Ultra-drawing of high molecular weight polyethylene cast from solution

III. Morphology and structure

P. Smith, P. J. Lemstra, J. P. L. Pijpers, and A. M. Kiel

(Received July 21, 1981)

Summary

The morphology and structure of gels produced by quenching semidilute solutions of high molecular weight polyethylene \( \langle M_w \rangle = 1.5 - 3.5 \times 10^6 \) in decalin is discussed. The drawing behavior of the dried gel films at room temperature and at 130 °C and the structural features of films drawn to ratios as high as 130 were examined with various microscopic techniques and wide-angle X-ray scattering.

Zusammenfassung

Morphologie und Struktur von Gelen, hergestellt durch Abschreckung halbverdünnter Lösungen von Polyethylen mit hohem Mol-Gewicht \( \langle M_w \rangle = 1.5 - 3.5 \times 10^6 \) in Decalin werden besprochen. Das Streckverhalten bei Raumtemperatur und bei 130 °C der trockenen Gelfilme und die Struktur-Eigenschaften von im Verhältnis bis 130:1 gestreckten Filme wurden unter Verwendung verschiedener Mikroskop-Techniken und der Weitwinkelstreuung von Röntgenstrahlen geprüft.

Key words

Ultra-drawing, Polyethylene, Morphology.

1. Introduction

Recently, it was demonstrated that semidilute solutions of high molecular weight linear polyethylene \( \langle M_w \rangle \sim 10^6 \) may set to form thermally reversible gels (1–3), as was also reported for branched polyethylene (4). Unlike covalently cross-linked networks, these gels have crystalline junction points. Barham et al. (3) investigated gelation/crystallization of polyethylene in connection with the mechanism of the fiber formation method known as surface growth (5). In our studies (1, 2) high-molecular-weight polyethylene gels were employed to produce high strength/high modulus fibers via a simple solution spinning/drawing route. The gels were prepared in the form of continuous fibers (1) or as gel films (2). It appeared that these polyethylene gels exhibited remarkably good drawability at elevated temperatures, even after complete removal of solvent, in comparison with melt-crystallized material. For example, films "gelled" from a 1 % w/w solution of high molecular weight polyethylene in decalin, which were subsequently freed from solvent, could readily be drawn to a draw ratio \( \lambda \) of 70 at 120 °C (2b), whereas the identical polymer sample crystallized from the melt already failed at \( \lambda = 6 \) under the same drawing conditions. The highly drawn films showed excellent axial orientation of the macromolecules and had a very high room temperature Young’s modulus of 120 GPa (2a, 6). The tensile strength of filaments produced by "gel"-spinning/drawing depended markedly on the molecular weight of the polyethylene, exceeding 3 GPa for molecular weights \( \langle M_w \rangle \) higher than \( 10^6 \) (1d). Clearly, gelation/crystallization is advantageous to improve the drawability of high molecular weight polyethylene, and, accordingly, to manufacture fibers having not only high modulus but also high tenacity.

The phenomenon of enhanced drawability of solution-crystallized high molecular weight polyethylene was discussed in Papers I and II of this series (2a, b). It was argued that the high entanglement density in melt-crystallized high molecular weight polyethylene hampers the achievement of high draw ratios at temperatures where the axial extension process is most effective. Reduction of the number of entanglements \( N \) may be accomplished by dilution and \( N \) is approximately related to the polymer volume
fraction $q_0$ in semidilute and concentrated solutions as (7):

$$N_{\text{solution}} = N_{\text{melt}} \cdot q_0.$$  [1]

Hence, by crystallization from exceedingly diluted solutions the number of entanglements trapped during solidification of the polymer is drastically reduced. Indeed, it was shown previously that the maximum draw ratio of high molecular weight polyethylene increased markedly with decreasing initial polymer concentration (2b). Obviously, a lower (molecular weight dependent) dilution limit is observed, because coherent gel structures are not normally generated at a polyethylene concentration below the onset or coil overlap (2b). Rather loose agglomerates of single crystals are then obtained, that is under quiescent conditions. These single crystals and annealed mats thereof exhibit excellent drawability, as was reported already many years ago by a number of authors (8-11). From a technological point of view this is, however, of limited value, because continuous films of fibers cannot be produced in this way. Therefore gelation, i.e. formation of macroscopically sufficiently coherent structures is a prerequisite

Although crystallization of linear polyethylene from dilute solutions is a widely studied topic in polymer physics (cf. 12), relatively few morphological investigations (notably those by Keith et al. (13)) were devoted to crystallization from more concentrated solutions, where gelation takes place. This is in particular remarkable since most industrial solution polymerization processes are operated in the high concentration range from 20-25% w/w polyethylene. Gelation of polyolefins, which featured only recently in the literature was already observed many years ago in various processes on technological scale (14-16).

