

Kinetics of enthalpy relaxation in polymeric glasses

Aleksey D. Drozdov

Institute for Industrial Mathematics, 4 Hanachtom Street, Beersheba, 84311 Israel

Received: 18 August 2000/Accepted: 18 September 2000

Summary

Constitutive equations are developed for the kinetics of enthalpy relaxation in polymeric glasses. An amorphous polymer is treated as an ensemble of cooperatively rearranged regions (CRR). Rearrangement of a CRR is modeled as a hop from one potential well on the energy landscape to another. The probability for changing traps in a hop is determined by the difference between the current and equilibrium concentrations of CRRs. A nonlinear parabolic equation is derived for the distribution function of CRRs. It is applied to predict entropy recovery after a thermal jump. Fair agreement is demonstrated between results of numerical simulation and experimental data for poly(vinyl acetate) and poly(methyl methacrylate) in the vicinity of the glass transition temperature.

Introduction

This note is concerned with the kinetics of enthalpy recovery in amorphous glassy polymers. Structural relaxation [physical aging (1)] in disordered media (spin glasses, supercooled liquids, structural and orientational glasses, etc.) has attracted substantial attention in the past decade (2-5). This phenomenon is conventionally studied in quench and wait tests, where a specimen equilibrated at some temperature T_0 above the glass transition temperature T_g is rapidly cooled to a temperature $T < T_g$ and is isothermally annealed at the temperature T ,

$$T(t) = T_0 \quad (T < 0), \quad T(t) = T \quad (T > 0). \quad (1)$$

It is evidenced as the strong effect of the waiting time t_w (the time elapsed upon quench before the beginning of a test) on physical properties of the sample.

Several molecular concepts have been developed for the out-of-equilibrium dynamics in disordered media (4-7). However, it is conventionally presumed that even the mode-coupling theory (the most advanced among molecular models) fails to adequately describe slowing down in the response of amorphous polymers below the glass transition temperature. This is explained by the neglect of cooperativity in reorientation of long chains that plays the key role in kinetic phenomena in the sub T_g region (6).

Our objective is to describe enthalpy relaxation in amorphous polymers using the trapping concept (8,9). We derive a nonlinear differential equation for diffusion of CRRs over the energy landscape. This equation is verified by comparing results of

numerical simulation with experimental data for poly(vinyl acetate) and poly(methyl methacrylate).

Diffusion over the energy landscape

Following Ref. (10), we treat an amorphous polymer as an ensemble of independent cooperatively rearranged regions (CRR). A CRR is thought of as a globule consisting of scores of strands of long chains (9). The characteristic length of a relaxing region in the vicinity of the glass transition temperature amounts to several nanometers (11). In the phase space, a CRR is modeled as a point located at the bottom level of its potential well. At random times, the point hops to higher energy levels as it is thermally agitated. We adopt the transition-state theory (12) and suppose that a CRR changes its trap [because of reorientation of chains caused by large-angle rotations of neighboring strands (6)] when it reaches some reference energy level. The energy of a potential well with respect to the reference state is denoted by w . For definiteness, it is assumed that $w > 0$ for any trap and $w = 0$ for the reference state.

Denote by $q(z)dz$ the probability for a CRR to reach the energy level that exceeds the bottom level of its potential well by some value located in the interval $[z, z + dz]$. In accord with Ref. (4), we set $q(z) = A \exp(-Az)$, where A is a constant. The probability for a CRR in a trap with potential energy w to reach the reference state in an arbitrary hop is given by

$$Q(w) = \int_w^\infty q(z)dz = \exp(-Aw).$$

With reference to (1), we suppose that the kinetics of rearrangement is governed by some material (internal) time τ and define the attempt rate γ as the average number of hops in a potential well per unit internal time. The quantity γ is assumed to be constant. Multiplying γ by the probability to reach the reference state in a hop Q , we find the rate of rearrangement

