

# Effect of the Reaction Conditions on the Photopolymerization of Methyl Methacrylate by Diethyl Dithiocarbamato-(1,2)-propane Diol

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**ABSTRACT:** The photopolymerization of methyl methacrylate (MMA) through the use of diethyl dithiocarbamato-(1,2)-propane diol (DCPD) was studied. The photoinitiator was synthesized from 3-chloro-1,2-propane diol and sodium diethyl dithiocarbamate in a solvent mixture of acetone and anhydrous ethanol. The photopolymerization was carried out in a Heber multilamp photochemical reactor (COMPACT-LP-MP88) (Heber Scientific, Chennai, India) at 254 nm. The effects of the reaction conditions on the polymerization of MMA were studied. The conversion and molecu-

lar weight increased with an increase in the monomer concentration and reaction time. However, for the DCPD-to-MMA molar ratio, a critical value was found for maximum conversion. The results suggested the living radical nature of the photoinitiator, which was further investigated by the preparation of a block copolymer with styrene. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2320–2328, 2005

**Key words:** block copolymers; initiators; photopolymerization

## INTRODUCTION

Photopolymerization is more advantageous than thermally initiated polymerization and has enormous commercial importance.<sup>1</sup> Techniques such as the curing of coatings on wood, metal, and paper, adhesives, printing inks, and photoresists are based on photoinitiated vinyl polymerization. Photopolymerizations in most cases are initiated by photoinitiators. The dithiocarbamate groups are known to act as photoinitiators in the free-radical polymerization of vinylic monomers. For the photochemical decomposition of the C—S bond, UV light between 254 and 366 nm is necessary.<sup>2</sup> Furthermore, compounds having *N,N*-diethyl dithiocarbamate groups such as benzyl-*N,N*-diethyl dithiocarbamate (BDC), *p*-xylenebis(*N,N*-diethyl dithiocarbamate), benzyl-*N*-ethyl dithiocarbamate, and *p*-xylenebis(*N*-ethyl dithiocarbamate) serve as good photoiniferters.<sup>3–5</sup> In 1982, the word *iniferters* was first used by Otsu<sup>6</sup> to name those substances that acted as an initiator, transfer agent, and terminator in radical polymerization. The polymerization is characterized by low polydispersities of the products typically ranging from 1.7 to 3, a linear increasing trend of the molecular weight with the conversion, and the formation of a related block copolymer. The polymerization of a vinyl monomer in the presence of an iniferters

results in a polymer end-capped with a group, which reversibly reacts with the propagating chain. The capped chain, however, dissociates thermally or photochemically into a propagating chain and a capping agent. The propagating chains, therefore, can undergo further reaction with the available monomers, and this leads to block copolymers.

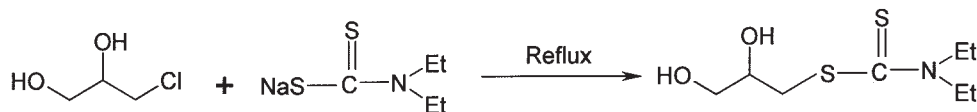
This research work describes the synthesis of a new photoinitiator, *N,N*-diethyl dithiocarbamato-(1,2)-propane diol, and the polymerization of methyl methacrylate (MMA) through its use. This particular photoinitiator is of interest because it can be used as a chain-extender diol in a two-step synthesis of polyurethane, which can be used as a macrophotoinitiator for the synthesis of polyurethane-*graft*-polyvinyl copolymers. The main objective of this work was to investigate the role of the reaction time, monomer concentration, and monomer-to-initiator molar ratio on the molecular weight distribution and conversion percentage of the poly(methyl methacrylate) (PMMA) being polymerized and hence to see whether the results indicated the iniferters nature of this photoinitiator. The block copolymerization of the resulting PMMA with the *N,N*-diethyl dithiocarbamyl (Et<sub>2</sub>NCSS) end group was also studied.

