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Synthesis of Poly (Amido-Amine) and Its Application for Removal of Metal Ions

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ABSTRACT

Poly (amido-amine) such as poly(acrylamide-acrylic acid-dimethylaminoethyl-methacrylate) P(AM-AA-DMAEM) was prepared by gamma irradiation induced template polymerization of acrylic acid on in the presence of poly(acrylamide-dimethylaminoethylmethacrylate) as a template polymer. The polymerization was studied by a free radical mechanism in aqueous solution and the hydrogel was obtained. The swelling degree of the formed hydrogel increases by increasing the polymer/monomer molar ratio and decreases with increasing the monomer concentration. The swelling degree was also found to depend on the radiation dose. The results showed that the capacity of the obtained hydrogel was found to be maximum at polymer/monomer molar ratio of 1.3. The capacity of the polymeric materials increases with increasing the monomer concentration and decreases with increasing the radiation doses. The metal cations interact with polymeric chains to form a cross-linked structure after cation build-up. This interaction occurs through complex formation between amide and amine groups with cations whereas the carboxylic group interacts by cation-exchange mechanism.

Key Words: Synthesis / Poly(amido-amine) / Hydrogyl / Heavy metals / Waste Water

INTRODUCTION

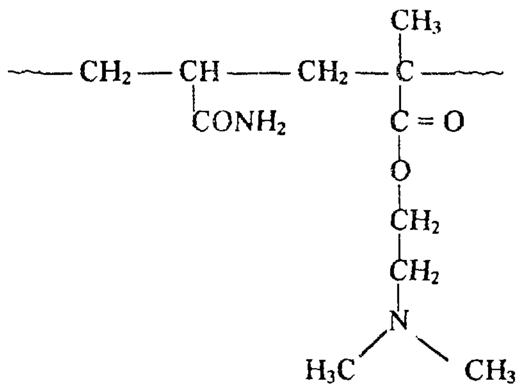
Hydrogel of poly(acrylic acid-dimethylaminoethylmethacrylate) P(AA-DMAEM) was prepared by a template polymerization of dimethylaminoethylmethacrylate (DMAEM) on poly(acrylic acid) PAA [1]. Poly(amido-amine) resins were prepared by a template polymerization of acrylic acid on cationic polymers such as: poly(acrylamide-diallylamine-hydrochloride) P(AM-DAA-HCl), poly(acrylamide-diallylethylamine-hydrochloride) P(AM-DAEA-HCl) and poly(diallylethylamine-hydrochloride) P(DAEA-HCl)[2-4]. These resins were used in treatment of waste water. In this work we have studied the template polymerization of acrylic acid on prepared poly(acrylamide-dimethylaminoethyl-methacrylate) as a template polymer. The effect of the experimental conditions such as radiation doses, polymer/monomer molar ratios and monomer concentrations on the swelling degree of the obtained polymeric material were investigated. The capacity of the hydrogel toward some cations was determined. The swelling degree of the obtained polymeric materials was investigated and the capacity of the hydrogel toward some cations was determined.

MATERIALS AND EXPERIMENTAL TECHNIQUE

Acrylic acid (AA) and dimethylaminoethylmethacrylate (DMAEM) inhibited by hydroquinonmono-ethylether which were used after distillation under vacuum. Reagent grade acrylamide (AM) was used as received.

1- Preparation of poly(acrylamide-dimethylaminoethylmethacrylate) p(AM-DMAEM):

P(AM-DMAEM) was preparated by gamma irradiation initiated copolymerization of acrylamide (AM) with dimethylaminoethylmethacrylate (DMAEM) in aqueous solution at molar ratio of 0.7 : 0.3 and total comonomer concentration of 12%. The mixture was subjected to radiation dose of 30 KGy. The formed copolymer was found to be gel with a swelling degree of 282. The structure of the copolymer can be represented as shown in structure (1):



Structure (1): P(AM-DMAEM)

2- Preparation of hydrogel:

Polymer/monomer mixture p(AM-DMAEM)/AA was prepared by dissolving p(AM-DMAEM) and AA at the requsite concentration in a de-oxygenated water. The prepared mexture was subjected to γ-irradiation from Co-60. After the irradiation the reaction mixture was then taken and poured into acetone to precipitate the formed copolymer. The hydrogel was dried under vacuum at 50°C to a constant weight.

