

Polymeric Antioxidant from Polyacrylic Acid

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Summary: Acrylic acid was polymerized and modified with some acids such as salicylic acid, benzalthiobarbituric acid and some amines such as aniline and α -naphthylamine. Modified polyacrylic acids (PA) were characterized with FT-IR spectroscopy and thermal analysis and their ability was tested to be antioxidants for PVC which contains sensitive terminal double bonds toward oxidative conditions. The extent of PVC discoloration is considered to follow up the degrading thermal oxidation. All the investigated polyacrylic acid derivatives showed ability as polymeric antioxidants better than the unmodified especially polyacrylylbenzalthiobarbituric acid. The results obtained are justified and discussed.

Keywords: Polymeric antioxidant; Thermal stability; Acrylic acid; PVC; Amines; Thiobarbituric acid.

Introduction

Polyacrylic acid (PA) is a big category of commercial polymers with widespread application directions such as medicine and agriculture [1]. PA and PA-based materials are utilized as smoothing agents for synthetic fibers, emulsifiers and thickeners for aqueous solutions and dispersions of latexes, sorbents and ion exchangers [2-5]. Acrylic-based hydrogels were used widely as a mucoadhesive system due to their elasticity and tremendous bio-adhesion [6]. Acrylic acid was used also to prepare stable, biocompatible and highly monodisperse polymer to be suitable for coating of cerium oxide nanoparticles which are efficient pH-dependent antioxidant with cytoprotection to the normal cell lines not to cancer cells against hydrogen peroxide and nitric oxide radical [7]. Adequate methods have been established to prepare aqueous CeO₂ sols by using biocompatible nontoxic stabilizers such as citric acid, polyacrylic acid, and polyvinylpyrrolidone [8]. A polymeric antioxidant nanoparticle was reported to suppress oxidative damage and cytotoxicity by iron oxide nanoparticles [9]. New antioxidants based on multiple hindered phenolic antioxidant pendants to unsaturated polymeric main chain were prepared and their application as antioxidants in polypropylene blends was examined [10]. Acrylamide and polyvinyl alcohol copolymers of acrylic acids are active to uptake metal ions and use for removal or preconcentration of metal ions [11]. Other acrylic acid based polymers are active as efficient flocculants useful to increase the strength of exceptional grades of paper [12]. Hydrophilic characteristics of PAs clarify their extensive

agricultural applications for seeds treatment, etc. Recently, PA derivatives attract much attention as substances of targeted physiological action [13]. Thiolated PAs on Mrp2 efflux protein pump showed inhibitory efficiency depending on their molar mass and extent of thiolation. Hence, the transport activity of the efflux pump transporter depends significantly on the modification extent and polymer molar mass [14]. PAs are extensively used also as enzyme carriers, proteins, drugs and other biologically active substances [15, 16]. Functionalization of iron oxide nanoparticles with commonly used functionalities such as amine, carboxylic and hydroxyl groups has been reported as contrast agents for MRI, magnetic separations, immobilizations of various bio-substances and targeted drug delivery [17]. Carboxymethylcellulose-g-PA synthesized with the assistance of microwave demonstrated flocculation efficiency higher than the ungrafted CMC proving the importance of PA in this direction. This makes them excellent flocculants for river water clarification [18]. Modified polyacrylic acids have been prepared by polymerization of modified monomers. However, starting with the monomer modification to obtain polymers with high purity is complicated and inappropriate for the waste recycling of PA [19]. Polyacrylates modified with ascorbic acid were achieved in two-steps process [20]. Another natural antioxidant-supported polyacrylate was prepared in a two-step process too [21]. The current study aims at preparation and characterization of derivatives of polyacrylic acid with some organic acids and amines through facile methods and

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application as thermal antioxidants for PVC as an example for the sensitive halogenated polymers.

Experimental

Acryloyl chloride; azobisisobutyronitrile (AIBN) and PVC (M.Wt.=100.000) and all chemicals used in this study were supplied by Bayouni Co., the Sigma-Aldrich agent in Saudi Arabia unless otherwise mentioned and used without further purification. FT-IR Spectroscopic analysis was carried out at Chemistry Department, King Abdulaziz University, Saudi Arabia using a Perkin-Elmer 1430 spectrophotometer. UV/Vis analysis was performed using double-beam spectrophotometer to determine the extent of PVC discoloration as an indication of the thermal oxidation. Thermogravimetric analysis (TGA) was performed on Shimadzu thermal analyzer (D-50), Japan, with 10 °C/min rate of heating in an inert atmosphere of nitrogen gas and by using sintered alumina (α -Al₂O₃) as a standard.

