

# Synthesis of PPC-graft-poly (PEOMA) Brush and PPC Gels via Post-polymerization Modification of Hydroxyl-functionalized Poly (Propylene Carbonate)

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## Research Article

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# Abstract

Post-polymerization modification offers a facile and effective tool for adapting polymer properties. However, it has not been applied to poly (propylene carbonate) (PPC) as traditional PPC lacks sufficient functional groups along the polymer chain. In the present work, for the first time, hydroxyl-functionalized PPC has been prepared and used to construct PPC-brush and cross-linked polymer gels through post-polymerization modification approach. PPC-brushes in the form of PPC-graft-poly (PEOMA) were obtained with controllable brush length and brush density via “grafting from” a PPC-macroinitiator which was synthesized from esterification reaction of PPC-OH with 2-bromoisobutyryl bromide. PPC permanent networks in the form of dioxane gels were prepared by cross-linking PPC-OH with 4,4'-diphenylmethane diisocyanate (MDI). Rheological measurement of the gels showed that the cross-linking density scales linearly with the hydroxyl group density in PPC-OH. This work not only offers a facile strategy to realize the post-modification of PPC but also spurs the devising of innovative biodegradable materials with tailored molecular architectures.

## Introduction

Poly (propylene carbonate) (PPC) is an ecofriendly biodegradable polymer synthesized from carbon dioxide ( $\text{CO}_2$ ) and propylene oxide (PO) [1, 2]. In consideration of largely available “greenhouse” gas  $\text{CO}_2$  can be utilized as a cheap carbon resource for PPC production, this copolymer has gained a continuous interest worldwide in the fields of academia and industry [3–5]. As a thermoplastic aliphatic polycarbonate, PPC has the properties of desirable biodegradability, good biocompatibility, excellent oxygen barrier performance and sufficient toughness at ambient temperature, which has potential applications in packaging, adhesives, biomedical material, etc [6–8]. However, the flexible molecular chains imparted by the considerable amount of ether bonds within PPC lead to extremely low glass transition temperature ( $T_g$ ), poor mechanical strength and inferior dimensional stability at temperatures above  $40^\circ\text{C}$  [9]. Besides, PPC tends to decompose into cyclic carbonate by the mechanism of “back biting” at a temperature of only about  $180^\circ\text{C}$  causing the narrow processing temperature [10, 11].

Changing the polymer structure of PPC by post-modification reaction or blending PPC with other polymers or fillers is effective in enhancing the thermal and mechanical properties [12–15]. Phillips et al. [16] reported, for example, that the thermal properties of PPC can be improved significantly after end-capping of hydroxyl groups. Using isocyanates such as polyaryl polymethylene isocyanate (PAPI) as cross-linker can improve the mechanical property due to the cross-linking network [17, 18]. Blending PPC with biodegradable polymers such as poly (lactic acid), poly (butylene succinate) or compounding PPC with fillers such as glass fiber, graphene offers effective approach to overcome the challenge in improving the mechanical property [19–21]. Besides, post-polymerization modification is proved to be a facile and effective tool for adapting polymer properties which require abundant functional groups along polymer side chain that is not applicable to traditional PPC [22–24]. We have reported the method of fabrication hydroxyl-functionalized PPC (PPC-OH) by first terpolymerization of  $\text{CO}_2$ , propylene oxide and *o*-nitrobenzyl-protected glycidol, and then deprotect the hydroxyl group via ultraviolet light irradiation [25].

The accessibility of hydroxyl group functionalized PPC has shed light on the adjusting of PPC properties via post-polymerization modification approach.

In this work, for the first time, by utilizing the primary hydroxyl groups along PPC-OH, various PPC-brushes were prepared by atom transfer radical polymerization (ATRP) of various monomers via “grafting from” approach. In addition, PPC gels were obtained by crosslinking PPC-OH with 4, 4'-diphenylmethane diisocyanate (MDI). The preparation and characterization of PPC-brushes and cross-linked PPC networks were discussed. And in this way, this kind of post-modification methodology not only achieved the improvement of  $T_g$  of PPC but also paved a new way to realize the attractive controllable architecture of polyester.

## Experimental Section

### Materials

All reagents were used without purification unless stated otherwise. Hydroxyl-functionalized poly(propylene carbonate)s (PPC-OHs) with hydroxyl group content from 2.1 to 12.1 mol% were prepared as described before [25]. Poly(ethylene glycol) methyl ether methacrylates,  $H_2C = C(CH_3)COO-(CH_2CH_2O)_nCH_3$  (PEOMA,  $MW_{av} = 188$  g/mol,  $DP_{PEO} = 2$ ;  $MW_{av} = 300$  g/mol,  $DP_{PEO} = 5$ ) were acquired from Sigma-Aldrich and used after purification by distillation. PPC used in this study was produced from PO and  $CO_2$  with a zinc glutarate catalyst. Solvent dichloromethane and 1,4-dioxane were purchased from Sigma-Aldrich, purified by distillation and dried over 4A molecular sieves. 4, 4'-diphenylmethane diisocyanate (MDI) was provided by BASF and distilled shortly before application. All other chemical were obtained from Sigma-Aldrich.

### Synthesis of PPC-OH

According to the experimental details reported in the reference [25], PO,  $CO_2$  and monomer A were added into a stainless steel reactor with a specific feed ratio to copolymerize at 3.0 MPa and 60°C for 24h. Obtained solid crude products (PPC-ONB) was purified by the method of repeated precipitating in methanol from acetone for three times. After drying, the PPC-ONB was dissolved in THF to form a solution with 10% (w/v) concentration. THF solutions were deoxygenated by stripping with argon gas and subsequently exposed to 313 nm UV light irradiation at room temperature to remove o-nitrobenzyl groups. The afforded PPC-OH was obtained and subsequently separated by repeated dissolving and precipitation in acetone and cold ligroin, respectively. The schematic illustration of the synthetic procedure of PPC-OH is shown in Fig. 1a.

### Synthesis of PPC-macroinitiator

PPC-OH with 10 mol% hydroxyl group was dissolved in dry dichloromethane and the solution was then cooled in an ice water bath. 2-bromoisobutyryl bromide (0.75 mL, 6 mmol) was dropwise to the mixture of 1 mL pyridine (0.0084 mol) and a DCM solution (20 mL) of PPC-OH (1.1 g PPC-OH polymer

corresponding to 1.2 mmol hydroxyl groups). The reaction mixture was stirred for 6 hours after which it was precipitated in methanol. Three times of reprecipitation from dichloromethane into methanol gave a pure product that was dried under a dynamic vacuum at 40 °C for 24 h before further processing. The PPC-macroinitiator was analyzed by <sup>1</sup>H-NMR to confirm the success of synthesis and determine the content of 2-bromoisotuyryl bromide units.

