Macromol. Symp. ***171,*** *253–264 (2001)*

Influence of Temperature, Pressure and Connectivity on the Dynamics of a Glass-Forming System Investigated by Dielectric Spectroscopy

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SUMMARY: A comparative study is reported on the dynamics of a glass-forming system when the glass transition is approached through different paths: cooling, compression, and polymerization. In particular, the influence of temperature, pressure and connectivity on the dynamics has been investigated by dielectric spectroscopy. A phenomenological description of the behavior of the dielectric response shows the existence of both differences and deep similarities between the change of some dielectric parameters during a polymerization reaction and during the temperature or pressure changes. A unified reading of our experimental results can be given in the framework of the Adam-Gibbs theory.

Introduction

One of the most prominent signs of approaching the glass transition is the strong increase of the structural relaxation time, changing over many orders of magnitude from less than picoseconds in the normal liquid state to more that hundreds of seconds in the frozen state, while the system circumvents crystallization and remains an amorphous phase.

If temperature is the variable most frequently used to drive a glass-forming system towards the glass transition, the use of pressure as an additional thermodynamic variable can provide an alternative route to the glassy state, being the effect of an isothermal increase of pressure on the slowing down of molecular motions quite similar to that produced by an isobaric decrease of temperature.[1,2] Beside this, polymeric systems provide a further interesting route to the glass transition, through the increase of connectivity as the result of a polymerization reaction.[3,4]

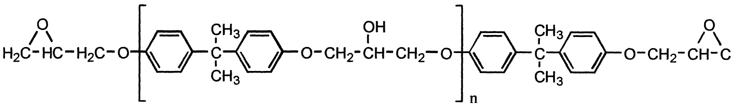
CCC 1022-1360/00/$ 17.50+.50/0

The natural question arises as to what extent is it possible to get a unified description of the glass-transition phenomenon produced by changing either thermodynamic variable, like temperature or pressure, or chemical variables, like the number of covalent bonds in a reacting system.

In this paper, we report a comparative study of the dynamics of a simple glass forming system investigated by wide band dielectric spectroscopy (10^{-1} – $2 \cdot 10^{10}$ Hz) under three different experimental conditions: (i) an isobaric condition by changing the temperature, (ii) an isothermal condition by changing the pressure, and (iii) during polymerization reactions under isothermal-isobaric conditions.

Experiments and Results

We considered a commercial grade sample (by Shell) of a common di-epoxy resin, diglycidyl-ether of bisphenol-A (DGEBA), equivalent epoxy weight ≈190 (**1**).



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DGEBA is a fragile glass-forming system with a relatively high glass-transition temperature at ambient pressure, $T_g \approx 257$ K by dielectric spectroscopy,5) and is a highly pressure-sensitive system with a relatively low glass-transition pressure at room temperature, $P_g \approx 270$ MPa.1) The system was studied at ambient pressure in the temperature range 163-363 K (Fig. 1a), and at room temperature in the pressure range 0.1-235 MPa (Fig. 1b).

DGEBA, if reacted with a bi-functional amine, like butylamine (BAM), yields a linear polymer, and if reacted with a tetra-functional amine, like ethylenediamine (EDA), yields a polymer network, through polymerization reactions. We reacted at 298 K the mixture DGEBA/BAM in stoichiometric ratio 1:1 (Fig. 1c), and the mixture DGEBA/EDA in non-stoichiometric ratio† 1:1 (Fig. 1d). More experimental details can be found elsewhere.4)

Some common features can be recognized in the behavior of the dielectric response of the system (Fig. 1). In all cases we have two dielectric processes: a secondary process at higher

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† In this case, the stoichiometric ratio is 2:1

frequencies and a structural process at lower frequencies. The structural peak shifts rapidly towards lower frequencies, either by decreasing the temperature, or by increasing the pressure, or by advancing the chemical reaction, and, in any case, it conventionally defines the glass transition when it reaches 10^2 s.

