

Effects of Humidity on the Dark Conductivity and Dielectric Properties of Poly(benzimidazobenzophenanthroline) Thin Films

H. Antoniadis,^{*,†,‡,§} M. A. Abkowitz,^{†,§} J. A. Osaheni,^{†,‡} S. A. Jenekhe,^{*,†,‡} and M. Stolka^{†,§}

Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York 14627; Department of Chemical Engineering, University of Rochester, Rochester, New York 14627-0166; and Xerox Corporation, Webster Research Center, 800 Phillips Rd, Webster, New York 14580

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The dark conductivity and the dielectric constant of thin films of the conjugated ladder polymer poly(benzimidazobenzophenanthroline) (BBL) are found to exhibit large sensitivity to the relative humidity (RH). Although the dc part of the conductivity shows the largest sensitivity, increasing from 4×10^{-14} to 5×10^{-11} S/cm when the relative humidity changes from 0% to 50%, the ac part varies much less under similar changes in RH. At RH approaching 0%, the dielectric constant was found to be frequency independent and close to 3 over the whole measured frequency range (10 – 10^6 Hz), whereas at 50% RH the dielectric constant was about 5 at the highest frequency. Thermogravimetric analysis has also confirmed these findings by detecting about 2% weight loss due to moisture removal from the films. The possible origins for these humidity effects on dark conductivity and dielectric properties are examined.

Introduction

Among the reported physical properties of ladder-type π -conjugated polymers, including poly(benzimidazobenzophenanthroline) (BBL), is their excellent thermal stability up to 700 °C in nitrogen atmosphere.¹⁻³ These polymers, in the form of films or fibers due to their high molecular weight ($\sim 100\,000$) and unique structural features, display good mechanical properties (high tensile strength, high modulus) and exceptional solvent and chemical resistance.^{3,4} The stability of the electronic and optical properties is also of crucial importance in the possible utilization of these materials for electronic and photonic applications.⁵⁻⁸ Humidity commonly affects the optoelectronic properties of various organic or inorganic materials and can limit the reliability of optoelectronic devices. In fact effects of humidity on the electronic properties of other conjugated polymers such as poly(alkylthiophenes) are not uncommon.⁹ In this paper we report the effects of relative humidity (RH) on the electronic properties of insulating BBL thin films prepared by spin coating from solutions of Lewis acid complexes of BBL.³

We describe here the effects of RH on the dark steady-state (dc) and ac conductivity and dielectric behavior. It is found that the steady-state dark conductivity increases more than 3 orders of magnitude from 4×10^{-14} to 5×10^{-11} S/cm when the relative humidity varies from 0% to 50%. The conductivity consisted of a frequency-independent, humidity-sensitive part and a frequency-dependent, humidity-insensitive component. Humidity was also found to affect the dielectric constant over the entire experimental frequency range. Careful thermogravimetric analysis confirmed these findings by detecting weight loss ($\sim 2\%$) due to release of water absorbed in the BBL thin films.

Experimental Methods

Thin films of benzimidazobenzophenanthroline-type ladder (BBL) polymer were prepared by solution casting on glass from an $\text{AlCl}_3/\text{CH}_3\text{NO}_2$ solution according to the complexation-mediated solubilization and film processing reported elsewhere.³ The free-standing films were obtained by peeling them away from the glass substrate. To facilitate electrical measurements, semitransparent (moisture permeable) gold (Au) electrodes (about 5 mm in diameter, and 200 Å in thickness) were vacuum evaporated onto the two opposite faces of free-standing films ranging in thickness from 1 μm to about 4 μm . The thicknesses of the free-standing BBL films were measured with a commercial profilometer, Tencor Inst. Model Alpha-Step 200, while they were still on the glass substrate.

All the electrical measurements presented here were performed inside a vacuum cell under dark conditions at room temperature. The cell was connected to external oxygen and nitrogen supply sources in order to study the effects of these gases on the dark conductive properties of BBL. In our experiments the 0% RH corresponds to conditions under vacuum of about 10^{-3} Torr and 50% RH to a nominal relative humidity at room ambient conditions verified by using a Vaisala Model HM132 humidity detector.

