

Photopolymerization of Methyl Methacrylate by 2,2'-Dithiodiethanol: Effect of Reaction Conditions

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Received 15 April 2005; accepted 16 September 2005

DOI 10.1002/app.23628

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The photopolymerization of methyl methacrylate (MMA) through the use of a novel disulphide, 2,2'-dithiodiethanol (DDE), was studied. This photoinitiator is of special interest because of its possible use in the synthesis of polyurethane macrophotoinitiator. The photopolymerization was carried out in the Heber multilamp photochemical reactor (COMPACT-LP-MP88) at 254 nm. The effects of reaction conditions on the polymerization of MMA were studied. It was observed that the percentage conversion and molecular weight increased with the increases of monomer

concentration and reaction time. However, for the initiator to monomer molar ratio, there was a critical molar ratio for maximum conversion. The results suggested the living radical nature of the photoinitiator, which was further investigated by the preparation of block copolymer with acrylonitrile. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1601–1606, 2006

Key words: living polymerization; photopolymerization; block copolymers

INTRODUCTION

Light-induced free-radical polymerization has enormous commercial importance,¹ and radical polymerization of vinyl monomers played an important role in the early development of polymerization. Blyth and Hoffmann reported the polymerization of styrene by sunlight more than 150 years ago.² Photopolymerization in most cases are initiated by photoinitiators. Aromatic carbonyl compounds, peroxy compounds, and azo compounds are commonly used as photoinitiators. The organic sulfur compounds like disulphides^{3–7} and dithiocarbamates^{8–14} are known to act as photoinitiators. These groups of photoinitiators are interesting in their action, as many of them are known to serve as good photoiniferters. In 1982, the word “iniferter” was first used by Otsu and coworkers,^{3,15} which acted as initiator, transfer agent, and terminator in radical polymerization. The polymerization was characterized by low polydispersities of the products typically ranging from 1.7 to 3, a linear increasing trend of molecular weight with conversion and formation of a related block copolymer. Polymerization of a vinyl monomer in the presence of an iniferter results in a polymer endcapped with a group, which reversibly reacts with the propagating chain. The capped

chain, however, dissociate thermally or photochemically into propagating chain and capping agent. The propagating chains, therefore, can undergo further reaction with the available monomers, leading to block copolymers.

This research describes the photopolymerization of methyl methacrylate (MMA) through the use of a disulphide 2,2'-dithiodiethanol (Scheme 1). The main objective of this work was to investigate the effect of reaction conditions on the percentage conversion of monomer, molecular weight, and molecular weight distribution, and hence to see whether the results indicate the iniferter nature of the photoinitiator. The block copolymerization of the resulting polymethylmethacrylate (PMMA) having thiyl end group with acrylonitrile has also been investigated. This particular photoinitiator is of our interest because it can be used as a chain extender diol in the two-step synthesis of polyurethane macrophotoinitiator, for vinyl polymerization.

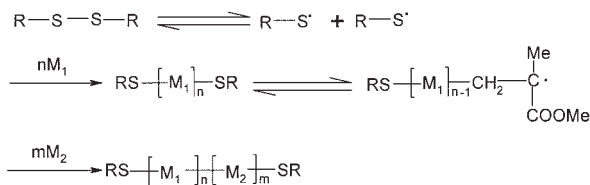
EXPERIMENTAL

Materials

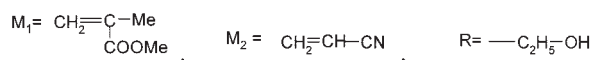
Dimethyl sulfoxide (DMSO, E-Merck, India) was dried over calcium hydride for 1 week and distilled under reduced pressure. *N,N'*-dimethyl formamide (DMF, E-Merck, India) was dried over powdered barium oxide for a few days and then distilled under reduced pressure. Methyl methacrylate (MMA, E-Merck, Germany) was washed with 5% aqueous

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Contract grant sponsor: University Grants Commission (New Delhi), India.



