Technology Section

Pak J Sci Ind Res 2000 43 (4) 262-266

Grafting of Polybutyl Acrylate Growing Chains to Gelatin

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(Received 29 June 1999; accepted 25 March 2000)

Modification of gelatin by grafting with butyl acrylate in the presence of potassium persulfate is accomplished and the results are discussed with respect to percent grafting, grafting efficiency and rate of grafting. The number and variety groups along the chain of gelatin act as grafting centres. Grafting efficiency is found to be the same at all monomeric gelatin ratio.

Keywords: Grafting, Polybutyl acrylate, Potassium persulfate, Gelatin.

Introduction

Gelatin is a water soluble protein resulting from the partial hydrolysis of collagen. Three reactive groups hydroxyl, carboxyl and amino fractions are present in gelatin 100g high quality gelatin contain hydroxyl, carboxyl and amino fractions as 100, 75 and 50 mole g^{-1} respectively. The industrial uses of gelatin may be divided into four major groups, in the order of their respective volumes e.g. foods, photographic films, pharmaceuticals and miscellaneous. Besides, technically inedible or reject gelatin products may be put to a wide range of varied applications. A potential use of gelatin is found in leather industry. For this purpose, gelatin is modified by grafting with vinyl monomers and the resulting product is used in the formulations of leather finishes (Nagabhushnum *et al* 1978). In our earlier paper (Khan and Khalil 1995), grafting of methyl methacrylate (MMA) onto gelatin is reported. The results are discussed with respect to grafting ratio and grafting efficiency. It is observed that the lower concentration of gelatin favour more grafting. This paper deals with the grafting of butyl acrylate onto gelatin using potassium persulfate as catalyst.

Experimental

Materials. Gelatin (food grade, Merck) and potassium persulfate (GR, Merck) were used without further purification. Butyl acrylate (Merck) was first washed with aqueous solution of alkali to remove inhibitor and then with water three times, dried on calcium chloride and finally distilled. The monomer was distilled for each use. Acetone, THF and other organic solvents were distilled before use.

Procedure of Grafting. Grafting reactions were accomplished in 250 ml reaction flask with nitrogen inlet and outlet. Stock solution of gelatin (10%) was prepared in warm water. Gelatin was precipitated from a portion of stock solution to confirm its percentage concentration. A known quantity of gelatin, n-BA and potassium persulfate were added in the reaction flask. The total volume was made up to 100 ml by adding water. The reaction was done at 60 °C. After completion of reaction time, the ingredients were transferred to a beaker already containing acetone (50 ml). Homopolymer and loosely bound homopolymer will be dissolved in acetone and graft copolymer will be precipitated. The product was further treated with THF to dissolve any homopolymer still present with the product. Finally it was dried in vacuum desiccator and weighed. The product was analyzed for nitrogen. The IR spectra of gelatin and product were recorded to ensure the linkage of poly (butyl acrylate) onto the backbone of gelatin from the appearance of characteristic absorption bands which were not present in the spectrum of pure gelatin.

Results and Discussion

Tables 1-4 show the results of graft copolymerization of butyl acrylate (n-BA) onto gelatin using potassium persulfate as catalyst. Various experiments were carriad out to identify the effects of monomer backbone initiator concentration and time, on grafting efficiency (GE), grafting ratio (GR) and grafting rate (Rg).

To ensure the grafting of n-BA onto gelatin the products were subjected to nitrogen estimation, solubility in different solvents and IR analysis. Gelatin and the 22 products were analysed for nitrogen. Gelatin contains 16.57% nitrogen whereas the products contain 3.80-12.23% nitrogen. This variation in nitrogen of both gelatin and products speculates the coupling of various number of growing polymer chains of poly (BA) onto activated sites of gelatin. Gelatin dissolved