Yet, little attention was paid to the morphological and structural characteristics of polyethylene gels, which appeared to be so useful in the formation of high strength/high modulus fibers and films (1-3).

The purpose of the present paper is twofold. First of all it is intended to discuss in some detail the structure of polyethylene gels. The second part of this study is concerned with the drawing behaviour of these gels, particularly in the Jumbo-range of ultradrawing (termed after Peterlin), i.e. draw ratios of 50-130, where major improvement of macromolecular orientation was still found to occur.

2. Experimental

2.1 Materials

The polyethylene used in the present study was Hostalen GUR 412 ($M_w = 3.5 \cdot 10^6$ kg/kmol). Some of the results quoted in this paper were obtained in earlier investigations where Hostalen GUR with $M_w = 1.5 \cdot 10^6$ kg/kmol was employed.

The solvent was decahydronaphthalene (decalin) from J. T. Baker Chemicals. It was used without purification.

2.2 Samples

Gel films of polyethylene/decalin were produced according to the methods that were described in Part II of this series (2b). Solutions containing 0.6, 2.0 or 10% w/w of the polymer were prepared at 160°C, and they were stabilized by 0.5% w/w of the anti-oxidant di-t-butyldiphenol. The more dilute solution (0.6 and 2%) was cast to form coherent gel films. The extremely viscous concentrated solution containing 10% w/w of polyethylene was compression moulded into a sheet, which was subsequently quenched to room temperature.

The as-cast and compression moulded gel films were allowed to dry on the air leaving films with a thickness in the range of 0.5 - 1.5 mm.

2.3 Techniques

2.3.1 Drawing

Drawing of the dried gel films was performed both at room temperature using a simple stretching frame, and at 130°C with the aid of an Instron tensile tester that was equipped with a temperature programmed oven. Elongation at elevated temperatures was carried out at a rate of 100 mm/min, and the initial specimen length was 20 mm. Draw ratios were determined in the usual way by measuring the displacement of ink marks placed 1 mm apart onto the specimens prior to drawing.

2.3.2 Microscopy

Polyethylene gels prepared onto copper grids were studied by conventional transmission electron microscopy.

Scanning electron microscopy was carried out on gels that were extracted with hexane, subsequently dried and fractured in liquid nitrogen.

The drawn films were examined in the polarizing microscope while immersed in oil and in the scanning electron microscope.

2.3.3 Wide-angle X-ray scattering

Wide-angle X-ray scattering was performed with aid of a Statton flat film camera, which was operated in vacuum. Ni-filtered Cu Kα-radiation was used. The exposed films were analysed with a micro-densitometer.
3. Results and discussion

The results obtained in this study will be presented and discussed in the following three sections: Gel structure, Drawing behavior and Structure of drawn films.

3.1 Gel structure

The gel state is perhaps the most versatile aggregation state of matter (cf. 17), and it is, accordingly, difficult to present a unifying definition of gels. In this paper the term gel refers to a macroscopically coherent structure, that is spatially cross-linked, comprises a major amount of low molecular weight liquid, and exhibits elastic properties not unlike those of solids.

Dissimilar to covalently bonded chemically cross-linked networks, or networks cross-linked physically by a few associated macromolecules or microcrystallites, the polyethylene gels that we are currently dealing with are stabilized by readily recognizable crystals. Evidence for the crystalline nature of the junction points was obtained by wide-angle X-ray scattering (WAXS). Figure 1 displays a WAXS-pattern of a gel that was prepared by quenching a 2 % w/w solution of high molecular weight polyethylene to room temperature. This X-ray pattern exhibits two rather sharp diffraction rings, which were identified as the (110) and (200) reflections of the orthorhombic polyethy-

Fig. 1. WAXS-patterns of gel produced by quenching a 2 % w/w solution of high molecular weight polyethylene in decalin to room temperature

Fig. 2. Scanning electron micrographs of extracted polyethylene/decalin gels. A. Polymer solution stored for 45 min at 160 °C before quenching to room temperature; magnification 1000 × B. Polymer solution mechanically agitated prior to gelation; magnification 2500 ×
lene unit cell, and a diffuse halo that was due to the solvent. This halo disappeared upon removal of the decalin from the gel (see fig. 5).

