Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information for

Copolymerization of alkyl diazoacetate with α,β-unsaturated aldehyde: synthesis and application

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Contents:

Supplementary Results and discussion

XRD curves

XRD curves (**Figure S1**) reveal that the obtained copolymers are all random.

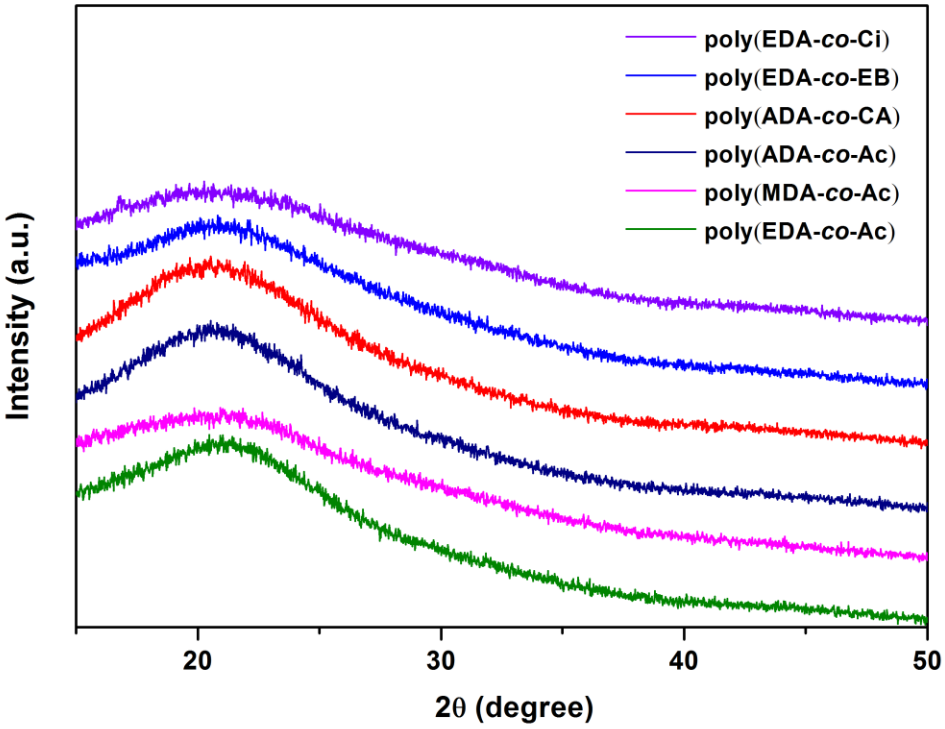

Figure S1. XRD curves of the copolymers.

^{1}H NMR and ^{13}C NMR spectroscopy

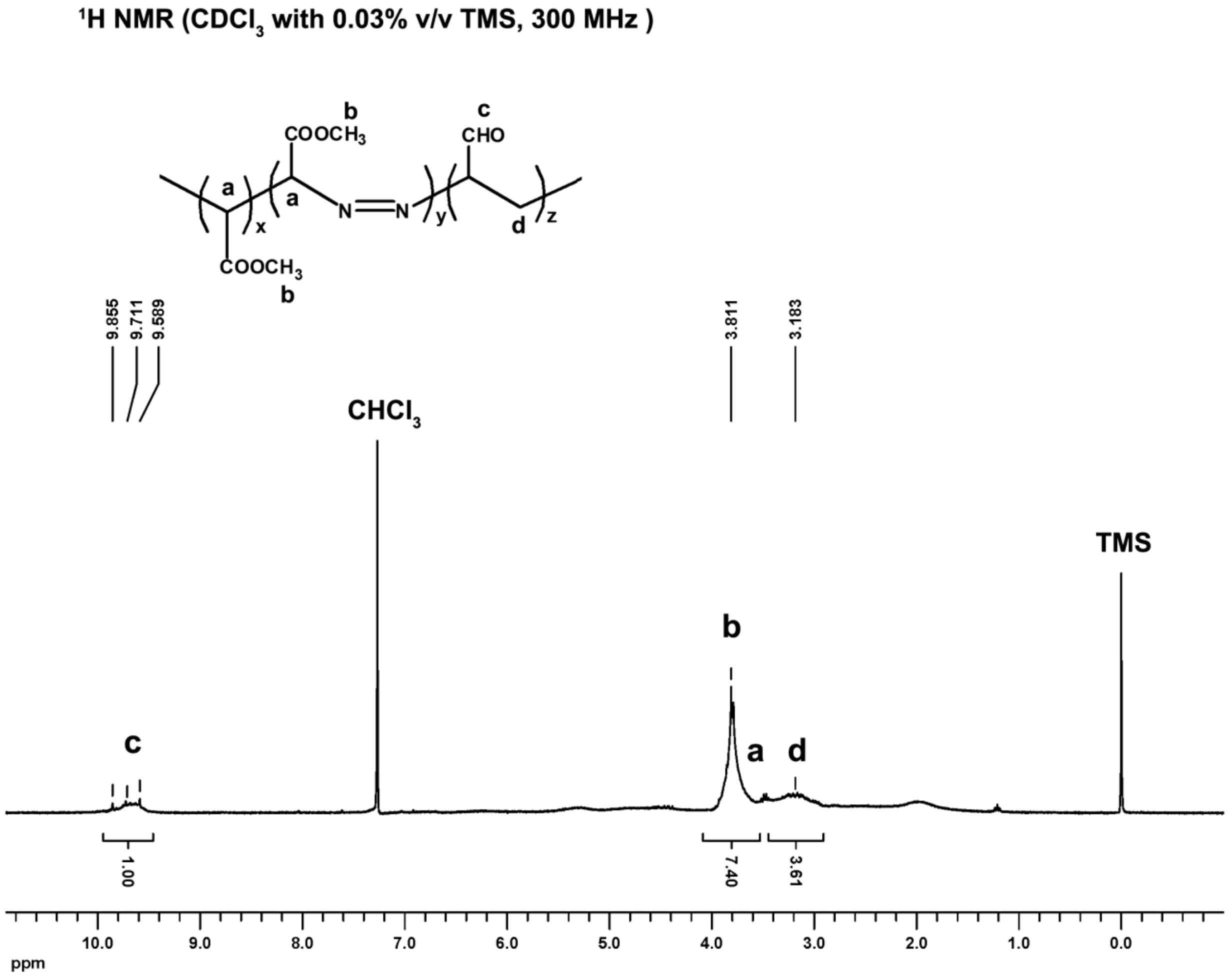

Figure S2. ^{1}H NMR spectrum of poly(MDA-*co*-Ac).

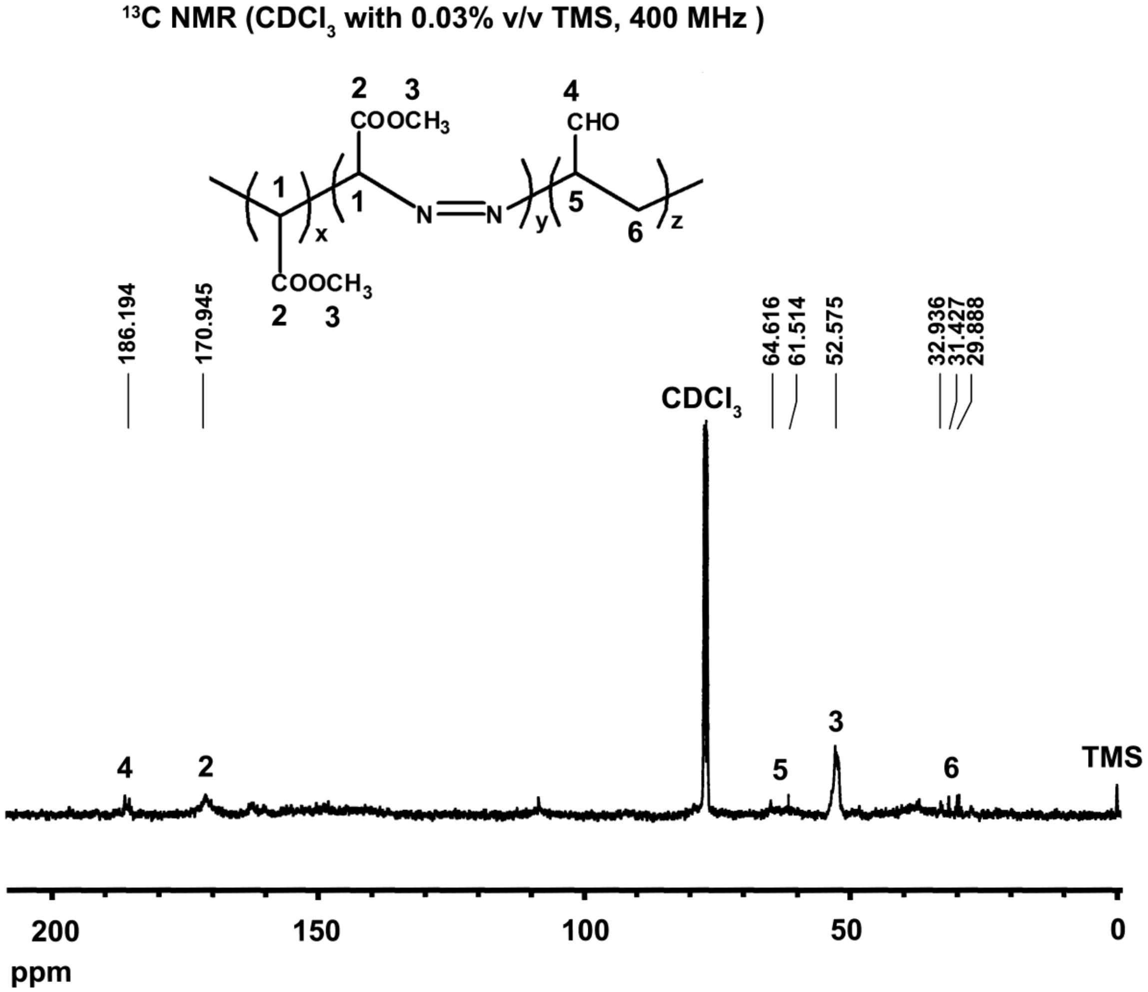

Figure S3. ^{13}C NMR spectrum of poly(MDA-*co*-Ac).

