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POLYMERIZATION OF 3-VINYL-5,5-DIMETHYLHYDANTOIN IN WATER

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Polymerization of 3-vinyl-5,5-dimethylhydantoin was carried out in water. The resulting polymer was insoluble in all solvents tested, while the polymers obtained in organic solvents were soluble in N,N-dimethylformamide. Polymerizations in water containing water-soluble polymers gave the polymers in which the water-soluble polymers were entrapped.

Poly(3-vinyl-5,5-dimethylhydantoin) [poly(3-V-DMH)] seems of much interest as a functional polymer but only a brief description has been published on the polymerization of 3-vinyl-5,5-dimethylhydantoin (3-V-DMH).$^{1)}$

Present paper outlines the anomalous behavior of the polymerization of 3-V-DMH in water.

3-V-DMH (mp 90-91°C) and 3-vinyl-1,5,5-trimethylhydantoin (3-V-TMH) (mp 50-52 °C) were synthesized according to the previously reported method.$^{2)}$ Poly(vinyl alcohol), gelatin and starch were commercial origin. Poly(acrylic acid) was obtained by bulk polymerization of acrylic acid and purified by pouring its methanol solution into benzene. Other chemicals were reagent grade. Unless otherwise stated, the polymerization was carried out at 50°C in glass tubes under nitrogen atmosphere. The monomer concentration in water was adjusted at a low value (0.25 mol/l) because both monomers were slightly soluble in water. [Solubility at 50°C was 6.7% (w/v) for 3-V-DMH and 5.4% (w/v) for 3-V-TMH].

Polymerizations of 3-V-DMH in organic solvents were carried out using 2,2'-azobisisobutyronitrile (AIBN) as initiator. All polymers obtained were soluble in N,N-dimethylformamide (DMF) and dimethyl sulfoxide, though the appearance of the polymerization medium varied with the solvents used, as shown in Table 1.$^{3)}$

Table 1 Polymerization of 3-V-DMH in organic solvents

Solvent	Polymer			
	Appearance of the polyn. medium	Yield (%)	Solubility in DMF	Intrinsic viscosity[a)]
DMF	Ho	~ 100	S	0.2
Acetic acid	Ho		S	
Methanol	He[b)]		S	
Ethanol	He[b)]	~100	S	0.2
Butanol	He[b)]		S	
t-Butanol	He[b)]	~ 100	S	0.9
Acetonitrile	He[b)]		S	
Acetone	He[b)]		S	
Dioxane	He[b)]	~100	S	0.2
Pyridine	He[c)]		S	
Benzene	He[c)]	~100	S	0.8

[Monomer]: 1.0 mol/l, [AIBN]: 4.7 X 10^{-3} mol/l, Polymerization time: 3 hr, temperature: 60°C. a) Measured in DMF at 30°C. b) Separated as a powder. c) Separated as a transparent, swollen mass. Ho: Homogeneous, He: Heterogeneous, S: Soluble.

Polymerization of 3-V-DMH in water was carried out using ammonium persulfate (APS) as initiator. The monomer solution became turbid after an induction period of few minutes. The turbidity increased with polymerization time and after about 10 min, the solution changed to a pudding-like product. The product was poured into methanol and the precipitated polymer was separated and dried under reduced pressure at room temperature. The polymer was broken into small pieces and extracted with DMF to remove a soluble part. Gel fraction was determined by weight ratio of the insoluble part toward the original polymer. The polymer thus obtained was infusible and insoluble in all solvents tested.

Fig. 1 shows the relation between gel fraction and conversion in the polymerization of 3-V-DMH in water.

