Polymer Bulletin 9, 114–120

Polymer Bulletin

Chemical Modification of Poly(Vinyl Chloroformate) and of its Copolymers Using Phase Transfer Catalysis

Sylviane Boivin, Abderrahmane Chettouf, Patrick Hemery and Sylvie Boileau

Laboratoire de Chimie Macromoléculaire associé au CNRS, Collège de France,
11 place Marcelin Berthelot, F-75231 Paris Cédex 05, France

ABSTRACT

The chemical modification of poly(vinyl chloroformate) and of its copolymers with compounds containing labile hydrogen atoms like amines, phenols, alcohols and 2-oxazolidone as well as with potassium cyanide and potassium fluoride has been investigated. Phase transfer catalysis conditions lead to soluble modified polymers with good substitution yields.

INTRODUCTION

The chemical modification of functional polymers has been extensively studied during the last decade. It has been shown that poly(vinyl chloroformate)(PVOCCl) can react with compounds containing labile hydrogen atoms like alcohols, phenols and amines (SCHAEFGEN, 1960 and 1968). Since we were able to prepare well-defined high molecular weight PVOCCl in quantitative yields (BOILEAU et al., 1980, MEUNIER et al., 1979, 1981, 1982 a) as well as copolymers of vinyl chloroformate (VOCCl) and vinyl acetate (VAC)(MEUNIER et al., 1981, 1982 b), we tried to find convenient conditions for the reaction of several amines, alcohols, phenols and KCN with PVOCCl in order to avoid degradation and to obtain soluble modified polymers with good substitution yields (MEUNIER et al., 1979, 1981, 1982 c). Other substituents have been tried and this work has been extended to copolymers of VOCCl with vinyl acetate (VAC). Moreover the use of phase transfer catalysis conditions led to higher substitution yields. Recent results in this area are described in this paper.

EXPERIMENTAL

PVOCCl samples were prepared by polymerization of VOCCl in

0170-0839/82/0009/0114/$01.40

CH_2Cl_2 at 35°C using dicyclohexyl peroxydicarbonate as initiator (MEUNIER et al. 1982 a). The same procedure was applied to the preparation of random copolymers of VOCCl with VAC (MEUNIER et al., 1982 b). Three samples were obtained, the composition of which was determined by elemental analysis. The molar fractions of VOCCl units in these copolymers were equal to 0.50 (COP 50), 0.18 (COP 18) and 0.05 (COP 5).

The procedure for the chemical modification of PVOCCl has been described previously (MEUNIER et al., 1979, 1982 c). The degree of substitution was determined by elemental analysis of the remaining Cl and C or N according to the substituent. Modified polymers and copolymers were characterized by IR, ^1H and ^{13}C NMR spectroscopy.

RESULTS AND DISCUSSION

Reaction with amines

Some typical experiments made with N-methylbenzylamine are shown in Table 1. Alkali carbonates were used as HCl scavengers since their excellent efficiency has been demonstrated for the reaction of amines with chloroformates (PITEAU et al., 1975). Since the amine is added in excess with respect to the chloroformate functions, some quaternary ammonium salt is formed which can act as phase transfer catalyst. Most of the chemical modifications were quantitative after 3 hours' reaction in the case of alkali carbonates. However, the use of 50% aqueous NaOH instead of alkali carbonates leads to quantitative yields of substitution after shorter reaction times, at lower temperatures.

Direct measurements of molecular weights of polymers containing chloroformate groups are difficult since these functions are very polar and reactive. The quantitative modification by N-methylbenzylamine leads to polymers which are soluble and stable in toluene and in THF. Thus it is possible to measure their molecular weight by osmometry and by GPC and to deduce those of the starting polymers (see Table 1). Moreover the values of $\overline{M}_n$ determined from those of polyvinylcarbamates prepared by different ways from a given batch of PVOCCl (runs 1 and 2 ; 3 and 4) are the same within the experimental errors.

