A New Photoiniferter/RAFT Agent for Ambient Temperature Rapid and Well-Controlled Radical Polymerization

MEHMET ATILLA TASDELEN, YASEMIN YUKSEL DURMAZ, BUNYAMIN KARAGOZ, NIYAZI BICAK, YUSUF YAGCI

Chemistry Department, Faculty of Science and Letters, Istanbul Technical University, Maslak, TR-34469, Istanbul, Turkey

Received 3 November 2007; accepted 9 February 2008
DOI: 10.1002/pola.22686

ABSTRACT: Phenacyl morpholine-4-dithiocarbamate is synthesized and characterized. Its capability to act as both a photoiniferter and reversible addition fragmentation chain transfer agent for the polymerization of styrene is examined. Polymerization carried out in bulk under ultra violet irradiation at above 300 nm at room temperature shows controlled free radical polymerization characteristics up to 50% conversions and produces well-defined polymers with molecular weights close to those predicted from theory and relatively narrow poyldispersities ($M_w/M_n \sim 1.30$). End group determination and block copolymerization with methyl acrylate suggest that morpholino dithiocarbamate groups were attained at the end of the polymer. Photolysis and polymerization studies revealed that polymerization proceeds via both reversible termination and RAFT mechanisms. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 3387–3395, 2008

Keywords: controlled/living radical polymerization; photoiniferter; photopolymerization; radical polymerization; reversible addition fragmentation chain transfer (RAFT)

INTRODUCTION

Photoinduced polymerizations, which utilize light energy to initiate chain reactions to form polymer materials, offer a number of advantages compared to thermally initiated ones. They can be conducted at room temperature, which is an outstanding advantage for both classical polymerization of monofunctional monomers and modern curing applications of di- and multifunctional monomers. By means of photopolymerization, for instance, monomers with low ceiling temperatures can easily be polymerized without depolymerization taking place. In curing of coatings or surfaces, where thermal polymerizations are not feasible, photopolymerizations can be employed with success. In photoinduced polymerization systems, the number of propagating radicals may be controlled by the choice of appropriate light intensities. However, since initiating species are generated continuously, growing polymer chains with large differences in chain lengths are present simultaneously in the medium. Therefore, polymers usually have a broad molecular weight distribution.

In the past two decades, controlled radical polymerization routes have been the focus of intense research owing to its versatility and potential commercial applications, such as controlled molar mass, narrow molecular weight distribution. The most versatile methods of controlled radical polymerization are atom transfer radical polymerization (ATRP),[1–5] nitroxide mediated polymerization (NMP),[6–8] and reversible addition-fragmentation chain transfer polymerization (RAFT).[9–12] Synthesis of various macromolecular architectures with well-defined properties can now be easily

---

Correspondence to: N. Bicak or Y. Yagci (E-mail: bicak@itu.edu.tr or yusuf@itu.edu.tr)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 46, 3387–3395 (2008)

achieved by the use of these techniques. An important advantage of RAFT over ATRP and NMP is its tolerance to a wide range of functionalities namely, —OH,[13] —COOH,[14] —CONR$_2$,[15] —NR$_2$,[16] —SO$_3$Na,[17] etc., in monomer and solvent. This provides possibility to perform the polymerization under a wide range of reaction conditions and polymerize or copolymerize a wide range of monomers in a controlled manner. The RAFT process can be induced not only thermally but also by ultraviolet (UV)[18–22] or γ-ray irradiation.[23–25] Photoinitiated controlled radical polymerization of vinyl monomers by RAFT process under UV radiation exhibit some limitations such as low conversions for a long polymerization time or addition commercially available photoinitiator in polymerization media for high monomer conversion. Among various RAFT agents, thiocarbonylthio compounds were found to be particularly useful in establishing a dynamic equilibrium between propagating radicals and dormant chains via RAFT mechanism.

In this connection, it should be pointed out that dithiocarbamates were initially used in the first studies of controlled radical polymerization and termed as iniferters by Otsu et al.[26–28] The main mode of action for these compounds was, however, a photochemical cleavage rather than bimolecular degenerative transfer.

In this article, we report the synthesis and characterization of phenacyl morpholine-4-dithiocarbamate (PMDC) and its application to RAFT polymerization of styrene (St). PMDC is sensitive to UV light that can initiate the polymerization under the irradiation of UV light and in the meantime plays a part in the RAFT process particularly at the early stages of the polymerization. Thus, controlled polymerization can successfully be performed at room temperature without an added photoinitiator at the wavelengths where the most of the conventional photoinitiators absorb the light. Moreover, photobleaching and polymerization studies in the presence of an added initiator and with the polymers were performed to provide information that would be useful in confirming either or both reversible termination and RAFT mechanisms were operative.

