Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Self-healable Functional Polymers based on Diels-Alder 'Click Chemistry' Involving Substituted Furan and Triazolinedione Derivatives; A Simple and Very Fast Approach

Prantik Mondal[a], Gourhari Jana[b], Tuhin Subhra Pal[a], Pratim K. Chattaraj[b, c], Nikhil K. Singha[a]*

[a] Rubber Technology Centre, Indian Institute of Technology Kharagpur, Kharagpur-721302, India
[b] Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India
[c] Department of Chemistry, Indian Institute of Technology Kharagpur, West Bengal-721302, India

Content

1. Materials

2-Hydroxyethyl methacrylate (HEMA) and *n*-butyl methacrylate (BMA) were purchased from Aldrich, USA and were purified by passing through a basic alumina column to make them inhibitor-free. 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTSPA), 4,4-azobis(4-cyanovaleric acid) (ABCVA), 5-Methyl-2-furoic acid (MFA, 97 %), and 4-Phenyl-1,2,4-triazoline-3,5-dione (PhTAD, 97%) were obtained from Sigma-Aldrich and used as received. DMF (> 99 %) and n-hexane (> 99 %) were purchased from Merck Specialties Private Limited, Mumbai, India and used as received. The distillation of THF solvent (obtained from Merck Specialties Private Limited, Mumbai, India) was carried out from the mixture of sodium and benzophenone under the nitrogen atmosphere to make it moisture-free. 4,4′-Methylenebis(phenyl isocyanate), 4-(Dimethylamino)pyridine (DMAP), and 1,4-Diazabicyclo[2.2.2]octane (DABCO) were purchased from Aldrich Chemical, USA and used as received. Bromine (>99 %) was purchased from S. D. Fine Chemical Ltd. Ethyl carbazate was purchased from Spectrochem, India and used as received. 2,5-Dimethyl furan (DMFu, > 98 %) was bought from Alfa Aesar and used as received. N, N′-Dicyclohexylcarbodiimide (DCC) was purchased from Spectrochem and used as received.

2. Characterization techniques

^{1}H-NMR, ^{13}C NMR, and ^{13}C DEPT-135 NMR spectra of all polymers and organic compounds were recorded on the Avance III HD 600-MHz (Bruker) spectrometer. Relative to solvent either $CDCl_3$ or DMSO-d_6 (δ_H = 7.27 and 2.50 ppm for $CHCl_3$ and DMSO respectively) containing a small amount of tetramethylsilane (TMS) as an internal standard, the chemical shifts were referenced in parts per million (δ).

The FTIR spectra of the polymers were recorded to analyze the inclusion of bisTAD in polymethacrylate within the wavenumber range of 4000-400 cm^{-1} in attenuated total reflection (ATR) mode in a Perkin-Elmer (Inc. version 5.0.1) spectrometer.

Differential Scanning Calorimetry (DSC) analysis of the polymer samples was carried out in a Discovery DSC 25 (TA) instrument. All the polymer samples were heated from 0 °C to 180 °C at a heating rate of 10 °C/ min under N_2 atmosphere. The glass transition temperature (T_g), retro-DA temperature (T_{rDA}) and its enthalpy (ΔH_{rDA}), and $T_{re\text{-}DA}$ were determined from the 1st heating and 1st cooling curves of the individual polymers.

Gel permeation chromatography (GPC) measurement polymers was performed at ambient temperature on the Viscotek GPC instrument (model VE 3580), equipped with a refractive index indicator. As eluent, Tetrahydrofuran (THF) was used with a flow rate of 1 mL/min. As an internal standard, linear poly(methyl methacrylate) (PMMA) of narrow polydispersity index was used for the calibration of the system.

The self-healing behavior of **P1Fu**, **P2Fu**, and DA polymethacrylates was monitored under optical microscopy (Leica DMLM, made in Germany). Using a razor, a scratch was deliberately made over the polymer surface prepared via drop-casting method (50 mg/ mL) on a glass slide, and healing was subsequently monitored at different time interval.

The hardness value of the polymethacrylates was determined by depth sensing indentation (DSI) using a TribroIndenter TI 950 (Hysitron Inc., Minneapolis, MN, USA) equipped with a diamond indenter tip of 150 nm radius. The polymethacrylate films (50 mg/ mL) were prepared

via a drop-casting method and dried under air or oven. The measurements were conducted in a single automated run at a fixed load of 50 μN under ambient temperature.

The healing efficiency (E_H) of all the polymer surfaces (50 mg/ mL) was monitored using a Contour GT 3D Optical Microscope, Bruker in vertical scan interferometry (VSI) mode.[1] HE of DA polymethacrylates was calculated using following formula:

$$Healing\ efficacy\ (E_H) = \frac{d_{healed} - d_{damaged}}{d_{undamaged} - d_{damaged}} X\ 100$$

For microscopy analyses, all the samples (50 mg/ mL) were prepared via a drop-casting method on a glass slide.

UV-Vis spectroscopy analysis of the organic compounds (20 mg/ mL) and polymer samples (50 mg/ mL) were carried out in Perkin-Elmer UV/Vis Spectroscopy Lambda 35, using THF as a solvent.

MALDI-TOF-MS analysis was performed using an Ultraflextreme mass-spectrometer (Bruker). 2,5-Dihydroxybenzoic acid (DHB) and trifluoroactetic acid (TFA) was used as matrix and cationic agent. The THF solution of organic compounds (≈ 25 mg) and matrix were mixed at 1:1 ratio by volume.

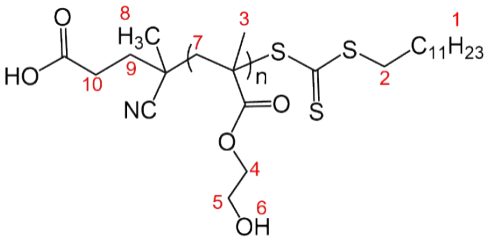
Computational Details

Geometry optimization and frequency calculation were performed using a long-range dispersion corrected highly parameterized density functional theory (DFT) based hybrid meta-GGA functional, M06-2X[2,3] in combination with 6-311+G(d, p) basis set[4,5] to study the reaction in the gas phase. The global hybrid meta-GGA functional M06-2X was used since it includes double the amount of the non-local exchange which is known to be well suited for calculations in main-group thermochemistry and kinetics.[4] The transition state (TS) search and subsequent intrinsic reaction coordinate (IRC) calculations were performed to confirm whether the located TSs are actually connected to the correct stationary points. Zero-point corrections were included in calculating the Gibbs free energies, thermal enthalpy corrections, and entropy. GAUSSIAN 16 software package[6] was used for all of the aforementioned calculations.

