Poly(vinyl chloroformate) and derivatives: 1. Polymerization of vinyl chloroformate, vinyl carbamates and vinyl carbonates

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(Received 10 August 1981)

The free-radical polymerization of vinyl chloroformate and of some of its derivatives, e.g., vinyl carbamates and vinyl carbonates, has been studied. Peroxydicarbonates are the most convenient initiators, especially for vinyl chloroformate polymerization carried out in bulk and in methylene chloride solution at 35°C since they lead to high molecular-weight polymers and quantitative yields. The structure of these polymers has been examined by i.r., ^{1}H and ^{13}C n.m.r. spectroscopy.

INTRODUCTION

The polymerization of vinyl chloroformate ($CH_2 = CHOCOCl$:VOCCl) has been little investigated[1,2], presumably because it was difficult to prepare a pure enough monomer in large enough yields[1-5]. Attempts to polymerize VOCCl by conventional free-radical initiators in bulk with azo compounds or benzoyl peroxide yielded brown or black low-molecular-weight resins in limited conversions. Schaefgen[1,2] found, however, that tri-n-butyl boron in the presence of small amounts of air is a good initiator of VOCCl polymerization, at 0° and at −80°C. High molecular-weight white polymers are formed in good yields and they were characterized by their inherent viscosities, i.r. spectra and X-ray diffraction patterns.

However, some derivatives of VOCCl like vinyl carbamates, vinyl carbonates and vinyl cyanoformates have been polymerized. Vinyl urethane gives a polymer on warming to 100°C[2] and the bulk polymerization of vinyl carbamates derived from cyclic amines like morpholine[6], aziridine, piperidine and pyrrole[7] initiated by AIBN or benzoyl peroxide have been mentioned. A colourless product has been obtained in the polymerization of methyl vinyl carbonate[8]. A variety of initiators have been tried for the polymerizations of t butyl vinyl carbonate and of vinyl cyanoformate[2]. The only initiator that gives any quantity of polymer with low yields (< 5%) is tri-n-butyl boron between −50° and −80°C.

It has recently been shown that pure VOCCl can be obtained with an 80% yield[9]. This prompted us to examine the polymerization of this monomer and of some of its derivatives as well as the chemical modification of poly(vinyl chloroformate) (PVOCCl)[10,11]. Use of peroxydicarbonates as free-radical initiators for the polymerization of VOCCl, in bulk and in solution, leads to high molecular-weight polymers[11,12]. The results concerning the polymerization of VOCCl and of some vinyl carbamates and vinyl carbonates as well as the characterization of these polymers are presented in this paper.

EXPERIMENTAL

Materials

The purity of VOCCl (Société Nationale des Poudres et Explosifs) was generally higher than 99% (main impurities: acetaldehyde, CCl_4 and benzene). This monomer was freed from the stabilizer by distillation just before use.

N-diethyl vinyl carbamate ($CH_2 = CHOCONEt$:VOCNEt$_t$) was prepared by the reaction of VOCCl with triethylamine according to the general procedure of dealkylation of tertiary amines developed by Schnur and Olofson[13-15] (Bp: 67°–68°C/19 mm Hg). N-butyl vinyl carbamate (VOCNHBu) was obtained from the reaction of VOCCl with n-butylamine using Na_2CO_3 as an HCl scavenger according to the procedure described for the synthesis of urethanes under heterogeneous conditions[16] (yield: 70%; Bp: 95°C/8 mm Hg).

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The reactions of methanol, phenol and menthol with VOCCl in the presence of NaOH gave the corresponding vinyl carbonates (VOCOMe, VOCOPh and VOCO Menthyl) as described previously[2,17], with 52%, 75% and 81% yields respectively. The use of pyridine instead of sodium hydroxide as the HCl scavenger led to a better yield (94%) for the reaction of phenol with VOCCl[13]. (Bp's: 96°C/760 mm Hg for VOCOMe; 85°C/3–4 mm Hg for VOCOPh and 75°C/1 mm Hg for VOCO Menthyl). VOCOMe thus prepared contained ~10% dimethyl carbonate as confirmed by ^{1}H n.m.r. which was impossible to eliminate by distillation.

THF was dried over calcium hydride and several sodium mirrors in glass apparatus sealed under high vacuum[18]. Methylene chloride was purified on P_2O_5 and then on several sodium mirrors as described previously[19].

