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Experimental Study of a Tetrafunctional Peroxide Initiator: Bulk Free Radical Polymerization of Butyl Acrylate and Vinyl Acetate

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Summary

This investigation examines the use of a tetrafunctional peroxide initiator in the bulk free radical homopolymerization of butyl acrylate and vinyl acetate. Rate of polymerization, molecular weights and in certain cases, gel fraction data were collected for selective experiments and compared to the results obtained with a monofunctional counterpart. In order to avoid the formation of insoluble gel material, further experiments were completed with varying concentrations of a chain transfer agent. Experimental results showed that when used at identical concentrations, the tetrafunctional initiator produced a faster rate in the polymerization of both butyl acrylate and vinyl acetate compared to the monofunctional initiator. Without the use of a chain transfer agent, runs with butyl acrylate produced significant amounts of gel material isolated by Soxhlet extraction. For a particular reaction time, the tetrafunctional initiator produced higher levels of gel compared to its monofunctional counterpart. When a chain transfer agent was used, the molecular weights were determined by its concentration and in turn, initiator functionality did not have an impact. In the polymerization of vinyl acetate, similar observations were made and no discernable difference could be seen between the molecular weight results of samples produced with either initiator.

Introduction

The potential advantages of multifunctional initiators in the free radical polymerizations of styrene have been documented by several groups [1-7]. These investigations have found that simultaneously obtaining high rates of polymerization and high molecular weights is possible by increasing an initiator's functionality. However, recent work has shown that these advantages depend greatly upon the nature of the monomer being polymerized [8,9]. Specifically, it has been observed during the polymerization of methyl methacrylate (MMA) that a tetrafunctional initiator can be used to produce a faster rate of polymerization; however, the polymer molecular weights were lower when compared to samples produced with a monofunctional counterpart employed at an equivalent concentration. The most significant difference between the polymerization mechanism of styrene and MMA is their modes of termination. Styrene chains typically terminate by radical coupling while in the case of MMA, chains terminate predominantly by disproportionation. The next step in our investigation of the behaviour of multifunctional initiators in various monomer systems was to examine polymerizations dominated by other transfer reactions.

Butyl acrylate (BA) is an important acrylic monomer used in many commercial products such as latex paints, adhesives and coatings. Its polymerization mechanism is greatly influenced by transfer reactions, especially transfer to polymer. Propagating chain-end radicals have been found to either wrap around and abstract a hydrogen from an acrylate unit on its own backbone (backbiting or intramolecular chain transfer) or the radical may abstract a hydrogen from a nearby polymer chain (intermolecular chain transfer). In the case of the former, the transfer reaction results in the production of short branches. However, when intermolecular chain transfer occurs, a tertiary radical may be formed at any point along the backbone resulting in long chain branching. Overall, transfer to polymer reactions can lead to the formation of highly branched polymers and it is not uncommon to observe the formation of insoluble gel early in the polymerization of butyl acrylate. Similarly, the polymerization mechanism of vinyl acetate (VAc) is greatly influenced by transfer reactions. It is well known that branching occurs in vinyl acetate as the result of transfer reactions with both monomer and polymer and that the formation of insoluble gel material is observed at high conversions.

In this study, we extend our investigation of the behaviour of a tetrafunctional peroxide initiator, JWEB50, by examining its impact on the polymerization of butyl acrylate and vinyl acetate. A suitable monofunctional counterpart to the tetrafunctional initiator is used in order to evaluate the performance of JWEB50. Due to the nature of the polymerization of butyl acrylate to form significant amounts of gel, some runs have investigated the use of a chain transfer agent (CTA) with each initiator.

Experimental

Initiators

Produced by ATOFINA Chemicals Inc., Luperox JWEB50 is a multifunctional initiator with four monoperoxycarbonate functional groups. Its structure and decomposition are shown in Figure 1. JWEB50 is shipped in a 50 wt. % solution of ethyl benzene and has a molecular weight of 965.0 g/mol. With respect to the tetrafunctional initiator's thermal stability, the functional groups are found to have 1-hour and 10-hour half-life temperatures of 119ºC and 100ºC in ethyl benzene and an approximate 1-hour half-life temperature of 121ºC in dodecane.

