

Functionalization of Carbon Nanotubes by Surface-Initiated Immortal Alternating Polymerization of CO₂ and Epoxides

Yi-Ming Wang*, Xiao-Yu Song, Song-Hai Shao, Peng-Xiang Xu, Wei-Min Ren, Xiao-Bing Lu*

Address: State Key Laboratory of Fine Chemicals, Dalian University of Technology E-330 West Campus, 2 Linggong Rd., Dalian 116024, China. Email: chemwym@dlut.edu.cn, lxb-1999@163.com.

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1. Synthesis of complex SalenCo(III)Cl^[1]

To a stirred mixture of SalcyCo(II) complex (0.6040g, 1 mmol) in CH₂Cl₂ (15 ml) was added p-toluenesulfonic acid monohydrate (0.1997 g, 1.05 mmol, 1.05 equiv.) in acetone (15 ml). The solution was stirred under dry oxygen atmosphere at room temperature for 60 min. The solvents were removed by rotary evaporation and the solid was further dried in vacuum. The resulting solid was suspended in hexane and filtered to afford dark green SalenCo(III)OTs in 95% yield. ¹H NMR (DMSO-d₆, 400 MHz) δ 1.30 (s, 18H, CMe₃), 1.55-1.65 (m, 2H, CyH), 1.74 (s, 18H, CMe₃), 1.87-1.97 (m, 2H, CyH), 1.97-2.05 (m, 2H, CyH), 2.28 (s, 3H, CH₃), 3.04-3.10 (m, 2H, CyH), 3.58-3.65 (m, 2H, CyH), 7.10 (d, J=7.6Hz, 2H, PhH), 7.44-7.48 (m, 6H, ArH and PhH), 7.80 (s, 2H, HC=N).

SalenCo(III)OTs (0.4000g) was dissolved in CH₂Cl₂ of 30 ml and then transferred into a 125 mL separatory funnel. The organic layer was rinsed with saturated aqueous NaCl solution (3×50 ml). The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The resulting solid was further suspended in hexane and filtered to afford dark green complex in 80% yield. ¹H NMR DMSO-d₆, 400 MHz) δ 1.30 (s, 18H, CMe₃), 1.53-1.63 (m, 2H, CyH), 1.74 (s, 18H, CMe₃), 1.85-1.97 m, 2H, CyH), 1.97-2.05 (m, 2H, CyH), 3.04-3.11 (m, 2H, CyH), 3.58-3.66 (m, 2H, CyH), 7.44 (s, 2H, ArH), 7.47 (s, 2H, ArH), 7.80 (s, 2H, HC=N). ESIMS (m/z, M⁺ + H): 603.3362; Calcd. For C₃₆H₅₂N₂O₂Co]⁺: 603.3361.

