

PROGRESS IN COLLOID & POLYMER SCIENCE

Editors: H.-G. Kilian (Ulm) and G. Lagaly (Kiel)

Volume 78 (1988)

***Relationships
of Polymeric Structure
and Properties***

***Guest Editor:
I. Chudáček (Prague)***



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Preface

The 5th International Seminar on Polymer Physics was organized by the Department of Polymer Physics at Charles University, Prague, 21–27 April, 1987. We present in this volume the main plenary lectures, short lectures, and posters from that seminar. The reader will obtain an overview of the principal scientific efforts in the field of polymer physics from many European universities and institutes. This book comprises two main scientific approaches:

1. The superstructure of polymer systems;
2. The electronic properties of thin polymer films.

It seems to me that the “heterogenous” state formed by these two approaches represents a few

inconveniences, but it has had a stimulating influence on each scientist present. The study of the polymeric state of condensed matter will in the future attract more scientists to its strange architecture, beautiful movements, and unexpected interactions. Also, new applications for polymers will emerge in future years and support existing ones.

In closing, I would like to thank each contributor, and the journal “Colloid and Polymer Science”, which made this publication possible.

Ivo Chudáček

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Equilibrium stress-strain properties and topological constraint release effects in end-linked model networks

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Abstract: The interpretation of the equilibrium mechanical properties of polyurethane model networks in the large elongation region has been performed within a theory of tube-like topological constraints. This theory describes the small-strain properties as well as the large-strain properties of the networks in terms of the number of elastically active network chains (EANCs) and structural features contained in the structural parameters T_e (trapping factor) and w_s (sol content).

Key words: Model networks, topological constraints, network defects, network theory, stress-strain measurements.

1. Introduction

In a recent paper [1] a theory of polymer networks was proposed which uses a tube-like mean field concept for simulating the strength and deformation dependence of the topological constraints of the network chains. The effectiveness of these constraints depends on the external deformation. It has been explained that network defects (e.g., dangling ends) and the sol content, w_s , favor constraint release effects (CRE) of network chains which tend to return the configurational tubes to the configurations they had before deformation.

In the following we investigate experimental data of polyurethane model networks [2] within the theory of tube-like topological constraints. Attention is devoted to the prediction of large-strain Mooney-Rivlin parameters C_1 and C_2 in terms of molecular characteristics of the network.

The equilibrium mechanical properties (small-strain and large-strain behavior) of polyurethane model networks have been investigated in [2]. The networks were prepared from poly(oxypropylene) triols (PPT) and 4,4'-diphenylmethane diisocyanate (MDI) at various initial molar ratios of reactive groups, r_H . The experimental small-strain data have been compared with theoretical dependences of the equilibrium

modulus, G , on the sol content, w_s . The calculations were based on the theory of branching processes [2, 3] and used the Langley-concept of trapped entanglements [4, 5] to correlate the equilibrium modulus with the concentration of elastically active network chains (EANCs), and with the so-called trapping factor, T_e , which characterizes the permanent topological interactions between segments in EANCs.

2. Theory

The statistical mechanics of polymer networks with deformation dependent tube-like topological constraints leads to the following dependence of the reduced stress σ_{Mg} on elongation λ [1]

$$\sigma_{Mg} \equiv \frac{\sigma_g(\lambda)}{\lambda - \lambda^{-2}} = G_{cg} + G_{Ng} \tilde{f}(\lambda) \quad (1)$$

where σ_g is the stress related to initial cross-section of the sample.

$$G_{cg} = \frac{f - 2}{f} RT v_{eg} \quad (1a)$$

is the "chemical" contribution to the total shear modulus (f = functionality),

$$G_{Ng} = a G_N^0 \beta_e^2 \quad (1b)$$

is the "topological" contribution to the total modulus and

$$\tilde{f}(\lambda, \nu, \beta_e) = \frac{1}{\nu \beta_e} \frac{\lambda^{\nu \beta_e} - \lambda^{-2\nu \beta_e}}{\lambda^2 - \lambda^{-1}}, \tilde{f}(\lambda = 1) = 1. \quad (1c)$$

The quantity ν_{eg} denotes the "chemical" number of EANCs in the unit volume of gel. In Eq. (1c) the parameter ν describes the constraining mechanism ($-1 \leq \nu \leq +1$) of network chains. The model of trapped entanglements may be viewed as a special case of (tube-like) topological constraints which is mainly based on the assumption of dominating local constraints. This assumption fails increasingly if CREs allow local constraints to relax. Then, the effect of the remaining global entanglements can be described successfully by the trapping concept. This picture of trapped pure entanglements yields $\nu = -1$ [1].

The quantity β_e ($0 \leq \beta_e \leq 1$) characterizes the deformation dependence of the constraining tubes (deformed tube radius $d_\mu = d_0 \lambda_\mu^{\beta_e}$, d_0 is the undeformed tube radius, $\mu = x, y, z$) and the relaxed microscopic deformation λ_{mic} of the *rms* end-to-end distance of network strands $((\lambda_{mic})_\mu = \lambda_\mu^{\beta_e})$. The time dependence of this relaxation process to the final (equilibrium) state after a sudden external deformation will be discussed in a separate paper [10].

