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Redox-Initiated Grafting of Acrylic Monomers onto Poly(vinyl Alcohol)

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ABSTRACT

Loss of capacity of magnetic micro ion-exchange resins has been suggested to be caused by cleavage of unstable linkages formed during the graft polymerization reaction. The nature of the grafting process was investigated by using a series of model compounds having the same structural features as the glutaraldehyde-crosslinked poly(vinyl alcohol) core matrix. These compounds were then subjected to hydrogen peroxide oxidation, followed by the addition of monomer in the presence of iron(II). The identity and extent of peroxidation of the intermediate compounds was determined. In each of the peroxidation reactions the tertiary acetal hydrogen was oxidized to a hydroperoxy derivative. Some of these derivatives were able to dimerize to form peroxy compounds. The reactions occurred rapidly at room temperature when an acetal compound was shaken with hydrogen peroxide. Good yields could be obtained by precipitation of the sodium salts of the hydroperoxides. The hydroperoxy derivatives were shown to initiate polymerization of methyl acrylate, acrylic acid, and acrylamide when in the presence of iron(II).

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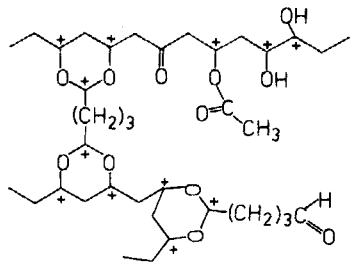


FIG. 1. Structures possibly present in resin core: (1) acetal structures; (2) residual hydroxy groups; (3) residual acetate groups; (4) anomalous head-to-head type linkages; (5) residual aldehyde groups; (6) oxidized groups, ketone groups. Not shown in diagram: (7) noncyclic interchain acetal structures; (8) anomalous condensed glutaraldehyde resin species. The symbol + denotes an asymmetric carbon; each of these will have two possible configurations. This is determined by the tacticity of the poly(vinyl alcohol) chain.

INTRODUCTION

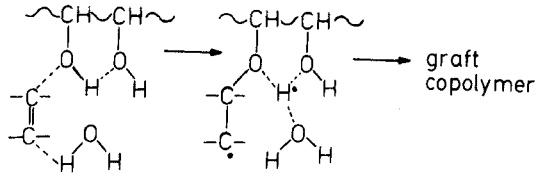
Acrylic acid has been grafted onto an inert polymeric core containing submicron particles of γ-Fe_2O_3 [1, 2]. The final material consists of a shell of essentially uncrosslinked weak acid polymer chains attached to the magnetic core and has been termed a "whisker resin." These resins have been observed to show a reduced capacity after several months of pilot plant trials. This paper describes an investigation of the structure of these resins with respect to the mechanism of the acrylic acid grafting. The method chosen to investigate the structure of the resin structure was to prepare model compounds having the same structural features as were expected to be present in the glutaraldehyde-crosslinked poly(vinyl alcohol) matrix. Structures probably present in the resin core structure are shown in Fig. 1.

These compounds were then subjected to the same reactions as the resin core, to determine structural changes taking place during the graft copolymerization process.

The mechanism (1) has been proposed [3] for the polymerization of methyl methacrylate in the presence of aqueous poly(vinyl alcohol) solution.

The presence of a 1,2-glycol content in poly(vinyl alcohol) is reported [4, 5] and estimated at 0.6-2.2 mole % [6]. Such 1,2-glycol units are oxidized more readily than the remaining head-to-tail polymer repeat units [5], the mechanism (2) being given for oxidation in the presence of cerium(IV) [7].

Carbonyl and carboxy endgroups are reported to be formed by



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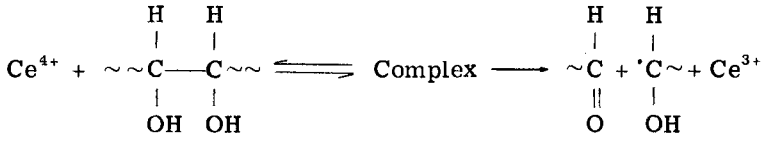
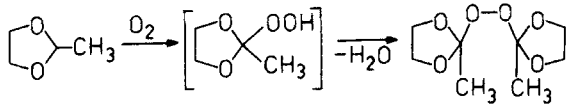


(2)

oxidation of poly(vinyl alcohol) [8]. Keto groups are reported to be present at the points where cleavage occurs [9]. Graft initiating activity is observed due to the presence of initial carbonyl and/or residual acetate groups in the poly(vinyl alcohol) [10]. One mole of methyl methacrylate graft was reported for every five moles of main chain cleavage of poly(vinyl alcohol) in an Fe^{3+}-H_2O_2 aqueous solution. The "grafts" were considered to be due to main-chain cleavage and to be block copolymers. A water-soluble graft copolymer of acrylic acid has been prepared by using aqueous cerium (IV) ammonium sulfate and poly(vinyl alcohol) [7].

