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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

The Electrophilic Effect of Thiol Group on Thiol-yne Thermal Click Polymerization for Hyperbranched Polythioether

Bo Zhao,[a] Yaochen Zheng,[a,b] Zhulin Weng,[a,c] Shengying Cai,[a] and Chao Gao[a]*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

This paper firstly revealed the electrophilic effect of thiol groups on thiol-yne polymerization. For it, we designed and synthesized five kinds of α-thiol-ω-alkynyl AB_2 type intermediates with different electrophilicity of thiols. The thiol electrophilic effect can be assessed by chemical shift (δ) and measured directly by nuclear magnetic resonance (NMR) spectroscopy. As the evidence by gel permeation chromatography (GPC) and NMR tracking measurements, the polymerization rate and molecular weight (MW) significantly enhanced with the reducing of electrophilic effect of thiol. On the contrary, increasing electrophilicity of thiol, the resultant degrees of branching (DBs) enhanced. The semiquantitative relation between reactive rate constant (k) and δ (or electrophilicity of thiol) can be expressed by $k = 2.41 - 1.34\ \delta$. Therefore, important features of thiol-yne polymerization and HPTEs, such as, rate constant (k), MW, DB, *etc*., can be roughly estimated in advance by the NMR measurement of thiol electrophilic effect.

1. Introduction

Hyperbranched polymers (HPs) have highly branched specific three-dimensional architecture, abundant intramolecular cavities, and peripheral functional groups for diverse potential applications.[1-19] Recently, hyperbranched polythioether (HPTE) has attracted significant interest due to large molecular weight (MW) and high degree of branching (DB), as well as simple, rapid, and scalable synthesis.[18-21] In addition, since the chain transfer constant of thiol group is much larger (about 70 times) than those of functional groups such as, hydroxyl, carboxyl, amino, epoxy, azide groups, and so on, these available functional groups could be facilely introduced into HPTEs via radical initiated thiol-yne polymerization of AB_2 or A_2+CB_2 type small monomers or macromonomers.[21-24]

As declared by Finzi et al. in 1930,[25] two-step consecutive additions, that is, the first addition of a thiol to an alkyne and the subsequential addition of another thiol to the resultant vinyl thioether, were involved in a complete thiol-yne reaction. Thiol-yne addition is a classic nucleophilic addition in nature,[26-28] therefore, electrophilicity of thiol, alkynyl or vinyl thioether must play an important role in thiol-yne polymerization and the structure of product. Using six kinds of alkynes including 1-octyne, butyl 3-mercaptopropionate, ethyl propiolate, propargyl acetate, methyl propargyl ether, methyl propargylamine, 2-octyne, and cyclooctyne as model compounds, Lowe and Bowman *et al*. have revealed the influence of electrophilicity, sterical hindrance and strain-promoted effect of alkynyl on photo-initiated thiol-yne addition in 2010.[29] However, the role of thiol group in thiol-yne polymerization still remains largely unexplored till now.

Within our previous work, we reported the facile synthesis of HPTEs via A_2+CB_2 strategy in one-pot and found the employed thiol compound with different chemical structure have an effect on yield and MW of products.[30] To figure out the effect of thiol electrophilicity on thiol-yne polymerization, we designed and synthesized five kinds of α-thiol-ω-alkynyl AB_2 like intermediates *via* thiol-ene click reaction of selected dithiol compounds and propargyl acrylate. Combined NMR and GPC detections, the influence of the thiol electrophilic effect on both polymerization rate and architecture of HPTEs was systemeticall investigated. The results show that reaction rate and MW decreased with the increasing electrophilicity of thiols, whereas the theoretically calculated DB increased with the increasing of thiol electrophilicity. As the necessary theory supplement for thiol-yne addition, it contributes to obtain a full understanding for the relation of thiol-yne polymerization and the structure of starting material.

Experimental Section

Materials

Octane-1,8-dithiol (**1**), 3,6-dioxaoctane-1,8-dithiol (**2**), 1,4-butanediol bis(thioglycolate) (**3**), 1,5-pentanedithiol (**4**), 1,2-ethanedithiol (**5**), propargyl acrylate, and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Aladdin Chemical Co. Prior to use, AIBN was recrystallized twice from absolute ethanol solution, and propargyl acrylate was passed through a column filled with basic alumina to remove the inhibitor. Tetrahydrofuran (THF), ethyl acetate, dichloromethane (DCM), and triethylamine (TEA) were of chemically pure grade, and were obtained from Sinopharm Chemical Reagent Co. Ltd. Unless specially indicate, all other organic reagents were used without further purification.

