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Highly Oriented, Low-Modulus Materials from Liquid Crystalline Polymers: The Ultimate Penalty for Solubilizing Alkyl Side Chains

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ABSTRACT: This paper describes a brief study of the effect of solubilizing, flexible alkyl side groups on the mechanical properties of highly oriented rigid-chain polymers. Experimental results obtained with poly(hexyl isocyanate) show that the side chains have a ruinous effect on the tensile modulus and stress at break. Simple calculations reveal that the attachment of *n*-hexyl side chains reduces the theoretical axial modulus of rigid-chain polyamides by about 90%.

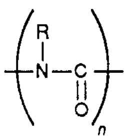
Introduction

The inventions, in the late 1960s, of the synthesis of rigid-chain aramids and the processing of these relatively intractable materials into high-strength, modulus fibers by Kwolek[1] and Blades[2] have sparked a major research endeavor to develop other, potentially strong, rigid-rod polymers. In particular, efforts have been directed to produce more tractable polymers that, unlike aramids, can be processed from the melt or from common solvents. A most popular route has been reduction of the stiffness of the polymer backbone by, for instance, incorporating kinks, crankshafts, or flexible main-chain spacers, which lowers the melting temperature of the polymers (for an outstanding review see ref 3). As a result, a vast variety of processable thermotropic polyesters have emerged. Unfortunately, but not surprisingly, the decreased chain stiffness generally resulted in lower modulus materials.[3] More recently, improved processability has been sought by attaching flexible side chains, such as *n*-alkyl groups, to rigid main-chain polymers.[4–6] It is of interest to point out that this technique has been utilized also to increase the processability of conjugated, electrically conductive polymers, notably of polythiophenes.[7–9]

It is well established that the mechanical properties of oriented polymers of finite chain length are dominated by secondary interactions, viz. van der Waals, polar, hydrogen, π–π bonds, etc. It would seem, therefore, that improvement of the processability of rigid-chain molecules through use of alkyl side chains, which interact through very weak van der Waals bonds, would come only at the expense of the mechanical properties.

In this note we re-emphasize that solubilizing alkyl side groups attached to rigid polymer backbones may indeed have a detrimental effect on the mechanical properties (see also earlier work of Aharoni on polyisocyanates[10] and Young et al. on substituted poly(diacetylenes)[11]. We selected poly(*n*-hexyl isocyanate) (PHIC) as a model species. This polymer has a helical character,[12] and the rigid macromolecular backbone is surrounded by a sheath of the solubilizing alkyl side chains. Consequently, the secondary bonds between the macromolecules are formed only through interaction of the side chains, revealing most clearly their effect on the mechanical properties. This is in contrast to previous studies on more planar side-chain derivatives of for instance poly(diacetylene),[11] for which complicating, anisotropic secondary bonds effects and remnants of main-chain interactions have to be taken into account. Additional advantages of the choice of PHIC are its well-documented lyotropic behavior, simple synthesis, and good solubility in many common solvents.[12–18]

PHIC is a polymer of the type



$$\left(-\overset{\displaystyle R}{\overset{|}{N}}-\underset{\underset{\displaystyle O}{\|}}{C}-\right)_n$$

with R = *n*-hexyl. This polymer, of molecular weight of 65×10^3, is reported to form lyotropic phases in various solvents at concentrations exceeding 35% v/v.[13] In this work ultraoriented monofilaments were prepared of this model polymer and their mechanical properties were measured and contrasted against those of high-strength, modulus poly(*p*-phenylene terephthalamide) (PPTA) fibers.