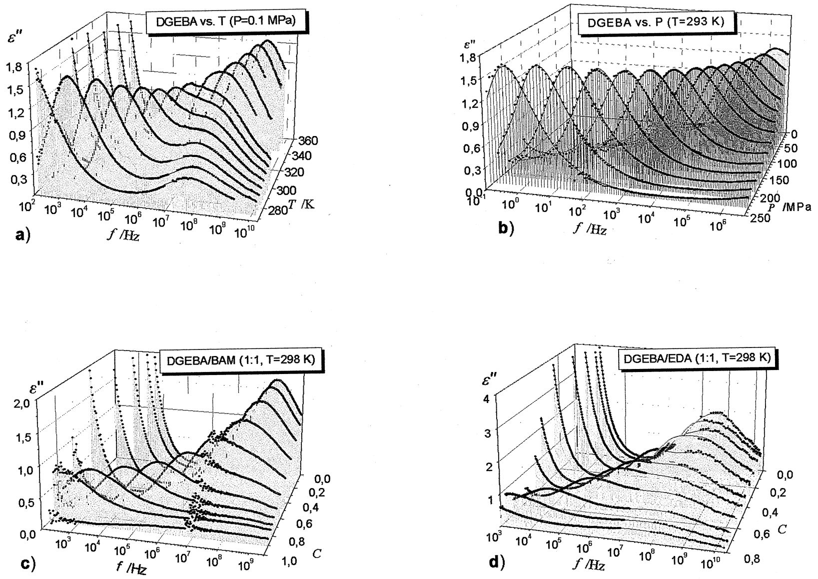


Fig. 1: Spectra of the dielectric loss factor, ε'', of DGEBA (a) during the isobaric (P=0.1 MPa) experiment at different temperatures; (b) during the isothermal experiment (T=293 K) at different pressures; (c) during the linear reaction with BAM (1:1, at 298 K) and (d) during the crosslinking reaction with EDA (1:1, at 298 K), at different values of conversion, C.

A pronounced decrease of the conductivity contribution, appearing as a tail $\propto\omega^{-1}$ in the lower frequency side of the spectral window, accompanies the increase of the structural relaxation time. On the contrary, the secondary process is far less affected by this phenomenon.

We fitted the complex dielectric permittivity, $\varepsilon = \varepsilon' - i\varepsilon''$, by the superposition of two Havriliak-Negami (HN) functions, accounting for the presence of two relaxation processes, plus a conductivity term $-i\sigma/\omega\varepsilon_V$ (ε_V is the vacuum permittivity), accounting for the ionic drift:

$$\varepsilon(\omega) - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_1)L_1(\omega) + (\varepsilon_1 - \varepsilon_\infty)L_2(\omega) - i\sigma / \omega\varepsilon_V; \qquad (1)$$

ε_0 and ε_∞ represent the low and high frequency limits of the complex dielectric permittivity; ε_0-ε_1 and ε_1-ε_∞ are the structural and secondary dielectric strengths; $L(\omega)=[1+(i\omega\tau)^{1-\alpha}]^{-\beta}$ is the normalized HN function, with τ the relaxation time, $0\leq\alpha\leq1$ and $0\leq\beta\leq1$ the shape parameters and the indexes 1 and 2 refer to the structural and secondary relaxations, respectively. The fitting procedure, carried out on both ε' and ε'' simultaneously, was adopted to describe the spectra when the temperature or the pressure was changed, or at different times during the polymerization reactions.

Discussion

At constant T and P, the number of chemical bonds formed between monomers induces the changes occurring in a reacting system. We expect that the most suitable independent variable for monitoring the physical changes in the polymerizing system is the conversion $C(t)=N_t/N_0$ (N_t= functional groups that have reacted, N_0= functional groups at the beginning of the reaction), that measures, at any time t, the advancement of the reaction through the fraction of functional groups that have actually reacted at that time. In the following, the behavior of dielectric parameters during a polymerization reaction will be considered as a function of C.

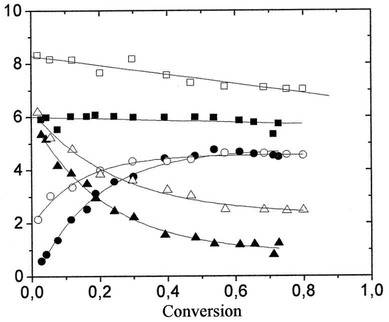


Fig. 2: Total (squares), structural (circles) and secondary (triangles) dielectric strengths of DGEBA/BAM 1:1 (solid symbols) and DGEBA/EDA 1:1 (open symbols), vs. conversion.