In Eq. (1b), G_N^0 is the plateau modulus of the corresponding linear uncrosslinked polymer. The quantity $a \approx 0.13 (d_0^m/d_0)^2$ contains the ratio of the lateral tube radius in the melt (d_0^m) and in the corresponding network, respectively. The theory yields [1, 7, 9] $d_0^m/d_0 \approx 2-4$ which leads to the relation

$$G_{Ng} \approx (0.5 - 2) \beta_e^2 G_N^0. \quad (2)$$

From comparison of Eq. (1b) with the entanglement contribution to the shear modulus according to the Langley-concept it is necessary to write $T_{eg} \equiv T_e/w_g \approx \beta_e^2 \cdot T_e$. T_e is the trapping factor and w_g is the weight fraction of the gel. The ratio $d_0^m/d_0 \approx 2-4$ differs from the conclusions of Gaylord [11] and Marrucci [12] who assumed the relation $d_0^m/d_0 = T_e^{1/2} < 1$. Without discussing CRE they expected that a dilution effect of network defects leads to a cross-sectional area of the tube in the network larger than the cross-sectional area of the tube surrounding the same chain in the uncrosslinked system. Our model [1, 7, 9] gives an additional effect of the crosslinks to the strength of the topological constraints and, therefore, $d_0^m/d_0 > 1$. The strength of topological constraints depends on the space density of polymer contour length (or the local segment number density) and not on structural details of the system [7, 13].

In the following, we use the equality $\beta_e^2 = T_{eg}$. The quantities ν_{eg} , T_{eg} , and w_g were calculated for PUR model-networks using the theory of branching processes [2, 3]. The value $a G_N^0 \approx 1.4 \text{ MPa}$ is taken from [2]. The Mooney-Rivlin parameters C_1 and C_2 are calculated by linear regression in the regime of moderate extensions ($\lambda = 1.1 - 2.5$) and use the relations

$$\begin{aligned} \sigma_{Mg}(\lambda) &= G_{cg} + G_{Ng} \tilde{f}(\lambda, \nu = -1, \beta_e = T_{eg}^{1/2}) \\ &= C_{1g} + C_{2g} \lambda^{-1}. \end{aligned} \quad (3)$$

The calculations were performed only in the case of networks characterized by the molar ratio $r_H \geq 1$ (samples No. 7-18 (PPT-LHT-240) and No. 28-40 (PPT-LG-56) of [2]). In the opposite case, $r_H < 1$, excess crosslinking took place, obviously due to the formation of allophanate groups. When determining C_{1g} and C_{2g} by

Eq. (3), the correlation coefficients of all samples have been estimated to be in the range $r = 0.950$ and $r = 0.993$.

3. Results and Discussion

The calculated parameters C_{1g} and C_{2g} have been compared with the corresponding values $C_1^* \equiv C_1^{\text{exp}}/w_g$ and $C_2^* \equiv C_2^{\text{exp}}/w_g$. The quantities C_1^{exp} and C_2^{exp} denote the measured Mooney-Rivlin constants of the unextracted networks [2]. The quantities C_1^* and C_2^* consider the lowering of the elastic constants due to the volume fraction of the sol. The correlation between C_{1g} and C_1^* is reflected in the linear regression result $C_{1g} [\text{MPa}] = 0.985 C_1^* [\text{MPa}] - 0.033 [\text{MPa}]$ with a correlation coefficient $r = 0.997$.

When comparing the calculated values of C_{2g} with the corresponding values of C_2^* , we observe a non-linear decrease of $c = C_2^*/C_{2g}$ with increasing sol content, w_s (Fig. 1). This effect qualitatively agrees with the result of previous studies of dry extracted and non-extracted networks prepared from different polymers [14]. The similar effect is obtained in swollen networks in which the C_2 -parameter at higher swelling degrees decreases non-linearly with increasing amount of solvent [1]. In the present paper the effect can be explained as the influence of the sol content on the CRE. Increasing amount of w_s (and, therefore, decreasing values of β_e) favors the knot rearrangement processes [15] which tend to return the configurations of tubes to those they had before deformation. The value of C_{2g} is determined by the amount of defects connected with the gel and their influence on the CRE. The value of C_2^* is additionally determined by the sol content.

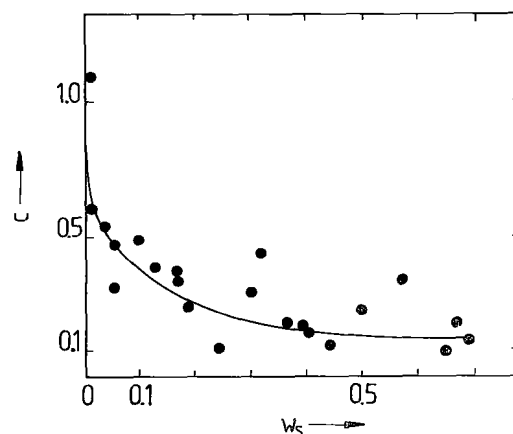


Fig. 1. The influence of sol content on the Mooney-Rivlin parameter C_2

Quantitatively, the curve in Fig. 1 is proposed to follow a power law dependence $c \sim (1 - w_s)^\alpha$. A similar result was found in [14]. A linear correlation analysis of a $\log c - \log w_g$ plot yields $\alpha \approx 1.42$ with a correlation coefficient $r = 0.660$.

On a molecular level the results can be interpreted as follows: The undeformed tube radius, d_0 , mainly depends on the segment number density and not on structural details, whereas the deformation dependence of the tube radius ($d_\mu = d_0 \lambda_\mu^{-\beta_e}$) depends considerably on structural parameters. Physically, this effect has been explained by the concept of constraint release of network chains. A large content of sol fraction w_s (and, hence, a small value of β_e) leads to (nearly) deformation independent tube dimensions. It is well known that polymer networks in which the topological restrictions are nearly independent of deformation have small (in comparison with C_1) values of the C_2 constants [1]. Similar effects can be found in swollen networks.

