Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Novel Orientation Techniques for the Preparation of High-Performance Materials from Semiflexible Polymers

J. E. Mark[a]
[a] Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio, USA

To cite this Article Mark, J. E.(1996) 'Novel Orientation Techniques for the Preparation of High-Performance Materials from Semiflexible Polymers', Journal of Macromolecular Science, Part A, 33: 12, 1783 — 1790
To link to this Article: DOI: 10.1080/10601329608011004
URL: http://dx.doi.org/10.1080/10601329608011004

J.M.S.—PURE APPL. CHEM., A33(12), pp. 1783–1790 (1996)

NOVEL ORIENTATION TECHNIQUES FOR THE PREPARATION OF HIGH-PERFORMANCE MATERIALS FROM SEMIFLEXIBLE POLYMERS

J. E. MARK

Department of Chemistry and the Polymer Research Center
The University of Cincinnati
Cincinnati, Ohio 45221-0172, USA

ABSTRACT

A technique is described for postponing the formation of anisotropic domains in semiflexible polymers so as to better orient them along a common direction. A theory has been developed to provide a foundation for this approach and guidance on carrying it out experimentally, and is described in outline form. The primary advantage of this processing route is the improved mechanical properties accompanying the increased orientation. This is illustrated by increases in moduli and ultimate properties of films of some cellulosics, polyisocyanates, and the protein collagen in the form of gelatin.

INTRODUCTION

The materials investigated were prepared by the following sequence of steps: 1) identifying polymer chains of sufficient stiffness to give liquid-crystalline, anisotropic phases (either homopolymers or block copolymers consisting of stiff and flexible sequences); 2) crosslinking the chains, in the presence of solvent, thus conferring sufficient solidity for the polymer to remain in a deformed state for any length of time, with the solvent preventing the premature ordering of the stiff chains or sequences; 3) deforming the swollen network uniaxially or biaxially to induce segmental orientation; and 4) removing the solvent, at constant length or at constant force, possibly causing a first-order transition to a *single-phase*, homogeneous, and

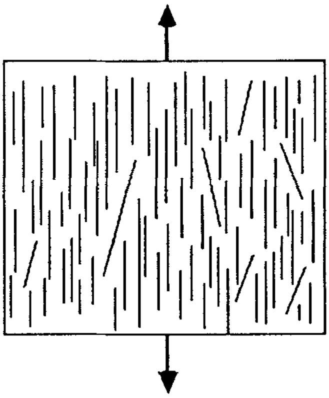


FIG. 1. Alignment of anisotropic domains possibly obtainable by drying under uniaxial orientation [5].

highly-ordered material [1-3]. The expected effects for the case of drying under uniaxial extension are shown in Fig. 1, and those under biaxial extension in Fig. 2.

Films prepared using this technique have been characterized by polarizing microscopy, birefringence, and stress-strain measurements in uniaxial and biaxial extension to rupture. Some of the polymers that are processible by these techniques have the additional advantage of being biodegradable. The utility of these techniques is illustrated using recent results obtained on cellulosic esters [8, 9], cellulose ethers [8, 9, 11], polyisocyanates [12], and gelatin [13].

THEORY

The theoretical aspects of these methods have been described in detail in a number of original papers and reviews [1-7, 10] and are therefore given in only outline form in this report.

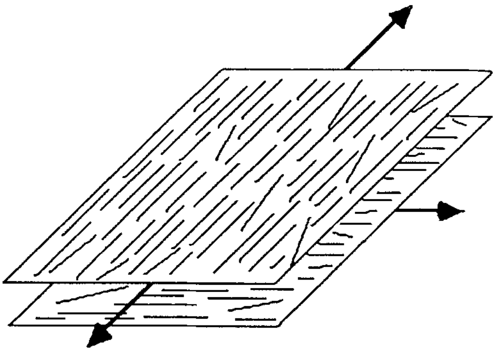


FIG. 2. Alignment of anisotropic domains possibly obtainable by drying under biaxial orientation [5].

It has been known that real polymer chains might be described in terms of freely jointed chains with a properly defined Kuhn segment length. The length-to-width ratio x for such a segment is usually around 3, but would be considerably larger for the semiflexible chains of interest in these studies. A successful method for the calculation of the combinatory ("steric") factor and the orientational factor of the configuration partition function for a system of freely jointed rods has been proposed by Flory and coworkers. This lattice theory has been used to enumerate the combinatory factor, although the orientation of rods is allowed to be continuous. This is done by considering a rod oriented in the kth direction (at angles θ_k, ϕ_k). According to theory, it can be represented by y_k sequences of x/y_k segments, where x is the axial ratio already mentioned and X is the direction of stretching.

