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With contributions by

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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* (α- and β-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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Intrinsic Molecular Mobility and Toughness of Polymers II

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