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Research Article

SYNTHESIS, CHARACTERIZATION AND THERMAL PROPERTIES OF NEW OXOETHYL ACRYLATE CONTAINING POLYMER

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ABSTRACT

In this study, 2-(bis(cyanomethyl)amino)-2-oxoethyl acrylate (CMA2OEA) monomer, which does not exist in the literature, was synthesized and characterized. Elemental analysis technique, along with classical spectroscopic methods such as FTIR, ^{1}H and ^{13}C NMR, is used in the characterization of the monomer. Further, homopolymer of the CMA2OEA monomer [poly(CMA2OEA)] is synthesized by free radical chain polymerization reaction. Homopolymer synthesized is also characterized by spectroscopic techniques and thermal characterization is investigated by TGA/DTA/DTG thermal analysis methods.
Keywords: 2-(bis(cyanomethyl)amino)-2-oxoethyl acrylate (CMA2OEA), poly(CMA2OEA), monomer, homopolymer, synthesis and characterization, thermal stability.

1. INTRODUCTION

The areas of polymer usages have been increasing with developing industrialization in recent years. Therefore it is important to develop polymers with different physical and chemical properties needed in the industrial field. Scientific studies to develop new products have been increasing in recent years [1]. Polymeric materials are widely used due to their low density, poor heat and electrical conductivity, high mechanical strength and flexibility, and low costs [2,3].

Studies on functional polymers have shown that the structure of the substituent, which is bound to the monomer, changes many properties of the monomer and its polymer depending on this structure [3-6]. One of the most commonly used species to improve the functionality of polymers is acrylate and methacrylate derivatives. Acrylate monomers have a wide range of applications due to their optical permeability, good mechanical and thermal resistance [5-8]. Due to biological activities of acrylate group monomers, it has been found in many different fields such as medical applications, orthopedics, dental filling applications, drug delivery systems and biochemical sensor studies [9-10].

Our team is conducting monomer and polymer studies on acrylate and acrylate derivatives. In our previous studies, we have synthesized and characterized the 2-(bis(cyanomethyl)amino)-2-oxoethyl methacrylate (CMA2OEM) monomer and compared the experimental-theoretical results [11]. We also studied the interaction of CMA2OEM with human anti-apoptotic proteins, and

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investigate d the ability of the monomer to inhibit these proteins in silico. Thus, a new molecule was synthesized to obtain the new drug active molecule [12].

In this study, it is aimed to synthesize and characterize the 2-(bis(cyanomethyl)amino)-2-oxoethyl acrylate (CMA2OEA) monomer, which has a similar structure to the CMA2OEM monomer and has not yet been synthesized in the literature. It is thought that the synthesized monomer and its polymer may find application in different working areas.

2. EXPERIMENTAL

2.1. Materials

Triethylamine (NR_3), Iminodiacetonitrile, chloroacetyl chloride, sodium acrylate, Triethylbenzylammoniumchloride (Tebac) as a phase transfer catalyst, Acetonitrile and 1,4-dioxane as solvent, and Azobisisobutyronitrile as free radical initiator (Sigma) were used as received.

2.2. Instrumental Measurements

The FTIR spectrum of all samples were performed with a PerkinElmer Spectrum Two (UATR) IR spectrometer in the range of 4000-450 cm^{-1}. Elemental analysis was carried out by a Leco CHNSO-932 auto elemental micro analyzer (St. Joseph, MI). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature in $CDCl_3$. Thermal analyze of the CMA2OEA homopolymer was obtained with a Hitachi 7000 TGA/DTA/DTG (Thermal Gravimetric Analysis/Differential Thermal Analysis/Differential Thermogravimetric Analysis) simultaneous system a heating rate of 10 ^{o}C min^{-1} in nitrogen atmosphere, from room temperature to 600 ^{o}C temperatures.

