

Supporting Information for

“A Simple Route to Synthesis of Branched and Cross-linked Polymers with Clickable Moieties by Photopolymerization”

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Experimental

Materials

Methyl acrylate (MA, Aldrich, 99%) was passed through a column of basic alumina to remove the inhibitor. Propargyl acetate (Aldrich) was purified by distillation prior to use. Propargyl acrylate (Aldrich, 98%), trimethylbenzoyl diphenylacetylphosphineoxide (TMDPO), bisacetylphosphine oxide (BAPO, Ciba Specialty Chemicals), 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Ciba Specialty Chemicals), 1-pyrenemethanol (98%, Sigma-Aldrich), toluene-4-sulfonyl chloride (>97%, Fluka), sodium azide (98.5%, Carlo-Erba), copper(I)bromide (≥97.0%, Riedel-de Haën), 1-octene (Aldrich), 1-octyne (Aldrich), 1,9-decadiene (Aldrich), 1,9-decadiyne (VWR, Alfa Aesar), 1,7-octadiene (VWR, Alfa Aesar), 1,7-octadiyne (VWR, Alfa Aesar) and toluene (C₆H₅CH₃, Aldrich, 99.5%) were used as received. 2-(Azidomethyl)pyrene (Py-N₃) was synthesized from 1-pyrenemethanol by tosylation and following azidation as described elsewhere.¹ *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich) used as a ligand, was distilled before use.

Laser Flash Photolysis

Laser flash photolysis experiments (LFP) were carried out exciting at 355 nm with a nanosecond Nd-YAG laser (Powerlite 9010, Continuum), operating at 10 Hz. The transient absorption analysis system (LP900, Edinburgh Instruments) uses a 450-W pulsed Xe arc lamp, a Czerny-Turner monochromator, a fast photomultiplier, and a transient digitizer (TDS 340, Tektronix). The instrumental response was about 7 ns.² Experiments were performed in *t*-butyl benzene under Ar bubbling.

Photopolymerization

A typical photopolymerization procedure for methyl acrylate (MA) and propargyl acrylate (PA) was as follows. MA (1 mL, 11 mmol), toluene (2 mL, 18.8 mmol), propargyl acrylate (5 % mol) and the photoinitiator (either BAPO or DMPA) were put in a Pyrex tube and filled with dry nitrogen prior to irradiation by a Ker-Vis blue photoreactor equipped with 6 lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm at room temperature. At the end of irradiation, polymer was precipitated in 10-fold excess methanol and dried in vacuum. Conversions for all samples were determined gravimetrically. All the other polymerizations were performed under identical experimental conditions. Depending on the conditions (Table 2), lightly branched, highly branched or partially cross-linked polymers were obtained. In the case of cross-linked polymer, the soluble part was extracted by THF. See Supporting Information for further experimental procedures.

Click Reaction

In a typical click reaction, branched polymer (105 mg) (concentration of alkyne groups determined theoretically = $1.2 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$), CuBr ($1.8 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$), PMDETA ($1.8 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$), 2-(azidomethyl)pyrene ($1.8 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$) and 5 mL of dimethylformamide (DMF) were placed in a Schlenk tube. The reaction mixture was degassed by three freeze-pump-thaw cycles and stirred at 60 °C for 20 h. After click reaction, the reaction mixture *passed through* a column filled with neutral *alumina to remove the copper salt*, precipitated into methanol, and finally dried in a vacuum at room temperature.

Analysis

¹H NMR spectra of the polymers were recorded in deuterated chloroform containing Si(CH₃)₄ as an internal standard using a Bruker AC250 (250.133-MHz).

FT-IR analyses were performed on a Perkin-Elmer FT-IR Spectrum One B spectrometer.

In order to characterize branching architecture of the polymers, both apparent and absolute molecular weights were measured. The apparent molecular weights ($M_{n,\text{GPC}}$) and polydispersities (M_w/M_n) were determined by gel permeation chromatography (GPC) using a Viscotek GPCmax auto-sampler system consisting of a pump, three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR} and G4000H_{HR}) (7.8 mm internal diameter, 300 mm length), a Viscotek differential refractive index (RI) detector with THF as eluent at a flow rate of 1.0 mL·min⁻¹ at 30 °C. The effective molecular weight separation of the columns are ranging 456–42,800 g·mol⁻¹ for G2000H_{HR}; 1050–107,000 g·mol⁻¹ for G3000H_{HR}; and 10,200–2,890,000 g·mol⁻¹ for G4000H_H. The detector was calibrated with polystyrene standards having narrow molecular weight distribution and so the quoted molecular weights of the polymers therefore are

expressed in terms of polystyrene equivalents. Data were analyzed using Viscotek OmniSEC Omni-01 software.

