

# Dithioester (ZC(=S)SR) mediated ‘controlled/living’ free-radical polymerization of methyl acrylate under $^{60}\text{Co}$ $\gamma$ -ray irradiation. Structure effect of Z-group

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## Abstract

The free-radical polymerizations of methyl acrylate (MA) have been systematically studied under  $^{60}\text{Co}$   $\gamma$ -ray irradiation using benzyl propane(dithioate) (**a**), benzyl phenylethane(dithioate) (**b**), benzyl benzenecarbodithioate (**c**), benzyl 4-cyanobenzenecarbodithioate (**d**) and benzyl 4-methoxybenzenecarbodithioate (**e**) as control agents. The results indicate that Z-group of dithioester plays an important role in the polymerization behavior. When Z-group is alkyl or alkyl derivative, in the case of dithioester **a** and **b**, the polymerizations reveal quite good living characteristics except for a similar inhibition period of about 40 min, which may be attributed to the lower propagation rate coefficients during the initialization period. However, for dithioesters **c**, **d** and **e**, aryl as Z-group, the polymerizations show very strong inhibitions in the processes. The strong inhibition may be associated with the formation of probable 3 or 4-arm structure compounds. It is worth noting that it is the first report for dithioester **a** to be used as control agent in ‘controlled/living’ free radical polymerization under  $\gamma$ -ray irradiation.

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*Keywords:* Dithioester; Living polymerization; Radiation

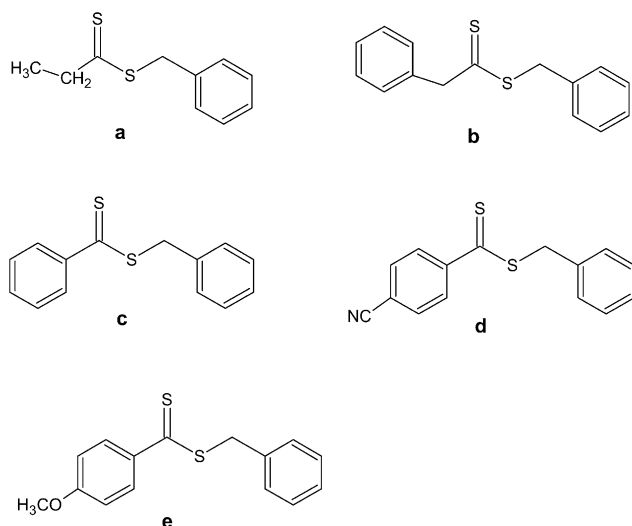
## 1. Introduction

Over the past decade, great progress has been made in controlled/living free radical polymerization, such as living free radical nitroxide-mediated polymerization (NMP) [1–3], atom transfer radical polymerization (ATRP) [4–6] and reversible addition-fragmentation chain transfer (RAFT) [7,8] process. Most of them are carried out under thermal or UV condition. For  $\gamma$ -ray irradiation, it is well known to initiate polymerizations of most monomers, such as methyl acrylate, methyl methacrylate and styrene. However, the polymerization is very difficult to control and the resulting polymers have uncontrolled molecular weights with broad molecular weight distributions. Recently Bai et al. achieved controlled/living free radical polymerizations of vinyl monomers under  $^{60}\text{Co}$   $\gamma$ -ray irradiation in the presence of dibenzyl trithiocarbonate [9–11] and dithiobenzoic acid [12]. And subsequently Davis et al. reported the living free radical polymerizations of styrene [13] and methyl methacrylate [14], and the graft

polymerization of styrene onto a polypropylene solid phase [15,16] under  $\gamma$ -ray irradiation with cumyl phenyldithioacetate and cumyl dithiobenzoate. Pan et al. [17] successfully prepared cyclic poly(methyl acrylate) with controlled ring size and narrow ring size distribution by the  $\gamma$ -ray irradiation polymerization of methyl acrylate at  $-30^\circ\text{C}$  in the presence of cyclic initiator. The  $\gamma$ -ray irradiation living free radical polymerization is a promising process for the practical application because of its advantages, such as being environmentally friendly, running at room temperature, involving no metal contamination, without additional initiators, and high penetrating ability.

