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Synthesis and Characterization of Ureidopyrimidone Telechelics by CuAAC "Click" Reaction: Effect of T_g and Polarity

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S *Supporting Information*
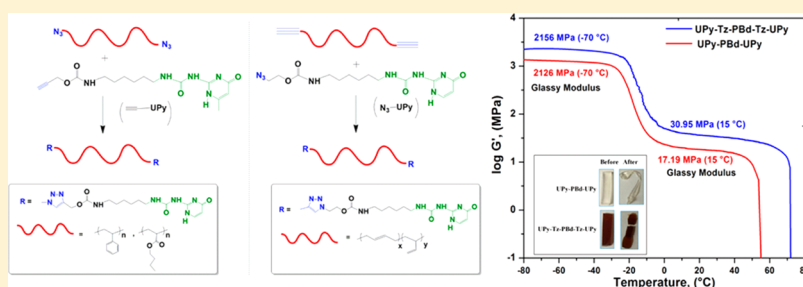
ABSTRACT: Telechelic oligomers functionalized with 2-ureido-4[1H]-pyrimidone (UPy), a quadruple hydrogen bonding group, have been synthesized using a combination of atom-transfer radical polymerization and click reaction. Ureidopyrimidone (UPy) synthons with propargyl and azide functionality were used for clicking with azido and propargyl telechelic oligomers, respectively. The effect of triazole linker and types of oligomers differing in T_g and polarity, such as poly(n-butyl acrylate) (PnBA), polystyrene (PS), and polybutadiene (PBd) on UPy hydrogen bonding have been examined. High solution viscosity and deviation from the normal terminal relaxation in melt state were observed, suggesting the presence of UPy aggregates that are in equilibrium between linear and network polymers. Differential scanning calorimetry studies confirm dissociation of UPy aggregates as an endothermic peak for PBd system, whereas the high T_g and polar polymers (PS and PnBA) had no such peaks associated with T_m indicating the significance of the polymer chain dynamics in supramolecular hydrogen bonding. The triazole linker interferes with the UPy association and reduces the sizes of hydrogen-bonded UPy aggregates and thereby improves the physical property of supramolecular polymers.

INTRODUCTION

Supramolecular polymers (SPs)[1] based on self-complementary quadruple hydrogen bonded 2-ureido-4[1H]-pyrimidone (UPy) telechelics oligomers[2−5] exhibit versatile material properties depending on the nature of linking oligomers, and they can be used as thermoplastic elastomers,[6] self-healing polymers[7] and in bioscaffolding applications. A high association constant ($K_{dim} = 6 \times 10^7$ M^{-1} in chloroform and 6×10^8 M^{-1} in toluene) of UPy groups and inexpensive synthesis using commercial reagents make UPy synthons indispensable for preparation of SPs.[8] Telechelic polymers functionalized with UPy groups are synthesized using chain end modification and often via reaction of hydroxyl terminal groups with a suitable excess UPy-synthon, a compound containing UPy and reactive isocyanate linker (UPy-R-NCO), where R is a linear alkyl chain or cyclic aliphatic chain.[6] By using this approach a variety of UPy telechelics based on low molecular weight oligomers such as, poly(ethylene-co-poly(propylene oxide)) (PEO−PPO),[6] poly(ethylene-co-butylene) (PEB),[9,10] polytetrahydrofuran (PTHF),[9] polycarbonates (PC)[6,11] and polyesters[6,12] have been prepared, and their properties are found to vary depending on different polymer backbone. More recently, the

UPy-NCO approach was employed by Delgado and co-workers in the preparation of UPy-poly(lactide)-b-PBd-b-poly(lactide)-UPy.[13]

Enhanced properties of SPs resulting from UPy telechelics are, in general, attributed to the linear chain extension resulting to very high molecular weight polymers.[6] Recent studies showed the importance of additional secondary interactions due to urethane or urea linkers and the formation of UPy aggregation contributing to the properties of SPs.[10,14] Our broader focus is to understand and compare the effect of polymer polarity and chain-dynamics on the UPy hydrogen-bonded polybutadiene (PBd) with acrylic and other polymers. However, the synthesis of SPs using UPy-functionalized telechelics has a prerequisite that the precursor polymer should have a specific chain end functionality (hydroxyl, or amine, or carboxylic). The attachment of UPy synthon becomes problematic for polymers that are difficult to synthesize, or which are not commercially available, with the above-

Scheme 1. Synthesis of UPy Telechelics of PS, P*n*BA, and PBd by Combination of ATRP and CuAAC Click Reactions
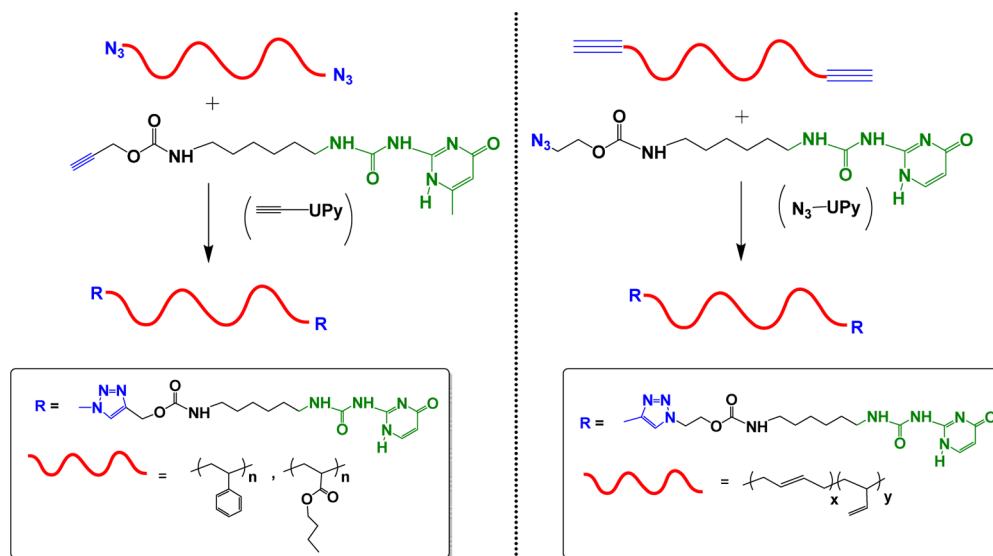
mentioned chain end groups. These polymers include, telechelic poly(alkyl) acrylates, poly(alky) methacrylates, and polystyrenic derivatives.

Synthesis of acrylic and styrenic based hydroxyl telechelics by anionic polymerization requires protected initiator, end-capping with ethylene oxide and deprotection. Moreover the conversion of hydroxyl functionality into UPy using isocyanate functionalized UPy (UPy-NCO) is complicated due to its high sensitivity towards polar impurities such as alcohol and water, which are difficult to remove from precipitated polymers. In the literature, excess amount of UPy-NCO has been used to drive the reaction and to improve the functionalization efficiency.[6,13] Although the controlled radical polymerization techniques can produce hydroxyl telechelics,[15−17] the transformation of hydroxyl telechelics into UPy telechelic still requires dry reaction condition. Moreover, these reactions often lead to incomplete UPy chain end modifications ($f < 2$) resulting to chains without UPy groups and broad polydispersity index.[18]

On the other hand, using atom-transfer radical polymerization (ATRP), it is possible to prepare monochelic ω-bromide, or telechelic α,ω-bis-bromide functionalized polymers from monofunctional or bifunctional initiators, respectively. The α,ω-bis-bromide end groups of the telechelics can be easily transformed into azide, which make them ideal candidates for the copper(I) catalyzed alkyne−azide (2 + 3) Huisgen cycloaddition (CuAAC) reaction.[19−26]

Herein, we have used a combination of ATRP and CuAAC click chemistry for the synthesis of telechelic oligomers functionalized with UPy (Scheme 1). Three different oligomers, with a similar molar mass (<3.0 kg/mol), were targeted to examine the effect of T_gs and the polarity characteristics on the hydrogen bonding association. These oligomers include telechelic polybutadiene (low T_g = −36 °C, nonpolar), P*n*BA (low T_g = −37 °C, polar), and PS (high T_g = 60 °C, nonpolar).

■ EXPERIMENTAL SECTION

Materials. The reagents CuBr (**I**), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA), tetrahydrofuran (THF, HPLC grade), chloroform (HPLC grade), *n*-hexane, methanol, 2-bromoethanol, propargyl alcohol, propargyl bromide, sodium hydride (60%), sodium azide, dimethylformamide (DMF), *n*-butyl acrylate, styrene, silica gel (230−400 mesh), 2-amino-4-hydroxyl-6-methylpyrimidine (6-Me-

Iso), neutral aluminum oxide, diethyl meso-2,5-dibromoadipate (DEBAD), calcium hydride, sodium sulfate, and dibutyltin dilaurate (DBDTL) were purchased from Aldrich. Hydroxyl-terminated polybutadiene (M_n = 2400 g/mol, 57% 1,2-vinyl) was kindly donated by Cray Valley. Deuterated chloroform was purchased from Cambridge isotopes laboratories Inc. Monomers were passed through neutral alumina column to remove the inhibitor. Deionized water (DI) was used wherever applied. All other chemicals were used as received unless stated otherwise. All reactions were done under inert condition by using a combination of high vacuum technique and N_2 atmosphere.

