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Kinetic Aspects of Styrene Polymerization with an Acyloxyamine

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The present paper evaluates largely unstudied kinetic aspects of styrene polymerization with a (relatively new) acyloxyamine over several temperature levels and contrasts these features with regular styrene polymerization and styrene polymerization with TEMPO. These comparisons show that the system behaves rather like regular thermal polymerization of styrene at temperatures between 120–180°C. However, at higher temperatures (> 180°C), acyloxyamine has an initiator-like contribution, giving the rate of polymerization an extra boost while decreasing molecular weights. This is further corroborated by mathematical modeling for both conversion and molecular weight averages.

Keywords: Acyloxyamine, styrene, thermal polymerization, polymerization kinetics

1 Introduction

Hindered amines have various applications as "chemical additives." They are well-known as powerful stabilizers to protect plastics from the negative influence of light and heat. Recently, tailor-made hindered amines have been introduced with applications beyond stabilization. By adjusting the structure and the substitution pattern adjoining the functional group, these nitroxyl compounds can have a broad area of application. For example, they can be used as flame retardants, as mediators in controlled radical polymerization (CRP), and as alternatives to peroxides for degradation of polypropylene (PP) (1).

PP degradation for production of controlled-rheology polypropylenes (CRPP) is well established and has been studied extensively (2–4). This process (industrially referred to as "vis-breaking") is usually done in an extruder at elevated temperatures by adding peroxides as a source of radicals, which effect the breakdown of the chains. The most common free radical initiators used in CRPP production are mono- and di-functional peroxides. Recently, work carried out in our group studied the effect of a tetra-functional initiator in CRPP (5) in order to investigate whether branching could also be imparted by a tetra-functional peroxide. However, a peroxide-free process is more desirable from the perspective of chemicals, handling, safety and potentially improved product quality. As a result, a relatively new hindered amine (trade name Irgatec CR76) with the structure of an acyloxyamine has been tailor-made by Ciba Specialty Chemicals (now part of BASF, however referred to as Ciba throughout the text herein) and potential uses of this chemical in PP degradation have been described by Pfaendner et al. (1, 6). Aside from the preliminary proprietary Ciba evaluations, use of this radical generator as a potentially safer radical source in CRPP production was recently investigated by Psarreas et al. (7) and the effect of processing temperature and acyloxyamine concentration on molecular weight averages, molecular weight distribution and rheological properties was reported.

In Pfaendner (1), several potential uses of the new acyloxyamine along with other radical generators are briefly mentioned, however, detailed kinetic investigations and information in the literature are scarce. Hence, given the prior experience we have had with the acyloxyamine, described in (7) but for a totally different application, the next logical step was to evaluate largely unstudied kinetic aspects of this new acyloxyamine for polymerization applications. In this paper, a kinetic study of styrene polymerization with the acyloxyamine (from now on simply referred to as AcAm)

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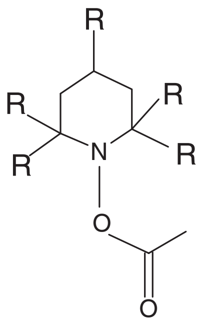


Fig. 1. Structure of acyloxyamine (AcAm).

Table 1. Summary of experimental runs

EXP #	*Recipe*	*T (°C)*	*Initial Concentration, M*
1	STY + AcAm	120	$[AcAm]_0 = 0.036$
2		150	$[AcAm]_0 = 0.036$
3		180	$[AcAm]_0 = 0.036$
4		210	$[AcAm]_0 = 0.036$
5		230	$[AcAm]_0 = 0.036$
6	STY + TEMPO	120	$[TEMPO]_0 = 0.0396$
7		180	$[TEMPO]_0 = 0.0396$
8	STY	120	-
9		210	-

is presented and the results are contrasted with regular free radical styrene polymerization (as in Gao and Penlidis (8)) and also with styrene polymerization under controlled radical conditions (as in Nabifar et al. (9)).

2 Experimental

2.1 Reagent Purification

Styrene (Aldrich Canada Ltd., Oakville, ON) was washed three times with a 10 w/v % sodium hydroxide solution and three times with distilled water, dried over calcium chloride and distilled under vacuum. Solvents (tetrahydrofuran, ethanol, dichloromethane, and acetone) needed during experimental analysis were used as received. Both benzoyl peroxide (BPO) initiator and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) controller were used as received from suppliers (ATOFINA Chemicals, King of Prussia, PA and Aldrich, respectively) without further purification.

