

Synthesis and properties of a stimulus-responsive block polymer

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1. Experimental

1.1. Materials

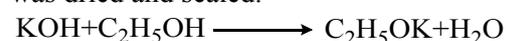
Sodium hydroxide-d (NaOD, >99.5%, 30 wt%) and deuterium chloride (DCl, >99.5%, 35 wt%) were supplied by Beijing Merida Technology Co., Ltd; deuterium oxide (D₂O, >99.9%) and tetrahydrofuran (THF, >99.5%) were purchased from Shanghai ZIQI Laboratory Equipment Co., Ltd; carbon disulfide (CS₂, >99%) and N-vinyl-2-pyrrolidone (NVP, >99%) were supplied by Shanghai McLean Biotechnology Co., Ltd; azobisisobutyronitrile (AIBN, >99%) was purchased from Bailiwei Technology Co., Ltd. and dimethylaminoethyl methacrylate (DMAEMA, >99.5%) was supplied by Qingdao Renas Polymer Materials Co., Ltd. CS₂ was purified by nitrification. AIBN was recrystallized twice with ethanol, prepared as absolute ethanol. THF was refluxed on potassium before use. Benzophenone was collected once it turned blue. NVP and DMAEMA were dried over calcium hydride and distilled under vacuum overnight.

1.2. Synthesis of small molecule initiators

1.2.1. Preparation of potassium ethyl xanthate

Under the ice bath conditions, 5.6 g KOH and 20 ml absolute ethanol were magnetically stirred and refluxed for 5 h, under continuous N₂ atmosphere until the solution turned slightly yellow. An excess amount of CS₂ was slowly added (4 h) dropwise to the solution using a dropping funnel, followed by the continuation of the reaction for 24 h. After completion of the reaction, petroleum ether was added and stirred for 30 min. Subsequently, the product was filtered, followed by the removal of ethanol and unreacted CS₂ as well as washing with petroleum ether. The steps were repeated thrice to obtain pure potassium alkylxanthate (yield: 91.94%).

4.0 g potassium alkylxanthate was dissolved in 40 ml acetone and stirred for 10 min. The solution was filtered, and 15 ml petroleum ether was added to the filtrate, resulting in a pale yellow flocculent precipitate appearing immediately. The contents were stirred for 10 min and filtered, resulting in pale yellow alkyl potassium orthoate after vacuum drying. The product was purified twice by following the method described earlier. After purification, the product was dried and sealed.

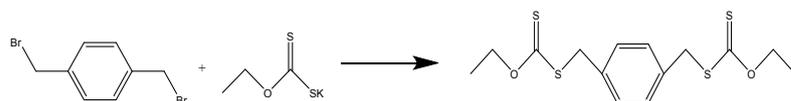




Scheme SI1. Preparation of potassium ethyl xanthate

1.2.2. Synthesis of small molecule initiators

In a three-necked flask, 8.8165 g ethyl ethylxanthate was dissolved in an appropriate amount of the solution of absolute ethanol and THF. Subsequently, 6.600 g dibromobenzyl (dissolved in THF) was added dropwise to the three-necked flask using a dropping funnel. The flask was placed in a water bath heated at 50°C, and the contents were magnetically stirred. With the addition of p-dibenzyl bromide, the reaction system gradually became opaque with a yellow precipitate. The reaction was continued for 48 h, followed by purification. For this, the reaction mixture was subjected to rotary evaporation to obtain a yellow solid. The solid material was dissolved in dichloromethane, followed by filtrations. The filtrate was extracted with water to remove the unreacted potassium xanthate. After extracting four times with deionized water, the lower organic layer was taken for rotary evaporation and vacuum drying. Finally, the product was obtained with a yield of 67.78%.



Scheme SI2. Synthesis of small molecule initiators

1.2.3. Synthesis of small molecule initiators by “One-pot” method

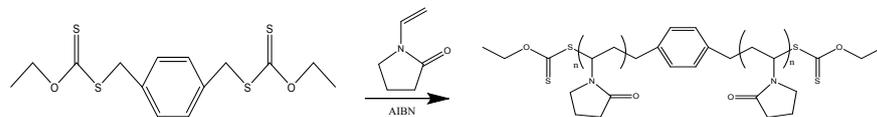
Under ice water bath conditions, KOH and absolute ethanol were magnetically stirred and refluxed, with continuous flow of N₂. The excess CS₂ was added dropwise to the solution using a dropping funnel. It should be noted that the addition process must be very slow. The reaction was continued for 24 h. Dichloromethane was dissolved in an appropriate amount of 1,4 – bis (bromomethyl) benzene, followed by the continuous addition of ethanol. The solid was dissolved by vigorous stirring, and the reaction was carried out at 38 °C for 36 h.