EXPERIMENTAL

Materials

Carbon disulfide (99.5%, Merck), 2-bromoacetophenone (98%, Acros), and (2, 4, 6-trimethylbenzoyl) diphenylphosphine oxide (TMDPO, Ciba) were used as received. Morpholine (99%, Merck) was stored over metallic sodium under nitrogen atmosphere for 24 h and finally distilled under reduced pressure. Styrene (St, 99%, Aldrich) and methyl acrylate (MA, 99%, Aldrich) were passed through basic alumina column to remove the inhibitor. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over benzophenone-Na. Other solvents were purified by conventional procedures.

Synthesis of Phenacyl Morpholine-4-dithiocarbamate

To a 100 mL of Erlenmeyer flask there were added (17.40 g, 0.20 mol) morpholine and 20 mL methanol. The solution was cooled to 0 °C in ice bath. Carbon disulfide (7.60 g, 0.10 mol) was introduced by drop wise addition through a pressure equalizing dropping funnel over 30 min under vigorous stirring. Then the solution of (4.00 g, 0.10 mol) NaOH in 20 mL methanol was added and the mixture was stirred at 60 °C for 1 h. About [3/4] of methanol was removed by rotavapor. The mixture was chilled and poured into 40 mL diethyl ether. The white precipitate (sodium salt of morpholine dithiocarbamic acid) was filtered and dried at 40 °C for 2 h under vacuum. The yield was 15.70 g (84.90%).

Methanolic solution of this salt (11.10 g, 0.06 mol in 35 mL methanol) was added to phenacyl bromide (lachrymatory, the reaction must be carried out under efficient fume cupboard) solution (11.90 g, 0.06 mol in 20 mL methanol). Progress of the reaction was followed visually by precipitation of NaBr. The turbid mixture was stirred at 60 °C for 1 h, cooled, and poured into 200 mL water. The white crystalline mass was filtered washed with excess of water (2 × 200 mL) and dried under vacuum for 24 h at room temperature. Yield 11.60 g (68.80%), mp: 129.5°C.

UV (CH$_2$Cl$_2$): λ_{max}., nm (ε, mol^{-1} L cm^{-1}); 300 (4882).

FTIR (ATR): 3055, 2920, 2830, 1702, 1470, 1390, 1310, 1280, 1140, 1065, 860, 820, 790, 690 cm^{-1}.

^{1}H NMR (250 MHz, CDCl$_3$, ppm): 7.8 aromatic; 5.0 C—CH$_2$—S; 3.8–4.4 CH$_2$.

^{13}C NMR (62.5 MHz, CDCl$_3$, ppm): 44.8, 46.9, 47.3, 50.1, 51.3, 66.2 CH$_2$; 128.5, 128.7, 133.5, 136.1 aromatic; 193.0 C=O; 195.9 C=S.

Photopolymerization

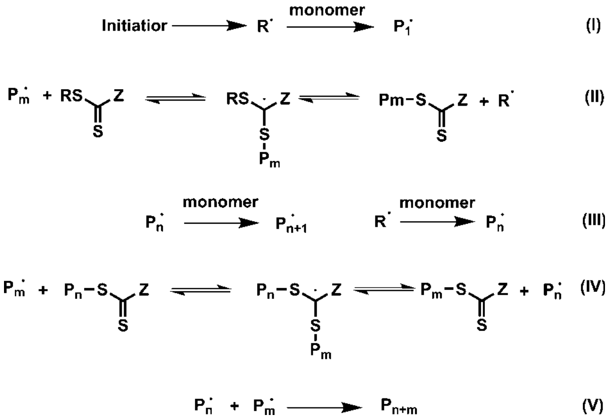
Typical procedure: Phenacyl morpholine-4-dithiocarbamate (PMDC, 1.22×10^{-2} g, 4.35×10^{-2} mol L^{-1}) and monomer (St, 1.0 mL, 8.70 mol L^{-1}) solution in bulk were put into a Pyrex tube (i.d. = 9 mm) that flushed with dry nitrogen. The mixture was irradiated a photoreactor (Rayonet) equipped with 16 lamps emitting light nominally at 350 nm at room temperature. The light intensity was 6×10^{-3} mW cm^{-2} as measured by Delta Ohm model HD-9021 radiometer. After given time, the resulted polymers were precipitated in the methanol and then dried under reduced pressure. Conversion of monomer was determined gravimetrically (yield: 12.90 ± 0.2%; $M_n = 3800$ g mol^{-1}). All the other polymerizations were performed under identical experimental conditions. Additional experiments by using added photo- and thermal initiators, and macro-RAFT agent were performed in the same manner. The detailed conditions are given in the related tables and figures.

Characterization

^1H NMR and ^{13}C NMR spectra of 5–10% (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 and 62.5 MHz, respectively, on a Bruker DPX 250 spectrometer. FTIR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0, 3 mL min^{-1} and a Waters 410 differential refractometer detector.