## EXPERIMENTAL

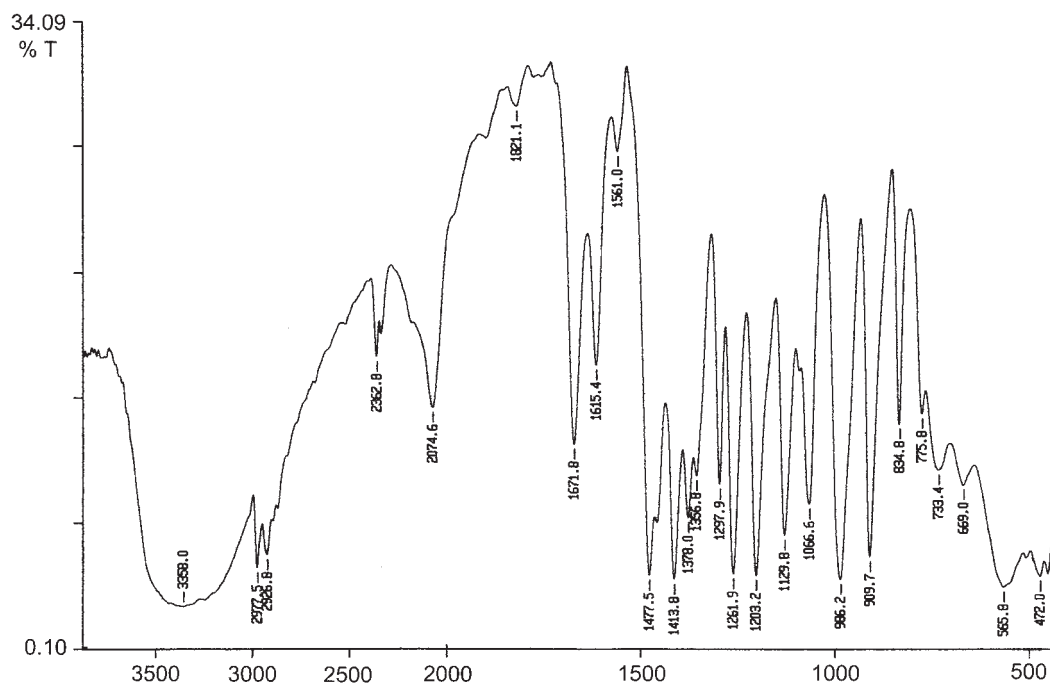
### Materials

3-Chloro-1,2-propane diol (CPD; E. Merck) was distilled before use. MMA (E. Merck) and styrene (St; E.

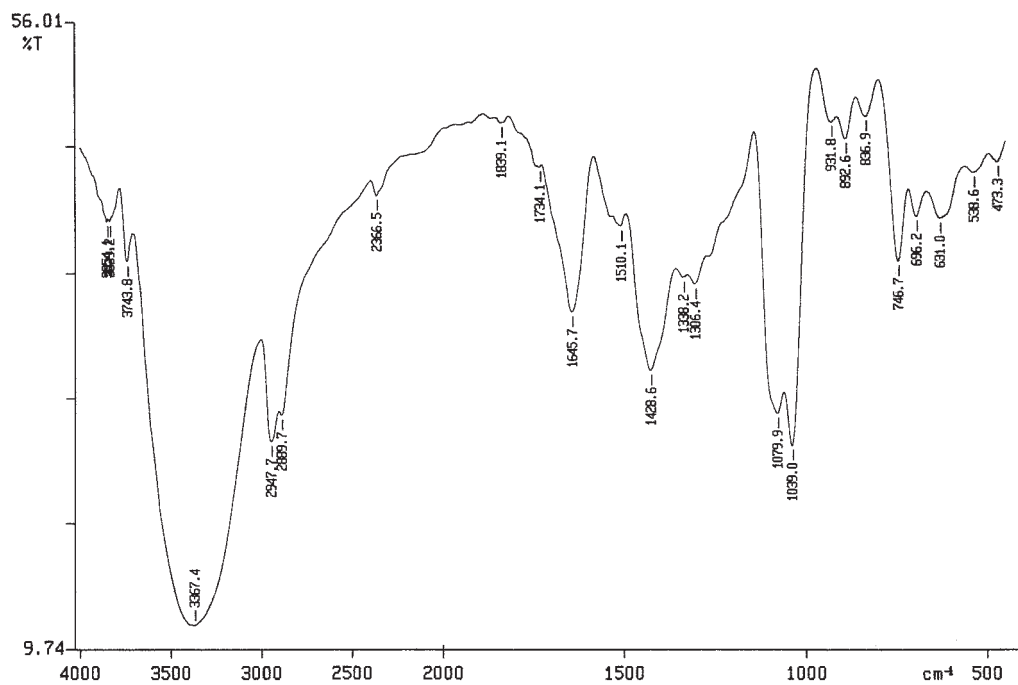
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Scheme 1



(a)



(b)

Figure 1 FTIR spectra of (a) NaSR, (b) CPD, and (c) DCPD.