The hindered amine (structure shown in Figure 1) was also used as received. It is a sterically hindered N-acyloxyamine in the form of a stable concentrate with a molecular weight of 638 g/mol. It has low volatility and can be safely transported or stored at ambient temperature.

2.2 Polymer Synthesis and Characterization

Experimental steps, namely, polymer synthesis (procedures and recovery of the polymer product from ampoules) and polymer characterization, carried out for the experiments reported herein, were the same as described previously in Nabifar et al. (9, 10), hence not reported again for the sake of brevity.

2.3 Summary of Experiments

Table 1 summarizes the operating conditions of experimental runs. To investigate polymerization kinetics, runs 1 to 5 were conducted with styrene and AcAm (with the AcAm concentration being at a level typical of what is employed for peroxides). Run 1 was conducted at 120°C, while runs 2, 3, 4 and 5 were conducted at 150, 180, 210 and 230°C, in order to investigate the effect of temperature and relate to other styrene polymerization conditions.

For comparison purposes, regular (purely) thermal polymerization of styrene was conducted in the absence of initiator or AcAm at 120 and 210°C (runs 8 and 9, respectively). Experimental data for thermal polymerization of styrene at 180 and 230°C were borrowed from Gao and Penlidis (8). For additional comparisons, runs were conducted with styrene but in the presence of TEMPO (a frequently used mediator in nitroxide-mediated radical polymerization (NMRP)), at 120 and 180°C (runs 6 and 7, respectively). The initial TEMPO concentration for these runs was as typically used in NMRP processes (9, 10).

3 Results and Discussion

Figure 2 shows conversion vs. time data for styrene polymerization with 0.036 M of the acyloxyamine at different temperatures (runs 1 to 5 of Table 1). It can clearly be seen that increasing the temperature increases the rate of polymerization (as expected for any radical polymerization). Rate of polymerization is extremely fast at higher temperatures, especially at 210 and 230°C in which polymerizations are completed almost after 20–30 minutes. The insert in Figure 2 shows the first 100 min of the reaction. It can be seen that for example, after 30 min, conversion is 6% for 120°C, 27% for 150°C, 77% for 180°C and 99% for both 210 and 230°C. Comparing further the runs at 210 and 230°C, one can see in the insert of Figure 2 that in the first 10–15 min of the reaction, the rate of polymerization at 210°C is only slightly lower than the rate at 230°C, however, after that initial stage, the profiles of conversion vs. time for these two temperatures are overlapping. These observations suggest that at temperatures between 120 and 180°C, the profiles of conversion vs. time are affected predominantly by the change in temperature, however, at higher temperatures (above 180°C), the corresponding profiles of conversion vs. time are not significantly influenced by temperature changes.

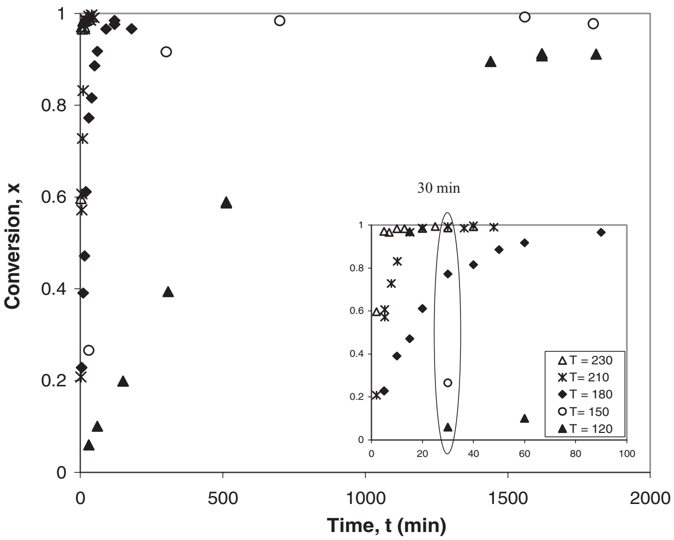


Fig. 2. Effect of temperature on rate of styrene polymerization with AcAm.

