2-Oxo-tetrahydrofuran-3-yl 9H-carbazole-9-carbodithioate Mediated Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

Di Zhou,[1,2] Xiulin Zhu,[1] Jian Zhu,[1] Lihua Hu,[1] Zhenping Cheng[1]

[1]*School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, China*
[2]*Department of Chemical Engineering, Jiangsu Key Laboratory of Advanced Functional Materials, Changshu Institute of Technology, Changshu 215500, China*

ABSTRACT: The 2-oxo-tetrahydrofuran-3-yl 9H-carbazole-9-carbodithioate (OTCC) mediated reversible addition-fragmentation chain transfer (RAFT) polymerizations of styrene and methyl acrylate were investigated. The results showed that OTCC was an effective RAFT agent for the polymerizations of styrene and methyl acrylate. The polymerizations exhibited ''living''/controlled characters. The resulting carbazole and 2- oxo-tetrahydrofuran-3-yl groups end-labeled polymer exhibited stronger fluorescence in *N*, *N*-dimethyl formamide, compared with those of OTCC under the same conditions. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2913–2918, 2007

Key words: polystyrene; fluorescence; radical polymerization; kinetics (polym)

INTRODUCTION

Many synthetic methods have been developed to synthesize end-labeled polymer, such as living anionic polymerization[1,2] and living radical polymerization: atom transfer radical polymerization,[3–6] nitroxyl-mediated polymerization.[7,8] However, to our best knowledge, there are few reports about the synthesis of end-labeled polymer via reversible addition-fragmentation chain transfer (RAFT) polymerization. Actually, according to the RAFT mechanism (Scheme 1), Z and R groups of RAFT agents will be capped at the ends of the polymer.[9,10] Thus, expectant end-labeled polymer can be prepared via RAFT polymerization conveniently by designing proper Z and R groups of RAFT agents. The R group of RAFT agents is required to be a good leaving group in comparison with the growing polymeric chain and a good reinitiating species toward the monomer used.[9–14] Benzyl,[15–19] cumyl,[20–23] and cyanoisopropyl[24–26] groups are widely used for the RAFT polymerizations of different monomers. Esters group shown in Scheme 2 also possess the above exhibited properties. The synthetic methods of these esters type compounds are convenient and easy to introduce the functional groups.[13,14,27,28] The various substituents at the α-carbon of the carbonyl group contribute toward the stabilization of the radical intermediate (Scheme 1, **I, II**), and also lead to generate radicals of various stabilities during the addition-fragmentation step shown in Scheme 1.[29] The reported efficiency of ester leaving groups (Scheme 2) for the polymerizations of styrene (St), acrylates, and methacrylates is shown in the following order: E1 < E2 < E3 < E4.[13,14,28–31] In this study, a new ester leaving group 2-oxo-tetrahydrofuran-3-yl (E5 in Scheme 2), was synthesized and used as the RAFT agent for the polymerizations of St, methyl acrylate (MA), and methyl methacrylate (MMA). The obtained polymers linked with the 2-oxo-tetrahydrofuran-3-yl group have some potential applications, such as macro-monomer of ring-open polymerization under the proper conditions. The optical properties of polymer bearing carbazole unit were also studied.

