Functionalizable polyurethane networks based on hydroxy-modified poly(chloroalkyl vinyl ether)s. 1

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Summary

This paper describes the synthesis of polyurethane networks based on partly hydroxy-modified poly(chloroethyl vinyl ether)s and examines the possibility to introduce various amounts of hydroxy groups in the network. Poly(chloroethyl vinyl ether)s are prepared by living-type cationic polymerization initiated by the $HI/ZnCl_2$ system. Introduction of hydroxyl groups along the chain, in controlled amount, is then achieved in a two-step process involving the reaction of a fraction of the pendant chloride groups with a carboxylic salt, followed by alkaline hydrolysis. Finally the corresponding polyurethane networks- with or without remaining hydroxy functions- are obtained by reaction with hexamethylene diisocyanate in different proportions. Preliminary study of the mechanical properties of the networks are also reported.

Introduction

The synthesis of polymer networks constituted or partly constituted of monomer units bearing functional groups, able to develop specific properties with the surrounding media or one of its constituent, are of interest for different application domains. Some illustrative examples are: development of complexation ability, catalytic and chemical activity, improvement of adhesive properties, adjustment of the hydrophylic/lypophylic balance, compatibilisation towards a given substrate (1), etc...

We have recently investigated the preparation and the use of poly(chloroethyl vinyl ether)s -poly(CEVE)- as chain precursors for the preparation of a series of poly(vinyl ether) chains having side functional groups (2).

This paper describes the synthesis of polyurethane networks based on partly hydroxy-modified poly(CEVE)s and examines the possibility to introduce various amounts of hydroxy groups in the network. A preliminary study of the mechanical properties of the networks is also reported.

Experimental:
Materials

Toluene and chloroethyl vinyl ether -CEVE- (Nisso Maruzen Chemical Co., Ltd.) were distilled over calcium dihydride and stored in glass flasks under dry nitrogen. Zinc dichloride was degassed under vacuum and dissolved in distilled dry diethyl ether $(1,2.10^{-1} \text{ mol.l}^{-1})$. The hydrogen iodide was obtained from a 57% aqueous solution by dehydration in toluene with phosphorus pentoxide. The organic HI solution was twice cryodistilled and stored under nitrogen at -30°C in the dark $(0,2 \text{ mol.l}^{-1})$.

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Polymerization procedures

Polymerizations were carried out under dry nitrogen, in toluene, at -40°C, in glass flasks equipped with PTFE stopcoks. CEVE and toluene were first introduced in the glass reactor through canula, then the HI and $ZnCl_2$ solutions were successively added, in this order, to the monomer solution. The monomer conversion was followed by SEC analysis of samples, quenched with ammoniacal methanol and taken from the polymerization system at increasing time. After 12 to 18 hours, the polymerization systems were deactivated by adding ammoniacal methanol to the reaction mixture maintained at -40°C. After concentration of the solution, the polymer was fully re-dissolved in methylene dichloride, neutralized with acetic acid and washed several times with an aqueous sodium thiosulfate solution. The polymer solution was finally dried over $MgSO_4$, filtered and vacuum dried to give the poly(CEVE)s.

Chemical transformation of the Polymer

* Poly(CEVE) (6g) was dissolved in dimethyl formamide (100 ml), and calculated amounts of potassium benzoate (1,05 equivalent per Cl to substitute) and of tetrabutylammonium hydrogen sulfate ([TBAHS]/[PhCO$_2$K]=0,1) were added successively. The mixture was stirred for one day at 80°C. The solution was washed with water several times, dried and the solvent evaporated under reduced pressure. The PCl-OBz intermediate was then characterized.
* To get the hydroxyl derivative, PCl-OBz was dissolved in acetone and an aqueous potassium hydroxide solution (10 equivalents, [KOH]=10 M) was added. The mixture was refluxed for one day. The system was neutralized, washed, dried, and the polymer was finally recovered by solvent evaporation. The quantitative removal of benzoate groups was confirmed by ^{1}H NMR spectroscopy.

Synthesis of poly(CEVE) urethane networks

PCl-OH was first dissolved in methylene dichloride or tetrahydrofuran (4ml/g), prior to introduce HMDI under nitrogen. The solvent fluidifies the polymer and allows to obtain an homogeneous mixture. The latter was poured into a mould, slowly raised to 60°C to evaporate the solvent and kept at this temperature for a week, under vacuum.

