Polymer Chemistry

PAPER

Metal-free click polymerization of propiolates and azides: facile synthesis of functional poly(aroxycarbonyltriazole)s†

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Azide–alkyne click polymerization is generally catalyzed by the Cu(I) complex, in which the removal of metallic residues after reaction remains challengeable. In this work, a metal-free click polymerization method was developed to avoid this problem. The diazide monomers (**9** and **10**) could readily react with aromatic and aliphatic dipropiolates (**1** and **2**) under simple heating to produce functional poly(aroxycarbonyltriazole)s (PACTs), a kind of polyester, with high molecular weights (M_w up to 23 500) and regioregularities (fraction of 1,4-disubstituted 1,2,3-triazole in polymers up to ∼90%) in excellent yields (up to ∼99%). The metal-free click polymerization also propagates smoothly in an open atmosphere without protection from oxygen and moisture. The PACTs are thermally stable, with 5% loss of their weights at temperatures higher than 335 °C. Thanks to the contained ester groups, the polymers can be rapidly degraded in the presence of potassium hydroxide aqueous solution. The PACT containing tetraphenylethene units exhibits a unique feature of aggregation-induced emission and can function as a fluorescent chemosensor to detect explosives in a superamplified manner.

Introduction

The development of new polymerization reactions is of critical importance in polymer science.[1] As we know, most of the new polymerization reactions, if not all, are derived from the established organic reactions of small molecules. One of the basic requirements is that the organic reaction should be highly efficient. The Cu(I)-mediated azide–alkyne cycloaddition, *i.e.* the click reaction, enjoys such advantageous characteristics as high efficiency, atom economy, regioselectivity, and functionality tolerance as well as mild reaction conditions, fast reaction rates and simple product isolation procedures.[2] Thus, it is an ideal reaction to be developed into a new polymerization method. Since the discovery independently by the research groups of Sharpless and Meldal in 2002,[3] this reaction has attracted considerable attention as a powerful modular synthesis approach and has been widely used in the areas of organic and medicinal chemistry, chemical biology, material science, *etc.*[4]

The click reaction has also been utilized in polymer science, but the research activity has been mainly on the post-functionalization of preformed polymers.[5] Meanwhile, the high efficiency of the click reaction also encourages polymer chemists to foster it into a powerful click polymerization technique.[6] The first attempt was reported by Voit and coworkers in 2004. They tried to synthesize hyperbranched polytriazoles by click polymerization of an AB₂ monomer of 3,5-bis(propargyloxy)benzyl azide in the presence of CuSO₄ and sodium ascorbate in aqueous solution, which only yielded insoluble products.[7] We and others have proven that soluble hyperbranched polytriazoles could be obtained by avoiding or minimizing the amount of water in the solvent mixture during the polymerization.[6i,8] Although impressive progress has been made by optimization of reaction conditions, the utilization of the click reaction to synthesize functional polytriazoles with linear and hyperbranched structures is still challengeable.[9] The Cu(I)-catalyzed click polymerization often leads to insoluble products in commonly used organic solvents, and moreover, the copper residues in the polymers can cause cytotoxicity and deteriorate their photophysical properties, which greatly limits the polymer application in biological and optoelectronic areas.[10] It is thus highly desirable to develop a click polymerization without transition-metal catalysts, *i.e.* metal-free click polymerization.

In recent years, the strain-promoted alkyne–azide cycloaddition (SPAAC) has been widely investigated and found an array of applications in the area of biological research because it does not use a poisoning Cu(I)-catalyst and it is cytocompatible.[11] No polymers, however, have been reported from this fast metal-free

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† Electronic supplementary information (ESI) available: IR spectra of **PII–PV** and their monomers (Fig. S1–S4), ¹H NMR spectra of **PII–PV** and their monomers (Fig. S5–S8), and ¹³C NMR spectra of **PII–PV** and their monomers (Fig. S9–S12). See DOI: 10.1039/c2py00586g

reaction, probably due to the synthetic difficulty in the preparation of cyclooctyne derivatives.

During the course of exploration of new polymerization methods based on triple-bond building blocks, we have established an efficient metal-free click polymerization.[12] Heating the mixtures of bis(aroylacetylene)s, a kind of active alkynes, with azides in polar solvents, such as DMF/toluene, at a moderate temperature of 100 °C for a short reaction time (6 h) readily produces soluble poly(aroyltriazole)s (PATAs) with high molecular weights (weight-average molecular weight, M_w up to 26 700) and regioregularities [the fraction of 1,4-disubstituted 1,2,3-triazole in PATAs ($F_{1,4}$) up to 92%] in high yields (up to ~98%) (Scheme 1A). As no metal catalyst is used, such a polymerization process enjoys the advantages of being less toxic, environmentally friendly, and the photophysical properties and cytotoxicities of resultant PATAs are free from the detriment by the metallic residues, making this method promising for biological application like SPAAC.

The preparation of aroylacetylenes, however, starts from aromatic aldehydes, requires many reaction steps and involves the use of reactive reagent of ethynylmagnesium bromide and toxic heavy metal oxidants of CrO_3 or MnO_2 under harsh reaction conditions (Scheme 1A), which will limit the application of such polymerization.[10b,c,13] However, the propiolates, in which the triple bond is adjacent to an electron-withdrawing ester group, are structurally similar to aroylacetylenes. Preliminary results indicated that such alkynes possess reactivity similar to aroylacetylenes when reacting with azides.[14] It is noteworthy that the propiolates can be readily synthesized from commercially available propiolic acid and aromatic or aliphatic diols via a one-step and one-pot esterification procedure under mild reaction conditions (Schemes 1B and C).

