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Reversible addition–fragmentation chain transfer polymerization of styrene initiated by tetraethylthiuram disulfide

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Abstract

The RAFT polymerization of styrene in bulk was carried out using tetraethylthiuram disulfide (TETD) as an initiator and 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) as a chain transfer agent at different temperatures. The results of the polymerization showed that TETD could initiate the RAFT polymerization of styrene in the living way. The kinetics of the polymerization showed first order. The molecular weights of the polymers increased linearly with conversions and were close to the theoretical values ($M_{n,th}$). The polydispersities of the polymers remained relatively narrow (<1.3). The structure of the polymer was characterized by ^{1}H NMR. The result showed that there were moieties of CPDN and TETD attained at the end of the polymer. Using these double functional end capped polymers, the chain-extension experiments were successfully carried out not only in the conventional RAFT polymerization way, but also under UV irradiation.

Keywords: Reversible addition–fragmentation chain transfer (RAFT) polymerization; 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN); Tetraethylthiuram disulfide (TETD)

1. Introduction

Since reversible addition–fragmentation chain transfer (RAFT) polymerization was reported by Rizzardo in 1998 [1], great attention has been paid by researchers [2–7]. Up to now, the RAFT polymerization has been successfully applied to many monomers including functional and water-soluble monomers [8–11]. Furthermore, the RAFT polymerization can be conducted in dispersed phase under controlled manner [12,13]. Many complex architecture polymers have also been synthesized via RAFT process, such as block [14], comb [15], star [16] and graft polymer [17].

The RAFT polymerization of styrene is usually performed using thermal initiator such as azobisisobutyronitrile (AIBN), and it can be also initiated by the radical derived from monomer at the high temperature without adding any initiator [18]. Obtained polymer contains corresponding moiety derived from initiator in the one end of the polymer chain and dithiocarbonyl structure in the other end [19]. When the functional chemicals are applied to initiate the RAFT polymerization, bifunctional end group polymers would be prepared. With these functional structures, polymers can be chain extended at both end of polymer chain [20,21]. However, few details about the proportion of the moiety from the initiator and the R group of RAFT agent which attached to the polymer were described in the published papers.

It is widely known that tetraethylthiuram disulfide (TETD) is an excellent thermal and photo-initiator for the polymerization of many monomers. Otsu et al. researched the effect of TETD on the polymerization and found that TETD acted not only as an initiator but also as a retarder, terminator and transfer agent. They put forward the concept 'Iniferter' and eventually explained the reaction mechanism [22]. Qiu et al. reported the atom transfer radical polymerization (ATRP) of styrene initiated by TETD and proposed the mechanism in which TETD really acted as the initiator in the process [20]. The results showed that TETD was an efficient initiator in ATRP and the TETD moiety was attached to the polymer chain.

In this paper, we report the application of TETD as an

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initiator in the CPDN mediated RAFT polymerization of styrene to examine that how many groups derived from TETD are left in the polymer. On the other hand, TETD is sensitive to UV light that can be initiated by the irradiation of UV light. We can obtain the bifunctional polymer which can be chain extended via RAFT process and under UV irradiation.

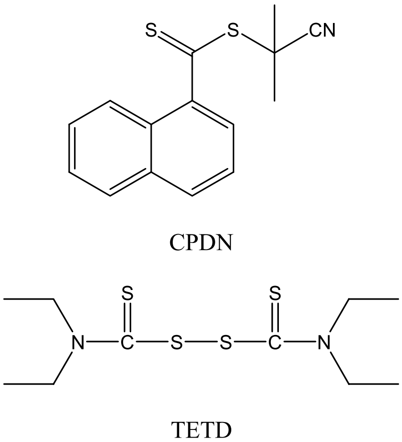
2. Experiment

2.1. Materials

All chemicals (analytical grade) were purchased from Shanghai Chemical Reagents Co. Ltd. China. Styrene (St) was washed with 5% NaOH solution and deionized water until neutralization, dried overnight with anhydrous $MgSO_4$, then distilled twice under reduced pressure, and stored in the refrigerator. Tetraethylthiuram disulfide (TETD, the structure was shown in Scheme 1) was recrystallized from ethanol and dried at room temperature under vacuum. 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN, the structure was shown in Scheme 1) was synthesized according to the literature [23]. All the other materials were used as received.

