Taylor & Francis
Taylor & Francis Group

Polyethylene Structure as a Function of Temperature: An EDXD Investigation

R. CAMINITI,[1] P. BALLIRANO,[2] AND M. CARBONE[3]

[1]Dip. di Chimica, Università La Sapienza, Roma, Italy
[2]Dip. di Scienze della Terra, Università La Sapienza, Roma, Italy
[3]Dip. di Scienze e Tecnologie Chimiche, Università Tor Vergata, Roma, Italy

Polyethylene structure has been investigated by energy dispersive X-ray diffraction (EDXD) as a function of temperature below the melting point, via Rietveld refinement. The behavior was studied at four temperatures, namely 25, 40, 70, and 88°C. In this range the structure undergoes a regular volume expansion that may be expressed in terms of specific volume ratio as $V_E/V_{25°C} = 0.991(2) + 4.0(5) \times 10^{-4} \times T(°C)$. The variation is almost completely taken up by the a cell parameter and results, apart for minor intrachain arrangements, in an increased distance between polymer chains.

1. Introduction

Polyethylenes are semicrystalline materials with good fatigue and wear resistance. Furthermore, they have a good resistance to organic solvents, degreasing agents, and electrolytic attack, are lightweight, resistant to staining, and have low moisture absorption rates. Because of their wide range of properties they are the most used polymers worldwide. In general their properties are related to differences in length of the polymer chain. Three classes are usually distinguished: low and high-density polyethylene (L- and H-DPE) and ultra high molecular weight polyethylene (UHMW-PE). Typical parameters characterizing the polyethylene are melt index, density, and mixture, either with other monomers to yield copolymers or with polyethylenes of different weight to yield bimodal resins.

The understanding of the physical and technological properties of polymers is strongly related to their structural identification. The degree of crystallinity, for instance, which is related to the chain branch number, affects their melting point, flexibility, and toughness. The polyethylene properties as a function of the operative conditions were first investigated by X-ray diffraction by Brown and Eby,[1] who determined lamellar thickness, melting temperature, and density as a function of crystallization conditions and heat treatments. Eby also investigated the variation of transition temperature as a function

of comonomer content, molecular weight, and lamellar thickness,[2] as well as the diffusion of ethane in polyethylene.[3]

X-ray studies of polyethylene structure were also performed as a function of temperature and the data analysis includes the least squares method and line-profile analysis in several temperature ranges. Swan[4] showed, in an early study, polyethylene unit cell variations in the temperature range $-196°C$ to $130°C$, with a different behavior along the three directions of the orthorhombic cell. In particular, he found that the parameter a shows a nonlinear expansion, b a small expansion, and c is rather constant. Iohara et al.[5] performed measurements in the temperature range $-165°C$ to $120°C$ and found a maximum displacement of the carbon atom in the direction perpendicular to the skeletal zigzag plane and a minimum displacement in the direction along the molecular axis.

Kobayashi and Keller[6] performed a line profile analysis of X-ray polyethylene spectra in the temperature range $-165°$ to $120°C$, where they hypothesized an actual shrinkage of the c parameter with the temperature. The line-shape analysis was also employed to monitor the polyethylene lattice distortions in the temperature range $-269°$ to $67°C$.[7] An increase of the line width was found with the increasing temperature. An explanation for this effect is related to the stress parallel to the plane of the lamellae produced by the differences of thermal expansion coefficients of the crystalline and amorphous domains in the lamellar two-phase system.

The lattice parameters, degree of crystallinity, dimensions of micro-paracrystals, and their lattice defects were studied in the temperature range $20°$ to $106°C$ by Asbach and Wilke.[8] They found that the density of the crystals decreases in steps in the measured ranges, that the micro-paracrystals show a large extension in the b direction above $90°C$, and that they are characterized by a prominent extension perpendicular to the 110-planes at lower temperatures.

The expansion of a polyethylene monocrystal was investigated by Li-Shen et al.[9] in order to determine the nature of flexible vibrations of the crystalline lattice of isolated polyethylene crystals in the range $-50°$ to $135°C$.

