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Polymerization and Copolymerization of Vinyl Carbamates and Vinyl Carbonates

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ABSTRACT

Poly(vinyl carbamates) and poly(vinyl carbonates) of high molecular weight have been obtained by polymerization of the corresponding monomers prepared from vinyl chloroformate. Poly(vinyl carbonates) can also be prepared by chemical modification of poly(vinyl chloroformate) with alcohols and phenols. Copolymerization parameters of phenyl vinyl carbonate with vinyl acetate have been determined in methylene chloride, at 35°C, with dicyclohexyl peroxydicarbonate as initiator.

INTRODUCTION

The polymerization and copolymerization of vinyl carbamates and vinyl carbonates have received little attention. Polymerization of vinyl urethane (SCHAEFGEN, 1968) and of vinyl carbamates derived from cyclic amines like morpholine (OVERBERGER, 1962), aziridine, piperidine or pyrrole (DOW CHEMICAL Co., 1966) has been mentionned. Low molecular weight products have been obtained by polymerization of methyl vinyl carbonate (KÜNG, 1945) and tertiobutyl vinyl carbonate (SCHAEFGEN, 1968). Copolymerization parameters of N-diethyl vinyl carbamate with vinyl acetate, styrene (RINGSDORF, 1963), acrylic acid, methyl acrylate and maleic anhydride (VON HÄGELE, 1964) have been determined as well as those of ethyl vinyl carbonate with p-chlorostyrene and vinyl acetate (KIKUKAWA, 1967).

We have recently examined the polymerization of vinyl chloroformate (VOCCl) and of its derivatives, namely of phenyl vinyl

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carbonate, as well as the chemical modification of poly(vinyl chloroformate) (PVOCCl) (MEUNIER et al., 1979;MEUNIER , 1981). This paper will describe the results concerning the polymerization and copolymerization of some vinyl carbamates and vinyl carbonates.

POLYMERIZATION OF VINYL CARBAMATES AND VINYL CARBONATES.

N-diethyl vinyl carbamate (I) was prepared by reaction of VOCCl with triethylamine (SCHNUR, 1973); N-butyl vinyl carbamate (II) was obtained from reaction of VOCCl with butylamine using Na_2CO_3 as HCl scavenger (PITEAU et al., 1975). Reaction of methanol, phenol and menthol with VOCCl leads to the corresponding vinyl carbonates (III), (IV) and (V) according to the described procedures (STRAIN et al., 1945; SCHAEFGEN, 1968; SCHNUR, 1973). These monomers have been polymerized in bulk and the results are shown in Table. 1.

TABLE 1

Polymerization of vinyl carbamates (I, II) and vinyl carbonates (III, IV, V) in bulk.

Monomer	Initiator	$\frac{[\text{Initiator}]}{[\text{Monomer}]}$	Temp. °C	Time h.	Yield %	$\overline{M}_n$ osm
I	DCPD [a]	0.5 %	35	18	-	37,000
I	AIBN	0.5 %	60	18	84	79,000
II	AIBN	0.5 %	60	18	65	35,000
III	AIBN	3 %	60	50	32.5	4,800
IV	BP [b]	0.1 %	80	19	23	65,000
IV	BP	0.1 %	87	19	32	40,000
IV	DCPD	0.5 %	35	20	65	92,000
V	BP	0.1 %	87	33	14	27,000
V	DCPD	0.5 %	35	16	44	73,000
V	DCPD	1 %	35	6	54	53,000

a) dicyclohexyl peroxydicarbonate ; b) benzoyl peroxide.

(I) : N-diethyl vinyl carbamate ; (II) : N-butyl vinyl carbamate;

(III) : methyl vinyl carbonate ; (IV) : phenyl vinyl carbonate ;

(V) : menthyl vinyl carbonate.

High molecular weight polymers were obtained except for methyl vinyl carbonate which is difficult to purify and for which the ratio : [initiator] / [monomer] was high. These new polymers have been characterized by IR, ^1H and ^{13}C NMR spectroscopy. As in the case of PVOCCl, the tertiary carbon atom in the main chain is sensitive to triad effects. A detailed study of the properties of these polymers will be published in a subsequent paper.

