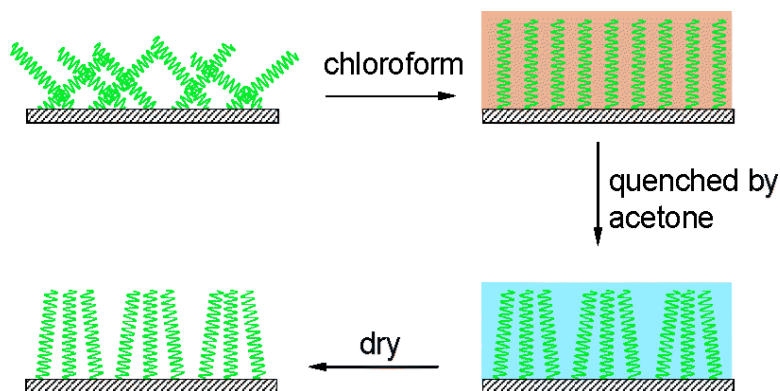


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J. Am. Chem. Soc., **2003**, 125 (21), 6376-6377 • DOI: 10.1021/ja034428k • Publication Date (Web): 03 May 2003

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Preparation of Unidirectional End-Grafted α -Helical Polypeptides by Solvent Quenching

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Polypeptide monolayers having distinct α -helical structures, as opposed to the random coils in common polymer films, are capable of forming highly organized molecular assemblies. Each helical chain is a macromolecular dipole attributed by the additive small dipoles of the amino acid repeats along its molecular axis. In theory, when helical chains are designed to chemically affix through their C-termini (or N-termini) at a surface, the resulting film consists of a huge net dipole arising from the collection of noncancelable individual dipoles. It is useful to form an electrically or optically active surface.

Among polypeptide materials, poly(γ -benzyl L-glutamate) (PBLG) has been studied most comprehensively as the helical rod model because of its stable helical structure. End-grafted PBLG films have been successfully fabricated and demonstrated strikingly high electromechanical and electrooptical efficiency;^{1,2} however, regardless of the synthetic approaches,^{3–9} their molecular orientation was found to be disordered, with average tilt angles $\langle\theta\rangle$ of 33–65° from the surface normal.^{10,11} Previous attempts to apply solvent treatments, or poling electrically or magnetically, failed to provide any long-term re-alignment effects.¹² Thus, to realize the potential use of the unidirectional rodlike polypeptide thin films, current challenges are to find a method to form a highly ordered molecular assembly.

Our observation from ellipsometry thickness measurements has found that end-grafted PBLG chains are preferentially stretched away from the surface when they are solvated in a good solvent such as chloroform, while they collapse in a bad solvent such as acetone. For example, for a 95 nm thick PBLG film in air, its thickness doubles to 186 nm in chloroform, but retains almost identical thickness of 98 nm in acetone. On the basis of this observation, our initial attempt was to first treat the films with chloroform and then dry them in air, in the hope of manipulating the molecular orientation by solvent. However, the molecular chains collapse after they are removed from chloroform, resulting in no thickness change in air (i.e., 95 nm).

Hence, a “solvent quenching” method that involves the use of both good solvent to stretch out the molecular chains and bad solvent to “freeze” up their upright orientation was proposed. The first experimental example was performed under the following conditions: An end-grafted PBLG monolayer was first “wetted” by a drop of chloroform and subsequently quickly immersed in a cup of acetone and mildly stirred for 30 s before being purged with dry air or nitrogen.

The out-of-plane orientation of helical PBLG chains can be best characterized by the external reflection Fourier transform infrared spectroscopy (ER-FTIR). Figure 1 shows ER-FTIR spectra for an end-grafted PBLG monolayer on an aluminum substrate¹³ before and after the “quenching” treatment. For PBLG, the transition dipole moments of amide I (1653 cm^{-1}), amide II (1549 cm^{-1}), amide A (3290 cm^{-1}), and the ester side chain (1733 cm^{-1}) are anisotropic,

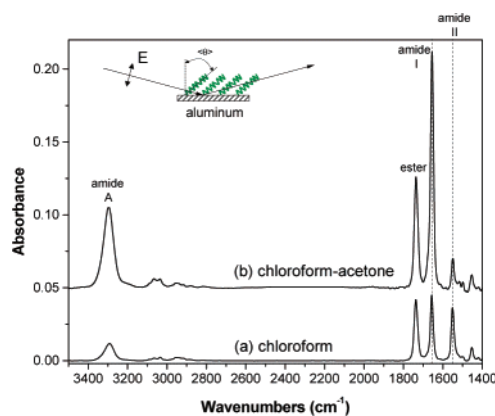


Figure 1. ER-FTIR spectra of an end-grafted PBLG monolayer on the aluminum substrate in air after treating with (a) chloroform only and (b) chloroform–acetone “quenching”. Note the relative intensity changes for amide I over amide II in these two spectra.

