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Development and characterization of melt-processable rigid-rod polymers with improved mechanical properties

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Abstract

The aim of the investigations was to develop a better understanding of the relation between the molecular structure and the resulting mechanical properties of rigid-rod polymeric systems. This understanding could eventually lead to an improvement of commercial, melt-processable liquid-crystalline polymers (LCPs). The aim was pursued by the successive synthesis, molecular characterization and macroscopic characterization of poly(*p*-phenylene)s, polyesters and polyamides with a systematically varying sequence of rigid-rod units in the main-chain and with flexible side chains. From the molecular characterization persistence lengths were found to increase from 7-9 nm (polyesters), to, about 14 nm (polyimide) and up to at least 22 nm (poly(*p*-phenylene)), in agreement with the expected molecular stiffness based on the main-chain structure. The determination of the macroscopic tensile stiffness of oriented samples resulted in actually achieved main-chain moduli (corrected for the cross-section of the side chains) in the order of 150 GPa, without a specific dependence on the molecular rigidity. An increasing discrepancy was observed between the experimental values and the theoretical main-chain modulus for higher molecular rigidity. This important effect was ascribed to increasing processing difficulties. On the other hand, the orientation development was found to be highly efficient in the investigated polymers.

Keywords:

rigid-rod polymers, synthesis, processing, chain modulus, characterization techniques

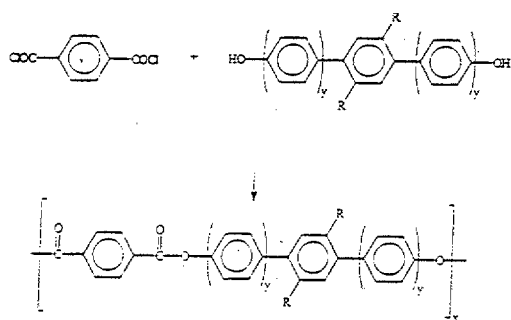
INTRODUCTION

Melt-processable liquid-crystalline polymers (LCPs) possess the unique combination of high mechanical properties and thermal resistance, and improved processability into highly oriented structures. These favorable properties are all related to the rigid-rod nature of the polymeric chain: the inherent chain rigidity directly accounts for the achievable mechanical and thermal properties, while the processing advantages proceed from the occurrence of a thermotropic liquid-crystalline state [1]. The presently available commercial LCPs are in fact random copolymers based on rigid aromatic units (mostly phenyl or bi-phenyl) and e.g. ester linkages. The melting temperatures of these commercial LCPs are in the range 250-400 °C and the mechanical stiffness varies from about 10 GPa in injection moulded parts to about 100 GPa in highly oriented fibres. Further improvement of the mechanical properties of LCPS requires a basic understanding of the relation between the chain parameters, with the emphasis on the persistence length, and the macroscopic mechanical properties, viz. the tensile modulus in the orientation direction. In commercial LCPS the study of this relation is hampered by the random nature. Therefore we have chosen to investigate this relation in rigid-rod polymers with a well defined structure of the main chain and with flexible side chains for achieving the melt-processability [2]. The molecular structure of the polymers under investigation is based on well defined sequences of *p*-phenylene units, either coupled directly or by means of ester or imide groups. Aliphatic side chains of different lengths were included.

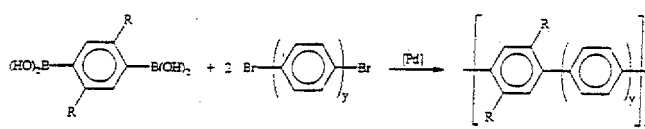
SYNTHESIS

The syntheses were successfully performed using a novel Pd-catalyzed polycondensation reaction, yielding a wide range of poly(*p*-phenylene)s (including oligo-*p*-phenylenes), polyesters and polyamides with (mostly) hexyl or dodecyl side chains [3-5]. In scheme 1 the reactions are shown leading to representative polyesters and poly(*p*-phenylene)s included in the research. Following these high-yield synthetic routes degrees of polymerization were achievable in the range 50-80. The synthesis of rigid-rod polyamides composed of pyromellitic diimide and *p*-terphenylene moieties was found to be less efficient with degrees of polymerization up to 15 [4]. All polymers were thoroughly characterized with respect to the molecular constitution (nmr, viscosimetry), thermal and phase behaviour (DSC).

