

Electronic Supplementary Information for **A Mussel-inspired
Adhesive with Stronger Bonding Strength at Underwater
conditions than at Dry conditions**

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Experimental section

Materials

Propargyl bromide (80 wt% solution in toluene, Aldrich), trimethylsilyl chloride (Sigma-Aldrich), azobis(isobutyronitrile) (AIBN, Sigma-Aldrich, 99%), *n*-butyllithium (*n*-BuLi, 2.5 M in hexane) were used as received. Diisopropylamine (Beijing Chemicals Co.) was refluxed with CaH₂ under argon for 6 h, followed by distillation. Tetrahydrofuran (THF, Beijing Chemicals Co.) was refluxed under argon with Na and diphenylmethanone until the solution became dark blue, and then it was distilled. *N*-Vinyl-2-pyrrolidone (VP, Sigma-Aldrich, 95%) was distilled under reduced pressure prior to use. 3,4-Bis-(*tert*-butyl-dimethyl-silanyloxy)-benzyl azide was synthesized according to our previously published works.¹ All the other solvents and reagents were purchased from Sigma-Aldrich and used as received unless otherwise stated. Seawater was obtained from the seaside in Qingdao (Yellow Sea of China) without any further treatment.

Instrumentation

¹H NMR spectra were recorded on a Bruker AV600 MHz spectrometer using TMS as an internal standard. GPC data was obtained on a Polymer Laboratories PL-GPC 120 system equipped with a refractive index detector. A combination of two polystyrene gel columns of PL gel-MIXEDC was used, with THF as the eluent at a flow rate of 1.0 mL/min and a temperature of 40 °C. The columns were calibrated using polystyrene standards. Lap shear test was conducted on a TY-8000 universal material testing system equipped with a 2000 N load cell.

Synthesis of 3-(3-trimethylsilylpropargyl)-*N*-vinyl-2-pyrrolidone (TMSPG-VP)

TMSPG-VP was synthesized according to the reported work.²

Synthesis of P(VP_x-*co*-TMSPG-VP_y) (copolymer 1)

VP and TMSPG-VP were copolymerized at different feeding ratio (90:10, 80:20, 70:30) via radical polymerization to produce the copolymers. The general procedure of radical polymerization was carried out according to the reported work.²

Deprotection of copolymer 1 to afford P(VP_x-co-PG-VP_y)

Deprotection of copolymer **1** was conducted according to the published work with modifications.² Taking P(VP_{81.3%}-co-TMSPG-VP_{18.7%}) for an example. Copolymer (0.50 g) was dissolved in 25 mL of methanol. Then, K₂CO₃ (0.20 g, 2 equiv. to TMSPG) was added into the solution and the resulting mixture reacted at ambient temperature overnight. Water (25 mL) was added to the reaction mixture. Then, it was extracted with chloroform (3 × 40 mL) and the extract was washed with brine (40 mL), dried over anhydrous MgSO₄ and concentrated. Yield: 85%.

Synthesis of protected catechol grafted copolymer 3

Using P(VP_{81.3%}-co-PG-VP_{18.7%}) as an example: 3,4-bis-(*tert*-butyldimethylsilanyloxy)-benzyl azide (0.31 g, 0.79 mmol), CuSO₄·5H₂O (19.74 mg, 0.08 mmol), ascorbic acid (27.84 mg, 0.16 mmol) were added to a solution of copolymer (0.42 g, 0.66 mmol) in 10 mL of DMF. The resulting mixture was heated at 80 °C for 48 h under argon atmosphere. Then, the mixture was added drop-wise into 200 mL of ethyl ether under stirring to precipitate the polymer. The precipitate was dissolved in methanol (10 mL) and precipitated out again in ethyl ether (200 mL). The crude product was purified by repeating precipitation. The precipitate was dried under vacuum to afford protected catechol grafted copolymer **3**. Yield: 89.5%.

Synthesis of catechol grafted copolymer 4

In a general procedure, concentrated HCl (5 equiv. to catechol) was added to a solution of protected catechol grafted copolymer **3** in methanol (0.01 g/mL) under argon atmosphere at room temperature. The resulting mixture was stirred at room

temperature overnight. The resulting mixture was added drop-wise into 200 mL of ethyl ether under stirring. The precipitate was dissolved in methanol and precipitated out again in ethyl ether (200 mL). The precipitate was dried under reduced pressure to afford catechol grafted copolymer **4**. Yield: 91.0%.

Adhesion experiments

Glass was selected as the adherend for lap shear test. Glass slides ($10 \times 2 \text{ cm}^2$) were activated by soaking in a 2-propanol/KOH bath for 30 min followed by rinsing with water and ethanol and then dried before use. Stainless steel was polished followed by rinsing with water and ethanol and then dried before use. The adhesion tests both at dry conditions and at underwater conditions were carried out at room temperature. For adhesion at dry conditions, the surfaces of adherends were kept dry in all cases during the whole process, from the usage of adhesive to lap shear test; for adhesion at underwater and under-seawater conditions, the adherends were firstly dipped in water to assure the surfaces humid. Then, 100 μL of catechol grafted copolymer **4** solution in methanol and dichloromethane (V:V, 1:1) (0.03 g/mL) was spread on two adherends with an area of 2 cm^2 . Then 20 μL of FeCl_3 solution in methanol was added on one of the adherends. The adherends were then allowed to stand in the air for about 30 s, and the ends applied with the adhesives and FeCl_3 were overlapped and fastened by two binder clips and placed underwater or under-seawater immediately and kept at room temperature for 24 h. Two aluminum sheets were bonded on the glass adherends using Krazy Glue before test. Lap shear adhesion measurements were conducted on a universal material testing system. Adherends were pulled apart at a rate of 10 mm/min. At least five samples were measured for each test and the average value of the bonding strength was adopted, with the error bar showing the maximum deviation of the measured data.

Equation

$$M_n(\mathbf{4}) = M_n(\mathbf{1}) + 92.97 \times \{M_n(\mathbf{1}) \div [(111.14 \times x) + (221.37 \times y)] \times y\} \quad \text{Equation S1}$$

$M_n(\mathbf{4})$ stands for the number-average molecular weight of synthetic adhesive **4**; $M_n(\mathbf{1})$ stands for the number-average molecular weight of copolymer **1**; 92.97 is the increased molecular weight per alkyne group after catechol modification; 111.14 is the molecular weight of VP and 221.37 is the molecular weight of TMSPG-VP.

1 (a) A. Li, M. Jia, Y. Mu, W. Jiang and X. Wan, *Macromol. Chem. Phys.*, 2014, DOI: 10.1002/macp.201400513. (b) M. Jia, A. Li, Y. Mu, W. Jiang and X. Wan, *Polymer*, 2014, **55**, 1160.

2 G. Chen, C. Wang, J. Zhang, Y. Wang, R. Zhang, F. Du, N. Yan, Y. Kou and Z. Li, *Macromolecules*, 2010, **43**, 9972.



(a)



(b)

Figure S1. Images of the interfaces before (a) and after (b) lap-shearing experiments.

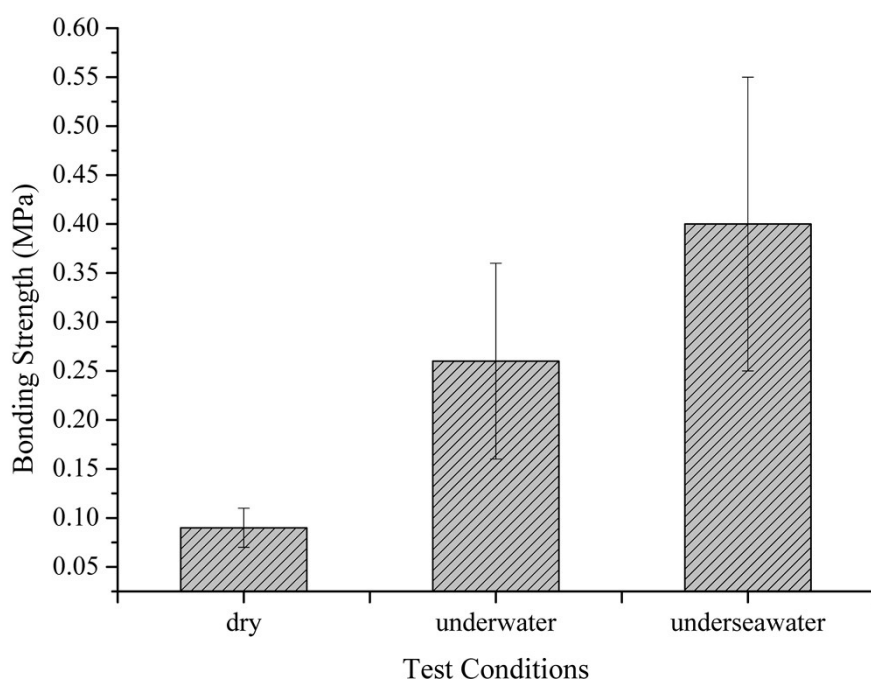


Figure S2. Bonding strength of synthetic copolymer **4** ($M_n = 8000$ Da, catechol content = 16.5%) on stainless steel at dry, underwater and under-seawater conditions.

