

Polypropylene-based graft copolymers *via* CuAAC click chemistry

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Abstract. Graft copolymers from commercial chlorinated polypropylene (PP-Cl) possessing either poly(ethylene glycol) (PEG) or poly(ϵ -caprolactone) (PCL) grafts are synthesized by copper (I)-catalyzed azide-alkyne cycloaddition ‘click’ reaction (CuAAC). For this purpose, azido-functional polypropylene is prepared by nucleophilic substitution of chlorine groups of PP-Cl with azidotrimethylsilane-tetrabutylammonium fluoride. Whereas, the clickable alkyne end-functional PEG and PCL are independently synthesized by esterification reaction of poly(ethylene glycol) methyl ether with 4-pentynoic acid at room temperature and ring-opening polymerization of ϵ -caprolactone using stannous octoate as catalyst and propargyl alcohol as initiator. Finally, the corresponding graft copolymers, PP-g-PEG and PP-g-PCL, with different surface properties were successfully synthesized by CuAAC ‘click’ reaction under mild condition. Spectral, chromatographic and thermal analyses at various stages prove the formation of desired polypropylene-based graft copolymers with well-defined properties. Furthermore, the water contact angle values of PP-Cl, PP-g-PEG and PP-g-PCL are found as $90\pm 1^\circ$, $78\pm 1.8^\circ$ and $83\pm 2.1^\circ$, respectively.

Keywords: polymer synthesis, chlorinated polypropylene, copper (I)-catalyzed azide-alkyne cycloaddition, graft copolymers, water contact angle

1. Introduction

Polyolefins comprising polypropylene, polyethylene, polyisobutylene, poly-1-butene, ethylene propylene diene rubber and ethylene propylene elastomer are known as the most widely used polymers in particular applications such as automotive, bottles, containers, hoses, garbage and bread bags etc. [1, 2]. The low cost, good mechanical and physical properties, both superior recyclability and processability are the key factors for selecting the polyolefins compared to other polymers in these applications. Since all polyolefins are aliphatic hydrocarbons consisting of only hydrogen and carbon atoms, they show poor wettability and adhesion characteristics. To overcome these limitations, the modification of polyolefins as a serious research area in polymer science has come into

prominence [3, 4]. Due to the absence of polar groups, semi-crystalline morphology, resistance to polar or ionic chemicals and limited chemical substitution, oxidation and free radical reactions, these modifications are quite challenging and usually are difficult to maintain [5]. There are two main modification methods in the literature: (i) direct copolymerization of either α -olefin [6, 7] or polar monomers [8, 9] and (ii) chemical modification of preformed polymers [10, 11]. For example, antibacterial [12], antifouling [13] and hydrogen storage [14] properties of polypropylene were enhanced *via* surface-initiated atom transfer radical polymerization [15]. Chlorine atoms on the polymer chains both develop polarity and allow reactive sites for a series of monomer such as acrylates, methacrylates and styrenes [16–19]. Polymers

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containing chlorine atoms, such as chlorinated poly(vinyl chloride) (CPVC), poly(vinyl chloride) (PVC), chlorinated polyethylene and polypropylene exhibit high fire and cold resistance as well as plasticity. These beneficial properties make them good choices for a number of industrial applications [20–25]. Among them, chlorinated polypropylene (PP-Cl) has been found many applications including paints, printing ink binders, overprint varnishes, sealing compounds and waterproof agents, due to its superior abrasive, ageing chemical resisting properties, and heat and light stability.

After successful discovery of click chemistry concept by Sharpless and Meldal, it is easy to perform polymer modification with high yield under mild conditions, such as rapid, stereospecific, orthogonal and no by-product coherent with the green chemistry [26]. Today, a series of reactions including Huisgen type Cu(I) catalyzed cycloaddition (CuAAC) [27, 28], thiol-ene [29–31] and Diels-Alder [32] are recognized as well-known click chemistry reactions [33]. Modification of polymers with CuAAC click reaction is very general, robust and particularly simple compared to other click chemistry reactions [34–37]. During the recent years, these reactions have been extensively applied for the modification of commercially available polymers such as PVC [38–41], polyethylene [42] and polypropylene [43, 44].

In the frame of our continuous interest in developing novel polymeric materials from commercially available polymers, here, the modification of chlorinated polypropylene with poly(ethylene glycol) and poly(ϵ -caprolactone) was achieved by CuAAC click chemistry under mild conditions. In this case, clickable azide functionality was introduced to commercial chlorinated polypropylene by using azidotrimethylsilane-tetrabutylammonium fluoride. In addition, the alkyne-functionalized poly(ethylene glycol) and poly(ϵ -caprolactone) were independently produced by esterification of poly(ethylene glycol) methyl ether by using 4-pentynoic acid and classical ring opening polymerization of ϵ -caprolactone initiated by propargyl alcohol and catalyzed by tin(II) 2-ethylhexanoate. The subsequent CuAAC click reactions of these polymers enabled to attain graft copolymers based on polypropylene. The successful formation of graft copolymers were confirmed by spectral, chromatographic and thermal analyses. Furthermore, the surface properties of obtained graft copolymers were also investigated by water contact angle measurement.