## Synthesis of PPC-graft-PPEOMA

In the preparation of grafted polymers, typically 120 mg of PPC-macroinitiator (0.08 mmol initiator groups), PEOMA,  $MW_{av} = 188$  g/mol (4.5 g, 24 mmol) or  $MW_{av} = 300$  g/mol (7.2 g, 24 mmol) and 28 mg of ATRP ligand 2,2'-bipyridine (dNbpy, 0.18 mmol) were dissolved in 5 mL of anisole and purged with argon for 10 min. The mixture was transferred to a Schlenk flask with Cu(I)Br (15 mg, 0.1 mmol) as catalyst ( $[PEOMA]_0/[Initiator]_0/[CuBr]_0/[dNbpy]_0 = 300:1:1:2$ ). The mixture was heated (40°C – 60 °C) and stirred for 2 to 6 hours. The reaction was terminated by cooling with cold water and diluting with DCM. The content was then filtered over a short pad of neutral alumina to remove the copper catalyst followed by three times of precipitation from DCM into methanol. After drying in dynamic vacuum at 40 °C overnight, the final product was characterized by <sup>1</sup>H NMR and GPC.

## Synthesis of cross-linked PPC network with MDI

The cross-linking was carried out by dissolving 2 g of PPC-OH polymer in 20 mL dry dioxane, heating to 70 °C and addition of MDI (-OH/-NCO = 1:1). Subsequently, 0.02 mL of stannous octoate (tin(II) 2-ethylhexanoate) catalyst solution in toluene (0.06 mmol) was added to the stirred mixture. After 2–4 hours, the mixture transformed into a gel. This gel was characterized by its rheological properties. Gel products were also dried under dynamic vacuum at 70 °C for 48 hours before thermal analysis. The preparation of cross-linked PPC network from PPC-OH is illustrated in Fig. 1b.

## Characterization

<sup>1</sup>H NMR spectra (300 MHz) were recorded on a Bruker 300 MHz FT-NMR spectrometer in chloroform-d<sub>1</sub>. Gel permeation chromatography (GPC, Agilent: Intelligent pump AI12, RI detector RI 101, set of two columns 2 × 5 μm Polypore from Varian) was used to determine the molecular weights distribution of the polymer samples relative to polystyrene standards in tetrahydrofuran as solvent. Differential scanning calorimetry (DSC, Mettler instruments) was used to determine the glass transition temperature. Rheometry was performed on an AR 2000ex controlled stress rheometer (TA Instruments, New Castle, Germany, USA) by using a cone-plate geometry (diameter = 60 mm, angle = 2°). Small amplitude oscillatory shear (SAOS) experiments were performed in a frequency range from 0.1 to 100 rad·s<sup>-1</sup> and the applied strain was kept within the limits of the linear viscoelastic regime.

## Results And Discussion

# Synthesis of PPC brushes

Hydroxyl groups on side chain enable the post-polymerization modification of PPC. A PPC based macroinitiator used for ATRP was prepared by reacting the hydroxyl groups on PPC-OH with 2-bromoisobutyryl bromide in the presence of pyridine as base (Fig. 2). The PPC-OH was obtained by deprotecting the ortho nitrobenzyl ether entities in the corresponding PPC-ONB, which was prepared by terpolymerization of propylene oxide, *o*-nitrobenzyl glycidyl ether and carbon dioxide. The esterification reaction was successfully conducted that most of the hydroxyl entities were transformed into 2-bromomethylpropionyloxy groups. The <sup>1</sup>H NMR spectrum (Fig. 3) of the purified PPC-macroinitiator allows to conclude that the overall functionality of the backbone adds up to 8% mol/mol of building blocks. This corresponds to a conversion of over 80% conversion of the initially presented OH groups.

It is anticipated that the main chain is not notably degraded during the PPC-macroinitiator synthesis process. The PPC-OH and the corresponding PPC-macroinitiator show about the same hydrodynamic volume according to a GPC analysis in THF (Fig. 4). The PPC-macroinitiator shows a slightly larger average number molecular mass of  $M_n = 2.9 \times 10^4$  ( $M_w/M_n = 2.4$ ) against PS standards, while PPC-OH displays an  $M_n$  of  $2.6 \times 10^4$  ( $M_w/M_n = 2.9$ ). Without knowledge of the Mark Houwink parameter this result is taken as an indication that the main chain was not degraded substantially in the process, i.e. was not nucleophilic attacked by pyridine [26].

Table 1  
GPC results of PPC-OH and PPC macroinitiator.

NO.	PEOMA <sup>a</sup> DP <sub>PEO</sub>	M:I:CuBr:dNbpy mole ratio	Temp °C	Time (h)	Mn × 10 <sup>-4</sup> (GPC) <sup>b</sup>	Mw/Mn (GPC)	DP n=
R1	2	100:1:1:2	60	6	Cross-linked Gel		
R2	2	100:1:1:2	50	4	Cross-linked Gel		
R3	2	150:1:1:2	40	4	Cross-linked Gel		
R4	2	300:1:1:2	50	2	15.5	2.6	7
R5	5	300:1:1:2	50	2	17.5	2.9	7

a, PEOMA, DP<sub>PEO</sub> = 2, MW<sub>av</sub> = 188 g/mol, DP<sub>PEO</sub> = 5, MW<sub>av</sub> = 300 g/mol; b, PPC-macroinitiator, Mn = 2.9 × 10<sup>4</sup> g/mol, M<sub>w</sub>/M<sub>n</sub> = 2.4.

A grafting from the PPC-macroinitiator was accomplished under ATRP conditions with polyethylene oxide methyl ether methacrylate PEOMA with Mn = 188 g/mol and Mn = 300 g/mol as monomer (Fig. 2). The products appear partially as gels (Table 1), especially when using lower ratios of monomer to initiator at

longer reaction times. This gelation is attributed to reactions of the ethylene oxide side chains due to the inner and inter radical-radical coupling reactions as showed in Scheme 1. The radicals are known to readily form after alpha hydrogen abstraction reactions at the polyethylene oxide entity [27]. Radical-radical coupling terminations are more likely to happen intramolecular due to the high concentration of grafted chains which extend from the PPC back backbone. Various polymerization conditions were screened with the objective to prevent the formation of interchain cross-links. These involve lowering the temperature from 60°C to 40°C, decreasing the catalyst concentration and screening various monomer/initiator ratios (from 100:1 to 300:1). The radical-radical coupling reaction could be minimized (**R4** and **R5**) at temperature of 50°C and with molar ratios of M:I:CuBr:dNbpy = 300:1:1:2 in 5 mL anisole as solvent and short reaction times (2 hours). This leads to lower monomer conversion. The <sup>1</sup>H-NMR spectrum of **R4** showed the presence of PEOMA units after purification of the polymeric reaction product (Fig. 5). The average degree of polymerization in the brushes was calculated to be 7 for **R4** and **R5** by comparing the integral values of signals of PPEOMA and the PPC backbone. The GPC trace of **R4** and **R5** is indicative of some residual “macroinitiator” (Fig. 6). This could be explained by the presence of residual PPC-OH which was not or only partially functionalized by the acyl bromide, probably because it was not completely dissolved in the reaction with bromoisobutyryl bromide (only 80% of initial hydroxyl groups were converted successfully). The GPC trace of the polymer brushes tend to be a multimodal distribution. This may be the result of sterically crowded growing during polymerization and intramolecular terminations, leading to an unequal distribution of the monomer PEOMA over the initiator entities.

