Effects of Reaction Conditions on Poly(methyl methacrylate) Polymerized by Living Radical Polymerization with Iniferter

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ABSTRACT: Living radical polymerization of methyl methacrylate (MMA) through the use of benzyl diethyl dithiocarbamate (BDC) was studied. The aim was to investigate the role of the concentration, BDC-to-MMA mol ratio, and reaction time upon the molecular weight, polydispersity, and conversion of the product. It was found that the molecular weight and the conversion increase with increase of the concentration at the expense of low polydispersity. The reaction time also played a significant role, especially at a relatively long reaction time where molecular weight, polydispersity, and conversion increased with increasing reaction time. In terms of the mol ratio effect, it was found that there was a critical mol ratio for maximum conversion. The results indicate that the kinetics of polymerization of MMA through the use of a BDC inifeter is different from that in the presence of a conventional initiator. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 938–944, 2000

Key words: living radical polymerization; iniferter; methyl methacrylate; benzyl diethyldithiocarbamate

INTRODUCTION

It is well known that various block copolymers can be used to improve interfacial adhesion in various multiphase polymeric systems such as blends[1] and laminate joints.[2] The conventional techniques for the preparation of block copolymers from vinyl monomers, such as anionic polymerization and group-transfer polymerization (GTP), have precluded widespread industrial applications, owing to its vigorous and demanding reaction conditions.[3] GTP has also been limited to use with acrylic-based monomers only.[4] As a result, there has been considerable interest in new synthesis routes for the preparation of block co-

polymers and narrowed polydispersity homopolymers from vinyl monomers.[5] One of the novel techniques for these purposes is "living" free-radical polymerization. Although normal free-radical polymerization cannot be used to achieve the block polymers, if the reaction conditions are controlled so that the propagating chains are free from bimolecular termination and a chain-transfer reaction, then the "living" mechanism can be approached. The strategy to achieve such conditions is to find a capping agent that reversibly reacts with the propagating chain. With the presence of capping agents, the propagating chains are temporary capped and prevented from a chain-transfer reaction and termination. The capped chains, however, dissociate thermally or photochemically into the propagating chains and the capping agents, depending on the type of agents. The propagating chains, therefore, can undergo further reaction with the available monomers, leading to block coplymers. There are

several methods that can be employed to obtain capping agents, including the use of nitroxide inert radicals,[6] atomic-transfer radical polymerization,[7] and the use of iniferters.[8] The use of nitroxide inert radicals was studied extensively by Georges et al.[9,10] The technique worked well with styrene and related monomers, whereas it was not the case for others monomers such as butyl acrylate. However, the cost for a commercailly available nitroxide radical, typically 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), is considerable high.

Atomic-transfer radical polymerization (ATRP) is one of the widely used techniques that can be used to obtain polymers having low polydispersities. ATRP is a reversible redox of the transition-metal compound being used as a catalyst. An alkyl halide, typically 1-phenyl ethylbromide, is used as a source for an initiator and a capping agent. Under appropriate conditions, the compound is dissociated into a reactive alkyl radical and a halide radical. The former acts as an initiator while the latter will reversibly combine with the metal compound catalyst. ATRP was studied extensively by Matyjaszewski et al.[7,11–13] It was found that styrene was polymerized via a living mechanism, and polydispersity of the polymer as low as 1.3 was reported.[7]

The iniferter concept was discovered by Otsu et al.[8] Iniferters are basically organic sulfur compounds with low decomposition energy. Under suitable conditions, the compounds are dissociated into reactive radicals and inert radicals, the latter serving as capping agents. Otsu et al. showed that the polymerization of styrene and methyl methacrylate (MMA) in the presence of an iniferter such as benzyl diethyldithiocarbamate (BDC) could proceed via the living mechanism.[14–16] The evidence used to support this included the low polydispersities of the product (typically ranging from 1.7 to 3), a linear increasing trend of molecular weight with the conversion, and a formation of a related block copolymer. For relatively strong electron-deficient monomers such as butyl acrylate and methyl acrylate, polymerization will not occur. Otsu et al., however, polymerized these monomers via a living mechanism successfully through the use of a two-component iniferter, that is, BDC in combination with tetraethyl thiuram disulfide.[17]

This research work concerns a controlled polymerization of MMA through the use of the BDC iniferter in order to optimize the product prepared from the technique. The main objective of this work was to investigate the role of the reaction time, monomer concentration, and monomer-to-iniferter mol ratio on the molecular weight, molecular weight distribution, and percentage conversion of the PMMA being polymerized.

