Eur. Polym. J. Vol. 23, No. 4, pp. 283–286, 1987
Printed in Great Britain

0014-3057/87 \$3.00 + 0.00
Pergamon Journals Ltd

PRODUCTION AND PROPERTIES OF POLYACENAPHTHYLENE—VII

UNPERTURBED DIMENSIONS AND CHAIN CONFORMATIONAL STUDIES OF POLYACENAPHTHYLENE*

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(*Received* 22 *July* 1986)

Abstract—The unperturbed dimensions of polyacenaphthylene in solution were determined from light scattering, osmotic and viscometric data in thermodynamically good solvents and in the theta solvent, 1,2-dichloroethane, using direct and indirect evaluation methods. The estimated value of the steric factor, σ, shows polyacenaphthylene to be a relatively rigid polymer in contrast to the results obtained from hydrodynamic investigations. An attempt was made to explain this discrepancy in terms of a tightly coiled conformation is solution due to weak links in the polymer chain.

INTRODUCTION

As reported in a previous communication [1], polyacenaphthylene (PACE) was synthesized, fractionated and characterized. Fractions with $M > 10^6$ [g/mol] were found to be branched. The theta-temperature was determined from light scattering experiments in 1,2-dichloroethane.

Although PACE is expected to show considerable stiffness because of its bulky substituent, it was found that theories relating to flexible coils could be applied in determinining its dilute solution properties.

In this paper we report on the determination of the unperturbed dimensions of PACE using direct and indirect evaluation methods. Furthermore, an attempt is made to assess the rigidity of PACE chains.

RESULTS AND DISCUSSION

The results of viscometric, gel permeation chromatographic, osmotic and light scattering experiments have been reported [1]. Data obtained from these experiments have been used to evaluate the unperturbed dimensions.

Unperturbed dimensions

The unperturbed dimensions were experimentally derived by two methods:

(1) direct, i.e. from experiments in theta-solvent at the theta-temperature, and

(2) indirect. By means of empirical- or semi-empirical equations, the perturbed dimensions were determined in thermodynamically good solvents and extrapolated to the unperturbed state.

Both methods have been the subject of numerous investigations and have been thoroughly probed and applied, e.g. [2–7]. From a theoretical point of view, it is preferential to use the direct method, which however has certain disadvantages. Experimenting at or close to the theta-temperature becomes quite tedious because of the tendency of some polymers, in particular stereoregular polymers, to fractionally precipitate or to crystallize from solution. Furthermore characteristic errors associated with the method of investigation may affect the results, e.g. the inaccuracy in determining the radius of gyration from light scattering experiments or the question of polymer solubility in viscosity measurement at the theta-temperature. Such problems may not arise when the indirect method is applied but, since empirical or semi-empirical equations are used for the estimation of the unperturbed dimensions, other uncertainties may arise. Questions may be raised about the validity or applicability of a particular empirical or semi-empirical equation for a particular polymer–solvent system.

The unperturbed dimensions of PACE were determined by both direct and indirect methods, and the results compared and analyzed.

Direct method

Light scattering. The unperturbed mean square radius of gyration $\langle r_0^2 \rangle_z$, which is obtained directly from light scattering experiments at the theta-temperatue, is a z-average. To calculate the weight-average $\langle r_0^2 \rangle_w$, the effect of heterogeneity for the molar mass distribution was taken into account. Since the molar mass distribution of PACE [8] only slightly differed from a Schulz–Flory distribution [9], for simplicity such a distribution was assumed.

The unperturbed average dimension A* is related to the unperturbed mean square radius of gyration $\langle r_0^2 \rangle_w$ and mean square end-to-end distance $\langle h_0^2 \rangle_w$ by the equation

$$A^{*2} = 6\langle r_0^2 \rangle_w / \bar{M}_w = \langle h_0^2 \rangle_w / \bar{M}_w. \qquad (1)$$

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*Part VI: J. Schmelzer and J. Springer. *Eur. Polym. J.* **23**, 243 (1987).

The values of $\bar{M}_w$, $\langle r_0^2\rangle_z$, $\langle h_0^2\rangle_w$ and A* of a branched PACE (fraction 1) and linear PACE (fractions 4–7) are summarized in Table 1.

The values obtained for the unperturbed average dimension show reasonable consistency and give an arithmetic mean for linear PACE of $6.7 \pm 0.3 \times 10^{-9}$ [cm mol$^{1/2}$/g$^{1/2}$].

