GAMMA RADIATION-INDUCED PREPARATION OF POLY(DIMETHYLAMINOETHYL METHACRYLATE-ACRYLAMIDE-ACRYLIC ACID) AS EXCHANGER

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GAMMA RADIATION-INDUCED PREPARATION OF POLY(DIMETHYLAMINOETHYL METHACRYLATE-ACRYLAMIDE-ACRYLIC ACID) AS EXCHANGER

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ABSTRACT

The polymeric material of poly(acrylamide-acrylic acid-dimethylaminoethylmethacrylate) "PAM-AA-DMAEM" was prepared by gamma radiation-induced polymerization of dimethylaminoethylmethacrylate (DMAEM) in the presence of prepared poly(acrylamide-acrylic acid) "PAM-AA" as a template polymer by using a template polymerization technique.

The effect of gamma radiation on the polymerization process showed that the conversion increases with increasing the radiation dose. The obtained polymer is water-soluble polymer at low

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doses <10 KGy. On increasing the radiation dose, the polymer was converted into a gel and the swelling degree was found to vary from 15 to 36. It was found that the capacities of the obtained polymeric gels toward Cu^{2+} increase with increasing the radiation dose, monomer concentration and the template polymer/ monomer molar ratio.

Spectroscopic studies showed that the mechanism of the floc formation after cation build-up is due to the interaction between the polymer and copper sulfate is a bond formation between the active groups of polymer chains and ions of copper sulfate. The amide and tertiary amino groups form complex with Cu^{2+} while carboxylic group interacts with Cu^{2+} through cation-exchange mechanism.

INTRODUCTION

Template or matrix polymerization, also termed replica polymerization, may be defined as the polymerization of monomer molecules in an organized array. One major objective in studying matrix polymerization is to devise system in which the properties of the template are replicated in the daughter polymer, thus conferring special characteristics on the product. The rate of polymerization was found to be dependent on the ratio of template to the monomer. The macromolecular matrix thus permits chain growth at lower temperatures. The monomer chosen must be capable of interacting with and polymerizing along, preferably linear template macromolecules. The interaction may be covalent, ionic, hydrogen bond or a van weals type. In addition, the distance between consecutive monomer units, mutual steric orientation and mobility of the monomer are important factors [1]. In this type of polymerization, complexes can be formed between two different type of polymer under suitable conditions [1-5].

For a template polymerization initiated by initiator, Smid *et al*. [6-11]. suggested the mechanism for initiation reaction (Equations 1 and 2).

$$I \longrightarrow 2R` \qquad\qquad\qquad (1)$$

$$R` + M \longrightarrow RM` \qquad\qquad\qquad (2)$$

where I is an initiator and R` is the formed free radical.

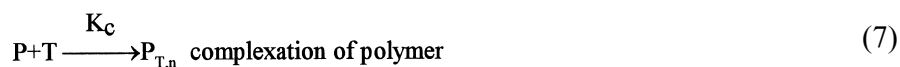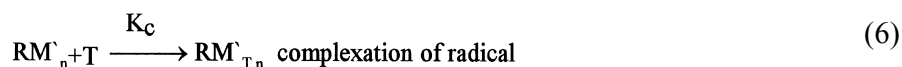In gamma radiation-initiated the polymerization in the presence of added template (T), the initiation reactions can be written according to Chapiro's suggestion [12] as shown in Equations 3 and 4.

$$A \longrightarrow 2R` \tag{3}$$

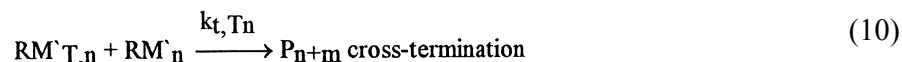$$T \longrightarrow 2T` \text{ or } T`+R` \text{ (R` small radical)} \tag{4}$$
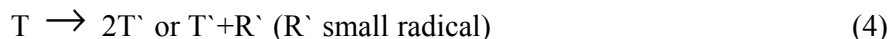
where A is a monomer or a solvent and T is the added template polymer. All the radicals generated are available to contribute to the chain initiation.

