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STUDIES ON GRAFT COPOLYMERIZATION OF METHYLMETH-ACRYLATE ONTO CASEIN

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The graft copolymerization of polymethylmeth-acrylate onto casein has been investigated using potassium persulfate initiator in aqueous medium. The effects of monomer, backbone and ascorbic acid (as activator) have been discussed in the light of percent grafting (GR), grafting efficiency (GE)and rates of Rg, Rp, Rh. The proof of grafting has also been established.

Key words: Graft copolymerization, Methylmeth-acrylate, Potassium persulfate, Activator.

Introduction

Earlier, the graft copolymerization of methylmeth-acryalte onto neoprene [1], acrylamide onto casein [2] and acrylonitrile onto PVA [3] have been reported. It has been found that graft copolymerization of vinyl monomers onto neoprene, casein and PVA is an effective tool for imparting desired properties. Different aspects of this technique have been revealed by several researchers through radical initiation [4-6]. Survey of the literature provides potassium persulfate alone or with ascorbic acid to be a good initiator system for grafting vinyl monomers onto casein [6,7]. Casein contains H bonds between C=O and - NH groups which have negative influence on the flexibility of films formed. This bonding is weakened and makes possible free rotation of some groups to give more elastic casein films [8]. This may be obtained by introducing growing polymer chain of acrylate monomer on the backbone of casein. This paper deals with the graft copolymerization of methylmethacrylate(MMA) onto the backbone of casein using potassium persulfate with or without ascorbic acid (AA) as initiator.

Experimental

Materials. Methylmethacrylate (E. Merck) was washed with 5% sodium hydroxide to remove inhibitor and dried over calcium chloride and distilled in the atmosphere of nitrogen. Acetone and other organic solvents were distilled before use. Casein (E.Merck, Art. 2241, alkali soluble), potassium persulfate (E.Merck, GR), ascorbic acid (BDH) were used without further purification.

*Procedure of polymerization.*The reaction was accomplished in a round flask provided with nitrogen inlet and outlet arrangements. Known quantity of casein was added in the reaction vessel already containing 20ml water. The casein was dispersed by constant stirring under nitrogen atmosphere. After 30 min. required quantity of MMA was added to the reaction vessel followed by potassium persulfate (in 10 ml water) and ascorbic acid (when required) in succession. The total volume of the reaction was made 60 ml by addition of more water. The reaction was then allowed to proceed for 45 min at 60°C. After required reaction time the contents were cooled at 5°C. The product was then filtered through a sintered crucible and dried to a constant weight under vacuum. The product then soxhlet extracted with acetone to remove loosely bound PMMA was dried to a constant weight. The product was analysed for nitrogen on elemental analysis equipment. IR spectrum of the product was recorded to identify the attachment of growing polymer chain of PMMA on the backbone of casein from the appearance of characteristic absorption bands which were not present in the spectrum of pure casein.

The total conversion, grafting efficiency (GE), grafting ratio (GR), rate of graft polymerization (Rg), rate of polymerization (Rp) and rate of homopolymerization (Rh) are calculated by using the following simple relations.

$$\text{Total conversion \%} = \frac{\text{Total weight of vinyl polymer formed x 100}}{\text{Weight of vinyl monomer used}}$$

$$\text{GE \%} = \frac{\text{Wight of vinyl polymer in graft x 100}}{\text{total weight of vinyl polymer formed}}$$

$$\text{GR \%} = \frac{\text{Weight of vinyl polymer in graft x 100}}{\text{Weight of backbone}}$$

$$\text{Rg} = \frac{\text{Grafted monomer (in mole)}}{\text{Time of polymerization (in second)}}$$

$$\text{Rp} = \frac{\text{Total conversion of monomer (in mole)}}{\text{Time of polymerization (in second)}}$$

$$\text{Rh} = (\text{Rp} - \text{Rg})$$

Results and Discussion

Tables 1, 2 and 3 include the data obtained from graft copolymerization of MMA onto casein using potassium

persulfate as initiator and ascorbic acid as an activator.

