Pak J Sci Ind Res 2001 44 (3) 132-136

GRAFTING OF GROWING POLYMERIC CHAINS

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(Received 23 February 1999; accepted 24 August 2000)

Growing polymer chains of vinyl acetate were grafted onto casein in an aqueous medium at 60°C using $K_2S_2O_8$ as initiator. The effects of monomer concentration, backbone concentration and activator concentration were determined. Grafting was confirmed by elemental analysis, solubility, IR spectroscopy and intrinsic viscosity.

Key words: Grafting efficiency, Hetrogenous protein, Swelling uptake.

Introduction

Grafting of vinyl monomers onto casein has been the subject of extensive investigations for the last several years (Mohan *et al* 1980; Somanathan *et al*1987). These reactions can bring about a variety of chemicals property changes depending upon the nature of the monomers used for grafting. Earlier the synthesis of graft copolymers of acrylamide and methylmethacrylate on neoprene (Khan *et al*1995) have been reported. This paper describes the grafting of poly (vinyl acetate) chains on the backbone of casein using potassium persulfate as initiator and ascorbic acid (AA) as activator at 60°C.

Experimental

Materials. Vinyl acetate (E. Merck) was distilled before use. Casein (E. Merck, alkali soluble), potassium persulfate (E. Merck, GR) and ascorbic acid (BDH) were used without further purification. Other organic solvents were distilled before use.

Procedure of polymerization. Polymerization reactions were carried out in a round bottom flask provided with nitrogen inlet and outlet arrangements. Known quantity of casein was added in the reaction flask already containing 25 ml water. The casein was dispersed by constant stirring under nitrogen atmosphere. After 40 min required quantity of vinyl acetate, potassium persulfate (in 10ml water) and ascorbic acid (when required) were added simultaneously to the reaction flask. The total volume of reactants was made to 60 ml by the addition of more water. The reaction was allowed to process for 20 min at 60°C. After required reaction time, the contents were cooled down to 5°C to terminate the reaction. The product was then filtered through sintered glass crucible and dried to a constant weight under vacuum. The unbound polyvinyl acetate was removed by soxhelet extraction using acetone as a solvent for 65 h. The resulting graft copolymer thus obtained was dried in vacuum at 50°C to a constant weight. The product was analyzed for nitrogen by elemental analysis. IR spectrum of the product was recorded to identify the grafting of growing polymer chain of vinyl acetate on the backbone of casein from the appearance of characteristics absorption bands which were not present in the spectrum of pure casein. The intrinsic viscosity of grafted product was measured at 30°C using Ostwald's type viscometer. For the measurement of viscosity of dilute solutions of product samples, the solutions were prepared in phosphate buffer (pH=8.4). Some undissolved polymer (0.8%) was seen in the bottom which was removed by filtration. Number average molecular weight Mn was determined by using the following relation (Khan *et al* 1994).

$$[h] = 9.25 \times 10^{-6} \bar{M}_n^{0.99}$$

where [h] is the intrinsic viscosity in dlg^{-1}. It is an intercept of the plot h_{sp}/C V_sC. Here h_{sp} is specific viscosity of the product samples and C is the concentration of their dilute solutions.

The rate of graft copolymer (R_g), rate of homopolymerization (R_h) rate of total conversion (R_p), Grafting ratio (GR) and Grafting efficiency (GE), were calculated from the following relations:

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

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

$$R_h = R_p - R_g$$

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

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$$GE\% = \frac{\text{Weight of vinyl polymer in graft}}{\text{Weight of vinyl monomer used}} \times 100$$

Results and Discussion

Data collected from the graft copolymerization of vinyl acetate onto the backbone of casein using potassium persulfate as an initiator and ascorbic acid as activator have been summarized Table 1-4.

