

12-1-2012

Section: Chemistry

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FAHIM NASSAR

Department of Applied Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.

H. NASSAR

Department of Applied Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.

F. HAI

Department of Applied Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.

G. AHMED

Department of Applied Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.

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NASSAR, FAHIM; NASSAR, H.; HAI, F.; and AHMED, G. (2012) "Synthesis of multifunctional acrylate monomers (MFAMs) and their applications," *Al-Azhar Bulletin of Science*: Vol. 23: Iss. 2, Article 13. DOI: <https://doi.org/10.21608/absb.2012.7208>

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SYNTHESIS OF MULTIFUNCTIONAL ACRYLATE MONOMERS (MFAMS) AND THEIR APPLICATIONS

FAHIM NASSAR, H. S. NASSAR, F. ABDEL HAI, G. I. AHMED

Department of Applied Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.

Abstract

Novel multifunctional acrylate monomers (MFAMs) were synthesized by reaction of acryloyl chloride with 3,4,5-trihydroxybenzoic (Gallic) acid and diethanolamine in the presence of triethylamine as catalyst. The prepared multifunctional acrylate monomers were used as cross-linkers for the synthesis of polyacrylic acid by precipitation polymerization using 2,2'-azobisisobutyronitrile (AIBN) as free radical initiator. Differential scanning calorimetry studies showed that the glass transition temperature behavior is significantly affected by the type and amount of MFAM employed. Viscosity measurements showed that the thickening effect depend upon the cross-linker type and concentration.

Keywords: Multifunctional acrylate monomers, Gallic acid, diethanolamine, precipitation polymerization, Azobisisobutyro-nitrile, and Differential scanning calorimetry.

1. Introduction

Acrylic acid polymers and copolymers are widely used as dispersants, thickeners, flocculants and superabsorbent polymers. The most prevalent commercial process to make such polymers is solution polymerization of acrylic acid in water.¹ Other processes, such as suspension polymerization, dispersion polymerization and precipitation polymerization, are carried out in organic media.² Precipitation polymerization is one of the methods to prepare stabilizer-free particles. This method requires only monomer, radical initiator, and solvent.^{3,4} Upon the discovery of precipitation polymerization in organic media, a variety of monomers including methacrylate, maleic anhydride, and chloromethylstyrene were copolymerized with divinyl-benzene as the cross-linkable monomer using this technique.⁵ Multifunctional monomers (MFMs) are used to make cross-linked polymers in free radical polymerization. Only small amounts of MFM are required to produce a cross-linked network.⁶

The aim of this work was to synthesize novel multifunctional acrylate monomers and describe the crosslinking polymerization of acrylic acid in 1,2-dichloroethane (DCE) using the prepared (MFAMs) as cross-linkers. The effect of crosslinking on polymer properties was evaluated and the thickening effect of the water-soluble cross-linked polymers was studied.

2. Experimental

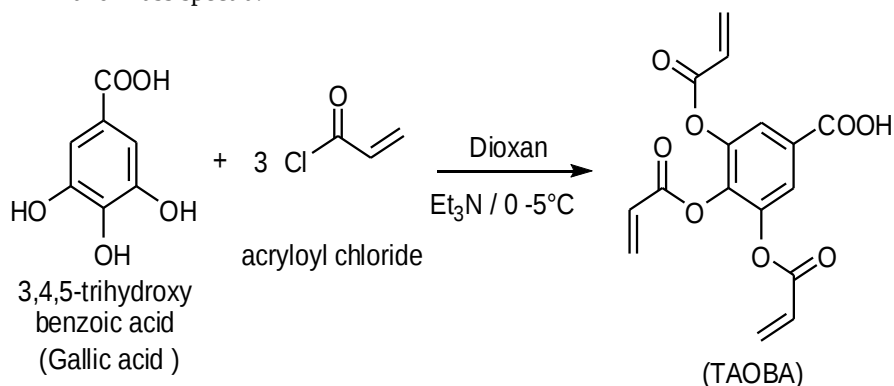
2.1. Materials

Gallic acid, diethanolamine, triethylamine and acryloyl chloride were purchased from Sigma-Aldrich Company Ltd, England. 1,2-dichloroethane and The initiator, 2,2'-azobisisobutyronitrile (AIBN) were obtained from El-Naser pharmaceutical chemical company, Egypt. Acrylic acid (inhibited with 180-220 ppm methyl ethyl hydroquinone) was obtained from EIF chem. (ATO) company, France. All chemicals were used as received.

