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GRAFTING OF VINYLIDENE CHLORIDE. MODEL STUDIES WITH POLY(VINYL ALCOHOL) AS SUBSTRATE

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ABSTRACT

The modification of coatings resins by graft polymerization of vinylidene chloride should produce a coatings binder with improved barrier properties. For superior color stability, vinylidene chloride must be copolymerized with other monomers such as alkyl acrylates and methacrylates. Ceric ion initiation was used to graft vinylidene chloride free-radically onto a model alcohol-containing polymer, polyvinyl alcohol. The effects of various reaction parameters on vinylidene chloride grafting were studied. Graft copolymers were characterized using selective solvent extraction, FTIR, SEM, XES, DSC, and x-ray diffraction.

INTRODUCTION

The incorporation of vinylidene chloride (VDC) into conventional solvent-borne coatings, such as alkyds, can potentially enhance barrier properties and improve gloss, flame retardation, and oil and solvent resistance [1]. A possible method for incorporation of VDC into alkyds is by free-radical solution grafting. Due to the thermal instability of homopoly(vinylidene chloride) (PVDC) chain segments, it would be necessary to graft copolymerize VDC with acrylic monomers. Free-radical grafting is commonly initiated with peroxides [2, 3]. With an alkyd as the substrate, grafting could occur through the double bonds

in the fatty-acid portions of the molecule. Potential problems with peroxide-induced grafting are production of substantial amounts of nongrafted polymer and premature gelation.

We have begun to explore the possibility of grafting vinylidene chloride with ceric ion initiation in an aqueous medium. This grafting process requires an oxidizable alcohol function on the polymer backbone from which a graft segment can be polymerized. Alkyds typically contain hydroxyl groups, and previous work with ceric ion grafting has shown that very little nongrafted polymer is produced [4-6]. To determine if incorporation of PVDC into conventional alkyd resins is feasible, poly(vinyl alcohol) (PVA) was used as a model backbone polymer. If grafting from PVA is successful, model compounds and then alkyds themselves will be graft modified.

EXPERIMENTAL

Materials

PVA (Air Products, Inc.) of molecular weight 108 000 was 96% hydrolyzed according to the manufacturer. It was dissolved in reverse osmosis (RO) water at 90°C. The PVA solution was cooled to room temperature and precipitated into reagent-grade acetone (Baker Chemical). The precipitate was collected by filtration and the process repeated two more times. The purified PVA was dried to constant weight in a vacuum oven at 60°C.

VDC (Dow Chemical) was washed with 5% NaOH, washed twice with RO water, and dried over magnesium sulfate. It was then vacuum distilled such that the temperature of the monomer never exceeded 26°C.

Ceric ammonium nitrate, $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ (CAN), (Fisher Scientific) and nitric acid (Fisher Scientific) were used as received. A standard solution of 1 M CAN in 1 N HNO_3 was prepared for grafting reactions.

Procedure

In a typical grafting reaction, appropriate amounts of aqueous PVA solution and VDC monomer were charged into an 80-mL Pyrex ampule. CAN solution was added to the reaction system, and the total volume was adjusted to 25 mL with 1 N nitric acid. Precautions were taken to keep the reaction mixture cool to avoid any loss of monomer due to evaporation. Three freeze-pump-thaw cycles were applied to the reaction mixture using liquid nitrogen for cooling, and the ampule was sealed under vacuum. The ampule was then

TABLE 1. Ceric Ion Grafting of Vinylidene Chloride (VDC) from PVA^a

Tube no.	VDC, mol/L	PVA, g/L	Reaction time, h	Ceric ion, mmol/L	Weight gain, %
2-1	0.97	10.4	2.5	2.01	18.4
3-1	0.97	16.0	2.5	4.01	18.5
4-1	0.97	16.0	2.5	4.20	43.0
4-2	0.97	16.0	2.5	6.30	51.3
4-3	0.97	16.0	2.5	8.40	34.0
4-4	0.97	16.0	2.5	10.05	24.6
5-1	1.95	16.0	3.0	6.13	43.2
5-2	2.09	16.0	3.0	6.13	34.6
5-3	3.89	16.0	3.0	6.13	30.8
5-4	4.87	16.0	3.0	6.13	18.9

