Macromolecules

ARTICLE

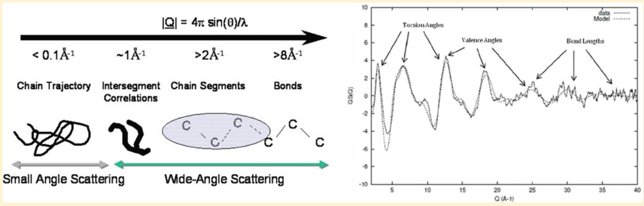
pubs.acs.org/Macromolecules

Three Dimensional Picture of the Local Structure of 1,4-Polybutadiene from a Complete Atomistic Model and Neutron Scattering Data

Thomas Gkourmpis*,§ and Geoffrey R. Mitchell

Polymer Science Centre, J. J. Thomson Physical Laboratory, Department of Physics, University of Reading, Reading, RG6 6AF, U.K.

ABSTRACT: An efficient method of combining neutron diffraction data over an extended Q range with detailed atomistic models is presented. A quantitative and qualitative mapping of the organization of the chain conformation in both glass and liquid phase has been performed. The proposed structural refinement method is based on the exploitation of the intrachain features of the diffraction pattern by the use of internal coordinates for bond lengths, valence angles and torsion rotations. Models are built stochastically by assignment of these internal coordinates from probability distributions with limited variable parameters. Variation of these parameters is used in the construction of models that minimize the differences between the observed and calculated structure factors. A series of neutron scattering data of 1,4-polybutadiene at the region 20−320 K is presented. Analysis of the experimental data yield bond lengths for C−C and C═C of 1.54 and 1.35 Å respectively. Valence angles of the backbone were found to be at 112° and 122.8° for the C−C−C and C−C═C respectively. Three torsion angles corresponding to the double bond and the adjacent α and β bonds were found to occupy *cis* and *trans*, s±, *trans* and g± and *trans* states, respectively. We compare our results with theoretical predictions, computer simulations, RIS models, and previously reported experimental results.



INTRODUCTION

Within a polymer chain, a wide range of length scales exist, each of which exhibits its own properties and special characteristics. The shortest of those length scales can be associated with the chemical structure, as it is seen through the local organization of chain segments. The chain trajectory can be seen as a continuous assembly of those segments. By restricting the analysis in homogeneous on the large scale materials, the length scales of the order 0.1−100 Å can be considered as the region of the local structure. The reciprocal Q ($Q = 4\pi \sin \theta/\lambda$, where 2θ is the scattering angle and λ is the incident wavelength) space is used, to reflect on the formalism used in broad Q X-ray and neutron scattering experiments.

In macromolecules the basic building block is the chemical bond, and the freedom of rotation it enjoys gives rise to the rich and unique polymeric structures. Usually torsion rotations for particular bonds are treated in terms of rotation states,[1,2] although this is not restrictive and in principle a large number of such states can be considered. The chain segment can be thought as a part of the chain over which the local properties (chain conformation) can be assumed to be broadly constant.[3]

Scattering techniques represent a valuable tool in the experimental determination of the local structure and chain conformation of amorphous polymers. Despite the fact that a wide range of experimental data on glassy and liquid polymers have been obtained, the majority of scattering studies is concentrated in the role of dynamics of the glass transition[4] and the large scale properties probed by SANS.[5] Most of the broad Q scattering studies of amorphous polymers, probing the details of the local conformation have been made for a number of polymeric systems,[6,7] using wide-angle X-ray scattering techniques. In recent years diffraction techniques using pulsed neutron sources have become available. Neutrons due to their high penetration and their capability to see light atoms like hydrogen using selective deuterium labeling, offer a unique opportunity to probe structural features over an extended reciprocal range. The spatial resolution using neutron scattering is much higher than the one traditionally seen in X-ray sources.

The experimentally observed structure factor from both neutrons and X-rays consists of a wide range of correlations. These structural correlations can be separated in to those arising from correlations within the chain (intrachain) and those arising by different chains (interchain).[6] The interchain correlations yield information on the extent and type of packing in the bulk. The intrachain contribution to the scattering can be extracted from the observed structure factor at values of the momentum transfer $Q \geq 2-2.5$ Å^{-1}, using atomistic modeling techniques.

Polybutadiene is a material of vital importance to rubber industry and technology due to its simple microstructure, well-defined chemical characteristics and low glass transition temperature. Using a range of polymerization techniques different microstructures of linear (1,4) and vinyl (1,2) chains can be produced. Although dynamic and relaxation properties of molten and glass 1,4-polybutadiene have been extensivelly studied through dielectric spectroscopy,[8,9]

Received: December 20, 2010
Revised: March 2, 2011
Published: March 23, 2011

ACS Publications © 2011 American Chemical Society

dx.doi.org/10.1021/ma102840p | *Macromolecules* 2011, 44, 3140–3148

NMR spin−lattice relaxation[10,11] and various neutron scattering methods[12−17] there is a lack of published information with respect to the conformational characteristics in the bulk.

The rotational isomeric state of polybutadiene is based on models developed by Flory[18] and Mark.[19,20] Both these models were developed for a single conformation of the rotational state of the double bond C═C, and it is assumed that there is no important coupling between conformations on either side of it. In the case of 1,4-*cis*-polybutadiene though Mark[19] assumes the existence of strong coupling between the pairs of the α bonds in their *trans* state on either side of the double bond. Recent quantum mechanical calculations though could not confirm this.[21] Both simulations[21] and RIS models[18−20] indicate the existence of strong second-order interactions in the $\alpha\beta\alpha$ conformations.

In this study a wide temperature range covering most of the experimentally accessible glass and liquid regime of 1,4-polybutadiene was performed, using broad Q neutron scattering. Intrachain correlations reflecting the chain conformation were extracted using a structural refinement technique, giving a picture of the changes on the local conformation as a function of temperature. The technique's output is compared with previously reported computer simulations, force field predictions based on quantum mechanical and RIS-based calculations and experimental data.

■ MODELING TECHNIQUE

Basics. The basic problem in a broad Q scattering experiment lies in the intrinsic difficulty of extracting structural information from the diffuse diffraction pattern. The Fourier transform of the structure factor can provide information on high confidence, concerning the near neighbor distances. The intrachain region of the scattering that contains all the information regarding the conformational characteristics of the chain remains hidden.

An alternative way of extracting the relevant information is by direct comparison of the experimental data to computer generated statistical models. The basic idea of this approach is that if the radial distribution function can be reconstructed and directly compared with the actual data a large volume of structural parameters can be probed and their effect on the scattering pattern can be established.

