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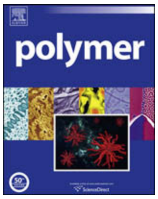

RAFT polymerization of styrene mediated by naphthalene-containing RAFT agents and optical properties of the polymers

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ABSTRACT

In this paper, we designed and synthesized five novel reversible addition–fragmentation chain transfer (RAFT) agents bearing naphthyl moieties in the Z or R groups, including 3,4,5-trimethoxy-benzyl dithio-2-naphthalenoate (TOBDN), 4-nitrobenzyl dithio-2-naphthalenoate (NBDN), 1-menaphthyl 4-cyanodithiobenzoate (NCDB), 1-menaphthyl dithiobenzoate (NDB) and 1-menaphthyl dithio-2-naphthalenoate (NDN). The RAFT polymerizations of styrene mediated by these RAFT agents with AIBN as the initiator at 80 °C were conducted and evaluated. Except for NCDB, the RAFT agents showed good control over the polymerization at different RAFT agent concentrations: the $M_{n,GPC}$ increased linearly with the monomer conversion, and the PDIs of the polymers were relatively low (PDI = 1.20–1.50). The structure of RAFT agents bearing three different R groups with naphthyl as the Z group showed less effects on the polymerization rate, while those bearing different Z groups with 1-menaphthyl as the R• group presented significant effects on the polymerization rates. The polymerization rate with phenyl as the Z group was higher than that with 2-naphthyl as the Z group, and it decreased significantly when using 4-cycno phenyl as the Z group. Retardation effects were observed with all the RAFT agents. ^{1}H NMR spectra and chain extension results confirmed that most of the polymer chains were "living". Ultraviolet (UV) absorption of naphthyl moieties at the R• group showed blue shifts compared with those of naphthyl at the Z group. The UV absorption intensity of PS was uniformly lower than that of the corresponding RAFT agent, while the fluorescence intensity of PS was higher than that of the corresponding RAFT agent.

1. Introduction

Reversible addition–fragmentation chain transfer (RAFT) polymerization, which was developed in 1998 [1,2], assimilated the advantages of radical polymerization and living polymerization. RAFT can produce polymers with well-defined architectures, predetermined molecular weights and narrow molecular weight distributions. RAFT polymerization can also be performed in bulk, solution, suspension and emulsion conditions as those used in conventional radical polymerization. Furthermore, the fact that a large variety of monomers can be polymerized by the RAFT method makes RAFT predominant over other "living"/controlled free radical polymerization methods, such as atom transfer radical polymerization (ATRP) [3–5], and stable free radical polymerization (SFRP) [6,7]. RAFT is expected to be one of the most promising methods among the "living"/controlled free radical polymerizations in terms of practical applications.

The mechanism of RAFT polymerization was firstly proposed by Rizzardo et al. [1,2], in which the repeated reversible transfer events of the RAFT agents, e.g., dithioesters, during polymerization induce equilibria between the dormant and living chains, resulting in the "living"/controlled behavior of the polymerization (Scheme 1) [8].

A RAFT agent usually has the structure of Z–C(=S)–S–R, and the selection of the Z and R groups is crucial in order to obtain a well-behaved polymerization [9,10]. For a given monomer, to achieve effective control, the Z group of a RAFT agent should be selected such that the C=S double bond be activated toward free radical addition. It has been reported that electron-withdrawing groups, which make the thiocarbonyl more electrophilic, can facilitate free radical addition to the C=S double bond and provide effective control even at the early stage of polymerization [11]. Meanwhile, the R• group must be a good homolytic leaving group relative to the attacking radical P_n• (Scheme 1). The rate of fragmentation of intermediate 3 (Scheme 1) can be enhanced by the increase in steric hindrance, the presence of electron-withdrawing groups and the stability of the radical R [8]. The R• formed must be able to re-initiate polymerization. Therefore, for a desired R group of the RAFT agent, an appropriate balance between the leaving ability of the substituent R and the ability of the re-initiation should be considered. Rizzardo et al. elaborately constructed guidelines for selecting RAFT agents for the polymerization of various monomers, and they

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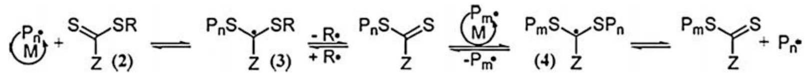
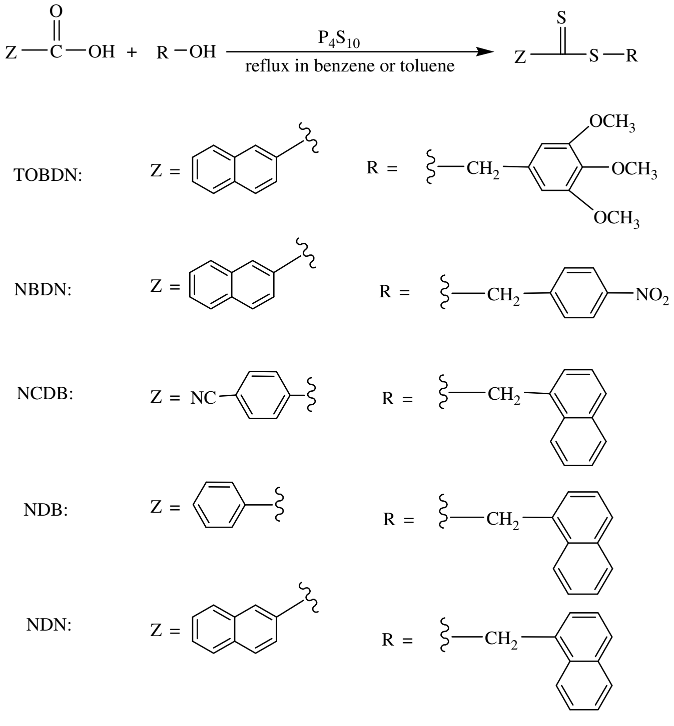


Scheme 1. Mechanism of RAFT polymerization.

reported the effects of R and Z on the effectiveness and the transfer coefficients of RAFT agents [9,10,12,13]. According to the RAFT mechanism, most of the polymer chains from the RAFT polymerization are end-capped by the Z and R groups at the ω and α chain-ends, respectively. Hereby, RAFT polymerization provides a means of introducing functional groups into the ends of a polymer chain by selecting appropriate RAFT agents [14,15].

Naphthyl-containing polymers have received increasing attention since they are useful optical materials for use in ultraviolet (UV) radiation and intramolecular excimer fluorescence [16–21]. Until now, most of the naphthyl moieties have been incorporated into the polymer chains as side groups [22–27]. The attachment of naphthyl moieties at the ω or α polymer chain-ends can be achieved by the "living"/control radical polymerization method with the functional initiator of ATRP, functional alkoxyamine in SFRP or functional chain transfer agent in the RAFT process. The RAFT polymerization is superior to other "living"/control radical polymerizations since it can modify the polymer with naphthyl moieties at the ω, or α, or both chain-ends, which is difficult to attain by ATRP or SFRP. Thus, the optical performance of the polymers arising from the naphthyl groups can be investigated and compared with the different positions of the naphthyl groups at the polymer chain-ends, such as ω, or α, or both. To the best of our knowledge, the comparison of the optical performance of naphthyl groups at different positions of the polymer chain-ends has not been reported.

The present work is aimed at the synthesis of well-defined polymers with naphthyl moieties attached at the chain-ends by RAFT polymerization. Five RAFT agents bearing naphthyl moieties at the Z, or R, or both positions were synthesized. Profiles of the polymerization of styrene with these RAFT agents were then investigated. The optical performance of end-functionalized polymers with naphthyl groups was explored and compared by UV–Vis and fluorescence measurements.



Scheme 2. Illustration of the structures and synthetic routes of RAFT agents.