In order to examine the effect of initiator functionality, a suitable monofunctional initiator was chosen such that when varying initiator type, there would be minimal variation in the structure and stability of the labile groups. As such, the monofunctional counterpart used in this study is tert-butylperoxy 2-ethylhexyl carbonate (Luperox TBEC, ATOFINA Chemicals Inc.). Figure 2 shows the structure and decomposition of TBEC. This monofunctional initiator has a similar thermal stability to JWEB50 as it has 1-hour and 10-hour half life temperatures of 121°C and 100°C in dodecane. Luperox TBEC is diluted with 5 wt. % of 2-ethylhexanol.

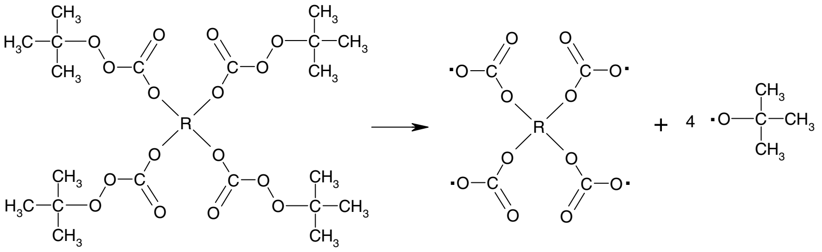

Figure 1. Decomposition of tetrafunctional initiator, JWEB50.

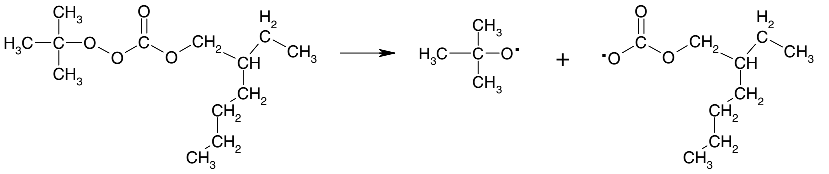

Figure 2. Decomposition of monofunctional initiator, TBEC.

Reagent Purification

Butyl acrylate (Sigma-Aldrich Canada Ltd.) was washed three times with a sodium hydroxide solution (10 w/v %), washed three times with distilled water, dried over calcium chloride and distilled under vacuum. Due to its high water solubility, vinyl acetate (Sigma-Aldrich Canada Ltd.) was purified by vacuum distillation only. All other materials such as solvents and initiators were used as received from suppliers. Dodecanethiol (Sigma-Aldrich Canada Ltd.) was utilized as a chain transfer agent in certain experiments with butyl acrylate. Hydroquinone (Sigma-Aldrich Canada Ltd.) was used to help quench the reactions and prevent additional polymerization. Both chemicals were used without further purification from suppliers.

Polymer Synthesis

Experiments were carried out in borosilicate glass ampoules (capacity ~4mL) where a solution of reagents (monomer, initiator and in some cases CTA) was prepared and pipetted into ampoules. Ampoules were then degassed by vacuum-freeze-thaw cycles, sealed under vacuum and immersed in a silicon oil bath. Ampoules were removed at selected time intervals and placed in liquid nitrogen to quench the reaction. Due to the fact that the samples were typically in a gel-like state, the removal of residual monomer was not possible using conventional methods. As such, after thawing and weighing the ampoules, they were broken and placed in stoppered flasks containing toluene and an inhibitor (hydroquinone). Approximately one day later, the broken pieces of the ampoule were removed from the flask, cleaned and weighed. The polymer solutions were then precipitated in ethanol and dried in a vacuum oven. In the polymerization of vinyl acetate, dichloromethane was used as the solvent to dissolve the polymer and petroleum ether as the nonsolvent to precipitate.

Polymer Characterization

Gel content was determined for poly(butyl acrylate) (PBA) samples using Soxhlet extraction. Prior to the extraction procedure, the paper thimbles were placed inside the Soxhlet apparatus, refluxed with toluene for one hour, dried under vacuum and then weighed. This was done to help reduce any error associated with the loss in weight of the paper thimble before and after the extraction of soluble material from the polymer. In the extraction process, toluene was refluxed over approximately 1 gram of polymer for 8 hours. The thimble and insoluble polymer were removed from the setup, dried under vacuum and then weighed to allow for the calculation of the gel content. The soluble fraction of the polymer (sol fraction) was recovered from the solvent reservoir.