Polymer brushes have been studied over the past three decades, and presented the potential applications in patterned surfaces, biomedical fields, coatings, solar cells, etc. benefited from their inherent flexibility in highly customization [28]. However, researches and applications are mainly focused on vinyl-based monomer-derived polymer brushes. Accordingly, we synthesized the non-vinyl-based polymer brushes via “grafting from” strategy taking biodegradable CO<sub>2</sub>-derived PPC molecules as backbones which contain abundant functional ester groups. The adopted method not only shows good operability and controllability to prepare PPC brush but also sheds some light on the development of post-processing design of polyester material.

## Preparation of PPC gels

The appeared gelation during synthesis of brush-shaped PPC drew our attention in consideration of the potential value in preparing high-performance PPC materials with network structures. But for the purpose of crosslinking, the reaction of ATRP seems to be a little overqualified and overcomplicated while facile one-step method is ought to be adopted. Aiming to preparing netlike PPC with crosslinking structure, MDI was chosen to be utilized as a crosslinker which can easily react with hydroxyl groups of PPC-OH.

Table 2  
Cross-linking of PPC-OHs with MDI in 1,4-dioxane\*

entry	-OH content (mol %)	-NCO/-OH (mol/mol)	T <sub>g</sub> (DSC)
M1	2.7	1:1	32.3
M2	3.3	1:1	30.2
M3	6.0	1:1	32.6
M4	7.1	1:1	31.3

\*Conditions: 10% g/ml PPC-OHs in 1,4-dioxane, 2–4 h reaction time at 70°C.

Firstly, PPC-OHs featuring different hydroxylation ratio (2.7 ~ 7.1 mol%) were synthesized whose detailed process can be found in our previous work. Then MDI was added into PPC-OH/1,4-dioxane solution (10g/ml) to crosslink PPC-OH macromolecules using Tin (II) octoate as the catalyst. The preparation process of MDI crosslinked PPC is illustrated in Fig. 7 and Table 2. Under the premise of the same ratio of reaction functional groups (-NCO/-OH = 1:1), various PPC-OHs with different hydroxylation ratio react with MDI to produce gels in 1,4-dioxane. The transformation from solution to gel suggests the formation of PPC-network. For further evidence, the dynamic rheological properties of the mixture system before and after transformation into gel were investigated. As shown in Fig. 8, the storage modulus G' and complex viscosity of the gel are both higher than the solution before transformation. This can be explained by the formed cross-links restrict the mobility of polymer chains. For gel-state sample, its G' is signally larger than the loss modulus G'' and meanwhile G' is consistently around 85 Pa, regardless of the increase of angle frequency, which confirms the soft-solid-like behavior of gel and proves the existing network structures [29–31].

It's worth noting that conventional PPC is hydroxy-terminated and the -OH groups on both ends of macromolecules would influence the judgement on whether the cross-linking reaction is induced by hydroxyl end groups or contributed by inserted -OH functionalities on the backbone of PPC-OH. Hence, conventional PPC was treated with MDI at various -NCO/-OH ratios in 1,4-dioxane to study the potential crosslinking reaction between end hydroxyl groups and isocyanate. Obviously, combining unmodified PPC with MDI results in the absence of gelation phenomena no matter how -NCO/-OH ratio is varied (Table 3). Besides, the number-average molecular weight and molecular weight distribution coefficient of PPC processed by MDI do have not changed a bit (Fig. 9). This verifies that -OH groups of hydroxy-functionalized PPC play the key role in the design and regulation of molecular structures.

Table 3  
Results of reactions of PPC with MDI.

NO. <sup>a</sup>	-NCO/-OH (mol/mol)	MDI (g)	$M_n^b \times 10^{-4}$	$M_n/M_w^b$
PPC	-	-	5.9	1.74
MP1	0.5/1	0.061	5.7	1.75
MP2	0.8:1	0.098	5.6	1.74
MP3	1:1	0.122	5.9	1.74
MP4	2:1	0.245	5.8	1.75
MP5	3:1	0.366	5.8	1.74

a, In each sample, 20 g PPC was treated with MDI in 1,4-dioxane at 70°C;

b, Molecular weight were determined by GPC calculation in THF.

The hydroxyl contents of PPC-OHs should have an influence on the crosslinking between MDI and PPC-OHs. Therefore, the gel samples M1 ~ M4 from PPC-OHs with various hydroxylation ratio were measured to analyze the relative crosslinking density. From the rheological behaviors of gels as shown in Fig. 10, it's suggested that storage modulus  $G'$  increases with hydroxylation ratio of PPC-OHs. Notably, the logarithm of the plateau storage modulus  $G_p'$  (taken at angle frequency  $\omega = 1 \text{ rad}\cdot\text{s}^{-1}$ ) is in linear proportion to the concentration of the OH functionalities which reveals the crosslinking density of obtained netlike PPC increases with the hydroxylation ratio of PPC. Thus, it's controllable to obtain PPC networks with special crosslinking density which have potential to be applied in the design of interpenetrating polymer networks (IPNs) and semi-interpenetrating polymer network (sIPN) or used for material reinforcing [32, 33]. Scheme 2 presents the potential application of net-shaped PPC in the preparation of PPC based sIPN. Importantly, there are plenty of degradable ester bonds on the backbone of net-shaped PPC which endow the PPC networks with biodegradable properties [34].

## Conclusions

Post-polymerization modification of hydroxyl-functionalized PPC (PPC-OHs) is reported to prepare PPC-brushes and cross-linked polymer networks. PPC-g-PPEOMA is accessible after esterification of PPC-OHs and 2-bromoisobutryl bromide to yield a PPC-macroinitiator suitable for ATRP. Various PPC-g-PPEOMA brushes with controllable brush length and brush density were prepared via "grafting from" method. The success of this synthesis provided a general method for preparing various PPC brush through ATRP of different monomers "grafting from" PPC-based macroinitiator. Cross-linked PPC networks were prepared by cross-linking PPC-OHs with 4, 4'-diphenylmethane diisocyanate (MDI) as cross-linking agent. Gel structures were formed in 1,4-dioxane. The cross-linking density/concentration increases linearly with the concentration of the OH functionalities on the PPC backbone. PPC was not cross-linked by MDI under the

same cross-linking reaction conditions. A mixture of PPC and PPC-OH treated with MDI as cross-linking agent would be transformed into semi-interpenetrating polymer network (sIPN).

