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Living free radical polymerization of styrene with 2-cyanoprop-2-yl dithionaphthalate as RAFT agent

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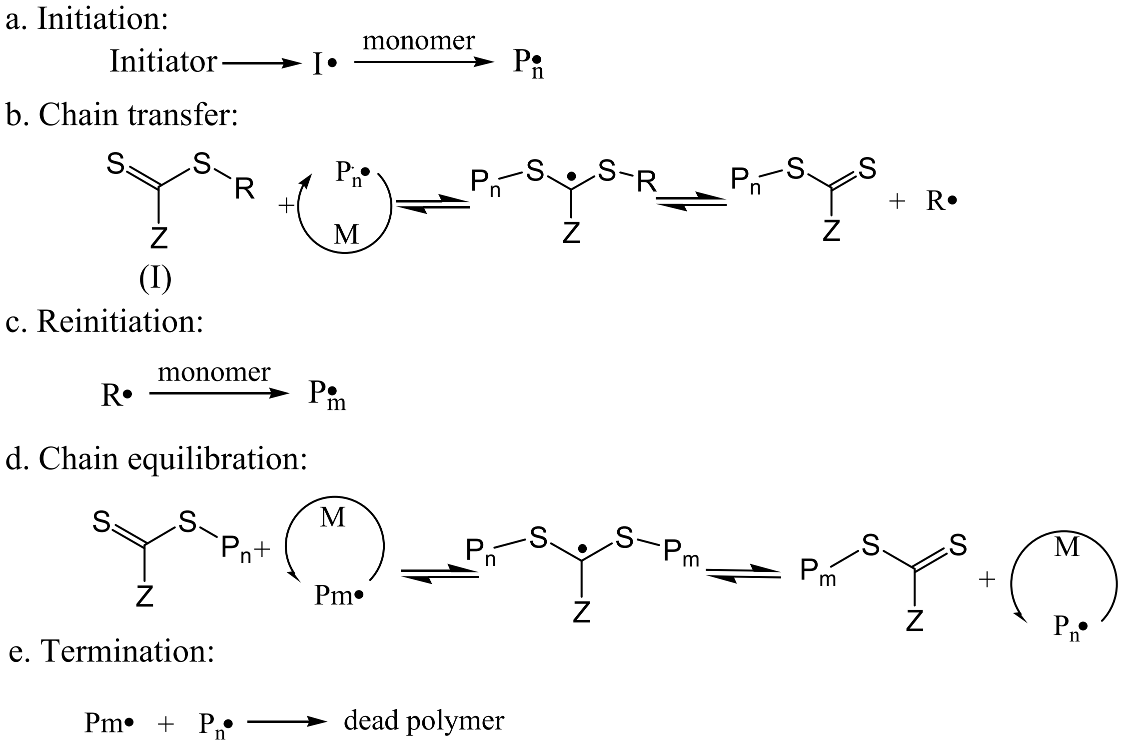
Abstract: The reversible addition-fragmentation chain transfer (RAFT) bulk polymerization of styrene was studied using 2-cyanoprop-2-yl dithionaphthalate (CPDN) as RAFT agent in the presence or absence of 2,2'-azoisobutyronitrile (AIBN). The results of both thermally and AIBN-initiated styrene (St) polymerizations show that St can be polymerized in a controlled way using CPDN as RAFT agent; i.e., the polymerization rate is first order with respect to monomer concentration, and molecular weight increases linearly with monomer conversion. The molecular weights obtained from gel permeation chromatography are close to the theoretical values and molecular weight distributions are relatively narrow (M_w/M_n < 1.2). It is confirmed by chain extension reaction that the polymer prepared via RAFT polymerization can be used as a macroRAFT agent. The effects of reaction temperature and mole ratios $[St]_0/[CPDN]_0/[AIBN]_0$ on the polymerization were investigated. The results indicate that the reaction temperature has a positive effect on the polymerization rate, but little effect on molecular weight and molecular weight distribution, and the optimum mole ratios were found to be $[CPDN]_0/[AIBN]_0 > 4/3$ and $[St]_0/[CPDN]_0 < 800$.

Introduction

In recent years, considerable effort [1-7] has been expended to develop free radical polymerizations that display the essential characteristics of living polymerizations. Several processes have been reported such as stable free radical polymerization (SFRP) [6], atom transfer radical polymerization (ATRP) [2-5], and reversible addition-fragmentation chain transfer (RAFT) [7,8]. RAFT is the youngest of these new methods, and appears as the most versatile way. The RAFT process is a polymerization in the presence of a dithio derivative, which reacts by a series of reversible addition-fragmentation steps (Scheme 1). With appropriate choice of RAFT agent and reaction conditions, RAFT polymerization can be used to produce narrow-polydispersity polymers with molecular weights predetermined by conversion and RAFT agent concentration [9-22].

