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Synthesis and reactivity of monodisperse prepolymers with blocked isocyanate end groups

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Summary : We describe the synthesis of monodisperse prepolymers containing one or two blocked isocyanate groups on the chain extremities.

The prepolymers containing blocked isocyanate in one end and hydroxyl group in the other end are obtained by chemical transformation of undecylenic acid to acid chloride. This later was converted to the isocyanate by the CURTIUS reaction and blocked with nonyl-phenol. Finally the blocked isocyanate was telomerized with mercapto-ethanol. The resulting product is deblocked at T≈105°C.

By action of pure 2.4 T.D.I. (Tolylene diisocyanate) on the later product, we obtain a product containing blocked isocyanate end groups. The removal of the blocking agent could be effected at 100°C or less depending on the compound used to remove the blocking agent (amine).

INTRODUCTION

Generally, the polyurethanes and polyurethane-ureas are obtained by two methods : the first consists of the reaction of stoechiometric diol amounts of diol and diisocyanate (called the one shot process). The second process uses intermediate prepolymers, obtained by reaction of an excess of diisocyanate and diol (called two shot process). This prepolymer is extended with diol (to obtain pure polyurethane) or diamine (to obtain polyurethane-ureas). In the case of (R.I.M.), rapid injection molding process, the second step is employed.

The stability of isocyanate to hydrolysis is always a problem. For this, Bayer proposed prepolymers with blocked isocyanate groups (DESMOCAP 11 and 12). With this process, the prepolymer is stable at ambiant temperature but react with diamines which displace the blocking agent and gives a polyurethane-urea. The free blocking agent has a low vapour tension, and can be used as plastifier. Using monodisperse difunctional compounds, we synthesized diol (1), and recently diisocyanate (2). Our works and those of EISENSBACH (3), HARELL (4), BILL (5), on polyurethanes with monodispersed soft and hard segments show a net improvement of properties, especially mechanical ones (6), due to the more regular structure of the polymer and increased phase segregation (7). In this study, we describe blocked isocyanate monodisperse prepolymers.

RESULTS AND DISCUSSION

Telomerization of the undecylenic acid derivatives with functional dithiols (1) was done according to the following reaction scheme :

$$CH_2=CH-(CH_2)_8-CO_2H \xrightarrow{SOCl_2} CH_2=CH-(CH_2)_8-COCl \qquad I$$

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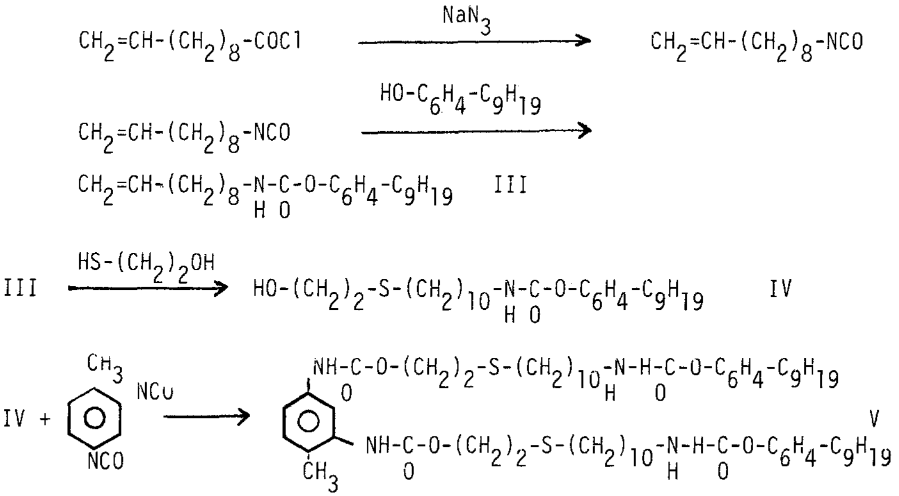


$$CH_2{=}CH{-}(CH_2)_8{-}COCl \xrightarrow{NaN_3} CH_2{=}CH{-}(CH_2)_8{-}NCO \quad \text{II}$$

$$CH_2{=}CH{-}(CH_2)_8{-}NCO \xrightarrow{HO{-}C_6H_4{-}C_9H_{19}} CH_2{=}CH{-}(CH_2)_8{-}\underset{H}{N}{-}\underset{O}{C}{-}O{-}C_6H_4{-}C_9H_{19} \quad \text{III}$$

$$\text{III} \xrightarrow{HS{-}(CH_2)_2OH} HO{-}(CH_2)_2{-}S{-}(CH_2)_{10}{-}\underset{H}{N}{-}\underset{O}{C}{-}O{-}C_6H_4{-}C_9H_{19} \quad \text{IV}$$

The structures were determined by ^1H NMR. The ^1H NMR analysis of the unsaturated acid chloride (I) are summed up in the following table :

structure	CH_2	$=CH$	$-CH_2$	$-(CH_2)_7$	$-CH_2$	$-\underset{O}{C}-Cl$
multiplicity	(m)	(m)	(t)	(m)	(t)	
chemical shift (ppm)	(5.9)	(5.1)	(2)	(1.3-1.7)	(2.3)	

Table 1 : N.M.R. data on acid chloride

When the acid chloride is converted to isocyanate, only the protons of carbon α to C-Cl is deshielded, and now absorb at 3.3.ppm. We note also the appearance of an intensive band in the I.R. Spectrum at $2250cm^{-1}$ characteristic of N=C of the isocyanate groups. After blocking NCO groups with substituted phenol, we observe the appearance of a signal H-N at 5.3ppm . Then protons α to the urethane absorb at 5.35ppm and we note the modification of multiplicity of protons α to nitrogen which absorb at 3.25ppm as a false quadruplet form, and the appearance of aromatic protons at 7.2ppm.