The commercially available solution of tri-n-butylboron in THF (25% by volume) (Aldrich) was used without purification. Azobisisobutyronitrile (AIBN), benzoyl peroxide (BP), dicyclohexyl peroxydicarbonate (DCPD) and bis(4-tertiarybutylcyclohexyl) peroxydicarbonate (TBCPD) were dried under high vacuum before use.

Polymerization procedure

Most of the experiments were carried out in glass apparatus sealed under high vacuum according to the procedure used for anionic polymerizations[20]. The monomer (VOCCl) was slowly condensed into a side tube in order to remove the inhibitor before its introduction by distillation together with the solvent into the polymerization vessel containing the catalyst and immersed in liquid nitrogen. Some experiments were performed under argon in apparatus linked to a high vacuum line. The monomer was introduced with a syringe through a serum cap and then degassed several times. In all cases, the reaction mixture was magnetically stirred at the desired temperature and the polymers were recovered after precipitation in petroleum ether. They were purified by dissolution in THF and precipitation in petroleum ether and dried under high vacuum. PVOCCl samples were kept in the dark at $-30°C$ in order to avoid cross-linking side reactions.

Monomer and polymer characterization

The purity of monomers was checked by gas chromatography. Most of the monomers and polymers were examined by i.r. spectroscopy with a Perkin Elmer 577 apparatus and by ^{1}H and ^{13}C n.m.r. with a Jeol C-60 HL, a Varian HA-100 and a Cameca 250 spectrometer. Assignments of the peaks to specific carbon atoms were made by using partial C–H decoupling. Molecular weights of polymers were measured by osmometry in toluene at 37°C and by g.p.c. in THF at 25°C using the calibration of polystyrene.

RESULTS AND DISCUSSION

Polymerization of VOCCl

Preliminary experiments were made with tri-n-butylboron as initiator. The results shown in *Table 1* are in good agreement with those found by Schaefgen[2] (see runs 1 and 5).

Direct measurements of PVOCCl molecular weights are difficult to perform since the chloroformate groups are very polar and reactive. We found that PVOCCl can be modified with a 100% yield by N-methylbenzylamine to give a polymer which is soluble in toluene and in THF[10,11]. We were thus able to measure molecular weights by osmometry and by g.p.c., and to deduce those of the starting PVOCCl's. For instance, the $\bar{M}_n$ of the completely modified polymer obtained in run 4 was found to be equal to 164 000 which corresponds to $M_n = 94000$ for the starting PVOCCl sample. The values of $\bar{M}_n$ and $\bar{M}_w$ deduced from g.p.c. measurements made on the same modified polymer were equal to 41 000 and 145 000 respectively.

Although tri-n-butylboron is very effective for the polymerization of VOCCl, its handling is rather difficult and dangerous. This prompted us to try other initiators like peroxydicarbonates, AIBN and benzoyl peroxide (BP). The results are shown in *Table 2*.

When the catalyst concentration was low ([initiator]/[monomer] < 0.1%) polymer yields were not quantitative. This is due to the fact that the concentrations of initiator and of monomer impurities are of the same order of magnitude. Although VOCCl is kept in the dark at $-30°C$ with an inhibitor, acetaldehyde formation is observed with time. Thus an [initiator]/[monomer] ratio of about 0.5% is necessary to avoid these problems. However, a gel effect is sometimes observed (runs 7 and 8) which provokes an increase in temperature and leads to coloured polymers. The results of runs 9 and 10 show that DCPD and TBCPD (defined in *Table 2*) have the same efficiency.

The use of peroxydicarbonates as initiators does not require special handling, contrary to tri-n-butylboron, and also allows us to work at a relatively low temperature (35°C) thus avoiding degradation reactions of PVOCCl. High molecular-weight colourless polymers can be prepared in this way.

More conventional free-radical initiators like BP and AIBN also gave nearly quantitative yields of PVOCCl at 54°–56°C after 15 h and 17 h (runs 11 and 12), contrary to the findings of Schaefgen[1,2]. This discrepancy may be explained by the fact that the monomer prepared by Schaefgen was less pure than ours. However, it should be mentioned that the crude polymers thus prepared are slightly yellow in colour. This is due to the higher polymerization temperature (~55°C) required by BP and AIBN than by peroxydicarbonates.

