

Chain Transfer Constants of Mercaptans in the Emulsion Polymerization of Styrene

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Synopsis

The chain transfer reaction and overall consumption of three mercaptans (*n*-decyl mercaptan, *n*-dodecyl mercaptan, and *tert*-dodecyl mercaptan) were studied in batch and semibatch seeded emulsion polymerizations of styrene. Seventy to ninety-five percent of the mercaptans reacted by chain transfer. The apparent chain transfer constants of mercaptans in the batch process decreased with increasing carbon chain length of the mercaptans. This tendency is connected with the analogous difference of the distribution coefficients of these mercaptans between the water phase and monomer droplets. The values of the chain transfer constant are independent of the amount of mercaptans used and reaction temperatures from 60°C to 90°C. The chain transfer constant of *tert*-dodecyl mercaptan had the same value in both the batch and semibatch processes. This indicates that varying the concentrations of initiator and monomer had negligible effects on the chain transfer reaction.

INTRODUCTION

Mercaptans have been recognized as the most important chain transfer agents in polymerization reactions. They are of great commercial importance, especially in the emulsion polymerization of dienes to synthetic rubbers, where the molecular weight must be controlled for ease of processing.^{1,2} Selection of a chain transfer agent (CTA) with a chain transfer constant near unity ensures that the transfer agent is consumed at about the same rate as the monomer. When the transfer constant is much lower than unity, high quantities of the transfer agent are required. On the other hand, a chain transfer constant greater than about five results in early consumption of the chain transfer agent, leaving the polymer unmodified in the high conversion range. Therefore, knowing the chain transfer constants of modifiers is essential in formulating a recipe for emulsion polymerization.

In emulsion polymerizations there are additional complications not seen in bulk polymerizations. Mercaptan chain transfer agents are usually added with the monomer and must diffuse through the water phase to get to the latex particle, the focal point for chain transfer activity. It has been shown that diffusion is the rate-limiting process for mercaptans with greater than 12 carbon atoms unless the mercaptan is pre-emulsified with the monomer.³ Also, mercaptans may be oxidized by an inorganic free radical or initiator in the water phase before reaching the latex particle. These water-phase reactions do not result in polymer chain transfer, hence both reactions reduce the efficiency of the chain transfer process.

The following reactions were considered in the analysis:

- A. $M_n^{\cdot} + M \rightarrow M_{n+1}^{\cdot}$ Propagation
- B. $M_n^{\cdot} + S \rightarrow M_n + S^{\cdot}$ Polymer-phase chain transfer
- C. $X^{\cdot} + S \rightarrow HX + S^{\cdot}$ Aqueous-phase transfer

In these reactions, M_n^{\cdot} denotes a propagating polymer radical containing n monomer units and M , S , and X represent monomer, chain transfer agent, and an inorganic, aqueous phase initiator or free

radical ($S_2O_8^{2-}$, $SO_4^{\cdot-}$, or OH^{\cdot}), respectively.

If the monomer that is consumed by other reactions is neglected then we can write eqs. (1), (2), and (3).

Since we will be comparing reactions in different phases, all equations are written in extensive variables, for example, $(-dM/dt)_p$ in eq. (1) is the rate of monomer reaction in the polymer phase (mol/s) in the reactor.

$$(-dM/dt)_p = k_p[M]_p[M_n^{\cdot}]_p\nu_p = k_p[M]_pM_n^{\cdot} \quad (1)$$

$$(-dS/dt)_p = k_{ct}[S]_p[M_n^{\cdot}]_p\nu_p = k_{ct}[S]_pM_n^{\cdot} \quad (2)$$

$$(-dS/dt)_{aq} = k_x[S]_{aq}[X^{\cdot}]_{aq}\nu_{aq} = k_x[S]_{aq}X^{\cdot} \quad (3)$$

where ν is the phase volume and the p and aq subscripts denote the polymer and aqueous phases. Adding eqs. (2) and (3) gives eq. (4a) the total consumption rate for mercaptan in the reactor.

