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Development of novel poly(phenylacetylene) network polymers and their mechanical behaviour

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Auxetics exhibit the anomalous property of getting wider rather than thinner when uniaxially stretched, i.e. have a negative Poisson's ratio. This work presents the results of simulations performed on a number of hypothetical poly(phenylacetylene) networks which are meant to mimic the behaviour of rotating scalene triangles. It was shown that such systems do indeed exhibit a negative Poisson's ratio being as low as *c.* -1.2, i.e. lower than the *c.* -1 found in earlier systems. This negative Poisson's ratio is due to the relative rotation of nanoscopic units.

1 Introduction The first auxetic system (i.e. a material which expands laterally when uniaxially stretched) was reported by Voigt [1], when single crystals of iron pyrites were described as having a negative Poisson's ratio. However, at that time this phenomenon was regarded as an anomaly, and the behaviour was attributed to twinning defects [2]. It was only in the 1980s that interest in such auxetic behaviour started to grow, especially through the important contributions made by pioneers such as Lakes [3], Evans [4] and Wojciechowski [5].

Since then, a wide range of auxetic systems have been discovered, including partially auxetic metals [6], cubic metallic alloys of extremely negative ($\nu < -1$) Poisson's ratios [7], completely auxetic metallic sulphides (showing negative ν in all directions) [7], zeolites [8–14] and silicates [15–21], which have been found to occur in nature. Other auxetic materials have been proposed or processed [4, 22–24], and auxetic foams have been produced from conventional foams by a number of different conversion processes [3, 25, 26]. It has also been recently discovered that cellulose, a major constituent of plant tissues, demonstrates auxetic properties [27, 28]. All of the above-mentioned systems can be characterised as having macro-, micro- or nanostructures with specific geometric features, which undergo particular deformation mechanisms. In all cases, the auxetic behaviour has been explained through the geometrical changes (deformation mechanisms) taking place as a result of uniaxially applied loads.

A significant corpus of work has also been conducted on hypothetical molecular networks which have geometries that resemble well-known larger scale auxetic structures. The best-known of these molecular structures are the reflexyne networks [29], proposed by Evans et al. [30] so as to mimic the re-entrant honeycombs. Other examples of such nano-level auxetics include the triangular networks developed by Grima and Evans [8], called the polytriangles-*n*-yne systems with *n* being the number of triple bonds in the chains (see the polytriangles-2-yne shown in Fig. 1a as an example). The deformation mechanism which leads to auxetic behaviour in this structure is the 'connected rotating rigid triangles' model, highlighted in Fig. 1b, which is an example of many rotating rigid unit mechanisms now known to be responsible for auxeticity in a wide range of materials, including the well-known auxetic naturally occurring silicate α-cristobalite and the zeolite natrolite [21, 31].

The work presented here explores a number of new structures which are based on the phenylacetylene chemistry, yet having more viable substitutions of the benzene ring, where their auxetic potential is assessed with the aim of identifying any systems which could exhibit interesting auxetic properties. These novel network-type polymers are

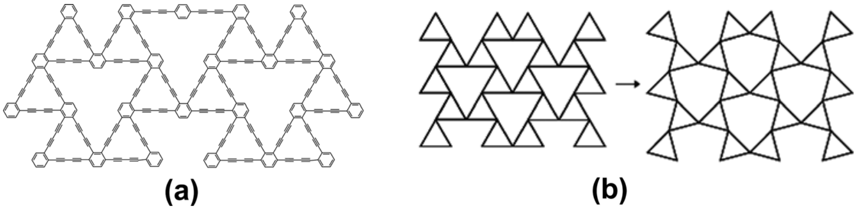


Figure 1 (a) The chemical structure of polytriangles-2-yne [8]; (b) the 'rotating triangles' model which depicts the idealised deformation mechanism of polytriangles-2-yne.

inspired by the generalised polytriangles networks studied by Grima et al. [32] and Chetcuti et al. [33] and are similar to molecular-level systems that already exist in the literature [34]. However, these new systems possess additional versatility imparted to them through some chemical structural variations that give rise to interesting systems with different mechanical properties from the parent systems.

