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Spherulite formation in a "noncrystalline" two-dimensional hydrogen-bond assembly

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Dedicated to the memory of Ingrid Hoffmann (died 12. 6. 1993)

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Summary

4-Urazoyl benzoic acid groups **1** are attached as terminal end group to an oligoisobutene. According to wide-angle X-ray scattering the material is amorphous. Differential scanning calorimetry, small-angle X-ray scattering, transmission electron microscopy, and polarizing microscopy show that the polar head groups form ordered two-dimensional assemblies which organize into spherulites. Temperature-dependent SAXS measurements and the d.s.c. analysis give a close insight into the order-disorder ("melting") process of the two-dimensional clusters which form macroscopic spherulites. The order-disorder transition of the clusters is closely related to the dynamics and order of the polyisobutene chain.

Introduction

In previous work we have demonstrated that 4-urazoyl benzoic acid groups **1**, which are attached randomly to polybutadiene (R: polymer chain), give rise to the formation of supramolecularly ordered assemblies[1]. These assemblies are characterized by an order-disorder transition ("melting" endotherm) around 80 - 100°C, if the groups are attached to a 1,4-polybutadiene. Up to this temperature the 4-urazoyl benzoic groups (U4A) within the ordered clusters are rigid[2] and the polar clusters act as efficient junction zones of a thermoreversible polybutadiene network[3]. Based on IR-dichroism experiments[4] and the X-ray-structure of a low molar-mass model compound **1b**[5], the formation of the ordered urazoyl benzoic acid assemblies could be attributed to the formation of "association chains" via urazole:urazole (U:U) and acid:acid (A:A) hydrogen bonds, which aggregate laterally into a two-dimensional cluster. In the original work which describes the X-ray analysis, the lateral aggregation between these "association chains" was attributed to the formation of additional dipole-dipole-interactions between urazole groups[5].

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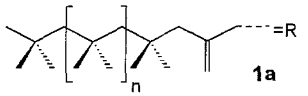
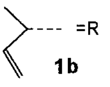
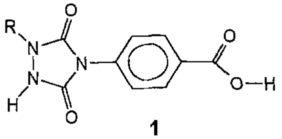


1a

n = 8 (number average)



1b



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This interpretation was based on the unusually close arrangement of those carbonyl groups of neighbored heterocyclic units which are not involved in hydrogen bonding. Very recently the X-ray analysis of model compounds of other urazoyl-aryl-acids, which also show this type of supramolecular self assembling in polymer matrices, lead us to revisit the X-ray structure of butenyl-urazoyl benzoic acid **1b**: The "dipole-dipole"-interaction is only observed in the crystal structure **1b** (R: 2-but-1-en-yl), while all crystal structures (including **1b**) give evidence of the formation of hydrogen bonds between the aromatic C-H (carbon atom in ortho position to the carboxylic acid group) and the urazole heterocycle[6]. Thus the formation of a two-dimensional layer may rather result from the lateral aggregation of the U:U4A:A4U:U association chains via aryl-urazole-hydrogen bonds (Ar:U) (Figure 1). If the U4A-stickers are randomly attached to a polybutadiene the two chains emerging from each polar group have to pack on top and on the bottom of the 2D-layer. As a consequence, the assembly of the stickers sensitively depends on the nature of the polymer backbone. Stickers attached to chains with larger average diameter than 1,4-polybutadiene (like polyisoprene or 1,2-polybutadiene) do not assemble into ordered layers[7], while α-olefin-derivatives (C10 - C20) have a melting point around 150°C, independent of the chain length[8].