Characterization. ^{1}H NMR spectra were recorded on Varian Mercury Vx 300 spectrometer at 300 MHz. The samples were prepared in CDCl$_3$. IR analysis was performed on a Nicolet IS 10 FTI −ATR spectrometer and data were analyzed using OMNIC software. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined using size exclusion chromatography (SEC) equipped with Knauer's K-501 HPLC pump, K-2301 RI detector, K-2501 UV detector, and with a set of two columns; Polymer Standards Services, SDV-gel, 60 cm length (5 μm) 100 Å and a linear 10^2−10^6 Å. Tetrahydrofuran (THF) with toluene as a solvent flow marker was used as an eluent at a flow rate of 1.0 mL/ min, and the SEC was calibrated using polystyrene (PS) standards obtained from Pressure Chemicals (Pittsburgh, PA). The $M_{n,SEC}$ of PBd was obtained against calibrated PS standards and corrected by multiplying with the correction coefficient of 0.50, a value typically used for PBd with 1,2-vinyl contents less than 10%.[27] However, Grubbs and co-workers reported that the $M_{n,NMR}$ matches with $M_{n,SEC}$ obtained with 0.50 as correction factor for ~90% *trans*-1,4 PBd.[28] Thus, we used 0.50 as the correction factor for the synthesized PBd, which has a higher (57%) 1,2-vinyl content, owing to a close agreement observed between the $M_{n,SEC}$ and $M_{n,NMR}$. The molecular weight of PBA is reported as apparent and relative to PS calibration. Thermogravimetry analysis (TGA) was performed using a TA Q-50 instrument (25 to 1000 °C), with a heating rate of 10 °C/min under nitrogen atmosphere.

Atomic force microscopy (AFM) was performed with a Nanoscope IIIa Microscope with Multimode Controller (Veeco Instrument) at ambient temperature. Drop cast films were prepared on freshly prepared mica using a sample concentration of 1 mg/mL in chloroform; and films were annealed for 24 h at room temperature. The tapping mode was employed with an antimony-doped Si tip (radius <10 nm) at a line scanning frequency of 1 Hz.

Differential scanning calorimetry (DSC) analysis was performed with a TA-Q1000 and TA Q-2000 instrument from −90 to 150 °C at a scan rate of 10 °C/min. Three repeated heating and cooling scans were run with a 5 min isotherm at −90 °C. Solution viscosity in

toluene was measured by an automatic viscometer using a Schott Instruments AVS 370 and a type 531-10 viscometer (0.64 mm capillary with $K = 0.01$).

Rheological measurements of PBd-UPy were performed on an AR2000ex rheometer (TA Instruments) with 25 mm disposable parallel plates and an environmental testing chamber (ETC). Nitrogen was used the gas source of ETC to prevent sample degradation at high temperature. Both small amplitude oscillatory shear and creep measurements were used to evaluate the viscoelastic properties of the samples.

Dynamic mechanical spectra were recorded on a TA 800 dynamic mechanical analyzer. A small rectangular bar of the polymer (thin films were prepared from melt), size approximately $2 \times 5 \times 10$ mm were subjected to a sinusoidal deformation at a constant frequency, using the extension clamp method. Measurements were carried out at a frequency of 1 Hz and a heating rate of 3 °C/min. The amplitude of the sinusoidal deformation was kept the same (15 μm) and the static force 10% more than the dynamic force in order to ensure a good contact between the sample and the probe.

Synthesis of Functional UPy Tags. *NCO-UPy.* UPy-NCO synthon was synthesized by following the reported procedure.[6] In a typical experiment, 15 g of 6-methyl isocytosine was added into a 250 mL round-bottom flask and kept under high vacuum at 110 °C. After 4 h the flask was cooled to room temperature, filled with nitrogen, and 1,6-HDI was added under nitrogen. The reaction was kept under stirring in an oil bath at 110 °C. After 20 h, the flask was cooled to room temperature and the product was isolated by precipitation in 1L hexane. UPy-synthon was obtained as while solid and thoroughly washed with hexane. Yield: 34 g (96.8%). FT-IR (ATR): v 1520, 1572, 1664, 1697, 2279, 2931 cm^{-1}.

Propargyl-UPy (UPy-Pg). A 10 g (34 mmol) sample of NCO-UPy synthon was reacted with 10 g (178 mmol) of propargyl alcohol in 200 mL of dry chloroform at 70 °C for 5–6 h in the presence of 100 mg of DBDTL. The reaction was monitored using IR until the peak at 2279 cm^{-1} (-NCO group) disappeared completely. After the reaction (6 h), the Pg-UPy was recovered by precipitation in 1 L of hexane. The product was washed with excess hexane and dried at 50 °C under vacuum for 24 h. Yield: 7.5 g (62.9%), ^{1}H NMR (300 MHz, CDCl$_3$): (δ, ppm) 13.13 (s, 1H, CH_3CNH), 11.86 (s, 1H, $-CH_2NH(C=O)$ NH), 10.12 (s, 1H, $-CH_2NH(C=O)NH$), 5.88 (s, 1H, $-CH=$ CCH_3), 5.26 (s, 1H, $-NH-COO-$, urethane group), 4.67 (s, 2H, $-COO-CH_2-$, propargyl group), 3.1–3.3 (m, 4H, $NH(C=O)$ $NHCH_2 + -CH_2NHCO$), 2.45 (s, 1H, $-CH_2-C\equiv CH$, 2.23 (s, 3H, $CH_3C=CH$), 1.5–1.6 (m, 4H, $-NCH_2CH_2CH_2CH_2-CH_2N-$), 1.36 (m, $-NCH_2CH_2CH_2CH_2CH_2-CH_2N-$). IR (ATR): v 1526, 1574, 1660, 1706, 2110 ($-C\equiv CH$), 2854, 2931, 3205 cm^{-1}.

Azido-UPy (UPy-N$_3$). In a first step, 10 g (34 mmol) of NCO-UPy synthon was reacted with 40 g (320 mmol) of 2-bromo ethanol in 200 mL of dry chloroform at 70 °C in the presence of a catalytic amount of DBDTL (0.100 g). The reaction was monitored by IR until all the $-NCO$ groups were consumed. The bromoethanol adduct of UPy was recovered by precipitation in 1L of hexane and washed and dried at 50 °C under vacuum for 24 h. Yield: 11 g, 77.3%. ^{1}H NMR (300 MHz, CDCl$_3$): (δ, ppm) 13.11 (s, 1H, CH_3CNH), 11.85 (s, 1H, $-CH_2NH(C=O)NH$), 10.12 (s, 1H, $-CH_2NH(C=O)NH$), 5.85 (s, 1H, $-CH=CCH_3$), 5.13 (bs, 1H, $-NH-COO-$, urethane group), 4.35 (m, 2H, $-NHCOO-CH_2-CH_2Br$), 3.50 (m, 2H, $-NHCOO-$ CH_2-CH_2Br) 3.1–3.3 (m, 4H, $NH(C=O)$ $NHCH_2 +$ $-CH_2NHCO$), 2.22 (s, 3H, $CH_3C=CH$), 1.5–1.6 (m, 4H, $-NCH_2CH_2CH_2CH_2CH_2-CH_2N-$), 1.36 (m, $-NCH_2CH_2CH_2CH_2CH_2CH_2N-$).

Subsequently, the bromoethanol UPy adduct, 5.5 g (13.3 mmol) was dissolved in 100 mL of DMF and reacted with 3 g (46 mmol) of sodium azide at 25 °C for 24 h. The product, azido-UPy was recovered by precipitation in deionized water, washed with excess water to remove traces of DMF, and dried at 50 °C under vacuum for 24 h. Yield: 4.5 g (90.0%), ^{1}HNMR (300 MHz, CDCl$_3$): (δ, ppm) 13.11 (s, 1H, CH_3CNH), 11.83 (s, 1H, $-CH_2NH(C=O)NH$), 10.12 (s, 1H, $-CH_2NH(C=O)NH$), 5.83 (s, 1H, $-CH=CCH_3$), 5.14 (bs, 1H, $-NH-COO-$, urethane group), 4.21 (m, 2H, $-NHCOO-CH_2-$

CH_2N_3), 3.43 (m, 2H, $-NHCOO-CH_2-CH_2N_3$) 3.1–3.3 (m, 4H, $NH(C=O)$ $NHCH_2 + -CH_2NHCO$), 2.22 (s, 3H, $CH_3C=CH$), 1.5–1.6 (m, 4H, $-NCH_2CH_2CH_2CH_2CH_2-CH_2N-$), 1.36 (m, $-NCH_2CH_2CH_2CH_2CH_2-CH_2N-$). IR (ATR): v 1521, 1582, 1665, 1697, 1741, 2095 (azide group), 2861, 2936, 3422 cm^{-1}.

