

MOLECULAR DESIGN OF NEW KINDS OF AUXETIC POLYMERS AND NETWORKS*

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Abstract Three new kinds of molecular networks are designed and predicted to exhibit negative Poisson ratios. Molecular mechanics calculations on these networks show that the magnitude of Poisson ratios depends on the relative flexibility of beam and arm structures. Several new kinds of auxetic polymers, whose successful synthesis should be easier than that of the corresponding auxetic networks, are then proposed. It is found that the kabob-like polymers with auxogens lying vertically on the main chain can acquire auxeticity while those with auxogens lying horizontally on the main chain cannot. Besides, a half kabob-like or pseudo-ladder polymer with auxogens linked at the intersection of the beam and the arm does show auxeticity when adopting constrictive conformers. It is, however, worthwhile noting that the origins of auxeticity still await and strongly deserve further experimental and theoretical investigations.

Keywords Auxetic, Auxeticity, Negative Poisson ratio, Auxetic polymer, Molecular modeling

INTRODUCTION

Most materials will shrink or expand laterally when stretched or compressed, *i.e.* they have positive Poisson ratios, but materials with negative Poisson ratios will undergo lateral expansion when stretched longitudinally and become thinner when compressed. Materials exhibiting this novel and counterintuitive behavior, now known as auxetic materials^[1], have attracted increasingly great scientific and industrial interest^[2–4] after the appearance of the first man-made auxetic polymer foam in 1987^[5]. As a new class of both structural and functional materials, auxetic materials are finding many practical and technologically important potential applications due to the novel auxetic effect itself and concomitant enhancements in other material properties.

Recently, the design and synthesis of molecular auxetics, namely auxetic materials at the molecular level, have become the most exciting endeavor^[6–13] in the development of auxetic materials since such systems can solve the problem associated with low Young's moduli inherent in any existing auxetic cellular foams while having the advantage of possessing a predesigned set of mechanical properties. However, the efforts made to synthesize such molecular auxetics have encountered great difficulties, even for the simplest case of auxetic liquid crystalline polymers^[11]. We hereby provide some alternatives for making molecular auxetic polymers and its corresponding networks and perform their molecular mechanics (MM) calculations on a SGI workstation using the Cerius²4.2 software package developed by MSI, now known as Accelrys. The synthetic work of these new auxetic polymers is relatively easy and some of them are being synthesized in our laboratory.

COMPUTATIONAL METHOD

Three basic methods are available for calculating mechanical properties in the Cerius²4.2 software package: second derivative calculation, constant stress minimization, and constant strain minimization^[14]. These techniques can all be used to obtain the stiffness matrix as well as its inverse, called the compliance matrix. These

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two matrices are then used to derive the other properties such as Young's moduli, bulk modulus, volume compressibility, and Poisson ratios. The second derivative method is generally considered the best method of the three; its principal drawback is that for large systems it is both slow and memory-hungry. The constant stress method works more efficiently for larger systems but is still quite slow. The constant strain method is the quickest for large systems but is the least likely to be accurate. Here we select the second derivative method since our systems are not very large.

The second derivative method uses a single-point energy calculation to obtain the second derivatives of the lattice energy with respect to the lattice parameters and the atomic coordinates. The following energy expression is used:

$$U = U_0 + \sum_i \frac{\partial U}{\partial \varepsilon} \varepsilon_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \varepsilon_i \varepsilon_j + \text{Higher order terms}$$

where U_0 is the equilibrium energy and ε is strain. When the structure is at an energy minimum (that is, all first derivatives of the lattice energy are zero), the second derivative term can be used to calculate the components C_{ij} of the stiffness matrix:

