A new approach to controlled/living radical polymerization by DPE method

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A B S T R A C T

Controlled free radical polymerizations of methyl methacrylate and styrene in bulk by 1,1-diphenylethene (DPE) were demonstrated in a two-step process, preheating treatment of initiators followed by a living polymerization of monomers. Over the course of polymerization, continuous growing of polymers with unimodal molecular weight distribution and a relatively small polydispersity index (around 1.5 even in the range of Mn ~ 10^5 g/mol) on GPC diagrams was observed. In our previous study, the DPE controlled radical polymerization with constant molecular weight throughout the polymerization was caused by the intrinsically low reactivation rate constant (k_2) of DPE capped dormant chains. To raise the reaction temperature in order to increase k_2, a continuous molecular weight growing but broader or bimodal molecular weight distribution was obtained if the living polymerization was conducted in a one-step process. In this work, a two-step polymerization process was proposed. In the first step, the initiator 2,2′-azobisisobutyronitrile (AIBN), control agent DPE, and small amount of monomer were mixed and heated for a specific time period. Then a living polymerization of monomers was conducted in the second step of polymerization. This two-step new approach had minimized the imperfections of the DPE system; thus the polymerization showed better living characters and revealed its enhanced control abilities.

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1. Introduction

A new alternative for controlled radical polymerization (CRP) by using 1,1-diphenylethene (DPE) was developed by Nuyken and co-workers [1] in 2001. Three main classes of controlled/living polymerization techniques, such as nitroxide mediated polymerization (NMP) [2–6], reversible addition-fragmentation transfer (RAFT) [7–11] and atom transfer radical polymerization (ATRP) [12–16] are rather mature in academic research and are in widespread use globally. However, drawbacks in three main techniques of CRP impede the mass production on an industrial scale. For example, the NMP system has to be carried out at high temperatures (>120 °C), due to its inherently slow reaction rate and it works better in styrene derivatives. The difficulties of catalyst removal from the polymer for ATRP and relatively complicated synthesis pathway as well as the unpleasant odor in RAFT are known defects.

Most of the radical polymerizations are controlled if small amounts of DPE are added, even applied to vinyl acetate and N-vinyl compounds. Furthermore, DPE is known for its inability to form homopolymers because of the steric hindrance [19]. Hence, it also acts as a molecular weight retarder during polymerizations. As mentioned, controlled radical polymerization based on DPE has attracted some interest because it is commercially available, odorless, and without known toxicity. Furthermore, the detailed mechanisms were proposed [17,18]. The DPE methods also apply to the production of multi-block copolymers: for instance, amphiphilic block copolymers. Tons of productions via DPE methods are achievable in a one pot reaction and the synthesis can be carried out in bulk or solvents as well as emulsions, which is attractive from an industrial viewpoint. In our previous work, we conducted DPE controlled radical polymerizations in homogeneous and mini-emulsion systems at 80 °C [20], and concluded that polymerization carried out in a miniemulsion system exhibited higher reaction rate and better controlled living character than those in a homogeneous system. Nevertheless, according to the published papers, constant molecular weight of the polymer throughout the reaction was still unanswered [1,21]. Therefore, some kinetic studies have been carried on in our group and the rate constants involved in the DPE-PMMA mechanisms were estimated [22]. The rate constant k_2, corresponding to the reactivation of the DPE capped dormant chains was found to be very small at 80 °C (1×10^{-5}/s), which

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successfully accounted for the constant molecular weight of polymers throughout the DPE controlled radical polymerizations.

