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Synthesis of Well-defined Carbazole Group Labelled Polymer via RAFT Polymerization and Study on the Optical Properties

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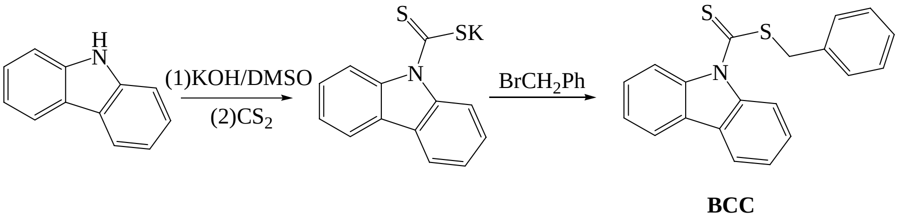
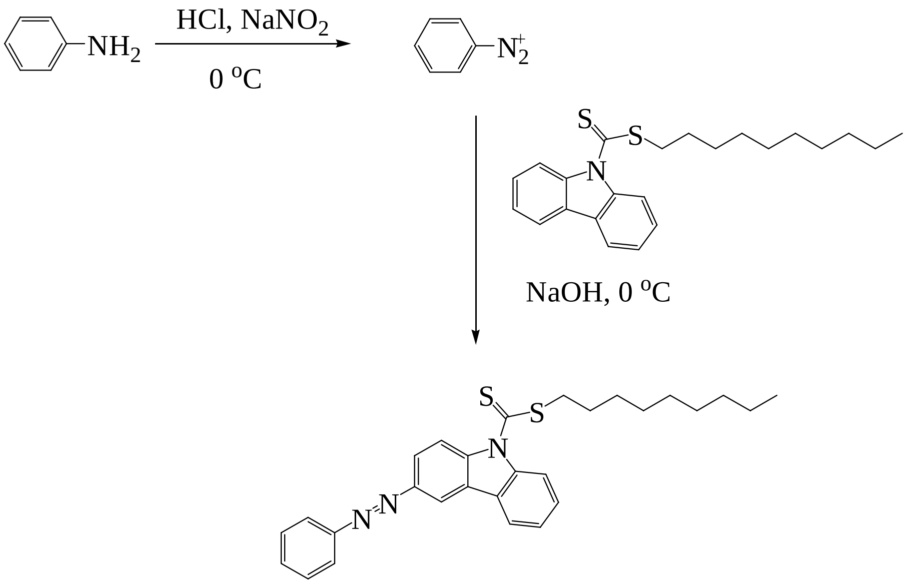
Abstract: Benzyl 9H-carbazole-9-carbodithioate (BCC) was synthesized and characterized. The single-crystal structure of BCC was first reported. The RAFT polymerizations of styrene and acrylates using BCC as the RAFT agent under conventional polymerization conditions were investigated. The results showed that the BCC was an effective RAFT agent for the polymerizations of styrene and acrylates. The well-controlled polymers were labelled with carbazole group, which was confirmed by ^{1}H NMR and the chain extension of the obtained polymer. Azo modified poly(methyl acrylate) (PMA) was synthesized through a post-polymerization azo-coupling scheme. The optical properties of obtained polymer were also characterized. The results showed that the carbazole group labelled polymer exhibited fluorescence and the azo polymer exhibited UV absorption behaviour in N,N-dimethyl formamide (DMF).

Introduction

End-labelled polymer has attracted the attention of polymer chemists for their special characters, especially fluorescence which has been widely used in the field of biochemistry and polymer chemistry [1-4]. Many synthetic methods have been developed to synthesize end-labelled polymer, such as living anionic polymerization [5, 6], and living radical polymerization, especially atom transfer radical polymerization (ATRP) [7-12]. However, to our best knowledge, there are few reports about synthesis of end-labelled polymer via reversible addition-fragmentation chain transfer (RAFT) polymerization. RAFT polymerization is one of the most recent of the living radical polymerization techniques [13, 14]. RAFT process is a polymerization which proceeds by a series of reversible addition-fragmentation steps in the presence of chain transfer agent (RAFT agent). Finally, RAFT agent moieties will be capped at both ends of the polymer. Thus, expected end-labelled polymer can be prepared via RAFT polymerization conveniently by designing proper RAFT agents. General structures of RAFT agents are dithioester [13, 14], xanthate [15-17], trithiocarbonate [18, 19] and dithiocarbamate [20-23]. For the dithiocarbamate used in RAFT polymerization, such as those derived from pyrrole and imidazole, the nonbonded electron pair on nitrogen must be involved in the aromatic system and thus less available for conjugation with the thiocarbonyl group. Benzyl 9H-carbazole-9-carbodithioate (BCC) has the character stated above. Furthermore, it also has been used as an effective RAFT agent for RAFT polymerization [24-26]. In this work, we synthesized BCC by the way as shown in Scheme 1 and first characterized its single-crystal structure by X-ray. We investigated the RAFT polymerizations of styrene and acrylates (MA, BA, OA) using BCC as RAFT agent. And the azo modified PMA was synthesized through a post-polymerization azo-coupling scheme (Scheme 2). The optical properties of obtained polymer were also characterized.