$$-dS/dt = k_{ct}[S]_pM_n^{\cdot} + k_x[S]_{aq}X^{\cdot} \quad (4a)$$

If it is assumed that $[S]_{aq}$ is proportional to $[S]_p$ (i.e., phase equilibrium is achieved), and that the ratio of X^{\cdot}/M_n^{\cdot} is nearly constant over the first 30% of monomer conversion, then the phase subscripts may be dropped and dS/dt may be written with a lumped rate constant, k_s .

$$-dS/dt = k_s[S]_pM_n^{\cdot} \quad (4b)$$

where $k_s = k_{ct} + k_x([S]_{aq}/[S]_p)(X^{\cdot}/M_n^{\cdot})$

The chain transfer constant (C_{ct}) is defined as the ratio of rate constants for the transfer reaction, k_{ct} , and the propagation reaction, k_p . Likewise a mercaptan reaction constant (C_s) may be defined as the ratio of k_s to k_p . The permissibility of lumping the aqueous and polymer mercaptan reactions can be tested by noting the constancy of k_s and hence C_s up to 30% of monomer conversion.

Division of eq. (4b) by eq. (1) gives eq. (5), which for batch reactions can be integrated to give eq. (6), where $C_s = k_s/k_p$.

$$\frac{dS}{dM} = \frac{d[S]}{d[M]} = \frac{k_s[S]}{k_p[M]} = C_s \frac{[S]}{[M]} \quad (5)$$

$$\log \frac{[S]}{[S_o]} = C_s \log \frac{[M]}{[M_o]} \quad (6)$$

In these equations, $[S_o]$ and $[M_o]$ are the initial concentrations of chain transfer agent and monomer, respectively, and $[S]$ and $[M]$ are the corresponding concentrations at various reaction times. As shown in eq. (6), a plot of $\log[S]/[S_o]$ against $\log[M]/[M_o]$ should give a straight line whose slope is equal to C_s , the mercaptan reaction constant.

The chain transfer constant, C_{ct} , can be found from the molecular weight of the polymer. Normally, the equation below is used to extract C_{ct} from the number average molecular weight of polymers made with and without added CTA.

$$\frac{1}{W_n} = \frac{1}{W_{no}} + C_{ct} \frac{[S]}{[M]}$$

where W_n and W_{no} are the number average molecular weights of polymer made with and without CTA.

However, since the ratio of $[S]/[M]$ varied throughout the course of the reaction, a different method was used to analyze the molecular weight data. A dynamic emulsion polymerization model was used to predict the number and weight average molecular weights as a function of polymerization time. The polymerization model was a modification of that proposed by Kao for styrene with a variable free radical efficiency.⁴ The model was modified by adding a mass balance for mercaptan using the reaction constant C_s , as determined above. The number and weight average molecular weights were calculated by including differential equations for the zero, first, and second polymer moments following a procedure first suggested by Bamford and Tompa⁵ and expanded by Broadhead et al.⁶ for use in their copolymerization model. The calculated molecular weight averages were then used to fit the chain transfer constant, C_{ct} , to the molecular weight data using the Nelder-Mead direct search method.

Three major systems are often used in emulsion polymerizations: batch, semibatch, and continuous. In the batch process, all of the recipe ingredients are added at the beginning of the batch cycle. Semibatch systems are designed like batch systems, but part of the initiator and/or monomer are added in a programmed manner after the reaction has started. In this study, the chain transfer and reaction constants of three mercaptans, *n*-decyl mercaptan, *n*-dodecyl mercaptan, and *tert*-dodecyl mercaptan (*t*-DDM) were determined under both batch and semibatch conditions.

TABLE I
Recipes used for Batch and Semibatch Emulsion Polymerization

Component	Batch	Semibatch	
Initial charge (pphm ^a)			
Styrene	100.	100.	10.
Deionized water	400.	300.	300.
1% Versenex 80 chelating agent	5.0	5.0	5.0
Aerosol MA	1.25	1.25	1.25
Seed	1.5	1.5	1.5
Sodium persulfate	0.5	0.2	0.2
Mercaptan	Varied	1.0	0.1
Continuous addition (pphm ^a)			
Sodium persulfate ^b	—	0.48	0.48
Deionized water ^b	—	100.	100.
Styrene ^c	—	—	90.
Mercaptan ^c	—	—	1.0

^aParts per one hundred parts monomer by weight.