Molecular weight averages and molecular weight distributions for poly(butyl acrylate) samples were determined using a Waters size exclusion chromatograph (SEC) equipped with a refractive index (RI) detector (2410 RI, Waters) and a multi-angle laser light scattering (MALLS) detector (DAWN DSP, Wyatt Technology Corp.) in series. Poly(vinyl acetate) (PVAc) samples were characterized with a different SEC setup equipped with low- and right-angle laser light scattering detectors (LALLS/RALLS), differential refractometer and viscometer in series (Viscotek). For both systems, the columns (one PLgel 10 μm guard column and three PLgel 10 μm MIXED-B columns (Polymer Laboratories Inc.)) and detectors were maintained at 30ºC. The mobile phase was filtered tetrahydrofuran (THF) (HPLC Grade, Caledon Laboratories Inc.) at a flowrate of 1 mL/min. Polymer solutions of approximately 0.2 wt. % were prepared and injected at volume of 100 μL. PBA samples were filtered prior to injection with 0.45 μm filters while 0.20 μm filters were used for the PVAc samples (GHP Acrodisc GF, Waters). The MALLS wavelength was 633 nm and the light-scattering intensity was measured at 18 angles between 14 and 152º. The LALS used a wavelength of 670 nm and the light scattering was measured at 7º. Specific refractive index increments of 0.063 mL/g and 0.055 mL/g were used for poly(butyl acrylate) and poly(vinyl acetate) in THF.

Experimental Design

A series of BA experiments were conducted in order to examine the behaviour of the tetrafunctional initiator in the polymerization of a monomer dominated by transfer to polymer. Due to the nature of the homopolymerization of butyl acrylate to form significant amounts of gel, some runs have investigated the use of a chain transfer agent with each initiator. Table 1 lists the various polymerizations of butyl acrylate and vinyl acetate carried out in this study. Unlike our previous work with styrene and methyl methacrylate, only selective experiments were chosen. In the case of BA and VAc, a comparison between initiators of equal concentrations and not "potential" radical concentrations (i.e., employing the monofunctional initiator at a concentration four times that of the tetrafunctional initiator) was performed.

Table 1. Butyl Acrylate and Vinyl Acetate Experiment Conditions.

Experiment	CTA Concentration, wt. %	Temperature, ºC	Initiator Type	Initiator Concentration, mol/L
BA-M1	0	80	TBEC	0.0005
BA-T1	0	80	JWEB50	0.0005
BA-M2	0.05	80	TBEC	0.0005
BA-T2	0.05	80	JWEB50	0.0005
BA-M3	0.5	80	TBEC	0.0005
BA-T3	0.5	80	JWEB50	0.0005
VAC-M	0	100	TBEC	0.0005
VAC-T	0	100	JWEB50	0.0005

Results and Discussion

Butyl Acrylate

Figure 3 is plot of conversion versus time for the bulk BA polymerization experiments. Looking at the data for each experiment a curved profile is observed with an initial rise in conversion and a leveling off as the reaction progresses.

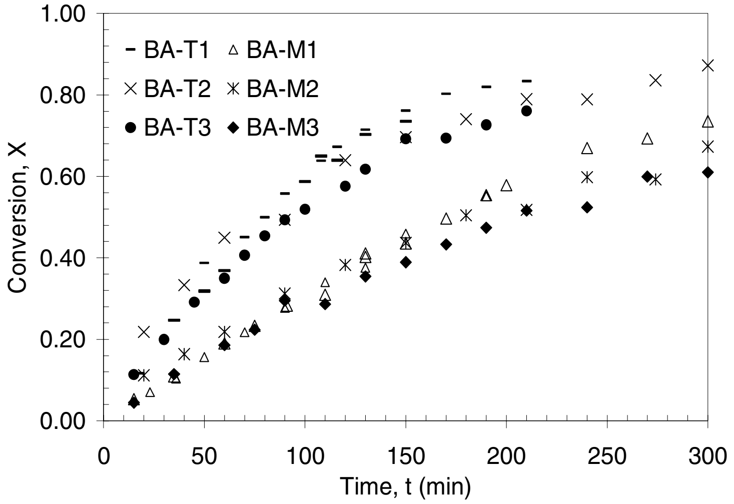

Figure 3. Monomer conversion as a function of time for the bulk polymerization of butyl acrylate at 80ºC.

