

INVESTIGATIONS ON VINYLENE CARBONATE I. PREPARATION AND PROPERTIES OF POLY-(VINYLENE CARBONATE)

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ABSTRACT

Bulk polymerization of vinylene carbonate using *t*-butylperoxypivalate at 40 °C gave colourless, high molecular weight poly(vinylene carbonate) (PVCA). Solutions of PVCA in acetone and DMF are not stable at 25 °C and this degradation was studied. From measurements in DMF with unfractionated PVCA a Mark-Houwink equation was obtained:

$$[\eta] \text{ (dl g}^{-1}\text{)} = 1.63 \times 10^{-4} \overline{M}_w^{0.736}$$

INTRODUCTION

Free radical polymerization of vinylene carbonate (VCA) was first studied by Newman and Addor^[1] and had been reported by Field and Schaeffgen^[2] to result in high molecular weight poly(vinylene carbonate) (PVCA).

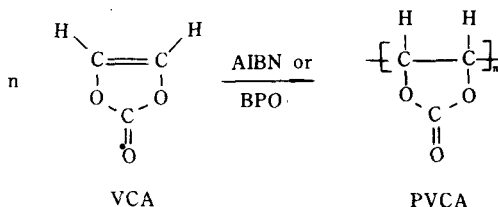


Fig.1 Structure of VCA and PVCA

The reactivity of the carbonate groups in PVCA offers the possibility of using various reactions to form new 1,2-disubstituted carbon chain polymers. Hydrolysis of PVCA yields poly(hydroxymethylene) (PHM), a polymer with a high degree of hydrogen bonding and reminiscent of cellulose in its solubility behaviour^[3]. Polymers with hydroxyl and carbamate groups were obtained from the reaction of PVCA with compounds containing amino groups^[2,4,5], whereas PVCA was converted into a polyelectrolyte after reaction with propansultone in a

strongly alkaline medium^[6].

Recently we started our research on PVCA and PHM (and copolymers of VCA) in order to investigate possible applications of these polymers, making use of the reactivity of the carbonate groups.

This paper gives details about the preparation and polymerization of VCA, resulting in PVCA with a substantially higher molecular weight than obtained by Field and Schaeffgen^[2]. Because it had been reported that PVCA degraded when dissolved in DMF at elevated temperatures^[2], the behaviour of PVCA in DMF (and also in acetone) was studied. Molecular weights of PVCA, reported by Field and Schaeffgen, were determined from η_{inh} and a $[\eta]-\overline{M}_n$ relationship given for solutions in acetone of low molecular weight PVCA (11,000–44,500)^[7]. Although PVCA ($\overline{M}_w = 150,000$) has been fractionated by Schulz and Vollkommer^[8], no Mark–Houwink equation has been reported. Therefore, in our study fractionation of high molecular weight PVCA was carried out and the relationship of $[\eta]$ vs. $\overline{M}_w$ in DMF was investigated. A detailed report about the synthesis of vinylene carbonate (VCA) will also be given because the polymerisation products had considerably improved properties compared to those mentioned in the literature^[8].

EXPERIMENTAL

Synthesis of vinylene carbonate (VCA)

A. Chloroethylene carbonate

Ethylene carbonate (500 g, 5.70 mol) was dissolved in 1000 ml CCl_4 and at $62 \pm 1^\circ\text{C}$ an equivalent amount of chlorine gas was introduced at a rate of 600 ml/min (UV lamp 350 W). After the chlorination a two phase liquid reaction product was obtained. The lower phase mainly consisted of CCl_4 with a small amount of chloroethylene carbonate, dichloroethylene carbonate and traces of CCl_4 . The monochloro compound was isolated by fractional distillation with a 60 cm Widmer column (b.p. $102-104^\circ\text{C}/10\text{ mm Hg}$; $n_D^{25} = 1.4520$). Yield 473 g (68%). $^1\text{H-NMR}$: 1.01 Cl/molecule chloroethylene carbonate.