2.2. Synthesis of multifunctional acrylate monomers

2.2.1. Synthesis of 3,4,5-tris(acryloyloxy)benzoic acid (TAOBA)

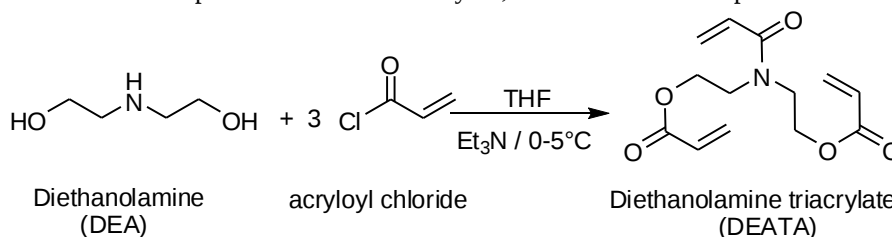
To a mixture of Gallic acid (10 gm, 0.058 mol) and triethylamine (24.75 ml, 0.176 mol) in 100 mL of dioxan was added acryloyl chloride (14.44 ml, 0.176 mol) dissolved in 10 mL dioxan dropwise under nitrogen atmosphere in an ice bath. After the mixture was allowed to warm to room temperature, it was stirred for 48 h. Dioxan and remaining acryloyl chloride were then evaporated under vacuum. Water was added to the residue, followed by two extractions with diethyl ether. The combined ether phases were washed with HCl (5 wt %) to remove the remaining triethylamine followed by washing three times with water. After drying on magnesium sulfate, filtration and removal of the solvent, the oily product was dried under vacuum pump, to remove the traces of acrylic acid. The reaction for the synthesis of TAOBA is shown in Scheme 1. The product was examined by IR, ¹H NMR and Mass spectra.



Scheme 1. Synthesis of TAOBA

2.2.2. Synthesis of Diethanolamine tri-acrylate (DEATA)

A mixture of freshly distilled Diethanolamine (9.6 ml, 0.1 mol), triethylamine (42 ml, 0.3 mol) and 100 ml THF was taken in a 250 ml one neck-round-bottom flask placed in an ice bath. The mixture was stirred well at 0-5 °C. Acryloyl chloride (24.55 mL, 0.3 mol) was added dropwise into the mixture under nitrogen atmosphere. After the addition the reaction mixture was allowed to be stirred in cold condition for 2 h and then at room temperature for 20 h. Then the precipitated triethylammonium chloride was filtered off and the solvent in the filtrate was removed using a rotary evaporator. The oily product was dried under vacuum to remove the acrylic acid residue. The reaction for the synthesis of DEATA is shown in Scheme 2. The product was examined by IR, ¹H NMR and Mass spectra.



Scheme 2. Synthesis of DEATA

2.3. Synthesis of cross-linked polyacrylic acid (cPAA)

In a typical thermally initiated free radical precipitation polymerization, a homogeneous mixture of acrylic acid, crosslinking agent and AIBN in DCE was added to a three-necked round bottom flask equipped with an overhead stirrer, nitrogen inlet, and condenser. The flask was placed in a thermostatic bath at 70±1°C. After 2-3 hr, polymer particles began to appear. The reaction was allowed to proceed for 5 hr to ensure a high percentage of monomer conversion. The precipitated slurry was filtered and washed with fresh DCE then dried. In this work two series of polymers were synthesized. The first series (SA) was synthesized by polymerization of fixed amount of acrylic acid and AIBN with different weight percentages (%) of TAOBA. The second series (SB) was synthesized by polymerization of fixed amount of acrylic acid and AIBN with different weight percentages (%) of DEATA. The Composition data of free radical polymerization are listed in table 1.

