A neutron reflectometry study of the production of thin polyphenylene films from precursor polymer

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(*Received 12 August 1991; revised 28 October 1991; accepted 23 January 1992*)

Neutron reflectometry has been used to study the formation of thin polyphenylene films produced by the aromatization of poly(5,6-*cis*-diacetocyclohexa-1,3-diene). It has been found that the process results in the production of films with non-uniform density in a direction normal to the surface. In addition, the aromatized films are found to have a much higher surface roughness than the precursor polymer film. This has been attributed to the disrupting effect of the volatile products of aromatization.

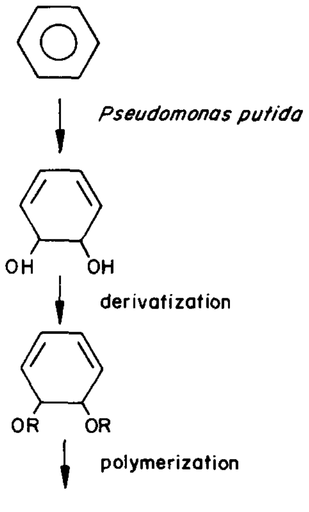
(Keywords: polyphenylene; neutron reflectometry; aromatization; thin films; precursor polymer)

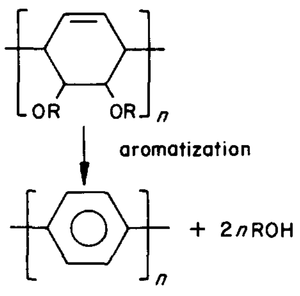
INTRODUCTION

Polyphenylene

It has recently been demonstrated that polyphenylene (PP), a rigid-rod-like polymer, may be synthesized from precursor polymer obtained initially from a biologically produced monomer[1].

Schematically, the process may be represented in the following manner:





The particular advantage of this route is that the precursor polymers (typically $R = CH_3CO$, CH_3OCO, etc.) are soluble in a range of common organic solvents. This facilitates the production of thin films by conventional processes such as spin coating or screen printing, which may then be aromatized to the intractable product, polyphenylene. Typical aromatization conditions employed in this final step involve heating to 400°C in an inert atmosphere for 5 min, although lower temperatures may be used at the sacrifice of longer aromatization times.

The process results in the production of a leaving group, typically an organic acid, which is volatile at these high aromatization temperatures. The escape of this product from a thin polymer film in which the polymer is simultaneously making the transition from a random coil to a rigid rod poses some interesting questions about the physical nature of the final film.

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0032-3861/92/194141-04

Neutron reflectometry

The theory of neutron reflectometry has been described in full detail in numerous references (e.g. ref. 2) and will not be repeated here. The neutron reflectivity of a sample consisting of discrete layers can be calculated using standard optical methods. Each layer is described by its thickness and its neutron scattering length density (*NSLD*) where:

$$NSLD = \frac{N_A b \rho}{MW} \qquad (1)$$

where N_A = Avogadro's number, b = the total neutron scattering length, ρ = the physical density (g cm^{-3}) and MW = the molecular weight.

Departures from ideality arising from surface roughness and interfacial diffuseness can be readily included by replacing the step-function change in *NSLD* between layers by a Gaussian distribution of width σ.

The technique thus provides information about isotopic composition and/or physical density normal to an interface.

Inversion of the measured data to extract *NSLD* profiles is not generally possible. Consequently, analysis usually proceeds by fitting model profiles to the data with iterative adjustment of layer thickness, *NSLD* and interfacial roughness until acceptable agreement with the experimentally observed reflectivity is achieved.

EXPERIMENTAL

The precursor polymer (PPP) used in this study was obtained from the diacetate derivative of *cis*-dihydrocatechol. The degree of polymerization was approximately 500.