^bAddition over a period of 2 h.

^cAddition over a period of 1 h.

EXPERIMENTAL

Materials

Styrene (Aldrich, 99 + %, inhibited with 10–15 ppm 4-*tert*-butylcatechol) was purified the day before use by washing with 10% potassium hydroxide solution to remove inhibitor, followed by distillation under a reduced pressure of nitrogen. Sodium persulfate, the initiator, was purified by recrystallization from warm water. The water used for polymerization was deionized and deoxygenated prior to use.

n-Decyl mercaptan, *n*-dodecyl mercaptan, *t*-DDM (Pennwalt technical grade*), seed latex, Aerosol MA (Trademark of The American Cyanamid Company), and Versenex 80 (Trademark of the Dow Chemical Company) chelating agents were used as received from The Dow Chemical Company without further purification. The seed was a polystyrene latex with an average particle diameter under .05 μm . The Aerosol MA [sulfobutanedioic acid 1,4-*bis*(1-methyl-pentyl) ester sodium salt] was used as the stabilizing surfactant. Versenex 80, which is an EDTA solution, was used as a chelating agent.

Polymerization Procedures

Batch emulsion polymerizations were carried out in a 1-L jacketed resin kettle fitted with a stirrer and a nitrogen inlet tube projecting into the reaction mixture. The recipe used is given in Table I.

*Technical *tert*-dodecyl mercaptan is the H₂S adduct with the C₁₂ cut from a propylene oligomerization. The product is a mixture of C₉ to C₁₄ mercaptans with 55–60% being C₁₂ mercaptan. Roughly 80% of the mercaptan is tertiary with the remainder being a secondary mercaptan.

All the ingredients, except styrene, mercaptan, and sodium persulfate, were mixed with most of the water and charged into the resin kettle. The resin kettle was kept at the desired temperature by circulating water of a constant temperature through the jacket of the kettle. The whole mixture was stirred with a stirring speed of 700 rpm and deoxygenated by bubbling with nitrogen for at least 30 minutes. The mixture of monomer and mercaptan was then added and after 5 min, the initiator dissolved in the remaining water was added to the kettle. The beginning of the reaction was taken to be the time of addition of the initiator.

At appropriate intervals, two samples were pipetted from the reaction kettle into tared flasks. One of the samples was poured into 150 mL of methanol containing 1 mL of 5% hydroquinone and 3 mL of 6 *M* sulfuric acid to coagulate the polystyrene for the polymer conversion measurement. The coagulated polystyrene was filtered through a tared fritted glass crucible, washed with methanol, and then dried at 50°C in a vacuum oven until a constant weight was reached.

The molecular weight distribution and averages were determined by using a Waters R401 GPC and Varian Micropack Columns. Dried latex samples were dissolved in tetrahydrofuran (0.5%) and the columns were calibrated with polystyrene standards.

The second sample was added dropwise with vigorous stirring into 100 mL of 95% ethanol containing 1 mL 0.1 *N* ferrous sulfate in 1 *N* sulfuric acid for residual mercaptan analysis. Mercaptan analysis of the coagulated latex in ethanol was performed amperometrically with silver nitrate using the method developed by Kolthoff.⁷ Concentrated ammonium hydroxide (2 mL) was added to the alcohol solution followed by amperometric titration with 0.005 *N* silver nitrate. In this titration, a rotating platinum electrode was used in conjunction with a half-cell prepared by dissolving 4.2 g of potassium iodide and 1.3 g of mercuric iodide in 100 mL saturated potassium chloride solution and with a mercury pool at the bottom of the flask.

Two types of semibatch emulsion polymerizations of styrene were performed using basically the same procedure as described for the batch polymerization. The main differences were the continuous addition of initiator or of initiator and monomer. The recipes are shown in Table I.

