Studies on Graft Copolymerization of Acrylate Monomers onto Casein

D. MOHAN, GANGA RADHAKRISHNAN, S. RAJADURAI, T. NAGABHUSHANAM, and K. THOMAS JOSEPH, *Polymer Division, Central Leather Research Institute, Adyar, Madras 600 020, India*

Synopsis

Poly(butyl acrylate) has been graft copolymerized onto casein using potassium peroxydisulfate–ascorbic acid as the initiating system. The proof of grafting has been obtained by ninhydrin test and IR studies. The effects of synthetic variables in the graft copolymerization have been discussed in the light of percent grafting, grafting efficiency, and the rates of polymerization.

INTRODUCTION

The milk protein, casein, contains H bonds between >C=O and —NH groups, which have a negative influence on the flexibility of the films formed.[1] These intermolecular bonds must therefore be weakened and thus make possible free rotation of some groups to give more elastic casein films. This can be achieved by grafting some acrylic ester groups onto casein.

The graft copolymerization of vinyl monomers onto bio and synthetic polymers has been the subject of innumerable publications.[2–10] However, the modification of casein by acrylate monomers has not been studied extensively. Potassium peroxydisulfates alone and in conjunction with other reducing agents were found to be good initiators for grafting vinyl monomers onto casein.[5,6,11]

Ascorbate anion radical, formed by the oxidation of ascorbic acid, was found to be effective for the initiation of polymerization.[12] Hashimoto and Sakaguchi[13] have used ascorbic acid–hydrogen peroxide system for the solution polymerization of vinyl acetate. The graft copolymerization of butyl acrylate onto gelatin has been recently reported[7] using this system. Ascorbic acid with peroxydisulfate has also been used for the solution polymerization of vinyl monomers.[14–17] Ascorbic acid–peroxydiphosphate initiator system has been used to graft methyl methacrylate onto silk.[9] No attempt has so far been made to synthesize graft copolymers of casein with butyl acrylate using potassium peroxydisulfate (KPS)–ascorbic acid (AA) redox system. In the present investigation, casein has been modified by poly(butyl acrylate) using the KPS–AA system in order to study the kinetics, mechanism, and also site of grafting reaction.

EXPERIMENTAL

Casein (E. Merck, G.R.), potassium peroxydisulfate (KPS) (E. Merck, G.R.), ascorbic acid (AA) (L.R. BDH, India), and pronase, B-grade (Cal, Bio-chem., United States) were used as such without further purification. Butylacrylate

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(Rohm and Hass, United States) was washed with sodium hydroxide, dried over anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen atmosphere and the middle fraction of the distillate was collected and used in the investigations.

Graft Copolymerization

The graft copolymerization reactions were carried out in a round-bottomed flask of 100 mL capacity provided with nitrogen inlet and outlet arrangements. In a typical experiment, casein was accurately weighed and dispersed in the reaction vessel containing 25 mL of H_2O, at constant stirring and thermostated at required temperature. After oxygen-free nitrogen was bubbled through the solution for 30 min, the required amount of butyl acrylate was added followed by potassium peroxydisulfate and ascorbic acid in succession. The total volume of the reaction was made up to 50 mL. The reaction was allowed to proceed for required time interval after which the contents were cooled to 5°C. The products were then filtered through a weighed sintered crucible and dried to a constant weight under vacuum. The resultant product was Soxhlet-extracted with acetone to remove the loosely bound homopolymer and dried to a constant weight *in vacuo*.

The rates of conversion of monomer (R_p) and homopolymerization (R_h) were calculated gravimetrically. The rate of graft copolymerization (R_g), percent grafting, and grafting efficiency (GE) were calculated as follows:

$$R_g = R_p - R_h$$

$$\text{percent grafting} = \text{PG} = \frac{W_2 - W_1}{W_1} \times 100$$

$$\text{grafting efficiency} = \text{GE} = \frac{R_g}{R_g + R_h} \times 100 = \frac{R_g}{R_p} \times 100$$

where W_1 is the weight of the casein dispersed and W_2 is the weight of the graft copolymers.

