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POLIMERY

Synthesis and photochemical stability of acrylamide and succinic anhydride copolymer with dyes

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Abstract: A copolymer of acrylamide (PAM) and succinic anhydride (SA) was obtained. The effect of dye (anthocyanin, bromophenol blue, thymol blue) on the photochemical stability of the copolymer (PAM-*g*-SA) was studied. X-ray diffraction, FT-IR, UV-Vis, NMR, DSC and TGA were used to evaluate PAM-*g*-SA. FT-IR analysis showed the disappearance of two bands at wavenumbers 3450 and 3380 cm^{-1} characteristic of the stretching vibrations of the primary amine, which indicates the formation of amides. UV photolysis of aqueous solutions with different concentrations of the copolymer was studied. PAM-*g*-SA showed an increase in the degree of polymerization under the influence of light (ca. 50%) for a solution of 200 mg/L after 10 h of irradiation. PAM-*g*-SA-anthocyanin also showed an increase in the degree of polymerization (26%) for the 1000 mg/L solution after 10 h of irradiation. Similar behavior was observed for anthocyanin (23%) at the dye concentration of 15000 mg/L. On the other hand, PAM-g-SA-bromophenol and PAM-*g*-SA-thymol were photodegraded after UV irradiation. It was shown that the photodegradation of PAM-*g*-SA can be prevented by the addition of appropriate dye.

Keywords: polyacrylamide, photodegradation, anthocyanin, bromophenol blue, thymol blue.

Synteza i stabilność fotochemiczna kopolimeru akrylamidu i bezwodnika bursztynowego z barwnikami

Streszczenie: Otrzymano kopolimer akrylamidu (PAM) i bezwodnika bursztynowego (SA). Zbadano wpływ dodatku barwnika (antocyjan, bromofenol, tymol) na stabilność fotochemiczną kopolimeru (PAM-*g*-SA). Do oceny PAM-*g*-SA stosowano dyfrakcję rentgenowską, FT-IR, UV-Vis, NMR, DSC i TGA. Analiza FT-IR wykazała zanik dwóch pasm przy liczbie falowej 3450 i 3380 cm^{-1} charakterystycznych dla drgań rozciągających aminy pierwszorzędowej, co wskazuje na tworzenie się amidów. Zbadano fotolizę UV roztworów wodnych o różnych stężeniach kopolimeru. PAM-*g*-SA wykazał wzrost stopnia polimeryzacji pod wpływem światła (ok. 50%) dla roztworu 200 mg/L po 10 h naświetlania. PAM-*g*-SA-antocyjan również wykazał wzrost stopnia polimeryzacji (26%) dla roztworu 1000 mg/L po 10 h naświetlania. Podobne zachowanie zaobserwowano w przypadku antocyjanu (23%) przy stężeniu barwnika 15 000 mg/L. Natomiast PAM-*g*-SA-bromofenol i PAM-*g*-SA- tymol uległy fotodegradacji po

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naświetlaniu UV. Wykazano, że fotodegradacji PAM-*g*-SA można zapobiec poprzez dodatek odpowiedniego barwnika.

Słowa kluczowe: poliakrylamid, fotodegradacja, antocyjany, błękit bromofenolowy, błękit tymolowy.

Acrylamide is a white, odorless crystalline solid that is highly soluble in water and other polar solvents, such as acetone and acetonitrile. The limited conjugation involving π electrons means that acrylamide lacks a strong chromophore for UV detection and does not fluoresce. Acrylamide exhibits both weakly acidic and basic properties. It is a bifunctional monomer, containing a reactive electrophilic double bond and an amid group [1, 2]. Because of the electron deficient double bond, acrylamide is susceptible to a wide range of reactions, such as nucleophilic additions, Diels-Alder, and radical reactions. Many of these reactions are reversible, and the rate of reaction depends on the strength of the nucleophile. Examples include the addition of ammonia, amines, phosphines, and bisulphites [3–5].

Acrylamide is the precursor to polyacrylamides, which are valuable polymers for water purification, mineral extraction, corrosion inhibition, food processing, agriculture, and paper making. Polyacrylamides (PAMs) are prepared through free radical polymerization of acrylamide through a variety of initiation systems (i.e., peroxides, persulfates, redox couples, and pho-

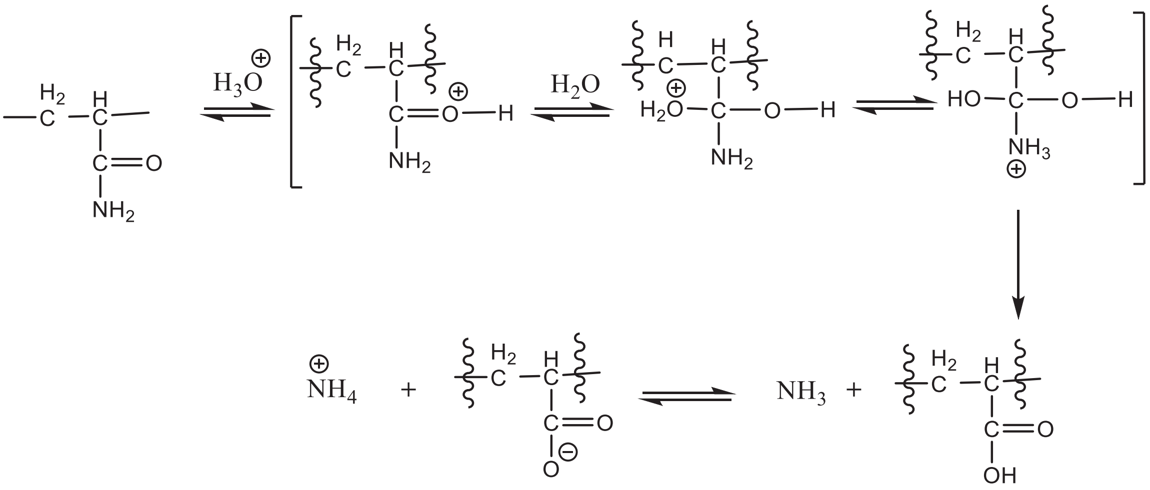

Fig. 1. Acidic hydrolysis of polyacrylamide

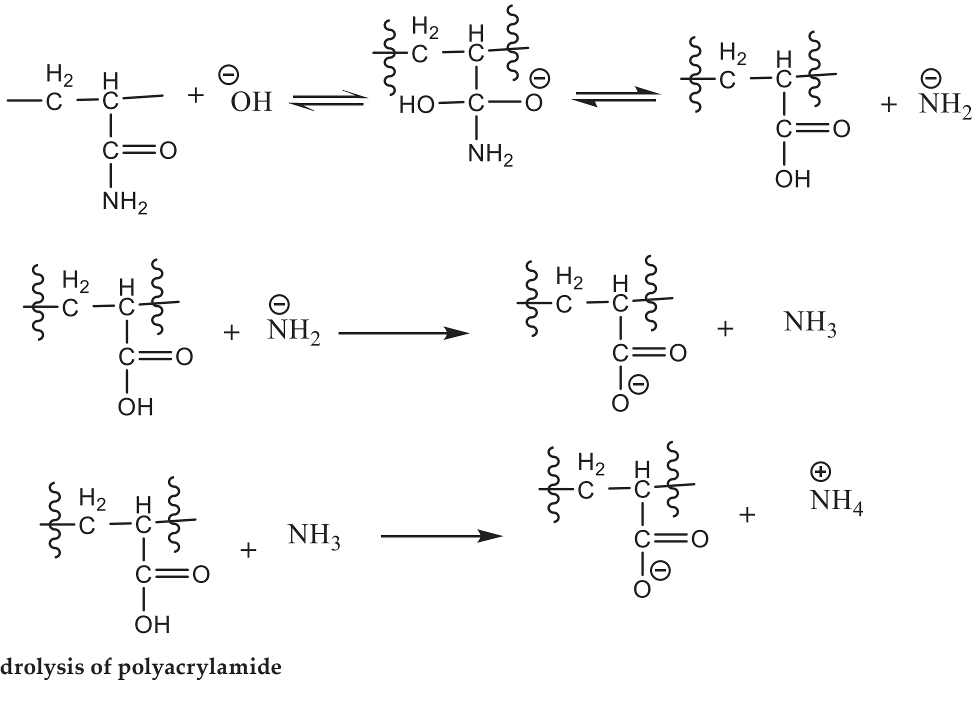

Fig. 2. Alkaline hydrolysis of polyacrylamide

tochemically) in aqueous solution or dispersions [6, 7]. The physical properties of each PAM product are usually different. For example, PAMs can be solid, emulsions, or solutions, with molecular weight ranges from thousands to over a million Daltons. PAMs are non-toxic to humans, animals, fish, or plants [4, 8]. In drinking water treatment, PAMs are usually added during coagulation or flocculation to destabilize particles and natural organic matter (NOM), and facilitate removal by sedimentation or filtration [9, 10]. Cationic PAMs are frequently used as primary coagulants to enhance the coagulation and deposition (or filtration) of negatively charged particles in natural water via adsorption and surface charge neutralization [11]. Non-ionic and anionic PAMs usually have a higher molecular weight (or longer chains) than cationic PAMs.