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in cold/hot water, dilute alkali solution and DMSO while the products did not dissolve in water, alkali solution and DMSO and showed swelling uptake of 5%, 42% and 17.3% respectively. Besides, gelatin swelled in DMF (swelling uptake 88%) and product gave paste with DMF. The swelling tests of gelatin and grafted material analysis are summarized in Table-5. Grafted gelatin showed solvent uptake; xylene (300%), acetone (0%), chloroform (102%), butyl acetate (27%), ethyl alcohol (47%) and carbon tetrachloride (66%). Gelatin showed uptake of solvents xylene (90%), acetone (6.8%), chloroform (0%), butyl acetate (20%), ethyl alcohol (0%) and carbon tetrachloride (19%). The solvent behaviour of the grafted product support the assumption for the formation of graft copolymer. IR spectra of the product (expt:2) and gelatin were also recorded as (Fig 1 and 2). The presence of ester carbonyl absorption band at 1720 cm^{-1} ensures the grafting of growing polymer chains of n-BA onto gelatin and establishes the formation of graft copolymer (BA-g-gelatin).

The total conversion of monomer grafting ratio (GR) and grafting efficiency (GE) were calculated as follows:

Total weight of vinyl polymer = yield-weight of backbone

Weight of vinyl polymer in graft = weight of vinyl polymer-weight of homopolymer

Total conversion = Total weight of vinyl polymer x 100 weight of vinyl monomer used

Grafting ratio (GR) % = Total vinyl polymer in graft x 100 weight of backbone

Grafting efficiency (GE) % = Weight of vinyl polymer in graft x 100 Weight of vinyl polymer formed

The effect of monomer concentration was determined by changing monomer concentration and keeping fixed concentration of gelatin and catalyst, temperature and time. The results (Table 1) indicate that an increase in monomer concentration increases the values of GR, Rp and Rg whereas the value of GE remains the same at all concentrations of monomer. This is due to the higher aggregate of growing polymer chains (radicals) of n-BA in the vicinity of gelatin radicals. The more growing polymer chains of monomer are available which couple onto the reactive sites of gelatin resulting more grafting. It is also evident Fig 2 'grafted n-BA' Vs n-BA, that rate of coupling of growing polymer chains onto active centres of backbone increases with an increase concentration of n-BA in the feed. The decrease in the percentage of nitrogen in the products also shows that the bigger polymer chains of n-BA attach on the reactive sites of gelatin which reduces the total content of nitrogen in the product. Similar results are also obtained for grafting of MMA on gela2tin using potassium persulfate as catalyst (Khan and Khalil 1995).

The effects of gelatin concentration on grafting of n-BA onto gelatin (Table 2). Show that grafting efficiency remains

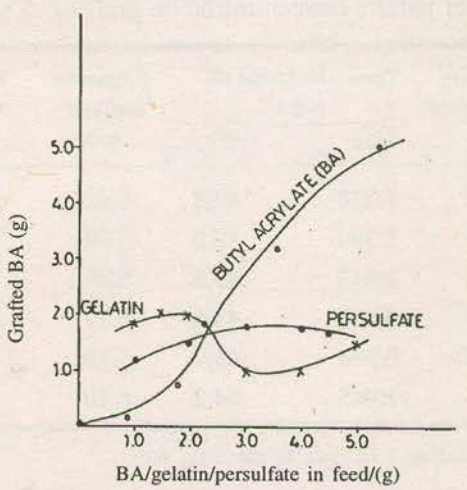

Fig 2. Effect of monomer, backbone and catalyst on graft yield.

