

Some Investigations of Graft Copolymer Formation in Aqueous Solutions of Vinyl Acetate in the Presence of Polyvinyl Alcohol

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INTRODUCTION

The emulsion obtained when vinyl acetate is emulsified and polymerized in water containing polyvinyl alcohol as a stabilizer, an alkaline buffer, and a persulfate catalyst should presumably contain graft copolymers between polyvinyl acetate and polyvinyl alcohol.

Encouraged by the results obtained by Hartley¹ on such graft copolymers, attempts were made to find the factors that would bring this emulsion to a higher content of grafting. Several emulsions were made, varying the degree of hydrolysis of the polyvinyl alcohol, the molecular weight of the same, and the pH value during the polymerization.

EXPERIMENTAL

Preparation of Aqueous Polyvinyl Acetate Dispersions

The recipe used by Hartley applied an 88% hydrolyzed polyvinyl acetate as a stabilizer, sodium carbonate as a buffer, and ammonium persulfate as the catalyst.² The polymerization lasted for 5 hrs. Thereafter the reaction mixture was kept at 90°C. for 1 hr.

This recipe, only slightly modified, was used in the present work with the following procedure: Twenty-one grams of polyvinyl alcohol and 1.875 g. of sodium bicarbonate were dissolved in 285 ml. of water. The aqueous solution was heated to 71°C., and during 3 hrs. 441 ml. of pure vinyl acetate and a solution of 1.5 g. of potassium persulfate in 30 ml. water was added dropwise and with constant stirring. Thereafter the reaction mixture was kept at 90°C. for 1 hr.

Fractionation of Polyvinyl Alcohol

Four polyvinyl alcohols of different degrees of hydrolysis were each fractionated into three parts based on molecular weight, so that twelve types of polyvinyl alcohol were obtained. The fractions were precipitated from an aqueous solution with a mixture of one part acetone and two

parts *n*-propyl alcohol. The molecular weight was controlled by use of an Ubbelohde viscosimeter with 80% acetic acid solution of polyvinyl acetate obtained after acetylation of the polyvinyl alcohol. The viscometric constants used were $K = 6.955 \times 10^{-1}$ and $a = 0.78$.

The four types of polyvinyl alcohol fractionated were:

1. 70% hydrolyzed polyvinyl acetate with medium to low molecular weight, Rhodoviol B.S. 200 (Rhone-Puolenc);
2. 88% hydrolyzed polyvinyl acetate with low molecular weight, Mowiol N 30-88 (Farbwerke Hoechst AG);
3. 88% hydrolyzed polyvinyl acetate with high molecular weight, Mowiol N 70-88 (Farbwerke Hoechst AG);
4. 99% hydrolyzed polyvinyl acetate with medium molecular weight, Elvanol 71-30 (Du Pont).

Each of the final twelve types was used as emulsifying agent when vinyl acetate was polymerized in emulsion.

Polymerizing Vinyl Acetate at Constant pH Value

When vinylacetate is polymerized in water at an elevated temperature, some hydrolysis of the ester occurs, and the emulsion becomes more and more acidic. When a buffer is added, as in the emulsion recipe just described, the pH value of the emulsion will follow an ordinary buffer titration curve. Several emulsions of polyvinyl acetate were made while the pH value was kept constant by adding a base dropwise into the emulsion during the polymerization. Two series were made; in Series 1 ammonium hydroxyde and acetic acid were used, and in Series 2 ammonium hydroxide and hydrochloric acid. The acids were used to obtain low

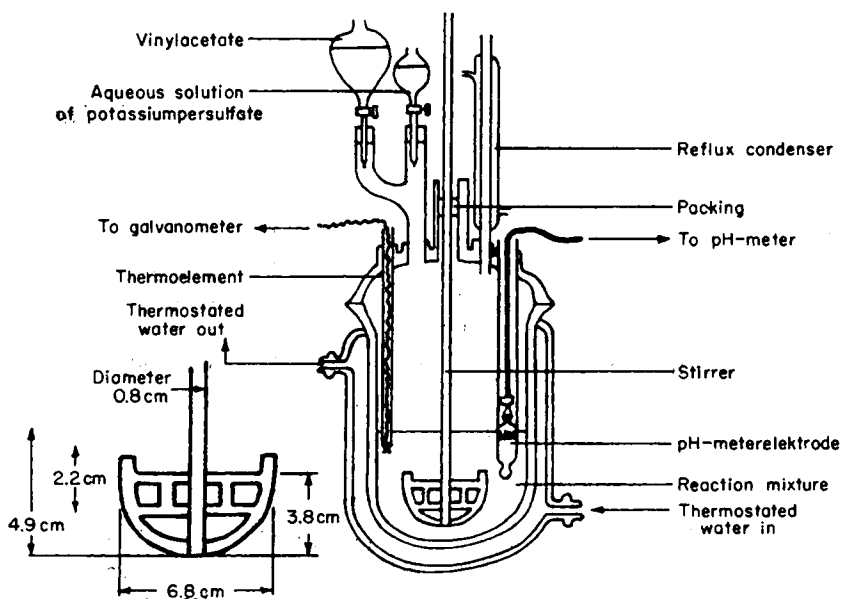


Fig. 1. The apparatus used.