There are five major degradation pathways for PAMs. These include thermal, photolytic, biological, chemical, and mechanical degradation [12]. Chemical degradation of PAMs can occur in water treatment. During water purification a variety of chemicals may be used in parallel with polyelectrolytes, including oxidants (i.e. chlorine, chloramines, ozone, permanganate, peroxide), coagulants (i.e. alum, ferric sulphate), chemicals to adjust pH (e.g. lime, caustic soda, soda ash, sulfuric acid), fluoride, and corrosion inhibitors. These chemicals, especially oxidants, may react with polyelectrolyte residuals in water and result in their degradation. The pH also influences the rate and extent of polymer degradation (13, 14). Under acidic or basic conditions, PAMs are susceptible to hydrolysis. The acidic hydrolysis reaction involves the nucleophilic addition of water to the protonated amid, followed by the elimination of NH_3 (Fig. 1). The basic hydrolysis (Fig. 2) involves the nucleophilic addition of hydroxide to the amide carbonyl, followed by loss of NH_2^- to form an acrylic acid residue. Then, a proton is removed by NH_2^- from the acrylic acid residue to form a more stable carboxylate anion and ammonium cation [15,16]. It is believed that only the amide group of PAMs is changed during acid or basic hydrolysis, while no reduction of the molecular weight has been observed.

Photodegradation of PAMs is believed to be a free radical process which may lead to cleavage of the polymer backbone (chain scission), cross-linking, introduction of new functional groups, and formation of lower molecular weight products [17, 18]. Caulfield *et al*. studied the stability of linear PAMs under thermal and irradiation conditions [17]. It was found that PAMs are stable under fluorescent lights and did not release detectable levels of acrylamide at 95°C, although hydrolysis of side-chain amide groups to acid groups was observed during the thermal aqueous degradation. Under UV irradiation at 254 nm, little amounts of acrylamide were released (below 50 ppm repeat monomer units in the polymer), and a drop in viscosity was observed. It was concluded that the acrylamide released was due to chain scission, and not unzipping of the polymer chain.

Dyes are widely used in several industries to color a wide range of products such as textiles and food, among others, while polymers were used as adsorbents to reduce the contamination of dyes in wastewater [19–21]. They also find use in technical applications such as fluorescent labelling, as laser dyes, for optical data storage, and as dyes for light-emitting diodes, among others. However, there is a need to improve their photochemical and photophysical properties [22]. One approach is to combine dyes with a polymer.

Polymer/dye blends have been of great interest since the 1980s. The process involves inserting dye molecules within polymer matrices, to produce new materials that differ depending on the preparation methods. The photochemical and photophysical properties of these materials have been studied [23]. Of importance to the optical performance and photostability of the resulting blend are: (1) the preparation method for the blend, (2) the selection of the polymer matrix, (3) the selection of an appropriate dye, and (4) the concentration of the dye.

In this study, PAM reacted with succinic anhydride to function as a spacer, and the reaction product was subsequently copolymerized with anthocyanin, thymol blue or bromophenol blue. The aim of the work was to prepare polyacrylamide derivatives resistant to photodegradation.

EXPERIMENTAL PART

Materials

Acrylamide was supplied by BDH (VWR Chemicals, Sanborn, USA), succinic anhydride was provided from Fluka (Honeywell, Charlotte, NC, USA), thymol blue dye (466.60 g/mol) was supplied by Thomas Baker (Maharashtra, India), bromophenol blue dye (669.96 g/mol) was supplied by HiMedia (Maharashtra, India), extracted anthocyanin dye, ethanol was supplied by BDH (VWR Chemicals, Sanborn, USA), dimethylformamide (DMF) was supplied by CDH (New Delhi, India), and diethyl ether was provided from Fluka (Honeywell, Charlotte, NC, USA).

Methods

Polymerization of acrylamide

3 g (0.041 mol) of acrylamide was dissolved in 10 mL of DMF in a screw-capped polymerization bottle, and 0.05% of the monomer mass of ammonium persulfate was added as initiator. The bottle was flushed with nitrogen gas for few minutes inside a glove box and firmly stopped. The solution was maintained at 70°C in a temperature-regulated water bath. After 1 h, the solvent was evaporated under vacuum, and the product was washed three times with diethyl ether and dried in a vacuum oven at 50°C (yield 90%, μ_{in} = 0.46 dLg) [24].

Preparation of PAM grafted-succinic anhydride-dye (PAM-*g*-SA-dye)

A round-bottom flask fitted with a condenser was charged with 2 g (0.027 mol) of polyacrylamide that was dissolved in 10 mL of DMF and mixed with 1.69 g (0.027 mol) of succinic anhydride dissolved in DMF. The mixture was refluxed about 6 hours at temperature in the range (75–80°C) and the product was purified by ethyl ether to remove purities then the product dried at room temperature.

2 g of co-polymer PAM-*g*-SA dissolved in 10 mL of ethanol: distilled water mixture (1:1 by volume) mix with 1 mg of anthocyanin, the mixture was added in a round flask equipped with reflux condenser and a magnetic stirrer, and refluxed for 5 hours at 78°, the violet viscous polymer washed with diethyl ether several times to remove the purities and then the product dried and collected at room temperature. The same procedure was used to prepare red crystals polymer with bromophenol (PAM-*g*-SA-bromophenol) and greenish crystals with thymol blue (PMA-*g*-SA-thymol).

Methods

The prepared polymers were characterized through various techniques. Fourier transform infrared (FT-IR) spectra were acquired with a Shimadzu FTIR-8400 (Kyoto, Japan) spectrometer in the form of KBr discs. Powder X-ray diffractograms were obtained with a Panalytical X'Pert Pro diffractometer (Amsterdam, Netherlands).

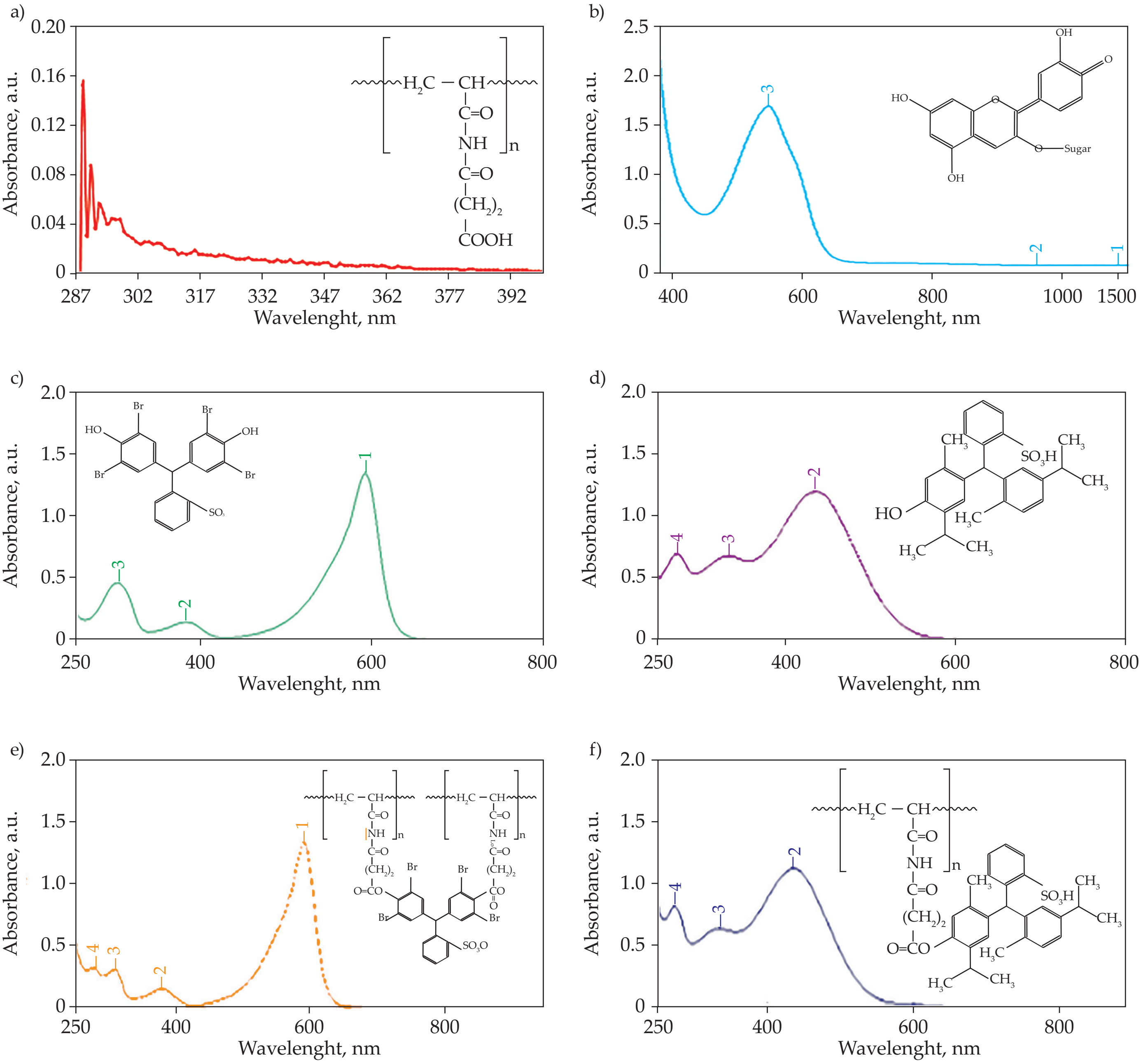

Fig. 3. UV/VIS spectra and structures: a) polyacrylamide, b) anthocyanin dye, c) bromophenol blue dye, d) thymol blue dye, e) polyacrylamide-*g*-succinic anhydride-bromophenol blue, f) polyacrylamide-*g*-succinic anhydride-thymol blue dissolved in distilled water

Thermal analyses were performed by means of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and derivative thermogravimetry (DTG) (Mettler Toledo 990, Columbus, OH, USA).

