Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis of Casein-g-Poly(methyl Acrylate)

D. Mohan[a]; Ganga Radhakrishnan[a]; S. Rajadurai[a]
[a] Polymer Division Central Leather Research Institute Adyar, Madras, India

To cite this Article Mohan, D. , Radhakrishnan, Ganga and Rajadurai, S.(1983) 'Synthesis of Casein-g-Poly(methyl Acrylate)', Journal of Macromolecular Science, Part A, 20: 2, 201 — 212
To link to this Article: DOI: 10.1080/00222338308069960
URL: http://dx.doi.org/10.1080/00222338308069960

J. MACROMOL. SCI.–CHEM., A20(2), pp. 201-212 (1983)

Synthesis of Casein-g-Poly(methyl Acrylate)

D. MOHAN, GANGA RADHAKRISHNAN, and S. RAJADURAI

Polymer Division
Central Leather Research Institute
Adyar, Madras 600020, India

ABSTRACT

The graft copolymerization of poly(methyl acrylate) onto casein was investigated using potassium peroxydisulfate initiator in aqueous medium. The effect of such variables as concentrations of monomer, initiator, and backbone, and temperature were studied and are discussed as they concern the rates of conversion of monomer, graft copolymerization, percent grafting, and grafting efficiency. Proof of grafting was also established.

INTRODUCTION

The modification of natural and synthetic polymers has been gaining interest from both the practical and fundamental points of view. It has been found that graft copolymerization of vinyl monomers onto proteins is an effective tool for imparting desired properties [1-5]. Different aspects of this technique have been revealed by several researchers [1-8] through radical initiation. Peroxydisulfate alone [5, 6] and in combination with suitable reducing agents [9, 10] was able to initiate the grafting reaction. However, very little work has been carried out on modifying the milk protein, casein [11-15].

In continuation of our earlier work [5, 6] on the modification of casein, the graft copolymerization of methyl acrylate onto casein has been investigated and is discussed in the light of rates of conversion

0022-233X/83/2002-0201$3.50/0

of monomer, graft copolymerization and homopolymerization, percent grafting, and grafting efficiency. The results are also compared with previous reports [5, 6].

EXPERIMENTAL

Materials

Casein (E. Merck, G.R.) and potassium peroxydisulfate (E. Merck, G.R.) were used as received. The monomer, methyl acrylate (BDH, England), was freed from inhibitor by washing successively with 5% sodium hydroxide and distilled water, dried over anhydrous sodium sulfate, and finally distilled under vacuum. The middle fraction of the distillate was used for the graft copolymerization reaction.

Procedures

The grafting reaction in heterogeneous medium was carried out in a three-necked flask equipped with a stirrer and a nitrogen inlet. In a typical experiment the required amount of casein was dispersed in water with constant stirring and thermostated at a specified temperature. After sufficient time a calculated amount of monomer was added to the reaction mixture followed by potassium peroxydisulfate. The total volume of the reaction mixture was maintained at 50 mL. After a specified reaction time, the reaction flask was removed from the thermostat and cooled to 5°C to stop the reaction. The resultant polymer was filtered and washed in a sintered crucible and dried in vacuum at 55°C to constant weight. The ungrafted homopolymer was then removed from the graft copolymer by exhaustive Soxhlet extraction with acetone for 70 h. The resultant graft copolymer thus obtained was dried in vacuum at 55°C to constant weight. The rates of conversion of monomer (R_p), graft copolymerization (R_g), percent grafting (PG), and grafting efficiency (GE) were calculated as reported [5, 6].

Characterization Technique

The graft copolymer was subjected to IR analysis after thorough extraction of the homopolymer. The IR spectra of casein and the graft copolymer were recorded in KBr using a Perkin-Elmer 337 grafting IR spectrophotometer.

RESULTS AND DISCUSSION

Studies of the effect of such experimental variables as concentrations of monomer, initiator, and backbone, and temperature have been carried out in order to understand the reaction mechanism of graft copolymerization.

