Efficient Polymerization of Azide and Active Internal Alkynes

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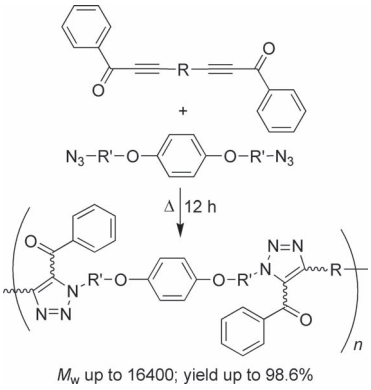
The 1,3-dipolar cycloaddition of azides and active internal alkynes has been well studied, but is rarely utilized as a tool for polymer preparation. In this work, an efficient polymerization route is developed. Polycycloaddition of diazide (**4**) and bis(benzoylethynyl)-benzenes and -butane (**3**) at elevated temperature has produced the first examples of soluble 1,4,5-trisubstituted polytriazoles P**I** with satisfactory molecular weights ($\overline{M}_w$ up to 16 400) in excellent yields (up to 98.6%). All the obtained polymers are thermally stable, losing merely 5% of their weights at temperatures higher than 367 °C. They exhibit higher refractive indices than some commercial plastics and can be crosslinked upon UV irradiation to generate a 3D photopattern with high resolution. The metal-free feature of such a methodology offers a facile tool to prepare functional materials free from the contamination of metal species.



1. Introduction

The Huisgen 1,3-dipolar cycloaddition of azides and alkynes is a well-known organic reaction, but received little attention after development because of its low reaction rate and regioselectivity.[1] This situation continued until Sharpless and Meldal and coworkers independently reported that Cu(I) species could remarkably accelerate the reaction and produce solely 1,4-disubstituted 1,2,3-triazoles.[2] The Cu(I)-catalyzed azide-alkyne cycloaddition enjoys such advantages as high regioselectivity, mild reaction conditions, economy efficiency, strong tolerance to functional groups and simple product isolation. The reaction was termed "click chemistry" by Sharpless and has found a variety of applications in diverse areas of research, including bioconjugate synthesis, surface modification, and dendrimer and polymer preparation.[3,4] The Ru(II)-catalyzed azide-alkyne cycloaddition, which produced only 1,5-disubstituted 1,2,3-triazole derivatives and was complementary to the Cu(I)-catalyzed reaction, was established in 2005. Besides the terminal alkynes, Ru(II) complexes can catalyze the reaction of internal alkynes with azides, which further widens the alkyne source and the application of click chemistry.[5]

Remarkable progress has been made in using the Cu(I)-catalyzed azide and alkyne click reaction to prepare functional polytriazoles.[6,7] Our groups have successfully adopted Cu(I)- and Ru(II)-catalyzed click polymerizations to synthesize functional 1,4- and 1,5-regioregular hyperbranched polytriazoles.[8] The complete removal of the catalyst residues from the resulting polymers has, however, been difficult.[9]

Since metallic species are detrimental to polymer properties, the best way to surmount this problem is to develop

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a click polymerization in the absence of transition-metal catalysts, i.e., metal-free click polymerization. As is well known, most new polymerization reactions, if not all, are derived from established organic reactions. Several metal-free click reactions or cycloadditions have been reported, among which the strain-promoted azide-alkyne cycloaddition is the most well-known one.[10] Few polymers, however, have been prepared using such a methodology, probably due to the synthetic difficulties in the preparation of cyclooctyne monomers.

During the course of our exploration of new polymerization reactions based on triple bond building blocks, our groups have established a metal-free click polymerization. Heating mixtures of active external alkynes, such as aroylacetylenes and propiolates, with azides in polar solvents at a moderate temperature of 100 °C for a short reaction time (6–12 h) readily produces soluble polymers with high molecular weights (weight-average molecular weight, $\overline{M}_w$ up to 26 700) and regioregularities (fraction of 1,4-disubstituted 1,2,3-triazoles up to 92%) in high yields (up to ~99%).[11]

According to the reaction mechanism of 1,3-dipolar cycloaddition, the azide monomer can react not only with the external alkynes but also the internal ones. Although reactions of azides and internal alkynes with electron-withdrawing groups have been reported,[12] to the best of our knowledge, no polymers have been reported in the literature from these monomers. In this paper, we established an efficient metal-free polymerization of active internal alkynes, named bis(benzoylethynyl)-benzenes or -butane, with diazide. The polymers were obtained in excellent yields and exhibited versatile properties, such as high thermal stability, high refractive index and photosensitivity.