^{1}H-NMR spectra were recorded on Varian Ultra Shield 300 MHz and 500 MHz spectrometers (Palo Alto, CA, USA), with tetramethylsilane as internal standard and the samples dissolved in deuterated DMSO.

Photolysis study

The photolysis experiments were conducted by irradiating all the polymers prepared with an ultraviolet lamp housed in a tube (Chain) (14 W) placed within a container (jar) with a volume of 250 mL. Stock solutions of all the synthetic polymers were prepared in distilled water and diluted to the required concentrations for photolysis. During the irradiation, a small amount of the irradiated solution was periodically withdrawn with a pipette and the absorbance of the aliquot taken was measured on a Biorad SmartSpec^{TM} Plus UV/VIS spectrophotometer. The measurements were made at the wavelength of maximum absorbance (λ_{max}) of the polymer or dyes. In the case of the acrylamide polymer the wavelength was 289 nm, for anthocyanin it was 547 nm, for bromophenol blue it was 591 nm, and for thymol blue it was 435 nm. Note that when the polymer plus succinic anhydride is bound to the dyes it exhibits the same λ_{max} as the dye alone. Figure 3 shows the absorption spectra and structures of the polymer and dyes. Standard calibration curves at the λ_{max} for the acrylamide polymer and for the dyes conjugated with the polymer were used to convert absorbance values to concentrations by making use of the Beer-Lambert law. The photodegradation percentage (%*D*) was calculated according to Equation 1 [25]:

$$\%D = \frac{C_0 - C_t}{C_0} \cdot 100 \qquad (1)$$

where C_0 is the initial concentration and C_t is the concentration at time *t* after irradiation.

RESULTS AND DISCUSSION

New grafted polymers were prepared by modifying polyacrylamide with succinic anhydride, as a spacer, and then grafting with anthocyanin, bromophenol blue and thymol blue dyes. The –NH_2 group in the polyacrylamide, which is a strong nucleophile, attacks the C=O group in the cyclic structure of succinic anhydride to form an amide. The carboxylic acid formed then binds to the dyes through ester formation, as shown in Figures 4 and 5.

Chemical structure analysis

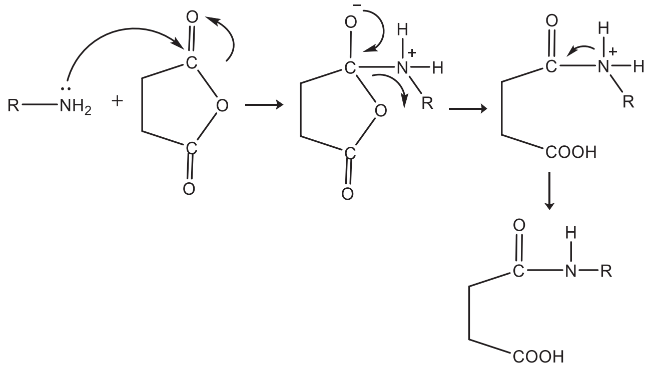

Fig. 4. Ring opening reaction of succinic anhydride with the amino group of acrylamides

The investigation of polymer grafted dyes' structures through FT-IR spectroscopy is a crucial process in understanding their chemical composition. In the FT-IR spectrum of PAM-*g*-SA, as depicted in Figure 6, a notable band emerges around 3355 cm^{-1}, attributed to the hydroxyl (OH) group inherent in the carboxylic group formed during the succinic anhydride ring-opening reaction. This observation underscores the significance of FTIR spectroscopy in elucidating the molecular structures of polymer grafted dyes, enabling a deeper insight into their properties and potential applications. The sp^3 CH absorptions are identified by frequencies lower than 3000 cm^{-1}, typically ranging from 2962 to 2856 cm^{-1}. These frequencies are attributed to the existence of CH, CH_2, and CH_3 groups within the compound. The distinctive peaks in the infrared spectrum at these frequencies serve as crucial markers in the identification and characterization of organic compounds, aiding in the elucidation of their molecular structure and composition. Understanding the significance of these absorptions provides valuable insights into the nature and properties of the molecules under study. The carboxylic group stretching vibration occurs at approximately 1718 cm^{-1}. The amide group appeared at 1656 cm^{-1} [26]. The FT-IR spectrum of PAM-*g*-SA-anthocyanin in Figure 7 presents notable peaks indicative of its molecular structure. Specifically, the spectrum reveals a prominent carbonyl peak at 1693 cm^{-1}, attributed to the ester group. Additionally, the spectral region between 2989-2935 cm^{-1} corresponds to the stretching vibrations of υ(CH-CH_2) aliphatic groups, while a distinct band at 3373 cm^{-1} is associated with hydroxyl (OH) functional groups. The bands of PAM-*g*-SA-bromophenol are depicted in Figure 8. The carbonyl of ester is observed at 1731 cm^{-1}, while CH-aromatic is evident at 3074 cm^{-1}, and the OH group appears at 3355 cm^{-1}. These specific spectral signatures provide valuable insight into the molecular structure and composition of the compound under investigation. In Figure 9, the FT-IR spectrum of PAM-*g*-SA-thymol revealed distinctive peaks indicative of various functional groups present in the sample. Specifically, the ester band was observed at 1697 cm^{-1}, highlighting the presence of ester linkages. Additionally, a band ranging from 3409 to 3357 cm^{-1} was attributed to the hydroxyl (OH) group within the structure. Furthermore, the spectrum displayed a distinct peak at 3224 cm^{-1} originating from the CH-aromatic group, and another band in the range of bonds.