Scheme 1. Synthetic route of benzyl 9H-carbazole-9-carbodithioate (BCC).



Scheme 2. Synthetic route of the azo modified PMA.

Results and Discussion

Crystal Structure of BCC

BCC crystallizes in the orthorhombic space group *Pca2₁* and the asymmetric unit contains one BCC molecule. Scheme 3 (Exp. Sec.) showed the molecular structure and the unit packing diagram of BCC. The bond length of C1=S1 (1.642(3) Å) is shorter than that of C1-S2 (1.727(3) Å). The moiety was nearly planar while the two C_6H_4 rings torsion for 4.78°. The angle between the pyrrole ring and the CS_2 plane was 44.56°. While the C2~C8 Ar moiety was nearly vertical to the CS_2 plane with a torsional angle of 86.41°.

The "living"/controlled polymerizations using BCC as RAFT agent

The "living"/controlled polymerizations of styrene and methyl acrylate in bulk using BCC as RAFT agent have been carried out. Fig. 1 shows the plots of $\ln([M]_0/[M])$ *vs* reaction time for the polymerizations of styrene ($[St]_0/[BCC]_0$ = 200:1, 100 °C) and methyl acrylate ($[MA]_0/[AIBN]_0/[BCC]_0$ = 500:1:3 and 1000:1:3, 60 °C), respectively. In the studied range of conversions, the plots were approximately linear without induction period, which indicated that the propagating radical concentrations were almost constant and had no significant termination reactions during polymerization.

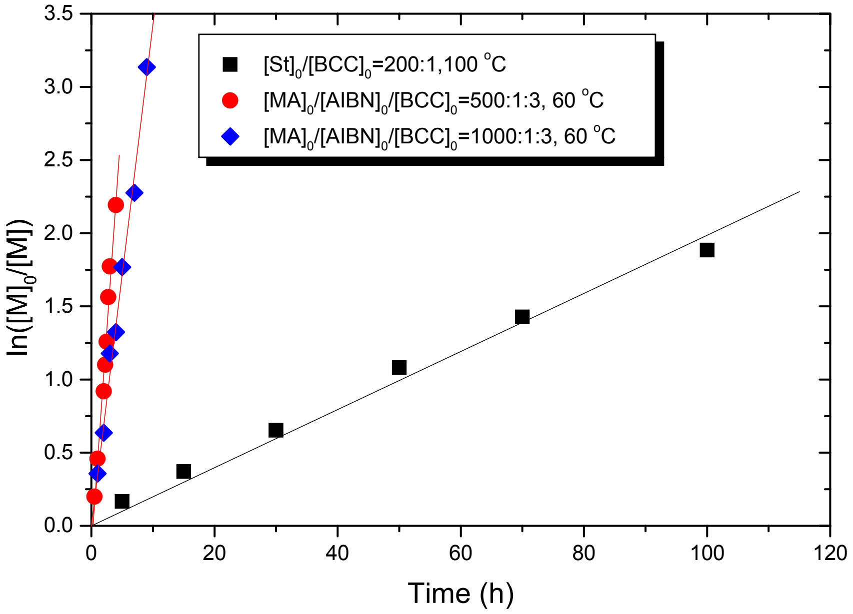


Fig. 1. Plots of $\ln([M]_0/[M])$ vs polymerization time for the RAFT polymerizations of styrene and methyl acrylate using BCC as RAFT agent.

In the case of styrene, the rate of polymerization by thermal initiation without any initiator was very slow. While methyl acrylate had a very reactive propagating radical with low steric bulk, which led to fast polymerizations with AIBN as an initiator.

