

CHANGES IN THE DEGREE OF POLYMERIZATION AND ACID AND BASE CONTENTS OCCURRING AT ROOM TEMPERATURE IN CAPROLACTAM POLYMERS*

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It has been found that a long-term storage of anionic caprolactam polymers at room temperature in the presence of oxygen leads to changes in the molecular weight and concentration of acidic and basic groups. These changes are dependent to a certain extent on the type of the catalytic system used; in particular, in the presence of water they are more pronounced for unextracted samples than for those extracted with water. However, even if the polymers are kept in dry air the changes in unextracted samples are so pronounced that as soon as after a weak some acid or base contents differ considerably from those obtained for fresh samples. These changes have been observed not only for anionic, but also for hydrolytic polymers.

Measurements of the degree of polymerization and of the concentration of acidic and basic groups in anionic caprolactam polymers carried out in our laboratories have revealed that measurements repeated after a few months differ in some cases from the results obtained immediately after preparation of the polymer. At first sight there was no regularity in the changes observed. The differences lay beyond the accuracy of analytical methods and could not be due to the inhomogeneity of samples, although only a few milligrams are used *e.g.* for the determination of the end groups. It is known that the anionic polymers of caprolactam contain irregular structures¹⁻⁴ (derived *e.g.* from substituted diamino ketone, 3-oxoamide, malonamide, uracil, barbituric acid). Such units are more frequent in amorphous than in crystalline regions. It is quite likely that some of them are more readily oxidized than regular monomer units. Participation of the individual irregular structures depends on the preparation conditions of the polymer, and particularly on the concentration of the catalytic components³.

Since the molecular weight and concentration of basic or acidic groups are important quantities characteristic of the given polymer, we thought it useful to elucidate the dependence of the changes in these quantities on the preparation conditions of the polymer. The changes occur even at room temperature and, therefore, also if the samples are stored as usual in a desiccator over phosphorus pentoxide, *i.e.* in dry air without cooperation of ultraviolet light. So far, the changes in the properties of polyamides have not been studied under these conditions. As a rule the changes

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in polyamides without cooperation of ultraviolet light have been investigated at temperatures above 100°C. At lower temperatures, changes in the UV spectra of hydrolytic polycaprolactam oxidized above 50°C^{5,6} have been studied. At temperatures above 90°C the formation of hydroperoxides together with changes in the IR spectra⁷ have been observed, while above 80°C structural changes have been investigated⁸.

EXPERIMENTAL

Polymers. Anionic polymers (1–8) were obtained by a technique described elsewhere⁹ (using caprolactam (crystallized five times from benzene). The hydrolytic polymer (H) was prepared from the same lactam by polymerization in the presence of aminocaproic acid (1% wt.) in a sealed ampoule, the volume of the liquid phase being equal to that of the gas phase. The conditions of polymer preparation and their characterization are given in Table I. The samples were used in the form of filings, 0.04 mm thick; after extraction with water at 20°C for 20 h (200 ml water/g) they were dried at 45°C/5 Torr for 24 h.

Polymer aging. All samples were kept in the dark at 25–30°C. One part of the samples was stored in a desiccator over phosphorus pentoxide (dry air); another part was kept over a water layer in desiccators filled with oxygen (wet oxygen); the third part was distributed into ampoules and on drying at 40°C/0.005 Torr (7 h) sealed *in vacuo* (pressure 0.005 Torr).

Analytical procedures. Intrinsic viscosities were calculated from a single determination at a concentration of 0.4 g/dl in tricresol at 25°C using Huggins' constant (k') 0.4.

The concentration of basic groups was determined by conductometric titration in the mixture phenol–propanol (1 : 1) (ref.¹⁰). The samples (10–50 mg) were dissolved at 60°C for 30 min in 15 ml of the mixture and titrated with 0.1M-HCl (aq.) on thermostating to 20°C; both dissolution and titration took place in a nitrogen atmosphere. The blank test of the titration medium (0.02–0.06 μmol/15 ml) was 10% at utmost of the amount of bases found.