Model Generation. A fully atomistic model is generated as a single chain containing 15 000 skeletal bonds, using the in-house software package *MESA*[22] developed in the University of Reading, Reading, U.K. Each atom is assigned a set of internal coordinates defining the chain conformation in terms of bond length, valence angle and torsion rotation. The conformational characteristics of interest in this case are of intrachain origin only. The chain in the model is build using a stochastic Monte Carlo method, leading to a number of different initial configurations, without taking into account the excluded volume. Ignoring the excluded volume is based on the Flory Principle that chains in the melt are unperturbed and their structural characteristics can be considered to be the sum of all possible configurations of a single chain.[23] Also by ignoring the excluded volume we could have faster computing times and convergence. After the chain is built all the interatomic distances are computed and the diffraction pattern is calculated using Debye's relationship[24]

$$S_C(Q) = \frac{1}{N}\sum_i \sum_{i \neq j} b_i b_j \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

with b_i, b_j the scattering lengths of atoms i and j, N the total number of atoms in the model, Q the reciprocal space wavevector, and r_{ij} the real space vector between atoms i and j. Since the correlations of interest are those of intrachain origin a window function was employed to exclude distant correlations that slow calculations and not contribute significantly to the structure factor. The window function calculates the interatomic distances of all atoms separated by less than a preset number of bonds and its use leads also to faster computation times. The use of a number of skeletal bonds rather than a simple radial distance means that the parameter, the number of bonds is directly related to the extent of intrachain correlations. The function is not a convolution, but simply a constraint on the atom pairs included in the calculation. Selection of the number of skeletal bonds is part of the multiparameter optimization. Clearly the window size needs to be longer than the correlation length along the chain. Initial estimates were based on the evaluation of the structure factor.

The experimental data used in this study were collected over a substantial period of time and they are assumed of having just systematic errors arising from the instrumentation. The experimental resolution for the SANDALS spectrometer $\Delta Q/Q \approx 4\%$. This constancy is typical for a time-of-flight instrument and applies to all scattering angles having an impact on the collected data. For this reason the calculated structure factor was smeared with a Gaussian function of width proportional to Q to simulate the average experimental resolution.

The scattering calculated from the model is *only* this of intrachain origin, and can then be compared with the one obtained by the diffraction measurement (only in the part of the curve that corresponds to intrachain correlations) and in order to ensure the impartiality of the test since the differences are very difficult to be seen with a naked eye a statistical χ^2 test was used

$$\chi^2 = \frac{1}{n}\sum_{i=1}^{n} [Q_i S_C(Q) - Q_i S_E(Q)]^2$$

with the subscripts C and E corresponding to the scattering from the model and the experimental data respectively, and n is the number of points considered. The experimental data that enter the χ^2 expression is dicretisised as a consequence of the binning process of the many detectors[26] (1070 at the time of the experiment). The calculated function is in principle available as a continuous function. However, due to the need for a speedy computation process to allow many models to be considered, we calculate the structure factor by fast Fourier transform techniques[22] which yield a discrete set of calculation points. Furthermore, the interatomic distances were binned; thus, the χ^2 relationship is a calculation between two discrete and not continuous functions.

The χ^2 test can give information on the impact the different length scales have on the scattering pattern, allowing the association of different parameters with different regions of the scattering. Having created the initial configuration the scattering is calculated and compared with the experimental data by means of the χ^2 test. By changing one chosen parameter at the time keeping all others to their initial values a number of possible configurations (models) can be explored and compared directly and quantitatively with the observed scattering pattern. The parameter's value that corresponds to the minimum value of the χ^2 test can then be inserted in the model as an initial value and another parameter can be searched in an iterative manner. Initially the "best fit" is quite broad and only the vicinity of the minima is identified, but as the search intervals become smaller a far better accuracy is obtained. This procedure continues until all parameters are searched and the statistical test result remains constant.

A version[25] of this procedure has been tried in the past for simpler polymers like polyethylene[26] and polytetrafluoroethylene (PTFE)[27] with a single chemical repeating unit with promising results. In this study we are applying this methodology to a much more complex and structurally inhomogeneous system like the polybutadiene.

■ EXPERIMENTAL SECTION

Fully deuterated (>99%) 1,4-polybutadiene $M_n = 75000$, $M_w = 79500$ was obtained by Polymersource Inc. in Canada. NMR analysis provided by the supplier gave a system of 37.1% and 55.9% 1,4-*cis* and -*trans* content respectively with 7% 1,2-polybutadiene. DSC analysis gave a glass transition of 170.15 K. The sample was dissolved in cyclohexane and casted into an aluminum container of 1 mm thickness and 36 mm diameter. All samples were left to dry under atmospheric pressure and vacuum for 48 h and solvent evaporation was checked by continuous weighting. As soon as the samples weight reached a constant value it was assumed that the majority of the solvent has been extracted. Neutron scattering measurements were performed in the ISIS Pulsed Neutron Source in the UK using SANDALS diffractometer.[26] Temperature control was achieved by a CCR cryogenic unit with temperature fluctuations of the order of ±2°, and all data were collected for a minimum of 500 to a maximum of 3500 μA integrated proton current (3.5−15 h).

Data collected in all 18 detector banks were normalized to the incident neutron beam and calibrated by a standard vanadium sample provided by the facility. Corrections for absorption, multiple and self-scattering, and attenuation were performed using the ATLAS data analysis routine.[27] Finally, the fully corrected data of each individual detector bank were merged to a total structure factor $S(Q)$.

■ RESULTS AND DISCUSSION

Neutron Scattering. Neutron scattering data for 1,4-polybutadiene were collected at a temperature range of 20−320 K covering a large part of the liquid and glassy regime. In Figure 1, the total structure factors in the glassy and liquid state can be seen. From these patterns, we can see that except for the main scattering peak (see inset in Figure 1) the rest of the pattern remains largely unchanged throughout the temperature range. This behavior can be associated with the two distinct areas of the diffraction pattern dominated by the interchain and intrachain scattering. In the area of the main peak (1−2 Å^{-1}) the scattering is dominated by interactions between segments of the same or different chains. Therefore, changes in this region indicate changes in the packing of the polymer in the bulk. The rest of the diffraction pattern is dominated by scattering between atoms joined by covalent bonds and the changes in that region cannot be directly observed from the relative changes in the pattern. By performing nonlinear peak fitting using a Gaussian function,[22] the relative position and width of the main scattering peak as a function of temperature can be deduced and the results are presented in Figures 2 and 3. From these figures the crossover between the liquid and glassy regime can be clearly seen and the intersection of the two fitting lines to the experimental data can be associated with the glass transition temperature. The experiment yields a value of approximately 175 K that is in very good agreement with values reported in the literature[4,12,30−32] and the value measured by DSC. The position and width of the peak as well as the total structure factor are in good agreement with previous reported data on a limited Q scale.[33−35] The change in the width of the main peak indicates the extent of the spatial correlations in the polymer and the change in position indicates changes in the distances between the elements that generate the scattering process (i.e. the chain segments). We can therefore associate the slope in the peak position as a function of temperature with the thermal expansion coefficient, and the experimental data yield a slope value of 6.634×10^{-4} K^{-1} that is in good agreement with values of thermal expansion coefficient reported for 1,4-*cis*-polybutadiene (6.63×10^{-4} K^{-1}),[36] for a copolymer of *cis*−*trans* 1,4-polybutadiene and vinyl 1,2 (7.5×10^{-4} K^{-1})[37] and from a molecular dynamics simulation(5.2×10^{-4} K^{-1}).[38] From the actual experimental results, using the

