

Copolymerization of Vinylene Carbonate

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The synthesis and some peculiar reactions of vinylene carbonate (VC) have been described recently by Newman and Addor.¹ From the organic point of view, vinylene carbonate acts as a dienophile in several Diels-Alder reactions, in spite of the absence of any conjugated carbonyl group with respect to the double bond. On polymerization by heating in the presence of benzoyl peroxide or azobisisobutyronitrile, high molecular weight polyvinylene carbonate can be obtained despite the symmetric 1,2 disubstitution of the olefinic bond. It seemed, therefore, interesting to characterize further the double bond of vinylene carbonate with the aid of copolymerization experiments, which offer the possibility of determining more quantitatively the polarity and the reactivity of the double bond.

Therefore, in the present paper, the results of the copolymerization of vinylene carbonate with several comonomers are described and their interpretation given. Moreover, some solubility properties of hydrolyzed co(vinyl acetate-VC) polymers will be examined in more detail.

I. COPOLYMERIZATION OF VINYLENE CARBONATE

(1) Experimental Results

(a) With Vinyl Acetate

The rate of copolymerization of VC with vinyl acetate has been followed dilatometrically at different molar ratios of both monomers in acetone solution at 70°C. In each experiment, the concentration of azobisisobutyronitrile (AIBN) was kept constant (0.024 mole/l.), while the total molar concentration of both monomers was always equal to 4.23 mole/liter. The copolymers were precipitated in dry ether, redissolved in acetone, and reprecipitated by pouring the solution in petroleum ether. After drying at 40°C. *in vacuo* at constant weight, the copolymers were analyzed by infrared spectrometry using the vinyl acetate $>\text{C}=\text{O}$ absorption band 5.77μ as analytical band. (The $>\text{C}=\text{O}$ band of VC, located at 5.46μ shifts by polymerization to 5.53μ .) The results of these experiments are given in Table I. The corresponding copolymerization diagram is given by curve (a) of Figure 1. The r_1 and r_2 reactivity ratios, calculated with the integrated equation are $r_1=3.0$, $r_2=0.27$. In regard to vinyl

TABLE I
Copolymerization of VC-Vinyl Acetate at 70°C.

(AIBN), 0.024 mole/l. $[(M_1) + (M_2)] = 4.23$ mole/l. Solvent, acetone.

Molar fract. VC in monomers	Molar fract. VC in copolymer	Yield, %	Time, min.	Rate, mole/l. sec. ⁻¹ $\times 10^4$
1.000	1.000	14.4	225	0.232
0.797	0.585	29.4	185	0.94
0.627	0.440	30.3	152	1.33
0.517	0.270	28.8	91	2.04
0.406	0.225	32.8	84	2.96
0.215	0.080	32.3	63	5.02
0.000	0.000	29.2	45	8.63

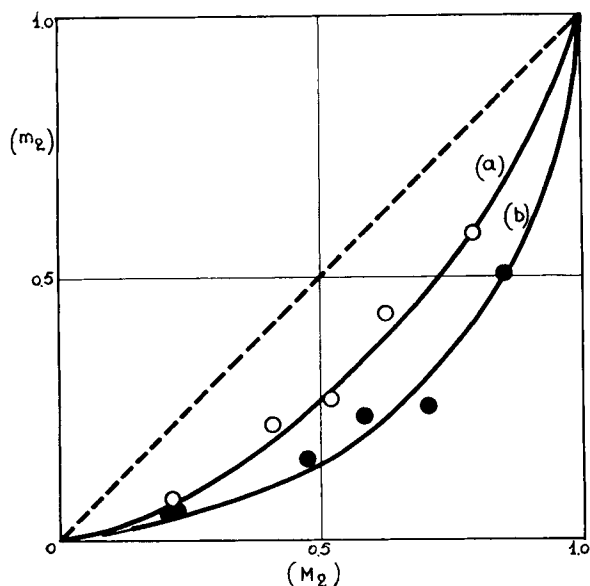


Fig. 1. Copolymerization of vinylene carbonate (M_2) with (a) vinyl acetate, (b) vinyl chloride.

acetate ($Q=0.028$ and $e=-0.3$)² the corresponding values of VC are equal to $Q=0.008$ and $e=-0.76$. From these r_1 and r_2 values and from the rate measurements described in Table I, $\delta_2/\delta_1=37.2$ the cross-termination rate constant:

$$\Phi = k_{t_{12}}/2(k_{t_{11}}k_{t_{22}})^{1/2}$$

may be estimated to about 1.