Surface modification by hexamethylene diisocyanate (HMDI)

The reaction was carried out at 30°C, under nitrogen, in cyclohexane. HMDI, dibutyl tin dilaurate (1% with respect to HMDI) and a piece of network were successively introduced, in a ratio such as HMDI was in large excess with respect to hydroxy functions. After five hours, the network was washed several times with dry cyclohexane and vacuum dried.

Polymer characterization

The molar mass and molar mass distribution (MMD) of the polymers were determinated by SEC, in tetrahydrofuran, on a Varian chromatograph equipped with three polystyrene gel columns (TSK GEL, G2000HXL, G3000HXL, G4000HXL), calibrated with polystyrene standards.
^{1}H NMR spectra (250 MHz) were obtained, in CDCl$_3$, at room temperature, on a Brüker AC250 spectrometer.
IRFT spectra were recorded on a Perkin-Elmer 683 spectrometer, using the ATR mode.
The mechanical tests were performed on a Adamel-Lhomargy DY22 dynamometer. The mechanical characteristics, e.g. the ultimate stress and the ultimate strain at break, were determined according to standard NF T 51-034 using H3 samples. Tests were realized at a strain rate of 2mm/min, with jaws of 50daN.

Results and discussion
a) synthesis of hydroxy-modified poly(CEVE) network precursors:
* Cationic living polymerization of CEVE :

HI/ZnCl$_2$ initiated living-type polymerization of CEVE (3,4) was carried out at -40°C in toluene, as depicted in scheme 1. Typical polymerization results are collected in Table 1.
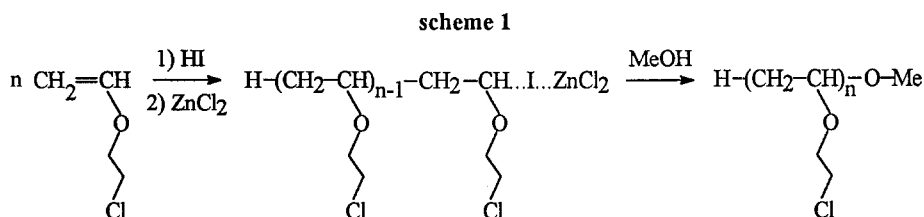
scheme 1

$$n \ CH_2=CH \xrightarrow[2)\ ZnCl_2]{1)\ HI} H\!-\!(CH_2\!-\!CH)_{n-1}\!-\!CH_2\!-\!CH...I...ZnCl_2 \xrightarrow{MeOH} H\!-\!(CH_2\!-\!CH)_{n}\!-\!O\!-\!Me$$

Cl ⟍ Cl Cl ⟍ Cl

Table 1:Synthesis and characteristics of poly(CEVE)s
prepared by HI/ZnCl$_2$ in toluene, at -40°C

[CEVE] (mol/l)	[HI] (mol/l)	$\overline{DP}_{n,th}$	$\overline{DP}_n$ (*)	$\overline{M}_w/\overline{M}_n$
2.76	2.00 10^{-2}	138	140 (a)	1.15
1.95	1.30 10^{-2}	150	145	1.15
1.89	0.63 10^{-2}	300	280	1.25
2.22	0.60 10^{-2}	370	347 (b)	1.20
2.00	0.40 10^{-2}	500	455	1.40
2.50	0.25 10^{-2}	1000	650	1.70

(a): PCl-1; (b): PCl-2
(*):calculated from $\overline{M}_n$ measured by size exclusion chromatography.

As shown in Table 1, a satisfactory correlation between the experimental and theoretical $\overline{DP}_n$, calculated assuming one polymer chain formed per HI molecule, is observed up to $\overline{DP}_n$'s of about 200-300. Then an increasing deviation of experimental $\overline{M}_n$ from predicted ones is observed, suggesting that chain transfer processes are not totally absent in these polymerization systems.

