

Synthesis of Casein-g-Poly(butyl Acrylate)

Grafting of vinyl polymers with bio-¹⁻⁶ and synthetic^{7,8} macromolecules has been the subject of interest of several workers. Considerable research has been carried out at the Central Leather Research Institute on the modification of biopolymers and their characterization with respect to collagen,^{9,10} gelatin,¹¹ and casein.¹²

Though casein has been used for various applications¹³⁻¹⁸ as is and in modified form and in combination with other polymers, few fundamental studies concerning its modification have been carried out. The present study was undertaken to understand the kinetics and mechanism of modification of casein and the characterization of the graft copolymer. The preliminary results on the modification of casein with poly(butyl acrylate) are discussed with respect to percent grafting, grafting efficiency (*GE*), rate of total monomer conversion (*R_p*), rate of graft copolymerization (*R_g*), and rate of homopolymerization (*R_h*).

EXPERIMENTAL

Materials

Casein (E. Merck, G.R.) and potassium persulfate (A.R., S.D.'s, India) were used as such without further purification. Butyl acrylate (Rohm and Haas, USA) was purified before use as reported in the literature.¹⁹

Grafting Procedure

Grafting reactions were carried out in 100-ml reaction vessels with nitrogen inlet and outlet arrangements. Casein was accurately weighed and placed in a reaction vessel containing 25 ml water thermostatted at 60°C. After a sufficient time, butyl acrylate was added, followed by the initiator, and the total volume was made up to 50 ml. The reaction was allowed to proceed for the required time interval. After the completion of the reaction, the contents were cooled to 5°C. The products were filtered through weighed sintered crucibles and then Soxhlet extracted.

The values of the rate of total monomer conversion and the rate of the homopolymerization were calculated gravimetrically. The rate of graft copolymerization (*R_g*) and the grafting efficiency (*GE*) were calculated from the following expressions:

$$R_g = R_p - R_h$$

$$GE = \frac{R_g}{R_p} = \frac{R_g}{R_g + R_h}$$

Isolation of Grafts

Acid Hydrolysis. The grafted copolymer was hydrolyzed by heating with 6*N* HCl for 18 hr. The separated poly(butyl acrylate) was filtered, washed, and dried for viscosity studies.

Viscosity. The viscosities of poly(butyl acrylate) side chains were determined in acetone, and the molecular weight of poly(butyl acrylate) was calculated from the equation reported in the literature.²⁰

Infrared Analysis. Pure casein and graft copolymer were subjected to infrared analysis using a Perkin-Elmer model 337 grating infrared spectrophotometer in the form of potassium bromide pellets (500 mg) containing 2-6 mg powdered polymers.

RESULTS AND DISCUSSION

To understand the grafting reaction of poly(butyl acrylate) onto casein, variations in monomer concentration, initiator concentration, backbone concentration, and temperature were effected.

