Graft copolymers of polysaccharides:
1. Graft copolymers of alginic acid

Hal S. Blair* and Kam Moon Lai
Department of Industrial Chemistry, The Queen's University of Belfast, 21 *Chlorine Gardens, Belfast, Northern Ireland*

(*Received* 21 *June* 1982)

Copolymers of alginic acid with acrylonitrile, methylacrylate, methylmethacrylate and ethylacrylate have been prepared and characterized by i.r. spectroscopy, differential thermal analysis and X-ray diffraction. Evidence is presented to indicate that the products are graft-copolymers and not simple mixtures of the two polymers.

Keywords Polysaccharides; alginic acid; acrylonitrile; methylacrylate; methylmethacrylate; ethylacrylate

INTRODUCTION

Algin or alginate is a water-soluble gum obtainable from brown algae. It is a copolymer consisting of D-mannuronic acid units linked β- (1→4), and L-guluronic acid units linked α- (1→4). The ratio of mannuronic acid to guluronic acid varies with the source of the algin, but the commercially important products are generally rich in mannuronic acid. Alginic acid and most of its salts with polyvalent metals are essentially insoluble, whereas the alkali metal salts are soluble. Insoluble metal alginates behave as typical ion-exchange resins, certain cations being more strongly bound than others. The affinities of divalent metal cations are dependent on the relative amounts of mannuronic and guluronic acid units present in the alginate. Studies of the interaction of polyvalent metal ions with alginic acid indicate that the hydroxyl groups may play an important role in ion binding. The isolation and properties of alginates have been reviewed extensively[1].

The present report is concerned with the preparation and characterization of graft copolymers of alginic acid.

EXPERIMENTAL

Sodium alginate was supplied by Alginate Industries Ltd. as 'Manutex F'. Solutions of Manutex F containing 2% by weight in distilled water were prepared at room temperature and filtered through a No. 1 porosity sintered glass filter.

Acrylonitrile and methyl acrylate were obtained from Aldrich Chemicals Ltd. and methyl methacrylate and ethyl acrylate from BDH Chemicals Ltd. The acrylonitrile (AN) and methyl acrylate (MA) were twice distilled under nitrogen at reduced pressure. The methyl methacrylate (MMA) and ethyl acrylate (EA) were purified by first washing with 5% sodium hydroxide solution to remove any inhibitor. The MMA was washed with distilled water, then dried over anhydrous sodium sulphate and distilled under nitrogen at reduced pressure. The EA was washed with saturated calcium chloride solution, dried over anhydrous calcium chloride and distilled under nitrogen at reduced pressure. For each polymerization reaction the monomer was freshly purified and the middle fraction of the distillate used.

Preparation of alginate graft copolymers

Sodium alginate solution (100 cm^3) in a 250 cm^3 three-necked flask was stirred while being flushed with nitrogen for 30 minutes. The solution was warmed to the required temperature and the vinyl monomer added with stirring, followed by the dropwise addition of the initiator[2]. The polymerization was allowed to proceed for the specified time after which the reaction mixture was poured into acetone (300 cm^3) with good stirring. After settling for one hour the product was separated by centrifuging. The product contained a mixture of alginate graft copolymer and homopolymer, the latter being removed by solvent extraction. PAN was removed by extraction with dimethylformamide for eighteen hours, PMA, PMMA, and PEA were removed by extraction with acetone for sixteen hours. The residual copolymer was dried for 16 h at 80°C under vacuum, using potassium hydroxide as a drying agent, and then weighed.

