A New Method for Determination of Percentage Grafting in Starch-Polyacrylonitrile Graft Copolymer

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The starch-polyacrylonitrile graft copolymer after complete removal of homopolymer and unreacted starch, is hydrolysed with 72% sulphuric acid. Glucose content of the hydrolysate is determined by titration against (a) periodate and (b) Fehling's solution. The percentage grafting is calculated from the amount of starch in the graft copolymer. Results obtained by this method compares well with those calculated from the percent nitrogen in the graft.

IN the case of cellulose and modified cellulose characterization of graft copolymers has been done by calculating increase in weight of the substrate after complete removal of homopolymer and unreacted substrate[1,2]. Such a method, however, is not convenient for characterization of grafted starch. Guglimell and coworkers[3] characterized starch-polyacrylonitrile (starch-pan) graft copolymer from the nitrogen analysis of the graft. In this note we report characterization of starch-pan graft copolymer by estimating glucose in the hydrolysate of the copolymer.

Graft copolymerization was carried out to give relatively low grafting. However, initiation with benzoyl peroxide afforded higher grafting values. Percentage grafting determined by the present method gave results which compared well with those determined by the standard method[3] reported for characterization of starch-pan graft copolymer. The present method is applicable to any given sample of starch-pan graft copolymer even when the initial amounts of starch and acrylonitrile used in the grafting experiment are not known. Besides, this method does not require quantitative recovery of the graft copolymer which is rather tedious and at times offers considerable difficulty. The present method may be applicable for characterization of cellulosic graft copolymer also.

The starch used was unmodified and dried prior to its use. Acrylonitrile (BDH) was fractionated under nitrogen. A centre cut was collected and stored at 5°C until used.

Catalyst — (a) Ceric sulphate (0·332 g) was taken in conc. nitric acid (6 ml) and diluted with distilled water to give the desired concentration.

(b) Benzoyl peroxide (0·5 g) was taken in dioxane (15 ml) and ethanol (15 ml) and the resulting solution added to the reaction mixture.

(c) Potassium persulphate (0·0966 g) and sodium bisulphite (0·5048 g) were dissolved in water and added to the reaction mixture. Ferrous ammo-

nium sulphate (0·0142 g) which acted as a promoter was added to the reaction mixture.

(d) Fenton's reagent was prepared by dissolving ferrous ammonium sulphate (20 mg) in minimum amount of water followed by addition of 30 vol% hydrogen peroxide (0·05 ml).

Graft copolymerization — Starch (10 g) was dissolved in hot deaerated water (500 ml) and placed into a three-necked flask fitted with mercury seal stirrer. The reaction flask was purged with nitrogen for 20 min and then a steady supply of nitrogen was maintained throughout the reaction. Required amount of catalyst was added to the stirred solution, followed by the addition of acrylonitrile during $2\frac{1}{2}$ hr. The reaction was carried out at 55-60° for 3 hr. After the completion of the reaction, the mixture was poured into methanol (1·5 litres) with constant stirring. A white grannular precipitate was formed which was filtered and air dried. The crude product was extracted with hot dimethylformamide to remove the homopolymer. The unreacted starch was removed by extraction with hot water. The resulting purified graft copolymer was dried at 50°. Evidence for grafting was obtained from the presence of nitrogen in the graft. Further, the IR spectrum showed a strong absorption for C≡N in the graft copolymer.

Estimation of percentage grafting — The purified graft copolymer (0·2 g) was hydrolysed with 72% sulphuric acid by refluxing for 3 hr. The volume was made to 100 ml with distilled water (stock solution). The liberated glucose in the stock solution was estimated in the following manner.

Aliquots (5 ml each) were taken and the glucose contents determined by titration against a standard (a) Fehling's solution and (b) sodium metaperiodate solution. In a controlled experiment, starch (0·2 g) was hydrolysed with 72% sulphuric acid and the glucose content was estimated as above. From the titre values the amount of starch was calculated. By substracting the amount of starch from the total amount of graft copolymer taken, the amount of polyacrylonitrile (pan) in the copolymer was obtained. Percentage grafting was then calculated as follows:

$$\% \text{ grafting} = \frac{\text{Amount of pan in the graft}}{\text{Amount of graft}} \times 100$$

The percentage grafting was also calculated from the amount of nitrogen present in the purified graft copolymer[3]. The results are presented in Table 1.