Synthesis of Telechelic Functional Polymers. *α,ω-Bisbromopolystyrene (Br-PS-Br).* To a 100 mL clean flame-dried round-bottom flask equipped with side arm (and Teflon stopcock) for attachment to the vacuum line was added 56 mL of styrene (489 mmol), 6.90 g of DBEAD (1.912 mmol), 0.68 g of PMDETA (3.90 mmol), and 0.56 g of CuBr (**I**) (3.09 mmol). This reaction mixture was degassed three times by freeze–pump–thaw cycles and the flask was kept in an oil bath maintained at 110 °C. After 110 min, the polymerization was terminated by cooling the flask with liquid nitrogen. The reaction mixture was diluted in 100 mL of THF and precipitated in 600 mL of methanol. Recovered polymer was dried and dissolved in 500 mL of THF and passed through alumina column to remove the copper catalyst. The eluted polymer solution was concentrated using rotatory evaporator at 40 °C under reduced pressure. The Br-PS-Br sample was further dried in vacuum oven at 50 °C for 24 h. Yield: 77%, $M_{n,th}$ = 2360 g/mol, $M_{n,GPC}$/ = 2400 g/mol, PDI = 1.13, and $M_{n\ NMR}$ = 2700 g/mol. ^{1}H NMR: δ, ppm, 0.9–1.9 (aliphatic protons, and $-COOCH_2-CH_3$), 3.6–3.9 ($-COOCH_2-$), 4.4 ($-PhCHBr$), 6.3–7.4 (Ar(H)). IR (ATR): v 1451, 1493, 1600, 1728, 2923, 3025 cm^{-1}

α,ω-Bisazidopolystyrene (N$_3$-PS-N$_3$). A 14 g sample of Br-PS-Br (11.66 mmol of Br) was dissolved in 100 mL of DMF under N$_2$ and reacted with 4.0 g (62.6 mmol) of sodium azide at 25 °C for 24 h. The reaction was monitored by ^{1}H NMR and IR. After a 100% conversion of bromide, the polymer was precipitated in excess water and filtered over buchnner funnel. The polymer was dissolved in chloroform, washed with water, dried over sodium sulfate, and the chloroform was removed using rotatory evaporator to give α,ω-azido terminated polystyrene. Yield: 13.5 g, (96.3%), $M_{n,th}$ = 2290 g/mol, $M_{n,GPC}$ = 2500 g/mol, PDI = 1.11, and $M_{n,NMR}$ = 2300 g/mol. ^{1}H NMR, δ, ppm, 0.9–1.9 (aliphatic protons, and $-COOCH_2-CH_3$), 3.6–3.9 ($-COOCH_2-$, and $-PhCHN_3$), 6.3–7.3 (Ar(H)). IR (ATR): v 1452, 1493, 1601, 1728, 2095 ($-$azide group), 2849, 2924, 3025 cm^{-1}

α,ω-Bisbromopoly(n-butyl acrylate) (Br-PnBA-Br). To a 100 mL clean flame-dried round-bottom flask, equipped with side arm (and Teflon stopcock) for attachment to the vacuum line, was added 60 mL of n-butyl acrylate (344.5 mmol), 7.0 g of DBEAD (1.944 mmol), 0.68 g of PMDETA (3.90 mmol), and 0.56 g of CuBr (**I**) (3.90 mmol). This reaction mixture was degassed three times by freeze–pump–thaw cycles, and the flask was kept in an oil bath maintained at 70 °C (it is advised to secure the rubber septum tightly by using copper wire, otherwise, due to a large vapor pressure, the integrity of the reactor may be lost). After 60 min the polymerization was terminated by cooling the flask with liquid nitrogen. The reaction mixture was dissolved in 500 mL of THF and passed through a column containing neutral alumina to remove the copper catalyst. The eluted solution was concentrated using rotatory evaporator at 50 °C under reduced pressure to remove the solvent and the residual monomer. Owing to the low molecular weight of the polymer and its good solubility in the methanol, the precipitation was avoided. Yield: 90%, $M_{n,th}$ = 2800 g/mol, $M_{n,GPC}$ = 3400 g/mol, PDI = 1.38. ^{1}H NMR: δ, ppm, 0.93 ($-COOCH_2-CH_2-CH_2-CH_3$), 1.37 ($-COOCH_2-CH_2-CH_2-$ CH_3) 1.57 ($-COOCH_2-CH_2-CH_2-CH_3$), 1.9–2.27 ($-CH$, and backbone proton), 4.04 ($-COOCH_2-CH_2-CH_2-CH_3$). IR (ATR): v 1454, 1729, 2873, 2933, 2958, cm^{-1}.

α,ω-Bisazidopoly(n-butyl acrylate) (N$_3$-PnBA-N$_3$). A 25 g sample of Br-PnBA-Br (14.7 mmol) was dissolved in 150 mL of DMF and reacted with 5 g of sodium azide (154 mmol) at 25 °C. After 24 h, the reaction mixture was precipitated in water, extracted in chloroform, dried over sodium sulfate and the chloroform was removed over rotatory evaporator to obtain 23.5 g of N$_3$-PnBA-N$_3$. The product was analyzed using FT-IR to determine the chain end functionality and the functionalization efficiency. The ratio of azide peak to the carbonyl peak was used to calculate the percent of chain end functionalization. Yield: 94%; $M_{n,th}$ = 2730 g/mol; $M_{n,GPC}$ = 3660 g/mol; PDI = 1.35. ^{1}H NMR: δ, ppm, 0.93 ($-COOCH_2-CH_2-CH_2-CH_3$), 1.37-

(−COOCH$_2$−CH$_2$−CH$_2$−CH$_3$), 1.57 (−COOCH$_2$−CH$_2$-CH$_2$−CH$_3$), 1.9−2.27 (−CH, and backbone proton), 4.04 (−COOCH$_2$−CH$_2$−CH$_2$−CH$_3$). IR (ATR): v 1452, 1729, 2109, 2736, 2873, 2934, 2959, cm^{-1}.

α, ω-Bispropargylpolybutadiene (PgO-PBd-OPg). In a typical experiment, a two neck round-bottom flask equipped with a stopcock and a ground joint connectivity to the high vacuum line, 50 g (42 mmol) (2400 g/mol) of α,ω-bishydroxyl-terminated polybutadiene was charged and dried under high vacuum at 70−80 °C for 2 h. After drying the polymer, ∼250 mL of THF was distilled in to it, from the vacuum line under reduced pressure using liquid nitrogen as coolant. After dissolution of the polymer at room temperature, 8.34 g of sodium hydride (209 mmol) and 7.0 g of 18-crown-6 ether (26 mmol) was added quickly, through the second neck under N$_2$ flow, and closed with a rubber septum. Immediate hydrogen gas liberation was seen. The reaction mixture was stirred for 1/2 h, while the flask was opened to the vacuum line slightly to remove the liberated hydrogen gas. After observing a complete cessation of hydrogen gas evolution, the flask was removed from the vacuum line and kept under N$_2$ atmosphere. Then, 18.6 mL of propargyl bromide (209 mmol) (80% in toluene) was added dropwise. Although the reaction goes to completion within ∼24−36 h, 18-crown-6 ether (which was not a perfect match for Na$^+$), was used to promote the reaction. The reaction was monitored by ^{1}H NMR. After 48 h, the reaction solution was left standing overnight to precipitate the salt, then the polymer solution was decanted and precipitated in to a large excess of acidic methanol (250 mmol of dilute HCl (6 M HCL) containing 1% BHT as antioxidant. The recovered dark-brown polymer was further purified by dissolving in chloroform and passing through a short silica column to remove any inorganic solids or suspended impurities. The chloroform was removed using rotatory evaporator to obtain 41 g of brown red colored viscous liquid of PgO-PBd-OPg. Yield: ∼ 80%. $M_{n,th}$ = 2580 g/mol. $M_{n,GPC}$/0.50 = 2730 g/mol; PDI = 1.13 and $M_{n,NMR}$ = 2500 g/mol. ^{1}H NMR: δ, ppm, 1.06−1.58 (aliphatic backbone from 1,2-vinyl), 1.80−2.02 (aliphatic backbone from 1,4-*cis*, and 1,4-*trans*), 2.38 (propargyl −CH$_2$−C≡CH), 3.50 (PBd−CH$_2$−CH$_2$−O−Pg), 4.09−4.12 (PBd−CH$_2$−CH$_2$−O−CH$_2$−C≡CH), 4.95 (1,2-vinyl =CH$_2$), 5.33−5.58 (1,4-*cis* and 1,4-*trans*, and 1,2-vinyl =CH). IR (ATR): v 1439, 1639, 2844, 2814, 3073 cm^{-1}.

