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Synthesis and Thermal Characterization of Copolymers Containing Amino Acids

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Abstract

Thee copolymers of amino acid were synthesized in two steps. First, the amino acids react with resorcinol to formation of azo monomers step. They led in a second condensation polymerization step to copolymeric materials. The structures of the copolymers were characterized by means of FT-IR and ^{1}H-NMR spectroscopy. The thermal properties were investigated by TGA and DTG.

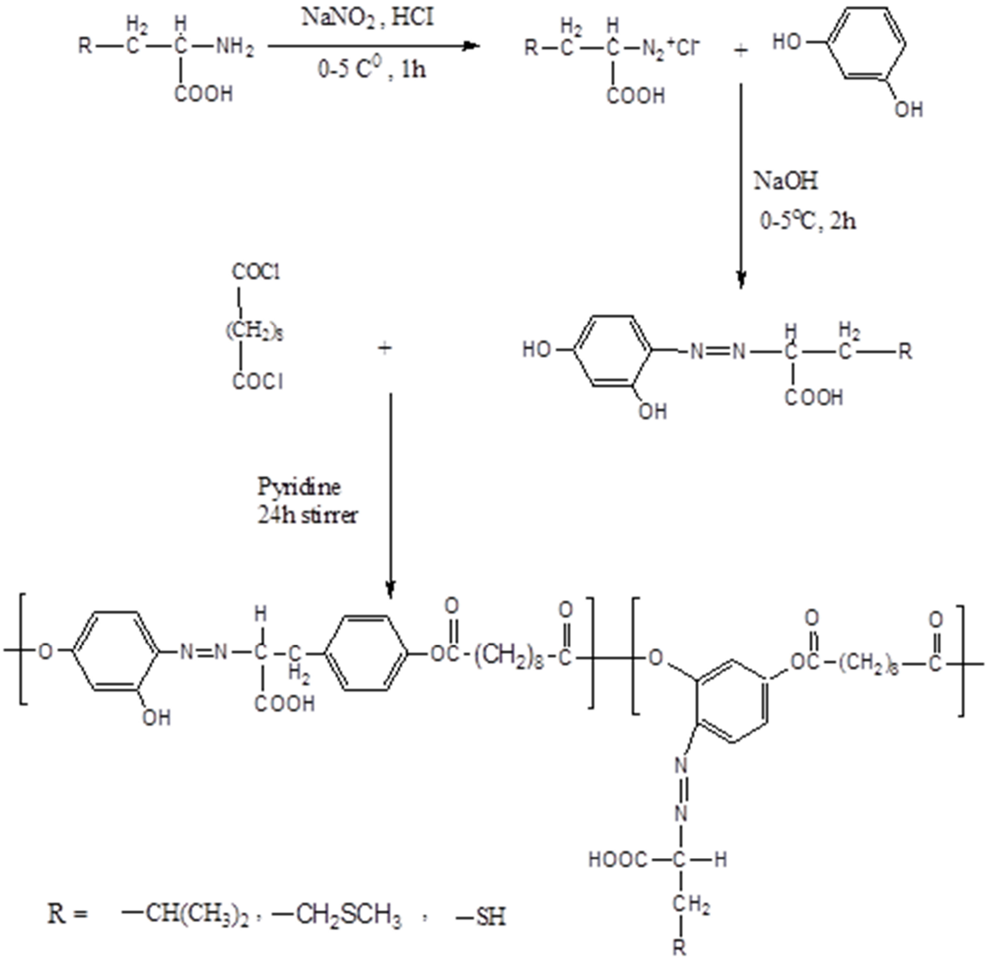
Keywords: copolymers, amino acid, thermal properties, azo compound

1. Introduction

For synthetic chemists, proteins can be regarded as the most superior polymers, as they have high molecular weights with uniform chain lengths and precisely controlled monomer sequences which lead to hierarchical folding and organization(Yuan et al. 2001 and Ladmiral et al. 2015). The primary structures of these biomacromolecules are constructed via the covalent linkage of the building blocks, and the molecular information, such as amino acid sequence, chain chirality, and amphiphilicity, encoded in the primary structures determines their highly ordered structures (Chen et al.2013). Recently, there has been a growing interest in preparing biodegradable, drug delivery system and biocompatible polymers, many studies have focused on the synthesis of polymers that will mimic the structure of naturally occurring polymers of amino acid and thus, the chemistry of amino acid(El-Newehy et al. 2013, Paik et al. 2012 and Ladmiral et al 2015). With the development of new approaches towards synthesis and study of polymerization, it has become possible to synthesize high molecular weight polypeptides derivative, due to the unique physical and structural properties of proteins**.** In literature different kinds of amino acid based on polymer were synthesized (Kudo et al. 2012 and Imanishi et al. 1989). On the other hand, although the amino acid unit has been used in polymers for many years, most reports concerned polymers with main chain units which have rigid-rods feature leads to the difficulties in solubility. The present work, we highlight on the design and synthesis of several side chains copolymers containing amino acid as a pendant groups.

