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Synthesis of 1,5-regioregular polytriazoles by efficient NMe_4OH-mediated azide-alkyne click polymerization

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Aromatic alkynes and azide were successfully polymerized under metal-free conditions using tetramethylammonium hydroxide (NMe_4OH) as organocatalyst at room temperature and soluble 1,5-regioregular polytriazoles P3a-P3e with high molecular weights (M_w up to 56000) were readily produced in high yields (up to 96%).

The development of facile and powerful polymerization reactions for the synthesis of new polymers through an efficient and universal way is of crucial importance to polymer science and material science.[1] As is known, most polymerization processes, if not all, are developed from the established organic reactions of small molecules. However, only some of the organic reactions could be developed into successful polymerization techniques. The efficiency of catalyst system, the availability of monomer, the yield, molecular weight, solubility and processability as well as the regio- and stereo-regularity of the resultant polymer should be considered. Thus, an ideal organic reaction to meet these specific concerns should be highly efficiency, modular, wide in scope and stereospecific.

In the past decade, the Cu(I)-catalysed azide–alkyne cycloaddition (CuAAC), *i.e.* the click reaction, was found to exactly meet this requirements.[2] Indeed, the CuAAC has been developed into a powerful Cu(I)-catalysed azide-alkyne click polymerization (CuAACP) under the enthusiasm efforts paid by the polymer scientists. Soluble linear and hyperbranched 1,4-regioregular polytriazoles (PTAs) with advanced functions have been facilely prepared.[3,4] Moreover, the efficient Ru(II)-catalysed azide-alkyne click polymerization to produced 1,5-regioregular PTAs was also reported.[5]

One potential problem for transition-metal catalysed azide-alkyne click polymerizations is that the metallic residues are hardly to be removed completely because the formed triazole rings have strong coordination with these species.[6] These metallic residues may worsen the solubility, cause cytotoxicity and deteriorate the photo-physical properties of the resultant PTAs.[7]

An alternative to circumvent this difficulty is to develop a polymerization in the absence of metallic species but remaining the click features at the same time, *i.e.* establishing a metal-free click polymerization (MFCP). Inspired by the results that bis(aroylacetylene)s could be facilely polycyclotrimerized in the presence of secondary amine instead of typical transition metal complex,[8] we successfully developed an efficient arolylacetylene-azide polycycloaddition, from which poly(aroyltriazole)s (PATAs) with high molecular weights were obtained in high yields.[9] More important, unlike previously reported thermal initiated cycloaddition, which produces 1,4-disubstituted and 1,5-disubstituted 1,2,3-triazoles in almost 1:1 ratio, our developed polymerization is highly regioselective and could produce PATAs with the fraction of 1,4-isomer ($F_{1,4}$) as high as 92%. Thus, it is a new kind of click polymerization, *i.e.* MFCP. Following the line of activated monomers, we further developed the MFCPs of propiolates and azides as well as 4,4'-diazidoperfluorobenzophenone and alkynes. Similarly, PTAs with $F_{1,4}$ ranged in 84.0-94.3% were obtained.[10]

However, There are no PTAs enriched in or solely containing 1,5-isomers are synthesized by the MFCP. As we demonstrated, PTAs solely containing 1,4- or 1,5-isomers exhibited different photophysical properties, which will be important for fundamental and application researches.[5]

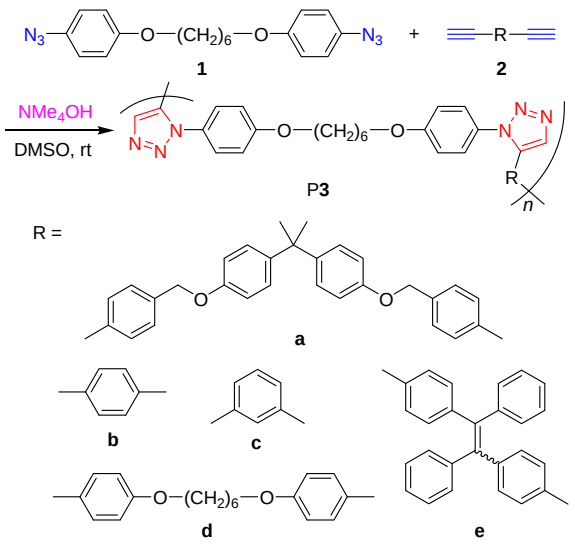
Recently, Fokin and co-workers reported an elegant click reaction that aromatic azides and terminal alkynes could undergo the cycloaddition in the presence of organocatalyst of tetramethylammonium hydroxide (NMe_4OH) at room temperature in

dimethylsulfoxide (DMSO), and solely 1,5-disubstituted 1,2,3-triazole derivatives were obtained in high yields.[11] The advantages of this reaction is that it does not need the help of expensive Ru catalyst, the monomers were traditional aromatic alkynes and aromatic azides, and the catalyst of NMe4OH is water soluble and can be removed easily after reaction.

