Synthesis and characterization of the graft copolymer including poly\(\beta\)-butyrolactone and polyvinyl chloride by ring-opening polymerization and "click" chemistry

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ABSTRACT
Synthesis of poly(vinyl chloride-g-\(\beta\)-butyrolactone) [poly(VC-g-BL)] graft copolymer was carried out by means of "click" chemistry of terminally propargyl poly\(\beta\)-butyrolactone ester (PBL-propargyl) and polyvinyl chloride with pendant azido group (PVC-N\(_3\)). PVC-N\(_3\) was synthesized by reaction of purified PVC and sodium azide. PBL-propargyl was obtained by the reaction of \(\beta\)-butyrolactone with propargyl alcohol by ring-opening polymerization. By using PVC-N\(_3\) and PBL-propargyl, poly(VC-g-BL) graft copolymer was synthesized. The concentration and amount of the solvent that influenced the reactions were evaluated. The characterization of the products was accomplished by using multi-instruments and methods such as \(^1\)H-NMR, FT-IR, TGA, DSC, static light scattering, and elemental analysis.

GRAPHICAL ABSTRACT

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1. Introduction
Graft copolymers are special types of copolymers consisting of a backbone and branches bonded covalently to the backbone.\(^{[1-3]}\) This feature of graft copolymers causes them to be used as drug delivery,\(^{[4]}\) hydrogel,\(^{[5]}\) thermoplastic elastomers,\(^{[6]}\) coating materials,\(^{[7]}\) and compatibilizers in polymer blends.\(^{[3,8]}\) Graft copolymerization is one of the methods to improve macromolecule properties.\(^{[9]}\) The syntheses of graft copolymers using "click" reaction philosophy are available in the literature.\(^{[10-12]}\) These days, the "click" chemistry methods, have emerged as the unique method for obtaining polymer.\(^{[13,14]}\) The main characteristics of "click" chemistry are indicated by simple product isolations, high tolerances of functional groups, superior regional selectivity, lack of by-products, and simple reaction conditions.\(^{[14-19]}\) The polymerization method is compatible with a wide variety of reaction conditions.\(^{[20]}\) Ring-opening polymerization (ROP) was widely used in the syntheses of new types of
Polymers. The method has been applied to many monomers with a lot of initiators and catalyst systems. Polymers obtained from lactones have some special features such as biocompatibility, good mechanical properties, biodegradability, and no toxicity. The production and consumption of polyvinyl chloride (PVC) is increasing day by day over the world. PVC is less linked on natural gas or petroleum comparing to other macromolecules, for example polyethylene terephthalate, polyethylene, polymethyl methacrylate.

This study showed the synthesis of poly(vinyl chloride-g-β-butyrolactone) by ring-opening polymerization (ROP) of β-butyrolactone (BL) using propargyl alcohol. PVC-N3 was synthesized by reaction of purified PVC and sodium azide as shown in the literature. The products were characterized by using spectroscopic and thermal methods in detail. The largest advantage of this work is that this study is a sample of combination reaction, from ROP to "click" chemistry. The current study can be a simple example of this point of view.

2. Experimental

2.1. Materials

Polyvinyl chloride with Mw ~ 43,000 g mol⁻¹ and Mn ~ 22,000 g mol⁻¹, methanol, N, N-dimethylformamide (DMF), sodium azide (NaN₃), propargyl alcohol, copper(I) bromide (CuBr), β-butyrolactone (BL), aluminum oxide, N,N,N′,N″,N‴-pentamethyldiethylenetriamine (PMDETA), and sodium chloride were supplied by Sigma-Aldrich. Diethyl ether and petroleum ether were bought from Carlo Erba Reagent. Chloroform was received from Aldrich. Triethylamine (TEA), sulfuric acid, tetrahydrofuran (THF), and ethanol were bought from Merck. PVC was purified as in the cited literature. 10 grams of PVC powder was dissolved in 100 mL of THF in 24 hours and sedimented in excess methanol and then dried under vacuum at 45 °C for 24 hours.

