

Thermally Reversible Gels from Carbonyl-Containing Water-Soluble Synthetic Polymers

GIFFIN D. JONES*

Central Research Laboratory, General Aniline and Film Corporation, Easton, Pennsylvania

The phenomenon of gelation is encountered widely with synthetic polymers, but it is usually irreversible because the crosslinking reactions which cause it usually are irreversible. A number of patents describe the use of gelling agents for polyvinyl alcohol to produce relatively stiff gels that can be melted and allowed to gel on cooling, for many cycles. Examples of these gelling agents are the polyhydric phenols, naphthylsalicylamide, and the diamide of salicylic acid and benzidine.¹ Presumably, these agents function by hydrogen bond formation. One might visualize crosslinks with the difunctional gelling agents; however, in the case of the naphthols, which function also, this explanation seems ruled out.

In an attempt to produce a synthetic substitute for photographic gelation, several approaches were successively tested and discarded. A study of gelation abilities of acrylamide-methacrylamide interpolymers,^{2a} poly-*N*-hydroxyethylacrylamide,^{2b} the interpolymer of methacryllsine and acrylamide, and the interpolymer of vinylpyridine and methacrylic acid^{2c} indicate that it is difficult, although not impossible, to produce a reversible gel by balancing attractive forces for the solvent with interchain hydrogen bonding. A more successful approach is that of introducing crosslinking by a reversible reaction. It was accomplished in work herein described by the use of carbonyl reagents and carbonyl polymers.^{2d}

Gels with sharp melting points were prepared by the use of polymers containing enolizable carbonyl groups together with a difunctional carbonyl reagent as gelling agent. The polymers were a partial acetoacetate of polyvinyl alcohol and some copolymers of polymerizable acetoacetates. The gelling agents were dihydrazides; polyamines could also be used and, in the case of a partially acetoacetylated polyethylenimine, no gelling agent

was required. This method of obtaining sharp melting gels is therefore a method based on the formation of crosslinks that are readily reversible thermally.

The homogeneous acylation of polyvinyl alcohol with diketene was carried out in hot dimethylformamide solution. The polyvinyl alcohol samples listed in Table I were acylated to the partial acetoacetate derivatives described in Table II. The acetoacetyl content was determined by a coupling reaction, which is referred to later. In this work the conversion was generally low and the product water-soluble; this was not the case in the work of Staudinger and Häberle,³ who subsequently prepared a highly acetoacetylated polyvinyl alcohol by reaction of diketene with polyvinyl alcohol in acetic acid suspension. The tendency to crosslink irreversibly on drying, reported by Staudinger and Häberle, was not observed when the conversion was less than 10 mole-%, with high-viscosity polyvinyl alcohol, or less than 30 mole-% with medium-viscosity polyvinyl alcohol.

It may be of some interest that, while polyvinyl alcohol solutions in dimethylformamide gel reversibly at about 100°, the acetoacetyl derivative at 30 mole-% conversion does not gel and remains soluble in dimethylformamide on cooling.

TABLE I
Polyvinyl Alcohol Grades

Sample	Grade ^a	$[\eta]$
Fully hydrolyzed		
A	90-25	0.75
B	71-24	0.85
C	72-51	1.02
Partially hydrolyzed (86-89%)		
D	51-5	0.32
E	52-22	

* Present address: Physical Research Laboratory, The Dow Chemical Company, Midland, Mich.

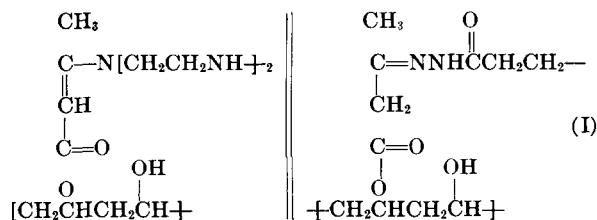
^a Elvanol, second number, is identified in supplier's bulletin as viscosity in centipoises of 4% solution.

TABLE II
Gel Strength and Fluid Point of Gels Prepared from Acetoacetyl Derivatives with Adipic Dehydrazide as Gelling Agent

Polyvinyl alcohol sample	Diketene used, mole-%	Acetoacetate found, mole-%	Gel strength at pH 4, g.	Fluid point, ^a °C.
A	16	12	—	—
A	11	10	85	100
A	5.6	3.5	45	60
B	13	6.6	—	—
B	6.6	5.3	172	55
B	5.7	4.7	15	33
C	6.8	6.7	62	—
C	4.5	4.5	119	—

^a Mean value of melting and setting points.