Determining whether the branches are included in the polyethylene crystallites was the subject of an early investigation of Swan,[10] who found that a polyethylene crystalline phase may include short branches of various kinds as interstitial imperfections. Later on Baker and Windle performed a detailed X-ray diffraction and modelling study[11−13] on the branch inclusion. As far as copolymerization is concerned, an example of investigation is the effect of propylene inclusion into polyethylene studied by wide-angle X-ray scattering (WAXS) and atomic force microscopy (AFM).[14]

A complete structural study, however, should provide information as close as possible to actual operative conditions, i.e., conditions under which the polymer will be used. Mechanical stress, temperature, and effects of corrosive agents affect the polymer's performance and need to be investigated in detail.

In order to fulfill those requirements, a few conditions need to be matched. A fast and dynamical data collection is advisable, although keeping accuracy in the structural determination. In this paper we approach the problem of polymer structural determination in dynamical conditions. In particular we performed an energy dispersive X-ray diffraction (EDXD) study of polyethylene structure as a function of temperature via Rietveld refinement. The advantages of this approach are the relatively fast data collection, large reciprocal lattice sampling, and the easier accessibility, when compared to neutron or synchrotron radiation equipment.

Furthermore, the prototype EDX diffractometer used in the present study is equipped with a sealed, thermostatic sample-holder that allows investigations as a function of

variable parameters such as temperature, reactants concentrations, etc. In this study we focused on thermal effects and collected polyethylene spectra at 25°, 40°, 70°, and 88°C, in order to obtain information of crystallite deformation below the melting point (134°C).

The first attempt to set up a laboratory energy-dispersive diffractometer to analyze a crystalline sample dates back to the end of the 1960s.[15] This technique is peculiar as it uses the unfiltered radiation generated by a commercial X-ray source. The radiation diffracted by the specimen is energy resolved by a solid-state detector at a suitable scattering angle. The modulus of the scattering vector, q, that depends on the energy of the photon, E, and the scattering angle, θ, is equal to

$$q\,(E, \theta) = 1.01354\,E\sin\theta = 4\pi\,(\sin\theta)/\lambda \tag{1}$$

So far, only a few studies have been published on the application of Rietveld refinements to EDXD patterns. The main limitation to the application of this type of analysis used to be the poor resolution and the need to use synchrotron sources that were privileged.[16−18]

On the contrary EDXD has been largely used for structural studies of low crystallinity, amorphous, or liquid materials,[19−22] or for the study of the kinetics of phase transitions.[23,24]

However, in a systematic investigation, the applicability of the Rietveld refinement to EDX diffraction patterns was checked for a few materials. In particular, corundum, rutile, and anatase nanocrystalline synthetic samples, and natural gypsum were studied by EDXD,[25] and the diffraction data were evaluated via the Rietveld refinement. The difference among cell parameters, bond distances and angles, and displacement parameters obtained by the Rietveld refinement on EDXD data and reference data from single crystal or conventional angular dispersive X-ray diffraction (ADXD) has been reported to be of the order of $1-3.5\sigma$.

The aim of this paper is to extend the Rietveld refinement to patterns collected by EDXD as a function of temperature. In order to check this opportunity, we selected a sample of polyethylene (PE) whose structural features were previously investigated[26] by means of conventional ADXD at room temperature (RT). Then, we heated the sample to several different temperatures (40, 70, 88°C) and for each of them we reiterated the data collection and the Rietveld analysis.

2.   Experimental

The EDXD instrument is characterised by a vertical θ/θ geometry.[27,28] The components of the instrument are:

- a commercial Seifert X-ray generator (x-ray source: W target);
- a collimating system composed of four adjustable (both vertically and axially) W slits;
- a thermostatic cell located at the common center of rotation of the diffractometer arms;
- step motors to move both X-ray tube and detector holding arms (reproducibility $>0.001°\,2\theta$);
- a solid-state detector EG&G liquid-nitrogen cooled ultrapure Ge ORTEC 92X linked via an electronic chain to a multichannel analyzer (MCA).

