Polymer Bulletin 7, 211-216 (1982)

Polymer Bulletin

A Non-Gaussian Statistical Treatment of Semicrystalline Polymers

F. Rietsch and J.P. Cavrot

Laboratoire de Structure et Propriétés de l'Etat Solide, LA 234,
Université des Sciences et Techniques de Lille,
F-59655 Villeneuve d'Ascq cedex, France

Summary

The purpose of this paper is to characterize the molecular parameters of a semicrystalline polymer by means of stress-strain-measurements. At low or moderate draw-ratios, the Gaussian theory of rubberlike elasticity of the amorphous regions allows to calculate the intrinsic birefringence of the amorphous region. At higher draw-ratios the non-Gaussian model makes it possible to define the number of statistical segments for any value of homogeneous draw-ratio, and then to estimate the maximum extensibility of the network chains.

Introduction

Because of its technological importance for the fiber and film manufacturing industry, uniaxial molecular orientation has been the subject of numerous investigations concerning in particular the characterization and measurement of the degree of orientation, in relation with the macroscopic deformation condition (SAMUELS 1974, WARD 1975). The importance of amorphous phase orientation, already recognized in early investigations has emphasized the need for characterization methods liable to distinguish between orientation distribution in both the crystalline and amorphous regions of a polymer. The major part of the present paper will deal with the uni-axial orientation of the amorphous region of the polymer, in order to determine the principal molecular parameters by application of the well defined kinetic theory of rubberlike elasticity in the more accurate non-Gaussian form (particularly for high extensions).

The Gaussian theory of rubber elasticity

The quantitative interpretation of rubber elasticity rests firmly on the use of Gaussian statistics to describe the behaviour of a single chain. The elastic network is then treated as an assembly of chains, with the assumption, with can be justified for Gaussian chains, of affine deformation of the junction points. Each network chain is assumed to consist of several statistical links that can freely rotate about their main chain bonds.

The stress-strain-birefringence relations obtained from the kinetic theory of rubber elasticity in simple extension are given below (TRELOAR 1975).

0170-0839/82/0007/0211/$01.20

$$\sigma = NkT(\lambda p^2 - \lambda p^{-1}) = \frac{\rho RT}{\overline{Mn}}(\lambda p^2 - \lambda p^{-1}) \qquad (1)$$

$$\Delta n = \frac{2\pi}{45}\frac{(\bar{n}^2+2)^2}{\bar{n}} N(\alpha_1 - \alpha_2)(\lambda p^2 - \lambda p^{-1}) \qquad (2)$$

where σ and N are the true stress (force per strained cross-section) and the number of elastic active chain per unit volume, $\overline{Mn}$ denotes the average molecular weight between crosslink points, λp, is the degree of stretch (homogeneous draw-ratio), $\bar{n}$ represents the mean refractive index of the polymer $|(n_1+2n_2)/3|$ and $(\alpha_1-\alpha_2)$ are the polarizability of the random link respectively along the direction of its length and the mean polarizability in the transverse direction.

Equations (1) and (2) together show that streee-optical coefficient $C = \Delta n/\sigma$ is strain-independent, and enables the optical anisotropy of the random link $(\alpha_1-\alpha_2)$ to be calculated.

$$C = \frac{\Delta n}{\sigma} = \frac{2.\pi}{45\ kT}\frac{(\bar{n}^2+2)^2}{\bar{n}}(\alpha_1 - \alpha_2) \qquad (3)$$

Semicrystalline polymers

Each phase of the semicrystalline polymer is assumed to have intrinsic properties and the physical unoriented property will be a result of the relative amount of the two phases present:

$$P_{unoriented} = \beta Pc + (1-\beta)Pa$$

where P is the observed property, β is the degree of crystallinity.

Any observed anisotropic property of the oriented semicrystalline polymer, ΔP oriented, is represented by a function of the properties of each oriented phases :

$$\Delta P\ oriented = \beta Pcfc + (1-\beta)Pafa$$

where fc and fa are the orientation function characterizing the average orientation of the crystalline and amorphous phases, respectively.