However, regarding  $\gamma$ -ray irradiation living free radical polymerization, two mechanisms have been proposed to explain the polymerization behavior. Although the reversible termination mechanism that is similar to the photoiniferter mechanism was first suggested several years ago [9], there is not enough experimental evidence to date. According to CAMD and CSIRO groups' works [14], the polymerization should proceed with RAFT mechanism that has been widely accepted in thermal condition. The initiating radical is first generated by the interaction of the radiation with the monomer, and initiates a propagating chain that then adds to the thiocarbonyl group in the dithio compound, creating the intermediate radical; this

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Scheme 1. Chemical structures of dithioesters.

step may release a leaving group radical that can initiate another polymer chain, the dithio moiety of the polymer chain formed during the process may then continue to act as a transfer agent, establishing the chain equilibrium. The rate of addition and fragmentation may be fast relative to the propagation, consequently maintaining the living character of the polymerization.

We have found that the structure of Z-group of xanthate [18] and dithiocarbamate [19] plays an important role in the polymerization control under  $\gamma$ -ray irradiation. The polymerizations have good living characteristics in the presence of xanthate or dithiocarbamate with the aryl conjugation structure of Z-group. In contrast, the polymerization with benzyl *N,N*-diethyldithiocarbamate or S-benzyl O-ethyl dithiocarbamate cannot be controlled and the resulting polymer has a broad molecular weight distribution or even crosslink occurs like traditional radical polymerization under  $\gamma$ -ray irradiation. In addition, the polymerization rate is markedly influenced by the conjugation structure of Z-group of dithiocarbamate and xanthate, and aromatic polycyclic groups on nitrogen or oxygen atom lead to pronounced retardation in the process.

Dithioester is an important class of control agent in living free radical polymerization under thermal condition and was first patented by Rizzardo et al. in 1998 [7]. It is well known that dithioester often inhibit the polymerization of acrylates under thermal condition. Considerable attention has been directed to the effect of dithioester structures on the polymerization behavior under thermal condition. It has been found that electron-withdrawing substitutes on Z-group can enhance the activity of dithioester [20] and that the steric factors, polar factors and the stability of R group appear to play an important role in determining its effectiveness [21].

However, to the best of our knowledge, dithioesters have not been systematically studied as control agents in living free radical polymerization under  $\gamma$ -ray irradiation to date. In order to well understand the polymerization process, it is necessary to investigate the structure influence of dithioester on the polymerization behavior under radiation. In this paper, we wish

to report the polymerization results with dithioester as control agent and the structure effect of Z-group of dithioester on living free radical polymerizations of methyl acrylate (MA) under  $\gamma$ -ray irradiation. The dithioesters employed in the present study are depicted in Scheme 1.

## 2. Experimental

### 2.1. Materials

MA was dried over CaH<sub>2</sub> overnight, and then distilled under reduced pressure, stored under N<sub>2</sub> at  $-20^{\circ}\text{C}$  prior to use. Tetrahydrofuran was refluxed with sodium for 24 h and distilled. The dithioesters (a–e) were synthesized according to the literature procedure [22]. All other chemical agents were used as received.

### 2.2. Polymerization

The polymerization was carried out in a sealed tube. The general procedure is as follows. A mixture of monomer and dithioester was placed in a 5 mL polymerization tube. After it was degassed with performing a freeze-evacuate-thaw cycle three times, the tube was sealed under vacuum. Then it was placed in an insulated room with a <sup>60</sup>Co source. The polymerization was carried out under <sup>60</sup>Co  $\gamma$ -ray irradiation at 60 Gy/min for a prescribed time at room temperature. After the polymerization, the reaction mixture was dissolved with THF, and then precipitated in 10-fold methanol. The polymer was collected by filtration and dried in a vacuum oven at  $40^{\circ}\text{C}$ . Conversion (Conv.) was calculated based on Eq. (1):

$$\text{Conv.}(\%) = \frac{(W_P - W_{\text{DTE}})}{W_M} \times 100\% \quad (1)$$

Where,  $W_P$ ,  $W_{\text{DTE}}$  and  $W_M$  respectively stand for the weights of the polymer, dithioester and monomer.

### 2.3. Characterization

Molecular weight and molecular weight distribution were determined by means of a Waters 150C gel permeation chromatography (GPC) equipped with  $10^3$ ,  $10^4$ ,  $10^5$  Å Waters Ultrastayragel columns, and using THF (1.0 mL/min) as the eluent, and the calibration was carried out based on polystyrene standard. <sup>1</sup>H and nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AVANCE-300 instrument with CDCl<sub>3</sub> as the solvent. <sup>13</sup>C NMR and <sup>13</sup>C DEPT-135 spectra were recorded by means of a Bruker AVANCE-400 instrument.

