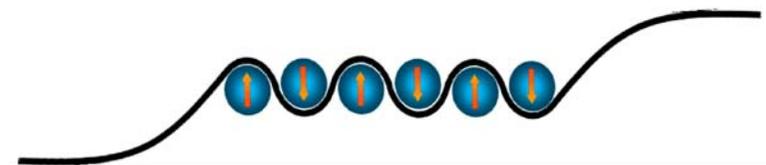
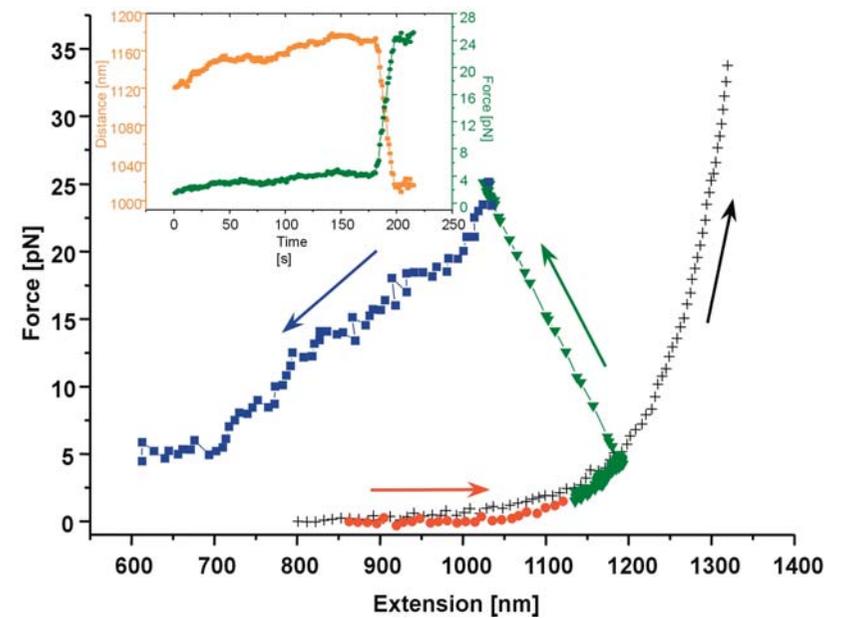


UNIVERSITY OF LEIPZIG

Faculty of Physics and Earth Sciences
Department of Experimental Physics I

GROUP “PHYSIK ANISOTROPER FLUIDE”



Annual Report 2005

Cover picture: The action (a) of the protein TmHU on a single chain of double-stranded DNA as measured by Optical Tweezers. (b) Scheme of the protein/DNA complex.

The year 2005

In the central research topics of our group i.e. Broadband Dielectric Spectroscopy, time-resolved FTIR-spectroscopy and experiments with optical tweezers good progress could be achieved: (i) Evidence could be found that in thin polymer films the glass transition temperatures as measured with different (microscopic and macroscopic) techniques do *not* coincide – in contrast to the bulk. (ii) refined experiments were carried out concerning structure, order and dynamics in self-supporting nematic liquid crystalline elastomers (Li, J. et al. 2005) and (iii) with optical tweezers novel experiments were carried out dealing with protein/DNA interaction but as well with microfluidics. In December 2005 I was awarded with the Karl Heinz Beckurts-prize for my contributions to dielectric spectroscopy and its applications. I take this as a great encouragement.

Friedrich Kremer

Contents

	page
Preface	1
1. Organization of the group	4
2. Projects	5
2.1 Molecular dynamics in thin films of polymers with special architecture (A. Serghei, F. Kremer)	5
2.2 Novel developments in the preparation of thin polymer films (A. Serghei, F. Kremer)	6
2.3 Dielectric properties of ionic liquids (A. Serghei, F. Kremer)	7
2.4 Molecular dynamics in semifluorinated side-chain Polyesters as studied by Broadband Dielectric Spectroscopy (J. Tsuwi, F. Kremer)	8
2.5 The microwave absorption of emulsions containing aqueous micro- and nanodroplets: A means to optimize microwave heating (J. Tsuwi, F. Kremer)	9
2.6 Spacer length dependent mesogen main chain alignment in liquid crystalline elastomer films (M. Tammer, P. Kölsch, F. Kremer)	10
2.7 Time resolved FTIR-spectroscopy on segmental reorientation of nematic elastomers under external mechanical fields (J. Li, M. Tammer, F. Kremer)	11
2.8 Structural analysis of films cast from recombinant spider silk proteins (M. Tammer, P. Kölsch, F. Kremer)	12
2.9 The flow resistance of single DNA-grafted colloids as measured by optical tweezers (C. Gutsche, M. Salomo, Y.W. Kim, R.R. Netz, and F. Kremer)	13
2.10 The flow resistance of one blank colloid in a polymer solution (C. Gutsche, M. Krüger, M. Rauscher, F. Kremer)	14
2.11 The interaction between colloids (diameter 2.2 μm) grafted with DNA of varying length (K. Kegler, F. Kremer)	15

4. Financial support

Prof. Dr. F. Kremer

Optische Pinzette als mikroskopische Sensoren und Aktuatoren zum Studium der Wechselwirkung zwischen einzelnen Biomolekülen
SMWK-Projekt 7531.50-02-0361-01/11 (2001-2006)

Prof. Dr. F. Kremer

DFG-Teilprojekt im Rahmen des Schwerpunktprogramms "Nano- und Mikrofluidik: Von der molekularen Bewegung zur kontinuierlichen Strömung"
DFG-Schwerpunktprogramm 1164, KR 1138/14-1 (2004-2006)

5. Graduations

Promotions:

Dipl.-Phys. Anatoli Serghei

23.01.2006 (colloquium on December 20, 2005)
"Confinement-effects on the molecular dynamics in thin polymer films"

6. Industry collaborations

Novocontrol

Hundsangen, Germany

Comtech GmbH

München, Germany

Freudenberg Dichtungs- und Schwingungstechnik KG

Weinheim, Germany

7. Patent application

Deutsches Patentamt, Nr.: 10 03 05 110.4-52

"Verfahren zur Feststellung wenigstens eines Zustandsparameters eines Dichtungssystems sowie Dichtungssystem"
Erfinder: Prof. Dr. F. Kremer