Modification of polyacrylic acid into polyacryloxy acids

About 2 mole of acrylic acid was polymerized under the conventional free radical polymerization conditions using 0.2 mole of AIBN in THF with stirring. After flushing out the mixture for 30 min at 70°C with nitrogen and cooling to the room temperature, enough amount of anhydrous diethyl ether was used to precipitate polyacrylic acid (PA). The obtained product was converted into polyacrylyl chloride (PAC) by treatment with thionyl chloride in a ratio of 1.4:1 of PA. After stirring for 1 h at 60°C and cooling down to 25 °C, the product was filtered off to be separated, washed with CH₂Cl₂ and dried in vacuum overnight at 40 °C.

About 0.5 mole of PAC was immersed for 6 h in 120 ml of acetonitrile and then treated with a mixture of 0.3 mole of 2-hydroxybenzoic acid and 0.9 mole of a solution of base such as triethylamine in 400 ml of acetonitrile. Stirring the mixture for 6 h at 25°C, pouring into dilute solution of HCl, filtration off followed by washing with methanol, 1M HCl, distilled water and finally with ether, poly-2-acryloxybenzoic acid (PABA) was obtained and dried overnight under vacuum at 40 °C. Poly-4-acryloxybenzothio-barbituric acid (PABTBA) was prepared similarly by using 4-hydroxybenzothio-barbituric acid instead of salicylic acid.

Modification of PA into poly-N-acrylamines

About 0.1 mole of PAC was soaked for 6 h in 40 ml CH₂Cl₂ in a 500 ml round bottomed flask and 0.2 mole of solution of cold aniline in 150 ml CH₂Cl₂ was slowly added while stirring. After further stirring for 30 min, poly-N-acrylaniline (PAAN) was separated by filtration, washed successively with CH₂Cl₂, acetone and methanol, dried for 24 h under vacuum at 40 °C to be ready for characterization. Similarly, poly-N-acrylnaphthylamine (PANA) was prepared.

Oxidative degradation of PVC in presence of modified polyacrylic acids

An amount of 0.2 gm of modified PA dissolved in THF and added to 10 g of PVC solution in 150 ml THF while stirring and degassed with sonication for 3 min. The mixture was then poured onto a polypropylene sheet fixed horizontally on a glass surface. The mixture was left until the solvent was evaporated at 25 °C. The produced film has been dried for 24 h at 25 °C under vacuum, cut into strips and left for different intervals at 100 °C. The absorbance of PVC film was measured at $\lambda = 400$ nm to estimate the average of discoloration extent which was calculated for 3 replicates in presence of PA, PABA, PABTBA, PAAN and PANA (Table-1).

Table-1: Influence of PA derivatives on PVC oxidative degradation.

