

Grafting of Ethyl α -Cyanacrylate on Poly(vinyl Alcohol)

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Synopsis

Because hydrophilic copolymers containing cyanacrylate elements should be useful as components of adhesives in surgery, the conditions of grafting of ethyl α -cyanacrylate on poly(vinyl alcohol) were studied. Two anthraquinone derivatives were applied as sensitizers in UV-initiated grafting; 2,6-disulfoanthraquinone sodium salt proved to be especially efficient. IR spectra and derivatograms of poly(vinyl alcohol-g-ethyl α -cyanacrylate) are described.

INTRODUCTION

α -Cyanacrylates are known as monomers rapidly and easily polymerizing by radical as well as by anionic mechanism. Owing to strong adhesive properties, which are the result of the outstanding adhesion to the majority of materials, α -cyanacrylates are used mainly as adhesives. Physiological inertness of poly(cyanacrylates) qualifies them for use in medicine.

The best results of two surfaces adhesion are obtained when the layer of the adhesive between both surfaces is very thin. It gives, additionally, particular advantage in medicine because in this case the thin polymer film can be resorbed faster. There are, however, some cases of application (e.g., orthopedic surgery) where it is very difficult to obtain adhesion by making the thin cover in the interosseous zone only. In these cases, it would be proper to use cyanacrylates with fillers. It is known that fillers have suitable mechanical resistance and good adhesion to the polymers; what is more, they often improve them.

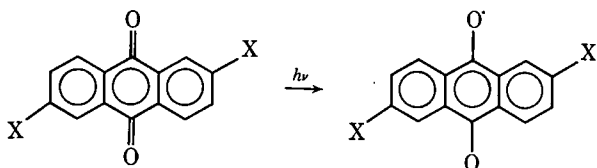
In research of such a model " α -cyanacrylate filler" we draw attention to the possibility of using the polymers soluble in water, e.g., poly(vinyl alcohol) and poly(vinyl pyrrolidone) as fillers. Poly(α -cyanacrylates) containing, as filling materials, easily soluble polymers should be of better quality for reason of resorption than the pure ones.

In this work, we deal with grafting of ethyl α -cyanacrylate (ECA) onto poly(vinyl alcohol) (PVA). This kind of copolymer seems to be particularly useful as filler for the polymerizing ECA.

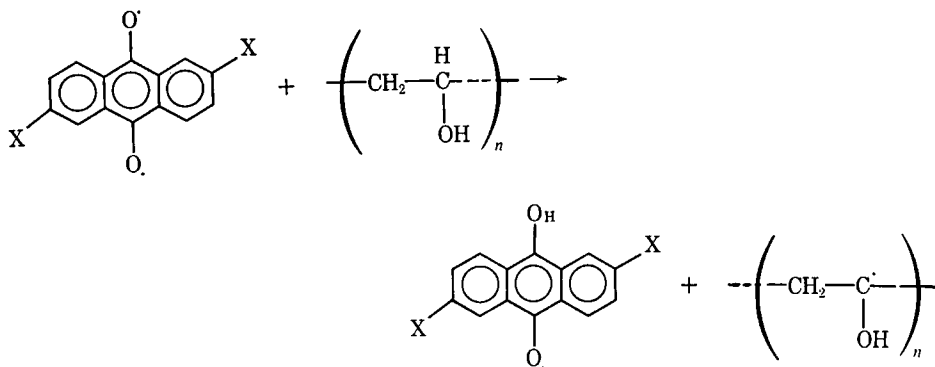
MECHANISM OF GRAFTING ETHYL α -CYANACRYLATE ONTO POLY(VINYL ALCOHOL)