Though the propiolates had been used to prepare triazole-containing polymers by the Huisgen 1,3-dipolar cycloaddition with azides,[15] there are no reports about the optimization of polymerization conditions, and detailed structure characterization and regioregularity of the resultant polymers, which are the key issues for the development of new polymerization techniques. In this paper, we systematically investigated the effects of polymerization conditions, such as reaction time, monomer concentration, and solvent, on the yields, molecular weights, and

regioregularities of the resultant poly(aroxycarbonyltriazole)s (PACTs). The PACTs can be also structurally regarded as polyesters. But unlike traditional polyesters that are usually synthesized by sluggish polycondensation of dicarboxylic acids and diols under severe conditions, such as high temperature and highly reduced pressure, PACTs can be efficiently prepared by this propiolate–azide metal-free click polymerization. Thus, we not only established a new kind of metal-free click polymerization but also provide a facile tool for the preparation of functional polyesters.

Results and discussion

Monomer synthesis

The diazide monomers **9** and **10** and diyne monomer **1** were prepared following our previously published procedures.[10a,16] The aliphatic dipropiolates **2** were prepared by an efficient one-step and one-pot esterification of commercially available aliphatic diols (**8**) with propiolic acid (**3**) in the presence of TsOH (Scheme 1C). All the monomers were carefully purified and characterized by spectroscopic methods, from which satisfactory analysis data corresponding to their molecular structures were obtained (see Experimental section for details).
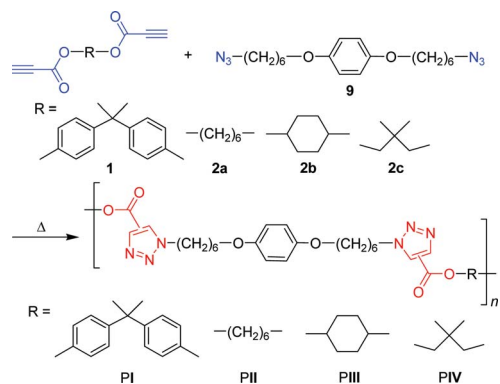
Click polymerization

According to our previously reported conditions of metal-free click polymerization of aroylacetylene and azide monomers, we have carried out the polymerization of aromatic dipropiolate **1** and tetraphenylethene (TPE)-containing diazides in a DMF/toluene mixture (1 : 1 by volume). The preliminary results showed that soluble PACTs with high molecular weights could be obtained in high yields.[14] Although the structures of propiolates are similar to aroylacetylenes, they are actually not the same. Thus, it is necessary to systematically study the polymerization reactions of dipropiolates with diazides by optimization of reaction conditions to establish a new kind of metal-free click polymerization (Scheme 2).

We first investigated the effect of monomer concentration on the 1,3-dipolar polycycloaddition of dipropiolate **1** and diazide **9** in a DMF/toluene mixture at 100 °C for 6 h on the basis of our previous paper.[12b] The M_w values of the PACTs generally
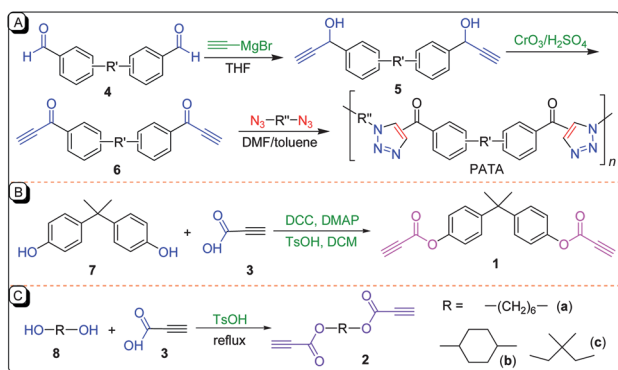
Scheme 1 Synthesis of active alkynes of aroylacetylenes and propiolates, as well as poly(aroyltriazole)s (PATAs) by metal-free, thermally activated, and regioselective click polymerization. DMF = *N,N*-dimethylformamide.

Scheme 2 Synthetic routes to poly(aroxycarbonyltriazole)s (PACTs) by metal-free click polymerization of dipropiolates and diazide.

enhance with increasing monomer concentration, but little changes in their polydispersity indices and yields were recorded (Table 1). The monomer concentration of 0.167 M was selected when taking the M_w and yield into account.

We then followed the time course of the polymerization reaction of **1** with **9** in a DMF/toluene mixture at 100 °C. Both the M_w and yields of the polymers are increased with reaction time except those for 24 h, in which the M_w decreases slightly (Table 2). Furthermore, all the polymers are completely soluble in commonly used organic solvents, such as THF, DCM, and chloroform. The results indicate that the polymerization of **1** and **9** possesses a fast reaction rate. Although the M_w (16 500) of the resultant polymers in 6 h is high enough for general purpose application, we chose 24 h as our optimal reaction time because higher yield was obtained.

Additionally, we studied the effect of solvents on the polymerization of **1** and **9** at 100 °C for 24 h at a monomer concentration of 0.167 M (Table 3). The solutions remained homogeneous during the polymerization in DMF, dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc) and their mixtures with toluene as well as in 1,4-dioxane, from which soluble polymers with high M_w were obtained in high yields. However, the precipitates appeared during the reaction when carried out in toluene and the products were partially soluble in THF and DMF. Furthermore, the soluble part of the polymer produced from toluene exhibits the highest M_w, and the reactions carried out in toluene containing polar mixtures also produced polymers with higher M_w compared to that in pure polar solvents, indicating that toluene may accelerate the polymerization. The $F_{1,4}$, one of the key parameters for click polymerization, of the polymers obtained in the polar solvents of DMF, DMSO and DMAc or their mixtures with toluene are all higher than 88.5%. The polymers conducted in nonpolar solvents of 1,4-dioxane and toluene, however, have low $F_{1,4}$ values. Thus, the polymerizations of dipropiolates and diazides are regioselective in polar solvents, which can also be termed as click polymerization. When considering the yield, molecular weight and $F_{1,4}$, we took the DMF/toluene mixture as our optimized solvent.