RESULTS AND DISCUSSION

Chain Transfer Constants of Mercaptans in the Batch Emulsion Polymerization of Styrene

Three mercaptans were used as chain transfer agents in the batch emulsion polymerization of styrene: *n*-decyl mercaptan, *n*-dodecyl mercaptan, and *t*-DDM. Reaction constants were calculated from the slopes of the plots of $[\log \text{ mercaptan remaining}]$ versus $[2 - \log \text{ styrene remaining}]$ according to eq. (6). (The 2 is included so that the increase in abscissa values corresponds to the increase percentage of the polymer yield.) Plots of the data obtained at various temperatures are shown in Figures 1 to 5. Figures 6 and 7 show the number and weight average molecular weights for two polymerizations and the dynamic simulation results from which C_{ct} was fit. Table II summarizes

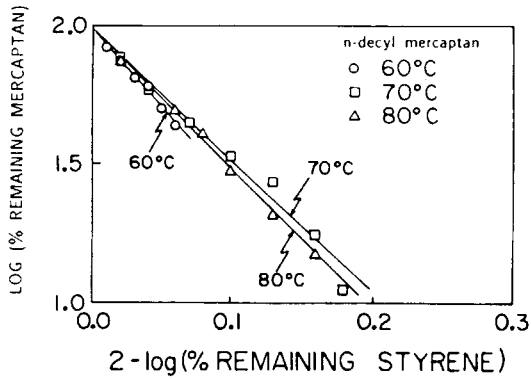


Fig. 1. Chain transfer constant plots for batch emulsion polymerization of styrene with addition of 0.5 ppm *n*-decyl mercaptan. (○) 60°C; (□) 70°C; (Δ) 80°C.

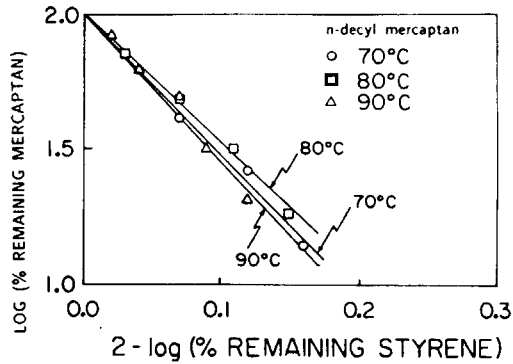


Fig. 2. Chain transfer constant plots for batch emulsion polymerization of styrene with addition of 1.0 ppm *n*-decyl mercaptan. (○) 70°C; (□) 80°C; (Δ) 90°C.

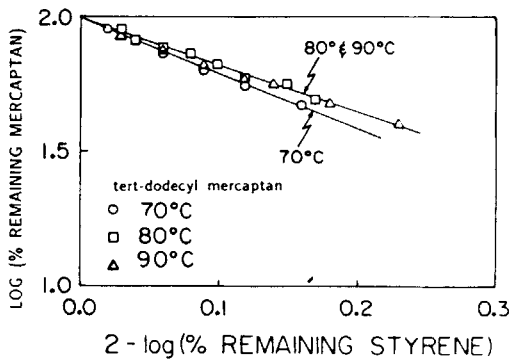


Fig. 3. Chain transfer constant plots for batch emulsion polymerization of styrene with addition of 0.5 ppm *tert*-dodecyl mercaptan. (○) 70°C; (□) 80°C; (Δ) 90°C.

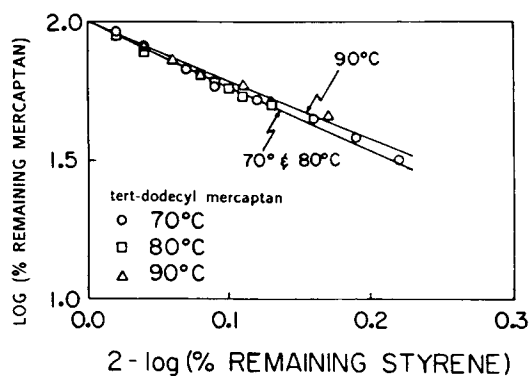


Fig. 4. Chain transfer constant plots for batch emulsion polymerization of styrene with addition of 1.0 ppm *tert*-dodecyl mercaptan. (○) 70°C; (□) 80°C; (Δ) 90°C.

