

GRAFT COPOLYMERISATION OF ACRYLONITRILE ON TO POLYVINYL ALCOHOL

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Acrylonitrile (AN) has been graft polymerised on to polyvinyl alcohol (PVA) in aqueous medium using potassium persulfate as an initiator. The grafting was characterised by elemental analysis, solubility, I.R. and intrinsic viscosity measurements. The rate of conversion of monomer, rate of graft copolymerisation (Rg), grafting ratio (GR) increased with increasing concentration of AN and decreased with increasing concentration of PVA. Increase in catalytic concentration was found to increase rate of conversion of monomer Rg and Gr. Some PVA is left unturned by growing polymer chain of PAN which increases with increasing concentration of AN PVA or potassium persulfate. The effects of concentration of AN, PVA and potassium persulfate on GR, Rg, rate of conversion of monomer and PVA used in grafting (PG) were studied.

Key words: Grafting efficiency, Mutual termination of radicals, High energy irradiation.

Introduction

The graft CO-polymers of vinyl monomers are extensively used in textile and plastic industries. Screen printing plates are prepared by coating a screen with a photosensitive resin containing graft copolymer obtained by grafting an acrylic monomer [1] to the backbone of poly vinyl alcohol (PVA). The screen printing plates prepared in the presence of graft copolymer of acrylic acid on PVA have better solvent resistance, abrasion resistance, better resolution and better processing in textile printing. The graft copolymers of vinyl monomers like styrene [2], methylmethacrylate [3,4] and methacrylic acid [5] onto the backbone of PVA and polyvinyl acetate have been found useful in textile industry. Most of these graft copolymers are prepared by high energy irradiation. The graft copolymers of acrylonitrile (AN) on PVA are also found useful in preparing screen printing plates [6,7]. This is due to excellent adhesive properties of PVA which holds the fabric in place during the printing process. In earlier publications the graft copolymerisation of MMA on natural rubber [8] and acrylamide on casein [9] have been reported.

In this report we describe the copolymerisation of An onto the backbone of PVA using water as a solvent and potassium persulfate as an initiator at 60°C.

Experimental

Materials. Acrylonitrile (BDH) was dried over Na_2SO_4 and distilled in an atmosphere of nitrogen. The middle fraction (b.p.76.°) was collected and stored at 0°C in the dark. Poly vinyl alcohol (molecular weight 61280) and GR grade $\text{K}_2\text{S}_2\text{O}_8$ (E. Merck) were used without further purification. Other organic solvents were distilled before use.

Procedure. The required amounts of PVA and water were transferred to four neck round bottomed flask fitted with con-

denser, stirrer, thermometer and separating funnel. The mixture was stirred at a temperature 58-60°C (for 1hr. Known quantity of monomer according to Tables 1-3 was then added following the addition of potassium persulfate (in 10 ml of water). The contents were continuously stirred. After required reaction time (4 hrs) the copolymer was precipitated with methanol and filtered through Buchner funnel, dried in vacuum desiccator and weighed. The dried sample was further soxhleted in water to remove unbound PVA. Nitrogen in the product was analysed to find out how much quantity of AN has been grafted on to the backbone of PVA. I.R. of this products was recorded to identify the grafting of growing polymer chain of AN on the backbone of PVA from the appearance of characteristic absorption bands which were not present in the spectrum of pure PVA.

The intrinsic viscosity of grafted products was determined at 25°C using Ostwald's type viscometer.

Results and Discussion

Table 1 summarizes the data for the effect of monomer concentration in the synthesis of graft copolymer of AN and PVA using potassium persulfate as catalyst and water as a solvent at 60°C for 4 hrs. Whereas the data shown in Table 2 obtained from the effect of backbone concentration in this synthesis. In Table 3, the data are given for the effect of catalyst concentration in the synthesis of graft copolymer of AN and PVA using water as a solvent at 60°C for 4hrs. The grafting was identified by means of elemental analysis, Solubility, I.R. spectral studies, intrinsic viscosity etc.

