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Thermal polymerization of methyl (meth)acrylate via reversible addition-fragmentation chain transfer (RAFT) process

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Abstract

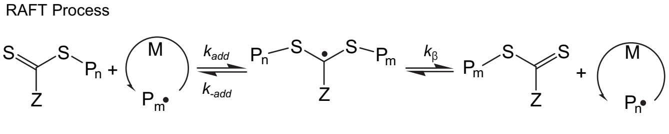
Thermal polymerization of methyl (meth)acrylate (MMA) was carried out using 2-cyanoprop-2-yl-1-dithionaphthalate (CPDN) and cumyl dithionaphthalenoate (CDN) as chain transfer agents. The kinetic study showed the existence of induction period and rate retardation, especially in the CDN mediated systems. The molecular weights of the polymers increased linearly with the monomer conversion, and the molecular weight distributions (M_w/M_ns) of the polymers were relatively narrow up to high conversions. The maximum number-average molecular weights (M_ns) reached to 351 900 g/mol ($M_w/M_n = 1.47$) and 442 400 g/mol ($M_w/M_n = 1.29$) in the systems mediated by CPDN and CDN, respectively. Chain-extension reactions were also successfully carried out to obtain higher molecular weight PMMA and PMMA-*block*-polystyrene (PMMA-*b*-PSt) copolymer with controlled structure and narrow M_w/M_n. Thermal polymerization of methyl acrylate (MA) in the presence of CPDN, or benzyl (2-phenyl)-1-imidazolecarbodithioate (BPIC) also demonstrated "living"/controlled features with the experimented maximum molecular weight 312 500 g/mol ($M_w/M_n = 1.57$). The possible initiation mechanism of the thermal polymerization was discussed.

Keywords: Thermal polymerization; Methyl (meth)acrylate; Reversible addition-fragmentation chain transfer (RAFT)

1. Introduction

The reversible addition-fragmentation chain transfer (RAFT) polymerization [1], together with other equally important "living"/controlled radical polymerization (LRP) techniques, such as nitroxide mediated polymerization (NMP) [2] and atom transfer radical polymerization (ATRP) [3], has received great attention because of its versatility in producing complex macromolecular architectures with narrow molecular weight distributions (M_w/M_ns) and controlled molecular weights. In general, LRP provided the polymers with controlled molecular weights and very narrow M_w/M_ns. However, number-average molecular weight of 200 000 g/mol may represent an upper limit for typical monomers [2–5], which prohibited further industrial application of polymers synthesized by LRP. As for RAFT polymerization, some researchers [6,7] demonstrated the RAFT polymerization of MMA under very high hydrostatic pressures (in the 1–10 kbar range), the polymers with very high molecular weights (1.25×10^6 g/mol) can be obtained, but the operation with very high pressure was limited for practical applications.

The RAFT process proceeds by a mechanism in which two equilibria (Scheme 1) are superimposed on the conventional radical polymerization scheme with all the elementary steps [8], i.e., initiation, propagation, and termination. The repeated reversible transfer events of the RAFT agents, e.g., dithioesters, during the polymerization induce equilibria between the dormant and living chains, which result in the living/controlled behavior of the polymerization.



Scheme 1. Mechanism of RAFT process.

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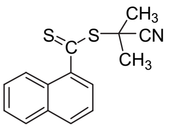
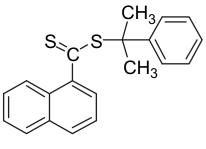
RAFT polymerization is usually carried out with conventional radical initiators. In principle, any source of free radicals can be used [9], but most often thermal initiators, e.g., 2,2′-azobisisobutyronitrile (AIBN), potassium persulfate (KPS) are used [10]. RAFT polymerization of styrene may be initiated thermally between 100 °C and 120 °C. UV irradiation [11], γ-source [12] and plasma initiation [13] have also been reported in RAFT polymerization. Unlike ATRP, the theoretical number-average molecular weight ($M_{n,th}$) is determined by the concentration ratio of the monomer to the initiator ($[M]_0/[I]_0$); the determining factor for the molecular weight in RAFT polymerization is the concentration ratio of the monomer and the RAFT agent [14]. According to RAFT polymerization mechanism, the concentration of the transfer agent is usually higher than that of initiator to ensure good controllability over the molecular weight through addition-fragmentation reactions [14].