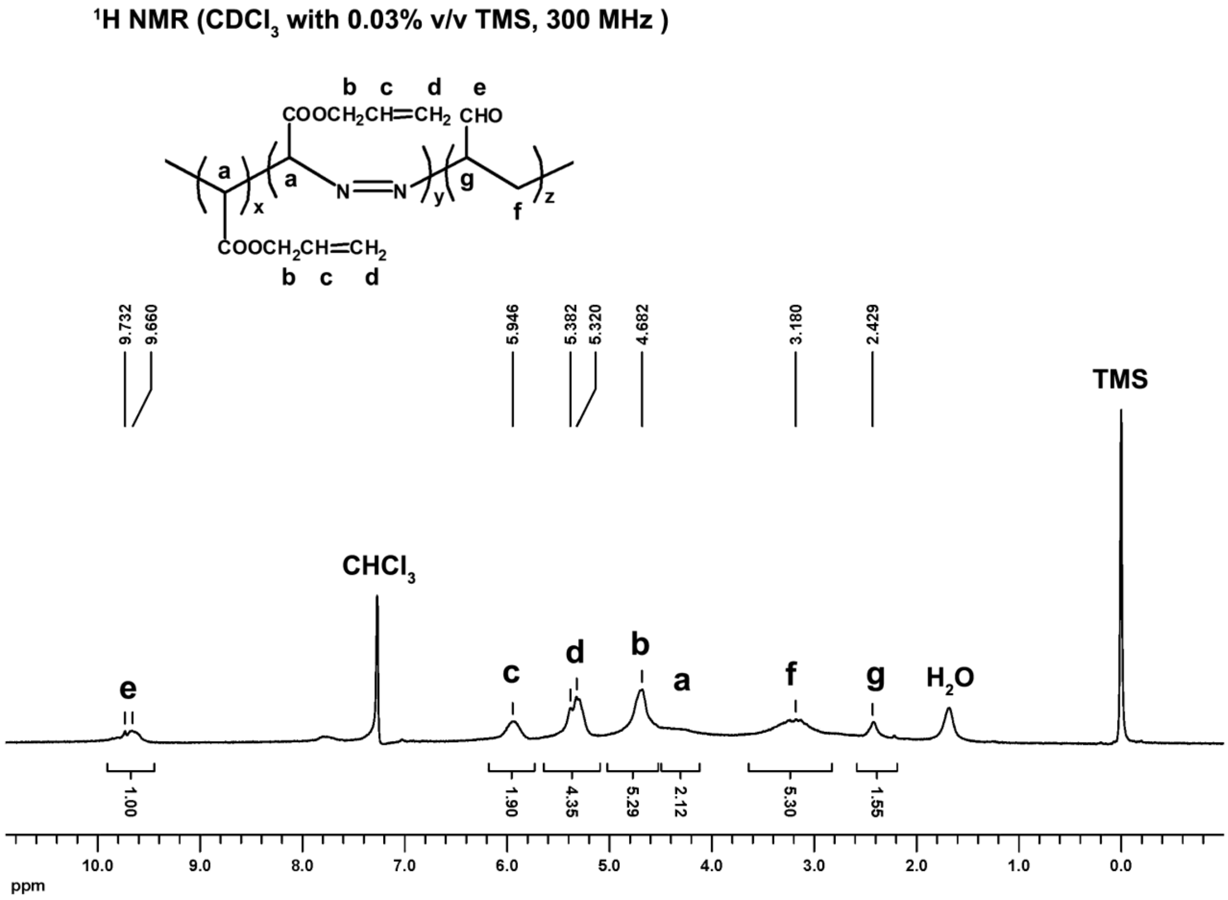

Figure S4. ^{1}H NMR spectrum of poly(ADA-*co*-Ac).

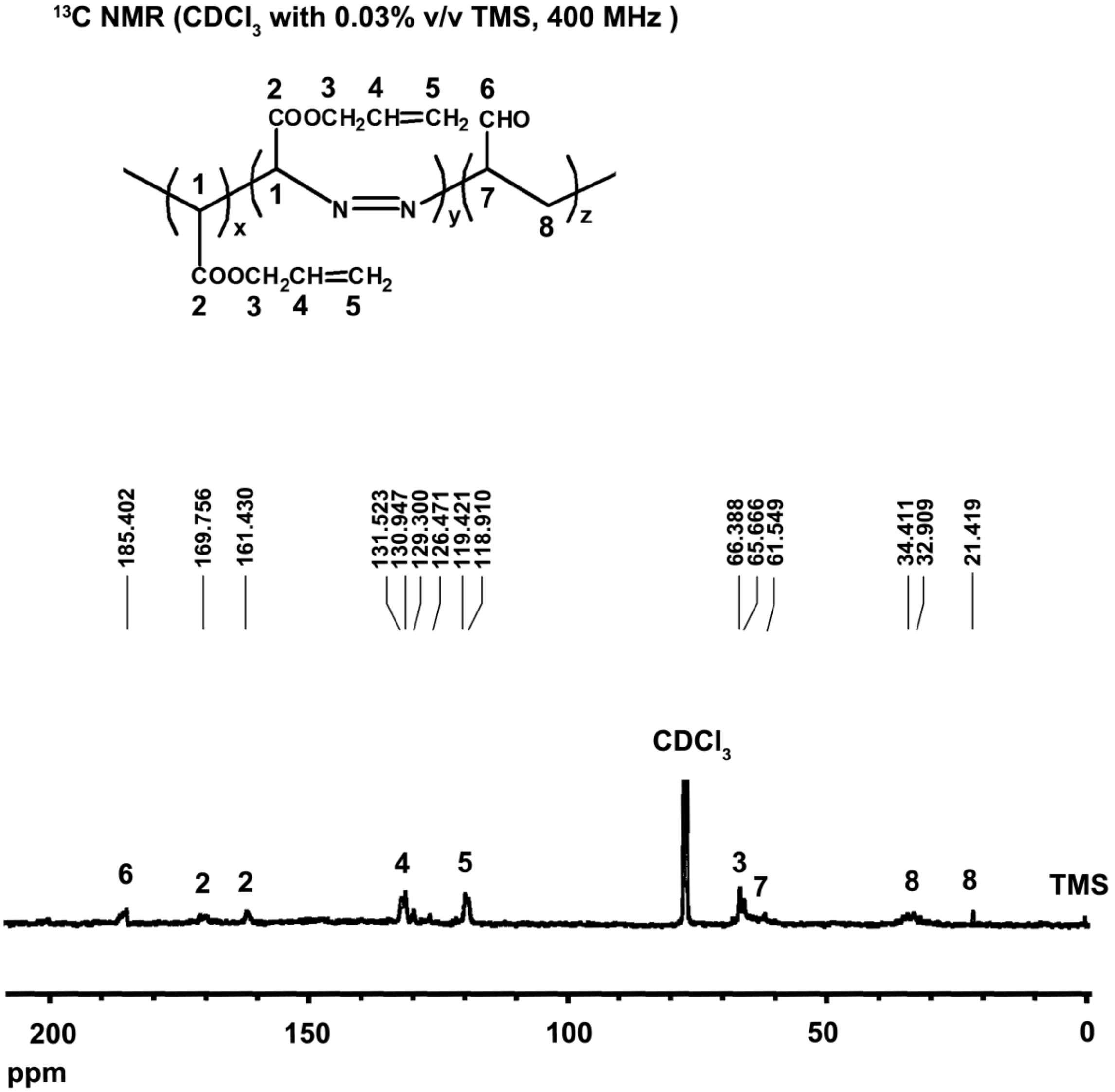

Figure S5. ^{13}C NMR spectrum of poly(ADA-*co*-Ac).