2. Experimental Section

2.1. Materials and Instrumentation

Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. Triethylamine (TEA) was distilled and dried over potassium hydroxide. Anhydrous *N*,*N*-dimethylacetamide (DMF), benzoyl chloride (**1**), 1,3-diethynylbenzene (**2a**), 1,4-diethynylbenzene (**2b**) and 1,7-octadiyne (**2c**) were purchased from Acros. 1,4-Bis(6-azidohexyloxy)benzene (**4**) was prepared according to our previous paper.[11d] Triphenylphosphine, bis(triphenylphosphine)-palladium(II) dichloride and copper(I) iodide were purchased from Aldrich. Pentamethylcyclopentadienyl-bis(triphenylphosphine)-ruthenium(II) chloride was purchased from STREM. All other solvents and reagents were used as received without further purification.

1D ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer in $CDCl_3$ using tetramethylsilane (TMS; δ = 0 ppm) as an internal standard. 2D ^{1}H-^{1}H NOESY spectra were obtained using a Bruker DMX-500 spectrometer. Fourier Transform infrared spectra were recorded on a Perkin Elmer 16 PC FT-IR spectrophotometer. Refractive index values of polymer thin films were detected on a Metricon model 2010 and 2010/M prism coupler thin film thickness/refractive index measurement system using five individual laser sources with wavelengths of 402.9, 473.0, 632.8, 933.5 and 1539.2 nm. Metriconfit software (Version 1.0.0) was employed to fit the acquired Ψ and Δ curves with the obtained five data points. The Cauchy dispersion law was applied to describe the polymer layer from the visible to IR spectral region. The thermal stability of the polymers was evaluated on a Perkin-Elmer TGA 7 analyzer under nitrogen at a heating rate of 10 °C min^{-1}. Thermal transitions were investigated by differential scanning calorimetry (DSC) using a TA DSC Q200 instrument under dry nitrogen at a heating rate of 10 °C min^{-1}. Weight- and number-average molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and polydispersity indexes ($\overline{M}_w/\overline{M}_n$) of the polymers were estimated in THF using a Waters 1515 gel permeation chromatography (GPC) system equipped with an interferometric refractometer detector, using a set of monodisperse polystyrenes for calibration and THF as the eluent at a flow rate of 1.0 mL min^{-1}. High resolution mass spectra (HRMS) were recorded on a Finnigan TSQ 7000 triple-quadrupole mass spectrometer operating in MALDI-TOF mode.

2.2. Monomer Synthesis

2.2.1. 1,3-Bis(benzoylethynyl)benzene (**3a**)

Into a 250 mL two-necked round-bottom flask purged with nitrogen were added $PdCl_2(PPh_3)_2$ (281 mg, 0.4×10^{-3} mol), CuI (152 mg, 0.8×10^{-3} mol), PPh_3 (105 mg, 0.40×10^{-3} mol), THF (60 mL) and triethylamine (20 mL). Then, 1.26 g of **2a** (10×10^{-3} mol, 1.32 mL) was injected by syringe. The mixture was cooled to 0 °C in an ice water bath, after which benzoyl chloride (**1**, 3.374 g, 24×10^{-3} mol, 2.783 mL) was injected dropwise. After stirring at room temperature for 12 h, the mixture was poured into ice water. The aqueous solution was extracted with 50 mL of dichloromethane three times. The organic phase was combined, washed with 100 mL of water three times and 100 mL of brine once, and then dried over anhydrous magnesium sulfate overnight. After filtration and solvent evaporation, the crude product was purified with a silica gel column using a petroleum ether/chloroform mixture (1:1 by volume) as the eluent. A grayish powder of **3a** was obtained in 94.2% yield (3.145 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.21 (d, 2H), 7.99 (s, 1H), 7.76 (d, 2H), 7.65 (t, 2H), 7.52 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 177.6, 133.9, 135.6, 134.7, 134.3, 129.5, 129.6, 128.7, 121.1, 90.6, 87.5; IR (thin film): ν = 3056, 2913, 2203, 1644, 1602, 1482, 1448, 1317, 1267, 1170, 1035, 898, 793, 688, 629 cm^{-1}; HRMS (MALDI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{14}O_2$, 335.1027; found, 335.1080.