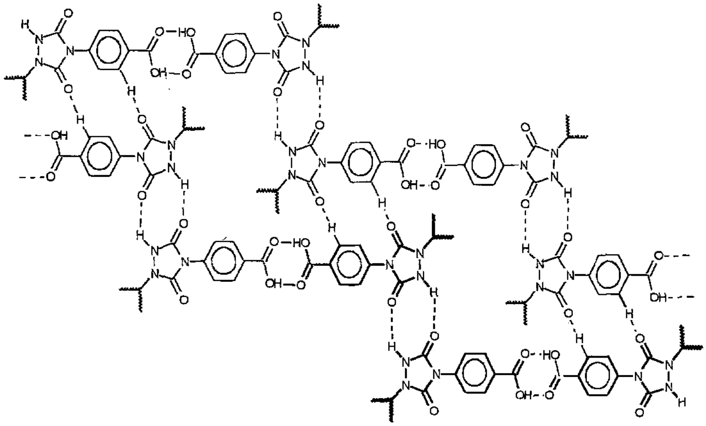


Figure 1: Two dimensional assembly of urazoyl benzoic acid groups formed by the lateral aggregation of association chains (U:U4A:A4U:U4A:A) via aryl-urazole hydrogen bonds[6]

To elucidate the details of the supramolecular assembling process, and to bridge the gap between low-molecular-weight compounds and the randomly substituted polymers, the present paper focuses on a model compound in which one U4A-sticker is attached to one chain end of a low-molecular-weight polyisobutene (P_n=13) **1a**.

Results

Excess oligoisobutylene with a vinylidene end group (Glissopal™ was kindly provided by Dr. Winkler, BASF) is reacted with 4-(3,5-dioxo-1,2,4-triazolin-4-yl)-benzoic acid to give 4-(1-oligoisobuten-1-yl-3,5-dioxo-1,2,4-triazolidin-4-yl)-benzoic acid (PIB-U4A) **1a. 1a** shows one of three possible isomers. The molecular weight of the starting PIB is around 800 g/mol, the molecular weight of the substituted material 1000 g/mol. Contrary to the PIB oligomer which is a low viscous liquid, PIB-U4A is a soft solid. The glass transition temperature of the PIB oligomer (-91°C according to DSC: inflection point of heat capacity change, extrapolated to heating rate zero) is shifted to -81°C in PIB-U4A. High molecular weight PIB has a glass transition of T_g^{∞}= -73°C. If one assumes the validity of the Fox-Flory equation to account for the variation of the glass transition with the number of chain ends (degree of polymerization), the observed increase of the glass transition corresponds to a reduction of the number of free chain-ends by a factor of two.

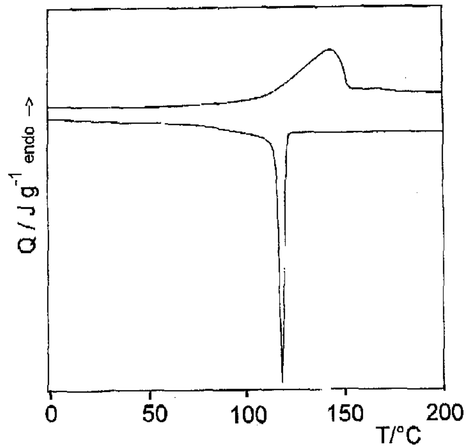


Figure 2: DSC-traces of the 1st heating-cycle of PIB-U4A (20K/min).

Figure 2 shows the DSC trace of PIB-U4A at a heating rate of 20 K/min in the temperature range from 0°C to 200°C (first heating cycle). The second and further heating cycles show the same behaviour with slightly deminished melting enthalpies: 1st **heating:** melting region: 112 - 178°C, maximum: 143°C, ΔH: 17.6 kJ/mol; 1st cooling: "crystallization": 124 - 90°C, maximum: 120°C, ΔH: -14.2 kJ/mol; **2nd heating:** melting region: 99 - 163, maximum: 143°C, ΔH: 14.2 kJ/mol; 2nd cooling: "crystallization": 122 - 90°C, maximum: 120°C, ΔH: - 12.3 kJ/mol. The melting enthalpies are given with respect to the concentration of U4A groups.

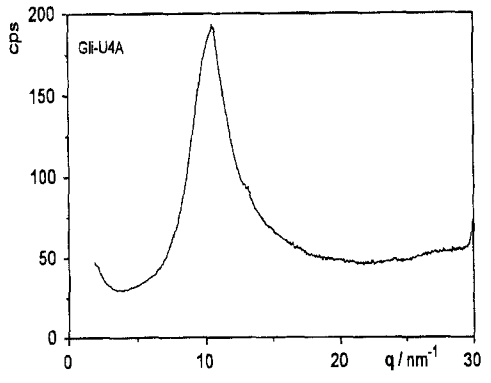


Figure 3: Wide-angle X-ray scattering profile of PIB-U4A.