EFFECT OF MONOMER CONCENTRATION

The effect of monomer concentration on the extent of polymerization of methyl acrylate with casein is shown in Figs. 1-4 (A). As the concentration of the monomer was increased, the rates of R_p, R_g, GE, and PG increased proportionately. Similar observations have been made by other investigators [16-18] for heterogeneous graft copolymerization. Increased grafting at higher monomer concentrations could be associated with the gel effect [19] due to an increase in the viscosity of the medium. In addition, the gel effect may also 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.

Due to the polar nature of the vinyl acetate monomer, lower R_p, R_g, PG, and GE were observed in an earlier system [6] compared to the present system. A similar trend has been reported in the literature [10].

EFFECT OF INITIATOR CONCENTRATION

Figures 1-4 (B) show the effect of peroxydisulfate concentration on the grafting of methyl acrylate onto casein. The rates of R_p, R_g, and PG were found to increase with the initiator concentration, while the grafting efficiency passed through a maximum. However, in the case of vinyl acetate [6], all the above parameters decreased after an initial increase because of the higher initiator concentration employed. The observed increase in R_p, R_g, and PG may be due to the fact that at lower initiator concentration, activation along the backbone takes place immediately, followed by graft copolymerization of monomers onto the backbone. The decrease in GE beyond the optimum concentration may be assumed to be due to chain transfer from the growing radicals to the monomers, resulting in a higher amount of homopolymer formation.

The higher R_p, R_g, GE, and PG in the case of methyl acrylate compared to butyl acrylate [5] and vinyl acetate [6] may be due to the higher reactivity of methyl acrylate toward graft copolymerization.