Hydrolysis of Graft Copolymer

Acid Hydrolysis. The casein graft copolymers (about 0.5 g) were weighed and then hydrolyzed for 18 h with 10 mL of 6*N* HCl, under vacuum in sealed reaction tubes at 100–105°C. The insoluble grafts were removed by filtration, washed with water, and dried *in vacuo* for viscosity studies.

Enzymatic Hydrolysis. Samples of casein-*g*-poly(butyl acrylate) (about 0.3 g) were heat denatured in water (50 mL). To the same, requisite amount of calcium chloride was added to make it a 0.02*M* solution and pH was adjusted to 8 with 0.1*N* sodium hydroxide. Pronase (10 mg) dissolved in water (0.5 mL) was then added together with a drop of toluene to prevent bacterial growth. The mixture was then incubated at 37°C for 18 h, while the pH was kept constant by addition of 0.01*N* sodium hydroxide. The insoluble graft was removed by centrifugation, washed and dried, and used for ninhydrin test.

Infrared Spectra

The infrared spectra of pure casein and grafted casein were measured with a Perkin-Elmer Model 337 Grating Infrared Spectrophotometer in the form of potassium bromide (KBr) pellets (500 mg) containing 2–6 mg powdered polymers.

Viscosity

Viscosities of the grafted poly(butyl acrylate) were determined at 25°C in an Ubbelohde type suspended level dilution viscometer with solution of polymer concentration ranging from 0.1 to 0.5 g/dL in acetone and the viscosity average molecular weights were estimated according to the equation[18]

$$[\eta] = 6.85 \times 10^{-3} \overline{M}_v^{0.75} \qquad \text{(dl/g, 25°C)}$$

Amino Acid Analysis

The hydrolysate of casein graft poly(butyl acrylate) with 6*N* HCl is evaporated on a rotary evaporator under vacuum at 40–50°C. The residue is dissolved in sodium citrate buffer at pH 2.2 and then analyzed with a BIOTRONIK Model L.C. 6000 E Amino Acid Analyzer to obtain insight into the active sites responsible for the graft copolymerization.

RESULTS AND DISCUSSION

With a view to understanding the reaction mechanism of grafting of poly(butyl acrylate) onto casein, the effects of synthetic variables such as concentration of monomer, initiator, activator (ascorbic acid), and backbone and temperature were investigated.

Effect of Monomer Concentration

It is observed from Figures 1–4(A) and Table I that with an increase in butyl acrylate concentration, the rates of conversion of monomer (R_p), graft copolymerization (R_g), and homopolymerization (R_h), molecular weight ($\overline{M}_v$) of side chain poly(butyl acrylate), percent grafting (PG), and grafting efficiency (GE) increase, which is in accordance with heterogeneous graft copolymerization.[6,8,19–22] At higher monomer concentrations, viscosity of the medium increases leading to gel effect.[23] Consequently, the biomolecular termination of the growing chains is hindered, while the other steps in the graft copolymerization process like initiation and propagation are not affected to the same degree due to the restricted mobility of the grafted polymer chain by the casein matrix. In addition, 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 favoring grafting reactions. Further, the relative increments in R_g is higher than that of R_h resulting in increasing grafting efficiency.