2.3. Synthesis of 2-(bis(cyanomethyl)amino)-2-oxoethyl acrylate (CMA2OEA)

Firstly, 2-chloro-N,N-bis(cyanomethyl)acetamide was synthesized. For this, Iminodiacetonitrile and NR_3 were dissolved in acetonitrile at 0–5^{o}C, and then chloroacetyl chloride was added dropwise to the solution by stirring. The precipitate was filtered off and solvent was removed and finally the reaction mixture was crystallized. The reaction scheme is shown in Figure 1(I). 2-choloro-N,N-bis(cyanomethyl)acetamide (1 mole), sodium acrylate (1.2 mole) Tebac and NaI as catalyst were stirred in acetonitrile a reflux condenser for 30 h in the presence of 100 ppm hydroquinone as inhibitor. Then it was removed from impurities and, thus 2-(bis(cyanomethyl)amino)-2-oxoethyl acrylate (CMA2OEA) monomer is synthesized (low yield) (Figure 1) [11,12].

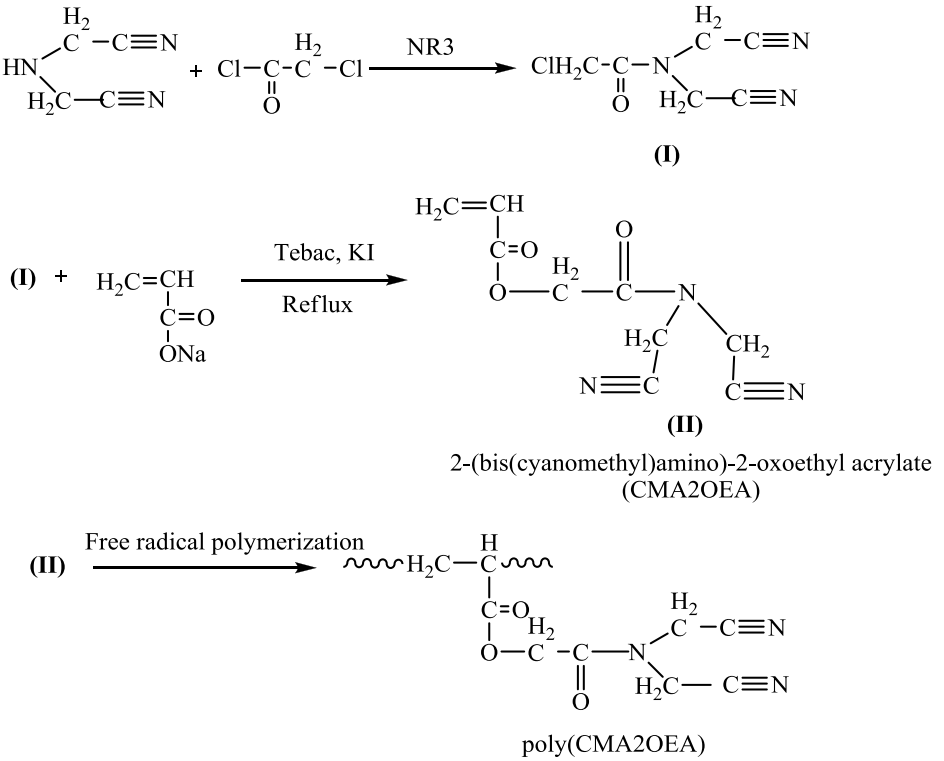

Figure 1. (I): Synthesis of the 2-chloro- N, N-bis(cyanomethyl)acetamide (II): Synthesis of the 2-(bis(cyanomethyl)amino)-2-oxoethyl acrylate (CMA2OEA), and Synthesis of homopolymer of CMA2OEA

2.4. Synthesis of the homopolymer of CMA2OEA (poly(CMA2OEA))

The monomer CMA2OEA in 1,4-dioxane solvent was polymerized at 70 °C for 36 hours using Azobisisobutyronitrile as the radical initiator and kept under inert gas. It was finally crystallized with ethanol to remove impurities. The chemical structure of homopolymer was characterized by spectroscopic methods (FTIR and ^{1}H NMR). The synthesis of homopolymer of CMA2OEA is shown in Figure 1.