3. Experimental Section

3.1 Preparation of PHEMA homopolymer via RAFT polymerization [$PHEMA_{65}$ (**P1**)]

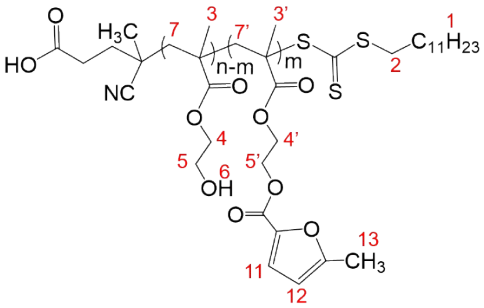
HEMA (1 g, 0.0076 mol), CDTSPA (0.0413 g, 1.02 x 10^{-4} mol), ABCVA (0.0072 g, 2.56 x 10^{-5} mol) and DMF (1 mL) were taken in a 25 ml round-bottomed (RB) flask having a magnetic stirring bar. Next, the RB flask was sealed with a silicone rubber septum and made oxygen-free by purging N_2 gas for 30 min. The polymerization reaction was carried out for 5 h at 70 °C and then quenched by immersing the tube in an ice bath and exposing to air. The viscous polymethacrylate was solubilized in a small volume of DMF and precipitated in diethyl ether. The re-precipitation process was continued for several times, and dried in a vacuum oven at 60 °C.



^{1}H NMR (600 MHz, DMSO-d$_6$) δ (ppm): 4.89-4.73 (H^6), 4.03-3.83 (H^4), 3.68-3.50 (H^5), 3.40 (H^2) 2.07-0.60 (alkyl Hs).

3.2 Modification of P1 polymer with 5-methyl-2-furoate groups [PHEMA$_{17}$-PMFMA$_{48}$ (**P1Fu**)]

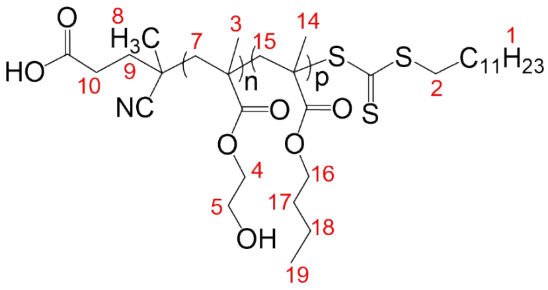
0.2 g **P1** (0.20 g, 0.0015 mol reactive HEMA), MFA (0.22 g, 0.0017 mol) and 4-dimethylamino pyridine (DMAP) (0.021 g, 0.0002 mol) were taken in a 10 mL RB flask and dissolved in 0.5 mL DMF and cooled in an ice bath. N, N-dicyclohexylcarbodiimide (0.37 g, 0.0018 mol) was dissolved in 0.5 mL DMF and then added dropwise to the above ice-cooled solution. The reaction was then continued for 36 h at room temperature (r.t.) for an increased extent of grafting. The polymer solution was then filtered and precipitated in ethanol. The modified polymer was dried in a vacuum oven at 40°C. The extent of conversion of HEMA units determined using ^{1}H NMR analysis (conversion = 73.8 %).



^{1}H NMR (600 MHz, DMSO-d$_6$) δ (ppm): 7.29-7.00 (H^{11}), 6.41-6.17 (H^{12}), 4.85-4.68 (H^6), 4.58-4.28 (H$^{5'}$), 4.26-4.00 (H$^{4'}$), 3.98-3.76 (H^4), 3.66-3.46 (H^5), 3.18 (H^2), 2.41-2.17 (H^{13}) 2.14-0.51 (alkyl Hs).

3.3 Preparation of PHEMA$_{28}$-*co*-PBMA$_{45}$ via RAFT polymerization (**P2**)

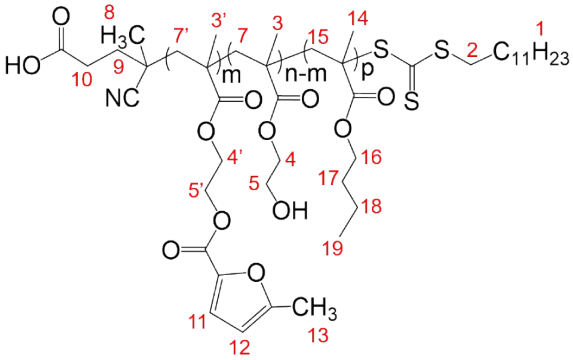
In a 25 mL RB flask, BMA (1 g, 0.007 mol) and HEMA (0.61 g, 0.0046 mol) monomers were dissolved in 2 mL of DMF followed by the addition of CDTPSA (0.047 g, 0.12 mmol) as a CTA and thermal initiator ABCVA (0.008 g, 0.03 mmol). After purging N_2 for 45 min at r.t., the polymerization was continued for 16 h at 80 °C. The gluey copolymer was solubilized in a little volume of DMF and precipitated from excess cold *n*-hexane. The precipitated polymer was washed several times and dried in a vacuum oven at 60 °C.



^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 4.26-4.06 (H^4), 4.03-3.92 (H^{16}), 3.91-3.79 (H^5), 3.25 (H^2) 2.16-0.73 (alkyl Hs).