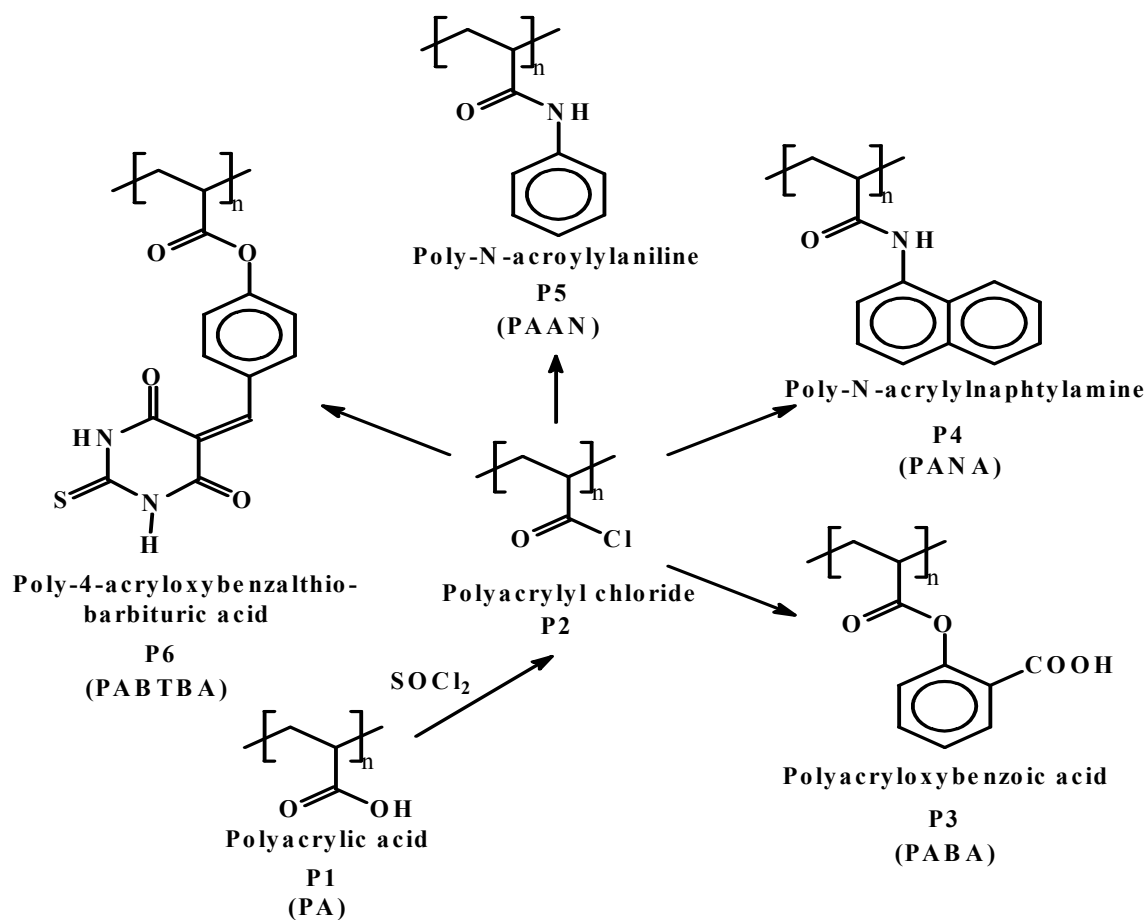
Time, min	PVC	PVC/PA	PVC/PABA	PVC/PABTBA	PVC/PAAN	PVC/PANA
0	0	0	0	0	0	0
12	0.47	0.40	0.22	0.16	0.23	0.27
24	1.23	1.12	1.10	0.20	0.73	0.82
72	1.96	1.86	1.73	0.29	1.19	1.30

Results and Discussion

Polyacrylic acid derivatives were prepared successfully according to Scheme-1 and characterized with different techniques. In the next context, the characterization of the polyacrylic acid derivatives will be discussed.

FT-IR Spectroscopy

Fig. 1a shows FT-IR spectrum of PABA with absorption peaks at 1615 cm⁻¹ and 1455 cm⁻¹ corresponding to aromatic residue; at 1690 cm⁻¹ and 1740 cm⁻¹ corresponding to carboxyl and ester C=O functionalities, respectively, and at 3030 cm⁻¹ corresponding to OH stretching. Fig. 1b shows FT-IR spectrum of PABTBA with absorption peaks at 1170 cm⁻¹, 1678 cm⁻¹ and 1725 cm⁻¹ correspondingly to C=S bonds and carbonyl functionalities for both ketonic and ester bonding.



Scheme-1: Functionalization of polyacrylic acid with different acids and amines.