2. Experimental part

2.1. Materials

Chlorinated polypropylene (PP-Cl, $M_{n, GPC} = 50000$ g/mol determined by GPC measurement), chlorine mass fraction: 29–32% [m/m] was purchased from Mark Zhang Shanghai Sunking Industry Incorporation (China). Azidotrimethylsilane (TMS- N_3 is flammable chemical, 95%), solution of tetrabutylammonium fluoride (TBAF, 1.0 M in THF), poly(ethylene glycol) methyl ether (mPEG, $M_n = 5000$ g/mol), 4-dimethylaminopyridine (DMAP, 99%), N,N' -dicyclohexylcarbodiimide (DCC, 99%), propargyl alcohol (99%), ϵ -caprolactone (ϵ -CL, 97%) and tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 92.5–100.0%), copper(I) chloride (CuCl, 99.99%) and N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Sigma Aldrich (Steinheim, Germany) and used as received. 4-pentynoic acid (98%, Alfa Aesar, Haverhill, ABD) used as received. Tetrahydrofuran (anhydrous, $\geq 99.9\%$, inhibitor-free, Sigma Aldrich, Steinheim, Germany), methanol (for HPLC, $\geq 99.9\%$, Sigma Aldrich, Steinheim, Germany), toluene (anhydrous, 99.8%, Sigma Aldrich, Steinheim, Germany), hexane (anhydrous, 95%, Sigma Aldrich, Steinheim, Germany), dichloromethane (anhydrous, $\geq 99.8\%$, Sigma Aldrich, Steinheim, Germany) and diethyl ether (for analysis EMSURE[®], Sigma Aldrich, Steinheim, Germany) were used without distillation. Glass cover slides sized 76 to 26 mm were purchased from ISOLAB (Istanbul, Turkey) and used for dip-coating.

2.2. Instrumentation

Fourier transform infrared (FT-IR) analyses were performed by Spectrum Two Spectrometer (Perkin-Elmer, Waltham, USA) equipped with a diamond ATR device for verify specific groups of intermediates and final products. 1H -NMR measurements were recorded by Varian 400 MHz NMR (Palo Alto, California, USA) spectrometer in chloroform-d with tetramethylsilane.

Gel permeation chromatography (GPC) analyses were determined by Viscotek GPCmax consisting of a refractive index (RI) detector (VE 3580, Viscotek) and a pump module (GPC max, Viscotek, Houston, TX) with flow rate 1 mL/min. In analyses injections auto-sampler system and 50 μ L injection volume were used. The calibration of RI detector was done by narrow molecular weight polystyrene standards. Two columns (LT5000L, Mixed, Medium Organic 300 \times 8 mm and

LT3000L, Mixed, Ultra-Low Organic 300×8 mm) with a guard column (TGuard, Organic Guard Column 10×4.6 mm) were used for the tetrahydrofuran eluent at 35 °C. Viscotek OmniSEC Omni-01 software were used to analyze the data. Differential scanning calorimetry (DSC) measurements were conducted to determine both melting temperatures and glass transition temperatures using Perkin-Elmer brand device (Waltham, USA) with diamond equipment with a heating rate of 10 °C/min under nitrogen flow (10 mL/min). Water contact angle (WCA) measurements was performed by KSV Attension Theta Optical Tensiometer (CAM-200, Vastra Frolunda, Sweden) using water for chromatography (LC-MS Grade) at room temperature.

2.3. General procedure for azide-functional polypropylene (PP-N₃)

According to a typical azidation procedure [45]; PP-Cl (1.0 g, 2·10⁻² mmol) was dissolved in THF (5 mL) and added in a 20 mL one necked flat bottomed flask, equipped with magnetic stirrer bar. Then, the TMS-N₃ (0.2 mL, 1.7 mmol) and TBAF (0.5 mL, 1.5 mmol) were added by drop-wise, respectively. Subsequently, purged with nitrogen gas for 10 min, formulation was left under vigorous stirring for 24 h heated up to 60 °C in oil bath. After the given time, the obtained PP-N₃ solution was precipitated with nearly 10 times excess methanol. This solution was filtered and dried under vacuum to remove residual solvent. (Yield = 90%, $M_{n,GPC} = 50\,000\text{ g}\cdot\text{mol}^{-1}$)