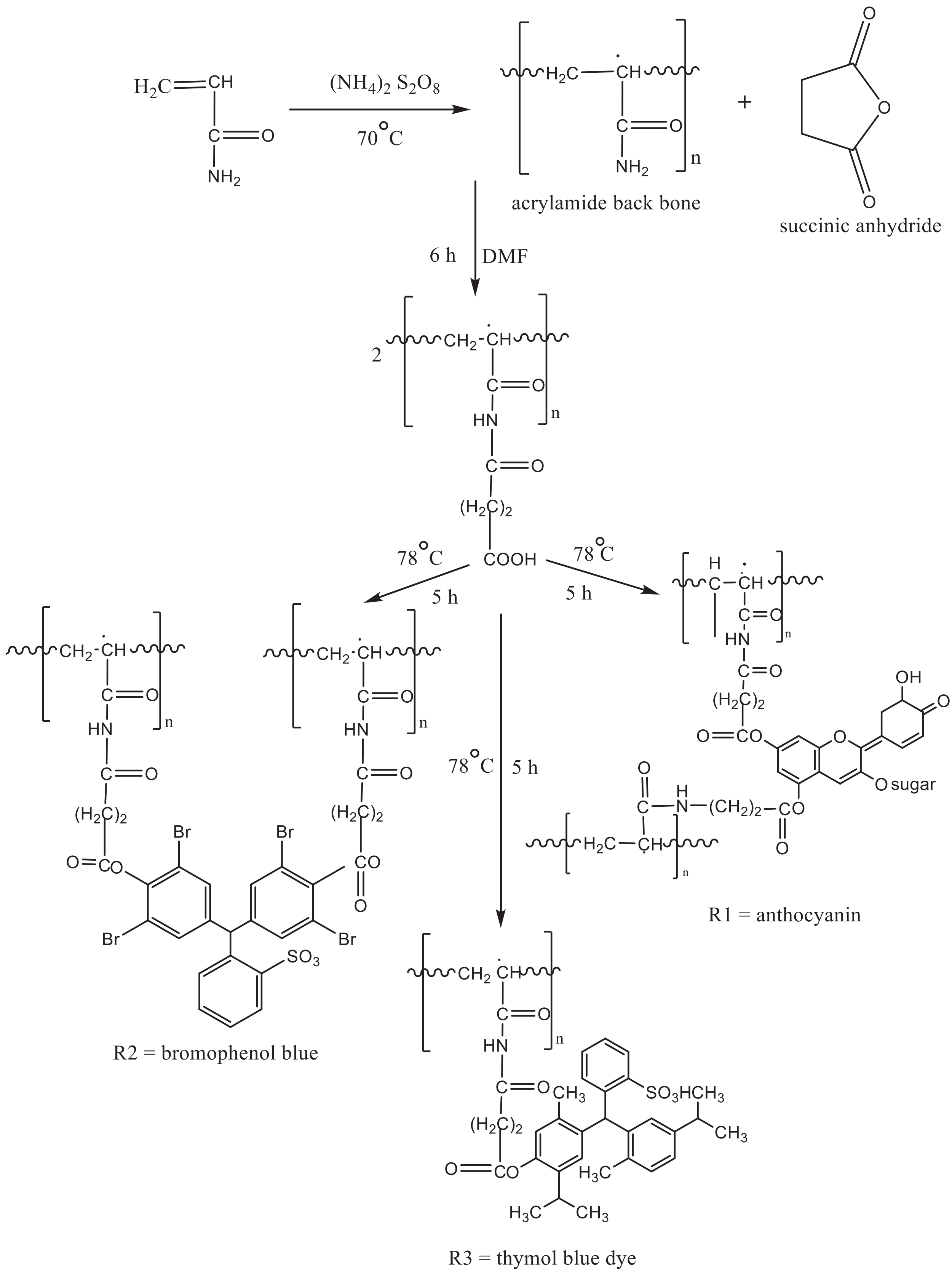

Fig. 5. Mechanism of the reaction with the three dyes of interest after the ring opening reaction of succinic anhydride with the amino group of acrylamides