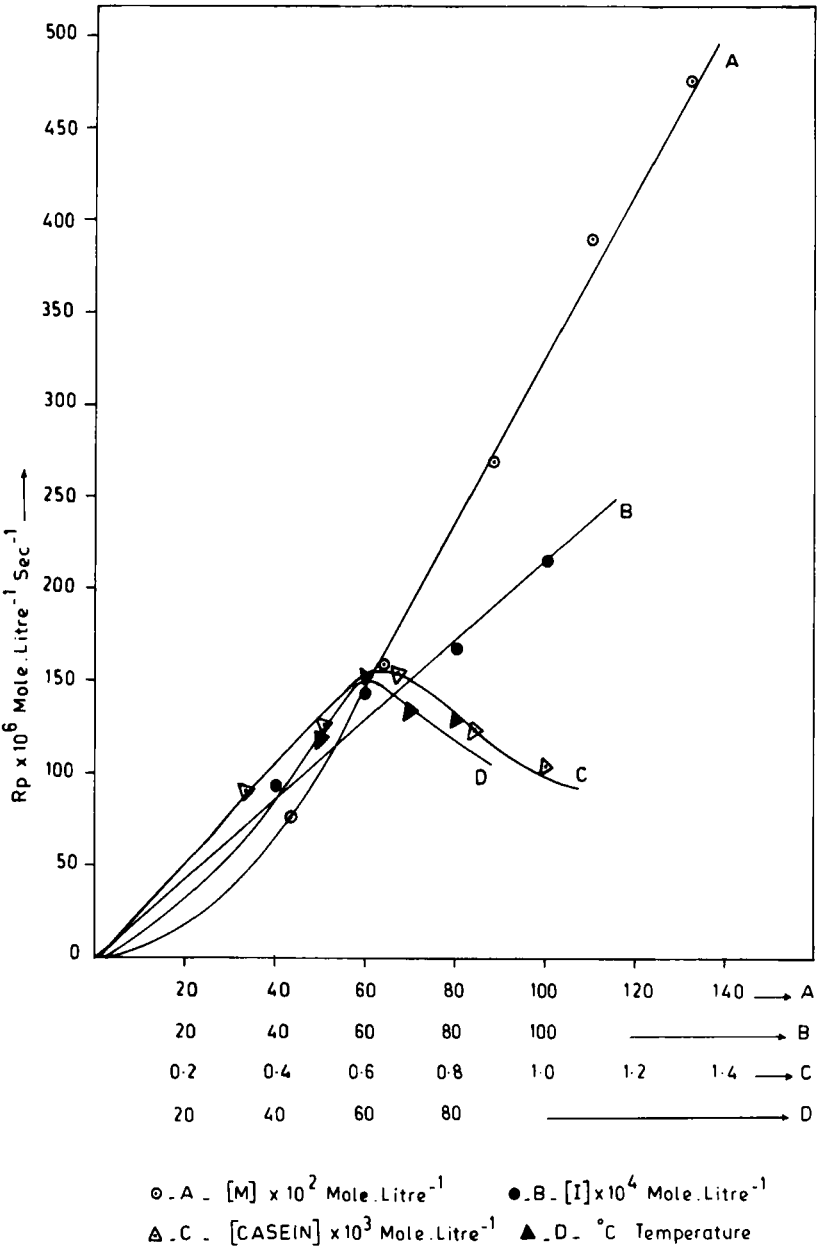

FIG. 1. A: Plot of rate of conversion of monomer versus monomer concentration. Reaction conditions: $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; [casein] $= 0.6667 \times 10^{-3}$ M; 60°C; time, 30 min; total volume 50 mL. B: Plot

EFFECT OF BACKBONE CONCENTRATION

The influence of casein concentration in the graft copolymerization of methyl acrylate has been studied. The results obtained for a given amount of monomer and various initiator concentrations are illustrated in Figs. 1-4 (C). An increase in backbone concentration was found to increase the rates of conversion of monomer and graft copolymerization initially. This may be attributed to the fact that an increase in backbone concentration leads to an increase in the number of grafting sites, thereby increasing R_p and R_g. Further, the relative increment in the rate of graft copolymerization is greater than that of homopolymerization, thereby leading to an increase in grafting efficiency.

However, the relative increment in the number of side chains grafted is less when compared to the relative increment in casein concentration. This leads to a decrease in percent grafting with increasing backbone concentration. Similar observations have also been made by several investigators [5, 6, 8, 20-24]. As expected, methyl acrylate has higher R_p, R_g, GE, and PG than butyl acrylate [5] which, in turn, is higher than vinyl acetate [6].

EFFECT OF TEMPERATURE

The role of reaction temperature in the graft copolymerization of methyl acrylate onto casein has been investigated. It was found that an increase in temperature accelerated the rates of conversion of monomer, graft copolymerization, and percent grafting up to 60°C.

An increase in temperature influences the activation of casein, the solubility of monomer, the diffusion of both monomer and initiator, the rates of peroxydisulfate decomposition, and the propagation of the grafting reaction, which results in an increase in R_p, R_g, and PG. However, an increase of temperature not only facilitated the rate of graft copolymerization but also accelerated the rate of homopolymerization, and hence there was a decrease in grafting efficiency.

FIGURE 1 (continued)
of rate of conversion of monomer versus initiator concentration. Reaction conditions: [MA] = 0.7268 M; [casein] = 0.6667×10^{-3} M; 60°C; Reaction time, 30 min; total volume, 50 mL. C: Plot of rate of conversion of monomer versus backbone concentration. Reaction conditions: [MA] = 0.7268 M; $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; 60°C; time, 30 min; total volume, 50 mL. D: Plot of rate of conversion of monomer versus temperature. Reaction conditions: [MA] = 0.7268 M; $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; [casein] = 0.6667×10^{-3} M; time, 30 min; total volume, 50 mL.