RESULTS AND DISCUSSION

Dithiocarbamates are kind of important control agents that have been widely used in controlled free radical polymerization, such as photoinifertters[29] and RAFT agents in thermal conditions.[30] The photochemical reactions of dithiocarbamate derivatives have been extensively studied experimentally and theoretically. They are known to undergo a reversible homolytic cleavage under UV radiation, and promote a controlled radical polymerization of vinyl monomers. Recently, Ishizu et al. estimated that density functional theory calculations provide a prediction of the trends in C—S bond dissociation energies for several model compounds as photoinitiator.[31–33]

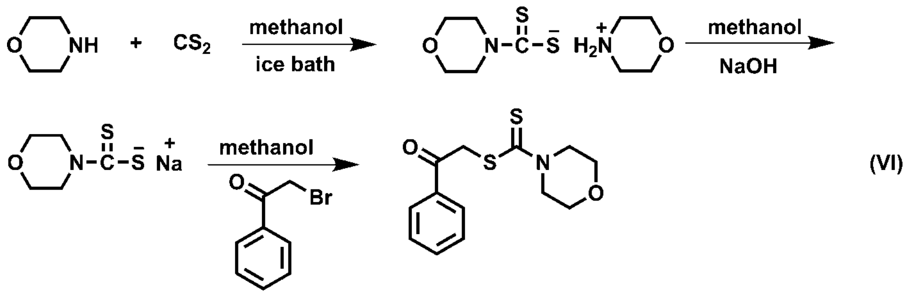


Scheme 1. Schematic for reversible addition-fragmentation chain transfer polymerization.

A number of photoinitiators possessing phenacyl chromophoric groups have been developed and used in both cationic[34–36] and free radical[37,38] polymerizations. Moreover, according to general scheme of RAFT polymerization as presented in Scheme 1, (R-S-C(S)-Z), phenacyl unit (as R component) appeared to be an easy leaving group which is desirable for fast transfer of radicals in early stage of the polymerization.

Morpholine ring can be considered as electron rich Z component for a potential RAFT agent. It seemed, therefore, appropriate to design and synthesize phenacyl ester of morpholino dithiocarbamate (PMDC) to act as both photoinitiator and RAFT agent in controlled free radical polymerization. PMDC was synthesized according to the conventional synthetic procedure,[39] applied for the synthesis of most of the RAFT agents, by reacting sodium salt of morpholino dithiocarbamate with commercially available phenacyl bromide (Scheme 2).

The structure of PMDC was confirmed by ^{13}C NMR, ^1H NMR, and UV–Vis spectral analysis. ^1H NMR spectrum of PMDC exhibits the signals at $\delta = 7.4$–8.2 ppm, and 4.9 ppm and 3.8–4.4 ppm corresponding to the aromatic protons, and methylene protons next to sulfur and morpholine moiety, respectively, [Fig. 1(A)]. As can be seen from Figure 2, the absorption spectrum of PMDC shows an n-π^* absorption with a maximum at about 300 nm characteristic of acetophenone derivatives.[34] Tail absorption at above 300 nm facilitates its use as photoinitiator at



Scheme 2. Synthesis of phenacyl morpholine-4-dithiocarbamate (PMDC).

wavelengths where the most commercial lambs emit the light and monomers do not absorb.

We have previously reported[34–38] that phenacyl group containing compounds undergo photoinduced decomposition when irradiated at appropriate wavelengths. This was further confirmed also for PMDC by the spectral changes on UV irradiation. Representative result for the decomposition of PMDC is shown in Figure 2.

UV spectra were recorded after the solution had been exposed to the light of the UV lamp for subsequent intervals.

The utilization of PMDC as photoinitiator and RAFT agent for polymerization of styrene was tested. The photopolymerizations of St were performed by UV irradiation at different time intervals with PMDC and $[St]_0/[PMDC]_0$ mole ratio of 200:1. Typical GPC profiles of these polymerization series are shown in Figure 3. All the GPC curves show a unimodal distribution. The elution peaks shift to the high-molecular weight-side increasing with reaction times.

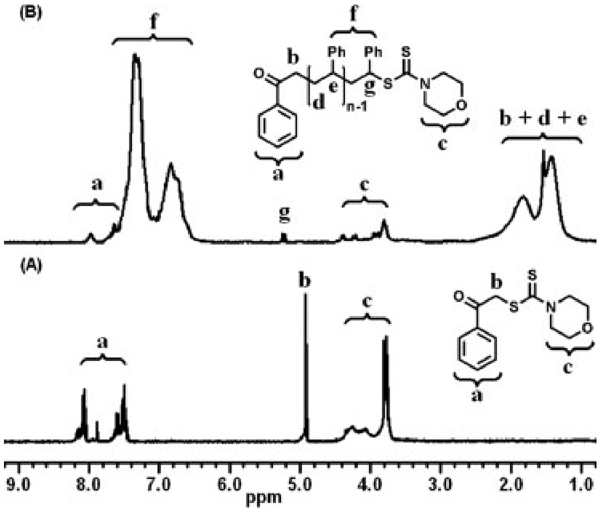


Figure 1. ^1H NMR spectra of the phenacyl morpholine-4-dithiocarbamate (A) and polystyrene, which was produced via RAFT polymerization with PMDC under UV irradiation (B) in $CDCl_3$.