α,ω-Bis-UPy Polybutadiene (UPy-PBd-UPy). Telechelic α,ω-bishydroxyl polybutadiene (HO-PBd-OH) was reacted with UPy-NCO synthon by using the reported procedure.[6]

UPy Functionalization of Telechelic Polymers Using CuAAC Click Chemistry. In a typical experiment, an equimolar amount of polymer and UPy derivatives with azide or alkyne functionality was taken in an appropriate round-bottom flask depending on the amount for reaction. The polymer and UPy derivative was dissolved in DMF or toluene and the required amount of PMDETA and CuBr (**I**) was added. The reaction mixture was stirred at room temperature for 24 h. In general, CuAAC requires a catalytic amount of copper salt (∼10%); however, owing to the coordination of the catalyst with UPy group and triazole, the reaction was performed with much higher concentration of copper salt.[29] A typical example is given below wherein the "*polymer*" represents telechelic oligomers (PS, P*n*BA, and PBd) used in this study.

Synthesis of UPy-Tz-polymer-Tz-UPy. In a 250 mL round-bottom flask, a required amount of N$_3$-polymer-N$_3$ or PgO-polymer-OPg (5.83 mmol) was dissolved in 100 mL of DMF for PS and P*n*BA and toluene for PBd. After obtaining a clear solution, an equivalent amount of Pg-UPy or N$_3$-UPy (5.87 mmol), depending on the functionality of telechelic polymers, CuBr (I) (5.87 mmol), and PMDETA (0.2 or 1 equiv catalyst-ligand complex) were added into the solution. The reaction mixture was purged with N$_2$ and the dark brownish greenish-brown colored reaction mass was stirred under N$_2$ for 24 h at RT. Reaction was monitored by IR (ATR) until the total disappearance of azide peak of either polymer or UPy-N$_3$. Then the product UPy-Tz-polymer-Tz-UPy was precipitated in a large amount of methanol for PS and PBd and water for P*n*BA. The UPy-Tz-polymer-Tz-UPys were isolated and dissolved in 500 mL of chloroform and washed with excess water until a neutral pH, dried over sodium sulfate and passed

through a short alumina column to remove the residual copper salt. The solvent was evaporated using rotatory evaporator to give the desired UPy functionalized telechelic polymers as white solids.

UPy-Tz-PS-Tz-UPy. Yield: ∼72%; $M_{n,th}$ = 2985 g/mol; $M_{n,GPC}$ = 2750 g/mol; PDI = 1.10; $M_{n\ NMR}$ = 2920 g/mol. ^{1}H NMR: δ, ppm (chain end group integration are multiplied by two), 13.09 (s, 2H, CH$_3$CNH), 11.84 (s, 2H, −CH$_2$NH(C=O)NH), 10.12 (s, 2H, −CH$_2$NH(C=O)NH), 6.33−7.33 (124H, Ar (H), 5.85 (s, 2H, −CH=CCH$_3$), 4.9−5.3 (8H), −CH (2H) (triazole ring), urethane −NH (2H), and −CH−Tz−CH$_2$− (4H)), 3.6−3.9 (−CH−Tz and −COOCH$_2$−CH$_3$). 3.1−3.3 (m, 8H, NH(C=O) NHCH$_2$ + −CH$_2$NHCO), 2.12 (s, 6H, CH$_3$C=CH), 1.5−1.6(m, 8H−N C H$_2$ *C H*$_2$ *C H*$_2$ *C H*$_2$ *C H*$_2$ − C H$_2$N−), 1.36 (8H m, −NCH$_2$CH$_2$*CH$_2$CH$_2$*CH$_2$CH$_2$N−) and aliphatic PS backbone. IR (ATR): v 1521, 1582, 1660, 1698 1724, 2853 3081 cm^{-1}.

UPy-Tz-PnBA-Tz-UPy. Yield: ∼67%; $M_{n,th}$ = 3430 g/mol,; $M_{n,GPC}$ = 3200 g/mol; PDI = 1.40; $M_{n\ NMR}$ = 5450 g/mol. ^{1}H NMR: δ, ppm (chain end group integration are multiplied by two), 13.09 (s, 2H, CH$_3$CNH), 11.84 (s, 2H, −CH$_2$NH(C=O)NH), 10.12 (s, 2H, −CH$_2$NH(C=O)NH), 7.33 (2H, triazole ring −CH), 5.85 (s, 2H, −CH=CCH$_3$), 5.16−5.25 (bs, 6H, (−NH−COO−, urethane group-(2H), and −OCH−Tz (4H)), 4.04 (−COOCH$_2$−CH$_2$−CH$_2$−CH$_3$ (50H)), 3.1−3.3 (m, 8H, NH(C=O) NHCH$_2$ + −CH$_2$NHCO), 0.93 (−COOCH$_2$−CH$_2$−CH$_2$−CH$_3$ (37H)). IR (ATR): v 1525, 1587, 1662, 1729, 2873 2958, 3216 cm^{-1}.

UPy-Tz-PBd-Tz-UPy. Yield: ∼79%; $M_{n,th}$ = 3340 g/mol; $M_{n,GPC}$ /0.50 = 2900 g/mol; PDI = 1.28; $M_{n\ NMR}$ = 3160 g/mol. ^{1}H NMR: δ, ppm (chain end group integration are multiplied by two), 13.09 (s, 2H, CH$_3$CNH), 11.84 (s, 2H, −CH$_2$NH(C=O)NH), 10.12 (s, 2H, −CH$_2$NH(C=O)NH), 7.56 (2H, triazole ring −CH), 5.80 (s, 2H, −CH=CCH$_3$), 5.33−5.58 ((54 H) 1,4-*cis* and 1,4-*trans*, and 1,2-vinyl =CH) 4.95 (1,2-vinyl =CH$_2$) (57H) and (−NH−COO−, urethane group (2H), 4.57 (8H), Tz-CH$_2$-CH$_2$−urethane), 4.44 ((4H) −O−CH$_2$−Tz), 3.50 (4H), PBd−CH$_2$−CH$_2$−O−Tz), 3.13−3.25 (m, 8H, NH(C=O)NHCH$_2$ + −CH$_2$NHCO), 2.12 (s, 6H, CH$_3$C=CH),1.80−2.02 (aliphatic backbone from 1,4-*cis*, and 1,4-*trans*)), 106−1.58 (aliphatic backbone from 1,2 vinyl). IR (ATR): v 1528, 1588, 1640,1664, 1698, 2846, 2916, 3141 cm^{-1}.

■ RESULTS AND DISCUSSION

In order to synthesize UPy-functionalized telechelic polymers with different linking chain, we prepared air and moisture stable UPy synthons with propargyl (Pg) and azido (N$_3$) functionalities and used for clicking with azido and propargyl telechelic
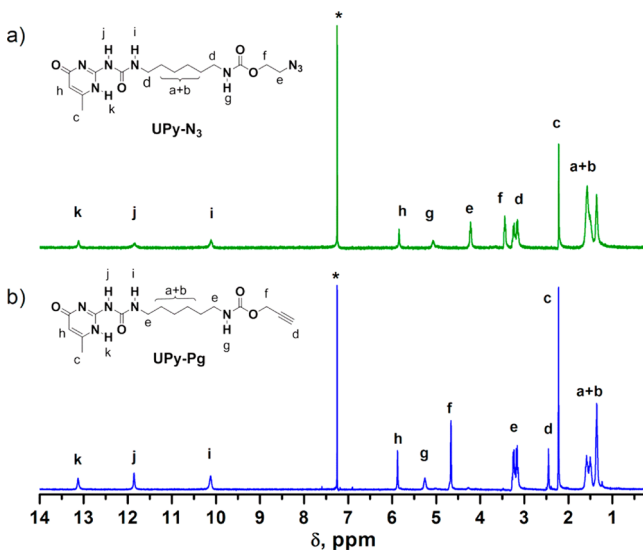
Figure 1. ^{1}H NMR spectra of (a) UPy-N$_3$ and (b) UPy-Pg. The star (∗) indicates residual protons of CDCl$_3$.

