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Molecular Origin of Supramolecular Self-Assembling in Statistical Copolymers[†]

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ABSTRACT: The X-ray structure of a derivative of urazoylbenzoic acid, i.e., 4-(1-but-1-en-3-yl-3,5-dioxo-1,2,4-triazolidin-4-yl)benzoic acid (1) proves the formation of an association polymer via intermolecular hydrogen bonding between either two carboxyl or two urazoyl groups. In addition, the X-ray structure shows the formation of an unusual dipole–dipole interaction between two antiparallel-oriented carbonyl groups of the heterocycle which has not been observed so far. The distance between the antiparallel-oriented carbonyl groups is only 2.980 Å. By the combination of hydrogen bonds and this dipole–dipole interaction, a two-dimensional highly ordered assembly of six-membered supramolecular rings is formed, where each of these supramolecular rings is built by six molecules of 1 interlinked by six noncovalent interactions. Such two-dimensional layers act as extended junction zones in substituted polydienes and explain the unusual mechanical properties of these materials.

Introduction

Due to their high reactivity in ene reactions, 4-substituted 1,2,4-triazolidin-3,5-diones have been used as modifying agents for various polydienes.[1] This polymer analogous reaction proceeds rapidly at room temperature up to conversions >90 mol %. At low degrees of substitution the highly polar 4-substituted urazole groups (4-R-3,5-dioxo-1,2,4-triazolidin-1-yl groups) are attached statistically along the polymer chain. In the case of R = $-C_6H_5$ binary hydrogen bond complexes are formed between the urazole groups,[1,2] leading to a thermoreversible network. These systems are useful as model systems for ionomers, because the degree of substitution is well-defined and the number of effective hydrogen bond junctions can be determined quantitatively from IR spectroscopy.[2e,f] If polybutadiene is modified with the corresponding benzoic acid derivative 4-(3,5-dioxo-1,2,4-triazolidin-4-yl)benzoic acid (2), each of the functional groups attached to the polymer is capable of forming two hydrogen bonds. Both {acid:acid} and {urazole··urazole} as well as {urazole·acid} hydrogen bonds may form,[3] resulting in an association polymer in the unpolar polybutadiene matrix (Figure 1a). On the basis of the unusual properties of these materials, which already are observed at rather low degrees of substitution (0.5–5 mol %), we have postulated the formation of an ordered supramolecular structure by the lateral aggregation of such association chains (Figure 1b, taken in part from ref 4c).[4,5] Evidence of the formation of an ordered structure by the polar side groups came from differential scanning calorimetry (DSC),[4b,c,e] small-angle X-ray scattering,[4b,f,5] IR spectroscopy,[4f,6] and mechanical measurements.[4a,d] From IR-dichroism experiments it has been concluded that only {urazole··urazole} and {acid:acid} dimers are forming the association polymers within the ordered clusters (Figure 1c).

However, the question remains open how an ordered aggregation of such association polymers can be possible in a polymer matrix. Recall that two nonpolar polybutadiene chains of each repeating unit of such an association chain are emerging. To get a more detailed picture about the molecular organization of these polar side groups in the modified polymer, 2 was reacted with *trans*-but-2-ene to give 4-(1-but-1-en-3-yl-3,5-dioxo-1,2,4-triazolidin-4-yl)benzoic acid (1, Scheme I).[7]