TABLE 1 — DETERMINATION OF PERCENTAGE GRAFTING IN STARCH-POLYACRYLONITRILE GRAFT COPOLYMER

Sample	Types of initiator	Percentage grafting	
		Present method	Nitrogen analysis[3]
I	Benzoyl peroxide	30·7	30·2
II	Fenton's reagent	18·8	19·5
III	Persulphate bisulphite	7·0	8·0
IV	Ceric sulphate	10·5	11·3

NOTES

References

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Hydrogen Bonding & Excess Volumes of Mixing of Phenol, o- & p-Chlorophenols & o- & p-Cresols with Tetrahydrofuran & Cyclohexanone

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Excess volumes (V^E) of binary liquid mixtures of phenol, o-chlorophenol, p-chlorophenol, o-cresol and p-cresol with THF and cyclohexanone have been measured at $30.0° \pm 0.01°C$. The data have been used to postulate (i) break-up of hydrogen bonds present in the polymers of phenols and (ii) formation of new hydrogen bonds between the molecules of phenols and the common components, THF and cyclohexanone. The experimental values of V^E have also been used to understand the influence of substituents on the strength of hydrogen bonds between the unlike components and also the relative basicities of THF and cyclohexanone.

THERE appears to be no satisfactory statistical theory, which deals with strong orientation effects introduced by hydrogen bonding from which one may deduce excess volumes of mixtures. However, Barker *et al.*[1] have presented a treatment based on lattice model for the calculation of excess free energy and excess heat of mixing. The excess volumes of binary liquid mixtures may be employed to understand, (a) the departure of a real mixture from ideal behaviour and (b) the nature of interaction between the molecules of components. In the present work excess volumes of mixing of phenol o- & p-chlorophenols, and o- and p-cresols with THF and cyclohexanone have been measured and the results have been used to study the structure breaking and structure making effects of the solvents THF and cyclohexanone. An attempt has also been made to ascribe the differences in excess volumes to the electrical effects of substituents in the phenols and the differences in the basicites of THF and cyclohexanone.

Measurement of excess volumes of mixing — The excess volumes were obtained from the densities of mixtures and pure liquids determined with the aid of a double stem pycnometer[2]. The density data obtained at $30° \pm 0.01°C$ were corrected for buoyancy and residual vapours and were reproducible with ± 0.0001. The excess volumes are accurate to ± 0.02 cm³/mole.

Purification of materials — Phenol, o-chlorophenol, p-chlorophenol, o-cresol, p-cresol, THF and cyclohexanone were purified by the methods described by Weissberger[3]. Their purity was checked by

TABLE 1 — EXCESS VOLUMES OF MIXING OF THE PHENOLS WITH THF AND CYCLOHEXANONE AT 30°C

Mole fr. (X_A)	Density g/ml	V^E cm³ mole⁻¹
PHENOL + THF		
0.1037	1.0568	−0.78
0.2383	1.0331	−0.85
0.3127	1.0207	−0.95
0.4088	1.0056	−1.32
0.5299	0.9836	−1.27
0.6385	0.9615	−1.26
0.7250	0.9429	−1.03
0.8356	0.9178	−0.75
0.8991	0.8766	−0.51
o-CHLOROPHENOL + THF		
0.1226	1.2242	−0.86
0.2376	1.1946	−1.48
0.3405	1.1635	−1.79
0.4372	1.1298	−1.83
0.5006	1.1108	−2.20
0.6511	1.0538	−2.27
0.7414	1.0135	−2.00
0.8344	0.9661	−1.34
0.9158	0.9221	−0.61
p-CRESOL + THF		
0.0829	1.0194	−0.24
0.2016	1.0083	−0.62
0.3017	0.9981	−0.89
0.4042	0.9858	−1.06
0.5030	0.9723	−1.14
0.6025	0.9561	−1.02
0.6963	0.9397	−0.87
0.8015	0.9215	−0.71
0.9014	0.8999	−0.45
o-CRESOL + THF		
0.0859	1.0298	−0.20
0.1988	1.0178	−0.67
0.3004	1.0068	−0.86
0.3974	0.9936	−1.04
0.5015	0.9783	−1.20
0.6019	0.9612	−1.05
0.6972	0.9442	−0.96
0.7991	0.9242	−0.81
0.9026	0.9010	−0.47
p-CHLOROPHENOL + THF		
0.1134	1.2367	−0.24
0.1989	1.2108	−0.48
0.2973	1.1790	−0.72
0.3941	1.1460	−0.93
0.4959	1.1091	−1.09
0.5966	1.0704	−1.23
0.7021	1.0266	−1.26
0.8008	0.9799	−0.96
0.8916	0.9336	−0.53
PHENOL + CYCLOHEXANONE		
0.0979	1.0543	−0.27
0.1989	1.0408	−0.37
0.3003	1.0275	−0.45
0.3456	1.0211	−0.44
0.4810	1.0041	−0.52
0.5891	0.9900	−0.49
0.6997	0.9756	−0.40
0.7916	0.9639	−0.31
0.9121	0.9488	−0.18