2.2. RAFT polymerization of styrene

A 1 mL ampoule was filled with predetermined concentration of St, CPDN and TETD, and was flame sealed after bubbled with argon for 10 min to eliminate oxygen and placed in an oil bath at the desired temperature. After a predetermined time, the ampoule was opened, and then the contents were diluted with a little THF and precipitated in 200 mL methanol. The polymer was collected and dried at 55 °C under vacuum. The conversion was determined gravimetrically.



Scheme 1. Structures of CPDN and TETD.

2.3. Chain extension using PSt as macro-RAFT agent

The same procedure of RAFT polymerization of styrene was used except that CPDN was substituted with PSt obtained from RAFT polymerization.

2.4. Chain extension using photopolymerization method

Monomer and predetermined concentration of PSt obtained from RAFT polymerization of styrene were added to the ampoule. After bubbled with argon for 10 min, the ampoule was flame sealed and left stand in the water bath at room temperature under a 1000 W UV lamp with the distance of 15 cm. The next operations were the same as stated in RAFT polymerization procedure.

2.5. Characterization

Molecular weights and polydispersities of the polymers were measured using Waters 1515 gel permeation chromatography (GPC) with THF as an eluent at a flow rate of 1.0 mL/min and column temperature at 30 °C, using HR 1, HR 3, and HR 4 column with molecular weight range 100–500,000. The molecular weights were calibrated with polystyrene standards. ^1H NMR spectra were recorded on an INOVA 400 MHz NMR using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. The purity of CPDN was determined on Waters 515 HPLC with methanol and water as eluent at the ratio of 80:20, and column temperature was 30 °C.

3. Results and discussion

3.1. RAFT polymerization of styrene

AIBN is usually applied as an initiator in the RAFT polymerization. In this work, TETD was used to initiate the RAFT polymerization of styrene in order to prepare bifunctional group ended polystyrene. The RAFT polymerization of styrene was conducted at 60 °C with the $[St]_0/[CPDN]_0/[TETD]_0$ ratio of 1000:3:1 in bulk. The results of $\ln([M]_0/[M])$ versus time were shown in Fig. 1. The kinetics was first order with respect to the monomer concentration, which indicated the propagating free radical concentration was stationary during the polymerization. The molecular weights increased linearly with conversion and were close to the theoretical values (Fig. 2). The relatively low values of polydispersity ($PDI < 1.2$) were also observed in Fig. 2. The theoretical molecular weights were calculated by the following equation (Scheme 2).

Comparison experiments were also carried out to investigate the effect of TETD on the polymerization of styrene. The results were listed in Table 1. The polymerization was hardly to take place with only CPDN added into Styrene. There was nothing precipitated in the methanol

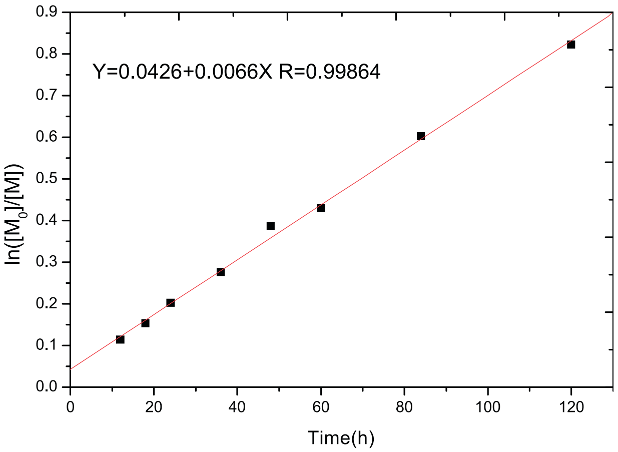


Fig. 1. Kinetic plot of RAFT polymerization of styrene initiated by TETD in bulk at 60 °C ($[St]_0/[CPDN]_0/[TETD]_0=1000:3:1$).