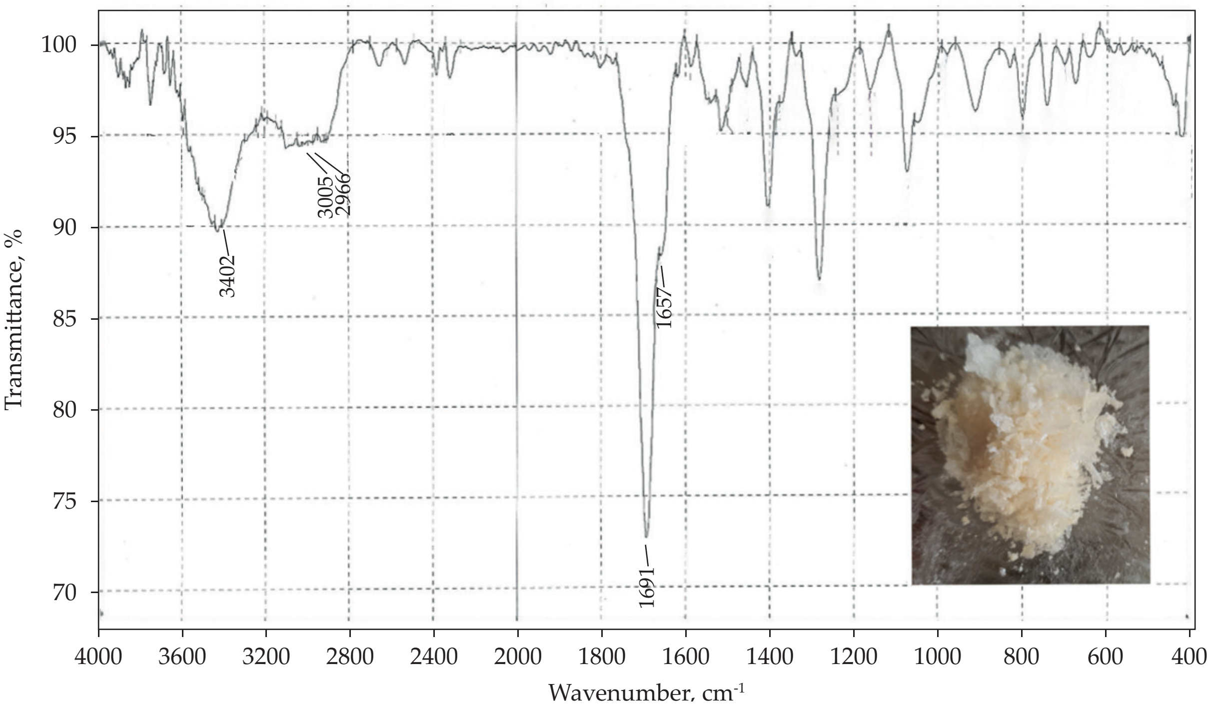

Fig. 6. FT-IR spectrum of PAM-*g*-SA

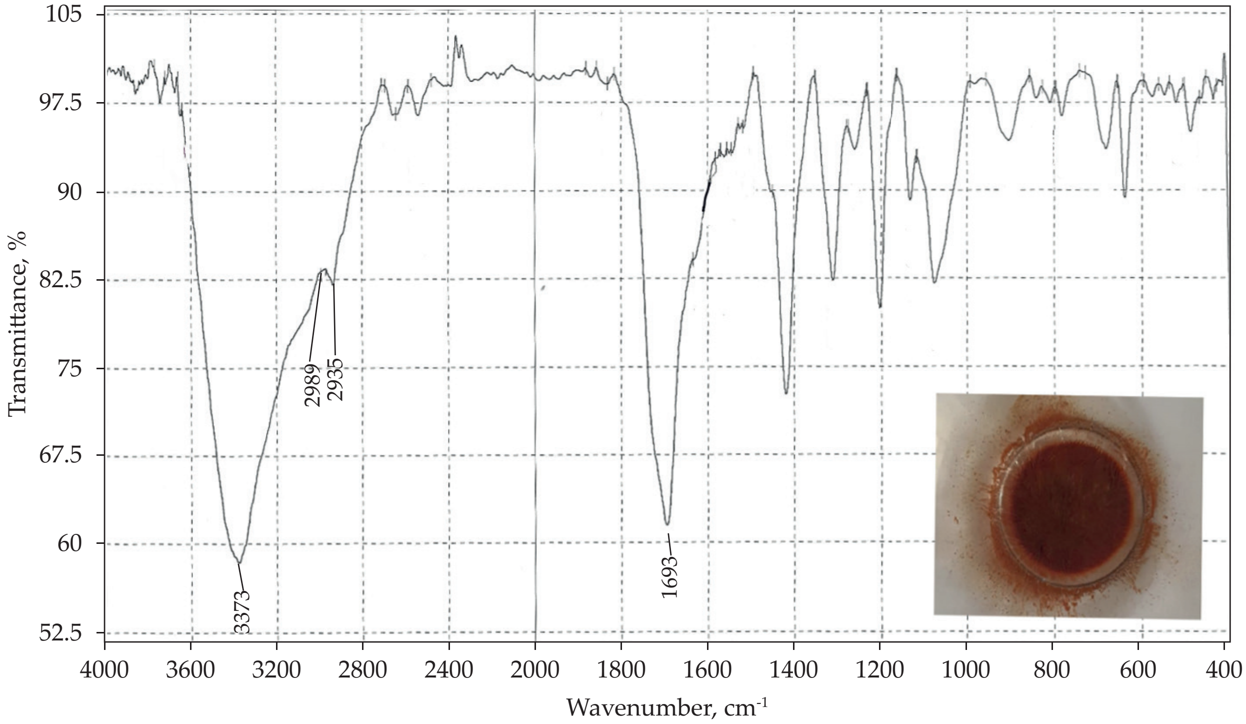

Fig. 7. FT-IR spectrum of PAM-*g*-SA-anthocyanin

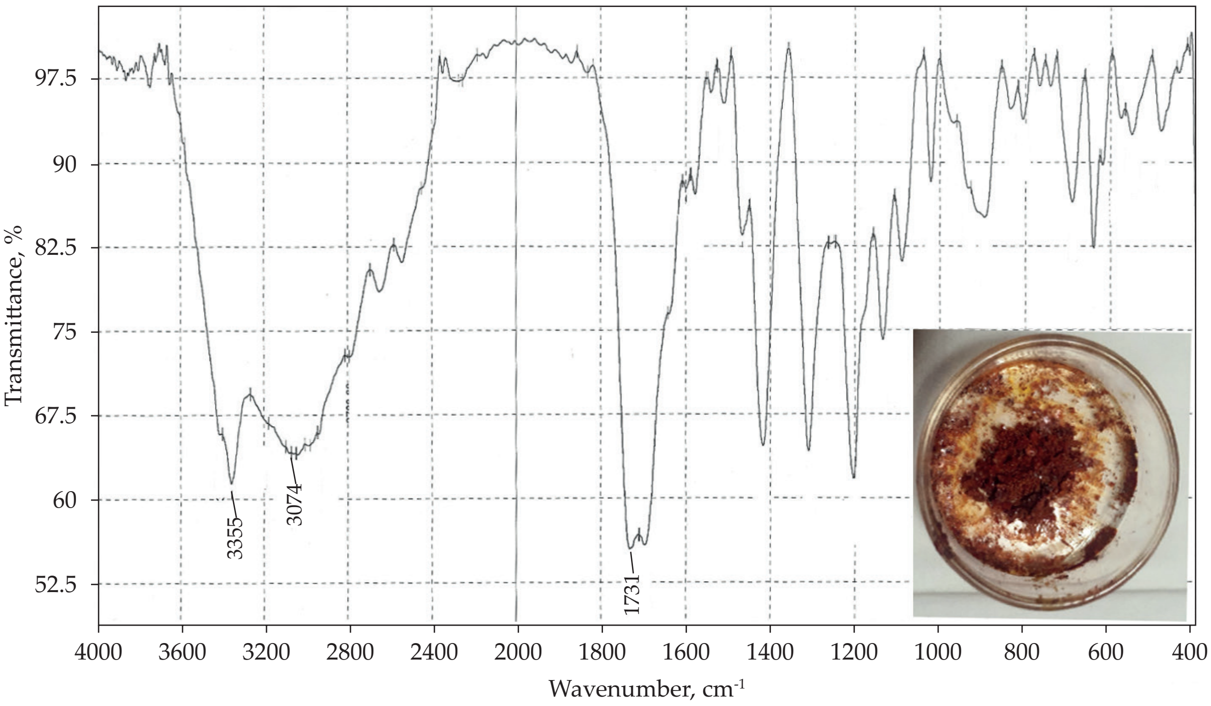

Fig. 8. FT-IR spectrum of PAM-*g*-SA-bromophenol blue

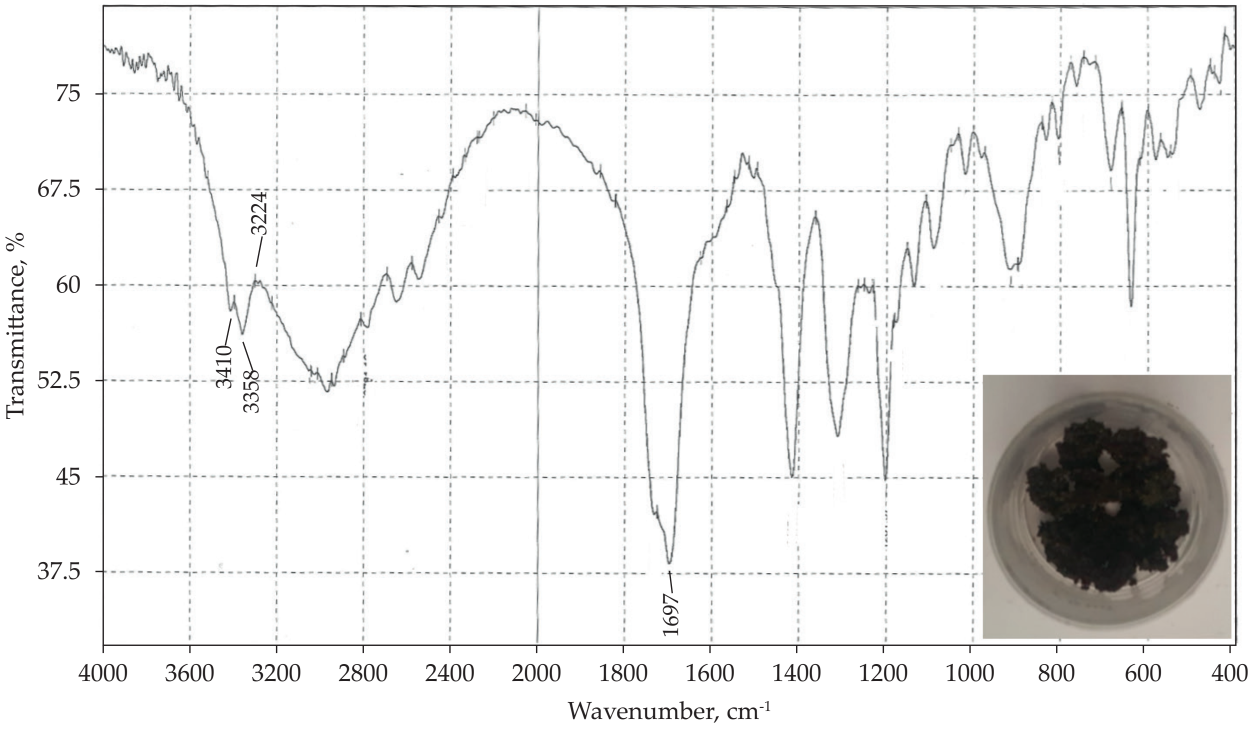

Fig. 9. FT-IR spectrum of PAM-*g*-SA-thymol blue

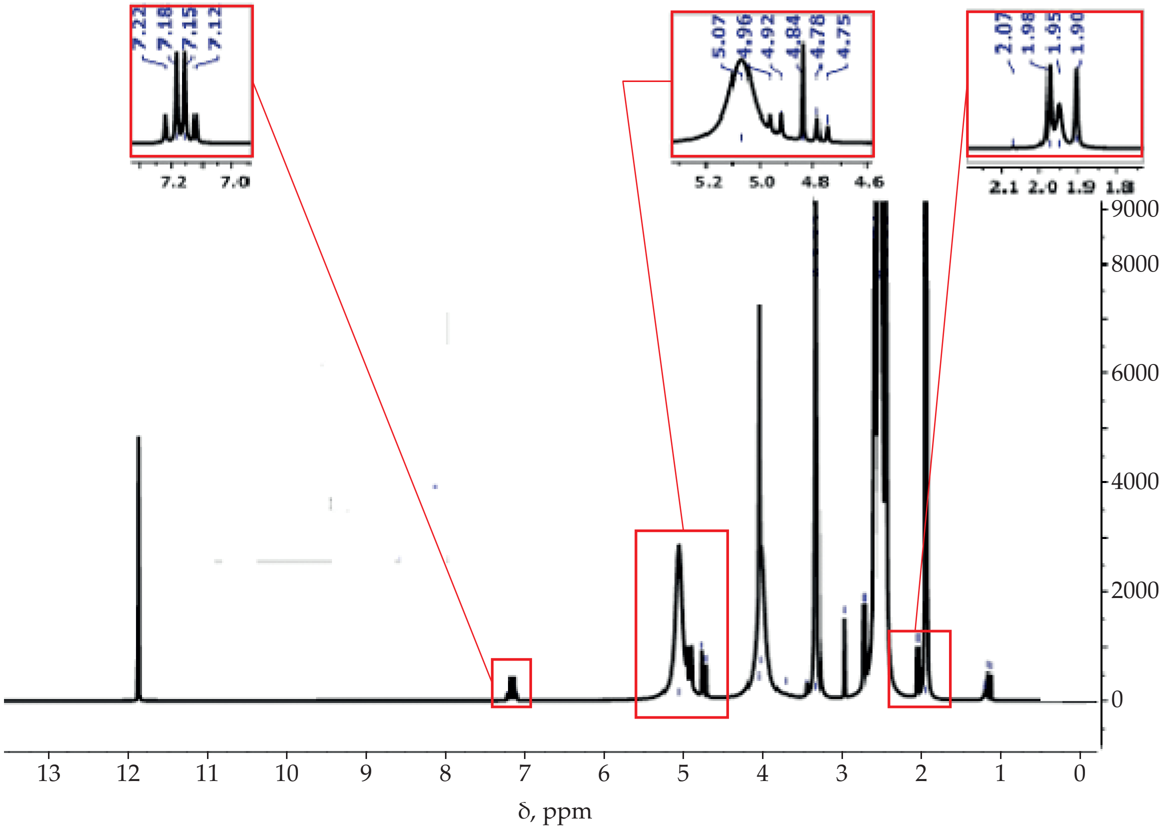

Fig. 10. ^{1}H-NMR spectrum of PAM-*g*-SA in deuterated DMSO

^{1}H-NMR of PAM-*g*-SA

The ^{1}H-NMR spectrum of PAM-*g*-SA recorded in deuterated DMSO solvent is displayed in Figure 10. It shows a broad signal at 5.07 ppm attributed to the ester groups. Furthermore, the spectrum shows a characteristic singlet signal at 11.86 ppm attributed to the proton of the carboxylic group. A quartet signal at 7.16 ppm is attributed to the proton of the amid group. Two doublet signals at 4.94 and 4.77 ppm are attributed to the protons of CH_2 groups. The doublet signal at 1.97 ppm is assigned to the CH_3(-).

Thermal stability

The thermal stability of PAM-*g*-SA-anthocyanin material was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). These measurements were conducted under an inert atmosphere of nitrogen gas. The TGA thermogram for this polymer in Figure 11 showed three stages of weight loss [27]. The first stage was found at approx. 168°C with a wt% loss of 59%. This stage of weight loss was attributed to the evaporation of water present in the form of moisture and decomposition of the succinic anhydride and anthocyanin. The weight loss was large, and this may be due to the degradation of all bonds that linked the added molecules to the acrylamide. The second stage, which was found at approx. 241°C, is attributed to the decomposition of acrylamide with a weight loss 16%. The third stage, which is the last stage, included a weight loss of 17.64% at a temperature greater than 400°C, which indicates the continued degradation of acrylamide and the emission of carbon dioxide, while the remaining wt% is carbonaceous char. The DSC analysis showed the presence of three stages, which correspond to the stages specified in the thermogravimetric analysis. At 104.5°C, which represents the temperature of dehydration, an endothermic process occurs with a value of 129.9 J/g. This is attributed to the loss of water absorbed on the hydrophilic groups in the copolymer of PAM-*g*-SA-anthocyanin dye. The temperature of 176.9°C represents the temperature needed to degrade the bonds between acrylamide and succinic anhydride and the anthocyanin. This is also an endothermic process with a value of 139.7 J/g. The change at 540°C is attributed to the thermal decomposition of the carbon structure of acrylamide and anthocyanin, which is an endothermic process with a value of 429.3 J/g.

