Synthesis and photophysical properties of fluorescent polystyrene containing 1,8-naphthalimide via atom transfer polymerization

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Abstract: Fluorescent polystyrene was synthesized by Atom transfer polymerization with a novel 1,8-naphthalimide derivative as initiator. The optical characteristics of initiator and obtained polystyrene in DMF solution are discussed. Results indicate that both initiator and polystyrene can emit intensive green luminescence at 520 nm, but the polymer has a higher quantum yield and energy yield.

Introduction

Recently, much attention have been paid to 1,8-naphthalimide derivatives because of their wide applications in structure coloration [1], light emitting diodes [2,3], laser media [4] and probes [5]. Compared to small molecules, polymeric 1,8-naphthalimide derivatives are more promising for they have better optical stability, chromaticity and processability. Presently, there are three approaches to prepare such fluorescent polymers: (1) synthesis from different fluorescent monomers containing 1,8-naphthalimide chromophore, then copolymerization with styrene, acrylonitrile or methyl methacrylate [6], Vladimir Bojinov and coworkers have done much in this aspect, they studied their fluorescent properties and chromaticity [7-9]; (2) use of Suzuki coupling or Yamamoto polycondensation reaction to get some conjugated polymers modified by 1,8-naphthalimide fluorophore, Lixiang Wang and coworkers have gotten some single polymers for white electroluminescence diode by this method [10-12]; (3) Utilize chemical modification of commercially available polymers containing reactive groups, Deyue Yan and coworkers synthesized a new functional fluorescent polymer through the reaction of Poly(styrene-co-maleic anhydride) and 4-amino-N-(2,4-dimethyl-phenyl)-1,8-naphthalimide, the polymer has good thermal and optical property [13]. However, all the three methods listed above are uncontrolled, which may have some effects on their performance or limit further modification. So, it is worthwhile to synthesis such polymeric 1,8-naphthalimide derivatives via living polymerization.

As a relatively new living radical polymerization, Atom transfer radical polymerization (ATRP) has caught much interest in the synthesis of polymers with well-defined structure, lowly polydispersity and controlled molecular weight [14-16]. Especially, by using functional initiator, block, comb, graft, star, hyperbranched and surface-anchored polymers can be easily prepared. If these initiators have optical and electronic properties, the obtained polymers may also have such properties. For example, Xiulin Zhu and coworkers used a number of azo-initiators capable of

initiating styrene to obtain a new kind of polymers containing azo groups [17]. In the same way, series of initiators containing pyrene [18], anthracene [19] and C₆₀ groups [20] were also applied to synthesis of polymers with special fluorescent properties. But as a material possessing strong luminance, 1,8-naphthalimides have never been reported in ATRP systems. Herein, we first used a novel kind of 1,8-naphthalimide derivative 2-(2,3-dihydro-2-(4-methoxy-phenyl)-1,3-dioxo-1H-phenalen-7-ylamino) ethyl-2-chloroacetate (DPDPECI) (the chemical structure is shown in Scheme 1) as initiator for atom transfer polymerization of styrene and obtained a greenish fluorescent polystyrene.

Scheme 1. The synthetic route for fluorescent polystyrene.

Results and discussion

Synthesis of initiator DPDPECI

The synthetic route of DPDPECI was outlined in Scheme 1. 6-bromo-2-(4-methoxy-phenyl)-benzo[de]isoquinoline-1,3-dione (BPBD) was prepared by condensation of 4-bromo-1,8-naphthalic anhydride with 4-methoxybenzenamine in ethanol solution. 6-ethanolamino-2-(4-methoxy-phenyl)-benzo[de]isoquinoline-1,3-dione (EPBD) was obtained by nucleophilic substitution of the Br group with ethanolamine in methoxyl ethanol solution. DPDPECI was obtained by the esterification of EPBD with acryloyl chloride.

In every reaction, TLC analysis was used to testify the purity. Compared to BPBD and EPBD, DPDPECI cannot be obtained by simple recrystallization from chlorobenzene, ethanol or ethyl acetate. Thus the pure DPDPECI was prepared by passing through a silica gel using CHCl₃/EtOAc as eluent. Figure 1 shows the ¹H-NMR spectrum of DPDPECI in CDCl₃, the singlets at 3.86 ppm originate from the protons of methoxy at position 1, the singlets at 3.76 ppm and 4.16 ppm are assigned to the protons of alkyl in the position 3 and 4, other singlets can also be well related to the rest of protons of DPDPECI.

Fig. 1. ^1H -NMR of DPDPECI in CDCl_3 .

Fig. 2. ^1H -NMR of PSt ($M_n=18614$, $\text{PDI}=1.421$) in CDCl_3 .

