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# Intrinsic Molecular Mobility and Toughness of Polymers II

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# **Intrinsic Molecular Mobility and Toughness of Polymers II**

Volume Editor: Hans-Henning Kausch

With contributions by

V. Altstädt · M. C. Baietto-Dubourg · C.-M. Chan · A. Chateauminois  
R. Estevez · E. Van der Giessen · C. Grein · L. Li



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## Preface

The enormous length of macromolecules and the low intra- and intermolecular barriers opposing rotation and displacement of molecular groups or of even longer segments are at the origin of the unique visco- and rubber-elastic behaviour of polymer solids. Molecular mobility influences all phases of processing and use of such materials. Thus segregation and phase separation in the melt as well as structure development through crystallization depend on chain dynamics. The same is true for most deformation mechanisms, sample stiffness and ultimate properties such as toughness. Considerable progress has been obtained in the last decade in the understanding of the mutual relationship between the primary molecular parameters chain configuration, architecture and molecular weight (MW) on the one hand, and the response of a loaded entanglement network, the nature of the processes limiting stress transfer and the resulting mode of mechanical breakdown on the other. In view of the large technical importance of mechanical performance it seems to be adequate to review this subject, the *Intrinsic Molecular Mobility and Toughness of Polymers*.

In their introductory contribution Kausch and Michler discuss the elementary, time-dependent molecular deformation mechanisms, the competition between them, and their influence on the different failure modes of thermoplastic polymers (crazing, creep, yielding and flow, fracture through crack propagation). By establishing a *micro-morphological model* of polymer deformation and durability the authors highlight the dual role of segmental jumps and displacements to improve toughness by energy dissipation and relaxation of critical stresses and to influence without exception all damage mechanisms.

The dynamic response of a chain segment to thermo-mechanical excitation strongly depends on in-chain cooperative motions. By combining the powerful techniques of multi-dimensional Nuclear Magnetic Resonance and of dielectric and dynamic mechanical analysis Monnerie, Lauprêtre and Halary have investigated the *intensity and molecular origin of sub- $T_g$  relaxations* and their degree of coupling for five structurally quite different amorphous polymers. Their important findings are reported in two comprehensive reviews treating the effect of chain configuration on segmental mobility and its effect on the toughness of these materials, respectively.

Essential features of the entanglement network and of the morphology of semi-crystalline polymers are determined through the crystallization process.

Chan and Li review homogeneous and heterogeneous nucleation. Using the new hot-stage in-situ AFM technique they particularly investigate the propagation of *founding lamellae*, their branching, interaction and development into lamellar sheaves and spherulites. In her contribution Grein gives a thorough *analysis of the influence of phase structure* ( $\alpha$ - and  $\beta$ -crystalline polypropylene) as compared to the effect of elastomeric modifier particles. She concludes that the capacity of a matrix to deform remains an essential requirement for high toughness materials.

Stress cracking environments are known to enhance the mobility in the affected surface regions. Altstädt shows that the rate of fatigue crack propagation at *constant stress intensity factor*  $K$  proves to be a sensitive quantitative measure of the influence of active media. He also points to the dual role of segmental mobility, permitting stress relaxation followed by strain hardening or unstable softening, respectively. The complex conditions of *fracture during sliding contact* are reviewed by Chateauminois and Baietto-Duboug. They arrive at the conclusion that the main wear mechanism of glassy polymers, asperity scratching, is strongly controlled by competition between crazing processes and shear yielding. In the final contribution Estevez and van der Giessen present a computational analysis of the fracture of glassy polymers. The *applied cohesive zone model* takes into consideration the three steps of crazing (initiation, thickening and breakdown) and seems to be sufficiently flexible to adapt to future refinements.

The editor wishes to thank all authors for their willingness to cooperate in this joint effort, which so heavily depended on the concourse of their special expertise. It is hoped that the resulting detailed overview will be of help to more fully exploit the large potential offered by polymeric systems. Unfortunately the comprehensive treatment has made it necessary to publish the above, closely related eight contributions in two consecutive volumes of the *Advances in Polymer Science*, Vols. 187 and 188. However, a common *Subject Index* in both volumes and the reproduction of the two *List of Contents* should make it easy for the reader to find the desired information.