A selection of the polymers, comprising at least one representative of each type, was synthesized with a range of molecular weights and in sufficient amounts to allow a characterization of both the molecular (persistence length) and the macroscopic properties (chain modulus). The structures of the essential polymers and their nomenclature is presented in figure 1.



$y=1$: PES1.3/R



$y=2$: PPP3/R

Scheme 1

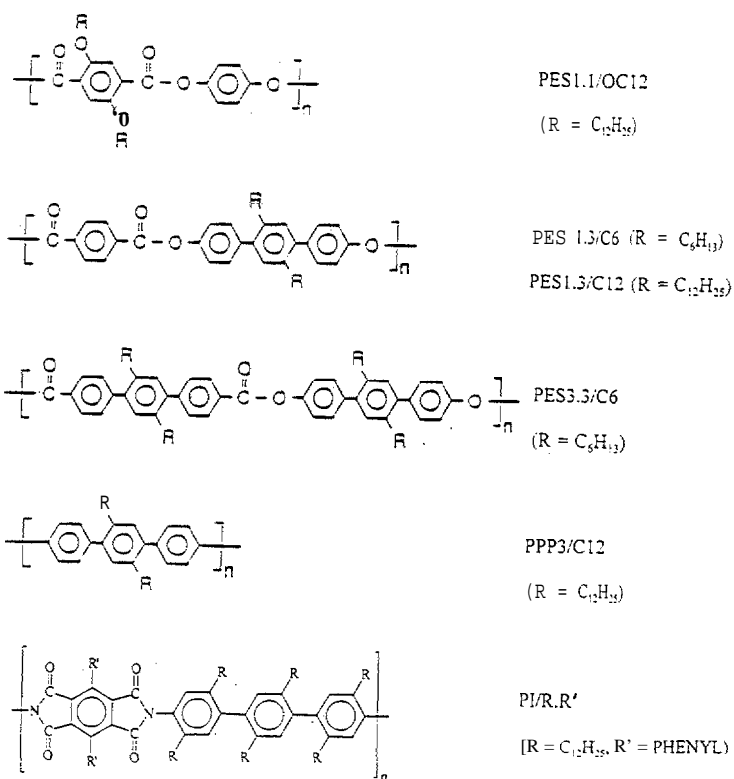


Figure 1 Structure of the polymers included in the molecular and macroscopic characterization

MOLECULAR CHARACTERIZATION

Apart from the structural analysis, the molecular characterization was directed towards the determination of the molecular rigidity, quantified by the persistence length. This molecular parameter, which is determined in solution, is very indicative for the ultimate chain modulus in the solid state and for the ability to form a liquid-crystalline state. The determination of the persistence length was pursued by using three different techniques, enabling a careful evaluation of the results. The Bohdanecky method, based on viscosimetric measurements, is already well-known. The other two methods, based on respectively magnetic birefringence measurements (also called Cotton-Mouton method, CM) and Depolarized Rayleigh Scattering (DRS), have the same physical background and were partly developed within the project.

The Bohdanecky method is based on the following relation between the inherent viscosity and the molecular weight:

$$\left(\frac{M_w^2}{[\eta]}\right)^{\frac{1}{3}} = A_\eta + B_\eta M_w^{\frac{1}{2}} \quad (1)$$

The persistence length l_p is calculated from the slope B_η , while the intercept A_η is used to estimate the hydrodynamic diameter of the polymer. In figure 2 the Bohdanecky plot is shown for the polyester PES 1.3/C6. From this plot a persistence length of approximately 8.5 nm was calculated for this polyester. In table 1 further results obtained with the Bohdanecky method for the polymers under investigation are presented. Since the persistence length is assumed to be mainly a main-chain property, the polymers are denoted by the main-chain code only.