8. Awards

Karl Heinz Beckurts-price to Prof. Dr. F. Kremer (December 2005)

- in press -

(10)	Serghei, A., and F. Kremer "Unexpected preparative effects on the properties of thin polymer films" in press: <i>Progress Colloid Polym. Sci.</i> (2005)			page
(11)	Kremer, F. "Broadband Dielectric Spectroscopy to study the molecular dynamics of polymers having different molecular architectures" chapter in the book "Physical properties of polymer handbook". J. E. Mark (Ed.) Springer-Verlag (2005), in press	2.12	Investigation of the DNA-binding protein TmHU with optical tweezers (M. Salomo, K. Kegler, M. Struhalla, J. Reinmuth, V. Skokow, <u>F. Kremer</u>)	16
(12)	Serghei, A., F. Kremer "Molecular dynamics in thin polymer films", chapter 1 in Fractals, diffusion and relaxation in disordered complex systems, <i>Advances in Chemical Physics ACP</i> , edited by Stuart A. Rice (guest editors: W.T. Coffey, Y.P. Kalmykov), John Willey & Sons, Inc., in press (2005).	3.	Publications	17
(13)	Gutsche, C., M. Salomo, Y.W. Kim, R.R. Netz and F. Kremer "The flow resistance of single DNA-grafted colloids as measured by Optical Tweezers" in press <i>J. Microfluidics and Nanofluidics</i> (2005)	4.	Financial Support	19
		5.	Graduations	19
		6.	Industrie collaboration	19
		7.	Patent application	19
		8.	Awards	19

- submitted -

(14)	Salomo, M., C. Gutsche, K. Kegler, M. Struhalla, K. Kroy, J. Reinmuth, W. Skokow, C. Immisch and F. Kremer "The binding of TmHU to single ds-DNA as observed by Optical Tweezers" submitted to <i>J. Mol. Biology</i> (2005)
(15)	Serghei, A., Y. Mikhailova, K.-J. Eichhorn, B. Voit, and F. Kremer "Faster" dynamics in thin polymer films" submitted to <i>J. Polym. Sci. B</i> (2005).
(16)	Salomo, M., K. Kegler, M. Struhalla, J. Reinmuth, W. Skokow, u. Hahn, F. Kremer "The elastic properties of single double-stranded DNA chains of different length" submitted to <i>J. of Single Molecules</i> (2005)

1. Organization of the group

Chairman: Prof. Dr. Friedrich Kremer

Academic staff and postdocs

Dr. Patrick Koelsch
Dr. Jianjun Li
Dr. Rongbiao Wang

Students

Dipl.-Phys. Christof Gutsche
M. Sc. Julius Tsuwi Kazungu
Dipl.-Phys. Kati Kegler
Dipl.-Biochem. Mathias Salomo
Dipl.-Phys. Anatoli Serghei
M. Sc. Michael Tammer

Technical staff

Karin Girke
Ines Grünwald
Dipl.-Ing. Jörg Reinmuth
Dipl.-Phys. Wiktor Skokow
Dipl.-Phys. Uwe Weber

Alumni

Prof. Dr. Siegbert Grande

3. Publications

- (1) Li, J.; D. Geschke
"Pyroelectric investigations of a hydrogen bonded ferroelectric liquid crystal gel by LMM"
Polym. Adv. Technol. **16**, 11 (2005)
- (2) Nikonorova, N.A., E.B. Barmatov, D.A. Pebalk, R. Diaz-Calleja, F. Kremer
"Dielectric relaxation of side-chain liquid crystalline ionomers containing alkaline metal ions"
Macromolecular Chem. Phys. **206**, 1630 (2005)
- (3) Tammer, M., J. Li, A. Komp, H. Finkelmann, F. Kremer
"FTIR-spectroscopy on segmental reorientation of a nematic elastomer under external mechanical fields"
Macromol. Chem.Phys. **206**, 709 (2005)
- (4) Li, Jianjun, M. Tammer, F. Kremer, A. Komp, H. Finkelmann
"Strain-induced reorientation and mobility in nematic liquid crystalline elastomers as studied by time-resolved FTIR spectroscopy"
Eur. J. Phys. E **17**, no.4, p 423-428 (2005)
- (5) Serghei, A., H. Huth, M. Schellenberger, C. Schick and F. Kremer
"Pattern formation in thin polystyrene films induced by an enhanced mobility in ambient air"
Phys. Rev. E **71**, 061801 (2005)
- (6) Serghei, A., Y. Mikhailova, K.-J. Eichhorn, B. Voit and F. Kremer
"Molecular dynamics of hyper-branched polyesters in the confinement of thin films"
Eur. Phys. J. E **17**, 199 (2005)
- (7) Tsuwi, J., D. Appelhans, S. Zschoche, R.-C. Zhuang, P. Friedel, L. Häußler, B. Voit, F. Kremer
"Molecular dynamics in fluorinated side-chain MI copolymers as studied by Broadband Dielectric Spectroscopy"
Colloid & Polymer Science **283**, 1321 (2005)
- (8) Weissflog, W.; U. Dunemann, M.W. Schröder, R.A. Reddy; H. Kresse, S. Diele, S. Grande, G. Pelzl
"Field-induced inversion of chirality in antiferroelectric and ferroelectric smectic phases formed by bent-core mesogens"
J. Mater. Chem. **15**, 939 - 946 (2005)
- (9) Weissflog, W.; U. Dunemann, M.W. Schröder,; S. Diele, G. Pelzl, H. Kresse, S. Grande
"Field-induced inversion of chirality in SmCPA phases of a new achiral bent-core mesogens"
In: *Journal of materials chemistry* : An interdisciplinary journal covering all aspects of materials chemistry. - Cambridge : Soc., ISSN 0959-9428, Bd. 15 (2005), S. 939-946

2.12 Investigation of the DNA-binding protein TmHU with optical tweezers

M. Salomo, K. Kegler, M. Struhalla, J. Reinmuth, V. Skokow, F. Kremer

We applied the advantages of optical tweezers to study the TmHU/DNA complex formation kinetics and the disruption of the protein from the DNA chain by mechanical forces. The histone-like protein TmHU from the hyperthermophilic eubacterium *Thermotoga maritima* belongs to the group of HU proteins that are small basic proteins occurring in all prokaryotes. Its major function consists in binding and compacting DNA into structures similar to eukaryotic chromatin. The functional form of TmHU contains two identical subunits having a monomeric molecular mass of 9.993 kDa and contains 90 amino acids. TmHU binds the DNA tightly ($K_D = 73$ nM) without detectable sequence specificity. It bends the DNA very ($\sim 160^\circ$) and simultaneously increases its flexibility.

