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Effect of Chain Rigidity upon Polymer Orientational Strengthening

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The IR spectroscopic study of molecular processes accompanying orientational strengthening of polymers with different rigidities is reported. Efficiency of orientational strengthening is shown to depend on the rigidity of macromolecules. Orientational strengthening of flexible- and rigid-chain polymers is always terminated because of fracture phenomena.

KEY WORDS Flexible and rigid-chain polymers, orientational strengthening, infrared dichroism, conformational transformations, chain scissions.

INTRODUCTION

Drawing is the basic technique of polymer strengthening. It can produce a several-fold increase in strength of flexible- and rigid-chain (FC and RC) polymers. Advances in the production of high-strength materials (fibers, films etc.) necessitate a deeper understanding of the crystallization and orientational phenomena that accompany fabrication of articles from polymers.

The aim of this work was to study drawing of polymers with different chain rigidity at the molecular level.

EXPERIMENTAL

Our objects were polymers with different chain rigidities, but identical molecular weights ($\bar{M}_w = 2 \times 10^4$): high-density polyethylene (HDPE), polypropylene (PP),

TABLE I
 Assignment of some infrared bands sensitive to conformations

Polymer	Frequency (cm ⁻¹)	Type of vibration	Phase	Conformation	Polarization
PE	720	$\gamma_r(\text{CH}_2)$	A, C	$T_m, m = 2-7$	σ
	730	$\gamma_r(\text{CH}_2)$	C	$T_m, m > 7$	σ
	1350	$\gamma_w(\text{CH}_2)$	A	GG	π
PET	845	$\gamma_r(\text{CH}_2)$	A, C	T	π
	900	$\gamma_r(\text{CH}_2)$	A	G	σ
PA-6	930	Amide IV	C	T	π
	980	Amide IV	A	G	σ
PPIA	935	Amide+ $\delta(\text{CH})$	C	T	π
PABI	3295	s (NH)	A, C	T	σ
PCHA	908	Amide IV	—	"armchairbath"	σ
	948	Amide IV	C	"armchair"	π

A and C are amorphous and crystalline phase, respectively.

T is *trans*-isomers, G is *gauche*-isomers.

m is the number of *trans*-isomers.

poly(vinylchloride) (PVC), poly(acrylonitrile) (PAN), polyamide-6 (PA-6), poly(ethylene-terephthalate) (PET), poly(*m*-phenyleneisophthalamide) (PPIA), poly(*p*-phenyleneterephthalamide) (PPTA), and poly(amidebenzimidazole) (PABI). The chain rigidity in PA-6 was varied by an initial quantity (before drawing) of extended chain *trans*-segments in macromolecules, and also by introducing a greater amount of rigid fragments (cyclohexane ring) into the backbone.¹ Drawing of fibers and films was performed at a lab-scale equipment above T_g . Strength of the samples was measured by an Instron-1121 device at a draw rate of 10 cm min⁻¹ and interclamp separation 20 cm.

The conformational composition, chain orientation and a number of chain scissions in polymers during orientational drawing were examined by IR polarization spectroscopy.² The molecular chain orientation was characterized by the $(D - 1)/(D + 2)$ ratio or orientation function F that are related by³

$$\frac{D-1}{D+2} = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \frac{3\langle \cos^2 \alpha \rangle - 1}{2} = \frac{3\langle \cos^2 \alpha \rangle - 1}{2} F, \quad (1)$$

where D is the infrared dichroism, θ is the angle between the chain axis and orientation direction, and α is the angle between the chain axis and direction of the transition moment. The IR absorption spectra were recorded on a DS-403G spectrophotometer. The IR absorption bands being analyzed and their attribution^{2,4} are listed in Table I. The number of molecular ruptures were calculated from the intensity of IR absorption bands with frequency 1718 and 1740 cm⁻¹ corresponding to end groups (C=O).

RESULTS AND DISCUSSION

Figure 1 shows $(D - 1)/(D + 2)$ as a function of the draw ratio λ for polymers with different chain rigidities at different draw temperatures T_{dr} . It is seen that for flexible-chain PE the orientation factor of the chains in the crystalline region reaches its limit at higher λ as compared with more rigid-chain polymers of the PABI and PA-6 types. A similar situation is observed for chains in the amorphous regions. It can therefore be concluded