EXPERIMENTAL

Monomer, Solvents, and Iniferter Preparation

A commercial grade of MMA was used in this work, supplied by the Siam Fine Chemicals Co. Ltd. (Bangkok, Thailand). The monomer was purified prior to use by an ordinary method.[18] The toluene used as a solvent in this work was an analytical grade from the JT-Baker (Phillipsburg, NJ), whereas a commercial grade of methanol used as a nonsolvent for precipitation of the product was supplied by the Siam Beta Group Co. Ltd. (Bangkok, Thailand). All the solvents were used as received. The BDC iniferter was synthesized from the reaction between benzyl chloride and sodium diethyldithiocarbamate in absolute ethanol at room temperature.[14] After the reaction was completed, the mixture was extracted from a mixture of dichloromethane and distilled water (1:1), three times, and the organic phase was collected and dried with anhydrous sodium carbonate overnight and solvent removed under reduced pressure.

Polymerization

The polymerization processes were conducted by varying three parameters: reaction time, monomer concentration, and iniferter/monomer mol ratio. The required amount of MMA was mixed with the BDC iniferter and the toluene solvent. Oxygen was removed from the mixture by nitrogen purging. The reaction tube was then sealed and exposed to ultraviolet radiation, using a Philips HPA-400 UV lamp, from a distance of 30 cm, at an ambient temperature (30°C). After polymerization for a given time, the product was isolated by precipitation in a large amout of methanol and dried under reduced pressure.

Characterization

The percentage conversion of MMA was determined by weighing the dried polymer. The molecular weight and polydispersity of the polymer was determined by size-exclusion chromatography (SEC) using a Waters 150 CV apparatus equipped with Styragel mixed B columns and two detectors,
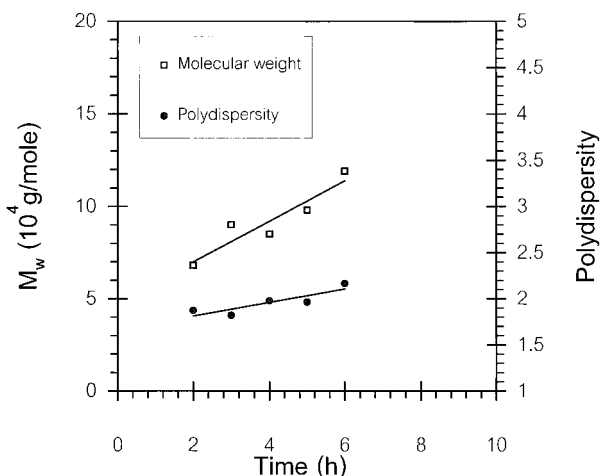
Figure 1 Molecular weight and polydispersity of PMMA as a function of time; [MMA] = 2.83 mol/L.

that is, a refractive index detector and a viscometer. The molecular weight resolving range of the columns ranged from 5×10^2 to 1×10^7. Polystyrene standards were used in order to generate a universal calibration curve. Tetrahydrofuran (THF) was used as an eluent at 1 mL/min, at 30°C.

RESULTS AND DISCUSSION

Figure 1 shows the effect of reaction time on the molecular weight and polydispersity of PMMA obtained by polymerization of MMA at a monomer concentration of 2.83 mol/L. It can be seen that the molecular weight considerably increased with increasing reaction time, while the polydispersity was slightly increased. Figure 2 shows that the percentage conversion of the monomer increased with increasing reaction time.

The results suggested that the polymerization proceeded via a living mechanism. In living polymerization, propagating chains are free from bimolecular termination. The longer the reaction time is, the more monomers consumed by the reactive propagating chains. The slight increase of the polydispersities with increasing reaction time also suggested that polymerization at a relatively short time, that is, 2–3 h, is an advantagein regard to a lower polydispersity of PMMA.

Control studies were conducted to investigate whether the MMA polymerized in the absence of BDC. The results in Table I show that the self-polymerization of MMA also occurred with con-

siderably low conversions (5.7 and 7.5%, after 4 and 7 h, respectively). The molecurlar weight of the products, however, was relatively high, compared with that from the polymerization with BDC. The polydispersity in the control experiments was slightly increased, for example, 2.3 and 2.4 for 4- and 7-h reaction times, respectively. A rational explanation for this effect was that there were no capping agents available for propagating chains. Therefore, these chains are capable of undergoing a combination termination, leading to a higher molecular weight of PMMA. The formation of the self-polymerized PMMA was, generally, unfavorable owing to the low purity and high polydispersity of the product being obtained.

