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Toward Negative Poisson Ratio Polymers through Molecular Design

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Like other materials, polymeric materials become thinner when stretched. That is, they have a positive Poisson ratio. In contrast to this expectation, a negative Poisson ratio polymer would expand laterally when stretched. Ashby[1] first suggested that a cellular structure having an inverted honeycomb geometry should lead to a negative Poisson ratio material. This suggestion was echoed later by Kolpakov.[2] The first structural model[3] was followed in 1987 by Lakes' report[4] of the first negative Poisson ratio material, a foam. Negative Poisson ratio (NPR) behavior has now been found in some bulk polymers[4−6] and metal foams[7] with certain macroscopical structures. Although some NPR metal foams can be strong,[7] the tensile strength and tensile modulus of these polymers are relatively low. A few inorganic crystals have been found to show NPR properties[8,9] due to atomic scale mechanisms; we are interested here, however, in a molecular scale examination of potential NPR behavior in polymeric materials. If the NPR behavior of a polymer can be induced through a molecular design approach, elastic properties of the resulting polymer could be uniquely controlled. Previously proposed molecular designs[10,11] for NPR polymers (sometimes called auxetic[10] polymers) have been based on an inverted honeycomb (reentrant cell) molecular structure. Although this structure can in principle provide a polymer with the desired auxetic properties, the combination of chemistry and mechanics to achieve it is fraught with difficulty. Furthermore, the highly cross-linked honeycomb structure could lead to a high melting temperature and poor tractability. Up to now, there has been no report of an auxetic polymer system based on this molecular structure approach.

Here we want to use a simple molecular design approach[12,13] based on site-connectivity driven rod reorientation in main chain liquid crystalline polymers to achieve auxetic behavior. We will also detail the critical molecular parameters to achieve this property. This proposed mechanism is tested experimentally using the X-ray scattering method.

In any molecular design approach, the fundamental factor enabling a polymer to exhibit auxetic behavior is the interchain packing distance, which should increase when the polymer is stretched. For a unit volume in which there are a fixed number of polymer chains, if the volume is to be increased while the number of polymer chains is kept constant, the only way to achieve this is to increase the overall interchain interaction distance (the distance between nonbonded atoms). The previous molecular design methods[10,11] are consistent with this principle. For example, the inverted honeycomb model under tensile strain provides an effective way to increase the intermolecular interaction distance.

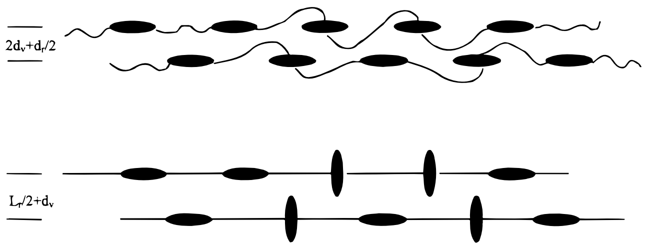

Figure 1. (Top) Arrangement of laterally attached rods in a main chain liquid crystalline polymer. The nematic field leads to orientation of the laterally attached rods parallel to the polymer chain axis. (Bottom) Under tensile stress, full extension of the polymer main chain forces the laterally attached rods normal to the chain axis. If the laterally attached rods are sufficiently long, the interchain distance could increase, leading to an expansion in the direction normal to the chain axis and hence to auxetic behavior.

The reason that natural and synthetic polymers virtually all exhibit a positive Poisson ratio is that polymers develop a more ordered and compact structure under tensile strain, for example, by interdigitation of groups along polymer chains or by perfection of local structuring leading to crystallization. However, a more ordered structure does not by necessity lead to a more closely packed structure. Nature has provided an excellent example: water is more dense in the liquid (amorphous) state than in its ice (crystal) form and the van der Waals close packing distance increases as water assumes a more ordered packing structure. There exist mechanical models[14,15] for the macroscopic origins of NPR behavior. We are concerned here with the behavior of individual polymeric chains for which van der Waals forces can dominate packing considerations and render prediction of a purely mechanical response to stress somewhat more complex.

Our proposed molecular-based approach to auxetic polymers is centered on laterally attached rods, which are incorporated into the polymer main chain. Figure 1 illustrates the proposed molecular-scale structure. Before orientation (or stretching), the laterally attached rods lie parallel to the polymer chain direction as shown in Figure 1 (top), due either to the nematic field (if the polymer is a nematic liquid crystalline polymer) or simply due to the packing efficiency consideration. Under a tensile force, the extension of the flexible spacers in the polymer main chain will force the laterally attached rods from a position roughly parallel to the tensile axis to a position normal to it, as shown in Figure 1 (bottom). This process would push the neighboring chains further apart. This mechanism assumes that the lateral forces (van der Waals) are not strong enough to prevent the mechanical reorientation of the laterally attached rods. If the length of the laterally attached rod is sufficiently long, the polymer would expand laterally.