Scheme 2. Schematic Synthesis of UPy Telechelic Polybutadiene, with and without a Triazole Ring
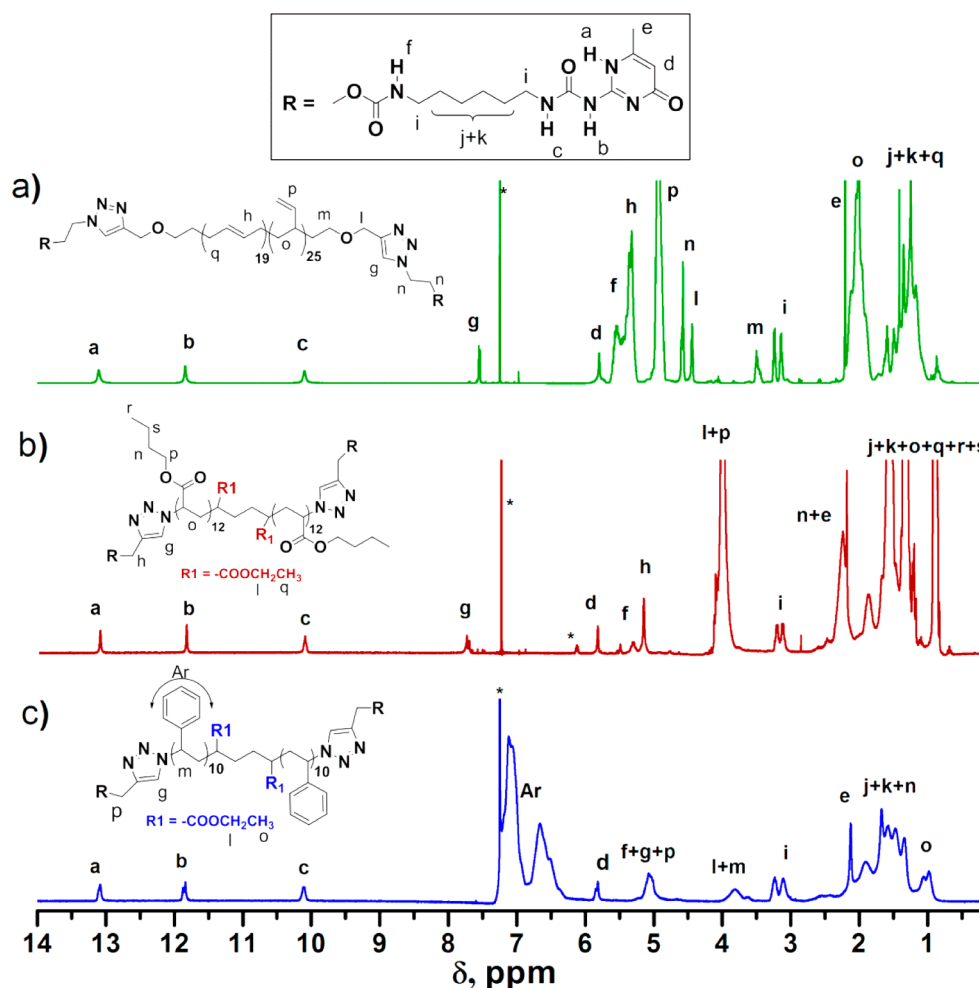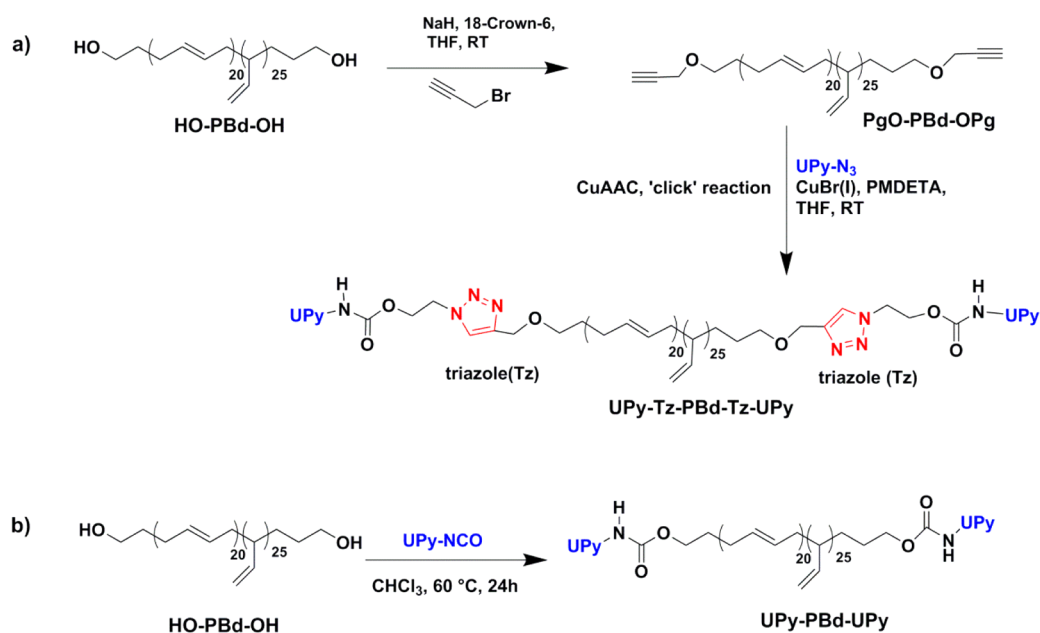
Figure 2. ^{1}H NMR spectra of UPy-telechelics prepared by CuAAC click reaction. (a) UPy-Tz-PBd-Tz-UPy, (b) UPy-Tz-PnBA-Tz-UPy, and (c) UPy-Tz- PS-Tz-UPy. The star (∗) indicates residual solvent CDCl$_3$.

oligomers, respectively to obtain UPy telechelic polymers (Scheme 1). Clickable UPy-Pg and UPy-N$_3$ synthons were

synthesized from UPy-NCO using an excess propargyl alcohol and 2-bromoethanol, respectively in the presence of dibutyltin

Table 1. Characterization UPy Telechelics Prepared by Combination of ATRP and CuAAC Click Reactions[a]

Polymers[a)]	M_n (kg/mol) of telechelics[b]			
	$M_{n,th}$[c]	$M_{n,NMR}$[d]	$M_{n,SEC}$[e]	M_w/M_n[e]
X-PS-X				
Br~~~Br	2.36	2.70	2.4	1.13
N₃~~~N₃	2.29	2.30	2.5	1.11
UPy–Tz~~~Tz–UPy	2.98	2.92	2.75	1.10
X-PnBA-X				
Br~~~Br	2.8	-	3.4	1.38
N₃~~~N₃	2.73	-	3.66	1.35
UPy–Tz~~~Tz–UPy	3.43	5.45	3.2	1.40
X-PBd-X				
HO~~~OH	2.0[f]	2.50	2.40	1.15
≡~~~≡	2.58	2.50	2.73	1.18
UPy–Tz~~~Tz–UPy	3.30	3.16	2.90	1.28
UPy~~~UPy	3.09	2.90	2.80	1.13

[a]Key: (a) Bulk ATRP of styrene and *n*-butyl acrylate were performed at 110 °C (for 1.8 h with 77% conversion) and 70 °C (for 1 h with 90% conversion), respectively, using difunctional initiator and telechelic hydroxyl functional PBd was obtained from Cray Valley with 57% 1,2 vinyl contents. (b) Conversion of end−group transformation is 100% based on NMR, the recovered yield is 80−90% in all cases, and reactions were performed over 24 h. (c) $M_{n,th}$ = (grams of monomer/mole of initiator) × conversion) + mol wt of chain-end functionality. (d) M_n calculated based on initiator or end group functionality (UPy, propargyl) from ^{1}H NMR in CDCl₃. (e) Determined from SEC. (f) Based on commercial specification.

dilaurate catalyst at 70 °C. Adduct of bromoethanol was converted to UPy-N₃ using sodium azide. The ^{1}H NMR of the products showed all the characteristic signals corresponding to UPy-Pg and UPy-N₃ (Figure 1). The transformation of −NCO group can be seen from the FT-IR spectra, which showed distinct vibration frequencies associated with −N₃ at 2095 cm⁻¹ and alkyne at 2110 cm⁻¹, for UPy-N₃ and UPy-Pg, respectively (Supporting Information, Figure S1).

α, ω-Bisazido telechelic PS and PnBA moieties were readily prepared by ATRP of styrene and *n*-butyl acrylate, respectively, and followed by treatment with sodium azide. On the other hand, propargyl end-functionalized PBd was prepared by etherification of hydroxyl-terminated PBd with propargyl bromide. The propargyl-functionalized telechelic PBd was reacted with UPy-N₃ to obtain UPy terminal PBd linked via triazole group (Scheme 2a). Also, hydroxyl terminated PBd was directly reacted with UPy-NCO to obtain UPy-PBd-UPy to evaluate the effect of triazole group on the UPy chain end association (Scheme 2b). Desired UPy telechelics were then prepared using click reaction in the presence of CuBr-PMDETA complex (Scheme 1). An excess of the catalyst complex (1:1 mol) was used in order to compensate

coordination of catalyst with UPy and triazole functionality of the product.

