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M. J. Scolah^a; R. Dhib^b; A. Penlidis^a

^a Institute for Polymer Research, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada ^b Department of Chemical Engineering, Ryerson University, Toronto, Ontario, Canada

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Use of a Novel Tetrafunctional Initiator in the Free Radical Homo- and Copolymerization of Styrene, Methyl Methacrylate and α -Methyl Styrene

M. J. SCORAH,¹ R. DHIB,² AND A. PENLIDIS¹

¹Institute for Polymer Research, Department of Chemical Engineering,
University of Waterloo, Waterloo, Ontario, Canada

²Department of Chemical Engineering, Ryerson University, Toronto, Ontario,
Canada

An investigation into the effect of initiator functionality on the free radical polymerization of various monomer systems including styrene, methyl methacrylate (MMA), styrene–MMA and α -methyl styrene–MMA with a tetrafunctional peroxide initiator (JWEB50) was completed. The performance of the tetrafunctional initiator was compared to a monofunctional counterpart (TBEC). Kinetic results showed that regardless of the monomer system studied, JWEB50 produced a faster rate of polymerization compared to TBEC at an equivalent concentration. Molecular weights, radii of gyration and intrinsic viscosities were obtained from two size exclusion chromatography setups: one equipped with a multi-angle laser light scattering detector and the other with low-angle laser light scattering and viscosity detectors. For the homopolymerization of styrene, JWEB50 produced polymer molecular weights similar to TBEC at the same concentration, while experiments with MMA indicated that JWEB50 produced molecular weights closer to those obtained with TBEC at a concentration four times as great. Runs with a feed mixture of styrene and MMA gave results that were a combination of the observations made for the individual homopolymerizations. The results for the feed mixture of MMA and α -methyl styrene were similar to the findings with pure styrene. Plots of radius of gyration, intrinsic viscosity and their corresponding branching factors provided evidence of branching for all cases except for the homopolymerization of MMA.

Keywords radical polymerization, kinetics (polym.), tetrafunctional initiation, radius of gyration, intrinsic viscosity, dilute solution properties, styrene, methyl methacrylate, α -methyl styrene

Introduction

Multifunctional initiators are seen to provide two advantages over traditional monofunctional initiators. Firstly, research has shown that they aid in increasing polymer production (1–7). It is known from free radical polymerization theory that the molecular weight is inversely proportional to the rate of polymerization. As such, with the use of a

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Address correspondence to A. Penlidis, Institute for Polymer Research, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.
E-mail: penlidis@cape.uwaterloo.ca

monofunctional initiator it is not possible to obtain high rates and high molecular weights for bulk or solution processes. Multifunctional initiators are seen as an alternative to this problem. It has been shown that initiators containing two or more functional groups can generate high rates of polymerization while producing polymer of similar or higher molecular weight when compared to a monofunctional initiator. Such an effect has been attributed to the sequential decomposition of the functional groups, thus allowing repeated initiation, propagation and termination of the same molecule.

The second advantage of multifunctional initiators is their ability to introduce branching into the final polymer product. When three or more labile groups are contained within a single molecule, the resulting polymer chain will have a structure resembling a star. Star polymers are the simplest class of branched structures and as such, they have received a great deal of interest (8, 9). The introduction of branching is seen as advantageous from the polymer processing viewpoint, especially in polymer stretching operations where branching has been found to improve such properties as melt strength (10, 11).

Multifunctional initiators is an area of research that has grown rapidly in the last few decades with the majority of studies dealing with controlled/living polymerizations such as atom transfer radical polymerization (ATRP), (12) reversible addition-fragmentation chain transfer polymerization (RAFT), (13) nitroxide-mediated polymerization (NMP), (14) anionic polymerization (15) and cationic polymerization (16). In comparison, there are relatively few studies that investigated the use of multifunctional initiators in free radical polymerizations. And those that have researched this area typically deal with difunctional initiators for the polymerization of styrene.

Interest in the use of multifunctional initiators for free radical polymerization began over three decades ago. Prisyazhnyuk and Ivanchev produced fundamental work on understanding the mechanism of polymerization with difunctional initiators (1). The authors examined the kinetics of several diperoxides having labile functional groups of differing thermal stability in the polymerization of styrene. Work was also completed on the use of unsymmetrical difunctional initiators to produce block copolymers. Polymerization was first carried out in styrene at a lower temperature to form polystyrene macroinitiators. These macroinitiators were then used in the polymerization of methyl methacrylate (MMA) at higher temperature to form block copolymers. Nearly a decade later, Ivanchev (1979) reviewed the current state of free radical polymerization initiation, summarizing most of the past work on difunctional initiators (17). Another significant review came from Simionescu et al. (1986) who compiled an extensive list of work involving the synthesis, decomposition and use of difunctional and multifunctional free radical polymerization initiators (18). Although some of the synthesis and decomposition studies dealt with initiators with a functionality greater than two, very little work was completed on the use of these initiators in actual polymerizations.

Similar to the earlier work, recent studies on multifunctional initiators are concerned more with difunctional molecules. The group of Choi and coworkers have written numerous articles starting with the employment of symmetrical difunctional initiators in the polymerization of styrene and developing a kinetic model of this system (3, 19). The group advanced to experimental and modeling work for unsymmetrical difunctional initiators, (20, 21) then to combinations of initiators (22) and finally, modified their batch model for a tubular reactor (23). Villalobos et al. (1991) found that previous models using difunctional initiation had serious limitations for the prediction of molecular weights and molecular weight distributions at high conversion. They modified and extended current models in the literature making comparisons to their experimental work (4). Similarly,

González et al. (1996) adapted a model to allow for the use of mixtures of mono- and difunctional initiators and compared their results to experimental data (5). Estenoz et al. (1996) evaluated several difunctional initiators for the synthesis of high-impact polystyrene and attempted to predict their experimental behaviour (24). More recently, Cavin et al. (2000) completed a thorough kinetic and modeling investigation of 2,5-dimethyl-2,5-bis(2-ethyl hexanoyl peroxy)hexane in the polymerization of styrene (6). By combining and adapting various models found in the literature, the group was able to accurately predict conversion data but molecular weights up to only 70% conversion. Dhib et al. (2000) compiled an extensive review of the work to date on difunctional initiators and incorporated the results into a computer simulation/database package (25). All of these studies have shown, either through experimental or modeling results, the ability of difunctional initiators over their monofunctional counterparts to reduce batch times while maintaining or increasing the polymer molecular weight.

As for initiators of functionality higher than two, a limited amount of work has been done in free radical polymerization. Menciloglu et al. (1992) reported on the synthesis of three tetrafunctional initiators based on the reaction of tetrakis(dimethylamino)titanium with either 2,2'-azoisobutyronitrile, tetracyanoethylene or isophorone diisocyanate (26). Very little polymerization information was reported. Cerna et al. (2002) reported a kinetic study showing that the use of difunctional and trifunctional cyclic initiators would allow for high rates of polymerization while producing high molecular weight polymer (7). Holzinger and Kickelbick (2002) are another group that has used multifunctional initiators in free radical polymerization (27). Their work examined the synthesis of various initiators for thermal or photoinduced free radical polymerization from modified cubic spherosilicate cages. The data showed that polymer with a broad polydispersity was being produced which the authors attributed to the formation of various molecular architectures. Kwon et al. (2003) synthesized a novel tetrafunctional photoiniferter for the production of star polystyrene by radical polymerization (28). The resulting polymer was found to have a broad molecular weight distribution (≥ 2.5) with roughly 3 out of the 4 arms retaining their functional groups. As such, this star polystyrene was used as a polymeric photoiniferter for further polymerization of styrene.

The purpose of this article is to continue our group's efforts towards the investigation of a tetrafunctional peroxide initiator designed for free radical polymerization. Previously, we reported on the use of the tetrafunctional initiator in the bulk free radical polymerization of styrene (29) and methyl methacrylate (30). This study expands the work in the area by investigating comonomer systems such as styrene-MMA and α -methyl styrene(α -MS)-MMA. In the work presented herein the performance of the tetrafunctional initiator is evaluated on the basis of the rate of polymerization, polymer molecular weight and evidence of branching compared to a monofunctional counterpart.

Experimental

Initiators

Produced by ATOFINA Chemicals Inc., Luperox JWEB50 is a multifunctional initiator with four monoperoxy carbonate functional groups. Its structure and decomposition are shown in Figure 1 with the R group shown in the diagram being a linkage ATOFINA has kept proprietary. 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 h and 10 h half-life

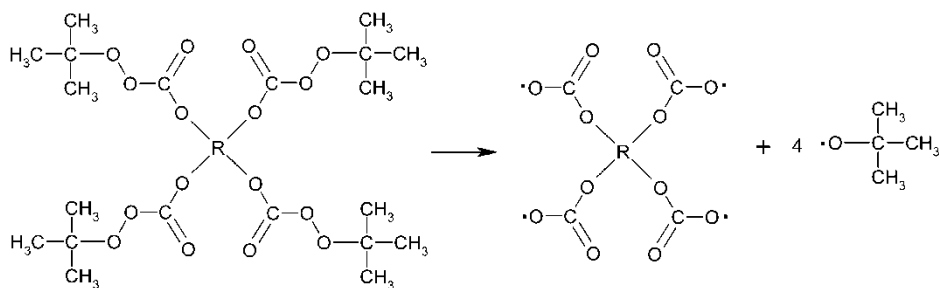


Figure 1. Decomposition of tetrafunctional initiator, JWEB50.

temperatures of 119°C and 100°C in ethyl benzene and an approximate 1 h half-life temperature of 121°C in dodecane.