$$C_{ij} = \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j}$$

Once the stiffness matrix has been obtained, several related mechanical properties can be derived from it. For example, the compliance matrix, $\mathbf{S}$, is calculated as the inverse of the stiffness matrix, *i.e.*, $\mathbf{S} = \mathbf{C}^{-1}$. Young's modulus is then calculated from the compliance matrix, with its principal components for three directions (x , y , and z) given by: $E_x = \frac{1}{S(1,1)}$, $E_y = \frac{1}{S(2,2)}$, $E_z = \frac{1}{S(3,3)}$, while Poisson ratios, which we are most interested in, are calculated from the compliance matrix as follows:

$$\begin{aligned} \nu_{xy} &= -\frac{S(2,1)}{S(1,1)}, \nu_{xz} = -\frac{S(3,1)}{S(1,1)}, \nu_{yx} = -\frac{S(2,1)}{S(2,2)} \\ \nu_{yz} &= -\frac{S(3,2)}{S(2,2)}, \nu_{zx} = -\frac{S(3,1)}{S(3,3)}, \nu_{zy} = -\frac{S(3,2)}{S(3,3)} \end{aligned}$$

RESULTS AND DISCUSSIONS

Currently, the design of molecular auxetics is mainly based upon the original macroscopic model invented by Gibson and Ashby *et al.*^[15, 16], which is further developed by Almgren^[17], *i.e.*, an inverted or re-entrant honeycomb-like network structure (see Fig. 1).

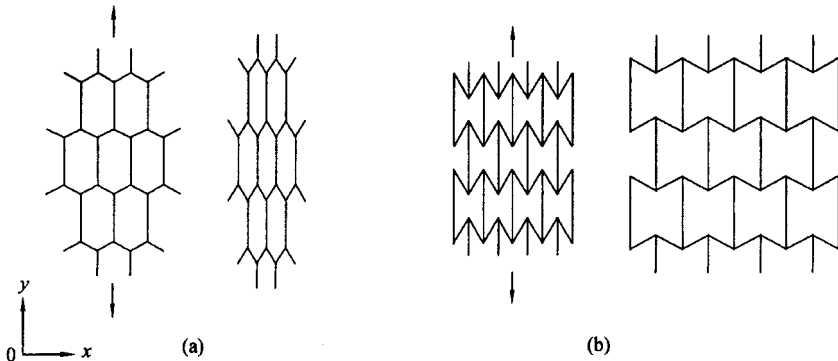


Fig. 1 (a) Conventional non-auxetic honeycomb network deformed by the hinging of the cell walls in response to tensile strain applied in the y direction; (b) Inverted or re-entrant honeycomb auxetic network expands in the x direction for the same deformation mechanism as for (a)