In order to more carefully control the polymerization of VOCCl initiated by peroxydicarbonates, some experiments were conducted in solution and the results

Table 1 Bulk polymerization of VOCC1 initiated by tri-n-butyl boron

Run	[Initiator]ᵃ/[Monomer]	Tempera-ture (°C)	Time	Yield (%)	η_{inh}.ᵇ
1	0.25%	−80	3 days	60	2.00
2	0.9%	0	1.25 h	96	0.28
3	0.4%	0	2 h	86	–
4	0.25%	−75	3 days	16.5ᶜ	0.63
5ᵈ	0.25%	−80	3 days	73	1.78

ᵃ % in volume
ᵇ Inherent viscosity measured on a solution of 0.5 g polymer in 100 ml acetone at 30°C
ᶜ Polymerization stopped by addition of oxygen
ᵈ Ref 2

Table 2 Bulk polymerization of VOCCl initiated by percarbonates, peroxides and azo compounds

Run	Initiator	[Initiator] / [Monomer]	Temperature (°C)	Time	Yield (%)	$\bar{M}_{n\ osm}$ [a]
6	DCPD[b]	0.05%	40	100 min	55	15 000
7[c]	DCPD	0.1%	40	8 min	>90	48 000
8[c]	DCPD	0.5%	35	70 min	~100	–
9	DCPD	0.5%	35	47 min	~100	68 000
10	TBCPD[d]	0.5%	35	40 min	98	72 000
11	BP[e]	0.5%	54	15 h	92	39 000
12	AIBN[f]	0.5%	56	17 h	98	59 000

[a] Calculated from the value obtained for the polymer quantitatively modified by N-methylbenzylamine
[b] Dicyclohexyl peroxydicarbonate
[c] Gel effect observed
[d] Bis(4-tertiarybutylcyclohexyl)peroxydicarbonate
[e] Benzoyl peroxide
[f] Azo-bis-isobutyronitrile

Table 3 Solution polymerization of VOCCl initiated by DCPD

Run[a]	Solvent	[M] mol l^{-1}	[Initiator] / [Monomer]	Temperature (°C)	Time (h)	Yield (%)	$\bar{M}_{n\ osm}$ [b]
13 (A)	THF	2.64	1.1%	42	3	31	–
14 (A)	CH_2Cl_2	3.54	0.5%	35	20	93	22 000
15 (B)	CH_2Cl_2	4.95	1.1%	35	1.75	100	70 000
16 (B)	CH_2Cl_2	5.34	0.8%	35	2	100	70 000
17 (C)	CH_2Cl_2	5.38	1.8%	35	2.2	100	20 000
18 (C)	CH_2Cl_2	5.34	1.9%	35	2	100	23 000

[a] Three different batches of monomer (A, B and C) were used
[b] Calculated from the value obtained for the polymer quantitatively modified by N-methylbenzylamine

Table 4 Bulk polymerization of vinyl carbamates and vinyl carbonates

Run	Monomer	Initiator	[Initiator] / [Monomer]	Temperature (°C)	Time (h)	Yield (%)	$\bar{M}_{n\ osm}$
19	VOCNEt$_2$	DCPD[a]	0.5%	35	18	–	37 000
20	VOCNEt$_2$	AIBN	0.5%	60	18	84	79 000
21	VOCNHBu	AIBN	0.5%	60	18	65	35 000
22	VOCOMe	AIBN	3%	60	50	32.5	4800
23	VOCOPh	BP[b]	0.1%	80	19	23	65 000
24	VOCOPh	BP	0.1%	87	19	32	40 000
25	VOCOPh	DCPD	0.15%	35	20	15	84 500
26	VOCOPh	DCPD	0.5%	35	20	65	92 000
27	VOCO Menthyl	BP	0.1%	87	33	14	27 000
28	VOCO Menthyl	DCPD	0.5%	35	16	44	73 000
29	VOCO Menthyl	DCPD	1%	35	6	54	53 000

[a] Dicyclohexyl peroxydicarbonate
[b] Benzoyl peroxide

are shown in *Table 3*. Methylene chloride is a convenient solvent and it is possible to prepare colourless, high molecular-weight PVOCCl's in quantitative yields after 2 h at 35°C. The results are reproducible using the same weight distribution of polymers deduced from g.p.c. distribution of polymers deduced from g.p.c. measurements made on modified samples is narrower ($\bar{M}_w/\bar{M}_n \simeq 2$) than that of polymers prepared in bulk ($3.5 < \bar{M}_w/\bar{M}_n < 4$). Kinetic studies of the radical polymerization of VOCCl initiated by peroxydicarbonates in CH_2Cl_2 are in progress.

