

Poly(vinyl chloroformate) and its derivatives: 5. New poly(vinyl carbamates) and poly(vinyl thiocarbonates)

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New poly(vinyl carbamates) and poly(vinyl thiocarbonates) have been prepared either by free radical polymerization of monomers or by chemical modification of poly(vinyl chloroformate) with appropriate amines and thiols using phase transfer catalysis. The structure of these polymers has been examined by i.r. and ^{13}C n.m.r. spectroscopy and their thermal behaviour has been studied.

(Keywords: vinyl carbamates; vinyl thiocarbonate; radical polymerization; chemical modification; phase transfer catalysis; ^{13}C n.m.r. spectroscopy; thermal analysis)

INTRODUCTION

The polymerization of vinyl chloroformate ($\text{CH}_2=\text{CHOCOC}l:\text{VOCC}l$) had been little investigated^{1,2} until a convenient synthesis leading to 80% yield of the pure monomer was discovered³. It has been recently shown that peroxydicarbonates are the most suitable initiators for VOCCl polymerizations carried out in bulk and in methylene chloride solution at 35°C, since they lead to high molecular weight polymers and quantitative yields^{4,5}.

Some derivatives of VOCCl like vinyl carbamates, vinyl carbonates and vinyl cyanoformate have been polymerized^{2,6-8}. Vinyl urethane gives a polymer on warming at 100°C² and the bulk polymerization of vinyl carbamates derived from cyclic amines like morpholine⁶, aziridine, piperidine and pyrrole⁷ initiated by AIBN or benzoyl peroxide have been mentioned. However, only recently, well defined high molecular weight poly(vinyl carbamates) and poly(vinyl carbonates) have been obtained by free-radical polymerization of *N*-diethyl vinyl carbamate, *N*-butyl vinyl carbamate, methyl vinyl carbonate, phenyl vinyl carbonate and menthyl vinyl carbonate⁵.

Some poly(vinyl carbamates), poly(vinyl carbonates) and poly(vinyl cyanoformate) have also been prepared by chemical modification of poly(vinyl chloroformate) (PVOCCl) with amines, alcohols, phenols as well as with potassium cyanide. Good substitution yields have been obtained especially on using phase transfer catalysis conditions⁹⁻¹¹.

The results concerning the preparation and the characterization of new poly(vinyl carbamates) and poly(vinyl thiocarbonates) obtained either by polymerization of

vinyl monomers or by chemical modification of PVOCCl are presented in this paper.

EXPERIMENTAL

The purity of VOCCl (Société Nationale des Poudres et Explosifs) was generally higher than 99%. This monomer was freed from the stabilizer by distillation just before use.

N-methylcyclohexyl vinyl carbamate (VOCN(CH₃)-C₆H₁₁, where VOC: CH₂=CH-O-C(O)-) was prepared by adding VOCCl (15 mmol) to a stirred suspension of MgO (15 mmol) and *B*-methylcyclohexylamine (17 mmol in 1:2 dioxane/water (15 ml). After 4 h at room temperature, the mixture was acidified to pH 3 and extracted with ether. The pure product was isolated from the dried (Na₂SO₄) ether extracts by vacuum distillation (yield: 85%; B.p.: 119°C/14 torr)¹².

N-piperidine vinyl carbamate (VOCNC₅H₁₀) was obtained from the reaction of *N*-ethylpiperidine with VOCCl according to the general procedure for dealkylating tertiary amines developed by Schnur and Olofson¹²⁻¹⁴ (yield: 90%; b.p.: 60°C-61°C/0.3 torr).

Vinyl phenyl thiocarbonate (VOCSPH) was prepared by the room temperature reaction of *S*-phenylthiochloroformate with (vinyloxy)trimethylsilane in the presence of KF complexed by 18-crown-6 in THF (according to literature method¹⁵) (yield: 66%; b.p.: 69°C-73°C/0.5 torr).