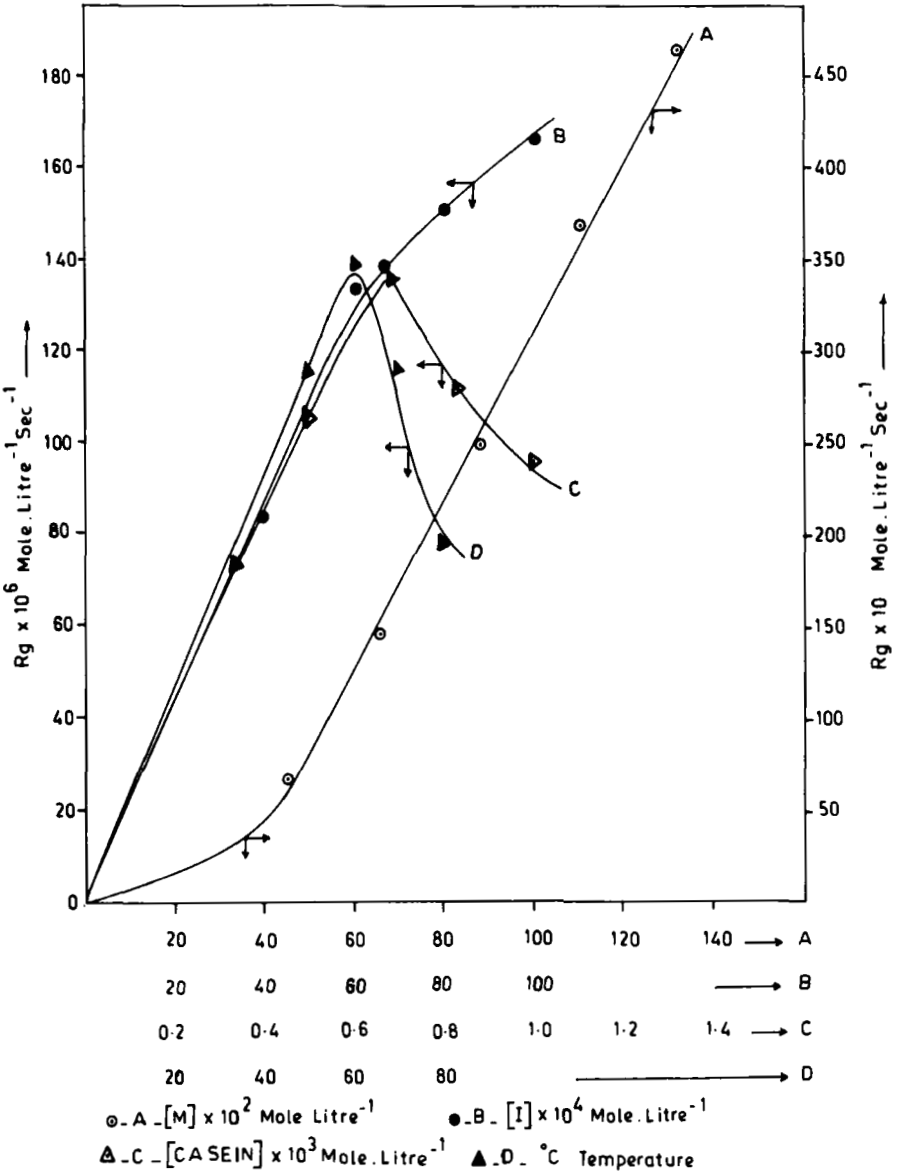

FIG. 2. A: Plot of rate of graft copolymerization versus monomer concentration. Reaction conditions: $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; [casein] $= 0.6667 \times 10^{-3}$ M; 60°C; time, 30 min; total volume, 50 mL. B: Plot of rate of graft copolymerization versus initiator concentration. Reaction conditions: [MA] = 0.7268 M; [casein] $= 0.6667 \times 10^{-3}$ M; 60°C; time, 30 min; total volume, 50 mL. C: Plot of rate of graft copolymerization versus backbone concentration. Reaction conditions: [MA] = 0.7268 M; $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; 60°C; time, 30 min; total volume, 50 mL. D: Plot of rate of graft copolymerization versus temperature. Reaction conditions: [MA] = 0.7268 M; $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; [casein] $= 0.6667 \times 10^{-3}$ M; time, 30 min; total volume, 50 mL.