Effective RAFT agents are certain thiocarbonylthio compounds (**I**, cf. Scheme 1) where Z is a group that modifies the reactivity of the thiocarbonyl group toward free radical addition and R is a free radical leaving group; moreover, $R^·$ must be reactive enough to reinitiate the polymerization efficiently [7]. The CSIRO group and others have reported that the effectiveness of RAFT agents (**I**) strongly depends on the nature of the groups Z and R, the monomer and the polymerization conditions [14-16, 23-25].



Scheme 1. Mechanism of the RAFT process

Our research group reported on the RAFT polymerization of methyl methacrylate (MMA) using 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) as chain transfer agent (CTA) [26]. The results showed that CPDN is an efficient RAFT agent in controlling free radical polymerization of MMA. In this work, we investigated RAFT bulk polymerization of St using CPDN as RAFT agent in the presence or absence of AIBN.

Experimental part

Materials

All chemicals (analytical grade) were purchased from Shanghai Chemical Reagents Co. Styrene (St) was washed with an aqueous solution of sodium hydroxide (5 wt.-%) three times and then with deionized water until neutralization. After drying with anhydrous magnesium sulfate, the monomer was distilled under reduced pressure and stored at 4°C. AIBN was recrystallized from ethanol and kept in a refrigerator at 4°C. CPDN was prepared according to the method described in ref. [26] and was purified by means of column chromatography on silica oxide with mixed petroleum ether and ethyl acetate as eluent.

^{1}H NMR (CDCl$_3$): δ = 1.95 (s, 6H); 7.42 (m, 2H); 7.51 (m, 2H); 7.85 (m, 2H) and 8.10 (m, 1H).

CPDN (C$_{15}$H$_{13}$NS$_2$)	Calc.	C 66.83	H 4.83	N 5.16
	Found	C 65.74	H 4.43	N 5.14

Other materials were used as received without further purification.

Polymerizations

RAFT polymerization of St using CPDN as RAFT agent

The polymerizations were performed as follows. A master batch of 10 mL St (87 mmol), 3.7 mg (0.022 mmol) AIBN (no AIBN in the case of thermal polymerization) and 23.6 mg (0.087 mmol) CPDN was prepared, and aliquots of 1 mL were placed in polymerization ampoules. The content was purged with argon to eliminate oxygen for approximately 10 min, and then the ampoules were flame sealed. The polymerization reaction was performed at the appropriate temperature. At the end of the reaction, each ampoule was quenched in cold water, and opened. The reaction mixture was diluted with a little tetrahydrofuran (THF), and precipitated in a large amount of methanol. The polymer was dried at room temperature in vacuum for several hours up to constant weight. Conversion of St was determined gravimetrically.

Polymerization of St using PSt as macroRAFT agent

The same procedure as for the RAFT polymerization of St was used except CPDN was substituted by polystyrene (PSt) obtained from the RAFT polymerization of St.

Characterization

The molecular weights and molecular weight distribution of the polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector, using HR 1, HR 3, and HR 4 columns with molecular weight range 100 - 500 000 calibrated with polystyrene standard samples. THF was used as the eluent at a flow rate of 1.0 mL/min operated at 30°C. ^{1}H NMR spectra of the polymers were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard.

Results and discussion

AIBN-initiated RAFT polymerization of St

The RAFT bulk polymerization of St was carried out using CPDN as RAFT agent and AIBN as an initiator. The kinetic plot of ln $[M]_0/[M]$ versus time is shown in Fig. 1. The straight line through the origin indicates that the steady state radical concentration is constant over the duration of polymerization in both of the experimented conditions. The polymerization shows that the molecular weights increase linearly with conversion and are close to the predicted values, and molecular weight distributions are relatively narrow ($M_w/M_n < 1.2$) (Fig. 2). The theoretical molecular weight is calculated via the following equation:

$$M_{n,\,calc.} = \frac{\text{monomer weight}}{\text{mole of CPDN}} \times \text{conversion} + M_{CPDN}$$

The ^{1}H NMR spectra of polymers prepared with RAFT polymerization are used to obtain qualitative and quantitative information on polymer end groups. A typical spectrum of PSt is shown in Fig. 3. The signals at $\delta = 7.4 - 8.1$ ppm correspond to the aromatic protons of CPDN units. The appearance of these signals indicates that the dithioester formed from CPDN reacted with primary or propagating radicals

