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

Studies on the Graft Copolymerization of Acrylonitrile Onto Sodium Alginate

N. Radhakrishnan[a]; Y. Lakshminarayana[a]; S. Uma Devi[a]; K. S. V. Srinivasan[a]
[a] Polymer Division Central Leather Research Institute Adyar, Madras, India

To cite this Article Radhakrishnan, N. , Lakshminarayana, Y. , Devi, S. Uma and Srinivasan, K. S. V.(1994) 'Studies on the Graft Copolymerization of Acrylonitrile Onto Sodium Alginate', Journal of Macromolecular Science, Part A, 31: 5, 581 — 591

To link to this Article: DOI: 10.1080/10601329409349740

URL: http://dx.doi.org/10.1080/10601329409349740

J.M.S.—PURE APPL. CHEM., A31(5), pp. 581-591 (1994)

STUDIES ON THE GRAFT COPOLYMERIZATION OF ACRYLONITRILE ONTO SODIUM ALGINATE

N. RADHAKRISHNAN, Y. LAKSHMINARAYANA, S. UMA DEVI,
and K. S. V. SRINIVASAN*

Polymer Division
Central Leather Research Institute
Adyar, Madras, India

ABSTRACT

Graft copolymerization of poly(acrylonitrile) onto sodium alginate was carried out in aqueous medium using potassium persulphate as an initiator. The effects of pH, time, monomer concentration, initiator concentration, temperature, and backbone concentration were investigated. Percent grafting and grafting efficiency were evaluated. Isolation of graft copolymer from unreacted sodium alginate was carried out using the selective solvent extraction technique. FTIR and thermogravimetric analysis for poly(acrylonitrile), sodium alginate, and sodium alginate-*graft*-poly(acrylonitrile) were studied to establish the occurrence of grafting. A probable mechanism for grafting is proposed.

INTRODUCTION

Alginic acid, a mucopolysaccharide of seaweed, is one of the important renewable resources available in the biosphere. Earlier, we reported [1] the grafting of alginic acid in heterogeneous medium using potassium persulphate as an initiator. Utilizing the advantage of sodium alginate being soluble in water, this paper deals with the modification of sodium alginate by graft copolymerization of acrylonitrile in aqueous medium using a free radical initiator. The polymers were isolated by the selective solvent extraction procedure. The effects of such variables as initiator concentration, reaction time, backbone concentration, pH, and temperature were studied during graft copolymerization. The functional groups incorporated, apart from that already present in alginate, are found to be useful as a retanning agent in leather processing by interaction with protein and chrome to impart fullness and grain-tightening effects on hides and skins. The complex formation of sodium alginate with chrome in chrome tanning also aids as a chrome exhaustion aid in the tanning of the hides and skins [2, 3].

EXPERIMENTAL

Materials

Sodium alginate (Loba Chemicals, India) was used as received.

Acrylonitrile (AN) (S.D. Fine Chemicals, India) was freed from inhibitors by washing successively with 5% NaOH solution and distilled water. The monomer thus extracted was dried over anhydrous sodium sulfate and distilled under vacuum. The middle fraction of the monomer was used in the present investigation.

Potassium persulfate (S.D. Fine Chemicals, India) was used as received.

The solvent dimethylformamide (DMF) (Sarabhai M. Chemicals, India) and acetone were commercial-grade solvents, purified according to standard procedures, and distilled before use.

Grafting Method

The grafting experiments were carried out in hard Pyrex glass tubes with a provision for passing nitrogen gas. The required amount of sodium alginate was dissolved in water in the Pyrex tube, and the pH was adjusted to 5. A known quantity of acrylonitrile was transferred into the polymerization tube, and purified nitrogen was passed through the solution. The tube was kept in a thermostatic water bath maintained at a required temperature. A known volume of potassium persulfate solution was pipetted into the reaction tube. After allowing the reaction to proceed for the required time, the contents of the reaction tube were poured into an excess of acetone to precipitate the polymer. The reaction tube was washed well with water in order to recover completely the adhering polymer sample. The precipitated polymer was allowed to settle down in a refrigerator. Then the contents were filtered through sintered crucibles. The gross polymer was dried in vacuum at 70°C to constant weight.

