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Polymerization and Copolymerization of Vinyl Chloroformate

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ABSTRACT

Use of peroxydicarbonates as free-radical initiators for the polymerization of vinyl chloroformate (VOCCl), in bulk and in solution, leads to high molecular weight polymers. Copolymerization parameters of VOCCl with vinyl acetate have been determined in methylene chloride, at 35°C, with dicyclohexyl peroxydicarbonate as initiator.

INTRODUCTION

The polymerization and copolymerization of vinyl chloroformate (VOCCl) have been little investigated (SCHAEFGEN, 1960 and 1968) until it has been recently shown that pure VOCCl could be obtained with 80 % yield (MALFROOT, 1978). We have examined in detail the polymerization of this monomer and of its derivatives as well as the chemical modification of poly(vinyl chloroformate)(PVOCCl) (MEUNIER et al., 1979 ; BOILEAU et al., 1980 ; MEUNIER , 1981). This paper will describe our recent results concerning the polymerization and copolymerization of VOCCl.

POLYMERIZATION OF VOCCl

VOCCl acquired from the SNPE (purity > 99 %) was polymerized in bulk with dicyclohexyl peroxydicarbonate (DCPD) and bis(4-tertiobutylcyclohexyl) peroxydicarbonate (TBCPD), at 35°-40°C. The results are shown in Table 1. 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. Molecular weights were deduced from the values of $\overline{M}_n$ mea-

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sured by osmometry in toluene at 37°C on PVOCCl modified with 100 % yield by N-methylbenzylamine as described previously (MEUNIER et al., 1979).

TABLE I

Bulk Polymerization of VOCCl initiated by free-radical catalysts.

Run	Initiator	$\frac{[\text{Initiator}]}{[\text{Monomer}]}$	Temp. °C	Time h	Yield %	$\overline{M}_n$ osm [a]
1	DCPD [b]	0.05 %	40	100 min	55	15,000
2 [c]	DCPD	0.1 %	40	8 min	>90	48,000
3 [c]	DCPD	0.5 %	35	70 min	∿100	-
4 [d]	DCPD	0.5 %	35	47 min	∿100	68,000
5 [d]	TPCPD [e]	0.5 %	35	40 min	98	72,000
6	BP [f]	0.5 %	54	15 h	92	39,000
7	AIBN	0.5 %	56	17 h	98	59,000

[a] calculated from the value obtained for the polymer quantitatively modified by N-methylbenzylamine ; [b] dicyclohexyl peroxy dicarbonate ; [c] gel effect observed ; [d] experiments made under high vacuum ; [e] bis(4-tertiobutylcyclohexyl) peroxydicarbonate ; [f] benzoyl peroxide.

More conventional free-radical initiators like benzoyl peroxide (BP) and AIBN were used. It was found that they lead to high molecular weight PVOCCl with good yields, contrary to the results of SCHAEFGEN (SCHAEFGEN, 1968). However the polymers were slightly colored, whereas the samples obtained with peroxydicarbonates at lower temperatures were colorless.

The remarkable efficiency of peroxydicarbonates for the bulk polymerization of VOCCl prompted us to make some experiments in solution, in apparatus sealed under high vacuum, with solvents purified on sodium mirrors (MEUNIER, 1981). Some results are shown in Table 2.

TABLE 2

Polymerization of VOCCl in solution initiated by DCPD

Run [a]	Solvent	[M] mol/l	[Initiator] / [Monomer]	Temp. °C	Time h	Yield %	$\overline{Mn}$ osm
8 (A)	THF	2.64	1.1 %	42	3	31	-
9 (A)	CH_2Cl_2	3.54	0.5 %	35	20	93	22,000
10 (B)	CH_2Cl_2	4.95	1.1 %	35	1.75	100	70,000
11 (B)	CH_2Cl_2	5.34	0.8 %	35	2	100	70,000
12 (C)	CH_2Cl_2	5.38	1.8 %	35	2.2	100	20,000
13 (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.

