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Cross-linking of PVC by Various Lengths of PEG via "Click" Chemistry

Çeşitli Uzunluklardaki PEG'ler Vasıtasıyla PVC'nin "Klik" Kimyası ile Çapraz Bağlanması

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Abstract

Cross-linked poly(polyvinyl chloride) (c-PVC) was synthesized by "click" reaction of polyvinyl chloride with azido pendant group (PVC-N3) and dipropargyllated polyethylene glycol (dp-PEG). For this purpose, dp-PEGs were obtained from polyethylene glycols with different molecular weights (400 Da, 600 Da, 1000 Da, 1500 Da, 2000 Da, 3000 Da, and 10000 Da) via treatment with propargyl chloride. PVC-N3 was synthesized through the substitution reaction between the pendant chloride on the PVC chains and azide ion. By using PVC-N3 and dp-PEGs with various lengths, c-PVCs with various degrees of cross-linking was obtained. The characterization of the PVC-N3, dp-PEG and c-PVC were performed using Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, thermogravimetric analysis, scanning electron microscopy and elemental analysis. Degrees of swelling of c-PVCs with different cross-linking densities in N,N-dimethylformamide were determined by quantitative measurements.

Keywords: "Click" chemistry, Cross-linking, Poly(vinyl chloride), Polyethylene glycol, Degree of swelling

Öz

Çapraz bağlı poli(vinil klorür) (c-PVC), azit grup ekli poli(vinil klorür) (PVC-N3) ile dipropargillenmiş polietilen glikolün (dp-PEG) "klik" kimyası reaksiyonuyla sentezlendi. Bu amaç için, dp-PEG'ler, farklı molekül ağırlıklarına sahip polietilen glikollerin (400 Da, 600 Da, 1000 Da, 1500 Da, 2000 Da, 3000 Da, and 10000 Da) propargil klorür ile muamelesinden elde edildiler. PVC-N3, PVC zincirleri üzerindeki asılı klorürlerle azid iyonu arasındaki yer değiştirme reaksiyonuyla sentezlendi. PVC-N3 ve çeşitli uzunluklardaki dp-PEG'ler kullanılarak farklı derecelerde çapraz bağlamaya sahip c-PVC'ler elde edildi. PVC-N3, dp-PEG ve c-PVC'nin karakterizasyonları, Fourier dönüşümlü kızılötesi spektroskopisi, nükleer manyetik rezonans spektroskopisi, termogravimetrik analiz, taramalı elektron mikroskobu ve elementel analiz teknikleri kullanılarak gerçekleştirildi. N,N-dimetilformamid içinde farklı çapraz bağlanma yoğunluklarına sahip c-PVC'lerin şişme dereceleri nicel ölçümlerle belirlendi.

Anahtar Kelimeler: "Klik" kimyası, Çapraz bağlanma, Poli(vinil klorür), Polietilen glikol, Şişme derecesi

1. Introduction

Poly(vinyl chloride) (PVC), one of the most common and important functional polymers, has been kept steady growth of the production and consumption over the world (Asan and Öztürk 2017, Grishin 2015). PVC is less dependent on crude oil or natural gas comparing to all other polymers, which are nonrenewable such as polyethylene, polyethylene terephthalate and polymethyl methacrylate. Copolymers have substantial interest due to their mechanical properties and practical applications (Savaş and Öztürk 2020). Copolymers, having polyethylene glycol (PEG) units, are very appealing substances for chemicals, industrial and biomedical practices, as PEG has unparallel features such superior hydrophilicity, flexibility, ion absorbability, and a superior grade of biocompatibility (Asan and Öztürk 2017, Wang et al. 1998, Aydinli et al. 2004, Riess 2003, Gacal et al. 2006, Pispas and Hadjichristidis 2003, Göktaş et al. 2014). In 2001, "click" chemistry described by Sharpless et al. (2001) has high yields, requires minimum purification, and proceeds in the existence of various functional groups