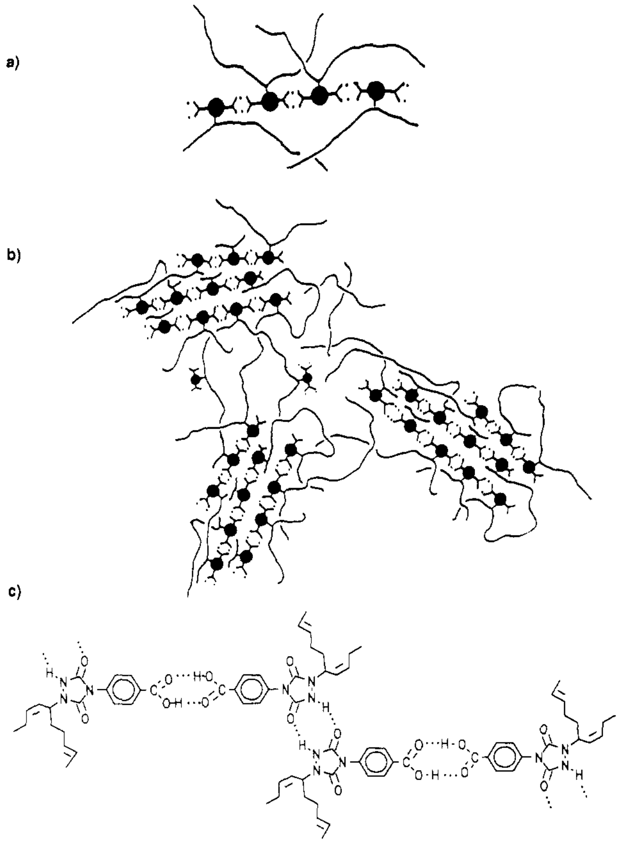

Figure 1. (a) Formation of association polymers in statistically modified polybutadiene. (b) Schematic representation of a domain formed by association polymers, according to ref 4c. (c) Sketch of an association polymer formed by the urazoylbenzoic acid groups attached to polybutadiene.[4e]

In the present paper we report on the crystal structure of 1.[8] So far only Butler et al. reported the structure of a urazole derivative, the brominated addition product of

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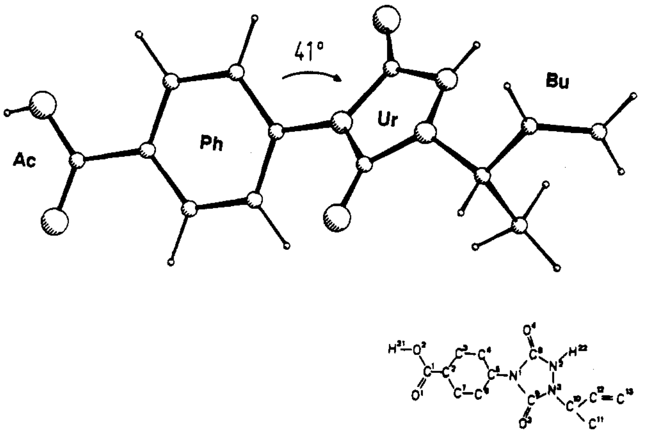
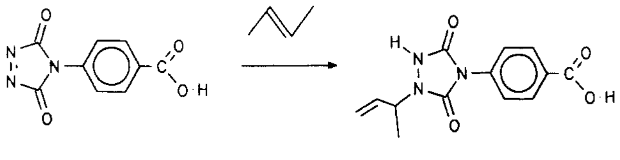


Figure 2. Structure of 1.[8] Benzoic acid moiety (Ph–Ac): C=O, 1.239 (6); C–OH, 1.271 (7) Å. 3,5-Dioxo-1,2,4-triazolidin-1-yl (urazoyl) moiety (Ur): N–N, 1.404 (6); N–C, 1.366 (5); C=O, 1.204 (6) ("dipolcarbonyl"; see Figure 3 and text); C–N, 1.394 (6); N–C, 1.389 (6); C=O, 1.218 (6) ("H-bridge carbonyl"; see Figure 3 and text); C–N, 1.352 (6) Å; torsional angles +13.1 (6), −10.6 (5), +4.8 (6), +3.1 (6), −9.7 (6)° (close to planar, approximately C_2 symmetry). Butenyl moiety (Bu): end group $=CH_2$, disordered. Torsion: Ac versus Ph, 4.1 (3)°; Ph versus Ur, 40.9 (3)°; Bu versus Ur, 79.6 (5)°.

Scheme I



S-(−)-4-(α-methylbenzyl)-1,2,4-triazolidin-3,5-dione with propene.[9] However, as will be discussed below, the situation in the chiral molecule is very much different from the urazoylbenzoic acid derivative.

Results and Discussion

Figure 2 shows the structure of 1 in the crystal. In the following discussion we will distinguish between the carboxylic acid (Ca), the phenyl ring (Ph), the urazoyl heterocycle (Ur), and the butenyl group (Bu). It is evident from Figure 2 that the carboxylic group and the phenyl ring are close to coplanar (torsional angle 4°). The heterocycle (Ur) is nearly planar with an approximated C_2 symmetry. Bond distances and angles are in good agreement with the data reported by Butler et al.[9] The torsional angle between Ur and Ph is 40.9°.[10] In the butenyl part (Bu) the final methylene unit is crystallographically disordered. Bu has a torsional angle with respect to Ur of 79.6°; i.e., the butenyl moiety, which represents a small portion of a polybutadiene chain, is about perpendicular to the plane of the urazole ring.