(b) With Vinyl Chloride

The experimental conditions and the results of the different experiments are given in Table II. The copolymers were precipitated in methanol and

TABLE II
Copolymerization of VC-Vinyl Chloride in Acetone at 80°C.

Molar fract. VC in monomers	Molar fract. VC in copolymer	Yield, %	Time, min.	(AIBN), mole/l.	[M ₁] + [M ₂], mole/l.
0.207	0.0535	33.6	55	0.033	8.7
0.224	0.0678	22.8	35	0.033	8.8
0.473	0.154	28.3	60	0.035	8.4
0.581	0.242	22.9	100	0.037	10.4
0.702	0.258	17.9	120	0.038	9.5
0.857	0.512	14.4	200	0.038	10.3

dried at constant weight *in vacuo*. Analysis of the copolymers was carried out by halogen determination following the method of Wurzschnitt.³ The corresponding diagram is given by curve (b) of Figure 1.

Using the integrated equation, the reactivity ratios r_1 and r_2 have been evaluated, respectively, as 5.2 and 0.09 (Fig. I, curve b). In regard to the Q and e values adopted for vinyl chloride, one finds:

Q	e	Vinyl chloride		
		Q	e	Ref.
0.004	-0.66	0.024	0.2	4
0.010	-0.46	0.074	0.4	2,5

(c) *With Methyl Methacrylate*

The rate of copolymerization of VC with methyl methacrylate has been measured at different molar ratios of both monomers in acetone solution at 70°C. In each experiment, the concentration of AIBN was 0.024 mole/l., while the total molar concentration of both monomers was always equal to 4.23 mole/l. After precipitation in ether, the polymers were redissolved

TABLE III
Copolymerization of VC-Methyl Methacrylate at 70°C.

(AIBN), 0.024 mole/l. $[(M_1) + (M_2)] = 4.23$ mole/l. Solvent, acetone.

Molar fract. VC in monomers	Molar fract. VC in copolymer	Yield, %	Time, min.	Rate, mole/l. sec. ⁻¹ $\times 10^4$
1.000	1.00	14.4	225	0.232
0.850	0.0776	12.9	179	1.15
0.712	0.0174	22.1	81	2.19
0.500	0.01	24.6	50	3.50
0.326	—	24.0	33	5.13
0.164	—	21.6	24	6.60
0.000	—	27.7	27	8.98

in acetone and reprecipitated in methanol. Their composition was determined, considering the intensity of the $>\text{C}=\text{O}$ absorption band ($5.77\ \mu$) of methyl methacrylate (Table III).

From these data, r_1 and r_2 were evaluated to 70.0 and 0.005; the value of ϕ , the cross-termination constant (calculated therefrom as from the rate measurements (δ_2/δ_1) = 38.8) must be very high (~ 100).

(d) *With Vinylpyrrolidone*

Copolymerization experiments of vinylpyrrolidone with VC were carried out and compared to similar experiments with vinyl acetate. In both cases, the copolymers were isolated by pouring the reaction mixture into dry ether; this procedure was repeated twice. The copolymers were dried at room temperature *in vacuo* in the presence of P_2O_5 ; their composition was determined by a nitrogen analysis (Kjeldahl). The results are given in Tables IV and V.

TABLE IV

Copolymerization of VC-Vinylpyrrolidone at 60°C.

(AIBN), 0.037 mole/l. $[(M_1) + (M_2)] = 5.77$ mole/l. Solvent, acetone.

Molar fract. VC in monomers	Molar fract. VC in copolymer	Time, min.	Yield, % (mole)
0.00	0	240	77.1
0.15	0.167	78	5.2
0.20	0.172	80	5.0
0.25	0.218	90	4.6
0.30	0.224	90	4.8
0.40	0.272	120	3.2
0.60	0.328	420	8.0
0.75	0.452	700	6.5
0.90	0.608	1110	5.5

TABLE V

Copolymerization of Vinyl Acetate-Vinylpyrrolidone at 70°C.