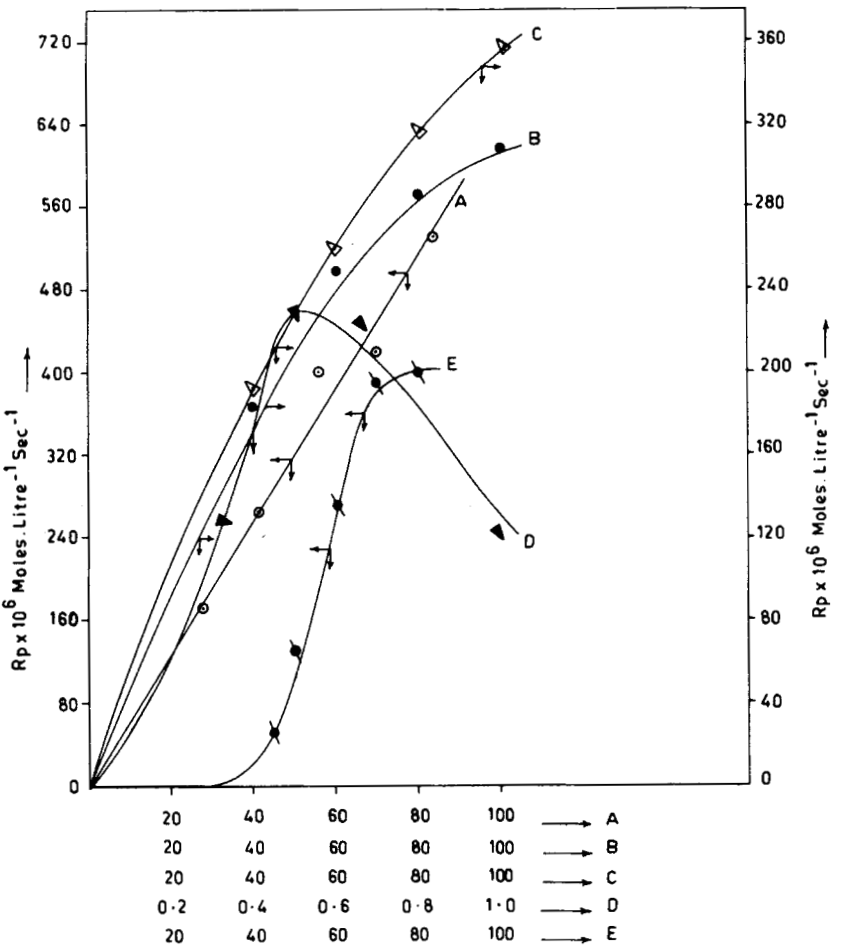

Fig. 1. (A) Plot of rate of conversion of monomer vs. monomer concentration: (⊙) [M] × 10^2 mol/L. Reaction conditions: [$S_2O_8^{-}$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (B) Plot of rate of conversion of monomer vs. initiator concentration: (●) [I] × 10^4 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (C) Plot of rate of conversion of monomer vs. activator concentration: (△) [AA] × 10^5 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^{-}$] = 6.0 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (D) Plot of rate of conversion of monomer vs. casein concentration: (▼) [B] × 10^3 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^{-}$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (E) Plot of rate of conversion of monomer vs. temperature: (◑) (°C). Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^{-}$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; reaction time = 15 min.

Effect of Initiator Concentration

The effect of concentration of peroxydisulfate by varying the concentration from 4.0 × $10^{-3}M$ to 10.0 × $10^{-3}M$ was found to increase the rates of conversion of monomer (R_p), graft copolymerization (R_g), and homopolymerization (R_h), percent grafting (PG), grafting efficiency (GE), and molecular weight ($\overline{M}_v$) of grafted poly(butyl acrylate) [Figs. 1–4(B) and Table I]. However, beyond an

