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Research Article

SYNTHESIS, SPECTROSCOPIC AND THERMAL CHARACTERIZATION OF NEW OXO METHACRYLATE-CONTAINING POLYMERS

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ABSTRACT

2-(bis(cyanomethyl)amino)-2-oxoethyl methacrylate (CMA2OEM) monomer was pre-synthesized and characterized. In this work, the homopolymer of CMA2OEM [poly(CMA2OEM)] and copolymer of CMA2OEM with methyl methacrylate [poly(CMA2OEM-co-MMA)] were synthesized by free radical chain polymerization reaction. Characterization of the synthesized poly(CMA2OEM) homopolymer and poly(CMA2OEM-co-MMA) copolymer were made by FT-IR and ^{1}H NMR spectroscopic methods. In addition, thermal stability of these new polymers was also investigated, and compared to each other. From the thermal results, it was found that the thermal stability of the homopolymer was higher than the copolymer.
Keywords: Homopolymer, copolymer, synthesis and characterization, thermal stability.

1. INTRODUCTION

With the increasing industrialization in recent years, the usage areas of polymers are increasing. 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. Polymeric materials are widely used due to their low density, poor heat and electrical conductivity, high mechanical strength and flexibility, and low costs [1-3].

Studies on functional polymers have shown that the structure of the substituent bound to the monomer and, depending on this structure, changes many properties of the monomer and its polymer. One of the most commonly used species to improve the functionality of polymers is acrylate and methacrylate derivatives. Meth/acrylate monomers have a wide range of applications due to their optical permeability, good mechanical and thermal resistance [4-7]. Due to the 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 [8, 9].

In previous studies, the 2-(bis(cyanomethyl)amino)-2-oxoethyl methacrylate (CMA2OEM) monomer was synthesized and characterized, and its experimental-theoretical results were compared [10]. In addition, the interaction of CMA2OEM with human anti-apoptotic proteins was studied and the ability of the monomer to inhibit these proteins in silico was investigated. Thus, a new molecule was synthesized to obtain the new drug active molecule [9]. In this study,

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synthesized and characterized the homopolymer of CMA2OEM, and its copolymer with methyl methacrylate. It is thought that the synthesized monomer, homopolymer, and copolymer may find application in different w orking areas. In addition, different mechanical and physical properties of these new synthesized polymers may be explored in future studies.

2. EXPERIMENTAL

2.1. Used Chemicals and Apparatus

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.

The FTIR spectrum of all samples were performed with a PerkinElmer Spectrum Two (UATR) IR spectrometer in the range of 4000-450 cm^{-1}. ^1H NMR spectrum was recorded on a Bruker 400 MHz spectrometer at room temperature in $CDCl_3$. Thermal analyze of the polymers were obtained with a Hitachi 7000 TGA/DTA/DTG (Thermal Gravimetric Analysis/Differential Thermal Analysis/Differential Thermogravimetric Analysis) simultaneous system a heating rate of 10 ^oC min^{-1} in nitrogen atmosphere, from room temperature to 600 ^oC temperatures.

2.2. Synthesis of 2-(bis(cyanomethyl)amino)-2-oxoethyl methacrylate (CMA2OEM) monomer and its homopolymer (poly(CMA2OEM))

For the synthesis of monomer firstly, 2-chloro-N,N-bis(cyanomethyl)acetamide was synthesized. 2-choloro-N,N-bis(cyanomethyl)acetamide (1 mol), sodium methacrylate (1.2 mol), and besides Tebac and NaI as catalyst were stirred in acetonitrile. Then it was removed from impurities and, thus CMA2OEM monomer is synthesized (Figure 1) [9,10].

For the synthesis of homopolymer, CMA2OEM monomer with the radical initiator-Azobisisobutyronitrile in 1,4-dioxane solution were added into polymerization flask. The system was kept under inert gas at 70 °C in 36 h. The resulting homopolymer was crystallized to remove impurities with ethyl alcohol. The chemical structure of homopolymer was characterized by spectroscopic methods by FTIR and ^1H NMR. The synthesis of the homopolymer of CMA2OEM is shown in Figure 1.