To further demonstrate the "controlled/living" character of the RAFT polymerization, the PSt sample obtained from photopolymerization was used as a macro-RAFT agent for block copolymerization with MA under similar experimental conditions. As shown in Figure 4, an obvious peak shift from the original PSt macroinitiator (M_n = 2400, PDI = 1.47) to the resultant copolymer polystyrene-*block*-poly(methyl acrylate) (M_n = 33,000, PDI = 1.37) was observed. The PDI of the block copolymer is slightly narrower than that of the initial polymer. This suggests most of the chains are still active during the process of the block polymerization reaction.

Figure 5 reveals an approximate linear relationship between conversion or $\ln([M]_0/[M]_t)$ and the reaction time of the RAFT photopolymerization of St. It should be pointed out that reasonable conversions were attained in much shorter times than those with the other RAFT agents

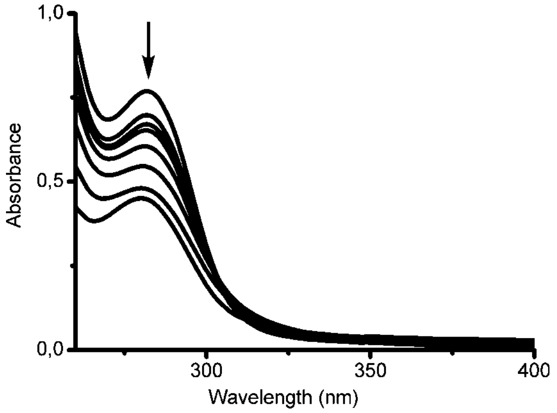


Figure 2. Typical UV/Vis spectral changes of phenacyl morpholine-4-dithiocarbamate (5.50 × 10^{-5} mol L^{-1}) on irradiation above 300 nm under nitrogen in CH_2Cl_2 at room temperature. UV spectra were taken at 0, 1, 2, 4, 8, 16, 32, 64 min.

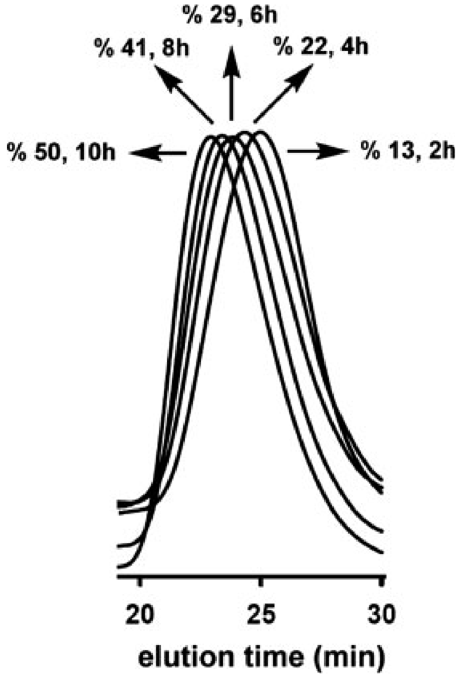


Figure 3. GPC traces for polystyrene obtained at different time interval [PMDC]/[St] = 1/200.

used in photopolymerizations alone[13,14] or in the presence of a photoinitiator.[15,16] Control of the chain growth, on the other hand must depend mostly on the equilibrium between radical addition to dithiocarbonyl group and leaving of the macro-ester component. The first-order kinetics implied that the concentration of the free radical remained constant during the polymerization.

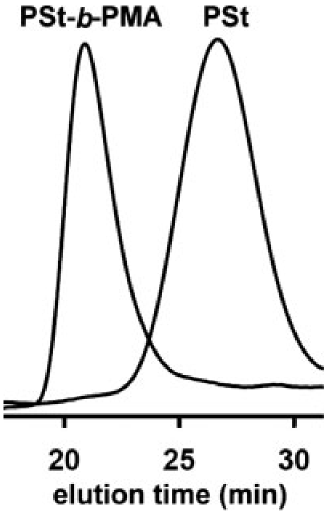


Figure 4. GPC traces for the PSt homopolymer (M_n = 2400, PDI = 1.44) and the corresponding PSt-*b*-PMA "block copolymer" (M_n = 33,000, PDI = 1.37).

