

**INFLUENCE OF THE STRUCTURE OF AZO COMPOUNDS DERIVED FROM 3-OXOAMIDE ON THEIR ACTIVATION EFFECT AND THE STABILITY OF CHROMOPHORE IN THE ANIONIC POLYMERIZATION OF CAPROLACTAM\***

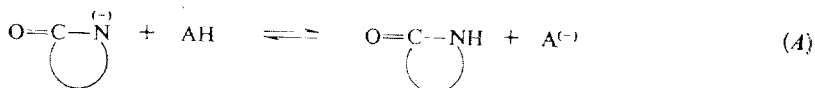
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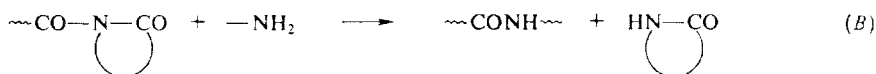
Received December 19th, 1974

The anionic polymerization of caprolactam in presence of compounds of the type  $R^1COCH_2 \cdot (CONHC_6H_5)-N=N-C_6H_4-R^2$  (*I*) and  $R-COC(CH_3)_2-CONHC_6H_4-N=N-C_6H_5$  (*II*) has been studied. Both types are characterized by a pronounced activating effect, the mechanism of which is discussed. The degree of incorporation of the azo group into the polymer and the colour stability under conditions of the anionic polymerization are better for *II* than for *I*.

Polyamides can be coloured by a number of organic and inorganic dyes (ref.<sup>1-6</sup>), the dye or pigment being usually added to the finished polymer. Only sporadically is the dye added before polymerization, because in this case it must be stable for long time and a high polymerization temperature needed for the usual hydrolytic polymerization. The anionic polymerization of lactams requires considerably shorter reaction times even at lower polymerization temperatures. In a suitable polymerization apparatus (*e.g.* extruder or pump) even pigment dyes can be used for colouration. However, there exist special requirements for dyes to be used in the colouration of anionic polyamides. The anionic polymerization is sensitive to the presence of compounds which neutralize lactam anions



or react with the growth centres such as amino compounds



Consequently, the above mentioned requirements are not fulfilled by the majority of azo compounds used which contain acid groups such as  $-\text{SO}_3\text{H}$  or  $-\text{COOH}$  or primary and secondary amino groups.

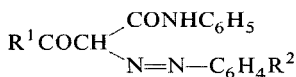
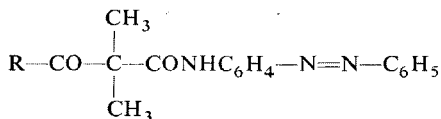
\* Part LVI in the series Alkaline Polymerization of 6-Caprolactam; Part LV; This Journal 39, 2393 (1974).

TABLE I  
2-Acyl-2-arylaazoacetanilides (I)

R <sup>1</sup>	R <sup>2</sup>	M.p., °C (ethanol)	Formula (m.w.)	Calculated/Found			$\lambda_{\max}$ nm	$\epsilon \cdot 10^4$ l/mol
				% C	% H	% N		
CH <sub>3</sub>	H	99—100	C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> (281.3)	63.55 63.40	4.50 5.38	14.86 14.94	373.5	2.80
CH <sub>3</sub>	4-CH <sub>3</sub>	125—126	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> (295.3)	69.14 69.24	5.80 5.86	14.23 14.48	380.0	2.82
CH <sub>3</sub>	3-CH <sub>3</sub>	116.5—117	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> (295.3)	69.14 69.24	5.80 5.83	14.23 14.46	376.4	2.93
CH <sub>3</sub>	4-CH <sub>3</sub> O	126—127.5	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> (311.3)	65.58 65.49	5.50 5.64	13.50 13.67	378.2	2.86
CH <sub>3</sub>	3-CH <sub>3</sub> O	93.5—945	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> (311.3)	65.58 65.50	5.50 5.60	13.50 13.48	391.4	2.95
CH <sub>3</sub>	4-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH—	136—138	C <sub>20</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> (352.5)	68.16 68.15	6.86 6.88	15.89 15.82	454.3	2.55
CH <sub>3</sub>	1-C <sub>10</sub> H <sub>7</sub>	172.5—174.5	C <sub>20</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> (332.4)	72.28 72.40	5.10 5.15	12.70 12.62	401.4	1.83
CH <sub>3</sub>	4-CH <sub>3</sub> CONH—	226—227 <sup>a</sup>	C <sub>18</sub> H <sub>17</sub> N <sub>4</sub> O <sub>2</sub> (321.4)	67.52 67.40	5.25 5.34	17.30 17.40	393.6	2.38
C <sub>6</sub> H <sub>5</sub>	4-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH—	172—173.5 <sup>b</sup>	C <sub>24</sub> H <sub>26</sub> N <sub>3</sub> O <sub>2</sub> (402.4)	71.95 71.80	6.60 6.50	13.65 13.90	468.5	2.26

<sup>a</sup> Dioxan. <sup>b</sup> Ethanol-toluene (7 : 3).