EXPERIMENTAL SECTION

Materials

All chemicals (analytical grade) used in this study were purchased from Shanghai Chemical Reagents Ltd. China and J and K-Acros. Monomers were
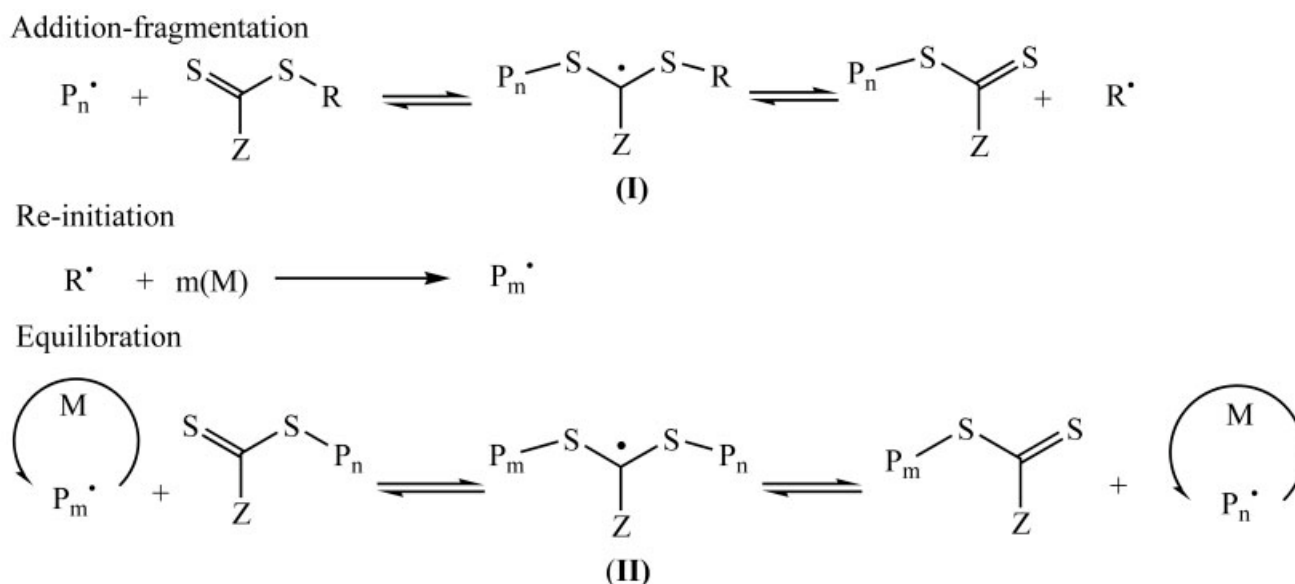
Scheme 1 Mechanism of RAFT Process, M is monomer, R is a radical that can initiate polymerization, Pm· and Pn· are polymer chains.

washed with an aqueous solution of sodium hydroxide (5 wt %) for three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, these monomers were distilled under reduced pressure and kept in a refrigerator under 4°C. 2-oxo-tetrahydrofuran-3-yl 9H-carbazole-9-carbodithioate (OTCC) was prepared by the following procedure: a suspension of potassium hydroxide (0.56 g, 0.01 mol) in dimethyl sulfoxide (50 mL) was prepared, and carbazole (1.67g, 0.01 mol) was added under vigorous stirring. The solution was stirred for 1 h at room temperature and then carbon sulfide (0.76 g, 0.01 mol) was added dropwise. The resultant reddish solution was stirred for 2 h at room temperature, and then 3-bromo-dihydrofuran-2(3H)-one (1.65 g, 0.01mol) was added. The mixture was stirred overnight at the room temperature. The resultant reaction mixture was precipitated in a large amount of water, and then a yellow solid was obtained. After being recrystallized from alcohol twice, the product was obtained as a yellow crystal (1.48g, dried, yield 45.2%). The product has been characterized by nuclear magnetic resonance (NMR), ele-

mentary analysis (EA), and high efficiency liquid chromatography (HPLC). The results were listed below: ^{1}H-NMR. δ:8.50–8.52 (d, 2H, cardazole-H), 7.98–8.00 (d, 2H, cardazole-H), 7.39–7.47 (m, 4H, cardazole-H), 5.10–5.12 (d, 1H, S—C—H), 4.48–4.57 (m, 2H, O—CH$_2$), 3.12 (s, 1H, C—CH$_2$—C), 2.52 (s, 1H, C—CH$_2$—C). EA. C$_{17}$H$_{13}$NO$_2$S$_2$, Calculated: C 62.36 H 4.00 N 4.28, found: C 62.53 H 4.07 N 4.16. The purity was above 96% by HPLC. Other materials were used without further purification.