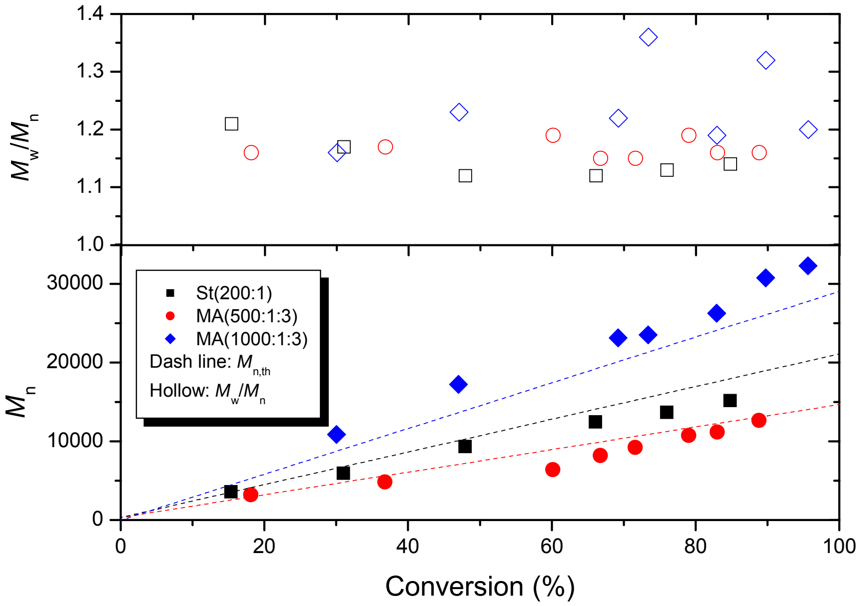


Fig. 2. Evolutions of the molecular weight and molecular weight distribution with monomer conversions. The conditions were the same as in Fig. 1.

The number-average molecular weight (M_n) of the polymer measured by GPC increased linearly with monomer conversion and was close to the calculated value $M_{n,th}$ ($M_{n,th}$ = $[St]_0 \times Mw_{st} \times$conversion/$[\text{RAFT agent}]_0$ + $Mw_{\text{RAFT agent}}$, Where $[St]_0$ and $[\text{RAFT agent}]_0$ are the initial concentrations of St and RAFT agent; Mw_{St} and $Mw_{\text{RAFT agent}}$ are molecular weights of St and RAFT agent, respectively.). The molecular weight distribution (M_w/M_n) was very narrow (Fig. 2).

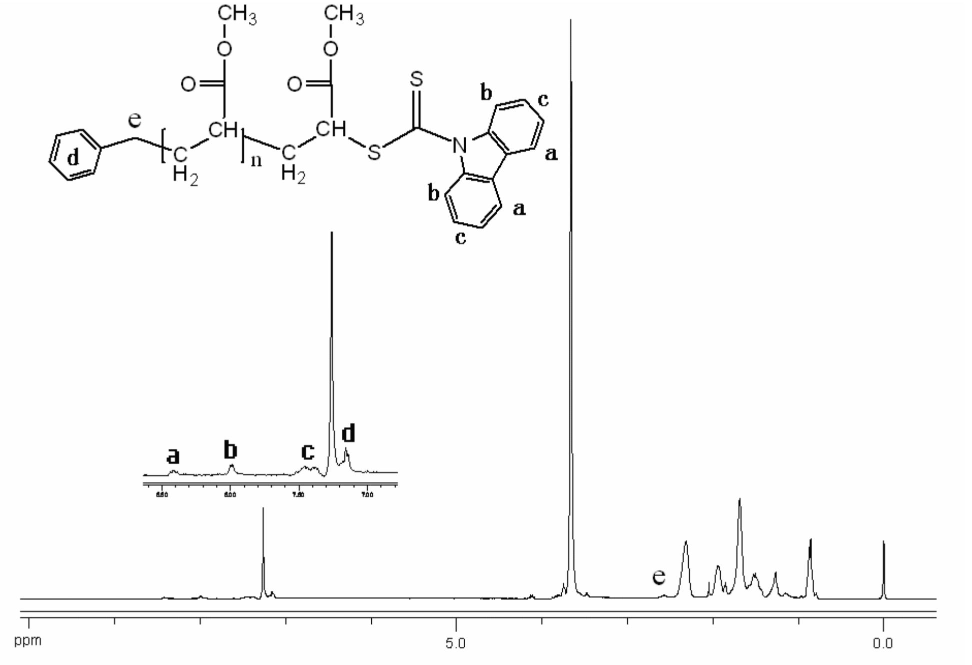


Fig. 3. Typical ^{1}H NMR spectrum of PMA obtained using BCC as RAFT agent.