The end-group transformations of azido-PS and azido-PnBA and propargyl-PBd into UPy group are accompanied by changes in physical characteristics of the polymers. For low T_g polymers, UPy-Tz-PBd-Tz-UPy (T_g = −36 °C) and UPy-Tz-PnBA-Tz-UPy (T_g = −37 °C), the viscosity enhancement was significant and became semisolid compared to their liquid precursors, PgO-PBd-OPg, and N₃-PnBA-N₃, respectively. More dramatic changes in the physical properties were seen in low T_g and nonpolar polymeric systems. In the case of UPy-Tz-PBd-Tz-UPy, the sample turned into a transparent thermoplastic elastomer. Similarly, UPy-PBd-UPy is a colorless transparent thermoplastic solid and the precursor hydroxyl PBd is a viscous liquid. Whereas, high T_g, nonpolar, and low T_g polar polymers have significant increase in the glass transition temperatures without changes in the physical state. The results indicate that the presence of Tz group between UPy and polymer backbone has significant effect for PBd, a low T_g and nonpolar polymer.

Figure 2 shows the ^{1}H NMR spectra of the products with the characteristic downfield signals of UPy group (10.2, 11.9, and 13.2 ppm) and triazole −CH group. The efficiency of the end-
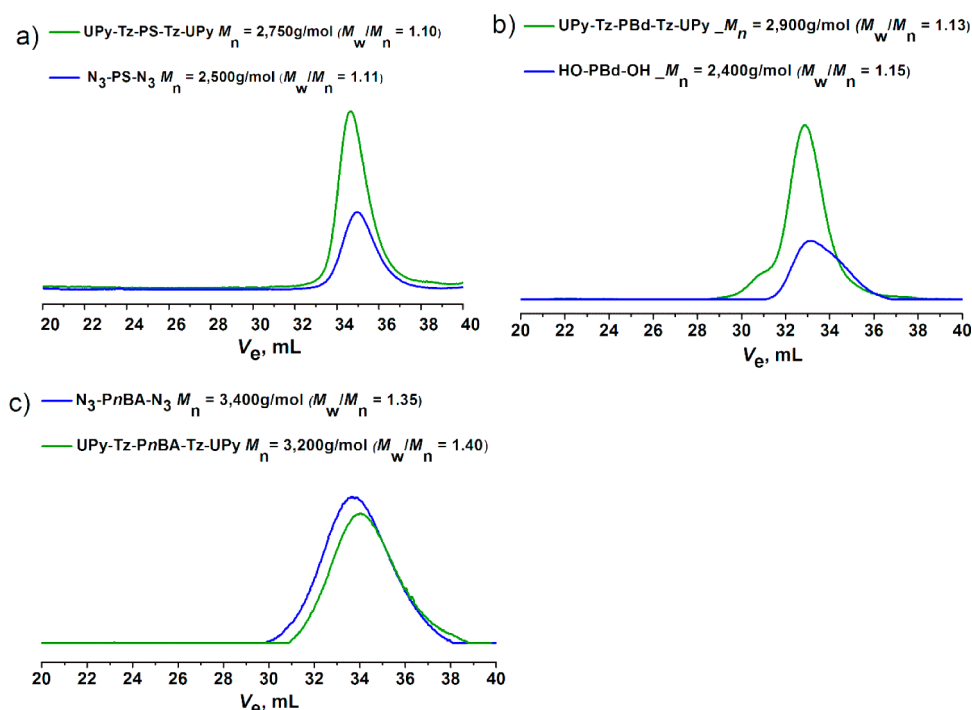
Figure 3. SEC eluograms of UPy telechelics prepared by CuAAC click reaction using RI detector. (a) UPy-Tz-PS-Tz-UPy-UPy, (b) UPy-Tz-PBd-Tz-UPy, and (c) UPy-Tz-P*n*BA-Tz-UPy, with all SEC sample concentrations being 1 mg/mL.
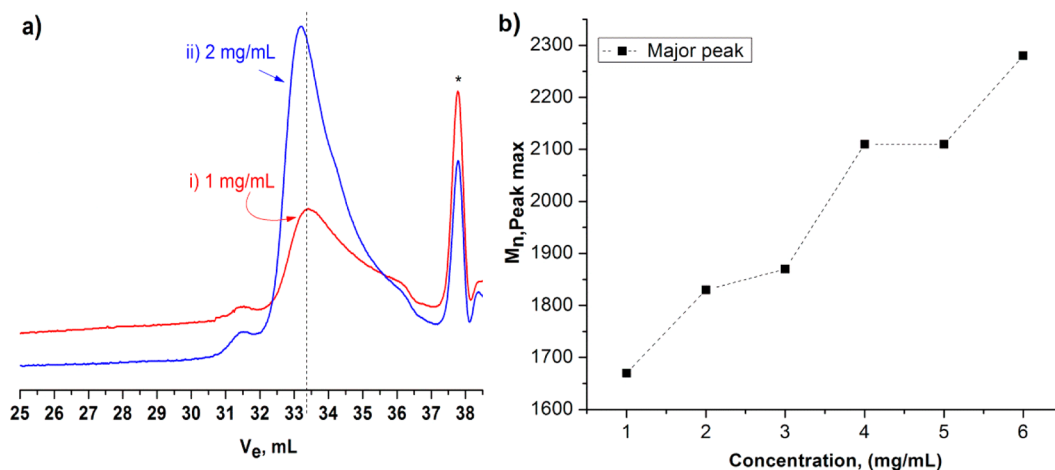
Figure 4. (a) SEC traces showing effect of concentration on the aggregation of UPy groups in UPy-Tz-PS-Tz-UPy (i) 1 mg/mL and (ii) 2 mg/mL and (b) a plot of peak-maximum molecular weight at different injection sample concentration with light scattering detector using d_n/d_c of 0.186.
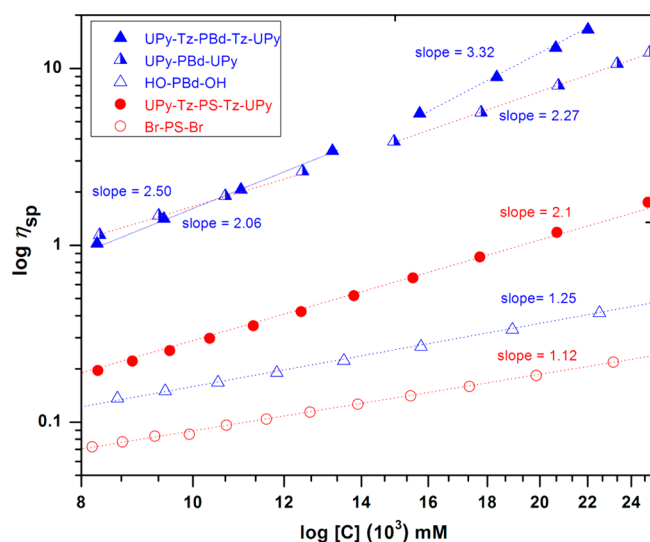
group transformation is also confirmed by the molecular weight determination by ^{1}H NMR and SEC as shown in Table 1. Propargyl and azide groups were totally absent in the IR spectrum of the polymer (Figure S2 and S3, Supporting Information); and the ratio of $M_{n,NMR}/M_{n,th}$ in all cases is close to unity indicating almost 100% functionality of these UPy telechelics.

Multiple Aggregation in SEC Elution Profile. SEC of UPy-Tz-PBd-Tz-UPy shows a small hump on the higher molecular weight $(2 \times M_p)$ side indicating the presence of dimers in THF solution (Figure 3b). Monotelechelic PBd–UPy samples also showed such a dimeric peak in SEC eluogram.[30] No such dimeric peaks were observed for PS and P*n*BA telechelic systems; however, when the UPy-Tz-PS-Tz-UPy was analyzed with a SEC equipped with the light scattering detector, it shows additional peaks corresponding to

the aggregation of UPy domains, which are dependent on the sample concentration in solution (Figures 3 and 4a). At very high concentrations (5 or 6 mg/mL), the elusion profile of the sample would also be influenced by the column overloading. However, the presence of UPy hydrogen-bonded association is evident as the peak-maximum molecular weight increases with increasing sample concentration in SEC (Figure 4b and Figure S4). Similar observations were reported by Wrue and co-workers[31] on telechelic UPy-PS-UPy prepared by a combination of ATRP and ATRC. No such observation was seen with UPy-P*n*BA-UPy, this was partly attributed to a weak hydrogen-bonding in the presence of polar ester pendants of the P*n*BA backbone and a broader molecular weight distribution of the sample.