After telomerization of the blocked product with the alcohol thiol, we observe the disappearance of the double bond of the undecylenic group, and the appearance of two triplets at 2.4 and 2.6ppm which characterize the protons of carbons α to sulfur, and also the triplet of protons of carbon to oxygen at 3.6ppm (Table 2).

Structure	$HO - CH_2$	$- CH_2$	$- S - CH_2$	$-(CH_2)_8$	$- CH_2$	$- \overset{H}{N}$	$- \underset{O}{C} - O$		$-C_9H_{19}$
Multiplicity	t	t	t	m	t	s		m	m
Chemical Shift (ppm)	3,6	2,6	2,4	1,3-1,8	3,1	5,4		6,9-7,1	0,8

Table 2 : N.M.R. data on the blocked isocyanate telomerized with alcohol thiol.

Finally, when we prepare product V, only the triplet of proton α to hydroxyl is deshielded to 4.2ppm as a triplet, and we observe also the appearance of a singlet at 2.1ppm which caracterizes the protons of the methyl groups of T.D.I. and a modification of aromatic proton intensity. Different prepared compounds have been caracterised by elemental analysis (Table 3). We note that theorical and pratical results are similar, what means that formulars determined by NMR^1 H are correct.

Compound	C		H		N		Cl	
	Theo.	Pract.	Theo.	Pract.	Theo.	Pract.	Theo.	Pract.
1	65,18	64,92	9,38	8,96	0	-	17,53	16
2	72,92	73,40	10,49	10,60	7,73	7,82	-	-
3	77,8	77,40	10,72	10,02	3,49	3,10	-	-
4	70,14	69,81	10,22	9,98	2,92	2,88	-	-
5	68,9	68,52	9,18	8,89	4,94	5,2	-	-

Table 3 : Elemental analysis results

In term of physical properties products IV and V are liquid while the prepared diisocyanate (3) in previous paper is solid :

$$OCN-(CH_2)_{10}-S-(CH_2)_2-O-(CH_2)_2-S-(CH_2)_{10}-NCO$$

Compound IV has been studied by differential scanning calorimetry. It present only a glass point at 18°C while compound V is semi-cristalline. The observed glass temperature and melting point are respectively -41°C and 51°C.

After, we studied the unlocked compounds IV, V by D.S.C.

Concerning IV, abviously we introduce primary alcohol and this compound undergoes polycondensation by itself at 105°C. We constate that this temperature is relatively mild which makes the product very interesting, since it does not require the addition of deblocking agent, not like the commercial compounds and product (V). In order to study compound (V), we prepared at first a model study (VI) :

Deblocking temperatures obtained with amines and compound (VI) are summed up in table 4.

These temperatures have been studied by differential scanning calorimetry and represent the beginning of the endothermic reaction.

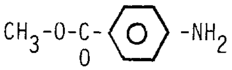
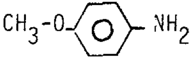
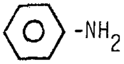
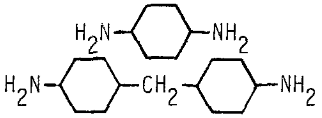
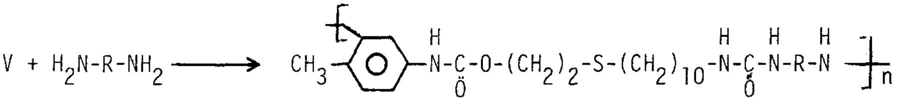
Used amines	Deblocking temperature (°C)
	180
	160
	150
$CH_3-(CH_2)_5-NH_2$	150
	70

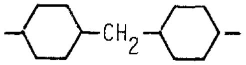
Table 4 : Study of deblocking reaction

From these results, we tested two cycloaliphatic diamines in deblocking the compound (V) :



The obtained products are :



with R =  or 

The unblocking temperatures are respectively 80°C and 100°C, which are relatively moderate.

REFERENCES

1 - B.Boutevin,E.El Idrissi et J.P.Parisi (1990), Die Makromol.Chem., 191, 445 .

2 - B.Boutevin, M.Chaib et J.J.Robin (1990), Polymer Bull. submitted to publication, accepted on March 1991.

3 - C.D.Eisenbach et C.L.Gunter (1983), ACS Orga.Coat.Appl.Polym.Sci.Proc, 49,239 .

4 - L.L.Harell, Macromolecules, (1969) 2(6),607.

5 - R.Bill, M.Droscher, G.Wegner (1981), Makromol.Chem.,182,1033.

6 - B.Boutevin, M.Chaib et J.J.Robin (1990), Makromol.Chem.,191,737.

7 - C.D.Eisenbach, W.Gronski (1983), Makromol.Chem.Rapid Commu., 4,707.

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