pH values at the start of the reaction. In each series the constant pH values varied from 7.0 to 2.0. The stabilizer was unfractionated polyvinyl alcohol no. 2.

RESULTS AND DISCUSSION

The twelve emulsions of polyvinyl acetate were all investigated for graftings.

According to Hartley, graftings with high content of polyvinyl acetate are soluble in acetone and will travel slower than pure polyvinyl acetate on a chromatography paper when the emulsion is eluted with acetone on a 4:1 acetone/water mixture. After spraying of the dried paper with a 0.01*N* aqueous iodine-potassium iodide solution, Hartley maintained that there should appear two spots, the upper red and the lower reddish purple. When the emulsions described were submitted to this test, the surprising fact was found, that they all showed one spot only this one having the same R_f value as pure polyvinylacetate.

The concentration of the applicated spot, the length of eluating time, and the eluating mixture was varied, but there never appeared a spot with the same R_f value that Hartley had found ($R_f = 0.2$). However, in some cases there appeared another spot, reddish to purple in color, with an R_f value of ca. 0.04. This spot could be shown to be due to the stabilizer.

The emulsions were then fractionated in a fractionating column similar to that described by Hartley.¹ The graftings with high content of polyvinyl acetate should according to previous data,¹ precipitate by the extracting solvent (water-ethyl alcohol) containing 38.5-53% alcohol.

The precipitation appeared within the same range of the solvent composition, but on examining the precipitate by paper chromatography and infrared spectroscopy it was found to be similar to pure polyvinyl acetate.

It was noticed that bulk-polymerized polyvinyl acetate, initiated by light, did not give the described precipitate. Apparently, this is a kind of dispersion phenomenon.

The graftings with a high content of polyvinyl alcohol could be isolated by immersing in water overnight a thin film made of an ethyl alcohol solution of emulsion on aluminum foil.¹ The mentioned graftings are soluble in water and can be isolated by evaporating the water.

Before further discussion, attention should be drawn to the colors on paper chromatogram of the different kinds of polyvinyl alcohol used in the present work. Number 1 had a red color similar to the color of pure polyvinyl acetate. Numbers 2 and 3 had the same bluish-red color and number 4 showed a distinct blue color. It appears that the hydroxyl groups cause blue color and the acetate groups red.

However, graftings with a high content of polyvinyl alcohol are said to have a blue-green color. This appears rather surprising since Hartley used an 88% hydrolyzed polyvinyl acetate as stabilizer. The polyvinyl alcohol shows a bluish-red color before any grafting takes place, and it was expected that the grafting would show a red spot.

By eluating the commercial 88% hydrolyzed polyvinyl acetate with a mixture of 55% acetone and 45% water the chromatogram showed a reddish-colored area at the top and an oblong bluish-green area below. This proved then that the polyvinyl alcohol consists of polyvinyl acetates of different degrees of hydrolysis.

The water containing the water-soluble parts of the emulsion also has a certain content of polyvinyl acetate colloiddally dispersed. This was also investigated by paper chromatography.

Due to this fact, it is very difficult to separate the polyvinyl alcohol or the presumed water-soluble graftings quantitatively from the polyvinyl acetate in the residue left after evaporating the water surrounding the polymer film.

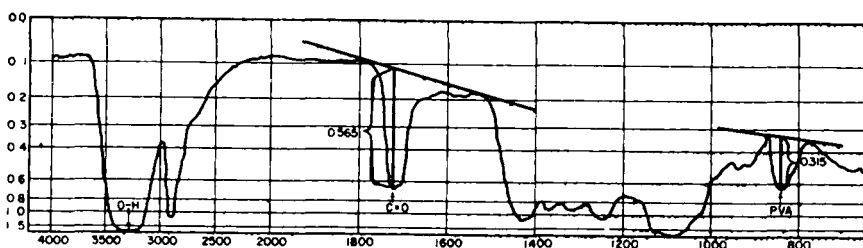


Fig. 2. The infrared absorption spectrum of the purified water-soluble part of the polyvinyl acetate emulsion which had the first fraction of polyvinyl alcohol no. 2 as stabilizer.

