

SYNTHESIS OF GRAFT COPOLYMER CASEIN-G-BUTYLACRYLATE

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Poly (butylacrylate) was graft copolymerised onto Casein in the presence of phosphate buffer using potassium persulphate as catalyst. The effects of concentration of monomers, backbone and catalyst on rate of conversion of monomer (R_p), rate of graft copolymerization (R_g), rate of homopolymerization (R_h), grafting efficiency (GE) and grafting ratio (GR) have been discussed.

Key words: Graft copolymer, Casein-g-butylacrylate, Homopolymerization.

Introduction

In our earlier papers (Khan *et al* 1994; Khan and Khalil 1995), the synthesis of graft copolymers of acrylamide, methylmethacrylate and vinyl acetate onto casein have been reported. These copolymers may be used in the finishing of artificial and synthetic leather. This paper describes the synthesis of graft copolymer casein-g-BA using potassium persulphate as catalyst at 60°C.

Experimental

Material. Butyl acrylate (BDH) was purified before use. It was first washed with 5% sodium hydroxide to remove added inhibitor and dried over calcium chloride, then distilled in the atmosphere of nitrogen. Casein (E Merck, alkali soluble) and potassium persulphate (E Merck, GR) were used without further purification. Solvents were used after distillation at their respective boiling points.

Procedure of polymerization. The reactions were accomplished in flange flask. In a typical experiment known quantity of casein was added in the reaction flask already containing 30ml H₂O. The casein was dispersed for 30 min by constant stirring under atmosphere of nitrogen. Butyl acrylate and potassium persulphate (in 10 ml water) were added in the reaction flask. Total volume of reacting mixture was made to 60 ml by the addition of water. The reaction was allowed to proceed for 30 min at 60 °C.

After completion of the reaction, the contents were cooled to 5°C to terminate the reaction. The product was filtered through weighed sintered crucible and then soxhlet extracted. The resulting product was dried in vacuum desiccator at 50°C to a constant weight. The product was estimated for nitrogen. IR spectrum of the product was recorded to identify the grafting

of BA onto casein from the appearance of prominent absorption bands which were not present in the spectrum of casein. The viscosity of dilute solutions of product samples in phosphate buffer (pH 8.4) was measured to determine the molecular weight.

Results and Discussion

Tables 1, 2, 3 include the data collected from graft copolymerization of BA onto casein using potassium persulphate as catalyst at 60°C for 30 mins. Elemental analysis, solubility, IR spectral studies and viscosity were used to identify the grafting of BA onto casein. The 13 samples of the product contain 11.2-14.01% nitrogen whereas casein contains 14.38% nitrogen. The variation and decrease in percentage of nitrogen show the attachment of growing polymer chain of BA onto activated sites of casein. The product samples and phosphate buffer were mixed to paste and dilute solutions were prepared by warming whereas casein was also dissolved in phosphate buffer. IR spectrum of one of the product sample (Expt No 2) was recorded in KBr. The absorption band at 1760-1700cm⁻¹ showed the characteristic of the ester carbonyl group of PBA which supported grafting of BA onto activated centres of casein.

The values of the rate of total monomer conversion (R_p), rate of graft copolymerization (R_g) rate of homopolymerization (R_h), grafting efficiency (GE) and grafting ratio (GR) were calculated from the following simple expressions.

$$R_p = \frac{\text{total conversion of monomer (mol)}}{\text{time of polymerization (sec)}}$$

$$R_g = \frac{\text{grafted monomer (mol)}}{\text{time of polymerization (sec)}}$$