The percent of AA in the hydrogel was determined using the following equation:

$$\text{The percent of AA} = \frac{\text{Weight of AA in the polymer}}{\text{Total weight of the polymer}} \times 100$$

The swelling degree is calculated using the following equation:

$$S = (W_S - W) / W$$

where W_S and W are the weight of the polymer after and before the polymer swelling, respectively.

3- Capacity determination:

The hydrogel was treated with 0.1 N NaOH to neutrolize the carboxylic groups then, the hydrogel was dried under vacuum at 50°C to a constant weight.

The capacity of the hydrogel was determined by a batch technique,[5] 20 ml of the metal salt solution (0.1 N) was added to 40 mg of the hydrogel. The percent of uptake on the gel for cations was determined spectro-photometrically [6]. The capacity of the hydrogel in m mol/g was calculated using the following equation:

$$\text{Capacity} = \frac{\%\ \text{uptake}}{100} \times C_o \times V/m \qquad \text{m mol/g}$$

where,

C_o is the initial concentration of the metal salt solution (mol/L)

V is the solution volume, ml and m is the weight of the polymer, gm.

RESULTS AND DISCUSSION:

Influence of Polymer/Monomer Molar Ratio:

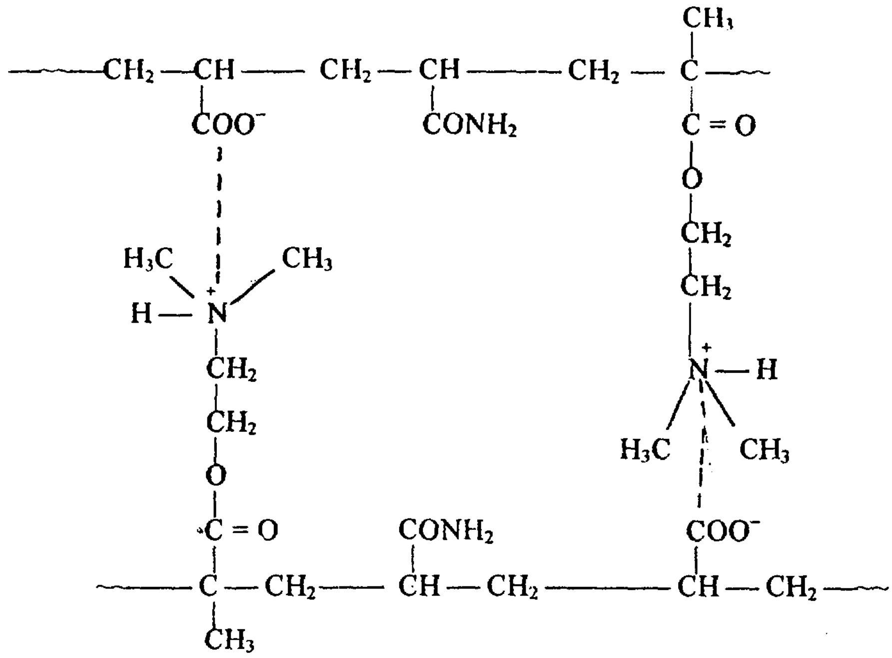
The influence of polymer/monomer (P/M) molar ratio on the template polymerization of AA oı p(AM-DMAEM) was studied at radiation dose of 20 KGy. The composition of the resultant polyme are calculated as shown in Table (1) which shows that that the percent and the molar ratio of A/ decreases with increasing P/M molar ratio. This can be attributed to increasing the concentration of th added p(AM-DMAEM) and decreasing the concentration of the monomer AA in the reaction mixture.