Polymerizations of vinyl carbamates and of VOCSPH were performed under nitrogen in an apparatus linked to a high vacuum line. The monomer was introduced with a syringe through a serum cap into the flask containing the catalyst (azobisisobutyronitrile:AIBN) which had previously been dried under high vacuum. The reaction mixture was magnetically stirred at the desired tempera-

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ture. The polymers were recovered after dissolution in methylene chloride and precipitation in petroleum ether. They were then dried under high vacuum.

The preparation of PVOCCI samples has been described in previous papers^{4,5}. Amines and 2-mercaptopyrimidine were commercial products used without special purification. *N*-methylbenzylamine and *N*-methylaniline were redistilled under nitrogen just before use. The procedure for the chemical modification of PVOCCI has been described previously⁹. The degree of substitution was determined by elemental analysis of the remaining Cl and N.

Most of the polymers were examined by i.r. spectroscopy with a Perkin Elmer 297 apparatus. The ¹³C n.m.r. spectra were obtained using a Bruker WP 250 spectrometer at 62.5 MHz on polymer solutions in a 90/10 mixture of 1,2,4-trichlorobenzene/perdeuterated nitrobenzene at 100°C. All the carbon chemical shift values were reported with respect to the internal reference HMDS. Molecular weights of polymers were measured by osmometry in toluene at 37°C. Glass transition temperatures were determined with a du Pont 1090 thermal analyser. They were taken as the intersection of the extrapolation of the baseline with the extrapolation of the inflexion on curves obtained with a heating rate of 20°C min⁻¹. Thermal stability of polymers was examined by thermogravimetry by heating the samples from 20°C to 700°C at 5°C min⁻¹ in air with a du Pont 990 thermal analyser.

RESULTS AND DISCUSSION

Polymerization of vinyl carbamates and of vinyl phenyl thiocarbonate

The polymerizations of *N*-methylcyclohexyl vinyl carbamate, *N*-piperidine vinyl carbamate and vinyl phenyl thiocarbonate (VOCSPH) were carried out in bulk with azobisisobutyronitrile (AIBN) as the initiator. The results are shown in Table 1.

High molecular weight polymers were obtained. The results of elemental analysis of these polymers are in good agreement with the theoretical values: Calculated for (C₁₀H₁₇NO₂)_n: C: 65.6%; H: 9.3%; N: 7.6%; O: 17.5%.

Found for poly(*N*-methylcyclohexyl vinyl carbamate): C: 65.0%; N: 9.3%; O: 18.1%. Calculated for (C₈H₁₃NO₂)_n: C: 61.9%; H: 8.4%; N: 9.0%; O: 20.7%. Found for poly(*N*-piperidine vinyl carbamate): C: 61.2%; H: 8.4%; N: 8.9%; O: 21.5%. Calculated for (C₉H₈SO₂)_n: C: 60.0%; H: 4.4%; S: 17.8%; O: 17.8%. Found for PVOCSPh: C: 59.8%; H: 4.5%; S: 18.0%; O: 17.7%. The carbonyl band observed in the i.r. spectra of these poly(vinyl carbamates) is located at 1700 cm⁻¹ whereas it is located at 1730 cm⁻¹ for PVOCSPh.

