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A Novel Initiator Containing Alkyne Group for the Polymerization of 2-Ethyl-2-oxazoline

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A novel trifunctional initiator with one alkyne and two trifluoromethanesulfonate moieties was synthesized from a protected alcohol 5-hydroxyl-2-phenyl-1, 3-dioxane. The alkyne functionalized intermediate with two protected alcohol groups was synthesized by reacting with propargyl bromide. The alcohol groups were cleaved using a mixture of tetrahydrofuran and hydrochloric acid aqueous solution. In the last step the initiator was synthesized using triflic anhydride in carbon tetrachloride. The initiator was characterized by ¹H NMR and used for the polymerization of 2-ethyl-2-oxazoline which gives polymers with narrow distribution. For comparison a similar initiator with two tosylates was prepared and used for the polymerization of the monomer 2-ethyl-2-oxazoline, the resulting product has a wide molecular weight distribution and most of the initiator remains unreacted after 24 h which may be due to the steric hindrance between the two tosylate groups. To further explore the steric hindrance phenomenon, a linear tosylate initiator was synthesized, but still some of the initiator remains unreacted, illustrating that both steric hindrance and electrophilic balance affect the efficiency of the cationic ring-opening polymerization. All of the polymers were characterized in detail by using ¹H NMR, matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy, and size exclusion chromatography to confirm the purity and distribution of the polymers.

Key words: Electrophile, 2-Ethyl-2-oxazoline, Steric hindrance, Triflate

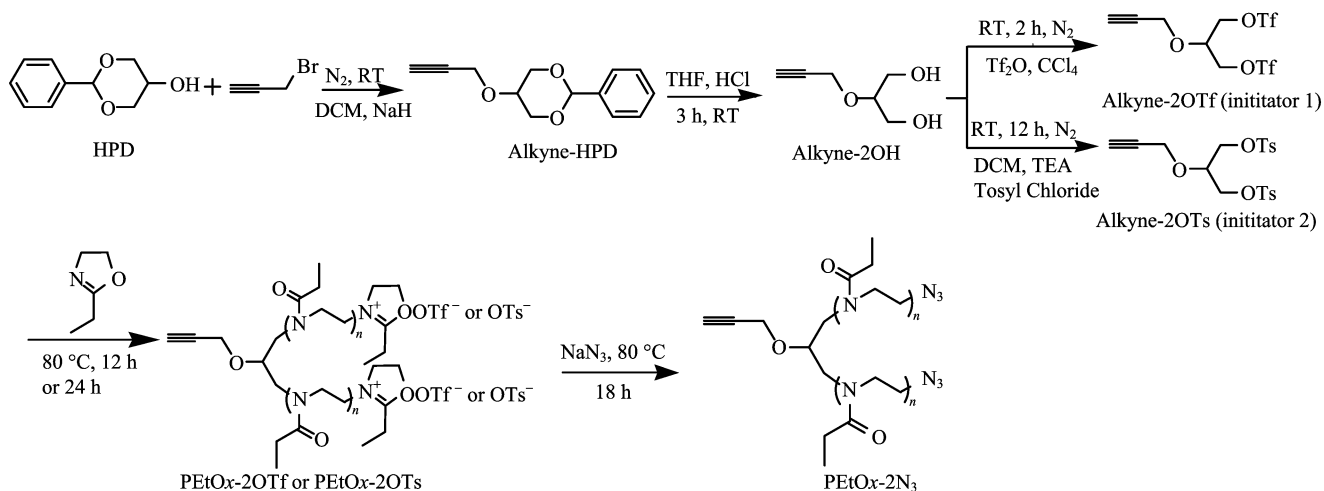
I. INTRODUCTION

Polyoxazolines has received much attention due to the potential applications as antifouling agents, dispersants for inks, and biomaterials [1, 2]. Different functional groups have been introduced via initiators, terminating agents, and monomers [3–7]. Among these methods, synthesis of monomers containing alkyne or alkene groups is time-consuming and also the number of the functional groups cannot be well controlled [8–11]. The functionality of polyoxazolines can be more than 80% using the initiation and termination route [12]. Interference of the polymerization of oxazoline monomers should be avoided during the introduction of functional groups through initiators. The alkyne functionality has special importance as alkyne groups can react with azide and thiol groups through alkyne-azide and thiol-yne click chemistry [13–15]. Strong electrophiles favor fast and clean initiation which leads

to well-defined polyoxazolines with narrow distribution [16, 17]. In the literature the alkyne functionality for polyoxazolines is mainly introduced either from the terminating or initiating group or in the side chain from a functionalized monomer [12, 18–25]. To the best of our knowledge, polyoxazolines with an alkyne group in the middle of the polymer have not been synthesized.