The controlled ability of the DPE system could be improved at elevated temperatures with more activation−deactivation cycles, but it was not good enough in narrowing the PDI compared to the well known CRP methods mentioned before. In those CRP processes, for example, NMP and ATRP, activation/deactivation cycles are fast enough to narrow down the molecular weight distribution. Therefore, two-step polymerizations with preheating treatment in such cases are less important. However in DPE mediated radical polymerizations, the rate constant of k_2 is much smaller than k_1, thus the activation/deactivation cycles are very slow and it is difficult to obtain a narrow molecular weight distribution without preheating treatment. Although some well defined multi-block copolymers and graft copolymers were synthesized successfully by the DPE method [23–27], there has been a very limited number of publications on DPE as a mediator for controlled radical polymerizations and the deficiencies of the DPE controlled system such as large polydispersity index, undesired chain terminations, and no expected increasing of molecular weight growing were still unsolved up to now. The aim of this work is to propose a new approach in order to enhance the performance of DPE controlled radical polymerization, so that living and growing of polymer chains with a smaller PDI throughout the course of polymerization could be obtained. A two-step process was first proposed to narrow down the molecular weight distribution of DPE controlled/living radical polymerizations. The reaction temperature, the amount of DPE, the addition of monomer in two steps, and the preheating time period were studied and are discussed in detail.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA; Acros), styrene (ST; Acros), and 1,1-diphenylethene (DPE; Acros) were distilled under a reduced pressure and stored at 5 °C before use. 2,2′-azobisisobutyronitrile (AIBN; Showa) was recrystallized from methanol. Tetrahydrofuran (ECHO), methanol (ECHO), and hydroquinone (HQ, Acros) were used without further purification.

2.2. Bulk polymerization

Monomers, initiator AIBN and control agent DPE following the molar ratios in Tables 1 and 2 were mixed in a 100 ml sealed three-necked glass reactor in one step or two steps. Nitrogen was purged for half an hour to drive out the oxygen and moisture before the reaction. Then the glass bottle was immersed in an oil bath to start

Table 1
Symbols and recipes of the DPE controlled bulk polymerization of MMA

Sample code	MMA:DPE:AIBN (molar ratio)	Reaction temperature	Process
A0	220:2:1	80 °C	One step
A1	220:12:1	95 °C	One step
A2	22:2:1$^{10 h, a}$ → 220:2:1	80 °C	Two steps
A2-1	22:2:1$^{2 h}$ → 220:2:1	95 °C	Two steps
A3	44:12:1$^{2 h}$ → 660:12:1	95 °C	Two steps
A4	22:12:1$^{2 h}$ → 660:12:1	95 °C	Two steps
A5	5.5:12:1$^{2 h}$ → 660:12:1	95 °C	Two steps
A6	5.5:12:1$^{1 h}$ → 660:12:1	95 °C	Two steps
A7	5.5:12:1$^{3 h}$ → 660:12:1	95 °C	Two steps
A8	22:4:1$^{2 h}$ → 660:4:1	95 °C	Two steps

^{a} Preheating time.

Table 2
Symbols and recipes of the DPE controlled bulk polymerization of styrene

Sample code	ST:DPE:AIBN (molar ratio)	Reaction temperature	Process
B1	220:2:1	90 °C	One step
B1-1	220:2:1	135 °C	One step
B2	22:2:1$^{10 min, a}$ → 220:2:1	135 °C	Two steps
B3	22:12:1$^{10 min}$ → 220:12:1	135 °C	Two steps
B4	22:12:1$^{30 min}$ → 220:12:1	135 °C	Two steps

^{a} Preheating time.

the polymerization. Temperature of the reaction mixture was monitored by a thermal couple. In the two-step process, the initiator was dissolved in a small amount of monomer in the presence of DPE, and was preheated for a specific period of time in the first step. Various time periods were chosen, basically depending on the dissociation rate of the initiator and polymerization rate. In the second step, the remaining monomers were then purged into the reaction bottle to continue the living polymerization. Certain amount of the sample was taken out into hydroquinone-containing methanol solution to precipitate polymers for the measurements of molecular weights and conversions.

2.3. Characterization

The conversion of monomer during polymerization was determined by gravimetric method. Molecular weight and molecular weight distribution of synthesized polymers at different conversions were measured by gel permeation chromatography (GPC), which was equipped with a solvent delivery system, two columns (300×7.8 mm, 5 micron, Phenomenex), and a differential refractometer (RI). Two columns were maintained at 40 °C. THF was used as the eluent and was kept at a flow rate of 1.0 ml/min. The sample concentration for GPC measurements was 2 mg/ml THF. Six polystyrene standards with molecular weights ranging from 104 g/mol to 382,100 g/mol were used for calibration.

