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SOME SOLUTION PROPERTIES OF POLYESTERAMIDE 6NT6

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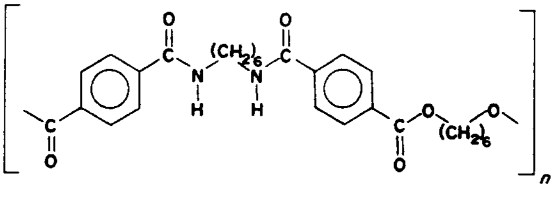
Abstract—The relationship between intrinsic viscosity and weight average molecular weight for an alternating polyesteramide of the type 6NT6 is reported. Weight average molecular weights were calculated by a trial and error method using osmotic pressure molecular weights and gel permeation chromatograms of polydispersed samples corrected for axial diffusion. Polydispersities of unfractioned samples are quoted. The unperturbed dimensions $(\langle \bar{r} \rangle_0^2/M)^{1/2}$ were derived by the method of Stockmayer–Fixman and the characteristic ratio C_∞ was obtained from experimental data.

INTRODUCTION

Polyesteramide 6NT6 (PEA) is a crystalline copolymer, substantially alternating, obtained by polycondensation some years ago in our laboratories [1]. The formula of the PEA is:



where n is the degree of polymerization. This polymer has a high melting point, is soluble in some protic liquid only, and shows interesting technological properties as a fibre [1, 2]. A previous paper [3] described some process parameters of polycondensation kinetics which optimize reaction conditions and product properties. This paper reports some solution properties of PEA obtained by viscometry, osmometry and GPC.

EXPERIMENTAL

(a) *Materials*

Samples of PEA were prepared by methods previously reported [1, 3]. Seventeen fractions were obtained by fractional precipitation from a dilute (1%) solution at 20° using *m*-cresol/*n*-heptane as the solvent/non-solvent pair.

(b) *Osmometry, viscometry and gel permeation chromatography (GPC)*

Osmotic pressures of *m*-cresol solutions at 70° were measured with a Mechrolab 502 Osmometer with S. & S. 08 membranes and the average molecular weight $\bar{M}_{osm}$ was determined by extrapolation to zero concentration. Intrinsic viscosities were determined from measurements on phenol-tetrachloroethane (50/50 by weight) solutions at 25° using Ubbelohde viscometers. All experimental results were evaluated by the least squares method. GPC measurements were obtained with a Waters apparatus Model 200 having four columns with nominal pore sizes from 10^2 to 10^5 Å. Elutions were performed with freshly distilled *m*-cresol at 115° at a flow rate of 1 cm³/min. The polymer concentration was 0.5 g/dl. The observed chromatograms, $F(v)$, were corrected for instrumental spreading in order to obtain the true distribution functions, $W(v)$, using the method suggested by Pierce and Armonas [4].

Axial diffusion coefficients, h, of our own GPC, as a function of elution volume, were evaluated using monodisperse Waters polystyrene samples as standards, and calculated by the method suggested by Balke and Hamielec [5]. The value of h was constant for the whole elution volume range of interest and was equal to 1 $(\text{count})^{-2}$. Number- and weight-average molecular weights and the polydispersity index, $\bar{M}_w/\bar{M}_n$, of each PEA sample were computed from $W(v)$ by means of a linear calibration curve which previously had been found by a trial and error numerical method which minimized the difference between experimental [6] ($\bar{M}_{osm}$) and calculated ($\bar{M}_n$) average molecular weights.

(c) *Differential scanning calorimetry (DSC)*

DSC measurements were performed with a Du Pont 900 thermal analyzer using a heating rate of 10°/min.

RESULTS AND DISCUSSION

Unfractionated and fractionated samples of PEA with a wide range of molecular weight have been characterized by viscometry, osmometry and GPC. Intrinsic viscosities, $\bar{M}_{osm}$, $\bar{M}_w$, and polydispersity indices determined by the above mentioned techniques are reported in Table 1. In Fig. 1, the relationships between $[\eta]$, $\bar{M}_{osm}$ and $\bar{M}_w$ are plotted. The differences among the three lines are due to different degrees of polydispersity in the samples. In fact, as is well known [7], the values of Mark–Houwink constants (K and α) depend on the degree of polydispersity in the samples. In order to obtain the true $[\eta]/\bar{M}_v$ relationship, use has been made of $\bar{M}_w$ because it is closer to the viscometric average, $\bar{M}_v$, as α approaches to 1. The relationship between $[\eta]$ and $\bar{M}_w$ is:

$$[\eta] = 3.64 \times 10^{-4} \bar{M}_w 0.75 \, (\text{dl/g})$$

from which $\bar{M}_v$ for PEA may be obtained for the molecular weight range 10^4 to 8×10^4. The fractions considered in Table 2 and Fig. 1 show an average polydispersity ratio $\bar{M}_w/\bar{M}_n \simeq \bar{M}_v/\bar{M}_{osm}$ of 1.7. Their melting points and melting heats (T_m and ΔH_m) are in the same range as those of parent polymer. The higher values of the second virial coefficient, A_2, (Tables 1 and 2) indicate that *m*-cresol at 70° is a "good" solvent for PEA which behaves as a flexible macromolecule. The validity of the trial and error method used to obtain the GPC calibration curve

