

Supporting Information

Syntheses of High Molecular Weight Hydroxy Functional Copolymers by Green and Selective Polycondensation Methods

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^1H NMR

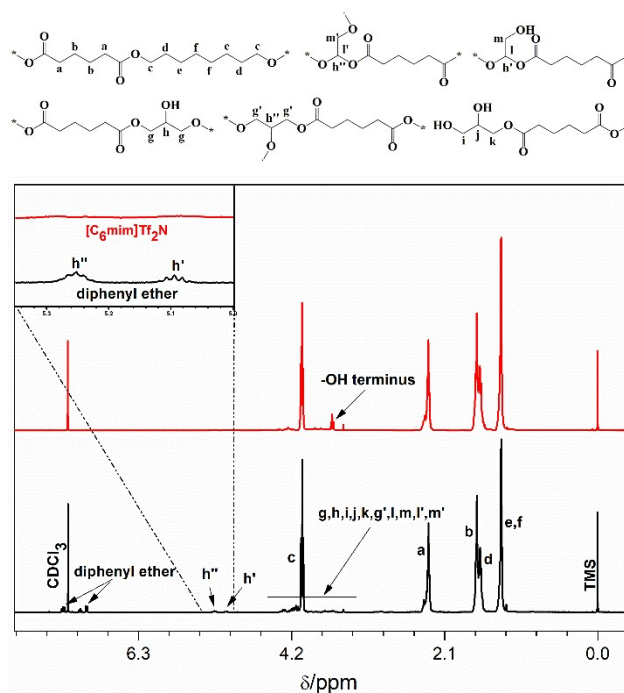


Fig. S1. P(OA-GA) macromolecular structure. ^1H -NMR spectrum of P(OA-GA) synthesized in [C₆mim]Tf₂N and diphenyl ether.

^{31}P NMR and Hydroxyl content

^{31}P NMR spectroscopy was performed on a Bruker 400 MHz spectrometer. The delay time was set at 3 s with the number of recorded scans of 1024. A stock solution was prepared by weighing exactly 530 mg Cr(acac)₃ (30.3 mM) and 150 mg cyclohexanol (30 mM) in a 50mL volumetric flask. These compounds were subsequently dissolved in a mixture of pyridine and CDCl₃(2.3:1 volume ratio). 4Å molecular sieves were added to protect the stock solution from moisture. Cyclohexanol was used as an internal standard for quantification purposes. Around 45-50mg of the polymer were accurately weighed into a vial, 0.6 mL of stock solution was added and the solution was transferred to a 5 mm NMR tube. Subsequently, 70 μL of phospholane reagent was added and HCl gas was formed, indicating that the

phosphorylation reaction took place. The reaction mixture was left to react for about 30 min at room temperature. Upon completion of the reaction, after the HCl formation had stopped, the solution was used to obtain the ^{31}P NMR spectra. Chemical shifts are reported in ppm relative to the residual peak of water-derivatized phospholane ($\delta = 132.2$ ppm).

Data analysis was performed using MestReNova software. Data afforded by the experiments are expressed in mg KOH/g sample.

$$\text{Hydroxyl dgroups} \left(\frac{\text{mg KOH}}{\text{g sample}} \right) = \frac{\text{mg}_{\text{cyclohexanol}} \frac{56100 \text{ mg KOH}}{\text{mol KOH}} \cdot \text{peak area hydroxyl group}}{\text{mg}_{\text{polyester}} \frac{100.2 \text{ g cyclohexanol}}{\text{mol cyclohexanol}} \cdot \text{peak area cyclohexanol}}$$

^{31}P NMR

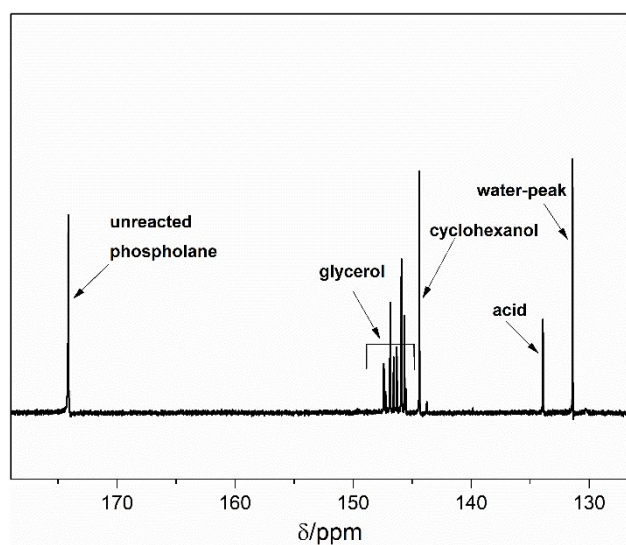


Fig. S2. ^{31}P -NMR spectrum of P(OA-GA)

Hydroxyl content

Table S1. Hydroxyl content of P(OA-GA) of different glycerol content.

