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Polymerization Studies with Allyl Starch*

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INTRODUCTION

Preparation and properties of allyl ethers of starch were actively investigated by Nichols and co-workers at the Eastern Regional Research Laboratory.[1,2] Their studies led to semicommercial production and marketing evaluations that relegated allyl starch to specialty uses. Application as a protective coating was discouraged because of the nonhomogeneity of the product, a tendency toward brittleness of the film, poor water resistance, and limited solvent solubility.[3] Because solubility was improved by preliminary degradation of starch to dextrins, degraded starch was used as substrates in preparing allyl dextrins for this study.

Despite its disadvantages, allyl starch retains a polymeric backbone with numerous unsaturated groups by which polymer characteristics may be modified. In view of the more recent advances in polymerization techniques and the availability of new unsaturated monomers, the potential exists for adequate modification of the allyl starch structure for use in the field of industrial coatings. This paper is concerned with the modification of the allyl substituent in allyl starch by homopolymerization and graft copolymerization reactions. Included in this study is the determination of the extent of participation of allyl groups in the curing of coatings, by the use of infrared spectroscopy, of the influence of dextrin molecular size and concentration upon the method and degree of homopolymerization, and of the effect of both homopolymerization and graft polymerization upon coating characteristics.

EXPERIMENTAL

Allyl Dextrin Preparation

The preparation of allyl starch dextrin has been adequately described.[1,2] Although considerable degradation occurs in the etherification procedure, further hydrolysis is usually required to obtain solvent-soluble products.

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Listed in Table I are substrates used to prepare products for polymerization studies. Substrates of varying intrinsic viscosities were used to compare not only the molecular weights obtained but also the yields of products. The ultracentrifugal weight-average molecular weights listed are the maxima in symmetrical broad-spectrum distributions. Dextrinization either before or after allylation lowers allyl dextrin yields considerably.

TABLE I
Preparation of Allyl Starch Dextrins

Substrate	$[\eta]$ of substrate (1N KOH)	Hydrolysis treatment	$\bar{M}_W$ Allyl dextrin	Allyl dextrin[a] yield, %
Pearl starch	1.7	pH 2 for 1 hr.[b]	300,000	70
Acid-hydrolyzed starch	0.3	pH 2 for 30 min.[b]	300,000	59
Enzyme-degraded starch	0.15	Water-insolubles centrifuged out and hydrolyzed for 10 min. at 90°C. with 1N HCl, recombined with water-solubles[c]	60,000	73
		Hydrolyzed for 30 min. at 90°C. with 1N HCl[c]	2,000	64

[a] Native starch without hydrolysis yields over 90% of allyl derivative.
[b] After alkylation.
[c] Before allylation.

Polymerization Techniques

All polymerizations were carried out in three-necked 100-ml. round-bottom flasks with electromagnetic stirring, no precautions being taken to eliminate air. For homopolymerization, solutions of the allyl dextrin at desired concentrations in either toluene or methyl isobutyl ketone were heated with 1 vol.-% tertiary butyl perbenzoate as a free-radical initiator at 110°C. In most instances, reactions were continued to the incipient gel point before adding hydroquinone to inhibit further reaction. Crude polymers were dried *in vacuo* for allyl group determinations.

For graft copolymerizations with acrylamide, acrylonitrile, and acrylic acid, the same techniques were applied, except that initiator concentration was 5% of the weight of the dextrin. Monomer concentration was limited to 1 mole of monomer per mole of allylated repeating unit, or approximately 50% of the allyl concentration. Thus, residual allyl groups were available for the curing cycle. Polymerized products were purified before functional group analysis either by reprecipitation with water or by extraction with solvents.

METHODS

Unsaturated groups were determined by the pyridine sulfate–dibromide method of Rowe et al.[4]

Free hydroxyl groups were acetylated with a pyridine and acetic anhydride (3:1) mixture according to the method of Ogg et al.[5]

Functional group analysis for measuring the extent of graft copolymerization was conventional analysis for acidic groups and the micro-Kjeldahl procedure for nitrogen.

Intrinsic viscosities of both allyl dextrins and unpurified polymerized products were determined in an Ostwald-Fenske viscometer with toluene at 25°C. Plots of ln η_r/c vs. c were constructed to extrapolate $[\eta]$ values. No kinetic corrections were made.