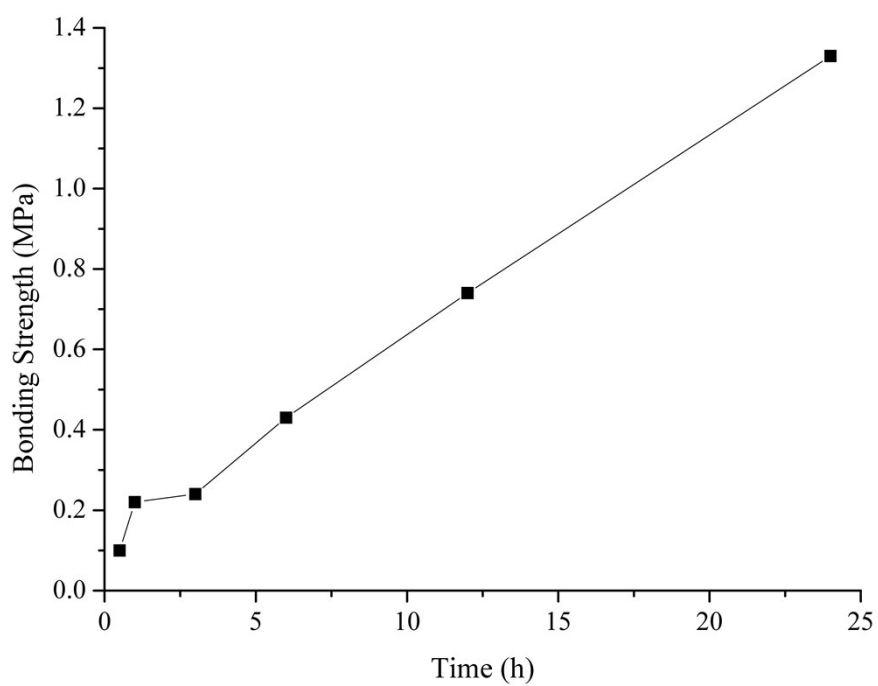


Figure S3. Underwater bonding strength of synthetic copolymer **4** with 16.0 mol% catechol grafted ($M_n = 10551$ Da) as a function of time (Tap water was used).

Spectroscopic data

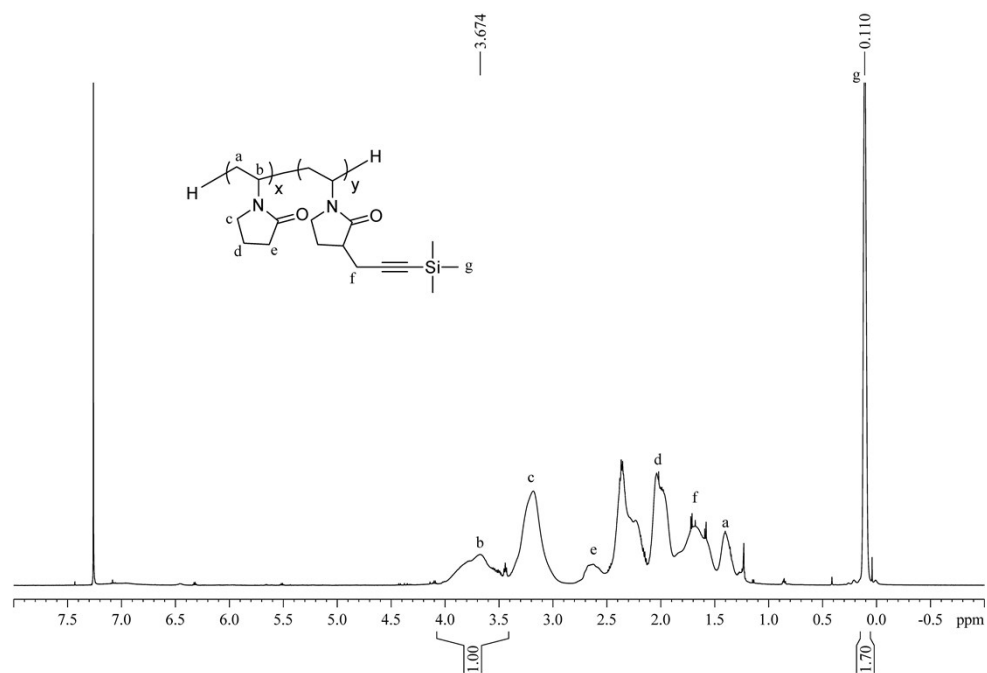


Figure S4. ^1H NMR spectrum of copolymer **1** P(VP_{81.1%}-co-TMSPG-VP_{18.9%}) in CDCl_3 .

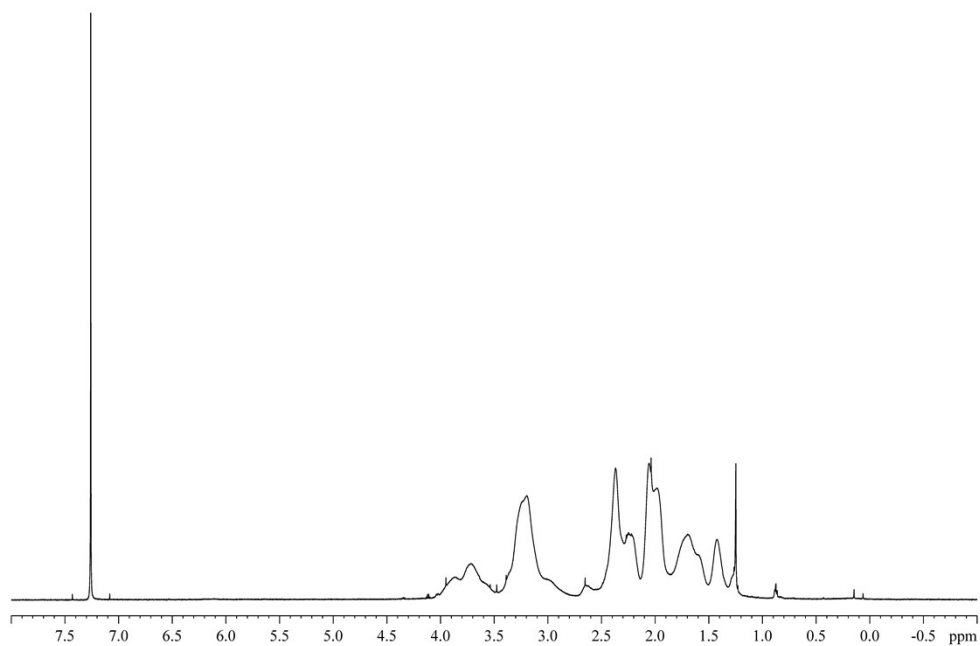


Figure S5. ^1H NMR spectrum of copolymer P(VP_{81.1%}-*co*-PG-VP_{18.9%}) in CDCl_3 .

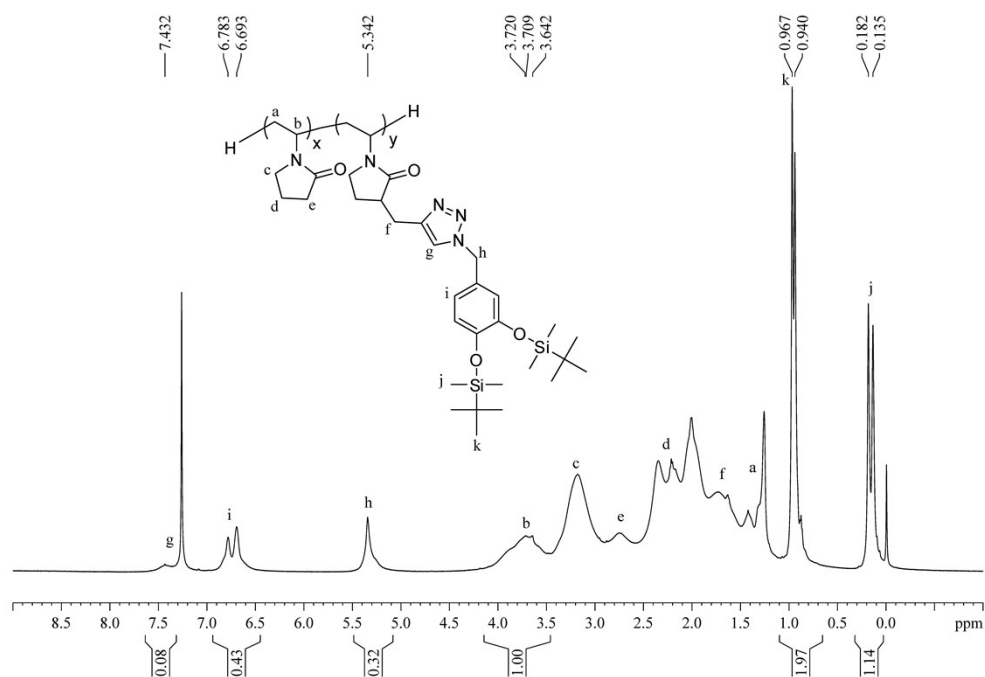


Figure S6. ¹H NMR spectrum of copolymer **3** with 16.0 mol% protected catechol grafted P(VP_{81.1%}-co-PG-VP_{18.9%}) in CDCl₃.

