

*Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

DIISOCYANATES REACTIVITY WITH DIOLS UNDER PSEUDO-HIGH DILUTION CONDITION

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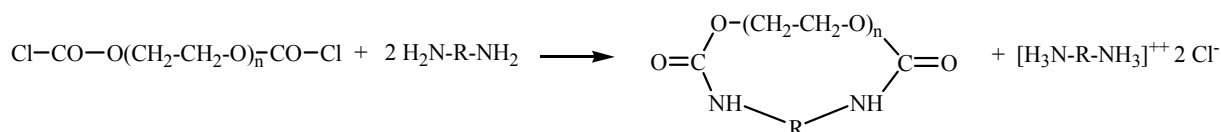
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In the last years the polymer science has been preoccupied with the synthesis and characterization of macromolecular compounds possessing unusual architectures. In this paper, we would like to report the synthesis of new oligomers bearing crown urethane structure, obtained by reacting diisocyanates with diols under pseudo-high dilution. The formed compounds could also be considered as a result of special reactivity of diols towards diisocyanates, verifying the previous hypotheses that the dimer alcohol and the free OH ends of the polymeric associates, exhibits the highest reactivity among the multiples alcohol associates.

INTRODUCTION

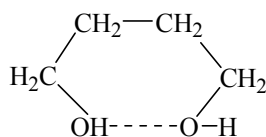
Syntheses and developments of cyclic oligomers are important in several fields of research including supramolecular chemistry and material science. In supramolecular chemistry, cyclic oligomers such as crown ethers,¹ calixarenes,² and cyclodextrins,³ are useful for molecular recognition, and in material science, cyclic oligomers are also useful for organic light-emitting diodes.⁴ Crown ethers represent still a subject of large interest, especially in the area of complexation and host-guest chemistry.^{5,6} They are utilized to extract alkali-metal cations from aqueous solutions into hydrophobic, nonpolar organic solvents⁷⁻¹⁸ and to carry these cations selectively through solvent-polymeric^{19,20} and liquid membranes.^{21,22} Crown ethers are mostly flexible and semirigid types. A naphthyl-substituted crown has been observed to have a folded U-shaped structure,²³ such that the naphthyl groups

are in a parallel orientation. Hence, aromatic substitution in crown ethers may give a folded or twisted shape, a negative factor in threading. Moreover, crown ethers possess a limited thermal stability. To overcome the main disadvantages of crown ethers, the present work highlights the synthesis of novel macrocyclic crown urethanes. Relative low-cost starting materials, a short synthesis route, and thermal stability are the attractive features of the present compounds. The first attempt to synthesize crown urethanes has been made by Kern and coworkers.^{24,25} The above mentioned authors, prepared several cyclic diurethanes by two different methods, applying Ruggli-Ziegler's principle of dilution. They reported,²⁴ that “good yields could be obtained” only by reaction of diamines and diol-bis-chloro-carbonate. Another approach consists in reacting bis-chloro-formiates and secondary amines, Scheme 1.



Scheme 1 – Reaction of bis-chloro-formiates with secondary amines.

Our previous work in the kinetic and reactions mechanisms of urethane formation,²⁶⁻³³ showed that the alcohol dimer as well as free OH ends exhibits the highest reactivity among all the alcohol autoassociation species. A supplementary test of this assertion can be made by the study of the diisocyanate's reaction with diols in pseudo-high dilution conditions, because at least three reasons: i) it is well-known that at low concentrations, in non polar solvents, the hydroxyl compounds are unassociated, or very little associate, thus unreactive, unlike the diols, which are intramolecular associated, and possess a higher reactivity, ii) the higher reactivity of diols in the first step (characterized by k_1) even at their very low concentrations (when bimolecular collisions are very sparse) produced the premise that the diisocyanate/diol reaction, would generate in the first step as intermediate: HO-R-O-CONH-R'-NCO, making possible in the second step (characterized by k_2 , and $k_2 \gg k_1$) the intermolecularly reaction, thus cyclic oligomers being generated, iii) the best candidate for such studies, among the diols, seems to be 1,4-butanediol. Its intrinsic structure, Scheme 2, favors, even at low concentrations the reaction with diisocyanates. Moreover, its particular intern structure resembles in a great extent with the linear dimer structure.



Scheme 2 – The 1,4-butanediol structure.

