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On the effect of solvent molecules on the structure and mechanical properties of organic polyphenylacetylene auxetic re-entrant network polymers

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Auxetics exhibit the unusual property of a negative Poisson's ratio, meaning they get wider rather than thinner when stretched. This work employs force-field based simulations to study the effect of solvent molecules on the structure and mechanical properties of porous polyphenylacetylene auxetic organic networked polymers. In particular, nano-level re-entrant honeycombs 1,4- and 2,8-reflexyne were exposed to three types of solvent molecules (ethanol, propanol and benzene) at different concentrations by performing Monte-Carlo based sorption simulations in two scenarios, one where the solvent was permitted into the pores of the system upon exposure, and one were the solvent could also enter in between the layers of the polymer. Results indicate that the presence of solvent molecules within the molecular framework of the networked polymers has a significant effect on their density and stiffness but does not influence the Poisson's ratio of the material. The effect on the stiffness was found to be highly dependent on various factors, including the properties of the network and the type and amount of solvent adsorbed. These results have important implications in future case scenarios which may involve the synthesis of such systems, and it throws light on how the mechanical properties could be affected due to contamination, while also identifying new methods on how to tailor such properties by exposing the material to specific solvents.

1 Introduction Most naturally occurring materials get thinner when stretched, *i.e.* have a positive Poisson's ratio. However, research has shown that unconventional materials exhibiting a negative Poisson's ratio, termed 'auxetic' [1] may also exist, and these materials exhibit the unexpected property of getting thicker when stretched. In recent years, there was a significant increase in research in auxetics and related fields [2–9]. Auxetic materials have not only been discovered in nature [10–15] but have also been designed and/or synthesised [16–21]. Auxetics have also been shown to possess improved mechanical and other macroscopic properties, such as increased indentation resistance and resilience [22–26], increased fracture toughness [27], improved pore size tunability [28–30] and better energy absorption and acoustic properties [31–36]. These improved properties have encouraged further research into these materials, which has led to the design of novel theoretical systems [37–41]. This helps us understand the deformation mechanisms taking place in such models, while giving insight to how the geometry of the structure can be tailored to produce specific mechanical properties.

In fact, it is now known that auxetic behaviour arises due to the specific structure of the system and the deformation mechanism taking place when the material is subject to uniaxial mechanical loading, something which can be perfectly exemplified by honeycomb systems (where re-entrant and non-re-entrant systems can exhibit either conventional or auxetic behaviour, depending on which deformation mechanism they undergo) [41, 42]. The deformation mechanism may involve changes in the structure at the molecular level, which in turn gives rise to a negative Poisson's ratio in the bulk material.

Examples of nano-auxetics include organic systems such as the hypothetical polyphenylacetylene molecular networked polymers [1, 41, 43–45] and auxetic liquid crystalline polymers [16–18], as well as metals [10] and other nanoscale inorganic crystalline materials such as zeolites [46–50] and silicates [12, 51–57].

Organic polyphenylacetylene networked polymers are some of the earliest examples in the history of nano-auxetics. Their geometric unit is based on the honeycomb structure [1], and the networks consist of branches of acetylene groups joined by benzene rings at the junctions, with each benzene ring having three polyacetylene arms. The geometry of the honeycomb depends on the connectivity of the polyacetylene arms to the benzene ring to give either the conventional honeycomb (where the arms are connected to alternate carbon atoms in the benzene ring) or the re-entrant structure (where the arms are connected to three adjacent carbon atoms in the benzene ring). These have been termed (*n*,*m*)-flexyne and (*n*,*m*)-reflexyne, respectively (with *n* and *m* denoting the number of triple bonds in the slanting and vertical chains of the unit), where the reflexynes exhibit auxetic behaviour whilst the flexynes exhibit conventional positive Poisson’s ratio behaviour.