Table 1
Physical properties of the
polyethylene sample

Density (g cm^{-3}) DIN 53479	0.945
Mw	300,000
Melting point, °C	134

The sample of PE we used was the commercial semicrystalline PE-HWST, previously investigated by angular dispersive X-ray diffraction,[26] supplied by SAPIG s.n.c., Rome, Italy. The same $20 \times 20 \times 2$ mm section used in Glazer et al.[26] was analysed.

The physical properties of the sample are reported in Table 1. Data were collected in symmetrical transmission mode[29] in order to simplify the evaluation of the coherent absorption which, for this geometry, is simply expressed as

$$A_{coh}(E, \theta) = \exp[-\mu(E)t \sec \theta] \tag{2}$$

Dead time was kept to $<2\%$ throughout the measurements.

3. Data Evaluation

The scattering angle θ of 10.8° was selected. Of the 1024 channels of the MCA, a total of 451 data points were evaluated. This is because the first 184 channels were not used as they contain the fluorescence L lines of W (8–10 keV range), and the last 390 channels
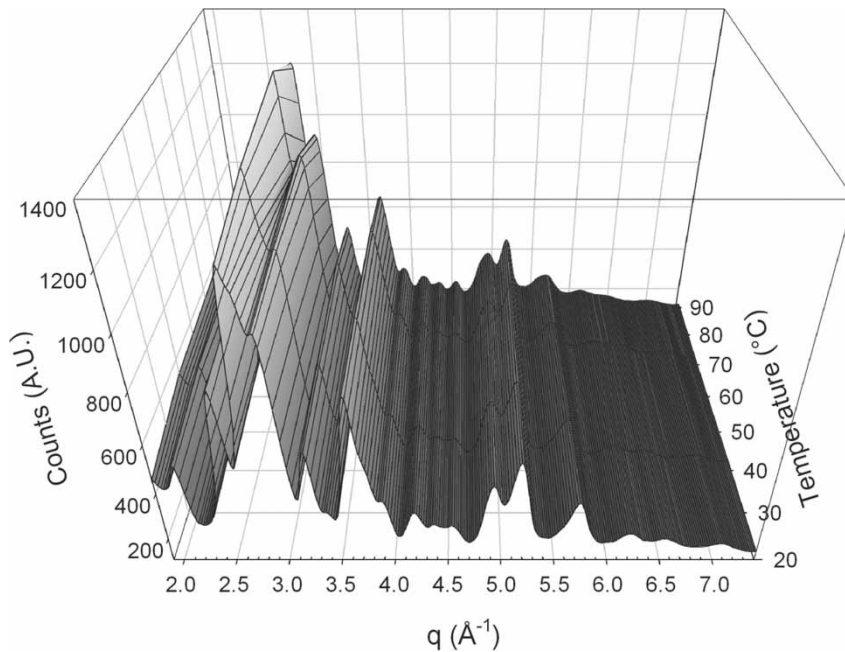

Figure 1. Evolution of diffraction data with increasing T.

Table 2

Miscellaneous data of the refinements. Agreement indices
and statistic indicators as defined in Young[34]

	R_p	wR_p	R_{Bragg}	Reduced χ^2
25°C	1.73	2.13	4.24	0.1688
40°C	1.62	2.03	2.29	0.1560
70°C	1.66	2.19	1.12	0.1862
88°C	1.72	2.27	1.57	0.1863

were not used because the counting statistics were considered inadequate. This data set covers the range $0.85 < d_{hkl} < 2.80$ Å. The X-ray source operated at 45 kV and 35 mA. A counting time of 6000 s was used. Slits apertures were, respectively, 500×8000 (post-Be window), 400×4000 (divergence), 400×4000 (antidivergence), and 800×4000 μm (receiving). Raw data were normalized to the incident white spectrum (fitted with a sixth-order polynomial) and corrected for absorption and escape peaks. The data were subsequently interpolated to obtain constant-θ data. Diffraction data as a function of temperature are reported in Fig. 1.

