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Synthesis and Semi-conducting Properties of Novel 2-(4-Chloro-1-naphtyloxy)-2-oxoethyl Methacrylate with 2-(Dimethylamino)Ethyl Methacrylate Copolymers, Quaternized Amino Groups

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Methacrylate based monomer, 2-(4-chloro-1-naphtyloxy)-2-oxoethyl methacrylate (ClNOEMA) was synthesized by reacting 4-chloro-1-naphthyloxychloromethylketone with sodiummethacrylate in acetonitrile solvent at 70°C in the presence of triethylbenzylammonium chloraid as phase transfer matter. The free-radical initiated copolymerization of (ClNOEMA), with 2-(dimethylamino)ethyl methacrylate (DMAEMA) was carried out in 1,4-dioxane solution at 70 ± 1°C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator with 50%–50% monomer-to-monomer ratio in the feed. This copolymer has been converted into a novel salts by reaction with the iodemethane (CH_3I). The copolymers and the corresponding salts have been characterized fully by a range of spectroscopic and thermal analysis techniques. The electrical conductivity dependence of temperature of the polymers were measured and the polymers exhibit the semiconducting behavior, confirming that the electrical conductivity increases with increasing temperature. The poly(CINOEMA-co-DMAEMA) polymer doped by CH_3I for 5 min shows the highest conductivity. The optical band gap, activation energy and room temperature conductivity values of this polymer were obtained to be 2.16 eV, 0.141 eV and 3.9×10^7 S/cm, respectively. These electronic parameters suggest that the poly(CINOEMA-co-DMAEMA) [0.23:0.77] polymer doped by CH_3I for 5 min is an organic semiconductor with the thermally activated conduction mechanism.

Keywords: 2-(4-chloro-1-naphtyloxy)-2-oxoethyl methacrylate, semi-conducting polymers, the electrical, optical and thermal properties

1 Introduction

Organic semi-conducting materials such as, monomer, polymer and some organic compounds are interesting as new materials. Organic compounds based on polymers and monomers capable of accepting electrons are potentially useful as semi-conductors in a number of new applications in microelectronic and electronic device technology. Among several organic systems, polymers, monomers and some other organic compounds have recently been shown to be a class of interesting organic semiconductors with interesting electrical and optical properties. In general, polymer and monomeric organic compounds having an extended delocalized π-system have intense absorption in the near infrared region and this information is associated with the charge transport properties of organic semiconducting materials (1–4). Methacrylate polymers are among the most important commercial polymers, with a very wide range of applications in products as diverse as glazing, lighting housings, bath tubs and structural adhesives. The success of these polymers in many of the applications is dependent on the versatility of the acrylic monomers in copolymerizing to produce a wide diversity of structures, which can be tailored to produce the desired properties. Of particular interest is the synthesis of copolymers with specific functionality, which can act as a locus for further reactions, or furnish the copolymer with specific chemical and/or physical characteristics. A system which has been studied extensively involves copolymers based on 2-(dimethylamino)ethyl methacrylate (DMAEMA) and methacrylates such as methyl methacrylate (MMA) (5–12). The basic character of the tertiary amino side chain in MMA-DMAEMA copolymers has inevitably led to studies of the acid-base behavior of the polymers using, for example, pH titration (1,2). Efimova *et al.* (1) have studied