Extraction of Graft Polymer

The homopolymer (PAN) was separated from the backbone polymer by extraction with DMF for 72 hours by the tumble bottle method. Percent grafting (PG) and grafting efficiency (GE) were evaluated by using the formulas given below.

$$\text{Percent grafting (PG)} = \frac{\text{weight of grafted polymer}}{\text{weight of backbone polymer}} \times 100$$

$$\text{Grafting efficiency (GE)} = \frac{\text{weight of grafted polymer}}{\begin{array}{c}\text{weight of total polymer}\\ \text{formed (graft + homopolymer)}\end{array}} \times 100$$

Infrared Spectra

The FTIR spectra of sodium alginate and the sodium alginate-*graft*-PAN were recorded using a Nicolet 20-DXB FTIR spectrophotometer.

Thermogravimetric Analysis

Thermogravimetric analysis of sodium alginate, PAN, and sodium alginate-*graft*-PAN were recorded from ambient temperature to 700°C in a nitrogen atmosphere using DuPont's 990 Model Thermal Analyzer.

RESULTS AND DISCUSSIONS

In order to optimize the conditions for grafting, the effects of pH, time, monomer concentration, initiator concentration, temperature, and backbone concentration on the grafting parameters were evaluated.

Effect of pH

The effect of pH plays an important role in the graft copolymerization of sodium alginate onto acrylonitrile. Below pH 4, sodium alginate converts into alginic acid and precipitates. In the present study, the maximum PG was observed at pH 5 on the graft copolymerization of acrylonitrile onto sodium alginate (Table 1).

TABLE 1. Effect of pH in the Graft Copolymerization of AN onto Sodium Alginate[a]

No.	pH	Percent grafting (PG)	Grafting efficiency (GE)
1	4	159.2	97.6
2	5	169.3	99.2
3	6	125.2	99.3
4	7	111.5	99.3

[a] Sodium alginate: 1.55 wt%. [AN]: 6.08 × 10^{-1} mol/L. [$K_2S_2O_8$]: 1.21 × 10^{-2} mol/L. Total volume: 55 mL. Time: 4 hours. Temperature: 70°C.

Hence, a pH of 5 was maintained in all subsequent experiments to optimize the grafting parameters.

Effect of Reaction Time

The effect of time on the graft copolymerization of acrylonitrile onto sodium alginate was studied by keeping the concentrations of the backbone, AN, and persulfate constant at 70°C (Table 2). The PG increased linearly up to 4 hours and then decreased almost steadily. This result indicates that the growing polymer chains and primary radicals are actively engaged in creating grafting sites throughout the backbone polymer. As the reaction time further increased above 4 hours, a stage may be reached at which the rate of formation of grafting sites becomes constant. As time progresses, chain transfer to monomer may take place with more homopolymer formation and decreasing PG. This type of trend has been observed by Anne et al. in the graft copolymerization of butyl acrylate onto gelatin [4].

Effect of Monomer Concentration

The influence of AN concentration on the graft copolymerization onto sodium alginate was studied at pH 5 and 70°C while keeping all the other variables constant. As the concentration of monomer (AN) is increased, the PG increases while the GE passes through a maximum and then decreases (Table 3). The GE is maximum at 10.77×10^{-1} mol/L monomer concentration and then decreases. This type of trend has been observed in other systems [4, 5].

Effect of Initiator Concentration

The effect of persulfate concentration on sodium alginate was studied at 70°C for 4 hours (Table 4). As the initiator concentration increased, PG and GE increased initially and then decreased. At an initiator concentration of 2.02×10^{-2} mol/L,

TABLE 2. Effect of Time Variation in the Graft Copolymerization of AN onto Sodium Alginate[a]

No.	Time, hours	Percent grafting (PG)	Grafting efficiency (GE)
1	1	108.3	91.2
2	2	140.7	95.3
3	3	154.7	97.1
4	4	157.9	96.5
5	5	148.5	96.9
6	6	142.7	97.0

[a] Sodium alginate: 1.55 wt%. [AN]: 6.08×10^{-1} mol/L. [$K_2S_2O_8$]: 1.21×10^{-2} mol/L. Total volume: 55 mL. Temperature: 70°C. pH: 5.