2. Experimental:

Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets on a Shimadzu 8400_S spectrometer (Japan). 1H-NMR spectra were recorded on a Bruker AMX-300 spectrometer at 300 MHz using deuterated DMSO as the solvent with TMS as an internal standard (Germany). The degradation characteristics of the prepared copolymers were determined by thermogravimetric analysis (TGA) using a TA-50Q. Measurements were carried out under a nitrogen atmosphere, from 25 to 700°C, at 20°C/min**.** The copolymers were prepared according to the reaction scheme 1.



Scheme1: The synthesis of copolymers

2.1. Preparation of azo compounds

Diazotization of amino acids

A solution of amino acids (10 mmol) and 3M HCl (8 mL) was heated gently, and then water (10 mL) was added in order to dissolve the solid. The mixture was cooled to 0 °C in an ice bath with stirring. Freshly prepared 1M sodium nitrite solution (10 mL) was then added slowly with stirring and the temperature of the solutions remains below 10 °C. The solution was kept in an ice bath and used immediately. (Al-Hamdani et al. 2010 and Furniss et al. 1989).

Coupling with resorcinol

A solution of resorcinol (10 mmol) in 1M NaOH (20 mL) was added and cooled in an ice bath. The suspension of diazonium salt from step 1 was then added slowly with stirring to the resorcinol solution. The reaction mixture was then kept in the ice bath for at least 20 minutes until the crystallization is complete (giving a colored solid). The pH of the solution was adjusted with dilute HCl or NaOH solutions (0.1M) in order to induce precipitation. The orange azo dye was collected and washed with cold water (Al-Hamdani et al. 2010 and Furniss et al. 1989).

2.2. Synthesis of copolymers

A suitable azo amino acid (6mmol) was dissolved in 10 ml of pyridine. To this solution was added sebacoyl chloride (4mmol).The reaction was carried out under an nitrogen atmosphere with vigorously stirred for 6h. Then 2-((2,4-dihydroxy phenyl)diazenyl)-3-(4-hydroxyl) propanoic acid (2mmol) were added to the same reaction vessel with vigorously stirred for 24h , the mixture was neutralized with 10% hydrochloric acid .The precipitate was filtered and washed several times with distilled water and dried at 60 ^{0}C under vacuum to yield 70-85% of copolymer (Furniss et al. 1989).

3. Results and discussion

3.1 FT-IR and ^{1}H-NMR Spectroscopy

The FT-IR spectra of azo compounds show a broad two bands around 3218 - 2550 cm^{-1} stretching vibrations of intramolecular hydrogen bonding for O-H groups and carboxylic acid, a two absorption bands appearing at1695 and 1658 cm^{-1} are attributed to carbonyl group and aromatic C=C observed at 1583cm^{-1} and the band at 1539 cm^{-1} due to -N=N- group(Stuart et al. 2004 and Akins et al. 2010). Figure1 shows FTIR spectra of azo compound (RC).