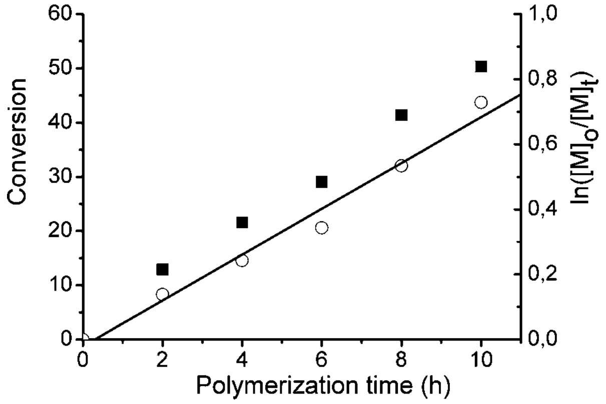


Figure 5. Plots of (■) the monomer conversion and (○) $\ln([M]_0/[M]_t)$ versus the polymerization time ([St] = 8.70 mol L^{-1}, [St]/[PMDC] = 200:1, wavelength = >300 nm, $I = 6 \times 10^{-3}$ mW cm^{-2}).

The photopolymerization results of St with PMDC showed that molecular weight were linearly increased with monomer conversion, while the molecular weight distribution became slightly narrower as monomer conversion increased (Fig. 6). All these results confirmed that the photopolymerization of St with PMDC proceeded in a controlled manner.

To confirm the polymerization mechanism, the chain ends of PSt prepared by the photopolymerization were analyzed by ^{1}H-NMR spectroscopy. The signal at $\delta = 7.8$ ppm and 3.8~4.4 were attributed to the aromatic protons of the phenacyl units and methylene protons of morpholine in PMDC [Fig. 1(B)]. The signals at $\delta = 6.2$~7.2 and 1.2~2.2 were attributed to the characteristic protons of polystyrene. Moreover,

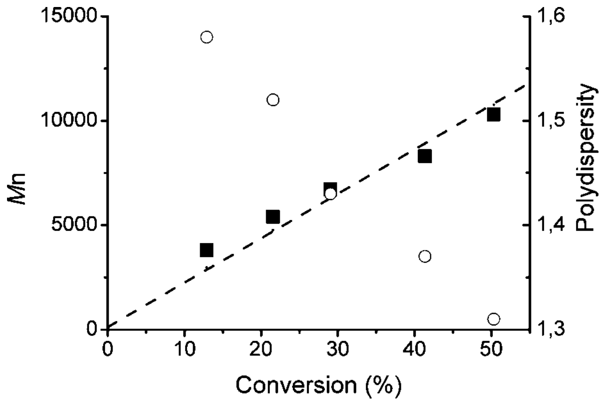
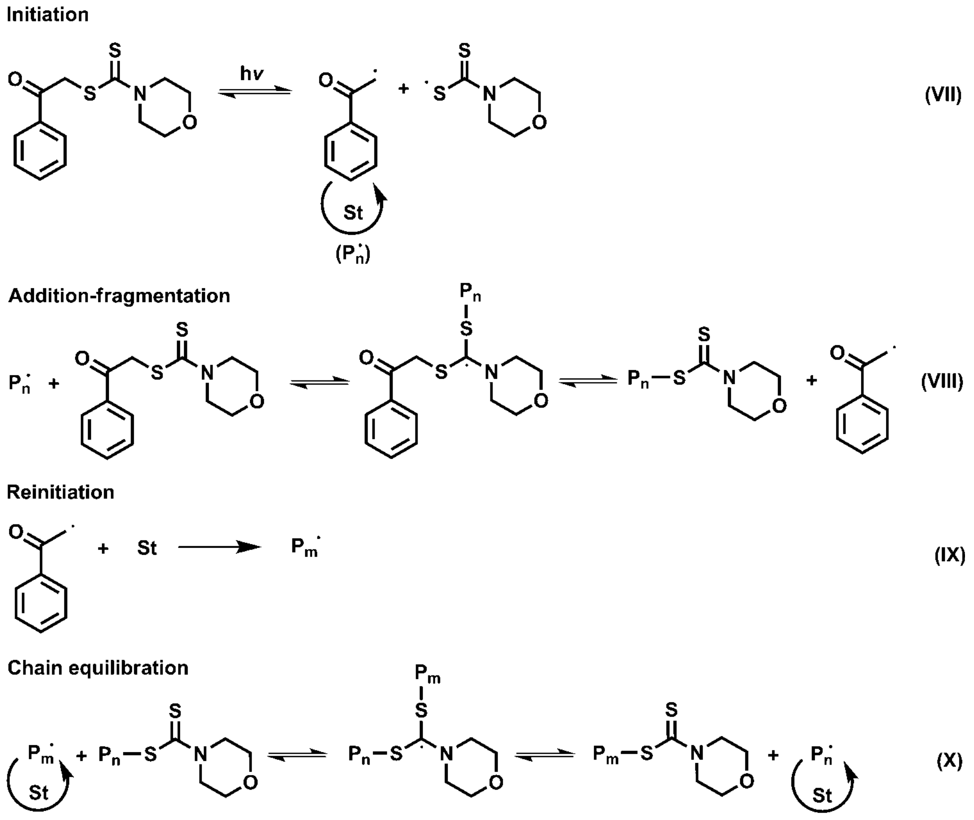


Figure 6. Plots of GPC experimental (■) and theoretical (- -) polymer molecular weight (M_n) values and (○) polydispersity (M_w/M_n) values versus the monomer conversion (experimental deteails are the same as given in Fig. 5).