3. RESULTS AND DISCUSSION

3.1. Characterization of 2-(bis(cyanomethyl)amino)-2-oxoethyl acrylate (CMA2OEA)

Elemental analysis of the monomer was carried out by an automatic micro elemental analysis device. In this system, 1 mg is taken from the sample to be analyzed. It was analyzed by burning in tin specimen container. The system is calibrated by sulfanilamide ($C_6H_8N_2O_2S$) standard material analysis to correct the results. The results of elemental analysis of synthesized monomer is as follows: Experimental found (%): C: 51.9, H: 4.3, O: 23.0, N: 20.1. The results showed a good agreement between experimental and theoretical values. The FTIR, ^{1}H and ^{13}C NMR spectra of the synthesized CMA2OEA monomer are indicated in Figures 2, 3 and 4. FTIR (cm^{-1}, the

most characteristic bands): 2999 (C-H stretch), 1713 (C=O ester stretch), 1690 (C=O amide stretch), 1627 (C=C olefinic stretch), 1162 (C-N stretch). ^{1}H-NMR spectrum (the most characteristic peaks): at 6.2 and 5.5 ppm for =CH_2 olefinic protons, 5.9 ppm for =CH protons, 5.1 ppm for O-CH_2 protons, 4.7 ppm for N-CH_2 protons. ^{13}C-NMR spectrum (the most characteristic peaks): at 167 ppm for ester and amide C=O, 134 ppm for =CH, 126 ppm for =CH_2 olefinic, 114 ppm for C≡N, 61 ppm for O-CH_2, 36 ppm for N-CH_2 carbons [13-16].