Further experimental studies on extracted and nonextracted samples would be useful to clarify the quantitative dependence of the ratio c on the sol content w_s .

The theoretical basis of the interpretation of experimental data can be improved by additional consideration (to the configurational restrictions of network chain segments) of restrictions of junction fluctuations [16, 17]. In the case of restricted chains and partially restricted junction fluctuations one obtains additional contributions to the elastic free energy of the network; and the front-factor depends on d_0 and has values between the free-fluctuation limit and fixed junction limit, respectively [17, 18].

We note that Andradý and Llorente [19] recently interpreted stress-strain properties of poly(oxyprop-

ylene) model networks by the Mooney-Rivlin approach and the theory of restricted junction fluctuations.

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Determination of mechanical parameters related to the kinetics of swelling in an electrically activated contractile gel

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Abstract: We report on an analytical model and related experiments to determine the mechanical parameters governing the kinetics of mechanical readjustment of a thermally crosslinked polyacrylic acid (20 % by weight) and polyvinylalcohol (80 % by weight) (PAA-PVA) gel.

Either thin films on spherical samples have been used in the experiments. The characteristic time of swelling in the case of a thin film has been found to be proportional to the square of a linear dimension of the sample divided by a diffusion coefficient D , defined as $D = \mu/f$, where μ is the shear modulus of the gel network and f is the friction coefficient between the network and fluid.

This constitutes an essential difference between the swelling of spherical samples reported in literature in which the diffusion coefficient is $D^* = (k + 4/3)/f$, where k is the bulk modulus of the gel network.

We have derived the value of the bulk modulus k , the shear modulus μ and the friction coefficient f by free swelling experiments performed on spherical and planar thin samples, and by direct measurement of water permeability across the gel.

Mechanical readjustment time constant and diffusion-reaction time constant, which has been previously determined, are then compared to evaluate the limiting rate phenomena which govern the kinetics of gel deswelling under electrochemical stimuli in different pH ranges.

Key words: Polyelectrolyte gels, polyacrylic acid + polyvinylalcohol, thermally cross-linked, swelling kinetics, electromechanochemistry.

Introduction

Recently, experiments have been conducted aimed at eliciting contractile activity in polyelectrolyte networks by electrical excitation, to eventually develop a new kind of "soft actuator". Muscle-like motors could be instrumental, among other possible applications, in the design of innovative artificial organs and limb prostheses [1] and dexterous effectors for advanced robots [2].

Although various physical effects can contribute to the observed electromechanical coupling [3], strongest contractile force density has been observed under provisions by which pH gradients are generated by electrode reactions and transported across the polymer network by electrodiffusion.

Several factors govern the electromechanochemical energy conversion performance of the system, such as

gel material parameters, composition and solute concentration of the supernatant solution, geometrical arrangements, electrode material, and potential difference at the electrodes.

The purpose of this work is to discuss an electromechanochemical swelling model which has been formulated to describe the kinetics of electrically activated contractile phenomena observed in a polyelectrolyte gel and to determine, by free swelling experiments and mechanical measurements performed on spherical and planar samples, material parameters which are relevant to a phenomenological description.

Electromechanochemical swelling model

To analyze and describe the transient mechanical behavior of a polyelectrolyte gel element in response

to proton and salt concentration gradients generated by electrode reactions and transported inside the gel by electrochemical potential differences, several rate processes should be taken into account, such as ion diffusion, diffusion limited chemical reaction, ion migration, and consequent electrical and mechanical readjustments of the polymer network [4].

Typically, proton diffusion-reaction and mechanical readjustment of the polymer network are the slowest phenomena, and a system of coupled differential equations is formulated to determine the kinetics of gel deswelling under electrochemical stimuli [5].

A comparison among proton diffusion and gel swelling characteristic time constants might prove very useful in decoupling the chemical and mechanical problems, particularly in the case of specific gel systems in which these limiting time constants are considerably different [6].

Analysis of the kinetics of free swelling

The kinetics of free swelling of a partially dehydrated gel is analyzed in the case of spherical and thin sheet samples; since no chemical change occurs in the gel during swelling; the kinetics is only governed by mechanical parameters.

An equation of motion of gel networks was formulated by Tanaka et al. [7] and proved to be adequate in describing free swelling phenomena either theoretically [8] or experimentally. Taking into account the chemical stress term β [9], which represents the zero-force strain generated by the proton concentration change, this equation is formulated

$$\partial u / \partial t = [(k + \mu/3) 1/f] \text{grad div } u + \mu/f \text{div grad } u + 1/f \text{grad } \beta. \quad (1)$$

The stress-strain relationship becomes

$$\sigma_{ij} = k \text{div } u \delta_{ij} + 2\mu(u_{ij} - 1/3 \text{div } u \delta_{ij}) + \beta \delta_{ij} \quad (2)$$

where

$$u_{ij} = (\partial u_j / \partial x_i + \partial u_i / \partial x_j) / 2$$

where u is the displacement vector of gel elemental volume from its position when the swelling process has gone to completion, k is the bulk elastic modulus of the gel polymeric component, μ its shear modulus, and f is the friction coefficient between the polymer network and the liquid medium.

