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Synthesis of monodisperse macromolecular diisocyanate

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Summary : The synthesis of a monodisperse macromolecular ($\overline{Mn}$=850) diisocyanate was done in three steps with an averall yield of 80%. The first one consist of the addition of the dithiol $HS-(CH_2)_2O(CH_2)_2SH$ to undecylenic acid, the diacid obtained $[(HO-CO-(CH_2)_{10}-S-(CH_2)_2]_2-O$ is then transformed to the acid dichloride by the action of thionyl chloride ($SOCl_2$), finally the acid dichloride is transformed to diisocyanate $[OCN-(CH_2)_{12}-S-(CH_2)_2]_2-O$ by CURTIUS reaction.

We note that the product is cristalline and its purity and that of the intermediates were determined by ^1H NMR.

INTRODUCTION

Telechelic polymers have been known for a long time (1) and they are used especially as prepolymers in polycondensation reaction. Generally diol chaines of polyester, polyether or diepoxide (DGEBA) are used and recently some diamines (from TEXACO and BASF).

The principal chaines are obtained by condensation or addition reaction. Lately other methods of synthesis appear, such as radical polymerization of butadiene with H_2O_2 (2), and polymerization of T.H.F. by cationic catalysts such as HSO_3F (3). Most of the oligomers obtained by these syntheses give higher polydispersity (order of 2), which interfer in the final properties of material.

Recently, various authors, Eisenbach (4), Bill (5), Harell (6) have applied organic synthetic methods to obtain monodisperse telechelic compounds which act as soft or hard segments (7). These authors show that the resulting polyurethanes materials have improved mecanical properties. PASCAULT et al. explained the improved mechanical properties were a result of increased segregation soft and hard phases (8).

We note that these syntheses were done in many steps and could not be applied industrially. They do permit a good comprehension of theoritical knowledge to polydisperse polymers.

In our case we synthesize a monodisperse diol (9) and its corresponding aromatic diamine (10) prepared by modification of the end groups.

Recently we confirm the improved performance of polyurethanes by comparing the mechanical properties of polyurethanes prepared with monodisperse diol, and their homologous polydisperse commercial T.H.F. (11).

The polyurethanes were obtained in the classical two step process from diisocyanate prepolymers. However the inconvenience of this technical preparation is that the prepolymers always contain traces of residual diisocyanate monomers, which are undesired because of their toxicity. Also this technical preparation leads to an increase in molecular weight and an undesirable rise in viscosity of the prepolymer. We present here a method

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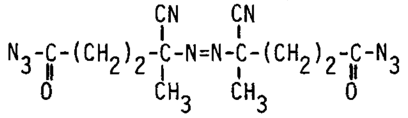
*To whom offprint requests should be sent to prepare a monodisperse diisocyanate free from residual diisocyanate monomers. This approach hasn't been well explored in litterature.

We mention the work of Heitz (12)(13) on the chemical modification of diisocyanated polystyrene obtained from A.I.B.N., and those of Gatge et al. (14) on the syntheses of diazic initiator precursor of diisocyanate

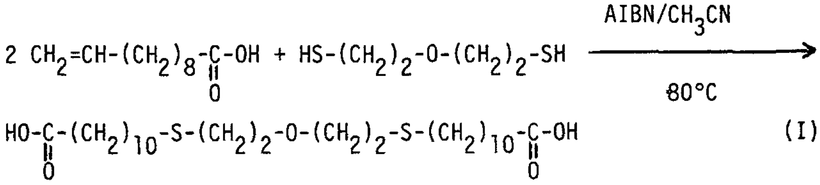


$$N_3-\overset{\displaystyle O}{\underset{\|}{C}}-(CH_2)_2-\underset{CH_3}{\overset{CN}{C}}-N=N-\underset{CH_3}{\overset{CN}{C}}-(CH_2)_2-\overset{\displaystyle O}{\underset{\|}{C}}-N_3$$

We note that the macromolecular diisocyanate obtained by these authors are polydisperse.

RESULTS AND DISCUSSION

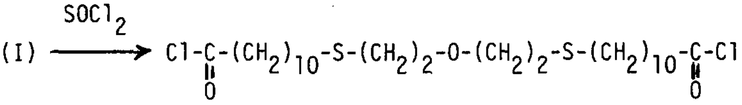
The telomerization of undecylenic acid with dithiol gives



$$2\ CH_2=CH-(CH_2)_8-\underset{\underset{O}{\|}}{C}-OH + HS-(CH_2)_2-O-(CH_2)_2-SH \xrightarrow[80°C]{AIBN/CH_3CN}$$

$$HO-\underset{\underset{O}{\|}}{C}-(CH_2)_{10}-S-(CH_2)_2-O-(CH_2)_2-S-(CH_2)_{10}-\underset{\underset{O}{\|}}{C}-OH \qquad (I)$$

the diacid (I) obtained is transformed to the diacid chloride by action of thionyl chloride ($SOCl_2$) on (I).

