built exclusively from N[2] bridges,[1] LiPN$_2$ (124°),[1] and HPN$_2$ (130°).[11]

The density of γ-P$_3$N$_5$ is 32% higher than the density of α-P$_3$N$_5$ (values from the X-ray structure determination: 2.77 (α-P$_3$N$_5$),[2] 3.65 g cm^{-3} (γ-P$_3$N$_5$)). Therefore the high-pressure phase could show interesting materials properties (e.g. great hardness or low compressibility) similar to those predicted for cubic γ-Si$_3$N$_4$ obtained under comparable conditions (1700 °C, 15 GPa).[3]

Experimental Section

The high-pressure synthesis of γ-P$_3$N$_5$ was carried out using the multianvil-technique and a hydraulic 1000 t press.[12, 13] Cr$_2$O$_3$-doped MgO octahedra (Ceramic Substrates & Components Ltd., Isle of Wight) with an edge length of 18 mm were used. Eight truncated tungsten carbide cubes (Toshiba Grade F, edge length: 32 mm, truncation edge length: 11 mm) separated by pyrophyllite gaskets served as anvils for the compression of the octahedra ("18/11 assembly" in conventional terminology). Partially crystalline P$_3$N$_5$, synthesized in accordance with reference [14], was loaded in a cylindrical capsule from hexagonal boron nitride (Henze, Kempten), (volume: ca. 35 mm^3) and sealed with a BN cap. The capsule was centered within two nested graphite tubes of different length, which acted as an electrical resistance heater. The remaining volume at both ends of the sample capsule was filled with two cylindrical pieces from MgO. This arrangement was placed into a ZrO$_2$ tube and then transferred into a pierced MgO octahedron. The electrical contact of the graphite tubes was arranged by two plates from molybdenum.

The assembly was compressed up to 11 GPa at room temperature over five hours and then heated up to 1500 °C within 30 min. The sample was held for five minutes at this temperature and then quenched to room temperature. Then the pressure was released over 15 h. The temperature was measured by using a W$_{97}$Re$_3$–W$_{75}$Re$_{25}$ thermocouple, which was attached coaxially to the resistance heater. Further details about pressure calibration and temperature measurement are described in reference [15].

After the removal of the BN capsule γ-P$_3$N$_5$ was obtained as a crystalline, sinterted, white product. Elemental analysis (%): calcd: P 57.02, N 42.98; found: P 54.8, N 41.6, O 2.3. The absence of hydrogen (N–H) was checked by IR spectroscopy. Owing to the weaker bonds the signals of the vibrations in the P–N network of γ-P$_3$N$_5$ are shifted to significantly lower wavenumbers than in α-P$_3$N$_5$. Moreover γ-P$_3$N$_5$ was characterized by ^{31}P-MAS-NMR spectroscopy ($\nu_0 = 202.473$ MHz). The investigation using a rotation frequency ν_{rot} of 30 kHz revealed two very sharp signals at $\delta = -12$ and -101 (reference: 85% H$_3$PO$_4$). The integration of the completely relaxed signals (recycle delay: 5000 s) showed an intensity ratio of 1:1.98, which is in good accordance with the results obtained from the X-ray investigations. This issue and the comparison with the ^{31}P-MAS-NMR data of α-P$_3$N$_5$[10] allow the assignment of signals at $\delta = -12$ to the tetrahedral site and the one at $\delta = -101$ to the PN$_5$ pyramids.

Received: March 5, 2001 [Z16712]

---

[1] W. Schnick, *Angew. Chem.* **1993**, *105*, 846; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 806.

[2] a) S. Horstmann, E. Irran, W. Schnick, *Angew. Chem.* **1997**, *109*, 1938; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1873; b) S. Horstmann, E. Irran, W. Schnick, *Z. Anorg. Allg. Chem.* **1998**, *624*, 620.

[3] a) A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fueß, P. Kroll, R. Boehler, *Nature* **1999**, *400*, 340; b) M. Schwarz, G. Miehe, A. Zerr, E. Kroke, B. Poe, H. Fuess, R. Riedel, *Adv. Mater.* **2000**, *12*, 883.

[4] a) K. Landskron, E. Irran, W. Schnick, *Chem. Eur. J.* **1999**, *5*, 2548; b) K. Landskron, W. Schnick, *J. Solid State Chem.* **2001**, *156*, 390; c) K. Landskron, S. Schmid, W. Schnick, unpublished results.