The acetoacetyl derivative was converted to pale yellow shreds by precipitation in ethylene glycol diethyl ether and air drying. Water solutions in the concentration range of 5 or 10% resembled those of polyvinyl alcohol except that they were gelled by the addition of a small amount of polyethyleneimine. The gel could be liquefied by being heated or by the addition of dilute acetic acid, and the solution could be regelled on cooling in neutral or alkaline solution. The gel was strongly yellow and probably vinylamine crosslinks were formed after the fashion of the formation of ethyl diethyliminocrotonate from diethylamine and ethyl acetoacetate.⁴ A more stable gel, also thermally reversible, was obtained by the use of the dihydrazide of a dibasic acid as gelling agent. These gels were no more colored than the solution of acetoacetyl derivative and it is presumed that the keto form is involved in the gelling reaction. The two gelling reactions are contrasted in reactions (I).



The maximum rate of gelling was found in the range normal for semicarbazone formation, i.e., pH 5. The useful pH range of reversibility is 3 to 7, as shown in Figure 1; in alkaline solution the gels do not melt. The range between melting and setting is 10 to 15°; the time for gelation either on cooling or on the addition of the gelling agent may be less than a minute. Of course, if the solution is

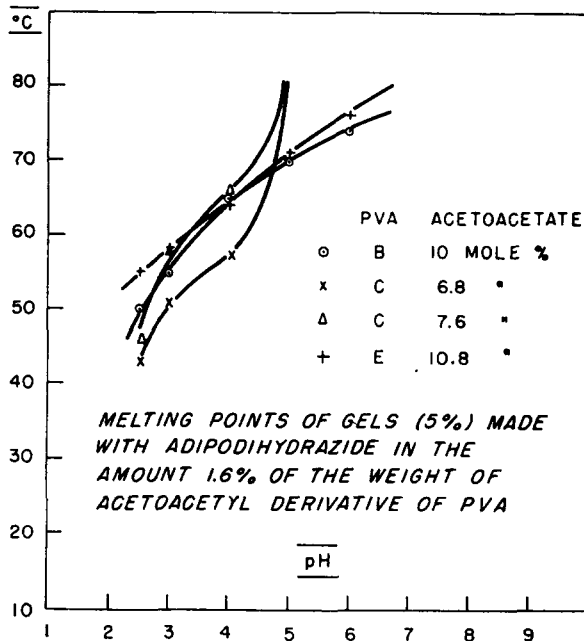


Figure 1

diluted there is a decrease in gel strength. The gel strength was measured by the weight required to thrust a 20 mm. test tube into the gel for a 10 mm. immersion. It was found that gel strength was higher with the acetoacetyl derivative of a medium-viscosity polyvinyl alcohol than with one of a higher-viscosity polyvinyl alcohol and a lower degree of acetylation. Within the range of water solubility, the more diketene used in acylating a given polyvinyl alcohol grade, the higher the melting point and greater the strength of the gel obtained in the gel test. Moreover, for the same gel melting point, a more dilute gel of a polymer having a higher acetoacetyl content is stiffer than a more concentrated gel of a polymer of lower acetoacetyl content. Thus, a 5% gel was obtained that melted at 65° at pH 3 and had a gel strength of 270 g. At pH 5 it melted at 73° in 5% concentration. When diluted to 2% concentration, it was twice as stiff at pH 5 as a 7% gel melting at the same temperature and made from a polymer having a lower proportion of acetoacetate.

It was found that the shorter the chain of the dihydrazide used as the gelling agent, the more efficient the action, although the standard tests were made with adipodihydrazide.

Some extensions of our tests were made. Allyl acetoacetate and *N*-allylacetoacetamide were made and copolymerized with acrylamide. These water-soluble copolymers with a minor amount of

TABLE III
Gelling of 5% Solution of 16 Mole-% Acetoacetyl Derivative
of PVA Sample A

Gelling agent	Concn., ^a %	Gel time, ^b min.	M.p., °C.	Gel p., °C.
Carbodihydrazide	0.8	2 ⁵ / ₆	80	—
Malonodihydrazide	1.6	5 ¹ / ₂	67	55
	3.2	4 ¹ / ₂	85	75
Adipodihydrazide	1.6	3 ¹ / ₄	62	50
	3.2	3 ³ / ₄	94	87

^a Relative to weight of acetoacetyl derivative of PVA.