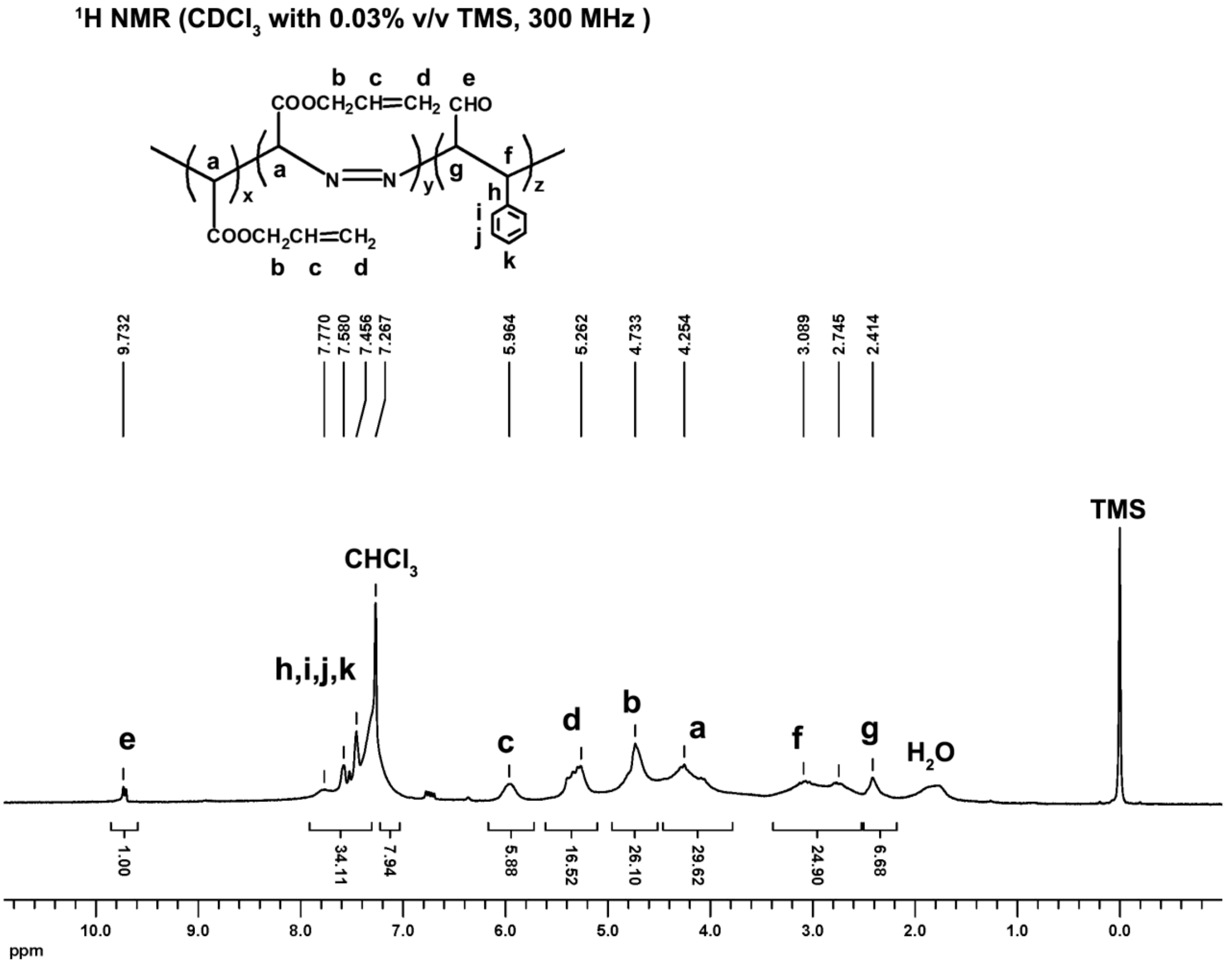

Figure S6. ^{1}H NMR spectrum of poly(ADA-*co*-CA).

^{13}C NMR ($CDCl_3$ with 0.03% v/v TMS, 400 MHz)

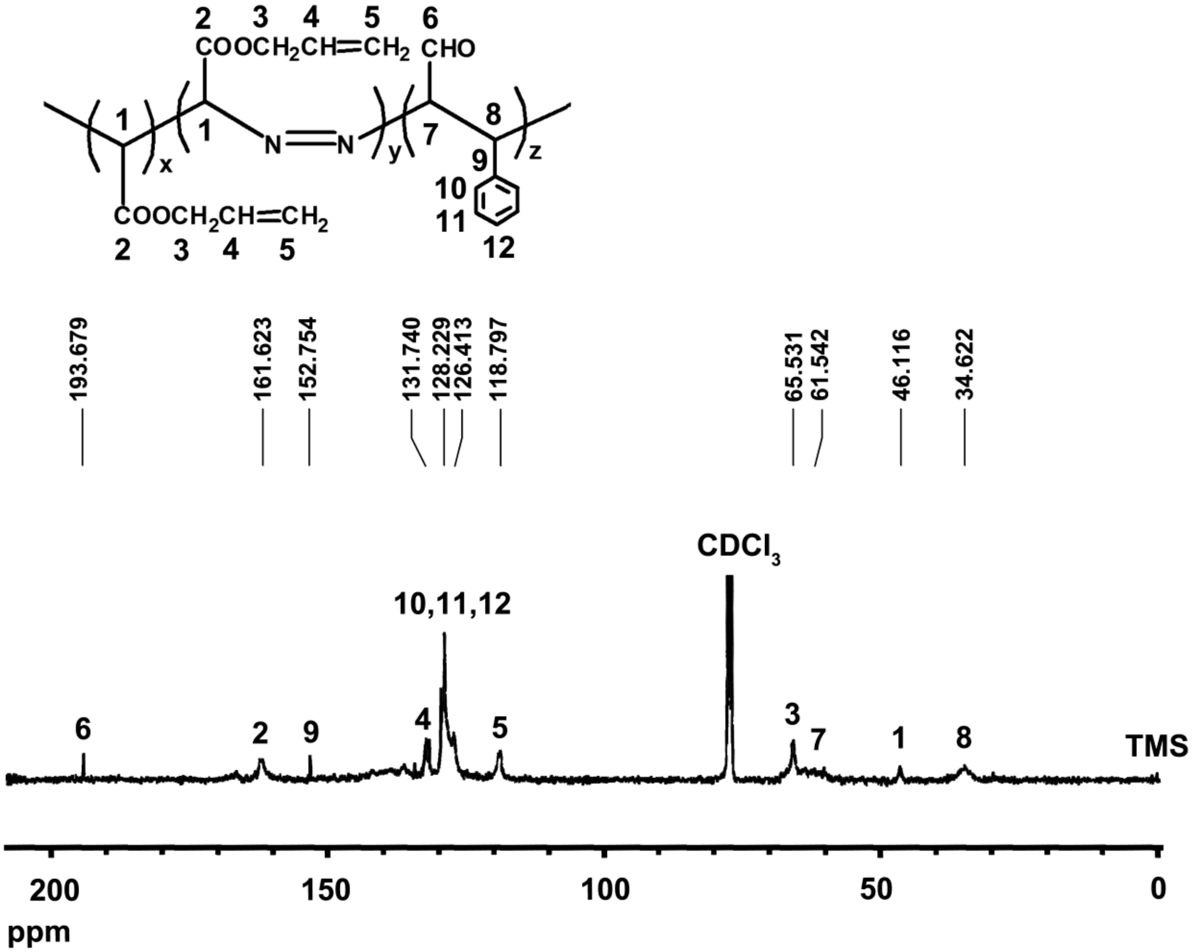

Figure S7. ^{13}C NMR spectrum of poly(ADA-*co*-CA).