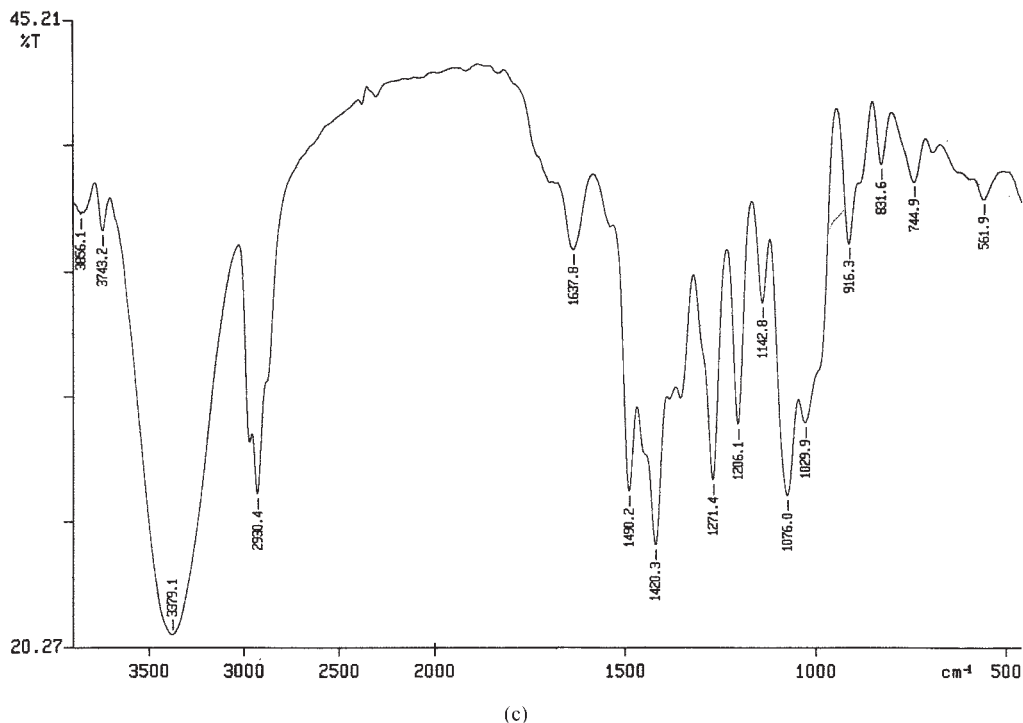


Figure 1 (Continued from previous page)

Merck) were purified by standard procedures. Dimethyl sulfoxide (E. Merck) was first dried over  $\text{CaCl}_2$  and then distilled under reduced pressure. Tetrahydrofuran (THF; E. Merck) was distilled before use. Acetone, methanol, ethanol (absolute), and cyclohexane were used as received.

#### Synthesis of *n,n*-diethyl dithiocarbamate-(1,2)-propane diol (dcpd)

DCPD was synthesized by the refluxing of CPD with sodium diethyl dithiocarbamate (NaSR) for 6 h in a solvent mixture of acetone and absolute ethanol (Scheme 1). At the end of the reaction, the sodium chloride formed was filtered out, the solvents were removed in a Bucci rotavapor, and the crude product was purified by distillation under reduced pressure.

#### Photopolymerization

The photopolymerization reactions were carried out in a Heber multilamp photochemical reactor at 254 nm. A mixture of MMA and DCPD in dimethyl sulfoxide was first purged with dry nitrogen. The reaction tube was then sealed and photoirradiated. At the end of the reaction time, the polymers were isolated by precipitation in water and dried in a vacuum oven.

#### Photoblock copolymerization

PMMA-*block*-PSt (where PSt is polystyrene) was synthesized by the irradiation of a mixture of PMMA and St in

THF in a nitrogen atmosphere for 6 h. The resultant polymer was precipitated in methanol and was Soxhlet-extracted with acetone and cyclohexane to remove the PMMA and PSt homopolymers, respectively. The block copolymer was then dried in a vacuum oven.

## RESULTS AND DISCUSSION

#### Characterization of DCPD

The formation of DCPD through the substitution reaction of chloropropane diol with NaSR was confirmed with the following observations:

1. Sodium chloride precipitated during the reaction.
2. ANAL. Calcd: C, 43.05%; H, 7.62%; N, 6.28%. Found: C, 39.51%; H, 7.17%; N, 6.48%.

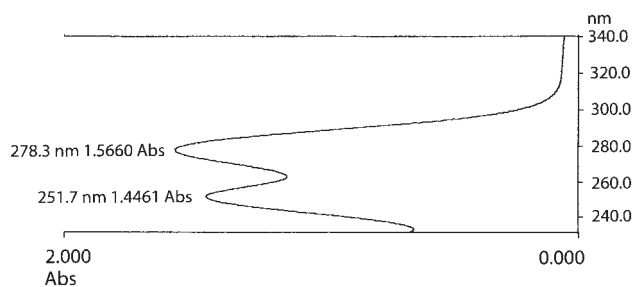


Figure 2 UV-vis spectrum of DCPD.