Synthesis of AB_2 type intermediates (6-10)

AB_2 like intermediates, **6-10**, were synthesized *via* thiol-ene Michael addition,[26,31,32] using triethylamine (TEA) as catalyst and undergoing a similar synthesis process. Typically, octane-1,8-dithiol (**1**) (10 mmol), 8 mL of THF, and TEA (10 mmol) were charged into a 25 mL round-bottom flask, and then cooled to 0 °C. The solution was purged with high purity N_2 for 30 min to eliminate oxygen. 2 mL THF solution of propargyl acrylate (10 mmol) was added dropwise to the aforementioned mixture over a period of 30 min by a syringe under vigorous stirring. Then the addition was conducted at 45 °C. At given intervals, the concentration of propargyl acrylate in the mixture was detected using ^{1}H NMR spectroscopy, until the proton signals of the CH_2=CH moiety totally vanished.[30] Cooling to room temperature, the mixture was diluted with 50 mL CH_2Cl_2, and then washed by 0.5M HCl solution (20 mL×2) and with distilled water (50mL×3). The organic phase was dried over $MgSO_4$, and filtered. The collected solution was concentrated by rotary evaporation and dried under vacuum, affording colorless liquid (2.59 g, 89.3%) which will be used as the intermediate, **6**, for the further synthesis of HPTE**1**.

Intermediate **6**, ^{1}H NMR (300MHz, $CDCl_3$, ppm): 4.70 (d, 2H, CH≡CC$\boldsymbol{H}_2$O), 2.80-2.70 (m, 2H, OCC$\boldsymbol{H}_2$CH$_2$S), 2.70-2.55 (m, 4H, HSC$\boldsymbol{H}_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$SC$\boldsymbol{H}_2$), 2.55-2.45 (m, 3H, C$\boldsymbol{H}$≡CCH$_2$OCOCH$_2$CH$_2$SC$\boldsymbol{H}_2$), 1.52-1.68 (m, 4H, HSCH$_2$C$\boldsymbol{H}_2$CH$_2$CH$_2$CH$_2$CH$_2$C$\boldsymbol{H}_2$CH$_2$S), 1.46-1.25 (m, 8H, HSCH$_2$CH$_2$C$\boldsymbol{H}_2$C$\boldsymbol{H}_2$ C$\boldsymbol{H}_2$C$\boldsymbol{H}_2$CH$_2$CH$_2$S), 1.31 (t, 1H, $\boldsymbol{H}$SCH$_2$).

Intermediate **7**, ^{1}H NMR (300MHz, $CDCl_3$, ppm): 4.70 (d, 2H, CH ≡ CC$\boldsymbol{H}_2$O), 3.73-3.53 (m, 8H, HSCH$_2$C$\boldsymbol{H}_2$OC$\boldsymbol{H}_2$C$\boldsymbol{H}_2$OC$\boldsymbol{H}_2$CH$_2$S), 2.84-2.75 (m, 4H, HSC$\boldsymbol{H}_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$SCH$_2$C$\boldsymbol{H}_2$), 2.75-2.62 (m, 4H, CH$_2$OCH$_2$C$\boldsymbol{H}_2$SC$\boldsymbol{H}_2$CH$_2$), 2.49 (t, 1H, C$\boldsymbol{H}$≡C), 1.53 (m, 1H, $\boldsymbol{H}$SCH$_2$),

Intermediate **8**, ^{1}H NMR (300MHz, $CDCl_3$, ppm): 4.70 (d, 2H, CH≡CC$\boldsymbol{H}_2$O), 4.16 (d, 4H, C$\boldsymbol{H}_2$CH$_2$CH$_2$C$\boldsymbol{H}_2$), 3.55-3.22 (m, 4H, HSC$\boldsymbol{H}_2$COOCH$_2$CH$_2$CH$_2$CH$_2$OCOC$\boldsymbol{H}_2$), 3.00-2.90 (m, 2H, CH$_2$ SCH$_2$ C$\boldsymbol{H}_2$), 2.81-2.70 (m, 2H, CH$_2$ SC$\boldsymbol{H}_2$ CH$_2$), 2.47 (t, 1H, C$\boldsymbol{H}$ ≡C), 1.74 (t, 4H, CH$_2$C$\boldsymbol{H}_2$C$\boldsymbol{H}_2$CH$_2$), 2.03 (t, 1H, $\boldsymbol{H}$S).