$$R(w) = \gamma \exp(-Aw). \quad (2)$$

Denote by Ξ the concentration of traps per unit mass, and by $p(\tau, w)$ the distribution function (at time τ) for traps with potential energy w . The number of relaxing regions (per unit mass) trapped in cages with energies belonging to the interval $[w, w+dw]$ and rearranged during the interval of time $[\tau, \tau+d\tau]$ is $\Xi R(w)p(\tau, w)dw d\tau$. Unlike previous studies (13, 15), we assume that not all relaxing regions change their traps when they reach the reference energy level and denote by $F(\tau, w)$ the ratio of the number of CRRs returning to their traps to the number of those reaching the reference state. The number of CRRs leaving their cages (with the energy located within the interval $[w, w + dw]$) per unit mass and unit internal time reads $\Xi[1 - F(\tau, w)]R(w)p(\tau, w)dw$. The exchange of CRRs is assumed to take place between the nearest neighbors on the energy landscape, that is between traps with the energy $[w, w + dw]$ and traps with the energies $[w - dw, w]$ and $[w + dw, w + 2dw]$. At the molecular level, this exchange is interpreted as creation and breakage of temporary links (entanglements, physical crosslinks, van der Waals forces, etc.) between strands forming a CRR. The balance law for the number of CRRs trapped in cages with the energy belonging to the interval $[w, w + dw]$ is given by

$$\frac{\partial p}{\partial \tau} = -(1 - F)Rp + \frac{1}{2}[(1 - F)Rp]_+ + \frac{1}{2}[(1 - F)Rp]_-, \quad (3)$$

where the subscript indices "-" and "+" refer to the intervals $[w - dw, w]$ and $[w + dw, w + 2dw]$. Expanding the right-hand side of Eq. (3) into the Taylor series, using

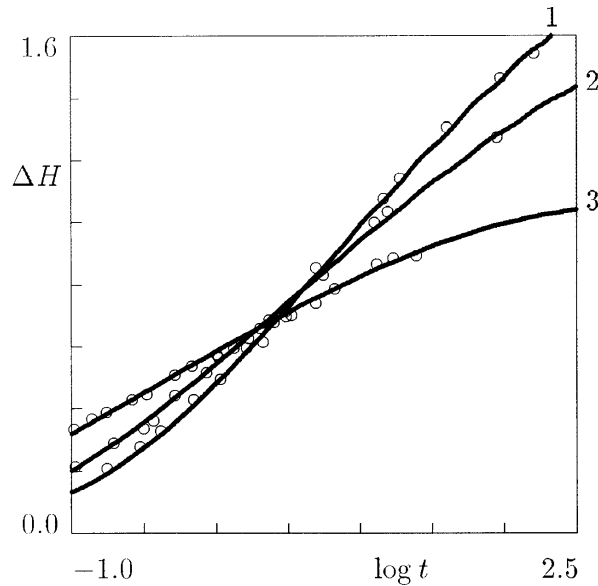


Figure 1: The relaxation enthalpy ΔH J/g versus time t h for PMMA ($T_g = 394.9$ K) quenched from $T_0 = 455$ to temperature T K. Circles: experimental data (30). Solid lines: prediction of the model with $\bar{W} = 2.0$ and $\Sigma_0 = 0.179$. Curve 1: $T = 375.0$; curve 2: $T = 380.0$; curve 3: $T = 387.5$

Eq. (2) and introducing the notation $\Gamma = \frac{1}{2}\gamma dw^2$, we arrive at the differential equation for diffusion over the energy landscape

$$\frac{\partial p}{\partial \tau} = \Gamma \frac{\partial^2}{\partial w^2} [(1 - F) \exp(-Aw)p]. \quad (4)$$

Formula (4) may be treated as an extension of multiparameter equations for the kinetics of structural relaxation (16,17), where a finite number of order parameters [with no transparent physical meaning (18)] is replaced by a continuous distribution of energies of traps. An important advantage of Eq. (4) over the relationships suggested in Refs. (19,20) is that it does not impose restrictions on the equilibrium density of traps $p_\infty(w)$, provided that $F = 1$ in the thermal equilibrium. Assuming this condition to be satisfied and referring to the Metropolis rule, we set

$$F(\tau, w) = \begin{cases} 1, & p(t, w) \leq p_\infty(w), \\ \exp[-\epsilon(p - p_\infty)], & p(t, w) > p_\infty(w), \end{cases} \quad (5)$$

where $\epsilon > 0$ is a material parameter. According to the random energy model (21), the initial distribution, $p_0(w)$, and the equilibrium distribution, $p_\infty(w)$, of CRRs are Gaussian.

