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A NOTE ON THE CHARACTERISTIC RATIO, C_∞, OF POLYMER CHAINS CONTAINING BENZENE RINGS AS MAIN-CHAIN SEGMENTS

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Abstract—A change of the spatial configuration of linear polymer chains brought about by benzene rings incorporated into chains of polyesters, polyamides and polyurethanes has been investigated. It is shown that the characteristic ratio, C_∞, of unperturbed dimensions is a decreasing function of the frequency of occurrence of the rings. An interpretation in terms of an increased rotational freedom conferred on nearby bonds by the rings is proposed.

INTRODUCTION

It has been found theoretically [1] that, due to their partial double bond character, the CO—NH and CO—O groups have an extended and rigid conformation so that, if incorporated into a polymethylene chain (as in polyesters and polyamides), they exert two opposing effects on the spatial configuration of the chain. Owing to their length and stiffness, they make the chain more extended (effect **I**). At the same time, however, they reduce the hindrance to rotation about the nearby bonds (effect **II**). As the latter effect predominates, the net result is a decrease in the characteristic ratio, C_∞, of unperturbed dimensions. Experimental data [2, 3] corroborate the prediction.

Aromatic rings are planar, rigid and more extended than the CO—NH and CO—O bonds and, therefore, they can be expected to have an effect which is qualitatively similar but quantitatively different. No theoretical treatment of the effect has been reported, except for poly(ethylene terephthalate) [1], so that an empirical analysis of the C_∞ values of aromatic polyesters, polyamides and polyurethanes presented here can provide the first guideline.

RESULTS AND DISCUSSION

The characteristic ratio, C_∞, is the ratio (in the limit of a high number of main-chain bonds) of the mean square end-to-end distance, $\overline{R_0^2}$, of the real chain and the corresponding quantity, $n\overline{l^2}$, calculated for a freely jointed chain having the same number of main-chain bonds, n, of a mean-square length, $\overline{l^2}$:

$$C_\infty = \lim_{n\to\infty} (\overline{R_0^2}/n\overline{l^2}) \qquad (1)$$

Both chains are assumed to be unperturbed by the excluded-volume effect. The product $n\overline{l^2}$ represents the value which $\overline{R_0^2}$ would assume in the absence of correlations between bond directions [1].

The characteristic ratio is calculated from experimental values of $(\overline{R_0^2}/M)_\infty$ by means of the equation

$$C_\infty = (\overline{R_0^2}/M)_\infty (M_b/\overline{l^2}) \qquad (2)$$

where M is the molecular weight of the chain and M_b is the mean molecular weight per skeletal bond. If various bonds of the chain differ in length, $\overline{l^2}$ represents the mean-square length of the skeletal bonds.

The values of $(\overline{R_0^2}/M)_\infty$ for polymers investigated here have been collected from the literature [3–13] and are listed in Table 1. The values of $M_b/\overline{l^2}$ were calculated taking into account the respective structure of the chain repeating unit (cf. Table 1) with the following values of bond length (expressed in nm): $l_{CH_2-CH_2} = 0.15$, $l_{CH_2-O} = 0.144$, $l_{CH_2-CO} = 0.151$, $l_{CO-O} = 0.133$, $l_{CO-NH} = 0.133$, $l_{CH_2-HN} = 0.146$ [1]. Because of their rigidity, the segments CO—Ph—CO, NH—Ph—NH, Co—Ph—O (where Ph stands for the *p*-phenylene group) were replaced by "virtual bonds" of length $l = 0.57$ nm (cf. [1]).

The characteristic ratio for the polymethylene chain at 25° was calculated from the value $C_\infty^{140} = 6.7$ [1] at 140° according to the equation

$$\ln C_\infty^{25} = \ln C_\infty^{140} + 115(\mathrm{d}\ln C_\infty/\mathrm{d}T) \qquad (3)$$

where $(\mathrm{d}\ln C_\infty/\mathrm{d}T) = -1.1 \times 10^{-3}$ [1].

The results of calculations, collected in Table 1, show that the C_∞ values for all polymers investigated here are lower than for polymethylene ($C_\infty^{25} = 7.6$). In Fig. 1a they are plotted against p defined as the fraction of bonds which, because of their length and/or stiffness, are expected to participate in the above effects **I** and **II**,

$$p = (n_1 + n_2)/S \qquad (4)$$

Here, S is the total number of skeletal bonds, n_1 is the number of "virtual" bonds associated with the benzene ring, and n_2 is the number of the CO—NH and/or CO—O bonds. All numbers refer to the chain repeating unit.

In calculating n_2, we face the problem of the conformation of the groups NH—CO—O and NH—CO—NH in polyurethane chains. Both CO—NH and CO—O have a partial double bond character so that, formally, the NH—CO—NH or NH—CO—O groups should be equivalent to two partial double bonds. We feel this is not very proba-

Table 1. Characteristics of polymers

Polymers*	$(\overline{R_0^2}/M)_\infty$ (nm^2)	$(M_b/l^2$ (nm^{-2})	C_∞	P	Type of segments†
Derivatives of terephthalic acid					
PET	0.91^{5,6}	446	4.05	0.43	
PBT	1.01^{5}	461	4.66	0.27	
PEA	1.00^{4,7,8}	471	4.71	0.30	
Trogamid T^{R}	0.85^{4}	550	4.67	0.30	
Polyester of p-*hydroxybenzoic acid*					
PEE	1.02^{4,9}	412	4.21	0.40	
Polyurethanes†, type $[A\text{-}\beta_m\text{-}C_n]$					
TPUR I	0.84^{3}	516	4.35	0.35	B1, C1, $m = 7$, $n = 2.9$
TPUR II	0.95^{3}	543	5.16	0.25	B1, C1, $m = 10$, $n = 3.1$
PUS	0.84^{3}	509	4.27	0.30	B2, C1, $m = 11.6$, $n = 7$
PUK	1.00^{3}	520	5.20	0.23	B3, C1, $m = 17.5$, $n = 5$
UB	0.92^{3,10}	525	4.83	0.20	B3, C2, $m = 11.4$, $n = 1$
UC	0.84^{3,10}	624	5.24	0.17	B3, C2, $m = 24.6$, $n = 1$
S	0.77^{11}	526	0.04	0.22	B3, C3, $m = 17.9$, $n = 5$
Polyurethanes†, type $[A\text{-}D(\text{k})]$					
PU-1	1.05^{3,12}	401	4.20	0.31	$k = 6$
PU-2	1.10^{3,13}	378	4.16	0.44	$k = 2$

