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Chain Transfer of Telogens with Styrene in Bulk and Emulsion Systems

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ABSTRACT

The chain transfer constants for selected telogens were determined with styrene in both bulk and emulsion polymerization systems. Since the locus of chain transfer, like polymerization, is primarily in the micelles or polymer particles, the chain transfer constants of water-insoluble telogens were similar in both systems. However, these values were different for water-soluble telogens and the difference was greatest for the most soluble telogens. The ratio of the chain transfer constants in bulk and emulsion systems is apparently related to the solubility parameters of telogens in a homologous series.

INTRODUCTION

It is generally accepted that the locus of polymerization of water-insoluble monomers in emulsion systems is primarily in the micelles or polymer particles [1]. It is also recognized that the polymerization of more water-soluble monomers in emulsion systems takes place both in the micelles and in solution.

Polymerization reactions in bulk and emulsion systems may also involve metathetical reactions in which the propagating macroradical is terminated by coupling with radicals that are abstracted from the initiator, monomer solvent, polymer, or other foreign substance. The new free radical which is produced by this abstraction may initiate a new chain reaction which may or may not have a propagation probability similar to that in which the original macroradical was produced. Thus Flory [2] defined this chain transfer as a reaction in which the growth of individual polymer molecules is limited but the number of active centers remains unchanged.

Additives under the names of chain transfer agents, telogens, regulators, or modifiers are widely used for the control of molecular weight and for the production of telomers. The values for the chain transfer constants for a large number of telogens have been published [3]. Most of these constants were obtained by bulk polymerization of specific monomers in the presence of varying concentrations of telogens while keeping all other variables constant.

While the chain transfer constants of several organic sulfur telogens [3] and benzene derivatives with styrene [4] have been reported for emulsion polymerizations, the corresponding values for bulk polymerization are not readily available. However, it has been reported that when all the telogen is dissolved in the polymer particles the chain transfer constant for octyl mercaptan is similar for bulk and emulsion systems at zero conversion [5]. The chain transfer constants for benzene with styrene have been reported as being 4×10^{-6} and 2×10^{-4} in bulk and emulsion, respectively [6].

The chain transfer constants of a water-insoluble telogen should be similar in bulk and emulsion systems providing the chain transfer with water is neglible. However, water-soluble telogens, like water-soluble monomers, should behave differently in emulsion than in bulk polymerization systems. This investigation was undertaken in order to determine the chain transfer constants of selected telogens in bulk and emulsion polymerization systems with the objective of showing that the locus of chain transfer in emulsion systems was primarily in the micelles or polymer particles.

DISCUSSION

It has been maintained that chain transfer to azobisisobutyronitrile is neglible, but Pryor [7] has shown that this initiator does have an appreciable chain transfer constant with styrene. This initiator was used in this investigation but since its concentration was constant, its effect in the bulk systems would be consistent. Likewise, there is some chain transfer to emulsifiers [8] but since the emulsifier content was constant, this effect in the emulsion polymerization systems in this investigation should be consistent.

It has been previously reported that there is little chain transfer to water [9, 10]. However, as shown in Table 1, the chain transfer constant for water to styrene in bulk polymerizations is measurable. The presence of the hydroxyl groups on the polystyrene produced can be demonstrated by a dyeing technique [11]. However, as shown in Table 1, no transfer to water was noted in emulsion polymerization and hence this effect is not significant in this investigation.

As evident from the Mayo equation [12]

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} - C_S \frac{[\text{telogen}]}{[\text{styrene}]}$$

the chain transfer constants (C_S) for styrene in both bulk and emulsion polymerization systems are dependent on the concentration of the styrene monomer and the telogen. Since the accessability of styrene to the locus of polymerization would be similar for comparable emulsion systems, the most important factor in these polymerizations would be the difference in the solubility parameter (δ) of the telogen and water [13]. It has been noted previously that the chain transfer constants for alkyl mercaptans in emulsion polymerization systems were related to their solubility [14, 15].