## Declarations

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### Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Note:

This work is based on the PhD thesis of Dr. Xiaojun Wu, one of the authors in this manuscript.

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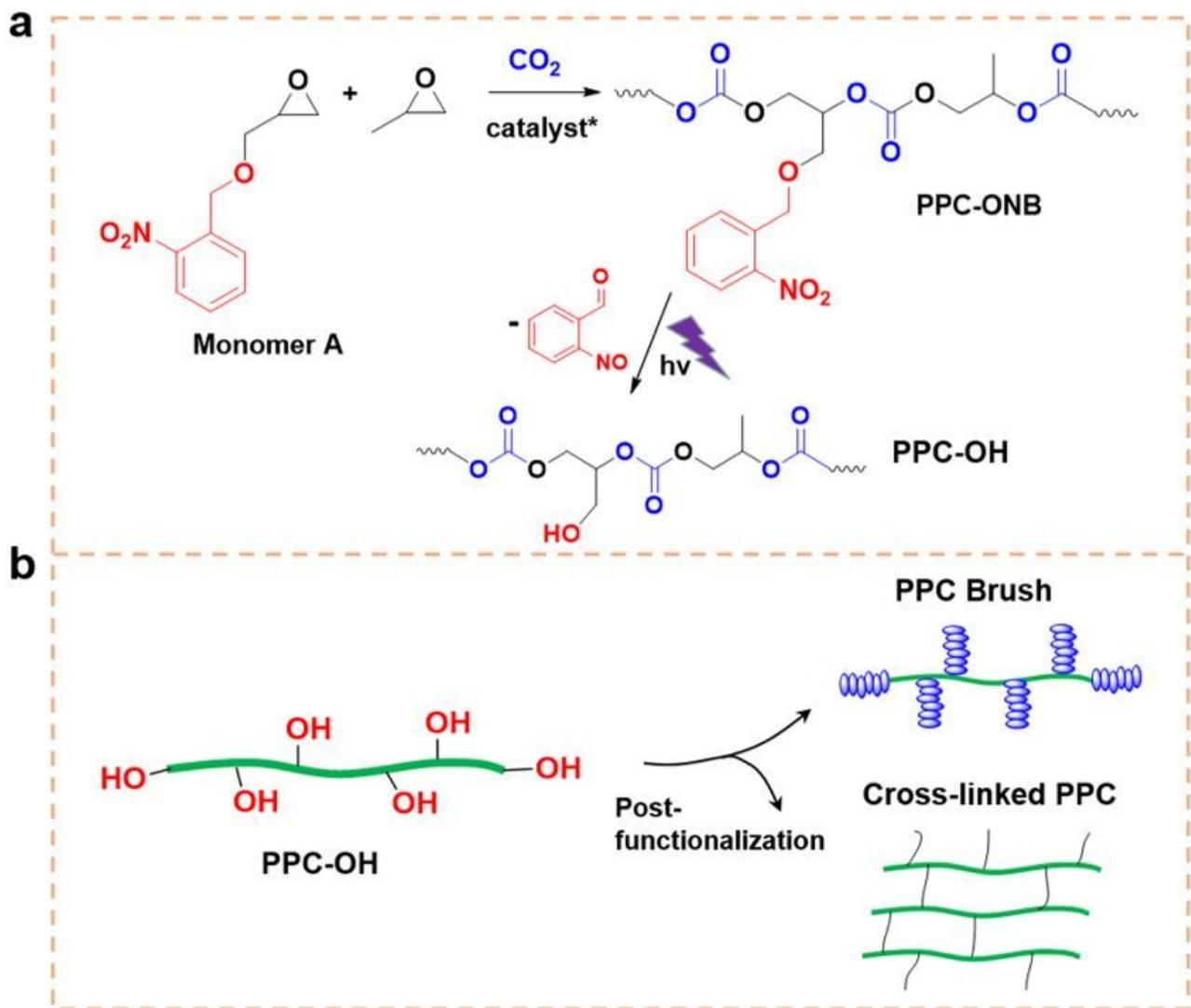
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## Schemes

Schemes 1 and 2 are available in the Supplementary Files section

## Figures



**Figure 1**

Schematic illustration of the synthetic procedure of PPC-OH (a) and the preparation of PPC brush and PPC network from PPC-OH via post-functionalization (b).