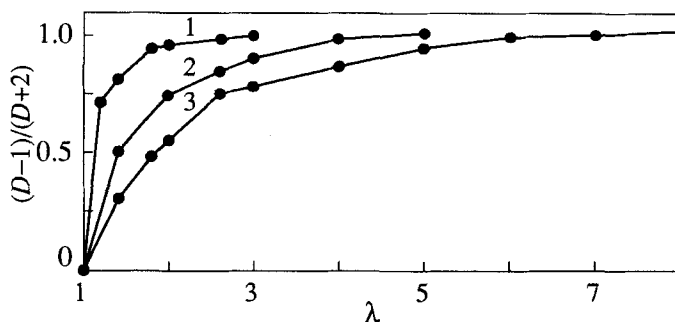


FIGURE 1 Change in orientation of molecular segments on drawing of PABI (curve 1, $\nu = 3295 \text{ cm}^{-1}$, $T_{\text{dr}} = 380^\circ\text{C}$), PA-6 (curve 2, $\nu = 930 \text{ cm}^{-1}$, $T_{\text{dr}} = 180^\circ\text{C}$) and PE (curve 3, $\nu = 720 \text{ cm}^{-1}$, $T_{\text{dr}} = 20^\circ\text{C}$).

that at one and the same λ the average-molecular chain orientation in rigid-chain polymers is higher than that in flexible-chain polymers. As follows from the Kratky model,⁵ which describes the orientational behavior of a polymer with rigid rod-like chains, they reach their maximum orientation already at draw ratio $\lambda \approx 3$. The experimental data also indicate that high chain orientation takes place in rigid-chain polymers even at $\lambda = 3$. Thus, it can be concluded that in drawing the elongation of rigid-chain polymers, in which conformational arrangements are limited, results mainly from orientation of rigid molecular chains as a whole. While the rotational-isomer fragments in flexible-chain polymers are several angstroms long, independent and non-deformable fragments in polymers of the semi-rigid type (poly(oxadiazol), poly(sulfonamide) etc.) are as long as several tens of angstroms. In more rigid polymers (polyhydrazines and some aromatic polyamides) these fragments are hundreds of angstroms in size. The process of deformation of these systems involves a decrease in the content of coiled conformations and increase in the amount of extended segments whose size and concentration depend on the rigidity of molecular chains. The higher the rigidity of a polymer chain, the larger the size of the rotational fragment and the lower the concentration of coiled isomers.

Figure 2 shows the relative contents of extended *trans*-isomers T and coiled *gauche*-isomers G as functions of draw ratio for polymers with different chain rigidity. It is seen that the conformational transformations become more intense with increasing rigidity of a polymer molecule (despite the activation barrier for conformational transformations grows in this case),⁶ i.e. at one and the same draw ratio the number of conformational transformations is higher in more rigid-chain polymers. This result is consistent with the rotational-isomer theory of stretching of polymer chains. For instance, the relative content of coiled isomers and draw ratio in rubber-like polymers were found to be related by

$$\frac{A - A_0}{A_0} = C \left(\lambda^2 + \frac{2}{\lambda} - 3 \right), \quad (2)$$

where parameter C depends on chain flexibility (the higher the chain flexibility, the lower the magnitude of C), and A_0 and A are the initial and current optical densities of IR absorption bands that characterize the content of coiled isomers.

Extrapolation of the relative content of isomers in Figure 2 to the limiting values ($(A - A_0)/A_0 = 1$ for T-isomers and $(A - A_0)/A_0 = -1$ for G-isomers) shows that this limit is reached at $\lambda = 15\text{--}30$ for HDPE, at $\lambda = 7$ for PET and PA-6, and at $\lambda = 5$