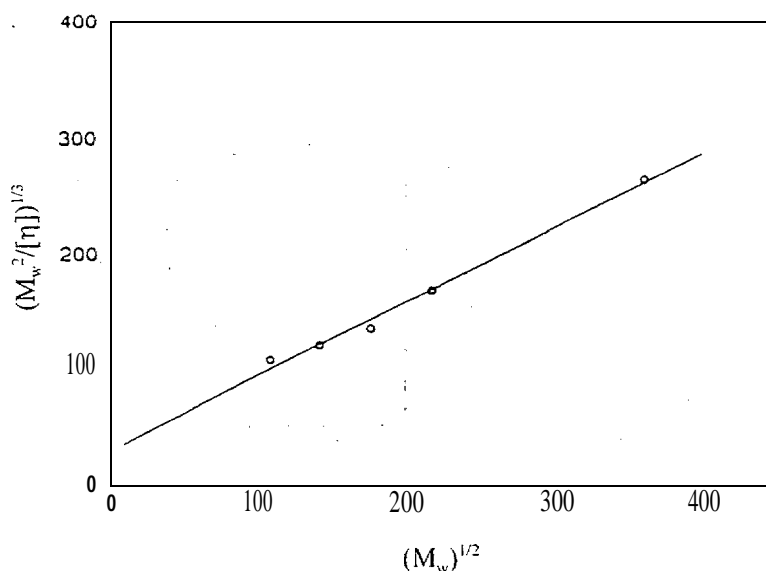


Figure 2 Bohdanecky plot for the polyester PES 1.3/C6

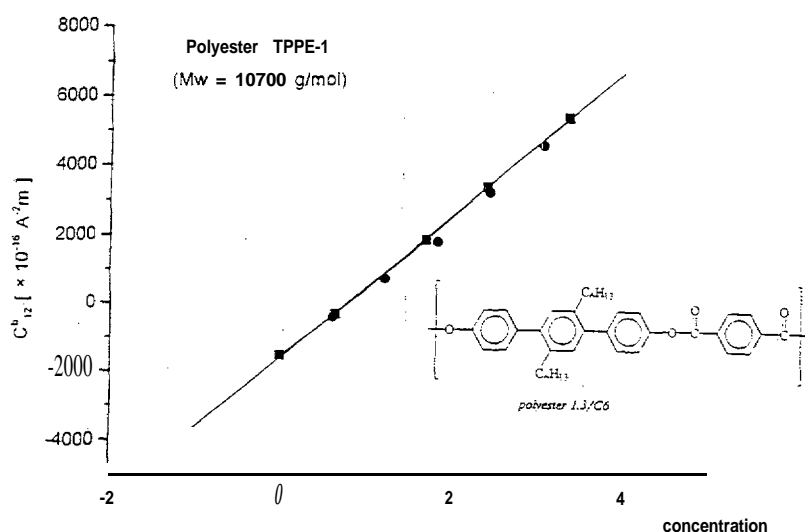
Table 1 Summary of persistence length values (in nm) obtained with various techniques

	PES1.1	PES1.3	PI	PPP3
Bohdanecky	7	8.5	13.7	21.5
Cotton-Mouton		9		
DRS		23.3		52.7

In the Cotton-Mouton method the magnetic birefringence An of a number of different solutions of the polymer is measured as a function of the magnetic field B . The CM constant C_{12}^b , corresponding to the slope of a plot of An versus B^2 , is then plotted against the concentration, leading to the specific CM constant C_2^b . In figure 3 an example of such a plot is presented for a low molecular weight polyester PES 1.3/C6. Following this procedure for a number of molecular weights, characterized by the contour length L_w , the persistence length can be derived from the following equation:

$$\frac{1}{C_2^b} = \frac{1}{Kl_p} + \frac{4}{3K} \frac{1}{L_w} \quad (2)$$

In this equation the constant K is determined by experimental conditions. The persistence length for the polyester obtained from the intercept of a plot according to equation 2 is included in table 1, Comparison with the data from the Bohdanecky method confirms the applicability of the CM method.

Figure 3 CM constant C_{12}^b vs. concentration for a low molecular weight PES1.3/C6

Depolarized Rayleigh Scattering is based on the measurement of the scattered laser intensity R_{VH} using Fabry-Perot Interferometry, as a function of the concentration c and the molecular weight of polymeric solutions. Largely analogous to the procedures followed in the CM method, the persistence length is derived according to the equation:

$$\left[\frac{c}{R_{VH}} \right]_{c \rightarrow 0} = \frac{1}{K_{DRS} l_p} + \frac{2}{3 K_{DRS}} \frac{1}{L_w} \quad (3)$$

Figure 4 presents an example of a plot based on this equation for the polyester PES 1.3/C6. The persistence length values obtained so far with this method can be found in table 1. It can be observed that these results follow the "right qualitative trend, but a systematic overestimation of the persistence length may be concluded. The complex character of the persistence length may well lead to somewhat different values from different techniques, as was also observed for poly(*p*-phenylene terephthalate) [6]. A further substantiation of the DRS results with data on different molecular weight polymers seems, however, necessary.

