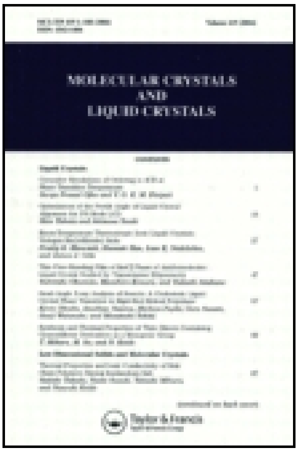

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Investigations of Stiff-Chain Polymers in Solution

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INVESTIGATIONS OF STIFF-CHAIN POLYMERS IN SOLUTION

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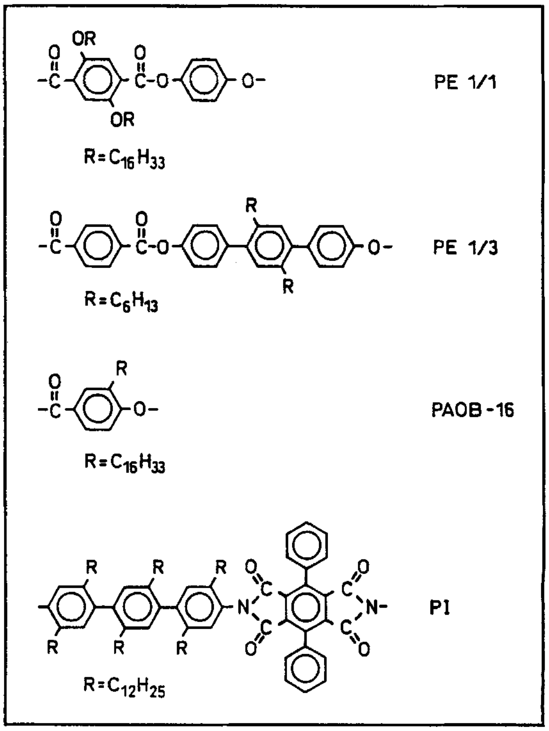
Abstract The shape and the conformation of stiff-chain polyesters and polyimides substituted by flexible side chains are reviewed and discussed. The shape of the dissolved macromolecules has been assessed by small-angle neutron scattering whereas the persistence length was determined by viscosimetric means. For all systems under consideration here the persistence length is found to be of the order of 10nm. This finding is in agreement with recent computer simulation indicating that bond angle and out-of-plane fluctuations lead to considerable deviations from the rodlike shape of the main chains.

Introduction

Stiff-chain polymers, i.e., macromolecules which assume a rodlike shape, present very interesting objects because of their ability to form thermotropic or lyotropic mesophases[1,2]. Since the stability and the type of the respective mesophase are intimately related to the shape and stiffness of the chains a thorough knowledge of the conformation of the various systems is required for a quantitative understanding of the phase behaviour.



Scheme 1

In this communication we discuss recent investigations on several stiff-chain polymers shown in scheme 1. All polymers under consideration here exhibit a sufficient solubility due to the alkyl or alkoxy side chains[2]. Hence, in all cases studies could be done in common organic solvents as e.g. chloroform or o-dichlorobenzene.

Systems: Polyesters PE1/1 have been investigated recently in solution and in bulk by Galda et al.[3]. Also, this system was studied[4] by small-angle neutron scattering (SANS) in the solid state, in the thermotropic mesophase and in dilute (isotropic) solutions. In order to obtain a higher stiffness of the main chain, the hydroquinone moiety was replaced by the respective 4,4''-terphenyldiol to obtain polyester PE1/3. The synthesis of these polyesters as well as their characterization has been given elsewhere[5,6]. Polyester PAOB-16 studied recently by Stern et al.[7] does not have a bulky substituent in the immediate neighbourhood of the carboxyl group. Thus it is interesting to compare its persistence length to the persistence length measured on polyester PE1/1. Finally, the terphenyl moiety and the pyromellitic unit are combined in polyimide PI synthesized recently[8]. Here the main chain should exhibit a high stiffness. A comparison between the measured persistence lengths of these systems therefore should give at least a qualitative insight into the factors governing chain stiffness.