In this work we investigated derivatives of 3-oxo amides (*I, II*) which can be regarded as suitable azo dyes. The type *I* compounds, called Hansa yellows<sup>7</sup>, with a characteristic 2-acyl-2-arylazoacetanilide, grouping can react in two tautomeric forms, namely, as 2-hydrazones of 2,3-dioxo amides and as 2-azo-3-oxo amides. In the latter case they could have an activating effect in the anionic polymerization of lactams, similarly to 2-mono- or 2,2-disubstituted 3-oxo amides<sup>8</sup>. Moreover, the amide group of the dye could participate in transamidation reactions, which would lead to the incorporation of the low-molecular weight coloured amide into the polymer chain and to the formation of a covalent bond between the chromophore and the polymer molecules.

*I**II*

## EXPERIMENTAL

### Chemicals Used

2-Acyl-2-arylazoacetanilides (*I*) were prepared by the coupling of diazotized aryl amines with 2-acyl amides according to ref.<sup>7</sup>. Their properties, analytical values and UV spectra are given in Table I. N,N-Dibutyl-2-phenylazoacetamide, m.p. 92.5–93.5°C (ethanol). For C<sub>18</sub>H<sub>27</sub>.N<sub>3</sub>O<sub>2</sub> (317.4) calculated: 68.2% C, 8.6% H, 13.25% N; found: 68.1% C, 8.7% H, 13.25% N.

Anilides of 3-oxo acids were prepared by addition of aniline to ketene dimers according to ref.<sup>9,10</sup>. 4'-Phenylazo-2,2,4-trimethyl-3-oxopentanamide, m.p. 103.5–104.5°C (heptane). For C<sub>20</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub> (337.4) calculated: 71.25% C, 6.85% H, 12.46% N; found: 71.45% C, 7.0% H, 12.6% N.

TABLE II

Anionic Polymerization of Caprolactam with Activators of the 2-Acyl-2-arylazoacetanilide (*I*)

Concentration of sodium caprolactam 0.6 mol%, concentration of activator 0.2 mol%, 180°C, 30 min.  $[\eta]$  intrinsic viscosity (cresol, 25°C).

R <sup>1</sup>	R <sup>2</sup>	Yield, %	$[\eta]$ , dl/g
CH <sub>3</sub>	H	92.8	2.59
CH <sub>3</sub>	4-CH <sub>3</sub>	91.2	2.55
CH <sub>3</sub>	3-CH <sub>3</sub>	89.5	2.60
CH <sub>3</sub>	4-CH <sub>3</sub> O	95.0	2.48
CH <sub>3</sub>	4-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	93.9	2.53
C <sub>6</sub> H <sub>5</sub>	4-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	95.2	2.30
CH <sub>3</sub>	1-C <sub>10</sub> H <sub>7</sub>	82.5	2.40

2-Alkyl acetoacetanilides were prepared by alkylation of acetoacetanilides according to ref.<sup>11</sup>.

Preparation of the polymerization mixture, filling of ampoules, polymerization and analysis of the reaction products have been described elsewhere<sup>8,12</sup>.

## RESULTS AND DISCUSSION

2-Acyl-2-arylazoacetamides (dyes of type I) exhibit an important activating effect on the anionic polymerization of caprolactam (Table II) and were therefore suggested as cocatalysts of the anionic polymerization of lactams<sup>13</sup>. Similarly to 3-oxo-amides<sup>8,14,15</sup>, their activating effect consists in the splitting to give reactive fragments which form growth centres with lactams:

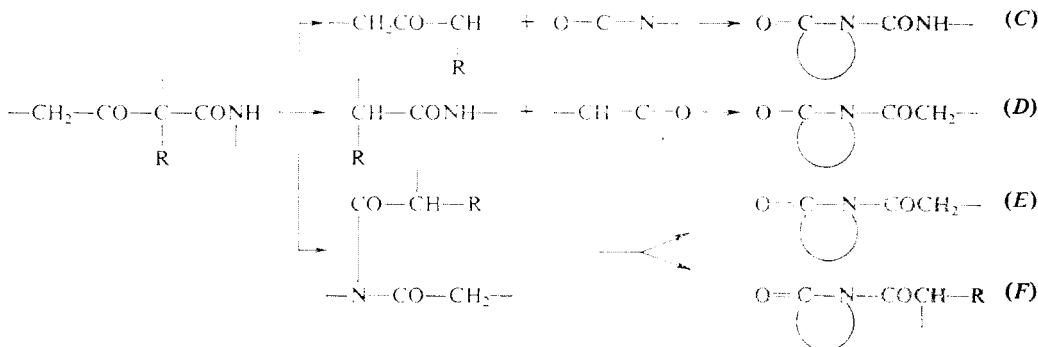


TABLE III

Time Needed for the Formation of 25 wt.% of Polymer in the Anionic Polymerization of Caprolactam in Presence of Sodium Caprolactam (0.6 mol.%) and of Azo Compounds (0.2%) of Type (I)

Azo compound I		Time <sup>a</sup> , min		
R <sup>1</sup>	R <sup>2</sup>	160°C	170°C	180°C
CH <sub>3</sub>	1-naphthyl	79	36	19
CH <sub>3</sub>	4-CH <sub>3</sub>	64	31	15
CH <sub>3</sub>	H	62	31	16
CH <sub>3</sub>	3-CH <sub>3</sub> O	55	28	14
CH <sub>3</sub>	3-CH <sub>3</sub>	44	26	19
CH <sub>3</sub>	4-CH <sub>3</sub> O	43	21	13
CH <sub>3</sub>	4-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	30	14	9
C <sub>6</sub> H <sub>5</sub>	4-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	21	11	6
	3-Oxoazoanilide <sup>b</sup>	7	9	4

<sup>a</sup> The time was determined by reading off 25% conversion on the plot of the time dependence of conversions similarly to Fig. 2. <sup>b</sup> 4'-Phenylazo-2,2,4-trimethyl-3-oxopentananilide.

### Effect of Activator Acidity

The rate of polymerization is strongly dependent on the sodium caprolactam/activator ratio. The azo compounds of type *I* have a high activating effect comparable to that of diacyl amines only at a sodium caprolactam/activator ratio higher than unity. On polymerization at 220°C with 2-[4-(N,N-diethylamino)benzene-1-azo]-2-benzoyl-acetanilide as activator the following yields were obtained:

Na-caprolactam, mol %:	0.6	0.6	0.6	0.8	0.8	0.8
Activator, mol %:	0.2	0.3	0.4	0.27	0.4	0.53
Yield, %:	90.1	90.6	66.7	90.9	91.8	88.7

The molecule of 2-acyl-2-arylazoacetamide contains two acid hydrogen atoms so that the cocatalytic effect can occur to a greater extent only in the presence of such an amount of base which in the neutralization equilibrium yields a sufficient quantity of lactamate anions needed for the growth reaction. Unlike azo compounds of type *I* azo compounds of type *II* possess only one acid hydrogen atom; as a consequence their activating ability does not depend so much on the sodium caprolactam/activator ratio (Fig. 1). The comparison of data in Fig. 1 and ref.<sup>8</sup> shows that the benzeneazo group raises the activity of the amide group more markedly than the phenyl group.

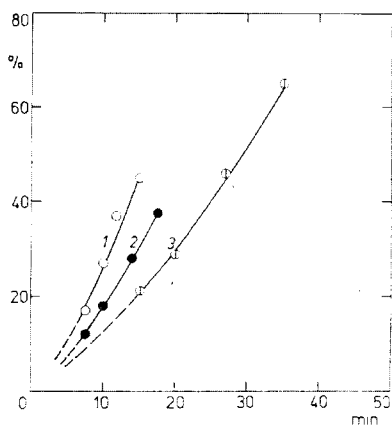


FIG. 1

Conversion to Polymer in Polymerization of Caprolactam at 170°C

Concentration of sodium caprolactam 0.15 mol %; concentration of 4'-phenylazo-2,2,4-trimethyl-3-oxopentananilide (mol %): ● 0.067, ○ 0.15, ◻ 0.30.