The structures of obtained polymers were characterized by ^{1}H NMR. A typical ^{1}H NMR spectrum of PMA (M_n = 11200, M_w/M_n = 1.16) is shown in Fig. 3. Fig. 3 showed the characteristic signals of BCC moiety at δ = 7.14-8.42, which indicated that the moiety of BCC was capped at the end of the polymer. Therefore, block copolymers were achievable and could validate the activity of the original polymer. Typical chain extension experiment had been carried out using obtained PMA as the macro-RAFT agent and styrene as the second monomer ($[St]_0/[PMA]_0$ = 1000:1, at 100 °C, with 42.0% conversion). GPC plots (Fig. 4) explicitly illustrated the changes in M_n and M_w/M_n before (a) and after (b) the chain extension reaction. There was an apparent peak shift compared with the original polymer. The experimental molecular weight increased from 8200 to 47100 which was close to calculated value $M_{n,th}$ ($M_{n,th}$ = 51900). The molecular weight distribution had no obvious change, which indicated the original polymer was almost active.

These observations were consistent with the mechanism of RAFT polymerization and the results showed that the BCC was an effective RAFT agent for the RAFT polymerization of styrene and methyl acrylate. Furthermore, the bulk polymerizations of butyl acrylate (BA) and octyl acrylate (OA) using BCC as the RAFT agent had also been carried out. The results were listed in Tab. 1. As shown in Tab. 1, the molecular weights of the obtained poly(butyl acrylate) (PBA) and poly(octyl acrylate) (POA) increased linearly with monomer conversion with relatively narrow molecular weight distributions. The molecular weights of POA were close to the calculated values, while for BA, the molecular weights were a little higher than calculated values.

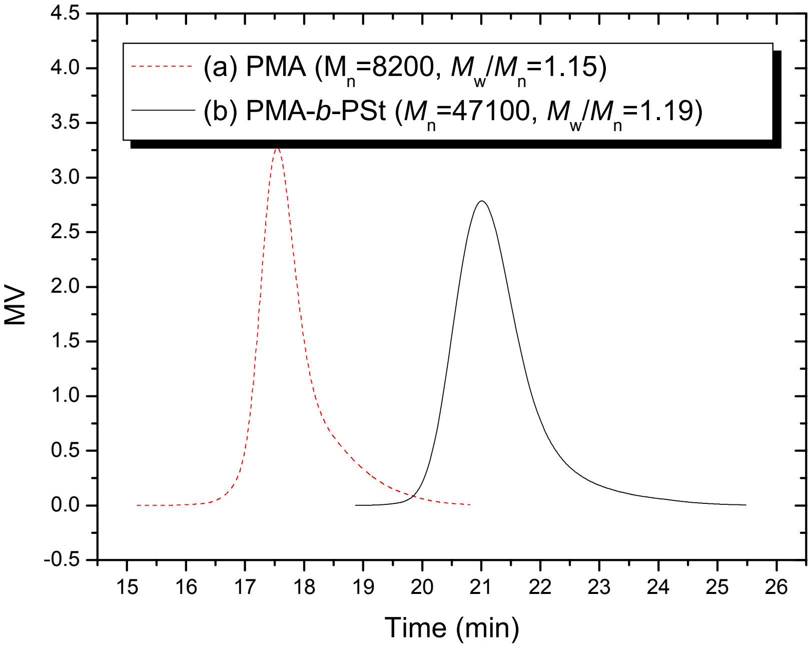


Fig. 4. GPC traces of polymer before (a) and after (b) chain extension reaction.

Tab. 1. Data of the RAFT polymerizations of butyl acrylate and octyl acrylate.

