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Synthesis and polymerization of fluorinated, chlorinated and deuterated vinyl carbonates

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ABSTRACT

The present paper deals essentially with the synthesis of new fluorinated and chlorinated poly(vinylcarbonates). Vinyl carbonates, $CH_2=CH-O-CO_2R$ (where $R=CH_2CCl_3$, CH_2CF_3, $C_2H_4C_6F_{13}$ and CD_3) were first prepared by reacting vinyl chloroformate with the corresponding alcohols. Their structures were identified by ^{13}C NMR. The action of ultraviolet light on these monomers resulted in the corresponding polycarbonates, the refractive indexes and Tg of which were measured. Polycarbonates possess Tg values between those of polyacrylates and polymethacrylates which contain the same substituents.

INTRODUCTION

We are interested in the synthesis of polymer materials as passive optical components. In the case of optical fibers, they are generally used in the production of the cladding but they are also under consideration for use in the core. In every case, the refractive index should be controlled which has to be lower for the cladding than for the core. Moreover, the polymer must show a very low attenuation. Taking into account the wavelengths being used (0.6 to 1.5 µm), the latter condition entails C-H bonds being replaced by bonds such as C-F, C-Cl or C-D. For this reason we carried out the syntheses and polymerizations of new halogenated or deuterated monomers (BOUTEVIN, 1984). Furthermore, polymer materials which constitute optical fibers must be amorphous, have a sufficiently high Tg and behave well from a mechanical point of view. Having prepared halogenated and deuterated acrylates and polyacrylates previously (ROUSSEAU, 1984), we have then investigated the syntheses of vinyl carbonates and corresponding poly (vinyl carbonates). The Tg of poly(phenyl acrylate) is known to be of 57° C while that of the corresponding poly(vinyl carbonate) is 82° C (BOIVIN, 1985). Moreover, polycarbonates are known to be good optical materials.

Some work has been carried out on poly(vinyl carbonates) during the last few years since vinyl chloroformate VO_2CCl has become an available monomer (MALFROOT, 1977). Consideration should be given to the work on radical polymerization (KASSIR, 1985) and anionic polymerization (BOILEAU, 1978) of vinyl carbonates

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as well as on copolymerization, one of the comonomers being a vinyl carbonate (GUYOT, 1984). Finally, it should be pointed out that poly(vinyl carbonates) can be prepared by chemical modification of poly(vinyl chloroformates) (MEUNIER, 1982) or by reaction of alkyl chloroformate with poly(vinyl alcohol) (SANCHEZ-CHAVES, 1985).

SYNTHESIS OF VINYL CARBONATES

Vinyl carbonates are prepared by reacting vinyl choroformate (which was supplied by the Société Nationale des Poudres et Explosifs) with the corresponding alcohol either using phase transfer catalysis (BOILEAU, 1984) or using pyridine in dichloromethane as the homogeneous phase. We preferred the latter method and a solid complex VO_2CCl-C_5H_5N was obtained in a first step. This pyridine-chloroformate complex was then destroyed by the selected alcohol resulting in the expected vinyl carbonate. Vinyl carbonates (I), (II) (III) and (IV) were obtained from alcohols CD_3OH, Cl_3C-CH_2OH, CF_3-CH_2OH and $C_6F_{13}C_2H_4OH$, respectively. They are reported in Table 1.
Because of the excellent agreement between the values given in the literature and our results, it was possible to identify the carbon atoms of the double bond by comparing our spectra with the ^{13}C NMR spectra of ethyl acrylate. Similarly, the spectrum of CH_2=CH-O-C-N$(C_2H_5)_2$ shows signals at 94.1 x 10^{-6} and 143.2 x 10^{-6} due to the (CH_2) and (CH) carbon atoms of the double bond, respectively (MEUNIER, 1982).
In the ^1H NMR spectrum, the signal of the vinyl group of the carbonate appears as an ABX system, the X part (-CH=) of which is centred at 7.1 x 10^{-6} and the AB part (CH_2=) at 4.7 x 10^{-6}, while in the case of an acrylate, the ABX system gives a single multiplet centred at 6.25 x 10^{-6}.
For the substituent R derived from alcohol, a 0.5 x 10^{-6} deshielding is observed when changing from alcohol to carbonate.