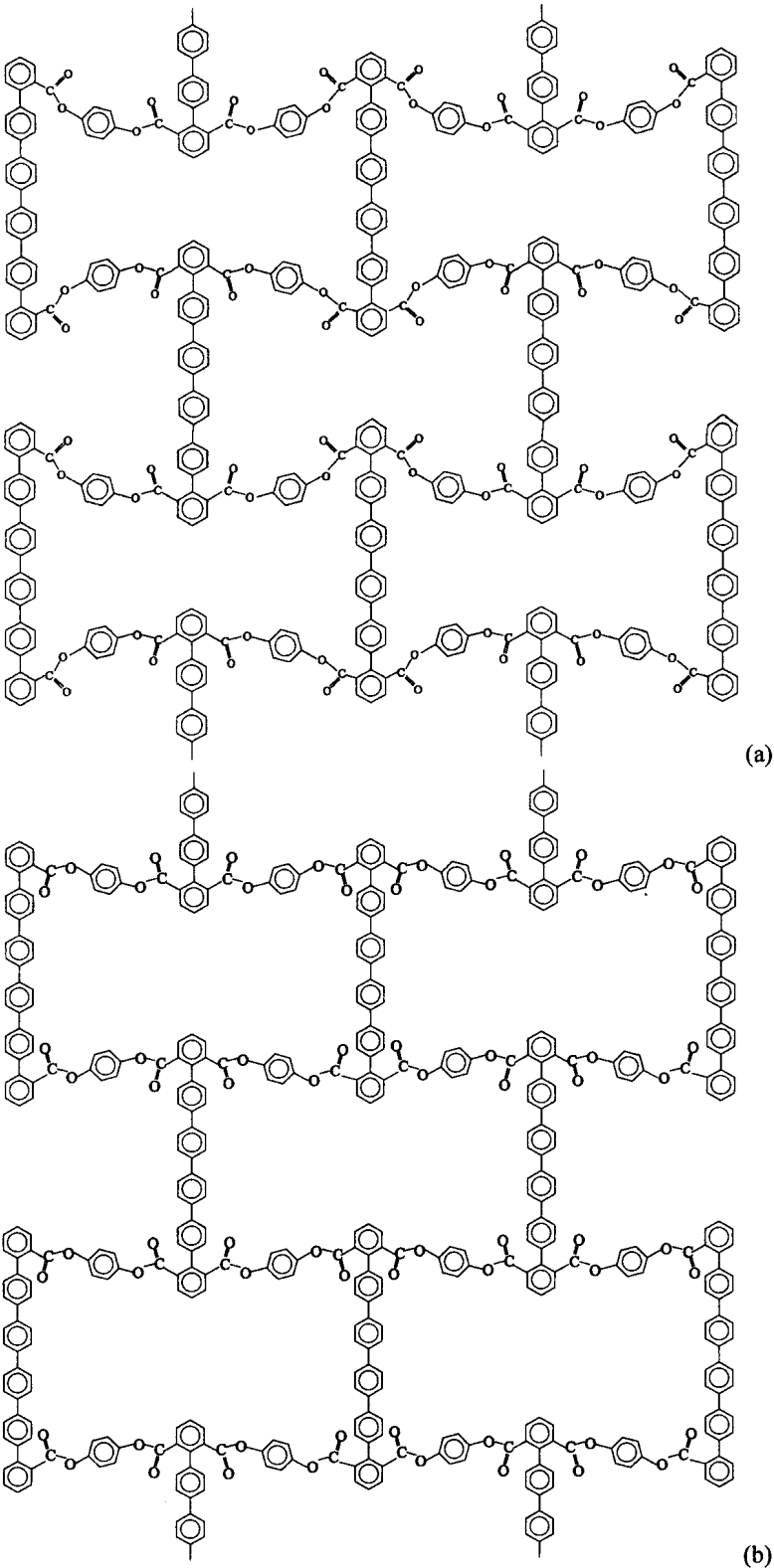


Fig. 2 Example of an auxetic network containing ester, amido ($-\text{CO}-\text{NH}-$) and ether ($-\text{CH}_2-\text{O}-$) links
(a) a constrictive starting conformer; (b) a patulous starting conformer

Let us look at a single hexamer in Fig. 1. We call the vertical side “beam” and the skew side “arm”. Then a natural speculation is: If the arm is more flexible than the beam, it should be more apt to deform when stretched, which should help acquire auxeticity.

So we first design some kinds of auxetic networks with similar reentrant-hexamer-like geometry, which are composed of same beam structures, *i.e.*, multi-phenyl but different arm structures with different functional groups, *i.e.*, ester, amido, and ether links. The arm structures considered here contain ester, amido, and ether links shown in Fig. 2.

After establishing molecular models, we first do MM calculation to get local energy-minimized conformers. The force field used is Dreiding 2.21. This is a generic force field that is verified to be suitable for general organic compounds^[18]. Figures 3–5 show some examples of these optimized structures. The optimized structures are then used to calculate mechanical properties including Poisson ratios, which we are most concerned about.

