ALKALINE POLYMERIZATION OF 6-CAPROLACTAM. XLVIII.*
FRACTION OF ACYL GROUPS OF THE ACTIVATOR INCORPORATED IN A HIGH-MOLECULAR WEIGHT POLYMER

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It has been found by using benzoylcaprolactam-[^{14}C] that approximately 90% of acyl groups from the activator become incorporated in the high-molecular weight polymer during polymerization at 175—280°C. The remaining fraction of benzoyl groups is present in the extractable oligomeric fraction. The relatively large fraction of oligomers can be assigned to fast side reactions which consume one part of the activator before it can participate in the growth reaction.

Side and consecutive reactions (condensation, disproportionation, hydrolysis)[1] occurring during the activated anionic polymerization of ε-caprolactam lead to the formation of basic and acidic agroups in polymer molecules. Moreover, the polymer also contains neutral end groups originating in the molecule of the activator used. A formula[2]

$$E = \varrho_A[A]_0/p + [B] + [C] \qquad (1)$$

has been suggested to evaluate the total end group concentration in a water-insoluble polymer; here, [B] and [C] are concentrations of basic and acidic groups which can be determined by titration methods; the fraction of neutral groups can be calculated from the initial concentration of the activator ($[A]_0$), the conversion of monomer into water-insoluble polymer, p, and a coefficient ϱ_A, representing the number of fragments of a molecule of the activator acting as chain end groups. The introduction of the factor p into the above term is based on earlier observations by Sekiguchi[3] who had found that during the low-temperature polymerization of 2-pyrrolidinone the activator was completely incorporated into the polymer. Activators of the acyllactam type are known to be subjected to condensation reactions under polymerization conditions. The subsequent side reactions can give rise to low-molecular weight compounds incapable of acting as growth centres. The fraction of the activator molecules which disappear to give inactive low-molecular

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weight compounds will generally depend on the type of the activator, the size of the lactam ring, and on the temperature and concentrations of the catalytic components.

It has been the objective of this work to check the calculated term of Eq. (*1*) by direct determination of the concentration of the activator acyl residues incorporated into high-molecular weight anionic polycaprolactam. Activators were N-(*p*-phenylazobenzoyl)caprolactam allowing the spectrophotometric analysis of the polymer, and N-benzoylcaprolactam with ^{14}C in the exocyclic carbonyl group suitable for radiometric analysis.

EXPERIMENTAL

Model Compounds and Activators

A number of model amides have been obtained by the Schotten-Baumann reaction from the respective amines and phenylazobenzoyl chloride (Table I) in order to determine the molar extinction coefficient of the *p*-phenylazobenzamide group at the end of the polycaprolactam chain in 100% formic acid; *p*-phenylazobenzoyl chloride was obtained from nitrobenzene *via* nitrosobenzene and *p*-phenylazobenzoic acid[4-6] in a yield of 25·4%.

N-(*p-Phenylazobenzoyl)caprolactam*: Caprolactam (3·0 g) was acylated with 3·0 g of *p*-phenylazobenzoyl chloride in 200 ml of toluene in the presence of 2 ml of pyridine at room temperature for 1·5 h and then at 90°C for 3·5 h. The yield was 3·7 g of red-brown crystals (Table I). N-(*p*-Phenylazobenzoyl) caprolactam was thermolyzed in N-ethylacetamide in ampoules having the volume about 0·04 ml at concentrations ranging from 8·0 to 11·6 mmol/kg, either in a neutral solution or with sodium caprolactam added in an amount equivalent to acylcaprolactam. The loss in colour density was followed in 96% ethanol or in a mixture of 96% ethanol and 0·4% acetic acid (for N-(*p*-phenylazobenzoyl)caprolactam, at λ_{max} 326 and 323 nm using $\varepsilon = 23\,520$ and 22 960 $mol^{-1}\,l\,cm^{-1}$, respectively) with a Unicam SP 100 apparatus.

N-*Benzoylcaprolactam*-[^{14}C]: The activator was obtained by a reaction of O-methyl-ε-caprolactim with benzoyl chloride-[^{14}C] in a yield of 73% (*cf.*[7]), m.p. 68—69°C, specific activity 51 Ci/μmol. Benzoic acid [$^{14}COOH$] was obtained after ref.[8] by carbonization of phenylmagnesium bromide with carbon dioxide [^{14}C] in a yield of 89% and transformed into benzoyl chloride-[^{14}C] with thionyl chloride in a 100% excess using pyridine as catalyst; the yield was 94%.