forming the angles of 39°, 75°, 28°, and 53° with the helical backbone, respectively.¹⁴ In particular, the dichroic ratio D of amide I over amide II absorption areas is useful in calculating the average tilt angle of α -helical rods from the surface normal.^{15,16} By using the equation described in the Supporting Information, we obtained the average tilt angle $\langle\theta\rangle$ of 49° before the quenching, which agrees with the previous literature.¹¹ Strikingly, after the “quenching”, the $\langle\theta\rangle$ becomes 3°, suggesting an almost perfect orientation of PBLG at surfaces.

The film thickness and refractive index measured by ellipsometry were shown in Table 1. After the “quenching”, the thickness of 94.6 nm and the refractive index of 1.560 change to 165.9 nm and 1.268, respectively, suggesting the transition from a densely to a loosely packed structure. Together with the results from ER-FTIR, we propose that the quenched PBLG film contains highly oriented molecular chains, thus increasing the film thickness and thereafter decreasing the film refractive index.

More evidence of the erected PBLG rods was observed by atomic force microscopy (AFM).¹⁷ Before the “quenching”, AFM images show a relatively smooth surface (Figure 2a), with a roughness of 5.9 nm. After the “quenching”, interesting ellipsoidal aggregates as shown in Figure 2b are formed. The aggregates have, on average, a half-height ellipsoid size of 200 nm and an ellipsoid height of 157 nm with surface roughness of 72.9 nm. The formation of the periodic molecular aggregates seems to suggest a “surface crystallization” process taking place by the “quenching”. Nevertheless, the AFM height estimates are consistent with the thicknesses measured by ellipsometry and small average tilt angles from ER-FTIR. The large space between mountains explains the low refractive index of the erected PBLG film measured by ellipsometry.

Furthermore, the “quenching” treatment consequently alters the surface properties of the grafted PBLG film. For example, the static

Table 1. Tilt Angles, Thicknesses, Refractive Indices, and Contact Angles of the End-Grafted PBLG Monolayers on the Solid Substrates before and after the Chloroform–Acetone “Quenching” Treatment

	before “quenching”	after “quenching”
average tilt angle (θ) (deg) ^a	49 ± 2	3 ± 2
ellipsometric thickness (nm) ^b	94.6 ± 0.8	165.9 ± 2.0
refractive index ^b	1.560 ± 0.004	1.268 ± 0.008
contact angle (deg) ^b	70 ± 3	113 ± 2

^a Aluminum substrate. ^b Silicon substrate.

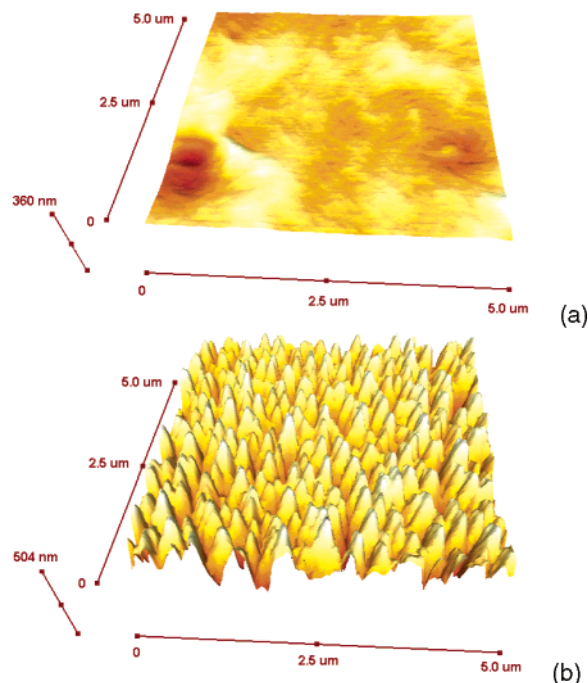


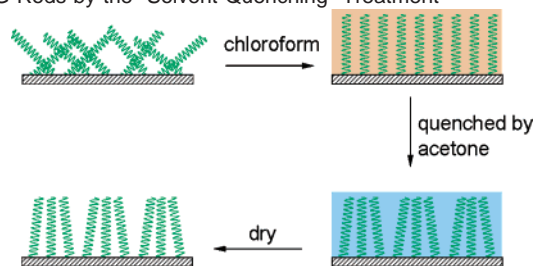
Figure 2. AFM images ($5 \times 5 \mu\text{m}^2$) of the end-grafted PBLG monolayer on a silicon substrate (a) before and (b) after the chloroform–acetone “quenching” treatment.

water contact angle changes from 70° to 113° (Table 1), suggesting different molecular organization: before, the molecular chains are disordered with the main chain amide groups exposed in air; after the treatment, the molecular chains erect with the phenyl side chains exposed, resulting in the drastic increase of surface hydrophobicity. On the other hand, the increase of surface roughness probably makes a contribution to the hydrophobicity too.¹⁸

The erected PBLG film is very stable at both ambient and aqueous conditions at least for months, unless it is treated with heat above 130°C or good solvents (e.g., chloroform, *N,N*-dimethylformamide (DMF), and dioxane).

