Chain Transfer Behavior of Fractionated Commercial Mercaptans in Emulsion Polymerization of Styrene

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SYNOPSIS

The chain transfer behavior of fractionated commercial tertiary mercaptans was investigated in batch and semicontinuous emulsion polymerization of styrene over the entire monomer conversion range. Four mercaptans were obtained by fractionation, which contained 9, 11, 12, and 13 carbons, respectively. The effect of the mercaptans was evaluated in terms of the consumption rates of the monomer and the chain transfer agents, the number average degree of polymerization, DP_n, and the polydispersity index, I, of the polymer. The batch experiments showed that the chain transfer efficiency decreases with increasing carbon number, which is due primarily to a lower diffusion rate of the chain transfer agent to the reaction sites (growing latex particles) through the aqueous phase. The partitioning ratio of the chain transfer agents between the aqueous phase and the monomer droplets also contributes, to a lesser extent, to the efficiency. The number average degree of polymerization and the polydispersity index are primarily controlled by the ratio of the mercaptan consumption rate over that of the monomer. In order to obtain a polymer with a constant DP_n and a narrow I, this ratio should be as close to unity as possible, as is the case for C_{11}. Otherwise, too high a ratio causes a severe increase in DP_n at the end of polymerization, and too low a ratio leads in the opposite direction. The semicontinuous experiments confirmed the batch results. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Mercaptans are commonly used as chain transfer agents (CTA) in free radical polymerization. In particular, they are used in emulsion polymerization for controlling the mass molecular weight of polymers that dictates their final properties. Although mercaptans have been used extensively in emulsion polymerization to prepare synthetic rubber, it is not clearly understood how they behave in dispersed systems. Little work has been performed in this area and only a few articles concerning mercaptans as CTA in emulsion polymerization have been published.[1-8] A kinetic analysis of the mercaptan consumption,[4,8] during emulsion polymerization, leads to eqs. (1) and (2).

$$\log \frac{M}{M_0} = C_S \log \frac{S}{S_0} \qquad (1)$$

where M_0 and S_0 denote the initial concentration of monomer and that of transfer agent, respectively, while M and S represent their concentrations at time t. C_S is the mercaptan reaction constant, which is defined as the ratio of the mercaptan chain transfer rate constant to the propagation reaction rate constant, that is,

$$C_S = \frac{k_S}{k_p} \qquad (2)$$

Emulsion polymerization is more complex than solution or bulk polymerization because the reactions of initiation, propagation, transfer, and termination take place simultaneously in several phases. Understanding the behavior of CTA in emulsion polymerization requires a knowledge of the partitioning of various substances among the phases

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and their diffusion rates from one phase to another. Generally, micelles in the medium are considered as the principle reaction loci during the initial stage of polymerization, and then the growing latex particles become the major reaction sites when conversions get higher. The monomer and the CTA droplets in the aqueous phase act as reservoirs that feed the reaction sites with monomer and CTA. The efficiency, whereby the CTA penetrates into the growing particles through the aqueous phase, is controlled by its diffusivity, the rates of the reactions that are occurring in the aqueous phase, and the partitioning coefficient between the aqueous and organic phases. When the CTA's molecular weight is so low that it diffuses at least as fast as the monomer, the monomer-to-mercaptan concentration ratio in the particles is expected to be the same as that in the bulk polymerization, provided that the conversion and the initial mercaptan content are the same. It is expected that the effect of such a CTA is the same for both polymerization processes. When the CTA's molecular weight is so high that it diffuses more slowly than the monomer, its efficiency will be reduced. In this case, it is conceivable that the apparent mercaptan chain transfer constant decreases and the average degree of polymerization increases, as shown for the emulsion polymerization of styrene. It was reported that primary mercaptans, containing at most ten carbon atoms, and tertiary mercaptans, containing not more than twelve carbon atoms, have a diffusion rate through water that is equal to their consumption rate in the emulsion polymerization of SBR.[2,3] This was also confirmed by the fact that the stirring rate has no effect on the reaction rate of mercaptans. The pH of the continuous phase influences greatly the diffusion rate of mercaptans. When the pH is high, mercaptans become ionized, displaying a higher diffusion rate. It was also found that pre-emulsification of high molecular weight mercaptans, or the preparation of soap in situ,[8,9] accelerates the consumption rate of CTA. Mercaptans may also have a significant effect on the kinetics of polymerization.[10] In an industrial emulsion po-

