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Structural properties of selected poly(azomethines)

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Abstract

Reasonable models for the crystalline structures of unsubstituted poly(azomethine) and methoxy substituted poly(azomethine) are proposed on the basis of X-ray diffraction and computer modeling. Both compounds exhibit a relatively high degree of crystallinity (~30%). The calculated diffraction patterns (almost identical to the experimental ones) show that the polymers investigated crystallize in a pseudomonoclinic or a triclinic lattice. The structural properties of the polymers studied, based on their crystalline structure models, are discussed.

Keywords: Conducting polymers; Poly(azomethines); X-ray diffraction

1. Introduction

Aromatic poly(azomethines) exhibit extremely interesting properties which are associated mainly with their polyconjugated backbone. Thus they show good thermal stability [1] and interesting non-linear optical properties [2,3]. They can also be used as a new type of catalytic support on which catalytically active centers are molecularly dispersed [4,5].

Aromatic poly(azomethines) are isoelectronic with poly(*p*-phenylene vinylenes), which are the most electroluminescent polymers [6]. For this reason they were tested as potential luminescent materials [7]. Unfortunately they are much less efficient than poly(*p*-phenylene vinylenes). Because of strong interchain interactions aromatic poly(azomethines) are very difficult to dissolve. However in recent years significant progress has been made in solution processing of these compounds. Due to the presence of basic sites of the imine type, poly(azomethines) can be complexed with Lewis acids such as $GaCl_3$. The resulting adducts are readily soluble in nitromethane and other nitroalkanes [2,3]. Similarly Bronsted acid–base chemistry can be used for the solubilization of poly(azomethines) [3]. Thus poly(azomethines) protonated with diphenyl phosphate or dicresyl phosphates are soluble in *m*-cresol. The complexed or protonated forms can be used for casting films. The treatment of these films with appropriate Lewis or Bronsted bases leads to pristine (uncomplexed) polymer. As the majority of conjugated polymers undoped poly(azomethines) show a relatively high crystallinity index [8]. In this paper we have undertaken the task of the elucidation of their crystalline structure using computer assisted modeling applied previously with success to other conjugated polymers [9,10]. Two polymers were studied: the simplest unsubstituted aromatic poly(azomethine) and dimethoxy ring substituted poly(azomethine).

2. Experimental

Unsubstituted poly(azomethine) (PPI) of the formula shown in Fig. 1(a) was prepared from *p*-phenylenediamine and terephthalaldehyde according to the method described earlier [11]. Ring substituted poly(azomethine) (PMOPI) of the formula shown in Fig. 1(b) was also obtained by polycondensation from *p*-phenylenediamine and 2,5 dimethoxyterephthaldehyde using the procedure described in detail in Refs. [2,12].

X-ray diffraction patterns were recorded on reflection from powder samples on a wide-angle SEIFERT-FPM XRD-7 diffractometer working in typical Bragg geometry. CuKα radiation was applied.

The experimental diffraction patterns obtained for PPI and PMOPI are presented in Figs. 2 and 3, respectively. These patterns are typical of semi-crystalline polymers

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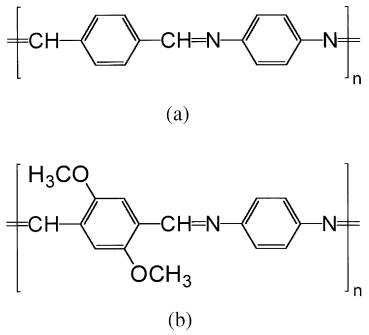

Fig. 1. (a) Formula of unsubstituted poly(azomethine) (PPI); (b) formula of dimethoxysubstituted poly(azomethine) (PMOPI).

and for this reason two components of the diffracted intensity can be easily distinguished: the crystalline one, related to the relatively sharp, Bragg-type reflection peaks, and the amorphous one, present as the broad and low-intense halo. This amorphous component, including the background and the low-angle scattering tail, can be fitted (somewhat arbitrarily) by the sum of a Lorentzian function and an exponential function, and subtracted. The solid lines in Figs. 2 and 3 indicate the amorphous components of PPI and PMOPI, respectively. As a result of this operation, the "pure" crystalline components of both diffractograms were obtained, and then compared with the theoretical results, calculated for the models (see below). Also, according to the method of Hindeleh and Johnson [13], the degree of crystallization for both polymers studied may be estimated, as the ratio of the integrated crystalline component intensity to the integrated total intensity. The following results were obtained: the degree of crystallization is close to 30% for PPI and almost 40% for PMOPI. These values show that the crystallinity of poly(azomethines) investigated in this study is relatively high compared to the typical values determined for other conjugated polymers which rarely exceed 20–30%.