To isolate the pure water-soluble parts of the residue from the colloidal polyvinyl acetate a purification process is necessary. A concentrated aqueous solution of the residue was filtered and pure acetone was added to the filtrate. The water-soluble parts then precipitated. The precipitate was redissolved in water, the solution concentrated, and acetone added. The procedure was repeated four to five times.

As the purification was difficult to follow by paper chromatography, a technique based on infrared spectroscopy was applied. The spectrometer used was a Perkin-Elmer Model 21.

The ratio concentration (C = O)/concentration (O — H) \approx extinction (C = O)/extinction (O — H) can be used as a measure of the content of C=O groups (acetate groups) in the polymer in relation to the content of O—H groups.

The absorption maximum marked with PVA is characteristic of polyvinyl alcohol and is used instead of that marked with O—H because possible traces of water would cause disturbances in the last absorption maximum.

In Figure 2 the mentioned ratio is $0.565/0.315 = 1.8$. Before purification of the water-soluble residue this ratio was approximately 6.0. This value decreased after each purification. When the described purification had been performed four or five times, the value became almost constant at a value very close to that of the original stabilizer of the emulsion.

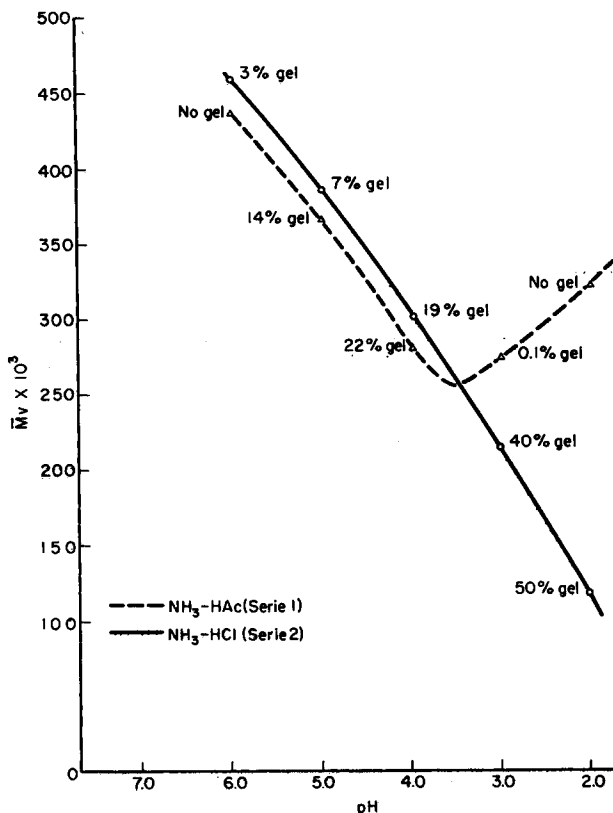


Fig. 3. Variations in molecular weight and gel formation in Series 1 and 2.

Although this method is not particularly exact, it suggests that the water-soluble parts of the emulsion are pure stabilizer.

In some cases where polyvinyl alcohol numbers 1, 2, or 3 were used as stabilizers, the value of the mentioned ratio of the purified water-soluble residues was slightly lower than the corresponding value of the original stabilizer. This could be due to the fact that some of the less hydrolyzed parts of the polyvinyl alcohol was removed by washing during the purification. If there had been a small part of graftings present, one would presume that these would be removed by washing during the purification process. However, this fact was difficult to establish because of the colloidal solution condition of the polymers.

The graftings and the polyvinyl alcohol removed by washing would only amount to approximately 5% of the total water-soluble residue.

The two series of polyvinyl acetate emulsions polymerized at constant pH showed some interesting features.

Figure 3 shows that parts of the emulsions form a gel. The amount of gel in Series 2 increased with decreasing pH value. At the same time, the molecular weight of the soluble part of the emulsions decreased.

TABLE I

		pH				
		6.0	5.0	4.0	3.0	2.0
Series 1, NH ₃ - HAc	Filtered 80% acetic acid solution	Clear	Opal	Opal	Strongly opal	Clear
	Huggins' <i>k'</i>	0.521	1.365	1.340	1.998	0.478
Series 2, NH ₃ - HCl	Filtered 80% acetic acid solution	Weakly opal	Opal	Opal	Weakly opal	Weakly opal
	Huggins' <i>k'</i>	0.830	1.426	1.410	-0.148	0.543

In Series 1 the formation of gel increased in amount until approximately pH 3.0 and then suddenly vanished. With the disappearance of the gel the molecular weight showed some increase.