Intermediate **9**, ^{1}H NMR (300MHz, $CDCl_3$, ppm): 4.70 (d, 2H, CH≡CC$\boldsymbol{H}_2$O), 2.82-2.70 (m, 2H, OOCC$\boldsymbol{H}_2$CH$_2$SCH$_2$), 2.7-2.55 (m, 4H, HSC$\boldsymbol{H}_2$CH$_2$CH$_2$CH$_2$CH$_2$SC$\boldsymbol{H}_2$CH$_2$), 2.55-2.45 (m, 2H, OOCCH$_2$CH$_2$SC$\boldsymbol{H}_2$), 2.48 (t, 1H, C$\boldsymbol{H}$≡C), 1.52-1.68 (m, 4H, HSCH$_2$C$\boldsymbol{H}_2$CH$_2$C$\boldsymbol{H}_2$CH$_2$S), 1.52-1.25 (m, 2H, HSCH$_2$CH$_2$C$\boldsymbol{H}_2$CH$_2$CH$_2$S), 1.34 (t, 1H, $\boldsymbol{H}$SCH$_2$).

Intermediate **10**, ^{1}H NMR (300MHz, $CDCl_3$, ppm): 4.70 (d, 2H, CH≡CC$\boldsymbol{H}_2$O), 2.90-2.60 (m, 8H, HSC$\boldsymbol{H}_2$C$\boldsymbol{H}_2$SC$\boldsymbol{H}_2$C$\boldsymbol{H}_2$), 2.49 (m, 1H, C$\boldsymbol{H}$≡C), 1.68 (t, 1H, $\boldsymbol{H}$SCH$_2$CH$_2$SCH$_2$).

Synthesis of HPTEs (HP 1-5)

Alkyne-capped HPTEs (HP **1-5**) were facilely synthesized *via* thermal initiated thiol-yne polymerization of the obtained α-thiol-ω-alkynyl AB_2 type intermediates, **6-10**, following the similar procedure, respectively. Typically, the intermediate, **6**, (50 mmol) were diluted with toluene to 0.5 M and mixed with AIBN (2.5 mmol). After purging N_2 to the flask for 30 min, the solution was heated at 65 °C for 24 h. To monitor the thiol-yne polymerization, at the given intervals, samples were collected through an air-tight syringe and directly measured using NMR and GPC. After twice precipitation with cooled methanol, the powders were offered and dried in vacuum at 30 °C over night. The chemical structures of the obtained HP**1**-HP**5** were further confirmed by ^{1}H NMR measurements, respectively.

Measurement and techniques

Nuclear magnetic resonance spectroscopy (NMR). The ^{1}H NMR spectra were recorded by a Varian Mercury Plus 300 MHz spectrometer. Samples were dissolved in deuterium chloroform ($CDCl_3$) with the tetramethylsilane (TMS) as an internal reference.

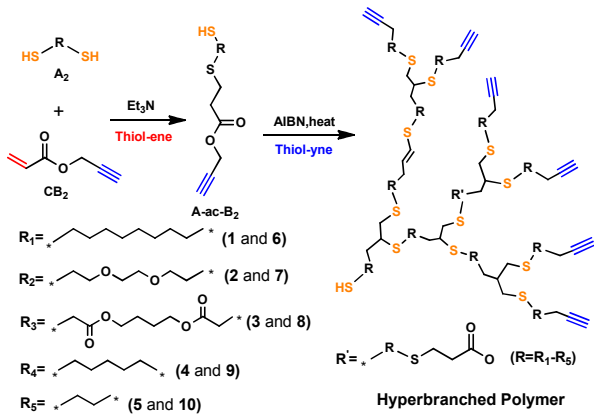
Gel permeation chromatography (GPC). The molecular weights and molecular weight distributions were measured on a PL-GPC220 with a refractive index detector. THF was used as eluent at a flow rate of 1.0 mL min^{-1}.