For our experiments we developed a special flow cell which enables us to immobilize a single DNA molecule between two functionalized polystyrene beads of which one is fixed at a micropipette and the other one is held by the optical trap. Further more it is possible to flush the cell with buffers or protein solution. After establishing a single DNA chain between two beads the force extension dependence of naked DNA was measured. After flushing the sample cell with TmHU solution of 5 nM concentration (in 10 mM $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ pH 7.5), a rapid decrease in the length of DNA is observed. Subsequent to the assembling of the TmHU/DNA complex, it was relaxed (Fig. 1). Afterwards the formed TmHU/DNA complex is stretched and relaxed again (Fig. 2). A distinct saw tooth pattern is observed being characterized by well defined disruption events. At higher force levels the length of naked DNA is recovered.

Binding and disruption of TmHU to and from DNA are found to take place in discrete steps of 4-5 nm length and $5 \cdot 10^{-20}$ J energy. This is in reasonable agreement with a microscopic model which estimates the extension of the binding-sites of the protein and evaluates the energetic mainly of the bending of DNA in the course of interaction.

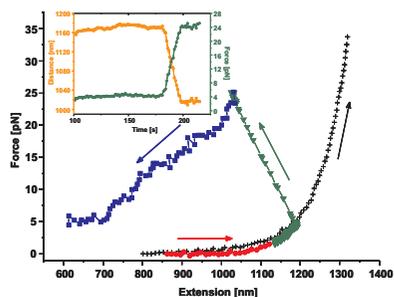


Fig. 1: Prior to incubation of the DNA with protein a force extension dependence of naked DNA is recorded (black crosses). Afterwards the DNA is stretched to a definite force level between 1-3 pN (full red circles). Flushing the sample cell with TmHU solution takes ~ 129 s and causes a slight drift of the bead on top of the micropipette (full green triangles, see as well insert). The action of the protein shows up as a rapid shortening of the DNA and an increase of its tension (see insert). At forces of about 20-25 pN the reaction is halted. Afterwards the protein /DNA complex is relaxed (blue squares).

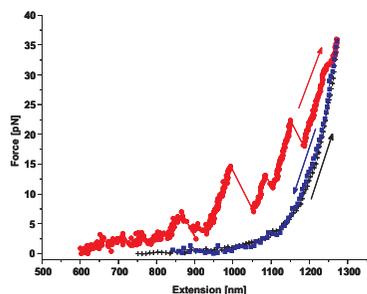


Fig. 2: When the TmHU/DNA complex is stretched distinct disruption events can be observed (full red circles). Subsequent relaxation (blue squares) of the chain delivers a force-extension dependence well comparable to that of naked DNA (black crosses). Repeated stretching cycles in the protein solution result in fully comparable disruption events as shown above.

2. Projects

2.1 Molecular dynamics in thin films of polymers with special architecture

A. Serghei*, F. Kremer

This projects aims to investigate confinement effects on the dynamic glass transition of polymers having special architectures. Thin films of hyper-branched polymers (Fig. 1a) and star-branched polymers are prepared and their molecular dynamics is investigated in dependence on the confinement size (film thickness). Two questions are addressed. The first one, what role plays the architecture of the macromolecular systems in the deviations of the dynamic glass transition from the bulk behaviour observed in thin films. For example, thin layers of hyper-branched polyesters show an increase of the average alpha relaxation rate with decreasing films thickness. This effect appears at much larger thicknesses (Fig. 1b) that those reported for linear polymers and therefore must be assigned to the special architecture of these dendritic macromolecules.

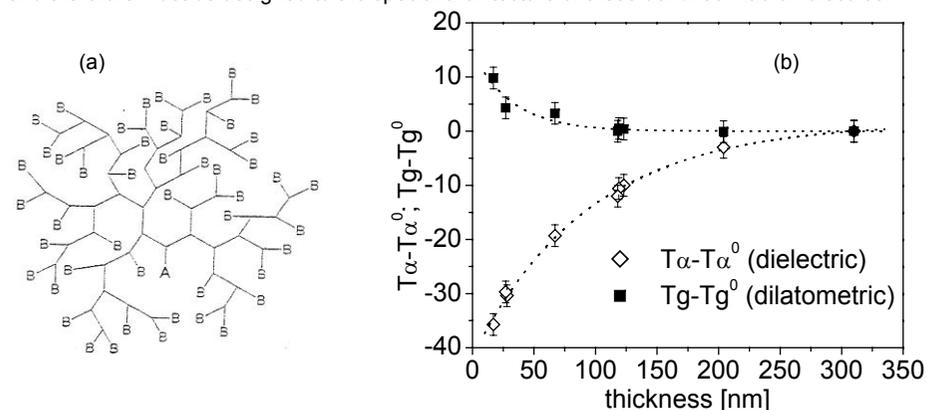


Fig.1: a) scheme showing the architecture of hyper-branched polymers b) the maximum temperature position of the alpha relaxation peak (by Broadband Dielectric Spectroscopy, at 0.6 Hz) and the glass transition temperature (by capacitive dilatometry), both normalized in respect to the values corresponding to 310 nm, as a function of film thickness.

The second question, to what extent different methods to investigate the glass transition provide comparable results when applied to thin films. For that, complementary measurements by Broadband Dielectric Spectroscopy, capacitive dilatometry and AC – calorimetry are employed. In the case of hyper-branched polyesters, the dielectric measurements show a faster dynamic glass transition with decreasing film thickness while simultaneous dilatometric determinations reveal a slight increase of T_g . Such an apparent controversy, reported for the first time for polymers in confinement, indicates that microscopic and macroscopic experimental techniques do not necessarily deliver similar results.