Monomer	Time (h)	Conversion (%)	$M_{n,th}$	M_n	M_w/M_n
BA[a]	0.5	17.4	4000	6200	1.21
	1	28.1	6300	8000	1.18
	2	50.3	11100	13900	1.12
	3	70.7	15400	19700	1.21
	4	80.1	17400	20100	1.18
OA[b]	1	18.1	11400	11500	1.43
	2	48.1	29900	29400	1.19
	4	57.2	35500	34000	1.29
	6	68.1	42200	43600	1.26
	10	87.0	53800	57600	1.24
	20	96.6	59700	60600	1.41

[a] $[BA]_0/[AIBN]_0/[BCC]_0$ = 500:1:3, 60 °C
[b] $[OA]_0/[AIBN]_0/[BCC]_0$ = 1000:1:3, 60 °C

The optical properties of the resulting polymers

Based on the RAFT mechanism, the carbazole unit, the rigid conjugated molecule, would exist at the end of the polymer. Therefore we characterized and compared the optical properties of the resulting polymers with BCC. The typical excitation spectra of BCC and the obtained well-controlled carbazole group labelled polymer in dimethyl formamide (DMF) at room temperature were shown in Fig. 5.

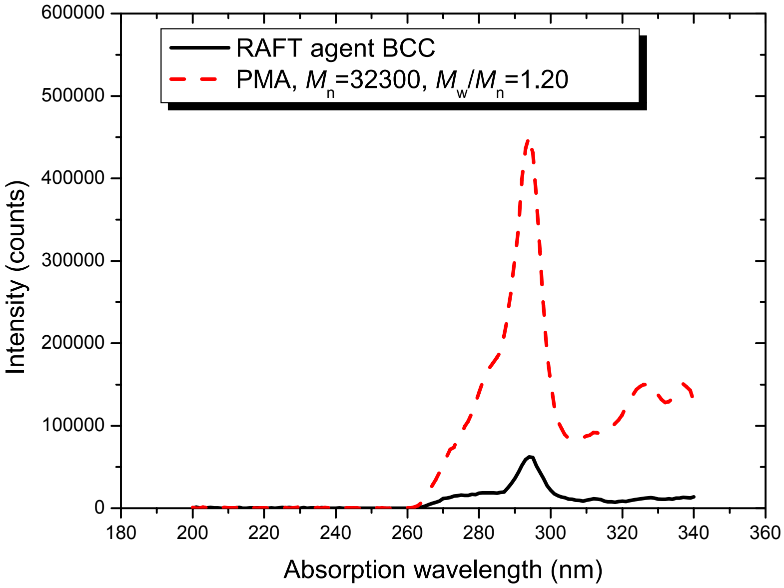


Fig. 5. Excitation spectra of BCC and carbazole group labeled polymer measured at the concentration of 1×10^{-4} carbazole unit mol·L^{-1} in DMF at room temperature.

The carbazole unit was excited strongly at 294 nm. Fig 6 showed the typical fluorescence spectra of BCC and end-labeled polymer in DMF. The strong emission peaks of PMA excited at 294 nm were observed at 344 and 358 nm. The fluorescence intensity of BCC was lower than PMA. This may be due to that the mobility of the RAFT agent should be stronger than that of obtained polymer, thus causing more molecular collision in RAFT agent solution than that of polymer's, leading to self-quench of fluorescence intensity.

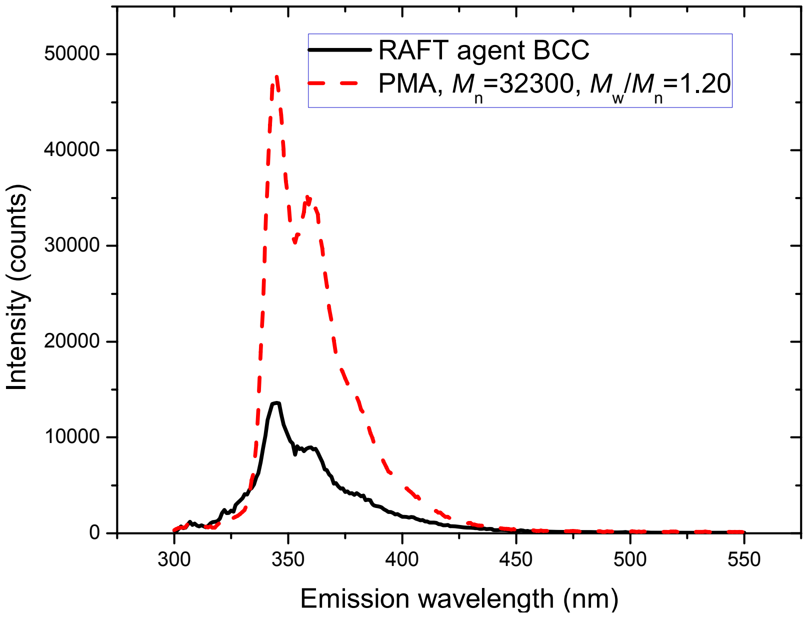


Fig. 6. Fluorescence spectra of BCC and carbazole group labeled polymer. The excitation wavelength was 294 nm and the conditions were same as in Fig. 5.