2. Experimental section

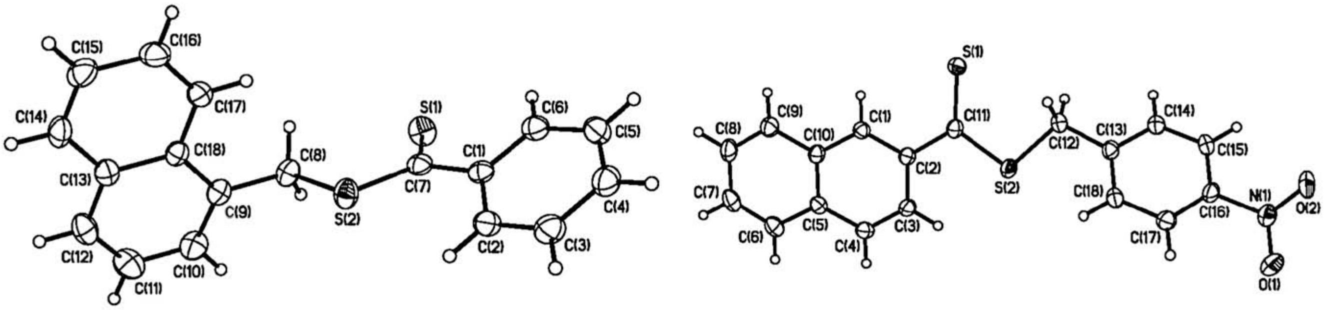
2.1. Materials

2-Formyl naphthalene (98%), 3,4,5-trimethoxyl phenylcarbinol (97%) and 4-cyano benzoic acid (97%) were purchased from Alfa Aesar Co. Ltd. 4-Nitro phenylcarbinol (98%) was purchased from Fluka Co. Ltd. 1-Naphthylcarbinol was purchased from Sigma–Aldrich Co. Ltd. Styrene (Shanghai Chemical Reagents Co. Ltd. China) was washed with an aqueous solution of sodium hydroxide (5 wt%) three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, the styrene was distilled under reduced pressure and kept in a refrigerator at 4 °C. Benzene was dried by a 4 Å molecular sieve and distilled before use. Other chemicals (analytical grade) used in this study were purchased from Shanghai Chemical Reagents Co. Ltd.

2.2. Synthesis of the RAFT agents

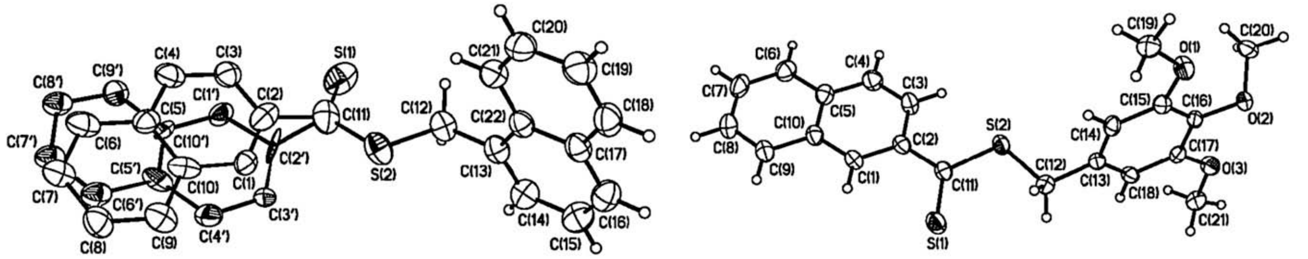
The RAFT agents were synthesized according to the literature [28–30]. The chemical structures and the synthetic routes of these RAFT agents are presented in Scheme 2. Typical procedures for the synthesis of TOBDN were as follows: 2-formyl naphthalene (2.5 mmol, 0.44 g), 3,4,5-trimethoxyl phenylcarbinol (2.5 mmol, 0.41 g), P_4S_{10} (1.25 mmol, 0.56 g), sodium acid carbonate (0.50 g) and benzene (20–25 mL) were added to a 50 mL three-neck-round bottom flask. The solution was then heated and refluxed for 10 h under argon atmosphere. Subsequently, the reaction solution was cooled and filtered. Solvent from the filtrate was removed by rotation evaporation. The crude product was purified by a column chromatogram of silica oxide with petroleum ether/acetic ether (v:v = 5:1) as the eluent. Then, it was recrystallized from petroleum ether. The purity of TOBDN was greater than 97.1% as determined by HPLC (Shimadzu 14B) with a yield of 30%. ^{1}H NMR ($CDCl_3$): 3.73 ppm (s, 9H), 4.50 ppm (s, 2H), 6.5 ppm (s, 2H), 7.3–8.7 ppm (m, 7H); Elemental analysis: Calcd. (%) C 65.60, H 5.24; Found (%) C 64.85, H 6.09; Melting point (M.p.): 104.3–107.4 °C. Other RAFT agents were synthesized with similar procedures. NBDN was obtained in 18% yield with a purity of 97.8%. ^{1}H NMR ($CDCl_3$): 4.8 ppm (s, 2H), 7.3–7.9 ppm (s, 2H), 7.3–8.5 ppm (m, 7H), M.p.: 97.8–99.3 °C. NCDB was obtained in 15% yield; ^{1}H NMR ($CDCl_3$): 5.0 ppm (s, 2H), 7.4–7.7 ppm (m, 8H), 7.8–8.1 ppm (m, 3H). Elemental analysis: Calcd. (%) C 71.44, H 4.10, N 4.38; Found (%) C 70.92, H 4.66, N 3.89; M.p.: 55.8–58.8 °C; NDB was obtained in 28% yield; ^{1}H NMR ($CDCl_3$): 5.0 ppm (s, 2H), 7.0–7.6 ppm (m, 9H), 7.7–8.0 ppm (m, 3H). Elemental analysis: Calcd. (%) C 73.43, H 4.79; Found (%) C 73.98, H 5.14; M.p.: 57.1–60.9 °C; NDN was obtained in 25% yield; ^{1}H NMR ($CDCl_3$): 5.1 ppm (s, 2H), 7.4–8.2 ppm (m, 13H), 8.6 ppm (s, 1H). Elemental analysis: Calcd. (%) C 76.70, H 4.68; Found (%) C 76.33, H 4.89; M.p.: 91.6–96.3 °C.

The single crystals of the RAFT agents shown above, with the exception of NCDB, have been obtained. Their crystal structures were confirmed by X-ray diffraction. Fig. 1 shows the crystal structures of NDB (1), NBDN (2), NDN (3) and TOBDN (4).



(1) NDB

(2) NBDN



(3) NDN

(4) TOBDN

Fig. 1. Single crystal structures of NDB, NBDN, NDN and TOBDN obtained by X-ray diffraction.

2.3. RAFT polymerization of styrene (St)

For RAFT polymerization, the following procedures were typical. A master batch of 10 mL (86.90 mmol) of St, 267.31 mg (0.69 mmol) of TOBDN and 22.83 mg (0.14 mmol) of AIBN was prepared, and an aliquot of 1 mL of the solution was placed in a 2 mL-ampoule. The content was purged with argon for approximately 10 min to eliminate oxygen. Then, the ampoule was flame-sealed. The polymerization reaction was performed at a predetermined temperature. After the prescribed reaction time, the reaction was quenched by immersing the ampoule in ice water. The reaction mixture was diluted with THF (about 2 mL), and precipitated in a large volume of