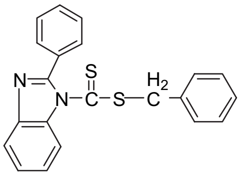
Up to the present, investigations of thermal polymerization have been almost entirely restricted to styrene. Since the rate of the thermal polymerization of MMA is sometimes too low to be taken into consideration, the living radical polymerization of MMA was usually initiated by initiators, such as alkyl halides [15–18] in ATRP, peroxides in reverse ATRP [19], alkoxyamines in NMP [20] and AIBN in RAFT polymerization [1,21,22]. However, it has been reported by several authors that MMA can homopolymerize at elevated temperatures to a significant extent without any additional initiator, irrespective of the care taken for purity of the MMA [23]. It is widely accepted that the thermal polymerization of methyl (meth)acrylate proceeds via a radical mechanism at relatively low rates, whereas, the mechanism of this kind of initiation is unsolved and still under investigation [24]. To our best knowledge, the thermal polymerization of methyl (meth)acrylate has not been reported in the field of living radical polymerization. It can be expected that in the thermal polymerization of methyl (meth)acrylate via RAFT process, the concentration of initiator radical, notwithstanding the unknown structure, is extremely low, polymerization can be well controlled with a low concentration of RAFT agent yielding polymer with high molecular weights, furthermore, the molecular weights can be controlled and predicted. This paper first focused on the utility of the RAFT methodology in the thermal polymerization of methyl (meth)acrylate systems to perform living polymerizations in order to obtain polymers with high molecular weights and narrow M_w/M_ns. The RAFT agents used were CPDN, CDN and BPIC, which had been confirmed in our lab as efficient RAFT agents for the polymerization of alkyl (meth)acrylate [25] and styrene [26].



CPDN



CDN



BPIC

2. Experimental part

2.1. Materials

The monomers, MMA (>99%) and St (>99%), were purchased from Shanghai Chemical Reagents Co. (Shanghai, China). They were washed with an aqueous solution of sodium hydroxide (5 wt%) three times, followed by deionized water until neutralization, and then dried over anhydrous magnesium sulfate. They were distilled twice under reduced pressure and stored at −18 °C. AIBN (97%, Shanghai Chemical Reagents Co.) was recrystallized from ethanol and dried at room temperature under vacuum and stored at 4 °C. Tetrahydrofuran (THF, analytical reagent) was obtained from Yangyuan Chemical Reagents Co. (Suzhou, China). BPIC was obtained according to the literature [27] as a yellow powder, and the purity was greater than 98% (HPLC). CPDN was synthesized according to the method reported in Ref. [25] with purity greater than 94%. CDN (96%) was prepared using a procedure similar to the one for CDB described elsewhere [28]. All other chemicals (reagent or analytical grade) were obtained from Shanghai Chemical Reagents Co. and used as received.

2.2. Characterization

M_ns and M_w/M_ns of the polymers were determined using Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector, using HR 1, HR 2, and HR 4 columns with molecular weights ranged 10^2–5×10^5 g/mol, HR 4, HR 5, and HR 6 columns with molecular weights ranged 5×10^3–10^7 g/mol. The columns were calibrated with PMMA standard samples. THF was used as an eluent at a flow rate of 1.0 mL/min and at 30 °C. ^{1}H NMR spectra of the precipitated polymers were recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard.

2.3. Thermal polymerization of MMA (MA) in the presence of RAFT agent

A typical polymerization procedure is as follows: a solution of MMA (MA) and RAFT agent (prescribed molar ratio) was added to a dried ampoule, the content was deoxygenated by bubbling argon for 20 min, then the ampoule was flame sealed and placed in an oil bath held by a thermostat at the desired temperature to polymerize. After the desired polymerization time, the ampoule was cooled by immersing it into icewater. Afterwards, it was opened and the contents were dissolved in THF and precipitated into a large amount of methanol. The polymer obtained as filtrate was dried under vacuum until a constant weight at room temperature. The monomer conversion was determined gravimetrically.

2.4. Chain extension of PMMA (PMA) with MMA or MA using thermal polymerization

A predetermined quantity of PMMA, obtained by thermal polymerization of MMA by RAFT process, was dissolved in predetermined quantity of MMA. The rest of the procedure was the same as described above, except that the RAFT agent was replaced by the PMMA synthesized above.

2.5. St–MMA copolymerization using PMMA as macroRAFT agent

A mixture of St, AIBN and PMMA, with predetermined concentration, was added to a 2 mL ampoule. The temperature was stabilized at 70 °C. The other procedures were the same as the RAFT polymerization of MMA described above.