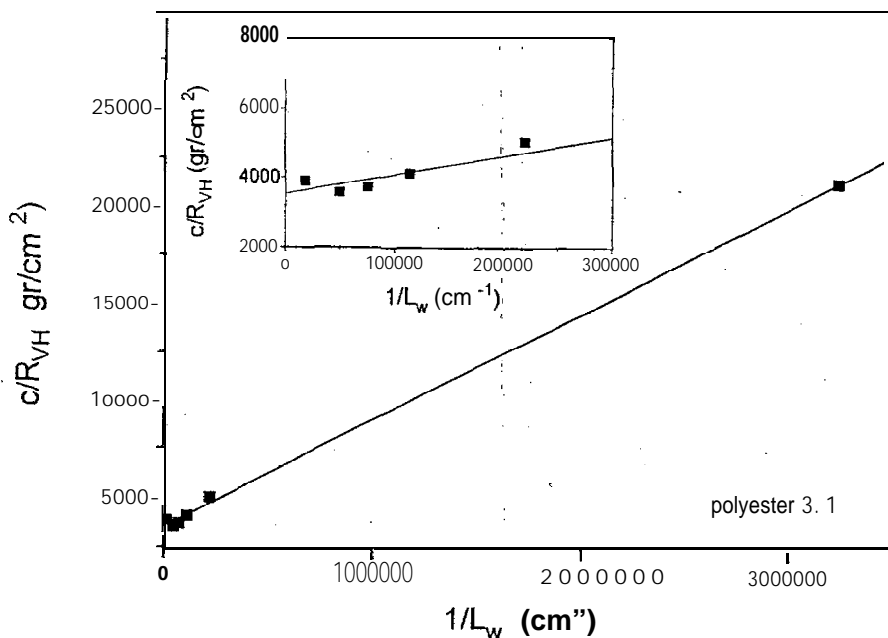


Figure 4 Determination of the persistence length of polyesters PES 1.3/C6, based on the linear relation between c/R_{VH} at $c \rightarrow 0$ and $1/L_w$

For commercial random copolyesters persistence length values in the order 6-9 nm were found [7], while in poly(*p*-phenylene terephthalate) values ranged between 15 and 29 nm, depending on the measurement technique [6]. Bearing this in mind, and with the above reservation concerning the DRS results, the values displayed in table 1 provide a consistent set of persistence length values, in the expected order of magnitude and increasing along with the theoretical chain stiffness. The persistence length measurements thereby confirm that the main-

chain of poly(*p*-phenylene)s is substantially stiffer than that “of the polyesters. with an intermediate position of the polyimide.

MACROSCOPIC CHARACTERIZATION

The main goal of the macroscopic characterization was the determination of the achievable chain modulus in oriented samples. By means of DSC recordings it was found that the main-chain melting of most polyesters occurred above 300 °C, with an exception for PES 1, 1/OC12, that melted to a mesophase at 170 °C. In the PPP polymer no melting could be observed. Since thermogravimetric measurements showed the onset of degradation effects around 200 °C for all polymers, thermotropic processing could in general be ruled out. Film casting and subsequent drawing was found to be a very efficient alternative, and highly oriented samples could be made of several polyesters (with increasing chain rigidity) and the poly(*p*-phenylene) displayed in figure 1. The degree of orientation of these samples was determined by various, complementary techniques. The derivation of the orientation parameter $P_2 = (3\langle \cos^2\theta \rangle - 1)/2$ from the azimuthal intensity distribution in wide angle X-ray diffraction (WAXD) recordings, is well-known, just like the use of FTIR spectroscopy. The third method, polarized laser Raman spectroscopy, based on the orientation dependent scattering of a specific vibration (C_1-C_4 of the benzene rings), is rather new and received special attention.

Using WAXD it was found that the oriented samples exhibit very high orientation levels. Already at a draw ratio $\lambda \approx 2$ an orientation given by $P_2 \geq 0.8$ was found, increasing to values $P_2 \geq 0.95$ at the maximum draw ratio $\lambda = 3$ to 4 in most polyesters, *even up to* $P_2 = 0.99$ for PES 1, 1/OC 12 ($\lambda = 6$). These high values turned out to be characteristic for oriented samples of the rigid-rod polymers under investigation, thereby demonstrating the high effectiveness of the drawing process. On the other hand, the spectroscopic techniques (Raman scattering and FTIR) resulted in systematically lower degrees of orientation in the range $P_2 = 0.4-0.8$, which develop rapidly at higher draw ratios ($\lambda > 2$). Figure 5 presents some combined results for the polyester PES3.3/C6. This behaviour can be understood by the fact that WAXD probes the orientation of larger units, consisting of ordered layers or clusters of polymeric chains (probably related to liquid-crystalline domains), while the spectroscopic techniques probe the orientation on a molecular level.