In order to examine the effect of initiator functionality, a suitable monofunctional initiator had to be chosen such that when varying initiator type, there would be minimal variation in 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 h and 10 h half-life temperatures of 121°C and 100°C in dodecane. Luperox TBEC is diluted with 5 wt% of 2-ethylhexanol.

The decarboxylation of the alkoxy-carbonyloxy radicals is not shown in Figures 1 and 2 as past studies have found that the rate of this step is relatively slow and is not competitive with the addition of an alkene (31, 32).

Reagent Purification

Monomers (styrene, methyl methacrylate, and α -methyl styrene) (Sigma-Aldrich Canada Ltd.) were washed three times with a 10 w/v% sodium hydroxide solution, washed three times with distilled water, dried over calcium chloride and distilled under vacuum. Solvents such as ethanol, dichloromethane and acetone used during the course of the experiment and both initiators (JWEB50 and TBEC) were used as received from suppliers without further purification.

Polymer Synthesis

Bulk polymerizations were completed in borosilicate glass ampoules (capacity ~4 mL) for a range of conversions. Monomers and initiator were weighed, mixed and pipetted

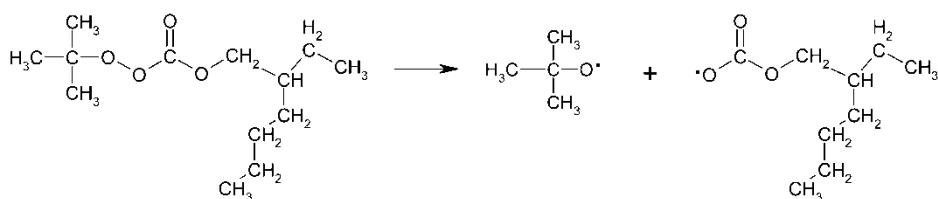


Figure 2. Decomposition of monofunctional initiator, TBEC.

into ampoules. Ampoules were then degassed by 4 vacuum-freeze-thaw cycles, sealed under vacuum with a gas/oxygen torch and then immersed in a silicon oil bath having a temperature control of $\pm 0.1^\circ\text{C}$. Ampoules were removed at selected time intervals and placed in liquid nitrogen to quench the reaction. The ampoules were then thawed, weighed, opened and the contents poured into a flask containing ethanol. The weights of the empty ampoules were also recorded. For the higher conversion levels where it became difficult to remove the reaction mixture, the ampoules were not thawed before being opened. In these cases, a frozen piece of the reaction mixture was removed from the ampoule, weighed, allowed to dissolve in dichloromethane and then precipitated with ethanol before being dried in a vacuum oven.

Polymer Characterization

Two size exclusion chromatographs (SEC) were used to characterize the polymer samples. The first setup (SEC1) is a Waters size exclusion chromatograph equipped with a multi-angle laser light scattering (MALLS) detector (DAWN DSP, Wyatt Technology Corp.) followed by a differential refractometer (2410 RI, Waters) in series. This SEC was maintained at 30°C and used to determine molecular weight and radius of gyration estimates. It was equipped with one PLgel $10\ \mu\text{m}$ guard column ($50 \times 7.5\ \text{mm}$) and three PLgel $10\ \mu\text{m}$ MIXED-B columns ($300 \times 7.5\ \text{mm}$) (Polymer Laboratories Ltd.). The laser operated at $633\ \text{nm}$ and the light-scattering intensity was measured at 18 angles between 14 and 152° . Molecular weight and radius of gyration estimates were determined using Astra version 4.7 software (Wyatt Technology Corp.).

The second size exclusion chromatograph (SEC2) consists of Waters solvent delivery system and autosampler followed by Viscotek's quad detector equipped with a UV detector, low- and right-angle laser light scattering detectors (LALLS/RALLS), differential refractometer and viscometer in series. One PLgel $10\ \mu\text{m}$ guard column ($50 \times 7.5\ \text{mm}$, Polymer Laboratories Ltd.) and three HR 5E columns ($300 \times 7.5\ \text{mm}$, Waters) were used with the detectors and columns maintained at 30°C . The laser operated at $670\ \text{nm}$ and the light-scattering intensity was measured at 7° (LALLS) and 90° (RALLS). Data analysis for this system was performed using OmniSEC version 3.0 (Viscotek).

Tetrahydrofuran (THF) (Caledon Laboratories Inc.) was filtered and used as the eluent at a flowrate of $1\ \text{mL}/\text{min}$ for both SEC setups. The polymer was dissolved in THF to obtain concentrations of $\sim 0.2\ \text{wt}\%$ and the injection volume varied between 100 and $200\ \mu\text{L}$. The second virial coefficient for the light-scattering equation was assumed to be negligible as very low concentrations of polymer were employed. Specific refractive index increment (dn/dc) values of $0.185\ \text{mL}/\text{g}$, $0.083\ \text{mL}/\text{g}$ and $0.2056\ \text{mL}/\text{g}$ were used in the light scattering analysis for PS, PMMA and poly(α -MS), respectively. In the case of copolymers, dn/dc values were determined from a weighted average based on copolymer composition. When using SEC2, copolymer composition was obtained from the UV signal while for SEC1 values were obtained from NMR.

A Bruker AVANCE 500 NMR spectrometer was employed for polymer composition analysis. Deuterated chloroform was used as the solvent and the measurements were taken at room temperature. The relative amounts of each monomer incorporated in the copolymer were estimated from absorption peaks of the spectra. In the case of MMA, the three protons in the $-\text{OCH}_3$ group were found at $\delta = 3.6\ \text{ppm}$ while for α -MS and styrene the five protons in the $-\text{C}_6\text{H}_5$ group were taken at 6.7 – $7.3\ \text{ppm}$.

Experimental Design

Tables 1 and 2 provide a list of the experiments completed with methyl methacrylate, styrene, α -methyl styrene and various comonomer mixtures. For the experiments listed in Table 1, the label starts with the feed type (S = styrene, M = methyl methacrylate, SM = 50/50 wt% mixture of styrene and MMA), then the type of initiator (M = monofunctional, T = tetrafunctional), followed by the initiator concentration (C = 0.004 mol/L, 4C = 0.016 mol/L). For the block of runs, which were conducted at the higher temperature, 120 is placed at the end of the label. A similar labeling code is used for the runs with α -MS as shown in Table 2.

Results and Discussion

Styrene–Methyl Methacrylate Copolymer

A total of nine experiment sets were completed in this section of the study with three experiments for styrene homopolymerization, three for MMA homopolymerization and three for the copolymerization of a 50–50 wt% mixture. In each of these sets, two runs employed the mono- and tetrafunctional initiators at identical concentrations. Looking at the decomposition of the initiators (see Figures 1 and 2) it can be seen that each JWEB50 molecule has the ability to produce four times as many radical sites as one TBEC molecule. Therefore, a third run was also performed for each feed composition with the monofunctional initiator at a concentration four times that of the tetrafunctional initiator. This would enable a comparison of the initiators at similar “potential” radical concentrations.

Table 1
Styrene-methyl methacrylate experiment conditions

Experiment	Styrene feed composition wt%	Temperature °C	Initiator type	Initiator concentration mol/L
S-MC	100	110	TBEC	0.004
S-M4C	100	110	TBEC	0.016
S-TC	100	110	JWEB50	0.004
M-MC	0	110	TBEC	0.004
M-M4C	0	110	TBEC	0.016
S-TC	0	110	JWEB50	0.004
SM-MC	50	110	TBEC	0.004
SM-M4C	50	110	TBEC	0.016
SM-TC	50	110	JWEB50	0.004
S-MC120	100	120	TBEC	0.004
S-TC120	100	120	JWEB50	0.004
M-MC120	0	120	TBEC	0.004
M-M4C120	0	120	TBEC	0.004
M-TC120	0	120	JWEB50	0.016

Table 2
 α -Methyl styrene–methyl methacrylate experiment conditions

Experiment	α -Methyl styrene feed composition wt%	Temperature °C	Initiator type	Initiator concentration mol/L
aMS-MMA-MC	20	110	TBEC	0.004
aMS-MMA-M4C	20	110	TBEC	0.016
aMS-MMA-TC	20	110	JWEB50	0.004

Conversion and Molecular Weight Results

Figure 3 presents conversion vs. time data for the bulk polymerization of styrene with JWEB50 and TBEC. By selecting linear regions of the low conversion data, estimates of the rate of polymerization were determined from the slope. When both initiators are employed at identical concentrations, it was observed that JWEB50 produced a higher rate of polymerization (rate for JWEB50 = 0.0051 min^{-1} , rate for TBEC = 0.0026 min^{-1}) and a limiting conversion of $\sim 98\%$ was achieved in half of the time required for TBEC (time for JWEB50 = 220 min, time for TBEC = 419 min). However, when the mono-functional initiator is added at a concentration four times that of the tetrafunctional, we found that the two data sets overlapped. In other words, when JWEB50 is used at a concentration of 0.004 M it produces a rate of polymerization similar to the rate obtained

