

How Symmetrical Molecules Can Induce Polarity: On the Paradox of Dilution

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Ⓜ This paper contains enhanced objects available on the Internet at <http://pubs.acs.org/crystal>.

ABSTRACT: Monte Carlo simulations show that solid solution $H_{1-X}G_X$ formation between dipolar (H) and symmetrical molecules (G) can yield a high degree of polar order, although both the structure of the dipolar and symmetrical component is assumed centrosymmetric. Previous studies have shown that polarity can evolve in a centric packing of dipolar molecules only if the difference in error probabilities for attaching the molecule in a faulted state “up” or “down” is not zero. This, however, is not necessary if a centrosymmetric growing seed of dipolar molecules is diluted by symmetrical molecules. Here, polarity arises from the presence of G molecules influencing the “up” and “down” states of dipolar H molecules. Most pronounced effects of polarity are predicted for molecules H and G undergoing a strong hydrogen-bond type interaction. As maxima of polarity can occur at relatively low values of X (molar fraction of symmetrical molecules), there is no need for finding systems undergoing solid solution formation over a wide range. Values of $X \leq 0.3$ may be sufficient to yield an X_{net} (net polarity, molar fraction of aligned dipoles) of about 0.4–0.6.

1. Introduction

It sounds like a paradox, but Monte Carlo simulations and the Markov-chain theory of polarity generation¹ make it clear: Increasing the molar fraction X of a symmetrical molecule G forming a solid solution $H_{1-X}G_X$ with the centrosymmetric lattice of a dipolar molecule H can induce polar properties (pyroelectricity) for the solid solution material ($0 < X < 1$).

In case a solid solution $H_{1-X}G_X$ exists for the entire range of composition, a maximum of net polarity can be obtained (Figure 1b,d), which corresponds to a concentration X of symmetrical G molecules inducing a significant dilution of H. The paradox refers to the fact that dilution of a centrosymmetric lattice by symmetrical molecules results in a vectorial physical property² not being allowed for the components H(s), G, and also G(s) (s stands for solid state). Furthermore, the phenomenon is predicted for conditions that do not fulfill the general criterion established for growth-induced polarity formation in molecular crystals such as channel-type inclusion compounds^{3,4} or single component materials.^{1,5} For these cases, it is a necessary condition for polarity formation upon growth of a centrosymmetric seed crystal to have a *difference* in the attachment probabilities (dipole up or down) P_{iu} and P_{ij} referring to distinct molecular fragments i and j , such as terminal functional groups ($i = A = \text{acceptor}$, $j = D = \text{donor}$).^{1,3} The present study shows that polarity can form during the growth of a solid solution $H_{1-X}G_X$ even if $P_{AA} = P_{DD}$.

The reason for this is simply that symmetrical G molecules give rise to orientational selection (up vs down) exceeded by dipolar species H. This orientational selectivity increases with the number of G molecules present in the solid solution. However, as X is increased,