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without the need for protection chemistry (Hein et al. 2008). After this time, "click" chemistry applications have been broadly studied (Moses and Moorhouse 2007, Savaş et al. 2020, Xu et al. 2007, Tunca 2013, Altıntas and Tunca 2011, Xi et al. 2014, Çatıker et al. 2019, Binder and Sachsenhofer 2007, Moshaverinia et al. 2012, Öztürk and Yörümez 2020, Öztürk et al. 2018). The Cu catalyzed azide-alkyne cycloaddition reactions are only the important one of these "click" reactions (Barner-Kowollik et al. 2011, Tunca 2018, Öztürk and Cavicchi 2018).

Firstly, polyvinyl chloride with azido pendant group (PVC-N_3) was carried out by the reaction of purified PVC and sodium azide as the literatures (Asan and Öztürk 2017, Savaş and Öztürk 2020, Kiskan et al. 2008, Pawlak et al. 2013, Zhang et al. 2020). Secondly, synthesis of dipropargyllated polyethylene glycol (dp-PEG) obtained by the reaction of PEGs with different molecular weights (400 Da, 600 Da, 1000 Da, 1500 Da, 2000 Da, 3000 Da, and 10000 Da) and propargyl chloride was presented as the similar procedures reported in the cited literatures (Pawlak et al. 2013, Öztürk et al. 2019, Öztürk and Meyvacı 2017). Lastly, PVC-N_3 and dp-PEG were utilized for "click" chemistry to obtain cross-linked poly(polyvinyl chloride) (c-PVC). Furthermore, the product characterization was provided in detail. Briefly, this paper demonstrates cross-linking of PVC by using difunctionalized PEGs with various lengths as novel cross-linking agents through "click" chemistry method.

2. Experimental

2.1. Materials

PVC (approximately Mn = 22,000 Da), copper(I) bromide (CuBr), *N,N*-dimethylformamide (DMF), sodium azide (NaN_3), 2,2′-bipyridyl (bpy), propargyl chloride, acetone, chloroform were received from Sigma-Aldrich and tetrahydrofuran (THF), PEGs with various molecular weights (400 Da, 600 Da, 1000 Da, 1500 Da, 2000 Da, 3000 Da, and 10000 Da), ethanol, petroleum ether, triethylamine (TEA) were supplied by Merck Millipore. Diethyl ether and petroleum ether were received from Carlo Erba Reagent, methanol was supplied by Kimetsan. All chemicals were used without further purifications.

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. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra of the products were detected using a Bruker Ultra Shield Plus, ultra-long hold time 400 NMR spectrometers. 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 sample was heated at a rate of 10 °C/min from 25 °C to 900 °C under N_2 gas. Scanning electron microscopy (SEM) images were taken on a Zeiss EVO LS 10 electron microscope. The cross-linked polymers were coated with a thin layer of gold on their surfaces to provide electrical conductivity.

2.3. Purification of PVC

PVC was purified as in the cited literatures (Asan and Öztürk 2017, Öztürk et al, 2014, Öztürk et al. 2020) as follow; 30 g of PVC powder was dissolved in 120 mL of THF in 48 hours and precipitated in excess methanol and dried under vacuum at 40 °C for 48 hours.

2.4. Synthesis of polyvinyl chloride with pendant azido group (PVC-N_3)

The similar procedures described in the cited literatures were applied for synthesis of PVC-N_3 (Asan and Öztürk 2017, Savaş and Öztürk 2020, Kiskan et al. 2008, Pawlak et al. 2013, Zhang et al. 2020, Jia et al. 2017, Ouerghui et al. 2016). For example, 30 g of purified PVC, 0.886 g of NaN_3, and 70 mL of DMF were placed into a flask. The flask was immersed in an oil bath fixed at 60 °C on a magnetic stirrer, and afterwards N_2 gas was introduced in the flask by a glass syringe. After 48 hours, the flask was opened, and the content was filtered. The solvent was evaporated by using a rotary evaporator. The mixture was poured into excess methanol to precipitate PVC-N_3. The product was filtered and dried at room temperature under vacuum for 2 days.