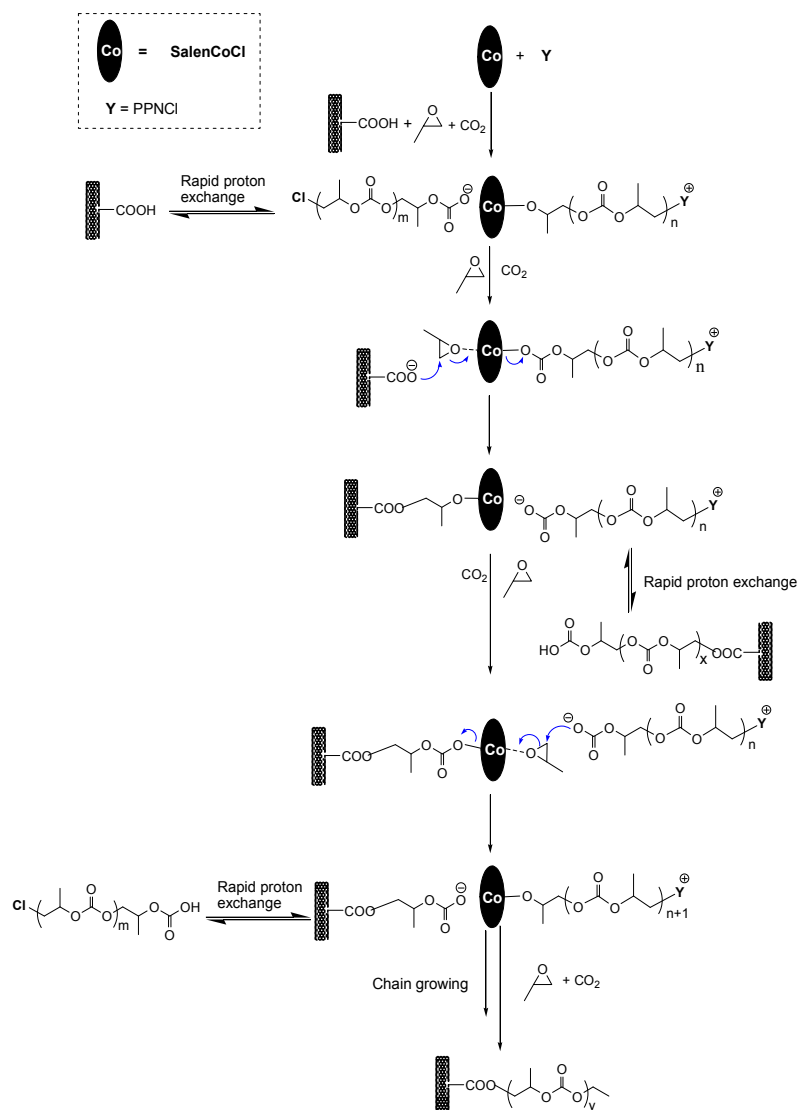
2. Gram Scale Procedure for the Copolymerization of CO₂ with Propylene Oxide.

To a stirred mixture of complex (0.52 g, 0.8 mmol, 1 equiv) was dissolved in propylene oxide (92.8 g, 1.6 mol, 2000 equiv) to form a red-brown solution, and then PPnCl (0.92 g, 1.6 mmol, 2 equiv) and MWNTs-COOH (1.2 g) were added into it in a nitrogen atmosphere respectively. The mixture was placed in an ultrasonic bath (40 kHz) for 30 min and then charged into a pre-dried 250 mL autoclave equipped with a magnetic stirrer. The autoclave was pressurized to the appropriate pressure with CO₂. In order to achieve the highest weight fraction of grafted polymer, the polymerization was stopped until the solution turned into solid phase. Then the resulting solid was dissolved and subsequently separated by vacuum-filtration using Millipore membrane filter. The product was obtained after drying overnight in vacuum at room temperature.

3. Mechanical understanding of chain transfer reaction and chain-growing on the surface of the MWNTs

On the basis of the facts previously described^[2], mechanistic understanding of chain transfer reaction between the polycarbonate anion and MWNTs-COOH, as well as chain-growing on the surface of the MWNTs in the binary catalyst system of SalenCo(III) and PPnCl was described in the scheme 1. Grafting chain-growth and dissociation of propagating carboxylate species on the surface of MWNTs take place at the one sides of the Co(III)-Salen center, and the cocatalyst takes turns at the other side. In the initial stage, the MWNTs-COOH is deprotonated by the anion at a growing-chain end of PPC, which becomes a dormant polymer chain. The forming carboxyl anion on the surface of

the MWNTs subsequently activates PO by its coordination to the central metal ion for further ring-opening. It is beneficial to the dissociation of the carboxylate species when the coordination of the epoxides and its further ring-opening simultaneously labilize the Co-carboxylate bond with regard to the anchored PPNCI on the other sides of cobalt center. The generated carboxylate anion chain attached by PPNCI could also be rapidly reversible with other dormant PPC immobilized on the MWNTs. Then, CO₂ rapidly inserts into the Co-O bond and another epoxide coordinates the central metal ion for the formation of carboxylate species. The insertion of CO₂ to Co-O bond produces the linear carbonate associated on the surface of MWNTs, which easily dissociates from the central metal at the activating PO by its coordination to the central metal ion with respect to the anchored PPNCI. Then the chains on the surface of MWNTs keep growing during the process of the insertion of CO₂ and epoxides, as well as rapid swapping between the neutral and deprotonated polymer chain.