(Scheme 1, b and d), and the CPDN moiety remained at the end of the polymer chain. Furthermore, we can estimate C_{PS} [27], the content of macromolecules capped with CPDN moiety in the product, on the basis of the number-average molecular weight, M_n (GPC), obtained by GPC measurement and the integral value of the peak at 7.4 - 8.1 ppm. Assuming that M_n (GPC) is the real molecular weight of polymer, the equations used are shown below:

$$C_{PS} = I_{7.4\text{-}8.1} / I'_{7.4\text{-}8.1}$$

$$I'_{7.4\text{-}8.1} = 5 \cdot 104 \cdot I_{6.2\text{-}7.3} / [5\ (M_n\ (\text{GPC}) - 271)]$$

C_{PS} of a typical polymer obtained with $[\text{St}]_0/[\text{CPDN}]_0/[\text{AIBN}]_0$ = 200:1:0.25 after 24 h polymerization at 60°C is 98%. Therefore, around 2% PSt did not contain the terminal dithionaphthalate group. This result agrees with refs. [28,29], which reported that there is less than 3% dead polymers remained in the product.

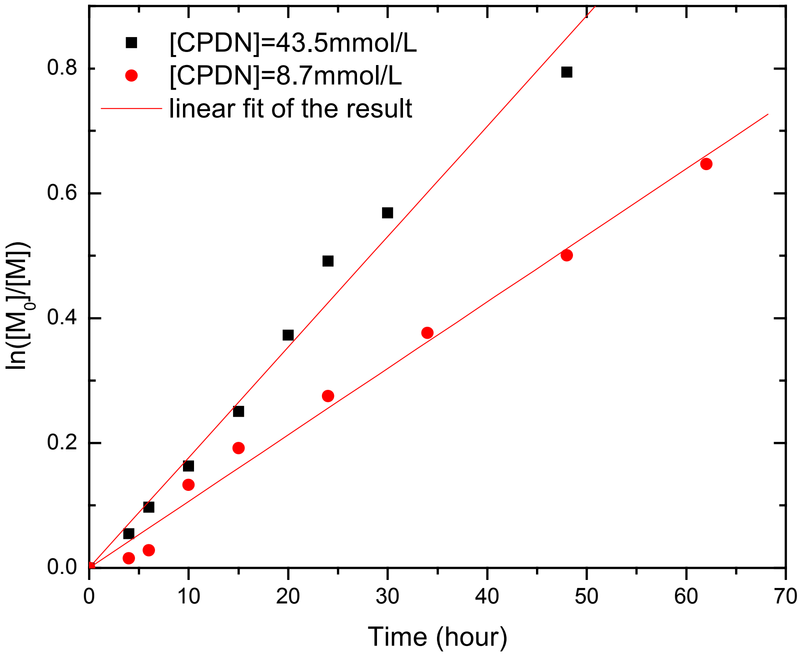


Fig. 1. Relationship of $\ln([M_0]/[M])$ versus reaction time for the polymerization of styrene with CPDN as RAFT agent and AIBN as initiator in bulk at 60°C. $[\text{St}]_0$ = 8.7 mol/L, $[\text{CPDN}]_0/[\text{AIBN}]_0$ = 4:1

The polymers obtained by the RAFT process have the moiety of CPDN in the end, which can be chain-extended. This chain extension was carried out using PSt as a macroRAFT agent and AIBN as initiator at 60°C. The results are shown in Fig. 4. The molecular weight of the original polymer increased from 9700 to 21 400 and 24 700 after 12 h and 24 h, respectively. There is an obvious peak shift from the original polymer to the chain extension products in Fig. 4. The peak of the original polymer disappears thoroughly, which indicates that the original polymers are fully reacted into new polymers in the chain extension reaction. On the other hand, the molecular weight distributions (M_w/M_n = 1.18 and 1.22) of the chain extension products are a little larger than of the original polymer (M_w/M_n = 1.12). This may be caused by the little portion of homopolymerization of St initiated by AIBN and the dead polymer that existed in the original polymer (macroRAFT agent), which was discussed above. On the other hand, there is a second shoulder appearing in the high molar mass domains in the last GPC trace (C, 24 h) in Fig. 4. This may be due to a combination between chains. Therefore, we are very confident that most of the chains are still living at the end of the polymerization.

