

# New Hydantoin Vinyl Ether Polymers

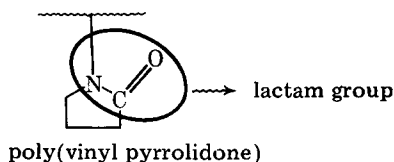
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## Synopsis

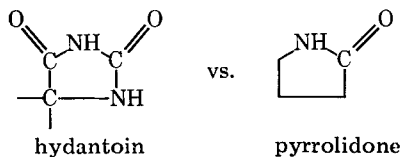
The title hydantoin vinyl ether polymers are water-soluble alternating copolymers of a hydantoin vinyl ether (HVE) and maleic anhydride (MA). The copolymerization parameters are  $\sim 0$  and 0.06, respectively. The HVE/MA polymers were compared with reference poly(vinyl pyrrolidone) (PVP) and methylvinylether (MVE)/MA polymers, of approximately the same specific viscosity, with regard to two key properties: solution viscosity and complexing capability (iodine). The HVE/MA polymers gave higher solution viscosities than PVP. When compared to MVE/MA, solution viscosity was lower initially but considerably higher after standing for a longer period of time. The inverse viscosity/time relationship observed for the MVE/MA polymer was not apparent in the case of HVE/MA. With regard to complexing capability the HVE/MA polymers proved to be clearly more effective. This is thought to be due to the HVE/MA polymer structure which offers two lactam groups plus two carboxyl groups for complexing vs. one lactam and two carboxyl groups, respectively, in the case of the reference polymers.

## INTRODUCTION

Poly(vinyl pyrrolidone) (PVP) is a well-established and highly successful water-soluble speciality polymer. PVP's commercial success is based on its almost universal complexing ability.<sup>1</sup> This complexing ability is in turn, primarily attributed to the pendant lactam group of the polymer<sup>1</sup>:



The hydantoin ring is structurally similar to the pyrrolidone ring:



This observation led to the investigation of various paths towards water-soluble hydantoin polymers, the assumption being that such polymers should also exhibit interesting complexing properties. One such path has led to the title hydantoin vinyl ether polymers based on 3-vinyloxyethyl-5,5-dimethylhydantoin (HVE) and maleic anhydride (MA).

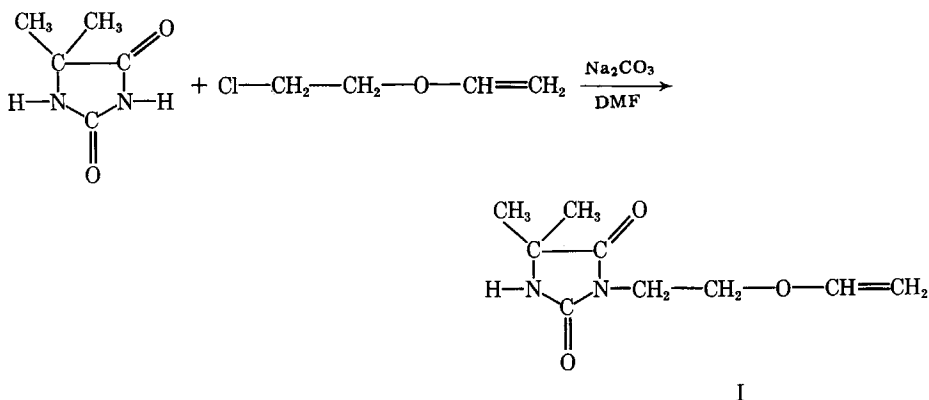
After a brief description of monomer and polymer synthesis this paper will

deal with the characterization of the HVE/MA polymers with regard to two key properties: complexing capability and solution viscosity/pseudoplasticity. The HVE/MA polymers are compared to PVP and to methylvinylether/maleic anhydride (MVE/MA) polymers.