(AIBN), 0.02 mole/l. $[(M_1) + (M_2)] = 5.77$ mole/l. Solvent, acetone.

Molar fract. Vin-OAc in monomers	Molar fract. Vin-OAc in copolymer	Time, min.	Yield, % (mole)
0.228	0.201	23	20.4
0.440	0.327	35	27.6
0.589	0.463	47	29.1
0.730	0.592	58	32.2
0.865	0.800	68	36.8

The corresponding copolymerization diagrams are given in Figure 2, where the composition of the copolymer is plotted as a function of composi-

tion of the initial monomer concentration. The r_1 and r_2 values have been calculated by the differential equation for the CO(VC-vinylpyrrolidone)

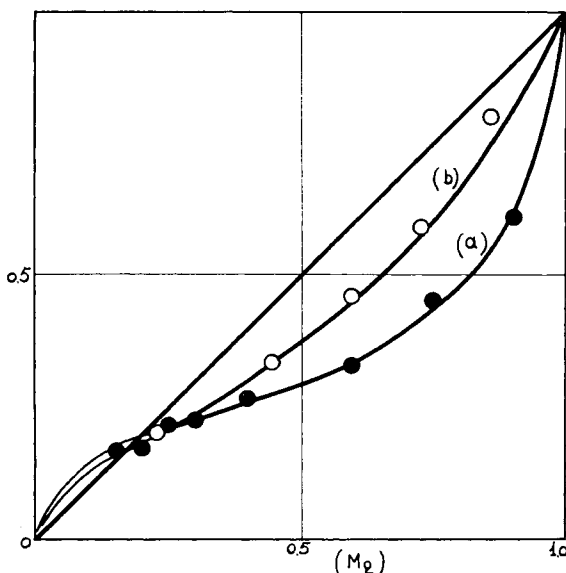


Fig. 2. Copolymerization of vinylpyrrolidone (M_1) with (a) vinylene carbonate, (b) vinyl acetate.

polymerization, while the integrated equation has been used for the second system.

$r_1 = 0.7$ and $r_2 = 0.4$ for the system vinylpyrrolidone (M_1) - VC (M_2).

$r_1 = 0.44$ and $r_2 = 0.38$ for the system vinylpyrrolidone (M_1) - vinyl acetate (M_2).

For vinyl acetate ($Q = 0.028$ and $e = -0.3$), the corresponding values of vinylpyrrolidone are $Q = 0.11$ and $e = -1.64$, while the values of VC indicate $Q = 0.025$ and $e = -0.51$.

From the experiments of Breitenbach and Edelhauser⁶ on the copolymerization of vinyl chloride (M_1) - vinylpyrrolidone (M_2), in which $r_1 = 0.53$ and $r_2 = 0.38$, values of $Q = 0.048$ and $e = -1.07$ are found for vinylpyrrolidone.

(e) With Styrene

Some experiments have been carried out in toluene solution at 85°C. at a total monomer concentration of 4.90 mole/l. in the presence of (AIBN) = 0.014 mole/l. The copolymers were precipitated in methanol, redissolved in acetone, and reprecipitated in methyl alcohol; their composition was determined by infrared spectrometry (14.30 μ phenyl-CH absorption band). See Table VI.

TABLE VI
Copolymerization of VC-Styrene at 85°C.

(AIBN), 0.014 mole/l. $[(M_1) + (M_2)] = 4.90$ mole/l. Solvent, toluene.

Molar fract. VC in monomers	Molar fract. VC in copolymer	Time, hr.	Yield, %
0.890	0.130	48	2.9
0.545	0.022	23	21.5

(f) *With Maleic Anhydride*

The yields of the copolymerization reactions are always very low; this must be attributed to important steric effects due to the ring structure of both monomers, and to a chemical reaction between both monomers, as shown by measuring the amount of carbon dioxide evolved during the reaction.

