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Structure and Dynamics of Glasses and Glass Formers

EDITORS:
C.A. Angell
K.L. Ngai
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T. Egami
G.U. Nienhaus

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Structure and Dynamics of Glasses and Glass Formers

Symposium held December 2–6, 1996, Boston, Massachusetts, U.S.A.

EDITORS:

C.A. Angell
Arizona State University
Tempe, Arizona, U.S.A.

K.L. Ngai
Naval Research Laboratory
Washington, D.C., U.S.A.

J. Kieffer
University of Illinois, Urbana
Urbana, Illinois, U.S.A.

T. Egami
University of Pennsylvania
Philadelphia, Pennsylvania, U.S.A.

G.U. Nienhaus
University of Ulm
Ulm, Germany

PITTSBURGH, PENNSYLVANIA

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Structure and Dynamics of Glasses and Glass Formers

PREFACE

The initiative for a symposium on this subject was taken by John Kieffer and, in response to his proposal to MRS, Austen Angell was asked by Karl Zeradski to play some part in its organization. He agreed to do so on the assurance that John, as well as several other experts in different areas such as Kai Ngai on polymers and liquids in general, Takashi Egami on metallic glasses and Uli Nienhaus on biophysical systems, would help. The brunt of the organization was borne by John Kieffer and we all owe him a strong vote of thanks for its ultimate success. A somewhat uncontrolled system of invitations, in judicious mixture with a selection of good contributed talks, seems by most accounts to have resulted in a satisfying, indeed exciting, scientific program.

This is a field in which the participants have failed to resolve the main questions despite an effort enduring over some 150 years, with 30-year recurrences of high activity. The latest of these cycles is in process and may not yet have peaked. It is, of course, unknown at this point whether the problems will be resolved in this cycle, though history is against it. Nevertheless, the presentations at this symposium, almost all of which are recorded in this volume, represent an excellent cross section of the attacks on the problem and will serve as essential reading to those who carry the torch to final success, or into the next cycle, as the case may be.

That we were able to cover the conference fees of all participants, and also give significant additional financial assistance in many cases where it was warranted, is thanks to the generous financial support of the Army Research Office, National Institute of Standards and Technology, National Science Foundation/Solid State Chemistry Program, and Office of Naval Research. We are indebted to Ms. Karen Nicholson of the Naval Research Laboratory for her valuable help over a period of three months in getting the manuscripts ready for publication.

C.A. Angell
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Part I

Short-Time Dynamics

DYNAMICS AT THE GLASS TRANSITION IN POLYMERS: RESULTS FROM NEUTRON SPECTROSCOPY

D. RICHTER*, A. Arbe**, J. Colmenero**

*Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, Jülich, Germany
**Departamento de Fisica de Materiales, Universidad del Pais Vasco, San Sebastian, Spain

ABSTRACT

This short review presents quasielastic neutron scattering and dielectric experiments on the α and β_{slow} relaxation in polybutadiene and polyvinylchloride. Exploiting the momentum transfer dependent dynamic structure factor, spatial information about the underlying molecular motions is obtained. While the β_{slow} process reveals itself as a local jump with average jump distances of about 1.5 Å, the α relaxation is diffusive and occurs statistically independently from the β_{slow} process. With this result a consistent interpretation of dielectric spectra on the same polymer is achieved. Finally some new results on the α process in PVC are presented.

INTRODUCTION

Glass forming polymers exhibit relaxation processes covering a huge dynamic range [1-3]. As an example Fig.1 displays the relaxation map for 1,4 polybutadiene [4-8]. The displayed data have been obtained by dielectric and mechanical spectroscopy as well as by dynamic light scattering and neutron spectroscopy. We observe a number of different relaxation processes. The structural α relaxation which supports the flow of the material slows down dramatically in the neighborhood of the glass transition temperature T_g. At a temperature about 20% above T_g a secondary relaxation (β_{slow}) splits from the primary α relaxation. This process exhibits an Arrhenius-like temperature dependence and persists into the glassy state. At very high frequencies in the picosecond regime anomalous vibrations, the so-called Boson peak, and associated with it a fast relaxation process termed β_{fast} is found. Both, the Boson peak as well as the β_{fast} process exhibit only very little temperature dependence. Though the relaxation processes, in particular the α_{slow} and β_{slow} relaxations, have been investigated by spectroscopic methods like dielectric and mechanical measurements since at least 50 years, still not very much is known about the molecular mechanism behind these relaxations. This deficiency relates to the fact that these spectroscopic methods although providing a very large dynamic range and high sensitivity in the time or frequency domain they do not reveal spatial information.