## EXPERIMENTAL

### Monomer Synthesis

3-Vinyloxyethyl-5,5-dimethylhydantoin was prepared from 5,5-dimethylhydantoin and 2-chloroethylvinylether<sup>2,3</sup>:



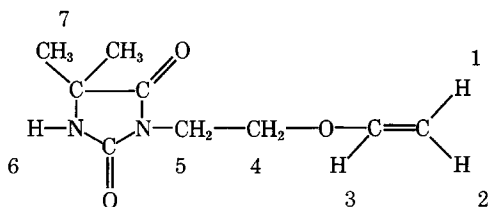
The 2-chloroethylvinylether precursor was obtained from 2,2'-dichlorodiethylether via dehydrohalogenation with sodium hydroxide, using triethanolamine as a catalyst.<sup>4</sup>

I was obtained in 95% yield and purified by distillation, bp 112°C/2 × 10<sup>-3</sup> mm Hg. It is a clear, yellowish viscous liquid which crystallizes on standing at room temperature after longer periods of time, mp 50°C.

ANAL. C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> Calcd: C, 54.54%; H, 7.12%; N, 14.13%; O, 24.22%. Found: C, 54.77%; H, 7.10%; N, 14.28%; O, 24.40.

### H-NMR

The H-NMR spectrum taken in CDCl<sub>3</sub> is in accord with the above structure:



<u>Proton(s)</u>	<u>ppm</u>	<u>Signal type</u>
1	4.19	d/d
2	4.02	d/d
3	6.43	d/d
4)	3.89	m
5)	3.81	m
6	6.02	s
7	1.45	s

Maleic anhydride (MA) was obtained in "synthesis" quality (99%) from Merck and used as supplied.

### Copolymerization

The copolymerization of 3-vinyloxyethyl-5,5-dimethylhydantoin and maleic anhydride was carried out either in toluene or in a mixture of toluene and cyclohexane at 60°C using azoisobutyronitril (AIBN) as initiator. The polymerization was of the solution/precipitation type. Polymerization in toluene alone led to polymers with low specific viscosity values. By carrying out the polymerization in the solvent mixture toluene/cyclohexane and varying the ratio between these two solvents, polymers with different specific viscosities could be obtained.<sup>5</sup>

A general polymerization procedure was as follows:

3-Vinyloxyethyl-5,5-dimethylhydantoin (HVE)	9.9 g (0.05 mol)
Maleic anhydride (MA)	4.9 g (0.05 mol)
AIBN	0.074 g (0.5 wt % based on monomers)
Cyclohexane + toluene	200 mL
Apparatus: 350 mL four-necked flask with stirrer, thermometer, condenser, and nitrogen inlet	

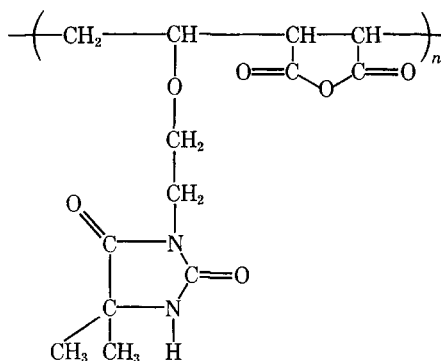
The apparatus was flushed twice with nitrogen and thereafter a light stream of nitrogen maintained throughout the polymerization. The polymer which precipitated from the monomer/initiator solution was filtered under vacuum and dried under reduced pressure at 50°C to constant weight.

The polymer was purified by repeated solution/precipitation from acetone/methanol until GC analysis of the mother liquor no longer showed any traces of monomer. The infrared spectrum (KBr) showed the following signals:

<u>Maleic anhydride</u>	<u>Hydantoin ring</u>
1860/1780 cm <sup>-1</sup> (1222): $\nu$ C=O	3400 cm <sup>-1</sup> $\nu$ N—H
928 cm <sup>-1</sup> : $\nu$ C—O—C	2980/2940 } cm <sup>-1</sup> $\nu$ aliphatic C—H
	2880 }
	1710 cm <sup>-1</sup> $\nu$ C=O

The <sup>13</sup>C spectrum showed a broad signal at 76.6 ppm, which was allocated to the asymmetric  $\alpha$ -C atom of the hydantoin-vinylether moiety and several transitions between 168 and 174 ppm, which were allocated to the carbonyl of the maleic

anhydride group. Both observations were interpreted as an indication that the steric configuration of the assumed 1:1 repeating unit (below) is not uniform.



