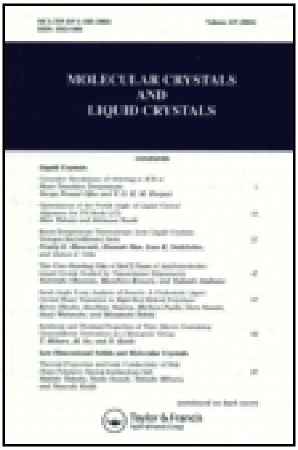

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Electronic Properties of Structurized Poly-1-Vinyl-1,2,4-Triazole

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Electronic Properties of Structurized Poly-1-Vinyl-1,2,4-Triazole

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For the first time, we have shown the possibility to obtain structurally ordered systems using structured (fractal) water as a solvent by taking a water-soluble polymer, poly-1-vinyl-1,2,4-triazole (PVT), as an example. When distilled water was used as a solvent, the films always have amorphous structure. The investigations of electronic properties of ordered PVT films show that the electronic properties of structured ordered PVT are similar as for crystal samples.

Keywords: fractal water; fractal polymer structure; structural order

INTRODUCTION

Today, we are dealing with new trends in the development of the scientific researches related to human activity. It is pertinent to mention here such new disciplines as nanophysics, nanoelectronics, nanobiology, nanochemistry, etc.

Nanotechnology produces the changes in the electronics of organic materials. Virtually, one can speak about the origin of the nanoelectronics of organic materials.

To meet the challenge, one needs to revise the properties of the known organic materials as nanoelectronic ones, synthesize new organic systems possessing unique electronic properties as special

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nanostructures, and elaborate new technological processes which would allow preparing new nanostructures for different applications.

In this work it is shown, on an example of water-soluble polymer, poly-1-vinyl-1,2,4-triazole (PVT), for the first time, that the structured water can define the structure of polymer. The electronic properties of structurally-arranged polymer correspond to the properties of the crystal, i.e., the anisotropy of properties is displayed.

MATERIALS

Triazoles, vinylazoles, and their polymer derivatives are interesting objects for scientific studies [1,2]. The practical importance of triazole compounds is widely known. Triazole derivatives, showing a wide spectrum of the biological activity, find an application as corrosion inhibitors, radioprotective agents, fungicides and pesticides in pharmaceutical chemistry and agriculture, and building blocks for the design of thermostable polymers. Homopolymers and copolymers of vinyltriazole can find a wide use in winemaking as flocculants and stabilizers of various wines, in medicine for the preparation of soft contact lenses and the manufacture of cartilaginous and bone tissue prostheses, in liquid chromatography as molecular sieves for the separation of proteins, enzymes, and nucleotides, in technical water supply and fire protection. Undoubtedly, these polymers should show the special properties, when they are used for the preparation of different nanostructures.

The introduction of a vinyl group to the triazole cycle does not drastically affect the π-electron charge of nitrogen in position 1. The polymerization of PVT has been carried out in DMFA under free-radical initiation in the presence of azobisisobutyric dinitrile (the initiator concentration was $3\ 10^{-2}$ mol/l) at 60°C.

The synthesized PVT ($M_w = 26000$) is a colorless powder, well solvable in water, dipolar organic solvents (DMFA, DMSO, DMAA), and acetic acid. It is hydrolytically stable, nontoxic, and capable to form complexes and salt. The nitrogen atoms of pyridine in PVT can participate (as donors of electrons) in the formation of hydrogen bonds with water molecules. The dissolution of PVT in water is accompanied by the high exothermic effect.

The thermodynamic investigations of the aqueous solutions of PVT have been performed in [1]. The exothermic effect of the PVT dissolution in water is apparently associated with the strong interaction of the polymer chains with water molecules due to the H-bonds formation, which involve unshared electron pairs of nitrogen atoms, heterocyclic and water hydrogen atoms. Since 1-substituted 1,2,4-triazole has maximal electronic density at N-4, it is reasonable to assume that the hydrogen bonds in PVT are formed with the participation of the unshared pair of just this atom. When PVT is mixed with water, the structures binding the chain with one water molecule are formed. The formation of a structure containing two water molecules per one chain of PVT is less energy favorable than the formation of a compound having one water molecule, which is explained by a small electronic density of the N-2 atom.

It has been shown [2] that PVT aqueous water solutions possess hydrophilic hydration.