Crystallinity

X-ray diffractograms for the polymers prepared are presented in Figure 12. Diffraction peaks are located at 2θ values of 23°, 26°, 31°, and 38° for PAM-*g*-SA. The diffractogram for PAM-*g*-SA-anthocyanin in Figure 12 b) shows the presence of an amorphous material, unlike the other three materials that were more crystalline. Figures 12(c) and 12(d) show the diffractograms for PAM-*g*-SA-bromophenol blue and PAM-*g*-SA-thymol blue, respectively where the characteristic peaks were observed at 2θ

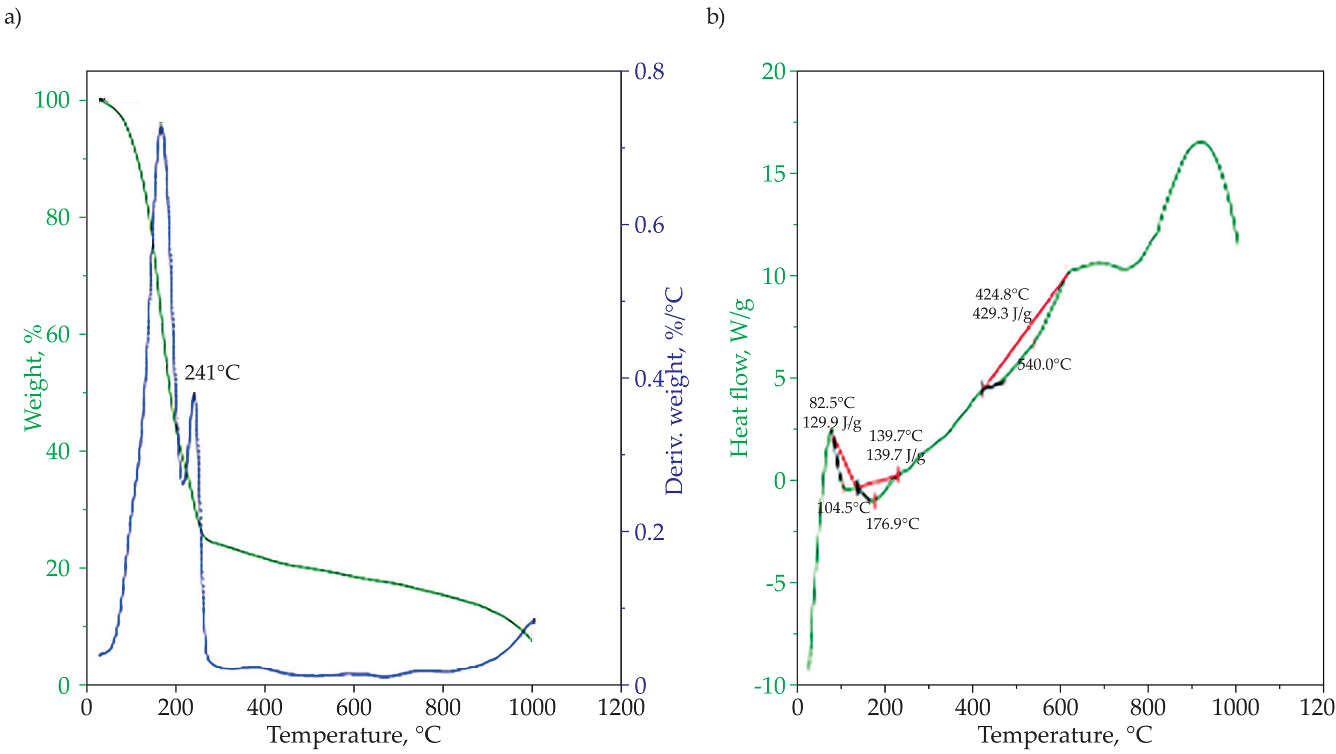

Fig. 11. Thermal properties of PAM-*g*-SA-anthocyanin: a) TGA, DTG, b) DSC

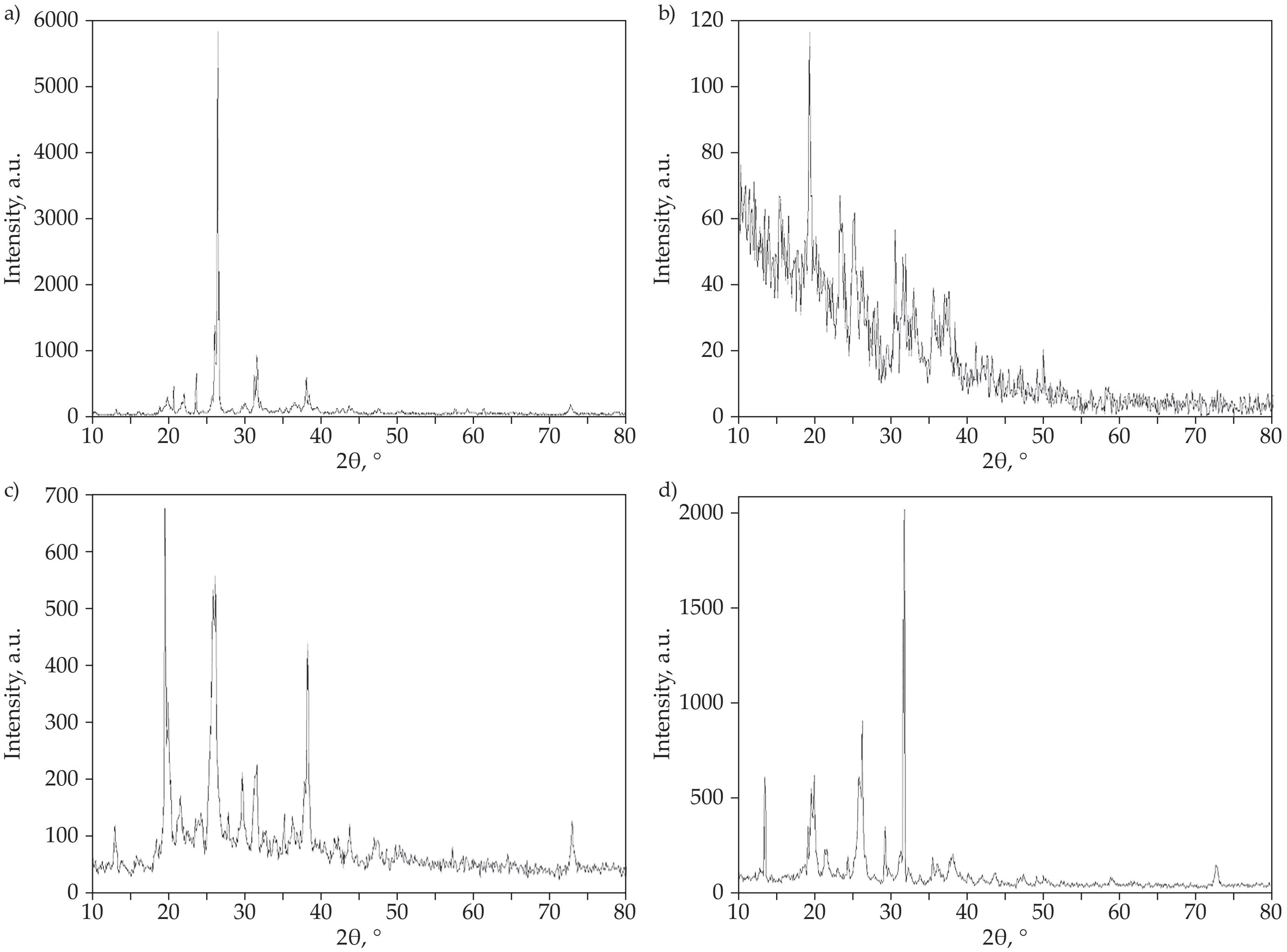

Fig. 12. X-ray patterns of PAM-*g*-SA with a) no dye, b) anthocyanin, c) bromophenol blue, d) thymol blue

values of 19°, 20°, 26°, and 38° for PAM-*g*-SA-bromophenol blue and at 20°, 25°, 26°, and 31° for the latter.

The crystallite size (*D*), which is not the particle size, was determined from the Scherrer equation [28] given in Equation 2:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{2}$$

where: *K* is the Scherrer constant, λ is the wavelength of the X-ray beam used (1.54184 Å), β is the full width at half maximum (FWHM) of the peak, and θ is the Bragg angle. The average crystallite sizes were determined from the peaks at 2θ values mentioned above and were found to be 26, 43, 20, and 27 nm for PAM-*g*-SA, PAM-*g*-SA-anthocyanin, PAM-*g*-SA-bromophenol blue, and PAM-*g*-SA-thymol blue, respectively.

