An experimental study of the effect of polymer molecular weight upon reaction rates in emulsion polymerization*

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Seed latices of poly(methyl methacrylate) of varying molecular weights, but of equivalent particle sizes, have been used to investigate the dependency of the reaction rate upon the polymer molecular weight. It was found that the molecular weight of the seed polymer and that of the polymer formed in the subsequent reaction both affected the reaction rate, with the latter effect more significant than the former. Reaction rates were found to decrease substantially as the polymer viscosity average molecular weight decreased from 5.8 to 0.4 million. These results are discussed in terms of the differences in the degree of entanglements of the various lengths of the polymer chains.

(Keywords: emulsion polymerization; kinetics; molecular weight; chain entanglements; poly(methyl methacrylate))

INTRODUCTION

It has been clear for some time that the Tromsdorff gel effect causes not only accelerating reaction rates but also simultaneous and dramatic increases in polymer molecular weight. Balke and Hamielec[1] have presented a wide range of data which clearly show these effects in the bulk polymerization of methyl methacrylate (MMA). More recently researchers such as Marten and Hamielec[2] and Soh and Sundberg[3] have offered descriptions of termination rate constants which are chain length dependent. While all of this work has been applied to bulk polymerization, there have been no detailed studies reported of the inter-relationship of the reaction rate and polymer molecular weight in latex systems. It is also of interest to note that some chain transfer agents used to substantially change the molecular weight of emulsion polymers have also appeared to have caused reductions in the reaction rate. Occasionally these chain transfer agents have been labelled as non-ideal by producing free radical groups with less inherent reactivity than those of the monomer and polymer. Another interpretation[4,5] has been that the oligomeric radicals produced by the chain transfer process can escape from the latex particles and cause a decrease in the number of free radicals in the particle. With this as background, the present study was undertaken to provide some experimental evidence of this effect in emulsion polymerization. The system chosen for study was that of MMA because it has such a strong gel effect and should thus offer a good chance to observe such effects. The technique used was to prepare several seed latices of widely different molecular weight (by using chain transfer agents in the base latex formulation) but at the same particle size, and then to observe the polymerization rate behaviour of subsequently added monomer under exactly the same reaction conditions.

The basic premise of this study was that the termination rate constant, k_t, is chain length dependent and that lower molecular weight polymer chains entangle less extensively than longer ones, thereby leading to higher values of k_t. In turn, the higher value of k_t should lead to lower radical populations in the particles (i.e. lower values of $\bar{n}$) and thus to lower reaction rates. However, as pointed out above, it must also be recognized that if the molecular weight is decreased by adding a chain transfer agent, it is likely that desorption of short, chain transferred radicals will increase and lower $\bar{n}$. This result has recently been reported for small particle sized latices (*ca.* 500 Å) by Lichti *et al.*[4] and (*ca.* 600–700 Å) by Lee and Poehlein[5]. In order to avoid this simultaneous effect, the present study made use of larger particle sized seed latices (1100–2000 Å) whose surface to volume ratio is such that radical desorption has much less effect upon the reaction kinetics. This would place these systems in the area of Ugelstad's[6] $\bar{n}$ vs. α' plot (for negligible water phase radical termination) in which α' is greater than about 0.10. It is acknowledged that if water phase radical termination is very significant, then one would have to consider both radical desorption and molecular weight effects.

EXPERIMENTAL

Seed latices were prepared by using standard batch and semi-continuous feed reaction techniques. Sodium lauryl sulphate was used as the only surfactant and potassium persulphate was used as the initiator. At the end of the seed latex preparation (carried out at 50°C), the latex was heated to 95°C for about an hour to deplete the unused initiator. The seed latices were produced at the same particle size but at differing polymer molecular weight by the use of tertiary dodecyl mercaptan (t-DM) as a chain transfer agent. These seed latices were subsequently swollen with fresh MMA monomer to the extent of 150 parts per hundred parts polymer. These latices were then

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cooled from room temperature to 5°C to prevent any polymerization from occurring when the initiator solution was added (this also at 5°C). Latices prepared in this fashion were added to tubular glass reactors (5 mm o.d. and 3 mm i.d.), sealed under vacuum and plunged into a water bath at 50°C to carry out the reaction. Each tube contained enough latex to provide a solids level determination (for measuring conversion level) and to yield polymer for molecular weight determination via dilute solution viscometry. The use of these tubular reactors ensured excellent temperature control even for very rapid reaction rates. The seed latices thus prepared are described in *Table 1*.

