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### “LIVING” RADICAL POLYMERIZATION OF MMA USING DIMETHYL 2,3-DICYANO-2,3-DIPHENYL SUCCINATE AS THERMAL INIFERTER

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**“LIVING” RADICAL POLYMERIZATION  
OF MMA USING DIMETHYL  
2,3-DICYANO-2,3-DIPHENYL SUCCINATE  
AS THERMAL INIFERTER**

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Graham Swift,<sup>2</sup> and ShuGuang Wu<sup>2</sup>**

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**ABSTRACT**

Dimethyl 2,3-dicyano-2,3-diphenylsuccinate (DMCPS), a good initiator, has been found to proceed via “living” free radical polymerization in the radical polymerization of methyl methacrylate. The average molecular weight of the polymethyl methacrylate increased while increasing both conversion and polymerization time, and its corresponding molecular weight distribution decreased with the increasing reaction time. Hence, it is inferred that DMCPS serves as a thermal iniferter and follows “living” free radical polymerization. Polymethyl methacrylate capped with the fragments initiated the polymerization of styrene to yield polymethyl methacrylate-polystyrene block copolymer, which has been characterized by proton nuclear magnetic resonance, infrared, and differential scanning calorimetry, respectively.

*Key Words:* “Living” radical polymerization; Iniferter; MMA; Dimethyl 2,3-dicyano-2,3-diphenylsuccinate.

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\*Corresponding author.

## INTRODUCTION

Radical polymerization is a very useful method for the large-scale preparation of various vinyl polymers, more than 70% of the vinyl polymers have been industrially produced by this method, which has a number of merits arising from the characteristics of intermediate free radicals. However, in the ordinary radical polymerization, polymers cannot usually be synthesized regio, stereo, and chemoselectively. Thus, the tacticity, molecular weight, molecular weight distribution, and end groups of the polymers are difficult to control. To improve the chemoselectivity of polymerization, Szwarc (1) first discovered living anionic polymerization in 1956, but its rigorous polymerization conditions, such as cryogenic polymerization temperature, highly purified solvents, monomers etc, increase the cost of the resulting polymers.

However, “living” radical polymerization, which has higher chemoselectivity, enables the preparation of narrow polydispersity resins and controlled block polymers. Two prerequisites, the low concentration of free radical and a relatively shorter chain length for a typical synthesis of well-defined polymers by radical polymerization can be achieved by the reversible deactivation of growing free radicals. Through this method, the concentration of the growing free radical is kept low enough to reduce the possibility of bimolecular termination, and the well-controlled or “living” free radical polymerization of vinyl monomers can be achieved.

One of the most important milestones in the development of living free radical polymerization reactions was the discovery of the iniferter reactions. The term “iniferter,” coined by Otsu *et al.* (2), is derived from initiation–transfer–termination. Iniferter avoids ordinary bimolecular termination and undergoes initiation, chain transfer to the initiator, and/or primary radical termination. Hence, the number of iniferter fragments per one polymer chain is always two. This type of radical polymerization may be simply considered as an insertion of monomer molecule into an iniferter. Some organic sulfur compounds (3,4), phenylazotriphenylmethane (5), azobisdiphenylmethane (6), and thiuram disulfides (7) serve as iniferters for the polymerization of vinyl monomers. Tetra- and hexaphenylethane derivatives (8–12) are capable of acting as iniferters and of following “living” radical polymerization due to the famous iniferter site tetra- or hexaphenylethane group. Diethyl 2,3-dicyano-2,3-diphenylsuccinate (DECPS) has been reported to be a thermal iniferter for the bulk polymerization of methyl methacrylate (MMA) (13). Dimethyl 2,3-dicyano-2,3-diphenylsuccinate (DMCPS), a diphenylethane derivative, is a good initiator (14) for free radical polymerization, but never recorded to be able to serve as an iniferter or proceed via “living” free radical polymerization before. In this article, a new conclusion that DMCPS proceeds via a “living” free radical polymerization mechanism in the polymerization of MMA is reported.