The graft substrate in the present study is an 86% hydrolyzed poly(vinyl alcohol) crosslinked by glutaraldehyde. Cyclic acetal groups are formed at the sites where crosslinking has occurred, and these groups are susceptible to oxidation. The autoxidation products of 1,3-dioxolanes have been used for initiation of vinyl polymerization [11, 12]. The peroxide of 2-methyl-1,3-dioxolane was obtained by room temperature autoxidation [13] [Eq. (3)].



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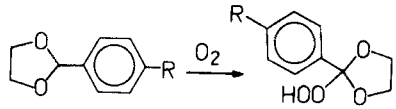
Oxygen in the presence of ultraviolet light [Eq. (4)] was used to obtain the hydroperoxides of substituted 2-phenyl-1,3-dioxolanes [14].



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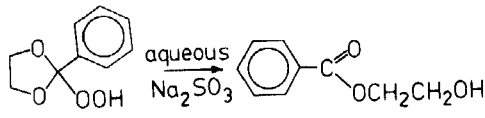
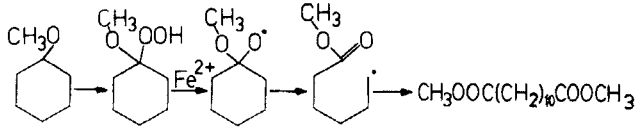
Hydrogen peroxide oxidation was also used to obtain the hydroperoxide, [Eq. (4), where R = H] [15, 16]. These compounds could be reduced [Eq. (5)] to form glycol esters [14].

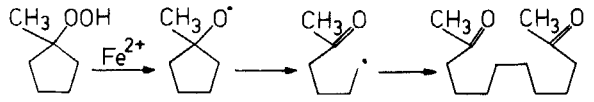


(5)

The cyclic acetal, 1,3-dioxane, structures in the crosslinked poly(vinyl alcohol) were postulated to form analogous hydroperoxide derivatives in the presence of hydrogen peroxide. In the presence of iron(II), these would form radicals which could initiate graft polymerization. Ring-opening reactions similar to the reaction (5) with Na_2SO_3 have been reported when Fe^{2+} is used as the reducing agent [12, 16b].



(6)



(7)

Thus the hydroperoxide of the cyclic acetal structures of the crosslinks could either initiate polymerization after reduction with Fe^{2+}, or, the radical could undergo a ring-opening reaction before initiating polymerization [Eqs. (6) and (7)].

EXPERIMENTAL

Preparation of Cyclic Acetals

Essentially the same method was used in each of the preparations, so the preparation of 2,4,6-trimethyl-1,3-dioxane will be used as an example. A mixture of 31.2 g of pentane-2,4-diol, 13.2 g of paraldehyde, and 0.15 g of 40% sulfuric acid was heated at 100°C for 6 hr. The solution was neutralized with aqueous potassium carbonate. Two phases separated, the upper organic phase was collected, and the lower aqueous phase was extracted twice with ether (2×, 25 ml). The

organic layer and the ether extracts were evaporated, and the oily residue was distilled using a short vigreaux column.

In the case of 2-methyl-1,3 dioxane, the distillate contained impurities as detected by the NMR spectrum.

A further distillation was carried out by using a 25 cm fractionating column packed with glass rings. The fraction boiling at 130-134°C was collected in 64% overall yield.

The corresponding glutaraldehyde derivatives were not all distilled but were purified by extraction with saturated aqueous sodium bisulfite solution. Infrared and NMR spectra before and after purification showed the residual free aldehyde reduced to a very small amount. Boiling points were determined on these glutaraldehyde derivatives by the Siwoloboff capillary tube method. Though the boiling points were very high, the compounds showed good stability with only very slight discoloration taking place.

Acetal of Poly(vinyl Alcohol)

Paraldehyde was reacted with Gelvatol 20-30, by adapting experiment 5.02 of Braun, Chedron, and Kern [17] dissolving the resultant polymer in hot methanol, and precipitating with water. The yield was 44% on the basis of poly(vinyl alcohol) taken = 100%. A firm, clear, moderately flexible film was obtained which was softened and swollen in water.