Scheme 3. Overall process for RAFT polymerization of styrene.

methylene protons next to sulfur was disappeared and overlapped with the characteristic signals of the PSt. These results revealed that the morpholino dithiocarbamate groups were attached to the polymer chain ends. These investigations, however, did not answer the question whether polymerization proceeded via RAFT or iniferter (reversible termination) mechanisms as polymers generated by either mechanisms share the same end group structure. First, we considered that the polymerization proceeded solely via reversible termination mechanism offered by Hong and coworkers[40,41] for living behavior under UV irradiation by using thiocarbonylthio compounds.

Under this scheme, UV irradiation induces the homolytic cleavage of the weak bond (C—S) of PMDC generates an active phenacyl radical and a resonance-stabilized dithiocarbamate radical. The phenacyl radical can initiate the polymerization to form the propagating radical, whereas the stable dithiocarbamate radical can only reversibly terminate the propagating radical to form a dormant polymer chain (Scheme 3, reactions VII). This reaction features a reversible chain termination mechanism. However, the RAFT mechanism might be operative in living polymerization as the PMDC possess a good living group which is critical for the success of the RAFT process (Scheme 3, reactions VIII–X). If the propagating chains were produced only by photoinduced cleavage continuously throughout the polymerization rather than through the R group of the PMDC, the polymerization would not be well controlled. The experimental results presented above on the photoinduced polymerization of St in the presence of PMDC gave strong evidence of living behavior. In our case, where the leaving group is a phenacyl radical (the same radical generated from the initial photodecomposition), there is an early release of initiating species into the polymerization, and the most of the chains are initiated through RAFT agent PMDC. Regardless of the mode of formation, either by photocleavage or RAFT processes, dithiocarbamate end groups can undergo chain transfer to any other active chain and resume growing itself. As a result of the continually occurring reversible chain transfer reactions, the growing radical chain does not encounter

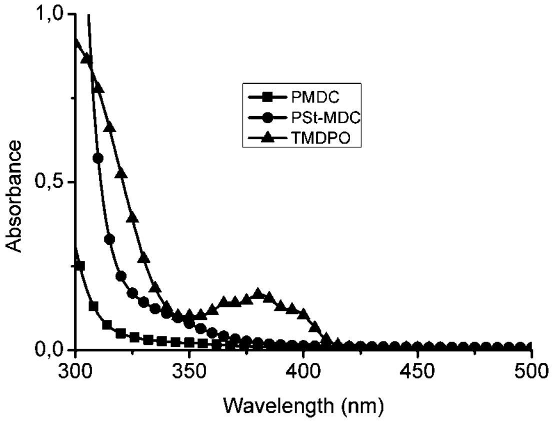


Figure 7. UV/vis spectra of (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TMDPO, ▲), macro-RAFT agent (PSt-MDC, ●) and phenacyl morpholine-4-dithiocarbamate (PMDC, ■) in CH_2Cl_2. The concentration of all compounds is 5.40×10^{-4} M.

the termination reactions which permanently deactivate the growing ends of polymers created by conventional free-radical polymerizations. It is clear that using photolysis to form initiating radicals is unlikely to lead polymerization to proceed completely via iniferter mechanism; radicals will still add to the thiocarbonyl group. This statement was further proved by control experiments using (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TMDPO) as photoinitiator in the polymerization system. As can be seen from Figure 7, TMDPO strongly absorbs light at 350–400 nm where the RAFT agent PMDC is transparent. Polymerization of St containing only TMDPO upon irradiation at $\lambda > 365$ nm resulted in the formation a polymer with bimodal molecular weight distribution (Fig. 8). However, photopolymerization with the addition of PMDC under identical experimental conditions produced a polymer with monomodal and narrow molecular weight distribution (Fig. 8). This result is taken as evidence for the fact that PMDC acts as RAFT agent. In this context, it is worth to mention the work Quinn et al. and Muthukrishnan et al.[18,42] who demonstrated that certain structurally designed thiocarbonyl compounds can initiate the polymerization photochemically and showed that polymerization proceeded via RAFT mechanism.