2.2. Instrumentation

Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra of the products were detected using a Jasco FT/IR 6600 model FT-IR spectrometer. A Bruker Ultra Shield Plus, ultra-long hold time 400 NMR spectrometer was used for obtaining the ¹H-nuclear magnetic resonance (¹H-NMR) spectra. The elemental analyses of the samples were performed on a Costech ECS 4010 instrument. Thermogravimetric analysis (TGA) measurements were conducted using a Seiko II Exstar 6000 TG/DTA 6200 instrument. The samples were heated at a rate of 10 °C/min from 25 °C to 600 °C under N₂ gas. Differential scanning calorimetry (DSC) measurement was obtained by Hitachi DSC 7000 series thermal analysis system under nitrogen flow. Static light scattering (SLS) was Malvern Zetasizer Nano Series Nano-ZS with Insmark IR120 model refractometer (solvent: DMF; concentration: 1 mg/mL, 0.5 mg/mL, and 0.25 mg/mL; temp.: 20 °C; λ = 633 nm). The measurements were performed in three times for 5 seconds. The results were evaluated according to the Berry and Guinier approach.

2.3. Synthesis of polyvinyl chloride with pendant azido group (PVC-N₃)

Similar procedures described in the cited literature were used for the synthesis of PVC-N₃. For example, 2.6465 g of purified PVC, 2.1486 g of NaN₃, and 50 mL of DMF were placed into a 250 mL flask. The glass flask was immersed in an oil bath fixed at 70 °C on a magnetic stirrer, and afterward, N₂ gas was introduced into the flask via a glass syringe. After 18 hours, the glass flask was opened, and the flask content was filtered. DMF was partially evaporated using a rotary evaporator. The mixture was poured into excess methanol to precipitate PVC-N₃ and then kept in the refrigerator for 1 day. After decantation, PVC-N₃ was dried at room temperature using a vacuum oven for 2 days.

2.4. Synthesis of terminally propargyl polyβ-butyrolactone ester (PBL-propargyl) by ring-opening polymerization (ROP)

PBL-propargyl was achieved via ROP as the procedure: 3.1680 gram of BL, 0.2889 g of propargyl alcohol, and 1–2 drops of Sn(Oct), as the catalyst were separately placed in a Schlenk tube, then, nitrogen gas was injected into the tube for 4–5 minutes. The tube was covered with a rubber septum and put into an oil bath at 120 °C. After 3 hours and 45 minutes, the content of the tube was mixed into cold excess diethyl ether/petroleum ether (1/1; v/v) to precipitate PBL-propargyl. And then the mixture was kept in the refrigerator for 1 day. After decantation, PBL-propargyl was dried at room temperature under a vacuum oven for 2 days.

2.5. Synthesis of poly(vinyl chloride-g-β-butyrolactone) [poly(VC-g-BL)] graft copolymer via "click" chemistry

The chemical amounts used in the graft copolymerization were showed in Table 1. Specified amounts of PVC-N₃, and terminally propargyl polychemistry of polyvinyl chloride with pendant azido group polyethylene terephthalate, polyethylene, polymethyl methacrylate.

| Table 1. Synthesis of poly(VC-g-BL) graft copolymer via “click” chemistry. |
|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Code        | PVC-N₃ (g) | PBL-propargyl (g) | DMF (mL) | Yield (g) | Yield (% wt.) | Mw (g mol⁻¹) | Decomposition temperature (°C) |
| TH1         | 0.1480     | 0.1501             | 20       | 0.2566    | 86.08        | –           | 239                        | 425                        |
| TH2         | 0.2044     | 0.1019             | 20       | 0.2550    | 80.62        | 110.000     | 223                        | 498                        |
| TH3         | 0.1060     | 0.2476             | 25       | 0.3536    | 72.20        | 112.000     | 227                        | 453                        |
| Polym. temp.: 30 °C; polym. time: 72 hours; CuBr = 0.001 g; PMDETA = 4 µL. | | | | | | | |
Scheme 1. The outline in the azidation reaction of PVC.