lymerization process, commercial mercaptans, used in emulsion polymerization, are usually a mixture of mercaptans having various numbers of carbon atoms. Moreover, each of them is a mixture of isomers. For example, the commercial tertio-dodecyl mercaptan (TDM) is composed of mercaptans with carbon atoms ranging from 10 to 13. It is believed that the TDM of Elf Aquitaine contains at least five components. Similarly, the commercial tertio-nonyl mercaptan (TNM) is a mixture of mercaptans ranging from C_7 to C_{11}. This is one of the reasons that the mercaptan content in emulsion polymerization recipes is chosen largely on the basis of empiricism in order to obtain a product with desired properties (mass molecular weights, particle sizes, and their distribution, etc.). The aim of this work is to investigate the chain transfer behavior of various single tertiary mercaptans in batch and seeded, semicontinuous emulsion polymerization of styrene.

EXPERIMENTAL

Materials

Styrene (Aldrich) was purified by passing it through a basic aluminium oxide column before use. Sodium dodecylsulfate (SDS), potassium persulfate, and sodium bicarbonate, all being purchased from Aldrich, were used as received. Deionized and distilled water was used for all polymerization runs. The tertiary mercaptans under investigation (C_9, C_{11}, C_{12}, and C_{13}) were obtained from commercial grades of mercaptans (TDM and TNM from Elf Aquitaine) through a carefully developed fractional distillation process under nitrogen and reduced pressure (1–2 mm Hg). Under those conditions, the boiling temperatures of the systems were lowered down to 110–150°C depending upon the CTA carbon chain length. Possible formation of polysulfide by oxidation was also reduced. Reflux rate was found to be important for a good fractionation of the products. Table I shows the compositions of the two original commercial TDM and TNM. After distillation, 95%

Table I   Compositions of the Commercial TDM and TNM Chain Transfer Agents from Elf Aquitaine (France)

	Light Products %	%C_7	%C_8	%C_9	%C_{10}	%C_{11}	%C_{12}	%C_{13}	Residues %
TDM	0.75[a]	—	—	—	1	17	77	5	0.05
TNM	1.4[b]	5.4	2.2	85.9	6.3	0.2	—	—	0.1

[a] Tetrapropylene.
[b] Tripropylene.

of the TNM was C_9-mercaptan. As for the TDM, a first distillation was not enough for a good separation of the mixtures. A second distillation of the first distillate was needed, which led to two fractions containing 93% C_{11} and 97% C_{12}, respectively. C_{10}-mercaptan could not be fractionated out because of its low content in the original product (1%). As for C_{13}-mercaptan, higher temperatures (130–150°C) and longer times were needed, causing possible degradation of the products. The remedy for this was to remove the most volatile compounds from the TDM quickly, followed by a reduction in the distillation rate. However, after distillation, the TDM contained only 45% C_{13} along with 11% C_{10}, 2% C_{11}, and 42% C_{12}.

Characterization Techniques

The mercaptans, obtained from the distillation, were analyzed by three techniques: gas chromatography for determining the weight percentage of mercaptans (i.e., in the form of R-SH), mass spectroscopy for the composition of thiols of different chain lengths, and potentiometry for the weight percentage of sulfur in R-SH form, using $AgNO_3$ as the titration agent. The titration was carried out in a mixture of ethanol (100 mL), cyclohexane (20 mL), and ammonia (2 mL) with a pair of silver-calomel electrodes. Mercaptan consumption during the emulsion polymerization was measured by a new titration technique that was developed in our laboratory and was proven to be more convenient than Kolthoff's[11] for quantifying residual mercaptans in latices. In Kolthoff's technique, latices were coagulated in ethanol, were stirred vigorously using a high speed mixer, and were then titrated with $AgNO_3$. The titration was monitored by an amperimeter. In the present work, latices (3 mL) were directly dissolved

in 100 mL tetrahydrofuran, followed by titration with $AgNO_3$. Here again, a pair of silver-calomel electrodes was used. Gel permeation chromatography was used to determine the DP_n and the polydispersity index of polystyrene.

Polymerization Procedure

Batch and seeded semicontinuous emulsion polymerizations of polystyrene were carried out in a jacketed glass reactor (2 L), fitted with a stirrer and an inlet tube for nitrogen purge of the system. Also attached to it was a condenser in order to prevent the removal of volatile compounds. The recipes used are reported in Table II. The surfactant (SDS), the buffer (sodium bicarbonate), and the water were fed into the reactor and were kept at 70°C for about 20 min, followed by the addition of styrene and mercaptan. The latter caused a temperature drop. After the temperature came back to 70°C, the initiator (potassium persulfate) was introduced and polymerization started. All the operations, including polymerization, were carried out under nitrogen purge in order to avoid oxygen induced inhibition. For the seeded, semicontinuous polymerization runs, the seed was prepared following the recipe given in Table II. The seed amounted to 20% of the final latex weight. After about 98% conversion, a continuous feed of ingredients started. The feeding rate was slow enough for the polymerization to proceed under starved conditions.