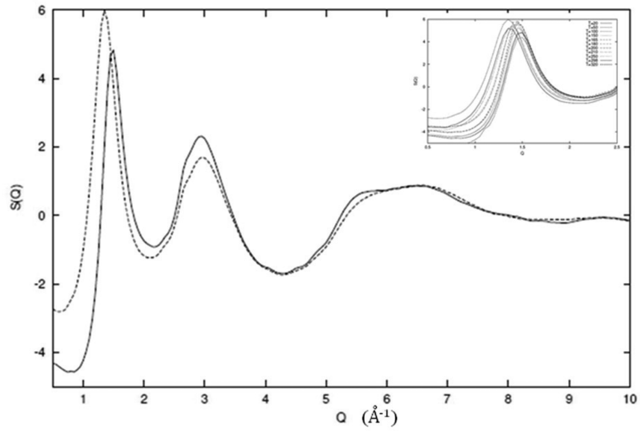


Figure 1. Neutron diffraction data for 1,4-polybutadiene in the liquid (320 K, solid line) and glassy regime (20 K, dotted line). Differences between the two structure factors are seen in the low Q region indicating differences in segmental mobility and packing in the bulk, something that can be seen from the inset where the first intense peak of the same pattern for all the different temperatures is presented. The high Q region pattern, corresponding to the local conformation is virtually unchanged.

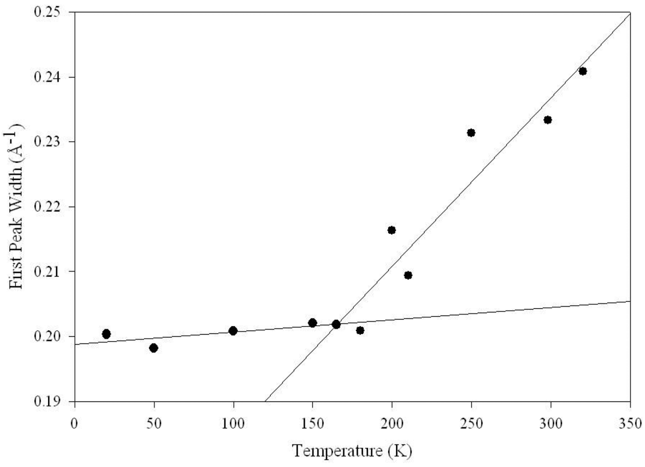


Figure 2. Width of the first intense peak of the diffraction pattern as a function of temperature (points). The solid lines have been added to facilitate the distinction between the glassy and liquid regime.

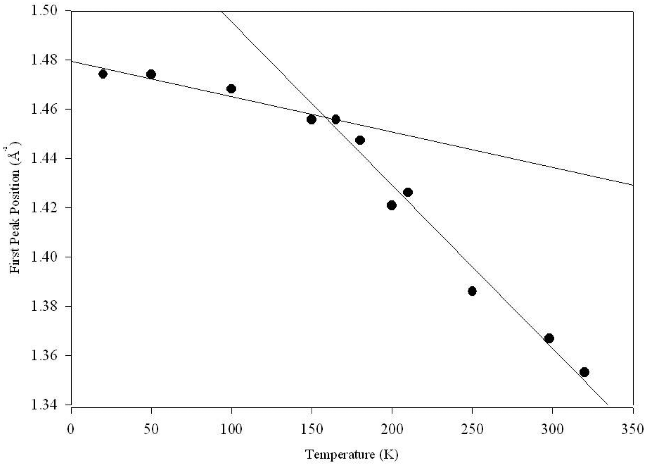


Figure 3. Peak position (points) of the first intense peak of the diffraction pattern of 1,4-polybutadine as a function of temperature. Liquid and glassy regimes can be identified by the crossover of the solid lines fitted to the data.

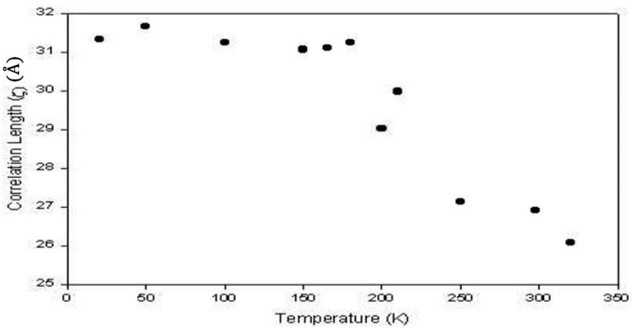


Figure 4. Correlation length ζ calculated from the width of the main scattering peak of 1,4-polybutadiene as a function of temperature. The different regimes (glassy and liquid) are visible with the value of the correlation length increasing with decreasing temperature and adopting an almost stable behavior below the glass transition.

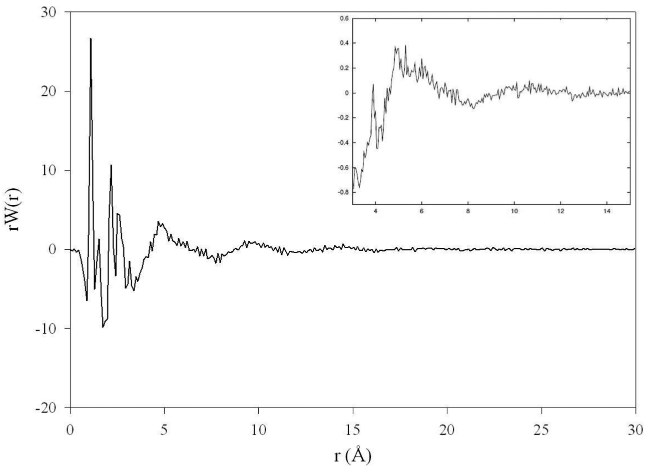


Figure 5. Radial distribution function for 1,4-polybutadiene obtained from neutron scattering experiment. The inset highlights the high r region.