The degree of grafting obtained was expressed as shown:

$$\%\,\text{graft} = \frac{\text{Total weight of graft copolymer} - \text{weight of alginate}}{\text{Weight of alginate}} \times 100$$

However as the alginate in a 2% solution is not completely recovered on precipitation with acetone, the equation is rewritten as:

$$\%\text{graft} = \frac{\text{Total weight of graft copolymer} - R\% \times \text{weight of alginate}}{R\% \times \text{weight of alginate}} \times 100$$

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* To whom all correspondence should be addressed

0032–3861/82/121838–04$3.00

Table 1 Effects of monomer concentration, temperature and time of reaction on the degree of grafting of PAN on alginate. In each case the H_2O_2 concentration was 7.96×10^{-3} M

Sample number	Monomer concentration (mole dm^{-3})	Temperature (°C)	Time (h)	Thiourea (10^{-3}M)	% Graft
I	3.79×10^{-1}	40	2.0	7.2	4.70
II	7.60×10^{-1}	40	2.0	7.2	55.30
III	11.38×10^{-1}	40	2.0	7.2	97.90
IV	15.00×10^{-1}	40	2.0	7.2	134.90
V	7.60×10^{-1}	40	0.5	7.2	17.00
VI	7.60×10^{-1}	40	1.0	7.2	49.20
VII	7.60×10^{-1}	40	3.0	7.2	65.20
VIII	7.60×10^{-1}	20	2.0	7.2	0.00
IX	7.60×10^{-1}	60	2.0	7.2	79.90
X	7.60×10^{-1}	40	2.0	2.4	4.00
XI	7.60×10^{-1}	40	2.0	14.4	65.00
XII	7.60×10^{-1}	40	2.0	24.0	113.70

Table 2 Effects of monomer concentration, temperature and time of reaction on the degree of grafting of MA on alginate. In each case the concentration of H_2O_2 was 7.96×10^{-3} M, and of thiourea 7.2×10^{-3} M

Sample number	Monomer concentration (mole dm^{-3})	Temperature (°C)	Time (h)	% Graft
XIII	2.8×10^{-1}	40	2.0	6.10
XIV	5.5×10^{-1}	40	2.0	25.10
XV	8.3×10^{-1}	40	2.0	29.30
XVI	11.0×10^{-1}	40	2.0	38.20
XVII	5.5×10^{-1}	40	0.5	16.80
XVIII	5.5×10^{-1}	40	1.0	22.80
XIX	5.5×10^{-1}	40	3.0	28.10
XX	5.5×10^{-1}	20	2.0	5.40
XXI	5.5×10^{-1}	60	2.0	28.60

where $R\%$ is the percentage recovery of alginate on addition of 100 cm^3 of a 2% solution of sodium alginate to 300 cm^3 of acetone. In the present work the average $\%R$ was 71.5.

Preparation of alginate/homopolymer blends

A known weight of homopolymer (0.5–1.5 g, depending on the composition of the graft copolymer), was dispersed in 100 cm^3 of a 2% alginate solution by stirring for 30 minutes. The dispersion was poured into acetone (300 cm^3), with stirring continued for 30 minutes. The mixture was allowed to settle for one hour and the precipitate separated by centrifuging. The product was then transferred to a sohxlet thimble and extracted using the same solvent as the corresponding graft copolymer. After extraction the product was dried as described and weighed.

Characterization of the copolymers

The copolymers were characterized by differential thermal analysis using a Perkin Elmer differential scanning calorimeter DSC 1B, infra-red spectroscopy using a Perkin Elmer 398 spectrophotometer with a data station and X-ray diffraction, using a Phillips X-ray generator model PW/1130/00/60 with a Proportional Detector Probe PW/1965/20/30 connected to goniometer PW/1050/25.

The grafted polymers used for d.t.a. were in the form of a fine powder, while those for i.r. and X-ray analysis were in the form of film.

RESULTS AND DISCUSSION

Tables 1–3 show the effects of monomer concentration and the temperature and time of reaction on the degree of grafting for each of the monomers used. With acrylonitrile at 40°C increasing the monomer concentration has a considerable effect on the degree of grafting, whereas the effect is much smaller with methyl acrylate and with methyl methacrylate the yield rises to a relatively low value. In the case of ethyl acrylate no graft copolymer was formed at 40°C.