Grafting was established by elemental analysis, solubility, IR spectral studies and intrinsic viscosity etc. The product samples were estimated for nitrogen. The 16 samples of the product contains 13.0-14.14% nitrogen whereas casein contains 14.38% nitrogen. The difference in percentage of nitrogen though little speculates the coupling of growing polymer chains of vinyl acetate onto the backbone of casein. Further the attachments of vinyl acetate molecules onto activated

Table 1
Effect of monomer concentration

Expt. no.	Vinyl acetate (mole)	Total conversion of vinyl acetate		Elemental analysis	Grafted monomer	GR%	GE%	$R_g \times 10^5 ms^{-1}$	$R_p \times 10^5 ms^{-1}$	$R_h \times 10^5 ms^{-1}$
		mole	%	% N						
1	0.051	0.0244	37.51	4.14	0.020	28.7	81.9	2.2222	2.71	0.49
2	0.0973	0.0262	40.20	13.92	0.022	31.5	84.0	2.4444	2.91	0.47
3	0.1302	0.0299	22.90	13.70	0.026	36.8	86.0	2.8888	3.32	0.44
4	0.1628	0.0327	20.10	13.02	0.029	41.3	88.3	3.2222	3.63	0.41

Casein, 16.67 x 10^{-5} mole; Persulphate, 1.48 x 10^{-3} mole; Temp, 60°C; Time, 15 min.

Table 2
Effect of ascorbic acid on monomer concentration

Expt. no.	Vinyl acetate (mole)	Total conversion of vinyl acetate		Elemental analysis	Grafted monomer	GR%	GE%	$R_g \times 10^5 ms^{-1}$	$R_p \times 10^5 ms^{-1}$	$R_h \times 10^5 ms^{-1}$
		mole	%	% N						
5	0.0651	0.0314	48.2	13.87	0.0280	40.2	89.3	3.11	3.49	0.38
6	0.0973	0.0362	37.2	13.92	0.0337	48.3	93.2	3.74	4.02	0.28
7	0.1302	0.0381	29.3	13.31	0.0358	51.3	93.9	3.98	4.23	0.25
8	0.1628	0.0412	25.3	13.10	0.0391	56.0	4.34	4.34	4.58	0.24

Casein, 16.67 x 10^{-5} mole; Persulphate, 1.48 x 10^{-3} mole; Temp, 60°C; Time, 15 min.

Table 3
Effect of backnone concentration

Expt. no.	Vinyl acetate (mole)	Total conversion of vinyl acetate		Elemental analysis	Grafted monomer	GR%	GE%	$R_g \times 10^5 ms^{-1}$	$R_p \times 10^5 ms^{-1}$	$R_h \times 10^5 ms^{-1}$
		mole	%	% N						
9	5.56	0.0207	21.3	13.31	0.0186	80.0	90.0	2.067	2.300	0.233
10	11.11	0.0246	25.3	13.87	0.0224	48.2	91.0	2.489	2.733	0.244
11	19.44	0.0186	19.1	13.00	0.0176	21.6	94.0	1.955	2.067	0.112
12	22.22	0.0238	24.5	13.87	0.0224	24.1	94.0	2.489	2.644	0.155

Vinyl acetate, 0.0973l; Persulphate, 1.48 x 10^{-3} mole; Temp, 60°C; Time, 15 min.

Table 4
Effect of ascorbic acid (AA) backbone concentration

Expt. no	Vinyl acetate (mole)	Total conversion of vinyl acetate (mole)	%	Elemental analysis % N	Grafted monomer (mole)	GR%	GE%	$R_g \times 10^5 ms^{-1}$	$R_p \times 10^5 ms^{-1}$	$R_h \times 10^5 ms^{-1}$
13	5.56	0.0228	23.4	13.30	0.0210	90.3	92.0	2.3333	2.5333	0.0200
14	11.11	0.0281	28.9	13.85	0.0259	55.7	92.0	2.8777	3.1222	0.2445
15	19.44	0.0221	22.7	13.92	0.0200	24.6	91.0	2.2222	2.4555	0.2333
16	22.22	0.0280	28.8	13.31	0.0267	28.7	95.0	2.9666	3.1111	0.1445

Vinyl acetate, 0.097 mole; Persulphate, 1.48 x 10^{-3} mole; AA, 1.42 x 10^{-4} mole; Temp, 60°C; Time, 15 min