## EXPERIMENT

### Materials

Commercial dimethyl carbonate from SIGMA Company was used as received. Commercial benzyl cyanide from SIGMA Company was purified by vacuum distillation. MMA and styrene (S) were washed with aqueous NaOH (10%) to remove inhibitor, dried over anhydrous  $\text{CaCl}_2$  for 5 h, and then CaH for 1 week, and distilled at reduced pressure, the middle portions were stored at 0~4°C before use. The other reagents were of analytical grade and used as received.

### Synthesis of DMCPs

DMCPs was prepared as described previously (15). Its two configurations, mesomer and dilomer, were not separated further and the ratio was 1:1, according to the integrity of the methoxyl peak in proton nuclear magnetic resonance ( $^1\text{H}$  NMR).

### Synthesis of the Low Molecular Weight PMMA-DMCPs and the Removal of Residual Initiator

To a refluxing solution of 1 g (2.87 mmol) of DMCPs in 6 mL of benzene was slowly added a solution of 3 mL (28.7 mmol) of MMA in 4 mL benzene in the course of 2 h, evaporation of benzene, and the residue was passed through a silica gel column (carbon tetrachloride: ethyl acetate = 9:1, V/V). The separated spots at  $R_f = 0.617$  and 0.0156 stand for DMCPs and PMMA-DMCPs, respectively.

### Synthesis of Block Copolymer PMMA-b-PS

In a typical experiment, 0.20 g of PMMA-DMCPs was synthesized by the above method, 1.81 g of styrene was placed in a glass tube. The tube was evacuated, sealed, and kept at 80°C for 3 h. When the polymerization was finished, the tube was cooled, opened, and the content was precipitated in the excess of methanol, and weighed 0.289 g after drying at 60°C in vacuum. Block copolymers were isolated from homopolymers by selective extraction with cyclohexane and acetonitrile of PS and PMMA, respectively, and 0.015 g dry block copolymer was obtained in the end.

### Polymerization

Kinetic measurement was performed using the gravimetric method. All rates were determined using time-conversion plots. For kinetic studies, required

amounts of MMA was charged into cylindrical pyrex tubes, degassed by three alternate freeze-pump-thaw cycles, sealed under vacuum, and placed in a thermostatic water bath controlled to  $\pm 0.1^\circ\text{C}$  for selected times. The tubes were removed from the water bath after a certain time. The viscous reaction mixtures were diluted with small amounts of benzene, poured into excess methanol, and twice reprecipitated from benzene to methanol to remove unreacted DMCPs, and weighted after drying at  $60^\circ\text{C}$  in vacuum.

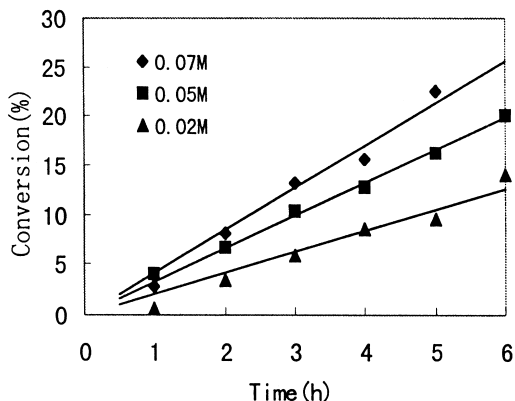
### Measurements

Molecular weight and molecular weight distribution were determined by a Waters gel permeation chromatography (GPC) model 150, equipped with refractive index (RI) detector using tetrahydrofuran (THF) as eluent at a flow rate of 1.0 mL/min, and molecular weight calibrations were done using polystyrene standards. The glass transition temperature ( $T_g$ ) was determined using a Mettler Toledo DSC821<sup>o</sup> Differential Scanning Calorimeter at a heating rate of  $10^\circ\text{C}/\text{min}$ . The thermogravimetric analysis (TGA) was carried out by a Mettler TA3000 thermal analyzer in nitrogen atmosphere at a rate of  $10^\circ\text{C}/\text{min}$ .  $^1\text{H-NMR}$  was carried out by VXR-300MHz, and infrared (IR) was determined by FT-5DX.

