

## Investigations on vinylene carbonate, 2<sup>a)</sup>

### Copolymerization with *N*-vinyl-2-pyrrolidone and ethyl vinyl ether

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#### Introduction

Functional monomers and polymers have received considerable attention in recent years, especially in the biomedical field. In this respect, poly(vinylene carbonate) is very interesting, because the reactive carbonate groups offer the possibility of coupling with bioactive compounds containing amino groups, e. g. proteins or enzymes. Copolymerization of vinylene carbonate with other vinyl monomers will affect the amount of carbonate groups as well as other properties of the copolymers. In a previous paper we described the preparation and properties of poly(vinylene carbonate)<sup>1)</sup>, and this paper reports the copolymerization of vinylene carbonate with *N*-vinyl-2-pyrrolidone and with ethyl vinyl ether.

Radical copolymerization of vinylene carbonate (VCA) was first reported by Price and Padbury<sup>2)</sup>. Several investigations on copolymerization of VCA with vinyl monomers were carried out, and in some cases the monomer reactivity ratios were determined<sup>3,4)</sup>. Copolymers of VCA (1) with vinyl compounds (2) in general contain only small amounts of VCA ( $r_1 < 1$  and  $r_2 > 1$ ) and show more or less characteristics of an ideal copolymerization ( $r_1 = 1/r_2$ ). The radical copolymerization of VCA with isobutyl vinyl ether, on the other hand, leads to predominantly alternating copolymers<sup>5)</sup>. However, in all these copolymerizations a relatively low reactivity of VCA was observed, due to the 1,2-disubstitution of the vinylene group.

Hayashi and Smets<sup>3)</sup> already studied the copolymerization of VCA (1) with *N*-vinyl-2-pyrrolidone (2), and they reported for the reactivity ratios:  $r_1 = 0,4$  and  $r_2 = 0,7$ , which means that, e. g. with 90 mol-% of VCA in the feed, an instantaneous copolymer composition of 80 mol-% VCA could be obtained. Because we were interested in high-molecular-weight copolymers containing high amounts of VCA, since this kind of materials might be interesting in biomedical applications (e. g. when grafted on polymeric surfaces), and because poly(*N*-vinyl-2-pyrrolidone) is known to be a good biocompatible polymer, copolymerization of VCA with *N*-vinyl-2-pyrrolidone (NVP) was studied. In addition to NVP, being a hydrophilic monomer, the less hydrophilic ethyl vinyl ether (EVE) was copolymerized with VCA, in order to study the

<sup>a)</sup> Part 1: cf. ref. 1)

effect of the difference in hydrophilicity on the properties of the copolymer and the influence of EVE on the arrangement of the monomeric units along the polymer chain.

## Experimental part

**Materials:** *N*-vinyl-2-pyrrolidone (NVP; Merck, Darmstadt, West Germany) and ethyl vinyl ether (EVE; Merck, Darmstadt, West Germany) were purified by distillation. Vinylene carbonate (VCA) was prepared according to a modification<sup>1)</sup> of the synthesis from ethylene carbonate as described previously<sup>6,7)</sup>. 2,2'-Azobisisobutyronitrile (AIBN; J. T. Baker, Deventer, The Netherlands) and *tert*-butyl peroxyvalate (Trigonox 25-75 C; AKZO, Deventer, The Netherlands) were used as received. Acetone (Merck, Darmstadt, West Germany), used as a solvent in the polymerization reactions, was distilled before use. Non-solvents, used for precipitating the copolymers, were of analytical grade.

**Methods:** Copolymers from VCA with NVP were obtained by solution polymerization in acetone at 50°C for 72 h in the presence of 0,25 mol-% of AIBN. Different amounts of both monomers were dissolved in acetone in thick-walled glass tubes, and after adding the initiator, the tube contents were degassed by freezing in liquid nitrogen and evacuating (3-4 times). After cooling the last time, the tubes were evacuated, sealed, and the polymerization was carried out by heating the tubes in an oil bath. The resulting products were precipitated in an excess of non-solvent (diethyl ether or ethyl acetate), filtered through a glass filter, washed several times, and dried in an oven at 40°C i. vac. for one night.

Solution polymerization of VCA with EVE was performed in acetone ( $[VCA] + [EVE] = 20 \text{ mol/L}$ ) at 50°C with 0,25 mol-% of *tert*-butyl peroxyvalate, according to the procedure described above. The copolymers produced were precipitated in an excess of diethyl ether. Overall conversions were kept low and never exceeded 15 wt.-%.

