Facile Prepared Bis(carbazyl thiocarbonyl) Disulfide as Chain Transfer Agent for RAFT Polymerization of Methyl Methacrylate

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ABSTRACT: The bis(thiocarbonyl) disulfide compounds are key intermediates for the preparation of the high-performance reversible addition-fragmentation chain transfer (RAFT) agents with 2-cyanoprop-2-yl or its homologous group as R group. In this article, a synthetic method in water was developed to prepare high-purity bis(carbazyl thiocarbonyl) disulfide (BCTD) based on a straightforward oxidation reaction using $K_3[Fe(CN)_6]$ as the oxidant. This method was proved to be a convenient, economical, and eco-friendly route to synthesize bis(thiocarbonyl) disulfides with high purity and high yield. Subsequently, the RAFT polymerizations of methyl methacrylate (MMA) have been studied by using BCTD and azobis(isobutyronitrile) (AIBN) to *in situ* generate RAFT agent 2-cyanoprop-2-yl N-carbazylcarbodithioate (CYCBD). After a very short initial nonliving phase, the polymerization exhibited typical living polymerization characteristics, including that the molecular weights of PMMA linearly increase with monomer conversions and PDI can remain in a relatively low range. The results further indicated that the ratio of BCTD to AIBN and the reaction temperature had a significant impact on the MMA polymerization, and the living features were most prominent when the ratio of BCTD to AIBN is in the range of 1–2 and polymerization temperature at 60°C. In addition, ^{1}H-NMR analysis and fluorescence spectroscopy of the resultant polymethyl methacrylate (PMMA) confirm the formation of carbazole end-labeled PMMA chains due to CYCBD generated *in situ* by the reaction of BCTD with AIBN. This can offer an alternative and complementary route to obtain well-defined polymers, especially for preparation of polymers with high molecular weight and a relatively low polydispersity. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: RAFT polymerization; bis(thiocarbonyl) disulfide; bis(carbazyl thiocarbonyl) disulfide; methyl methacrylate; fluorescence

INTRODUCTION

Reversible addition-fragmentation chain transfer (RAFT) process[1,2] has received a great deal of attention and refinement over the past few years as it can allow the synthesis of well-defined polymers with controlled chain architecture, predetermined composition, specific functionality, and hence unrivaled properties.[3–5] The key principle of the RAFT polymerization is to transfer the majority of active propagating species into dormant species, which can be achieved by employing appropriate thiocarbonylthio compounds (Z—C(=S)—S—R) with high chain transfer constants as chain-transfer agents (CTAs).[6,7] The dithiobenzoates with phenyl as Z group have the most versatility to mediate most commonly used monomers.[8] In addition, the dithiocarbamates, such as those originated from carbazole,[9–12] imidazole,[13,14] and triazole,[15] exhibit a sufficient controlling activity even toward the less reactive propagating radicals. Especially, the carbazyl dithiocarbamates with a large conjugation on Z group possess some special properties as RAFT agents.[15,16] They not only can efficiently mediate the RAFT polymerization of methacrylate, acrylate, and styrene monomers, but also can easily obtain polymer labeled with a carbazyl fluorescent terminal group.[17,18]
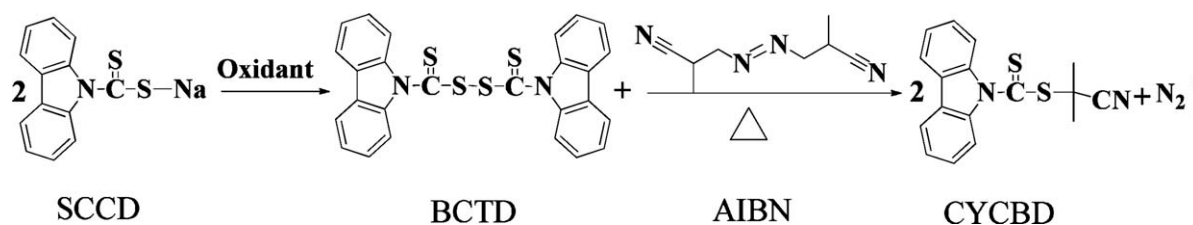
The largest obstacle to the generalization and application of RAFT polymerization is that the bulk of RAFT agents are currently not commercially and

Scheme 1 Synthetic route of CYCBD.

conveniently available. With regard to the carbazyl dithiocarbamates, our research group has reported a convenient, economical, and eco-friendly aqueous phase method, in which the high-purity RAFT agents in the form of crystal was precipitated and spontaneously separated from the aqueous solution.[9] However, the high-performance RAFT agents with 2-cyanoprop-2-yl or cyano-homologous as R group cannot be synthesized by aqueous phase method, and frequently are difficult to prepare, purify (usually use column separation), and preserve. These efficient CATs are crucial for the RAFT process of some less reactive monomers, for example, methyl methacrylate (MMA), so it is important to find a stable, easily synthetic route, or other alternative agents.[19,20] Some groups successively reported the RAFT homopolymerizations of styrene and (meth)acrylate monomers by using bis(thiobenzoyl) disulfide and azobis(isobutyronitrile) (AIBN) to synthesize CTA *in situ*.[21,22] Compared with dithioesters, the bis(dithiocarbonyl) disulfide is much stable and easier to prepare and purify. Thus, it may be used as an alternative of dithioesters to prepare well-defined polymers with controlled chain architecture and molecular weight as well as low polydispersity index.