For each of the three CTA concentration levels (0, 0.05 and 0.5 wt%), the data show that the tetrafunctional initiator requires less time to reach a particular conversion when compared to the monofunctional initiator at the same initiator concentration. For the comparison without CTA, the initial rate of polymerization was estimated by the slope of the conversion-time data at low conversion. The ratio of the rate of polymerization for the tetrafunctional initiator (0.00558 min^{-1}) to the rate with the monofunctional initiator (0.00283 min^{-1}) was determined to be 1.97. From theory it is known that the rate of polymerization is proportional to the square root of the initiator concentration. A ratio of two between rates implies that using the tetrafunctional initiator is equivalent to employing the monofunctional initiator at a concentration four times as great. This observation corresponds well with the fact that the tetrafunctional initiator has the potential to generate four times as many radical sites per molecule of initiator compared to its monofunctional counterpart.

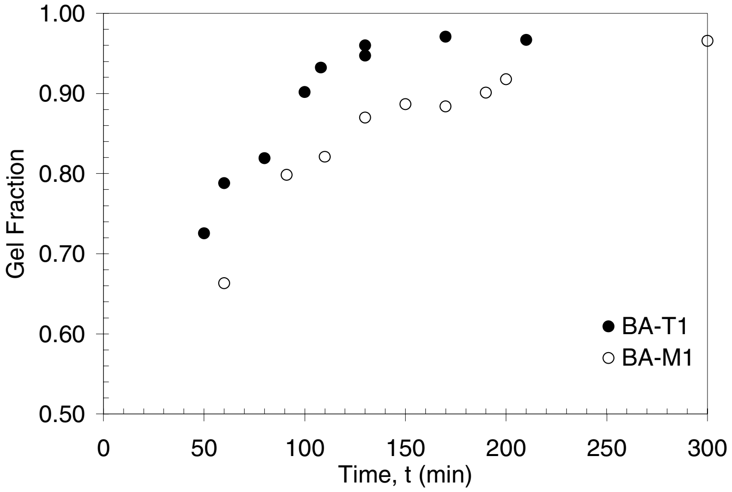

Figure 4. Gel fraction as a function of time for butyl acrylate experiments with no chain transfer agent.

The BA runs without CTA invariably produced polymer containing insoluble gel material. Using a Soxhlet extractor, the gel fraction of polymer samples was determined. Figure 4 is a plot of gel content versus time, illustrating the effect of initiator functionality on the amount of gel produced. The data indicate that higher levels of gel content are obtained with the tetrafunctional initiator compared to TBEC. As the structure of the tetrafunctional initiator leads to production of branched polymers, it is not unreasonable for this type of initiator to cause higher fractions of insoluble gel to be produced.

Molecular weight data for the soluble material extracted from PBA samples are presented in Figure 5. The samples were of extremely high molecular weight and the shape of the chromatograms (not shown here) indicated that the limit of the columns had been reached. In cases where the detector cell contains a polydisperse fraction (i.e., incomplete separation by the columns), light scattering will provide a weight average molecular weight estimate. Thus the weight average molecular weight of the entire sample can still be used while the other averages and polydispersity are not valid. The data in Figure 5 indicate that the molecular weight of the soluble fraction increases with conversion up to a certain point. At conversions greater than 60% and a corresponding gel fraction of >90%, the molecular weight of the soluble fraction begins to decrease. At this point, it is most likely that the growth of the gel fraction begins to incorporate the uncross-linked chains and hence, reduces the sol molecular weight.

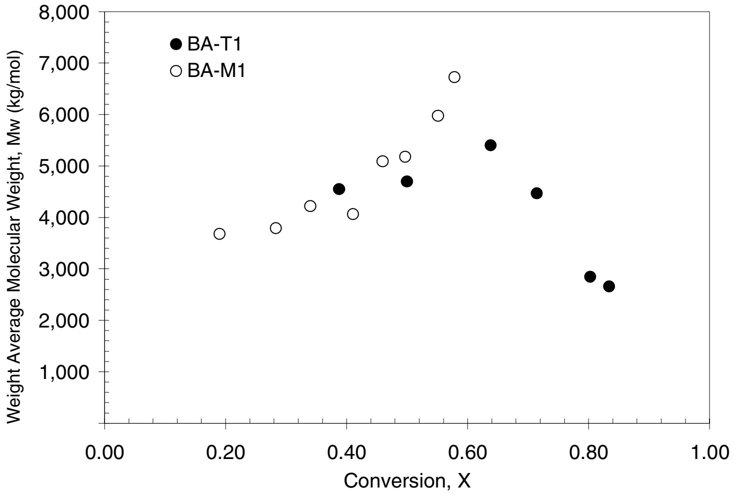

Figure 5. Weight average molecular weight of soluble material extracted from poly(butyl acrylate) samples.