The experimental space studied may be best viewed in matrix form. The seed latices were made at three different polymer molecular weights (High—5.8 million, Medium—1.2 million, and Low—0.4 million) and the polymer subsequently formed also produced at these three molecular weights. This gave a possibility of nine separate experiments and are designated below by the notation:

High Molecular Weight polymer formed in High Molecular Weight seed - H/H; Low Molecular Weight polymer formed in High Molecular Weight seed - L/H; etc.

The experimental matrix appears as:

H/H	H/M	H/L
M/H	M/M	M/L
L/H	L/M	L/L

with columns representing experiments utilizing the same seed latices in the presence of which polymer of varying molecular weight is produced, and rows representing different seed latices in the presence of which polymer of the same molecular weight is formed. All these reactions were carried out under the same exact conditions of solids and initiator levels, and temperature (50°C).

One unfortunate aspect of the use of t-DM was that it could not be stripped out of the M and L seed latices after their preparation. This prevented the formation of high molecular weight polymer in the presence of a low or medium molecular weight seed. Thus the actual experimental matrix was:

H/H		
M/H	M/M	
L/H	L/M	L/L

RESULTS

Matrix experiments were carried out for seed particle sizes at both 1100 Å and 2000 Å. The swollen particle diameters were approximately 26% larger than the seed particles and together with the other experimental parameters yielded values of α' of 1.0 or greater at the beginning of the reaction. Due to the presence of the gel effect in each experiment the value of α' increased with conversion and thus ensured that radical desorption need not be considered in assessing the reaction kinetics. This is corroborated by the results of measurements by Ballard, Napper and Gilbert[8] from which they concluded that even for much smaller PMMA latex particles than used here, virtually all of the desorbed free radicals undergo subsequent re-entry. Thus, the desorption phenomenon, while present, is not rate determining.

Table 1 Characteristics of seed latices

Particle diameter[a] (Å)	t-DM level (pphpm)[b]	Polymer mol.wt. × 10^{-6} (viscosity average)[c]
1180	zero	5.8
1150	0.45	1.2
1090	0.75	0.39
2000	zero	5.7
2000	0.75	0.34

[a] Measured via turbidity
[b] Parts per hundred parts monomer
[c] Measured in MEK at 30°C. Mark–Houwink constants[7] of $a=0.72$, $K=6.9\times10^{-5}$

