

## Effect of Substituent of Chain Transfer agent in the Free Radical Polymerization

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### 자유 라디칼 중합반응에서 사슬이동제의 치환기 효과

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**ABSTRACT** : Carbon tetrachloride is very reactive chain transfer agent due to the resonance stability of the trichlorocarbon radicals after breaking of C-Cl bond. Effect of benzylic radical comparing to trichlorocarbon radicals in the chain transfer reactions was investigated. From the structural point of view, cumyl chloride is a good candidate because it has the C-Cl bond with benzylic radicals after displacement of C-Cl bond. The reactivity of free radical polymerization of styrene in the presence of cumyl chloride was compared with that of carbon tetrachloride by calculating chain transfer constants. Results show that the cumyl chloride acts as a stronger chain transfer agent than carbon tetrachloride. The calculated chain transfer constant of cumyl chloride shows higher value (0.0463) than that of carbon tetrachloride (0.0011) in the styrene polymerization. High reactivity of cumyl chloride comparing to that of carbon tetrachloride is probably due to the higher resonance stability of benzylic radical than that of trichlorocarbon radicals after breaking of C-Cl bond. Monte Carlo simulation method is applied for characterizing the validity of kinetic constants according to the ratio of chain transfer agent to monomer.

**요약** : 사염화탄소는 C-Cl결합이 끊어진 후에 생성되는 삼염화탄소 라디칼의 공명 안정성에 의해 매우 반응성이 높은 사슬이동제로 알려져 있으며, 본 논문은 벤질 라디칼과 삼염화탄소 라디칼의 안정성을 비교연구하였다. 큐밀클로라이드는 C-Cl결합이 끊어진 후에 벤질 라디칼을 생성하므로 이 연구에 적합한 구조이다. 큐밀클로라이드와 사염화탄소의 반응성은 스티렌을 단량체로 한 자유라디칼 중합을 통해 계산된 사슬 이동 상수로 비교하였다.

실험 결과에 따르면 큐밀클로라이드는 사염화탄소보다 더 반응성이 높았다. 계산된 큐밀클로라이드의 스티렌에 대한 사슬이동상수 값이 약 0.0463으로 0.0011인 사염화탄소 보다 훨씬 높았다. 이 결과는 벤질 라디칼이 삼염화탄소 라디칼보다 훨씬 높은 안정성을 보여주기 때문인 것으로 추정된다. 큐밀클로라이드의 사슬이동상수의 유효성을 조사하기 위하여 Monte Carlo 모의 실험 방법을 사용하였다.

*Keywords* : free radical polymerization, cumyl chloride, chain transfer constants, Monte Carlo simulation method

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## I. Introduction

The mechanism of the free radical polymerization has been well defined since late of 1930.<sup>1</sup> From the kinetic point of view, the rate of the propagation reaction must be sufficiently higher than that of chain transfer reaction to get high molecular weight polymer during the brief lifetime of the propagating radical.

Although chain transfer reaction results in a decrease in the size of the propagating polymer chain, it can be practically used for controlling the polymer molecular weight in the industrial applications such as coatings, adhesives and thermoplastic elastomers.

Many authors have studied the relationship between reactivity and structure of chain transfer agents.<sup>2,3</sup> From these studies, it is shown that the bond strength and stability of resultant radicals after displacement reactions are the most important factors to determine the reactivities of chain transfer agents.

As an example, chain transfer constants for the polymerization of styrene with carbon tetrachloride and carbon tetrabromide are 0.011 and 2.2, respectively.<sup>4</sup> High reactivity of chain transfer reaction for carbon tetrachloride and carbon tetrabromide are due to the weak carbon-halogen bonds. These bonds are especially weak because of the excellent stabilization of the trihalocarbon radicals formed by resonance involving the halogen free pairs of electrons. The great chain transfer reaction for carbon tetrabromide compared to the carbon tetrachloride is due to the weak C-Br bond. Also, benzylic radical is one of the most stabilized radical due to the resonance effects.