2 The proposed new nano-networks

In the systems being proposed here, the triangular units are represented through a '1,3,5-triacetylenylbenzene'-like unit, connected together through *cis*-ethylene junctions as in Fig. 2a. Such a construction would not only avoid the 1,2,3,4-tetrasubstituted phenyl rings in the original nano-polytriangles network proposed by Grima [8], but more importantly, permit the triangles to assume a non-equilateral shape, meaning that it would become possible to construct a wider variety of triangular networks of the form as discussed in Grima, Chetcuti et al.'s work, giving significantly more versatility.

In fact in such systems, one is not constrained to having the triangles equilateral, an imposition previously imparted through the 60° internal angles at the vertices which result from the substitution pattern of the benzene rings in Grima's polytriangles [8]. In the novel systems, assuming that the triangles are of side lengths a, b, c defined as in Fig. 2b, then these lengths a, b, c can assume a much wider range of distinct values which may be approximated by

$$a = \sqrt{L_1^2 + L_2^2 - 2L_1L_2\cos\left(\frac{2\pi}{3}\right)} = \sqrt{L_1^2 + L_2^2 + L_1L_2}, \tag{1}$$

$$b = \sqrt{L_2^2 + L_3^2 - 2L_2L_3\cos\left(\frac{2\pi}{3}\right)} = \sqrt{L_2^2 + L_3^2 + L_2L_3}, \tag{2}$$

$$c = \sqrt{L_1^2 + L_3^2 - 2L_1L_3\cos\left(\frac{2\pi}{3}\right)} = \sqrt{L_1^2 + L_3^2 + L_1L_3}, \tag{3}$$

where L_i is the length indicated in Fig. 2b, which may be related to the length of the acetylene chain through

$$L_i = |C_R - C_R| + |C_R - C_1| + |C_2 - C_1| + |C_2 - C_2| + (2n_i - 1)|C_1 - C_1|, \tag{4}$$

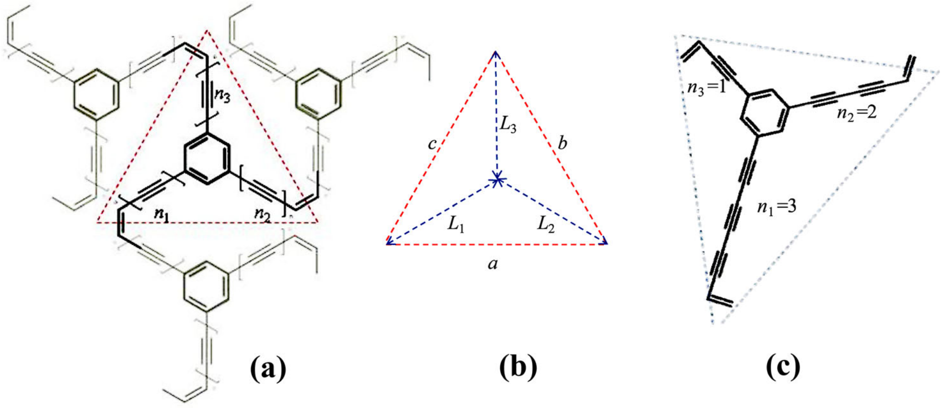


Figure 2 (a) The 1,3,5-triacetylenylbenzene group which makes up the triangular units that are connected together through *cis*-ethylene junctions; (b) the triangular unit, indicating triangle side lengths a, b and c, as well as the acetylene-chain-related lengths L_1, L_2 and L_3; (c) the 3,2,1-polytriangles-Type II system, indicating the location and assigned values of n_1, n_2 and n_3 which form the basis of the suggested nomenclature. (Note that the location of n_i is determined by referring to the 'generic rigid triangles' model proposed by Grima et al. [32].)