Copolymer compositions were calculated from <sup>1</sup>H NMR spectra recorded on a 200 MHz Nicolet NMR spectrometer (DMSO-*d*<sub>6</sub> as a solvent) and/or by elemental analysis (C, H or N). Viscometric measurements were carried out with solutions of poly(VCA-*co*-NVP) in freshly distilled *N,N*-dimethylformamide, using an Ubbelohde-type viscometer at 25°C. Limiting viscosity numbers  $[\eta]$  were evaluated by extrapolation to zero concentration (concentration range 1-5 mg/mL)<sup>8)</sup>.

## Results and discussion

### Poly(VCA-*co*-NVP)

Some characteristics of the synthesized VCA-NVP copolymers are listed in Tabs. 1 and 2. From Tab. 1 it can be seen that increasing the monomer feed concentration resulted in a marked increase in the limiting viscosity numbers,  $[\eta]$ . The effect of monomer feed composition upon the copolymerization is shown in Tab. 2.

From the data shown in Tabs. 1 and 2, it can be concluded that copolymerization of VCA with NVP resulted in copolymers with substantial amounts of VCA, depending on the reaction conditions. However, copolymers with higher contents of VCA were not obtained, and we therefore decided to reconsider the *r*-values, as given by Hayashi and Smets<sup>3)</sup> ( $r_1 = 0,4$  and  $r_2 = 0,7$ ). In doing so, our attention was attracted by the fact that the azeotropic composition  $F_{1,AZ}$ , as suggested in their copolymerization diagram, conflicted with the azeotropic composition calculated from the reactivity ratios given by Hayashi and Smets:  $F_{1,AZ} \equiv (1 - r_2)/(2 - r_1 - r_2) = 0,33$ . This is best illustrated by Fig. 1 in which both the experimental data of Hayashi and Smets and the curve corresponding to  $r_1 = 0,4$  and  $r_2 = 0,7$  are plotted. Hayashi and Smets

Tab. 1. Effect of monomer feed concentration upon the copolymerization of vinylene carbonate (VCA) (1) with *N*-vinyl-2-pyrrolidone (NVP) (2)<sup>a)</sup>

	Experiment number			
	1	2	3	4
Mass of VCA in g	4,27	4,36	4,32	4,68
Mass of NVP in g	5,70	5,58	5,62	5,97
([VCA] + [NVP])/(mol/L)	10	20	30	54
Yield of copolymer in g	6,92	8,00	7,94	8,62
in wt.-%	69	80	80	81
$F_1$ <sup>b)</sup>	0,32	0,37	0,36	0,39
Conversion of VCA in %	43	57	56	61
$[\eta]/(\text{dL} \cdot \text{g}^{-1})$ <sup>c)</sup>	0,73	1,82	2,05	2,39

a) Mole fraction of VCA in the monomer feed  $f_1 = 0,50$ .

b) Mole fraction of VCA in the copolymer, determined via elemental analysis.

c) Determined in *N,N*-dimethylformamide at 25 °C.

Tab. 2. Effect of monomer feed composition upon the copolymerization of vinylene carbonate (VCA) (1) with *N*-vinyl-2-pyrrolidone (NVP) (2)<sup>a)</sup>

	Experiment number					
	5	6	7	2	8	9
Mass of VCA in g	0,84	1,28	1,77	4,36	2,58	3,44
Mass of NVP in g	4,45	3,92	3,60	5,58	2,22	1,11
$f_1$ <sup>b)</sup>	0,20	0,30	0,39	0,50	0,60	0,80
Yield of copolymer in g	3,78	3,98	4,46	8,00	3,43	3,16
in wt.-%	71	77	83	80	71	69
$F_1$ <sup>c)</sup>	0,20	0,09	0,18	0,37	0,44	0,64
Conversion of VCA in %	73	22	37	57	50	53
$[\eta]/(\text{dL} \cdot \text{g}^{-1})$ <sup>d)</sup>	1,28	1,44	1,68	1,82	1,45	1,03

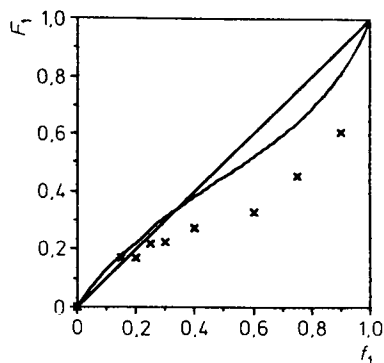
a) [VCA] + [NVP] = 20 mol/L.

b) Mole fraction of VCA in the monomer feed.

c) Mole fraction of VCA in the copolymer, determined via elemental analysis.

d) Determined in *N,N*-dimethylformamide at 25 °C.