The most characteristic feature of the "melting" process is the extreme width of the transition while "crystallization" occurs in a rather narrow temperature range with only a slight tailing. This already indicates that the endotherm is not a typical crystal melting process. Figure 3 shows the wide angle X-ray scattering of PIB-U4A in the **q**-range (**q**= scattering vector) from 2 to 30 nm^{-1}. Between $7 < \mathbf{q} < 20$ nm^{-1} a broad amorphous halo is observed. There is no indication of crystalline reflections. Obviously the material does not show 3-dimensional crystalline order.

Figure 4 shows the small angle X-ray profiles of PIB-U4A (HASYLAB (DESY) polymer beam-line A2; point collimation; monochromatic synchrotron radiation (λ = 0.150 nm); position sensitive detector set at 120 cm) in the temperature range from 80 to 145°C. Two pronounced scattering maxima are observed in the **q**-range between 0.25 $nm^{-1} < \mathbf{q} < 2.5$ nm^{-1}.

The weak maximum around 1.78 nm^{-1} obviously is the second order maximum of the main peak around 0.87 nm^{-1}. The scattering intensity remains constant up to 90°C. Above this temperature the scattering intensity slightly decreases, until it vanishes around 144°C. This decay occurs in a broad temperature range, similar to the broad melting observed by DSC. At 150°C only a very broad weak scattering maximum between $0.75 < \mathbf{q} < 1.75$ nm^{-1} is observed. Upon cooling (cooling rate 2 K/min) the two maxima form again. In accordance with the DSC trace, the development of the scattering peaks evolves in a narrower temperature intervall than melting. Upon slow cooling the scattering peaks are narrower than before heating. This is an indication of an increased structural perfection. If the positions of the scattering maxima are analyzed according to Bragg's law, the main peak corresponds to a spacing of 7.1 nm and the second peak to half of this value. As can be seen from Figure 4, the position of the maximum slightly shifts with temperature (Figure 5). During heating the long spacing increases from 7.1 nm (20°C) to 7.3nm (60°C) and then deacreases over a broad temperature range to 6.4 nm at 140°C, which is the highest temperature for which the SAXS peaks are observed. Upon cooling, the peak is first observed at 138°C (6.7 nm) and the long spacing increases to about 7.1 nm (80 - 90°C) before decreasing to 6.9 nm at room temperature.

The observation of the two SAXS-maxima strongly supports the model of two-dimensional layers of the polar groups which form extended stacks in the case of the endsubstituted PIB-oligomer. Direct evidence can be obtained from transmission electron microscopy. Ultrathin films were cast from dilute toluene solution directly onto gold grids. No conclusive TEM micrographs were obtained from unstained samples. Upon staining in RuO_4 vapor (30 minutes, RuO_4 attacks aromatic rings) the beam stability is improved. At very large magnification "lamellar stacks" can be observed in the micrographs. Figure 6 shows a typical micrograph with a stack of about 10 lamellae. Annealing of the stained ultrathin film improves the quality of the stacks. The periodicity of the lamellar stacks is $\approx$7nm. This value is in excellent agreement with the spacing obtained from SAXS.