Stanett and his co-workers¹⁻³ applied light initiated polymerization for grafting monomers onto cellulose and its derivatives. In this reaction, sensitizing dyes

were used. The anthraquinone dyes were adsorbed on cellulose which was next irradiated with UV light. The reaction starts with abstracting the hydrogen atom from cellulose by the light-activated dye molecule. The obtained cellulose free radicals initiated graft, block copolymerization. Homolytic breaking of the C-H bond in poly(vinyl alcohol) molecule requires much energy. Dealing with 2,6-substituted anthraquinone dyes with electrophilic groups, it is possible to abstract the hydrogen radical in an indirect way. The mechanism of the graft reaction in the presence of these dyes is as follows:



Nascent diradical is stable because of the stabilized influence of electrophilic groups (X) in positions 2,6; thus, it can react with poly(vinyl alcohol) according to the reaction

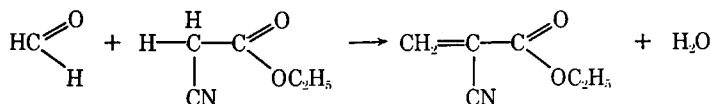


Similarly, it is expected that free-radical centers in the PVA chain initiate grafting of vinyl monomers.

EXPERIMENTAL

Ethyl α -Cyanacrylate (ECA)

ECA was obtained by condensation of formaldehyde with ethyl cyanacetate in alkaline medium:⁴



ECA was freed from the reaction mixture by vacuum distillation, followed by the depolymerization of the poly(ethyl α -cyanacrylate) formed as a by-product. Monomer was redistilled, and the fraction boiling at 66–67°C (3 mm Hg) was collected. Refraction $n_D^{20} = 1.4389$.⁵

Poly(vinyl Alcohol)

PVA with 88% hydroxyl groups and viscometric molecular weight $\bar{M} = 375,000$ was used.

Sensitizers Used

2,6-Dinitroanthraquinone (DNAQ), pure, melting 286–290°C with decomposition.

2,6-Disulfoanthraquinone sodium salt (DSAQ) Suchardt, pure.

PVA Films

PVA dissolved in water as 10% solution was poured out onto a polyethylene plate and dried in air at 45°C. Thus obtained films were dried in a desiccator with P_2O_5 to constant weight.

Films 0.02–0.03 mm thick were obtained. Different amounts of sensitizer were added to the PVA solutions (2,6-dinitroanthraquinone in the form of 5% DMF solution, and 2,6-disulfoanthraquinone sodium salt in the form of 2% water solution). Films containing 0.1–1% of the dye were obtained.

GRAFTING OF ECA ON PVA FILM

Grafting was carried out in quartz test tubes, 20 mm in diameter and 100 mm long. For this we used films obtained as mentioned above cut into strips ca. 2.5 cm² each. The film strips were placed in test tubes, and monomer was added. Nitrogen-filled test tubes were stoppered and irradiated with a 374-W quartz lamp, at a distance of 80 cm from the tubes. The test tubes were kept revolving to secure uniform irradiation effect.^{1,2}

The experiments were conducted according to the following systems: (a) 2,6-Dinitroanthraquinone DNAQ dissolved in nitrobenzene was added to ethyl α -cyanacrylate, and the quartz test tubes containing PVA foils were filled with this solution. (b) The test tubes with PVA film containing dispersed DNAQ, as described above, were filled with pure monomer ECA. (c) The test tubes with PVA foil containing DSAQ, as described above, were filled with pure monomer ECA.

All the experiments were conducted at a temperature of 25°C. The time of irradiation was always 24 hr.^{1,2} The variable parameters in this experiment were the kind and the percentage of sensitizer in the films (runs 2 and 3) or in monomer (run 1). We tested systems containing 0.1–1% sensitizer. Results of the experiments are shown in Table I. Irradiation of the above system in the absence of sensitizers produced no trace of the graft copolymer.

ANALYSIS OF THE GRAFTING PRODUCTS

The films, after being UV irradiated, were extracted with benzene using a Soxhlet apparatus to dissolve the benzene-soluble homopolymer ECA. The extraction was carried out for 48 hr until constant weight of the grafted product was obtained.

