Molecular weight distribution of polycaprolactam, anionically synthesized in presence of lithium chloride

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Samples of polycaprolactam, obtained by anionic polymerization of caprolactam in bulk under adiabatic conditions and in presence of different amounts of lithium chloride, have been fractionated using a method based on summative fractionation of the polyamide in the amorphous state. By increasing the amount of lithium chloride in the system, the limiting viscosity number of the as-polymerized material decreases; at the same time the integral distribution curves reveal a bimodal molecular weight distribution as a consequence of the complex pattern of main and side reactions. The high molecular weight peak is very narrow, both with and without lithium chloride in the polymerizing system. Lithium chloride considerably reduces the polydispersity of the low molecular weight portion, which is very broad for the non-salt treated polycaprolactam. The relative importance of the two peaks, which is almost even for polycaprolactam synthesized without salt, is shifted in favour of the lower molecular weight peak by increasing the salt content. This effect is also accompanied by a higher production of water-soluble oligomers.

INTRODUCTION

In the past few years studies on the synthesis and properties of ion-containing polymers have experienced a continuous growth of interest both at academic and industrial level[1]. Our research has been focused on the preparation of aliphatic polyamides modified by addition of lithium salts, which are dissolved in the polymer matrix and ionically bonded to the polar groups of the polyamide. Ciferri *et al.* has found that *salt-modified* polyamides show an enhancement of many physical properties, such as a higher Young's modulus[2], lower melting temperature[3], reduced crystallization rate[4], and higher melt viscosity[5]. The specific interactions between lithium ions and the polar groups of the polyamides are responsible for the above modifications of polymer properties. The possibility of polymerizing lactams in the presence of lithium salts has been attempted in order to obtain homogeneous distribution of the ions in the polymer matrix.

Preliminary data on the anionic polymerization of caprolactam in the presence of lithium chloride have been recently reported[6], and a detailed description of the role of lithium salts on kinetics and mechanism of the activated caprolactam polymerization will be described elsewhere[7]. We present here our data on molecular weights (*MW*) and their distributions (*MWD*) for polycaprolactam (*PCL*), anionically synthesized in presence of lithium chloride.

Compared to the large number of papers devoted to *MWD* of hydrolytically polymerized caprolactam, relatively few studies on *MWD* of anionically synthesized PCL have been published so far[8–16].

In the non-activated anionic polymerization the *MWD* is very broad[8–11] as a result of the continuous increase of *MW* during polymerization. In fact, the polymer chains initiated at the early stages of polymerization can grow much longer than those initiated at very high conversion. Further on, *side* reactions, such as depolymerization, disproportionation and transacylation, become increasingly important and cause a decrease of *MW* as well as a narrowing of *MWD*, which approaches the statistical one[8,9].

In the activated polymerization of caprolactam, *MW* and *MWD* are complex functions of the reaction conditions such as the polymerization temperature (below or above the polymer melting point), the concentration of the catalytic species, the activator to initiator ratio[8,12–16]. At temperatures below the polymer m.p. the *MWD* seems to be rather narrow[13] because of the crystallization of the polyamide, which largely reduces polymer–polymer exchange reactions, depolymerization and disproportionation.

EXPERIMENTAL SECTION

Our polymer samples have been synthesized by anionic polymerization of caprolactam in bulk, under anhydrous conditions, at the initial polymerization temperature of 154°C. First, known amounts of lithium chloride are mixed with the solid monomer at room temperature, warmed up and readily dissolved in the melt at 120°C. Then lithium metal is added and the initiator (lithium caprolactamate, 0.5 mole %) obtained *in situ*[6]. The activator (N-acetyl caprolactam, 0.5 mole %) is added at 154°C. The polymerization runs are performed under adiabatic conditions and the equilibrium

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Table 1 Limiting viscosity number (cm^3/g) of the fractionated polycaprolactam