2.5. Synthesis of dipropargyllated polyethylene glycol (dp-PEG)

Synthesis of dipropargyllated PEGs was performed by a synthesis protocol similar with the literatures (Pawlak et al. 2013, Öztürk et al. 2019, Öztürk and Meyvacı 2017, Goswami et al. 2013). The reaction parameters were given in Table 1. The specified amounts of PEGs (400 Da, 600 Da, 1000 Da, 1500 Da, 2000 Da, 3000 Da, and 10000 Da) and TEA were dissolved in chloroform under N_2 gas flux. The flasks were cooled below 0 °C by using ice-salt bath. Certain amounts of propargyl chloride (stoichiometrically equivalent to the PEGs) in 7 mL of chloroform were slowly added to the solutions via dropping funnels. The solutions were stirred at room temperature for certain times given in Table 1. The solutions were concentrated by a rotary evaporator and then cold excess diethyl ether was added to precipitate the dp-PEGs. The dp-PEGs were obtained from decantation and dried at room temperature under vacuum for 2 days.

2.6. Synthesis of cross-linked polyvinyl chloride (c-PVC) by "click" chemistry

The amounts of reactants used in the cross-linking were shown in Table 2. The specified amounts of PVC-N_3, dp-PEG, CuBr, bpy, and THF (as solvent) were charged separately into a flask and then the flask was purged with N_2 for 5 minutes. The flask was immersed in an oil bath at 35 °C until the times given in Table 2. The jelly mixture was poured into excess methanol to remove the unreacted chemicals and catalysts. The cross-linked polymer was dried at room temperature under vacuum for 2 days.

2.7. Degrees of swelling (q_v) values of c-PVC

The degrees of swelling (q_v) values of c-PVC were determined as in the literatures (Collins et al. 1973, Hamurcu and Baysal 1993, Hazer and Baysal 1986). Briefly, 0.2 g of the cross-linked sample was kept in 20 mL of DMF for 2 h at 25 °C. Then, sample was removed and weighed. q_v values of c-PVC samples were calculated by the equation:

$$q_v = \frac{m_{\text{swollen polymer}}}{m_{\text{dry polymer}}}$$

Here, $m_{\text{swollen polymer}}$ and $m_{\text{dry polymer}}$ are the masses of the swollen c-PVC and the dry c-PVC, respectively.

Table 1. Reaction parameters for the synthesis of dp-PEG.

Code	PEG (g)	PEG (mol)	Propargyl chloride (g)	Propargyl chloride (mol)	PEG/ Propargyl chloride (mol/mol)	Triethyl-amine (g)	Chloro-form (mL)	Time (hour)	Yield (wt %)
HH-2	15.002 (PEG-2000 Da)	0.008 (PEG-2000 Da)	1.120	0.015	0.533	2.287	60	56	82.91
HH-3	7.547 (PEG-1500 Da)	0.005 (PEG-1500 Da)	0.745	0.010	0.500	1.525	55	48	74.18
HH-4	8.094 (PEG-1000 Da)	0.008 (PEG-1000 Da)	1.192	0.016	0.500	2.440	45	48	66.52
HH-5	6.091 (PEG-600 Da)	0.010 (PEG-600 Da)	1.490	0.020	0.500	3.050	46	49	48.51
HH-6	5.005 (PEG-400 Da)	0.013 (PEG-400 Da)	0.931	0.012	1.083	1.906	47	53	58.96
HH-7	10.045 (PEG-10000 Da)	0.001 (PEG-10000 Da)	0.150	0.002	0.500	0.134	74	48	93.79

Table 2. Synthesis of c-PVC by "click" chemistry. Reaction temperature: 35 °C.