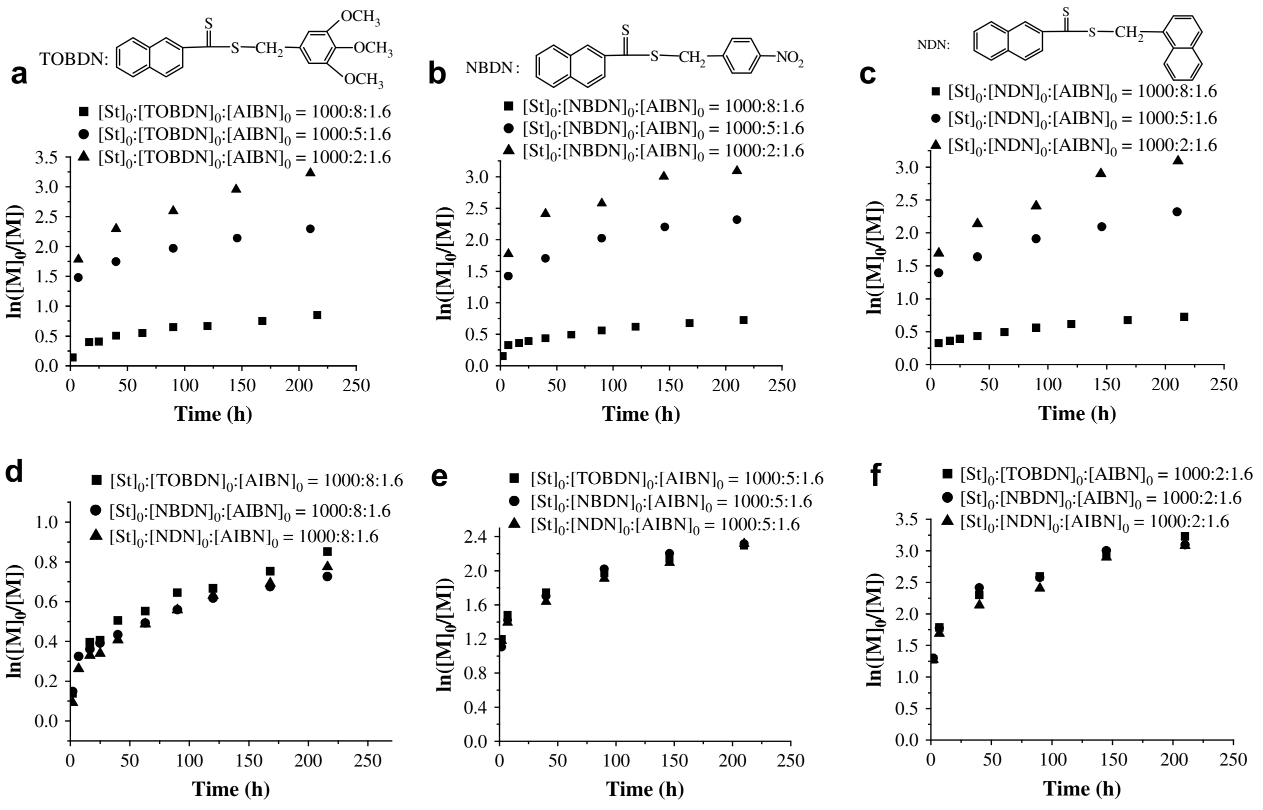


Fig. 2. Kinetic plots of the RAFT polymerization of styrene mediated by RAFT agents bearing different R groups with 2-naphthyl as the Z group at various concentrations of the RAFT agents at 80 °C. $[St]_0 = 8.74$ mol/L.

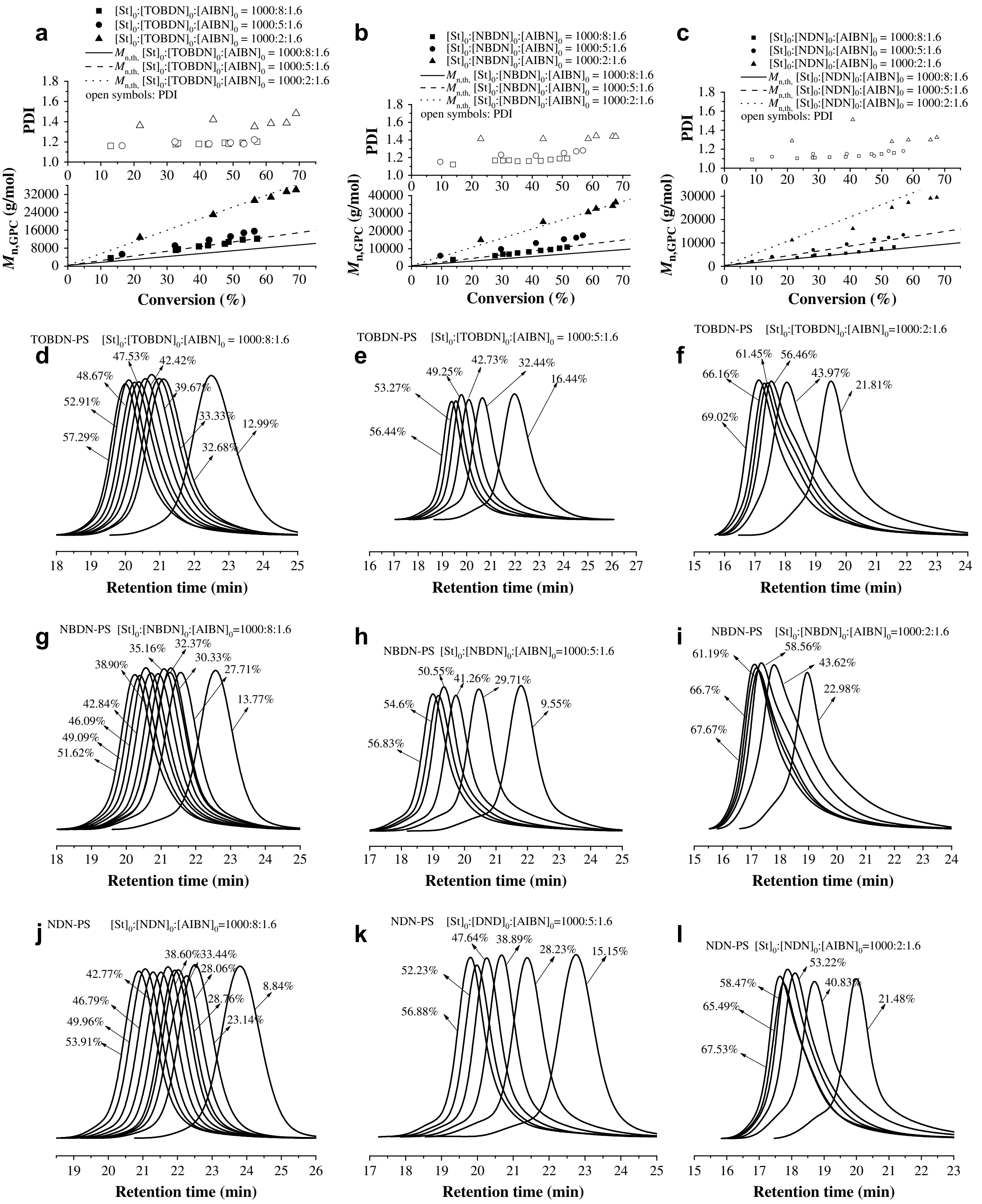


Fig. 3. Evolution of $M_{n,GPC}$, PDI and GPC curves with monomer conversion for the RAFT polymerization of styrene with three RAFT agents. Polymerization conditions are the same as those in Fig. 2. $M_{n,th} = [St]_0/[RAFT\ agent]_0 \times conversion \times M_{st}$ (104) + m. w. of RAFT agent. 104 refers to the molecular weight of styrene.

methanol (about 200 mL). The polymer was obtained by filtration and dried at room temperature under vacuum to a constant weight. The conversion of styrene was determined gravimetrically.

2.4. Chain extension of polystyrene (PS)

The procedure of the chain extension experiment was similar to that of RAFT polymerization except that the RAFT agent was replaced by PS synthesized via RAFT polymerization.

2.5. Characterization

The number-average molecular weight (M_n) and polydispersity (PDI) of the synthesized polymer were determined by a Waters 1515 gel permeation chromatographer (GPC) equipped with a refractive 494 index detector, using HR1, HR3, and HR4 columns with a molecular weight range of 100–5,00,000 calibrated with PS standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. ^{1}H NMR spectra of the polymers were recorded on an INOVA400 nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. Elemental analyses (EA) of C, H and N were conducted by the EA1110 CHND-S. The UV–Vis absorption spectra of the polymers in $CHCl_3$ solution were determined on a Shimadzu RF540 spectrophotometer. The fluorescence intensity was measured by fluorometry (FLS920, Edinburgh Instruments Co. Ltd.). The crystal structures of the RAFT agents were measured by CDD single crystal diffraction (Rigako Mercury CDD).

3. Results and discussions

3.1. RAFT polymerization of St mediated by RAFT agents bearing different R groups with 2-naphthyl as the Z group

In the RAFT polymerization process, the effectiveness of the RAFT agent depends on the nature of the combination of the monomer to be polymerized and the RAFT agent used [9,10,13]. The R and Z groups of the RAFT agent determine the effectiveness of the RAFT agent to a large extent [9,10,13]. In general, the R group is required to be a good leaving group in comparison with the growing polymeric chain and a better reinitiating species than the monomer used. The stability, steric bulk, and polarity of $R^\bullet$ should also be considered for the selection of the $R^\bullet$ group [9,31–33]. In the present work, RAFT agents bearing three different R groups with naphthyl as the Z group were designed and synthesized. The R groups were selected to be 3,4,5-trimethoxy-benzyl, 4-nitro-benzyl and 1-menaphthyl corresponding to TOBDN, NBDN and NDN, respectively. Fig. 2(a)–(c) illustrates the respective kinetic plots for the polymerizations of St mediated by TOBDN, NBDN and NDN at various concentrations at 80 °C.