References:

- [1] Y. H. Kim, *J. Polym. Sci., (A)* **36**, 1685 (1998).
- [2] A. Serghei et al., *Eur. Phys. J. E* **17**, 199 (2005).

Collaborators:

C. Schick (Rostock University), B. Voit (IPF Dresden, Germany)

*The underlined author is the principal investigator of the project.

2.2 Novel developments in the preparation of thin polymer films

A. Serghei, F. Kremer

In this work novel methods for the preparation of thin polymer films are developed. One approach is schematically described in Fig. 1. Silica nano-colloids are used as spacers between two ultra-flat highly conductive silicon wafers. On one of the two wafers a thin polymer film was previously deposited by spin-coating from solution. This preparation procedure enables one – for the first time – the investigation of the dynamic glass transition in thin films having a free upper interface.

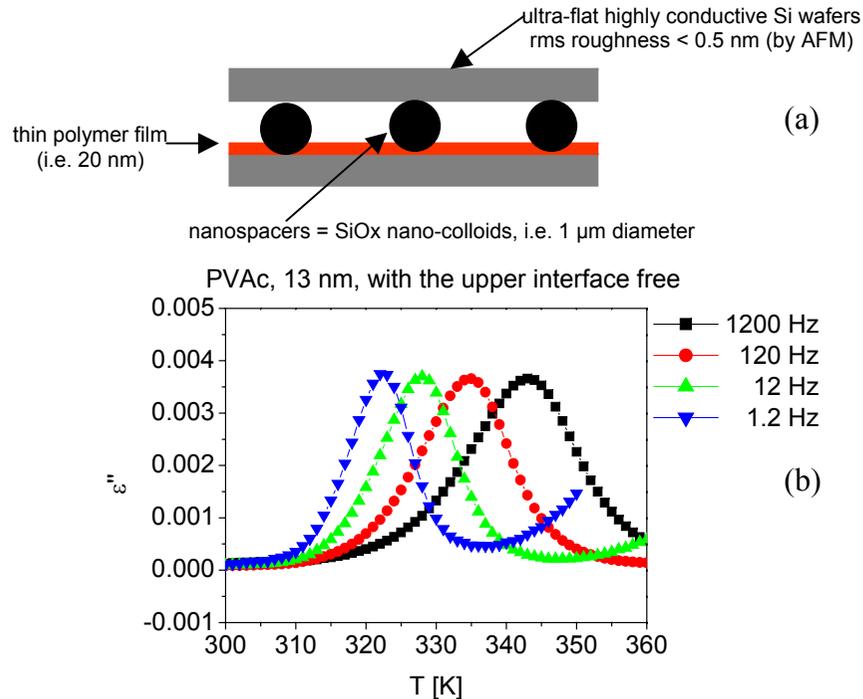


Fig. 1: a) schematic representation of the sample preparation; b) dielectric loss vs. temperature at different frequencies, as indicated, for a thin film of PVAc having a thickness of 13 nm.

This method is sensitive down to film thicknesses as small as 10 nm or even lower, depending on the size of the colloids used as spacers and on the dielectric strength of the investigated materials. Its advantages, over the standard preparation procedure for dielectric measurements on thin films, are: 1) one avoids the evaporation of metal electrodes; 2) the samples have a free upper interface; 3) the samples are spin-coated on silicon wafers, resulting in an identical sample geometry and interfacial interactions as in the case of ellipsometric studies.

2.11 The interaction between colloids (diameter 2.2 μm) grafted with DNA of varying length.

K. Kegler, F. Kremer

The forces of interaction between two colloids grafted with DNA varying in length between 1000 base pairs (bp) and 6000 bp is measured for a grafting density of 450 ± 50 chains per colloid corresponding to $0.03 \mu\text{m}^2/\text{chain}$. One colloid is held by a micropipette which the other is kept in the optical trap. The separation between the colloids can be adjusted in nm-steps. It is possible to exchange the medium and to measure the interaction with *one* single pair of DNA-grafted colloids in different media e.g for different ionic strengths. Furthermore the forces in x- and y-direction [Fig. 1] can be measured separately.

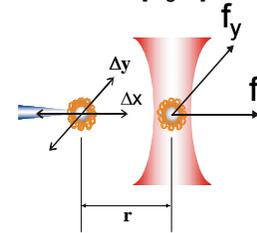


Fig. 1: Scheme of two of two colloid grafted with DNA of varying length. One colloid is fixed by a micropipette, the other is kept in the optical trap. The former can be moved in x- and y-direction and resulting forces f_x and f_y are measured separately.

The following results were obtained:

1. Measuring the forces in a salt free medium one finds pure repulsive interactions and no attraction if the colloids are withdrawn from each other. This changes in the presence of salts (e.g. in a medium of 150 mM NaCl): After contact between the colloids one has an attractive interaction which is caused by counter-ion condensation.
2. Moving the colloids in y-direction perpendicular to the x-axis delivers for colloids in contact for the forces in x-direction a smooth response while in y-direction stick-slip phenomena are observed (Fig. 2a). Exchanging the medium from 150 mM to 1M NaCl results in strongly reduced forces of interaction (Fig. 2b).

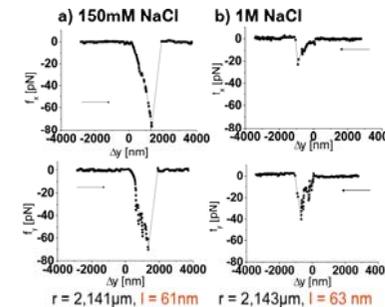


Fig. 2: Forces of interaction f_x in x-direction and f_y in y-direction between two DNA(4000 bp)-grafted colloids in NaCl-solution of different ionic strength as indicated. In (a) the separation between the solid surface of the colloid is $l=61$ nm in (b) it is $l=63$ nm. It is shown that for the measurement at 150 mM NaCl where the DNA is more swollen than at 1 M NaCl the forces are much stronger. In x-direction a smooth response is found while in y-direction stick-slip phenomena take place. The arrow indicates from which side in y-direction the colloids are approached to each other.

