

Supporting Information for

A Novel Polytriazole-based Organogel Formed by the Effects of Copper Ions

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EXPERIMENTAL DETAILS *Raw Materials*

4,4'-diamino diphenylmethane, sodium nitrite, sodium azide, DMF and DMSO (all of chemical purity), HCl, EDTA, triphenylphosphine and copper bromide (CuBr₂) (all of analytical reagent grade) were purchased from Sinopharm Chemical Reagent Co. Ltd and used as received.

Instrumentation

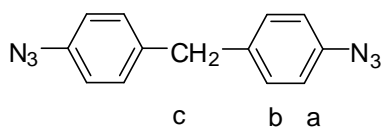
Proton nuclear magnetic resonance (¹H NMR) spectra were obtained in deuterium chloroform solvent on a BRUKER Avance500 (500 MHz, BRUKER, DE) instrument, employing tetramethylsilane (TMS) as an internal standard. FTIR spectra were recorded with a Nicolet 550 (TA, U.S.) infrared spectrometer. Rheological behavior was analysed using a RheoStress RS600 Rheometer (HAAKE, DE.). Differential scanning calorimetry (DSC) was carried out on a TA Q2000 (TA, U.S.) analyzer under nitrogen atmosphere at the heating rate of 10°C/min. Gel permeation chromatography (GPC) was carried out on Wyatt Technology Corporation Waters 515 (Wyatt Technology Corp., U.S.). DMF was used as the solvent. Scanning electron

microscope (SEM) analysis was performed on JSM-6360LV (JEOL, JP).

Preparation of Polytriazole (PTA) Gels

Synthesis of 4, 4'-Diazido diphenylmethane (A)^[1-2]

4,4'-diamino diphenylmethane (5.94 g, 0.03 mol), deionized water (210 mL), and concentrated HCl (120 mL) were added into a four-neck bottomed flask (1000 mL) with a mechanical stirring bar. When the reaction flask was cooled to 0°C in an ice bath, the sodium nitrite (6.18 g, 0.09mol) dissolved in deionized water (90 mL) was dropwise added into the flask. With the reaction processing, the mixture solution became homogeneous and converted into a dark brown one. After being stirred for 1 h, the reactant was cooled to 0°C again. The sodium azide (4.86 g, 0.075mol) in deionized water (90 mL) was added dropwise into the reaction system. Evolution of nitrogen gas was observed during this reaction process. After continuously stirring for 6 hours and waiting for 12 hours, we could get the brown solid product (A1), which was dried under vacuum, by washing up the precipitate with deionized water. The structure of the diazide was shown in Scheme S1. Yield: 87%, mp: 40~42°C (41~42°C, reported[11]), ¹H NMR(CDCl₃, TMS) δ: 7.18 (d, 4H, H_a), 6.98 (d, 4H, H_b), 3.97 (s, 2H, H_c), FT-IR(KBr, ν, cm⁻¹): 2089 (-N₃), 1468, 2926(-CH₂-); Elemental analysis for C₁₃H₁₀N₆, Found (Calcd) (%): C 33.19 (33.60), C 62.59 (62.40), H 3.83 (4.00).



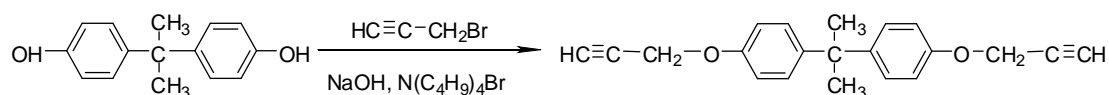
4,4'-Diazido diphenylmethane(A)

Scheme S1. The structure of the diazide

Synthesis of dipropargyl bisphenol A (B)^[3]

Dipropargyl bisphenol A was synthesized according to the literature [12] (Scheme S2).

Yield: 70%. m.p. 79~80°C; ¹H-NMR(CDCl₃, TMS) δ: 1.62 (s, 6H, -CH₃), 2.50 (tr, 2H, ≡CH), 4.65 (d, 4H, -CH₂), 6.86 (m, 4H, -O-Ar-H), 7.15 (m, 4H, -C-Ar-H); FT-IR (KBr): 3286cm⁻¹, 3260cm⁻¹(≡CH), 2110cm⁻¹(C≡C); Elemental analysis for C₂₁H₂₀O₂, Found (Calcd) (%): C 82.19 (82.87), H 6.63 (6.62), O 11.18 (10.51).