LiCl, 0%		LiCl, 1.32% w/w		LiCl, 2.44% w/w		LiCl, 3.55% w/w		LiCl, 11.99% w/w	
$C(M)$	$[\eta]^*$	$C(M)$	$[\eta]^*$	$C(M)$	$[\eta]^*$	$C(M)$	$[\eta]^*$	$C(M)$	$[\eta]^*$
0.050	39	0.085	92	0.102	59	0.090	56	0.140	62
0.132	93	0.194	116	0.268	119	0.245	99	0.306	73
0.217	153	0.258	129	0.354	143	0.334	126	0.363	83
0.326	190	0.323	137	0.433	156	0.415	142	0.455	94
0.455	210	0.388	145	0.539	182	0.495	161	0.579	109
0.569	266	0.461	172	0.633	196	0.598	185	0.661	130
0.651	282	0.537	187	0.729	206	0.716	194	0.745	143
0.755	292	0.633	197	0.832	213	0.780	197	0.845	148
0.900	320	0.741	205	0.927	224	0.860	209	0.923	160
0.990	346	0.857	224	0.985	232	0.961	223	0.985	175
		0.960	239						
1	212		168		155		149		106
$\Sigma_i W_i[\eta]_i$	217		168		156		149		105

conversion is achieved within few minutes. The final temperature is between 180° and 205°C. The polymer is freed of monomer, oligomers, initiator residues and lithium chloride by extraction with boiling water (4 h). The lithium chloride content is determined by argentometric titration (Mohr method).

The fractionation of PCL is performed by using, with minor modifications, the method recently adopted by Bianchi[17] and based on summative fractionation[18] of the polyamide in the amorphous state[19].

As compared to the other fractionation methods usually employed for polycaprolactam, such as fractional dissolution[13], turbidimetry[8,9,11], coacervation[20,21], the proposed summative fractionation has the advantage of being very rapid, unexpensive and reliable. The polymer in the amorphous state is obtained by dissolution of the polycaprolactam in formic acid (85% in water, v/v) and addition of lithium chloride to the solution. The polymer concentration is about 3%, w/v, and the salt to polymer ratio is 2.5. The phase separation is performed at 18° ± 0.1°C by dropwise addition of water containing lithium chloride (7.5% by weight), followed by centrifugation, filtration and drying.

Each summative fraction is characterized by viscometry in *m*-cresol at 25°C. In all cases the viscosity number data show a straight line dependence on dilution. For the correlation parameters between $[\eta]$ and M we used the values given by Tuzar *et al.*[22] ($K = 5.26 \times 10^{-2}$ cm^3/g; $a = 0.745$).

In order to evaluate the limiting viscosity number of each fraction from the summative fraction data the following relationships are assumed:

$$W_i = F(M)_i - F(M)_{i-1}$$

$$[\eta]_i = \frac{F(M)_{i-1}}{F(M)_i}[\eta]_{i-1} + \frac{W_i}{F(M)_i}[\eta]_i^*$$

where $F(M)_{i-1}$ and $F(M)_i$ are the summative weight fractions of the precipitate characterized by $[\eta]_{i-1}$ and $[\eta]_i$, respectively; W_i is the fraction of precipitated molecules by the i-th addition of the non solvent; $[\eta]_i^*$ is the calculated limiting viscosity number of the corresponding fraction.

After determination of each W_i and related $[\eta]_i^*$ a check can easily be done on the basis of the following relationship:

$$\sum_{i=1}^{n} W_i[\eta]_i^* = [\eta]_{F(M)=1}$$

where $[\eta]_{F(M)=1}$ corresponds to the limiting viscosity number of the original, unfractionated sample.

By using the well-known method of Schulz *et al.*[23], based on the equation:

$$C(M)_n = \frac{1}{2}W_n + \sum_{m=1}^{n-1} W_m$$

the integral distribution curves (*IDC*) are calculated.

RESULTS AND DISCUSSION

The cumulative weight fractions $C(M)$ and the corresponding $[\eta]^*$ values for five polycaprolactam samples, synthesized in presence of different amounts of LiCl, are given in *Table 1*.

The excellent agreement between the limiting viscosity number of the unfractionated samples and the value obtained from the summative fractionation experiments is evidenced by the data of the last two lines of *Table 1*. Furthermore, we can assume that no appreciable degradation or modification of the polymer chain length occurs during the fractionation runs. It is also evident that the presence of LiCl in the polymerizing system causes a decrease of $[\eta]$, i.e. of the polymer molecular weight. The dependence of $[\eta]$ on LiCl content is given in *Figure 1*.