Though this side process was restricting for a satisfactory functionalization of chain ends, it still allowed the synthesis of poly(CEVE)s with controlled molar masses and narrow molar masses distribution (MMD), at least in a certain polymer molar masses range, Table 1. These two characteristics were believed necessary, but also sufficient, to obtain, by topological modification of some of pendant chlorides, an hydroxy-functionality close to the desired average value, for the large majority of polymer chains: in particular, the presence of very low molar masses poly(CEVE) chains of lower functionality (5) is expected to be minimized in these conditions.

Two series of poly(CEVE), selected according to these criteria, see Table 1 (samples a and b) and Figure 1, have been partially hydroxylated by chemical transformation of some CEVE units and used as polyurethane network precursors.
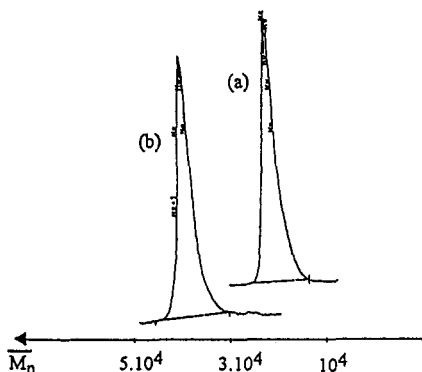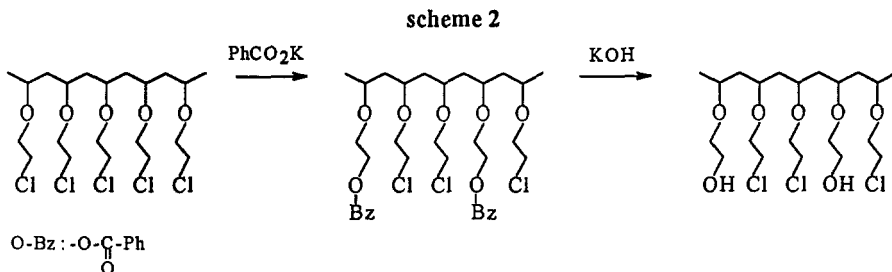
Figure 1: SEC chromatograms of PCl-1 (a) and PCl-2 (b), see Table 1.

* partial transformation of chloride side groups into hydroxyle

The direct hydrolysis of chloride groups, in strongly basic conditions, results in an elimination and partial cross-linking of the polymer; therefore the polymer modification was performed in two steps as depicted in scheme 2.

scheme 2

In the first step, substitution of a limited number of pendant chloride groups by a carboxylic acid salt, i.e. potassium benzoate or potassium acetate, was first achieved. The best results were obtained when the reaction was performed in dimethyl formamide, at 80°C, in the presence of a phase transfer catalyst (tetrabutylammonium hydrogen sulfate, TBAHS) : in these conditions the two salts react almost quantitatively and the substitution yield can be controlled by adjusting the amount of carboxylate salt with respect to that of chloride groups.

The benzoate derivative was however finally preferred because of its better leaving character and the ease to determine the chain modification rate by ^{1}H NMR, since the proton resonances of the benzoate group are well-resolved from those of poly(CEVE). A ^{1}H NMR spectrum of a poly(CEVE), before and after partial substitution of chlorides by benzoate groups, as well as peak assignments are presented in Figure 2 (a,b).