Where,



Scheme 1

sodium hydroxide solution to remove the inhibitor, and then washed with distilled water, dried over CaCl_2 , and distilled under reduced pressure. Acrylonitrile (AN, SRL, India) was purified by the standard procedure. 2,2'-dithiodiethanol (DDE, Fluka, Switzerland) was used as supplied. Acetone and methanol were used as received.

Photopolymerization

Photopolymerization of MMA was carried out in the Heber (India) multilamp photochemical reactor [COMPACT-LP-MP88] at 254 nm by changing the

- reaction time
- monomer concentration
- initiator/monomer molar ratio.

The required amount of MMA was mixed with the initiator in DMSO and purged with dry nitrogen. The reaction tube was then sealed and photoirradiated. At

the end of the reaction, the products were isolated by precipitating in a large amount of water, and then, filtered and dried under vacuum at 55°C for several days.

Photoblock copolymerization

PMMA block polyacrylonitrile (PMMA-*b*-PAN) was synthesized by irradiating a mixture of PMMA and AN in DMF in nitrogen atmosphere for 5 h. The resultant polymer was precipitated in methanol and soxhlet extracted with acetone to remove PMMA homopolymer, and then PAN homopolymer was removed by partial dissolution technique using a mixture of DMF and absolute alcohol. The remaining polymer was then dried in vacuum oven.

Characterization

The percentage conversion of MMA was determined by weighing the dried product. The molecular weights and polydispersity were determined by gel permeation chromatography, using a Waters (USA) apparatus equipped with Styragel column and refractive index and viscometric detectors. Polystyrene standards were used to generate a universal calibration curve. Tetrahydrofuran (THF) was used as the eluent at 1 mL/min at room temperature. FTIR spectra were recorded using PerkinElmer (UK) RX1 FTIR spectrophotometer. The polymers were analyzed in the form of KBr plate. $^1\text{H-NMR}$ spectra were recorded on a Bruker AC (Switzerland) 200 MHz spectrophotometer in $\text{D}_6\text{-DMSO}$ as solvent.

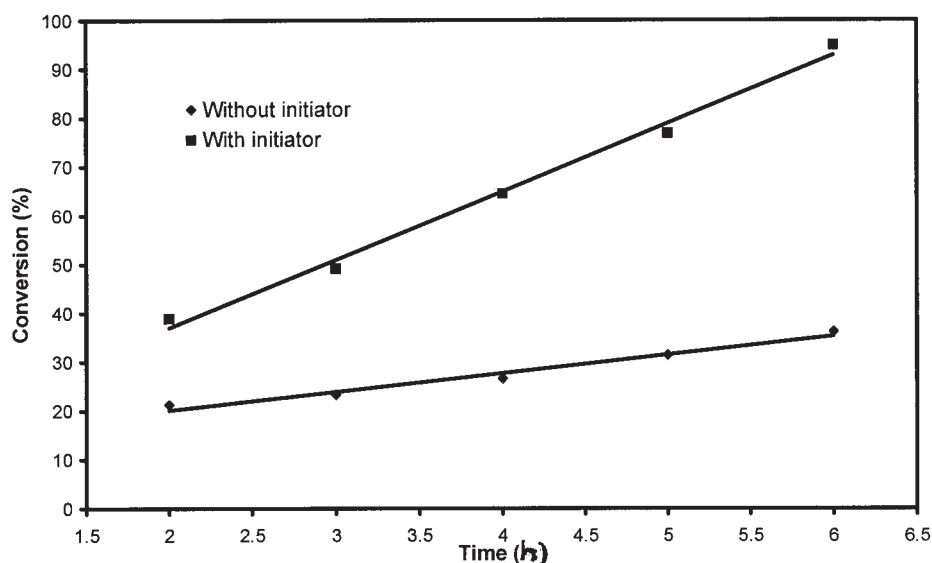


Figure 1 Conversion of monomer as a function of reaction time. $[\text{MMA}] = 0.5 \text{ mol/L}$.