Table (1): Influence of polymer/monomer (P/M) molar ratio on the composition of the polymer

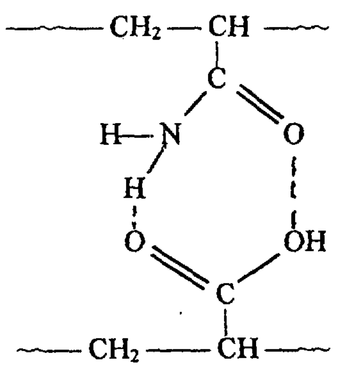
P/M molar ratio	Polymer composition					
	Percent			Molar Ratio		
	AM	AA	DMAEM	AM	AA	DMAEM
0.66	22	62	16	0.24	0.68	0.08
1.00	27	53	20	0.30	0.59	0.11
1.32	32	45	22	0.34	0.56	0.10
1.66	35	40	25	0.41	0.46	0.13

The template polymerization of AA in the presence of hydrogel of p(AM-DMAEM) as a templa polymer produces hydrogel of p(AM-AA-DMAEM) and the swelling degree of the obtained polym decreases relative to the original polymer p(AM-DMAEM). The swelling degree and the capacity of tl obtained polymeric gels toward Cu^{2+} were studied. The results are shown in Figure (1) which shows th the swelling degree increases with increasing P/M molar ratio. On increasing P/M molar ratio tl concentration of AA in the formed polymer decreases which leads to decrease both the compl formation between the carboxylic and the amino group [7], and the hydrogen bonding associati (plurimolecular aggradation) between -COOH and $-CONH_2$ groups. These complex formation and tl association between the functional groups of the polymeric chains lead to formation of crosslinki between the polymeric chains as shown in structures (1&2), respectively. When P/M molar rat increases. The degree of crosslinking decreases which increases the swelling of the formed polymer.

The results of Fig. (1) shows that the capacity increases with increasing P/M molar ratio whereas high P/M molar ratio the capacity decreases. At low polymer concentration syneresis occurs, yieldi strongly heterogeneous gel; even if syneresis is avoided large proportion of dangling chains and loop produced. Higher concentration of precursor polymer increase the probability for permanent trapp entanglements to occure. Moreover, at very high viscosity of the medium may be favorable for t formation of heterohomohenetities within the gel at which iterpenetration of chains begins(. Consequently, the capacity of the gel increases. In addition, on increasing P/M molar ratio, the compl formation [11-13] and the association between the polymeric chains increase which leads to increase in t extent of crosslinking between polymeric chains. Hence, the capacity of the gel increases. At high P/ molar ratio of 1.6 the capacity decreases may be attributed to higher increase in the extent crosslinking as a result of higher increase in the concentration of the template polymer.



Structure (1): Complex formation between the polymeric chains



Structure (2): Pluremolecular aggragation between the polymeric chains

2- Influence of Monomer Concentration:

The influence of monomer concentration on the swelling degree and the capacity toward Cu^{2+} for the obtained hydrogel as a result of template polymerization was studied at polymer concentration of 3% and radiation dose of 20 KGy. The results are shown in Fig.(2), which shows that the swelling degree decreases whereas the capacity of the hydrogel toward Cu^{2+} increases with increasing the monomer concentration. The swelling degree decreases with increasing the monomer concentration as discussed above in item 1 (Table (1) and Fig.(1)). On increasing the monomer concentration the probability of complex formation and the association increase. These increase the degree of corsslinking between the polymeric chains. In addition, the number of carboxylic groups increases which leads to increase the interaction with the cation. Hence, the capacity of the gel increases. At high monomer concentration the capacity decreases may be attributed to higher increase in the extent of crosslinking between the polymeric chains[13].