Polymerization

Sodium caprolactam and polymerization techniques used were the same as in an earlier communication[2]. The polymerizations with N-phenylazobenzoylcaprolactam were carried out by procedure *A* and those with N-benzoylcaprolactam by procedure *E* which differed from the described[2] procedure *C* in that the predried monomer was melted at 140°C for 10 min, and the initiator was dissolved each time one minute at the given temperature.

Analytical Methods

The non-extractable fraction of the polymerizate was determined by extraction with water as described in ref.[9] or with methanol or benzene under reflux and stirring (4 × 120 ml of methanol for 30 min each time, or 5 × 90 ml of benzene for one hour each time; the first benzene fraction

contained a trace of acetic acid). In some cases the extracts were evaporated in a vacuum rotating evaporator at a bath temperature below 50°C; the residue of water extracts was dehydrated by evaporation with 2 × 10 ml of benzene and 2 × 10 ml of hexane; the dry residue was dried before weighing at 25—30°C/3 Torr for 1—2 days.

The absorbance of solutions of coloured polymers and dry residue of the extracts in a 100% formic acid was measured with a Unicam SP 100 apparatus at 322 nm, using $\varepsilon = 22580\ \text{mol}^{-1} . .1 . \text{cm}^{-1}$ determined for *p*-phenylbenzamidocaproic acid.

The radioactivity of polymerizates, polymers and extracts was determined by a combustion method[10]. During combustion of 10—50 mg of the sample, 15 ml of the mixture 2-aminoethanol–2-methoxyethanol (12 : 88) was used for absorption; after the reaction, 10 ml of the resulting solution was mixed with 10 ml of a scintillation agent containing 6 g of 2,5-diphenyl-1,3-oxazole and 0·07 g of 1,4-bis(5-phenyl-1,3-oxazole-2-yl)benzene in 1000 ml of toluene, and the activity was determined with an SL20—Intertechnique, Plaisir—France scintillation spectrometer.

Thin layer chromatography: Kieselgel GF_{254} (Merck) layer 0·1 mm, development in the systems ether–methanol (10 : 1) or butanol–acetic acid (4 : 1), detection with ultraviolet light followed by iodination.

Gas liquid chromatography: The monomer was determined by means of benzophenone as an internal standard and methanol as solvent on a column 1 m × 3 mm packed with 10% Carbowax 20 M on Chromosorb W (80—100 mesh), nitrogen as carrier gas (50 ml/min), 185°C, flame ionization detector, Perkin-Elmer Fll apparatus with a D 26 integrator.

TABLE I

p-Phenylazobenzamides, (R = p-$C_6H_5N{:}NC_6H_4CO$)

Compound (yield, %)	M.p., °C (solvent)	Formula (mol. weight)	Calculated/Found % C	% H	% N	λ_{max}, nm ε^a
$RNH(CH_2)_5COOH$ (62)	157·5—159·0 (acetone)	$C_{19}H_{21}N_3O_3$ (339·4)	67·24 67·23	6·24 6·28	12·38 12·30	322 22 580
$RNH(CH_2)_5COC_6H_5$ (82)	147·0—148·5 (ethanol)	$C_{25}H_{25}N_3O_2$ (399·5)	75·16 75·17	6·31 6·38	10·52 10·84	322 24 960
$[RNH(CH_2)_5]_2CO$ (98)	227·0—228·5 (dimethylformamide)	$C_{37}H_{40}N_6O_3$ (616·7)	72·05 71·90	6·54 6·59	13·63 13·57	322 22 560[b]
$RNHC_4H_9$ (98)	143—144 (ethanol–cyclohexane)	$C_{17}H_{19}N_3O$ (281·4)	72·57 72·53	6·81 6·88	14·94 14·96	322 22 900
$RN(CH_2)_5CO$ (94)	137·5—139·0 (ether–acetone)	$C_{19}H_{19}N_3O_2$ (321·4)	71·01 71·14	5·96 5·93	13·08 13·04	—

[a] In 100% formic acid, $\text{mol}^{-1}\,1\,\text{cm}^{-1}$; [b] $\text{equiv}^{-1}\,1\,\text{cm}^{-1}$ (equivalent based upon R).