Rietveld refinement was carried out by the general structure analysis system (GSAS) crystallographic package.[30] This suite of programs is, in fact, able to handle constant-q data by conversion to conventional ADXD data using a fictitious, user-defined, wavelength ($MoK_{\alpha1} = 0.70926$ Å throughout this work). Peak shape was modeled by means of a pseudo-Voigt function modified for peak asymmetry.[31] Refined parameters included: Gaussian $\tan^2 \theta$- and $\tan \theta$-dependent, and θ-independent (GU, GV, and GW, respectively) parameters, Lorentzian $\tan \theta$-dependent parameter (LY), and two asymmetry parameters S/L and H/L (constrained to be equal). The peak cutoff was set to 0.005% of the peak maximum. The background was fitted with a nine-term Chebyshev polynomial of the first kind. A zero-correction for detector position was also refined. As in the case of the refinements of Glazer et al.[26] the structure of polyethylene was refined in the space group P*nam* and three soft constraints were imposed, with unit weight, during the minimization procedure: C–H1=C–H2 = 1.06(1) Å; H1–H2 = 1.70(3) Å, the C–C bond distance and the C–C–C bond angle being unconstrained. Displacement parameters of hydrogen atoms were constrained to be equal. The presence of texture was checked, during the last

Table 3

Evolution of cell parameters, volume, and specific volume ratio with temperature.
For comparison purposes data collected at room-temperature of Glazer et al.[26]
are reported

	a (Å)	b (Å)	c (Å)	V (Å^3)	$V_E/V_{25°C}$
Galzer et al.[26]	7.4240(8)	4.9470(6)	2.5526(2)	93.75(3)	—
25°C	7.424(2)	4.947(2)	2.5526(6)	93.75(7)	1.000
40°C	7.470(2)	4.953(2)	2.5526(5)	94.44(6)	1.007
70°C	7.563(3)	4.958(2)	2.5501(7)	95.62(9)	1.020
88°C	7.619(4)	4.953(2)	2.5462(8)	96.09(11)	1.025

Table 4
Evolution of relevant bond distances and angles
with temperature

	C–C (Å)	C–C–C (°)
Glazer et al.[26]	1.532(5)	112.8(6)
25°C	1.544(2)	111.5(2)
40°C	1.546(2)	111.3(2)
70°C	1.545(2)	111.2(2)
88°C	1.537(2)	111.8(2)

cycle of refinement, by means of a generalized spherical-harmonic description.[32] Nine terms up to the sixth order were introduced obtaining a significant improvement of the fit because of a texture index, J, of 1.45. The refined coefficients of the spherical harmonic terms at 25°C were subsequently used and kept fixed for the other refinements. The total number of refined parameters was 36. Miscellaneous data of the refinement are reported in Table 2, evolution of cell parameters with temperature in Table 3, evolution of relevant bond distances and angles with temperature in Table 4, and experimental, calculated, and difference plots for the data collected at 70°C (chosen as representative) in Fig. 2.

4. Discussion

The current investigation of polyethylene structure by EDXD via Rietveld refinement is a part of our studies on applicability of this analytical method to polymers. In a first stage, Rietveld refinements were performed on ADXD data obtained from polymers such as poly (*p*-phenylene sulfide)[33] and polyethylene.[26] In a second stage, the Rietveld method was applied to diffraction patterns of crystalline materials obtained by
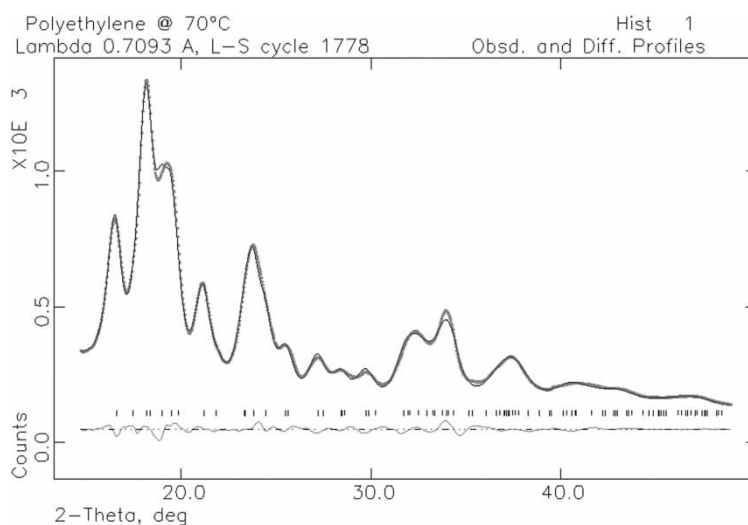