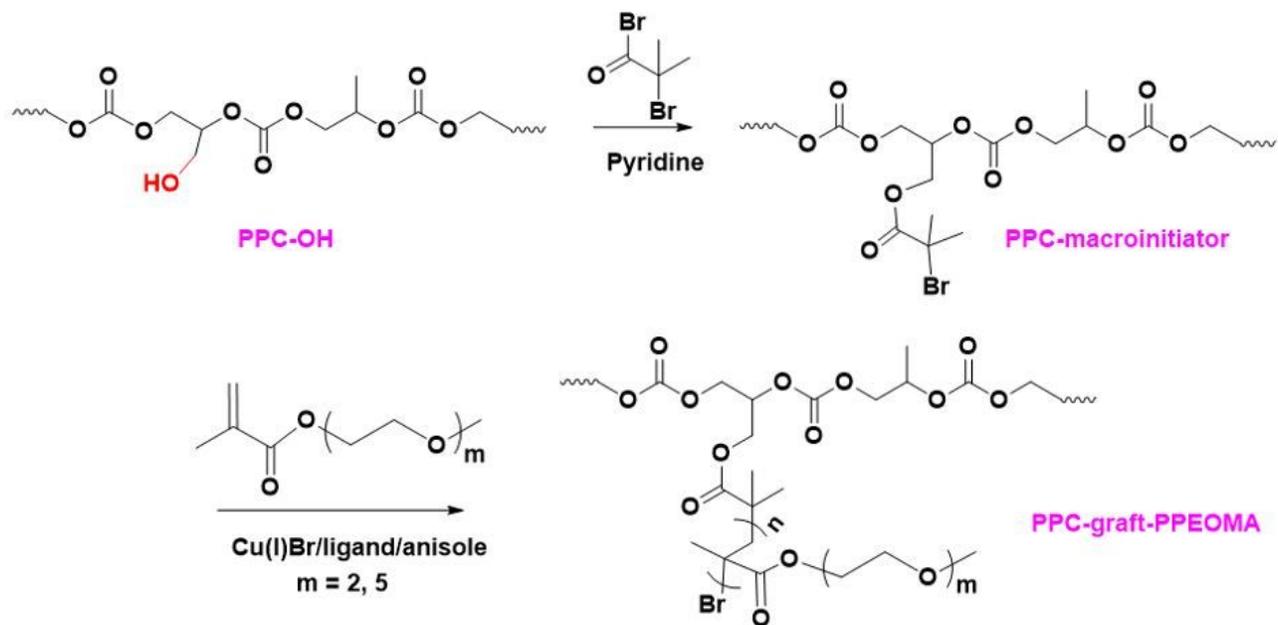
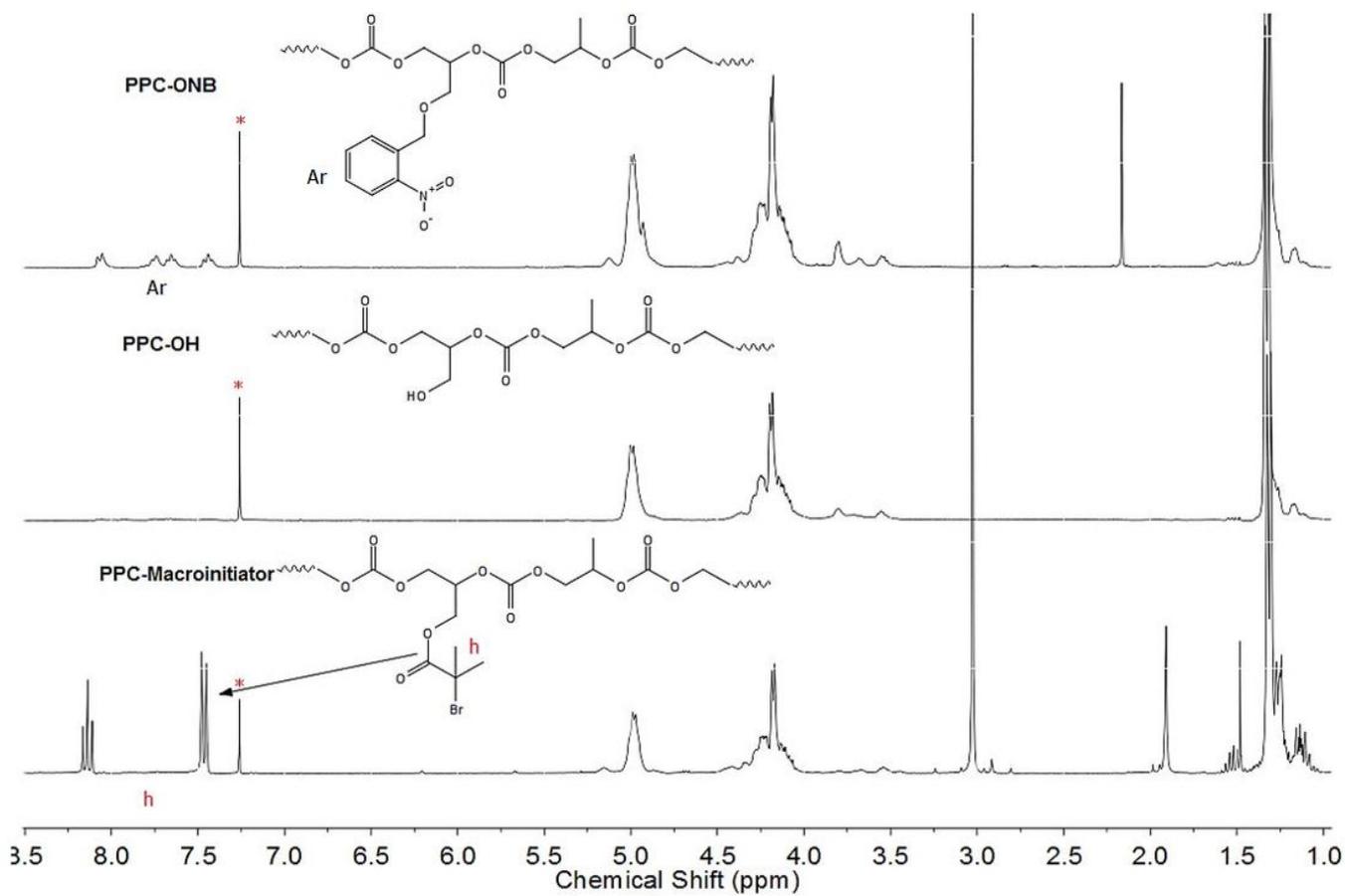


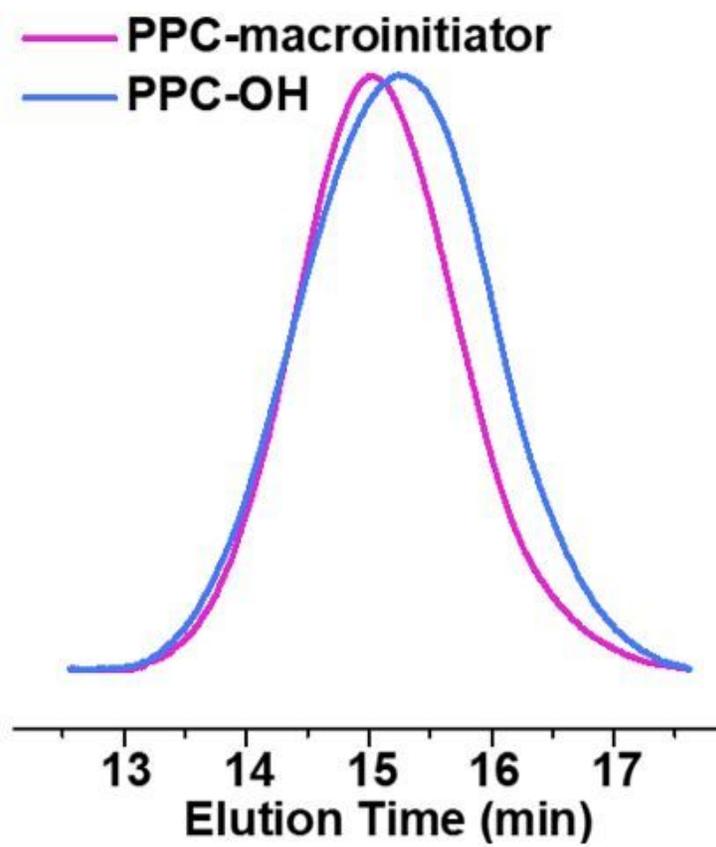
Figure 2

Synthesis of PPC-macroinitiator and PPC-graft-PPEOMA.