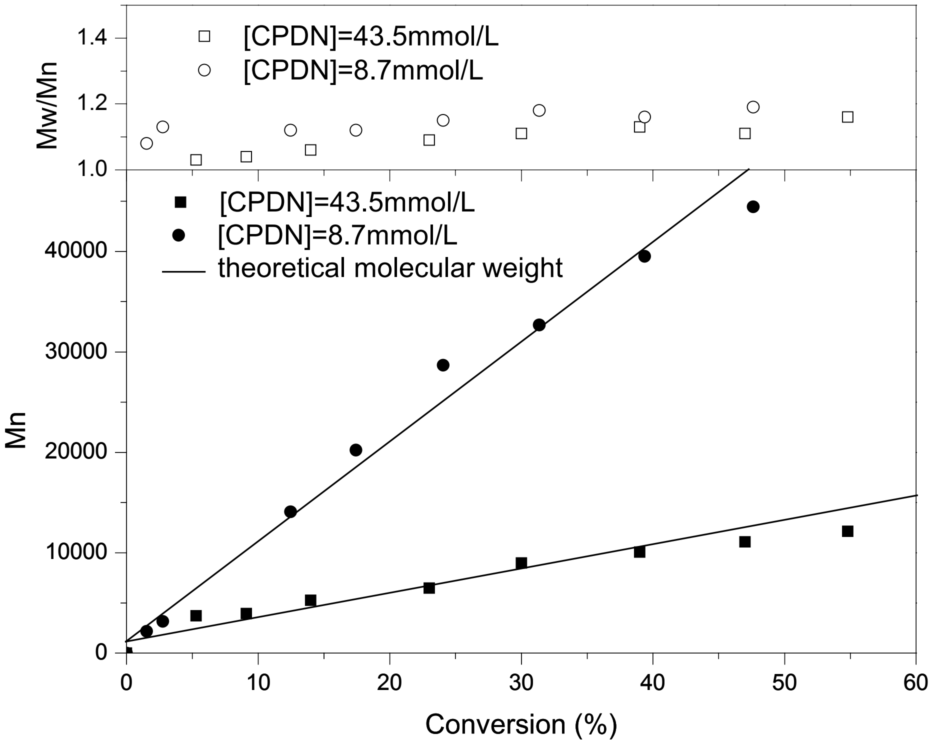


Fig. 2. Relationships of molecular weight and molecular weight distribution versus conversion for the polymerization of styrene. Experimental conditions are the same as in Fig. 1

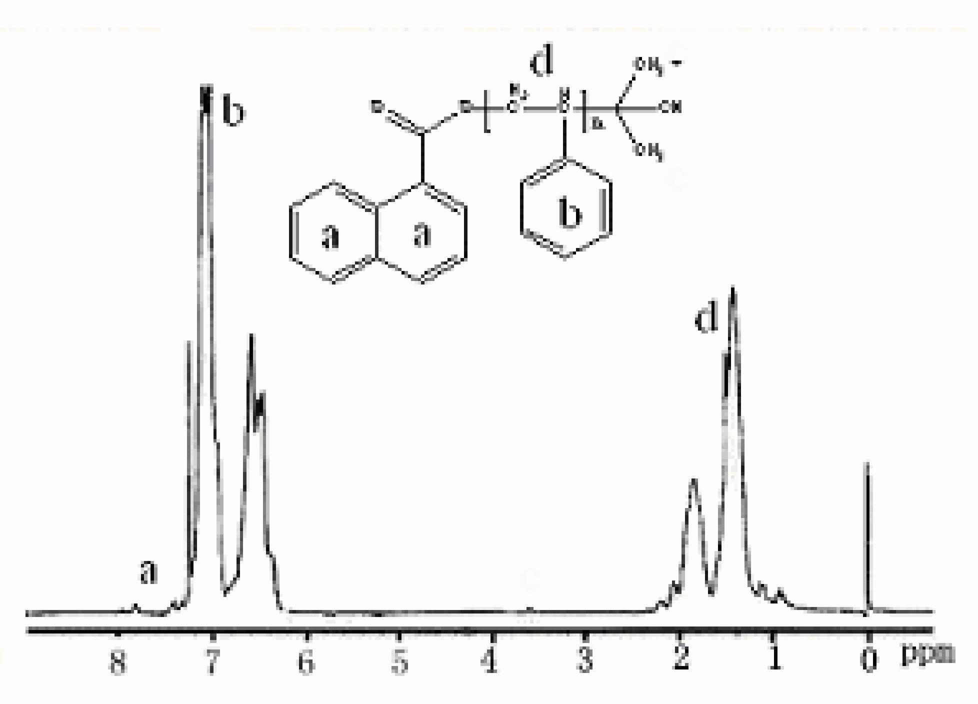


Fig. 3. ^{1}H NMR of PSt using CDCl$_3$ as solvent and tetramethylsilane as the internal standard. ([St]$_0$/[CPDN]$_0$/[AIBN]$_0$ = 200:1:0.25, 30 h, 60°C, M_n = 9700, M_w/M_n = 1.12)