Code	dp-PEG (g)	PVC-N_3 (g)	CuBr (g)	bpy (g)	THF (mL)	Time (hour)	Yield (wt %)	q_v (in DMF)	Decomposition Temperature (°C)		
									Td1	Td2	Td3
HK2	1.539	3.381	0.221	0.475	40	25	72.10	-	223	464	-
HK3	1.370	1.010	0.130	0.284	27	27	84.58	3.31	181	274	459
HK4	1.000	1.364	0.190	0.425	30	27	65.51	3.24	198	371	448
HK5	1.015	2.003	0.258	0.562	35	26	75.61	6.64	195	457	-
HK6	0.792	2.048	0.258	0.562	30	24	80.90	6.57	201	299	444
HK7	9.090	1.007	0.261	0.567	50	26	87.75	1.95	285	399	-

3. Results and Discussion

3.1. Synthesis of PVC-N_3

PVC-N_3 yield was 93.91 wt %. The first line in Scheme 1 includes the reaction pathway for synthesis of PVC-N_3. The FT-IR spectrum of PVC-N_3 in Figure 1A shows 2950 cm^{-1} and 2912 cm^{-1} for aliphatic -CH, and 2330 cm^{-1} for -N_3. Typical -N_3 signal at 2330 cm^{-1} appeared in polymer sample, which was confirmed the expected chemical structure. The ^{1}H-NMR spectrum of PVC-N_3 in Figure 2A shows 2.2 ppm for -$C\underline{H}_2$, 4.3 ppm for -$NC\underline{H}$, and 4.5 ppm for -$ClC\underline{H}$. The result of elemental analysis of PVC-N_3 shows 37.76 wt % C, 4.48 wt % H, and 0.25 wt % N, which confirms the successful azidation of PVC.

3.2. Synthesis of dp-PEG

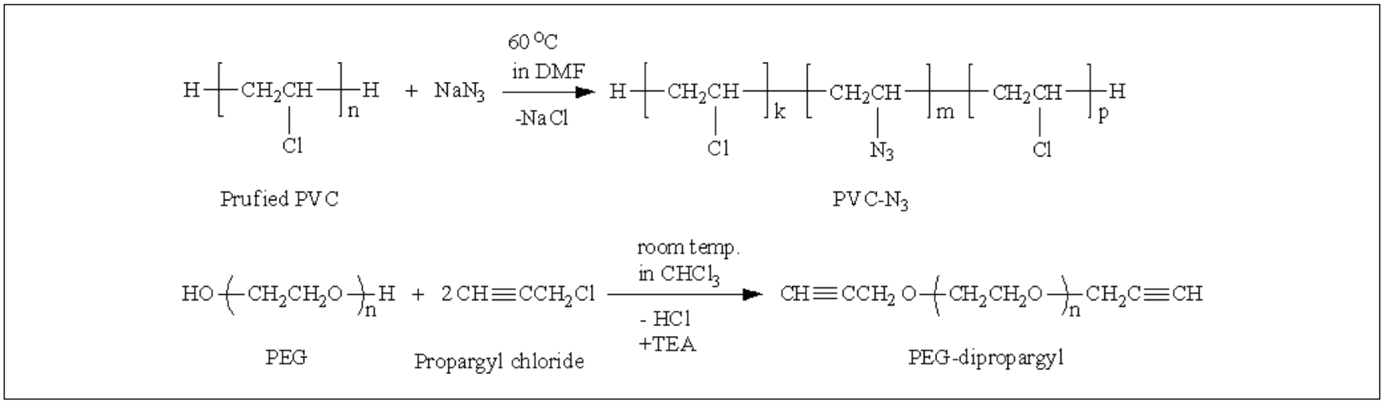
The second line in Scheme 1 includes the synthesis of dp-PEG. The yields of the propargylation reaction were found to be between 48.51 wt % and 93.79 wt % as shown in Table 1. Maximum yield of dp-PEG was obtained by using PEG with 10000 Da. Minimum yield of dp-PEG was obtained by using PEG with 600 Da. It is more probably that there will be a population of three types of PEG which possess zero, one, and two propargyl end-groups. As we used [propargyl chloride]/[PEG] = 2/1 (mol/mol) in the reaction, there could be zero and one propargyl end-groups at very little amounts. To the best of our knowledge, most of the product is PEG with two propargyl groups at chain-ends. However, we assumed that all the product was dp-PEG, namely, cross-linking agent. The FT-IR spectrum of dp-PEG (HH-7 in Table 1) in Figure 1B indicates the signals at 3411 cm^{-1} for C≡C, 2946 cm^{-1} for aliphatic -CH, 1115 cm^{-1} for -OC. The ^{1}H-NMR spectrum of propargyl-PEG (HH-3 in Table 1) in Figure 2B shows 2.5 ppm for $\equiv C\underline{H}$ of the propargyl part, 3.5 ppm and 4.1 ppm for -$OC\underline{H}_2$ of PEG block, 4.4 ppm for -$OC\underline{H}_2$ linked PEG block. The observed peak at 2.5 ppm for ≡CH proton in the ^{1}H-NMR spectrum and 3411 cm^{-1} for C≡C groups in the FT-IR spectrum of dp-PEG were further evidences that dp-PEG was successfully obtained.