2.2.2. 1,4-Bis(benzoylethynyl)benzene (**3b**)

This was prepared from 1,4-diethynylbenzene (**2b**) and benzoyl chloride (**1**) following a similar procedure. A white needle crystalline solid was obtained in 92.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.21 (d, 4H), 7.73 (s, 4H), 7.65 (t, 2H), 7.52 (t, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 177.6, 136.6, 134.3, 133.0, 129.5, 128.7, 122.3, 91.1, 88.8; IR

(thin film): ν = 3056, 2913, 2203, 1635, 1575, 1498, 1448, 1407, 1313, 1288, 1209, 1174, 1010, 838, 788, 692, 667, 553 cm^{-1}; HRMS (MALDI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{14}O_2$, 335.1027; found, 335.1069.

2.2.3. 1,4-Bis(benzoylethynyl)butane (**3c**)

This was synthesized from 1,7-octodiyne (**2c**) with benzoyl chloride (**1**) following a similar procedure. A brown needle crystalline solid was obtained in 90.9% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.12 (d, 4H), 7.59 (t, 2H), 7.47 (t, 4H), 2.59 (t, 4H), 1.88 (t, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 178.0, 136.7, 133.9, 129.4, 128.5, 95.3, 80.0, 26.9, 18.7; IR (KBr): ν = 3059, 2929, 2248, 2189, 1635, 1590, 1447, 1321, 1266, 1173, 1104, 1067, 978, 881, 794, 756, 697, 608, 521; HRMS (MALDI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{18}O_2$, 315.1340; found, 315.1387.

2.3. Model Synthesis

Into a baked 10 mL Schlenk tube with a stopcock in the side arm purged with nitrogen were added **3a** (55 mg, 0.15×10^{-3} mol) and pentamethylcyclopentadienylbis(triphenylphosphine)-ruthenium(II) chloride (14 mg, 0.015×10^{-3} mol). Freshly distilled THF (1 mL) and 6-azidohexyloxybenzene (**5**, 66 mg, 0.30×10^{-3} mol) were then injected. After stirring at 70 °C for 12 h, the mixture was concentrated. The crude product was purified with a silica gel column using petroleum ether/chloroform (1:1 by volume) as the eluent. A yellow solid was obtained in 91.2% yield (110 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.32, 7.70, 7.61, 7.50, 7.28, 6.93, 6.83, 4.46, 3.86, 2.02, 1.72, 1.28, 0.88.

2.4. Polymer Preparation

The polymerization reactions were carried out under nitrogen using standard Schlenk techniques. Typical procedures are given below. Into a baked 10 mL Schlenk tube with a stopcock in the side arm was added diacetylene (0.20×10^{-3} mol) and diazide (0.20×10^{-3} mol). The tube was evacuated and refilled with dry nitrogen three times through the side arm. Then, anhydrous DMF (1.0 mL) was injected via a syringe. After stirring at 150 °C for 12 h, the mixture was diluted with 5 mL of chloroform and added dropwise into 220 mL of hexane/chloroform (20:1 by volume) through a cotton filter under stirring. The precipitate was allowed to stand overnight, was collected by filtration, and then was dried under a vacuum at room temperature to a constant weight.

2.4.1. Characterization Data for PIa

The polymer was prepared from 1,3-bis(benzoylethynyl)benzene (**3a**) and 1,4-bis(6-azidohexyloxy)benzene (**4**). It was a yellow solid obtained in a 98.5% yield, with an $\overline{M}_w$ of 16 400, and an $\overline{M}_w/\overline{M}_n$ of 4.00 (GPC, polystyrene calibration). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.29, 8.24, 7.69, 7.56, 7.47, 6.74, 4.50, 4.21, 4.10, 3.80, 1.91, 1.67, 1.39, 0.90; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 186.48, 153.39, 143.40, 142.05, 140.07, 136.97, 134.38, 133.12, 130.57, 128.19, 126.94, 115.239, 67.94, 48.66, 31.48, 29.88, 28.69, 26.15, 25.05, 22.24, 14.00, 12.73; IR (thin film): ν = 3048, 2940, 2881, 2092, 1650, 1586, 1539, 1506, 1460, 1354, 1224, 1030, 914, 821, 747, 687, 525 cm^{-1}.