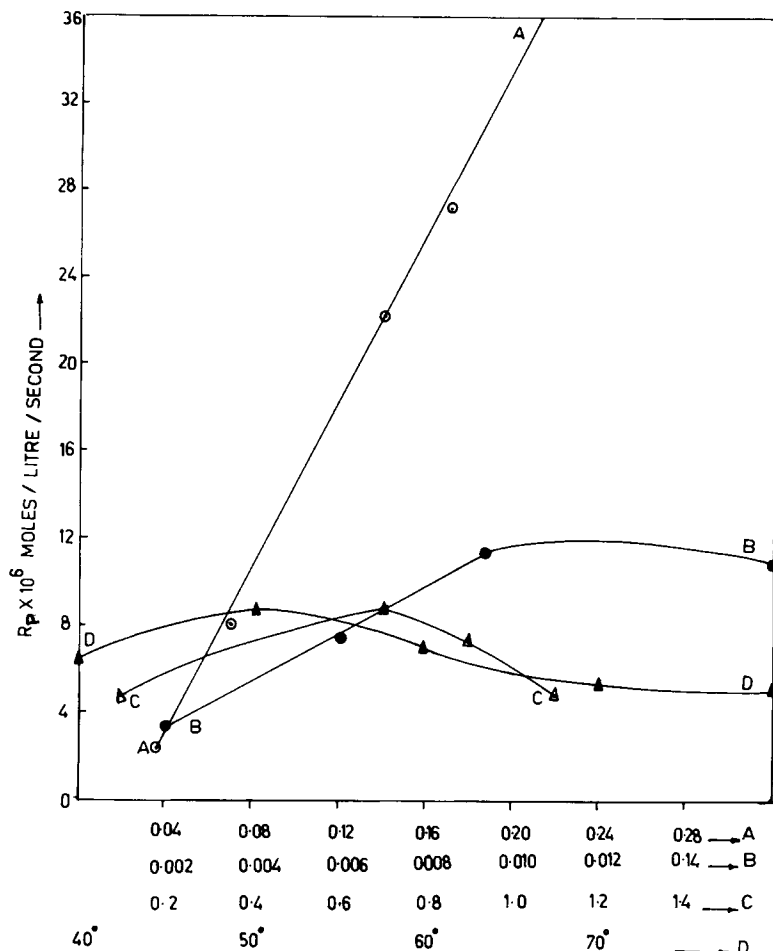


Fig. 1. A, Plot of rate of total monomer conversion vs. monomer concentration. Reaction conditions: $[S_2O_8^{2-}] = 10^{-2}M$; [casein] = 1% by weight of total volume; temperature = $60^\circ C$; reaction time = 60 min. B, Plot of rate of total monomer conversion vs. initiator concentration. Reaction conditions: $[BA] = 0.06975 \text{ mole/l.}$; [casein] = 1% by weight of total volume; temperature = $60^\circ C$; reaction time = 60 min. C, Plot of rate of total monomer conversion vs. backbone concentration. Reaction conditions: $[BA] = 0.06975 \text{ mole/l.}$; $[S_2O_8^{2-}] = 10^{-2}M$; temperature = $60^\circ C$; reaction time = 60 min. D, Plot of rate of total monomer conversion vs. temperature. Reaction conditions: $[BA] = 0.06975 \text{ mole/l.}$; $[S_2O_8^{2-}] = 10^{-2}M$; [casein] = 1% by weight of total volume; reaction time = 60 min.

Rate of total conversion of monomer, rate of graft copolymerization, rate of homopolymerization, percent grafting, and efficiency were calculated by gravimetric methods.

Monomer Variation

It was observed that an increase in monomer concentration in the system was found to increase the rate of total conversion (A in Fig. 1), thereby showing a possible increase in the rate of homopolymerization and the rate of grafting. This was confirmed by analysis of R_g and R_h ; R_g (A in Fig. 2) and R_h (Table I) were found to increase with increase in monomer concentration. But grafting efficiency (A in Fig. 3) was found to level off after a certain monomer concentration, showing that even when the percent grafting (A in Fig. 4) and R_g are increased, they have not contributed to a