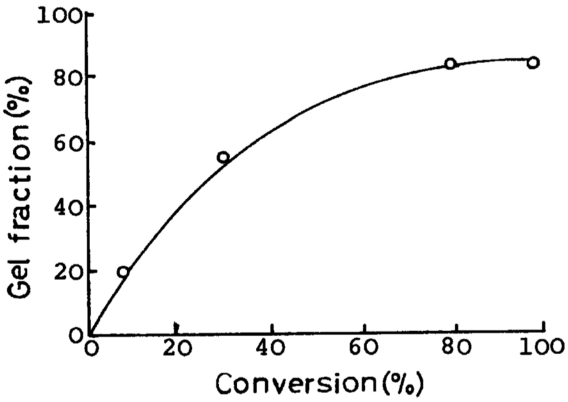

Fig. 1 Relation between gel fraction and conversion

[Monomer]: 0.25 mol/l, [APS]: 2.35 X 10^{-3} mol/l, Polymerization temp.: 50°C.

It can be seen that the gel fraction increases with increasing the conversion and ultimately exceeds 80%. A similar result was obtained in the polymerization of 3-V-DMH in water using suspended AIBN as initiator.

On the other hand, polymerization of 3-V-TMH in water using APS as initiator gave a pudding-like product as with 3-V-DMH, but the resulting polymer was completely soluble in DMF.

This leads to the assumption that the insolubilization of poly(3-V-DMH) obtained in water might be due to a pseudo crosslinking resulting from a strong hydrogen bonding between polymer molecules. This assumption, however, was rejected by the fact that the insoluble poly(3-V-DMH) remained insoluble after acetylation with acetic anhydride.

Thus, it will be sure that the insolubilization of poly(3-V-DMH) polymerized in water results from an exact crosslinking. The crosslinking is presumed to take place *via* the abstraction of the 1-position hydrogen atom of hydantoin pendants of dead polymers by a growing polymer radical. Although the reason why no crosslinking takes place in the polymerizations in organic solvents, is not completely explainable, the chain transfer of growing polymer radicals to the solvents might play an important role.

Polymerizations of 3-V-DMH in water were carried out in the presence of a small amount of organic additives. The results were shown in Table 2. Pudding-like polymers were obtained in almost quantitative yields, as with the polymerization in pure water but the gel fraction in the resulting polymers decreased appreciably and with some additives, it disappeared completely. The decrease in the gel fraction might be due to the chain transfer to the additives but the effect of

Table 2 Polymerization of 3-V-DMH in water

Additive	Polymer	
	Gel fraction (%)	Intrinsic viscosity[a)]
DMF	~48	-
Acetic acid	~41	-
Methanol	~70	-
Ethanol	~80	-
Butanol	~70	-
t-Butanol	~80	-
Acetonitrile	~45	-
Acetone	~0	0.62
Dioxane	~0	1.75
THF	~0	1.18
Pyridine	~0	0.78
None	~83	-

[Monomer]: 0.25 mol/l, [APS]: 2.35×10^{-3} mol/l, [Additive]: 0.25 mol/l, Polymerization time: 0.5 hr, temp.: 50°C.

a) Measured in DMF at 30°C.

acetone, dioxane, THF or pyridine as additive seems too drastic to ascribe it to only the chain transfer, considering their extremely low concentrations (0.25 mol/l). These additives, which have a high hydrogen bonding ability, might be attracted to the hydrogen atom of hydantoin pendant to protect the hydrogen atom from the attack of growing radicals.

The polymerization of 3-V-DMH was investigated in water containing a water-soluble polymer, such as poly(vinyl alcohol), poly(acrylic acid), gelatin and starch. The polymerization was carried out using APS as initiator under air. Rapid polymerization took place to form a pudding-like product, as with the polymerization of pure monomer. The product was broken up to small pieces and the pieces were extracted with water at room temperature until no more additive was detected in the extract. The poly(vinyl alcohol) and starch entrapped in poly(3-V-DMH) were confirmed by coloration with iodine, the gelatin and poly(acrylic acid) by IR spectroscopy. These results suggest that the polymerization of 3-V-DMH in water containing an enzyme is useful as a preparation method of immobilized enzyme.

References

1) M. Sato, Nippon Kagaku Zasshi, 83, 323 (1962).

2) M. Sashio, M. Tanaka and N. Murata, Kogyo Kagaku Zasshi, 74, 301 (1971).

3) The polymers melted at 340-360°C which was appreciably higher than that in lit. (1) (at 210-250°C).

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