$$\begin{aligned} p_0(w) &= \frac{1}{\sqrt{2\pi}\Sigma_0} \exp\left[-\frac{(w - W)^2}{2\Sigma_0^2}\right], \\ p_\infty(w) &= \frac{1}{\sqrt{2\pi}\Sigma_\infty} \exp\left[-\frac{(w - W)^2}{2\Sigma_\infty^2}\right], \end{aligned} \quad (6)$$

where $W, \Sigma_0, \Sigma_\infty$ are adjustable parameters. Equations (6) may be accepted, provided that for any $t > 0$.

$$\int_{-\infty}^0 p(t, w) dw \ll 1. \quad (7)$$

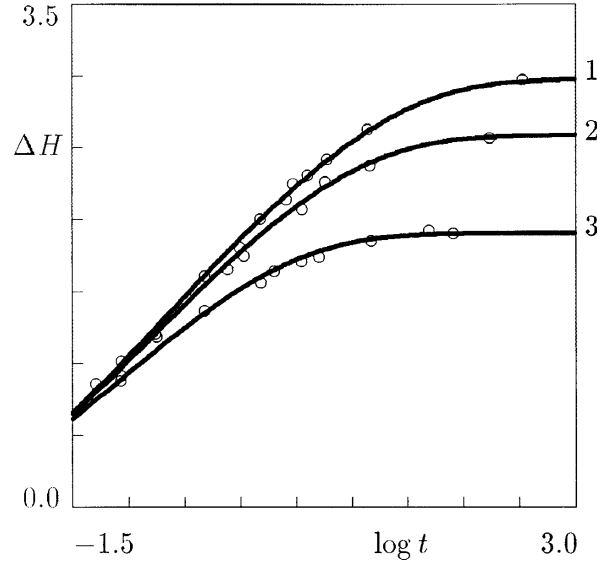


Figure 2: The relaxation enthalpy ΔH J/g versus time t h for PVA ($T_g = 315$ K) quenched from $T_0 = 353$ to temperature T K. Circles: experimental data (31). Solid line: prediction of the model with $\bar{W} = 0.9$ and $\Sigma_0 = 0.09$. Curve 1: $T = 303.0$; curve 2: $T = 305.0$; curve 3: $T = 308.0$

It follows from Eq. (6) that the average equilibrium energies of CRRs are independent of temperature, whereas their variances are strongly affected by T . This is in agreement with a conventional assumption regarding the growth in the ruggedness of the energy landscape with a decrease in temperature (4.22).

Enthalpy relaxation

The level of disorder in an ensemble of CRRs is characterized by the configurational entropy per CRR

$$s(t) = -k_B \int_0^\infty p(t, w) \ln p(t, w) dw,$$

where k_b is Boltzmann's constant (23). Adopting the concept of material time with an entropy driven internal clock (1), we set

$$\frac{d\tau}{dt} = a. \quad (8)$$

The shift fact or a reads

$$\ln a(t) = -\kappa_0 [s(t) - s(0)] = \kappa \int_0^\infty [p_0(w) \ln p_0(w) - p(t, w) \ln p(t, w)] dw, \quad (9)$$

where κ_0 is a material parameter and $\kappa = k_b \kappa_0$.

The configurational enthalpy per CRR, $h(t)$, is expressed in terms of the configurational entropy, $s(t)$, by means of the conventional formula

$$\frac{\partial h(t)}{\partial s(t)} = T(t).$$

Integration of this equality for a one-step thermal test. Eq. (1), implies the formula for the enthalpy per unit mass $H = \Xi h$. Our main hypothesis is that relaxing enthalpy

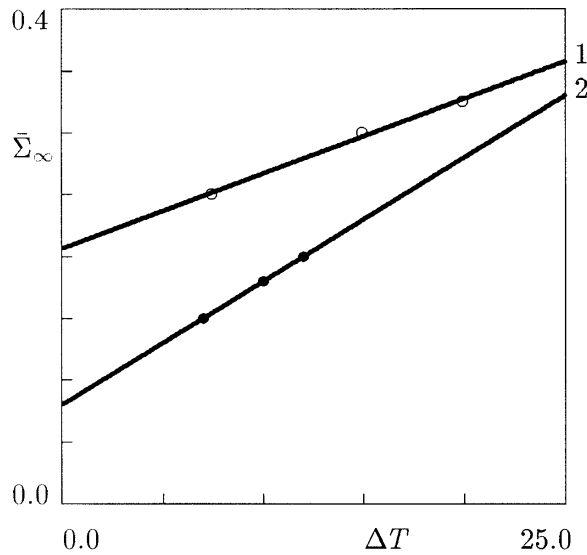


Figure 3: The parameter $\bar{\Sigma}_\infty$ versus the degree of supercooling ΔT K. Circles: treatment of observations. Solid lines: approximation of the experimental data by Eq. (11). Curve 1: PMMA, $a_0 = 0.2065$, $a_1 = 0.0061$; curve 2: PVA, $a_0 = 0.0800$, $a_1 = 0.0100$

