

RHEOLOGY OF SILICATE GLASSES

Jesper deClaville Christiansen* and Aleksey D. Drozdov

Center for Nanotechnology, Aalborg University
Fibigerstraede 16, DK-9220 Aalborg East, Denmark
*E-mail: i9ictus@iprod.auc.dk

Silicate glasses show a very intricate rheological behavior, where the complex mechanical response is strongly affected by structural relaxation. This paper is concerned with modeling the viscoelastic behavior of silicates together with the evolution of their structural state. Conventional phenomenological equations for structural recovery (Adam-Gibbs, Tool-Narayanaswamy, etc.) are discussed, and some unresolved problems are formulated.

Introduction

Rheology was a key parameter in the birth of our planet where geological silicates were melted and solidified in a process that is still ongoing today. The importance of this field to mankind is evident from phenomena such as explosive volcanism and earthquakes. It is estimated that about a billion people live under the shadow of active geological processes. The field of rheology of silicates is also of great importance for industrial applications ranging from production of rock wool and glasses for automobiles, windows and bottles to applications of vitreous silica in wave-guides and semiconductor wafers. A number of excellent studies have been conducted in this field in the past two decades. However, the interaction between the specialists in rheology and those in the fields of geology, chemistry and physics of silicates has been rather weak. In the present work, we focus on the inclusion of structural parameters into constitutive models, because viscosity and elastic moduli of silicates depend not only on temperature and pressure, but also of the structural state of the material.

Silicates

This paper is concerned with the rheology of silicates in the melt state, the state of supercooled liquid, and the glassy state. Most features of the melt are preserved in all the three states, in spite of significant differences in their physical properties. The structure of silicates is rather complex, and it strongly depends on the chemical composition: natural melts contain a number of different oxides that noticeably affect their response. For example, the mechanical behavior of a viscous silica-rich “granitic” melt differs substantially from that of a “basaltic” melt which is silica poor.

Structural relaxation

The term “structural relaxation” (and its synonyms, structural recovery and physical aging) is conventionally employed to describe slow changes in the internal structure of a glass with time [1,2]. Here, the adjective “slow” means that the rate of structure alteration is smaller than the characteristic rates of other time-dependent phenomena (such as the viscoelastic response observed in creep and relaxation tests, the viscoplastic effects revealed in tensile tests with various strain rates, the mass-transport rates measured in diffusion tests, and so on.).

It is presumed that above the glass transition temperature, the internal structure of a supercooled liquid changes so rapidly with temperature that the equilibrium state of a material is reached practically immediately (within the experimental time-scale). This means that a supercooled liquid may be treated as an equilibrated medium at any instant.

Below the glass transition temperature, the rate of change of the internal structure decreases severely, which implies that the time necessary for reaching an equilibrium state after a step change in temperature noticeably exceeds the time-scale of standard tests. Structural recovery is conventionally thought of as development of the internal structure of a glass with time driven by changes in temperature or pressure.

An excellent review on structural relaxation in silicates is provided by Stebbins et al. [3] where a number of complex phenomena are described. Previous work on silicate rheology focused mainly on characterizing systems in thermal equilibrium and extrapolating the effect of temperature on moduli and viscosities by means of the Arrhenius or WLF equation. The mechanical relaxation is traditionally represented using Maxwell models with a single relaxation time or a series of relaxation times. By analogy with this approach, structural relaxation (evolution of the internal structure to a new equilibrium state driven by a step change in temperature, pressure or chemical composition) is described by the function

$$\phi(t) = \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where τ is a structural relaxation time. At small departures from equilibrium, the temperature dependence of τ is approximated by an Arrhenius relationship

$$\tau = \tau_0 \exp\left(\frac{\Delta H^*}{RT}\right) \quad (2)$$

where τ_0 is a constant, ΔH^* is the activation enthalpy, R is the gas constant and T is the absolute temperature. As Equation (2) is not very good at quantitatively describing observations in a one-step thermal test, more sophisticated

phenomenological equations are often used. According to the Tool concept [4], the relaxation process depends not only upon the current temperature, but also on a fictive temperature, T_f that characterizes the internal structure of a silicate. T_f is conventionally thought of as a temperature at which the current internal structure of a glass is in equilibrium. As the current state of an amorphous material depends on the history of its treatment, the fictive temperature is a function of the entire thermal pre-history. With reference to the Narayanaswamy [5] equation, we write