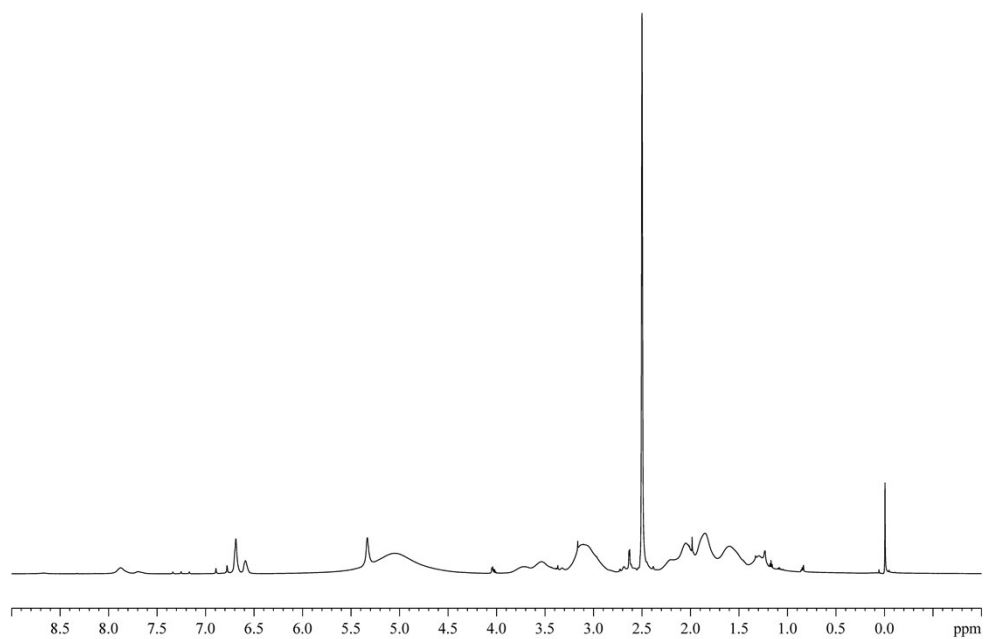


Figure S7. ¹H NMR spectrum of copolymer **4** with 16.0 mol% catechol grafted P(VP_{81.1%}-*co*-PG-VP_{18.9%}) in DMSO-*d*₆.

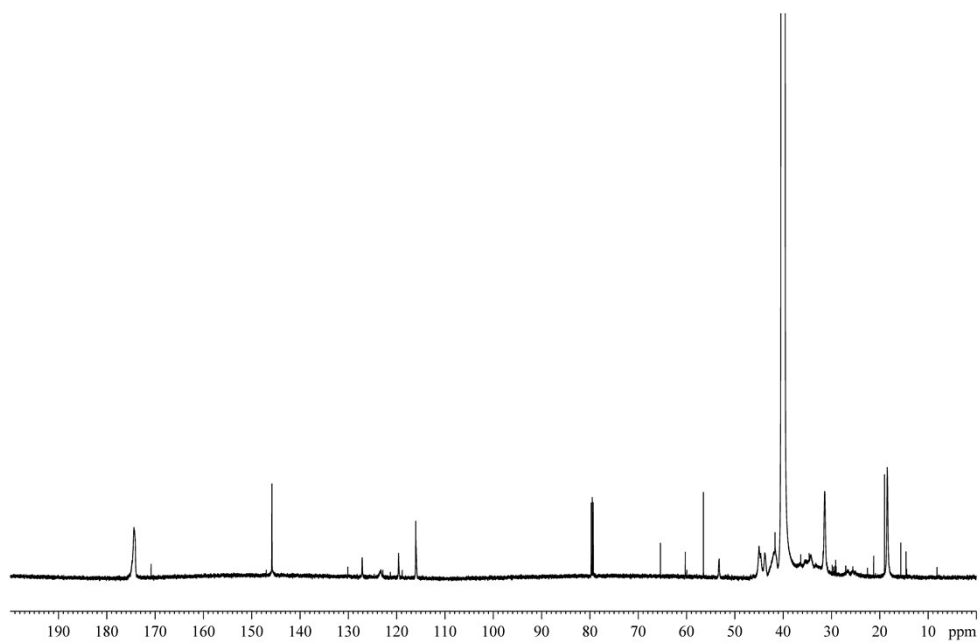


Figure S8. ^{13}C NMR spectrum of copolymer **4** with 16.0 mol% catechol grafted $\text{P}(\text{VP}_{81.1\%}\text{-co-PG-VP}_{18.9\%})$ in $\text{DMSO-}d_6$.

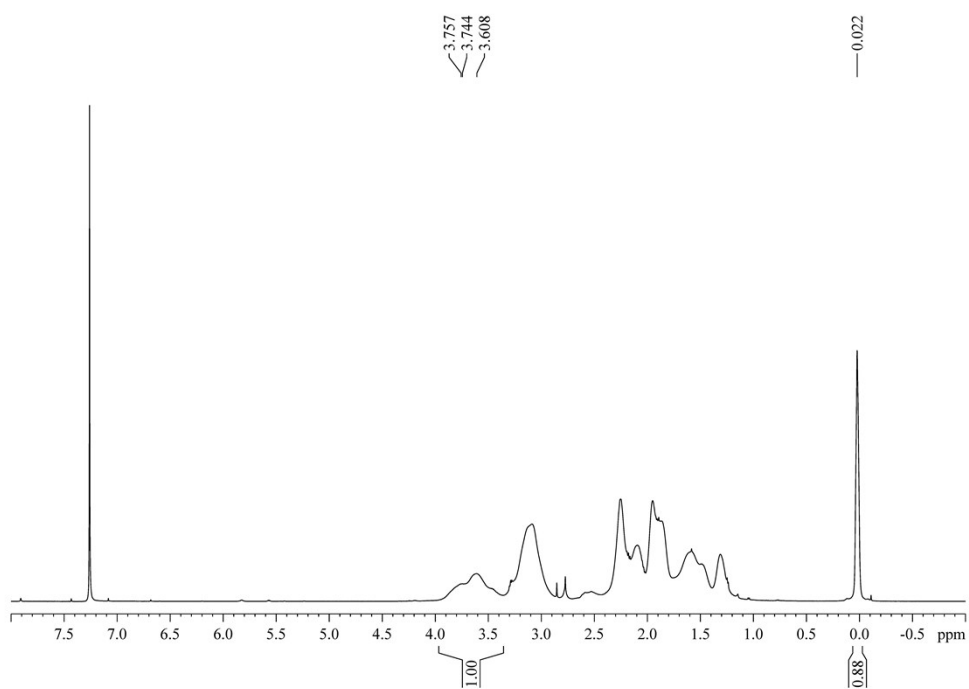


Figure S9. ¹H NMR spectrum of copolymer **1** P(VP_{90.2%}-*co*-TMSPG-VP_{9.8%}) in CDCl₃.

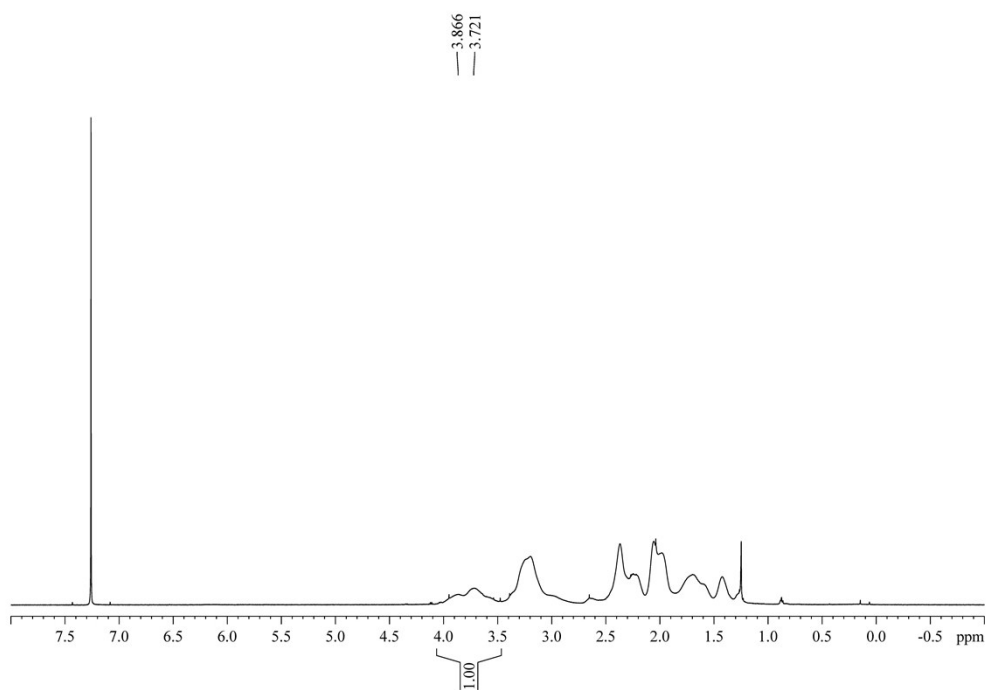


Figure S10. ¹H NMR spectrum of copolymer P(VP_{90.2%}-co-PG-VP_{9.8%}) in CDCl₃.