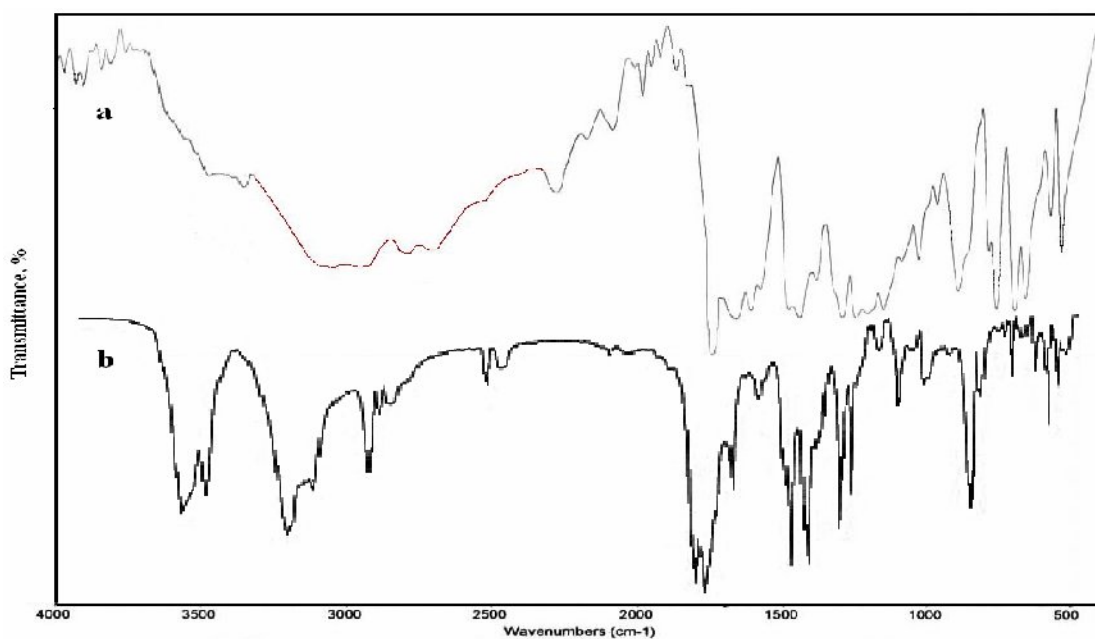


Fig. 1: FT-IR spectra of a) PABA and b) PABTBA.

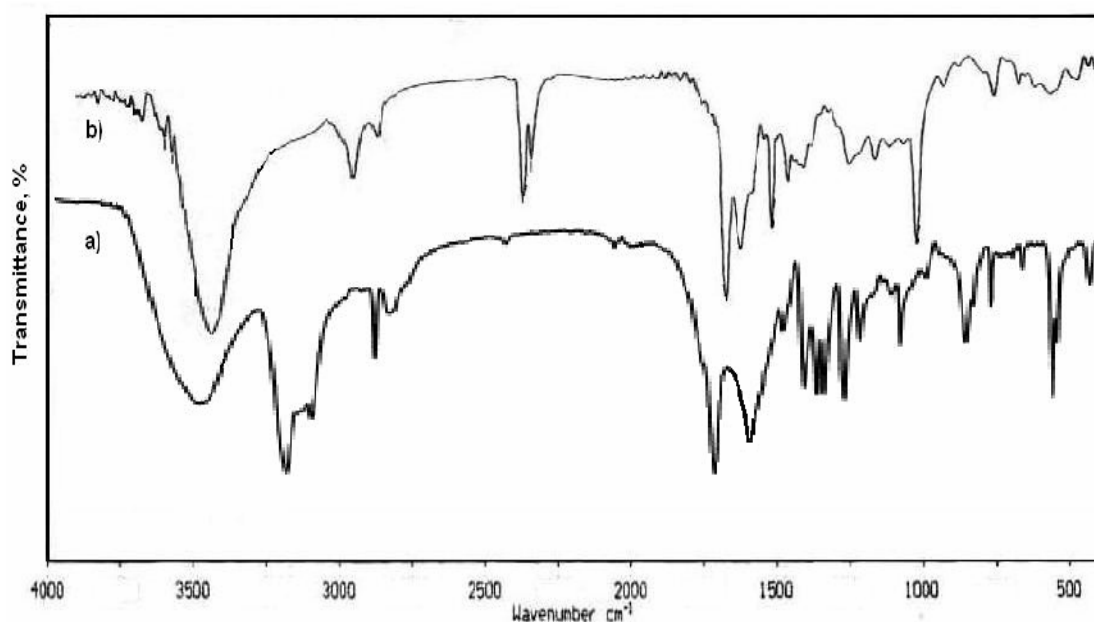


Fig. 2: FT-IR spectra of a) PAAN and b) PANA.