A Keithley 617 electrometer which included an integrated power supply was used for the steady-state dark current measurements. Ac conductivity and capacitance (dielectric constant) measurements were done using two multifrequency

* To whom correspondence should be addressed.

† Center for Photoinduced Charge Transfer.

‡ Department of Chemical Engineering, University of Rochester.

§ Xerox Corp.

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(1) Deusen, R. L. *J. Polym. Sci.: Polym. Lett.* **1966**, *4*, 211.

(2) Jenekhe, S. A.; Tibbetts, S. J. *J. Polym. Sci. B: Polym. Phys.* **1988**, *26*, 201.

(3) Jenekhe, S. A.; Johnson, P. O. *Macromolecules* **1990**, *23*, 4419.

(4) Wang, C.-S.; Lee, C. Y.-C.; Arnold, F. E. *Mater. Res. Soc. Symp. Proc.* **1992**, *247*, 747.

(5) Jenekhe, S. A.; Roberts, F. M.; Agrawal, A. K.; Meth, J. S.; Vanherzeele, H. *Mater. Res. Soc. Symp. Proc.* **1991**, *214*, 55.

(6) Meth, J. S.; Vanherzeele, H.; Jenekhe, S. A.; Roberts, F. M.; Agrawal, A. K.; Yang, C.-J. *SPIE Proc. Ser.* **1991**, *1560*, 13.

(7) Lindle, J. R.; Bartoli, F. J.; Hoffman, C. A.; Kim, O.-K.; Lee, Y. S.; Shirk, J. S.; Kafafi, Z. H. *Appl. Phys. Lett.* **1990**, *56*, 712.

(8) Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater.* **1990**, *26*, 649.

(9) Punkka, E.; Isotalo, H.; Ahlhog, M.; Stubb, H. *Mater. Res. Symp. Proc.* **1992**, *247*, 753.

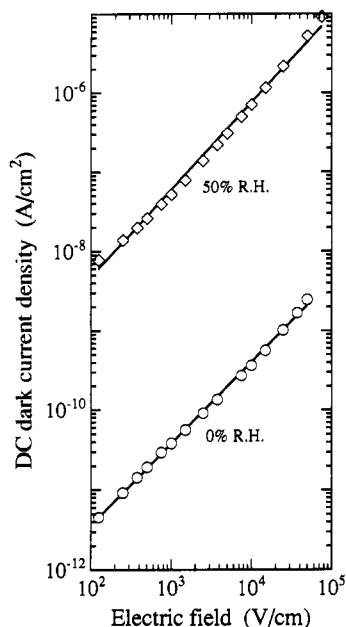


Figure 1. Steady-state dark current density as a function of electric field for a BBL film at ambient conditions (50% RH) and in vacuum of 10^{-3} Torr (0% RH).

(10 Hz to 1 MHz) GenRad 1689M and Hewlett Packard HP 4275A precision RLC meters controlled by a personal computer. The thermogravimetric analysis (TGA) was performed in flowing nitrogen at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ while monitoring the percent of weight loss with a commercial thermogravimetric analyzer: a du Pont Model 2100 Thermal Analyst based on an IBM PS/2-60 computer and equipped with a Model 951 thermogravimetric analyzer. The BBL sample used for the TGA experiments was in its initial as synthesized pristine form, that is, prior to film processing via the complexation-mediated solubilization.

Results

Steady-State Measurements: Dark Conductivity.

For these measurements BBL films were sandwiched between two transparent vacuum-evaporated gold electrodes which were permeable to moisture. A steady-state (dc) voltage was applied to the sample, and the in-series dark current was detected by an electrometer. The specimen was kept in vacuum (10^{-3} Torr at room temperature) for about 24 h before any measurement was taken. At 10^{-3} Torr the relative humidity in the vacuum cell is essentially zero. After this long equilibration in vacuum, the dark current response to an applied dc voltage was found to be constant with time for more than 1 day. As a result of this, ionic contributions to the measured current are excluded.