3. Results and discussion

3.1. Reaction temperatures and polymerization without preheating treatment

In sample A0, the reaction temperature was kept at 80 °C and its GPC diagram is shown in Fig. 1. Results showed that the Mn stayed constant throughout the reaction with consumption of the monomer and a narrow PDI (1.2 ∼ 1.3) was obtained in a small Mn range. It revealed that DPE capped on the polymer chains which were generated from the continuously dissociated initiator and were unable to reactivate owing to the extremely small k_2 [22], so that diversity of the molecular weights was not obvious. Livingness of this trial was also verified by a chain extension experiment [22]. Typically this case does not belong to the categories of CRP and shows no real features of controllable growth of molecular weight. Scheme 1 shows the DPE mechanism. P_n-D* and P_{2t} were suggested to be the dormant structures of DPE ended radicals. For the sake of more activation−deactivation cycles between P_n* and P_n-D*, we conducted polymerizations at higher temperatures and the corresponding samples were A1, B1, and B1-1. When the temperature was raised above 90 °C, continuous growth of molecular weight due to an elevated k_2 was observed from the GPC diagram. However, both the continuous generation of relatively small molecular weight polymer chains caused by the dissociation of initiator and chain terminations enlarged the PDI values throughout the reaction. In styrene systems, sample B1 has similar displays to sample A1 and sample B1-1 has bimodal molecular
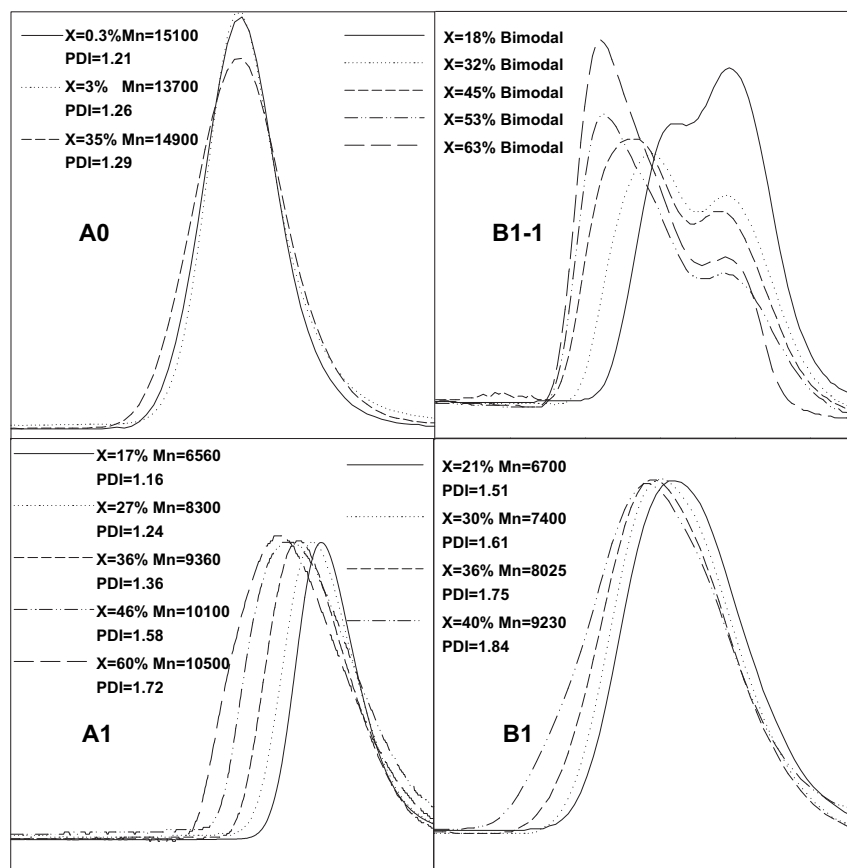
Fig. 1. GPC traces of sample A0, A1, B1, B1-1.

weight distributions over the course of polymerization on GPC traces. It was apparent that great differences between chain lengths were obtained under the conditions in the above mentioned samples.