The particular geometry of such honeycomb systems gives rise to pores within the structure, a property which has been the subject of investigation in various studies, including the macroscale honeycomb-glass bead host-guest system [58] and the molecular-level honeycomb-buckyball host-guest analogue [59].

Although these networks are hypothetical and their successful synthesis has not yet been reported, they still represent one of the more important classes of auxetics. Hence, it is important that one obtains a deeper understanding of their behaviour, including their mechanical properties in non-ideal but more realistic scenarios. Unfortunately, all studies conducted so far have focused on highly idealised versions of these networks. If these polymers had to be synthesised, it would be highly unlikely to obtain such ideal purity, and therefore it is crucial to understand how traces of foreign substances such as solvent molecules that may find their way into the system during synthesis, could affect the properties of the polymer. In this respect, it is also important to note that it is believed that solvent diffusion is generally quite difficult to take place in polymeric crystals, where solvent penetrates preferentially into the amorphous regions and only rarely into crystalline regions [60], however on the other hand, a study involving reflexynes should not be excluded due to the presence of pores within these systems.

In view of this, here we report on the use of force-field based simulations to study the mechanical properties of typical re-entrant polyphenylacetylene honeycombs in the presence of different typical solvent molecules, which are likely to be adsorbed within the pores and in between the layers of the network polymer with the aim of understanding the potential effect that any solvent contamination might have on the polymers in the eventuality of their synthesis.

2 Modelling methodology

Simulations were performed on the auxetic 1,4- and 2,8-reflexyne systems using the commercially available molecular modelling package Materials Studio V6.0 (Accelrys Inc., San Diego, USA). The simulations employed the PCFF force-field [61, 62] and the default force-field settings were applied, with the exception of non-bond (van der Waals and Coulombic) interactions summation method, for which the Ewald procedure was used [63]. The PCFF force-field has been adequately parameterised for all atom types used in this study, and has in fact already been used to successfully model the properties of reflexyne systems [45].

The starting unit-cell structures for the 2D polymeric molecular honeycomb networks containing $1 \times 1 \times 1$ repeat units were built using the Builder tools within Materials Studio and placed in the global *YZ*-plane with the vertical ligaments being placed parallel to the *Z*-direction. Periodic boundary conditions were applied with the [001] cell vector, which is parallel to the vertical ligaments, being aligned parallel to the global *Z*-direction, and the [010] direction aligned to lie in the *YZ*-plane (see Fig. 1). This alignment ensures that the networks remain aligned parallel to the *YZ*-plane in the simulations with the vertical ligaments being parallel to the global *Z*-direction, meaning that the cell vectors will be of the form:

$$\boldsymbol{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}, \quad \boldsymbol{b} = \begin{pmatrix} 0 \\ b_y \\ b_z \end{pmatrix}, \quad \boldsymbol{c} = \begin{pmatrix} 0 \\ 0 \\ c_z \end{pmatrix}. \qquad (1)$$

The potential energy of the structure (having P1 unit-cell symmetry) was then minimised as a function of the atomic coordinates and six cell parameters to the earlier of the default fine convergence criteria (energy change threshold of 0.0001 kcal mol^{-1} and maximum force of 0.005 kcal mol^{-1} Å^{-1}) or 5000 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, and quasi-Newton methods. This step was

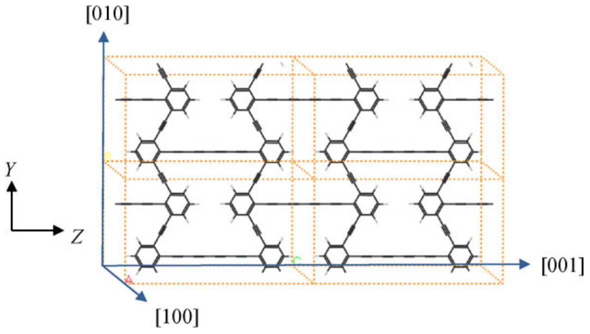


Figure 1 The structure of 1,4-reflexyne showing the alignment of the system, with the [001] cell vector being aligned along the global *Z*-direction, and the [010] cell vector aligned in the *YZ*-plane.

repeated three times to enable re-calculation of the non-bond list and to ensure complete minimisation of the structure.