The dependence of the dark current density on applied electric field in vacuum (0% RH) is shown in Figure 1. A strictly linear dependence is found over the entire electric field range. Using the definition of conductivity $J_d = \sigma E$ (where J_d is the dark current density, σ the dark conductivity, and E the applied field) and since Au forms a ohmic contact (due to similar I - V plots under positive and negative polarity) the dark conductivity of the BBL thin film was estimated to be 4×10^{-14} S/cm under vacuum and 0% RH. The electric field independent dark conductivity ($\sigma = en\mu$) suggests that the density of carriers n and their mobility μ are also electric field independent for BBL, at least for the specified electric field range.

Also shown in Figure 1 is the dark current density as a function of the electric field under ambient dark conditions (50% RH). It is obvious from the graph that the dark

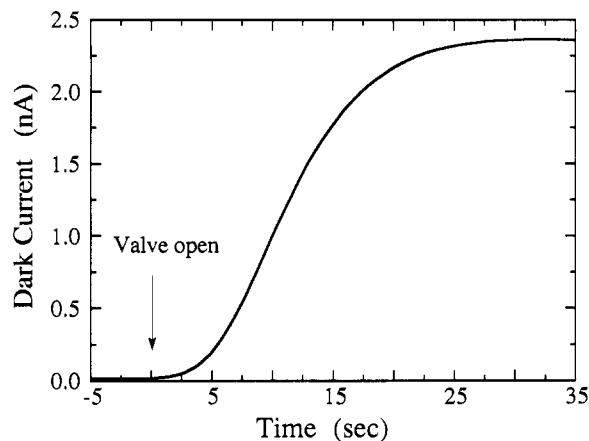


Figure 2. Time response of the dark current to air humidity. The sample is exposed to air (approximately 50% RH) immediately from vacuum (in 10^{-3} Torr) by opening a valve, indicated with an arrow at time zero.

conductivity upon exposure to air has changed more than 3 orders of magnitude. The slope of the J_d versus E plot gives a dark conductivity of approximately 5×10^{-11} S/cm. Even for these conditions, the dark current was found to be constant for more than 10 hours and therefore nonionic in nature. This extremely large and fully reversible change in the dc dark conductivity was successfully repeated many times not only on the same film but also on other BBL films.

It is conceivable that the change in dc dark conductivity with relative humidity could be the result of a reversible adsorption of molecular oxygen and/or nitrogen from air onto the surface or the bulk of the BBL film. Also, it can be argued that such physisorbed oxygen and/or nitrogen alters the conductive properties of the Au/BBL/Au device rather than the polymer film. This possibility was excluded by the following test. While the Au/BBL/Au device was under vacuum, dry oxygen gas was introduced into the vacuum cell at about 2 psi above atmospheric pressure for 15–20 min. During the exposure of the Au/BBL/Au device to dry oxygen, changes in the dark current were no more than 10% as measured by the electrometer. Similar small changes in the dark current were observed when the polymer device was exposed to dry nitrogen gas in the same way. However, when ambient air from the room was introduced into the cell by opening the valve to ambient, the dark current increased by many orders of magnitude, suggesting that moisture in the air was the key factor causing the change.

The time response of the dark current to atmospheric humidity was also examined as shown in Figure 2. This was done by introducing air to the vacuum cell, initially under 10^{-3} Torr, by simply opening a valve and exposing the sample to air containing approximately 50% RH. The whistling sound of incoming air persisted for approximately 10 s, essentially the time during which the maximum dark current was reached. This indicates that the delivery of air to the device is the limiting factor and not the device response. Because of the way the experiment was performed the measured response time of about 15–20 s constitutes only an upper limit for the true response time of Au/BBL/Au device. For comparison the commercial humidity detector used to measure the ambient humidity (Vaisala HMP 35) is rated to have a response time of about 5 s at $20\text{ }^{\circ}\text{C}$.