Table 1: feed composition data of free radical polymerization

Monomer(g) (AA)	AIBN(g)	SA series		SB series		DCE(g)
		TAOBA(% relative to monomer weight)	Polymer code	DEATA(% relative to monomer weight)	Polymer code	
10	0.1	0	SA ₀	0	SB ₀	100
10	0.1	0.05	SA1	0.1	SB1	100
10	0.1	0.1	SA2	0.4	SB2	100
10	0.1	0.2	SA3	0.8	SB3	100
10	0.1	0.6	SA4	2	SB4	100
10	0.1	1.5	SA5	4	SB5	100
10	0.1	3	SA6	6	SB6	100
10	0.1	6	SA7	-	-	-

Note: SA₀ and SB₀ are free radical polymerization of acrylic acid in absence of cross-linker

2.4. Viscosity studies

The polymer solution viscosity was measured in distilled water at concentration (2 wt. %) at 25 ± 1 °C with a LVDV –II+ Brookfield viscometer. A 28% ammonia solution (in different quantities) was used to adjust the pH of the polymer solution at 7.5-8. The Viscosity was measured at different rpm (3-100) to study the effect of shear rate.

3. Results and discussion

3.1. Characterization of MFAMs

The FT-IR spectrum for the (TAOBA) shows the following characteristic bands. 3492 cm^{-1} is attributed to the strong intermolecular hydrogen bond between the carboxylic groups, 2960 cm^{-1} (C–H aliphatic), 1736 and 1702 cm^{-1} (C=O ester and carboxylic groups, respectively), 1612 cm^{-1} (C=C aliphatic) and 1536 cm^{-1} (C=C aromatic).

The mass spectrum of the (TAOBA) was compatible with the molecular formula $\text{C}_{16}\text{H}_{12}\text{O}_8 \cdot \text{H}_2\text{O}$ and showed molecular ion peak at m/z (intensity %) 350(0.21), the base peak at 55(100) and other significant peaks at 332(0.29), 153(95.85) and 170(96.91).

^1H NMR spectrum of the (TAOBA) in DMSO and DMSO+ D₂O showed signals at $\delta(\text{ppm})=7.3(\text{br.s, H, COOH, exchangeable with D}_2\text{O})$, $7.03(\text{s, 2H, Ar-H})$, and $5.8-6.3(\text{m, 9H, 3 CH}_2=\text{CH-})$.⁷ Other signals at 4.1 ppm (residual water)⁸, and $3.6-3.8\text{ ppm}$ and 1.8 ppm (residual Et₂O).

The FT-IR spectrum for the (DEATA) shows bands at 2978 cm^{-1} (C–H aliphatic), 1736 and 1638 cm^{-1} are attributed to C=O stretching vibration of the ester and amide function,

respectively, and 1402 cm^{-1} (-C=C- aliphatic). The absence of the bands around 3300 cm^{-1} indicating complete acryloylation of (NH and OH) groups.

The mass spectrum of the (DEATA) was compatible with the molecular formula, $\text{C}_{13}\text{H}_{17}\text{O}_5\text{N}$. and showed molecular ion peak at m/z (intensity %) 267(3.49), the base peak at 55(100) and other significant peaks at 99(50.71) and 164(56.60).

^1H NMR spectrum of the (DEATA) in DMSO showed signals at $\delta(\text{ppm})= 5.8\text{-}6.4(\text{m}, 9\text{H}, 3\text{CH}_2=\text{CH})$, $4.19\text{-}4.29(\text{m}, 4\text{H}, 2\text{CH}_2\text{OCO})$ and $3.5\text{-}3.8(\text{m}, 4\text{H}, 2\text{CH}_2\text{NCO})$.

3.2. Characterization of the cross-linked polyacrylic acid

The FT-IR spectrum of polyacrylic acid (SA_0 , without any cross-linker) showed a strong band at 1698 cm^{-1} attributed to C=O Stretching vibration of the carboxyl function, very broad band having medium value 3484 cm^{-1} is attributed to OH stretching vibration and a band at 2950 cm^{-1} is assigned to aliphatic C-H stretching vibration of methylene and methine groups.

The FT-IR spectrum of cross-linked polyacrylic acid with (TAOBA) (SA) showed Very broad band having a medium value at 3216 cm^{-1} assigned to aromatic C-H stretching vibration coupled with OH stretching vibration of carboxylic group. The band at 2961 cm^{-1} is ascribed to aliphatic C-H stretching vibration and at 1712 cm^{-1} to C=O stretching of carboxylic group. The vinyl bands at 1680 cm^{-1} did not appear in spectra indicating that all monomeric groups are involved in polymerization reaction. The appearance of the aromatic C=C stretching at 1453 cm^{-1} indicate that the cross-linker (TAOBA) has involved in the polymerization process.