The effect of grafting temperature was investigated by carrying out the reaction at 20°C, 40°C and 60°C keeping the other variables constant. With acrylonitrile, methyl acrylate and methyl methacrylate there is a steady increase in yield of copolymer as the temperature is increased. Grafting of ethyl acrylate however only occurred at 60°C.

The reactivities of the monomers were calculated, methyl acrylate being taken as unity. *Table 4* shows the relative reactivities at three different monomer concentrations. The order of the reactivity is in agreement with that obtained by Simionescu and Oprea[3], who grafted acrylic monomers on to cellulose using ozone as initiator.

To establish that grafting had indeed occurred and that the products were not simply physical mixtures of the polymers, the copolymers and mixtures of the homopolymers were examined by solvent extraction and differential thermal analysis.

Table 5 shows the composition of the polymer mixtures and the copolymers used for solvent extraction and the weight changes after extraction. In all cases the physical mixtures showed a complete extraction of the added polymer, while the copolymer samples showed only a very small loss.

Table 6 shows the compositions of the polymer mixtures and the copolymers used for differential thermal

Table 3 Effects of monomer concentration, temperature and time of reaction on the degree of grafting of MMA on alginate. In each case the concentration of H_2O_2 was 7.96×10^{-3} M and of thiourea was 7.2×10^{-3} M

Sample number	Monomer concentration (mole dm^{-3})	Temperature (°C)	Time (h)	% Graft
XXII	2.4×10^{-1}	40	2	6.0
XXIII	4.7×10^{-1}	40	2	7.56
XXIV	7.1×10^{-1}	40	2	7.88
XXV	9.4×10^{-1}	40	2	7.66
XXVI	4.7×10^{-1}	40	0.5	4.90
XXVII	4.7×10^{-1}	40	1	6.30
XXVIII	4.7×10^{-1}	40	3	8.62
XXIX	4.7×10^{-1}	20	2	2.17
XXX	4.7×10^{-1}	60	2	9.22

Table 4 Relative reactivities of the monomers, at three different monomer concentrations (Reactivity of MA = 1.0)

	Monomer concentration (mole dm^{-3})		
Monomer	4×10^{-1}	7×10^{-1}	10×10^{-1}
AN	0.40	2.29	3.54
MA	1.00	1.00	1.00
MMA	0.50	0.29	0.31
EA	0.00	0.00	0.00

Table 5 Solvent extraction of alginate graft copolymers and physical mixtures of alginate and homopolymers

	Material	Composition		Extraction solvent time (h)		Wt. change after extraction (%)
M1	physical mixture	ALG[1]/PAN[2],	100/49	DMF[3]	18	50
VI	graft	ALG/PAN,	100/49	DMF	18	3
M2	physical mixture	ALG/PMA,	100/29	Acetone	16	30
XV	graft	ALG/PMA,	100/29	Acetone	16	2
M3	physical mixture	ALG/PMMA,	100/7.6	Acetone	16	8
XXV	graft	ALG/PMMA,	100/7.6	Acetone	16	0
M4	physical mixture	ALG/PEA,	100/28	Acetone	16	30
XXXI	graft	ALG/PEA,	100/28	Acetone	16	2

[1] ALG = alginate; [2] PAN = polyacrylonitrile, PMA = polymethyl acrylate, PMMA = polymethyl methacrylate, PEA = polyethyl acrylate;
[3] DMF = *N,N'*-dimethylformamide

Table 6 Sample of alginate graft copolymers and their physical mixture for differential thermal analysis

	Material	Composition	
M5	physical mixture	ALG/PAN,	100/55.0
V	graft	ALG/PAN,	100/17.0
II	graft	ALG/PAN,	100/55.0
IV	graft	ALG/PAN,	100/135.0
A	alginate only		
M6	physical mixture	ALG/PMA,	100/28.1
XIX	graft	ALG/PMA,	100/28.1
M7	physical mixture	ALG/PMMA,	100/8.0
XXV	graft	ALG/PMMA,	100/7.6
M8	physical mixture	ALG/PEA,	100/28.0
XXXI	graft	ALG/PEA,	100/28.0