Figure 2. Experimental (dots), calculated (line), and difference plots of the refinement of polyethylene at 70°C. Vertical markers refer to the position of calculated reflections.
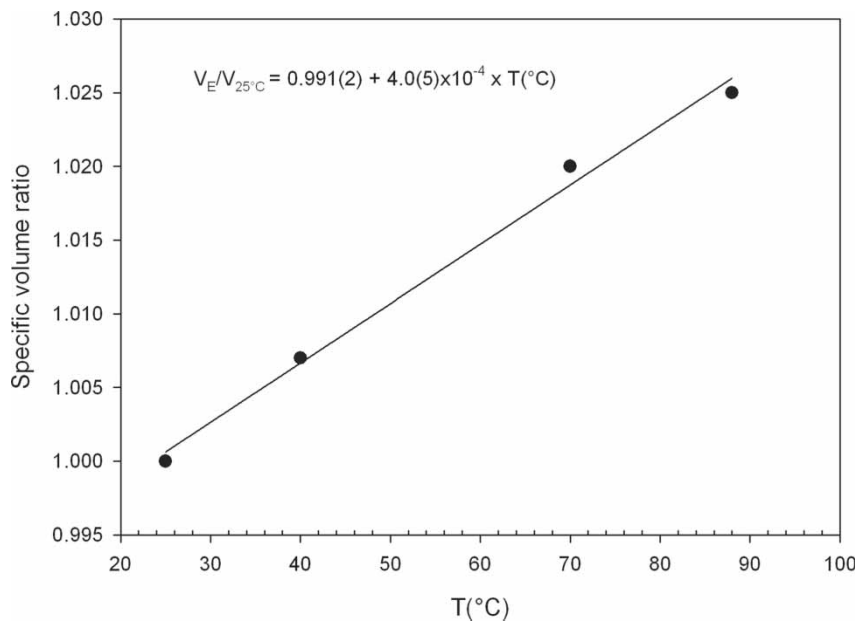
Figure 3. Specific volume ratio variation as a function of the temperature.

EDXD.[25] In both cases the structures obtained were compared to literature data and yielded a satisfactory level of accuracy.[25,26]

In the present study, the Rietveld refinement was applied to X-ray patterns of polymers obtained by EDXD. Furthermore, we performed this investigation as a
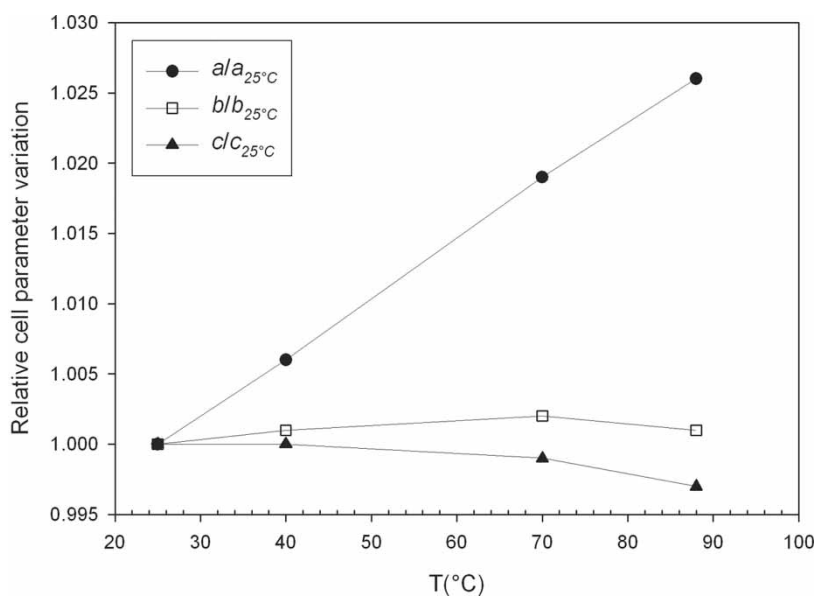