Entry	Molar ratio A:O:G ^[b]	Ter ^[c] (%)	L _{1,2} ^[d] (%)	L _{1,3} ^[e] (%)	Den ^[f] (%)	Mn ^[g] (g/mol)	PDI ^[g] (Mw/Mn)	OHV _{NMR} ^[h] [mg _{KOH} g ⁻¹]
1	1:0.8:0.2	13.78	15.11	44.44	26.67	29639	1.21	3259
2	1:0.84:0.21	20.42	19.58	40.83	19.20	34795	1.48	4702
3	1:0.53:0.53	14.8	18.4	40.00	26.80	15158	1.37	5963

[a] All products were synthesized through two-step method. Pre-condensation conditions: adipic acid : 1,8-octanediol : Glycerol = 1:0.84:0.21; 130, 140, 150°C for 1h and 160°C for 2h. Post-polycondensations conditions: 60°C, N-435(10wt% of monomers), reaction times were 24h in vacuum 1.5-3mmHg; [b]A=adipic acid; O=1,8-octanediol; G=Glycerol. Data were analyzed by ¹³C NMR and calculated based on [c]eq.2.; [d]eq.3.; [e]eq.4.; [f]eq.5. [g] Determined by GPC measurement in THF relative to poly(styrene). n.d.=not determined. [h] Determined by ³¹P NMR.

Comparisons of different polymerization methods

Table S2. The comparisons of different polymerization methods

Method	Temperature (°C)	Catalyst	Mn(g/mol)	Mw(g/mol)	PDI(Mw/Mn)	References
1	60	N-435(10wt%)	53937	96547	1.79	This work
2	60	Sc(OTf) ₃ (0.5mol%)	18600	44268	2.38	4
3	70	N-435(10wt%)	24387	75599	3.1	28
4	90	N-435(10wt%)	9120	30096	3.3	8
5	60	N-435(10wt%)	8900	31150	3.5	11

Method 1. Adipic acid: 1,8-octanediol: Glycerol(mol)=1:0.84:0.21, in solvent (diphenyl ether), under reduced pressure (1.5-3mm Hg), 24h.

Method 2. Dicarboxylic Acid: Glycerol: 1,9-nonanediol(mol)=1:0.8:0.2, bulk, under reduced pressure (0.3-3.0mmHg), 10h.

Method 3. Adipic acid: 1,8-octanediol: Glycerol(mol)=1:0.8:0.2, bulk, under reduced pressure (40 mmHg), 42h.

Method 4. Oleic diacid: Glycerol =1:1(mol), bulk, under reduced pressure (10 mmHg), 24h.

Method 5. Divinyl adipate: Glycerol=1:1(mol), in solvent (THF), normal pressure, 24h.

Repeatability of synthetic methods

Table S3. The proportion of glycerol repeat unit substitution of copolymer P (OA-GA) [a]

Entry	Molar ratio A : O : G ^[b]	Solvent	Ter ^[c] (%)	L _{1,2} ^[d] (%)	L _{1,3} ^[e] (%)	Den ^[f] (%)	Mn ^[g] (g/mol)	PDI ^[g] (Mw/Mn)
M5-1	1:0.84:0.21	diphenyl ether	12.89	15.11	44.44	27.56	53937	1.79
M5-2	1:0.84:0.21	diphenyl ether	13.46	17.32	45.92	23.30	52074	1.69
M8-1	1:0.84:0.21	[C ₆ mim]Tf ₂ N	20.42	19.58	40.83	19.20	13913	1.73
M8-2	1:0.84:0.21	[C ₆ mim]Tf ₂ N	19.81	20.05	41.33	18.81	12835	1.47

[a] All products were synthesized through two-step method; Pre-polymerization were conducted at 130, 140, 150°C for 1h and 160°C for 2h under N₂ atmosphere, respectively; Post-polymerization were conducted at 60°C, 24h, N-435(10wt% of monomers), in vacuum 1.5-3mmHg; [b]A=adipic acid; O=1,8-octanediol; G=Glycerol. Data were analyzed by ¹³C NMR and calculated based on [c] eq.2; [d] eq.3; [e] eq.4; [f] eq.5; [g] Determined by GPC measurement in THF.