3. Results and discussion

3.1. Thermal polymerization of MMA in the presence of RAFT agents

Thermal polymerizations of MMA were carried out using CPDN and CDN as the RAFT agents without the addition of any thermal- or photo-initiator. One of the purposes of this work is to obtain well-defined PMMAs with high molecular weights (>200 000 g/mol) and narrow M_w/M_ns. Thus, the RAFT agent was added at a low level concentration. In this work, the minimum concentration of the RAFT agent was reduced to 0.0016 M, hereby, the maximum theoretical molecular weight was about 600 000 g/mol. Kinetic plots of the thermal polymerization of MMA at 80 °C are shown in Fig. 1. The results showed that the polymerization rates were very slow in most of the experimented cases. The plots also uniformly showed acceleration in the polymerization rate after the conversion was higher than a level. As for the "living"/controlled radical polymerization, some researchers have demonstrated that the kinetics plots have shown acceleration instead of pseudo first-order plots because of the slow initiation of the initiator [29]. In our work, the acceleration was probably due to the slow initiation in thermal polymerization at a relatively low temperature. Another reason was probably the gel (or Trommsdorf) effect that occurred in the RAFT polymerization [4,5,10]. It can also be seen that the polymerization rates at the beginning stage did not change remarkably with the concentration of CPDN switching from 0.0063 M to 0.0016 M. While, the starting time of rate acceleration in the case of $[\mathrm{CPDN}]_0 = 0.0016$ M was earlier than that in the case of $[\mathrm{CPDN}]_0 = 0.0063$ M, which might be owing to the molecular weight of the polymer obtained at the low concentration of CPDN (0.0016 M) was much higher than that at high concentration of CPDN (0.0063 M) with the same conversion, resulting in the prior emergence of gel effect in the low concentration of CPDN (0.0016 M) [13]. However, in the case of the CDN, polymerization rate was dramatically enhanced with the concentration of CDN reducing from 0.0063 M to 0.0016 M. Similar retardation effects were reported in literatures [30–33] and there is currently vigorous debate on the causes of the retardation phenomena [10,28]. In our present work, CPDN with 2-cyanoprop-2-yl($^{\bullet}C(CH_3)_2CN$) as R group had much less retardation than CDN with cumyl($^{\bullet}C(CH_3)_2Ph$) as R group holding the same Z group (naphthyl) in both RAFT agents. This observation was consistent with the literatures [5,10,34], which reported that substantial retardation was observed with cumyl dithiobenzoate as the RAFT agent, while the retardation was absent or diminished with 2-cyanoprop-2-yl-dithiobenzoate as the RAFT agent in the MMA polymerization [35]. The discrepancy between the two R groups could be attributed to the very high reactivity of cumyl radicals towards the RAFT agent, i.e. the rate constant ($k_{-\beta}$) for $^{\bullet}C(CH_3)_2Ph$ was higher than that for $^{\bullet}C(CH_3)_2CN$. An obvious inhibition period of about several hours was also observed from Fig. 1, especially in the CDN mediated polymerizations. Some authors had reported an inhibition effect observed in certain RAFT-mediated polymerizations. The inhibition period corresponds to the time taken to convert the RAFT agent into the polymeric RAFT agent [36]. In our work, the inhibition period was likely due to the slow initiation in thermal polymerization of MMA, which would take much more time to consume the RAFT agent, especially at low temperature [23,24,37]. The prolonged inhibition period in the case of CDN might also be on account of the facile back reaction of the cumyl radical with the RAFT agent [10].

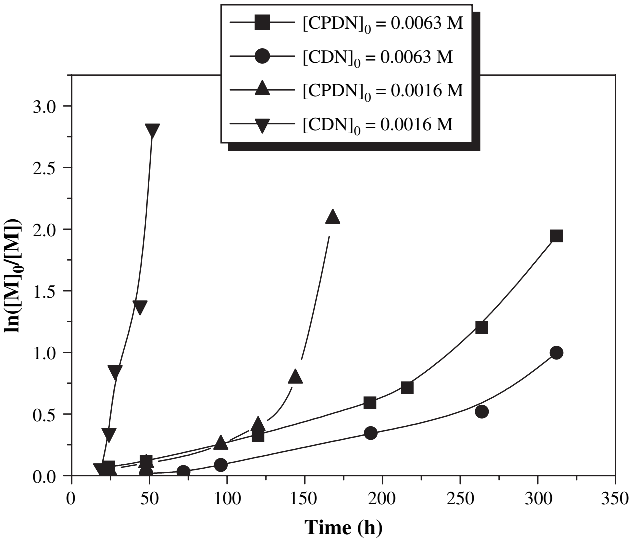


Fig. 1. Dependence of $\ln([M]_0/[M])$ on polymerization time in bulk; $[\mathrm{MMA}]_0 = 9.40$ mol/L, $[\mathrm{RAFT\ agent}]_0 = 0.0063$ M, 0.0016 M, 80 °C.