3.3. Synthesis of c-PVC by "click" chemistry

c-PVC was obtained at 35 °C by using "click" chemistry method of dp-PEG and PVC-N_3. Scheme 2 includes the reaction pathway for synthesis of c-PVC. The results of the polymerization were shown in Table 2. The yields of the c-PVC obtained from "click" chemistry were found gravimetrically between 65.51 wt % and 87.75 wt %. The yields may be assumed to be relatively high. The FT-IR spectrum of c-PVC (HK7 in Table 2) in Figure 1C indicates the characteristic signals at 2877 cm^{-1} for aliphatic -CH, 1095 cm^{-1} for -OC, 617 cm^{-1} -Cl. Furthermore, the observed peaks at 1462 cm^{-1} and 1342 cm^{-1} for triazole group were evidence that the "click" chemistry was fulfilled.

The morphological properties of c-PVC samples (HK2 and HK4 in Table 2) were examined by SEM analysis. The surface morphologies of the cross-linked polymers were given in Figure 3. Generally, fractured surface structure was seen in SEM images of c-PVC. SEM images of the c-PVC generally exhibited porous surfaces.

TGA analysis of c-PVC (HK4 in Table 2) was conducted to determine both the chemical compositions of the polymer and temperatures of thermal transitions belonging to each component in the polymer (Figure 4). PEG had one decomposition temperature (Td) at 371 °C. But PVC had two Td at 198 °C and 448 °C. In the case of c-PVC, PVC and PEG units have individual Td. As shown in Figure 4, TGA demonstrated fascinating characteristics of the



Scheme 1. Reaction pathways in the syntheses of PVC-N_3 and dp-PEG.