Solution Viscosity. Solution viscosity of the triazole containing sample in toluene is much higher than the sample

Figure 5. Viscosity profile of UPy telechelics and the effect of triazole on UPy chain end association of UPy-Tz-PBd-Tz-UPy and UPy-Tz-PS-Tz-UPy.

Effect of Heating Rate and Aging on DSC Analysis of UPy Telechelics.

Each DSC run has at least three heating and cooling cycles with a heating rate of 5, 10, and 20 °C/min. After the first DSC run, the sample was aged at room temperature for a given time interval before rerunning it for the second and the third heating cycles. The DSC profile of PBd-UPy samples at a heating rate of 10 °C/min shows the presence of endothermic peak at ~63 °C for UPy-PBd-UPy and at ~78 °C for UPy-Tz-PBd-Tz-UPy suggesting the presence of aggregated UPy domains (Figure S6). The UPy-Tz-PBd-Tz-UPy showed a higher melting peak supporting the presence of additional hydrogen bonding interactions involving the triazole group in the UPy domain aggregation. Enthalpy values of endothermic peak decrease in second and third heating cycle. However, a time-dependent DSC analysis of these two samples further supports the participation of triazole affects the reassociation dynamics of supramolecular association as the UPy-Tz-PBd-Tz-UPy sample shows a complete recovery of the melting peak after 6 h, whereas the UPy-PBd-UPy shows only a partial recovery of 33% in 6 h as evident from the corresponding enthalpies of dissociation (Table 2). This was calculated by using first heating cycle, and values of second and third run were divided by the enthalpy value of first cycle.

Since the hydrogen-bonded UPy dimers are in equilibrium with aggregated domains, the heating rates alter the dynamics significantly. For the heating cycle at 20 °C/min, the endothermic peak recovery is very low for UPy-Tz-PBd-Tz-UPy, and the peak position shifts from 69.36 to 103.5 °C (Figure 6). For the sample without the Tz linker, the second and third heating cycles do not show any endothermic peak at all. Moreover, the peak recovery is very small for UPy-Tz-PBd-Tz-UPy (4.426%). This clearly indicates, the time required to regenerate the original volume of UPy aggregated domains is not sufficient for higher heating/cooling rate. Meijer and co-workers in their earlier work on UPy-Kraton-UPy reported an absence of such a melting peak in the second heating cycle (20 °C/min) and considered an absence of crystalline aggregates, and chain extension leading to formation of very high molecular weight polymer were the attributes for the thermoplastic elastomeric properties of UPy-Kraton-UPy.[6] However, the dynamics of linking chain in the present study is much higher due to low M_n, it may be possible that the presence of endothermic peak in relatively higher M_n (4100 g/mol) material, UPy-Kraton-UPy, could be absent on the experimental time scale since the time in between the subsequent heating and cooling cycles were not sufficient at the rate of 20 °C/min for the formation of UPy aggregates. However, recent work by Kautz and co-workers has shown the presence of a small endothermic peak at 69 °C in UPy-Kraton-UPy sample (DSC run at 10 °C/min ramping rate), which was attributed to an incomplete aggregation of lateral urethane group.[10] The sample with a lateral urea linking group has a melting point of 129 °C, due to nanophase aggregated fiber formation by one-dimensional staking of urea groups.

without the triazole linker (Figure 5). The double logarithmic plot of specific viscosity, η_{sp} vs concentration gave slope values of 2.27 and 3.32 for UPy-PBd-UPy and UPy-Tz-PBd-Tz-UPy, respectively in a high concentration region ([C] >18 mM). As per the predictions of Cate's model of the reversibly linked SPs, the viscosity plot for UPy-telechelics with linear chain extension should have a slope in the range of 3.5−3.7, though a different slope than this prediction was also reported in SP networks.[5,32] Furthermore, normal viscosity plots, η_{sp} vs [C] for PS and PBd SPs show two distinct regions supporting the UPy chain-end network-dynamics change very fast at higher concentration (overlap concentration) indicating the onset of entanglements (Figure S5). It is evident from the plot, the viscosity increases rapidly above ~15 mM and expected to show a much higher slope >3.7 at higher concentration ([C] > 25 mM). Interestingly, the onset for the entanglement concentration for both the samples is similar ([C] ~ 15 mM). This indicates the chain-end extension is primarily driven by UPy dimerization. At a higher concentration, a much higher slope of UPy-Tz-PBd-Tz-UPy clearly indicating participation of triazole group, which results in much stronger entanglement of the UPy chain-extended network. Also, the crossover concentration can be assumed as an overlap concentration for this sample.[33]

On the contrary, the viscosity profile of the UPy-Tz-PS-Tz-UPy sample shows a very minimal increase in comparison to its precursor. This may be related to a low R_h of PS compared to PBd and a much higher overlap concentration of low molecular weight PS. The sample of UPy-Tz-PnBA-Tz-UPy was not used for the viscosity study and it is expected to have a similar viscosity behavior like UPy-Tz-PS-Tz-UPy.
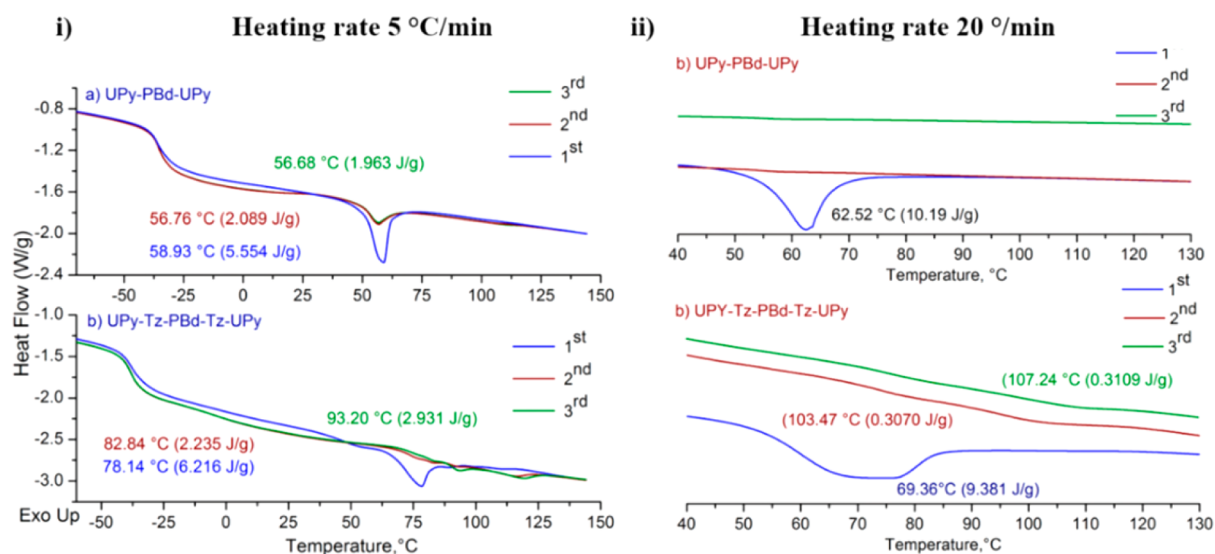
Table 2. DSC Analysis of UPy-PBd-UPy, Effect of Triazole on Hydrogen-Bonded Aggregation of UPy Groups

sample[a]	first run heating cycle		after 6 h aging		
	T_m (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)	% recovery[b]
UPy-Tz-PBd-Tz-UPy	77.95	12.46	76.19	12.67	100
UPy-PBd-UPy	63.21	15.32	59.42	4.987	33.0

[a]Analysis was performed at a heating/cooling rate of 10 °C. [b]Calculated based on the ΔH of the first heating cycle.

Figure 6. DSC profile of telechelic PBd UPy: (i) heating rate (5 °C), UPy-PBd-UPy (a) and UPy-Tz-PBd-Tz-UPy (b); (ii) heating rate 20 °C, UPy-PBd-UPy (a) and UPy-Tz-PBd-Tz-UPy (b).