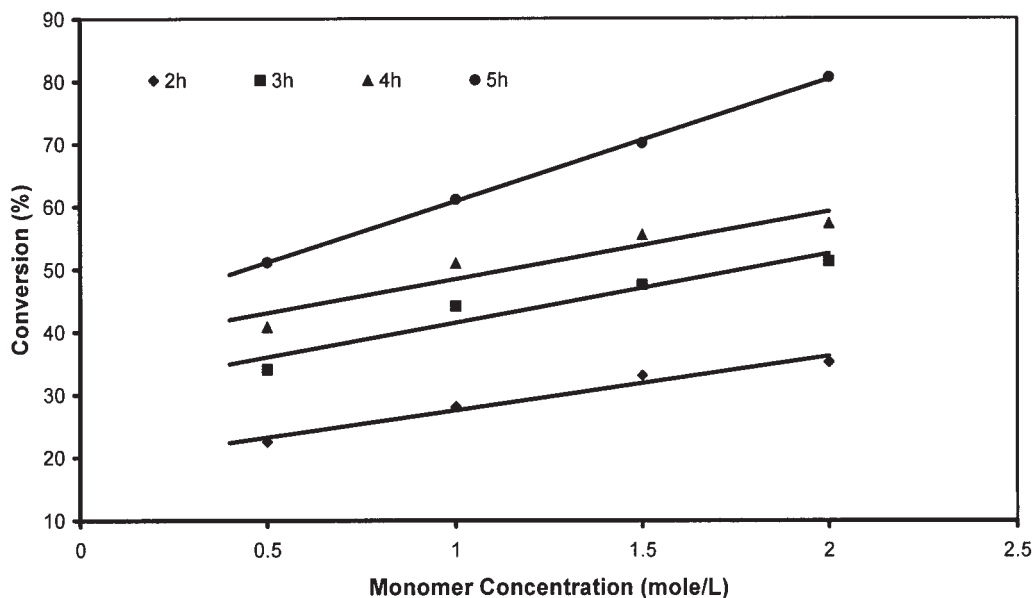


Figure 2 Relation between conversion and the concentration of the MMA at various reaction times.

RESULTS AND DISCUSSION

Polymerization of MMA was carried out in the presence of the initiator 2,2'-dithiodiethanol (DDE) in the photochemical reactor. The effects of varying reaction conditions on the percentage conversion of MMA were studied.

Effect of reaction time

Figure 1 shows the percentage conversion of MMA with reaction time at a monomer concentration of 0.5 mol/L. It was observed that with increasing reaction time, the percentage conversion of the monomer was increased. The result suggested that the polymerization proceeded through a controlled radical mechanism where the propagating chains are free from bimolecular termination. Hence, longer the reaction time, more monomers consumed by the reactive propagating chains. This results in increase in percentage conversion with increase in reaction time.

We also carried out controlled studies to investigate whether the MMA was polymerized in the absence of DDE. It was observed that MMA polymerized in the absence of DDE, but percentage of conversion was low. This is shown in Figure 1. These results were similar to those observed previously by Otsu and Kuriyama¹² for the bulk polymerization of styrene with benzyl diethyldithiocarbamate (BDC) and by Kongkaew and Woottikanokkhan¹⁶ in solution polymerization of MMA with BDC.

Effect of monomer concentration

The effect of monomer concentration on the percentage conversion of MMA is shown in Figure 2, at various reaction times. The percentage conversion of MMA increased with increasing monomer concentration. Variation of molecular weight and polydispersity with the monomer concentration was also investigated at reaction time 2 h and results are shown in Figure 3. Molecular weight of PMMA also increased with increasing monomer concentration. This is prob-

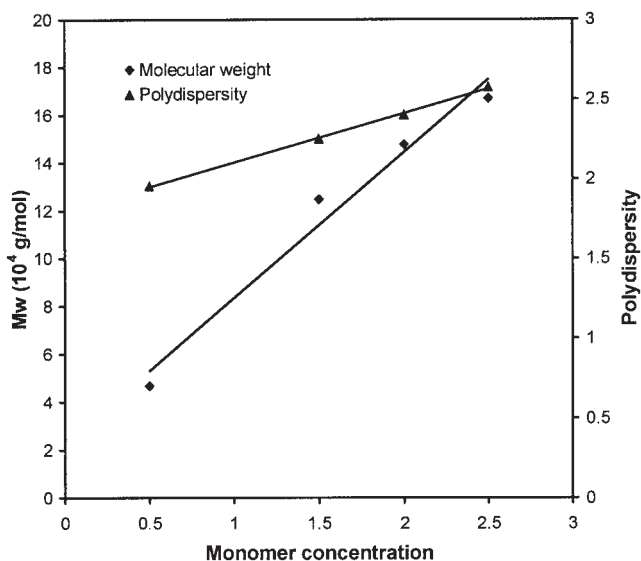


Figure 3 Molecular weight and polydispersity of PMMA as a function of concentration at 2 h reaction time.