B. Vinylene carbonate

Chloroethylene carbonate (360 g, 2.94 mol), 360 ml dry ethyl acetate and 3.2 g di-*t*-butyl-*p*-cresol were mixed and 448 ml (3.28 mol) triethylamine was added dropwise at 20°C with stirring. The heat of the reaction caused the temperature to increase, cooling was necessary to keep the temperature at 20°C . A voluminous precipitate of the amine salt was formed and the colour of the reaction mixture became dark brown. The mixture was heated at 55°C for 20 h and stirring became increasingly difficult. The precipitate was collected and washed 4 times with ethyl acetate, each time with 320 ml. The filtrate and washings were combined and the ethyl acetate was removed by distillation at 40°C (30 mm Hg). The remaining liquid was refluxed for purification with 4 g of NaBH_4 for 1 h at $64^\circ\text{C}/35\text{ mm Hg}$ and was fractionally distilled with a 30 cm Widmer column at 53.5°C and 13 mm Hg. After 5 h the distilled VCA became light brown and was treated again with NaBH_4 under the same conditions. After distillation

colourless VCA was obtained: 115.5 g (45.7%), $n_D^{20} = 1.4190$, m. p. 20.5°C . This product remained colourless in the refrigerator during 6 months and could still be used for polymerization yielding high molecular weight PVCA.

Polymerization of VCA

Different amounts of AIBN or *t*-butylperoxypivalate (Trigonox 25 — 75°C , AKZO, Deventer, The Netherlands) were dissolved in 20 g VCA in thick walled glass tubes. The tube contents were degassed by freezing and evacuating (5 — 6 times). After cooling for the last time, the tubes were evacuated and sealed prior to polymerization. After the polymerization the tube contents were dissolved in 500 ml DMF and the polymers were precipitated into 3000 ml ethanol and dried.

Fractionation of PVCA

10g PVCA (Exp. 7, Table 1) were dissolved in 500 ml DMF and subsequently 1500 ml of ethanol was added dropwise with stirring at 20°C . To this 0.5% solution a further 500 ml of ethanol was added dropwise under stirring. The solution became turbid and was heated to 30°C after which the PVCA dissolved. The solution was kept overnight at 20°C , the supernatant liquid was decanted and the viscous residue was dissolved in DMF (3 — 5%). This solution was dropped into a tenfold amount of ethanol with stirring. The precipitate was isolated by filtration, washed with ethanol and dried in vacuum at 20°C until constant weight. In this way six fractions could be obtained.

Viscometry and molecular weight determination

For the viscometric measurements, PVCA samples were used in concentrations of 0.1 — 0.5% at 25°C using an Ubbelohde viscometer.

Solutions of PVCA (0.05 — 0.25%) in DMF at 25°C were used for the weight average molecular weight determinations ($dn/dc = 0.076$, 25°C , KMX-6-LALLS apparatus).

RESULTS AND DISCUSSION

Polymerization of VCA

Data about the polymerization of VCA are given in Table 1.

Table 1 Free radical bulk polymerization of VCA^a

Exp.	Initiator (mol%)	Temp. ($^\circ\text{C}$)	Time (h)	Colour	Yield (%)	$[\eta]^c$ (dl g ⁻¹)	$[\eta]^f$ (dl g ⁻¹)
1	0.04 ^b	63	18	yellow	72	2.00	
2	0.07 ^b	63	18	yellow	76	2.33	
3	0.09 ^b	63	18	yellow	76	2.59	
4	0.52 ^b	60	18	brown	61	1.11	0.77
5	0.52 ^b	50	48	yellow	63	3.21	
6	0.26 ^b	24	24	yellow	48	1.02	0.60
7	0.25 ^b	40	72	colourless transparent	74	4.10	