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$$R_h = R_p - R_g$$

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

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

Table 1 illustrates the effect of monomer concentration on the grafting parameters. The results indicate that the values of GE, GR, Rp and Rg are increased with increasing concentration of BA. It is due to higher availability of BA growing polymer chain radicals in the close vicinity of casein activated sites or casein macro-radicals which are almost immobile. For grafting it is very necessary for monomer radicals to be in the reach of casein activated sites. The rate of conversion of BA is greater than the rate of grafting since at the early stage of reaction butylacrylate starts homopolymerising, although formation of homopolymer is little. Similar results are also

obtained in graft copolymerization of acrylamide, MMA, vinyl acetate on casein, wool, silk and nylon (Nayak 1976; Nayak *et al* 1980; Paradhan *et al* 1982; Khan *et al* 1994; Khan and Khalil 1995)

The effect of concentration of casein on the grafting of BA onto casein is shown in Table 2. It is very interesting to note that the values of GE, Rp and Rg exhibit increase with increase in concentration of casein whereas GR shows a downward drift. The increase in concentration of casein produce large number of grafting centres along the backbone resulting in an increase of GE, Rp, Rg. The decrease in grafting ratio might be due to the absolute decrease in the monomer to casein concentration ratio (monomer/casein). The number of grafting sites on the backbone of casein is more than that growing polymer chains and growing polymer radicals. The growing polymer chains of PBA utilize the grafting sites of casein partially and some unbound casein radicals are left behind which cause mutual termination between the backbone radicals (Joseph *et al* 1982; Khan *et al* 1994). Due to this reason,

Table 1

Effect of monomer variation in graft copolymerization of butyl acrylate (BA) onto casein using potassium persulphate as catalyst*

Expt No	Butyl acrylate mol	Total conversion of BA		Elemental analysis % N	Grafted monomer mol	GR %	GE %	Rate of polymerization x 10 ⁶ mol Sec ⁻¹		
		mol	%					Rp	Rg	Rh
1.	0.05859	0.01045	17.8	14.01	0.007914	8.4	75.70	5.8055	4.3967	1.4088
2.	0.07812	0.01781	22.80	11.20	0.01656	17.7	93.00	9.8944	9.2000	0.6944
3.	0.09765	0.02600	27.70	11.48	0.02437	26.0	93.73	14.4444	13.5388	0.9056
4.	0.11718	0.03890	33.2	12.04	0.03758	40.0	96.61	21.6111	20.8777	0.7334

* Casein 3.33 x 10⁻⁴ mol, persulphate 3.75 x 10⁻³ mol, temp 60°C, time 30 min.

Table 2

Effect of backbone variation in graft copolymerization of butyl acrylate (BA) onto casein using potassium persulphate as catalyst*

Expt No	Casein x 10 ⁵ e mol	Total conversion of BA		Elemental analysis % N	Grafted monomer mol	GR %	GE %	Rate of polymerization x 10 ⁶ mol Sec ⁻¹		
		mol	%					Rp	Rg	Rh
5.	20.833	0.01465	18.75	11.77	0.01305	22.3	89.1	8.1388	7.2500	0.8888
6.	27.778	0.01687	21.60	13.17	0.01586	20.3	94.0	9.375	8.8111	0.5639
7.	33.333	0.01781	22.8	11.20	0.01656	17.7	93.0	9.8944	9.2000	0.6944
8.	41.667	0.01850	23.7	12.61	0.01747	14.9	94.4	10.2777	9.7055	0.5722
9.	48.611	0.01930	24.7	13.67	0.01850	13.9	95.85	10.7222	10.2777	0.4445

* BA 0.0781² mol, persulphate 3.75 x 10⁻³ mol, temp 60 °C, time 30 min.

instead of obtaining pure graft copolymer as a product, a mixture of PBA casein macromolecule and graft copolymer is obtained. Similar results have been obtained in the graft copolymerization of BA on gelatin (Joseph 1982) and acrylamide on casein (Khan *et al* 1994).