It can be found from Fig. 2(a)–(c) that the polymerization rate decreased with an increase of the three RAFT agent concentrations, indicating the existence of retardation effects [34–46] in the polymerization process. The retardation has been frequently observed in common RAFT polymerization, although the causes for the retardation effect are still under debate [34–46]. There are two predominant theories on the retardation effects [41]. The theory proposed by Barner-Kowollik et al. [37] assumes that the

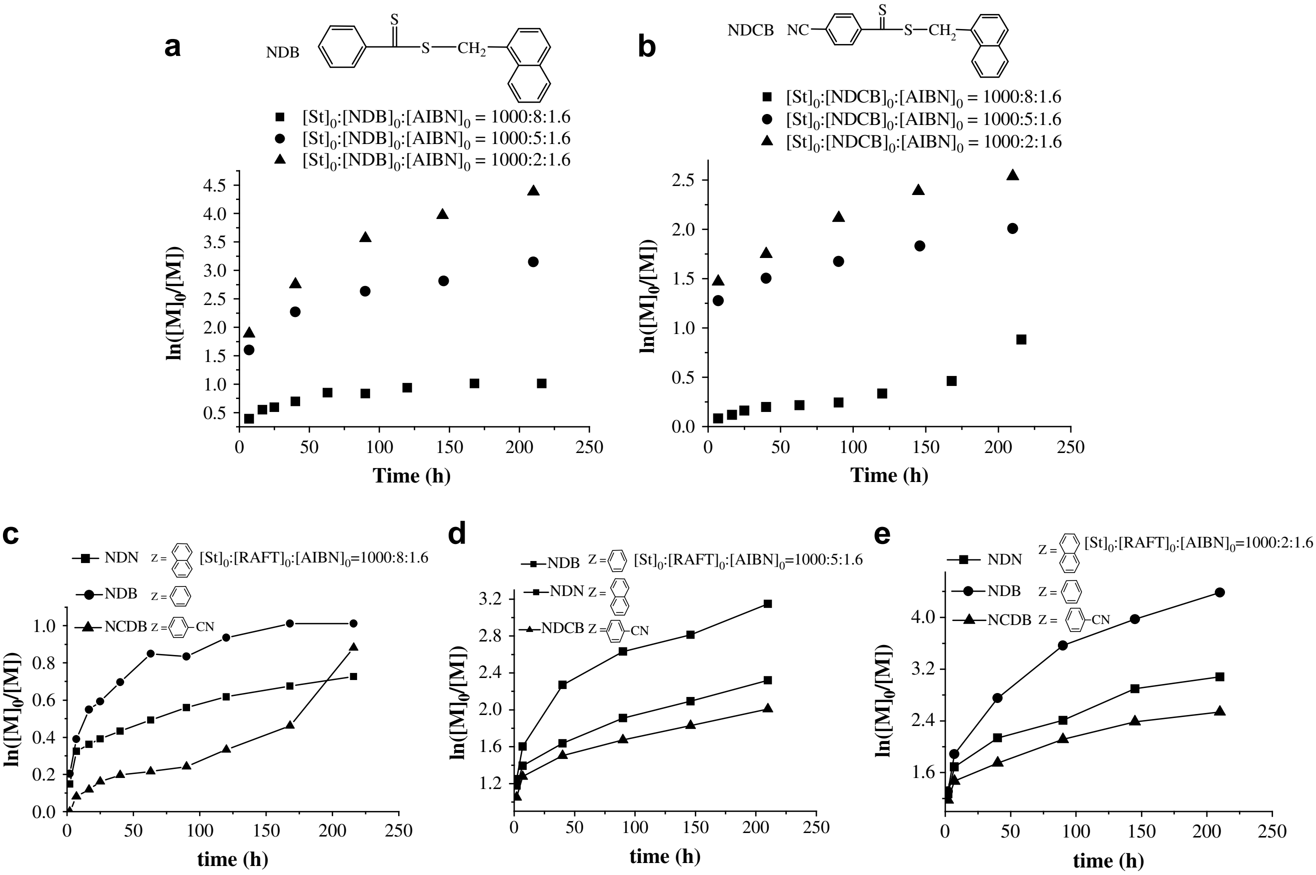


Fig. 4. Kinetic plots of the RAFT polymerization of styrene mediated by RAFT agents bearing different Z groups with 1-menaphthyl as the $R^\bullet$ group at various concentrations of RAFT agents at 80 °C. $[St]_0 = 8.74$ mol/L.

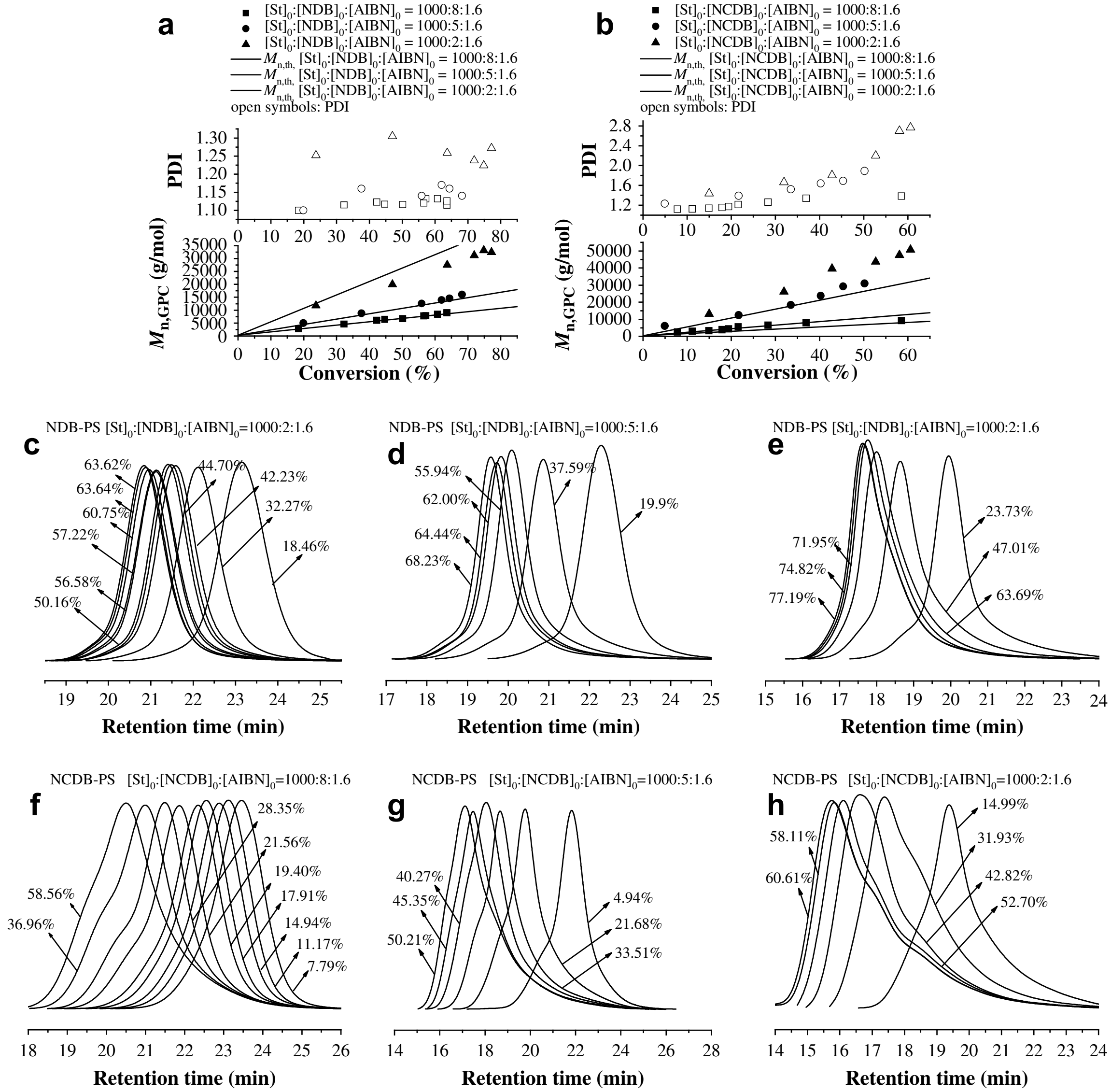


Fig. 5. Evolution of $M_{n,GPC}$, PDI and GPC curves with monomer conversion in the RAFT polymerization of styrene with three RAFT agents. Polymerization conditions are the same as those in Fig. 4. $M_{n,th} = [St]_0/[RAFT\ agent]_0 \times conversion \times M_{St}$ (104) + m. w. of RAFT agent. 104 refers to the molecular weight of styrene.

intermediate radical formed in the RAFT polymerization process is relatively stable and long-lived. The authors denote this theory as the slow fragmentation model. The theory of Monteiro et al. [35] for retardation of RAFT polymerization suggests that there is significant cross-termination of the intermediate radical with other free radicals existing in solution. The authors denote this theory as the intermediate radical termination model. Recently, Sébastien Perrier demonstrated that the above two conflicting theories on the retardation effect in RAFT polymerization can actually coexist [44]. In Fig. 2(d)–(f), it was found that the polymerization rate shows less dependence on the particular dithio-2-naphthoate derivative with different R groups at three concentrations of RAFT agents. Similar results were reported in the literature, mainly due to the smaller dependence of the rate constant for addition to the thiocarbonyl on the R group [8,9,34,41,43–47].