As shown in Table 1, the chain transfer constants for 1-propanethiol, 1-decanethiol, and carbon tetrachloride with styrene were similar for both bulk and emulsion systems. The differences between the chain transfer constants for other telogens in bulk and emulsion systems were related to the water solubility of the telogens. While there are not enough data to

TABLE 1. Chain Transfer Constants with Styrene in Bulk and Emulsion Systems

Telogen	Chain transfer constant C_S (10^4)		Solubility parameter (δ) telogen	$\frac{C_S \text{ bulk}}{C_S \text{ emulsion}}$
	Bulk	Emulsion		
Water	0.06	0.0	23.4	-
Methanol	2.96	0.16	14.5	19.0
Ethanol	16.11	2.76	12.7	5.8
Butanol	10.66	2.63	11.4	4.0
2-Methyl-1-propanol	4.97	1.49	10.5	3.1
Dodecanol	10.92	3.30	8.2	3.3
2-Butanol	5.62	1.29	10.8	4.4
2-Methyl-2-propanol	24.76	6.56	10.6	3.7
Ethylene glycol	13.31	0.19	14.6	71.0
Glycerol	28.64	0.3	16.5	95.0
1-Propanethiol	21,800	21,100	8.7	1.0
1-Decanethiol	17,100	16,200	6.6	1.1

Butylamine	7.00	1.20	8.5	5.8
Diethylamine	25.61	7.00	7.9	3.6
Triethylamine	17.17	6.00	7.4	2.8
Acetic acid	5.42	0.2	10.7	27.1
Octanoic acid	13.26	2.23	7.1	5.9
Monochloracetic acid	28.60	0.76	11.8	37.6
Dichloroacetic acid	35.00	1.0	11.5	35.0
Trichloroacetic acid	100.00	3.37	10.8	29.7
Ethyl acetate	5.70	1.52	6.8	3.7
Amyl acetate	17.83	3.87	8.1	3.9
Diethyl malonate	2.70	0.64	8.9	4.2
Carbon tetrachloride	144.08	130.89	8.6	1.1

justify drawing curves, the ratio of the chain transfer constants in bulk and emulsion systems is apparently related to the solubility parameters of telogens in a homologous series.

EXPERIMENTAL

Bulk polymerizations of styrene were conducted at 60°C in the presence of 2.5% azobisisobutyronitrile and with varying amounts of telogen. These telogens were also present when styrene was polymerized in emulsion at 60°C in the presence of potassium persulfate and a nonionic emulsifier.

The polymeric product was removed from these systems in the early stages of polymerization by precipitation or coagulation. The limiting viscosity number $[\eta]$ of benzene solutions of these polymers was calculated from the following relationship for the specific viscosity (η_{sp}), the relative viscosity (η_{rel}), and the concentration (C):

$$[\eta] = \frac{\eta_{sp} + 3 \ln \eta_{rel}}{4C}$$

The average degree of polymerization ($\overline{DP}$) was calculated from the limiting viscosity number of the benzene solutions using the equation: $\overline{DP} = 3.205 + 1.37 \log [\eta]$. A Fortran IV computer program was written as a computational aid for speed and accuracy. The least squares method was used for the calculation of the slope (C_s) and the intercept ($1/\overline{DP}_0$) in the Mayo equation given in the Discussion.

The presence of carboxyl groups in the telomers was verified by dye formation [10]. The presence of hydroxyl groups was demonstrated by dye formation of the reaction product of the telomer and maleic anhydride. The presence of other groups was determined by noting peaks not attributable to polystyrene in the pyrolyzates of the telomers. The areas of these peaks increased linearly as the concentration of telogens was increased [16].

Pyrolyzates were obtained by coating a platinum coil with a benzene solution of the telomers and characterizing the off-gases from the heated coil using a Wilkins Instrument and Research, Inc., Model A100C Chromatograph. Chromosorb W with 20% SE52 coating was used in a 3.05 m × 6.35 mm copper column with helium as the carrier gas. The pyrolyzates were identified by a comparison of the retention times of known compounds.

CONCLUSIONS

The chain transfer constants of water-insoluble telogens were similar when styrene was polymerized in either bulk or emulsion systems. These values differed when more water-soluble telogens were used. The ratio of the chain transfer constants in bulk and emulsion systems is apparently related to the solubility parameters of telogens in a homologous series.

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