These results were similar to those observed previously by Otsu and Kuriyama[19] for the bulk polymerization of styrene with BDC. According to the work of Otsu and Kuriyama, polymerization of styrene proceeded via the living mechanism as shown by an increase in molecular weight as well as conversion with the reaction time, up to 63,000 g/mol and 30% conversion after 15 h. However, the polydispersities were significantly high, ranging between 2.1 and 6.3, depending on the reaction time used. The result was probably related to the effect of monomer concentration.

Effect of Monomer Concentration

Figure 3 shows the effect of monomer concentration on the molecular weight of PMMA at various
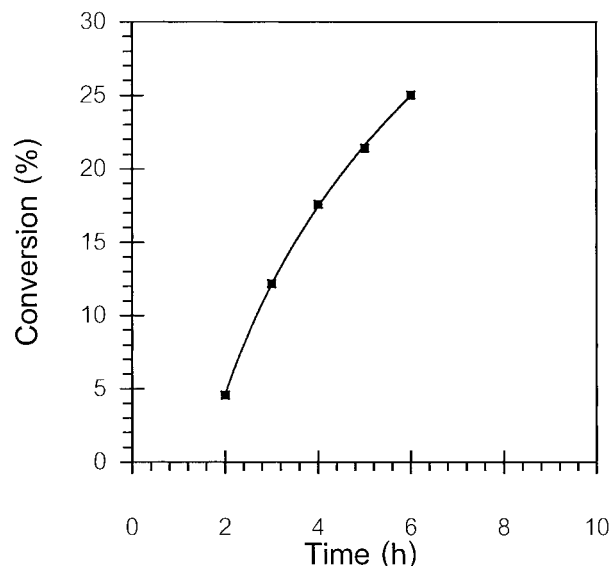

Figure 2 Conversion of MMA as a function of reaction time; [MMA] = 2.83 mol/L.

**Table I MMA Polymerization Data at Concentration 2.83 mol/L With and Without BDC Iniferter**

Condition	Reaction Time (h)	Conversion (%)	M_w (g/mol)	Polydispersity
With BDC	4	17.6	85,339	1.98
With BDC	7	23.9	120,403	1.96
Without BDC	4	5.7	256,006	2.31
Without BDC	7	7.5	434,032	2.41

reaction times. It can be seen that, in most cases, the molecular weight of the polymer tended to increase with increasing monomer concentration. The reaction time also showed a significant effect, that is, the molecular weights increased with reaction time, especially at a higher monomer concentration.

It should be noted that the ratio of MMA to BDC used in this work was constant, being 268. It can be observed that the molecular weight still increased with monomer concentration. This was probably related to the effect of monomer concentration upon the viscosity and temperature in the reaction. A higher concentration means that exothermic heat, occurring during the polymerization, can be less dissipated and, thus, the temperature increased. This statement was observed during the experiment in that the temperatures of the contents in the reactor at 2.83, 5.612, and 6.60 mol/L of MMA (at 4-h polymerization time)

were 46, 49, and 56°C, respectively. Temperature has a significant effect on both the rate of propagation and rate of termination. The rate constant for the propagation (k_p) appears to increase with increasing temperature more than that for the termination (k_t).[20] In relation to this work, MMA could polymerize faster at a relatively higher temperature, leading to a relatively high molecular weight product. The effect of monomer concentration on the percentage conversion of MMA is shown in Figure 4.