The purification was carried out as following: the reaction mixture was washed thrice with distilled water. Subsequently, the organic layer was separated, washed, and dried overnight over anhydrous MgSO₄. The solvent was removed using the rotary evaporator. Following this, the product was dissolved in chloroform (20 times volume). Finally, the product was obtained after precipitation with 80 volumes of petroleum ether. The yield of the product was 85.22%.

1.3. Synthesis of macroinitiator

The macroinitiator PVP-CTA-PVP(macro-CTA) and macroinitiator PDMAEMA-CTA-PDMAEMA was synthesized by using the tube sealing method, described as follows: the arm length of the macro-CTA was controlled by adjusting the ratio of n(NVP)/n(CTA) and n(DMAEMA)/n(CTA). Thus, CTA with different arm lengths were synthesized. For this, the corresponding monomer, CTA and AIBN initiator were weighed as per the calculations. The reagents were added to the Shrek tube with magnetons. An appropriate amount of ethanol was subsequently added, followed by stirring. After dissolution of the reagents, nitrogen gas was continuously introduced for 30 min. The contents were sealed after three cycles of freezing-thawing, followed by heating in a water bath at 65 °C. After carrying out the reaction for a

certain period of time, the reaction flask was taken out of the bath and swiftly frozen in liquid nitrogen. The post-treatment steps were as follows: after dissolving the product in ethanol, it was precipitated with diethyl ether thrice to remove the unreacted CTA and monomers. The yield of the product was ~75%.

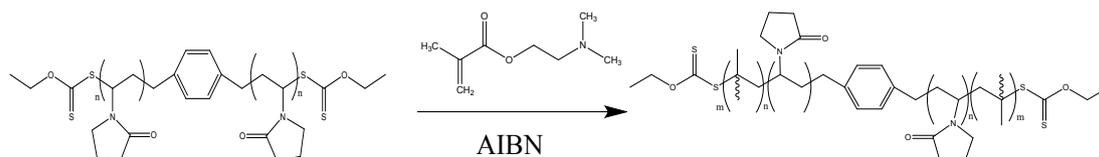


Scheme SI3. Synthesis of macroinitiator

1.4. Synthesis of PDMAEMA-*b*-PVP-CTA-PVP-*b*-PDMAEMA

The ratio of the components of the PDMAEMA segment with different repeating unit numbers for the same macro-CTA was calculated. Based on the calculations, the corresponding monomer, macro-CTA and AIBN initiator amounts were weighed, and the polymer was synthesized by following the method described earlier.

The post-treatment method was as follows: the product was dissolved in ethanol and subsequently precipitated with *n*-hexane. The secondary purification was carried out by dissolving the product in ethanol and precipitating it thrice with petroleum ether.



Scheme SI4. Synthesis of PDMAEMA-*b*-PVP-CTA-PVP-*b*-PDMAEMA

1.5 Characterization

Fourier-transform infrared spectroscopy (Nicolet 360) was used to monitor the functional groups in the products. The spectra were taken in the scanning range from 4000 cm^{-1} to 400 cm^{-1} , with 4 cm^{-1} resolution and 128 scans. The atomic proportion was obtained by using CHNSO elemental analyzer (Vario EL cube). Nuclear magnetic resonance (NMR, Avance300-DPX) was used to obtain the ^1H NMR spectra of the block polymer. The tests were carried out with the deuterated chloroform and heavy water as solvents and tetramethylsilane as the internal standard. The molecular weight of the synthesized macroinitiator was determined by gel permeation chromatography (GPC) using VE 3580 differential detector, with three malvin columns connected in series (T5000+T3000+T1000), and the column temperature set to 35°C. DMF (3.5 MM ttabr) was used as the mobile phase, with the flow rate of 0.8 mL min^{-1} , and polystyrene was used as the standard sample. Dynamic light scattering (DLS) was carried out using 0.5 mg/mL aqueous solution of the block polymer. The particle size distribution of the aqueous solution of the block polymer was analyzed using Malvern instruments Zetasizer Nano ZS90 instrument with the 4mW He-Ne laser of 633 nm wavelength and 173° test angle. Transmission electron microscopy (TEM) was performed on a JEM-2100F microscope with an accelerating voltage of 200 kV.