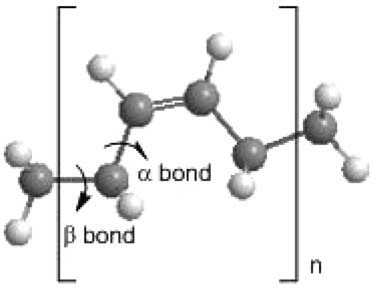
width of the main scattering peak we have calculated the correlation length. The change in position and width of the main scattering peak can be associated with interchain contribution to the polymer. The thermal change in the liquid phase is much larger than in the glassy region and by assuming that the width σ of the intersegmental peak arises from the distribution of the near-neighbor distances, the correlation length ζ can be defined as $\zeta = 4\pi/\sigma$. In the case of our experimental data the correlation length is seen (Figure 4) to decrease with increasing temperature, whereas below the glass transition it adopts an almost constant value of approximately 31.5 Å. Our calculation is based on the method of Frick, Richter, and Ritter[13] and our result is in good agreement with their reported value of approximately 34 Å for materials of similar molecular weight.

The second step in the structural analysis comes with the mathematical manipulation of the data by means of a Fourier transformation and the radial distribution function can be obtained. In Figure 5, the radial distribution function obtained from the experimental data can be seen. From this data set peaks at 1.1, 1.34, 1.51, and 1.54 Å correspond to C$-$D, C$=$C, $=$C$-$C, and C$-$C distances, and the results are in agreement with the ones reported previously.[38,39] Analysis of the radial distribution function to a series of pair correlation functions in a manner similar to the work done by Kim, Misra, and Mattice[40] exhibit peaks at 2.5 Å corresponding to the distance of two carbons separated by two bonds, 2.2 Å corresponding to C$-$D pairs not covalently bonded at neighboring atoms and 1.8 Å corresponding to the distance between two deuterium atoms connected to the same carbon atom. Peaks at larger distances arise from the conformational preferences of the chain. A broad peak at approximately 5 Å and almost no peaks after 7 Å are in good agreement with previously reported results.[47]

So far, we explored the information obtained by observation of the experimental data and by their mathematical manipulation in the form of the radial distribution function. Although the real space analysis yields information concerning the very localized topology, understanding of the chain conformation is still unattainable. One way to extract this vital piece of information is to "reconstruct" the radial distribution function using a computer model and compare the scattering with the experimental observation. The initial polybutadiene model was built as a single chain consisting of 15 000 atoms, and during the preliminary stages of this study the initial configuration was found to be totally independent of the final converged structure. Therefore, to speed up the computation time we started with a model based on RIS prediction of Flory[18] and Mark,[19,20] with equal proportions of *cis* and *trans* conformations around the double bond, a triple state of *cis*, $g\pm$ (180°, $\pm$60°) for the α bond[41-43] and *trans*, $s\pm$ (0°, $\pm$120°) for the β bonds (Chart 1). A vinyl 1,2 fraction of 7% per the NMR measurements was included in the calculation, distributed along the backbone in a random manner. Figure 6 shows the comparison of the initial model with the experimental data, and although the basic features of the scattering curve are represented there is a lack in the quantitative prediction of the relevant widths and intensities of the scattering peaks.

After this initial step, the structural refinement started by allowing one parameter at the time to be scanned at a given interval. Several models were build with the parameter under investigation set to the relevant scan value (based on the scan step used) while all other model parameters were kept constant at their original values. The diffraction pattern from each of these

Chart 1. Fragment of 1,4-polybutadiene indicating the geometrical parameters of the model.



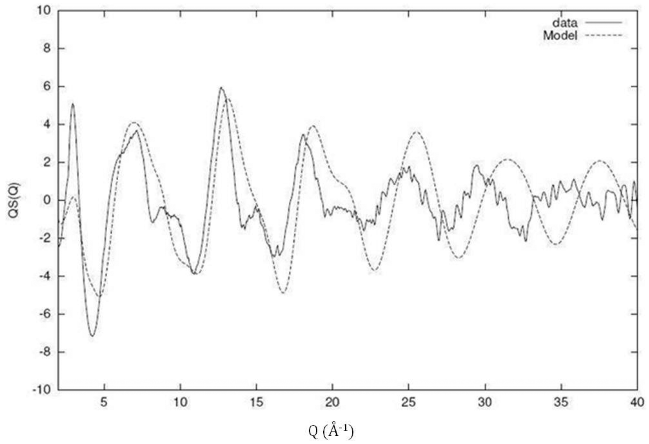


Figure 6. Comparison between the initial model (dotted lines) and the experimental data (solid lines) for 1,4-polybutadiene. The high Q region where covalent bond correlations are predominately dominant is following the general trend of the experimental data, despite the fact that peak positions and widths are not fully accurate. In the low Q region, dominated by torsion rotation correlations, the fit is far worse.

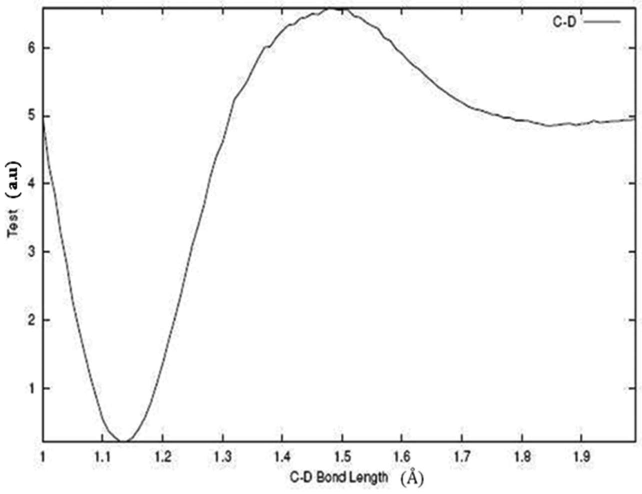


Figure 7. χ^2 test results for the carbon—deuterium bond.

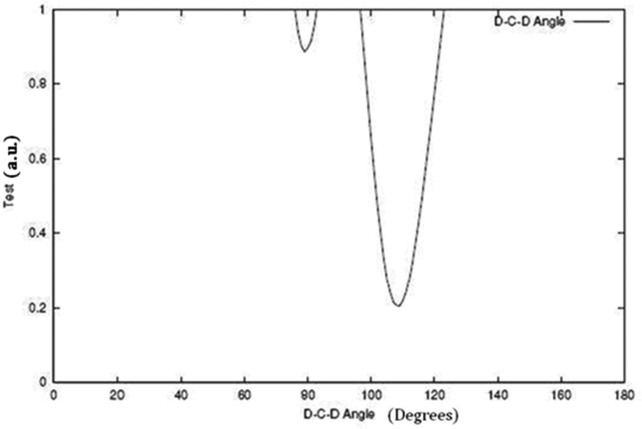


Figure 8. χ^2 test results for deuterium—carbon—deuterium valence angle.

models was then calculated and compared via a χ^2 test with the observed scattering curve. The region of the minimum χ^2 result was then identified and the procedure was repeated again with smaller intervals and scanning steps. This series of calculations were repeated until the scanning step corresponded to the desired accuracy of the parameter under investigation. The best value for the given parameter was then extracted as the one yielding the minimum χ^2 result between model and experiment. The procedure was repeated iteratively for all given parameters after the previous parameter was fixed to the value extracted by the χ^2 curve, and the overall search was repeated as many times as necessary to achieve convergence in the χ^2 values.