It is known that the aqueous solutions differ from non-aqueous ones by the specific feature of water, i.e., by the availability of a porous network of hydrogen bonds in water [3]. Hydrophilic and hydrophobic hydrations are distinguished. Both types of hydration are characterized by negative values of excess enthalpies and entropy. Hydrophilic hydration is considered to mean the interaction of water with polar groups of a diluted substance, in particular the groups capable to the formation of hydrogen bonds with water molecules. Such a hydration involves the ordering of water molecules, which are firmly bound to polar groups of the diluted substance. Under hydrophobic hydration, the molecules of the diluted substance penetrate into the pores of the open structure of water and increase the interaction of water molecules with one another, which also results in the structure ordering.

Hydrophilic and hydrophobic hydrations occur also in aqueous polymer solutions. Hydrophilic hydration dominates in the PVT-water system. The following thermodynamic parameters of the PVT dissolution in water were determined at 298 K: enthalpy $\Delta H = -68.9$; entropy $\Delta S = -31.1$; the Gibbs energy of the mixing of PVT with water $\Delta G = -37.8$. All thermodynamic parameters are negative, which is explained by the formation of hydrogen bonds between the nitrogen atoms of heterocyclic fragments and water molecules. The total number of hydrogen bonds with PVT ensures its high hydrophility. The values of the water diffusion coefficient in PVT films prove this fact. The kinetic curve of the water sorption on films is typical. In the initial stage of the penetration of water in a polymer film, a slight decrease of the diffusion coefficient is observed. When the water content is enhanced, the diffusion coefficient begins to rapidly increase. The sharp increase of diffusion with rise of the water content in PVT films is indicative of the absence of a significant association of water molecules, which confirms the domination of hydrophilic hydration.

The predominance of hydrophilic hydration in the aqueous solutions of PVT is in good accordance with the data obtained for the aqueous solutions of low-molecular amines [4].

EXPERIMENTAL

Solid films of PVT were obtained from a solution. Two following types of water as a solution were used: the one was distilled water, and the second was a good natural drinking water, which has ordered structure or fractal structure [5–7]. The second water is the matrix of molecules of water and the impurities as the components of drinking water composing a self-ordered system. Such naturally ordered structure of water is a lyotropic liquid crystal. From such structured water, it is possible to obtain the solid state of fractal structure [5] (the phase transition: liquid state–solid state). In the same manner, when we are using such structured water for solving the PVT, we can obtain the ordered films of the polymer. To investigate the structure of layers, an optical microscope NU-2E ≪Karl Zeiss≫ was employed; the average magnification of the microscope is close to 150.

The electronic absorption spectra of films and solutions on distillate and structured water in the spectral region 4.20–6.00 eV were measured. The spectra were recorded at room temperature using a double-beam spectrophotometer ≪Hitachi≫, Japan.