RESULTS AND DISCUSSION

A number of reactions between three diisocyanates, that is, bibenzyl-4,4'-di-yl diisocyanate (4,4'DBDI), methylene bis *p*-phenylisocyanate (MDI), and diphenyloxide *p,p'*-diisocyanate (DODI), and two diols: diethylene diol (DEG), and 1,4-butane diol, (BD) see Table 1,

were carried out. A typical cyclization reaction of diisocyanate and diol under pseudo-high dilution conditions affords essentially quantitative yield of cyclic crown urethanes without the formation of high molecular weight polymer, according with the reaction scheme, Scheme 3.

The structure a, describes the particularly case of diisocyanates reaction with diols, which lead to the formation of the simplest oligomer, that is, the cyclic diurethane. The b product, describes the structure of the large majority of formed cyclic oligomers. When $n = 0$, then $b = a$. When the cyclization reactions have been done, the crude reaction mixtures were subject of FTIR analyses.

Ring strain in the dimer is evident from a shift in the carbonyl absorption band, which occurs at 1780 cm^{-1} . The cyclic oligomer carbonyl band occurs at $1765\text{--}1770\text{ cm}^{-1}$, which is similar to the frequency observed in polycarbonate (1170.6 cm^{-1}). The cyclic oligomers have a strong C-O-C band at $1070\text{--}1140\text{ cm}^{-1}$. The aromatic C=C band is located around 1500 cm^{-1} .

For the DBDI-DEG and DBDI-BD syntheses, we performed a succession of separations, by using methanol, dioxane, and N,N-dimethylformamide (DMF).

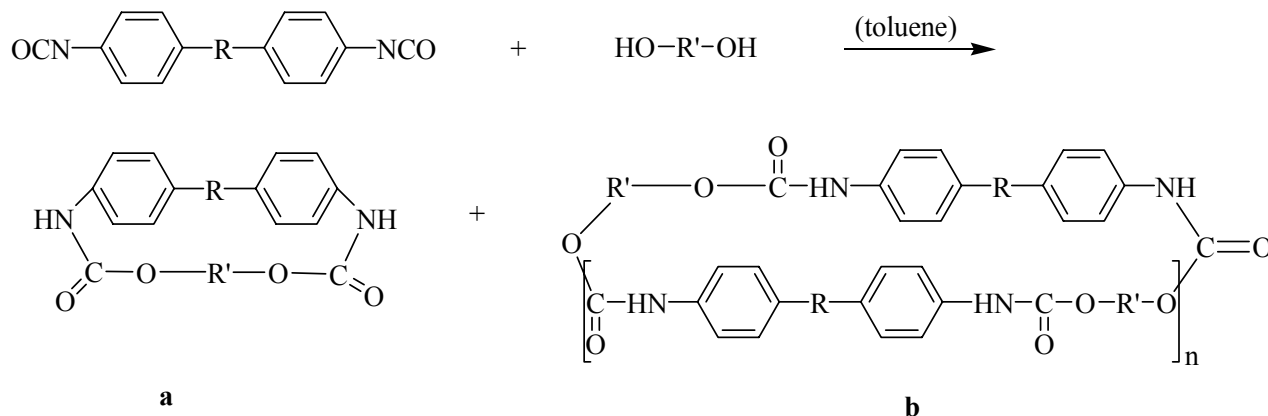
Figure 1 shows the percentages of the separated fractions after selective extractions in MeOH, (1ma, 1mb, and 2ma, 2mb, respectively) dioxane (1xa1, 1xa2, 1xb1, 1xb2, and 2xa, 2xb1, 2xb2 respectively) and DMF (1d, and 2d respectively). Fractions 1xa1, 1xb1, are obtained by precipitation in cold and refluxed dioxane, while the 1xa2 and 1xb2 are resulted by concentration of the solutions in cold and refluxed dioxane respectively. The highest percentage was obtained for the DBDI-DEG synthesis by extraction with DMF and precipitation with MeOH (70%).

The resulted mixtures after selective solvent extractions were further analyzed by means of molecular mass determination, by using two parallel methods, Table 2.

Table 1

Reagents pairs used in reaction to generate the crown urethanes compounds.

Nr. Crt.	Diisocyanate	Diol	Reaction code
1	4,4'DBDI	DEG	DBDI-DEG
2	4,4'DBDI	BD	DBDI-BD
3	MDI	BD	MDI-BD
4	MDI	DEG	MDI-DEG
5	DODI	DEG	DODI-DEG



R = -CH₂-; -(CH₂)₂-; -O-

R' = -(CH₂)₄-; -(CH₂)₂-O-(CH₂)₂-

Scheme 3 – A typical cyclization reaction of diisocyanate and diol under pseudo-high dilution conditions.