### Polymerization of vinyl carbamates and vinyl carbonates

The polymerizations of N-diethyl vinyl carbamate (VOCNEt$_2$ where V: $CH_2=CHO-$), N-butyl vinyl carbamate (VOCNHBu), methyl vinyl carbonate (VOCOMe), phenyl vinyl carbonate (VOCOPh) and menthyl vinyl carbonate (VOCO Menthyl) were carried out in bulk with free-radical initiators. The results are shown in *Table 4*.

High molecular weight polymers were obtained except for VOCOMe which was difficult to purify and for which the ratio :[initiator]/[monomer] was high. Dicyclohexyl peroxydicarbonate is a more efficient catalyst than benzoyl peroxide for the polymerization of VOCOPh and for VOCO Menthyl. The low yields of PVOCOPh obtained in runs 23, 24 and 25 are probably due to the low concentration of initiator as already observed by Tobolsky[21] in the case of the free-radical polymerization of styrene. On increasing the ratio :[DCPD]/[VOCOPh] from 0.15% to 0.5% (runs 25 and 26) the polymer yield increases from 15 to 65%. However, the molecular weight

Table 5 Chemical shifts (ppm) of carbon atoms for VOCNEt₂ and PVOCNEt₂

Compound	Solvent	Temperature (°C)	$>$C=O (1)	—CH= (2)	—CH— (2')¹	CH₂= (3)	—CH₂— (3')	—CH₂— (4)	—CH₃ (5)
VOCNEt₂[a]	–	30	152.7	143.2	–	94.1	–	$\begin{Bmatrix}41.7\\42.3\end{Bmatrix}$	13.4 14.4
VOCNEt₂[a]	–	50	152.8	143.3	–	94.1	–	42.1	14.0
VOCNEt₂[b]	C₆H₃Cl₃	110	157.2	141.3	–	92.3	–	40.1	11.8
PVOCNEt₂[b]	C₆H₃Cl₃	110	157.2	–	$\begin{Bmatrix}67.4\,i\\67.1\,h\\66.8\,s\end{Bmatrix}$	–	38.7	39.8	12.1

[a] Ref: TMS
[b] Ref: HMDS
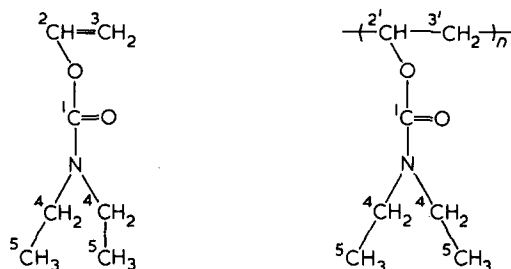
of PVOCO Menthyl decreases on increasing the catalyst concentration (runs 28 and 29). Menthyl vinyl carbonate is more reactive than menthyl isoprenyl carbonate which has been polymerized in bulk at 75°C, with BP as initiator in order to prepare a polymeric composition which can release menthol to tobacco smoke under normal smoking conditions[22]. We tried to polymerize this monomer under the conditions of run 27 without success. The ratio $\bar{M}_w/\bar{M}_n$ for PVCOPh's (runs 24, 25 and 26) is close to 2 as determined by g.p.c.

Monomer and polymer characterization

Polyvinylchloroformate. The i.r. spectra of the different PVOCCl samples are consistent with the expected vinylic structure: ν(C=O): 1770 cm⁻¹ (vs); ν(O–C): 1170 cm⁻¹ (s) and ν(C–Cl): 680 cm⁻¹ (s). The ¹H n.m.r. spectrum (CD₃COCD₃ 25°C, 60 MHz) shows two peaks at 2.4 ppm (methylene protons) and 5.4 ppm (methine protons) in the expected ratio 2/1. The ¹³C spectrum of PVOCCl displays two single peaks at 38.7 and 151 ppm assignable to the secondary and quaternary carbons respectively, whereas a triplet (76.9, 77.9 and 79.0 ppm) is observed for the tertiary carbon which corresponds to the triad structures (s, h, i). The determination of the percentages of different triads gives the following values: $i = (mm) = 0.23$; $h = (mr) = 0.51$ and $s = (rr) = 0.26$. This allows the application of the classical Bovey's equation[23]:

$$P_m/r = \frac{(mr)}{2(mm) + (mr)} = 0.52_5 \text{ and } P_r/m = \frac{(mr)}{2(rr) + (mr)} = 0.49_5.$$

Thus $P_m/r + P_r/m = 1.02$. It can be concluded that PVOCCl is an atactic polymer having a Bernouillian statistical distribution as expected from the free-radical polymerizations.