Figure 1. FT-IR spectra of (a) purified PVC, (b) PVC-N₃, (c) PBL-propargyl, (d) poly(VC-g-BL) graft copolymer.

Figure 2. ¹H-NMR spectra of (a) purified PVC, (b) PVC-N₃, (c) PBL-propargyl, (d) poly(VC-g-BL) graft copolymer.

Scheme 2. Reaction pathway for the synthesis of PBL-propargyl by ROP.
PMDETA, PBL-propargyl, and DMF as the solvent were separately put in a glass flask. After dissolution, CuBr was added followed by injecting nitrogen gas for 4–5 minutes. The flask was put into an oil bath at 30 °C temperature on a magnetic stirrer. After specific times, the glass flask content was filtered. DMF was partially removed using a rotary evaporator. The mixture was drained into excess methanol to separate precipitated poly(VC-g-BL) graft copolymer. The mixture was kept in the refrigerator for 1 day. After decantation, the graft copolymer was dried at room temperature using a vacuum oven for 2 days. Poly(VC-g-BL) graft copolymer yield was detected gravimetrically.

**Scheme 3.** Reaction outline in the synthesis of poly(VC-g-BL) graft copolymer by "click" chemistry.

**Figure 3.** DSC curve of poly(VC-g-BL) graft copolymer (TH-3 coded in Table 1).
3. Results and discussion

3.1. Synthesis of PVC-N3

PVC-N3 was obtained using PVC which was purified. PVC-N3 yield was 96.03 wt %. Scheme 1 contains the synthesis outline of PVC-N3. The FT-IR spectrum of purified PVC (Figure 1(a)) indicates 2970 and 2910 cm\(^{-1}\) for aliphatic -CH\(_2\) and -CH\(_3\), 610 cm\(^{-1}\) for -Cl. The FT-IR spectrum of PVC-N3 (Figure 1(b)) indicates 2920 and 2864 cm\(^{-1}\) for aliphatic -CH\(_2\) and -CH\(_3\), 2094 cm\(^{-1}\) for -N\(_3\). A typical -N\(_3\) signal at 2094 cm\(^{-1}\) appeared in the PVC-N3, that confirmed the estimated chemical structure. The 1H-NMR spectrum of purified PVC in Figure 2(a) shows 4.5 ppm for -ClCH\(_2\), and 2.3 ppm for -CH\(_3\). The 1H-NMR spectrum of PVC-N3 (Figure 2(b)) indicates 8.0 ppm for CDCl\(_3\), 3.4 ppm for -NCH and -CICH\(_3\), and 2.5 ppm for -CH\(_2\). The data of the elemental analysis of PVC-N3 shows 33.56 wt % C, 5.10 wt % H, and 2.04 wt % N, which confirms not only the formation of PVC-N3 but also the azide groups. The number of azide groups of PVC-N3 was calculated using 2.04 wt.% N and Mn value of PVC-N3 (~ 22,000 gmol\(^{-1}\)). About 9 azide groups per chain was determined.

3.2. Synthesis of PBL-propargyl by ROP

PBL-propargyl was obtained by reaction of BL and propargyl alcohol via ROP technique. Scheme 2 includes the polymerization pathway for the synthesis of PBL-propargyl. PBL-propargyl yield was 58.93 wt %. The FT-IR spectrum of PBL-propargyl (Figure 1(c)) shows about 3500 cm\(^{-1}\) for -OH, 3300 cm\(^{-1}\) for -C=O, 2900 cm\(^{-1}\), 2800 cm\(^{-1}\) and 2650 cm\(^{-1}\) for aliphatic -CH\(_3\), -CH\(_2\), -CH, 1700 cm\(^{-1}\) for -C=O, and 1100 cm\(^{-1}\) for -C-O. The 1H-NMR spectrum of PBL-propargyl (Figure 2(c)) shows 5.1 ppm for -OCH of the PBL group, 4.6 ppm for -OCH\(_2\) of the propargyl, 4.1 ppm for -OH of the PBL, 2.4 ppm for aliphatic -CH\(_2\) linked carbonyl group of the PBL, 2.0 ppm for \(\equiv\text{CH}\) of the propargyl group, and 1.2 ppm for aliphatic -CH\(_3\) of the PBL.
3.3. Synthesis of poly(VC-g-BL) graft copolymer