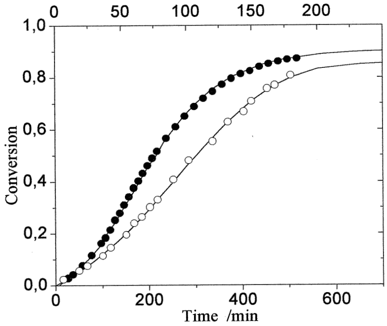


Fig. 3: Dielectric conversion, C_{diel}, of DGEBA/BAM (solid circles; bottom axis), and DGEBA/EDA (open circles; top axis). Solid curves represent the calorimetric conversion from DSC.

In a pure system, we have constant dipole concentrations as well as constant dipole moments. On the other hand, a polymerization reaction not only results in more or less complicated links between molecules, but usually also modifies the dipoles in the system; some dipoles may disappear, and sometimes molecular groups having a dipolar charge distribution may be replaced by different molecular groups with different dipoles. The dielectric analysis is seen to be very sensitive to such a difference, and from a comparison of dielectric quantities we can appreciate both differences and analogies between the different paths to the glass transition, i.e. *thermodynamic* and *chemical* vitrification.

Differences – The main differences can be recognized in (i) the behavior of the relaxation strengths, (ii) the monitoring of the chemical conversion, and (iii) the gel-transition phenomenon.

(i) While a linear trend is found as a function of both $1/T$ 5) and P,1) under polymerization a linear dependence on C is only found for the overall relaxation strength. The decrease of this last follows from the decrease of dipole concentration during the advancement of the reaction. The structural and secondary strengths are likely to be conditioned by the appearance of products and disappearance of reactants (Fig. 2).

(ii) The possibility of monitoring the chemical conversion by dielectric quantities is connected with the modification of dipoles associated with the formation of each chemical bond. For instance, when the mean-square dipole moments of the molecular groups involved in the reaction remain constant and only the dipole concentration, N, is modified. According to the Kirkwood-Frölich-Onsager relation6) the change of the static dielectric permittivity, ε_0, is linearly dependent on N and, therefore, on the chemical conversion. Under these conditions, the normalized value of the static permittivity, $C_{diel}(t)=[\varepsilon_0(t=0)-\varepsilon_0(t)]/[\varepsilon_0(t=0)-\varepsilon_0(t\to\infty)]$, closely parallels the calorimetric conversion (Fig. 3). This quantity can be interpreted as the dielectric conversion.

(iii) The sol-gel transition is due to the growth of a network structure forming a percolative cluster of macroscopic size; obviously, this phenomenon does not find a counterpart in the dynamics of the system under variable T or P.

Analogies - The relaxation times are far less sensitive to details of the chemical structure, although they are able to account for dynamic properties of the molecules. Accordingly, the main analogies between the different paths to the glass transition can be recognized in the following results: (i) the Debye-Stokes-Einstein (DSE) relation7,8) is fulfilled under cooling, compression, and polymerization (Fig. 4); (ii) the structural relaxation time is well described by a Vogel-Fulcher (VF) law, as a function of T, P and C (Fig. 5).

(i) The DSE relation was formulated on the basis of a hydrodynamic model and describes the connection between the relaxation and the transport properties in a fluid. In the highly viscous regime, it can be given as $\sigma \cdot \tau \cong$ const,$^{9)}$ and simply states that the conductivity, which probes the translational diffusion, is expected to be in inverse proportion to the dielectric relaxation time, which probes a rotational diffusion mechanism$^{10)}$. In a log-log plot, DSE behavior should correspond to a straight line of slope –1. The lines in Fig. 4a and 4b indicate that the DSE equation is fulfilled under cooling and compression.

According to Deng and Martin$^{11)}$, it should be possible to relate conductivity σ and structural relaxation time τ at any conversion through a similar relation, provided that the contribution from the number-average degree of polymerization, $\bar{x}_n(C)$, is taken into account. The term $\bar{x}_n(C)$ should account for the difference between the diffusion coefficient of the ionic species producing σ, and the diffusion coefficient of the growing macromolecular structures to which the relaxing dipoles are bound. Fig. 4c shows that if σ is replaced by $\sigma \cdot \bar{x}_n(C)^{-1}$, with $\bar{x}_n(C)=1/(1\text{-}C)$ in our case,$^{12)}$ a DSE-like relation is also fulfilled from polymerization. Those findings confirm that the changes in the structural relaxation time mirror the changes occurring in the diffusive dynamics of the macromolecular structure, due to the progressive linking of molecules.