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the acid-base properties of both monomeric and polymeric DMAEMA salts in aqueous and aqueous-ethanolic conditions. Monomeric and polymeric salts of DMAEMA were made by reaction with the acids HCl, HNO_3, H_2SO_4 or H_3PO_4. The ionization constants of the monomeric and polymeric ammonium salts were calculated and, from this, the electrostatic free energies of ionization, ΔG_{el}. The structural features of the anions (size, element, e.g. carbon or phosphorus) were observed to have a significant effect on the ionization constants and ΔG_{el} of the salts. It was also noted that the ionization constants for the monomers and polymers were reduced in an aqueous environment compared to an aqueous-ethanolic environment. The homopolymer and copolymers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) are used extensively as stabilizers for latex formation, as potential carriers for drug delivery systems and for a wide range of cosmetics applications (13–17). Poly DMAEMA is a useful carrier for non-viral gene delivery since its cationic charges can condense plasmid DNA by ion interactions (18). Poly DMAEMA-based block copolymers can be cross-linked to form nanospheres with a cross-linked shell, which can then act as nanoreactors and drug delivery vehicles (19). Furthermore, DMAEMA block copolymers exhibit reversible pH-, salt-, and temperature-induced micellization in aqueous media (20–22). By combining the bioactive properties of polyDMAEMA and the biocompatibility of polyHEMA, well-controlled poly(DMAEMA-b-HEMA) hydrophilic-hydrophilic block copolymers can be very useful for preparing nanostructural, "intelligent" materials and devices for biomedical applications. Many polyDMAEMA- or polyHEMA-based hydrophilic and amphiphilic diblock copolymers have been prepared using various living polymerization techniques. Well-controlled molecular architectures are essential to study the materials structure-property relationships, especially in biomedical applications (23). In the past decade, controlled radical polymerization (CRP) has been the focus of intense research owing to its versatility and potential commercial applications, such as controlled molar mass, narrow molecular weight distribution and well-defined architecture and functionalities (24–27).

On the other hand, recently, ionomers have been investigated due to the great interest which is both present from the point of view of basic research in polymer science and from a practical point of view of designing new composite materials for advanced technologies (28). We have evaluated that the electrical properties of insulating polymers can be changed to semi-conducting polymers by attaching in the structure of their macromolecules. With this aim, we report here the synthesis and characterization of monomer ClNOEMA, as well as copolymer of ClNOEMA with DMAEMA using 50%–50% by mole feed ratios. The electrical, optical and thermal properties of the synthesized polymers have been investigated by conductivity-temperature and optical characterization methods.

2 Experimental

2.1 Materials

2-(Dimethylamino)ethyl methacrylate (DMAEMA) (Merck) was each passed in turn through a basic alumina column in order to remove inhibitor. 4-Chloro-1-naphtol (Aldrich), sodium methacrylate Aldrich), chloracetylchloride (Merck), acetonitrile and anhydrous magnesium sulfate (Aldrich) were used as received.

2,2′-Azobisisobutyronitrile (AIBN) (Aldrich) was purified by successive crystallizations from chloroform-methanol mixture. Triethylbenzylammonium chloride (TEBAC) was prepared by reacting triethylbenzylamine (Aldrich) (1 mol) with ammonium chloride (Aldrich) (2 mol). Triethylamine, 1,4-dioxane, n-hexane, iodomethane, tetrahyrofurane, ethylacetate (Merck), were analytical grade commercial products and used as received.

2.2 Synthesis of 4-Chloro-1-naphtylchloracetate

The synthesis of 4-chloro-1-naphtylchloroacetate was carried out as follows:

4-chlor-1-naphtol (0.030 mol) and triethylamine (NR_3) (0.090 mol) were dissolved in 100 ml acetonitrile at 0–5°C, and then chloacetylchloride (0.032 mol) was added dropwise to the solution. The reaction mixture was stirred at room temperature for 15 h. The organic layer was washed several times with diethyl ether and dried over $MgSO_4$. After removing the ether, the resulting 4-chloro-1-naphtylchloracetate was crystallized from ethanol. A yellow product was obtained and recrystallized from ethanol as a yellow powder (yield 80%). The reaction scheme is shown in Figure 1.

2.3 Synthesis of 2-(4-Chloro-1-naphtyloxy)-2-oxoethyl methacrylate (ClNOEMA) (Monomer Synthesis)

4-Chloro-1-naphtylchloroacetate (1 mol) and sodium methacrylate (1.1 mol), along with TEBAC (0.1 mol) and NaI (0.1 mol) as the catalyst system, were stirred in 50 ml of acetonitrile at 75°C in a reflux condenser for 30 h in the presence of 100 ppm of hydroquinone as an inhibitor, then, the solution was cooled to room temperature and neutralized with a 5% KOH solution. The organic layer was washed several times with water and the water layer was then washed a number of times with diethyl ether. The acetonitrile and diethyl ether layers were collected and dried over anhydrous

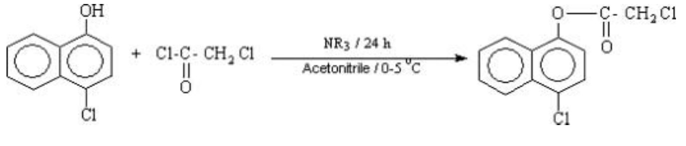

Fig. 1. Reaction scheme for the preparation of 4-chloro-1-naphtylchloroacetate.