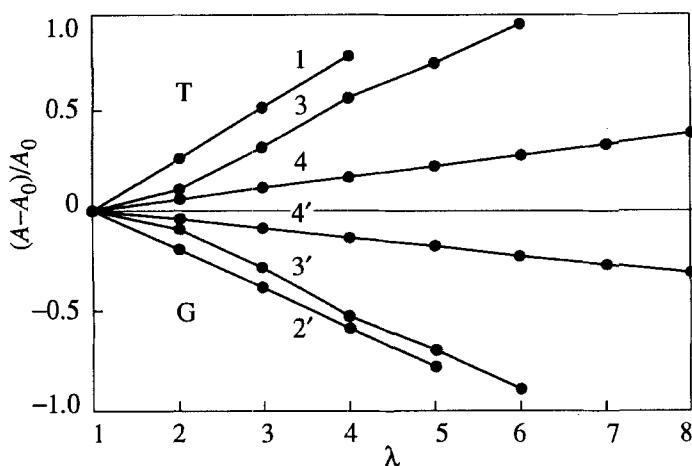


FIGURE 2 Change in relative content of T-isomers (curves 1, 3, 4) and G-isomers (curves 2', 3', 4') on drawing of PPIA (curve 1, $\nu = 935 \text{ cm}^{-1}$, $T_{\text{dr}} = 280^\circ\text{C}$), PA-6 (curve 2', $\nu = 980 \text{ cm}^{-1}$, $T_{\text{dr}} = 180^\circ\text{C}$), PET (curves 3, 3', $\nu = 900$ and 845 cm^{-1} , respectively; $T_{\text{dr}} = 100^\circ\text{C}$) and HDPE (curves 4, 4', $\nu = 720$ and 1350 cm^{-1} , respectively; $T_{\text{dr}} = 20^\circ\text{C}$).

for PPIA. Just at these draw ratios a full extension of chains must occur in the polymers under consideration (in case their slippage is absent). This result has been confirmed, for instance, in Reference 8, where it was shown that a high content of extended chains is achieved in PE at $\lambda = 30$.

In practice, however, it is difficult to obtain ultimate draw ratios and, hence, a full chain extension by drawing of polymers, and especially of flexible- and semi-rigid polymers, without taking special measures. This is due to the fact that on drawing the conformational transformations and chain orientation in a polymer are accompanied by the fracture process.² Accumulation of a definite concentration of chain scissions in a polymer leads to arresting the orientational strengthening of the sample and the macrofracture. Macromolecular scissions are mainly caused by the over stresses which they experience because of a nonuniform chain length distribution.⁹ The study of chain scission accumulation in polymers with different chain rigidity during orientational drawing has revealed (Figure 3) that the macrofracture of a rigid-chain polymer sample takes place at lower draw ratios λ_f than that of a flexible-chain polymer. For rigid-chain polymers the magnitude of λ_f at which the sample breaks down differs only slightly from the theoretically calculated draw ratio λ_t . For flexible-chain polymers, λ_f is well below λ_t . This is apparently due to the fact that a high chain coiling in flexible-chain polymers gives rise to a broad length distribution of chains that in turn leads to a nonuniform distribution of the external stress over bonds. The molecular coiling in rigid-chain polymers is low because of a poor conformational set, and therefore the chain length distribution is more narrow, and the stress distribution over bonds is more uniform. The concentrations of chain scissions at which a sample macrofracture occurs are approximately similar for polymers with different rigidities.

Thus, the experiment has shown that in polymers with higher chain rigidity the molecular orientation is more efficient and complete than in flexible-chain polymers, and this must undoubtedly affect the physical and mechanical properties of fibers and films obtained by drawing. Figure 4 shows the maximum strengths σ_{max} versus maximum draw ratios λ_{max}

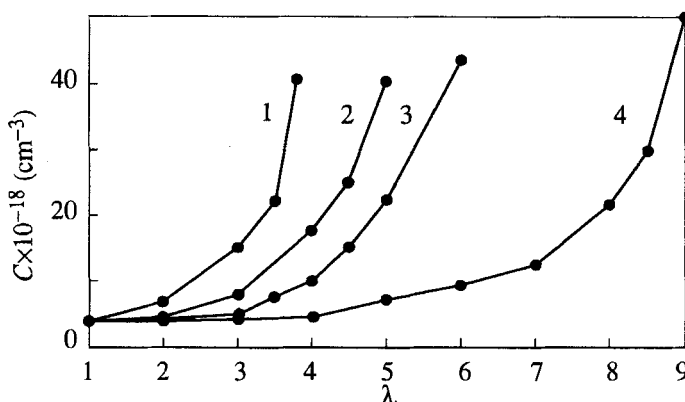


FIGURE 3 Accumulation of chain scissions on drawing of PABI (curve 1), PPIA (curve 2), PA-6 (curve 3), PE (curve 4). Chain scissions were calculated from accumulation of C=O end groups in polymers studied. Their concentration was estimated from IR-bands recorded in the frequency range 1700–1800 cm^{-1} .