(ii) When the system is cooled (Fig. 5a), the secondary relaxation time follows a thermal activated behavior described by an Arrhenius law, while the increase of the structural relaxation time shows a continuous change in the activation energy that is well described, in the range investigated, by a VF equation, $\tau=\tau_0\exp[B_T/(T\text{-}T_0)]$.

The behavior of the relaxation times as a function of pressure (Fig. 5b) shows a strong similarity with the behavior against reciprocal temperature. In particular, the pressure dependence of the structural relaxation time can be described to a good approximation by a phenomenological function that parallels the VF equation with P in place of $1/T$, $\tau=\tau_0\exp[B_P P/(P_0\text{-}P)]$.$^{1,2)}$ During polymerization, if conversion is used as independent variable, a VF-like function, $\tau=\tau_0\exp[B_C/(C_0\text{-}C)]$, can be still used to represent the increase of the structural relaxation time[3] (Fig. 5c). In general, a VF-like description is not suitable for describing the data as a function of time of reaction.

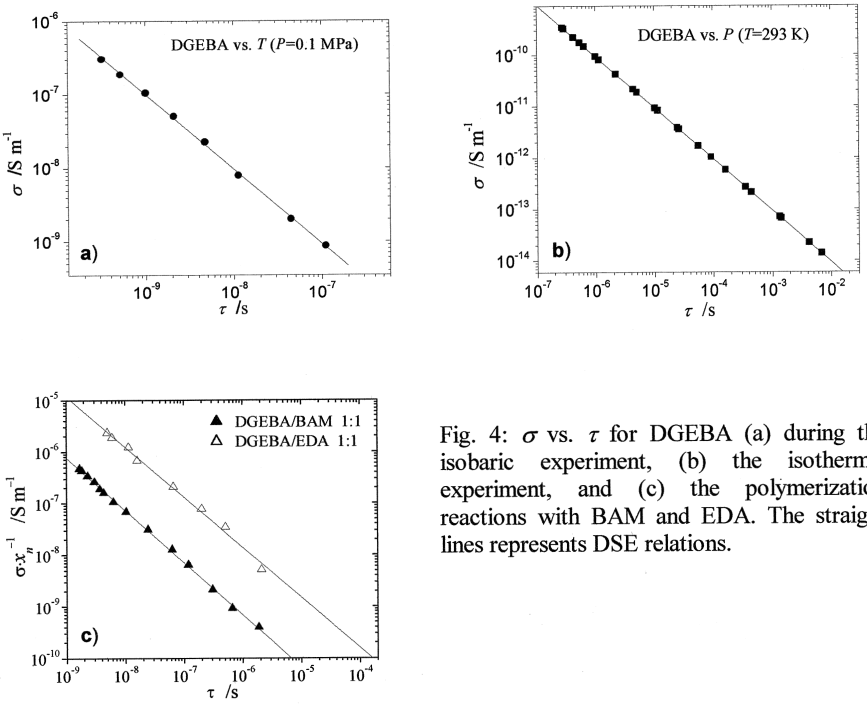
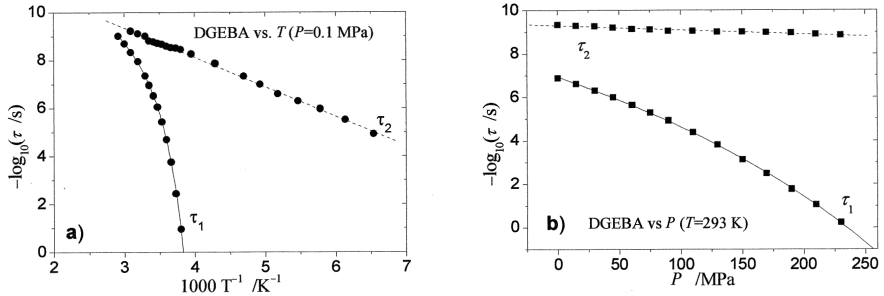


Fig. 4: σ vs. τ for DGEBA (a) during the isobaric experiment, (b) the isothermal experiment, and (c) the polymerization reactions with BAM and EDA. The straight lines represents DSE relations.