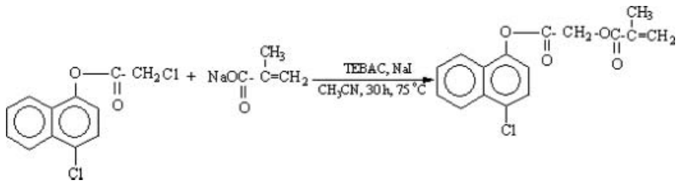

Fig. 2. Reaction scheme of 2-(4-chloro-1-naphtyloxy)-2-oxoethyl methacrylate monomer.

$MgSO_4$ overnight, after which the acetonitrile and diethyl ether were collected and finally crystallized from ethanol to give the methacrylate monomer. The reaction scheme is shown in Figure 2.

2.4 Copolymerization

Copolymerization reactions were conducted with AIBN as the initiator and 1,4-dioxane as the solvent at $70 \pm 0.1°C$ in Pyrex-glass ampoules sealed under a high vacuum. For feed composition, the calculated amount of the monomers and initiator were weighed and added to the required volume of 1,4-dioxane. We isolated the resulting copolymer by pouring the contents of the glass ampoules into n-hexane. The precipitated material was purified by reprecipitation from 1,4-dioxane as solvent/n-hexane as non-solvent and then filtered and dried until a constant weight was attained. The amounts of monomeric units in the copolymer was determined by elemental analysis, with the results obtained 0.23:0.77.

2.5 Characterization Techniques and Measurements

IR spectra were measured on a Jasco 460 Plus FT-IR spectrometer. ^{1}H-and ^{13}C-NMR spectra of the polymers were recorded in $CDCl_3$ with tetramethylsilane as the internal standard using a Bruker 400 MHz NMR spectrometer. Thermal data were obtained by using a Perkin-Elmer Diamond TG-DTA thermobalance in N_2 atmosphere. The thermal stabilities of the polymers were investigated by thermogravimetric analysis (TG) in a nitrogen stream at a heating rate of 10°C.min^{-1}. Elemental analyses were carried out by a LECO CHNSO-932 auto microanalyzer. For the electrical conductivity measurements, the poly(3-thiophene boronic acid) was prepared in the form of pellets having 0.143 mm thickness. Electrical conductivity was measured as a function of temperature by alternating polarity methods to eliminate electrical polarization, triboelectric and piezoelectric effects using a KEITHLEY 6517A electrometer. Absorption spectra of the polymer were recorded by a Shimadzu UV-VIS-NIR 3600 spectrophotometer with an integrating sphere attachment at room temperature.

3 Results and Discussion

3.1 Characterization of Copolymers

The copolymeric units of ClNOEMA with DMAEMA can be represented according to Figure 3:

3.2 FTIR Spectrum

The FTIR spectrum of the poly(ClNOEMA-co-DMAEMA) [0.23:0.77] is shown in Figure 4. The peak at 3050 cm^{-1} corresponds to the C-H stretching of the aromatic system. The symmetrical and asymmetrical stretching due to the methyl and methylene groups are observed at 2983, 2938 and 2863 cm^{-1}. The shoulder at 1740 cm^{-1} is attributed to the ester carbonyl stretching of two copolymeric