In a previous work, 2-cyanoprop-2-yl *N*-carbazylcarbodithioate (CYCBD) was synthesized based on a substitution reaction between bis(carbazyl thiocarbonyl) disulfide (BCTD) and AIBN (Scheme 1) and was used as the CTA in RAFT polymerization of MMA.[17] The results have confirmed that CYCBD was a high-performance RAFT agent for styrene and various acrylate monomers. However, the preparation and purification of CYCBD are relatively difficult. Compared with CYCBD, the preparation process of BCTD is considerably simpler, as the BCTD can be synthesized by a simple oxidation process in the aqueous solution of sodium carbazole-9-carbodithioate (SCCD). The high-purity BCTD can be easily obtained in the form of crystal that was precipitated and spontaneously separated from the aqueous solution of reaction mixture. In this article, the new synthetic method in water for the preparation of high-purity BCTD was studied. Subsequently, we, in detail, investigated the RAFT polymerization of MMA by the use of BCTD and AIBN to synthesize RAFT agent *in situ*.

EXPERIMENTAL

Materials

Carbazole purchased from Wenshui Chemical, Shanxi, China was recrystallized from methanol and then dried in a vacuum. Sodium hydride, carbon disulfide (CS_2), potassium ferricyanide ($K_3[Fe(CN)_6]$), anhydrous sodium sulfate, tetrahydrofuran (THF), toluene, and MMA were purchased from The First Chemical Reagents Factory of Tianjin, China. MMA was dried by CaH_2 overnight, and then distilled under reduced pressure and stored under N_2 at $-10°C$ prior to use. THF was refluxed with sodium for 48 h and then distilled, respectively. High performance liquid chromatography (HPLC) grade dichloromethane was purchased from Merck (Darmstadt, Germany), and deionized water was obtained from a UP water purification system (Shanghai Ultrapure Technology, Shanghai, China). All other chemical agents were used as received.

Synthesis of bis(carbazyl thiocarbonyl) disulfide

The high-purity aqueous solution of SCCD was prepared according to our previous study.[9] And then, an excess of $K_3[Fe(CN)_6]$ aqueous solution (100 mL, 0.5 mol/L) was slowly dropped in the aqueous solution of SCCD with a vigorous magnetic stirring for 2 h at room temperature. In this process, a large amount of yellow crystal precipitates were formed. The product BCTD was easily obtained after washing with excess deionized water and vacuum drying at room temperature. Pure BCTD: yellow crystals; yield: 97.3%; melting point: 146.1–147.8°C. ^{1}H-NMR (300 MHz, CDCl$_3$), δ (ppm): 8.42–8.39 (d, 4H), 8.18–8.01 (d, 4H), 7.46–7.40 (m, 8H); IR (KBr disc): 3000–3060 (C—H), 1041 (—C=S); elemental analysis calculated for $C_{26}H_{16}N_2S_4$: C 64.43%, H 3.33%, N 5.78%, S 26.46%; elemental analysis found: C 64.40%, H 3.34%, N 5.76%, S 26.50%.

Polymerization

The general procedure is as follows. A mixture of MMA, toluene, AIBN, and chain transfer agent (BCTD) was placed in a dry flask. After three freeze-pump-thaw cycles, the polymerization was carried out at a given temperature in the dark condition for a predetermined time. After the polymerization, the reaction was quenched by immersion of the reaction

flask into liquid N_2. Subsequently, the reaction mixture was diluted with THF, and then precipitated in excess ethanol. The polymer was collected by filtration and dried in a vacuum oven.

Conversion (Conv.) was determined by gravimetrical method and was calculated based on Eq. (1):

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

where, W_p, W_{CTA}, and W_m, respectively, stand for the weights of the polymer, RAFT agent, and monomer.

And the theoretical molecular weight ($M_{n,th}$) of polymethyl methacrylate (PMMA) was calculated according to Eq. (2):

$$M_{n,th} = \frac{W_m}{m_{CTA}} \times \text{Conv.} + M_{CTA}$$
$$= \frac{W_{MMA}}{2 \times m_{BCTD}} \times \text{Conv.} + M_{CYCBD} \quad (2)$$

where, W_m, m_{CTA}, and M_{CTA} are the weights of monomer in the feed, the initial moles of CTA added, and the molecular weight of CTA, respectively. W_{MMA}, m_{BCTD}, and M_{CYCBD} are the weights of MMA in the feed, the initial moles of BCTD added, and the molecular weight of CYCBD, respectively.