Scheme S1. Mechanistic understanding of Chain transfer reaction between the polycarbonate anion and MWNTs-Polycarbonate, as well as chain-growing on the surface of the MWNTs in the Binary catalyst system of SalenCo(III)Cl and PPnCl.

4. Representative Raman spectroscopy of MWNTs-COOH and MWNTs-PPC

Raman spectroscopy was used to probe the electronic properties of the modified MWNTs materials. In figure 1, the D-band at about 1332 cm^{-1} , related to scattering from defects present in the hexagonal framework of the nanotube walls, and the G-band at about 1590 cm^{-1} , ascribed to the tangential C-C stretching vibrational mode^[3], can be clearly observed for MWNTs-COOH and MWNTs-PPC, indicating that the functionalized MWNTs still preserves its basic structure. A shoulder around 1600 cm^{-1} assigned to the D' band is ascribed to disorder and defects arising from double resonance feature. Relative to the oxidized tubes, a slight increase of an intense ratio I_D/I_G after grafting reaction with PPC due to the influence of the grafted PPC on the electronic properties of the MWNT-COOH, as well as the production of field disturbance and physical strain in the graphite skeleton as reported^[4,5]. The intensity enhancement of D band in MWNTs-g-PPC samples proves the covalent bonding of PPC to MWNTs, instead of physical adsorption with the graphene layer.

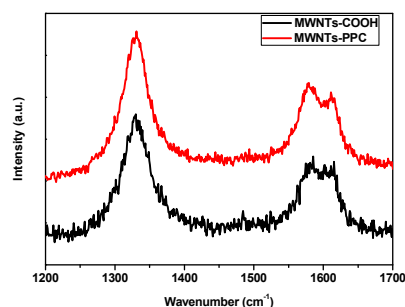


Figure 1. Raman spectra of MWNTs-COOH, $I_G/I_D=0.76$ and MWNTs-g-PPC,

$$I_G/I_D=0.85.$$

5. Representative TG plot of the resulted PPC

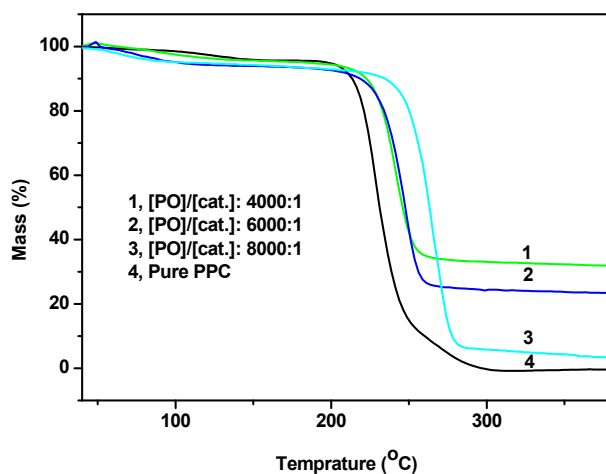


Figure 2. TGA curves: 1 , MWNTs-g-PPC, [PO]/[cat.]:4000:1; 2, MWNTs-g-PPC, [PO]/[cat.]:6000:1; 3, MWNTs-g-PPC, [PO]/[cat.]:8000:1; 4, Pure PPC.