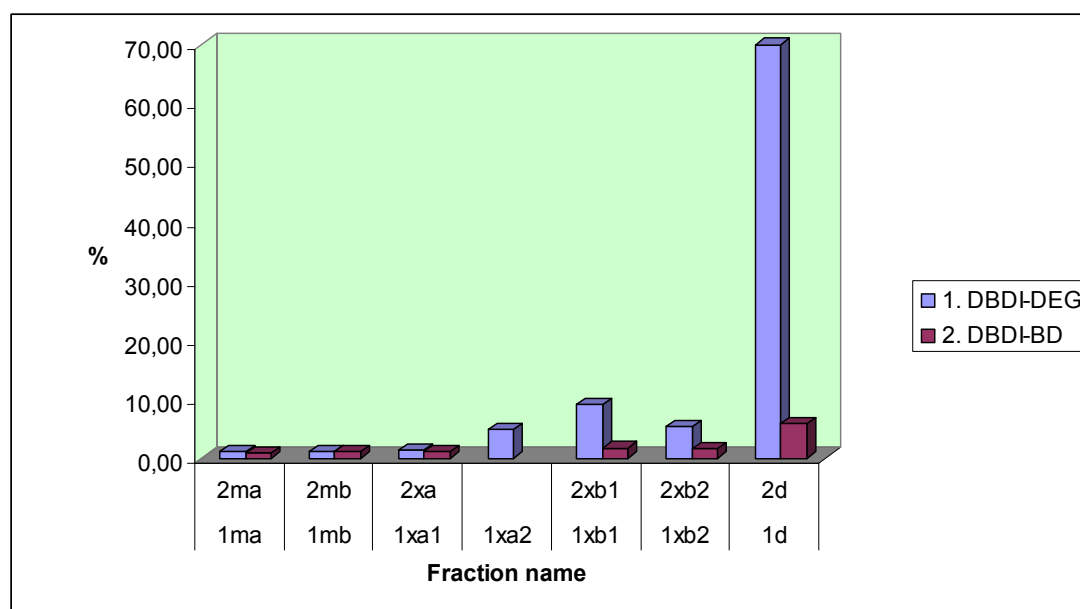


Fig. 1 – The percentages of the separated fractions after selective extractions in various solvents for DBDI-DEG and DBDI-BD syntheses.

Table 2

The founded molecular mass and melting points for the separated compounds of the DBDI-DEG syntheses

Mixture code (see Fig. 1)	Identified species (as determined by GPC)	Molecular mass (as determined by GPC)	% (GPC)	Molecular mass (as determined by osmometry)	Theoretical molecular mass	Melting point °C
1m _b	1m _{b1}	360	76.65	440	370 (n = 0)	170-173
	1m _{b2}	735	23.35		740 (n = 1)	182-185
1x _{a2}	1x _{a2}	755	99.90	730	740 (n = 1)	184
1x _{b1}	1x _{b1-1}	732	95.64	3121	740 (n = 1)	278-281
	1x _{b1-2}	7312	4.35		7400 (n = 10)	
1x _{b2}	1x _{b2-1}	701	77.91	1298	740 (n = 1)	248-251
	1x _{b2-2}	3542	22.09		2960 (n = 4)	
1d	1d ₁	10582	74.32	7958	10360 (n = 14)	262-266
	1d ₂	688	25.68		740 (n = 1)	

The osmometry method for the molecular mass determination will provide only an average value, since the use of Gel Permeation Chromatography (GPC) would deliver us the whole information linked with the total number of identified species and the molecular mass of any individual species.

As we can see from Table 2, generally, the separated mixtures of DBDI-DEG synthesis are mixtures by twos oligomers. Fortunately, there is one exception, namely, the 1xa₂, (fraction isolated by dioxane extract concentration) when the dimer of DBDI-DEG was isolated as a sole products.

Interestingly, the DBDI-DEG dimer is present in every mixture, accompanying the existence of DBDI-DEG monomer (1 mb fraction) and even larger oligomers (n = 10 in 1xb₁ fraction, n = 4 in 1xb₂ fraction, and n = 14 in 1d fraction). For the main products of the DBDI-DEG synthesis, supplemental analyses by means of minimized energy structures have been carried out. Minimize energy job type, force field: MM2, minimizer: Polak Ribiere, minimum RMS gradient: 0.100000, minimum step move: 0.000010. The obtained structures are depicted in Figures 2 and 3.