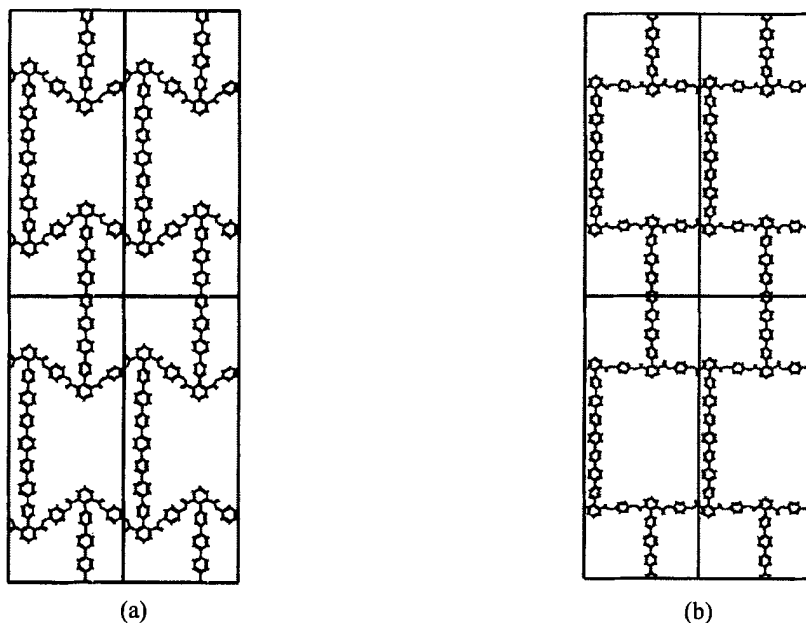


Fig. 3 Example of an optimized auxetic network containing ester links
a) T9 (here T means a constrictive optimized conformer while 9 is the number of benzene rings on the beam structure); b) S9 (here S means a patulous optimized conformer while 9 is the number of benzene rings on the beam structure)

The corresponding Poisson ratio results are listed in Tables 1–3. To our delight, we get negative Poisson ratios in all these cases, and these structures are relatively easier to synthesize than the multi-acetylene structure designed by Evans *et al.*^[1] And what is more important is that there are some interesting hints we can get from the data contrasts among Tables 1–3. First, as we expected at the beginning of the paper, different networks with different arm structures due to different links do result in different Poisson ratios. The networks with amido links seem to be more hopeful in achieving auxeticity than the other two kinds of networks. Secondly, the patulous conformers are much more likely to get negative Poisson ratios than the constrictive ones, which is surprisingly contrary to the prediction according to the Gibson-Ashby model. We believe that this is probably because, under very small deformation condition (the strain is less than 1%), the constrictive conformers, though having lower energies than the patulous conformers, have to climb higher energy barriers than the patulous conformers, while the moving abilities of atoms are very limited at 0 K and so the net result is that the patulous conformer will be more likely to get auxeticity than the constrictive conformers.

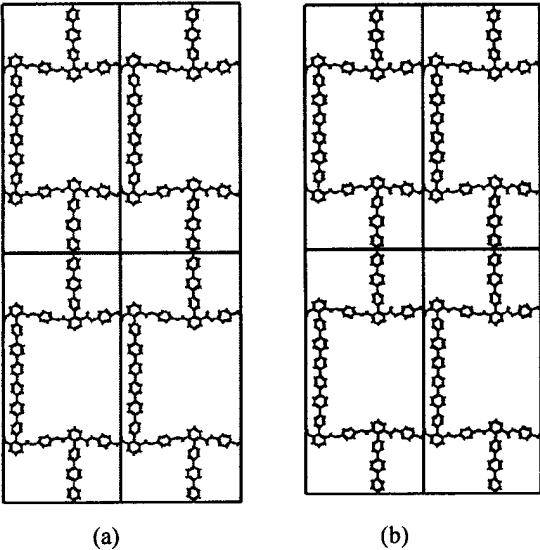


Fig. 4 Example of an optimized auxetic network containing amido links
(a) T8 (here T means a constrictive optimized conformer while 8 is the number of benzene rings on the beam structure); (b) S8 (here S means a patulous optimized conformer while 8 is the number of benzene rings on the beam structure)