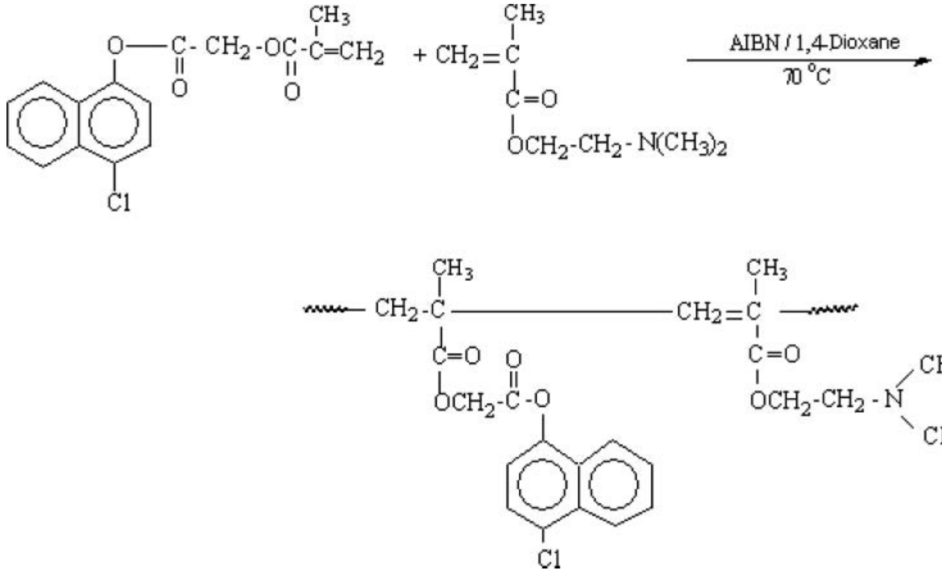

Fig. 3. Reaction scheme of copolymer.

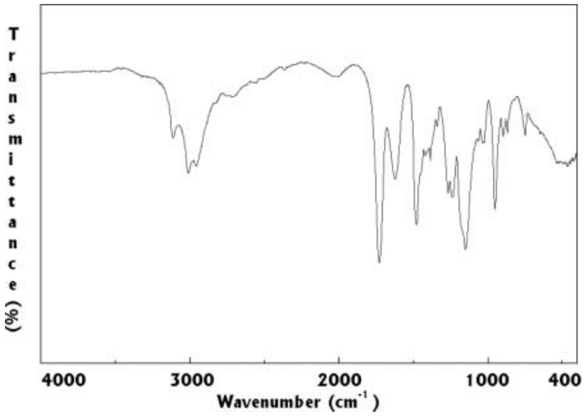

Fig. 4. FTIR spectra of copoly(ClNOEMA-DMAEMA): [0.23:0.77].

units. The ring breathing vibrations of the aromatic nuclei are observed at 1600, 1504 and 1470 cm^{-1}. The asymmetrical and symmetrical bending vibrations of methyl groups are seen at 1460 and 1385 cm^{-1}. The C-O stretching is observed at 1165 and 1200 cm^{-1}. The C-H and C=C out-of-plane bending vibrations of the aromatic nuclei are observed at 790 and 565 cm^{-1}, respectively.

3.3 ^{1}H-NMR Spectrum

The ^{1}H-NMR spectrum of the poly(ClNOEMA-co-DMAEMA) [0.23:0.77] is shown in Figure 5(A). The ^{1}H-NMR spectra of copolymer has the characteristic resonances corresponding to the general formula. All chemical shift data are also in agreement with the given molecular structure shown in Figure 3.

3.4 ^{13}C-NMR Spectrum

The proton decoupled ^{13}C-NMR spectrum of the poly(ClNOEMA-co-DMAEMA) [0.23:0.77] is shown in Figure 5(B). The ^{13}C-NMR spectra of copolymer has the characteristic resonances corresponding to the general formula. All chemical shift data are also in agreement with the given molecular structure shown in Figure 3.

3.5 Thermogravimetric Analysis

Figure 6 shows the thermal decomposition profile of the ClNOEMA-co-DMAEMA [0.23:0.77] copolymer. The initial degradation temperature and 99% weight loss of poly(ClNOEMA-co-DMAEMA) [0.23:0.77] was found to be 166°C and 600°C, respectively. Thermal degradation of copolymer was performed by two steps. The weight loss of the first step was found to be 75% between 165–260°C. The weight loss of the second step was found to be 14% between 260–600°C. In thermogravimetric analysis, the weight loss due to evolution of water, carbon monoxide and evaporation of other pyrolysis products are collectively measured as percentage of the original weight. In this investigation, poly(ClNOEMA-co-DMAEMA) [0.23:0.77] was heated at a steadily increasing temperature from 30–600°C in an atmosphere of nitrogen, the initial weight loss in the first step was due to the rupture of weak linkages and volatilization of low molecular weight species. The decomposition of polymers at higher temperature may be due to the breakage of main chain accompanied by volatilization of the cleaved products.