Poly(VC-g-BL) graft copolymer was synthesized at 30 °C for 72 hours via "click" chemistry of PBL-propargyl and PVC-N₃. The pathway of the polymerization is shown in Scheme 3. The yield was between 86.08 wt.% and 72.20 wt.%. The FT-IR of poly(VC-g-BL) graft copolymer as presented in Figure 1(d) presents distinctive signals which belong to the PBL-propargyl and PVC-N₃. The FT-IR spectrum of poly(VC-g-BL) graft copolymer (TH1 in Table 1) and Figure 1(d) shows 3407 cm⁻¹ for -OH, 2974 cm⁻¹ for aliphatic -CH₂, 1734 cm⁻¹ for -C = O, 1649 cm⁻¹ for -N = N-, and 1056 cm⁻¹ for -C-O. The disappearance of propargyl group (3300 cm⁻¹) and the appearance of triazole group (1649 cm⁻¹) can be appropriate for the "click" reaction. The ¹H-NMR spectrum of poly(VC-g-BL) graft copolymer (TH1 in Table 1) in Figure 2(d) shows 8.0 ppm for aromatic -CH of triazole, 5.1 ppm for -OCH of PBL, 3.2 ppm for -CHCl and -CHN of PVC, 2.5 ppm for aliphatic -CH₂ linked carbonyl of the PBL, 1.9 ppm for aliphatic -CH₂ of the PVC, and 1.3 ppm for aliphatic -CH₃ of the PBL. The signal at 8.0 ppm in the ¹H-NMR spectrum is a great evidence for aromatic -CH protons of triazole.[1,2,46–48]

The glass temperature (Tg) value of poly(VC-g-BL) graft copolymer (TH-3 coded in Table 1) was obtained by DSC. Two different Tg values were observed in the DSC thermogram of the graft copolymer as shown in Figure 3. Tg values were measured as about 14 °C attributed for PBL group and 79 °C attributed for PVC group. TGA analysis of poly(VC-g-BL) graft copolymer was conducted to determine both the chemical compositions of the copolymer and temperatures of thermal transitions belonging to each component in the copolymer (Figure 4). In this instance of poly(VC-g-BL) graft copolymer, PBL and PVC groups have got individual decomposition temperatures (Td). PBL and PVC had one Td at about 223 °C and 498 °C, respectively [Figure 4(a)]. TGA demonstrated continuous weight loss starting from about 184 °C to nearly 519 °C with maxima at about 227 °C and 453 °C (Figure 4(b)). Approximately 94.8 wt. % by weight of the copolymer decomposed between these temperature values. Mw values of poly(VC-g-BL) graft copolymer in Table 1 obtained from the SLS measurements were 110,000 g mol⁻¹ and 112,000 g mol⁻¹. The SLS measurements of poly(VC-g-BL) graft copolymer (TH-2 and TH-3 coded in Table 1) were given as supplemental data.

4. Conclusion

This work shows the synthesis of poly(VC-g-BL) graft copolymer from the two component homopolymers. The process used to obtain graft copolymer is simple, effective, and high-yielded. The approach could open the way for further and well-characterized materials employing a combination of "click" chemistry method and ROP method. Product characterization was obtained through ¹H-NMR, FT-IR, SLS, TGA, DSC, and elemental analysis and proved the synthesis of poly(VC-g-BL) graft copolymer.

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Disclosure statement

The authors declare no conflict of interest.

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