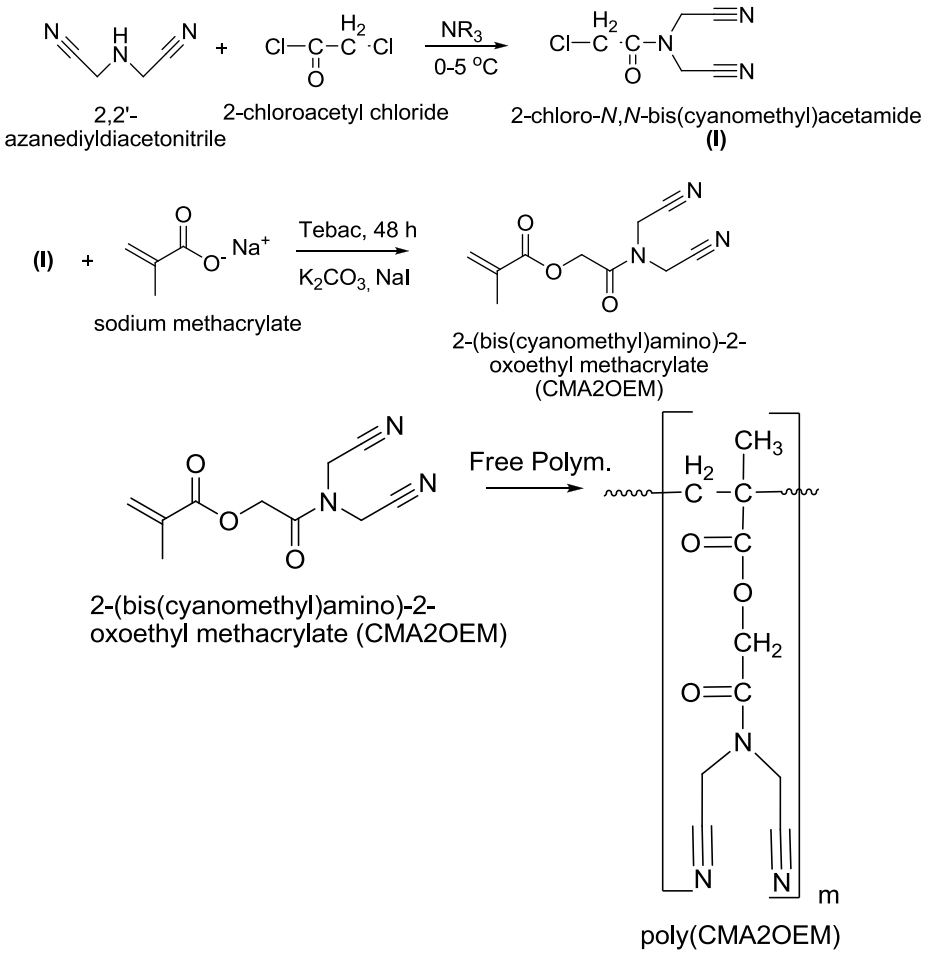

Figure 1. Synthesis of the CMA2OEM monomer [9,10] and its homopolymer

2.3. Synthesis of Copolymerization of Methyl Methacrylate with CMA2OEM (CMA2OEM-co-MMA)

The copolymerization of Methyl Methacrylate (MMA) and CMA2OEM was synthesized similar to the homopolymer synthesis. The two appropriate monomers, CMA2OEM (1 mmol) and MMA (1 mmol), with the radical initiator Azobisisobutyronitrile in 1,4-dioxane solution were added into polymerization flask. The system was kept under inert gas at 70 °C. The resulting copolymer was crystallized to remove impurities with ethyl alcohol. Synthesis of copolymer of CMA2OEM and MMA (CMA2OEM-co-MMA) is shown in Figure 2. The chemical structure of CMA2OEM-co-MMA was characterized by spectroscopic methods by FTIR, ^{1}H-NMR.