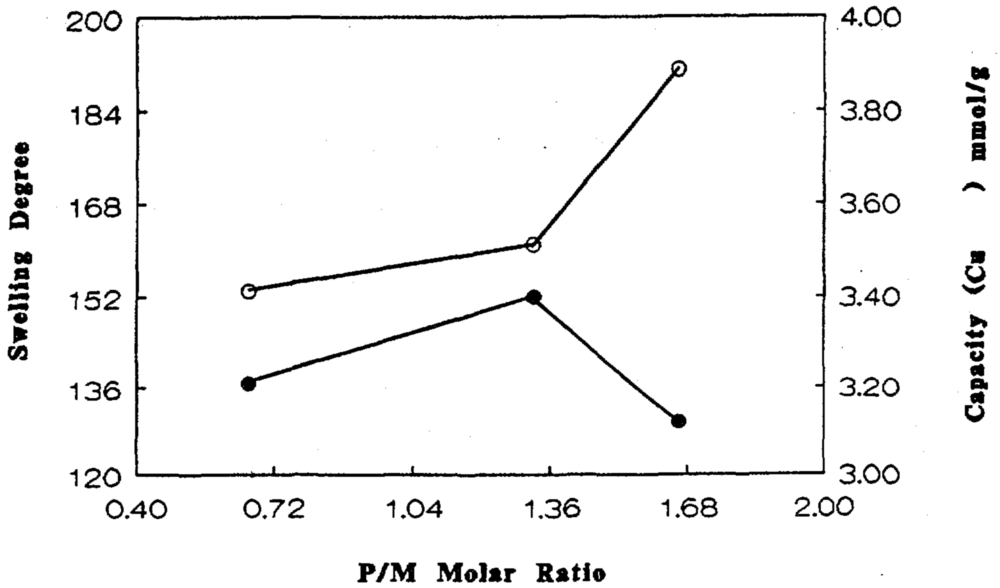


Figure (1): Influence of P/M molar ratio on the swelling degree and capacity,
o swelling degree & • capacity

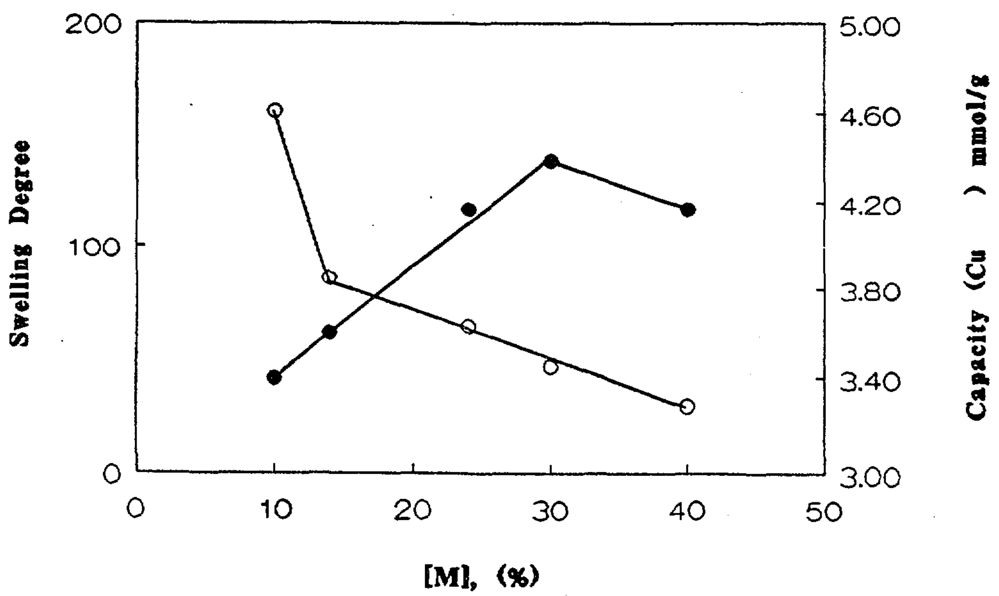


Figure (2): Influence of monomer concentration on the swelling degree and capacity,
o swelling degree & • capacity

3- Influence of Radiation Doses:

The influence of radiation on the swelling degree and the capacity of the hydrogel toward Cu^{2+} for the obtaind hydrogel from the template polymerization was studied at P/M molar ratio of 1.3 and monomer concentration of 10%.

The results are shown in Fig.(3) which shows that the swelling degree increases with increasing the radiation dose then decreases. The increase in the swelling degree can be attributed to the effect of γ-irradiation on the formed polymer. This increases the degree of branching [14-17] between the polymeric chains for gel formation [15-18]. In addition, the complex formation and the association between the functional groups of the polymeric chains increase as mentioned hereabove (item 1) which leads to higher branching between the polymeric chains. At higher dose the swelling degree decrease can be attributed to higher increase in the extent of crosslinking as a result of irradiation which hinders the swelling of the polymer.