2.4. Synthesis of alkyne end-functionalized poly(ϵ -caprolactone) (PCL-alkyne)

Synthesis procedure of alkyne end-functionalized poly(ϵ -caprolactone) was carried out according to previous literatures [46, 47]. Briefly, monomer ϵ -caprolactone (5 mL, 47 mmol), propargyl alcohol (0.1 mL, 1.2 mmol) as an initiator and Sn(Oct)₂ (three drops by using pasteur pipette) as a catalyst in 5 mL toluene were added in a 20 mL one necked flat bottomed flask that flamed previously and equipped with magnetic stirrer bar. The polymerization was conducted at 110 °C for 18 h. After the polymerization, the mixture was precipitated with nearly 10 times excess hexane. This solution was filtered and dried under vacuum. (Yield = 61%, $M_{n,theo} = 2800\text{ g}\cdot\text{mol}^{-1}$, $M_{n,GPC} = 3100\text{ g}\cdot\text{mol}^{-1}$, $M_{n,NMR} = 2700\text{ g}\cdot\text{mol}^{-1}$).

2.5. Synthesis of alkyne-end functionalized poly(ethylene glycol) methyl ether (PEG-alkyne)

Synthesis procedure of alkyne functionalized poly(ethylene glycol) methyl ether was performed according to previous literatures [48–50]. Briefly, the mPEG (3 g, 0.6 mmol) solution in 25 mL CH₂Cl₂, 4-pentynoic acid (0.22 g, 2.25 mmol), DMAP (0.09 g, 0.75 mmol) and DCC (0.45 g, 2.25 mmol) solution in 10 mL CH₂Cl₂ were added into a 250 mL one necked flat bottomed flask, equipped with magnetic stirrer bar. Then the mixture was left under vigorous stirring for 24 h. at room temperature. And then, the PEG-alkyne solution was purified by column chromatography. The solution was precipitated with nearly 10 times excess diethyl ether. Then, the precipitate was filtered and dried under vacuum. (Yield = 48%, $M_{n,theo} = 5100\text{ g}\cdot\text{mol}^{-1}$, $M_{n,GPC} = 4200\text{ g}\cdot\text{mol}^{-1}$, $M_{n,NMR} = 5500\text{ g}\cdot\text{mol}^{-1}$).

2.6. Synthesis of polypropylene-based graft copolymers via CuAAC click chemistry (PP-g-PCL and PP-g-PEG)

In a 25 mL flask pre-heated to 50 °C with magnetic stirrer, PP-N₃ (0.5 g, 1·10⁻² mmol), PCL-alkyne (0.48 g, 1·10⁻¹ mmol) or PEG-alkyne (0.5 g, 1·10⁻¹ mmol), ligand PMDETA (6.3 μ L, 3·10⁻² mmol) and catalyst CuCl (3 mg, 3·10⁻² mmol) were added and dissolved in THF (15 mL). Before the reaction mixture was left to refill with nitrogen for 10 min degassed by vacuum and stirred for 24 h. After the given reaction time final solution was diluted with THF and passed from neutral alumina to remove metal salts. This eluent was concentrated by evaporation and precipitated with cold methanol before dried under vacuum about overnight at room temperature.

2.7. Water contact angle measurement

A homemade mechanical dip coater was used to coating to glass substrate with solution of precursor and obtained polypropylene-based graft copolymers. Before the dip coating glass slides which are used as substrate in coating procedure were cleaned in chromic acid and then rinsed with de-ionized water two times. 150 mg/mL concentration of PP-Cl, PP-g-PCL and PP-g-PEG solutions were prepared in THF and glass cover slides dipped into them by using

homemade mechanical dip coater at room temperature (withdraw rate: 100 mm/min, waiting duration: 30 min) to obtain uniform surfaces. After given time coated glass slides were held under vacuum to remove residual solvents for 24 h before the WCA measurements.

3. Results and discussion

Graft copolymers with different topologies prepared since many decades for numerous applications are the general type of segmented copolymers that branches of different composition randomly linked to a linear polymer backbone. Due to their ultimate mechanical, thermal and solution properties compared with linear polymers, they have been utilized as surfactant, nano-carrier, emulsifier, biosensor, compatibilizer, resistance material and thermoplastic elastomer [1]. Generally, there are three type synthesis methods for graft copolymers including (i) grafting through or macromonomer method, (ii) grafting from and (iii) grafting onto methods [51–53]. After the discovery of click chemistry reactions, the use grafting onto method is more applicable than others. Thanks to click chemistry reactions, a series of difficulties such as poor selectivity, low grafting efficiency and tolerance to a variety of solvents and functional groups can be simply eliminated in the synthesis of graft copolymers. In the present paper, polypropylene based graft copolymers including PP-g-PCL and PP-g-PEG from chlorinated polypropylene were successfully prepared *via* grafting onto method using CuAAC click chemistry (Figure 1.)