Hydroperoxidation Reactions

Extraction Method. A 1-g portion of the cyclic acetal and 2 g of hydrogen peroxide (30%) were mechanically shaken together for 1 hr. The mixture was diluted with 10 cm^3 of water and extracted with ether (2×, 4 cm^3). The combined extracts were dried over anhydrous sodium sulfate and then the ether was evaporated. The residual hydroperoxide was stored in a refrigerator.

Sodium Salt Method. The acetal and hydrogen peroxide were allowed to react as described above. 40% (w/w) aqueous sodium hydroxide was added dropwise, and the resulting precipitate was filtered under reduced pressure. The solid sodium salt of the hydroperoxide was washed with ether, air dried and stored in a refrigerator.

The sodium salt of 2,4,6-trimethyl-1,3-dioxane-2-hydroperoxide was obtained as white flakes in 50% yield and melted with decomposition at 63-69°C. The sodium salt of 2,2-trimethylenebis(1,3-dioxane)-2-hydroperoxide was obtained as white crystals in 43% yield and melted with decomposition at 62-65°C.

Blanks. Blanks were performed to determine if all hydrogen peroxide was removed from the extracts. Some blanks were performed with the use of alkane solvent (bp 100-110°C) to simulate the substrate. Tests with iodide and starch solutions were negative for

the blanks, indicating that activity of the acetal products was due to the corresponding hydroperoxide only.

Initiation of Polymerization by the Hydroperoxides

With Acrylic Acid. A 2.5 g portion of 86% aqueous acrylic acid was dissolved in a solution of 0.2 g of iron(II) sulfate heptahydrate in 10 cm^3 of distilled water. The solution was shaken with 0.2 g of hydroperoxidized 2-methyl-1,3-dioxane for 30 min. An immediate exothermic reaction took place, and the solution turned an orange-brown color. The solution was made acid with hydrochloric acid and after standing the supernatant liquid was decanted and the residue washed with methanol. After drying, a yield of 45% was obtained and verified as poly(acrylic acid) by infrared spectroscopy.

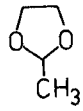
With Methyl Acrylate. The same quantities as described above for acrylic acid were mixed, the hydroperoxide being added last. The mixture again showed an immediate exothermic reaction and orange-brown coloration. The mixture was mechanically shaken for 1 hr, then extracted with ether. The ether extract was poured into hexane and the precipitated polymer was collected. After drying, a yield of 35% was obtained and verified as poly(methyl acrylate) by infrared spectroscopy.

The same procedures were used to test the other hydroperoxides and to evaluate other monomers for potential grafting activity.

RESULTS AND DISCUSSION

A series of model acetal compounds (I - X) was synthesized for testing in reactions with hydrogen peroxide. These included 2-methyl-1,3-dioxolane (I), 2-methyl-1,3-dioxane (II), 2,4,6-trimethyl-1,3-dioxane (III), 2,2-trimethylene(1,3-dioxolane) (IV), 2,2'-trimethylenebis(1,3-dioxane) (V), 2,2'-trimethylenebis(4,6-dimethyl-1,3-dioxane) (VI), acetaldehyde poly(vinyl alcohol) acetal (VII), 2-propyl-1,3-dioxane (VIII), 2-benzyl-1,3-dioxane (IX), and triethylidenemannitol (X).

Compounds I and II differ in ring size, which is an important consideration in the stability of cyclic acetals [18]. The five-membered ring structure could be formed only when head-to-head polymerization occurred in the poly(vinyl alcohol). In structure III the methyl groups at positions 4 and 6 represent the points of attachment of the polymer chain and provide two additional tertiary hydrogens. Structure III has four possible isomers, as does the acetal ring structure in crosslinked poly(vinyl alcohol). The structures are formed from the isomers of pentane-2,4-diol as shown. Steric effects would cause the methyl groups to preferentially occupy equatorial positions. Inversion of the ring must be slow, since the NMR of the proton at position 2 gives two well-separated quartets. The one most



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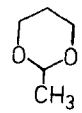

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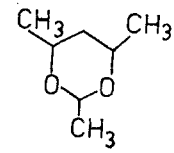
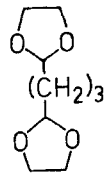


III



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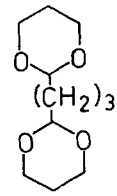

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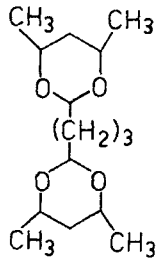