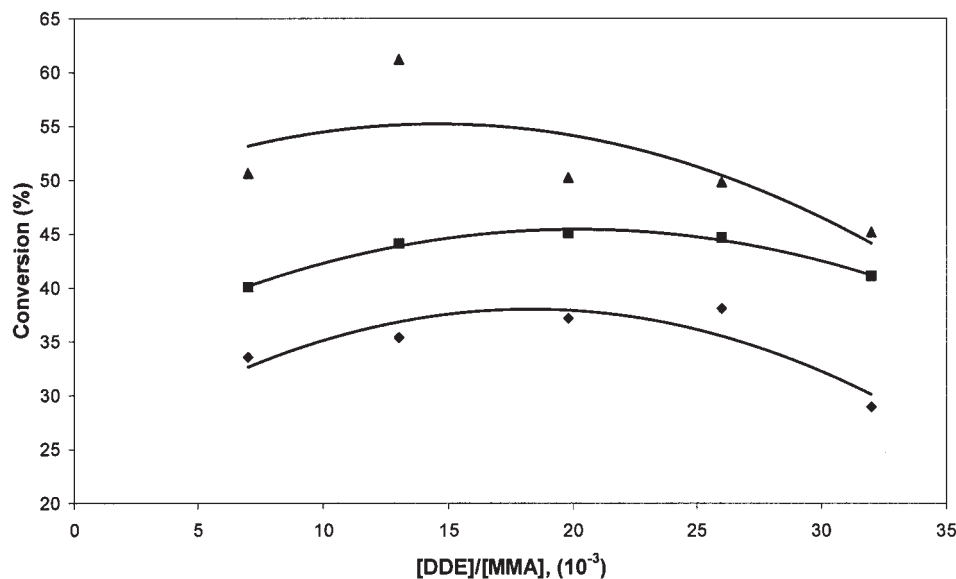


Figure 4 Relationship between [DDE]/[MMA] ratio and conversion of PMMA with polymerization time.

ably related to the effect of monomer concentration upon the viscosity and temperature in the reaction. A higher concentration means that increased exothermic heat occurring during the polymerization can be less dissipated, results in an increase in temperature. The rise in temperature increases the rate of reaction, which results in consumption of more amounts of monomers, leading to increase in percentage conversion. Further, 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 rise in temperature more than that for termination.¹⁶ In the present case, MMA could polymerize faster leading to relatively high-molecular weight products. Figure 3 shows the effect of monomer concentration on molecular weight and polydispersity.

Further, it was observed that, with increasing monomer concentration, the polydispersity of the respective products also increased in the range 1.84–2.54, which is a generally observed pattern in radical polymerization process. This suggested that there was a greater chance for bimolecular termination of the propagating chains at higher concentrations, which was probably because the iniferter could not act as a transfer agent and/or a terminator effectively at the higher concentrations. These results are similar to those reported by Kongkaew and Wootthikanokkhan,¹⁶ in the solution polymerization of MMA with BDC.

Effect of initiator to monomer molar ratio

The effect of rise in initiator/monomer molar ratio on the percentage conversion of MMA was also

investigated. The results are shown in Figure 4. Initially, with increasing molar ratio the conversion increased. But, with further increase in the molar ratio, the conversion showed a decreasing trend. This suggested that there was a critical value of DDE/MMA molar ratio for the maximum conversion. This result 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.¹⁷ This result is similar to results reported by Kongkaew and Wootthikanokkhan¹⁶ and Nair.¹⁸ The existence of a critical molar ratio is related to the nature of the iniferter, that is, the compound does not merely act as an initiator, but also act as a chain-transfer agent and a terminator. At low concentration of initiator to monomer molar ratio, the initiation process predominates, but at higher concentration, the transfer and termination processes predominate, and so the decrease in conversion. Alternatively, it could be possible that above the critical molar ratio, bimolecular termination between propagating chain dominated leading to the decrease in monomer conversion.