VINYL CARBONATE POLYMERIZATION

It was performed by ultraviolet irradiation in the presence of DAROCUR (0.5 % based on monomer) as photosensitiser using a PHILIPS HPK 125 W lamp for one hour. The respective polymers were obtained from monomers (I), (II), (III) and (IV). These were hard and transparent materials. Only the polymer prepared from compound (IV) showed some flexibility. The refractive indexes and the Tg of these polymers are given in Table 3.

Table 1 : Physical characteristics of vinyl carbonates

Monomer	Boiling point b.p.	Refractive index $n_D^{20°}$
(I) $CH_2{=}CH{-}O{-}\underset{\overset{\|}{O}}{C}{-}OCD_3$	99°C (760mmHg)	1.3990
(II) $CH_2{=}CH{-}O{-}\underset{\overset{\|}{O}}{C}{-}OCH_2CCl_3$	88°C (10mmHg)	1.4667
(III) $CH_2{=}CH{-}O{-}\underset{\overset{\|}{O}}{C}{-}OCH_2CF_3$	107°C (760mmHg)	1.3552
(IV) $CH_2{=}CH{-}O{-}\underset{\overset{\|}{O}}{C}{-}OC_2H_4C_6F_{13}$	52°C (0.4mmHg)	1.3441

As the monomers were identified by ^1H NMR and ^{13}C NMR, their purity was checked.

The chemical shift values are reported in Table 2.

Table 2 : ^{13}C NMR - ^{13}C chemical shifts (10^{-6}) for compounds $H_2C{=}CH_2{-}O{-}\underset{\overset{\|}{O}}{C}{-}OR$

Compound	$H_2C{=}$	$=CH$	$-\underset{\overset{\|}{O}}{C}-$	R
(I)	96.5	142.5	152.9	CD_3 53.37 (septet)
(II)	98.9	142.5	151.5	CCl_3 94.16 (singlet)
(III)	98.4	142.6	152	$CH_2{-}CF_3$ 63.6 (quartet; J=37.5Hz) 122.77 (quartet; J=276.29Hz)
(IV)	97.7	142.7	152.6	$-\overset{\beta}{C}H_2\overset{\alpha}{C}H_2C_6F_{13}$ Cα30.61 (triplet; J=21.97Hz) Cβ60.18 (triplet; J=4.88Hz)
$CH_2{=}CH{-}O{-}\underset{\overset{\|}{O}}{C}{-}CH_3$	96.3*	141.6*	167.7*	-
Ø-O-$\underset{\overset{\|}{O}}{C}$-O-Ø	-	-	152*	-
$CH_2{=}CH{-}\underset{\overset{\|}{O}}{C}{-}OC_2H_5$	130.4*	129.7*	164.5*	-

* (LEVY, 1972)

Table 3 : Polymer refractive indexes (at 20° C) and Tg

Polymer	$n_D^{20°}$	T_g^* (°C)
(I)	1.4619	55
(II)	1.4965	74
(III)	1.4045	57
(IV)	insoluble in common solvents	37

*Perkim Elmer DSC4 (20°C/mn)

Refractive indexes are seen to increase normally when changing from monomer to polymer. This increase is of an average order of 5 %. Nevertheless account must be taken of the poor solubility of certain solvents. Generally, the Tg values of polycarbonates are observed to be halfway between the values of the corresponding polyacrylates and polymethacrylates. For example, if we take into consideration fluorinated derivatives, a Tg of 57° C is obtained for polymer (III) while that of poly (trifluoroethylacrylate) is -10° C and that of poly(trifluoroethyl methacrylate) is 73° C. For the long chain fluorinated polymers, these values are 9° C, 49° C and 37° C for poly(perfluorooctyl acrylate), poly(perfluorooctyl methacrylate) and polycarbonate (IV), respectively.

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