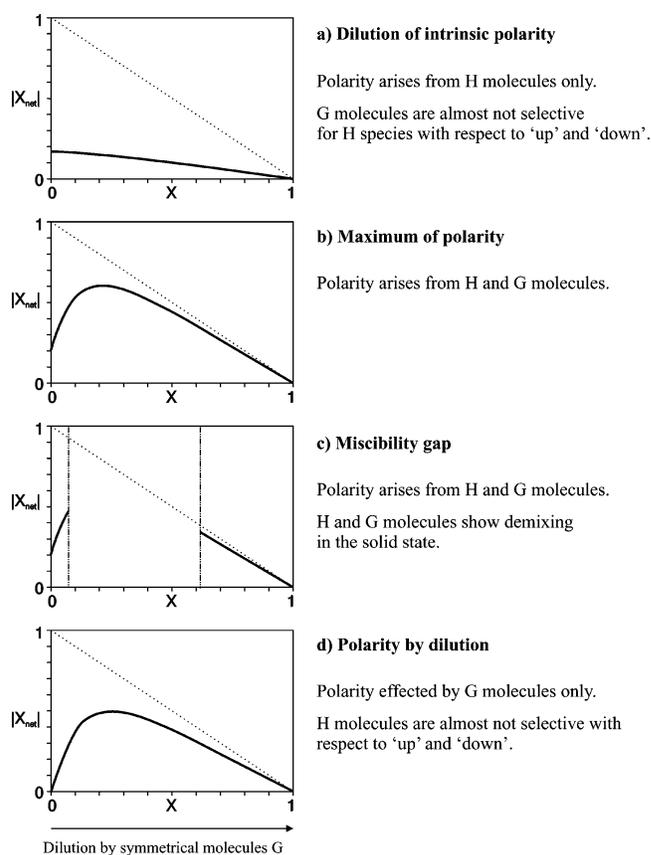


Figure 1. Four representative cases (a–d) showing the variation of polarity $|X_{\text{net}}|$ with respect to the molar fraction X of symmetrical molecules G in solid solutions $H_{1-X}G_X$ with polar molecules H.

the available fraction $(1 - X)$ of dipoles H being aligned in the same direction is reduced. Consequently, a

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maximum of net polarity is expected somewhere between $X \approx 0.2-0.6$ (Figure 1b,d).

In the following sections, we present a formal description of the system along with Monte Carlo simulations using assumed but realistic intermolecular interaction energies for input parameters.

2. Definitions and General Survey

For any detailed introduction concerning a general discussion of growth-induced polarity formation and its experimental confirmation, we refer here to original work and reviews.^{1,6} A survey of literature reporting on effects of polarity in solid solutions is given in ref 7.

For a demonstration of basic phenomena, we assume to have organic molecules featuring intermolecular interactions of the following type:

(i) Interactions of dipolar molecules H described as $A-\pi-D$ (two possible states for the dipole: \downarrow or \uparrow):

$E_{AA}(-A\cdots A-)$, $E_{DD}(-D\cdots D-)$, $E_{AD}(-A\cdots D-)$, where A/D are acceptor/donor fragments, respectively.

$E_p(\downarrow\cdots\downarrow)$, $E_{ap}(\downarrow\cdots\uparrow)$, where p/ap are parallel/antiparallel lateral interactions.

(ii) Interactions of symmetrical molecules G described as $N-\pi-N$ (single state: $|\cdot\rangle$), where $N \equiv A$ or D :

$E_{NN}(-N\cdots N-)$, $E_n(|\cdot\rangle)$, with n denoting the lateral interaction.

(iii) Interactions between dipolar and symmetrical molecules:

$E_{AN}(-A\cdots N-)$, $E_{DN}(-D\cdots N-)$, $E_m(|\cdot\rangle, |\cdot\rangle)$, where m is for mixed interactions.

We limit our discussion here to symmetrical molecules of the type $A-\pi-A$, ($N \equiv A$). Therefore, it is assumed to have $E_{NN} = E_{AN} = E_{AA}$ and $E_{DN} = E_{AD}$, whereas in general $E_p \neq E_{ap} \neq E_m \neq E_n$. To summarize, we will use the following energies and energy differences:

$$\begin{aligned} E_{AD} &= E_{DN}, \\ E_{DD}, \\ E_{AA} &= E_{AN} = E_{NN}, \\ E_{ap}, E_p, E_m, E_n \end{aligned}$$

and

$$\begin{aligned} \Delta E_A &= E_{AA} - E_{AD}, \\ \Delta E_D &= E_{DD} - E_{AD}, \\ \Delta E_{\perp} &= E_p - E_{ap} \end{aligned}$$

(A similar description holds for symmetrical molecules of the type $D-\pi-D$, ($N \equiv D$).

Referring to the introduction, we consider only cases where $\Delta E_{\perp} \geq 0$, i.e., where molecules exceed either no lateral alignment (channel-type inclusion compounds) or are aligned in antiparallel fashion (centrosymmetric single component structures).