Lausanne, September 2005

Hans-Henning Kausch

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## **Contents of Volume 187**

### **Intrinsic Molecular Mobility and Toughness of Polymers I**

**Volume Editor: Hans-Henning Kausch**

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#### **The Effect of Time on Crazing and Fracture**

H.-H. Kausch · G. H. Michler

#### **Investigation of Solid-State Transitions in Linear and Crosslinked Amorphous Polymers**

L. Monnerie · F. Lauprêtre · J. L. Halary

#### **Deformation, Yield and Fracture of Amorphous Polymers: Relation to the Secondary Transitions**

L. Monnerie · J. L. Halary · H.-H. Kausch

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# Contents

**Direct Observation of the Growth of Lamellae and Spherulites by AFM**  
C.-M. Chan · L. Li . . . . . 1

**Toughness of Neat, Rubber Modified and Filled  $\beta$ -Nucleated Polypropylene: From Fundamentals to Applications**  
C. Grein . . . . . 43

**The Influence of Molecular Variables on Fatigue Resistance in Stress Cracking Environments**  
V. Altstädt . . . . . 105

**Fracture of Glassy Polymers Within Sliding Contacts**  
A. Chateauminis · M. C. Baietto-Dubourg . . . . . 153

**Modeling and Computational Analysis of Fracture of Glassy Polymers**  
R. Estevez · E. Van der Giessen . . . . . 195

**Author Index Volumes 101–188** . . . . . 235

**Subject Index** . . . . . 259

# Direct Observation of the Growth of Lamellae and Spherulites by AFM

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1	Introduction . . . . .	2
2	Crystallization Processes . . . . .	6
2.1	Homogeneous Nucleation—Birth of Primary Nuclei . . . . .	6
2.2	Development of the Founding Lamella . . . . .	9
3	Development of the Lamellar Sheaf . . . . .	14
3.1	Branching of Lamellae . . . . .	14
3.2	Branching at Different Temperatures . . . . .	19
3.3	Propagation of Lamellae . . . . .	22
3.4	Lamellar Growth Rate . . . . .	25
4	The Effect of Film Thickness on Lamellar Growth Rate and Morphology . . . . .	29
5	Formation of Spherulites . . . . .	35
6	Heterogeneous Nucleation . . . . .	37
7	Summary . . . . .	39
	References . . . . .	39

**Abstract** This article describes some of the progress made in the understanding of the growth of polymer lamellae and spherulites using atomic force microscopy (AFM) in the last five years. High-resolution and real-time AFM phase imaging enables us to observe the detailed growth process of lamellae. During the early stage of crystallization, embryos appear and disappear on the film surface. A stable embryo develops into a single lamella, which develops into a founding lamella. Then, the founding lamella develops into a lamellar sheaf through branching and splaying. Through further branching and splaying, a lamellar sheaf develops into a spherulite with two eyes at its center.

**Keywords** Atomic force microscopy · Branching · Crystallization · Embryo · Lamella · Polymer · Spherulite

## Abbreviations

AFM	atomic force microscopy
EM	electron microscopy
$T_g$	glass transition temperature
<i>i</i> -PP	isotactic polypropylene
<i>i</i> -PS	isotactic polystyrene
OM	optical microscopy
BA-C10	poly(bisphenol A- <i>co</i> -decane)
BA-C8	poly(bisphenol A- <i>co</i> -octane)
PEO	poly(ethylene oxide)
PS[(S)-LA]	poly[(s)-lactide]
PCL	polycaprolactone
PE	polyethylene
PP	polypropylene
SEM	scanning electron microscopy
TM-AFM	tapping-mode atomic force microscopy
TEM	transmission electron microscopy
$\Delta G_{\text{edge}}$	free energy of formation for an edge-on primary nucleus
$\Delta G_b$	free energy change per unit of crystalline material formed
$\gamma_f$	interfacial energy between the folding surface and the melt
$\gamma_\ell$	interfacial energy between the lateral plane and the melt
$\gamma_{\text{cs}}$	interfacial energy between the crystal and the substrate
$\gamma_{\text{ms}}$	interfacial energy between the melt and the substrate
$a$	dimension of a nucleus;
$a_c$	critical dimension of a nucleus
$\ell$	dimension of a nucleus
$\ell_c$	critical dimension of a nucleus
$\Delta G_{\text{flat}}$	free energy of formation for a flat-on nucleus
$\Delta H_b$	enthalpy of melting per unit volume of crystal
$T_m^o$	equilibrium melting point of a polymer
$T_c$	crystallization temperature
$\bar{M}_W$	weight-average molecular weight
$g$	average growth rate of a lamella
$L_0$	length between the lamellar tip and the location at which an induced nucleus just appears
$t_i$	induction time for the formation of an induced nucleus