$$\tau = \tau_0 \exp\left(\frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f}\right) \quad (3)$$

where the parameter x lies between 0 and 1. Another conventional model for structural relaxation is provided by the Adam-Gibbs equation [6],

$$\tau = \tau_0 \exp\left(\frac{B}{TS_c(T_f)}\right) \quad (4)$$

where B is a constant and $S_c(T_f)$ is the configurational entropy. An important advantage of Eq. (4) is that the configurational entropy can be found experimentally, for example, from calorimetric experiments [7] and FTIR (Fourier transform infrared spectroscopy) measurements [8]. The configurational entropy is expressed in terms of the fictive temperature as:

$$S_c(T_f) = \Delta C_p \ln\left(\frac{T_f}{T_k}\right) \quad (5)$$

where ΔC_p is the difference between the liquid and the glass heat capacities in regions close to T_g and T_k is the Kauzmann temperature (the temperature at which the configurational entropy vanishes in equilibrium). Several experimental studies have proven that Eq. (1) describes the isothermal relaxation rather poorly. To improve the quality of data fitting, a model with a distribution of relaxation times can be employed [9]

$$\phi(t) = \sum_i g_i \exp\left(-\int_0^t \frac{dt'}{\tau_i}\right) \quad (6)$$

where g_i are temperature-independent coefficients that satisfy the condition $\sum g_i=1$. Despite the advantage of Eq. (6) compared to Eq. (1) in the approximation of experimental data, the description of the micro-mechanisms corresponding to various relaxation times for structural relaxation in Eq. (6) still remains a challenge for researchers. For transient experiments, where temperature varies with time, the above

equations can be used in combination with the Boltzmann superposition principle.

At T_g the viscosity for all glasses is in the range of 10^{12} Pa s and the typical shear modulus is of order of 30 GPa. The characteristic time for mechanical relaxation is, consequently, around 100 s, and the structural relaxation time is of order of 200 s [6], while a significant part of structural changes occur after 400 s [1]. These estimates reveal that structural relaxation times are quite long compared to the time-scale of many industrial processes in the vicinity of T_g .

Viscosity functions accounting for structural relaxation

To take into account structural changes in a rheological model, we combine Eqs. (4) and (5)

$$\eta = A_e \exp\left(\frac{B_e}{TS_c}\right) = A_e \exp\left(\frac{B_e}{T\Delta C_p \ln\left(\frac{T_f}{T_k}\right)}\right) \quad (7)$$

Here A_e is a pre-exponential coefficient and the constant B_e is proportional to the free energy. Eq. (7) was tested by several authors and was found to be acceptable for the analysis of Newtonian fluids. For a non-Newtonian flow, one can combine the Adam-Gibbs formula (4) with e.g. a Carreau type [11] model for shear viscosity to obtain

$$\eta = \eta_0^* (1 + \lambda^2 \dot{\gamma}^2)^{-N} \exp\left(\frac{B_e}{T\Delta C_p \ln\left(\frac{T_f}{T_k}\right)}\right) \quad (8)$$

where λ is a characteristic time, and the viscosity plateau at high shear rates is neglected. Equation (8) is proposed here for the first time, and it has to be further evaluated in viscosity tests on non-Newtonian fluids.

Rheometry

High temperatures and very corrosive melts combined with large variations in viscosity (typically more than 10 decades from T_g to the temperatures above liquidus) make rheometry of stone a challenge. Due to crystallization of melts, viscosity can be directly measured above the liquidus temperature and in some limited range above T_g (for rapidly quenched melts) only, whereas in the interval between these temperatures it has to be extrapolated. Several methods exist for determining viscosities of silicate melts and glasses. In our laboratory, the concentric cylinder method is commonly used. Adopting the

DIN standard geometry for spindle heads, the crucible is chosen to provide a medium gap size ($0.5 < R_{\text{spindel}}/R_{\text{crucible}} < 0.99$). The spindle shaft is extended to reach out of an oven and is connected to a Paar-Physica MC1 rheometer. Both crucible and spindle are made of 80% Platinum and 20% Rhodium by weight. The oven can reach temperatures of over 1900 K. Some data obtained by this method are plotted in Figure 1. Other methods that have been used include capillary rheometry [12, 13] at temperatures above 1500 K in a graphite rheometer under inert gas. At lower temperatures near T_g , available methods are ball indentation, biaxial compression and solid bar oscillatory rheometry. Fiber elongation is used to measure the response in tensile tests. The high-frequency behavior is analyzed by ultrasonic methods.