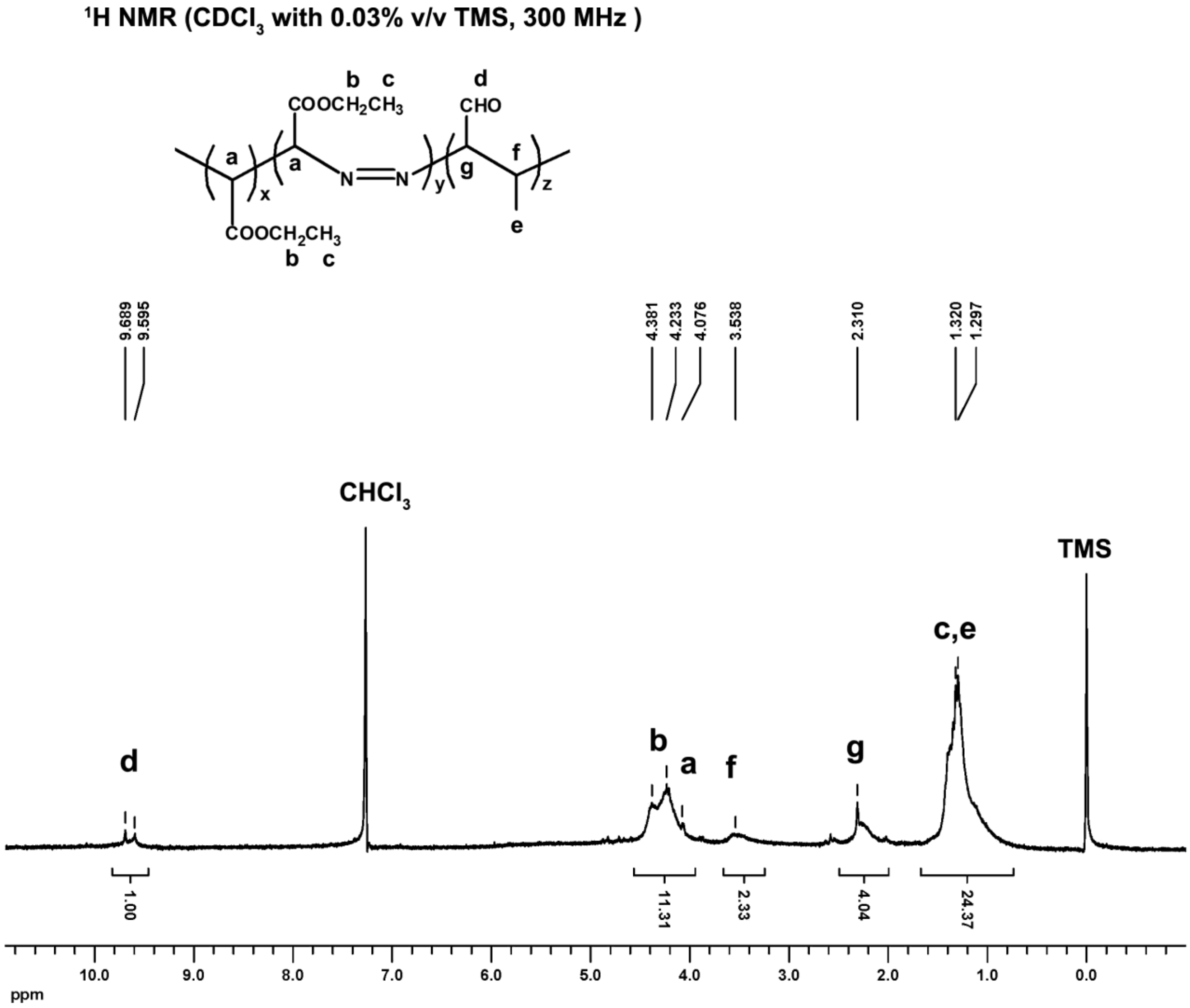

Figure S8. ^{1}H NMR spectrum of poly(EDA-*co*-EB).

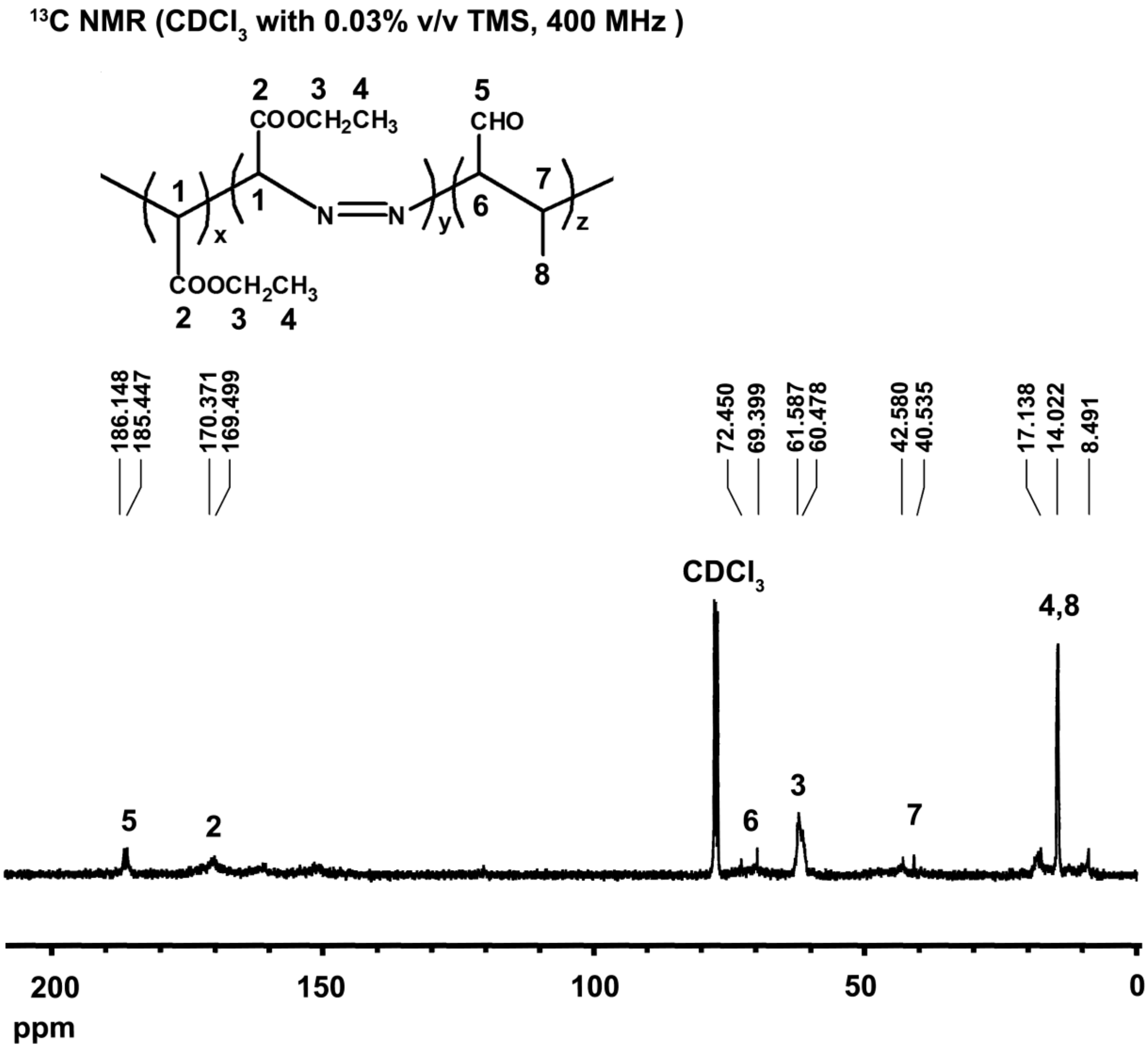

Figure S9. ^{13}C **NMR spectrum of poly(EDA-*co*-EB).**

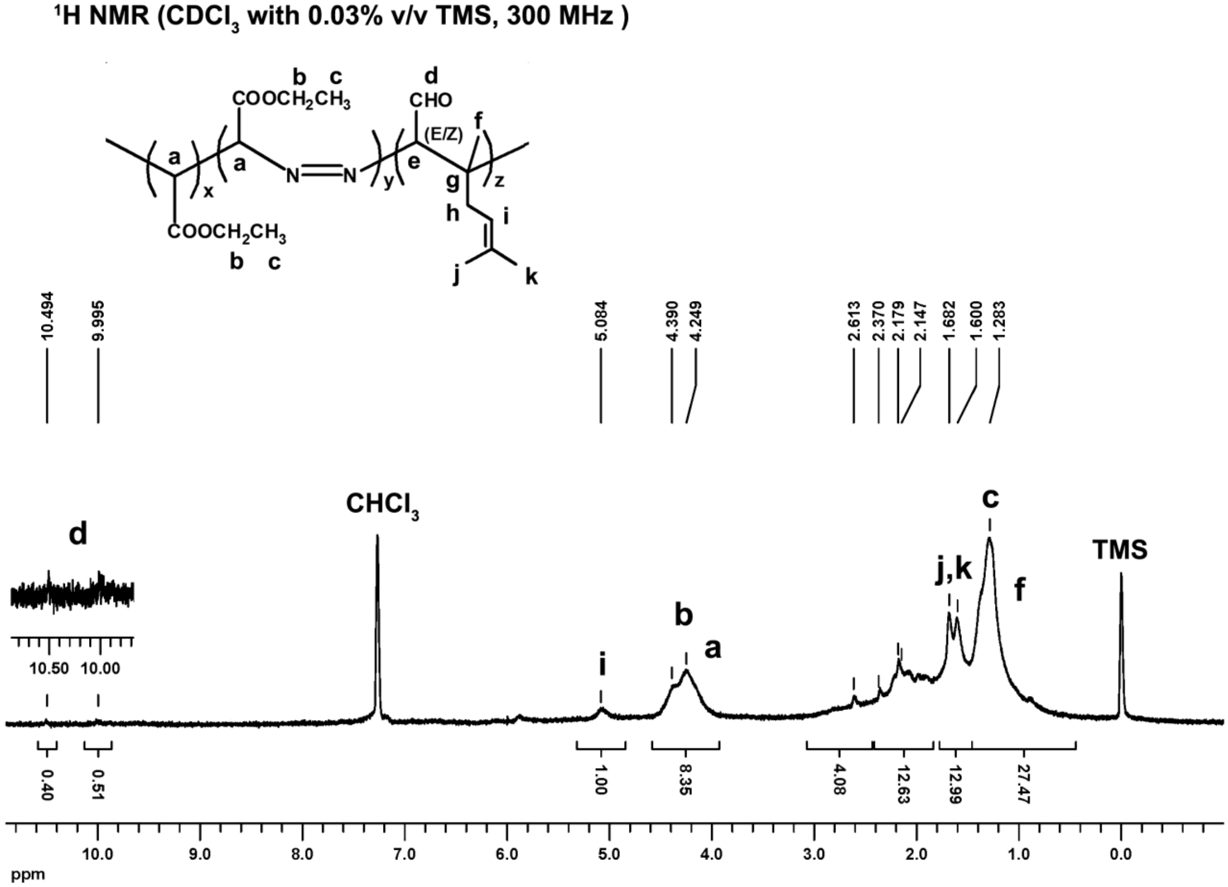

Figure S10. ^{1}H NMR spectrum of poly(EDA-*co*-Ci).