Partially hydroxylated poly(CEVE) could then be readily obtained by hydrolysis of benzoate groups, in acetone, at 80°C, under basic conditions. ^{1}H NMR analysis of the polymer allowed us to confirm the quantitative elimination of benzoate, leading to the formation of pendant hydroxyle, as shown by the complete disappearance of the aromatic proton signals and the shift of the methylene attached to the benzoate group $-CH_2-O-CO-Ph$ on the polymer spectrum, Figure 2c. Besides, the absence of any other proton NMR signal, as well as no change in the apparent $\overline{M}_n$ and in the MMD of the polymers measured by SEC, are in agreement with the absence of any noticeable side reaction.
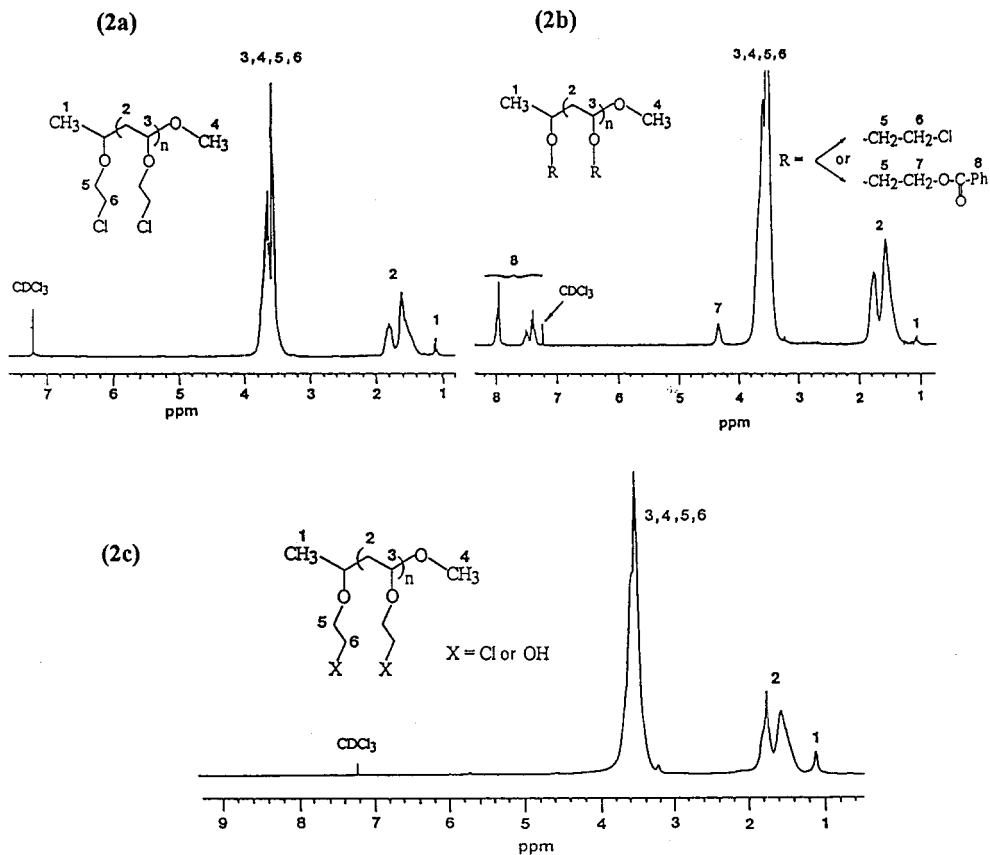
(2a)

(2b)

(2c)

Fig.2: 250 MHZ ^{1}H NMR spectra in CDCl3
(2a): PCl-1; (2b): PCl-1-OBz, (2c): PCl-1-OH

b) synthesis of poly(CEVE) urethane networks

Poly(CEVE)-based polyurethane networks were prepared by reacting hydroxy-modified poly(CEVE)s, (PCl-OH), with HMDI either using a stoechiometric proportion of isocyanate functions with respect to hydroxy functions of the polymer, or in the presence of a default of diisocyanate in order to obtain networks containing remaining hydroxy groups, see scheme 3.

Scheme 3
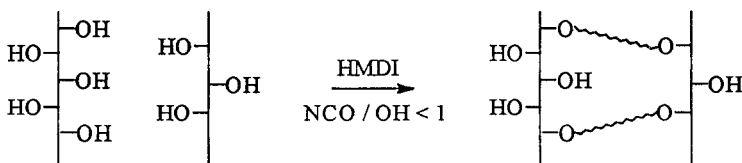
The IRFT spectra of two different networks, recorded in ATR mode are shown in Figure 3. The first one (N1) was obtained from a PCl-1-OH precursor, containing 10% of hydroxylated monomer units using a stoechiometric ratio NCO/OH. The second (N2) was prepared from a PCl-1-OH precursor, containing 20% of hydroxylated monomer units with a ratio NCO/OH equal to 0,5 .
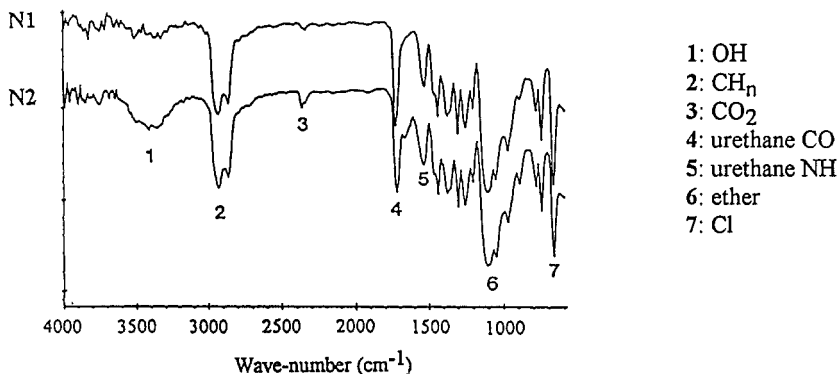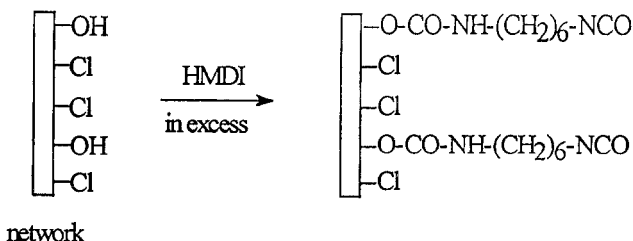