It is intuitively apparent from Figure 1 that the minimum length for laterally attached rods to be able

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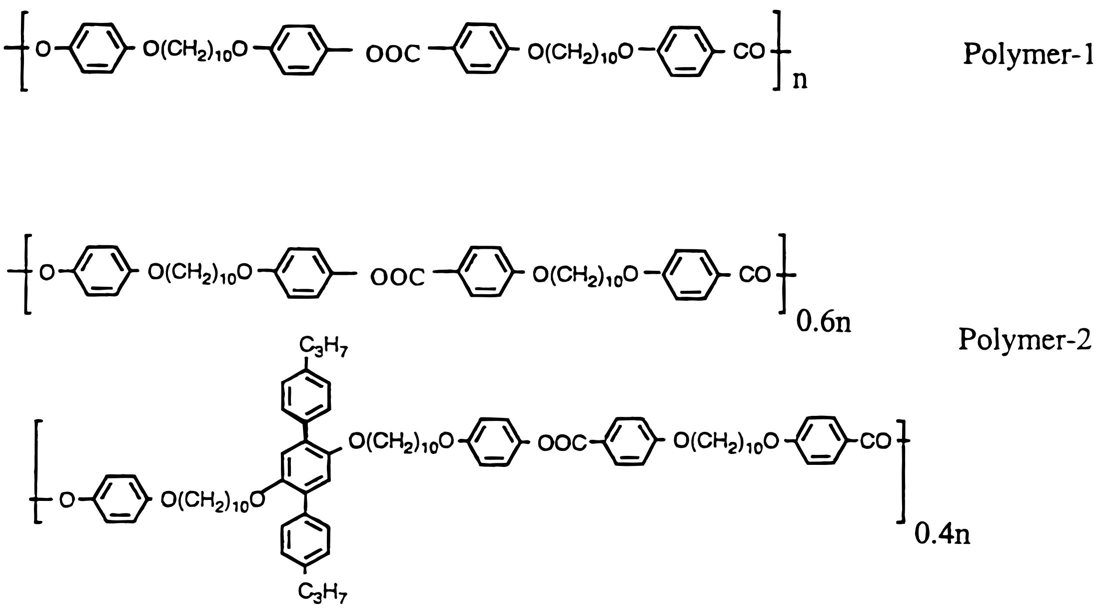

Figure 2. Chemical structures of polymers 1 (parent polymer) and 2 (polymer having laterally attached rods).

to induce auxetic behavior is

$$d_r/2 + 2d_v < L_r/2 + d_v \tag{1}$$

$$L_r > d_r + 2d_v \tag{2}$$

L_r and d_r are the length and diameter of the laterally attached rod, respectively, and d_v is the van der Waals close packing distance, which is typically about 4 Å. Given that the diameter of the rod is approximately 5 Å, a minimum length of the laterally attached rod that could enable a polymer to exhibit auxetic behavior is

$$L_r > 13\ \text{Å} \tag{3}$$

A linear terphenyl rod has a length of about 13 Å, which puts it at the critical threshold for such a polymer to show auxetic properties.

It is worth noting, however, that Figure 1 (top) represents the ideal situation for the packing of laterally attached rods before stretching. In this situation, the polymer would achieve its maximum auxetic efficiency. In the general (non-liquid crystalline) case, the laterally attached rods would pack somewhat randomly in the polymer: only some will be oriented in the direction of the chain axis, as shown in the Figure 1 (top). As to the packing efficiency consideration, the likelihood for a laterally attached rod to be oriented normal to the chain axis decreases as the length of rod increases. Nevertheless, the statistical packing of laterally attached rod structures can only decrease the extent of auxetic response of these polymers but should not eliminate it. One way to maximize the effectiveness of the laterally attached rods is to modify the intrinsic character of the polymer chain structure. If mesogenic groups were to be introduced in the polymer main chain, the polymer will likely exhibit liquid crystallinity, preferably, for our needs, a nematic phase.[11] As a result of the nematic field acting to orient all rods parallel to neighboring rods, the majority of laterally attached rods are forced to orient parallel to the chain axis direction, as shown in Figure 1 (top).

In addition to the requirement of a minimum length of the laterally attached rod, the preferred connection between the rods are flexible chains, such as alkyl chains. These flexible linkages enable the laterally attached rods to assume the preferred orientation (as shown in Figure 1 (top)), which is critical for the polymer to exhibit auxetic behavior. Moreover, the flexible nature of alkyl chains allows them to act as “solvent”, which can facilitate the reorientation of transverse rods under tensile stress.

Although there are similarities in our mechanistic design to the tilting rod mechanism for NPR behavior, as described by Evans[16] and Wojciechowski,[17] our design has the laterally attached rods tethered at their centers, not at their ends as in Evans’ mechanism. Furthermore, we are here involved with a simple linear chain polymer, not with a networked structure. To test the viability of this proposed molecular engineering approach to auxetic polymers, two polymers, prepared in our laboratory, were examined: one (polymer 2) contains laterally attached rods and the other one (the parent polymer, 1) contains only terminally attached rods, the classical (rigid/flexible)$_n$ main chain liquid crystalline polymer. Both polymers 1[18] and 2[19] are nematic liquid crystalline polymers and both have a common chemical structure. The specific chemical structures are shown in Figure 2.

