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

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To cite this Article Joseph, Anne , Radhakrishnan, Ganga , Nagabhushanam, T. and Joseph, K. Thomas(1981) 'Graft Copolymerization of Acrylic Monomers onto Biopolymers. Part I. Grafting of Poly(butyl Acrylate) onto Gelatin', Journal of Macromolecular Science, Part A, 15: 3, 515 — 525
To link to this Article: DOI: 10.1080/00222338108074390
URL: http://dx.doi.org/10.1080/00222338108074390

J. MACROMOL. SCI.–CHEM., A15(3), pp. 515-525 (1981)

Graft Copolymerization of Acrylic Monomers onto Biopolymers. Part I. Grafting of Poly(butyl Acrylate) onto Gelatin

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ABSTRACT

Gelatin was graft copolymerized with poly(butyl acrylate) using potassium peroxy disulfate in aqueous medium. Effects of temperature, time, monomer concentration, and backbone concentration were studied. The percent grafting was found to increase initially and then decreased in all cases. Infrared, viscosity, and thermal analysis were carried out on the graft copolymers, and the mechanism of the graft copolymerization reaction was discussed.

INTRODUCTION

Even though the modification of bio [1-6] and synthetic polymers [7] has been studied extensively in order to achieve better mechanical properties, the research work on modification of gelatin by synthetic polymers is scanty. The graft copolymerization of vinyl monomers onto starch [1], cellulose [2], wool [3], rubber [4], and collagen [5] have resulted in good industrial applications. The modification of gelatin by synthetic polymers should throw more light on the development of new biomaterials. The dissociation of polypeptide chains of collagen by thermal or chemical process leads

to gelatin. Gelatin is unique among proteins owing to the absence of appreciable internal order.

In continuation of our previous work [8, 9], gelatin has been modified by poly(butyl acrylate) in order to impart its flexible characteristics to brittle gelatin with a view to improve the physical properties of gelatin.

EXPERIMENTAL

Materials

Gelatin (Riedel, Germany) was used as such in the investigations. Monomer, butyl acrylate (Rohm and Haas, U.S.A.), was washed with sodium hydroxide dried over calcium chloride and distilled under reduced pressure in an atmosphere of nitrogen, and the middle fraction of the distillate was collected and used in the investigations. Potassium peroxydisulfate (G.R., E. Merck) was used as such without further purification. Double distilled water was used in the preparation of the solutions and reagents.

Procedures

A 10% gelatin solution was prepared as reported earlier [9] and used in the investigations. Every time freshly prepared gelatin solution was used to avoid any bacterial growth. The gelatin solution was taken in a 50 mL reaction vessel with nitrogen inlet and outlet arrangement and thermostated at 60°C. Monomer was then added followed by the initiator. After the completion of the reaction the contents were poured in acetone and the precipitated products were filtered and dried.

The dried products were Soxhlet extracted for the removal of homopolymer poly(butyl acrylate) using acetone. The extraction was repeated for complete removal of homopolymer.

The extracted dried product was then analyzed for total nitrogen content by Kjeldahl's method.

Acid hydrolysis of the graft copolymer was carried out by refluxing in 6 N HCl to remove the gelatin moiety. The remaining poly(butyl acrylate) was filtered, washed, and dried for viscosity measurements.

Characterization

Infrared Analysis

The graft copolymer films made from m-cresol solution were subjected to IR analysis for the proof of grafting (Figs. 1 and 2) using Perkin-Elmer Model 337 grating infrared spectrophotometer.

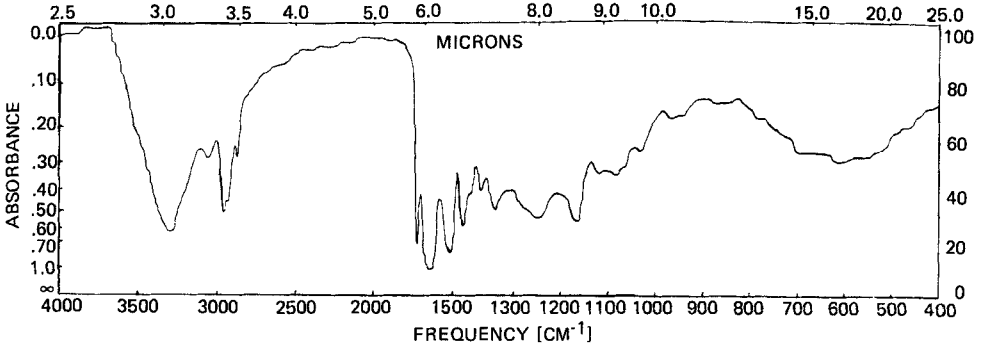

FIGURE 1.