where n_i is the number of triple bonds in the chain whilst $|C_R - C_R|$ is the average length of a C–C bond in a benzene ring, $|C_R - C_1|$ is the average bond length between a C atom in a benzene ring and a C atom in an acetylene chain, $|C_2 - C_1|$ is the average length between bonded sp^2 and sp hybridised C atoms, $|C_2 - C_2|$ is the average length between two bonded sp^2 hybridised C atoms, whilst $|C_1 - C_1|$ is the average length between two bonded C atoms in an acetylene chain. Taking parameters from standard force-fields, such as the Dreiding force-field [35], this length becomes approximately equal to:

$$L_i = (1.39\,\text{Å}) + (1.29\,\text{Å}) + (1.26\,\text{Å}) + (1.33\,\text{Å}) + (2n - 1)(1.19\,\text{Å}) = [4.08 + 2.38n_i]\,\text{Å}. \quad (5)$$

For example, a triangle made from systems having $n_1 = 1$, $n_2 = 2$ and $n_3 = 3$ would have side lengths of:

$$[a \times b \times c] \approx [9.86 \times 13.96 \times 12.08]. \quad (6)$$

Once again, to simplify the discussion, a simple nomenclature system will be used for these systems, which will be termed (n_1,n_2,n_3)-polytriangles-Type II, where (n_1,n_2,n_3)- refer to the number of triple bonds per acetylene chain, as indicated in Fig. 2c. Note that the Type II suffix is being used to distinguish these novel systems from the ones described originally by Grima [8].

Given the large number of systems that may be constructed in the manner described above, modelling was only performed on a small sub-section of the possible systems. This was also done in order to identify any issues which could potentially reduce the auxetic character of these systems.

3 Simulations A number of (n_1,n_2,n_3)-polytriangles-Type II organic networks having the connectivity illustrated in Fig. 2 were constructed with the number of carbon–carbon triple bonds in each of the three acetylene chains (n_1,n_2,n_3) being (1,1,1), (2,2,2), (3,3,3), which systems where meant to result in equilateral triangles, or (2,1,1), (1,2,2), (2,2,3), (2,3,3), (3,2,1), which systems where meant to result in non-equilateral triangles.

For all systems, the starting unit-cell structures for the 2D networks listed above were constructed using the Builder tools in Materials Studio V.6.0 (Accelrys, Inc. USA) and placed in the global *YZ* plane, with the alignment shown in Fig. 3. This alignment ensured that the networks remained aligned parallel to the *YZ* plane as much as possible in the simulations and is not dissimilar to that employed by Grima et al. in the analytical model of the general polytriangular systems.

Periodic boundary conditions were applied with the [001] cell vector being aligned parallel to the global *Z* direction, while the [010] direction was aligned to lie in the *YZ* plane. An energy expression was set up for each of the constructed systems using three different force-fields: Dreiding [35], PCFF [36, 37] and COMPASS [38–40]. These force-fields were chosen since they have all been adequately parameterised for all atom types used in this study, and they have in fact already been used to successfully model the properties of the related molecular-level reflexyne and flexyne systems [41–43]. In all cases the default force-field settings were applied, with the exception of non-bond interactions (Van der Waals and Coulombic interactions) summation method, for which the Ewald procedure [44] was used. Note that charge equilibration [45] was performed prior to using the Dreiding force-field, since this force-field does not include a list of partial charges to be used in formulating the energy expression.

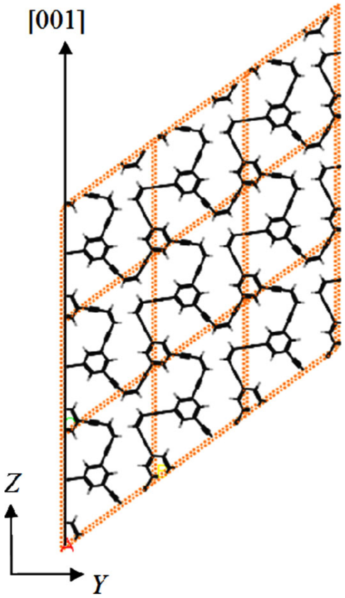


Figure 3 A representative example of the newly designed networked polymer, the (1,1,1)-polytriangles-Type II system.