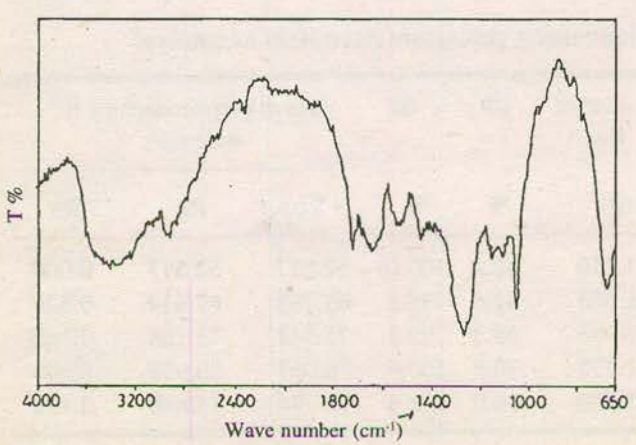

Fig 1. IR spectrum of (BA-g-Gelatin)

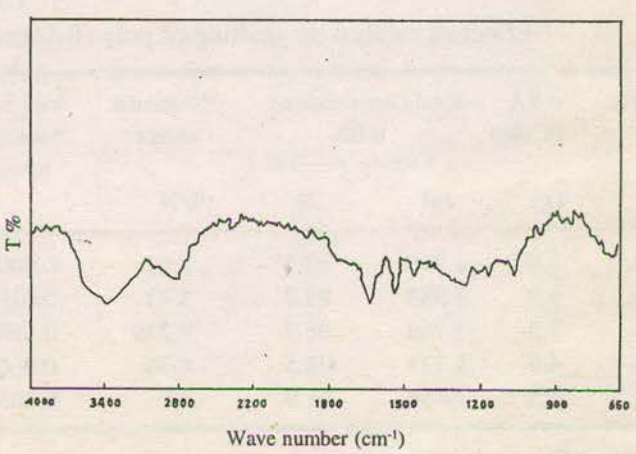

Fig 3. IR Spectrum of gelatin

Table 1

Effect of monomer concentration on grafting of poly (BA) onto gelatin using potassium persulfate as catalyst

S. No.	n-BA in feed	Total conversion of n-B		Elemental analysis	Weight of homo-polymer	Grafted BA	GR	GE	Rate of polymerization x 10^7 mole sec^{-1}		
	(g)	(g)	%	%N		(g)	%	%	Rp	Rg	Rh
1.	0.90	0.135	15.0	7.33	0.000	0.135	13.5	100.0	5.859	5.859	0.000
2.	1.80	0.750	41.7	6.80	0.200	0.748	74.8	99.7	32.552	32.465	0.086
3.	2.25	1.870	83.0	5.80	0.000	1.870	187.0	100.0	81.163	81.163	0.000
4.	3.60	3.168	88.0	5.30	0.001	3.167	316.7	99.70	137.500	137.456	0.044
5.	4.05	4.030	99.5	4.62	0.002	4.028	402.8	99.95	174.913	174.826	0.087
6.	5.40	5.015	92.8	3.80	0.000	5.015	501.5	100.00	217.664	217.664	0.000

Gelatin, 1g; persulfate, 2.7g; time, 30 min; temp, 60°C.

Table 2

Effect of gelatin concentration on grafting of poly (BA) onto gelatin using potassium persulfate as catalyst

S.No.	n-BA in feed	Total conversion of n-BA		Elemental analysis	Weight of homopo-lymer	Grafted BA	GR	GE	Rate of polymerization x 10^7 mole sec^{-1}.		
	(g)	(g)	%	% N		(g)	%	%	Rp	Rg	Rh
7.	1.0	1.870	92.8	5.80	0.000	1.87	187.0	100.0	81.163	81.163	0.000
8.	1.5	1.980	88.0	5.93	0.000	1.98	132.0	100.0	85.937	85.937	0.000
9.	2.0	2.010	89.3	5.98	0.10	2.00	100.0	99.5	87.239	86.805	0.434
10.	3.0	0.980	43.6	6.27	0.000	0.98	32.7	100.0	42.534	42.534	0.000
11.	4.0	0.938	41.7	5.70	0.000	0.938	23.5	100.0	40.711	40.711	0.000
12.	5.0	1.445	64.2	6.80	0.000	1.445	28.9	100.0	62.716	62.716	0.000

BA, 2.25g; persulfate, 2.7g; time, 30 min; temp, 60°C.