3.6 Preparation of the Ionomers

The ionomers of copolymers were prepared as follows: A quantity of copolymer 0.25 g (for each ionomer)) was placed in a 100 ml reaction tube and dissolved in tetrahydrofurane 10 ml (for each ionomer)). Methyl iodide (CH_3I) 1 ml (for each ionomer)) was distilled on copolymer dropwise using a distillation funnel while the solution was stirred with magnet stirring. The reactions were performed for various times (5, 15, 30, 60 and 180 min). Each mixture was precipitated in n-hexane and washed by ethylacetate. The products were dissolved in dimethylsulfate (DMS) and precipitated in the ethylacetate and then dried at 45°C. Ionomers prepared at the times 5, 15, 30, 60 and 180 min were named as I1, I2, I3, I4 and I5, respectively, and the chemical structure is given in Figure 7. CH_3I molecule was attracted by copolymer for transformation times. Thus, Iodine loading in the ionomers follows the order of I1 $<$ I2 $<$ I3 $<$ I4 $<$ I5.

The chemical structure of the ionomer can be represented according to Figure 7:

3.7 Characterization of Ionomer by ^{1}H-NMR Spectra

The ^{1}H-NMR spectrum of the poly(ClNOEMA-co-DMAEMA) [0.23:0.77] ionomer is shown in Figure 8. The chemical shift assignments for the ionomers were based on the chemical shifts observed for the respective copolymers. The structure of ionomer is confirmed by ^{1}H-NMR spectral data.

3.8 Semi-conducting Properties of the Poly(ClNOEMA-co-DMAEMA) Ionomers

Figure 9 shows the electrical conductivity plots of the ionomer. The electrical conductivity of the poly(ClNOEMA-co-DMAEMA) [0.23:0.77] polymer doped by CH_3I increases with an increase of temperature. The electrical conductivity of the poly(ClNOEMA-co-DMAEMA) polymer was fitted by Arrhenius model:

$$\sigma = \sigma_o \exp\left(-\frac{\Delta E}{kT}\right) \qquad (1)$$

Where σ_0 is a constant, ΔE is the activation energy for conductivity, T is the temperature. As seen in Figure 9, the poly(ClNOEMA-co-DMAEMA) polymer doped by