The product obtained before and after soxhleting in water was estimated for nitrogen. The prepared sample of PAN contains 26.1% N. On the other hand 12 samples of the product before soxhletion contains 17.5-18.7% N, whereas the

TABLE 1. EFFECT OF MONOMER VARIATION.

Exp. no.	AN in feed mole	Total conversion of AN		PVA in product x 10 ⁵ mole	Elemental analysis % N		% GR*	R _g x 10 ⁶ ms ⁻¹
		Mole	%		Non-soxhelated	Soxhelated		
1.	0.2264	0.1887	83	1.9745	18.05	18.82	830	13.1042
2.	0.3057	0.2642	86	2.3056	17.80	18.37	990	18.3472
3.	0.3820	0.3547	93	2.7923	17.90	18.10	1100	24.6319
4.	0.7642	0.6792	89	2.9545	18.3	18.40	1990	47.1667

Gr: grafting ratio; R_g: rate of graft copolymerization PVA = 3.2637x10⁻³ mole, persulfate= 2%, water= 60ml; temp= 60°C, time= 4hr.

TABLE 2. EFFECT OF BACKBONE VARIATION.

Exp. no.	PVA in feed x10 ⁵ mole	Total conversion of AN		PVA in product x 10 ⁵ mole	Elemental analysis % N		% GR*	R _g x 10 ⁶ ms ⁻¹
		Mole	%		Non-soxhelaeted	Soxhelated		
5.	2.4478	0.2830	92.6	1.6684	18.0	18.54	1470	19.6527
6.	3.2637	0.2642	86.0	2.3056	17.8	18.37	990	18.3472
7.	4.0796	0.2358	77.0	3.5917	18.5	19.20	570	16.3750
8.	4.8956	0.2311	76.0	4.5070	18.7	19.32	440	16.0486

Gr: grafting ratio; R_g: rate of graft copolymerization AN = 0.3057 mole; persulfate 2%; water = 60ml; temp= 60°C, time= 4hr.

product after soxhletion estimates 18.1-19.32% N. This lowering and variation in the percentage of nitrogen suggests the attachment of PVA in the growing polymer chain of PAN or vice versa. Nitrogen contents of the product sample before and after soxhletion also indicate that some quantity of backbone is left unturned by combining with growing polymer chain of PAN. Solubility of the product in different solvents was tested to ascertain that the product is a graft copolymer. The product dissolves in hot Dimethyl formamide (DMF) and dimethyl Sulfoxide (cold) whereas PVA gets dissolved in cold or hot water. Further, PAN dissolves in cold or hot DMF. It shows that PAN combines on the backbone of PVA resulting a graft copolymer. The most effective solvent for this graft copolymer is DMSO. I.R. spectral studies have also been carried out to evidence the formation of graft copolymer. The spectra of PVA and grafted PVA are shown in Fig. 1 and 2 respectively. In Fig.2 the absorption band at 2250 cm⁻¹ indicates the presence of nitrile (C=N) group whereas this band (2250 cm⁻¹) is absent in the spectrum of PVA (Fig.1). The presence of nitrile group in the spectra of PVA indicates the association of growing polymer chains of acrylonitrile on to the backbone of PVA.

The grafting ratio (GR) and PVA used in grafting (PG) were calculated by using the following relations.

$$GR = \frac{\text{Weight of PAN in product}}{\text{Weight of PVA in product}}$$

The effect of concentration of AN in the grafting of AN on the backbone of PVA is depicted in Table 4. These results

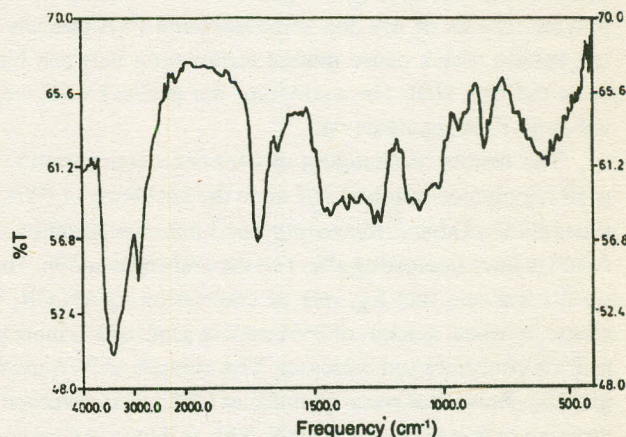


Fig. 1. I.R. Spectrum of PVA.