Polymer 1[18] has a glass transition temperature, T_g, of 40 °C, a solid to nematic transition temperature, T_{K-N}, of 185 °C and a nematic to isotropic transition temperature, T_{N-I}, of 215 °C. Polymer 2[19] has a T_{K-N} of 142 °C and a T_{N-I} of 155 °C.

Since an increase of interchain packing distance is the basis for these polymers to exhibit auxetic behavior, one way to probe this property is to use the X-ray scattering method. In this study, X-ray analysis was carried out on a Siemens X-ray diffractometer with nickel-filtered Cu Kα radiation (1.5418 Å). A 2-D detector was used to record the diffraction images. The data sampling step was 0.05° (2θ). Polymer fibers were drawn from their nematic phases. Polymer powder samples were obtained by heating the polymer samples to their isotropic melts and then slowly cooling to room temperature.

In X-ray scattering, the equatorial scattering provides information regarding interchain packing distances.

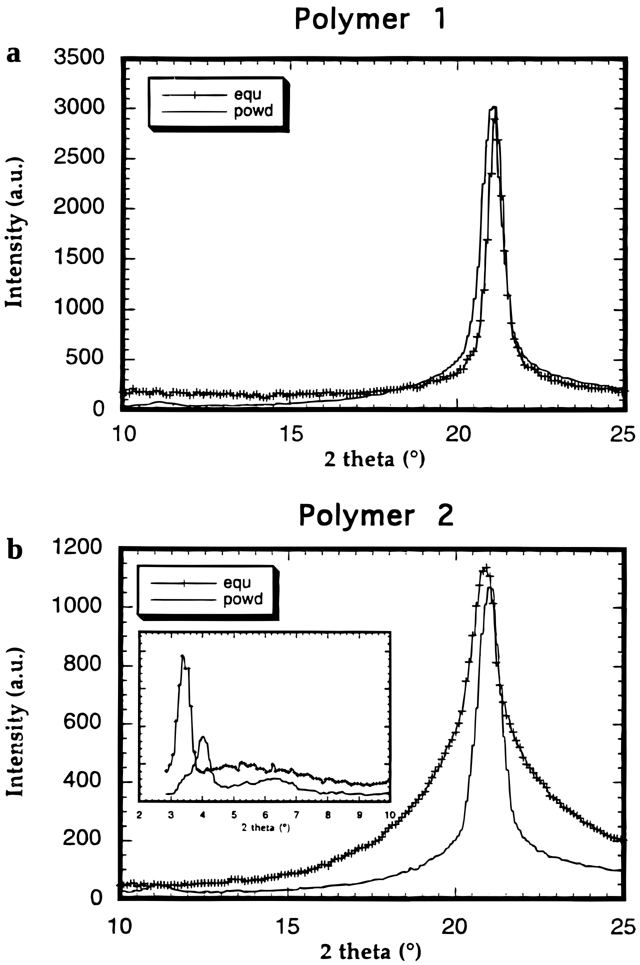

Figure 3. (a) X-ray scattering of polymer without incorporation of laterally attached rods. "equ" is the equatorial scattering of oriented polymer 1, representing the interchain distance of the polymer under stress (stretched). "powd" is the powder scattering of polymer 1, representing the interchain distance of unstretched polymer. The shift of scattering position to a higher angle for the oriented polymer clearly indicates that the interchain distance decreases when the polymer is stretched. This can be interpreted macroscopically that the polymer should become thinner. (b) X-ray scattering of polymer with incorporation of laterally attached rods. "equ" is the equatorial scattering of oriented polymer 2, representing interchain distance of the polymer under stress (stretched). "powd" is the powder scattering of polymer 2, representing the interchain distance of un-stretched polymer. The shift of scattering positions to lower angles for the oriented polymer clearly indicates that the interchain distances increase when the polymer is stretched. This can be interpreted macroscopically that the polymer should become thicker.

Parts a and b of Figure 3 show the X-ray scattering from these two polymers. For polymer 1, without laterally attached rods, the position of equatorial scattering from an oriented fiber (at about 21°, 2θ) is at a higher angle compared with that of the powder sample, indicating that the interchain distance decreases upon orientation. This is the typical behavior observed for a polymer fiber, since a more ordered and compact structure is developed under orientation. For polymer 2, having laterally attached rods, the equatorial scatterings of an oriented fiber (at about 3.5° and 21°, 2θ) move to lower angles, compared with that of the unoriented sample (powder scattering), indicating an increase of interchain distance when the polymer is stretched. The low angle equatorial scattering represents the interaction distance between two main chains and the high angle equatorial scattering represents the interaction distance between side chains and side chains and/or between side chains and main chains.

The laterally attached rod structure and the criterion for the laterally attached rod to induce auxetic behavior in a polymer described here represent a conceptually simple molecular-level approach to achieving negative Poisson ratio materials. The X-ray scattering study supports the proposition that an auxetic polymer can be obtained by incorporating laterally attached rods into main chain liquid crystalline polymers. The details of synthesis and the structure and deformation behavior of the resulting polymers are currently being studied and will be reported in due course.

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