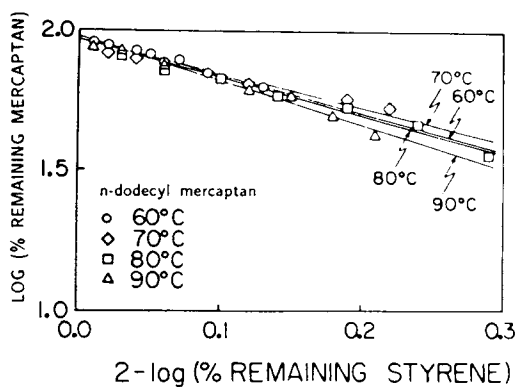


Fig. 5. Chain transfer constant plots for batch emulsion polymerization of styrene with addition of 1.0 ppm *n*-dodecyl mercaptan. (○) 60°C; (◇) 70°C; (□) 80°C; (Δ) 90°C.

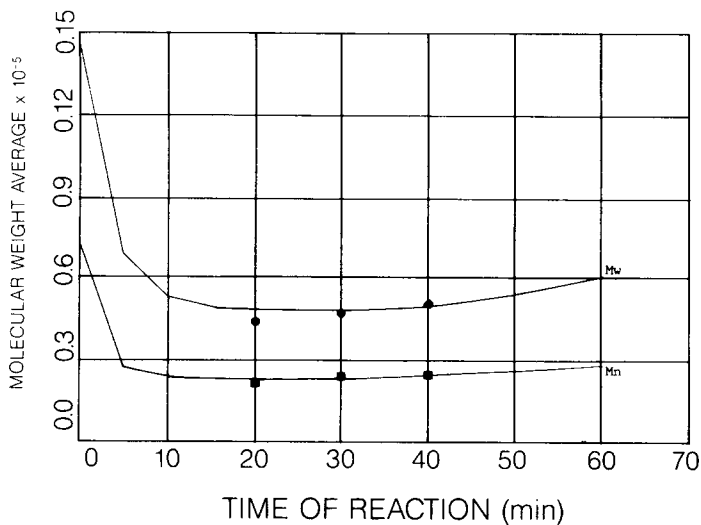


Fig. 6. Molecular weight of polystyrene at 90°C and 0.5% *tert*-dodecyl mercaptan.

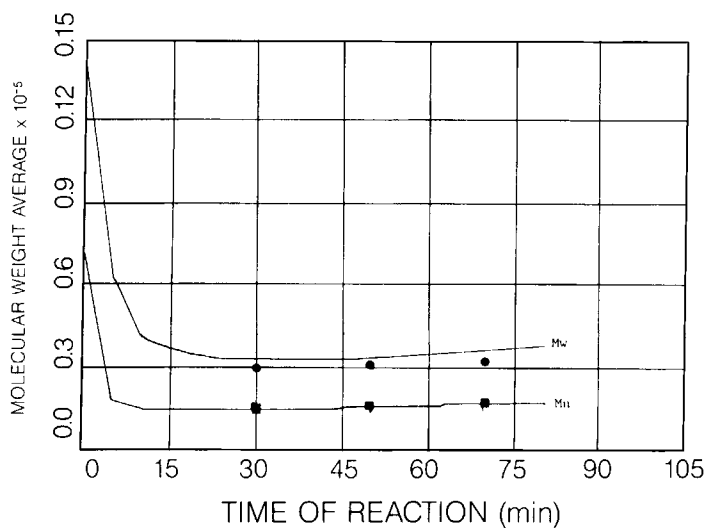


Fig. 7. Molecular weight of polystyrene at 70°C and 1.0% *tert*-dodecyl mercaptan.