after 18 h, and the conversion was 13.5% after 60 h (entry 1). When TETD and CPDN were both added into the polymerization system, the conversion reached 64.6% after 60 h (entry 2). The polymerization was obviously accelerated by TETD and this was one of the evidence that TETD acted as an initiator. The polymerization of styrene just with the presence of TETD showed ill controlled characters (entry 3, PDI = 1.68, $M_n = 78{,}400$). This result was consistent with the literature [20]. While adding CPDN into the system, the molecular weight was much less and in good agreement with the theoretical one, and the polydispersity decreased to a low value (entry 4, PDI = 1.10, $M_n = 8400$). The polymerization rate decreased obviously when CPDN was added, which showed a significant retardation. The retardation phenomenon was also observed in various RAFT polymerization systems [24,25].

The conversion of polymerization for CPDN/AIBN system (entry 5) was higher than that for CPDN/TETD system (entry 4). It indicated that the rate of polymerization with AIBN as an initiator was higher than that with TETD. At almost the same conversions, the molecular weights of polymers in the cases of CPDN/AIBN and CPDN/TETD were both close to theoretical values and the values of polydispersity remained relatively low (entry 5 and entry 6). These results indicated that the similar controllability of polymerization was obtained using TETD or AIBN as the initiator in the RAFT polymerization of styrene; however, the polymerization rate of styrene initiated by TETD was slower than that by AIBN.

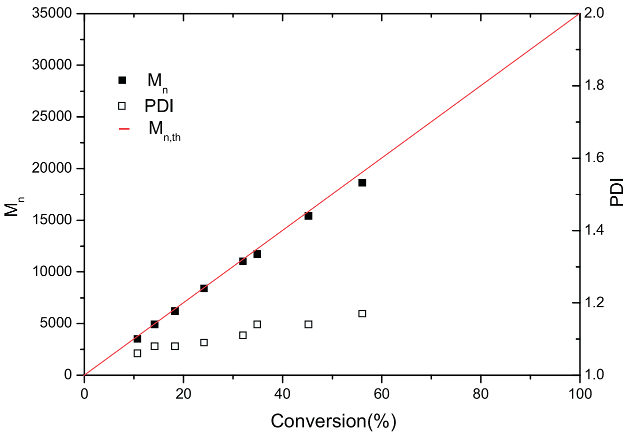


Fig. 2. M_n and polydispersity vs. monomer conversion for RAFT polymerization of styrene initiated by TETD at 60 °C ($[St]_0/[CPDN]_0/[TETD]_0=1000:3:1$).

$$M_{n,th}=\frac{M_{n,St}[St]_0\text{Conversion}}{[CPDN]_0}+M_{n,CPDN}$$

Scheme 2. The equation to calculate the theoretical molecular weight.

The proportion of dithiocarbonyl group in the polystyrene chain end can be calculated by comparing the molecular weight obtained by ^1H NMR and by GPC [26]. The polymer was characterized by ^1H NMR with DMSO as the solvent so as to distinguish the peaks of naphthyl to phenyl. The molecular weight calculated by the integral peak area ratio of naphthyl and phenyl in the NMR spectrum was 2221, and the value measured by GPC was 2182, so 98.2% polymer was end-functionalized by dithiocarbonyl group, which was in accord with that reported by Rizzardo et al. [27].

In order to calculate the ratio of moieties of CPDN to TETD, the RAFT polymerization was carried out using deuterium styrene (St-D) as monomer with the $[St\text{-}D]_0/[CPDN]_0/[TETD]_0$ ratio of 300:3:1 at 60 °C in bulk. The ^1H NMR spectrum of the polymer was shown in Fig. 3. The signals at $\delta=7.8$–8.1 ppm assigned to the naphthalene protons in positions 4, 5 and 8. The signals at $\delta=3.5$–4.2 ppm attributed to the methylene protons of $-S_2CNEt_2$ units [20]. The ratio of these two integral peak area was about 1:1, which meant that if there was one dithiocarbonyl group at one end of every polymer chain, there would be about 75% polymer chains containing $-S_2CNEt_2$ unit at other end of the polymer chain. The additional polymer chains (about 25%) are end-capped with other structures, such as isobutyronitrile. The exact end group structure of every polymer chain was difficult to confirm with ^1H NMR and was still under investigation in our group.