Table 5
Intrinsic viscosity [h] and number average moleculer weight ($\overline{M}_n$) of poly (vinyl acetate-g-casein)

Expt. no	[h](dlg^{-1})	$\overline{M}n \times 10^{-4}$
1	0.58	7.0
2	0.73	8.8
3	0.74	9.0
4	0.84	10.2
5	0.50	6.0
6	0.39	4.7
7	0.39	4.7
8	0.37	4.5
9	0.40	4.8
10	0.38	4.6
11	0.34	4.1
12	0.60	7.3
13	0.56	6.8
14	0.48	5.8
15	0.42	5.1
16	0.80	9.7

centres of casein decrease nitrogen contents from 14.38 to 13.02% in the product. Solubility also helps in the identification of grafting between casein and growing polymer chains of vinyl acetate. The product samples make paste in phosphate buffer (pH = 7.5-8.0) and dilute solutions may be prepared on warming whereas casein dissolves in the phosphate buffer (pH=8). Swelling tests were also carried out in different organic solvents. The product shows a little swelling uptake in MEK (2%), methylene chloride (4%), isopropanol (8%), ethanol (15%), cyclohexane (16.0%), carbon tetrachloride (17%) and chloroform (26%) whereas casein does not show any tendency to swell in these solvents. The solvent behaviour of the grafted product supports the assumption for the formation of graft copolymer. IR spectra of casein and one of the product samples were recorded to know the addition of growing polymer chain to casein macromolecule. The absorption band at 1720 cm^{-1} shows the characteristics of the ester carbonyl group of polyvinyl acetate which supports grafting of polyvinyl acetate molecules on the activated centres of casein. It establishes the grafting of polyvinyl acetate side chains to casein.

The effect of monomer concentration of the grafting of vinyl acetate onto casein has been shown in Table-1. These results show that with an increase in monomer concentration, the values of R_g, R_p, GE and GR get increased. This is due to higher aggregation of vinyl acetate molecules in the vicinity of casein macro-radicals. The more growing polymer chains of vinyl acetate are available which attach onto the activated centres of casein resulting more grafting. The rate of conversion of vinyl acetate is greater than the rate of grafting since at the early stage of reaction homopolymerization of vinyl acetate also takes place. The same things happen in the graft copolymerization of acrylamide (Khan *et al* 1994) and methyl methacrylate (Khan and Khalil Ahmed 1995) on casein and nylon (Lenka 1982).

The influence of ascorbic acid with variation on graft copolymerization of vinyl acetate onto casein has been summarized in Table-2. These results indicate that in the presence of activator, the values of R_p, R_g, GR and GE increase with the increasing vinyl acetate concentration as it was happened in the absence of activator (Table-1) whereas rate of homopolymerization gets decreased with increase in concentration of vinyl acetate. Further the presence of ascorbic acid enhances the values of R_p, R_g, GR and GE. The addition of ascorbic acid results the formation of ascarbate ion radicals in addition to the persulfate ion radicals which enhanced the values of these parameters.

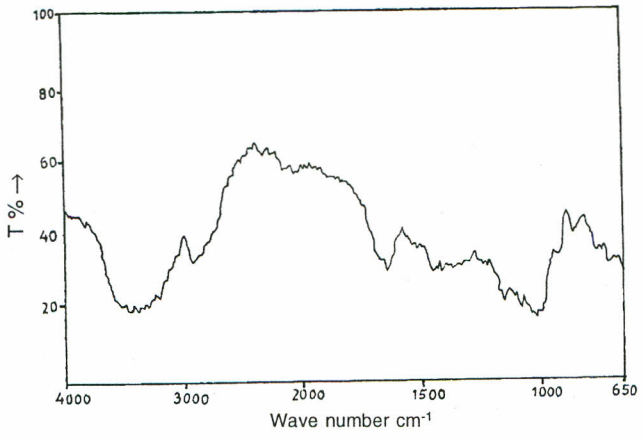

Fig 1. IR Spectrum of casein.