*Abbreviations; PET = poly(ethylene terephthalate); PBT = poly(tetramethylene terephthalate); Trogamid T^{R} = poly(trimethylhexamethylene terephthalate); PEA = polyesteramide $[COPhCOO(CH_2)_6OCOphCONH(CH_2)_6NH]_x$; PEE = polyesterether $[COPhO(CH_2)_6OPhCO(Ch_2)_6O]_x$ where Ph is the *p*-phenylene group.

†Segments of polyurethane chains: A $[CONHPhCH_2PhNHCOO]$;
B1 $[(CH_2)_4OCO(CH_2)_4COO]$; B2 $[(CH_2)_2OCO(CH_2)_4COO]$;
B3 $[(CH_2)_5COO]$; C1 $[CONHPhCH_2PhNHCOO(CH_2)_4O]$;
C2 $[CONHPhCH_2PhNHCONH(CH_2)_4NH]$; C3 $[CONHPhCH_2PhNHCO(CH_2)_5O]$;
D(k) $[(CH_2)_kO]$.

ble. In the lack of better knowledge, we consider the NH—CO—NH and NH—CO—O groups as equivalent to one double and one single bond, admitting that the p values for polyurethanes are somewhat uncertain. (By setting these groups equivalent to two double bonds, we would increase p by about 15%, which would have no consequences for the conclusions of this paper.)

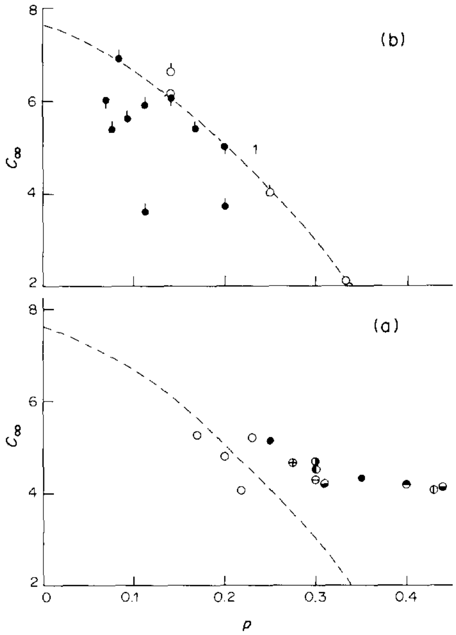

Fig. 1. Plot of the characteristic ratio C_∞ against the fraction p of stiff bonds. (a) Data points: ⦶PET: ⊕PBT: ◑PEA: ◐Trogamid T®;◓PEE: ●TPUR I and II; ⊖PUS: ○PUK, UB, UC, S; ◒PU 1 and 2 (for abbreviations see Table 1). (b) Data points for aliphatic polyesters (⫰theor. [15], ●exp. [3, 14]) and polyamides (⫯theor. [1, 16], ●exp. [2]). Curve 1 in (a) and (b) is drawn through theoretical points for aliphatic polyamides and polyesters.

The use of p as a variable characterizing the chain structure may seem arbitrary but the smoothness of curve 1 in Fig. 1b, which is a fit to the theoretical values of C_∞ for aliphatic polyesters and polyamides, offers justification for this choice.

In order to have a reference basis for the subsequent discussion, we have calculated C_∞ for purely aliphatic polyesters and polyamides [1, 14–16] and plotted them against p (with $n_1 = 0$) in Fig. 1b. Curve 1 fits theoretical data. Experimental values for most polyamides are close to it, whereas the majority of data points for polyesters lie below. The reason for this finding is unknown but it might be connected with the method of evaluating C_∞ from the intrinsic viscosity in good solvents. In spite of this discrepancy, curve 1 can be used as a reference dependence for an assessment of the effect of benzene rings.

The data in Fig. 1a for polymers with benzene rings originate from various laboratories. Very little is known about the polydispersity of the samples. The C_∞ values have been obtained by eliminating the excluded-volume effect from the intrinsic viscosity data in good solvents. All these facts can affect the accuracy of the correlation. Despite that, the plot in Fig. 1a is smooth, especially at $p \gtrsim 0.25$.

Figure 1a shows that, by increasing the frequency of occurrence of stiff segments or bonds, we reduce the characteristic ratio. Effect II (i.e. the enhancement of rotational freedom conferred on nearby bonds by the benzene ring and CO—NH or CO—O bonds) obviously prevails over effect I. Anyway, the latter is here stronger than with purely aliphatic polyamides or polyesters as indicated by the data points (for $p > 0.25$) lying above curve 1. That can be assigned to the "virtual" bonds (associated with the benzene rings) being longer than the bonds CO—NH and CO—O.

This explanation seems reasonable but a theoretical analysis is needed. On the other hand, the correlation in Fig. 1a for chains containing benzene rings is good enough to be useful for predictive purposes, e.g. for estimating C_∞ for new polymers and copolymers of this type.

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