Weight-average molecular weights were calculated from sedimentation constants determined from ultracentrifugal patterns of allyl dextrin at 0.5% concentrations in acetone.

Curing properties of coatings were evaluated as to the rate of drying tack-free at room temperature and the pencil hardness after curing at 150°C. for 20 min. Resistance of the cured coatings to water, 5% NaOH, 10% NH_4OH, 4% HOAc, and 50% ethanol was determined by spot tests.[6]

Homopolymerization

The development of insoluble infusible coatings during the curing cycle suggests the formation of a three-dimensional network. Mechanisms proposed for curing allyl groups are based upon formation of hydroperoxides on the α-carbon to the unsaturated group.[7] More direct evidence of the fate of unsaturated groups in representative allyl dextrins was sought by infrared absorption analysis. Spectra before and after curing at 150°C. for 20 min. show a loss of approximately 50% of the allyl groups, as determined by the terminal methylene group at 10.75 μ. Cobalt naphthenate added to increase curing efficiency may increase the rate but does not alter the extent of allyl groups participating in the curing process. Concurrent with the loss in allyl groups was a comparable increase in carbonyl groups similar to that of the ester carbonyl groups at 5.8 μ.[8]

A peroxide-initiated prepolymer (60,000 $\bar{M}_W$ at 7% concn.), 34% of its allyl groups polymerized, as found by chemical analysis, showed under infrared examination on silver chloride plates that an additional 20% loss in allyl groups occurred during curing for 20 min. at 150°C. Certainly, a major portion of the allyl groups participate in the curing process.

A more critical evaluation of homopolymerization was obtained by polymerizing allyl dextrins of three different molecular weights at different solute concentrations. Extensive crosslinking of allyl polymers was sought without gelation at high solute concentrations. Actual measurement of the extent of polymerization was expressed as the percentage of reacting allyl groups. The mode of polymerization was indicated by the

TABLE II
Homopolymerization of Allyl Starch Dextrins

Allyl groups per Anhydroglucose unit	$\bar{M}_w$	Polymeriz. time, hr.	Dextrin concn., g./100 ml.	Allyl groups reacting, %	Intrinsic viscosity	
					Before polym.	After polym.
1.8	300,000	0.25	30	28	0.13	0.25
		0.5	15	34		0.29
		1.5	7	61		0.23
2.0	60,000	1.25	30	14	0.05	0.15
		2.75	15	25		0.25
		6	7	35		0.09
2.4	2,000	3	30	25	0.015	0.02
		11	15	42		

magnitude of change in intrinsic viscosities of the crude polymers. Normally, these free-radical reactions were inhibited at the incipient gel state.

The most interesting observation from the results in Table II concerns the effect of concentration upon the type of polymerization. Decreasing the dextrin concentration from 30 to 7% favors intra- over intermolecular polymerization. Actually, the polymerization appears intramolecular in nature because greater proportions of allyl groups react without appreciably increasing intrinsic viscosity. An intrinsic viscosity of about 0.3 is the maximum currently believed obtainable that will still allow solvent solubility to be retained. Polymerizations at 30% concentration gel rapidly when less than 30% of the allyl groups react, because of the initially high solution viscosity. Much of this percentage of allyl groups reacting is undoubtedly intramolecular in nature.

Influence of the molecular weight of allyl dextrins on polymerization is not so conclusive. Lower molecular weight fractions (60,000) should allow more interpolymerization before the limiting solvent solubility is exceeded. However, lowering the molecular weight lessens the tendency to crosslinking, increases the polymerization time, and favors chain termination.

The tendency to intramolecular polymerization at low dextrin concentrations (7%) was examined more thoroughly by following the rate of

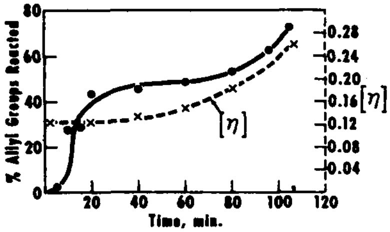

Fig. 1. Rate of polymerization of 300,000 molecular weight dextrin at 7% (w/v) concentration.