The FT-IR spectrum of cross-linked polyacrylic acid with (DEATA) (SB) showed strong band at 1713 cm^{-1} assigned to C=O stretching vibration of the carboxylic group, a band at 2960 cm^{-1} attributed to aliphatic C-H stretching vibration of methylene and methine groups, very broad band extending from 3480 cm^{-1} to 3000 cm^{-1} attributed to OH stretching vibration of carboxylic group.

3.3. Solubility studies

The polymers were soluble in DMSO, DMF, and hydroxyl containing solvents such as (methanol, ethanol, and isopropanol), but insoluble in chloroform, methylene chloride, carbon tetrachloride, 1,2-dichloroethane and hydrocarbons solvents such as (n-hexane, benzene, toluene and xylene).

3.4. Differential scanning calorimetry

The thermal properties of the polymers synthesized have been investigated by A differential scanning calorimeter (DSC-60, SHIMADZU, TA Instruments, Japan). The reported values of glass transition temperature (T_g) for PAA are $105\text{ }^\circ\text{C}$ ¹⁰, $123.7\text{ }^\circ\text{C}$ ¹¹ and $122.4\text{ }^\circ\text{C}$.⁵ In the present work the T_g of PAA, as seen in Fig. 1, is $98.22\text{ }^\circ\text{C}$ and the melting temperature is $262\text{ }^\circ\text{C}$.

The DSC curves of TAOBA and DEATA cross-linked polymers are shown in figures (2-10). As shown in Table 2, the melting temperatures T_m of cPAA with TAOBA lie between 245 and 263.5 °C while The T_m of cPAA with DEATA lies between 240.5 and 249.5 °C.

Table 2. DSC data of TAOBA and DEATA cross-linked PAA

Cross-linker Wt %	TAOBA					DEATA			
	0.05	0.2	0.6	1.5	6	0.1	0.8	2	6
Polymer Code	SA1	SA3	SA4	SA5	SA7	SB1	SB3	SB4	SB6
Glass transition Temp., T_g (°C)	120	122	122.5	117.37	132	85	114.83	111.81	117
Melting Temp., T_m (°C)	263.5	250.7	241.9	245.3	246.4	249.1	238.3	243.6	241.0
Onset flow Temp., T_{of} (°C)	180.4	194.4	184.1	178.2	184.8	184.7	180.6	179.0	180.4

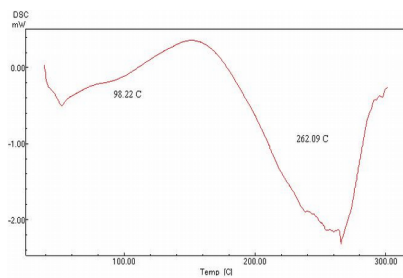


Fig.1. DSC of polyacrylic acid (SA₀)

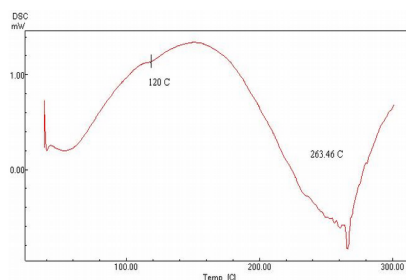


Fig.2. DSC of cPAA with 0.05% of TAOBA (SA1)

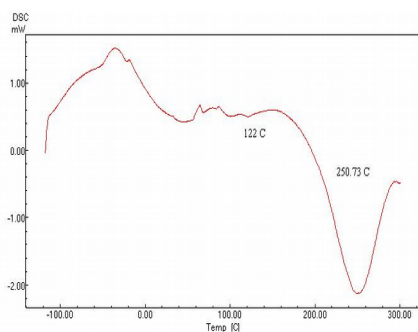


Fig.3. DSC of cPAA with 0.2% of TAOBA (SA3)

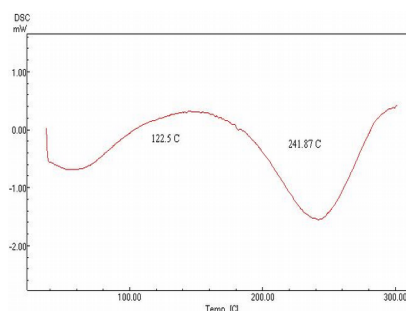


Fig.4. DSC of cPAA with 0.6% of TAOBA (SA4)