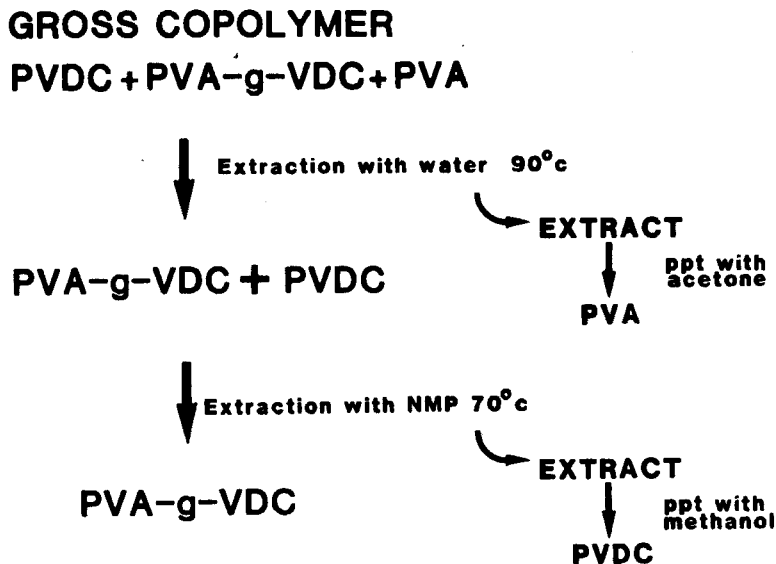
^aTotal volume, 25 mL; temperature, $40 \pm 0.1^\circ\text{C}$.

placed in a thermostated bath maintained at $40 \pm 0.1^\circ\text{C}$, and the ampule was shaken every 20 min. The reaction was quenched by precipitating the reaction mixture into cold methanol. The reaction product was collected on a sintered glass crucible and dried to constant weight in a vacuum oven at 40°C . Table 1 lists specific conditions for representative runs.

The crude copolymer was isolated by the solvent extraction method shown in Scheme 1. Loss of weight of the graft product after this procedure was less than 1%. Exhaustive extraction procedures, i.e., high temperatures and long extraction times, could not be used in this case because of the thermal instability of PVDC. However, ceric ion has been reported to produce negligible amounts of nongrafted homopolymer for many systems [4-6].

Scanning electron micrographs (SEM) were taken using an Advanced Metals Research 100A scanning electron microscope. The samples were dried in a vacuum desiccator and sputter-coated with gold under argon at 2.5 kV and 20 mA. SEM scans were taken at 20 kV.

X-ray energy spectrograms (XES) were recorded with a XES Model 5100 (KeveX Corp.) for graft copolymer samples. The IR spectra were recorded on a Nicolet 5DX FTIR using KBr pellets.



SCHEME 1. Isolation of graft copolymer by selective solvent extraction.

Differential scanning calorimetry (DSC) was carried out with a DuPont DSC attached to a 9900 thermal analyzer. Samples were scanned at 16°C/min under nitrogen.

Wide-angle x-ray scattering (WAXS) was produced on a Philips PW 1720 x-ray generator. The samples were placed in a nickel-filtered $\text{CuK}\alpha$ collimated beam at a distance of 5.00 cm for 12 h.

RESULTS AND DISCUSSION

The conditions for grafting were chosen to maximize grafting efficiency, i.e., to minimize the proportion of nongrafted PVDC homopolymer produced. Percent grafting is defined as the ratio of the weight of grafted polymer chains to the weight of polymer backbone. For systems which produce low fractions of nongrafted homopolymer, % weight gain serves as a good approximation for % grafting.

All grafting reactions were run at $40 \pm 0.1^\circ\text{C}$ because of the high grafting efficiency at this temperature reported by Sudhakar [7] for the ceric ion-initi-

ated heterogeneous grafting of methyl methacrylate onto cellulose nitrate. Consideration of the relative inaccessibility of the cellulose nitrate substrate, which is insoluble in aqueous acid solution, suggests the extreme resistance toward homopolymer initiation by ceric ion. Since PVA is water soluble, the relative tendency toward homopolymer formation may be even less in the present studies. Sudhakar [7] compared a physical mixture of homopolymers with the graft copolymer and observed that a solvent extraction scheme similar to ours was efficient for extracting the homopolymers and that ceric ion initiation gave very high grafting efficiencies.