RAFT polymerizations in bulk

The following procedure was typical: a stock solution of 16 mL (139 mmol) of styrene and 90.9 mg (0.278 mmol) OTCC (for acrylates, proper amount of AIBN was added) were prepared, and then aliquots of 2 mL were placed in 5 mL ampules. The content was purged with argon for ~ 10 min to eliminate the dissolved oxygen. Then the ampules were flame sealed. The polymerization reaction was performed at the appropriate temperature. After the desired reaction time, each ampule was quenched in ice water, and
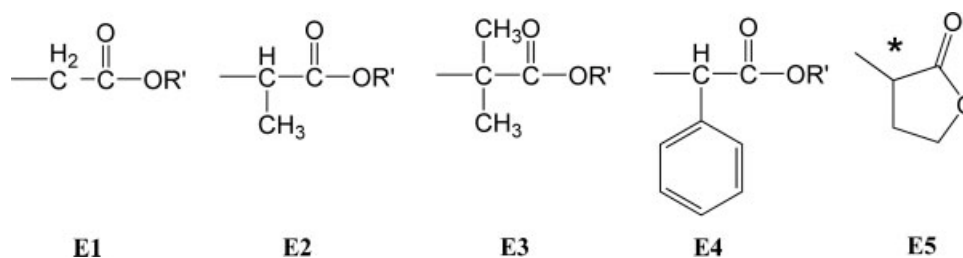
Scheme 2 Chemical structures of ester leaving groups (R groups).

Time (h)	Conversion (%)	$M_{n, th}$[a]	$M_{n, GPC}$	M_w/M_n
1	13.2	4700	121,000	2.10
3	34.0	11,700	128,000	2.21

[a] $M_{n,th} = [M]_0 \times M_w \times$ conversion/[RAFT agent]$_0$ + $M_{wRAFT\ agent}$, where $[M]_0$ and [RAFT agent]$_0$ are the initial concentrations of monomer and RAFT agent, and M_w and $M_{wRAFT\ agent}$ are molecular weights of monomer and RAFT agent, respectively.

opened. The reaction mixture was diluted with a little of tetrahydrofuran (THF) (about 2 mL), and precipitated in a large amount of methanol (about 300 mL, for acrylates using ligroin). The polymer was obtained by filtrating and dried at room temperature under vacuum to constant weight. Conversion was determined gravimetrically.

Characterization

The molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector, using HR 1, HR 3, and HR 4 column. Calibrated was performed with polystyrene or poly(methyl methacrylate) (molecular weight range 100–500,000) as standard samples. THF 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 NMR instrument using CDCl$_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. Elemental analyses (EA) of C, H, and N were measured by the EA1110 CHND-S. The purity of dithiocarbamates was determined by Waters 515 HPLC: the mixture of methanol and water ($V_{methanol} : V_{water} = 80 : 20$) was used as the eluent at a flow rate of 0.8 mL min^{-1} operated at 30°C using C18 column and using Waters 996 as a detector. The fluorescence intensity was measured by FLS920.