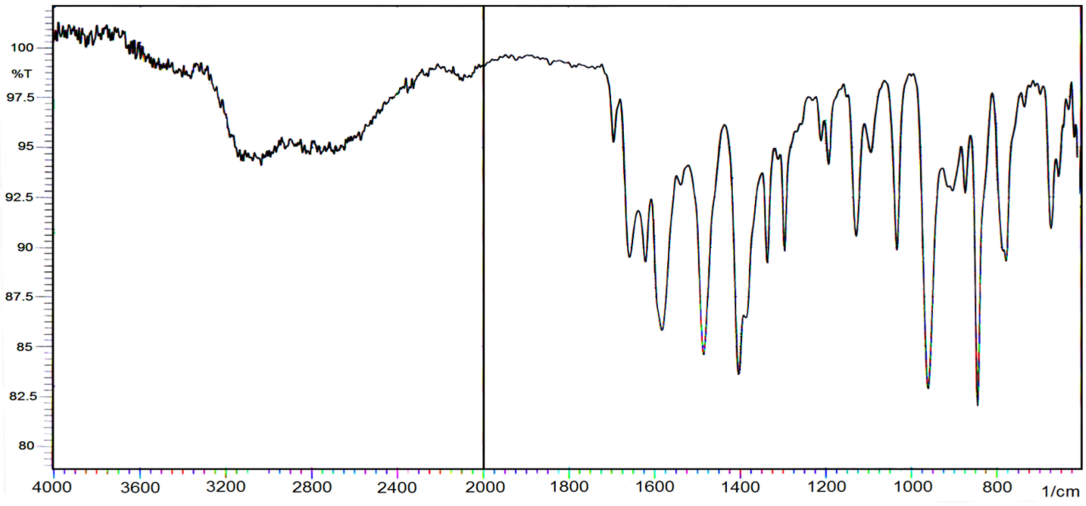


Figure1. FTIR spectra of azo compound (RC)

The ^{1}H-NMR spectra of azo compounds shows clear characteristic spectral. The main feature of these spectra is the appearance of low field resonance for the proton of hydroxyl groups which gives signal at 9.65 - 9.90 ppm, the protons of the phenyl rings give a complex absorption in the range 6.0-8.13ppm and the protons of CH gives signals at 2.53- 2.74ppm. The azo compound (RT) shows protons of CH_2 and CH gives signals at 3.02 and 2.74 ppm respectively. RM shows proton of CH_2, CH_2S and CH_3 at 1.89, 1.69 and 1.24 ppm respectively. RL shows protons of CH_2, CH and CH_3 gives signals at 2.93, 1.76 and1.24 ppm respectively (Stuart et al. 2004 and Akins et al. 2010). Typical ^{1}H-NMR spectrum for RT and RM are shown in Figures.2 and 3.