The absolute molecular weights ($M_{n,TDGPC}$) were determined by a second GPC setup (TD-GPC) equipped with an Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector including RI, dual laser light scattering ($\lambda = 670$ nm, 90° and 7°), and a differential pressure viscometer was conducted to measure the absolute molecular weights ($M_{n,TDGPC}$) in THF with a flow rate of $0.5 \text{ mL}\cdot\text{min}^{-1}$ at 35°C . Three detectors were calibrated with a polystyrene standard with narrow molecular weight distribution ($M_n = 115,000 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.02$, $[\eta] = 0.519 \text{ dL}\cdot\text{g}^{-1}$ at 35°C in THF, $dn/dc = 0.185 \text{ mL}\cdot\text{g}^{-1}$) provided by Viscotek company.

The ratio between $M_{n,GPC}$ and $M_{n,TDGPC}$ ($R_M = M_{n,GPC}/M_{n,TDGPC}$) gives qualitative information about the branching density of the polymers since branched structures are more compact than linear polymers for a given molecular weight.³ As can be seen in Table S1, the normalized $R_{M,n}$ value significantly differs as polymer architecture moves from linear ($R_{M,n} = 1.000$) to highly branched architectures ($R_{M,n} = 0.178$). This parameter thus indicates a trend of branching density of the synthesized polymers.

Results

Laser Flash Photolysis

Before proceeding to the synthesis of the desired branched polymers, a systematic kinetic study was performed to examine the addition of radicals either on the triplet bond or the double bond of PA. Such a study, revealing the relative reactivity of radicals with respect to these two functional groups would support the mechanism of formation of the branched polymers. As radical addition onto triple bonds has not received considerable attention, there is a lack of reliable rate constants available from the literature. Therefore, it was decided to study the reactivity of the phosphinoyl radical with different alkynes and the corresponding alkenes. The most widely used methodology to study the reactivity of radicals towards unsaturated compounds is to probe the absorbance of phosphinoyl radical. These radicals are formed from the excitation of trimethylbenzoyl diphenylacetyl phosphineoxide (TMDPO) which is known to undergo fast homolytic scission after irradiation (Scheme 1). This leads to the formation of a trimethylbenzoyl radical and a diphenylphosphinoyl radical.

The transient absorption spectrum obtained immediately after laser excitation at 355 nm of TMDPO in *t*-butyl benzene is shown in Figure S1 and is attributed to the diphenylphosphinoyl radical.⁴ The kinetics observed at 330 nm for several 1-octyne concentrations are displayed in Figure S2 showing that the kinetics decay faster with increasing concentrations of 1-octyne. The quenching rate constants k_q for the different alkenes and alkynes can then be determined by applying the Stern -Volmer relation:

$$1/\tau = 1/\tau_0 + k_q [Q] \quad (1)$$

where $[Q]$ is the molar concentration of quencher. τ and τ_0 are the measured radical lifetimes in the presence and in the absence of quencher, respectively. The Stern-Volmer plot obtained for 1-octyne is displayed in Figure S2. Due to the bimolecular recombination of radicals in the absence of quencher, the decay of the phosphinoyl radical at low concentration of quencher is not strictly pseudo-first order and contains a part of second order kinetics. This explains the deviation from linearity for the corresponding data on Figure S2. These data were not taken into account for the determination of the rate constant.

Table S1. Quenching rate constants of phosphinoyl radical by selected double and triple bonds.

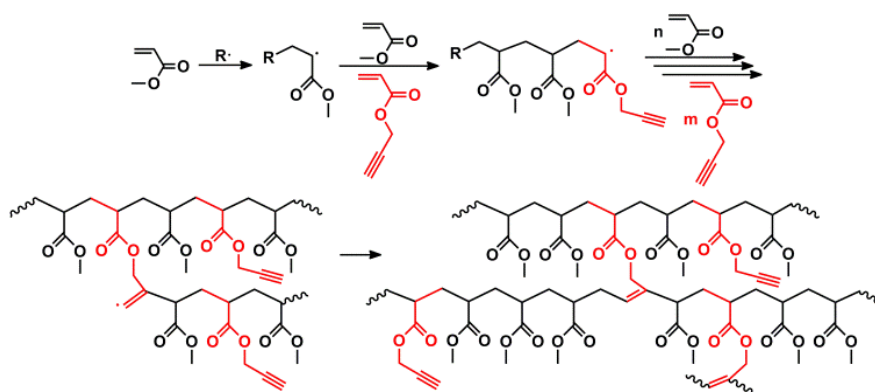
[Quencher]	$k_q (\times 10^6 \text{ M}^{-1} \text{ s}^{-1})$
methyl acrylate	26
1-octene	2.4
1-octyne	1.5
1,7-octadiene	4.4
1,7-octadiyne	4.8
1,9-decadiene	4.2
1,9-decadiyne	3.3
propargyl acetate	0.92
propargyl acrylate	32