Figure 3 illustrates the corresponding number-average molecular weights and polydispersities vs. conversion. As can be seen in the upper plot, there is production of high molecular weight polymer right from the start of the reaction and molecular weights stay almost constant with conversion for all temperatures. Increasing the temperature decreases the molecular weights, a typical feature in any radical polymerization. For example, at 60% conversion, number-average molecular weight is decreasing from the order of 280,000 g/mol for 120°C to around 22,000 g/mol for 230°C. A point to note here is that the decrease in molecular weight values is less pronounced at higher temperatures. As can be seen in Figure 3, the difference between number-average molecular weights for 210 and 230°C is not as large as the corresponding differences for the temperature range between 120 and 180°C. Independently replicated measurements for average molecular weight values were also conducted at 210°C, and as can be seen in the upper plot of Figure 3, there is a very good agreement between the two replicated runs.

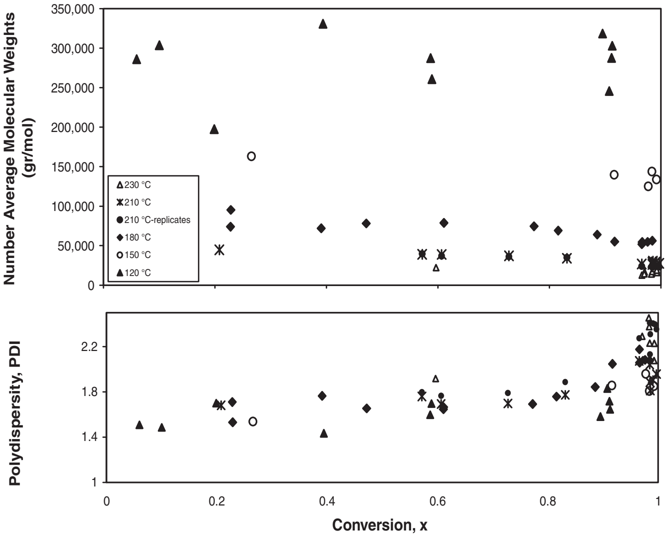


Fig. 3. Effect of temperature on number-average molecular weights and polydispersity of styrene with AcAm.

The corresponding polydispersity values, shown in the lower plot, are in the range of 1.4 to 2.4, which are in the same range as values for purely thermal polymerization of styrene. At this point one can speculate that the behavior of styrene polymerization with AcAm is identical to that of regular (purely) thermal polymerization of styrene (no initiator added). To further check this, the next subsection compares experimental results of styrene with added AcAm, with experimental results and modeling simulations for thermal polymerization of styrene.

3.1 Comparison with Thermal Polymerization of Styrene

In this subsection styrene polymerization with AcAm is contrasted with regular thermal polymerization of styrene in order to appreciate better the effect of AcAm. At 180 and 230°C, our results with AcAm are contrasted with data from the literature (Gao and Penlidis (8) reviewed and discussed a large number of experimental data sources on regular thermal polymerization of styrene). For further clarification, our experimental results on styrene polymerization with AcAm are selectively contrasted with model predictions for regular (purely) thermal styrene polymerization. The modeling predictions presented herein are from a general comprehensive model developed by Jung (11), where more details can be found.

Figure 4 compares conversion versus time data for styrene with AcAm with the corresponding data for (purely) thermal polymerization of styrene, at 120°C (runs

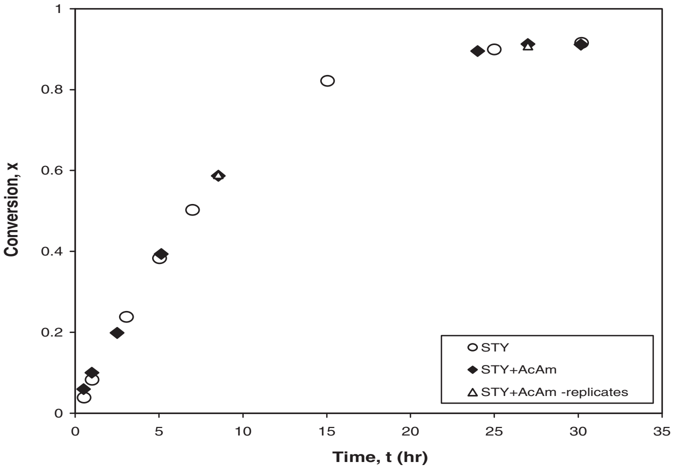


Fig. 4. Conversion vs. time data at 120°C: experimental results of styrene with AcAm vs. experimental results for thermal styrene.