^a 20 g monomer, ^b AIBN; ^c UV lamp 10W, 254 nm; ^d *t*-butylperoxypivalate; ^e in DMF, 25°C ; ^f in acetone, 25°C

At low AIBN concentration polymers were obtained with a high $[\eta]$ (Table 1, exp. 1 — 3). These polymers were only partially soluble in DMF and were slightly coloured because the heat of reaction was low as the result of the relatively

low polymerization rate. However, the properties of these polymers were better than those in ref. 1 and 2 as far as colour, yield and intrinsic viscosities are concerned. At higher initiator concentration (exp. 4) and at a higher temperature (60 °C) the obtained PVCA was brown, indicating heat instability of the polymer. With the same AIBN concentration (exp. 5) but at a lower temperature (50 °C), only slightly yellowish coloured PVCA was obtained, with a higher molecular weight. Using UV, the decomposition temperature could be lowered, however, the results shown in Table 1 (exp. 6) indicate that even at 24 °C chain degradation had taken place under the influence of UV.

It is obvious from Table 1 that using AIBN at various temperatures always coloured products were obtained. However, polymerization of VCA with *t*-butylperoxypivalate at 40 °C resulted in colourless PVCA (exp. 7) in a high yield and with a considerably higher molecular weight than obtained in the other experiments.

Behaviour of PVCA in acetone and in DMF

Acetone and DMF are good solvents for PVCA. It has been reported^[2] that acetone has only a limited solubility for PVCA (about 1%) with an $\eta_{inh} > 100 \text{ ml g}^{-1}$ whereas we observed that the solubility was higher than 1%, with an η_{inh} of 1340 ml g^{-1} in a 0.5% solution. There are reasons to assume that the PVCA used by the authors had a lower solubility due to partial hydrolysis.

As part of our study on PVCA we were interested in the evaluation of a $[\eta] - \bar{M}_w$ relationship for PVCA in acetone and in DMF. A $[\eta] - \bar{M}_n$ relationship for solutions in acetone of unfractionated PVCA has been published^[7] for molecular weights from 11,000 — 44,500. However, solutions of our PVCA samples in acetone had much higher η_{red} values and we therefore could not use this Mark-Houwink relationship.

PVCA (Table 1, exp. 7) was fractionated using DMF/ethanol in a similar way as had been described by Schulz and Vollkommer^[8]. Data about the fractions are shown in Table 2.

Table 2 Fractionation of PVCA with DMF /ethanol

Fraction	Weight (g)	η_{inh}^a
unfractionated	10.0	4.31
7-F1	0.9	13.40
7-F2	1.3	7.04
7-F3	1.3	4.46
7-F4	1.5	2.41
7-F5	1.3	1.26
7-F6	0.6	0.64

^a dl g^{-1} , $C = 0.5\%$ (W/W), acetone, 25 °C

Study of the relationship between η_{red} and C for PVCA fractions in acetone gave results as shown in Fig. 2.

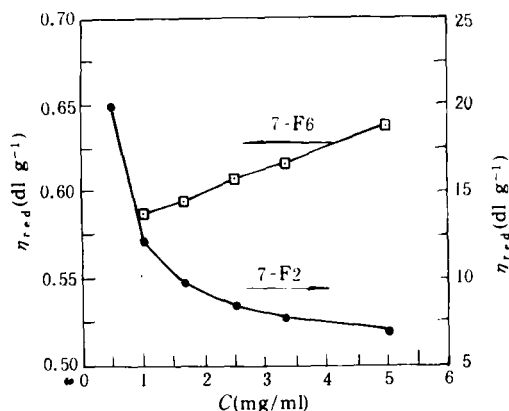


Fig. 2 Relationship between η_{red} and C of PVCA with different molecular weight (acetone, 25 °C)

Solutions of 7-6F in acetone showed a linear relationship of η_{red} with concentration ($[\eta] = 0.58 \text{ dl g}^{-1}$, $\overline{M}_w = 113,500$). However, with higher molecular weight PVCA in acetone (e. g. 7-F2) a decrease of η_{red} with increasing concentration was observed.