To confirm that the azo group was attached to PMA, we characterized the PMA modified by azo. Its ^1H NMR spectrum was showed in Fig. 7. Compared to Fig. 3 in Fig.7, a new peak (δ: 8.57, a) should be because of carbazole-H after azo group has been attached, and the benzyl-H (j, k) was still found and its peak was not shifted, which indicated that azo group was successfully attached to the carbazole group and not the benzyl group. In addition, according to the high sensitivity of the azo group to the ultraviolet light, we carried out the examination of the UV spectra of the azo PMA in DMF (Fig. 8). From the results of reported papers, the typical absorption of azobenzene attached to usual polymer was under 400nm [27-30].

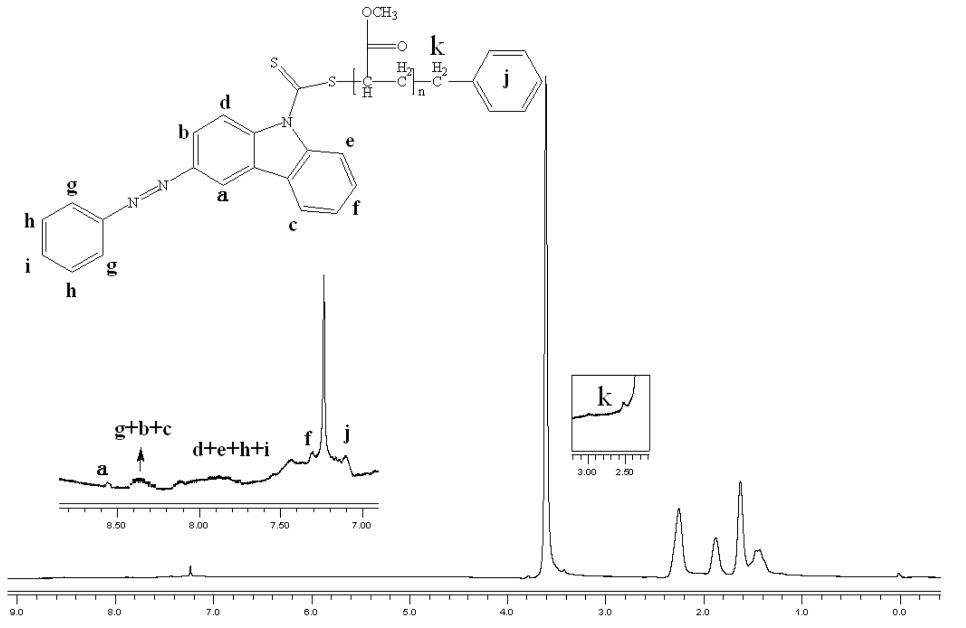


Fig. 7. ^1H NMR spectrum of the azo modified PMA.