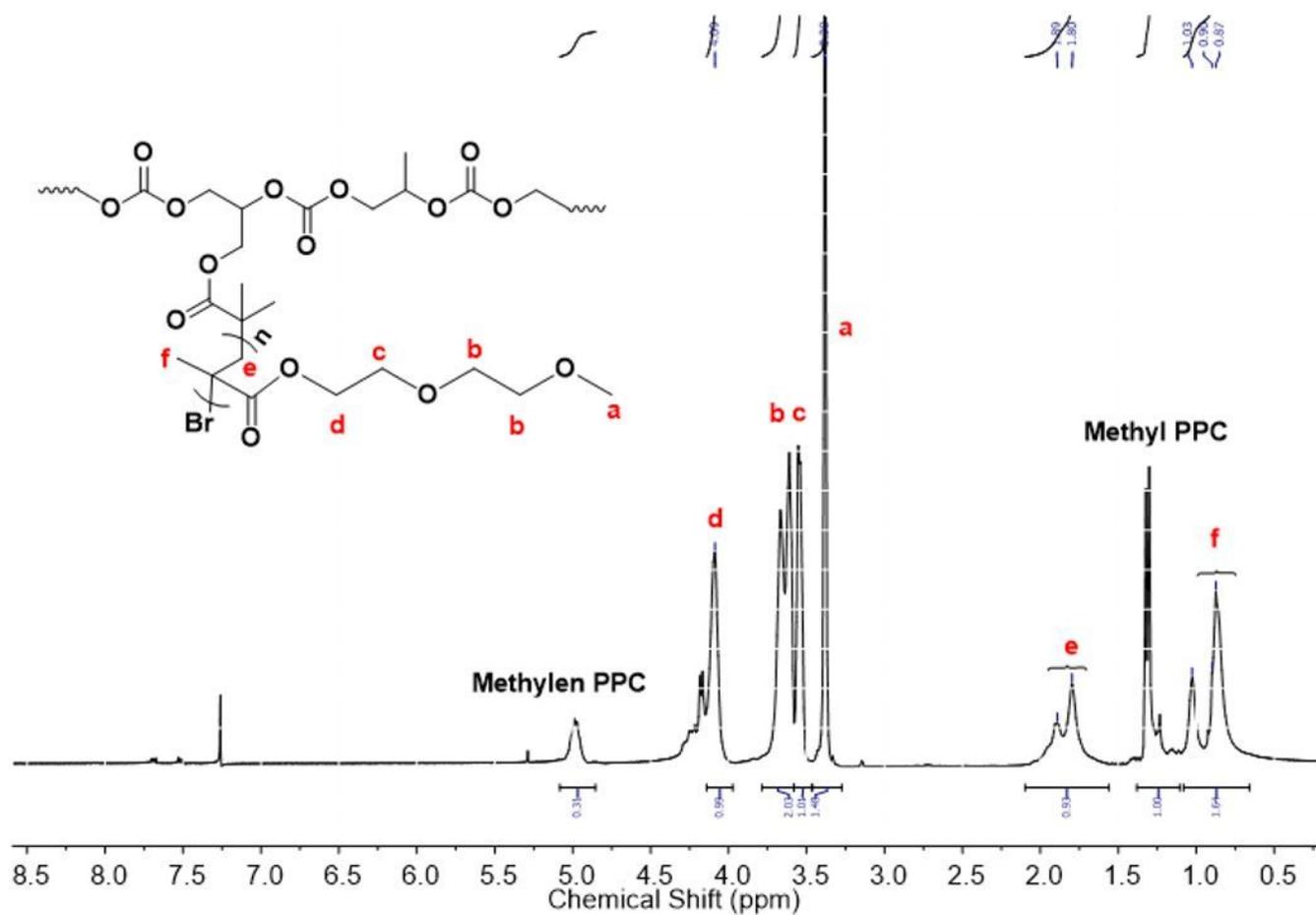
**Figure 3**

$^1\text{H}$  NMR spectra of PPC-ONB, PPC-OH and PPC-macroinitiator.



**Figure 4**

GPC trace of PPC-OH and the corresponding PPC-macroinitiator.



**Figure 5**

$^1\text{H}$  NMR spectra of PPC-graft-PPEOMA brush (sample **R4**,  $n = \text{DP}_{\text{PEO}} = 7$ ).

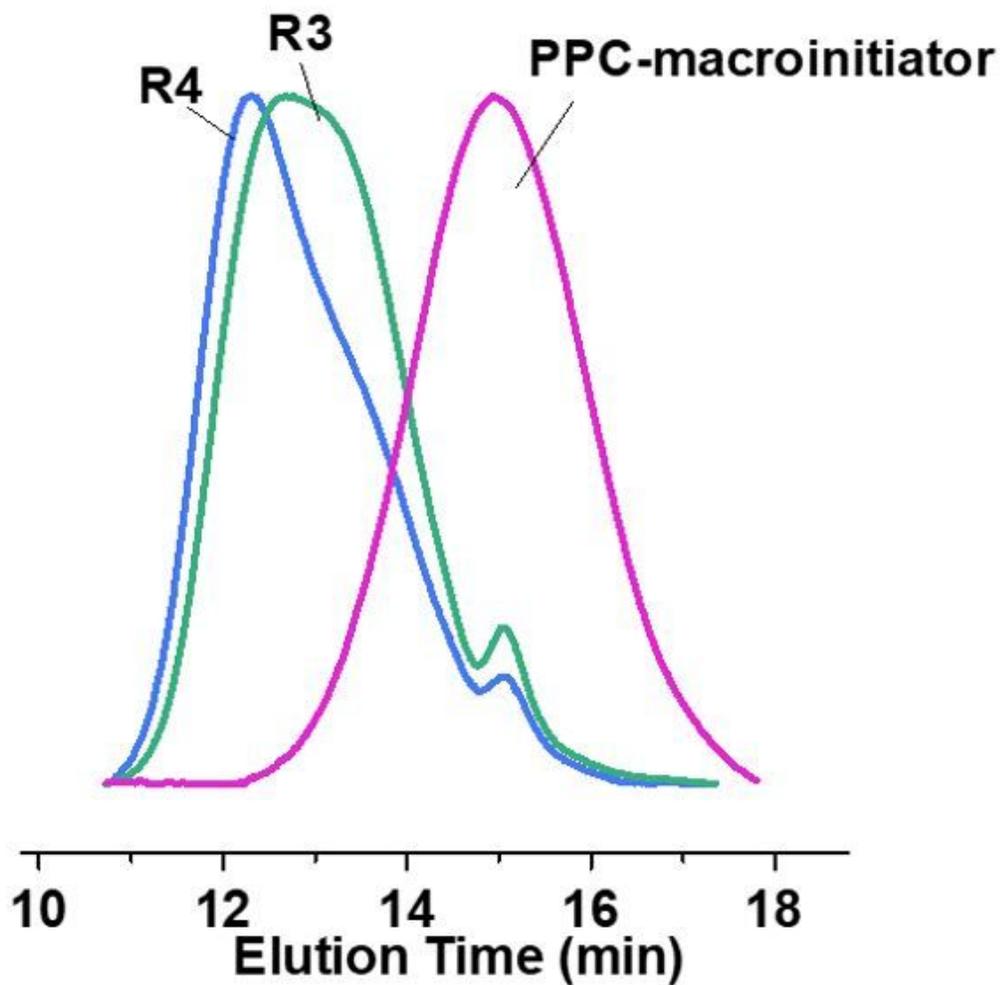


Figure 6

GPC trace of PPC-macroinitiator and PPC-brushes.