The structures of obtained PP-g-PCL, PP-g-PEG and intermediates were firstly confirmed by both FT-IR and $^1\text{H-NMR}$ spectroscopies. In Figures 2 and 3, it can be seen that characteristic C-Cl band of PP-Cl at around 730 cm^{-1} were disappeared, while a sharp peak corresponding to $-\text{N}_3$ group at around 2095 cm^{-1} was appeared after the azidation reaction. Moreover, the stretching alkyne peaks of the PCL-alkyne or PEG-alkyne appeared in both spectrums at around

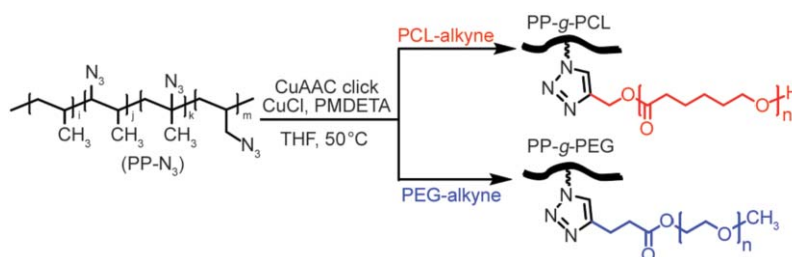


Figure 1. Polypropylene-based graft copolymers from PP-Cl *via* CuAAC click chemistry.

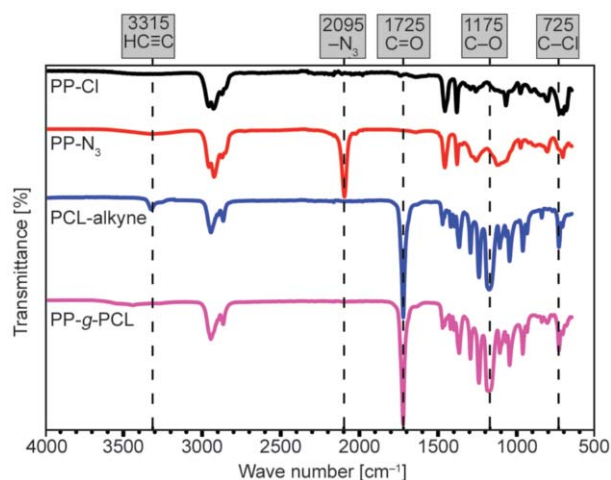


Figure 2. FT-IR spectra of PP-Cl, PP- N_3 , PCL-alkyne and PP-g-PCL.

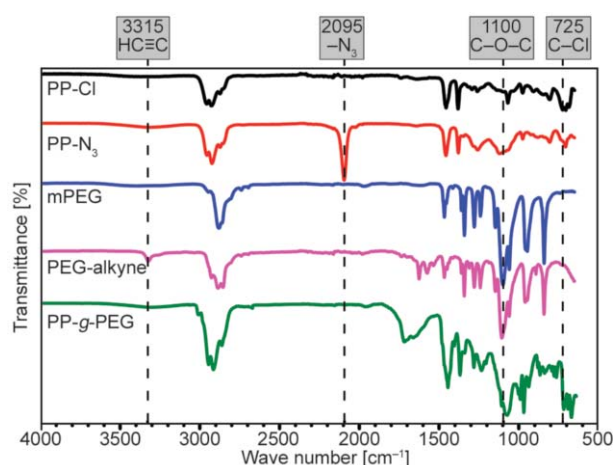


Figure 3. FT-IR spectra of PP-Cl, PP- N_3 , mPEG, PEG-alkyne and PP-g-PEG.

3315 cm^{-1} after ring opening polymerization and esterification reaction, respectively. According to FT-IR analysis, the complete disappearances of azide and alkyne peaks as well as appearance of $>\text{C}=\text{O}$ band at around 1725 cm^{-1} for PP-g-PCL, etheric C-O-C band at around 1100 cm^{-1} and $-\text{C}-\text{O}$ band at around 1175 cm^{-1} for PP-g-PEG indicated the successive formation of desired polypropylene based graft copolymers.