Dynamic tensile measurements were used to assess the mechanical behaviour. The ultimately achievable chain modulus was derived from tensile measurements as a function of the draw ratio at the lowest accessible temperature of -175 °C. The ultimate chain modulus could be measured directly in the case of PES 1.1 /OC12 (about 50 GPa, corresponding to a main-chain value of about 180 GPa when corrected for the cross-section of the side chains), and was estimated using an extrapolation method for the other polymers. This extrapolation procedure was based on the aggregate model [8]:

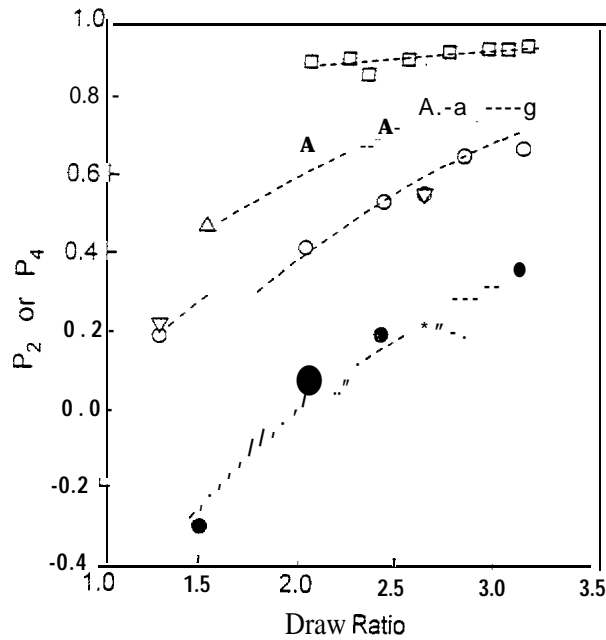


Figure 5 Orientation parameter values determined by various techniques; (O) P_2 Raman (1616 cm^{-1}); (V) P_2 FTIR (1605 cm^{-1}); (●) P_1 Raman (1616 cm^{-1}); (Δ) P_2 FTIR (860 cm^{-1}); (□) P_2 WAXD; lines are drawn to guide the eye

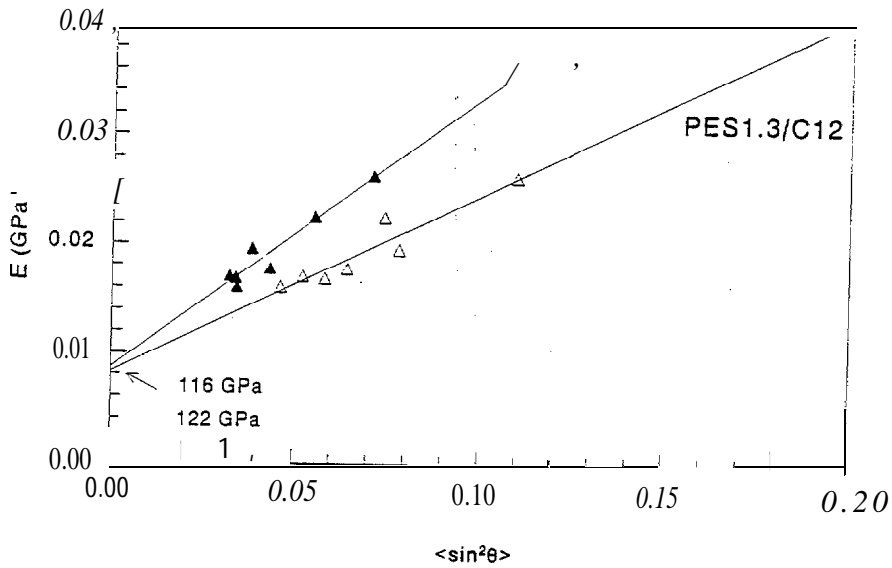


Figure 6 Aggregate model plot for PES1.3/C12, based on the respective orientation values $\langle \sin^2\theta \rangle_{exp}$ (A) and $\langle \sin^2\theta \rangle_{fit}$ (Δ)