Ac Measurements: Dark Conductivity and Dielectric Constant. *Dark Conductivity.* The dark conduc-

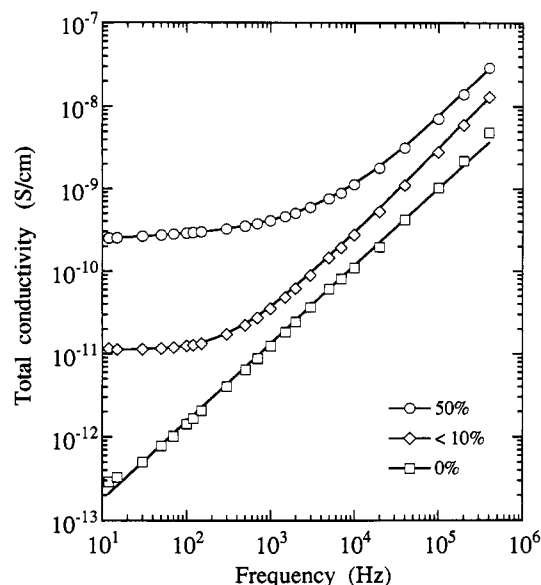


Figure 3. Total conductivity as a function of frequency of the ac applied voltage at three different levels of relative humidity. The best straight line fit corresponding to the lowest humidity (0% RH) has a slope of 0.94.

tivity as a function of frequency (for the same BBL film configured as above) is shown in a log-log plot in Figure 3 for three different humidity levels. The measurements were performed using the RLC meters described earlier. It is clear from the plots (especially for the 50% RH) that the measured total conductivity σ_{TOT} consists of two components: a frequency independent part σ_{DC} and an almost frequency-proportional part σ_{AC} , or $\sigma_{TOT} = \sigma_{DC} + \sigma_{AC}$. However, as the humidity level is lowered, approaching 0%, only the frequency-proportional part ($\sigma_{AC} \sim f^{0.94}$) prevails over the entire frequency range. As shown in Figure 3, humidity primarily affects the dc part of conductivity; it changes more than three orders of magnitude just as shown previously (see Figure 1). The ac part is clearly much less sensitive to humidity changes. The dark conductivity at 10 Hz and 50% RH is somewhat larger ($\sim 2 \times 10^{-10}$ S/cm) than the corresponding dc conductivity (5×10^{-11} S/cm) presented in Figure 1. We attribute this difference to small fluctuations of relative humidity. In fact this variation is small in comparison with the total change of conductivity between 50% RH and 0% RH.

This kind of frequency dependence of the dark ac conductivity has also been observed in other π -conjugated polymers, such as conducting polyethylene/poly(3-ocetylthiophene) polymer gels,¹⁰ poly(phenylacetylene) doped with iodine,¹¹ and polyacetylene;¹² it has also been common in amorphous inorganic semiconductors.¹³ Although this dependence is not completely understood, it has been suggested that the frequency-dependent part of conductivity is related to electron (hole) pair hopping among localized states, where there is a wide distribution of hopping rates.^{12,13} The power law dependence of the ac

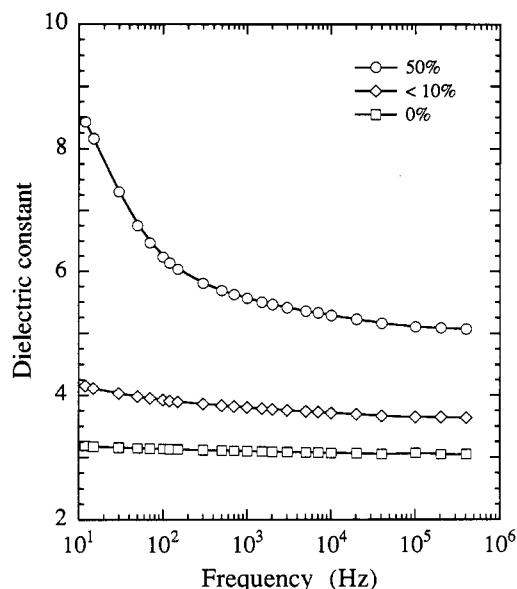


Figure 4. Dielectric constant as a function of frequency (of the ac applied voltage) at three different levels of relative humidity. At lowest humidity (0% RH) the dielectric constant is frequency independent and equal to 3.

conductivity with frequency, according to dispersive transport theories,¹⁴ can be induced by disorder in the structure of the polymer. This is in agreement with the time-dependent behavior of persistent photocurrents observed in the same BBL thin films.¹⁵ The persistence of photocurrents in BBL was attributed to a broad range of release times of the trapped carriers due to the distribution of trapping sites induced by disorder.¹⁵