Inspired by the features of this organic reaction, we tackled the challenge to prepare 1,5-regioregular PTAs by the MFCP. After systematically optimizing the reaction conditions, we successfully developed a new tetramethylammonium hydroxide (NMe_4OH)-mediated azide-alkyne MFCP and 1,5-regioregular PTAs with high molecular weights were obtained in high yields.

In order to get familiar with this reaction, we firstly repeated the reaction using phenylacetylene (**4**) and azidobenzene (**5**) as the reactants in the presence of NMe_4OH under the reported conditions (Scheme S1, electronic supplementary information, ESI†). For comparison, we also synthesized 1,4-disubstituted 1,2,3-triazole (**7**) using the same substrates by $Cu(PPh_3)NO_3$-catalysed click reaction (Scheme S2, ESI†).[12] According to our previous finding that the ^{1}H NMR spectra of triazoles enjoy better resolution in DMSO-d_6 than in $CDCl_3$,[8a] we thus performed the ^{1}H NMR analysis of the crude products in the former. Their ^{1}H NMR spectra were shown in Fig. S1 (ESI†). The resonance of proton of triazole in 1,5-isomer **6** was observed at δ 8.13 as a singlet peak, whereas, that of 1,4-isomer **7** appeared at δ 9.31 as a single peak, too.

Encouraged by this preliminary results, we thus tried to develop this promising click reaction to a new kind of MFCP and to prepare 1,5-regioregular PTAs. First, we prepared the diazide monomer **1** by facile reactions (see ESI for details)†. The diynes **2** were either synthesized according to the reported methods as shown in ESI† or are commercially available. Then, we used diazide **1** and diyne **2a** as model monomers to optimize the polymerization conditions (Scheme 1).



Scheme 1. NMe_4OH-mediated click polymerizations of diazide **1** and diynes **2** in DMSO at room temperature.

We first investigated the effect of reaction temperature on the polymerization of **1** and **2a** at NMe_4OH and monomer concentrations of 0.01 and 0.05 M, respectively, in DMSO. Delightfully, soluble polymers with weight-averaged molecular weights (M_w) of 23000 were obtained in high yield (80%) at room temperature (r.t.) in 2 h. However, increasing the reaction temperatures from r.t. to 60, 80, and 100 °C affected little on the M_w of the products but their yields were sharply decreased (Table S1, ESI†). We thus chose r.t. as the preferable polymerization temperature.

Next, we studied the effect of the concentration of catalyst on the polymerization. When the amount of catalyst was increased from 0.01 to 0.05 M while other parameters remain unchanged, the M_w increased from 23000 to 31000 and the yields kept almost the same (Table S2, ESI†). Continually increasing the catalyst concentration to 0.05 M affect little on the M_w but the residues of the ethynyl groups of **2a** were greatly decreased as indicated by the weakened absorption at 3269 cm^{-1} (Fig. 1) and proton resonance at δ 4.20 in the ^{1}H NMR (Fig. 2). To simply the structure characterization of the product, we used the equivalent amount of NMe_4OH to the monomers as the catalyst.

Finally, we followed the time course and the results were showed in Table S3 (ESI†). The experiments showed when **1** and **2a** were polymerized for 12 h, PTAs with higher M_w (36000) and yield (86%) could be obtained. Further lengthening the reaction time to 24 h will enhance the M_w to 44000. Thus, 24 h was adopted as the optimized reaction time.

With these optimized reaction parameters in hand, we polymerized other diynes **2b**-**2e** with diazide **1**. All the polymerizations propagated smoothly, producing PTAs of P**3b**–P**3e** with high M_w (up to 56000) in excellent yields (up to 96%) (Table 1), manifesting the universality of this powerful and efficient polymerization. All the freshly prepared P**3a**-P**3e** are soluble in commonly used organic solvents, such as tetrahydrofuran, chloroform, dichloromethane, DMSO, dimethyl formamide. They are also thermally stable. The temperatures for 5% loss of their weights (T_d) are higher than 245 °C (Fig. S2, ESI†).