As most crystalline gels, the polyethylene gels were thermally reversible. Upon heating the gel reverted into a fluid, or sol, at the gel-melting temperature of about 90 °C. Generally the structure of thermally reversible cross-links is less well-defined than that of covalent junction points, and it depends largely on the thermal and rheological history of the solutions that the gels were generated from. This was also very much true of the present polyethylene gels, as is illustrated by the photographs presented in figure 2. This figure displays two scanning electron micrographs of gels (extracted with hexane and subsequently dried) of high molecular weight polyethylene prepared from a 2 % w/w solution in decalin under different rheological conditions. The micrograph in figure 2A reveals the structure of a gel obtained from a solution that was kept at 160 °C for 45 minutes after dissolution of the polymer. This structure comprised interconnected lamellar crystals. The photomicrograph in figure 2B was taken from an extracted and dried gel that was generated from a 2 % w/w solution which was stirred at 160 °C prior to quenching to room temperature. Now the cross-linking loci of the gel appeared to consist of fibrillar shish-kebab-like crystals. Clearly, orientation of the macromolecules induced by the mechanical agitation was the underlying cause of fibrillar crystallization in the latter gel. Storage at 160 °C for 45 minutes ensured relaxation of the polymer chains that might have been oriented during the dissolution procedure. Precocious quenching of not fully relaxed solutions that contained remnants of flow-induced orientation resulted in the formation of rather complex gel structure comprising lamellar crystals, row-nucleated crystals and, in the extreme case, shish-kebabs (see fig. 3).

The structure of gels obtained from stirred solutions and the memory-effect of agitated solutions of high molecular weight polyethylene where extensively studied and discussed in connection with fiber formation from flowing solutions by Barham et al. (3). These authors demonstrated that upon stirring a network of bundle-like nuclei was generated which set to form a clear transparent gel at remarkably high temperature, well above 90 °C (18). Upon further cooling to room temperature lamellar crystals developed, giving rise to an opaque appearance of the final gel. The morphology of these gels was disclosed by Barham et al. (3) and closely resembles the structure presented in figure 2B.

Such composite morphologies, comprising fibrillar and lamellar crystals, usually are unfavourable for drawing (19), since the various crystalline entities have different optimum drawing temperatures. Therefore, we tried in our preparations to avoid excessive fibrillar crystallization by storage of the polyethylene solutions at high temperature under quiescent conditions prior to quenching. Connectedness within the gels thus produced is provided to some extent by intercrystalline links (13) and much more by ramified lamellar crystals (see figures 2A and 4) of the kind that is commonly observed in spherulites.

Next we will address the structural changes that occurred upon removal of the decalin from the as-set gels. There are two distinct ways in which the solvent could be removed from the polyethylene gels, each resulting in a different morphology of the remaining polymer structure. The first method, which, in fact, was applied to produce the scanning electron micrographs in figures 2 and 4, consisted of extraction of decalin with a low boiling solvent such as

Fig. 3. Transmission electron micrographs of a row-nucleated structure (A, 9000 ×) and shish-kebab (B, 9000 ×, Pt-shadowed) observed in polyethylene gels obtained from stressed solutions.
hexane, and subsequent drying. This procedure yielded a highly porous, completely opaque material (see fig. 2, 4). Compression at room temperature produced a semi-transparent film with drawing properties no different from the original porous structure (2b). The second method involved evaporation of the decalin at ambient conditions, upon which a dense film was generated containing 3-4 % w/w residual solvent. Usually this last trace of decalin was removed by extraction with methanol or hexane. Reduction of the gel volume occurred primarily in the direction of the film thickness. This caused the lamellar crystals in the gel to orient preferentially with the chain axis perpendicular to the surface of the polymer film. The $a$ and $b$-axes were distributed randomly in the plane parallel to the film. This was deduced from wide-angle X-ray patterns of these dried gels, presented in figure 5. This preferred orientation, which is commonly observed in sedimented single crystal mats (8-11), was not found in the extracted gel films. In our studies we were unable to trace differences in drawing behavior between gels dried by either of the methods.