It can be seen from Figure 4 that the conversion of MMA increased with increasing monomer concentration. This effect could be explained in the same manner as that discussed for Figure 3. There was a relationship between the viscosity and the propagation rate constant (k_p). The reaction time also had an effect, especially for higher concentrations. The viscosity of the mixture in the
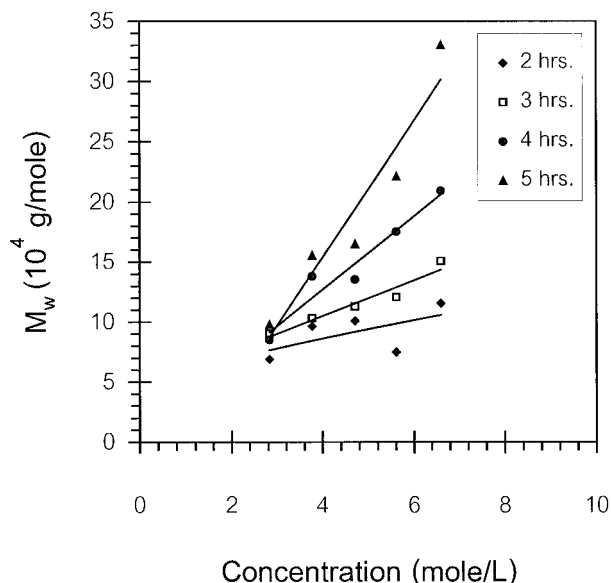
Figure 3 Molecular weight of PMMA as a function of monomer concentration at various reaction times.
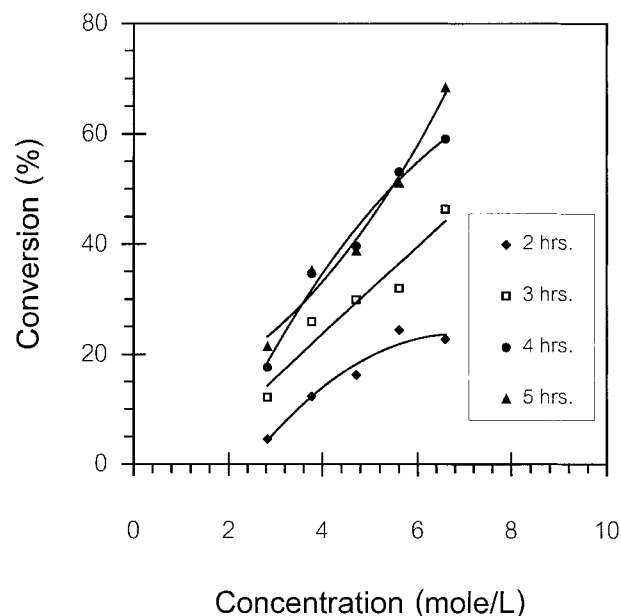
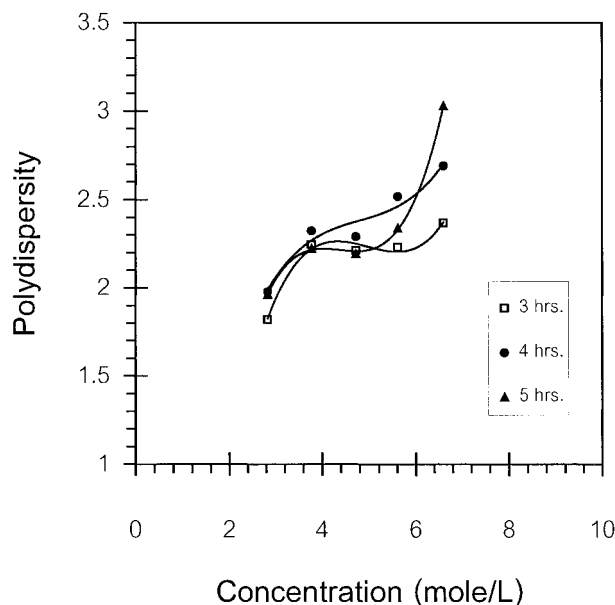**Figure 4** Relationship between conversion and the concentration of the MMA at various reaction times.

Figure 5 Polydispersity of PMMA as a function of concentration at various reaction times.

reaction tube will increase as the reaction time increases, due to longer polymer chains being produced. As a result, the conversion and molecular weight increase. From this work, it seemed that polymerization at a relatively high monomer concentration was preferred in order to obtain a higher molecular weight and higher conversion of the product. However, the effect of concentration on the polydispersity of the polymer also deserves consideration.

Generally, it can be seen in Figure 5 that the polydispersity increased with increasing monomer concentration, irrespective of the reaction times. For example, at 3-h reaction time, the polydispersities at minimum and maximum concentrations were 1.8 and 2.4, respectively. This suggested that there was a greater chance for bimolecular termination of the propagating chains at higher concentrations. This was probably because the iniferter could not act as a transfer agent and/or a terminator effectively at the higher concentrations. The reaction time also showed a significant effect, especially at higher concentrations. For example, at the concentration of 6.60 mol/L, as the reaction time increased from 3 to 5 h, the polydispersity increased from 2.3 to 3.0. This was because the length of the propagating chains and the viscosity of the mixture in the reaction tube increased with the reaction time, as previously discussed. As a result, the propagating chains had more chances to undergo bimolecular

termination with their neighboring reactive chains.