Figure (3) shows also that the capacity increases with increasing the radiation whereas at high dose the capacity decreases. The increase in the capacity by increasing the radiation dose may be attributed to increasing the degree of crosslinking between the polymeric chains due to irradiation [2,3,6,13-17]. The decrease in the capacity at high doses may be attributed to imidiation of amide groups [14-18] and the decrease in the number of carboxylic groups [6,19].

In addition at high dose the higher increase in the extent of cross-linking between the polymeric chains decreases the capacity of the hydrogels [19,20].

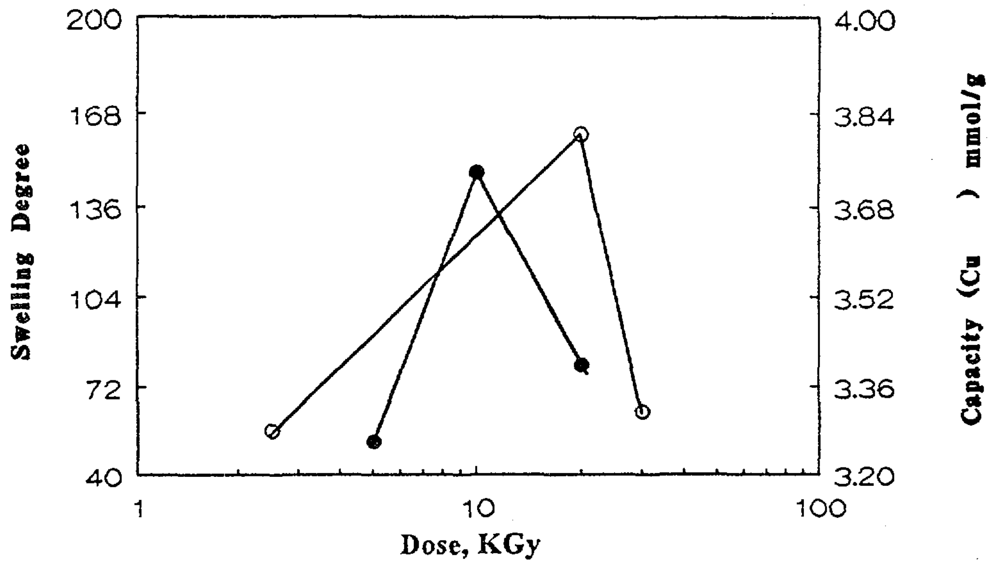


Figure (3): **Influence of radiation dose on the swelling degree and capacity,**
o swelling degree & • capacity

4- Sorption of Metal Ions on Polymers:

The sorption of metal ions such as Co^{2+}, Cu^{2+}, Ni^{2+}, UO_2^{2+} and Th^{4+} on the hydrogel was studied at different pH. The capacity of the hydrogel toward Th^{4+} and UO_2^{2+} was determined at pH ~2 to prevent the hydrolysis of these metal salts. The capacity was determined and the results are given in Table (2) which shows that the capacity of the investigated metals follows the order:

$$Co^{2+} > Cu^{2+} > Ni^{2+} > Th^{4+} > UO_2^{2+}$$

This order reflects agreement with the stability constant of metal complexes with ligands containing donor atom such N and O [21]. P(AM-AA-DMAEM) contains N and O is similar to other polymers [2-5,8,22-27] which can bind or complex metal ions.

Table (2): Variation of capacity of p(AM-AA-DMAEM) toward metal ions

Metal salts	pH	Capacity, mmol/g
$CoCl_2.6H_2O$	4.23	6.57
$CuSO_4.5H_2O$	4.16	4.17
$NiSO_4.7H_2O$	4.80	3.50
$Th(NO_3)_4$	2.47	1.33
$UO_2(NO_3)_2.6H_2O$	2.20	1.22

