

## CPP 30: Polymerphysics II

Time: Thursday 14:00–17:00

Location: C 130

CPP 30.1 Thu 14:00 C 130

**Study of rubber network structure by low field  $^1\text{H}$  double-quantum NMR experiments** — ●JUAN LOPEZ VALENTIN and KAY SAALWACHTER — Martin-Luther-Universität Halle-Wittenberg, Institut für Physik; Friedemann-Bach-Platz 6, D-06108 Halle (Germany)

Elastic properties of rubber are closely related with the network structure, and Solid-state nuclear magnetic resonance (NMR) is a successful tool to obtain this local information. Proton double-quantum (DQ) is one of the most recent and versatile approach towards the measurement of weak residual dipolar couplings (the NMR observable) associated with "NMR submolecules" (related to the Kuhn segments). It provides in the same experiment not only quantitative information on semi-local chain order (thus cross-link density) and its distribution, but also about chain dynamics [1].

Based on this methodology, natural rubber networks, which were vulcanized with different cure systems (sulphur and organic peroxide), were studied. Important variations in the quantity of non-coupled network defects (which are not elastically active), crosslink distribution as well as chain dynamics were found according to the different vulcanization reactions. They could partially explain the variation in the elastic properties of these samples. Note that we never observe any influence of Gaussian chain statistics on network chain dynamics. Cooperativity between polymer chains reduces and homogenise the conformational space that ultimately governs the chain entropy.

[1] K. Saalwachter, Prog. NMR Spectrosc., 2007, 51, 1-35.

CPP 30.2 Thu 14:15 C 130

**Structure and Dynamics of silicone networks as investigated by  $^1\text{H}$  low field double-quantum NMR** — ●WALTER CHASSÉ and KAY SAALWACHTER — Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, Friedemann-Bach-Platz 6, D-06108 Halle, Germany

The existence of cross-links and other topological restrictions lead to non-isotropic fast segmental fluctuations, and therefore some residual dipolar couplings persist, which are directly related to the crosslink density. Based on this principle, we have used static  $^1\text{H}$  double-quantum NMR spectroscopy to measure quantitatively these residual dipolar couplings and their distribution<sup>1</sup>.

Usually the easiest method to study network structure (crosslink density) is the swelling experiment based on Flory-Rehner-Theory. In this view we have compared the molecular weight between cross-links MC obtained from DQ-NMR with results of as well performed swelling experiments for PDMS networks with different topologies. Independently of this, the crosslink density can also be taken from  $^1\text{H}$  MAS experiments. With these results, we obtained information not only about the network structure of the rubber but also about the validity of the model used to analyze the DQ-NMR data, thermodynamics of swelling (polymer solvent interaction parameter  $\chi$ ), and the influence of network heterogeneities in that process. In conclusion we could show that DQ-NMR in combination with swelling experiments is a powerful method to characterize structure and dynamics of rubber.

[1] K. Saalwachter, Prog. in NMR Spectr., 2007, 51, 1-35.

CPP 30.3 Thu 14:30 C 130

**Dynamics in polymer networks containing liquid crystal** — ●RACHID HADJI<sup>1,2,3</sup>, SILKE RATHGEBER<sup>1</sup>, AMINA NÉGADI<sup>2</sup>, and ULRICH MASCHKE<sup>3</sup> — <sup>1</sup>Max-Planck-Institute for Polymer Research, Polymer Physics, 55128 Mainz, Germany. — <sup>2</sup>Université Aboubakr Belkaid, Laboratoire de Recherche sur les Macromolécules, 13000 Tlemcen, Algeria. — <sup>3</sup>Université des Sciences et Technologies de Lille, Laboratoire de Chimie Macromoléculaire, 59655 Villeneuve d'Ascq Cedex, France.

Polymer networks filled with liquid crystal are of interest due to their actuatoric properties but also due to their possible optical applications. Their anisotropic optical properties allow the switching from a transparent to an opaque state by alignment in an external electrical field. Changing the temperature through the disorder/order transition of the liquid crystal leads to a deswelling/swelling of the network which can be used for actuatoric applications. We studied the molecular dynamics of polymer networks containing different amounts of liquid crystal with dielectric spectroscopy (DS) and mechanical spectroscopy at the nematic-isotropic transition of the liquid crystal. We

also followed the phase transitions of the systems by dynamic scanning calorimetry. The networks under investigation were poly(*n*-butyl acrylate) networks filled with the commercial liquid crystals 5CB and E7, respectively. We were able to follow the dynamical changes occurring in the polymeric matrix as well as in the liquid crystalline solvent at the nematic-isotropic transition. In addition we studied the effect of the degree of sterical hindrance by changing the crosslink density.

CPP 30.4 Thu 14:45 C 130

**Topological aspects in random copolymer globules** — ●DANIEL BÖLINGER, HSIAO-PING HSU, and PETER VIRNAU — Institute of Physics, Johannes Gutenberg-University, 55099 Mainz

Although globular homopolymers display an abundance of knots [1], little is known about the topology and the degree of entanglement in copolymer globules. To this end we investigated globular structures which were generated with numerical simulations of the HP model using the nPERMis algorithm [2]. In this talk we will highlight structural and topological differences between homopolymer and random copolymer globules and demonstrate that entanglements are greatly reduced in copolymer structures. These results also shed some light on the longstanding controversy why only few knots have been observed in experimentally determined protein structures.