Fig. 1. Mole fraction of VCA (1) in poly(VCA-co-NVP),  $F_1$ , vs. mole fraction of VCA in the monomer feed,  $f_1$ . ×: Experimental data by Hayashi and Smets<sup>3)</sup>; —: Curve based on  $r_1 = 0,4$  and  $r_2 = 0,7$



calculated the reactivity ratios by using the copolymer composition equation. However, after a trial and error procedure with their data and this equation, we found for the reactivity ratios  $r_1 \approx 0,05$  and  $r_2 \approx 1$ . These recalculated  $r$ -values are in agreement with the values more recently reported by Greenley<sup>9)</sup>:  $r_1 = 0,055$  and  $r_2 = 1,082$ . When applying the method of Kelen and Tüdös<sup>10)</sup> (KT-method) to the data of Hayashi and Smets, we calculated the  $r$ -values as  $r_1 = 0,01$  and  $r_2 = 0,94$ . Although Greenley also calculated the  $r$ -values from the data of Hayashi and Smets using the KT-method, still some deviation occurs from the  $r$ -values we calculated, which may be explained by the fact that the KT-curve did not show a good fit with the experimental data of Hayashi and Smets (regression coefficient = 0,90). More accurate  $r$ -values can only be obtained by using more experimental data over a wider range of monomer feed compositions than Hayashi and Smets used.

### Poly(VCA-co-EVE)

The results of the copolymerizations of VCA with EVE are listed in Tab. 3. The reactivity ratios for the VCA-EVE system were deduced from the composition data derived from the NMR-spectra (using the data from all samples except from experiment 12 because of the deviation between the  $F_1$ -values from NMR-data and from carbon content determination via elemental analysis) by two graphical methods, according to Fineman and Ross (FR)<sup>11)</sup>, and Kelen and Tüdös<sup>b)</sup>.

The monomer reactivity ratios deduced from the plots based on these two methods are presented in Tab. 4. From this table it can be shown that both methods lead to about

Tab. 3. Copolymerization of vinylene carbonate (VCA) (1) with ethyl vinyl ether (EVE) (2)<sup>a)</sup> (for explanation of symbols see Tab. 2)

	Experiment number						
	10	11	12	13	14	15	16
Mass of VCA in g	0,88	1,73	2,60	3,46	4,30	6,04	7,81
Mass of EVE in g	6,48	5,75	5,07	4,32	3,60	2,16	0,76
$f_1$	0,10	0,20	0,30	0,40	0,50	0,70	0,90
Yield of copolymer in g	0,60	1,04	0,55	0,61	0,47	0,55	0,89
in wt.-%	8,2	13,9	7,2	7,8	5,9	6,7	10,4
C-content in %	58,2	56,1	53,4	54,0	53,1	51,4	48,6
H-content in %	8,3	7,5	6,8	6,9	6,4	5,9	5,0
$F_1$ <sup>b)</sup>	0,27	0,37	0,40	0,46	0,49	0,54	0,67
$F_1$ <sup>c)</sup>	0,30	0,38	0,49	0,47	0,50	0,57	0,69
$f_{VCA}$ <sup>d)</sup> (after polymerization)	0,09	0,17	0,29	0,40	0,50	0,71	0,92
Conversion of VCA in %	20,9	24,8	9,4	8,9	5,8	5,3	8,1
Conversion of EVE in %	6,4	10,6	6,0	7,0	6,0	10,6	34,2

a)  $[VCA] + [EVE] = 20 \text{ mol/L}$ .

b) Calculated from NMR data.

c) Calculated from C-content determination via elemental analysis.

d) Calculated from the initial amount of VCA minus amount of VCA in the copolymer.

Tab. 4. Reactivity ratios  $r_1$  and  $r_2$  for the copolymerization of vinylene carbonate (1) with ethyl vinyl ether (2)

Calculation method	$r_1$	$r_2$	Regression coefficient
Fineman-Ross-1 <sup>a)</sup>	0,12	0,19	1,00
Fineman-Ross-2 <sup>a)</sup>	0,13	0,19	1,00
Kelen-Tüdös	0,11	0,19	1,00

<sup>a)</sup> Based on two different Fineman-Ross equations, given in ref. <sup>11)</sup>.