Viscosity

The unperturbed dimensions were evaluated from intrinsic viscosities $[\eta]$ measured in 1,2-dichloroethane at the theta-temperature using the Flory–Fox equation [2].

$$[\eta] = K_\theta \bar{M}_w^{1/2} = \phi_0 A^{*3} \cdot \bar{M}_w^{1/2}. \qquad (2)$$

Flory's viscosity factor, ϕ_0 free from polydispersity effects has been estimated experimentally [10, 11] and theoretically [12] to be 2.5 and 2.6×10^{23} [mol^{-1}] respectively.

For our purpose, this factor is corrected for polydispersity using a polymolecularity correction factor $q_{r_zM_w}$. According to Bareiss [12], for polymer fractions with $\bar{M}_w/\bar{M}_n \leqslant 1.3$, the type of molar mass distribution is of much less importance than the effect of molar mass distribution breadth on $q_{r_zM_w}$. One can therefore, for $\bar{M}_w/\bar{M}_n \leqslant 1.3$, use the polymolecularity correction factors calculated for a Schulz–Flory distribution. With $\bar{M}_w/\bar{M}_n = 1.3$ for the PACE fractions, $q_{r_zM_w} = 0.712$ and Eqn (2) becomes

$$[\eta] = \phi_0 \cdot q_{r_zM_w} \cdot \mathrm{A}^{*3} \cdot \bar{M}_w^{1/2}. \qquad (3)$$

In a previous communication [1] the conformation factor K_θ was estimated from $[\eta]/M$ measurements at the theta-temperature to be 42.7×10^{-3} [cm^3·mol$^{1/2}$/g$^{3/2}$]. The unperturbed dimension A* for linear PACE was calculated according to Eqn (3) to be 6.21×10^{-9} [cm mol$^{1/2}$/g$^{1/2}$].

Indirect methods

The unperturbed dimensions were determined indirectly from viscosity measurements in toluene, tetrahydrofuran (THF), and benzene. The following semi-empirical equations, based on excluded volume theories, were then used to evaluate the unperturbed dimensions:

—the Stockmayer–Fixman–Buchard equation [5] (S–F–B)

$$[\eta]/M^{1/2} = K_\theta + 0.51\,\mathrm{B}^*\phi_0 M^{1/2} \qquad (4)$$

allows the determination of the conformational factor K_θ and the polymer–solvent interaction parameter B*, which represents the long range interactions. From $[\eta]/M^{1/2}$ vs $M^{1/2}$ plots, K_θ and B* can be evaluated from the intercept and slope respectively.

—the Kurata–Stockmayer relationship [3] (K–S)

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.363\phi_0 \cdot \mathrm{B}^* \times [g(\alpha_\eta) \cdot \bar{M}_w^{2/3}/[\eta]^{1/3}]. \qquad (5)$$

Plots of $[\eta]^{2/3}/M^{1/2}$ vs $g(\alpha_\eta) \cdot M^{2/3}/[\eta]^{1/3}$ yield K_θ and B* from the intercept and slope respectivley.

These plots for linear PACE fractions (fractions 4–11) are illustrated in Figs 1 and 2, $[\eta]$ being expressed in cm^3/g. The plots show good linearity. Least scattering of the experimental data is observed in the K–S plot.

Table 1. Unperturbed dimensions of PACE

Fraction	$\bar{M}_w \times 10^{-5}$ [g/mol]	$\langle r_0^2\rangle_z^{1/2} \times 10^6$ [cm]	$\langle h_0^2\rangle_w \times 10^{11}$ [cm^2]	A* × 10^9 [cm mol$^{1/2}$/g$^{1/2}$]
1	21.30	4.83	11.46	7.35
4	10.40	3.13	5.03	6.95
5	8.28	2.49	3.33	6.34
6	6.07	2.35	2.83	6.82
7	4.90	2.07	2.24	6.76

In both plots, the values for 1,2-dichloroethane give straight lines with a slightly negative but nearly zero slope confirming this solvent to be a theta solvent for PACE. The intercepts of the K–S and the S–F–B plots for PACE in benzene and 1,2-dichloroethane are identical. However, these values are higher than those for toluene and (THF), which have common intercepts in both plots. No common point of intersection for all the lines was obtained. Linear regression gave intercepts from which the K_θ-values listed in Table 2 were calculated.

The K_θ-values obtained by the indirect method in toluene, THF and benzene are all of the same magnitude. The values differ for each specific solvent by less than 3% and, compared to the K_θ-value obtained by the direct method, vary more or less by *ca* 5%.

