Phys. Status Solidi B **248**, No. 1, 111–116 (2011) / **DOI** 10.1002/pssb.201083979

physica status solidi pss b
www.pss-b.com
basic solid state physics

Molecular networks with a near zero Poisson's ratio

Joseph N. Grima* **and Daphne Attard**

Faculty of Science, Department of Chemistry, University of Malta Msida, Malta

Received 10 June 2010, revised 26 July 2010, accepted 30 July 2010

Keywords molecular networks, mechanical properties, zero Poisson's ratio, auxetic, negative Poisson's ratio

---

* Corresponding author: e-mail joseph.grima@um.edu.mt, Phone: +356 2340 227, Fax: +356 2133 0400

A series of polyphenylacetylene networks are predicted to exhibit the not so common property of a near-zero Poisson's ratio, a property which is highly desirable in various practical applications. This behaviour is explained qualitatively in terms of a simple honeycomb model involving flexure, hinging and/or stretching of acetylene chains.

1 Introduction The Poisson's ratio of a material describes how the dimensions of the material change as it is uniaxially loaded. Most common materials have a positive Poisson's ratio, i.e. they contract laterally when stretched. However, materials can also have negative Poisson's ratios (auxetic materials [1]), i.e. expand when stretched [1–33] (e.g. certain foams [5–8], polymers [1, 2–4, 9–15], metals and minerals [16–21], honeycombs and models [22–26]) or a zero Poisson's ratio (ZPR), i.e. their lateral dimensions remain unchanged during uniaxial loading (e.g. cork [34], beetle's wing's membrane [35], scaffold-type and rectangular cellular structures [36, 37] and polymer gels [38] were found to have a zero or near-ZPR). In this respect we note that although in recent years there have been much attention being given to materials exhibiting negative Poisson's ratios in view of their superior properties when compared to conventional materials [5, 27, 28], the area of ZPR materials have so far been greatly ignored, probably because of the fact that such property is not easy to achieve. Nevertheless, it should be noted that ZPR is a highly desirable property especially in applications where changes in the lateral dimensions are detrimental to a system's performance. ZPR materials are also particularly useful in the manufacture of cylindrical surfaces, something which neither conventional nor auxetic materials can do very well (auxetics tend to form doubly curved surface [1, 5, 39] whilst conventional materials tend to form saddle shaped surfaces).

In this work we present new type of molecular systems which have been predicted to exhibit a (virtually) ZPR. These systems are designed to mimic the geometry of the honeycomb illustrated in Fig. 1c-i, which honeycomb has both non-re-entrant and re-entrant features (normally associated with conventional and auxetic behaviour, respectively, see Fig. 1a and b) and is henceforth referred to as a 'semi re-entrant honeycomb'. It has been shown that such honeycombs exhibit ZPR for stretching in the Ox_1 direction if the honeycombs deform through flexure or hinging of the honeycomb cell walls (idealized flexure/hinging models) or even through stretching of the cell walls (idealized stretching model) [40–43]. Deformation for loading in the Ox_2 direction of the idealized honeycomb model is more restrained: by virtue of the periodicity of the structure, only stretching of the vertical ribs would be permitted (idealized stretching model) as other deformations would introduce distortions that are not allowed in perfectly planar honeycombs. In fact, an idealized network would have resisted deformations through in-plane hinging or flexure of the cell walls for loading in the Ox_2 direction since the re-entrant layer has a tendency to expand whilst the non-re-entrant layer has a tendency to contract laterally when stretched in the Ox_2 direction, two properties which obviously cannot occur simultaneously. Such 'idealized stretching model' is also expected to exhibit ZPR for uniaxial loading in the Ox_2 direction.

These idealized 'hinging/flexure/stretching' models [40–43] for the semi re-entrant honeycomb suggest that the Poisson's ratio is scale independent, meaning that the ZPR effect can be manifested at any length scale. Thus, in theory, it is possible to achieve the desired ZPR even at the molecular level by designing molecular networks with similar geometric features.