For a template polymerization system in which the monomer is preferentially interacted with the template polymer. Challa *et al.* [6] and Smid [7-10] suggested the following mechanism for interaction of the added template polymer (T) with the monomer (M), the radical ($RM`_n$) and the formed polymer (P). The complexation reaction can be written as seen in Equations 5-10.

$$M+T \underset{}{\overset{K_L}{\rightleftharpoons}} M.T \text{ adsorption equilibrium of monomer} \tag{5}$$

$$RM`_n+T \xrightarrow{K_C} RM`_{T,n} \text{ complexation of radical} \tag{6}$$

$$P+T \xrightarrow{K_C} P_{T,n} \text{ complexation of polymer} \tag{7}$$

Reactions steps associated with the template (Equations 8, 9, 10).

$$RM`_{T,n} + M \xrightarrow{k_p,T} RM`_{T \ n+1} \text{ template propagation} \tag{8}$$

$$RM`_{T,n} + RM`_{T,n} \xrightarrow{k_p,T} RM`_{T \ n+m} \text{ template termination} \tag{9}$$

$$RM`_{T,n} + RM`_n \xrightarrow{k_t,Tn} P_{n+m} \text{ cross-termination} \tag{10}$$
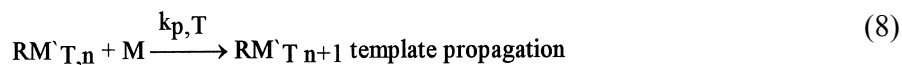
Consequently, the propagation reactions occur by possible steps [11]:

a) the monomer may be propagated by the free radicals R` or T`; b) the monomer may be complexed with the added polymer (Equation 5) and propagated according to the "Zipping-up" mechanism [4, 13-15] in which the monomer is aligned in a regular manner on the polymer; c) the monomer may be complexed with the formed polymer and also propagated by the "Zipping-up"

mechanism [16,17]; and d) the growing radical may be complexed with the added polymer (Equation 6) and attacking the monomer molecules from the bulk (template propagation, Equation 8).

All propagating radicals are terminated with each other according to Equations 9 and 10 or complexed according to Equation 7 to form dead polymers containing the chains of the polymerized monomer which are associated (complexed) or linked with the chains of the template polymer.

In the present work, we have studied the effect of radiation dose, the polymer/ monomer molar ratio and the monomer concentration on the polymerization of DMAEM in the presence of poly(acrylamide-acrylic acid) "PAM-AA". The capacities of the obtained polymeric materials toward Cu^{2+} were determined.

EXPERIMENTAL

Poly(acrylamide-acrylic acid) PAM-AA was prepared by the copolymerization of acrylamide with acrylic acid at the optimum conditions for the copolymerization process [18]. Dimethylaminoethyl methacrylate (DMAEM) was a product of Koch-light Laboratories Ltd. inhibited by hydroquinonmonoethylether which was used after distillation under vacuum. The template polymerization technique for the polymerization process was carried using gamma irradiation from Co-60 with a dose-rate of 3KGy/hr as described previously [11]. The conversion percent was determined gravimetrically. The percent of DMAEM in the obtained gel was determined using Equation 11.

The percent of MDMAEM = Weight of DMAEM/Total weight of polymer.

The swelling degree(s) is calculated using Equation 11

$$S = (Ws - W)/W \qquad\qquad (11)$$

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

The capacity of the obtained polymeric gel toward Cu^{2+} was also determined as described previously [19] at pH ~6 using NaOH, and copper sulfate concentration of 0.04 M/L at room temperature (25°C).

RESULTS AND DISCUSSION

Influence of the Radiation Dose on the Polymerization Process

The influence of the radiation dose on the polymerization of DAMAEM in the presence of PAM-AA (0.86:0.14) was studied at equal molar ratio of monomer and polymer $[M] = [T] = 0.64$ M/L. The results are shown in Figure 1 which shows that the conversion percent increases with increasing the radiation dose. At higher doses, the conversion percent increases slowly. The increase in the conversion can be attributed to the gel-effect of such system and the complex formation between the monomer and the polymer as shown in Structure 1.