Although the optimization of reaction conditions was performed using aromatic propiolate and azide, such optimal conditions can also be employed to polymerize aliphatic dipropiolates **2** with azide **9**. The polymerizations are shown in Scheme 2 and the results are listed in Table 4. All the polymerizations proceeded smoothly, producing PACTs with high molecular weights and regioregularities in high yields. Furthermore, oxygen

Table 1 Effect of monomer concentration on the click polymerization[a]

No.	$[M]_0^b$/M	M_w^c	PDI[c]	Yield (%)
1	0.050	9700	1.37	62.3
2	0.100	15 300	1.50	93.4
3	0.125	15 500	1.50	97.3
4	0.167	17 000	1.51	96.0
5	0.250	20 900	1.55	92.2

[a] Carried out in a DMF/toluene mixture (1 : 1, v/v) at 100 °C under nitrogen for 6 h. [b] Monomer concentration. [c] M_w and PDI of polymer were estimated by GPC in THF on the basis of a polystyrene calibration.

Table 2 Time course on the click polymerization[a]

No.	t/h	M_w^b	PDI[b]	Yield (%)
1	1	11 200	1.41	76.4
2	2	14 700	1.55	90.2
3	4	15 300	1.50	90.9
4	6	16 500	1.51	89.8
5	12	18 900	1.55	91.6
6	24	17 800	1.52	96.7

[a] Carried out in a DMF/toluene mixture (1 : 1, v/v) at 100 °C under nitrogen at a monomer concentration of 0.167 M. [b] M_w and PDI of polymer estimated by GPC in THF on the basis of a PS calibration.

Table 3 Effect of solvent on the click polymerization[a]

No.	Solvent[b]	Yield (%)	S^c	M_w^d	PDI[d]	$F_{1,4}^e$ (%)
1	DMF	90.9	√	15 600	1.57	94.3
2	DMF/toluene[f]	96.7	√	16 500	1.50	90.1
3	DMSO	96.0	√	13 200	1.46	91.7
4	DMSO/toluene[f]	94.6	√	17 700	1.51	88.5
5	DMAc	97.4	√	15 100	1.48	91.7
6	DMAc/toluene[f]	96.2	√	17 200	1.50	89.3
7	1,4-Dioxane	93.8	√	11 500	1.41	78.7
8	Toluene	100	Δ	43 800	1.51	78.1

[a] Carried out at 100 °C for 24 h under nitrogen at a monomer concentration of 0.167 M. [b] Abbreviations: DMF = N,N-dimethylformamide, DMSO = dimethyl sulfoxide, and DMAc = N,N-dimethylacetamide. [c] Solubility (S) tested in THF, chloroform, DMF and DMSO; √ = completely soluble, Δ = partially soluble in THF and DMF. [d] M_w and PDI of polymer estimated by GPC in THF on the basis of a PS calibration. [e] Fraction of 1,4-regioisomer in the reaction products determined by ^{1}H NMR. [f] Volume ratio: 1 : 1.

Table 4 Click polymerization of dipropiolates and diazide[a]

PACTs	Monomer	S^b	Yield (%)	M_w^c	PDI[c]	$F_{1,4}^d$ (%)
PI	**1 + 9**	√	96.1	15 100	1.49	90.1
PII	**2a + 9**	▲	85.3	$10\ 500^e$	1.28^e	87.0
PIII	**2b + 9**	√	88.6	18 700	1.53	84.0
PIV	**2c + 9**	Δ	91.2	$11\ 400^e$	1.27^e	84.7
PI(o)[f]	**1 + 9**	√	89.2	16 700	1.32	89.3

[a] Carried out in a DMF/toluene mixture (1 : 1, v/v) at 100 °C for 24 h under nitrogen at a monomer concentration of 0.167 M. [b] Solubility (S) tested in THF, chloroform, DMF and DMSO; √ =completely soluble, ▲ = insoluble in THF, partially soluble in DMF, but completely soluble in chloroform, and Δ = partially soluble in THF and DMF, but completely soluble in chloroform. [c] M_w and PDI of polymer estimated by GPC in THF on the basis of a PS calibration or in DMF on the basis of PMMA calibration (for **PII**). [d] Fraction of 1,4-regioisomer determined by ^{1}H NMR. [e] Data for soluble part. [f] Carried out in air for 6 h.

and moisture exert little effect on the polymerization [*cf.* Table 4, **PI(o)**], which will help simplify the reaction procedures.

Structural characterization

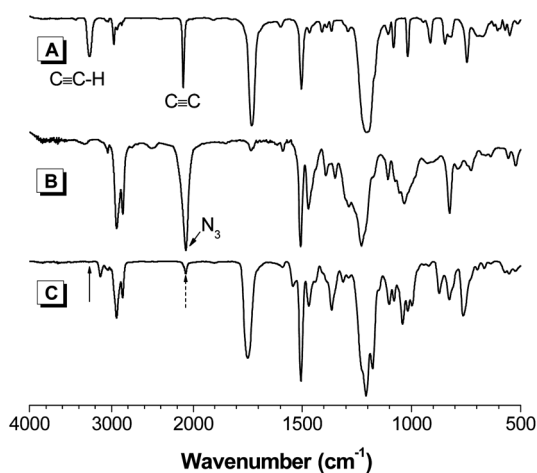The polymer structures were characterized by spectroscopic methods and satisfactory results corresponding to their

Fig. 1 IR spectra of monomers **1** (A) and **9** (B) and their polymer **PI** (C).

structures are obtained (see Experimental section and ESI† for details). Examples of the IR spectra of **PI** and its monomers are given in Fig. 1. The stretching vibration bands of ≡C–H at 3276 cm^{-1} and C≡C and N$_3$ at 2094 cm^{-1} in the spectra of monomers became much weaker after reaction, indicating that most of the acetylene and azide groups in monomers **1** and **9** have been consumed by the metal-free click polymerization and transformed to triazole rings in polymer **PI**. The spectral profiles of **PII–PIV** are similar to that of **PI** (Fig. S1–S3 in the ESI†), implying that the metal-free click polymerization exerts the same effect on the reaction of aromatic or aliphatic propiolates with azides.