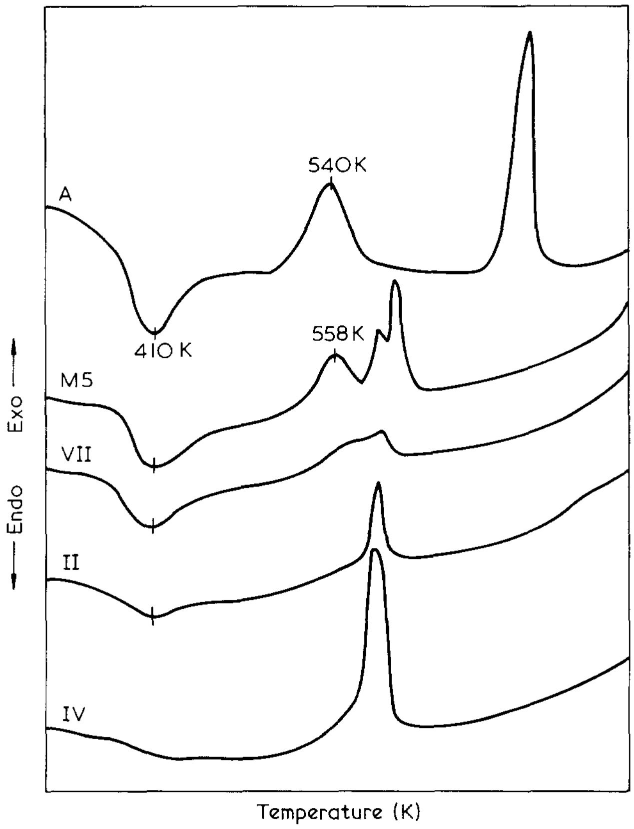

Figure 1 Differential thermograms of alginate (A), PAN-*g*-alginate (II, IV and VII) and a physical mixture of PAN and alginate (M5)

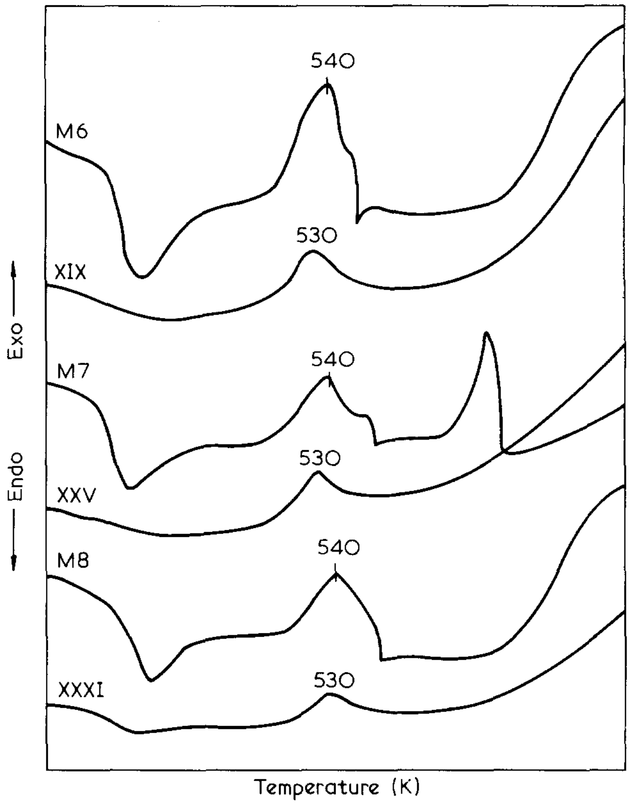

Figure 2 Differential thermograms of PMA-*g*-alginate (XIX), PMMA-*g*-alginate (XXV) and PEA-*g*-alginate (XXXI) and the corresponding physical mixtures (M6, M7 and M8)

analysis and *Figures 1* and *2* show the thermograms obtained for a physical mixture of alginate and PAN and several copolymers. The endothermic peak at 410 K and the exothermic peak at 540 K appear to be characteristic of the non-grafted alginate. As the proportion of PAN in the copolymer increases the peaks at 410 K and 540 K decrease while the one at 558 K increases and appears in all the samples containing PAN. The results suggest that the changes in the thermal behaviour are due to the PAN being chemically bonded to the alginate and not simply a physical mixture.

