Poly(vinyl chloroformate) and derivatives: 2. Copolymerization of vinyl chloroformate and of phenyl vinyl carbonate with vinyl monomers

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Vinyl chloroformate and phenyl vinyl carbonate have been copolymerized with vinyl acetate in methylene chloride at 35°C, using dicyclohexylperoxydicarbonate as initiator. The copolymerization parameters obtained show that vinyl chloroformate and vinyl acetate have nearly the same reactivity whereas phenyl vinyl carbonate is slightly less reactive than vinyl acetate.

Keywords Vinyl chloroformate; phenyl vinyl carbonate; vinyl acetate; copolymerization; reactivity ratios; characterization

INTRODUCTION

Few investigations have been made on the copolymerization of vinyl chloroformate ($CH_2=CHOCOCl$: VOCCl) and of its derivatives like vinyl carbamates and vinyl carbonates. The copolymerization parameters of *N*-diethylvinyl carbamate ($CH_2=CHOCONEt_2$: $VOCNEt_2$) have been determined in bulk at 66°C with vinyl acetate (VAC) and with styrene[1], and in benzene at 80°C with acrylic acid, methyl acrylate and maleic anhydride[2], in the presence of free-radical initiators. $VOCNEt_2$ is much less reactive than styrene and shows a smaller copolymerization tendency than acrylic monomers and VAC. Reactivity ratios have been also determined for the copolymerization of ethyl vinyl carbonate (VOCOEt) with *p*-chlorostyrene and with VAC, in benzene at 60°C[3]. VOCOEt and VAC have nearly the same reactivity whereas *p*-chlorostyrene is much more reactive than VOCOEt. However, Schaefgen[4,5] carried out some copolymerization experiments of VOCCl with VAC and with acrylonitrile, in bulk at 0°C, using tri-n-butylboron as initiator. In the first system a substantial proportion of VOCCl units was found in the copolymer apart from about 30% homo poly(vinyl acetate). The copolymerization experiments with acrylonitrile were not rewarding, since less than 1% of the VOCCl units were found in the copolymer obtained with a low yield.

An advantage in copolymerizing VOCCl with a second monomer would be to introduce reactive sites that could be modified later on with dyes, drugs, cross-linking agents etc. We have recently shown that high molecular weight poly(vinyl chloroformates) (PVOCCl) can be prepared in high yields[6-9]. The best results are obtained in CH_2Cl_2 at 35°C, with peroxydicarbonates as initiators. It was found that these catalysts are also convenient for the polymerization of vinyl carbamates and vinyl carbonates[6,8,9]. This prompted us to examine in detail the copolymerization of VOCCl and of phenyl vinyl carbonate (VOCOPh) with VAC. The results are presented in this paper.

EXPERIMENTAL

VOCCl (Société Nationale des Poudres et Explosifs, purity >99%) and vinyl chloride (Rhône–Poulenc) were deinhibited by distillation in apparatus sealed under high vacuum just before their introduction into the polymerization vessel. VOCOPh, prepared by reaction of VOCCl with phenol[5,10], and VAC (Prolabo) were distilled under nitrogen. Styrene was purified over calcium hydride and several sodium mirrors. Monomers were sealed under high vacuum in tubes fitted with break-seals. Methylene chloride (SDS Pestipur) was purified on P_2O_5 and then on several sodium mirrors as described previously[11]. Dicyclohexylperoxydicarbonate (DCPD) was dried under high vacuum before use. A commercially available solution of tri-n-butylboron in THF (25% by volume) (Aldrich) was used without purification. Some preliminary experiments were made under argon in apparatus linked to a high vacuum line. Most of the experiments were performed in glass apparatus sealed under high vacuum. The copolymerization procedure was the same as that described for the homopolymerization of VOCCl[8,9]. Polymers were recovered after precipitation in petroleum ether and dried under high vacuum. All the copolymers containing VOCCl units were kept in sealed tubes at −30°C in the dark, in order to avoid degradation reactions. The composition of the copolymers was determined by elemental analysis and by ^1H n.m.r. In one experiment with VOCCl and VAC, the mixture of volatile products was recovered by distillation into a side flask fitted with a n.m.r. tube which was immersed in liquid nitrogen and then sealed under vacuum. The composition of the unreacted monomers was determined by ^1H n.m.r.