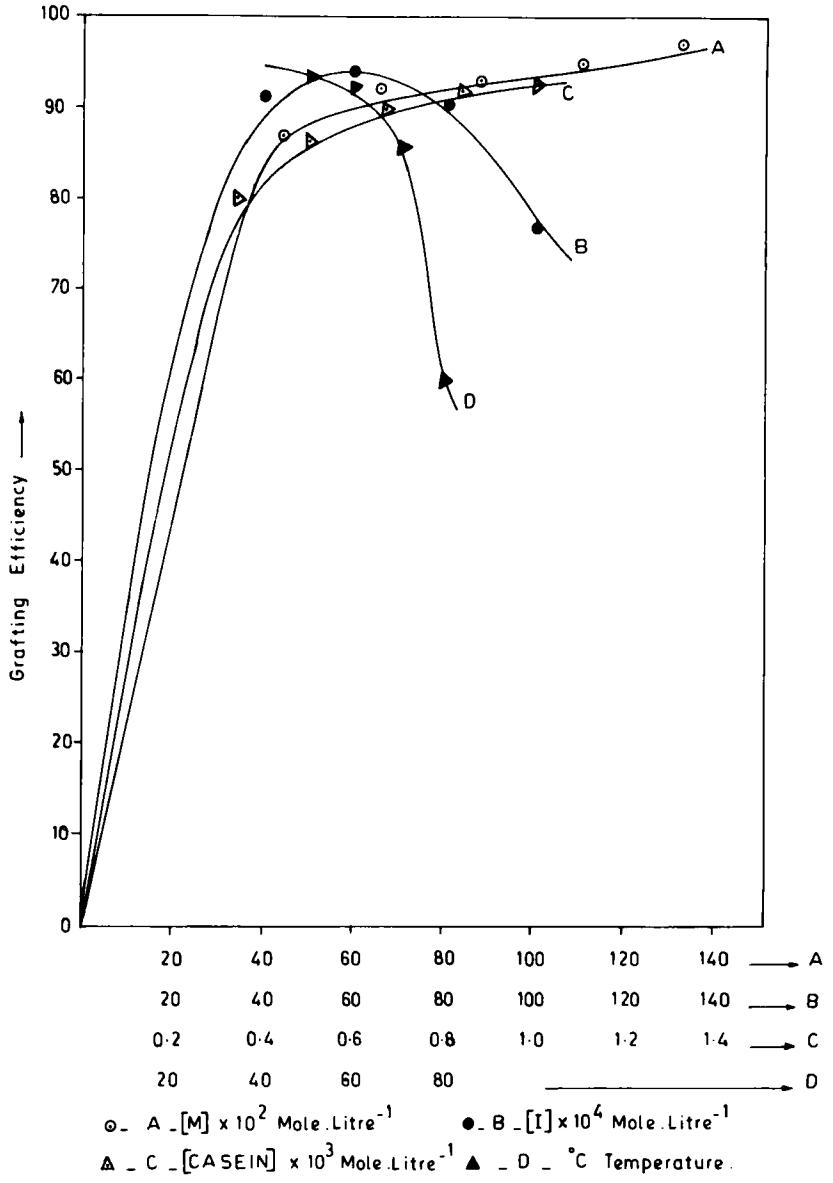

FIG. 3. A: Plot of grafting efficiency versus monomer concentration. Reaction conditions: $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; [casein] = 0.6667×10^{-3} M; 60°C; time, 30 min; total volume, 50 mL. B: Plot of grafting efficiency versus initiator concentration. Reaction conditions: [MA] = 0.7268 M; [casein] = 0.6667×10^{-3} M; 60°C; time, 30 min; total volume, 50 mL. C: Plot of grafting efficiency versus backbone concentration. Reaction conditions: [MA] = 0.7268 M; $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; 60°C; time, 30 min; total volume, 50 mL. D: Plot of grafting efficiency versus temperature. Reaction conditions: [MA] = 0.7268 M; $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; [casein] = 0.6667×10^{-3} M; time, 30 min; total volume, 50 mL.