2.4.2. Characterization Data for PIb

The polymer was synthesized from 1,4-bis(benzoylethynyl) benzene (**3b**) and 1,4-bis(6-azidohexyloxy)benzene (**4**). It was a yellow solid obtained in a 97.0% yield, with an $\overline{M}_w$ of 11 400 and an $\overline{M}_w/\overline{M}_n$ of 3.14 (GPC, polystyrene calibration). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.28, 7.77, 7.60, 7.52, 7.46, 7.36, 7.29, 7.25, 6.75, 6.74, 4.52, 4.51, 4.34, 4.33, 3.82, 1.93, 1.76, 1.69, 1.40; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 186.50, 152.64, 146.97, 143.53, 136.97, 135.58, 134.44, 130.57, 129.72, 128.88, 115.26, 68.01, 49.68, 47.82, 31.42, 30.05, 29.76, 29.38, 26.14, 21.87, 14.14; IR (thin film): ν = 3050, 2923, 2856, 2194, 1652, 1594, 1504, 1454, 1350, 1225, 1104, 1002, 915, 825, 749, 693, 598, 504 cm^{-1}.

2.4.3. Characterization Data for PIc

The polymer was constructed from 1,4-bis(benzoylethynyl) butane (**3c**) and 1,4-bis(6-azidohexyloxy)benzene (**4**). It was a light yellow solid obtained in 93.2% yield, with an $\overline{M}_w$ of 15 600 and an $\overline{M}_w/\overline{M}_n$ of 3.55 (GPC, polystyrene calibration). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.32, 7.71, 7.56, 6.77, 4.50, 4.32, 3.84, 3.13, 2.93, 1.97, 1.86, 1.75, 1.64, 1.52, 1.43; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 187.78, 162.71, 153.27, 142.87, 137.72, 133.06, 130.83, 130.79, 129.40, 129.26, 128.38, 115.56, 77.44, 68.41, 49.86, 47.96, 36.93, 30.31, 28.48, 25.84; IR (thin film): ν = 3070, 2940, 2856, 2104, 1650, 1603, 1547, 1501, 1469, 1353, 1233, 1048, 914, 826, 732, 687, 515 cm^{-1}.

2.5. Photopatterning

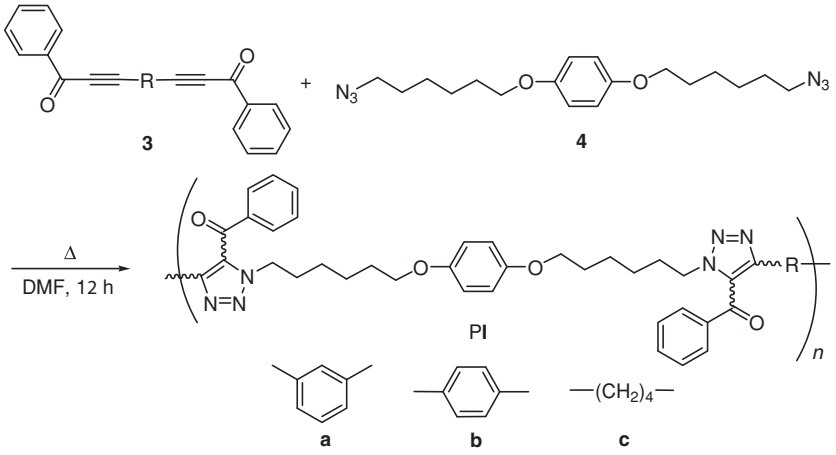
The photo-crosslinking reaction of the polymer film was conducted in air at room temperature using a 365 nm light obtained from a Spectroline ENF-280C/F UV lamp at a distance of 5 cm as the light source. The incident light intensity was ~18.5 mW cm^{-2}. The film was prepared by spin-coating the polymer solution (10% w/w in 1,2-dichloroethane) at 2000 rpm for 1 min on a silicon wafer. The polymer film was dried in a vacuum oven at room temperature overnight. The photoresist pattern was generated using a copper photomask and taken on an optical microscope (Nikon 80i equipped with Nikon Digital Sight DS-5Mc-L2 Cooled CCD camera) using a normal light source.