This anomalous behaviour of PVCA solutions of higher concentrations is possibly due to association of PVCA molecules in acetone, because in acetone a lower $[\eta]$ was observed than in DMF (Table 1, exp. 4 and 6).

Because of this phenomenon, acetone was not suitable for the evaluation of a Mark-Houwink relationship for PVCA with molecular weights higher than about 120,000 Daltons. Moreover, acetone could not be used because of another reasons. Solutions of PVCA in acetone showed a substantial decrease of the viscosity as a function of time, indicating a degradation of the polymer chains (Fig. 3).

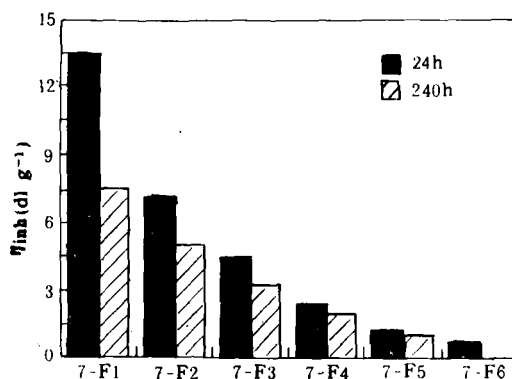


Fig. 3 Degradation of PVCA in acetone at 25 °C (η_{inh} at $C=0.5\%$ (W/W))

In contrast to the results obtained with acetone as a solvent, solutions of PVCA in DMF showed a linear relationship of η_{red} vs. C , irrespective of the molecular weight of the fractions. Obviously in DMF the interaction between solvent

and polymer molecules is less molecular weight dependent than in acetone.

Because viscometric measurements indicated a degradation of PVCA in acetone, solutions of PVCA in DMF were also studied, although degradation of PVCA in DMF had only been observed at elevated temperatures^[2]. During fractionation of PVCA with DMF /methanol, Schulz and Vollkommer used temperatures of 45—50 °C, but no reports were given about degradation of PVCA^[8]. Viscosities of solutions of PVCA in DMF were measured at 25 °C as a function of time (Fig. 4).

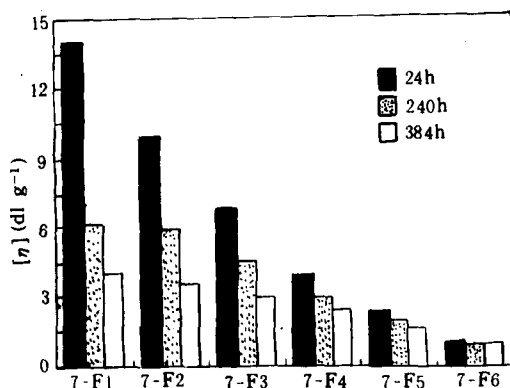


Fig. 4 Degradation of PVCA in DMF at 25 °C

The results show that DMF had a similar effect on PVCA as acetone and that degradation in DMF had occurred even at 25 °C. Degradation of PVCA molecules in acetone and in DMF might be the result of a considerable steric hindrance because the carbon atoms in the PVCA backbone are also part of the five-membered rings. Such rigid polymer chains will easily be broken in solution especially in strong polar solvents, resulting in degradation of the polymer chains. Degradation of PVCA in DMF was observed as a function of time which meant that degradation had also taken place during the fractionation (10 days), resulting in a change of the molecular weight distribution. Therefore $[\eta]$'s and weight average molecular weights were determined with unfractionated PVCA samples after 1 day in DMF at 25 °C. The polymers were obtained by bulk polymerization of VCA using different monomer/initiator ratios (cf. exp. 7, Table 1).