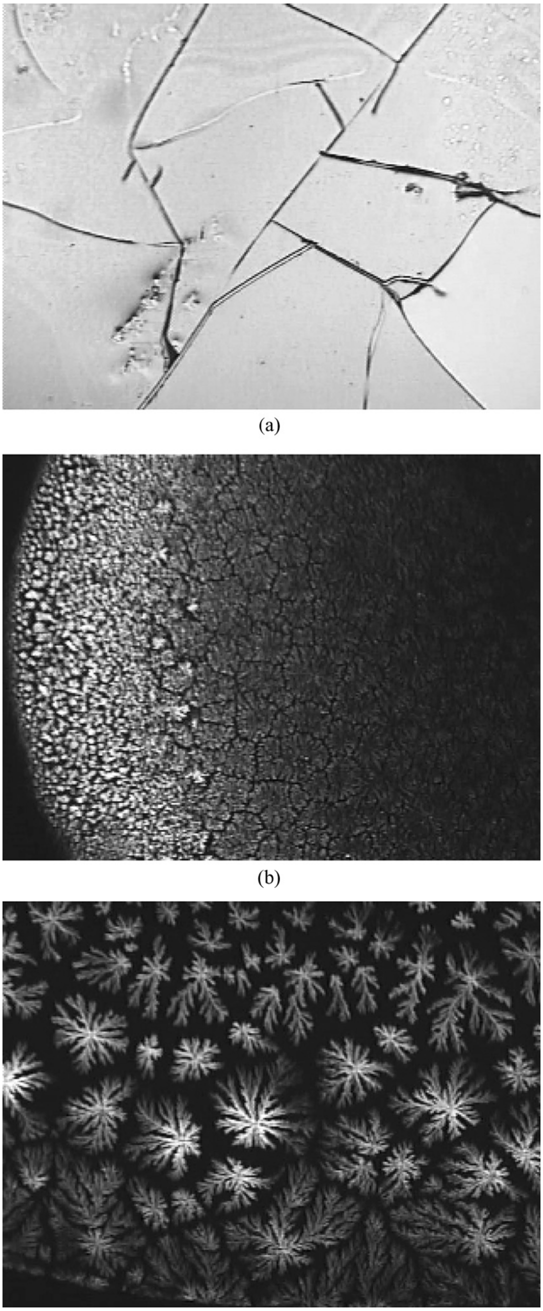
RESULTS

The structures of polymer layers in polarized light are shown in Figure 1. When distillated water was used as a solvent, the solid layers had amorphous structure (Fig. 1a). The films are glass-like with characteristic dislocations as typical lines. In polarized light, the films are isotropic. On the photo, we show the film obtained when a polarizer and an analyzer were not strictly crossed but were rotated relative to each other by 7–10 degrees.

Figure 1b shows the edge of the film obtained from a solution on structured water. It is evident from the picture that the film has optical bisymmetry. The bisymmetry of films is exceptionally due to the water structure. In this case, the water orders the film structure of PVT.

Figure 1b gives the structure of the solid phase of the solvent-fractal water [6]. It is a dry residue, which is formed on the substrate after the evaporation of water by a specific method.

In Figure 2 (a and b), the examples of the structure of solid layers obtained under specific conditions are shown. The structure (Fig. 2a) is polydispersal. It was obtained for a wedge-shaped film in the region of a wedge edge by the usual method of evaporation of a solvent (no additional heating of a solution was used; natural lyophilization). The film has fractal, optically active (or bisymmetric) structure.



(a)

(b)

(c)

FIGURE 1 Amorphous (a) and fractal (b) structures of PVT film; Fractal structure of water (solid state) (c).

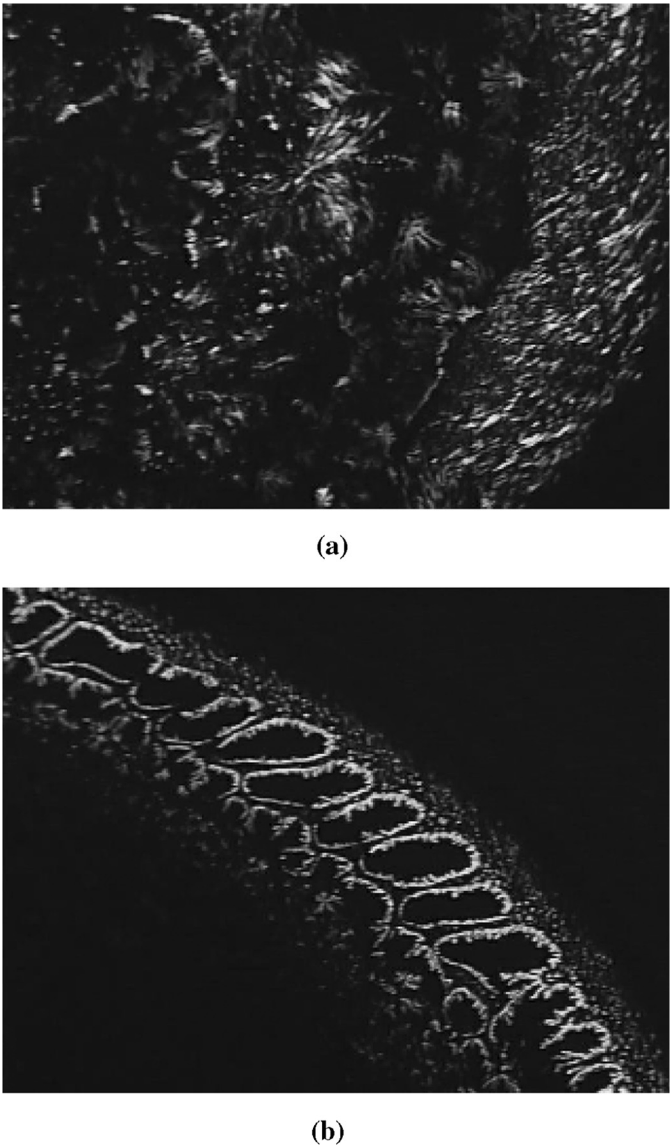


FIGURE 2 Structures of PVT solid layers obtained under specific conditions of films preparation.