According to our previous finding that the ^{1}H NMR spectra of poly(aroyltriazole)s and polytriazoles have better resolution in DMSO-d_6 than in CDCl$_3$, we thus performed the ^{1}H NMR analysis of **PI** in DMSO-d_6. Fig. 2 shows the ^{1}H NMR spectra of polymer **PI** and its monomers **1** and **9** as an example. The resonances of the acetylene protons of **1** and the methylene protons adjacent to the azide group of **9** at δ 4.84 and 3.32, respectively, almost disappeared in the spectrum of **PI**. Additionally, new peaks resonating at δ 8.99, 8.49, 4.67 and 4.45 are observed. The strong peaks at δ 8.99 (c) and 4.45 (a) are associated with the resonances of the protons in the triazole ring and its neighboring methylene group in the 1,4-isomeric units, while the weak signals at δ 8.49 (d) and 4.67 (b) are stemmed from those in the 1,5-isomeric units. The results suggest that most of the alkyne and azide groups of the monomers have been transformed to the triazole rings of the polymers by the click polymerization, further substantiating the conclusion drawn from the IR spectral analysis. Since the resonance peaks at δ 8.99 and 8.49 are well separated in **PI**, we used their integrals to calculate the $F_{1,4}$ values, which are as high as 90.1%. **PII–PIV** also possess high $F_{1,4}$ according to their ^{1}H NMR spectra, which were measured in CDCl$_3$ because they are partially soluble in DMSO (Fig. S5–S7 in the ESI†).

^{13}C NMR spectroscopy offers more informative characterization data of polymers (Fig. 3, and S9–S11 in the ESI†). For example, the spectrum of **PI** shows almost no acetylene carbon resonance at δ 81.8 and 74.7 compared to those of its monomers (Fig. 3). Meanwhile, two new peaks appear at δ 138.3 and 130.3, which are assigned to triazole carbon resonances of **PI**. Similar
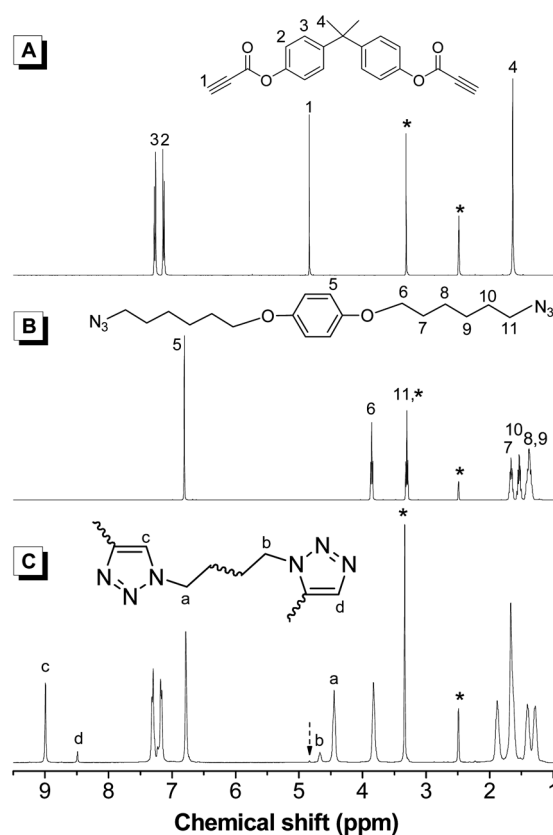

Fig. 2 ^{1}H NMR spectra of DMSO-d_6 solution of monomers **1** (A) and **9** (B) and their polymer **PI** (C). The solvent and water peaks are marked with asterisks.

phenomena were observed in the ^{13}C NMR spectra of **PII–PIV**. This once again proves that most of the alkyne and azide groups of the monomers have been transformed to the triazole rings in the polymers by the metal-free click polymerization.

Stability and optical transparency

The thermal stabilities of the PACTs were evaluated by thermogravimetric analysis (TGA). The results show that all the polymers are thermally stable. As can be seen from Fig. 4, the temperatures for 5% weight loss (T_d) are higher than 335 °C under nitrogen, which indicates their strong resistance to the thermolysis and oxidation at the elevated temperatures regardless of their aromatic or aliphatic nature.

The PACTs are highly transparent in the visible spectral region and allow the light at wavelengths longer than 375 nm to transmit through (Fig. 5). This excellent optical transparency is because the alkyl spacers and ester groups of the repeat units in the PACTs weaken the electronic communications and shorten the effective conjugation lengths. The high optical transparency makes the PACTs promising for photonic applications.[17]

Polymer hydrolysis

Degradable polymers are of growing interest in the fields of biomedical applications and environment protection.[18] One of the well-known synthetic hydrolysable polymers is polyester, which is generally synthesized by sluggish polycondensation of
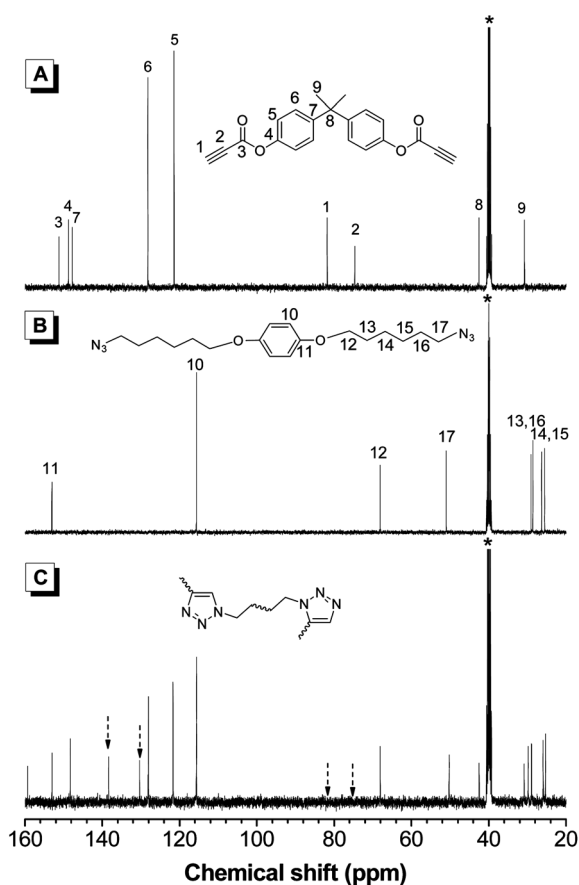
Fig. 3 ^{13}C NMR spectra of DMSO-d_6 solution of monomers **1** (A) and **9** (B) and their polymer **PI** (C). The solvent peaks are marked with asterisks.
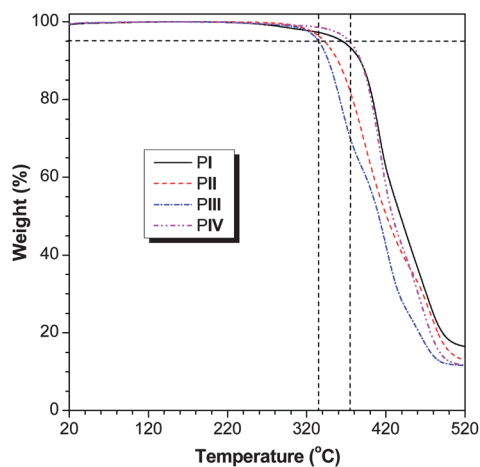