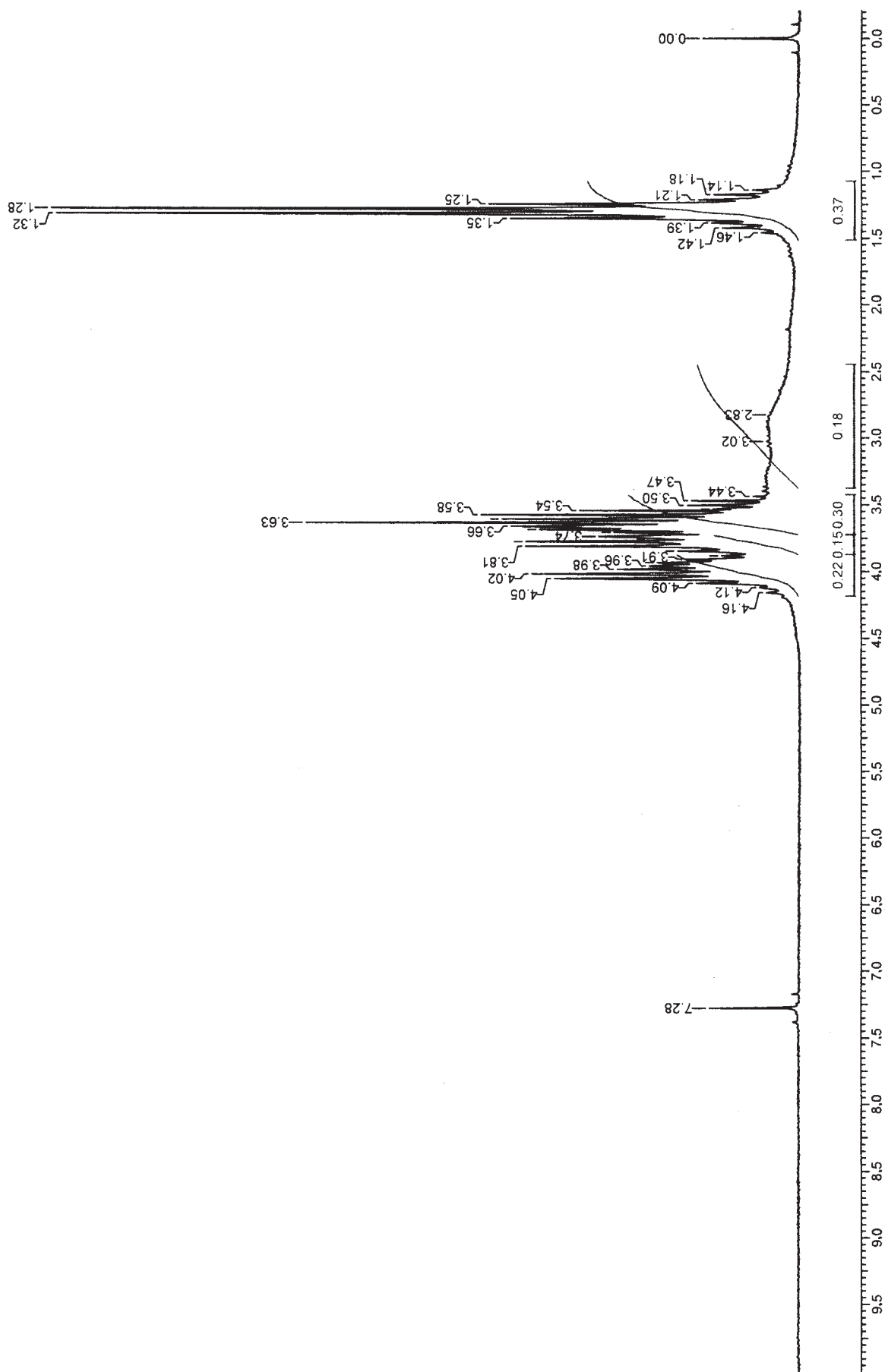


Figure 3 <sup>1</sup>H-NMR spectrum of DCPD.

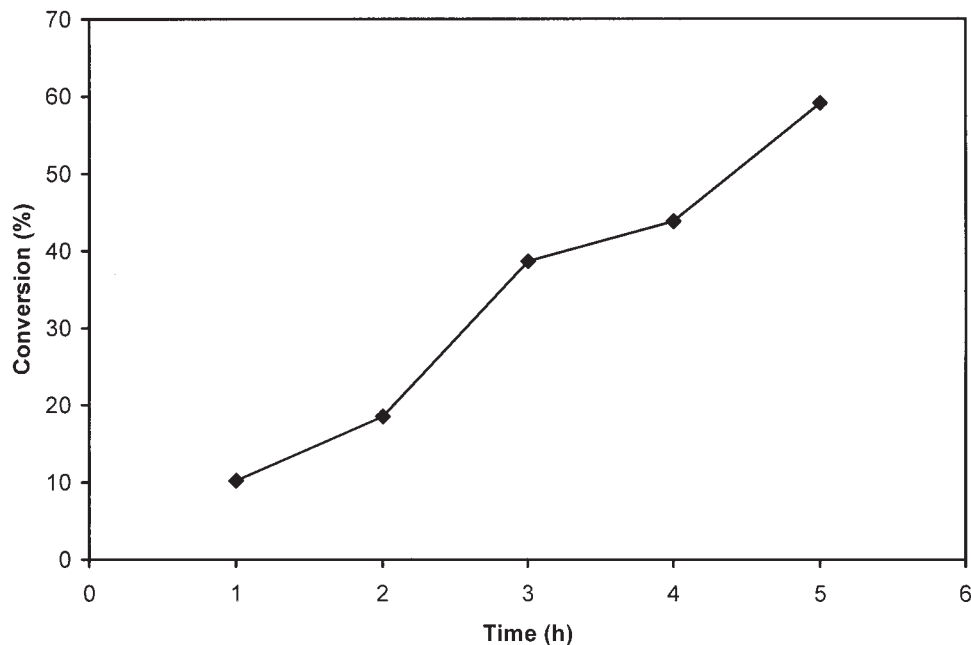


Figure 4 Conversion of MMA as a function of the reaction time ( $[MMA] = 0.55 \text{ mol/L}$ ).