Scheme S2. Synthesis of bispropargyl ether of bisphenol-A (BPEBA)

Synthesis of Cu(PPh₃)₃Br^[4]

The Cu(I) complex, Cu(PPh₃)₃Br, was prepared using a previously published method [13]. Cu(PPh₃)₃Br: yield 87%, mp.: 168~170°C. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.24-7.33 (m, Ph(*meta*, *ortho*), 36H), 7.33-7.40 (m, Ph(*para*), 9H).

Formation of polytriazole gels

The synthesis of new polymeric organogel (GelT) prepared by 'click' chemistry is described as Scheme 3. A (0.250g, 1 mmol) and B (0.304g, 1 mmol) was dissolved in DMF or DMSO (10.526g, 5% wt), and then Cu(PPh₃)₃Br (0.035g, 2% M) was added. After 48h heating at 60°C, GelT was formed. Other gels were prepared as the same way except that CuSO₄/sodium ascorbate (0.025g, 0.04g, 2% M), CuBr (0.006g, 2% M) and CuI (0.008g, 2% M) substituted Cu(PPh₃)₃Br (0.035g, 2% M) as catalyst,

respectively. Finally, the reactions all formed polytriazole gels in DMF or DMSO with $\text{Cu}(\text{PPh}_3)_3\text{Br}$, $\text{CuSO}_4/\text{sodium ascorbate}$, CuBr and CuI as catalysts. It indicates that diverse Cu(I) source all have the ability to form gel in this reaction.

SUPPORTING RESULTS

FTIR Analysis.

GelT was illustrated by FTIR (Fig. S1). Absorption peaks of $\equiv\text{CH}$ (3290cm^{-1}) and $-\text{N}_3$, $\text{C}\equiv\text{C}$ (2110cm^{-1}) disappear in the gel. The peaks at 3130cm^{-1} which is assigned to C-H in the triazole ring occurs in the polytriazole gel. It indicates that the reaction between the azide and alkyne groups has taken place and the poly(1,2,3-triazole) has been formed.

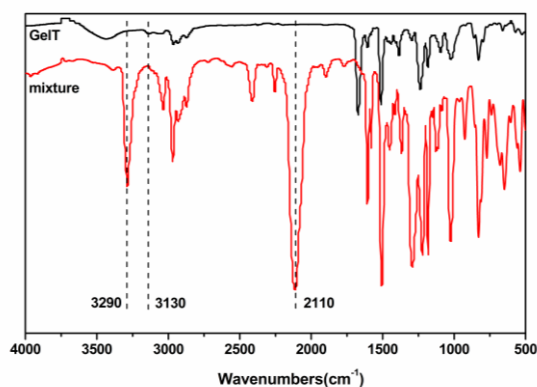


Figure S1. FTIR spectra of polytriazole gel

Rheology experiments

In order to expose the gel nature of GelT, rheology measurements including Dynamic Time Sweep (DTS), Dynamic Frequency Sweep (DFS), and Dynamic Strain Sweep (DSS) were carried out.

The following three experiments were carried out for GelT:

a. Dynamic Time Sweep (DTS): plot of storage modulus (G' , elastic component) and loss modulus (G'' , viscous component) with time. In this experiment the strain (1%) and the frequency (1Hz) were kept constant. The magnitude of G' is an indication of the extent of cross-linking leading to material rigidity. The material is considered a gel if $G' > G''$.

b. Dynamic Frequency Sweep (DFS): plot of G' and G'' with frequency (0.01 to 100 Hz), performed to make sure that the frequency used in DTS is within the linear viscoelastic regime. The results show that the gels here are viscoelastic for frequencies ranging from 0.01 to 100 Hz; we chose 1 Hz for DTS.

c. Dynamic Strain Sweep (DSS): plot of G' and G'' with strain (from 0.01 to 100%), performed to make sure that the strain used in DTS is within the linear viscoelastic regime. The results show that the gels here fracture at slightly less than 2% strain; we used 1% strain for DTS.

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