3. Comparing the frictional forces for grafted colloids having a length of 1000 bp and 4000 bp it is shown that the interaction sets in a correspondingly shorter separation.

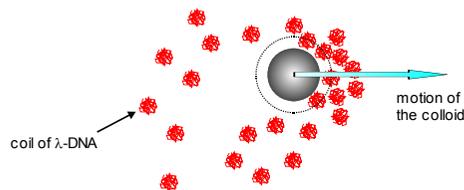
This project is supported within the DFG-Schwerpunktprogramm SPP1164.

Collaborators:

A. Pich (TU Dresden, Germany), M. Stamm, P. Uhlmann (IPF Dresden, Germany), R. Netz (LMU Munic, Germany)

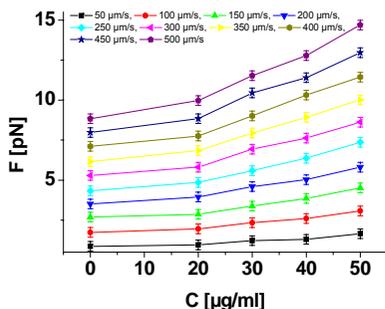
2.10 The flow resistance of one blank colloid in a polymer solution

C. Gutsche, M. Krüger, M. Rauscher and F. Kremer



A dependence according to the Stoke's law is found with a flow resistance which increases by more than 100% in going from 0 µg/ml to 50 µg/ml. This pronounced effect cannot be explained on the basis of measurements of the macroscopic viscosity as determined with the flow viscosimeter.

Fig. 2: Force acting on *single* colloids (1.32µm, 2.23 µm and 3.00 µm diameter) in solutions with different λ-phage-DNA concentrations as indicated. The measurements were carried out at 25°C.



References:

- [1] Bustamante C. et al.; *Science* **265**, 1599-1600. (1994)
- [2] Strick T.R. et al.; *Science* **271**, 1835-1837 (1996)
- [3] Bustamante C., Bryant Z., Smith C.B.; *Nature* **421**, 423-427. (2003)
- [4] Meiners J.-C., Quake S.R.; *Physical Review Letters* **84**, 5014-5017 (2000)

Collaborators:

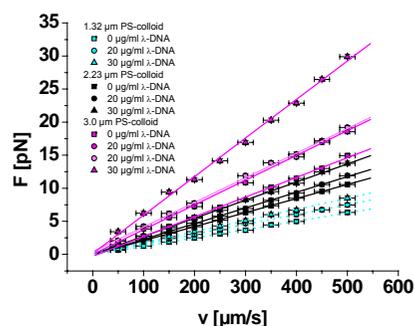
Dr. M. Rauscher (Max-Planck-Institut für Metallforschung, Stuttgart).

Funding:

DFG priority programm 1164 (Nano- & Microfluidics)

The flow resistance of one *blank* colloid in a solution of λ-DNA (48000 bp, contour length of $L_0=16 \mu\text{m}$, radius of gyration $R_g=500 \text{ nm}$) was measured for concentrations between 0 to 30 µg/ml (Fig. 2).

Fig. 1: Assumed distribution of DNA coils with respect to a colloid in motion.



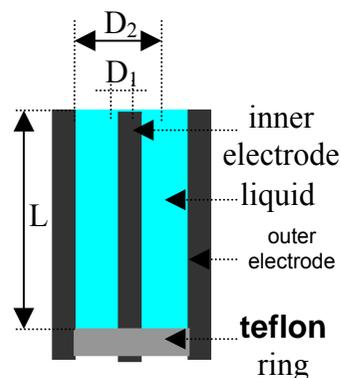
It is assumed that this finding has its molecular origin in the heterogeneous nature of the DNA solution [1-4]. The DNA-coils are in size not negligible compared to the colloids. Furthermore absorption of DNA on the colloid might play a role and must be ruled out

Fig. 3: Force acting on a *single* colloids (2.23 µm diameter) in dependence of different λ-phage-DNA concentrations at different flow velocities.

2.3 Dielectric properties of ionic liquids

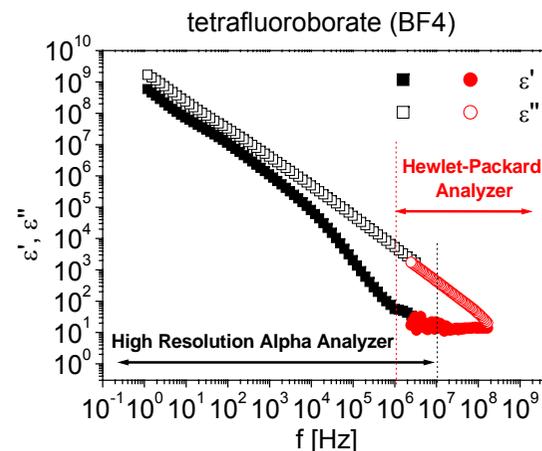
A. Serghei, F. Kremer

The chemical reactions which take place in ionic solvents exhibit – in comparison to those in molecular solvents – modified properties. They lead to better yields and higher conversion rates, and the regio- and enantioselectivity are improved. Although a variety of reactions, as enzymatic, transition metal catalysed and non-catalized reactions have been optimised in ionic solvents, only a little is known about the mechanisms underlying these “ionic liquid effects”. The aim of this project is to investigate whether and how the reactivity and regioselectivity correlate with the permittivity of the ionic solvents. For that, dielectric measurements are performed by means of Broadband Dielectric Spectroscopy in a wide frequency range covering ten decades (0.1 Hz – 1 GHz). Due to the high conductivity of these materials, the geometry of the sample cell has to be optimised. A first approach is schematically illustrated in Fig. 1 a. Preliminary measurements on tetrafluoroborate using this sample geometry (Fig. 1b) show an excellent agreement between the low and the high frequency experimental curves.



$$C = \epsilon_0 \epsilon' \frac{2\pi L}{\ln \frac{D_2}{D_1}}$$

(a)



(b)

Fig. 1: a) schematic illustration of the sample cell; b) real ϵ' and imaginary part ϵ'' of the complex permittivity vs. frequency at room temperature for tetrafluoroborate (BF4).