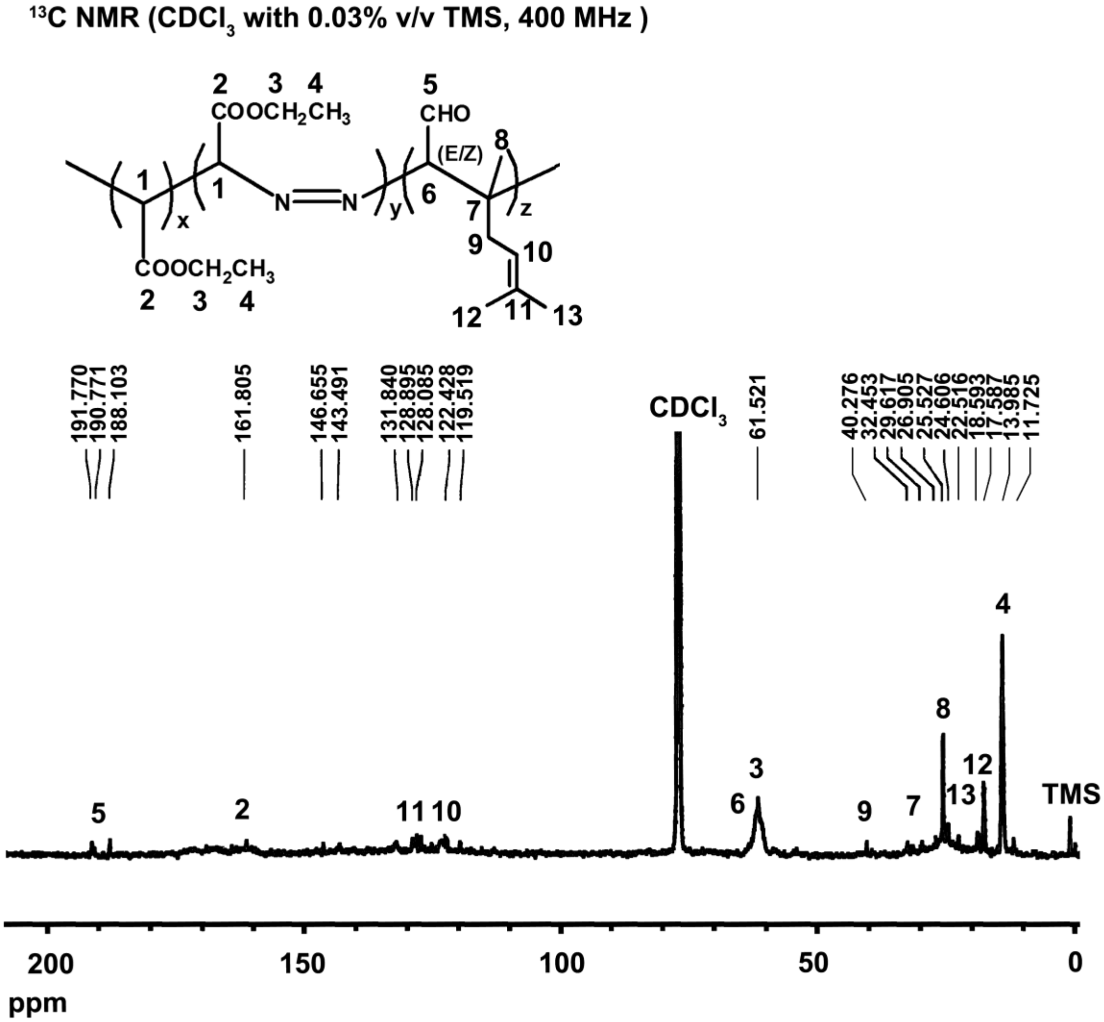

Figure S11. ^{13}C NMR spectrum of poly(EDA-*co*-Ci).

FT-IR spectroscopy

The FT-IR spectra of the obtained copolymers (**Figure S12**) show that the intense bands at approximately 1700 cm^{-1} belong to the carbonyl and aldehyde groups. The peak at approximately 1550 cm^{-1} can be assigned to the azo group derived from EDA.[1]

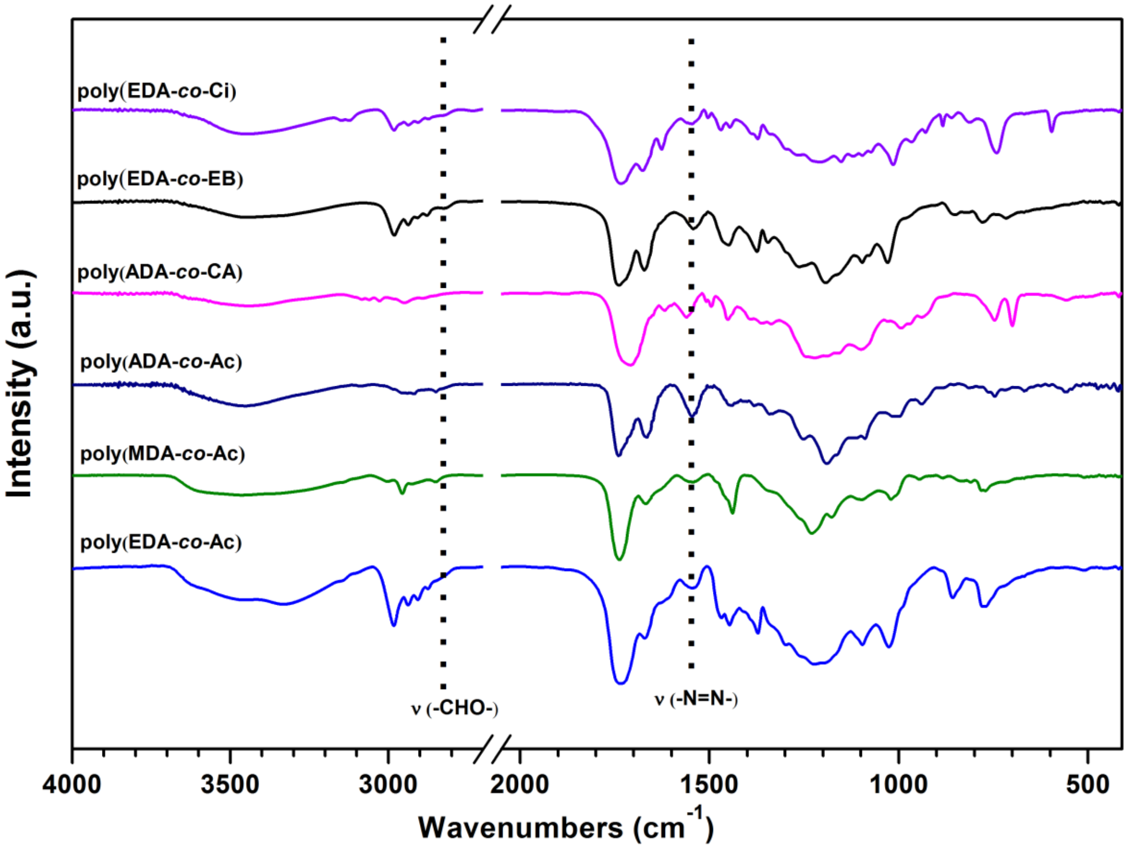

Figure S12. FT-IR spectra of the copolymers.