Fig. 4 TGA thermograms of **PI–PIV** recorded under nitrogen at a heating rate of 20 °C min^{-1}.

dicarboxylic acids and diols under severe conditions, such as high temperature and highly reduced pressure.[19] The PACTs with one ester linkage in each repeat unit can be structurally viewed as polyesters.

The PACTs synthesized in this work can be hydrolyzed in a time scale of minutes in the presence of KOH aqueous solution. As
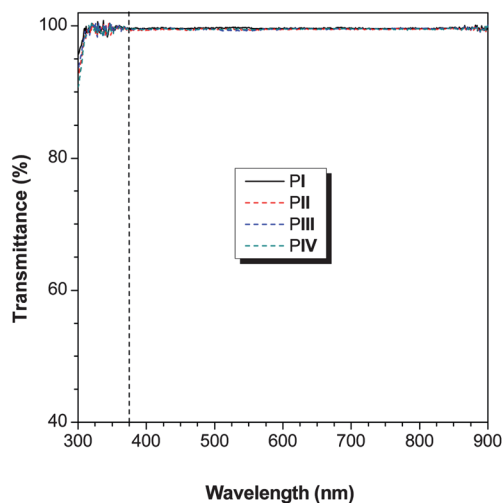

Fig. 5 Light transmission spectra of PACTs in chloroform. Polymer concentration: 10 μM.

shown in Fig. 6, the M_w of **PI** decreased from 15 700 to 14 000 during the first 3 min. Afterwards, the degradation became faster, which was also proven by their GPC curves, in which shoulder peaks clearly appeared especially after 4 min. The M_w of the **PI** became too small to be precipitated out from hexane, thus no GPC data were obtained after hydrolysis for 10 min, indicating that the polymer is fully degraded. Generally, the degradation of conventional linear polyesters often takes a long period of time. The rapid hydrolysis of the PACT may be due to the existence of triazole rings in the polymer, which allow the water molecules and alkaline species to penetrate into the polymer and to react with ester groups *via* weak interactions of hydrogen bonds, *etc.* This attribute makes the PACTs promising biomedical materials and environmentally friendly engineering plastics.

Preparation of functional PACT

Encouraged by the success in development of the metal-free click polymerization of aromatic and aliphatic dipropiolates and
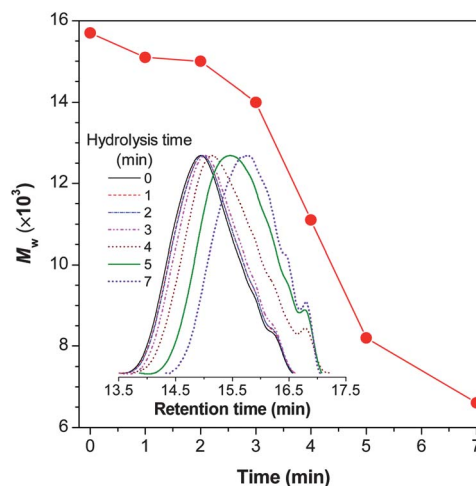
Fig. 6 The plot of M_w of **PI** versus hydrolysis time in the presence of KOH aqueous solution. Inset: GPC curves of degraded products of **PI**.
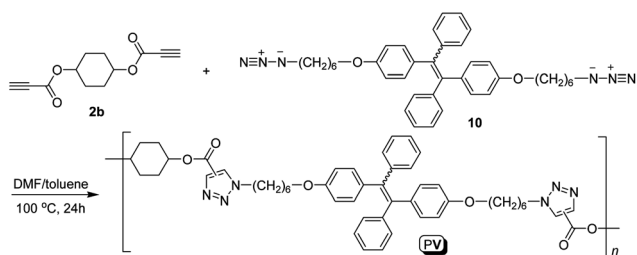
diazides, we tried to widen the application of this reliable method to prepare functional materials. In our previous research, we found that TPE exhibits the unique feature of aggregation-induced emission (AIE) and can be functionalized with ease.[20] We have also incorporated TPE moieties into the polymer backbone to prepare AIE-active polytriazoles and poly(aroyltriazole)s by Cu(I)-mediated and metal-free click polymerization.[16,21]

In this work, we adopted the aliphatic dipropiolate (**2b**) to react with the TPE-containing diazide (**10**) to prepare functional PACT under our optimal reaction conditions (Scheme 3). **PV** with high molecular weights (M_w: 23 500) and regioregularities ($F_{1,4}$: 86.2%) in high yields (99.2%) was thus obtained, further confirming the fidelity of our developed propiolate–azide metal-free click polymerization. Its structure was fully characterized by IR (Fig. S4 in the ESI†), [1]H (Fig. S8) and ^{13}C NMR (Fig. S12 in the ESI†) spectra and satisfactory analysis data were obtained. **PV** is readily soluble in commonly used organic solvents, such as DCM, chloroform, THF, DMF and DMSO and is thermally stabile (T_d: 342 °C).
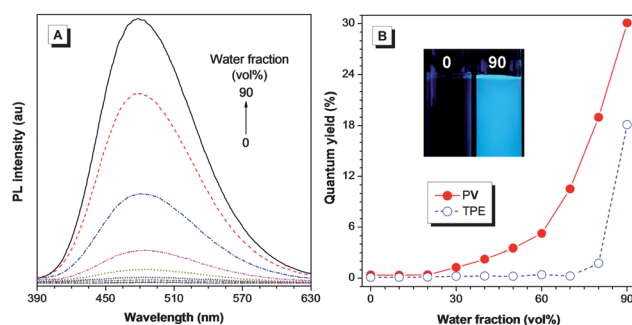
Aggregation-induced emission

