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Aromatic Polyureas and Polythioureas by a New Polycondensation Reaction Using Ethylene Chlorophosphite as Reagent

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Summary

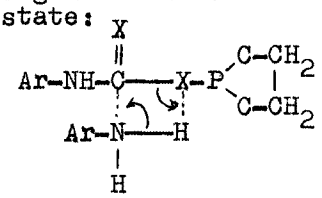
Aromatic polyureas and polythioureas are prepared from aromatic diamines and carbon dioxide or carbon disulfide, by a new direct polycondensation reaction with ethylene chlorophosphite as reagent in pyridine as solvent and acceptor for hydrochloric.

Introduction

In the last time, reagents with phosphorus have been applied with success for syntheses of polyureas and polythioureas. Thus N.Yamazaki and coworkers[1] used diphenyl or triphenyl phosphite (reagents with aromatic structure) in this field, obtaining polymers with high viscosities.

Results and discussion

In our previous papers[2,3] we showed that ethylene chlorophosphite (reagent with aliphatic structure) was able to promote the reaction of carbon disulfide or gaseous carbon dioxide with aromatic amines, resulting thioureas or ureas in high yields, involving a mechanism with the following four-centred transition state:



X = O, S

In this paper we present a new application of this reagent for syntheses of polyureas and polythioureas.

For the synthesis of aromatic polyureas, the polycondensation reaction was carried out by introducing gaseous carbon dioxide into a 300 ml autoclave containing ethylene chlorophosphite (ECP) and a diamine in pyridine. The best results were obtained with 4,4'-diaminodiphenylether (DADPE) in pyridine as solvent and acceptor for hydrochloric acid. The unsatisfactory results in the presence of N-methylpyrrolidone or dimethylformamide (table 1) may be due to a reaction of ECP with this solvents, similar to other cases.[4,5]

Table 1. Polyureas from DADPE and carbon dioxide (20-25 atm.) in the presence of ECP and various amounts of solvents.[a]

Solvent ml	Polymer	
	Yield %	$\eta_{inh.}$[b]
15 (Py)	97	0.49
30 (Py)	98	0.85[c]
40 (Py)	100	1.10[c]
50 (Py)	100	1.15[c]
20/20(Py/NMP)	92	0.38
30/10(Py/NMP)	97	0.51
20/20(Py/DMF)	94	0.42
30/10(Py/DMF)	96	0.56

[a] DADPE = ECP = 10 mmol., temperature 50-60°, time 6-7 h.

[b] Measured at a concentration of 0.5% in NMP.

[c] The polymer has been dissolved in NMP by heating.

The polycondensation reactions effectuated at higher temperatures than 60°, give lower viscosities (at 70-80°, η_{inh}=0.5-0.6 for DADPE), because the reactive intermediary with ECP is sensitive at high temperature. Also, a pressure of carbon dioxide higher than 20-25 atm did not improve the viscosity.

In a similar manner to the reaction with carbon dioxide, polythioureas result from carbon disulfide and aromatic diamines, but with lower viscosities. Our investigations show that the polycondensation reaction is completed during 6-7 hours at 50-60° under pressure of nitrogen (15-20 atm.). In this conditions DADPE gives polythiourea with η_{inh} 0.32. When the same reaction is kept 6-7 hours at 75-85°, the viscosity decreases.

The obtained polyureas and polythioureas present characteristic absorption bands in IR spectra at 1650 and 1530 cm^{-1} due to $\nu_{C=O}$ and $\nu_{C=S}$

Experimental

The following materials were used: 4,4'-diaminodiphenylether was recrystallized from ethanol and 4,4'-diaminodiphenyl methane from benzene, while p-phenylenediamine and m-phenylenediamine were distilled.[6,7]

Polycondensation of DADPE with carbon dioxide

To 30 ml dry pyridine in 100 ml three-necked flask, 2g (0.01 mole) DADPE were added. Then under stirring and cooling, 1.8 ml (0.02 mole) ethylene chlorophosphite were added. After stirring one hour at room temperature, the obtained mixture was poured into 300 ml autoclave. The flask was washed with 10 ml dry pyridine and the resulted solution was poured in autoclave too. The reaction was carried out under pressure of carbon dioxide (20-25 atm.) at 50-60° for 6-7 hours. At the

end of reaction, the obtained polymer was precipitated in 300 ml methanol, collected by filtration and washed with 30-40 ml methanol. Then, the obtained polyurea was stirred one hour with 200 ml water, filtered and washed with 35-40 ml water. After drying under vacuum at 60-80°, 2.26 g polymer with viscosity 1.1 were obtained. Yield 100% (calculated on DADPE employed).

Anal: Calculated for: $C_{13}H_{10}N_2O_2$; C, 69.00; H, 4.50; N, 12,38%. Found: C, 68.11; H, 4.31; N, 11.63%

In similar conditions, the other aromatic polyureas (presented in table 2) were prepared.

Polycondensation of DADPE with carbon disulfide

To 30 ml dry pyridine in a 100 ml three-necked flask, 2 g(0.01 mole) DADPE were added under stirring. When the solution was clear, 0.6 ml (0.01 moles) carbon disulfide were added and the stirring was continued for one hour at room temperature. Then 1.8 ml (0.02 mole) ethylene chlorophosphite were added. After stirring one hour in the same condition, the reaction was carried out as above under pressure of nitrogen (15-20 atm.) in autoclave. At the end of reaction, the desired product was dried in the same conditions, affording 2.37 g polythiourea with viscosity 0.32. Yield 98% (calculated on DADPE employed).

Anal: Calculated for: $C_{13}H_{10}N_2OS$; C, 64.44; H, 4.16; N, 11.56%. Found: C, 63.58; H, 4.06; N, 10.83%.

In similar conditions, the other polythioureas (presented in table 2) were prepared.

Table 2. Polyureas and polythioureas obtained by means of ethylene chlorophosphite as reagent.[a]

Diamine	CO_2 or CS_2	Yield %	η inh.[b]
p,p'-Diaminodiphenylether	CO_2	100	1,10[c]
p,p'-Diaminodiphenylmethane	CO_2	98	0,47
p-Phenylenediamine	CO_2	98	0,35
m-Phenylenediamine	CO_2	97	0,23
p,p'-Diaminodiphenylether	CS_2	98	0,32
p,p'-Diaminodiphenylmethane	CS_2	97	0,27
p-Phenylenediamine	CS_2	95	0,20
m-Phenylenediamine	CS_2	96	0.25

a) The polymers were identified by elementary analysis and IR spectra.

b) In NMP (0.5%) at 20°.

c) The polymer has been dissolved in NMP by heating.

By this new synthesis we obtained aromatic polyureas and polythioureas, which are difficult to obtain by the heating of aromatic diamines with carbon dioxide or carbon disulfide.

REFERENCES

1.N.Yamazaki, T.Iguchi and F.Higashi, J.Polym.Sci.,Polym. Chem.Ed.,13,785(1975); 20,103 (1982).
2.C.I.Chiriac, Rev.Roumaine Chim.,29,329 (1984).
3.C.I.Chiriac, Rev.Roumaine Chim.,(in press).
4.S.Klutchko and R.I.Meltzer, J.Org.Chem.,30,3454 (1965).
5.H.H.Boshard; H.Schmidt and H.Zollinger, Helv.Chim.Acta,42, 1653 (1959).
6.C.I.Chiriac and J.K.Stille, Macromolecules,10,710 (1977).
7.C.I.Chiriac, Polymer Bulletin,11,371 (1984).

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