The minimum concentration observed for gelation of polyethylene solutions appeared, not unexpectedly, to depend on the molecular weight of the polymer sample. This concentration was always found in the vicinity of the critical concentration for the onset of coil overlap, which is roughly given by (see e.g. ref. 7):

$$[\eta] \cdot c \sim 1$$

where $[\eta]$ is the intrinsic viscosity and $c$ the polymer concentration (in g/dl). Thus, gels of lower molecular weight polyethylene were obtained, provided that the polymer concentration was sufficiently high. The latter gels became increasingly brittle at lower molecular weights. The use of such gels is rather limited, since improvement of drawability by disentangling through gelation crystallization is drastically reduced due the high initial polymer concentration (2b) needed for the formation of the gels. Moreover, low molecular weight polyethylene exhibits excellent drawability when crystallized from the melt and a beneficial change thereof is not needed (20).

As was already mentioned in the introduction to this paper, at polymer concentration below
the onset of coil overlap loose aggregates of single crystal were generated upon cooling under quiescent conditions.

3.2 Drawing behavior

Drawing of polymers may proceed with a distinct transition – the neck – from the isotropic to the oriented structure, a process generally referred to as cold drawing, or by homogeneous deformation of the entire specimen. In both cases the original material is transformed into a fibrous structure. For polyethylene this process is completed at a draw ratio ($\lambda$) of about 8–10. Our understanding of this transition itself as well as the phenomena occurring during further drawing of the fibrous structure is primarily due to Peterlin. Excellent reviews concerning these processes are given in references (21, 22), and these topics will not be elaborated on in the present paper.

This section is intended to demonstrate the marked effect of the initial polymer concentration on the drawing behavior of solution “gel-led” films of high molecular weight polyethylene. Figure 6 shows optical micrographs of polyethylene films that were cast from 0.6 and 10 % w/w solutions, as well as melt-crystallized material, all drawn at room temperature. The melt-crystallized film, drawn approximately 3 times, exhibited homogeneous deformation, i.e. without necking or apparent fibril formation (fig. 6A). Drawing of the film gelled from the 10 % solution proceeded with multiple necking (fig. 6B) and, finally, the film obtained from the 0.6 % solution showed one sharp neck (fig. 6C).

The scanning electron micrograph presented in figure 7 was taken from the drawn 10 %-film. This micrograph illustrates very clearly the abundance of micronecks throughout the sample. Drawing of the various films at 130 °C advanced much in the same manner as at room temperature, that is with respect to the necking behavior. Naturally (2b), the maximum draw ratio increased drastically at higher temperatures, as was the tendency towards fibrillation reduced in comparison with drawing at room temperature. This is obviously due to enhanced plastic deformation at high temperatures.

The differences observed in necking behavior of the films obtained from the 0.6 and 10 % solution and the melt-crystallized material can readily be understood in terms of interconnect-

Fig. 6. Optical micrographs of high molecular weight polyethylene films drawn at room temperature: A – melt crystallized; B – cast from 10 % solution; C – cast from 0.6 % solution. Magnification 200 ×

edness of the macromolecules in the various samples. In the melt-crystallized film the very long polyethylene chains are not only incorporated in many crystallites, but, more important, they are connected to one another by numerous trapped entanglements, which act as friction centres during drawing. Hence, the applied drawing force is very effectively transmitted to the majority of the macromolecules, giving rise to homogeneous deformation. If, on the other
hand, the high molecular weight polyethylene is “gelled” from semi-dilute solution particularly the number of trapped entanglements is drastically reduced, and the macromolecules can readily be extended and aligned since they need not drag along numerous other chains in this process. Only when the force required for further extension of partly aligned molecules exceeds the force to initiate plastic flow within the unoriented material new macromolecules will become extended, i.e. the neck proceeds. Drawing of the film obtained from the 10 % solution represents the intermediate case.