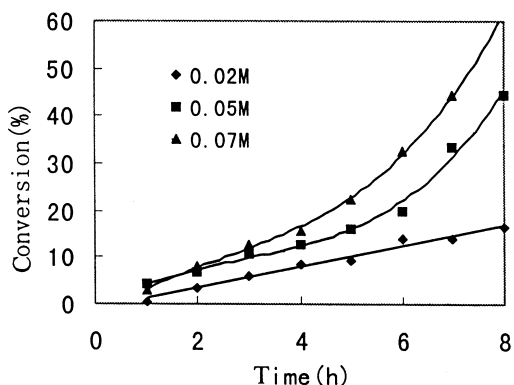
## RESULTS AND DISCUSSION

### Kinetic Studies

As is seen from Figure 1, all of the observed conversion was found to increase linearly from the origin with reaction time. In these relations, no distinct induction period was found. From Figure 2, the auto-acceleration effect could be



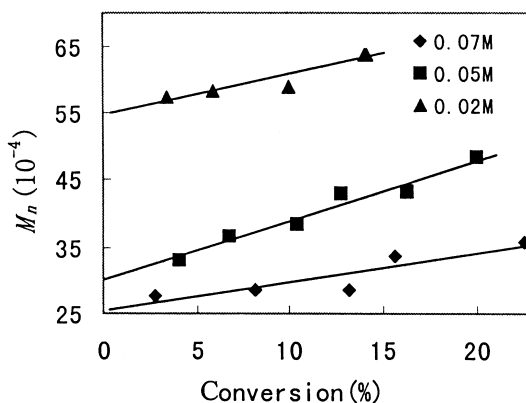
**Figure 1.** Time-conversion relations at initial stage in the bulk polymerization of MMA with DMCPs as initiator at  $50^\circ\text{C}$ .



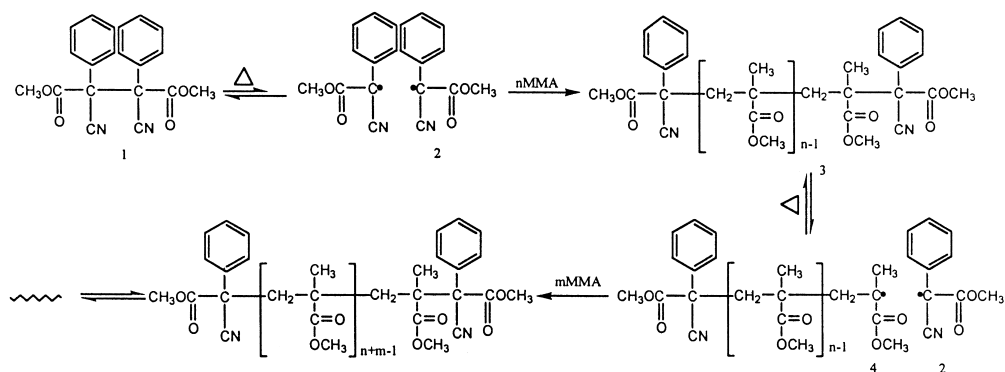
**Figure 2.** Time-conversion relations in the bulk polymerization of MMA with DMCPs as initiator at different concentrations at 50°C.

observed. Figure 3 showed that the time-molecular weight relations for bulk polymerization of MMA with different concentrations' DMCPs. As seen from Figure 3, the  $M_n$  of the polymers increased with conversion, i.e., reaction time. Such findings may be taken to indicate that this compound can serve as iniferter to induce a “living” radical polymerization according to the model (Sch. 1).

Namely, the hexa-substituted C-C bond in 3 is dissociated into propagating radical 4, and a less-reactive radical 2, the former reacts with MMA to induce polymerization, whereas the latter undergoes primary radical termination by recombination leading to 3 (polymer with a thermally labile C-C bond end group). The thermal dissociation of the hexa-substituted C-C at the resultant polymer chain end followed by further propagation can take place repeatedly in the same manner, and a polymer with a high molecular weight can be formed stepwise by its active end group.