As already extensively studied,^{1,4,5} a basic requirement for polarity formation in a centric structure of dipolar species is to have a difference of energy $\Delta E_f = \Delta E_A - \Delta E_D$ being nonzero. Considering that the preferred longitudinal interaction is $-A\cdots D-$, ΔE_f can be interpreted as the difference between the appearance

of two types of defects, namely, $-A\cdots A-$ (probability of appearance P_{AA} driven by E_{AA}) and $-D\cdots D-$ (probability P_{DD} driven by E_{DD}). Moreover, it has to be emphasized that these defects may arise only for differences ΔE_A and ΔE_D , which are sufficiently small. This can be easily understood by the example of strong synthons $-A\cdots D-$ leading to almost no creation of defects, even if $\Delta E_f \neq 0$. A real example is *p*-nitroaniline (centrosymmetric structure) featuring strong $-\text{NH}\cdots\text{O}-$ interactions and showing almost no second harmonic generation effect for chemically very pure samples.⁸

In case of solid solutions, $\Delta E_f \neq 0$ is not anymore a necessary condition for polarity formation, because the deviation from 50:50 up/down can be effected by symmetrical molecules: For $\Delta E_f = 0$, polarity can arise if the difference in the probabilities between docking a molecule H up ($-A\cdots N-$) or down ($-D\cdots N-$) and a molecule G is sufficiently high. This corresponds to the energy difference $E_{AN} - E_{DN}$. As we limit the study to $N \equiv A$, here the difference is described by $E_{AA} - E_{AD} = \Delta E_A$.

The creation of polarity by the symmetrical molecules G (ΔE_A) can interfere with that arising from the dipolar molecules (ΔE_f), leading thus to four cases represented in Figure 1. On the vertical axis, $X_{\text{net}} = X_A(\downarrow) - X_D(\uparrow)$ (X_A, X_D , molar fractions of H molecules in the solid with the acceptor- and donor-terminal oriented toward the nutrient, respectively) is a measure for net polarity.¹ On the horizontal axis, we have the molar fraction X of symmetrical molecules in the solid solution. The dotted line with derivative -1 is the asymptotic limit for any of the curves in (a) to (d): All curves in the lines ($\lim_{X \rightarrow 1} X_{\text{net}}$) join this line and no curve of X_{net} can surpass it after any X . The four cases presented in Figure 1 can be interpreted as follows.

(a) In many centrosymmetric crystal structures, dipolar molecules pack into sites where on average the molecular orientation is 50:50%. In such structures, there is obviously no strong ΔE_{\perp} responsible for an antiparallel alignment, nor are there strong synthon interactions to form, for example, polar chains. However, already a small ΔE_f can introduce a significant polarity for $X = 0$.¹ Because of the absence of a strong synthon interaction $-A\cdots D-$, the insertion of symmetrical molecules will essentially give rise to a *dilution*, i.e., *reduction of the intrinsic polarity*. In terms of energy, absence of selectivity effected by symmetrical molecules G can be explained by $E_{AN} - E_{DN} = \Delta E_A \approx 0$. Recently, this was demonstrated for 4-chloro-4'-nitro-stilbene, forming a solid solution with 4,4'-dinitrostilbene over the entire range of composition.⁷

(b) In that case, polarity arises from H but also from G molecules. Because of $\Delta E_A \neq \Delta E_D$ ($\Delta E_f \neq 0$) there is an intrinsic polarity at $X = 0$. Moreover, the nonzero difference between E_{AN} and E_{DN} ($\Delta E_A \neq 0$) enhances the selectivity for up vs down, leading to a *maximum of polarity for $X > 0$* . This case corresponds to molecules exhibiting moderately strong $-A\cdots D-$ interactions, i.e., ΔE_A and ΔE_D are sufficiently small to give rise to polarity, but ΔE_A is sufficiently high to give selectivity in the mixed interactions (note that $\Delta E_A = E_{AN} - E_{DN}$ is responsible of polarity induced by G molecules).