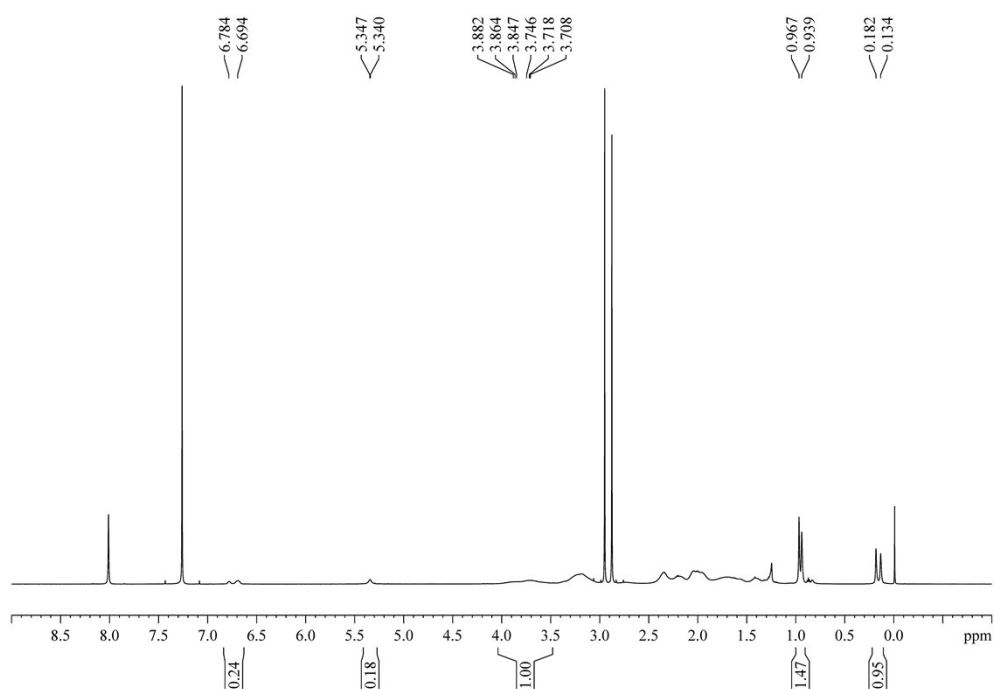


Figure S11. ¹H NMR spectrum of copolymer **3** with 9.0 mol% protected catechol grafted P(VP_{90.2%}-co-PG-VP_{9.8%}) in CDCl₃.

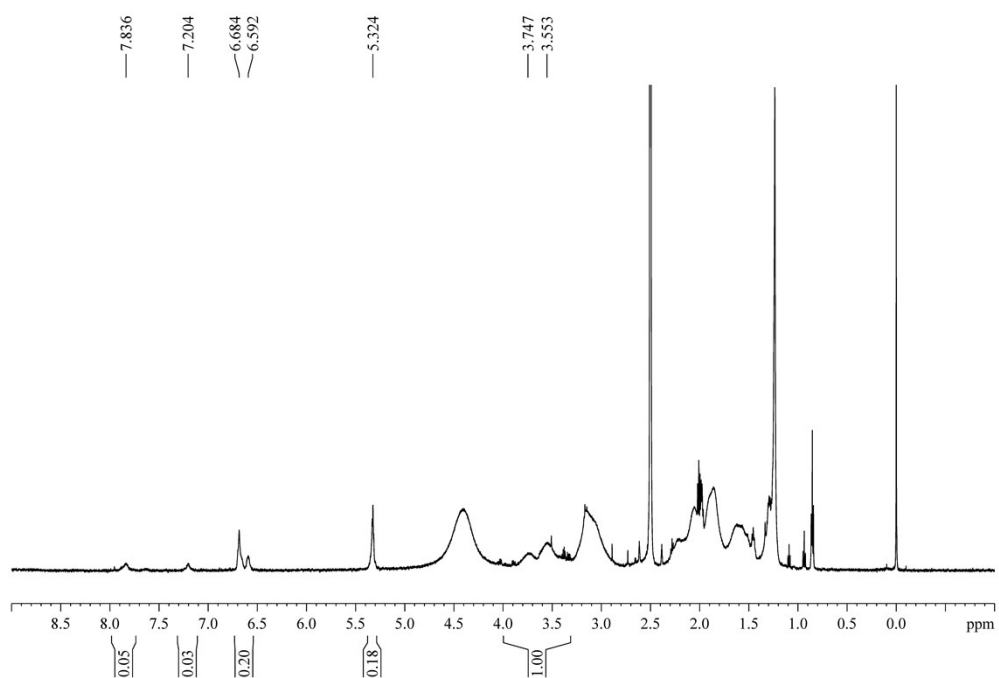


Figure S12. ¹H NMR spectrum of copolymer **4** with 9.0 mol% catechol grafted P(VP_{90.2%}-co-PG-VP_{9.8%}) in DMSO-*d*₆.

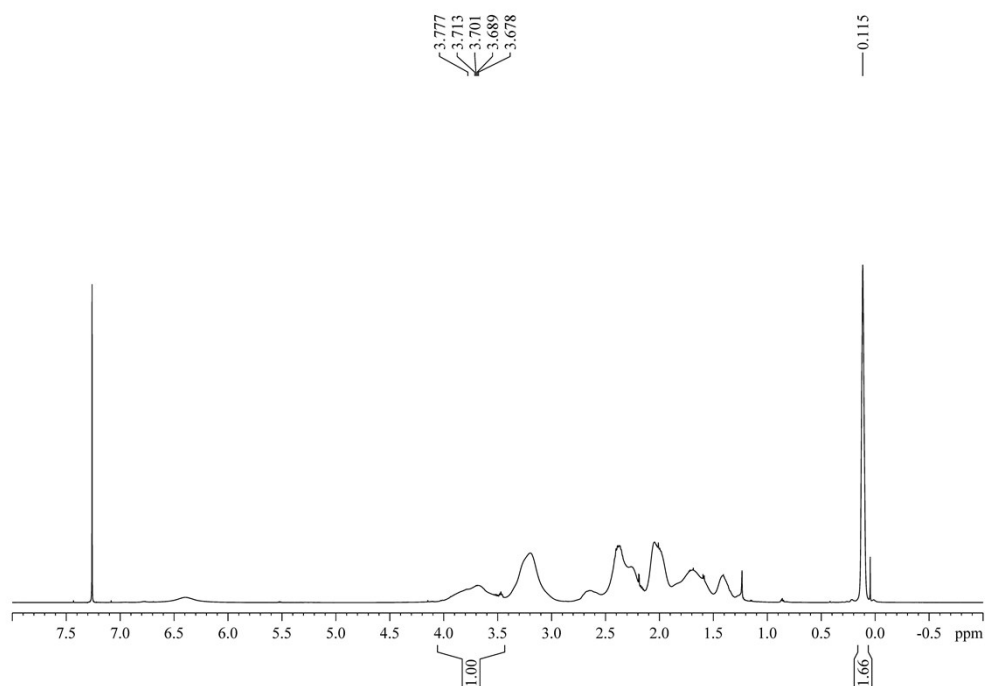


Figure S13. ¹H NMR spectrum of copolymer **1** P(VP_{81.6%}-co-TMSPG-VP_{18.4%}) in CDCl₃.