Fourier transform infrared spectroscopy (FTIR). All the FTIR spectra were carried out on a Bruker VECTOR-22 IR spectrometer at room temperature. In all cases, the spectra were collected over 32 scans at a spectral resolution of 4 cm^{-1}.

Results and Discussion

Synthesis of AB_2 type intermediates (6-10)

To get a clear idea of the electrophilicity influence on thiol-yne polymerization, we select five dithiols (**1-5, Scheme 1**) and design two series of AB_2 type intermediates (**6-10**): 1) similar atom numbers in their backbones with the different thiol substituents, such as **6-8**; 2) identical thiol substituent groups with different atom numbers, such as **6**, **9** and **10**. Here, we employed thiol-ene Michael addition to synthesize α-thiol-ω-alkynyl AB_2 type intermediates, due to its mild reaction condition, high efficiency, reliability and atom economy (Scheme 1).[22,31,32] Furthermore, five kinds of dithiols (**1-5**) reacted with the same propargyl acrylate ensure all the products with identical alkynyl group to eliminate its impact on the propagation.



Scheme 1 Thiol-ene and thiol-yne sequential click reactions for HP**1**-HP**5** via $A_2 + CB_2$ strategy.

Based on ^{1}H NMR tracking measurements, it takes 6 h to complete additions of **1** and **4** to CH_2=CH, whereas it needs 8 h to carry out reactions of **2**, **3** and **5** to CH_2=CH, following the anti-Markovnikov rule.[26,33] Their corresponding chemical structures were also characterized by ^{1}H NMR spectroscopy (Figs. 1 and 2). As shown in ^{1}H NMR spectra, all proton signals of resultant AB_2 intermediates were assigned and labeled with different alpha codes, respectively. No proton signals of C$\underline{H}_2$=C$\underline{H}$- moiety appeared at 5.6-6.6 ppm, suggesting the thiol-ene click reactions completed. Moreover, based on the ratio of

the integration of the proton signals of -OC$\underline{H_2}$C≡CH to that of the proton signals of the terminal group, HSC$\underline{H_2}$- (1:1), it further confirmed that all the intermediates were successfully synthesized. The proton signals of alkynyl and thiol groups were labeled with "a" and "k" (Fig. 1). Notably, the locations of "a" in **6-10** were identical, indicating protons of alkynes exist in the similar chemical environment. However, there was significant difference of those of "k" (ascribed to thiol protons) in two series of intermediates, caused by the different substituent groups. As shown in Figs. 1, 2 and S1, the proton signals of thiols in **6-10** located at 1.31, 1.53, 2.03, 1.34 and 1.68 ppm, which were similar to those of thiols in starting materials (1.34, 1.58, 2.00, 1.35 and 1.67 ppm). In order of decreasing electrophilicity of thiol, there was **8** > **10** > **7** > **9** > **6**. Moreover, this result implied that we can exactly infer the electrophilicity of thiol in corresponding intermediate as long as we have got the chemical shift in starting material by the ^{1}H NMR measurement.

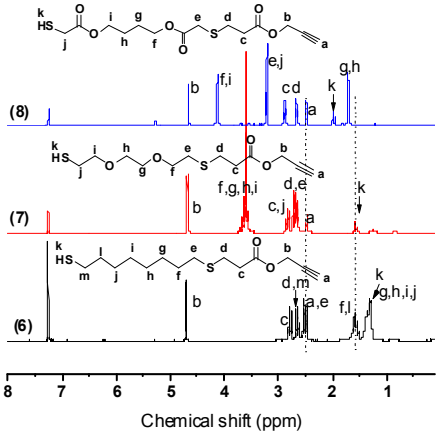


Fig. 1 ^{1}H NMR spectra of intermediates **6-8**.

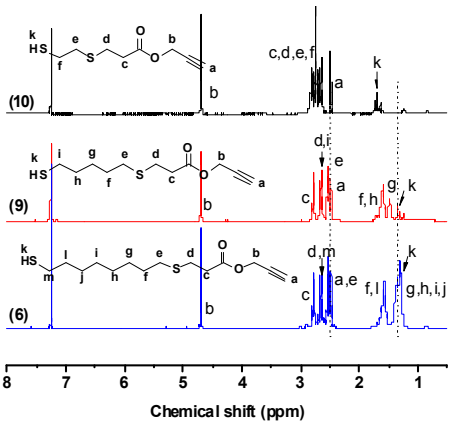


Fig. 2 ^{1}H NMR spectra of intermediates **6**, **9** and **10**.