Block copolymerization

The capability to form block copolymer is also considered as a characteristic behavior of living-radical polymerization. If a disulphide behaves as an iniferter, then the polymer will end with a sulfur end group, which should be capable of initiating further polymerization with vinylic monomers. In

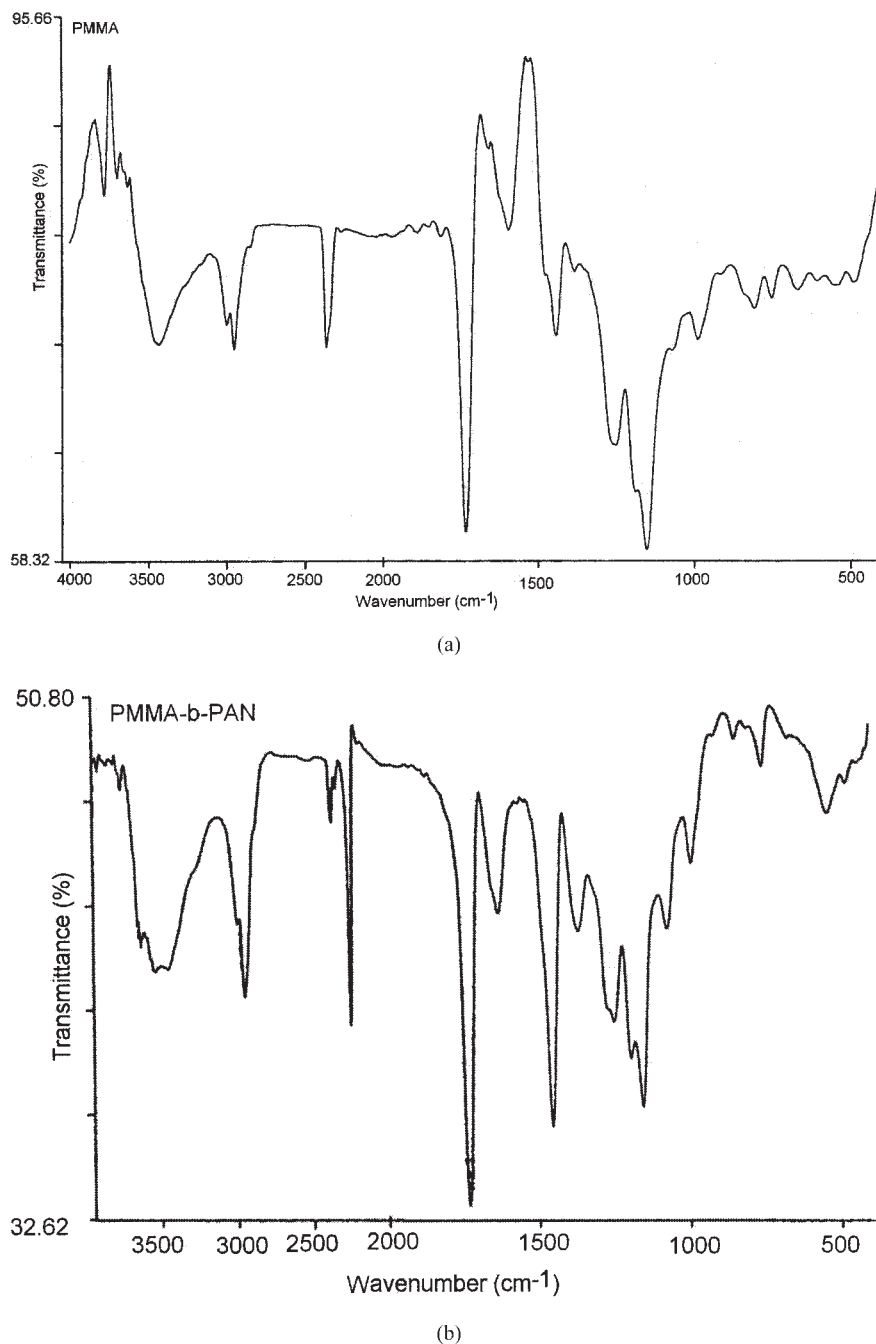


Figure 5 IR-spectra of (a) PMMA and (b) PMMA-*b*-PAN.