SANS-Studies: In general, studies of the conformation by light scattering or by small-angle neutron or x-ray scattering are capable to give the most direct information on the shape and the persistence of the above systems[9]. This requires, however, the determination of the radius of gyration from the scattering intensities in the Zimm-region with high precision[9]. As shown[4] recently for polyesters PE1/1, however, this region corresponding to lowest angles in SANS-studies is severely disturbed by excess scattering. This effect which can be modelled by a Debye-Bueche correlation function[10] points to a residual association of the chains despite the fact that PE1/1 dissolves easily in the solvent used for these studies (deuterated nitrobenzene). One reason for this problem may be located in the necessity of using rather high concentration of the polymer as compared to a typical light scattering experiment. As shown[11] by light scattering experiments on polyimide PI another reason for the excess scattering is located in association due to open endgroups. Closing the endgroups by chemical means thus relieves this problem. Hence, the SANS-study of PE1/1 given in reference [4] does allows neither the determination of the radius of gyration nor of the persistence length of this system.

SANS-investigations, on the other hand, give highly useful information on the shape of the chains in various states of aggregation. This is due to the strong contrast between protonated and deuterated macromolecules[12]. Also, in the region of higher angles the effect of intermolecular interaction on the scattering intensity vanishes. Hence, in this region the evaluation of structural data from the SANS data is not hampered anymore by association.

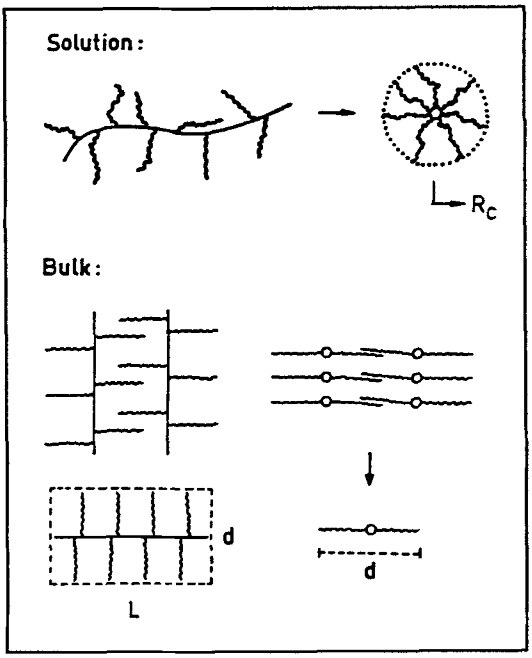


Fig. 1 Scheme of the different shapes of polyesters PE1/1 as revealed by SANS [4]

An analysis along these lines given in reference [4] clearly reveals the following (cf. fig. 1): In solution the side chains can adopt any conformation and the entire molecule assumes an approximately cylindrical shape. A measure of cross section of the polyesters in solution can be derived from the radius of gyration R_c perpendicular to the main chain axis[9]. In bulk the packing constraints exerted by the neighbouring polymer molecule and the microphase separation of the incompatible main and side chains (cf. ref.[13] and [3] for a discussion of the structure in solid state) lead to a planar conformation of the side chains. Thus the entire molecule exhibit a plate-like shape under these condition. These SANS experiments therefore clearly show that polyester PE1/1 assume a boardlike shape only to comply with the boundary conditions in solid state; without the restrictions imposed by neighbours the polyester molecules undergo a drastic change of shape. Up to now there is no similar study on the other systems available but there is no reason why the other systems depicted in scheme 1 should behave in a different way.

Viscosimetric Studies: The preceding paragraph has shown that SANS can provide highly interesting information on the overall shape of stiff-chain polymers with flexible side chains. The angular range of the SANS-data used for this analysis refer to a length scale in which the PE1/1 chains behave as rigid rods. In order to assess the deviations from the ideal cylindrical shape a quantity has to be determined which is sensitive to a length scale of the order of the contour length of the chains. The intrinsic viscosity as function of molecular weight is such a property. It can be interpreted in terms of the theory of worm-like chain model of Yamakawa and Fuji[14] to yield the persistence length. Bohdanecky[15] has shown that this evaluation can be done elegantly by the following plot:

$$\left(\frac{M^2}{[\eta]}\right)^{\frac{1}{3}} = A_\eta + B_\eta M^{\frac{1}{2}}$$

where A_η is a quantity depending on the hydrodynamic diameter of the chains and B_η can be expressed as function of the unperturbed end-to-end distance of the chains. Thus the slope of such a plot allows the determination of the persistence length whereas the intercept gives the hydrodynamic radius of the chains.

