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Synthesis of an ABC Type Triblock Copolymer on MWCNT Surface: Structural, Thermal, Electrical and SEM Characterization

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Abstract: Multi-walled carbon nanotubes (MWNTs) attached to ethylene glycol (MWNT-OH) were grafted with ring-opening polymerization of ε-caprolactone (MWNT-pCL). Initiating sites for atom transfer radical polymerization (ATRP) were formed by end acylation of MWNT-pCLwith α-bromopropionyl bromide. After styrene was polymerized by ATRP on the surface of the macroinitiator (MWNT-pCL-Br) in presence of CuBr/2,2′-bipyridine as catalyst at 110 oC, the triblock copolymer (MWNT-pCL-b-PS-b-pGMA) was prepared by the aid of the same technique using glycidyl methacrylate as monomer, at the same catalyst and temperature conditions, by using the diblock copolymer (MWNT-pCL-b-PS) as macroinitiator. The 1HNMR studies show that structure in terms of mer number per molecule of the ABC type triblock copolymer is MWNT-p(CL)$_6$-b-P(S)$_{36}$-b-p(GMA)$_{1080}$. The determination of chemical structure of the triblock copolymer was carried out using Fourier transform infrared (FT-IR), proton nuclear magnetic resonance (1H NMR) and scanning electron microscopy (SEM). Thermal properties were investigated by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The Tg value estimated from the temperature dependence of the dielectric constant, the dielectric loss factor, and the ac conductivity for the triblock copolymer, is in agreement with the DSC value. The results of the dielectric constant and ac conductivity of the triblock copolymer were also discussed.

Keywords: ε-caprolactone, GMA, MWNT, styrene, triblock copolymer.

MWCNT Yüzeyinde bir ABC Tipi Üç Bloklu Kopolimer Sentezi : Yapısal, Termal, Elektriksel ve SEM Karakterizasyonu

Özet: Etilen glikol bağlı (MWNT-OH) çok-duvarlı karbon nanotüp (MWNTs) ε-kaprolaktonun halka açılması polimerizasyonuyla aşılandı (MWNT-pCL). Atom transfer radikal polimerizasyonu (ATRP) için başlatma ucu, MWNT-pCL´nun α-bromopropiyonil bromür ile uç açillemesiyle hazırlandı. Katalizör olarak CuBr/2,2´-bipridin yanında 110 ^{o}C de makrobaşlatıcının (MWNT-pCL-Br) yüzeyinde ATRP ile stirenin polimerizasyonundan sonra, aynı sıcaklıkta aynı katalizör yanında glisidil metakrilatın makrobaşlatıcı olarak iki bloklu kopolimer (MWNT-pCL-b-PS) kullanılarak yapılan ATRP polimerizasyonuyla üç bloklu kopolimer (MWNT-pCL-b-PS-b-pGMA) hazırlandı. ^{1}HNMR çalışmaları ABC tipi üç bloklu kopolimerin molekül başına mer sayılarının MWNT-p(CL)$_6$-b-P(S)$_{36}$-b-p(GMA)$_{1080}$ şeklinde olduğu belirlendi. Üç bloklu kopolimerin kimyasal yapısının belirlenmesi Fourier dönüşümlü infrared (FT-IR), proton nükleer manyetik rezonans (^{1}H NMR) ve taramalı electron mikroskopuyla (SEM) gerçekleştirildi. Termal özellikler termogravimetrik analiz (TGA) ve diferesiyel taramalı kalorimetre (DSC) ile incelendi. Üç bloklu kopolimerin dielektrik sabiti, dielektrik kayıp faktörü ve ac iletkenliğinin sıcaklık bağımlılığından tahmin edilen T_g değerinin DSC den bulunan değerle uyuştuğu görüldü. Üç bloklo kopolimerin dielektrik sabiti ve ac iletkenliği de ayrıca tartışıldı.

Anahtar kelimeler: E-kaprolakton, GMA, MWNT, stiren, triblok kopolimer.

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1. Introduction

There has been intense interest on carbon nanotubes (CNTs) due to their unusual physical properties and large application potential, covering a broad range in nanotechnology [1,2]. The poor solubility of CNTs in organic solvents restricts them to be used as drug delivery agents into living systems in drug therapy. Thus, more research on area surface modification of CNTs attracted significant interest recently [3-8]. Hence, many modification approaches like physical, chemical or combined have been exploited for their homogeneous dispersion in common solvents to improve solubility [9-11]. Various methodologies were reported in the literature in order to achieve covalent functionalization of nanotubes. Electrochemically assisted covalent modification of carbon substrate material has become a new era in the field of chemically modified electrodes, which involves the formation of covalent bond between the substrate and the modifier molecule [12-14]. The other method for functionalization of CNTs is electrochemical polymerization on surface of CNT [15].The main perspective of this modification involves the generation of oxygen containing functionalities, more specifically carboxylic groups commonly called surface oxides formed by the aggressive oxidation treatment using strong acids. The carboxyl functionalized carbon nanotubes could be further grafted with functional moieties with terminal amine or thiol groups, which can effectively control the particle size and dispersion of noble metal CNTs on the surface of tubes [16-18]. Another way to attach the polymer to the nanotube surface is by the "grafting from" method, which means that the reactive groups were covalently attached to the nanotube surfaces as well as the polymers graft from the reactive groups. It is also the reaction between the reactive groups in the surfaces of nanotubes and monomers. An example of grafting from method is the atom transfer radical poymerization on the surface of CNT [5,7,19-21].

This study describes preparation of an ABC type triblock copolymer using ε-caprolactone, styrene and glycidyl methacrylate by a combination of ring opening polymerization and atom transfer radical polymerization techniques. Also Structural, thermal, electrical and surface characterization of the triblock copolymer was investigated.