Additionally, via thiol-ene click chemistry, all the yields of **6-10** were over 89.3%. With different thiol electrophilic effect, these intermediates were used to carry out the sequential thiol-yne addition for the synthesis of HPTEs.

Synthesis of HPTEs (HP1-HP5)

A series of HPTEs (HP**1**-HP**5**) were synthesized via radical initiated thiol-yne step-growth polymerization using the obtained **6-10** as model compounds in toluene at 65 °C (Scheme 1). To eliminate coupling reactions between macromolecular radicals as far as possible,[21,34,35] we control the concentrations of **6-10** are low enough (about 0.5 M).[30]

As shown in NMR and FTIR (Figs. 3, 4 and S2-S8), the signals intensity of thiol and alkynyl group gradually weakened and the reaction system increasingly became viscous along with reaction time extending, implying the thiol-yne polymerization of **6** was effectively triggered by free radical yielded from the hemolysis of AIBN.

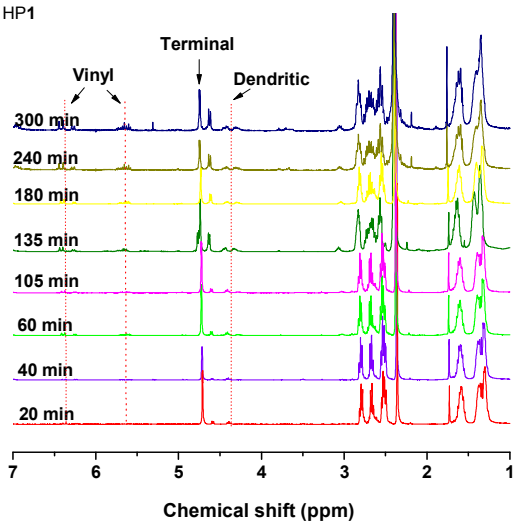


Fig. 3 ^{1}H NMR spectra of HP**1** at different reactive time.

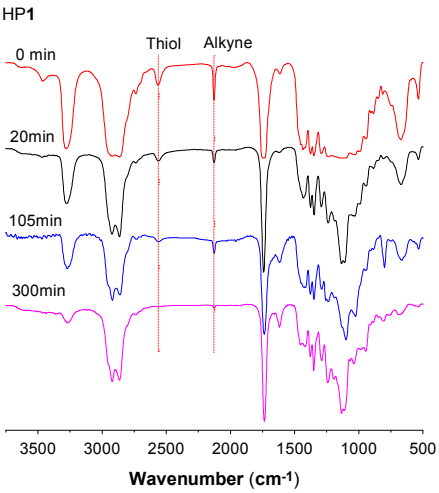


Fig. 4 FTIR spectra of HP**1** at different reactive time.

Moreover, the results of GPC measurements (Figs. 5 and 6) showed that weight-average molecular weights (M_ws) of products also increased with the prolongation of reaction time. Only within 5 h, the M_w of HP**1** reaches 128,900 g mol^{-1} with the yield of 96.4% and PDI of 17.3. Under the same reactive conditions, the yield, M_w and PDI of HP**2** are 85.4%, 10,200 g mol^{-1} and 2.2, respectively. Nevertheless, the case of **8** is totally different. Even after 24 h, the obtained M_w of HP**3** is only 2,500 g mol^{-1} with the PDI of 1.2. For HP**4**, the similar values to those of HP**1** with yield, M_w and PDI are 95.5%, 106,200 g mol^{-1} and 17.2. With respect to **10**, the resulted HP**5** with the yield of 58.7%, the M_w of 4,600 g mol^{-1} and the PDI of 1.7 was achieved in 24 h. Notably,

the orders of M_w and conversion (as presented in Table 1) are in coincidence with those of the electrophilicities of thiol groups.