Atom transfer radical polymerization of styrene

The polymerization was carried out using DPDPECI/CuCl/PMDETA as initiating system, styrene as monomer and cyclohexanone as solvent. The well-known mechanism of ATRP can be characterized by ^1H -NMR spectrum, kinetic plots, polydispersity index and block extension copolymerization.

As per the character of ATRP, DPDPECI should be incorporated at one end of the polymer chain, while the other end remains a terminal halide. It can be testified by ^1H -NMR spectrum. In Figure 2, signals at 3.90 ppm are attributed to the protons in position 1, including the protons of methoxy, the protons in the ester ethyl, signals at 4.4 ppm are assigned to the protons in position 2, the protons of alkyl next to the ester carbonyl, signals at 3.5 ppm are attributed to the terminal protons next to the halogen atoms.

Fig. 3. Kinetic plot for the polymerization of styrene in cyclohexanone solution (50%v/v) at 100 °C ($[\text{styrene}]/[\text{DPDPECI}]/[\text{CuCl}]/[\text{PMDETA}]=200:1:1:1$).

Fig. 4. Dependence of M_n and PDI with conversion for the polymerization of styrene initiated by DPDPECI. The condition was given in the caption of Figure 3.

The kinetic plot of polymerization at 100 °C is presented in Figure 3. It shows a typical linear variation of conversion and $\ln[M]_0/[M]$. ($[M]_0$ and $[M]$ denote the monomer concentrations at time 0 and t with time). Such a behaviour indicates that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to monomer. Figure 4 illustrates the dependences of number molecular weight and polydispersity index on monomer conversion. The M_n s increase linearly with the conversion and the PDIs are in the region of 1.43 to 1.65. In addition, it should be noted that the M_n s measured by GPC are deviated from the theoretical values $M_{n(th)}$ ($M_{n(th)}=[\text{St}]/[\text{DPDPECI}]\times\text{Conversion}\times 104$), which indicates a relatively slow initiation with respect to the fast propagation of monomer [21-23]. All of these results suggest a controlled polymerization.

To verify the living character of polymerization initiated by DPDPECI further, the resulting polystyrene was used for chain extension. The polymerization was carried

out in solution (cyclohexanone) at 80 °C, with MMA as the second monomer and $[MMA]/[PSt]/[CuCl]/[PMDTA] = 200:1:1:1$. After 3 hours, the molecular weight measured by GPC increased from 15300 to 21200 and the PDI changed from 1.4 to 1.6 with the conversion up to 50%. The GPC traces (Figure 5) show that the polymerization of the second monomer MMA for chain extension was successful.

Fig. 5. GPC traces of PSt and relative PSt-b-PMMA copolymer.

Spectral characteristics of PSt

Due to the electron donor-acceptor interaction between the substituents at C-4 position and the carbonyl group from the imide structure, 1,8-naphthalimide derivatives have good fluorescent properties. For the polystyrene initiated by DPDPECl, every polymer chain contains one 1,8-naphthalimide group, and should have similar luminescence as the initiator DPDPECl. Table 1 presents the photophysical characteristics of DPDPECl and polystyrene in DMF solution.

Tab. 1. Photophysical Characteristics of DPDPECl and PSt.

Substance	λ_A , nm	$\log \epsilon$	λ_F , nm	$\nu_A - \nu_F$, cm^{-1}	ϕ^a	E_F
DPDPECl	420	4.04	520	4578	0.61	0.49
PSt ^b	430	3.47	520	4025	0.71	0.59

^a Relative to Fluorescein [24]

^b The PSt refers to the polymer with $M_n = 18600$ and $PDI = 1.4$

Both DPDPECl and PSt in DMF solvent displayed a yellow-green colour and showed intensive green fluorescence under the radiation of UV light. The absorption maxima (λ_A) were in the visible region, 420 nm and 430 nm, respectively. The small distinction was probably caused by the chemical environment of chromospheres in DPDPECl and PSt. The fluorescent emission maxima for the initiator and polymer were the same ($\lambda_F = 520\text{nm}$).

For 1,8-naphthalimide derivatives, Stokes shift ($\nu_A - \nu_F$) is an important parameter, which indicates the difference in properties and structure of the dyes between the ground state S_0 and the first excited state S_1 . The Stokes shift is calculated by Equation (1):

$$(V_A - V_F) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^7 \quad (1)$$

Value for DPDPECl is larger than PSt, illustrates that more energy loss occurs during the transition from S_0 to S_1 in the small molecules.