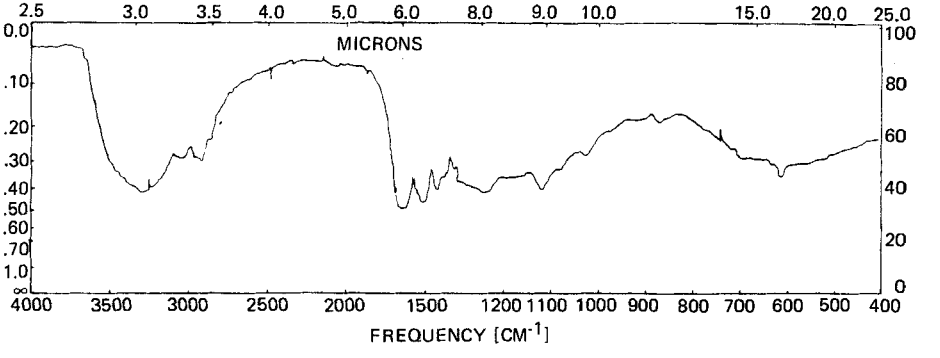

FIGURE 2.

Thermogravimetric Analysis

TGA analysis of the grafted and ungrafted gelatin was made using a Stanton thermobalance and the results are presented in Fig. 3.

Viscosity

The viscosities of poly(butyl acrylate) branches after acid hydrolysis were determined in order to calculate the molecular weight. A 0.1% solution (by weight) of the polymer was made using acetone as the solvent, and the viscosity was measured at 25°C using an Ubbelohde viscometer. The molecular weight of poly(butyl acrylate) was calculated using the Mark-Houwink equation [10]: $[\eta] = KM^a$, where $K = 6.85 \times 10^{-3}$ (mL/g) and $a = 0.75$. The values are given in Tables 1-4.

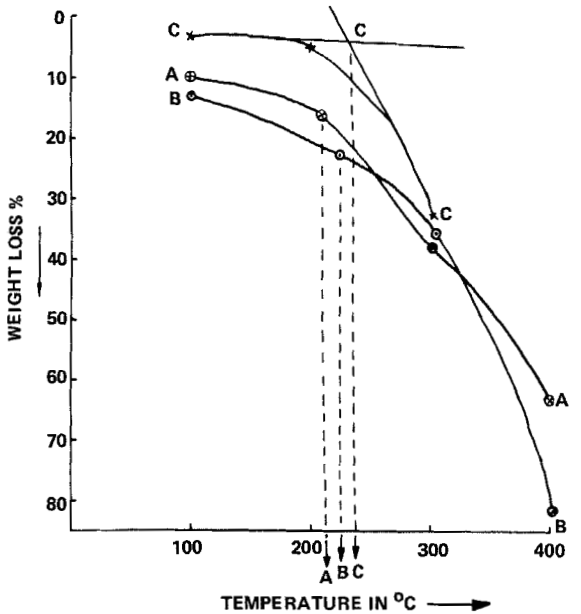

FIG. 3. Temperatures: A, 210°C; B, 225°C; C, 235°C.

TABLE 1. Effect of Initiator Concentration on Molecular Weight of Poly(butyl Acrylate)

[Initiator] × 10^3 mol/L	$[\eta]$ (mL/g)	Molecular weight
2	1.320	1114
6	1.449	1256
16	1.416	1227

TABLE 2. Effect of Temperature on Molecular Weight of Poly(butyl Acrylate)

Temperature (°C)	$[\eta]$ (mL/g)	Molecular weight
40	0.890	657
70	1.744	1607
80	1.912	1824

TABLE 3. Effect of Gelatin Percent on Molecular Weight of Poly-(butyl Acrylate)

% gelatin	$[\eta]$ (mL/g)	Molecular weight
7	0.629	409
8	1.135	907
10	2.284	2307
12	1.570	1403
15	1.194	971

TABLE 4. Effect of Time on Molecular Weight Poly(butyl Acrylate)

Time (min)	$[\eta]$ (mL/g)	Molecular weight
15	1.320	1114
45	1.231	1014
60	1.318	1109
75	1.060	827

RESULTS AND DISCUSSION

Even though the chemical modification of functional groups on the amino acids was studied both on gelatin [8] and collagen [5] in order to understand the conformational and structural aspects of collagen, the modification of gelatin by synthetic polymers is new. Free radical polymerization is the most common method of producing graft copolymers. The graft copolymerization of gelatin with vinyl monomers is easier to its parent precursor collagen which is insoluble in aqueous medium. Tropocollagen, though soluble in aqueous acetic acid system, has a cost which prevents its use in industrial applications. Even though Nagabhushanam et al. [8] in India and Kuwajima et al. [11] in Japan graft copolymerized vinyl monomers onto gelatin and demonstrated the formation of true grafts, further studies are necessary to gain insight into the mechanism of graft copolymerization using this substrate. The effect of time on the grafting reaction has shown interesting results. The percent grafting was found to increase initially (Fig. 4, Abscissa A) with increasing reaction time and finally decreased. This observation may be attributed to the following facts. The primary radicals formed by the decomposition