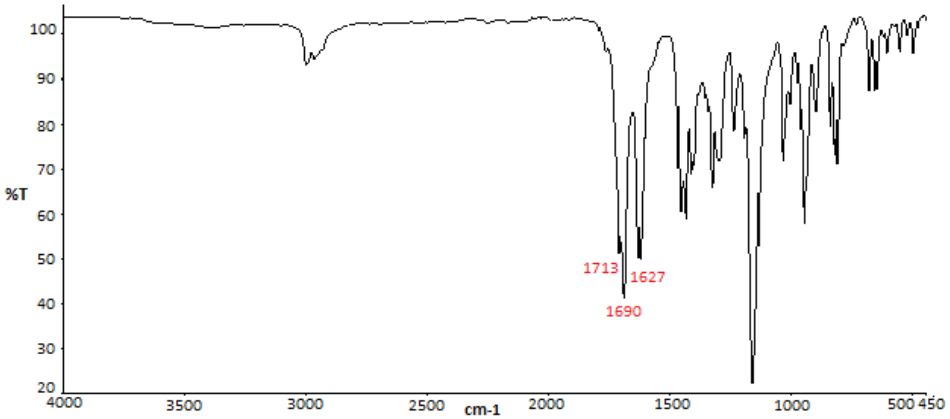

Figure 2. The FTIR spectrum of the CMA2OEA

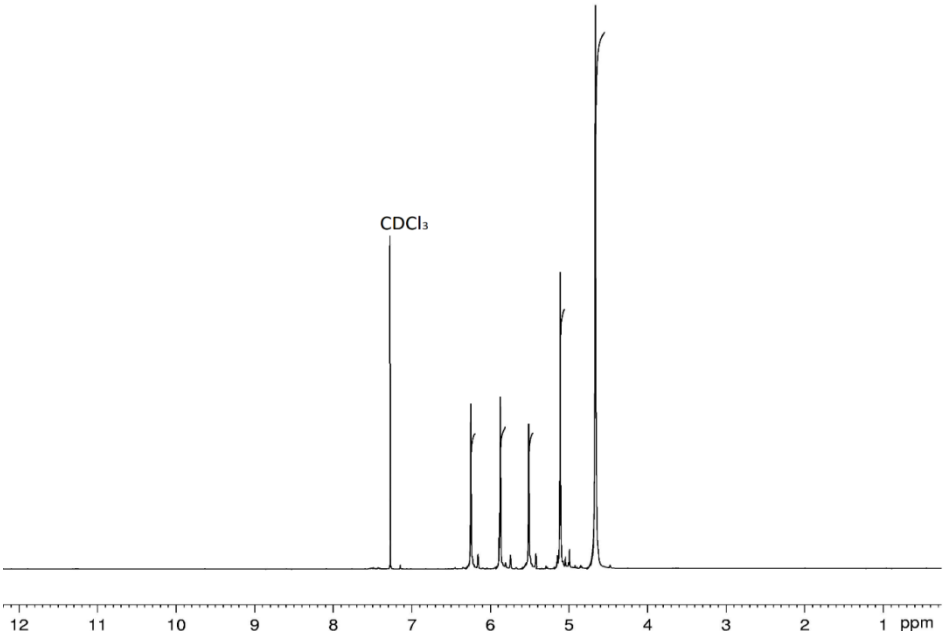

Figure 3. The ^{1}H NMR spectrum of the CMA2OEA

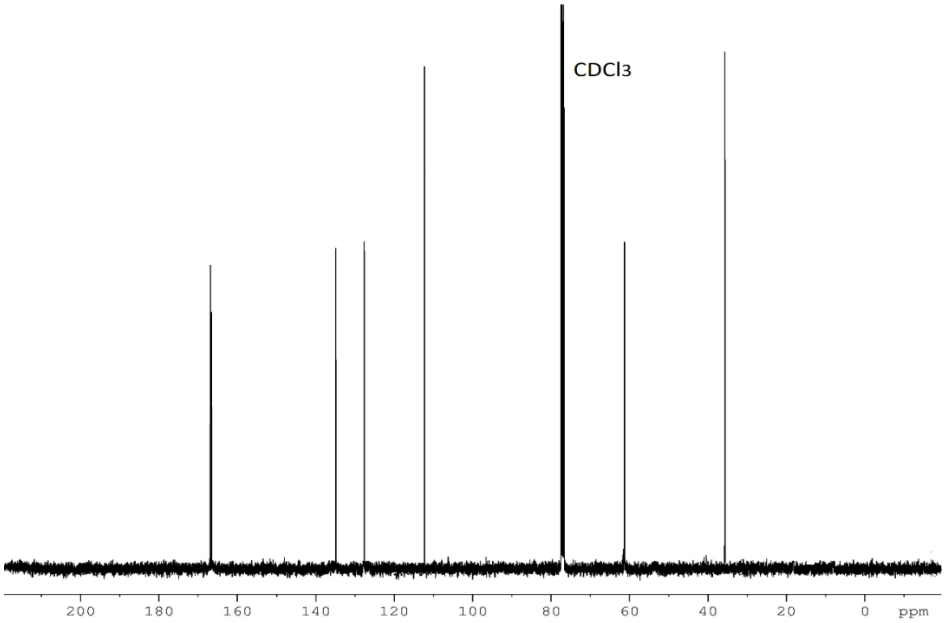

Figure 4. The ^{13}C NMR spectrum of the CMA2OEA

3.2. Spectroscopic Characterization of CMA2OEA homopolymer

The FTIR and ^{1}H NMR spectra of the synthesized CMA2OEA homopolymer are indicated in Figures 5 and 6. FTIR (cm^{-1}, the most characteristic bands): 1720 (C=O ester stretch), 1685 (C=O amide stretch), 1161 (C-N stretch). ^{1}H-NMR spectrum of homopolymer following peaks appears; at 7.3 ppm for d-chloroform (solvent) and its satellite protons, 5.1 ppm for N-$\underline{CH_2}$ protons, 4.6 ppm for O-$\underline{CH_2}$ protons, 2.0 ppm for -C-$\underline{CH}$ attached to the polymer chain, 1.6 and 1.3 ppm for polymer chain -CH_2 protons [13-16].