The concentration of acidic groups was determined by conductometric titration with 0.1M sodium propoxide (in propanol)¹⁰. The polymers (10–30 mg) were dissolved at 150°C for 5 min in 10.4 ml of benzyl alcohol; the solution was then cooled to 75°C, diluted with 1.6 ml of propanol and titrated at 75°C. The dissolution and titration occurred under nitrogen. The blank test of the titration medium (0.15–0.30 μmol) amounted to as much as 25% of the amount consumed in the titration of polymers. The blank tests (for the determinations of both the basic and acidic groups) were calculated from four titrations of different amounts of the standard polymer (the weighed amounts ratio being 1 : 2 : 3 : 4). The linear plot of the reagent consumed (y , mol) against the weighed amount (x , kg) was used to calculate the blank test (a , mol) from the relationship $y = a + bx$ and the concentration of the basic resp. acidic groups in the polymer (b , mol/kg).

RESULTS AND DISCUSSION

Several anionic and one hydrolytic polymer were kept for three years *in vacuo*, in dry air and in wet oxygen. One part of each sample was stored in the original unextracted form; the remaining part was extracted immediately on preparation. Since hydrolyzable structural units such as *e.g.* diacyl amine or 3-oxoamide units, may also be incorporated in anionic polymers, the samples were extracted at room

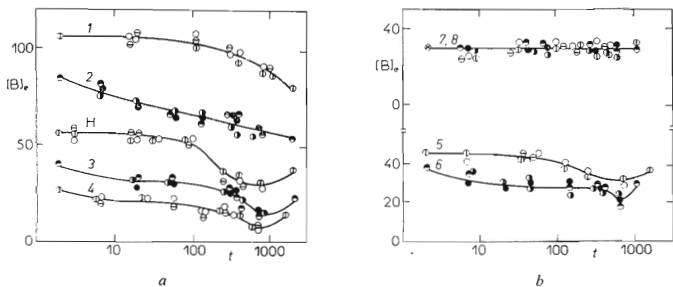


FIG. 1

Apparent Concentration of Basic Groups, $[B]_e$ (mmol/kg) in Extracted Samples 1-4 and H (a) and 5-8 (b)

Curve numbers correspond to samples of anionic polymers, H designates hydrolytic sample, t is time in days (logarithmic scale); \circ , \ominus dry air, $\omin�$, \bullet wet oxygen, \circ , \bullet vacuum (in Fig. 1b \circ , $\omin�$ and $\omin�$ refer to samples 5 and 7, \bullet , $\omin�$ and \bullet correspond to samples 6 resp. 8).

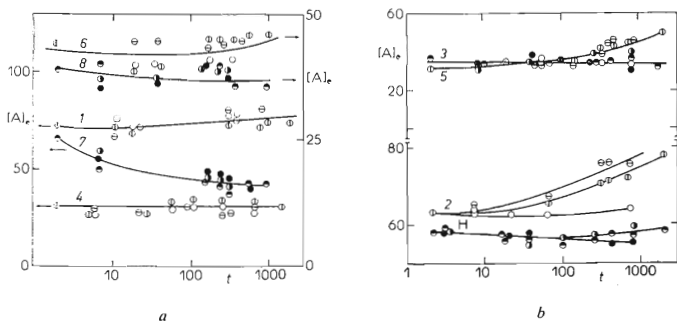


FIG. 2

Apparent Concentration of Acidic Groups, $[A]_e$ (mmol/kg), in Extracted Samples 1, 4, 6-8 (a) and 2, 3, 5, H (b)

Meaning of symbols cf. text to Fig. 1 (in Fig. 2b \circ , $\omin�$ and $\omin�$ correspond to samples 2 and 3, \bullet , $\omin�$ and \bullet correspond to samples 5 and H).

temperature to minimize the extent of their hydrolysis, if any. After some time both unextracted and extracted samples were titrated conductometrically, both acidometrically and alkalimetrically, and their intrinsic viscosity was determined.