To check whether TPE-containing **PV** still retains the AIE characteristics, we investigated its PL spectra in the solution and aggregate states. When excited at 328 nm, the maximum absorption wavelength, the PL curve of **PV** in dilute THF solution shows almost a flat line parallel to the abscissa (Fig. 7A), indicating that the polymer is virtually nonemissive. The emission is progressively intensified with gradual addition of water into its THF solution, but its spectral profiles remain unchanged. The maximum emission intensity was recorded in the THF/water mixtures with a water fraction (f_w) of 90%. Evidently, **PV** has been endowed with the AIE feature.

We then estimated the fluorescence quantum yield (Φ_F) of **PV** in the THF/water mixtures with different f_w. For comparison, the Φ_F values of TPE were also measured under the same experimental conditions. In THF solution, both **PV** and TPE exhibit negligibly small Φ_F values of 0.37 and 0.11%, respectively (Fig. 7B). The Φ_F values of **PV** increase gradually with water addition. The highest value (30.09%) was recorded in the THF/water mixture with a f_w of 90%, which is 81-fold higher than that in THF solution. The changes in the Φ_F values further confirm that **PV** is AIE-active. On the other hand, there is almost no change in Φ_F values of TPE with addition of water until f_w is larger than 70%. The highest value (18.11%) was also obtained in the THF/water mixture with a f_w of 90%, but it is much smaller than that of **PV**.
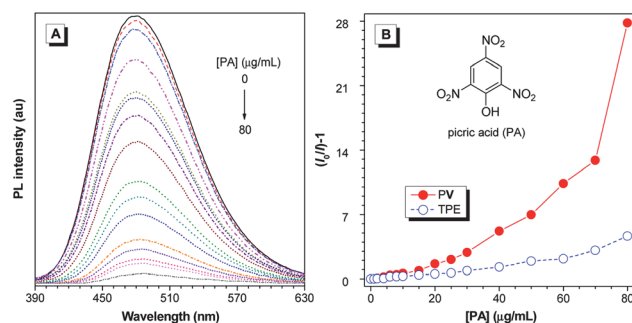

Fig. 7 (A) PL spectra of **PV** in THF and THF/water mixtures. Concentration: 10 μM; λ_{ex}: 328 nm. (B) Variation in the quantum yields (Φ_F) of **PV** and TPE in THF/water mixtures with different water fractions. Φ_F values were estimated using quinine sulfate in 0.1 M H_2SO_4 (Φ_F = 54.6%) as a standard. The inset in panel (B): solutions of **PV** in pure THF and a THF/water mixture with 90% water; photographs taken under illumination of a handheld UV lamp.

Thus, even though the TPE units have been knitted together by the triazole rings in **PV**, their peripheral phenyl rings can still actively rotate when molecularly dissolved, making the polymer nonemissive. In the aggregate state, the intramolecular rotation of the phenyl rings is restricted, which blocks the nonradiative channel and turns on the light emission of the polymer.[22] Compared to the TPE molecule, the rotations of phenyl rings of TPE units in **PV** are more tightly restricted due to the additional confinement of polymer chains in the aggregate state, making it more emissive.

Explosive detection

The novel AIE characteristics of **PV** prompted us to explore its potential application as a fluorescent chemosensor to detect explosives, which has received extensive interest because of the homeland security and *anti*-terrorism implications.[23] Because 2,4,6-trinitrophenol (picric acid, PA) is commercially available among the explosive nitroaromatic compounds, we thus use it as a model. The aggregates of **PV** in a THF/water mixture with a f_w of 90% were utilized as the fluorescent probes. For comparison, the nanoaggregate of TPE was also used to detect PA.

Scheme 3 Synthetic route to functional PACT *via* metal-free click polymerization.

Fig. 8 (A) PL spectra of the TPE-containing polymer in THF/water mixtures (f_w: 90%) containing different amounts of picric acid (PA). Concentration: 10 μM; λ_{ex}: 328 nm. (B) Stern–Volmer plots of $I_0/I - 1$ of the **PV** and TPE *versus* PA concentration, where I = peak intensity and I_0 = peak intensity at [PA] = 0 μg mL^{-1}.

As shown in Fig. 8A, the PL intensities of **PV** aggregates are progressively decreased with PA addition. The fluorescence quenching can be clearly discerned at a PA concentration of 1 µg mL^{-1}. In sharp contrast to the Stern–Volmer plot of TPE, which is almost linear (quenching constant of 8300 M^{-1}) with increase of PA concentration, the plot of **PV** shows a linear correlation with a quenching constant of 14 200 M^{-1} only when the PA concentration is lower than 15 µg mL^{-1} (Fig. 8B). Afterwards, the curve deviates from linearity and bends upward, manifesting a unique superamplified quenching effect.[24]

Conclusion

In this work, we have developed an efficient metal-free click polymerization of dipropiolates and diazides through optimization of polymerization conditions. The diyne monomers can be aromatic and aliphatic propiolates. The click polymerizations of dipropiolates (**1** and **2**) with diazides (**9** and **10**) are carried out in a polar solvent of DMF/toluene (1 : 1 by volume) at a moderate temperature of 100 °C for 24 h, affording soluble **PI–PV** with high molecular weights and regioregularities in high yields. Furthermore, this polymerization is insensitive to oxygen and moisture and can be carried out in an open atmosphere.

The resultant PACTs are thermally stable, optically transparent, and could be chemically degraded rapidly. The TPE-containing PACT shows unique AIE characteristics and its aggregates can work as a fluorescent chemosensor for super-amplified detection of explosives. It is anticipated that this polymerization technique will be a versatile synthetic tool for the generation of new functional materials, which can find an array of applications in biological, environmental, and optoelectronic fields.