Poly(vinyl carbamates). The results of the elemental analysis of PVOCNEt₂ and of PVOCNHBu are in excellent agreement with the theoretical values: Calculated for (C₇H₁₃NO₂)ₙ: C, 58.7%; H, 9.1%; N, 9.8%; O, 22.4%. Found for PVOCNEt₂: C, 58.7%; H, 9.2%; N, 9.8%; O, 22.3%. Found for PVOCNHBu: C, 58.6%; H, 9.1%; N, 9.6%; O, 22.7%.

The main absorption bands observed on the i.r. spectrum of PVOCNEt₂ are located at 1695 cm⁻¹ (vs),

ν(C=0) and 1160 cm⁻¹ (s), ν(C–N). However some characteristic bands of the monomer are also observed at ν(CH$_{\text{vinyl}}$):3060 cm⁻¹ and ν(C=C):1640 cm⁻¹. It has not been possible to eliminate the residual monomer either by selective precipitation of the polymer or by evaporation under high vacuum. The remaining amount of monomer (15%) was determined by ¹H n.m.r. spectroscopy. Whereas the methyl and methylene protons of the side groups cannot be distinguished in the monomer and the polymer spectra, methylene protons of the polymer chain give a large peak located at 1.8 ppm and the spectrum of the vinyl protons of the monomer is composed of a quadruplet (7.24 ppm) and two doublets (4.69 and 4.36 ppm).

The ¹³C spectrum of VOCNEt₂ was recorded at 62.9 MHz at 30° and 50°C. The results are given in *Table 5*. It can be seen that the two methyl and methylene carbons of the N-ethyl groups give doublets at 30°C which collapse at 50°C. This phenomenon is due to a partially fixed conformation effect which disappears on heating at 50°C. The ¹³C spectrum of PVOCNEt₂ was recorded at 62.9 MHz in 1,2,4-trichlorobenzene at 110°C. Assignments and chemical shifts of the different carbons of this polymer as well as those of the monomer are given in *Table 5*. As for PVOCCl, a triplet is observed for the tertiary carbon of the chain which corresponds to the triad structures. However it has not been possible to determine the percentages of the different triads with accuracy.

The characteristic bands of the i.r. spectrum of PVOCNHBu are located at 1690 cm⁻¹ (vs), ν(C=O); 3310 cm⁻¹ (s) and 1520 cm⁻¹ (vs), ν(N–H).

The assignments and chemical shifts of the different carbons for VOCNHBu and for the corresponding polymer are shown in *Table 6*. The tertiary carbon of the chain is sensitive to triad effects. However, only two peaks instead of three are observed due to the overlapping of two signals. The methylene carbon of the chain is sensitive to diad effects and the highest peak can be attributed to racemic diads since this polymer is presumably atactic. Moreover the percentages of diads can be determined: $r = 0.62$ (37.2 ppm) and $m = 0.38$ (37.9 ppm). If we assume that PVOCNHBu has a Bernouillian statistical distribution, as expected in the case of free-radical

Table 6 Chemical shifts (ppm) of carbon atoms for VOCNHBu and PVOCNHBu

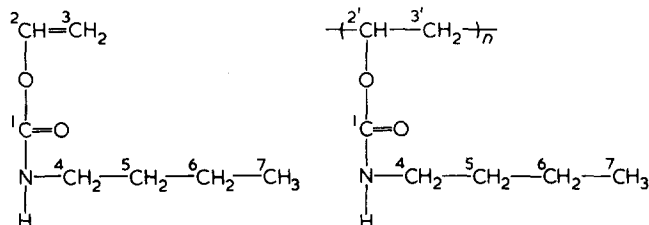| Compound	$\rangle$C=O (1)	–CH= (2)	–CH– (2')	CH$_2$= (3)	–CH$_2$– (3')	–CH$_2$– (4)	–CH$_2$– (5)	–CH$_2$– (6)	–CH$_3$ (7)
VOCNHBu[a]	154.5	142.8	–	94.3	–	41.0	32.2	20.2	13.8
PVOCNHBu[b]	154.4	–	67.6 i 67.3 h+s	–	37.2 r 37.9 m	39.2	30.5	18.2	11.7