A molecular system which could possibly mimic this behaviour is one which replaces the ribs by acetylene chains which are connected together by benzene rings that act as junctions as shown in Fig. 1c-ii. Similar molecular networks which consist of only the re-entrant or the non-re-entrant feature have already been studied and shown to exhibit negative and positive Poisson's ratios, respectively [1, 2–4].

Table 1 Simulated Poisson's ratio for different (*m*,*n*)-semiflexynes, (*m*,*n*)-flexynes and (*m*,*n*)-reflexynes. Note that the results confirm that the Poisson's ratio for the semi-flexynes are approximately zero in sharp contrast to those obtained for the flexynes and reflexynes which are very similar to ones published elsewhere by Evans et al. and Grima et al.

	(*m*,*n*)-	(1,4)-	(1,5)-	(1,6)-	(2,4)-	(2,5)-
semi re-entrant	ν_{23}	0.03	0.03	0.02	0.00	0.00
(*m*,*n*-semiflexynes)	ν_{32}	0.06	0.08	0.05	−0.01	0.00
non-re-entrant	ν_{23}	0.29	0.27	0.25	0.54	0.49
(*m*,*n*-flexynes)	ν_{32}	0.56	0.52	0.85	0.93	1.05
re-entrant	ν_{23}	−0.40	−0.37	−0.31	n.a.	−0.77
(*m*,*n*-reflexynes)	ν_{32}	−0.34	−0.41	−0.46	n.a.	−0.50

2 Simulations Referring to Fig. 1, a series of (*m*,*n*)-flexyne, (*m*,*n*)-reflexyne and (*m*,*n*)-semiflexyne polyphenyl acetylene honeycombs with $m = 1$, 2 and $n = 4$–6 were modelled through molecular mechanics simulations. Simulations of the minimum energy configurations for the systems discussed here were carried out using the Cerius^2 V4.1 (Accelrys, Inc., San Diego, USA) molecular modelling package. Using periodic boundary conditions, the networks where represented as infinite layers aligned parallel to the *YZ* plane in such a way that the vertical *n* chains align approximately to the *Z* directions (i.e. the Ox_2 direction in Fig. 1 was aligned with the *Z* direction and the Ox_1 was constrained to lie in the *YZ* plane) and were permitted to stack freely on top of each other along the third direction (*X*), without imposing any restraints on the lattice parameters. The energy expressions *E* were set up using parameters from the PCFF force-field [44]. Non-bond terms were added using the Ewald summation technique [45]. The mechanical properties were also calculated from the 6 × 6 stiffness matrix ***C*** (and its inverse, the compliance matrix ***S***) for the minimum energy configuration of the polyphenylacetylene systems obtained from the second derivative of the potential energy function since:

$$c_{ij} = \frac{1}{V}\frac{\partial^2 E}{\partial\varepsilon_i\partial\varepsilon_j}, \quad i,j = 1,2,\dots,6, \tag{1}$$

where *E* is the energy expression, *V* the volume of the unit cell and ε_i, ε_j are strain components. The Poisson's ratios