### Polyamide/Ammonium Salt (PAAS)

The polyanhydride was suspended in benzene or trichloroethylene and anhydrous ammonia bubbled into the suspension until a sample taken from the suspension was completely water soluble. The salt was filtered, dried at 50°C to constant weight and purified by repeated precipitation in acetone/water. Infrared allocations (KBr):

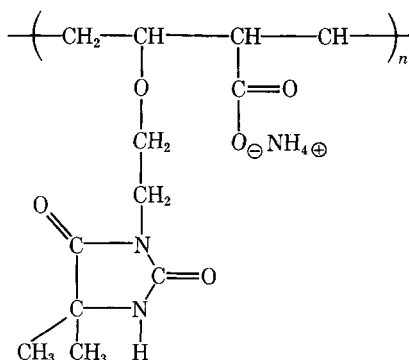
$$3420/3200 - 2800 \text{ cm}^{-1} : \nu \text{ N—H} + \overset{\oplus}{\text{N}}\text{H}_4$$

$$\left. \begin{array}{l} 1768 \text{ cm}^{-1} \nu \text{ C=O} \\ 1710 \text{ cm}^{-1} \nu \text{ C=O} \end{array} \right\} \text{hydantoin ring}$$

$$1670 \text{ cm}^{-1} \nu \text{ C=O amide}$$

$$\left. \begin{array}{l} 1580 \text{ cm}^{-1} \\ 1400 \text{ cm}^{-1} \end{array} \right\} (\text{COO}^-) \begin{array}{l} \nu \text{ asymm.} \\ \nu \text{ symm.} \end{array}$$

$$1100/1070 \text{ cm}^{-1} \nu \text{ C—O—C}$$



### Copolymerization Parameters

The copolymerizations were carried out in toluene at 60°C with AIBN as initiator and were terminated by cooling to 0°C. Copolymer yields were within

the range 4–11%. The polymers were filtered, dried at 50–55°C under vacuum, and then repeatedly precipitated from DMF/acetone until gas-chromatographic analysis of the mother liquor no longer showed any trace of monomers. Copolymer composition was then determined via nitrogen analysis.

### Reference Materials

Poly(vinyl pyrrolidone) (PVP) and poly(methylvinylether)/maleic-anhydride (MVE/MA) were obtained commercially and used as supplied. The specific viscosities of the samples obtained, measured according to the procedure outlined below, were as follows:

PVP “low molecular weight grade”:0.27

PVP “high molecular weight grade”:1.76

MVE/MA “low molecular weight grade”:0.90

MVE/MA “high molecular weight grade”:8.17

### Complexing Capability

Complexing capability was determined as the ability to solubilize and complex iodine. Iodine was chosen as representative for the many dyestuffs, physiological and toxic chemicals which are solubilized and detoxified by the structurally similar polyvinylpyrrolidone.

Equal portions of sublimized, pulverized iodine were added to 1% aqueous polymer solutions kept under a sealed glass bell and the time until dissolution and “complexation” of the iodine portions had taken place noted, total test duration being limited to 150 h. “Complexation” was assumed to have taken place when the polymer/iodine solution had become colourless.

At this stage,  $I_2$  is no longer present in the solution, as can easily be demonstrated by solvent extraction and/or titration and is assumed to have been complexed by the polymer.

Polymers which had been tested together, under identical experimental conditions, were compared by comparing the slopes  $\Delta t/\Delta I_2$  of their respective  $t/I_2$  plots, as determined by linear regression. Statistically significant correlation coefficients  $> 0.99$  were obtained in all cases.

### Specific Viscosity

All (specific) viscosity measurements were carried out in dimethylformamide (pa) at 25°C in an Ubbelohde-type viscosimeter. The solution concentration was 1 g/100 mL in all cases.

### Viscosity and Pseudoplasticity

The measurements were carried out with a Brookfield Viscometer Model LVT at ambient temperature. The polymer solutions were compared pairwise, under identical experimental conditions. In the case of viscosity/time plots the solutions were not stirred between measurements.