TABLE 3. Effect of Monomer Concentration in the Graft Copolymerization of AN onto Sodium Alginate[a]

No.	[AN], mol/L × 10^{-1}	Percent grafting (PG)	Grafting efficiency (GE)
1	3.04	67.2	92.7
2	4.56	115.7	95.4
3	6.08	157.9	96.5
4	7.71	220.7	96.6
5	10.77	326.1	97.1
6	12.15	353.1	93.1

[a]Sodium alginate: 1.55 wt%. [$K_2S_2O_8$]: 1.21 × 10^{-2} mol/L. pH: 5. Temperature: 70°C. Time: 4 hours. Total volume: 55 mL.

the PG was 165; above this concentration the PG decreased. This may be due to the fact that a higher initiator concentration facilitates not only the functions of more active centers on the backbone but also facilitates the preferential attack of primary radicals on the monomer, leading to a larger amount of homopolymer formation in the graft copolymerization.

Effect of Temperature

The influence of temperature on the graft copolymerization of AN onto sodium alginate was studied by keeping the concentrations of AN and persulfate constant at 70°C for 4 hours (Table 5). With an increase of temperature from 60 to

TABLE 4. Effect of Initiator Variation in the Graft Copolymerization of AN onto Sodium Alginate[a]

No.	[$K_2S_2O_8$], mol/L × 10^{-2}	Percent grafting (PG)	Grafting efficiency (GE)
1	0.41	127.6	96.6
2	0.81	146.1	96.9
3	1.21	157.9	96.5
4	1.61	160.9	95.2
5	2.02	165.7	90.1
6	2.42	164.6	84.8

[a]Sodium alginate: 1.55 wt%. [AN]: 6.08 × 10^{-1} mol/L. Temperature: 70°C. Total volume: 55 mL. Time: 4 hours. pH: 5.

TABLE 5. Effect of Temperature Variation in the Graft Copolymerization of AN onto Sodium Alginate[a]

No.	Temperature, °C	Percent grafting (PG)	Grafting efficiency (GE)
1	60	140.9	97.8
2	65	155.5	97.1
3	70	157.9	96.5
4	75	184.9	95.2
5	80	176.5	94.3

[a] Sodium alginate: 1.55 wt%. $[K_2S_2O_8]$: 1.21×10^{-2} mol/L. [AN]: 6.08×10^{-1} mol/L. Total volume: 55 mL. Time: 4 hours. pH: 5.

75°C, PG and GE increase. A further increase of temperature to 80°C favors the formation of more homopolymer and consequently decreases the PG and GE. The percent grafting was found to be maximum at 75°C.

Effect of Backbone Concentration

The effects of sodium alginate (backbone) concentration on the graft copolymerization of AN onto sodium alginate was studied by keeping the concentrations of AN and persulfate constant at 70°C for 4 hours (Table 6). The PG and GE decrease with an increase in backbone concentration. The optimum backbone concentration for grafting of AN onto sodium alginate is 4.55 wt% sodium alginate.

TABLE 6. Effect of Backbone Concentration in the Graft Copolymerization of AN onto Sodium Alginate[a]

No.	[Backbone], in wt%	Percent grafting (PG)	Grafting efficiency (GE)
1	1.55	157.8	96.5
2	1.82	134.2	96.4
3	2.73	111.5	96.7
4	4.55	129.4	94.6
5	5.46	140.1	91.1
6	6.36	142.4	80.5

[a] $[K_2S_2O_8]$: 1.21×10^{-2} mol/L. [AN]: 6.08×10^{-1} mol/L. pH: 5. Temperature: 70°C. Time: 4 hours. Total volume: 55 mL.

However, a further increase in backbone concentration above 4.55 wt% sodium alginate decreases the GE. This could be due to the fact that sodium alginate radicals are utilized in termination at higher backbone concentrations. Further the PG decreases up to 2.73 wt% backbone concentration and then increases slightly. This could be explained on the basis that the relative increment in backbone concentration is very much higher than the relative increment of grafting chain.

Characterization of Graft Copolymer

The FTIR Spectra of Graft Copolymer

The FTIR spectra of sodium alginate as well as of sodium alginate-*graft*-PAN in KBr pellet were given in Fig. 1. The isolated graft copolymer showed a characteristic $-C\equiv N$ absorption peak at 2249 cm^{-1} of PAN, indicating that the acrylonitrile has been grafted onto sodium alginate.

Thermogravimetric Analysis

The thermogram of sodium alginate, PAN, and sodium alginate-*graft*-PAN are shown in Figs. 2 and 3.