This complex formation helps the monomer to be adsorbed on strongly ionized PAA. The adsorbed monomer is excited by induced polarization aggregates to generate an initiation radical species [20]. However, the formation of the complexed polymer radical retards the termination and enhances both the polarization rate and the average molecular weight [13, 20-22].

In the gel-state, as the conversion percent increases the viscosity of the medium highly increased is due to the presence of the template polymer [23]. The growing chains are trapped in the viscous medium. So, the conversion percent is suddenly increased. At high conversion, the propagation reaction is reduced as a result of slower migration of monomer molecules to react with the active growing chains. When the active chain end is buried in a polymer domain of the template polymer, the monomer has to penetrate into the domain in order
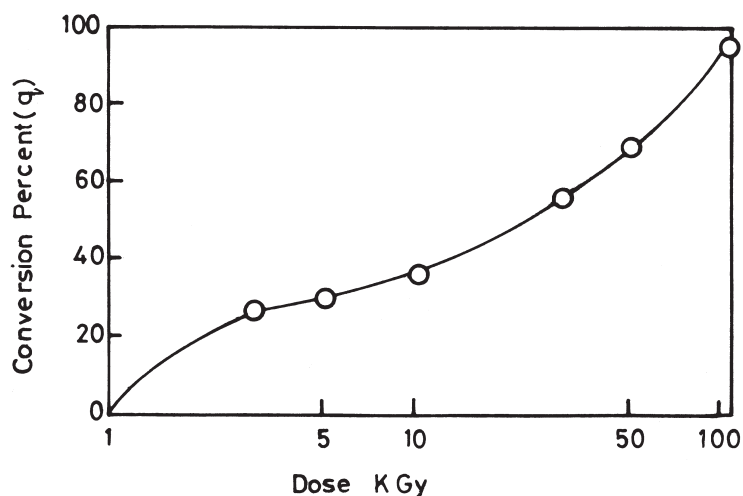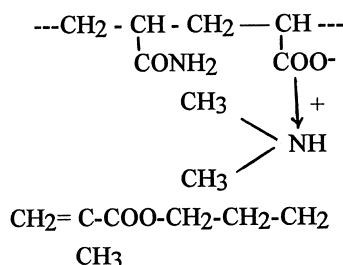

Figure 1.   Influence of radiation dose on the polymerization of DMAEM.

$$---CH_2 - CH - CH_2 \longrightarrow CH ---$$

$$CONH_2 \qquad COO^-$$

$$CH_3$$

$$\searrow \quad |^+$$

$$NH$$

$$CH_3 \nearrow$$

$$CH_2= C\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}CH_2$$

$$CH_3$$

Structure 1.   Monomer-polymer complex

to react with the active center. The penetrating monomer may complex with the polymer in the process decreasing its mobility and chemical reactivity [24]. This leads to a decrease in the conversion percent at high doses. Termination may be hindered when the active site is buried in the polymer domain [21]. This is similar to the previous findings [11, 25, 26] in the template polymerization of acrylic acid on poly(diallyethylamine-hydrochloroide) "PDAEA-HCL", polyacrylamide "PAM", poly(acrylamide-diallylamine-hydrochloride) "PAM-DAA-HCl", and poly(acrylamide-diallylethylamine-hydrochloride) "PAM-DAEA-HCl".

The composition of the formed polymer is shown in Table 1, which shows that the percent of the polymerized DMAEM increases with increasing the radiation dose. This is due to increasing the conversion percent. The percent of DMAEM in the copolymer reaches its maximum value at complete conversion. At dose >30 KGy, the complex copolymer is converted into a gel and the swelling degree varying from 15 to 36. The structure of the obtained polymeric gel is shown in possible Structures 2 and 3.

