

SHORT COMMUNICATION

Polythioamides by Room-Temperature Polycondensation

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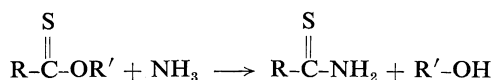
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KEY WORDS Room-Temperature Polycondensation / Dithiocarboxylic Acid Esters / Diamines / Polythioamides /

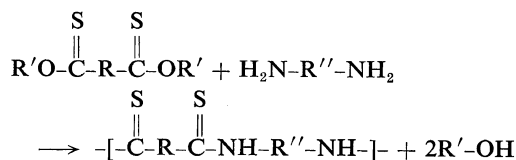
Polycondensation reaction is usually carried out by heating monomers in a molten state and the reaction is accompanied by equilibrium which is continually displaced to the polymer formation by removal of the more volatile product such as water or alcohol from the reaction system. Therefore, the rate of polycondensation is apparently influenced by the elimination rate of these volatile products from the reaction vessel.

However, when an active substituent is introduced in a monomer structure, the reactivity of functional groups such as amine or carboxylic acid increases^{1,2,3,4} to such a great extent that the polycondensation reaction is apparently not influenced by equilibrium.

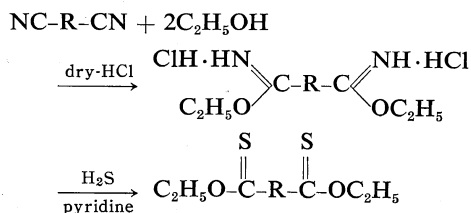
Thiocarboxylic acid-O-ester is known⁵ to react easily with ammonia at low temperature to form thioamide compound.





It is expected that this reaction could be extended to the polycondensation reaction of dithiocarboxylic acid-O,O-diester with diamines to form polythioamide at a relatively low temperature.



Dithiocarboxylic acid-O,O-diester were synthesized by the following route



Physical constants of the obtained diesters are as follows

	Yield	Anal.				
		C, %		H, %		
		Found	Calcd	Found	Calcd	
EtOCS-(CH ₂) ₄ -CSOEt	10% bp	125—128°C (2 mm)	51.79	51.27	7.72	7.75
EtOCS-  -CSOEt	61% mp	87—88°C	57.02	56.66	5.80	5.55
EtOCS-  -CSOEt	66% mp	62—63°C	55.71	56.66	5.57	5.55

Polythioamides by Room-Temperature Polycondensation

Diesters and diamines were dissolved in various solvents in a given concentration in the presence of 5 mol% of lithium ethoxide and the solution was kept at a constant temperature. The rate of the polycondensation reaction was determined either by titration of residual amine in the solution or by gas-chromatographic analysis of yielded alcohol in the solution. Polymer was collected by pouring the solution into water, followed by filtration and washing with benzene.

The rates of polycondensation of various di-

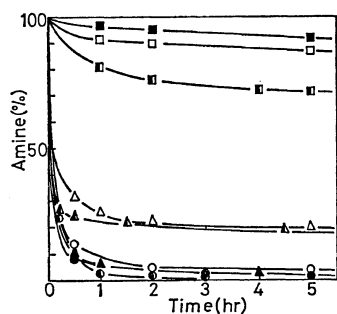


Figure 1. Rates of polycondensation of EtOC-R-S-COEt and $\text{H}_2\text{NR}'\text{NH}_2$ in DMF at 30°C: monomer concn, 0.25 mol/l; catalyst, EtOLi, 5 mol%.

R	R'
○, $-(\text{CH}_2)_4-$	$-(\text{CH}_2)_6-$
△, $-(\text{CH}_2)_4-$	$-(\text{CH}_2)_2-$
□, $-(\text{CH}_2)_4-$	
●,	$-(\text{CH}_2)_6-$
▲,	$-(\text{CH}_2)_2-$
■,	
◐,	$-(\text{CH}_2)_6-$
△,	$-(\text{CH}_2)_2-$
■,	

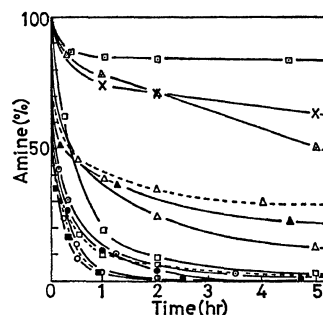


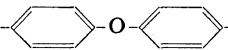
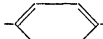

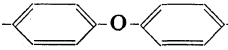
Figure 2. Rates of polycondensation of EtOC-S-COEt (---) or EtOC-S-COEt (—) and $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ in various solvents at 30°C: monomer concn, 0.25 mol/l; catalyst, EtOLi, 5 mol%; ○, DMF; △, EtOH; □, THF; ●, DMAc; ▲, HMPA; ■, DMSO; ◐, NMP; △, EtOH/H₂O = 1/1; ◑, DMSO/H₂O = 1/1; ×, DMAc/H₂O = 1/1.