TABLE 1

Reaction of N-Methylbenzylamine with PVOCCl and with copolymers VOCCl/VAC in CH_2Cl_2 ([amine]/[Cl] = 1.5 ; [Base]/[Cl] = 2)

Run	Polymer	Base	t (°C)	Time (min)	D.S. (%)	$\overline{M}_n$ osm. [a)]
1	PVOCCl	Na_2CO_3	40	165	99	19000
2 [b)]	PVOCCl	50% NaOH [c)]	20	20	100	20000
3	PVOCCl	Na_2CO_3	40	155	98	18000
4 [b)]	PVOCCl	50% NaOH [d)]	20	10	100	18500
5	COP 50	Na_2CO_3	40	150	96	16000
6	COP 18	Na_2CO_3	40	180	100	27500
7	COP 5	Na_2CO_3	40	165	98	21500

a) calculated from the value obtained for the modified polymer ; b) [amine]/[Cl] = 2.3 ;
c) [base]/[Cl] = 1 ; d) [base]/[Cl] = 1.5

This shows that no significant degradation of PVOCCl occurs by using a strong base like 50% aq. NaOH during its modification by amines.

Reaction with phenols and alcohols

Some results are shown in Table 2. The use of phase transfer catalysis conditions leads to an excellent yield of substitution (96%) in the case of the reaction of phenol with PVOCCl by using SO_4HNBu_4 (TBAH) as catalyst. It was also possible to modify a copolymer of VAC with VOCCl (COP 18) by p-nitrophenol in a good yield (83%). Moreover soluble polymers containing ferrocene groups linked to the backbone via carbonate functions were obtained by reaction of PVOCCl and of its copolymer (COP 18) with ferrocenic alcohol (runs 13 and 14). In all cases no hydroxyl band could be detected by IR showing the absence of significant hydrolysis of the polymers during the modification.

Reaction with 2-oxazolidone

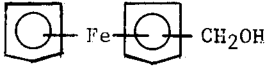
The chemical modification of PVOCCl (5 mmol) with 2-oxazolidone (5.5 mmol) was made under phase transfer catalysis conditions (CH_2Cl_2/50% aq. NaOH : 50ml/0.3ml ; SO_4HNBu_4 : 5 mol % of the chlorine content of PVOCCl). After 3 h at 20°C, the degree of substitution was equal to 79 %. The characteristic bands of the IR spectrum are located at 1755 cm^{-1} (vs) and 1820 cm^{-1} (vs) which correspond to the two carbonyl vibrations of the linear and cyclic carbamate functions.

Reaction with KCN

We were able to prepare poly(vinyl cyanoformate)(PVOCCN) by reaction of PVOCCl with KCN, using dicyclohexyl-18 crown-6 (DCHE) as phase transfer catalyst (MEUNIER et al., 1979, 1982 c). However it was necessary to operate in acetonitrile in order to obtain a 80% yield of substitution. The use of SO_4HNBu_4 combined with the presence of a small amount of water instead of the crown-ether leads to excellent yields of substitution in a less polar solvent like CH_2Cl_2 (runs 17, 19 and 20, Table 3). The rôle of water was noticed for the reaction of chloroformates with KCN catalyzed by 18-crown-6 (CHILDS and WEBER, 1976; WEBER and GOKEL, 1977). It was assumed that water was needed to assist

TABLE 2

Reaction of alcohols and phenols with PVOCCl and with copolymers VOCCl/VAC in CH_2Cl_2. ([ROH]/[Cl] = 1.5 ; [Base]/[Cl] = 2)

Run	Polymer	ROH	Base	Catalyst (mol %)[a]	t (°C)	Time (min)	D.S. (%)
8[b]	PVOCCl	C_6H_5OH	pyridine	no	-10	180	88
9	PVOCCl	C_6H_5OH	50% NaOH[c]	TBAH(5)	20	85	96
10	COP 18	C_6H_5OH	pyridine	no	0	180	83
11	COP 5	C_6H_5OH	pyridine	no	0	180	82
12	COP 18	$NO_2C_6H_4OH$	50% NaOH[c]	TBAH(5)	0	210	83
13	PVOCCl		pyridine	no	0	180[d]	69
14	COP 18	"	50% NaOH[c]	TBAH(5)	0	300	70

[a] mol % of the chlorine content of polymer ; [b] ref. MEUNIER et al., 1981 ; [c] [base]/[Cl] = 2.5 for run 9 and 8.3 for runs 12 and 14 ; [d] +18h at 20°C

in degrading the KCN crystal lattice. Kinetic studies on this type of reaction is in progress.