RESULTS AND DISCUSSION

Polymerizations using OTCC as RAFT agent

To study the effectiveness of OTCC as RAFT agent, the St, MA, and MMA were performed in the presence of OTCC respectively. From the experimental results listed in Table I, it can be found that the OTCC is not efficient enough to control over the polymerization of MMA. The number average molecular weight (M_n) obtained from GPC is much more larger than the calculated value $M_{n,th}$. The molecular weight distribution (M_w/M_n) is very broad ($M_w/M_n > 2.0$). Researchers attributed the results to the low leaving capacity in
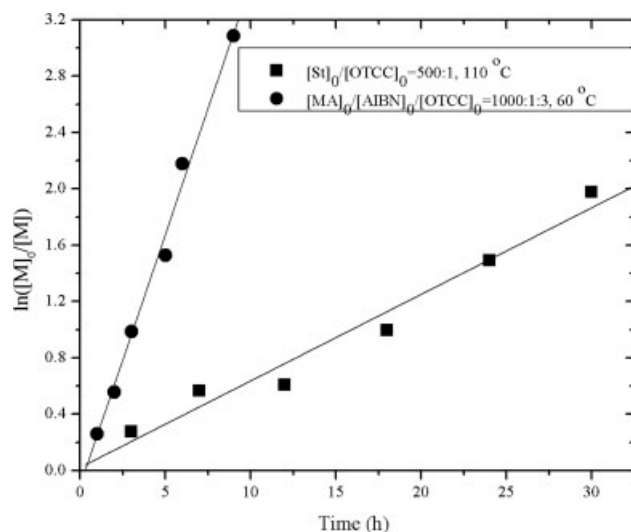

Figure 1 Plots of ln([M]$_0$/[M]) versus polymerization time for the RAFT polymerizations of styrene and methyl acrylate using OTCC as RAFT agent.

comparison with that of poly(methacrylate) radicals during the RAFT process shown in Scheme 1 and leading to the equilibrium of RAFT process to be strongly shifted to the left.[32]

While in the case of styrene and methyl acrylate, the ''living''/controlled polymerizations using OTCC as RAFT agent were carried out successfully. Figure 1 shows the plots of ln([M]$_0$/[M]) versus reaction time for the polymerizations of styrene ([St]$_0$/[OTCC]$_0$ = 500 : 1, 100°C) and methyl acrylate ([MA]$_0$/[AIBN]$_0$/[OTCC]$_0$ = 1000 : 1 : 3, 60°C), respectively. In the studied range of conversions, the plots are approximately linear without induction period, which indicates that the propagating radical concentrations were almost constant and without significant termination
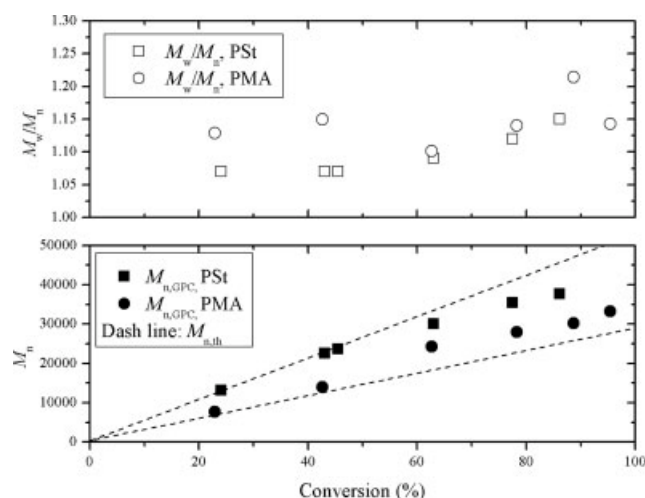