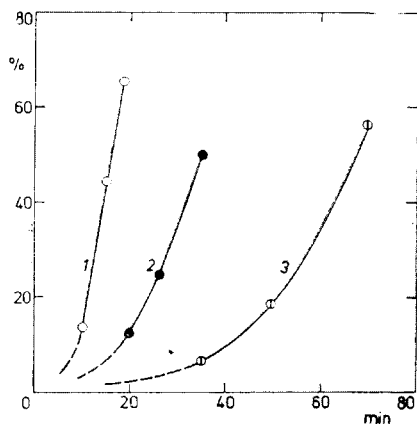
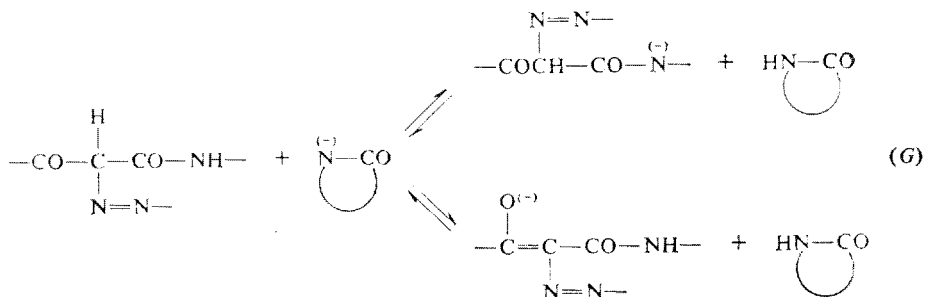


FIG. 2

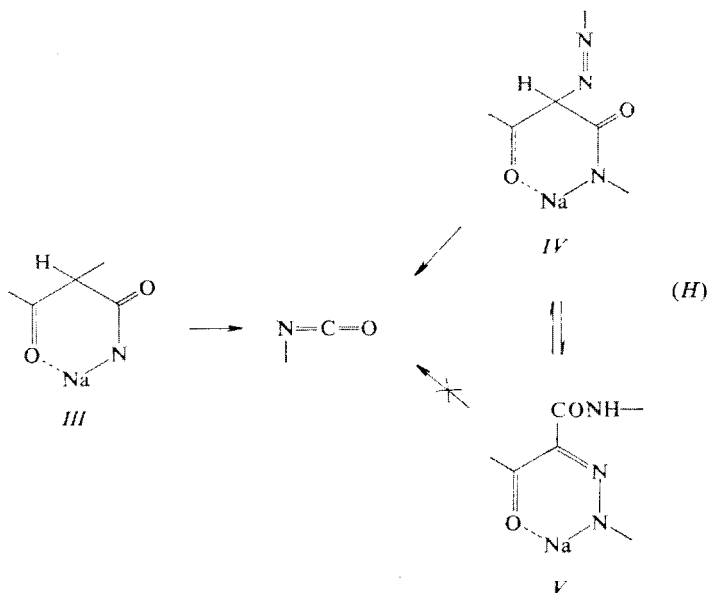
Polymerization of Caprolactam with Sodium Caprolactam (0.6 mol.%) and 2-Acetyl-2-(3-methoxybenzene-1-azo)acetanilide (0.2 mol %)

Polymerization temperatures, °C: ○ 160, ● 170, ◻ 180.



### Effect of Activator Structure

In the cocatalysis with 3-oxo amides in a basic medium isocyanate cleavage (H) via the cyclic structure III or its dissociated form plays the predominant part. In the case of 2-acyl-2-arylaazoacetamides another structure (V), which does not contribute to the formation of growth centres via intermediate isocyanate, competes with the structure IV which is analogous to III:



This helps to explain differences in the mechanism of cocatalysis existing between 2-acyl-2-arylaazoacetamides and 3-oxo amides, the structures of which are otherwise very similar to each other. The isocyanate cleavage of 3-oxo amides is influenced by substituents on the carbon atom in position 2 and increases with increasing +I

effect of the alkyl groups<sup>8</sup>. A similar effect can be observed for 2-aryazoacetamides, in which the cocatalytic influence increases in the series of substituents of the arylazo group in an order indicated in Table III. Thus, the activating effect increases with increasing electron density on the nitrogen atom of the azo group adjacent to the aryl group, because acidity becomes reduced and the content of the hydrazone V (in (H)), which does not contribute to the activating effect, is suppressed. The activating effect of 2-acyl-2-aryazoacetamides is affected by the character of the acyl group (Table III) similarly to 3-oxo amides, the activating effect of which increases with increasing +I effect of substituents of the carbonyl group in the acyl part (Table IV).

N,N-Dibutyl-2-phenylazoacetoacetamide did not activate the anionic polymerization of caprolactam, similarly to 3-oxo amides from which no N-anion can be formed<sup>15,16</sup>.