Fig. 2a shows FT-IR spectrum of PAAN with no absorption peaks at 1660 cm^{-1} for COCl functionality while there are absorption peaks at 3270 cm^{-1} and 1610 cm^{-1} corresponding to N-H stretching and amidic C=O groups, respectively. This means that the modification of polyacrylyl chloride into polymer-supported amines was achieved successfully and the same is true also for PANA where the absorption peaks appeared at 1625 cm^{-1} and 1570 cm^{-1} related to olefinic C=C and aromatic C=N double bonds, respectively, as represented in Fig. 2b.

Thermal Analysis

Fig. 3a shows the thermal analysis (TGA) of PABTBA indicating the degradation of about 52% of the sample at reasonably high temperature of $325\text{ }^{\circ}\text{C}$. The first weight loss stage may be mainly due to the cracking of C-O bond and release of thiobarbituric acid moiety. Upon increasing the temperature, the sample suffers a slight weight loss of about 12.8.0% begins at $420\text{ }^{\circ}\text{C}$. This can be due to C-C bond fission and the behavior of PABTBA can be considered as a characteristic trend of typical polyolefins at high temperatures. Fig. 3b shows TGA of PA as a reference. Also, Fig. 3c shows the thermal analysis (TGA) of PABA where the sample suffered a weight loss of 62% within the temperature range from $95\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$. Further 14% at was also lost at $410\text{ }^{\circ}\text{C}$ reflecting the stability of PABA up to $250\text{ }^{\circ}\text{C}$. This can be attributed mainly to decarboxylation while C-

C fission of the main chain began at temperature of $420\text{ }^{\circ}\text{C}$.

Fig. 4 shows TGA of PAAN and PANA where PAAN is stable against thermal degradation up to $235\text{ }^{\circ}\text{C}$ with 48% weight loss followed by slight weight loss of 9.6% at $530\text{ }^{\circ}\text{C}$ which may be due to the facile oxidation of the amine functionality with possible separation of this moiety from the matrix. This means that the thermal stability of PAAN is relatively not very high. Conversely, PANA shows 52% weight loss at $265\text{ }^{\circ}\text{C}$ indicating the relative higher stability in comparison to PAAN. However, both PAAN and PANA are thermally more stable than PABA which may be due to the ease of decarboxylation.

Application polyacrylic acid derivatives as antioxidants for PVC

All the derivatives of polyacrylic acid involved in this study were investigated as thermal stabilizers for PVC against thermal oxidative degradation. This degradation involves autocatalytic dehydrochlorination of PVC causing rigorous staining and weakness of mechanical properties [22-24]. On thermal treatment of PVC in the presence of the modified polyacrylic acid, the extent of discoloration of PVC varies from derivative to another. On comparison with blank PVC, the role of modified polyacrylic acids was clear.