$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ in various solvents at 30°C: monomer concn, 0.25 mol/l; catalyst, EtOLi, 5 mol%; ○, DMF; △, EtOH; □, THF; ●, DMAc; ▲, HMPA; ■, DMSO; ◐, NMP; △, EtOH/H₂O = 1/1; ◑, DMSO/H₂O = 1/1; ×, DMAc/H₂O = 1/1.

thiocarboxylic acid-O,O-diethyl esters with diamines were determined in *N,N*-dimethylformamide (DMF) in the concentration of 0.25 mol/l at 30°C and results are shown in Figure 1 where it is seen that the polycondensation reaction took place rapidly at room temperature. In particular, the polycondensation reaction of dithioisophthalic acid-O,O-diethyl ester (DTIP) with hexamethylenediamine (HD) was completed within a few hours and the rate of the polycondensation reaction was greatly influenced by solvents in the following decreasing order: DMSO > DMF > DMAc > NMP > THF > EtOH > EtOH-H₂O(50/50), as shown in Figure 2.

On the other hand, solvents have a marked influence on the structure of obtained polymers and an insoluble polymer with a rubber-like elasticity was formed in THF and particularly in ethanol during the polycondensation, while the reaction in solvents such as DMSO, DMF or DMAc proceeded in an homogeneous phase and the obtained polymers were soluble in these solvents, as indicated in Table I. However, when water was added to DMSO, DMF or DMAc, the reaction was retarded with the precipitation of insoluble polymer out of the solution.

Table I. Polycondensation of EtOC(=S)-R-COEt and H₂N-R'-NH₂ in various solvents^a

Monomer		Condition		Polymer			
R	R'	Solvent	Time, day	Yield, %		PMT, °C	
				Soluble	Insoluble		η_{sp}/c^b
-(CH ₂) ₄ -	-(CH ₂) ₂ -	DMF	2	38.0	0	0.08*	136—140
"	-(CH ₂) ₆ -	EtOH	10	0	100		(260)
"	"	THF	10	0	100		(260)
"	"	DMF	10	0	100		(260)
"		DMF	48	67.3	0	0.09*	(300)
	-(CH ₂) ₂ -	DMF	1	90.0	0	0.09*	190—200
"	-(CH ₂) ₆ -	DMF	1	75.3	0	0.22*	150—155
"	"	DMSO	1	100	0	0.22	150—155
	-(CH ₂) ₂ -	THF	1	49.7	33.5	0.09	
"	"	DMF	1	91.1	0	0.12	184—220
"	"	DMSO	1	84.7	0	0.13	
"	"	DMAc	1	78.1	0	0.11	
"	-(CH ₂) ₆ -	EtOH	1	0	100		(210)
"	"	THF	1	84.6	13.9	0.17	81—115
"	"	DMF	1	96.8	2.9	0.24	98—125
"	"	DMSO	1	94.2	0	0.18	98—125
"	"	DMAc	1	98.1	1.4	0.27	106—132
"	"	NMP	1	93.5	0	0.15	
"	"	HMPA	1	84.9	0	0.14	
"	"	DMSO-H ₂ O (50/50)	2	7.4	13.7		
"	"	DMAc-H ₂ O (50/50)	2	13.8	30.2	0.11	
"		DMSO	9	69.6	0	0.08	167—185

^a Monomer concn, 0.25 mol/l; temp, 30°C; catalyst, C₂H₅OLi, 5 mol%.

^b 0.05 g/10 ml in DMF(*H₂SO₄) at 30°C.

^c PMT, polymer melting temperature; (), decomposition temperature.

Aliphatic dithiocarboxylic acid ester tended to react with diamine to form insoluble polymer and the reaction with hexamethylenediamine resulted in the formation of insoluble polymer even in such low concentrations as 0.1 mol/l and at 0°C.

Effects of monomer concentration and temperature on the polycondensation reaction of DTIP with HD are summarized in Table II. It is interesting to note in Table II that the amount of soluble polymers increased with increasing monomer concentrations and with rising tem-

peratures.

Soluble polymers could dissolve in THF, *m*-cresol, DMF, DMAc, and concentrated sulfuric acid and they were insoluble in benzene, chloroform or acetone. Insoluble polymers which were precipitated out of the solution during the polycondensation reaction could not dissolve in any common organic solvents, suggesting a highly crosslinked structure.

Elementary analyses of soluble and insoluble polymers were in close agreement with the expected structure as follows.