2. Experimental Method

2.1. Synthesis of MWNT-COOH

Carboxyl-functionalized MWNTs (MWNT-COOH) were prepared by oxidation of MWNTs in a mixture of conc. HNO_3 and H_2SO_4 in 1:3 ratio (by volume).

The procedure: MWNT (2 g), 40 mL of the acid mixture was added into a 250 mL flask equipped with a condenser, and the mixture was stirred vigorously. The flask was then immersed in an ultrasonic bath at room temperature for 20 min. The stirring of the mixture was continued under reflux for 10 h in an ultrasonic bath. The mixture was allowed to cool at room temperature and was then diluted with 250 mL of water, followed by neutralization with conc NaOH to pH 7 and then filtered. The residue was washed with water several times, washed with THF to remove the water, and then dried under vacuum for 24 h at 50 ^oC.

2.2. Synthesis of MWNT-OH

An excess amount (10 mL) of thionyl chloride were added on 300 mg of MWNT-COOH. The mixture was refluxed for 24 h at 70-75 ^oC after passing through argon gas. Then the solid product (MWNT-COCl) was filtered, washed with THF for a few times, and dried under vacuum for overnight at 40 ^oC.

The mixture of 200 mg of MWNT-COCl and 5 mL of ethylene glycol were added into a 25 mL flask, and then was refluxed by magnetically stirring at 120 °C in an oil bath for about 48 h. The mixture was allowed to cool at room temperature, and the solid product of (MWNT-OH) was filtered, washed with THF for a few times, and dried under vacuum at 50 °C until constant weight was obtained.

2.3. Synthesis of MWNT-ε-Polycaprolactone

Into a reaction flask, 100 mg of MWNT-OH, 550 mg ε-caprolactone, 10 mL of toluene and a few drops of $Sn(Oct)_2$ as catalyst were added. After passing through argon gas, the mixture was refluxed in an oil bath for 24 h. After cooling at room temperature, the catalyst was filtered and the filtrate was added dropwise into excess n-hexane to precipitate the polycaprolactone (MWNT-pCL). The polymer was filtered off and dried under vacuum at 45 oC until constant weight was observed.

2.4. Preparing of Macroinitiator Using α-Bromopropionyl Bromide From MWNT-pCL

The mixture of 70 mg MWNT-pCL, 10 mL dried THF, and 250 mg Na_2CO_3 were added into a 25 mL reaction flask and then the mixture was cooled to 0 °C. 500 mg α-bromopropionyl bromide was added dropwise by magnetically stirring and the acylation was continued at room temperature for about 24 h. At the end of the reaction the precipitated salt was filtered, and the filtrate was dropped into excess n-hexane to precipitate the polymer. After filtration, the macroinitiator (MWNT-pCL-Br) was dried under vacuum at 40 °C for 24 h.

2.5. Synthesis of MWNT-pCL-b-PS Diblock Copolymer

CuBr (6.8 mg, 0.047 mmol) and 2,2′-bipyridine (bpy) (14.9 mg, 0.094 mmol) and a few mL dichloromethane were added into the polymerization tube, followed by the addition of MWNT-pCL-Br (20 mg) and 500 mg (4.810 mmol) styrene. After purging with argon for 15 min, the tube was sealed with screw cap and kept in an oil bath at 107-110 °C for 24 h. The mixture was diluted with dichloromethane, and the polymer was precipitated in slightly acidic ethanol. The polymer (MWNT-pCL-b-PS) was filtered off, dried under vacuum at 40 oC for 24 h.

2.6. Synthesis of MWNT-pCL-b-PS-b-pGMA Triblock Copolymer

CuBr (30 mg, 0.209 mmol) and 2,2′-bipyridine (66 mg, 0.418 mmol) and a few mL of dichloromethane were added to the polymerization tube, followed by the addition of MWNT-pCL-b-PS (60 mg) and 3000 mg GMA (21.0 mmol. After purging with argon for 15 min, the tube was sealed with screw cap and kept in an oil bath at 107-110 °C for 1 h. After the mixture was diluted with dichloromethane, and the polymer was precipitated in slightly acidic ethanol. Triblock copolymer (MWNT-pCL-b-PS-b-pGMA) was filtered, and dried under vacuum at 40 °C for about 24 h.

2.7. Measurements

1H NMR analysis were performed with 400 MHz by Bruker A VIII 400 machine, using $CDCl_3$ as the solvent, and a tetramethylsilane as standard. Fourier transform infrared spectra (FT-IR) were recorded on Perkin-Elmer Spectrum One FTIR spectrometer. Calorimetric measurements were carried out using a Shimadzu DSC-50 thermal analyzer under N_2 flow at heating rate of 20 °C/min., while thermal stability studies were carried out using Shimadzu TGA-50 thermobalance under N2 flow with a heating rate of 10 °C/min.

For capacitance measurements according to the previous work [22], the polymer was grinded with an agate mortar and pestle, and the final fine powder was pressed at four tons of pressure into disk-shaped samples with a thickness of 0.72 mm for the diblock copolymer and 0.75 mm for the triblock copolymer with a surface of 1.13 cm^2. The entire surface of the disk was coated with silver cake, which acts as a good contact for capacitance measurements.

The measurements were carried out at room temperature using a QuadTech 7600 precision LRC meter impedance analyzer at the frequency range of 40 Hz-2 kHz. The dielectric features against the frequency and temperature were examined. Furthermore, ac conductivity of the triblock copolymer against the temperature were also examined.