- The Fourier transform infrared (FTIR) spectra of NaSr, CPD, and DCPD are shown in Figure 1(a–c), respectively. Characteristic peaks due to the  $-\text{SC(S)N}$  group appeared at  $1076$ ,  $1206$ , and  $1271 \text{ cm}^{-1}$ , respectively, in the FTIR spectra of DCPD.
- The ultraviolet–visible (UV–vis) spectrum of DCPD is shown in Figure 2. Conjugated absorbent peaks due to  $-\text{S}-\text{C}=\text{S}$  and  $\text{S}=\text{C}-\text{N}$  appeared at wavelengths of  $251$  and  $278 \text{ nm}$ , respectively.
- The  $^1\text{H-NMR}$  spectrum of DCPD was recorded in a  $200\text{-MHz}$  instrument in  $\text{CDCl}_3$  and is shown in

Figure 3. The two methyl groups in the  $(\text{CH}_3-\text{CH}_2)_2\text{N}$  group appear as a closely spaced triplet in the range of  $1.22\text{--}1.35 \text{ ppm}$ .<sup>7</sup> The rest of the protons appear as a complex multiplet in the region of  $3.4\text{--}4.2 \text{ ppm}$ .

#### Effect of the reaction conditions on the photopolymerization

The effects of various reaction conditions on the conversion percentage of MMA and the molecular weight

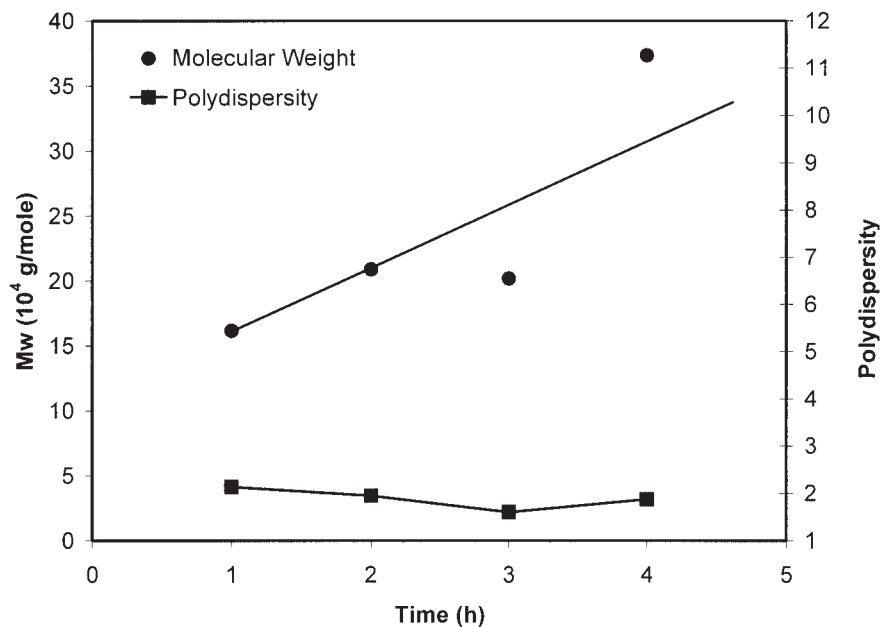


Figure 5 Molecular weight and polydispersity of PMMA as a function of the time ( $[MMA] = 0.55 \text{ mol/L}$ ).

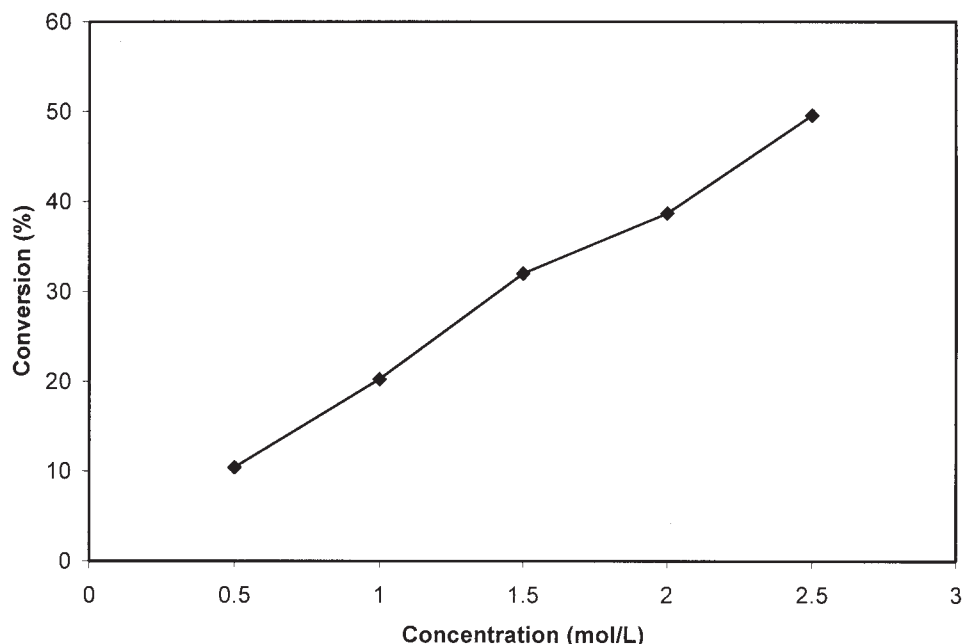


Figure 6 Conversion of MMA as a function of the monomer concentration.

of PMMA were studied. The conversion percentage of MMA was determined from the dry weight of PMMA. The molecular weights were determined with a Waters gel permeation chromatography (GPC) apparatus with THF as the eluent.