2.1 Sorption Sorption simulations were then carried out using three different solvent molecules: ethanol, propanol and benzene. An attempt was made to simulate two different situations where:

(i) The polymer layers were separated prior to sorption so that the solvent molecules could enter within the void as well as penetrate in between layers (Type A);
(ii) The solvent molecules could only enter the void of the polymer networks without any layer separation prior to sorption (Type B).

These two systems were studied in order to simulate two possible case scenarios, one where solvent molecules enter in between the layers of the polymer while synthesis is taking place, and the other where the molecules accommodate themselves within the pores after the polymeric layers have already been closely packed.

For the Type A, the length of the lattice vector **a** which corresponds to the [100] direction was increased to 10 Å, so as to separate the layers and permit solvent molecules to enter between them, and then a super-lattice of 8 × 2 × 2 was created. For the Type B, a super-lattice of 8 × 2 × 2 was created from the original 1 × 1 × 1 minimised systems, but this time the cell parameters were left as obtained through the minimisation process.

For each of these polymeric systems (the sorbent), and for each solvent (the sorbate), the concentration of the sorbate was varied in order to allow the sorption of a specific number of molecules within the polymer system: 2, 4, 8, 16, 32, 64 and 96 molecules. The Sorption tool within Materials Studio was used to perform Monte-Carlo based sorption simulations. The Monte-Carlo algorithm is a stochastic (or non-deterministic) technique, thus making use of randomly generated numbers, which are used both to move the sorbates in space, as well as to decide which energy configurations are acceptable. The Metropolis algorithm [64] was used and calculations were carried out in the canonical ensemble, which enables fixed loading of a specific number of sorbate molecules. The quality of the simulations settings was set to 'Fine' so that the number of equilibration steps was equal to 100 000 and the number of production steps was 1 000 000. A sorption temperature of 298 K was used throughout and values of 1 Å and 50° were employed for the maximum translation and rotation steps, respectively. Each of the sorption simulations produced a trajectory containing the configurations sampled at specified intervals of the production stage, which was then used to extract representative samples of systems containing the solvent molecules.

2.2 Mechanical properties Following the sorption simulations, a representative sample of ten structures was extracted from each trajectory and these were re-minimised using the same energy expression described above.

The mechanical properties of each re-minimised system were then computed using the Forcite module within Materials Studio, which makes use of the constant-strain approach. These simulations generated the 6 × 6 stiffness matrix **C**, which relates the stress $\boldsymbol{\sigma}$ and the strain $\boldsymbol{\varepsilon}$ through $\boldsymbol{\sigma} = \mathbf{C}\boldsymbol{\varepsilon}$. The maximum strain amplitude was set to 0.003 *i.e.* 0.3% strain and four 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 $\mathbf{S} = \mathbf{C}^{-1}$ as shown below:

$$\begin{aligned} E_x &= \frac{1}{s_{11}}, \quad E_y = \frac{1}{s_{22}}, \quad E_z = \frac{1}{s_{33}}, \\ \nu_{yz} &= -\frac{s_{32}}{s_{22}}, \quad \nu_{zy} = -\frac{s_{23}}{s_{33}}, \quad G_{yz} = \frac{1}{s_{44}}, \end{aligned} \tag{2}$$

where 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 shear modulus in the YZ-plane whilst s_{ij} are the elements of the compliance matrix **S**.

3 Results and discussion In all of the systems simulated, with the exception of the Type B 1,4-reflexyne systems, it was observed that the solvents molecules can penetrate in the pores of the systems and also in between the layers. The only system which did not adsorb any of the solvents was Type B 1,4-reflexyne, probably because the solvent molecules are too large to enter the pores of this particular system.