The proof of grafting of MMA molecules onto the backbone of casein can be obtained by elemental analysis, IR spectrum and solubility etc. The elemental analysis of the product samples was carried out for nitrogen. The 15 samples of the product contain 7.26-14.17% nitrogen whereas casein contains 14.5% nitrogen. The variation in % of nitrogen is simply due to the coupling of growing polymer chains of PMMA onto casein. This attachment of monomer molecules on the activated sites of casein causes decrease in % of nitrogen from 14.52 to 7.26% (Tables) resulting graft copolymer. Solubility is another important tool which helps in deciding grafting between MMA molecules and casein. Casein dissolves in phosphate buffer (pH8) whereas the product simply swells and thus gets dispersed into pieces on agitation. Swelling tests were carried out in different organic solvents. The product shows a little solvent uptake in methylene chloride (5%), MEK (6%), ethanol (10%), cyclohexan (12%), carbontetrachloride (22%) and chloroform (30%) etc., whereas casein does not show any tendency to swell in these solvents. Furthermore the solvent uptake of casein in acetone increases from 22 to 37% and in tetrahydrofurane it becomes from 9 to 40%. The solvent behaviour of the grafting product towards organic solvents supprots the assumption for the formation of MMA-g-casein. An IR spectrum of a product sample is shown in Fig. 1. The presence of an absorption band at 1730 cm^{-1} which is a characteristic of ester carbonyl groups in graft copolymer supports the formation of casein-g-MMA graft copolymer.

The influence of monomer concentration on the graft-

TABLE 1. EFFECT OF MONOMER CONCENTRATION IN GRAFT COPOLYMERIZATION OF MMA ONTO THE BACKBONE OF CASEIN (0.167×10^{-3} MOLE) USING POTASSIUM PERSULFATE (1.48×10^{-3} MOLE) AS CATALYST AT 60°C FOR 45 MIN.

Expt. No.	MMA mole	Total conversion of MMA		Elemental analysis	Grafted monomer	GR	GE	Rg x 10^6	Rp x 10^6
		Mole	%	% N	mole	%	%	ms^{-1}	ms^{-1}
1.	0.06	0.0121	20.2	13.57	0.0090	15.0	74.0	3.33	4.48
2.	0.07	0.0130	18.6	13.95	0.0098	16.0	75.0	3.63	4.81
3.	0.08	0.0139	17.4	13.90	0.0105	17.5	75.7	3.89	5.15
4.	0.09	0.0148	16.4	13.61	0.0112	18.7	77.7	4.15	5.48
5.	0.10	0.0150	15.0	13.87	0.0116	19.3	77.3	4.29	5.55
6.	0.11	0.0168	15.3	13.75	0.0140	23.3	83.3	5.18	6.22
7.	0.12	0.0175	14.6	13.62	0.0146	24.3	83.4	5.41	6.48

TABLE 2. EFFECT OF ASCORBIC ACID (2.48×10^{-4} MOLE) IN GRAFT COPOLYMERIZATION OF MMA ONTO CASEIN (0.167×10^{-3} MOLE) USING POTASSIUM PERSUFATE (1.48×10^{-3} MOLE) AS CATALYST AT 60°C FOR 45 MIN.

Expt. No.	MMA mole	Total conversion of MMA		Elemental analysis	Grafted MMA	GR	GE	Rg x 10^6	Rp x 10^6
		Mole	%	% N	mole	%	%	ms^{-1}	ms^{-1}
8.	0.06	0.0200	27.1	13.58	0.0183	30.5	91.5	6.78	7.40
9.	0.07	0.0215	28.1	13.12	0.0197	32.8	91.6	7.29	7.96
10.	0.08	0.0217	58.5	13.85	0.0203	33.8	93.5	7.52	8.04
11.	0.09	0.0253	44.2	13.7	0.0239	39.8	94.5	8.85	9.37

TABLE 3. EFFECT OF BACKBONE CONCENTRATION IN GRAFT COPOLYMERIZATION OF MMA (0.09 MOLE) USING POTASSIUM PERSULFATE (1.48×10^{-3} MOLE) AS CATALYST AT 60°C FOR 45 MIN.

Expt. No.	Casein x 10^4 mole	Total conversion of MMA		Elemental analysis	Grafted monomer	GR	GE	Rg x 10^6	Rp x 10^6
		Mole	%	% N	mole	%	%	ms^{-1}	ms^{-1}
12.	1.67	0.0148	15.0	13.64	0.0112	18.7	75.7	4.15	5.48
13.	1.94	0.0186	20.7	14.17	0.0163	23.3	87.7	6.03	6.89
14.	2.22	0.0222	24.7	13.95	0.0197	24.6	88.7	7.29	8.22
15.	2.50	0.0248	27.6	13.31	0.0223	24.8	89.6	8.26	9.18

ing of MMA onto casein is shown in Table 1 and Figs. 2 and 3. An increase in monomer concentration was found to increase the rates of Rp, Rg, Rh, GR and GE. This increase might be due to higher availability of the monomer molecules in the vicinity of casein macroradicals. The more growing polymer chains of MMA are available which combine onto the activated centres of casein resulting more grafting. The rate of conversion of MMA is greater than the rate of grafting since at the early stage of reaction homopolymerization of MMA takes place.