The appearance of CPDN moiety in the ^1H NMR spectrum of polymer indicated that the polymerization of styrene in the presence of TETD and CPDN was according to the RAFT mechanism. It was to say that in the presence of CPDN, TETD acted as an initiator in the RAFT polymerization of styrene, instead of an Iniferter. We proposed the reaction mechanism of the polymerization of styrene in the presence of CPDN and TETD as described in Scheme 3.

Based on the RAFT polymerization mechanism, the polymer obtained from the RAFT polymerization of styrene contains dithiocarbonyl group at one end of polymer chain,

Table 1
Data of styrene polymerization in the different conditions at 70 °C

Entry	$[St]_0/[CPDN]_0/[I]_0$	Time (h)	$M_{n,GPC}$	$M_{n,th}$	Conv (%)	PDI
1	1000:3:0	60	5000	4600	13.5	1.08
2	1000:3:1[a]	60	21,200	22,400	64.6	1.18
3	1000:0:1[a]	9	78,400	21,400[b]	20.3	1.68
4	1000:2:1[a]	9	8400	7800	15.0	1.10
5	1000:2:1[c]	9	21,400	23,000	41.2	1.18
6	1000:2:1[a]	24	19,400	20,700	39.3	1.18

[a] I is TETD.

[b] $M_{n,th}$ is calculated according to the Iniferter mechanism. ($M_{n,th}=(\text{monomer weight}\times\text{Conversion})/2[I]_0+M_I$).

[c] I is AIBN.

which can be used as a macro-RAFT agent. Therefore chain extension was carried out using PSt as a macro-RAFT agent with the $[St]_0/[PSt]_0/[TETD]_0$ ratio of 1000:2:1 at 60 °C, and the GPC traces of polymers were shown in Fig. 4. The molecular weight increased from 8400 to 24,600. The GPC trace obviously shifted from (a) to (b), which indicated that most of the polymer chains contain a $-S_2CNa$ unit at the end. However, the GPC trace of chain-extended polymer showed a slight tail and the polydispersity was broader than before. These results may be caused by the dead chains existed in macro-RAFT agent or a small amount of homopolymer initiated by TETD [27].

Furthermore, as shown in the Fig. 3, the polymer contained the moiety of TETD at the other end of polymer chain, which was a UV light sensitive structure and could initiate polymerization under UV light irradiation [28]. Here, the polymer obtained from RAFT polymerization of styrene initiated by TETD was used as the photo-initiator to initiate the polymerization of styrene under the irradiation of UV light. The polymerization was carried out for 39 h at the $[St]_0/[PSt]_0$ ratio of 500:1 and the GPC traces were shown in Fig. 4 as the peaks (c). The GPC curve showed a bimodal peak, one with high molecular weight (c-1, M_n increased from 8400 to 62,700), and the other with lower molecular weight (c-2, $M_n=8300$) being closed to the original peak ($M_n=8400$). We inferred that most of the polymers containing TETD moiety (namely $-S_2CNEt_2$) had been chain extended, while a little portion of polymer was inactive in this situation. This was consistent with the result of ^1H NMR spectrum (Fig. 3).