(c) There is a *miscibility gap*, because of two different structures for H(s) and G(s). At both ends of the

Table 1. Influence of the Strength of an $-A\cdots D-$ Interaction on the Resulting Polarity (X_{net}) for Solid Solutions between a Dipolar Molecule H ($A-\pi-D$) and a Symmetrical Molecule G of the Type $A-\pi-A$

$-A\cdots D-$ interaction	weak	moderate	strong	moderate to strong
$\Delta E_f = \Delta E_A - \Delta E_D$	$\Delta E_f \neq 0$	$\Delta E_f \neq 0$	$\Delta E_f \neq 0$	$\Delta E_f = 0$
creation of defects	high $E_{AD} \approx E_{AA}, E_{DD}$	moderate $E_{AD} < E_{AA}, E_{DD}$	low $E_{AD} \ll E_{AA}, E_{DD}$	moderate to low
polarity at $X = 0$	yes	yes	almost no	no
selectivity effected by G molecules	no $E_{DN} \approx E_{AN}$	yes $E_{DN} < E_{AN}$	yes $E_{DN} \ll E_{AN}$	yes
corresponding figure	1a dilution	1b maximum	1d polarity by dilution	

horizontal axis polarity increases due to the effect of ΔE_f and ΔE_A . Preliminary results for 4-cyano-4'-ethynylstilbene (H) and 4,4'-dicyano-stilbene (G) showed such kind of behavior.

(d) This is the case of special interest, because *polarity is effected only by G molecules*. The curve starts at both sides with zero polarity and passes through a maximum, just because of the effect of E_{AN} vs E_{DN} ($\Delta E_A \neq 0$). This case is typical either for strong $-A\cdots D-$ interactions, or for molecules presenting no significant difference between $-A\cdots A-$ and $-D\cdots D-$. In the first case, a highly negative E_{AD} prevents the formation of any kind of defects between dipolar molecules (so that X_{net} is zero at $X = 0$), but provides a high selectivity for H molecules effected by G entities with respect to up vs down. In the second case, no polarity may arise at $X = 0$ because $\Delta E_f = 0$.

The influence of the strength of an $-A\cdots D-$ interaction on the polarity formation in solid solution is summarized in Table 1: For a symmetrical molecule of type $A-\pi-A$ (assuming that the interactions $-A\cdots A-$ and $-D\cdots D-$ are weak), tuning of polarity in solid solutions is possible just by modifying the interaction strength $-A\cdots D-$. Indeed, this interaction is responsible for $\Delta E_A = E_{AN} - E_{DN}$, and therefore responsible for a modification of polarity by symmetrical molecules G. It has to be noted that the same kind of results can be obtained for G molecules of the type $-D\cdots D-$.

In the next sections, we illustrate basic phenomena for case (d) by use of Monte Carlo simulations and an analytical stochastic theory.

3. Monte Carlo Simulations

For Monte Carlo simulations,⁹ we consider the following model: Starting from a substrate layer, the growth of crystals is described by the attachment of entire layers of molecules one after another. Each layer consists of a square lattice with lattice sites being occupied either by an H molecule, oriented down or up (with respect to the growth direction), or by a symmetrical molecule G. Therefore, a site can be in one of three possible states (down, up, neutral), while empty sites are not allowed. The molecules of the uppermost layer are subjected to thermal relaxation with respect to (i) the orientation of the dipole in case of the H molecules, (ii) an exchange of an H molecule with a G molecule and vice versa. Thermalization of molecules at defined sites is effected by taking into account four nearest neighbor interactions to molecules within the layer and the longitudinal interaction with the corresponding molecule of the previous layer. As crystal

growth is assumed to take place near equilibrium (slow growth rate), the chemical potentials of the two molecules are considered to be equal in the solid and in the gas phase, i.e., $\mu_{\text{H}}^{\text{solid}} = \mu_{\text{H}}^{\text{gas}}$ and $\mu_{\text{G}}^{\text{solid}} = \mu_{\text{G}}^{\text{gas}}$. The chemical potentials of the gas phase are given by those of a mixture of two ideal gases with the molar fractions $1 - X_{\text{gas}}$ for the H molecules and X_{gas} for the G molecules, respectively (see ref 10 for further details). After equilibration, the state of the surface layer is frozen, and a subsequent layer is attached, defining the new surface layer for undergoing thermalization. This process is repeated until a stationary state (concerning polarity) is reached by a subsequent addition of layers.