Matrix assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS) spectrum was recorded in the reflector mode on a Bruker BIFLEX™ III using a nitrogen laser (337 nm) and an accelerating potential of 20 kV. Samples were prepared by mixing a solution of matrix (2,5-dihydroxybenzoic acid: DHB) in THF (40 mg/mL) and a solution of oligomer in THF (1 mg/mL). Then, 1  $\mu\text{L}$  of the resulting

Table 1  
 Polymerization results of MA polymerized under  $^{60}\text{Co}$   $\gamma$ -ray irradiation (60 Gy/min, [Dithioester]=0.019 mol/L)

Entry	Dithioester	Time (min)	Conv. (%) <sup>a</sup>	$M_{n,th}$ <sup>b</sup>	$M_{n,NMR}$ <sup>c</sup>	$M_n$ <sup>d</sup>	$M_w$ <sup>d</sup>	$M_w/M_n$ <sup>d</sup>
1	<b>a</b>	30	4.8	2400	2360	2500	3100	1.24
2	<b>a</b>	60	12.7	6350		7500	8200	1.09
3	<b>a</b>	110	46.5	23,300		29,600	31,500	1.06
4	<b>b</b>	45	6.6	3300	3600	4000	5600	1.37
5	<b>b</b>	90	34.6	17,300		27,500	28,600	1.04
6	<b>b</b>	120	51.6	25,800		36,000	38,200	1.06
7	<b>c</b>	180	1.1			–	–	–
8	<b>c</b>	210	Partly crosslink	–	–	–	–	–
9	<b>d</b>	120	1.3			–	–	–
10	<b>d</b>	150	Partly crosslink	–	–	–	–	–
11	<b>e</b>	145	1.0			–	–	–
12	<b>e</b>	180	Partly crosslink	–	–	–	–	–

<sup>a</sup> Determined gravimetrically, calculated according to Eq. (1).

<sup>b</sup> Calculated according to Eq. (2).

<sup>c</sup> Calculated according to Eq. (3).

<sup>d</sup> Determined by gel permeation chromatography (GPC).

mixture was deposited onto the target plate and the solvent was evaporated at room temperature. Internal standards (peptide derivatives) were used to calibrate molecular weight.

### 3. Results and discussion

The polymerizations of MA were carried out under  $^{60}\text{Co}$   $\gamma$ -ray irradiation (60 Gy/min) in the presence of dithioesters (**a–e**) respectively at room temperature, and the results were listed in Table 1. As can be seen from the table, the polymerization behaviors are quite different with the different dithioesters. When Z-group is alkyl or alkyl derivative, for dithioester **a** and **b**, the polymerizations were ‘controlled’ very well according to the ‘controlled’ molecular weight and narrow distribution (entries 1–6, Table 1); whereas, when Z-group is changed into aryl, for dithioesters **c**, **d** and **e**, the heavy inhibitions of the polymerizations were observed, and there

was almost no polymer obtained before crosslink (entries 7–12, Table 1).

It was found that for dithioester **a** and **b** mediated polymerizations, the molecular weights were very close to the theory value within a reasonable error, which can be calculated according to the Eq. (2):

$$M_{n,th} = \text{Conv.} \frac{W_M}{M_{DTE}} + M_{m,DTE} \quad (2)$$

Where,  $W_M$  and  $M_{DTE}$  are, respectively, the weight of monomer in the feed and the moles of dithioester added,  $M_{m,DTE}$  is the molar mass of dithioester. It should be explained that the relatively large difference between the experimental and theory molecular weights for entries 5 and 6 in Table 1 may be ascribed to the following probable reasons: (1) the dithioester may be destroyed at relatively high conversion in the polymerization under gamma radiation, (2) polystyrene