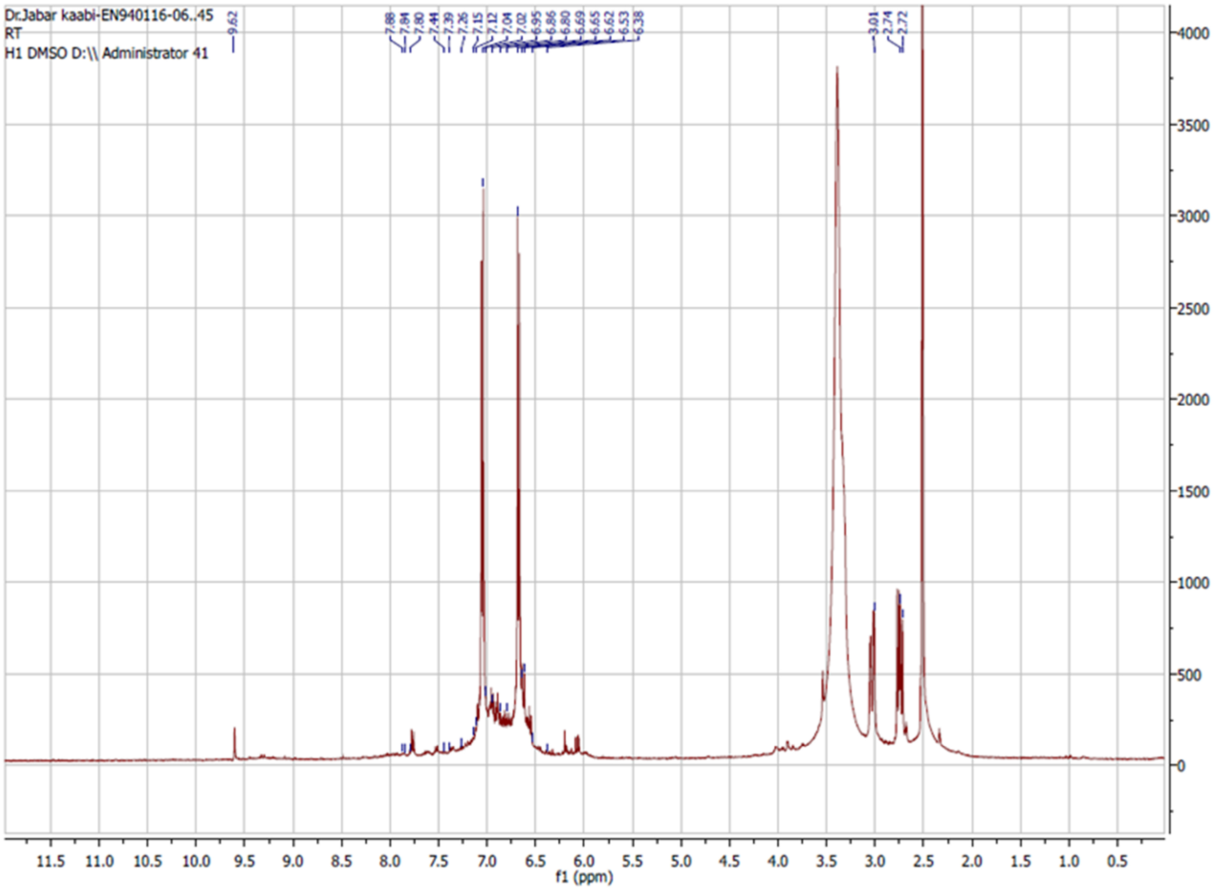


Figure 2. ^{1}H-NMR spectrum for azo compound RT

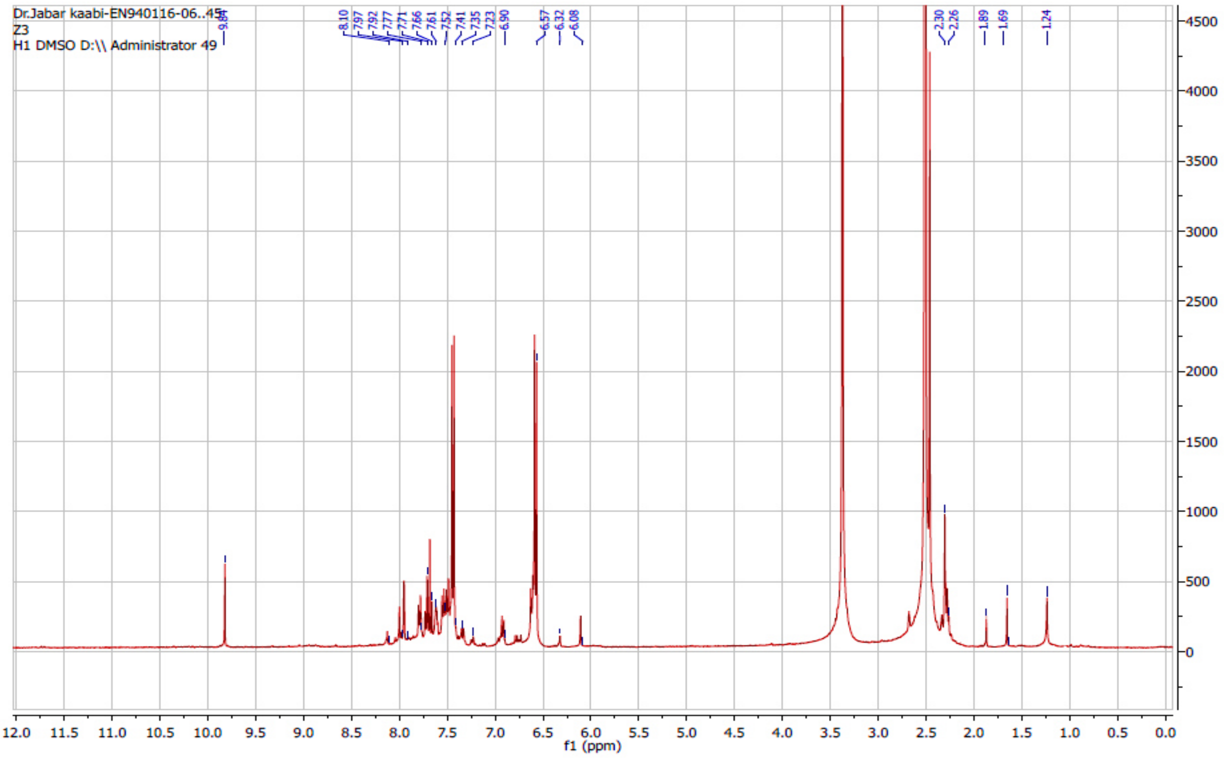


Figure 3. ^{1}H-NMR spectrum for azo compound RM

The FT-IR spectra of copolymers show two bands at 2929 and 2854 cm^{-1} attributed to C-H stretching vibrations of aliphatic group asymmetry and symmetry respectively, a strong band at 1705 cm^{-1} characteristic of carbonyl group of ester group, a two absorption bands appearing at1691and 1610 cm^{-1} are attributed to carbonyl group and aromatic C=C observed at 1591 cm^{-1} and the band at 1514 cm^{-1} due to -N=N- group (Stuart et al. 2004 and Akins et al. 2010). Figure 4 shows FTIR spectra of copolymer P-MC.