3. Results and Discussion

3.1. Polymer Synthesis

The azide monomer (**4**) was synthesized according to our previous publication.[11d] For comparison, three bis(benzoylacetylene)s (**3**) with different linkers and substitution patterns were designed and prepared by a modified Sonogashira coupling of benzoyl chloride and diynes **2** in high yields (up to 94.2%) (Scheme S1).[13] All the monomers were carefully purified and characterized by spectroscopic methods, from which satisfactory analysis data corresponding to their molecular structures were obtained.

In our previous works, we conducted the metal-free click polymerization of aroylacetylenes and azides at 100 °C for



Scheme 1. Synthesis of polytriazoles by efficient 1,3-dipolar polycycloadditions of active internal alkynes and azide.

6 h in polar solvents.[11] Considering the steric effect of the internal alkynes, we further raised the reaction temperature to 150 °C for the polymerization. All the polymerization reactions propagated smoothly and furnished PI with satisfactory molecular weights (up to 16 400) in excellent yields (up to 98.6%, Scheme 1, Table 1) after 12 h. The results were comparable to those achieved in our previous investigation, indicating the reactivity of internal alkynes was quite similar to that of aroylacetylenes and propiolates. The obtained polymers were completely soluble in common organic solvents, such as THF, chloroform, DMF and DMSO. The polymers were thermally stable, losing merely 5% of their weights at temperatures higher than 367 °C (Figure S1A). They showed moderate glass transition temperatures (68.5, 65.4 and 39.3 °C for PI**a**, PI**b** and PI**c**, respectively) (Figure S1B), which is understandable because they are largely constructed from alkyl chains.

3.2. Structural Characterization

Thanks to the good solubility of the polymers in common organic solvents, we could characterize their molecular structures by "wet" spectroscopic techniques and obtained satisfactory results corresponding to their structures (see Experimental Section and Supporting Information for details). The IR spectra of PI**a** and its monomers are given in Figure S2 as an example for discussion. The stretching vibration bands of C≡C of **3a** and N_3 of **4** occured at 2204 and 2098 cm^{-1}, respectively. They became much weaker after polymerization, indicating that most of the acetylene and azide groups in the monomers were consumed and transformed into the triazole rings in PI**a**. Similar phenomena were observed when a comparison was made between the IR spectra of PI**b** and PI**c** with their monomers (Figure S3 and S4).

One key issue for the azide-alkyne cycloaddition is the regioregularity of the resulting product, which can generally be calculated using ^{1}H NMR spectroscopy. We also used this technique to complete calculations for our polymers and to deduce the fractions of regioisomers. Figure 1 shows the ^{1}H NMR spectra of PI**a** and its monomers **3a** and **4**. For better assignment of the resonance peaks, a model compound **6** was prepared by a Cp*Ru(PPh$_3$)$_2$Cl-catalyzed click reaction of **3a** and **5** (Scheme S2). The methylene protons adjacent to the azide groups of **4** resonated at δ 3.28, but this resonance almost disappeared in PI**a**. Comparing the spectrum of **6** with that of PI**a**, it is clear that the peak at δ 4.42 (peak a) was associated with the proton resonance of structure A.[5b] On the other hand, the peak at δ 4.51 was assigned to that of structure B.