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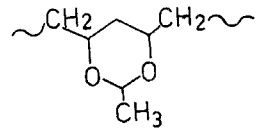
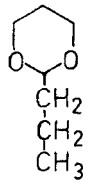
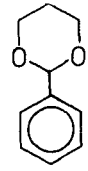


VII



VIII



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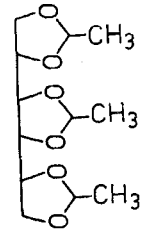
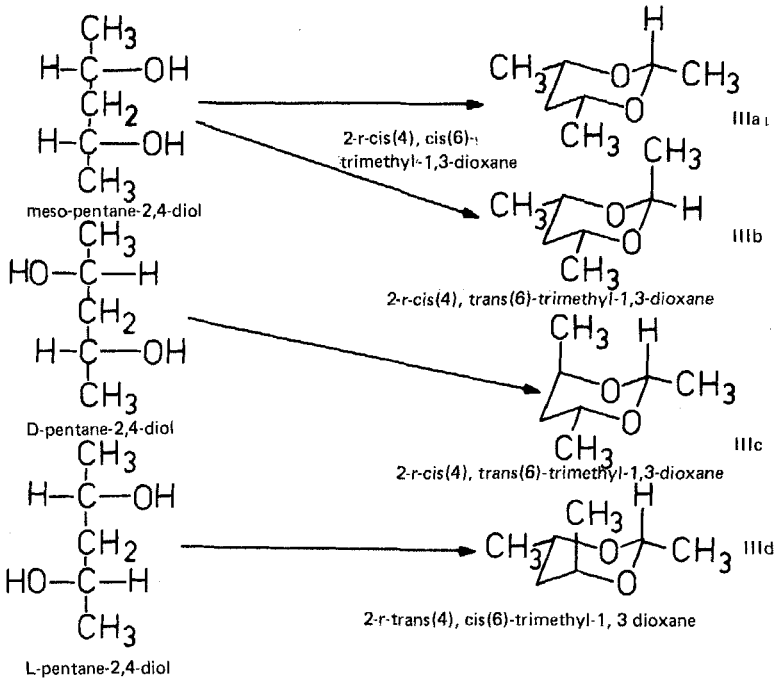


X



downfield was ascribed to an equatorial hydrogen and the other to an axial hydrogen [19, 20]. The starting material was a mixture of the isomeric pentane-2,4-diols. Resolution of the products was not attempted.

Compounds IV, V, and VI introduce the variable of glutaldehyde into the models. For compound VI, considering isomer possibilities for compound III, there will be 10 possible isomers. Thus the glutaraldehyde-crosslinked poly(vinyl alcohol) will have 10 isomeric crosslinks.

Poly(vinyl alcohol) was reacted [17] with acetaldehyde (paraldehyde form) to the acetal which had an infrared spectrum as indicated by Lindemann [21]. This preparation was then used to study the peroxidation reaction in a polymeric system having solubility, although with the possibility of some intermolecular acetalization [22].

Low yields were obtained when isolating some of the peroxidized derivatives of the acetals, so structures VIII and IX were synthesized. The propyl and benzyl groups made the hydroperoxy derivatives easier to extract from hydrogen peroxide solution. Triethylidene mannitol (X) was a solid of high melting temperature and low water solubility; its hydroperoxy derivative was able to be isolated as an insoluble solid. Physical properties for the compounds are listed in Table 1.

TABLE 1. Physical Data for Cyclic Acetals

Structure	Yield (%)	Boiling point (°C)	NMR spectral characteristics, microanalytical data
I	9.2	79-80 (82-87)[a]	2-H, δ = 4.97 ppm (quartet)
II	17	108-110 (108-110)[a]	2-H, δ = 4.61 ppm (quartet) (lit.[b] δ = 4.61 ppm)
III	64	130-134 (135-136/745 mm)[c]	2-H_{axial}, δ = 4.70 ppm (quartet) (lit.[c] δ = 4.55 ppm) 2-$H_{equat.}$, δ = 4.98 ppm (quartet) (lit.[c] δ = 5.17 ppm)
IV	49	236-239	Anal. Found: C = 53.4%, H = 8.2% (Calcd: C = 57.4%, H = 8.5%) 2-H, δ = 4.75 - 5.00 ppm (multiplet)
V	12	266-270 97-100/2 mm	Anal.: Found: C = 60.2%, H = 9.3% (Calcd: C = 61.1%, H = 9.3%) 2-H, δ = 4.42-4.67 ppm (multiplet)
VI	11	261-262 (mp = 40-43)	Anal. Found: C = 65.5%, H = 9.9% (Calcd: C = 66.1%, H = 10.4%) 2-H, δ = 4.72-4.94 ppm (multiplet)
VII	44	Clear, moderately flexible film	
VIII	24	158-160 (154-157)[a]	2-H, δ = 4.52 ppm (triplet)
IX	27	95/4 mm, 250/760 mm (mp = 45)	Anal. Found: C = 73.2%, H = 7.3% (Calcd: C = 73.1%, H = 7.4%)