^b Time for gelation at 32°C.

acetoacetyl derivative, even though undoubtedly not uniform in composition, could be gelled reversibly by adipodihydrazide. The copolymers made with these monomers had the gel strengths given in Table IV. The less favorable showing of the amide was ascribed to a lower copolymerizability and the production of an acrylamide copolymer of lower viscosity. A copolymer of acrylamide and methyl vinyl ketone made with a monomer ratio of 7 to 1 by weight was water-soluble and could be gelled reversibly with adipodihydrazide; however, the gelling and melting behavior was sluggish in comparison to that of the acetoacetyl derivatives.

TABLE IV
Gel Strength Tests (Adipodihydrazide, 25%, pH 5): Weight
Required to Immerse 20 mm. Test Tube

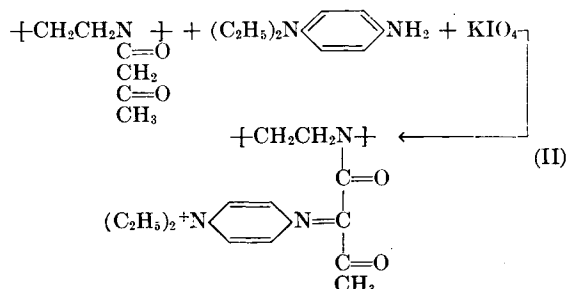
Sample ^a	Weight, g.			M.p., °C.
	5 mm.	10 mm.	15 mm.	
A	11	27	50	80
B	11	30	47	40

^a A: 5% gel acrylamide copolymer with 10% allyl acetoacetate; 1.6% gelling agent. G: 10% gel acrylamide copolymer with 20% allyl acetoacetamide; 0.8% gelling agent.

The reaction of diketene with ethyleneimine can be carried out without polymerization but, in one case in which the ethyleneimine was added dropwise to the diketene, there was a sudden and vigorous polymerization after the reaction had been completed. The reaction of diketene with polyethyleneimine gave a product which, if only partially acetoacetylated, gelled reversibly in neutral or alkaline solution and the gel was colorless. With a high degree of acetoacetylation the polymer can be gelled reversibly with adipodihydrazide.

Acetoacetyl polymers contain active methylene linkages and can be converted to azo and azo-

methine dyes. A yellow dye was obtained by the reaction of dianisidine diazonium chloride-zinc chloride complex with a partially acetoacetylated polyethyleneimine. The formation of a yellow azomethine dye is illustrated in reaction (II).



EXPERIMENTAL

Reaction of Diketene with Polyvinyl Alcohol

Diketene, 18 g., (freshly distilled to eliminate yellowness) was diluted with 18 g. of anhydrous dimethylformamide and added during the course of 15 min. to a stirred solution of 150 g. of polyvinyl alcohol (Elvanol 72-51) in 1350 g. of anhydrous dimethyl formamide at 140°C. The reaction was carried out in a hood and with provision for refluxing. The reaction temperature could be as low as 110°; if it was much lower the polyvinyl alcohol solution would gel. The polymer was precipitated while still hot in benzene (3500 g.). After drying, the yellowish fibrous polymer was redissolved with stirring and heating to 100° in 1400 g. of water. Analysis by a standard diazo coupling test showed the polymer to have been acetoacetylated to the extent of 6.8 mole-%. In other experiments, methanol or ethylene glycol dimethyl ether were used as precipitating solvents.

Dihydrazide

After the directions of Borsche et al.,⁵ a solution of 0.1 mole of the diethyl ester of the dibasic acid and 0.3 mole of hydrazine hydrate dissolved in 15 cc. of methanol was heated on a steam bath for 4 hr. On cooling, the dihydrazide crystallized. A 2% solution of dihydrazide adjusted to pH 5 with acetic acid was used for gelling tests. The standard test was the addition of 1 cc. of 2% solution of adipodihydrazide to 25 cc. of a 5% solution of the acetoacetylated polyvinyl alcohol. This amount of gelling agent is equivalent in stoichiometric reaction to a mole per cent acetoacetylation of 0.8.

Gelling Test

A 25 cc. sample of a 5% solution of acetoacetyl derivative of Elvanol 91-65 having 6.8 mole-% acetoacetylation was treated with 1 cc. of the adipodihydrazide gelling agent solution. Gelation occurred within 1 min. After storage overnight at 25°, the weight required to thrust a 20 mm. test tube into the gel a distance of 10 mm. was 257 g.