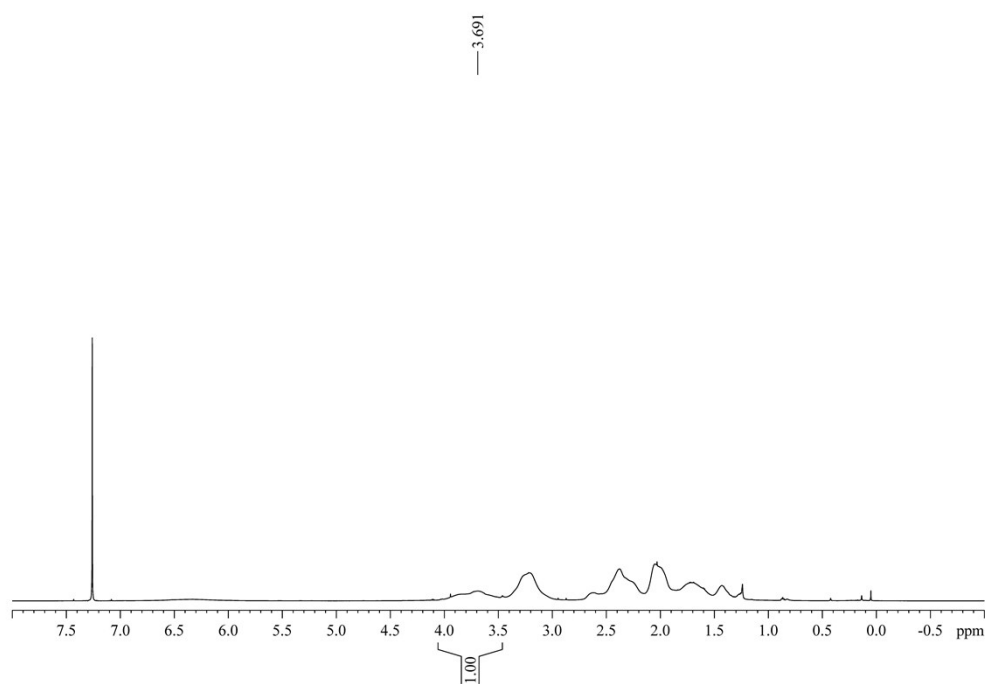


Figure S14. ^1H NMR spectrum of copolymer P(VP_{81.6\%}-*co*-PG-VP_{18.4\%}) in CDCl_3 .

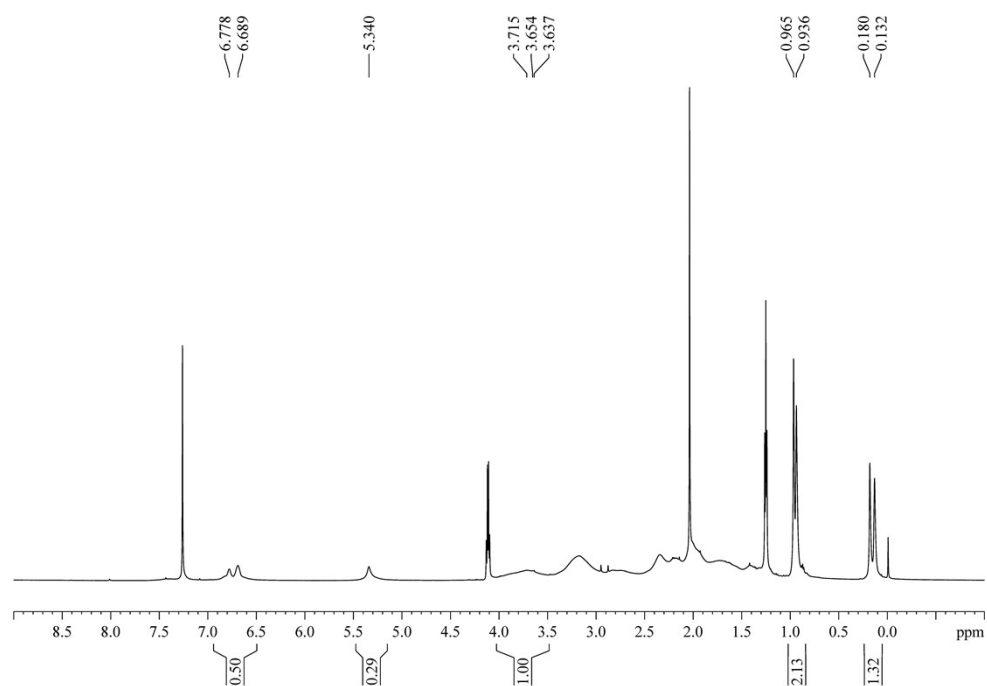


Figure S15. ¹H NMR spectrum of copolymer **3** with 14.5 mol% protected catechol grafted P(VP_{81.6%}-co-PG-VP_{18.4%}) in CDCl₃.

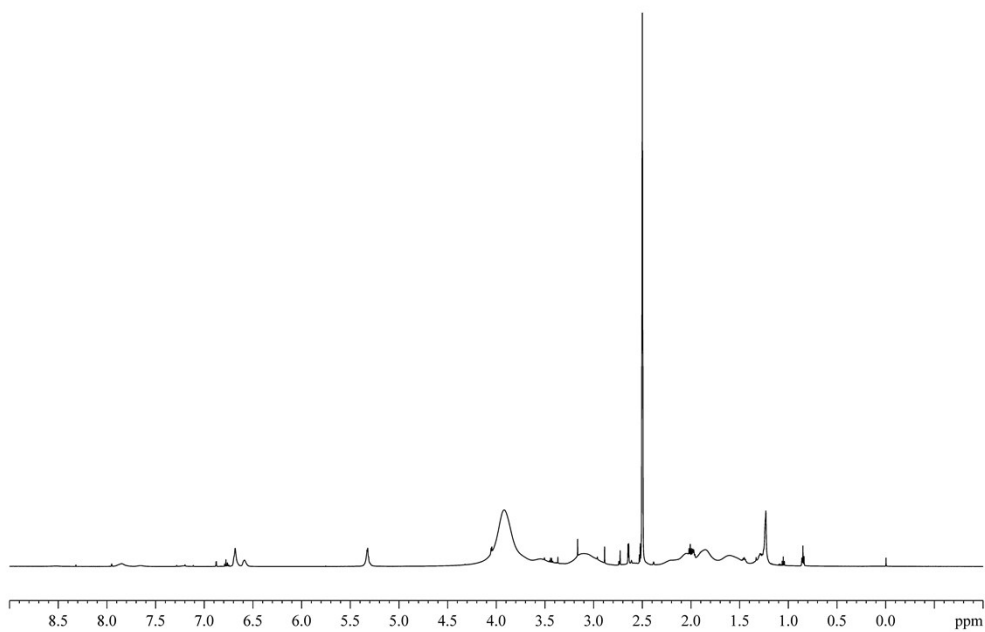


Figure S16. ¹H NMR spectrum of copolymer **4** with 14.5 mol% catechol grafted P(VP_{81.6%}-*co*-PG-VP_{18.4%}) in DMSO-*d*₆.

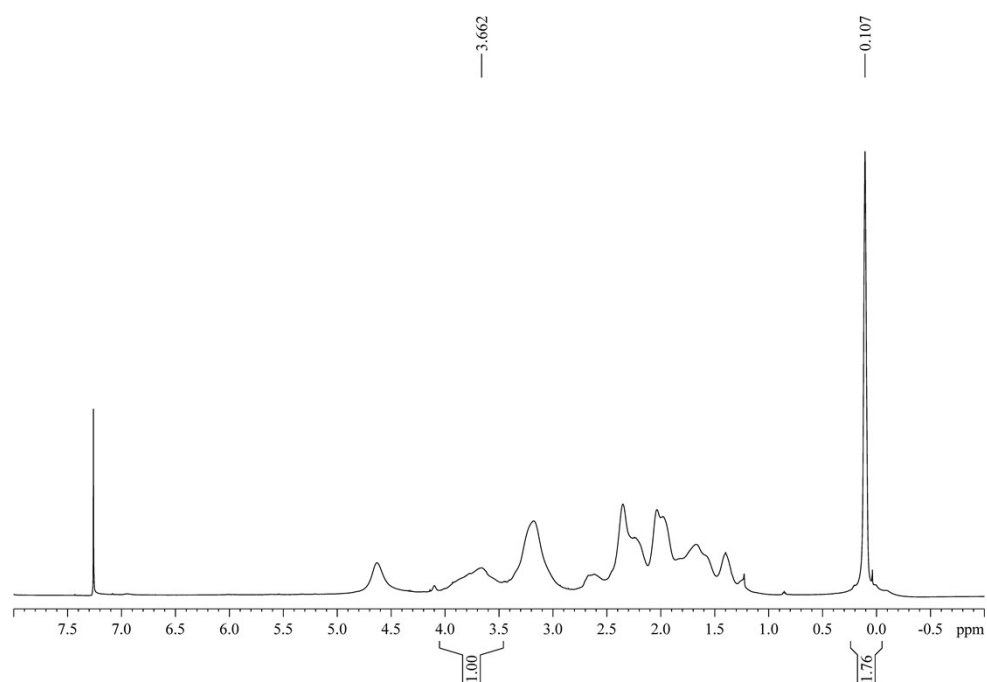


Figure S17. ¹H NMR spectrum of copolymer **1** P(VP_{80.4%}-co-TMSPG-VP_{19.6%}) in CDCl₃.