3.4 Functionalization of **P2** copolymer with 5-methyl-2-furoate groups [**P2**-$PMFMA_{26}$ (**P2Fu**)]

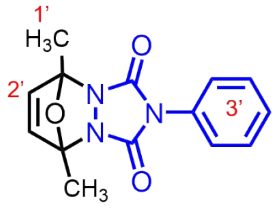
0.5 g **P3** polymer (0.0013 mol reactive HEMA), MFA (0.25 g, 0.0019 mol) and 4-dimethylamino pyridine (DMAP) (0.024 g, 0.0002 mol) were taken in a 10 mL RB flask and dissolved in 1 mL DMF and cooled in an ice bath. N, N-dicyclohexylcarbodiimide (DCC) (0.431 g, 0.0021 mol) was dissolved in 0.5 mL DMF and then added dropwise to the above ice-cooled solution. The reaction was then continued for 36 h at r.t. for an increased extent of grafting. The polymer solution was then filtered and precipitated in ethanol. The modified polymer was dried in a vacuum oven at 40 °C. The extent of conversion of HEMA units was measured via ^{1}H NMR analysis (conversion > 95 %).



^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 7.23-7.03 (H^{11}), 6.38-6.18 (H^{12}), 4.56-4.28 ($H^{5'}$), 4.27-4.01 ($H^{4'}$), 4.00-3.95 (H^4), 3.95-3.71 (H^{16}), 3.61-3.49 (H^5), 3.19 (H^2), 2.43-2.20 (H^{13}) 2.13-0.46 (alkyl Hs).

3.5 Reaction of 2,5-Dimethyl furan (DMFu) with PhTAD

DMFu (0.026 g, 0.27 mmol, 0.4 mL THF solvent) and freshly powdered PhTAD (0.052 g, 0.29 mmol, 0.4 mL THF solvent) were taken and dissolved in THF solvent separately. The TAD solution was added to the solution of the furan derivative. The completion of the reaction was evidenced from the fast discoloration of red-colored TAD derivative within less than 20 sec. The solution was allowed for further spectroscopy analyses. A similar sort of reaction was carried out in $CDCl_3$ solvent to analyze the final reaction product via UV-Vis, ^{1}H NMR, and ^{13}C NMR spectroscopy.

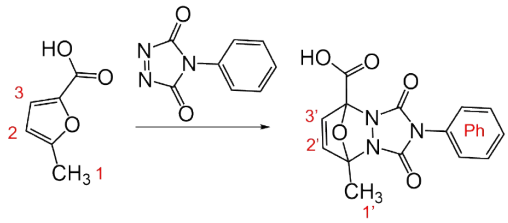


^{1}H NMR (600 MHz, CDCl3) δ (ppm): 7.58–7.33 (H3'), 6.81 (H2'), 2.38 (H1').

MALDI-MS of DMFu-PhTAD DA-click adduct: [M + H$^+$] = 272.68 (F.W = 271.27)

3.6 Reaction of 5-methyl-2-furoic acid (MFA) with PhTAD

MFA (0.023 g, 0.18 mmol) and freshly powdered PhTAD (0.0031 g, 0.018 mmol) were taken and dissolved in $CDCl_3$ solvent separately. The TAD solution was added to the solution of the furan derivative. The completion of the reaction was evidenced from the gradual disappearance of red colored TAD derivative within 1 h under r.t.



^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.59–7.33 (H^{Ph}), 7.26 (residual H^3), 6.79 ($H^{3'}$), 6.35 ($H^{2'}$), 6.19 (residual H^2), 2.48 ($H^{1'}$), 2.42 (residual H^1).

3.7 Modification of **P1Fu** with PhTAD via DA-click chemistry

The polymer modified with substituted furan groups, 0.1 g (0.34 mmol reactive MFMA units) of **P1Fu** was reacted with 0.0059 g (0.034 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione (PhTAD) (molar ratio of reactive MFMA: PhTAD = 10:1) were dissolved separately in 0.2 ml of THF solvent (or $CDCl_3$ solvent for ^{1}H NMR analysis). The two solutions were mixed at r.t. (~30 °C). It took 90 min for the complete disappearance of the red color of the TAD derivative. The completion of the 'click' reaction was evidenced by the ultimate disappearance of the red color of the PhTAD. The resultant polymer solution was further analyzed via UV-Vis and ^{1}H NMR spectroscopy analyses.

3.8 Preparation of chemical network of **P1Fu** with bisTAD via DA-click chemistry

0.1 g of **P1Fu** (0.34 mmol reactive MFMA units) and 0.012 g (0.034 mmol) of bisTAD (molar ratio of MFMA: bisTAD = 10:1) were dissolved separately in 0.3 ml of THF solvent. The two solutions were mixed at r.t. (~30 °C). The solvent of the overall solution was evaporated under an ambient condition, which ultimately resulted in a gelled adduct within 2 h. The crosslinked polymer was dried in a vacuum oven and kept for further analyses.

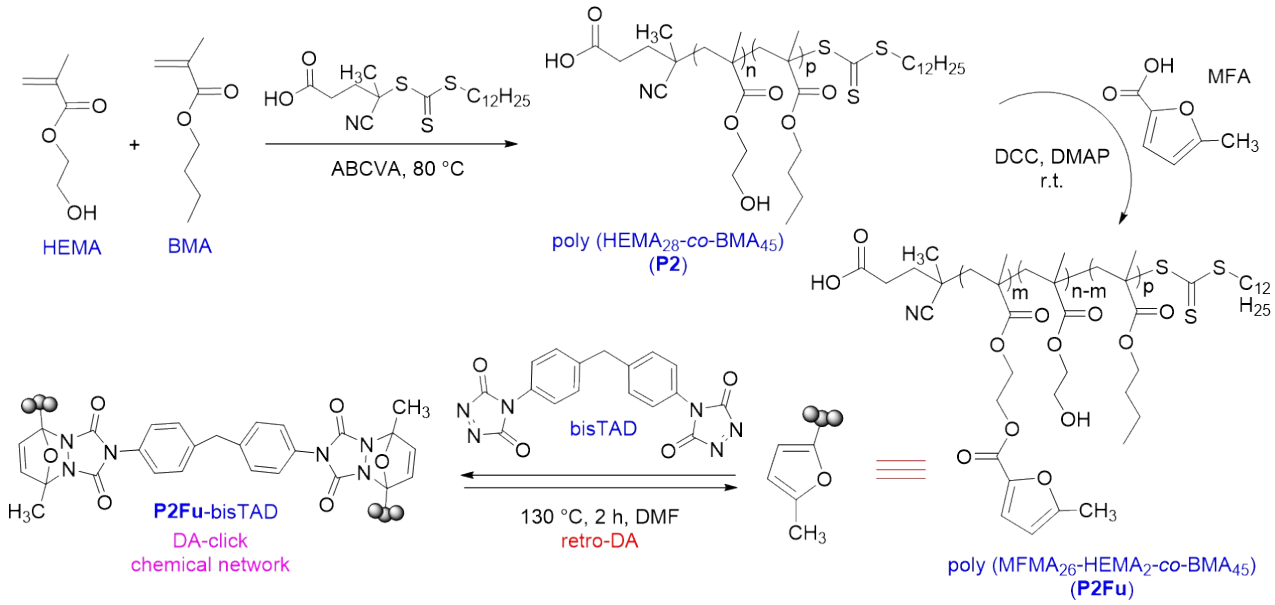
3.9 Preparation of bisTAD

The bisTAD was prepared according to the methodology mentioned in previous literature.[1]