The relatively small influence of the degree of crystallinity on the short-time modulus is explained on the basis of the two-phase series model, which assumes linear additivity of the compliances of the amorphous and the crystalline phase (SAMUELS 1974, TAKAYANAGI et all 1966). The influence of the amorphous phase will become predominant if the value of its modulus is much lower than that of the crystalline phase. Consequently, if the polymer sample is held at constant length to prevent shrinkage, a shrinkage force develops. This force reflects the mobility of the segments in the amorphous region. Thus, for a semicrystalline polymer, the shrinkage force per unit amorphous phase becomes :

$$\frac{\sigma}{1-\beta} = \frac{\rho RT}{\overline{Mn}}(\lambda p^2 - \lambda p^{-1}) \qquad (4)$$

By the usual additivity rule expressed here, the additive effect of the anisotropy of each phase is represented by the following equation :

$$\Delta n = \beta fc\Delta \overset{o}{c} + (1-\beta)fa\Delta \overset{o}{a} + \Delta nf \;= \Delta a + \Delta c$$

where Δnf is the (often assumed negligible) contribution of form birefringence, $\Delta \overset{o}{c}$ and $\Delta \overset{o}{a}$ are the intrinsic birefringences per unit volume of the crystalline region and the amorphous region respectively.

The birefringence of the amorphous phase is the appropriate parameter to be used in eq. 2, if this contribution, defined per unit volume of the two-phase material, is reduced to the contribution per unit amorphous volume, i.e., $\Delta a/(1-\beta)$.

The Gaussian representation of $\sigma/(1-\beta)$ and $\Delta a/(1-\beta)$ versus $(\lambda p^2-\lambda p^{-1})$, and $\Delta a/(1-\beta)$ versus $\sigma/(1-\beta)$, according eqs (1), (2), (3), enables the optical anisotropy of the random link $(\alpha_1-\alpha_2)$, the number of repeat units per network chain, and then the number of random links to be determined if the optical anisotropy of the monomer unit can be calculated. This analysis is made with the assumption of low or moderate degree of elongation, i.e., that the end-to-end distance is very much less than the fully extended length of the chain. At high extensions the Gaussian approximations are not valid.

Non-Gaussian chain statistic of oriented semicrystalline polymer

The non-Gaussian statistical treatment takes into account the finite extensibility of the chains, and thus of the network; the maximum extension being proportional to the square root of the number of n of random links in an amorphous chain between crosslinks.

In the non-Gaussian strain, the formula derived by JAMES and GUTH (1943) appears to be more appropriate :

$$\sigma = \frac{\rho RT}{\overline{Mn}}\,\frac{n^{1/2}\lambda p}{3}\left|L^{-1}\left(\frac{\lambda p}{n^{1/2}}\right) - \lambda^{-3/2}L^{-1}\left(\frac{1}{\lambda_p^{1/2}n^{1/2}}\right)\right| \qquad (5)$$

where L^{-1} is the inverse Langevin function of the fractional elongation $\lambda p/\lambda p,max$.

For high extended chains, that is to say for $\lambda p \to \lambda p,max = n^{1/2}$, the ultimate extensibility of the network corresponds to a strong upward curvature $(\sigma \to \infty)$.

The value of $\overline{Mn}$ automatically determines the number n of equivalent random links :

$$\overline{Mn} = KnMo$$

where K is the number of monomer units of molecular weight Mo,per random link, define in the region of small or moderate strain (eqs. (1) and (2)).

Thus : $$\frac{\sigma}{1-\beta} = \frac{\rho RT}{KMo}\,\frac{n^{-1/2}\lambda p}{3}\left|L^{-1}\left(\frac{\lambda p}{n^{1/2}}\right) - \lambda^{-3/2}\,L^{-1}\left(\frac{1}{\lambda p^{1/2}n^{1/2}}\right)\right| \qquad (6)$$

The shrinkage stress-extension relation is thus determined by one parameter, n, which is specific to the non-Gaussian theory and controls the behaviour in the high-strain region and the ultimate extensibility of the network.