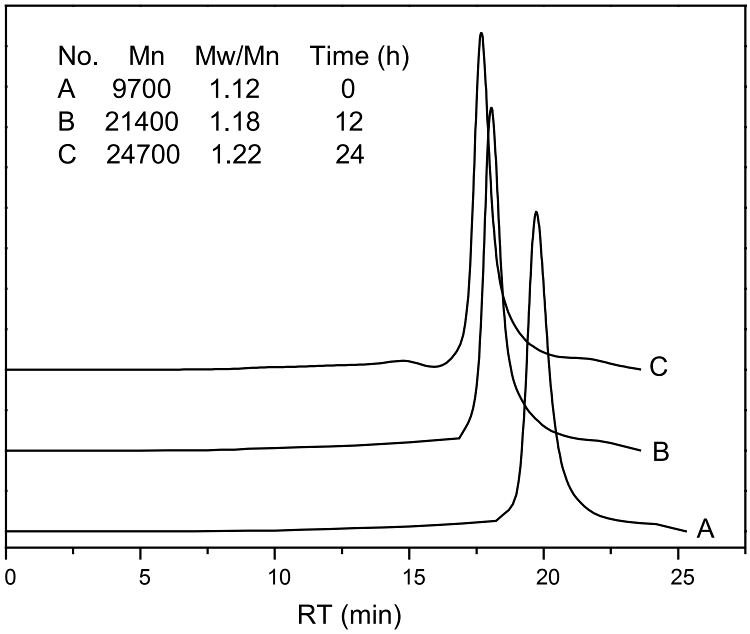


Fig. 4. GPC curves for the chain extension of PSt used as macroRAFT agent. A: original polymer, B: after 12 h, C: after 24 h, $[St]_0 = 8.7$ mol/L, in bulk at 60°C, $[\text{macro-CPDN}]_0 = 8.7 \cdot 10^{-3}$ mol/L, $[\text{AIBN}]_0 = 2.18 \cdot 10^{-3}$ mol/L

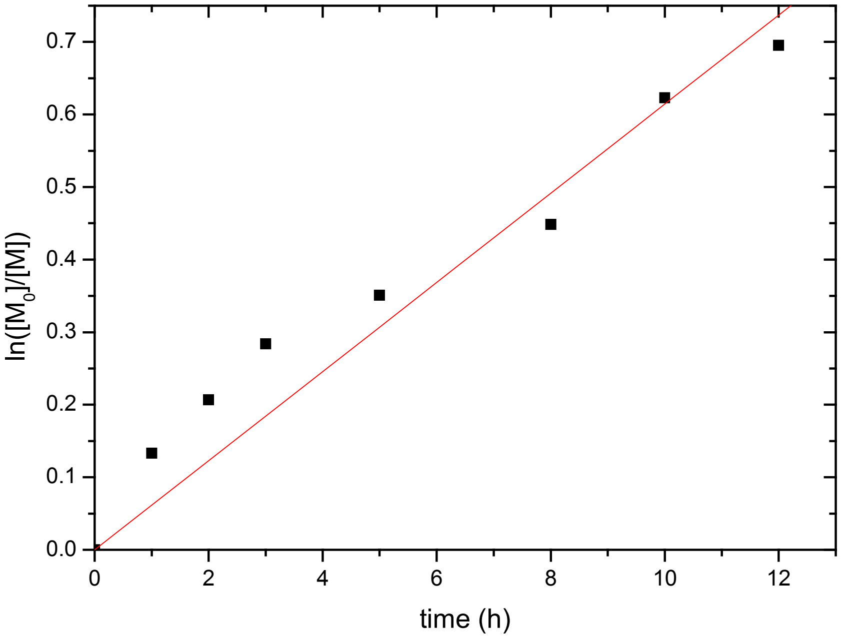


Fig. 5. Relationship of $\ln([M_0]/[M])$ versus reaction time for the thermally initiated RAFT polymerization of St with CPDN as RAFT agent in bulk at 100°C. $[St]_0 = 8.7$ mol/L, $[\text{CPDN}]_0 = 4.35 \cdot 10^{-2}$ mol/L

Thermally initiated RAFT polymerizations of St

The thermally initiated RAFT polymerization of St was performed at 100°C using CPDN as RAFT agent. The results are shown in Figs. 5 and 6. A linear relationship between $\ln([M_0]/[M])$ and the reaction time is observed in Fig. 5. Fig. 6 shows the linear evolution of molecular weight with conversion. The molecular weights obtained by GPC are larger than the predicted values, but the molecular weight distributions are relatively narrow (M_w/M_n = 1.1). These results show that CPDN is an effective RAFT agent for the thermally initiated RAFT polymerization of St. However, both the kinetics and molar mass evolution shown in Figs. 5 and 6 indicate a particular behaviour compared to the AIBN-initiated polymerization, e.g., a relatively high polymerization rate at the beginning and also that the average molecular weights are larger than expected. This may be caused by some non-controlled polymers formed at the beginning [23,24].