The integral distribution curves of our polycaprolactam samples as functions of the molecular weight of each fraction are plotted in *Figure 2*. The shape of the curves reveals a bimodal *MWD* for all samples. Bimodal distribution for anionic polycaprolactam has already been found, but only at polymerization temperatures higher than the polymer melting point and for relatively short polymerization times. For longer times the inflection point in the integral distribution curve disappears, in connection with a remarkable shift toward lower molecular weights[16].

The *MWD* of anionic PCL synthesized at low temperature, i.e. below the polymer melting point, is claimed to be

very narrow[13]. In our opinion, however, a careful inspection of those data suggests the presence of inflection points in the integral distribution curves.

From our data, it seems reasonable to attribute the bimodal behaviour of the IDC to the complex pattern of main and side reactions which take part in the course of the anionic polymerization. The most relevant side reactions responsible for the bimodal *MWD* are Claisen-type condensation reactions, which are very likely to occur in the early stages of the polymerization, i.e. when the reaction system is markedly basic. We can reasonably exclude any significant contribution of branching to the bimodal behaviour of our fractionation data. From the work of Pavlova *et al.*[24], it seems that monofunctional activators, such as N-acetyl caprolactam, minimize the extent of the branching reactions.

Various methods of analysis of the fractionation data have been proposed so far. Analytical functions of two or more parameters, based either on polymerization kinetics or empirical fitting of the data, are widely used. Due to the complexity of the kinetic scheme for our polymerizing system, we have adopted an empirical approach.

Integral and differential distribution curves and *MWD* indices have been evaluated by using Tung's method[25], where:

$$I(M) = 1 - e^{-aM^b}$$

$$W(M) = \frac{d}{dM}[I(M)] = ab\,M^{b-1}\,e^{-aM^b} = abM^{b-1}[1 - I(M)]$$

with:

$I(M)$ = Integral *MW* distribution function, which can be identified with $C(M)$
$W(M)$ = differential distribution function
M = molecular weight of the fraction
a,b = constants

a and b are evaluated from the log [log $1/1 - C(M)$] vs. log$M$ plot, b being the slope and log (a log e) the intercept of the straight line. For a bimodal distribution two distinct lines are obtained, each characterized by a specific set of a and b values[25].

As an example the log–log plots relative to some of our fractionation experiments are reported in *Figure 3* and clearly confirm the bimodal *MW* distribution.

From the calculated values of a and b, reported in *Table 2*, integral and differential curves have been obtained, as shown in *Figures 4* and *5*, respectively.

The b value is related to the polydispersity ratio Q by the following relationship:

$$Q = \frac{\bar{M}_w}{\bar{M}_n} = \Gamma\left(1 + \frac{1}{b}\right) \cdot \Gamma\left(1 - \frac{1}{b}\right) = \frac{\pi/b}{\mathrm{Sin}(\pi/b)}$$

where $\Gamma(\,)$ is the Gamma function. Q values are given in *Figure 5*.

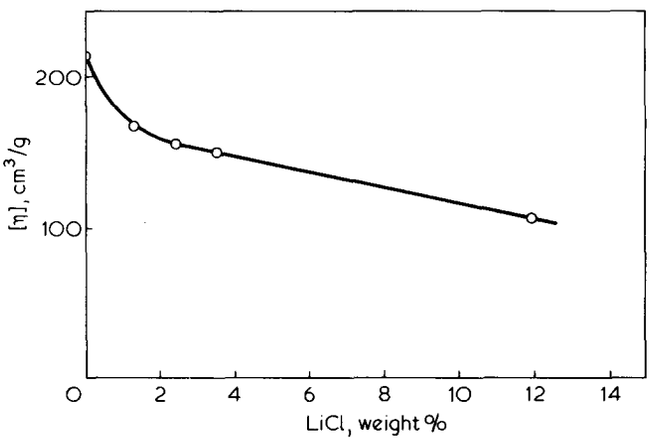

Figure 1 The effect of LiCl content of the polymerizing mixture on the limiting viscosity number of polycaprolactam