The chemical to mechanical coupling is provided by the proton concentration dependence of the phenomenological coefficients k , μ , f , and β . The kinetics of free swelling of a gel sample depends upon its geometry and material parameters as it is analyzed in the following in the case of spherical and thin planar samples.

Spherical samples

By referring to Eq. (1) in which the β term is omitted since no chemical change occurs, the kinetic of swelling is described when the function $u(r, t)$, (r being the sample radius), is determined in the space domain occupied by the gel (in the state at $t = \infty$).

By solving Eq. (3) in spherical coordinates, it has been shown [10] how the characteristic relaxation time τ_s of the polymer network is proportional to the square of the radius a of the sphere when fully swollen and inversely proportional to the diffusion coefficient of the polymer network into the solution

$$\tau_s = a^2 / (D_s \pi^2) \quad \text{where } D_s = (k + 4\mu/3) / f. \quad (3)$$

During the swelling process, $r(t) = a - \Delta r(t)$, where

$$\Delta r(t) = \Delta r_0 (6\pi) \sum_n n^{-2} \exp(-n^2 t / \tau_s) \quad (4)$$

and

$$\Delta r_0 = -u_{(r=a, t=0)}.$$

At $t > \tau_s/4$ in the time dependence of Δr the exponential term having $n = 1$ becomes preponderant.

Thin planar samples

We analyze the kinetics of swelling of a thin, planar sample whose thickness is negligible in respect to other dimensions, and we assume that the system is invariant in respect to translations along the planar coordinates x and y during the swelling process.

Under these assumptions, the strain components do not depend on the x and y coordinates; the following identities hence hold:

$$\begin{aligned} \partial u_{xx} / \partial x &= \partial u_{yy} / \partial x = \partial u_{xx} / \partial y = \partial u_{yy} / \partial y \\ &= \partial u_{zz} / \partial x = \partial u_{zz} / \partial y = 0. \end{aligned} \quad (5)$$

By integrating the first four equations in relation to Eq. (5), we obtain $u_x = u(z) x$ and $u_y = u(z) y$.

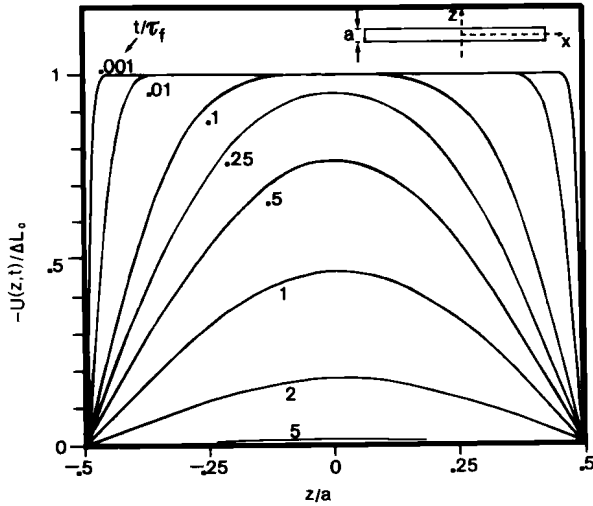


Fig. 1. Calculated fractional strain along x direction in a planar sample during the swelling process at various parametric values of the reduced time of swelling

Adhering to the definition of the strain tensor, it follows that $u_{xy} = 0$.

Since the system is invariant in interchanging x and y , the equality $u_{xx} = u_{yy}$ also holds. By introducing these relationships into the gel equation of motion we obtain

$$\partial u_x / \partial t = \mu / f \partial^2 u_x / \partial z^2 \quad (6)$$

$$\partial u_y / \partial t = \mu / f \partial^2 u_y / \partial z^2 \quad (7)$$

$$\partial u_z / \partial t = (k + \mu/3) / f \partial(\text{div } u) / \partial z + \mu / f \partial^2 u_z / \partial z^2. \quad (8)$$

We now are able to solve Eq. (6) by defining initial and boundary conditions which are congruent with the free swelling experiments.

Initial conditions, in the hypothesis of isotropic swelling, are defined as

$$u_i(x, y, z, t = 0) = u_0 i \quad i = x, y, z \quad (9)$$

where u_0 indicates the percent change of sample dimensions referred to the final state at $t = \infty$.

Boundary conditions are defined by assuming that at time $t = 0^+$ the sample is immersed into the solution and "freed" from the virtual pressure which confines it to its actual dimensions.

Hence, at any t , $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 0$ at the sample surfaces perpendicular to the z axis at $z = \pm a/2$ (see

Fig. 1 for the definition of the coordinate system). It follows

$$\sigma_{zz} = (k + 4/3\mu)u_{zz} + (k - 2/3\mu)(u_{xx} + u_{yy}) = 0$$

$$\text{at } t > 0 \text{ and } z = \pm a/2 \quad (10)$$

$$\sigma_{xx} = (k + 4/3\mu)u_{xx} + (k - 2/3\mu)(u_{yy} + u_{zz}) = 0.$$

By solving Eq. (10) in u , we obtain $u(\pm a/2, t) = 0$.

We can now find a solution of Eq. (6); introducing the initial and boundary conditions defined above

$$u = \sum_n \exp(-(2n+1)^2 t/\tau_f) (-1)^n [4u_0/(2n+1)\pi] \cos[(2n+1)z\pi/a], \quad (11)$$

where $\tau_f = a^2 f / \pi^2 \mu = a^2 / \pi^2 D_f$.