Chemical modification of PVOCCI by amines and by 2-mercaptopyrimidine

PVOCCI samples coming from the same polymerization batch were allowed to react with *N*-methylbenzylamine, carbazole, *N*-methylaniline, 2,3-dimethylindole and 2-mercaptopyrimidine, in methylene chloride, with a small amount of 50% aqueous NaOH, at room temperature. A phase transfer catalyst (Bu₄N⁺HSO₄⁻:TBAH) was used in some cases. The results are shown in Table 2. Nearly quantitative substitution yields were observed in the case of aromatic amines like *N*-methylbenzylamine⁹ and *N*-methylaniline in the absence of TBAH. The mechanism typically involves a nucleophilic attack at the carbonyl carbon of the chloroformate group by the unshared pair of electrons of the nitrogen atom of these amines. In contrast, nitrogen's extra pair of electrons in heterocyclic compounds like carbazole or 2,3-dimethylindole is involved in the π cloud, and is not available for a nucleophilic attack at the carbonyl carbon. Thus, in the absence of TBAH, no reaction occurs between PVOCCI and carbazole at room temperature in CH₂Cl₂ after 0.5 h whereas a quantitative yield of substitution is observed after 3 h on adding a catalytic amount of TBAH (runs 6 and 7 in Table 2). The mechanism in this case is the formation of carbazyl tetrabutylammonium which reacts very rapidly with the carbonyl of PVOCCI in the same manner as proposed for the *N*-alkylation reactions of carbazole by chloromethylated polystyrene or polyepichlorhydrin¹⁶.

The carbonyl band observed in the i.r. spectra of PVOCCI modified by carbazole, *N*-methylaniline and 2,3-dimethylindole is located at 1725, 1705 and

Table 1 Bulk polymerization of vinyl carbamates and of vinyl phenyl thiocarbonate initiated by AIBN ([AIBN]/[monomer] = 0.5%)





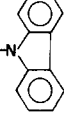



Run	Monomer	Temperature (°C)	Time (h)	Yield (%)	\bar{M}_n osm
1		60	18	70	80 000
2		60	18	63	46 500
3 ^a		65	3	53	53 000
4	VOC-SPh	60	18	57	43 000

^aPolymerization carried out in glass apparatus sealed under high vacuum; [AIBN]/[monomer] = 1%

Table 2 Reaction of amines and of 2-mercaptopyrimidine with PVOCCI under PTC conditions at room temperature (PVOCCI : 5×10^{-3} mole; CH_2Cl_2 : 35 ml; 50% aq. NaOH : 0.4 ml; magnetic stirring)

Run	Amine	[Amine] / [PVOCCI]	TBAH ^a (mol%)	Time (h)	Degree of substitution (%)
5	<i>N</i> -methylbenzyl amine	2.6	—	0.25	97
6	<i>N</i> -methylaniline	2.5	—	0.33	100
7	Carbazole	2.5	—	0.50	0
8	Carbazole	2.5	5	3	100
9	Carbazole	1.0	5	5	100
10	2,3-dimethylindole	2.5	5	7	90
11 ^b	2-mercaptopyrimidine	1.5	5.5	3.66	98

^aReferred to the Cl content of polymer^b CH_2Cl_2 : 50 ml**Table 3** Thermal properties of some poly(vinyl chloroformate) derivatives
$$\text{---} \left[\text{CH}_2\text{---CH} \left(\text{---O---C(=O)---R} \right) \right]_n \text{---}$$

Run	R	T_g (°C)	$T_{\text{decomposition}}^a$ (°C)	\overline{M}_n
3		45	285	53 000
1		37	270	80 000
5		40	273	58 000
9		62	264	58 000
8		65	247	~78 000 ^b
11		35	219	~60 000 ^b
4		74	240	43 000
12 ^c		82	257	42 000

^aMaximum of the derivative thermodynamic curve; ^bCalculated from \overline{M}_n of PVOCCI ($\overline{M}_n = 34\,000 \pm 1\,000$) deduced from \overline{M}_n measured for samples modified by *N*-methylbenzylamine (run 5) and by *N*-methylaniline (run 9); ^cSample obtained by bulk polymerization of VOCOPh at 60°C with AIBN as initiator⁵.

1725 cm^{-1} respectively whereas it is located at 1735 cm^{-1} in the case of PVOCCI modified by 2-mercaptopyrimidine.