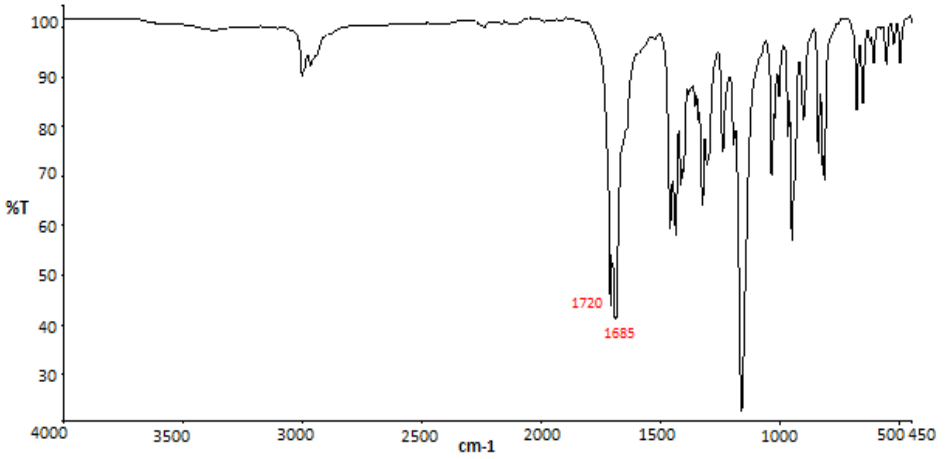

Figure 5. The FTIR spectrum of the CMA2OEA homopolymer

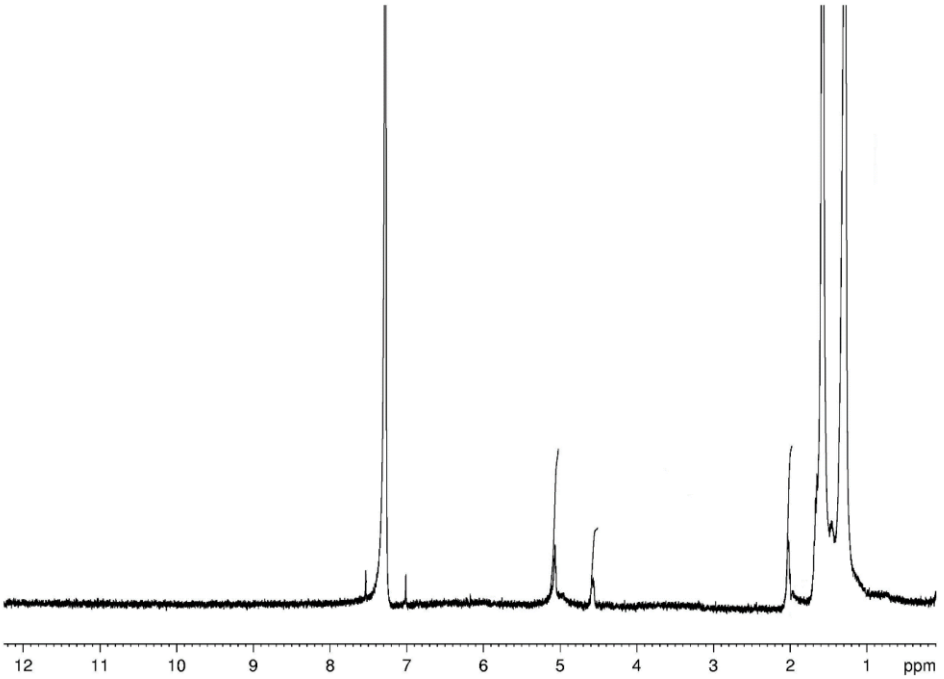

Figure 6. The ^{1}H NMR spectrum of the CMA2OEA homopolymer

3.3. Thermal Characterization of CMA2OEA homopolymer

Thermal analysis methods help determining the thermal stabilities of polymers and provide information about their thermal behavior. The decomposition temperature and the temperature at weight loss are taken as a measure of thermal stability. The thermal properties of homopolymer were determined by TGA/DTA/DTG simultaneous system. The degradation of homopolymer from thermogram was observed at two levels. Important thermal results for homopolymer; decomposition temperature at 20% is 303°C, decomposition temperature at 50% is 429°C, weight loss at 400°C, 450°C, and 500°C is 38%, 56%, and 61% respectively, residue at 550°C and 600°C is 37% and 35% respectively. Also, the first and second maximum decomposition temperature is 285°C and 418°C respectively. The thermal curves of homopolymer is given in Fig.7 [15-19].