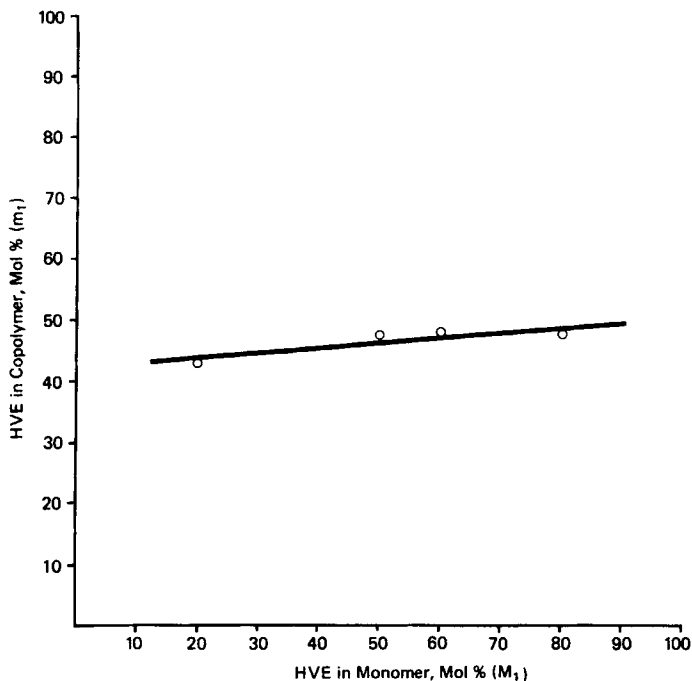


Fig. 1. Copolymerization composition curve of hydantoinvinylether (HVE) and maleic anhydride (MA) at 60°C in toluene.

## RESULTS AND DISCUSSION

### Copolymerization Parameters

Figure 1 shows the copolymerization composition curve in toluene at 60°C in which the ratio of hydantoinvinylether (HVE) to maleic anhydride (MA) was varied from 20/80 to 80/20. With the exception of the 20/80 experiment—in which the copolymer contained approximately 43 mol % of the HVE—the resulting copolymers were composed of both monomer components in equimolar amounts within a limit of  $\pm 5\%$ . This suggests an alternating—ABAB—polymerization.

The copolymerization parameters were determined according to the Fineman and Ross procedure.<sup>6</sup> Treatment of the experimental data according to

$$(F/f)(f - 1) = r_1 \cdot (F^2/f) - r_2 \quad (1)$$

[where  $F = M_1/M_2$  (monomer composition) and  $f = m_1/m_2$  (polymer composition)] gave the following parameters:

$$r_1 = -0.016$$

$$r_2 = 0.080$$

The  $r_1$  value is negative but close to zero. As neither  $r$  can be negative,  $r_1$  was assumed to be zero. For this case the following equation applies:

$$(1 - f) = r_2(f/F) \quad (2)$$

In this equation, when  $(1 - f)$  is plotted against  $f/F$ , the slope of the resulting straight line is equal to  $r_2$ . This new treatment of the data gave

$$r_1 = 0$$

$$r_2 = 0.06$$

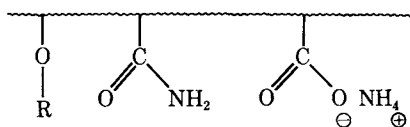
$r_2$  was calculated by linear regression. The correlation coefficient of the  $(1 - f)$  ( $f/F$ ) straight line was 0.98, and this value was statistically significant at the 95% level.

An alternating copolymerization between the HVE and MA monomers was to be expected. Classical copolymerization theory shows vinyl ethers in the lower right-hand corner of the  $\epsilon/q$  diagram, i.e., high induced negative charge and practically no resonance stabilization. Maleic anhydride on the other hand is at the top left of center of the diagram, i.e., high induced positive charge and relatively high resonance stabilization.<sup>7</sup>

### General

The starting point for the work described in this paper was the supposition that water-soluble hydantoin polymers should exhibit similar complexing properties to those of PVP. It is clear therefore that a comparison of the HVE/MA polymers with this reference polymer should be undertaken. As the HVE/MA polymers are, in a broader sense, vinyl ether/maleic anhydride polymers a comparison with the already existing methylvinylether/maleic anhydride (MVE/MA) products was also indicated. The specific viscosities of the reference products were measured and then HVE/MA polymers synthesized to match (i.e., HVE/MA polymers exhibiting  $\eta_{sp}$  values as close as possible to those of the reference products). These product pairs were then compared with regard to the key property in question.

PVP is directly water-soluble; the HVE/MA and MVE/MA polymers were tested in the form of their directly water-soluble amide/ammonium salts:



### Complexing Capability

Results are given in Table I. The numerical values given in Table I under the heading complexing capability are relative and represent the difference between the slopes of plots of "complexation time" against iodine concentration (see Experimental).