The energy of the systems was minimised as a function of the atomic coordinates and six cell parameters to the earlier of reaching the default fine convergence criteria (including an energy change threshold of 0.0001 kcal mol^{-1} and maximum force of 0.005 kcal mol^{-1} Å^{-1}) or 15,000 minimisation steps, whichever occurs first. The SMART minimiser implemented in Materials Studio was used to perform the energy minimisation calculation, which is a cascade of the steepest descent, ABNR (Adjusted basis set Newton–Raphson), and quasi-Newton methods. This step was repeated three times to enable re-calculation of the non-bond list and to ensure complete minimisation of the structure.

The resulting systems were visually analysed and the mechanical properties were calculated using the 'constant-strain' approach (using the Forcite module within Materials Studio). The maximum strain amplitude was set to 0.010 i.e. 1.0% strain and seven distorted structures were generated for each strain pattern. The on-axis Young's moduli and in-plane on-axis Poisson's ratios and shear modulus for these systems were then calculated from the compliance matrix as shown below:

$$E_x = \frac{1}{s_{11}}, \quad E_y = \frac{1}{s_{22}}, \quad E_z = \frac{1}{s_{33}}, \tag{7}$$

$$\nu_{yz} = -\frac{s_{32}}{s_{22}}, \quad \nu_{zy} = -\frac{s_{23}}{s_{33}}, \quad G_{yz} = \frac{1}{s_{44}}, \tag{8}$$

where s_{ij} are the elements of the compliance matrix **S**, E_x, E_y and E_z are the Young's moduli in the X, Y and Z directions, ν_{yz} and ν_{zy} are the Poisson's ratios in the YZ plane for loading in the Y and Z directions respectively and G_{yz} is the on-axis shear modulus in the YZ plane.

From the simulated on-axis stiffness matrix, the in-plane off-axis properties were calculated using standard axis transformation techniques as described in Nye [46] and implemented and coded for the Maple package by Grima [47].

Note that all simulations were performed using just two triangular units per unit cell, thus resulting in a parallelogramic unit cell, since a preliminary convergence study suggested that this system is sufficient to adequately model the properties of such system.

4 Results

The simulated structural properties of the constructed polytriangles systems are summarised in Fig. 4, while their simulated mechanical properties are given in Fig. 5 together with plots of the off-axis Poisson's ratio upon rotation around the X-axis. These results immediately show that for all the studied systems, most combinations of $n_i = 1$, 2 or 3 in the structure can give a negative Poisson's ratio in the YZ plane, with ν being more negative off-axis.

The structural properties were first analysed and compared by obtaining information on the sizes of the unit cell and also by visually observing the YZ and XY projections of the minimised structures. It can be noted that in general, each system minimised with different force-fields achieved similar conformations and characteristics, including volume and density. A few exceptions were noted though, particularly in systems having longer acetylene chains such as (3,2,1)- and (3,3,3)-polytriangles systems. In these cases, slightly different packing was achieved with different force-fields. The acetylene chains, for example, overlapped each other in some cases but did not in others.

It can also be noted from the XY projections that all the systems adopted a slightly out-of-plane configuration, the extent of which seems to be dependent on the length of the acetylene chains, n. For example, this out-of-plane bending was very significant in the (3,3,3)-polytriangles-Type II system, where long acetylene chains overlap in order to be able to pack within a small space so as to maximise the density. Other systems such as the (2,3,3)-polytriangles-Type II system, also packed in a highly dense manner but they tend to pack without the need of any chains overlapping. Such packing is less efficient and gives rise to rather large pores. In contrast to this, the (1,1,1)-polytriangles-Type II system packs more efficiently due to the short acetylene chains (having only one carbon–carbon triple bond), thus having relatively smaller pores in the minimised structure. Nevertheless, despite this out-of-plane bending, the systems generally still retained their expected geometric features when viewed down their YZ plane, in the sense that one can still visualise the expected 'connected triangles' motif. One should also note that the properties of the (1,1,1)-polytriangles system showed significant consistency when simulated with different force-fields, something which to a certain extent was not entirely evident in most of the other systems. This may be attributed to the greater degree of freedom imparted on the systems by the longer acetylene chains in cases where $n_i > 1$.