CHEMICAL MODIFICATION OF PVOCCl

It has been shown that PVOCCl reacts with compounds containing labile hydrogen atoms like alcohols, amines and phenols (SCHAEFGEN, 1968). We have found convenient conditions for the reaction of several amines with PVOCCl in order to avoid degradation and to obtain soluble modified polymers with nearly quantitative yields of substitution (MEUNIER et al., 1979; MEUNIER , 1981). Poly(butyl vinyl carbamate) was thus prepared by reaction of n-butyl amine with PVOCCl, in methylene chloride at 42°C, using Na_2CO_3 as HCl scavenger. After 4 hours of reaction, the yield of substitution was equal to 95 % and the resulting polymer had the same IR and NMR spectra as the sample prepared by polymerization of the corresponding vinyl carbamate.

Poly(vinyl carbonates) can also be obtained by reaction of PVOCCl with alcohols and phenols.

TABLE 2

Reaction of alcohols and phenols with PVOCCl ([ROH] / [Cl] = 1.5; [HCl scavenger] / [Cl] = 2).

ROH	Solvent	HCl scavenger	Temp. °C	Time h.	Degree of substitution %
$NO_2C_6H_4OH$	CH_2Cl_2	K_2CO_3 a)	40	2	23
C_6H_5OH	CH_2Cl_2	pyridine b)	-10	3	88
$CH_3OC_6H_4CH_2OH$	CH_2Cl_2	pyridine b)	0	3	93
quinine	THF	K_2CO_3 a)	20	1.25	45 c)

a) with dicyclohexyl-18 crown-6 : 1.5 mol % of the chlorine content of PVOCCl;
b) added dropwise to the mixture during 1 h ; c) insoluble polymer.

TABLE 3

Copolymerization of vinyl acetate (M_1) and VOCOPh (M_2) in CH_2Cl_2 at 35°C initiated by DCPD [a)]

Run	$[M_1]_o + [M_2]_o$ mol/l	M_1 mole fraction in monomers	Polymerization time h.	Yield %	M_1 mole fraction in copolymer [b)]
1	2.19	0.79	0.5	2.5	0.79_5
2	2.13	0.59	2	4.9	0.63
3	2.16	0.49_5	4.5	21.2	0.54
4	2.21	0.39_5	2.5	3.2	0.52
5	2.15	0.24	3.3	4.8	0.36

[a)] [Initiator] / [Monomers] = 0.5 % ; [b)] determined from ^1H NMR Spectra of the copolymers.

The procedure for the chemical modification of PVOCCl has been described previously (MEUNIER et al., 1979 ; MEUNIER , 1981). The degree of substitution was determined by elemental analysis of C or N and of remaining Cl. Some results are indicated in Table 2.

The best results are obtained by using pyridine as HCl scavenger. Contrary to the observation made by SCHAEFGEN (SCHAEFGEN, 1968), no hydrolysis occurs during the reaction of PVOCCl with phenol since no hydroxyl absorption is detected in the IR spectrum of the modified polymer.

COPOLYMERIZATION OF PHENYL VINYL CARBONATE

The monomer reactivity ratios r_1 and r_2 were determined in copolymerization of vinyl acetate (VA) and phenyl vinyl carbonate (VOCOPh) in CH_2Cl_2 at 35°C with DCPD as initiator. The results are given in Table 3. The KELEN-TÜDÖS method extended to high-conversion data was used for the treatment of the experimental data (KELEN et al., 1975 ; TÜDÖS et al., 1976 ; KELEN et al., 1977). The reactivity ratios r_1 (VA) and r_2 (VOCOPh) are equal to 0.83 ± 0.10 and 0.38 ± 0.10, respectively. Vinyl acetate is slightly more reactive than phenyl vinyl carbonate. From the ^{13}C NMR spectrum and the GPC curve of such a copolymer, it can be concluded that the phenyl side groups are randomly distributed along the macromolecules.

CONCLUSION

High molecular weight poly(vinyl carbamates) and poly(vinyl carbonates can be obtained by polymerization of VOCCl derivatives with free-radical initiators. They can also be prepared by chemical modification of PVOCCl. Random copolymers of vinyl acetate and phenyl vinyl carbonate have been obtained, and their reactivity ratios have been determined at 35°C in CH_2Cl_2 with dicyclohexyl peroxydicarbonate as initiator. Vinyl acetate is slightly more reactive than phenyl vinyl acetate. Further work on the polymerization and copolymerization of new VOCCl derivatives is in progress.

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