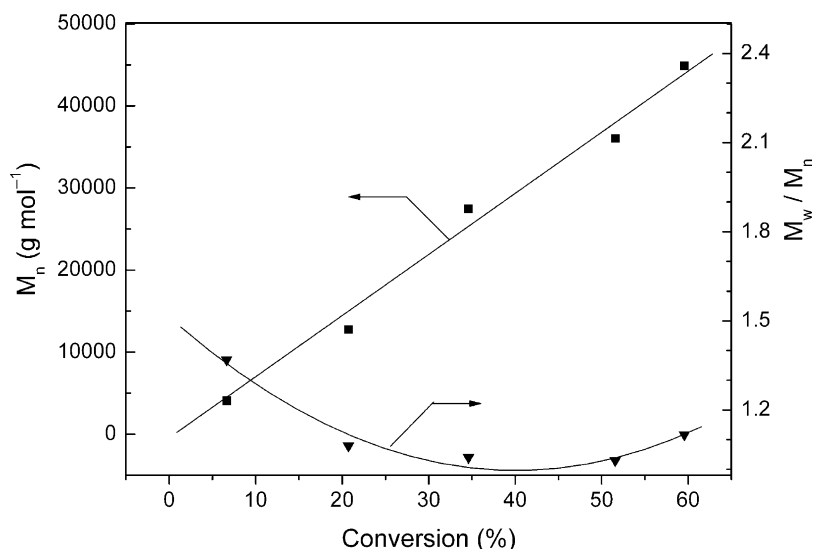


Fig. 1. Molecular weight and molecular weight distribution as a function of monomer conversion for the polymerization of MA in the presence of dithioester **b** (60 Gy/min, [b]=0.019 mol/L).

standards are used for GPC calibration, and (3) there exists an experimental error to some extent during the experiment.

Fig. 1 shows the evolution of the molecular weight and molecular weight distribution with monomer conversion for the polymerization with dithioester **b** as an example for a successful living polymerization. It can be clearly seen that the molecular weight of the obtained polymer increases linearly with monomer conversion, and the molecular weight distributions remains very narrow throughout the process. Typical GPC curves for different reaction times are depicted in Fig. 2. It is obvious that the molecular weight distributions become narrower and narrower with the growth of molecular weight. These chain length distributions demonstrate the ‘controlled’ nature of the polymerizations.

On the other hand, it is noticed that there exist the similar linear relationships between  $\ln([M]_0/[M])$  and polymerization time for dithioester **a** and **b** mediated polymerizations (solid line, Fig. 3), which indicates that the polymerizations are first order reactions with respect to monomer concentration. All of the evidences indicate that the polymerization is a ‘living’ free radical process. In addition, the plots both show a similar inhibition period of about 40 min. During the period, the monomer conversion remains very low.

The polymer structures were characterized by  $^1\text{H}$ NMR and two typical  $^1\text{H}$ NMR spectra of PMA as examples were shown in Fig. 4. The peaks at  $\delta=3.20\text{--}4.50$  ppm are assigned to the methylic protons of the MA units. In Fig. 4(A), the signals at  $\delta=7.13\text{--}7.30$ , 4.70, 2.99, 2.57 and 1.36 ppm show that the existence of benzyl and ethyl group of dithioester **a** in the polymer chain; In Fig. 4(B), the peaks at  $\delta=7.35\text{--}7.10$ , 4.78, 4.60 and 2.55 ppm indicate that benzyl groups of dithioester **b** are retained in the polymer chain. Provided that each macromolecule contains one dithioester residue, number-average molecular weight,  $M_{n,\text{NMR}}$ , can be calculated according to Eq. (3):

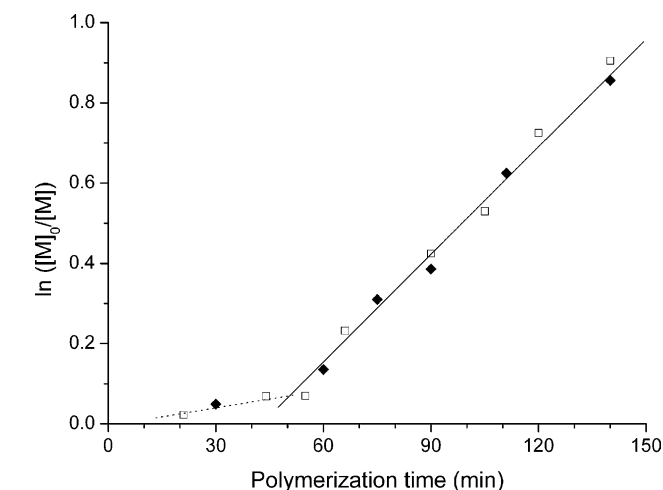


Fig. 3.  $\ln([M]_0/[M])$  as a function of time for the polymerization of MA in the presence of dithioester **a** ( $\blacklozenge$ ) and **b** ( $\square$ ) (60 Gy/min, [Dithioester] = 0.019 mol/L).

$$M_{n,\text{NMR}} = \frac{86I_{3.75}}{(3I_{\text{S-CH-}})} + M_{m,\text{DTE}} \quad (3)$$

Where,  $I_{3.75}$  are the integral values of the peaks at  $\delta=3.20\text{--}4.50$  ppm,  $I_{\text{S-CH-}}$  is the integral value of the peaks corresponding to the proton of S-CH-, 86 is the molar masses of MA. The calculated values of molecular weight are listed in Table 1. The close agreement within a reasonable error between  $M_{n,\text{NMR}}$  and  $M_n$  is an additional evidence for the ‘living/controlled’ character of the polymerization.