TABLE II
Chain Transfer Constants of Mercaptans in the Batch Emulsion
Polymerization of Styrene at Various Temperatures

Mercaptan	Mercaptan conc. (pphm)	Reaction temperature (°C)	Reaction constant, C_s	Chain transfer constant C_{ct}	C_{ct}/C_s
<i>n</i> -decyl mercaptan	0.5	60	5.5		
	0.5	70	4.8		
	0.5	80	5.0	4.3	.85
	1.0	70	5.2		
	1.0	80	4.9	4.2	.85
	1.0	90	6.0		
<i>tert</i> -dodecyl mercaptan	0.5	70	2.0	1.5	.76
	0.5	80	1.7		
	0.5	90	1.6	1.5	.93
	1.0	70	2.2	1.5	.66
	1.0	80	2.3		
	1.0	90	2.1	1.6	.76
<i>n</i> -dodecyl mercaptan	0.5	60	1.7		
	1.0	60	1.4		
	1.0	70	1.1	.69	.63
	1.0	80	1.3		
	1.0	90	1.5	1.3	.86
	1.0	90	2.5 ^a		

^a Experiment performed at pH = 10.

TABLE III
Dependence of the Change in the Molecular Weights of Polymers on
the Extend of Polymerization of Styrene in the Presence of Mercaptans

Thiol	Amount pphm ^a	Reaction temp. (°C)	Reaction time (min)	% Conversion	Mw	Mn	Mw/Mn
—	—	80	40	24.4	239,000	95,000	2.5
			80	61.2	314,000	124,000	2.5
<i>n</i> -decyl mercaptan	0.5	80	36	25.5	25,000	14,000	1.8
			48	34.5	27,000	15,000	1.9
	1.0	80	40	27.5	15,000	9,000	1.7
			80	54.5	45,000	13,000	3.5
<i>tert</i> -dodecyl mercaptan	0.5	70	30	13.6	53,800	27,400	2.0
			50	24.6	57,100	27,100	2.0
			70	35.2	55,900	27,800	2.0
	1.0	70	30	14.2	29,300	15,000	2.0
			50	25.0	30,600	15,700	2.0
			70	35.9	32,300	17,100	1.9
	0.5	90	20	12.8	44,100	22,200	2.0
			30	23.8	47,300	24,300	2.0
			40	34.1	50,800	25,700	2.0
	1.0	90	20	17.0	27,500	14,300	1.9
			30	26.3	30,000	15,900	1.9
			40	34.8	28,000	14,100	2.1
<i>n</i> -dodecyl mercaptan	1.0	70	30	13.5	77,000	27,800	2.8
			50	24.2	80,700	27,000	2.8
			70	35.0	71,500	28,000	2.6
	1.0	90	20	19.1	42,400	15,400	2.8
			30	28.8	40,200	16,400	2.5
			40	38.0	41,200	17,500	2.4

^aPart per one hundred parts monomer by weight.

the chain transfer and reaction constants calculated from these plots. Also listed in Table II is the ratio of C_{ct}/C_s , which represents a chain transfer efficiency for the mercaptan. Table III lists the molecular weight average and % conversions for the samples that were submitted for molecular weight determination.

Examination of the data in Table II shows that varying the mercaptan concentration twofold has a negligible effect on the chain transfer constants, as expected from the theory of chain transfer. Temperature also has only a very slight influence on the values of these constants, indicating that the activation energies for propagation and transfer are quite similar. This same phenomenon has also been reported by Smith.⁸

Also the mercaptan reaction constants show no clear dependence on the initial mercaptan concentration. This and the linearity of the plots in Figures 1 through 5 support the approximation made in lumping reactions (2) and (3). However, the chain transfer efficiencies, C_{ct}/C_s , show more variation, being lower at the lower temperatures. This may be due to a lower activation energy for the nonchain transfer reactions or to less diffusion resistance in the water phase for the C_{12} mercaptans at the higher temperatures leading to lower loss of mercaptan by side reactions in the water phase.

In an emulsion polymerization, the traditional view is that the micelles are the principal loci of reaction during the early stages of polymerization, while

