

CONFORMATION OF SUBSTITUTED POLYACETYLENES IN SOLUTION

J.P. AIME

Laboratoire de Cristallographie et Physique Cristalline, Université Bordeaux I, 351
Cours de la Libération, F-33405 Talence Cedex, France

T. MASUDA

Department of Polymer Chemistry, Kyoto University
Kyoto 606-01, Japan

ABSTRACT

A small angle neutron scattering (SANS) study on substituted polyacetylenes in good solvent has been performed. The two polymers considered are composed of mono- and disubstituted monomer units. The SANS results show unambiguously the influence of the steric interaction between neighbouring substituents on the magnitude of the statistical length. Attempt is also done to relate the magnitude of the torsional fluctuations to the optical properties.

INTRODUCTION

Conjugated polymers with large molecular weights can be solubilized in common organic solvents by adding appropriate substituents. Most exhibit thermochromism and solvatochromism, which has stimulated extensive studies on the relation between optical properties and chain conformation. Recent studies have shown that the substituents and the torsion between monomer units play a key role in understanding the statistical conformation [1,2] and an increasing amount of theoretical work has paid special attention to the effects of torsional fluctuations, emphasizing their influence on the π -electrons delocalization [3,4].

In this note we report experiments aiming to establish as accurately as possible the description of the chain statistics, and to predict its link with the π -electron delocalization. Small Angle Neutron Scattering (SANS) was used to provide structural information at intermediate and local scales, that is between 200 and 10 Å.

Here we focus our work on substituted polyacetylenes synthesized following the Masuda route [5]. The generic formula is $(RC=CR')_n$. Two polymers are considered, one is poly[o-(trimethylsilyl)phenyl acetylene] (hereafter abbreviated P1) [6], where $R = H$ and $R' = C_6H_4-O-Si(CH_3)_3$ IN which an additional bulky substituent at the ortho position of the phenyl ring enhances the steric interaction, and the other is the poly[1-(trimethylsilyl)-1-propyne] (hereafter abbreviated P2) [7], where $R = CH_3$ and $R' = Si(CH_3)_3$, from which a strong repulsive interaction between neighbouring monomer units is expected. The results obtained with these two polymers are compared with the previous results obtained on polyphenylacetylene (hereafter abbreviated PPA), where $R = H$ and $R' = C_6H_5$ and the poly(2-octyne), where $R = CH_3$ and $R' = CH_2)_4CH_3$ [1].

EXPERIMENTAL RESULTS

The samples used have a very high air stability, their molecular weight and polydispersity are: $M_w = 1.4 \times 10^6$, $M_w/M_n = 2.35$ and $M_w = 2.3 \times 10^5$, $M_w/M_n = 1.8$ respectively for P1 and P2. A detail description of the synthetic routes used and properties of these polymers is given in references [6] and [7]. SANS data have been collected at the Institut Laue Langevin (Grenoble-France) and Laboratoire Léon Brillouin (Saclay-France). Absolute measurements have been performed following the usual routines described in details elsewhere [2]. The scattering vector range used is $6 \times 10^{-3} \text{ \AA}^{-1} < q < 0.25 \text{ \AA}^{-1}$.

Considering a chain as an infinitely thin thread, we focus attention on conformation at the local scale. In other words, we are interested in the asymptotic regime of the scattering function, that is, $g(q) \propto q^{-\alpha}$ for $q \rightarrow \infty$. The purpose of the dimensionless scattering function $g(q)$ is to obtain the scattering density of the macromolecule in the asymptotic regime. For the case of the rod conformation, one have a q^{-1} law, the limit of $g(q)$ is given by :

$$\lim_{q \rightarrow \infty} q g(q) \sim \frac{\pi}{a} \quad (1)$$

where a is the monomer unit length. Therefore the plateau height in a $qg(q)$ plot gives the linear density of the macromolecule in a rod conformation. For an actual wormlike chain, the angular correlation along the backbone can be large enough such that a rigid conformation is observed. The rigidity is measured by the statistical length b . For a worm-like chain, the asymptotic behavior is given by [8]:

$$\lim_{q \rightarrow \infty} q g(q) = \frac{\pi}{a} + \frac{C(N)}{qab} \quad (2)$$

Where $C(N) = -2 N^{-1}$ for a rod and $C(\infty) = 4/3$ for an infinite worm-like chain [8].

The lower the q value at which a q^{-1} behavior is observed, the larger is the rigidity of the macromolecule. We do not need more sophisticated approach for understanding the properties of the different polyacetylenes studied. In figure 1 are reported the three scattering curves measured for P1, P2 and PPA. A hierarchical order appears, the lowest curve (P2 sample) shows the most rigid behavior, the P1 sample (a monosubstituted acetylene polymer) shows an intermediate stiffness while PPA exhibits a flexible conformation. We thus observe a progressive change on the magnitude of the local stiffness; the theoretical structure factors calculated following the method given in reference [9] gives quantitative values of that change. The statistical lengths obtained are: 110 Å, 70 Å, and 45 Å respectively for P2, P1 and PPA chains with an error of about ± 5 Å.

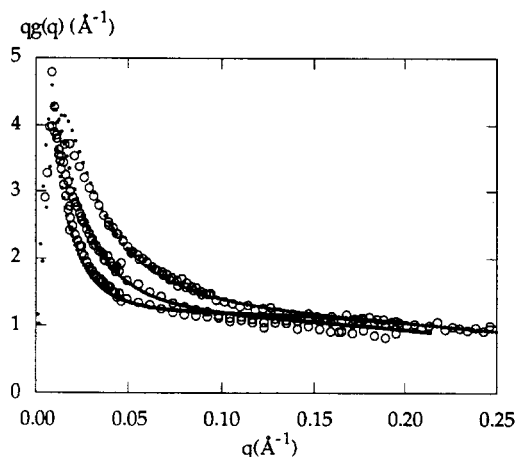


Figure 1: $q g(q)$ plots of the scattering functions. The lowest curve corresponds to the P2 sample, the intermediate curve to the P1 sample and the highest curve (ref [1]) to the PPA sample. The filled circles corresponds to theoretical computation [9] providing the statistical length (see text).