disappearance of allyl groups in high molecular weight dextrin with time. Figure 1 shows the fast initial intrapolymerization during the first 20 min. For the next 60 min., more gradual, and apparently concurrent, intra- and interpolymerizations continue; then the interpolymerization rate increases and the polymerization goes to the gel state. This slow interpolymerization is confirmed by intrinsic viscosities of crude solution samples removed and inhibited at various time intervals, as shown in Figure 1. A type of intrapolymerization often termed cyclic polymerization has been observed with diallyl phthalate; in this, 10- or 12-membered rings were formed without a viscosity increase.[9]

Homopolymerized products of allyl dextrins when cured maintain their 6H pencil hardness but show increased susceptibility to water, solvents, and alkali at the concentrations specified (under Methods). Resistance to solvents lasted for less than an hour in most instances. Apparently, extensive homopolymerization failed to provide products suitable for coatings. This failure may result from the major tendency toward intra- rather than interpolymerizations.

Graft Copolymerization of Allyl Dextrin

Failure to obtain desired coating properties in homopolymerized allyl dextrins led to an evaluation of an alternative procedure of grafting different monomers to pendant allyl groups of the starch backbone by free-radical mechanisms. Preparations and properties of an allyl starch–styrene copolymer have been reported without any evidence of the type of polymerization obtained.[10] In our studies, preliminary grafts were limited to those monomers whose functional groups were easily determined and whose homopolymer was either water-soluble or insoluble in the polymerizing solvent (an aid in the purification of polymers).

Data in Table III compare the total allyl groups polymerized with the types of polymerization occurring. Functional group analysis indicates the quantity of monomer attached. The amount of allyl homopolymerization is obtained by difference. The original allyl dextrin homopolymerizes to an incipient gel state in about 40 min. Monomer grafting reduces this polymerization time to as low as 11 min.

Since an intramolecular reaction is detrimental to coating properties, desirable monomers should limit this type of reaction. Of the three

TABLE III
Graft Copolymerization of Ally Starch Dextrins

Monomer	Polymeriz. time, min.	Allyl groups reacting, %	Allyl groups, %	
			Copol.	Homopol.
Acrylonitrile	30	30	10	20
Acrylamide	15	40.5	40.4	0
	13	32.5	32.5	0
Acrylic acid	11	32.5	16.3	16.2

monomers investigated, only acrylamide was preferentially polymerized to the complete exclusion of allyl homopolymerization. With the other monomers, the extent of copolymerization never exceeded that of homopolymerization.

With acrylic acid and maleic anhydride monomers, esterification occurs during the free-radical reactions. Monofunctional acids, such as acrylic acid, show only slight esterification, and a comparison can be made concerning the quantity of monomer grafted through the unsaturation. Copolymerizations with maleic anhydride are not tabulated because side reactions, such as esterification, are so extensive that the extent of grafting could not be determined.

Functional group analysis indicates that 7.5% of acrylic acid (0.45 g. acrylic acid in 6 g. copolymer), 15–18% of acrylamide (2.87–3.54% N), and 3.6% of acrylonitrile (0.95% N) monomers were grafted to the allyl dextrin in the reactions summarized in Table III. Graft copolymers prepared from these monomers have poorer coating properties than the original allyl dextrins. Functional groups, such as the acid and amides, would be expected to lower water resistance unless they react with more active sites on the polymer. From the results obtained, these secondary reactions during the curing cycle must be quite limited.

DISCUSSION OF RESULTS

Heat-cured coatings of allyl starch dextrins prepared with or without cobalt driers were shown by infrared absorption to have 50% of the allyl groups polymerized by oxidiative mechanisms. Despite this extensive polymerization, these products were unsuited for industrial coatings.

Solution polymerization at 110° with peroxide initiators provides an alternate approach route for allyl polymerization without the concurrent degradation associated with the above described oxidative polymerization. Thus, a prepolymer, in which 35% of the allyl groups had reacted, was made by heating a 15% solution of allyl dextrin in toluene at 110° with added peroxide. Analysis of a cured coating made from this prepolymer showed that 50% of the allyl groups had reacted, as was also the case when the allyl dextrin was cured directly by oxidative polymerization. However, these products, as well as those at 7% concentration in which 60% (Table II) and 70% (Fig. 1) of the allyl groups had reacted, actually produced coatings inferior in water and organic-solvent resistance to coatings prepared from the original allyl dextrin by cobalt-catalyzed polymerization. Intrinsic viscosity data on the highly polymerized products obtained by polymerization of 7% solutions of allyl dextrin in toluene establish that the type of polymerization achieved does not produce materials with desirable coating properties.