In Fig. 1 the strain in the planar sample during the swelling process is reported at various parametric values of the reduced time of swelling. The sample length along x coordinate $L(t)$ can be calculated

$$L(t) = L \cdot \{1 + 4u_0 \sum_n \exp(-(2n+1)^2 t/\tau_f) (-1)^n / [(2n+1)\pi]\} \quad (12)$$

where L is the gel dimension when fully swollen.

It can be noted that for $t > \tau_f/9$, the term having $n = 0$ becomes predominant in the summation series.

Experimental

Sample preparation

Thermally crosslinked gel samples were prepared in thin sheet and spherical form using polyvinylalcohol (PVA) and polyacrylic acid (PAA). PVA with a degree of hydrolysis of 98% and an average molecular weight of 10 000 (AnalytiCals, Carlo Erba, Milano, Italy) and PAA with an average molecular weight of 250 000 (Aldrich Chemical Co., Milwaukee, Wisconsin USA) were dissolved separately into bidistilled water and subsequently mixed in the relative proportion of respectively, 80% and 20% by weight. After 20 min of stirring at 60 °C, the homogeneous solution was dehydrated in a thermostatic oven at 40 °C under mild vacuum. The sample was removed from the original container and thermally crosslinked at 130 °C for 45 min. The samples are then equilibrated with bidistilled water.

Free swelling experiments

Spherical samples (average diameter 0.05 cm) and square shape, thin sheets (average thickness 0.02 cm, 0.5 cm side) were partially dehydrated up to the point where linear dimensions reduced 8%. At $t = 0$, partially dehydrated samples were immersed into bidistilled water and allowed to free swell to equilibrium at 20 °C. Linear

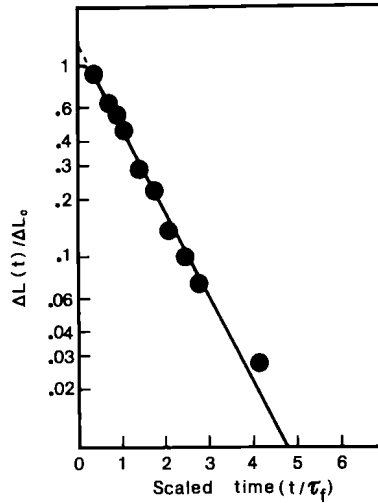


Fig. 2. The change in the length of a planar sample in respect to its length when fully swollen, at various scaled time of swelling. The solid curve is calculated using Eq. (11)

dimension changes were measured in time by using a graduated eyepiece. In Fig. 2 the change in the length of a planar gel sample $\Delta L(t)/\Delta L_0$ during swelling is reported, plotted as a function of relative time t/τ_f . The solid line represents the theoretical behavior calculated using Eq. (12). The extrapolated intercept with the ordinate axis of the line-fitting experimental data gives the value $4/\pi$, as theoretically predicted. A value of $\tau_f = 86 \pm 2$ sec has been obtained after averaging measurements performed on 10 gel samples. In Fig. 3, the change in the radius of a spherical sample is reported under the same condition illustrated for Fig. 2. Here again the theoretical prediction is quite accurate and the intercept at $t/\tau_s = 0$ gives the calculated value of $6/\pi^2$. A value of $D_f = 1/\pi^2 \cdot 4.7 \pm 0.4 \cdot 10^{-6}$ cm²/sec has been obtained after averaging measurements performed on 10 samples. A value of $D_s = 1/\pi^2 \cdot 2.0 \pm 0.3 \cdot 10^{-5}$ cm²/sec has been obtained for spherical samples.

Measurements of the friction coefficient and of the elastic moduli

Measurement of polymer-water friction coefficient was performed using the apparatus and technique indicated by Tanaka et al. [7]. A gel sample in the form of a disk (diameter = 0.8 cm; thickness = 0.018 cm) is contained in a glass apparatus as illustrated in Fig. 4 and located in a thermostatic oven at 20 °C. The time dependence of the capillary water column height is recorded using a cathetometer and it is shown in Fig. 5 in a logarithmic scale. Fitting of experimental points permits us to obtain the value of $\tau = 2.6 \cdot 10^5$ sec for the exponential time dependence $h = h_0 \exp(-t/\tau)$.

The value of the friction coefficient f can be calculated [8] from the relationship

$$f = \rho g A_g \tau / (\delta A_c) \quad (12)$$

where ρ is the density of water, g is the acceleration of gravity, A_g is the gel surface area, δ is the gel thickness, and A_c is the cross-sectional

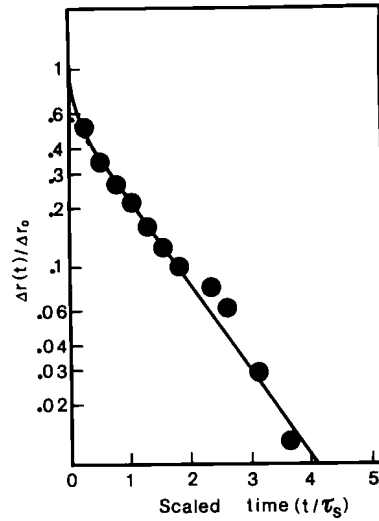


Fig. 3. The change in the radius of a spherical sample during swelling, plotted as a function of the scaled time of swelling. The solid curve is calculated using Eq. (4)

area of the capillary column. The calculated value is $f = 3.1 \pm 0.8 \cdot 10^{13}$ dyne sec/cm⁴. Since, as it has been calculated in this paper, $f = \mu/D_f$ for planar samples, the combined measurement of D in free swelling experiments f and of the shear elastic modulus may provide a control of the theoretical arguments by comparing the independently measured and calculated values of f .