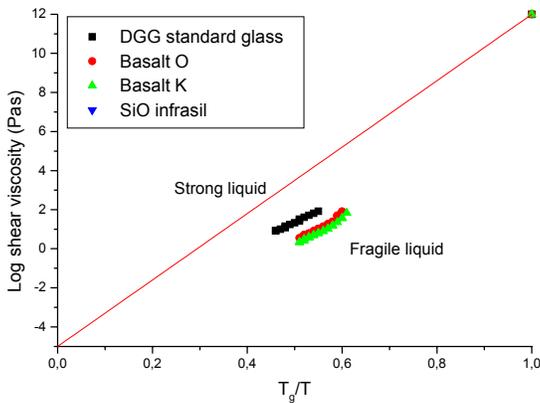


Figure 1. Viscosity versus the inverse normalized (with T_g) temperature. DGG is a German standard glass (wt%: 71.7 SiO₂, 1.2 Al₂O₃, 0.1 TiO₂, 0.2 FeO, 6.7 CaO, 4.2 MgO, 15.0 Na₂O, 0.4 K₂O, 0.4 SO₃), Basalt O (wt%: 49.3 SiO₂, 15.6 Al₂O₃, 1.8 TiO₂, 11.7 FeO, 10.4 CaO, 6.6 MgO, 3.9 Na₂O, 0.7 K₂O), Basalt K (wt%: 48.9 SiO₂, 14.0 Al₂O₃, 2.0 TiO₂, 11.9 FeO, 7.0 CaO, 10.0 MgO, 2.9 Na₂O, 1.0 K₂O, 0.6 P₂O₅). SiO₂ data are taken from [3]. Data in the entire temperature range should reach the same end point at 10^{12} Pas at $T_g/T=1$. For all measurements $T=T_f$.

The advantages of the plot in Figure 1 were first discussed by Angell, see also [14]. The straight line corresponds to a strong liquid (whose behavior follows the Arrhenius law), whereas curved lines reflect the response of fragile (non-Arrhenius) liquids. In terms of the Adam-Gibbs equation (7), a strong liquid has a small ΔC_p , whereas a fragile liquid possesses a large ΔC_p . Figure 2 presents experimental data in a torsional oscillatory test at 760 °C and their approximation by a model derived in [15]. Fair agreement is shown between the observations for the storage and loss moduli and the results of numerical simulation. The model treats a stone melt (glass) as an ensemble of relaxing units with various activation energies for rearrangement. The effect of thermal treatment is accounted for in terms of the fictive temperature.

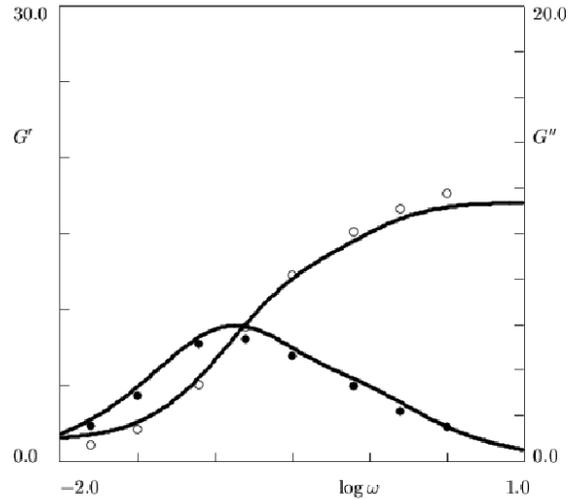


Figure 2. The storage modulus G' in GPa (unfilled circles) and the loss modulus G'' GPa (filled circles) versus frequency ω rad/s. Symbols: experimental data. Solid lines: numerical simulation.