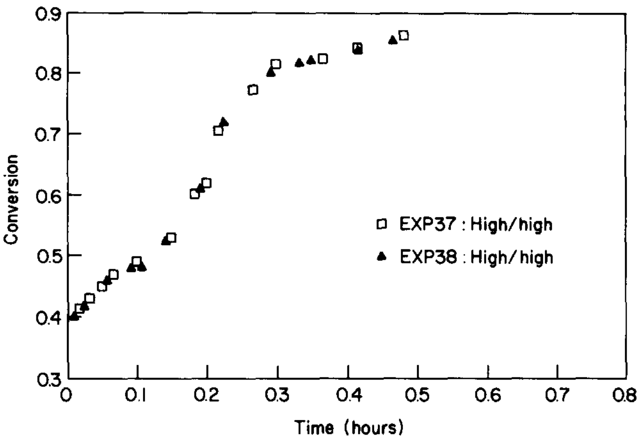

Figure 1 Reproducibility of experimental data

The reproducibility of the experimental data can be assessed from *Figure 1*, which shows duplicate runs of the H/H experiment (no t-DM) at the 1100 Å seed particle size. Since some of the differences in conversion profiles for the matrix experiments using the 1100 Å seed latices may not be too great, this level of reproducibility is important. Both sets of data in *Figure 1* were corrected[9] for inhibition which is present at the beginning of all the reactions. The small differences between the seed latex particle sizes at the 1100 Å range (i.e. 1180, 1150 and 1090 Å seen in *Table 1*) can be shown to lead to only 2 or 3% difference in rates when all other parameters are the same. This results because the experiments were all carried out at values of α' greater than unity. One may notice that the data in *Figure 1* and subsequent Figures indicate a conversion level of 40% at the start of the experiment, rather than 0%. This is because 'conversion' in this study using seed latices has been determined as the total weight fraction of polymer at any time during the experiment. By using a formulation of 150 parts of monomer per 100 parts of seed polymer, this gives a weight fraction of polymer of 0.4 at the beginning of the experiment. The reason for doing this is that it puts the conversion–time plot on the same basis as those experiments which start with only monomer.

In general terms it was anticipated that the reaction rates would be slower as one moves down a column of the experimental matrix and as one moves to the right along a row of the matrix. Thus the H/H run should be the fastest and the L/L run should be the slowest. *Figure 2* shows the results for column 1 using the high molecular weight seed latex producing post-formed polymer at high, medium and low molecular weights. The lower molecular weights were produced by adding t-DM to the monomer used to swell the H seed latex. As expected, the rates decreased as the post-formed polymer molecular weights decreased.

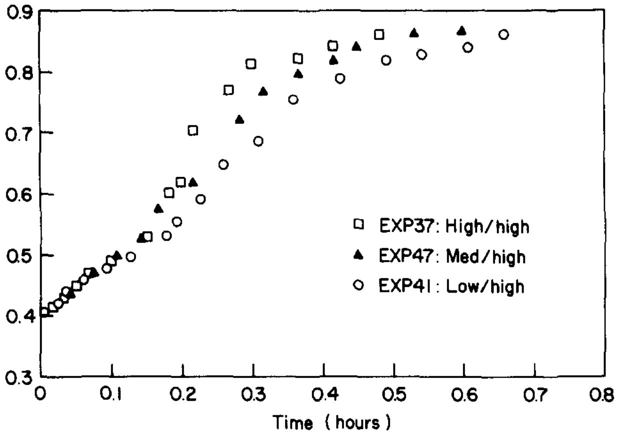

Figure 2 Conversion profiles for column 1 experiments, H/H, M/H and L/H

Table 2 Molecular weights of seed and combined seed/post-formed polymers

Experiment	Seed M.Wt. (measured)	Post-formed M.Wt. (expected)	Combined M.Wt. (measured)
H/H	5.8×10^6	5.8×10^6	6.0×10^6
L/H	5.8×10^6	0.39×10^6	2.1×10^6
L/L	0.39×10^6	0.39×10^6	0.41×10^6

Although polymer fractionation was not performed prior to measurement of the combined seed and post-formed polymer molecular weight, the combined viscosity average molecular weight of the resultant L/H emulsion polymer was 2.1 million vs. the 5.8 million of the seed polymer. This contrasts with the measurement of the combined molecular weights of the H/H polymer as 6.0 million vs. the 5.8 million of the H seed and the expected 0.39 million of the post-formed polymer in the L/H experiment. *Table 2* shows the measured molecular weights for the seed and combined polymers of several experiments in the matrix.

The bottom row experiments represented the formation of equivalent molecular weight post-formed polymer in the presence of various molecular weight seed polymers. In these experiments the same level of t-DM was used in each. The conversion profiles are displayed in *Figure 3* and show lower rates associated with lower molecular weight seed polymers, although the differences in rates between the row experiments are more subtle than those in the column experiments. Since the chain length of the growing macroradicals in each of the L/H, L/M and L/L experiments should be the same, the results in *Figure 3* suggest that the chain length of the diluent polymer can affect the rate. This result was not entirely expected but appears to be real.