On the other hand, sometimes modification of an initiator to introduce a functional group disturbs the electrophilic balance of the initiator and the resulting initiator fails to give polymers with narrow distribution [26]. For example, Kobayashi *et al.* [27] used 1,4-dibromobutane for the polymerization of 2-methyl-2-oxazoline, but the polydispersity of the polymer was high which represents the inefficiency of the initiator. Fijten *et al.* [28] used propargyl tosylate and butynyl tosylate to introduce alkyne functionality for the azide-alkyne click reaction [15, 29]. The initiator with longer carbon chain gives polymers with high polydispersity and incomplete initiation due to the lower electrophilic nature of the carbon attached to the tosyl group. Recently, Hoogenboom *et al.* [26] used tetra and hexatosylates for the synthesis of star polyoxazolines of different arms.

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Scheme 1 Schematic diagram of the synthesis of the trifunctional initiator and corresponding alkyne containing poly(2-ethyl-2-oxazoline).

These initiators do not give clean polymers and most of the initiator remains unreacted due to both steric hindrance and lower electrophilicity. To overcome this problem, they introduced a porphyrin core and synthesized porphyrin-cored tetratosylate initiator.

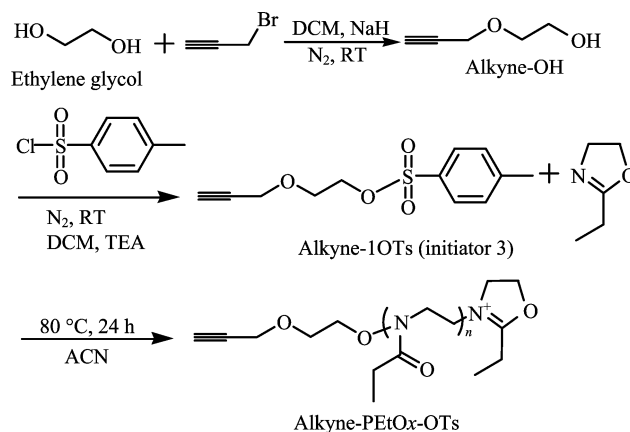
In this study, we synthesized a novel trifunctional initiator with one alkyne and two triflate arms for the polymerization of 2-ethyl-2-oxazoline, as shown in Scheme 1. Starting from a protected alcohol, alkyne moiety was introduced using propargyl bromide and the cleavage of the resulting product gave a compound with one alkyne group and two hydroxyl groups. The alcohol groups were transformed to triflates using triflic anhydride and used for the polymerization of 2-ethyl-2-oxazoline. A similar initiator with tosylate groups was also synthesized and compared with the triflate initiator.

To compare steric hinderance and electrophilicity, a linear tosylate initiator similar to the trifunctional tosylate initiator was synthesized and used for the polymerization of the monomer 2-ethyl-2-oxazoline, as shown in Scheme 2. The trifunctional initiator alkyne-2OTf gives polymers with narrow distribution while the polymers from the initiators alkyne-2OTs and alkyne-1OTs have broader distribution.

II. EXPERIMENTS

A. Materials

Acetonitrile (ACN, Sinopharm, 99%) was distilled twice from KMnO₄ and then from calcium hydride (CaH₂) just before use. 2-Ethyl-2-oxazoline (Alfa, 99%) was stirred for 6 h with CaH₂ and fractionally distilled for polymerization. Dichloromethane (DCM, Sinopharm, 99%) was distilled from CaH₂. *N,N*-



Scheme 2 Schematic diagram of the synthesis of the difunctional tosylate initiator and corresponding poly(2-ethyl-2-oxazoline).

dimethylformamide (DMF, Sinopharm, 99%) was dried by stirring over MgSO₄ for 24 h and then distilled under a reduced pressure at 50 °C. Tetrahydrofuran (THF, Sinopharm, 99%) was dried by refluxing over sodium for 24 h and distilled. In all the experiments the water used was of ultra-pure grade with a resistivity of 18.2 MΩ·cm. Other reagents were used without further purification unless otherwise stated.