Fig. 3 exhibits the evolution of number-average molecular weight ($M_{n,GPC}$), polydispersity index (PDI), as well as the corresponding GPC traces of the styrene with the monomer conversion in RAFT polymerization mediated by TOBDN, NDN and NBDN at different RAFT agent concentrations. In the context, PS obtained by TOBDN, NBDN and NDN are referred as TOBDN–PS, NBDN–PS and NDN–PS, respectively. From Fig. 3(a)–(c), at three concentrations of RAFT reagents, the GPC molecular weights ($M_{n,GPC}$) of TOBDN–PS, NBDN–PS and NDN–PS increased linearly with monomer conversion and were close to the predicted molecular weight ($M_{n,th}$). PDIs from the polymers were lower than 1.5. These results indicated the “living” behavior of the polymerizations mediated by these three RAFT agents. Concentrations of RAFT agents were also found to have some effect on the PDIs of the polymers. The PDIs increased from 1.2 to 1.5, when depressing the molar ratios of St to RAFT agent from 1000:8 to 1000:2. The $M_{n,GPC}$ values of TOBDN–PS and NBDN–PS were slightly higher than the calculated values ($M_{n,th}$) at high molar ratios of RAFT agent. The deviation may be due to relative low chain transfer coefficients with incomplete consumption of the RAFT agents [8,47]. The $M_{n,GPC}$ of NDN–PS agreed well with the predicted value. The control of NDN can be due to the fact that the R group of NDN was a large conjugate system of menaphthyl, which produced a more stable R• compared with those of TOBDN and NBDN. The stable R• induced a higher fragmentation rate and higher chain transfer coefficients [8,47]. In Fig. 3(d)–(l), the GPC elution profiles of three

RAFT agents under various concentrations with monomer conversion showed mono-distributions, indicating the living character of the polymerizations.

3.2. RAFT polymerization mediated by RAFT agents bearing different Z groups with 1-menaphthyl as the R group

The Z group strongly influences the stability of the intermediate radical (Scheme 1). An activated Z group to the thiocarbonyl double bond will improve the stability of intermediate radicals and hence favor the formation of the intermediate. However, the stability of the intermediate also needs to be balanced with its reactivity toward fragmentation which frees the reinitiating group (R•). Numerous groups have investigated with respect to the effects of the Z group on the polymerization of a variety of monomers [9,16,50–55]. It has been concluded that an aryl group was one of the best candidates for the control over a wide range of monomers, such as styrene, methacrylates, acrylates, etc. It has also been reported that the electron-withdrawing groups in Z can enhance the rate of radical addition to the C=S double bond and produce polymers with narrow polydispersity from the early stage of polymerization [11].

In this work, phenyl, naphthyl and 4-cycno phenyl were selected as three different Z groups connecting in NDB, NDN and NCDB, respectively. The polymerization results of NDN at various concentrations at 80 °C are shown in Figs. 2(c), 3(c), and (j)–(l). The polymerization results of NDB and NCDB at various concentrations at 80 °C are shown in Fig. 4(a) and (b). It was found from Fig. 4(a) and (b) that retardation effects were also observed with NDB and NCDB as RAFT agents. In Fig. 4(c)–(e), the polymerization rate of NDB with phenyl as the Z group, at various concentrations, was higher than that of NDN with 2-naphthyl as the Z group. It can also be seen from Fig. 4(c)–(e) that the polymerization rate was significantly lower when NCDB was used as the RAFT agent. Earlier efforts by Rizzardo et al. demonstrated that electron-withdrawing substituents on Z could enhance the stability of the intermediates [8,10,41,43,45,46]. However, very stable intermediates did not form free radicals easily, which resulted in the slow fragmentation of the intermediates as well as the increase to some extent of the polymerization retardation [35,44,48].

Fig. 5 shows the evolution of the $M_{n,GPC}$, PDI and GPC curves of polystyrene obtained by NDB and NCDB with monomer conversion at various concentrations of the RAFT agent at 80 °C. The polystyrene obtained from NDB and NCDB is referred to as NDB–PS and NCDB–PS, respectively. "Living" attributes were observed in the NDB (Fig. 5(a), (c)–(e)) and NDN (Fig. 3(c), (j)–(l)) mediated systems: $M_{n,GPC}$ increased with monomer conversion and agreed well with $M_{n,th}$. The PDIs values from the polymers were below 1.40. It was found from Fig. 3(j)–(l) and Fig. 5(c)–(e) that the GPC traces of polystyrene mediated by NDN and NDB showed Gaussian distributions with conversion evaluation. In the NCDB mediated system, poor control over the polymerization was found by the indication of the $M_{n,GPC}$ deviating from the theoretical ones and PDI values increasing from 1.11 to 2.8, as well as the non-monomudal distribution of the GPC traces (Fig. 5(f)–(h)). Such an observation may be due to presence of highly stable intermediate radicals arising from NCDB, enhancing their probability of termination with propagating radicals or themselves, potentially resulting in the formation of 3 or 4-arm structure compounds [35,41,44,49].

3.3. End group analysis and chain extension experiments

The chain-ends of the polystyrene prepared by the RAFT agents bearing naphthyl moieties were analyzed by ^{1}H NMR spectra. As

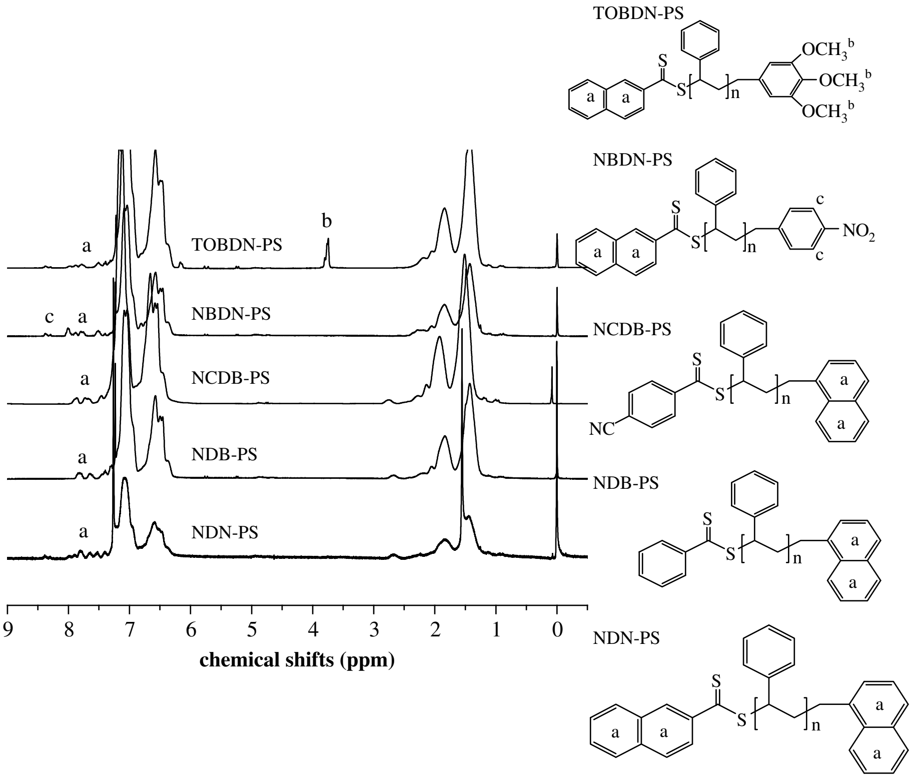


Fig. 6. ^{1}H NMR spectra of polymers prepared by RAFT agents with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. TOBDN–PS: $M_{n,GPC} = 8000$ g/mol, PDI = 1.14; NBDN–PS: $M_{n,GPC} = 4200$ g/mol, PDI = 1.08; NCDB–PS: $M_{n,GPC} = 6180$ g/mol, PDI = 1.18; NDB–PS: $M_{n,GPC} = 4980$ g/mol, PDI = 1.09; NDN–PS: $M_{n,GPC} = 2250$ g/mol, PDI = 1.16.