Table 1. Polymerizations of diazide **1** and diynes **2**.[a]

monomer	polymer	yield (%)	M_w[b]	PDI[b]	$F_{1,5}$ (%)[c]
1 + **2a**	P**3a**	86	44000	1.41	92
1 + **2b**	P**3b**	91	56000	1.62	100
1 + **2c**	P**3c**	96	41000	1.33	100
1 + **2d**	P**3d**	89	17000	1.22	100
1 + **2e**	P**3e**	85	40300	1.45	100

[a] Polymerizations were carried out in DMSO under nitrogen at room temperature for 24 h; [M] = 0.05 M; [NMe_4OH] = 0.05 M. [b] Estimated by gel permeation chromatography (GPC) in DMF containing 0.05 M LiBr on the basis of a polystyrene calibration, PDI = M_w/M_n. [c] Fraction of 1,5-disubstituted 1,2,3-triazole isomers in the polymers.

Thanks to the good solubility of P**3a**-P**3e**, their structures were characterized by spectroscopic techniques and satisfactory analysis data corresponding to their expected structures were obtained (see

experimental section and Fig. S3-S15 in ESI for details)†. An example of the FT-IR spectrum of P**3a** is shown in Figure 1. Its monomers **1** and **2a** were also presented for comparison. In the spectra, the stretching vibration bands of N_3, C≡C, ≡C-H appeared at 2122, 2107 and 3269 cm^{-1}, respectively. They became much weaker after polymerization, indicating that most of the ethynyl and azide groups in monomers had been converted into triazole rings in polymer. Similar results were obtained from the analysis of the FT-IR spectra of P**3b**–P**3e** (Fig. S3–S6, ESI†).

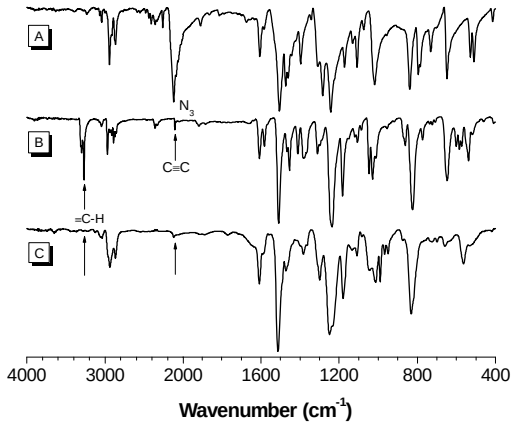


Figure 1 IR spectra of monomers (A) **1**, (B) **2a** and (C) their polymer P**3a**.

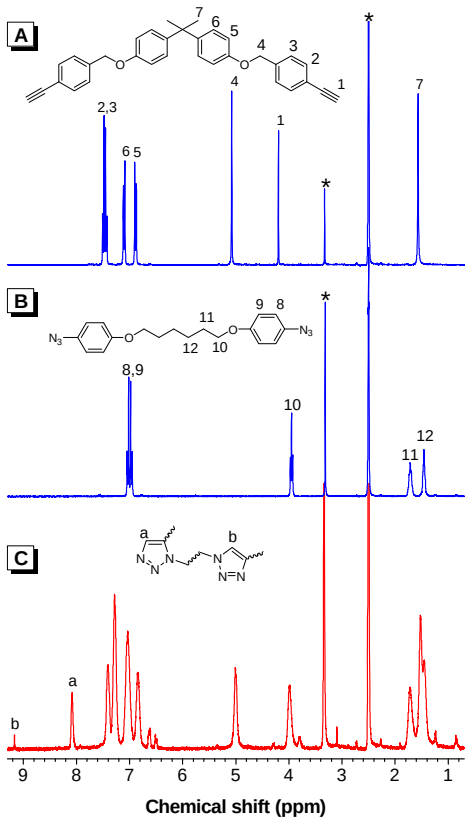


Figure 2. ^{1}H NMR spectra of monomers (A) **2a**, (B) **1** and (C) their polymer P**3a** in DMSO-d_6. The solvent peaks are marked with asterisks.