The combined effect of varying seed molecular weight and post-formed molecular weight can be seen from the diagonal set of experiments H/H, M/M and L/L. Here the post-formed and pre-formed molecular weights were measured to be the same, as shown in *Table 2*. *Figure 4* displays the conversion profiles and shows a very significant dependency of rate upon molecular weight. Since the seed and post-formed polymer molecular weights were varied in the same direction, it appears that the individual contributions of the diluent and growing polymer chains to reaction rate control combine in a synergistic fashion. This produces rate differences between experiments along the diagonal in the matrix that are greater than either of those seen along a row or a column.

In order to test whether the pre-formed and post-formed polymer contribute independent effects upon the reaction rate, a comparison should be made between the L/H and M/M experiments. Here the respective changes between seed and post-formed polymer vary in opposite directions. *Figure 5* displays the results of these two experiments and indeed shows a significant degree of counteraction, as opposed to the synergism seen in *Figure 4*.

Larger sized seed latices were also made in order to increase the difference in the rates seen as molecular weight was changed in the smaller sized latices. An H seed was produced at 2000 Å and 5.7 million molecular weight and an L seed was produced at the same particle size but at 0.34 million molecular weight. The resultant conversion profiles for H/H and L/L experiments are shown in *Figure 6*, where the difference in the two curves is quite dramatic. It is also noted in passing that the seed latices produced at 2000 Å utilized the same levels of t-DM as did the seed latices at 1100 Å and resulted in the same molecular weights (see *Table 1*). This is consistent with the idea that emulsion polymer molecular weights are predominantly controlled by chain transfer processes rather than chain termination processes.