Experimental Section

Poly(*n*-hexyl isocyanate) was synthesized[19] by ionic polymerization of 7 mL of freshly distilled *n*-hexyl isocyanate (made from heptanoyl chloride and sodium azide by means of a Curtius reaction[16,18,20]) in a 30-mL dimethylformamide/toluene (1:3) mixture (dried over KOH and $MgSO_4$), at −78 °C, under nitrogen. The catalyst, 0.1 mL of sodium cyanide solution (0.3 wt % in DMF), was slowly added (in 3 min); subsequently the solution was stirred for 30 min, at −78 °C. The reaction was terminated by adding 50 mL of cold methanol. The precipitated polymer was subsequently filtered, washed with methanol, reprecipitated from toluene, and dried. The viscosity-averaged molecular weight, M_v, of the sample was estimated from the intrinsic viscosity, $[\eta]$, in chloroform at 25 °C according to the relationship:[21] $[\eta] = 3.74 \times 10^{-5} M_v^{0.99}$.

One set of fibers was prepared by dry-spinning, at room temperature, 5–50% w/v solutions of PHIC in chloroform at an extrusion rate of 0.5 m/min (spinneret diameter 0.5 mm). The as-spun fibers were drawn over a hot plate at 190 °C to their maximum draw ratio. In agreement with previous findings,[10,21] the dried filaments displayed a low maximum draw ratio resulting in modest orientation only.

A second series of (highly oriented) PHIC monofilaments was produced at room temperature by pulltrusion of lyotropic solutions of 50% w/v PHIC in chloroform (rate = 10–15 cm/s).

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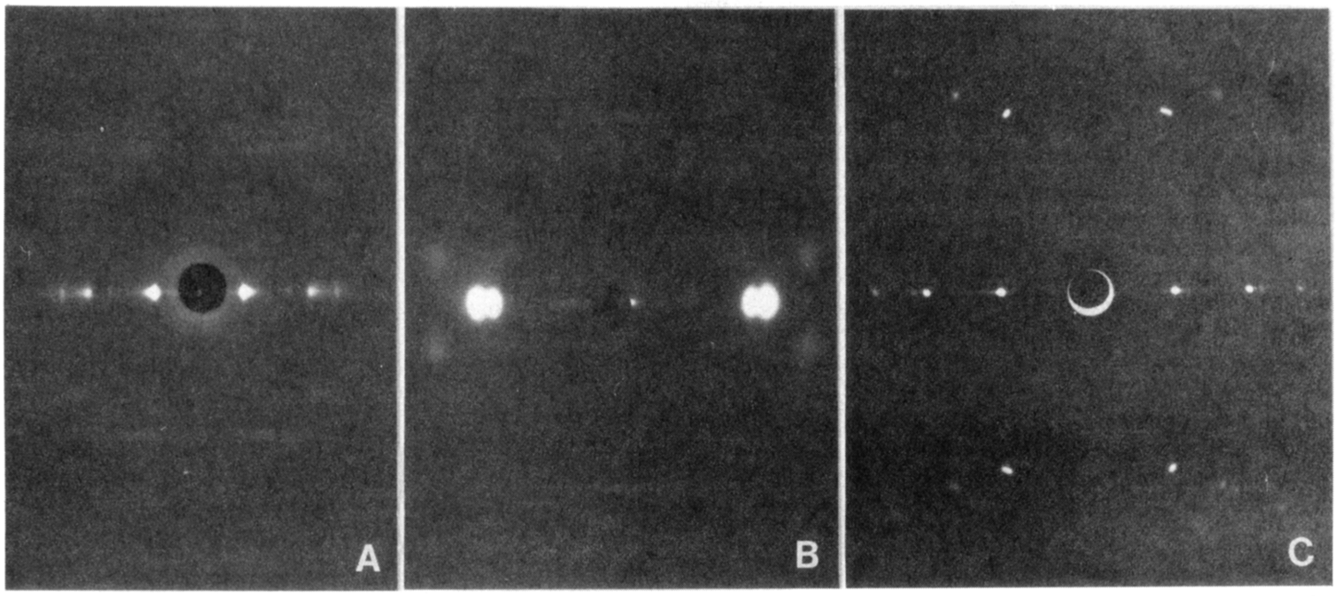

Figure 1. Wide-angle X-ray pattern of pulltruded PHIC fibers (A), PPTA fibers (B, Kevlar 49), and ultra-oriented PE fibers (C). Fiber axis is vertical; the camera length was not constant for each pattern.