Using Scherrer's formula the average size of the crystalline regions in the polymer can be estimated from the width

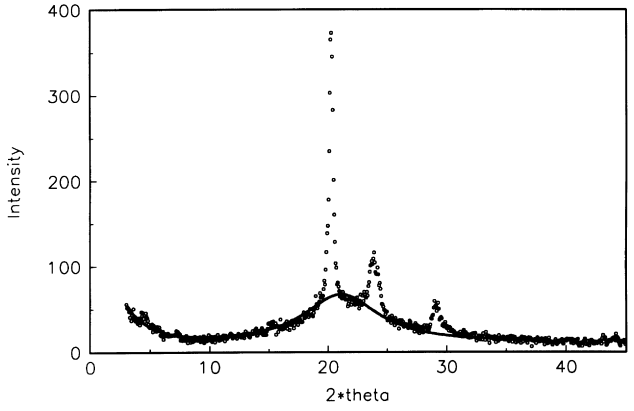

Fig. 2. Experimental diffraction pattern (dots) obtained for PPI. The solid line represents the amorphous component and background (see text).

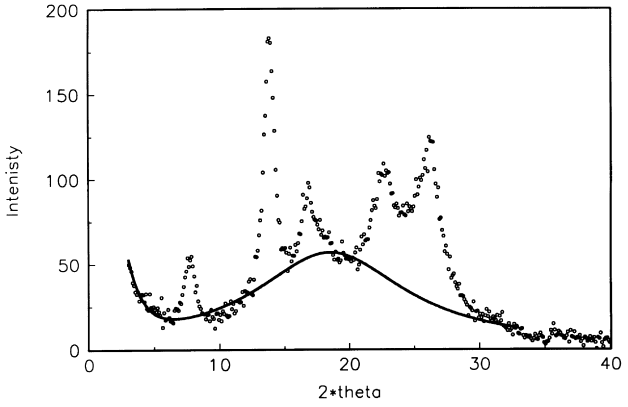

Fig. 3. Experimental diffraction pattern (dots) obtained for PMOPI. The solid line represents the amorphous component and background (see text).

of the crystalline reflections. The observed diffraction peaks are relatively narrow (especially for PPI, in comparison to other conjugated polymers, such as polyaniline), with the FWHM equal 0.4° for PPI and 0.9° for PMOPI. Thus, the average diameters of the crystalline areas are of the order of 100 Å for PMOPI and 200 Å for PPI.

In order to determine the crystalline structure of the polymers studied, we performed computer modeling. Several points have to be taken into account during the construction of the models:

- the chemical structure of both compounds which can be extracted from the literature [12,14];
- the broadening of the reflection peaks due to the crystallite dimensions was incorporated by using the resolution window of the appropriate width;
- due to their low scattering formfactor, all hydrogen atoms were neglected both in the calculations, as well as in the pictures presented below.

The modeling was performed using our own computer program designed for the determination of the poly(azomethines) structure as well as the commercially available POWDERCELL package [15]. None of these programs incorporated any fitting procedure.

For both polymers, the influence of the twisting of the aromatic rings on the calculated diffraction pattern was tested. It turned out that these patterns are fairly insensitive to the twist angle of aniline as well as the benzylidene rings with respect to the C–N=C–C plane. For this reason in the following figures we have sketched flat polymer chains (for obtaining a better clarity of the pictures), having in mind that in reality both types of rings are definitely twisted.

3. Crystalline structure of unsubstituted poly(azomethine)

Because of the same number of electrons in the CH group and in the nitrogen atom, they are indistinguishable

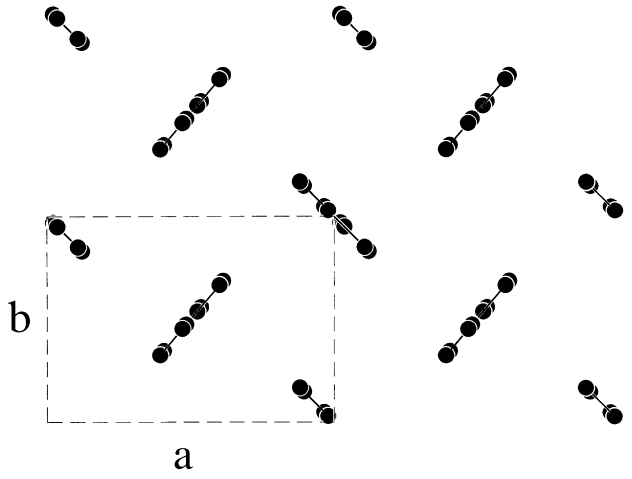

Fig. 4. Model of the crystalline structure of PPI—view along the chains (*c* axis).