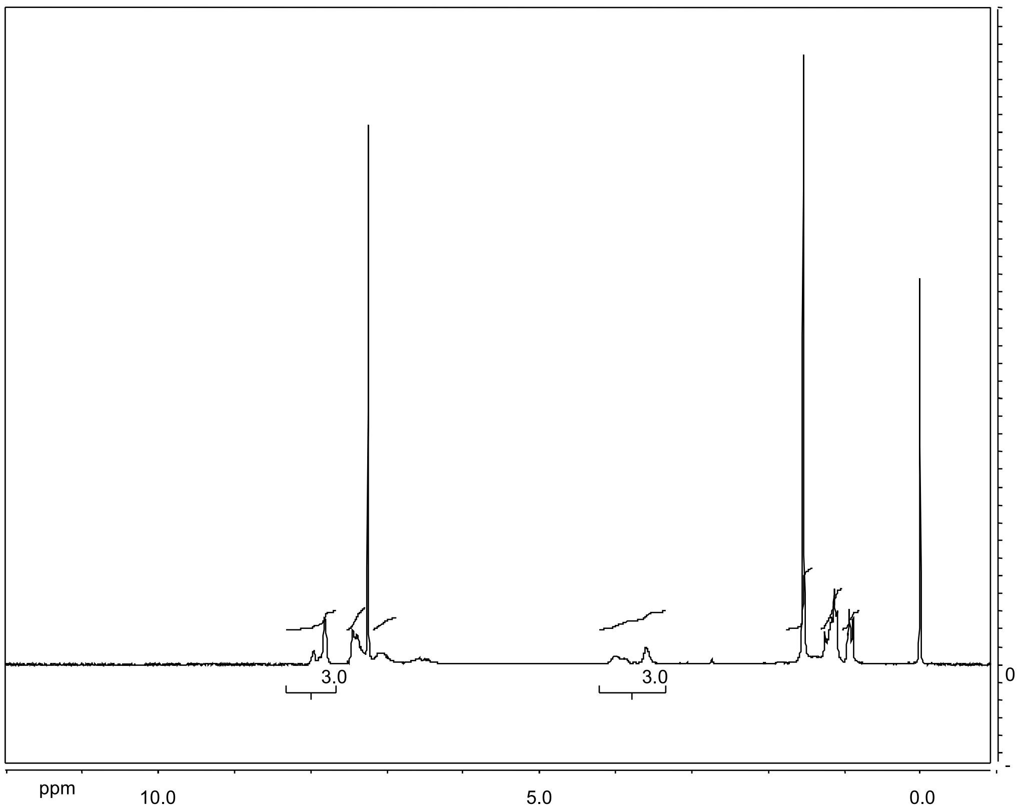
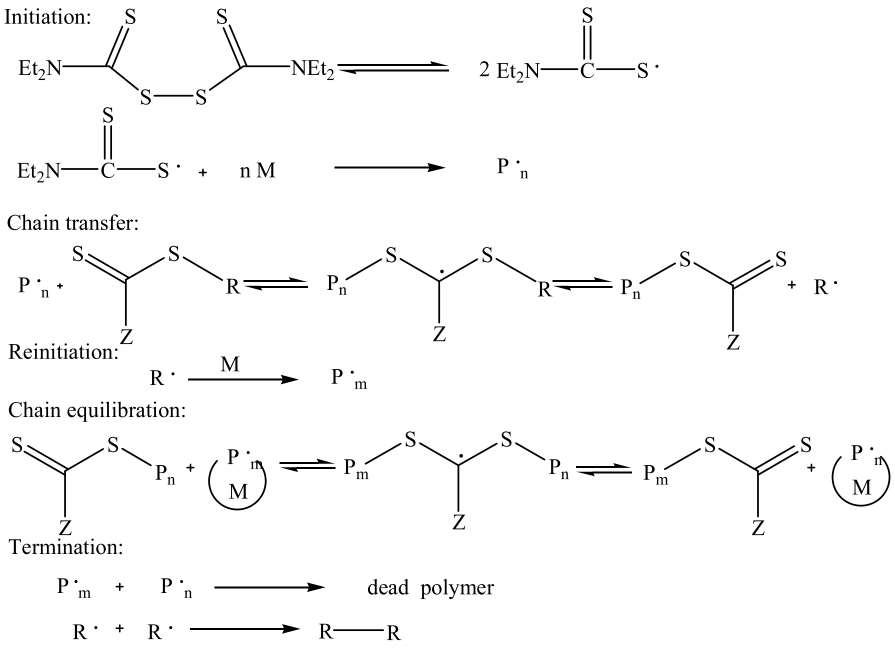


Fig. 3. ^1H NMR spectra of PSt-D, $[St\text{-}D]_0/[CPDN]_0/[TETD]_0=300:3:1$, 60 °C.