[5] The X-ray investigations of γ-P$_3$N$_5$ were performed with a conventional powder diffractometer STOE Stadi P in Debye–Scherrer geometry using Cu$_{K\alpha 1}$ radiation. The powder diffraction pattern was indexed unambiguously in orthorhombic symmetry by using the program WERNER. From systematic absences the space groups $I222$, $I2_12_12_1$, $Imm2$, and $Immm$ were considered. The integration and extraction of the intensities as well as the structure solution by direct methods was carried out by using the program EXPO. The position of all atoms in chemically plausible locations was only achievable in the space group $Imm2$. The Rietveld refinement of the crystal structure data was performed with the program GSAS. The scaling factor, the lattice constants, the zero point, and the background were refined initially. The profile was fitted by a pseudo-Voigt function corrected for asymmetry. All atom positions and thermal displacement factors were refined. $Imm2$, $a = 1287.20(5)$, $b = 261.312(6)$, $c = 440.04(2)$ pm, $V = 148.0 \times 10^6$ pm^3, $Z = 2$, $\rho_{calcd} = 3.657$ g cm^{-3}, $\lambda = 154.05$ pm, measured range $10° < 2\theta < 85°$, 7500 data points, 41 reflections, $R_p = 0.073$, $wR_p = 0.094$, $R_F = 0.048$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411847.

[6] F. Liebau, *Structural Chemistry of Silicates*, Springer, Berlin, **1985**.

[7] A. Neuhaus, *Chimia* **1964**, *18*, 93.

[8] W. Kleber, K.-T. Wilke, *Krist. Tech.* **1969**, *4*, 165.

[9] a) R. Day, A. Schmidpeter, R. Holmes, *Inorg. Chem.* **1983**, *22*, 3696; b) D. Schomburg, U. Wermuth, R. Schmutzler, *Phosphorus Sulfur Silicon* **1986**, *26*, 193; c) D. Schomburg, U. Wermuth, R. Schmutzler, *Chem. Ber.* **1987**, *120*, 1713; d) P. G. Jones, A. Meyer, R. Schmutzler, *Z. Naturforsch. B* **1990**, *45*, 175; e) J. Breker, P. G. Jones, R. Schmutzler, *Phosphorus Sulfur Silicon* **1990**, *53*, 193.

[10] W. Schnick, J. Lücke, F. Krumeich, *Chem. Mater.* **1996**, *8*, 281.

[11] a) W. Schnick, J. Lücke, *Z. Anorg. Allg. Chem.* **1992**, *610*, 121; b) H. Jacobs, R. Nymwegen, S. Doyle, T. Wroblewski, W. Kockelmann, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1467.

[12] D. Walker, M. A. Carpenter, C. M. Hitch, *Am. Mineral.* **1990**, *75*, 1020.

[13] D. Walker, *Am. Mineral.* **1991**, *76*, 1092.

[14] V. Schultz-Coulon, W. Schnick, *Z. Anorg. Allg. Chem.* **1997**, *623*, 69.

[15] D. C. Rubie, *Phase Transitions* **1999**, *68*, 431.

Physically Cross-Linked Ultrathin Elastomeric Membranes**

Frank Mallwitz and Werner A. Goedel*

Thin, freely suspended membranes are of great interest for use in micromechanical devices, sensors, and actuators that require repeated elastic deformation, such as accelerometers or membrane valves. The ongoing miniaturization of these devices creates a demand for progressively thin membranes with a broad range of mechanical properties, especially with

---

[*] Dr. W. A. Goedel
Universität Ulm
Organische und Makromolekulare Chemie OC3
89069 Ulm (Germany)
Fax: (+49) 731-502-2883
E-mail: werner.goedel@chemie.uni-ulm.de

Dr. F. Mallwitz
Humboldt-Universität zu Berlin
Fachbereich Physik
Berlin (Germany)

[**] This work was supported by the Max-Planck Gesellschaft, the Deutsche Forschungsgemeinschaft (project Gö 693/2), and the Kalhof-Rose Stiftung. The experiments were conducted at the Max-Planck-Institut für Kolloid- & Grenzflächenforschung, Berlin. We thank H. Möhwald (MPI-KGF), M. Antonietti (MPI-KGF), M. Möller (Universität Ulm), and J. Rabe (Humboldt Universität Berlin) for support and fruitful discussions.