3.3 Structure of drawn films

The structure of ultradrawn polyethylene (draw ratios up to 30–40) has been the subject of a great many studies, notably by Peterlin, Ward, Porter and Keller, and their respective co-workers. Accordingly, this topic will not be dwelled upon in this paper; for comprehensive reviews by these authors the reader is referred to reference (22). The general conclusion arrived at is, broadly speaking, that the structure of ultra-drawn polyethylene has a fibrous nature. Although somewhat different views exist about the microstructure of the fibrillar entities, it is generally believed that the fibrils comprise highly oriented and extended macromolecules. This favorable packing of chains is the underlying cause of the high stiffness of these drawn materials, which may exhibit axial Young’s moduli as high as 70 GPa, measured at room temperature (22). The structure of films of high molecular weight polyethylene, cast from a semi-dilute solution and subsequently drawn to similar high draw ratios of 30–40 appeared to be no different from the melt-crystallized/drawn material mentioned above, when viewed in the optical microscope or examined by scanning or transmission electron microscopy or X-rays. Also the Young’s modulus of the solution cast/30 times drawn high molecular weight polyethylene films was found to be in the range from 70–100 GPa (2a, 6).

As was already noted previously (2b), the maximum draw ratio of a single polyethylene chain varies roughly with the molecular weight as:

$$\lambda_{\text{max}} \propto M W^{0.5}.$$

Hence, application of high molecular weight polyethylene permits higher draw ratios, that is when appropriate “dis-entanglement” of the long chains is accomplished prior to drawing, as in the present study. It was demonstrated in Part II of this series that the maximum draw ratio of solution-cast high molecular weight polyethylene increased drastically with decreasing initial polymer concentration (2b). In the present work polyethylene with $M_w = 3.5 \cdot 10^6$ kg/kmol was gelled from a 0.6 % w/w solution in decalin. The maximum draw ratio of the dried film amounted to $\sim 130$ at $130 \, ^\circ C$, which is very well in agreement with a prediction made with the previously derived relation between $\lambda_{\text{max}}$ and the initial polyethylene volume fraction $\varphi$ (2b):

$$\lambda_{\text{max}} = \lambda_{\text{max}}^1 \cdot \varphi^{-0.5}.$$

Here $\lambda_{\text{max}}^1$ refers to the maximum draw ratio of melt-crystallized material, which had the value of 9.5 at $130 \, ^\circ C$ for the present polyethylene sample. Substitution of the initial polymer vol-
volume fraction of 0.006 (which is at the dissolution temperature of 160 °C roughly equal to the weight fraction) in equation (4) leads to a calculated maximum draw ratio at 130 °C of 123 for the solution cast film. This value compares favorably with the experimental value of about 130.

This section deals in particular with changes in structure and morphology occurring upon increasing the draw ratio from 30 to 130. Tensile measurements performed at room temperature revealed that the mechanical properties of these Jumbodrawn films were still markedly enhanced in comparison with those of the ultra-drawn specimens. An axial Young's modulus of 150 GPa, measured at a strain rate of 0.1 min⁻¹, was found for films drawn to a ratio of 130.

Direct evidence for improvement of chain orientation is provided by wide-angle X-ray scattering. Figure 8 displays WAXS-patterns of films cast from a 0.6 % solution that were drawn at 130 °C to draw ratios of 25, 50 and 130 (film thickness resp. 9, 5 and 2 μm). The polyethylene unit cell appeared to be orthorhombic in all samples. Although it is generally assumed that near complete chain alignment in the direction of draw is already achieved at relatively low draw ratios of 15-20, figures 8B and C illustrate that at very high draw ratios major improvement of the macromolecular orientation occurred. In fact, the WAXS-pattern of the 130 times drawn film comprises reflection spots of a perfection that is usually observed for single crystals. Calculation of the well-known orientation functions here is no longer meaningful.

Comparison of patterns B and C reveals that reflections such as (200) and (201), which are present in B, are absent in the latter. As a matter of fact, the intensity of the (200)-reflection gradually decreased with increasing draw ratio, as becomes apparent from the equatorial microdensitometer traces of the WAXS-patterns of figure 8B and C and of figure 5A (undrawn). In addition to the absence of the (200) spot, pattern C is characterized by a strongly increased intensity of the (020) reflection, in comparison with A and B. These observations point to a double orientation of the polyethylene lattice in the 130 times drawn film. Apart from near perfect c-axis orientation in the direction of draw, this Jumbodrawn film exhibited strong orientation of the b-axis in the plane of the film and, accordingly, a-axis orientation perpendicular to the film.