3.2. Preheating treatment

A two-step process was performed to solve this problem. In the first step, i.e., preheating step, the initiator almost completely

Scheme 1. The DPE mechanism.

decomposed into radicals followed by the second step of polymerization. In other words, the living chains were born in the preheating step and growing into living polymer chains in the second step. In order to let the initiators dissociate under a monomer deficient condition in the presence of DPE, and to obtain DPE capped precursors for the following second step living polymerization, only a small amount of monomer was involved in the first-step reaction. After a specific time period, the remaining monomer was then added and we proceeded with the second step of polymerization. In sample A2, the molar ratio of MMA:DPE:AIBN was fixed as 22:2:1 in the first step and the mixture was heated at 80 °C for 10 h, then the remaining MMA monomers were added and the molar ratio of MMA:DPE:AIBN became 220:2:1. The dissociation rate constant (k_d) of the initiator AIBN at 80 °C was taken as 1.1×10^{-4}/s from Refs. [28,29], in which greater than 98.5% of the initiator had been dissociated in 10 h through the calculations from k_d. The chain propagations in the second step of polymerization in sample A2 could be explained by Le Chatelier's principle. As soon as the monomers were added, the bulk concentrations of P_n^*, D, and P_n-D* dropped from the previous level. According to the stoichiometry among the above three species, the reaction moved towards the left in the equilibrium of k_1 and k_2, which caused the decapping of P_n-D*, thus propagation of polymer chains occurred. From the GPC diagram in Fig. 2, maximum PDI during the middle stage of the reaction was about 2.2. The trend of the molecular weight distributions as well as the relatively large PDI values implied a small frequency of activation–deactivation cycle under 80 °C, and not all the polymer chains were activated at the same time. Once it reached a specific molecular weight which was determined by the amount of the monomer added, the propagation stopped. These phenomena were verified by the behavior of the stagnant
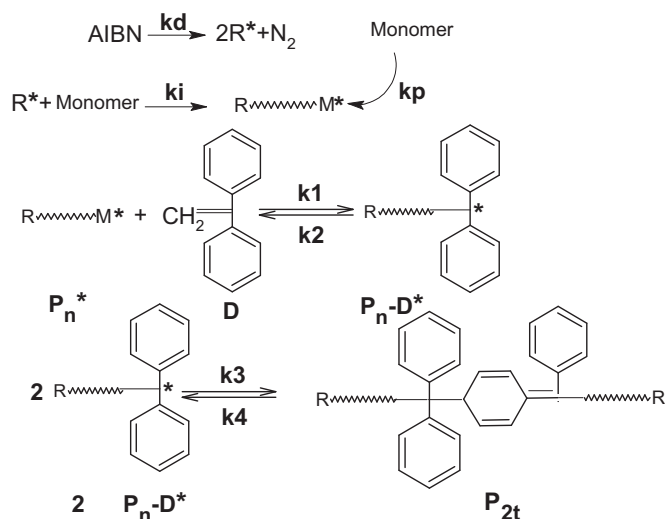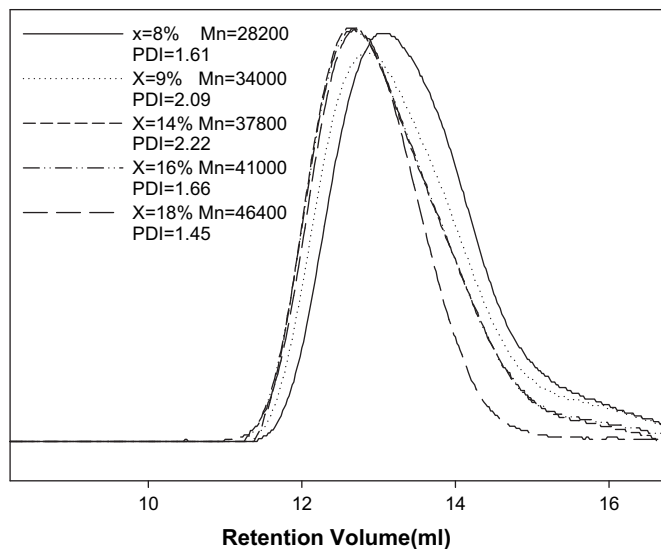
Fig. 2. GPC traces of sample A2.