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Table 1 Copolymerization of VAC (M_1) with VOCCl (M_2) in bulk, initiated by tri-n-butylboron (Initiator/Monomers = 0.6% in volume)

					M_1 mole fraction in copolymer[a]	
Run	M_1 mole fraction in monomers	Temperature (°C)	Time (days)	Yield (%)	Soluble in benzene	Insoluble in benzene
1[b]	0.50	0	–	70	0.91 (30%)	0.29 (70%)
2	0.50	–80	3	96	– (<10%)	0.56 (>90%)
3	0.50	–80	3	60	– (<5%)	0.50_5 (>95%)

[a] Determined from chlorine content
[b] Ref: 7

Table 2 Copolymerization of VAC(M_1) and VOCCl(M_2) in CH_2Cl_2 at 35°C initiated by DCPD ([Initiator]/[Monomers] = 0.5% except for run 9: 0.23%)

					M_1 mole fraction in copolymer	
Run	$[M_1]_0 + [M_2]_0$ (mol l^{-1})	M_1 mole fraction in monomers	Time (h)	Yield (%)	From Cl %	From n.m.r.
4	2.40	0.83	1	43.3	0.81	0.80
5	2.32	0.58_5	1	17.4	0.55_5	0.58_5
6	2.43	0.49_5	0.75	20.6	0.50	0.50_5
7	2.40	0.39	0.50	12.1	0.43_5	0.45_5
8	2.31	0.20	0.55	11.8	0.25_5	0.24_5
9	10.86[a]	0.50	1.25	90.0	0.53	–

[a] In bulk

Copolymers were analysed by ^1H and ^{13}C n.m.r. with Jeol C-60 HL, Varian HA-100 and Cameca 250 spectrometers. G.p.c. measurements were performed in THF at 25°C using u.v. and refractometric detections.

RESULTS AND DISCUSSION

VOCCl Copolymers

Preliminary copolymerization experiments were conducted with VOCCl and VAC in conditions similar to those described by Schaefgen[5]. It can be seen from the results shown in *Table 1* that the copolymer composition is quite different from that obtained by Schaefgen. In spite of the discrepancy observed for the copolymer yields of runs 2 and 3 which is due to the fact that different batches of VOCCl were used, one can conclude that the percentage of polymer soluble in benzene, i.e. of homopoly(vinyl acetate), is very low. Moreover the composition of the copolymer obtained in run 3 is nearly the same as that of the initial feed. The results of run 2 are questionable since the chlorine content was determined 2 months after the experiment on a sample kept at room temperature in air, and we have since observed that the chlorine content of PVOCCl decreases with time if polymers are kept without special care.

More convenient conditions have been recently found for the polymerization of VOCCl[6-9]. Therefore, the copolymerization parameters of VOCCl and VAC were determined in CH_2Cl_2 at 35°C with dicyclohexyl peroxydicarbonate as initiator. The results are shown in *Table 2*. The molar composition of the copolymers was determined from chlorine content and by ^1H n.m.r. analysis from integrations of the peaks at 5 ppm (methine protons of the chains) and at 2 ppm (methylene protons of the chains and methyl protons of VAC units). Both methods gave the same results within experimental error and average values have been taken for the calculation of the reactivity ratios r_1 and r_2. Moreover, the VAC mole fraction in the copolymer of run 4 was also determined by ^1H n.m.r. analysis of the unreacted monomers. The value found by this method is equal to 0.80_5 and fits quite well with the values determine from chlorine content and from n.m.r. analysis of the copolymer.