## 1

### Introduction

When a polymer crystallizes from the melt without disturbance, it normally forms spherical structures that are called spherulites [1, 2]. The dimensions of spherulites range from micrometers to millimeters, depending on the structure of the polymer chain and the crystallization conditions, such as cooling rate, crystallization temperature, and the content of the nucleating agent. The structure of spherulites is similar regardless of their size; they are aggregates of crystallites [1–6].

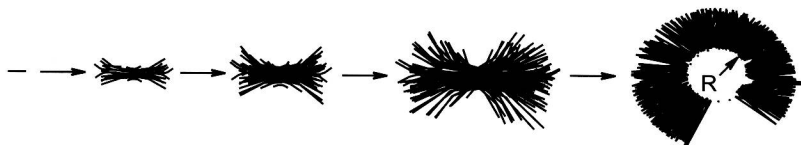
Much effort has been devoted to investigating the detailed architectures and the construction of spherulites. Early investigations of the crystallization of polymers through optical microscopy (OM) [7, 8] posited that polymer spherulites consisted of radiating fibrous crystals with dense branches to fill space. Later, when electron microscopy (EM) became available, spherulites were shown to be comprised of layer-like crystallites [9, 10], which were named lamellae. The lamellae are separated by disordered materials. In the center of the spherulites, the lamellae are stacked almost in parallel [5, 6, 11–15]. Away from the center, the stacked lamellae splay apart and branch, forming a sheaf-like structure [11, 13–15]. It was also found that the thicknesses of lamellae are different [5, 6, 11, 12]. The thicker ones are believed to be dominant lamellae while the thinner ones are subsidiary lamellae.

EM and OM have a few drawbacks, making them unsuitable for application in real-time studies of spherulitic growth at the lamellar level. The resolution of OM is too low to detect lamellae. The required sample preparation techniques for scanning electron microscopy (SEM) and transmission electron microscopy (TEM) usually stop the crystal growth. Examining the internal structure of growing spherulites in a partially crystallized and quenched polymer sample overcomes this drawback to a certain extent, and the process of spherulite formation has been deduced [4, 6, 11]. A spherulite is believed to develop from a stack of lamellae. During the growth process, the stacked lamellae splay apart continually and branch occasionally. The continuous growth of the dominant lamellae leads to the formation of a spherical skeleton and the subsidiary lamellae fill up the space between the dominant lamellae.

Phillips and Edwards studied the spherulitic morphology and the growth kinetics of natural, isomerized, and synthetic *cis*-polyisoprene under different pressures with TEM [16–23]. The polymer thin films were stained with osmium tetroxide vapor to stop the crystallization and enhance the phase contrast. Heterogeneous nucleation and homogeneous nucleation were both observed [18]. Heterogeneous nucleation was identified by the observations of lamellae growing in all directions normal to the surface of the nucleus. In homogeneous nucleation, lamellae were observed to grow in two directions. The growth rates of dominant and subsidiary lamellae were found to be the same and constant [19]. The spherulitic morphologies of melt-crystallized poly(4-methyl pentane) [24], polyethylene (PE) [10, 11, 13, 25–27], isotactic polypropylene (*i*-PP) [11], and isotactic polystyrene (*i*-PS) [28] were investigated using OM and TEM. The main points made by the authors concerning the spherulitic growth were that dominant lamellae first grew into the melt to form a skeleton of a spherulite by splaying and branching; inter-dominant lamellar regions were filled with subsidiary lamellae; and branching was mainly through giant screw dislocations. The pressure build-up by molecular cilia between lamellae caused the splaying.

Splaying apart and branching of lamellae to form spherulites due to the repulsion of the amorphous materials between the lamellae are the general features of polymer spherulites [4, 11, 14, 15]. It is understood that to achieve a spherical shape, primary lamellae have to splay apart and branch. Even so, the origins for the splaying and branching processes have not been confirmed. The early investigations of polymer crystallization suggested that the accumulation of noncrystallizable impurities in the front of growing lamellae was the reason for branching [29]. But several authors have queried this diffusion-control mechanism. On the basis of the morphology of growing spherulites in quenched samples, Bassett and his colleagues proposed that branching is a result of secondary nucleation on primary lamellae [11]. They also suggested that the mutual repulsion between the adjacent primary lamellae, resulting from the protruding cilia of the lamellae, is the origin for splaying of the stacked lamellae. However, the secondary nucleation and splaying processes have never been observed directly owing to the limitations of EM.