Table 1. Solution properties of some unfractioned PEA samples

Sample	$[\eta]$ (dl/g)	$\bar{M}_{osm}$	$A_2 \cdot 10^3$ (ml mol/g^2)	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$	$\bar{M}_{osm}\ \bar{M}_n/\bar{M}_{osm}$ (%)
A	1.84	32100	3.7	—	—	—
B	1.59	24100	3.8	3.1	73800	0.0
C	1.52	25800	3.2	2.5	70800	8.6
5*	1.46	35500	4.2	2.1	65000	−9.8
D	1.22	18000	2.3	2.3	42600	4.3
E	1.10	16500	2.1	2.7	43100	−5.9
F	0.75	11700	4.1	2.9	26400	−18.9
G	0.72	10000	1.8	2.5	27000	6.9
H	0.52	7000	1.4	2.3	16400	0.0

* is a fraction of sample D.

Table 2. Some solution and bulk parameters characterizing polymer D and some of its fractions

Fraction	% Weight	$[\eta]$ (dl/g)	$\bar{M}_{osm}$	$A_2 \cdot 10^3$ (ml mol/g^2)	$\bar{M}_v/\bar{M}_{osm}$	T_m C	ΔH_m (cal/g)
D	100	1.22	18000	2.3	2.8	261	16
2	3.5	1.64	45800	4.2	1.6	259	15.5
3	3.5	1.60	—	—	—	258	15
5	6.0	1.46	35500	3.9	2.1	260	15
7	4.7	1.34	33500	3.4	1.7	260	14.5
12	4.6	1.14	26200	3.7	1.8	260	15.5
15	4.4	0.95	22900	4.0	1.5	259	15.5

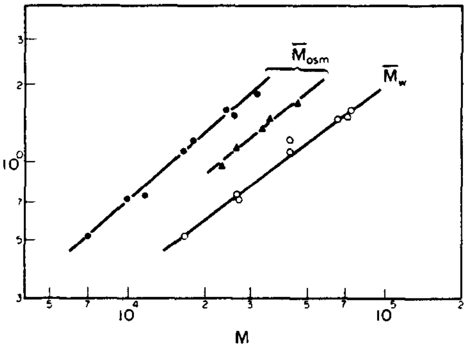


Fig. 1. Relation between $[\eta]$ and $\bar{M}_w$ for unfractioned samples (● osm $\bar{M}_w$, ○ weight average $\bar{M}_w$) and for some fractions (▲ osm $\bar{M}_w$).

from nine pairs of $W(v)$ and $\bar{M}_{osm}$ is shown at the right of Table 1 in which the error between the experimental $\bar{M}_{osm}$ and the calculated $\bar{M}_n$ is normally less than 10%. This method is substantially an extension of that of Balke [6] to polymers showing a fairly narrow distribution and requiring a correction of GPC chromatograms for instrument spreading.

Polydispersities quoted in Table 1 for unfractionated PEA exceed 2, the value usually observed for polycondensation polymers. These higher polydispersities are related to a slight broadening of the distributions towards the low molecular weights. Unperturbed chain dimensions $(\langle r^{-2}\rangle_0/M)^{1/2}$ and the corresponding characteristic ratio C_∞ [8] have been obtained by $K_\theta = 2.5 \times 10^{-3}$, which has been derived from $[\eta]$ and $\bar{M}_w$ data by the procedure of Stockmayer and Fixman [9]. They have been corrected for polydispersity by assuming a Schulz distribution function, taking the average $\bar{M}_w/\bar{M}_n$ value of 2.5 and ϕ_0 value of 2.6×10^{21}. Unperturbed chain dimensions $(\langle r^{-2}\rangle_0/M)^{1/2} = (K_\theta/\phi_0)^{1/3} q_w^{-1/3}$ were found equal to 1.00 Å $(\mathrm{g\,mol})^{-1/2}$ and C_∞ was equal to 4.76. This comparatively low value of C_∞ indicates fair chain flexibility for PEA such as that reported for polyamide 6.6 and polyethyleneterephtalate [8].

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