Plots of a_x, b_y and c_z, the projections in the X, Y and Z directions as a function of N_s (number of solvent molecules adsorbed) as well as a typical portion of the corresponding structures with the maximum number of adsorbed solvent molecules, are shown in Fig. 2. These results clearly suggest that the Type A 1,4-reflexyne systems respond very differently from either of the 2,8-reflexyne systems. In fact, in the case of the 1,4-reflexyne system, as the number of sorbate molecules adsorbed in between the layers was increased, the layers minimised to separations where they are increasing further apart in order to accommodate the molecules. Therefore, there was an increase in the projection of the 1,4-reflexyne system in the X-direction as the number of solvent molecules was increased (see Fig. 2a). This layer separation increased even further when larger solvent molecules such as benzene were adsorbed: it increased by 65.4% (from 25.7 to 42.5 Å) in the presence of 96 benzene molecules per 8 × 2 × 2 cell. Another very interesting observation that can be made is the fact that for the Type A 1,4-reflexyne, the benzene molecules, in general, tend to be located in between the planes and orient themselves almost parallel to the planes, *i.e.* with a face-to-face orientation (see Fig. 3a), this being one of the two preferred orientations for maximising π–π interactions. The other orientation (which was not manifested in 1,4-reflexyne), is one where the

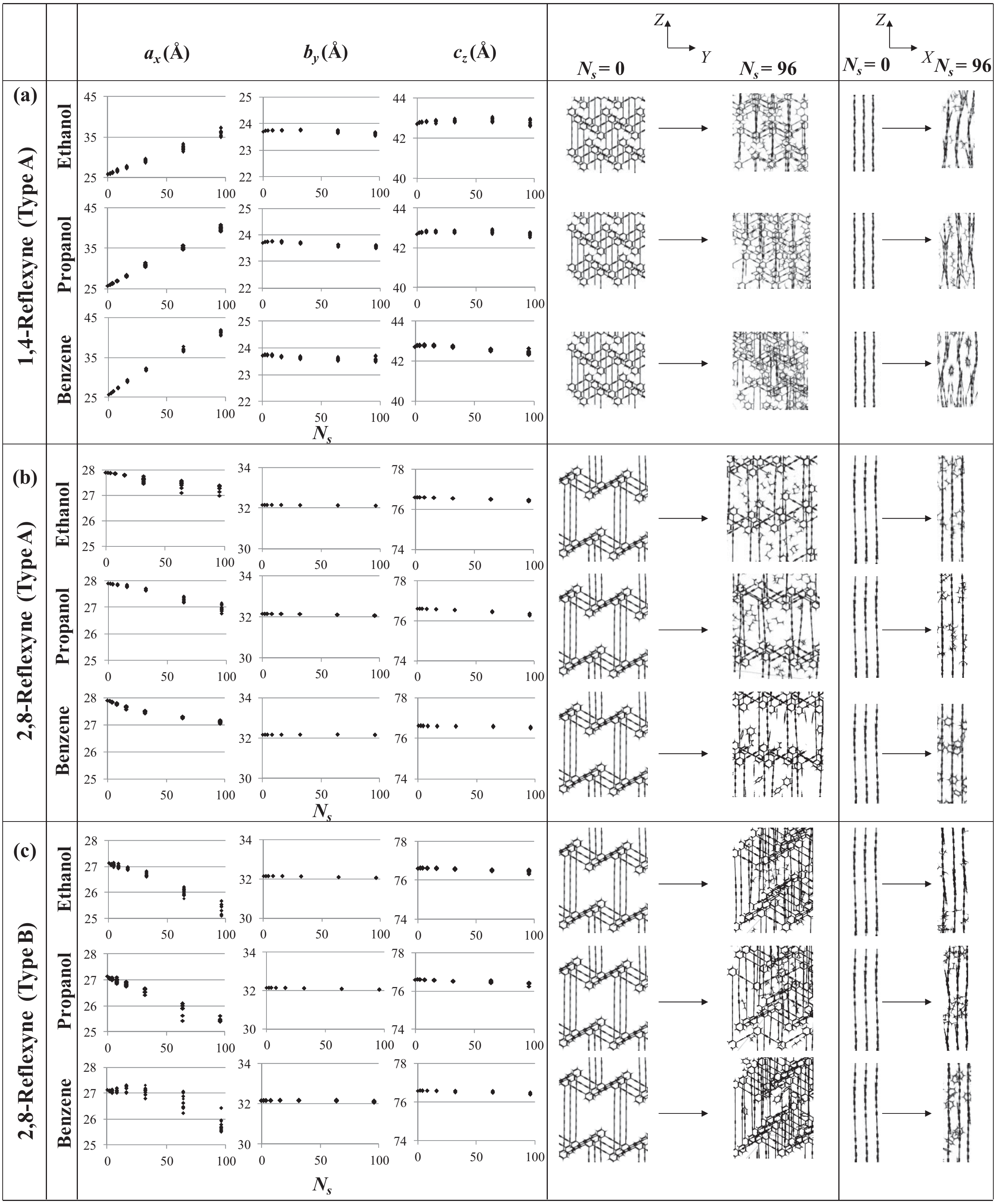
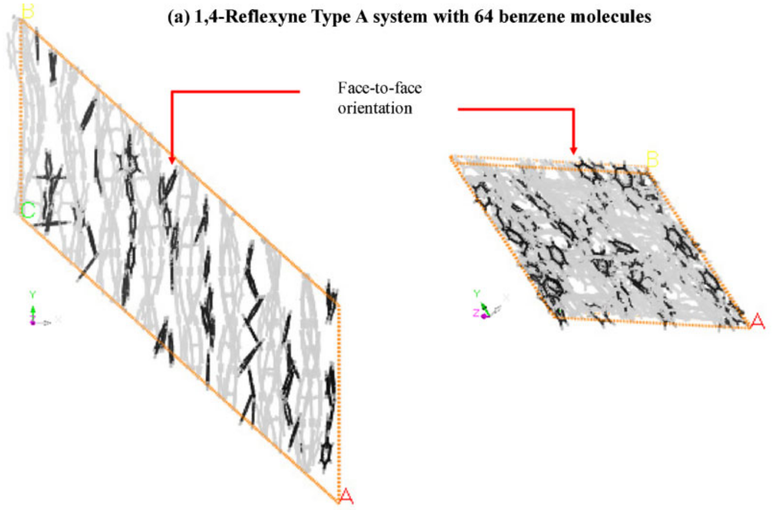


Figure 2 Plots of the 8 × 2 × 2 unit cell projections in X, Y and Z directions as a function of N_s, the number of adsorbed solvent molecules. The figure also shows views in the ZY and ZX plane of a typical portion of the original reflexyne systems prior to sorption (showing only three layers of the super-lattice for clarity) and also a portion of the corresponding structure with the maximum number of adsorbed solvent molecules (96 molecules per 8 × 2 × 2 unit cell).