high stress resistance and elasticity. One way of making extremely thin, usually rigid, membranes is to assemble monolayers of non-water-soluble amphiphiles at the air–water interface, and then transfer them by Langmuir–Blodgett (LB) transfer to cover holes in solid substrates.[1–4] In previous publications we reported that monolayers of liquid polymers with ionic head groups can be covalently cross-linked by irradiation on the water surface[5] and then transferred to solid substrates to form nanometer-thin elastomeric membranes.[6] Unfortunately, using these procedures, one generates a solid monolayer already on the water surface. Thus, the monolayer is unable to undergo the two-dimensional flow neccessary for LB transfer.[7] It is therefore desirable to have substances that form fluid monolayers at the air–water interface, that can be transferred to form freely suspended membranes, and that can be stabilized by cross-linking shortly after transfer.

Herein, we report for the first time that this goal can be achieved by using physical instead of covalent cross-linking: In bulk or in nonpolar solvents, ionic groups attached to nonpolar polymers have a tendency to form aggregates that are composed of several ionic groups and the corresponding counterions. These aggregates act as cross-linking sites and give rise to elastic behavior provided that each polymer chain has at least two ionic groups.[8–10] In contrast to covalent cross-linking, however, these aggregates can be broken up upon addition of polar solvents. In the polymer monolayers considered here, the ionic head groups bind to the water surface (see Figure 1top). In this polar environment, aggregation of the ionic groups is unlikely. Thus the monolayers behave as viscous liquids and can be transferred to a substrate with holes to form initially a fluid membrane with a water core. Once the residual water drains or evaporates, however, the ionic groups of the polymer chain aggregate and thus effectively cross-link the membrane (Figure 1).

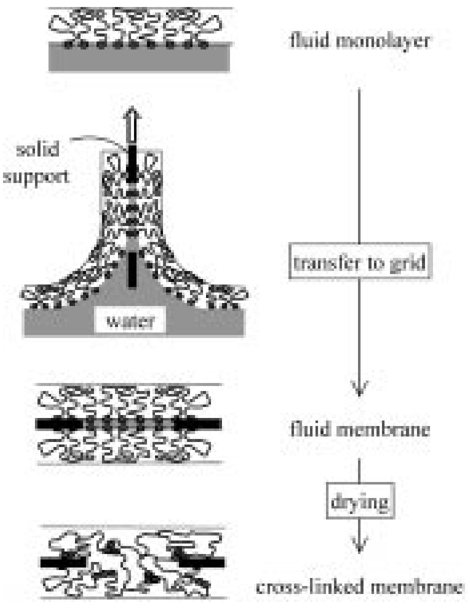

Figure 1. Scheme of the formation of a freely suspended membrane made from monolayers of polymers with ionic head groups. Langmuir–Blodgett transfer of the monolayer generates a freely suspended membrane, which is physically cross-linked by aggregation of ionic head groups after drying.

Linear polyisobutenes with a single sulfonate head group, and three-armed star polyisobutenes with an ionic head group on each arm have been prepared by "living" carbocationic polymerization.[11–13] The structures of the molecules and the associated chain lengths are depicted in the inset of Figure 2. The polymers, which have a glass transition temperature well below room temperature,[14] were spread at 15 °C from 4×10^{-4} wt% solutions in ethanol/pentane mixtures (1/50 by weight) and transferred at 20 °C to copper electron microscopy grids under conditions similar those used previously.[6]

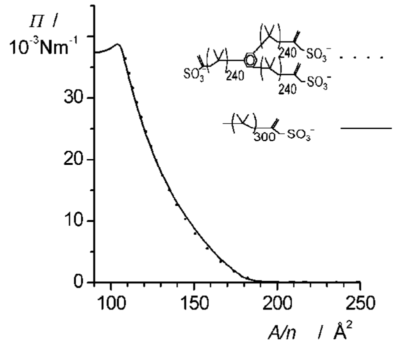

Figure 2. Plot of lateral pressure (Π) versus area per head group (A/n) of polyisobutenes with ionic head groups. ——: linear polymers with one sulfonate group at one end; ••••: three-armed star polymers with three sulfonate groups (one at the end of each arm).