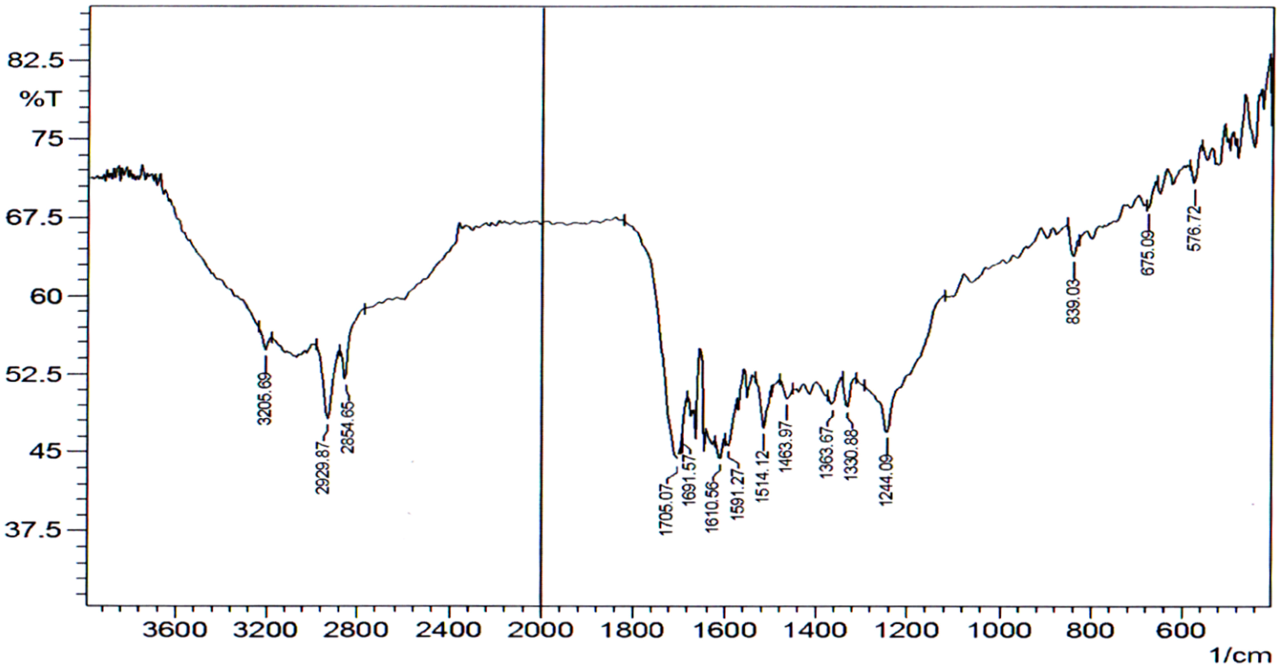


Figure1. FTIR spectra of copolymer P-MC

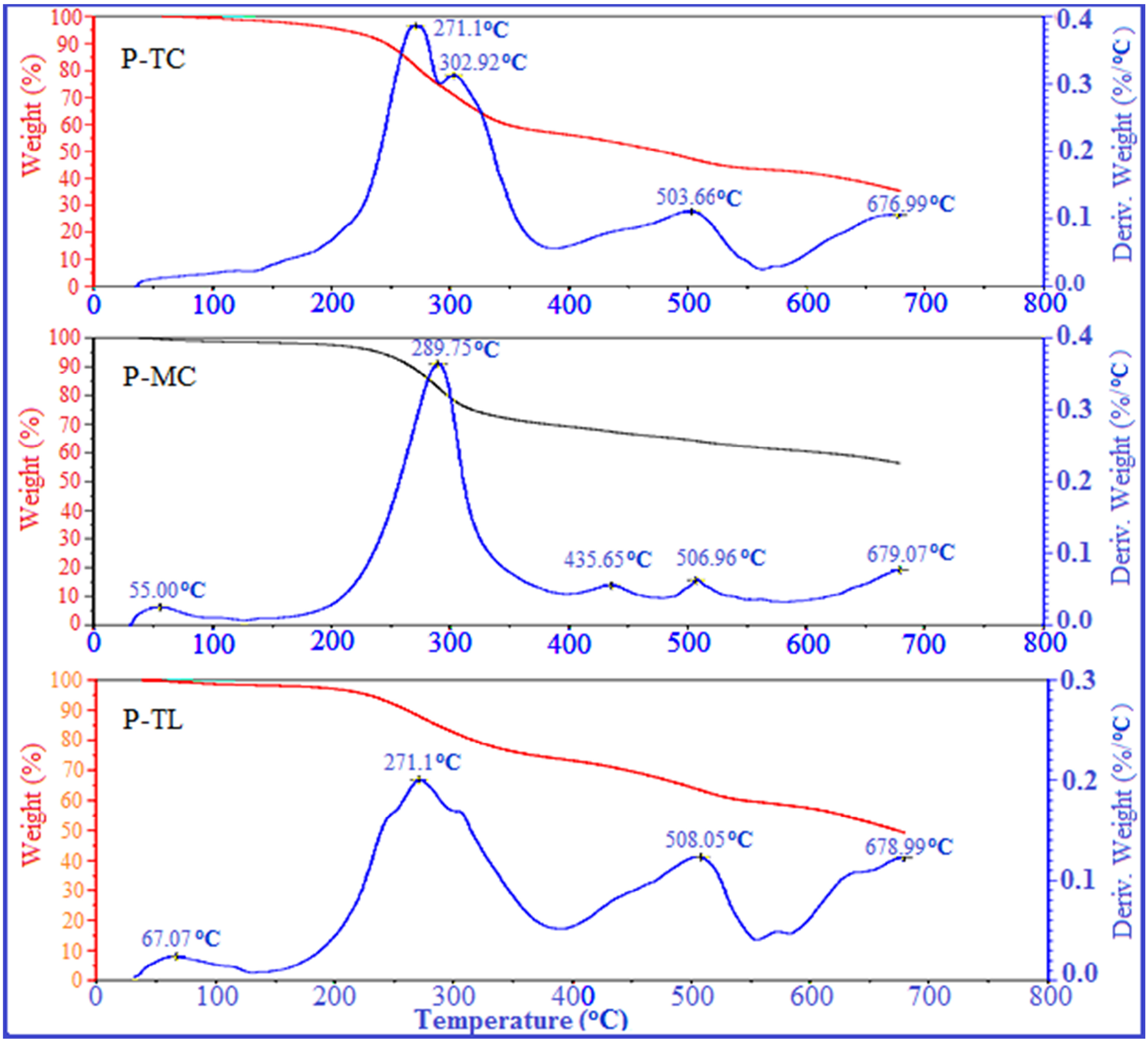
3.2 Thermal analysis

Table 3 shows the data on thermal analysis for some of prepared copolymers. TGA and DTG curves of the prepared P-TC, P-MC and P-TL copolymers showed that repeated units begin to decompose at 271.1, 289.75, and 271.1 °C respectively, on the DTG curves. The copolymers exhibited weak peaks below T=70 °C due to the loss of moisture (Bednarek et al. 2013). P-TC showed a broad peak between 150 and 376 °C. There are two stages of decomposition with maxima at 271.1, and 302.92 °C on the DTG curve, and a corresponding mass loss of 43 % on the TGA curve, are due to the decomposition of repeated units, and a second mass loss of 18 % , was seen with a peak at around T=508.05 °C. P-TL showed a first mass loss of 27 % on the TG curve, was seen with a broad peak at around T=271.1 °C on the DTG curve, and a second mass loss of 18 %, was seen with a peak at around T=508.05 °C. The TGA and DTG curves of P-MC showed three stages of decomposition with maxima at 289.75, 435.65, and 506.96 °C on the DTG curve, and a corresponding mass loss of 47 % on the TGA curve (Al-Lami 2015). Figure 4 shows TGA and DTG curves of some prepared copolymers.

Table 5. Data for thermal analysis

copolymer	Char content % at 700 °C	Temp. of 50% weight loss(°C)	Rate of decomposition %/min
P-TC	*41*	*469*	*7*
P-MC	*59*	*>700*	*10.5*
P-TL	*57.2*	*665*	*7.5*

Figure 4. shows TGA and DTG curves of some prepared copolymers



4. Conclusions

New copolymers containing amino acid as a side chain were synthesized via two stages, first the azo compound as monomer was prepared and the second stage, copolymers were prepared by condensation polymerization. The copolymer structures obtained were identified with common spectroscopic measurements. Then, the thermal stability was studied via TGA and DTG measurements**.**

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