To confirm the chemical structures of polypropylene-based copolymers and intermediates, $^1\text{H-NMR}$

studies were conducted. As depicted in Figures 4 and 5, there were mainly two types of protons belonging to PP-Cl samples; the protons attached to –Cl bounded carbons (–CH₂–Cl and –CH–Cl) and aliphatic protons (–CH₂– and –CH–) of the main chain. The aliphatic protons (1–3 and 5–10) were appeared resonance between 1.71 and 2.81 ppm, while the other protons (4 and 11) were seen at 3.55 and 3.68 ppm, respectively [20]. After the azidation process, new peaks (a and b) belonging to protons attached to –N₃ bounded carbon atoms were appeared at 2.24 and 3.22 ppm, whereas the remaining –Cl bounded carbon protons (4 and 11) were still observed in the PP-N₃ sample. The ¹H-NMR spectra of PCL-alkyne and corresponding PP-g-PCL samples were also presented in Figure 4. As can be seen that the disappearances of characteristic alkyne and azide peaks; methine (c) 4.7 ppm and methylene (d) protons at 2.5 ppm of PCL-alkyne and methine (a) and methylene (b) as well as the appearance of triazole proton (c) at 8.12 ppm were great evidences for the

successful formation of clicked product PP-g-PCL [54]. Also in Figure 5, the structure of another PP-g-PEG copolymer was also analyzed by ¹H-NMR spectroscopy and the similar results were observed [45, 55–58]. Furthermore, the composition of graft copolymers were also calculated from integration ratios of specific resonances belonging to each segments by using following formulas Equations (1) and (2) for PP-g-PCL and PP-g-PEG and the result summarized in Table 1. The molar content of the polypropylene in the PP-g-PCL was found 88%, while it was 72% for PP-g-PEG. This difference could be explained by the higher chain length of PEG-alkyne, which partially increase the PEG content as well as decrease the PP content in the PP-g-PEG. All of these results confirmed the chemical structures of PP-g-PCL and PP-g-PEG.

$$PP[\%] = \left[\frac{\left(\frac{3+6+7+9}{10} \right)}{\left(\frac{0}{2} \right) + \left(\frac{3+6+7+9}{10} \right)} \right] \cdot 100 \quad (1)$$

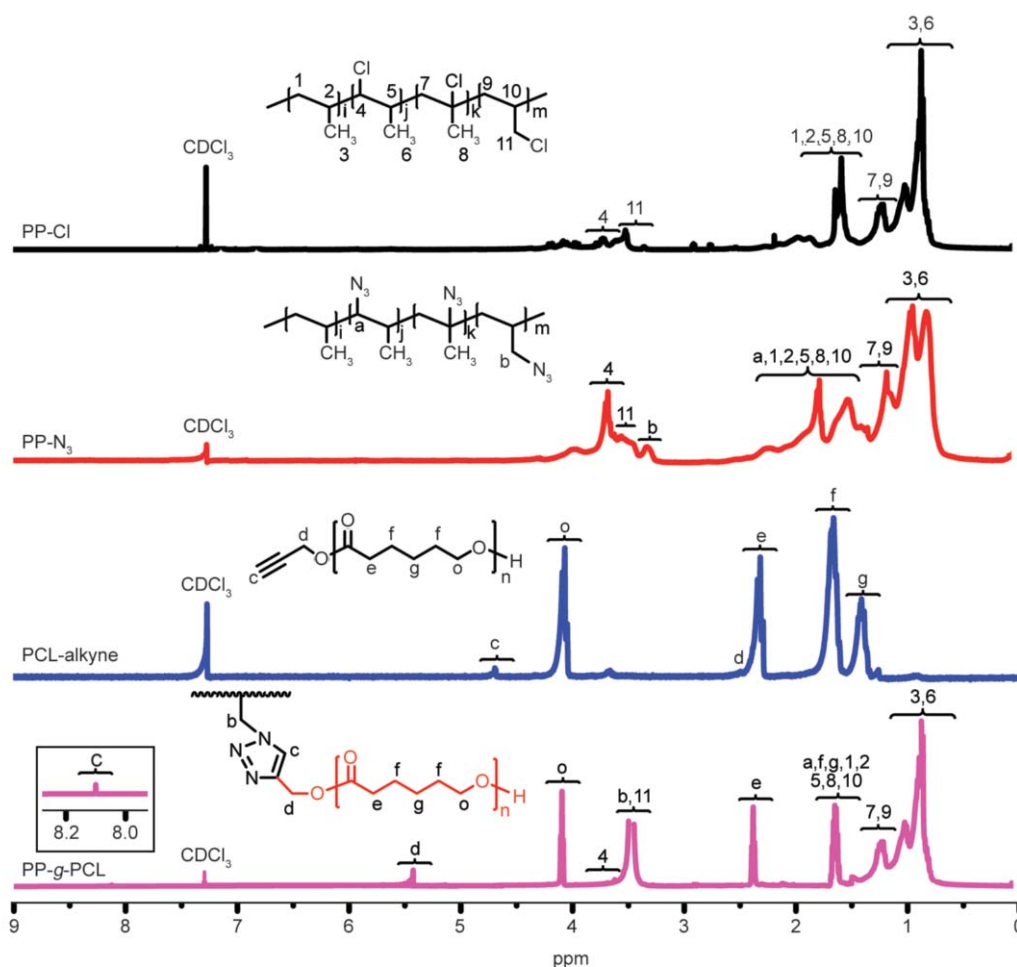


Figure 4. ¹H-NMR spectra of PP-Cl, PP-N₃, PCL-alkyne and PP-g-PCL.