Methylene chloride was found to be a convenient solvent and it was possible to prepare high molecular weight PVOCCl in controlled conditions. The results are reproducible using the same batch of monomer. Moreover the molecular weights distribution is narrower in this case ($\overline{M}_w/\overline{M}_n \simeq 2$) than in bulk.Kinetic studies of the radical polymerization of VOCCl initiated by peroxydicarbonates in CH_2Cl_2 are in progress.

COPOLYMERIZATION OF VOCCl

Results of SCHAEFGEN (SCHAEFGEN, 1968) for copolymerization of VOCCl and vinyl acetate (VA) at 0°C with 0.6 % tri-n-butylboron as initiator show the presence of 30 % of homopoly (vinyl acetate) besides the copolymer. Preliminary experiments were made in the same conditions as those described by SCHAEFGEN and we did not observe the formation of homopoly(vinyl acetate).

Since we were able to prepare high molecular weight PVOCCl in CH_2Cl_2 at 35°C with DCPD as initiator, we decided to determine

TABLE 3

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

Run	$[M_1]_o + [M_2]_o$ mol/1	M_1 mole fraction in monomers	Polymerization time h	Yield %	M_1 mole fraction in copolymer	
					from Cl %	from NMR
14	2.40	0.83	1	43.3	0.81	0.80
15	2.32	0.58_5	1	17.4	0.55_5	0.58_5
16	2.43	0.49_5	0.75	20.6	0.50	0.50_5
17	2.40	0.39	0.50	12.1	0.43_5	0.45_5
18	2.31	0.20	0.55	11.8	0.25_5	0.24_5
19	10.86 b)	0.50	18	16.2	0.50	0.53_5

[a] [Initiator] / [Monomers] = 0.5 % except for run 19 (0.23 %) ; b) experiment made in bulk.

the monomer reactivity ratios r_1 and r_2 in copolymerizations of VA and VOCCl in these conditions (MEUNIER, 1981). 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 (VOCCl) are equal to 0.7 ± 0.1 and 0.6 ± 0.1, respectively. From the ^{13}C NMR spectrum and the GPC curve of such a copolymer modified quantitatively by N-methylbenzylamine, it can be concluded that the distribution of chloroformate side groups along the macromolecules is random.

Vinyl acetate and vinyl chloroformate have nearly the same reactivity towards free radicals. Therefore, one can predict the behavior of VOCCl on the copolymerization with other vinyl monomers. For instance, styrene is much more reactive than VOCCl, as determined by the copolymerization of 50/50 mixture of these two monomers : only 3 % of VOCCl units are present in the copolymer obtained with 25 % yield. Vinyl chloride is also more reactive than VOCCl since the molar fraction of VOCCl in a copolymer obtained with 6 % yield is equal to 25 % whereas the initial molar composition of the monomers was 50/50.

CONCLUSION

We have shown that usual free-radical initiators can be used for the polymerization of pure VOCCl. Among them, peroxydicarbonates are the most convenient since they lead to high molecular weight, colorless polymers with quantitative yields, at 35°-40°C in bulk and in CH_2Cl_2 solutions. Random copolymers of VOCCl and vinyl acetate have been prepared, and their reactivity ratios have been determined at 35°C in CH_2Cl_2. These two monomers have nearly the same reactivity. It is therefore possible to prepare a large variety of copolymers containing reactive sites. Further work in this domain is in progress.

REFERENCES

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

KELEN, T. and TÜDÖS, F. : J. Macromol. Sci. Chem. A9, 1 (1975).

KELEN, T. , TÜDÖS, F., TURCSANYI, B. and KENNEDY, J.P. : J. Polym. Sci., Polym. Chem. Ed. 15, 3047 (1977).

MALFROOT, T. and PITEAU, M. : Belg. Patent 864, 309 (1978).

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

MEUNIER, G. : Thèse Docteur-Ingénieur, Paris (1981).

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

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

TÜDÖS, F., KELEN, T., FÖLDES-BEREZSNICH, T. and TURCSANYI, B. : J. Macromol. Sci. Chem. A 10, 1513 (1976).

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