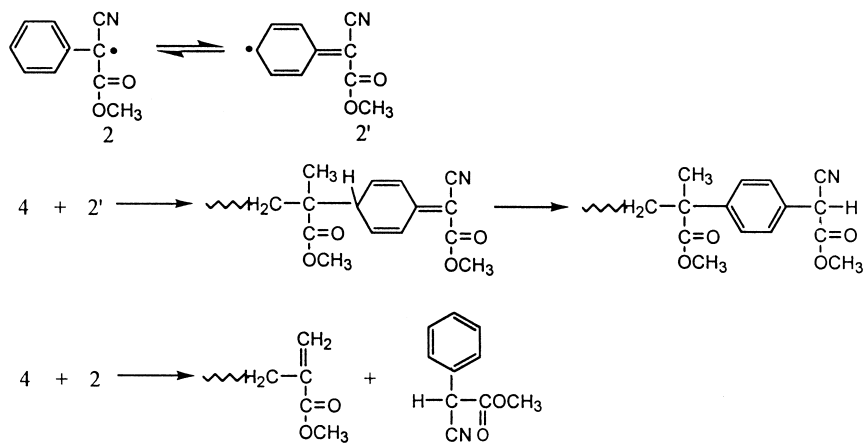
**Figure 3.** The conversion- $M_n$  plot for the polymerization of MMA with DMCPs as initiator at different concentrations at 50°C.



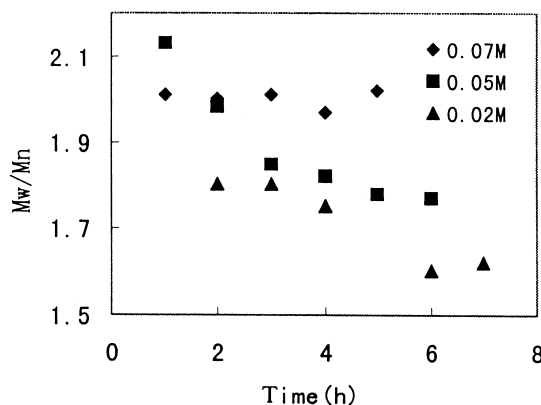
Scheme 1.

However, the observed relations between  $M_n$  and conversion shown in Figure 3 do not pass the origin and the increase in  $M_n$  is not great enough. These observations may be accounted for by the fact that the living nature of DMCPs is not so high, because undesirable side reactions (deactivation reaction) lead to the deactivation of the active chain end in competition with that in Scheme 1. The possible side reactions are ordinary bimolecular termination between 4, primary radical termination by disproportionation between 4 and 2, as well as coupling reaction at the phenyl group, which forms a dead polymer not to be able to grow continuously (see Sch. 2).

As mentioned above, the induction period was not observed in the polymerization of MMA with DMCPs, even at higher concentration. The higher initiating activity and lower dissociation rate of DMCPs probably can explain this observation.



Scheme 2.



**Figure 4.** Time-molecular weight distribution ( $M_w/M_n$ ) relation of the polymerization of MMA with DMCPS at various concentrations at 50°C.

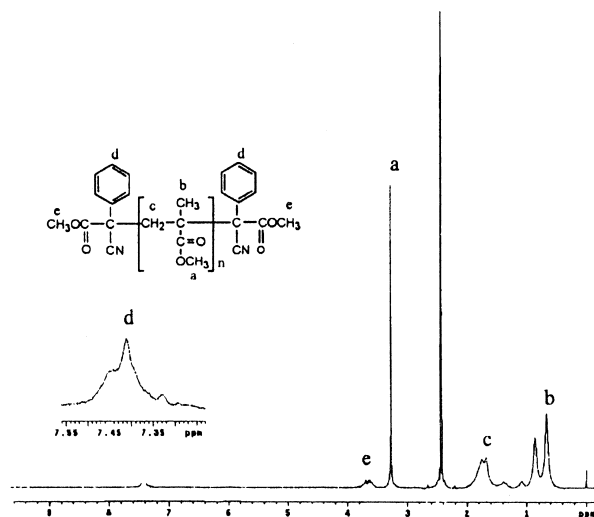
As seen from Figure 4, the molecular weight distribution of the resultant polymer gradually decreases with the reaction time or conversion, which is one of the characteristics of living radical polymerization. This was because the length of the propagating chains and the viscosity of the mixture in the reaction tube increased with the reaction time. As a result, the propagating chains had fewer chances to undergo bimolecular termination with their neighboring reactive chains, and the primary radical termination became more and more important. But the molecular weight distribution was almost not lower than 1.50, which shows that the bimolecular termination between propagating radicals is maybe still very important despite of the primary radical termination.