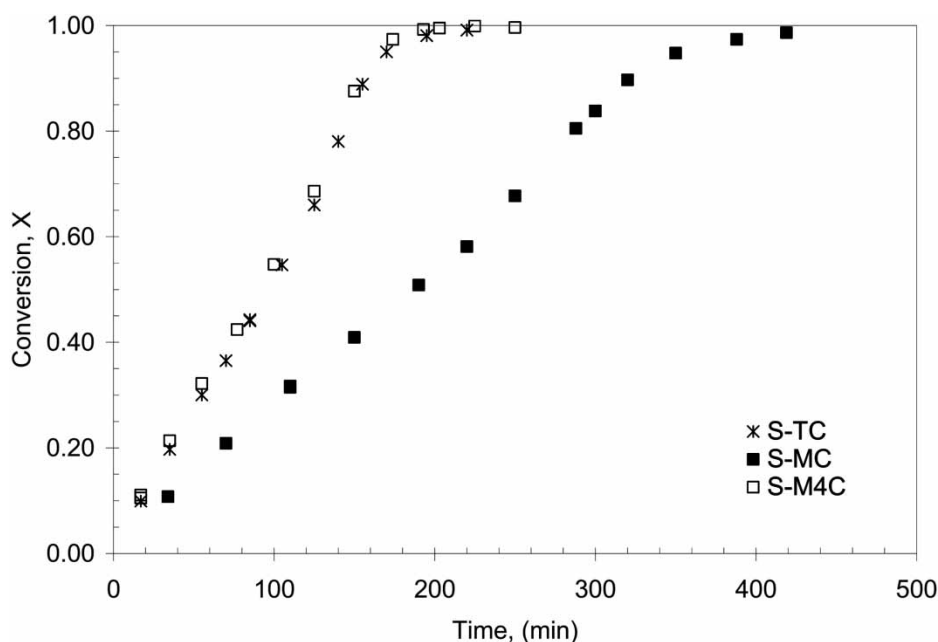


Figure 3. Monomer conversion as a function of time for the bulk polymerization of styrene at 110°C ($C = 0.004 \text{ M}$, $4C = 0.016 \text{ M}$).

with TBEC at a concentration of 0.016 M. This result would suggest that the tetrafunctional initiator's labile groups are decomposing and reacting in a way similar to TBEC's functional group.

Figure 4 is plot of the weight-average molecular weight estimates for the three styrene homopolymerization runs. Results from both SEC setups are plotted and agree very well showing good reproducibility. When examining the molecular weight results, it can be seen that by increasing the concentration of the monofunctional initiator, a polymer of lower molecular weight is produced. This is the dilemma facing polymer manufacturers where an increase in the rate of polymerization causes a noticeable decrease in the polymer molecular weight. Looking at the data for the tetrafunctional initiator, it can be seen that the molecular weights are comparable to those produced when the monofunctional initiator is used at the same concentration. These results are similar to what has previously been observed with multifunctional initiators and styrene: high rates of polymerization are obtained while maintaining or increasing the molecular weight (1–7, 11, 18, 25, 29).

Figure 5 is a plot of the polydispersity results for the styrene experiments. The curves indicate that at low conversions each of the three conditions ($[JWEB50]_0 = 0.004$ M, $[TBEC]_0 = 0.004$ M, and $[TBEC]_0 = 0.016$ M) produce polymer with a similar polydispersity. However, at higher conversions it was found that the tetrafunctional initiator produced polymer with a somewhat broader molecular weight distribution. This effect is clearly shown when examining the evolution of the SEC traces as the reaction progresses. Figures 6 and 7 provide the chromatograms obtained from SEC1 for several samples from experiments S-TC and S-MC. The RI and 90° LS signals are shown in arbitrary units. For the case of the tetrafunctional initiator we find that as conversion increases a shoulder appears at lower elution volumes indicating a high molecular

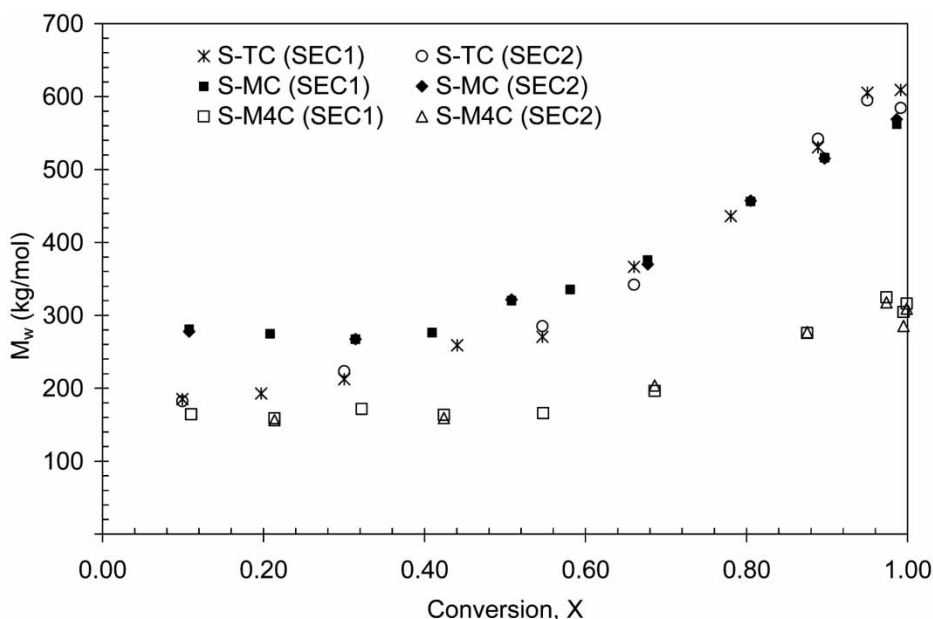


Figure 4. Weight-average molecular weight as a function of conversion for the bulk polymerization of styrene at 110°C ($C = 0.004$ M, $4C = 0.016$ M).

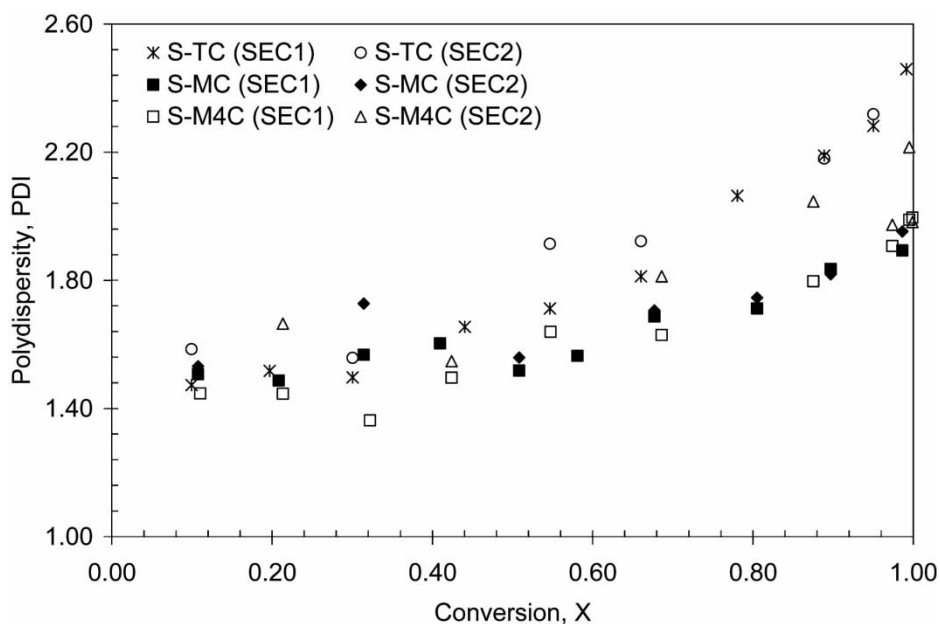


Figure 5. Polydispersity as a function of conversion for the bulk polymerization of styrene at 110°C ($C = 0.004$ M, $4C = 0.016$ M).

weight fraction. This shoulder can be seen in both the refractive index and the light scattering signals. This phenomenon is not seen when we examine the evolution of chromatograms for polymer produced with the monofunctional initiator.

Conversion vs. time results for the homopolymerization of MMA are shown in Figure 8. Again, it is observed that the tetrafunctional initiator produces a higher rate of polymerization compared to the monofunctional initiator when used at the same concentration. Similar to the homopolymerization of styrene, the curve for JWEB50 overlaps that of TBEC at a concentration four times that of the tetrafunctional initiator. In contrast, when we examine the molecular weight results for MMA we do not find the same trends previously observed with styrene. Figure 9 presents the weight-average molecular weight estimates for the three MMA homopolymerization experiments. The data show that the polymer produced with the tetrafunctional initiator has molecular weights much

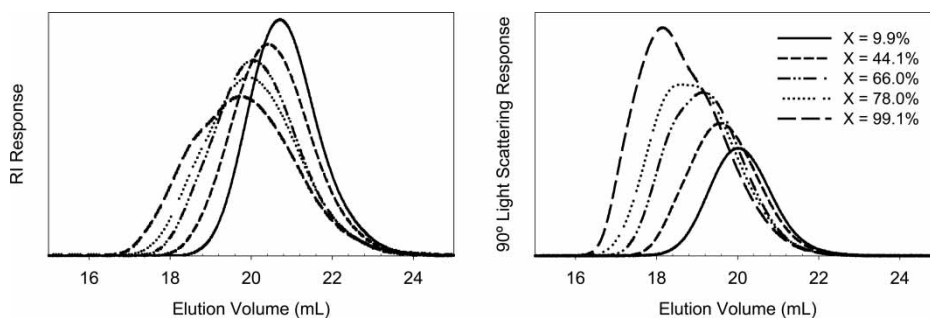


Figure 6. SEC chromatograms for polymer samples from experiment S-TC (from SEC1).