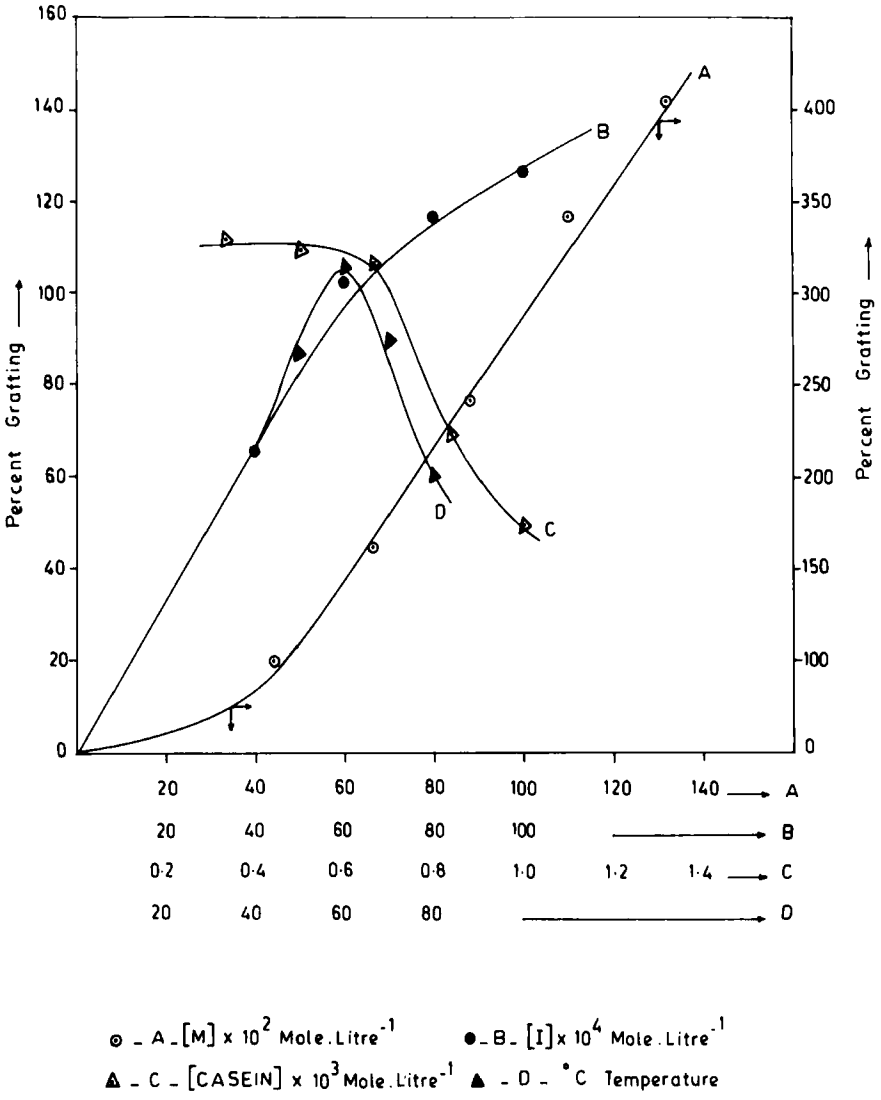

FIG. 4. A: Plot of percent grafting versus monomer concentration. Reaction conditions: $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; [casein] = 0.6667×10^{-3} M; 60°C; time, 30 min; total volume, 50 mL. B: Plot of percent grafting versus initiator concentration. Reaction conditions: [MA] = 0.7268 M; [casein] = 0.6667×10^{-3} M; 60°C; time, 30 min; total volume, 50 mL. C: Plot of percent grafting versus backbone concentration. Reaction conditions: [MA] = 0.7268 M; $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; 60°C; time, 30 min, total volume, 50 mL. D: Plot of percent grafting versus temperature. Reaction conditions: [MA] = 0.7268 M; $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ M; [casein] = 0.6667×10^{-3} M; time, 30 min; total volume, 50 mL.

Beyond the critical temperature, 60°C, an increase in temperature favors fast termination between graft, primary, and homopolymeric radicals, resulting in decreased R_p, R_g, and PG. Similar observations were cited in our earlier work [5, 6].

Proof of Grafting

Selective solvent extraction, a method based on differences in solubilities between the graft copolymer and the unbound homopolymer, has provided evidence for the graft copolymerization of acrylate monomers onto proteins [25]. In the present investigation the unbound homopolymer, poly(methyl acrylate), was Soxhlet extracted from the graft copolymer using acetone as solvent.

However, homopolymer chains may be entangled with macromolecules of the substrate, casein, without covalent bonding to form a copolymer of modified properties. This situation was proven to be absent in the present system by extracting the homopolymer from the physical blends of casein with poly(methyl acrylate). This establishes proof that pure casein graft copolymers are formed.