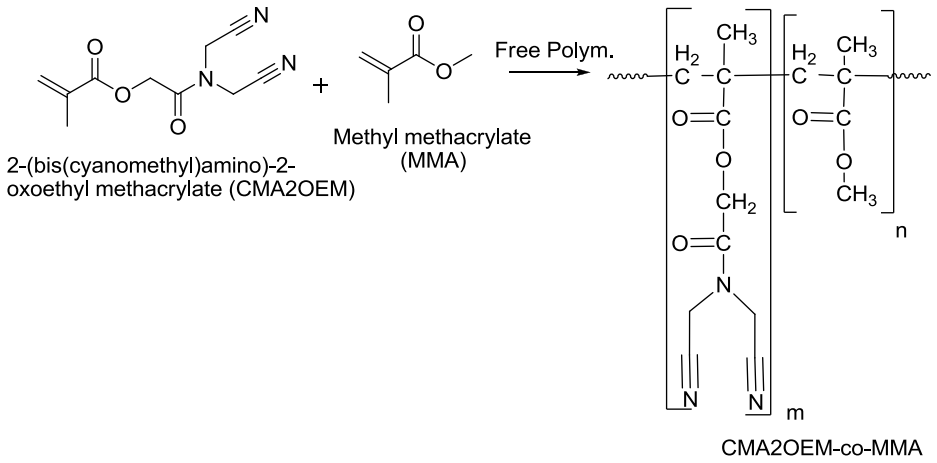

Figure 2. Synthesis of CMA2OEM-co-MMA

3. RESULTS AND DISCUSSION

3.1. Spectroscopic Characterization of CMA2OEM Homopolymer

The FTIR and ^{1}H NMR spectra of the synthesized CMA2OEM homopolymer are indicated in Figure 3 and 4. FTIR (cm^{-1}, the most characteristic bands): 2960 (C-H stretch), 2200 (C≡N stretch), 1736 (C=O ester stretch), 1689 (C=O amide stretch), 1450 (C-H bend), 1165 (C-N stretch). Figure 3 shows comparatively FTIR spectra of monomer and homopolymer. The C = C peak of 1627 cm^{-1} is not observed in the homopolymer. This is proof that the polymer is properly synthesized. ^{1}H-NMR spectrum of homopolymer following peaks appear; at 7.3 ppm for $CDCl_3$ (solvent) protons, 5.4 ppm for N-CH_2 protons, 4.1 ppm for O-CH_2 protons, 1.6 and 1.3 ppm for polymer chain -CH_2 protons, 0.9 ppm for C-CH_3 protons [10, 11].

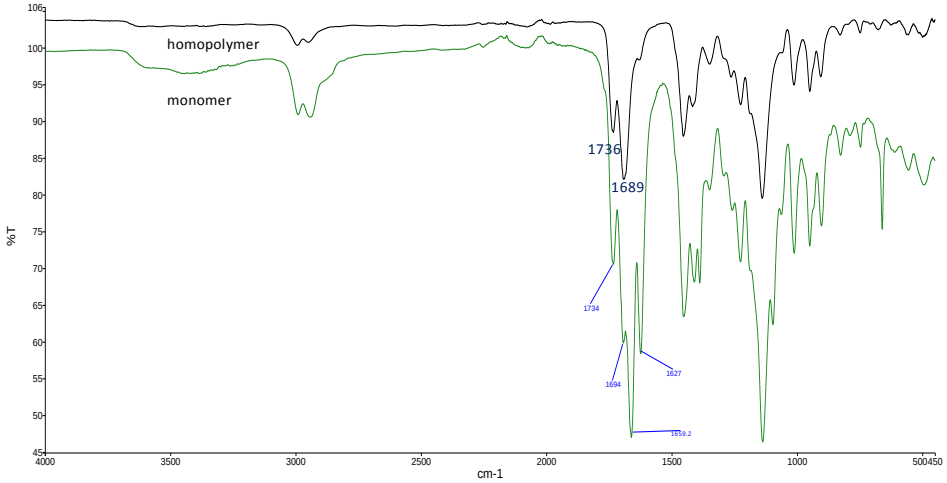

Figure 3. The FTIR spectrum of the CMA2OEM monomer and its homopolymer, comparatively