It is interesting to study the effect of benzylic radical comparing to trichlorocarbon radicals in the chain transfer reactions. Structure's point of view, cumyl chloride has the C-Cl bond with benzylic radicals after displacement of C-Cl bond.

In this study, chain transfer reaction of cumyl chloride by using styrene as a monomer was studied

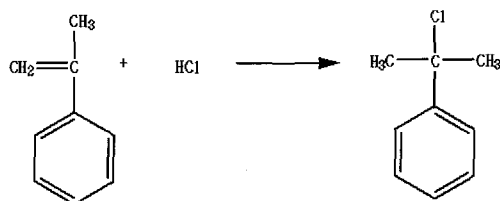
and compared with the effect of chain transfer reaction with carbon tetrachloride in the styrene polymerizations. Monte Carlo simulation method was applied for validating the kinetic constants of chain transfer reaction of cumyl chloride in the styrene free radical polymerization.

## II. Experimental

Cumyl chloride was synthesized in a 1000 ml three-neck flask equipped with a gas out-let tube, a magnetic stirrer, and a dry tube placed in an ice bath. After the system was flushed with dry nitrogen, the gas outlet tube was connected to a HCl generator. The HCl generator was a 500 ml flask containing 100 g of dry sodium chloride and equipped with a gas outlet tube and a dropping funnel containing 120 ml concentration sulfuric acid. HCl was generated by slowly adding sulfuric acid to the sodium chloride. After adding both freshly distilled  $\alpha$ -methylstyrene (50 ml) and dry  $\text{CH}_2\text{Cl}_2$  (450 ml) to the flask, HCl was bubbled into the  $\text{CH}_2\text{Cl}_2$  solution with stirring for two hours at 0 °C. After being stirred overnight below 15 °C,  $\text{CH}_2\text{Cl}_2$  solution was distilled by using a rotary evaporator. The complete conversion to cumyl chloride and absence of  $\text{CH}_2\text{Cl}_2$  were confirmed by the <sup>1</sup>H-NMR spectrum of the product which is shown in Figure 1 and Scheme 1.

The methyl (2.1 ppm) and aromatic (7.3~7.8 ppm) proton resonances have resonance areas in the ratio of 6:5, as expected. This cumyl chloride was used without further purification.

Azo-bis(isobutyronitrile) (AIBN) was recrystallized from methanol and dried under vacuum prior to use.



Scheme 1. Mechanism of the synthesis of cumyl chloride.

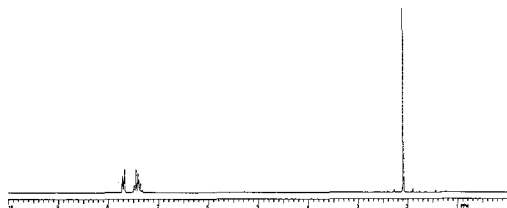


Figure 1.  $^1\text{H-NMR}$  spectrum of cumyl chloride.

Styrene was purified by washing three times with aqueous 10 % NaOH, then six times with distilled water, dried with  $\text{MgSO}_4$  and distilled in the presence of calcium hydride under reduced pressure prior to use. All polymerizations were done in solution containing various amounts of cumyl chloride and styrene along with AIBN as an initiator at a concentration of 0.2 mol %. The mixtures were flushed with dry nitrogen and the tubes were sealed. The polymerizations were conducted for 68 hours at 50 °C water bath and the reactions were terminated by freezing them in liquid  $\text{N}_2$ . The polymer was separated from monomer by precipitation of the reaction mixture in a large excess of methanol followed by evaporation, re-dissolution, filtration, and drying.

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (Water Associates, Model 150 C) having different refractive index detector and styragel columns with pore sizes ranging from 100– $10^6$  Å. Calibration curves were made by using well-fractionated polystyrene samples with narrow molecular weight distributions ( $M_w/M_n=1.1$ ).