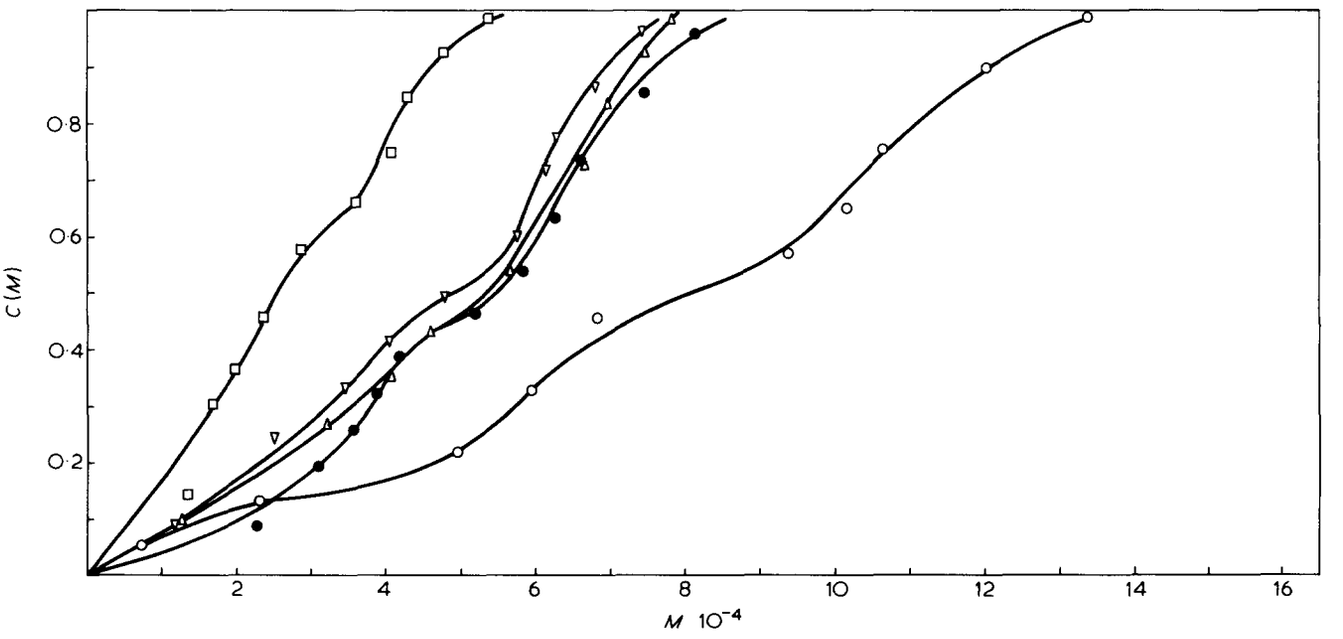

Figure 2 Cumulative weight fraction of polycaprolactam samples, synthesized in presence of different amounts of LiCl, as a function of molecular weight (○ = 0%; ● = 1.32%; △ = 2.44%; ▽ = 3.55%; □ = 11.99 weight % LiCl)

Obviously, the polydispersity indices evaluated on the basis of the above equation implicitly involve extrapolation beyond the actual regions of the experimental data points, i.e. they imply integration over M values between 0 and ∞. Therefore, they cannot be compared with indices obtained from direct summation of the experimental values.

From the data of *Figure 5* it appears that the anionic polycaprolactam synthesized in the absence of lithium chloride shows a bimodal distribution, with a very broad low MW peak ($Q \sim 40$) and a very narrow high MW peak ($Q \sim 1.1$).

The addition of lithium chloride does not appreciably affect the distribution of the higher molecular weights which remains quite narrow, but considerably reduces the polydispersity of the low molecular weight portion. However, the relative importance of the two peaks (see *Figure 4*), is shifted in favour of the lower MW peak by increasing LiCl content. This effect is also accompanied by a higher production of water-soluble oligomers, as shown in *Table 3*. A detailed study on the effect of lithium chloride on oligomer production is in progress[26].

Of course, it is hard to distinguish in the MWD curves the true fractionation based on the differences in the chain length from the spurious contributions related to inhomogeneity of the chemical structure and/or branching. However, from the trend of the Q values we may suggest that the very narrow high MW peak corresponds to the pure propagation process, which is of the 'living polymer' type. Side reactions are responsible for the low MW peak formation and bimodality. A fraction of the high molecular weight chains is involved in these side reactions, which cause polymer degradation and chemical irregularities, show autocatalytic character and strongly reduce the polymer chain length.