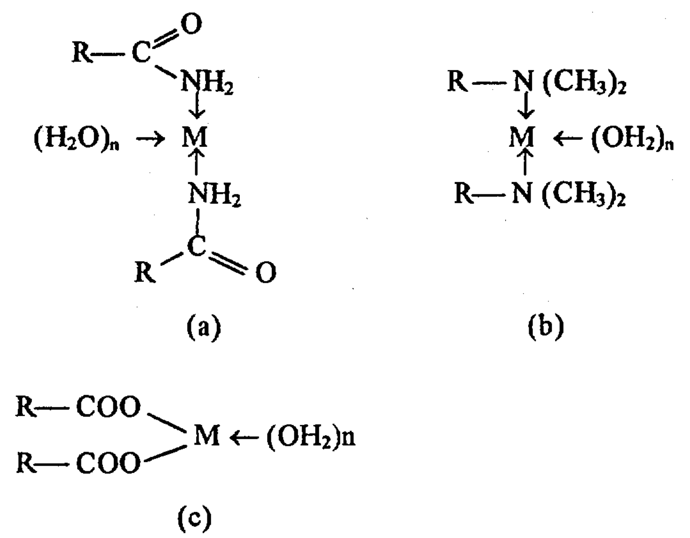
The lower the value of the capacity of the gel toward UO_2^{2+} and Th^{4+} may be attributed to the effect of pH. At lower pH-values the amide and the amino group of the polymeric chains are mostly present in the protonated from leading to imidation of amide groups with the formation of intermolecular crosslinking between the polymeric chains as mentioned above. By increasing the pH, the degree of protonation and imidation of amide and amine groups decrease, this leads to increasing the probability of interaction between the gel and the cations in the aqueous solution with the complex formation.

P(AM-AA-DMAEM) interact with metal ions to form a crosslinked structure according to the possible mechanisms which can be represented in structures (3&4).

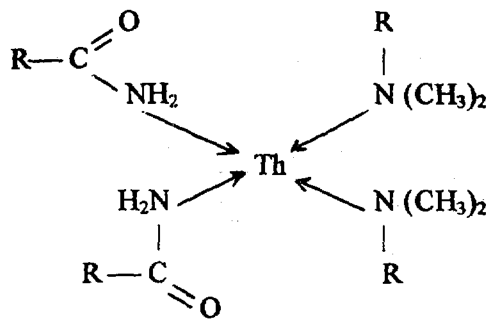
a- Amide and amino groups form complex with metal ions.

b- Carboxylic carboxylate group interact with metal ions through cation-exchange mechanism.

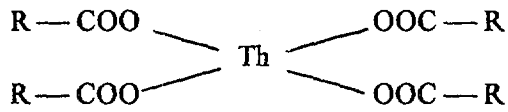
This is in agreement with the suggested mechanisms for interaction of poly(amido-amine)[2,3,8,9,27,28-31], polyacrylamide [32] and poly(acrylamide-acrylic acid)[2-4,8,9,13] with cations.



Structure (3): Formation of crosslinked between P(AM-AA-DMAEM) with cations, where M= Co^{2+}, Cu^{2+}, Ni^{2+} and UO_2^{2+} and n is number of water of crystalization.



(a)



(b)

Structure (4): Formation of Crosslinked between P(AM-AA-DMAEM) and Th^{4+}

REFERENCES

(1) Z.H. Abd-Elatif, Polym. Internat., 28, 301 (1992).

(2) T. Siyam, 3rd Arab Intern. Conf. on Polymer Science and Technology, 4-7 Sept., I, 43, Mansoura Univ., Mansoura, Egypt (1995).

(3) T. Siyam, I.M. El-Naggar and H.F. Aly, Nuclear and Hazardous Waste Management Intern. Topical Meeting, Spectrum'96, 18-23, Aug., Seattle, Washington, p.66 (1996).

(4) T. Siyam, Macromolecular Reports, A31 (Suppls. 3&4), 383 (1994).

(5) T. Siyam, M.M. Abdel-Hamid and I.M. El-Naggar, Macromolecular Reports, A32 (Suppls, 5&6) 871 (1995).

(6) Z. Marczenko, Spectrophotometric Determination of Elements, Eillis Horwood Ltd Chichester, 310 (1976).

(7) Z.H. Abd-Elatif, 1st Arab Intern. Conf. on Polymer Applications, p.67, Fac. of Sci. Mansoura Univ. Mansoura, Egypt Sept. (1991).