TABLE 1.   Influence of the Radiation Dose on the Composition and the Capacity of the Obtained p(AM-AA-DMAEM)

| Dose, Kgy	Composition percent			Capacity,
	AM	AA	DMAEM	m mol/g
5	49.6	9.6	40.73	-
10	46.2	9.2	44.59	-
30	44.0	5.9	50.10	3.68
50	42.0	6.4	51.60	3.67
70	24.5	6.5	69.01	3.91
100	21.4	4.18	74.42	4.57
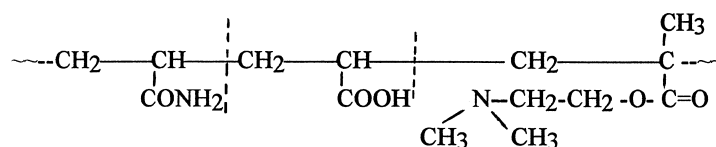
Structure 2.   PAM-AA-DMAEM

The influence of the radiation dose on the capacity of the obtained polymer is shown in Table 1, which shows that both the capacity of the gel toward Cu^{2+} increases with increasing the radiation dose. The increase in the capacity may be attributed to the increase in the degree of crosslinking between polymer chains as a result of irradiation. In the previous work [14, 25, 26], we have studied gamma irradiation initiated template polymerization of acrylic acid (AA) on polyacrylamide and poly(amido-amine) for preparation of poly(acrylamide-acrylic acid) resin PAM-AA, poly(acrylamide-acrylic acid-diallylamine-hydrochloride) resin p(AM-AA-DAA-HCl) and poly(acrylamide-acrylic acid-diallylethylamine-hydrochloride) resin p(AM-AA-DAEA-HCl). The capacities of the obtained resins increase with increasing the radiation dose. At high doses, the capacity decreases may be due to the higher increase in the extent of crosslinking.

Influence of Polymer/Monomer Ratio

The influence of the polymer/monomer molar ratio on the capacity of the obtained polymer toward Cu^{2+} was studied at monomer concentration 0.64 M/L and radiation dose of 30 KGy. The results are shown in Figure 2, which shows that the capacity increases with increasing the polymer/monomer molar ratio to reach its maximum value at molar ratio of 1.5. At very low polymer concentration, syneresis occurs, yielding strongly inhomogeneous gel; even if syneresis is avoided, a large proportion of dangling chains and loop is produced. A higher
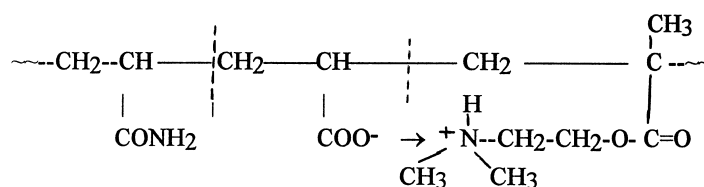
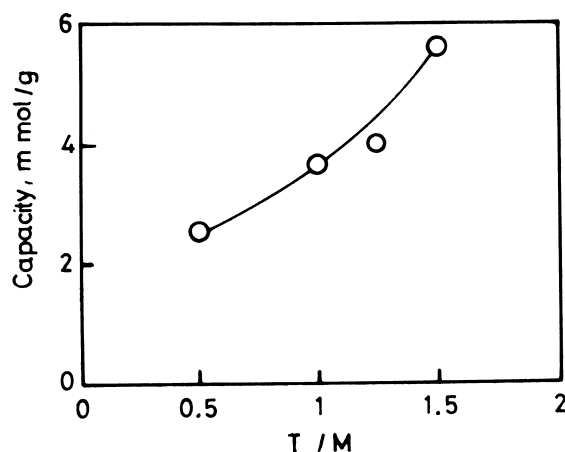Structure 3.   PAM-AA-DMAEM (Complex Form)

Figure 2.   Influence of T/M molar ratio on the capacity of the obtained polymer gel.

concentration of precursor polymer increases the probability for permanent trapped entanglements to occur. Moreover, a very high viscosity of the medium may be favorable for the formation of inhomogeneities within the gel at which interpenetration of chains begins [27]. Consequently, the capacity of the gel increases. In addition, on increasing the amount of added polymer, the complex formation [28, 29] between the monomer and polymer increases which leads to increase the extent of crosslinking between polymeric chains. Consequently, the capacity of the gel increases.