Conversion Measurement

Conversion measurement was performed by sampling latex mixtures successively at chosen time intervals. They were weighed quickly (W_{wet}), and then were placed in a solution (1 mL), containing 0.1%

Table II   Recipes Used for the Batch and Semibatch Polymerization Experiments[a]

Components (g)	Batch	Semicontinuous Polymerization	
		Seed Formation	Continuous Feeding
Styrene	100	100	100
Deionized water	397.7	397.7	398.7
Sodium dodecylsulfate	2.00	2.00	1.00
Sodium bicarbonate	0.15	0.15	0.15
Potassium persulfate	0.15	0.15	0.15
Mercaptan	1.00	1.00	1.00

[a] The weights are based on part per hundred monomer (pphm).

by weight hydroquinone, in order to stop the reaction. After drying in a vacuum oven for 24 h, the samples were weighed again (W_{dry}). Because W_{wet} and W_{dry} included the weights of the surfactant, the buffer, the initiator, and the inhibitor, they were corrected for the calculation of the conversion of styrene into polystyrene:

$$p = \frac{W'_{dry}}{W'_{wet}/5} \times 100\% \qquad (3)$$

where the factor 5 takes into account the fact that the system is made of $\frac{1}{5}$ of monomer; W'_{wet} and W'_{dry} are the corrected weights for W_{wet} and W_{dry}, respectively.

EXPERIMENTAL RESULTS

Four tertiary mercaptans (C_9, C_{11}, C_{12}, and C_{13}) were studied as the chain transfer agents in the batch emulsion polymerization runs, while only C_9 and C_{12}-mercaptans were used in the seeded emulsion polymerization runs.

The conversion of styrene into polystyrene, the amount of residual mercaptans, the number average degree of polymerization (DP_n) and the polydispersity index of the resulting polymer for the batch experiments, are shown in Figures 1–4, respectively; those experiments, except for the polydispersity index for the seeded semicontinuous experiments, are shown in Figures 5–7, respectively.
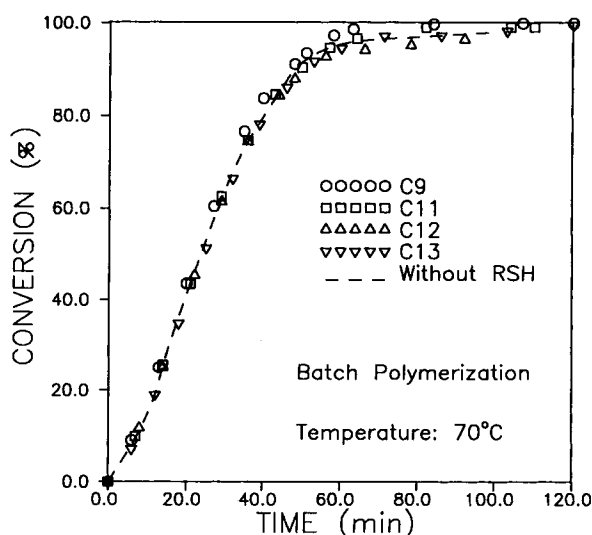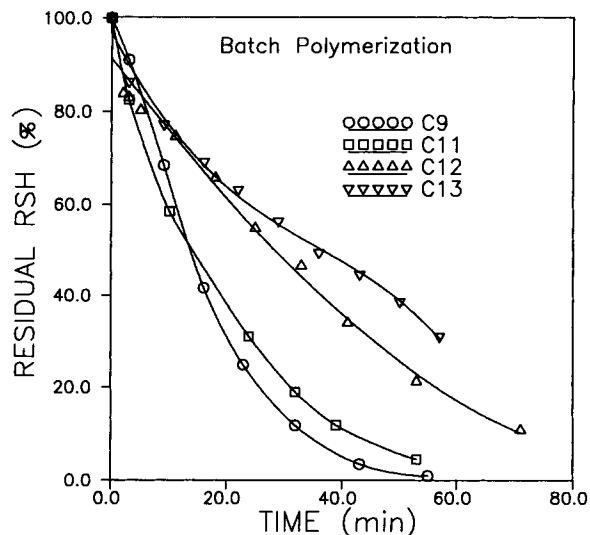

Figure 2   Residual mercaptans (%) vs. time for the batch experiments.