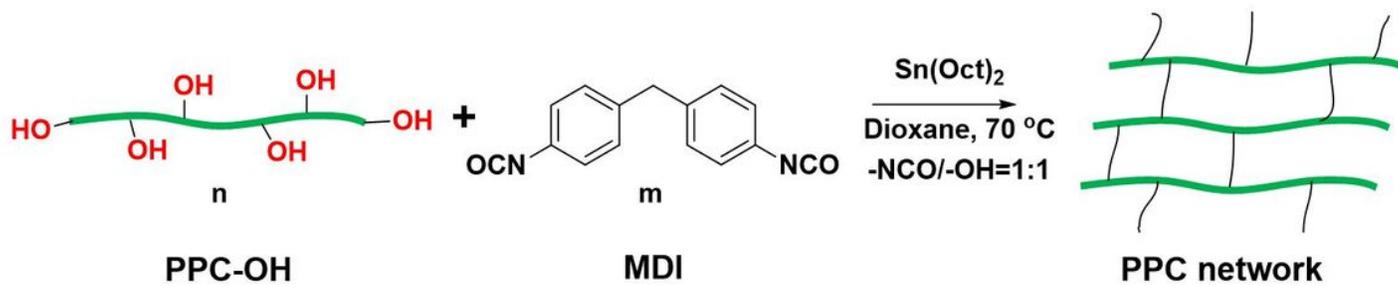


Figure 7

Synthesis of cross-linked PPC-OHs using MDI as cross-linking agent.

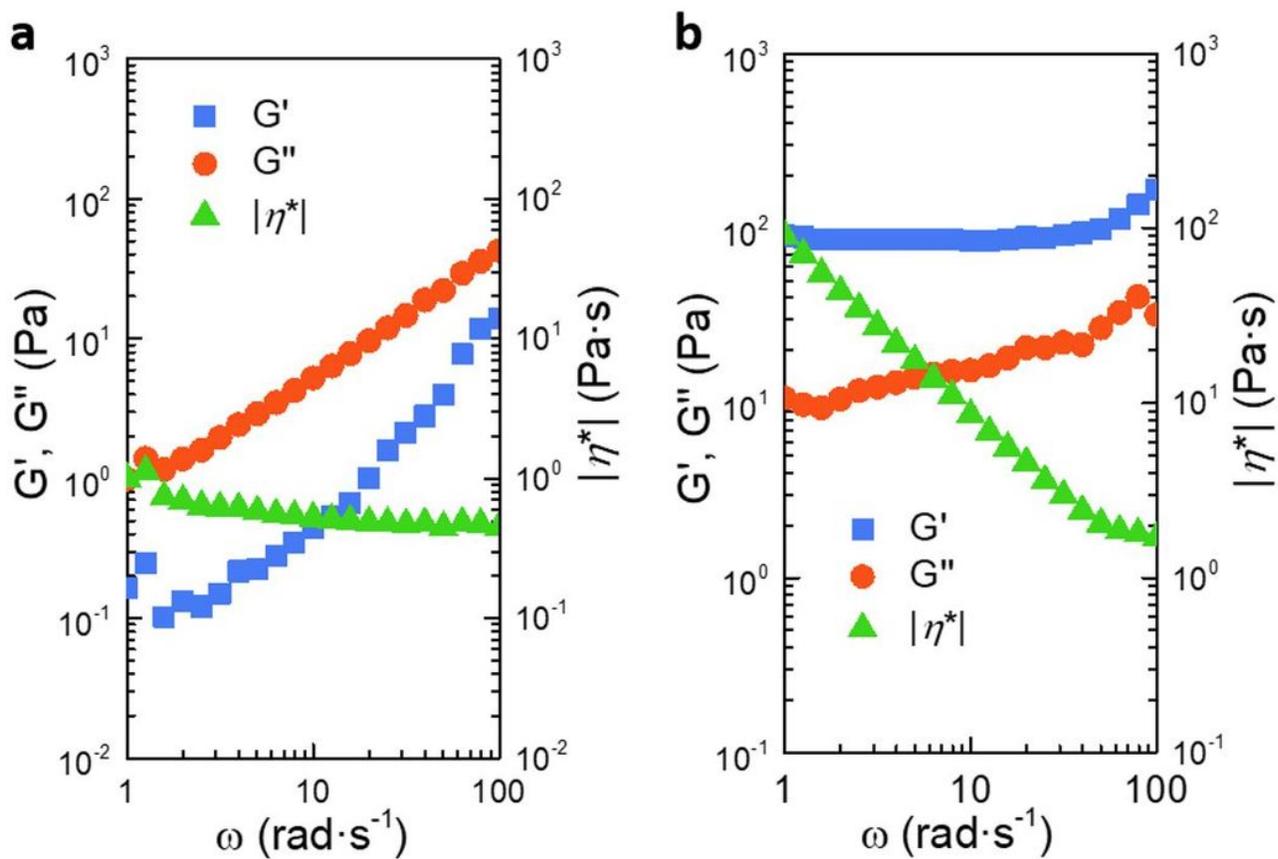
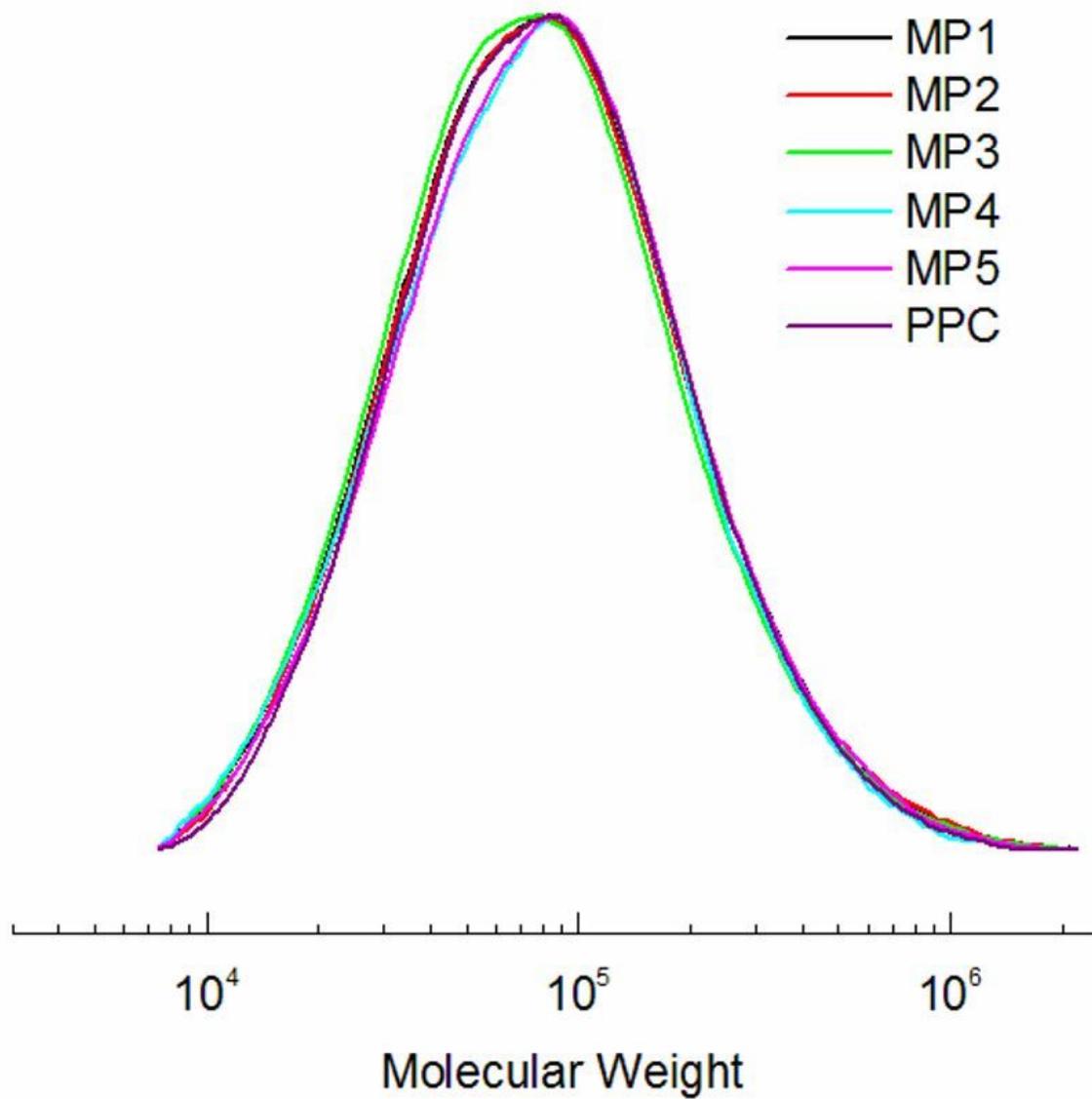