Effect of Mol Ratio Between Iniferter and Monomer

The effect of the BDC/MMA mol ratio was investigated. It can be seen in Figure 6 that the conversions did not change linearly with the mol ratio. For example, at the monomer concentration of 2.83 mol/L, the conversion initially increased as the BDC/MMA mol ratio was increased from 0.0037 to 0.0074. However, with further increases in the mol ratio (i.e., from 0.0074 to 0.0149 and 0.0224), the conversion tended to decrease again. This suggested that there was a critical value of the BDC/MMA mol ratio for the maximum conversion. These results also suggested that polymerization kinetics in the presence of an iniferter is different from that in the presence of a conventional initiator, where the polymerization rate is proportional to the square root of the initiator concentration.[21] However, the trend found in this work seemed to be supported by that previously discussed by Reghunadhan Nair.[22] The existence of a critical mol ratio is, actually, related to the nature of an inifeter, that is, the compound does act not only as an initiator, but also as a chain-transfer agent and a terminator. Therefore, the increasing trend of the conversion with the
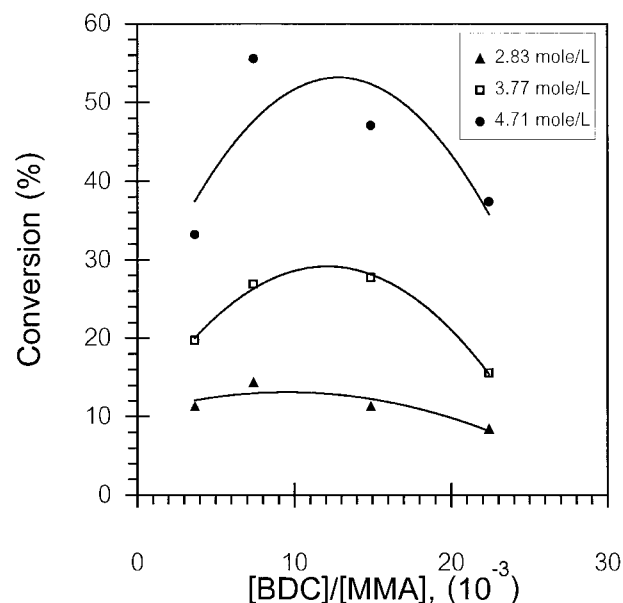

Figure 6 Relationship between [BDC]/[MMA] ratio and conversion of PMMA with polymerization time of 3 h at various monomer concentrations.

Table II   Relationship Between BDC]/MMA Mol Ratio and Molecular Weights of PMMA with Polymerization Time of 3 h and Monomer Concentration of 4.71 mol/L

BDC/MMA Mol Ratio	M_w (g/mol)	Polydispersity
3.7	140,557	1.90
7.4	131,642	1.80
14.9	62,001	1.75
29.8	45,498	1.70

[BDC]/[MMA] mol ratio could only be observed at the initial stage of the graph in Figure 6. At this stage, the concentration of the *N,N*-diethyldithiocarbamyl (DC) radical, being obtained from a dissociation of BDC, is insufficient to cap all the propagating chains and the initiation process predominates the kinetics. However, as the concentration of BDC was increased further, there were more DC radicals available to cap with the propagating chains. The propagating chains, therefore, have less chance to react with the monomers. The transfer and termination processes were more dominate than was the kinetics and so the conversion decreased with the mol ratio.

The explanation in Figure 6 as to the critical BDC/MMA mol ratio discussed above corresponds to the results shown in Table II showing that the polydispersity decreased with increasing mol ratio. The lowest polydispersity, obtained at the monomer concentration of 4.71 mol/L, was 1.7. This corresponded to the highest value of the BDC/MMA mol ratio (i.e., 0.0298), indicating that the higher mol ratio of BDC to MMA, the more chance to approach the living polymerization mechanism due to the predominant transfer and termination processes at this stage.

Table II also shows that the molecular weight of PMMA decreased with an increasing mol ratio of BDC to MMA, as expected. This was because at the higher mol ratio the propagating chains have less chance to react with the monomer, as previously discussed. Therefore, the higher the mol ratio is, the lower the polymer molecular weight obtained.

CONCLUSIONS

To achieve low-polydispersity PMMA from living radical polymerization through the use of the BDC iniferter, the polymerization should be carried out under the following conditions:

- Low monomer concentration (typically, 2.83 mol/L);
- Short period of reaction time (typically, 2–3 h);
- High BDC/MMA mol ratio (typically, 0.02–0.03).

On the other hand, if high molecular weight and high conversion of the PMMA are to be considered, polymerization under a relatively high concentration, longer reaction time, and relatively low BDC/MMA mol ratio was recommended.

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