Photographic Test

A derivative of Elvanol 71-24 with 18.9 mole-% acetoacetylation was dissolved in water to a 10% concentration by weight. The following solutions were prepared:

Solution 1: 100 parts of distilled water, 14 parts of potassium bromide, 0.2 parts of potassium iodide, 0.4 parts of sodium chloride, and 40 parts of the 10% water solution of the acetoacetyl derivative.

Solution 2: 200 parts of water, 20 parts of silver nitrate, 20 parts of 29% ammonium hydroxide

Solution 3: 460 parts of a 10% water solution of the product obtained above, 220 parts of a 10% water solution of citric acid.

Solution 4: 33 parts of a 2% solution of adipodihydrazide.

A photographic emulsion was prepared by adding, during the course of 15 min. Solution 2 maintained at 40°C. to Solution 1, also at 40°C. To Solution 3 was added the mixture of Solutions 1 and 2 and the resultant mixture was stirred for 4 min., after which Solution 4 was added. The pH of the resultant emulsion was 4.7 and gelation took place in about 2.5 min. After chilling, the emulsion was washed for 1½ hr. with distilled water. The emulsion became fluid when heated to 55-60°C. and was coated onto photographic paper at 65°C.

The coated paper was exposed to a negative photographic image and developed by standard photographic procedures. There was thus obtained a photographic print exhibiting clear highlight portions, good gradation, and deep black in the shadow portions of the image, and having speeds equal to or slightly greater than that of standard soft photographic contact-printing developing-out paper. The finished print, upon immersion in boiling water for 5 min., showed no deleterious results.

Allylacetamide

To a solution of 83 g. of diketene in 210 cc. of absolute ether was added 57 g. of anhydrous

allylamine in dropwise fashion over a period of half an hour. The temperature was maintained at 0°. On distillation of the reaction mixture, *N*-allylacetamide was obtained as a pale yellow liquid boiling at 122-125° at 1 mm. and solidifying to a yellow solid that melted at 28°.

Reaction of Polyethyleneimine with Diketene

To 180 cc. of an aqueous solution of 20 g. of polyethyleneimine was slowly added 37.5 cc. of diketene during the course of half an hour. The temperature rose to 75°C. The reaction mixture was kept alkaline by the periodic addition of 40% caustic. On cooling, the solution did not gel but could be gelled at pH 6 by the addition of adipodihydrazide. When a smaller proportion of diketene was used—for example, 0.5 cc. to 3 g. of polyethyleneimine in 25 cc. of water—there was obtained a solution that gelled on cooling. The stiff colorless gel melted at 75° and regelled at 65°.

Gelling of Polyvinyl Alcohol with Disalicylbenzidide and *N*-β-Naphthylsalicylamide

Gelling tests were made according to the directions given in U.S. Patent 2,249,537.¹ A 5.4% solution of polyvinyl alcohol was prepared, and to 50 g. of this solution at 50°C. was added a solution of 0.25 g. of *N*-β-naphthylsalicylamide in 3.2 cc. of 0.5*N* sodium hydroxide. A shroud of precipitate formed which was slow to dissolve on being stirred. After standing overnight at room temperature, a slightly milky gel formed and seemed about as stiff as 10% gelatin.

A 5.6% solution of polyvinyl alcohol was prepared, and to 50 g. was added a solution of 0.1 g.

TABLE V
Gel Tests with Disalicylbenzidide

Polyvinyl alcohol		Gel	
Sample	D.P.	M.p., °C.	Clarity
300 B 0-15-1 film, reprecipitated	370	48°	Clear
Elvanol 51-05	115	No gel	Milky
A ^a	380	52	Clear
B	280	59	Turbid
C	130	No gel	Clear

^a Samples A, B, and C were prepared from polyvinyl acetate: samples of DP, 940, 310, and 96, respectively, which were made by polymerization as follows and hydrolyzed with alcoholic potassium hydroxide. A, bulk 0.2% benzoyl peroxide, 80°; B, methanol solution, UV light, 40°; C, dimethylformamide solution, 0.2% benzoyl peroxide, 80°.

of *N,N'*-disalicylbenzidide in 1.6 cc. of 0.5*N* sodium hydroxide. It was necessary to make the addition at about 70°C. and to stir well to dissolve the precipitated globules. The product gelled at about 40°; the gel melted at about 60° and was insoluble in water at room temperature. It was very stiff and was less cloudy and much quicker in setting than the product formed with *N*- β -naphthylsalicylamide.