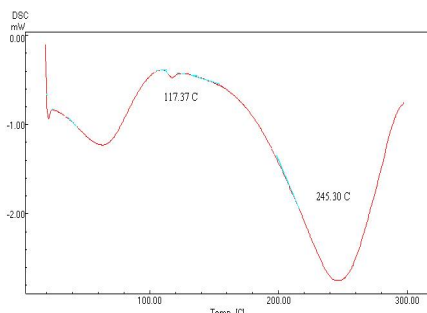


Fig.5. DSC of cPAA with 1.5% of TAOBA (SA5)

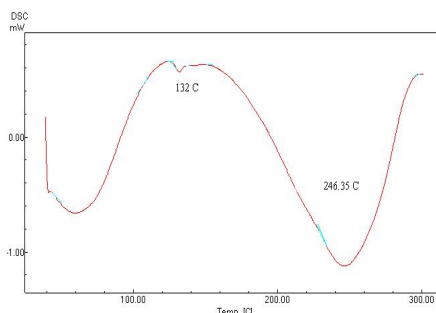


Fig.6. DSC of cPAA with 6% of TAOBA (SA7)

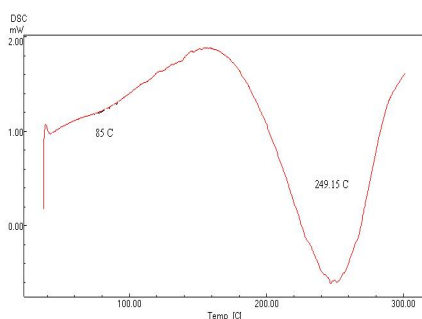


Fig.7. DSC of cPAA with 0.1% of DEATA (SB1)

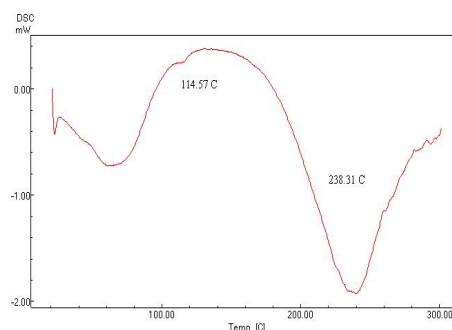


Fig.8. DSC of cPAA with 0.8% of DEATA (SB3)

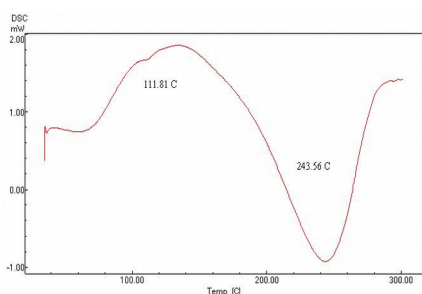


Fig.9. DSC of cPAA with 2% of DEATA (SB4)

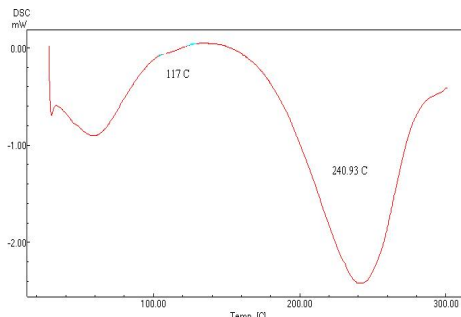


Fig.10. DSC of cPAA with 6% of DEATA (SB6)

The plots of T_g versus cross-linker concentration are shown in Fig. 11(a and b). The T_g of the cPAA with TAOBA crosslinking agent was increased as the concentration of crosslinking agent was increased. This behavior can be explained by the formation of cross-linked polymer. The mobility of the polymer chains in the networks become difficult, causing the T_g to increase. Different behavior for the T_g values of cPAA with DEATA was observed. When the concentration of DEATA was low (0.1%), the T_g decreased as compared with the T_g of PAA. This is probably

because low concentration of DEATA may produce only branched polymer. As the DEATA concentration increased further, Tg began to increase indicating the formation of cross-linked polymer.