The living behavior was demonstrated by the linear evolution of the number-average molecular weight with conversion (Fig. 2). The M_w/M_n values of the obtained polymers were relatively low (<1.4) when the concentration of RAFT agent was 0.0063 M. As the concentration of RAFT agent was reduced to 0.0016 M, the M_w/M_n values increased slightly, and at the same time, the $M_{n,GPC}$ negatively deviated from the $M_{n,th}$, which indicated that the initiator-derived chains were significant at low concentration of RAFT agent [10]. Decreasing the amount of RAFT agent, the concentration of

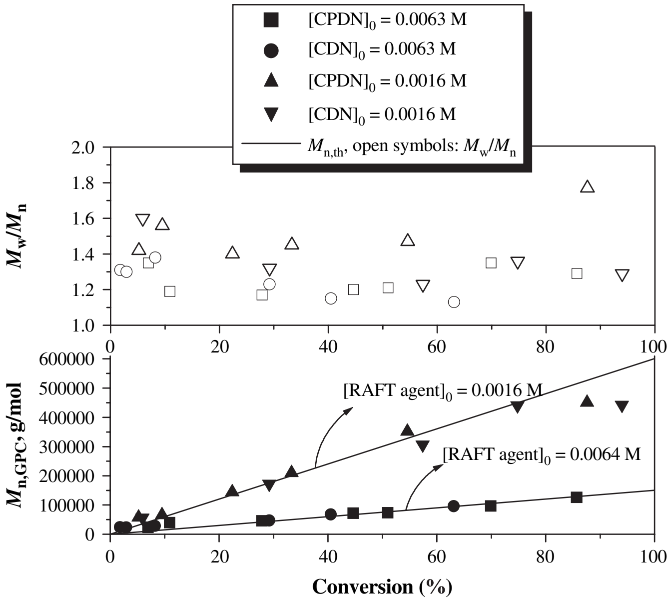


Fig. 2. Dependence of M_n and M_w/M_n on conversion for thermal polymerization of MMA, same reaction condition as in Fig. 1. $M_{n,th} = ([MMA]_0/[RAFT\ agent]_0) \times Mw_{MMA} \times \text{conversion} + Mw_{RAFT\ agent}$.

initiator species, despite the undefined structure in the present work, may be higher than the RAFT agent concentration. Considerable chains derived from the initiators were not adequately regulated through the addition-fragmentation equilibrium [10,14], resulting in high M_w/M_n values and negative deviations of the molecular weights. At the beginning of the polymerization (<10% conversion), the $M_{n,GPC}$ was greater than $M_{n,th}$, the deviation was pronounced especially in the CDN systems. The reason may be that the RAFT agent was slowly consumed while the $M_{n,th}$ was calculated based on the complete consumption of the RAFT agent during this period [10,28,38]. From the kinetic characters of the polymerization and molecular weight/conversion data, it can be demonstrated that the thermal polymerization of MMA in the presence of RAFT agents had the similar living features compared with conventional RAFT polymerization initiated by some thermal initiators.

The chain ends of the PMMA prepared by thermal polymerization in the presence of RAFT agents were analyzed by ^{1}H NMR spectroscopy (Fig. 3). The signals at $\sigma = 7.4$–8.1 ppm corresponded to the aromatic protons of the naphthalene units in CPDN (Fig. 3A), the ^{1}H NMR of the PMMA mediated by CDN (Fig. 3B) was similar to that of CPDN, expect for the signals at 7.18 ppm which were ascribed to the aromatic protons of the phenyl group in CDN. These aforementioned results revealed that the RAFT agents were attached to the polymer chain ends.

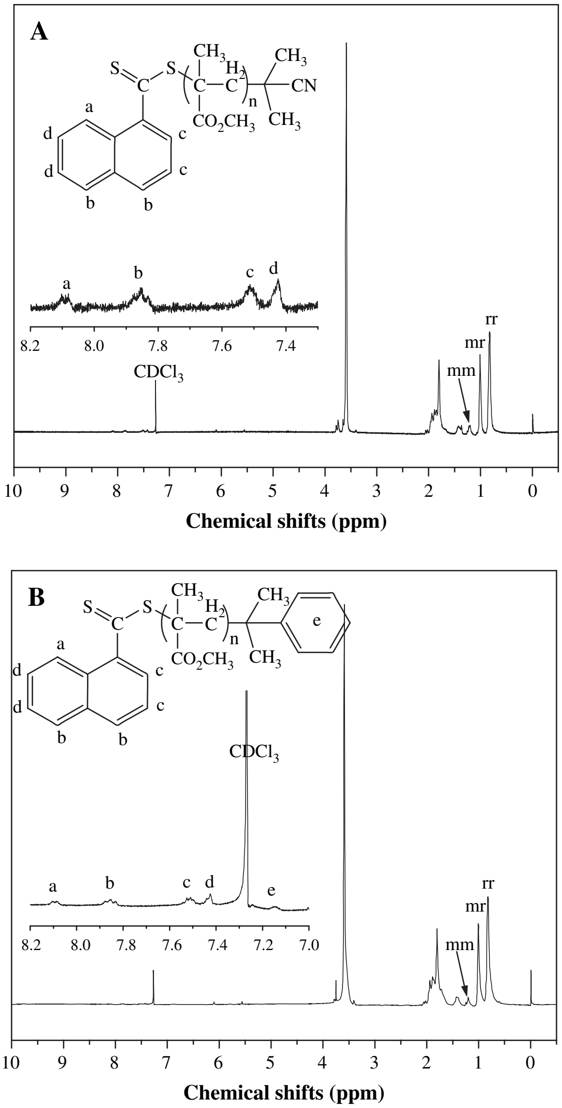


Fig. 3. ^{1}H NMR spectra of PMMA with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. A: CPDN end-capped PMMA, $M_{n,GPC} = 8300$ g/mol, PDI = 1.27; B: CDN end-capped PMMA, $M_{n,GPC} = 28\,600$ g/mol, PDI = 1.38.