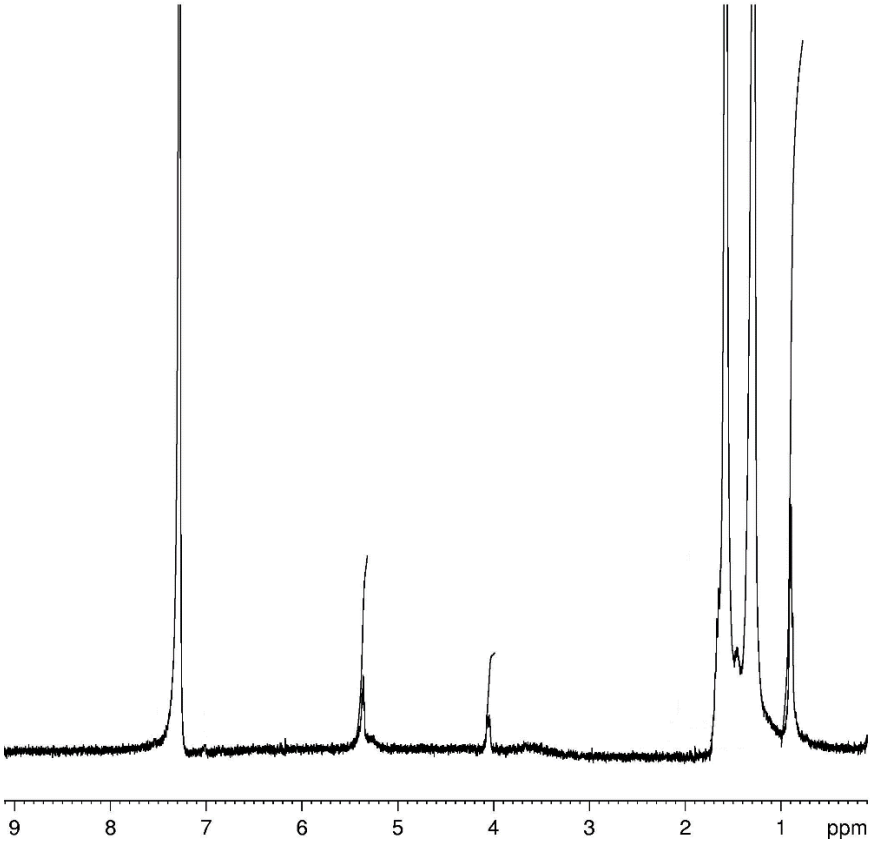

Figure 4. The ^{1}H NMR spectrum of the CMA2OEM homopolymer

3.2. Spectroscopic Characterization of CMA2OEM-co-MMA Copolymer

The FTIR and ^{1}H NMR spectra of the synthesized CMA2OEM-co-MMA copolymer are indicated in Figure 5 and 6. FTIR (cm^{-1}, the most characteristic bands): 2951 (C-H stretch), 2170 (C≡N stretch), 1723 (C=O ester stretch), 1662 (C=O amide stretch), 1390 (C-H bend), 1151 (C-N stretch). ^{1}H-NMR spectrum of copolymer following peaks appear; at 7.3 ppm for $CDCl_3$-solvent protons, 5.4 ppm for N-CH_2 protons, 4.4 ppm for O=C-O-CH_2 protons, 3.5 ppm for O-CH_3 protons, 1.9 ppm for C-CH_2-C protons, 1.6-1.3 ppm for polymer chain protons, 1.1 ppm for C-CH_3 protons.