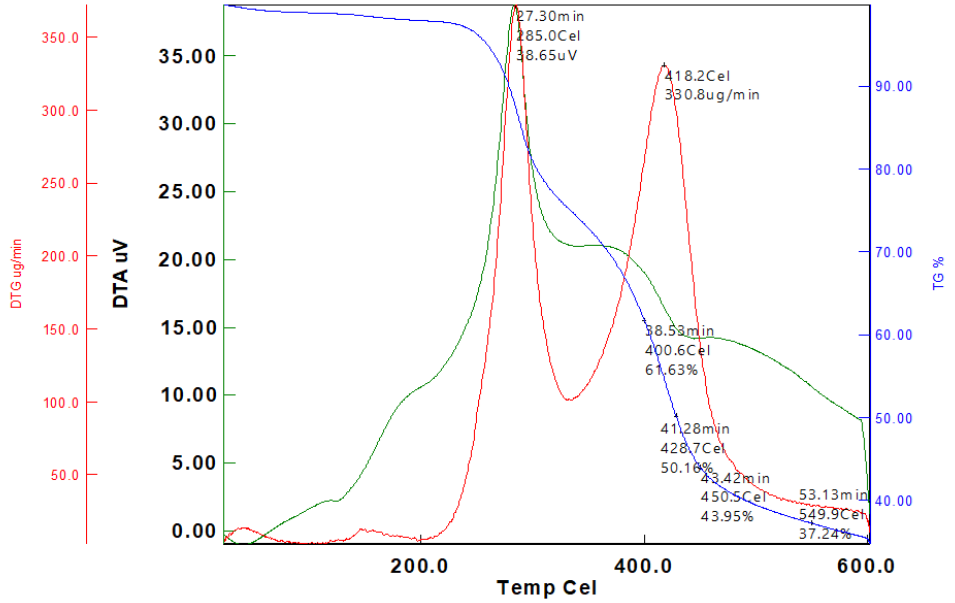

Figure 7. The TGA/DTA/DTG curves of the CMA2OEA homopolymer

4. CONCLUSION

In this study, 2-(bis(cyanomethyl)amino)-2-oxoethyl acrylate (CMA2OEA) monomer was synthesized. It has not yet been made in the literature. Characterization of the monomer was performed by FTIR, elemental analysis and ^{1}H and ^{13}C NMR spectroscopy techniques. Then, CMA2OEA homopolymer was synthesized, and its characterization was performed by the same spectroscopic techniques. Thermal behavior of homopolymer was investigated by the TGA/DTA/DTG simultaneous system. The thermal decomposition of homopolymer was found to occur at two levels, and it was also found that the first maximum decomposition temperature was 285 °C and the second maximum decomposition temperature was 418 °C. The newly synthesized monomer and homopolymer may be increasingly applied to the areas of materials and biomaterials in the future.

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