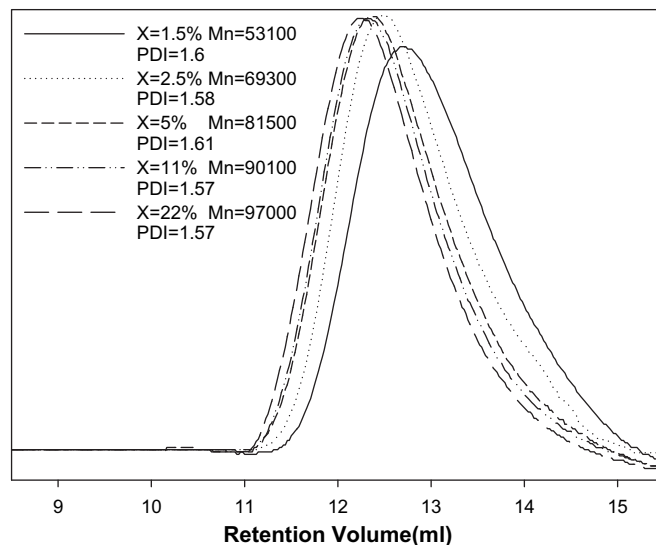Fig. 3. GPC traces of sample A7.

movement of peaks laid in the larger Mn zone on the GPC diagram after a certain extent of monomer consumption, and a smaller PDI value (1.45) was obtained at a "non viscous" 18% low monomer conversion when the propagations ended. Data indicated that at 80 °C, the small reactivation constant k_2 not only lessened the cycles between P_n^* and P_n-D* but increased the PDI values throughout the course of polymerization.

To conduct polymerizations at a higher temperature 95 °C with preheating treatment, such as sample A7, continuous growth of molecular weight with narrow distributions was observed throughout the course of polymerization. The GPC traces of A7 are shown in Fig. 3. Details are discussed in Section 3.3.

3.3. Preparation of large molecular weight polymers with a narrow distribution

3.3.1. Influence of monomer concentration in the step of preheating treatment

In samples A3–A5, the first step of preheating treatment was conducted in various small amounts of monomer at 95 °C with a fixed molar ratio of DPE/AIBN and preheating time of 2 h. The PDI values under the given molecular weight were in an order of A3 > A4, and A5 > A4. The reason for A3 > A4 was due to the increases of polymerization rate and chain length of DPE capped precursors in the step of preheating treatment in A3. The concentration of the monomer was higher in A3, thus the polymerization rate increased and the chain length increased in the preheating treatment step. As the activation–deactivation cycles did not proceed fast enough in the second step living polymerization, the chain length of precursors would influence the PDI of the final product polymers. The increase of the chain length of precursors would enlarge the PDI of the final polymers. However, minimizing the amount of monomer in the first step might not guarantee a smaller PDI because of the altered initiator efficiencies. Under conditions of lacking in monomer such as sample A5, the effective initiation of monomers largely decreased. The number of growing chains diminished. As a result, the molecular weight and PDI of polymers in A5 were larger than those of A4 during the second step of living polymerization. The order of molecular weights at a given conversion was A5 > A4 > A3 as shown in Fig. 4.