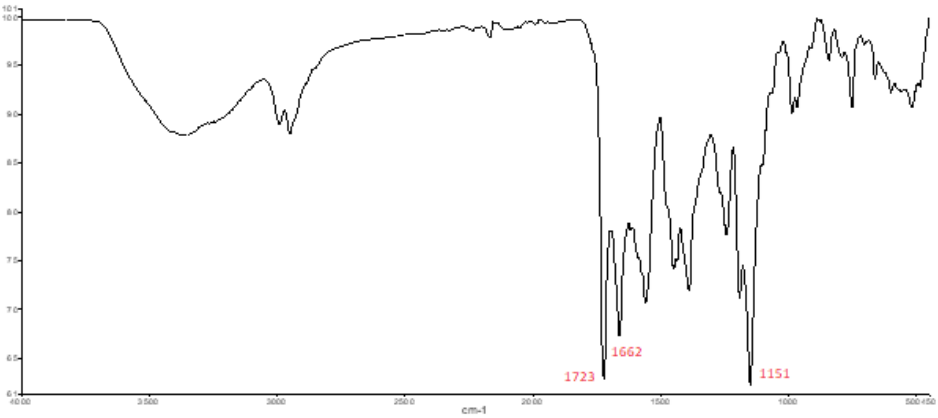

Figure 5. The FTIR spectrum of the CMA2OEM-co-MMA

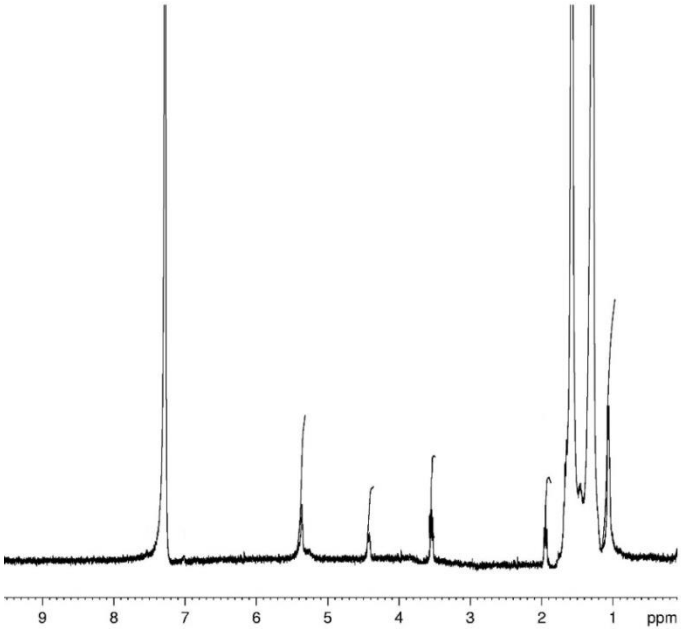

Figure 6. The ^{1}H NMR spectrum of the CMA2OEM-co-MMA

3.3. Thermal Characterization of CMA2OEM 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 was determined by TGA/DTA/DTG simultaneous system. The degradation of the homopolymer from the thermogram was observed at two levels. Important thermal results for the homopolymer are given in Table 1, and the thermal curves of the homopolymer are given in Figure 7 [11-14].