B. Synthesis of the compounds alkyne

1. Synthesis of the compound alkyne-HPD

5-Hydroxyl-2-phenyl-1,3-dioxane (HPD) was prepared using a previously described method [30]. HPD (10 g, 55.50 mmol) was dissolved in 25 mL of DCM

and then NaH (1.81 g, 66.46 mmol) was added in three successive batches at 0 °C under N₂. Propargyl bromide (8.04 g, 66.46 mmol) in 10 mL DCM was added dropwise to the above mixture using a separating funnel and the reaction was allowed to proceed at room temperature. The progress of the reaction was monitored using thin layer chromatography. After completion, the reaction mixture was filtered and then the solvent was removed using a rotary evaporator. The mixture was dissolved in toluene/petroleum ether mixture (1:1, 100 mL) and recrystallized three times. The product was dried in a vacuum oven for 24 h at room temperature.

2. Synthesis of the compound alkyne-2OH

Alkyne-HPD (5 g, 23 mmol) was dissolved in 40 mL THF/HCl 1 mol/L (1:1) in a round bottom flask and the reaction was allowed to stir at room temperature for 4 h. After confirmation from thin layer chromatography the reaction was stopped and the solvent was removed under a reduced pressure. The crude product was purified by column chromatography using *n*-hexane/ethyl acetate (1:3) as an eluent. The solvent was removed using a rotary evaporator to get a yellowish oily product.

3. Synthesis of the trifunctional initiator 1 (alkyne-2OTf)

Alkyne-2OH (0.2 g, 1.53 mmol) and pyridine (0.304 g, 3.84 mmol) was dissolved in 5 mL carbon tetrachloride in a three necked round bottom flask with N₂ inlet and outlet. Triflic anhydride (1.10 g, 3.90 mmol) was dissolved in 4 mL carbon tetrachloride and was added dropwise to the above mixture at 0 °C. The reaction was carried out at room temperature and the progress of the reaction was monitored by using TLC. After 2 h the reaction was stopped and the product was purified by filtration through anhydrous Na₂SO₄. The solvent was removed under a reduced pressure to get a pinkish oily product. ¹H NMR (400 MHz, CDCl₃) δ/ppm, 4.68–4.56(m, 4H), 4.36 (d, 2H), 4.25 (m, 1H), 2.58 (t, 1H).

4. Synthesis of the two arm alkyne functionalized macromonomer (alkyne-PEtOx-2OTf)

Alkyne-2OTf initiator (0.2 g, 0.51 mmol), 2-ethyl-2-oxazoline (1.06 g, 10.15 mmol) and 3 mL of acetonitrile were added to a pre-dried polymerization tube. Air was removed using three freeze-pump-thaw cycles and the tube was sealed. The polymerization reaction was carried out at 80 °C for 12 h. After completion of the reaction, the polymer was used directly in the next step.

5. Azidation of Alkyne-PEtOx-2OTf (alkyne-PEtOx-2N₃)

Alkyne-PEtOx-2OTf (0.8 g, 0.4 mmol) in 5 mL acetonitrile was transferred to a round bottom flask with N₂ inlet and outlet. Sodium azide (NaN₃, 0.520 g, 8 mmol) was added to the reaction mixture and the reaction was carried out at 80 °C for 18 h. The excess salt was removed by centrifugation and the polymer was precipitated from tenfold excess ice cold diethyl ether three times. The polymer was dried in a vacuum oven at room temperature overnight.

6. Synthesis of the polymer alkyne-PEtOx-triazole-1,1'-bis(4-phenyl)

Alkyne-PEtOx-2N₃ (100 mg, 0.050 mmol) was dissolved in 24 mL DMF and degassed by bubbling N₂ for about an hour. Phenyl acetylene (64 mg, 0.66 mmol) and PMDETA (200 μL, 0.94 mmol) was added to a three necked round bottom flask under N₂ blanket and the mixture was degassed for about an hour by bubbling N₂. CuBr (134.4 mg, 0.94 mmol) was added to it. The polymer/DMF solution was added to phenyl acetylene/PMDETA/CuBr solution at a rate of 1 mL/h at 60 °C. After completion of the reaction the solvent was removed under a reduced pressure and the residue was dissolved in 50 mL DCM. The reaction mixture was washed with NH₄Cl three times to remove copper salt. The organic phase was collected and dried with anhydrous Na₂SO₄. The solvent was removed using a rotary evaporator. The polymer was precipitated from diethyl ether and dried in a vacuum oven at room temperature overnight.