From the data in Figure 3 it can be seen that the addition of dodecanethiol had a slight effect on the rate of polymerization. The trends show that with increasing CTA concentration, the conversion-time trends are slightly lowered. The effect of dodecanethiol on molecular weight and gel fraction was quite evident. Weight average molecular weight estimates for the four experiments run with CTA are shown in Figures 6 and 7. Samples were filtered prior to injection into the SEC. No significant difference was found when comparing the mass of injected polymer to the mass of polymer estimated from the RI signal. This result along with the observation that the samples could be filtered without applying significant pressure was taken as an indication that the samples did not contain insoluble microgels. At both CTA levels, molecular weight curves for the tetrafunctional and monofunctional initiator coincided well. A significant effect on the molecular weight was observed when increasing the CTA concentration. At the higher concentration, both initiators produced polymer molecular weights starting at approximately 50 kg/mol and increasing with conversion to an upper limit of 80 kg/mol. At the lower CTA concentration, polymer molecular weights were much higher and increased dramatically after 50% conversion was reached (see Figure 6).

The polydispersity (PDI) values at the higher CTA concentration (data of Figure 7) were determined to be similar for both initiators and remained constant for the course of the reaction. Figure 8 provides the polydispersity index values for the two experiments completed at the lower CTA concentration. From low to mid conversions where the molecular weight estimates do not vary considerably, it was found that the PDI values remained fairly constant. After reaching ~50% conversion, polymer with much broader molecular weight distributions is produced and the PDI is found to noticeably increase. These results would suggest that at the higher CTA concentration, transfer to CTA is the dominant factor controlling molecular weight for the entire course of the reaction. At the lower CTA concentration, the data indicate that transfer to CTA is the controlling factor up until ~50% conversion where enough dodecanethiol has been consumed such that transfer to polymer and monomer becomes significant. Although radius of gyration (R_g) plots for the poly(butyl acrylate) samples are not shown here, the results were examined in order to determine the extent of branching. A comparison of R_g data between polymer samples produced with JWEB50 and TBEC did not show any marked differences.

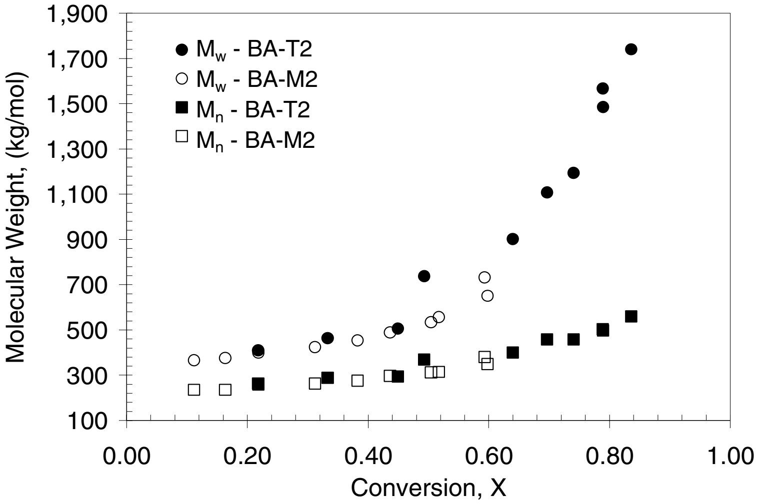

Figure 6. Molecular weight averages as a function of conversion for the bulk polymerization of butyl acrylate with [CTA] = 0.05 wt.%.