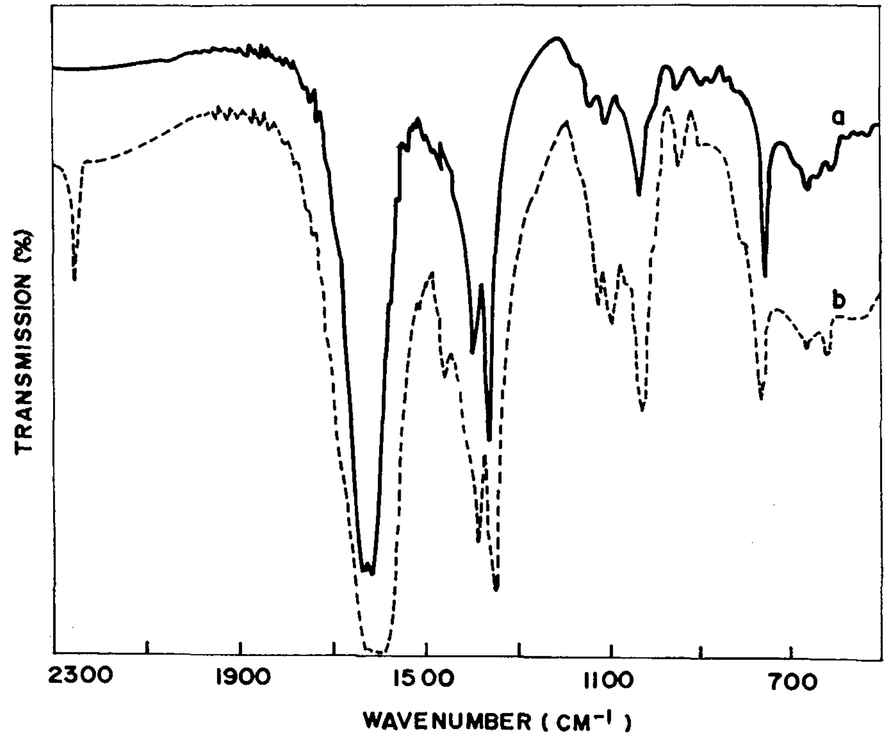

FIG. 1. Infrared (IR) spectra of (a) pure sodium alginate and (b) sodium alginate-*graft*-polyacrylonitrile.

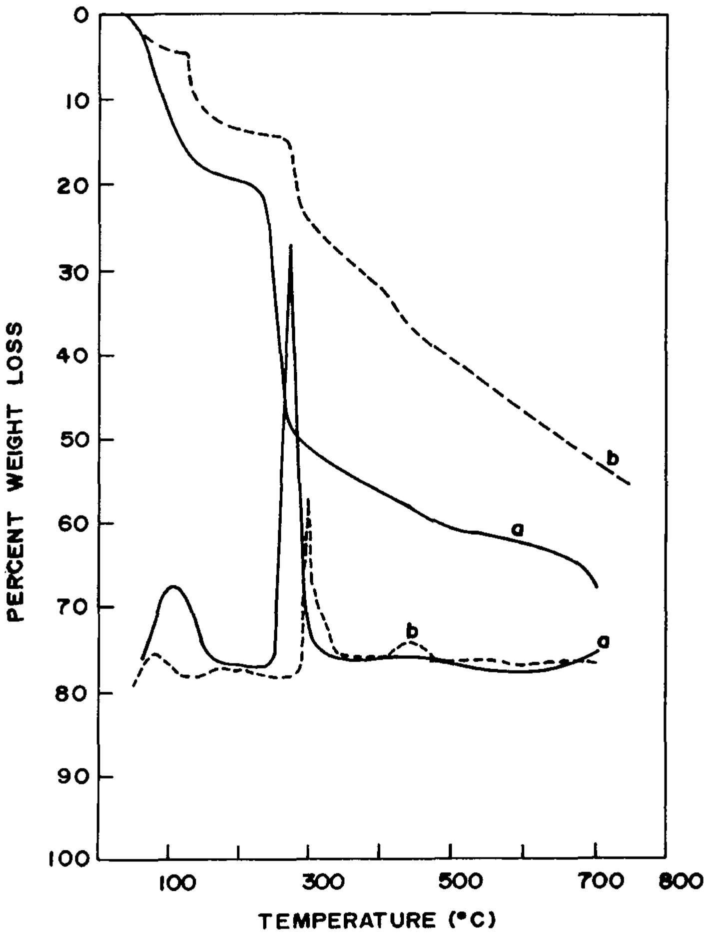

FIG. 2. Thermogram of (a) pure sodium alginate and (b) poly(acrylonitrile).