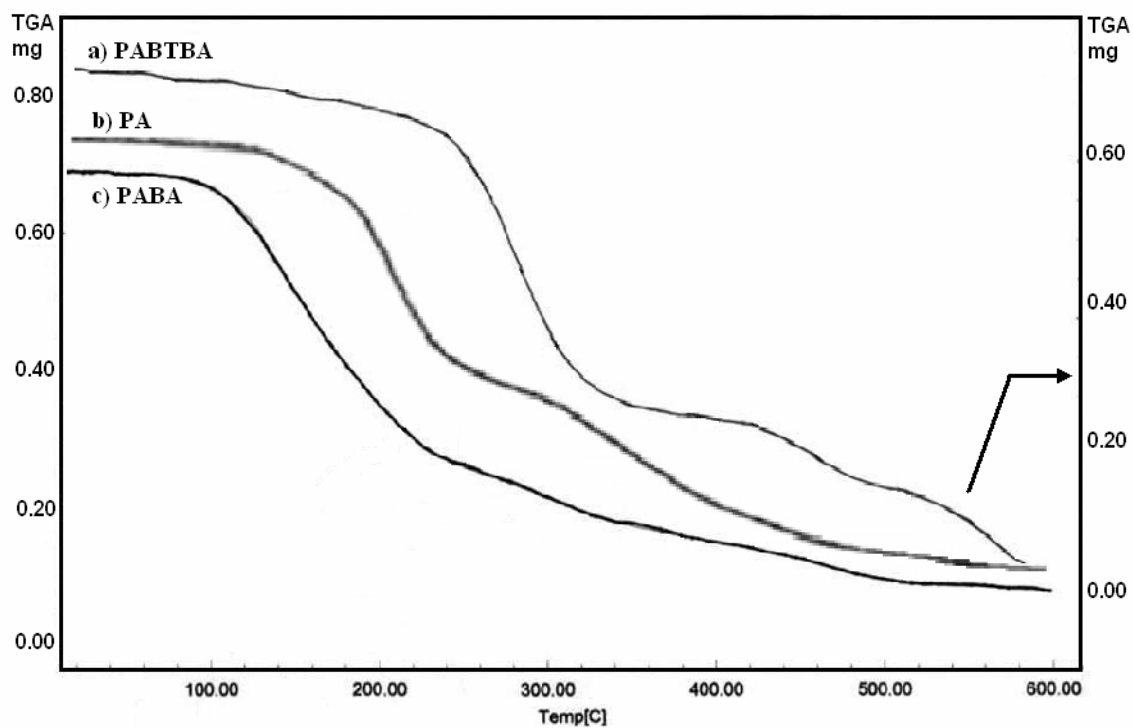


Fig. 3: TGA analysis of **a)** Poly-4-acryloyloxybenzalthiobabaturic acid (**PABTBA**); **b)** Polyacrylic acid (**PA**), and **c)** Poly-2-acryloyloxybenzoic acid (**PABA**).

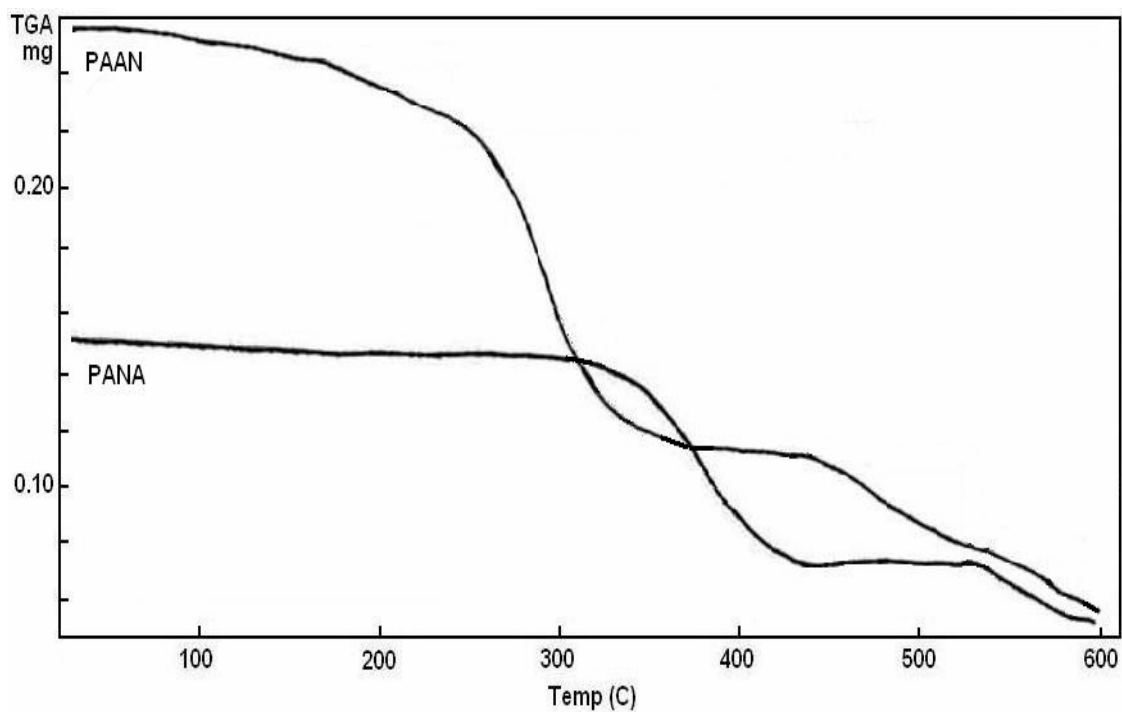


Fig. 4: TGA diagrams of PAAN and PANA.