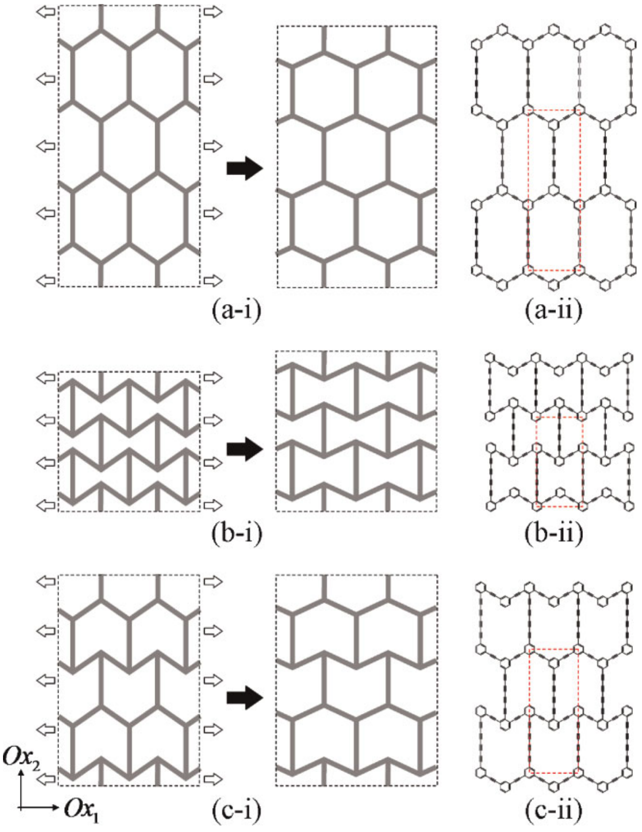


Figure 1 (online colour at: www.pss-b.com) The geometry of (a-i) a non-re-entrant, (b-i) re-entrant and (c-i) semi re-entrant honeycombs deforming through hinging and their respective molecular equivalent: (a-ii) (*m*,*n*)-flexyne, (b-ii) (*m*,*n*)-reflexyne and (c-ii) the new (*m*,*n*)-semiflexynes where in accordance with existing nomenclature, *m* and *n* are the number of triple bonds in the inclined and vertical acetylene chains, respectively.

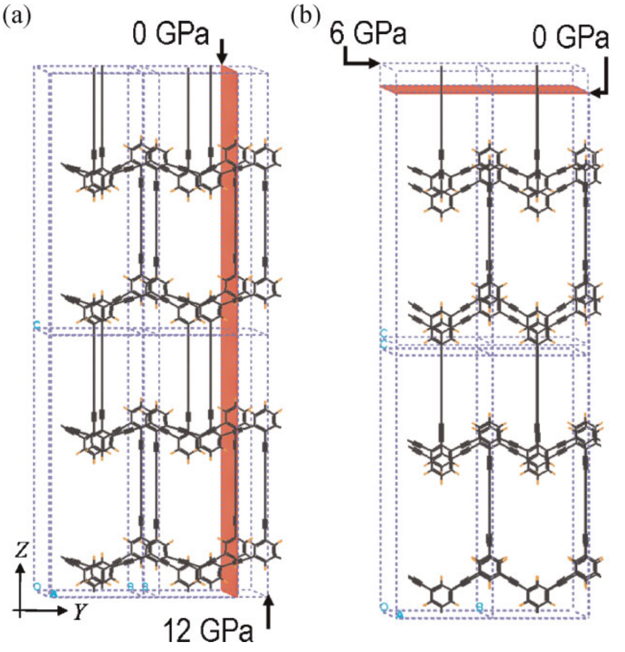
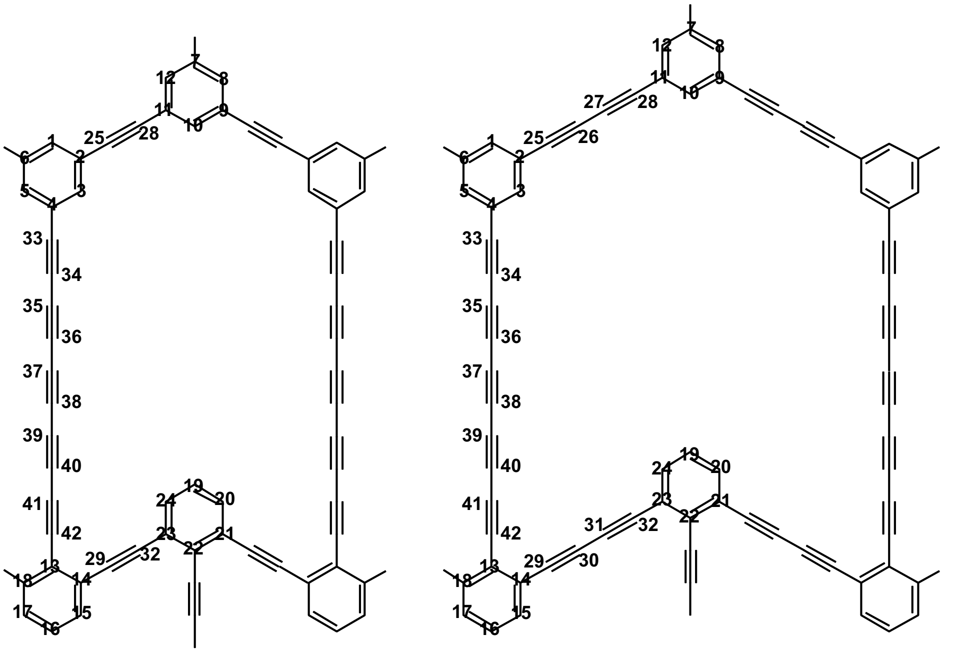