Collaborators:

Prof. F. Bordusa (University of Halle), C. Wespe (University of Halle)

2.4 Molecular dynamics in semifluorinated side-chain Polyesters as studied by Broadband Dielectric Spectroscopy

J. Tsuwi, F. Kremer

Structural segments consisting of alkyl and perfluoroalkyl groups covalently linked by a C-C bond are well known for their microphase separation resulting in highly ordered bulk structures. The use of such materials for surface modification is numerous because of the resulting low surface free energy. We are employing Broadband Dielectric Spectroscopy to study the molecular dynamics in fluorinated side-chain polyesters.

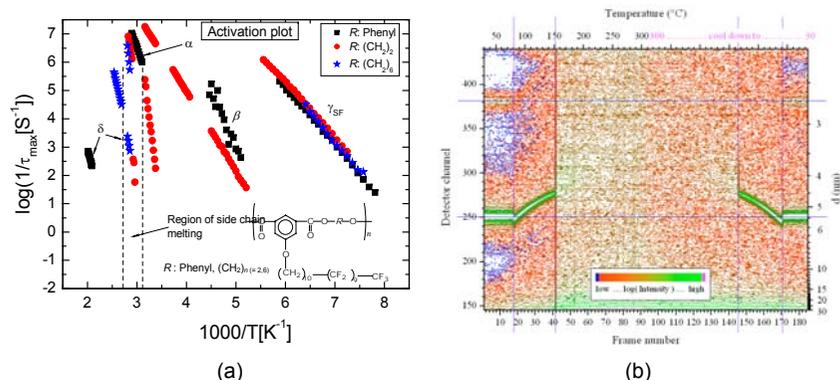


Fig. 1: (a) Activation plot showing four relaxation processes γ_{SE} , β , α and δ in order of their mean relaxation times. (b) Temperature dependent small angle X-ray (t -SAXS)

The polymers comprise of non-substituted main chain polyesters and polyesters with semifluorinated (oxydecylperfluorodecyl) side chains. Combining temperature-dependent small angle X-ray scattering (T-SAXS), differential scanning calorimetry (DSC) and BDS it can be shown that the microphase separated semifluorinated polymers exhibit independent dynamic glass transition relaxations taking place in the separate microphases. Additionally in the glassy state, the non-substituted polymers show an Arrhenius type relaxation whose activation energy decreases gradually from 52 kJ/mol to 40 kJ/mol with increasing main chain flexibility. The semifluorinated polymers exhibit a relaxation assigned to fluctuations of the perpendicular component of the fluoroalkyl end group with activation energies between 38-40 kJ/mol. With increasing flexibility of the main chain, the dynamics of the backbone becomes faster for the non-substituted polymers while an opposite trend is observed in the oxydecylperfluorodecyl substituted side chain materials. The dielectric results are analyzed in the context of micro-phase separated layered structures, supported by DSC and t -SAXS studies (Fig. 1).

References:

- [1] Tsuwi J, Pospiech D. et al., *J. Polym. Sci. B: Polym.*, (2006), in preparation
- [2] Tsuwi, J.; Appelhans, D.; Zschoche, S.; Zhuang, R.C.; Friedel, P.; Häußler, L.; Voit, B.; Kremer, F., *Colloid & Polym. Sci.* **283**, 1321-1333 (2005)
- [3] Tsuwi J., Appelhans D., Zschoche S., Friedel P., Kremer F., *Macromol.* **37**, 6050 (2004)
- [4] Gottwald A, Pospiech D, et al. *Macromol. Chem. Phys.* 203 (5-6), 854 (2002)

Collaborator:

D. Pospiech (IPF Dresden, Germany)

2.9 The flow resistance of single DNA-grafted colloids as measured by optical tweezers

C. Gutsche, M. Salomo, Y.W. Kim, R.R. Netz and F. Kremer

In rheological experiments the flow resistance of *single* blank or DNA-grafted colloids is determined and compared. The length of the double-stranded (ds)-DNA varies between 1000 base pairs (bp), 4000 bp and 6000 bp corresponding to contour lengths between 340 nm and 2040 nm at a grafting density of $0.03 \pm 0.01 \mu\text{m}^2/\text{chain}$. The degree of swelling of the grafted DNA is adjusted by exchanging the ion concentration of the surrounding medium. For all examined flow velocities ranging between $100 \mu\text{m/s}$ to $1200 \mu\text{m/s}$ one observes an interesting deviation from Stokes law which can be traced back to a shear-dependent conformational change of the brush layer. The ratio of the effective hydrodynamic radii of DNA-grafted and blank colloids shows a pronounced dependence on the flow velocity, but as well on the length of the grafted DNA and the ionic strength of the solvent. The experimental findings are in qualitative agreement with hydrodynamic simulations based on an elastically-jointed chain model.

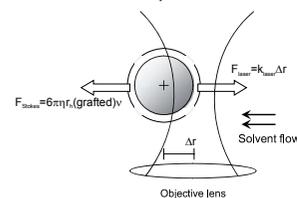


Fig. 1: Forces acting on a grafted colloid in flow

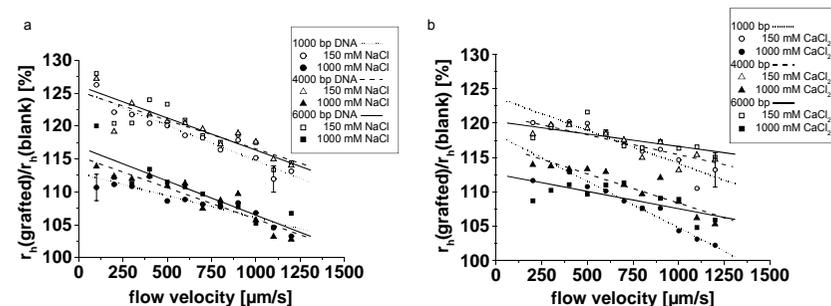


Fig. 2: ratio of the effective hydrodynamic radii for DNA-grafted and blank colloids versus flow velocity. Three single colloids with different DNA-grafting (1000 bp, 4000 bp and 6000 bp, same grafting density) are measured in two NaCl/CaCl₂-media ((a): 1000 bp DNA-chains: light blue ○ – 150 mM NaCl, blue ●, 1000 mM NaCl, 4000 bp DNA-chains --- : light pink Δ 150 mM NaCl, red ▲ 1000 mM NaCl, 6000 bp DNA-chains — : green □ 150 mM NaCl, ■ 1000 mM NaCl, (b): as (a) but for CaCl₂-solutions).