Tensile properties of the dried, dense fibers were measured at room temperature with an Instron tensile tester (Model 1122), at a cross-head speed of 10 mm/min. The gauge length of the specimen was 15 mm. The cross-sectional areas of the fibers were determined by using a Nikon microphot-FX microscope. The tensile strength at break (σ), the Young's modulus (E), and the elongation at break (ϵ) of each filament were measured and reported as the averages of at least five measurements.

Wide-angle X-ray scattering (WAXS) experiments were carried out on PHIC single filaments with a Philips PW 1729 X-ray generator operated at 30 kV and 40 mA.

Results and Discussion

PHIC fibers were dry-spun from chloroform solutions of different concentrations ranging from 5 to 50% w/v polymer. Extrusion of solutions of higher concentrations yielded highly irregular and inhomogeneous fibers. The as-spun fibers were hot drawn to their maximum draw ratio of ~3. The diameters of the drawn fibers were 100–400 μm. Independent of the initial concentration the tenacities of the fibers were in the range from 25 to 40 MPa and Young's moduli were 1.0–1.3 GPa. WAXS experiments and polarized optical microscopy revealed only little orientation and alignment of the polymer chains. Surprisingly, fibers obtained from a 50% w/v solution of PHIC in chloroform, which was lytropic, did not exhibit significantly improved chain alignment and mechanical properties over those derived from less concentrated, isotropic solutions. We are inclined to attribute this result to the occurrence of flow irregularities during extrusion of the long-chain, lyotropic phase.

Highly oriented monofilaments were readily obtained, however, by *pulltrusion* of the lyotropic PHIC solutions. The fibers (of 40-μm diameter) were highly birefringent and showed near perfect orientation when viewed in the polarizing optical microscope. Figure 1A shows a WAXS pattern of a typical PHIC fiber. This pattern is indicative of a high degree of crystallinity and outstanding alignment of the macromolecules along the fiber axis. It is instructive to contrast the perfection of the orientation of PHIC macromolecules against that observed in the commercial rigid-chain aramid PPTA fibers (Kevlar 49, Du Pont Co.) and in ultra-oriented polyethylene (PE). WAXS patterns of PPTA and PE are shown in parts B and C, of Figure 1, respectively. The polyethylene sample was prepared with the gel-spinning/drawing method; the draw ratio was 150 (for details see ref 22). The average orientation angles, derived from the half-width at half-maximum intensity of the major equatorial reflections, are ~4.6, 6.0, and 2.1° for PHIC, PPTA, and PE, respectively. Clearly, the orientation of the PHIC molecules favorably compares with PPTA and approaches the orientation of the ultra-drawn PE specimen.

Table I
Mechanical Properties and Orientation Angle (φ) of Various Highly Oriented Fibers

material	M_v, kg/mol	E, GPa	σ, GPa	ϵ, %	φ,[a] deg
PPTA	40	125	3.6	3.0	6.0
PE	2000	150	5.0	5.0	2.1
PHIC	490	4	0.2	6.6	4.6

[a] From half-width at half-maximum.

The mechanical properties of the PHIC, PPTA, and PE samples are collected in Table I. The ultra-oriented PHIC fibers exhibited a tensile strength of 0.2 GPa and Young's modulus of 4.3 GPa, which significantly exceed previously reported properties of moderately oriented and unoriented specimens.[10,21] Nevertheless, these values are exceptionally low; they only slightly exceed the strength and stiffness of many common, unoriented crystallizable polymers. The mechanical properties of the ultra-oriented PHIC fibers most certainly are far from those usually found for the highly oriented structures exemplified by PPTA and PE (Table I).