To achieve good statistics and to allow for a good representation of all relevant conformational characteristics a series of averages from a number of individual models was used. In this procedure we used an average of 10 models (15000 skeletal bonds) for the identification of the bond lengths, 50 models for the search of the valence angles and 100 models for the identification of the torsional characteristics. In Figures 7 and 8 the results for a number of the relevant parameters obtained during this study can be seen. For each curve the value of the parameter corresponding to the minimum χ^2 was obtained by direct examination of the curve. An effort to identify the absolute minimum in the vicinity of the parameter space by use of derivatives was made but the difference between this approach and the direct examination was smaller than the requested accuracy so it was not used.

Bond Lengths and Angles. In a scattering pattern the parameter with the most profound effect (in terms of shapes and positions of the peaks in the curve) is the bond length. This is natural as in terms of conformational characteristics (length, angle and torsion) the bond length is the most populated so it is expected that by finding the value in the vicinity of the χ^2 test for the bond length should have a very large impact on the scattering pattern. To visualize how important the impact of the bond length is in the scattering pattern we can see Figure 9 where a series of models of different C—D bond lengths are compared with the experimental data. It can be seen that for a C—D bond of 1.13 Å the comparison of the output of the model with the scattering data is far better than for a absurd value of 1 and 1.5 Å respectively. It is therefore expected that the position and width of the bond length distribution will be predicted with high level of accuracy.

For the entire temperature range (20—320 K) the positions of the distributions defining the C—D, C—C, C═C, C—C═ and ═C—C bonds were found to be totally stable and fixed to a single value. Table 1 summarizes the results obtained from this procedure along with predictions from quantum mechanical calculations, molecular dynamics simulations, and X-ray diffraction studies of crystalline compounds. As expected the results obtained with this procedure are in good agreement with previously reported values obtained by X-ray diffraction studies of crystalline 1,4-*cis*-polybutadiene[19,44,45] and 1,4-*trans*-polybutadiene.[20] The molecular dynamics simulation results presented here are not the only ones. There are a number of simulations of 1,4-polybutadiene investigating thermodynamic and conformational properties[46,47] as well as conformational dynamics[48] and the force fields used give results similar to the ones obtained by our method. Recently a set of parameters defining a united atom force field for 1,4-polybutadiene was developed based on quantum mechanical calculations.[21] The validation of this force field was performed through molecular dynamics simulations of molten 1,4-polybutadiene and its results were compared with C^{13} NMR and neutron spin echo experimental results.[49] An even more recent atomistic Monte Carlo simulation of 1,4-*cis*-polybutadiene[39] exhibits the same results as our approach. In terms of the widths of the distributions defining the bond lengths it has been discovered that the relative error in the observed result is very sensitive to the Q range and the data quality. The refinement's output exhibits negligible change with temperature as most values are in the range of 0.03−0.07 Å. This can be attributed to the experimental resolution not being high enough to allow for the extraction of such high detailed information. During the validation of the refinement procedure it has been seen, even in the case of "perfect data" that the minimum of the width of a distribution defining the bond length was lying in a shallow curve with a level of uncertainty of the order of 0.02−0.04 Å. In the case of the experimental data apart from the intrinsic limitations of the technique itself, the existence of noise as well as other factors depending on the data analysis have to be taken into consideration. Therefore, it can be expected that the uncertainty in the values of the fluctuations of the bond lengths must be considered high.

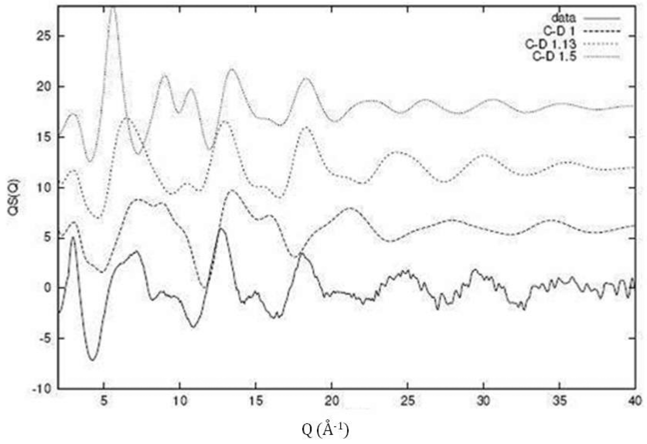


Figure 9. Effect of the carbon−deuterium bond on the overall picture of the diffraction pattern. The best fit distance of 1.13 Å (short-dashed line) shows a significant resemblance to the experimental data (solid line) when compared with two artificial C−D values of 1 Å (dotted line) and 1.5 Å (short dashed line). All the curves have been shifted for clarity.

In Figure 10, the positions of the valence angles distributions for the whole temperature range can be seen, and in Table 1 the average valence angle positions can be see compared with previously reported results and predictions. The position of the valence angle distributions obtained with this technique are in good agreement with experimental data,[19,44,45] RIS models,[18,50] and computer simulations.[21,39,46,47] Unlike the bond lengths, the positions of the distributions of the valence angles are not totally constant with temperature and a small level of fluctuation exist, possibly indicating a slight level of unharmonicity of the valence potential.

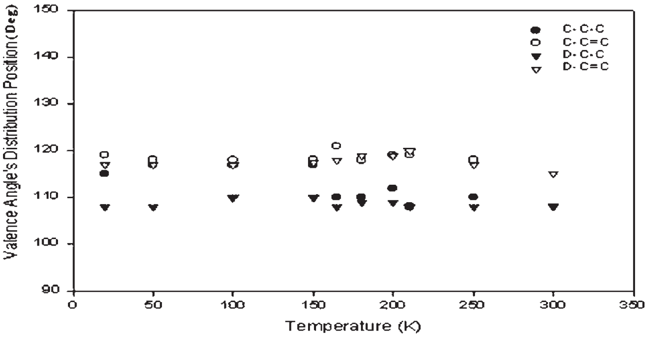


Figure 10. Valence angle distribution's peak position for the different configurations along the 1,4-polybutadiene chain as a function of temperature. Throughout the experimentally accessible range the valence angle position appears to be almost constant with slight fluctuations of the order of few degrees.