The measurement of the shear elastic modulus of the gel has been performed on planar samples under sinusoidal (3 Hz) uniaxial tensile stress using a commercially available instrument (Rheograph Piezo, ToyoSeiki, Tokyo, Japan); a value of $\mu = 1.4 \cdot 10^7$ dyne/cm² has been obtained. Hence $f = \mu/D_f = 3.0 \pm 0.6 \cdot 10^{13}$ dyne sec/cm⁴, which is in reasonable agreement with the directly measured value of $f = 2.5 \pm 0.8 \cdot 10^{13}$ dyne sec/cm⁴. Finally, since $D_s = (k + 4\mu/3)/f$, the value of the elastic bulk modulus k is calculated to be $k = 3.5 \pm 1.5 \cdot 10^7$ dyne/cm².

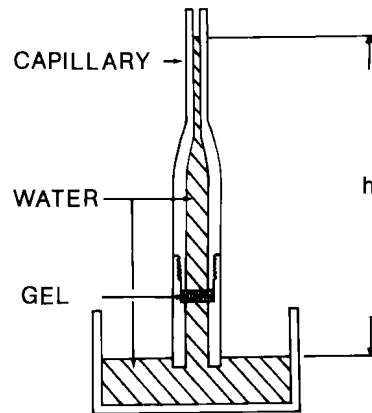


Fig. 4. Apparatus for measuring the friction coefficient f between the polymer network and water. After reference [7]

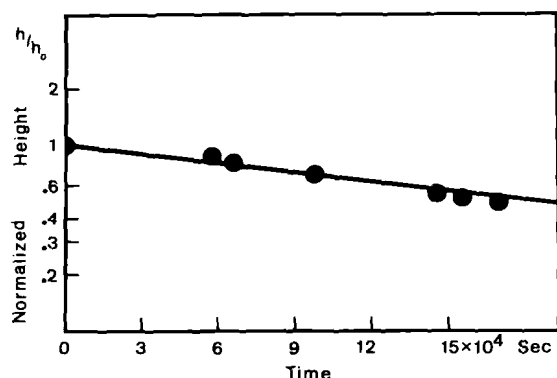


Fig. 5. Normalized height (logarithmic scale) of the capillary water column vs time of application of hydrostatic load

Conclusions

The time constant for free swelling of PAA-PVA gel samples having different geometry can be calculated using different combinations of the parameters k , μ and f .

A comparison between the proton diffusion-reaction time constant [5] and the mechanical readjustment time constant evaluated here shows that the kinetics of electrochemically activated PAA-PVA gels is limited by proton diffusion-reaction or by mechanical readjustment depending on the pH range. In the case of small pH increments, the proton diffusion-reaction time constant τ_c has been theoretically and experimentally found [5] to follow the relationship

$$\tau_c = (\pi^2 D_+)^{-1} [1 + K \cdot n / (K + c^D)^2] \quad (13)$$

where K is the intrinsic dissociation constant (mean value) of the carboxyl groups bound to the polymer network, c^D is the free proton concentration inside the gel, n is the total concentration of ionizable groups per liter of membrane water, and D_+ is the proton diffusion coefficient inside the gel.

The measured values of $K = 1.28 \cdot 10^{-5}$ mole/liter, $n = 0.568$ mole/liter, and D_+ comprised between $1.5 \cdot 10^{-9}$ and $3.8 \cdot 10^{-9}$ m²/sec (depending on the gel water content) [5] allow us, by using Eq. (13), to assert that the mechanical readjustment time constant, as evaluated for a planar sample, is shorter than the diffusion-reaction time constant when the pH of the solution in

equilibrium with the gel is higher than 2.9. At pH higher than 3.2 the kinetics are governed by the proton diffusion-reaction and the electromechanochemical problem can be decoupled. The polymer network, from a mechanical point of view, can be so considered at any time to be in equilibrium at the local proton concentration. In this context the mathematical description of gel kinetics under electrochemical stimuli is greatly simplified.

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Dielectric and thermal relaxations in amorphous and semicrystalline poly(ethylene terephthalate)

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Abstract: Undrawn PET was crystallized using several temperature programs to get samples of different crystalline structure, as indicated by a varying thickness of the amorphous layer between neighboring lamellae. The fluctuation model proposed by Donth was used to estimate the size (1–3 nm) of the cooperative, rearranging regions connected with the glass transition in these samples. There occurs a hindrance of the cooperative motions due to the crystalline structure, as shown by the correlation between the size of the cooperative, rearranging regions and the thickness of the layer of mobile amorphous material.

The WLF-curves are shown for the amorphous and the semicrystalline PET in the frequency range from 10^{-15} to 10^8 Hz. A deviation from these curves, expected for the hindrance, is not observed.

Key words: Semicrystalline PET, amorphous fraction, glass transition, cooperative motion, characteristic length.