Structural relaxation, background and future

Three main approaches are conventionally employed to describe transformation of the internal structure of a glass. The first was proposed about half a century ago, see [2] and the references therein, and it is based on the introduction of a structural parameter (or several structural parameters) whose evolution reflects changes in the microstructure. Traditionally, the free volume (the difference between the total volume and the volume occupied by molecules) and the fictive temperature (the temperature at which the current microstructure would be in the equilibrium state) are used as structural variables. According to common practice, the kinetics of their development is described by phenomenological differential (the KAHR relation [16] for the free volume, the Tool formula [4] for fictive temperature) or integral (the Moynihan concept [9]) equations.

To reduce the number of material constants, first-order kinetics are conventionally postulated to derive differential models that are determined by only one parameter (the characteristic time for structural relaxation, τ_s). To account for the nonlinearity and the non-exponentiality of structural transformations, τ_s is treated as a function of a structural variable or variables (as an example, we refer to the Narayanaswamy equation, Eq. (3), where an analog of the Arrhenius formula is applied to describe the effect of fictive temperature on τ_s).

The other approach is grounded in the energy-landscape concept [17]. The energy landscape is a hypersurface in the phase space that corresponds to a constant free energy of an amorphous medium. It is presumed that this surface has a relatively simple shape when the temperature, T , exceeds the

glass transition temperature T_g (which means that the surface possesses only a few points of minima), whereas below T_g , the topological structure of the hypersurface becomes more and more complicated when temperature drops [18]. Given a temperature, $T < T_g$, the energy landscape is treated as a surface with a large number of minima (potential wells) separated by barriers. The points of local minima are gathered into groups (that correspond to the same valley), while valleys, in turn, are assumed to be separated by barriers with larger heights (compared to the energy of thermal fluctuations). Structural evolution of a glass is treated as motion of a point (its position characterizes the current state of the internal structure) that hops from one potential well to another over barriers (searching for a global minimum corresponding to the equilibrium state), as well as from one valley to another (this motion becomes available when the point reaches a saddle point that separates two contiguous valleys). Hops over barriers are assumed to be driven by thermal excitations and are described by the theory of thermally activated processes. Transition from one valley to another is attributed either to reaching a saddle point between the existing valleys, or to changes in the shape of a hypersurface. The latter transformations are associated with a dependence of the energy landscape on the current state of a glass, which implies that new valleys arise (become available for the travelling point) when it reaches some local minima. The current state of the energy landscape is determined by a configurational entropy that is associated with the number of local minima (inherent structures) available for a glass in a non-equilibrium state. The topology of an energy landscape has been adequately described only in the past several years [19], whereas the dynamics of motion along the free-energy hypersurface have not yet been unambiguously determined. A convenient approach was proposed by Bouchaud [20], who treated a glass as a set of points located in potential wells with various depths and described the hopping process by a distribution function for occupied wells. The evolution of the distribution function is attributed to jumps to new potential wells, when the points reach some reference level in their hops.

According to the third approach, the glass transition temperature is associated with changes in the time-dependent behavior of some basic elements from which a glass is composed. It is assumed that the response of these basic elements (whose physical meaning is determined by the chemical composition of a glass) is not affected by their interactions above the glass transition temperature. Below T_g , these elements are organized into flow units: cooperatively rearranging regions (CRR) which relax when all elements in a group change their positions with respect to each other simultaneously [6]. Cooperative organization of the basic elements (a few tetrahedra in silicate glasses or several nearby strands in polymer glasses) is induced by a severe reduction (with a decrease in temperature) in the volume available for rearrangement.

Two scenarios were suggested for the non-Debye structural relaxation in glasses (that presume organization of flow units in parallel and in sequence). According to the first picture [21], elements with small activation energies relax first preparing a necessary place for rearrangement of elements with higher activation energies. Then, elements with higher potential energies are rearranged, providing new opportunities for the small-energy elements (opening new valleys on the energy landscape for these elements). These multi-step processes (where more and more elements rearrange in sequence) are repeated until an equilibrium state is reached. The other scheme is based on rearrangement of cooperative regions in parallel [22] (which presumes that various regions are characterized by various activation energies, and the higher the activation energy is, the longer a region waits for a rearrangement event). Rearrangement of a CRR does not necessarily result in its equilibration (which means that the equilibrium state of a region is reached by an infinite sequence of rearrangement events only). The current state of a CRR is characterized by its configurational entropy that is thought of as a measure of irregularity in mutual positions of basic elements in a group. The higher is this irregularity, the smaller is the activation energy necessary for rearrangement, and the larger the rate of structural recovery is. A simple and convenient formula that accounts for these correlations is provided by the Adam-Gibbs equation.