Scheme 3. Mechanism of the RAFT polymerization of styrene initiated by TETD using CPDN as the chain transfer agent.

3.2. Influence of the polymerization temperature and the ratio of CPDN to TETD

RAFT polymerizations of styrene were performed using CPDN as a RAFT agent and TETD as an initiator at different temperatures and the results were shown in Figs. 5 and 6. As shown in Fig. 5, the rate of polymerization increased obviously with the temperature. The kinetic plots of ln($[M]_0/[M]$) versus time were all linear. The molecular weights were close to the theoretical values. The molecular weight distributions at 60 °C were narrower than those at 70 and 80 °C. These results revealed that the increase of temperature could accelerate the rate of the RAFT polymerization of styrene, but the side reactions also increased.

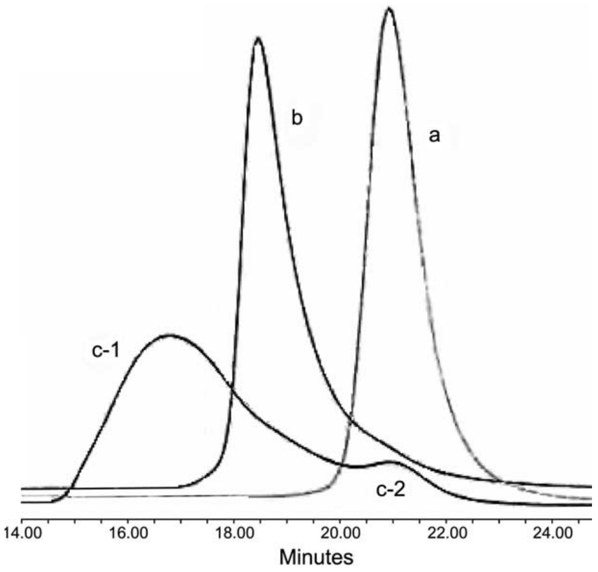


Fig. 4. GPC curves of chain-extensions initiated via thermal and UV irradiation. (a) PSt, $M_n=8400$, PDI = 1.10, 15.0%, 9 h, 70 °C; (b) thermo-initiated chain extension, $M_n=24{,}600$, PDI = 1.32, 46.6%, 48 h, 70 °C; (c) UV radiation initiated chain extension, c-1, $M_n=62{,}700$, PDI = 2.53; c-2, $M_n=8300$, PDI = 1.09, 51.2%, 39 h.

According to the RAFT polymerization mechanism, the different ratios of CPDN to TETD have a great effect on the control of polymerization. As shown in Table 2, molecular weights decreased significantly and the rate of the polymerization was decelerated as increasing the concentration of RAFT agent in the polymerization system, while the values of polydispersity remained at low values (<1.3).

The results shown in Fig. 7 indicated that the initiator concentration had no obvious effect on the molecular weight in current researched polymerization system. The ratios of

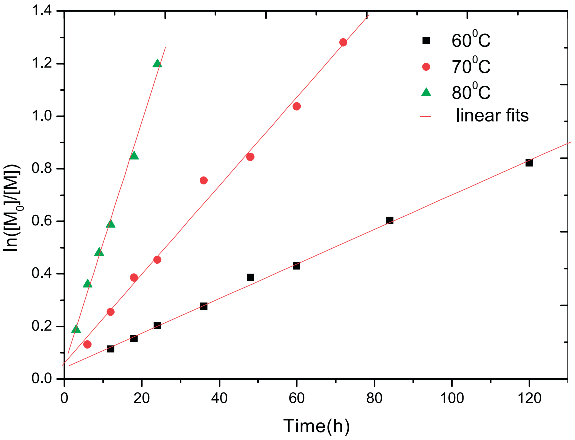


Fig. 5. Kinetic plots of RAFT polymerization of styrene at different temperatures ($[St]_0/[CPDN]_0/[TETD]_0=1000{:}3{:}1$).