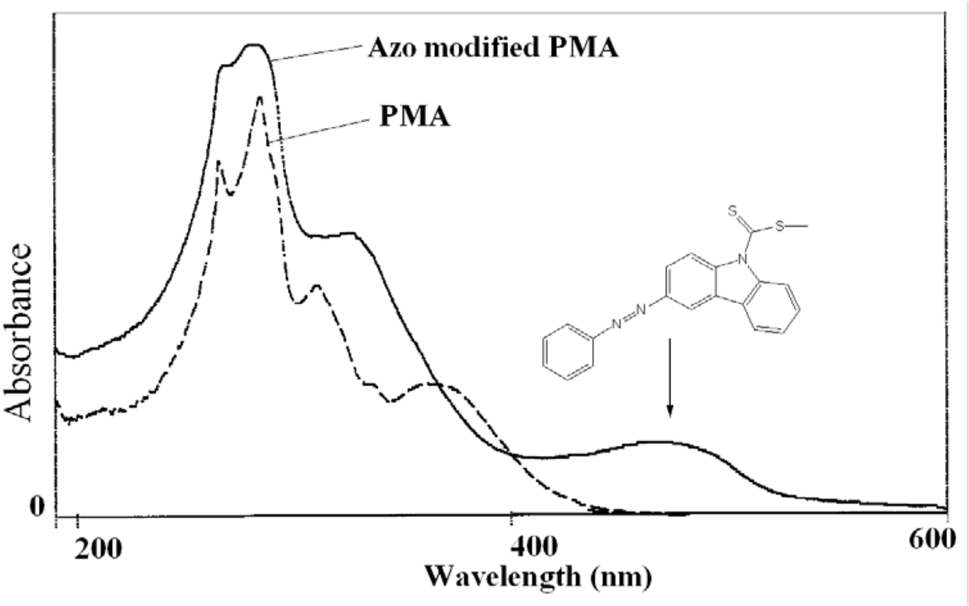


Fig. 8. UV spectra of PMA and the azo modified PMA in DMF. The concentration was 2×10^{-5} mol L^{-1}.

In Fig.8, a new absorption at round 480 nm suggested azobenzene had attached to the carbazole group at the end of PMA. The obvious red shift was caused by the azo chromophore conjugated with carbazole group [31-33]. Reference 33 also reported the shift in absorption spectra before and after azo modified on carbazole group.

Conclusions

The experimental results showed that the benzyl 9H-carbazole-9-carbodithioate was an effective RAFT agent in control of free radical polymerization of styrene and acrylates (MA, BA and OA) under conventional polymerization conditions. The molecular weights increased linearly with monomer conversion with relatively narrow molecular weight distributions, and were close to the calculated values. Obtained polymer had optical properties: the strong fluorescence emissions of the obtained well-designed PMA labeled with carbazole group excited at 294 nm were observed at 344 and 358 nm; both obtained PMA and the azo modified PMA strongly absorbed UV light in DMF.