This basic theory by Flory has now been extended to such systems in a state of deformation. The result of greatest importance centers on the orientational order parameter

$$S = \langle P_2(\cos\theta)\rangle = \frac{3}{2}\langle\cos^2\theta\rangle - \frac{1}{2} \tag{1}$$

where θ is the angle between the rod and the X axis. For uniaxial deformation, this parameter is given by

$$S \cong \frac{1}{5m}(\lambda^2 - 1/\lambda v_2)\left(1 + \frac{5xv_2}{64\left[1 - \left(\frac{x}{x_c}\right)v_2\right]}\right) \tag{2}$$

where m is the number of Kuhn segments, λ is the elongation, and v_2 is the volume fraction of polymer in the swollen, crosslinked network. The quantity $x_c = 3/[4/\pi - 1] \cong 10.98$ is the critical or "bifurcation" value of x in the Flory–Ronca model described above. When the ratio x/x_c becomes significantly large, then the factor in square brackets becomes important and phase separation occurs.

The theory has also been applied to thermotropic systems by elaborating the mean-field approach proposed by Flory and Ronca. The attractive dispersion forces related to the anisotropy of the polarizability tensors for chain segments contribute to the mean field, which gives an additional contribution to the alignment of polymer segments in the direction of stretch. The result is now

$$S = \frac{1}{5m}\left(\lambda^2 - \frac{1}{\lambda v_2}\right)\left(1 + \frac{5xv_2}{64\left[1 - \left(\frac{x}{x_c}\right)v_2\right]}\right) \left\{1 - \frac{1}{5}\tilde{T}^{-1}\left[1 - \frac{5xv_2}{64\left(1 - \frac{x}{x_c}v_2\right)}\right]\right\}^{-1} \tag{3}$$

where $\tilde{T}$ is the reduced temperature. The quantity in the braces represents the mean-field correction for the orientation function S. With decreasing temperature, S increases in comparison with the athermal case (for which $\tilde{T}^{-1} = 0$). Similarly, knowledge of the free energy enables calculation of the stress and chemical potentials.

The above analysis yields plots of segmental orientation S against axial ratio x, composition v_2, and extent of deformation λ. The information thus obtained provides guidance on how to control the phase separation so that the entire sample becomes anisotropic, with all of the chains in a given layer very nearly aligned in the same direction.

The phase separations exhibited by undeformed semiflexible and rigid-rod polymers are now well understood in terms of the thermodynamics and statistical mechanical theories of the liquid-crystalline state, as is documented elsewhere [5]. These extensions of the basic theories to polymeric systems in the *deformed* state are also showing considerable promise.

EXPERIMENTAL RESULTS

Cellulose Acetate and Hydroxypropylcellulose

Cellulose ester cellulose acetate [8, 9] and cellulose ether hydroxypropyl cellulose [8, 9, 11] have been studied using this novel orientation technique. Well-ordered liquid-crystalline states have been observed under a variety of conditions for these cellulosics. Some typical results obtained on a film sample of hydroxypropyl cellulose (HPC) having a molecular weight between crosslinks M_c of 20.3×10^3 $g \cdot mol^{-1}$ are shown in Fig. 3. Drying the sample while under uniaxial elongation is seen to greatly increase its modulus and ultimate strength in the direction parallel to the extension direction maintained during drying. The system is, of course, anisotropic, and this is evidenced by the decrease in some of the mechanical properties in the perpendicular direction.

Figure 4 shows the relationship between the tensile modulus and tensile strength, and the birefringence of the oriented films. The relationship is seen to be

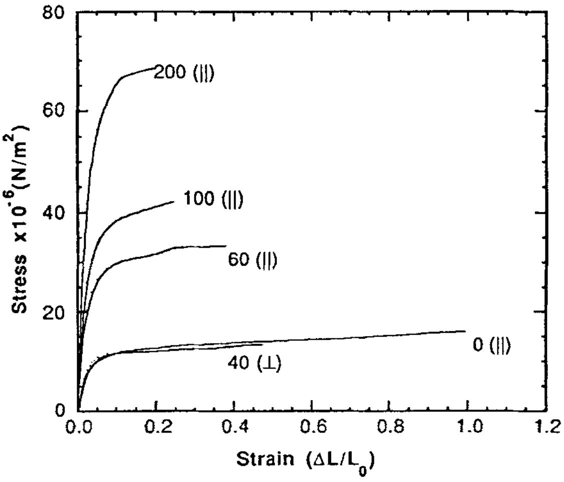


FIG. 3. Stress-strain behavior of oriented films prepared from HPC [9]. Labels on the curves are the values of the extension ratio maintained during drying under uniaxial elongation. The mechanical testing was carried out either parallel (||) or perpendicular (⊥) to the orientation axis of the sample.