The thermograms of sodium alginate and PAN show a two-stage decomposition pattern, the first stage occurring at 100°C extending up to 150°C with a 16% weight loss, and the second stage at 280°C with a 48% weight loss. The weight loss at 100°C is due to the elimination of either absorbed water or bound water. In the decomposition of alginic acid, the weight loss at 100°C may be attributed to the elimination of a water molecule either by lactonization of the carboxyl group with the hydroxyl groups in C_2 and C_3 carbon atoms or by transglucosination [1]. Perlin [6] pointed out that alginic acid lactonizes around 50–200°C by eliminating a water molecule. The decomposition of alginic acid at 240°C may be due to the elimination of carbon monoxide. Sodium alginate shows a two-stage decomposition pattern (Fig. 2), the first stage occurring at 100°C and extending up to 150°C with a 16% weight loss and the second stage at 280°C with a 48% weight loss. The weight loss at 100°C is due to the elimination of either absorbed water, bound water, or water generated from the reaction. The decomposition of sodium alginate occurs at 280°C

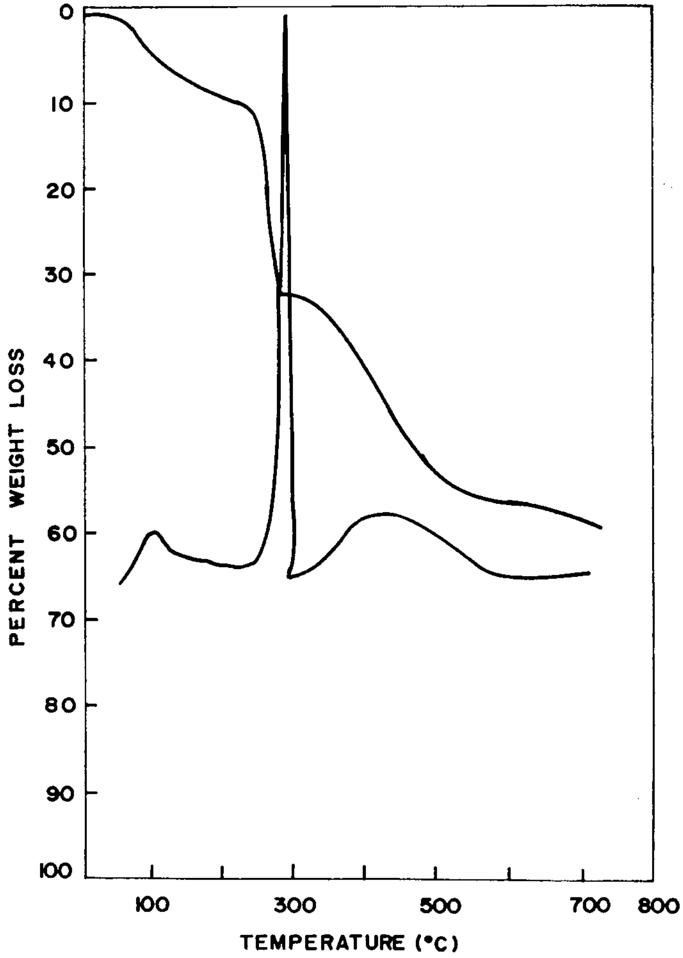

FIG. 3. Thermogram of sodium alginate grafted with poly(acrylonitrile).

compared to that of alginic acid at 240°C, indicating the higher thermal stability of sodium alginate compared to that of alginic acid [1].

The percent weight losses of sodium alginate, PAN, and sodium alginate-*graft*-PAN at different temperatures are given in Table 7. It is observed that the thermal stability of the graft copolymer is higher than that of sodium alginate and lower than that of PAN. The weight loss of sodium alginate at 380°C is 55% compared to sodium alginate-*graft*-PAN occurring at a very high temperature of 550°C, indicating that sodium alginate-*graft*-PAN has a higher thermal stability than pure sodium alginate.