On analysing the mechanical properties results (Fig. 5), it is immediately evident that various values of negative Poisson's ratio were obtained, ranging up to -1.2 in the (3,2,1)-polytriangles system. Exceptionally low Poisson's ratios were also obtained in the (2,1,1)-system (when simulated with the Dreiding force-field) and the (2,2,2)-system (when simulated with the PCFF force-field), which exhibited ν of up to -1.5 and -2, respectively. This is very significant as this high magnitude of auxeticty had not been demonstrated in the earlier work by Grima [8], as expected since those systems had triangular units which were equilateral, i.e. even in their most idealised scenario, are only expected to achieve maximum auxeticity corresponding to Poisson's ratios of -1. Such bounds in the Poisson's ratio are relaxed for the more general models built from scalene triangles, with the result that Poisson's ratios which are more negative than -1 may be obtained, as is the case reported here. It is however unfortunate that these more general systems are no longer isotropic, as discussed in detail elsewhere [33]. Here it should be noted that in the study performed here, such anisotropy was very evident, as expected. Anisotropy was also found in the systems having $n_1 = n_2 = n_3$, such as the (1,1,1)-, (2,2,2)- and (3,3,3)-polytriangles systems even if such systems were meant to mimic the isotropic -1 behaviour, however this was not the case. This unexpected behaviour is probably because of the out-of-plane bending which did not allow the triangular units to behave as ideal units in a single plane.

5 Deformation mechanism

In attempt to understand the reason behind this auxetic behaviour, additional simulations were performed where the systems were uniaxially stretched in the Y and Z directions and the minimum energy configurations of the stretched structures were obtained. These simulations were performed through the Cerius^2 modelling environment (Accelrys, Inc.) using the previously minimised structures as starting points. Here we report only a sample of these simulations, namely those performed on the (1,1,1)-polytriangles-Type II system when this was stretched by application of a uniaxial stress of 1.0 GPa in the Y direction.