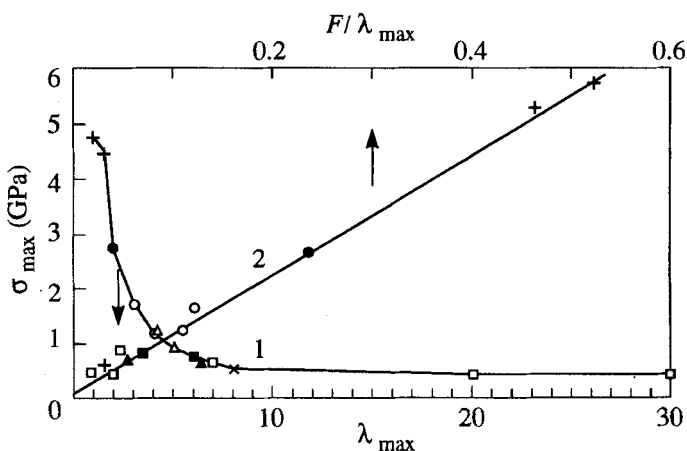


FIGURE 4 Maximum strength σ_{\max} as a function of λ_{\max} (curve 1) and of F/λ_{\max} (curve 2) for PABI (+), PPTA (●), PA-6 (○), PET (▲), PAN (Δ), PVC (■), PP (×) and PE (□).

for polymers with different chain rigidities. The dependence is hyperbolic. Despite a low drawability of rigid-chain polymers, their strengths at λ_{\max} is higher than those achieved for flexible-chain polymers that can be drawn to considerably higher draw ratios. The relationship between the strength of polymers σ_{\max} and F/λ_{\max} ratio has a universal linear character, because all polymers fit a straight line with a satisfactory accuracy. Extrapolation of F/λ_{\max} to unity ($F = 1$, $\lambda_{\max} = 1$), which corresponds to the case of fully extended and oriented chains in polymers gives strength $\sigma = 10$ GPa. The ultimate strength of 10 GPa that can be achieved in case of perfect orientation of extended chains proves to be close to the theoretical estimates.

The data shown in Figure 4 are consistent with the experimental data on variation of the orientation of conformers (Figure 1) and their relative content (Figure 2) with draw ratios for polymers with different types of rigidities. It follows from Figure 4 that strengthening of a polymer depends on the efficiency of drawing. The efficiency of the orientational

strengthening of rigid-chain polymers is higher than in the flexible-chain ones, because the degree of molecular coiling in them is lower, and the degree of chain orientation is higher. Therefore, the strength of rigid-chain polymers is higher and is achieved at lower draw ratios than in flexible-chain polymers.

It should be noted in conclusion that it is rather difficult to obtain high strength flexible-chain polymers by a conventional orientational drawing, because many of these polymers crystallize with formation of folded crystallites.¹⁰ This leads to a decrease of the number of tie chains and their nonuniform distribution in the amorphous regions, and, hence, to a low tensile strength.

The strength of rigid-chain polymers can be increased by a thermal treatment alone, without using the orientational drawing. This is due to the fact that kinetic chain rigidity and strength of rigid-chain polymers are strongly affected by the intermolecular interaction that increases after thermal treatment.¹¹ The thermal treatment of rigid-chain polymers can give rise to selforientation of chains and, hence, to an increase in strength.

To achieve high strength of rigid-chain polymers, chain orientation is often carried out in the polymer solution, and not in the bulk.

Drawing of bulk rigid-chain polymers is performed at temperatures over T_g (300°C and higher) at which fracture processes are very intense. For rigid-chain polymers in solution, low shear stresses are needed to produce high enough orientation because of a considerable degree of chain extension and as a result the intensity of fracture processes reduces sharply. The fibers produced by this technique exhibit strength and elastic characteristics close to the theoretical ones.¹²

The degree of rigidity of a macromolecule in PA-6 was varied by introducing more rigid fragments (for instance, cyclohexane rings) into the backbone. The Kuhn segment for poly(cyclohexanamide) (PCHA) is higher than 200 Å (see Reference 13), i.e. it is an order of magnitude higher than for PA-6. By gradually substituting flexible-chain methylene links by more rigid cyclohexane rings we can follow the change of character of rotation-isomer transformations during drawing (Figure 5). In case of an equimolar content of flexible links and rigid rings in a copolymer the fraction of coiled isomers in flexible spacers (the 980 cm^{-1} band) decreases sharply with draw ratio as in a homopolymer PA-6, while the amount of *trans*-fragments (the 930 cm^{-1} band) and ordered portions of cyclo(hexanamide) links (the 948 cm^{-1} band) increase. A higher chain rigidity in a copolymer hinders isomer transformations and, for the ratio of 1 : 9 between the links, orientation becomes inefficient, because the content of extended isomers remains unaltered or even decreases with drawing.