Figure 2 shows the thermograms for physical mixtures of alginate and PMA, PMMA and PEA, and also the corresponding graft copolymers. The endothermic peak at 410 K and the exothermic peak at 540 K appear in all the mixtures, but not in the copolymers. The exothermic peak at 540 K in the mixtures has been shifted to 530 K in the copolymers.

In all four copolymers the i.r. absorption spectra show bands which are typical of the grafted polymer and which are not present in alginate. With the copolymers of PAN, PMA and PMMA the typical absorption bands increase with time of reaction, increase in temperature and with increasing concentration of initiator. *Figures 3–5* show the i.r. spectra of typical alginate copolymers.

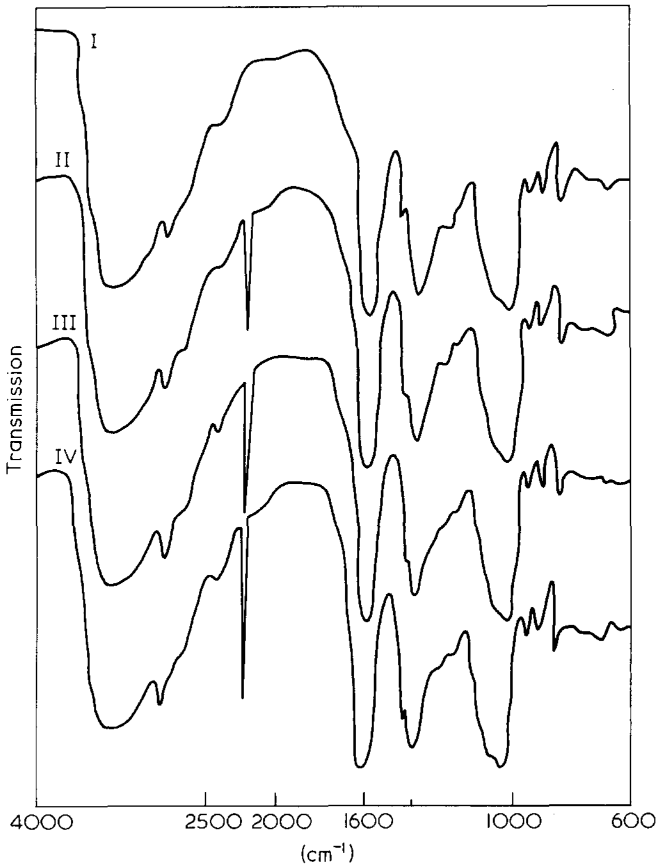

Figure 3 I.r. absorption spectra of PAN-*g*-alginates

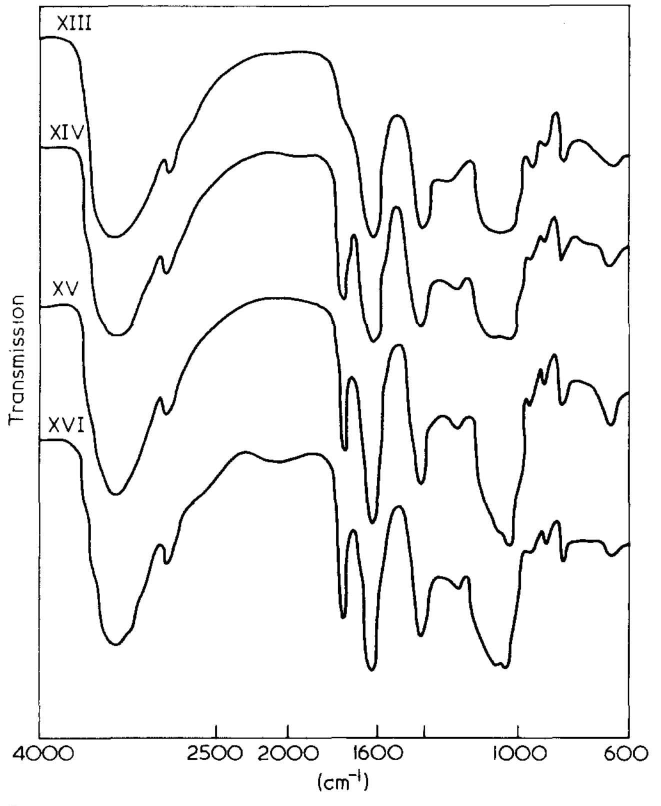

Figure 4 I.r. absorption of PMA-*g*-alginates

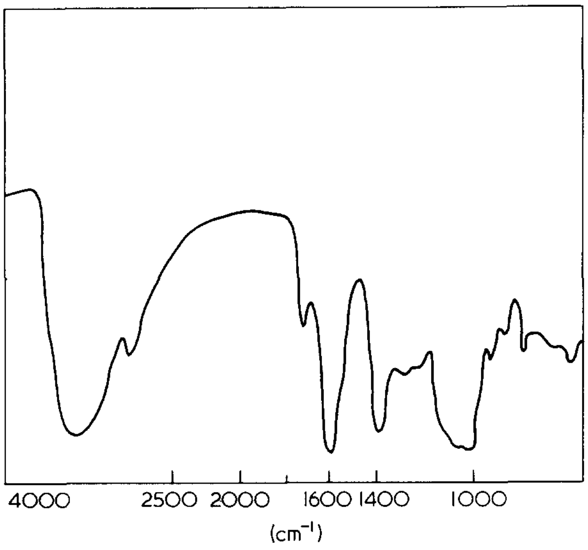

Figure 5 I.r. absorption spectrum of PMMA-*g*-alginate (sample XXII)

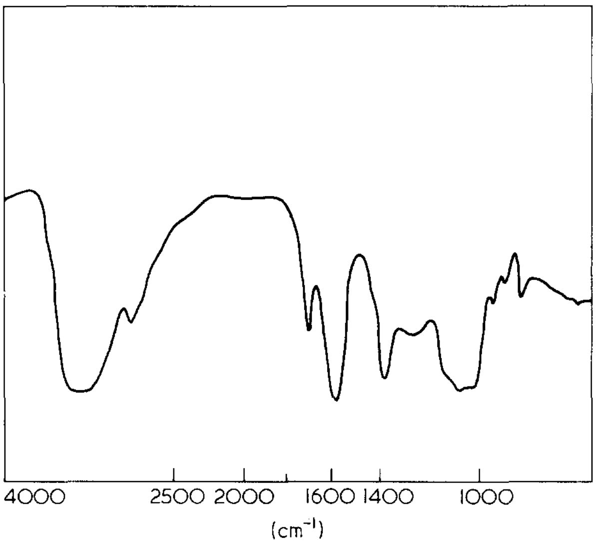

Figure 6 I.r. absorption spectrum of PEA-*g*-alginate (sample XXXI)

The spectra of PMA, PMMA and PEA graft copolymers (*Figures 4* and *6*) all have an absorption band at around 1730 cm^{-1} characteristic of a carboxylic ester carbonyl and not present in the alginate spectrum, while that of the PAN grafted samples show a peak at 2240 cm^{-1} attributed to nitrile absorption (*Figure 3*). This peak becomes stronger as the degree of grafting increases. The intensity of the OH band in the spectrum of each of the copolymers is less than that in the spectrum of alginic acid, indicating that some of the grafted polymer is linked through OH groups.

The results of X-ray diffraction measurements, although difficult to interpret quantitatively, indicate that the PAN-, PMA- and PMMA-graft copolymers had more crystalline character than the original alginate. In the case of the PAN- and PMA-grafted samples, the crystallinity appeared to increase with the degree of grafting.

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