References:

- [1] Gutsche C. et al.; *Microfluidics and Nanofluidics*, in press (2006)
- [2] Baumann C. et al.; *Proc. Natl. Acad. Sci.* **97**, 6185-6190 (1997)
- [3] Brochard-Wyart F.; *Europhys. Lett.* **23**, 105-111 (1993)
- [4] Brochard-Wyart F. et al.; *Europhys. Lett.* **26**, 511-516 (1994)
- [5] X. Schlagberger and R. R. Netz, *Europhys. Lett.* **70**, 129 (2005)
- [6] Y.W. Kim and R.R. Netz, *Europhys. Lett.* in press (2005)

Collaborators:

R.R. Netz (TU München)

Funding:

DFG priority programm 1164 (Nano- & Microfluidics)

2.8 Structural analysis of films cast from recombinant spider silk proteins

M. Tammer, P. Kölsch, F. Kremer

Silks are one of nature's best performing protein fibers. Spiders produce silk with outstanding mechanical properties, getting spidersilk in the focus of possible technical applications. Silk proteins can not only be processed into threads as found in nature, but can also be cast artificially into films in vitro. We investigated films of bacterially produced proteins mimicking the two dragline silk components ADF-3 and ADF-4 of the garden cross spider *Araneus diadematus* [1] in cooperation with Thomas Scheibel at the TU-Munich. The secondary structure for such silk films can be analyzed using FTIR spectroscopy to measure the absorbance spectra. A deconvolution of the amide I absorbance band between 1600 cm^{-1} and 1700 cm^{-1} , representing primarily the C=O stretching vibrations, with Lorentzian oscillators is used for determining the ratio of e.g. α -helical or β -sheet structure.

ADF-2 and ADF-3 consist mainly of repetitive sequences with characteristic polyalanine and glycine-rich motifs as well as non-repetitive (NR) regions at their carboxylterminus. We investigated whether the NR-regions play a decisive role in assembly, structure and stability of films cast therefrom. There had been no significant difference between the spectra of the proteins with or without NR-regions (Fig. 1, left). Furthermore, the influence of methanol and potassium phosphate treatment on the secondary structure has been studied. A shift of the maximum of the absorbance to lower wavenumbers ($\sim 1630\text{ cm}^{-1}$) indicating the formation of β -sheet structures at the expense of α -helices ($\sim 1660\text{ cm}^{-1}$) was found in all treated samples (Fig. 1, right)[4].

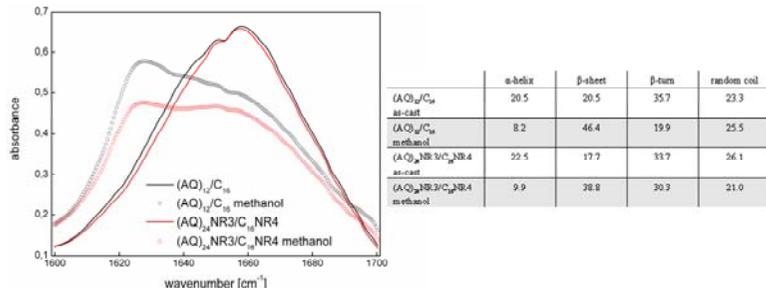


Fig. 1: Left: IR spectra of untreated samples without (AQ)₁₂C₁₆ and with NR-regions (AQ)₂₄NR3/C₁₆NR4 and of the same material treated with methanol; Right: resulted content of secondary structure for the films as derived by deconvoluting the amide I band.

References:

- [1] T. Scheibel; *Microbial Cell Factories*; **3**, 14 (2004)
- [2] U. Slotta, M. Tammer, F. Kremer, P. Koelsch, T. Scheibel; (2006), submitted to *Supramolecular Chemistry*

Collaborators:

T. Scheibel (Technische Universität München, Germany)

2.5 The microwave absorption of emulsions containing aqueous micro- and nanodroplets: A means to optimize microwave heating

J. Tsuwi, F. Kremer

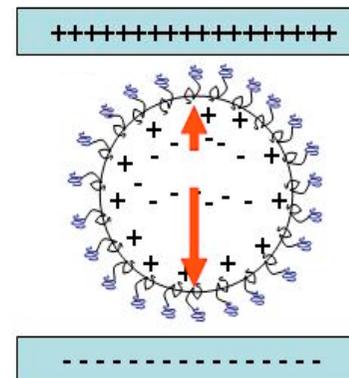


Fig. 1: A droplet containing aqueous solution placed between two charged electrodes

The microwave absorption of frequencies between 10 MHz - 4 GHz is measured for aqueous brine droplets dispersed in a dielectric medium ($\epsilon' = 2.0$). By varying the size of the droplets, ion type and ion concentration, it is found that the absorption goes through a maximum which depends as well on the type of ions and their concentration. The absorption process is attributed to the polarization of the microdroplets through surface charges. Means to optimize microwave heating in these systems is discussed.