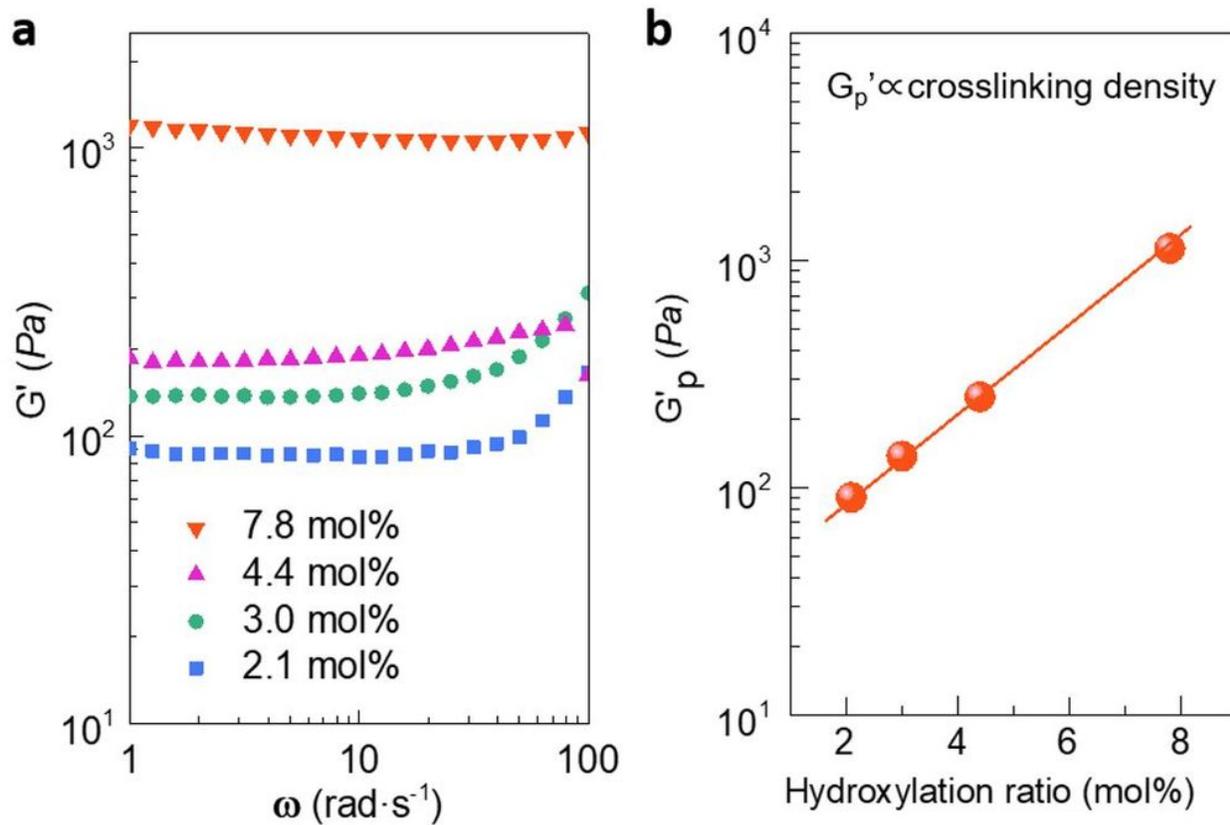
Figure 8

Rheological behaviors of the PPC-OH/MDI mixture system before (a) and after (b) the transformation into gel.



**Figure 9**

GPC traces of PPC after treating with MDI.



**Figure 10**

Rheological properties of cross-linked gels from PPC-OHs with various hydroxylation ratio (a) and the relationship between the plateau storage modulus and hydroxylation ratio of PPC-OH (b).

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.jpg](#)
- [Scheme2.jpg](#)