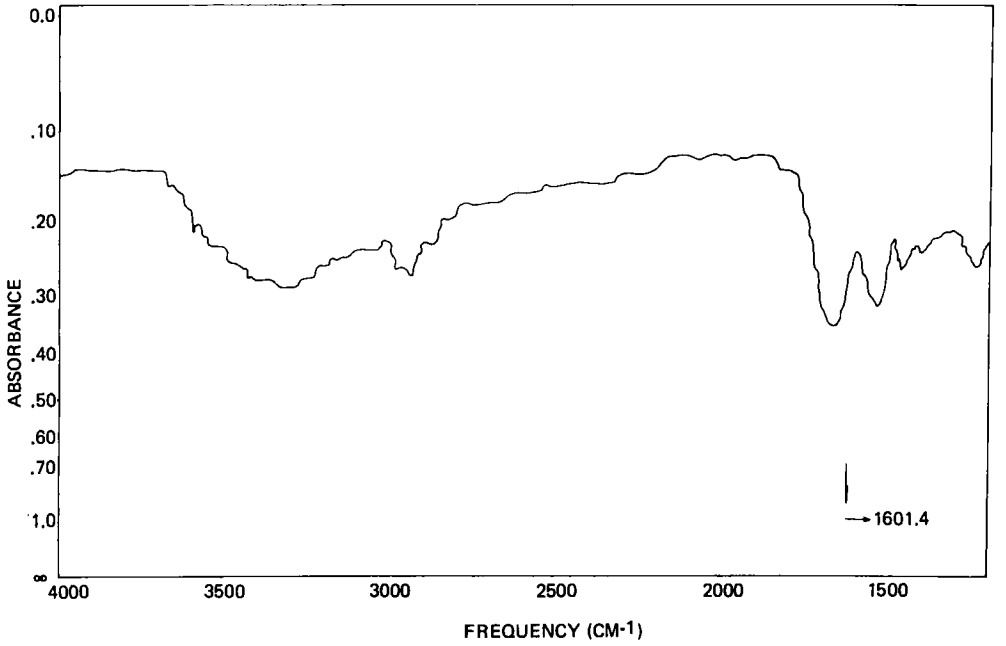

FIG. 5. Infrared spectra of pure casein.

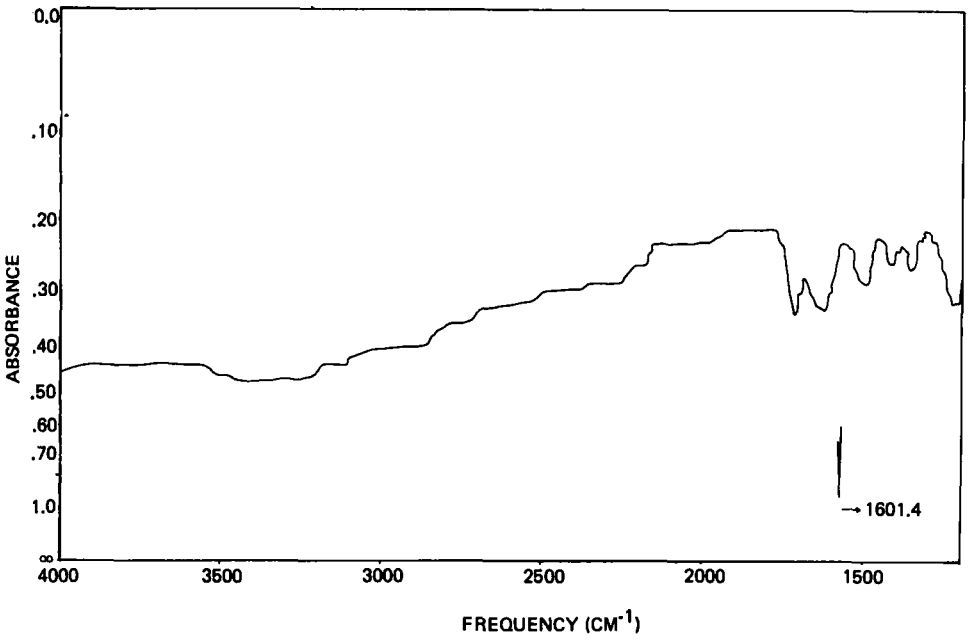

FIG. 6. Infrared spectra of casein-g-poly(methyl acrylate).