Dielectric Constant. The real part of the complex permittivity (dielectric constant) in BBL was estimated by measuring the capacitance of the sandwich device Au/BBL/Au in the frequency range between 10 Hz and 1 MHz. For estimation of the dielectric constant ϵ , the relation $\epsilon = Cd/\epsilon_0 A$ was used, where C is the measured (frequency dependent) capacitance, d is the thickness of the BBL film, ϵ_0 is the vacuum permittivity, and A is the area of the Au electrodes. Because of the observed increase of the capacitance with moisture we exclude thickness changes due to possible swelling of the BBL film. Figure 4 shows the dielectric constant versus frequency of the applied ac voltage for three humidity levels.

In the absence of humidity the dielectric constant of BBL films is frequency independent over the whole frequency range and is close to 3 as expected for nonpolar π -conjugated polymers. At relative humidity of 10% or less, the dielectric constant is only weakly dependent on frequency, with values of about 4 at 10 Hz and 3.75 at 10^5 Hz. The effect of humidity on the dielectric constant is rather pronounced at 50% RH. It consists of two parts, a strongly frequency-dependent part (at low frequencies) and an asymptotic frequency-independent part (at higher frequencies).

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was also used in order to address and verify the moisture sensitivity of BBL thin films observed through conductivity and dielectric constant measurements. TGA was intentionally performed on a BBL sample in its initial powder form prior to film processing, to exclude weight losses due to the extraction of the organic

(10) Fizazi, A.; Moulton, J.; Pakbaz, K.; Rughooputh, D. D. V.; Smith, P.; Heeger, A. J. *Phys. Rev. Lett.* **1990**, *64*, 2180.

(11) Ehrlich, P.; Anderson, W. A. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; Vol. 1, p 441.

(12) Epstein, J. A. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; Vol. 2, p 1041.

(13) Mott, N. F.; Davis, E. A. *Electronic Processes in Non-Crystalline Materials*; Clarendon Press: Oxford, 1979; p 300.

(14) Scher, H.; Schlesinger, M. F.; Bender, J. T. *Physics Today*, **1991**, *Jan*, 26.

(15) Antoniadis, H.; Abkowitz, M. A.; Osaheni, J. A.; Jenekhe, S. A.; Stolka, M. *Synth. Met.* **1993**, *60*, 149.

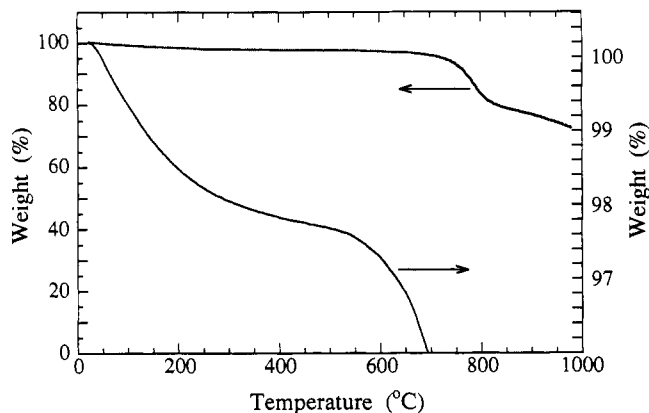


Figure 5. TGA thermogram for BBL films under flowing nitrogen at a heating rate of 10 °C/min. The enlarged version of the TGA plot corresponds to the right y axis and is plotted between 96 and 100 wt %, where it is clear that about 2 wt % is lost in the temperature range between 20 and 300 °C.

solvents remaining in the film after solubilization. The sample was previously exposed to ambient (laboratory) conditions for six weeks. Figure 5 shows the TGA thermogram of a BBL sample. The sample starts to decompose at about 730 °C, indicative of its high thermal stability² compared to other rigid rod polymers.¹⁶ However, Figure 5 also shows an enlarged portion of the thermogram close to 100 wt % which shows that BBL exhibits about 2 wt % loss in the temperature range 25–300 °C. This 2 wt % loss is most probably due to absorbed moisture. In fact, a rigorously dried sample did not show any weight loss in this temperature region. Similar TGA experiments on poly(*p*-benzobisoxazole phenylene) (PBO) and poly(*p*-benzobisthiazole phenylene) (PBZT) did not reveal any weight loss both in the pristine form or the thin film form (processed with Lewis acid complexation) in the temperature range 25–300 °C, suggesting that the observed effect is intrinsic to BBL.