per unit mass $\Delta H(t)$ coincides with changes in the configurational enthalpy, $\Delta H(t) = H(t) - H(0)$, which results in the formula

$$\Delta H(t) = \Lambda \int_0^\infty [p_0(w) \ln p_0(w) - p(t, w) \ln p(t, w)] dw \quad (10)$$

with $\Lambda = k_b T \Xi$. Introducing the dimensionless variables $\bar{w} = Aw$, $t = \bar{t}/t_0$, where t_0 is the characteristic time of aging, and setting $\bar{\Gamma} = A^2 \Gamma t_0$, $\bar{W} = AW$ and $\bar{\Sigma}_k = A \Sigma_k$, we arrive at constitutive equations (4) to (6) and (8) to (10) with 7 adjustable parameters: \bar{W} , $\bar{\Sigma}_0$, $\bar{\Sigma}_\infty$, $\bar{\Gamma}$, ϵ , κ and Λ . It follows from Eq. (4) that the quantities \bar{W} and $\bar{\Gamma}$ are interrelated: when one of them is chosen arbitrarily, the other characterizes the time scale. For convenience of numerical simulation, we fix the parameter \bar{W} (which ensures that Eq. (7) is satisfied) and determine $\bar{\Gamma}$ by matching observations. Because both constants, $\bar{\Gamma}$ and ϵ , characterize the time scale, one of them may be chosen *a priori*. For definiteness, we assume that $\epsilon = 1.0$. To determine the constant Λ , we adopt the free volume concept and assume that any CRR contains some amount of free volume (hole). Because the volume concentrations of holes for poly(methyl methacrylate) and poly(vinyl acetate) are unknown, we accept the value $\xi = 7.3 \cdot 10^{26} \text{ m}^{-3}$ found for polyethylene near its glass transition temperature by PALS (24). Taking mass density $\rho = 1.2 \text{ g/cm}^3$ and $T = 350 \text{ K}$, we obtain $\Lambda = 3.2 \text{ J/g}$. This estimate reduces the number of material constants to four. The latter number is comparable with the number of adjustable parameters in phenomenological models where observations are fitted using the stretched exponential function. As examples, we refer to a model with 4 constants (25.26) that combines the Kohlrausch–Williams–Watts (KWW) formula with the Adam–Gibbs equation for the characteristic time of structural relaxation \mathcal{G} and to a model with 5 constants (27.28) that employs the KWW equation together with the Narayanaswamy formula for \mathcal{G} .

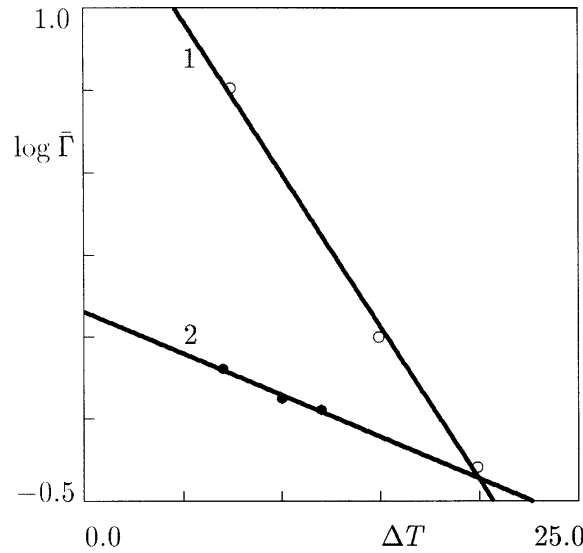


Figure 4: The parameter $\bar{\Gamma} \text{ h}^{-1}$ versus the degree of supercooling ΔT K. Circles: treatment of observations. Solid lines: approximation of the experimental data by Eq. (11). Curve 1: PMMA, $b_0 = 1.4272$, $b_1 = 0.0930$; curve 2: PVA, $b_0 = 0.0768$, $b_1 = 0.0254$

Validation of the model

We begin with fitting observations for poly(methyl methacrylate) in the sub- T_g region. For a description of specimens and the experimental procedure, we refer to (29). First, we match experimental data at the lowest temperature $T = 375$ K and determine $\bar{\Sigma}_0$, $\bar{\Sigma}_\infty$, $\bar{\Gamma}$ and κ (which ensure the best approximation of observations) by using the steepest-descent procedure. We fix the parameter $\bar{\Sigma}_0 = 0.179$ and proceed approximation of experimental data at higher temperatures with three adjustable parameters, $\bar{\Gamma}$, $\bar{\Sigma}_\infty$ and κ . Figure 1 reveals fair agreement between observations and results of numerical analysis.