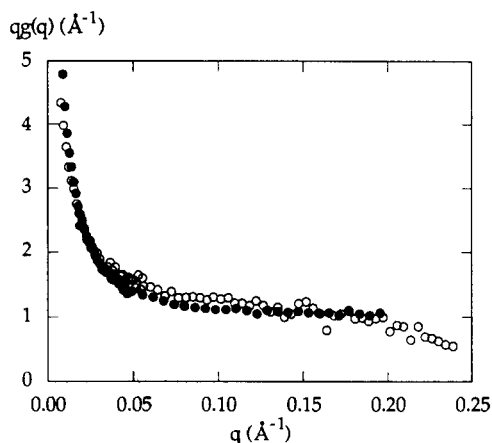


Figure 2: Comparison between the two $qg(q)$ plots of disubstituted polyacetylene: P2 (•) and from ref. [1] poly(2-octyne) (o).

The size of the side-groups are not large enough for having a noticeable influence on the scattering function at large q values ($q > 0.1 \text{ Å}^{-1}$) [2]. Therefore except for poly(2-octyne) [1], we do not have access at the conformation of the substituents with respect

to the backbone. Nevertheless, it is not quite difficult to establish a link between the stiffness increase and the chemical structure of the substituent side-groups. The larger the size of the substituents and the steric interaction, the larger is the magnitude of the statistical length. Since we may reasonably expect an increase of the average rotation between monomer units as the substituent size increases, the evolution shown in figure 1 evidence the direct relation between the chain rigidity and the chain twist along the backbone. The latter proposal is in complete agreement with the prediction of the model given in [2].

The comparison of the two scattering functions of the disubstituted acetylene polymers (figure 2) gives an additional experimental proof. Quantitative values of the average torsion between monomer units have been obtained for poly(2-octyne), $\phi = 50^\circ$, providing that we have an helical structure at the local scale. The height of the plateau does not reach the expected value as it is for the P2 sample. This result and the way we have deduced an helical structure has been discussed at length in reference [1]. Here we shall only note that the two polymers show a very close stiffness, suggesting that the average rotation between monomer units must be in the same range. The fact that the plateau height of the P2 is not as high as for poly(2-octyne) can be understood either by considering an helical structure without central hollow part or a random distribution of the sign of the average torsion along the backbone.

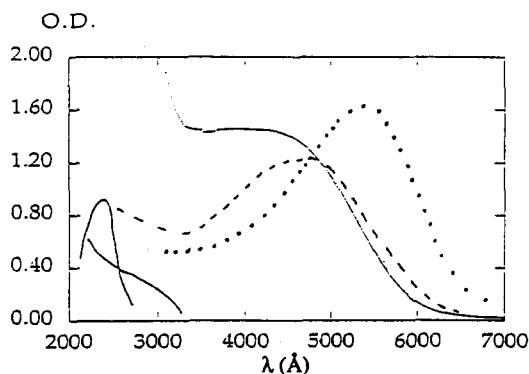


Figure 3: UV-Visible absorption spectra of PPA (continuous line), poly(o-MePA) (- -) P1 sample (dotted line). P2 sample and poly(2-octyne) show an absorption in the U.V range.

In figure 3 are reported the optical spectra of the polymers in solution. For the samples of disubstituted acetylene polymer, the solution are transparent and the absorption only occurs in the UV range. This result is in full accordance with the existence of large torsion that reduces the conjugation length down to the monomer unit scale. In spite of the existence of the alternating C=C bond structure on the main chain, we observe an absorption spectrum similar to the one of saturated polymers. Incidentally we show, at least for the substituted polyacetylenes, that the most rigid polymers have the smallest conjugation length.

For the monosubstituted polymers, the relation between the optical absorption and the chain conformation is less straightforward. As already noted in reference [10], the absorption spectrum of poly(o-MePA) and P1 sample have a maximum at a longer wavelength than that of PPA. Similar results have also been observed for other polymers with substituent at the ortho position of phenyl group. Since our main result is that the chain rigidity is governed by the magnitude of the torsion and that a substituent at the ortho position of phenyl group should enhance the average torsion between monomer units, we expect an opposite result.

A possible explanation may be found by considering the stability of the different polymers involved. While poly(o-MePA) and P1 have a very good stability, PPA has a poor stability [1,5]. This is particularly obvious in solution at room temperature, the SANS measurements shows a drastic loss of the molecular weight as a function of time [1]. The existence of more numerous chemical defects for PPA may in part obscure the direct relation between the chain twist, reducing the conjugation length, and the optical properties.

CONCLUSIONS

The study of the chain statistic of soluble substituted polyacetylenes provides a clear picture allowing to secure the description of the local stiffness of conjugated polymers in good solvent. The torsional fluctuations have a sizeable influence on the π electron localization such that polymers with disubstituted units give a visible transparent solution. They are also responsible of the chain rigidity; the conjugated polymers with disubstituted units are more rigid than those with monosubstituted units. Their statistical lengths are approximately twice larger than the ones of polymers built with monosubstituted units. Moreover the polymer with units having a substituent at the ortho position of phenyl group exhibits an intermediate stiffness.

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