[a] Neat at 30°C, ref: TMS
[b] In C$_6$H$_3$Cl$_3$ at 110°C, ref: HMDS

Table 7 Chemical shifts (ppm) of carbon atoms for VOCOPh and PVOCOPh

Compound	$\rangle$C=O (1)	–C– (4)	–CH= (2)	–CH– (2')	CH$_2$= (3)	–CH$_2$– (3')	CH$_{ar}$ (5)	CH$_{ar}$ (6)	CH$_{ar}$ (7)
VOCOPh[a]	151.7	151.6	143.3	–	98.7	–	121.5	130.1	127.8
PVOCOPh[b]	153.7	151.1	–	73.9 i 72.1 h 70.7 s	–	39.3	121.3 121.6 121.8	129.2	125.9
PVOCOPh[c]	151.2 i 151.5 h 151.7 s	149.9	–	71.9 i 70.7 h 69.6 s	–	37.7 37.9 38.1	119.3 119.5 119.7	127.2	123.7

[a] In CD$_3$COCD$_3$, at 25°C, ref: TMS
[b] In CDCl$_3$, at 50°C, ref: TMS
[c] In C$_6$H$_3$Cl$_3$ at 110°C, ref: HMDS
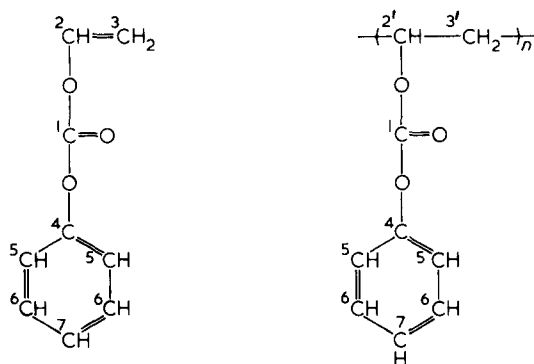
polymerization, it is possible to calculate the percentages of triads[23]. $P_m = m$ and $i = P_m^2 = 0.14$; $h = 2P_m(1 - P_m) = 0.47$ and $s = (1 - P_m)^2 = 0.39$. The observed percentages for the two peaks corresponding to the tertiary carbon of the chain are equal to 0.18 (67.6 ppm) and 0.82 (67.3 ppm) respectively. Thus it seems reasonable to assign the smallest peak to isotactic triads and the highest one to hetero and syndiotactic triads.

Poly(vinyl carbonates). The main absorption bands observed on the i.r. spectrum of PVOCOMe are: ν(C = O): 1745 cm^{-1} (vs), ν(O–C): 1260 cm^{-1} (vs) and ν(C–H): 2960 cm^{-1} (vs). Those of PVOCOPh are located at 1750 cm^{-1} (vs), ν(C = O); 1585 cm^{-1} (s) and 1485 cm^{-1} (s), ν(C = C$_{ar}$); 1270 cm^{-1} (vs), ν(O–C) and 1200 cm^{-1} (vs), ν(O–C$_{ar}$).

The ^{1}H spectrum of PVOCOPh (CDCl$_3$, 25°C, 60 MHz) displays three large peaks at 2.5 ppm (methylene protons), 6.4 ppm (aliphatic methine protons) and 7.1 ppm (aromatic protons) in the expected ratio 2/1/5. The ^{1}H spectrum of the same polymer recorded at 250 MHz (CDCl$_3$, 50°C) shows two large doublets for the aliphatic methylene and methine protons. No stereosensitivity of the protons could be observed.