TABLE 3

Reaction of KCN with PVOCCl and with copolymers VOCCl/VAC in CH_2Cl_2 at 20°C. ([KCN]/[Cl] = 1.5)

Run	Polymer	Catalyst (mol %) [a]	Time (h)	D.S. (%)
16 [b]	PVOCCl	DCHE (5)	5	29
17 [d]	PVOCCl	TBAH (5.3) [c]	3.7	92
18	COP 18	TBAH (5)	28	67
19	COP 18	TBAH (10) [c]	0.75	88
20	COP 18	TBAH (10) [c]	1.25	93

[a] mol % of the chlorine content of polymer ; [b] ref. MEUNIER et al., 1982 c ; [c] +0.2 ml H_2O; [d] [KCN]/[Cl] = 1

Reaction with KF

Some results are indicated in Table 4. As in the case of the reaction of KCN with chloroformate functions, a small amount of water increases the reaction rate. Chloroformate groups can

TABLE 4

Reaction of KF with copolymers VOCCl/VAC in CH_2Cl_2 at 40°C ([KF]/[Cl] = 3.5)

Run	Polymer	Catalyst (mol %) [a]	Time (h)	D.S. (%)
21	COP 5	TBAH (8) [b]	1	45
22	COP 18	TBAH (8) [b]	5	83

[a] mol % of the chlorine content of polymer ; [b] + 0.2 ml H_2O

be converted into fluoroformate groups in a high yield (run 22). The characteristic IR bands of the modified copolymer (run 22) are located at 1740 cm^{-1} (vs), ν(C=O) acetate and 1830 cm^{-1} (vs), ν(C=O) fluoroformate.

CONCLUSION

Phase transfer catalysis conditions are quite convenient for the preparation of a large variety of new polymers by reaction of different functional molecules with PVOCCl as well as with copolymers containing chloroformate side groups. Further work in this field is in progress.

ACKNOWLEDGMENTS

The Société Nationale des Poudres et Explosifs is gratefully acknowledged for its financial support. The authors thank D^{r} J.P. SENET for many stimulating discussions.

REFERENCES

BOILEAU,S., JOURNEAU,S. and MEUNIER,G. : Fr. Patent 80/02651 (1980)

CHILDS,M.E. and WEBER,W.P. : J. Org. Chem., 41, 3486 (1976)

MEUNIER,G., HEMERY,P., SENET,J.P. and BOILEAU,S. : Polymer Bulletin, 1, 809 (1979) and 4, 699 (1981)

MEUNIER,G., HEMERY,P., BOILEAU,S., SENET,J.P. and CHERADAME,H. : Polymer, 23, 849 (1982)

MEUNIER,G., HEMERY,P. and BOILEAU,S. : Polymer, 23, 855 (1982)

MEUNIER,G., BOIVIN,S., HEMERY,P., BOILEAU,S. and SENET,J.P. : Polymer, 23, 861 (1982)

PITEAU,M., SENET,J.P. and VITRANT,A.M. : Fr. Patent 75/25470 (1975)

SCHAEFGEN,J.R. : U.S. Patent 3, 118, 862 (1960)

SCHAEFGEN,J.R. : J. Polym. Sci. C, 24, 75 (1968)

WEBER,W.P. and GOKEL,G.W. : Phase Transfer Catalysis in Organic Synthesis, Berlin, Heidelberg, New York : Springer 1977

Received November 5, accepted November 16, 1982