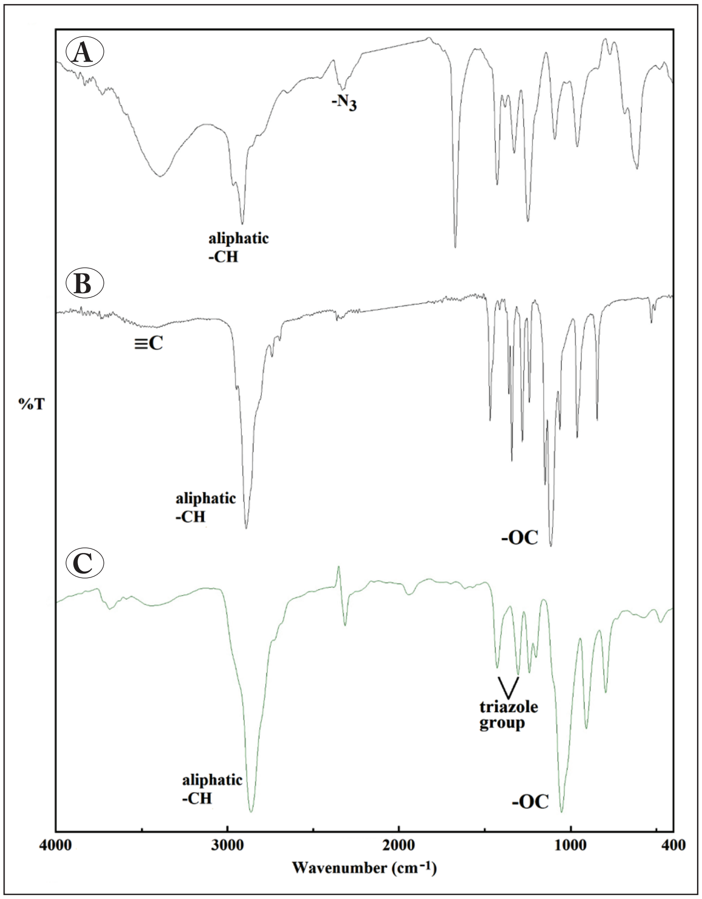


Figure 1. FT-IR spectra of **(A)** PVC-N_3, **(B)** dp-PEG (HH-7 in Table 