DISCUSSION

The data presented in this study indicate that there

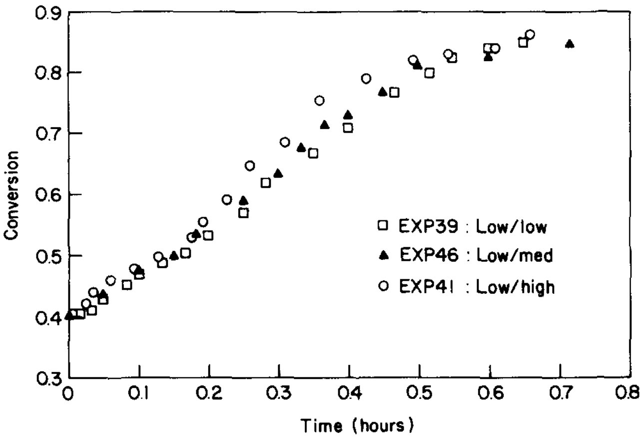

Figure 3 Conversion profiles for bottom row experiments, L/H, L/M and L/L

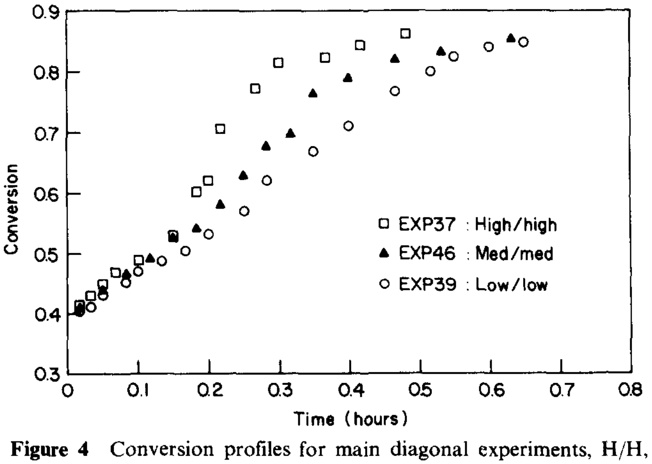

Figure 4 Conversion profiles for main diagonal experiments, H/H, M/M and L/L

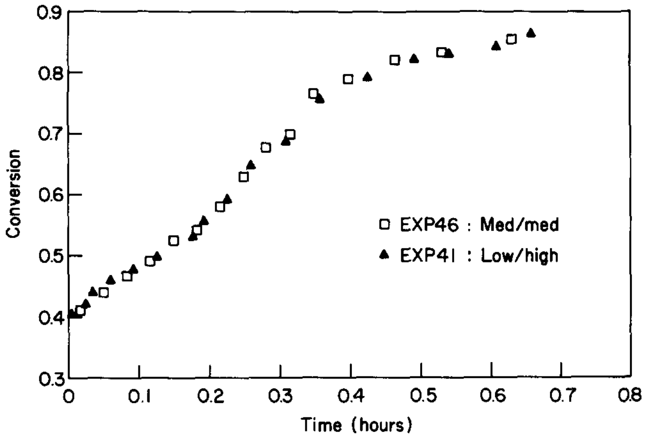

Figure 5 Conversion profiles for cross-diagonal experiments, L/H and M/M

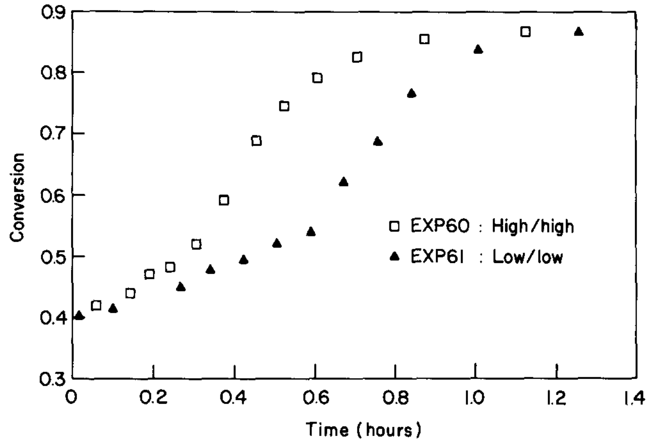

Figure 6 Conversion profiles for large particle sized latices, H/H and L/L

appears to be no doubt that polymer chain length can substantially affect emulsion polymerization kinetics. Since it has been shown that desorption of oligomeric free radicals from latex particles is not a rate determining step for these experiments, one must attribute these rate differences to changes in the termination rate between free radicals. This in turn supports the idea that the termination reaction rate should be chain length dependent. As noted earlier, both Marten and Hamielec[2] and Soh and Sundberg[3] have offered models of the termination rate process in free radical polymerization which are molecular weight dependent, the latter description using the concept of chain entanglements of the macroradical chain to describe this dependency. This chain entanglement concept has also led to the idea that beyond a certain level of chain entanglements the termination rate process loses its chain length dependency, being controlled instead by the movement of the radical chain end due to the propagation steps[3]. Thus what is envisaged is a termination rate process which has no chain length dependency when the chains are too short to entangle significantly (never seen in emulsion polymerization but frequently encountered in bulk, solution and suspension polymerization), no chain length dependency when they are very highly entangled, and significant chain length dependency at intermediate levels of entanglement. The data presented in this study fall into the last category of entanglement density, at least during the early part of the reactions. Later in the reactions the entanglement density may have become so high that the termination rate loses its chain length dependency. This may be the case for the data in *Figure 6*, which shows a very significant rate (slope of the conversion–time curve) difference early in the reaction and a very small rate difference at about 65% conversion. Further studies in this laboratory are directed towards applying the chain entanglement based model[3] to these data, although it appears that more precise data will be required in order critically to evaluate the contribution of the pre-formed molecular weight to the overall control of the termination process.

In conclusion, the authors suggest that for most practical emulsion polymerization systems it should be common to find rate reductions when chain transfer agents are added to an otherwise high molecular weight system. Tulig and Tirrell[10] have made similar comments for bulk polymerizations when chain transfer reactions are made to be more prominent. The rate reductions seen in emulsion polymers may also be different depending upon particle size due to the nature of the dependency of the free radical population, $\bar{n}$, upon the characteristics of the system as seen through plots such as presented by Ugelstad[6]. In general it would appear that rate reductions seen in large particle sized latices are due primarily to molecular weight effects, while those occurring in small particle sized latices may be due to the combined effect of molecular weight and radical desorption.

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