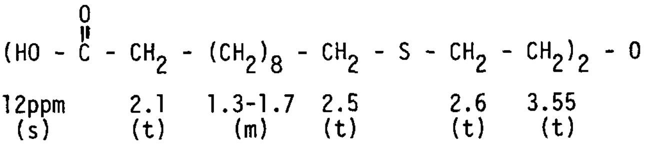


$$(I) \xrightarrow{SOCl_2} Cl-\underset{\underset{O}{\|}}{C}-(CH_2)_{10}-S-(CH_2)_2-O-(CH_2)_2-S-(CH_2)_{10}-\underset{\underset{O}{\|}}{C}-Cl \qquad (II)$$

Finally, by action of an aqueous solution of sodium azide on the diacid chloride (II) in toluene (CURTIUS-REACTION) we obtained the corresponding diisocyanate (III).

$$(II) \xrightarrow[toluene/80°C]{NaN_3} OCN-(CH_2)_{10}-S-(CH_2)_2-O-(CH_2)_2-S-(CH_2)_{10}-NCO \qquad (III)$$

Concerning the syntheses of the diacid (I) the yield after 12 hours is greater than 90%, and the purity of the product was determined by ^1H NMR.



$$(HO-\overset{\overset{O}{\|}}{C}-CH_2-(CH_2)_8-CH_2-S-CH_2-CH_2)_2-O$$

HO-C	CH₂	(CH₂)₈	CH₂	CH₂	CH₂
12ppm	2.1	1.3-1.7	2.5	2.6	3.55
(s)	(t)	(m)	(t)	(t)	(t)

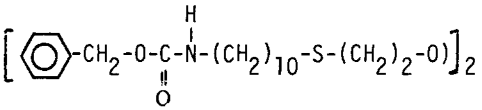
s = singlet ; t = triplet ; m = multiplet

The total absence of insaturation at (4.9 and 5.9ppm) and the presence of only one peak on GPC confirm the purity of (I).

When we pass to the diacid chloride (II) we observe by ^{1}H NMR the total disappearance of the peak at 12ppm, and the deshielding of the protons of carbon α to the acid group which absorb at 2.3ppm.

The corresponding diisocyanate is obtained in two steps. First, at temperature less than 10°C, by action of NaN$_3$ in toluene on product (II), the resulting product (diazid) is not isolated, and by heating at 80°C for two hours gives the diisocyanate at yield of 85% essentially. On ^{1}H NMR we note the isocyanate group (3.3ppm), and the appearance of an intensive band in I.R. at 2250cm^{-1} characteristic of the isocyanate group.

A confirmation of the structure was made by the syntheses of the diurethane derivative from benzyl alcohol (IV), which caracterise the isocyanate group :



The diisocyanate (III) prepared is a solid with a melting point of 50°C ; this product is cristalline and doesn't exhibit a glass transition temperature, which differentiates it from the majority of classic diisocyanate prepolymers.

It is then an interesting syntheses since it leads easily to a monodisperse diisocyanate of molecular weight of 850 with a yield of about 80%, where the mecanical properties are in studing.

REFERENCES

1 C.A.Uraneck H.L.Hsieh O.G.Bruck (1960) J.Polym.Sci. 46 535.

2 J.C.Brosse D.Derouet F.Epaillard J.C.Soutif G.Llegay K.Dusek (1987) Advances in Polym.Sci. 289 167.

2 Dupont de Nemours, US Patent 994900x.

4 C.D.Eisenbach W.Gronski (1983) Makromol. Chem. Rapid. Commun. 4, 707.

5 R.Bill M.Droscher G.Weyner (1981) Makromol. Chem. 182 1033.

6 L.L.Harell (1969) Macromolecules 2 (6) 607.

7 C.D.Eisenbach C.L.Gunter (1983) ACS. Orga. Coat. Appl. Polym. Sci. Proc. 49 239.

8 Y.Camberlin J.P.Pascault (1982) Journal of Polymer Sciences Polym. Chem. Td. 20 383.

9 B.Boutevin A.El Idrissi J.P.Parisi (1990) Die. Makromol. Chem. 191,445.

10 C.Bougherara B.Boutevin J.J.Robin (1990) Makromol. Chem. Rapid. Commun. (submitted to publication).

11 B.Boutevin M.Chaib J.J.Robin (1990) Die. Makromol. Chem. 191, 737.

12 W.Konter B.Boner KH.Kohler W.Heitz (1981) Makromol.Chem. 182, 2619.

13 W.Guth W.Heitz (1976) Makromol. Chem. 177, 1835.

14 N.D.Ghatge S.P.Vernekar P.P.Wadgaonkr (1983) Makromol Chem Rapid Commun. 4, 307.

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