LiCl apparently enhances the polymer degradation through a complex mechanism which is at present under investigation. A relevant contribution, however, should be related to the lower extent of crystallinity caused by the salt addition. The higher mobility of the polymer chains (in the amorphous regions) contributes significantly to the side reactions.

The bimodal behaviour of the distribution curves for PCL synthesized at temperatures higher than the polymer m.p. has been attributed by Roda *et al.*[11] to Claisen-type condensations. Similar interpretations can be proposed for our low-temperature polymerization system. Following Roda's findings[11], we are synthesizing PCL with an activator to initiator concentration ratio of 3. This would balance the pre-

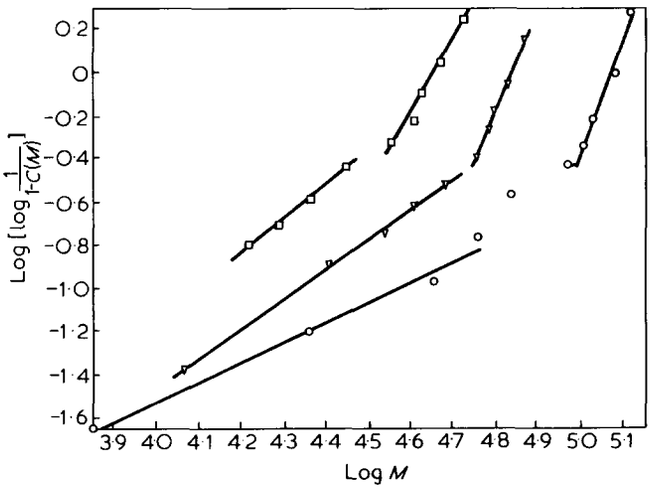

Figure 3 log[log(1/1−$C(M)$)] vs. log M plot according to Tung's method[25], (symbols as in *Figure 2*)

Table 2 Parameters of Tung's equation[25]

LiCl weight %	Low MW peak		High MW peak	
	a	*b*	*a*	*b*
0	1.39×10^{-5}	1.02	9.68×10^{-25}	4.81
1.32	7.98×10^{-14}	2.77	6.10×10^{-21}	4.22
2.44	1.58×10^{-8}	1.62	8.88×10^{-31}	6.26
3.55	2.25×10^{-7}	1.38	3.43×10^{-24}	4.92
11.99	5.01×10^{-8}	1.62	5.55×10^{-16}	3.35