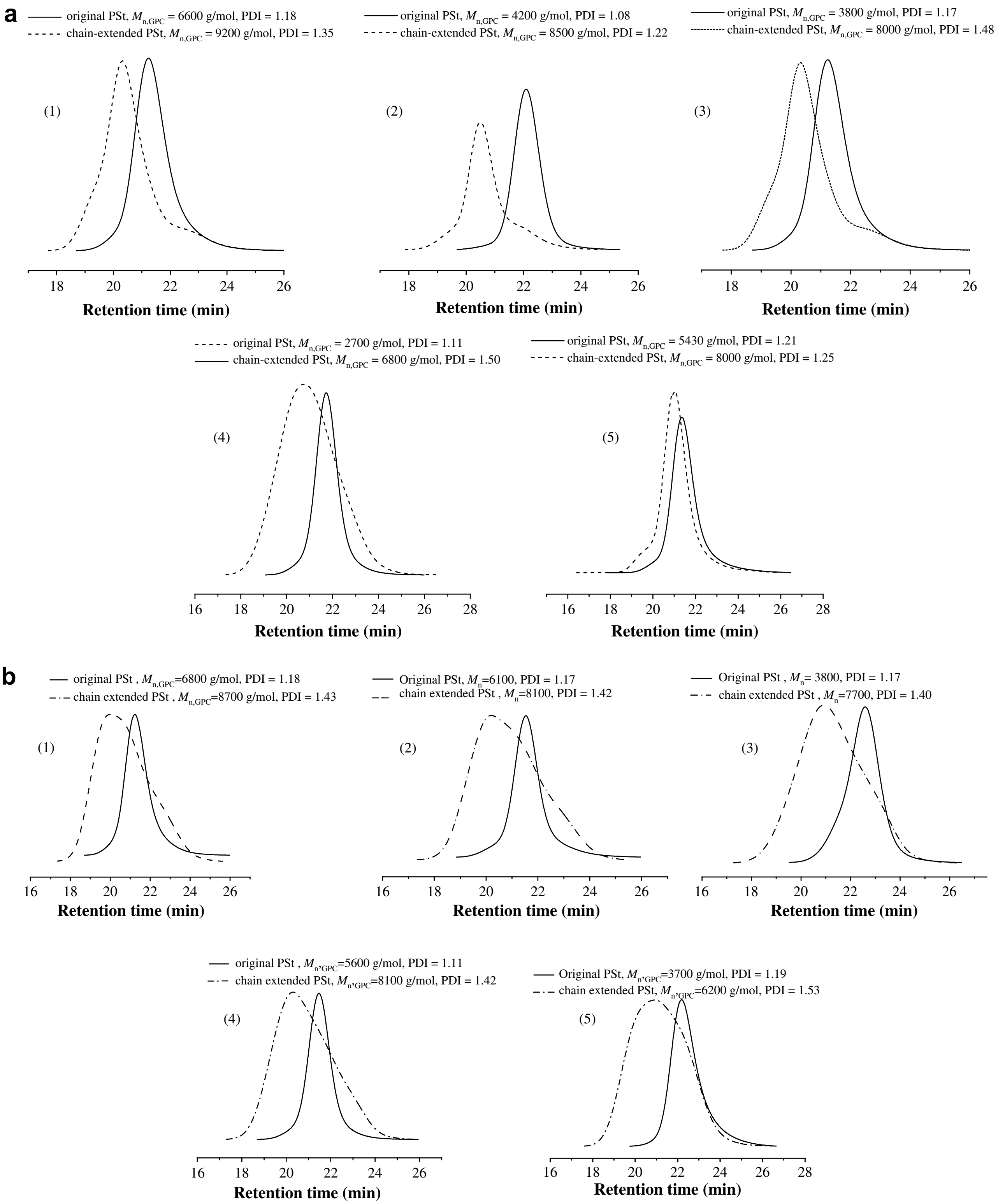


Fig. 7. (a) GPC curves of the original PS and chain extension polymers using styrene as the monomers with the molar ratio of $[St]_0$:[macro-RAFT agent]$_0$:$[AIBN]_0 = 500:3:1$. (1) TOBDN–PS $T = 80\,^\circ C$, $t = 1.5$ h, conversion = 37.1%; (2) NBDN–PS, $T = 90\,^\circ C$, $t = 3.5$ h, conversion = 49.7%; (3) NCDB–PS, $T = 80\,^\circ C$, $t = 1.4$ h, conversion = 46.6%; (4) NDB–PS: $T = 80\,^\circ C$, $t = 2.7$ h, conversion = 61.3%; (5) NDN–PS, $T = 90\,^\circ C$, $t = 1.0$ h, conversion = 24.9%. (b) GPC curves of the original PS and chain extension polymers using styrene as the monomers with the molar ratio of $[St]_0$:[macro-RAFT agent]$_0$:$[AIBN]_0 = 500:1.5:1$, at 80 °C. (1) TOBDN–PS, $t = 1.1$ h, conversion = 34.0%; (2) NBDN–PS, $t = 1.0$ h, conversion = 31.3%; (3) NCDB–PS, $t = 2.2$ h, conversion = 43.1%; (4) NDB–PS, $t = 2.0$ h, conversion = 37.7%; (5) NDN–PS, $t = 1.4$ h, conversion = 30.4.

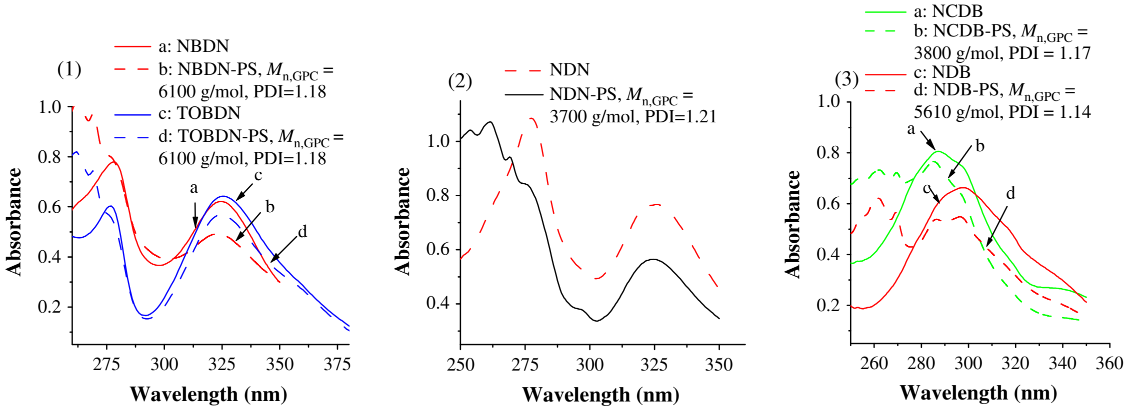


Fig. 8. UV–Vis spectra of the RAFT agents and the corresponding polymers with $CHCl_3$ as the solvent at room temperature. The concentrations of all solutions are 3.0×10^{-5} mol/L. (1) NBDN, TOBDN, NBDN–PS and TOBDN–PS; (2) NDN and NDN–PS; (3) NCDB, NDB, NCDB–PS and NDB–PS.

presented in Fig. 6, all of the ^{1}H NMR spectra showed the signals of the corresponding RAFT agents at 7.4–8.1 ppm, arising from the aromatic protons of the naphthyl units in the RAFT agents. With respect to the TOBDN-mediated PS, the signals at 3.70 ppm (b) corresponded to the methoxyl protons of the TOBDN units, and the $\delta = 8.4$–8.5 ppm (c) in the NBDN-mediated PS can be ascribed to the phenyl protons neighbored at the nitro group of the NBDN units. These results indicate that most of the moieties from the RAFT agent were attached to the polystyrene ends.

To further demonstrate the “living” nature of the RAFT polymerization, the polystyrene samples obtained were used as macro-RAFT agents for chain extension reactions. In Fig. 7(a) and (b), the molar ratio of $[St]_0/[\text{macro-RAFT agent}]_0/[AIBN]_0$ was 500:3:1 and 500:1.5:1, respectively. It was found from Fig. 7(a) and (b) that there were obvious peak shifts from the macro-RAFT agents to the chain extended polymers, and Gaussian distribution of the chain extended polymers was found. These results demonstrated that most of the polystyrene from RAFT polymerizations with the five different RAFT agents were living and can be active for chain extension reactions.