the swollen polymer particles are the principal reaction sites in the late stages, as proposed by Harkins.⁹ The emulsified monomer droplets (oil phase) act as reservoirs for supplying both monomer and chain transfer agent to the reaction loci. In such a picture, the aqueous phase behaves as a boundary between the reaction loci and oil phase. The effectiveness of the transport of the chain transfer agent from the reservoir oil phase to the reaction loci is determined by the diffusion constant of the chain transfer agent in water, and its susceptibility to reaction while traversing the aqueous phase. The effectiveness is also determined by the distribution coefficient of the transfer agent between the water and the monomer droplets. The diffusion constants of all the mercaptans studied here should be fairly similar; however, the distribution coefficient is very dependent upon the number of carbon atoms in the mercaptan. For example, Yabroff¹⁰ found that the distribution coefficients of a homologous series of primary mercaptans (ethyl mercaptan to heptyl mercaptan) between water and isooctane decrease by a factor of 4.3 for each additional carbon atom. This decrease in the distribution coefficient is no doubt largely responsible for the reduced values of the chain transfer constant for *n*-dodecyl mercaptan and *t*-DDM relative to *n*-decyl mercaptan, as shown on Table II.

Another factor important in determining the rate of transport of mercaptans to the reaction loci through the water phase during the polymerization is the pH value of the aqueous phase. Being a weak acid, aliphatic mercaptans ionize in a solution of high pH. Increasing the pH of the solution will decrease the distribution coefficient of mercaptan, which will aid the transport of the mercaptans to the reaction loci. This effect of pH is illustrated in Figure 8 where the mercaptan consumption versus time curves for two batch runs at different pH values are shown. For *n*-dodecyl mercaptan, the rate of mercaptan consumption at pH = 10 is higher than that at low pH, indicating that

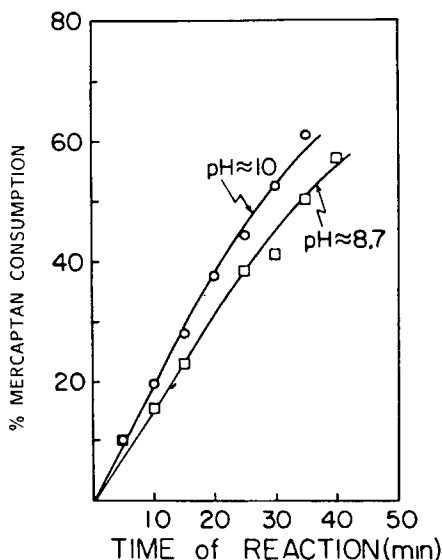


Fig. 8. Effect of pH on the consumption of mercaptan in the emulsion polymerization of styrene at 90°C with addition of 1.0 ppm *n*-dodecyl mercaptan. (○) pH ≈ 10; (□) pH ≈ 8.7.

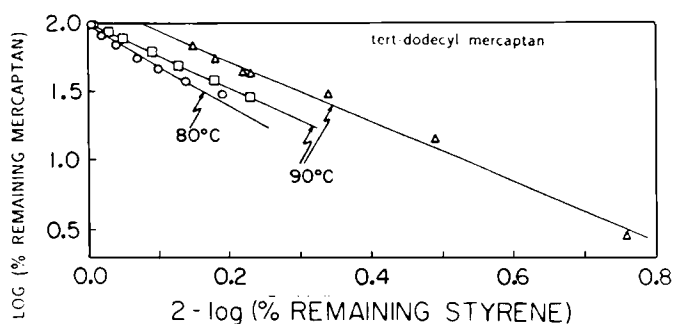


Fig. 9. Chain transfer constant plots for semibatch emulsion polymerization of styrene with addition of 1.0 ppm *tert*-dodecyl mercaptan. (○, □: continuous addition of initiator; △: continuous addition of initiator and monomer.)

pH indeed is a controlling factor for chain transfer action. Consequently, the reaction constant of *n*-dodecyl mercaptan at high pH is 30 to 60% higher than the value at low pH, as shown in Table II.

Chain Transfer Constants of Mercaptans in the Semibatch Emulsion Polymerization of Styrene

n-Dodecyl mercaptan and *t*-DDM were chosen for further study as chain transfer agents in the semibatch emulsion polymerization of styrene since these mercaptans had chain transfer constants close to unity in our batch experiments. Figures 9 and 10 show the chain transfer constant plots; the reaction constants calculated from the plots are summarized in Table IV.