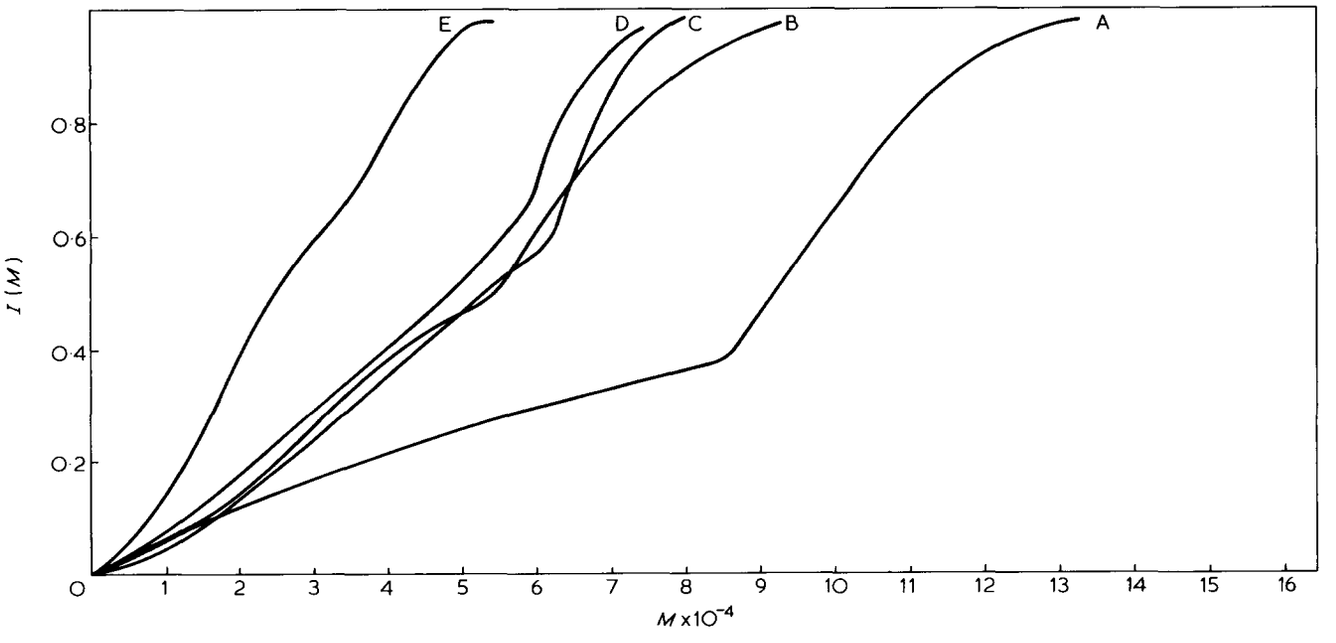

Figure 4 Integral distribution curves of polycaprolactam samples synthesized in presence of different amounts of LiCl (weight %). A: 0; B, 1.32; C, 2.44; D, 3.55; E, 11.99%