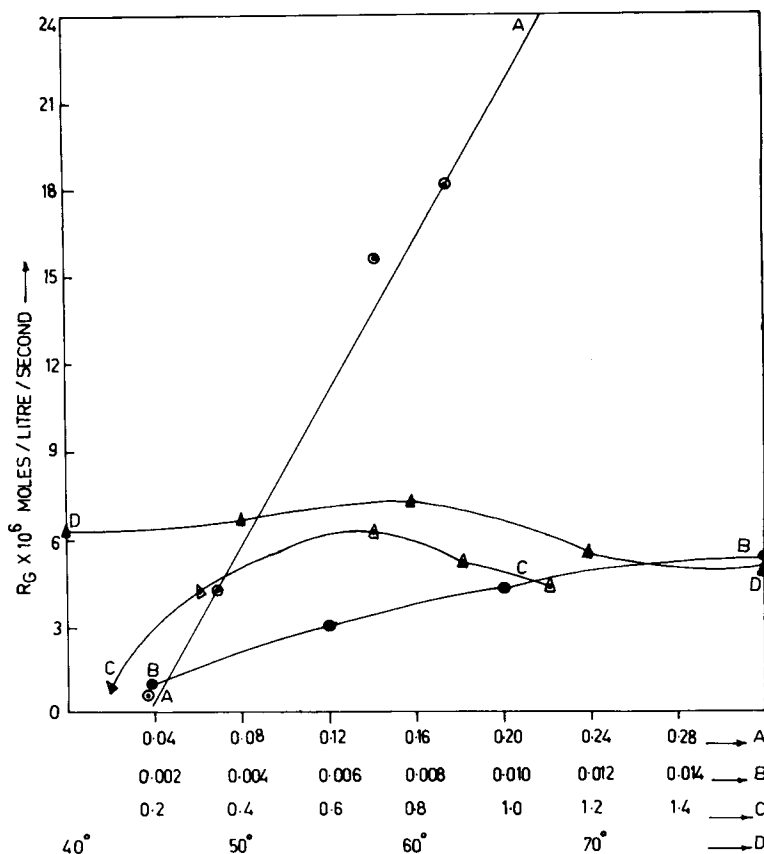


Fig. 2. A, Rate of graft copolymerization vs. monomer concentration. Reaction conditions: $[S_2O_8^{2-}] = 10^{-2}M$; [casein] = 1% by weight of total volume; temperature = $60^\circ C$; reaction time = 60 min. B, Rate of graft copolymerization vs. initiator concentration. Reaction conditions: [BA] = 0.06975 mole/l.; [casein] = 1% by weight of total volume; temperature = $60^\circ C$; reaction time = 60 min. C, Rate of graft copolymerization vs. backbone concentration. Reaction conditions: [BA] = 0.06975 mole/l.; $[S_2O_8^{2-}] = 10^{-2}M$; temperature = $60^\circ C$; reaction time = 60 min. D, Rate of graft copolymerization vs. temperature. Reaction conditions: [BA] = 0.06975 mole/l., $[S_2O_8^{2-}] = 10^{-2}M$; [casein] = 1% by weight of total volume; reaction time = 60 min.

progressive increase in grafting efficiency. This may be due to the fact that the relative increment in R_g after this limit is less compared to the relative increment in R_h . This may be due to the grafted chains acting as diffusion barriers which may impede diffusion of monomer into the backbone. As a result, less monomer would be available for grafting and most of it may be used for homopolymerization.

Initiator Variation

Variation in initiator concentration was found to increase R_p initially (B in Fig. 1) and then decrease it, which in turn might be due to the increase in R_h and R_g up to a certain limit and then a decrease either in R_h or R_g or in both. In agreement with these results, grafting efficiency increased initially and then decreased (B in Fig. 3) owing to the relative increment in the values of R_h compared to R_g .

The decrease in R_p with increasing initiator concentration may be due to annihilation of primary radicals formed in the system without being utilized for grafting and homopolymerization reactions and to termination of growing radicals by the primary radical.²¹

TABLE I
Rate of Homopolymerization and Molecular Weights of Side Chain Poly(butyl Acrylate)

Variation	$R_h \times 10^6$, mole/l. sec	Molecular weight $\bar{M}_v \times 10^{-5}$
Monomer, mole/l.		
[M] concentration		
0.03488	1.7969	3.27493
0.06975	3.9019	3.20546
0.13950	6.5929	6.22835
0.17440	9.2101	6.90515
0.20930	10.1128	7.21460
0.24410	11.5625	9.19943
[S ₂ O ₈ ²⁻] = 10 ⁻² M; [casein] = 1% by weight of total volume; temperature = 60°C; time = 60 min		
Initiator, mole/l.		
[I] concentration		
0.002	2.3655	5.59597
0.006	4.4922	8.51472
0.010	7.6736	5.52973
0.016	5.3342	4.54805
[BA] = 0.0698 mole/l.; [casein] = 1% by weight of total volume; temperature = 60°C; time = 60 min		
Temperature; °C		
40	0.0998	6.105962
50	2.1398	4.534959
60	2.5781	3.205467
70	3.0208	—
80	3.7500	—
[BA] = 0.0698 mole/l.; [S ₂ O ₈ ²⁻] = 10 ⁻² M; [casein] = 1% by weight of total volume; time = 60 min		
Backbone concentration [B]		
0.1	3.9887	—
0.3	2.6649	—
0.5	2.0486	—
0.7	2.5781	—
0.9	2.5564	—
1.1	0.5685	—
[BA] = 0.0698 mole/l.; [S ₂ O ₈ ²⁻] = 10 ⁻² M; temperature = 60°C; time = 60 min		

Variation of Backbone Concentration

Increasing backbone concentration was found to have interesting effects on the grafting reaction. The rate of total conversion (C in Fig. 1) increased initially and then decreased with increase in the backbone concentration (C in Fig. 1). This shows that the rate of graft copolymerization and the rate of homopolymerization should increase initially and then decrease. This was confirmed by Table I and C in Fig. 2.