RESULTS AND DISCUSSION

Polymerization in the temperature range from 125 to 225°C in the presence of sodium caprolactam ($[I]_0 = 22-26$ mmol/kg of the polymerization mixture) and N-(*p*-phenylazobenzoyle)caprolactam ($[A]_0 = 22-66$ mmol/kg) at ratios $[A]_0/[I]_0$ ranging from 0·5 to 1·5 has shown that 10–20% of all groups of the polymerizate absorbing in the region 300–350 nm are present in water-soluble oligomers. The results could not be evaluated in detail, since the total content of the coloured component decreases during the polymerizations; at the same time, the extent of the polymerization reaction (p) also decreases compared to the equilibrium values for the given temperatures. A similar decrease in colour density occurs during the thermolysis of N-(*p*-phenylazobenzoyl)caprolactam in N-ethylacetamide, both in alkaline (after 120 min at 175°C by 3·5%) and neutral (after 90 min at 225°C by 7%) solutions. Since the extinction falls off continuously during thermolysis, the process

TABLE II

Characteristics of Anionic Polymerizates of Caprolactam

$[A]_p$ Activator concentration in water-insoluble fraction determined radiometrically, $\sigma = [A]_p \cdot p/[A]_0$.

Sample	$[I]_0$	$[A]_0$	T	t	p	$[A]_p$	σ
	mmol/kg		°C	min		mmol/kg	
1	43·51	43·56	280	28·25	0·8825	44·54	0·90
2	43·51	43·46	280·0	87·25	0·8775	44·91	0·91
3	43·51	43·47	282·1	177	0·8804	43·90	0·89
4	43·51	43·55	224·7	26·5	0·9147	42·48	0·89
5	43·51	43·59	224·8	87	0·9145	41·37	0·87
6	43·51	43·53	225·4	176·25	0·9148	39·40	0·83
7	43·06	86·27	224·6	26·5	0·9147	91·26	0·97
8	43·72	21·82	225·2	26·5	0·9155	22·54	0·95
9	86·93	21·75	225·7	26·5	0·9144	19·63	0·83
10	86·52	43·26	225·4	26·5	0·9128	40·26	0·85
11	85·71	85·70	224·5	26·5	0·9117	86·51	0·92
12	21·93	21·82	224·7	26·5	0·9170	20·11	0·85
13	21·82	43·70	225·0	26·5	0·9152	43·43	0·91
14	21·62	86·39	224·9	27·5	0·8088	95·68	0·90
15[a]	43·51	43·46	175·1	30	0·9697	39·34	0·88

[a] Prepared by procedure *A*.

involved does not consist only in a change of the chromophore at the initiation step of polymerization, and a loss of chromophoric groups during the polymerization must be taken into account.

A convincing information on the activator distribution in the polymerizate has been provided by experiments with labelled N-benzoylcaprolactam. The benzoyl derivative was chosen among N-acyllactams because, unlike the case of activation with acyllactams having methylene group at the α-position of the exocyclic acyl group, no losses of ^{14}C may occur in the form of carbon dioxide evolved[11] during the polymerization due to the possible hydrolysis of 3-oxoamide structural units in the polymer chain[1]. In the case of samples obtained within the temperature range 175–280°C (at 225°C with various polymerization times or with various ratios of the catalytic components on three concentration levels of the initiator), 89% on the average of the initial activator is incorporated into the water-insoluble polymer (Table II); relative mean deviation ±3% of this conversion (σ) is given by the accuracy of radiometry. The checks by total balances of labelled benzoyl groups (determination in the polymerizate, on the one hand, and in both the polymer and the extract, on the other) were quite satisfactory, not only for water extractions, but also for extractions with methanol or benzene (Table III). In no case has the comparative technique revealed the presence of N-benzoylcaprolactam in thin-layer chromatograms of the extracts; only trace amounts could be suspected in the case of benzoic acid. Consequently, the whole amount of the activator present reacts during the polymerization, and the benzoyl groups are incorporated both in the polymer and in the water-soluble low-molecular weight compounds; no perceptible hydrolysis of the end benzamide groups takes place during the extraction of the polymerizate.

It follows from Table II that approximately 11% of the activator is transformed by polymerization into water-soluble benzoylated compounds. The examples of poly-

TABLE III

Activator Concentration (mmol/kg) in Polymerizate ([A]), Extract ($[A]_e$), and in Polymer ($[A]_p$) Determined Radiometrically

e Extractable fraction of polymerizate, $q = ([A]_e \cdot e + [A]_p \cdot p)/[A]$.