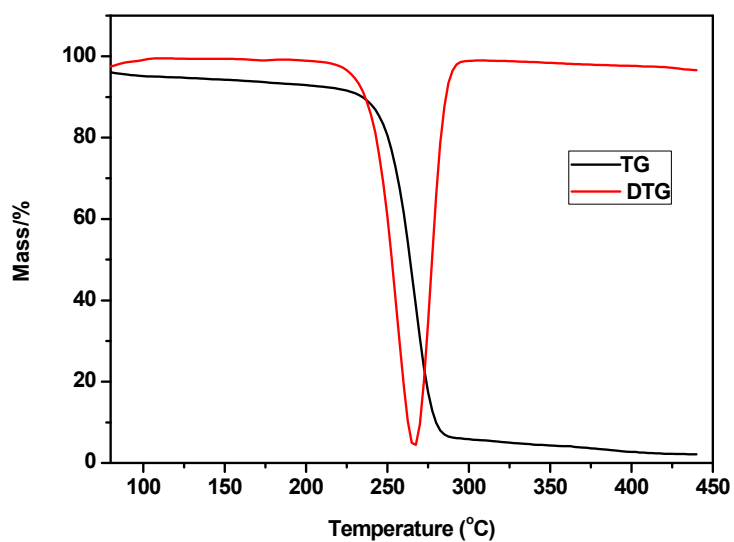


Figure 3. The TG and DTG curves of the MWNTs-g-PPC containing 92.7 weight % PPC.

6. Representative DSC plot of the MWNTs-g-PPC

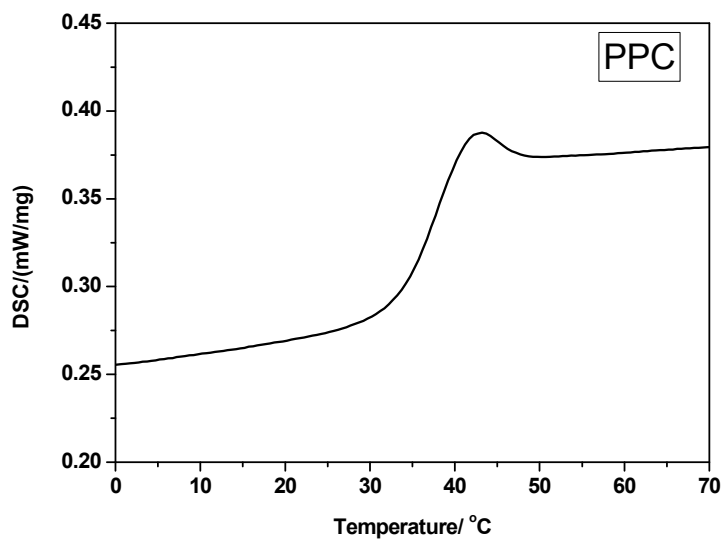


Figure 4. The DSC curves of the PPC.