Characterization

The molecular weights and polydispersity index (PDI) of the polymers were measured with a Waters 1515 gel permeation chromatographer (GPC; Waters company, Milford, USA) equipped with a refractive index detector, using PLgel MIXED C (MW 200-3M), PLgel C (MW500-20K), and PLgel C (MW4-400K) column with molecular weight range 100–500,000 calibrated with polystyrene standard samples. THF was used as an eluent at a flow rate of 1 mL/min. ^{1}H-NMR spectra of the products were recorded on a Varian Mercury Vx300 NMR instrument (Varian, Palo Alto, USA) with CDCl$_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. Fourier transform infrared spectroscopy (FTIR) was carried out using KBr disks in the region of 4000–500 cm^{-1} by using BIO-RAD FTIR 3000 (BIO-RAD Company, Hercules, USA). Elemental analysis was determined by oxygen flask combustion on an Elementar Vario Micro cube (Elementar Analysis, Hanau, Germany). The fluorescence spectra were measured by the fluorescence spectrometer on Varian Cary Eclipse (Varian, Palo Alto, USA) with THF as solvent at room temperature and using 5 nm bandpass, 6 s response time.

High performance liquid chromatography (HPLC) analysis

The purity of BCTD was analyzed by HPLC with an Agilent 1100 series systems consisting of quaternary gradient pump, variable wavelength UV-detector, online vacuum degasser, thermostatted column compartment, and autosampler with variable injection volume. The applied solvents were HPLC grade dichloromethane. The column was a Kromasil silica gel column (100 Å, 150 × 4.6 mm, 5 μm, Scienhome Science Instruments, Tianjin, China). The applied column temperature was 30°C. The samples were dissolved in dichloromethane and the sample solutions were filtered through a 0.23 μm membrane filter and injected in the chromatograph. The flow rate during analysis was constant with 1.0 mL/min and the injection volume was 20 μL. UV spectra were recorded in range 200–600 nm.

RESULTS AND DISCUSSION

The preparation of BCTD by aqueous phase method

It is well-know that the RAFT process depends on a reversible addition-fragmentation reaction mediated by a suitable thiocarbonylthiol compound. A great variety of compounds have been designed and synthesized with different kinds of substituents. The previous reports have confirmed that 2-cyanoprop-2-yl is an effective R group for RAFT polymerization of most vinyl monomers, as the 2-cyanoprop-2-yl is an excellent leaving group and, at the same time, a good reinitiating radical. Generally, RAFT agents bearing a 2-cyanoprop-2-yl as R group could be synthesized via a radical addition-fragmentation process from the reaction of bis(thiocarbonyl) disulfide compounds with AIBN.[23] Therefore, bis(thiocarbonyl) disulfide is currently of great importance for the preparation of tertiary dithiobenzoates. The synthesis of bis(thiocarbonyl) disulfide compounds via oxidation by iodine systems under anhydrous conditions is quite common.[2,22,24] However, the iodine oxidation generally provides poor results due to the sensitivity of the oxidation reaction to impurities and specific conditions.[25] In addition, the removal of the excess iodine from the resultant bis(thiocarbonyl) disulfide compounds often results in numerous inconveniences for the industrialized production. The use of a more convenient and economical method to produce bis(thiocarbonyl) disulfides would be a welcome addition to the production of these compounds.

BCTD, the precursor used for the preparation of CYCBD (Scheme 1), can be very simply obtained by an improved aqueous phase method based on a straightforward oxidation reaction using $K_3[Fe(CN)_6]$ as the oxidant in the aqueous solutions of SCCD. In the whole reaction system, the reactants $K_3[Fe(CN)_6]$ and SCCD are both water soluble while the reaction product BCTD is insoluble in water and
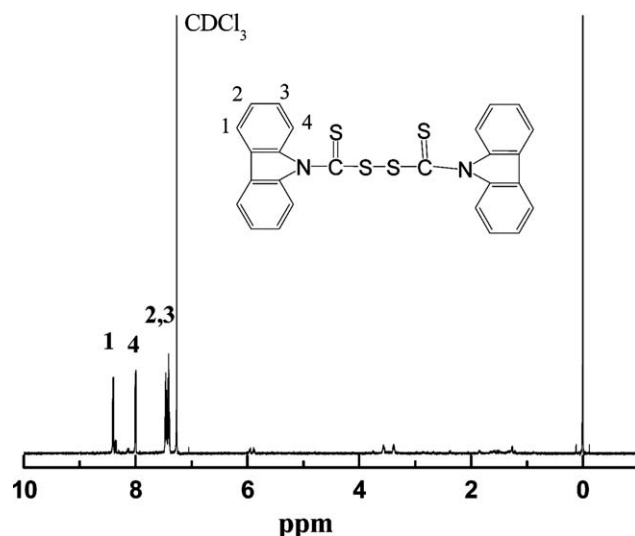
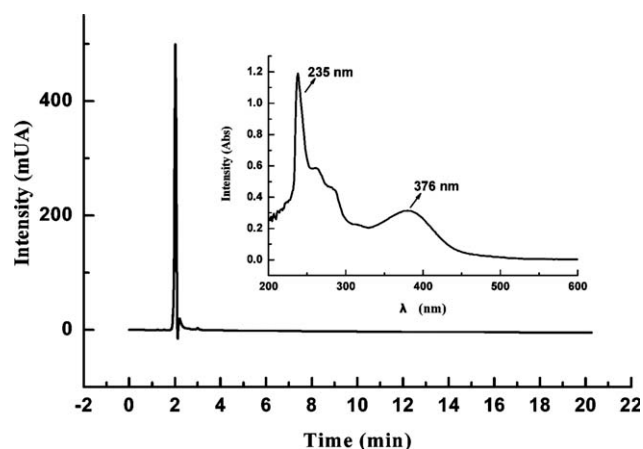**Figure 1** ¹H-NMR spectra of raw BCTD prepared by aqueous phase method.