Figure 2 (online colour at: www.pss-b.com) Deformations for loading in the (a) *Y* and (b) *Z* directions.

Table 2 Measurements for the changes in bond angles characterizing (b-i) hinging and (b-ii) flexing and (b-iii) the fractional changes in the bond lengths quantifying the extent of stretching in (a-i) (1,5)- and (a-ii) (2,5)-semiflexynes for loading at a stress equivalent to 10% of the Young's modulus. The deformations in the benzene rings are also shown in (c-i) and (c-ii).



(a-i) (a-ii)

hinging

bond angles (°)	∠3–2–25	∠28–11–10	∠24–23–32	∠29–14–13	∠14–13–42	∠33–4–3
(1,5)-	−5.4	8.6	−5.1	8.5	−1.1	−0.3
(2,5)-	−5.4	7.1	−5.2	7.1	−0.4	0.0

(b-i)

flexing

bond angles (°)	∠2–25–28 ∠25–28–11	∠14–29–32 ∠29–32–23	∠2–25–26 ∠27–28–11	∠25–26–27 ∠26–27–28	∠14–29–30 ∠31–32–23	∠29–30–31 ∠30–31–32
(1,5)-	−1.6	−1.4	–	–	–	–
(2,5)-	–	–	−2.8	−0.9	−2.4	−0.7

(b-ii)

stretching in m-linkages

fractional change	2–25 28–11	14–29 32–23	25–26 27–28	29–30 31–32	26–27	30–31	25–28	29–32
(1,5)-	5.5	5.7	–	–	–	–	2.6	2.7
(2,5)-	3.3	3.3	1.6	1.6	1.6	1.7	–	–

(b-iii)

deformations in benzene rings:

stretching

fractional change	1–2 6–1 15–16 16–17	2–3 5–6 14–15 17–18	3–4 4–5 13–14 18–13	7–8 12–7 21–22 22–23	8–9 11–12 20–21 23–24	9–10 10–11 19–20 24–19
(1,5)-	3.6	−0.3	−0.4	3.5	−0.3	−0.4
(2,5)-	2.3	−0.2	−0.5	2.2	−0.2	−0.5

(c-i)

Table 2 (Continued)

	hinging			
bond angles (°)	∠6–1–2 ∠15–16–17	∠1–2–3 ∠5–6–1 ∠14–15–16 ∠16–17–18	∠2–3–4 ∠4–5–6 ∠13–14–15 ∠17–18–13	∠3–4–5 ∠18–13–14
(1,5)-	1.9	−3.3	2.0	0.7
(2,5)-	0.5	−1.8	1.5	0.0
bond angles (°)	∠12–7–8 ∠21–22–23	∠7–8–9 ∠11–12–7 ∠20–21–22 ∠22–23–24	∠8–9–10 ∠10–11–12 ∠29–20–21 ∠23–24–19	∠9–10–11 ∠24–29–20
(1,5)-	2.2	−3.4	1.8	0.9
(2,5)-	0.7	−1.9	1.5	0.1
(c-ii)				

were then calculated from these matrices since it is given by:

$$\nu_{ij} = -\frac{\varepsilon_j}{\varepsilon_i} = -\frac{s_{ij}}{s_{jj}}, \tag{2}$$

where *i* indicates the loading direction and *j* the transverse direction. Convergence tests were also performed to ensure that the mechanical properties of the system are not dependent on the size of the unit cell considered.