This process described, as shown schematically in Fig. 1, is still hypothetical because the description is not based on direct observations of the formation of spherulites. Furthermore, how the stacked lamellae are generated is still not clear, though nucleation of a supercooled melt can be predicted from thermodynamics [4]. The invention of atomic force microscopy (AFM) [30–36] has made direct observation of the crystallization of polymers possible. In addition to its high resolution, contact-mode AFM can record real-time images of a dynamic process. The disadvantage of contact-mode AFM is the considerable pressure exerted by the probe tip on the sample surface, causing sample deformation and induced nucleation. In particular, such damage to soft samples such as polymers and biological specimens limits the applicability of AFM. In recent years, the development of tapping-mode AFM (TM-AFM) has enhanced the capability of AFM as a surface analysis technique [35, 36]. In TM-AFM, a fast oscillating probe is used for surface imaging. During the operation, the tip makes contact with the surface briefly in each cycle of oscillation. Many studies have been performed to interpret the height and phase images recorded by TM-AFM [37–40]. The results clearly indicate that phase images can provide enhanced contrast on heterogeneous surfaces. TM-AFM has been shown to be a powerful tool to study the surfaces of polymer blends, copolymers, and semi-crystalline polymers [36–38, 41–44].



**Fig. 1** Schematic showing the formation of a spherulite from a lamella



By utilizing the advantages of AFM, the spherulites and lamellae of various semi-crystalline polymers have been investigated [45–84]. The lamellar thickness [49, 68] and hedritic morphology [54] of polypropylene (PP) were studied by Vancso and colleagues and the thickness of the lamellae was found to be identical to the values in the literature as revealed by other techniques. The growth rates of a spherulite and the internal lamellae of a poly(hydroxybutyrate-co-valerate) copolymer have been determined by Hobbs and colleagues with TM-AFM [58]. The result indicated that the overall gross growth front of a spherulite can propagate at a constant rate although internal lamellae cannot propagate in the same way. It was posited that the spherulite growth rate is dependent on the rate of secondary nucleation on the existing lamellae but not on the growth rate of the lamellae. Melting and crystallization of poly(ethylene oxide) (PEO) [47, 57], PEO in PEO/poly(methyl methacrylate) blends [48], poly(ether ether ketone) [53], and PE [55] have been studied by an AFM equipped with a hot stage.

In order to record the dynamic polymer crystal growth process in-situ, two factors are significantly important. One is the use of a very high resolution technique. Such a technique can repeatedly record the same area without damage to or significant interactions with the sample. AFM has been proved to be a successful tool to fulfill this task. The other key factor is that the polymers must have an appropriate crystallization rate. It generally takes an AFM several minutes to produce an image. This requires that the polymer has a very slow crystallization rate. The crystallization rates of most semi-crystalline polymers at room temperature are too fast.

It is well known that the crystallization rate and crystallinity of a polymer are strongly dependent on the crystallization temperature and polymer chain structure. A polymer can be controlled to have a slow crystallization rate by crystallizing at a high temperature close to its melting point or a lower temperature near its glass transition temperature. It is much more difficult to obtain high-quality AFM images of polymers at high temperatures because the melt may interact with the AFM tip which may induce crystallization as well. To run AFM at low temperatures, a cooler is required to keep the sample cool. As a result, the operation at or near room temperature is preferred. Modifying the polymer chain structure can reduce the crystallization rate. Varying the flexible segment length can control the flexibility of the polymer chain, which affects its crystallization rate significantly. Li et al. prepared a series of polymers (BA- $C_n$ ) by phase-transfer catalyzed polyetherification of 1,  $n$ -dibromoalkane ( $C_n$ ,  $n = 4, 6, 8, 10, 12, 14$ , and 18) with bisphenol A (BA), with a hard BA segment, and a flexible  $C_n$  segment [85]. The synthesis is described in Scheme 1. BA-C8 and BA-C10, which crystallize slowly, are ideal candidates for in-situ AFM crystallization studies. Their physical properties are summarized in Table 1.