We have reported the structure effects of xanthates and dithiocarbamates on the polymerization of MA under  $\gamma$ -ray irradiation [18,19]. For the dithioesters, we also find that there is a remarkable influence of Z-group of dithioester on the polymerization behavior. For dithioester **c**, **d** and **e** with phenyl or phenyl derivatives as Z-group, the polymerizations show a very strong inhibition (i.e. almost complete inhibition) in the process, there is almost no polymer obtained before crosslink (entries 7–12, Table 1). We attempted to investigate the effect of substituent on phenyl, but unfortunately there is no marked effect of the substitutes, whether electron-pulling or electron-pushing group (i.e. CN and  $\text{OCH}_3$ ), observed on the polymerization behavior within a reasonable experimental error. Whereas, for dithioester **a** and **b**, as mentioned above, the polymerizations are the good ‘controlled/living’ processes though they have inhibition periods to some extent. Since R group was the same for each of the dithioesters, the different results of the polymerizations should be ascribed to the effect of Z-group. It is obvious that the conjugation structure of Z-group of dithioester has a pronounced influence on the polymerization behavior under  $\gamma$ -ray irradiation.

There have been some debates regarding the inhibition mechanism in dithioester mediated acrylate polymerizations under thermal condition. Davis and Barner-Kowollik attributed it to either slow fragmentation of the intermediate RAFT radicals appearing in the pre-equilibrium or the slow re-initiation of the leaving group radical of the initial RAFT agent [23,24]. On the other hand, Tonge and Klumperman et al.

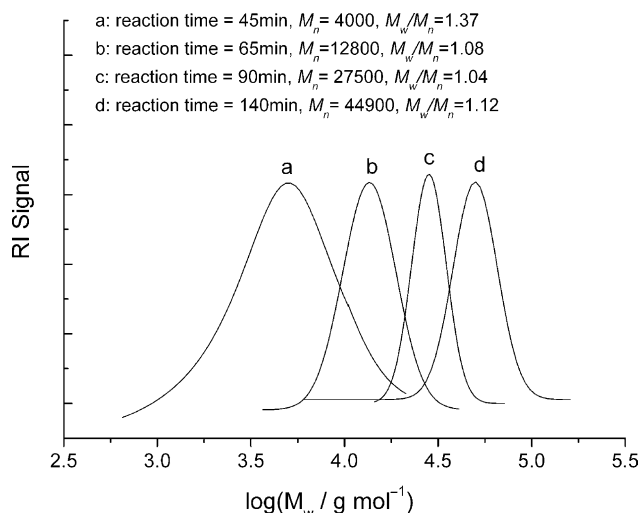


Fig. 2. GPC curves of PMA samples from the polymerizations under  $^{60}\text{Co}$   $\gamma$ -ray irradiation in the presence of **b** (60 Gy/min) for different reaction times.

suggested that the inhibition is due to the lower propagation rate coefficients of oligomeric radicals during the initialization period, and the length of the period is dependent on the RAFT agent concentration [25]. For dithioester **a** and **b**, the Z-groups, i.e. ethyl and benzyl, are almost equally favorable for a relatively less stable disulfur alkyl radical intermediate; and furthermore, the dithioesters have the apparent larger transfer