3.10 Preparation of chemical network of **P2Fu** with bisTAD via DA-click chemistry

In the case, 0.1 g of **P2Fu** (0.15 mmol reactive MFMA) and 0.0054 g (0.015 mmol) of bisTAD (molar ratio of MFMA: bisTAD = 10: 1) were dissolved separately in 0.2 ml of THF solvent. The two solutions were mixed at r.t. (~30 °C), and the solvent of the resultant solution was evaporated under r.t. As the solvent was evaporating, the color of the TAD derivative gradually faded away and finally resulted in a gelled adduct within a duration of 2 h. The crosslinked polymer was dried in a vacuum oven and kept for further analyses.

4. Figures and tables



Scheme S1. Schematic illustration of the synthesis of the **P2Fu**-bisTAD DA network

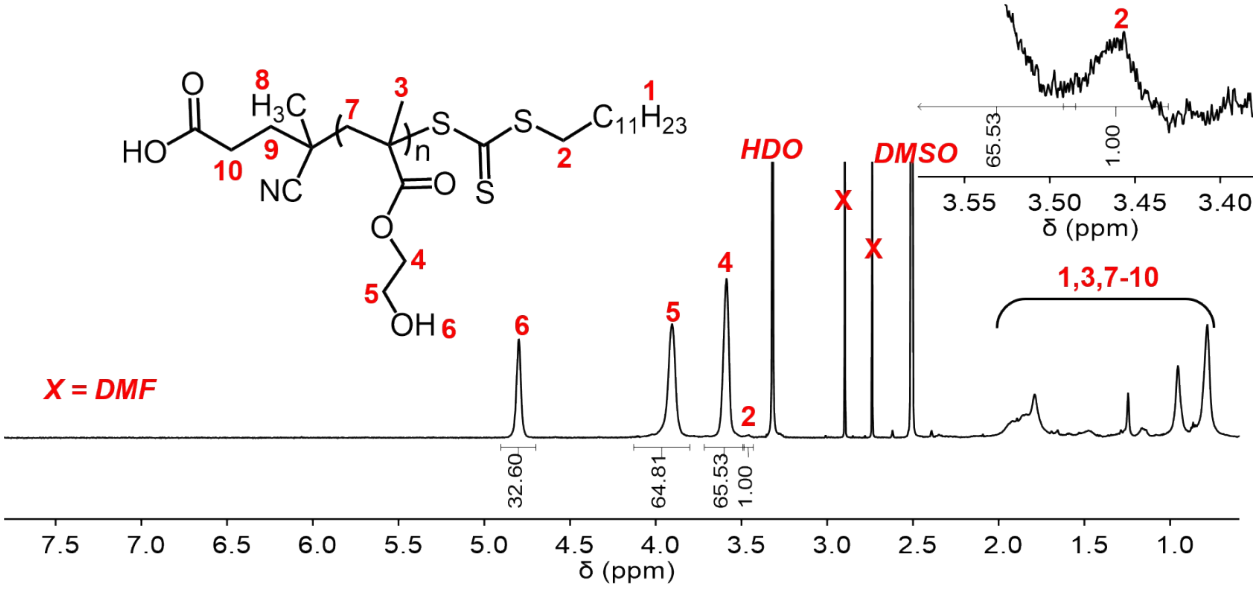


Figure S1. ^{1}H NMR analysis of the **P1** polymer in DMSO-d_6 solvent

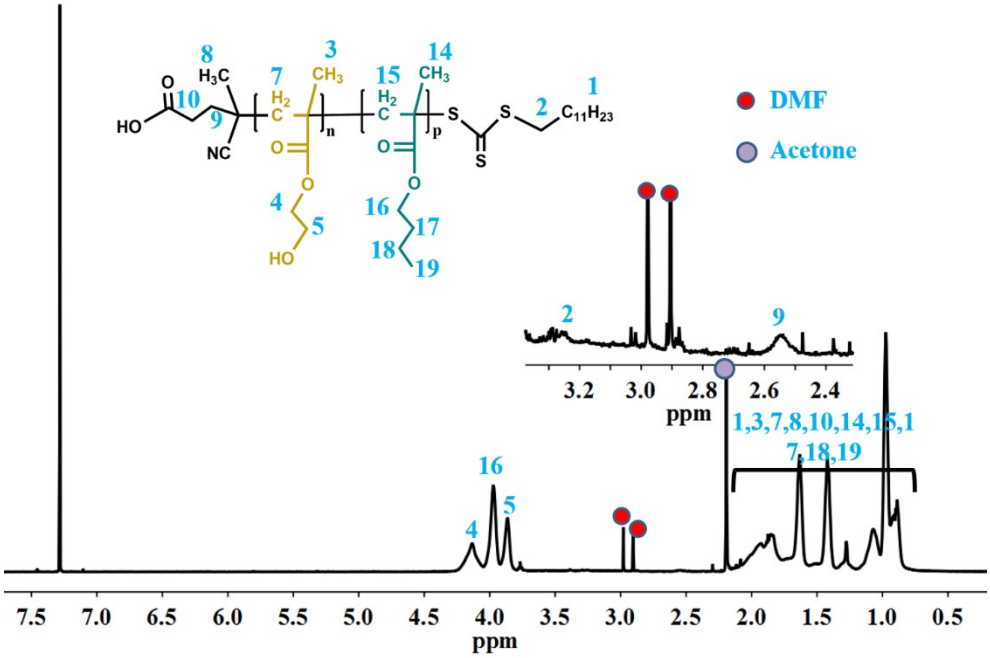


Figure S2. ^{1}H-NMR spectroscopy of **P2** copolymer in $CDCl_3$ solvent.