These rates are in following order:

$$Rp > Rg > Rh$$

Similar observations were obtained for hetrogenous graft copolymerization of acrylamide onto casein [2] and different acrylates on casein [6,8].

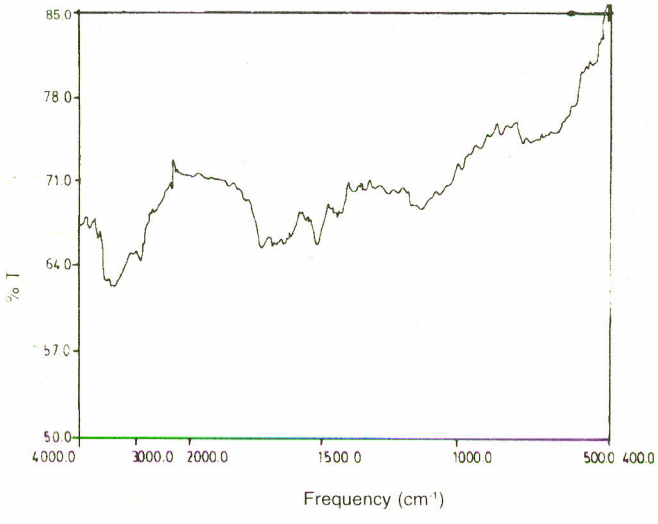

Fig. 1. IR spectrum of graft copolymer of methylmethacrylate onto casein.

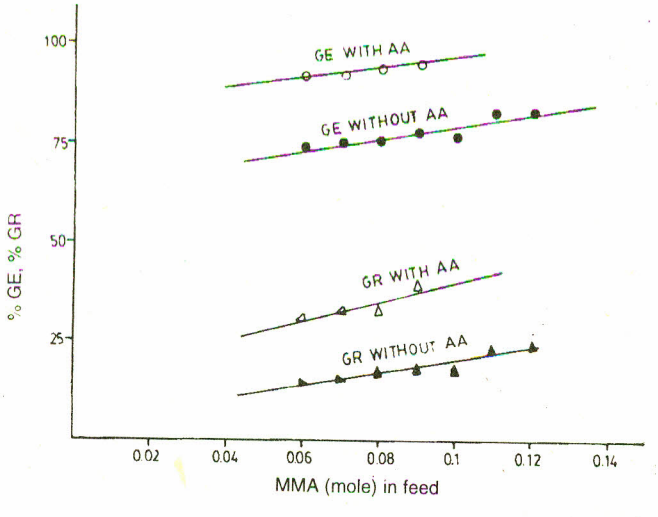

Fig. 2. Effect of MMA on % GE and % GR in the graft copolymerization of MMA onto casein with or without ascorbic acid.

The effect of ascorbic acid on graft copolymerization of MMA onto casein is summarized in Table 2 and depicted in Fig.2 and 3. These results indicate that in the presence of activator, the value of Rg, Rp, GR and GE get increased with the increase of monomer concentration as it was observed in the absence of activator (Table 1) whereas the rate of homepolymerization (Rh) decreases with the increase in concentration of MMA. Further, the presence of ascrobic acid enhances the value of Rg, Rp, GR and GE and decreases the value of Rh as shown in Fig.1. Due to presence of ascorbic acid, ascorbate ion radicals are formed in addition to the sulfate ion radicals and hence increases the value of Rp, Rg, GE and GR.

Table 3 includes the observations obtained from the effect of backbone concentration on the graft copolymerization of MMA onto casein. These results show that an increase in backbone concentrations was found to increase the rates of conversion of monomer, graft copolymerization, homopolymerization, GE and GR (Fig.4). With the increasing concentration of casein a large number of active sites are formed along the backbone thereby increasing Rp, Rh, Rg, PG and GE. The relative increment in Rg is greater than that of Rh and resulted in increasing the value of GE.