3.3.2. Influence of preheating time period

Based on sample A5 with a minimized amount of monomer, an extended preheating treatment for 3 h was conducted in sample A7 and a contrast of 1 h in A6. The dissociation rate constant (k_d) of AIBN at 95 °C was taken as 6.5×10^{-4}/s, hence more than 99% of the AIBN had been dissociated within 2 h and about 90% dissociation occurred within 1 h. As mentioned, in such a monomer deficient condition, the efficiency of initiation was low. How the preheating time affected the growth of living polymers would be discussed in this series of experiments. It was found that increasing the preheating time in A7 would decrease the PDI value. The order of molecular weight at a given conversion was A7(3 h) > A5(2 h) > A6 (1 h) during the second step of living polymerization because the
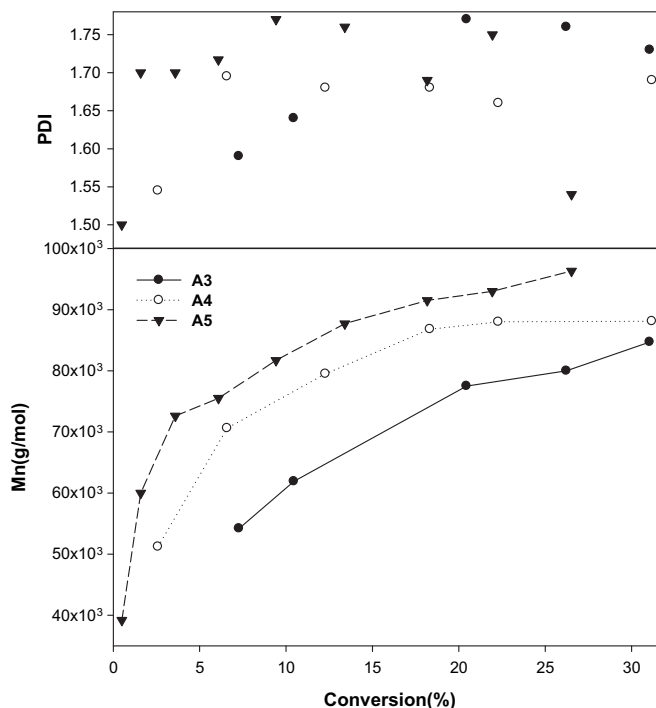

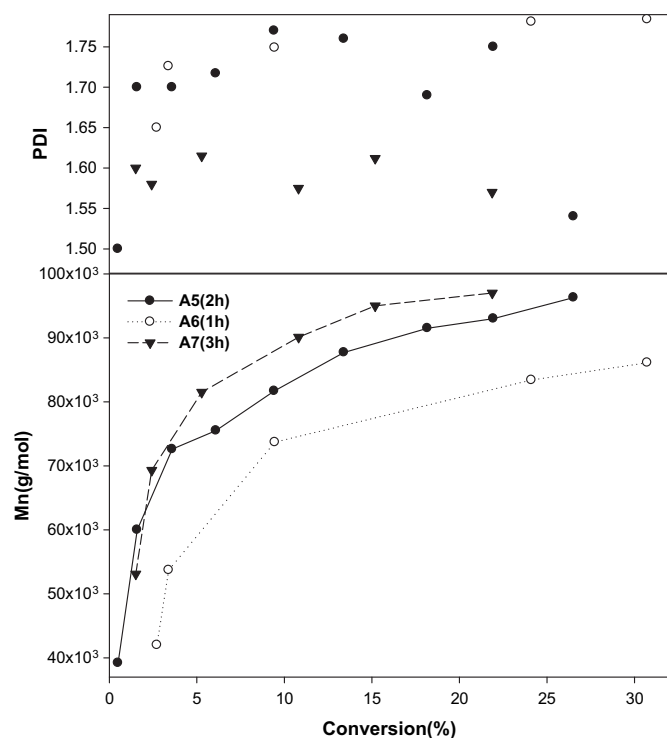Fig. 4. Molecular weights and PDI versus conversion of sample A3–A5.

Fig. 5. Molecular weights and PDI versus conversion with various preheating time periods of MMA system.

Fig. 7. Molecular weights and PDI versus conversion of sample A4, A8.

chain termination in extension of the preheating time period could be increased especially when a little monomer was present. As for the smaller PDI observed in A7 was due to the reason that a few irreversibly terminated oligomers with molecular weights below 10³ g/mol were neglected in GPC measurement. Results showed that, under extremely low monomer concentrations, to extend the preheating time led to a better living character. The PDI values of

sample A7 stayed relatively small with the consumption of monomer even in the range of Mn ∼ 10⁵ g/mol. The molecular weight and PDI values versus conversion of samples A5 ∼ A7 are shown in Fig. 5. Similar results between sample B3 and B4 in a styrene system with different preheating times are shown in Fig. 6. The order of molecular weights and PDI values at a given conversion were B4(30 min) > B3(10 min) and B3 > B4, respectively.