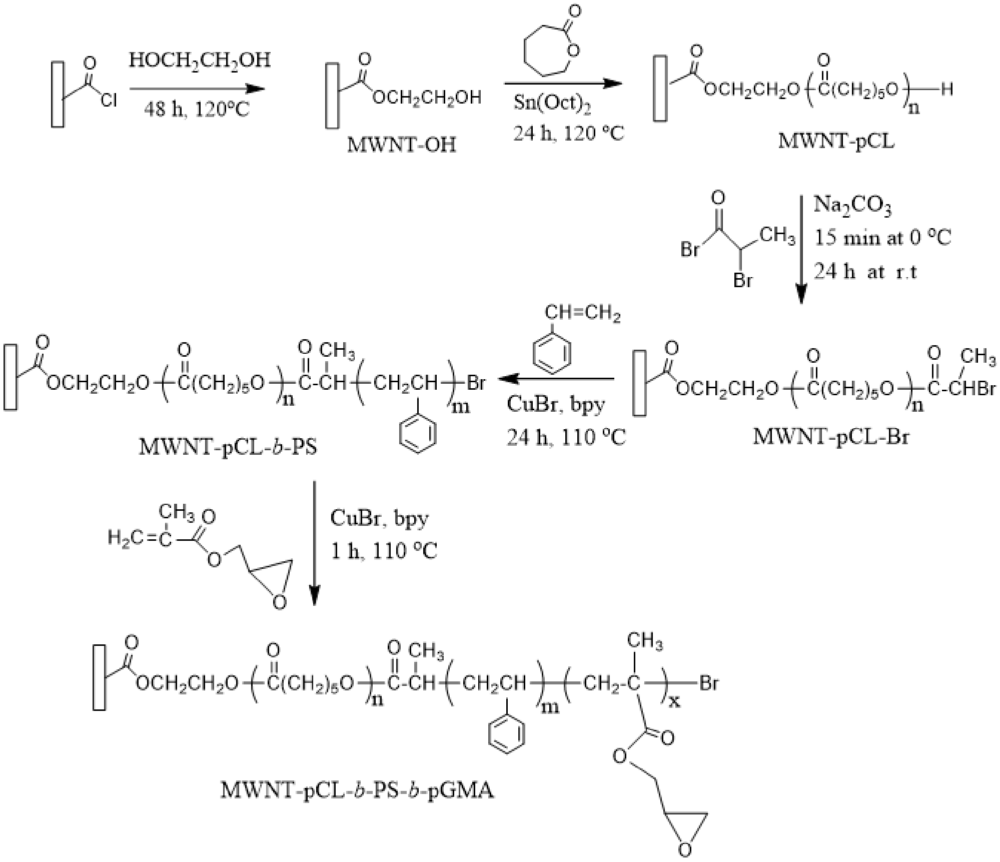


Figure 1. Synthesis of the triblock copolymer by grafting from on surface of MWNT

3. Results and Discussion

3.1. Synthesis and structural characterization studies

FTIR spectrum (Fig 2a) of MWNT-COOH shows the bands at 1718 cm^{-1} (C=O stretching vibration) and 1128 cm^{-1} (C-O stretching vibration). These bands are not presence that of original MWNT (This spectrum has not been text). MWNT-OH was obtained with mono acylated of ethylene glycol after MWNT-COOH was converted to MWNT-COCl with thionyl chloride. FTIR spectrum of (Fig 2b) MWNT-OH shows the small bands at 1730 cm^{-1} (stretching vibration of C=O in ester), at 2923 and 2846 cm^{-1} (aliphatic C-H stretching vibration), 1077 and 1180 cm^{-1} [C-C(=O)-O symmetric and asymmetric vibrations, respectively]. MWNT-pCL was prepared by grafting of ε-CL on MWNT-OH in presence of Sn(Oct)2 as catalyst by aid of ring opening polymerization. The FTIR spectrum (Fig 2c) of MWNT-pCL shows characteristic bands at 1730 cm^{-1} (stretching vibration of C=O in ester), at 2949 and 2859 cm^{-1} (aliphatic C-H stretching vibration), 1192 and 1256 cm^{-1} [C-C(=O)-O symmetric and asymmetric vibrations, respectively].

MWNT-pCL was converted to the macroinitiator for ATRP (atom transfer radical polymerization) by acylation of OH group at the end of MWNT-pCL with α-bromopropionyl bromide. O-H Stretching vibration at 3462 cm^{-1} (Fig 2d) was disappeared by the acylation. MWNT-pCL-b-PS was prepared by ATRP of styrene using the macroinitiator in presence of CuBr/bpy as catalyst. This diblock copolymer shows new bands at 3000-3100 cm^{-1} (aromatic =C-H stretching vibration), 761 and 705 cm^{-1} (out off plane =C-H bending vibration in monosubstituted aromatic) and three of weak overtone and combination bands between 2000-1660 cm^{-1} (one of them is covered by carbonyl peak), in addition to the bands of the ε-caprolactone units (Fig 1e). In FT-IR spectra (Fig 2f) triblock copolymer (MWNT-pCL-b-PS-b-pGMA) obtained by ATRP technique shows characteristic bands at 3000 cm-1 (C-H stretching vibration of epoxy ring), 1731 cm^{-1} (C=O), 1260 cm^{-1} (symmetrical epoxy ring stretching or epoxy ring breathing frequency), 915 cm^{-1} (asymmetrical epoxy ring stretching) and 846 cm^{-1} (epoxy C-H bending vibration). Triblock copolymer shows also characteristics bands of styrene units.