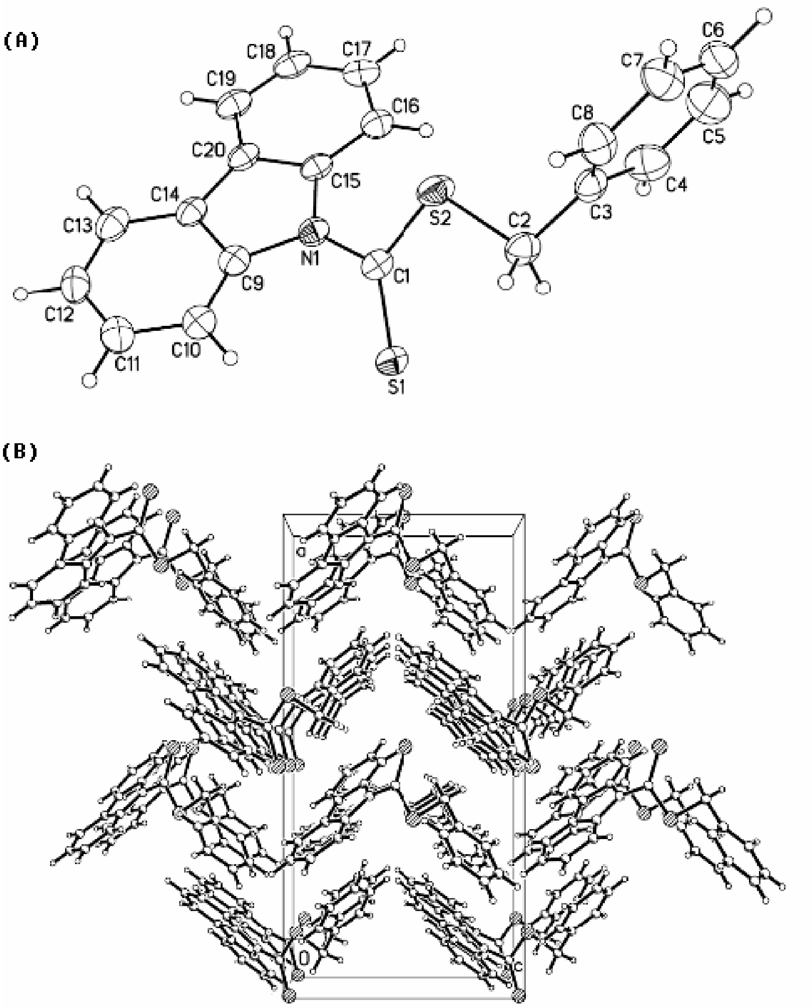
Experimental

Materials

All chemicals (analytical grade) used in this study were purchased from Shanghai Chemical Reagents Co. China and J&K-Acros. Monomers were 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 ^{o}C. Benzyl 9H-carbazole-9-carbodithioate (BCC) was prepared by the following procedure: a suspension of KOH (0.56 g, 0.01mol) in DMSO (50 mL) was prepared, and carbazole (1.67g, 0.01 mol) was added under vigorous stirring. The solution was stirred for 1 hour at room temperature and then carbon sulfide (0.76 g, 0.01 mol) was added dropwise. The resultant reddish solution was stirred for 2 hours at room temperature, and then bromomethyl-benzene (1.70 g, 0.01mol) was added. The mixture was stirred further for a night at the room temperature. The resultant reaction mixture was precipitated in large amount of water, and then a yellow solid was obtained. After being recrystalized from alcohol twice, the product was obtained as a yellow crystal (0.66g, dried, yield 20%). The product has been characterized by nuclear magnetic resonance (^{1}H-NMR), elementary analysis (EA), high efficiency liquid chromatography (HPLC) and single-crystal X-ray crystallography. The results were listed below: ^{1}H NMR. δ: 4.73(s, 2H), 7.23-7.48(m, 7H), 8.00(d, 2H, J = 7.6 Hz), 8.09 (d, 2H, J = 8.0 Hz), 8.66 (d, 2H, J = 6.8 Hz). EA. $C_{20}H_{15}NS_2$, Calculated: C 72.03 H 4.53 N 4.20, found: C 71.77 H 4.55 N 4.48. The purity was above 99% by HPLC. Other materials were used without further purification.

X-ray Crystallography

The measurement was performed on a Rigaku Mercury CCD X-ray diffractometer (3KV, sealed tube) at -80°C, using graphite monochromated Mo-Kα (λ = 0.71070 Å). A dark brown prism of BCC with dimensions 0.35 × 0.30 × 0.09 mm was mounted on a glass fiber with grease. Diffraction data were collected at ω mode with a detector distance of 35 mm to the crystal. Indexing was performed from 6 images, each of which was exposed for 15 s. A total of 720 oscillation images for each were collected in the range 6.48° < 2θ < 50.70°.



Scheme 3. Perspective view showing atom-numbering scheme (A); the unit cell packing diagram of BCC looking down the a-axis (B).

The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver. 1.3, 2001), and an absorption correction (multi-scan) was applied, which resulted in transmission factors raging from 0.898 to 0.972. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structure was solved by direct methods [34a], and expanded using Fourier techniques [34b]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically idealized positions (C-H = 0.98 Å for methyl groups) and constrained to ride on their parent atoms with Uiso(H) = 1.2Ueq(C). All the calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku/MSC, Ver. 3.60, 2004). Important crystal and data collection parameters for are summarized in supporting information.

Polymerizations

The following procedure was typical. A stock solution of 8 mL (69.5 mmol) of styrene and 115.7 mg (0.348 mmol) BCC (for acrylates, proper dose of AIBN was added) was prepared, and then aliquots of 1mL were placed in ampoules. The content was purged with argon for approximately 10 minutes to eliminate the oxygen. Then the ampoules were flame sealed. The polymerization reaction was performed at the appropriate temperature. After the desired reaction time, each ampoule was quenched in ice water, and opened. The reaction mixture was diluted with a little of THF (about 2 mL), and precipitated in large amount of methanol (about 300 mL, for MA using ligroin). The polymer was obtained by filtrating and dried at room temperature under vacuum to constant weight. Conversion was determined gravimetrically.

Synthesis of the azo modified poly(methyl acrylate)

The azo modified poly(methyl acrylate) was prepared by a post-polymerization azo coupling reaction. Aniline (0.0031g, 0.033mmol) was diazotized by the method described in scheme 2. The diazonium salt solution was added dropwise into a solution of PMA (M_n=26200, M_w/M_n = 1.19) (0.786g, 0.03mmol), in dimethylformamide (DMF) at 0 °C.

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. Calibration was performed with polystyrene or poly(methyl methacrylate) (molecular weight range 100-500,000) as standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 $mLmin^{-1}$ operated at 30 ^{o}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 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 $mL\cdot min^{-1}$ operated at 30 ^{o}C using C18 column and using Waters 996 as detector. The fluorescence intensity was measured by FLS920. The UV absorption spectra of the sample were determined on a Shimadzu-RF540 spectrophotometer.

Acknowledgements

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