The lateral pressure/area isotherms on the water surface (Figure 2) show that the area per head group occupied by a three-armed star polymer is very similar to the area occupied by a linear polymer with a single head group. Thus, the star architecture and the presence of several head groups does not hinder spreading of the anchored polymers.

If monolayers of polymers with only one head group are transferred to copper grids with 70 µm holes, they initially cover the holes, as a 40 nm[15] thin bilayer formed during the transfer. However, these membranes rupture within minutes after transfer. As an example a membrane made by LB transfer of polyisobutene with a single head group and a chain length of 300 repeat units is shown in Figure 3top). Within 30 min, all membrane-covered holes in the grid rupture (see Figure 3bottom). Presumably these membranes are stabilized only by a temporary network formed by entanglements of the polymer chains. These entanglements, however, cannot stabilize the membrane on a longer time scale and thus rupture occurs. This assumption is supported by rheological investigations of monolayers at the water–air inter-

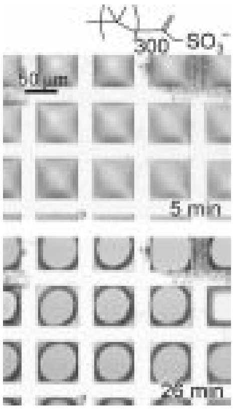

Figure 3. A freely suspended membrane generated by LB transfer of a monolayer of polyisobutene with a single ionic head group per polymer chain (300 repeat units per chain). The membranes rupture within 30 min (light microscopy image with top and bottom illumination.)

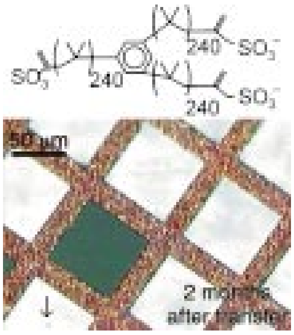

Figure 4. A freely suspended membrane generated by LB transfer of a monolayer of a three-armed polyisobutene star polymer with an ionic head group at each arm (240 repeat units per arm). The membrane is stable for months (light microscopy images with top illumination).

face before transfer[16] and by the fact that the stability of these membranes decreases with decreasing chain length.

Monolayers of three-armed star polymers with an ionic head group at each arm can be transferred to copper grids to generate freely suspended membranes as in the previous case. However, these membranes are stable for months. For example, Figure 4 depicts a light microscopy image of a freely suspended membrane of a three-armed star polymer two months after its generation by LB transfer. Immediately after transfer approximately 80 % of the holes were covered with a freely suspended membrane. (The dark window in the middle left of Figure 4 was not covered by a membrane.) Two months later these membranes still cover the holes of the grid. In the lower left of Figure 4, an approximately 5 µm wide hole is visible as a dark spot (arrow). Even though the membrane in this part of the image is punctured, it does not rupture. Similar membranes transferred to grids with 250 µm holes are still intact 12 months after preparation.

This behavior is only observed in the case of polymers with more than one ionic group per chain and the stability increases with the number of ionic groups per chain. In addition, the membranes rupture when exposed to vapor of polar solvents such as dimethyl sulfoxide (within 3 min if exposed 1 h after transfer, within 30 min if exposed to DMSO 11 months after transfer). Therefore, it is likely that in the freely suspended membranes the ionic head groups form aggregates and thus give rise to physical cross-linking. We note, however, that the monolayers on the water surface before LB transfer do not appear to be cross-linked permanently but can undergo a two-dimensional flow towards the substrate during the transfer process.[17] Evidently, the cross-linking takes place by aggregation of the ionic groups only after the transfer—as schematically depicted in Figure 1. In this respect the monolayer investigated here offers an advantage compared to photochemically cross-linked monolayers[6] which are unable to undergo two-dimensional flow on the water surface.

As indicated schematically in Figure 5 the freely suspended membranes can be deformed reversibly by applying an asymmetric overpressure. In Figure 6a–c a continuously increasing overpressure of approximately 100–1000 Pa is applied to an initially flat freely suspended membrane from below. As a result of the overpressure, the membrane bulges upward. Upon release of the overpressure this deformation is completely reversible and can be repeated multiple times.

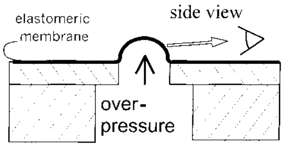

Figure 5. Test of the elastic properties of freely suspended membranes by applying an overpressure from below.