But, interestingly, grafting efficiency increased steadily with increasing backbone concentration. This may be attributed to the fact that the relative increment in R_g is higher than the relative increment in R_h at any concentration of backbone in the reaction system under the conditions studied.

The decrease in R_g might be due to the destruction of radical activity on the backbone soon after it is formed due to its higher concentration. Deactivation of backbone radicals may also occur through combination and/or interaction with the primary radicals.

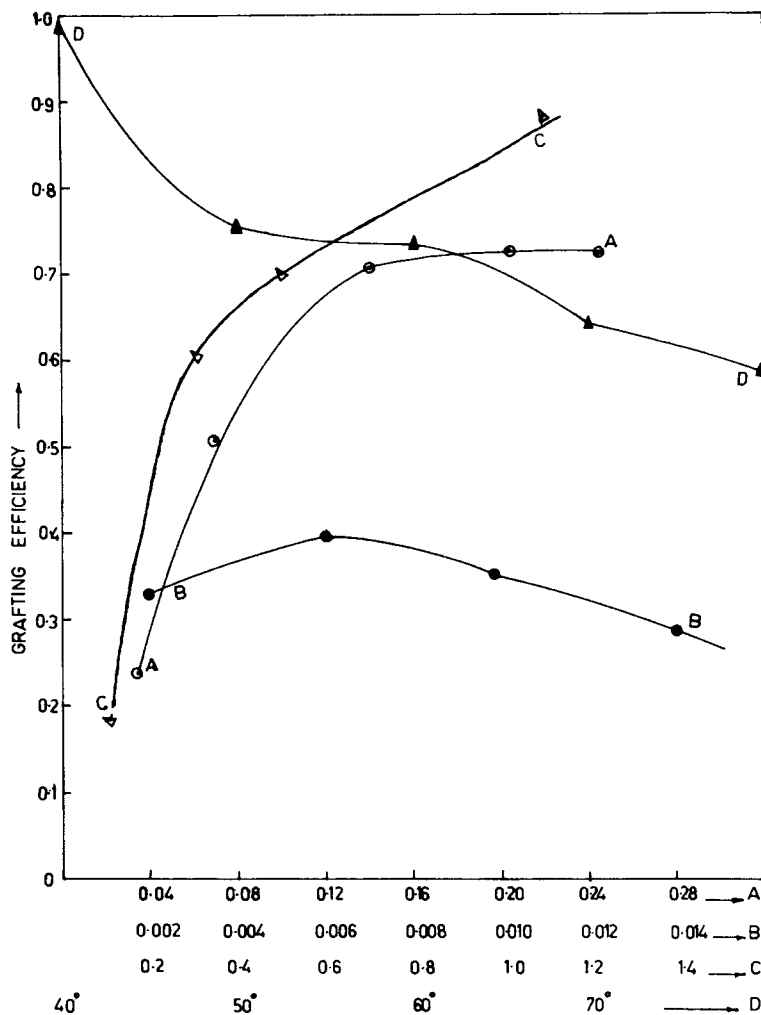


Fig 3. A, Grafting efficiency vs. monomer concentration: $[S_2O_8^{2-}] = 10^{-2}M$; [casein] = 1% by weight; B, Grafting efficiency vs. initiator concentration: [BA] = 0.06975 mole/l.; [casein] = 1% by weight; C, Grafting efficiency vs. backbone concentration: [BA] = 0.06975 mole/l.; $[S_2O_8^{2-}] = 10^{-2}M$; D, Grafting efficiency vs. temperature ($^{\circ}C$): [BA] = 0.06975 mole/l.; $[S_2O_8^{2-}] = 10^{-2}M$; [casein] = 1% by weight. Reaction time ABCD = 60 min; temp. A, B, C = 60 $^{\circ}C$.