#### Effect of the reaction time

Figure 4 shows the conversion percentage of MMA with the reaction time. The conversion percentage of

the monomer increased with increasing reaction time. The result suggests that the polymerization proceeded through a controlled radical polymerization mechanism, in which propagating chains were free from bimolecular termination. Hence the longer the reaction time was, the more monomer was consumed by the reactive propagating chains. This resulted in an increase in the conversion percentage as well as the molecular weight with an increase in the reaction time. Figure 5 shows the effect of the reaction time on

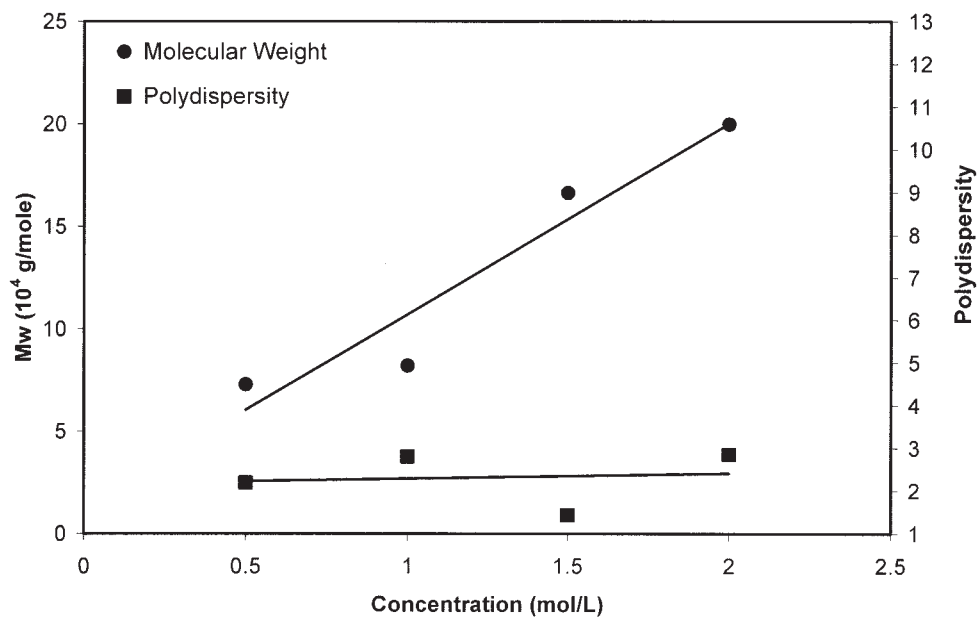
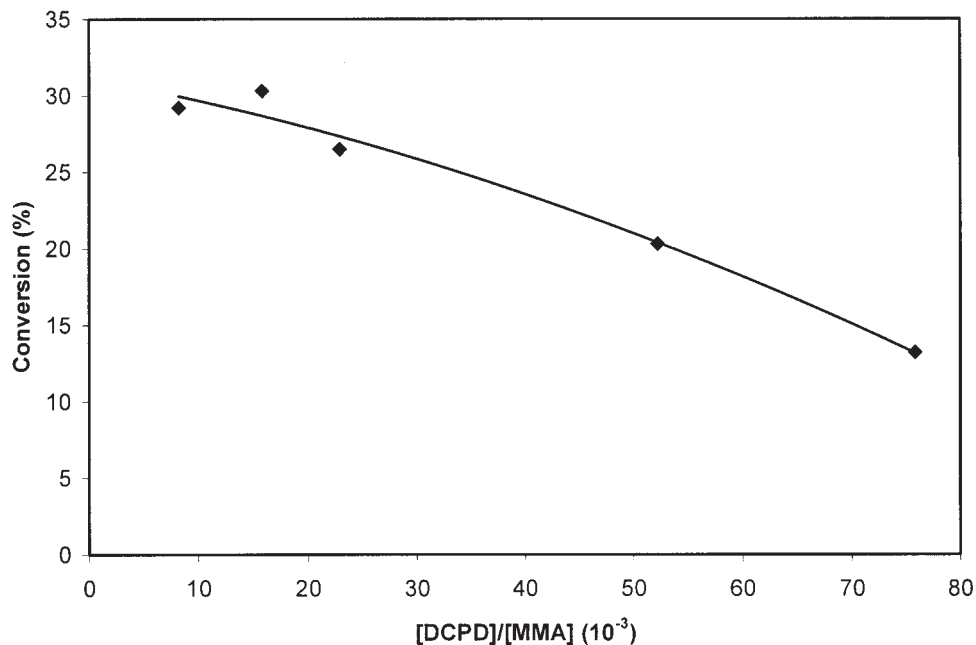


Figure 7 Molecular weight and polydispersity of PMMA as a function of the monomer concentration at 6 h.