Figure 2 Evolutions of the molecular weights (M_n) and molecular weight distribution (M_w/M_n) with monomer conversion. The conditions were the same as in Figure 1.
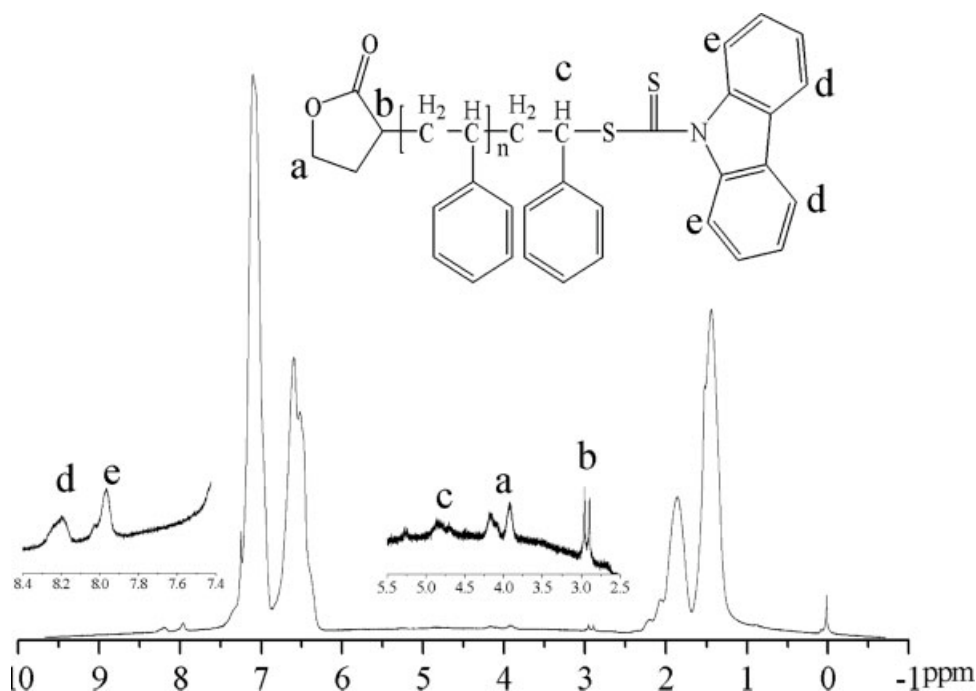
Figure 3 Typical ^{1}H-NMR spectrum of PSt ($M_n = 13,200$, $M_w/M_n = 1.07$) obtained using OTCC as RAFT agent.

reactions during the polymerization. The polymerization rate of styrene initiated by thermal initiation is very slow. While the polymerization rate of methyl acrylate is fast because of the AIBN initiated and the very reactive propagating radical with low steric bulk. Figure 2 shows that the number average molecular weight (M_n) of the polymer measured by GPC

increases linearly with monomer conversion and is close to the calculated value, and the molecular weight distribution (M_w/M_n) is narrow (<1.20).

The structures of the obtained polymers were characterized by ^{1}H-NMR. The typical ^{1}H-NMR spectra of PSt ($M_n = 13,200$, $M_w/M_n = 1.07$) and PMA ($M_n = 7700$, $M_w/M_n = 1.12$) are shown in Figures 3 and 4,
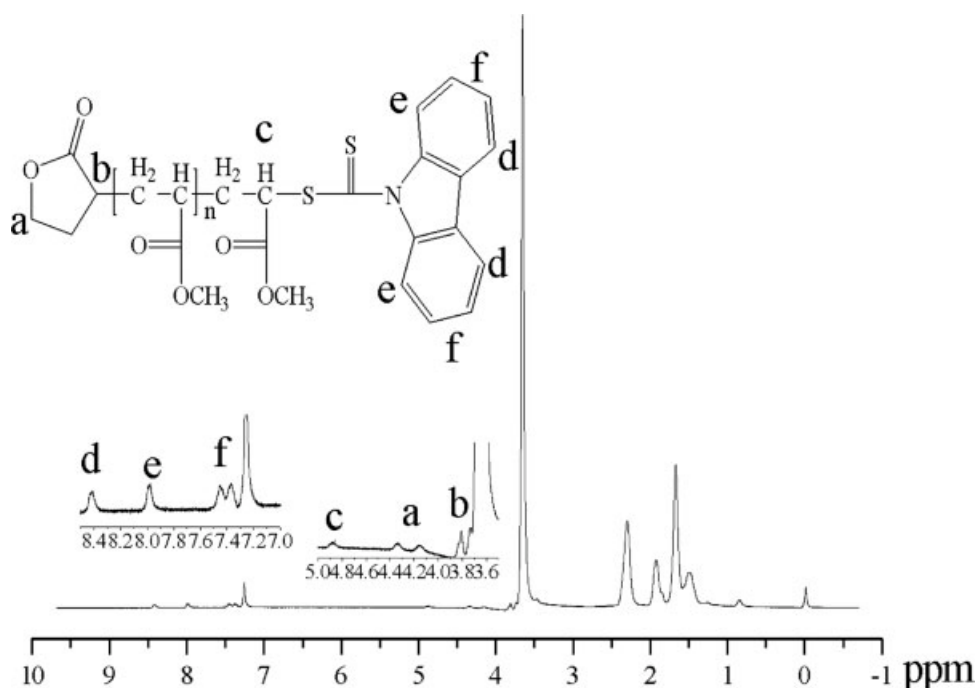