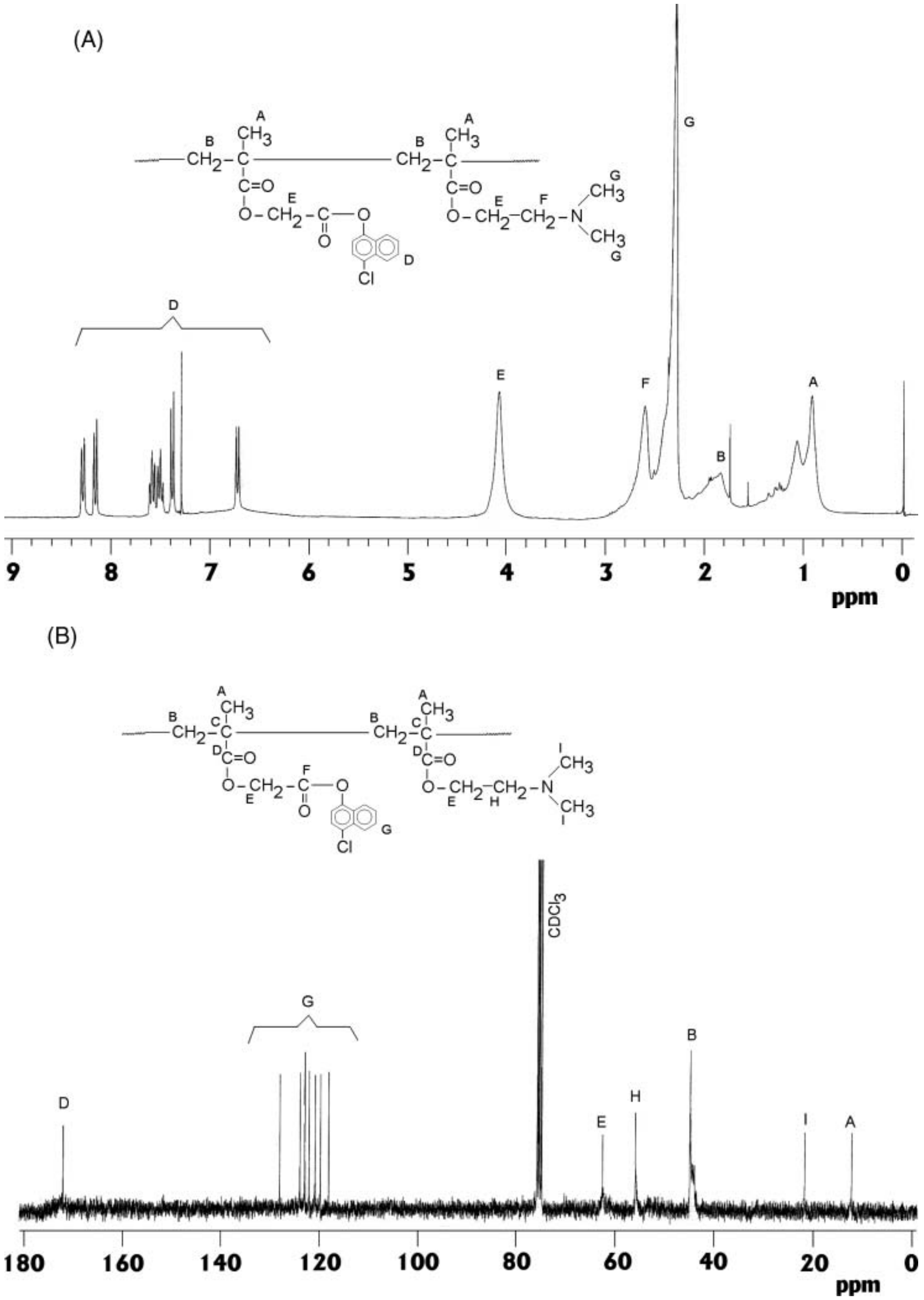

Fig. 5. ^{1}H- and ^{13}C-NMR spectra of poly(ClNOEMA-co-DMAEMA)[0.23:0.77].

CH_3I for 5 min. shows the highest conductivity. The ΔE and room temperature conductivity values of this polymer were obtained to be 3.9×10^7 S/cm and 0.141 eV, respectively. These electronic parameters suggest that the poly(CINOEMA-co-DMAEMA) polymer doped by CH_3I for 5 min is an organic semiconductor and the conductivity mechanism is controlled by the thermally activated conduction mechanism. It is evaluated that the electrical conductivity properties of the insulating poly(CINOEMA-co-DMAEMA) changed from insulating state to semiconducting state using methyl iodide dopant. The other important parameter of any organic semiconductor material is the optical band gap. In order to obtain this parameter, we were measured the absorption spectra of poly(CINOEMA-co-DMAEMA) polymer doped by CH_3I for 5 min to determine optical band gap, because this polymer only indicates the good conductivity for an organic semi-conductor. Figure 10 shows the absorption spectra of the polymer. This spectrum shows a absorption edge and in the strong absorption edge, the absorption coefficient dependence of photon

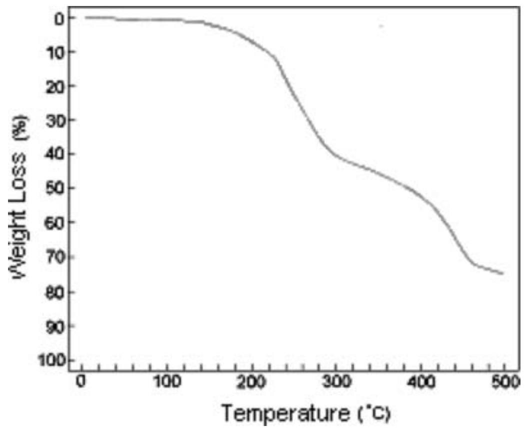

Fig. 6. TG curve of poly(ClNOEMA-co-DMAEMA): [0.23:0.77].