Table S2. Effect of irradiation time on branching density ($R_{M,n}$) during copolymerization of methyl acrylate (95 % mol) and propargyl acrylate (5 % mol) by irradiation ($\lambda = 350$ nm) of DMPA (0.25 % mol) at room temperature in toluene.

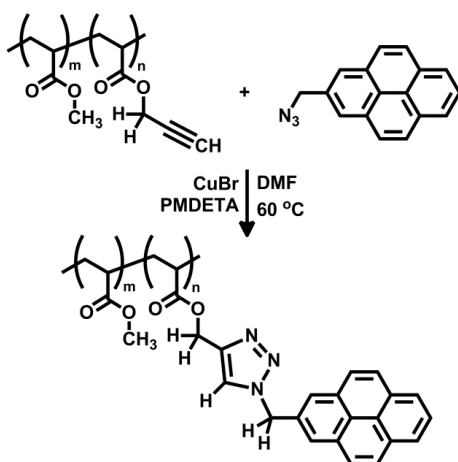
Run	Time (sec.)	Conv. (%)	Linear polym. cont. (%)	PDI	$M_{n,RI}$ (g/mol)	$M_{n,DLS}$ (g/mol)	$R_{M,n}$
1	150	49	100	6.92	26860	179900	0.194
2	180	58	100	5.64	44550	315250	0.184
3	210	58	8.5	5.00	42030	307200	0.178

Table S3. Effect of photoinitiator type on branching density ($R_{M,n}$) during copolymerization of methyl acrylate and propargyl acrylate by irradiation of DMPA ($\lambda = 350$ nm) (0.25 % mol) or BAPO ($\lambda = 415$ nm) (0.25 % mol) at room temperature in toluene. All resulted polymers were completely soluble. (Irradiation time = 150 sec.)

Run	Initiator	PA (% mol)	Conv. (%)	PDI	$M_{n,RI}$ (g/mol)	$M_{n,DLS}$ (g/mol)	$R_{M,n}$
4	DMPA	5	49	6.92	26860	179900	0.194
5	BAPO	5	26	3.48	51100	124760	0.532



Scheme S1. Branching mechanism in photoinduced copolymerization of methyl acrylate with propargyl acrylate.



Scheme S2. Functionalization of the branched polymers with pyrene by Cu(I)-catalyzed click reaction .

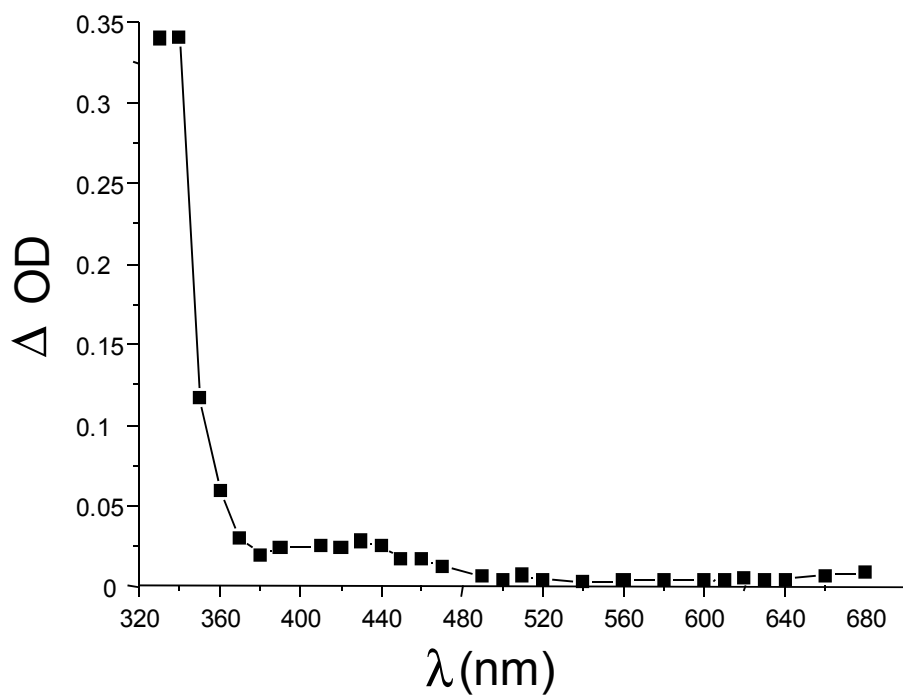


Figure S1: Transient spectra of the phosphinoyl radical just after laser excitation of trimethylbenzoyl diphenylacetylphosphineoxide (TMDPO) in *t*-butyl benzene.