DISCUSSION

Batch Polymerization

Note first from Figure 1 that none of the four mercaptans (1 pphm) has a visible effect on the conversion rate of styrene. The consumption rate of mercaptan increases with decreasing carbon chain length (Fig. 2). This implies that the consumption rate of mercaptans is controlled by their diffusion rate from monomer droplets, where they reside at first, to growing latex particles through the aqueous
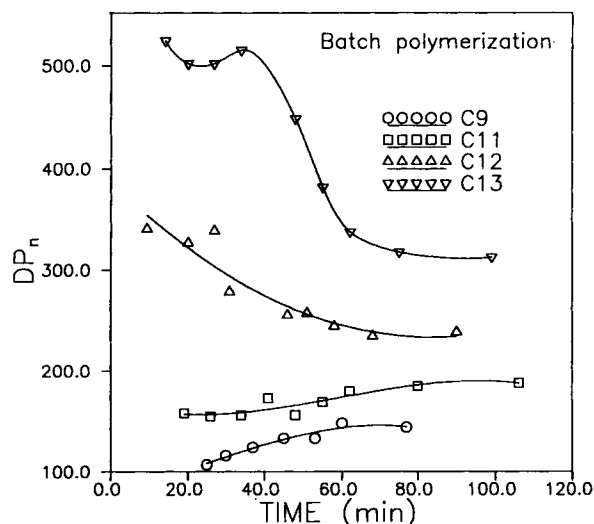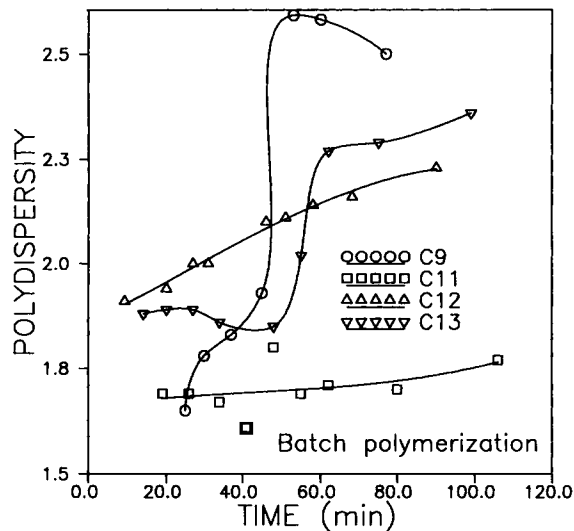

Figure 1   Effect of 1 pphm mercaptan on the styrene conversion for the batch experiments.

Figure 3   Effect of 1 pphm mercaptans on DP_n for the batch experiments.

Figure 4 Effect of 1 pphm mercaptans on the polydispersity index for the batch experiments.

Figure 6 Residual mercaptans vs. time for the semi-continuous experiments.

phase. Moreover, the partitioning ratio of mercaptans between the aqueous and the organic phases decreases with increasing carbon chain length, leading to a lower concentration of mercaptan in the aqueous phase. Therefore, the CTA tends to remain in monomer droplets instead of going into water. A lower concentration of CTA in the aqueous phase increases its diffusion length from the aqueous phase to the growing latex particles.