Figure 4. Relative cell parameters variation as a function of the temperature.

function of temperature. The necessary first step of this investigation is the comparison of RT polyethylene structures obtained by EDXD and ADXD. We found out that cell parameters, bond distances, bond angles, and displacement parameters obtained in the two studies agree within 3σ. Hence, we can conclude that EDXD is able to provide reliable data in polymer structural studies.[26]

The previously-mentioned parameters are compatible with a polyethylene structure at RT consisting of parallel polymer chains that develop along the c axis. The C−C−C angle we found in the present study is 111.5(2)° and the C−C distance is 1.543(2) Å, also in good agreement with the previous ADXD study.

We performed the structural study as a function of temperature in a range well below the melting point, in order to understand better how the polyethylene structure absorbs the thermal stress in typical working conditions. In particular, we heated the polyethylene sample up to 40°, 70°, and 88°C and in each case recorded the EDXD pattern, while keeping the sample at a constant temperature.

The parameters calculated according to the Rietveld refinement give a clear picture of the temperature-induced deformation in the polyethylene structure. The increase of the cell volume when heating the polyethylene sample from 25 to 88°C is 2.5%. Furthermore, the expansion is rather linear with the temperature and may be expressed in terms of
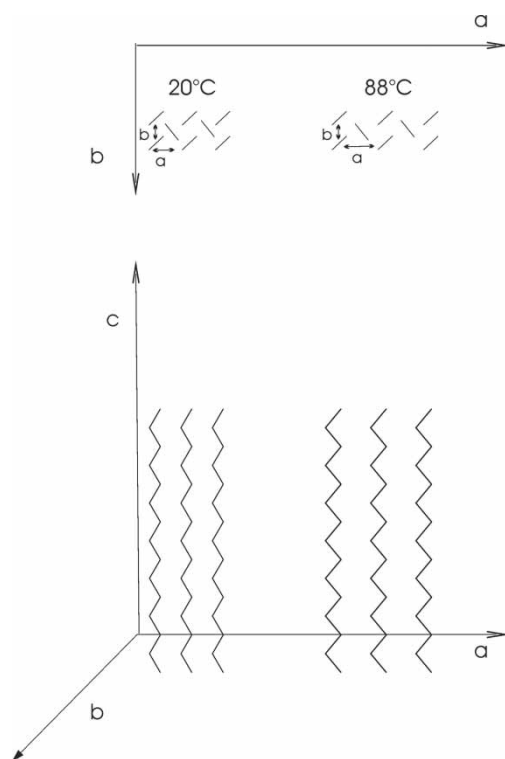

Figure 5. A sketch of the temperature effects on the polyethylene chains arrangement. The chains are aligned along the c direction. When heating the sample, apart for minor intrachain arrangements, the chains get more distant from each other. This accounts for the increase of the cell parameter a. The top part of the figure shows a [001] projection of the polyethylene chains as well as the increase of the cell parameter a as a function of temperature.

specific volume ratio ($V_E/V_{25°C}$: V_E = relative excess volume, $V_{25°C}$ = volume at 25°C) as $V_E/V_{25°C} = 0.991(2) + 4.0(5) \times 10^{-4} \times T(°C)$ (Fig. 3). The distribution of the cell expansion over the cell parameters is quite interesting. The expansion is almost completely taken up by parameter *a*. In fact, in the temperature range 25–88°C it increases by about 2.5%. The increase of cell parameter *b* is very small and is counterbalanced by a slight compression of cell parameter *c*. The relative variation of cell parameters is illustrated in Fig. 4.