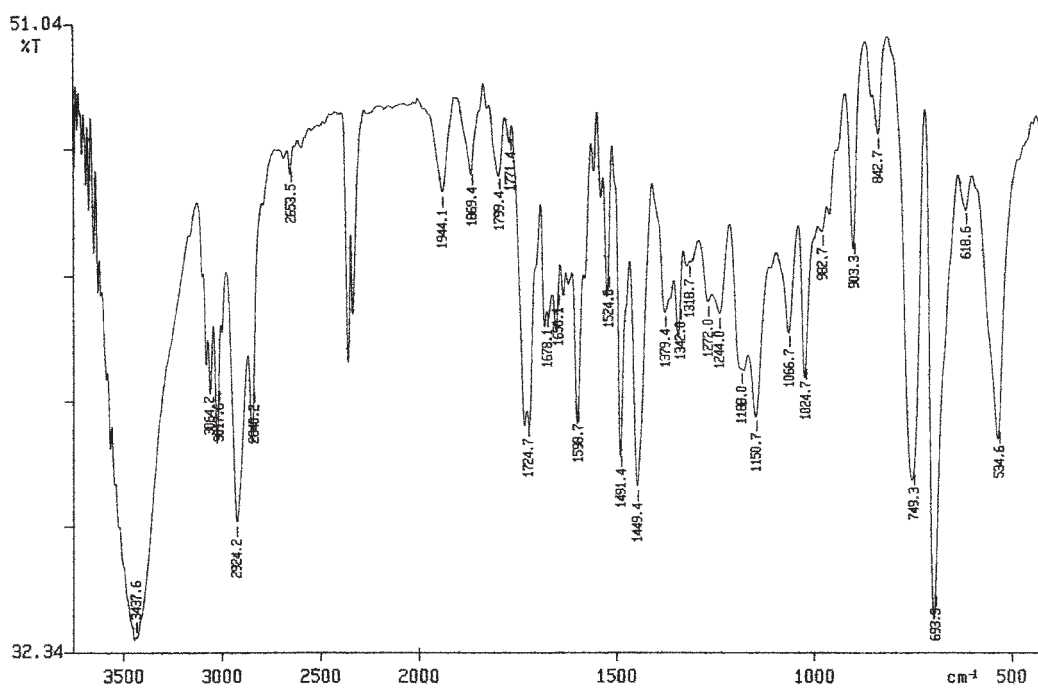
**Figure 8** Relationship between the [DCPD]/[MMA] ratio and the conversion of MMA with a polymerization time of 4 h at a monomer concentration of [MMA] = 2.02 mol/L.

the molecular weight and polydispersity of PMMA. Although the molecular weight increased considerably with the reaction time, the polydispersities remained in the range of 1.6–2.1, as expected in a living radical polymerization process. These results were similar to those reported by Otsu and Kuriyama<sup>8</sup> for the bulk polymerization of St with BDC and by Kong-

kaew and Wootthikanokkhan<sup>3</sup> for the solution polymerization of MMA with BDC.

#### Effect of the monomer concentration

Figures 6 and 7 show the conversion percentage of MMA and the molecular weight and polydispersity of