For all systems modelled, the minimum energy separation between adjacent layers was found to range between 3.34 and 3.36 Å (*cf.* 3.35 Å for graphite [46]), confirming that the inter-layer π–π interactions are correctly modelled. Also, mechanical properties simulations, the results of which are illustrated in Table 1, suggest that the novel semi re-entrant networks exhibit Poisson's ratios which are very close to zero as opposed to the flexynes and reflexynes which were confirmed to exhibit conventional and auxetic behaviour, respectively, for loading on-axis as suggested elsewhere [1, 2–4]. This in-plane almost ZPR is in general accompanied by a non-ZPR out of plane, which results from deformations that aim at restoring the interlayer π–π interactions.

In an attempt to understand the underlying deformations which lead to this behaviour, we simulated the minimum energy configuration at different values of applied uniaxial stresses and measured several bond lengths and angles at different stress levels for loading in the *Y* and *Z* directions. In all cases, an attempt was made to ensure that the applied strains were less than 10%. In particular, the applied stresses where always less that 10% of the Young's modulus in the stretching direction.

The simulations (see Fig. 2) suggest that the molecular level honeycombs mimic the behaviour of the idealized 'hinging/flexing/stretching' model which explains the values of the Poisson's ratios obtained. It is evident from Table 2, which shows the changes in some of the bond lengths and angles most affected by deformation, that in general, the dominant deformation mechanism for loading in the *Y* direction is hinging at the junction between the acetylene chain and benzene ring for which changes of up to 8.5° for $m = 1$ systems and 7.1° for $m = 2$ systems were measured. Stretching of the acetylene chains occurs to a lesser extent and is mostly concentrated at the bonds directly connected to the benzene ring which experience a strain which is approximately twice that of the bonds in the rest of the *m*-linkage (see Table 2). The extent of hinging and stretching is slightly smaller for the larger systems with $m = 2$, while flexure becomes more significant. Also interesting is the fact that for loading in the *Y*-direction, $m = 2$ systems have a Poisson's ratio that is closer to zero than that of the corresponding $m = 1$ systems. This is presumably because the benzene rings in the smaller $m = 1$ systems contribute significantly to the overall dimensions of the system. Thus, any distortion of the benzene rings may lead to deviations from ideal behaviour. As evident from Table 2 (c-i) and (c-ii) such deformations occur to a larger extent in the smaller systems and thus deviation from ideal behaviour is expected to be most significant for the smaller $m = 1$ systems (see Table 1). For the larger systems, such distortions become negligible when compared to the size of the unit cell such that any deformations that occur as a result of such distortions which are not accounted for in the idealized model, have little effect on the overall behaviour of the system.

The simulations also suggest that the way the molecular networks deform for loading in the *Z* direction (see Fig. 2b) is slightly more complex. In particular, they suggest that the molecular level honeycombs deform primarily due to stretching of the vertical ribs, a mechanism which as explained above leads to ZPR. This mode of deformation is expected since as discussed elsewhere [47], the 'stretching mechanism' would have been the sole mechanism in an idealized perfectly planar honeycomb model. Nevertheless, in these nanoscale honeycombs, stretching of the ribs is also accompanied with some flexure and hinging of the *m*-acetylene chains where the opposing deformation