When MMA and casein were heated in the presence of persulfate with or without ascorbic acid (as an activator) three or four types of radicals are formed. These are persulfate radicals, monomer radicals, backbone radicals and ascorbate ion radicals. Persulfate radicals create active sites onto the backbone of casein to form casein radicals and react with monomer resulting in monomer radicals. The ascorbate ion radicals react with monomer as well as backbone radicals to speed up the reaction. At the early stage of reaction, mutual termination of growing polymer chain radicals takes place form-

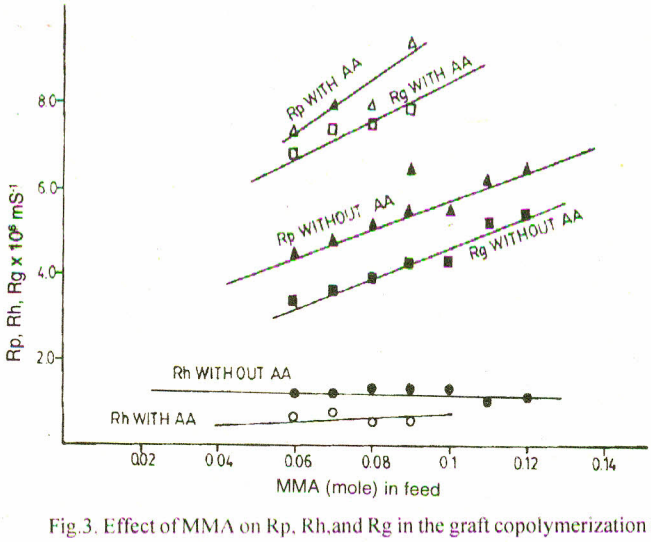

Fig.3. Effect of MMA on Rp, Rh,and Rg in the graft copolymerization of MMA onto casein with or without ascorbic acid.

ing polymethylmethacrylate and these mutual termination of monomer radicals and casein radicals to casein radicals take place forming graft copolymers and macromolecules of casein. The termination race between homopolymer radicals is faster than that between casein and homopolymer radicals. This is because the homopolymer radicals are almost immobile [2, 9] due to reduced segment movement. The homopolymer radicals couple to all available activated sites of casein. In addtion, the gel effect may cause swelling of casein which assists in the diffusion of monomer to the growing chains and active sites on the casein thereby favouring grafting reactions. The relative increments in Rg is higher than that of Rh resulting in increasing grafting efficiency. With the increase of backbone concentration, large number of active centres become available along the backbone for coupling of growing polymer chain radicals of monomers and enhances the value of Rp, Rg, Rh, GE and GR. Ascorbate ion radicals cause in forming more monomer and casein radicals result in enhancing the value of Rp, Rg, GE and GR.

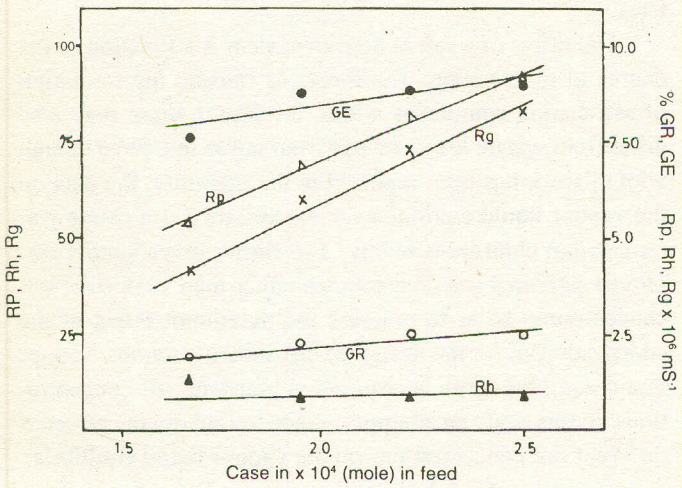

Fig. 4. Effect of casein concentration on % GR, % GE, Rp, Rh and Rg in the graft copolymerization of MMA onto casein.

The grafted casein is creamy tough substance which may be powdered. It decomposes at 160±1°C. It becomes light brown when it was kept at 170°C in an ovan for an hour with loss in weight as 10.5%. On further keeping at 200°C for an hour, the product becomes dark brown with loss in weight as 0.7%. After keeping at 230°C for an hour the product becomes black in colour. This black material does not dissolve or swell in any solvent. It might be due to intramolecular and intermolecular rearrangements of amide groups in the polymer chains.

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