1: OH
2: CH_n
3: CO_2
4: urethane CO
5: urethane NH
6: ether
7: Cl

Wave-number (cm^{-1})

Figure 3: IRFT spectra of networks N1 and N2.

In the two cases the isocyanate vibration band at 2260 cm^{-1} has totally disappeared, suggesting that the reaction of HMDI gets close to completion. This is further supported by the almost complete vanishing of the OH band in N1 prepared at the 1:1 stoechiometry, whereas its presence is still clearly observed in the spectrum of N2, in agreement with the ratio OH/NCO used.

In order to further examine the presence of OH groups at the N2 network surface, the latter was reacted with a large excess of HMDI in cyclohexane, according to the procedure described in scheme 4. Since cyclohexane is a non-solvent of hydroxy-modified poly(CEVE)s and does not swell the corresponding networks, we may assume that the reaction mostly proceeds at the material surface. After several careful washing of the sample with an hydrocarbon, solvent of HMDI, the presence of remaining NCO, indicative of the anchoring of HMDI by one of it ends, was confirmed by ATR (see Figure 4). Analogous results were obtained with the PCl-OH cross-linked at a ratio NCO/OH of 0,75 (N3): the higher the calculated initial proportion of free OH, the higher the final NCO band intensity (see Figure 4).
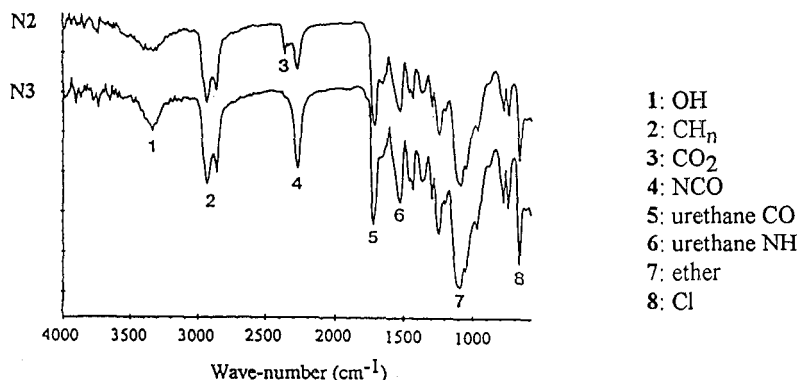
scheme 4

network

N2

N3

1: OH
2: CH$_n$
3: CO$_2$
4: NCO
5: urethane CO
6: urethane NH
7: ether
8: Cl

Wave-number (cm^{-1})

Figure 4: IRFT spectra of networks N2 and N3.

c) Study of the mechanical properties of the poly(CEVE) urethane networks:

A first series of poly(CEVE) networks, without residual hydroxy function, was prepared from PCl-OH samples, hydroxylated at different extent in order to obtain networks with various average molar masses of the randomly cross-linked network chains ($\overline{Mc}$). By this procedure, the average distance between OH groups ($\overline{M}_{OH}$) was varied from 980 to 8500g/mol. In a first approach, we may assume that the average molar mass between network junctions, $\overline{Mc}$, is close to $\overline{M}_{OH}$, considering a complete reaction of hydroxyl groups with HMDI.