Samples were prepared by spin coating a 16% w/w solution of precursor polymer dissolved in *N*-methyl-2-pyrrolidone onto optically polished silica microscope slides using a Headway Research Inc. model 1-EC101D photo-resist spinner. Spinning solutions were filtered through 0.5 μm PTFE membrane filters and the process was undertaken in a clean air Class 100 cabinet. The slides were flooded with solution, the excess spun off at 1000 rpm and then accelerated to 6000 rpm over 2 min. The films were then dried in an air-circulated oven for 30 min at 170°C. An approximate measure of layer thickness was obtained by profilometry (X-step model 200) on films lightly scratched with a scalpel.

Samples were prepared using identical spinning procedures and aromatized to varying degrees under previously determined conditions. Samples were aromatized in a stream of dry nitrogen in a temperature-programmed furnace (Thermco Mini-Brute). Duplicate samples were prepared on microscope slides previously sputtered with a thin layer of gold to enable specular reflectance *FT*i.r. to be undertaken. A Nicolet 5ZDX *FT*i.r. instrument with a fixed-angle (80°) reflectance attachment (Spectra-Tech) was used.

The actual degrees of aromatization achieved were then checked by i.r. spectroscopy utilizing the characteristic carbonyl stretch of the precursor polymer at 1750 cm^{-1} and the *para*-CH at 810 cm^{-1} (two pairs of adjacent hydrogens) in the polyphenylene units produced.

Neutron reflectivity measurements were made using the CRISP spectrometer at the Rutherford Appleton Laboratory[4]. The reflectivity profiles were measured at an incident angle of 0.33° using neutrons in the wavelength range 2–6.4 Å.

The data were analysed by the time-of-flight method to produce plots of reflectivity *versus* wavelength. These reflectivity profiles were then modelled using Abeles' method[3,5,6] and the parameters refined using the method of incremental parameter variation. It has been found that this simple method is very effective in locating a good solution from an initially poor starting point and provides a useful alternative to non-linear least-squares refinement.

RESULTS AND DISCUSSION

The samples prepared for study by neutron reflectometry are detailed in *Table 1*. Aromatization results in a reduction in film thickness of about 70–80%. Therefore, a fairly thick film, by neutron reflectometry standards, of about 3000 Å was prepared for the precursor film so that subsequent partially and fully aromatized films would fall into a thickness range more ideally suited to study.

The reflectivity profile for the unaromatized starting material is shown in *Figure 1*. The interference fringes of this thick film are well resolved and enable an unambiguous determination of the model parameters. These are given in *Table 2*. The interfacial roughness parameter relating to the polymer/substrate interface was found to be the same as the surface roughness obtained for the bare substrate. In order to reduce the number of variable parameters in the remaining samples, this factor was fixed at this value. Similarly, the instrumental

Table 1 Sample details

Sample code	Aromatization conditions	Aromatization (%) by i.r.	Layer thickness[a] (Å)
PPP	–	0	3000
PP400/5	400°C/5 min	100	660
PP300/30	300°C/30 min	38	2400
PP300/60	300°C/60 min	66	1930
PP300/120	300°C/120 min	98	1310
PP300/360	300°C/360 min	99	990

[a] As measured by profilometry

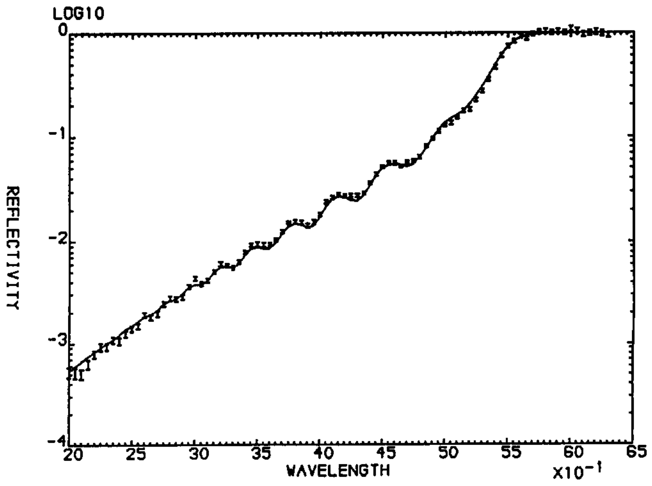

Figure 1 Reflectivity profile for sample PPP. The experimental data are indicated by the error bars. The full curve represents the best calculated fit to these data according to the parameters given in *Table 2*