1), and **(C)** c-PVC (HK7 in Table 2).

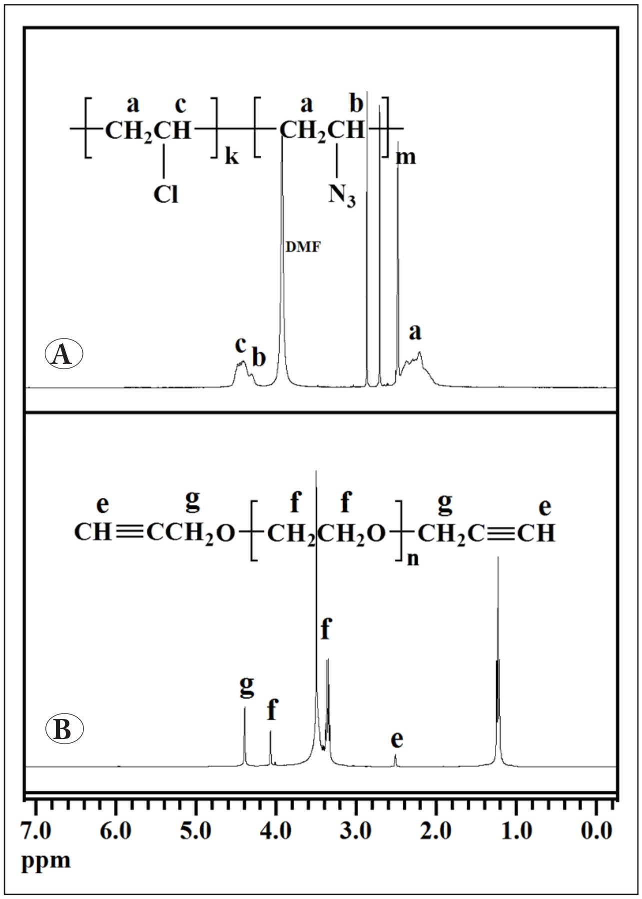
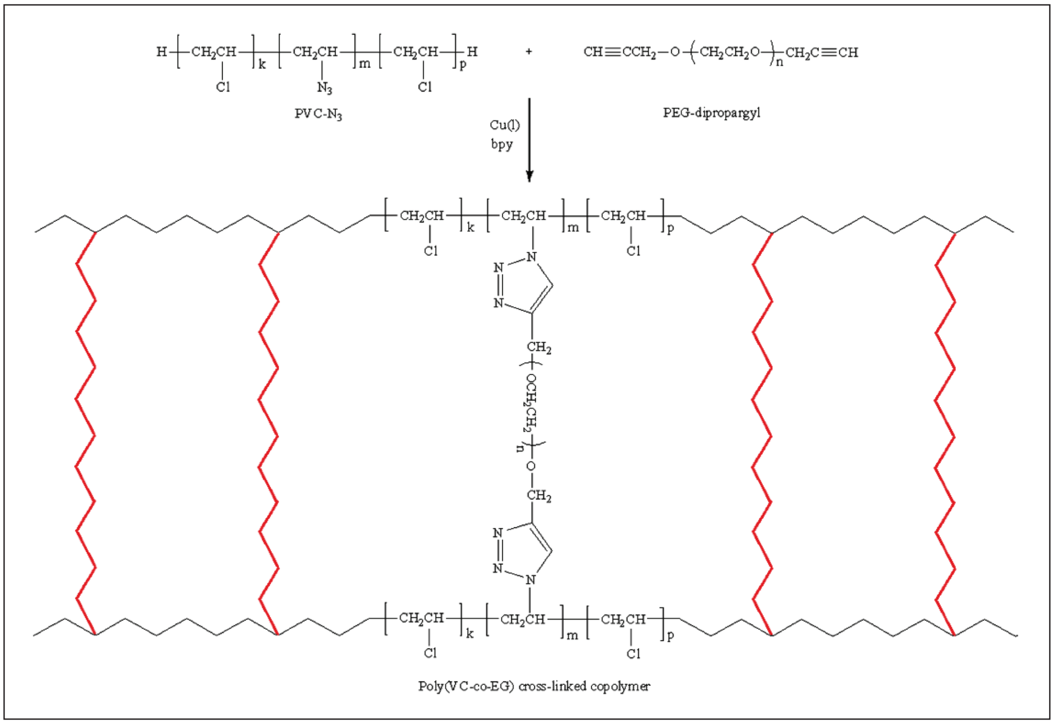