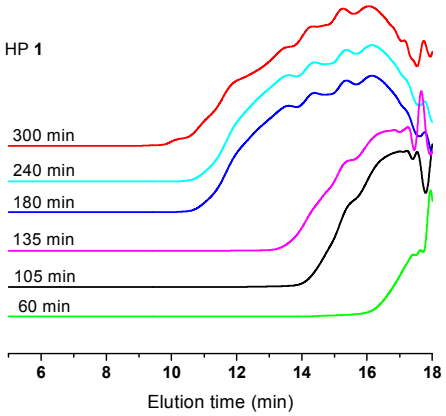


Fig. 5 GPC profiles of HP**1** at different reaction time.

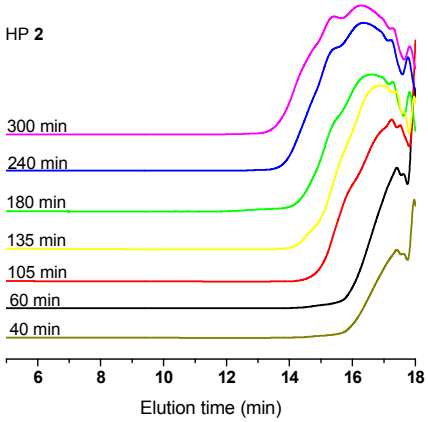


Fig. 6 GPC profiles of HP**2** at different reaction time.

Effect of electrophilicity of thiols on polymerization rate

During thiol-yne addition, hydrogen abstraction of radical to thiol is the controlling step, which mainly depends on the stability of thiols. Attacked by free radical, the sulphur atom with higher electron density can be easier fracture of S-H bond and faster formation of thiyl radical. With regard to a complete addition cycle of thiol-yne, three times hydrogen abstractions were involved, that is, primary radical to thiol, vinyl sulfide radical to thiol, and dithioether radical to thiol.[21,26-29] Since the thiol-yne polymerization was composed by multiple thiol-yne and thiol-ene addition cycles, the tiny difference among repeated hydrogen abstractions will lead to remarkable difference of the final M_w and conversion of monomers (see Table 1).

To build the quantitative or semiquantitative relation between thiol electrophilic effect and polymerization rate, we investigate the kinetics of thiol-yne polymerization of these intermediates. As there were no homopolymerizations of alkynes or alkenes involved in thiol-yne polymerization, the thiol consumption rate will equal to the polymerization rate, R_p. It can be expressed by:

$$R_p = -\frac{d[SH]}{dt} = k[SH]_t^{\alpha}[C\equiv C]^{\beta} \quad (1)$$

where k represents the rate constant for polymerization and [SH] is the concentration of thiol groups. $[SH]_t$ is defined as the concentration of thiol at t, which equals to ($[SH]_0$ - Δ [SH]). At the early stage of thiol-yne addition, $[SH]_t \approx [C\equiv C]$ and $\alpha + \beta \approx 1.0$.[28,29] With a little rearrangement, Eq. (1) leads to

$$k \cdot dt \approx -\frac{d[SH]}{[SH]_t} \quad (2)$$

The integral form of Eq. (2) can be described by:

$$k \cdot \Delta t \approx \ln\frac{[SH]_0}{[SH]_t} = \ln\frac{[SH]_0}{[SH]_0 - \Delta[SH]}$$

$$= \ln\frac{1}{1-\mathrm{conv}_{[SH]}} = -\ln(1-\mathrm{conv}_{[SH]}) \quad (3)$$

in which $conv_{[SH]}$ is the conversion of thiol groups, and Δt is the sampled interval. $Conv_{[SH]}$ can be calculated, according to the results of ^{1}H NMR measurements.

Table 1. Reaction conditions and results for HP**1**-HP**5**.