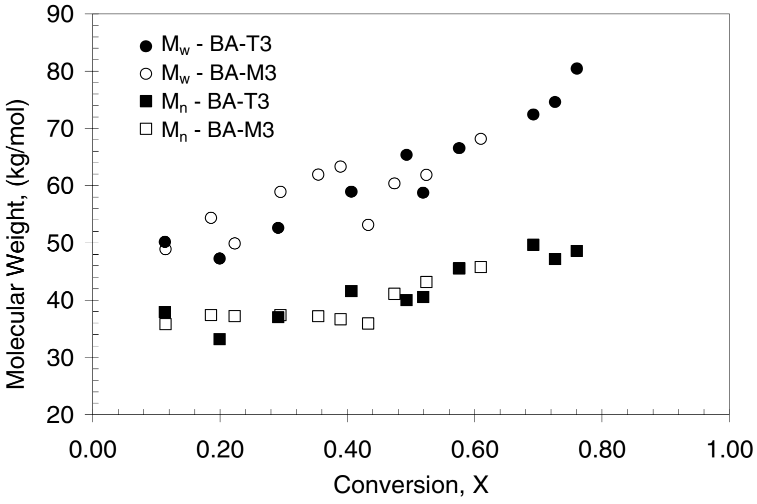

Figure 7. Molecular weight averages as a function of conversion for the bulk polymerization of butyl acrylate with [CTA] = 0.5 wt.%.

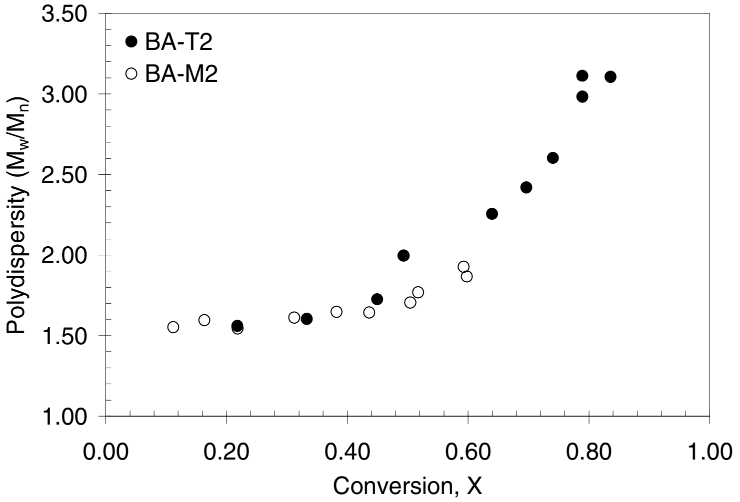

Figure 8. Polydispersity index as a function of conversion for the bulk polymerization of butyl acrylate with [CTA] = 0.05 wt.%.

Vinyl Acetate

Conversion versus time trends for the bulk polymerization of vinyl acetate initiated with JWEB50 and TBEC are shown in Figure 9. The curves show that the tetrafunctional initiator produced a faster rate of polymerization compared to the monofunctional initiator at an equivalent initial concentration of initiator. Using the linear portion of the conversion versus time data, the initial rate of polymerization was estimated. JWEB50 produced an initial rate of polymerization of 0.0152 min^{-1} while TBEC generated a rate of 0.00810 min^{-1}. The ratio of the initial rate of polymerization produced with JWEB50 to the rate generated by TBEC at the same concentration level is approximately 2. According to theory, this result would suggest that employing JWEB50 is equivalent to using TBEC at a concentration four times as great. This observation agrees with those findings made with other monomer systems (e.g., styrene [7], MMA [8], styrene/MMA [9] and α-methyl styrene/MMA [9]).

Weight average molecular weight results are shown in Figure 10 for the two vinyl acetate experiments. The data for each experiment show similar trends with molecular weights starting near 300 kg/mol and increasing dramatically with conversion towards 4,000 kg/mol and above. The polymerization of vinyl acetate is characterized by high rates of transfer to monomer and polymer. As the act of either transfer reaction leads to a branched molecule, very high molecular weights are obtained as the reaction progresses. The data in Figure 10 shows that the effect of initiator functionality has very little effect on molecular weight. In order to see if there is a difference between curves at lower conversions, the insert of Figure 10 is scaled for 60% conversion. At low conversion and hence low polymer concentrations, the extent of transfer to polymer is less of a factor. The molecular weight data for the polymerization with TBEC appear to be slightly higher than the other run. The data suggests that transfer to monomer and polymer control the molecular weight more so than changes in initiator functionality. Although not shown here, plots of number average molecular weight or polydispersity as a function of conversion were similar for the two experiments. As well, intrinsic viscosity versus molecular weight data for samples of similar conversion from the two experiments showed similar levels of branching.