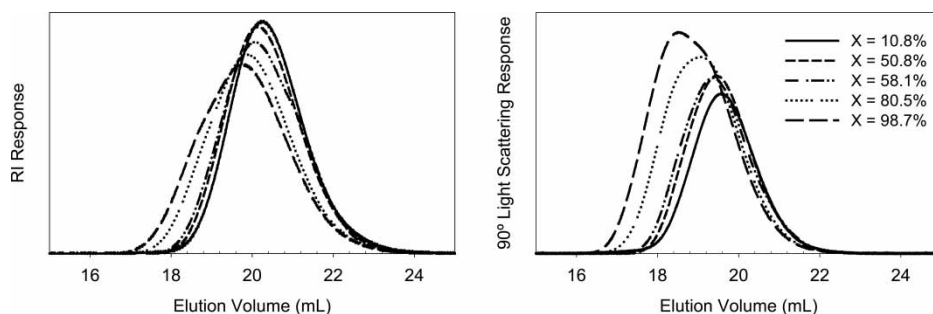


Figure 7. SEC chromatograms for polymer samples from experiment S-MC (from SEC1).

lower than when the monofunctional initiator is employed at the same concentration. In fact, the results for JWEB50 are similar to the curve observed for TBEC at a concentration four times as high.

In the case of MMA, differences between the polydispersity for polymer produced with the tetrafunctional initiator compared to the monofunctional counterpart were not observed. As well, a comparison between the SEC chromatograms for the PMMA samples did not show a high molecular weight shoulder for the polymer produced with JWEB50. In fact, no discernible differences were observed between the SEC traces for polymer produced with JWEB50 compared to those samples initiated with TBEC.

These observations with styrene and MMA are comparable to what has previously been reported (29, 30). With styrene, the tetrafunctional initiator would produce higher

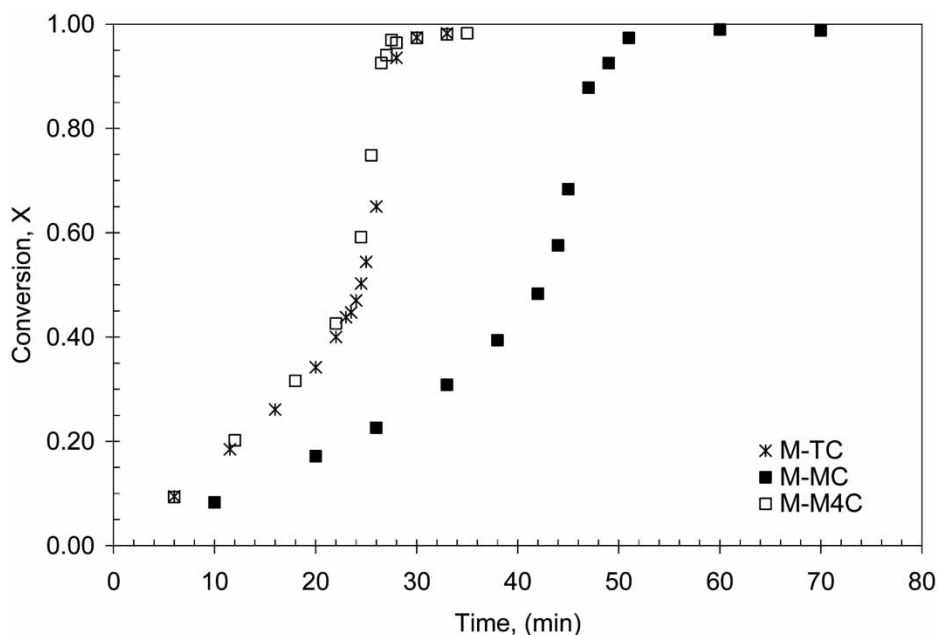


Figure 8. Monomer conversion as a function of time for the bulk polymerization of MMA at 110°C ($C = 0.004$ M, $4C = 0.016$ M).

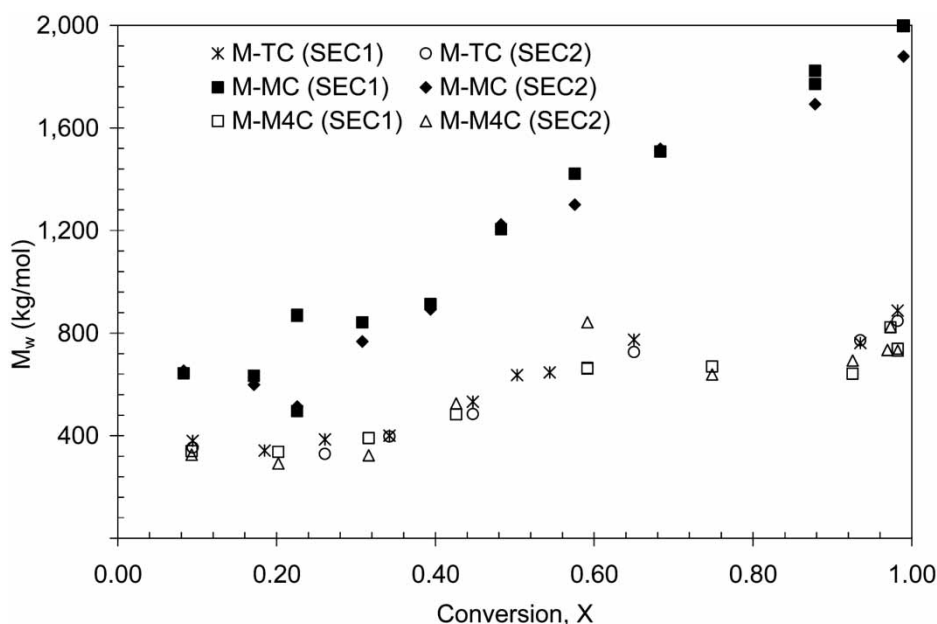


Figure 9. Weight-average molecular weight as a function of conversion for the bulk polymerization of MMA at 110°C ($C = 0.004$ M, $4C = 0.016$ M).

rates of polymerization while maintaining similar molecular weights compared to the monofunctional counterpart. However, this benefit was not observed with MMA and it was found that using the tetrafunctional initiator is equivalent to employing the monofunctional initiator at a concentration four times as high. The varying results between the two monomers have been attributed to their different modes of termination. For the temperature range studied, styrene is known to terminate predominately by radical coupling while in the case of methyl methacrylate radicals terminate mostly by disproportionation. Figure 10 provides an example of the influence the mode of termination will have on the degree of polymerization. We consider a theoretically simple situation where a tetra-radical has n monomer units for each arm and terminates with four linear radicals with n monomer units. If radical termination occurs by combination, a star polymer with four arms, each with a $2n$ monomer units, would be formed. Alternatively, if disproportionation was the dominant mode of termination, a star polymer with n monomer units per arm would be produced along with four linear chains comprised of n monomer units. In the case of the former, the degree of polymerization would be $8n$ while for the latter, it would be $8n/5$. This simple example indicates that coupling of the linear chains with the multifunctional core would help the tetrafunctional initiator to produce polymer of a higher molecular weight. As such, multifunctional initiators have the potential to allow higher reaction rates without lowering the polymer molecular weight when radicals predominantly terminate by coupling.