Table 1. Comparison between the Structural Parameters Obtained for 1,4-Polybutadiene with Previously Reported Experimental and Theoretical Data

model parameter	this work	Flory[a]	simulation[b]	simulation[c]	X-ray[d]
C−C	1.54 ± 0.01 Å	1.53 Å	1.53 Å	1.54 Å	1.53 Å
C−C=	1.51 ± 0.01 Å	1.51 Å	1.51 Å	1.505 Å	1.51 Å
C−D	1.13 ± 0.01 Å		1.1 Å	1.09 Å	1.1 Å
C=C	1.35 ± 0.01 Å	1.34 Å	1.34 Å	1.32 Å	1.34 Å
C−C−C	112.8° ± 0.5°	112°	112°	112.1°	112°
C−C=C	122.8° ± 0.5°	125°	124.7°	128.5°	125°
D-C=C	117.4° ± 0.5°	117.5°		117.1°	117.5°
D−C−C	108.6° ± 0.5°	110°		108.9°	110°
α bond	*cis*, ± 60° ± 1−2°	*cis*, ± 60°	*cis*, ± 60°	*cis*, ± 60°	*cis*, ± 60°
β bond	*trans*, ± 120° ± 5°	*trans*, ± 120°	*trans*, ± 120°	*trans*, ± 120°	*trans*, ± 120°

[a] Reference 18. [b] Reference 21. [c] Reference 38. [d] Reference 44 and 45.

C−C=C−C Double Bond. The bond with the most paramount effect in the chain conformation of 1,4-polybutadiene is the C−C=C−C double bond, that can adopt *cis* and *trans* states. The population of *trans* states was evaluated by the refinement

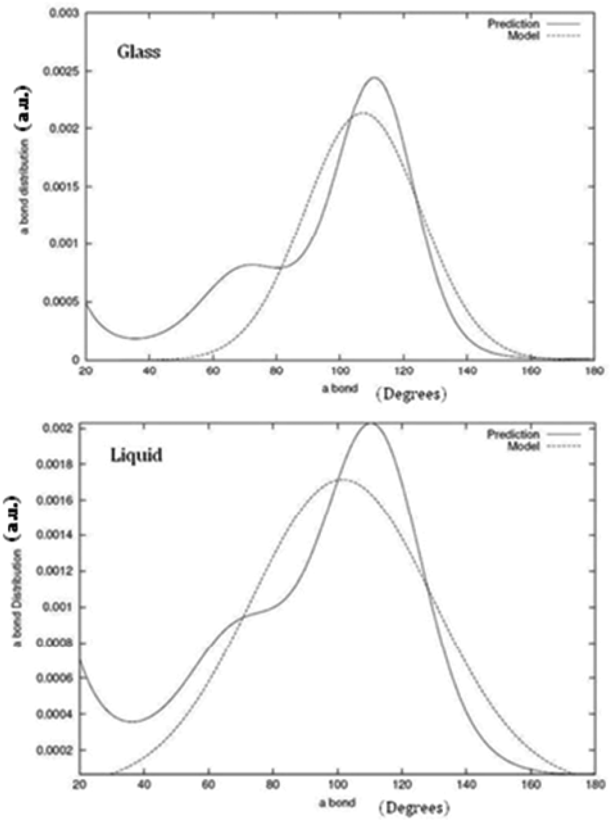


Figure 11. *s*± conformer's distribution taken from a force field, with both states of the α bond weighted according to the double bond prediction in the glass and liquid state (prediction, solid lines) compared with the refinement technique (model, dotted lines). In the glass state, the small second peak of the α bond that arises from the specific rotational state adjacent to the *cis* double bond is not sampled by the model, something that is partially achieved in the liquid state.

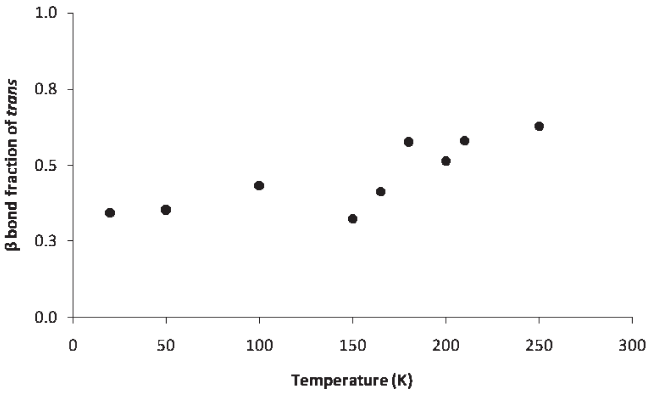


Figure 12. Fraction of *trans* states of the β bond obtained by the structural refinement technique as a function of temperature.

technique at 50 ± 10%, a value that was supported by independent NMR measurements. Since the energetic barrier between the *trans* and the *cis* states is predicted to be between 14 and 24.2 kcal/mol,[21] conformational changes of the double bond are not expected to occur. Because of that the fraction of the *trans* state used in our analysis was taken to be 55.9% per the NMR measurement. Both *cis* and *trans* states were simulated with Gaussian distributions of fixed position and variable width. During the scan in the χ^2 test both widths were treated simultaneously and the uncertainty in the values obtained was of the order of 4−5 deg.

C−C−C=C and C=C−C−C α bonds. The α bond in 1,4-polybutadiene was found to occupy *cis* (180°) and *s*± (60 ± 1−2°) states in good agreement with the RIS states predicted by Fory[18] and Mark.[19,20] In this study each torsion angle was assigned individually without taking into account neighboring conformations. Since the energetic barrier between *cis* and *trans* states is high it is expected that the coupling between torsion states to be constrained between the double bonds. This means that the set of $\alpha\beta\alpha$ torsions will be strongly coupled something that should be visible in the scattering pattern. Quantum chemical calculations in model compounds show that the potential of the α bond will be significantly different depending of the state of the adjacent double bond.[21] It is therefore expected that a certain amount of internal overcompensation from the parameters will take place in order to minimize the χ^2 result. This is manifested in terms of the width of the *s*± distribution that gets large trying to cover all possible configurations. This can be seen in Figure 11 where the combined distribution of *s*± conformer taken from a force field prediction[21] with both states of the α bond (adjacent to *cis* or *trans*) weighted according to the NMR data with respect to the double bond can be seen for two different states of the molecule, glass and liquid. In the same figures the given distribution of the α bond used by the refinement technique at the appropriate temperature is presented for comparison. In the glass the distribution of the combined α bond seems to be split in two peaks quite far from each other. Consequently our approach although it models the majority of the given populations misses the small but significant second peak that arises from the specific rotational state of the α bond with respect to the adjacent *cis* double bond. In the liquid state the approach used is more accurate as the distributions become broader and the two peaks show evidence of merging in one. The simplified distribution used by us appears to be adequate to represent the complex nature of the α bond in the melt, something that can be seen from the lower χ^2 values observed. The fraction of the *cis* population of the α bond has been predicted to be in the range of 0−15% from RIS models[18−21] and atomistic simulations,[39] a value in good agreement with 0 ± 5−10% established from our analysis. On the basis of this it can be argued that although the approach is simplistic the fraction of the population of the α bonds is in relatively good agreement with previously reported predictions.