(a) 1,4-Reflexyne Type A system with 64 benzene molecules

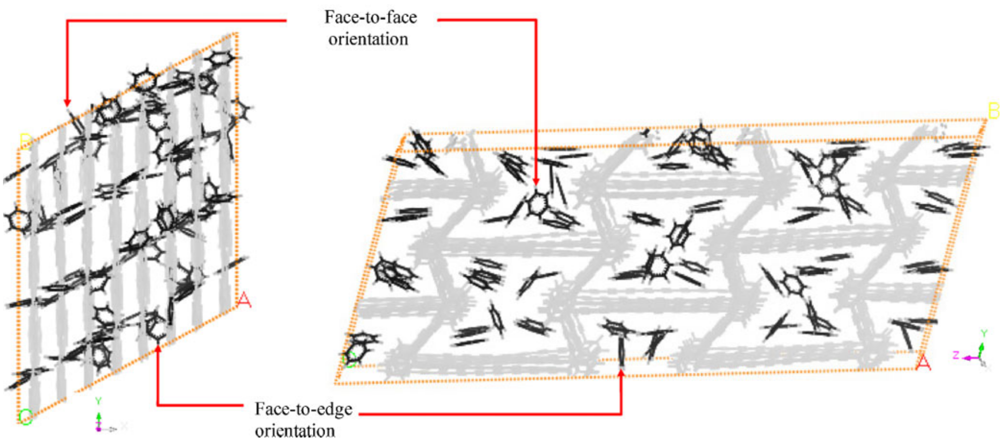

(b) 2,8-Reflexyne Type B system with 96 benzene molecules

Figure 3 The orientations adopted by benzene sorbate molecules within (a) 1,4-reflexyne (face-to-face orientation), and (b) 2,8-reflexyne (both face-to-face and face-to-edge orientations).

benzene rings are perpendicular to each other, a face-to-edge orientation, which would have resulted in a much greater increase in the dimensions. In fact, in this case the inter-layer separation increased from an average of 3.1 Å to around 5.3 Å, *i.e.* an increase which is concordant with an observation that an additional benzene layer is being placed between most of the original network layers.

In contrast to 1,4-reflexyne, in both Type A and Type B 2,8-reflexyne systems, the layers were pushed even closer to each other as the amount of sorbate molecules increased. The presence of these molecules within the pores seems to increase the attraction between the layers, hence allowing them to pack closer together. In fact, for the Type A systems in the presence of 96 solvent molecules per $8 \times 2 \times 2$ unit cells, the cell vector a_x decreased to an average of around 3.7, 3.4 and 2.8%, respectively, in the case of ethanol, propanol and benzene, whilst in the case of the Type B, this decrease was around 6.5, 7.0 and 4.9%, respectively. In all cases considered, the other dimensions, represented by b_y and c_z, remained more or less constant, showing that the in-plane molecular structure of the network polymer was not significantly affected by the presence of sorbate molecules in the sense that there was neither an opening up nor a closure of the pores in the system. Besides, a most interesting result is that in 2,8-reflexyne (both Types A and B), the benzene rings adopt a conformation where the molecules are located inside the pores and are generally approximately perpendicular to the layers, with a face-to-side orientation (see Fig. 3b). The only exception to this is that some benzene molecules are accommodated almost in the centre of the pores, where they tend to adopt a face-to-face orientation. The preferred face-to-side orientation is feasible this time, since the benzene rings are being located inside the pores of the system, and not between the layers themselves. In such locations, this highly stable conformation [65] is preferred since, given the shape of the pores, it permits a greater number of benzene molecules to be accommodated within the pointed corners of the pores.