Fig. 3 shows three distinct peaks appearing at the highest field, which represent MMA groups of different tacticities. The bands at about 0.82, 1.02, and 1.18 ppm arose from syndiotactic (rr), atactic (mr), and isotactic (mm) methyl groups, respectively [39]. The tacticity of the PMMA was calculated from the integrated ratios of rr, mr, and mm from Fig. 3. The ratios of the triad tacticity for rr, mr, and mm were 64.6, 34.3, and 1.1 as in Fig. 3A. As for the Fig. 3B, the ratios were 66, 32.7, and 1.3, respectively. The tacticity distributions were in good agreement with the tacticity for benzoyl peroxide (BPO)-initiated polymerization [40]. These results suggested that the thermal polymerization of MMA in the presence of RAFT agent was via a radical-mediated mechanism.

To further demonstrate the living fashions of the thermal polymerization of MMA in the presence of RAFT agents, the obtained PMMA samples were used as macroRAFT agents for reactions of chain extension and block copolymerization. The results of chain extension and block copolymerization of the PMMAs end-capped by CPDN and CDN are shown in Fig. 4A and B, respectively. As shown in Fig. 4A, the PMMA with $M_n = 8300$ g/mol ($M_w/M_n = 1.27$) was successfully chain-extended with MMA to result PMMA with higher molecular weight, $M_n = 75\,800$ g/mol ($M_w/M_n = 1.23$) after

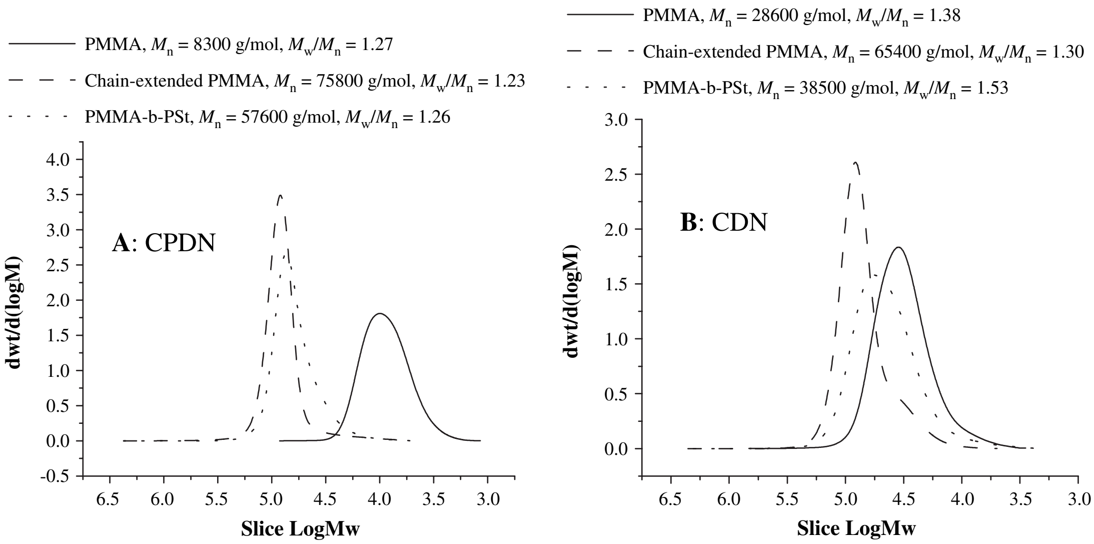


Fig. 4. GPC curves before and after chain extension or block copolymerization using PMMA samples prepared by the deoxygenated RAFT polymerization of MMA as macroRAFT agent. CPDN–PMMA: chain-extended with MMA, $[MMA]_0 = 9.40$ mol/L, $[MMA]_0/[PMMA]_0 = 1000/1$, 80 °C, 21 h, 63.6% conversion; block copolymerization with St, $[St]_0/[PMMA]_0/[AIBN]_0 = 1000/1/0.3$, 70 °C, 21 h, 54.3% conversion; CDN–PMMA: chain-extended with MMA, $[MMA]_0 = 9.40$ mol/L, $[MMA]_0/[PMMA]_0 = 1000/1$, 80 °C, 45 h, 21.3% conversion; block copolymerization with St, $[St]_0 = 8.90$ mol/L, $[St]_0/[PMMA]_0/[AIBN]_0 = 1000/1/0.3$, 70 °C, 51 h, 8.1% conversion.