2. Results and Discussion

2.1. Small molecule CTA

2.1.1 Elemental analysis

Theoretically, the content of each element should be: C: 48.52%, H: 5.23% and S: 37.01%. As shown in Table SI1, the experimentally measured values are observed to be consistent with the theoretical values under ideal conditions. Thus, it can be concluded that ethyl xanthate was successfully synthesized.

Table SI1 Elemental analysis of the CTA

Name	C (%)	H (%)	S (%)
CTA	48.52	5.207	36.254
CTA	48.46	5.181	36.665
Mean value	48.49	5.194	36.595
Deviation, abs	0.04	0.018	0.099
delta	0.06	0.026	0.141

2.1.2 Infrared characterization

As shown in Fig. SI1 and Table SI2, the corresponding functional groups of ethyl xanthate are reflected in the product.

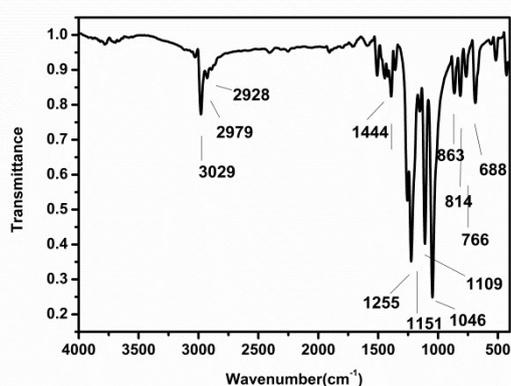
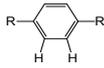


Fig. SI1 Infrared spectra of the small molecule CTA

Table SI2 Analysis of the infrared spectra of the small molecule CTA

Wave Numbers (cm ⁻¹)	Type
3029	C-H stretching vibration in 
2979	C-H stretching vibrations of methyl groups in $\text{CH}_3\text{-C-}$ H_2
2928	C-H stretching vibrations of methylene groups in $\text{CH}_3\text{-C-}$ H_2
1444	-CH ₂ - deformation vibration and -CH ₃ stretching vibration in $\text{CH}_3\text{-C-}$ H_2
1390	C-H deformation vibration in -CH ₃
1255	C-O stretching vibrations in 

1046	C-S stretching vibrations in 
1151	C=S stretching vibrations in 
863	out-of-plane deformation vibration of the para-substituted benzene ring
688	vibration of the in-plane ring deformation of the para-substituted benzene ring
814	plane deformation vibration of the adjacent two hydrogen atoms at para position in 
766	rocking vibration of C-C skeleton

2.1.3 ¹H NMR spectrum

To further determine the product structure, NMR characterization was carried out, shown in Fig. SI2 and Table SI3. The integral area ratio a:b:c:d is observed to be 1:1:1:1.5, and the proton number is 4:4:4:6, which are observed to be completely consistent. Thus, the NMR analysis reconfirmed that ethyl xanthate was successfully synthesized.

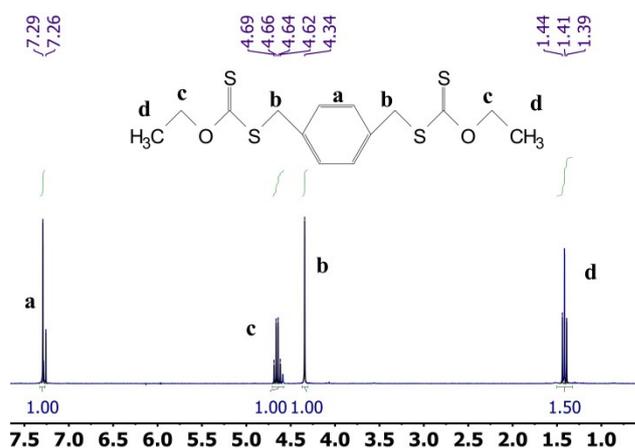


Fig. SI2 ¹H NMR spectrum of ethyl xanthate synthesized by One-pot method.

Table SI3 Analysis of the ¹H NMR spectra of ethyl xanthate synthesized by One-pot method..

Chemical Shift (ppm)	Type
1.44, 1.41 and 1.39	hydrogen proton absorption peaks of the terminal methyl group of -OCH ₂ -CH ₃
4.34	methylene proton absorption peak at the benzylic position
4.69, 4.66, 4.64 and 4.62	hydrogen proton absorption peaks of the methylene group attached to the methyl group in -OCH ₂ -CH ₃
7.29	hydrogen proton absorption peak of the methine group on the phenyl group