Influence of Monomer Concentration

The influence of the monomer concentration on the capacity of the obtained gel toward Cu^{2+} was studied at polymer/monomer equal molar ratio and at radiation dose of 30 KGy. The results are shown in Figure 3, which shows that the capacity increases with increasing the monomer concentration. On increasing the monomer concentration, the probability of complex formation increases. This increases the degree of crosslinking between the polymeric chains. In addition, the number of amino groups increases which leads to an increase in the interaction with the cation. These increase the capacity of the gel. This is similar to the previous finding in the polymerization of AA on PMA. It was found that the capacity of the resin increases with increasing the concentration of the polymerized monomer along the template polymer [25].
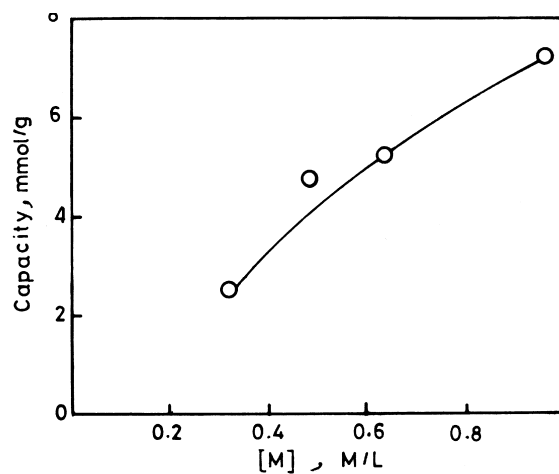
Figure 3.   Influence of monomer concentration on the capacity of the obtained gel.

TABLE 2.   IR Spectral Data of p(AM-AA-DMAEM)mer gel

Absorption Bands of Original Groups, Cm^{-1}	Experimental Absorption Bands, Cm^{-1}
Amide: Free NH stret., 3500, 3500 (Amide II) Bonded NH stret., 3350, 3180 NH bond, 1620-1590 C=O stret., 1650 (Amide I)	3453 1560 1638
Carboxylate: 1610-1550 -COO$^-$ 1410-1300	1560 1412
Hydroxyl: Free -OH stret., 3650-3590 Bonded -OH stret., 3400-3200	3685, 3666
Amine: C-N stret., 1410	1412

Interaction between the Gel and Ions

The formed gel was treated with $CuSO_4.5H_2O$ as described previously [11]. The infrared spectrum of the formed floc after cation build-up which produced from the interaction of p.(AM-AA-DMAEM) with $CuSO_4.5H_2O$ is summarized in Table 2. The spectrum shows absorption bands at: 1560 and 1412cm^{-1} characteristic for COO$^-$ indicate that the carboxylic group of the polymer chain forms bonds with Cu^{2+}.

The absorption bands show that:

a. Amide group like tertiary amino group interact with Cu^{2+} through a complex formation. This is in agreement with the finding of other investigators in interaction of Cu^{2+} with acrylamide polymers [25, 26, 30-34] and with the finding of other authors [35-38] in interaction of poly(4-vinylpyridine) (PVP), poly(ethyleneimine)   "PEI",   poly(vinylamine),   poly-(amidoamines), poly(N,N,N`,N`,tetramethylethane-1,2-diamine),   (4-(3,4-dihydroxyl phenyl-L-alanine) and polydioximes with cations such as: Cu, Ni, Cd, Fe, Cr and Hg.

b. Carboxylic group interacts with Cu^{2+} through chemical reaction or cation-exchange mechanism. This is also in agreement with the previous findings (26, 27, 31-33) in interaction between the polymeric materials with copper sulfate.

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