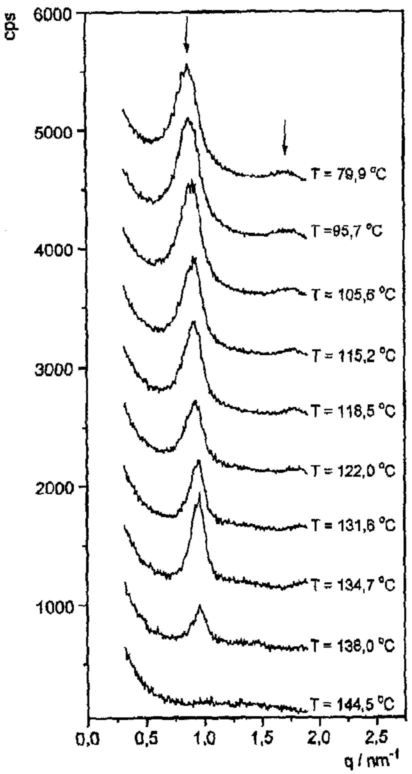
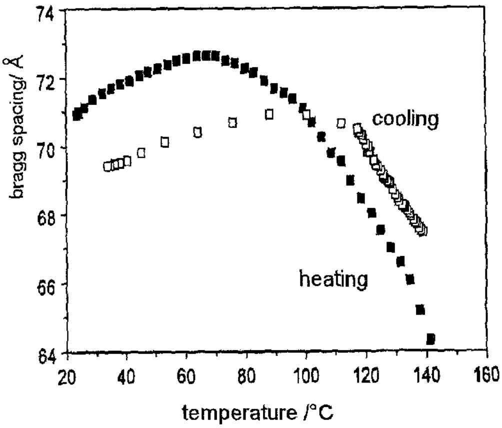


Figure 4: SAXS-profiles of PIB-U4A at various temperatures (synchrotron radiation, 0.150 nm); arrows indicate position of primary and secondary scattering maximum.

Figure 5: Temperature dependence of the Bragg-distance obtained from the SAXS-peak during one heating ■/cooling □ cycle.



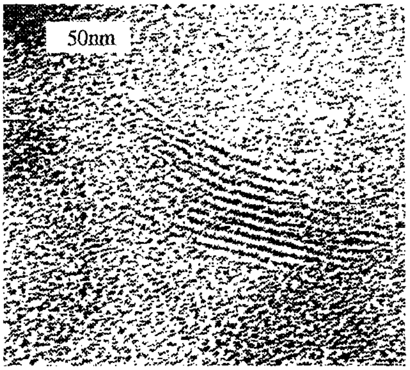


Figure 6: Transmission electron micrograph of PIB-U4A (sample cast from solution, stained with RuO_4)

Besides TEM, polarizing light microscopy was used for the direct observation of the supramolecular assembly process. Above the "melting" temperature the material is isotropic. Upon cooling from the melt, birefringent spherulitic objects form. Figure 7 shows an intermediate stage of such an isothermal (T_c= 130°C, after 20 minutes) spherulitic growth. At larger magnification it becomes evident that the material is rather different from "conventional" spherulites. The spherulites appear to consist of loose fringes. The absolute value of the birefringence is rather low if it is compared to the birefringence of crystalline materials of the same thickness.

Discussion

There are various interesting aspects involved in the physics of the order-disorder transition in PIB-U4A. On the one hand WAXS is a direct proof that long-range order is absent, while the d.s.c. data show that the order-disorder transition resembles a first-order transition. The disorder-order transition is characterized by a strong undercooling and ordering occurs in a rather narrow temperature interval (with some slight tailing to lower temperatures). On the other hand, the broad "melting" transition clearly shows the difference from a "typical" first order transition. This broad transition obviously is related to the SAXS-data. The long spacing observed at room temperature in both SAXS and TEM is in excellent agreement with a value estimated according to $2*L_{PIB} + D_{U4A}$ where L_{PIB} is the length of the oligoisobutene. For the given degree of polymerization (≈ 13) a stretched chain would have a length of approximately L_{PIB}= 3.3 nm. From molecular models the thickness of the layer of U4A-groups can be estimated to be in the order of D_{U4A}= 0.4 - 0.5 nm. The experimentally observed long period of 7.1nm thus would be in agreement with a layered structure involving rather stretched PIB-chains as a result of the dense packing of the chains on the two-dimensional U4A-surface. It has been shown independently by ^{2}H-NMR-experiments on U4A-substituted polybutadiene that at least two monomer segments which are directly linked to the polar group are glassy even at room temperature[2]. This can only be explained as a consequence of the dense chain-packing on the cluster surface. This situation is schematically shown in Figure 8 (left). Upon heating, the density becomes smaller and as in most systems, the "lattice" parameter, i.e. the Bragg spacing slightly increases (Figure 5). Increase of the temperature, i.e. increase of the kinetic energy, will tend to increase the population of gauche conformations in the PIB-segment and thus a more coiled conformation. This will cause a force on the two-dimensional assemblies, which may disrupt as indicated in Figure 8 (right) in a side view. As a consequence, the chains can adopt the more favored coiled conformation and the Bragg spacing decreases.