The consumption rate of CTA inherently has a direct effect on the number average degree of polymerization (DP_n). The faster the CTA reacts, the
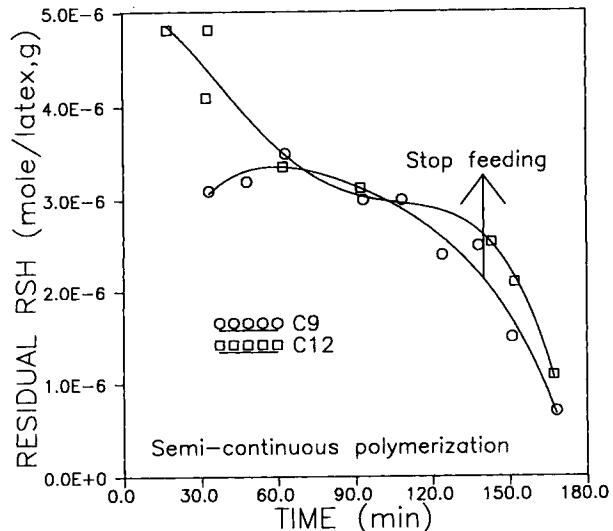
lower the DP_n. The DP_n of polystyrene increases with increasing carbon chain length of CTA from C_9 to C_{13} (Fig. 3) over the entire monomer conversion. It is also important to note that, for a given amount of mercaptan introduced in the batch recipe (1 pphm), the total depletion of CTA occurs at different monomer conversions, depending upon the CTA carbon chain length. This is better illustrated when the residual R-SH is plotted against the monomer conversion by combining the data in Figures 1 and 2 to obtain Figure 8. While the consumption rate of C_{11}-mercaptan matches that of the
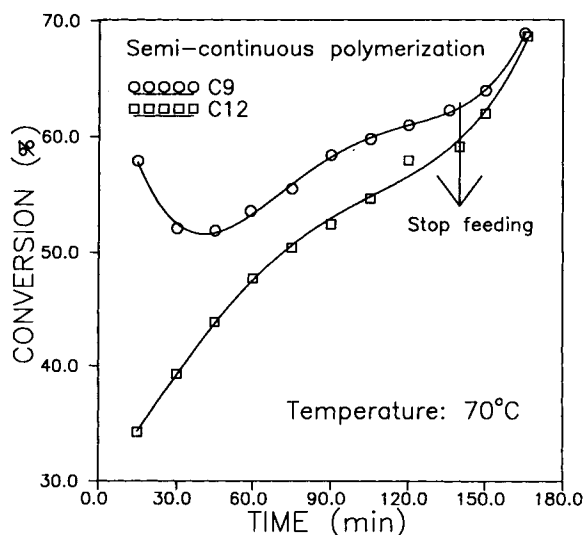

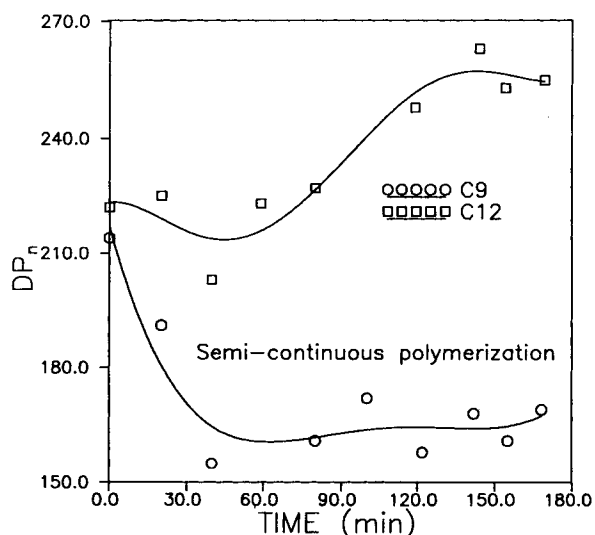**Figure 5** Styrene conversion vs. time for the semicontinuous experiments.

Figure 7 Effect of mercaptans on DP_n for the semicontinuous experiments.
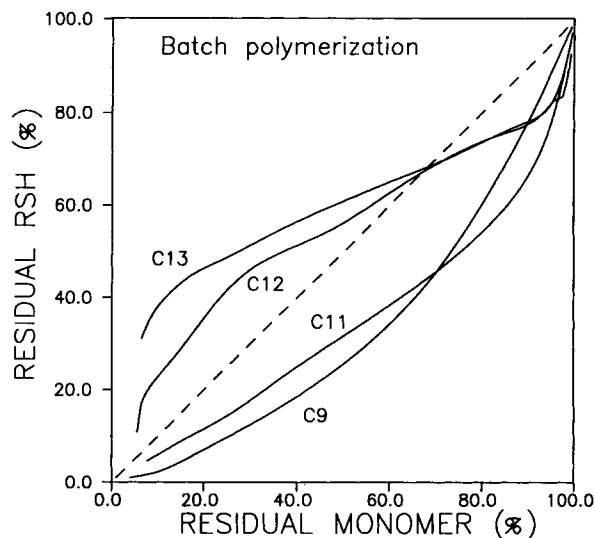
Figure 8 Residual mercaptans (%) vs. residual styrene (%) for the batch experiments. The solid lines are obtained by interpolation of the data in Figures 1 and 2.
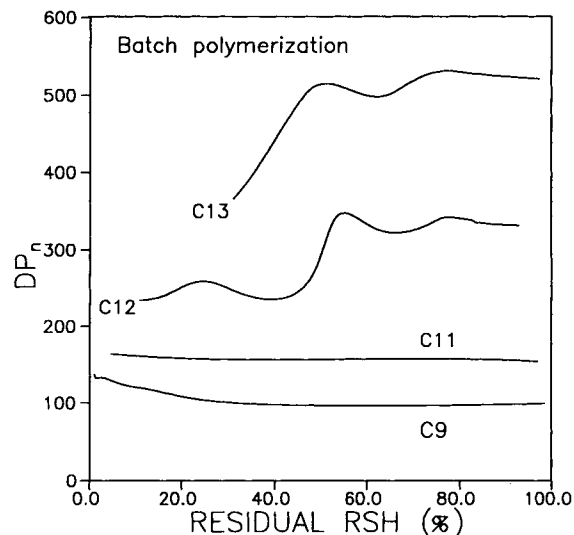