Figure 4 also shows the molecular weight distribution decreases with the reaction time proportionally at 0.02 M and 0.05 M. However, when the concentration of DMCPS is up to 0.07 M, the molecular weight distribution doesn't decrease with reaction time. Such findings are taken to indicate that the increase of the concentration of the initiator causes more growing radical and the more coupling termination than the corresponding primary termination, or probably the iniferter could not act as a transfer agent and/or a terminator effectively at the higher concentrations.

### Postpolymerization Studies

In some cases, postpolymerization can not give a reliable proof owing to a little of the residual initiator. In this study, the residual initiator has been removed completely by silicon gel column chromatography according to the preceding mentioned method, and the PMMA-DMCPS obtained was characterized by  $^1\text{H}$  NMR spectroscopy (Fig. 5). Besides the characteristic chemical shifts of the repeat units of MMA, there are characteristic signals from DMCPS. The signal



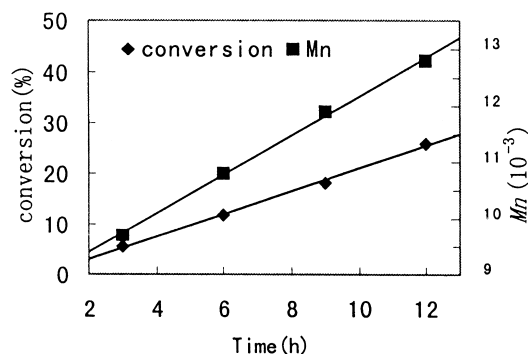


**Figure 5.** The  $^1\text{H}$  NMR spectroscopy of the macro-initiator PMMA-DMCPS,  $M_n = 2348$ ;  $M_w/M_n = 1.82$  (in  $\text{DMSO-d}_6$ , 300 MHz).

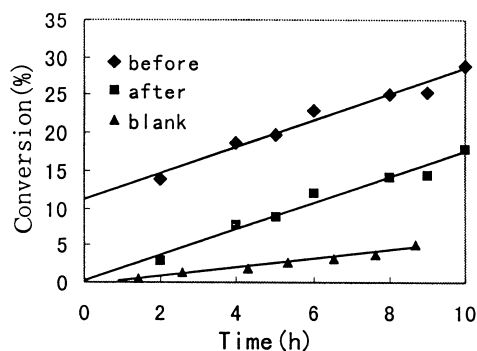
from phenyl group of DMCPS was seen clearly at 7.47 PPM, which indicated the end group of the polymer obtained contains the fragment of DMCPS.

The polymerization of MMA in the presence of PMMA-DMCPS was carried out, and the results are shown in Figure 6. As seen from Figure 6, the plots of time-conversion and time- $M_n$  for the postpolymerization of PMMA-DMCPS for MMA at  $70^\circ\text{C}$ . The conversion and number molecular weight increase linearly with time. These findings can explain that the resultant polymer has the dormant “living” radical species (i.e., iniferter site) at the chain end.

The method as described above can give a pure block copolymer, but the large loss makes the relations of  $M_n$  and conversion of block copolymer with time impossible. Figure 7 gives the rough relations of conversion with time before and after subtracts of the mass of macroinitiator. By comparison with blank experi-