Introduction

The study of relaxation processes in semicrystalline polymers is a current topic of great scientific and technological interest. A large number of investigations have been undertaken to characterize relaxations in these materials, and there has been much scientific interest in the elucidation and detailed description of the molecular processes underlying them. Of particular interest is the main relaxation process or glass transition. There is some evidence that the molecular motion connected with this relaxation process is a cooperative one. The fluctuation model proposed by Donth [1, 2] is used to estimate the size of the cooperatively rearranging regions (CCR) at the glass transition:

$$V_a = k T_g^2 (1/c_v)/\rho(\delta T)^2 \quad (1)$$

where k is Boltzmann's constant, T_g is glass transition temperature, $(1/c_v)$ is the step in the reciprocal specific heat at T_g , ρ is the density of the amorphous material and δT is the mean temperature fluctuation. A great

effort is necessary in order to extract δT from thermograms [2, 3]. Therefore, very rough approximations must be made [4]. From reference [3] a mean value of about 0.4 can be extracted for the ratio $\delta T/\Delta T$ (for three amorphous polymers), where ΔT is the temperature interval between 16 % and 84 % of the c_p step height for the heating thermogram. A variation, or shift, of this value is not believed to influence the qualitative results of the present paper.

Considering V_a as a sphere with a radius ξ , which is considered as a characteristic length, we obtain

$$\xi = (3 V_a/4\pi)^{1/3}. \quad (2)$$

The characteristic lengths ξ calculated according to Eqs. (1) and (2) for amorphous polymers are in the nm range (2–3 nm) [1–3]. If this is really the case, the question arises: What will happen if the dimension of the amorphous region is reduced to a value comparable with the characteristic length of cooperative motion? In semicrystalline polymers it should be possible to form this reduction which would hinder the cooperative motion.

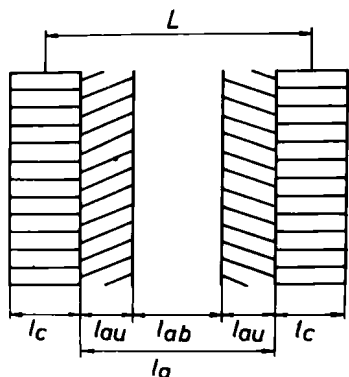


Fig. 1. Schematic representation of the arrangement of lamellae inside a regular crystalline structure (see text and Table 1)

Experimental

We used commercial PET (ORWO K36, $\bar{M}_w \approx 23000$) as a model system since it allows us to estimate the size of the CRR in the totally amorphous material and in samples of different crystalline structure as well. In order to obtain the dimension of the amorphous regions inside the semicrystalline material we used the following simplified model (Fig. 1). The mean distance between the center of the lamellae equals the long period L , as it is determined by small angle x-ray scattering, in connection with the methods described by Vonk [5]. The long period varies from 7 to 9 nm for the samples investigated. From wide angle x-ray scattering we obtain the mass fraction of crystalline material and calculate the volume fraction α_v . Using this simple one-dimensional model it is possible to estimate the mean size of the lamella l_c and of the amorphous layer l_a (see Table 1). In addition to these crystallinity parameters we know from molecular mobility measurements (as NMR or calorimetric investigation of the step height of the specific heat, and by Raman spectroscopy as well) that the amorphous layer in the investigated PET samples is not a homogeneous one [6]. Here we are able to obtain the volume fraction β of the mobile amorphous material and the volume fraction γ of the rigid amorphous material with higher and lower molecular mobility, respectively. One possibility to estimate β and the thickness of the corresponding layer l_{ab} is given by

$$\beta = \Delta C_p / \Delta C_{pa} \quad l_{ab} = L \cdot \beta \quad (3)$$

where ΔC_p is the step height of the specific heat at T_g for the observed semicrystalline sample and ΔC_{pa} is that for an amorphous one. The quantities we obtained [6] are given in Table 1. In our opinion the rigid amorphous material is located in the interfacial region. Its value of about 2 nm corresponds to the literature data for other polymers [7]. The figures shown in Table 1 correspond to three different crystallization regimes. These are:

1. Isothermal crystallization using temperatures between 120 °C and 220 °C;

2. Stepwise crystallization in the same temperature range in accordance with Groeninckx [8];

3. A long time secondary crystallization at 220 °C up to 500 h.

In this way we produced samples with different thicknesses of the layer of the mobile amorphous material. Table 1 reveals that

Table 1. Parameters describing the crystalline structure 6 (see Fig. 1)

Material	Volume-fraction	Corresponding layer
crystalline	α_v 0.2 – 0.4	$l_c = L \cdot \alpha_v$ 2–4 nm
noncrystalline (amorphous)	$1 - \alpha_v$ 0.6 – 0.8	$l_a = L \cdot (1 - \alpha_v)$ 5–7 nm
mobile amorphous	β 0.1 – 0.3	$l_{ab} = L \cdot \beta$ 1–3 nm
rigid amorphous	γ_v 0.4 – 0.6	$2l_{au} = L \cdot \gamma$ 3–4 nm

they fall into the nm range so that they are of the same order of magnitude as the CRR.