(continued)

TABLE 1 (continued)

Structure	Yield (%)	Boiling point (°C)	NMR spectral characteristics, microanalytical data
X		(mp = 163-165)	

[a]Data of Hibbert and Timm [18].
[b]Data of Jackman and Sternhell [23].
[c]Data of Eliel and Nader [20].
[d]Some disparity due to differences in solvent, see also Pihlaja and Ayras [24].

TABLE 2. Hydroperoxide Content of Oxidation Products

Starting compound	Hydroperoxy content (mole O_2/mole product)[a]
2-Methyl-1,3-dioxolane	0.67
2-Methyl-1,3-dioxolane	0.15
2,4,6-Trimethyl-1,3-dioxane	0.66
2-Propyl-1,3-dioxane	0.11
2,2'-Trimethylenebis(1,3-dioxolane)	0.04
2,2'-Trimethylenebis(1,3-dioxane)	0.42
Triethylidene mannitol	0.30
Poly(vinyl alcohol) acetaldehyde acetal	0.07

[a]Mean of from two to five determinations; accuracy ± 10% mainly due to difficulty in achieving a consistent degree of hydroperoxidation.

Hydroperoxidation Reactions

Each of the acetal model compounds was subjected to treatment with hydrogen peroxide. Some of the compounds were soluble in 30% hydrogen peroxide and so no physical change was observed during 1 hr at room temperature. Others, such as 2,4,6-trimethyl-1,3-dioxane, formed a cloudy suspension which gradually cleared to a colorless solution within 1 hr, indicating that a reaction had taken place.

After an extraction procedure the products were analyzed for hydroperoxy content. In each case the product contained a quantity of starting material. Another method used to obtain the products was by precipitation of the sodium salt of the hydroperoxide with 40% sodium hydroxide solution. This yielded a relatively pure hydroperoxide, whereas extraction always provided a mixture. The hydroperoxide content of the products is shown in Table 2. The analyses were carried out essentially as described by Miller and Mayo [25].

Though the hydroperoxidation appeared to occur very readily a surprising observation of the selectivity of the reaction was made with 2,4,6-trimethyl-1,3-dioxane. The NMR spectra of this compound and the oxidation product (Fig. 2) showed that isomers with 2-H in an equatorial position did not show a proton in the product spectrum while those with an axial 2-H were present in the product spectrum. Only the less hindered equatorial position is oxidized to a hydroperoxy group.

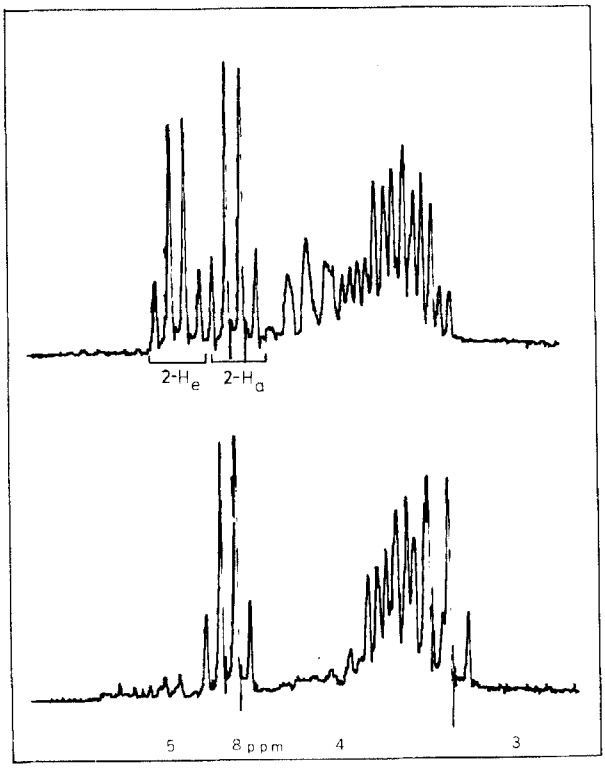


FIG. 2. NMR spectra of (top) 2,4,6-trimethyl-1,3-dioxane and (bottom) its oxidation product.