The Kelen–Tüdös method extended to high-conversion data was used for the treatment of experimental data[12-14]. O'Driscoll *et al.*[15] have compared the precision of estimation of copolymerization reactivity ratios by different methods[15]. They concluded that for a new monomer pair, a linear method such as that of Kelen–Tüdös may be used. In the Kelen–Tüdös equation:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \qquad (1)$$

η and ξ are variables obtained from the charge and copolymer composition and α is a parameter which serves to distribute uniformly and symmetrically the experimental points between 0 and 1. The η *versus* ξ plot shown in *Figure 1* is linear and r_2 (i.e. r_2/α) and r_1 are obtained from the intercepts at $\xi = 0$ and $\xi = 1$, respectively, computed using the least squares method. The reactivity ratios r_1 (VAC) and r_2 (VOCCl) were found to be 0.7 ± 0.1 and 0.6 ± 0.1, respectively. The chloroformate units of a 50/50 copolymer were quantitatively modified by *N*-methylbenzylamine in order to obtain a more stable material which could be studied more easily[6,8,9]. The ^{13}C spectrum of this modified copolymer was recorded at 62.9 MHz, in 1,2,4-trichlorobenzene at 120°C. Assignments and chemical shifts of the different carbons are given in *Table 3* together with those for the corresponding homopolymers prepared and recorded in the same conditions. From the spectra relative to the methine and methylene carbons of the chains for the copolymer and the two homopolymers, it can be seen that the methine and methylene carbons resonances in the copolymer are quite different from those observed in the homopolymers. Effects due to stereosensitivity and to the vicinity of two different units are responsible for these complex resonances. It can be concluded that such a copolymer is presumably composed of randomly distributed VOCCl and VAC units. This conclusion was confirmed by the g.p.c. analysis of the same copolymer. Unimodal distributions were observed by using either refractometric or u.v. detection as shown in *Figure 2*. Moreover, the ratio of the responses given by these two types of detection was constant at any elution volume. This means that chromophores (i.e. benzene rings of carbamate units) are randomly distributed along the macromolecules. However, the copolymer composition was found to be the same over the whole range of molecular weights if one accepts that the extinction coefficient does not vary with the number of adjacent chromophores.

VOCCl and VAC have nearly the same reactivity. One can thus predict the behaviour of VOCCl with other comonomers from the results obtained for the copolymerization with VAC. For instance, styrene is much more reactive than VOCCl, as determined by the copolymerization of 50/50 mixture of these two monomers: only 3% of VOCCl units are present in the copolymer obtained at 25% yield. Vinyl chloride is also more reactive than VOCCl since the molar fraction of VOCCl in a copolymer obtained at 6% yield is equal to 25% while the initial molar monomers feed was 50/50. The results are shown in *Table 4*.

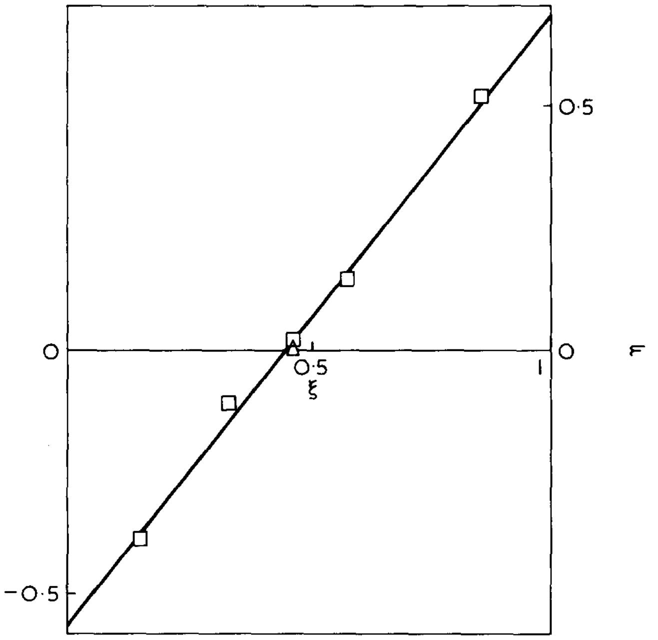

Figure 1 η *versus* ξ plot for the system: VAC/VOCCl/dicyclohexylperoxydicarbonate/CH_2Cl_2/35°C (Δ: in bulk)