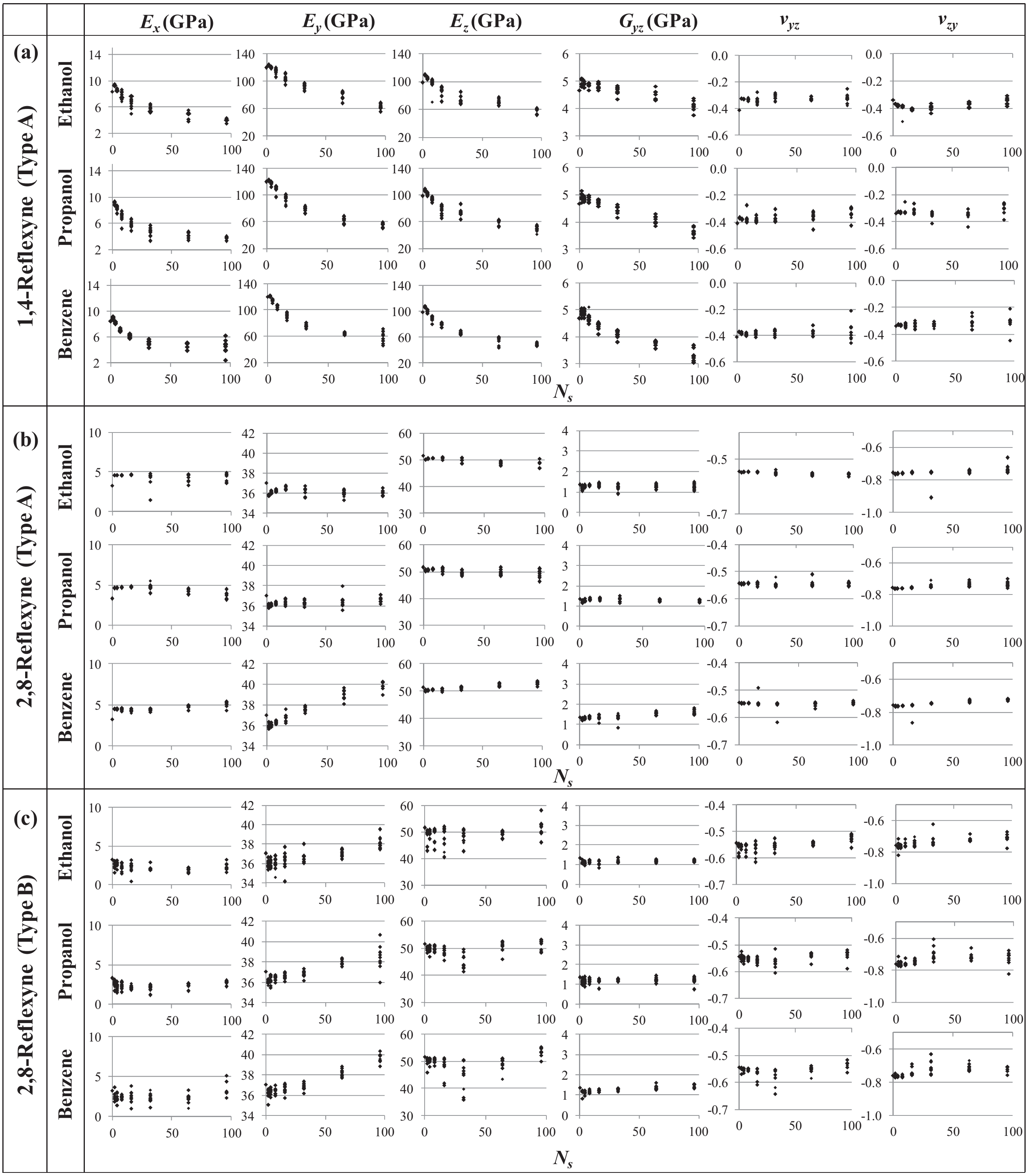


Figure 4 The variation of Young's moduli, E_x, E_y and E_z, shear modulus, G_{yz}, and Poisson's ratios ν_{yz} and ν_{zy} as a function of the number of solvent molecules N_s within (a) Type A 1,4-reflexyne, (b) Type A 2,8-reflexyne and (c) Type B 2,8-reflexyne systems.