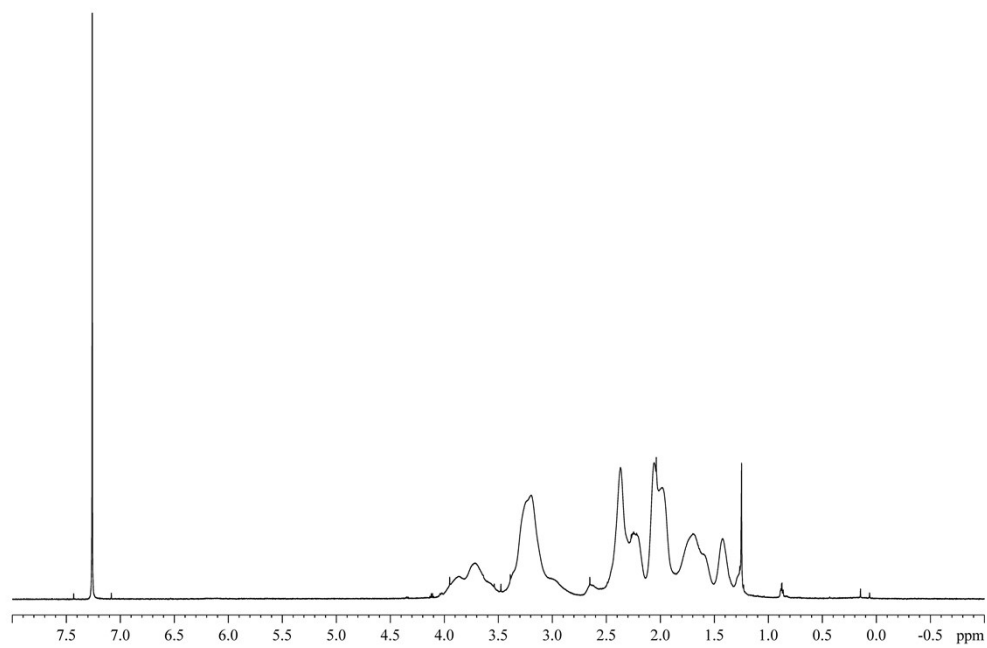


Figure S18. ¹H NMR spectrum of copolymer P(VP_{80.4%}-co-PG-VP_{19.6%}) in CDCl₃.

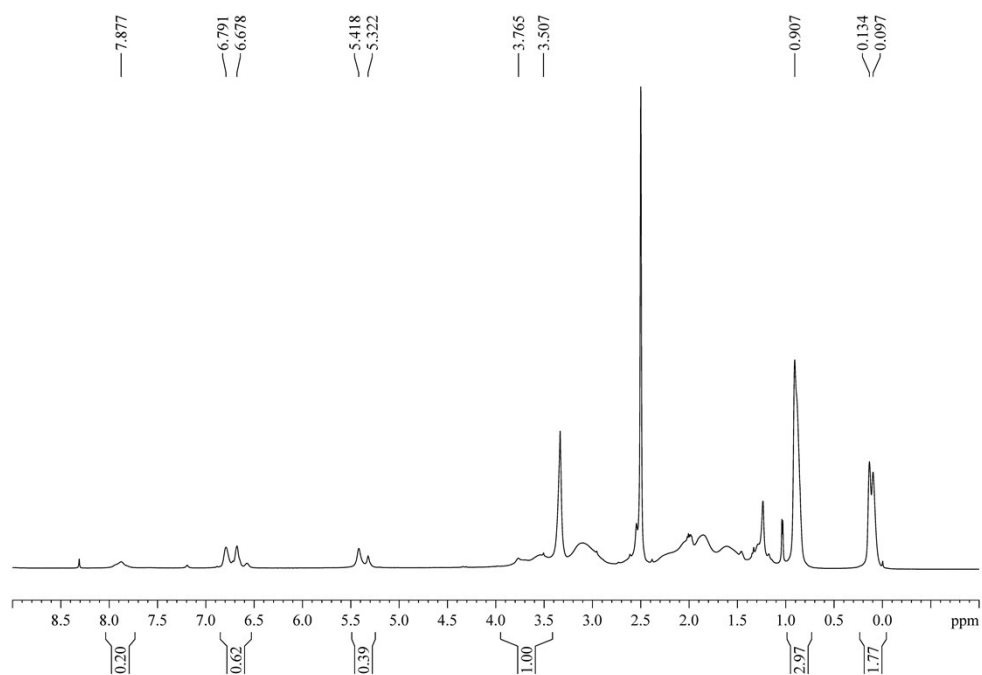


Figure S19. ¹H NMR spectrum of copolymer **3** with 16.5 mol% protected catechol grafted P(VP_{80.4%}-co-PG-VP_{19.6%}) in DMSO-*d*₆.

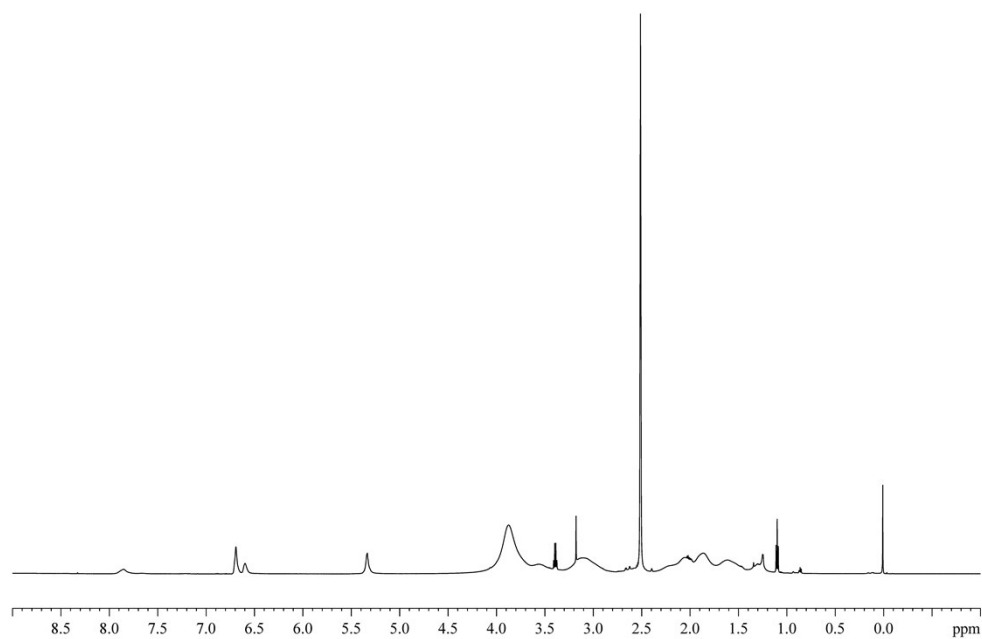


Figure S20. ¹H NMR spectrum of copolymer **4** with 16.5 mol% catechol grafted P(VP_{80.4%}-co-PG-VP_{19.6%}) in DMSO-*d*₆.

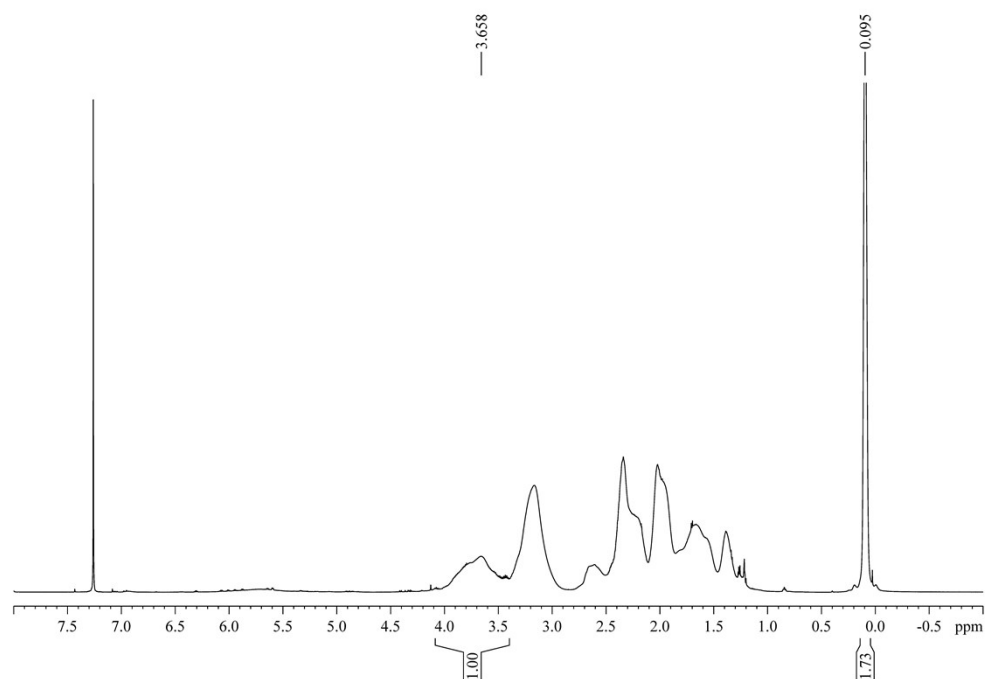


Figure S21. ¹H NMR spectrum of copolymer **1** P(VP_{80.8%}-*co*-TMSPG-VP_{19.2%}) in CDCl₃.