(2) **Interpretation**

The copolymerization reactivity ratios of vinylene carbonate with the different comonomers are summarized in Table VII. The very high value

TABLE VII
Copolymerization Reactivity Ratios of Vinylene Carbonate

r_2	r_1	Comonomer (M_1)	Cross-termination rate const. ^a
0.27	3.0	Vinyl acetate	1
0.09	5.2	Vinyl chloride	
(0.005)	(70)	Methyl methacrylate	Very high (~ 100)
0.4	0.7	Vinylpyrrolidone	

of the cross-termination rate constant with respect to methyl methacrylate must be related to the opposite sign of the polarities of both monomers (MMe: + 0.4; VC: -0.6).

TABLE VIII
Reactivity and Polarity of Vinylene Carbonate

Vinylene carbonate		Comonomer	
Q	e	Q	e
0.008	-0.76	0.028	-0.3 vinyl acetate ²
0.004	-0.66	0.024	0.2 vinyl chloride ²
0.010	-0.46	0.074	0.4 vinyl chloride ^{2,5}
0.025	-0.51	0.11	-1.64 vinylpyrrolidone ^a
(0.020)	(0.06)	(0.048)	(-1.07) vinylpyrrolidone ⁶
Mean 0.012	-0.60		

^a Q and e values obtained from the r_1 and r_2 values (0.44 and 0.38) of vinylpyrrolidone-vinyl acetate copolymers.

The values of the reactivity Q and the polarity e of the double bond of VC calculated therefrom in agreement with the Alfrey-Price equation⁷ depend on the nature of the comonomer and on the corresponding Q and e values admitted for this latter (Table VIII). The very low reactivity of vinylene carbonate results from the cyclic structure and the symmetric disubstitution of the double bond. In comparison with vinylacetate, the negativity of the double bond is more pronounced, as could be expected by the simultaneous presence of two electron donor groups.

II. CO(VINYLENE ALCOHOL-VINYL ALCOHOL) POLYMERS

Polyvinylene carbonate was hydrolyzed in acetone-water solution (85/-15) either in acid or in alkaline medium. After precipitation by addition of ethanol and further purification of the polymer, the polyalcohol, $(\text{CHOH})_x$, is completely insoluble in H_2O , in dimethyl formamide, and even in Schweizer's cuprammonium solution. This insolubility was attributed to the existence of strong intermolecular hydrogen bonding, and possibly to the presence of some crosslinking due to ether $-\text{O}-$ bridge formation.

Contrarily, co(vinylene carbonate-vinyl acetate) polymers yield on alkaline hydrolysis copolymers which are soluble in water if the vinylene alcohol content is relatively low.

Viscometric and osmotic measurements on aqueous solutions of the hydrolyzed copolymers show, however, that the Huggins k' constants⁹ and the slopes of the osmotic diagrams of the reduced osmotic pressure as a function of the concentration (χ_1 values¹⁰) decrease with increasing vinylene

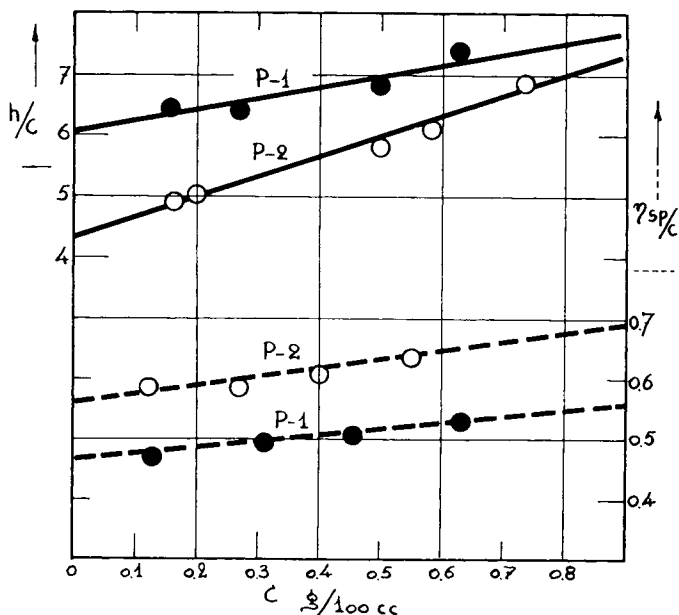


Fig. 3. Viscometric and osmotic diagrams of co(vinylene alcohol-vinyl alcohol) polymers.

TABLE IX
Viscosity and Osmotic Pressure Measurements in Aqueous Solution at 25°C.