It was found from Fig. 7 that the PDI values of the chain extension polymers were larger than those of the original polymers. The results can be caused by a fraction of the dead polymer chains in the original polymer and the side reactions during the chain extension. The GPC traces of the chain extension polymers obtained from higher concentrations of macro-RAFT agents had better symmetry and smaller PDI values than those obtained from lower concentrations of macro-RAFT agents. The results can be caused by more side reactions during the chain extension at lower concentrations of macro-RAFT agents.

3.4. *Optical properties of PS end-capped by a naphthyl chromophore*

3.4.1. *UV spectroscopy of PS*

In this work, the naphthyl species was designed and incorporated into the Z or R groups of the RAFT agents. As a result, the polymers obtained in the present experiments were end-capped with naphthyl units as confirmed in Fig. 6. Measurements of UV spectroscopy of the naphthyl-based RAFT agent and the corresponding polymers in $CHCl_3$ were carried out according to the high sensitivity of the naphthyl group to ultraviolet light (UV). The results are presented in Fig. 8. It can be found from Fig. 8(1) that TOBDN, NBDN, TOBDN–PS and NBDN–PS exhibited strong absorption peaks at 325 nm resulting from the naphthyl moieties. It can also be found from Fig. 8(1) that strong absorption peaks appeared at 275 nm arising from the phenyl moieties of TOBDN and NBDN. The incorporation of $-NO_2$ and $-OCH_3$ groups into phenyl ring at the respective R• group of TOBDN and NBDN resulted in red shifts of the phenyl species. In Fig. 8(2), NDN exhibited two strong absorption peaks at 325 nm and 275 nm. The strong absorption

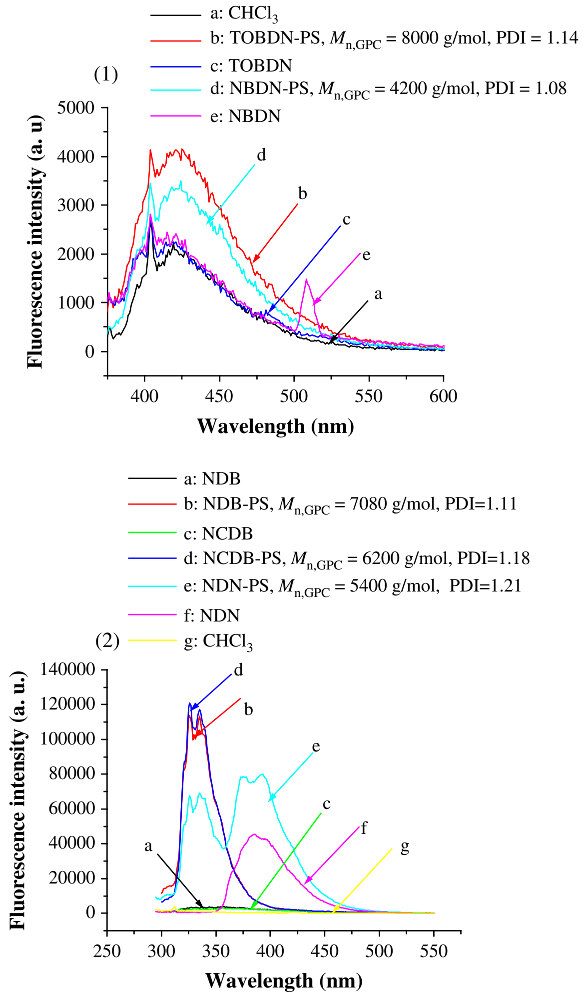


Fig. 9. Fluorescence emission spectra of RAFT agents and the corresponding polymers. (1) TOBDN, NBDN and the corresponding polymers with $CHCl_3$ as solvent at room temperature, $\lambda_{ex} = 360$ nm; (2) NDN, NDB, NCDB and the corresponding polymers, $\lambda_{ex} = 285$ nm. The chromophoric concentrations of all solutions are 3.0×10^{-5} mol/L.

peak at 325 nm was ascribed to the naphthyl moiety at the Z group, which connected directly with the thiocarbonyl group. The absorption peak at 275 nm can be attributed to the naphthyl moiety at the R group, which overlapped with the absorption peak of the phenyl from the PS backbone, resulting in a broad absorption peak between 250 nm and 290 nm. With respect to NDB, NCDB, NDB–PS and NCDB–PS, the UV absorption spectra are presented in Fig. 8(3). The absorption peaks of the naphthyl moieties showed blue shifts compared with those in Fig. 8(1) (naphthyl at the Z group). The naphthyl moieties at the R groups of NDB and NCDB did not connect directly with the thiocarbonyl group, which may be the cause of blue shifts. The naphthyl at the Z group of NDN (Fig. 8(2)) conjugated with the thiocarbonyl to a larger degree in comparison with the phenyl at the Z groups of NDB and NCDB (Fig. 8(3)), which may have resulted in the blue shifts of the naphthyl moieties at the R group in NDN (at around 275 nm) relative to NDB and NCDB (at around 290–300 nm).

Furthermore, it can be found from Fig. 8 that the absorption intensity of PS was uniformly lower than the corresponding RAFT agent. Two factors may be responsible for this result. First, in the polymer, the thiocarbonyl species were separated from the naphthyl groups at the R group by the polymer chain, which could have eliminated the interaction between the thiocarbonyl and the naphthyl ring at the R group, as well as the interaction between the naphthyl ring at the Z group and some groups at the R group, such as NO_2–, OCH_3–. The absorption of the naphthyl was thus depressed. The other factor lies in that, although most of the polymer chains were end-capped by the moieties of the RAFT agents, there was also a small fraction of dead polymer chains without naphthyl moieties, which led to the decreased concentration of naphthyl in the polymer system. As a consequence, the UV absorption of the polymer was lower than that of its corresponding RAFT agent.

3.5. Fluorescence emission of PS

It is well known that naphthyl is one of the typical fluorophores. In this work, the fluorescence emissions of the obtained polymers, together with the relevant RAFT agents, were investigated. Fig. 9 shows the typical fluorescence emission spectra of the polymer and the corresponding RAFT agent in $CHCl_3$ solution. Fig. 9(1) shows that TOBDN, NBDN and the corresponding PS exhibited extremely weak fluorescence emission intensity ($\lambda_{ex} = 360$ nm), and the fluorescence emission intensity of the polymer was a little higher than that of the corresponding RAFT agent. In Fig. 9(2), it can also be seen that NDB and NCDB exhibited very weak fluorescence emission; however, NDB–PS and NCDB–PS had strong fluorescence emission intensity at 330 nm ($\lambda_{ex} = 285$ nm). In the case of NDN–PS, two strong fluorescence emission peaks were observed at 330 nm and 380 nm, respectively. However, the intensity at 330 nm was lower than that of NDB–PS and NCDB–PS. NDN presented a transmitted fluorescence at 380 nm and its intensity was approximately half of that of NDN–PS.

The sulfur atom is a well-known fluorescence-quenching agent. It has been also reported by some authors that the fluorescence attached to the polymers obtained by RAFT polymerization is strongly quenched by the thiocarbonyl [56–61]. With regard to Fig. 9(1), TOBDN, NBDN and the PS derived from them exhibited fluorescence emissions with low intensities, which can be due to the fact that the naphthyl at the Z group connected directly with the thiocarbonyl group. Therefore, the intensity of the fluorescence emission was remarkably quenched by the thiocarbonyl. As for Fig. 9(2), compared with the RAFT agents, the thiocarbonyl in PS was far separated from the naphthalene group by the polymer chain. The quenching effects on the fluorescence were thus depressed, resulting in higher fluorescence intensity for polymers compared with the relevant RAFT agent. With respect to NDN, it incorporated two naphthyl rings both at the Z and R groups. Hereby, the interaction between the molecule of the excited state and the molecule of the ground state may form an exciplex, which can cause specific fluorescence emission distinguished from that of naphthyl. Therefore, NDN may offer a unique fluorescence emission at 380 nm, which is a new fluorescence emission peak different from that of naphthyl. As for NDN–PS, both naphthyl rings were partitioned by the polymer chain; thus, they presented two fluorescence emission peaks with high intensity. One was at 330 nm, which was similar to that of NDB–PS and NCDB–PS with lower intensity; the other was at 380 nm, which was similar to NDN with higher intensity. The reasons for this are not clear at this stage, and further investigation is needed to completely understand the mechanism.