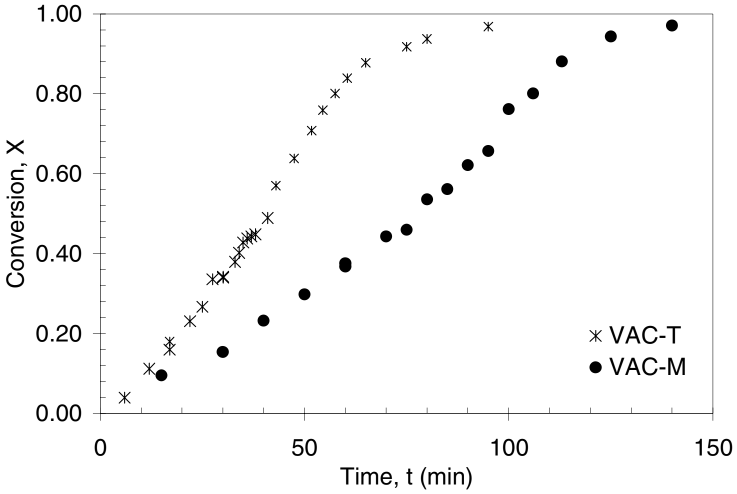

Figure 9. Conversion as a function of time for the bulk polymerization of vinyl acetate at 100ºC.

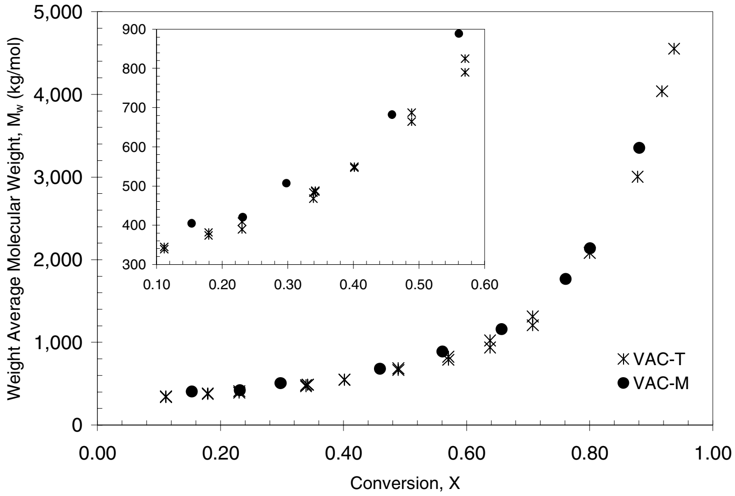

Figure 10. Weight average molecular weight as a function of conversion for the bulk polymerization of vinyl acetate at 100ºC. Insert: weight average molecular weight for less than 60% conversion.

Due to the importance of transfer reactions in the polymerization of vinyl acetate, the formation of gel material would not be unexpected. Unlike the PBA samples, all of the poly(vinyl acetate) samples dissolved and no swollen material was ever observed.

However, it was suspected that the PVAc samples might contain soluble microgels. In each run, the very high conversion samples could not pass through the 0.2 μm filter. For VAC-T, the highest conversion sample that could be filtered was 93.7% while for VAC-M, a maximum conversion of 88.1% was reached. For those samples that could pass through the disposable filters, a comparison of the mass of injected polymer to the mass of polymer calculated from the RI signal showed no statistical differences. This observation suggested polymer was not being lost to the filtering processes (offline or inline) and that the existence of extremely high molecular chains could be ignored. However, further testing did prove otherwise. The samples were injected again without prior filtration. Several phenomena occurred that would suggest the presence of highly branched molecules including large negative peaks in the inlet pressure of the detector array, spiking of the pump pressure, and extremely noisy data. These observations indicated that the samples which could be filtered did contain a very low amount of extremely high molecular weight material.

Conclusions

The experiments in this study were chosen as a selective investigation on the use of a tetrafunctional initiator with monomer systems dominated by transfer reactions. Experimental results have shown that the tetrafunctional initiator, JWEB50, can produce a faster rate in the polymerization of both butyl acrylate and vinyl acetate compared to TBEC. The experiments for both monomers lead to the production of highly branched polymer. Without the use of a CTA, the bulk polymerization of butyl acrylate inevitably produced insoluble gel material. Results from Soxhlet extraction indicated that for similar reaction times, JWEB50 produced higher levels of gel material compared to TBEC. When a CTA was used, the molecular weight results were dominated by the CTA concentration and initiator functionality did not have an impact. In the polymerization of vinyl acetate, a similar observation was found and no discernable difference could be seen between the molecular weight versus conversion results of samples produced with JWEB50 and TBEC.

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