The polyethylene structure rearrangement as a function of temperature, as can be deduced from Table 4, is not related to significant intrachain modifications, because the C–C–C angle and the C–C bond length are substantially unchanged. The main effect of the distortion is the increased distance between polymer chains that leads to the increase of cell parameter *a*. A sketch of the temperature effect on the polymer chains is given in Fig. 5, which describes a [001] projection as well.

5. Conclusions

Rietveld refinement was carried out to obtain the polyethylene structure as a function of temperature by EDXD. This technique is largely employed for the determination of liquid and amorphous materials local structure. However, several tests have indicated that it can be sufficiently accurate in the case of crystalline samples too. In the present study, polyethylene structure was investigated by EDXD as a function of temperature, below the melting point (134°C), via Rietveld refinement. Four temperatures were investigated, 25, 40, 70, and 88°C. In this range, the structure undergoes a regular volume expansion that may be expressed in terms of specific volume ratio as $V_E/V_{25°C} = 0.991(2) + 4.0(5) \times 10^{-4} \times T(°C)$. In agreement with previous studies,[4−6] we find that the variation is almost completely taken up by the *a* cell parameter and results in an increased distance between polymer chains.

References

1. Brown, R.G.; Eby, R.K. Effect of crystallization conditions and heat treatment on polyethylene: lamellar thickness, melting temperature, and density. J. Appl. Phys. **1964**, *35* (4), 1156.
2. Eby, R.K. First-order transition temperatures in crystalline polymers. J. Appl. Phys. **1963**, *34* (8), 2442.
3. Eby, R.K. Diffusion in a polymer with lamellar morphology, polyethylene. J. Appl. Phys. **1964**, *35* (9), 2720.
4. Swan, P.R. Polyethylene unit cell variations with temperature. J. Polym. Sci. **1962**, *56*, 403.
5. Iohara, K.; Imada, Takayanagi, M. Determination of displacement of polyethylene molecules in crystal lattice. Polym. J. **1972**, *3* (3), 357.
6. Kobayashi, Y.; Keller, A. A temperature coefficient of the *c* lattice parameter of polyethylene; an example of thermal shrinkage along the chain direction. Polymer **1970**, *11*, 114.
7. Krenzer, E.; Ruland, W. Temperature dependence of lattice distortions in polyethylene. Colloid Polym. Sci. **1981**, *259*, 405.
8. Asbach, G.I.; Wilke, W. Temperaturabhängigkeit der Realstruktur des kristallinen Anteils von LPDE. Colloid Polym. Sci. **1982**, *260*, 113.
9. Li-shen, L.; Andreeva, N.S.; Kargin, A. X-ray studies of polyethylene monocriystals at various temperatures. Vysokomolekularnyie Soedinenya **1961**, *III*, 1238.
10. Swan, P.R. Polyetylene unit cell variations with branching. J. Polym. Sci. **1962**, *56*, 409.
11. Baker, A.M.E.; Windle, A.H. The effects of branching and fibre drawing on the crystal structure of polyethylene. Polymer **2001**, *42*, 651.

12. Baker, A.M.E.; Windle, A.H. Evidence for a partially ordered component in the polyetylene from wide-angle X-ray diffraction. Polymer **2001**, *42*, 667.

13. Baker, A.M.E.; Windle, A.H. An X-ray diffraction and modeling study of short chain branch location within the structure of polyehylene. Polymer **2001**, *42*, 681.

14. Chang, A.C.; Tau, L.; Hiltner, A.; Baer, E. Structure of blown fil from blends of polyethylene and high melt strength polypropylene. Polymer **2002**, *43*, 4923.

15. Giessen, B.C.; Gordon, G.E. X-ray diffraction: new high-speed technique based on X-ray spectrography. Science **1968**, *159*, 973.

16. Glazer, A.M.; Hidaka, M.; Bordas, J. Energy-dispersive powder profile refinement using synchrotron radiation. J. Appl. Cryst. **1978**, *11*, 165.

17. Buras, B.; Gerward, L.; Glazer, A.M.; Hidaka, M.; Staun Olsen, J. Quantitative structural studies by means of the energy-dispersive method with X-rays from a storage ring. J. Appl. Cryst. **1979**, *12*, 531.