Experimental section

General information

Tetrahydrofuran (THF), toluene, and 1,4-dioxane were distilled from sodium benzophenone ketyl in an atmosphere of nitrogen immediately prior to use. Dichloromethane (DCM) was distilled under nitrogen over calcium hydride. *N,N*-Dimethylformamide (DMF) was pre-dried over calcium hydride, distilled under reduced pressure and kept under nitrogen. Other solvents were purified by standard methods. 1,3-Dicyclohexylcarbodiimde (DCC) and *p*-toluenesulfonic acid monohydrate (TsOH) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (China). 1,6-Hexanediol and 1,4-cyclohexanediol were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). All other chemicals were purchased from Acros, Alfa or Aldrich and used as received without further purification.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ADVANCE2B 400 NMR spectrometer in CDCl$_3$ or DMSO-d_6 using tetramethylsilane (TMS; $\delta = 0$) as an internal reference. IR spectra were taken on a Bruker Vector 22 spectrometer. UV spectra were measured on a Varian VARY 100 Bio UV-visible spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Fluorescence quantum yields (Φ_F) were estimated using quinine sulfate in 0.1 N H$_2$SO$_4$ ($\Phi_F = 54.6\%$) as a standard. The absorbance of the solutions was kept 0.04–0.06 to avoid the internal filter effect.

Element analysis was conducted on a Thermo Finnigan Flash EA1112 system. Thermo-gravimetric analysis (TGA) measurements were carried out on a Perkin-Elmer TGA 7 under dry nitrogen at 20 °C min^{-1}. Relative weight-average (M_w) and number-average (M_n) molecular weights of the polymers and their polydispersity indices (PDI, M_w/M_n) were estimated by a Waters 1515 gel permeation chromatography (GPC) system equipped with an interferometric refractometer detector, using a set of monodisperse polystyrenes or poly(methyl methacrylate) as calibration standards and THF or DMF as the eluent at a flow rate of 1.0 mL min^{-1}.

Monomer preparation

4,4′-Isopropylidenediphenyl dipropiolate (**1**), 1,4-bis(6-azido-hexyloxy)benzene (**9**) and 1,2-bis[4-(6-azidohexyloxy)phenyl]-1,2-diphenylethene (**10**) were prepared according to our previous papers.[10a,16] Aliphatic dipropiolates (**2**) were prepared by esterification of aliphatic diols with propiolic acid in the presence of TsOH (Scheme 1C). Detailed experimental procedures for the synthesis of 1,6-hexanediol dipropiolate (**2a**) are given below as an example.

In a 250 mL round-bottom flask equipped with a Dean–Stark apparatus were added 1.18 g (10 mmol) of 1,6-hexanediol (**8a**), 2.10 g (30 mmol) of propiolic acid (**3**), 0.19 g (1 mmol) of TsOH, and 100 mL of dry toluene. The mixture was allowed to reflux for 36 h with constant removal of yielded water. The solution was concentrated by a rotary evaporator, and the residue was dissolved in 100 mL of DCM. The organic phase was washed with 5% aqueous solution of NaHCO$_3$ (30 mL × 3) and water (50 mL × 1), and then dried over MgSO$_4$ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using petroleum ether (60–90 °C)/ethyl acetate (10 : 1, v/v) as eluent. 1,6-Hexanediol dipropiolate (**2a**) was obtained in 91.0% yield (2.02 g) as a white solid. IR (thin film), ν (cm^{-1}): 3279 (≡C–H stretching), 2944, 2119 (C≡C stretching), 1714 (C=O stretching), 1464, 1233. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 4.20 (t, 2H), 2.91(s, 1H), 1.70 (m, 2H), 1.41(m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 152.7, 74.6, 74.5, 66.1, 28.1, 25.3. Anal. Calcd for C$_{12}$H$_{14}$O$_4$: C, 64.85; H, 6.35. Found: C, 64.77; H, 6.41%.

Aliphatic dipropiolates **2b** and **2c** were prepared by similar procedures, and their characterization data are given below.

1,4-Cyclohexanediol dipropiolate (2b). This monomer was prepared from 1,4-cyclohexanediol (**8b**) and propiolic acid (**3**). White solid; yield 95.4% (2.10 g). IR (thin film), ν (cm^{-1}): 3282 (≡C–H stretching), 2957, 2119 (C≡C stretching), 1716 (C=O stretching), 1447, 1354, 1257. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 4.96 (m, 1H), 2.91 (s, 1H), 1.91 (m, 2H), 1.77 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 152.0, 74.8, 74.5, 72.1, 26.8. Anal. Calcd for C$_{12}$H$_{12}$O$_4$: C, 65.45; H, 5.49. Found: C, 65.77; H, 5.52%.

2,2-Dimethyl-1,3-propanediol dipropiolate (2c). This monomer was prepared from 2,2-dimethyl-1,3-propanediol (**8c**) and pro-piolic acid (**3**). White solid; yield 67.7% (1.41 g). IR (thin film), ν (cm^{-1}): 3282 (≡C–H stretching), 2972, 2121 (C≡C stretching), 1720 (C=O stretching), 1471, 1375, 1256. ^{1}H NMR (400 MHz,

CDCl$_3$), δ (TMS, ppm): 3.98 (s, 2H), 2.87 (s, 1H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 152.5, 75.1, 74.3, 70.4, 34.6, 21.4. Anal. Calcd for C$_{11}$H$_{12}$O$_4$: C, 63.45; H, 5.81. Found: C, 63.40; H, 5.79%.

Polymer synthesis

All the polymerizations of dipropiolates and diazides were carried out under nitrogen using a standard Schlenk technique in a vacuum line system, unless otherwise stated. Typical experimental procedures for the click polymerization of **1** with **9** are described below.