Assignments and chemical shifts of the different carbons for VOCOPh and PVOCOPh are given in *Table 7*. The ^{13}C spectrum of PVOCOPh was recorded at 110°C in 1,2,4-trichlorobenzene, at 62.9 MHz. In these conditions, aliphatic methine carbon and methylene carbon as well as carbonyl carbon are stereosensitive. The percentages of different triads can be determined from the area of the three peaks corresponding to the methine carbon resonance: $i = 0.18$; $h = 0.48$ and $s = 0.34$. The classical Bovey's calculation[23] leads to

$$P_m/r = \frac{h}{2i + h} = 0.57 \quad \text{and} \quad P_r/m = \frac{h}{2s + h} = 0.41, \quad \text{and}$$

$P_m/r + P_r/m = 0.98$. Thus PVOCOPh has a Bernouillian statistical distribution. This polymer is predominantly atactic as shown by the high percentage of heterotactic triads. However, the syndiotactic triads are slightly predominant and this might be explained by steric hindrance phenomena due to the bulkiness of phenyl

groups. The relative order of triads for the carbonyl carbon is the reverse of that observed for the methine carbon as in the case of poly(methyl methacrylate)[23]. The percentage of different triads found in this case is in good agreement with that found for the methine carbon. Four peaks are observed for the methylene carbon resonance. This carbon is sensitive to tetrads effects but only four of the expected six peaks are observed due to some overlapping. A detailed analysis of the percentage of the different tetrads is rather difficult and would require more data with samples of different tacticities.

In conclusion, we have shown that typical free-radical initiators can be used for the polymerization of pure VOCCl. Among them, the peroxydicarbonates are the most convenient since they lead to high molecular-weight colourless polymers in quantitative yield, at 35°–40°C in bulk and in methylene chloride solution. High molecular-weight polymers have also been obtained by free-radical bulk polymerizations of *N*-diethyl vinyl carbamate, *N*-butyl vinyl carbamate, phenyl vinyl carbonate and menthyl vinyl carbonate. The structure of these polymers has been analysed by ^{13}C n.m.r. spectroscopy. The tertiary carbon of the chain is sensitive to triads effects and these polymers have a Bernouillian statistical distribution, as expected in the case of free-radical polymerizations. The results concerning the copolymerization of VOCCl and VOCOPh with vinyl monomers as well as the chemical properties of PVOCCl will be described in forthcoming papers.

REFERENCES

1 Schaefgen, J. R. U.S. Patent 1964, 3 118 862
2 Schaefgen, J. R. *Am. Chem. Soc. Polym. Prepr.* 1967, **8**(1), 723 and *J. Polym. Sci. C*, 1968, **24**, 75
3 Küng, F. E. U.S. Patent 1945, 2 377 085
4 Strain, F. and Küng, F. E. U.S. Patent 1945, 2 377 111
5 Lee, L. H. *J. Org. Chem.* 1965, **30**, 3943
6 Overberger, C. G., Ringsdorf, H. and Weinshenker, N. *J. Org. Chem.* 1962, **27**, 4331
7 Dow Chemical Co. Fr. Patent 1966, 1 478 633
8 Küng, F. E. U.S. Patent 1945, 2 370 549
9 Malfroot, T. and Piteau, M. Belg. Patent 1978, 864 309
10 Meunier, G., Hémery, P., Senet, J. P. and Boileau, S. *Polym. Bull.* 1979, **1**, 809
11 Meunier, G. *Thèse Docteur-Ingénieur*, Paris 1981
12 Boileau, S., Journeau, S. and Meunier, G. Fr. Patent 1980, 80/02651
13 Schnur, R. C. *Ph.D. Thesis*, Pennsylvania State Univ., 1973
14 Olofson, R. A., Schnur, R. C. and Bunes, L. A. U.S. Patent 1973, 3 905 981
15 Olofson, R. A., Schnur, R. C., Bunes, L. and Pepe, J. P. *Tetrahedron Lett.* 1977, 1567
16 Piteau, M., Senet, J. P. and Vitrant, A. M. Fr. Patent 1977, 2 371 486
17 Strain, F. and Küng, F. E. U.S. Patents 1945, 2 370 589; 2 377 111 and 2 384 143
18 Hémery, P., Boileau, S. and Sigwalt, P. *J. Polym. Sci. Polym. Symp.* 1975, **52**, 189
19 Chéradame, H. and Sigwalt, P. *Bull. Soc. Chim. Fr.* 1970, 843
20 Boileau, S., Champetier, G. and Sigwalt, P. *Makromol. Chem.* 1963, **69**, 180
21 Tobolsky, A. V. *J. Am. Chem. Soc.* 1958, **80**, 5927
22 Grubbs, H. J., VanAuken, T. V. and Johnson, W. R. U.S. Patent 1978, 4 127 601
23 Bovey, F. A. 'High Resolution NMR of Macromolecules', Academic Press, New York, 1972