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EFFECT OF DEGREE OF SUBSTITUTION ON GRAFTING OF ACRYLONITRILE ONTO SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED AMYLOSE

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ABSTRACT

In order to study the effect of degree of substitution, the grafting of acrylonitrile (AN) onto sodium salt of partially carboxymethylated amylose (Na-PCMA) samples of varying degrees of substitution has been carried out using ceric ammonium nitrate (CAN) as an initiator. The percentage of grafting (% B), percentage grafting efficiency (% GE) and % add-on are found to decrease with increase in degree of substitution. The molecular weights of the grafted homopolymer (PAN) have been determined from viscosity measurements and are found to decrease with increase in degree of substitution of Na-PCMA sample. The results on the thermal studies of all the Na-PCMA samples and their graft

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copolymers also showed that the thermal stability decreases with increasing degree of substitution of Na-PCMA.

INTRODUCTION

As a part of our research programme we have successfully grafted different vinyl monomers onto sodium salt of partially carboxymethylated amylose using chemical [1-4] as well as radiation [5] methods. We have also measured the water absorbency of saponified Na-PCMA-g-PAN samples of different degrees of substitution [6] and studied the thermal behaviour of different graft copolymers of sodium salt of partially carboxymethylated amylose [7]. In the present work we have studied the effect of degrees of substitution on grafting of acrylonitrile onto Na-PCMA.

EXPERIMENTAL

Materials

Amylose used for the preparation of Na-PCMA was extracted from the potatoes with usual procedure [8]. The method of Abdel-Akher et al [9] was followed for the preparation of Na-PCMA of varying degrees of substitution. The methods of purification and measurement of degree of substitution (\overline{DS}) were followed as discussed earlier [10]. The samples of Na-PCMA had \overline{DS} values 0.313, 0.493, 0.604, 0.816, 1.157 and 1.836 respectively.

The optimum reaction conditions for affording maximum percentage of grafting of acrylonitrile (AN) onto Na-PCMA ($\overline{DS} = 0.313$) using ceric ammonium nitrate (CAN) as

redox initiator were determined as discussed elsewhere [1]. The optimum reaction conditions obtained were : Na-PCMA ($\overline{DS} = 0.313$) = 2.0 g (dry basis), $[HNO_3] = 0.5$ mol/L, $[AN] = 1.169$ mol/L, $[CAN] = 0.20$ mol/L, Temperature = $30^\circ C$, Time = 4 hr and Volume of solvent (H_2O) = 50 mL.

By using the same optimized reaction conditions, the grafting of AN onto Na-PCMA samples having varying degrees of substitution (viz. $\overline{DS} = 0.493, 0.604, 0.816, 1.157$ and 1.836) was carried out. The experimental procedure followed was identical one followed for the preparation of Na-PCMA ($\overline{DS}=0.313$)-g-PAN [1]. All the different graft copolymers were purified by soxhlet extraction with DMF for 48 hr. After removal of the homopolymer (PAN), all the pure graft copolymer samples were dried at $40^\circ C$ under vacuum until constant weight was obtained.

The percentage grafting (% G) and grafting efficiency (% GE) were evaluated by the following expressions :

$$\text{Percentage grafting (\% G)} = \frac{\text{Weight of polymer grafted}}{\text{Initial weight of backbone}} \times 100$$

$$\text{Percentage grafting efficiency (\% GE)} = \frac{\text{Weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{Weight of homopolymer grafted}} \times 100$$

Side Chain Separation

The grafted samples viz. Na-PCMA ($\overline{DS} = 0.313$)-g-PAN, Na-PCMA ($\overline{DS} = 0.493$)-g-PAN, Na-PCMA ($\overline{DS} = 0.604$)-g-PAN,

Na-PCMA ($\overline{DS} = 0.816$)-g-PAN, Na-PCMA ($\overline{DS} = 1.157$)-g-PAN, and Na-PCMA ($\overline{DS} = 1.836$)-g-PAN were hydrolyzed by refluxing them for six hours in 1N HCl solution [11]. After all the Na-PCMA went into the solution, resinous masses were obtained and were separated by filtration, washed with water and with ethanol and dried under vacuum at 40°C. All the isolated side chains were characterized by IR as PAN.