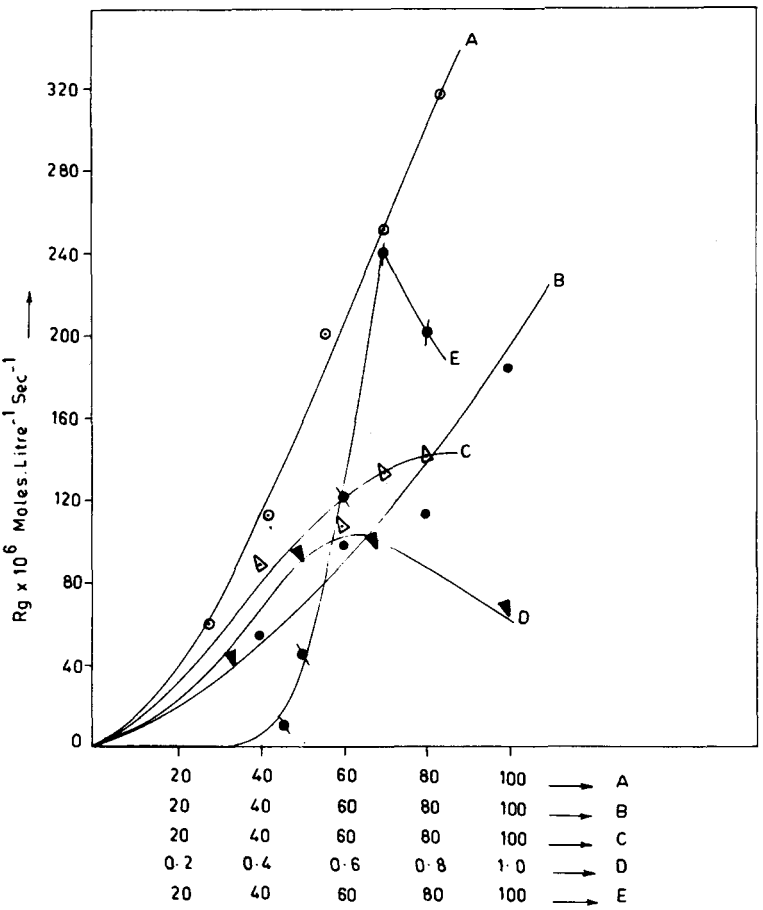

Fig. 2. (A) Plot of rate of graft copolymerization vs. monomer concentration: (⊙) [M] × 10^2 mol/L. Reaction conditions: [$S_2O_8^-$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (B) Plot of rate of graft copolymerization vs. initiator concentration: (●) [B] × 10^4 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (C) Plot of rate of graft copolymerization vs. activator concentration: (▲) [AA] × 10^5 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^-$] = 6.0 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (D) Plot of rate of graft copolymerization vs. casein concentration: (▼) [B] × 10^3 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^-$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (E) Plot of rate of graft copolymerization vs. temperature: (◑) (°C). Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^-$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; reaction time = 15 min.

optimum initiator concentration of 8.0 × $10^{-3}M$, the rate of homopolymerization was found to increase. These may be explained as follows: The reduction of peroxydisulfate in presence of ascorbic acid involves the formation of ascorbate radicals. In presence of the radicals, the ascorbate ($\dot{A}\bar{H}$) and sulfate ion ($SO_4^{\cdot-}$) radicals are the active species,[15,24] which activates the backbone and monomer and thereby initiates the polymerization. At relatively higher concentration of initiator, the primary radicals are produced, however, at a faster rate, which are mainly utilized for graft copolymerization. Hence, an increase in initiator