Table 2 Parameters for precursor polymer corresponding to best fit to data: dθ = angular resolution, nb_x = neutron scattering length of layer x (s = substrate), σ_{xy} = interfacial roughness between layers x and y (0 = air), d_x = thickness of layer x

dθ	nb_s (Å^{-2})	σ_{01} (Å)	d_1 (Å)	nb_1 (Å^{-2})	σ_{12} (Å)
5.8%	0.343×10^{-5}	11	3352	0.160×10^{-5}	20

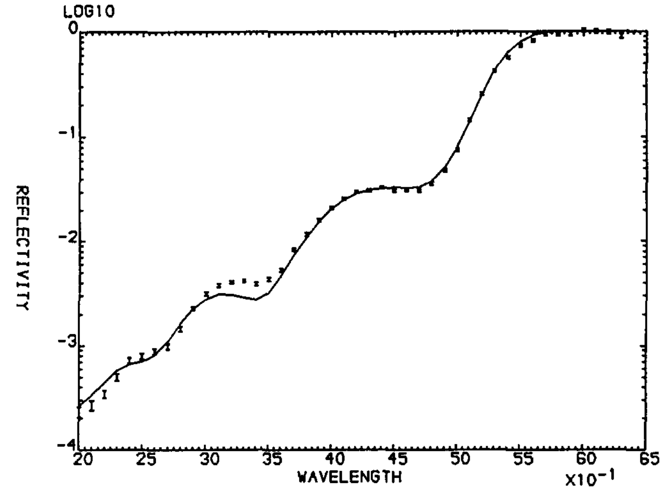

Figure 2 Reflectivity profile for sample PP400/5. The full curve represents the best fit obtained using a single-layer model

resolution factor, dθ, which is also sensitive to macroscopic sample flatness, was constrained to 6.5 ± 1.0%.

The *NSLD* of the precursor polymer was found to be in close agreement with the calculated value, indicating that the film density is similar to that of bulk polymer (1.16 g cm^{-3}).

The calculated *NSLD* of polyphenylene is about 14% larger than the precursor polymer on the basis of isotopic composition alone. However, it is known that, while the precursor is amorphous, the aromatized product can crystallize, leading to an even greater anticipated difference in *NSLD*.

Figure 2 shows the reflectivity profile obtained for the fully aromatized sample PP400/5. The reduction in film thickness expected from the loss of mass is clearly evident from the lower frequency of the interference fringes. However, repeated attempts to fit these data with a simple model of a single layer on a substrate yielded only poor agreement such as that illustrated in the figure.

In order to fit these data it was necessary to invoke a model in which the polymer film was represented by two layers of differing *NSLD*. This approach yielded the much more satisfactory fit to the data shown in *Figure 3*. The parameters corresponding to this fit are given in *Table 3*.

There are several points worthy of comment with regard to this model. First, it will be observed that the lower half (layer 2) of the film has a *NSLD* very close to that of the precursor polymer. One possible explanation for this could therefore be that only the top half of the film is aromatized. However, this can be discounted by the absence of any carbonyl stretch bands in the i.r. spectrum of this sample. Rather, it would seem that the bottom half of the film consists of polyphenylene of substantially lower physical density than the top half (0.82 g cm^{-3} compared to 1.08 g cm^{-3}). It is interesting to note that the theoretical maximum possible density for polyphenylene calculated from the contents of the unit cell is 1.33 g cm^{-3} (ref. 7).

The next feature of interest in this model is the value obtained for the surface roughness of 83 Å. This high value should be compared with the 11 Å obtained for the precursor film. The originally fairly smooth surface of the precursor film has presumably been disrupted by the escape of acetic acid during aromatization at 400°C.

The value obtained for the interfacial diffuseness between the top and bottom halves of the polymer film and the precise layer thicknesses are impossible to determine with certainty. However, it is clear that the interface is very diffuse as interference effects that may be expected to arise from it are entirely suppressed. Indeed, the model should be interpreted as representing a polymer film in which there is a density gradient normal to the surfce. It was regarded as inappropriate to attempt to model the form of this profile more accurately due to the absence of higher-resolution data. The model we have chosen fits the data to the resolution collected and we feel gives a better representation of the shape of the profile than one based on invoking an arbitrary function.