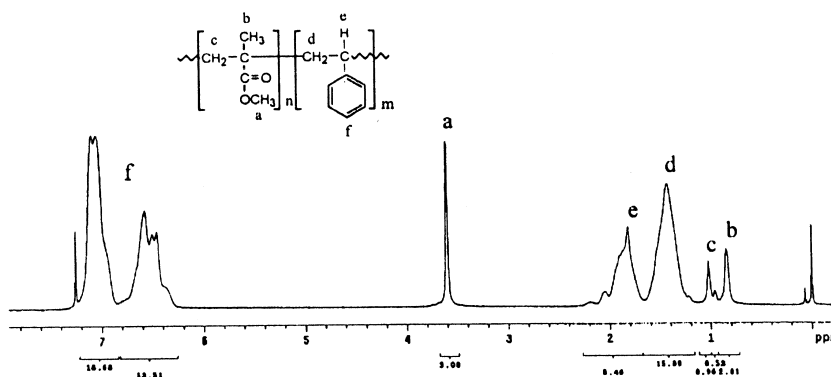
**Figure 6.** The plot of time-conversion and time- $M_n$  for the postpolymerization of PMMA-DMCPS for MMA at  $70^\circ\text{C}$  [ $\text{PMMA-DMCPS}$ ] = 0.043 g/mL.



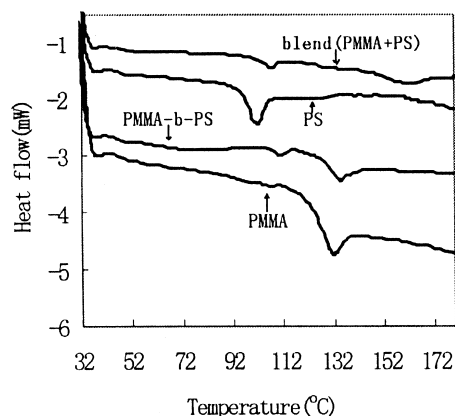
**Figure 7.** The postpolymerization of styrene by PMMA-DMCPS at 80°C [PMMA-DMCPS] = 0.10g/mL. “before” stands for the conversion-time relation before the subtract of the mass of macroinitiator; “after” stands for the conversion-time relation after the subtract of the mass of macroinitiator.

ment, the faster polymerization rate initiated by PMMA-DMCPS may give additional proof of “living” radical polymerization. Figure 8 shows the <sup>1</sup>H-NMR spectrum of the block copolymer, which exhibits signals at 0.80 to 1.1 ppm (CH<sub>3</sub>), 1.3 to 2.3 ppm (backbone CH<sub>2</sub> and CH), 3.6ppm (O-CH<sub>3</sub>), and 6.33-7.1 ppm (phenyl protons). <sup>1</sup>H-NMR spectrum is an effective tool to determine percentages of PMMA and PS present in the block copolymer. The backbone phenyl protons of PS and -OCH<sub>3</sub> protons of PMMA can be used to determine the composition. By comparing integral values, it was determined that ~13% PMMA (weight percentage) is present in the PMMA-PS block copolymer.

The block copolymers were further characterized by Fourier transform infrared (FT-IR) and DSC techniques. In the FT-IR spectrum of PMMA-PST block copolymer, the characteristic peaks at 1736 and 3084~3029 cm<sup>-1</sup> correspond to the ester carbonyl of PMMA segment and the -C-H stretching of the benzene ring. The glass temperatures of PMMA-DMCPS, PS-DMCPS, and



**Figure 8.** The <sup>1</sup>H NMR spectroscopy of the block copolymer PMMA-b-PS,  $M_n = 17464$ ,  $M_w/M_n = 3.23$  (in CDCl<sub>3</sub>, 500 MHz).



**Figure 9.** The differential scanning calorimetry (DSC) of PS, PMMA, the blend of PS and PMMA, and block copolymer (PMMA-b-PS).

PMMA-PS block copolymers appeared at 133°C, 103°C, and 110°C, 135°C, respectively, and the glass temperatures of the blend by the corresponding PMMA and PS are 108°C and 162°C.

## CONCLUSION

DMCPS can be used as a thermal iniferter for the “living” radical polymerization of MMA. The PMMA obtained contains the hexa-substituted C-C bond end group, which is thermally labile, and can be used as macroinitiator to initiate the polymerization of styrene for the preparation of the block copolymer PMMA-b-PS. However, undesirable side reactions make the reaction initiated by DMCPS low “living” characteristic.

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