### III. Simulation technique

The basic theory for the stochastic approach to reaction kinetics is described elsewhere.<sup>5</sup> After applying the stochastic method to simulate the free radical polymerization,<sup>6,7</sup> they concluded that stochastic method is a useful tool for characterizing the behavior of the free radical polymerization. In this study, Monte Carlo method is used for the validity of kinetic constants assumed in the polymerization

Table 1. The Rate Constants Used in The Simulation

Rate constant	value
$k_d$	$3.0 \times 10^{-6}$
$k_a$	10
$k_p$	150
$k_{tr,s}$	6.9
$k_t$	$1.5 \times 10^8$

of styrene in the presence of cumyl chloride. The rate constants for the simulation are listed in Table 1.

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

$$k^{st} = k^{de} \quad (\text{for first order reactions}) \quad (1)$$

$$k^{st} = \frac{k^{de}}{V \cdot N_a} \quad (\text{for second order reactions}) \quad (2)$$

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,  $\tau$  and  $\mu$ , must be generated. Time interval for reaction  $\tau$  can be calculated from the random number  $r_1$  from the uniform distribution in the unit interval.

$$\tau = (1/a_0) \ln(1/r_1) \quad (3)$$

$a_0$  is the sum of rates of reactions,  $a_0 = \sum_{\mu=1}^M a_\mu$ , where  $a_\mu$  is the rate of the  $\mu$ -th reaction.

The certain kind of reaction  $\mu$  during time interval  $\tau$  can be determined from the random number  $r_2$  by uniform distribution in the unit interval by following relations.

$$\sum_{\nu=1}^{\mu-1} a_\nu < r_2 \cdot a_0 \leq \sum_{\nu=1}^{\mu} a_\nu \quad (4)$$

where  $\mu$  is the number of the possible kinds of reaction and  $a_\nu$  is the rate of reaction  $\nu$ .

In this simulation, the rates of the reactions are as follows :

$$a_1 = k_d^{st} [\text{AIBN}] \quad (5)$$

$$a_2 = k_a^{st} [\text{R} \cdot][\text{M}] \quad (6)$$

$$a_3 = k_p^{st} [\text{RM} \cdot][\text{M}] \quad (7)$$

$$a_4 = k_x^{st} [\text{RM} \cdot][\text{YZ}] \quad (8)$$

$$a_5 = k_t^{st} [\text{XM} \cdot][\text{XM} \cdot] \quad (9)$$

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  $a_1, a_2, \dots, a_5$  for the current molecular populations.

Step 3: calculate and store as  $a_0$ , the sum of the  $M a_\mu$  values.

Step 4: generate two independent random numbers  $r_1$  and  $r_2$  uniformly between 0 and 1, and calculate  $\tau$  and  $\mu$  according to (3) and (4).

Step 5: using the  $\tau$  and  $\mu$  values obtained in step 4, advance  $t$  by  $\tau$ ,  $t = t + \tau$ .

Step 6: adjust the molecular population levels to reflect the occurrence of reactions

- 1) decomposition of initiator(Eq. 1) : decrease [AIBN] by 1 and increase [R ·] by 2
- 2) initiation (Eq 2) : decrease [R ·] and [M] by 1, increase [RM ·] by 1
- 3) propagation (Eq 3) : decrease [YM<sub>i</sub> ·] and [M] by 1, increase [YM<sub>i+1</sub> ·] by 1 ( $i = 1 - n$ )
- 4) chain transfer (eq 4) : decrease [RM<sub>i</sub> ·] and

[YZ] by 1, increase [RM<sub>i</sub>Z] and [Y ·] by 1 ( $i = 1 - n$ )

5) termination (eq 5) : decrease [RM<sub>n</sub> ·] and [RM<sub>m</sub> ·] by 1, increase [RM<sub>n+m</sub>Y] by 1

Step 7: recalculate the quantities  $a_\nu$  corresponding to reactions, increase the reaction counter by 1 and return to Step 2

## IV. Results and Discussion

Figure 2 and 3 summarize the effects of yield and molecular weight on the polymerization of styrene in the presence of cumyl chloride.