Discussion

The origins of the observed humidity effects on the electronic and dielectric properties of BBL films may be fairly complicated processes, requiring more studies for a more detailed microscopic understanding. To our knowledge, there are no data available in the literature for BBL (such as solubility/diffusivity data) to further confirm our observations. In the following we will only *speculate* on the mechanisms by which the water gets absorbed into BBL films and how this can give rise to the increase of dark conductivity and dielectric constant.

The observed humidity sensitivity of BBL is likely due to water (H₂O) that is preferentially hydrogen bonded to the carbonyl oxygen¹⁷ as illustrated in Figure 6. The detection of about 2 wt % of absorbed moisture (cf. Figure 5) indicates that water is hydrogen bonded to only a small fraction of the carbonyl oxygen sites in the polymer backbone. If all the available carbonyl oxygen sites absorb water molecules as the illustration in Figure 6 suggests, the maximum amount of water uptake is expected to be 10.5 wt % based on the repeat unit of BBL. Thus only about 20% of the carbonyl oxygen sites in the polymer film have absorbed water molecules, which might suggest that only the molecules close to the surface of the thin film are affected by humidity.

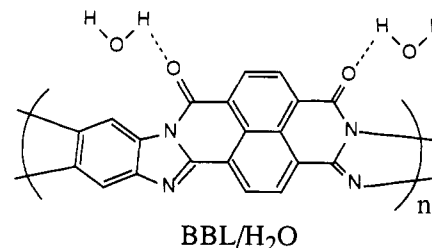


Figure 6. Chemical structure of BBL showing possible water attachment to the chain through hydrogen bonding to the carbonyl oxygen.

It is also possible that the surface of the films react with oxygen, forming a very high energy surface, or in other words, the material has a highly oxidized surface, upon which water is easily adsorbed. Such an accumulated absorbed water layer on the surface might considerably alter the space charge layer adjacent to the surface of the film and thus conduction along this layer.¹⁸

A nonhomogeneous distribution of water across the polymer film, for example, a surface richer in water than the bulk, could give rise to a frequency dependent dielectric constant similar to that observed at 50% RH. This is consistent with a Maxwell–Wagner effect,¹⁵ according to which a dielectric consisting of conglomerates of macroscopic volume elements with different dielectric constants (heterogeneous dielectric) would give rise to a frequency dependent dielectric constant.

It is also possible that humidity is affecting the bulk of the BBL film rather than just the surface layer. At 50% RH the dielectric constant was found to be frequency independent in the range 10⁴–10⁶ Hz (cf. Figure 4). The higher value of dielectric constant in this frequency range indicates that there is some water involvement (since the dielectric constant of H₂O is ~80) throughout the bulk of the film.

Conclusions

Our study of the dark conductivity and dielectric properties of insulating BBL thin films in vacuum and ambient atmospheric conditions show that humidity has a large effect on these properties. In vacuum, the BBL thin films are insulating materials with a dark conductivity of 4 × 10⁻¹⁴ S/cm and a frequency independent dielectric constant of 3. In ambient humid atmosphere, the dark conductivity increases dramatically more than 3 orders of magnitude to 5 × 10⁻¹¹ S/cm and the dielectric constant consists of two parts, a strongly frequency-dependent part (at low frequencies) and an asymptotic frequency-independent part (at higher frequencies) close to 5. This frequency dependence of the dielectric constant indicates the importance of the surface effects on the observed humidity effect. More detail experimental studies are underway in order to further understand the mechanism under which water affects the electronic and dielectric properties of BBL films.

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(16) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* 1992, 4, 95.

(17) Gupta, R. R. *Physical Methods in Heterocyclic Chemistry*; John Wiley: New York, 1984; pp 22.

(18) Tanielian, M.; Chatani, M.; Fritzsche, H.; Smid, V.; Persans, P. D. *J. Non-Cryst. Solids* 1980, 35–36, 575.