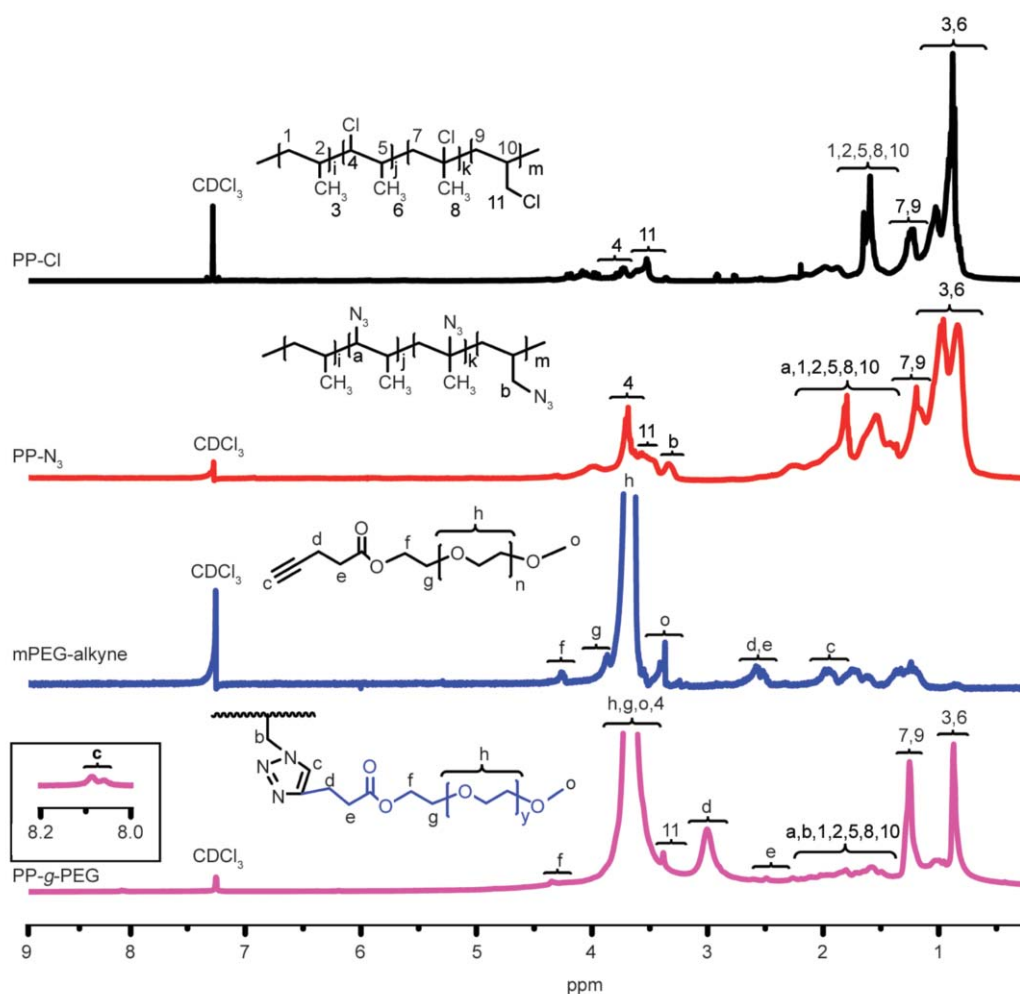


Figure 5. $^1\text{H-NMR}$ spectra of PP-Cl, PP- N_3 , PEG-alkyne and PP-g-PEG.

$$\text{PP}[\%] = \left[\frac{\left(\frac{3+6+7+9}{10} \right)}{\left(\frac{4+11+b+h+g+o}{4} \right) - \left(3 \cdot \frac{3+6+7+9}{10} \right) + \left(\frac{3+6+7+9}{10} \right)} \right] \cdot 100 \quad (2)$$

Table 1. The molecular weight and thermal properties of PP-g-PCL and PP-g-PEG, and their precursors.