the present study, the PMMA was irradiated in the presence of acrylonitrile. The formation of PMMA-PAN block copolymers was observed from IR spectroscopy and $^1\text{H-NMR}$ spectroscopy, as shown in Figures 5(b) and 6, respectively. The IR spectrum of PMMA-PAN block copolymer has the characteristic peak of PAN at 2246.7 cm^{-1} (CN) and of PMMA at 1732.5 cm^{-1} (C=O) and 1154.3 cm^{-1} (C—O—C), respectively. The $^1\text{H-NMR}$ spectrum of PMMA-*b*-PAN shows a peak at around 2.13 ppm, which can

be attributed to NC—CH—^{19} , and the peak centered at 3.47 ppm is due to the —COOCH_3 group of PMMA.

CONCLUSIONS

The present work described the use of a new polymerizable photoiniferter 2,2'-dithiodiethanol (DDE) for polymerization of MMA. The result obtained from the study of varying reaction conditions on the percentage

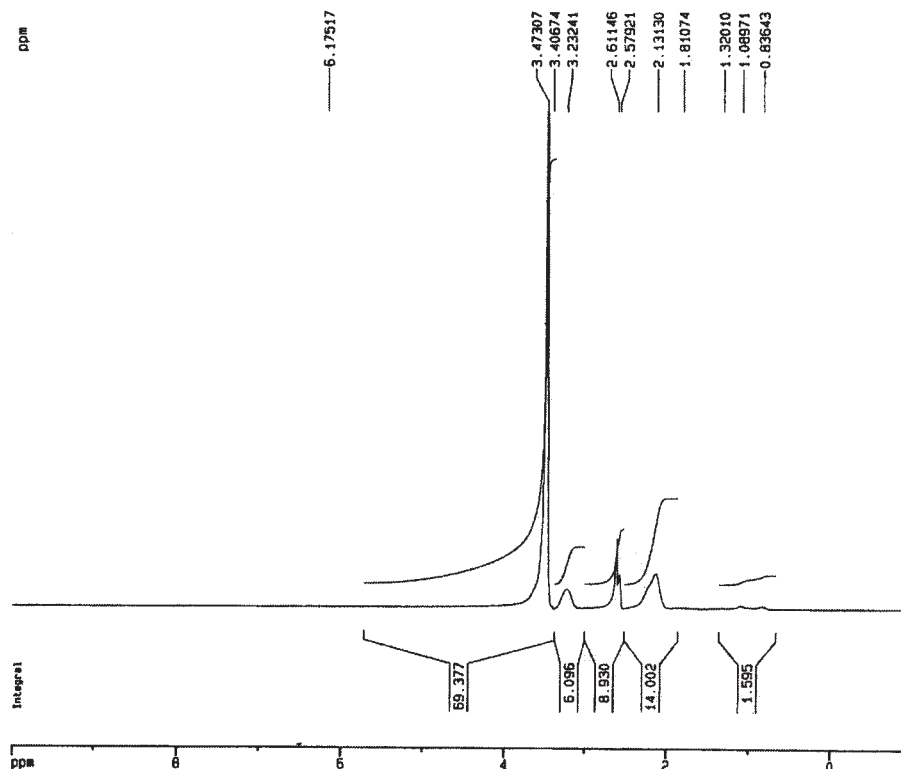


Figure 6 $^1\text{H-NMR}$ spectra of PMMA-*b*-PAN.

conversion of MMA and molecular weight of PMMA indicated that DDE behaved as a photoiniferter giving rise to living/controlled-radical polymerization. This aspect was further supported by the observed capability of PMMA to further polymerize AN to form PMMA-PAN block copolymer.

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