Probable Mechanism

Extensive work has been reported on the mechanism of grafting of vinyl monomers onto cellulose and cellulose derivatives [7–11], and a mechanism has

TABLE 7. Weight Percent Loss of Sodium Alginate, PAN, and Sodium Alginate-*graft*-PAN at Different Temperatures[a]

	Weight percent loss at a temperature (°C) of					
Sample	10	20	30	40	50	60
Sodium alginate	90	200	250	260	290	380
PAN	145	290	375	490	650	720
Sodium alginate-*graft*-PAN	235	270	280	395	475	550

[a] Figures 2 and 3.

been proposed. Arthur [11] studied the mechanism in the graft copolymerization of vinyl monomers onto cellulose using a redox initiator and proposed hydrogen abstraction from the cellulose, thereby creating an active center. In a similar way it is likely that hydrogen abstraction with the formation of a free radical on the sodium alginate could occur with the creation of a radical site for the initiation of graft copolymerization:

$$\mathrm{M{-}H} + \mathrm{R} \rightarrow \mathrm{M}^{\cdot} + \mathrm{RH}$$

$$\mathrm{M}^{\cdot} + n\mathrm{M} \rightarrow \mathrm{M}_n\mathrm{M}^{\cdot}$$

$$\mathrm{M}_n\mathrm{M}^{\cdot} + \mathrm{M}^{\cdot} \rightarrow \mathrm{M}_{n+2}$$

$$\mathrm{M}_n\mathrm{M}^{\cdot} + \text{alginate} - \mathrm{H} \rightarrow \text{alginate}{-}\mathrm{M}_{n+1} + \mathrm{H}^{\cdot}$$

where M = monomer, R = initiator.

CONCLUSION

The graft copolymerization of AN onto sodium alginate using potassium persulfate in an aqueous medium has been reported. The graft copolymerization is pH-dependent, and the maximum PG was observed at pH 5. The optimization of grafting parameters has also been studied. The thermal stability of grafted sodium alginate is higher than that of backbone polymer. The resultant product is useful as a chrome exhaustion aid cum retanning agent in leather processing [2, 3].

REFERENCES

[1] M. T. Vijayakumar, C. R. Reddy, and K. T. Joseph, *Eur. Polym. J.*, *21*, 415 (1985).

[2] Y. Lakshminarayana, N. Radhakrishnan, K. Parthasarathy, and K. S. V. Srinivasan, *J. Am. Leather Chem. Assoc.*, *85*, 425 (1990).

[3] Y. Lakshminarayana, K. S. V. Srinivasan, N. Radhakrishnan, S. Ramalingam, T. Ramasami, K. Parthasarathy, K. T. Joseph and K. S. Jayaraman,

"Water-Soluble Acrylic Syntan," Indian Patent Application Del. 1104/89 (1989).

[4] A. Joseph, G. Radhakrishnan, T. Nagabhushanam, and K. T. Joseph, *J. Macromol. Sci.—Chem.*, *A15*, 515 (1981).

[5] K. S. V. Srinivasan, N. Radhakrishnan, and M. K. Pillai, *J. Appl. Polym. Sci.*, *37*, 1551 (1989).

[6] A. S. Perlin, *Can. J. Chem.*, *30*, 278 (1958).

[7] K. Bardhan, S. Mukhopadhyay, and S. R. Chatterjee, *J. Polym. Sci., Polym. Chem. Ed.*, *15*, 141 (1977).

[8] D. Sudhakar, K. S. V. Srinivasan, K. T. Joseph, and M. Santappa, *J. Polym. Sci., Polym. Lett. Ed.*, *16*, 457 (1978).

[9] J. T. Guthrie, N. B. Huglin, and G. O. Philips, *Eur. Polym. J.*, *8*, 747 (1972).

[10] D. N. S. Hon and H. C. Chan, in *Graft Copolymerization of Lignocellulosics Fibers ACS Symp.*, *187*, 101 (1982).

[11] J. C. Arthur Jr., "Photo-initiated Grafting of Monomers onto Cellulose Substrates," in *Developments in Polymer Chemistry*, Vol. 1 (N. S. Allen, Ed.), Applied Science, Barking, 1980, p. 69.

Received May 17, 1993
Revision received August 24, 1993