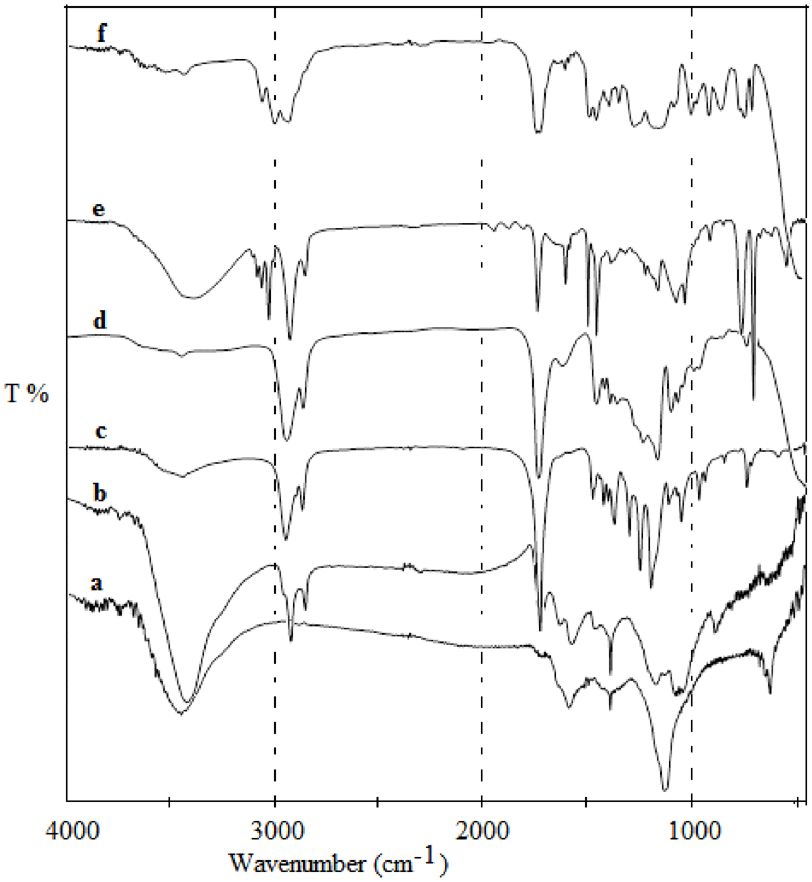
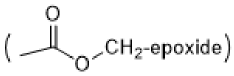
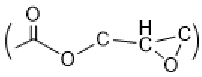
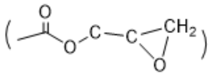


Figure 2. FT-IR spectrum of (a)MWNT-COOH, (b) MWNT-OH, (c) MWNT-pCL-OH, (d) MWNT-pCL-Br, (e) MWNT-pCL-b-PS, (f) MWNT-pCL-b-PS-b-pGMA)

The 1H NMR spectrum (Fig 3a) of MWNT-pCL shows characteristic signals at 4.30 ppm (MWNT-COOCH$_2$-), 4.09 ppm (-OCOC-C-C-C-CH$_2$OCO-), 3.70 ppm (OCOC-C-C-C-CH$_2$-OH end group), 2.34 ppm (-OCOCH2-C protons on α-carbon), 1.67 ppm (-OCOC-CH$_2$-C-CH$_2$-C-O) and 1.41 ppm (-OCOC-C-CH$_2$-C-C-O). When the integral heights of –CH$_2$- in the –CH$_2$OH (end group) and –CH2- bounded the ester oxygen compared, repeating CL units can be estimated as approximately 6 units per MWNT-pCL. After acylation of OH group at the end of MWNT-pCL with α-bromopropionyl bromide, that is, after it transformed to macroinitiator for ATRP, the signal at 3.70 ppm (C-CH$_2$-OH) of MWNT-pCL was disappeared, and new signals at 4.35 ppm [-CH$_2$-O-C(=O)-C(CH$_3$)$_2$Br, integral height 0.09, end group] and 1.85 ppm [-C-O-C(=O)-C(CH3)$_2$Br, integral height 0.26, end group] appeared (Fig 3b). In the ^{1}H NMR spectrum (Fig 3c) of

MWNT-pCL-*b*-PS obtained from ATRP of styrene in presence of the macroinitiator, the characteristic signals of PS block were observed at 6.3-7.4 ppm (phenyl ring protons in styrene units), at 1.25-2.20 ppm (aliphatic protons of styrene units and the protons far from oxygen in CL units). In CL units of diblock copolymer, -CH2- proton signals bounded to carbonyl and -CH$_2$- proton signals bounded to oxygen in ester group were at 2.34 and 4.09 ppm, respectively. When the integral heights of –CH$_2$- at 2.34 ppm or 4.09 ppm those of aromatic protons compared, it is calculated that styrene units are nearly 6 times of the caprolactone units. That is, the diblock copolymer contains 6 units CL and 36 units styrene per the molecule. In ^{1}HNMR spectrum of MWNT-pCL-*b*-PS-*b*-pGMA (Fig 3d) the proton signals of glycidyl methacrylate unit mainly appeared, though the proton signals for CL and styrene unit were observed in the weak intensity. Namely; at 4.34 ; 3.84 ppm  , 3.26 ppm  and 2.87; 2.66 ppm  . The resonance signal of the methylene protons on the main chain of GMA units and the –CH- protons of styrene units were observed at 2.01 and 1.93 ppm. The α-methyl groups in methacrylate polymers are sensitive to the stereochemical configuration [23,24]. The resonance signal of the α-methyl splits into three well resolved peaks at 0.97, 1.12 and 1.31 ppm, which have been assigned to syndiotactic (rr), atactic (mr + rm) and isotactic (mm) triads, respectively. It is calculated that the differences in chemical shifts between the two signals, ($\delta_{mm} - \delta_{rm+mr}$) = 0.19 ppm and ($\delta_{rm+mr} - \delta_{rr}$) = 0.15 ppm, are very close to that of PGMA homopolymer (0.18 and 0.14 ppm) [24] and that of PMA (0.15 ppm) [23]. The ^{1}HNMR signal intensity of the triads shows that the GMA block of the triblock copolymer contains 52.0 % syndiotactic rr, 38.8 % atactic