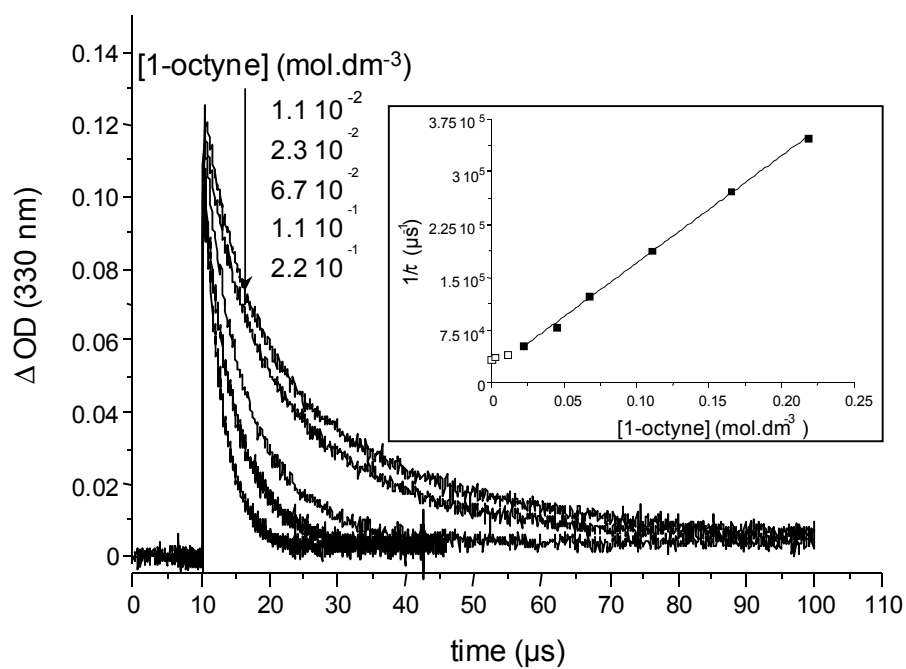


Figure S2: Phosphinoyl radical decays measured at 330 nm as a function of 1-octyne concentration in *t*-butyl benzene. Insert: Corresponding Stern-Volmer plots.