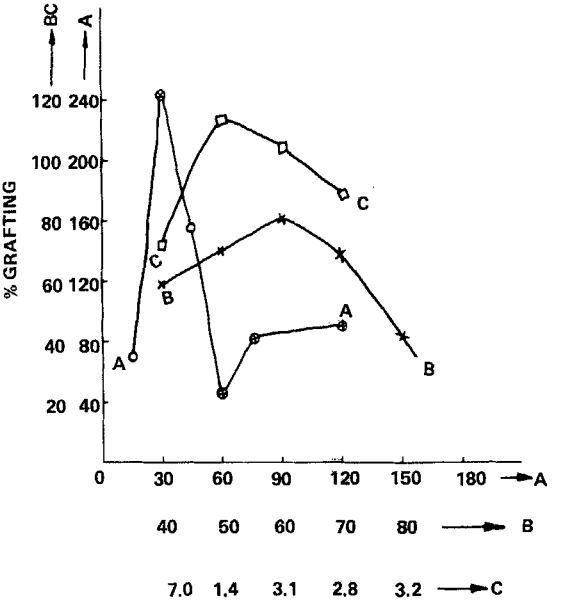

FIG. 4. Abscissas: A, time in minutes; B, temperature in °C; C, [monomer] $\times 10^2$ mol/L.

of initiator are active and interact with gelatin to give gelatin macroradicals which in turn react with butyl acrylate to give the gelatin-g-poly(butyl acrylate) radical. Then further incorporation of poly(butyl acrylate) takes place and thus the percent grafting increases initially. When the reaction time is further increased, chain transfer to monomer may take place, thus decreasing the percent grafting and forming homopolymer. Added to this is the high activation of gelatin-g-poly(butyl acrylate) growing radicals. The primary radicals may interact to terminate the graft. Similar observations were also noted in the homopolymerization reaction [12].

The temperature of the reaction normally plays an important role in graft copolymerization reactions. Lower reaction temperatures favored higher percent grafting (Fig. 4, Abscissa B) in agreement with reported results [8, 11]. An increase in temperature up to 60°C increased the percent grafting and then decreased and finally increased. The primary radicals formed by the decomposition of the initiator preferentially attacked gelatin, but on further increase the grafting percent decreased, thereby showing an increase in homopolymerization formation.

As reported by earlier workers [11], potassium peroxydisulfate was found to be an effective initiator for grafting of poly(butyl acrylate)

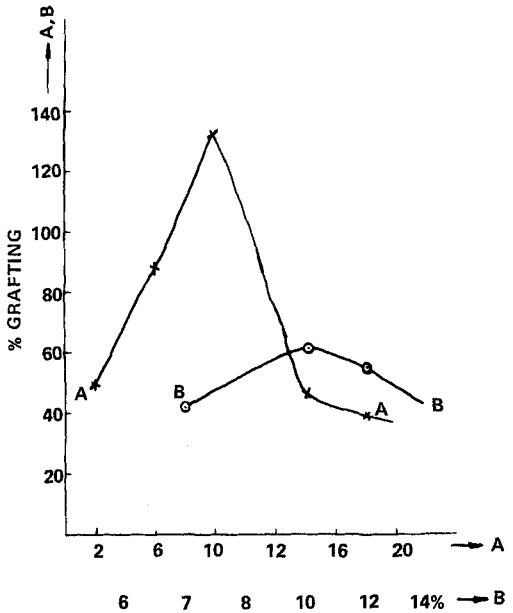

FIG. 5. Abscissas: A, [initiator] $\times 10^3$ mol/L; B, [gelatin].

onto gelatin. As gelatin and potassium peroxydisulfate are soluble in aqueous medium, the approach of initiating radicals to gelatin is facilitated, which may result in an interaction with the functional groups of gelatin to produce backbone radicals. Further, primary radicals may also form a redox system on the backbone itself as in the case of potassium peroxydisulfate initiated grafting of PMMA onto polyvinyl alcohol [13] and thus resulting in higher percent grafting. The percent grafting reached a maximum (Fig. 5, Abscissa A) which suggests that by adding more initiator, more grafting sites are formed and a further increase may facilitate the rate of homopolymerization rather than the rate of grafting [14].

In agreement with the findings of Mehrotra and Ranby [15, 16] in the grafting of polyacrylonitrile onto starch, Nagabhushanam et al. on the grafting of methyl acrylate onto gelatin, and Kojima et al. on the grafting of methyl methacrylate onto hemoglobin [17], an increase in backbone concentration decreased the percent grafting (Fig. 5, Abscissa B). This may be due to the decrease in the monomer-to-backbone ratio when the amount of gelatin concentration increased or all the monomer present was utilized in the graft copolymerization. A further increase in gelatin concentration does not play a major role in grafting.