Thermal properties of poly(vinyl chloroformate derivatives)

Glass transition temperatures and thermal stability for several poly(vinyl carbamates) and poly(vinyl thiocarbonates) have been determined and the results are shown in Table 3. For comparison, the thermal behaviour of a poly(vinyl phenyl carbonate) sample prepared by free radical polymerization of the corresponding monomer⁵ also has been examined (run 12, Table 3).

The thermal stability of these polymers seems to decrease slightly in the following way: poly(vinyl carbamates) > poly(vinyl carbonates) > poly(vinyl thiocarbonates). The values of T_g for the polymers $[\text{CH}_2\text{---CH}(\text{OCOR})_n$ decrease according to the following order for R: $-\text{O}-\text{Ph} > -\text{S}-\text{Ph} > -\text{N}(\text{CH}_3)-\text{Ph}$. Among the T_g values



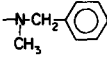

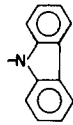


for poly(vinyl carbamates) the slight differences observed could be explained by differences afforded by the side groups which could affect the torsional mobility of the skeletal bonds¹⁷.

¹³C n.m.r. spectra of poly(vinyl chloroformate) derivatives

The ¹³C chemical shifts of the carbon atoms of the main chains and of the carbonyl groups for some poly(vinyl chloroformate) derivatives are given in Table 4.

In all cases, the stereosensitivity of all carbons of the main chains is observed. The methine carbons of the chains exhibit mainly triad effects whereas the methylene carbons of the chains are sensitive to at least tetrad effects and probably in the case of polymers 1 and 5 to hexad effects giving complicated multiplets. The areas of the three peaks of the rather symmetrical triplets given by the methine carbons of the chains correspond approximately to the 1:2:1 ratio. Thus it can be deduced that all the

Table 4 ^{13}C n.m.r. chemical shifts (ppm; ref: HMDS) of carbon atoms of the main chains and of carbonyl groups for some poly(vinyl chloroformate) derivatives: $-\text{CH}_2-\text{CH}(\text{O}-\text{C}(=\text{O})-\text{R})-\text{CH}_2-$ (m = multiplet)

Run	R	$\text{C}=\text{O}$	$-\text{CH}-$ ↑	$-\text{CH}_2-$
3		153.1	67.8 67.5 67.2	(m) 38.7
1		153.5	67.5 67.2 67.0	(m) 38.6
5		154.2	68.1 67.6 67.3	(m) 38.8
9		153.1 153.0 152.9	68.3 67.7 67.4	(m) 38.4
8		149.8 149.7	70.8 69.9 69.4	(m) 38.1
4		167.1 166.9	70.8 69.9 69.3	(m) 38.0
12		151.2 151.5 151.7	71.9 70.7 69.6	(m) 37.9

polymers are predominantly atactic and that they probably correspond to $P_m=0.5$ of the Bernoullian statistical distribution. The accuracy of the determination of areas of the peaks corresponding to the methine carbon resonances is a little marred by the fact that sometimes these triplets are slightly splitted showing pentad effects. This assumed random distribution is quite expected since these polymers have been prepared according to a free-radical process in solution.

Concerning the carbonyl resonances, all the shifts are within the 149–154 ppm range except for that corresponding to polymer 4 for which a deshielding effect due to the neighbouring sulphur atom is observed. It is worth noting that the stereosensitivity exhibited by the carbonyl groups is observed in the case of polymers having the highest T_g , i.e. the less mobile side groups.

A detailed analysis of the percentage of the different n -ads was not possible since not only the meso and racemic contents seem to be identical but the variation of stereospecificity of the polymerization process which allows the assignments has revealed to be quite difficult.

In conclusion, new poly(vinyl carbamates) and poly(vinyl thiocarbonates) have been prepared either by free radical polymerization of monomers or by chemical modification of poly(vinyl chloroformate) with the appropriate amine or thiol using phase transfer catalysis conditions. The structure of these polymers has been analysed by ^{13}C n.m.r. spectroscopy and their thermal behaviour has been examined. Further work in this field is in progress.

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