The influence of $\overline{Mc}$ on the breaking stress σ_r and the breaking strain $(\Delta l/lo)_r$ is shown in Table 2 and in Figure 5, in the case of two precursors PCl-1 and PCl-2 of different $\overline{M}_n$ (see Table 1). Except for the lowest $\overline{Mc}$ (980g/mol), σ_r remains almost constant with increasing $\overline{Mc}$, whatever the precursor used. On the other hand, as it may be seen (Figure 5), $(\Delta l/lo)_r$ not only depends on $\overline{Mc}$, but also on the molar mass of the PCl precursor. For a same polymer precursor, the higher $\overline{Mc}$, the higher the breaking strain, but for different precursors, the higher their $\overline{DP}_n$, the lower the breaking strain.

Different hypothesis can be postulated to explain this last behaviour:

-despite the absence of the isocyanate band in IRFT spectra, an important limitation of the reaction between hydroxyle and HMDI with precursors of higher $\overline{DP}_n$, due to viscosity effect. However, this should lead to a reverse effect, i.e., higher Mc values should lead to higher breaking strain.

-more entanglements of polymer chains at hight precursor $\overline{DP}_n$. This would lead to apparent $\overline{Mc}$ lower than estimated and also to lower elongation properties (Table 2).
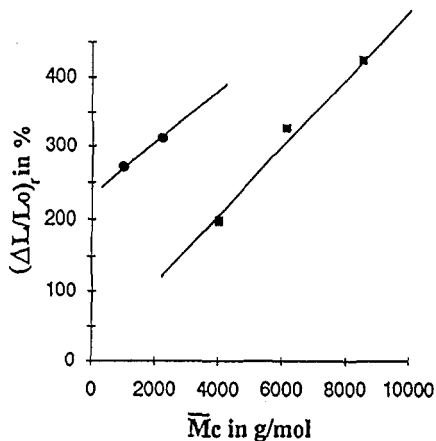
Table 2: Mechanical properties of Poly(CEVE)-based polyurethane networks

sample	$\overline{Mc}$ (g.mol^{-1})	σ_r (MPa)	$(\Delta l/lo^*)_r$ (%)
PCl-1	980	2.80	271
-	2 200	1.40	312
PCl-2	4 000	0.93	198
-	6 100	1.45	326
-	8 500	1.23	424

*:lo=17mm (rectilinear party of the H3 sample)
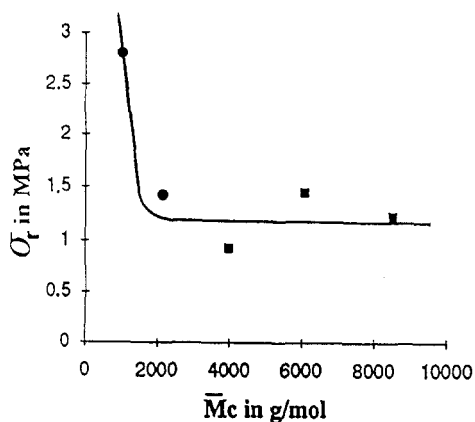
(5a)   (5b)

● : $\overline{M}_n$, PCl precursor = 15000 g.mol^{-1};   ■ : $\overline{M}_n$, PCl precursor = 37000 g.mol^{-1}

Figure 5: (5a): effect of $\overline{M}c$ on stress at break; (5b): effect of $\overline{M}c$ on elongation rate at break

Besides, some preliminary measurements, performed on networks containing residual hydroxy functions, tend to indicate an effect of OH on the mechanical properties: for a network containing 10% of remaining OH group, σ_r remains in the same range of magnitude, but the elongation is reduced by a factor of about two, suggesting the influence of hydrogen bonding interactions in the bulk.

In conclusion, the present study shows that poly(CEVE)-based polyurethane networks can be obtained from precursors prepared by controlled topological hydroxylation of poly(CEVE). The corresponding partially hydroxylated poly(CEVE) polyurethane networks can also be obtained by the same procedure. The preparation, by chemical modification of poly(CEVE), of a series of poly(vinyl ether)s bearing "active" side groups and the synthesis of the corresponding functional polyurethane networks will be reported in a following paper.

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