7. Synthesis of the trifunctional initiator 2 (alkyne-2OTs)

Alkyne-2OH (1.0 g, 7.69 mmol) and triethylamine (1.94 g, 19.23 mmol) was dissolved in 20 mL DCM in a round bottom flask under N₂ blanket. Tosyl chloride (3.70 g, 19.23 mmol) was dissolved in 10 mL DCM and added dropwise to the reaction mixture from a separating funnel. The reaction was carried out at room temperature under N₂ atmosphere and the progress of the reaction was monitored by TLC. The reaction mixture was filtered and the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using *n*-hexane/ethyl acetate 3:1 as an eluent.

8. Synthesis of alkyne functionalized macromonomer with two arms (alkyne-PEtOx-2OTs)

The tosylate initiator alkyne-2OTs (0.10 g, 0.23 mmol), 2-ethyl-2-oxazoline (0.453 g, 4.60 mmol) and 1.40 mL of acetonitrile were added to a long neck

predried polymerization tube. The reaction mixture was deoxygenated by three freeze-pump-thaw cycles. The reaction was carried out at 80 °C for 24 h. The polymer was precipitated from ice cold diethyl ether and dried in a vacuum oven at room temperature overnight.

9. Synthesis of the compound alkyne-OH

Ethylene glycol (10.0 g, 161.20 mmol) was dissolved in 30 mL DCM in a three necked round bottom flask under inert atmosphere. NaH (2.4 g, 105.50 mmol) was added in three successive batches at 0 °C. Propargyl bromide (12.66 g, 105.50 mmol) in DCM was added dropwise to the above mixture from a dropping funnel and the reaction was carried out overnight. The salt was filtered and the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using *n*-hexane/ethyl acetate 1:1 as an eluent to get an orange color oily product.

10. Synthesis of the difunctional initiator 3 (alkyne-1OTs)

Alkyne-OH (2.5 g, 25.00 mmol) and triethylamine (3.03 g, 30.10 mmol) were dissolved in 20 mL DCM. Tosyl chloride (5.75 g, 30.10 mmol) in 15 mL DCM was added dropwise under N₂ atmosphere to the above mixture at 0 °C and the reaction was carried out overnight. The crude product was purified by flash chromatography with *n*-hexane/ethyl acetate (5:1).

11. Synthesis of the alkyne functionalized macromonomer (alkyne-PEtO x -OTs)

The tosylate initiator (0.25 g, 0.988 mmol), 2-ethyl-2-oxazoline (1.95 g, 19.76 mmol) and 6 mL of acetonitrile were charged to a long neck predried round bottom flask. The polymerization mixture was degassed by using three freeze-pump-thaw cycles. The reaction was carried out at 80 °C for 24 h. The polymer was precipitated from diethyl ether and dried in a vacuum oven at room temperature for 24 h.

C. Characterization

Nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AV400 spectrometer using deuterated chloroform (CDCl₃) as a solvent and tetramethylsilane (TMS) as an internal standard. Matrix-assisted laser desorption ionization time of flight mass spectra (MALDI-TOF-MS) were recorded using a Bruker Autoflex III instrument in positive ion mode. 2-[(2E)-3-(4-tert-Butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) and potassium trifluoroacetate (KTFA)

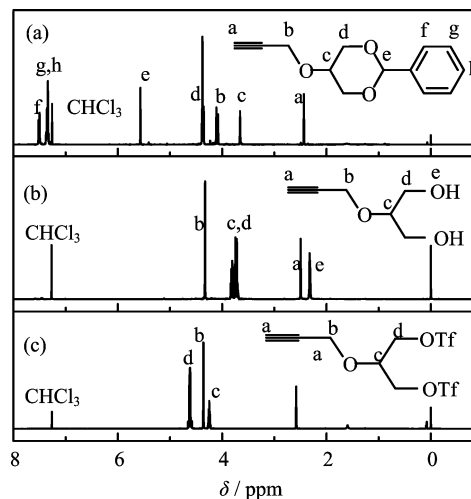


FIG. 1 ¹H NMR spectra (400 MHz, CDCl₃) of (a) alkyne-HPD (b) alkyne-2OH, and (c) alkyne-2OTf initiator.

were used as a matrix. SEC (Waters 1515) apparatus was used to determine the weight average molar mass (M_w), number average molar mass (M_n) and the distribution (M_w/M_n). The apparatus has three styragel columns (HR2, HR4 and HR6) with a universal refractive index (RI, Wyatt WREX-02) detector and an advanced multiangle laser light scattering detector (MALLS, Wyatt DAWN EOS) at 35 °C. THF was used as an eluent at a flow rate of 1.0 mL/min and the standards are polystyrene with narrow distribution.