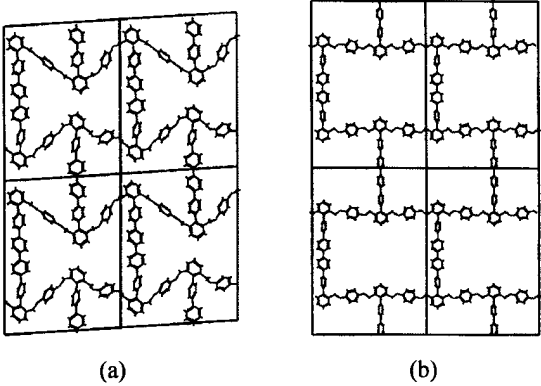


Fig. 5 Example of an optimized auxetic network containing ether links
(a) T6 (here T means a constrictive optimized conformer while 6 is the number of benzene rings on the beam structure); (b) S6 (here S means a patulous optimized conformer while 6 is the number of benzene rings on the beam structure)

Table 1. Poisson ratios of auxetic networks containing ester links

N	ν_{xy}	ν_{yx}	ν_{xz}	ν_{zx}	ν_{yz}	ν_{zy}
S6	-0.4943	-0.1307	0.4252	0.2382	0.1212	0.2568
S7	-0.5423	-0.1165	0.7422	0.1619	0.3144	0.3191
S8	-0.4781	-0.0718	0.1195	0.1834	0.0452	0.4619
S9	-0.1270	-0.0298	0.1369	0.1772	0.0266	0.1470
T6	-0.1028	-0.1246	-0.0057	-0.0184	0.0793	0.2125
T7	-0.0126	-0.0610	0.2921	0.3987	0.4699	0.1321
T8	-0.2068	-0.2037	0.0741	0.2693	0.0022	0.0081
T9	-0.1498	-0.1649	0.0804	0.2154	0.0040	0.0098

Table 2. Poisson ratios of auxetic networks containing amido links

N	ν_{xy}	ν_{yx}	ν_{xz}	ν_{zx}	ν_{yz}	ν_{zy}
S6	-1.7629	-0.1775	0.6631	0.2777	0.2566	1.0675
S7	-0.9911	-0.1987	0.5341	0.2178	0.1915	0.3895
S8	-1.1234	-0.2024	0.1684	0.3488	0.0670	0.7707
S9	-0.9146	-0.2849	0.1504	0.3674	0.0713	0.5593
T6	-0.2988	-0.6745	0.3181	0.5293	0.4603	0.3393
T7	-0.5459	-0.3000	0.5245	0.1495	-0.1916	-0.0994
T8	-0.2117	-0.1945	0.3954	0.2113	-0.0557	-0.0324
T9	-0.1027	-0.1105	0.5232	0.1717	-0.1241	-0.0379

Although the above results are somewhat encouraging, the successful syntheses of these networks still remain a challenge to polymer chemists, especially for a beam structure with 6–9 benzene rings. So next we propose two kinds of linear polymers containing reentrant building blocks, which we call *auxegens*, and the difference between these two kinds of linear polymers lies in the arrangement of auxegens on the main chain (see the optimized model examples in Figs. 6, 7). Also we started from two main starting conformers, *i.e.* the

constrictive conformer and the patulous conformer, and the corresponding Poisson ratios are listed in Tables 4, 5, respectively.