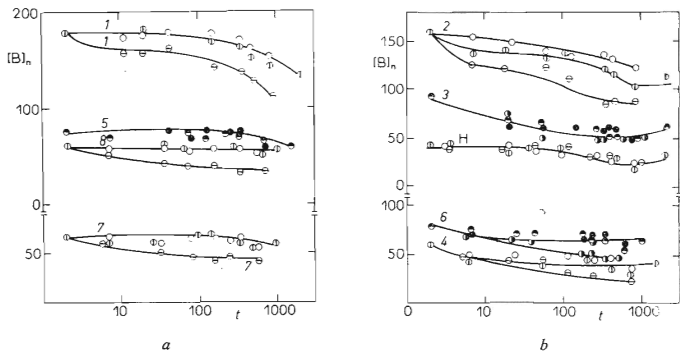


FIG. 3

Apparent Concentration of Basic Groups, $[B]_n$ (mmol/kg), in Unextracted Samples 1,5,7-8 (a) and 2-4,6,H (b)

Meaning of symbols *cf.* text to Fig. 1.

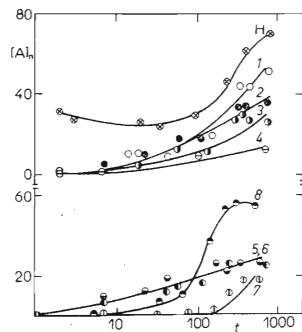


FIG. 4

Changes in the Apparent Concentration of the Acidic Groups, $[A]_n$ (mmol/kg), in Unextracted Samples 1-8 and H in Wet Oxygen

Samples: ○ 1, ● 2, ⊙ 3, ⊖ 4, ⊕ 5, ⊗ 6, ⊕ 7, ● 8, ⊗ H.

The conductometric titration in benzyl alcohol and in the mixture phenol-propanol was developed for the determination of carboxylic or amine groups respectively in hydrolytic polyamides. However, the anionic polymers of caprolactam may contain different types of acidic or basic groups which cannot be distinguished in the given medium; neither can it be said with certainty that the conductometric method used in a given medium reveals the content of all acidic and basic groups. Therefore, the

TABLE I

Preparation Conditions and Characterization of the Polymerization Products

c_i Concentration of sodium caprolactam as initiator (mmol/kg), c_a concentration of activator (mmol/kg), E water extractable fraction (% wt.), $[A]$ and $[B]$ apparent concentrations of acidic and basic groups respectively (mmol/kg), $[\eta]$ intrinsic viscosity (dl/g); indexes e and n designate data on extracted and unextracted samples, respectively.

Sample	Activator	c_a	c_i	E	$[A]_n$ $[A]_e$	$[B]_n$ $[B]_e$	$[\eta]_n$ $[\eta]_e$
1	—	—	70	8.9	0 73	178 106	0.87 0.97
2	N,N,N',N'-Tetraacetyl-hexamethylenediamine	70	70	9.5	0 46	159 85	0.68 0.74
3	N,N,N',N'-Tetraacetyl-hexamethylenediamine	70	35	9.1	0 30	92 40	0.78 0.85
4	N,N,N',N'-Tetraacetyl-hexamethylenediamine	70	28	8.7	0 31	60 27	0.82 0.87
5	N,N,N',N'-Tetraacetyl-hexamethylenediamine	35	35	8.5	0 35	75 46	0.83 0.89
6	N-Benzoylcaprolactam	35	35	8.5	0 44	79 38	1.41 1.54
7	N-Phenylcarbamoyl-caprolactam	35	35	8.5	0 66	67 29	1.61 1.76
8	N-p-Toluy-2-ethyl-3-oxohexanamide	35	35	9.3	0 39	60 29	1.22 1.31
H ^a	—	—	88	18.6	31 ^b 37 ^b	42 ^c 46 ^c	1.23 1.53

^a 6-Aminocaproic acid as initiator. ^{b,c} Concentration of ^b carboxylic groups or ^c amino groups.

consumption of acid or base during conductometric titration need not necessarily always correspond to the actual concentration of basic or acidic groups, and the concentrations thus obtained are only apparent.