Treatment of Isolated Grafts with Ninhydrin Reagent

Casein in the graft copolymer was hydrolyzed by the enzyme pronase. The grafted side chains were isolated by dialyzing and finally by freeze-drying the hydrolyzed sample. The isolated grafts were then treated with ninhydrin reagent [5]. The development of the blue color normally associated with amino acids confirmed grafting of methyl acrylate onto casein.

Infrared Spectra

Typical IR spectra of casein and the graft copolymer are presented in Figs. 5 and 6. The presence of a band at 1750 cm^{-1}, which is characteristic of ester carbonyl groups in the graft copolymer, supports the formation of casein graft copolymer.

REFERENCES

[1] C. E. Brockway and P. A. Seaberg, J. Polym. Sci., Part A-1, 5, 1313 (1967).
[2] Y. Iwakura and Y. Imai, J. Polym. Sci., Part C, 23, 461 (1968).
[3] H. L. Needles, J. Polym. Sci., Part A-1, 5, 1 (1967).
[4] T. Kuwajima, H. Yoshida, and K. Hayashi, J. Appl. Polym. Sci., 20, 967 (1976).
[5] D. Mohan, G. Radhakrishnan, and T. Nagabhushanam, Ibid., 25, 1799 (1980).
[6] D. Mohan, G. Radhakrishnan, and S. Rajadurai, Makromol. Chem., 183, 1659 (1982).
[7] K. Kojima, S. Iwabuchi, K. Murakami, K. Kojima, and F. Ichikawa, J. Appl. Polym. Sci., 16, 1139 (1972).
[8] R. Mehrotra and B. Ranby, Ibid., 16, 1139 (1972).
[9] M. Negishi, K. Arai, S. Okada, and I. Nagakura, Ibid., 9, 3465 (1966).
[10] B. N. Misra, R. Dogra, I. K. Mehta, and A. S. Singha, Angew. Macromol. Chem., 90, 83 (1980).
[11] V. Svoboda and V. Novotny, Czechoslovakian Patent 162,063 (c1-CO8111/00), (November 15, 1976), Appl. 71/1,174 (February 17, 1971); Chem. Abstr., 85, 160853p (1976).
[12] W. Friedrich and J. Benn, East German Patent 49,469 (c1-C 09g), (August 5, 1966), Appl. November 9, 1964; Chem. Abstr., 66, 11891e (1967).
[13] V. Svoboda, V. Novotny, T. Dederle, and M. Ambroz, Czechoslovakian Patent 154,531 (c1-C 14C), (August 15, 1974), Appl. 5076/72 (July 18, 1972); Chem. Abstr., 82, 141629s (1975).
[14] F. Belohradsky, M. Kulhanek, L. Blazek, and V. Navratil, Czechoslovakian Patent 87,983 (December 15, 1958); Chem. Abstr., 55, 3997 (1961).
[15] F. Belohradsky, M. Kulhanek, and L. Blazek, Czechoslovakian Patent 87,983 (December 15, 1958); Chem. Abstr., 54, 5176 (1960).
[16] B. N. Misra, I. K. Mehta, and R. Dogra, J. Macromol. Sci.-Chem., A12, 1513 (1978).
[17] L. J. Wolfram and J. B. Speakman, J. Soc. Dyers Colour., 77, 477 (1961).
[18] A. K. Pradhan, G. Panda, N. C. Pati, and P. L. Nayak, J. Appl. Polym. Sci., 26, 3511 (1981).
[19] S. Dilli, J. L. Garnett, E. C. Martin, and D. H. Phvoc, J. Polym. Sci., Polym. Symp., 37, 57 (1972).
[20] A. Hebeish and P. C. Mehta, J. Appl. Polym. Sci., 12, 1625 (1968).
[21] R. Mehrotra and B. Ranby, Ibid., 21, 1647 (1977).
[22] R. Mehrotra and B. Ranby, Ibid., 21, 3407 (1977).

[23] R. Mehrotra and B. Ranby, Ibid., 22, 2991 (1978).
[24] K. Kojima, S. Iwabuchi, and K. Kojima, Bull. Chem. Soc. Jpn., 44, 1891 (1971).
[25] R. J. Ceresa, Block and Graft Copolymerization, Vol. I, Wiley, New York, 1972.

Accepted by editor November 20, 1982
Received for publication January 12, 1983