Other good–bad solvent pairs, including DMF–water, tetrahydrofuran–hexane, and dioxane–methanol, are also capable of bringing up molecular orientations of surface PBLG.¹⁹ The results suggest that the proposed “solvent quenching” method is universal and the only requirement is that the solvent pair has to be miscible. Accordingly, a simplified model that summarizes the molecular orders and mechanisms during the quenching process is proposed in Scheme 1: The originally disordered grafted PBLG chains are first stretched out in chloroform, which is followed by the acetone

Scheme 1. Schematic Model of the Alignment of Surface-Grafted PBLG Rods by the “Solvent Quenching” Treatment^a



^a The film is first “wetted” with chloroform (the good solvent), and then the upstanding configuration is frozen by immediately “quenching” with acetone (the bad solvent).

treatment, during which the chains form periodic aggregates to minimize the surface contact with the acetone molecules, and thus the aggregates remain after being dried in air.

In conclusion, we have demonstrated a very simple “solvent quenching” approach to promote oriented PBLG aggregates by sequentially treating the films with good and bad solvents. Both good and bad solvents are proven to be essential for the success of the experiments. In one case, the proposed procedure only requires one drop of chloroform and a subsequent dip in a cup of acetone to alter the final molecular orientation. The total operation time is less than 1 min. The change of molecular order has altered the surface properties and is anticipated to improve the electromechanical and electrooptical properties of PBLG films, which is upon further investigation.

Supporting Information Available: (1) Synthesis of end-grafted PBLG films; (2) calculation of tilt angle; (3) transmission FTIR spectra of PBLG on silicon before and after chloroform–acetone “quenching” (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Jaworek, T.; Neher, D.; Wegner, G.; Wieringa, R. H.; Schouten, A. J. *Science* **1998**, *279*, 57.
- Chang, Y.-C.; Frank, C. W.; Forstmann, G. G.; Johannsmann, D. *J. Chem. Phys.* **1999**, *111*, 6136.
- Whitesell, J. K.; Chang, H. K. *Science* **1993**, *261*, 73.
- Heise, A.; Menzel, H.; Yim, H.; Foster, M. D.; Wieringa, R. H.; Schouten, A. J.; Erb, V.; Stamm, M. *Langmuir* **1997**, *13*, 723.
- Wieringa, R. H.; Schouten, A. J. *Macromolecules* **1996**, *29*, 3032.
- Chang, Y.-C.; Frank, C. W. *Langmuir* **1998**, *14*, 326.
- Wieringa, R. H.; Siesling, E. A.; Geurts, P. F. M.; Werkman, P. J.; Vorenkamp, E. J.; Erb, V.; Stamm, M.; Schouten, A. J. *Langmuir* **2001**, *17*, 6477.
- Wang, Y.; Chang, Y.-C. *Langmuir* **2002**, *18*, 9859.
- Wang, Y.; Chang, Y. C. *Adv. Mater.* **2003**, *15*, 290.
- Higashi, N.; Koga, T.; Niwa, M. *Langmuir* **2000**, *16*, 3482.
- Wieringa, R. H.; Siesling, E. A.; Werkman, P. J.; Angerman, H. J.; Vorenkamp, E. J.; Schouten, A. J. *Langmuir* **2001**, *17*, 6485.
- Worley, C. G.; Linton, W. R.; Samulski, E. T. *Langmuir* **1995**, *11*, 3805.
- The synthesis of the end-grafted PBLG monolayer on both aluminum and silicon substrates is described in the Supporting Information.
- Tsuboi, M. *J. Polym. Sci.* **1965**, *59*, 139.
- Enriquez, E. P.; Samulski, E. T. *Mater. Res. Soc. Symp. Proc.* **1992**, *255*, 423.
- Miura, Y.; Kimura, S.; Imanishi, Y.; Umemura, J. *Langmuir* **1999**, *15*, 1155.
- AFM images were obtained using a Nano-R AFM (Pacific Nanotechnology, Tustin, California) in material sensing mode.
- Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D. *Adv. Mater.* **2002**, *14*, 1857.
- Wang, Y.; Chang, Y. C. MRS Spring Meeting, April 21–25, 2003, San Francisco, CA.

JA034428K