Table 3. Poisson ratios of auxetic networks containing ether links

N	v_{xy}	v_{yx}	v_{xz}	v_{zx}	v_{yz}	v_{zy}
S6	-0.2302	-0.0347	0.6628	0.0628	0.0220	0.0138
S7	-0.1456	-0.0422	-0.2412	-0.0299	0.0225	0.0096
S8	-0.3408	-0.1046	0.1089	0.1369	0.0543	0.2223
S9	-0.1849	-0.0959	0.0116	0.0145	0.0259	0.0626
T6	-0.0993	-0.1334	0.6351	0.2024	0.4736	0.1123
T7	-0.3156	-0.3773	0.3389	0.2604	0.1363	0.0876
T8	-0.2414	-0.3102	0.4171	0.2190	0.1654	0.0676
T9	-0.1793	-0.4572	0.9198	0.4470	0.1545	0.0294

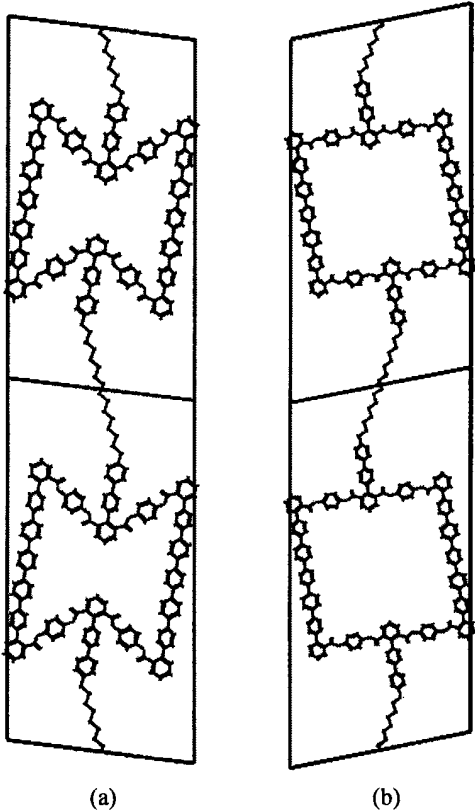


Fig. 6 Optimized model examples of kabob-like polymers with auxegens lying vertically on the main chain
a) T16 (here T represents a constrictive conformer while 16 is the number of carbon atoms on the flexible segment chain); b) S16 (here S represents a patulous conformer while 16 is the number of carbon atoms on the flexible segment chain)

As can be seen from the results in Tables 4, 5, the kabob-like polymers with auxegen lying vertically on the main chain can retain auxeticity to some extent while those with auxegen lying horizontally on the main chain cannot. A possible explanation is that for the latter, when stretched, the main deformation will occur along the main chain, while the arm structure of the auxegen hardly feels the tensile force because these auxegens are linked at the center of the beam structure. If so, then we might as well design a kind of polymer in which only half the auxegens on the main chain are linked together at the intersection of beam and arm structures (see Fig. 8). We suppose this kind of polymers should show auxeticity if the arm structure can feel the stretching when stretched.

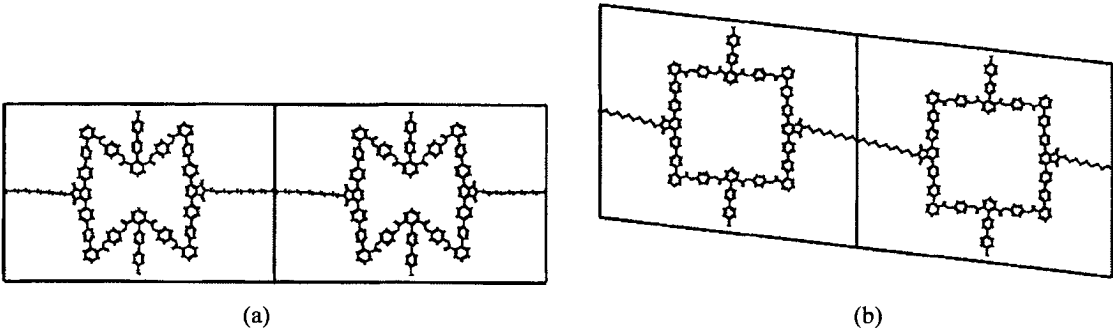


Fig. 7 Optimized model examples of kabob-like polymers with auxogens lying horizontally on the main chain
a) T20 (here T represents a constrictive conformer while 20 is the number of carbon atoms on the flexible segment chain);
b) S20 (here S represents a patulous conformer while 20 is the number of carbon atoms on the flexible segment chain)