The experiments with TMDPO can not prove the intended assertion that the operative mechanism of control in the other polymerizations was RAFT or simultaneous photo-driven reversible termination. There are still unclear points in the mechanism after the initial RAFT-agent (PMDC) is consumed. Therefore, we performed photo- and thermal polymerization of MA using conventional initiators with (PSt-MDC) as a macro-RAFT agent. As can be seen in Table 1, by using TMDPO in the presence of macro-RAFT agent, the less controlled polymer was obtained with broad molecular weight distribution than that of without using TMDPO. This result suggested that morpholino dithiocarbamate end functional polystyrene is still photoactive above 365 nm even at the later stages of the polymerization. Similar experiments under thermal conditions were also performed (see experiments 3 and 4 in Table 1). Notably, the polymerization does not proceed in the absence of an added initiator indicating that PSt-MDC does not act as a thermal iniferter. In the presence of AIBN as free radical initiator, however, polymerization occurs in a controlled manner.

In summary, the well-controlled polymerization of styrene was achieved using PMDC under UV irradiation at ambient temperature. The living character of this polymerization was confirmed by both the linear tendency of molecular weight evolution with conversion and a blocking experiment. The occurrence of RAFT mechanism was proved by polymerization experiments performed at various conditions, that is, polymerizations in the presence of an added photoinitiator and polymerization of second monomer by using

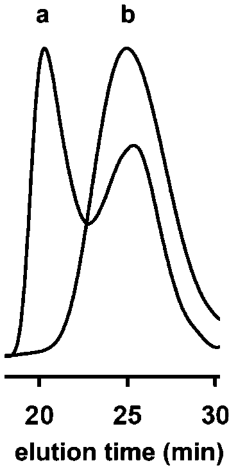


Figure 8. GPC traces for polystyrene formed by photopolymerization of styrene (bulk) using TMDPO in the absence (a) (M_n = 7300, PDI = 4.83), and presence of PMDC (b) (M_n = 5100, PDI = 1.51). Photopolymerization carried out above 365 nm using TMDPO as photoinitiator (interference filter: Cupric sulfate aqueous solution).

Table 1. Results of Photo- and Thermal Polymerization of Methyl Acrylate Using Conventional Initiators with PSt-MDC (conv: 18%; M_{nth}: 4000 g mol^{-1}, M_{nNMR}: 4600 gmol^{-1}, M_{nGPC}: 5200 g mol^{-1}, M_w/M_n: 1.65) as a Macro-RAFT Agent, [PSt-MDC]: 2.88 × 10^{-2} mol L^{-1}

No	[MA]/[PSt-MDC]/[I]	Time (min)	Conv.[a] (%)	$M_{\mathrm{n,th}}$	$M_{\mathrm{n,NMR}}$[b]	M_{nGPC}[c]	M_w/M_n[c]
1[d]	200/1/0.1	15	60	14,800	42,100	18,300	1.80
2[d]	200/1/0	15	7.2	5700	10,600	6500	1.72
3[e]	200/1/0.1	60	17	7400	6900	17,700	1.53
4[e]	200/1/0	60	–	–	–[f]	5250	1.60

[a] Determined by gravimetrically.

[b] Calculated from ^{1}H NMR of the corresponding polymers.

[c] Determined by GPC based on polystyrene standart.

[d] Photopolymerization carried out above 365 nm using TMDPO as photoinitiator in the presence of CH_2Cl_2 (interference filter: Cupric sulfate aqueous solution).

[e] Thermal polymerization carried out at 70 °C using AIBN as thermal initiator in the presence of toluene.

[f] ^{1}H NMR analysis did not indicate the addition of PMA segment.

macro RAFT agent. It was concluded that both RAFT and reversible termination mechanisms are operative in the system. In addition, PMDC possesses excellent optical absorption properties in the near UV spectral region, ensuring efficient light absorption from most UV light sources. These properties suggest that it may find use in a variety of practical applications where thermounstable monomers and monomers containing thermodenaturalizable biomolecular moieties are used.