Polymerizing vinyl acetate at pH = 7.0 gave a very low yield of polymer because nearly all the monomer was hydrolyzed. Only a dilute brown solution was obtained.

The stirrer used in the polymerization was made of stainless steel and, as ferric ions are known to cause gelation in an emulsion of polyvinyl acetate,

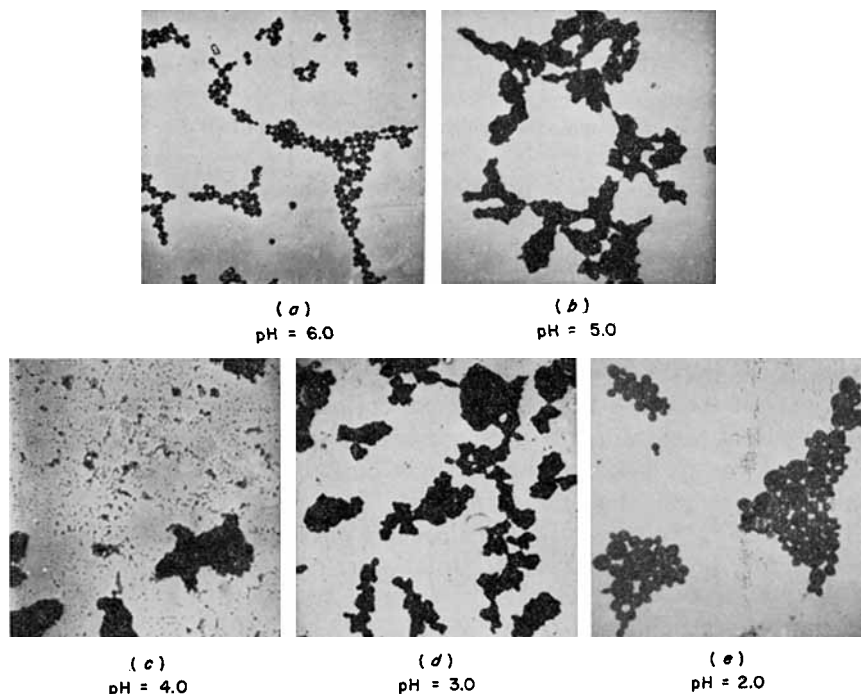


Fig. 4. Photomicrographs showing the emulsions in Series 1. 1325 \times .

a stirrer made of chromium-brass was tried³; there was no difference in the results.

Table I seems to show that Huggins' $k' = (\eta_{sp}/c - [\eta])/([\eta]^2c)$ and, correspondingly, the degree of branching of the molecules increases at the start and then decreases as the pH value changes from 6.0 to 2.0.⁴

The photomicrographs in Figure 4 show the emulsions in Series 1.

One may observe that the polymer particles in *b*, *c*, and *d* are sintered together, and that the particles in *e* are considerably larger than those in *a* which has polymer particles of "normal size."

On investigation of the soluble parts of the emulsions in Series 1 and 2 for graftings, the result was negative.

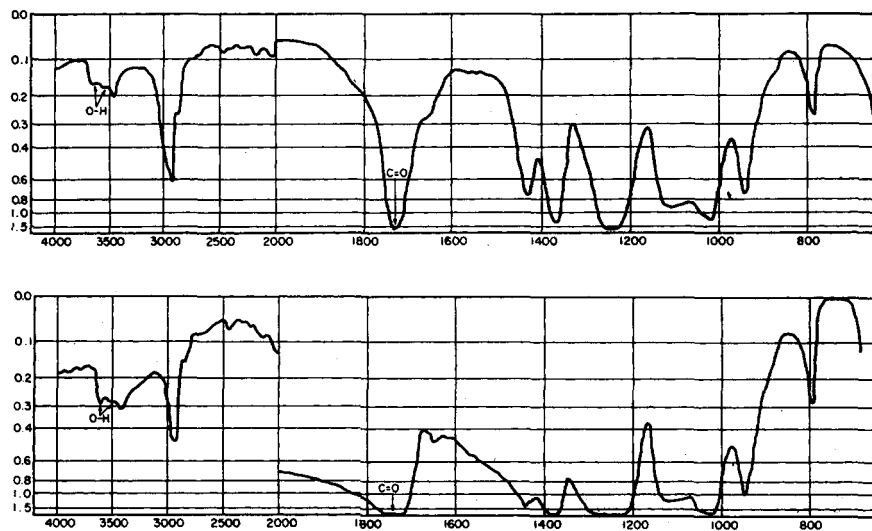


Fig. 5. (A) Infrared absorption spectrum of a film of polyvinyl acetate 150 μ thick. (B) Infrared absorption spectrum of a film of gel approximately 150 μ thick.