The $>C^{(8)}=O^{(4)}$ carbonyl group in the neighborhood of N–H has a length of 1.218 Å, which is slightly longer than the $>C^{(9)}=O^{(3)}$ group. This already may be taken as an indication that the $>C^{(8)}=O^{(4)}$ carbonyl group is involved in the hydrogen bond. Contrary to this result, Butler et al. reported a length of 1.185 Å for the carbonyl group in the neighborhood of the N–H group and 1.236 Å for the carbonyl group analogous to $>C^{(9)}=O^{(3)}$ and concluded from this that a single hydrogen bond between $>C^{(9)}=O^{(3)}\cdots H-N^{(2)}$ is formed.[11]

Figure 3 shows the arrangement of 1 in the crystal. The intermolecular distances prove the formation of binary cyclic hydrogen bond complexes involving two hydrogen bonds between acid groups on the one hand and two –CONH– units of urazole rings on the other hand. The

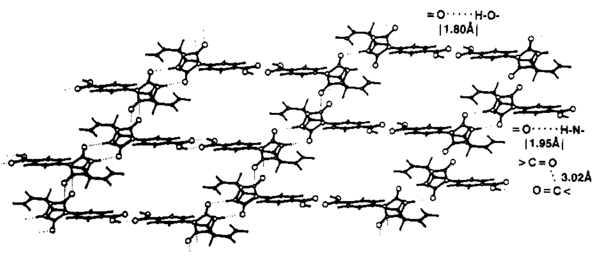


Figure 3. Sketch of the crystal structure of 1.[8] Threefold interlinking of 1 molecules (around three symmetry centers (SC): (I) Ac part (O–H···O hydrogen bond, –OH, 0.85 (8) Å; –OH··O, 1.80 (7) Å; O*H*··O, 2.616 (5) Å; angle, OH·∧·O=C 162 (8)°; SC at 1/2, 0, 1/2 (*f*)), two times at the Ur ring. (II) >NH···O=C< hydrogen bond, NH, 0.89 (8) Å; >NH··O=C<, 1.95 (9) Å; >N*H*··O=C, 2.820 (6) Å; angles, >NH·∧·O=C<, 164 (7)°; SC at 0, 1/2, 0 (*c*). (III) Dipole–dipole interaction: C=O··C, 3.021 (6) Å; angle, >C=O·⌟·C 99.3 (3)°; SC at 1/2, 0, 0 (*d*)). Layer structure formed by a six-membered ring: one ring consisting of six molecules of 1 + six noncovalent interactions = "supramolecular" analogon to graphite).

hydrogen bond between the carboxylic acid groups $-COO^{(1)}H\cdots O^{(2')}=C<$ has the following characteristic dimensions: –OH, 0.8 Å; H··O=C, 1.8 Å; O*H*··O=C<, 2.616 Å. The two carboxylic groups are in a plane; the angle –OH·∧·O= is 162°. These data are in excellent agreement with the structure of the hydrogen bonds of benzoic acid.[12] In contrast to this, the five-membered urazole rings are not coplanar. The urazole rings are shifted parallel with respect to each other. The two $>N^{(2)}H\cdots O^{(4')}=C^{(8)}<$ hydrogen bonds have the following characteristics: >NH, 0.89 Å; >NH··O=C, 1.95 Å; >NH··O=C<, 2.82 Å. The NH·∧·O=C angle is 164°. Due to the parallel shift of the five-ring planes and the torsion between Ph and Ur, the resulting association polymer resembles a stairway, formed by {acid:acid} and {urazole··urazole} linkages. This is the "secondary structure" that has been proposed for the association polymer in the polybutadiene matrix on the basis of IR-dichroism experiments.[6] The X-ray structure gives no evidence for further hydrogen bonds or π–π interactions between the phenyl rings. However, an unexpectedly small distance in combination with a geometry which has not been described so far[13] is observed for the carbonyl groups $>C^{(9)}=O^{(3)}$ which are not involved in hydrogen bonding: The two carbonyl groups form a parallelogram with antiparallel-oriented carbonyl groups. The distance between $>C^{(9)}\cdots O^{(3')}$ is only 3.021 Å. The angle $C^{(9)}=O^{(3)}$·⌟·$C^{(9')}$ is 99.3°; i.e., the two carbonyl groups form a slightly distorted rectangle with a distance of only 2.98 Å between the antiparallel carbonyl groups. This distance is considerably shorter than the van der Waals distance, which is estimated to be on the order of 3.2–3.3 Å for C···O. This low distance indicates a rather strong bonding dipole–dipole (i.e., quadrupole) interaction.[14]

