest value of average chain length.

Table 3
Chain length distributions of various chain transfer agent as a function of ratio R

		CCl_4	$CHCl_2Br$	$CHCl_3$	CH_2Cl_2	CH_3CH_2I
0.8	X_n	2.19	1.14	2.27	5.57	1.08
	X_w	2.37	1.25	2.67	5.78	1.15
	PI	1.08	1.10	1.17	1.04	1.07
0.5	X_n	2.35	1.20	2.57	5.71	1.12
	X_w	2.57	1.34	3.04	5.85	1.24
	PI	1.09	1.12	1.18	1.02	1.11
0.3	X_n	2.56	1.29	2.96	5.80	1.19
	X_w	2.83	1.47	3.52	5.90	1.37
	PI	1.10	1.14	1.19	1.02	1.16

Fig. 7 shows the chain length distribution of chain length distribution as a function of chain transfer agent at the ratio of 0.5.

Comparing the results of chain length distribution of telomers when $CHCl_3$, which absolute value of slope is low ($\alpha = -25.8$), and CCl_4, which absolute value of slope is high ($\alpha = -45.7$), is used as chain transfer agent, the average chain length have similar values but the broadness of chain length distribution becomes narrow as absolute value of α increases. The ratio of chain transfer agent to monomer affects the average chain length and broadness of telomer. Average chain length and broadness (PI) slightly increase as the ratio of chain transfer agent to monomer decreases.

Table 4 shows the effect of the differentiation of chain transfer constant as a function of chain length. In Table 4 we can categorize three types to study the effect of differentiation of chain transfer constant as a function of chain length. Firstly, the value of C_1 is below 1.0 while C_2 and after are above 1.0. In this case C_∞ could not consider the change of value of C_1 and C_2 which is very important factor for determining the average chain length of resulting telomer at 1 and 2 units. Secondly, the all values of C are below 1.0. Thirdly, the values of C are above 1.0.

Comparing the results of chain length distributions when CCl_4 and $CHCl_3$ is used as chain transfer agent, which is belonging to the first case, average chain length of resulting telomers when C_∞ is used as chain transfer constant is

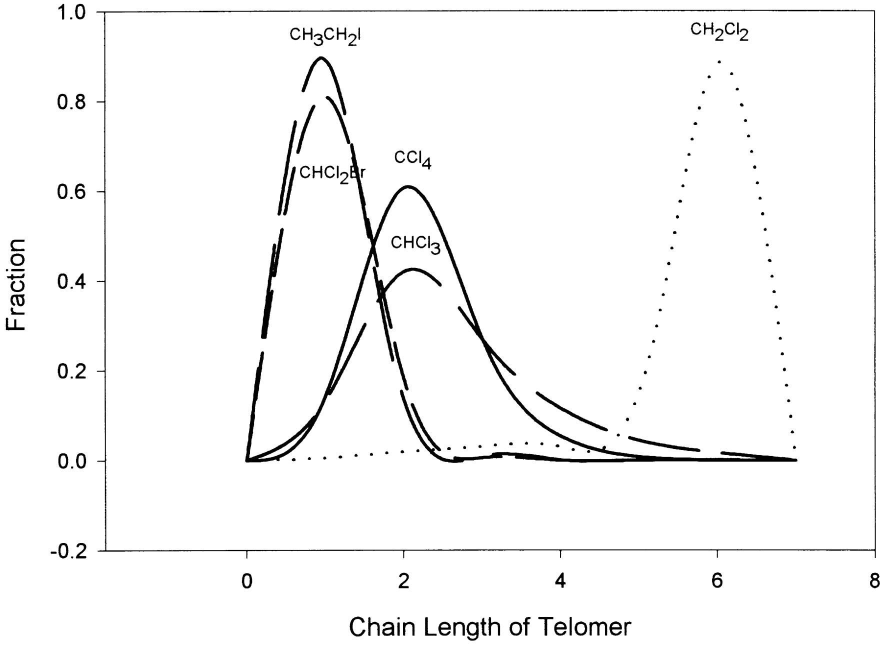

Fig. 7. Chain length distributions as a function of chain transfer agent when the ratio of chain transfer agent and monomer is 0.5.

almost half of that when chain transfer constant used is the value which differentiated with chain length.

For the other chain transfer agent, which is belonging to the second or third case, average chain length of resulting telomers when C_∞ is used as chain transfer constant does not affect the properties significantly except broadness of chain length distributions.

4. Conclusions

Free radical telomerization is studied by Monte Carlo method. In these studies, rate constants for growing radicals of less than five monomer units is considered. Monte Carlo simulation method is successfully applied for characterizing the telomerization such as validity of kinetic constants depending on the size of chain length and chain length distribution.

Average number and weight chain length are mainly determined by the value of C_1 and broadness of distributions (PI) are determined by the slope of plots of $\log(C_n)$ vs. $1/(2n+1)^2$.

Effect of differentiation of chain transfer constant as a function of chain length is studied by categorizing three types of chain transfer agents. Firstly, the value of C_1 is below 1.0 while C_2 and after are above 1.0. Secondly, the values of all the C are below 1.0. Thirdly, the values of all the C are above 1.0.

For the first case, average chain length of resulting telomers when C_∞ is used as chain transfer constant is almost half of that when chain transfer constants used are the value differentiated with chain length. For the second and third case, average chain length of resulting telomers when C_∞ is used as chain transfer constant do not affect significantly except broadness of chain length distributions which is determined by the absolute value of slope α. For telomers,

Table 4
Effect of differentiation of chain transfer constant as a function of chain length. (*S*: use C_∞. *D*: use differentiated *C* as a function of chain length)

		CCl_4		$CHCl_2Br$		$CHCl_3$		CH_2Cl_2		CH_3CH_2I	
		S	*D*	*S*	*D*	*S*	*D*	*S*	*D*	*S*	*D*
0.8	X_n	1.05	2.18	1.01	1.13	1.26	2.22	5.35	5.56	1.05	1.07
	X_w	1.10	2.36	1.02	1.23	1.51	2.61	5.73	5.77	1.11	1.13
	PI	1.04	1.08	1.01	1.09	1.20	1.18	1.07	1.04	1.06	1.06
0.5	X_n	1.07	2.34	1.02	1.20	1.38	2.58	5.55	5.69	1.11	1.12
	X_w	1.13	2.56	1.04	1.35	1.72	3.05	5.81	5.85	1.22	1.23
	PI	1.06	1.09	1.02	1.13	1.25	1.18	1.05	1.03	1.10	1.10
0.3	X_n	1.11	2.55	1.03	1.28	1.63	2.95	5.76	5.79	1.17	1.16
	X_w	1.22	2.80	1.06	1.45	2.23	3.50	5.88	5.90	1.32	1.33
	PI	1.10	1.10	1.03	1.14	1.37	1.19	1.02	1.02	1.13	1.14

which the value of C_1 is below 1.0 while the value of C_2 and after are above 1.0, are showed the importance for differentiating the chain transfer constant as a function of chain length for the characterization of kinetic behavior of telomerization.

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