Table 4. Poisson ratios of kabob-like polymers with auxogens vertically lying on the main chain

N	ν_{xy}	ν_{yx}	ν_{xz}	ν_{zx}	ν_{yz}	ν_{zy}
T10	-0.2384	-0.1103	0.1263	0.4189	0.0442	0.3170
T12	-0.3955	-0.1709	0.1349	0.4622	0.0734	0.5814
T14	-0.4697	-0.2118	0.0952	0.3925	0.0258	0.2356
T16	-0.5284	-0.2915	0.0712	0.3134	0.0181	0.1447
S10	-0.3465	-0.1284	0.0589	0.3458	0.0412	0.6522
S12	-0.4732	-0.3452	0.0427	0.2906	0.0332	0.4360
S14	-0.4715	-0.1881	0.0335	0.1857	0.0302	0.4199
S16	-0.7149	-0.4513	0.0068	0.0980	0.0113	0.2555

Table 5. Poisson ratios of kabob-like polymers with auxogens horizontally lying on the main chain

N	ν_{xy}	ν_{yx}	ν_{xz}	ν_{zx}	ν_{yz}	ν_{zy}
S14	0.3709	0.3229	0.0035	0.0963	0.0116	0.3636
S18	0.3666	0.3448	0.0054	0.1567	0.0110	0.3390
S20	0.3452	0.3452	0.0043	0.1335	0.0111	0.3465
S24	0.3324	0.2653	0.0047	0.1308	0.0079	0.2767
T14	0.0921	0.1965	0.0312	0.4120	0.0359	0.2219
T18	0.1147	0.1132	0.2845	0.2790	0.1139	0.1132
T20	0.2182	0.1404	0.2025	0.3402	0.0090	0.0234
T24	0.1579	0.3940	0.0368	0.1852	0.0020	0.0041

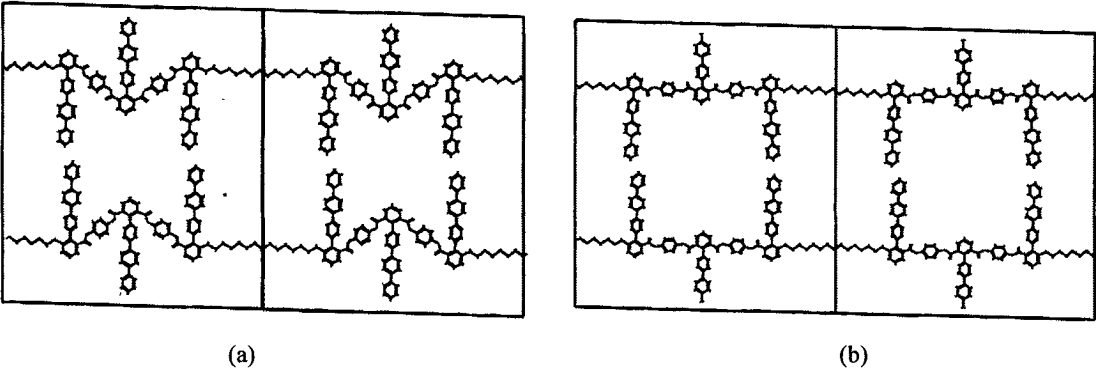


Fig. 8 Optimized model examples of half-kabob or pseudo-ladder-like polymers linked at the intersection of beam and arm structures
a) T15 (here T represents a constrictive conformer while 15 is the number of carbon atoms on the flexible segment chain)
b) S15 (here S represents a patulous conformer while 15 is the number of carbon atoms on the flexible segment chain)