Thermal properties

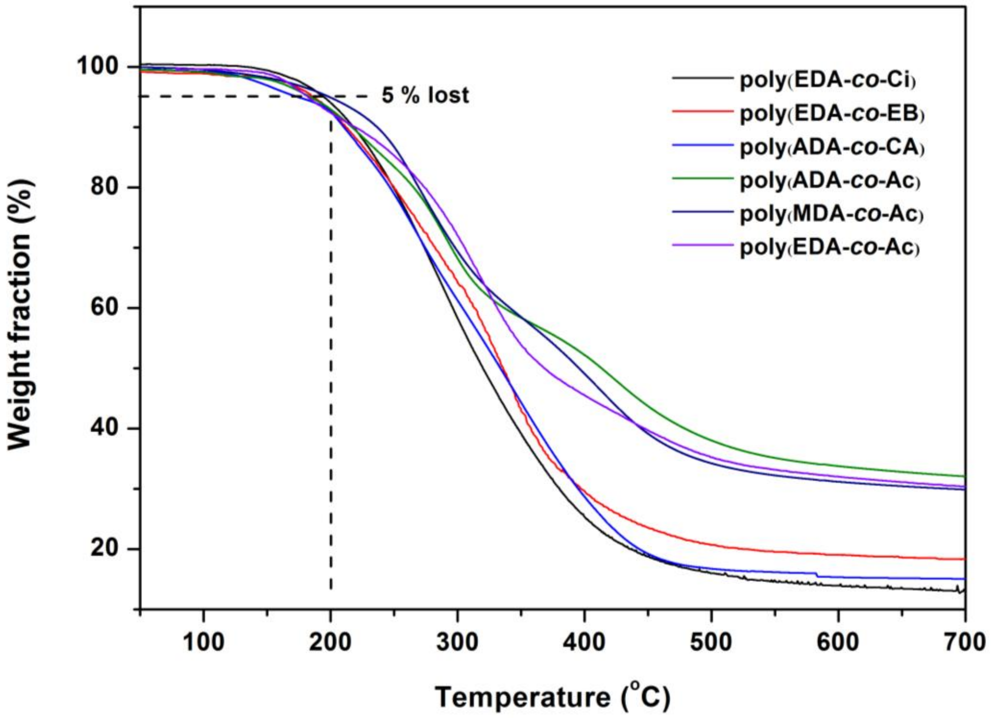

Figure S13. TGA curves of the copolymers under nitrogen atmosphere.

Table S1 TGA data of the copolymers

Copolymer	$T_L/^oC^a$
poly(EDA-*co*-Ci)	194.8
poly(EDA-*co*-EB)	186.7
poly(ADA-*co*-CA)	174.5
poly(ADA-*co*-Ac)	184.2
poly(MDA-*co*-Ac)	199.2
poly(EDA-*co*-Ac)	182.2

[a] T_L is defined as the temperature for 5% loss of weight of the copolymer.

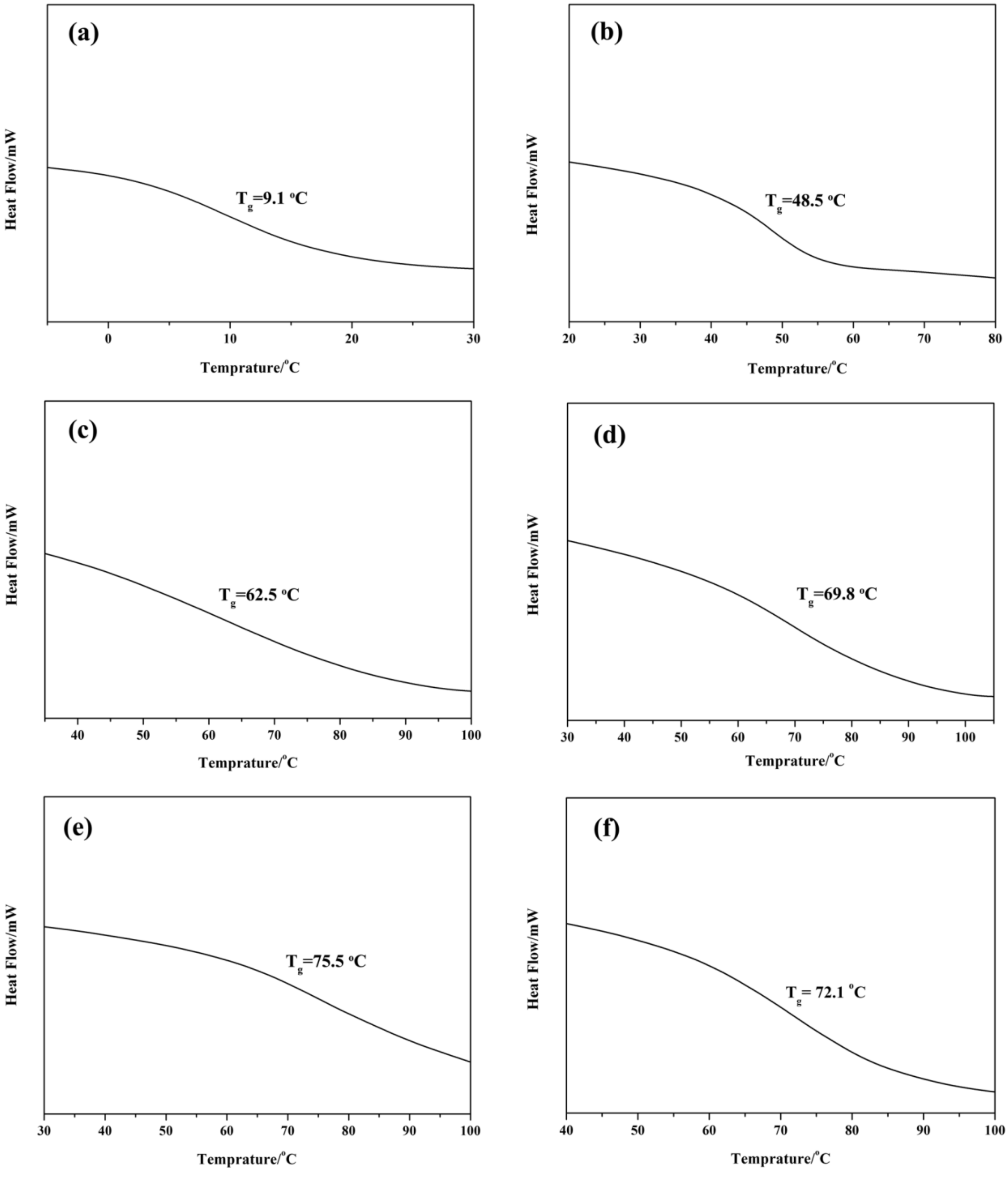

Figure S14. DSC curves of the copolymers. a, poly(EDA-*co*-Ci); b, poly(EDA-*co*-EB); c, poly(ADA-*co*-CA); d, poly(ADA-*co*-Ac); e, poly(MDA-*co*-Ac); f, poly(EDA-*co*-Ac). These data are recorded in the 2nd round. T_g means glass transition temperature.

The thermal properties of the obtained copolymers are examined by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). **Figure S13** is the TGA curves of the copolymers, which shows that all the obtained copolymers are thermostable, losing merely 5% of their weights at temperatures higher than 174.5^{o}C (T_L). The details are summarized in **Table S1**. **Figure S14** is the DSC curves of the obtained copolymers, and the glass transition temperatures (T_g) between 9.1 and 75.5 ^{o}C are observed.

Mechanism studies of copolymerization of EDA and Ac by inhibition of TEMPO

The radical inhibitor 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) retards the copolymerization of EDA and Ac significantly. The proton signals of CH_2=CH in Ac disappear in ten minutes without TEMPO, but sixty minutes should be taken with 0.5 equiv TEMPO (**Figure S15**). In addition, in the reaction with TEMPO, the gas isn't released so extensively and the temperature doesn't rise so rapidly as in that without TEMPO. In conclusion, the copolymerization is a possible radical mechanism. [2]

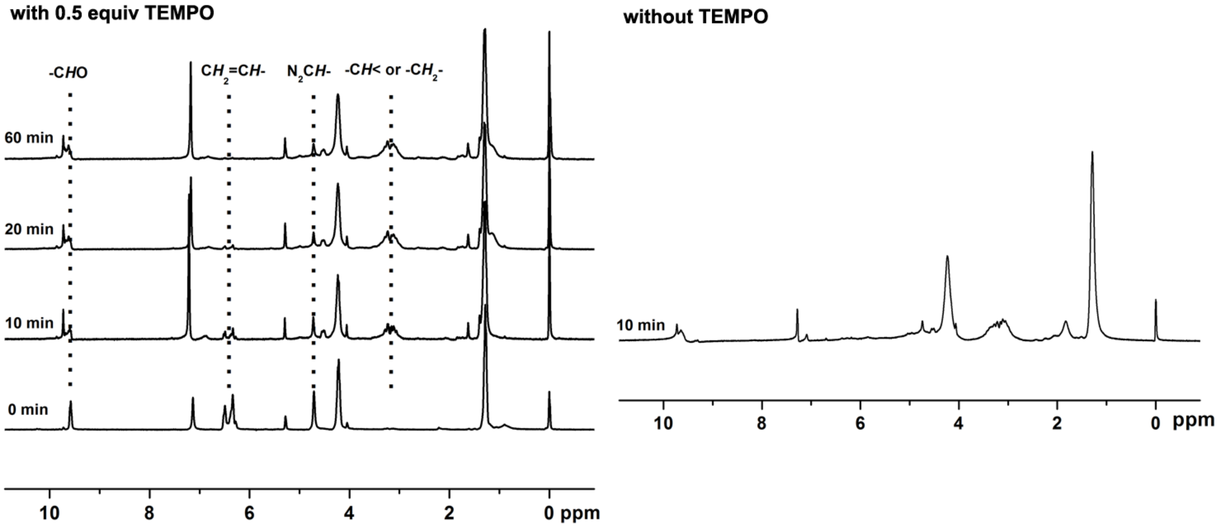

Figure S15. TEMPO inhibition effects on the copolymerization of EDA and Ac. Conditions: Ac (5.0 mmol, 1.0 equiv), EDA (5.0 mmol, 1.0 equiv) are mixed at room temperature under blowing nitrogen.