### *Incorporation of Chromophore into the Polymer*

In the anionic polymerization of lactams 2-acyl-2-aryazoacetamides take part in the transamidation reactions by which the polymer chains split to give two polymer particles:



In the above transamidations the coloured part of azoacetoacetamide of type I is incorporated into one of the two polymer molecules. As illustrated by Table V,

TABLE IV

Effect of Substituent on the Activation Effect of 3-Oxoamides  $\text{R}^1\text{COCH}(\text{R}^2)\text{CONHC}_6\text{H}_5$  in the Adiabatic Polymerization of Caprolactam

Concentration of initiator and activator 0.3 mol.%;  $t_{0.5}$  is halftime in the adiabatic polymerization<sup>8</sup>,  $[\eta]$  intrinsic viscosity (cresol, 25°C).

$\text{R}^1$	$\text{R}^2$	$t_{0.5}, \text{s}$	Yield, %	$[\eta], \text{dl/g}$
$\text{CH}_3$	$\text{CH}_3$	1 975	93.9	2.106
$\text{CH}_3$	$\text{C}_4\text{H}_9$	1 114	93.5	1.950
$\text{C}_2\text{H}_5$	$\text{CH}_3$	1 472	93.1	2.254
$\text{C}_3\text{H}_7$	$\text{C}_2\text{H}_5$	898	92.9	2.212
$\text{C}_5\text{H}_{11}$	$\text{C}_4\text{H}_9$	891	93.2	2.356
$\text{C}_7\text{H}_{15}$	$\text{C}_{16}\text{H}_{33}$	860	94.5	2.500

TABLE V

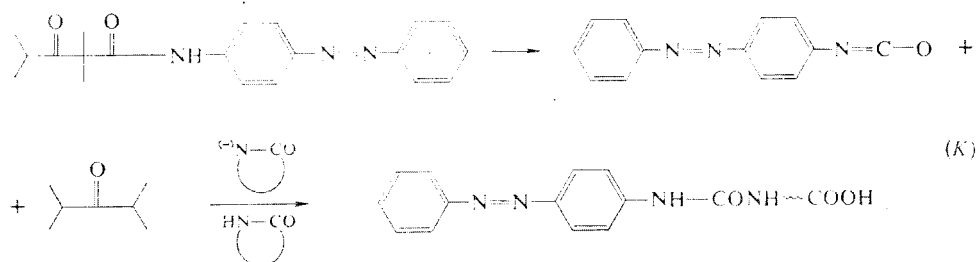
Stability and Participation of Incorporated Chromophore in the Polymer (0.4 mol.% sodium caprolactam, 0.3 mol.% azo compound, 180°C)

$Q$  is ratio  $100E/E_0$ , where  $E$  is extinction of the solution of polymerizate in  $CF_3CH_2OH$  ( $c = 10$  mg/ml) at  $\lambda_{max}$ ;  $E_0$  is theoretical extinction, subscripts  $n$  and  $e$  denote unextracted and extracted polymerization product, respectively.

$t$ , min	Yield, %	$Q_n$	$Q_e$	$t$ , min	Yield, %	$Q_n$	$Q_e$
2-Phenylazo-2-benzoylacetonilide				4'-Phenylazo-2,2,4-trimethyl-3-oxopentananilide			
5	17.1	81.1	45.1	15	89.5	100	95.0
10	88.4	16.2	6.9	60	96.8	84.8	77.5
15	90.4	9.6	2.7				
30	95.2	5.4	1.2				
60	97.3	0.9	0.2				

the portion of the incorporated chromophore is comparatively low and decreases further with increasing time of reaction. The destruction of the chromophore can be attributed to the instability of the grouping  $RCOCH_2N=N-$  at elevated temperatures, particularly under the conditions of the anionic polymerization of lactams. A similar decomposition was observed for  $N$ -(*p*-phenylazobenzoyl) caprolactam<sup>17</sup>. About one half of all the chromophores present is incorporated into the polymer at the beginning of polymerization (Table V), which suggests that the isocyanate cleavage ( $C$ ) proceeds at a rate similar to the transacylation reaction ( $J$ ) and to reactions ( $D-F$ ) ( $R$  stands for  $-N=N$ -aryl).

Chromophores derived from aminoazobenzene are much more stable. In the anionic polymerization of caprolactam in presence of 4'-phenylazo-2,2,4-trimethyl-3-oxopentananilide (type II) reaction ( $C$ ) yields a coloured isocyanate which provides coloured growth centres on which coloured polyamide with a covalently bonded chromophore is formed:





A chromophore of this type is incorporated into the polymer in a high extent and is more stable under the conditions of anionic polymerization than the chromophore  $C_6H_5N=N-CH_2-CONH-$  (Table V).

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Translated by L. Kopecká.