Table 6. Poisson ratios of half-kabob or pseudo-ladder-like polymers linked at the intersection of beam and arm structures

N	ν_{xy}	ν_{yx}	ν_{xz}	ν_{zx}	ν_{yz}	ν_{zy}
T9	-0.5339	-0.2712	0.3038	0.5276	0.0426	0.1455
T11	-0.3879	-0.1833	0.2568	0.5269	0.0162	0.0703
T13	-0.6134	-0.2097	0.2150	0.3765	0.0566	0.2900
T15	-0.6301	-0.1584	0.0748	0.2505	-0.0010	-0.0140
T17	-0.9727	-0.2451	0.0348	0.1970	0.0026	0.0583
S9	-0.1119	-0.0069	0.1455	0.2209	0.0213	0.5271
S11	-0.0121	-0.0008	0.1550	0.2358	0.0204	0.4728
S13	0.1973	0.0095	0.0973	0.1519	0.0101	0.3287
S15	0.0590	0.0043	0.1566	0.3157	0.0210	0.5805
S17	0.0256	0.0010	0.1237	0.1963	0.0065	0.2694

The values of the resulting Poisson ratios are listed in Table 6. It is very interesting to notice that for the constrictive conformers, they do show auxeticity as we expected while the situation seems less satisfactory for the patulous conformers (only two structures show auxeticity). And yet this is consistent with the prediction of the Gibson-Ashby model.

We therefore conclude that the acquisition of auxeticity depends greatly on the main deformation mechanism and the moving abilities of all atoms in a molecular structure, and a better understanding of them requires further experimental and theoretical investigations.

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REFERENCES

- 1 Evans, K.E., Nkansah, M.A., Hutchinson, I.J. and Rogers, S.C., *Nature*, 1991, 353: 124
- 2 Wei, G.Y., *Polym. Bull. (in Chinese)*, 1995, (4): 234; *Mater. Rev. (in Chinese)*, 2003, 17(1): 8
- 3 Alderson, A., *Chem. Ind.*, 1999, (10): 384
- 4 Evans, K.E. and Alderson, A., *Adv. Mater.*, 2000, 12(9): 617
- 5 Lakes, R.S., *Science*, 1987, 235: 1038
- 6 Wojciechowski, K.W., *Mol. Phys.*, 1987, 61: 1247
- 7 Wei, G.Y. and Edwards, S.F., *Comput. Polym. Sci.*, 1992, 2: 44
- 8 Baughman, R.H. and Balvao, D.S., *Nature*, 1993, 365: 735
- 9 Guo, Y. and Goddard III, W.A., *Chem. Phys. Lett.*, 1995, 237: 72
- 10 Baker, J.B., Douglass, A.G. and Griffin, A.C., *Abstr. Pap. Am. Chem. Soc.*, 1995, 210: 146
- 11 He, C.B., Liu, P.W. and Griffin, A.C., *Macromolecules*, 1998, 31: 3145
- 12 Grima, J.N., Jackson, R., Alderson, A. and Evans, K.E., *Adv. Mater.*, 2000, 12(24): 1912
- 13 Wu, H.M. and Wei, G.Y., *Acta polymerica sinica (in Chinese)*, 2004, (2): 201
- 14 "Cerius2 4.0 User Guide—Property Prediction", Molecular Simulations Inc., San Diego, 1999
- 15 Gibson, L.J., Ashby, M.F., Schajer, G.S. and Roberson, C.I., *Proc. R. Soc. London*, 1982, A382: 25
- 16 Gibson, L.J. and Ashby M.F., "Cellular Solids: Structure and Properties", Pergamon Press, Oxford, 1988, p.69
- 17 Almgren, R.F., *J. Elasticity* 1985, 15: 427
- 18 Mayo, S.L., Olafson, B.D. and Goddard III, W.A., *J. Phys. Chem.* 1990, 94: 8897