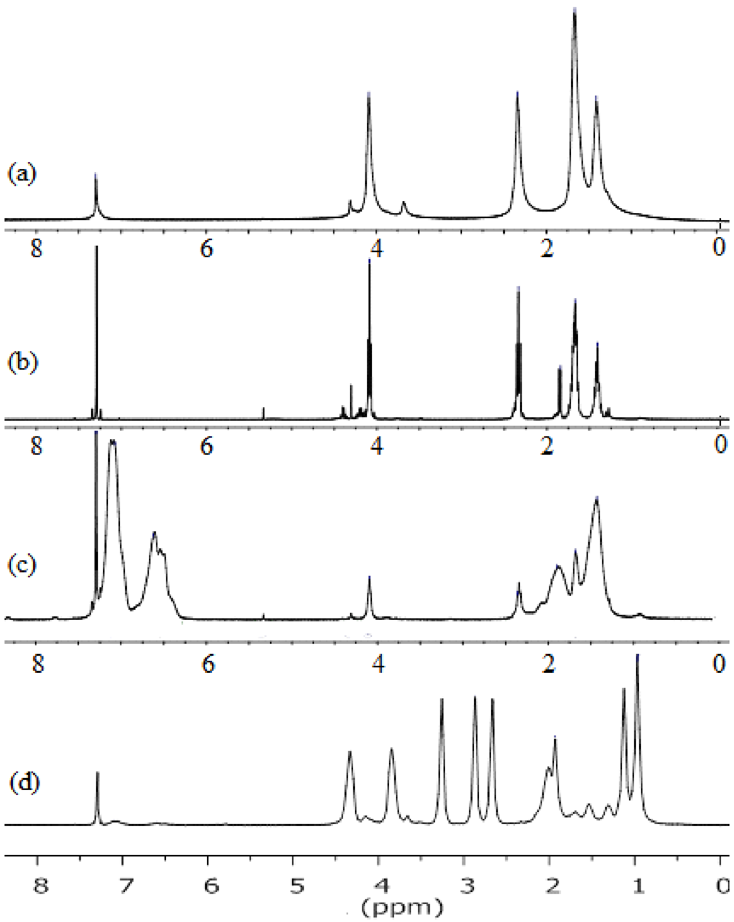


Figure 3. ^{1}H NMR spectrum of (a) MWNT-pCL, (b) MWNT-pCL-Br, (c) MWNT-pCL-b-PS, (d) MWNT-pCL-b-PS-b-pGMA

(heterotactic) mr + rm and 9.2 % ısotactic mm sequences. Phenyl ring protons in styrene units and methylene proton of ester group in CL units were observed between 6.3-7.4 ppm and at 4.09 ppm, respectively. When integral height of anyone from five signals among at 4.34 ppm and 2.66 ppm of glycidyl group those of aromatic protons compared, it can be estimated that the GMA units in the triblock copolymer are nearly 30 times of styrene units. That is, triblock copolymer is in the structure of MWNT-p$(CL)_6$-*b*-P$(S)_{36}$-*b*-p$(GMA)_{1080}$.

3.2. SEM Investigation

MWNT distribution is not regular, some areas show the sparse distribution, some areas shows dense distribution (Figure 4a). SEM image of MWNT-pCL-*b*-PS (Figure 4b) shows that MWNT particles were mostly covered with the polymer, and were distributed randomly in the block copolymer. Figure 4c shows that the lengths of MWNTs in the triblock copolymer shortened and they are present in the form of aggregation in the structure.

3.2.1. Thermal Analysis Studies

The DSC thermograph of MWNT-pCL (Fig 5) shows that the melting point of polycaprolactone units is 52 °C. This value is highly lower than such as 61°C and 67°C given in literature [25,26].