Photostability studies

Aqueous solutions of the polymer/dye materials prepared were irradiated with ultraviolet light and the concentrations of the materials monitored at regular intervals by UV-visible spectrophotometry.

Photolysis of PAM-*g*-SA

Irradiation of an aqueous solution of PAM-*g*-SA under UV-light led to an increase in the concentration of the polymer since an increase in the absorbance of the aqueous solution of the polymer, when was observed at (λ_{max}) 289 nm (Fig. 13). Table 1 illustrates the percentage increase in concentration of the polymer. The increase in concentration was higher at the lower concentration (200 mg/L) than at the higher concentration of polymer (600 mg/L). The suggested mechanism of reaction can be explained as follows: when the aqueous solution of PAM-*g*-SA is irradiated with UV-light, free radicals can be produced from breaking the carboxyl bond in the polymer leading to the formation of either carbonyl or hydroxyl radicals and because of the low polymer concentration, the polymeric chain propagation is more accessible for attack by the radicals formed, and this promotes the formation of new polymeric chains. The percentage increases were smaller at the larger concentrations due to the restriction on the movement of the polymeric chains because of the presence of a greater number of molecules.

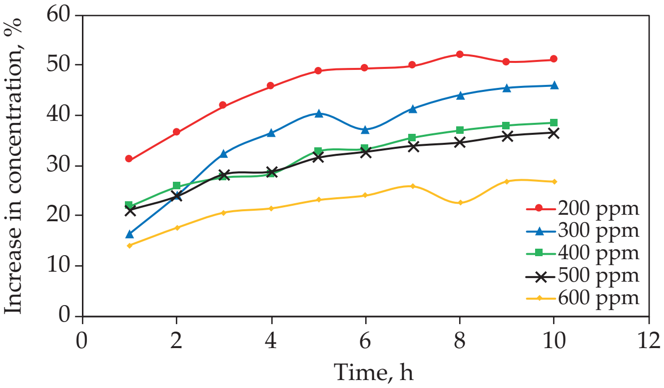

Fig. 13. Changes in the concentration of aqueous solutions of PAM-*g*-SA during photolysis

Photolysis of anthocyanin dye and PAM-*g*-SA-anthocyanin

Anthocyanin is a natural dye, found in flowers, fruits, stems, leaves and roots of plants. Investigations have shown that anthocyanin has more properties apart from its coloring nature, such as antimicrobial properties [34]. The color of the dye and its structure change with the pH of the medium (red at pH < 3, violet at pH 7, and blue at pH > 11) [35]. In this work, the anthocyanin dye was extracted from cabbage leaves and the color of the dye was violet since the dye was extracted in ethanol and prepared in distilled water where the pH was about 6.8.

The photolysis of the anthocyanin dye in aqueous solution was studied at different dye concentrations (15 000, 20 000, and 25 000 mg/L). It was found that irradiation of the dye by UV-light causes an increase in the absorbance of the dye (Fig. 14). This behavior differs from that of the other dyes used in this study.

Table 1. Photolysis-induced changes in the concentration of aqueous solutions of PAM-*g*-SA

Time, h	Concentration, %				
	200 mg/L	300 mg/L	400 mg/L	500 mg/L	600 mg/L
1	31.16	16.49	22.00	21.13	14.10
2	36.60	24.05	25.79	23.84	17.60
3	41.80	32.41	27.67	28.25	20.62
4	45.68	36.56	28.39	28.77	21.46
5	48.76	40.37	32.84	31.55	23.13
6	49.28	37.26	33.28	32.71	24.03
7	49.80	41.37	35.49	33.91	25.87
8	51.98	44.10	36.91	34.56	22.55
9	50.65	45.54	37.91	35.92	26.84
10	50.98	46.01	38.44	36.56	26.84

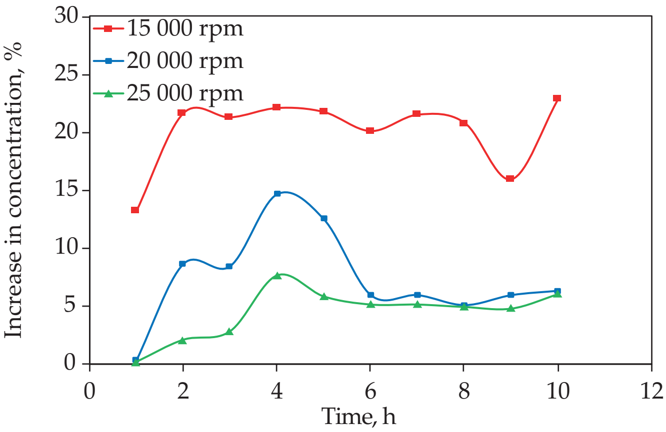

Fig. 14. Concentration changes of aqueous solutions of anthocyanin dye during photolysis

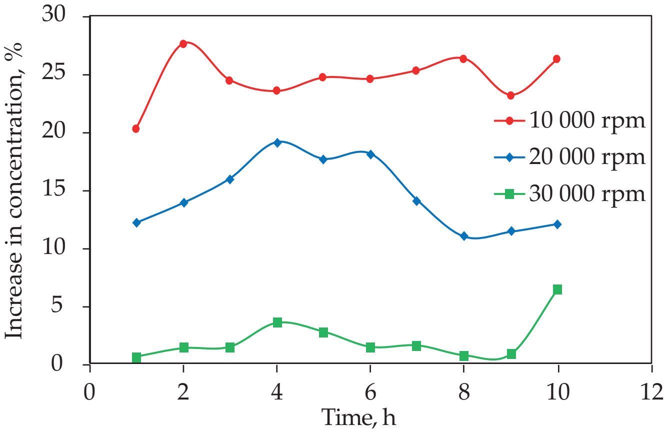

Fig. 15. Concentration changes of aqueous solutions of PAM-*g*-SA-anthocyanin during photolysis

T a b l e 2. Concentration changes during photolysis of aqueous solutions of anthocyanin dye and PAM-*g*-SA at different concentrations

Anthocyanin concentration, mg/L	Increase in concentration after 10 h of irradiation, %	PAM-*g*-SA-anthocyanin concentration, mg/L	Increase in concentration after 10 h of irradiation, %
15 000	22.8	10 000	26.2
20 000	6.3	20 000	12.0
25 000	6.04	30 000	6.4

Furthermore, Figure 14 and Table 2 indicate that the polymerization was higher at lower concentration (22.8% at 15 000 mg/L) than at higher concentrations (6% at 25 000 mg/L). The mechanism of reaction can be explained by the formation of radicals in three positions of the anthocyanin molecule upon UV-irradiation in a weakly acidic medium (pH c.a. 6.8). The three hydroxyl groups in the dye lose a proton leading to the formation of oxide radicals, a chain connection will be obtained in the mentioned positions by hydroxyl groups from other dye molecules to form polymeric chains and, hence, the concentration increases.

The same behavior can be noticed during the UV photolysis of an aqueous solution of PAM-*g*-SA-anthocyanin. Irradiation of different concentrations (10 000, 20 000, and 30 000 mg/L) of this polymer did not lead to bond breaks in the structure. On the contrary, it led to an increase in concentration as the results illustrated in Figure 15 and Table 2 show. The expected mechanism of this behavior can be explained based on the formation of radicals in the anthocyanin dye as mentioned earlier. From Table 2, the percentage increase in concentration after 10 h of irradiation for PAM-*g*-SA-anthocyanin was higher than for the anthocyanin dye, because of the increase in the number of polymeric chains in the case of PAM-*g*-SA-anthocyanin. Also, the latter showed poor crystallinity which allows for a greater degree of movement.

Photolysis of bromophenol blue dye and PAM-*g*-SA-bromophenol blue

Bromophenol blue dye is commonly used in a range of textile industries, and it can cause ecological hazards when disposed [29]. The photocatalytic degradation of blue bromophenol with different photocatalysts has been studied [30–33]. In this work the photolysis of PAM-*g*-SA-bromophenol blue polymer was studied, as well as the dye. It was found that UV-irradiation of bromophenol blue dye at different concentrations (10–40 mg/L) led to photodegradation of the dye. Figure 16 shows the percentage degradation of dye. It was observed that the highest percentage degradation was 65% for 10 mg/L of dye after one hour of irradiation, and the percentage degradation reduced with increasing concentration of bromophenol dye due to blocking of the light by the increase in the number of dye molecules. Also, with an increase in concentration the dye molecules aggregate, so the percentage degradation is reduced.

The results of the photolysis of PAM-*g*-SA-bromophenol blue polymer under UV-light and for different concentrations are shown in Figure 17. It is clear from Fig. 17 that the degradation of the polymer is much slower than for the dye: an equivalent percentage degradation occurs in 6 h for the polymer but only 1 h for the dye. The polymer concentration is much higher, so you expect more blocking of the light and, hence, less degradation.