Effect of Reaction Conditions on Percent Grafting

Grafting Time

It is seen in Fig. 1 that % weight gain increases with time up to about 3 h, after which conversion begins to level off with little or no additional graft copolymerization. This trend is commonly seen in ceric ion grafting reactions

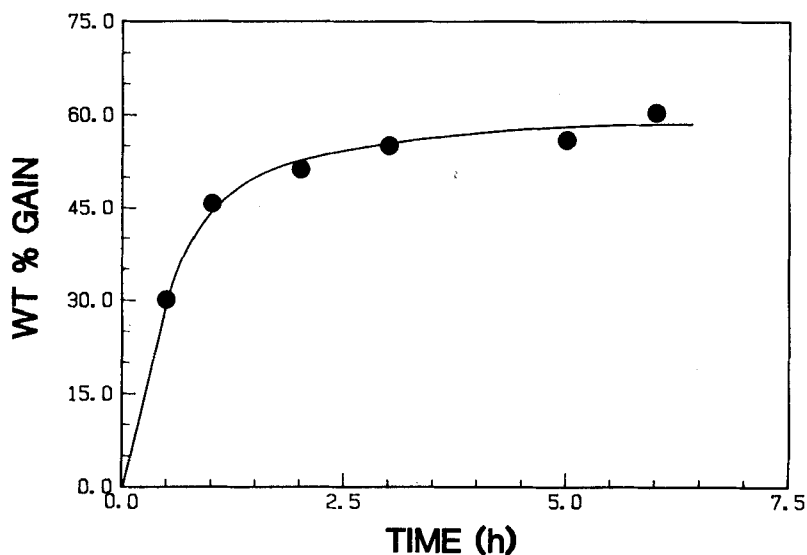


FIG. 1. Effect of grafting time on weight gain: [CAN] = 6.3 mmol/L; [VDC] = 1.00 mol/L; [PVA] = 16 g/L.

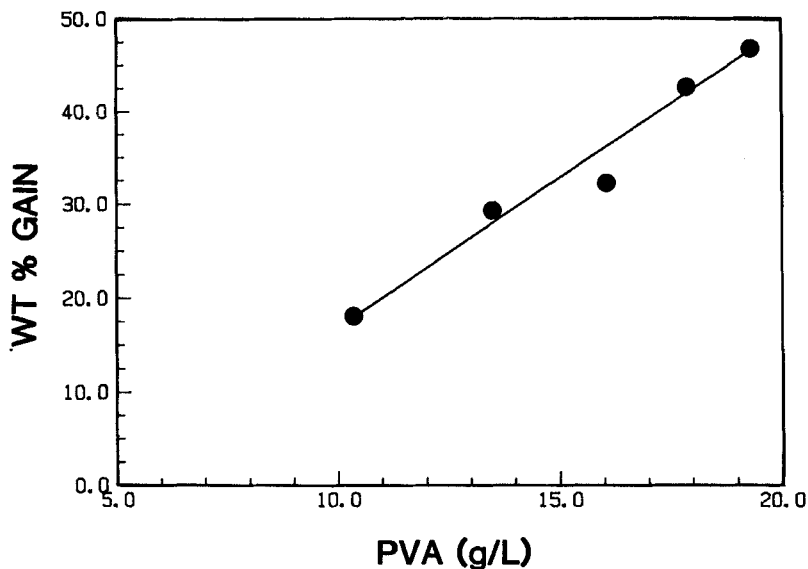


FIG. 2. Effect of PVA concentration on weight gain: $[\text{VDC}] = 1.00 \text{ mol/L}$; $[\text{CAN}] = 6.3 \text{ mmol/L}$; reaction time = 2.5 h.

[6]. For example, in grafting methyl methacrylate onto cellulose nitrate with ceric ion, it was observed that percent grafting increased rapidly at first and then became constant after a certain reaction time. Further increase in grafting time did not alter either the number of grafting sites or the number-average molecular weight of grafted chains [7].