To demonstrate that the model adequately describes observations for other polymers as well, we fit experimental data for poly(vinyl acetate) near its glass transition point. The experimental procedure and specimens are exposed in detail in (30). First, we fit experimental data at the lowest temperature $T = 303$ K and determine the parameter $\bar{\Sigma}_0 = 0.09$ which ensures the best approximation of observations. Afterwards, we repeat calculations for other temperatures and find $\bar{\Sigma}_\infty$, $\bar{\Gamma}$ and κ as functions of temperature T . Figure 2 demonstrates good correspondence between results of numerical simulation and experimental data.

The quantities $\bar{\Sigma}_\infty$, $\bar{\Gamma}$ and κ are plotted versus the degree of supercooling $\Delta T = T_g - T$ in Figures 3 to 5. The dependences $\bar{\Sigma}_\infty(T)$, $\bar{\Gamma}(T)$ and $\kappa(T)$ are correctly approximated by the "linear" functions

$$\bar{\Sigma}_\infty = a_0 + a_1 \Delta T, \quad \log \bar{\Gamma} = b_0 - b_1 \Delta T, \quad \kappa = c_0 - c_1 \Delta T, \quad (11)$$

where a_k , b_k and c_k are adjustable parameters. Following Ref. (31), we define the critical temperature T_{cr} as a temperature at which the energy landscape becomes homogenous and $\bar{\Sigma}_\infty$ vanishes. It follows from Eq. (11) and Figure 3 that for poly(vinyl acetate), $T_{cr} = T_g + 8.0$ K which is quite close to $T_{cr} = T_g + 9.4$ K found by using experimental data in mechanical tests (31). In the vicinity of T_g , the apparent

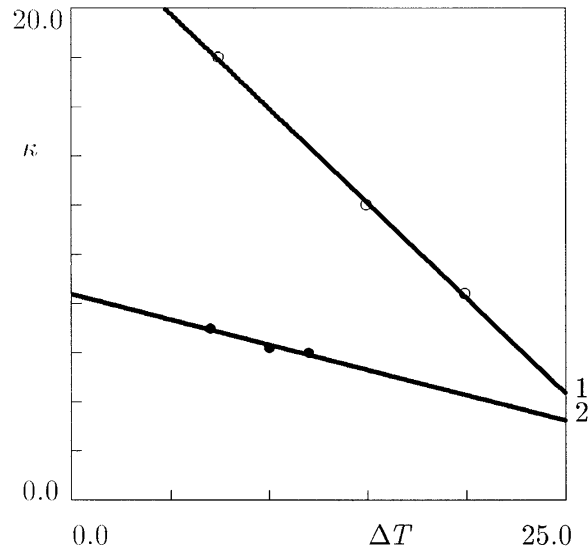


Figure 5: The parameter κ versus the degree of supercooling ΔT K. Circles: treatment of observations. Solid lines: approximation of the experimental data by Eq. (11). Curve 1: PMMA, $c_0 = 23.639$, $c_1 = 0.7705$; curve 2: PVA, $c_0 = 8.3842$, $c_1 = 0.2053$

activation energy ΔE is given by

$$\Delta E = -R \left. \frac{d \ln \bar{\Gamma}}{d(1/T)} \right|_{T=T_g},$$

where R is gas constant. This formula together with Eq. (11) implies that $\Delta E = b_1 R T_g^2 \ln 10$. It follows from this equality and Figure 4 that $\Delta E = 277.71$ kJ/mol for PMMA and $\Delta E = 48.26$ kJ/mol for PVA, which are typical values of the activation energy for these polymers (32). According to Figure 5, the parameter κ vanishes (i.e. the internal time τ coincides with the absolute time t) at the temperatures $T_\kappa = T_g - 30.68$ K for PMMA and $T_\kappa = T_g - 40.84$ K for PVA, which belong to the thermal interval between the Kauzmann temperature and the glass transition point.