(8) T. Siyam, Gamma Radiation-Induced Preparation of Polyelectrolytes and Its use for Treatment of Wastewater, in Chermisnoff (ed.) Handbook of Engineering Polymeric Materials Ch.9, 119-135, Marcel Dekker Inc. (1997).

(9) T. Siyam, H.A. Youssef and I.M. El-Naggar, 6th Intern. Conf. on Energy and Environment, 18-21 May, p.II, 609 Cairo, Egypt. ( )

(10) S.Candau, J. Bastide and M. Delsanti, Structureal, Elastic and Dynamic Properties of Swolen Polymer Networks, In: Advances in Polymer Science (Polymer Netwarks) Springer-Verlag Berlin Heidelberg N.Y. (1982).

(11) K. Fujimore, Polym. Bull., 8, 207 (1982).

(12) K. Fujimore, G.T. Trainor & M.J. Costigan, J. Polym. Sci., A-1, 22, 2479 (1984).

(13) T. Siyam and R. Ayoub, J.M.S. -Pure Appl. Chem. A34(9), 1727 (1997).

(14) T. Okuda, I. Ishigaki, T. Suwa and S. Machi, J. Appl. Polym. Sci., 24, 1713 (1979).

(15) A. Chapiro, Radiation Chemistry of Polymeric Systems Interssci. Publ. Inc. N.Y., Ch. IV, pp.130-155 (1962).

(16) H.J.J., W.K.Zhang, Z.W. Sun., J.J. Che, and Z.H.Li, Radiat. Phys. Chem., 42 (1-3), 81 (1993).

(17) T. Siyam, Egypt. J. Chem. 38(1), 91 (1995).

(18) T. Wada, H. Sekiya and S.Mchi, J. Appl. Polym. Sci., 20, 3233 (1976).

(19) E.V. Egorov and P.D. Novikov, Action of Ionizing Radiation on Ion-Exchange Materials, A tomizat, Moscow (1965).

(20) A.M. Semushin and I.A. Kuzin, Zhur Prikl. Khim., 33, 2323 (1960).

(21) L.G. Sillen and A.E Martell, Stability Constants of Metal-Ion Complexes, Supplement No. 1, The Chemical Society, London, Special Publication No. 25 (1971).

(22) M.M. Jones, H.D. Coble, T.H. Partt and R.D. Harbison, J. Inorg. Nucl. Chem., 37, 2409 (1975).

(23) G.A. Nyssen, M.M. Jones, J.D. Jernigan, R.D. Harbison and J.S. MacDonald, J. Inorg. Nucl. Chem., 39, 1889 (1977).

(24) K.A.K. Ebraheem, J.A.Al-Duhan and S.T. Hamid, Eur. Polym. J., 21, 97 (1985).

(25) M.M.Jones, J. Inorg. Nucl. Chem., 25, 40, 1235 (1978).

(26) K.A.K. Ebraheem, S.T. Hamid and J.A. Al-Duhan, J.M.S. -Pure Appl. Chem., A34 (9), 1691 (1997).

(27) I. Karatans and G. Iraz, Macromolecular Reports, A30 (Suppls. 3&4), 341 (1993).

(28) T. Siyam and E. Hanna Macromolecular Reports (Suppls 3&4), A31, 349 (1994).

(29) E. J. Goethals, Polymeric Amines and Ammonium Salts, (International Symposium on Polymeric Amines and Ammonium Salts), Ghent, Belgium, 24-26 Sept. 1979, pp.229, 255, 263271, 282, Pregamon Press (1979).

(30) S.Savost'yanov, V.V.Pbyugin, D.A.Kvitskays and A.N.Pohmarev, Bvestiya-I3 Vestiya Akademii-Nauk-Seria-Khimich, 6, 1070 (1993).

(31) T. Siyam, H.A. Youssef and I.M. El-Naggar, J.M.S.-Pure Appl. Chem. A34(11), 2379 (1997).

(32) M.A.Moharram, S.M. Rabie and A.Y. Daghistumi, J. Appl. Polym. Sci., 50(3), 459 (1993).

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