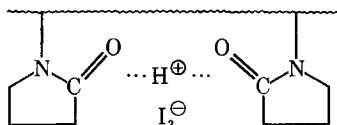
In the first part of the table the results obtained with a low molecular weight PVP polymer and an HVE/MA polymer with similar specific viscosity are given. The complexing capability of the HVE/MA polymer is almost three times higher than that of the corresponding PVP polymer. In the second comparison the HVE/MA polymer is almost 60% more efficient than its MVE/MA reference product. Finally, two HVE/MA polymers with different specific viscosities are

TABLE I  
 "Complexing Capability" of HVE/MA and Reference Polymers

Polymer	Specific Viscosity $\eta_{sp}^a$	Complexing capability (relative values)
PVP	0.27	100
HVE/MA	0.25	296
MVE/MA	0.90	100
HVE/MA	0.93	159
HVE/MA	0.93	100
HVE/MA	0.17	137

<sup>a</sup>  $\eta_{sp} = \eta_{sp}/c$  ( $c = 1$  g/100 mL).

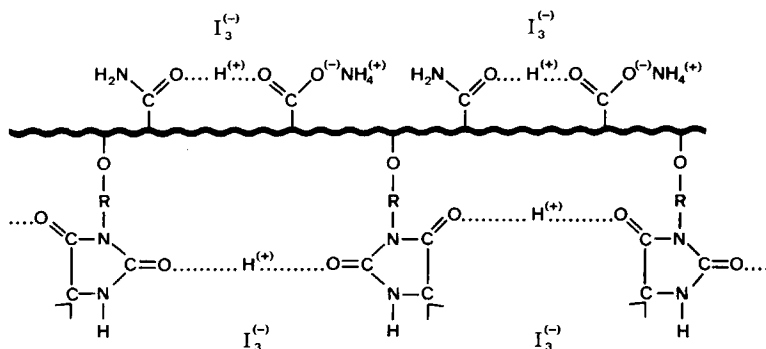
compared. The results indicate that the complexing capability of the HVE/MA copolymer can be enhanced by decreasing the specific viscosity. The complexing capability of PVP is well known in the literature.<sup>8-15</sup> With regard to the PVP/iodine complex in particular, detailed recent investigations have led to the proposal that a PVP/H<sup>+</sup>/I<sub>3</sub><sup>-</sup> complex is formed in which the proton is held between two PVP-carbonyl groups via hydrogen bonding<sup>16,17</sup>:



If this is indeed so, then the HVE/MA polymer might offer additional hydrogen bonding possibilities as shown in Scheme I.

Here each HVE/MA repeating unit would offer hydrogen bonding facilities for 1½ protons as opposed to ½ proton in the case of PVP. This might conceivably be the theoretical explanation for the superior complexing ability of the HVE/MA polymers when compared to PVP.

The MVE/MA polymers are known to be iodine complexing agents. The exact nature of the MVE/MA-iodine bond has not been revealed, but it has been suggested that the complexing effect is due to the fact that the MVE/MA polymers contain a substantial amount of oxygen.<sup>18</sup> (It is possible that the authors

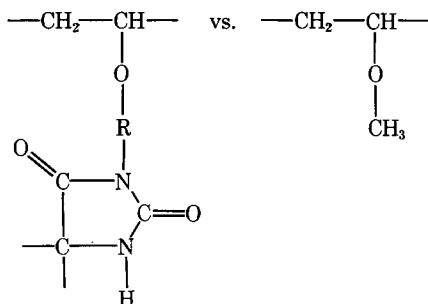


Scheme I.



are referring to hydrogen bonding via the two free electron pairs of the oxygen atom.)

The HVE/MA polymer should, *a priori*, offer the same "oxygen" complexing capacity plus additional complexing contributions from the lactam groups of the hydantoin ring:



(the amide/ammonium group being, of course, the same for both polymers.)