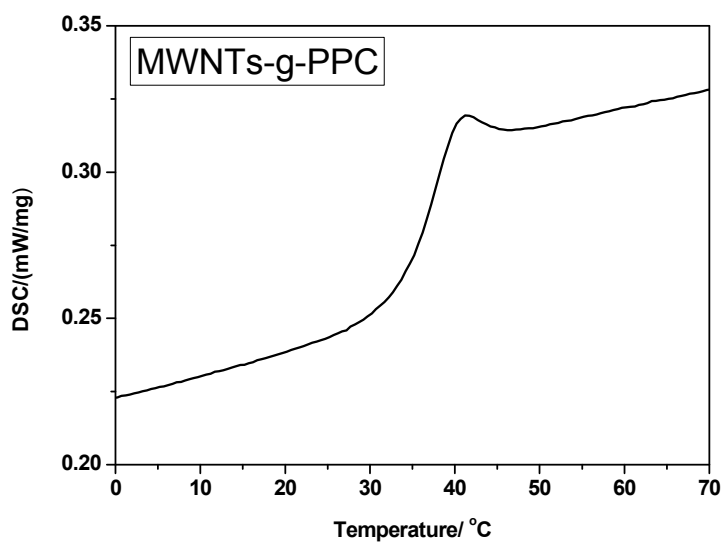
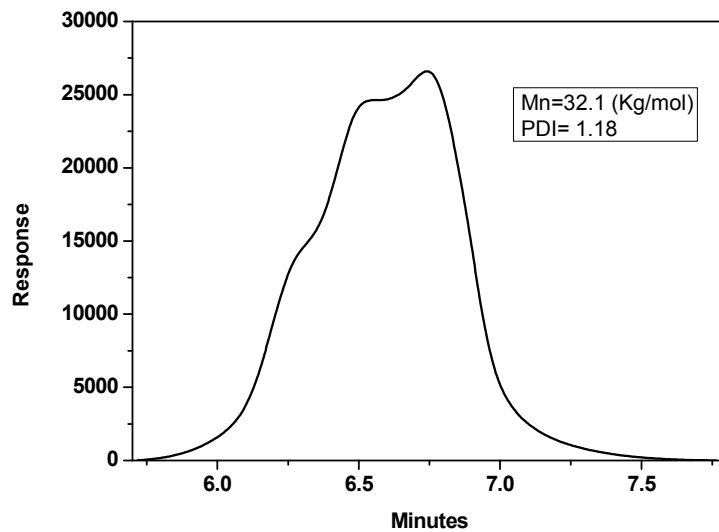
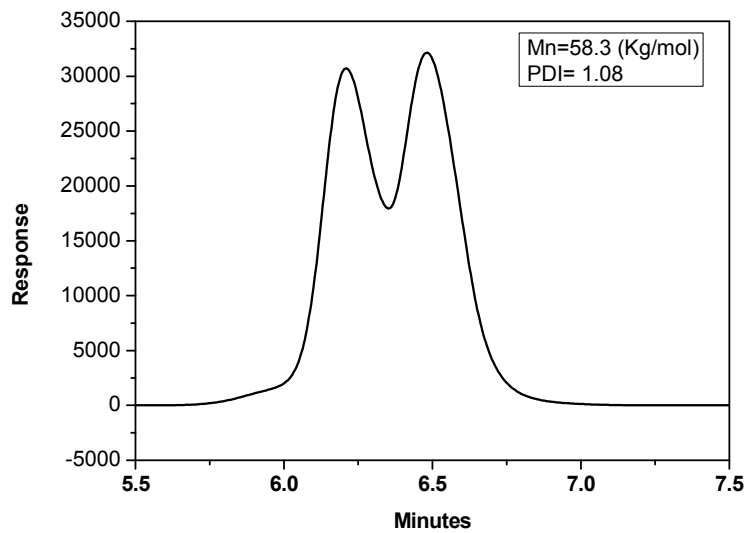
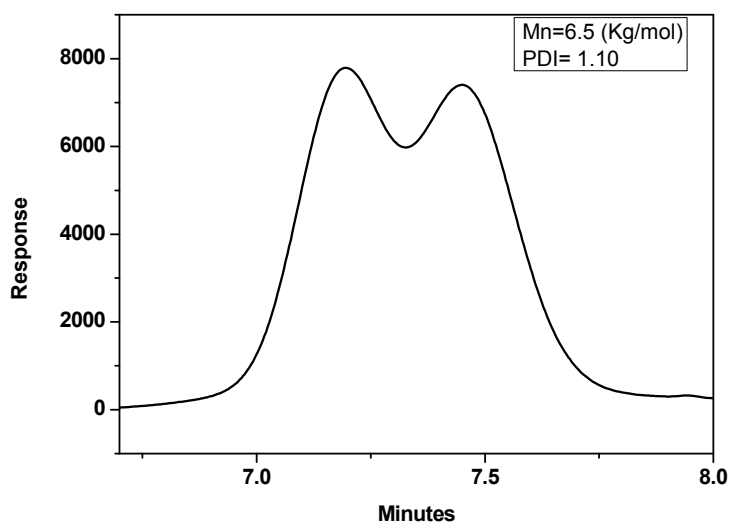


Figure 5. The DSC curves of the MWNTs-g-PPC.

7. GPC data for CO₂/PO copolymerization at various ratios of monomers to

catalysts





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