Polymer	Conv. ^a [%]	$M_{n,\text{GPC}}^b$ [g·mol ⁻¹]	D^b	Comp. ^c [PP%]	T_g^d [°C]	T_m^d [°C]
PP-Cl	–	50 000	3.21	100	39	not determined.
PP- N_3	–	52 000	3.23	100	36	not determined.
PCL-alkyne	61	3 100	1.85	–	not determined.	58
PEG-alkyne	48	4 200	1.21	–	not determined.	55
PP-g-PCL	45	88 000	1.98	88	not determined.	54
PP-g-PEG	53	38 000	2.29	72	not determined.	49

^aCalculated gravimetrically; ^bThe molecular weight ($M_{n,\text{GPC}}$) and distribution (D) were determined by gel permeation chromatography; ^cThe compositions were calculated by $^1\text{H-NMR}$ using Equations (1) and (2); ^dDetermined by differential scanning calorimetry.

The molecular weights and distributions of obtained graft copolymers and intermediates polymers were investigated by GPC analysis. According to Figures 6, both graft copolymer and precursor samples displayed unimodal peaks without a shoulder. Interestingly,

after the click reactions, the GPC chromatogram of PP-g-PCL sample shifted to higher molecular weight (from 50 000 to 88 000 g·mol⁻¹), but the other chromatogram belonging to PP-g-PEG sample were moved to lower molecular weight (from 50 000 to

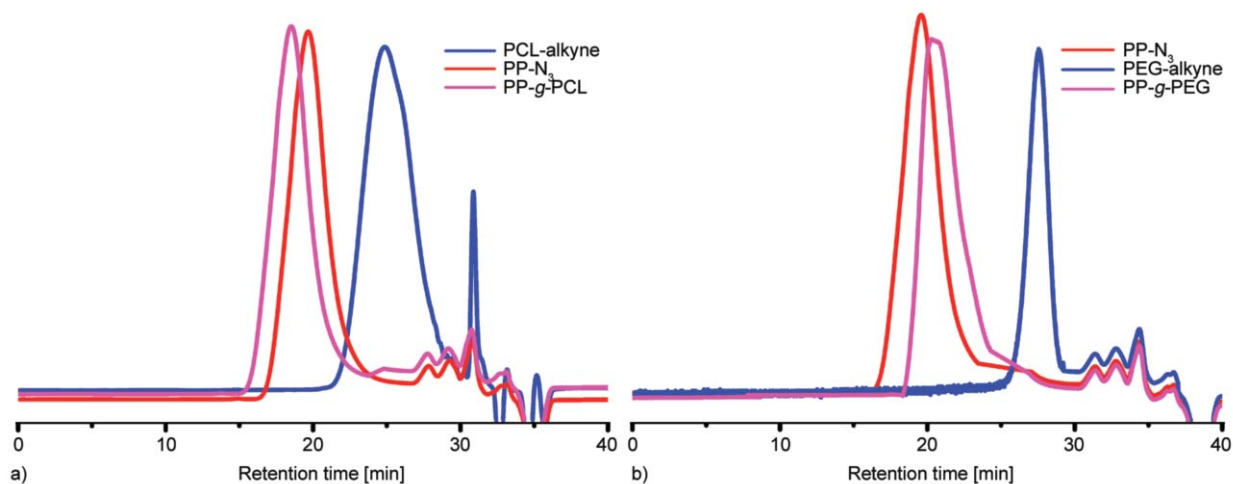


Figure 6. GPC traces of precursor PCL-alkyne, PP-N₃ and PP-g-PCL (a), PP-N₃, PCL-alkyne and PP-g-PEG (b).

38 000 g·mol⁻¹). This decrease might be due to the hydrophilic behavior of PEG segments, which strongly interacted with the stationary phase [59]. Therefore, the molecular weight of PP-g-PEG sample was decreased with respect to linear PP-N₃. The similar behaviors were also reported by previously published studies [60–62]. For example, the molecular weight was decreased to 21 520 g·mol⁻¹ in the synthesis of well-defined amphiphilic polysulfones-g-poly(ethylene glycol) starting from PSU-N₃ (25 600 g·mol⁻¹) and PEG (550 g·mol⁻¹) precursors [63]. It was also noted that polydispersities of the obtained PP-g-PCL (\bar{D} = 1.98) and PP-g-PEG (\bar{D} = 2.29) were narrower than the PP-Cl sample (\bar{D} = 3.21) and these data were acceptable for graft copolymers. (Table 1). Notably, the combination of well-defined side chains with commercial PP-Cl could decrease the polydispersities of obtained graft copolymers [63]. These results together with ¹H-NMR spectroscopy confirmed the successful synthesis of graft copolymers from commercially available precursors. The thermal properties of the graft copolymers and precursor backbone were further analyzed by differential scanning calorimeter (DSC). The neat PCL and PEG segments exhibited semi-crystalline characteristics having a glass transition (–60 and –55 °C) and a melting (58 and 55 °C) temperatures. As shown in Figure 7, while the PP-Cl and PP-N₃ displayed a glass transition temperature (T_g) at 39 and 36 °C respectively, after CuAAC click reactions, this T_g was not detected in both PP-g-PCL and PP-g-PEG samples. This might be explained by overlapping of T_g with the melting peaks of PP-g-PCL and PP-g-PEG that were detected at 54 and 49 °C, respectively. On the other hand, the melting points of PCL and PEG