It can be seen that small amount of cumyl chloride has a dramatic effect on the yield and molecular

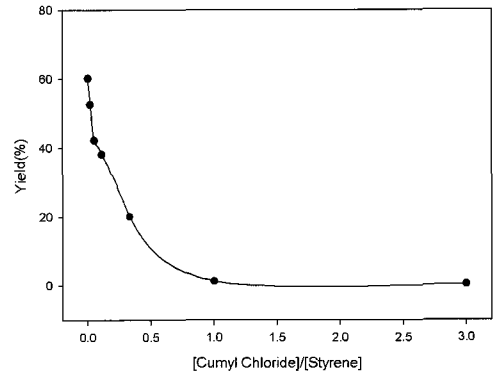


Figure 2. Effect of yields on the polymerization of styrene in the presence of cumyl chloride.

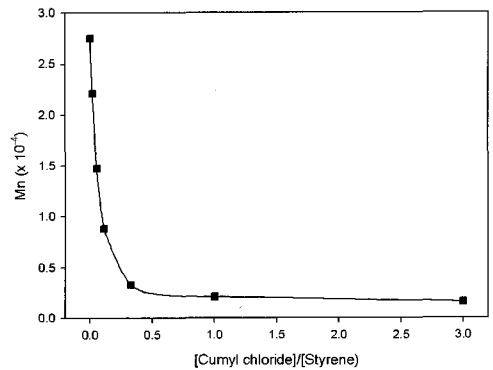


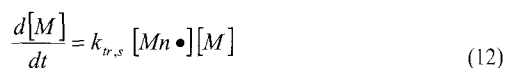
Figure 3. Effect of molecular weights on the polymerization of styrene in the presence of cumyl chloride.

weight of the polymer produced. These results indicate that the overall rate of polymerization decreases with increasing cumyl chloride content. Furthermore, the molecular weight of polymer decreases with increasing cumyl chloride content. Mayo equation is used to determine chain transfer constants for these materials. The form of the Mayo equation used in this work is given below.

$$\frac{1}{DP} = \frac{1}{DP_0} + C_s \frac{[S]}{[M]} \quad (10)$$

In this equation,  $C_s$  is the chain transfer constant

for a substance, S, this being equal to  $\frac{k_{tr,s}}{k_p}$ , where  $k_{tr,s}$  and  $k_p$  are the rate constant for the following reactions:



$$C_s = \frac{k_{tr,s}}{k_p} \quad (13)$$

Other term in the equation included DP and  $DP_0$ , the degree of polymerization of polymer obtained in the presence and absence of chain transfer agent, respectively, [S], the concentration of chain transfer agent, and [M], the concentration of monomer in the polymerization experiment. According to this modified Mayo equation, a plot  $\frac{1}{DP}$  versus  $\frac{[S]}{[M]}$  should be a straight line having a slope of  $C_s$  and an intercept of  $DP_0$ .

Figure 4 shows Mayo plot for the results obtained from polymerization of  $\frac{[cumyl\ chloride]}{[Styrene]}$  mixtures.

By working with this curve, chain transfer constant for cumyl chloride in styrene polymerization was evaluated from the slope of the linear line of

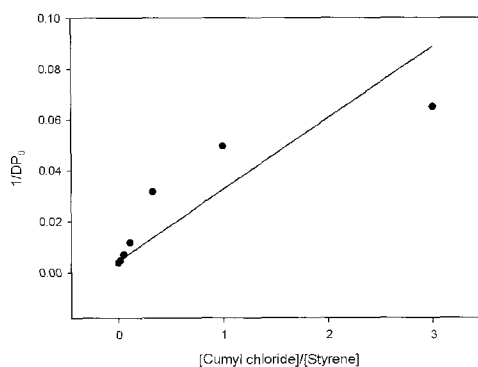
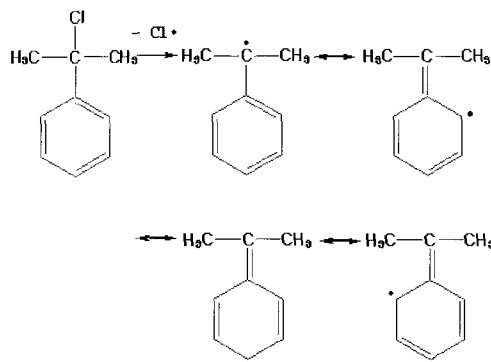