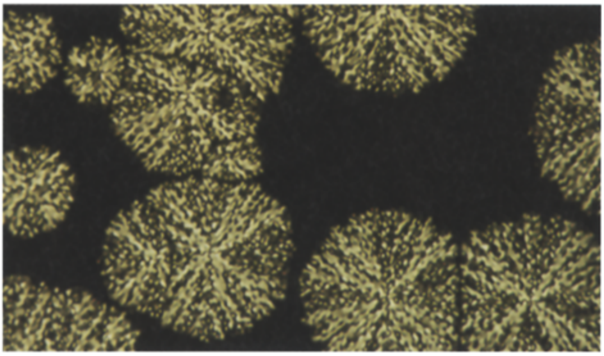


Figure 7: Polarizing light microscopy of PIB-U4A; sample kept at T_c =130°C for 20 minutes (crossed polarizers) (x64)

As we know from temperature dependent IR-spectroscopy[8] the fraction of urazole-urazole and acid-acid hydrogen bonds changes only slightly in the temperature range below the order-disorder transition. We thus conclude that the transition can be mainly attributed to the rupture of the aryl-urazole hydrogen bonds (Figure 1). Rupture of some of these secondary interactions would cause considerable removal of the internal stress acting on the clusters due to the enhanced thermal agitation of the PIB chains. This results in the very broad order-disorder transition. Upon cooling, the cooperative disorder-order transition will occur as soon as the nuclei of the 2D-structure are stable. These will grow and cause the formation of spherulites in this X-ray-amorphous material. The d.s.c. data show that the heat evolved upon cooling at 20K/min is always smaller than the "melting endotherm". This result is valid despite the uncertainties in the determination of the transition enthalpies if the temperature range of the transition is broad. Obviously the structure does not form perfectly from the melt within the cooling cycle.

The spherulitic texture is very much different from conventional crystalline spherulites. Obviously the structure is highly distorted and the bended structure of the spherulite gives evidence that the number of laterally aggregated association chains is limited. Such a structure may be described more adequately as a ribbon, which may twist or bend and thus cause the birefringent texture.

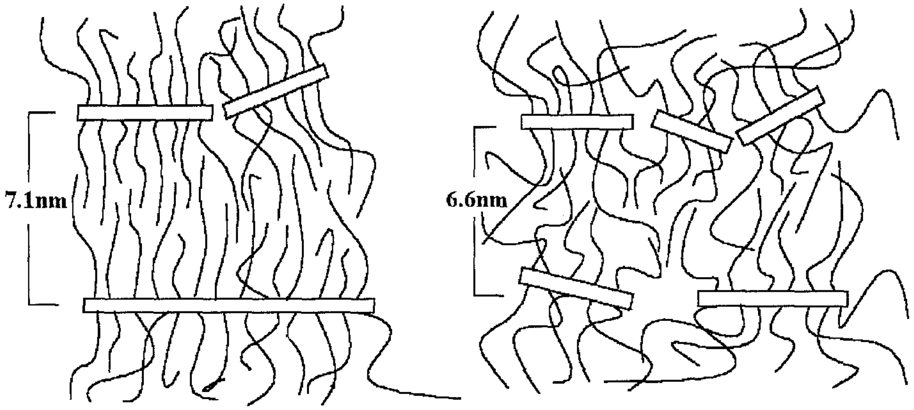


Figure 8: Side view of the two-dimensional layer structure of PIB-U4A. (left): "stretched" PIB-chains at low temperature; (right): coiling of PIB-chains at higher temperature causes a rupture of the 2D-assembly and a thus a reduction of the size of the 2D-clusters. To maintain the density the distance between the (less ordered) layers decreases.