Sample	Time (min)	Conv[a] (%)	M_w (g mol^{-1})	PDI[b]	DB
HP**1**-1	20	23.4	-	-	0.97
HP**1**-2	40	32.2	-	-	0.91
HP**1**-3	60	42.3	2,700	1.48	0.87
HP**1**-4	105	47.3	3,700	1.50	0.85
HP**1**-5	135	58.6	5,800	2.01	0.80
HP**1**-6	180	79.2	17,500	5.46	0.73
HP**1**-7	240	92.2	95,800	15.95	0.66
HP**1**-8	300	96.4	128,900	17.25	0.62
HP**2**-1	20	16.9	-	-	0.99
HP**2**-2	40	25.1	1,200	1.08	0.99
HP**2**-3	60	34.2	1,400	1.14	0.96
HP**2**-4	105	45.7	1,900	1.18	0.89
HP**2**-5	135	48.7	2,600	1.21	0.87
HP**2**-6	180	61.0	4,700	1.80	0.81
HP**2**-7	240	81.4	8,000	2.02	0.77
HP**2**-8	300	85.4	10,200	2.21	0.74
HP**3**	1,440	-	2,500	1.19	0.99
HP**4**-1	20	23.8	-	-	0.96
HP**4**-2	40	30.2	1,100	1.10	0.94
HP**4**-3	60	38.1	3,300	1.44	0.90
HP**4**-4	105	45.3	3,500	1.53	0.88
HP**4**-5	135	59.8	4,400	1.63	0.79
HP**4**-6	180	76.7	16,600	5.22	0.73
HP**4**-7	240	89.5	82,800	13.85	0.67
HP**4**-8	300	95.5	106,200	17.22	0.64
HP**5**	1,440	58.7	4,600	1.70	0.69

[a] Conversion of thiol groups. [b] Polydispersity index (M_w/M_n). [c] DB was calculated by the equation, DB = (D+T)/(D+T+L).[19]

As showed in Fig. 7, the relations of $conv_{[SH]}$ and reaction time were approximately linear when $conv_{[SH]}$ < 40 %. Here, we defined k_{30} to be the thiol-yne reaction rate constant at $conv_{[SH]}$ of 30%. The corresponding reaction times at $conv_{[SH]}$ = 30% of **6**, **7**, **9** and **10** were 35.10, 39.28, 50.68 and 169.0 min, respectively.

According to Eq. (3), the k_{30} values were calculated and summarized in Table 2.

Table 2. Results for thiol-yne polymerizations of **6-10**.

AB_2 type intermediate	**6**	**9**	**7**	**10**	**8**
$\delta_{[SH]}$ (ppm)	1.31	1.34	1.53	1.68	2.03
t_{30} (min)	35.10	39.28	50.68	169.0	-
k_{30} (h^{-1})	0.583	0.539	0.419	0.124	-
DP_w	447.0	431.2	35.6	22.5[a]	7[a]

[a] Reaction time was 24 h.

As shown in Table 2, the k_{30} values of polymerizations of **6**, **9**, **7** and **10** were 0.583, 0.539, 0.419 and 0.124 h^{-1}, giving rise to weight-average degree of polymerization (DP_w) of 447.0, 431.2, 35.6 and 22.5, which were agreed with the increasing order of thiol chemical shifts ($\delta_{[SH]}$). The significant differences among k_{30}s and DP_ws are ascribed to their different electrophilicities of thiols, since it is the only distinction among thiol-yne reactions of **6-10**. Reported by Bowman *et al.*, the first addition rate of different thiols (such as, butyl 3-mercaptopropionate and octanethiol) to alkyne is without any difference.[29] Therefore, it can be inferred that the thiol electrophilic effect exclusively works during the addition of thiol to vinyl thioether.

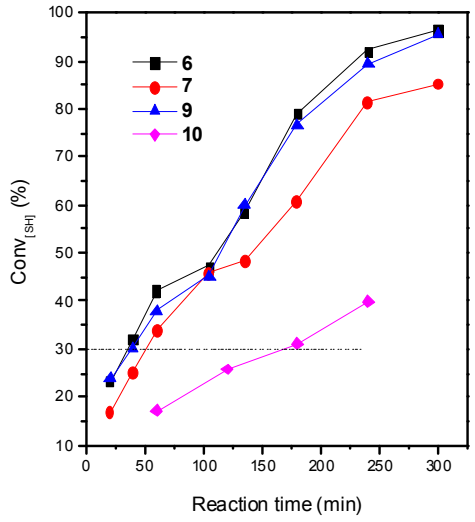


Fig. 7 Reaction time dependence of $conv_{[SH]}$ of **6**, **7**, **9** and **10**.