For a more exact form of equation (2) relating birefringence to higher strain, the TRELOAR (1954) modification of the KUHN and GRÜN result appears as show :

$$\frac{\Delta a}{1-\beta} = \Delta \overset{o}{a} F$$

where $$\Delta \overset{o}{a} = \Delta Po \, \frac{2\pi}{9} \, \frac{(\bar{n}^2+2)^2}{\bar{n}} \qquad (7)$$

and $\Delta Po = Nn(\alpha_1-\alpha_2)$ is equal to the maximum difference in polarizability of the material per unit volume.

F is the optical orientation function. TRELOAR's(1954) expression for the orientation function is defined by the corresponding series expression :

$$F = \frac{1}{5n}(\lambda p^2-\lambda p^{-1}) + \frac{2}{175n^2}(6\lambda p^4+2\lambda p-\frac{8}{\lambda p^2}) + \frac{6}{875n^3}(10\lambda p^6+6\lambda p^3-\frac{16}{\lambda p^3})+\ldots \qquad (8)$$

The non negligible contribution of the higher-order terms in this expression, involves introduction of a closer approximation.

The TRELOAR (1954) modification appears more satisfactory in the followed expression which differs from equation (8) by the use of a finite number of three terms which has been found to be numerically accurate to within 1 per cent over the whole range of the network strain :

$$F = \frac{1}{5n}(\lambda p^2-\lambda p^{-1}) + \frac{1}{150n^2}(6\lambda p^4+2\lambda p-8/\lambda p^2) + \frac{1}{350n^3}(10\lambda p^6+6\lambda p^3-16/\lambda p^3) \qquad (9)$$

However, if such an analysis is extended to the maximum extensibility of the network chains, it must necessary obey of the limit condition : $F \to 1$ for $\lambda p \to \lambda p,max = n^{1/2}$

It appears from equation (9) that :

$$\text{Lim.}F_{\lambda p \to n^{1/2}} = \frac{282}{1050} - \frac{178}{1050}\, n^{-3/2} < 0.268$$

which leads to a maximum birefringence $\Delta n\text{max} = \Delta \overset{o}{a} F < 0.27\, \Delta \overset{o}{a}$.

This theoretical limiting value is much less than the values of a lot of experimental results of semicrystalline polymers. Consequently the Treloar's relation is clearly not appropriate to use for such an optical analysis and it is necessary to introduce other numerical values for the equation (9):

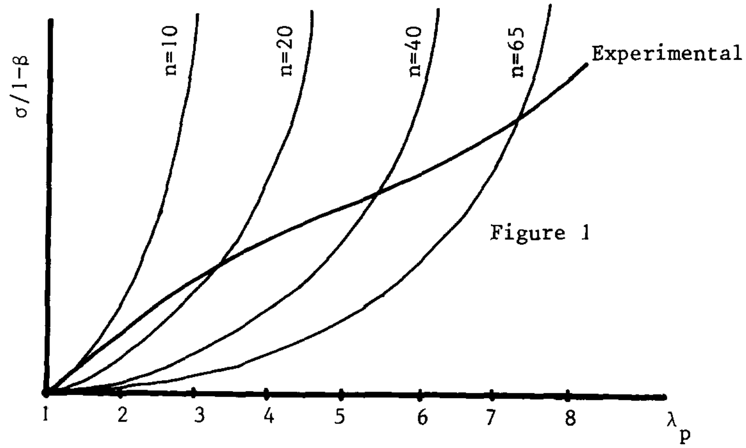
$$F = \frac{1}{5n}(\lambda p^2-\lambda p^{-1}) + \frac{1}{10n^2}(6\lambda p^4+2\lambda p-8/\lambda p^2) + \frac{1}{50n^3}(10\lambda p^6+6\lambda p^3-16/\lambda p^3) \qquad (10)$$