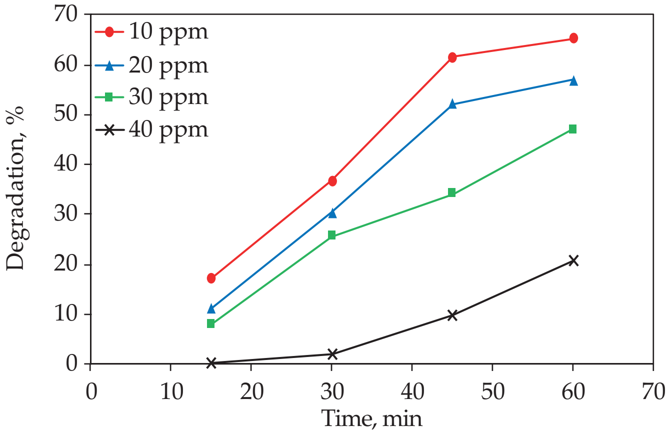

Fig. 16. Photolysis of aqueous solutions of bromophenol dye at different concentrations

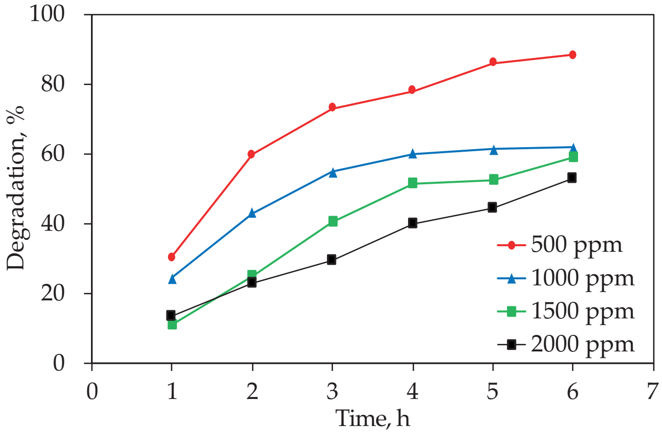

Fig. 17. Photolysis of aqueous solutions of PAM-*g*-SA-bromophenol blue at different concentrations

Table 3. Concentration changes during photolysis of aqueous solutions of bromophenol blue dye and PAM-*g*-SA-bromophenol blue at different concentrations

Dye concentration, mg/L	Degradation after 1 h of irradiation, %	PAM-*g*-SA-dye concentration, mg/L	Degradation after 1 h of irradiation, %
10	65	500	88
20	57	1000	61.8
30	47	1500	59
40	20	2000	52

The mechanism of the degradation of bromophenol blue dye has been proposed to occur because of the attack of hydroxyl radicals on the double bond of the carbons which link the three benzene rings. This causes the formation of a colorless compound, as shown in Fig. 18 [34–37].

Photolysis of thymol blue dye and PAM-*g*-SA-thymol blue

Thymol blue dye is one of the sulfonphthalein dyes that are used as an acid-based indicator. Its color changes with pH, and this color change refers to a change in the structure of the dye [38]. In this study, all the samples of thymol blue dye were prepared in distilled water, and the color of the aqueous solutions was yellow. The aqueous solutions of thymol blue dye and PAM-*g*-SA-thymol blue polymer were irradiated with UV-light at different concentrations of dye (20-50 mg/L) and synthetic polymer (150–300 mg/L). Figures 19 and 20 show the results of the photolysis of dye and synthetic polymer, respectively. Both materials were found to photodegrade. It was found that thymol blue dye resisted the photodegradation process, as the highest percentage degradation was

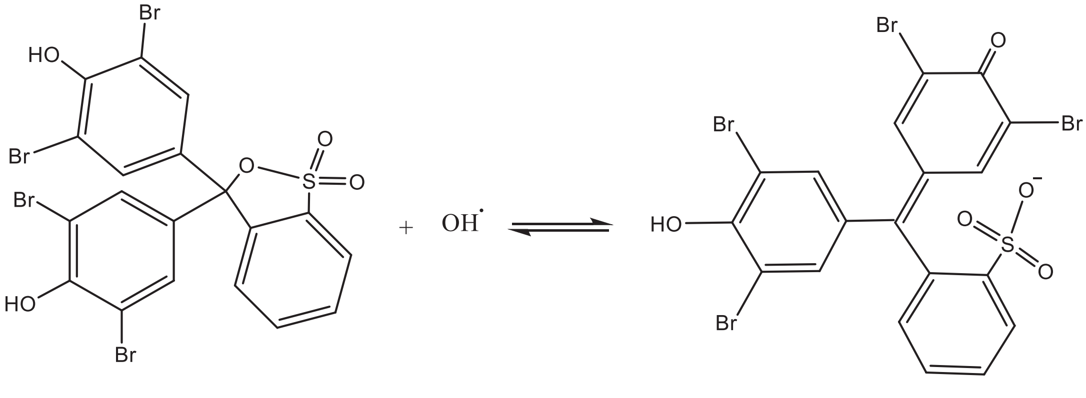

Fig. 18. Mechanism for the degradation of bromophenol blue dye

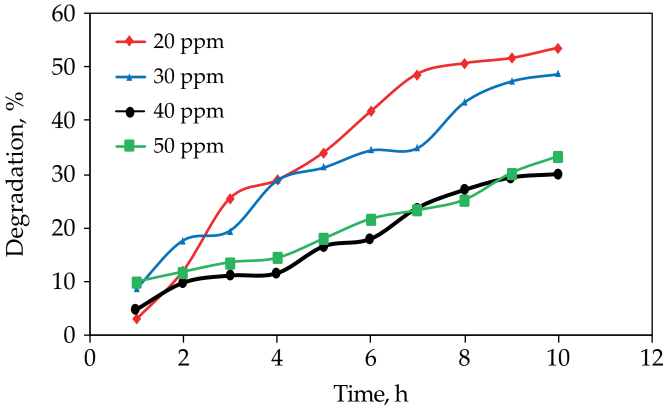

Fig. 19. Degradation of thymol blue dye in aqueous solutions during photolysis

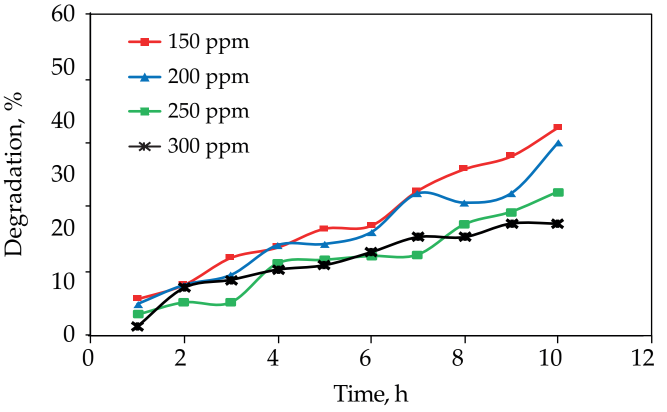

Fig. 20. Degradation of thymol blue dye in aqueous solutions of polymer dye during photolysis

Table 4. Concentration changes due to photolysis of different concentrations of aqueous solutions of thymol blue dye and PAM-*g*-SA-thymol blue

Dye concentration, mg/L	Degradation after 10 h of irradiation, %	PAM-*g*-SA-dye concentration, mg/L	Degradation after 10 h of irradiation, %
20	53.36	150	39.44
30	48.68	200	36.59
40	29.90	250	27.24
50	33.20	300	21.33

(53.36 %) at 20 mg/L for the dye and (39.44%) at 150 mg/L for PAM-*g*-SA-thymol blue after 10 h of irradiation under UV-light. It was noticed that the degradation of dye reduced when it was grafted onto the mentioned polymer. Table 4 shows the percentage degradation of these two materials after 10 h of illumination. The mechanism of degradation occurs via the attack by hydroxyl radicals generated upon irradiation on various positions of the dye, such as the isopropyl segment, benzene ring, and exo-double bond, which change the compact arrangement of linkages in the ring structure. All the mentioned routes finally lead to CO_2 and H_2O [39, 40].

CONCLUSIONS

In this research, a copolymer was synthesized from the reaction of polyacrylamide with succinic anhydride, followed by the reaction of the PAMs with dyes (anthocyanins, bromophenol, and blue thymol). The synthesized polymers were characterized using FT-IR, X-ray diffraction, UV-visible spectroscopy and TGA. The photolysis of the synthesized polymers was also studied to determine the photostability of the polymers and to identify the best polymer that resists light. Studying the photolysis of the synthetic polymers shown that the best polymers which resisted photodegradation were PAM-*g*-SA and PAM-*g*-SA-anthocyanin, which did not photodegrade upon UV-illumination, but rather showed an increase in polymerization. On the other hand, PAM-*g*-SA-bromophenol blue and PAM-*g*-SA-thymol blue polymer photodegraded. Thus, it was demonstrated that the photodegradation of PAM-*g*-SA can be prevented by a reasonable choice of dye.

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Authors contribution

S.A.M – research concept, methodology, investigation, validation, visualization, writing; S.H.A – research concept, methodology, investigation, validation, visualization, writing; B.S.M - validation, visualization, writing. M.A.B – writing.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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