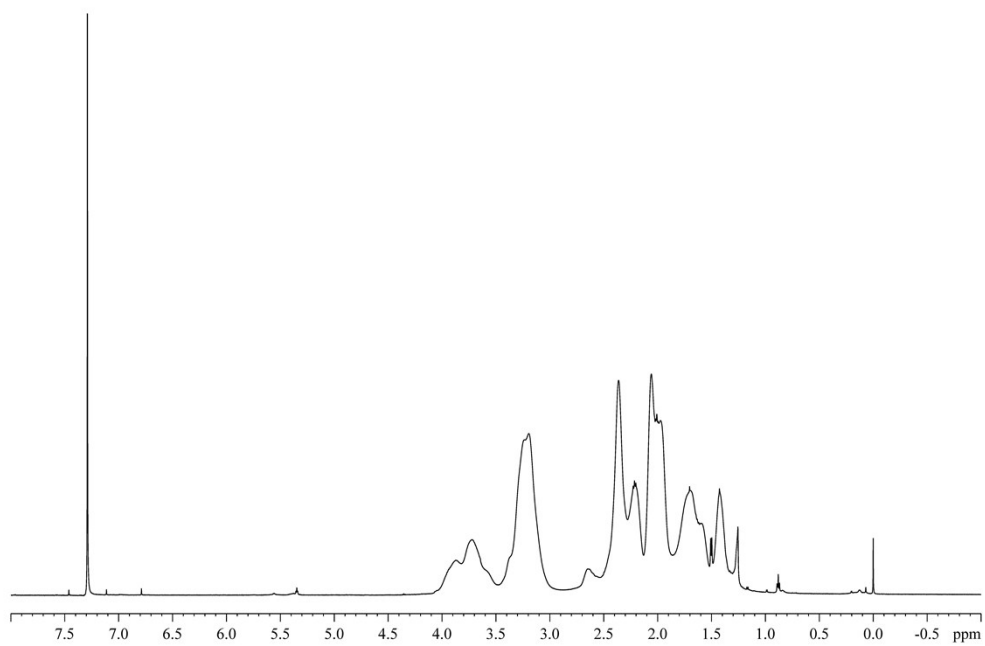


Figure S22. ¹H NMR spectrum of copolymer P(VP_{80.8%}-*co*-PG-VP_{19.2%}) in CDCl₃.

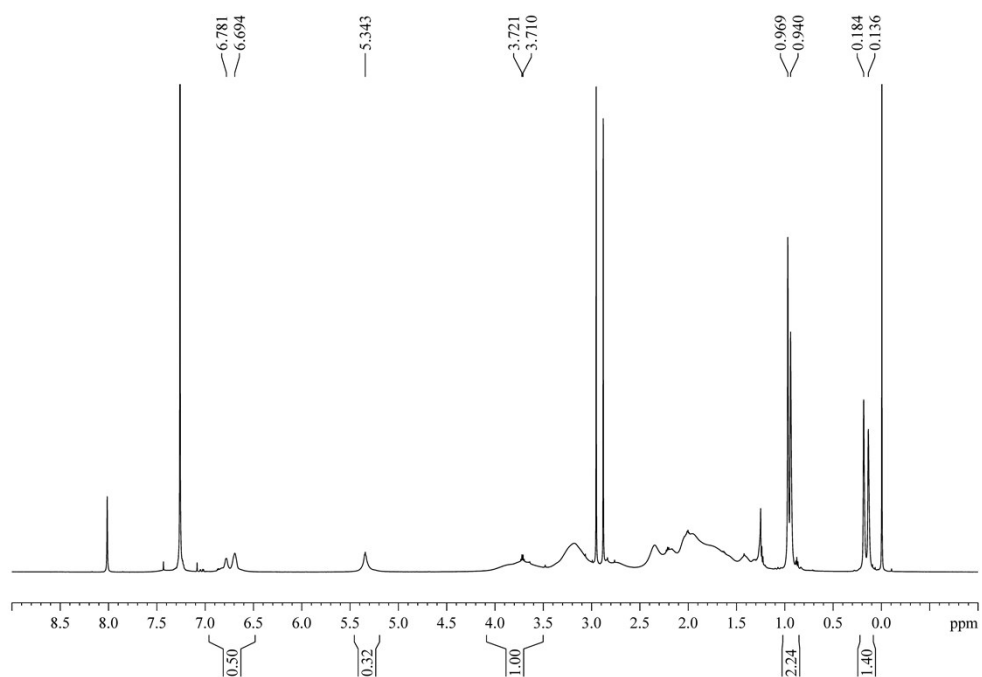


Figure S23. ¹H NMR spectrum of copolymer **3** with 16.0 mol% protected catechol grafted P(VP_{80.8%}-co-PG-VP_{19.2%}) in CDCl₃.

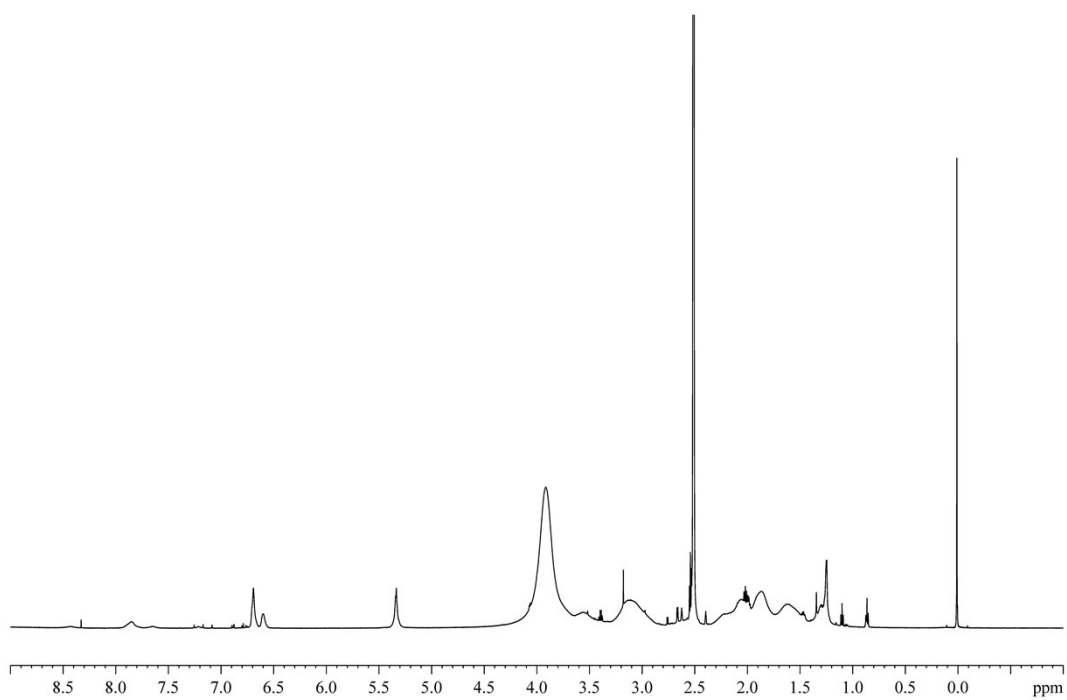


Figure S24. ¹H NMR spectrum of copolymer **4** with 16.0 mol% catechol grafted P(VP_{80.8%}-*co*-PG-VP_{19.2%}) in DMSO-*d*₆.