**Figure 9** FTIR spectrum of the PMMA-PSt block copolymer.

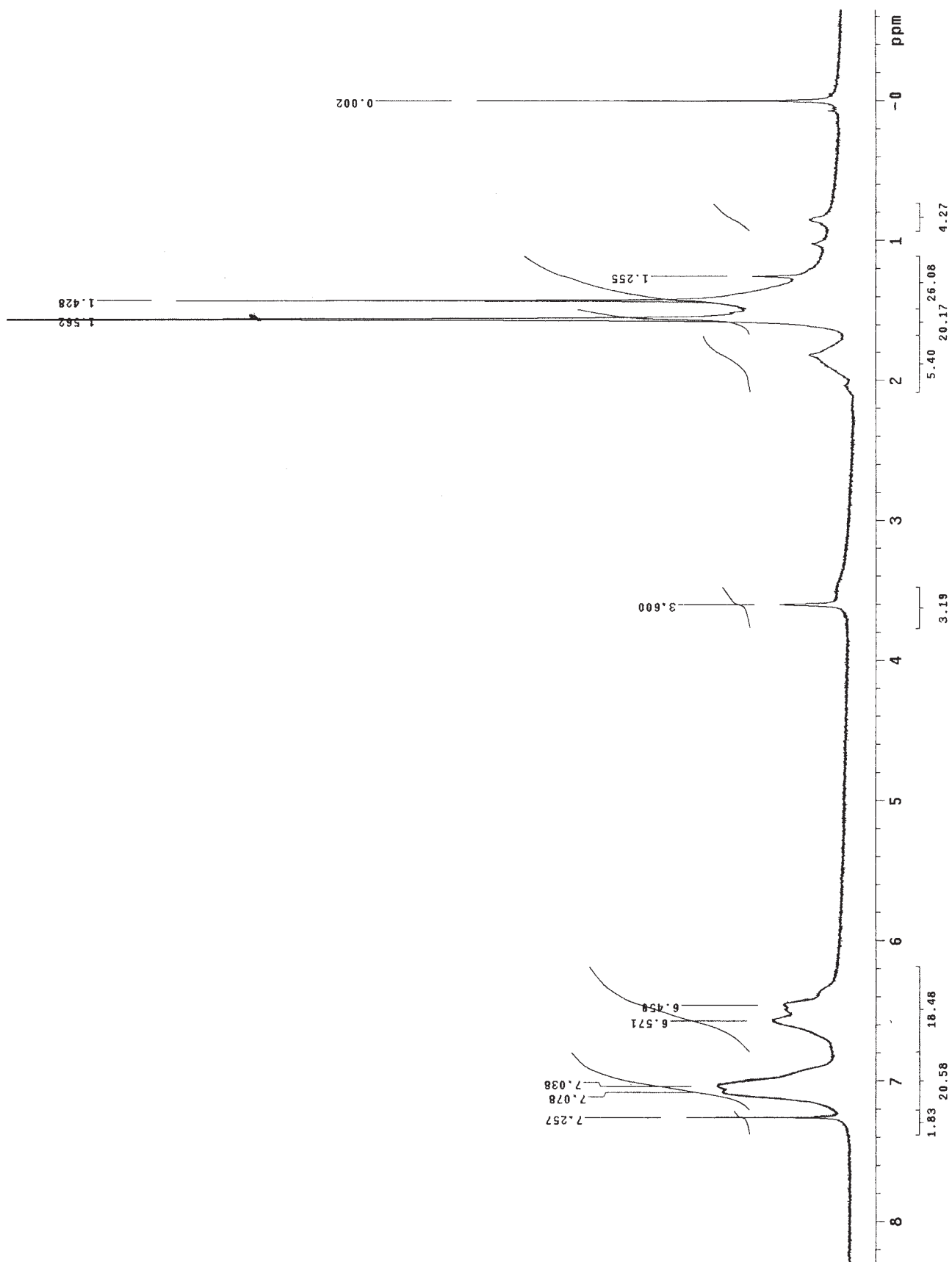


Figure 10 <sup>1</sup>H-NMR spectrum of the PMMA-PSt block copolymer.



PMMA with increasing monomer concentration. Both the conversion percentage of MMA and the molecular weight of PMMA increased with the monomer concentration. This is probably related to the effect of the monomer concentration on the viscosity and temperature in the reaction. A higher concentration means that increased exothermic heat, occurring during the polymerization, could be less dissipated, and this resulted in an increase in the temperature. The rise in the temperature increased the rate of reaction, and this resulted in the consumption of more monomer, leading to an increase in the conversion percentage. Furthermore, the temperature has a significant effect on both the rate of propagation and the rate of termination. The rate constant for propagation appears to increase with a rise in the temperature more than that for termination.<sup>9</sup> In this case, MMA could polymerize faster, and this led to relatively high-molecular-weight products.

#### Effect of the DCPD/MMA molar ratio

The effect of the rise in the initiator/monomer molar ratio on the conversion percentage of MMA was investigated. The results are shown in Figure 8. The conversion did not change in a linear manner with an increase in the molar ratio. The results suggest that there is a critical value of the DCPD/MMA molar ratio for the maximum conversion. The trend found in this work is similar to earlier reported work.<sup>3</sup> The existence of a critical molar ratio is an indication of the fact that the initiator is acting not as a mere initiator but also as a chain-transfer agent and terminator; that is, it is acting as an iniferter. Although at a low initiator-to-monomer molar ratio, the initiation process dominated, at a higher molar ratio, the transfer and termination dominated, and this led to the fall in the conversion with the molar ratio. Alternatively, it could be possible that above the critical molar ratio, bimolecular termination between propagating chains dominated, and this led to the decrease in the monomer conversion.

#### Block copolymerization

The ability to form block copolymers is also considered a characteristic behavior of living radical polymerization. PMMA formed through DCPD should end up with a  $-S-C(=S)-NEt_2$  group, which should further polymerize vinylic monomers upon irradiation<sup>10</sup> to form block copolymers. In this case,

PMMA was irradiated in the presence of St. The formation of PMMA-*block*-PSt was observed from the FTIR spectrum (Fig. 9) and <sup>1</sup>H-NMR spectrum (Fig. 10). The FTIR spectrum of the PMMA-*block*-PSt copolymer shows the characteristic peaks of PMMA at 1724.7 (C=O) and 1150.7 cm<sup>-1</sup> (C—O—C) and of PSt at 1598.7 cm<sup>-1</sup> (C=C, aromatic). In the <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum of the PMMA-*block*-PSt copolymer, the observed chemical shifts may be assigned in the following manner: 6.45–6.57 (—C<sub>6</sub>H<sub>5</sub> of PSt), 3.6 (—OCH<sub>3</sub> of PMMA), 1–2 (—CH<sub>2</sub>—CH— of PSt and  $\alpha$ -methyl and methylene protons of PMMA), and 7.02–7.25 ppm (due to CDCl<sub>3</sub>). This is further supported by the GPC studies. The rise in the molecular weight of the block in comparison with that of PMMA was indicated from the elution times of the GPC measurements [PMMA (weight-average molecular weight = 424,176 g/mol, peak value = 18.50 min) and PMMA-*block*-PSt (peak value = 16.867 min)]. These results indicated the living radical nature of PMMA end-capped with the diethyl dithiocarbamyl group.

#### CONCLUSIONS

This work describes the successful preparation of the photoinitiator DCPD. It was used in the polymerization of MMA. The results obtained from the study of the effects of various reaction conditions on the conversion percentage of MMA and the molecular weight of PMMA indicated that, like other diethyl dithiocarbamate photoinitiators, DCPD also behaves as a photoiniferter, giving rise to living radical polymerization. This aspect was further confirmed by the observed ability of PMMA to further polymerize St to form the PMMA-PSt block copolymer.

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