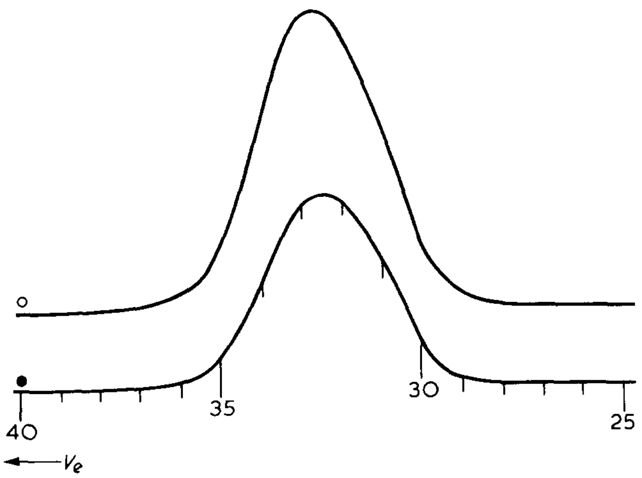

Figure 2 G.p.c. chromatograms for a 25/75 mol % VAC/VOCCl copolymer quantitatively modified by *N*-methylbenzylamine (○: u.v. detection; ●: refractometric detection)

Table 3 Chemical shifts (ppm from HMDS) of carbon atoms for a VAC/VOCCl copolymer (50/50) modified by *N*-methylbenzylamine (Spectra recorded at 62.9 MHz in $C_6H_3Cl_3$ at 120°C)

	>C=O		−CH−		−CH₂−			−CH₃	
Compound	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
PVAC	167.6	–	65.7 65.9 66.5	–	37.6 37.9 38.3	–	–	18.8	–
PVOCNMe Benzyl	–	154.1	–	67.5 67.8 68.2	–	38.4 38.8	51.0	–	32.0
Modified copolymer	167.6	154.0	66.2 66.9 67.1 67.4		38.0 38.4 38.7		50.9	18.9	31.9

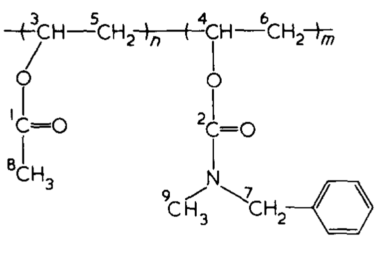

Table 4 Copolymerization of VOCCl (M_1) with styrene and with vinyl chloride (M_2) initiated by DCPD

Runs[a]	$[M_1]_0 + [M_2]_0$ (mol l^{-1})	M_1 mole fraction in monomers	[Initiator] / [Monomers]	Temperature (°C)	Time (h)	Yield (%)	M_1 mole fraction in copolymer[b]
10	9.69[c]	0.49	0.15%	40	72	25	0.03
11	4.60[d]	0.49	1%	35	1	6	0.25

[a] Run 10: M_2 = styrene; run 11: M_2 = vinyl chloride
[b] Determined from Cl%
[c] In bulk
[d] In CH_2Cl_2

Table 5 Copolymerization of VAC(M_1) and VOCOPh(M_2) in CH_2Cl_2 at 35°C initiated by DCPD ([Initiator]/[Monomers] = 0.5%)

Run	$[M_1]_0 + [M_2]_0$ (mol l^{-1})	M_1 mole fraction in monomers	Time (h)	Yield (%)	M_1 mole fraction in copolymer[a]
12	2.19	0.79	0.5	2.5	0.79_5
13	2.13	0.59	2	4.9	0.63
14	2.16	0.49_5	4.5	21.2	0.54
15	2.21	0.39_5	2.5	3.2	0.52
16	2.15	0.24	3.3	4.8	0.36