To determine the solvent dependency of K_θ, the values obtained from the K–S plots were examined. K_θ-values in toluene and THF are quite similar, but differ considerably from K_θ-values obtained from benzene and 1,2-dichloroethane. These differences are however not large enough to clearly account for

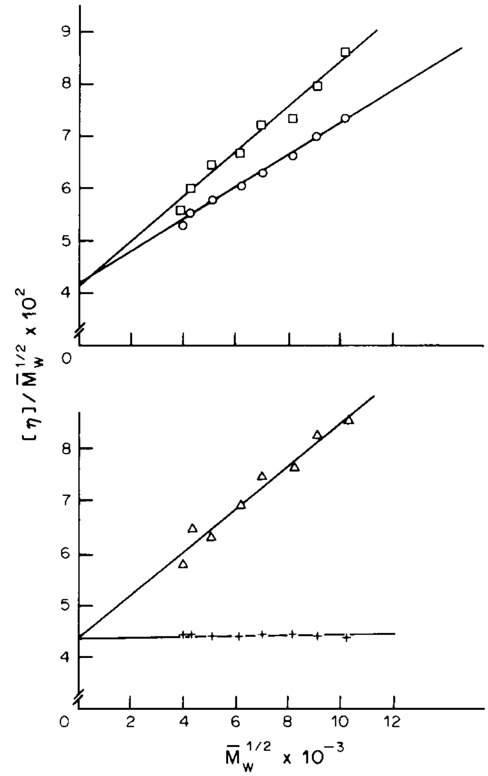

Fig. 1. Kurata–Stockmayer plot for PACE in toluene, benzene and THF at 25°C and in 1,2-dichloroethane at the theta-temperature. ○ Toluene; □ THF; △ Benzene, + 1,2-Dichloroethane.

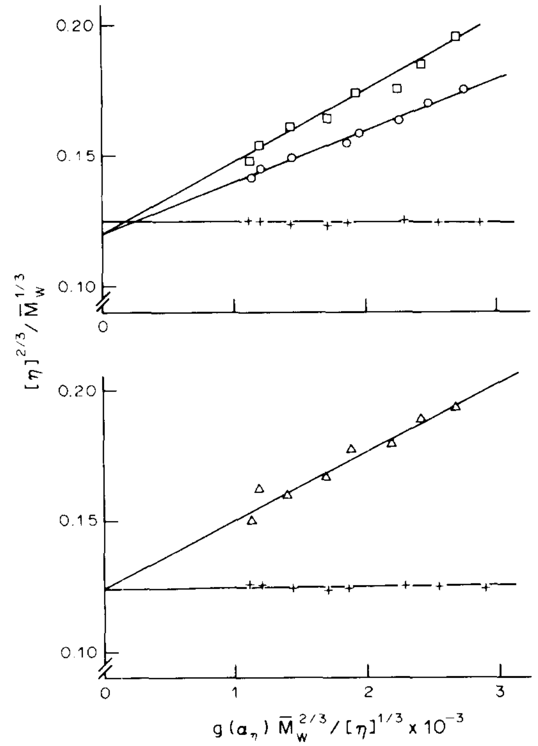

Fig. 2. Stockmayer–Fixman–Buchard plot for PACE in toluene, benzene and THF at 25°C and in 1,2-dichloroethane at the theta-temperature. Symbols as for Fig. 1.

solvent effects and, in view of the data-scattering, could result from experimental error. Rather, it can be assumed that all plots yield approximately the same K_θ-values for all solvents.

The values of B* (Table 2) show normal behaviour, i.e. they increase with the thermodynamic solvent power and become zero under theta-condition. The K_θ-values, with $\phi_0 = 2.5 \times 10^{23}$ [mol^{-1}], yield unperturbed dimensions A* given in Table 2. In comparison, the A*-values from the indirect method are almost equal to the A*-value derived directly from viscosity measurements in 1,2-dichloroethane, but deviate by about 0.5×10^{-9} [cm mol$^{1/2}$/g$^{1/2}$] from the A*-value derived from light scattering experiments. This difference may arise from experimental errors in the determination of the radius of gyration due to the small angular dependence of the reduced scattering intensity of PACE, e.g. relative to polystyrene [17].