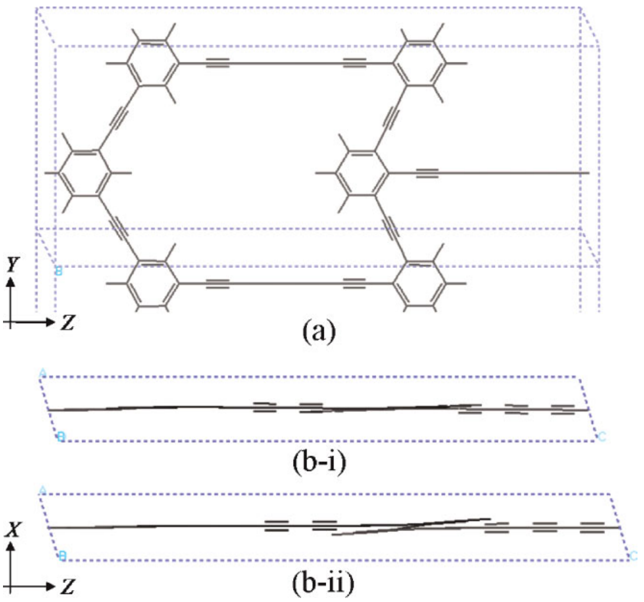


Figure 3 The undeformed network viewed in the (a) *YZ* and (b-i) *XZ* plane and (b-ii) the out of plane deformation at the re-entrant part of the network for loading in the *Z* direction.

tendencies are accommodated by out-of-plane deformations. In fact, the simulations suggest that the re-entrant part of the network tilt in a manner to accommodate the deformations at the non-re-entrant part (Fig. 3). However, despite these deformations which are not predicted by the idealized model [47], the molecular networks still exhibit a near-ZPR for loading in the *Z* direction.

All this is very significant since for the first time, we have shown that nanostructures can be made to exhibit the very useful property of ZPRs. These materials have some useful potential applications, for example they can be used as a substitute to naturally occurring materials such as cork, as an alternative to composite materials that are specifically designed to exhibit ZPRs thereby eliminating problems related to interface failure arising from mismatch of the properties of the materials and also used in the manufacture of cylindrical shaped surfaces (e.g. pipes), something which neither conventional nor auxetic materials can do very well [40–43].

3 Conclusion In this work we have proposed a polyphenylacetylene networks and have shown the potential of these simple molecular system to exhibit a ZPR. We hope that given the many advantages of such materials when compared to conventional materials, these predictions will encourage further research into their chemistry so as to enable the synthesis of the first man-made ZPR.

Acknowledgements This work was supported by the Government of Malta through an MGSS grant awarded to Daphne Attard.