[a] Determined by ^1H n.m.r. on the copolymer

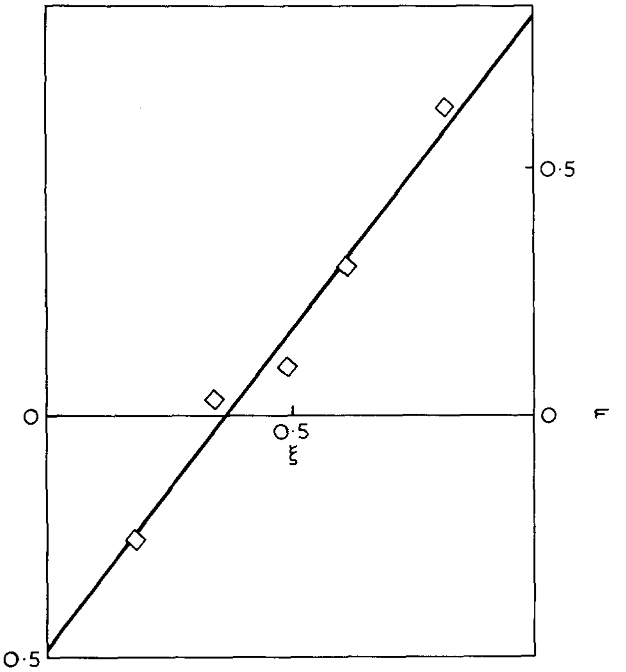

Figure 3 η *versus* ξ plot for the system: VAC/VOCOPh/dicyclohexylperoxydicarbonate/CH_2Cl_2/35°C

G.p.c. analysis was made on the styrene–VOCCl copolymer and on the vinyl chloride–VOCCl copolymer. The latter had been modified by *N*-methylbenzylamine. Unimodal distributions were observed by using refractometric and u.v. detection. Moreover, the ratio of the responses given by these two types of detection was constant at any elution volume, suggesting that the chromophores (i.e. benzene rings of styrene units in the first copolymer and carbamate units in the second one) are randomly distributed along the macromolecules. However this type of analysis is not accurate for the styrene–VOCCl copolymer due to the very low content of VOCCl units.

VOCOPh Copolymers

The copolymerization parameters of VOCOPh and VAC were also determined for reactions in CH_2Cl_2 at 35°C with DCPD as initiator. The results are given in *Table 5*. Molar composition of the copolymers were determined by ^1H n.m.r. analysis from integrations of the peaks at 7.2 ppm (aromatic protons) and at 2 ppm (methylene protons of the chains and methyl protons of VAC units).

The Kelen–Tüdös method was used for the treatment of experimental data. The η *versus* ξ plot shown in *Figure 3* is linear. The reactivity ratios r_1(VAC) and r_2(VOCOPh) were found to be 0.83 ± 0.10, and 0.38 ± 0.10, respectively. The ^{13}C spectrum of the copolymer obtained in run 14 (VAC/VOCOPh = 54/56) was recorded at 62.9 MHz in 1,2,4-trichlorobenzene at 120°C. Assignments and chemical shifts of the different carbons are given in *Table 6* together with those for the corresponding homopolymers prepared in the same conditions. If we look at the spectra corresponding to the methine and methylene carbons of the chains for the copolymer and the two homopolymers, the peaks observed for the copolymer are quite different from those of the corresponding homopolymers. The well defined triplet of the methine carbon in PVOCOPh which corresponds to triads effects[6,8,9] is perturbed by the close vicinity of VAC units. Thus, it seems reasonable to conclude that VAC and VOCOPh units are randomly distributed in the macomolecules. This was confirmed by g.p.c. analysis made with u.v. and refractometric detections since they show a unimodal distribution. Moreover, the ratio of the responses given by these two types of detection was constant at any elution volume indicating that the chromophores (benzene rings of VOCOPh units) are randomly distributed along the macromolecules.

Determination of Q *and* e *parameters*

The copolymerization parameters (r_1,r_2) of VAC with VOCCl and VOCOPh are collected in *Table 7*. The reactivities Q_2 of the monomers and the polarities (e_2) of

Table 6 Chemical shifts (ppm from HMDS) of carbon atoms for a VAC/VOCOPh copolymer (54/46) (Spectra recorded at 62.9 MHz, in $C_6H_3Cl_3$ at 120°C)

	$>C{=}O$		$-\overset{\vert}{C}H-$		$-CH_2-$		$-CH_3$
Compound	(1)	(2)	(3)	(4)	(5)	(6)	(7)
PVAC	167.6	–	65.7 65.9 66.5	–	37.6 37.9 38.3	–	18.8
PVOCOPh	–	151.2 151.5 151.7	–	69.6 70.7 71.9	–	37.7 37.9 38.1	–
Copolymer	168.0	151.2 151.4	66.5 66.3	71.1 72.2	37.7 37.9		18.8