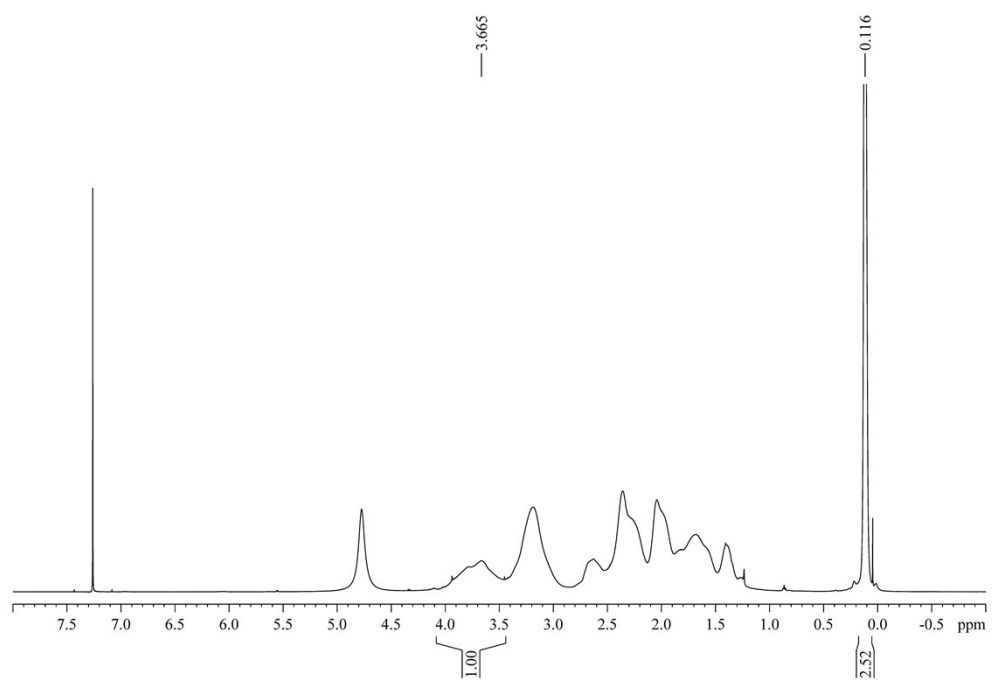


Figure S25. ^1H NMR spectrum of copolymer **1** P(VP_{72.0%}-*co*-TMSPG-VP_{28.0%}) in CDCl_3 .

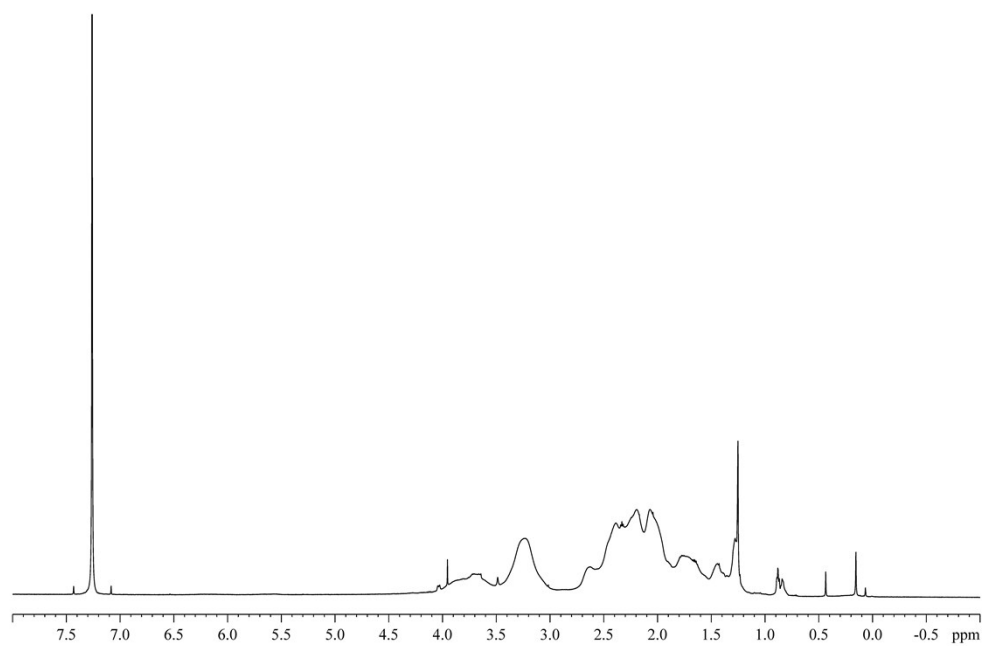


Figure S26. ¹H NMR spectrum of copolymer P(VP_{72.0%}-*co*-PG-VP_{28.0%}) in CDCl₃.

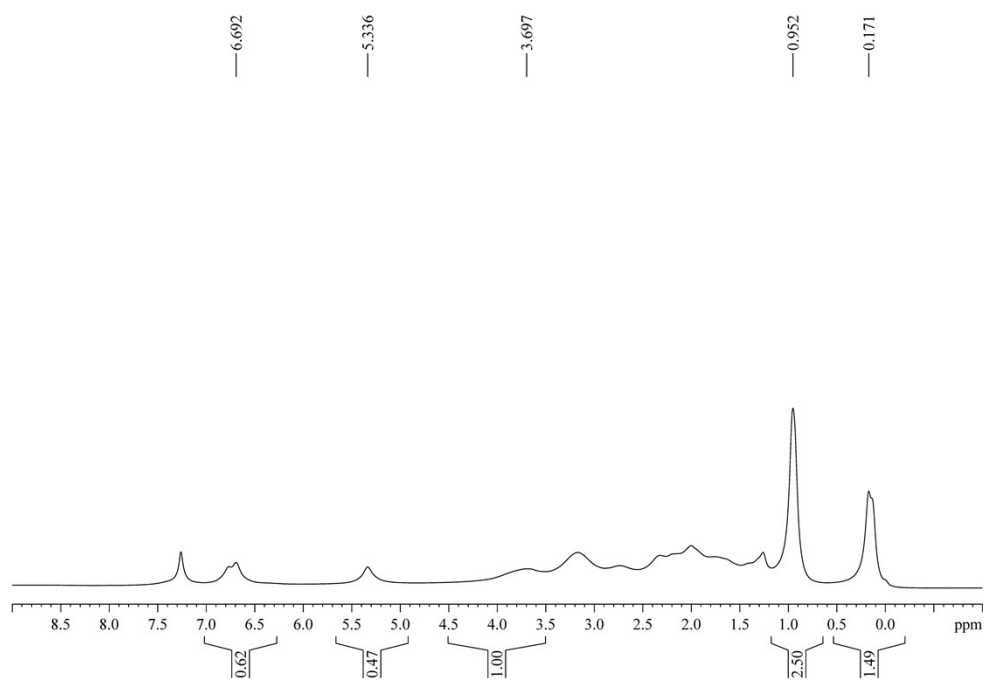


Figure S27. ¹H NMR spectrum of copolymer **3** with 23.5 mol% protected catechol grafted P(VP_{72.0%}-co-PG-VP_{28.0%}) in CDCl₃.

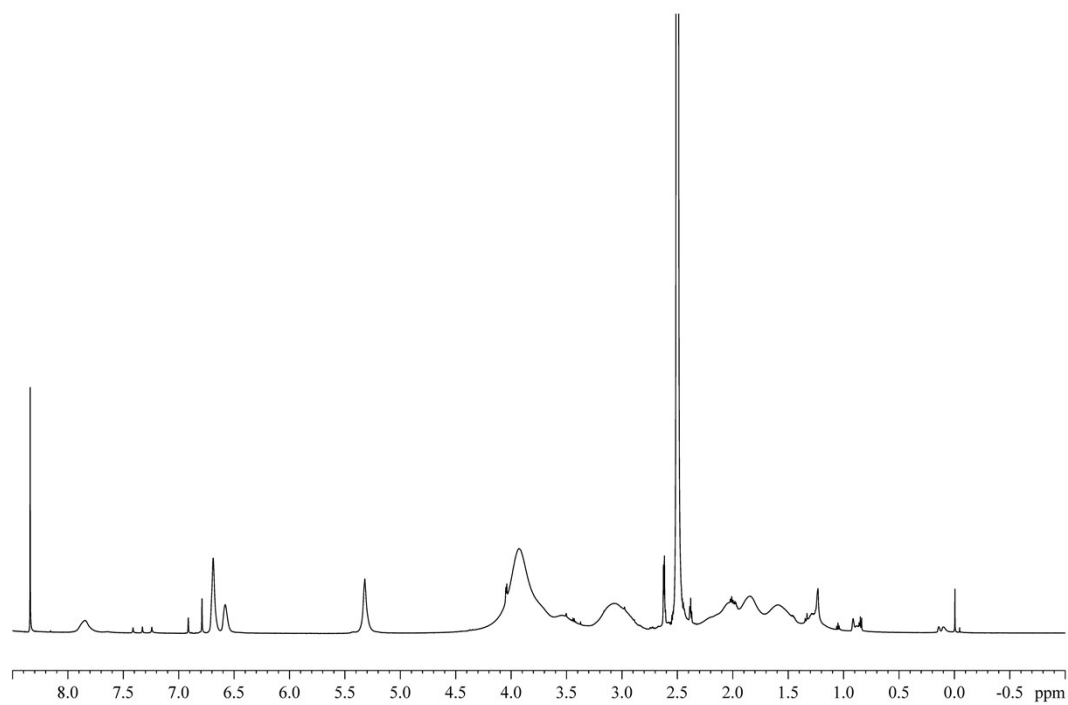


Figure S28. ¹H NMR spectrum of copolymer **4** with 23.5 mol% catechol grafted P(VP_{72.0%}-co-PG-VP_{28.0%}) in DMSO-*d*₆.