Viscosity measurements

The molecular weight of grafted homopolymer (PAN) was determined from the intrinsic viscosity measurements. The intrinsic viscosity measurements were carried out at 25°C in DMF solution by using Ubbelohde viscometer.

Thermogravimetric analysis

The thermal behaviour of Na-PCMA samples having varying degrees of substitution and their graft copolymers was studied in air at a heating rate of 10°C/min by using the DuPont 951 thermogravimetric analyzer.

RESULTS AND DISCUSSION

In the present study, the Na-PCMA samples of varying degrees of substitution have been prepared in order to study the effect of \overline{DS} on the graft yields. It is expected that the presence of two functional groups, hydroxyl and carboxyl, in Na-PCMA affords attractive sites for further chemical modification such as grafting. The presence of $-\text{CH}_2\text{COONa}$ groups in the Na-PCMA may open up the structure, thus increasing the diffusion of the initiator

and the monomer. There is neither significant effect on the availability of the amylose hydroxyls nor on their reactivity by the $-\text{CH}_2\text{COONa}$ groups. On the other hand, the accessibility of remaining hydroxyl groups of Na-PCMA to grafting is greater, since higher graft yields are obtained with the latter.

The grafting yields obtained in the graft copolymerization of AN on all the samples of Na-PCMA with different degrees of substitution have been tabulated in Table-1. It can be seen from this table that the values of % G and % GE decrease with increasing $\overline{\text{DS}}$. It appears that introduction of $-\text{CH}_2\text{COONa}$ groups into the amylose molecules results into two opposing effects : (a) opening up of the amylose structures, and thereby enhancing diffusion and adsorption of both the monomer and the initiator and (b) blocking some of the hydroxyl groups along the amylose chains. Effect (a) leads to increase in the grafting yields, where as effect (b) gives rise to a decrease. The factor predominating out of the two will control the graft yield.

From the results of Table-1, it can be said that for Na-PCMA sample-A effect (a) predominates while for other samples (B to F), effect (b) is predominating. Thus the effect of introducing the increasing amounts of carboxymethyl groups in the amylose molecule, leads to the decrease of swellability and blocking of the amylose hydroxyls. In addition to this, the free hydroxyl groups, in

TABLE 1 : Effect of Degree of substitution (\overline{DS})^a in the graft copolymerization of AN onto Na-PCMA samples

Sample(s)	\overline{DS}	% Grafting (% G)	% Grafting Efficiency (% GE)
A	0.313	181.50	82.97
B	0.493	177.80	81.85
C	0.604	171.56	80.22
D	0.816	165.38	78.80
E	1.157	156.90	75.74
F	1.836	139.80	71.31

a. **Reaction Conditions** : Na-PCMA (all \overline{DS}) = 2.0 g (dry basis); $[HNO_3]$ = 0.5 mol/L; $[AN]$ = 1.169 mol/L; $[CAN]$ = 0.20 mol/L; Temperature = 30°C; Time = 4 hr; Volume of solvent (H₂O) = 50 mL and Total volume = 65 mL

the Na-PCMA samples with increasing amount of carboxymethyl groups, appear to be inaccessible for grafting, perhaps because of steric hindrance. Therefore, for Na-PCMA samples B, C, D, E and F, the graft yield decreases with increasing \overline{DS} .

The weight average molecular weight (\overline{M}_w) and number average molecular weight (\overline{M}_n) were calculated from intrinsic viscosity measurements of the grafted homopolymer

TABLE 2 : Effect of Degree of substitution (\overline{DS}) of Na-PCMA on molecular weight averages and polydispersity of grafted PAN.

\overline{DS}	% Grafting (% G)	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w / \overline{M}_n$
0.313	181.50	6.04	3.02	2.00
0.493	177.80	5.88	2.94	2.00
0.604	171.56	5.41	2.71	2.00
0.816	165.36	5.26	2.63	2.00
1.157	156.90	5.11	2.55	2.00
1.836	139.80	4.50	2.25	2.00

(PAN) using the Cleland-Stockmayer equation [1] :

$$[\eta] = 2.33 \times 10^{-4} \overline{M}_w^{0.75} \text{ dl g}^{-1}$$

$$[\eta] = 3.92 \times 10^{-4} \overline{M}_n^{0.75} \text{ dl g}^{-1}$$

Thus the values of \overline{M}_w , \overline{M}_n and polydispersity obtained in the case of all the Na-PCMA samples of different degrees of substitution are tabulated in Table-2. The values of \overline{M}_w and \overline{M}_n are found to decrease with increase in \overline{DS} of Na-PCMA sample, which is in accordance with the variation of % grafting with \overline{DS} .