For all polyesters and polyimide PI the data of the intrinsic viscosity as function of the weight-average molecular weight give linear Bohdanecky-plots within prescribed limits of error[3,5-7,11]. Figure 2 and 3 show the plots for polyester PE1/3 (references [5,6]) and for polyimide[11] PI, respectively.

From these plot a persistence length of approximately 6.5nm results for PE1/1 in chloroform together with a hydrodynamic radius of 0.7nm. For PE1/3 the respective values are 8.5nm and 0.9nm; for polyester PAOB-16 the persistence length results to

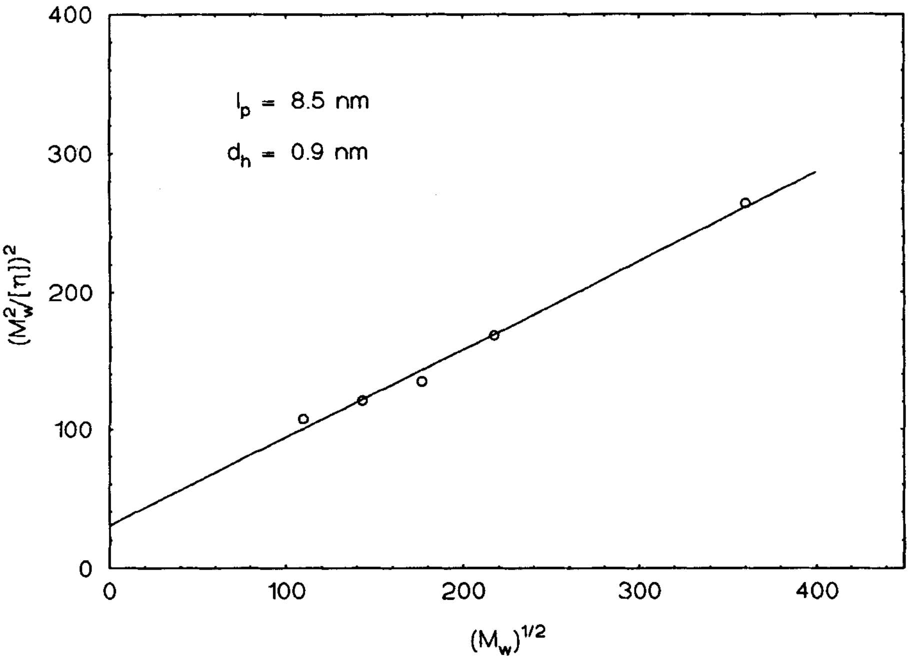


Figure 2 Bohdanecky-plot of polyester PE1/3 [5,6].

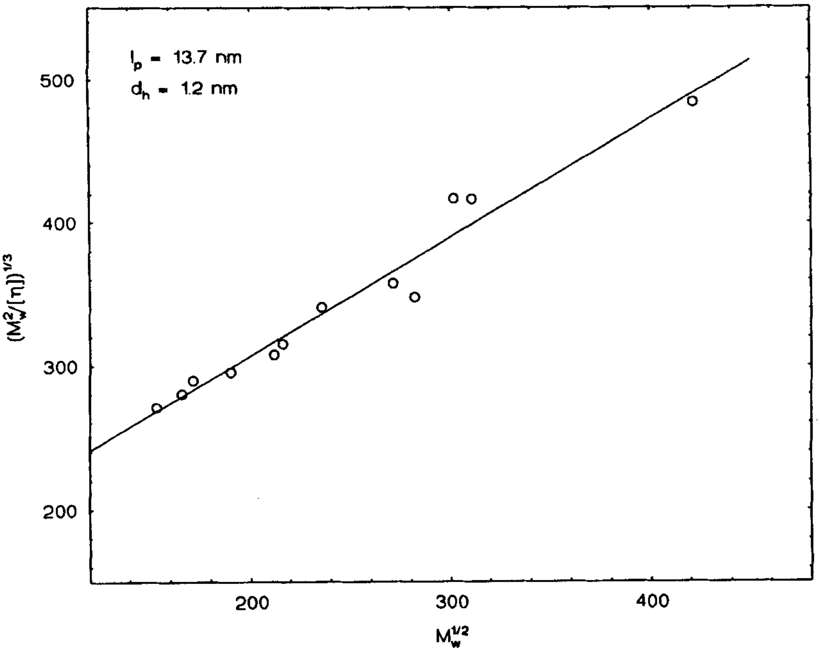


Figure 3 Bohdanecky-plot for polyimide PI [11].