Table 3 $[\eta]$ and $\overline{M}_w$ for unfractionated PVCA

Polymer	$[\eta]^a, b$	$\overline{M}_w^b$	$\log [\eta]$	$\log \overline{M}_w$
P1	1.83	323.000	0.262	5.509
P2	2.18	405.000	0.338	5.607
P3	2.42	465.000	0.384	5.667
P4	3.17	680.000	0.501	5.833

^a dl g⁻¹; ^b in DMF, 25 °C, after 1 day

The data from Table 3 were plotted in Fig. 5 and a Mark-Houwink relationship was calculated as the following equation,

$$[\eta](\text{dl g}^{-1}) = 1.63 \times 10^{-4} \overline{M}_w^{0.736}$$

to be used for molecular weights from 300,000 — 700,000 Daltons.

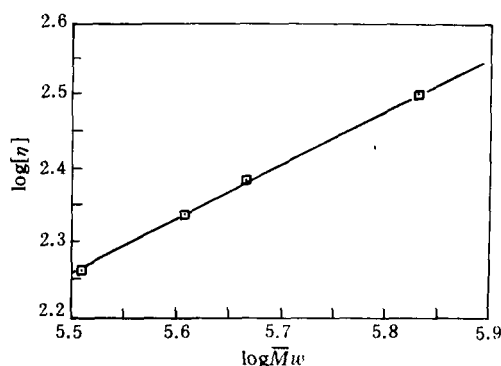


Fig. 5 $\log[\eta]$ vs. $\log \bar{M}_w$ for unfractionated PVCA in DMF, 25 °C

Field and Schaeffen^[2] mentioned the possibility of obtaining PVCA with a $\bar{M}_n > 10^6$. This assumption was based upon viscosity measurements in DMF with $n_{inh} \geq 2 \text{ dl g}^{-1}$. However, assuming their η_{inh} to be equal to $[\eta]$, we calculated with our M-H equation a molecular weight of 360,000. This value is quite different from that of Field and Schaeffen and it is likely that their calculation was incorrect.

The value for α in the Mark-Houwink equation is not unexpected when looking at the molecular structure of PVCA. In addition this value is in accordance with the observation that DMF is a good solvent for PVCA.

CONCLUSIONS

From the results of the polymerizations of VCA, it is obvious that the temperature and the initiator concentration play an important role for the quality of the polymer. Colourless, high molecular weight PVCA could be obtained in high yields in contrast with results reported in the literature.

PVCA dissolved in acetone or DMF appeared to be strongly susceptible to degradation, which was shown by viscosimetry. Using PVCA samples with weight average molecular weights from 300,000 — 700,000 a Mark-Houwink relationship was found: $[\eta] (\text{dl g}^{-1}) = 1.63 \times 10^4 \bar{M}_w^{0.736}$ (DMF, 25 °C).

Keywords:

Vinylene carbonate, Polymerization, High Molecular Weight, Degradation, Mark-Houwink Equation.

REFERENCES

- [1] Newman, M. S. and Addor, R. W., *J. Am. Chem. Soc.*, **1955** 77, 3789.
- [2] Field, N. D. and Schaeffen, J. R., *J. Polym. Sci.*, **1962**; 58, 533. *Macromol. Synth.*, **1966** 2, 15.
- [3] Hass, H. C. and Schuler, N. W., *J. Polym. Sci.* **1958** 31, 237.
- [4] Nemirowsky, V. D. and Skorokhodov, S. S., *J. Polym. Sci., Part C* **1967** 16, 1471.
- [5] Dynamit Nobel A-G, *Neth. Appl.* 6, 601, 339, **1966**, *Chem. Abstr.*, 3354a, **1967**.
- [6] Schulz, R. C. and Vollkommer, N., *Macromol. Chem.*, **1970**, 133, 307.
- [7] Smets, G. and Hayashi, K., *J. Polym. Sci.*, **1958** 29, 257.
- [8] Schulz, R. C. and Vollkommer, N., *Macromol. Chem.*, **1968** 116, 288.