PVA Concentration

Figure 2 illustrates the relationship between % weight gain and PVA concentration. This trend is expected because the number of available hydroxyl groups grows with increasing PVA concentration. If the PVA concentration were increased further, the weight gain would be expected to level out at some optimum PVA/ceric ion ratio.

Initiator Concentration

The weight gain goes through a maximum at a CAN concentration of approximately 6 mmol/L (Fig. 3). Such behavior has been reported for other ceric ion grafting systems [6] and can be explained as follows. Increases in ceric ion

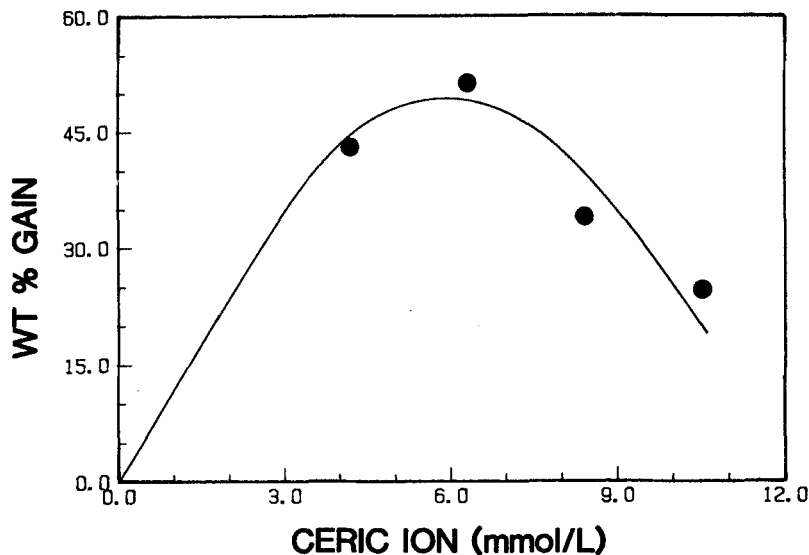


FIG. 3. Effect of ceric ion concentration on weight gain. [PVA] = 16 g/L; [VDC] = 1.00 mol/L; reaction time = 2.5 h.

concentration when its concentration is still low result in an increase in initiation. However, ceric ion is also known to terminate growing free radicals by oxidation [8-10]. Thus, when the ceric ion concentration gets too high, termination of radicals becomes important, and the weight gain is less.

No increase in weight was observed in control reactions conducted without ceric ion. In other words, thermal polymerization of VDC did not take place under the present experimental conditions.

Characterization of Graft Copolymers

Differential Scanning Calorimetry (DSC)

DSC thermograms of homo-PVA, homo-PVDC and PVA-g-VDC are shown in Fig. 4. The melting points observed for PVA and PVDC, i.e., 229 and 199°C, respectively, agree well with literature values [1, 11].

The DSC thermogram of the graft sample shows a shift in the melting point of PVDC to 200°C. This shift in temperature is indicative of graft copolymer