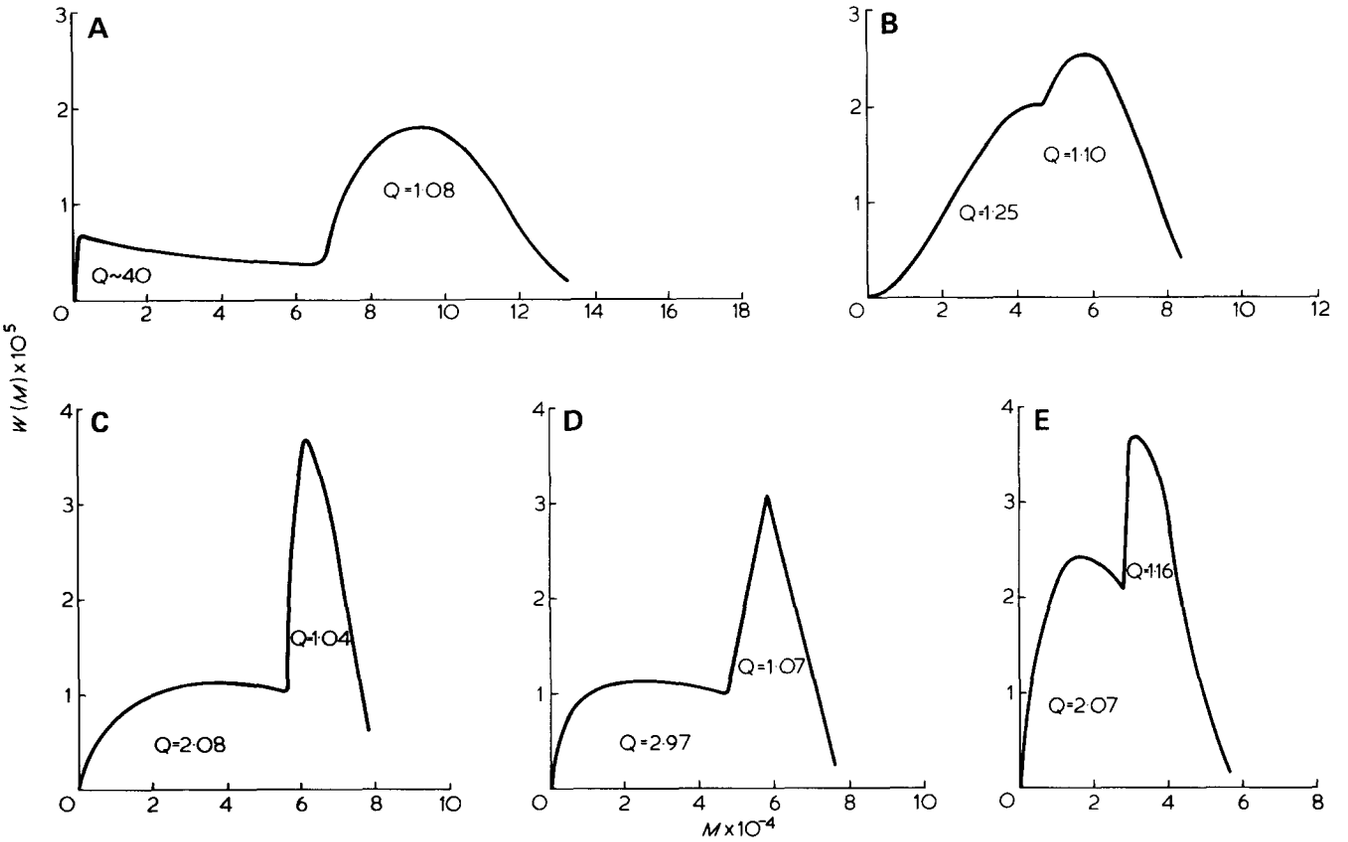

Figure 5 Differential distribution curves of polycaprolactam samples, synthesized in presence of different amounts of LiCl (weight %)

Table 3 Water-soluble oligomers present in polycaprolactam samples, synthesized in presence of different amounts of LiCl

LiCl weight %	Oligomers weight %
0	1.36
1.32	3.54
2.44	5.82
3.55	7.70
11.99	–

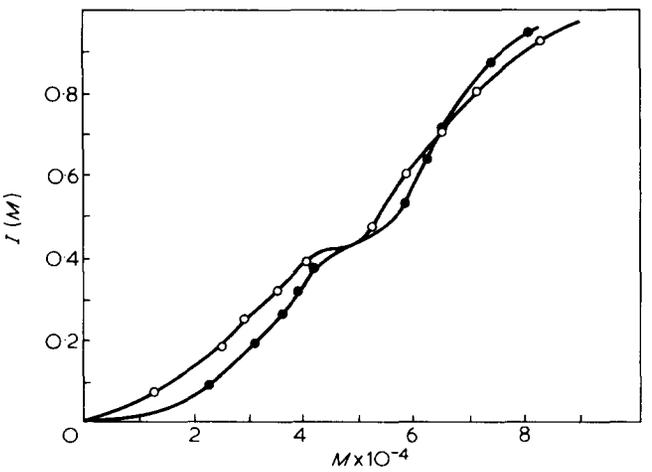

Figure 6 Integral distribution curves of polycaprolactam synthesized in presence of 1.32 weight % LiCl. (open circles = $C(M)$ from fractional precipitation; full circles = $C(M)$ from summative fractionation)

ferred consumption of activator and eliminate the residual basicity of the system. Data on *MWD* for this polymer are in progress and will be related to relevant information from kinetic data (rate of polymerization, equilibrium conversion, heat of polymerization, etc.).

LiCl also controls molecular weights of PCL. Both peaks are displaced toward lower *MW*s by increasing the amount of the salt. The higher oligomer production parallels this behaviour and fully accounts for the *apparent* increase of the low *MW* peak from the unsalted PCL to the salted ones.

In order to verify the validity of the summative fractionation method, we have performed a fractional precipitation on one of our samples. The solvent–precipitant pair has been the same as for the summative fractionation runs.

In *Figure 6* the integral distribution curve evaluated from fractional precipitation data (open circles) is compared to the full circles corresponding to the summative fractionation method.

A full confirmation of the bimodal *MW* distribution is evident. The agreement between the two methods is excellent in the higher *MW* portion of the curve, whereas remarkable deviations are present at lower molecular weights, with higher *MW* values when the summative fractionation method has been employed.

In our opinion this difference can be due to some degradation of the polymer, which remains for about two weeks in formic acid solutions, as required by the lengthy method of fractional precipitation. In this case, indeed, $\Sigma W_i[\eta]_i$ gives a value of 1.61, whereas $\Sigma W_i[\eta]_i^*$ from the summative fractionation gives 1.68, i.e. the same value as for the unfractionated sample. Obviously, the degradation affects to a greater extent the lower molecular weights, which stay in the acidic solution for a longer time.

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