Table 3

Effect of catalyst on grafting of poly (BA) onto gelatin using potassium persulfate as catalyst

S.No.	n-BA in feed	Total Conversion of n-BA		Elemental analysis	Weight of homopo-lymer	Grafted BA	GR	GE	Rate of polymerization x 10^7 mole sec^{-1}.		
	(g)	(g)	%	% N		(g)	%	%	Rp	Rg	Rh
13.	1.0	1.210	67.2	7.61	0.000	1.210	48.4	100.0	52.517	52.517	0.000
14.	2.0	1.584	88.0	8.42	0.019	1.565	62.6	98.8	68.763	67.934	0.829
15.	3.0	1.740	96.7	9.240	0.008	1.731	69.3	99.5	75.548	75.164	0.382
16.	4.0	1.773	98.5	8.70	0.000	1.773	70.9	100.0	76.953	76.953	0.000
17.	4.5	1.654	91.9	8.7	0.003	1.650	66.0	99.8	71.796	71.640	0.156

Gelatin, 2.5g; n-BA, 1.8; time, 30 min; temp, 60°C.

Table 4

Effect of time on grafting of poly (BA) onto gelatin using potassium persulfate as catalyst

S.No.	n-BA in feed	Total Conversion of n-BA		Elemental analysis	Weight of homopo-lymer	Grafted BA	GR	GE	Rate of polymerization x 10^7 mole sec^{-1}.		
	(g)	(g)	%	%N		(g)	%	%	Rp	Rg	Rh
18.	10	0.108	3.6	11.70	0.000	0.108	7.2	100	2.343	2.343	-
19.	20	0.540	18.0	10.9	0.000	0.540	21.6	100	5.859	5.859	-
20.	30	0.831	27.7	09.80	0.000	0.831	33.2	100	6.011	6.011	-
21.	45	1.380	46.0	12.23	0.000	1.380	55.2	100	6.655	6.655	-
22.	55	1.800	60.0	11.41	0.000	1.800	72.0	100	7.102	7.102	-

Gelatin ,2.5g; n-BA, 3.0; persulfate, 2.7g; temp, 60°C.

Table 5

Solvent uptake of gelatin and (Gelatin-g-BA)

Name of solvent	Solvent uptake % gelatin	(Gelatin-g-BA)
Acetone	6.8	0.0
Alkali % (cold/hot)	Soluble	42.0
Butyl acetate	20.0	27.0
Carbon tetrachloride	19.0	66.0
Chloroform	0.0	102.0
DMF	88.0	Paste
DMSO	Soluble	173.0
Ethyl alcohol	0.0	47.0
Xylene	90.0	300.0
Water (cold/hot)	Soluble	5.0

the same with the increase in concentration of gelatin. It is because the reactive sites of gelatin are utilized by all growing polymer chains formed during the reaction. Furthermore, the value of GR decreases with the increase in concentration of gelatin. Values of Rp and Rg are same in at all concentrations of gelatin and increase progressively at 1.0, 1.5 and 2.0 g gelatin in feed and suddenly drop after these concentrations. This may be due to the fact that with higher gelatin concentration more grafting sites are formed which may interact and lead to termination. The lower concentration of gelatin favours more grafting as obvious from the amount of grafted n-BA onto gelatin (Fig 3). The homopolymerization of monomer is negligible (Roy and Kumar 1991) which conforms the attachment of all growing polymer chains formed (during the reaction) onto gelatin.

In Table 3 the effect of catalyst concentration on grafting of poly (n-BA) onto gelatin are shown. The results indicate that the values of GR, Rp and Rg are enhanced with increas in concentration of catalyst. The primary radicals which are prejudiced by decomposition of persulfates (SO_4, OH) facilitate in activating the reactive sites of gelatin and form monomer radicals. For more catalyst concentration, more monomer radicals are formed which result in the enhancement in the values of GR, Rp and Rg (Fig 3). The values of GE at all catalyst concentrations is same showing that the growing polymer chains of n-BA are no2t ungrafted.