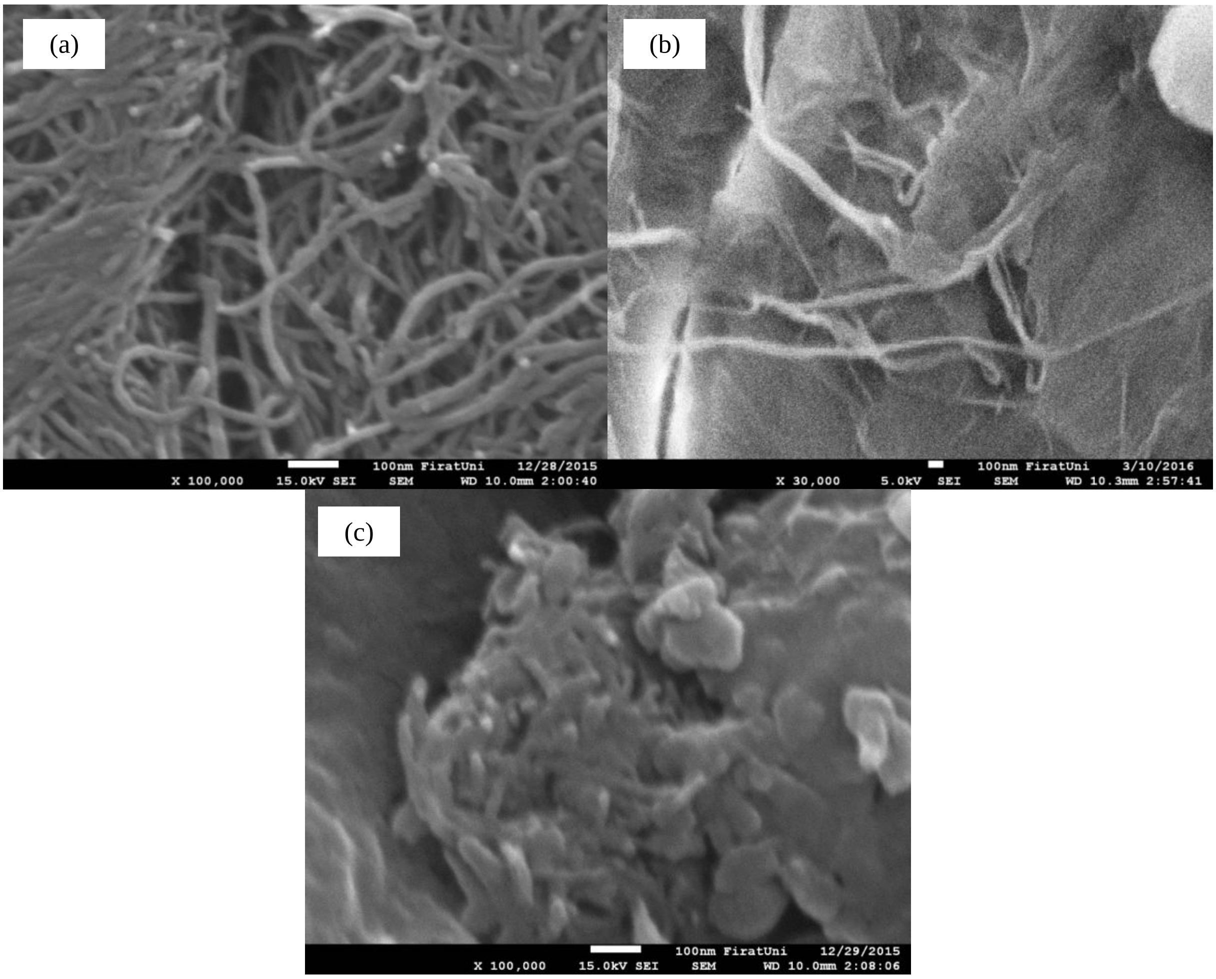


Figure 4. SEM images of (a) untreated MWNT, (b) MWNT-pCL-b-PS and (c) MWNT-pCL-b-PS-b-pGMA

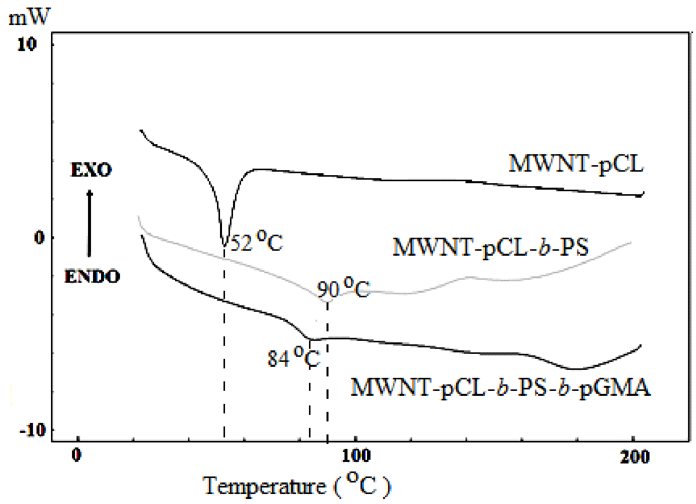


Figure 5. DSC thermograms of MWNT-pCL, MWNT-pCL-b-PS and MWNT-pCL-b-PS-b-pGMA

The melting point of polycaprolactone increases rapidly depending on molecular weight until about 8000 g/mol [27]. According to the values given in the literature, pCLs with molecular weight of 578, 1750, 3950 g/mol show a melting point of 45°C, 57°C and 60 °C, respectively.

Number of repeating CL units in MWNT-pCL is about 6 units as a result of ^{1}H NMR. This result shows that the number average molecular weight is about 700 g/mol, and according to the literature data [27] a melting point of 52 °C is a suitable value for this polymer. The DSC curves show that the glass transition temperatures of MWNT-pCL-*b*-PS and MWNT-pCL-*b*-PS-*b*-pGMA are 90°C and 84°C, respectively.

The thermal stability of the polymers was studied by programmed thermogravimetric analysis over a temperature range from room temperature to 500 °C under nitrogen atmosphere (Fig 6). The thermogravimetric curve shows that there is no weight loss until 410 °C, and between 410-500 °C only a weight loss of 2% for original MWNT. While MWNT-COOH show very slow decomposition step with a weight loss of about 5 % between 300 - 390 °C, after that a weight loss of totally 22 % shows until 500 °C. The thermal behavior and decomposition

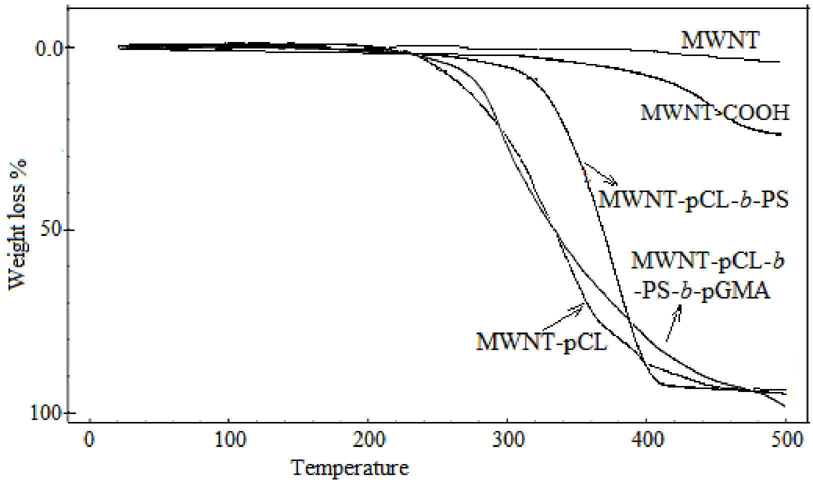


Figure 6. TGA thermograms of untreated MWNT, MWNT-COOH, MWNT-pCL, MWNT-pCL-b-PS, MWNT-pCL-b-PS-b-pGMA