In total the individual molecule 1 experiences three noncovalent interactions. Both binary hydrogen bond complexes as well as the quadrupole are located around crystallographic symmetry centers {Ac:Ac symmetry center (SC) at 1/2, 0, 1/2; Ur··Ur (H-bridge) SC at 0, 1/2, 0; Ur·Ur (quadrupole) at 1/2, 0, 0; locations with respect to the elementary cell dimensions}. Six molecules of 1 form a ring, kept together via six noncovalent interactions. These rings represent the basic motif of a two-dimensional network involving three different types of interactions. It may be regarded as a supramolecular analogon to graphite. The X-ray structure gives no indication for any unexpectedly low distance between two of these layers. The alkenyl chains (Bu) are located alternating above and below this layer.

Conclusions

The two-dimensional supramolecular layer structure as given in Figure 3 represents the key to understanding how these polar groups, even if they are attached statistically along a polybutadiene chain, arrange in an ordered domain. Hydrogen bonds form the association chains; these are linked together via dipole–dipole interactions. The polybutadiene chains are located above or below this two-dimensional structure of the urazoylbenzoic acid units. However, the size of these supramolecularly ordered domains is limited due to topological constraints which result from the fact that the polar groups are attached statistically to the polymer backbone.[15]

IR spectroscopy on amphiphilic molecules, which were obtained from the reaction of **2** with long-chain α-olefins, shows that the same type of supramolecular arrangement is retained, irrespective of the length of the olefin. Melting of these molecules is associated with the cooperative breakup of the quadrupolar interaction, while the hydrogen bonds are still intact to a major extent.[14b]

In contrast to other supramolecular structures based on hydrogen bonding between low molar mass molecules,[16] the combination of hydrogen bond motifs with other directed noncovalent interactions like the dipole–dipole interaction in the present system provides additional degrees of freedom to design defined supramolecular structures. In the present system the functional groups are attached easily to chain molecules, and the formation of domains of highly ordered polar groups results in unexpected material properties.

One main question is how sensitive this structure is with respect to the chemical structure of the urazole derivative. In parallel work we have shown that the formation of the supramolecular structure is suppressed if the urazoyl groups are shifted from the para to the meta position of the aromatic ring.[17] On the other hand, by suitable variation of the substitution pattern, the stability of the supramolecular arrays can be further increased.[18] Further variation may result in supramolecular structures which can be switched optically.[19] In addition, such polymers carrying these types of interacting groups with a strong tendency toward cooperative self-organization are expected to show a very peculiar behavior in dilute and semidilute solutions.

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Supplementary Material Available: Tables of X-ray structure data, atomic coordinates, and bond lengths and angles and torsion angles of 4-(1-but-1-en-3-yl-3,5-dioxo-1,2,4-triazolidin-4-yl)benzoic acid (4 pages); table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(3) Simple molecular modeling calculations show that comparable enthalpies of formation are expected for urazole··urazole and acid:acid hydrogen bonds, as well as for urazole·acid contacts.[4f]

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(5) On the basis of DSC and SAXS experiments, the number of functional groups which form such a domain of association polymers has been estimated to be on the order of 80–100.[4f] The length of an association polymer can be estimated either from mixtures of mono- and difunctional polar groups[4e] or from the analysis of the DSC transition according to an order–disorder transition. The experimental data show that the actual length of an association chain varies between 8 and 20 units, depending on the degree of substitution and the number of functional groups per polymer chain. Between 4 and 8 association chains form a single domain (Hilger, C.; Stadler, R., to be submitted to *Macromolecules*).

(6) Abetz, V.; Hilger, C.; Stadler, R. *Makromol. Chem., Makromol. Symp.* **1991**, *52*, 131. On the basis of the different dichroism of the benzoic acid unit and the urazole–amide-II vibration, we could show unambiguously that urazole·acid contacts play no role in the formation of the supramolecular ordered structure. In addition, the orientation behavior of the association polymer as well as SAXS data on oriented samples[4c] shows that the polar domains dispersed in the polymer matrix are highly anisotropic (Abetz, V. Doctoral dissertation, Universität Freiburg, 1990).