Infrared Analysis

IR spectroscopy has been found to be a valuable tool in studying graft copolymerization reactions. This technique has been extensively used to study the proof of grafting [18] and to determine the structure of grafted products. IR spectra showed the characteristic amide absorption at 1550 and 1660 cm^{-1} in addition to carbonyl peaks at 1730 cm^{-1}. This provides proof for grafting (Figs. 1 and 2).

Added to this is the insolubility of the grafted gelatin in water compared with native gelatin, which also suggests that grafting has taken place.

Thermogravimetric Analysis

Several claims [19] are made in the literature on the melting temperature of collagen and gelatin. The most discussed values appear to be $\gtrsim 200$. Several methods [20-22] were employed to study the melting point. In the present investigation the gelatin graft copolymers were subjected to thermal gravimetric analysis. The samples chosen had different amounts of poly(butyl acrylate) grafted onto gelatin. The percent grafting of the samples are (A) 71.33, (B) 157.3, and (C) 264.3, and the melting points obtained (Fig. 3) are 210, 225, and 235°C, respectively. It appears that by the incorporation of the poly(butyl acrylate) moiety, the melting temperature is changed. Further work is being carried out in this field to arrive at a general understanding of the melting point.

Viscosity studies were carried out on the side chain of poly(butyl acrylate) after hydrolyzing away the gelatin backbone. The results are presented in Tables 1-4.

The molecular weights of all the side chains of poly(butyl acrylate) appears to be in the range of 10^3. The lower molecular weight value and the higher percent grafting value show that side chain growth is limited to a certain extent but the number of sites would have to be more on the backbone, in general, and even this reaches a maximum value and then decreases (Figs. 4 and 5). Since the chain lengths measured are for unfractionated polymer side chains, the results must be treated with caution.

Mechanism

Chemical grafting involves the activation of the substrate. Once the substrate has been activated, chains of monomers linked by covalent bonds grow on the substrate, resulting in branches.

As far as the activation of the backbone is concerned, the following possibilities can be visualized:

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\cdot-}$$

$$SO_4^{\cdot-} + H_2O \longrightarrow HSO_4^- + OH^{\cdot}$$

$$2OH^{\cdot} \longrightarrow H_2O + \tfrac{1}{2}O_2 \qquad (a)$$

$OH^{\cdot} + SO_4^{\cdot-}$ radicals can initiate to produce backbone radicals:

$$OH^{\cdot} + \text{gel} \longrightarrow \text{gel}^{\cdot}$$

$$SO_4^{\cdot-} + \text{gel} \longrightarrow \text{gel}^{\cdot}$$

Alternatively, a complex might also be expected to form between gelatin and initiator systems:

$$\text{gel} + \text{initiator} \longrightarrow \text{complex}$$

$$\text{complex} \longrightarrow \text{gel}^{\cdot} + \text{products} \qquad (b)$$

This is followed by the decomposition of the complex to yield gelatin radicals.

Once the gelatin radical is produced, the monomer adds onto it to give a graft copolymer. In addition to graft formation, we have also seen the possibilities of formation of homopolymer. This is favorable in the case of (a) where both $OH^{\cdot}$ and $SO_4^{\cdot-}$ may initiate homopolymerization which progressively increases by an increase in initiator concentration rather than by percent grafting as observed in Figs. 4 and 5.

The possibility of a complex can be visualized from the high percent grafting yield. Thus grafting may be taking place by both mechanisms.

Further, the lower percent grafting with the progress of the reaction might be due to chain transfer from the backbone radicals:

$$\text{gel–P}^{\cdot} + M \longrightarrow \text{gel–P} + M^{\cdot}$$

where gel–$P^{\cdot}$ is a growing gelatin graft radical.

$$M^{\cdot} + M \longrightarrow \text{homopolymer}$$

Termination may take place in different ways:

$$\text{graft}^{\cdot} + \text{graft}^{\cdot} \longrightarrow \text{nonradical products}$$

$$\text{graft}^{\cdot} + \text{homopolymer} \longrightarrow \text{nonradical products}$$

$$\text{homopolymer}^{\cdot} + \text{homopolymer}^{\cdot} \longrightarrow \text{homopolymer}$$

Further work is in progress to elucidate the mechanism of grafting reactions.

ACKNOWLEDGMENT

Our thanks are due to Prof. Aravamudam, Indian Institute of Technology, Madras, India, for thermogravimetric analysis of our samples.

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Accepted by editor August 3, 1979
Received for publication November 13, 1979