Table 1. Thermal behavior and decomposition temperatures of the polymers

Polymer	IDT* (^{o}C)	A weight loss of 50 % at (^{o}C)	Weight loss at 350 ^{o}C	Residue at 500 ^{o}C
MWNT	410	?	0	98
MWNT-COOH	300	?	2	78
MWNT-pCL	225	335	65	6
MWNT-pCL-*b*-PS	300	370	30	6
MWNT-pCL-*b*-PS-*b*-pGMA	260	335	60	4

*IDT: Initial decomposition temperature

3.3 Electrical properties

Dielectric constant, property of an electrical insulating material (a dielectric) equal to the ratio of the capacitance of a capacitor filled with the given material to the capacitance of an identical capacitor in a vacuum without the dielectric material. A material with a high dielectric constant is placed in an electrical field, the magnitude of the field will be reduced within the volume of the dielectric. Dielectric constant (ε′) is evaluated from the capacitance measurement using the following equation:

$$\varepsilon' = \frac{C.d}{A.\varepsilon_o} \qquad (1)$$

where ε_o is permittivity in free space, which is equal to ε_o = 8.856x10^{-14} F/cm, *C* is parallel capacitance, *d* and *A* are thickness and area of the sample, respectively.

The dielectric loss (ε′′), which is a measure of the loss of energy in a dielectric material, is obtained from the equation

$$\varepsilon'' = \varepsilon' \tan\delta \qquad (2)$$

where tan δ is the loss tangent and is measured by the ac impedance bridge.

In the frequency range between 100 and 2500 Hz, for MWNT-pCL-*b*-PS up to about 400 Hz and MWNT-pCL-*b*-PS-*b*-pGMA up to about 800 Hz, the dielectric constant degrease very slow with increasing frequency at room temperature (Fig 7).

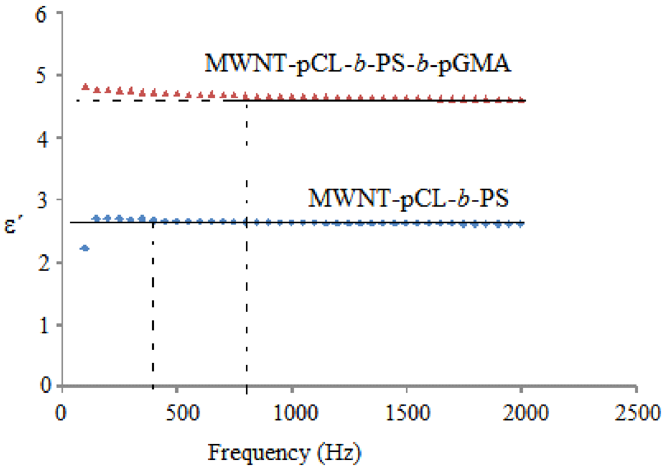


Figure 7. Frequency dependence of dielectric constants of MWNT-pCL-b-PS and MWNT-pCL-b-PS-b-pGMA at room temperature.

After these frequency values the dielectric constants reach a constant value at 2.6 for MWNT-pCL-*b*-PS and at 4.6 MWNT-pCL-*b*-PS-*b*-pGMA. This may be due to very low orientation and oscillation of permant dipoles in the applied field. The variation of dielectric constant with temperature at 1 kHz fixed frequency for the triblock copolymer is seen in Fig 8. The Figure shows that dielectric constant of the triblock copolymer increases with temperature due to an increase of total polarization arising from dipoles and trapped charge carriers. After 340 K the increasing is rapid, between 340-365 K is probably α-relaxation region associated to the glass transition region of the triblock copolymer. The intersection point of the straight line drawing from points before 340 K with the straight line drawing from points after 365 K obtained as 80 ^{o}C (353 K) which corresponds to T_g temperature of the triblock copolymer (it is obtained as 84 oC from DSC curve). The variation of dielectric loss factor (ε´´) with temperature at 1 kHz fixed frequency for the triblock copolymer is seen in Figure 9.

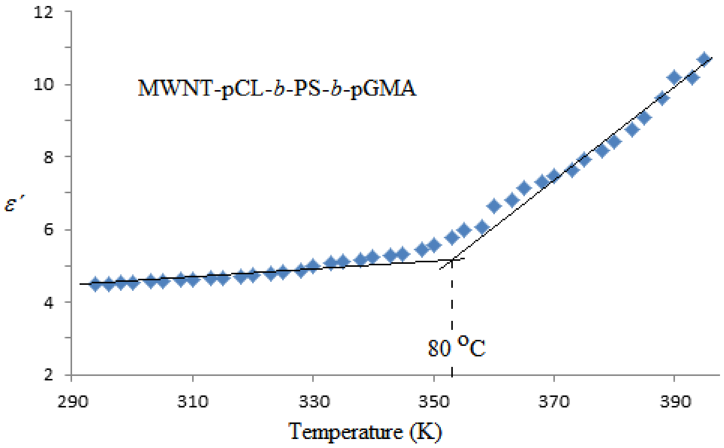


Figure 8. Temperature dependence of dielectric constant of MWNT-pCL-b-PS-b-pGMA at 1 kHz