Detailed inspection of pattern (8C) disclosed the absence of the following reflections: (200), (210), (310), (400) and (201), which normally are observed in specimens with random distribution of the a and b-axis. This lead us to the conclusion that the angle between the a-axis and the film surface normal was less than 38°.
It should be noted that double or biaxial orientation in drawn polyethylene films was reported already a number of years ago by Ishikawa et al. (10). These authors observed this type of orientation in sedimented mats of single crystals that were drawn at 90 °C to ratios of 25–35, and they attributed this phenomenon to preferential tilting of the polymer chains about the \( b \)-axis. It is, however, remarkable that in our studies and in investigations by other authors (22) on the structure of polyethylene drawn to \( \lambda = 35 \) no double orientation of the crystalline lattice was observed. Moreover, a 130 times drawn film of high molecular weight polyethylene with a final thickness of 0.1 mm produced for X-ray examination in the direction of draw

![Fig. 9. Equatorial densitometer traces of WAXS-patterns presented in figure 8B and C and 5A](image)

\( \lambda = 1 \) (A)

\( \lambda = 50 \) (B)

\( \lambda = 130 \) (C)

Fig. 9. Equatorial densitometer traces of WAXS-patterns presented in figure 8B and C and 5A

![Fig. 10. Scanning electron micrographs of films of high molecular weight polyethylene cast from a 0.6 % solution in decalin, dried and drawn at 130 °C to draw ratios of 35 (A) and 130 (B). Magnification 3000 ×](image)
did not exhibit the biaxial orientation mentioned above. These observations, in our opinion, point to the conclusion that the origin of the double orientation of the polyethylene crystalline lattice may be found in the thickness of the drawn film or in a correlation between the aspect ratio of the cross-sectional areas of the film and of the fibrillar (possibly lath-shaped) crystalline entities, rather than in a particular deformation mode of the macromolecules or in an increased tendency towards multi-axial perfection upon extended drawing. An estimation of the final thickness of the drawn films produced by Ishikawa et al. (10) yielded a value of about 3–5 μm, which is in close accord with that of our Jumbodrawn films showing biaxial orientation.

Apart from improvement of chain orientation upon increasing the draw ratio from 25 to 130, also the surface morphology showed a small, but distinct, enhancement. Figure 10 displays two scanning electron micrographs of films of high molecular weight polyethylene cast from a 0.6 % solution that were drawn at 130 °C to draw ratios of 35 and 130. Although both micrographs exhibit a highly oriented fibrillar morphology, the surface of the 130 times drawn film appeared to be considerably more smooth and regular. The striations observed in this picture (fig. 10B) show only few interruptions or imperfections. The morphology of this film closely resembles that observed for extended chain crystals produced at high pressure (23).

Finally, a few remarks need to be made about the transverse properties of the drawn films. As was already noted by other authors (22), polyethylene exhibits exceedingly poor transverse mechanical properties and a strongly increased fibrillation tendency at increasing draw ratios. Figure 11 shows a scanning electron micrograph of a film drawn 35 times that was partly spliced at room temperature. It is seen in this micrograph that the fibrillar structure was still highly interconnected and that severe lateral deformation occurred prior to tearing. At increasing draw ratios this deformability perpendicular to the draw direction was highly reduced and the Jumbodrawn films were readily spliced. Figure 12 shows a high resolution scanning electron micrograph of fibrils and microfibrils that were generated upon splicing the 130 times drawn film. The thickness of the microfibrils was estimated to be about 40 nm. Whether or not these microfibrils are the elementary entities
constituting the oriented structure remains a question to be dealt with in the future.

Acknowledgement

The authors are indebted to their colleagues of the Department of Physical Chemistry (DSM), in particular to Mr. S. M. G. Nadorp, for their valuable assistance in the preparation of this manuscript. They also wish to thank Dr. C. G. Vonk (DSM) and Dr. P. J. Barham and Professor A. Keller (University of Bristol) for their continuous interest in this work and for their helpful suggestions. This manuscript was partly written during a stay of one us (P. S.) at the Centre de Recherches sur les Macromoléculles Végétales, Grenoble, with Dr. H. Chanzy, to whom this author is indebted for his warm hospitality.

References


Author's address:
P. Smith et al.
DSM, Concerndienst Research en Octrooien
Central Laboratory
Postbus 18
6160 MD Geleen (The Netherlands)