Figure 9 DP_n vs. residual mercaptans (%) for the batch experiments. The solid lines are obtained by interpolation of the data in Figures 2 and 3.

monomer during the entire polymerization process, except for the initial stage, that of C_{12} or C_{13}-mercaptan falls behind due to a lower reaction rate. On the other hand, the consumption rate of C_9-mercaptan exceeds that of the monomer. Thus, there is an accumulation of mercaptan at the end of polymerization in the case of C_{12} or C_{13}-mercaptan, and a lack of mercaptan in the case of C_9-mercaptan.

Obviously, the change in DP_n is affected directly by the behavior of mercaptans. When the consumption rate of mercaptan falls behind that of monomer, the DP_n is expected to decrease. The opposite result is expected when the mercaptan consumption rate exceeds that of monomer. These expectations were indeed verified experimentally and are shown in Figure 9, in which the DP_n of polystyrene is plotted against the residual mercaptan. The change in DP_n becomes more significant when the CTA is larger than the C_{11}-mercaptan. This is due to a more important accumulation of CTA at the end of polymerization.

A change in DP_n is accompanied by a change in polydispersity index. This is shown in Figures 3 and 4 and is better seen in Figure 10, in which the polydispersity index is plotted against the DP_n. This means that, in order for a polymer to have a narrow weight distribution and a constant DP_n during the entire emulsion polymerization process, the consumption rate of mercaptan should match that of monomer as closely as possible. Unlike C_9, C_{12}, and C_{13}, the use of C_{11} as the chain transfer agent yielded a polymer product with a quasiconstant DP_n and a

small polydispersity index. Correspondingly, of the four mercaptans investigated, C_{11}-mercaptan best meets this requirement. If this requirement is not satisfied, too high a C_S causes a severe increase in DP_n at the end of polymerization (in the case of C_9-mercaptan), and too low a C_S brings about a significant increase in DP_n (in the case of C_{13}-mercaptan). This teaches us that in order to reduce the polydispersity index of the final product, the initial concentration of CTA in the polymerization recipe has to be so chosen that the rate of depletion of
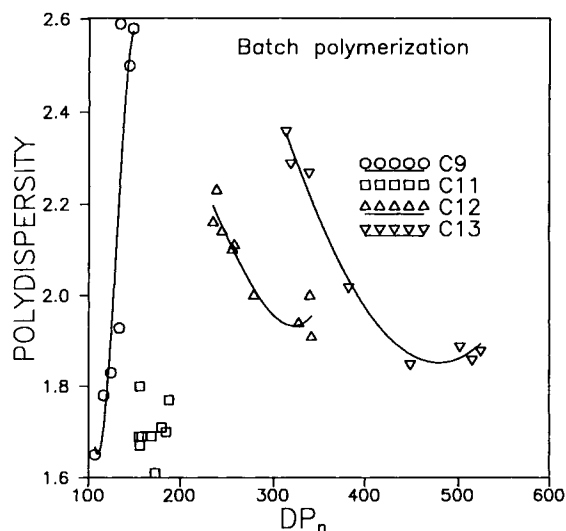

Figure 10 Polydispersity index vs. DP_n for the batch experiments.

CTA matches that of monomer. This is the case for the polymerization of styrene carried out with 1 pphm of C_{11}-mercaptan. In principle, the final DP_n of the polymer can also be chosen at will, but this is usually difficult to achieve without disturbing the polydispersity index. Industrially, it is more difficult to control both DP_n and polydispersity index, because mercaptans are generally mixtures of CTA.