For the thermalization of a layer, the following single molecule flip/exchange was applied by using a modified Metropolis algorithm:

(1) A lattice site is selected randomly.

(2) Given the *actual* state of this site, a *trial* state is defined by choosing one of the two other possible states randomly (i.e., with equal probability of 0.5).

3. The acceptance ratio r between these two states is calculated:

$$r = e^{(\Delta\mu - E_{\text{trial}} + E_{\text{actual}})/k_{\text{B}}T}, \Delta\mu = \mu_{\text{trial}} - \mu_{\text{actual}}$$

where k_{B} is the Boltzmann constant and T is the temperature of the system. E_{trial} and E_{actual} are the energies of the two states. Note that the chemical potential of H molecules is the same for both dipole orientations.

(4) If $r \geq 1$, the *trial* state is accepted, otherwise it is taken with probability r .

(5) Steps 1–4 are repeated until thermal equilibrium is reached. As we are interested in the polar properties of as-grown crystals and not in details of the process itself, thermodynamical arguments are sufficient for the simulation and therefore no kinetic aspects were included here.

In addition to Monte Carlo simulations, an analytical description for the system has been undertaken in terms of a Markov mean-field process for the three different states (down, up, neutral). For a detailed description of the analytical theory and a thorough discussion comparing the two approaches, see ref 10.

4. Results

For an illustration of the theoretical discussion given above, we show the influence of (i) the longitudinal energy difference $\Delta E_A = \Delta E_D$ (see Figure 2) and (ii) the lateral energy difference ΔE_{\perp} (see Figure 3) on the formation of polarity (X_{net}). All energies are given in kJ/