III. RESULTS AND DISCUSSION

Scheme 1 represents the synthesis of the novel trifunctional initiator with one alkyne and two triflate groups, and the polymerization of 2-ethyl-2-oxazoline. The synthetic process started from a protected alcohol due to the easy handling of the required products.

In the first step one of the alcohol group of the compound 5-hydroxyl-2-phenyl-1, 3-dioxane was used to introduce an alkyne moiety in the structure. After reaction with propargyl bromide, FIG. 1(a) shows that the characteristic peaks located at ~2.43 ppm (“a”) and ~4.10 ppm (“b”) are attributed to the protons of alkyne and alkyne-CH₂-O-, indicating the successful introduction of the alkyne moiety into the compound (alkyne-HPD). All the other peaks in FIG. 1(a) are the same as those in the starting compound (HPD). In the second step, the two protected alcohol groups were cleaved using the mixture of 1 mol/L HCl and THF. After cleavage, we can see that the peaks at 5.55, 7.33, and 7.49 ppm from the benzene group completely disappear, while a new peak representing the OH group appears at 2.32 ppm. The peaks (“d”, -CH-(CH₂-O)₂) at 4.37 ppm and (“b”, alkyne-CH₂-O-) at 4.10 ppm shift to 3.72 ppm and 4.33 ppm, respectively. The peak (“c”, -CH-(CH₂-

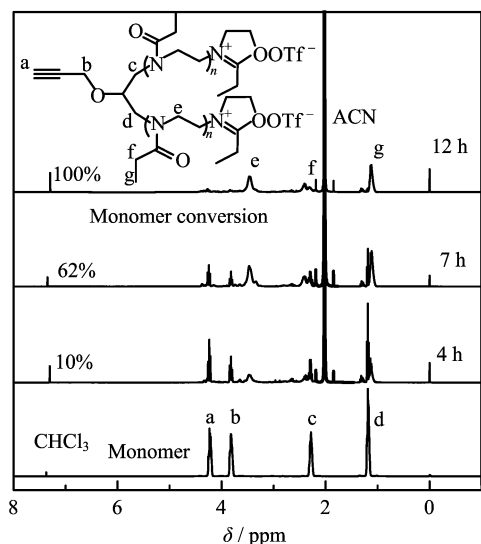


FIG. 2 ^1H NMR spectra of the kinetics of 2-ethyl-2-oxazoline polymerization initiated by Alkyne-2OTf initiator at 80°C in acetonitrile.

$\text{O})_2$) shifts from 3.65 ppm to 3.73 ppm. The triflate initiator was synthesized using a similar previously described method [31]. After replacement of the two OH groups with triflates, the peak at 2.32 ppm disappears and the peak (the proton of alkyne, “a”) at 2.48 ppm shifts to 2.57 ppm. The peaks c and d at ~ 3.73 ppm split and shift to 4.22 and 4.60 ppm, respectively. The introduction of the triflate was also confirmed from ^{19}F NMR, as shown in FIG. S1 in the supplementary materials. As alkyne-2OTf is unstable due to its sensitivity to moisture, it was used within 2 h after preparation.

FIG. 2 shows the ^1H NMR spectra of the poly(2-ethyl-2-oxazoline) samples that were obtained after different polymerization times and the monomer 2-ethyl-2-oxazoline. FIG. 3 shows that the plot is linear before the completion of the reaction when alkyne-2OTf was used as the initiator, indicating fast initiation and first order kinetics. Using alkyne-2OTf as the initiator, the polymerization reaches 100% conversion in about 12 h. Previously, for most of the initiators using the common heating system, longer time was required for simple tosylate, bromide and nosylate initiators [32, 33]. For example, Einzmann *et al.* [33] reported that a little modification in the structure of the initiator with tosylates gave polymers incomplete initiation. When the same tosylate groups were replaced by triflates, then most of the initiators represented fast initiation system. Hoogenboom *et al.* [26] reported that the multi-tosylate initiators were inefficient because of the steric hindrance. Our results suggest that both the electrophilic balance and steric hindrance control the efficiency of the initiators for the polymerization of the 2-alkyl-2-oxazoline monomers. Fik *et al.* [34] used a longer bromide initiator with a dodecyl carbon chain and they found that the kinetics and end group functionality along with the dis-