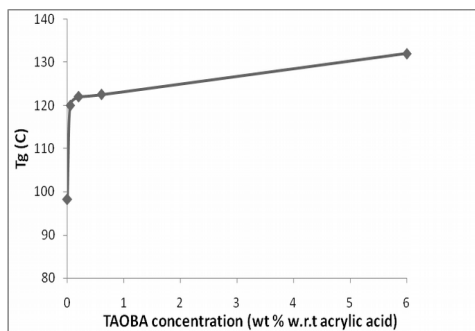


Fig.11 (a). Effect of (TAOBA) conc. on the Tg

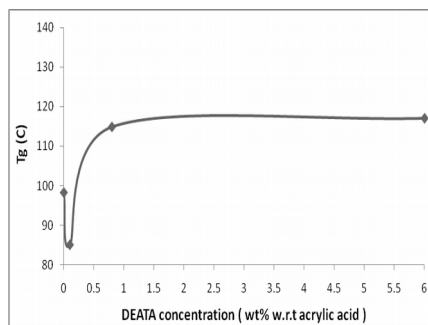


Fig.11 (b). Effect of (DEATA) conc. on the Tg

3.5. Viscosity study

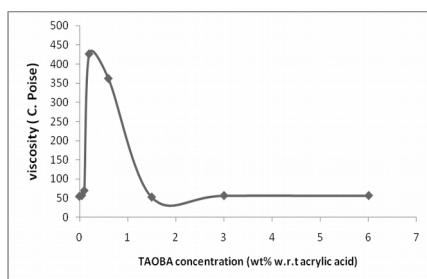
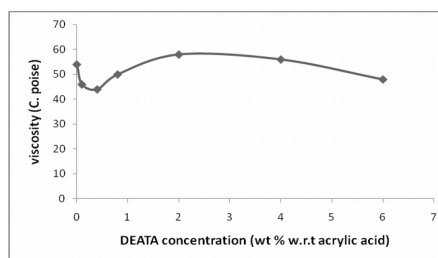
Cross-linked, water soluble PAA is good thickener. To evaluate the water solubility of the present polymers, 0.1g polymer was dispersed in 10 ml distilled water. The mixture was stirred for 24 hr. at room temperature. The mixture then was allowed to stand for a week at room temperature. For (SA) polymers SA1, SA2, SA3 and SA4 were completely soluble in water, SA5 and SA6 were partially soluble but SA7 was insoluble (i.e., a settled layer at the bottom of the vial was observed). For (SB) polymers SB1, SB2 and SB3 were completely soluble in water, SB4 and SB5 were partially soluble but SB6 was insoluble.

The viscosity of the polymer solutions was studied by dissolving 2 g polymer in 100 ml distilled water. The pH was raised to 7.5 by addition of ammonia solution (28 %). The viscosity of these solutions then measured at $25\pm 1^\circ\text{C}$ with a LVDV-II+ brookfield viscometer at 3 rpm using spindle 61. Measurements were carried out at 3 rpm because at low rpm the effect of shear rate on the viscosity is not significant and the influence of the chemical structure of cross-linked polymers can be studied. The viscosity results are listed in Table 3.

Table 3. Viscosity results (SA and SB) at (2% solid content, 3 rpm, and spindle 61)

Polymer code	Conc.(%) (TAOBA)	Vis. (cp)	Polymer code	Conc.(%) (DEATA)	Vis. (cp)
SA ₀	0	54	SB ₀	0	54
SA1	0.05	56	SB1	0.1	46
SA2	0.1	69	SB2	0.4	44
SA3	0.2	426	SB3	0.8	50
SA4	0.6	362	SB4	2	58
SA5	1.5	52	SB5	4	56
SA6	3	56	SB6	6	48
SA7	6	56	-	-	-

The effect of cross-linkers on the viscosity of polyacrylic acid (PAA) solutions is shown in Figs.12 and 13. When the concentration of the cross-linker (TAOBA) was less than 0.2 % the viscosity of the aqueous solutions increased dramatically with the cross-linker concentration, as shown in Fig 12. As the cross-linker concentration increase, the viscosity went through a maximum (426 cp) and began to decrease. This behavior can be explained as follows: when the cross-linker concentration was greater than 0.2 wt %, the polymers were at least partially insoluble in water, decreasing the thickening effect of the polymer.

**Fig.12. The effect of (TAOBA) concentration on the polymer thickening effect.****Fig.13. The effect of (DEATA) concentration on the polymer thickening effect.**

Out of the cross-linked polymers listed in Table 3, SA3 containing 0.2wt% TAOBA which having the maximum viscosity was chosen for studying the effect of shear rate.