These geometric isomers correspond to the tacticity of the poly-(vinyl alcohol) chain as well as the orientation of the acetal cross-links. It can be concluded that not all the tertiary acetal hydrogens in the crosslinked resin will be oxidized to hydroperoxy groups. Thus the available sites for grafting will be restricted by the axial or equatorial orientation of this hydrogen.

All of the acetal model compounds oxidized readily when shaken with 30% hydrogen peroxide at room temperature. It would appear that this same reaction also occurs in the resin core and provides hydroperoxy sites which are the initiators of grafting. Some of the hydroperoxides are capable of dimerizing to form peroxides but this is not likely to occur in the resin core since such groups are not free to come together because of the rigid matrix formed by dense cross-linking.

The presence of γ-Fe_2O_3 in the hydrogen peroxide agitation stage did not cause any difference in the yield or NMR of the product obtained using 2-methyl-1,3-dioxane. The site of hydroperoxidation was verified by reduction with aqueous sodium sulfite. The result of this is a ring-opening reaction to give the corresponding glycol ester. Thus 2-propyl-1,3-dioxane was oxidized with hydrogen peroxide to form the hydroperoxide. The hydroperoxide was not isolated, but the reaction mixture was allowed to react with sodium sulfite. The solution was acidified with dilute sulfuric acid and refluxed for 6 hr to hydrolyze the glycol ester. Ether extraction gave a material which had an odor strongly suggesting butanoic acid and infrared and NMR spectra identical with those of an authentic sample of butanoic acid. This is the product expected from hydroperoxidation of the 2-position.

Initiation of Acrylate Polymerization by the Hydroperoxides

The ability of the acetal hydroperoxides to initiate polymerization was tested using methyl acrylate and acrylic acid. The hydroperoxides were found to be active initiators in the presence of iron(II). For example, when 2,4,6-trimethyl-1,3-dioxane-2-hydroperoxide was added to an aqueous solution of acrylic acid containing a small quantity of iron(II) sulfate, an exothermic reaction accompanied by an intense orange-brown color was immediately observed. The polymers could be isolated and verified by infrared spectroscopy.

When hydroperoxidized poly(vinyl alcohol) acetaldehyde acetal was treated with methyl acrylate in the presence of iron(II) a 56% increase in mass was obtained after washing with methanol and drying.

Acrylamide was also found to polymerize rapidly, while methacrylic acid polymerized only slowly as indicated by reaction exotherms. N,N-Dimethylaminoethyl methacrylate and 2-vinylpyridine showed no observable reaction.

Hydrogen peroxidized poly(vinyl alcohol) and poly(vinyl acetate) were also active in initiating grafting. However several hours were required for the reaction with hydrogen peroxide, and in the case of poly(vinyl alcohol) much chain scission occurred, significantly lowering the viscosity molar mass [9].

CONCLUSION

The site of grafting is predominantly the tertiary acetal carbon arising from the crosslink structure. This forms either an ortho ester structure or rearrangement may take place, at the radical stage prior to initiation, to provide an ester graft linkage. Other

graft sites may occur due to oxidative cleavage of the main poly(vinyl alcohol) chain. Essentially block copolymer would form if cleavage occurs. The linkage in this case would be an ether or carbon-carbon bond which would yield a more stable graft but at the expense of degradation of the poly(vinyl alcohol) core.

That the predominating graft linkages are ortho ester or ester structures would render them susceptible to hydrolysis. Extraction experiments with dilute hydrochloric acid have shown that acrylic acid grafts can be removed from samples of the resin.

By analogy with 2,4,6-trimethyl-1,3-dioxane, the site of grafting is stereospecific. The tertiary acetal hydrogen only reacts when in an equatorial position in the six membered acetal ring. This requires the two acetalized hydroxyls on the poly(vinyl alcohol) backbone to be in the same configuration (isotactic) and the crosslink chain to be trans to each of them.

A number of monomers were tested for ability to polymerize in the presence of the hydroperoxides and iron(II). Methyl acrylate, acrylic acid, and acrylamide reacted rapidly; methacrylic acid to much lesser extent; and N,N-dimethylaminoethyl methacrylate and 2-vinylpyridine showed no reactivity.

ACKNOWLEDGMENT

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