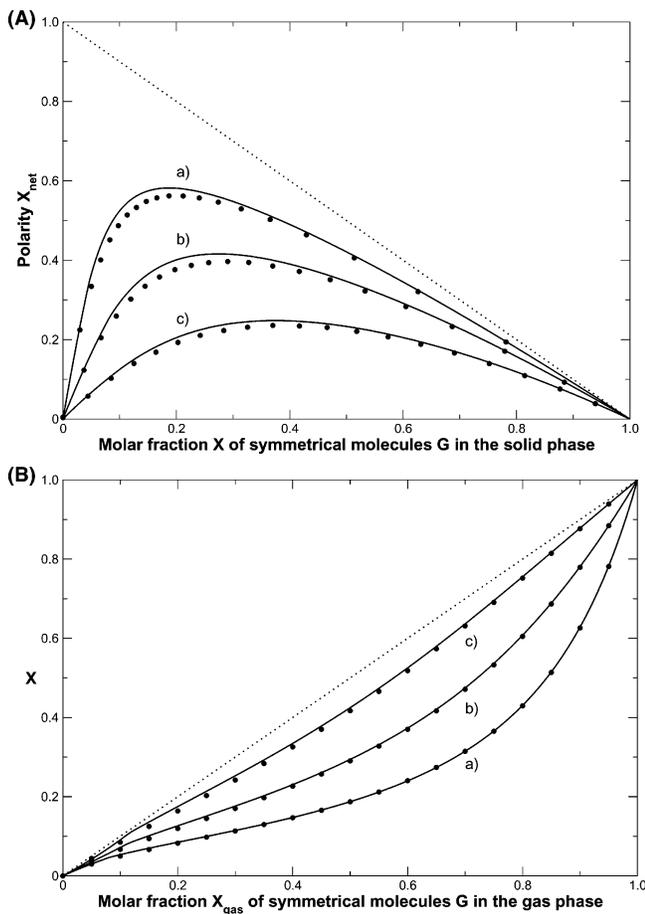


Figure 2. (A) Polarity X_{net} vs dilution X by symmetrical molecules G in the solid state. Longitudinal energy differences $\Delta E_{\text{A}} = \Delta E_{\text{D}}$: 8, 6, 4 [kJ/mol], (a–c). $\Delta E_{\perp} = 1$ kJ/mol, $T = 300$ K. Points: Monte Carlo simulations. Lines: Markov mean-field model.¹⁰ Error bars for results of the Monte Carlo simulations are too small to be shown here. Dotted line: Asymptotic limit for X_{net} vs X . (B) Molar fraction X of symmetrical molecules G in the solid phase vs X_{gas} of symmetrical molecules G in the gas phase. Longitudinal energy differences $\Delta E_{\text{A}} = \Delta E_{\text{D}}$: 8, 6, 4 [kJ/mol], (a–c). $\Delta E_{\perp} = 1$ kJ/mol, $T = 300$ K. Points: Monte Carlo simulations. Lines: Markov mean-field model.¹⁰ Note that the Monte Carlo points are uniformly distributed over the X axis. Dotted line: distribution coefficient of one.

mol. For the entire analysis, the following interaction energies were kept constant:

$$E_{\text{AA}} = E_{\text{DD}} = E_{\text{AN}} = E_{\text{NN}} = -2$$

$$E_{\text{ap}} = -2$$

$$E_{\text{m}} = -2, E_{\text{n}} = -3$$

Note, that the condition $E_{\text{AA}} = E_{\text{DD}}$ leads to zero polarity at $X = 0$ as explained above ($\Delta E_{\text{f}} = 0$). Sufficiently negative values for E_{m} and E_{n} ensure formation of a solid solution at least for a small range of X .

In case (i), the series $E_{\text{AD}} = E_{\text{DN}} = -10, -8, -6$ was chosen with $E_{\text{p}} = -1$, leading to the following energy differences: $\Delta E_{\text{A}} = \Delta E_{\text{D}} = 8, 6, 4$ and $\Delta E_{\perp} = 1$ (Figure 2).

In case (ii), the series $E_{\text{p}} = -1, 0, 1$ was chosen with $E_{\text{AD}} = E_{\text{DN}} = -10$, resulting in $\Delta E_{\perp} = 1, 2, 3$ and $\Delta E_{\text{A}} = \Delta E_{\text{D}} = 8$ (Figure 3). The temperature was set to $T = 300$ K.