Data obtained in respect of the effect of time on grafting of n-BA onto gelatin (Table 4) shows that at initial stages the rate of formation of primary radicals is very slow but increase progressively with time. With greater intervals of time the primary radicals may form redox system with reducing groups present in the gelatin thereby increasing the percent of grafting considerably , (Nagabhushnam *et al* 1978). The reactive groups on the backbone of gelatin are mostly hydroxyl, carboxyl and amino fractions. Due to presence of these reactive groups at lower concentration of gelatin, the percent grafting increases and the groups are not left unturned by primary radicals which stop homopolymerization of n-BA. Similar results are also reported in the grafting of MMA onto gelatin with different catalyst including persulfate (Ikada *et al* 1974) grafting of PVA with potassium persulfate and grafting of ethyl acrylate ontop gelatin using hydrogen peroxide and ascorbic acid in aqueous medium (Thomes 1985), grafting efficiency is maximum (100%) at all intervals of time.No homopolymerization of n-BA takes place. But sometimes if more gelatin is available in the system monomer radicals can't turn each activated centres of backbone and backbone radicals mutually terminate themselves forming backbone radicals resulting decrease in grafting ratio. Same happened in the present case (Khan and Khalil 1995; Mohan *et al* 1989).

The graft copolymer obtained is a yellow solid substance which becomes powdery on crushing. When copolymer sample (expt. 12) is heated at 50-75°C for an hour it retains its original colour and loose its weight (3.8%). On further heating, the same sample at 100°C for an hour, retains the colour and looses its weight 4%. When the temperature reaches to 150°C, it starts becoming brown and in 90 min it looses its weight (4.5%). This decomposed product at 200°C becomes dark brown with loss in weight 0.5%. At 250°C charring of the decomposed products begins, which is found insoluble in the solvents give in Table 5. It does not make paste with DMF.

The loss in weight even at 200°C (0.5%) and insolubility of the heated copolymer may have been caused by the crosslinking of the degraded copolymer and the intermolecular rearrangements of the reactive groups (particularly amide) of the undegraded copolymer. Moreover in the presence of air, copolymer might have undergone chain scission and oxidation reaction in addition to other reactions (Mullik and Khan 1970; Grassie and Hay 1962).

References

Grassie N, Hay J N 1962 Thermal degradation of polymethyl vinyl ketone and its copolymers with acrylonitrile. *J Polymer Sci* **56** 189.

Ikada Y, Nishizaki Y, Sakurada I 1974 Reaction of PVA with potassium persulfate and graft copolymerization. *J Polymer Sci Polymer Chem* Ed.**12** 1829.

Khan A R, Khalil A 1995 Studies on graft copolymerization of MMA onto casein. *Pak J Sci Ind Res* **38** 292.

Kuwajima T, Hoshida H, Hayashi K 1974 Grafting of PMMA onto gelatin with different initiators. *J Appld Polymer Sci* **20** 967.

Mohan D, Radhakrishnan G, Rajdurai V R, Cameron G 1989 Graft copolymerization of acrylamide onto casein, A kinetic study. *J Polymer Sci Polymer Chem* Ed.**16** 3287.

Mullik S U, Khan A R 1970 Copolymerization of acrylonitrile and tetrachloroethylene. *Pak J Sci Ind Res* **12** 186-190.

Nagabhushanam T, Thomas J K, Santapa M 1978 Graft copolymerization of methyl acrylate onto gelatin. *J Polymer Sci Polymer Chem* Ed.**16** 3287.

Roy P, Kumar A 1991 Graft copolymerization of gelatin with PMMA on aqueous medium. *Polymer Eng Sci* **31**(14) 1001-8.

Thomas G A 1985 Graft copolymerization of ethyl acrylate onto gelatin using H_2O_2 ascorbic acid in aqueous medium. *J Polymer Sci Polymer* Ed. **23** (11), 2865-74.