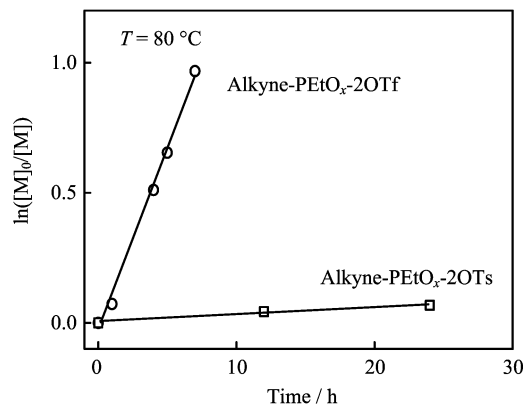


FIG. 3 Kinetic plots for the polymerization of 2-ethyl-2-oxazoline with the ratio of monomer to initiator (M/I) of 20:1 in acetonitrile at 80°C using the initiators alkyne-2OTf and alkyne-2OTs.

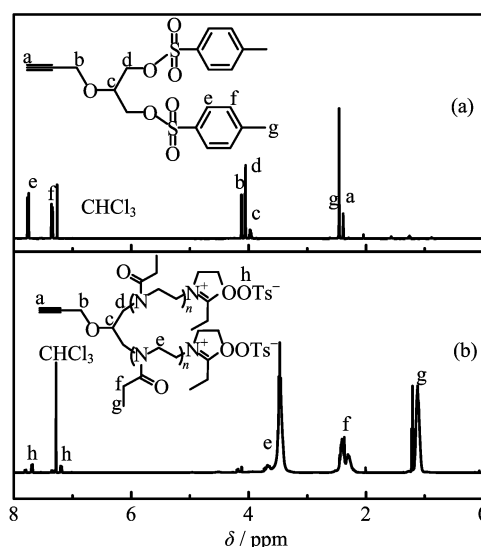


FIG. 4 ^1H NMR spectra (400 MHz, CDCl_3) of (a) alkyne-2OTs and (b) alkyne-PEtOx-2OTs. The initial M/I was 20/1, polymerization was carried out at 80°C for 24 h. The polymer was obtained after precipitation in diethyl ether.

tribution were excellent, presumably because the benzene ring between the long carbon chain and the bromide did not affect the electrophilicity of the initiator [36]. Recently, Rasolonjatovo *et al.* [35] used a tetra-triflate initiator for the synthesis of poly(THF)-block-poly(2-methyl-2-oxazoline) and obtained well-defined narrow distributed star polymers. Kowalczyk *et al.* [17] used a hexanosylate initiator for the synthesis of star poly(2-ethyl-2-oxazoline). Although the initiator is multifunctional, but efficient which may be due to the strongest nosylate group which is electron withdrawing and also the steric hindrance between the nosylate groups is negligible like triflates.

For comparison, we synthesized a ditosylate initiator as shown in Scheme 1 and its ^1H NMR are shown

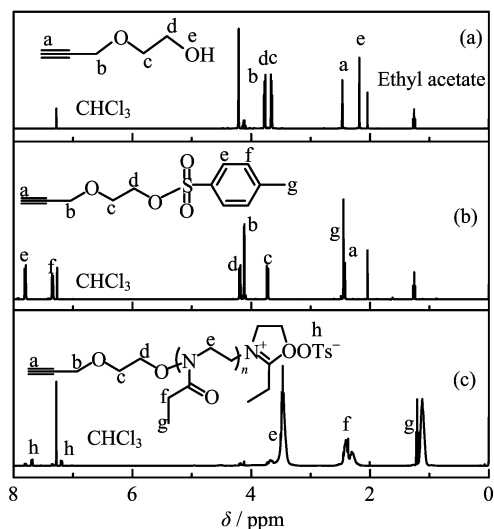


FIG. 5 ^1H NMR spectra (400 MHz, CDCl_3) of (a) alkyne-OH (b) alkyne-1OTs and (c) alkyne-PEtOx-1OTs. The initial feed M/I was 20/1. Polymerization was conducted at 80°C for 24 h and the polymer was obtained after precipitation in diethyl ether.

FIG. 4. After tosylation and purification of the product using column chromatography, FIG. 4(a) shows the appearance of two peaks at 7.37 and 7.73 ppm, representing the benzene protons of tosyl moiety. Similarly, the peak at 2.32 ppm from the two OH groups disappears, illustrating the successful synthesis of the initiator. The pure initiator was used for the polymerization of 2-ethyl-2-oxazoline. From FIG. 4(b), we can see that the signals from the tosylates at 7.37 and 7.73 ppm in the initiator shift to 7.26 and 7.69 ppm, respectively. Small peaks at 7.37 and 7.73 ppm still exist, which is from the unreacted initiator.