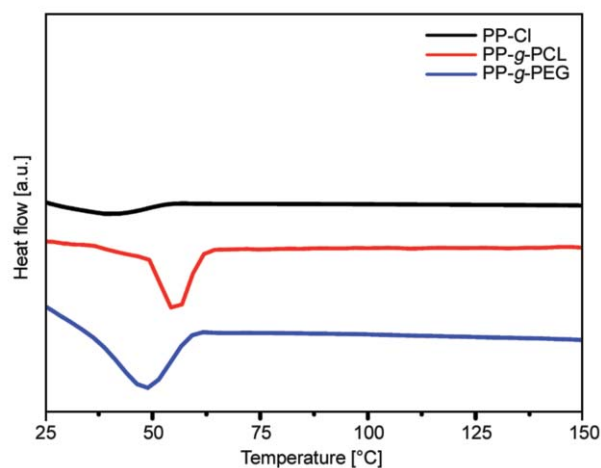


Figure 7. DSC thermograms of PP-Cl, PP-g-PCL and PP-g-PEG samples.

segments were slightly shifted to lower temperatures. These change could be due to the segmental mobility, polarity and rigidity of backbone compared with the other segments [64, 65].

The surface properties of graft copolymers and initial PP-Cl sample were investigated by water contact angle (WCA) analysis at room temperature (Figure 8). While, the average WCA of a droplet of positioned on PP-Cl coated substrate was in the range of 90±1° that was in good agreement with the literature values [66–68].

By introduction of either hydrophilic PCL-alkyne (determined as 65±1.5°) [69–71], or PEG-alkyne (determined as 42±1.9°) units on the PP-Cl backbone, the WCA values of corresponding graft copolymers were decreased down to 83±2.1° and 78±1.8°, respectively. The difference observed in the graft copolymers could be explained by the interaction of the polymer surface chains with the water. The apparently

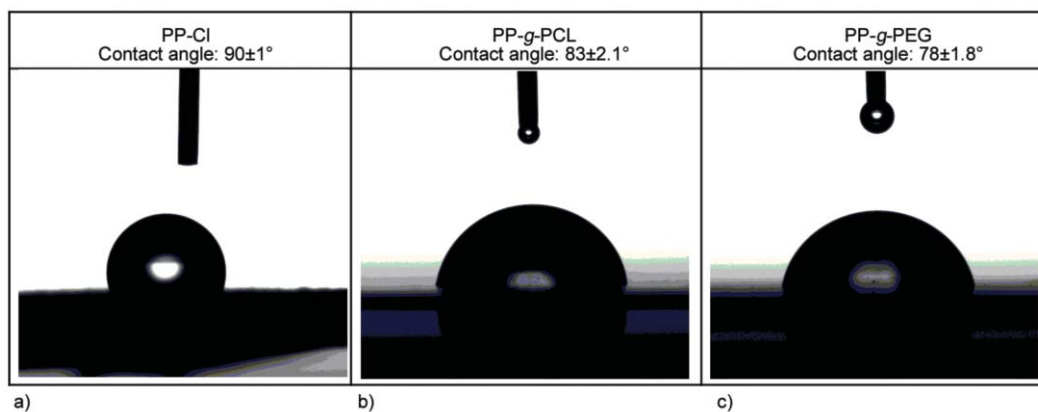


Figure 8. Shape of water drops on PP-Cl (a), PP-g-PCL (b) and PP-g-PEG (c) surfaces and their WCA measurements (Each measurement has been repeated ten times).

lower hydrophilicity of PP-g-PEG more likely resulted from a lower WCA value of PEG-alkyne [18, 72]. Overall, this simple route enabled to tailor the wettability of commercially available PP-Cl by inclusion of different type of polymers as pendant groups.

4. Conclusions

In summary, a simple and efficient method was described to obtain graft copolymers from commercially available sources normally required hard conditions due to the lack of polarity. Spectral FT-IR and $^1\text{H-NMR}$ analysis proved that chemical structures of all intermediates and formation of polypropylene-based graft copolymers. Based on the GPC and DSC analyses, the molecular weight and thermal transition changes also confirmed the successful synthesis of graft copolymers. Furthermore, the desired properties such as wettability can be simply introduced onto polypropylene backbones that was clarified by WCA measurements. This facile route enables to expand the potential applications of commercially available chlorinated polypropylene such as particularly packaging, toys, building, automotive, transport and medical. Further studies in this line are now in progress.

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