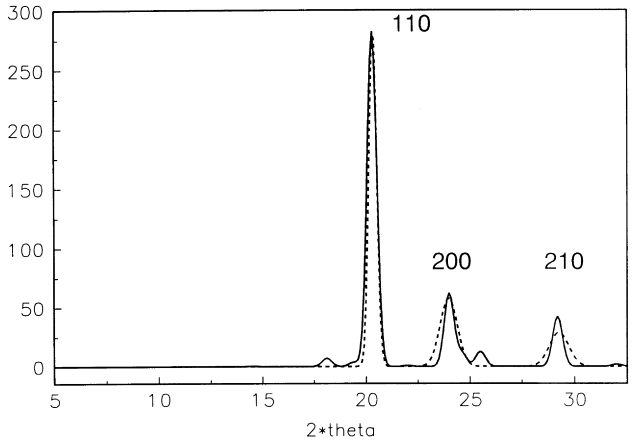

Fig. 6. Diffraction pattern calculated for the model structure of PPI (solid line) and the experimental crystalline component obtained for PPI (dashed line). The numbers give the crystalline indices.

for X-rays and therefore the period along chains (*c* axis) is shortened twice. This assumption is well confirmed by the fact, that in the experimental diffraction pattern obtained for PPI the reflection related to the expected repetition distance (~12.2 Å) is absent due to the extinction rule. The model of the crystalline structure of PPI is described by a pseudomonoclinic unit cell with the following parameters: $a = 7.42$, $b = 5.39$, $c = 6.11$ Å, $\beta = 94°$. The unit cell consists of two parallel polymer chains: the first one is located on the edge of the unit cell, and the second one in its center. Both chains are tilted in the opposite directions with an angle equal ~35–40° (see Fig. 4). Such an arrangement of the polymer chains is quite common for many polymers (e.g. polyethylene), because it allows to obtain a well packed system with appropriate distances between the adjacent macromolecules. The calculated density is equal 1.31 g/cm^3, which is a reasonable value.

Fig. 5 shows the arrangement of the polymer chains in the perpendicular direction. It is demonstrated that every second chain is shifted along the *c* axis by a distance equal to half of the lattice constant in this direction. Such a displacement significantly improves the packing as it gives a larger free volume to the relatively bulky rings.

The comparison of the calculated diffraction pattern with the experimental crystalline component is presented in Fig. 6. The numbers give the crystalline indices. The agreement between both curves allows us to state that the proposed model describes the real structure of PPI well.

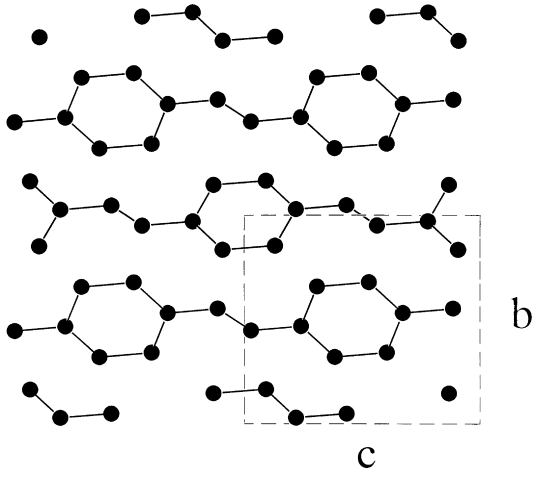

Fig. 5. Model of the crystalline structure of PPI—view in the direction perpendicular to the chains (along the *a* axis).

4. Crystalline structure of methoxy substituted poly(azomethine)

In this case there exist no reasons for the shortening of the repetition distance along the polymer chains, because the two adjacent rings are distinctly different due to the presence of the methoxy substituents in the benzylidene one. Indeed, the Bragg reflection related to the expected distance appears in the experimental diffraction pattern. Both the lower symmetry of the polymer backbone as well as the larger number of diffraction peaks suggests a lower symmetry of the crystalline structure of PMOPI. Indeed, the results of the computer modeling show that its structure can be described by the triclinic unit cell with the following parameters: $a = 7.47$, $b = 7.93$, $c = 12.40$ Å, $\alpha =$

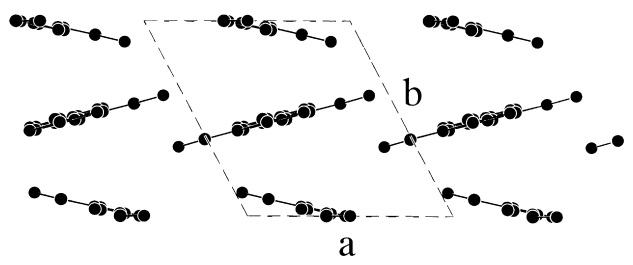

Fig. 7. Model of the crystalline structure of PMOPI—view along the chains (*c* axis).