It also can be noted that all the four chain transfer agents used in this study were consumed faster at the initial stage of polymerization (Fig. 9). This is possibly due to the presence of some CTA in the micelles prior to initiation. This amount of CTA is ready for reaction as soon as initiation starts, whereas CTA contained in the monomer droplets has to diffuse through the aqueous phase to reach the main reaction loci. Since the consumption rate of mercaptan in the early stage of polymerization is not in a steady state, C_S cannot be determined from the data generated during this period. The data generated at high monomer conversions are not good for the C_S determination either, because of a reduced polymerization rate induced by the depletion of monomer. These two phenomena can be seen by a shift of the slope of the plots [2 + $\log_{10}(S/S_0)$] vs. [2 + $\log_{10}(M/M_0)$] (Fig. 11). Theoretically, if the ratio between $\log_{10}(S/S_0)$ and $\log_{10}(M/M_0)$ is equal to unity ($C_S = 1$), the slope of the plot is not sensitive to monomer depletion, even at the end of polymerization. This is the case for the polymerization of styrene in the presence of C_{11}-mercaptan as the CTA (Fig. 11).
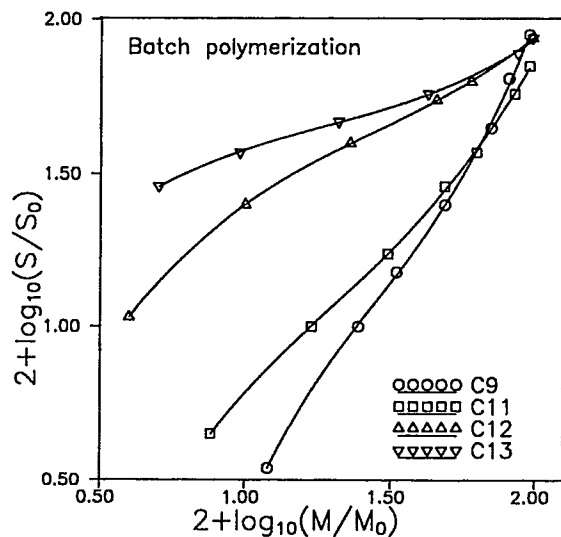
Table III   Mercaptan Reaction Constants, C_S, for the Fractionated Mercaptans in the Batch Polymerization

Mercaptan	C_S
C_9	2.00
C_{11}	1.00
C_{12}	0.51
C_{13}	0.29

The mercaptan reaction constant, C_S, for all the four mercaptans used in this study for the batch polymerization was determined from the slopes of the curves in Figure 11, when the ratio of the logarithm of the consumption rate of mercaptan to that of monomer was constant. The values are presented in Table III.

What still remains to be understood is how a bulky CTA accumulates during polymerization, especially at high conversions. A possible explanation is that, after the initiation period, the polymerization proceeds under the steady state conditions. During this period, the CTA resides in the monomer droplets. When the latter disappear, the CTA is squeezed out and forced to diffuse rapidly through water to the growing latex particles. This diffusion process is then controlled by the partitioning ratio of CTA between the aqueous phase and the particles containing swollen polymer. This sudden increase of CTA in the particles causes a significant increase in the transfer reaction rate of CTA at high monomer conversions.

Seeded Semicontinuous Polymerization

The seed (80 g) was prepared according to the recipe in Table II in the presence of the same mercaptan as that in the emulsion that was to be fed to the reactor continuously. The continuous feeding of emulsion began when the conversion of the seed polymerization reached 98%. In order to avoid the formation of new particles during the continuous feeding, the surfactant concentration in the emulsion (2.5 g per 1000 g water) was chosen to be below the critical micellar concentration (for SDS, it is 2.6 g per 1000 g water). The feeding rate was chosen to be 4.8 g/min, such that the system was under monomer-starved conditions. Scanning and transmission electron microscopes were used to count the number of the latex particles, and they confirmed that there were no new particles formed. Under those conditions, it is believed that the number of particles was

Figure 11   Determination of the mercaptan reaction constant, C_S, from the batch experiments: [2 + $\log_{10}(S/S_0)$] vs. [2 + $\log_{10}(M/M_0)$].

about the same as that of the above-mentioned batch system at a 20% conversion. The latex particle number is important because it determines the rate of diffusion of mercaptan through water into latex particles, and is necessary for calculating starved conditions in the seeded, semicontinuous process, based upon the kinetics of the batch system.

The relatively moderate increase in conversion (Fig. 5) as compared to the batch reactions, is due to the fact that the overall rate of polymerization is proportional to the number of latex particles per unit volume. Although in the semicontinuous polymerization, the number of latex particles is close to the batch systems, the continuous feeding of emulsion increases the overall volume of the system, reducing therefore the number of latex particles per unit volume.