Figure 2b shows the formation of characteristic periodic fractal structures on the edge of the film. Such a structure of the film points to the nonlinear processes at the phase transition from a solution to the solid phase, when the peculiarities of the polymer self-assembling in the initial solution are observed.

The formation of such specific structure is defined by the role of structured water (Fig. 1c) used as a polymer solvent.

In Figure 3, the absorption spectra of the solutions of PVT and solvent (water) are shown (it is a spectrum from [1]). The curve "albumin" presents the spectrum of serum albumin, which is structured using the fractal water in the same manner as for PVT (optically active samples). The absorption spectra of structural PVT and albumin testify that their energetic structures are similar.

The absorption spectra are typical of solvents (distillate and structured drinking water). They represent the long-wave part of the water absorption band, whose maximum is at 7 eV. (Fig. 3).

The absorption spectrum consists of two parts. The region of 4.25–5.25 eV corresponds to the absorption by impurities. The peculiarities of the absorption in this spectral range for the solutions of polymer and solvent are well seen in the case of a linear scale for the absorption (Fig. 3).

For the second spectral region (5.25–6.25 eV) the absorption obeys the Urbach rule (exponention dependence absorption on energy

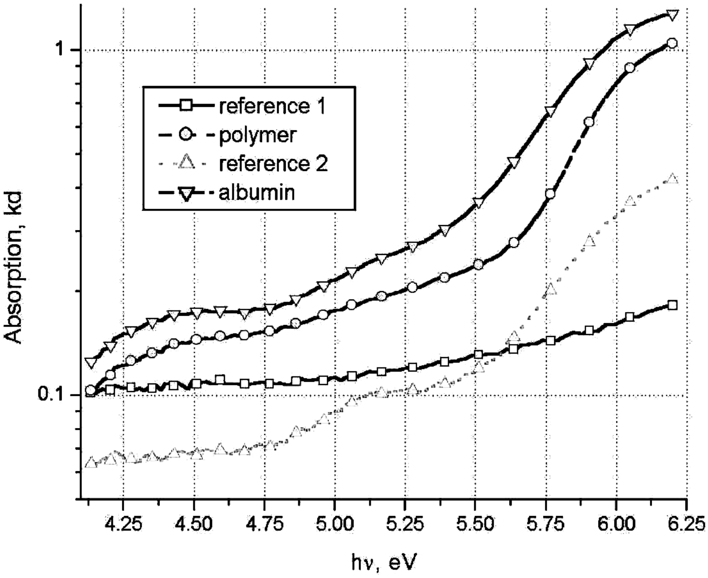


FIGURE 3 The absorption spectra of PVT – polymer and spectrum of serum albumin.

photons and temperature) [8]. The parameters of such dependence for polymer obtained from distillate and structured water are various.

The absorption spectra for polymer films in the same region are given in Figure 4. The difference in the electronic spectra of structured and amorphous polymer films is displayed in the region of the edge of PVT ≪natural≫ absorption (4.0–5.5 eV).

The spectra of a surface photoconductivity (ITO electrodes) coincide with absorption spectra, and the integral photosensitivity is higher (an order) for structured polymer, than for an amorphous sample.

The frequency dependences of dark resistance of amorphous and structured PVT films are shown in Figure 5. It is obvious, that the spectral dependences R(ω) for amorphous and structurally arranged films are various. This difference is connected, first of all, to the feature of processes of a charge carriers scattering on different structural defects of polymer films. The dispersion R(ω) is defined by the structural arrangement of polymer on the relaxation of charge carriers in the range of a spectrum 10^2–10^4 Hz. The low frequency range of R(ω) spectrum (10^0–10^2 Hz) is defined by the exhibition of a disordered (amorphous) part of the film structure.