The question arises whether or not the gel consisted of graftings. After pressing the insoluble gel to a thin plate, approximately 150 μ thick, by applying 10,000 kg. of pressure, it could be examined by the infrared spectroscopy. A film of pure polyvinyl acetate was examined in the same manner, and the results of the examination are shown in Figure 4(a) and (b).

The two absorption spectra appear to be equal, proving that the gel consists of polyvinyl acetate only.

No turbidimetric titrations were performed.

CONCLUSION

The results of the investigations for graftings between polyvinyl acetate and polyvinyl alcohol in the desired emulsions were all negative.

There is a slight possibility, however, that graftings will be found in 5% of the total water-soluble residue which is washed away during the purification.

Hartley does not mention what kind of 88% hydrolyzed polyvinyl acetate he used, but it may be suggested that the reddish-purple spots he mentioned are due to the stabilizer. The blue-green color, which Hartley suggests is indicated by the water-soluble graftings, may be explained as the more hydrolyzed part of the stabilizer.

The gel formation can be interpreted in the following manner: Vinyl acetate has only one reactive double bond, and an ordinary gel formation would therefore be impossible. The formation of a gel is most probably a consequence of chain transfer reactions. Numerous chain transfer reactions would increase the possibility of bonds between the molecular chains.

On this basis it appears that the number of chain transfer reactions increases when the pH value in the emulsion decreases.

One may assume that there is no gel formation at pH = 2.0, when acetic acid is used as acidifying agent, because the molecules of acetic acid penetrate the polymer particles and make it impossible for a chain transfer reaction to occur between the molecular chains.

Considering the fact that the gel was found to contain no polyvinyl alcohol, it may be concluded that there were no chain transfers in the polyvinyl alcohol.

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References

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Synopsis

Encouraged by the results obtained in the field of graftings between polyvinyl acetate and polyvinyl alcohol, attempts were made to find factors that would bring a polyvinyl acetate emulsion to a higher content of such graftings. In this work vinyl acetate was emulsified and polymerized in water containing polyvinyl alcohol as stabilizer, potassium persulfate as catalyst, and sodium bicarbonate as a buffer. Emulsions were made, with varying degrees of hydrolysis of the polyvinyl alcohol, molecular weight, and pH during the polymerization. Paper chromatography and infrared absorption spectra were used to identify the graftings, but the results proved negative: no graftings were found.

Résumé

Encouragés par les résultats obtenus dans le domaine des greffages entre l'acétate de polyvinyle et l'alcool polyvinylique, nous avons fait des essais dans le but de trouver des facteurs, qui pourraient augmenter le greffage d'une émulsion d'acétate de polyvinyle. Dans ce travail l'acétate de vinyle est émulsifié et polymérisé dans l'eau contenant de l'alcool polyvinylique comme stabilisateur, du persulfate de potassium comme catalysa-

teur et du bicarbonate de sodium comme tampon. Plusieurs émulsions ont été faites, en variant le degré d'hydrolyse de l'alcool polyvinylique, le poids moléculaire de celui-ci et le pendant la polymérisation. Afin d'identifier les polymères greffés on a examiné les spectres infra-rouges et la chromatographie sur papier, mais les résultats étaient tous négatifs. Aucun greffage n'a été constaté.

Zusammenfassung

Ermutigt durch die bei der Aufpfropfung von Polyvinylacetat auf Polyvinylalkohol erhaltenen Ergebnisse wurden Versuche zur Ermittlung der Faktoren unternommen, die eine Polyvinylacetatemulsion auf einen höheren Gehalt an einer solchen Aufpfropfung bringen könnten. In der vorliegenden Arbeit wird Vinylacetat in Wasser, das Polyvinylalkohol als Stabilisator, Kaliumpersulfat als Katalysator und Natriumbikarbonat als Puffer enthält, emulgiert und polymerisiert. Durch Variierung des Hydrolysegrades des Polyvinylalkohols, seines Molekulargewichts und des pH während der Polymerisation wurde eine Reihe von Emulsionen hergestellt. Es wurde versucht die Aufpfropfung durch Papierchromatographie und Infrarotabsorptionsspektren nachzuweisen, die Versuche verliefen aber alle negativ. Es konnte keine Aufpfropfung festgestellt werden.

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