21 h at 80 °C under the thermal initiation. As shown in Fig. 4B, the PMMA with $M_n = 28\,600$ g/mol ($M_w/M_n = 1.32$) was successfully chain-extended with MMA to result PMMA with $M_n = 65\,400$ g/mol ($M_w/M_n = 1.30$) after 45 h at 80 °C under thermal initiation. Furthermore, two block copolymers of MMA and styrene were also successfully prepared using the PMMA as the macroRAFT agent and AIBN as initiator at 70 °C. These results further showed that most of the chain ends were attached with dithioester moieties.

For a comprehensive understanding of the thermal polymerization of MMA in the presence of RAFT agents, the effects of the concentration of RAFT agent and reaction temperature on the polymerization rate, the molecular weight and molecular weight distribution of the polymers were also investigated. The results are summarised in Table 1. It can be seen that the polymerization was obviously retarded when the concentration of RAFT agent increased from 0.0063 M to 0.0315 M (entries 1–4 and 9–12), which could be owing to the higher concentration of RAFT agent used [5,28,35]. The molecular weight distribution of PMMA narrowed with an increase of the CPDN concentration (entries 1–6), which indicated that the polymerizations were well controlled at the higher CPDN concentration. Earlier efforts by other researchers [10,38] confirmed that the higher polymerization temperature increased the propagation rate constant and the chain transfer constant, resulting in very narrow M_w/M_ns from the beginning of the process. In our work, there appeared no dramatic effect of temperature on the M_w/M_n (entries 3,4,7,8 and 9,10,13,14), which was probably because of the low concentrations of initiator species.

Table 1
The results of thermal polymerization of MMA in the presence of dithionaphthalate derivatives

Entry[a]	$[\text{RAFT agent}]_0$ (mol/L)	Temperature (°C)	Time (h)	Conv. (%)	$M_{n,GPC}$ (g/mol)	M_w/M_n	$M_{n,th}$[b] (g/mol)
1	0.0315	80	48	5.1	5970	1.26	1800
2			504	81.5	27 090	1.08	24 700
3	0.0063	80	48	10.9	39 800	1.19	16 600
4			312	85.7	126 200	1.29	128 800
5	0.0016	80	48	9.5	65 800	1.56	57 300
6			168	87.6	450 800	1.77	525 900
7	0.0063	40	240	5.5	24 500	1.33	8500
8			1176	87.1	126 500	1.20	130 900
9	0.0063	80	48	1.8	24 300	1.31	3020
10			312	63.1	95 900	1.13	95 000
11	0.0016	80	24	29.2	172 200	1.32	175 500
12			52	94	442 400	1.29	564 300
13	0.0063	40	384	5.5	24 200	1.38	8250
14			576	86.9	131 700	1.33	130 700

[a] $[MMA]_0 = 9.40$ mol/L. Entries 1–8: CPDN as RAFT agent; entries 9–14: CDN as RAFT agent.

[b] $M_{n,th} = ([MMA]_0/[\text{RAFT agent}]_0) \times Mw_{MMA} \times \text{conversion} + Mw_{\text{RAFT agent}}$.

3.2. Thermal polymerization of MA in the presence of RAFT agents

To examine the generality of the RAFT polymerization of other acrylate monomers by thermal initiation method, the thermal polymerizations of MA mediated by CPDN and BPIC were carried out under the similar reaction conditions to those for MMA. The polymerizations were conducted with low concentration of RAFT agents (0.00094 M) at 80 °C. The polymerization rate in the case of CPDN was lower than that in case of BPIC (see Fig. 5). The naphthyl as the Z group enhanced the stability of the intermediate radicals compared with that of BPIC, which incurred the polymerization retardation in CPDN mediated system [10,38]. Well-defined PMAs with narrow M_w/M_ns were also obtained (Fig. 6). The maximum molecular weight of PMA reached to 312 500 with a low M_w/M_n value (1.57). Chain-end analysis (Fig. 7) and successful chain-extension reactions (Fig. 8) also suggested well-controlled characters of the thermal polymerization of MA in the presence of RAFT agents.

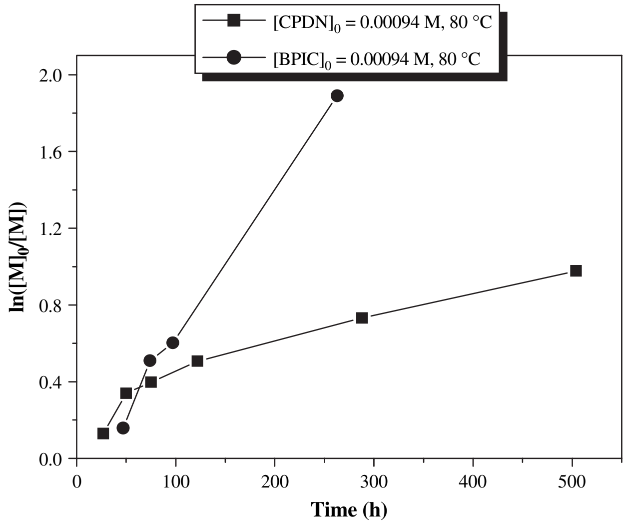


Fig. 5. Dependence of ln($[M]_0/[M]$) on polymerization time, $[MA]_0 = 5.66$ M, $[CPDN]_0([BPIC]_0) = 0.00094$ M, 80 °C, 50% (v/v) MA in benzene solution.