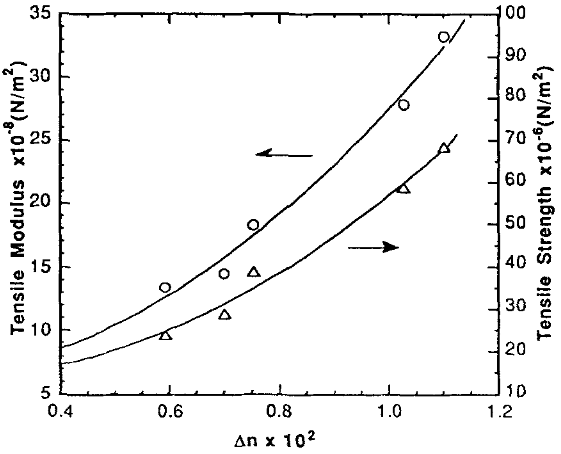
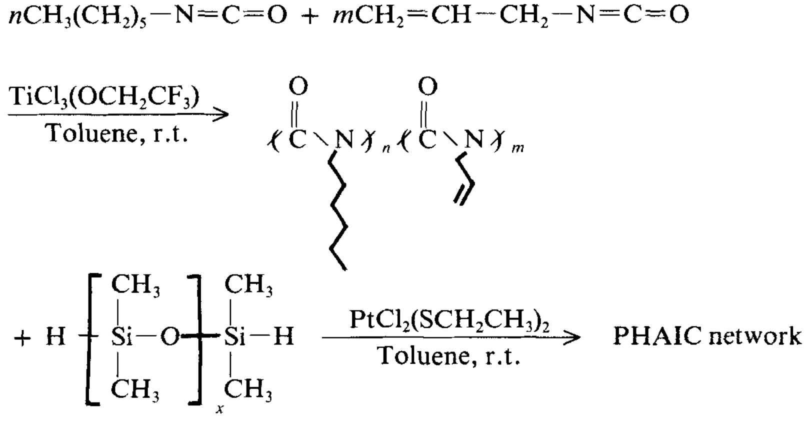


FIG. 4. Correlation between the tensile modulus (○) and tensile strength (△) and the birefringence of oriented films prepared from HPC ($M_c = 20.3 \times 10^3$ g·mol^{-1}) [9].

nonlinear, with the modulus increasing more rapidly with an increase in birefringence at higher degrees of orientation.

Poly(Isocyanates)

These polymers are also known to form liquid-crystalline phases, and films prepared from one of them have been treated by these orientation techniques [12]. In this case the polymer was obtained by copolymerizing *n*-hexyl isocyanate with allyl isocyanate to obtain samples of poly(hexylallyl isocyanate) (PHAIC). The allyl groups were included to provide unsaturated sites for introducing the required crosslinks for the desired network structure. The crosslinking was carried out either free-radically by thermolysis of an organic peroxide or by direct addition to the double bonds in a hydrosilation reaction. The preparation of the copolymer and its crosslinking through the hydrosilation reaction are illustrated in Scheme 1 [12].



SCHEME 1.

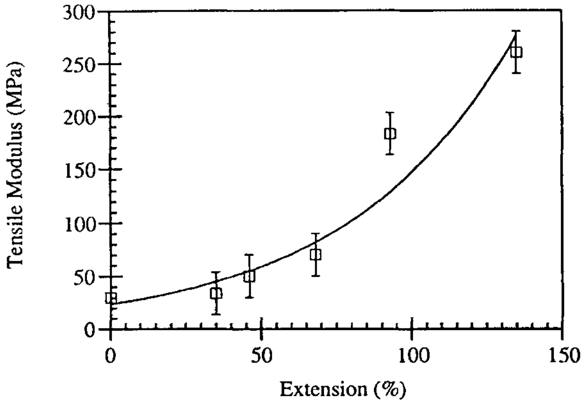


FIG. 5. Tensile modulus as a function of the extension ratio during drying for oriented films of PHAIC [12].

Some of the increases in modulus obtained by drying the samples in the uniaxially extended state are shown in Fig. 5 [12].

Gelatin

This material is composed of the protein collagen, which is a naturally-occurring material and thus has the considerable advantage of biodegradability. Films prepared from samples of it have been given this orientation treatment, both in uniaxial extension and in biaxial extension (through inflation of a sheet of the material). Values of the tensile strength and modulus obtained at different values of the uniaxial extension ratio during drying are shown in Fig. 6 [13]. Again, very large increases are seen to result from the uniaxial treatment.