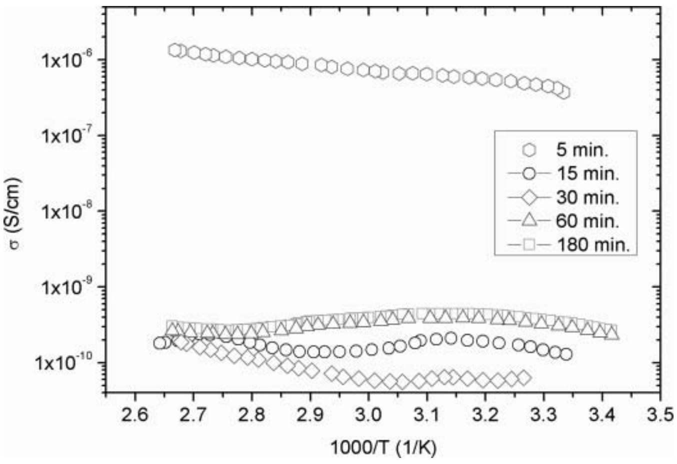

Fig. 9. Electrical conductivity plots of the poly(CINOEMA-co-DMAEMA) [0.23:0.77] ionomer.

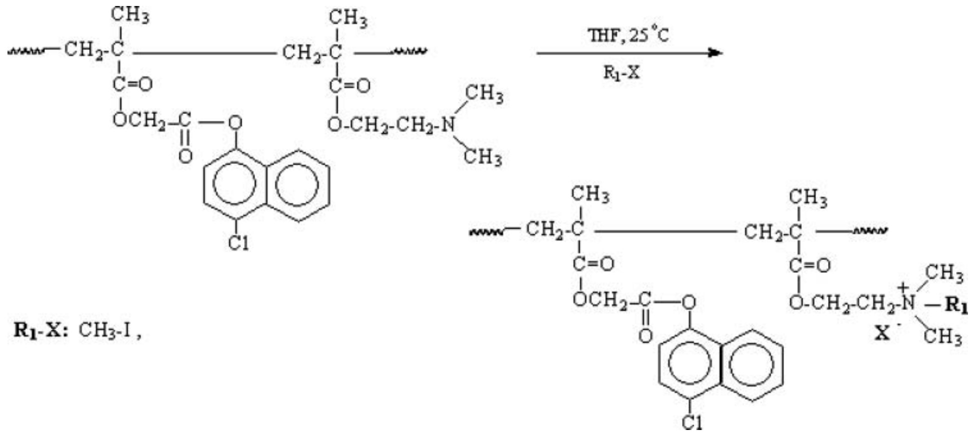

Fig. 7. Reaction scheme of ionomer.

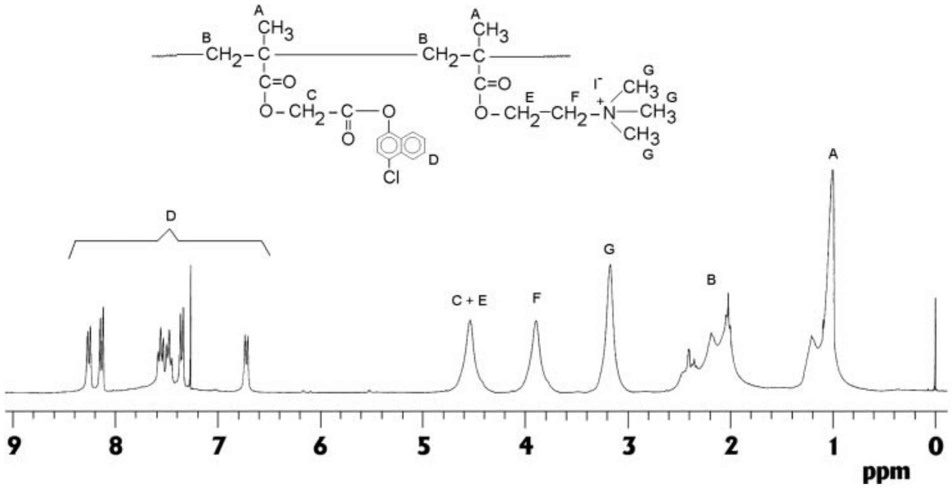

Fig. 8. ^{1}H-NMR spectra of copoly(ClNOEMA-DMAEMA) [0.23:0.77] ionomer.