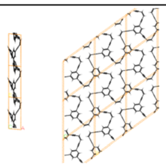
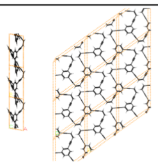
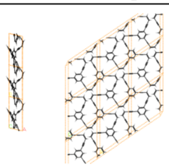
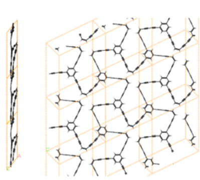
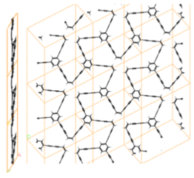
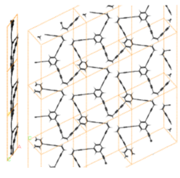
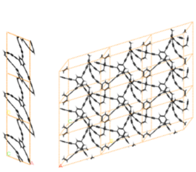
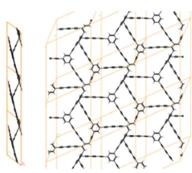
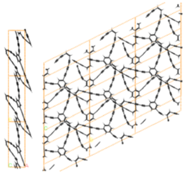
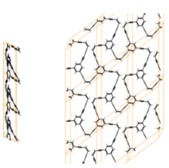
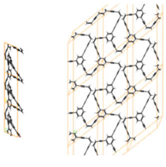
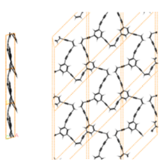
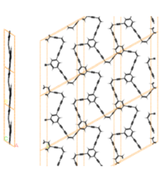
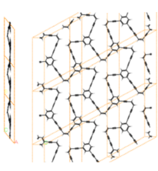
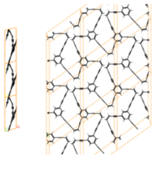
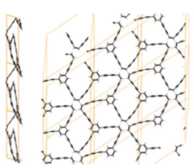
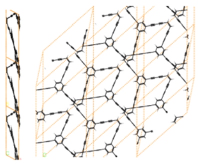
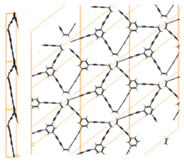
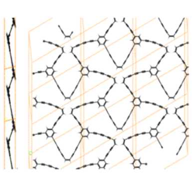
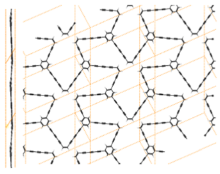
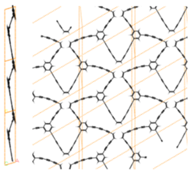
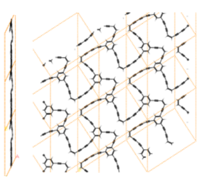
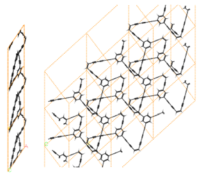
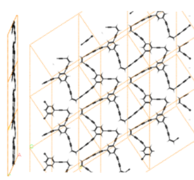
(n_1,n_2,n_3)-polytriangles Type II systems		**a_x (Å)**	**b_y (Å)**	**c_z (Å)**	**Density ($\mathrm{g\ cm^{-3}}$)**	**Volume ($\mathrm{cm^{-3}}$)**	**Dreiding** Y X Z Y	**PCFF** Y X Z Y	**Compass** Y X Z Y
(1,1,1)-system	Dreiding	3.96	10.3	12.75	1.19	520.46			
	PCFF	4.36	10.06	12.36	1.14	542.21			
	Compass	4.29	9.92	11.97	1.21	509.05			
(2,2,2)-system	Dreiding	3.36	14.75	17.91	0.97	886.48			
	PCFF	3.44	15.57	17.91	0.9	957.82			
	Compass	3.4	14.62	17.13	1.01	852.2			
(3,3,3)-system	Dreiding	7.15	13.02	10.09	1.08	938.64			
	PCFF	4.25	14.21	18.86	0.89	1139.18			
	Compass	5.37	14.85	10.91	1.17	870.42			
(2,1,1)-system	Dreiding	3.87	9.83	16.52	1.11	628.01			
	PCFF	4.21	9.49	16.46	1.06	658.47			
	Compass	4.17	9.29	16.1	1.12	624.25			
(2,2,1)-system	Dreiding	3.26	11.91	17.81	1.07	691.56			
	PCFF	3.25	12.29	17.69	1.05	706.04			
	Compass	3.56	10.7	16.55	1.17	629.35			
(2,2,3)-system	Dreiding	3.85	15.06	16.4	0.99	951.47			
	PCFF	4.02	14.63	15.71	1.01	924.53			
	Compass	3.29	15.25	18.29	1.02	917.61			
(2,3,3)-system	Dreiding	3.36	16.69	19.66	0.92	1104.36			
	PCFF	3.27	21.02	18.35	0.81	1260.96			
	Compass	3.36	16.71	19.67	0.92	1105.39			
(3,2,1)-system	Dreiding	3.41	15.23	16.69	0.99	866.95			
	PCFF	5.05	13.29	11.97	1.07	803.16			
	Compass	3.35	15.55	16.92	0.97	880.86			

Figure 4 Structural properties of the resulting minimised (n_1,n_2,n_3)-polytriangles-Type II systems obtained with Dreiding, PCFF and COMPASS force-fields, including views of the systems in the *YX* and *ZY* planes.