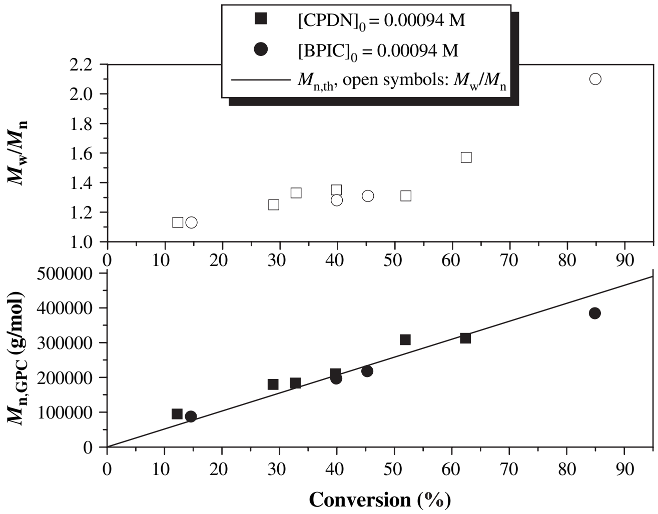


Fig. 6. Dependence of M_n and M_w/M_n on conversion for thermal polymerization of MA with CPDN or BPIC as RAFT agent, reaction conditions as in Fig. 5, $M_{n,th} = ([MA]_0/[CPDN]_0 \text{ or } [BPIC]_0 \times Mw_{MA} \times \text{conversion} + Mw_{CPDN \text{ or } BPIC}$.

3.3. RAFT polymerization mechanism

The experimental results proved that the polymerization was via a RAFT mechanism. The key problem is that where does the initiation source come from? According to previous literatures, three initiation sources are suspected for the initiation behavior. First, the initiation behavior is probably from the classical thermal initiation, i.e., intermolecular reactions. In the case of methyl (meth)acrylate, the reaction is very slow and will take several hours to produce little conversions [24,41], therefore, it cannot be the main initiation source.

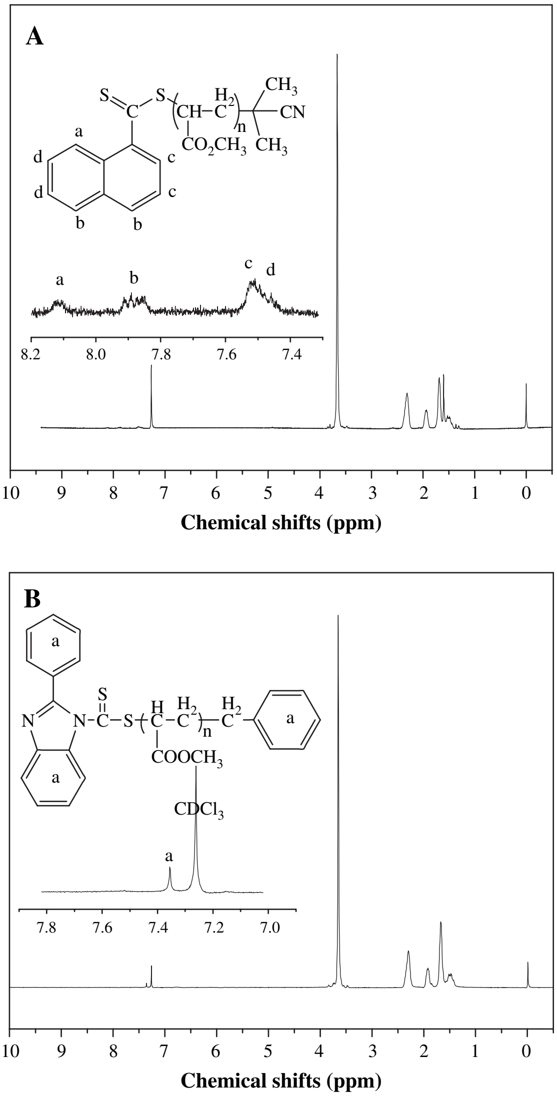


Fig. 7. ^{1}H NMR spectra of PMA with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. A: CPDN end-capped PMA, $M_{n,GPC} = 12\,400$ g/mol, $M_w/M_n = 1.15$; B: BPIC end-capped PMA, $M_{n,GPC} = 87\,400$ g/mol, $M_w/M_n = 1.13$.