### Viscosity and Pseudoplasticity

Figure 2 shows viscosity (2.5% solution) against rpm (Brookfield) for a "high molecular weight" PVP polymer and an HVE/MA polymer with approximately

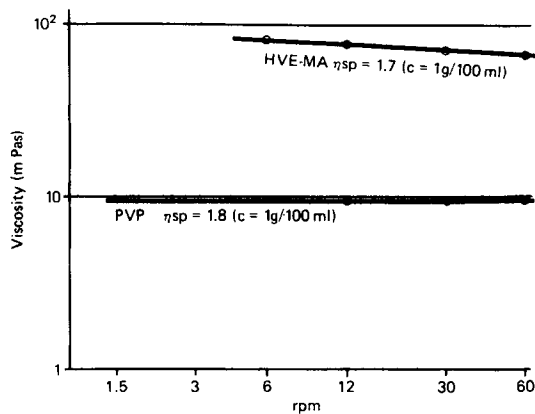
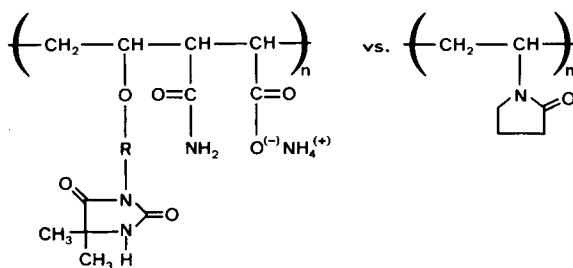


Fig. 2. Viscosity (2.5% aqueous solutions) against rpm (Brookfield) for a "high molecular weight" poly(vinyl pyrrolidone) (PVP) polymer and a hydantoinvinylether/maleic anhydride (HVE/MA) copolymer with approximately the same specific viscosity.

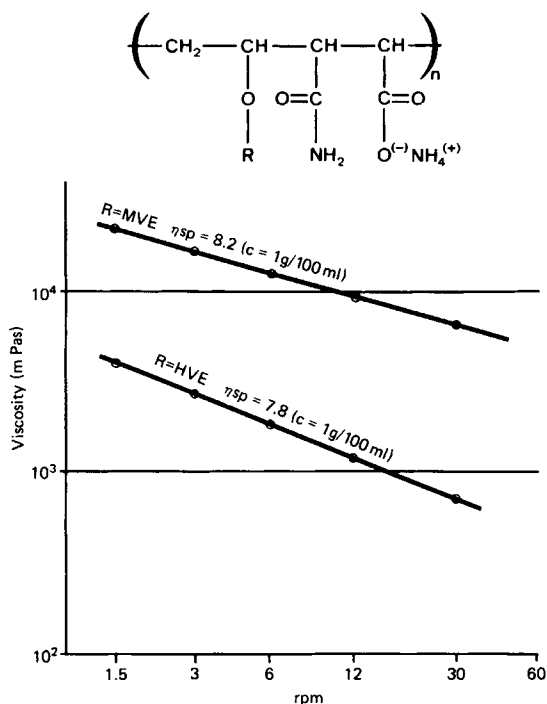


Fig. 3. Viscosity (2.5% aqueous solutions) against rpm (Brookfield) for a "high molecular weight" methylvinylether/polyamide-ammonium salt (R = MVE) and a hydantoinvinylether/polyamide-ammonium salt (R = HVE) with approximately the same specific viscosity.

the same specific viscosity. The two polymers show different solution viscosities with that of the hydantoin polymer being approximately eight times higher. The HVE/MA polymer has two pendant lactam groups in the form of the hydantoin ring plus an amide and an ammonium group per repeating unit as opposed to the one lactam group in the case of PVP. All three pendant groups in the HVE/MA polymer backbone are probably contributing to solution viscosity, with the ammonium groups likely to be making the largest contribution. The PVP polymer shows no pseudoplasticity, the HVE/MA polymer a slight dependency of viscosity on shear.

In Figure 3 the viscosity and pseudoplasticity of a "high molecular weight" methylvinylether polymer with a HVE/MA polymer of approximately the same specific viscosity are compared. The two polymers show almost the same degree of pseudoplasticity but the thickening efficiency of the MVE polymer is clearly superior.