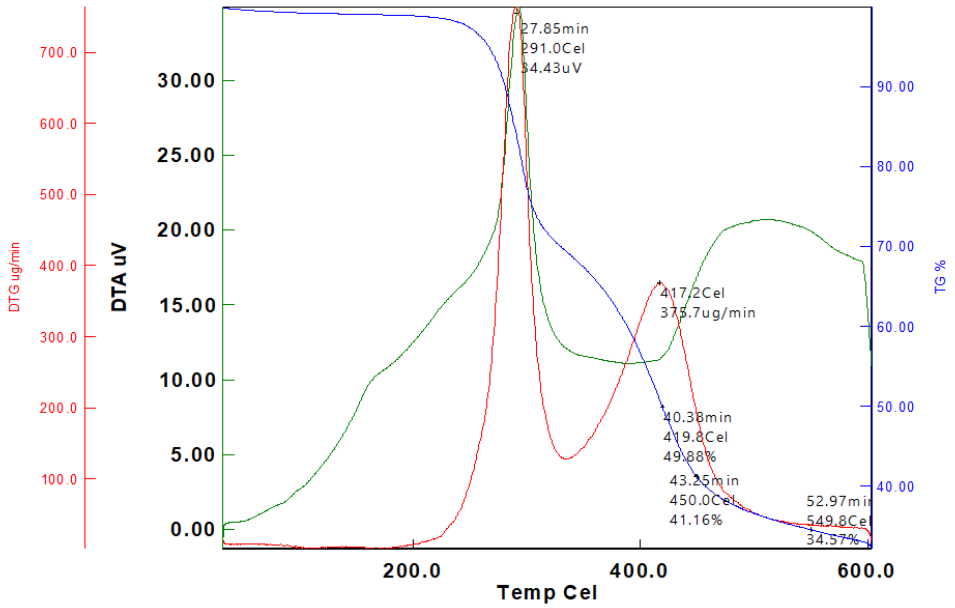

Figure 7. TGA/DTA/DTG curves of the CMA2OEM homopolymer

3.4. Thermal Characterization of CMA2OEM-co-MMA Copolymer

The thermal properties of copolymer were determined by TGA/DTA/DTG simultaneous system. The degradation of the copolymer from the thermogram was observed at two levels. From the results such as maximum decomposition temperatures, % weight loss, and% residue, it was seen that the thermal stability of the homopolymer was higher than the copolymer. The thermal curves of the homopolymer and copolymer are given in Figure 8, comparatively. Important thermal results for homo and copolymer are given in Table 1 [11-14].

Table 1. TGA data of the homopolymer and copolymer

Sample	Max. Dec.Temp. (ºC)	Temp. of 20% weight loss (°C)	Temp. of 50% weight loss (°C)	%Weight loss (400 ºC)	%Weight loss (450 ºC)	%Weight loss (500 ºC)	%Residue (550 ºC)	%Residue (600 ºC)
poly(CMA2OEM)	291 and 417	296	420	43	59	63	35	33
CMA2OEM - co-MMA	238 and 397	238	370	65	81	83	16	15

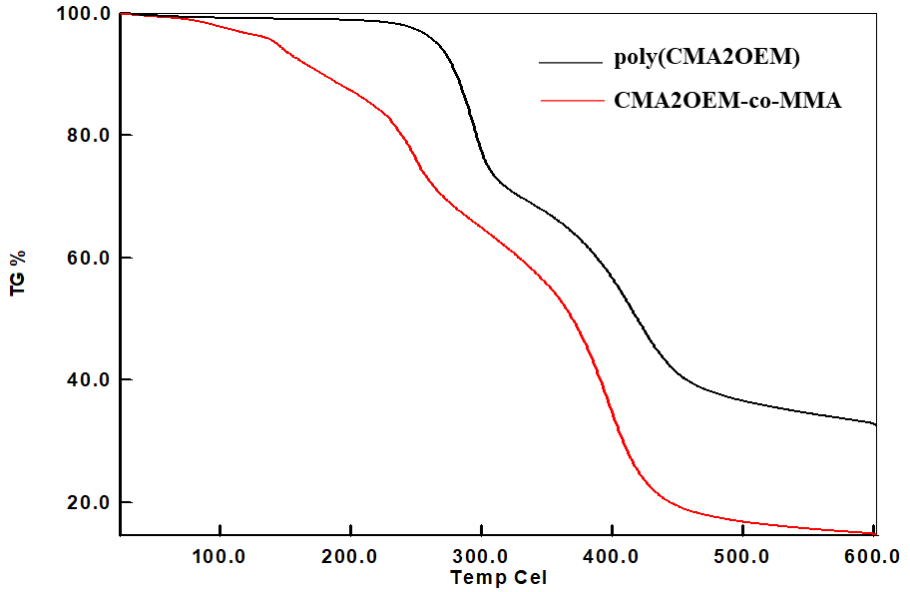

Figure 8. TGA curves of the homopolymer and copolymer, comparatively.

4. CONCLUSION

In this study, the new copolymer [CMA2OEM-co-MMA], and homopolymer of 2-(bis(cyanomethyl)amino)-2-oxoethyl methacrylate (CMA2OEM) monomer, which has not yet been made in the literature, were synthesized by the free radical chain polymerization reaction and, then characterized. Characterization of the homopolymer and copolymer were performed by FTIR, and ^{1}H NMR spectroscopy techniques. The results obtained from spectroscopic techniques were in agreement with the literature. Thermal behavior of homo and copolymer were investigated by the TGA/DTA/DTG simultaneous system. The thermal decomposition of homo and copolymer were found to occur at two levels, and it was also found that the maximum decomposition temperatures were 291°C-417°C, and 238°C-397°C, respectively. From the thermal results, it was found that the thermal stability of the copolymer was lower than the homopolymer. This result may vary depending on the chemical structure of the polymer and different functional groups in the polymer. These new polymers which were first synthesized in the literature are considered to attract attention in the material sector.

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