# NOTE

## Low-Frequency Raman Evidence for Straight Chain Segments in an UHMW Polyethylene Gel

## KATHERINE KOBER,<sup>1</sup> S. KHIZHNYAK,<sup>2</sup> P. PACHOMOV,<sup>2</sup> A. TSHMEL<sup>1</sup>

<sup>1</sup> Fracture Physics Department, Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia

<sup>2</sup> Tver State University, 170002 Tver, Russia

### INTRODUCTION

The gel-formation method is one of the most promising routes for obtaining high-performance materials, such as ultrahigh-molecular-weight (UHMW) polyethylene (PE) fibers of a tensile strength up to 5-7 GPa and a Young's modulus about 200 GPa.<sup>1</sup> High strength of the gel-derived products is achieved by drawing a preform under temperature-force conditions thoroughly accomodated to properties of a given polymer sample. The first steps of gel-to-oriented-structure transformation are of great importance because at the initial stage of the gel formation, a molecule of the flexible-chain semicrystalline polymer takes the form of a statistic ball. Nucleation of regular sites (including sequences of trans-isomers) in the wet gel would provide optimal conditions for further development of the oriented structure. Therefore, if one could succeed to produce in a gel some quantity of straight chain segments (SCS), a presence of these units would stimulate a more rapid evolution of the ordered regions at subsequent drawing of the sample, with probable gain in strength.

In polyvinyl alcohol gels, incipient crystallites of 4-7 nm in diameter were observed with the help of the wide-angle neutron scattering.<sup>2</sup> A presence of *trans*-sequences (i.e., straight-chain segments) in the PE gels was concluded from the infrared (IR) spectroscopic study,<sup>3</sup> where the intensity of the doublet at 720 and 731 cm<sup>-1</sup>, representing the crystalline regions in PE, had been measured.

In this work, the structure of UHMW PE macromolecules in gel and block-oriented states was studied using the longitudinal acoustic modes (LAM) analysis. The Raman-active LAM are localized on the straight chain segments of polymeric molecules, and the LAM

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band contour brings information on the SCS distribution in a sample. The length of the ordered sequence (L), planar zigzag in the case of PE, and the LAM frequency,  $\nu_L$ , are related as

$$\nu_L = (2cL)^{-1} (E/\delta)^{1/2} \tag{1}$$

where *c* is the speed of light,  $\delta$  is the density, and *E* = 370 GPa<sup>4</sup> is the Young's modulus in the chain direction.

One can find also the SCS length distribution function F(L) using the following relation where the Boltzmann factor of the energetic levels population is taken into account, as follows:

$$F(L) \sim [1 - \exp(-hc \nu_L/kT)] \nu_L^2 I_L$$
 (2)

Here,  $I_L$  is the scattering intensity at the frequency  $\nu_L$ ; T is the temperature.

#### **EXPERIMENTAL**

#### Samples

The experiments were performed on a UHMW PE with molecular weight of  $2.4*10^6$ . The polymer solution in a decaline was prepared in a cylindrical flask with a helical stirrer. The suspension of the polymer powder in solvent was slowly heated from 20 to 140°C with intensive stirring. The polymer particles exhibited swelling at 90 to 110°C, then dissolved at 110 to 115°C. The 2% UHMW PE solution at 140°C was poured into a glass Petri plate. The rapid cooling resulted in gel-film formation.

#### Equipment

The spectra were excited by the line at 632.8 nm of a 60-mW He–Ne laser. The light scattered at

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90° was registered by a Raman triple monochromator Spex Model Ramalog 5 equipped with a cooled RCA C31034 electric multiplier and a photon counting system.

#### **RESULTS AND DISCUSSION**

In Figure 1, the low-frequency spectra of the gel and drawn samples are shown. A wide band stretching from 20 to 180 cm<sup>-1</sup> with a maximum near 100 cm<sup>-1</sup> is seen in the spectrum of a gel. A band at 30 cm<sup>-1</sup> in the spectrum of weakly oriented sample (the draw ratio  $\lambda = 3$ ) exhibits an apparent difference in the bandwidth as compared to the gel spectrum. Further drawing (to  $\lambda = 39$ ) results in the band shift to 18 cm<sup>-1</sup> becoming the band's contour of a complicated shape. The band maximum positions gave us, according to eq. (1), the average SCS lengths in the samples, which appeared to be 3 nm in the gel, 10 nm at  $\lambda = 3$ , and 17 nm at  $\lambda = 39$ .

The whole LAM band contour reflects, in the end, the SCS length distribution. However, due to a reciprocal correspondence between  $\nu_L$  and L, the Raman band contour is far from being adequate to the true F(L) profile. In Figure 2, the calculated SCS length distribution functions for initial and drawn samples are shown. One can see that, in spite of the great



**Figure 1** Low-frequency Raman spectra of a PE gel and drawn fibers in the range of LAM bands.



**Figure 2** SCS length distribution profiles calculated from the Raman spectra shown in Figure 1.

narrowing of the LAM band, the F(L) width increases as sample drawing.

The maximum of the function F(L) is close to the average size of the crystalline regions in polymers.<sup>4</sup> At  $\lambda = 39$ , in addition to SCS responding the domal part of the distribution profile, a certain amount of straight segments of more than 40 nm in length appear. This is more than two times longer than the average crystal size (17 nm) responding to the main maximum. We tentatively ascribe the long-length wing of the F(L) profile of the most stretched fibers to a contribution of taut tie chains involving two crystals separated by an amorphous layer.

#### CONCLUSION

The low-frequency Raman (LAM) study evidenced a presence of a certain amount of straight chain segments in a gel prepared from weakly concentrated UHMW PE solution. Average length of the SCS was about 3 nm. In the fibers drawn from the gel-derived preforms, the appearance of the taut tie chains stretching over two crystals and an amorphous layer situated between them was observed.

#### REFERENCES

- Marikhin, V. A.; Myasnikova, L. P. in Oriented Polymeric Materials; Fakirov, S.; ed. Hufhis & Wept: Heidelberg, Germany, 1996.
- 2. Kanaya, T. KEK Prog Rep 1993, 92, 136.
- Pakhomov, P. M.; Larionova, N. V.; Alekseev, V. G. Polym Sci B 1995, 37, 241.
- 4. Peterlin, A. J Appl Phys 1979, 50, 838.