Concluding remarks

A model has been derived for enthalpy relaxation in amorphous glassy polymers after thermal jumps. Adjustable parameters in constitutive equations are found by fitting experimental data for poly(methyl methacrylate) and poly(vinyl acetate). The following conclusions are drawn from numerical simulation:

1. constitutive equations adequately describe structural relaxation in the sub- T_g region.
2. the growth of the degree of supercooling ΔT leads to an increase in $\bar{\Sigma}_\infty$ (the growth of ruggedness of the energy landscape), a decrease in the attempt rate Γ (in agreement with the concept of thermally activated processes) and a decrease in the parameter κ (at high levels of supercooling, the internal time τ approaches the absolute time t).
3. some critical temperature T_{cr} exists at which the energy landscape becomes homogeneous. The location of the critical point (about 10 K above T_g) is in fair

agreement with data provided by fitting observations in mechanical tests and with predictions of the mode-coupling theory.

Acknowledgement: Financial support by the Israeli Ministry of Science through grant 1202-1-98 is gratefully acknowledged.

References

1. Struik LCE (1978) Physical ageing in amorphous polymers and other materials. Elsevier, Amsterdam
2. Ediger MD, Angell CA, Nagel SR (1996) *J Phys Chem* 100: 13200
3. Debenedetti PG (1996) *Metastable liquids: Concepts and principles*. Princeton Univ. Press, Princeton
4. Bouchaud J-P, Cugliandolo LF, Kurchan J, Mezard M (1998) In: Young AP (Ed) *Spin glasses and random fields*. World Scientific, Singapore, p. 161
5. Mezard M, Parisi G (2000) *J Phys: Condens Matter* 12: 6655
6. Dyre JP (1995) *Phys Rev B* 51: 12276
7. cummins HZ, Li G, Hwang YH, Shen GQ, Du WM, Hernandez J, Tao NJ (1997) *Z Phys B* 103: 501
8. Monthus C, Bouchaud J-P (1996) *J Phys A* 29: 3847
9. Sollich P (1998) *Phys Rev E* 58: 738
10. Adam G, Gibbs JH (1965) *J Chem Phys* 43: 139
11. Rizos AK, Ngai KL (1999) *Phys Rev E* 59: 612
12. Goldstein M (1969) *J Chem Phys* 51: 3728
13. Robertson RE (1978) *J Appl Phys* 49: 5048
14. Chow TS (1983) *J Chem Phys* 79: 4602
15. Drozdov AD (2000) *Polym Bull* 44: 353
16. Moynihan CT, Eastal AJ, Wilder J, Tucker J (1974) *J Phys Chem* 78: 2673
17. Kovacs AJ, Aklonis JJ, Hutchinson JM, Ramos AR (1979) *J Polym Sci: Polym Phys Ed* 17: 1097
18. Rendell RW, Ngai KL, Fong GR, Aklonis JJ (1987) *Macromolecules* 20: 1070
19. Feltham P (1968) *Phys Stat Sol* 30: 135
20. Dobeš F (1980) *Acta Metall* 28: 377
21. Richert R, Bässler H (1990) *J Phys: Condens Matter* 2: 2273
22. Angell CA (1997) *Physica D* 107: 122
23. Avramov I, Milchev A (1988) *J Non-Cryst Solids* 104: 253
24. Dlubek G, Saarinen K, Fretwell HM (1998) *J Polym Sci B: Polym Phys* 36: 1513
25. Gomez Ribelles JL, Monleon Pradas M (1995) *Macromolecules* 28: 5867, 5878
26. Cowie JMG, Harris S, Gomez Ribelles JL, Meseguer JM, Romero F, Torregrosa C (1999) *Macromolecules* 32: 4430
27. Hodge IM, Berens AR (1982) *Macromolecules* 15: 762
28. Hutchinson JM, Smith S, Horne B, Gourlay GM (1999) *Macromolecules* 32: 5046
29. Cowie JMG, Ferguson R (1993) *Polymer* 34: 2135
30. Cowie JMG, Harris S, McEwen IJ (1998) *Macromolecules* 31: 2611
31. Drozdov AD (2000) *Europhys Lett* 49: 569
32. Ferry JD (1980) *Viscoelastic properties of polymers*. Wiley, New York