The possibility to recognize a VF-like behavior of the structural relaxation time for all the three routes to the glass transition can be regarded as an important indication of the existence of some common factor controlling the dynamics of glass-forming systems close to the glass transition. In order to have an indication on what this factor may be, we consider the origin of VF-type behavior. The search for a theoretical basis for this behavior has stimulated much work, and different concepts have been invoked to rationalize it.[13-15] One of the most interesting interpretations was put forward by Adam and Gibbs,[13] based on the concept of configurational entropy and the assumption of cooperatively rearranging regions (CRRs). Starting from the observation that the sluggish relaxation behavior governing the glass transition is a manifestation of the smallness of entropy (dearth of configurations), the theory explains the behavior of the structural relaxation time in terms of the size of the CRR. The size of this CRR is determined by configuration restrictions and is expressed in terms of the configurational entropy of the system. The outcome is a link between the transition probability, W, to a different configuration of the CRR, and the configurational entropy of the system, S_c:

$$W \propto \tau^{-1} = \tau_0^{-1} \exp(-A/TS_c). \tag{2}$$



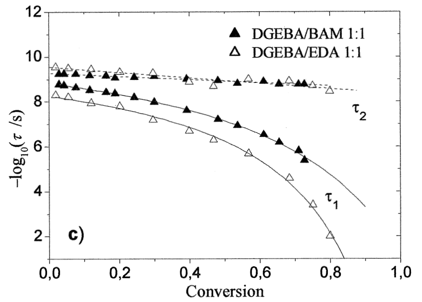


Fig. 5: Structural, τ_1, and secondary, τ_2, dielectric relaxation times during (a) the isobaric experiment, (b) the isothermal experiment, and (c) during the polymerization reactions with BAM and EDA. The dashed lines are Arrhenius-like fitting curves, the solid lines are Vogel-Fulcher fitting curves.

In this equation is $A \propto \Delta\mu$ ($\Delta\mu$ is the energy barrier hindering the rearrangement per molecule), and $S_c = S^{melt} - S^{crystal} = \int_{T_K}^{T} (\Delta C_p / T) dT$, with $S_c(T_K) = 0$ and $\Delta C_p = C_p^{melt} - C_p^{crystal}$. As the dependence of $\Delta\mu$ on T, P and C is reasonably negligible,[13)] τ will depend on T, P and C through the quantities $\Delta C_p(T, P, C)$ and $T_K(P, C)$. At constant P and C, if $\Delta C_p \propto 1/T$ is assumed, then it can easily be shown[16)] that eq.(2) gives a VF relation for $\tau(T)$ with $T_0 = T_K$:

$$\tau = \tau_0 \exp\left[B/(T - T_K)\right] \tag{3}$$

Here, we observe that if the dependence of ΔC_p on P[17,18)] and C can be neglected, then eq.(2) results in:

$$\tau = \tau_0 \exp\left[B/(T - T_K(P, C)\right] \tag{4}$$

According to this equation, it is expected that P and C mainly influence the temperature where S_c vanishes, i.e T_K. In particular, it is enough to require in eq.(4) that $T_K(P)$ and $T_K(C)$

are hyperbolas, in order to reproduce a VF-like relation for $\tau(P)$ and $\tau(C)$ respectively.

Extended calorimetric measurements as a function of P and C that allow a direct check of eq.(2) are not available. However, concerning the pressure dependence, an indirect check comes from experimental results1) showing that for DGEBA the influence of P on T_0, in the VF equation, overwhelms the effect on B, and the dependence $\tau(T,P)$ is accounted for by a simple correction of T_0. Moreover, the pressure-extended model of Gibbs and DiMarzio19) gives a numeric result, for the change with pressure of the temperature where S_c goes to zero, that is in qualitative agreement with the required behavior of $T_K(P)$. Concerning the conversion dependence, an indirect check comes from experimental values of $T_g(C)$,20-24) a quantity closely related to T_0. All the experimental findings are consistent with an increasing dependence of $T_g(C)$ that can be suitably described by a hyperbolic behavior.

Accordingly, during an isothermal-isobaric polymerization the growth of the number of covalent bonds, i.e. conversion, in the reacting system plays a role that is quite similar to that of temperature decrease or pressure increase; this role is to reduce the number of configurations available to the system, thus forcing the molecules to move cooperatively over an increasing length scale. In the light of this, it makes sense that the size of the CRR, and, hence, S_c, is controlled by conversion rather than the time of reaction. In fact, in order to reduce the number of configurations available to the system it doesn't matter how long one has to wait, but rather how many constraints are made between molecules.

Conclusion

We have reported broad-band dielectric measurements on DGEBA as a function of temperature, pressure and conversion; in particular, we have shown how glass formation can be driven by both physical processes, like cooling and compression, and chemical processes, like polymerization reactions.