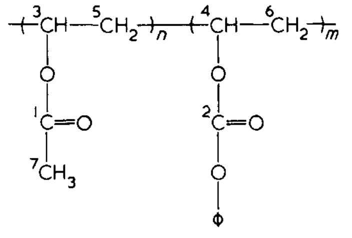

Table 7 Copolymerization parameters of VAC(M_1) with VOCCl and its derivatives (M_2)

M_2	r_1	r_2	Q_2	$e_2{}^a$	δ $\underline{C}H_2$= (ppm from TMS)	$e_2{}^b$
VOCCl	0.7 ± 0.1	0.6 ± 0.1	0.084	−1.81	101.0	−0.93
VOCOPh	0.83 ± 0.10	0.38 ± 0.10	0.080	−1.98	98.7	−1.07
VOCOEt^c	0.87 ± 0.04	0.79 ± 0.07	–	–	–	–
$VOCNEt_2{}^d$	1.700	0.126	0.028	−1.10	94.1	−1.35

[a] Determined from the Alfrey-Price equation[16]
[b] Determined from equation (3)
[c] Ref: 3
[d] Recalculated by Greenley[17] from the data of ref 1

their double bond were calculated from the parameters r_1 and r_2 using the Alfrey–Price equation[16]. The Q_1 and e_1 values of vinyl acetate recently recalculated by Greenley[17] ($Q_1 = 0.026$ and $e_1 = -0.88$) were used. The r_1 and r_2 values for VAC and $VOCNEt_2$[1] are also included in *Table 7* together with the Q_2 and e_2 parameters calculated by Greenley[17] from copolymerization data of $VOCNEt_2$ with four different monomers.

Another empirical method of determination of e parameters from ^{13}C n.m.r. data has been proposed[18]. A linear relationship between e and the chemical shift of the methylene carbon of the double bond of vinyl monomers, viz:

$$e(\text{vinyl X}) = \frac{\delta(\underline{C}H_2)(\text{ppm/TMS}) - 113.5}{22} \qquad (2)$$

was found to apply to fourteen monomers, but with e values calculated from r_1 and r_2 data determined by inaccurate methods. Since Greenley[17] recalculated a large number of r_1 and r_2 values using the Kelen–Tüdös method extended to high conversion data[12–14], more precise values for Q and e are now available[17]. Equation (2) was thus modified with these e values by using a least squares method:

$$e(\text{vinyl X}) = \frac{\delta(\underline{C}H_2)(\text{ppm/TMS}) - 116.2}{16.4} \qquad (3)$$

and e_2 values were then determined from ^{13}C n.m.r. data for VOCCl, VOCOPh and $VOCNEt_2$ using equation (3). The results are given in *Table 7*.

The reactivity ratios r_1 and r_2 determined for the copolymerization of VAC with VOCCl and with VOCOPh are less than 1 indicating that the copolymers approach an alternating structure. A comparison of the r_1 and r_2 values found, for the copolymerization of VAC with VOCCl, VOCOPh, VOCOEt and $VOCNEt_2$ (*Table 7*) shows that r_2 values for VOCCl and its derivatives are nearly the same as r_1 values for VAC except in the case of $VOCNEt_2$.

The Q_2 values of VOCCl and its derivatives are very low thus pointing to the low reactivity of these compounds. Discrepancies are observed between the e_2 values determined from the Alfrey–Price equation and from ^{13}C n.m.r. data for VOCCl and VOCOPh. This can be explained by the fact that in the former method of calculation, copolymerization data with only one monomer (VAC) were used. Other r_1 and r_2 data are needed in order to determine Q_2 and e_2 more accurately. If we consider the e_2 values obtained from ^{13}C n.m.r. data for VOCCl, VOCOPh and $VOCNEt_2$, it can be noticed that the electron-donating power of the substituent on these monomers follows the order $-O-C-NEt_2 > -O-C-OPh > -O-CCl$.

In conclusion, we have shown that VOCCl and VAC have nearly the same reactivity and that it is possible to prepare a large variety of copolymers containing reactive sites. Further work in this field is in progress.

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