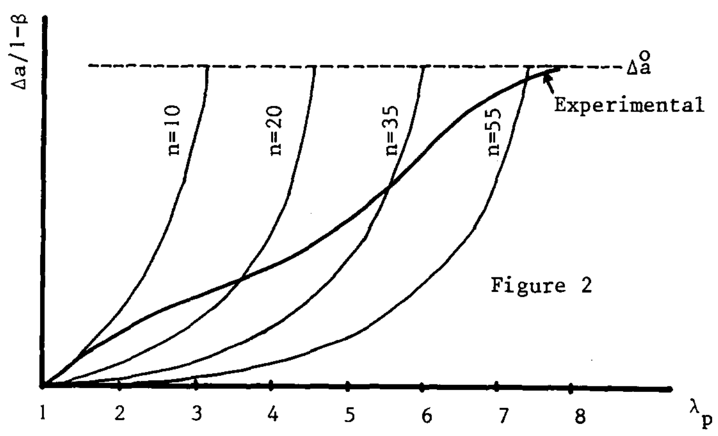
with : $\text{Lim } F_{\lambda p \to n^{1/2}} = 1 + \frac{3}{25}\, n^{-3/2} - \frac{4}{5}\, n^{-3} \approx 1.$

All the features considered above suggest that :

i) for drawing of semicrystalline specimens at low or moderate draw ratios, the application of Gaussian theory of rubberlike elasticity of the amorphous regions, allowed to characterize the molecular parameters, particularly, the number of active network chains per unit volume and the number of statistical segments in an amorphous chain between crosslink. According to equation (7), the intrinsic birefringence $\Delta \overset{o}{a}$ per unit volume of the amorphous region can be calculated.

ii) at higher draw ratios, the non-Gaussian model makes it possible to define the number of statistical segment for any given value of λp. The stress-strain (eq. 6) and birefringence-strain (eq. 10) theoretical datas, superimposed on experimental values must fit the same value of n, for a given draw ratio λp (Figures 1 and 2). The increase of n involves necessarily a certain amount of slip between physical entanglements until the limiting homogeneous draw ratio. This results in an increase in the length of each network chain (CAVROT et al, ENGELAERE et al., in press).





A plot of equations (6) and 10), for various number of statistical segments, n, superimposed on experimental values

iii) for a given value of the number of statistical segments, n, the maximum extensibility can be estimated by the relation : $\lambda p,max \simeq n^{1/2}$. It is thus interesting to characterize λp,max by a two stage drawing in which the first stage induces a specific homogeneous deformation (λp) and consequently the number of statistical segments (Figures 1 and 2). The second stage refers to a cold drawing at constant value of network chains (and also n) which leads to the maximum extensibility, λp,max. Such an analysis has been extended to oriented semicrystalline poly(ethylene terephthalate), where the presence of chain entanglements and crystallines results in an effective molecular network structure.

References

CAVROT, J.P., ENGELAERE, J.C., and RIETSCH, F., : J. Polym. Sci. in press
ENGELAERE, J.C., CAVROT, J.P., and RIETSCH, F., : Polymer in press
JAMES, H.M., and GUTH, E., : J. Chem. Phys. 11, 455 (1943)
SAMUELS, R.J., : "Structural Polymer Properties, New-York : John Wiley & Sons (1974)
TAKAYANAGI, M., IMADA, K., and KAJIYAHA, J., : J. Polym. Sci. C 15, 263 (1966)
TRELOAR, L.R.G., : "The Physics of Rubber Elasticity" Oxford University Press, London (1975)
TRELOAR, L.R.G., : Trans. Faraday Soc., 50, 881 (1954)
WARD, J.M., : "Structure and Properties of Oriented Polymers", Applied Science Publishers LTD, London (1975)

Received April 5, accepted April 7, 1982