Other peaks were assignable except that at δ 4.10, which was also observed in the ^{1}H NMR spectrum of PI**b** but was absent in that of PI**c** (Figure S5), implying that it was associated with the aromatic linkers. To clarify its origin, we further characterized PI**a** by 2D Nuclear Overhauser Effect spectroscopy (NOESY) and the spectrum is given in Figure S6. Enlarging the spectrum showed that an interaction existed between the triazole bridged methylene and phenyl protons in structure A. The crowded molecular structure may force them into close proximity, and their coupling generated a new peak at δ 4.10. A similar observation was also reported in the literature[14] The fractions of structure A in PI**a**, PI**b** and PI**c** were thus calculated to be 68.8, 67.5 and 74.0%, respectively, using the peak integrals at δ 4–5 as they did not overlap with other resonance peaks. The ^{13}C NMR spectra of the polymers exhibited almost no azido methylene and acetylene carbon resonances of their monomers. (Figures S7–S9). Meanwhile, new peaks emerged in the aromatic absorption region, further proving that most of the alkyne and azide groups of the monomers were transformed into the triazole rings in the polymers by the polycycloaddition reactions.

Table 1. Synthesis of polytriazoles PI by efficient 1,3-dipolar polycycloaddition of active internal alkynes **3** and azide **4**.[a)]

No.	Monomer	Polymer	$\overline{M}_w$[b)]	$\overline{M}_w/\overline{M}_n$[b)]	Yield [%]
1	**3a** + **4**	PI**a**	16 400	4.00	98.6
2	**3b** + **4**	PI**b**	11 400	3.14	97.1
3	**3c** + **4**	PI**c**	15 600	3.55	93.2

[a)] Polymerization reactions were carried out at 150 °C for 12 h. [3] = [4] = 0.2 M.[b)] Determined by gel permeation chromatography (GPC) in THF on the basis of a linear polystyrene calibration.

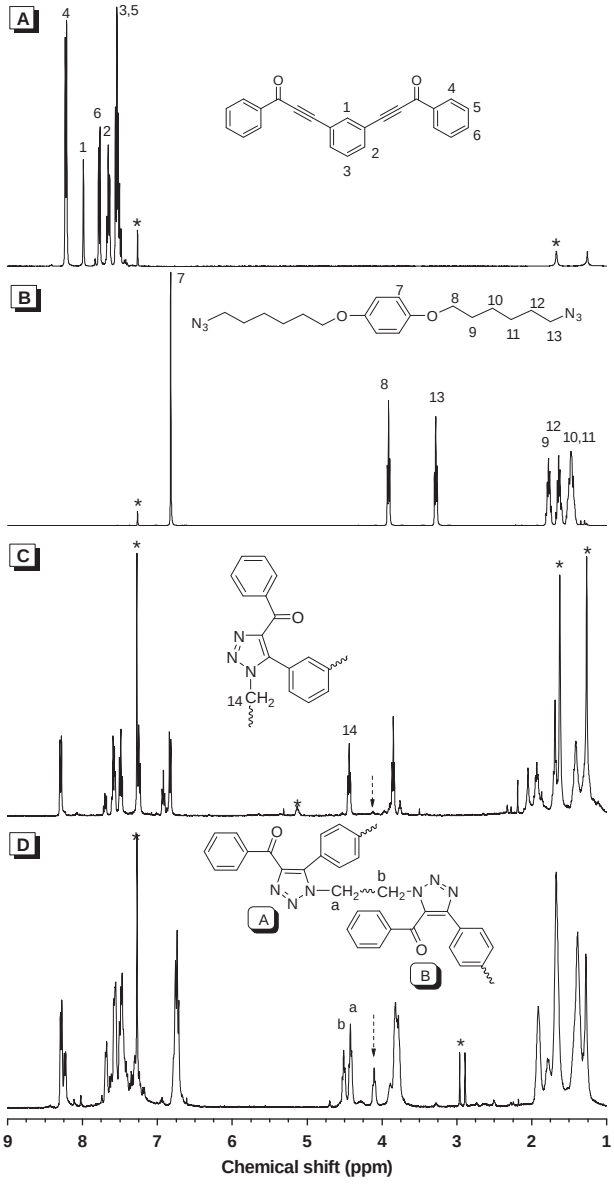


Figure 1. ^{1}H NMR spectra of chloroform-*d* solutions of monomers (A) **3a** and (B) **4**, (C) model compound **6**, and (D) polymer P**Ia** measured at room temperature. The solvent peaks are marked with asterisks.