In a 15 mL Schlenk tube with a stopcock in the side arm was placed 33.2 mg (0.1 mmol) of **1** and 36.0 mg (0.1 mmol) of **9**. The tube was evacuated and refilled with dry nitrogen three times through the side arm. Freshly distilled DMF (0.3 mL) and toluene (0.3 mL) were injected into the tube to dissolve the monomers. After stirring at 100 °C for 24 h, the reaction mixture was diluted with 5 mL of chloroform and added dropwise into 200 mL of hexane through a cotton filter under stirring. The precipitates were allowed to stand overnight and then collected by filtration. The polymer was washed with hexane and dried to a constant weight at ambient atmosphere.

Characterization data for PI. White powder; 96.1% yield. M_w 15 100; M_w/M_n 1.49 (GPC, determined in THF on the basis of PS calibration). $F_{1,4}$: 90.1%. IR (thin film), ν (cm^{-1}): 2939, 2859, 2089 (N$_3$ and C≡C stretching), 1748 (C=O stretching), 1505, 1207. ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 8.99, 8.49, 7.30, 7.16, 6.78, 4.67, 4.45, 3.83, 3.34, 2.49, 1.88, 1.67, 1.40, 1.28. ^{13}C NMR (100 MHz, DMSO-d_6), δ (TMS, ppm): 159.3, 153.0, 148.2, 138.3, 130.3, 128.1, 121.7, 115.6, 68.1, 50.1, 42.4, 31.0, 29.6, 28.8, 25.9, 25.3.

PII. The polymer was prepared from 1,6-hexanediol dipropiolate **2a** (44.4 mg, 0.2 mmol) and 1,4-bis(6-azidohexyloxy)benzene **9** (72.0 mg, 0.2 mmol) in 1.2 mL of DMF/toluene (1 : 1 by volume). White powder; 85.3% yield. **PII** is completely soluble in chloroform, partially soluble in DMF, but insoluble in THF. M_w 10 500; M_w/M_n 1.28 (soluble part, GPC, determined in DMF on the basis of poly(methyl methacrylate) (PMMA) calibration). $F_{1,4}$: 87.0%. IR (thin film), ν (cm^{-1}): 3119, 2938, 2862, 2089 (N$_3$ and C≡C stretching), 1727 (C=O stretching), 1509, 1467, 1360, 1224. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 8.26, 8.07, 6.78, 4.71, 4.42, 4.25, 3.89, 1.95, 1.72, 1.51, 1.40, 1.12. ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 160.6, 153.2, 139.7, 127.7, 115.4, 70.2, 68.2, 50.5, 35.6, 30.1, 29.0, 26.1, 25.5, 21.8.

PIII. The polymer was prepared from 1,4-cyclohexanediol dipropiolate **2b** (44.0 mg, 0.2 mmol) and 1,4-bis(6-azidohexyloxy)benzene **9** (72.0 mg, 0.2 mmol) in 1.2 mL of DMF/toluene (1 : 1 by volume). White powder; 88.6% yield. M_w 18 700; M_w/M_n 1.53 (GPC, determined in THF on the basis of PS calibration). $F_{1,4}$: 84.0%. IR (thin film), ν (cm^{-1}): 3116, 2942, 2864, 2076 (N$_3$ and C≡C stretching), 1726 (C=O stretching), 1507, 1224. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 8.09, 8.03, 6.78, 4.72, 4.42, 4.35, 3.87, 1.96, 1.79, 1.73, 1.49, 1.39. ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 160.5, 153.1, 140.1, 127.2, 115.3, 68.1, 65.0, 50.5, 30.0, 29.0, 28.5, 26.1, 25.5.

PIV. The polymer was prepared from 2,2-dimethyl-1,3-propanediol dipropiolate **2c** (41.6 mg, 0.2 mmol) and 1,4-bis(6-azidohexyloxy)benzene **9** (72.0 mg, 0.2 mmol) in 1.2 mL of DMF/toluene (1 : 1 by volume). White powder; 91.2% yield. **PIV** is completely soluble in chloroform but partially soluble in THF. M_w 11 400; M_w/M_n 1.27 (soluble part, GPC, determined in THF on the basis of PS calibration). $F_{1,4}$: 84.7%. IR (thin film), ν (cm^{-1}): 3132, 2940, 2865, 2082 (N$_3$ and C≡C stretching), 1732 (C=O stretching), 1508, 1469, 1383, 1225. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 8.12, 8.07, 6.77, 5.17, 4.72, 4.42, 3.86, 2.06, 1.96, 1.86, 1.72, 1.38. ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 160.1, 153.0, 140.2, 127.3, 115.3, 70.8, 68.2, 50.5, 30.0, 29.0, 27.3, 26.1, 25.4.

PV. The polymer was prepared from 1,4-cyclohexanediol dipropiolate **2b** (44.0 mg, 0.2 mmol) and 1,2-bis[4-(6-azido-hexyloxy)phenyl]-1,2-diphenylethene **10** (123.0 mg, 0.2 mmol) in 1.2 mL of DMF/toluene (1 : 1 by volume). White powder; 99.2% yield. M_w 23 500; M_w/M_n 1.58 (GPC, determined in THF on the basis of PS calibration). $F_{1,4}$: 86.2%. IR (thin film), ν (cm^{-1}): 2938, 2861, 2092 (N$_3$ and C≡C stretching), 1730 (C=O stretching), 1606, 1507, 1236. ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 8.82, 8.28, 7.04, 6.91, 6.79, 6.60, 5.04, 4.64, 4.38, 3.78, 1.83, 1.60, 1.39, 1.24. ^{13}C NMR (100 MHz, DMSO-d_6), δ (TMS, ppm): 160.2, 157.3, 144.1, 139.8, 139.3, 135.9, 132.1, 131.2, 129.4, 128.1, 126.8, 113.8, 70.6, 67.4, 50.1, 29.6, 28.4, 27.2, 25.8, 25.3.

Polymer hydrolysis

The hydrolysis of the polymer was carried out in air. To a 10 mL tube were added 30 mg of **PI** and 2.9 mL of freshly distilled THF. Then, 0.1 mL of 30 wt% KOH aqueous solution was injected. The resultant mixture was stirred at room temperature. The molecular weight of the polymer was monitored by GPC.

Acknowledgements

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