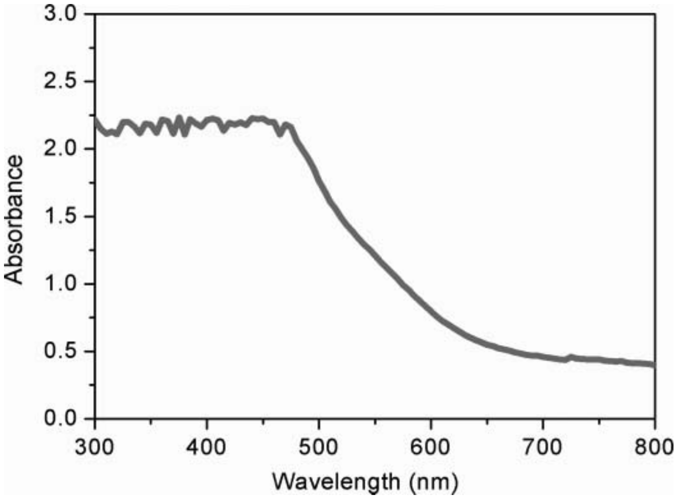

Fig. 10. UV-VIS spectra of the poly(CINOEMA-co-DMAEMA) [0.23:0.77] polymer doped for 5.

energy is defined as (29),

$$\alpha h\nu = A(h\nu - E_g)^m \qquad (2)$$

Where $h\nu$ is the photon energy, A is a constant depending on the transition probability and E_g is the optical band gap and m determines the type of optical transitions and for direct transitions, $m = 1/2$ and 2, for indirect transition $m = 2$ and 3. It is well known that the optical transitions occurring at the fundamental edge of semiconductors are direct and indirect. If m value is known, the type of optical transition can be determined. In order to determine value of the optical band gap, we plotted $(\alpha h\nu)^2$ as a function of photon energy (Figure 11). The optical band gap of the polymer was determined by extrapolating the linear portion of the plot to $(\alpha h\nu)^2 = 0$. The optical band gap of the polymer was found to be 2.16 eV. This value is a typical for organic semiconductor (30).

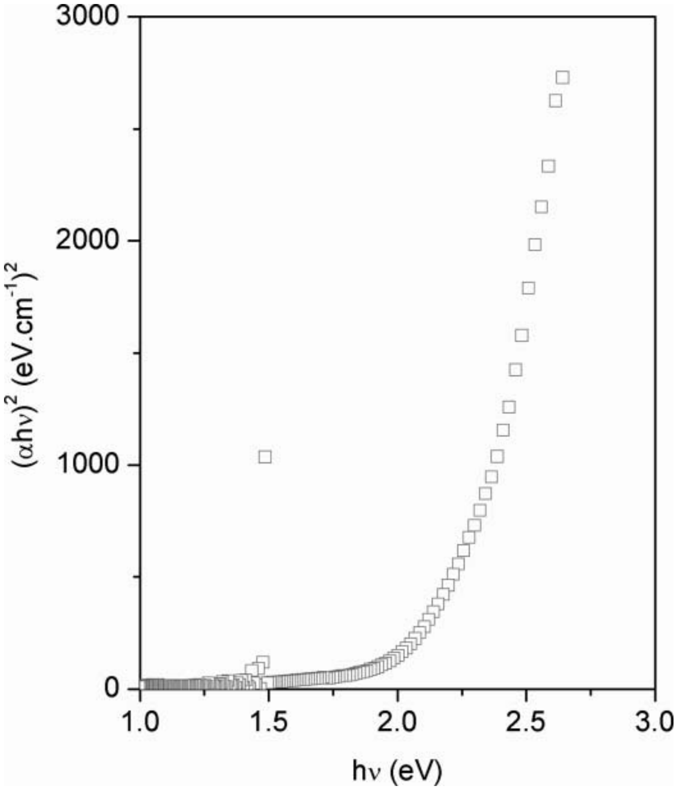

Fig. 11. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for poly(CINOEMA-co-DMAEMA) [0.23:0.77] polymer doped for 5.

4 Conclusions

The free radical chloro copolymer containing amino group and quaternized were successfully prepared by methyl iodide. Structure of the ClNOEMA and its copolymer with DMAEMA was confirmed by FTIR and ^{1}H-and ^{13}C-NMR spectroscopic techniques. The electrical conductivity properties of the insulating poly(CINOEMA-co-DMAEMA) changed from insulating state to semiconducting state using methyl iodide dopant.

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