8nm whereas it hydrodynamic radius follows as 1.1 to 1.3nm. Thus the stiffness of the three polyesters under consideration here is approximately the same. Only the polyimide exhibits the slightly higher value of 13.7nm together with a hydrodynamic radius of 1.2nm.

Given the various approximations in the theory[15] it seems to be rather difficult to assess the accuracy of these figures. It has to be noted that the hydrodynamic diameters compare favourably with the R_c value measured[4] by SANS for PE1/1. Here approximately 0.6nm has been determined which is slightly smaller than the above figures for the hydrodynamic radii as expected. Furthermore, the hydrodynamic diameters of the polyesters PE1/1 (cf. [3]) and PAOB (cf. [7]) exhibit an increase with increasing length of the side chains above the limits of error. Additional confidence into the above figures can be derived from the fact that a recent determination[6] of the persistence length of PE1/3 by measurements of the magnetic birefringence lead to a value of 10.7nm. The result obtained for the polyimide PI is corroborated by an analysis of chain conformation by light scattering[11]. Thus, the data for the chain stiffness as obtained by Bohdanecky's plot seem to be a reliable base for the discussion of the various factors influencing the persistence length.

Discussion: The above analysis has shown that the sufficient solubility of the polyesters and the polyimide under consideration here allows the determination of their shape and stiffness. The strong change of the shape when going from bulk to solution as revealed by SANS has been already expected from the structural analysis of the solid state. The figures of persistence length obtained in the course of the viscosimetric analysis, however, are considerably smaller than anticipated by the analysis of Flory and coworkers[16]. It must be remarked in this context, however, that the figure of 50nm for the persistence length of poly(4-hydroxybenzoic acid) holds only true if the subsequent monomer units are assumed to be colinear; otherwise a drastic reduction of chain stiffness will result (cf. figure 3 of ref. [16]).

In this context it is furthermore interesting to note the polyester PAOB-16 exhibits nearly the same stiffness as polyester PE1/1 which bears a bulky substituent in the o-position to the carboxyl-group. Thus the influence of such a substituent seems to be marginal. Also, the large structural changes when going from polyester PE1/1 to PE1/3 do not result in a marked increase of the persistence length. Even the imide unit often regarded as absolutely rigid leads only to a moderate increase of chain stiffness.

To the authors knowledge Jung and Schürmann[17] were the first to show convincingly by computer simulations that bond angle fluctuations not taken into account by the calculation of Hummel and Flory[16] will reduce the persistence length considerably. In particular, out-of-plane fluctuation of the ester bond must not be disregarded when discussing the stiffness of the polyester main chains. The calculations of Jung and Schürmann[17] predict a value for the persistence length exactly in range observed here. Experimental studies[18,19] on related systems and recent computer simulations[17,20,21] have corroborated this prediction. Thus, Farmer et al.[20] came to the conclusion that even poly(p-phenylene) which often is regarded as an example of an ideal rigid rod polymer has a persistence length of only 22nm.

In conclusion, the survey given herein has demonstrated that the stiffness of the systems shown in scheme 1 are of the order of 10nm. Even the polyimide PI only exhibits a persistence length of 13.7nm and cannot be regarded as a truly rigid rod polymer. This finding is in accord with recent computer simulations[20,21] showing that the reduction of chain stiffness is due to deviations from rectilinearity caused by e.g. bond angle fluctuations and out-of-plane distortions of the chains. One is therefore forced to the conclusion[20] that a truly rigid rod polymer cannot be made by a one-dimensional chain. It must consist of a three-dimensional structure which is much less prone to bending fluctuation than the single-stranded structures discussed herein.

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