Since solution polymerization is predominantly intra in nature, monomers were sought that would graft to the allyl groups and thereby decrease the intrapolymerization. Curing depends upon both the unreacted allyl groups and the functionality of the groups introduced. Copolymers with acrylic acid and acrylonitrile were made, but some homopolymerization of dextrin allyl groups occurred during the reaction. With acrylamide, copolymerization was the only reaction. Coatings made from all the copolymers were inferior to those obtained with the original allyl dextrin.

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Synopsis

Industrial evaluation of allyl starch as a coating material in the late 1940's established that properties such as brittleness, nonhomogeneity of product, solvent solubility, and poor water resistance limited its potentialities to specialty uses. Infrared absorption analysis of allyl dextrin coatings before and after curing established that 50% of the allyl groups oxidatively polymerized. Since some degradation occurs in this process, attempts were made to limit this degradation and to improve coating properties by polymerizing pendant allyl groups with free-radical initiators. Homopolymerization studies involving effects of molecular size and dextrin concentration indicated that intramolecular polymerization dominated early stages of the reaction. Graft copolymerization of a few unsaturated monomers resulted in products containing 3.6% acrylonitrile, 8.5% acrylic acid, and 15–18% acrylamide. Only with the acrylamide did no concurrent homopolymerization of dextrin allyl groups occur. Neither variations in method for polymerizing the allyl dextrins nor use of copolymers was effective in producing suitably cured coatings.

Résumé

Une évaluation industrielle de l'amidon allylique comme matériel de recouvrement, avait montré dès la fin de 1940, que des propriétés telles que la fragilité, la non-homogénéité du produit, la solubilité dans les solvants et la faible résistance à l'humidité limitent ces possibilités à des usages spéciaux. L'analyse d'absorption infra-rouge de revêtement de dextrines allyliques avant et après vulcanisation établit que 50% de groupes allyliques polymérisent par oxydation. Comme une dégradation s'effectue lors de ce procédé, on a cherché à limiter celle-ci et à améliorer les propriétés du revêtement par polymérisation des groupes allyliques restent par des initiateurs radicalaires. Des études d'homopolymérisation comportant des effets de dimension moléculaire et de concentration en dextrine indiquent que la polymérisation intramoléculaire est prépondérante lors des premières étapes de la réaction. La polymérisation par greffage de quelques monomères insaturés donne des produits contenant 3.6% d'acrylonitrile, 8.5% d'acide acrylique et 15 à 18% d'acrylamide. A l'exception de l'acrylamide, il ne se présente pas d'homopolymérisation concurrente des groupes allyliques de la dextrine. Aucune variation dans la méthode de polymérisation des dextrines allyliques pas plus que l'utilisation de copolymères ne sont efficientes pour produire des revètements vulcanisès utilisables.

Zusammenfassung

Die technische Erprobung von Allylstärke als Überzugsmaterial in den späten vierziger Jahren zeigte, dass Eigenschaften wie Sprödigkeit, Nichthomogenität der Produkte, Löslichkeit in Lösungsmitteln und geringe Wasserbeständigkeit ein Hindernis für die Anwendung für spezielle Zwecke bildet. Infrarotanalyse von Allyldextrinüberzügen vor und nach der Härtung zeigte für 50% der Allylgruppen das Auftreten einer oxydativen Polymerisation. Da bei diesem Vorgang ein gewisser Abbau stattfindet, wurden Versuche zur Begrenzung dieses Abbaus und zur Verbesserung der Bedeckungseigenschaften durch Polymerisation der anhängenden Allylgruppen mit radikalischen Startern unternommen. Homopolymerisationsversuche mit Variierung der Molekülgrösse und Dextrinkonzentration zeigten, dass in den frühen Stadien der Reaktion intramolekulare Polymerisation vorherrscht. Pfropfcopolymerisation mit einigen ungesättigten Monomeren führte zu Produkten mit 3,6% Acrylnitril, 8,5% Acrylsäure und 15–18% Acrylamid. Nur bei Acrylamid trat keine Homopolymerisation der Dextrinallylgruppen als Konkurrenzreaktion auf. Weder eine Variation der Polymerisationsmethode für die Allyldextrine noch die Verwendung von Copolymeren lieferte eine brauchbare Härtung der Uberzüge.

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