References:

- [1] Holtze C., Tsuwi J., Sivaramakrishnan, R., Kramer K. D., Kremer F., Antonietti M., (2006), submitted to *Langmuir*
- [2] Antonietti, M.; Landfester, K. *Prog. Polym. Sci.* **27**, 689-757 (2002)
- [3] Sjöblom J.; Førdedal H.; Skodvin T., *J. Disp. Sci. and Techn.* **20**, 921-943 (1999)
- [4] Hanai T, In: Sherman P (Ed) *Emulsion Science* Academic Press, London (1968) Chapter 5

Collaborators:

Markus Antonietti (MPI of Colloids and Interfaces, Golm, Germany)
Christian Holtze (Experimental Soft Condensed Matter Group, Harvard University, U.S.A)

2.6 Spacer length dependent mesogen main chain alignment in liquid crystalline elastomer films

M. Tammer, P. Kölsch, F. Kremer

There are multiple ways of embedding liquid crystalline molecules into a polymer network. One of the most common techniques is a connection between one end of the mesogens and the main chain with an alkyl spacer chain, so called side chain liquid crystalline elastomers (SC-LCE). Polarized Fourier transform infrared (FTIR) spectroscopy is a powerful tool to determine the mean orientation and the order for the various molecular segments [1]. We applied this method to investigate the reorientation of the mesogens and spacer groups upon mechanically stretching the polymer network of thin nematic and cholesteric SC-LCE films*. For both systems the mesogens are found to form an oblate (director perpendicular to the main chain) or prolate (director parallel to the main chain) preferred orientation depending on whether the number of atoms in the spacer chain is even or odd. For the cholesteric films with no initial preferred orientation of the mesogens in the film plane, the strength of the coupling between the liquid crystal molecules and the polymer chain was compared for different spacer length. The shortest spacer with a length of four atoms revealed the highest coupling. Additionally for films with equally mixed spacer lengths (even and odd), the results after stretching showed an oblate conformation due to the stronger influence of the shorter spacer chains [2].

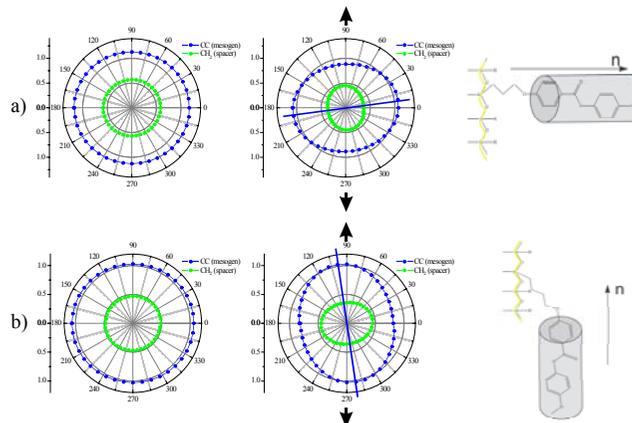


Fig. 1: Polar plot of the absorbance for cholesteric films with (a) an even and (b) an odd number of aliphatic units in the spacer chain. Left: initial state; Middle: stretched; Right: molecular picture.

References:

- [1] J. Li, M. Tammer, A. Komp, H. Finkelmann, F. Kremer, *Eur. Phys. J. E* **17**, 423-428 (2005).
 [2] M. Tammer, A. Komp, H. Finkelmann, P. Kölsch, F. Kremer; in preparation.

Collaborators:

H. Finkelmann (University of Freiburg, Germany)

*synthesized in the group of Prof. Finkelmann

2.7 Time resolved FTIR-spectroscopy on segmental reorientation of nematic elastomers under external mechanical fields

J. Li, M. Tammer, F. Kremer

Fourier transform infrared (FTIR) spectroscopy [1-3] is an especially suitable method for obtaining molecular level information for liquid crystalline networks. Time resolved FTIR spectroscopy with polarized light is employed to study the segmental orientation and the order parameters of nematic liquid crystalline elastomers (NLCEs, Fig. 1) with a monodomain structure in response to an external mechanical field [4,5]. Detailed results about the reorientation of the mesogens, the spacer molecules and the main chain are obtained due to the specificity of the FTIR measurements.

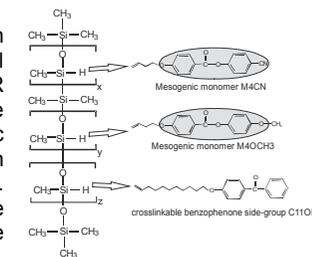


Fig. 1: NLCE material

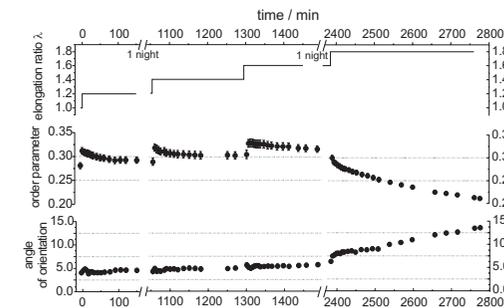


Fig. 2: Orientation and order parameters for the CC group (mesogens) at perpendicular strain

Mechanical strain is applied to thin NLCE films parallel and perpendicular to the initial mesogen orientation and the evolution of the orientation and the molecular order parameter with time is obtained for the different molecular moieties after each increase of the elongation ratio. While at parallel strain neither a reorientation nor a significant change of the order parameters takes place for all groups, the molecular units react differently to a strain applied perpendicular to the initial mesogen orientation (Fig. 2). Below a threshold

value of the elongation ratio the orientation and order parameters remain nearly constant. Above this value a continuous reorientation is found for all molecular segments while the order parameters decrease. The network is not stable anymore and flows until the film breaks.

References:

- [1] H. W. Siesler, K. Holland-Moritz, *Infrared and Raman Spectroscopy of Polymers*, Practical Spectroscopy Volume 4; Marcel Dekker: New York, 1980.
 [2] S. V. Shilov, S. Okretic, H. W. Siesler, M. A. Czarnecki, *Appl. Spectrosc. Rev.* **31**, 125 (1996)
 [3] H. Skupin, F. Kremer, S. V. Shilov, P. Stein, H. Finkelmann, *Macromolecules* **32**, 3746 (1999)
 [4] M. Tammer, J. Li, A. Komp, H. Finkelmann, F. Kremer, *Macromol. Chem. Phys.* **206**, 709 (2005)
 [5] J. Li, M. Tammer, A. Komp, H. Finkelmann, F. Kremer, *Eur. Phys. J. E* **17**, 423 (2005)

Collaborators:

H. Finkelmann (University of Freiburg, Germany)