It is evident from the data in Table I that the solubilizing *n*-alkyl side groups have a devastating effect on the mechanical properties. Clearly, chain rigidity, the appearance of liquid crystallinity, and high degrees of orientation should not be interpreted as an insurance for high strength or stiffness of the materials obtained from mesophases. The extraordinary mechanical properties of materials such as PPTA and the PBX family[3] result not only from their intrinsic chain stiffness, which promotes effective molecular orientation, but also in particular from their ability to form strong intermolecular secondary bonds, e.g. hydrogen and π–π bonding. These bonds overcome the stress concentrations caused by the large number of chain ends resulting from the modest molecular weight of these polymers and contribute to improved shear moduli. In this context, it is interesting to note that, because of its weak secondary (van der Waals) bonds, PE requires a significantly higher molecular weight (approximately 20×[23]) and a higher degree of orientation than PPTA to match the strength and stiffness of aramids. This requirement is even more pronounced for polymers with *n*-alkyl side chains as discussed below.

In the following section we attempt to estimate the theoretical axial modulus of PHIC, which, to our knowledge, is not reported in the literature. It is assumed that the uniaxially oriented fiber is a composite of rigid rods (the polymer backbones) covalently bonded to a low modulus matrix (the flexible side chains), which, in turn, interacts through secondary bonds. According to the widely used Halpin–Tsai equation[24] for multiphase composite solids, the stiffness, E_c, in the fiber direction of uniaxially oriented composites is given by

$$\frac{E_c}{E_m} = \frac{(1 + \xi\eta v_f)}{(1 - \eta v_f)} \qquad (1)$$

Here $\eta = (E_f/E_m - 1)(E_f/E_m + \xi)^{-1}$, $\xi = 2(l/d)$, v_f = volume fraction fibers, and subscripts f and m refer to fiber and matrix, respectively; (l/d) = aspect ratio of the fiber. For large aspect ratios (a condition met in the present system) the equation reduces to the so-called Voight average

$$E_c = E_f v_f + E_m(1 - v_f) \qquad (2)$$

If we depict oriented PHIC as uniaxially aligned rigid-rod C–N backbones, embedded in a alkyl matrix, the volume fraction v_f can be calculated from the cross-sectional areas of the main chain and the interchain spacing. The cross-sectional area of the backbone is of the order of 20 Å^2.[25] Earlier X-ray studies by Aharoni[26] showed, in agreement with our observations, that the spacing between the closest parallel aligned polymer backbones is about 15 Å. Taking the effective cross-sectional area of the entire molecule to be 15^2 Å^2, it follows that $v_f \sim 0.09$.

The large distance of 15 Å between the polymer backbones indicates that no overlap and packing exists between side chains of adjacent macromolecules. Consequently, the modulus of the alkyl matrix, E_m, will be dominated by interactions between alkyl chain ends and will be much lower than the lowest shear modulus for polyethylene crystals (1.6 GPa[27]). Equation 2 can then be further simplified to

$$E_c = E_f v_f \qquad (3)$$

This implies that the attachment of *n*-hexyl side chains to the rigid-chain polymer reduces the axial modulus to a mere 9% of the value of the backbone modulus (E_f).

The backbone modulus of polyisocyanates is unknown. A first approximative upper limit could be the theoretical modulus of nylon-1. However, due to the large side groups, the polyisocyanate backbone reportedly has a helical character.[12] Therefore, the main-chain modulus of polyisocyanates is well below the stiffness of amide polymers (~200 GPa)[25] and closer to that of, for example, isotactic poly(propylene) (60 GPa).[28] Employing relation 3, the theoretical axial modulus of PHIC is estimated to be of the order of 6 GPa. The maximum value of the Young's modulus (4.3 GPa) that was achieved by the pulltrusion technique is about 70% of this approximative "theoretical" value. Gratifyingly, this is not unlike the fraction of the theoretical modulus that is generally attained for highly oriented aramids and polyolefins.

Concluding Remarks

The data presented in this paper clearly illustrate that attachment of solubilizing alkyl side groups to rigid-chain polymers may have a devastating effect on the mechanical properties of liquid crystalline polymers. This is due to reduction of the number of (uniaxially oriented) covalent bonds per unit cross-sectional area and weakening of secondary interactions. Obviously, these results were obtained for the worst possible configuration, in which all interactions between the rigid backbones are replaced by weak van der Waals bonds. A lesser reduction of the mechanical properties is observed when such bonds are present in only one plane, and strong main-chain interactions are preserved in other directions, as was already pointed out in the Introduction.