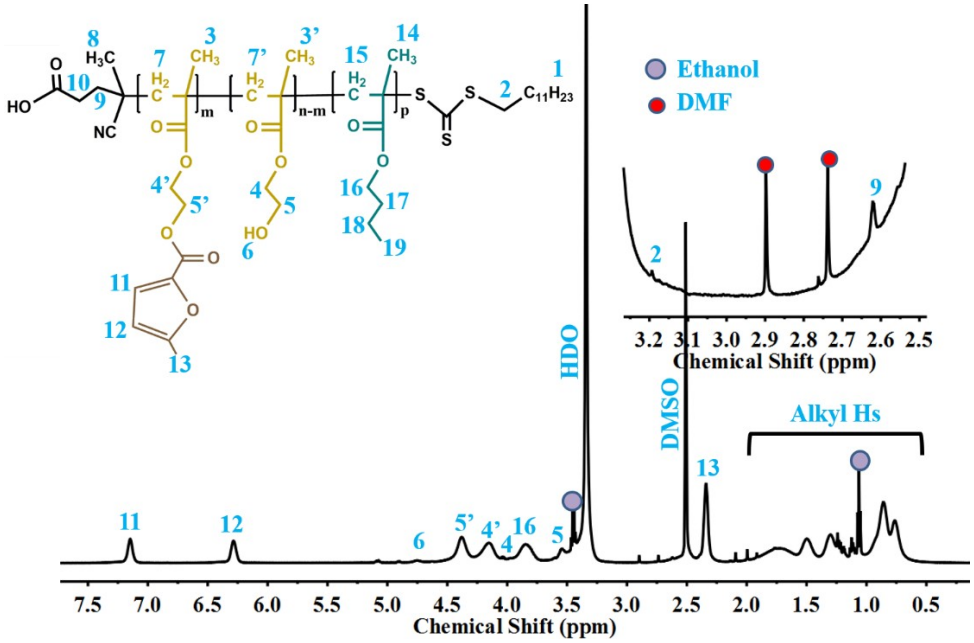


Figure S3. ^{1}H-NMR spectroscopy of **P2Fu** copolymer in DMSO-d_6 solvent.

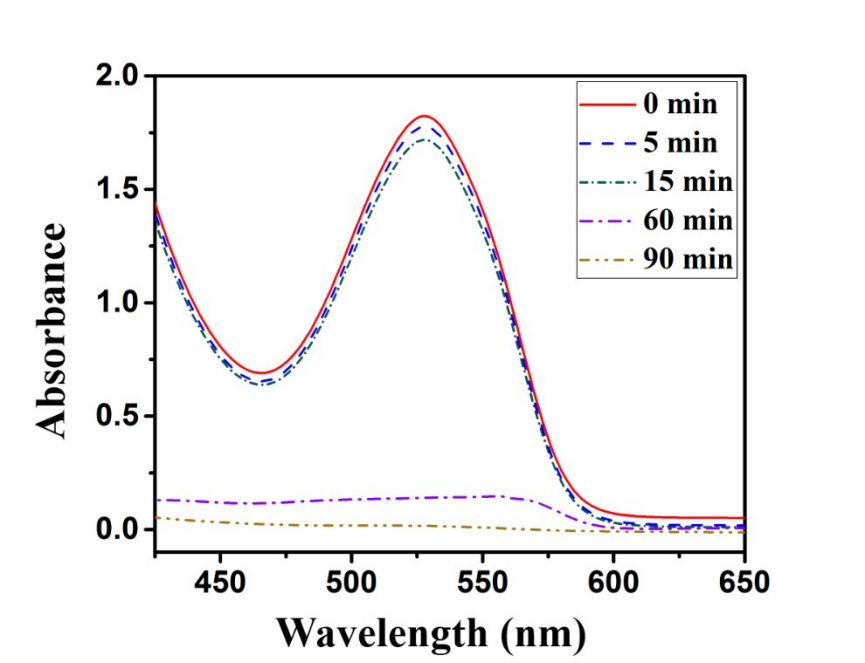


Figure S4. UV analysis of **P1Fu**-PhTAD polymer.

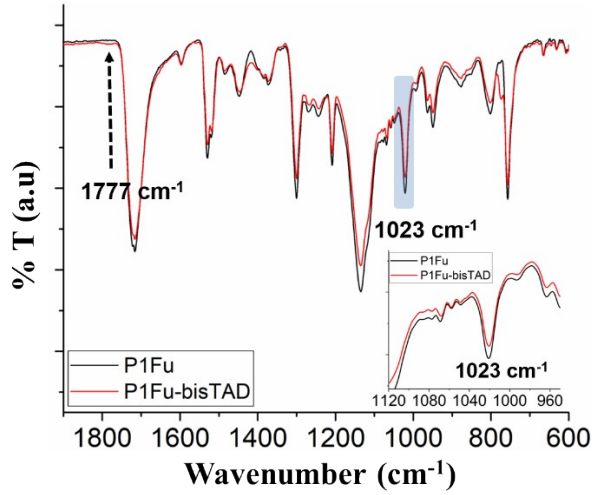


Figure S5. FTIR analysis of **P1Fu** and **P1Fu**-bisTAD DA polymer.