Table 3 shows the influence of persulphate concentration in the graft copolymerization of BA onto casein. The results indicate that the increase in concentration of catalyst increases the values of GR, Rp, Rg. Since casein and persulphate are soluble in the reaction medium, the approach of initiating radicals to casein is facilitated. As a result persulphate radicals interact with the functional group of casein and produce backbone radicals. It is very interesting to note that the value of GE drops from 93.5 to 91.5% with increasing the concentration of persulphate from 7.4×10^{-4} to 22.2×10^{-4} mole and then it increases (GE = 97.3%) at the catalyst concentration 29.6×10^{-4} mole. Again GE (94%) decreases at the persulphate concentration 37.5×10^{-4} mole which might be due to the nonavailability of sufficient grafting sites on casein from coupling of growing polymer chain of PBA with the casein. It results in the formation of homopolymer of BA which is also indicated from the value of Rh (Table 3). The values of Rh increase with the decrease in the value of GE. In brief, the order of Rp, Rg & Rh in all the three cases is:

$$R_p > R_g > R_h$$

Intrinsic viscosity $[\eta]$ in dlg^{-1} of dilute solutions of graft copolymer were determined at 30°C in an Ostwald's type viscometer. Phosphate buffer of pH 8.4 was used as solvent. Number average molecular weight \overline{M}_n was determined by using following relationship (Khan *et al* 1994).

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

Intrinsic viscosity is the intercept of the plot η_{sp}/C vs C where

C is the concentration of the dilute solution and η_{sp} is its specific viscosity. The intrinsic viscosity of the product samples obtained from these plots were 0.46-1.5 dlg^{-1} . The number average molecular weight calculated from these values were 55470-186750. The molecular weight of casein is 36000 ($[\eta] = 0.3 \text{ dlg}^{-1}$). The increase in molecular weight as compared with molecular weight of casein indicates that both casein and BA have participated in the reaction resulting graft copolymer (Fig 1). Further increase in the molecular weight also shows that there is possibility of mutual termination of casein radicals resulting in the formation of casein macromolecules. The product obtained after soxhlet extraction is the mixture of grafted casein and grafted casein macroradicals enhance the molecular weight of the product as shown in Table 4.

Swelling tests were accomplished in different solvents at room temperatures. Grafted casein (casein-g-BA) swells with different solvents uptake in acetone (18%), benzene (4%), chloroform (32%), carbon tetrachloride (20%), ethanol (16%),

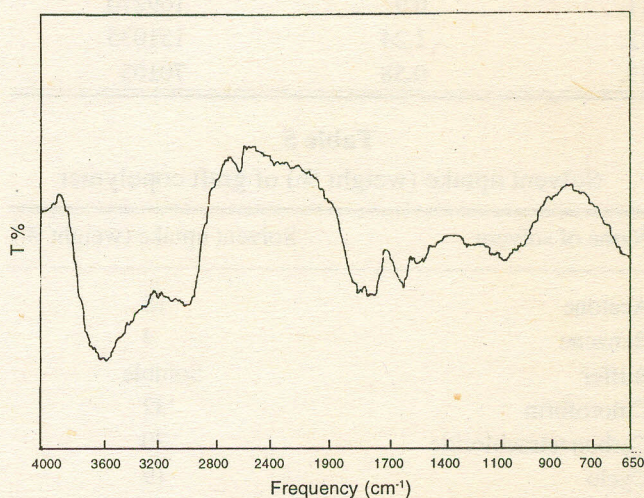


Fig 1. IR spectrum of graft copolymer casein-g-BA.

Table 3

Effect of catalyst variation in graft copolymerization of butyl acrylate (BA) onto casein using potassium persulphate as catalyst*

Expt No	Persulphate $\times 10^4$ mol	Total conversion of BA		Elemental analysis % N	Grafted monomer mol	GR %	GE %	Rate of polymerization $\times 10^6 \text{ mol Sec}^{-1}$		
		mol	%					Rp	Rg	Rh
10.	7.4	0.01312	16.8	13.17	0.01227	15.7	93.5	7.2889	6.8166	0.4723
11.	22.2	0.01391	17.8	12.90	0.01273	16.3	91.5	7.7257	7.0746	0.6511
12.	29.6	0.01429	18.3	13.73	0.01391	17.8	97.3	7.9389	7.7278	0.2111
13.	37.5	0.01687	21.6	13.17	0.01586	20.3	94.0	9.375	8.8111	0.5639