The error in the determination of the apparent concentration of acidic groups in this paper was 4 mmol/kg; the determination of basic groups was subjected to an error of 2 mmol/kg. The intrinsic viscosity was determined with an accuracy of 1%.

While the apparent concentrations of the acidic ($[A]$) and basic ($[B]$) groups of extracted anionic samples stored in dry air, wet oxygen and *in vacuo* vary in the same way (Figs 1 and 2), the changes in unextracted samples (particularly of $[A]$) depend on the mode of storage (Figs 3a, 3b, 4). In none of the unextracted polymers stored *in vacuo* did titration reveal any acidic groups even after three years. If the polymers were kept in dry air, the acidic groups were formed at such a negligible rate that only after more than a thousand days low values of $[A]$ could be detected in the individual polymers (2–8 mmol/kg). However, a remarkable increase of $[A]$ was observed for unextracted samples stored in wet oxygen (Fig. 4). This increase is much higher than for extracted samples and is not accompanied by a corresponding decrease in molecular weight. Also $[B]$ is subjected to a deeper change in the case of unextracted samples than in that of extracted samples; similarly to the acidic groups, the changes in bases are not correspondingly reflected in the molecular weight. Thus, it seems evident that the reactions accompanied by changes in $[A]$ and $[B]$ occur prevalently in low-molecular weight fractions or in the monomer¹¹. Besides low-molecular weight fractions, the unextracted anionic polymers also contain a fraction of the strongly basic initiator (*i.e.* alkaline salts of lactam or amide) and the respective carbonate¹². Thus, in the presence of water there occurs alkaline hydrolysis of amide or other hydrolyzable groups (*e.g.*, imide, isocyanate and 3-oxoamide groups). The rate of acid formation in unextracted samples 1–5 (Fig. 4) is actually proportional to the residual basicity of the polymer (c_i)_r given by¹³ $(c_i)_r = c_i - 0.4c_a$, where c_i is the initiator concentration and c_a is the activator concentration in the anionic polymerization of caprolactam. It can be concluded, therefore, that in any case it is better to extract and dry the samples as soon as possible instead of keeping them in the original unextracted state.

Effect of Composition of the Anionic Catalytic System on Changes in Extracted Polymers

The extracted polymers 1–8 differed from each other as to the time variation of $[A]$ and $[B]$ (Figs 1a, 1b, 2a, 2b). The different course of $[A]$ for the hydrolytic and anionic samples indicates (Fig. 2) that acidic groups in the anionic polymers are not represented prevalently by carboxylic groups attached to a sequence of methylene groups, but that they are rather acidic products of decomposition of the catalytic polymerization components⁴. It is also possible, however, that they are in fact carboxylic groups

TABLE II

Intrinsic Viscosities (dl/g) of Unextracted and Extracted Polyamide Samples ($[\eta]_n/[\eta]_e$) after Storage in Various Media