3.3.3. Influence of DPE

The polymerization of sample A8 was carried out with less DPE than in sample A4. The molar ratio of MMA:AIBN was fixed, but the
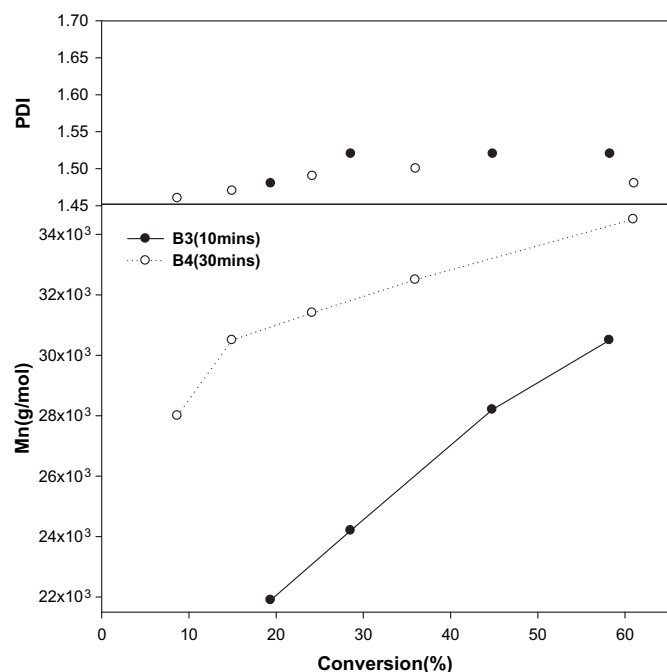

Fig. 6. Molecular weights and PDI versus conversion with various preheating time periods of the styrene system.
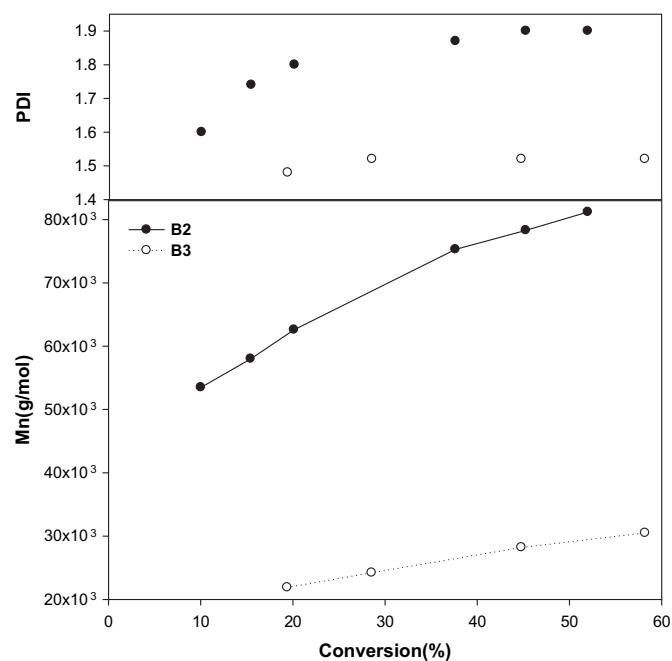

Fig. 8. Molecular weights and PDI versus conversion of sample B2, B3.
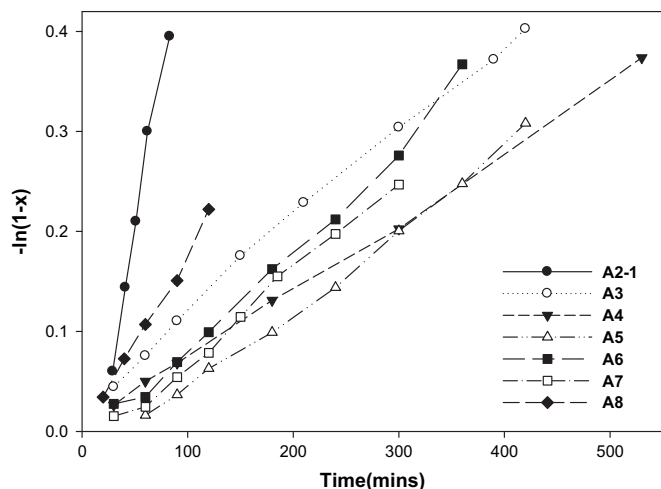
Fig. 9. $-\ln(1-x)$ versus polymerization times for samples A2-1 to A8.