$$\frac{1}{E} = \frac{1}{E_c} + \frac{1}{G} \langle \sin^2\theta \rangle \tag{4}$$

with E the measured tensile modulus, E_c the ultimate chain modulus, G the shear modulus and θ the orientation angle. In figure 6 an example of this extrapolation procedure is given

for the polymer PES 1.3/C12. In this figure two differently obtained values for the orientation parameter $\langle \sin^2\theta \rangle$ are included, based on a direct numerical integration of the WAXD intensity distribution ($\langle \sin^2\theta \rangle_{\text{exp}}$) and on the use of a fitting procedure ($\langle \sin^2\theta \rangle_{\text{fit}}$), respectively. In this case the values of the extrapolated chain modulus indicated in the figure appear rather accurate, but in general it was concluded that the uncertainties involved in this procedure do not allow a detailed interpretation of the resulting values.

An illustrative way of presenting the obtained results is to make a comparison between the actually achieved modulus and the theoretical value. Figure 7 shows a diagram in which the maximally obtained chain modulus (at -175 °C), corrected for the cross-section of the side chains, is compared to the theoretical main-chain modulus (calculated according to [9]). The commercial poly(*p*-phenylene terephthalamide) fiber (PPTA) is included. The diagram clearly shows that a (theoretically) stiffer main-chain does not result in proportionally higher experimental moduli. The discrepancy between theory and practice increases with increasing molecular stiffness. This important effect can mainly be attributed to the increasing processing difficulties. As a consequence, the actually achieved main-chain moduli were found to stagnate in the order of 150 GPa.

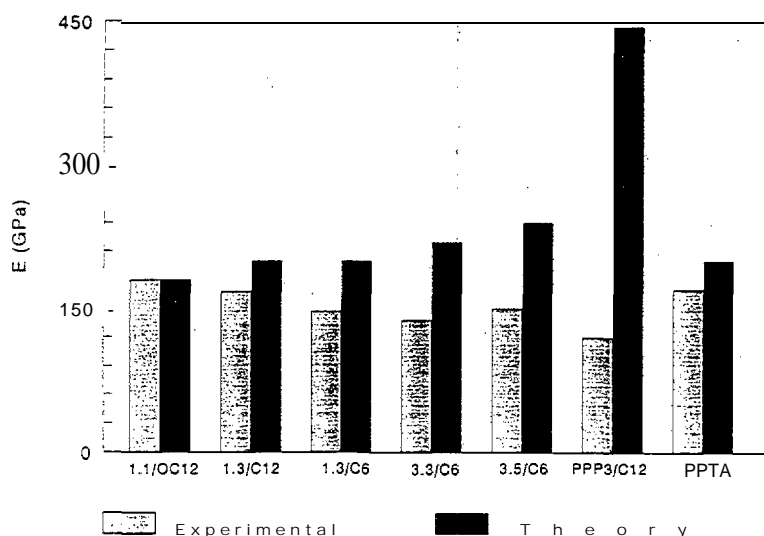


Figure 7 Comparison of the experimentally achieved and theoretical main-chain moduli of the polymers under investigation

CONCLUSIONS

The investigations described in overview in this report, have led to a quantitative assessment of both the molecular rigidity and the macroscopic stiffness of a range of rigid-rod polymers. By measuring the persistence length in solution, with several techniques, it was conclusively established that the molecular rigidity increases in the order polyester [PES 1.1/R, PES 1.3/R], polyimide, poly(*p*-phenylene) (PPP3/R). The results with respect to the actually achieved

experimental moduli showed main-chain values (corrected for the side-chains) around 150 GPa, without a specific relation with the anticipated molecular rigidity. An increasing discrepancy is observed between the actually achieved main-chain moduli and the theoretically predicted values in the order PES 1.1/R, PES 1.3/R, PES 3.3/R, PES 3.5/R, PPP3/R, which could mainly be ascribed to increasing processing difficulties. Consequently, a higher rigidity of the molecular chain does not unambiguously result, in proportionally higher macroscopic main-chain moduli. On the other hand, the orientation process as observed in the drawing of films, turned out to be highly efficient for the polymers under investigation. Optimized rigid-rod polymers with flexible side chains might therefore present a unique combination of processing and performance characteristics.

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