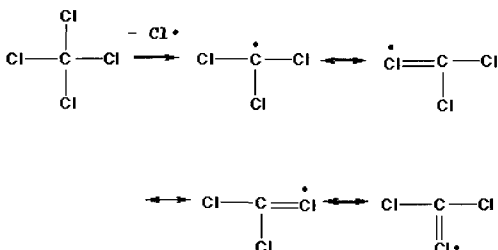
Figure 4. Mayo plot for the polymerization of styrene in the presence of cumyl chloride.

the plot  $\frac{1}{DP}$  versus  $\frac{[S]}{[M]}$ . The result obtained was 0.0463. The value of the chain transfer constant is in the range between the chain transfer constants for carbon tetrachloride (0.0011), and carbon tetrabromide (2.20). From these results, we can conclude that the resonance of benzylic radical (Scheme 2) contribute more in the stability of resulting radical comparing to that of trichloro-carbon radicals (Scheme 3) after breaking of C-Cl bond. Also, we can assume that the substituents of chain transfer agent affect tremendously, but it can not prevail the bond strength such as C-Cl vs. C-Br in the reactivity of chain transfer reactions.

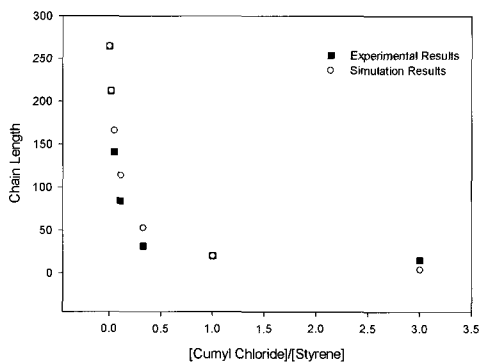
Figure 5 shows the comparison between the simulated results of number average chain length and experimental results.



Scheme 2. The resonance stability of the benzylic radical.



**Scheme 3.** The resonance stability of the trichloro radicals.



**Figure 5.** Comparison between the simulated results of number average chain length and experimental results.

As shown in Figure 5, the simulated results of the number average chain length are quite good agreement with experimental results.

These simulations verify that the result of the calculated chain transfer constant of cumyl chloride is in the range of reasonable kinetic values in the free radical polymerizations.

## V. Conclusion

Effect of benzylic radical comparing to trichloro-carbon radicals in the chain transfer reactions was investigated. From the structural point of view, cumyl chloride is a good candidate because it has the C-Cl bond with benzylic radicals after displacement of C-Cl bond.

Cumyl chloride was synthesized using  $\alpha$ -methylstyrene and HCl gas in the solution of  $\text{CH}_2\text{Cl}_2$ . Polymerization behavior of styrene as a monomer

was studied by using cumyl chloride as chain transfer agent. Small amount of cumyl chloride has a dramatic effect of on the yield and molecular weight of the polymer produced. These results indicated that the overall rate of polymerization decreased with increasing cumyl chloride content. Furthermore, the molecular weight of polymer decreased regularly with increasing cumyl chloride content. The calculated value of chain transfer constant for the styrene was about 0.0463 which was in the range between carbon tetrachloride (0.0011) and carbon tetrabromide(2.20). From these results, we can conclude that the resonance of benzylic radical contribute more in the stability than that of trichlorocarbon radicals after breaking of C-Cl bond. Results of the Monte Carlo simulation showed that the number average chain length were quite good agreement with experimental results. These simulations verified that the result of the calculated chain transfer constant of cumyl chloride was in the range of reasonable kinetic values in the free radical polymerizations.

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