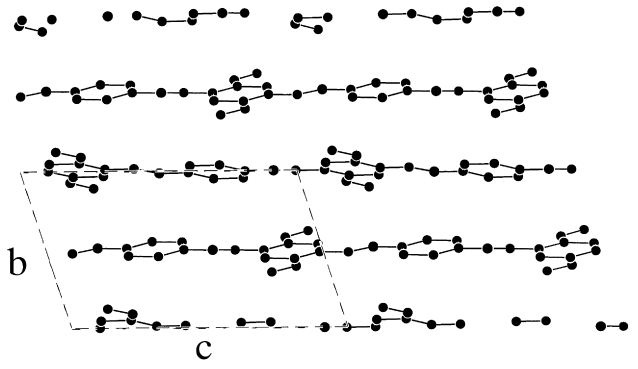

Fig. 8. Model of the crystalline structure of PMOPI—view in the direction perpendicular to the chains (along the *a* axis).

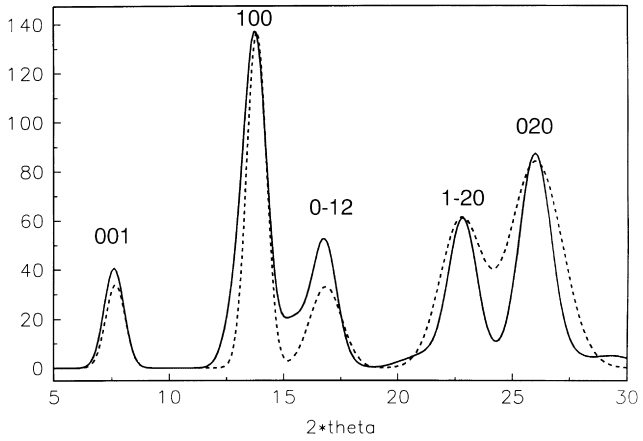

Fig. 9. Diffraction pattern calculated for the model structure of PMOPI (*solid line*) and the experimental crystalline component obtained for PMOPI (*dashed line*). The numbers give the crystalline indices.

100, $\beta = 102$ and $\gamma = 115°$. The calculated density is equal 1.35 g/cm^3. The structure consists of two types of polymer chain layers and in each layer the chains are tilted in the opposite directions with an angle equal ~20° (see Fig. 7). The view of the structure along the *a* axis (shown in Fig. 8) demonstrates that in this case also every second polymer layer is shifted along the direction of the polymer chains, which is caused by the necessity of finding enough empty space for the bulky methoxy group. Such an arrangement of the polymer chains allows us to fulfil the condition concerning the sufficient distances between atoms from the adjacent macromolecules, which is not easy in this case.

The diffraction pattern calculated for this model is compared with the experimental data in Fig. 9. The agreement between both curves may not be perfect in this case, however, one can suggest that the proposed model explains the basic features of the PMOPI crystalline structure quite well.

5. Discussion and conclusions

The crystalline structures of PPI and PMOPI were determined by the use of X-ray diffraction and computer modeling. Both systems exhibit a remarkably high degree of crystallinity and quite large average dimensions in their crystalline regions. In this sense they are very different from poly(*p*-phenylene vinylene) (PPV), which is isoelectronic with PPI, but is a much less ordered system—in general PPV is almost amorphous.

Unfortunately, very low solubility of both polymers is a major problem in any future applications, and in making use of their high crystallinity.

In this work it was shown once more, that computer modeling is a very powerful tool for crystal structure determination of complex polymer systems, for which the common crystallographic procedures (including fitting procedures, e.g. Rietveld's types) are not useful, because of the large number of atoms within a unit cell and a very small number of experimental diffraction peaks. However, one should realize, that the models obtained in such a way are only hypothetical (they are not unique) and they can be replaced by other models, for which the agreement between the calculated diffraction patterns with the experimental ones would be very good or even better.

Acknowledgements

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