As far as the concentration of mercaptan is concerned, a significant difference between C_9 and C_{12} mercaptans is noted at the beginning of the continuous feeding (Fig. 6). This is a result of the seed polymerization, which leads to an accumulation of mercaptan in the case of C_{12} and a depletion in the case of C_9. A plateau (roughly $2.5 \times 10^{-6} \sim 3.2 \times 10^{-6}$ mole R-SH per gram of latex) is observed for both mercaptans after about 60 min of reaction and before the cessation of feeding at 140 min, implying that the amount of mercaptans that is fed to the reactor is less than that in the latex particles by the diffusion process through the water phase. At this CTA concentration, the system is working under steady state conditions, that is, the mercaptan con-
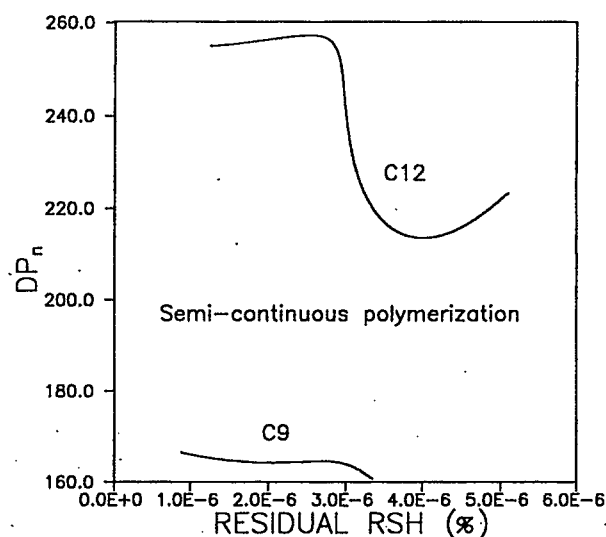
sumption rate matches its feeding rate. All the polymer molecules formed during this period are expected to have the same molecular weight. This is confirmed experimentally (Figs. 6 and 7), and is better illustrated in Figure 12, in which the DP_n is plotted against the residual mercaptan concentration. The difference of DP_n between C_9 and C_{12} is related to the mercaptan concentration difference in the reactor after seed formation.

During a seeded, semicontinuous polymerization of styrene, DP_n can be controlled by adjusting the concentration of mercaptan in the seed recipe and in the emulsion that is to be fed continuously. The feeding rate of mercaptan has to be controlled in order to meet appropriate concentration requirements. CTA-free seed and mercaptan starved feeding are the conditions that lead to a low polydispersity index.

CONCLUSION

The aim of this work was to investigate the behavior of four chain transfer agents containing, respectively, 9, 11, 12, and 13 carbons in emulsion polymerization processes. Those chain transfer agents were obtained by fractionating industrial products through an optimized distillation process under vacuum and nitrogen, and they contained 95% C_9, 93% C_{11}, 97% C_{12}, and (11% C_{10} + 2% C_{11} + 42% C_{12} + 45% C_{13}), respectively. Batch and semicontinuous emulsion polymerizations of styrene were chosen as the processes. The batch process allowed for the determination of their apparent chain transfer constants, C_S, which decrease with increasing chain carbon length, as does the chain transfer efficiency. The latter corresponds to a decrease in the diffusion rate of mercaptan to the reaction sites (latex particles) through the aqueous phase when the mass molecular weight of the chain transfer agent increases.

It was shown that the ratio of the consumption rate of mercaptan, over that of monomer, determines directly the change of the number average degree of polymerization, DP_n, and the polydispersity index. If the ratio is greater than unity ($C_S > 1$), the mercaptan will be totally consumed before the polymerization is over, thus DP_n increases. This is the case for C_9 mercaptan. If the ratio is less than unity ($C_S < 1$), the monomer will be totally polymerized before the mercaptan is depleted. DP_n then decreases, as is the case for C_{12} and C_{13}. In order to obtain a constant DP_n, the ratio should be as close

Figure 12 DP_n vs. residual mercaptans (%) for the semicontinuous experiments. The solid lines are obtained by interpolation of the data in Figures 6 and 7.

to unity as possible, and the results with C_{11} (C_S = 1) confirmed the point. It was shown that a change in DP_n is always accompanied by a change in polydispersity index. Our results showed that it is virtually impossible to obtain a polymer product with a prerequested DP_n and a narrow weight distribution.

The semicontinuous experiments showed that the behavior of the chain transfer agents, C_9 and C_{12}, is identical to that in the batch polymerization. This implies that, again, the kinetics of chain transfer are mostly controlled by the rate of diffusion of mercaptans to the latex particles through the aqueous phase.

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