Sample	D_{min} (nm)	D_{max} (nm)	D_{avg} (nm)
UPy-PBd-UPy	49	85	78.5
UPy-Tz-PBd-Tz-UPy	34	79	55.0
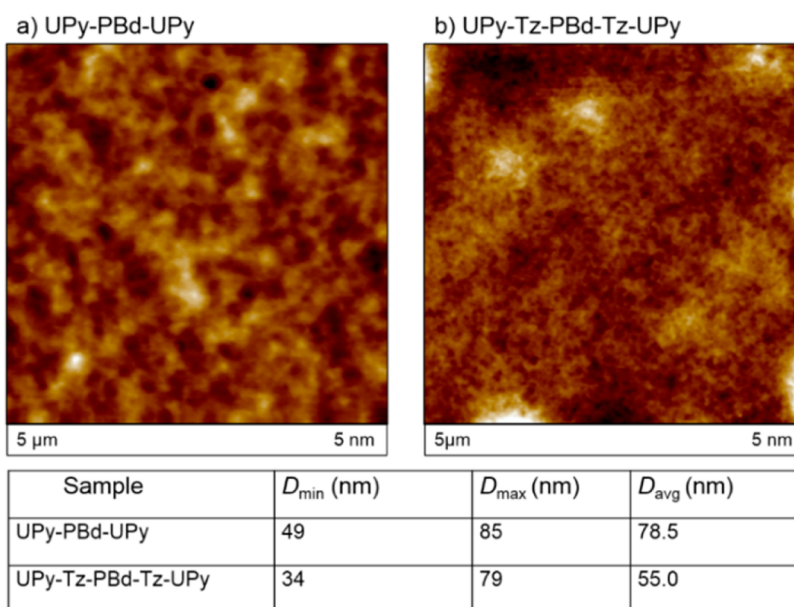
Figure 7. AFM phase images of UPy-PBd-UPy (a) and UPy-Tz-PBd-Tz-UPy (b), and size of aggregated domains.
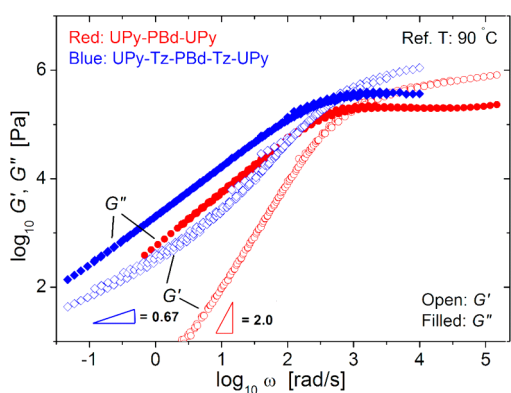

Figure 8. Complex viscosity master curves of UPy-Tz-PBd-Tz-UPy and UPy-PBd-UPy at reference temperature 90 °C.

The T_g values of UPy-Tz-PS-Tz-UPy and UPy-Tz-PnBA-Tz-UPy are in close agreement with the literature values considering their end-group modification (Figure S7)[29,34,35] Interestingly, there is no endothermic peak in high T_g and nonpolar PS sample attributable to the formation of UPy associated domains up to 150 °C. The polar PnBA system also has an absence of endothermic peak. The combined effect of triazole and UPy association appears to be weak in PnBA and PS systems. The polar ester pendants in PnBA system can compete with hydrogen bonding and diminish the UPy hydrogen bonding association.[36] In the case of PS linking chain, the motion of the chains is frozen below the T_g, which does not facilitate the growth of extended, and stronger hydrogen bonded domain formation. The hydrogen bonding in this case appears to be limited due to the nature of the polymer chain, especially in solid state. Nevertheless, the existence of
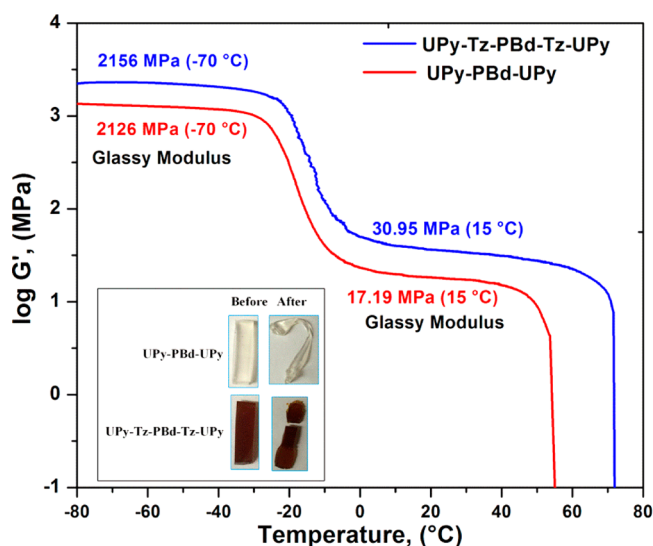
Figure 9. Temperature dependence of modulus for UPy-PBd-UPy and UPy-Tz-PBd-Tz-UPy.

UPy associated domain formation is evident in the solution too (Figure 5).

Thin-Film Surface Morphology. Participation of Tz in the UPy network was further supported by AFM analysis of the drop cast film of UPy-PBd-UPy and UPy-Tz-PBd-Tz-UPy. Both samples show a random network consisting of micellar aggregated domains indicative of UPy chain end associations. The formation of networks is more favorable at room temperature at which the experiments were performed. However, the sizes of the aggregated domains are smaller in the case of UPy-Tz-PBd-Tz-UPy (Figure 7). This indicates that the triazole takes part in the chain end association, thereby reducing the UPy micellar cluster sizes in solid-state morphology. It is worth mentioning here that the model studies carried out with the mixture of C6UPy (made from Me-Iso and hexyl isocyanate) and triazole compound (made from octyl azide and 1-hexyne) indicated only minute changes in ^{1}H NMR in diluted concentration ($\sim$5 mg/mL) and due to merging bands of functional groups, it is difficult to discern the triazole interaction in the FT-IR spectra. Moreover, ^{1}H NMR spectrum in CDCl$_3$ shows characteristic UPy peaks indicating triazole does not disturb the dimerization of UPy in solution. A comparison of the domain sizes indicates the participation of triazole group leading to the formation of smaller domains with uniform distribution across the PBd matrix. However, a high T_m and a modulus (see below, Figure 8) of triazole containing sample indicate that the net strength of the resulting cluster network is higher than UPy-PBd-UPy, probably due to a positive interference either by the hydrogen bonding of the triazole group or steric hindrance around the UPy dimeric clusters.

Complex Viscosity and Modulus of UPy Telechelics. In order to evaluate the effect of Tz on the UPy group association, both the UPy-PBd-UPy and UPy-Tz-PBd-Tz-UPy samples were analyzed by rheology using 90 °C as reference temperature (Figure 8). The complex modulus master curves show distinct differences for the UPy-PBd-UPy and UPy-Tz-PBd-Tz-UPy. A higher complex modulus was observed for UPy-Tz-PBd-Tz-UPy compared to the sample without Tz linking group.

Moreover, the low-frequency slope 0.67 also deviates from 2 for G' clearly suggesting that the system is not able to completely relax its mechanical stress at low frequency due to network formation. Thus, we believe that the interference of Tz in UPy aggregation domains promotes larger network formation with smaller clusters. The effect of Tz group on the property enhancement was also seen in the DMTA analysis of the thin films of these samples (Figure 9). Both the glassy ($\Delta G = 400$ MPa) and rubbery ($\Delta G = 13$ MPa) modulus values of the triazole containing sample are much higher than the sample without the Tz. The value of the rubbery modulus is almost twice for the UPy-Tz-PBd-Tz-UPy. As seen earlier from the DSC analysis, the sample UPy-Tz-PBd-Tz-UPy has a higher T_m, which was further confirmed by the DMTA plot. Thin film of UPy-Tz-PBd-Tz-UPy with Tz linker retains its strength up to $\sim$70 °C and undergoes brittle-break at $\sim$72 °C. Whereas the UPy-PBd-UPy film starts yielding at $\sim$54 °C and finally breaks at $\sim$57 °C(Figure 9, inset). Therefore, the preliminary rheology and DMTA studies strongly support the participation of the triazole ring in the hydrogen bonded aggregates of UPy dimers, which changes the size and distribution of UPy aggregated domains as confirmed by AFM images. More detailed studies on the rheology of the UPy telechelics are currently under progress in our lab and will be published elsewhere.

■ CONCLUSIONS

In this report, a modular approach for the synthesis of UPy telechelics by combination of ATRP and click reaction has been introduced. Using this approach, three different telechelic polymers of PS, PBd, and PnBA have been synthesized and characterized. The presence of triazole group positively interferes with the hydrogen bonding of UPy domains. Solution, melt and solid-state characterizations of triazole-containing UPy telechelics indicate that the resulting SPs exhibit higher viscosity and modulus. As ATRP allows preparation of various molecular architectures using block copolymers containing suitable pendant or side groups, which can be directly used for clicking UPy moiety, this combination of ATRP and click approach would be a very useful synthetic tool. Also, selection of propargyl amine and hydroxyl amine will provide an easy path for UPy telechelics with urea linkage through the approach described herein.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

FT-IR spectra of UPy-NCO, Pg-UPy, and UPy-N$_3$ synthons and UPy-Tz-PBd-Tz-UPy, SEC traces of UPy-Tz-PS-Tz-UPy at different concentrations, viscosity plots of UPy-Tz-PBd-Tz-UPy and UPy-Tz-PS-Tz-UPy, DSC of telechelic PBd-UPy and PS-UPy systems with and without Tz linker, and glass transition temperatures of the three polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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