The NMR spectroscopy could provide more valuable and detailed information for the illustration of the polymer structures. In view of that P**3a**-P**3e** are soluble in DMSO and polytriazoles have good resolution in DMSO-d_6, the ^{1}H NMR spectra and ^{13}C NMR spectra of P**3a**-P**3e** were measured in DMSO-d_6. Figure 2 shows the ^{1}H NMR spectra of P**3a** and its monomers as an example. The resonances of ethynyl protons of **2a** were hardly observed in the spectrum of P**3a**. This result could further confirmed by its ^{13}C NMR spectrum, in which the carbon resonances at δ 83.29 and 80.85 of **2a** are disappeared (Fig. S7, ESI†). Meanwhile, new peaks resonating at δ 9.16 (b) and 8.08 (a) are observed in ^{1}H NMR spectrum of P**3a**. Compared with the spectra of model compounds (Fig. S1, ESI†), the former is readily assigned to the resonance of the protons of the triazole rings in the 1,4-isomeric units while the latter is associated with that of 1,5-isomers. Thanks to the well resolution of these two peaks, the fraction of the 1,5-isomer ($F_{1,5}$) could be accurately calculated by comparing their integrals. The value of 92% was thus deduced.

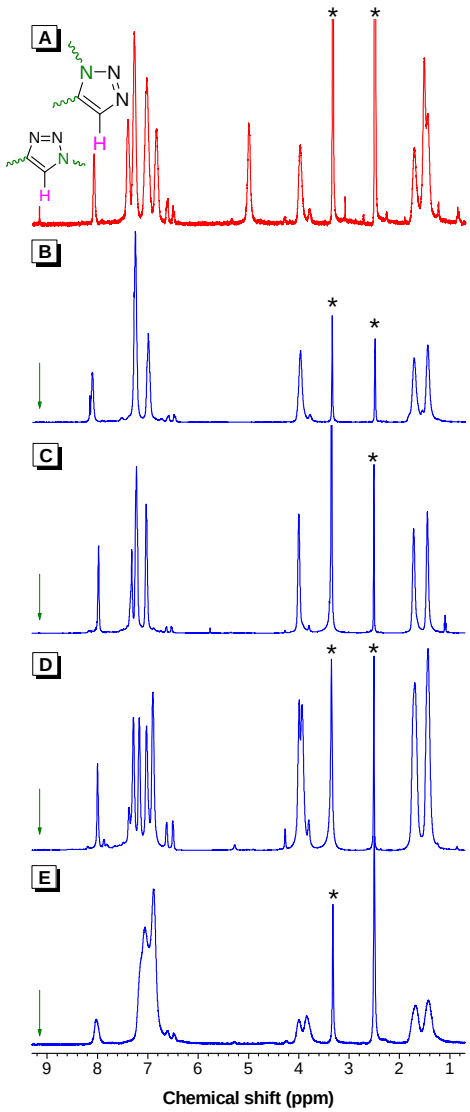


Figure 3. ^{1}H NMR spectra of polytriazoles of (A) P**3a**, (B) P**3b**, (C) P**3c**, (D) P**3d**, and (E) P**3e** in DMSO-d_6. The solvent peaks are marked with asterisks.

Similar results were obtained for P**3b**-P**3e** (Fig. S8-S15, ESI†). Excitingly, the resonance peaks of the protons of 1,4-disubstituted 1,2,3-triazoles are absent and only those of 1,5-isomers were observed in the ^{1}H NMR spectra of P**3b**-P**3e** (Fig. 3), suggesting that the $F_{1,5}$ values are 100% for these PTAs. Thus, this NMe_4OH-mediated azide-alkyne polycycloaddition is efficient and region-selective, and is a new kind of MFCP.

Conclusions

In summary, a new kind of efficient NMe_4OH-mediated aromatic azide and alkynes click polymerization is established and 1,5-regioregular PTAs with M_w up to 56000 were obtained in high yields (up to 96%). The resultant PTAs are soluble and thermal stable, which enable them to find broad applications. The mechanism understanding of this highly efficient MFCP and its application to prepare advanced functional materials are ongoing in our research group.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details; FT-IR, ^{1}H and ^{13}C NMR spectra; reaction condition optimization data. See DOI: 10.1039/c000000x/

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The efficient and region-selective NMe_4OH-mediated aromatic azide ad alkynes click polymerization to generate 1,5-regioregular polytriazoles was successfully established.