Using Eqs. (1) and (2) it is possible to estimate the size of the CRR of these samples by analyzing a thermogram in the glass transition interval [9]. Since we investigated one polymer only, we think that the error in ξ of the order of 20% is a systematic one. Hence it does not influence the linearity shown in Fig. 2. Dielectric relaxation in these samples has been measured in the frequency range from 10^{-5} to 10^8 Hz and mechanical relaxation at about 1 Hz as well as in the temperature range from –60 °C to 220 °C. The position of relaxation (as $\log f_{\max}$ vs. $1/T$) for amorphous and semicrystalline PET are depicted in an Arrhenius-plot (Fig. 3). In order to include the thermal measurements, Eq. (4) [1,2] was used to transform the cooling rate \dot{T} into a frequency

$$f \approx \dot{T} / 2\pi\delta T. \quad (4)$$

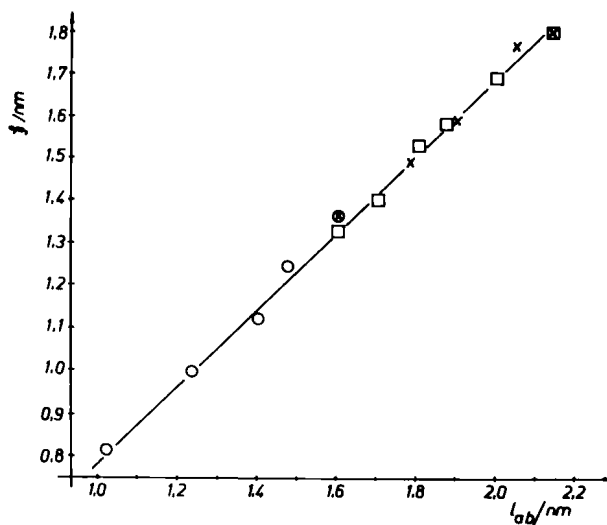


Fig. 2. Characteristic length of the cooperative motion versus thickness of the mobile amorphous layer for specimens of different thermal treatment; x: isothermal; O: stepwise; □: long time crystallization

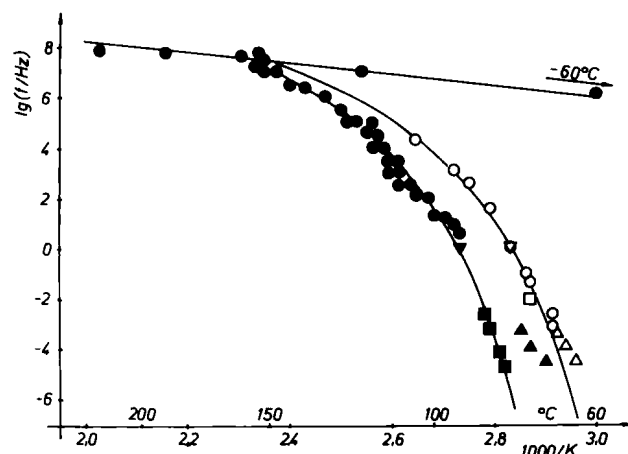


Fig. 3. Relaxation map of amorphous (open symbols) and semicrystalline (solid symbols) PET. O, ●: dielectric; ▽, ▼: torsion pendulum; □, ■: glass temperature (Eq. (4)); △, ▲: enthalpy relaxation. ▽, ■, ▲: one sample crystallized at 120 °C for 16 h; ●: different crystallized samples

Results and discussion

Figure 2 depicts the dependence of the characteristic length (Eqs. (1) and (2)) for the cooperative motion in the semicrystalline samples on the thickness of the mobile amorphous layer (Eq. (3)). In any case the characteristic length is smaller than that determined for an amorphous sample (2.5 nm) and it is smaller than the width of the amorphous layer. It shows that the crystalline structure hinders the cooperative motions connected with the glass transition. Furthermore, it is a hint for the existence of CRR in the nm range as well. This hindrance of the cooperative motions should appear in the temperature-frequency relation for dynamic experiments, too. Since cooperativity of the motions connected with the glass transition increases as frequency decreases, a deviation from the WLF-curve will occur in the range where the hindering starts [10]. Figure 3 shows the WLF and Arrhenius behavior for the amorphous and semicrystalline samples. The secondary relaxation process was measured down to -60°C and its location is the same for both samples. That means that there is no influence of crystalline structure on the local motions connected with this secondary relaxation process. The calculated activation parameters are $E_a = 43 \text{ kJ/mol}$ and the pre-exponential factor $A = 6 \cdot 10^{12} \text{ Hz}$. Near 150°C for both samples, the main relaxation, i.e., the cooperative motion, separates from this local relaxation process.

The WLF equation (Eq. (5)) fits the curves using the parameters as

$$C_2 = 37 \text{ K and } f_0 = 10^{-2} \text{ Hz,}$$

$$C_1 = 14 \quad T_0 = 347 \text{ K (amorphous)}$$

$$C_1 = 14,5 \quad T_0 = 361 \text{ K (semicrystalline)}$$

$$\log(f/f_0) = C_1 \cdot (T - T_0)/(C_2 + T + T_0). \quad (5)$$

A deviation from the WLF-curve can be observed only for the enthalpy relaxation, but not in the frequency region around 10 Hz, where the hindering of the cooperative motions starts. In this region we only observe a drastic increase of DC conductivity so that it is not possible to perform dielectric measurements at lower frequencies. One might imagine that there exists a connection between charge transport and the hindering of the cooperative motions. Unfortunately, we have no experimental proof for this hypothesis at the moment and further investigations would be welcome.

Conclusions

PET proved to be a good model system for investigation of the influence of crystalline structure on the glass transition. On the basis of the fluctuation model of the glass transition proposed by Donth, it is possible to understand the correlation between the characteristic length of cooperative motions connected with the glass transition, and the dimensions of the crystalline structure. It is not clear why no deviation from the WLF-curve was found in the low frequency range for the semicrystalline samples. Probably there exists a small deviation but it is covered by the scatter of the measuring points which is relatively high and hence the fit of the WLF-curve does not reveal all details.

In our opinion these measurements support the picture of cooperatively rearranging regions in the nm range and the possibility to influence these motions by the dimensions of the crystalline structure.

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