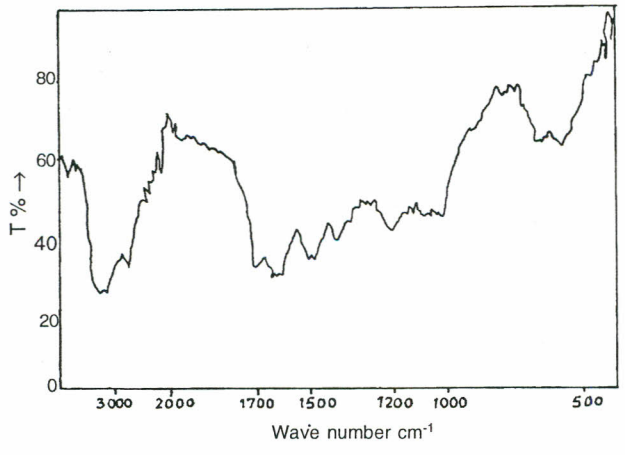

Fig 2. IR Spectrum of poly (vinyl acetate-g-casein).

Table-3 includes the observations obtained from the effect of backbone concentration on graft copolymerization of vinyl acetate onto casein. From these results, an interesting situation is observed. The values of R_g, R_h, N and quantity of grafted monomer increase with increasing concentration of casein from 5.56×10^{-5} to 11.11×10^{-5} mole and then drop at 19.44×10^{-5} mole. Again these values increase at the concentration of casein 22.22×10^{-5} mole. On the other hand the value of GE increases with increasing concentration of backbone though the difference is not appreciable. The results in Table-4 indicate the effect of activator on backbone variation. The addition of ascorbic acid increases in value of GR, GE, R_h, R_g, N and quantity of grafted monomer but the trend of increasing backbone concentration on these values except GE is the same as observed in the absence of activator (Table-3).

With the increase in backbone concentration, a large number of active centres are produced along the backbone for coupling of growing polymer chains radicals of monomer and enhances the values of R_p, R_g, R_h, N and quantity of monomer. But at certain concentration of casein, perhaps required quantity of active centres could not be formed for cupling the growing polymer chains of monomer. In addition the gel effect may cause swelling of casein which assist in the diffusion of monomer to the growing polymer chains but active centres on the casein don't favour grafting reactions at this concentration (Khan *et al* 1995; Mohan *et al* 1989). It is because as the concentration of casein increases, the values of above mentioned parameters get increased showing that swelling of casein definitely help in the diffusion of monomers to the growing polymer chains and active centres on the casein thereby favour grafting reactions. The values of GE supports this belief.

The intrinsic viscosity of dilute solutions of product samples prepared in phosphate buffer (pH 8.4) were determined to find out their number average molecular weight Mn. These values are determined as 0.34-0.84 dl g^{-1}.

The number average molecular weights calculated from these values were $4.1\text{-}9.7 \times 10^4$ (Table-5). The molecular weight of casein is 3.6×10^4 ([n] = 0.3 dl g^{-1}). These results indicate that the molecular weight of each product sample is higher than the molecular weight of casein. It means that both vinyl acetate and casein are participated in the reaction and growing polymer chains of vinyl acetate are attached to the available active centres of casein resulting grafted product. Further the increase in molecular weight shows that there is also possibility of mutual termination of backbone radicals resulting in macroradicals of casein. The product obtained after soxhelet extraction is the mixture of grafted casein and grafted casein macroradicals. During the formation of reaction some undisolved portion of copolymer was settled down in the bottom which was 0.8%. it is rather due to crosslinking of the product.

The graft copolymer samples are light brown powdery substances soluble in phosphate buffer (pH 8.4). They start decomposing above 190°C. One of the sample (exp. 2) was kept in an oven. When temperature reached to 200°C, it became from light brown to brown. On further heating, a dark brown polymeric material is obtained at 260°C with a loss in weight as 12% which does not dissolve in any solvent. Insolubility of decomposed material might be due to the intermolecular and intramoleculer rearrangement of the amide group in the polymer chain.

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