molar ratio of DPE:AIBN was 4:1 and 12:1 in A8 and A4, respectively. The molecular weight and PDI versus conversion are shown in Fig. 7. The results revealed that, as more DPE was employed into the system, the polymerization rates were retarded not only in the first step of the reaction but also in the second step of living polymerizations. In other words, a larger molecular weight of A8 in comparison with A4 under the given monomer conversion was expected. As less DPE is present, there are more probabilities for the decapping of P_n-D^* and lower probabilities for P_n^* to be capped again over the course of living polymerization, the propagation of polymer chains and thus the molecular weight of A8 increased significantly.

The trend of molecular weights and PDI values versus conversion in B2 and B3 is shown in Fig. 8, in which molar ratios of DPE: AIBN were 2:1 and 12:1, respectively. Results showed that, under low DPE concentration such as B2, the PDI values increased with the growing of molecular weight. However, controlled PDI values throughout the course of polymerizations were demonstrated if adequate DPE was present. Consequently, controlled molecular weight distributions with consecutive chain growing were obtained in DPE mediated radical polymerizations. Figs. 9 and 10 showed the relationship in the plot of $-\ln(1-x)$ versus polymerization time for MMA and styrene systems. Better linearity of

logarithmic profiles was observed for two-step processes (all cases in Fig. 9 and B2 ~ B4 in Fig. 10) compared to the one-step process (B1 in Fig. 10). The living characters of polymers during polymerization were well controlled in this two-step polymerization process.

4. Conclusions

In this study, the performance of DPE controlled radical polymerizations is shown to be improved substantially through a two-step polymerization process. More activation–deactivation cycles occurred at higher temperatures, which caused continuous growth of molecular weight during polymerization. It was found that a preheating treatment of initiators was necessary for a better living character of DPE controlled systems. In our experimental results, the PDI of the final polymers decreased with lowering of the amount of monomer concentrations in the preheating step. Furthermore, increasing the preheating time in monomer deficient conditions has led to an enhanced controlled living character. Also, the influences of the amount of DPE on the reaction rate, molecular weights, and the trend of PDI values were investigated. Controllable chain extensions were achievable and smaller PDI values were obtained through this new approach.

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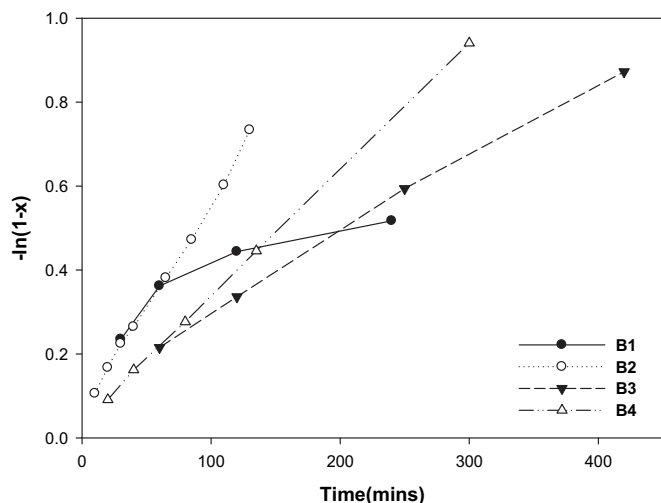[29] Brandup JI, Grulke E. Polymer handbook. New York: Wiley and Sons; 1989.

Fig. 10. $-\ln(1-x)$ versus polymerization times for samples B1–B4.