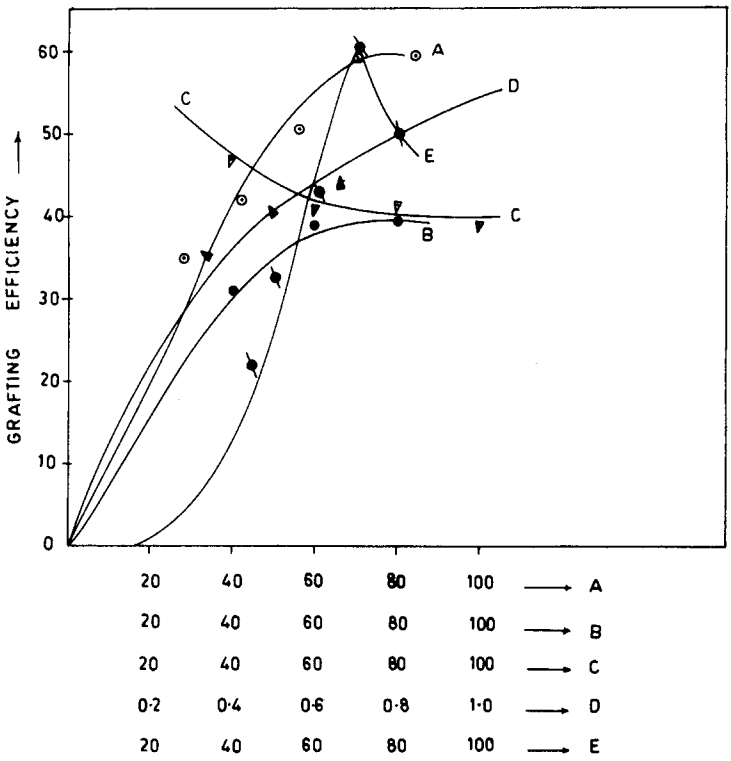

Fig. 3. (A) Plot of grafting efficiency vs. monomer concentration: (⊙) [M] × 10^2 mol/L. Reaction conditions: [$S_2O_8^{-}$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (B) Plot of grafting efficiency vs. initiator concentration: (●) [I] × 10^4 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (C) Plot of grafting efficiency vs. activator concentration: (▽) [AA] × 10^5 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^{-}$] = 6.0 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (D) Plot of grafting efficiency versus casein concentration: (▲) [B] × 10^3 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^{-}$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (E) Plot of grafting efficiency vs. temperature: (◑) (°C). Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^{-}$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; reaction time = 15 min.

concentration increases R_p, R_g, PG, and GE. Similar observations were also made in our earlier systems.[6,19,20]

In contrast to the homopolymerization systems, where the molecular weight of the polymer decreases with increasing initiator concentration under mutual termination conditions, the slight increase in $\overline{M}_v$ of the grafted polymers in the present system may be explained by taking into account the termination of grafted chain radicals by homopolymer radicals, whose concentration will be bound to increase with increasing initiator concentration.[25]

Effect of Activator Concentration

The effect of ascorbic acid concentration on graft copolymerization of butylacrylate onto casein is depicted in Figures 1–4(C) and Table I. The rates of