Our main hypothesis was that the major factor determining the initiator efficiency is the electrophilicity of the initiator. Therefore, we designed a similar initiator with one tosylate to decrease the steric hindrance, as shown in Scheme 2 and FIG. 5. An alkyne moiety was introduced from ethylene glycol by using the same method mentioned above. FIG. 5 shows that two new peaks (“a”, “b”) appear at 2.46 and 4.20 ppm respectively, representing the protons of alkyne and alkyne- $\text{CH}_2\text{-O-}$ groups. In the second step, a tosylate group was introduced by replacing the OH group. The ^1H NMR shows that after tosylation the peak (“e”, $\text{CH}_2\text{-CH}_2\text{-OH}$) at 2.18 ppm from OH completely disappears while two new peaks at 7.38 and 7.80 ppm appear which corresponds to the protons in the benzene from the tosyl group. Similarly, the protons of alkyne- $\text{CH}_2\text{-O-}$ at 4.20 ppm shift to 4.10 ppm while the protons next to the tosyl group ($-\text{CH}_2\text{-OTs}$, “d”) at 3.73 ppm shift to 4.19 ppm. Polymerization of 2-ethyl-2-oxazoline was carried out with this initiator, after polymerization three new peaks appear at 1.12, 2.37, and 3.45 ppm,

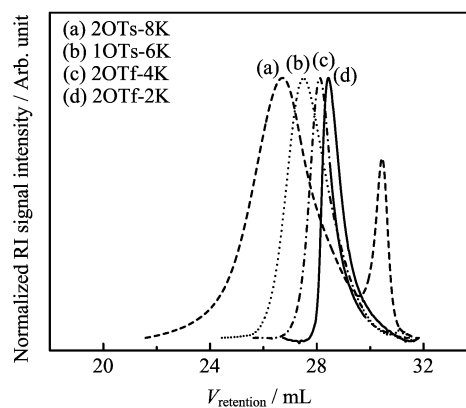


FIG. 6 SEC traces of (a) alkyne-PEtOx-2OTs-8K (b) alkyne-PEtOx-1OTs-6K (c) alkyne-PEtOx-2OTf-4K (d) alkyne-PEtOx-2OTf-2K. For alkyne-PEtOx-2OTs and alkyne-PEtOx-1OTs, the M/I was 20/1, while for alkyne-PEtOx-2OTf two different initial M/I feed ratios 20/1 and 50/1 was used. All the polymerizations were conducted in ACN at 80°C . SEC analysis was done at different time intervals.

representing methyl, methylene and backbone protons from the polymer. Similar to the results using the alkyne-2OTs initiator, there are still some signals from the unreacted initiator. Because this initiator has less steric hindrance, this experiment suggests that electrophilicity governs the initiator’s efficiency. Hoogenboom *et al.* [26] used the porphyrin cored tetratosylate initiator to decrease the steric hindrance and control the electrophilicity of the carbon attached to the tosylate and they found that the initiator is efficient for the polymerization.

The molecular weight distributions of all the polymers from the three different initiators were determined using SEC. As shown in FIG. 6, the polymer initiated with the alkyne-2OTf initiator is narrowly distributed with a polydispersity index (PDI) less than 1.20 and the molecular weight is close to the theoretical value. The polymer initiated with alkyne-2OTs initiator has the highest distribution with a PDI of 2.20 and the molecular weight is also almost five times of the theoretical value, indicating that most of the initiator remains unreacted. The peak at lower retention volume from the alkyne-2OTs initiator is due to the unreacted initiator, as this peak disappeared after dialysis (data not shown) [26]. The polymer initiated with the alkyne-1OTs initiator has also a broader molecular weight distribution with a PDI of 1.58 which further supports that although there is less steric hindrance, due to the chain extension of the initiator backbone the electrophilicity becomes lower compared to the smaller tosylate initiator like propargyl tosylate. This electrophilic character was explained by Kobayashi *et al.* [27], by using computational and experimental study and found that electrophilicity affected the efficiency of the initiator for the polymerization of poly(2-methyl-2-oxazoline).