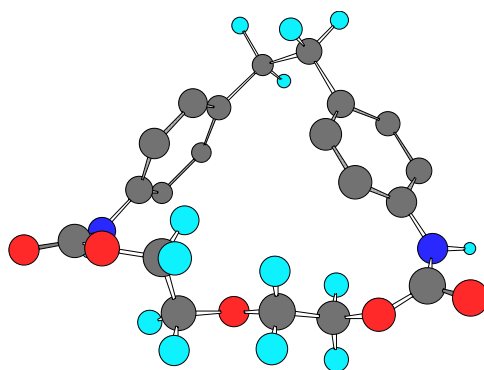


Fig. 2 – The optimized structure for the DBDI-DEG monomer.

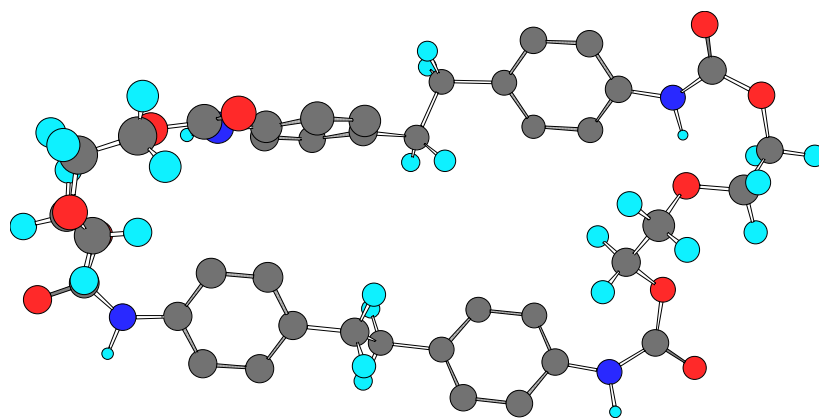


Fig. 3 – The optimized structure for the DBDI-DEG dimer.

EXPERIMENTAL

Preparation of cyclic oligomers. The cyclization reactions were conducted in a 2 L three-neck round-bottom flask which was equipped with a Dean-Stark trap and condenser, a thermometer and a nitrogen inlet. The reaction vessel was charged with toluene (1000 mL), diisocyanate (8.5 mmol), and diol (8.5 mmol). 1,4-diaza-bicyclo [2.2.2] octane (DABCO) (0.5 %) was added. The mixture was vigorously stirred and heated to reflux under nitrogen for eight hours. The reaction mixture was then cooled to room temperature and magnetically

stirred for another 18 h. Finally, the desired oligomers were filtered off and have been subject of a sequence of separations, by using a succession of solvents, that is: methanol, dioxane, and N,N-dimethylformamide. The resulted oligomers were dried in a vacuum oven (120 °C) for 24 h.

¹H NMR (500 MHz, Chloroform) for the DBDI-DEG monomer:

δ 7.31 (d, J = 7.5, 4H), 7.11 (d, J = 7.5, 4H), , 6.03 (s, 0H), 4.30 (ddd, J = -11.5, 4.7, 8.4, 2H), 4.28 (ddd, J = -11.5, 4.0, 8.5, 2H), 3.68 (ddd, J = -11.5, 4.7, 8.5, 4H), 2.72 (ddd, J = -12.5, 2.6, 3.6, 2H), 2.71 (ddd, J = -12.5, 3.6, 12.7, 2H)

¹H NMR (500 MHz, Chloroform) for the DBDI-DEG dimer:

δ 7.53 (d, J = 7.5, 8H), 7.17 (d, J = 7.5, 8H), 6.25 (s, 0H), 4.25 (ddd, J = -11.5, 3.8, 11.0, 8H), 3.65 (ddd, J = -11.5, 1.5, 9.9, 8H), 2.76 (ddd, J = -12.5, 1.4, 5.8, 8H).

Instruments and procedures. The FTIR spectra were recorded on a Perkin Elmer 1760 Infrared Spectrophotometer. The GPC analysis on cyclic oligomer mixtures were carried using six 500 Å pore size ultragels columns in series, each 300 mm x 7.8 mm i.d.; effective MW range from 100 to 10000; minimum efficiency 12000 plates/300 mm column. The carrier was DMF; the UV detector was set at 230 nm / 0.50 AUFS. Reversed-phase HPLC was carried out using a Vydac – C18, semi-prep. size column, 250 mm x 9.4 mm i.d., 5 µ packing. Flow rate 30 mL / min at 60 °C. Vapour Pressure Osmometry (VPO) analyses were carried out using a Gonotec instrument, solvent DMF.

CONCLUSION

The diisocyanates reactions with diols in pseudo-high dilution condition, formed complex mixtures of oligomers. The DBDI-DEG system was detailed analyzed and the DBDI-DEG monomer and dimer have been separated and characterized. Supplementary separations procedures for another's diisocyanate-diol reactions are in progress and will be further reported.

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