In order to study the effect JWEB50 would have with comonomer feeds, experiments were completed with a 50–50 wt% mixture of styrene and methyl methacrylate. Figure 11 is plot of the conversion versus time results for the three initiator conditions ($[JWEB50]_0 = 0.004$ M, $[TBEC]_0 = 0.004$ M, and $[TBEC]_0 = 0.016$ M). Similar to the homopolymerizations of MMA and styrene, we observe that the tetrafunctional initiator

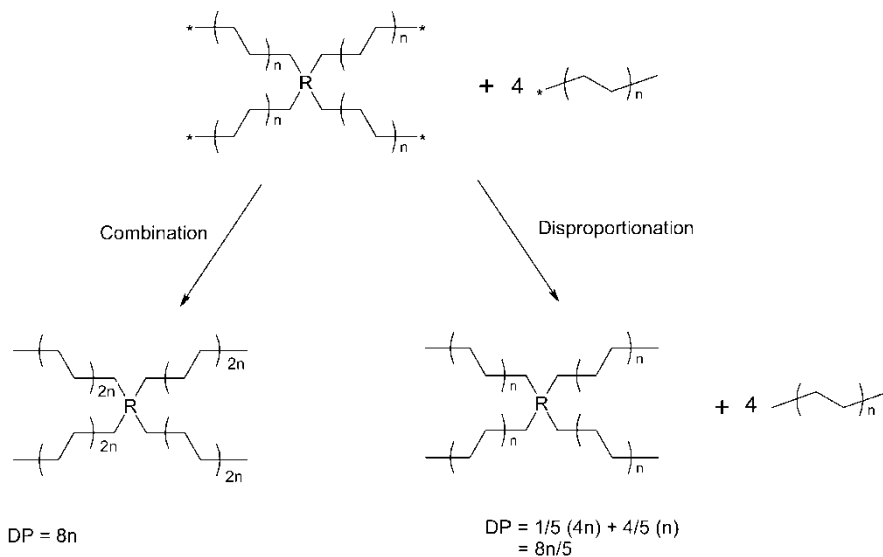


Figure 10. Effect of mode of termination on degree of polymerization.

yields a rate of polymerization similar to that of the monofunctional initiator at a concentration four times as high. Molecular weight results for this comparison are shown in Figure 12. The data show trends that are a mixture of what has been observed for the homopolymerization of styrene and methyl methacrylate. Initiating the polymerization with the tetrafunctional initiator has produced polymer with molecular weights in

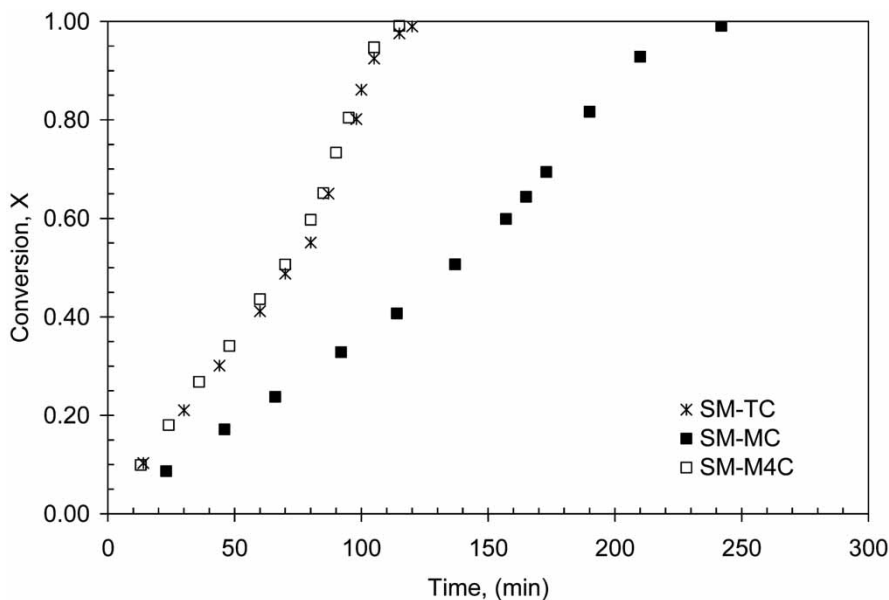


Figure 11. Monomer conversion as a function of time for the bulk copolymerization of styrene and MMA at 110°C ($C = 0.004$ M, $4C = 0.016$ M).

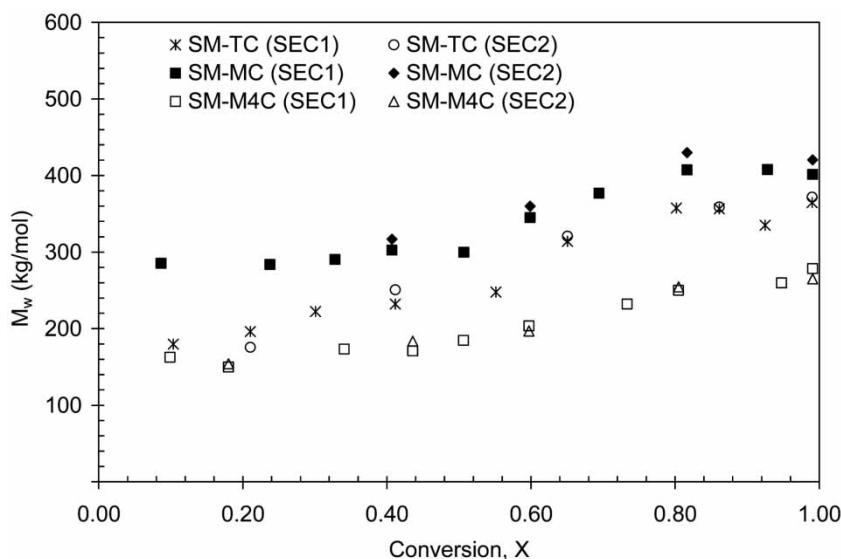


Figure 12. Weight-average molecular weight as a function of conversion for the bulk copolymerization of styrene and MMA at 110°C ($C = 0.004$ M, $4C = 0.016$ M).

between those trends observed for the monofunctional initiator at the high and low concentrations (0.004 M and 0.016 M). The polydispersity of the polymer was calculated and no difference was observed between the three runs. Figure 13 shows the accumulated polymer composition as a function of conversion for the copolymerization experiments of styrene and MMA. As expected, the data indicate that the tetrafunctional initiator does not influence copolymer composition.

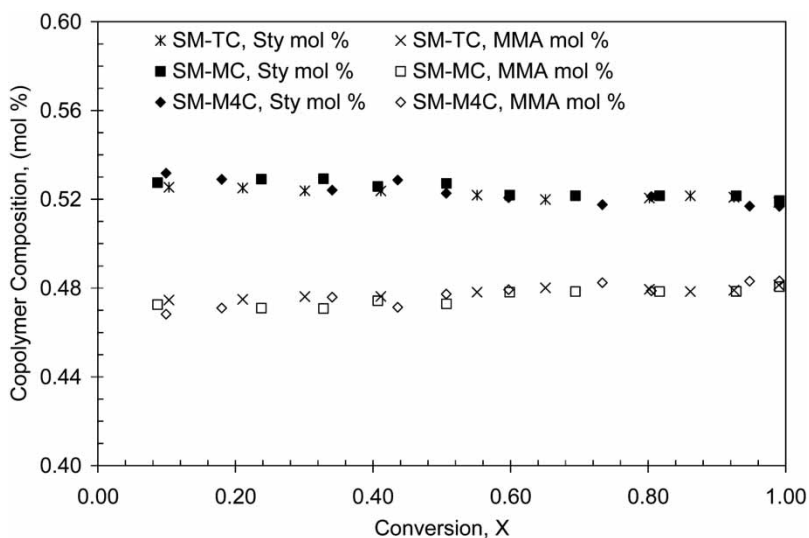


Figure 13. Copolymer composition as a function of conversion for the bulk copolymerization of styrene and MMA at 110°C ($C = 0.004$ M, $4C = 0.016$ M).

Evidence of Branching

The examination of dilute solution properties is a common method for discovering evidence of branching within a polymer sample and has been the subject of a variety of experimental and theoretical studies (33–37). One of the most fundamental properties that can be obtained from dilute solution methods is the size of a polymer molecule, normally measured as the mean-square radius:

$$\langle S^2 \rangle = \left\langle \sum_{i=1}^N \frac{r_i^2}{N} \right\rangle \quad (1)$$

where the polymer molecule is separated into N small elements of identical mass and r_i is the distance of the i th unit from the polymer molecule's center of gravity. The angled brackets denote that the mean-square radius is averaged over all possible conformations. The term radius of gyration is commonly used when referring to a polymer molecule's size and is simply the square root of the mean-square radius:

$$R_g = \langle S^2 \rangle^{1/2} \quad (2)$$

The influence of branching on the size of a polymer chain is that for a particular molecular weight, an increase in branching will decrease the radius of gyration. To assess the decrease in size due to branching, the mean-square radius of a branched polymer is compared to its linear analog of identical molecular weight. Quantitatively, this is expressed through the following contraction factor:

$$g = \frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l} = \frac{(R_g^2)_b}{(R_g^2)_l} \quad (3)$$

where the subscript b denotes that it is the branched polymer and l is for the linear polymer of identical molecular weight. Values of g less than unity are an indication of branching.

The mean-square radius can be determined experimentally from static light scattering experiments through the angular dependence of the intensity of scattered light. However, when the sample is polydisperse, scattering experiments provide the z-average mean-square radius. A broad molecular weight distribution can undoubtedly impact polymer properties and it has been found that the influence of branching can be completely masked by a large polydispersity. As such, differences between results for an unfractionated branched sample and its linear counterpart will be indiscernible. Coupling a light scattering device with SEC is a method to overcome this problem. Assuming that SEC adequately fractionates the polymer sample, the LS detector cell should contain monodisperse fractions at any particular time and a distribution of the radius of gyration as a function of molecular weight can be obtained.