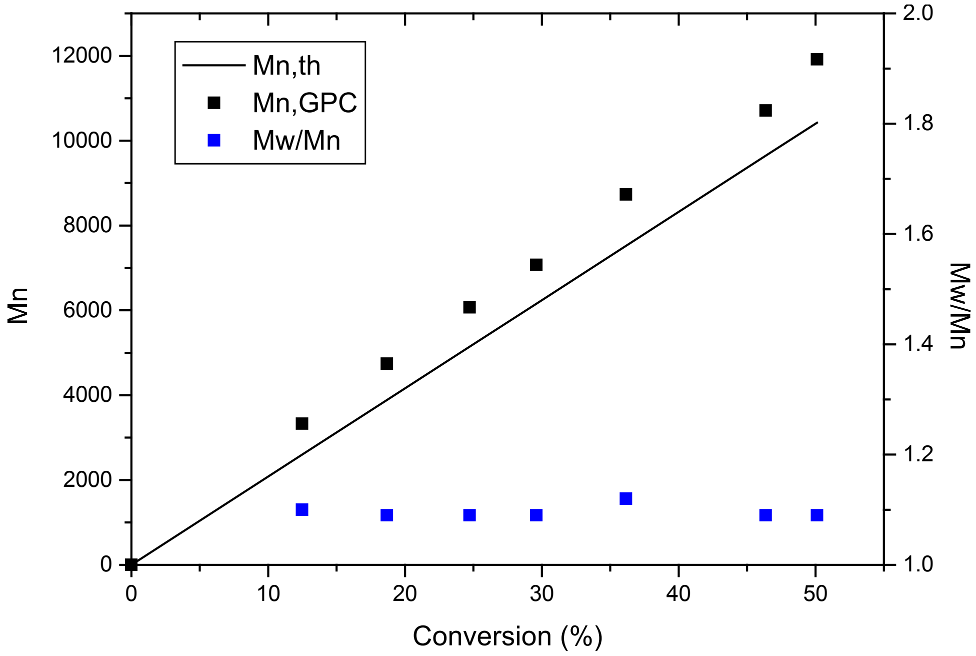


Fig. 6. Relationships of molecular weight and molecular weight distribution vs. conversion for the polymerization of styrene. Exptl. conditions were the same as in Fig. 5

Influence of the CPDN/AIBN ratio

The kinetic plots of the RAFT polymerization at different ratios of CPDN/AIBN are shown in Fig. 7. Examination of the data revealed that the polymerization rate at a CPDN/AIBN ratio of 4/1 is significantly slower than that performed at a CPDN/AIBN ratio of 4/3 or 1/1. This is, of course, attributed to the increased probability of generated radicals to react with RAFT agent or macroRAFT agent rather than monomer. The linear relationships between number-average molecular weight and conversion are shown in Fig. 8. The value of M_w/M_n is small at high ratio of CPDN/AIBN (M_w/M_n < 1.17 at CPDN/AIBN = 4:1), and increases with decreasing ratio of CPDN/AIBN (M_w/M_n < 1.28 at CPDN/AIBN = 4:3 and < 1.36 at CPDN/AIBN = 1:1). The result suggests that the mole ratio of CPDN/AIBN should be higher than 4/3 for a better control of the radical polymerization of St using CPDN as RAFT agent. However, the molecular weight distribution of the resulting polymer increases from relatively low values (M_w/M_n = 1.03, 1.05 and 1.09) to higher values (M_w/M_n = 1.16, 1.27 and 1.30) in the course of conversion from 2.5, 8.1 and 16.1% to 59.3, 68.3 and 69.3, respectively. Laus et al. reported the same results found for the RAFT polymerization of styrene using phosphoryl dithioester as the RAFT agent [15] and de Brouwer et al. found the same behaviour in the emulsion RAFT polymerization of many monomers [19]. The reason may be due to the portion of unexpected termination accumulated to a higher level with increasing conversion. At the same time, the viscosity of the reaction system will be high at higher conversion, which is obviously unfavourable to the activation and deactivation equilibrium eventually resulting in more side reactions.