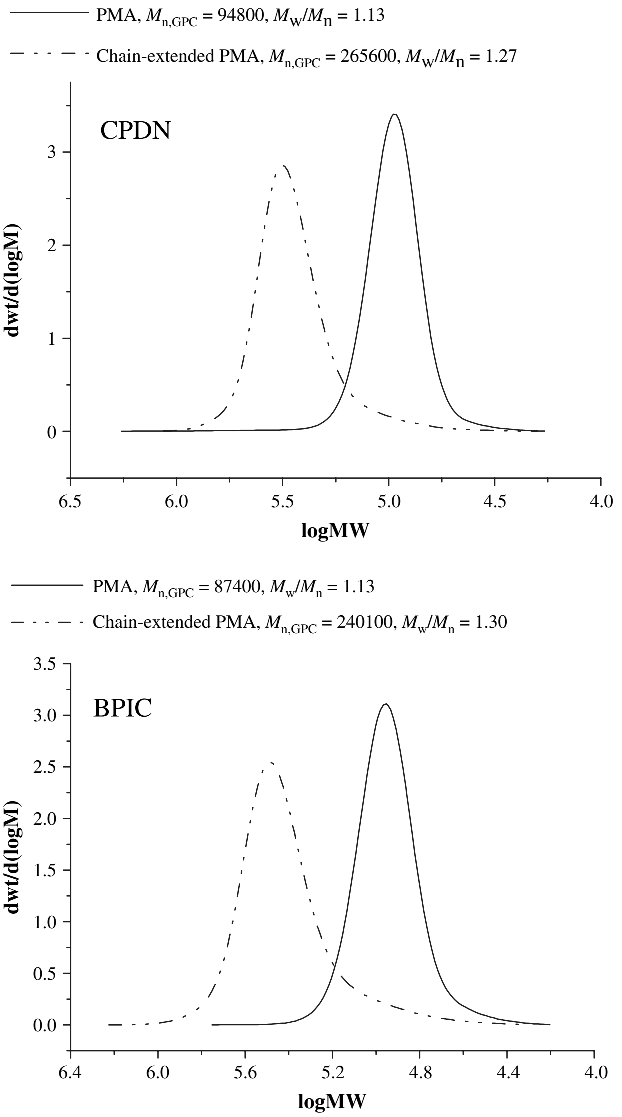


Fig. 8. GPC curves before and after chain extension using PMA samples as macroRAFT agents. PMA mediated by CPDN as macroRAFT agent: $[MA]_0 = 5.66$ M, $[PMA]_0 = 0.00094$ M, 50% (v/v) MA in benzene, 80 °C, 47 h, 33.5% conversion; PMA mediated by BPIC as macroRAFT agent: $[MA]_0 = 5.66$ M, $[PMA]_0 = 0.00094$ M, 50% (v/v) in benzene, 80 °C, 22 h, 40.2% conversion.

Another suspicious resource of initiation radicals may be generated directly from the RAFT agent under heat [10], however, the visible decomposition temperature of the RAFT agents such as dithiobenzoate under heating is higher than 90 °C [42,43], and the resulted unsaturated compound and dithiobenzoic acid cannot act as initiators. Therefore, the decomposition of the RAFT agent is ruled out from the initiation source. Finally, the most possible initiation source may be the MMA peroxide containing species formed from monomer and molecular oxygen. We have known that the mechanism of MMA thermal polymerization has been the subject of long controversy and is still unsolved [24,37,44]. It is widely accepted that the initiation of the thermal polymerization of MMA is due to the formation and decomposition of the peroxide containing species that are formed from dissolved oxygen even at ambient temperature [23,24,37,44], and at relatively higher temperature, these peroxides decompose quickly and initiate the radical polymerization [24]. In our experiment, oxygen was eliminated by the argon flushing, however, it may not be exhaustive, molecular oxygen dissolved in monomer reacted with molecular monomer resulting in the formation of the peroxide, which then acted as initiators for the thermal polymerization of MMA [23,24]. The low concentration of peroxide thus resulted in low polymerization rates.

4. Conclusion

Well-defined PMMA or PMA with high molecular weights and narrow M_w/M_ns could be synthesized using thermal polymerization of MMA or MA in the presence of low concentration of RAFT agents. The polymerizations demonstrated ‘‘living’’/controlled characters. Chain-extension reactions were also successfully carried out to obtain higher molecular weight PMMA, PMA and PMMA-*b*-PSt copolymer with controlled structure and narrow M_w/M_ns. The most possible initiator may be the peroxide containing species formed from monomer and molecular oxygen. It opened a way to perform living/controlled radical polymerization of methyl (meth)acrylate by the thermal initiation method; however, extensive researches are needed to clarify the initiation mechanism.

Acknowledgments

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