=C−C−C−C= β Bond. The =C−C−C−C= β bond was found to occupy a 3-fold potential with minima occurring in the *trans* (0°) and *g*± (120°) states in good agreement with the RIS model,[18−20] and the fraction of *trans* populated states was found to be 40 ± 5−10%. On the basis of the observations of the refinement on the scattering function it was found that the β bond has more significant impact on the diffraction pattern than the subtle effect observed by the α bonds. In Figure 12 the fraction of the *trans* population of the β bond obtained in this study as a function of temperature can be seen. In the glassy regime the fraction is approximately 40% and it reaches to values close to 60% in the molten state. This behavior is the exact opposite of what was expected based on force fields predictions,[21] and this difference can probably be attributed to the complex potential of the α bond attached to a *cis* double bond and the significant level of coupling of the $\alpha\beta\alpha$ torsions.

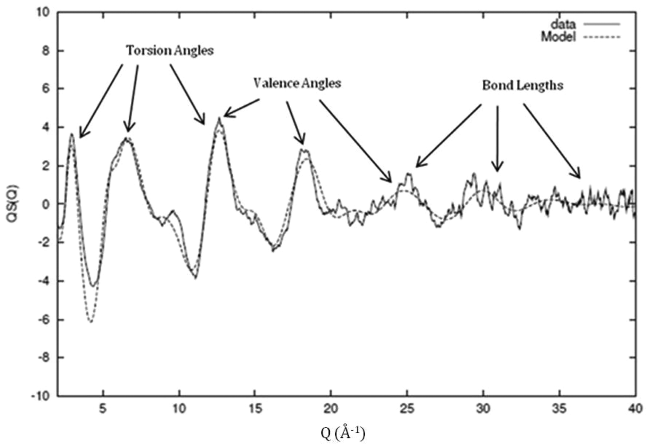


Figure 13. Comparison of the experimental data for 1,4-polybutadiene (data, solid line) and the best fit model results (model, dotted line). The different regions of the scattering curve predominately affected by the different structural parameters can also be seen.

Characteristic Ratio. Extrapolation of the results obtained during this study from local to large scale was performed by the calculation of the characteristic ratio. A series of optimized models (1000 models) for each temperature were generated with a different number generator. That way an average polymeric chain was stochastically created with similar local structure. In this case all models had the same set of initial parameters taken from the best fit result for the given temperature, and the mean squared root end to end length was calculated for each of them. The characteristic ratio of the combined chain was extracted using the formula $c_n = \langle r_0^2\rangle/(\sum_{i=1}^{X-1} l_1^2)$ where $X - 1$ is the number of links in the backbone and l^2 the average squared skeletal bond length. Using Flory's formulation[18] for an 1,4-polybutadiene chain we have $\sum_i l_i^2 = 88.697x - 2.3409$ Å where $x = X/4$ is the numbers of monomers in the chain. The characteristic ratio calculated from the optimum model exhibits a slight downward trend with temperature and has an average value of 4.6 in relative agreement with previously reported values.[18,21,51] The level of discrepancy in the C_∞ calculation can be attributed in the sensitivity of the torsion angles in the dimensions of the chain. 1,4-*trans*-polybutadiene seem to be more sensitive to the rotation of the β bond and its first order interactions with its neighbors.[21] 1,4-*cis*-polybutadiene on the other hand is more sensitive to the conformational energies of the α bonds and especially its small but important *cis* population. Finally the position of the $g\pm$ conformation of the α bond has been reported to have a direct impact in the chain dimensions of both *cis*- and *trans*-1,4-polybutadiene.[21] Therefore, it can be said that the noninclusion of conditionality in the assignment of the torsion angles as well as in the strong coupling of the $g \pm$ dihedral angle of the α bond with its neighbors is expected to have a significant effect in the chain dimensions as manifested by the results of the characteristic ratio.

Diffraction Pattern. Since the whole structural refinement procedure depends on the comparison between the calculated and the observed structure factor, an association of the different parameters of the model can be made with different regions of the diffraction pattern. Obviously all parameters affect the entire intrachain region, but there are subregions of the scattering curve that are more affected by the optimization of parameters that correspond to different length scales. We found that parameters that correspond to atoms joined together by covalent bonds (especially C—D bonds) have the most profound effect on the shape of the scattering curve. This effect although dominant throughout the entire range manifests itself more on the high Q region ($Q > 20-25$ Å^{-1}). Parameters that affect the valence and torsion angles have a somehow dominant effect on the lower Q region and almost no effect on the high Q area, as can be seen from Figure 13 where the schematic representation of the impact of the various structural parameters on the structure factor can be seen.

SUMMARY

In this study, we have demonstrated the feasibility of carrying out a detailed structural analysis of an amorphous polymer through a combination of scattering measurements over an extended Q range and atomistic modeling. We have shown that the high sensitivity of neutrons to fully duterated polymers can be used to extract details of intrachain correlations from a relatively simple statistical model by direct comparison to the diffraction pattern over the entire Q region (once the interchain part of the scattering is removed). The technique presented in this paper provides information on the structural characteristics of the repeat unit, and on the degree of stiffness of the polymer chain itself.

Broad Q neutron scattering data covering the entire experimentally accessible temperature range (20—320 K) in the liquid and glass state of 1,4-polybutadiene has been presented. Each of the data sets can be considered an independent measurement and has been used to validate the modeling procedure while yielding information regarding the local conformation ant any given temperature. Bond lengths and angles are almost in total agreement with previously reported predictions and experimental findings. It has been concluded that a normal distribution is modeling with very high accuracy the bond lengths and angles and the experimental data indicate an almost total harmonic potential for the bond length and a slight unharmonisity of the valence angle distribution. Fully accurate extraction of information regarding the chain conformation faces difficulties posed by the complex nature of the α bond adjacent to a *cis* double bond as well as the strong coupling between different conformations of the $\alpha\beta\alpha$ torsional sequence. A high level of overcompensation between the parameters of the torsion distributions attempting to minimize the statistical test is attributed to the lack of conditionality in the assignment of the torsion probabilities. From this study it is assumed that the basic RIS model where rotational states are assigned in terms of single values of each population cannot represent the local structure of 1,4-polybutadiene accurately. This is because the chain conformation has been found to be more irregular than the random coil model, something seen in natural rubber in the past.[21,41] The structural refinement technique indicates that for the case of a random copolymer of 1,4-polybutadiene with almost equal fractions of *cis* and *trans* populations of the double bond the local structure can be best represented by a set of delocalized rotation states for the α and β bonds. Consequently the torsion angles need to have a greater level of rotation allowed, generating a very narrow channel of excluded conformations. This level of constraint in the rotational state appears to be screened in the large scale regime, something seen from the calculation of the characteristic ratio. It will though be present and have a direct impact on the local scale. Extrapolation of the characteristic ratio using the local chain conformation is in relative agreement with previously reported values and the level of discrepancy can be attributed to the sensitivity it exhibits to the nature of the α and β bonds. Finally, the technique's capability of extracting structural information and its sensitivity is manifested by the prediction of the fraction of *trans* populations of the double bond present in the material, in very good agreement by independent NMR measurements.