Figures 14 (a), (b) and (c) are radius of gyration plots for the three different styrene-MMA feed mixtures. The plots provide a comparison between polymer produced with the tetrafunctional initiator and polymer produced with the monofunctional initiator. In the case of the homopolymers, an extra curve is included for a polydisperse linear polystyrene standard (American Polymer Standards Corp.). The polystyrene data show that the broad standard and the polymer produced with the monofunctional initiator have identical curves for radius of gyration as a function of molecular weight. The results for these two samples show the expected linear trend in a double logarithmic plot as R_g is related to molecular weight by the following equation:

$$R_g = aM^b \quad (4)$$

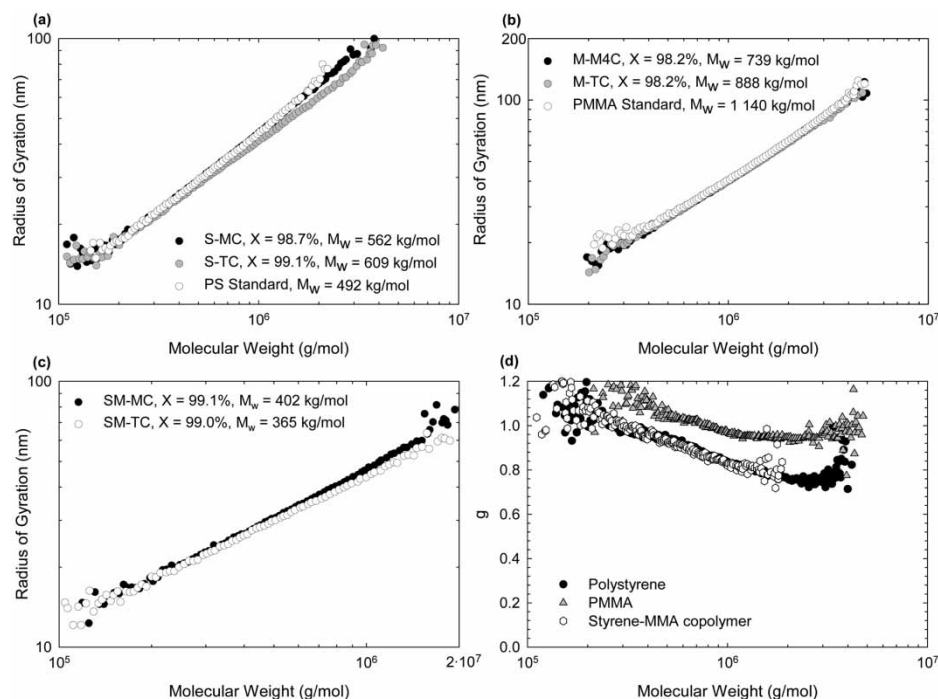


Figure 14. Radius of gyration and corresponding branching factor as a function of molecular weight: (a) polystyrene, (b) poly(methyl methacrylate), (c) styrene–methyl methacrylate copolymer, (d) g values for PS, PMMA and copolymer samples produced with the tetrafunctional initiator.

A value of 0.5 or greater for the exponent is expected for linear polymers in a good solvent. Using nonlinear regression, estimates of a and b were obtained for the broad molecular weight standard and the sample produced with the monofunctional initiator (see Table 3). These estimates are comparable to what has been previously reported in the literature (36, 38, 39).

When examining the data for the polymer produced with the tetrafunctional initiator, it can be seen that at low molecular weights the three curves overlap (Figure 14 (a)). This is an indication that in the low molecular weight range, the polymer produced with JWEB50 is linear. However, in the high molecular weight range, the data for the tetrafunctional

Table 3
Power law coefficients for radius of gyration-molecular weight relationship and Mark-Houwink-Sakurada coefficients

Sample	a (nm)	b	K (dL/g)	α
S-MC (sample 14)	0.0103	0.606	1.38×10^{-4}	0.705
Broad PS	0.00987	0.609		
M-M4C (sample 14)	0.00616	0.636	1.55×10^{-4}	0.747
Broad PMMA	0.00501	0.652		
SM-MC (sample 12)	0.0103	0.610	1.16×10^{-4}	0.722

initiator curves away and downwards from the data for the broad standard and for the polymer produced with TBEC. The fact that at a particular molecular weight, the polymer produced with JWEB50 has a lower radius of gyration than the polymer generated with TBEC is an indication that the former is more branched.

Figure 14 (b) provides the comparison for the poly(methyl methacrylate) samples. Unlike the case of polystyrene, deviations between the curves for the broad standard and the polymer samples produced with the tetra- and monofunctional initiators were not found. Based on these results we do not see any evidence of branching when the tetra-functional initiator is employed with methyl methacrylate. This observation was somewhat unexpected. A comparison of the rate data for the two initiators suggested that the functional groups for the tetrafunctional initiator were fully decomposing and behaving similar to those of the monofunctional initiator. From this, we would expect that branched polymers had formed. If this was the case, then it could be that SEC-MALLS is not sensitive enough to detect low levels of branching in these samples.

A characteristic of SEC is that separation occurs based on hydrodynamic size. If the polymer sample contains a mixture of branched and linear chains, each with their own molecular weight distribution, it is possible for branched and linear molecules to have the same hydrodynamic size but differing molecular weights. When this occurs, the branched and linear polymer chains will not be separated by SEC. The detector cells will then no longer contain monodisperse fractions and the results will represent an average. As previously mentioned, the R_g estimate obtained from light scattering experiments is a z-average and the effect of polydispersity can counterbalance any reduction in R_g caused by branching.

Because JWEB50 was employed in a free radical process, the final polymer will have a branching distribution due to several factors including the structure of JWEB50, coupling of multi-radicals, and in a more general case, also due to chain transfer to polymer and terminal double bond polymerization, with each fraction having its own molecular weight distribution. However, revisiting the example shown in Figure 10 may explain why branching is not seen with MMA. In the case of styrene, the fact that radicals terminate predominantly by coupling means that the tetra-chains have the potential to grow much larger than the linear chains. As well, radical coupling helps reduce the number of linear chains compared to radicals terminating by disproportionation. These two factors would help branching to be detected because the branched chains would be significantly larger than the linear chains and the fraction of linear chains would be smaller, thus limiting coelution.

The radius of gyration plot for the styrene–MMA copolymer data is shown in Figure 14(c). The results are a combination of what was seen with the homopolymers. The data for the polymer produced with the tetrafunctional initiator only curve slightly away from the linear sample. Using the relationship given by Equation (4) and the parameters in Table 3, the branching factor, g , for each of the three samples produced with JWEB50 has been calculated and the results are shown in Figure 14(d). Noise in the detector signals in the low molecular weight and low radius of gyration range contributes to the scatter in the data and to the values of g being greater than unity. The data indicate that the PMMA sample is not branched while the PS and copolymer samples show similar levels of branching.

In addition to the LS results, the viscometer can provide similar information about branching as it allows for the determination of the polymer intrinsic viscosity, $[\eta]$, and its appropriate contraction factor:

$$g' = \frac{[\eta]_b}{[\eta]_l} \quad (5)$$

where the intrinsic viscosity values are for branched and linear polymers of identical molecular weight. Coupled with SEC, the viscometer produces a Mark-Houwink-Sakurada (MHS) plot for each sample (see Figures 15 (a), (b) and (c)). The MHS plots show similar trends to those observed with the radius of gyration plots. Evidence of branching was detected for PS and the styrene–MMA copolymer produced with the tetrafunctional initiator. However, in the case of PMMA no discernible difference was detected between polymer produced with the monofunctional and tetrafunctional initiators. In order to estimate values of g' , the MHS coefficients were obtained from nonlinear regression and used to calculate the intrinsic viscosity of the linear polymer (see Table 3). The estimates of K and α are similar to those reported in the literature (34, 36, 40)

Figure 15(d) provides a plot of g' as a function of molecular weight for the three samples produced with the tetrafunctional initiator. One point to note is the results indicate that the PMMA sample could be slightly branched in the very high molecular weight range. However, this sample is no more branched than the PMMA sample produced with TBEC as both their MHS plots overlap (see Figure 15(b)). In fact, the g' curve for the PMMA sample produced with TBEC (not shown) and the curve for the sample produced with JWEB50 completely overlap, thus indicating that both samples have the same level of branching. A certain amount of branching can be generated with a monofunctional initiator because of the nature of the free radical polymerization. For example, terminal double bonds formed by radicals terminating through disproportionation can eventually be consumed and form trifunctional branches.

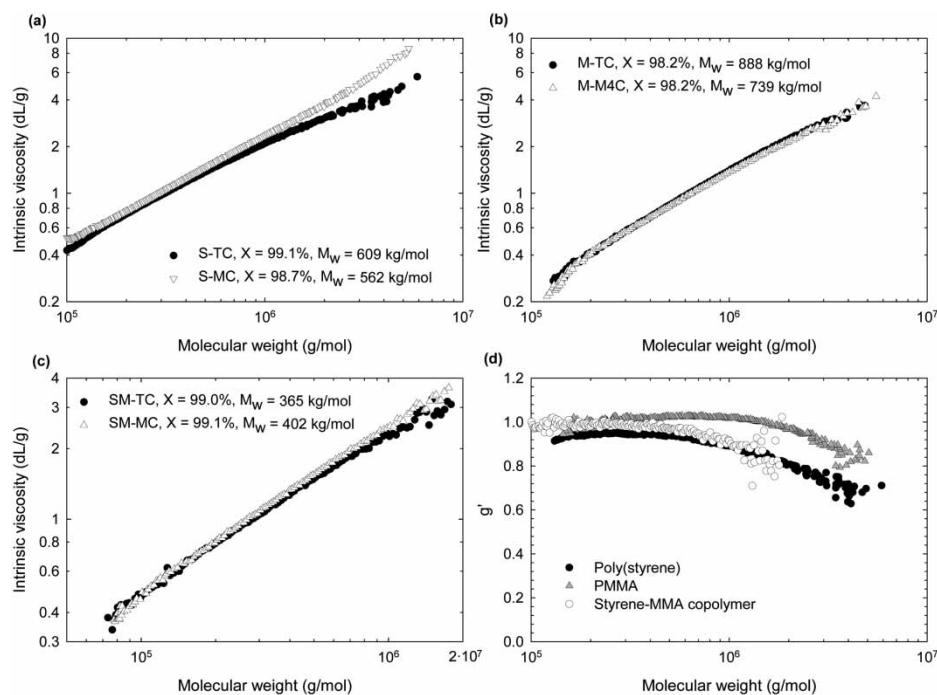


Figure 15. Intrinsic viscosity and corresponding branching factor as a function of molecular weight: (a) polystyrene, (b) poly(methyl methacrylate), (c) styrene–methyl methacrylate copolymer, (d) g' values for PS, PMMA and copolymer samples produced with the tetrafunctional initiator.