will precipitate spontaneously as a crystal from aqueous solution. Therefore, the expected high-purity BCTD is eventually easily obtained after filtering and washing the yellow crystal precipitate. It is worth pointing out that the yield of product is very high (>95%) due to the fact that the equilibrium is strongly shifted toward the formation of product BCTD. In brief, compared with the traditional iodine oxidation in organic solvent, the new method is more simple, economical, and eco-friendly, as the inconvenient purification treatments and vast organic solvents can be avoided. It is worth pointing out that the other bis(thiocarbonyl) disulfide compounds can also be successfully prepared by this new aqueous phase method when the dithiocarbamates or carbodithioates salt can be soluble in water, whereas the expected bis(thiocarbonyl) disulfides have a low solubility in water.

BCTD prepared in water without further purification was directly characterized by ¹H-NMR and HPLC. The ¹H-NMR spectrum of raw BCTD is shown in Figure 1. It can be seen that the signal at 8.42–8.39 ppm, 8.18–8.01 ppm, and 7.46–7.40 ppm corresponds to the carbazyl proton of BCTD units. According to the ¹H-NMR spectra, the purity of the obtained compound is over 97.5%. The HPLC chromatogram recorded by a UV detector at 376 nm corresponding to the maximum UV absorbance of —S—C=S chromophore as shown in Figure 2 was performed to measure the purity of the raw BCTD. Only one peak with a retention time of 2 min was visible in the HPLC chromatogram and the impurity almost cannot be detected. These results indicated that the improved aqueous phase method provides a more feasible and simple route to reduce the various impurities and thus to prepare high-purity bis(thiocarbonyl) disulfide compounds.
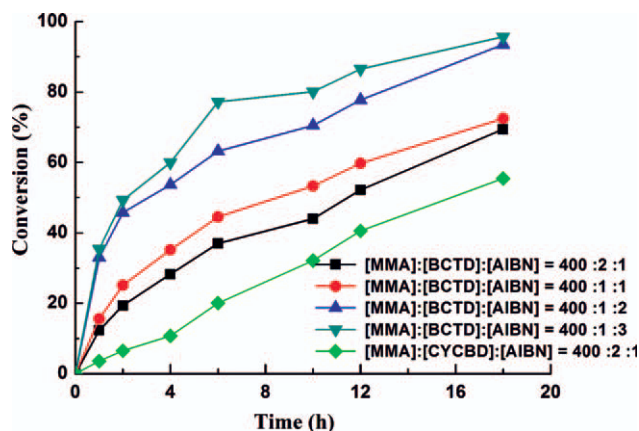
RAFT polymerization of MMA mediated by CYCBD generated *in situ* from BCTD and AIBN

It was pointed out that the RAFT polymerization of MMA is of a rigorous demand for RAFT agents.[24] CYCBD proved to be an efficient CAT in RAFT polymerization of MMA was prepared based on a substitution reaction between BCTD and AIBN (Scheme 1).[17] Considering that AIBN is a usually used initiator in the free-radical polymerization, it is very possible to produce RAFT agent *in situ* through the reaction of BCTD and AIBN. Accordingly, BCTD was introduced into the AIBN initiated free-radical polymerization of MMA to *in situ* generate CYCBD with carbazyl as Z group and 2-cyanoprop-2-yl as R group. A series of experiments, in which BCTD and AIBN concentrations were varied while all the other reaction conditions were held constant, were carried out to estimate their influence on the RAFT polymerization of MMA. A control experiment was carried out by using CYCBD as the RAFT agent. The plots of conversion vs. polymerization time for RAFT polymerization of MMA using CYCBD generated *in situ* as the RAFT agent at 60°C in toluene are shown in Figure 3. It can be found that CYCBD can induce a typical living RAFT polymerization of MMA. In the whole polymerization process, the molecular weight of resultant PMMA in the presence of CYCBD increases linearly with monomer conversion throughout the polymerization. Moreover, the molecular weight of PMMA closely approached the theoretical values and the PDI of all PMMAs prepared by CYCBD, except the PDI at low conversion, is generally lower than 1.2 (shown in Fig. 4).