Temperature Variation

Increase in the reaction temperature was found to increase R_p initially and then to decrease it (D in Fig. 1). R_g followed the same trend,¹¹ whereas the grafting efficiency steadily decreased from the beginning. The decrement in R_p and R_g with temperature may be due to the fast rate of termination. Even though there is a slight increase in R_g initially, this increment is relatively small compared to the relative increment in R_h (Table I) and D in Fig. 2. Thus it appears that an increase in reaction temperature favors homopolymerization rather than graft copolymerization.

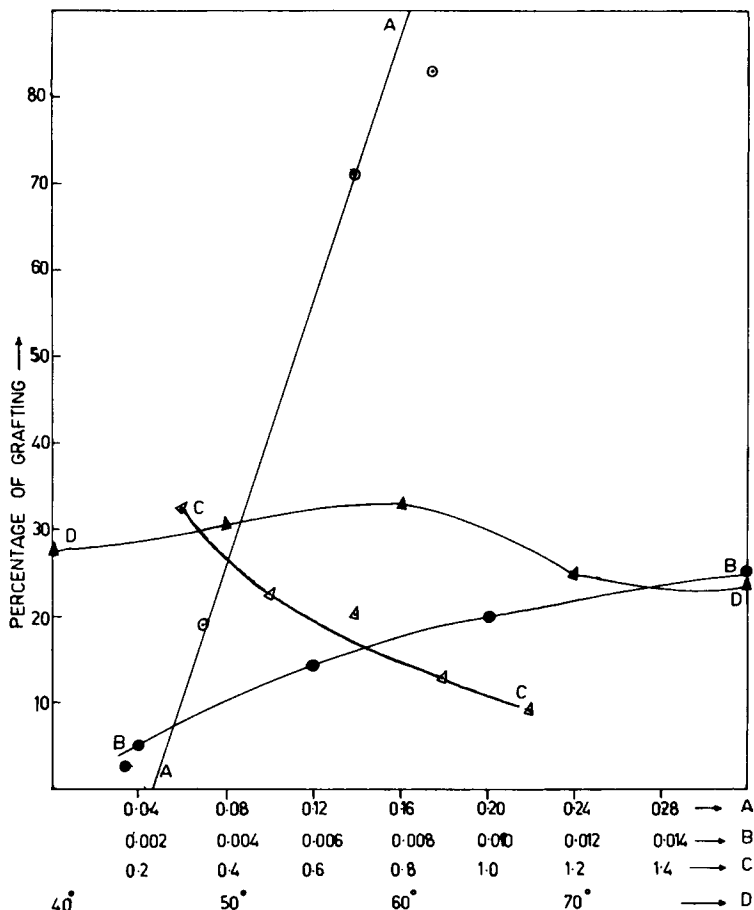


Fig. 4. A, Percent grafting vs. monomer concentration. Reaction conditions: $[S_2O_8^{2-}] = 10^{-2}M$; $[\text{casein}] = 1\%$ by weight of total volume; temperature = 60°C ; reaction time = 60 min. B, Percent grafting vs. initiator concentration. Reaction conditions: $[\text{BA}] = 0.06975 \text{ mole/l.}$; $[\text{casein}] = 1\%$ by weight of total volume; temperature = 60°C ; reaction time = 60 min. C, Percent grafting vs. backbone concentration. Reaction conditions: $[\text{BA}] = 0.06975 \text{ mole/l.}$; $[S_2O_8^{2-}] = 10^{-2}M$; temperature = 60°C ; reaction time = 60 min. D, Percent grafting vs. temperature. Reaction conditions: $[\text{BA}] = 0.06975 \text{ mole/l.}$; $[S_2O_8^{2-}] = 10^{-2}M$; $[\text{casein}] = 1\%$ by weight of total volume; reaction time = 60 min.

Viscosity

The poly(butyl acrylate) side chains were subjected to viscosity measurements in order to determine the molecular weight of side chains.