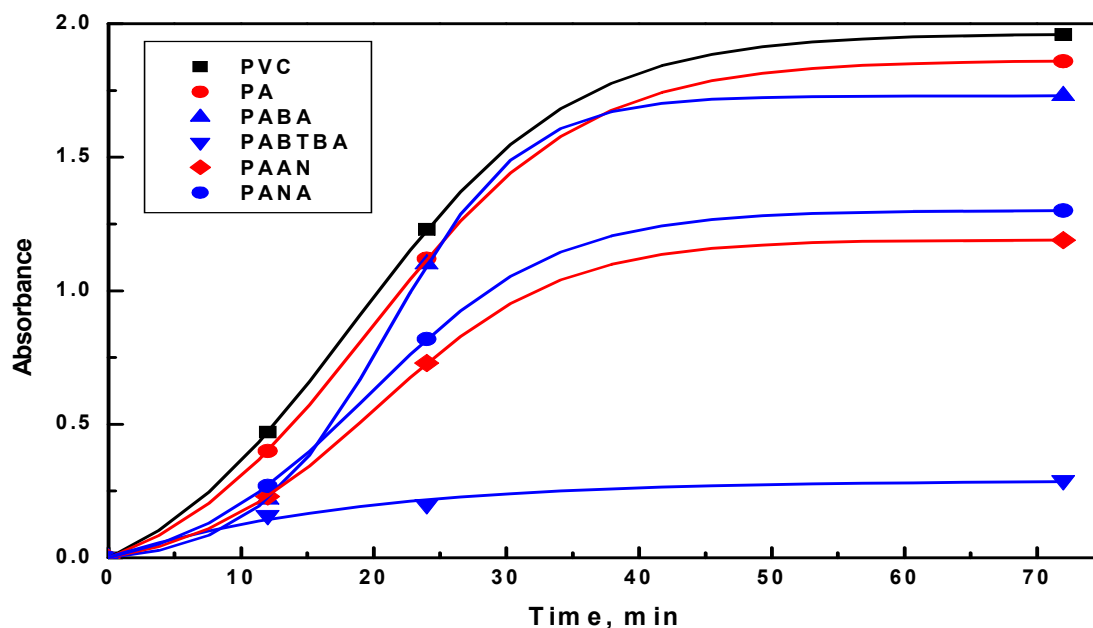


Fig. 5: Dependence discoloration extent of PVC represented by its absorbance on the time of thermal treatment at 100 °C in presence polyacrylic acid derivatives.

PABTBA has different functionalities able to hinder the reaction of degradation and to absorb HCl resulted in by the degradation. This can reduce the hazards of acidic degradation products [25]. Fig. 5 shows that the discoloration extent of PVC treated with modified polyacrylic acid is lower than that of the reference PVC. These findings prove the role of the thiobarbituric acid moiety in the polymeric antioxidant where it interacts with the chlorine atoms released from PVC, hence; obstruct the sites of odd electron on PVC main chains. This interaction hinders the conjugation process and gives better chance for HCl to be evolved. The spacer group in PABTBA helps also to increase mobility of the side chains to grab the emitted HCl. For PAAN and PANA, they are expected to serve as reasonable antioxidants for PVC due to their basic characteristics helping to trap the evolved HCl released from PVC during the thermal treatment. The results represented in Fig. 5 confirm this expectation and the efficiency of PAAN and PANA was better than that of PABA while it was still lower than that for PABTBA.

Conclusion

From the current study one can conclude that PA derivatives, especially PABTBA, are able to serve as thermal stabilizers for PVC. The investigated PA derivatives showed good thermal stability where PABTBA showed thermal stability up to 325 °C against 250 °C for PABA. Also, PAAN showed

stability against thermal degradation up to 235 °C while it was up to 265 °C for PANA. All PA derivatives showed good efficiency as polymeric antioxidants and thermal stabilizers for PVC better than the unmodified PA. PABTBA showed higher efficiency than PABA while PAAN showed higher efficiency than PANA as polymeric antioxidants for PVC. Amine-modified PA showed efficiency between PABA and PABTBA as antioxidant for PVC.

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