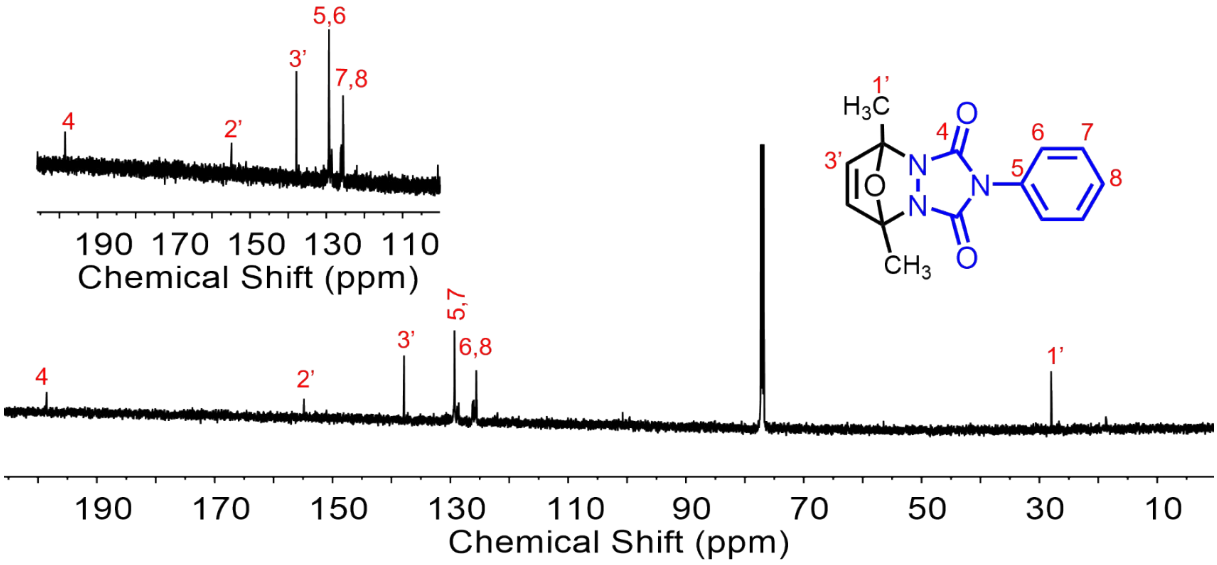


Figure S6. ^{13}C NMR analysis of DMFu-PhTAD DA adduct.

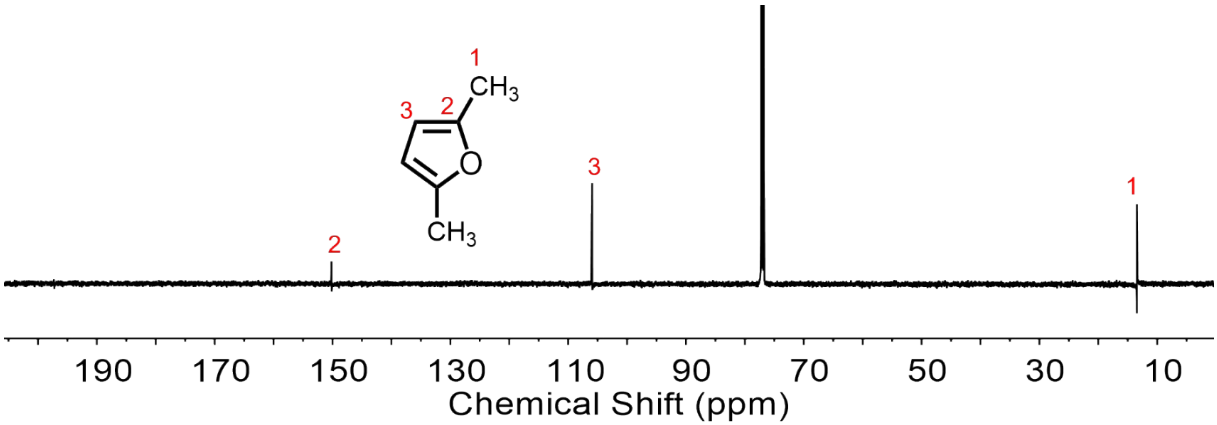


Figure S7. ^{13}C NMR spectrum of DMFu.

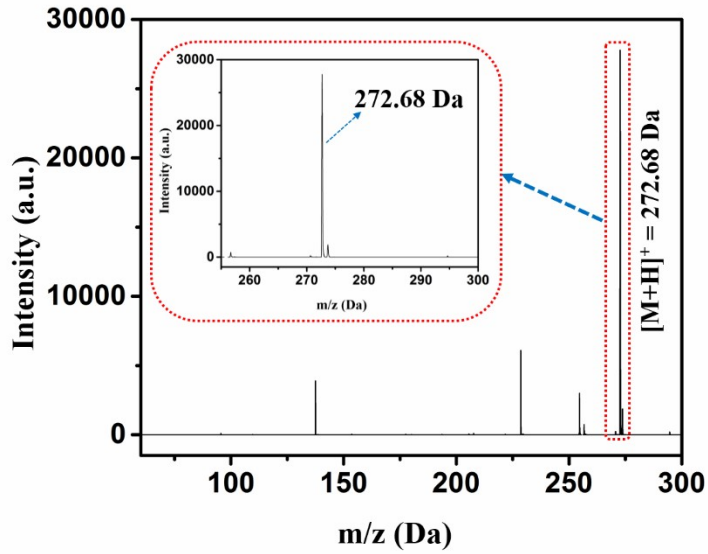


Figure S8. MALDI-MS analysis of DMFu-PhTAD DA-click adduct.

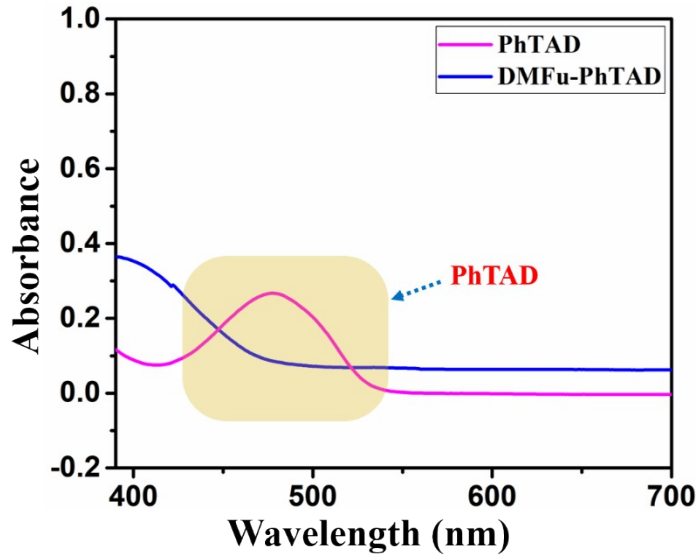


Figure S9. UV analysis of PhTAD and DMFu-PhTAD.