Days	Dry air	Wet oxygen	Vacuum	Days	Dry air	Wet oxygen	Vacuum
Sample 1				Sample 6			
12	—/—	0.88/0.94	0.86/0.97	21	1.41/1.53	1.45/1.54	1.40/1.52
148	0.87/0.97	0.90/0.97	0.86/0.98	43	1.41/1.53	1.45/1.54	1.41/1.54
333	0.88/0.98	0.94/0.97	0.86/0.97	183	1.45/1.53	1.51/1.54	1.41/—
398	0.89/0.98	0.95/—	0.87/0.97	233	1.45/1.50	1.50/1.55	1.44/—
770	0.90/0.98	0.95/1.00	0.87/0.97	345	1.45/1.45	1.50/1.54	1.42/1.55
1 200	0.98/1.06	—/—	—/—	610	1.45/1.44	1.52/1.52	1.42/1.56
				1 000	1.49/1.49	—/—	—/—
Sample 2				Sample 7			
61	0.68/0.76	0.73/0.78	—/0.75	7	—/1.74	1.61/1.74	1.62/1.75
132	0.69/0.75	0.72/0.74	0.70/0.76	33	1.62/1.75	1.65/1.76	1.61/1.78
313	0.69/0.76	0.73/0.76	0.71/0.76	79	1.61/1.74	1.67/1.72	—/—
366	—/0.78	0.76/0.76	—/0.76	167	1.61/1.72	1.65/1.74	1.63/1.76
750	0.70/0.73	0.74/0.73	0.71/0.75	247	1.59/1.69	1.65/1.72	1.62/1.76
1 200	0.74/—	—/—	—/—	330	1.57/1.69	1.66/1.70	1.63/—
				600	1.52/1.64	1.59/1.68	1.65/1.75
				1 000	1.62/1.77	—/—	—/—
Sample 3				Sample 8			
54	0.74/0.85	0.78/—	0.78/0.83	7	—/1.31	1.24/1.33	1.22/1.32
134	0.80/0.86	0.81/0.85	0.78/0.86	36	1.21/1.32	1.25/1.33	1.21/1.33
294	0.78/0.87	0.82/0.86	0.78/—	67	1.21/1.32	1.25/1.32	1.21/1.31
365	0.78/—	0.82/0.83	0.79/0.87	150	1.18/1.33	1.28/1.32	1.23/1.33
450	0.79/0.86	0.83/0.85	0.80/0.87	233	1.21/1.29	1.29/1.32	1.24/1.31
720	0.79/0.86	0.82/0.86	0.80/0.87	320	1.18/1.30	1.28/1.32	1.24/1.31
1 200	0.82/0.95	—/—	—/—	585	1.20/1.29	1.28/1.33	1.24/1.34
				1 000	1.19/1.35	—/—	—/—
Sample 4				Sample H			
26	—/0.87	0.82/0.86	0.81/0.87	2	1.23/1.53	1.23/1.53	1.23/1.53
58	0.84/0.84	0.82/0.85	0.82/0.87	20	—/—	—/—	1.32/1.56
109	0.82/0.88	0.83/0.86	0.81/0.87	99	—/1.61	1.29/1.51	1.36/1.59
262	0.82/0.89	0.83/0.88	0.82/0.88	250	1.37/1.60	—/1.44	1.33/—
337	0.82/0.87	0.84/0.88	0.82/0.87	408	1.33/1.57	1.24/1.42	1.33/1.61
690	0.81/—	0.86/0.85	0.81/0.88	790	1.37/1.57	1.10/1.34	1.35/1.56
1 100	0.83/0.89	—/—	—/—	1 200	1.38/1.57	—/—	—/—
Sample 5							
40	1.06/1.13	—/—	1.06/1.13				
56	1.05/—	1.07/—	1.06/1.15				
125	1.05/1.14	1.09/—	1.03/1.14				
238	1.06/1.15	1.12/1.17	1.05/1.13				
318	1.07/1.14	1.10/1.15	1.05/1.13				
670	1.04/1.14	1.10/1.15	1.06/1.14				
1 100	1.11/1.20	—/—	—/—				

pendant on irregular structures. It can be deduced from the variation of $[B]$ that the basic groups in anionic polymers are not represented exclusively by primary amino groups¹² and that the ratio of concentrations of the individual types of bases differs for the individual polymers. As far as the changes in intrinsic viscosity are concerned, the anionic polymers are more stable than the hydrolytic polymer (Table II). The viscosity changes in the anionic polymers are always lower than changes in $[A]$ or $[B]$. This seems to indicate that labile acidic and basic groups are either end groups or groups contained in very short side chains.

