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SHORT COMMUNICATION

Polythioamides by Room-Temperature Polycondensation

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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 $known^5$ to react easily with ammonia at low temperature to form thioamide compound.

S	S	
$\overset{\parallel}{\mathbf{R-C-OR'}} + \mathbf{NH}_3$	$\longrightarrow \mathbf{R} - \mathbf{C} - \mathbf{N}\mathbf{H}_2 + \mathbf{R}' - \mathbf{O}\mathbf{H}$	

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

$$S S$$

$$R'O-C-R-C-OR' + H_2N-R''-NH_2$$

$$S S$$

$$\longrightarrow -[-C-R-C-NH-R''-NH-]- + 2R'-OH$$

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

$$\begin{array}{c} \text{NC-R-CN} + 2C_2H_5\text{OH} \\ \xrightarrow{\text{dry-HCl}} & \begin{array}{c} \text{ClH} \cdot \text{HN} \\ \hline C_2H_5\text{O} \end{array} \\ \xrightarrow{\text{C-R-C}} & \begin{array}{c} \text{NH} \cdot \text{HCl} \\ \hline \text{OC}_2H_5 \\ \hline \text{OC}_2H_5 \\ \hline \end{array} \\ \xrightarrow{\text{H}_2\text{S}} & \begin{array}{c} \text{S} \\ \hline \\ \hline \\ \text{pyridine} \end{array} \\ \end{array} \\ \begin{array}{c} \text{C}_2H_5\text{O} - \text{C} - \text{R} - \text{C} - \text{OC}_2H_5 \end{array} \end{array}$$

Physical constants of the obtained diesters are as follows

					And	al.	
Y	ield			С,	%	Н,	%
				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

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Diesters and diamines were dissolved in various solvents in a given concentration in the presence of $5 \mod \%$ 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-

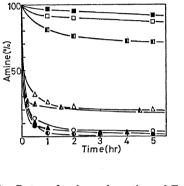
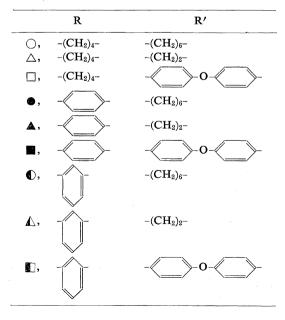


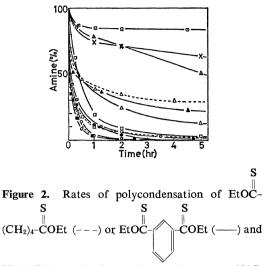
Figure 1. Rates of polycondensation of EtOC-R-S

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COEt and $H_2NR'NH_2$ in DMF at 30°C: monomer concn, 0.25 mol/*l*; catalyst, EtOLi, 5 mol%.



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H₂N-(CH₂)₆-NH₂ in various solvents at 30°C: monomer concn, 0.25 mol/*l*; catalyst, EtOLi, 5 mol%; ○, DMF; △, EtOH; □, THF; ●, DMAc; \blacktriangle , HMPA; \blacksquare , DMSO; ④, NMP; △, EtOH/H₂O =1/1; ④, 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.

Monomer		Conditi	Condition		Polymer					
			Time,	Yield, %						
R	R′	Solvent	day	Soluble	Insoluble	$\eta_{ m sp}/c^{ m b}$	PMT,° °C			
-(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			
\square	$-(CH_2)_2-$	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				
"	"	$\begin{array}{c} DMSO-H_2O\\ (50/50) \end{array}$	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			

Table I. Polycondensation of EtOC-R-COEt and H_2N -R'-NH2 in various solvents a

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

^b 0.05 g/10 ml in DMF ($^{*}H_{2}SO_{4}$) at 30°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/land 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 temperatures.

Soluble polymers could dissolve in THF, mcresol, 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.

Polymer		C, %	Н, %	N, %	
-[-CS(CH ₂) ₄ CSNH(CH ₂) ₆ NH-]-	{Found Calcd	47.53 47.52	6.19 6.98	13.63 13.86	
-[- CS - C SNH(CH ₂) ₆ NH-]-	{Found Calcd	59.80 60.42	6.56 6.52	9.41 10.07	

Infrared spectrum of insoluble polymers showed weak absorptions at 3200 and 1560 cm^{-1} which could be assigned to absorptions due to the N-H group and thioamide II, respectively. New absorptions appeared at 1660 and 650 cm⁻¹ which could be attributed to absorptions to -C=N- and

ightarrow C-S- groups, when compared with that of soluble polymers. Therefore, a cross-linking reaction might occur among thioamide groups of polymer chains to form insoluble polymers as follows

$$[-CS-R-CSNH-R'-NH-]-$$

$$-[-N=C-R-C=N-R'-]-$$

$$i$$

$$S$$

$$S$$

$$i$$

$$i$$

$$-[-N=C-R-C=N-R'-]-$$

reaction of dithiocarboxylic acid ester with diamine took place at room temperature even in alcohol, which indicates that the polycondensation reaction is apparently not under the control of chemical equilibrium since it is not influenced by the presence of the elimination product. The reaction mechanism and the role of the thiocarbonyl group on the polycondensation reaction needs to be elucidated and detailed study is now in progress.

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It is very interesting that the polycondensation 5. M. Matsui, Mem. Coll. Eng. Kyoto, 1, 285 (1908).

Solvent		Temp, °C	Time, hr	Yiel	(1	
	Concn, mol/l			DMF-soluble	DMF-insoluble	$\eta_{ m sp}/c^{ m b}$
DMAc	0.10	30	24	57.1	16.7	0.14
DMAc	0.25	30	24	98.1	1.4	0.27
DMAc	0.50	30	24	98.6	0	0.30
DMF	0.50	0	24	90.8	4.5	0.25
DMF	0.50	30	26	98.3	0	0.26
DMF	0.50	60	22	99.4	0	0.32
DMF	0.50	100	5	99.8	0	0.31
DMF	0.50	154	5	99.6	0	0.28

 Table II. Effects of monomer concentration and temperature on the polycondensation reaction of DTIP with HD^a

^a Catalyst, $C_2H_5OLi=5 \text{ mol}\%$.

^b 0.05 g/10 ml in DMF at 30°C.

 $\circ 0.05 \text{ g}/10 \text{ m}l$ in H₂SO₄ at 30°C.