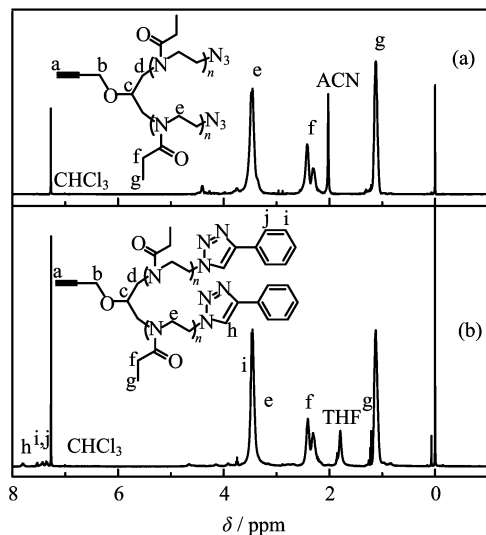


FIG. 7 ¹H NMR spectra (400 MHz, CDCl₃) of (a) alkyne-PEtOx-N₃ (b) PEtOx-triazole-1,1'-bis(4-phenyl).

Due to the increasing interest in click chemistry because of its ease and efficiency for the synthesis of polymers with different topologies and the combination of different polymers, we converted the triflate groups into azide group and then used a small phenyl acetylene compound to react with the polymer as a model reaction. After click reaction, we can see from FIG. 7, that two new peaks appear at 7.36–7.53 and 7.81 ppm, respectively. The peaks at 7.36–7.53 ppm corresponds to the protons in the benzene ring from the small phenyl acetylene molecule while the peak at 7.79 ppm represents the triazole ring proton. According to the peak ratio of the polymer backbone to the triazole ring, the percentage of conversion was ~67%.

The structures before and after click reaction were also confirmed using MALDI-TOF-MS spectrometry. We can see from FIG. 8, that the azide terminated polymer during MALDI-TOF-MS converts to a terminated polymer with the evolution of N₂ [37], the calculated mass is 2145.7 g/mol and the mass analysis gives 2145.34 g/mol. Similarly, for the polymer after click reaction the theoretical and calculated masses agree with each other, which further supports the ¹H NMR analysis.

IV. CONCLUSION

A novel trifunctional initiator with one alkyne and two triflate moieties was synthesized and used for the polymerization of 2-ethyl-2-oxazoline monomer. The kinetics and polymer distribution show that the system follows fast initiation and slow propagation. The steric hindrance between the two arms was negligible and also the electrophilicity of the carbons attached to the triflate groups was high, which results in a well-defined

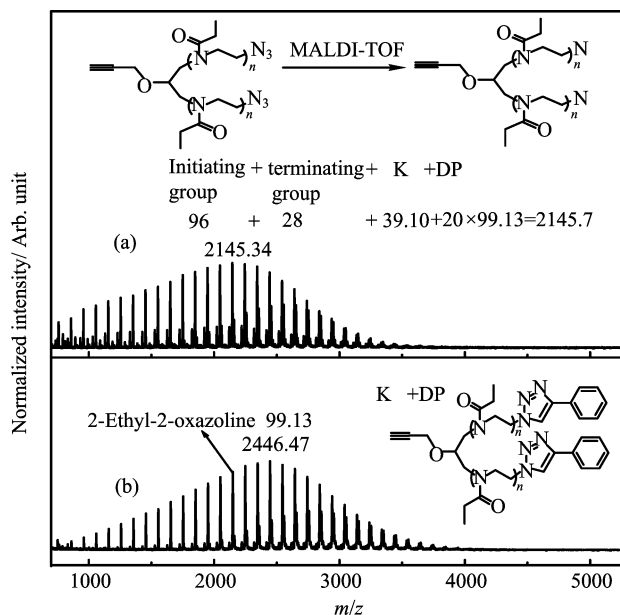


FIG. 8 MALDI-TOF-MS spectra of (a) alkyne-PEtOx-N₃ (b) alkyne-PEtOx-triazole-1,1'-bis(4-phenyl).

polymer with a narrow distribution. The resulting initiator was compared to a tosylate initiator, which gives incomplete initiation and polymers with broader distribution. A linear tosylate initiator with longer carbon chain was synthesized. The results from that initiator shows that both the factors steric hindrance and electrophilicity affects the polymerization of 2-ethyl-2-oxazoline. This work will be helpful for synthesizing telechelic polyoxazolines with well-defined M_w and one alkyne group in the middle of the polymer.

Supplementary materials: ¹⁹F NMR spectrum of the alkyne-2OTf initiator is shown in FIG. S1.

V. ACKNOWLEDGEMENTS

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