The introduction of solvent molecules in the system seemed to have a significant effect on some of the mechanical properties of these systems, particularly their stiffness (see Fig. 4). These changes are also dependent on the system being modelled. In fact, in the case of the Type A 1,4-reflexyne, the Young's moduli, E_x, E_y and E_z, as well as shear modulus, G_{yz}, were predicted to decrease with increasing sorbate concentration as shown in Fig. 4a, respectively. This can be attributed to enlargement of the unit cell in the presence of solvent in between the layers, which reduces the stiffness of the material in all directions. In contrast to this, in the case of the Type B 2,8-reflexyne systems, for all the sovents used, there was an increase in the Young's moduli for loading in the *Y*-direction whilst the moduli for loading in the *X* and *Z* directions remained on-average constant in the presence of any solvent, with one exception. This increase in E_y could be partially explained by the observation that the layers of 2,8-reflexyne were allowed to pack closer to each other with sorption. This increase in E_y was most pronounced in the case of benzene where as shown in Fig. 4, there was an increase in Young's modulus in the *Y*-direction from 37 GPa to around 40 GPa. This, as well as the decrease in thickness a_x can also be attributed to the high degree of π–π interactions between the benzene solvent molecules the phenyl groups making up the polymeric framework, as is expected when one considers the possible interactions present in such systems [65]. E_y also increased in the presence of a high concentration of ethanol and propanol within the pores of 2,8-reflexyne (in the Type B system) and this can be attributed to the polar–π interactions between the solvent molecules and benzene rings in the polymeric system. All of this can also be related to the decrease in projection a_x which results as the number of adsorbed solvent molecules is increased. This gives rise to a densification of the system and hence an increased stiffness. In the case of the Type A 2,8-reflexyne, the increase in the modulus was only observed in case of benzene as a solvent, something which may be partially explained by the lesser extent of decrease in the inter-layer separations.

Also very significant is the fact that the presence of solvent molecules in between the layers or within the pores of the polymer does not seem to have any significant effect on the Poisson's ratio of these systems which on average remained constant for all system types and in the presence of all solvent types. This is very significant since it suggests that should these polymers be indeed synthesised, one would still expect that the predicted auxeticity, which is the most interesting property of these systems, would still be retained even if they are not in their fully dried and pure form. This may be indicative that the deformation mechanism of the system when this is stretched is not being significantly affected by the presence of the solvent molecules, since it is a well known fact that the Poisson's ratio is highly dependent not only on the geometric features of the system, but also how these change upon the application of uniaxial stress. All this is of great practical importance, since it is known that it is sometimes not easy for experimentalists to obtain materials in their pure form, and it is not unknown that the presence of external species would have a significant effect on the mechanical properties, including any auxetic potential of real materials [66, 67]. More importantly, it is being shown that it could be possible to further modify the properties of these systems, in particular their stiffness to auxeticity ratio though the introduction of foreign solvent species with the result that the resulting species would be better adapted to real practical applications requiring tailor-made properties. Also, this discovery also suggests that these materials could be highly suited in nano-filtration applications since their auxeticity may be retained even in the presence of sorbate molecules. From a more academic point of view, the finding that the change in density is not affecting the Poisson's ratio is also noteworthy.

Before concluding, it should be emphasised that this study on the effect of solvent species on reflexyne systems is characterised by a number of assumptions. For example, it may be argued that in real systems, more than one type of solvent is likely to be present, or that the solvent would be unevenly distributed within the system, scenarios which are not being represented here and are beyond the scope of this preliminary study. Nevertheless, it is hoped that the discovery that auxetic behaviour may be retained in the reflexyne systems even if they are not in the solvent-free form, will further encourage experimentalists to attempt to synthesise these systems with the aim of producing man-made auxetic materials having properties which are tailor-made for practical applications.

4 Conclusions This study investigated the effect of the presence of solvent molecules in different concentrations on the structure and mechanical properties of 1,4- and 2,8-reflexyne nano-networks. It was shown that in general, the presence of solvent affects more the density of the systems and their moduli than their Poisson's ratios, with the auxetic characteristics being retained. This has important implications in future case scenarios which could possibly involve synthesis of such network polymers since this study simulated the behaviour of the system in a non-ideal but more realistic situation, where the material is contaminated by foreign solvent molecules, which are likely to enter the system during and after the synthetic procedure. It was also suggested that since the stiffness can be easily altered by introducing specific solvent molecules, one may use this route in order to produce systems with the desired characteristics for specific practical applications.

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