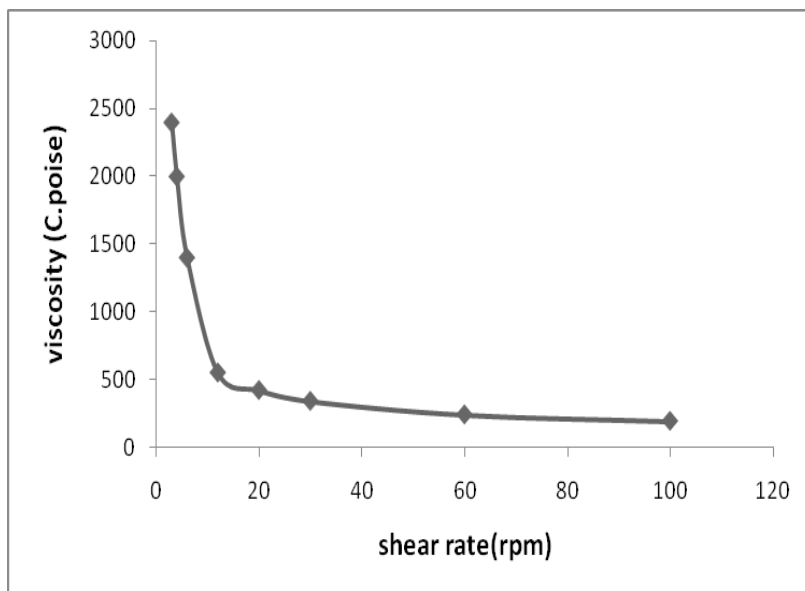
Effect of shear rate on viscosity

The effect of shear rate on the viscosity of selected SA3 polymer was studied at 3-100 rpm using spindle 64 (solid content 2%) and the data are listed in Table 4.

Table 4. Effect of shear rate on the viscosity of SA3 polymer.

Shear rate(rpm)	100	60	30	20	12	6	4	3
Viscosity (cp)	192	240	340	420	550	1400	2000	2400

The plot of viscosity versus shear rate is shown in Fig.14. The lowest viscosity (192 cp) was observed at 100 rpm but the highest viscosity (2400 cp) was observed at 3 rpm. The observed drop in the viscosity values with increase in shear rate may be related to the break down of the hydrate or solvent enveloped network polymer in the solutions by the mechanical action.¹²

**Fig.14. Effect of shear rate on viscosity of SA3**

3.6. Gel permeation chromatography (GPC)

The selected SA3 polymer was characterized in term of weight, number average molecular weight (M_w and M_n) and polydispersity using GPC technique. As shown in Fig.15. The number average molecular weight (M_n) was 447057, the weight average molecular weight (M_w) was 784714 and the polydispersity (M_w / M_n) was 1.75. GPC data showed that one of the main reasons for the higher thickening efficiencies of the cross-linked PAA in many systems is attributable to the higher molecular weight.

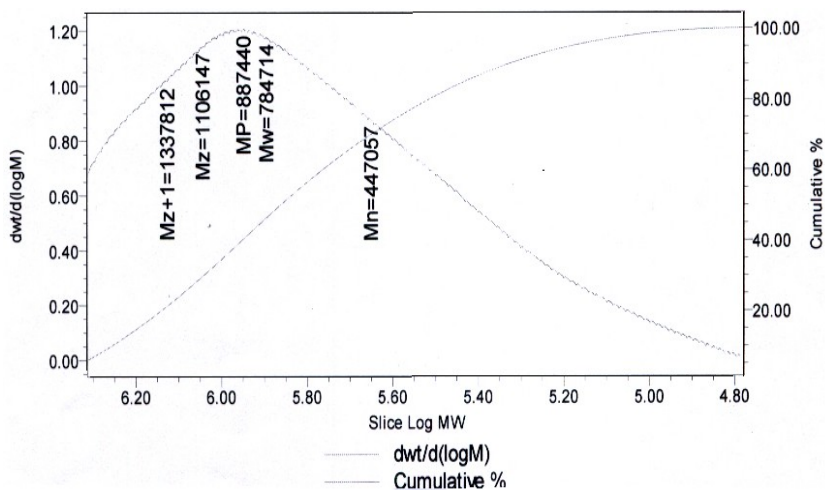


Fig.15. GPC data of SA3 polymer

3.7. Storage stability

The Brookfield viscosity of SA3 polymer was measured at 24 h intervals for 7 days. Where no change in the viscosity of the stock was observed, thus establishing the high shelf life of the thickeners.

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