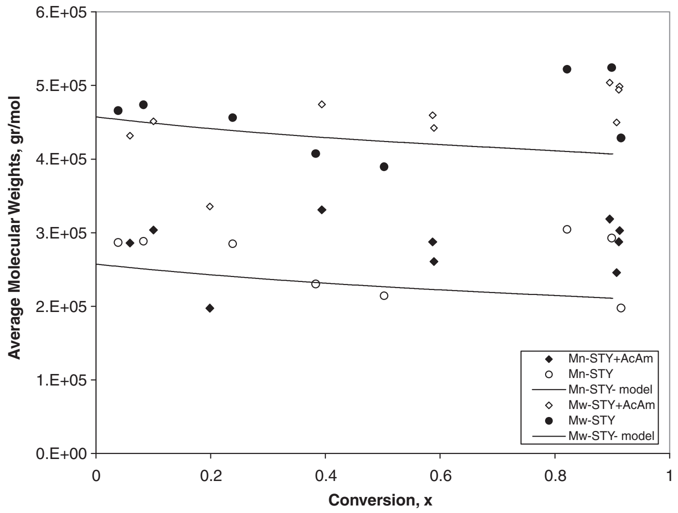


Fig. 5. Average molecular weight data at 120 °C: experimental results of styrene with AcAm vs. experimental results and model predictions for thermal styrene.

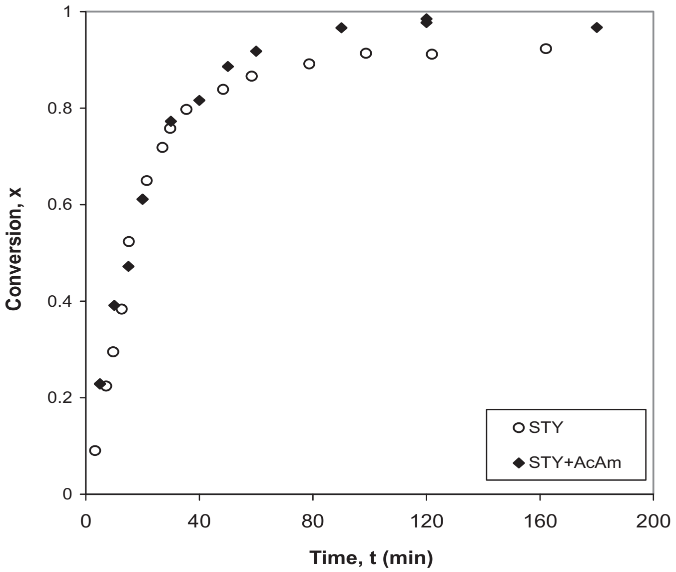


Fig. 6. Conversion vs. time data at 180°C: experimental results of styrene with AcAm vs. experimental results for thermal styrene.

1 and 8 of Table 1). As can be seen, the polymerization with AcAm is acting as regular thermal polymerization of styrene, as if they were two 'replicate' runs. Two independent replicates were analyzed for styrene polymerization with AcAm, to check for reproducibility; as can be seen, the results from the replicates are in good agreement (white triangles vs. black diamonds).

The corresponding comparisons for number-average molecular weights (M_n) and weight-average molecular weights (M_w) are shown in Figure 5. The molecular weight experimental data for the run with AcAm are again almost identical with the ones from regular thermal polymerization of styrene. Figure 5 also illustrates molecular weight model predictions for regular thermal styrene; it can be seen that model predictions capture the general behaviour, being acceptably close to the corresponding experimental results.

Figure 6 contrasts conversion versus time data for styrene polymerization with AcAm at 180°C, with the corresponding data for regular thermal polymerization of styrene from Arai et al. (reported in Gao and Penlidis (8)), at 179.5°C. It can be seen that the two data sets are in excellent agreement up to about 85% conversion, after which point conversion levels for regular thermal polymerization of styrene become lower. In this case, our speculation is that since the two experiments were carried out in two different laboratories, the source of discrepancy after 85% conversion could be attributed to typical measurement error and hence one could claim that there is no significant difference between styrene polymerization with AcAm and regular thermal polymerization of styrene at this temperature level.

The corresponding comparisons for average molecular weights are shown in Figure 7. There is excellent agreement between weight-average molecular weight data, as if again there were two independent "replicate" experiments. For number-average molecular weights, the literature data on regular thermal styrene polymerization are slightly lower than styrene polymerization with AcAm (black circles vs. open diamonds). The corresponding model predictions for styrene polymerization slightly overestimate the molecular weight experimental data for both styrene polymerization with AcAm and purely thermal polymerization of styrene. However, the predictions capture the general behavior of the molecular weights, and again they are acceptably close to the corresponding experimental results.