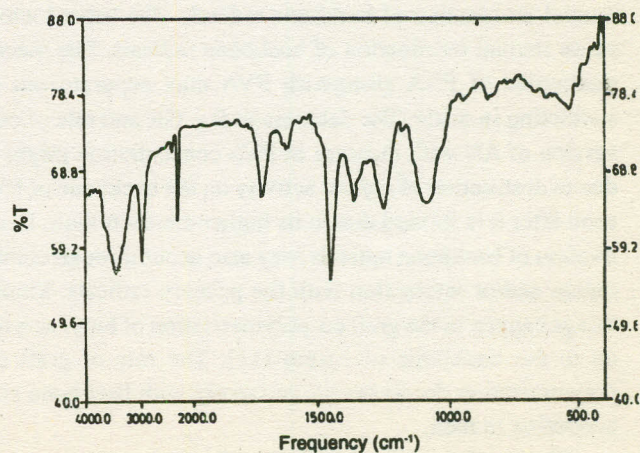


Fig. 2. I.R. Spectrum of graft Co-polymer of AN onto PVA.

TABLE 3. EFFECT OF CATALYST VARIATION.

Exp. no.	Catalyst %	Total conversion of AN		PVA in product x 10 ³ mole	Elemental analysis % N		% GR*	R _g x 10 ⁶ ms ⁻¹
		Mole	%		Non-soxhelaeted	Soxhelaeted		
9.	1.0	0.2094	68.5	2.0739	18.10	18.9	870	10.5416
10.	1.5	0.2315	76.0	2.2519	17.95	18.45	890	16.0763
11.	2.0	0.2642	86.4	2.3009	17.80	18.37	990	18.3472
12.	2.5	0.2849	93.2	2.3662	17.50	18.40	1040	19.784

Gr: grafting ratio, R_g: rate of graft copolymerization PVA = 0.2637x10⁻³ mole AN = 0.3057 mole, water = 60 ml, temp = 60°C 2, time = 4hr.

indicate that with an increase in concentration, of monomer the rate of conversion of AN, rate of graft copolymerisation (R_g), grafting ratio and PG increase. Which might be due to higher availability of the monomer molecules in the vicinity of Vinyl alcohol macro radicals. The more growing polymer chains of AN are available which attach on to the activated sites of PVA resulting more grafting. But the amount of PVA used in grafting (PG) shows that some amount of PVA are left unconverted by monomer radicals. It might be due to utilisation of required grafting sites of PVA by the growing polymer chains of AN and some unbound PVA radicals are left behind which cause mutual termination between backbone radicals [10]. On soxhleting the product with water, unbound PVA separates out.

The results of changing of backbone concentration on graft copolymerisation of AN on to the backbone of PVA are illustrated in Table 2. Increasing backbone concentration was found to have interesting effect on the grafting reaction. These results indicate that R_g, rate of conversion of AN, GR, decrease, whereas amount of PVA used in grafting PG increases as PVA concentration increases. The amount of PVA used in grafting shows that some quantity of PVA is left unturned by growing polymer chains of PAN. This is due to utilisation of required grafting sites of PVA by the growing polymer chains of AN and unbound PVA radicals are left behind which cause mutual termination of backbone radicals. The behind which cause mutual termination of backbone radicals. The macromolecules of PVA alongwith PVA may separate out on soxhleting in water. The decrease in R_g, GR and rate of conversion of AN with increase in PVA concentration might be due to destruction of radical activity on the backbone of PVA soon after it is formed due to its higher concentration. Deactivation of backbone radicals may also occur through combination and/or interaction with the primary radicals. Similar things happen in the graft co-polymerisation of butyl acrylate on to the backbone of casein [11]. The rate of graft copolymerisation decreases progressively with backbone concentration in feed.