Table 3. Conformation factor of PACE and similarly structured polymers

Polymer	σ	Source
PACE	2.78	This work
Poly(1-vinylnaphthalene)	2.46	13
Poly(2-vinylnaphthalene)	2.95	14
Poly(4-vinyl-biphenyl)	2.63	14
Polystyrene	2.28	15
Poly(*N*-vinylcarbazole)	2.82	16

Chain conformation

The steric factor σ can be used to measure the hindrance to internal rotation about the single bonds of the chain. σ is obtained from the relationship,

$$\sigma = \langle h_0^2 \rangle / \langle h_0^2 \rangle_{\text{of}} = \text{A}^*/\text{A}^*_{\text{of}} \qquad (6)$$

where $\langle h_0^2 \rangle$ and $\langle h_0^2 \rangle_{\text{of}}$ are the mean square end-to-end distance in the unperturbed state for a freely rotating chain and A^*_{of} is the unperturbed dimension of a freely rotating chain.

A^*_{of} for PACE was estimated to be [8] 2.23×10^{-9} [cm mol$^{1/2}$/g$^{1/2}$]. Taking A* as 6.21×10^{-9} [cm mol$^{1/2}$/g$^{1/2}$], the steric factor was calculated according to Eqn (6). The calculated value and those of other similarly structured polymers are summarized in Table 3.

Even though the results of hydrodynamics studies showed PACE in dilute solution to behave in a manner similar to linear flexible polymers, the above result indicates that PACE is a relatively rigid molecule.

Chain rigidity can be attributed to the hindrance to molecular rotation around the polymer main chain. The chain rigidity of linear vinyl polymers, e.g. polystyrene, is due to steric interaction of the neighbouring side groups of the polymer chain. Under similar conditions of polymer/solvent interaction, e.g. in the unperturbed state, the steric factor and the chain rigidity increases with size of the side groups, i.e. with increasing monomer unit molecular weight. This can be seen from the σ-values of polystyrene and poly(1-vinylnaphthalene) (P1VN) in Table 3. In accordance, polymers with bulky or spatial substituents, e.g. poly(*N*-vinylcarbazole) and poly(2-vinylnaphthalene) have been reported to have very large σ-values, 2.82 and 2.95 respectively. If on the other hand, the σ-values of PACE and P1VN are compared, in spite of similar monomer unit molecular weight, the σ-value of PACE (2.78) is found to be much larger than that of P1VN (2.46).

Table 2. Unperturbed dimension A*, conformation factor K_θ and thermodynamic parameter B* for PACE in various solvents

Solvent	Method	$K_\theta \times 10^2$ [cm^3 mol$^{1/2}$/g$^{3/2}$]	A* $\times 10^9$ [cm^3 mol$^{1/2}$/g$^{1/2}$]	B* $\times 10^{28}$ [cm^3 mol^2/g^2]
1,2-Dichloroethane	Direct	4.27	6.21	—
Benzene	Indirect			
	K–S	4.37	6.26	4.10
	S–F–B	4.32	6.24	4.76
Toluene	K–S	4.20	6.18	3.07
	S–F–B	4.12	6.14	3.45
THF	K–S	4.20	6.18	4.14
	S–F–B	4.08	6.12	4.73

This is not a surprising result as the structural difference between PACE and P1VN is that every alternate PACE main chain bound is locked in the polymer chain.

If the σ-values of P1VN, PACE and poly(4-vinylbiphenyl) (PVB), are compared, it can be concluded that the main contribution to PACE chain stiffness is the hindrance to free rotation about the main polymer chain. Both polymers (PACE and P1VN) have similar spatial configurations and contributions due to steric hindrance are expected to be of the same order of magnitude. In PACE, only half of all the main chain valence bonds can participate in a free molecular rotation about the main chain. Every other bond is part of the cyclic repeating unit.

Contrary to results obtained from hydrodynamic studies, the above results confirm that PACE exhibits considerable stiffness, as indicated by examination of molecular models. Conclusively PACE can be described as an appreciably rigid polymer exhibiting non-draining character.

This contradictory description can possibly be explained with the help of results obtained by Stelter and Springer [18] during photodegradation studies of PACE. Thermally prepared PACE were found to contain *ca* 13 so-called weak links for 1000 structural units. It can be assumed that in solution stiff segments of the PACE main chain are linked together by flexible links permitting the PACE molecule to assume a less expanded dimension than would have been expected. A relatively small proportion of irregular links would suffice to change the macroconformation of a rod-like molecule into that of a coil [19]. This explains the "normal" values (0.65–0.7) of the constant a in the Mark–Houwink equation $[\eta] = kM^a$. PACE therefore consists of rigid regular chain segments interrupted by coil-enhancing irregular chain structures.

Acknowledgements—One of us, Henry Agbaje, acknowledges financial support by the German Academic Exchange Service (DAAD) and we thank the Chemische Fabrik Weyl AG, Mannheim, for the kind gift of acenaphthylene.

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