It is natural to assume that these three different approaches to the description of evolution of the microstructure of a glass should be mutually dependent. Some correlations between them may be easily established by using phenomenological relations. For example, assuming the configurational entropy, S_c , to be expressed in terms of the fictive temperature, T_f , by means of a conventional formula that connects entropy and temperature, see Eq. (5), a relation may be developed between the phenomenological approach and the concept of cooperative relaxation. In another example, the configurational entropy of an ensemble (that characterizes topology of an energy landscape) is assumed to coincide with the configurational entropy of a cooperative region. Despite the convenience of these assumptions for applied research, their physical basis is rather questionable, and their justification requires a serious revision of the fundamental concepts.

This brief survey of constitutive models for structural relaxation in glasses leads to several questions that remain to be answered even at the present stage of our knowledge:

1. Our experimental data [23] reveal striking similarity between changes in the configurational entropy (that characterizes an ensemble of relaxing domains with various activation energies) and changes in relaxation times (found by fitting observations in mechanical tests) for several amorphous and semicrystalline materials. It was also found that the graphs of the mechanical relaxation time versus temperature (recalculated using

data in rheological tests on equilibrated silicate melts) and of the structural relaxation time versus fictive temperature (obtained from DSC measurements on silicate glasses) plotted on a semi-log scale coincide after their shift along the time-axis. These findings lead to a hypothesis that the short-term response of a glass (measured when its internal structure remains unchanged) and the long-term behavior (observed as structural recovery of a glass) are governed by the same physical mechanism at the micro-level. What the nature of this mechanism is, and in which way experimental data in short-term tests may be used to predict structural relaxation remain unclear.

2. Within the energy-landscape concept (where the configurational entropy is treated as a measure of distribution of cooperatively relaxing units with various activation energies), changes in the ensemble of CRRs driven by mechanical factors should result in alteration of the average rate of structural recovery. Some attempts have been undertaken in the past decade to observe slowing down of structural relaxation (rejuvenation of a glass) induced by loading [24]. Unfortunately, the experimental data on polymeric glasses do not provide an unambiguous answer to whether the equilibration process decelerates. Silicate glasses, where structural recovery occurs in a larger interval of temperatures compared to polymeric glasses, provide excellent opportunity to check the applicability of the energy-landscape theory.
3. There are no doubts that the configurational entropy (irrespective, whether it is defined in terms of the energy-landscape theory or within the concept of cooperative rearrangement) reflects the evolution of the internal structure of a glass. However, the kinetics of changes in the configurational entropy should noticeably differ for these two approaches. As the configurational entropy in the Adam-Gibbs theory cannot be calculated ab initio, the only way to predict its evolution with time is based on the phenomenological equation (5) and an appropriate (Tool-like) kinetic equation for the fictive temperature. The energy-landscape concept together with physically transparent hypotheses regarding transformations of the free-energy hypersurface ensures additional opportunities that lead to new classes of governing equations. For example, assuming that transformation of the micro-structure is governed by the fragmentation-aggregation mechanism [25, 26] (which means that several CRRs with small activation energies can aggregate to form a region with higher activation energy and a CRR with a large potential energy can be broken into several smaller parts being exited by thermal fluctuations), one can describe in a unified fashion such interesting phenomena as over-shooting of DSC traces on aged samples and a non-monotonic dependence of elastic moduli and strength of silicate glasses on time and temperature of annealing. We believe that development of

constitutive equations for the evolution of the energy landscape (based on this or similar scenarios) and their experimental validation is a challenging task to be performed in the coming years.

Acknowledgements

We acknowledge the contributions of our research group and Rockwool International A/S, especially Dr. S. Lund Jensen.