Major improvement of the stiffness and strength is expected, of course, when after processing the solubilizing side groups are chemically or thermally removed and strong secondary bonds are restored. In the present case of polyisocyanates this may yield a route toward high-strength, modulus nylon-1 fibers. It is apparent from eq 2 that the mechanical properties can also be improved by increasing the modulus of the "solubilizing" matrix, for instance, by cross-linking of the side chains or by improving the secondary interactions between side chains. However, only moderate enhancement is expected for the present PHIC material, since the side-chain structures will be loaded, at best, in the transverse direction, and not axially.

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Registry No. PHIC (homopolymer), 26746-07-6; PHIC (SRU), 37727-37-0.

On the Relation between Structure and Dynamics of Star Polymers in Dilute Solution

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ABSTRACT: Studying star polymers in solution, where the inner core, the outer shell, or the full star was labeled, we investigated in detail the relation between the architecture of a star polymer and its initial dynamic response. In the framework of the RPA approach we evaluate the initial relaxation rates for the inner and outer part of a Gaussian star including the hydrodynamic interaction. Furthermore, we point out a general relation between the structure of stars with arbitrary arm statistics and their dynamic response. We present small-angle neutron scattering data on 12-arm partially and fully labeled polyisoprene stars and evaluate the corresponding partial structure factors. The best description of these data is given by the recent molecular dynamics simulations. The star dynamics were investigated by neutron spin–echo spectroscopy. The relaxation behavior of the star core and shell were found to differ qualitatively. While the reduced relaxation rates of the star core as well as of a fully labeled star undergo a pronounced minimum at intermediate Q values, the respective shell relaxation rates undergo a maximum in the same Q range. On the basis of the measured partial and full static structure factors within the random-phase approximation (RPA) approach, the Q dependence of the initial star relaxation rates under all contrast conditions can be quantitatively accounted for. On the other hand, the time scales of the relaxation process reflect also dynamic features such as hydrodynamic screening. At longer times further dynamic processes like the disentangling of interarm entanglements appear to come into play.

I. Introduction

Long flexible polymers in dilute solutions have been a subject of long-standing interest from both an experimental and a theoretical point of view.[1,2] While the static and dynamic properties of linear chains have been widely investigated and appear to be well understood, much less is known on branched polymers. Star polymers, where several linear chain molecules of nearly identical molecular weight are attached at one end to a center molecule, may be considered as prototype materials for branched systems. The star structure implies a very inhomogeneous polymer density profile: starting from the crowded star center, where we have to consider strongly stretched chains, the density profile decreases to the outer regions of the star. If scaling ideas are introduced, according to Daoud and Cotton[3] and Birshtein et al. this may be pictured in terms of the concept of semidilute solutions with a blob size decreasing from the rim to the center. Explicit calculations on the star structure are available for Gaussian stars,[6] while molecular dynamics calculations yielded results for real systems.[7] The internal star dynamics have been treated on the level of initial slope calculations on the basis of Kirkwood's diffusion equation, which takes into account the hydrodynamic interaction between chain segments.[6] These calculations are also available for partially labeled systems like stars built from diblock copolymers of different scattering contrast.[8] Lately, considerations on the structure and dynamics of diblock copolymers of arbitrary architecture put these calculations into a general context.[8-11]

On the other hand, progress in anionic polymerization made it possible to synthesize star polymers with a narrow distribution of molecular weight and functionality.[12] These achievements triggered intense experimental efforts to investigate these well-characterized, monodisperse, branched polymers. Elastic light scattering,[13] small-angle neutron (SANS),[14] and X-ray scattering[15] addressed structural aspects, while quasielastic light scattering[13] and NMR[16] dealt with diffusional prop-

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