3.3. Polymer Properties

The development of new processable materials with high refractive indices (RIs) has attracted much attention owing to their potential applications in photonic and optoelectronic devices.[15] **PI** contain numerous aromatic rings and polarized benzoyltriazole units and thus may show high RIs.[11c] Wavelength-dependent refractive index measurements showed that the polymers indeed displayed high RI values (n = 1.682–1.572) in a wide wavelength region (400–1560 nm) (Figure 2). RI values at longer wavelengths are missing due to the equipment limitations. The RI values of P**Ia**, P**Ib** and P**Ic** at 633 nm were 1.621, 1.621 and 1.596, respectively, which are

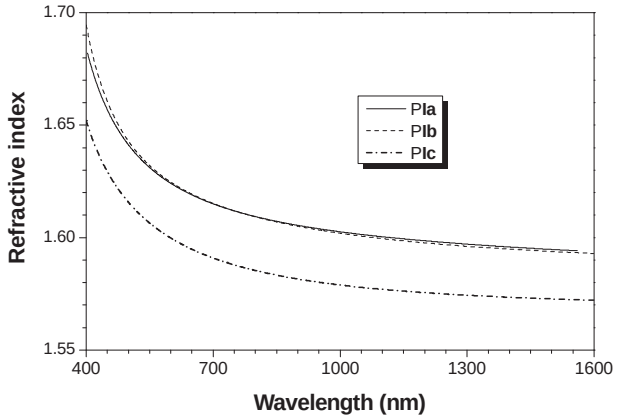


Figure 2. Wavelength dependence of refractive indices of thin films of PI.

much higher than those of commercially important optical plastics such as polyacrylate (n = 1.492), polycarbonate (n = 1.581) and polystyrene (n = 1.587).[16] The difference in the refractivity at 633 nm indicates that the RI value of the polymer can be tuned by simply varying the type of linker.

We have proven that benzoyltriazole, being structurally similar to benzophenone, is photosensitive and can be crosslinked upon UV irradiation to generate 3D photopatterns with high resolution.[11c] The present polymers contain many benzoyltriazole units and they are thus anticipated to be photosensitive and readily crosslinkable. Indeed, when a thin solid film of P**Ia** spin-coated on a silicon wafer was UV-irradiated in air through a copper photomask for only 3 min, the exposed region became insoluble. A well-resolved 3D photopattern was thus generated after development in 1,2-dichloroethane (Figure 3), making the polymers promising for applications in the fabrication of printed circuit boards, sand carving, microelectronics, etc.

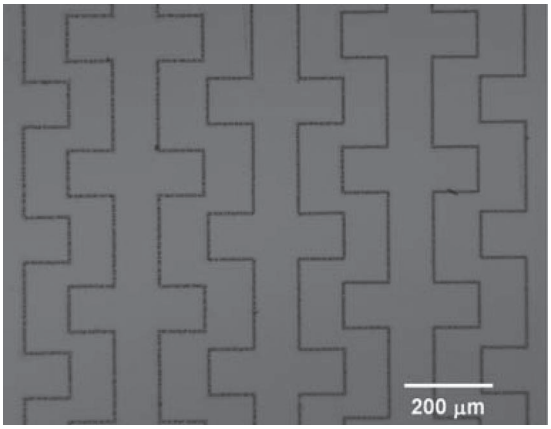


Figure 3. Negative photopattern generated by UV-irradiation of P**Ia** for 3 min. The photograph was taken under normal room lighting.

4. Conclusion

In this work, we presented the first example of polymer preparation from azide and active internal alkynes using efficient 1,3-dipolar polycycloaddition. The polymerizations of alkynes (**3**) and azide (**4**) were carried out in DMF at 150 °C for 12 h, affording soluble P**Ia**–P**Ic** with satisfactory molecular weights in excellent yields. The polymers were thermally stable with high degradation temperatures. Thanks to the benzoyltriazole units, the polymers exhibited high refractive indices. They were also photosensitive and could generate 3D photopatterns with high resolution. Thus, this work not only establishes a new efficient 1,3-dipolar polycycloaddition reaction but also provides a facile tool for the synthesis of 1,4,5-trisubstituted functional polytriazoles that are free from metal residue contamination. Such a methodology and materials are promising for use in biological, environmental and optoelectronic areas.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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