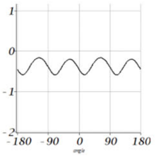
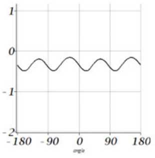
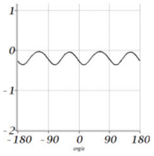
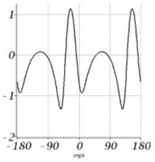
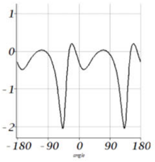
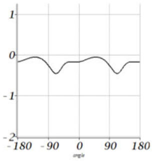
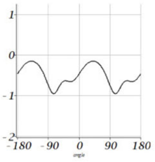
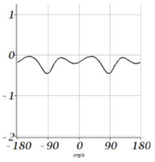
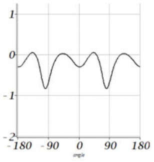
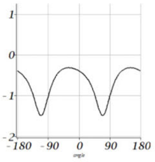
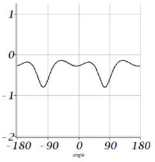
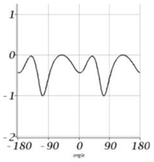
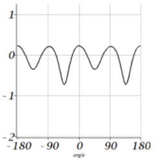
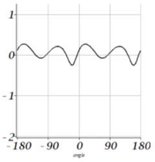
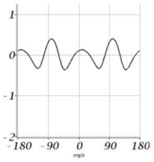
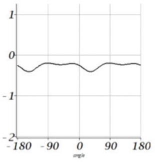
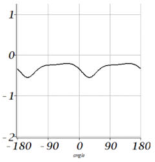
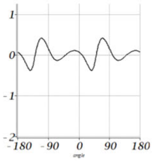
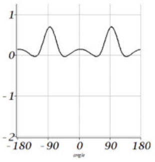
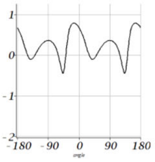
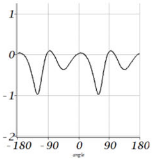
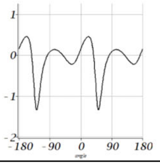
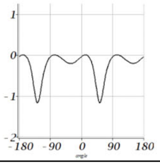
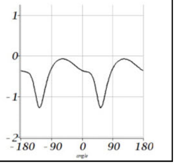
(n_1,n_2,n_3)-polytriangles-Type II systems		Mechanical Properties					Off-axis plots		
		E_y (GPa)	E_z (GPa)	G_{yz} (GPa)	ν_{yz}	ν_{zy}	Dreiding	PCFF	Compass
(1,1,1)-system	Dreiding	10.71	9.37	6.58	-0.45	-0.40			
	PCFF	8.73	10.06	5.99	-0.35	-0.40			
	Compass	11.43	9.52	5.41	-0.27	-0.22			
(2,2,2)-system	Dreiding	12.44	1.62	1.59	-0.67	-0.09			
	PCFF	5.16	1.44	1.68	-0.29	-0.08			
	Compass	5.57	8.16	3.36	-0.18	-0.26			
(3,3,3)-system	Dreiding	2.10	3.29	1.38	-0.48	-0.74			
	PCFF	3.70	9.00	2.39	-0.19	-0.46			
	Compass	3.81	8.66	1.77	-0.31	-0.70			
(2,1,1)-system	Dreiding	2.43	6.21	3.43	-0.40	-1.03			
	PCFF	5.16	11.26	3.82	-0.28	-0.62			
	Compass	5.59	7.40	2.24	-0.44	-0.59			
(2,2,1)-system	Dreiding	3.51	3.22	6.01	0.22	0.20			
	PCFF	22.77	9.67	5.97	0.11	0.05			
	Compass	6.30	19.80	9.34	0.10	0.31			
(2,2,3)-system	Dreiding	6.25	4.98	4.17	-0.26	-0.21			
	PCFF	4.78	3.58	2.98	-0.34	-0.26			
	Compass	2.59	5.96	2.36	0.07	0.16			
(2,3,3)-system	Dreiding	2.98	14.84	3.40	0.13	0.66			
	PCFF	10.96	10.08	7.81	0.59	0.54			
	Compass	1.81	5.80	3.86	0.02	0.06			
(3,2,1)-system	Dreiding	2.19	1.18	1.15	0.14	0.08			
	PCFF	2.38	2.51	2.08	-0.05	-0.05			
	Compass	2.30	1.98	1.17	-0.31	-0.70			

Figure 5 Mechanical properties of (n_1,n_2,n_3)-polytriangles-Type II systems, including the on-axis Young's moduli and shear modulus, as well as the in-plane on-axis Poisson's ratios and off-axis plots of the Poisson's ratio upon rotation around the *X*-axis.

Figure 6 depicts the resulting deformation which ultimately gave rise to auxetic behaviour. These images confirm that the rotating triangles mechanism is indeed taking place, thus explaining the observed negative Poisson's ratio.