Sample	Extraction agent	*e*	*p*	[A]	$[A]_e$	$[A]_p$	*q*
1	water	0·110	0·882	43·40	33·42	44·54	0·9899
2	benzene	0·040	0·958	41·40	24·20	43·16	1·0221
4	methanol	0·081	0·907	43·73	51·83	43·37	0·9955
6	water	0·086	0·915	40·41	47·13	39·40	0·9924
15	water	0·019	0·970	40·00	109·65	39·34	1·0061

mers having $[A]_0 = [I]_0 = 43{\cdot}5$ mmol/kg illustrate the rather surprising fact that the above fraction is virtually independent of temperature and molecular weight of the polymer. If the benzoyl groups were present in the extractables in the form of benzamide groups of regular linear oligomers, their participation should increase with decreasing degree of polymerization of the polymers (having comparable molecular weight distribution). The molecular weight distribution of anionic polymers obtained at 220°C is not too remote from the statistical distribution[12] of hydrolytic polymers, so that the content of extractable linear oligomers (c_{lin}) should be similar. For a low-molecular weight polymer (sample 3, $[\eta] = 0{\cdot}68$ dl g^{-1}, $\bar{P}_\eta \approx 80$) the content of extractables other than the monomer and cyclic oligomers corresponds to $c_{lin} \approx 1{\cdot}4\%$ (ref.[13]) of the hydrolytic polymerizate. However, for sample 4 with $\bar{P} \approx 220$ (*cf.*[2]) the content of these compounds is considerably higher, $c = e - c_m - c_c = 2{\cdot}2\%$ (extract $e = 8{\cdot}4\%$, monomer $c_m = 4{\cdot}4\%$ according to GLC, cyclic oligomers $c_c = 1{\cdot}8\%$ according to ref.[13,14]) than in an analogous hydrolytic polymerizate, $c_{lin} < 0{\cdot}2\%$ (ref.[13,15]). The difference between c and c_{lin} can be attributed to the presence of other low-molecular weight compounds which are probably formed in side reactions of the activator. It was found that the acylation of the lactam anion with the acyclic carbonyl of the activator (growth reaction) proceeds only about five times faster than the decay of the activator due to condensation[16]. The assumption seems justified, therefore, that one part of the activator or of growing molecules disappears at the given temperatures *via* irreversible reactions to yield extractables which – in contrast with regular linear oligomers – do not participate in the equilibrium any more. The proportion of these compounds (amount, molecular weight) obviously depends on the polymerization conditions.

The results thus obtained are not at variance with the conclusions arrived at by Sekiguchi[3] concerning the incorporation of the bulk of N-benzoyl-2-pyrrolidinone in the polymer within a very short time after the onset of the anionic polymerization of 2-pyrrolidinone at 30°C. Sekiguchi investigated spectrometrically the loss of aromatic nuclei in a solution containing only the monomer after the polymer had been precipitated by the mixture ethanol–ether 1 : 9 (diethyl ether is used analytically to separate the monomer from its mixture with oligomers[14], but is not sufficiently effective for the extraction of the monomer from a high-conversion polymerizate). In the case of polycaprolactam they are linear oligomers whose solubility in the chosen extraction solvent (water, methanol, benzene) is also responsible for the presence of the activator fragments in the extract.

It follows from the above that Eq. (*1*) should be rearranged to become

$$E = \sigma \,.\, \varrho_A [A]_0/(1 - e) + [B] + [C]\,, \qquad (2)$$

where both the member corresponding to the extractable fraction (e) and the constant σ depend on the extraction agent (0·89 for water). The relationship between the degree of polymerization

and intrinsic viscosity

$$2/M_0 \,.\, E = 105{\cdot}6[\eta]^{1{\cdot}90}\,, \tag{3a}$$

which was determined by using Eq. (*1*) for an assembly of 36 polycaprolactam samples[2] was revised with respect to Eq. (*2*); the resulting equation was

$$2/M_0 \,.\, E = 112{\cdot}3[\eta]^{1{\cdot}179}\,. \tag{3b}$$

Owing to the rather small correction and to the on the average balanced weight of the individual concentrations added in Eq. (*2*), the revaluation has led only to small changes in the constants for anionic polycaprolactam.

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