In order to understand better how the density profile of these polyphenylene films develops, a study of the partially aromatized samples listed in *Table 1* was made. A lower aromatization temperature of 300°C was used in this series of samples. This has the effect of slowing down the process sufficiently to exercise better control over the production of partially aromatized films. Fits to these reflectivity profiles similar in quality to those of *Figures 1* and *3* were obtained and details of the parameters derived are given in *Table 4*. It was found that, as aromatization proceeds, the *NSLD* initially drops from 1.60×10^{-6} Å^{-2} to approximately 1.30×10^{-6} Å^{-2}. This occurs probably due to the polymer swelling in the presence of hot, gaseous acetic acid. The surface roughness is also observed to increase rapidly to high values.

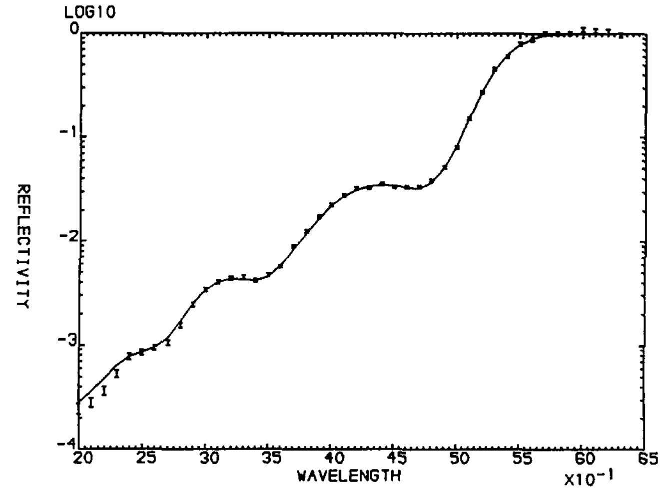

Figure 3 Reflectivity profile for sample PP400/5. The full curve represents the best fit obtained using a two-layer model as given in *Table 3*

Table 3 Two-layer parameter fit to PP400/5

nb_s (Å^{-2})	σ_{01} (Å)	d_1 (Å)	nb_1 (Å^{-2})	σ_{12} (Å)	d_2 (Å)	nb_2 (Å^{-2})	σ_{23} (Å)
0.348×10^{-5}	83	388	0.214×10^{-5}	82	489	0.162×10^{-5}	20

Table 4 Details of final fits to reflectivity data

Sample code	σ_{01} (Å)	d_1 (Å)	nb_1 (Å^{-2})	σ_{12} (Å)	d_2 (Å)	nb_2 (Å^{-2})	σ_{23} (Å)
PP300/30	95	2289	0.129×10^{-5}	40	–	–	–
PP300/60	106	1795	0.130×10^{-5}	20	–	–	–
PP300/120	135	1210	0.125×10^{-5}	20	–	–	–
PP300/360	93	511	0.245×10^{-5}	105	557	0.159×10^{-5}	20

It is only when the degree of aromatization approaches 100% that the film settles down, forming a higher-density top layer with a slightly smoother surface. In this case, the much slower aromatization results in the production of a surface layer of rather higher density than was found for sample PP400/5. In this instance the density of the polyphenylene nearer the surface is found to be 1.24 g cm^{-3}. The likelihood is that this represents a largely crystalline form of polyphenylene forming a sort of skin over a lower layer of severely disordered polymer, which may contain considerable voiding.

CONCLUSION

It has been demonstrated that neutron reflectometry can be used to yield a detailed description of the aromatization of precursor polymer films to form polyphenylene. Despite the complexity of the processes involved, the experimental reflectivity profiles may be reproduced using relatively simple but informative models.

ACKNOWLEDGEMENTS

The authors gratefully ackowledge valuable discussions with Dr P. A. Holmes and Dr J. Nehring.

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