The thermal behaviour of all the Na-PCMA samples having different degrees of substitution and their graft

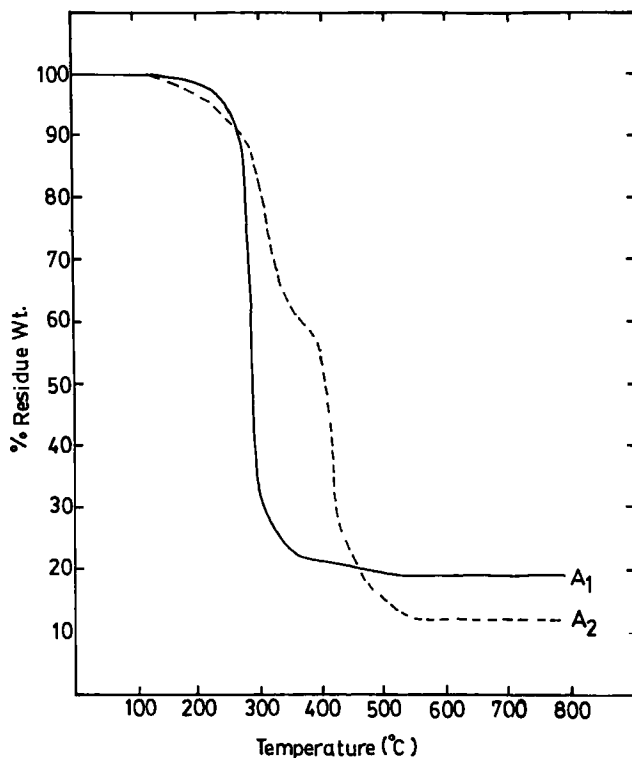


Fig.1 : TG thermograms for A₁ : Na-PCMA ($\overline{DS} = 0.313$),
A₂ = Na-PCMA ($\overline{DS} = 0.313$)-g-PAN in air.

copolymers at a heating rate of 10°C/min in air atmosphere was studied using DuPont 951 thermogravimetric analyzer. The typical primary thermograms obtained for Na-PCMA ($\overline{DS}=0.313$) and Na-PCMA ($\overline{DS}=0.313$)-g-PAN samples are shown in Fig-1. The values of the temperature characteristics and IPDT for the Na-PCMA samples having different degrees of substitution and their graft copolymers are also reported in Table-3. The

TABLE 3 : Thermogravimetric analysis of Na-PCMA samples of different degrees of substitution and their graft copolymers

Sample	% Grafting (% G)	T_0 °C (IDT)	T_f °C (FDT)	T_{max} °C		T_{10} (°C)	T_{50} (°C)	IPDT (°C)
				Step-I	Step-II			
Na-PCMA ($\overline{DS}=0.313$)	-	125	525	290.0	-	270.0	287.0	319
Na-PCMA ($\overline{DS}=0.313$)-g-PAN	181.50	115	550	302.5	415	275.0	405.0	343
Na-PCMA ($\overline{DS}=0.604$)	-	155	710	315.0	625	300.0	325.0	485
Na-PCMA ($\overline{DS}=0.604$)-g-PAN	171.56	150	450	315.0	390	260.0	372.5	285
Na-PCMA ($\overline{DS}=0.816$)	-	150	640	310.0	625	310.0	315.0	429
Na-PCMA ($\overline{DS}=0.816$)-g-PAN	165.38	105	450	325.0	415	242.5	385.0	273
Na-PCMA ($\overline{DS}=1.836$)	-	150	605	320.0	545	300.0	390.0	423
Na-PCMA ($\overline{DS}=1.836$)-g-PAN	139.80	125	425	330.0	370	240.0	347.5	263

examination of the table reveals that the overall thermal stability of all the grafted samples decreases compared to the corresponding Na-PCMA samples except Na-PCMA sample having $\overline{DS}=0.313$. It can be further seen that with increasing \overline{DS} of Na-PCMA, IPDT value of the corresponding graft copolymer decreases which is also quite in accordance with the values of % grafting.

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