In the case of BCTD, it can be observed that the polymerization rates are drastically higher as compared with CYCBD, especially in initial polymerization stage (<2 h). Furthermore, the initial polymerization rates of MMA were unreasonably high in the case of a higher concentration of AIBN,


Figure 2 HPLC chromatogram and UV spectrum of raw BCTD prepared by aqueous phase method.
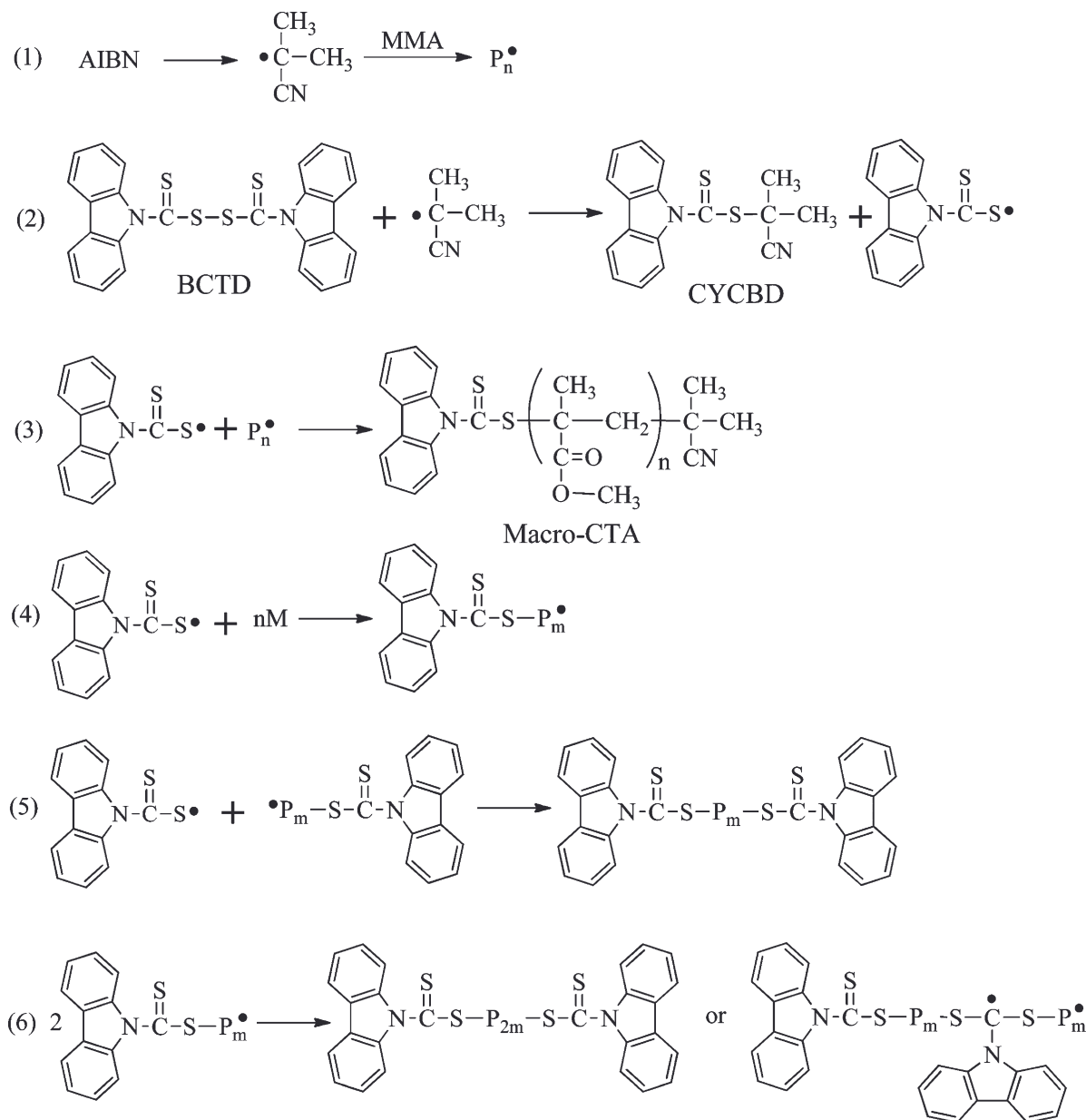
Figure 3 Conversion vs. polymerization time plots for RAFT polymerization of MMA using CYCBD generated *in situ* by the reaction of BCTD with AIBN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicating uncontrolled, nonliving polymerization. This may be due to the fact that the thimbleful of CYCBD in initial polymerization phase, if any, is not enough to capture promptly the propagating radicals to form deactivated dormant polymer species. However, the polymerization rates decreased to a low value in the next duration of polymerization