To explore the relationship of thiol electrophilicity and their reactivities within thiol-yne polymerization, the corresponding k_{25}s and k_{35}s at thiol conversions of 25% and 35% were also calculated according to Eq. (3), respectively. In this work, the rate constant at early polymerization stage, k, was approximately expressed by the arithmetic mean value of k_{25}, k_{30} and k_{35}. The dependence of k on δ (or electrophilicity) of thiols was shown in Fig. 8. As it can be seen in the plot, polymerization rate constant decreased gradually with the increasing of chemical shift. The semiquantitative relation can be given by the fitting linear equation, $k = 2.41 - 1.34\ \delta$. When the electrophilicity of thiol is small enough, δ approaches zero and k_{30} maybe reach the maximum, 2.41 h^{-1}. On the contrary, the incorporation of electron-withdrawing substuents into thiol compound will reduce polymerization rate. Theoretically, as $\delta_{[SH]}$ trends to 1.80, the k will reach zero, which means no thiol-yne polymerization can proceed. Because the electron affinity of thiol substuent is so strong that hydrogen abstraction between thiol and free radical can't carry out smoothly at all. Hence, no thiol-yne polymerization can be triggered. It can be predicted the chemical shift of reactive thiols is lower than 1.80.

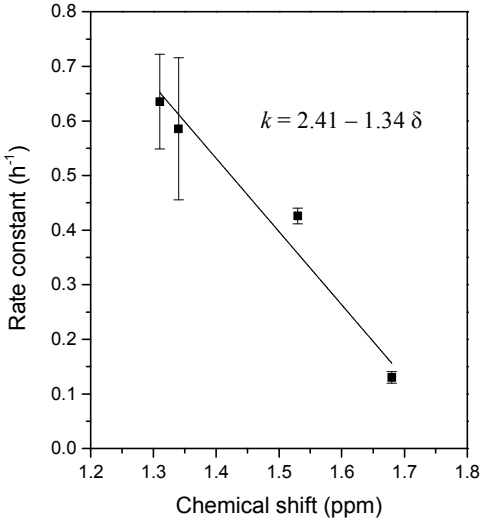


Fig. 8 Rate constant (k) as a function of chemical shift (δ) of thiols.

Effect of electrophilicity of thiols on structure

Except polymerization rate, electrophpility of thiol has an important effect on the structure of HPTE. As shown in Table 1, DBs of HP**1**-HP**3** were 0.62, 0.74 and 0.99. The order of DB of HPTE was in accordance with that of thiol electrophilic effect of monomer. All the calculated DBs were higher than the theoretical one (0.5), which were attributed to the faster addition rate (r_2) of thiol to vinyl thioether than that (r_1) of thiol to alkynyl ($r_2/r_1 \approx 3$).[29] Besides, polydispersity index (PDI) of the resultant HPTE reduced with the increasing of thiol electrophilic effect (Table 1). For example, δ values of **6** and **8** were 1.31 and 2.03. Obtained PDIs of corresponding HPTE**s** were 17.25 and 1.19, respectively. These results indicated the weaker thiol electrophpilic effect of monomers will lead to the larger difference in structure of products.

Conclusions

We synthesized five kinds of α-thiol-ω-alkynyl AB_2 type intermediates to explore the effect of thiol electrophilicity on thiol-yne polymerization. The electrophilic effect of thiol in synthesized intermediate was similar to that of thiol in starting material, which can be facilely detected by the ^1H NMR analysis. Our experimental results showed that the thiol electrophilic effect played a significant role in thiol-yne polymerization. Both the polymerization rate and the structure of resultant HPTEs were influenced by it. With the increasing of electrophilicity of thiols, polymerization rate, MW, and yield or conversion of functional groups decreased; instead, the DB of HPTEs improved. The semiquantitative relation between thiol electrophilic effect and reaction rate constant can be expressed by $k = 2.41 - 1.34\ \delta$. According to the equation, we can infer that the δ of reactive thiols is not more than 1.80. This work mainly highlighted the

importance of electrophilic effect of thiol groups within thiol-yne polymerization and it is helpful to get a complete understanding for the thiol-yne polymerization, paving a way for design and synthesis of novel polythioethers.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51173162 and No. 21325417), and China Postdoctoral Science Foundation (No. 2014M551724).

Notes and references

[a] *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China. Tel: +86-0571-87952088. E-mail: chaogao@zju.edu.cn*

[b] *Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Yantai University, 30 Qingquan Road, Yantai 264005, P. R. China*

[c] *School of Mathematical and Physical Sciences, Hubei University for Nationalities, Enshi, 445000, P. R. China*

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