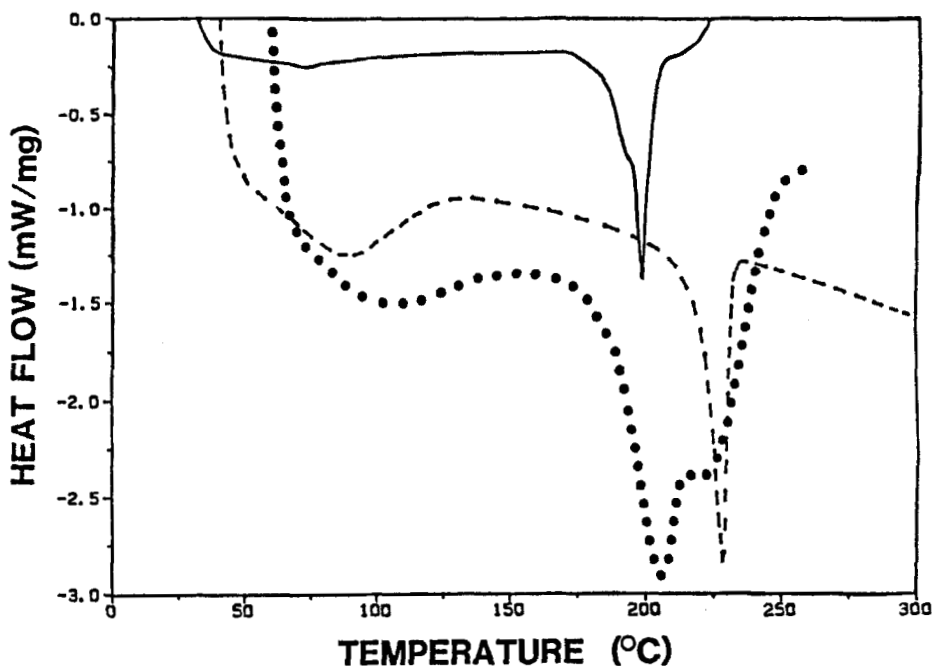


FIG. 4. DSC scans of PVDC (—), PVA (---), and PVA-g-VDC (···).

[7]. If the sample was simply a physical mixture of the two homopolymers, there should be no shift in the melting peak. The shoulder on the graft copolymer melting peak at 225°C is thought to be the melting transition of PVA segments within the graft copolymer. Quantitative measurements yielded values of 43 and 87 J/g for the melting peaks of homo-PVDC and homo-PVA, respectively. Surprisingly, the total heat of melting per unit weight of the copolymer was much higher. We have no explanation for this observation at present, but it does imply either an increase in crystallinity or a change in the crystal structure of PVDC or PVA or both. Further investigations in this direction are in progress.

Scanning Electron Microscopy and X-Ray Energy Spectroscopy

The scanning electron micrographs of PVA and PVA-g-VDC, shown in Figs. 5 and 6, show a change in the surface of the PVA, which can be attributed to grafting of VDC.



FIG. 5. Scanning electron micrograph of PVA.

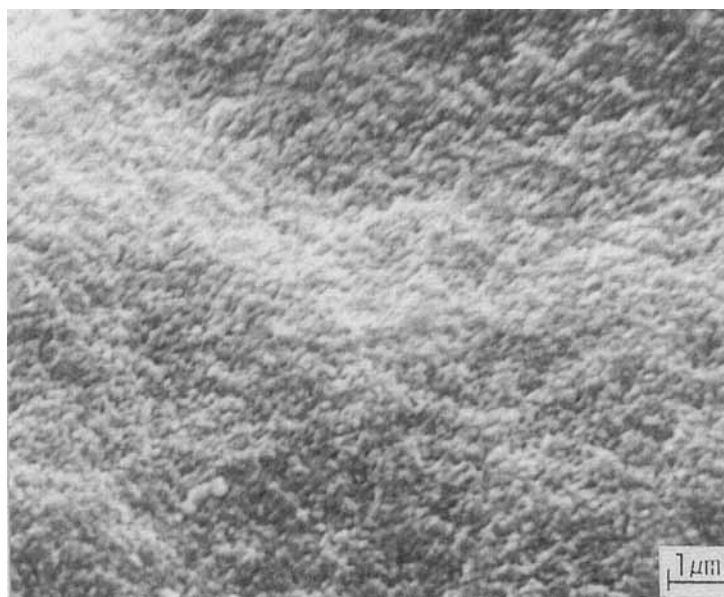


FIG. 6. Scanning electron micrograph of PVA-g-VDC.