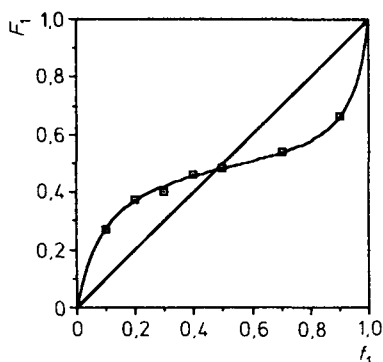


Fig. 2. Mole fraction of VCA (1) in poly(VCA-co-EVE),  $F_1$ , vs. mole fraction of VCA in the monomer feed,  $f_1$  (curve based on  $r_1 = 0,11$  and  $r_2 = 0,19$ )

the same results. Although there was no considerable deviation between the corresponding  $r$ -values derived from two different FR-equations, which is usually the case, because the experimental data are unequally weighted by the FR-equations, the reactivity ratios as calculated with the KT-method were used in further calculations.

The copolymer composition curve, calculated with  $r_1 = 0,11$  and  $r_2 = 0,19$ , is shown in Fig. 2, along with the experimental data. It should be noted that in our calculation of the reactivity ratios the initial, instead of the average monomer feed ratio was used, which is not recommended by some authors because of the error introduced <sup>12)</sup>. However, recalculation of the monomer reactivity ratios with the KT-method using the average monomer feed ratio resulted in only relatively small deviations in the  $r$ -values:  $r_1 = 0,11$  and  $r_2 = 0,17$ .

It can be demonstrated, e.g. by calculating diad and triad fractions using the nomograph of Izu and O'Driscoll <sup>13)</sup> that VCA-EVE copolymers have predominantly alternating structure, because fractions of alternating diads and triads exceed 0,80 and 0,65, respectively, for a wide range of monomer feed compositions (from  $f_1 = 0,30$  to  $f_1 = 0,70$ ). This behaviour of VCA in the polymerization with EVE is in agreement with previously reported data on the copolymerization of VCA with another vinyl ether, viz. isobutyl vinyl ether <sup>5)</sup>.

## Conclusions

Solution polymerization in acetone at 50 °C in the presence of 2,2'-azoisobutyronitrile is a suitable route for the synthesis of high-molecular-weight VCA-NVP copolymers. Reconsidering the work of Hayashi and Smets, it appeared that the curve in their copolymerization diagram is not in accordance with the reported  $r$ -values. Based on our recalculations, it can only be concluded that the copolymerization of VCA (1) with NVP (2) meets the general rule for copolymerizations of VCA with more reactive vinyl compounds:  $r_1 < 1$  and  $r_2 > 1$ . From the reactivity ratios for the copolymerization of VCA (1) with EVE (2) ( $r_1 = 0,11$  and  $r_2 = 0,19$ ) it is clear that the copolymers show an increasing tendency towards alternation as well as they contain relatively larger amounts of VCA compared with other copolymers of VCA.

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- 1) J. X. Huang, G. H. Chen, E. J. Tijsma, L. van der Does, A. Bantjes, *Chin. J. Polym. Sci.*, in press
- 2) U.S. 2 722 525 (1955), American Cyanamid Company, invs.: J. A. Price, J. I. Padbury; *Chem. Abstr.* **50**, 3011h (1956)
- 3) K. Hayashi, G. Smets, *J. Polym. Sci.* **27**, 275 (1958)
- 4) J. M. Judge, C. C. Price, *J. Polym. Sci.* **41**, 435 (1959)
- 5) R. C. Schulz, R. Wolf, *Kolloid Z. Z. Polym.* **220**, 148 (1967)
- 6) N. D. Field, J. R. Schaeffgen, *J. Polym. Sci.* **58**, 533 (1962)
- 7) M. S. Newman, R. W. Addor, *J. Am. Chem. Soc.* **75**, 1263 (1953)
- 8) J. F. Rabek, "Experimental Methods in Polymer Chemistry", John Wiley & Sons, Chichester-Toronto 1980, p. 127
- 9) R. Z. Greenley, *J. Macromol. Sci., Chem.* **A14**, 445 (1980)
- 10) T. Kelen, F. Tüdös, *J. Macromol. Sci., Chem.* **A9**, 1 (1975)
- 11) M. Fineman, S. Ross, *J. Polym. Sci.* **5**, 259 (1950)
- 12) F. L. M. Hautus, H. N. Linssen, A. L. German, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 3487 (1984)
- 13) M. Izu, K. F. O'Driscoll, *J. Appl. Polym. Sci.* **14**, 1515 (1970)