AUTHOR INFORMATION

Corresponding Author

*E-mail: thomas.gkourmpis@borealisgroup.com.

Present Addresses

§Borealis AB Polyolefin Research Stenungsund SE 444−86 Sweden.

ACKNOWLEDGMENT

This work was supported by University of Reading and the Science and Engineering Research Council. We would like to acknowledge CCLRC for providing access to the RAL neutron facility, thank Alan Soper and Chris Benmore for all their help during the neutron scattering experiments and Fred Davis, Robert Olley, and Clark Balague for all their help with the sample preparation and characterisation.

REFERENCES

(1) Volkenstein, M. V. *Configurational Statistics of Polymer Chains*; Wiley-Interscience: New York, 1963.

(2) Flory, P. J., *Statistical Mechanics of Chain Molecules*; Wiley-Interscience: New York, 1969.

(3) Lovell, R.; Mitchell, G. R.; Windle, A. H. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 46.

(4) Frick, B.; Richter, D. *Science* **1995**, *267*, 1939.

(5) Richter, D. *Physica B* **2000**, *276*−*278*, 22.

(6) Mitchell, G. R. In *Order in the Amorphous State of Polymers*; Keinath, S. E., Miller, R. L., Rieke, J. K., Eds.; Plenum: New York, 1987.

(7) Mitchell, G. R. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Booth, C., Price, C., Eds.; Pergamon: Oxford, U.K., 1989.

(8) Deegan, R. D.; Nagel, S. R. *Phys. Rev. B* **1995**, *52*, 5653.

(9) Arbe, A.; Richter, D.; Colmenero, J.; Farago, B. *Phys. Rev. E.* **1996**, *54*, 3853.

(10) Guillermo, A.; Dupeyre, R.; Cohen-Addad, J. P. *Macromolecules* **1990**, *23*, 1291.

(11) Dejan de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1989**, *22*, 122.

(12) Richter, D.; Frick, B.; Farago, B. *Phys. Rev. Lett.* **1998**, *61*, 2465.

(13) Frick, B.; Richter, B.; Ritter, C. *Europhys. Lett.* **1989**, *9*, 557.

(14) Kanaya, T.; Kaji, K.; Inoue, K. *Macromolecules* **1991**, *24*, 1826.

(15) Zorn, R.; Richter, B.; Frick, B.; Farago, B. *Physica A* **1993**, *201*, 52.

(16) Arbe, A.; Buchenau, U.; Willner, L.; Richter, D.; Farago, B.; Colmenero, J. *Phys Rev lett* **1996**, *76*, 1872.

(17) Zorn, R.; Kanaya, T.; Kawaguchi, T.; Richter, D.; Kaji, K. *J. Chem. Phys.* **1996**, *105*, 1189.

(18) Abe, Y.; Flory, P. J. *Macromolecules* **1971**, *4*, 219.

(19) Mark, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 4354.

(20) Mark, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 6829.

(21) Smith, G. D.; Paul, W. *J. Phys. Chem. A* **1998**, *102*, 1200.

(22) Mitchell, G. R. *MESA, A Molecular Ed. for Structural Analysis*; Reading, U.K., 1996.

(23) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.

(24) Warren, B. E. *X-Ray Diffraction*: Addison-Wesley: Reading, MA, 1969.

(25) Mitchell, G. R.; Rosi-Schwartz, B. *Physica B* **1992**, *180*−*181*, 558.

(26) Rosi-Schwartz, B.; Mitchell, G. R. *Nucl. Instrum. Methods Phys.* **1995**, *A 354*, 17.

(27) Rosi-Schwartz, B.; Mitchell, G. R. *Polymer* **1994**, *35*, 3139.

(28) Turner, J. Z.; Soper, A. K.; Howells, W. S.; Hannon, A. C.; Ansell, S. *SANDALS Survival Guide*; ISIS Facility, Rutherford-Appleton Laboratory: U.K., 1999.

(29) Soper, A. K.; Howells, W. S.; Hannon, A. C. *ATLAS Analysis of Time of Flight Diffraction Data for Liquid and Amorphous Samples*; ISIS Facility, Rutherford-Appleton Laboratory: U.K., 2001.

(30) Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Interscience: New York, 1989.

(31) Robertson, C. G.; Roland, C. M. *Macromolecules* **2000**, *33*, 1262.

(32) Grebowicz, J.; Aycock, W.; Wunderlich, B. *Polymer* **1986**, *27*, 575.

(33) Buchenau, U.; Wischnewski, A.; Richter, D.; Frick, B. *Phys. Rev. Lett.* **1996**, *77*, 4035.

(34) Frick, B.; Farago, B.; Richter, D. *Phys. Rev. Lett.* **1990**, *64*, 2921.

(35) Richter, D. *J. Phys. Condens. Mat.* **1996**, *8*, 9177.

(36) Paul, D. R.; DiBenedetto, A. T. *J. Polym. Sci. C* **1965**, *10*, 17.

(37) Valentine, R. H.; Ferry, F. D.; Homma, T.; Nonmiya, K. *J. Polym. Sci.* **1968**, *A2*, 479.

(38) Okada, O.; Furuya, H. *Polymer* **2002**, *43*, 971.

(39) Getoso, P.; Nicol, E.; Doxastakis, M.; Theodorou, D. N. *Macromolecules* **2003**, *36*, 6925.

(40) Kim, E.; Misra, S.; Mattice, W. L. *Macromolecules* **1993**, *26*, 3424.

(41) Mattice, W. L.; Suter, U. W. *Conformational Theory of Large Molecules: The Rotational Isomeric State Model in Macromolecular Systems*: Wiley: New York, 1994.

(42) Lide, D. R.; Mann, D. E. *J. Chem. Phys.* **1957**, *27*, 868.

(43) Lide, D. R. *Annu. Rev. Phys. Chem.* **1964**, *15*, 225.

(44) Natta, G.; Corradini, P. *Angew. Chem.* **1956**, *68*, 615.

(45) Natta, G.; Corradini, P. *Nuovo Cimento, Suppl.* **1960**, *15*, 111.

(46) Li, Y.; Mattice, W. L. *Macromolecules* **1992**, *25*, 4942.

(47) Tsolou, G.; Harmandaris, V. A.; Mavrantzas, V. G. *Macromol. Theory Simul.* **2006**, *15*, 381.

(48) Gee, R. H.; Boyd, R. H. *J. Chem. Phys.* **1994**, *101*, 8028.

(49) Smith, G. D.; Paul, W.; Mokenbusch, M.; Willner, L.; Richter, D.; Qiu, X. H.; Ediger, M. D. *Macromolecules* **1999**, *32*, 8857.

(50) Allegera, G. *Makromol. Chem.* **1967**, *110*, 58.

(51) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.