Such space-time sensitivity can be provided by inelastic and quasielastic neutron scattering because cold and thermal neutrons possess wavelengths corresponding to the interatomic distances and at the same time thermal energies. Other than X-rays providing structural information neutrons reveal knowledge where an atom is situated and in which direction it moves at what speed. In this way space-time observation of individual molecules is facilitated. In particular, the neutron spin echo (NSE) method reveals information about the time-dependent dynamic structure factor $S(Q,t)$ which reflects the time-dependent density-density correlations

$$\frac{S(Q,t)}{S(Q)} = \langle \delta\rho(Q,t)\delta\rho(Q,0)\rangle \qquad (1)$$

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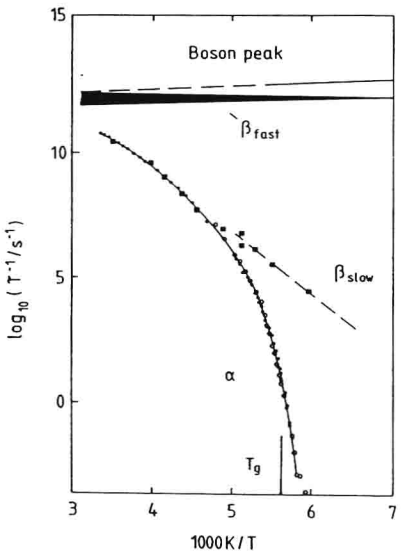

Fig.1: Relaxation map for (1,4) polybutadiene covering the prevailing dynamical features around the glass transition. The frequency range for the Boson peak and the associated fast relaxation like dynamics (β_{fast}) are indicated schematically [15]. The full and open circle along the α relaxation trace represent dielectric [7] and mechanical [8] results respectively. The full squares display characteristic rates obtained from neutron spin echo spectroscopy [5,6]. The time scale of the α process has been shifted to match that of the microscopic data. The dashed line represents the temperature dependence of the β_{slow} process observed by dielectric spectroscopy [9].

$\delta\rho(Q,t)$ is the Fourier component of a density fluctuation to the wave vector Q at a time t. $S(Q)$ denotes the static structure factor and $Q=4\pi/\lambda \sin(\Theta/2)$ is the scattering vector, where λ is the neutron wave length and Θ the scattering angle.

In this work we present neutron spin echo results on the Q-dependent dynamic structure factor of polybutadiene [9,10] and some new results on PVC [11]. First, these data are analyzed in the β relaxation regime revealing spatial information about this relaxation process. Thereafter, we consider the merging regime of the α and β relaxation and show the statistical independence of both relaxation processes. We revisit dielectric results on polybutadiene and interpret them consistently on the basis of the insight gained from the NSE investigations. Finally, we present some new results on PVC which are interpreted in the same spirit resolving an old puzzle on the seemingly very strongly stretched relaxation function of the α process.

EXPERIMENTAL RESULTS: POLYBUTADIENE

The experiments were performed on deuterated 1,4 polybutadiene (PB) which was synthesized anionically yielding a random microstructure of 52% cis, 41% trans, and 7% vinyl groups. The glass transition occurs in this sample at 178 K. The neutron spin echo experiments have been performed at the spectrometer IN11 of the ILL Grenoble. In order to access a wide Q range, different neutron wave lengths have been employed.

Fig.2 displays the static structure factor of 1,4 PB. In the low Q regime, $Q \leq 3.5$ Å^{-1} $S(Q)$ exhibits two maxima. The first maximum at around $Q=1.5$ Å^{-1} shifts strongly with temperature and relates to interchain correlations depending on the soft van der Waals interactions. On the other