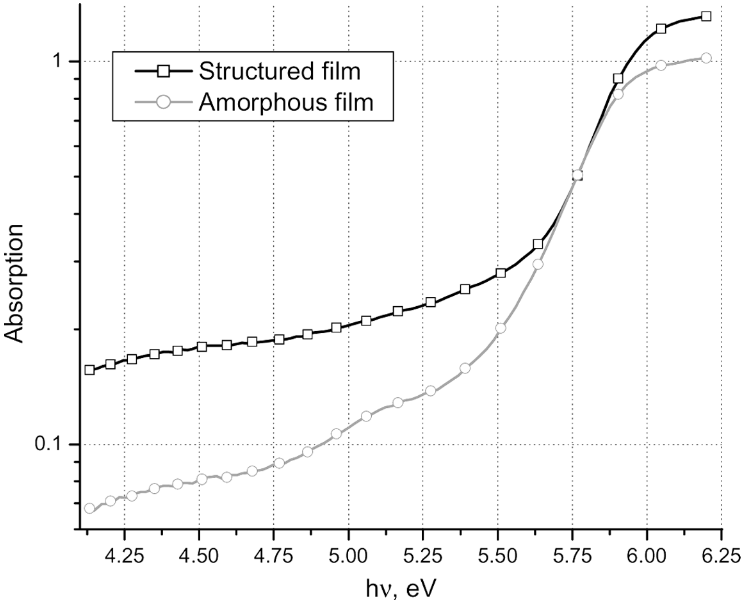


FIGURE 4 The absorption spectra of PVT films.

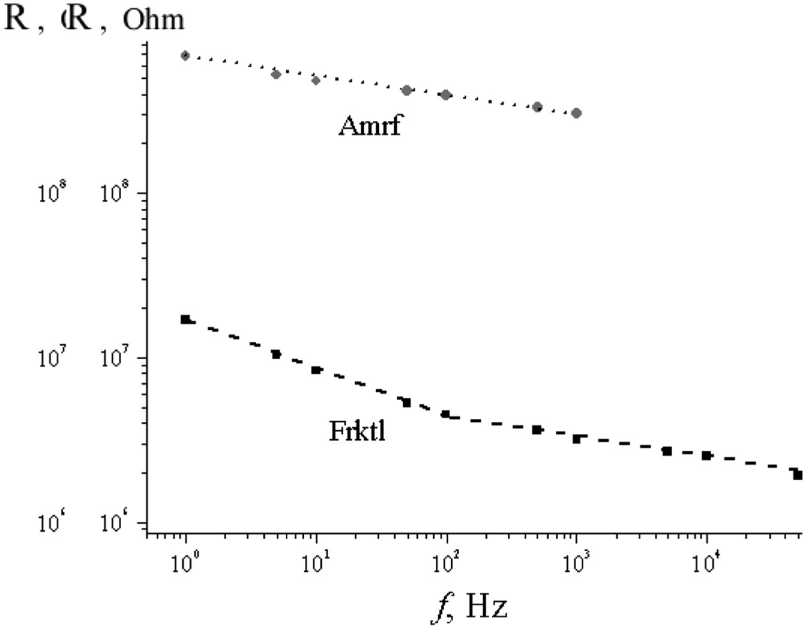


FIGURE 5 The frequency dependences of resistance of amorhous (Amrf) and structured, fractal (Frktl) PVT films.

CONCLUSIONS

On an example of water-soluble polymer PVT, it is experimentally shown for the first time, that structurally-ordered water, as a solvent for the polymer, defines the structure of the polymer solution, that results in the preparation of structured films (with optical bisymmetry) from such solution.

The water sets the structural arrangement of polymer and therefore the optical bisymmetry of films. The basic electronic properties of optically bisymmetrical PVT films are on an order higher, than for amorphous samples of the polymer.

We suppose that such structural arrangement of polymer films due to the structure of the solvent will have the applications in the electronics of organic materials, in the nanoelectronics as a whole.

REFERENCES

[1] Tager, A. A., Safronov, A. P., Lopyrev, V. A., Ermakova, T. G., *et al*. (1987). *Vysokomol. Soed., Ser. A.*, *29*, 2421.

[2] Safronov, A. P., Tager, A. A., Sharina, S. V., Lopyrev, V. A., Ermakova, T. G., *et al*. (1989). *Vysokomol. Soed., Ser. A*, *31*, 2662.

[3] Franks, F. (Ed.) (1972). *Water: Comprehensive Treatise*, Vol. 1, Plenum Press: New York.

[4] Belousov, V. P. & Panov, I. Yu. (1983). *Thermodynamics of Electrolyte Aqueous Solutions*, Leningrad.

[5] Kurik, M. V. (1991). *Izv. AN SSSR*, *55(a)*, 1798.

[6] Kurik, M. V. (2001). *Cosmol. Astroph.*, *3*, 45.

[7] Kuzmenko, O. G. & Kurik, M. V. (2006). *Eniology*, *1*, 71.

[8] Kurik, M. V. (1972). *Phys Stat. Sol.*, *8*, 9.