Molecular weights (\bar{M}_v) of side chains were found to increase with monomer concentration (Table I). In agreement with this observation, percent grafting also (A in Fig. 4) increased with increasing monomer concentration. This shows that the monomer units were progressively added to the side chain of the backbone during the reaction. Increase in the initiator concentration was found to lower the molecular weight (Table I) of the side chain, but percent grafting increased steadily (B in Fig. 4). This may be explained by the fact that while more monomer is graft copolymerized along the backbone, the growing side chain may interact with the excess of primary radicals present in the system due to rise in the primary radical concentration.

Increase in temperature was found to decrease the molecular weights of the side chain poly(butyl acrylate) (Table I). Thus, it appears that the rise in temperature of the reaction system leads to

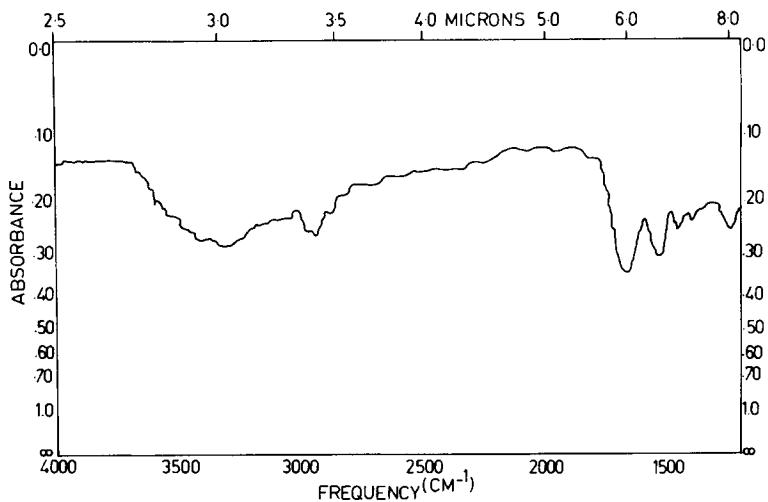


Fig. 5. Infrared spectrum of pure casein.

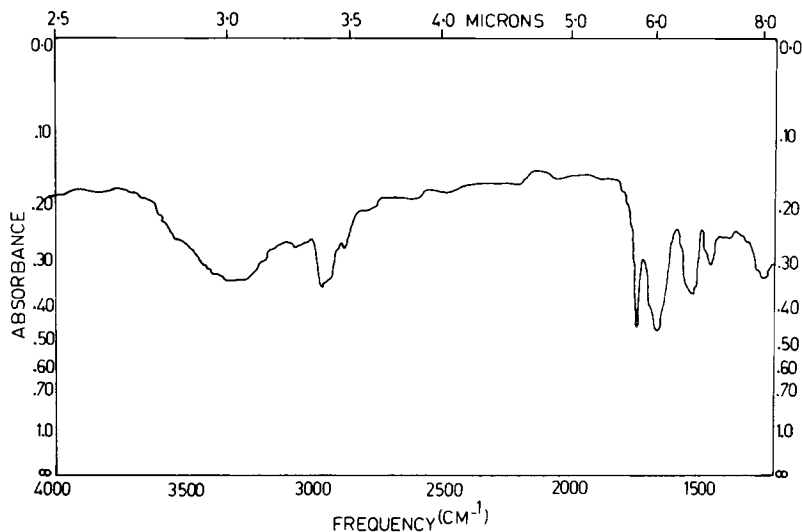


Fig. 6. Infrared spectrum of grafted casein.

termination involving the mutual annihilation of the growing radicals and interaction of growing radicals with primary radicals in the system.

Proof of grafting was obtained by the ninhydrin test and by infrared analysis. The grafted side chains were subjected to the ninhydrin test.¹² The appearance of a blue color showed the incorporation of amino groups, indicating grafting.

Further, IR spectra of pure casein and grafted casein after exhaustive Soxhlet extraction with acetone for poly(butyl acrylate) were taken (Figs. 5 and 6, respectively). The IR spectrum of graft copolymer showed an additional peak at 1745 cm⁻¹ due to the ester carbonyl group of poly(butylacrylate).

The authors thank Dr. K. Thomas Joseph and Dr. S. Rajadurai for their useful discussions.

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Received November 4, 1979
Revised February 12, 1980