Figure 2. ^{1}H-NMR spectra of **(A)** PVC-N_3 and **(B)** dp-PEG (HH-3 in Table 1).



Scheme 2. Reaction outline in the synthesis of c-PVC.

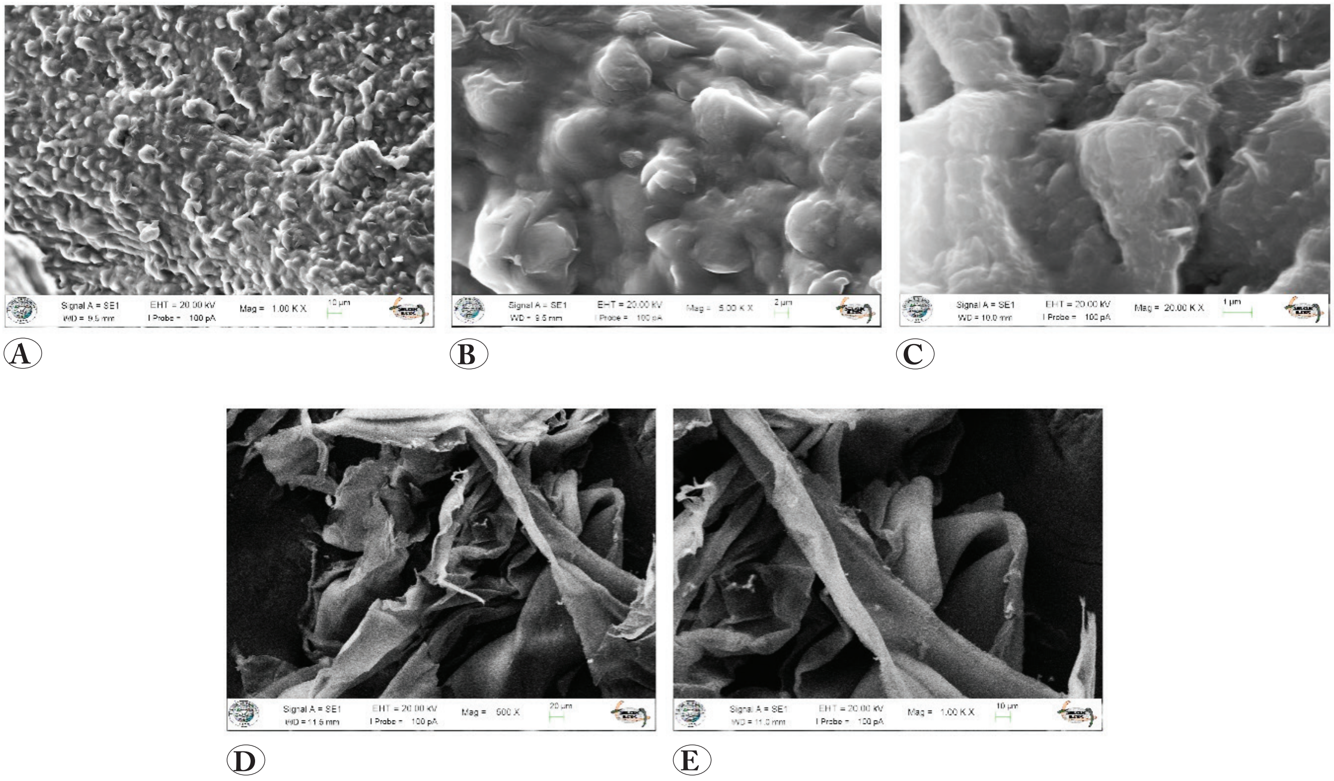


Figure 3. SEM images of c-PVC; **(A)** X1000 (HK2 in Table 2), **(B)** X5000 (HK2 in Table 2), **(C)** X20000 (HK2 in Table 2), **(D)** X500 (HK4 in Table 2), and **(E)** X1000 (HK4 in Table 2).

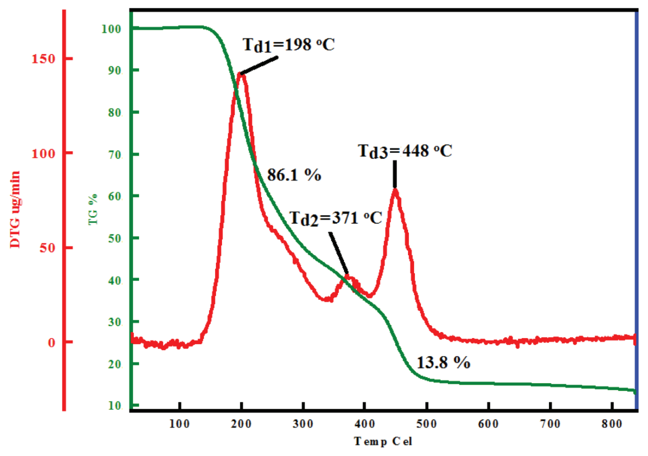


Figure 4. TGA thermogram of c-PVC (HK4 in Table 2).

polymer such as continuous weight loss starting from about 140 °C to nearly 550 °C with maxima at 198 °C, 371 °C, and 448 °C.

The “click” chemistry synthesis of c-PVC from the two constituent homopolymers was acquired. In other word, this paper demonstrates cross-linking of PVC by using difunctionalized PEGs with various lengths as novel cross-linking agents through “click” chemistry method. This procedure used to synthesize cross-linked polymer is easy and effective. This work can pioneer for further and well-conceived cross-linked polymers used for many applications. The calculation of q_v, a very reliable and practical method, could be applied to verify the cross-linked polymer formation. The swelling ratios of c-PVCs in DMF varied from 1.95 to 7.26.

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