[1] P. Virnau, Y. Kantor, and M. Kardar, J. Am. Chem. Soc 127, 15102 (2005).

[2] H.P. Hsu, V. Mehra, W. Nadler and P. Grasberger, J. Chem. Phys. 118, 441 (2003).

CPP 30.5 Thu 15:00 C 130

**Effects of molecular shape and flexibility on the permittivity ratio of a model polymer network** — ●HENNING HÖRSTERMANN and REINHARD HENTSCHKE — Bergische Universität, Wuppertal, Germany

Sorption and diffusion of binary mixtures of small molecules in randomly crosslinked amorphous model polymer networks is studied via computer simulation. Three types of molecules identical in volume but different in shape and flexibility (compact, linear-stiff, and linear-flexible) are combined into binary mixtures (compact/linear-stiff) and (linear-stiff/linear-flexible). The relative effects of shape and flexibility on separation factor and diffusion coefficient inside random polymer networks are studied using a Molecular Dynamics/Gibbs-Ensemble Monte Carlo hybrid technique. In addition the effects of temperature, pressure, and network strand length are considered. We find that the compact molecules are preferentially absorbed into the network at all strand lengths and temperatures considered. Flexibility only leads to minor preferential sorption under most conditions. Diffusion coefficients of the competing species inside the network are found to agree within the error bars.

Additionally, the relation between connectivity ratio and network shrinkage is studied over a wide range of temperatures and pressures. The simulation results are compared to a mean-field Flory-Huggins lattice model.

CPP 30.6 Thu 15:15 C 130

**On the statistics of Gaussian two and three-dimensional networks: Fluctuations of junctions and collapse driven by structure.** — ●MICHAEL LANG<sup>1,2</sup>, SERGEY PANYUKOV<sup>3</sup>, MICHAEL RUBINSTEIN<sup>2</sup>, and JENS-UWE SOMMER<sup>1</sup> — <sup>1</sup>Leibniz-Institute for polymer Research, Hohe Str. 6, 01069 Dresden, Germany — <sup>2</sup>Department of Chemistry, University of North Carolina, 27599 Chapel Hill, N.C., USA — <sup>3</sup>P. N. Lebedev Physics Institute, Russian Academy of Sciences, Moscow, Russian Federation

We investigate ideal Gaussian networks both analytically and with computer simulations using the Bond Fluctuation model with and without excluded volume interactions. The focus of this study is on fluctuations and the collapse of networks with different connectivity and dimensionality.

We show that the size of a perfect square 2D network made from  $n^2$  Gaussian chains with  $N$  monomers each is  $R_g \sim N^{1/2} \cdot \log(n)$ . Thus, fluctuations in two-dimensional networks diverge logarithmically with the size of these films while fluctuations of three-dimensional networks with cubic structure is  $\sim N^{1/2}$  and do not increase with their size. We study the cross-over between two and three-dimensional networks by

following the dependence of junction fluctuations on the thickness of films.

The results of model systems are compared with more realistic networks in order to understand the effect of disorder on the properties of the network and fluctuations of network junctions.

break

CPP 30.7 Thu 15:45 C 130

**Influence of Electric Fields on the Phase Behavior of Concentrated Block Copolymer Solutions** — ●HEIKO G. SCHOBERTH<sup>1</sup>, KRISTIN SCHMIDT<sup>2</sup>, and ALEXANDER BÖKER<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany — <sup>2</sup>Materials Research Laboratory, University of California, Santa Barbara, USA

We investigate the influence of the electric field on the phase behavior of diblock copolymer morphologies in concentrated solutions using Synchrotron SAXS. We observe a decrease of the order-disorder-transition temperature and phase separation with increasing electric field strength. This shift is found in  $T_{ODT}$  even at moderate field strengths and follows a linear dependence.

Furthermore we can also induce an order-order-transition. We synthesized different block copolymers with compositions close to the predicted phase boundaries. Due to the lower free energy of aligned anisotropic microdomain structures parallel to the electric field, we can induce a transition from the metastable hexagonally perforated lamellae to the lamellae phase under strong electric fields. In addition for an isotropic cubic gyroid phase, which cannot be aligned, a transition to aligned cylinders is found.