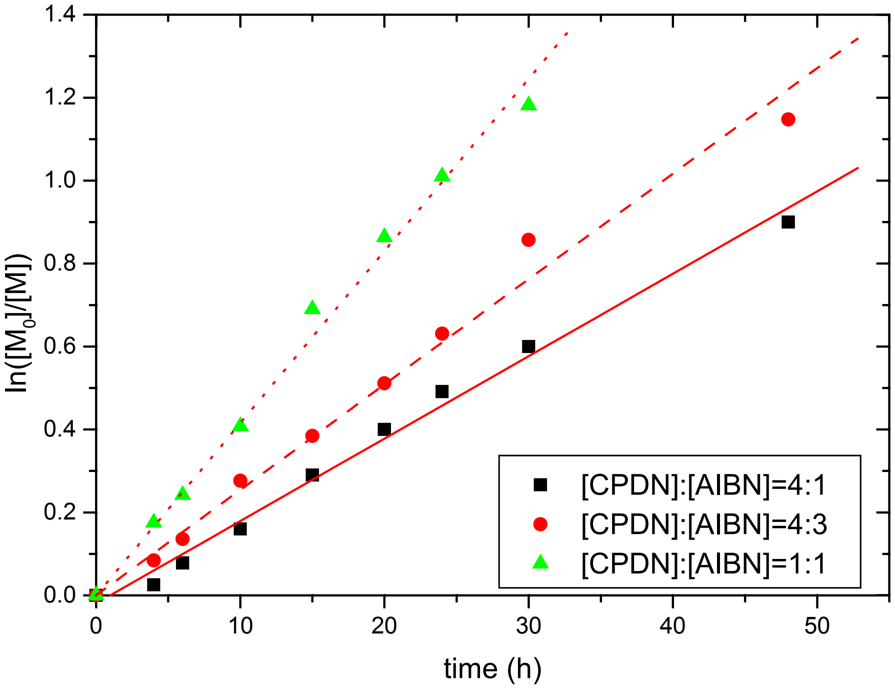


Fig. 7. Relationships of ln([M$_0$]/[M]) versus reaction time for the polymerization of St with CPDN as RAFT agent and AIBN as initiator in bulk at 60°C. $[St]_0$ = 8.7 mol/L, $[CPDN]_0 = 4.35 \cdot 10^{-2}$ mol/L

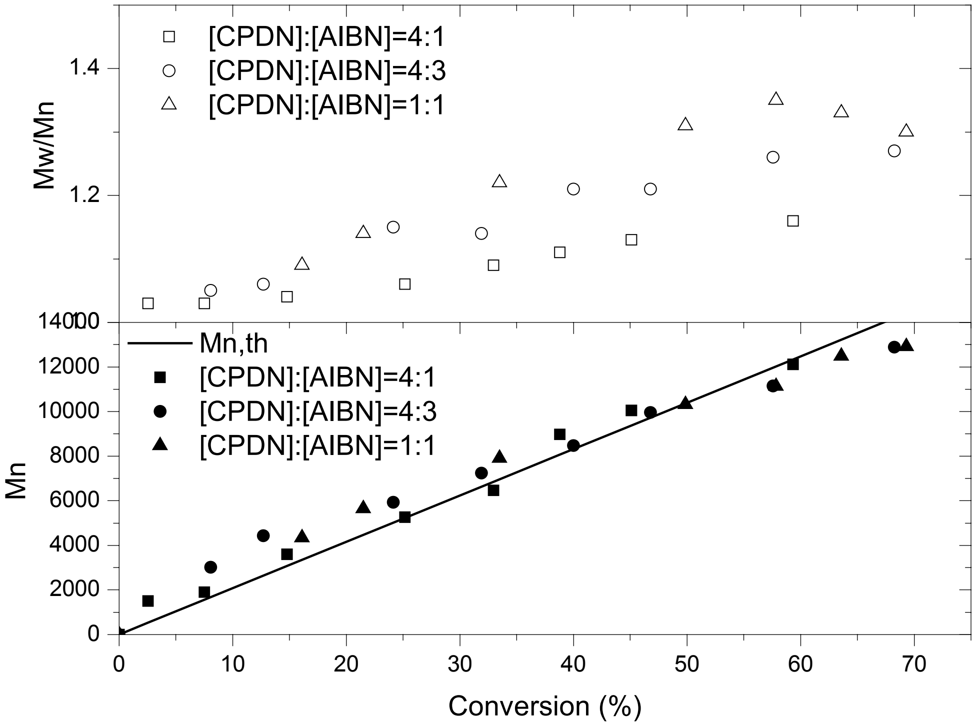


Fig. 8. Relationships of molecular weight and molecular weight distribution vs. conversion for the polymerization of styrene. Exptl. conditions were the same as in Fig. 7