Single-photon fluorescence spectra of monomers

Figure S16 shows that only EB and CA exhibit rather weak fluorescence, and other monomers are almost non-luminescent.

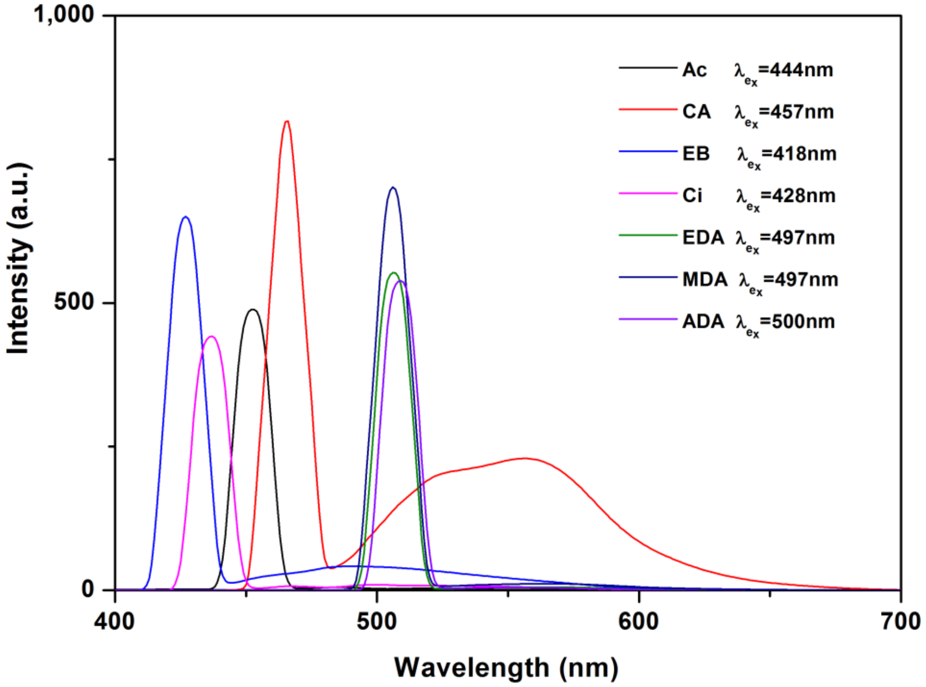

Figure S16. Fluorescence emission spectra of the monomers with slit width of 5.0/5.0 nm. All monomers are measured without solvent. λ_{ex} represents the excitation wavelength here.

Single-photon fluorescence spectra of the copolymers

The single-photon fluorescence spectra of the copolymers, poly(EDA-*co*-Ac), poly(MDA-*co*-Ac), poly(ADA-*co*-Ac), poly(ADA-*co*-CA), poly(EDA-*co*-EB) and poly(EDA-*co*-Ci), are given in **Figure S17**. These polymers not only exhibit down-conversion fluorescence, but also emit up-conversion fluorescence. The maximum emission wavelengths of both down- and up-conversion spectra are the same.

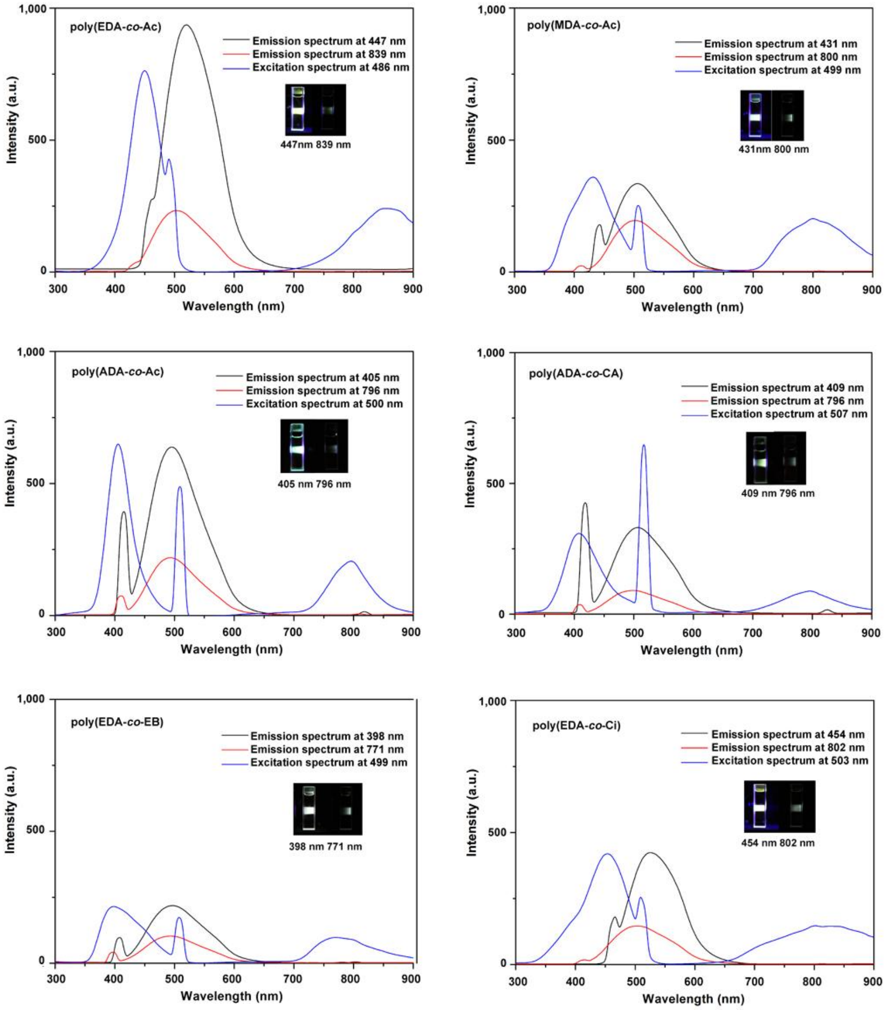

Figure S17. Fluorescence spectra of the copolymers. Concentrations: 1 mg/mL in chloroform and slit width is 5.0/5.0 nm.