The polarization measurements of anisotropy of IR absorption have revealed that efficiency of orientational phenomena depends on the initial ordering in polyamide. Figure 6 shows the dependence of dichroism and relative intensity of the 948 cm^{-1} band corresponding to the content of ordered PCHA regions. The degree of initial ordering was varied in wide limits by the conditions of precipitation of fibers made of the copolymer PA-6 and PCHA with a ratio of 2 : 8. Orientation was estimated at a definite draw ratio for the ordered regions and all polymer chains separately (948 and 908 cm^{-1}). It can be seen that there is a certain optimum initial ordering at which the orientation is the highest. For disordered regions, the optimum orientation was reached at a lower initial order than for the ordered regions where a higher initial order in polyamide chains is needed to obtain the highest orientation. The observed effects can be attributed to the fact that the efficiency of orientation grows up to a certain limit with increasing degree of crystallinity (i.e. rigidity

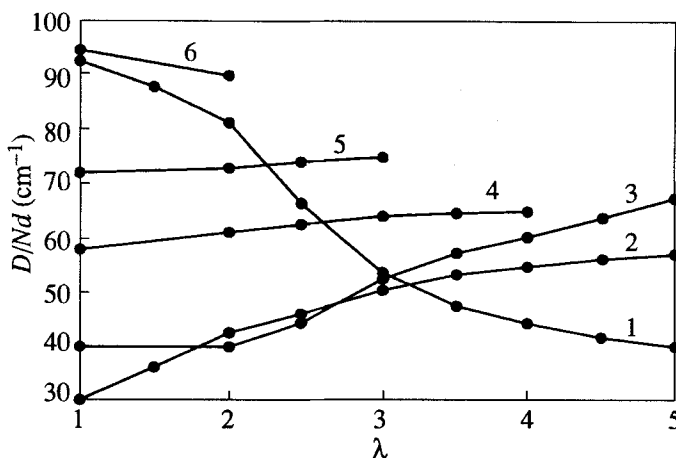


FIGURE 5 Relative intensity of structure-sensitive absorption bands at $\nu = 980 \text{ cm}^{-1}$ (curve 1), $\nu = 930 \text{ cm}^{-1}$ (curve 2), and $\nu = 948 \text{ cm}^{-1}$ (curves 3–6) versus draw ratio λ for PA-6/PHCA based fibers with different content N of PCHA: $N = 50\%$ (curves 1–3), $N = 80\%$ (curve 4), $N = 90\%$ (curve 5), and $N = 100\%$ (curve 6). d is fiber diameter, $T_{dr} = 220^\circ\text{C}$.

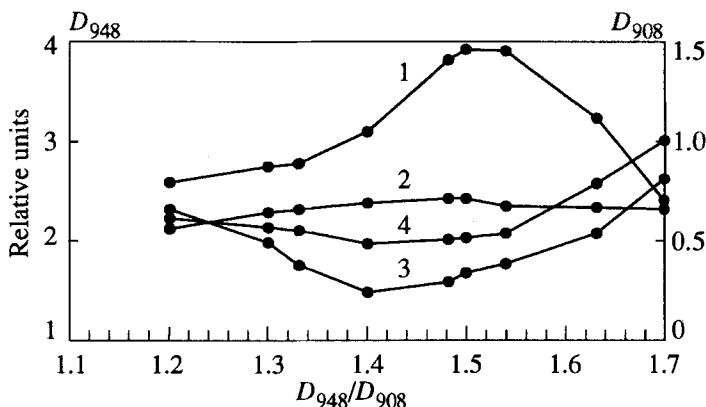


FIGURE 6 Relationship between orientation of fibers based on PA-6/PHCA (2 : 8) with $\lambda = 5$ (curves 1, 3) or $\lambda = 3$ (curves 2, 4) and degree of preliminary ordering. D_{948} is a dichroism of "crystalline" band (curves 1, 2), D_{908} is a dichroism of the band corresponding to orientation of all polymer chains (curves 3, 4).

as well) of an undrawn system, and then, on "recrystallization", an elevated rigidity of the system does not favour the conditions for efficient orientation.

CONCLUSION

It is shown that strengthening of flexible- and rigid-chain polymers is associated with extension of coiled molecules and orientation of chains in the draw direction. The efficiency of orientational strengthening in rigid-chain polymers is higher, since the molecules therein are already extended to a considerable degree. Drawing is terminated because of fracture phenomena. No doubt, the orientational and fracture phenomena in polymers should be

taken into account in polymer strengthening.

For flexible-chain polymers, an increase in the rigidity of the system initially increases the efficiency of orientation, then, as the set of coiled conformers in the chains becomes poorer, the potential barriers for transition of macromolecules from coiled to extended forms grow, and efficiency of orientation drops sharply. Orientation of polymers with rigid chains requires that other technological methods (conversion of a sample into a liquid-crystalline state in solution or temperature treatment, in particular) be used.

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