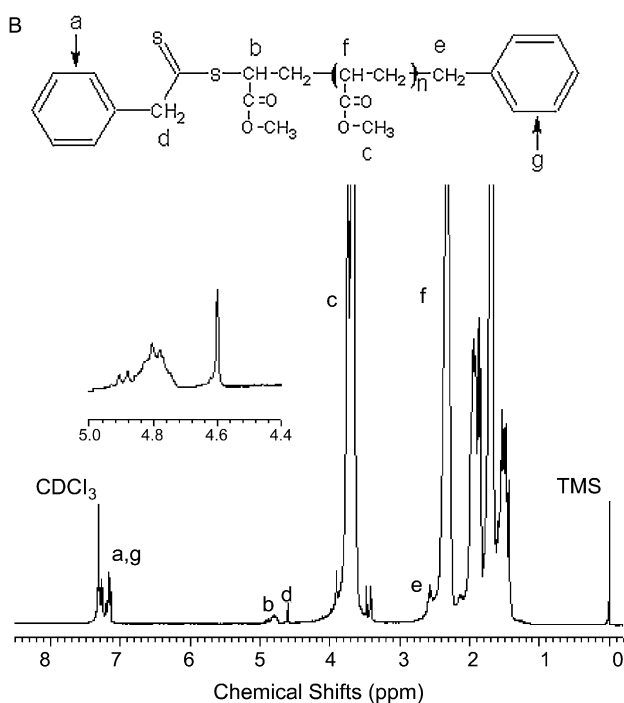
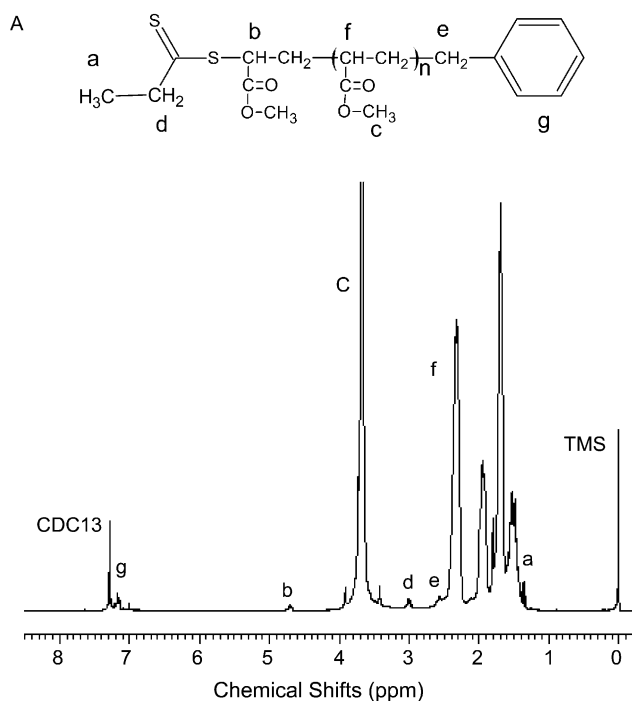


Fig. 4.  $^1\text{H}$  NMR spectra (300 MHz,  $\text{CDCl}_3$ ) of PMA prepared by the polymerization in the presence of dithioesters: (A) **a** (entry 1, Table 1), and (B) **b** (entry 4, Table 1) under  $^{60}\text{Co}$   $\gamma$ -ray irradiation.

constants [26]. Therefore, the inhibition for dithioester **a** and **b** mediated polymerizations may be ascribed to the lower propagation rate coefficients during the initialization period, not to the slow fragmentation of the intermediate RAFT radicals, and the similar inhibition period within a reasonable experimental error is related to the same dithioester concentration. Fig. 3 further demonstrated the inference. Because the radical concentration should be a constant under  $\gamma$ -ray irradiation at the prescribed dose rate, the slope of the straight line in Fig. 3 is proportional to the apparent polymerization rate constant. So the plots (from the dot to solid line) show that there is a low apparent polymerization rate constant at the start of the reaction, after the period, the radical changes to a faster propagating species.

For dithioesters **c**, **d** and **e**, the strong inhibition phenomena in the processes are similar with that of cumyl dithiobenzoate mediated styrene and MA polymerizations under a source of gamma irradiation at low dose rates [16,27]. Davis et al. [16] proposed that a significant free radical storage effect (or a stable radical sink) may be responsible for the almost complete inhibition due to stable intermediates (either radical or nonradical), and the color change observation was provided.

To further investigate the point, some experimental observations were obtained in dithioester **c**, **d** and **e** mediated polymerizations. For the crosslinked samples (entries 8, 10 and 12, Table 1), it was noticed that the crosslinked part was colorless while the liquid part had the red color. The monomer in the red liquid part (entry 12, Table 1) was removed under reduced pressure at 40 °C to afford a red solid, and then it was characterized by MALDI-TOF MS,  $^{13}\text{C}$  NMR and  $^{13}\text{C}$  DEPT-135 spectra.