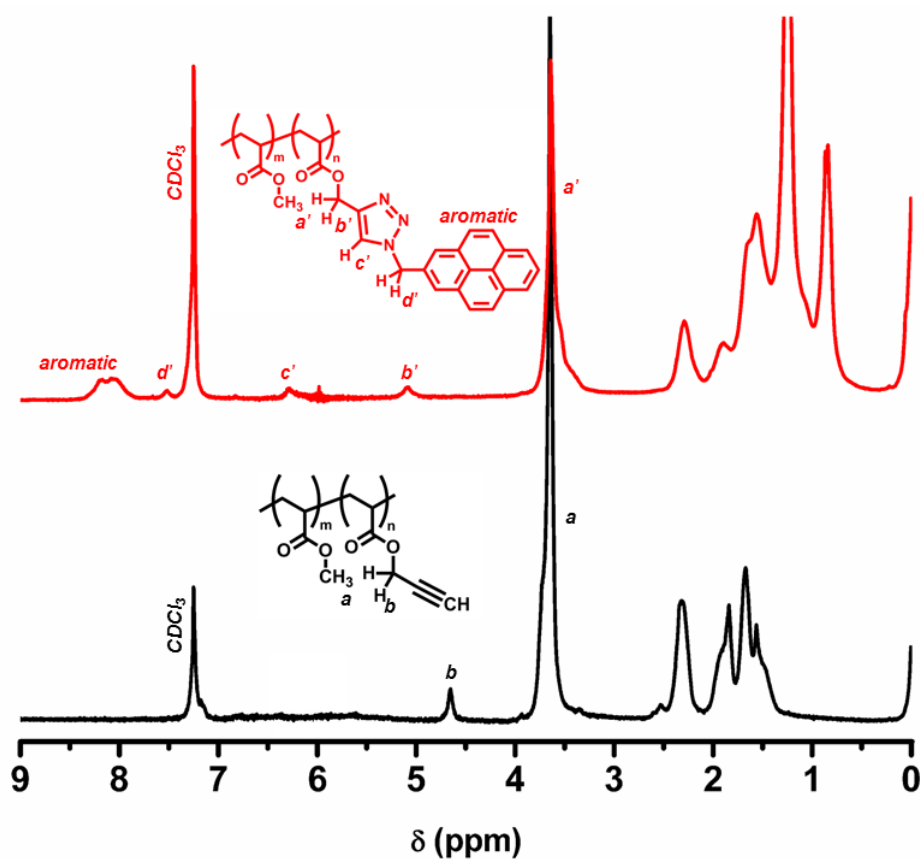


Figure S3. ¹H-NMR spectra of the copolymer of methyl acrylate and propargyl acrylate obtained by photopolymerization using BAPO (0.25 % mol; $\lambda = 415$ nm) (0.25 % mol) at room temperature in toluene, and its pyrene functionalized analogue (Irradiation time = 150 sec.).

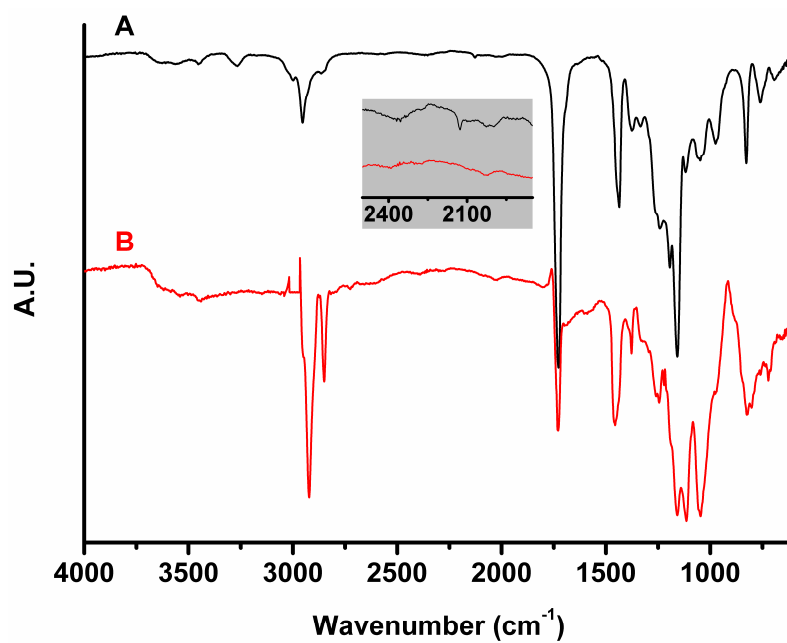


Figure S4. FT-IR spectra of the copolymer of methyl acrylate and propargyl acrylate obtained by photopolymerization using BAPO (0.25 % mol; $\lambda = 415$ nm) (0.25 % mol) at room temperature in toluene (**A**), and its pyrene functionalized analogue (**B**) (Irradiation time = 150 sec.).

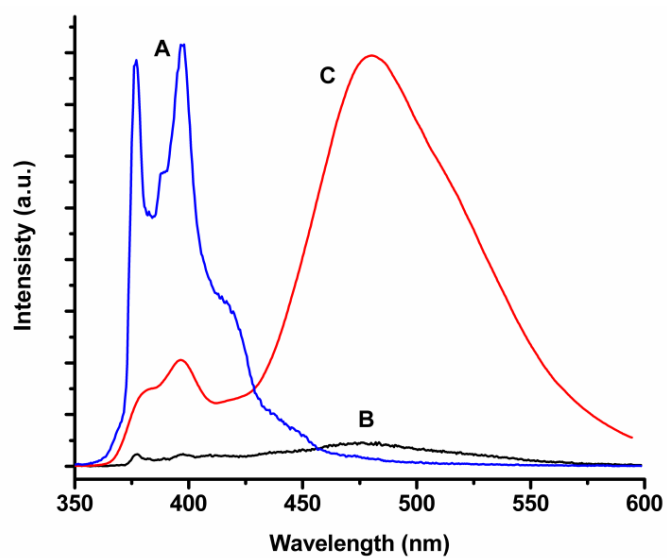


Figure S5. Fluorescence emission spectra of 1-pyrenemethanol (**A**), the clickable branched polymer (see Table S2 Run 5) (**B**) and corresponding pyrene-conjugated polymer (**C**) ($\lambda_{\text{excitation}} = 340 \text{ nm}$).

References:

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