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Poly(vinyl Chloroformate and Derivatives

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ABSTRACT

Poly(vinyl chloroformates) of high molecular weight have been successfully modified by amines and by KCN. Poly(vinyl carbonates) have been prepared by polymerization of phenyl vinyl carbonate.

INTRODUCTION

The polymerization and copolymerization of vinyl chloroformate (VOCCl) have been little investigated (Schaefgen, 1960 and 1968) presumably because it was difficult to prepare the monomer without impurities, with a good yield (Schaefgen, 1968 ; Küng, 1945 a ; Strain et al., 1945 a ; Lee, 1965). Some alkyl and aryl vinyl carbonates derived from vinyl chloroformate have been synthetized (Schaefgen, 1968 ; Küng, 1945 b ; Strain et al., 1945 b, c ; Olofson et al. , 1977) which can be polymerized in low molecular weight products (Schaefgen, 1968 ; Küng, 1945 b). Copolymerization parameters of ethyl vinyl carbonate with p-chlorostyrene and vinyl acetate have been determined in bulk and in benzene, at 60° C with azobisisobutyronitrile (AIBN) as initiator (Kikukawa, 1967).

It has been recently shown that pure VOCCl could be obtained with 80% yield (Malfroot, 1978). This prompted us to examine in detail the polymerization of this monomer and of its derivatives, namely of phenyl vinyl carbonate (VOCOPh), as well as the chemical modification of poly(vinyl chloroformate) (PVOCCl).

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POLYMERIZATION OF VOCCl

VOCCl acquired from the Société Nationale des Poudres et Explosifs (purity > 99%) was polymerized in bulk with tri-n-butylboron as initiator, at -80° or 0°C, according to Schaefgen (1968). Polymer samples were purified by several dissolutions in THF and precipitations in petroleum ether. They were then dried under high vacuum and kept in the dark at -30°C in order to avoid a decomposition which leads to insolubility. The results shown in Table 1 are in good agreement with those found by Schaefgen (1968).

TABLE 1

Bulk polymerization of VOCCl initiated by tri-n-butyl boron [a).]

Run	Initiator / Monomer [b)]	Temp. °C	Time h.	Yield %	η inh.[c)]	Cl %[d)]
1	0.25 %	- 80	3 days	60	2.00	31.6
2	0.9 %	0	1.25 h	96	0.28	31.7
3	0.4 %	0	2 h	86	-	33.0
4	0.25 %	- 75	3 days	16.5 [e)]	0.63	-

a) 25% by volume $(C_4H_9)_3B$ in THF ; b) % in volumes ; c) inherent viscosity measured on a solution of 0.5 g polymer in 100 ml acetone at 30°C ; d) theoretical value : 33.3% ; e) polymerization stopped by addition of oxygen.

The IR spectra of the different samples are consistent with the theoretical structure (C = O : 1770 cm^{-1} ; O - C : 1170 cm^{-1} ; C - Cl : 680 cm^{-1}). The ^1H spectrum shows two peaks at 2.4 ppm ($C\underline{H_2}$) and 5.4 ppm

(C<u>H</u>) in the expected ratio 2/1. The ^{13}C spectrum displays two single peaks at 38.7 and 151 ppm assignable to the secundary and the quaternary carbons respectively whereas a triplet (76.9, 77.9 and 79.0 ppm) is observed for the asymetric tertiary carbon which corresponds to triad structures.

CHEMICAL MODIFICATION OF PVOCCl

It has been shown that poly(vinyl chloroformate) reacts with compounds containing labile hydrogen atoms, such as alcohols, amines and phenols (Schaefgen, 1968). We have tried to find convenient conditions for the reaction of several amines with PVOCCl in order to avoid degradation and to obtain soluble modified polymers with a good yield of substitution. Use of alkaline carbonates as hydrogen chloride scavengers is quite convenient for this type of reaction (Piteau et al., 1975). In a typical experiment, the substituent (7.5 mmol) is added to a PVOCCl solution (5 mmol in 100 ml of solvent : acetonitrile (ACN) or CH_2Cl_2) together with alkaline carbonate (10 mmol). The heterogeneous mixture is vigorously stirred for a few hours at a given temperature. It is then filtered and the polymer is recovered by precipitation of the solution in water and purified by several dissolutions and precipitations. The degree of substitution is determined by elemental analysis of N and of remaining Cl. The results are shown in Table 2.