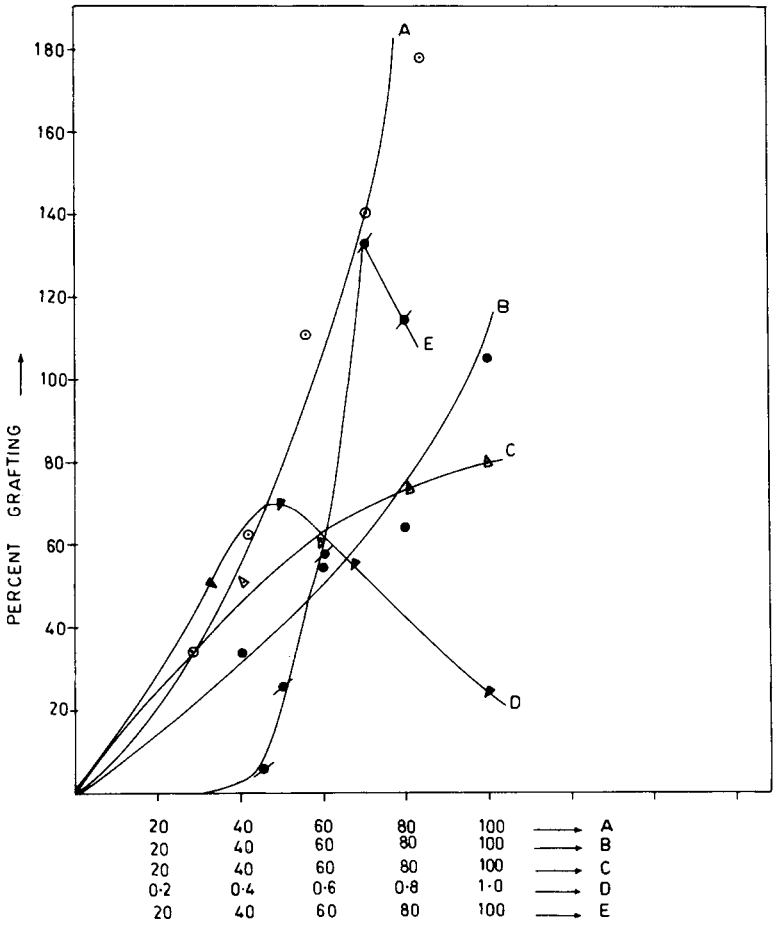

Fig. 4. (A) Plot of percent grafting vs. monomer concentration: (⊙) [M] × 10^2 mol/L. Reaction conditions: [$S_2O_8^{=}$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (B) Plot of percent grafting vs. initiator concentration: (●) [I] × 10^4 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (C) Plot of percent grafting vs. activator concentration: (▲) [AA] × 10^5 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^{=}$] = 6.0 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (D) Plot of percent grafting vs. casein concentration: [B] × 10^3 mol/L. Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^{=}$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; temp = 60°C; reaction time = 15 min. (E) Plot of percent grafting vs. temperature: (◑) (°C). Reaction conditions: [BA] = 0.4610 mol/L; [$S_2O_8^{=}$] = 6.0 × 10^{-3} mol/L; [AA] = 0.6 × 10^{-3} mol/L; [casein] = 0.6667 × 10^{-3} mol/L; reaction time = 15 min.

conversion of monomer (R_p), graft copolymerization (R_g), homopolymerization (R_h), and percent grafting (PG) were found to increase, while the grafting efficiency (GE) continuously decreases. With increase in ascorbic acid concentration, a larger number of active species, i.e., ascorbate ion ($\dot{A}\bar{H}$) radicals are formed in addition to the sulfate ion ($SO_4^{\dot{-}}$) radicals,[15,24] and hence the observed increase in R_p, R_g, R_h, and PG. However, since the ascorbate radicals are mainly utilized for homopolymerization,[20] the relative increment in R_h is higher than that of R_g and resulted in decreased grafting efficiency.

TABLE I
Results on the Rate of Homopolymerization and Molecular Weights of Side Chain Polybutylacrylate

Variation	$R_n \times 10^6$ (mol/L-s)	Molecular weight ($\overline{M}_v \times 10^{-6}$)
Monomer (m/L), [M]		
0.2794	110.11	—
0.4191	153.72	—
0.5588	196.31	21.77
0.6985	169.78	24.67
0.8382	217.68	27.92
$[S_2O_8^-] = 6.0 \times 10^{-3}M$: [AA] = $0.6 \times 10^{-3}M$		
[Casein] = $0.6667 \times 10^{-3}M$, temp = 60°C; time = 15 min Initiator (m/L), [I] $\times 10^3$		
4	127.20	—
6	152.03	10.06
8	170.91	12.58
10	122.97	16.26
[BA] = $0.4610M$; [AA] = $0.6 \times 10^{-3}M$		
[Casein] = $0.6667 \times 10^{-3}M$: temp = 60°C; time = 15 min Activator (m/L), [AA] $\times 10^4$		
4	100.70	—
6	153.54	—
8	186.84	—
10	219.78	—
[BA] = $0.4610M$; $[S_2O_8^-] = 6.0 \times 10^{-3}M$		
[Casein] = $0.6667 \times 10^{-3}M$, temp = 60°C; time = 15 min Backbone (m/L), [B] $\times 10^3$		
0.33	83.24	—
0.50	136.84	7.30
0.67	124.48	9.36
1.00	56.33	7.40
[BA] = $0.4610M$; $[S_2O_8^-] = 6.0 \times 10^{-3}M$		
[AA] = $0.6 \times 10^{-3}M$; temp = 60°C; time = 15 min Temperature (°C)		
45	39.93	—
50	84.15	—
60	151.65	10.76
70	155.05	23.23
80	199.70	19.26
[BA] = $0.4610M$; $[S_2O_8^-] = 6.0 \times 10^{-3}M$; [casein] = $0.6667 \times 10^{-3}M$		
[AA] = $0.6 \times 10^{-3}M$; time = 15 min		