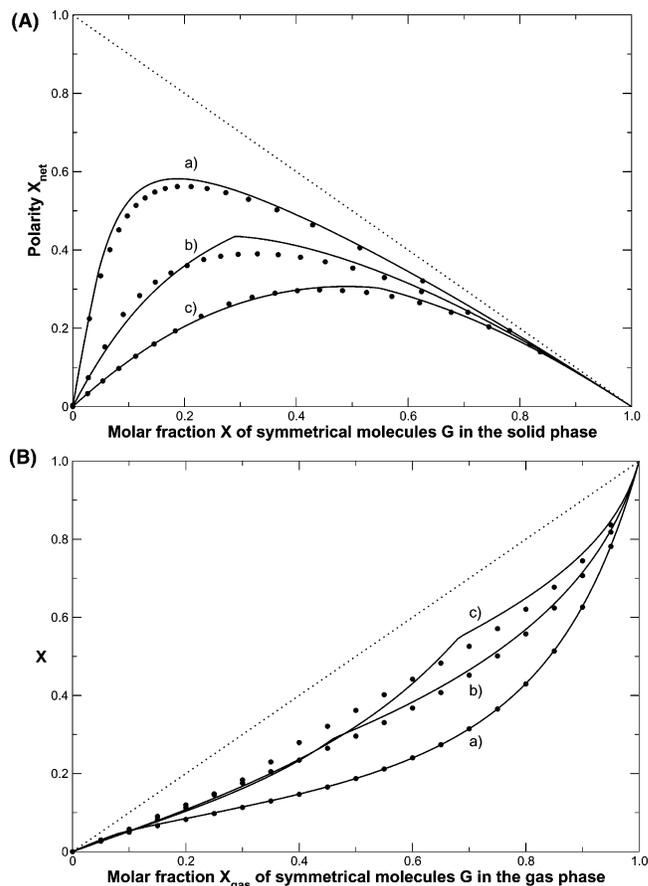


Figure 3. (A) Polarity X_{net} vs dilution X by symmetrical molecules G in the solid state. Lateral energy differences ΔE_{\perp} : 1, 2, 3 [kJ/mol], (a–c). $\Delta E_{\text{A}} = \Delta E_{\text{D}} = 8$ kJ/mol, $T = 300$ K. Points: Monte Carlo simulations. Lines: Markov mean-field model.¹⁰ Error bars for results of the Monte Carlo simulations are too small to be shown here. Dotted line: asymptotic limit for X_{net} vs X . (B) Molar fraction X of symmetrical molecules G in the solid phase vs X_{gas} of symmetrical molecules G in the gas phase. Lateral energy differences ΔE_{\perp} : 1, 2, 3 [kJ/mol], (a–c). $\Delta E_{\text{A}} = \Delta E_{\text{D}} = 8$ kJ/mol, $T = 300$ K. Points: Monte Carlo simulations. Lines: Markov mean-field model.¹⁰ Note that the Monte Carlo points are uniformly distributed over the X axis. Dotted line: Distribution coefficient of one.

Calculations were done with the Monte Carlo method (lattice size: 100×100 ; single layer equilibration time: 1000 Monte Carlo steps per lattice site on average; growth equilibrium time: 50 layers; measurement interval: one layer; measurement range: 200 layers; see ref 10 for details) and the Markov mean-field model presented in ref 10.

The variation of X_{net} with respect to the concentration X of symmetrical molecules G is shown (Figures 2a and 3a). Starting by $X_{\text{net}} = 0$ and $X = 0$, polarity is formed by the inclusion of symmetrical molecules G, passing a maximum within $0 < X < 1$, decreasing and approaching a gradient of -1 in the limit $X \rightarrow 1$. As expected, a larger value for the energy difference $\Delta E_{\text{A}} = E_{\text{AN}} - E_{\text{DN}}$ enhances the selectivity between up and down states for the polar molecules H and, therefore, leads to a higher maximum X_{net} (Figure 2a). On the other hand, larger values of ΔE_{\perp} stabilize the centric orientational state of the crystal (because $E_{\text{ap}} \ll E_{\text{p}}$) and consequently weaken the effect of polarity formation (Figure 3a).

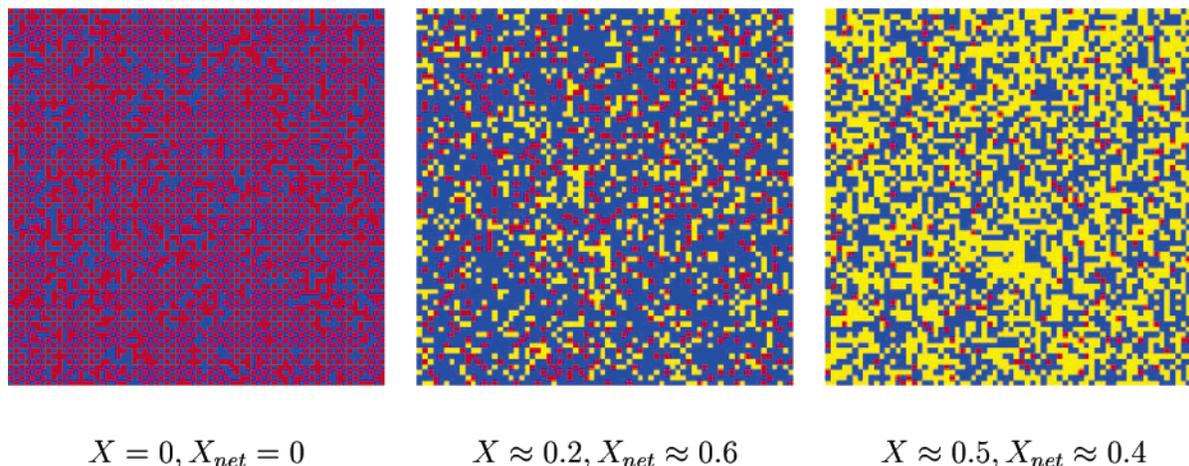


Figure 4. Snapshots of Monte Carlo simulations for three different cases of X_{gas} (0, 0.53, 0.85).¹⁰ Energies [kJ/mol]: $E_{AD} = -10$, $E_{AA} = E_{DD} = -2$, $E_p = -1$, $E_{ap} = -2$, $E_n = -3$, $E_m = -2$. Blue: polar molecule H in state down; red: polar molecule H in state up; yellow: symmetrical molecule G. Temperature: 300 K; lattice size: 70×70 ; snapshots taken after 100 layers of growth.