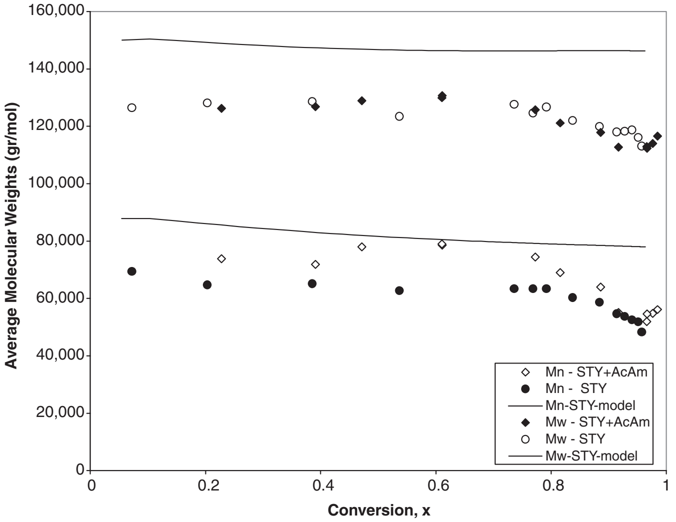


Fig. 7. Average molecular weight data at 180°C: experimental results of styrene with AcAm vs. experimental results and model predictions for thermal styrene.

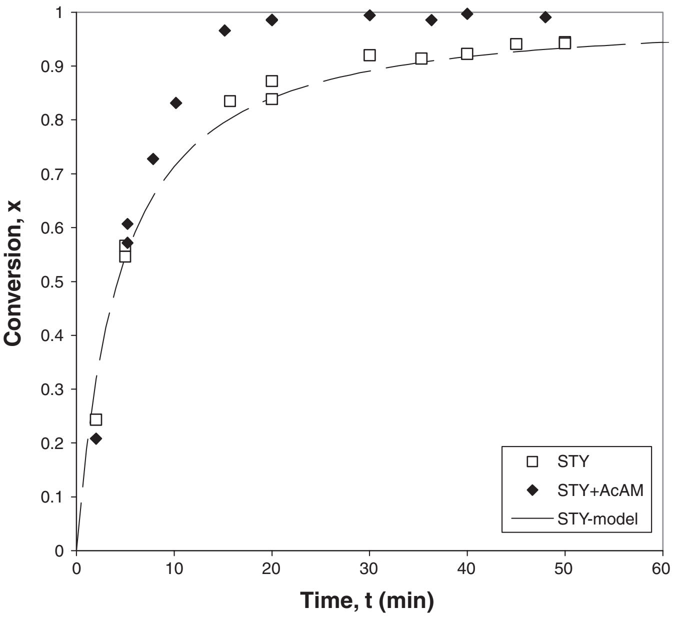


Fig. 8. Conversion vs. time data at 210°C: experimental results of styrene with AcAm vs. experimental results and model predictions for thermal styrene.

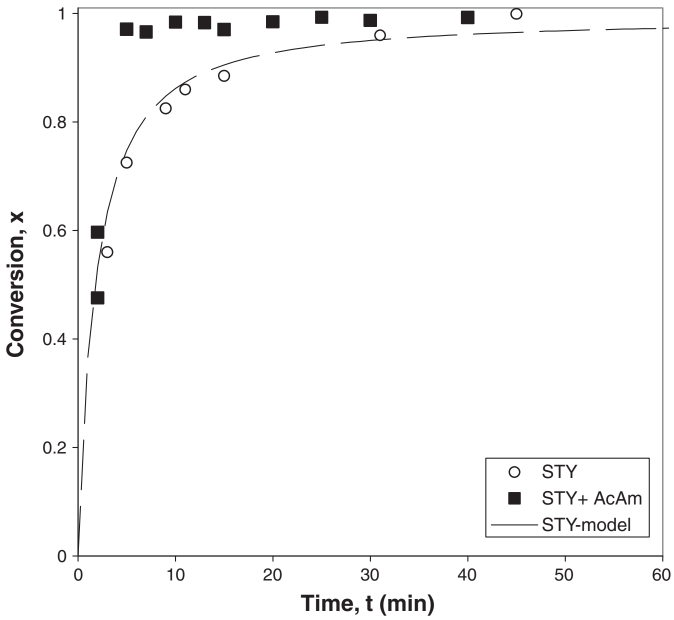


Fig. 10. Conversion vs. time data at 230°C: experimental results of styrene with AcAm vs. experimental results and model predictions for thermal styrene.