The present work has shown that the polar U4A groups attached to the chain end of an oligomeric polyisobutene forms two-dimensional lamellar assemblies which arange to large scale spherulites. The molecular state of order within the polar aggregates is the same as in randomly substituted polydienes, where they cause an efficient cross-linking. One of the interesting physical features of this material is that the size of the clusters is controlled by the segmental dynamics of the PIB-segments.

Experimental

Sample preparation: 4-(3,5-Dioxo-1,2,4-triazolin-4-yl)-benzoic acid (Td4A) was synthesized according to literature3. 1.64 g of oligoisobutene (Glissopal™, from BASF) are dissolved in 100 ml of dry ! toluene. 0.2 mmol of the freshly prepared Td4A (dissolved in 20 ml of dry ethylacetate) are added. The solution is stirred at room temperature until the red colour of Td4A has disappeared (about 48 h). The solvent is completely removed under vacuum. To remove excess of unreacted oligoisobutene, the raw product is dissolved in a low amount of THF and added onto a column (silica/petrol ether). Unreacted oligoisobutene is removed by elution with petrol ether. Then the solvent is changed to THF to remove the product from the column. The product is dried under high vacuum. The product is a white waxy product which forms a solid foam from the vacuum drying. The material is characterized by NMR, IR and elemental analysis. The data are in agreement with structure 1a: ^{1}H-NMR: 7.96ppm AABB, (4 aromatic protons); 5.61 ppm, 5.24 ppm and 5.09 ppm (2 olefinic methylene protons, various isomers); 4.44ppm and 4.22ppm (2 methylene protons neighbored to heterocycle and double bond); 2.05 ppm (methylene protons neighbored to double bond); 1,38ppm, chain-CH_2, 1.08 ppm chain-CH_3, 0.96 ppm end group-CH_3.

Differential scanning calorimetry (d.s.c.) was performed with a Perkin Elmer DSC7. Standard heating rate: 20 K/min. Other heating rates where appropriate (see text). The instrument was calibrated using Naphthalin and Indium standards.

Wide- angle X-ray scattering WAXS: Goniometer PW1078, Philips with a proportional counter (PW1710, Philips); Ni-filtered Cu-K_α.

Small angle X-ray scattering SAXS: Temperature-dependent SAXS-profiles were obtained at HASYLAB (DESY, Hamburg) at polymer beamline A2 using monochromatic synchrotron radiation at 0.150 nm using a position sensitive detector. Distance between sample and detector: 120cm. The heating/cooling rate was 2 K/min.

Transmission electron microscopy: Zeiss TEM 90, 80kV (de Broglie wave length 4.18 pm); Samples were cast from dilute solution (Toluene) onto the gold-grid. The ultrathin samples were stained for 30 minutes in RuO_4 vapor.

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References

[1] a) Hilger, C.; Stadler, R. *Macromolecules 1990*, **23**, 2095

b) Hilger, C.; Stadler, R. *Macromolecules 1992*, **25**, 6670

[2] Dardin, A.; Stadler, R.; Boeffel, C.; Spiess, H. W. *Makromol. Chem. 1993*, **194**, 3467

[3] a) Hilger, C.; de Lucca Freitas, L.; Stadler, R. *Polymer 1990*, **31**, 818

b) Hilger, C.; Stadler, R. *Makromol. Chem. 1990*, **191**, 1347

[4] Abetz, V.; Hilger, C.; Stadler, R. *Makromol. Chem. Makromol. Symp. 1991*, **52**, 131

[5] Hilger, C.; Dräger, M.; Stadler, R. *Macromolecules 1992*, **25**, 2498

[6] Seidel, U.; Hellmann, J.; Schollmeyer, D.; Hilger, C.; Stadler, R. *Supramolecular Science, in print*

[7] Schirle, M.; Beckmann, J.; Stadler, R. *Angew. Makromol. Chem. 1992*, **202-203**, 261

[8] M. Schirle, Doctoral Dissertation, Johannes Gutenberg-Universität Mainz 1994