REFERENCES AND NOTES

1. Wang, J. S.; Matyjaszewski, K. Macromolecules 1995, 28, 7572–7573.
2. Wang, J. S.; Matyjaszewski, K. J Am Chem Soc 1995, 117, 5614–5615.
3. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. Macromolecules 1995, 28, 1721–1723.
4. Matyjaszewski, K.; Xia, J. Chem Rev 2001, 101, 2921–2990.
5. Kamigaito, M.; Ando, T.; Sawamoto, M. Chem Rev 2001, 101, 3689–3745.
6. Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y. Miyamoto, T. Macromolecules 1996, 29, 3050–3052.
7. Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. J Am Chem Soc 1999, 121, 3904–3920.
8. Hawker, C. J.; Bosman, A. W.; Harth, E. Chem Rev 2001, 101, 3661–3688.
9. Ganachaud, F.; Monteiro, M. J.; Gilbert, R. G.; Dourges, M.-A.; Thang, S. H.; Rizzardo, E. Macromolecules 2000, 33, 6738–6745.
10. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffrey, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559–5562.
11. Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1999, 32, 2071–2074.
12. Moad, G.; Chiefari, J.; Krstina, J.; Postma, A.; Mayadunne, R. T. A.; Rizzardo, E.; Thang, S. H. Polym Int 2000, 49, 993–1001.
13. Albertin, L.; Stenzel, M.; Barner-Kowollik, C.; Foster L. J. R.; Davis, T. P. Macromolecules 2004, 37, 7530–7537.
14. Schilli, C. M.; Zhang, M. F.; Rizzardo, E.; Thang, S. H.; Chong, Y. K.; Edwards, K.; Karlsson, G.; Muller, A. H. E. Macromolecules 2004, 37, 7861–7866.
15. Mori, H.; Sutoh, K.; Endo, T. Macromolecules 2005, 38, 9055–9065.
16. Sahnoun, M.; Charreyre, M. T.; Veron, L.; Delair, T.; D'Agosto, F. J Polym Sci Part A: Polym Chem 2005, 43, 3551–3565.
17. Mitsukami, Y.; Donovan, M. S.; Lowe, A. B.; McCormick, C. L. Macromolecules 2001, 34, 2248–2256.
18. Quinn, J. F.; Barner, L.; Barner-Kowollik, C.; Rizzardo, E.; Davis, T. P. Macromolecules 2002, 35, 7620–7627.
19. Junkers, T.; Theis, A.; Buback, M.; Davis, T. P.; Stenzel, M. H.; Vana, P.; Barner-Kowollik, C. Macromolecules 2005, 38, 9497–9508.
20. Lu, L. C.; Yang, N. F.; Cai, Y. L. Chem Commun 2005, 5287–5288.
21. Lu, L. C.; Zhang, H.; Yang, N. F.; Cai, Y. L. Macromolecules 2006, 39, 3770–3776.
22. Jiang, W. D.; Lu, L. C.; Cai, Y. L. Macromol Rapid Commun 2007, 28, 725–728.
23. Bai, R. K.; You, Y. Z.; Pan, C. Y. Macromol Rapid Commun 2001, 22, 315–319.
24. Barner, L.; Quinn, J. F.; Barner-Kowollik, C.; Vana, P.; Davis, T. P. Eur Polym Mater 2003, 39, 449–459.
25. Barner-Kowollik, C.; Vana, P.; Quinn, J. F.; Davis, T. P. J Polym Sci Part A: Polym Chem 2002, 40, 1058–1063.
26. Otsu, T. J Polym Sci Part A: Polym Chem 2000, 38, 2121–2136.
27. Otsu, T.; Yoshida, M. Macromol Chem Rapid Commun 1982, 3, 127–132.

28. Otsu, T.; Yoshida, M.; Tazaki, T. Macromol Rapid Commun 1982, 3, 133–140.
29. Otsu, T.; Matsunaga, T.; Doi, T.; Matumoto, A. Eur Polym Mater 1995, 31, 67–78.
30. Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. Macromolecules 1999, 32, 6977–6980.
31. Ishizu, K.; Khan, R. A.; Ohta, Y.; Furo, M. J Polym Sci Part A: Polym Chem 2004, 42, 76–82.
32. Ishizu, K.; Katsuhara, H.; Kawaguchi, S.; Furo, M. J Appl Polym Sci 2005, 95, 413–418.
33. Ishizu, K.; Katsuhara, H. Design Mon Polym 2006, 9, 99–115.
34. Kasapoglu, F.; Onen, A.; Bicak, N.; Yagci, Y. Polymer 2002, 43, 2575–2579.
35. Kasapoglu, F.; Yagci, Y. Macromol Rapid Commun 2002, 23, 567–570.
36. Yonet, N.; Bicak, N.; Yagci, Y. Macromolecules 2006, 39, 2736–2738.
37. Kasapoglu, F.; Aydin, M.; Arsu, N.; Yagci, Y. J Photochem Photobiol A Chem 2003, 159, 151–159.
38. Nese, A.; Sen, S.; Tasdelen, M. A.; Nugay, N.; Yagci, Y. Macromol Chem Phys 2006, 207, 820–826.
39. Favier, A.; Charreyre, M. T. Macromol Rapid Commun 2006, 27, 653–692.
40. Hong, C. Y.; You, Y. Z.; Bai, R. K.; Pan, C. Y.; Borjihan, G. J Polym Sci Part A: Polym Chem 2001, 39, 3934–3939.
41. You, Y. Z.; Hong, C. Y.; Bai, R. K.; Pan, C. Y.; Wang, J. Macromol Chem Phys 2002, 203, 477–483.
42. Muthukrishnan, S.; Pan, E. H.; Stenzel, M. H.; Barner-Kowollik, C.; Davis, T. P.; Lewis, D.; Barner, L. Macromolecules 2007, 40, 2978–2980.