The differences between the effects of the physical and chemical processes mainly mirror the continuous modification of dipole moments while new chemical bonds are formed in the growing macromolecular structure. The similarities mainly mirror the fact that conductivity and structural relaxation time are not very sensitive to details of the chemical structure, while they probe the dramatic changes in the diffusive dynamics at the molecular level.

An unified intrepretation of our experimental results can be given in the framework of the Adam-Gibbs theory, where P and C mainly influence the temperature at which S_c vanishes. Such an interpretation leads to the conclusion that an increase of connectivity has the same effect on the molecular mobility of the motion-freezing resulting from cooling and compression, through the reduction of configurations available to the system and the consequent cooperative motion. It seems that forcing the molecules to move cooperatively, either by reducing the energy or the volume at their disposal, or by chemically linking them, makes the system spontaneously approach the glassy state.

How general are the findings has to be tested on more systems, and the occurrence of further effects could be checked. For instance, in experiments where the kinetics of reaction can be controlled, a kinetics effect on the glass-transition conversion is expected, similar to that observed on the glass-transition temperature by changing the cooling rate; in particular, a lower glass-transition conversion should be associated with a higher reaction rate.

References

1. S. Corezzi, P.A. Rolla, M. Paluch, J. Ziolo, D. Fioretto, *Phys. Rev. E* **60**, 4444 (1999)
2. Paluch, S.J. Rzoska, P. Habdas, J. Ziolo, *J. Phys.: Condens. Matter* **10**, 4131 (1998); and references therein
3. R. Casalini, S. Corezzi, D. Fioretto, A. Livi, P.A. Rolla, *Chem. Phys. Lett.* **258**, 470 (1996)
4. R. Casalini, S. Corezzi, A. Livi, G. Levita, P.A. Rolla, *J. Appl. Polym. Sci.* **65**, 17 (1997)
5. R. Casalini, D. Fioretto, A. Livi, M. Lucchesi, P.A. Rolla, *Phys. Rev. B* **56**, 3016 (1997)
6. C.J.F. Böttcher, *Theory of Electrical Polarization*, Elsevier Publ., Amsterdam 1973
7. A. Einstein, *Ann. Phys.* (N.Y.) **17**, 549 (1905)
8. F. Stickel, E.W. Fischer, R. Richert, *J. Chem. Phys.* **104**, 2043 (1996)
9. S. Corezzi, S. Capaccioli, G. Gallone, M. Lucchesi, P. A. Rolla, *J. Phys.: Condens. Matter* **11**, 10297 (1999)
10. The DSE relation has been widely verified in ordinary liquids, although a generalized fractional-DSE relation, $\sigma \cdot \tau^m \cong const$ with $m<1$, is not unusual in polymers and in simple molecules at high viscosity.
11. Y. Deng, G.C. Martin, *Macromolecules* **27**, 5141 (1994)
12. F. Ciardelli ed., *Macromolecuole*, published by Pacini Editore, Pisa 1986
13. G. Adam, J.H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965)
14. M.H. Cohen, D. Turnbull, *J. Chem. Phys.* **31**, 1164 (1959)
15. M.H. Cohen, G.S. Grest, *Phys. Rev. B* **20**, 1077 (1979)
16. I.M. Hodge, *J. Non-Cryst. Solids* **169**, 211 (1994)
17. S. Takahara, O. Yamamuro, H. Suga, *J. Non-Cryst. Solids* **171**, 259 (1994)
18. S. Takahara, M. Ishikawa, O. Yamamuro, T. Matsuo, *J. Phys. Chem. B* **103**, 792 (1999)
19. E.A. DiMarzio, J.H. Gibbs, P.D. Fleming, I.C. Sanchez, *Macromolecules* **9**, 763 (1976)

20. T. Atake, C.A. Angell, *J. Phys. Chem.* **83**, 3218 (1979)
21. S.A. Bidstrup, N.F. Sheppard jr., D.S. Senturia, *Polym. Eng. Sci.* **29**, 325 (1989)
22. S. Carrozzino, G. Levita, P.A. Rolla, E. Tombari, *Polym. Eng. Sci.* **30**, 366 (1990)
23. J.O. Simpson, S.A Bidstrup, *J. Polym. Sci. B* **33**, 53 (1995)
24. J. Wei, M.C. Hawley, M.T. Demeuse, *Polym. Eng. Sci.* **35**, 461 (1995)