The product was dried and weighed every 6 hr. Thus, the mass of the grafted poly-ECA together with unchanged PVA was found. Next, the grafted product

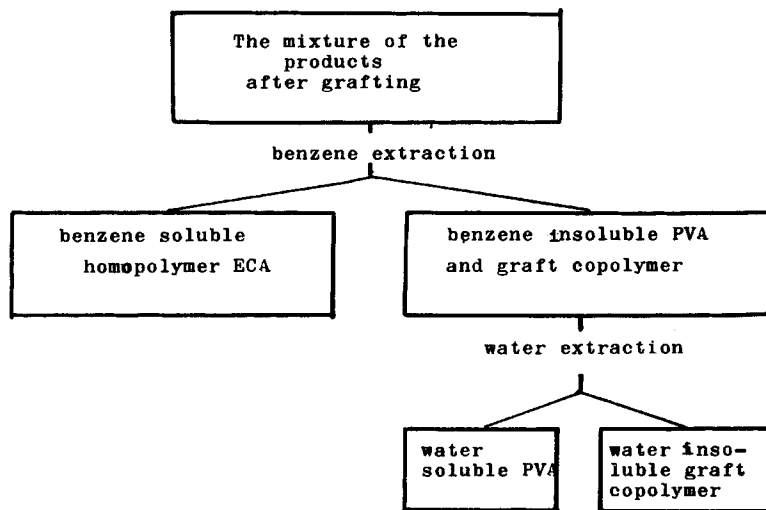


Fig. 1. Scheme of extraction sequence.

was extracted with water in order to dissolve the unreacted PVA. The water extraction was also held in the Soxhlet apparatus for 24 hr until constant weight of the product was reached. The extraction scheme is shown in Figure 1. Suspecting possible "snake in cage" blend of both homopolymers present in the copolymer, the following test was made: purified samples (2 g) were dissolved in molten phenol (50 cc) and precipitated with 40 cc water, centrifuged, washed with water, then with benzene, and analyzed. Analysis: sample 1a 4.20% N before the test, 4.07% N after the test; sample 3a 6.41% N before the test, 6.53% N after the test. Almost no change in the composition was found. An example of the mass balance of the extractions is given in Figure 2.

The IR spectrum of the poly(vinyl alcohol-g-ethyl α -cyanacrylate) is based on the IR spectrum of PVA, the characteristic features of which are distinctly marked (1100 cm^{-1} , 3350 cm^{-1}). In this spectrum one can easily see the absorption maxima derived from the grafted acrylonitrile units.

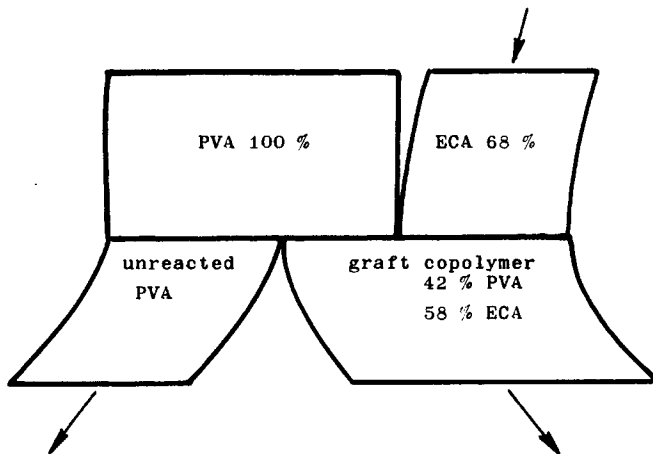


Fig. 2. Mass balance of extraction (example of run 3a).