The results obtained from the effect of catalyst concentration in the graft copolymerisation of AN onto the back-

bone of PVA. are shown in Table 3. Variation in the concentration of catalyst was found to increase R_g, GR, PG only slightly and rate of conversion of AN. Since PVA and persulphate are soluble in reaction medium (water) the process of initiating radicals to PVA is facilitated. With increased concentration of catalyst, more and more free radicals are formed which produce more activated centres on to the backbone of PVA and monomer radicals. The mode of increase in rate of conversion of AN PG value at all the catalyst concentration under discussion is not found appreciable.

When a heterogeneous mixture of AN, PVA, water and potassium per sulfate are heated, persulfate radicals, monomer radicals and form monomer radicals and create the activated sites on to the backbone of PVA to form backbone radicals. Mutual termination of monomer radicals to PVA radicals and PVA radicals to PVA radicals (forming macro radicals) take place producing graft Co-polymers and macroradicals of PVA [10]. Homopolymer radicals couple to all available activated centres of PVA. Some times if more PVA is available in the system the homopolymer radicals can't turn each activated site of PVA and thus PVA radicals mutually terminate themselves forming PVA macroradicals which results a decrease in GR. The viscosity of CO-polymer

TABLE 4. INTRINSIC VISCOSITY [η] AND NUMBER AVERAGE MOLECULAR WEIGHT (M_n) OF PVA-G-AN.

Exp No.	[η] dl/g	M _n
1.	2.00	87833
2.	2.60	124620
3.	2.50	118269
4.	1.80	76325
5.	1.90	82030
6.	2.60	124620
7.	3.00	150816
8.	2.30	105825
9.	1.70	70720
10.	1.85	79160
11.	2.60	124620
12.	2.30	105825

solutions in DMF was measured at 25°C. The number average molecular weight (\bar{M}_n) was calculated by using the following relationship of intrinsic viscosity $[\eta]$, and \bar{M}_n [12],

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_n^{0.75}$$

the intrinsic viscosities of product samples were found to be 1.7-3.0 dl/g. The number average molecular weight calculated from that values were 70720-150816 (Table 4). From these results it is evident that the molecular weight of the product samples are higher than that of PVA 61280 indicating that both AN and PVA are participating in the reaction and growing polymer chains of An are attached to the available activated centres on the backbone of PVA. The increase in molecular weight may be due to grafting of monomer molecules on the backbone of PVA.

The swelling tests of grafted PVA were carried out at room temperature. Grafted PVA swelled with different solvent uptake in acetone (26%), benzene (75%) ethyl acetate (40%), ethyl alcohol (74%) cyclohexanone (80%), toluene (70%), Dioxane (78%) and water (87%), whereas it does not swell in THF. It dissolves in DMF (hot) and DMSO. On the other hand PVA dissolves in water. It shows very poor solvent uptake with the above mentioned solvents. It may be due to the attachment of acrylonitrile molecules on to the backbone of PVA in the form of branches.

All the CO-polymer samples shown in Tables 1-3, were white powdery substances which were soluble in DMSO and DMF. Grafted PVA decomposes at 160°. When kept at 170°C, in air, for 1/2 hr, The product turned into pale brown materials with a loss in weight about 2%. It was further kept at 180°C, without loss in weight and turned into brown colour which was mostly insoluble in DMF and DMSO. Finally the

product sample was kept at 250°C when it decomposes into dark black material. The insolubility of the decomposed product in these solvents is due to the crosslinking of the degraded graft copolymer and the intermolecular rearrangements of the nitrile groups of the grafted polyacrylonitrile. More over in the presence of air, the CO-polymer might have undergone chain scission and oxidation reactions.

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