and the curves presented in Figure 3 yielded close-to-linear correlations between conversion and polymerization time. Especially in the case of a high concentration of BCTD ([BCTD] : [AIBN] $\geq$ 1 : 1), the polymerization in the second polymerization phase exhibited first-order kinetic, which suggested that the number of the propagating radicals originated from the decomposition of initiator has decreased due to the presence of CYCBD generated *in situ* by the reaction of BCTD with AIBN. Increasing the BCTD concentration would increase the probability of the reaction between BCTD and AIBN, which can decrease the concentration of the propagating radical and eventually lead to decreasing the polymerization rate. These results are in agreement with the previous work of Monteiro and de Brouwer,[26] and Zhou and coworkers,[21] in which bis(benzyl thiocarbonyl) disulfide and bis(thionaphthoyl) disulfide were used to *in situ* produce RAFT agent, respectively. In the same way, the reaction possibility of AIBN and BCTD would increase when increasing the AIBN concentration while keeping BCTD concentration constant. However, a similar decrease in the polymerization rates was not observed. The polymerization rates in the case of a high concentration of AIBN were significantly higher than that in the case of a high concentration of BCTD. This may be due
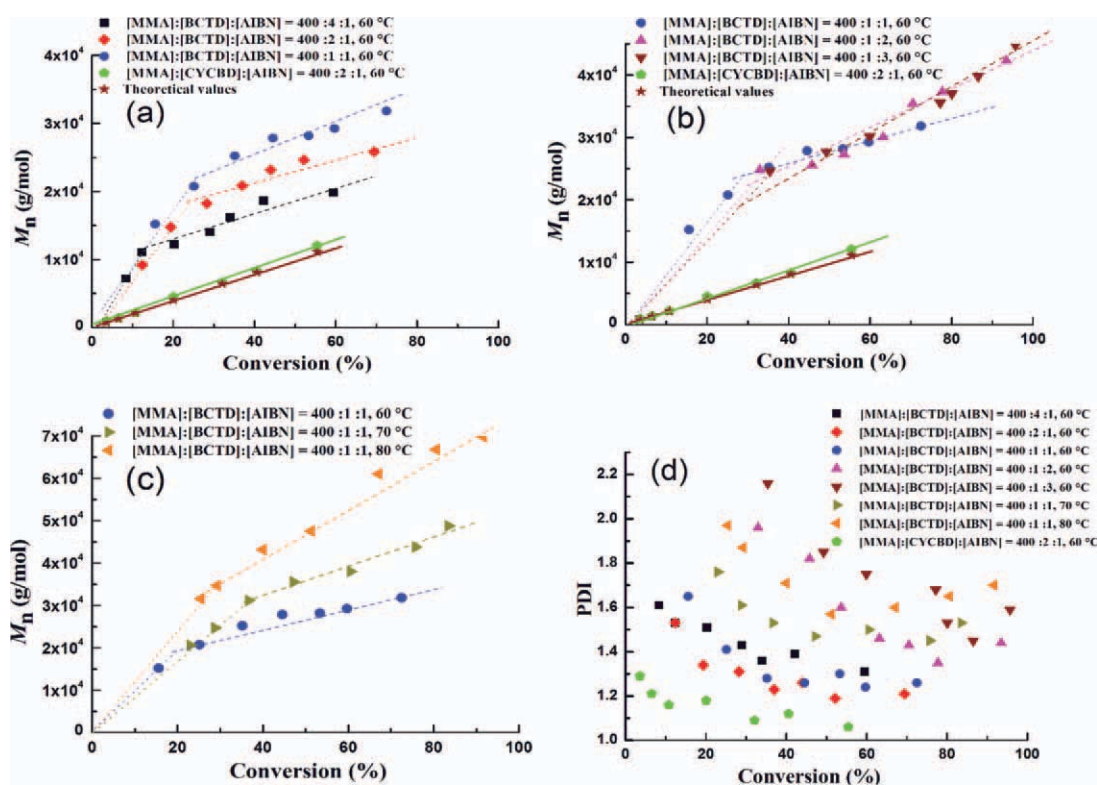
Figure 4 Molecular weight and PDI vs. monomer conversion plots for RAFT polymerization of MMA using CYCBD generated *in situ* by the reaction of BCTD with AIBN. The theoretical molecular weight of PMMA prepared by CYCBD at 60°C was calculated according to Eq. (2), which is equated to the theoretical values of [MMA] : [BCTD] : [AIBN] = 400 : 1 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 2 Possible RAFT polymerization mechanism mediated by CYCBD generated *in situ* by the reaction of BCTD and AIBN.

to the fact that the high AIBN concentration means more propagating radicals and thus faster polymerization rates. In addition, it was worth pointing out that, regardless of the BCTD concentration, nearly no retardation was observed in the RAFT polymerization of MMA in the presence of BCTD.

The concentration of BCTD and AIBN can have a significant impact on the polymerization rates, and undoubtedly influence the property parameters of the obtained PMMA. The molecular weight and PDI vs. monomer conversion plots for RAFT polymerization of MMA using CYCBD generated *in situ* by the reaction of BCTD with AIBN were shown in Figure 4. It can be seen from Figure 4(a,b) that the

RAFT polymerizations of MMA for all concentrations of BCTD displayed a hybrid behavior between living and conventional free-radical polymerization. In initial polymerization phase, the polymerization behavior of MMA followed conventional free-radical polymerization. The monomer conversion, depending on the AIBN concentration, reached to about 11–35% in relatively short polymerization time (1 h). And the initial polymerization also formed high-molecular-weight PMMA ($M_n > 10{,}000$ g/mol) with a relatively high polydispersity (PDI > 1.6). The reason can be ascribed to the fact that less RAFT agent is available for the polymerization in initial phase due to the incomplete conversion of BCTD to CYCBD. Subsequently, the polymerization exhibited

some typical living characters of RAFT in the next polymerization stage. Molecular weights linearly increased with monomer conversion while the PDI remained relatively low. It can be seen from Figure 4(d) that the PDI of most of these PMMA was below 1.4 when the ratio of BCTD to AIBN was 2 : 1 or 1 : 1. Furthermore, both of the molecular weights and the polydispersities decreased at the same monomer conversions with the increase of the ratio of BCTD to AIBN. These results indicated that the formation of CYCBD should occur during the polymerization process and the polymerizations were processed according to a RAFT mechanism.