N- β -Naphthylsalicylamide and *N,N'*-Disalicylbenzidide

To a suspension of 108 g. (0.755 mole) of β -naphthylamine and 104.3 g. (0.755 mole) of salicylic acid in 1500 cc. of dry toluene was added 29 cc. (45.7 g., 0.332 mole) of phosphorous trichloride. The mixture, which soon became pasty, was stirred and refluxed for 2 hr. and then steam-distilled to remove the toluene and filtered. The precipitate was washed with 10% hydrochloric acid, water, and 10% sodium bicarbonate; it was recrystallized from absolute alcohol with Darco decolorization. This was carried out in four portions with 3000 cc. of alcohol being used over. The yield was 125 g., m.p. 183–184°; with recrystallization, m.p. 187–188°. A second crop, 20 g., was obtained by evaporation of the mother liquor to half-volume.

In the same way, 73 g. of benzidine (0.397 mole) was acylated with 109.5 g. of salicylic acid (0.794 mole) and 30 cc. of phosphorous trichloride. The mixture did not become pasty although stirred and refluxed for 2 hr., steam-distilled, and washed with 10% hydrochloric acid and 10% sodium bicarbonate. The blue-gray precipitate was insoluble in alcohol and soluble in hot nitrobenzene, cold dimethylformamide, or alkali, but crystals could not be obtained. The material was recrystallized as a tan powder from pyridine⁶ and this tan powder was washed with ether.

This work was carried out under the direct supervision of Dr. C. E. Barnes and the indirect supervision of Dr. F. W. H. Mueller, of AnSCO, and Dr. Willy Schmidt. At the time of this work, Dr. Barnes and Dr. Schmidt were at the Central Research Laboratory.

References

1. McDowell, W. H., and Kenyon, W. O., U.S. Pat. 2,234,186 (1941), 2,249,536 (1941), 2,249,537 (1941), and

2,249,538 (1941). Lowe, W. G., U.S. pat. 2,286,215 (1942), 2,311,058 (1943), and 2,311,059 (1943).

2. (a) Jones G. D., U.S. Pat. 2,504,074 (1950). (b) Jones, G. D., U.S. Pat. 2,533,166 and (c) Jones, G. D., U.S. Pat. 2,508,718 (1950), and 2,611,763 (1953), and (d) Jones, G. D., U.S. Pat. 2,480,810 (1949), 2,536,980 (1951), 2,555,646 (1951), 2,561,205 (1951), and 2,587,329 (1952).

3. Staudinger, H. and M. Häberle, *Makromol. Chem.*, **9**, 52 (1952).

4. Roll, L. J., and R. Adams, *J. Am. Chem. Soc.*, **53**, 3469 (1931).

5. Borsche, W., W. Müller, and C. A. Bodenstein, *Ann.*, **475**, 120 (1929).

6. Fargher, R. G., L. D. Galloway, and M. E. Proger, *J. Textile Inst.*, **21**, 245 (1930).

Synopsis

The reversible reaction with di-hydrazides in acidic solution or polyamines in alkaline solution is used to cause synthetic polymers containing labile carbonyl groups to gel with sharp thermoreversibility in dilute water solution. Some of the polymers described contain active methylenes, for example, partially acetoacetylated polyvinyl alcohol and polyethylenimine, and copolymer of allyl acetoacetate with acrylamide. These polymers function also as couplers for azo and azomethine dye formation.

Résumé

La réaction réversible de dihydrazides en solution acide ou de polyamines en solution alcaline a été employée pour former des polymères synthétiques renfermant des groupes carbonyles labiles, qui se gélifient avec une thermoreversibilité élevée en solution aqueuse diluée. Quelques-uns des polymères décrits contiennent des méthylènes actifs, par exemple l'alcool polyvinylique partiellement acétoacétylé et le copolymère d'acétoacétate d'allyle et d'acrylamide. Ces polymères fonctionnent aussi comme agent de couplage pour la formation de colorant azoïque et azométhinique.

Zusammenfassung

Die reversible Reaktion mit Dihydraziden in saurer Lösung oder mit Polyaminen in alkalischer Lösung wurde verwendet, um synthetische Polymere, die reaktionsfähige Carbonylgruppen enthalten, zu einer scharf thermoreversiblen Gelbildung in verdünnter wässriger Lösung zu veranlassen. Einige der beschriebenen Polymeren enthalten aktive Methylengruppen, zum Beispiel teilweise acetoacetylierter Polyvinylalkohol und Polyäthylenimin, und das Copolymer von Allylacetoacetat mit Acrylamid. Diese Polymeren fungieren auch als Kupplungskomponenten für Azo- und Azomethinfarbstoffbildung.

Received March 1, 1961