This finding is very significant because it confirms that the novel designs proposed here contribute to the regime of molecular-level auxetic systems and also provide a better understanding of the behaviour of such systems through the combined information of their structural and mechanical

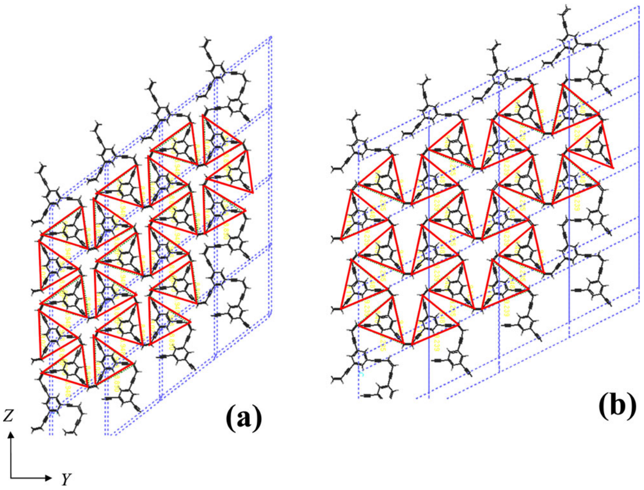


Figure 6 The rotating-triangles model which explains the deformation mechanism taking place in the novel polytriangles-Type II systems, in this case the (1,1,1)-polytriangles-Type II system, where (a) is the initial structure at 0.0 GPa and (b) is the stretched structure at 1.0 GPa stress along the Y direction.

properties. The resulting auxetic potential of the (n_1,n_2,n_3)-polytriangles-Type II systems arising from the 'rotating triangles' mode of deformation is particularly important, since it confirms that the 'rotating rigid units mechanism' is indeed one of the more superior deformation mechanisms which drives the system towards a negative Poisson's ratio.

On closer inspection of the results from these simulations, one may note that the deformation mechanism also involves the flexure of the acetylene chains during stretching, which not only bring about the rotation of the triangular units, as highlighted in Fig. 6, while keeping their connections through the *cis*-ethylene bond, but also result in some deformations of the triangles themselves. These deformations of the triangular units themselves would not have been accounted for in the derivation of the analytical model, which only considers the highly idealised scenario where the triangles are perfectly rigid, and are the most likely cause for the deviations from the predictions of the analytical model.

Before concluding, it is important to point out that this study was based on static mechanical simulations, and it would be very interesting to understand the behaviour of such systems at various temperatures and pressures, since these factors may have a significant effect on the structural properties, and hence also on the mechanical behaviour, of these systems. Besides, such a modelling study also assumes that the networks under consideration are perfect networks, with no random defects (such as lack of connectivity). Work we and others performed on non-perfect systems suggests that in general, imperfections may result in significant changes to the Poisson's ratio [48–51]. Therefore, it would also be interesting to study such systems from a more realistic point of view in order to understand how such defects may ultimately affect their mechanical properties.

Finally it is also important to highlight that all the systems studied here are hypothetical and it is still unknown whether they can be successfully synthesised, which is a problem that has already been encountered with reflexyne and flexyne systems. However, it is very important to further the research of such hypothetical networks since they provide a better understanding of the behaviour of molecular-level systems, while also leading to the design of new auxetic systems.

6 Conclusions This study has shown that the novel molecular-level (n_1,n_2,n_3)-polytriangles-Type II systems have auxetic potential, with all the systems exhibiting negative Poisson's ratio through the 'rotating triangles' deformation mechanism. These systems were found to be anisotropic, even in systems were $n_1 = n_2 = n_3$, which unexpected behaviour can be attributed to their lack of planarity. These poly(phenylacetylene) networks show very promising auxetic properties, and these predictions encourage further research into similar systems and their chemistry, with the hope of having them successfully synthesised and mechanically tested in the future. Bearing in mind that these systems are also likely to benefit from additional other interesting properties, such as high electrical connectively due to their extensive π-bonding, we hope that this work will provide an impetus to such further studies.

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