However, compared with the results shown in Figure 4(a,b), it can be found that the living features were promoted with the increase of BCTD concentration, whereas increasing AIBN concentration led to a less control of polymerization reactions. According to Vosloo et al.'s argumentation,[22] the reaction mechanisms of the polymerization of MMA in the presence of AIBN and BCTD are shown in Scheme 2. Increasing the concentration of either BCTD or AIBN will raise the probability of the reaction between BCTD and AIBN, thus leading to an increase in the concentration of CYCBD generated *in situ*. Moreover, the fragments of BCTD can react with the growing polymer radicals to form Marco-CTA. As a result, the increase of BCTD concentration can increase not only the concentration of CYCBD but also the amount of Marco-CTA. On the contrary, although the increasing AIBN concentration will raise the number of CYCBD, meanwhile, it can also increase the amount of propagating radicals. Consequently, only the increase of the concentration of BCTD but not AIBN can markedly promote the living features of MMA polymerization. Nevertheless, compared to [BCTD] : [AIBN] = 2 : 1 or 1 : 1, the PMMA obtained using a higher concentration of BCTD ([BCTD] : [AIBN] = 4 : 1), despite showing lower molecular weight, had slightly higher polydispersities. This result can be deduced that the ratio of BCTD to AIBN in the range of 1–2 might be a more appropriate selection for RAFT polymerization of MMA. Generally, the characteristics of living polymerization increases with raising the ratio of the RAFT agent concentration to the initiator concentration, which leads to narrowing the molecular weight distributions and lowering the PDI values. For example, increasing the ratio of BCTD to AIBN from 1 : 3 to 2 : 1, demonstratively, led to a lower molecular weight and PDI. The high concentration of BCTD ([BCTD] : [AIBN] = 4 : 1) results in a slightly broader polydispersity, which can be ascribed to that the increase in the concentration of BCTD may increase the occurrence of side reactions. The polymers produced by these side reactions, as shown in Scheme 2, may have different chain length and
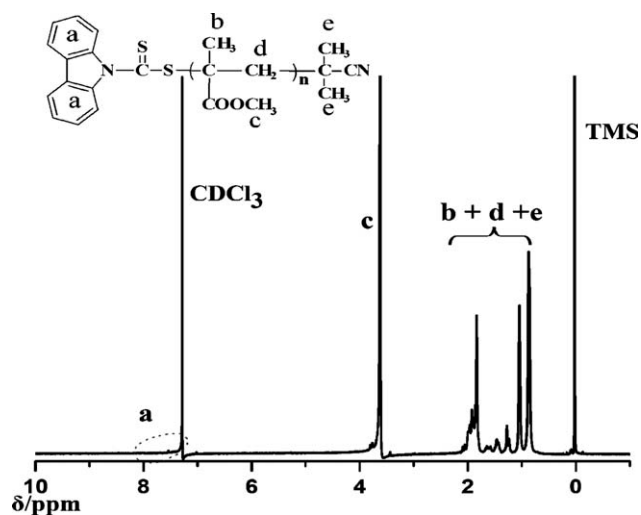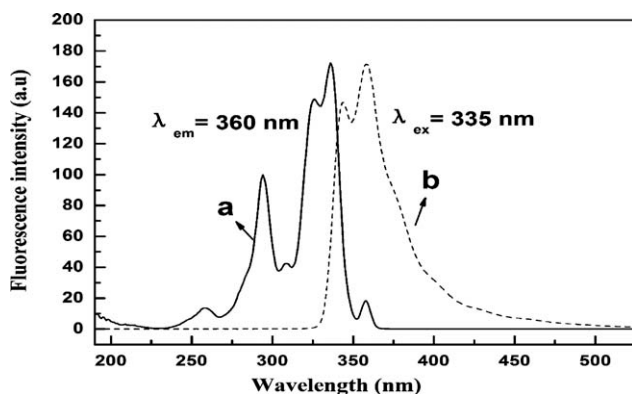

Figure 5 ^{1}H-NMR spectrum of PMMA mediated by CYCBD generated *in situ* by the reaction of BCTD with AIBN ([MMA] : [CTA] : [AIBN] = 400 : 2 : 1; temperature = 60°C; Conv. = 36.98 %; $M_n = 2.08 \times 10^4$ g/mol).

architecture, leading to broadening of the molar mass distributions.[22]

In addition, it should be noted that the experimental molecular weights of PMMA mediated by BCTD were significantly larger than the molecular weights of PMMA prepared by CYCBD or the corresponding theoretical values. It is clearly indicated in Scheme 2 that only a part of the initiator fragments can react with BCTD to produce CYCBD and another part will initiate the growing polymer radicals. The fragments of BCTD may undergo some side reactions other than directly producing CYCBD. All these factors result in that the amount of CYCBD obtained from the reaction of BCTD and AIBN varied during the polymerization process and was also significantly lower than that of the theoretical yield of CYCBD. As a result, it is no wonder that the experimental molecular weights of PMMA mediated by BCTD were significantly larger than the corresponding theoretical values.