A MALDI-TOF MS (Fig. 5) analysis was made with the sample to give details on their probable structures (Scheme 2). In Table 2, the peaks (P1–P6) correspond well to the probable 3 or 4-arm structures (A–I) respectively. The structures may be similar to the low mass model 3 or 4-arm star polymers reported by Fukuda et al. [28,29] and Monteiro et al. [30], and can not act as a transfer agent to react with the propagating

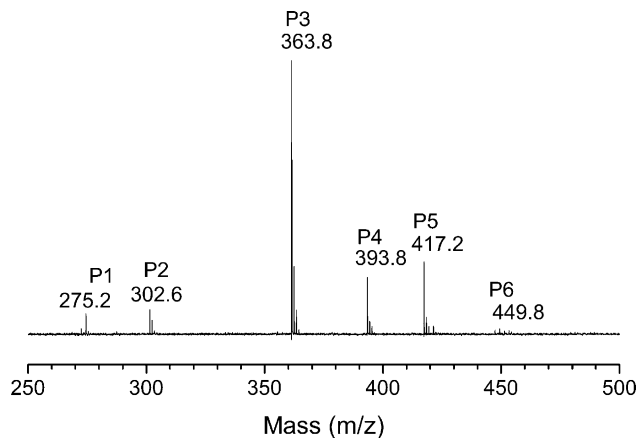
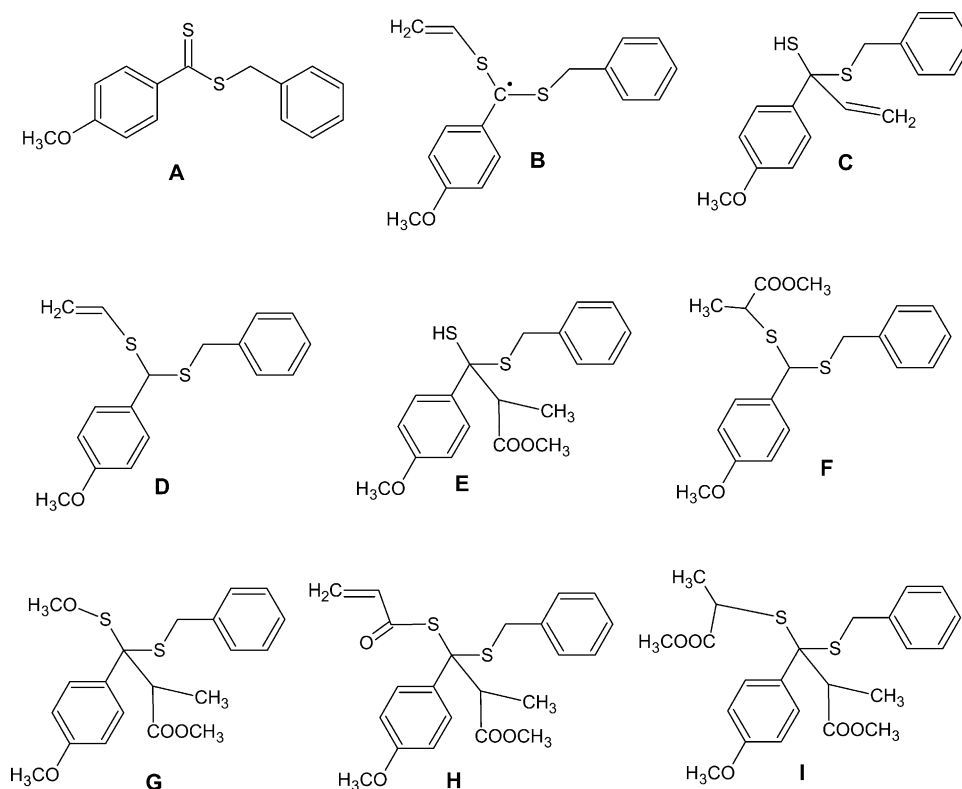


Fig. 5. MALDI-TOF MS spectrum acquired from the noncrosslink part of the sample prepared by the polymerization with dithioester **e** (entry 12, Table 1) dispersed in a matrix of 2,5-dihydroxybenzoic acid.



Scheme 2. Probable structures derived from the MALDI-TOF MS distributions for the noncrosslink part of the sample prepared by the polymerization with dithioester **e** (entry 12, Table 1).

radical any more. The compounds might result from dithioester **e** reacting with corresponding radicals produced by the interaction of the radiation with the monomer. It was noticed that P2 could correspond to an intermediate radical itself (**B**) (302.6 mass units), and the similar phenomenon had been observed by Charreyre et al. [31]. In addition, from Fig. 5, we could also find that a little dithioester **e** (i.e. **A**) still existed and a very small amount of adduct (**I**) formed.