Two-photon fluorescence spectroscopy

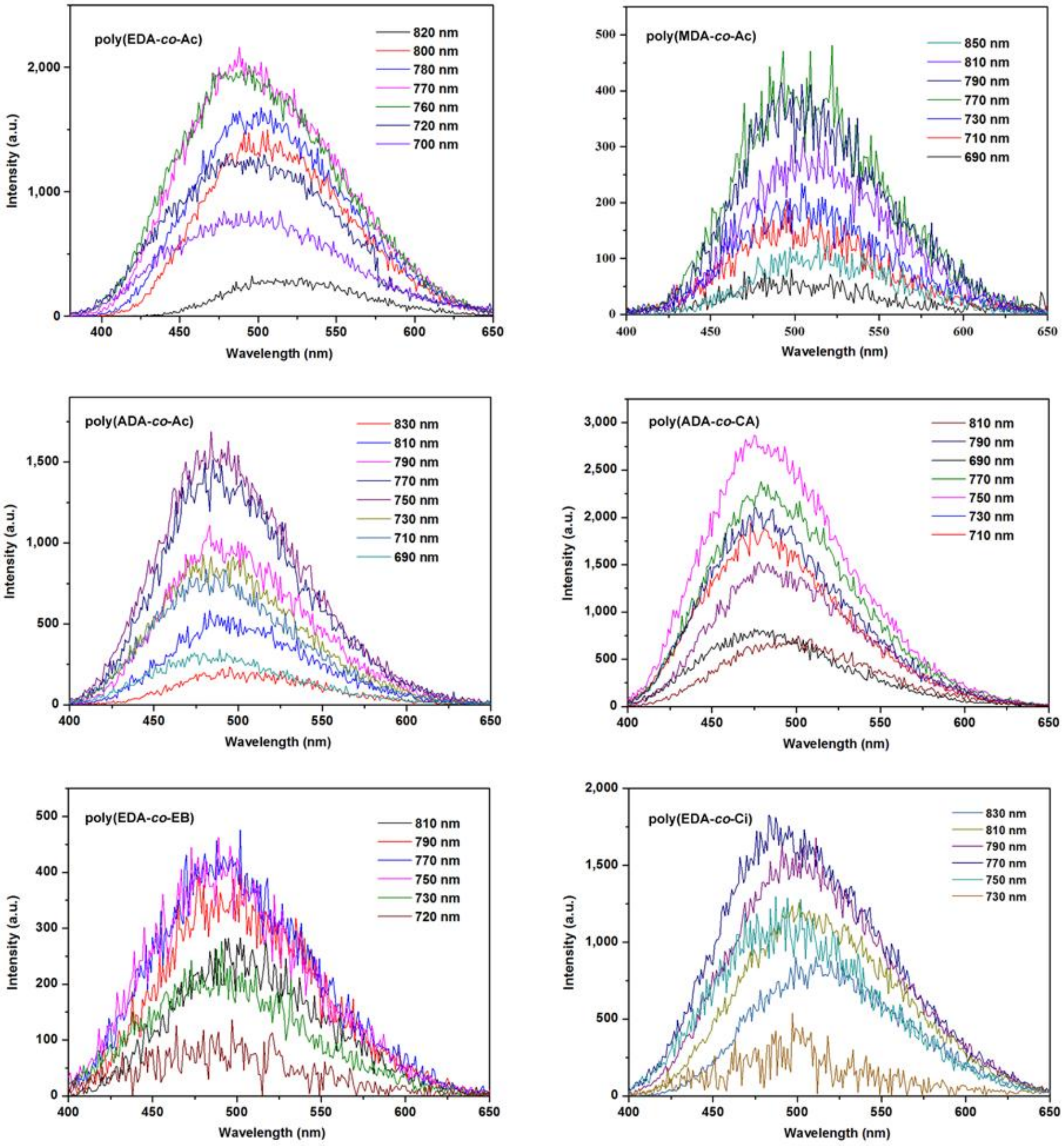

Figure S18. Two-photon fluorescence spectra of the copolymers. Concentrations: 1 mg/mL in dimethyl sulfoxide (DMSO) excited by different wavelengths.

Table S2. Maximum excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of the copolymers in two-photon fluorescence spectra

Copolymer	λ_{ex}/nm	λ_{em}/nm
poly(EDA-*co*-Ac)	760	500
poly(MDA-*co*-Ac)	770	505
poly(ADA-*co*-Ac)	750	485
poly(ADA-*co*-CA)	750	480
poly(EDA-*co*-EB)	770	490
poly(EDA-*co*-Ci)	770	490

All copolymers can emit fluorescence excited under NIR by a two-photon laser. (**Figure S18**) All the emission signals can be detected in a wide range from 690 nm to 850 nm. The λ_{ex} and λ_{em} of each copolymer are presented in **Table S2**.

Femtosecond pulsed laser excited up-conversion emission spectroscopy

Excited by a femtosecond pulsed laser, the quadratic dependence between the laser power and photoluminescence intensity of poly(EDA-*co*-Ac) (**Figure S19a** and **S19b**) and between that of poly(ADA-*co*-Ac) (**Figure S19c** and **S19d**) implies that the emission is the result of a two-photon excitation process.

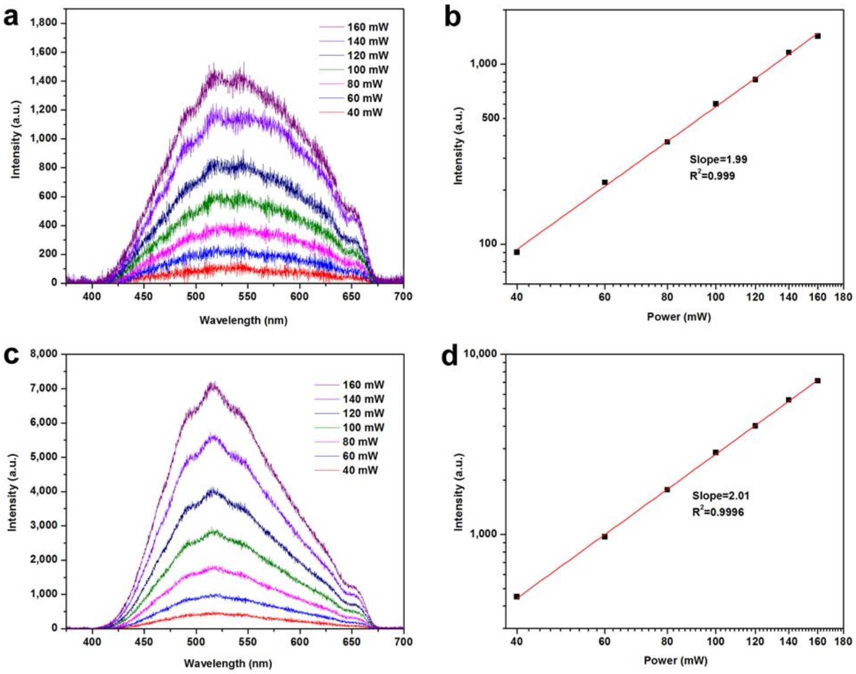

Figure S19. Femtosecond pulsed laser excited up-conversion luminescence spectra of poly(EDA-*co*-Ac) and poly(ADA-*co*-Ac). a, Emission spectra of poly(EDA-*co*-Ac) at 780 nm. **b,** Logarithmic plots of the dependence of relative two-photon excited fluorescence intensity on excitation power for poly(EDA-*co*-Ac) at 520 nm. **c**, Emission spectra of poly(ADA-*co*-Ac) at 760 nm. **d,** Logarithmic plots of the dependence of relative two-photon excited fluorescence intensity on excitation power for poly(ADA-*co*-Ac) at 515 nm. The concentration of poly(EDA-*co*-Ac) and poly(ADA-*co*-Ac) is 1 mg/mL in DMSO.

DFT calculations

According to DFT calculations of a EDA-EDA-Ac trimer (T) (**Figure S20**), the electrons are mainly distributed in the delocalized electronic orbitals on the backbone of the ring system, forming a highest occupied molecular orbital (HOMO), a HOMO-1, a lowest unoccupied molecular orbital (LUMO), and a LUMO+1. The HOMO and HOMO-1 are generated from the π-π interaction of one -N=N- group, while the LUMO and LUMO+1 derive from the conjugation of two -N=N-s. Thus, the fluorescence is mainly because of the electron radiation transition between intramolecular -N=N- conjugations.

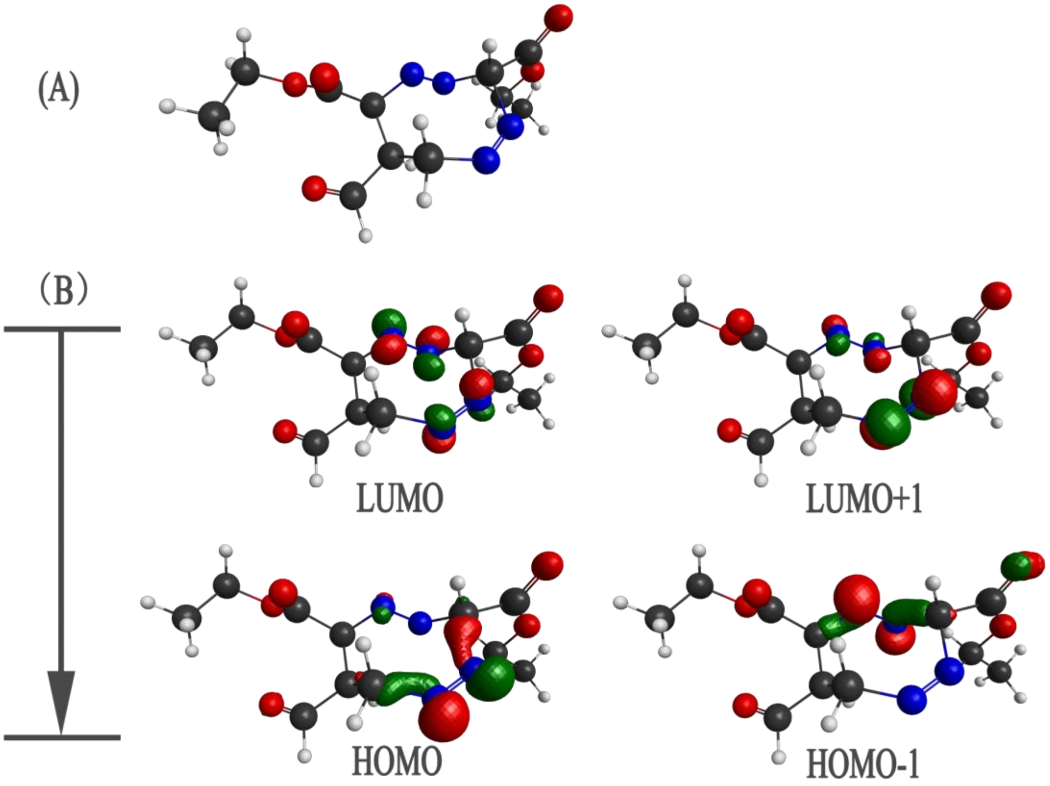

Figure S20. The optimized geometry (A) and molecular orbitals (B) of T by B3LYP/6-31G(d,p).

Supplementary Reference:

1. K. Maruoka, M. Oishi and H. Yamamoto, *Macromolecules*, 1996, **29**, 3328-3329.

2. H. Lu, W. I. Dzik, X. Xu, L. Wojtas, B. de Bruin and X. P. Zhang, *J. Am. Chem. Soc.*, 2011, **133**, 8518-8521.