Effect of Backbone Concentration

Figures 1–4(D) and Table I illustrate the effect of casein concentration in the graft copolymerization of butylacrylate onto casein. An increase in backbone concentration was found to increase the rates of conversion of monomer, graft copolymerization, homopolymerization, and percent grafting initially, while grafting efficiency increases continuously. However, the molecular weight ($\overline{M}_v$) of poly(butyl acrylate) does not vary very much. With increasing backbone concentration, a larger number of active sites are formed along the backbone, thereby increasing R_p, R_g, R_h, and PG. Further the relative increment in R_g is greater than that of R_h and resulted in increasing grafting efficiency. The decrease in percent grafting beyond the optimum value of backbone concentration may be interpreted as being due to slower addition of grafted side chain than the amount of casein increased.[26–30] The downward drift of the rates of

conversion of monomer and graft copolymerization beyond the optimum concentration may be due to mutual termination between backbone radicals and the deactivation of backbone radicals by the primary radicals.

The molecular weight ($\overline{M}_v$) of the grafted polymer chains does not seem to vary very much with backbone concentration, because this results only in an increase in the total number of grafting radical sites along the backbone, which does not affect the molecular weight at a higher monomer concentration employed. However, the increasing grafting efficiency with increasing backbone concentration may be attributed to the fact that the relative decrease in R_g is much less than the relative decrease in the rate of homopolymerization (R_h).

Effect of Temperature

The grafting of poly(butyl acrylate) onto casein has been investigated at various temperatures and the results are depicted in the Figures 1–4(E) and Table I. The rates of conversion of monomer, graft copolymerization, homopolymerization, percent grafting, grafting efficiency, and molecular weight of bound poly(butyl acrylate), $\overline{M}_v$, increase with increase in temperature as in normal polymerization. It is interesting to note that the rate of conversion of monomer increased with increase in temperature, while R_g, PG, GE, and $\overline{M}_v$ passed through a maximum. These results could be associated with (i) a faster rate of decomposition of peroxydisulfate in the presence of ascorbic acid giving more $SO_4^{\dot{-}}$ and $\dot{A}\overline{H}$ and $\dot{O}H$ radicals in close proximity of the casein and (ii) the increased mobility of monomer in the vicinity of the trunk polymer. The combined effect of the above factors will necessarily lead to increase in R_p, R_g, PG, GE, and $\overline{M}_v$.

However, a further increase in temperature favors homopolymerization to give relatively higher rates, thereby decreasing R_g, PG, GE, and $\overline{M}_v$.