References

[1] K. E. Evans, M. A. Nkansah, I. J. Hutchinson, and S. C. Rogers, Nature **353**, 124 (1991).
[2] K. E. Evans, A. Alderson, and F. R. Christian, J. Chem. Soc., Faraday. Trans. **91**, 2671 (1995).
[3] A. Alderson, P. J. Davies, M. R. Williams, K. E. Evans, K. L. Alderson, and J. N. Grima, Mol. Simul. **31**, 897 (2005).
[4] J. N. Grima, D. Attard, R. N. Cassar, L. Farrugia, L. Trapani, and R. Gatt, Mol. Simul. **34**, 1149 (2008).
[5] R. Lakes, Science **235**, 1038 (1987).
[6] N. Chan and K. E. Evans, J. Mater. Sci. **32**, 5945 (1997).
[7] J. N. Grima, D. Attard, R. Gatt, and R. N. Cassar, Adv. Eng. Mater. **11**, 533 (2009).
[8] S. McDonald, N. Ravirala, P. Withers, and A. Alderson, Scr. Mater. **60**, 232 (2009).
[9] R. H. Baughman and D. S. Galvão, Nature **365**, 735 (1993).
[10] K. L. Alderson and K. E. Evans, Polymer **33**, 4435 (1992).
[11] A. Alderson and K. E. Evans, J. Mater. Sci. **32**, 2797 (1997).
[12] C. He, P. Liu, and A. C. Griffin, Macromolecules **31**, 3145 (1998).
[13] J. N. Grima and K. E. Evans, Chem. Commun. 1531 (2000).
[14] J. N. Grima, J. J. Williams, and K. E. Evans, Chem. Commun. 4065 (2005).
[15] B. D. Caddock and K. E. Evans, J. Phys. D, Appl. Phys. **22**, 1877 (1989).
[16] J. N. Grima, R. Gatt, A. Alderson, and K. E. Evans, J. Mater. Chem. **15**, 4003 (2005).
[17] R. H. Baughman, J. M. Shacklette, A. A. Zakhidov, and S. Stafström, Nature **392**, 362 (1998).
[18] A. Yeganeh-Haeri, D. J. Weidner, and J. B. Parise, Science **257**, 650 (1992).
[19] J. N. Grima, R. Jackson, A. Alderson, and K. E. Evans, Adv. Mater. **12**, 1912 (2001).
[20] A. Alderson and K. E. Evans, J. Phys.: Condens. Matter **21**, 025401 (2009).
[21] C. Sanchez-Valle, S. V. Sinogeikin, Z. A. D. Lethbridge, R. I. Walton, C. W. Smith, K. E. Evans, and J. D. Bass, J. Appl. Phys. **98**, 053508 (2005).
[22] L. J. Gibson, M. F. Ashby, G. S. Schajer, and C. I. Robertson, Proc. R. Soc. Lond. A **382**, 25 (1982).
[23] A. Alderson, K. L. Alderson, D. Attard, K. E. Evans, R. Gatt, J. N. Grima, W. Miller, N. Ravirala, C. W. Smith, and K. Zied, Compos. Sci. Technol. **70**, 1042 (2010).
[24] F. Scarpa, P. Panayiotou, and G. Tomlinson, J. Strain Anal. **35**, 383 (2000).
[25] I. G. Masters and K. E. Evans, Compos. Struct. **35**, 403 (1996).
[26] K. W. Wojciechowski and A. C. Brańka, Mol. Phys. Rep. **6**, 71 (1994).
[27] F. Scarpa, L. G. Ciffo, and J. R. Yates, Smart Mater. Struct. **13**, 49 (2004).
[28] K. E. Evans and N. Chan, J. Cell. Plast. **34**, 231 (1998).
[29] C. Remillat, F. Scarpa, and K. W. Wojciechowski, Phys. Status Solidi B **246**, 2007 (2009).
[30] J. N. Grima and K. W. Wojciechowski, Phys. Status Solidi B **245**, 2369 (2008).
[31] C. W. Smith and K. W. Wojciechowski, Phys. Status Solidi B **245**, 486 (2008).
[32] K. W. Wojciechowski, A. Alderson, K. L. Alderson, B. Maruszewski, and F. Scarpa, Phys. Status Solidi B **244**, 813 (2007).

[33] K. W. Wojciechowski, A. Alderson, A. Braka, and K. L. Alderson, Phys. Status Solidi B **242**, 497 (2005).
[34] L. J. Gibson, K. E. Easterling, and M. F. Ashby, Proc. R. Soc. Lond. A **377**, 99 (1981).
[35] T. Jin, N. S. Goo, S. C. Woo, and H. C. Park, J. Bionic Eng. **6**, 224 (2009).
[36] R. Olympio and F. Gandhi, in: 48th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Honolulu, Hawaii, 23–26 April, 2007.
[37] C. Lira, F. Scarpa, M. Olszewska, and M. Celuch, Phys. Status Solidi B **246**, 2055 (2009).
[38] E. Geissler and A. M. Hecht, Macromolecules **13**, 1276 (1980).
[39] A. Alderson, Chem. Ind. 384 (1999).
[40] J. N. Grima, L. Oliveri, D. Attard, R. Gatt, B. Ellul, G. Cicala, and G. Recca, 6th Int. Workshop on Auxetics and Related Systems, Bolton, UK, 2009.
[41] J. N. Grima, L. Oliveri, D. Attard, B. Ellul, R. Gatt, G. Cicala, and G. Recca, Adv. Eng. Mater., in press.
[42] L. Oliveri, PhD Thesis, University of Catania (2009).
[43] D. Attard, PhD Thesis, University of Malta, in preparation.
[44] H. Sun, S. Mumby, J. Maple, and A. Hagler, J. Am. Chem. Soc. **116**, 2978 (1994).
[45] P. P. Ewald, Ann. Phys. **64**, 253 (1921).
[46] A. Hunter, J. Singh, and J. Thornton, J. Mol. Biol. **218**, 837 (1991).
[47] D. Attard and J. N. Grima, Phys. Status Solidi B **248**, 52 (2011), this issue.