References

1. M.D. Ediger, C.A. Angell, S.R. Nagel, Supercooled liquids and glasses. *J. Phys. Chem.* 100 (1996) 13200-13212.
2. E.-J. Donth, *Relaxation and Thermodynamics in Polymers: Glass Transition*. Akademie, Berlin, 1992.
3. J.F. Stebbins, P.F. McMillan, D.B. Dingwell, *Structure, Dynamics and Properties of Silicate Melts*, Rev. in Mineral. Vol. 32, Mineralogical Society of America, 1995.
4. A.Q. Tool, Relation between inelastic deformation and thermal expansion of glass in its annealing range. *J. Am. Ceram. Soc.* 29 (1946) 240-253.
5. O.S. Narayanaswamy. A model for structural relaxation in glass. *J. Am. Ceram. Soc.* 54 (1971) 491-498.
6. G. Adam, J.H. Gibbs, On the temperature dependence of cooperative relaxation properties in glassforming liquids near the glass transition temperature. *J. Chem. Phys.* 43 (1965) 139-146.
7. Y.Z. Yue, J.deC. Christiansen, S.L. Jensen, Determination of the fictive temperature for a hyperquenched glass. *Chem. Phys. Lett.* 357 (2002) 20-24.
8. A. Argawal, K.M. Davis, M. Tomozawa, A simple IR spectroscopic method for determining fictive temperature of silica glasses. *J. Non-Cryst. Solids* 185 (1995) 191-198.
9. C.T. Moynihan, A.J. Easteal, J. Wilder, J. Tucker, Dependence of the glass transition temperature on heating and cooling rates. *J. Phys. Chem.* 78 (1974) 2673-2677.
10. R. von der Ohe, Y. Yue, J. deC. Christiansen, S. Lund Jensen. Finite-Elemente-Simulationen des Glasfaserziehvorgangs. Proceedings of Deutsche Glastechnische Gesellschaft e.V. (DGG), 76. Glastechnische Tagung, Bad Soden/Taunus, Germany, 2002.
11. P.J. Carreau, D. De Kee, M. Daroux, *Can. J. Chem. Engng.* 57 (1979) 135.
12. J. deC. Christiansen, Y.Z. Yue, Overview of capillary rheometry and discussion of vortex vs. round/sharp entrance. *Glasknisk Tidskrift* 54 (1999) 1-8.
13. M. Solvang, PhD-thesis. Aalborg University, 2002, to be published.
14. L.M. Martinez, C.A. Angell, A thermodynamic connection to the fragility of glass-forming liquids,

- Nature 410 (2001) 663-667.
15. A.D. Drozdov, J.deC. Christiansen, Modelling the linear viscoelastic behavior of silicate glasses near the glass transition point. E-preprint cond-mat/0205365
 16. A.J. Kovacs, J.J. Aklonis, J.M. Hutchinson, A.R. Ramos, Isobaric volume and enthalpy recovery of glasses. 2. A transparent multiparameter theory. J. Polym. Sci.: Polym. Phys. Ed. 17 (1979) 1097-1162.
 17. M. Goldstein, Viscous liquids and the glass transition: a potential energy barrier picture. J. Chem. Phys. 51 (1969) 3728-3739.
 18. F.H. Stillinger, T.A. Weber, Dynamics of structural transitions in liquids. Phys. Rev. A 28 (1983) 2408–2416.
 19. E. La Nave, S. Mossa, F. Sciortino, Potential energy landscape equation of state. Phys. Rev. Lett. 88 (2002) 225701.
 20. J.P. Bouchaud, Weak ergodicity breaking and aging in disordered systems. J. Phys. I France 2 (1992) 1705-1713.
 21. R. G. Palmer, D. L. Stein, E. Abrahams, P. W. Anderson, Models of hierarchically constrained dynamics for glassy relaxation. Phys. Rev. Lett. 53 (1984) 958-961.
 22. A.D. Drozdov, Modeling structural recovery in amorphous polymers. Math. Comput. Model. 31 (2000) 79-95.
 23. A.D. Drozdov, J. deC. Christiansen, The nonlinear time-dependent response of semicrystalline polymers: correlations between the configurational entropy and the rate of rearrangement of chains. Macromol. Theory Simul. (2002) submitted.
 24. G.B. McKenna, Dynamics and mechanics below the glass transition: the non-equilibrium state. Comput. Mater. Sci. 4 (1995) 349-360.
 25. A.D. Drozdov, Structural relaxation in polymeric glasses. Chem. Phys. Lett. 327 (2000) 54-60.
 26. A.D. Drozdov, A model for structural relaxation in amorphous glassy polymers based on the aggregation-fragmentation theory. J. Polym. Sci. B: Polym. Phys. 39 (2001) 1312-1325.