Figure 8 compares conversion vs. time data for styrene polymerization with AcAm and styrene thermal polymerization at 210°C (runs 4 and 9 of Table 1). As can be seen, the two data sets are in good agreement up to 60% conversion but after that there is a jump in conversion values for styrene with AcAm. For example, after only 15 minutes, the conversion level is 96% for styrene with AcAm, while only 83% for (purely) thermal styrene polymerization. The model predictions capture the behavior of styrene thermal polymerization almost perfectly. The observations now start suggesting that AcAm seems to have an initiator-like contribution to styrene polymerization. However, the corresponding average molecular weights in Figure 9 do not yet reflect the expected decrease in molecular weights due to AcAm's initiator-like behavior, although one can argue that the data for styrene with AcAm are slightly lower than the ones for thermal polymerization.

To clarify our speculations, another experiment for styrene polymerization with AcAm was carried out at even a higher temperature (230°C; run 5 in Table 1). Figure 10

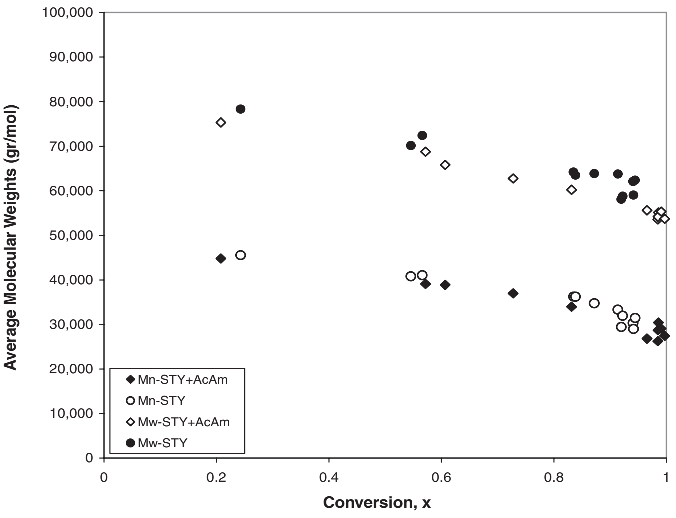


Fig. 9. Average molecular weight data at 210°C: experimental results of styrene with AcAm vs. experimental results for thermal styrene.

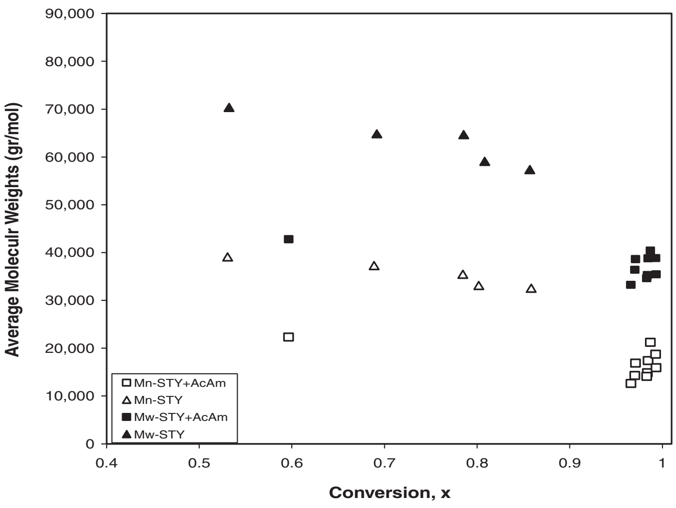


Fig. 11. Average molecular weight data at 230°C: experimental results of styrene with AcAm vs. experimental results for thermal styrene.