Effect of Longer Reaction Times

In several of the experiments for the homopolymerization of styrene, it was observed that at low and mid conversions, both initiators produced polymer of similar molecular weight. However, towards the end of the reaction it was found that the polymer molecular weights were increasing more with the tetrafunctional initiator than the monofunctional initiator. As a result, a final block of experiments with styrene and MMA were completed to study the use of the tetrafunctional initiator at longer reaction times. It was found in the polymerization of styrene with JWEB50 that the molecular weight increased further even though full conversion had been reached. Figure 16 shows the weight-average molecular weight results for the homopolymerization of styrene at 120°C where each of the samples analyzed had reached a conversion of 99% or greater. The molecular weight data show an increasing trend for the polymerization initiated with the tetrafunctional initiator. However, in the case of the monofunctional initiator, it was found that the molecular weight of the polymer did not change over time (note that at 600 minutes three data points are plotted for three different samples). Figure 17 provides chromatograms for three samples produced with JWEB50 for various reaction times. The curves show that the high molecular shoulder increases with time even though full conversion has been reached. Looking at the data for the homopolymerization of MMA a different trend was observed. The tetrafunctional initiator did not cause the polymer molecular weight to increase after the final limiting conversion had been reached (see Figure 18).

Methyl Methacrylate and α -Methyl Styrene Copolymer

Three experiments were performed with a comonomer feed mixture of α -methyl styrene and methyl methacrylate to examine the behavior of the tetrafunctional initiator with a

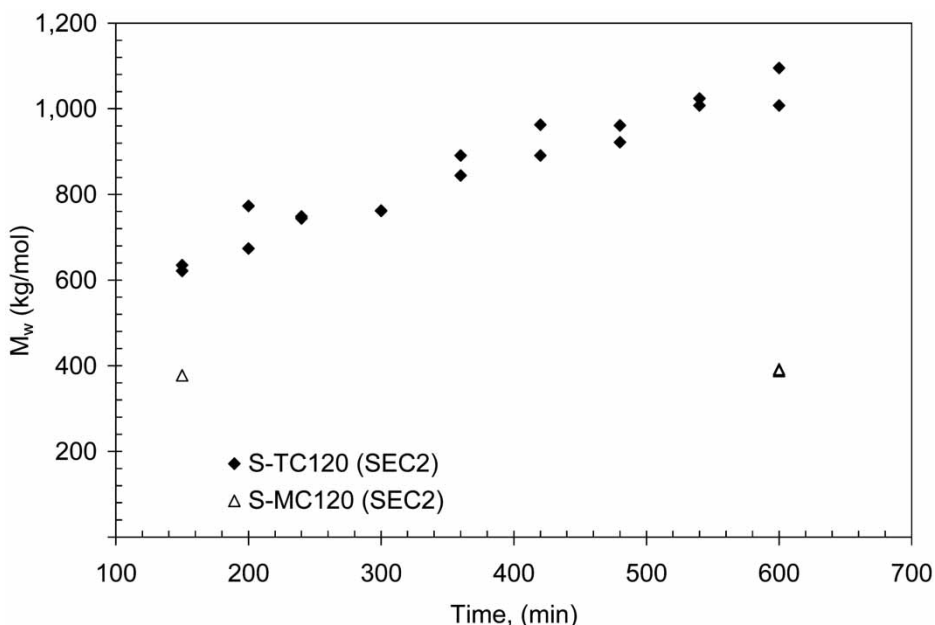


Figure 16. Weight-average molecular weight as a function of conversion for the bulk polymerization of styrene at 120°C (all samples are >99% conversion).

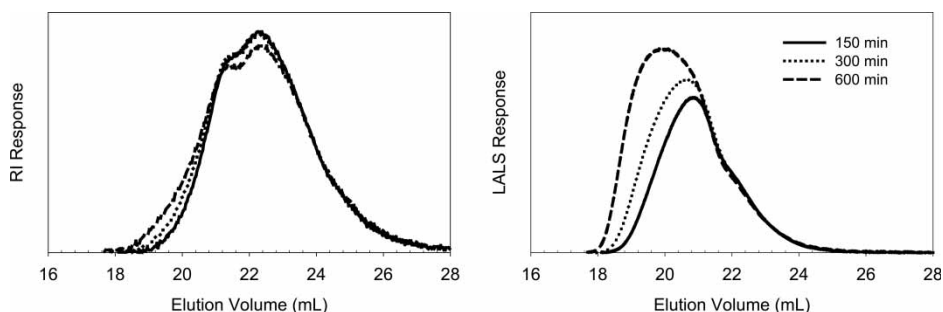


Figure 17. SEC chromatograms for polymer samples from experiment S-MC120 (from SEC2).

monomer that readily depropagates. α -MS is known to have a low ceiling temperature of 61°C for the pure monomer. Its use as a comonomer has several advantages including its ability to act similar to a chain transfer agent and lower the polymer molecular weight, and its ability to increase the polymer glass transition temperature (poly(α -MS) $T_g = 177^{\circ}\text{C}$ compared to PS $T_g = 100^{\circ}\text{C}$). However, the use of α -MS does have drawbacks as it can significantly lower the rate of polymerization. These features are evident when comparing the conversion and molecular weight data of the homopolymerization of MMA (see Figures 8 and 9) to the copolymerization of MMA with α -MS (see Figures 19 and 20). Looking at the experiments with TBEC as an example, the addition of

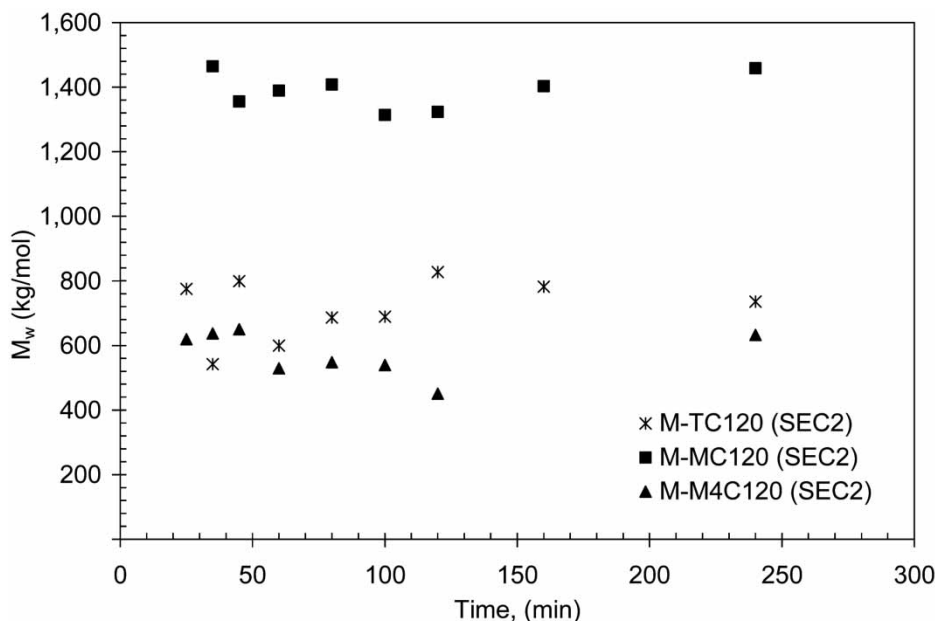


Figure 18. Weight-average molecular weight as a function of conversion for the bulk polymerization of MMA at 120°C (all samples are $>99\%$ conversion).