Primary amines react as well as secundary amines leading to excellent yields of substitution. In the case of ethylethanolamine, a selective N-alkylation is observed as shown by the IR spectrum of the modified polymer. Moreover, since the PVOCCl modified with 100% yield by benzyl methylamine is soluble in toluene, we have been able to measure its molecular weight by osmometry : $\overline{M_n}$ osm. = 164 000 which corresponds to

TABLE 2

Reaction of amines with PVOCCl.

Substituent	Solvent	HCl scavenger	Temp. °C	Time h	Degree of substitution %
$C_6H_5CH_2NHCH_3$	ACN	K_2CO_3 [a]	55	3	100
$C_6H_5CH_2NHCH_3$	ACN	no	55	3	100
$C_2H_5NHCH_2CH_2OH$	CH_2Cl_2	Na_2CO_3	42	2	84
η-$C_4H_9NH_2$	CH_2Cl_2	Na_2CO_3	42	1	94
$NH_2CH_2COOC_2H_5$, HCl [b]	CH_2Cl_2	$(C_2H_5)_3N$ [c]	40	2	95

[a] Dicyclohexyl-18 crown-6 added : 1.5 mol % of the chlorine content of polymer ;

[b] 6 mmol for 5 mmol of PVOCCl ;

[c] 10 mmol added dropwise to the mixture during 1 h. at 20°C.

$\overline{M_n}$ = 94 000 for the starting PVOCCl sample (run 4, Table 1). It is the first time that the molecular weight of PVOCCl could be evaluated since direct measurements on PVOCCl are very difficult.

Cyanoformates can be easily prepared by reaction of chloroformates with KCN, using phase transfer catalysis (Childs et al., 1976). This method has been successfully applied for the chemical modification of chloromethylated polystyrene by NaCN (N'Guyen et al., 1979). The results of some experiments made on PVOCCl are shown in Table 3. Use of crown ether is necessary for this type of reaction.

TABLE 3

Reaction of KCN with PVOCCl in acetonitrile.

Catalyst [a)] (mol %)	Temp. °C	Time h	Degree of substitution %
no	30	2.5	2
DCHE (2.2)	20	3	79
DCHE (1.1)	30	3	74
DCHE (2.8)	40	3	80

a) DCHE : dicyclohexyl-18 crown-6, mol % of the chlorine content of polymer.

POLYMERIZATION OF PHENYL VINYL CARBONATE

Phenyl vinyl carbonate (VOCOPh) prepared by reaction of VOCCl with phenol (Strain et al., 1945 b, c ; Schnur, 1973) was polymerized in bulk, under nitrogen, using AIBN or benzoyl peroxide (BP) as initiator. White powders were obtained after dissolution of the polymers in THF and precipitation in petroleum ether. The results are given in Table 4.

TABLE 4

Free-radical polymerization of VOCOPh.

Initiator (%) [a]	Temp. °C	Time h.	Yield %	$\overline{M_n}$	$\overline{M_w}$
AIBN (1.4)	85	0.75	42	4 700 [b]	10 400 [b]
BP (0.15)	80	20	30	28 000 [b]	60 000 [b]
BP (0.10)	80	19	23	65 000 [c]	-
BP (0.10)	87	19	32	40 000 [c]	-

[a] mol % initiator ; [b] measured by GPC in THF at 30°C

[c] measured by osmometry in toluene at 37°C.

The ratio $\overline{M_w}/\overline{M_n}$ is nearly equal to 2 as expected for a free radical polymerization. The IR spectra of the different samples are consistent with structure (C = O : 1760 cm^{-1}, characteristic aromatic absorptions at 3040, 1580, 1485 and 765 cm^{-1}). No hydroxyl absorption is detected whereas an important OH band is observed for the PVOCCl sample modified by phenol which has been prepared by Schaefgen (1968). The ^1H spectrum displays three large peaks at 2.5 ppm (CH_2), 6.4 pmm (aliphatic $C\underline{H}$) and 8 ppm (aromatic protons) in the expected ratio 2/1/5. As in the case of PVOCCl, the ^{13}C spectrum shows a triplet for the asymetric tertiary carbon which corresponds to triad structures.

A detailed study of the properties of high molecular weight poly(vinyl chloroformates) and of its derivatives is presently being carried out and will be published in a subsequent paper.

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