Figure 4 Typical ^{1}H-NMR spectrum of PMA ($M_n = 7700$, $M_w/M_n = 1.12$) obtained using OTCC as RAFT agent.

	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n	$M_{n,NMR}$	$M_{n,GPC}/M_{n,NMR}$
Sample in Figure 3	12,900	13,200	1.07	15,600	0.85
Sample in Figure 4	6900	7700	1.12	9900	0.78

respectively. In Figure 3, the peaks at $\delta = 3.95$–4.20 (a), 2.90–2.96 (b) are ascribed to the protons of the leaving group 2-oxo-tetrahydrofuran-3-yl, and the signals at $\delta = 8.20$ (d), 7.98 (e) indicate the existence of carbazole group; in Figure 4, the moieties at $\delta = 4.15$–4.34 (a), 3.47 (b) are assigned to R group 2-oxo-tetrahydrofuran-3-yl, and the peaks at $\delta = 8.41$ (d), 7.98 (e) and 7.37–7.45 (f) are ascribed to Z group carbazole. And the c peaks both in Figures 3 and 4 correspond to the proton of S—CH—. The number–average molecular weight from NMR, $M_{n,NMR}$, can be calculated according to equations: $M_{n,NMR} = M_{St} \times 2/5 \times I_{6.80}/I_{8.20}$, $M_{n,NMR} = M_{MA} \times 2/3 \times I_{3.67}/I_{8.41}$, respectively, providing that each macromolecule contains a OTCC residue. Where $I_{8.20}$ is the integral values of the peaks at $\delta = 8.20$ ppm corresponding to the two protons of the carbazole and and $I_{6.80}$ is the integral values of the peaks at $\delta = 6.51$–7.08 ppm which correspond to the five protons of benzene group in St structure (showed in Fig. 3); $I_{8.41}$ and $I_{3.67}$ are the integral values of the peaks at $\delta = 8.41$ ppm corresponding to the two protons of the carbazole and at $\delta = 3.67$ ppm that correspond to the three protons of the ester methyl group in MA structure (showed in Fig. 4). The results are listed in Table II. The close agreement within a reasonable error between $M_{n,th}$, $M_{n,GPC}$, and $M_{n,NMR}$ provides additional evidence for the "living"/controlled character of the polymerization. Furthermore, block copolymers are available and could validate the activ-

ity of the original polymer. Typical chain extension experiment was carried out using the obtained PMA as the macro-RAFT agent and styrene as the second monomer ($[St]_0/[PMA]_0 = 800 : 1$, at 110°C, after 12 h with 55.1% conversion). GPC plots (Fig. 5) explicitly illustrate the changes in M_n and M_w/M_n before (a) and after (b) the chain extension reaction. There is an apparent peak shift comparing with original polymer. The experimental molecular weight increases from 7700 to 50,000, which is close to the calculated value ($M_{n,th} = 53,600$) with a little increase of the molecular weight distribution value (from 1.12 to 1.24), which indicate almost all chains of original polymer are active. These above results agree with the experimental criteria of a "living"/controlled polymerization, and the moieties of OTCC are successfully capped at the ends of obtained polymer.