	Molar fract. VC in copolymer ^a	(η) hydrolyzed copolymer	k'	MW ^b (osm. press.)	ξ^c
P-1.....	0.342	0.47	0.41	41.200	0.478
P-2.....	0.082	0.56	0.54	58.300	0.461

^a Determined by infrared spectrometry on the C=O band (5.77 μ) before hydrolysis.

^b Fuoss-Mead osmometer with cellulose membrane ("Membran Gesellschaft Göttingen").

^c Density of the polymer = 1.3.

alcohol content (Table IX, Fig. 3). These results are in agreement with an increasing tendency of association of the polymer molecule as a consequence of a higher concentration of —CHOH— groups.

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Synopsis

The copolymerization of vinylene carbonate VC (M_2) with several vinyl monomers (M_1) has been examined. The reactivity ratios r_2 and r_1 have been determined in the systems VC-vinyl acetate (0.27 and 3.0), VC-vinyl chloride (0.09 and 5.2), VC-vinylpyrrolidone (0.4 and 0.7), VC-methyl methacrylate (<0.01 and ~ 70). These values indicate for vinylene carbonate in the Alfrey-Price scheme a reactivity Q equal to 0.012 and a polarity e of -0.6 . From the r_1 and r_2 parameters of the system vinyl acetate-vinylpyrrolidone (0.38 and 0.44, respectively) the Q and e values of vinylpyrrolidone have also been determined: $Q = 0.11$ and $e = -1.6$. The copolymers of vinylene carbonate and vinyl acetate yield on hydrolysis polyalcohols $-(CH_2CHOH)_x-(CHOH)_y-$ of which the solubility decreases with increasing content of hydroxyl groups.

Résumé

On a étudié la copolymérisation du carbonate de vinyène VC (M_2) avec plusieurs monomères vinylique (M_1). Les rapports de réactivité r_2 et r_1 ont été déterminés dans

les systèmes VC-acétate de vinyle (0,27 et 3,0), VC-chlorure de vinyle (0,09 et 5,2), VC-vinylpyrrolidone (0,4 et 0,7), VC-méthacrylate de méthyle ($<0,01$ et ~ 70). Ces valeurs permettent d'attribuer au carbonate de vinylène une réactivité $Q = 0,012$ et une polarité $e = -0,6$, conformément au schéma d'Alfrey-Price. Aux dépens des paramètres r_1 et r_2 de la copolymérisation acétate de vinyle-vinylpyrrolidone (0,38 et 0,44 respectivement), on peut calculer pour la vinylpyrrolidone une réactivité et une polarité, égales à $Q = 0,11$ et $e = -1,6$. La copolymérisation de carbonate de vinylène et d'acétate de vinyle permet d'obtenir après hydrolyse des polyalcools $-(CH_2-CHOH)_x-(CHOH)_y-$ dont la solubilité décroît avec une teneur croissante en groupes oxyhydriles.

Zusammenfassung

Die Copolymerisation von Vinylencarbonat VC (M_2) mit mehreren Vinylmonomeren (M_1) wurde untersucht. Die Reaktivitätsverhältnisse r_2 und r_1 wurden in den Systemen VC-Vinylacetat (0,27 und 3,0), VC-Vinylchlorid (0,09 und 5,2), VC-Vinylpyrrolidon (0,4 und 0,7) und VC-Methylmethacrylat ($<0,01$ und ~ 70) bestimmt. Diese Werte erlauben es, dem Vinylencarbonat eine Reaktivität $Q = 0,012$ und eine Polarität $e = -0,6$ in Übereinstimmung mit dem Alfrey-Price-Schema zuzuschreiben. Mittels der Parameter r_1 und r_2 der Copolymerisation von Vinylacetat-Vinylpyrrolidon (0,38 und 0,44) kann man für Vinylpyrrolidon eine Reaktivität und eine Polarität von $Q = 0,11$ und $e = -1,6$ berechnen. Die Copolymerisation von Vinylencarbonat und Vinylacetat führt nach Hydrolyse zur Erhaltung von Polyalkoholen $-(CH_2CHOH)_x-(CHOH)_y-$ deren Löslichkeit mit zunehmendem Gehalt an Oxyhydrilgruppen abnimmt.

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