CPP 30.8 Thu 16:00 C 130

**Multiscale Simulations of Polybutadiene Solutions** — ●THOMAS STRAUCH, PETER VIRNAU, and WOLFGANG PAUL — Johannes Gutenberg-Universität Mainz

Polymer processing relies in general on detailed knowledge of the polymer solvent phase diagram. Computer simulations have become a powerful tool to investigate complex systems and particularly their phase behavior. However, it is often impossible to treat the polymer solvent mixture in complete chemical detail within simulations. To avoid this problem, one can coarsen the fully atomistic model. We present a new, systematic coarse-graining procedure applied to the Polybutadiene(1,4)-Butane solution. For the polymeric component, the procedure uses an equation of state known from atomistic simulations or experiment to validate the choice of the coarse grained potentials. Furthermore structural quantities are compared with results from chemically detailed simulations or experiments. The solvent's nonbonded potential can be determined by mapping the critical point of the model system onto the experimental critical point of the substance. To investigate the phase diagram of the polymer solution, a potential for the interaction between the two components is chosen by using Lorentz-Berthelot mixing rules. In addition to the systematic coarse-graining procedure, results for the phase behavior of the Polybutadiene(1,4)-Butane solution obtained by grand canonical Monte Carlo simulations will be shown.

CPP 30.9 Thu 16:15 C 130

**Calculation of the segmental order parameter for a polymer chain in good solvent** — ●ZORYANA USATENKO<sup>1,2</sup> and JENS-UWE SOMMER<sup>1</sup> — <sup>1</sup>Leibniz Institute for Polymer Research Dresden e.V., 01069 Dresden, Germany — <sup>2</sup>Institute for Condensed Matter Physics, NAS Ukraine, 79011 Lviv, Ukraine

We have calculated the segmental tensor order parameter of flexible polymer chains in weak good solvent. This quantity is directly observ-

able in multi-quantum NMR experiments. We have used the Edwards model for polymer chains and have applied direct perturbation expansion with respect to excluded volume interactions in one loop order. The obtained results indicate that the distribution of the tensor order parameter is not homogeneous along the chain as expected for ideal Gaussian statistics. Overall segmental order is lower as compared to Gaussian chains and decays towards the chain ends [1]. These results are in agreement with computer simulation studies on single chains with fixed ends in good solvent. The overall reduction of the tensor order parameter has been also observed in NMR experiments on swollen polymer networks [2].

[1] Z.Usatenko, J.-U.Sommer, *Macromolecular theory and simulations*, 2007 (in press).

[2] K. Saalwächter and J.-U. Sommer, *Macromol.Rapid Commun.* 28, 1455 (2007).

CPP 30.10 Thu 16:30 C 130

**From simple liquid to polymer dynamics: a field cycling NMR study on linear polymer melts of different molecular weights** — ●AXEL HERRMANN, SOBIROH KARIYO, CATALIN GAINARU, HARALD SCHICK, JULIA HINTERMEYER, ALEXANDER BRODIN, VLADIMIR N. NOVIKOV, and ERNST A. RÖSSLER — Universität Bayreuth, Experimentalphysik II, 95440 Bayreuth

We utilize fast field cycling NMR relaxometry to investigate the crossover from glassy dynamics through Rouse to reptation behavior in a series of polybutadienes (PB) and polydimethylsiloxanes (PDMS) with molecular weights  $M$  ranging from the low  $M$  (simple liquid dynamics) to the high  $M$  limit (reptation dynamics). The dispersion data  $T_1(\omega)$  are transformed into the susceptibility  $\chi''(\omega) \propto \omega/T_1$  and master curves are constructed for each  $M$ . By extracting the polymer spectra through subtracting the glass spectrum from the total spectra and comparing them to Rouse theory, we are able to determine the Rouse unit  $M_R$  and entanglement weight  $M_e$ . These characteristic molecular weights also show up in the  $M$  dependence of the dynamic order parameter  $S$ , a measure of the relative correlation loss due to polymer dynamics, and the glass transition temperature  $T_g$ . Thus, the glass process is specifically modified by the polymer dynamics. We find similar results for the samples of PDMS. For partially deuterated PB our approach yields the common polymer dynamics although the values of  $S$  are different. Hence in order to provide a coherent interpretation of NMR dispersion data of polymers, the contribution of the glass dynamics has to be taken explicitly into account.

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**Dynamics of n-alkyl-cyanobiphenyl and cyano-n-alkylbenzoate molecules in a surface layer adsorbed onto aerosil** — STEFAN FRUNZA<sup>1</sup>, LIGIA FRUNZA<sup>1</sup>, and ●ANDREAS SCHÖNHALS<sup>2</sup> — <sup>1</sup>National Institute of Materials Physics, R-077125 Magurele, Romania — <sup>2</sup>Federal Institute of Materials Research and Testing, D-12205 Berlin, Germany

Composites prepared from aerosil and n-alkyl-cyanobiphenyl (nCB, n=2 - 8) or cyano-n-alkylbenzoate (CPnB; n= 4 - 7) molecules are investigated by dielectric spectroscopy (10 MHz to 1 GHz) in a large temperature range. The selected high silica density allows the observation of the behavior of a thin layer (with nearly a one or two-monolayer structure) adsorbed on the silica particles. For the composites one relaxation process is observed at frequencies much lower than that of the processes found for the corresponding bulk. It is assigned to the dynamics of molecules in a surface layer. The temperature dependence of its relaxation rates obeys the Vogel/Fulcher/Tammann law, characteristic for glassy dynamics liquids. For both systems they vary continuously with the length of alkyl chain. This is discussed in detail in the frame work of quasi two-dimensional character of glassy dynamics of molecules adsorbed on a surface.