TABLE I
Grafting Mass Balance Analysis^a

Run no.	System: polymer + monomer + dye	m , g	m_1 , g	Δm_1 , %	m_2 , g	Δm_2 , %	Graft copolymer composition				N, %		
							PVA		ECA		Found	Calcd.	
							mass-%	mole-%	mass-%	mole-%			
1a	PVA film + ECA containing DNAQ												
	0.2% based on PVA	0.1161	0.1346	16	0.0442	38	58	80	42	20	4.20	4.65	
1b	PVA film + ECA												
	containing DNAQ												
	0.3% based on PVA	0.1072	0.1341	21	0.0461	43	42	67	58	33	6.13	6.51	
1c	PVA film + ECA												
	containing DNAQ												
	0.4% based on PVA	0.1234	0.1401	13	0.0396	32	58	80	42	20	4.91	4.72	
2a	PVA film containing												
	0.2% DNAQ + ECA	0.2396	0.2727	14	0.0892	37	63	83	37	17	3.92	4.18	
2b	PVA film containing												
	0.3% DNAQ + ECA	0.2690	0.3013	12	0.0724	30	60	81	40	19	4.62	4.47	
2c	PVA film containing												
	0.4% DSAQ + ECA	0.2118	0.2477	17	0.0825	39	56	79	44	21	5.07	4.92	
3a	PVA film containing												
	0.2% DSAQ + ECA	0.3002	0.5047	68	0.3510	117	42	67	58	33	6.41	6.51	
3b	PVA film containing												
	0.3% DSAQ + ECA	0.2987	0.4932	65	0.3410	114	43	68	57	32	6.05	6.38	
3c	PVA film containing												
	0.4% DSAQ + ECA	0.2974	0.5114	72	0.4190	140	49	73	51	37	5.63	5.72	

^a m = Weight of PVA before grafting; m_1 = weight of PVA after grafting after benzene extraction; Δm_1 = gain in weight based on weight of PVA before grafting; m_2 = weight of copolymer after water extraction; Δm_2 = weight of copolymer based on the PVA weight before irradiation.

The spectrum of the poly(ethyl α -cyanacrylate) taken for comparison shows the characteristic absorption maximum at 2250 cm^{-1} relating to $-\text{C}\equiv\text{N}$ group vibrations and two maxima at 3000 cm^{-1} and at 1070 cm^{-1} . The last two peaks cannot be clearly explained, although Hummel⁶ shows the relation between the last range and the vibrations of the C-C chain which can be observed in polyacrylonitrile. It is significant that both these maxima appear clearly only in the copolymer spectrum. In the spectrum of pure PVA, no absorption is observed in these ranges.

The thermal analysis of the copolymers showed that their decomposition begins at the decomposition temperature of the poly-ECA, which is the less temperature-resistant component (the maximum of the endothermic process at 196°C).

CONCLUSIONS

a. The graft copolymerization of ethyl α -cyanacrylate onto poly(vinyl alcohol) proceeds only during UV irradiation in the presence of sensitizer (2,6-dinitroanthraquinone and 2,6-disulfoanthraquinone sodium salt). Interruption of the irradiation stops the process.

b. The grafting proceeds only on the surface of the films, because compositions of the copolymers in runs 1 and 2 are similar. It does not matter if the sensitizer was in the film or in the monomer.

c. The grafting proceeded more effectively when DSAQ (run 3) was used as sensitizer. The gain in weight of the grafted PVA was $\Delta m_1 = 68\text{--}72\%$. Applying DNAQ (run 2) as the reaction sensitizer, the gain in weight of PVA, Δm_1 , after grafting was only 12–17% (Table I).

d. Between 0.2 and 0.4% of sensitizer, no influence of its concentration on the grafting efficiency was noted.

e. Poly(vinyl alcohol-g-ethyl α -cyanacrylate) is soluble only in molten phenol or tricresol; it swells strongly in water and slightly in benzene and acetone, being insoluble in these solutions. The copolymer obtained has strong hydrophilic properties, and as such corresponds to the model mentioned in the introduction to this paper.

f. It is characteristic for the thermal properties of the copolymer that the decomposition begins at 160°C . This is the temperature of depolymerization of poly(ethyl α -cyanacrylate).

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