4. Conclusions

In this paper, five novel RAFT agents bearing naphthyl moieties at the Z or R groups were designed and synthesized. The investigation of the polymerization behavior by RAFT agents demonstrated that, with the exception of NCDB, RAFT agents presented good “living”/controllability on the polymerization of styrene: the $M_{n,GPC}$ increased linearly with the monomer conversion, and the PDIs of the polymers were lower than 1.2 at different concentrations of RAFT agents. The RAFT polymerization rates decreased with an increase in RAFT agent concentrations due to the retardation effect in the RAFT polymerization. Three RAFT agents using 3,4,5-trimethoxy-benzyl, 4-nitro-benzyl and 1-menaphthyl as the R group with naphthyl as the Z group showed lesser effects on the RAFT polymerization rate. The RAFT polymerization rates mediated by three RAFT agents using phenyl, naphthyl and 4-cycno phenyl as the Z groups, respectively, with 1-menaphthyl as the R group showed significant differences. The polymerization rate with phenyl as the Z group was higher than that observed with 2-naphthyl as the Z group, and decreased significantly when using 4-cycno phenyl as the Z group. ^{1}H NMR spectra and chain extension results confirmed that most of the polymer chains were “living”. The obtained PS showed typical UV absorption and fluorescence emission arising from the naphthyl moiety. The UV absorption of PS was lower than its corresponding RAFT agent, while the fluorescence of the PS was higher than that of the RAFT agent.

Acknowledgments

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References

[1] Le TP, Moad G, Rizzardo E, Thang SH. PCT Int Appl 1998, WO 98/01478.

[2] Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT. Macromolecules 1998;31:5559–62.

[3] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28:1721–3.

[4] Kamigaito M, Ando T, Sawamoto M. Chem Rev 2001;101:3689–745.

[5] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614–5.

[6] Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661–88.

[7] Georges MK, Veregin PRN, Kazmaier PM, Hamer GK. Macromolecules 1993;26:2987–90.

[8] Moad G, Rizzardo E, Tang SH. Aust J Chem 2005;8:379–410.

[9] Chong BYK, Krstina J, Le TPT, Graeme M, Postma A, Rizzardo E, et al. Macromolecules 2003;36:2256–72.
[10] Chiefari J, Mayadunne RTA, Moad CL, Moad G, Rizzardo E, Postma A, et al. Macromolecules 2003;36:2273–83.
[11] Benaglia M, Rizzardo E, Alberti A, Guerra M. Macromolecules 2005;38:3129–40.
[12] Rizzardo E, Chiefari J, Mayadunne RTA, Moad G, Thang SH. ACS Symp Ser 2000;768:278–96.
[13] Moad G, Chiefari J, Krstina J, Postma A, Mayadunne RTA, Rizzardo E, et al. Polym Int 2000;49:993–1001.
[14] Charles L, Mccormick ABL. Acc Chem Res 2004;37:312–25.
[15] Shim S, Lee H, Choe S. Macromolecules 2004;37:5565–71.
[16] Merle-Aubry L, Holden DA, Merle Y, Guillet JE. Macromolecules 1980;13:1138–43.
[17] Holden DA, Jordan K, Safarzadeh-Amiri A. Macromolecules 1986;19:895–901.
[18] Holden DA, Shephard SE, Guillet JE. Macromolecules 1982;15:1481–5.
[19] Spyros A, Dais P. Macromolecules 1992;25:1062–7.
[20] Pasch NF, Webber SE. Macromolecules 1978;11:727–32.
[21] Somersall AC, Guillet JE. Macromolecules 1973;6:218–23.
[22] Sun J, Tang HD, Jiang JQ, Zhou XS, Xie P, Zhang RB, et al. J Polym Sci Part A Polym Chem 2003;41:636–44.
[23] Naikwadi KP, Wadgaonkar PP. J Chromatogr A 1998;811:97–103.
[24] Liu CQ, Liu Y, Xie P, Zhang RB, Zhu CF, Wang C, et al. Macromol Chem Phys 2001;202:1581–5.
[25] Fox MA, Thompson HW. Macromolecules 1997;30:7391–6.
[26] Colak D, Cianga I, Muftuoglu AE, Yagc Y. J Polym Sci Part A Polym Chem 2006;44:727–43.
[27] Jin YH, Zhu J, Zhang ZB, Cheng ZP, Zhang W, Zhu XL. Eur Polym J 2008; 44:1743–51.
[28] Dureault A, Gnanou Y, Taton D, Destarac M, Leising F. Angew Chem Int Ed 2003;42:2869–72.
[29] Dureault A, Taton D, Destarac M, Leising F, Gnanou Y. Macromolecules 2004; 37:5513–9.
[30] Sudalai A, Kanagasabapathy S, Benicewicz BC. Org Lett 2000;2:3213–6.
[31] Schilli C, Lanzendoerfer MG, Mueller AHE. Macromolecules 2002;35:6819–27.
[32] Perrier S, Barner-Kowollik C, Quinn JF, Vana P, Davis TP. Macromolecules 2002; 35:8300–6.
[33] Donovan MS, Lowe AB, Sumerlin BS, McCormick CL. Macromolecules 2002; 35:4123–32.
[34] Perrier S, Takolpuckdee P. J Polym Sci Part A Polym Chem 2005;43:5347–93.
[35] Monteiro MJ, De Brouwer H. Macromolecules 2001;34:349–52.
[36] Kwak Y, Goto A, Komatsu K, Sugiura Y, Fukuda T. Macromolecules 2004;37: 4434–40.
[37] Barner-Kowollik C, Quinn JF, Morsley DR, Davis TP. J Polym Sci Part A Polym Chem 2001;39:1353–65.
[38] Wang AR, Zhu S, Kwak Y, Goto A, Fukuda T, Monteiro MS. J Polym Sci Part A Polym Chem 2003;41:2833–9.
[39] Coote ML. Macromolecules 2004;37:5023–31.
[40] Barner-Kowollik C, Quinn JF, Nguyen TLU, Heuts JPA, Davis TP. Macromolecules 2001;34:7849–57.
[41] Barner-Kowollok C, Buback M, Charleux B, Coote M, Drache M, Fukuda T, et al. J Polym Sci Part A Polym Chem 2006;44:5809–31.
[42] Monteiro MJ. J Polym Sci Part A Polym Chem 2005;43:3189–204.
[43] Barner-Kowollok C. Handbook of RAFT polymerization. Weinheim: Wiley-GmbH & Co, KGaA; 2008.
[44] Konkolewicz D, Hawkett BS, Gray-Weale A, Perrier S. Macromolecules 2008;41:6400–12.
[45] Barner-Kowollok C, Perrier S. J Polym Sci Part A Polym Chem 2008;46:5715–23.
[46] Geelen P, Klumperman B. Macromolecules 2007;40:3914–20.
[47] Moad G, Rizzardo E, Thang SH. Aust J Chem 2006;59:669–92.
[48] Barner L, Quinn JF, Barner-Kowollik C, Vana P, Davis TP. Eur Polym J 2003;39:449–59.
[49] Hua DB, Ge XP, Bai RK, Lu WQ, Pan CYD. Polymer 2005;46:12696–702.
[50] Destarac M, Brochon C, Catala JM, Wilczewska A, Zard SZ. Macromol Chem Phys 2002;203:2281–9.
[51] Destarac M, Bzducha W, Taton D, Gauthier-Gillaizeau I, Zard SZ. Macromol Rapid Commun 2002;23:1049–54.
[52] Mayadunne RTA, Rizzardo E, Chiefari J, Chong YK, Moad G, Thang SH. Macromolecules 1999;32:6977–80.
[53] Quinn JF, Davis TP, Rizzardo E. Chem Commun 2001:1044–5.
[54] Destarac M, Charmot D, Franck X, Zard SZ. Macromol Rapid Commun 2000; 21:1035–9.
[55] Davis TP, Barner-Kowollik C, Nguyen TLU, Stenzel MH, Quinn JF, Vana P. ACS Symp Ser 2003;854:551–69.
[56] Chen M, Ghiggino KP, Mau AWH, Rizzardo E, Thang SH, Wilson GJ. Chem Commun 2002:2276–7.
[57] Chen M, Ghiggino KP, Launikonis A, Mau AWH, Rizzardo E, Sasse WHF, et al. J Mater Chem 2003;13:2696–700.
[58] Chen M, Ghiggino KP, Mau AWH, Rizzardo E, Sasse WHF, Thang SH, et al. Macromolecules 2004;37:5479–81.
[59] Chen M, Ghiggino KP, Mau AWH, Sasse WHF, Thang SH, Wilson GJ. Macromolecules 2005;38:3475–81.
[60] Zhou N, Lu L, Zhu X, Yang X, Wang X, Zhu J, et al. Polym Bull 2006;57:491–8.
[61] Farinha JPS, Relogio P, Charreyre MT. Macromolecules 2007;40:4680–90.