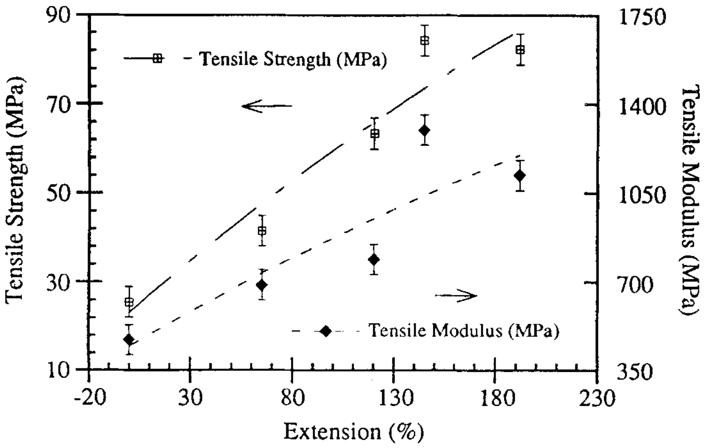


FIG. 6. Tensile strength and modulus vs extension ratio at drying for gelatin networks [13]. Swelling solvent: H_2O.

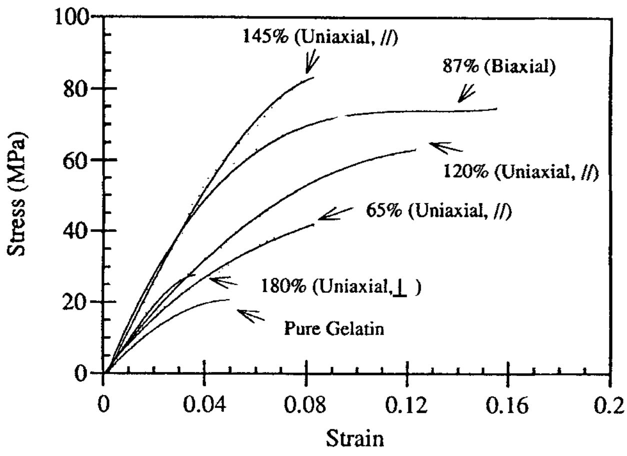


FIG. 7. Stress–strain curves for uniaxially and biaxially oriented gelatin films [13]. Swelling solvent: H_2O.

Figure 7 shows the results obtained on films dried while in either the uniaxially oriented or biaxially oriented state [13]. The latter gives the most impressive results in that the film is isotropic within its plane and is seen to have a better balance of properties than the films treated by the simpler uniaxial-orientation technique.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the financial support provided by the Procter & Gamble Company through its University Exploratory Research Program and by the National Science Foundation through Grant DMR 94-22223 (Polymers Program, Division of Materials Research), and the fellowship support provided by the Raychem Corporation.

REFERENCES

[1] B. Erman, I. Bahar, A. Kloczkowski, and J. E. Mark, *Macromolecules, 23*, 5335 (1990).
[2] I. Bahar, B. Erman, A. Kloczkowski, and J. E. Mark, *Ibid., 23*, 5341 (1990).
[3] B. Erman, T. Haliloglu, I. Bahar, and J. E. Mark, *Ibid., 24*, 901 (1991).
[4] B. Erman, I. Bahar, A. Kloczkowski, and J. E. Mark, in *Elastomeric Polymer Networks* (J. E. Mark and B. Erman, Eds.), Prentice-Hall, Englewood Cliffs, NJ, 1991.
[5] B. Erman, I. Bahar, Y. Yang, A. Kloczkowski, and J. E. Mark, in *Polymer Solutions, Blends, and Interfaces* (I. Noda and D. N. Rubingh, Eds.), Elsevier, Amsterdam, 1992.
[6] A. Kloczkowski, J. E. Mark, B. Erman, and I. Bahar, in *Polymer Solutions, Blends, and Interfaces* (I. Noda and D. N. Rubingh, Eds.), Elsevier, Amsterdam, 1992.

[7] B. Erman, I. Bahar, A. Kloczkowski, and J. E. Mark, in *Synthesis, Characterization, and Theory of Polymeric Networks and Gels* (S. M. Aharoni, Ed.), Plenum, New York, NY, 1992.

[8] Y. Yang, A. Kloczkowski, J. E. Mark, B. Erman, and I. Bahar, *Colloid Polym. Sci., 272*, 284 (1994).

[9] J. E. Mark, Y. Yang, A. Kloczkowski, B. Erman, and I. Bahar, *Ibid., 272*, 393 (1994).

[10] Y. Yang, A. Kloczkowski, J. E. Mark, B. Erman, and I. Bahar, *Macromolecules, 28*, 4920 (1995).

[11] Y. Yang, A. Kloczkowski, J. E. Mark, B. Erman, and I. Bahar, *Ibid., 28*, 4927 (1995).

[12] W. Zhao, H. Zimmer, and J. E. Mark, *Prepr., Div. Polym. Mater. Sci. Eng., 71*, 399 (1994).

[13] W. Zhao, A. Kloczkowski, J. E. Mark, B. Erman, and I. Bahar, *J. Macromol. Sci.—Pure Appl. Chem., A33*, 525 (1996).