Figure 4 shows viscosity against time for the same two polymers. It is interesting to note that the MVE polymer solution shows a pronounced decrease, whereas the HVE polymer solution shows practically no change in viscosity over the 8-week period of observation. Taking the difference in initial solution viscosity first and assuming that our match of specific viscosities ( $\pm 5\%$ ) is good enough in order not to bias the result, we have the vinylether moiety R as the only differing factor between the two polymers. It is not felt that either the methyl or ethyl-hydantoin groups *per se* could be making a major contribution towards

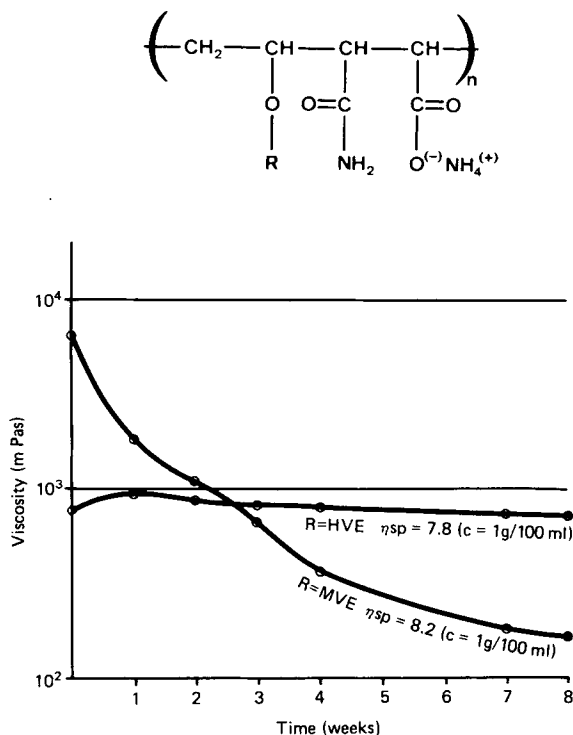


Fig. 4. Viscosity (2.5% aqueous solutions) against time (without stirring between measurements) for a "high molecular weight" methylvinylether/polyamide-ammonium salt ( $R = \text{MVE}$ ) and a hydantoinvinylether/polyamide-ammonium salt ( $R = \text{HVE}$ ) with approximately the same specific viscosity.

the solution viscosity. Polyanions, on the other hand, are known to produce a marked thickening effect when dissolved in water. This is generally attributed to electrostatic repulsion along the polymer coil. This repulsion is supposed to lead to a pronounced expansion of the coil and thus to an increase in hydrodynamic volume.<sup>19</sup>

In addition, there is the so-called "electroviscous effect" mainly caused by the repulsion between the ionic shells of different polymer coils.<sup>19</sup> If this line of thinking is correct, it might be concluded that the hydantoin moiety is in some way hindering or lessening intra- or intermolecular repulsion possibly via association with the copendant amide groups.

Association may, indeed, be the explanation for the difference in viscosity/time dependence observed for the two polymer solutions (Fig. 4). The suggestion here would be that the solution viscosity of the MVE/MA polymer is attributable solely to electrostatic repulsion. With time the polymer coils in solution might rearrange in such a manner that electrostatic repulsion is considerably reduced—thus the reduction in hydrodynamic volume and, consequently, in solution viscosity. One would also expect electrostatic repulsion to be primarily responsible for solution viscosity in the case of the HVE/MA polymer. Here, however, lactam/amide association might be making an additional, largely time-independent, contribution to solution viscosity.

## CONCLUSION

The new HVE/MA polymers have been compared with PVP and MVE/MA polymers with regard to complexing capability and solution viscosity. These two properties were singled out because it was felt that they are, *inter alia*, the key to a vast number of different applications in which the state of the art PVP and MVE/MA polymers are used.

In the first case (i.e., complexing capability) the HVE/MA polymers have proven to be clearly more effective. With regard to solution viscosity they showed higher values than PVP. When compared to MVE/MA, solution viscosity was lower initially but considerably higher after standing for a longer period of time, i.e., the inverse viscosity/time relationship observed for the MVE/MA polymer was not apparent in the case of HVE/MA. This effect could be of interest for certain applications.

As only products with practically identical specific viscosities have been compared, thereby eliminating molecular weight as a bias, it seems reasonable to assume that the improvements shown by the HVE/MA polymers are due to their unique chemical structure.

As mentioned at the beginning of this paper, PVP's success as an extremely versatile speciality polymer is based on its almost universal complexing ability—this last being attributed to the pendant lactam group. The active element behind the success of the MVE/MA polymers is, in all probability, the pendant anhydride group. In the HVE/MA polymers these two structural elements have, in effect, been combined: (2) lactam groups, in the form of the hydantoin ring, plus the anhydride group. Results seem to indicate that this combination is more effective than either one of these groups alone or, schematically: lactam + anhydride > lactam alone and lactam + anhydride > methyl + anhydride.

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