18. Yamanaka, T.; Ogata, K. Structure refinement of GeO_2 polymorphs at high pressures and temperatures by energy-dispersive spectra of powder diffraction. J. Appl. Cryst. **1991**, *24*, 111.

19. Rossi Albertini, V.; Bencivenni, L.; Caminiti, R.; Cilloco, F.; Sadun, C. A new technique for the study of phase transitions by means of energy dispersive x-ray diffraction. Application to polymeric samples. J. Macromol. Sci. Phys. **1996**, *B35*, 199.

20. Rossi Albertini, V.; Caminiti, R.; Cilloco, F.; Croce, F.; Sadun, C. Temperature dependance of PEO phase transition rate by energy dispersive x-ray diffraction. J. Macromol. Sci. Phys. **1997**, *B36*, 221.

21. Caminiti, R.; Gleria, M.; Lipkowitz, K.B.; Lombardo, G.M.; Pappalardo, G.C. Molecular dynamics simulations combined wih large angle x-ray scattering technique for the determination of the structure, conformation and conformational dynamics of polyphosphazenes in amorphous phase: study of poly(di-(4-methylphenoxy)phosphazene). J. Am. Chem. Soc. **1997**, *119*, 2196.

22. Sugiyama, K.; Shinkai, T.; Waseda, Y. High Temp. Mater. Proc. **1998**, *17*, 155.

23. Ballirano, P.; Caminiti, R.; Ercolani, C.; Maras, A.; Orrù, M.A. X-ray powder diffraction structure reinvestigation of α and β forms of cobalt phthalocyanine and kinetics of the $\alpha \Rightarrow \beta$ phase transition. J. Am. Chem. Soc **1998**, *120*, 12798.

24. Caminiti, R.; Rossi Albertini, V. The kinetics of phase transitions observed by energy-dispersive X-ray diffraction. Int. Rev. Phys. Chem. **1999**, *18*, 263.

25. Ballirano, P.; Caminiti, R. Rietveld refinements on laboratory energy dispersive X-ray diffraction (EDXD) data. J. Appl. Cryst. **2001**, *34*, 757.

26. Caminiti, R.; Pandolfi, L.; Ballirano, P. Structure of polyethylene from X-ray powder diffraction: influence of the amorphous fraction on data analysis. J. Macromol. Sci. Phys. **2000**, *B39* (4), 481.

27. Caminiti, R.; Sadun, C.; Rossi, V.; Cilloco, F.; Felici, R. XXV National Congress of Physical Chemistry, Cagliari, Italy, June 17th–21st 1991, Pat. Appl., 01261484, June 23, 1993.

28. Caminiti, R.; Sadun, C.; Bionducci, M.; Buffa, F.; Ennas, G.; Licheri, G.; Musinu, A. Energy dispersive x-ray diffraction applied to isothermal crystallization of the amorphous alloy Ni60B40. Gazz. Chim. Ital. **1997**, *127*, 59.

29. Wilson, A.J.C. Note on the aberrations of a fixed-angle energy-dispersive powder diffractometer. J. Appl. Cryst. **1973**, *6*, 230.

30. Larson, A.C.; Von Dreele, R.B. GSAS General Structure Analysis System. LAUR 86–748. Los Alamos National Laboratory, 1986.

31. Finger, L.W.; Cox, D.E.; Jephcoat, A.P. A correction for powder diffraction peak asymmetry due to axial divergence. J. Appl. Cryst. **1994**, *27*, 892.

32. Von Dreele, R.B. Quantitative texture analysis by Rietveld refinement. J. Appl. Cryst. **1997**, *30*, 517.

33. Ballirano, P.; Caminiti, R.; D'Ilario, L.; Martinelli, A.; Piozzi, A.; Maras, A. Crystallization condition influence on the structural characteristics of poly(p-phenylene sulfide): Rietveld refinement. J. Mater. Sci. **1998**, *33*, 3519.

34. Young, R.A; Ed. In *The Rietveld Method*; Oxford Science Publications: Oxford, 1993; 1.