* Casein 27.778×10^{-5} mol, BA = 0.0781 mol, temp 60°C, time 30 min.

isopropanol (30%), MEK (5%), methyl chloride (25%), petroleum ether (7%), toluene (18%), THF (45%) and xylene (12%). Casein swells in water with 50% solvent uptake but the

Table 4

Intrinsic viscosity $[\eta]$ and number average molecular weight (mn) of casein g-BA

Expt No	$[\eta]$ dl/g	Mn
1.	0.95	115400
2.	1.36	165805
3.	1.40	170730
4.	1.53	186750
5.	1.03	125220
6.	0.58	70105
7.	1.36	165805
8.	0.70	84770
9.	1.27	154725
10.	0.46	55470
11.	0.9	109270
12.	1.24	151035
13.	0.58	70105

Table 5

Solvent uptake (weight %) of graft copolymer

Name of solvent	Solvent uptake (weight %)
Acetone	18
Benzene	4
Buffer	Soluble
Chloroform	32
Carbon tetrachloride	20
Cyclo	19
Ethanol	16
Isopropanol	30
MEK	5
Methylene chloride	25
Petroleum ether	7
Toluene	18
THF	45
Water	Insoluble
Xylene	12

grafted casein does not dissolve in water even does not show any swelling tendency in water. Grafted casein gets dissolved in phosphate buffer (pH 8.4). It might be due to the attachment of BA molecules to the backbone of casein.

The graft copolymer samples are creamy powdery substances soluble in phosphate buffer (pH 8.4). One of the sample starts decomposing from 150°C. When 1g sample (No 2) is kept in an oven at 100°C for 2h, it does not change its colour with 9% loss in weight. On further heating at 150°C for 2h, it becomes light brown with 4% loss in weight. When temperature reaches to 206-210°C, the substance becomes dark brown with 8% loss in weight. The material becomes insoluble in phosphate buffer. The change in weight and solubility of decomposed product might be due to crosslinking of the degraded polymer and intermolecular rearrangements of the amide group of the undegraded polymer. Moreover in addition to other reaction the copolymer might have undergone chain scission and oxidation reactions in the presence of air. (Grassie and Hay 1962; Jellinek 1962; Mullik and Khan 1970).

References

- Grassie N and Hay J N 1962 Thermal coloration and insolubilization in polyacrylonitrile. *J Polymer Sci* **58** 189.
- Jellinek H H G 1962 *Macromolecular chemistry IUPAC*, Butterwarths and Co. London.
- Joseph A, Radhakrishnan G, Joseph K T and Santappa 1982 Grafting of polymeric side chain to gelatin. *J Appl Polym Sci* **27** 1313.
- Khan A R, Khalil A, Yousufzai A H K 1994 Synthesis of graft copolymer of casein with acrylamide. *Pak J Sci Ind Res* **37** 92.
- Khan A R, Khalil A 1995 Studies on graft copolymerization of MMA on casein. *Pak J Sci Ind Res* **38** 292.
- Khan A R, Khalil A, Iffrahim A F K Grafting of growing polymer chains onto casein. *Pak J Sci Ind Res* (in press).
- Mullik S U and Khan A R 1970 Copolymerization of acrylonitrile and tetrachloroethylene. *Pak J Sci Ind Res* **12** 186.
- Nayak P L 1976 Grafting of vinyl monomers on wool fibres. *J Macromole Sci Rev Macromole Chem* **14** (2) 193.
- Nayak P L, Lenka S, Misra M K 1980 Copolymerization of MMA onto wool. *J Appl Polym Sci* **25** 1323.
- Pardhan A, Pati N C and Nayak P 1982 Grafting vinyl monomers onto polyester fibres **27** 2131-2138.