(7) The synthesis of **2** is described in ref 4b. A saturated solution of *trans*-but-2-ene is prepared by bubbling the gas into about 50 mL of CH_2Cl_2 at −78 °C. A total of 400 mg of **2** (1.82 mmol) is dissolved in ethyl acetate and added to the solution of the butene (olefin is present in about 20-fold excess). After disappearance of the red color of **2**, the mixture is stirred for another 2 h at room temperature. Solvent and excess olefin are evaporated under vacuum. The remaining powder of **1** was isolated in analytical quality. Yield: 97.9% Fp: 225 °C. Anal. Found (calcd for $C_{13}H_{13}N_3O_4$ (275.2)): C, 56.99 (56.72); H, 4.95 (4.76); N, 15.11 (15.27). ^1H NMR (90 MHz, acetone-d_6, 25 °C, TMS): δ 1.4 (3 H, d, CH_3), 4.77 (1 H, m, >CHN), 5.27 (2 H, t, CH_2), 6.0 (1 H, m, =CH–), 7.9 (4 H, AA′BB′, H_{ar}). IR (KBr): 3450 (br, m), 3156 (s), 3070 (s), 2986 (s), 2920 (s), 2850 (s), 2675 (m), 2550 (m), 1775 (m), 1703 (vs), 1683 (vs),1648 (sh, w), 1607 (s), 1583 (w), 1520 (m), 1425 (s), 1380 (sh, w), 1320 (m), 1290 (m), 1180 (m), 1130 (m), 925 (m), 860 (w), 840 (w), 785 (m), 760 (w), 730 (w), 690 (w) cm^{-1}. Single crystals for X-ray analysis were obtained from slow crystallization from benzene.

(8) Crystal structure analysis of **1**: triclinic $P\bar{1}$; $a = 6.561$ (1), $b = 8.687$ (2), $c = 12.677$ (1) Å; $\alpha = 93.68$ (1)°, $\beta = 104.97$ (1)°, $\gamma = 102.78$ (1)°; $V = 675$ (1) Å^3; $Z = 2$. 1540 reflections with $I > 1.5\,\sigma(I)$, 194 variables, $R = 0.0803$. Further details about the crystal structure analysis may be obtained as supplementary material.

(9) Mallakpour, S. E.; Butler, G. B.; Aghabozorg, H.; Palenik, G. J. *Macromolecules* **1985**, *18*, 342.

(10) This strong torsion is the result of the steric hindrance between the carbonyl oxygens of the heterocycle and the hydrogen atom (H_3 and H_5) of the phenyl ring. Molecular modeling calculations using the program PC model from Serena Software give an angle of 45°. If the hydrogen bonds are neglected in the calculation, the torsional angle is 0°.

(11) The thermodynamic parameters, determined for the binary urazole·urazole complex, are $\Delta H = -27$ kJ mol^{-1} and $\Delta S = -52$ J mol^{-1} K^{-1}.[2e] Similar values have been observed for other highly ordered cyclic binary hydrogen bond complexes. The different hydrogen bond reported by Butler et al.[9] in the crystal is the result of the fact that their molecule is chiral. Chirality excludes the formation of a centrosymmetric structure which is present if the cyclic binary hydrogen bond complex is formed.

(12) Simm, G. A.; Robertson, J. M.; Goodwin, T. H. *Acta Crystallogr.* **1955**, *8*, 157.

(13) A computer search of similar structural units in the Cambridge Structural Database has been unsuccessful. There are no reported crystal structures which show a similar short antiparallel arrangement of two carbonyl groups.

(14) (a) Such a strong binding interaction should also be observable by other techniques, i.e., by spectroscopy. Indeed for both 1[3f] and substituted polybutadiene a splitting is observed for the characteristic asymmetric carbonyl ring vibration of the urazole ring, which is located at about 1703 cm^{-1}, if the urazole ring is part of a hydrogen bond complex.[2e] For temperatures below

the melting of 1 or below the order–disorder transition observed for the urazole acid groups attached to polybutadiene, this carbonyl vibration splits into two absorptions at 1690 and 1720 cm^{-1}. This splitting disappears at high temperatures at the order–disorder transition. Thus it must be concluded that this splitting, which is explained by the coupling of the vibrations of the individual urazole rings, is related to the existence of an ordered structure (Hilger, C.; Abetz, V.; Schirle, M.; Stadler, R. in preparation). (b) Schirle, M. Diplomarbeit, Universität Mainz, 1990.

(15) The fraction of functional groups which are not incorporated into the ordered domains depends on the distance between the functional groups along the chain, on the number of groups per chain, and on the chain flexiblity.[2c,4f,5]

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