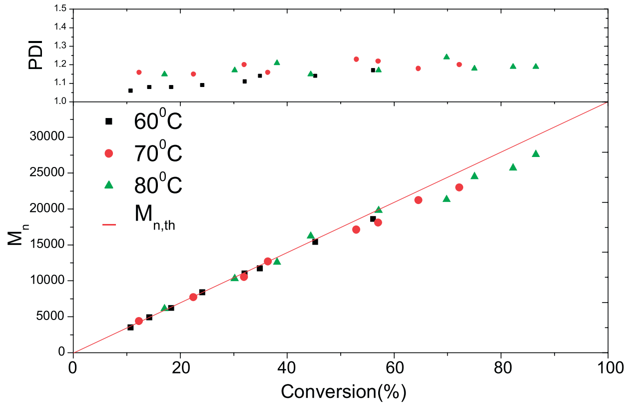


Fig. 6. M_n and PDI vs. monomer conversion of RAFT polymerization of styrene at different temperatures ($[St]_0/[CPDN]_0/[TETD]_0 = 1000:3:1$).

Table 2
The results of RAFT polymerization of styrene at different molar ratios of CPDN to TETD at 70 °C, 60 h, $[TETD]_0 = 8.77$ mmol/L

$[CPDN]_0$/ $[TETD]_0$	$M_{n,GPC}$	$M_{n,th}$	Conv (%)	PDI
1:1	61,300	74,200	71	1.49
1.5:1	31,600	48,100	69	1.31
2:1	30,800	35,600	68	1.19
3:1	21,200	22,700	65	1.18

CPDN to TETD ranging from 4:1 to 4:4, the measured molecular weights were rather close to the theoretical values and the molecular weights increased linearly with conversion in all experimented cases.

4. Conclusion

The polymerizations of styrene in bulk were conducted in the presence of CPDN and TETD. The results indicated that the polymerizations were undertaken via RAFT polymerization mechanism and TETD acted as an initiator. The polymerizations exhibited controlled polymerization characters: molecular weights increasing linearly with conversion and closed to the theoretical values, polymers prepared had narrow polydispersities (<1.3). This polymerization could be well controlled in $[CPDN]_0/[TETD]_0$ ratios of 2:1 or 3:1. 98.2% polymer chain was end-functionalized by dithiocarbonyl group and about 75% polymer chain contained TETD moiety in the end according to the ^{1}H NMR spectrum. The obtained polymers could be chain-extended both in the conventional RAFT way and under UV light irradiation.

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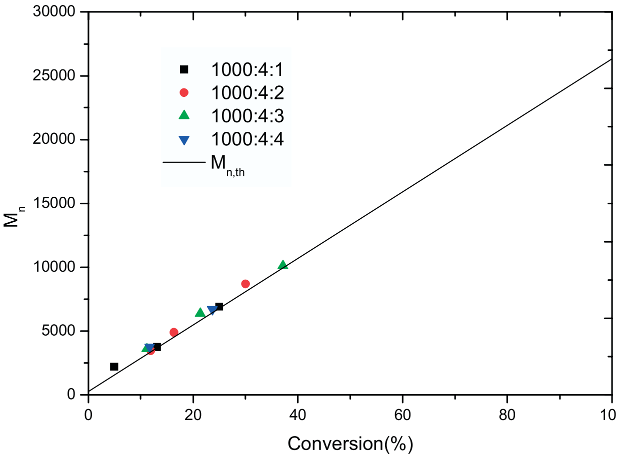

Fig. 7. M_n vs. monomer conversion of RAFT polymerization of styrene at different concentrations of TETD ($[St]_0/[CPDN]_0 = 1000:4$).

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