Fluorescent quantum yield (ϕ) and energy yield of fluorescence (E_F) show the ability of fluorescent materials to emit the absorbed light energy. ϕ was determined using Fluorescein as a standard; E_F is calculated by Equation (2):

$$E_F = \phi_F \frac{\lambda_A}{\lambda_F} \quad (2)$$

For PSt, the values of ϕ and E_F are 0.71 and 0.59, higher than those of DPDPECl. Such phenomenon was caused by the macromolecular structure of PSt, which hinder the conformational changes in the chromophoric system. This result is in agreement with the value change of Stokes shift; all this means less energy loss and stronger emitting strength for PSt [9].

Conclusions

In this paper, we have prepared a novel fluorescent polystyrene containing 1,8-naphthalimide chromophore with atom transfer polymerization of styrene using DPDPECl/CuCl/PMDETA as initiating system and cyclohexanone as solvent. The initiator DPDPECl and polystyrene can emit intensive green fluorescence, but the polymer has higher quantum yield and energy yield.

Experimental

Materials

4-bromo-1,8-naphthalic anhydride (Liaoning Liangang Dyes Chemical Co. Ltd), 4-methoxy-benzenamine (Sinopharm Chemical Reagent Co. Ltd), ethanolamine (Sinopharm Chemical Reagent Co. Ltd), Copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (Shanghai Zhenxing Chemical Reagent Factory), methoxyl ethanol (Sinopharm Chemical Reagent Co. Ltd) and acryloyl chloride (Sinopharm Chemical Reagent Co. Ltd) were used as received. Styrene (CP, Shanghai Chemical Reagent Co. Ltd) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with deionized water and drying with magnesium sulphate anhydrous overnight, and finally distilled in vacuum. Copper (I) chloride (CuCl) (Shanghai Zhenxing Chemical Reagent Factory) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with ethanol absolute, dried in vacuum. PMDETA (98%, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4-Å molecular sieve and distilled in vacuum. Cyclohexanone (AR) was dried with magnesium sulphate overnight and distilled in vacuum. Triethylamine (Sinopharm Chemical Reagent Co. Ltd) was distilled in vacuum. Other reagents were used without any further purification.

Synthesis of 6-bromo-2-(4-methoxy-phenyl)-benzo[de]isoquinoline-1,3-dione (BPBD)

4-bromo-1,8-naphthalic anhydride 2.5g (9mmol) and 4-methoxybenzenamine 2.5g (25mmol) were refluxed in 100ml ethanol with vigorous stirring for 6 hours. The suspension was filtered to give a brown solid; recrystallization from chlorobenzene gave pale gray powder 3.0g (88%).

Synthesis of 6-ethanolamino-2-(4-methoxy-phenyl)-benzo[de]isoquinoline-1,3 dione (EPBD)

A mixture of BPBD (1.5 g, 3.9 mmol), ethanolamine (2.0 ml) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.5 g) was stirred in 50 ml methoxyl ethanol to give a brown solution; the solution was allowed to reflux for 4 hours before it was poured into water, and a orange solid precipitated. After filtration, this solid was dried and recrystallized from chlorobenzene to give 1.2 g of orange-red powder (87%).

Synthesis of 2-(2,3-dihydro-2-(4-methoxyphenyl)-1,3-dioxo-1H-phenalen-7-ylamino) ethyl 2-chloroacetate (DPDPECI)

EPBD 1.0 g (2.8 mmol) was dissolved in 100ml THF, dehydrated triethylamine 0.5 g (5 mmol) and acryloyl chloride (0.3 g) in 15 ml THF were added subsequently. The mixture was stirred at room temperature for 15 hours, poured into 500 ml water. Filtered and dried, then the yellow powder was passed through a silica column using $\text{CHCl}_3/\text{EtOAc}$ as eluent. Finally, DPDPECI 0.3 g was obtained (25%).

General polymerization

CuCl , PMDETA, cyclohexanone, DPDPECI, styrene, and a small magnetic stirrer were added to a pressure tube. The tube was sealed and cycled between vacuum and N_2 four times. Then the tube was sealed under N_2 and placed in a thermostatically controlled oil bath. Samples were taken periodically for conversion and molecular weight analysis. The samples were dissolved in THF and precipitated into a large amount of hot methanol with several drops of HCl aqueous solution, filtrated and dried under vacuum. This process was repeated three times and then the greenish powder was used for analysis.

Characterizations

^1H -NMR spectra were measured by INOVA 400 MHz NMR spectrometer, CDCl_3 as solvent. Purity of initiator was analyzed by TLC. Conversions for monomer were determined by gravimetry. Molecular weights and the polydispersity relative to polystyrene were measured using Waters1515 GPC with THF as a mobile phase and with column temperature of 30°C . UV-vis spectra were recorded on a Perkin-Elmerl-17 UV-vis instrument. Room temperature emission and excitation spectra were carried out using Edinburgh-920 fluorescence spectra photometer.

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