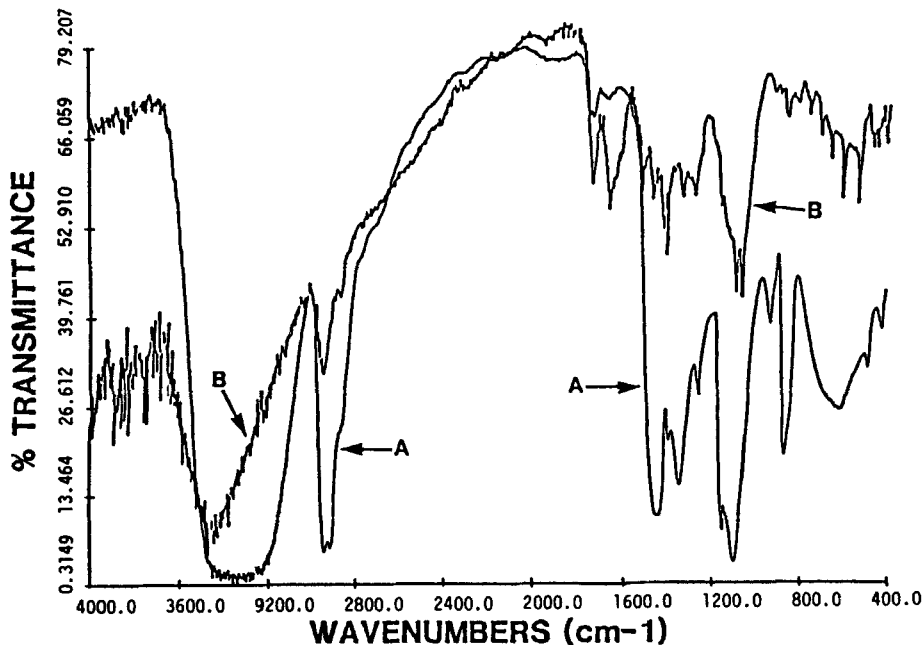


FIG. 7. FTIR spectra of PVA (A) and PVA-g-VDC (B).

X-ray energy spectroscopy (XES), a technique to identify chemical elements by measuring the dispersive x-ray energy that is a unique characteristic of each element, was used to identify chlorine in the VDC graft copolymers. The energy peak located at 2.62 keV in the x-ray energy spectrum of the graft copolymer confirmed the presence of chlorine.

Fourier-Transform Infrared Spectroscopy (FTIR)

The large absorbance in the FTIR spectrum of the graft copolymer (Fig. 7) at $3300\text{--}3500\text{ cm}^{-1}$ is characteristic of O-H stretching in PVA. The four sharp peaks between $500\text{--}800\text{ cm}^{-1}$, due to the C-Cl stretching motions in PVDC [1], and the reduction of OH stretch in the spectrum of graft copolymer are evidence for the presence of PVDC graft segments in the copolymer.

Wide-Angle X-Ray Scattering

Wide-angle x-ray diffraction patterns of PVDC, PVA, and their graft copolymers are presented in Fig. 8. PVDC, a highly crystalline material, produced a number of relatively sharp concentric circles superimposed on a background of scatter. On the other hand, a transparent film of PVA yielded a diffuse ring characteristic of amorphous materials (Fig. 8d). The x-ray diffraction patterns of PVA grafted with PVDC (Figs. 8b and 8c), as expected, show that an increase in the PVDC content of the copolymer results in higher crystallinity. The analogous bands at 5.66 and 2.79 Å for both PVDC and the graft copolymers (Table 2) suggests crystallization of PVDC graft segments. The band of d -spacing 5.66 Å is attributed to the 100 and 102 reflections while the d -spacing 2.81 Å accounts for the 200 and 204 reflections [12, 13]. This is consistent with a proposed helical structure for PVDC [12]. The d -spacing 1.75 due

TABLE 2. Wide-Angle X-Ray Spectrometry Data for PVDC and Graft Copolymers

Sample	Distance, cm	Angle, degrees	d -spacing, Å
PVDC ^a	1.40	7.80	5.66
	2.27	12.35	3.60
	3.17	15.90	2.81
	3.94	19.12	2.35
PVA-g-VDC ^b (60% VDC)	1.40	7.82	5.66
	1.74	9.65	4.60
	2.19	12.11	3.67
	3.13	16.04	2.79
PVA-g-VDC ^b (30% VDC)	1.34	7.56	5.86
	1.73	9.52	4.66
	3.18	16.23	2.76

^aPowder.

^bFilm.