However, according to the  $^{13}\text{C}$  DEPT-135 spectrum (Fig. 6(b)), there is only one peak (66.2 ppm) corresponding to the quaternary carbon in  $^{13}\text{C}$  NMR (Fig. 6(a)), which may be assigned to structure E of the main peak P3 in MALDI-TOF MS [32]. On the other hand, the structures (B–D and F–I) was not found from Fig. 6. This may be attributed that the content of

the structures is too low or they might be generated by the laser power in the process of mass spectroscopy.

The results indicated that dithioester **c**, **d** and **e**, due to phenyl or phenyl derivatives as Z-groups that are favorable for a stable disulfur alkyl radical intermediate, scavenged the initial radical to give 3 or 4-arm structure compounds until completely consumed at room temperature, then

Table 2  
Probable structures corresponding to the peaks of MALDI-TOF MS

Peak	Monoisotopic mass experimental	Monoisotopic mass theoretical	Structures in Scheme 2	Cationization
P1	275.2	275.4	<b>A</b>	$\text{H}^+$
P2 <sup>a</sup>	302.6	302.4	<b>B</b>	$\text{H}^+$
		303.4	<b>C; D</b>	$\text{H}^+$
P3	363.8	363.5	<b>E; F</b>	$\text{H}^+$
P4	393.8	393.5	<b>G</b>	$\text{H}^+$
P5	417.2	417.5	<b>H</b>	$\text{H}^+$
P6	449.8	449.6	<b>I</b>	$\text{H}^+$

<sup>a</sup> P2 might also correspond to the structures **C** and **D** due to their theoretical monoisotopic masses (303.4 mass units) very close to **B**'s isotopic mass (303.6 mass units).

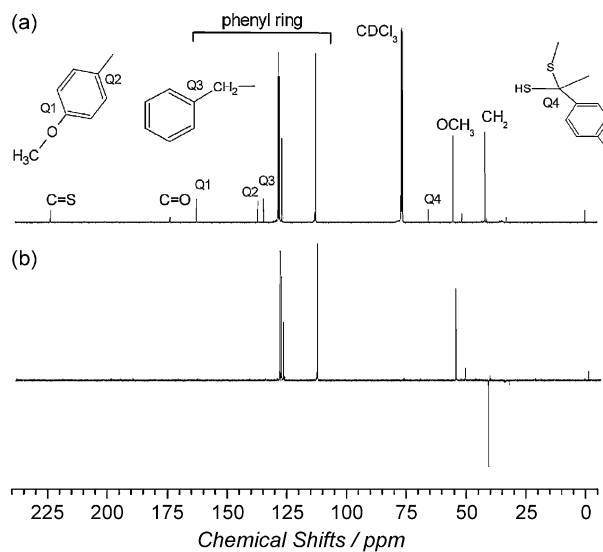


Fig. 6. (a)  $^{13}\text{C}$  NMR and (b) DEPT-135 spectra (400 MHz,  $\text{CDCl}_3$ ) of the red solid from the noncrosslink part of the sample prepared by the polymerization with dithioester **e** (entry 12, Table 1).

the polymerization proceeded as the conventional radical process did, and crosslink easily occurred.

#### 4. Conclusions

The free radical polymerizations of methyl acrylate have been systematically studied under  $^{60}\text{Co}$   $\gamma$ -ray irradiation with dithioesters as control agents. It was found that the structure of Z-group of dithioester plays an important role in the polymerization behavior. The polymerizations have good 'living' characteristics when Z-group is alkyl or alkyl derivatives in the case of dithioesters **a** and **b**. The molecular weight of the obtained polymer increases linearly with monomer conversion, molecular weight distribution is very narrow, and a linear relationship between  $\ln([M]_0/[M])$  and polymerization time exists. In addition, the systems both show a similar inhibition period of about 40 min, which may be attributed to the lower propagation rate coefficients during the initialization period, and the similar inhibition period is related to the same dithioester concentration. On the other hand, for dithioesters **c**, **d** and **e**, aryl as Z-group, the polymerizations show very strong inhibitions (almost complete inhibition) in the processes, there is almost no polymer obtained before crosslink. The strong inhibition may be associated with the generation of probable 3 or 4-arm structure compounds. It is worthy noticing that it is the first report for dithioester **a** to be used as control agent in 'controlled/living' free radical polymerization under  $\gamma$ -ray irradiation.

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