The dielectric loss factor increases slowly with increasing temperature up to about 330 K, but after about 355 K the increase is very rapid. Between 330-355 K is probably a α-relaxation region which corresponds to the glass transition temperature of the triblock copolymer. The T_g is estimated as 83 ^{o}C from this diagram, it is very close to the value estimated from DSC. Minor differences between the T_g values obtained from electrical properties and DSC data have been observed in some other studies [28,29]

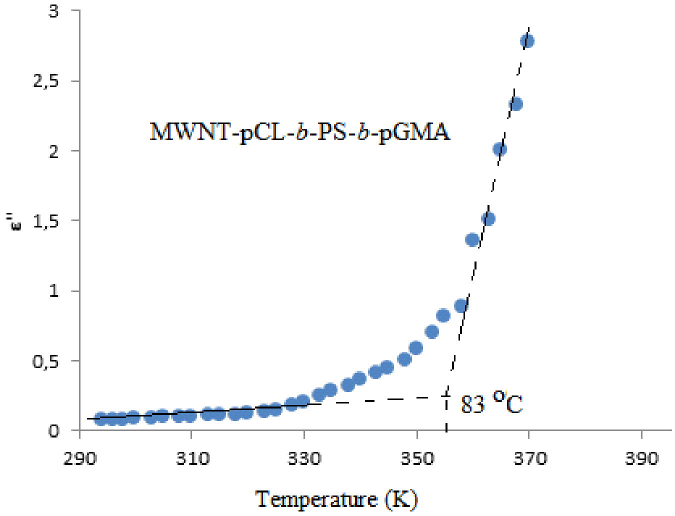


Figure 9. Temperature dependence of dielectric loss factor MWNT-pCL-b-PS-b-pGMA at 1 kHz

Electrical conductivity (σ) is evaluated from the conductance (G) measurement using the following equation:

$$\sigma = \frac{G \, . \, d}{A} \tag{3}$$

where d and A are thickness and area of the sample, respectively.

For nonmetallic materials the ac electrical conductivity (σ) depends on the absolute temperature (T) according to the Arrhenius equation.

$$\sigma = \sigma_o \exp\left(- E_a / k_B \, T\right) \tag{4}$$

where σ_o is a constant, E_a is the activation energy for conduction and k_B is the Boltzmann constant. The variation of ln σ versus inverse absolute temperature (1/T) of the triblock copolymer is given in Fig. 10. The plot shows that as temperature increases the conductivity value also increases. This Figure shows that the relation is linear with two different slopes which suggest two different activation energies, one with moderate temperature dependence and the other with strong temperature dependence. Similar results were seen in the literature [29]. The intersection point of two straight line is about 86 ^{o}C which corresponds the glass transition temperature (the value obtained from DSC curve is 84 ^{o}C) of the triblock copolymer.

The activation energy was calculated as 0.31 eV from slope the straight line in low temperature region (310-359 K), it was calculated as 1.79 eV from slope the straight line in high temperature region (359-435 K). This different behavior can be rationalized by recognizing the free-volume model. As the temperature increases, the polymer can expand easily and produce free volume. Thus, polymer segments can move into the free volume [30] and the resulting conductivity represented by overall mobility of polymer is determined by the free volume around the polymer chains.

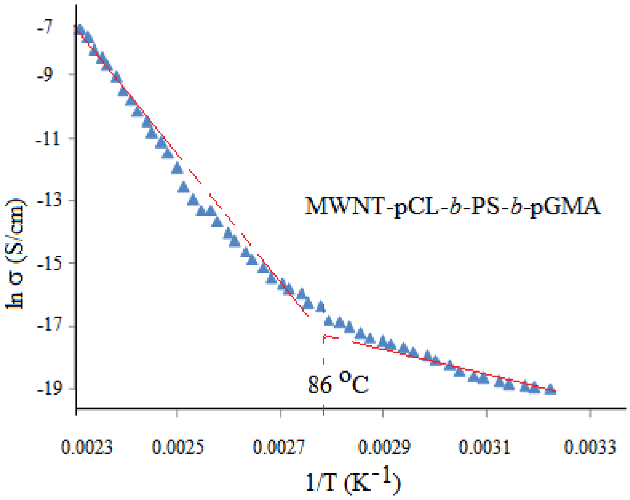


Figure 10. Variation of ac conductivity with temperature of the triblock copolymer

Therefore, as temperature the increases, free volume increases. This leads to an increase in ion mobility and segmental mobility that will assist charge transport [31].

4. Conclusions

After strong acid oxidation, derivatization with ethylene glycol of MWNT transformed acid chloride with $SOCl_2$ gave MWNT-OH. Ring opening polymerization of ε-caprolactone (CL) using $Sn(Oct)_2$ as catalyst resulted in MWNT attached to pCL. After acylation reaction of MWNT-pCL with α-bromopropionyl bromide, the realization of ATRP first with styrene and then with GMA in presence CuBr/bpy gave the block copolymer (MWNT-pCL-*b*-PS) and the triblock copolymer (MWNT-pCL-*b*-PS-*b*-pGMA), respectively. The ^{1}HNMR studies show that structure in terms of mer number per molecule of the ABC type triblock copolymer is MWNT-p(CL)$_6$-*b*-P(S)$_{36}$-*b*-p(GMA)$_{1080}$. Chemical structures of all the polymers were defined FT-IR, ^{1}H NMR and SEM. It was found that the GMA block of the triblock copolymer contains 52.0 % syndiotactic rr, 38.8 % atactic (heterotactic) mr + rm and 9.2 % ısotactic mm sequences. It was determined that the glass transition temperatures were 90^{o}C for the diblock copolymer and 84 ^{o}C for the triblock copolymer as DSC data. For the triblock copolymer ıt was observed that dielectric constant dependence on frequency is very weak, but that dielectric constant, dielectric loss factor and ac conductivity dependence on temperature is remarkable.

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