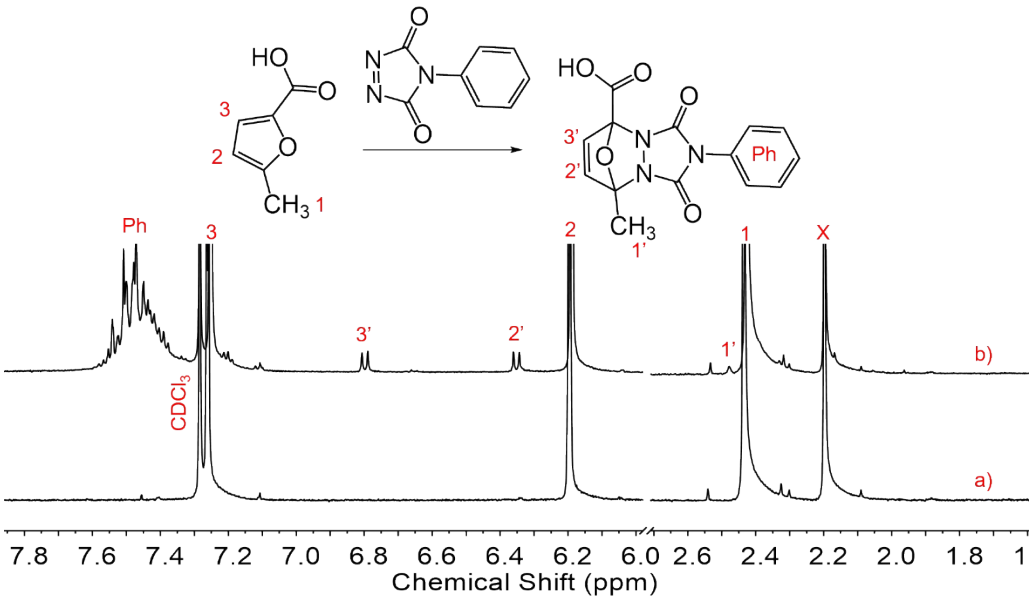


Figure S10. 1H NMR analysis of a) MFA and b) MFA-PhTAD (molar ratio of MFA: PhTAD = 1: 0.125) in $CDCl_3$ solvent.

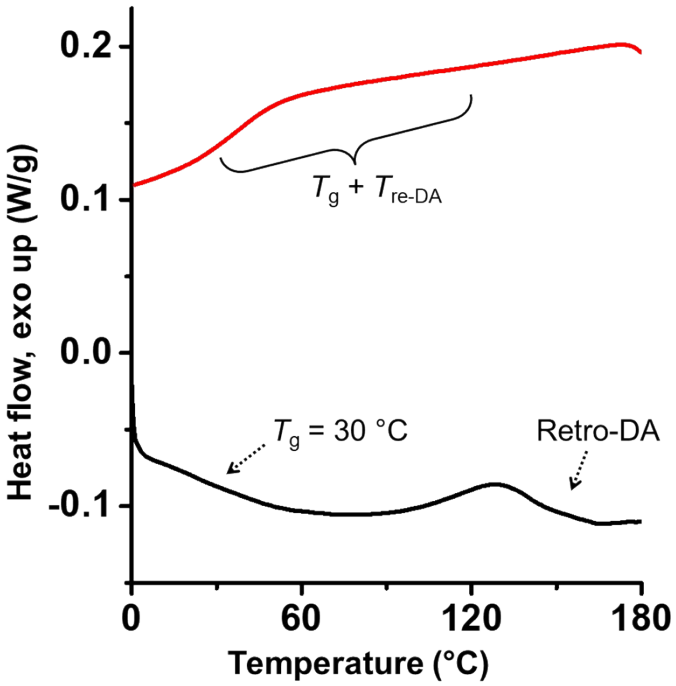


Figure S11. DSC analysis of **P2Fu**-bisTAD DA adduct.

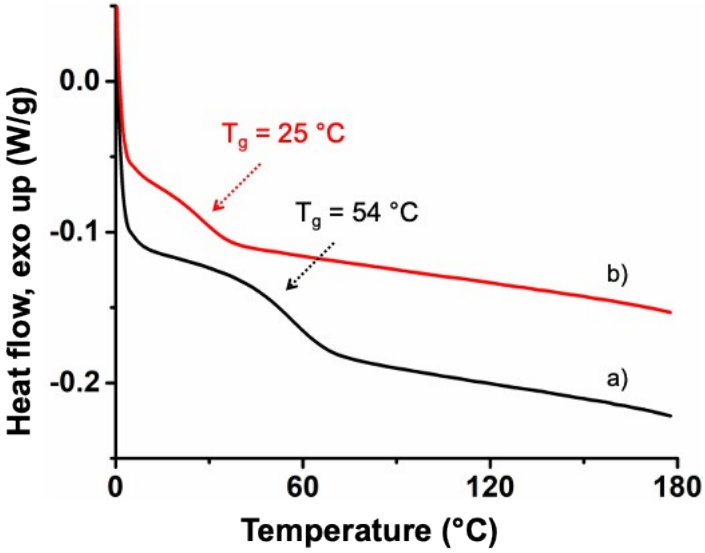


Figure S12. DSC analysis of a) **P1Fu** and b) **P2Fu**

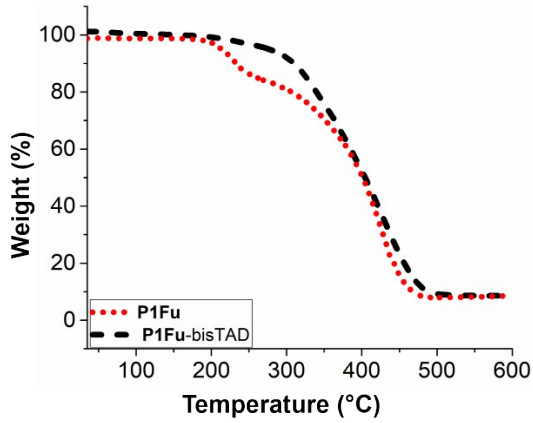


Figure S13. TGA analysis of **P1Fu** and **P1Fu**-bisTAD DA adduct.