The values of the reaction constant for *t*-DDM at 80°C and 90°C are virtually the same in both semibatch emulsion polymerization processes. This indicates that varying the initiator and monomer concentrations during the reaction has negligible effects on the chain transfer constants. According to the Smith-Ewart¹¹ theory, the steady-state rate of polymerization is affected

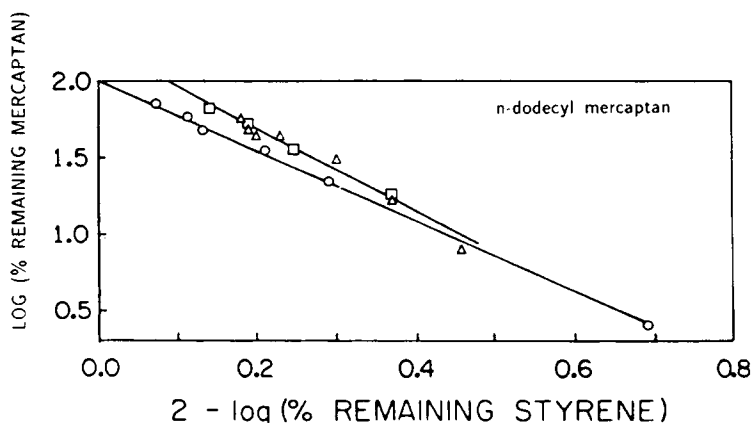


Fig. 10. Chain transfer constant plots for semibatch emulsion polymerization of styrene at 90°C with addition of 1.0 ppm *n*-dodecyl mercaptan. (○: continuous addition of initiator; □, △: continuous addition of initiator and monomer.)

TABLE IV
Chain Transfer Constants of Mercaptans in the
Semibatch Emulsion Polymerization of Styrene

Mercaptan	Mercaptan conc. (pphm)	Reaction temperature (°C)	Reaction constant, C_s
<i>tert</i> -dodecyl mercaptan	1	80	2.8 ^a
	1	90	2.2 ^a
	1	90	2.2 ^b
<i>n</i> -dodecyl mercaptan	1	90	2.2 ^a
	1	90	2.7 ^b , 2.9 ^b

^aContinuous addition of initiator, see Table I.

^bContinuous addition of both initiator and monomer, see Table I.

by the initial initiator concentration only because of its effect on the number of reaction loci which form during the locus-initiation stage. Therefore, variation of the initiator concentration has no measurable effect upon the rate of polymerization if the number of reaction loci is fixed. Since the recipe used in this study is seeded, the number of polymer particles was fixed at the beginning of the reaction, and varying the concentrations of initiator and monomer had no effect on the rates of the polymerization and the chain transfer reactions.

As for *n*-dodecyl mercaptan, the reaction constants of semibatch emulsion polymerization at 90°C are higher than those obtained in the batch process. This puzzling phenomenon indicates that the chain transfer action of *n*-dodecyl mercaptan was increased in the semibatch process; we have no explanation for this observation.

CONCLUSIONS

Three mercaptans *n*-decyl mercaptan, *n*-dodecyl mercaptan, and technical grade *tert*-dodecyl mercaptan (*t*-DDM) were studied as chain transfer agents in batch emulsion polymerizations of styrene at reaction temperatures ranging from 60°C to 90°C using a seeded recipe. The chain transfer and mercaptan reaction constants obtained (Table II) are independent of the reaction temperature. The small values for the transfer constants of the higher mercaptans (*n*-dodecyl mercaptan and *t*-DDM) in emulsion polymerization are due to the slow transport rate of mercaptan from the monomer droplet reservoir to the reaction loci, the polymer particles. Chain transfer efficiencies were 95% for the C₁₀ mercaptan and 70% to 90% for the C₁₂ mercaptans, indicating significant levels of side reactions for the less soluble mercaptans.

n-Dodecyl mercaptan and *t*-DDM were also studied as chain transfer agents in semibatch polymerization of styrene. The mercaptan reaction constant of *t*-DDM had virtually the same value in the semibatch experiments as in the batch emulsion polymerization at reaction temperatures of 80°C and 90°C. This indicates that varying the concentrations of initiator and monomer has a negligible effect on the chain transfer constants. For *n*-dodecyl mercaptan, higher values for the chain transfer constant were obtained in the semibatch emulsion polymerization, for a reason that is not clear.

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