The labile sites which in anionic polymers are responsible for the changes in the concentration of the acidic and basic groups are products of side reactions of the catalytic species. It is known that during the activated anionic polymerization above the melting temperature of the polymer the majority of the growth centres and strong bases decay as soon as in the first few minutes of polymerization¹³. It is also during this time that the main portion of irregular structures is formed; the formation of further irregular structures due to the strong base proceeds at a much slower rate³. The assembly of side reactions by which catalytic components are decomposed and irregular structures arise is very intricate⁴; the results obtained so far suggest that the reaction order with respect to the initiator and activator is not uniform. Thus, it may be assumed that the ratio of the individual irregular structures in a fresh polymer will depend on the initial concentrations of the initiator and activator. The $[A]$ and $[B]$ values in samples 1–8 are the higher the higher concentration of the initiator and the lower the initial activator to initiator ratio (Table I). The same proportionality is found when comparing samples 1–5 as to the rate of changes in $[A]$ and $[B]$ (Figs 1 and 2). This suggests that also the ratio of the individual basic or acidic foreign structures is strongly dependent on the ratio of the catalytic components.

The changes in $[A]$ and $[B]$ in samples 5–8 (Figs 1 and 2) indicate that the type of the polymerization activator also affects the character and number of the individual irregular structures. In this case too the main role is played by the basicity level during polymerization or further heating. Of the polymers under investigation, sample 8 seems to be the most stable one, with α -monosubstituted 3-oxoamide used as activator for its preparation. Compounds of this type are more acidic than caprolactam by several orders of magnitude, so that from the very onset of polymerization the concentration of strongly basic lactam anions is greatly reduced, which in turn reduces the extent of side reactions leading to the formation of labile (acidic or basic) groups. During three years neither $[A]$ nor $[B]$ have changed in the extracted sample 8 (Figs 1b, 2a); the intrinsic viscosity has increased by mere 5% and only toward the end of the period under investigation (Table II), regardless of the mode of storage.

While polymers obtained with activators of the acyllactam or diacylamine type behave in a similar manner (Figs 1b, 2 and Table II, samples 5 and 6), the extracted sample 7 (obtained with N-phenylcarbonylcaprolactam as activator) differs from all the other polymers by a comparatively fast decrease in $[A]$ during the first year

without, however, this fast rate being affected by the mode of storage of the polymer (Fig. 2a). In contrast with all the other unextracted polymers (Fig. 4), the apparent concentration of acidic groups in unextracted sample 7 was increasing at the lowest rate probably because the fast decrease in the acidic groups in the polymer (Fig. 2a) compensated for the similarly fast formation of these groups in the low-molecular weight fraction. The value of $[B]$ in extracted polymer 7 was constant over the whole time interval similarly to sample 8 (Fig. 1b). This seems to indicate that the ratio of various types of basic groups in these polymers is different from the ratio of the individual bases in polymers obtained with activators of the imide type.

It is interesting that in most of the extracted polymers the value of $[B]$ varied also *in vacuo*. So far, the loss of basic groups in an inert atmosphere has been observed only at higher temperatures^{11,14}.

Hydrolytic Polymer

The molecule of a nonstabilized hydrolytic polycaprolactam should consist of units of one kind and should be terminated by amino- and carboxy groups. Such polymer, free from irregular structures, could be more stable at room temperature than anionic polymers with irregular units, so that it could be used as a reference standard. It appears, however, that even in the absence of oxygen reactions take place in the hydrolytic polymer which cause changes in the concentration of the end groups (Figs 1a and 2b) and of the degree of polymerization (Table II), both in the extracted and in the unextracted polymer (Figs 3b and 4). The hydrolytic polymer is even less stable as compared to some anionic polymers. The initial extracted polymer itself contains less acids than bases, the acid content being lower than would correspond to the chain number calculated from the viscometric data; obviously, one part of the acids have vanished during polymerization. Both acid and base contents first decrease with time; the decrease of bases lasts longer.

In contrast with anionic polymers the changes of the end groups of the hydrolytic polymer correspond to the changes in the molecular weight (Table II, Figs 1a and 2b). The initial increase in molecular weight, particularly *in vacuo*, may be assigned to the condensation reactions of the amino and carboxy groups. Further on, in the presence of oxygen, the acid and base contents increase and their numbers approach each other (Fig. 1a and 2b).

It follows from the results described here that none of the caprolactam polymers is stable enough during storage to be used in a long run as a reference sample for the determination of the end groups or of the degree of polymerization.

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