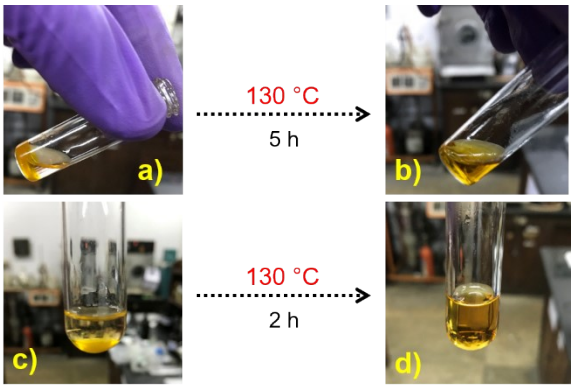


Figure S14. Solubility of **P1Fu**-bisTAD DA network at a) r.t., b) 130 °C (after 5 h); and **P2Fu**-bisTAD DA network c) at r.t., and d) 130 °C (after 2 h).

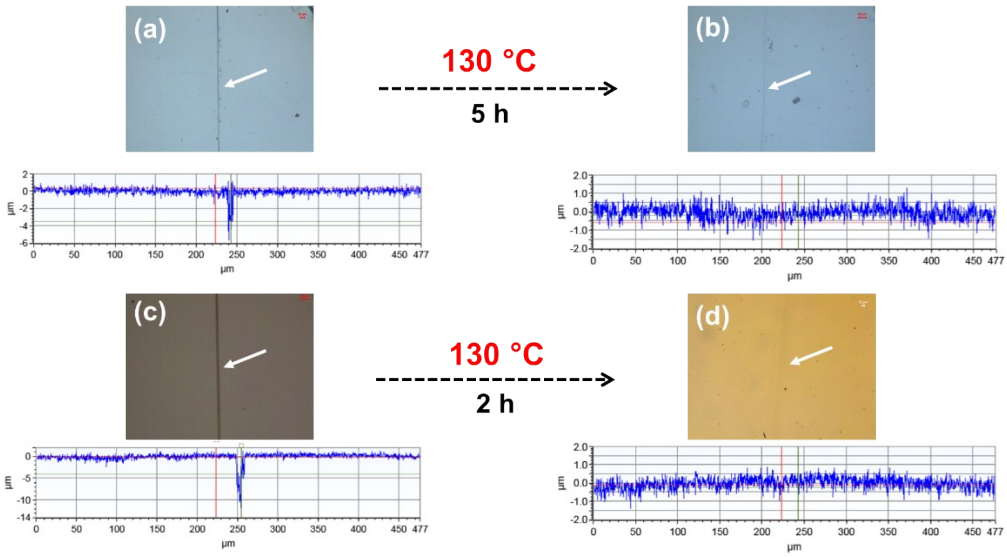


Figure S15. 3D-OSP images of **P1Fu**-bisTAD a) scratched at r.t. and b) after heating at 130 °C for 5 h, **P2Fu**-bisTAD c) scratched at r.t. and d) after heating at 130 °C for 2 h.

Table S1. Summary of healing efficiencies of all crosslinked polymer films

Crosslinked Polymers [a)]	Post-notch Depth (μm)	Post-heal Depth (μm)	E_H (%) [b)]	Duration of healing
P1Fu-bisTAD network	3.8	0.7	81.5 ± 0.8	5 h
P2Fu-bisTAD network	3.1	0.1	93.3 ± 1.9	2 h

[a)] The initial depth of all the polymer samples was ~0.0 μm.

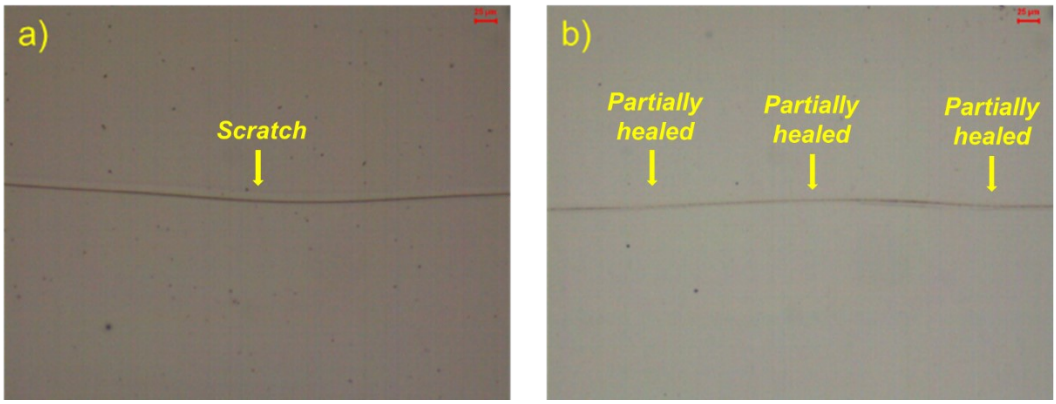


Figure S16. OM images of **P2Fu**-bisTAD after a) scratch at r.t. and b) heating at 100 C for 2 h (followed by cooling it to r.t.).

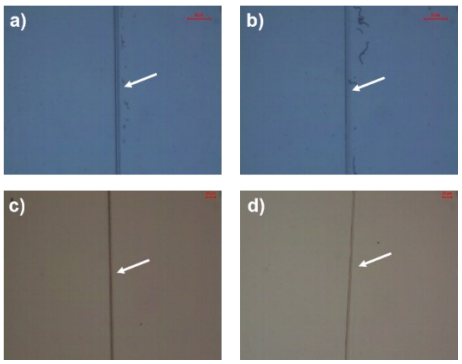


Figure S17. Optical microscopy images of P1Fu a) scratched at r.t. and b) after heating at 130 °C for 5 h, P2Fu c) scratched at r.t. and d) after heating at 130 °C for 2 h.

5. References

1. P. Mondal, S. K. Raut, N. K. Singha, *J. Polym. Sci. Part A: Polym. Chem.* 2018, **56**, 2310.
2. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.
3. L. P. Liu, D. Malhotra, R. S. Paton, K. Houk and G. B. Hammond, *Angew. Chem. Int. Ed.*, 2010, **49**, 9132.
4. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, 72, 650.
5. T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294.

6. Gaussian 16, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. 34 Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.