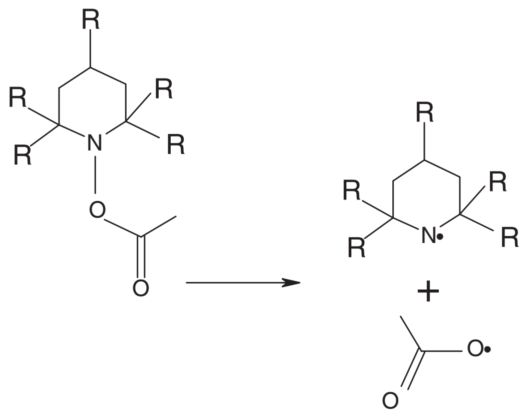
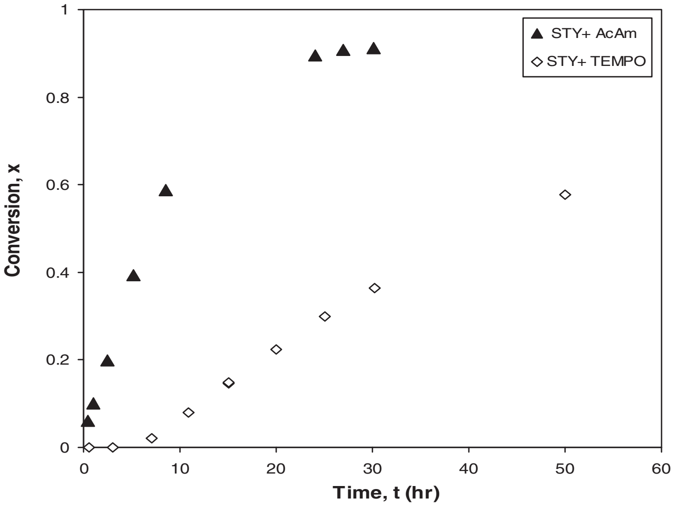


Fig. 12. Thermal cleavage of AcAm.

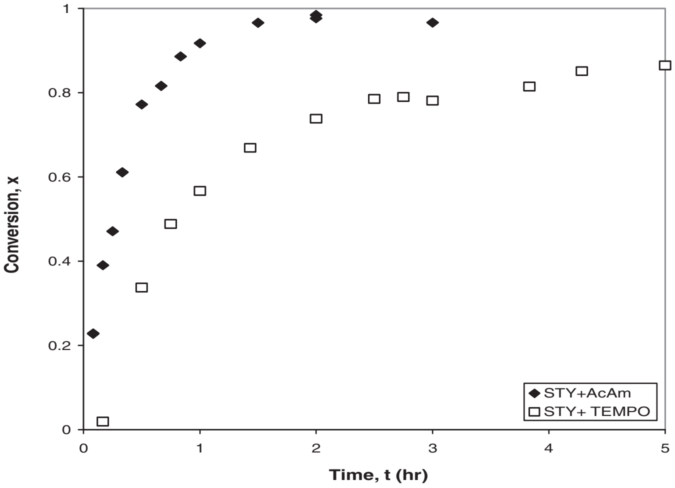
compares the corresponding conversion versus time data with data for styrene thermal polymerization. As can be seen, the run with AcAm is definitely faster than the purely thermal one (after only 5 min have elapsed, the run with AcAm shows 97% conversion). The model predictions follow once more the styrene thermal polymerization behavior almost perfectly. The corresponding molecular weight data are shown in Figure 11. As can be seen, both number- and weight-average molecular weights for styrene with AcAm are lower compared to the values for purely thermal polymerization of styrene. These results show that at 230°C, AcAm again contributes as an initiator to styrene polymerization (increasing the rate of polymerization while decreasing molecular weights). This contribution had possibly started manifesting itself even at 180 and 210°C (see Figures 6 to 9 and the discussion around them), but was not as evident at lower temperatures. According to Rutsch and Cech (12), AcAm dissociates to aminyl and acyloxy radicals at high temperatures (more preferably at the higher temperature levels of polymer degradation operations, above 200 °C), as shown in Figure 12, and that is why AcAm exhibits this additional initiator-like contribution at temperature levels above 180–200°C.

3.2 Comparison with Thermal Polymerization of Styrene in the Presence of TEMPO

Figure 13 compares conversion vs. time data for styrene polymerization with AcAm and styrene polymerization with TEMPO, at 120°C and 180°C (runs 1 and 6, and 3 and 7 of Table 1). It can be observed that the run with AcAm is much faster than the one with TEMPO, however, the difference between polymerization rates at 180°C is not as significant as at the 120°C level. At 120°C (Fig. 13a), after 24 h, the conversion level is 90% with AcAm and only 30% with TEMPO, while at 180°C (Fig. 13b) after 2 h, conversion is 98% with AcAm and 73% with TEMPO. Other observations for the 180°C temperature level are a plateau in conversion level for styrene polymerization with TEMPO after about 2.5 h, and a much shorter (almost negligible) induction period at the beginning of the reaction compared to the run with TEMPO at 120°C.