Ⓜ Monte Carlo animations of Figure 4 (Ⓜ left, Ⓜ middle, Ⓜ right) in animated gif format are available.

In both cases, Monte Carlo simulations and the analytical stochastic approach¹⁰ are in very good agreement. As shown in Figure 4, snapshots of Monte Carlo simulations for three different values of X_{gas} indicate that symmetrical molecules G are randomly distributed within the layer, showing virtually no tendency for clustering. Given this condition, the system can be described satisfactorily by a mean-field approach.

Because chemical potentials were taken into account in both models (Monte Carlo simulations and analytical theory), the fractions of H and G molecules in the solid phase can differ from those in the gas phase. This effect is shown in Figures 2b and 3b, which represent the distribution between the molar fractions of the symmetrical molecules G in the two phases, (X_{gas} vs X). Further insight to the systems can be gained by viewing Monte Carlo animations (Figure 4).

5. Conclusion

The effectiveness of the concept growth and design is made evident by Monte Carlo simulations which show for the first time that polarity in solid solutions can be tuned for a wide range of X_{net} . These calculations are considered a base for the search of real molecules. Fortunately, maximum net polarity is obtained for a system with relatively low X as the limiting asymptote in Figure 1 features a negative derivative. This makes it much more probable for finding real systems, because dipolar and symmetrical molecules do in general not crystallize in isomorphous structures. Therefore, a miscibility gap (Figure 1c) is likely to be encountered. This may not be a problem if X can be kept sufficiently

low, as high X_{net} values may be reached before a miscibility gap is limiting further increase.

Calculations support the idea that in the case of polarity tuning by solid solutions, the interaction E_{AD} is most important (Table 1): Best molecules feature low energies $|E_{AA}|$, $|E_{DD}|$ and a largest possible $E_{ND} < 0$ ($N \equiv A$). Consequently dipolar molecules which can undergo hydrogen bridging are most interesting for being tested. Experiments along these lines are in progress. Preliminary results for *p*-nitroaniline and other centrosymmetric structures of H molecules support present theoretical findings.

References

- (1) Hulliger, J.; Bebie, H.; Kluge, S.; Quintel, A. *Chem. Mater.* **2002**, *14*, 1523–1529.
- (2) Nye, J. F. *Physical Properties of Crystals*; Clarendon Press: Oxford, 1992.
- (3) Hulliger, J.; Roth, S. W.; Quintel, A. In *Crystal Engineering: From Molecules and Crystals to Materials*; Braga, D., et al., Eds.; Kluwer Academic Publishers: The Netherlands, 1999; pp 349–368.
- (4) Hulliger, J.; Roth, S. W.; Quintel, A.; Bebie, H. *J. Solid State Chem.* **2000**, *152*, 49–56.
- (5) Hulliger, J. *Chem. Eur. J.* **2002**, *8*, 4579–4586.
- (6) Hulliger, J. *Chimia* **2001**, *55*, 554–561.
- (7) Kluge, S.; Dohnke, I.; Budde, F.; Hulliger, J. *CrystEngComm* **2003**, *5*, 67–69.
- (8) Kato, M.; Kiguchi, M.; Sugita, N.; Taniguchi, Y. *J. Phys. Chem. B* **1997**, *101*, 8856–8859.
- (9) Newman, M. E. J.; Barkema, G. T. *Monte Carlo Methods in Statistical Physics*; Clarendon Press: Oxford, 1999.
- (10) Wüst, T.; Hulliger, J. *J. Chem. Phys.* **2004**, submitted.

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