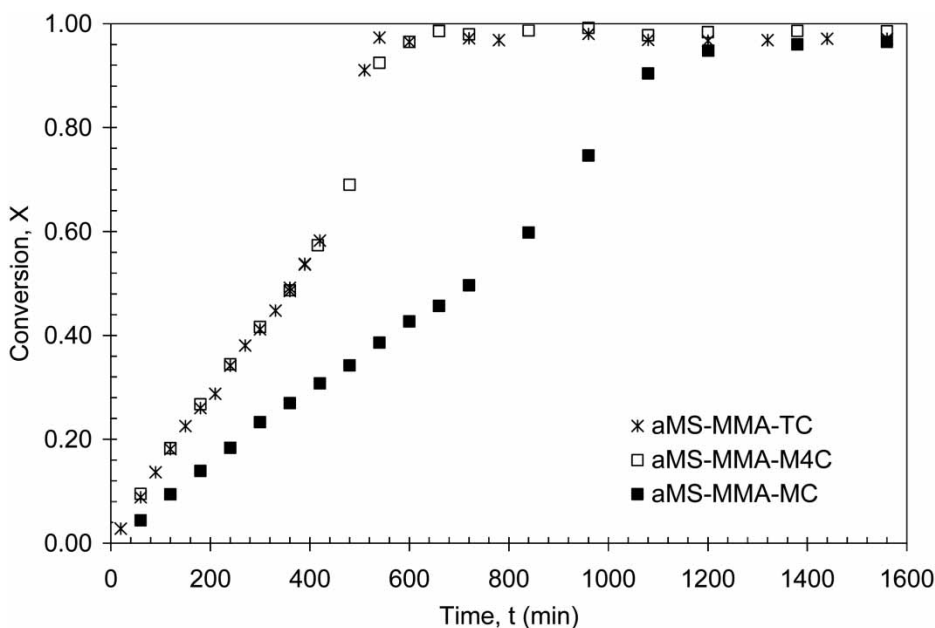


Figure 19. Monomer conversion as a function of time for the bulk copolymerization of α -methyl styrene and MMA at 110°C ($C = 0.004$ M, $4C = 0.016$ M).

20 wt% α -MS significantly extended the reaction times to reach a limiting conversion (~ 20 times longer) and molecular weights were noticeably reduced (full conversion: no α -MS, $M_w \approx 2 \times 10^6$; with α -MS, $M_w \approx 5 \times 10^5$).

When comparing the conversion, molecular weight and composition results for the α -MS–MMA experiments to those observed for the copolymerization of styrene and MMA, several similarities were observed. The conversion data again indicated that the tetrafunctional initiator produced a faster rate of polymerization compared to the monofunctional initiator and that similar rates can be obtained when the monofunctional initiator is employed at a concentration four times as great (see Figure 19). The molecular weight results showed that the use of JWEB50 produced polymer of similar molecular weight to when TBEC is used at the same concentration (see Figure 20). As well, the intrinsic viscosity data indicate that the polymer produced with the tetrafunctional initiator is more branched than the polymer produced with the monofunctional initiator (see Figure 21). An interesting point to note is that for the copolymerization of an equal feed mixture of styrene and MMA, we observed trends that were halfway between those of pure styrene and pure MMA (i.e., JWEB50 produced polymer molecular weights that were bounded by the trends for TBEC). However, in the case of the copolymerization with α -MS, we do not see a combination of the trends found with styrene and MMA. In fact, with a small amount of α -MS, we see trends similar to those observed with pure styrene. Therefore, with the addition of α -MS, the polymerization of MMA with the tetrafunctional initiator produced high rates and high molecular weights compared to TBEC. Although not shown here for the sake of brevity, the copolymer composition was again not affected by initiator functionality.

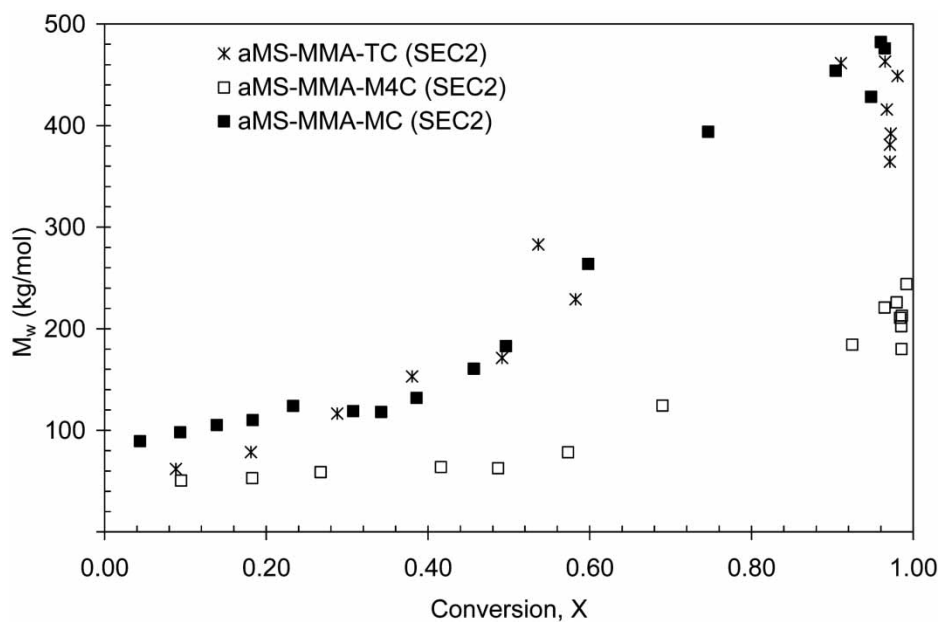


Figure 20. Weight-average molecular weight as a function of conversion for the bulk copolymerization of α -methyl styrene and MMA at 110°C ($C = 0.004\text{ M}$, $4C = 0.016\text{ M}$).

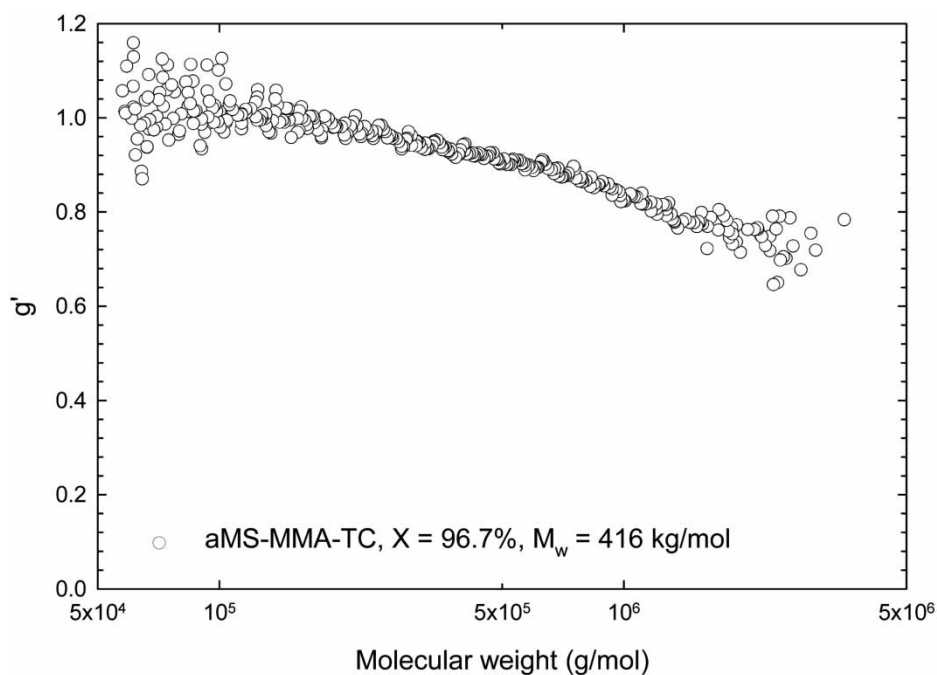


Figure 21. Intrinsic viscosity contraction factor as a function of molecular weight for polymer produced with the tetrafunctional initiator.

Conclusions

The use of JWEB50, a tetrafunctional peroxide initiator, in the bulk polymerization of various systems including styrene, MMA, styrene–MMA and α -MS–MMA was investigated. Comparisons with respect to the rate of polymerization and polymer molecular weight were made to TBEC, a monofunctional initiator with a functional group of similar structure and thermal stability to those of JWEB50. For every monomer and comonomer feed mixture studied, JWEB50 produced similar conversion-time data to that obtained with TBEC at a concentration four times as great. The results demonstrate that regardless of monomer type, the tetrafunctional initiator generates a higher rate of polymerization compared to its monofunctional counterpart.

Examination of the molecular weight results showed varying trends for the different feeds. In the case of styrene, JWEB50 produced molecular weight averages similar to those obtained with TBEC at the same concentration. As well, towards the end of the polymerization, higher polydispersities were observed with JWEB50 and inspection of the SEC traces showed the appearance of a high molecular weight shoulder not seen when using the monofunctional initiator. Experiments completed at longer reaction times with styrene showed that even after the final limiting conversion had been obtained, the polymer molecular weights kept on increasing when JWEB50 was employed. This was not observed with the monofunctional initiator. In contrast, for the homopolymerization of MMA, JWEB50 was found to decrease the molecular weight to a level similar to the results for TBEC at a concentration four times as great. SEC traces for polymer generated with the two initiators did not show any differences. As well, the increase in molecular weight after a limiting conversion was reached with JWEB50 was not observed with MMA. When a similar set of experiments were conducted with a 50/50 mixture of styrene and MMA, the molecular weight results were a combination of the trends observed for the two homopolymer cases. JWEB50 was found to produce molecular weights in between those for TBEC at the high and low concentrations. Plots of radius of gyration, intrinsic viscosity and their corresponding branching factors showed samples produced with JWEB50 were more branched than those for TBEC in the case of styrene and its copolymers. No evidence of branching was found with MMA. With a relatively small addition of α -MS to MMA, the use of JWEB50 allowed high molecular weight polymer to be produced and evidence of branching was shown via the g' estimates.

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