The optical properties of the resulting polymers

Based on the RAFT mechanism and the above experimental results, fluorescent carbazole unit are attached to the ends of the polymer. Therefore the optical properties of the resulting polymers are characterized and compared with that of OTCC. Figure 6 shows the typical fluorescence spectra of OTCC and obtained polymer in DMF. The strong emissions excited at 294 nm are observed at 344 and 359 nm. The fluorescence intensity is in the following order: PSt > PMA > OTCC
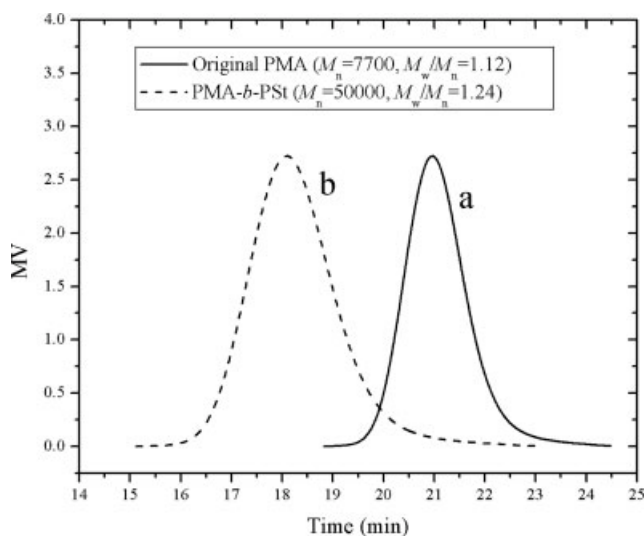

Figure 5 GPC traces of polymers before (a) and after (b) chain extension reaction.
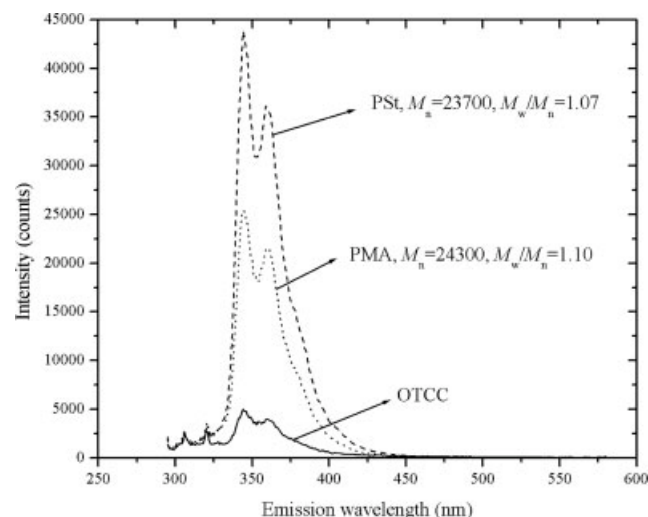

Figure 6 Fluorescence spectra of OTCC and resulting carbazole group labeled polymer measured at the concentration of 2×10^{-5} carbazole unit mol L^{-1} in DMF.

at the same measuring conditions. The fluorescence intensity of the polymer is stronger than the RAFT agent OTCC. This may be due to the stronger molecular movement of the RAFT agent than that of its corresponding polymers and thus caused more molecular collision and led to self-quench of fluorescence intensity. The intensity of PSt is stronger than the intensity of PMA for its contribution of styrene unit.

CONCLUSIONS

In summary, 2-oxo-tetrahydrofuran-3-yl, bearing a chiral carbon, was first used as the R group for the RAFT polymerizations of styrene, methyl acrylate and methyl methacrylate. OTCC was an effective RAFT agent for the polymerizations of styrene and methyl acrylate, i.e., the polymerizations exhibited ''living''/controlled characters, but it was not effective to control over the polymerization of methyl methacrylate. The strong emissions of obtained polymer excited at 294 nm were observed at 344 and 359 nm and the fluorescence intensity was in the following order: PSt > PMA > OTCC.

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