The polymerization temperature is one of the important parameters in living free-radical polymerization. The effect of reaction temperature on the RAFT polymerization of MMA has been probed using cyanoisopropyl dithiobenzoate as RAFT agent.[24] The research has confirmed that the higher temperature can increase both the rate of polymerization and the transfer constant of the RAFT agent, leading to lower polydispersities at a given conversion. It can be seen from the Figure 4(c,d) that the polymerization temperature also can exert significant effects on the BCTD-mediated MMA polymerization. The molecular weights and the polydispersities of PMMA obtained at higher reaction temperature (70°C and 80°C) were quite higher than those

Figure 6 Fluorescence spectra of PMMA mediated by CYCBD generated *in situ* by the reaction of BCTD with AIBN [(a): fluorescence excitation spectra emitted at 360 nm; (b): fluorescence emission spectra excited at 335 nm; [MMA] : [CTA] : [AIBN] = 400 : 2 : 1; temperature = 60°C; Conv. = 36.98%; $M_n = 2.08 \times 10^4$ g/mol; The concentration of PMMA in THF = 6.6 μmol/mL).

obtained at 60°C, indicating a faster but less controlled polymerization. These results seemed inconsistent with the previous finding that the higher temperature proved beneficial in all the important aspects, including faster polymerization and narrower PDI. This may be due to the following facts: the high temperature favors AIBN decomposition leading to an increase in radical formation and consequently increases the probability of termination reactions. In addition, the high temperature may increase the likelihood of the side reactions of BCTD other than directly producing CYCBD and RAFT-end capped chains.

Structure characterization of PMMA by ^{1}H-NMR and fluorescence spectrometer

As mentioned earlier, the polymerizations of MMA in the presence of BCTD and AIBN were performed according to the RAFT mechanism. Furthermore, the color of PMMA prepared by BCTD and AIBN possessed the characteristic yellow of the polymers produced by RAFT technique. It can be deduced from these results that the formation of CYCBD and carbazole end-labeled PMMA chains should occur during the polymerization process. The end-groups of PMMA mediated by CYCBD generated *in situ* by the reaction of BCTD with AIBN were characterized and analyzed by ^{1}H-NMR, as shown in Figure 5. The signal above 7.0 ppm corresponding to the aromatic protons of CBTD and the signal at 1.0–2.1 ppm assigning to the methyl and methylene protons can provide certain pieces of evidence to confirm the formation of the CYCBD by the reaction of BCTD with AIBN. However, the evidence was not conclusive enough, since the NMR signals of **a** and **e** corresponding to the terminal groups were very weak. In

order to further verify the above conclusions, the fluorescence spectroscopy of the resultant PMMA was measured. As mentioned earlier, the carbazyl group would be capped at the end of PMMA chain if the MMA polymerization was mediated by CYCBD generated *in situ* from BCTD with AIBN. The fluorescence excitation and emission spectra of the resultant PMMA in dilute THF solution was shown in Figure 6. The PMMA obtained using BCTD and AIBN exhibited an excitation with peaks at about 294, 325, and 335 nm at the emitting wavelength of 360 nm, and showed an emission with peaks at about 342 and 360 nm at the exciting wavelength of 335 nm. The appearances of these characteristic peaks confirmed the formation of CYCBD and carbazole end-labeled PMMA chains.

CONCLUSION

Bis(thiocarbonyl) disulfide compounds are one of the most popular intermediates for the synthesis of the high-performance RAFT agents with 2-cyano-prop-2-yl or its homologous group as R group. In this article, an aqueous phase method was developed to prepare high-purity BCTD based on a straightforward oxidation reaction using $K_3[Fe(CN)_6]$ as the oxidant in water. This new aqueous phase method was proved to be a convenient, economical and eco-friendly route to synthesize bis(thiocarbonyl) disulfides with high purity and high yield. Subsequently, the RAFT polymerizations of MMA have been carried out by using CYCBD as CTA generated *in situ* by the reaction of BCTD with AIBN. The polymerization performed according to a conventional free-radical polymerization in initial reaction phase and subsequently switched to a typical controlled/living polymerization. In the second polymerization phase, the molecular weights of PMMA linearly increase with monomer conversions and PDI can remain in a relatively low range. Furthermore, ^{1}H-NMR analysis and fluorescence spectroscopy of the resultant PMMA confirmed the formation of CYCBD *in situ* by the reaction of BCTD with AIBN and carbazole end-labeled PMMA chains. RAFT polymerization using BCTD and AIBN to synthesize CTA *in situ* may provide an alternative and complementary path to obtain well-defined polymers, especially for preparation of polymers with high molecular weight and a relatively low polydispersity.

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