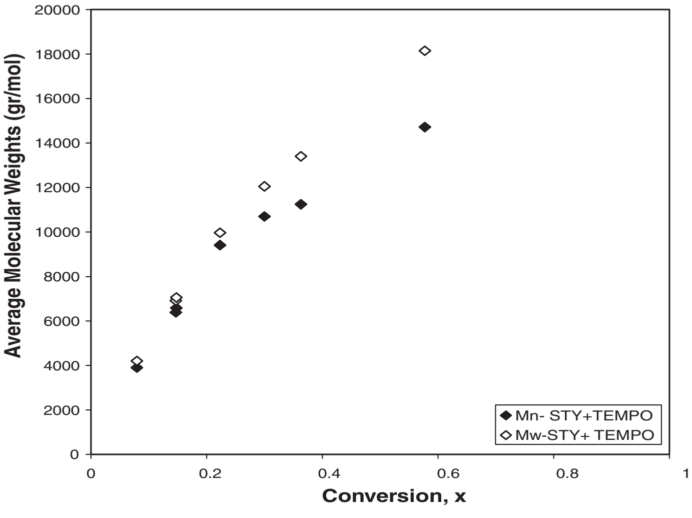
(a)



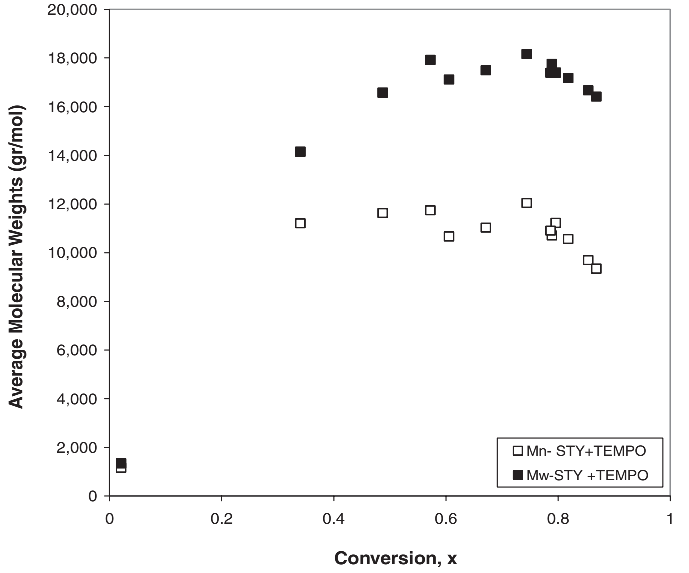
(b)

Fig. 13. Rate comparison for polymerization of styrene with AcAm and TEMPO, at (a) 120°C, (b) 180°C.

The corresponding molecular weights for polymerization of styrene with TEMPO at 120°C are shown in Figure 14(a), showing an almost linear increase of molecular weights with conversion, typical of any controlled radical polymerization. Comparing these data with molecular weights obtained from polymerization of styrene with AcAm (Fig. 5), one can see that the molecular weights are much lower. Figure 14(b) illustrates molecular weight vs. conversion for styrene polymerization with TEMPO at 180°C. As can be seen, polymerization is not controlled at these conditions, since molecular weights are not increasing linearly with conversion. Comparing these results with styrene polymerization with AcAm (Fig. 7), one again can see that molecular weights are much lower; at 60%



(a)



(b)

Fig. 14. Molecular weights vs. conversion for styrene with TEMPO at (a) 120°C and (b) 180°C.

conversion, the number-average molecular weight is about 10,000 g/mol for styrene polymerization with TEMPO (Fig. 14(a)), while at the same conversion level, the molecular weight is about 78,000 g/mol for styrene with AcAm (Fig. 7).

Although styrene polymerization with TEMPO had been classified as controlled radical polymerization at lower temperatures (see Nabifar et al. (9)), at elevated temperatures it could not be classified as controlled. However, comparing the molecular weight results to styrene polymerization with AcAm shows that the presence of TEMPO lowers the molecular weights dramatically. Radicals generated through thermal polymerization of styrene are trapped by TEMPO and the duration that the radicals are in the dormant mode is relatively long, thus causing the dramatic decrease in molecular weights. Although both AcAm and TEMPO can be categorized as hindered amines, they contribute very differently in styrene polymerization.

4 Conclusions

Selective kinetic investigations on styrene polymerization using an acyloxyamine over several temperature levels showed that the system behaves rather like regular (purely) thermal polymerization of styrene at temperature levels between 120–180°C, whereas at temperatures above 180–200°C AcAm seems to have an initiator-like contribution, thus increasing the rate of polymerization while decreasing molecular weights.

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