In summary, Langmuir–Blodgett transfer of monolayers of hydrophobic polymers with low glass transition can generate elastomeric freely suspended membranes, provided that the polymer chains bear more than one ionic group per polymer molecule. Most likely these membranes are stabilized by physical cross-linking due to the aggregation of the ionic head groups *after* draining and drying of the transferred monolayers.

Received: October 25, 2000
Revised: April 4, 2001 [Z15990]

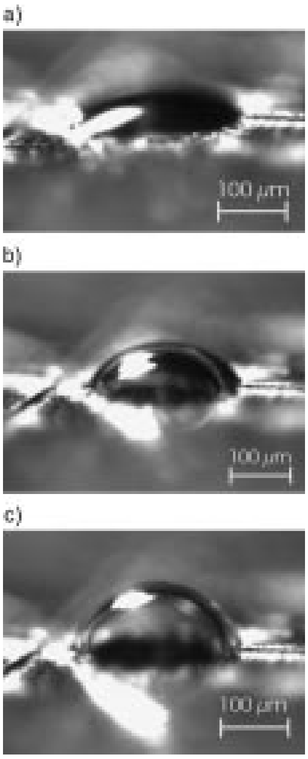

Figure 6. Light microscopy images (side view, side illumination) of a freely suspended membrane of a three-armed star polymer with ionic head groups on each arm, which spans a 300 µm hole. A small overpressure (approximately 100–1000 Pa) is applied from below and the membrane bulges upwards (a→c). This deformation is reversible upon release of the overpressure and can be repeated multiple times.

---

[1] O. Albrecht, A. Laschewsky, H. Ringsdorf, *J. Membr. Sci.* **1985**, *22*, 187.

[2] M. Seufert, C. Fakirov, G. Wegner, *Adv. Mater.* **1995**, *7*, 52.

[3] M. Kunitake, T. Nishi, H. Yamamoto, K. Nasu, O. Manabr, N. Nakashima, *Langmuir* **1994**, *10*, 3207.

[4] W. A. Goedel, C. Peyratout, L. Ouali, V. Schädler *Adv. Mater.* **1999**, *11*, 213.

[5] R. Heger, W. A. Goedel, *Prog. Colloid Polym. Sci.* **1997**, *105*, 167.

[6] W. A. Goedel, R. Heger, *Langmuir* **1998**, *14*, 3470.

[7] F. W. Embs, G. Wegner, D. Neher, P. Albouy, R. D. Miller, C. G. Willson, W. Schrepp, *Macromolecules* **1991**, *24*, 5068.

[8] G. Bronze, R. Jerome, P. Teyssie, C. Marco, *Polym. Bull.* **1981**, *4*, 241.

[9] M. Möller, E. Mühleisen, J. Omeis in *Physical Networks—Polymers and Gels* (Eds.: W. Burchard, S. B. Ross-Murphy), Elsevier, London, **1990**, pp. 45–64.

[10] a) S. Bagrodia, Y. Mohajer, G. L. Wilkes, R. F. Storey, J. P. Kennedey, *Polym. Bull.* **1983**, *9*, 174; b) M. R. Tant, G. L. Wilkes, R. Storey, J. P. Kennedey, *Polym. Bull.* **1985**, *13*, 541.

[11] R. Santos, J. P. Kennedy, M. Walters, *Polym. Bull.* **1984**, *11*, 261.

[12] a) J. P. Kennedy, L. R. Ross, J. E. Lackey, O. Nuyken, *Polym. Bull.* **1981**, *4*, 67; b) J. P. Kennedy, L. R. Ross, O. Nuyken, *Polym. Bull.* **1981**, *5*, 5.

[13] R. F. Storey, Y. Lee, *J. Polym. Sci. Polym. Chem.* **1991**, *29*, 317.

[14] The glass transition temperature of the polymer ($T_g = -63\,^{\circ}C$) was determined by differential scanning calorimetry (DSC).

[15] The thickness of a monolayer is equal to the surface concentration divided by the density of the polymer. The surface concentration is given by the molar mass of polymer divided by (Avogadro's constant × area per molecule).

[16] C. Luap, W. A. Goedel, *Macromolecules* **2001**, *34*, 1343.

[17] The fluidity of the monolayer can be checked by applying dust particles to the surface and by monitoring their displacement during transfer.