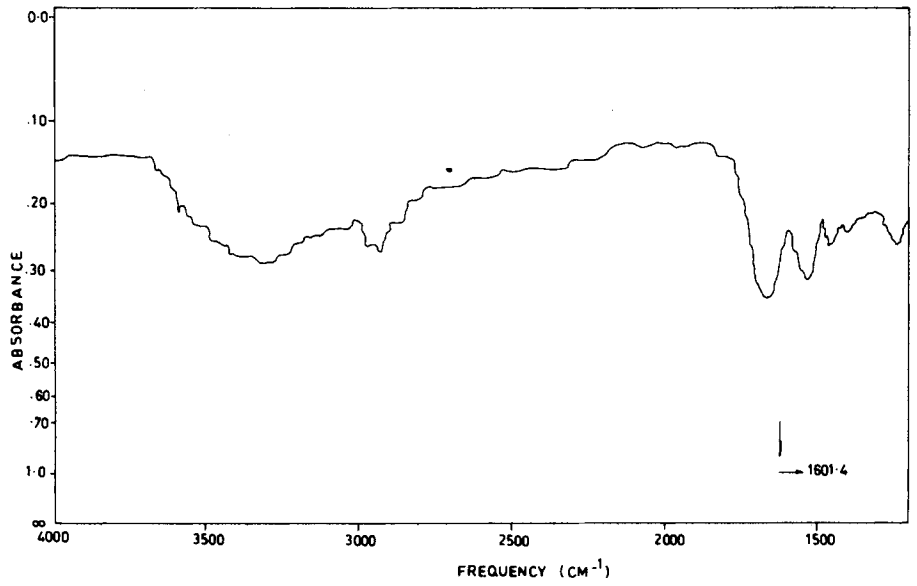

Fig. 5. Infrared spectrum of pure casein.

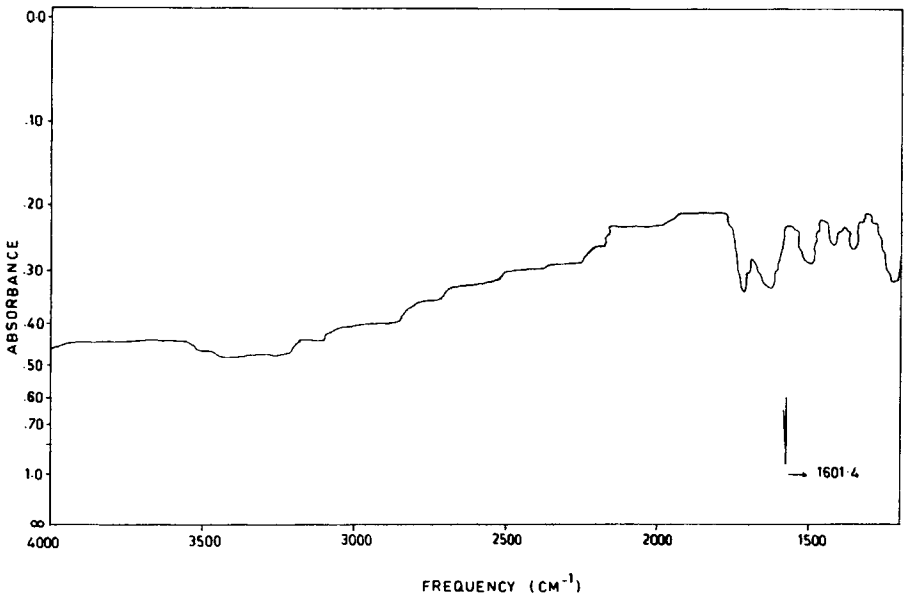

Fig. 6. Infrared spectrum of grafted casein.

The proof of grafting can be obtained by the detection of amino acid end groups in the grafted polymer, isolated by enzymatic hydrolysis of the graft copolymer. The isolated grafts were treated with ninhydrin reagent. The development of blue color normally associated with the amino acids confirmed the grafting of poly(butyl acrylate) onto casein.

Further proof of grafting was obtained from the IR spectra of pure casein and the casein-*g*-poly(butyl acrylate) after exhaustive Soxhlet extraction with acetone (Figs. 5 and 6, respectively). The presence of an additional band at 1745 cm^{-1}, which is characteristic of the ester carbonyl group (Fig. 6), supports the formation of casein graft copolymers.

Further, comparison of amino acid analyses of pure and grafted casein indicates that the amino acids cystine, methionine, and arginine have been affected up to 85–100% in grafted casein, which shows that these are the sites at which poly(butyl acrylate) have been attached.[25] Our findings are in good accordance with the earlier reports[31,32] on the grafting of casein with acrylics.

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