Influence of the St/CPDN ratio

The effects of different ratios of St/CPDN on polymerization were studied. The results are listed in Tab. 1, which shows that the polymerizations in all entries were conducted in a controlled way by RAFT polymerization. However, with increasing the mole ratio of $[St]_0/[CPDN]_0$, the molecular weight distribution increases and the polymerization rate decreases. The concentration of radicals would decrease as the ratio of $[St]_0/[CPDN]_0$ increased, therefore this resulted in a low polymerization rate, e.g., conversion decreased from 56.3 to 46.9% after 48 h polymerization at 60°C with the mole ratio of $[St]_0/[CPDN]_0$ increasing from 300:1 to 1000:1. At the same time, the molecular weight distribution increased from 1.17 to 1.34 as the mole ratio of $[St]_0/[CPDN]_0$ increased from 300:1 to 1000:1, which may be caused by more side reactions as a result of the decreasing concentration $[CPDN]_0$. These results show that in order to successfully carry out the RAFT polymerization of St with CPDN as RAFT agent and AIBN as initiator, the suitable ratio of $[St]_0/[CPDN]_0$ should be smaller than 800:1.

Tab. 1. Data from the RAFT polymerization of St at different ratios of $[St]_0/[CPDN]_0$ at 60°C, $[St]_0$ = 8.7 mol/L, time = 48 h

Entry	$[St]_0/[CPDN]_0/[AIBN]_0$	M_n (GPC)	M_n (calc.)	M_w/M_n	Conversion in %
11	300 : 1 : 0.5	17 140	17 591	1.17	56.3
12	500 : 1 : 0.5	24 740	25 838	1.16	49.7
13	800 : 1 : 0.5	33 100	39 836	1.29	47.9
14	1000 : 1 : 0.5	38 000	48 786	1.34	46.9

Tab. 2. Data from the RAFT polymerization of St at different temperatures, $[St]_0/[CPDN]_0/[AIBN]_0$ = 200 : 1 : 0.25

Entry	Temp. in °C	Time in h	Conv. in %	M_n (calc.)	M_n (GPC)	M_w/M_n
21	60	6	7.5	1833	1900	1.03
22	60	10	14.8	3345	3600	1.04
23	60	24	38.8	8343	8900	1.11
24	80	1	18.8	4195	4300	1.12
25	80	6	34.1	7351	7600	1.16
26	80	10	42.3	9069	9100	1.13
27	100	1	27.8	5799	6300	1.11
28	100	3	40.2	8380	8400	1.16
29	100	6	60.7	10 955	10 900	1.14

Influence of reaction temperature

The influence of the reaction temperature on the RAFT polymerization of St was studied. The results are listed in Tab. 2. The results indicate that the reaction temperature has a positive effect on the polymerization rate, and that the conversion increases with the reaction temperature, indicating a faster rate of polymerization at higher reaction temperature. The reaction temperature has little effect on molecular weight and molecular weight distribution.

Conclusions

CPDN was employed in the controlled radical polymerization of St. Thermally initiated and AIBN-initiated RAFT polymerizations of St were conducted. Both in the thermally initiated and AIBN-initiated systems, the molar mass increased linearly with time as expected for a controlled polymerization process; molecular weight progressively increased with time, and the molecular weight distributions were narrow ($M_w/M_n < 1.2$). Obtained PSt was successfully used as a macroRAFT agent to carry out a chain extension reaction with freshly added St, which confirmed the ‘living’/controlled nature of the polymerization system. The molecular weight distributions of the chain extension polymers were a bit broader than of the original polymer. The reason is attributed to the dead polymer remained in the macroRAFT agent and a portion of homopolymerization caused by AIBN initiation. The dead polymer fraction, which does not contain CPDN moiety in the end, is calculated as about 2% by comparing molecular weights obtained by ^{1}H NMR and GPC. The mole ratios of $[St]_0/[CPDN]_0/[AIBN]_0$ have an effect on the polymerization. The suitable mole ratios are $[CPDN]_0/[AIBN]_0 > 4:3$ and $[St]_0/[CPDN]_0 < 800:1$. Within the reaction temperature range of 60 to 100°C, the AIBN-initiated polymerization rate of St increases with increasing reaction temperature, however, the reaction temperature has little effect on molecular weight and molecular weight distribution.

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