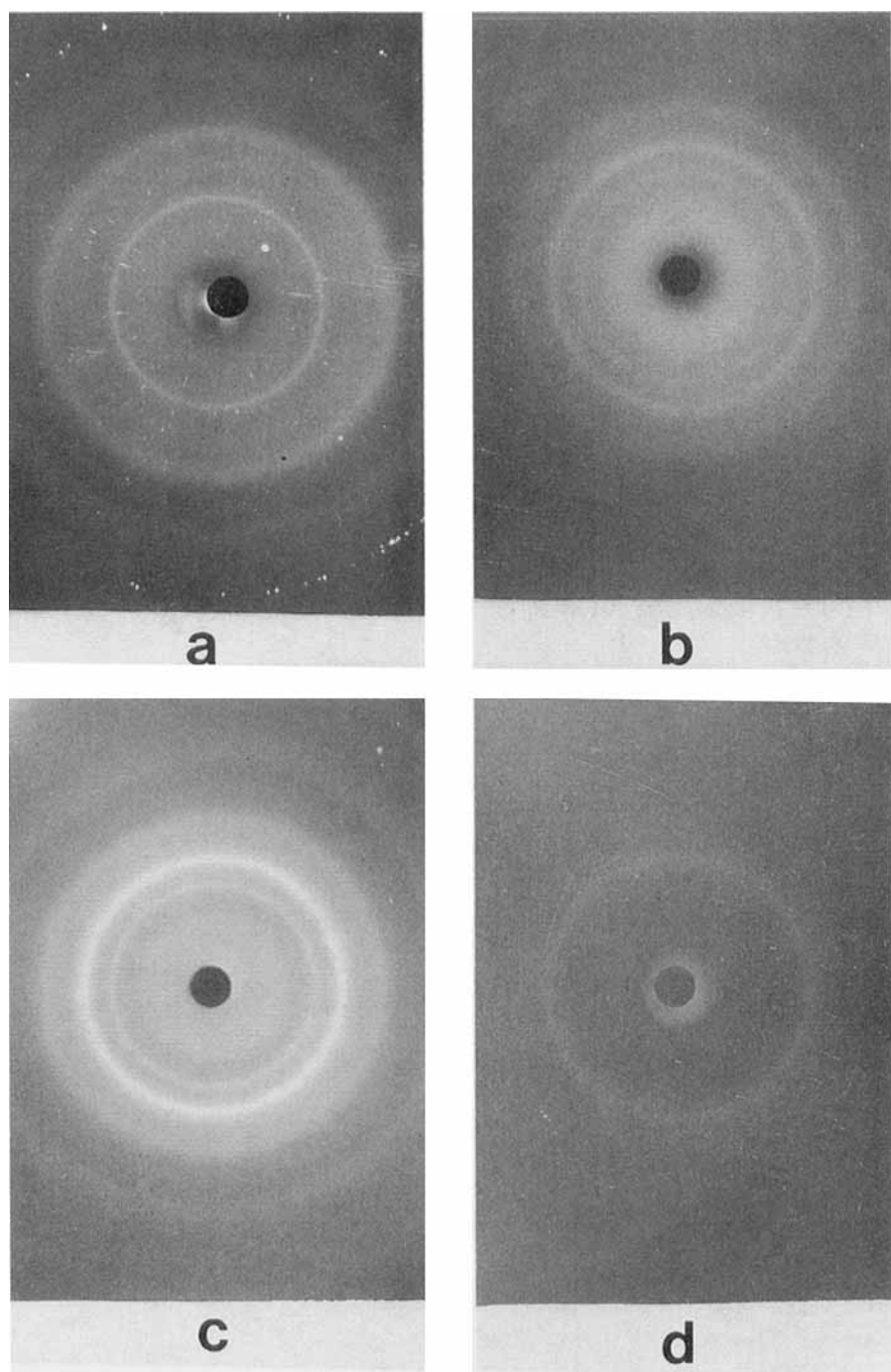


FIG. 8. Wide-angle x-ray diffraction pictures of (a) PVDC, (b) PVA-g-VDC (60%), (c) PVA-g-VDC (30%), and (d) PVA.

to PVA is seen in both PVA and graft copolymer x-ray patterns. Further investigation of the crystal structure of graft copolymers is in progress.

CONCLUSION

It has been shown that vinylidene chloride can be graft polymerized onto a model alcohol-containing polymer, PVA, by use of ceric ion initiation. Solvent extraction indicated that essentially no homopolymer is formed during the grafting reaction. Characterization by DSC, SEM, FTIR, WAXS, etc. indicates that a phase-separated graft copolymer was produced which displayed high crystallinity. The amount of crystallinity was found to be a function of the extent of grafting. However, details of the crystalline morphology have not been fully elucidated. Future work will involve grafting VDC or copolymers of VDC with acrylic monomers onto other hydroxy-containing substrates.

ACKNOWLEDGMENT

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