

Polymere Netzwerke: Struktur, Theorie und Anwendung



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Durch die Vernetzung von Polymeren werden Flüssigkeitseigenschaften (Viskosität) mit Festkörpereigenschaften (Formbeständigkeit, Lösungsmittelbeständigkeit) kombiniert. In der modernen Polymerforschung und -technologie werden Vernetzungsprozesse zur gezielten Beeinflussung dieser Materialeigenschaften im Zusammenspiel mit strukturierenden Präparations- oder Selbstorganisationsprozessen eingesetzt. Hinsichtlich technischer Anwendungen sind dabei elastomere Werkstoffe ein unverzichtbarer Bestandteil für zukünftige energieeffiziente Leichtbau- und Mobilitätstechnologien. Polymergele erlangen dagegen insbesondere im Bereich der biomedizinischen Anwendungen sowie der Smart Materials für die Aktorik, Sensorik und Mikrofluidik/Mikrosystemtechnik eine zunehmende Bedeutung mit neuen Herausforderungen bezüglich des Verständnisses dieser Materialien.

In 2012 wurden Ergebnisse vorgestellt, bei denen zeitabhängige Vorgänge in Netzwerken mittels modernster Röntgenstreutechniken analysiert wurden. Im Rahmen von Arbeiten innerhalb der DFG-Forschergruppe (FOR 597) konnte ein Zusammenhang zwischen der Kinetik der dehnungsinduzierten Kristallisation in Naturkautschuk und der Rissausbreitung hergestellt werden. Ebenso konnten durch zeitaufgelöste Messungen zwei Phasen der Kristallisationskinetik nachgewiesen werden (Macromolecules 45, 7914 (2012)). Mit Hilfe von Röntgen-Korrelationsspektroskopie wurden die Füllstoffdynamik in Elastomeren und die Alterungsmechanismen der Materialien untersucht. Hierbei konnten – in Zusammenarbeit mit Partnern in Frankreich und USA – Zusammenhänge mit der Dynamik in Kolloidgelen und weichen Gläsern hergestellt werden (doi.org/10.1021/ma3013674 Macromolecules). In Zusammenarbeit mit der Arbeitsgruppe von Prof. Kay Saalwächter (Halle/S.) wurden grundlegende Quellungseigenschaften von Polymernetzwerken als Funktion der Lösungsmittelqualität experimentell und theoretisch untersucht. Unter Nutzung des Flory-Rehner-Modelles wurde ein expliziter analytischer Zusammenhang zwischen der Segmentorientierungs-Ordnung und dem Quellgrad gefunden, welcher durch NMR-Experimente bestätigt werden konnte (Macromolecules 45, 5513 (2012)).

Neuartige Netzwerke ohne chemische Netzknoten können durch Verschlaufung von Ringpolymeren erzeugt werden. In Computersimulationen wurden erstmals verschiedene Präparationsstrategien für solche „Olympischen Gele“ analysiert. Simulationen gestatten ebenso die direkte topologische Analyse von Lösungen und Schmelzen aus Ringpolymeren. In diesem Zusammenhang konnte ein neues Modell zur Beschreibung der Konformationseigenschaften von Ringpolymeren entwickelt werden (Macromolecules 45, 7542 (2012)). Seit mehr als einem Jahr werden auch Simulationsmethoden zur Untersuchung der Kinetik und der Quellungseigenschaften von Superabsorbentnetzwerken im Rahmen eines Industrieprojektes gefördert.

Bei feld-kontrollierbaren Funktionsnetzwerken lassen sich Form und mechanische Eigenschaften durch Anlegen eines äußeren Feldes ändern. Prominente Beispiele, die hier untersucht werden, sind photosensitive azobenzolhaltige Elastomere und magneto-sensitiven Elastomere. Faszinierendes Potenzial für technische Anwendungen findet man bei künstlichen Muskeln, Sensoren, Mikrorobotern, Mikropumpen, Aktuatoren. So wurden neue analytische Ansätze entwickelt, welche die chemische Struktur von azobenzolhaltigen Polymernetzwerken mit deren photo-mechanischen Eigenschaften in Beziehung setzen (J. Phys. Chem. B 116, 913 (2012), J. Chem. Phys. 137, 024903 (2012)). Die Erweiterung dieser Arbeiten auf photoinduzierte Deformationsdynamik von Azoelastomeren wird im Rahmen eines 2012 eingeworbenen DFG-Projekts fortgesetzt. Neuere analytische Ansätze zur Beschreibung mechanischer Eigenschaften von magnetosensitiven Elastomeren (Condensed Matter Physics 15, 33601 (2012)) sollen in Zusammenarbeit mit der TU Dresden experimentell verifiziert werden.

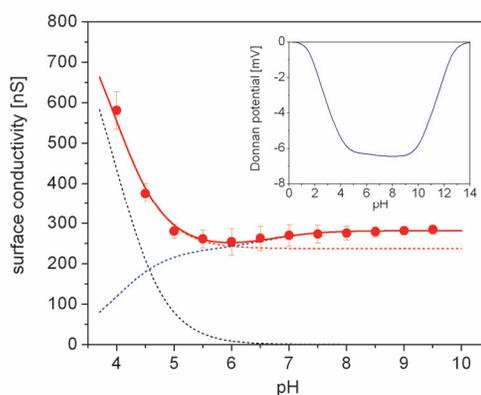
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Electrokinetic analysis to reveal composition and structure of biohybrid hydrogels

Ralf Zimmermann, Susanne Bartsch,
Uwe Freudenberg, Carsten Werner

Hydrogels, 3-dimensional matrices of physically or chemically cross-linked polymers, are instrumental to progress in tissue engineering [1]. These materials can be adapted in their mechanical properties to various tissues [2] and incorporate biomolecular constituents of extracellular matrices (ECM) to stimulate embedded cells by specifically orchestrated signals [3]. Biohybrid hydrogels, consisting of synthetic and biologically derived polymeric constituents, are increasingly developed and employed for this purpose [4]. Among these systems, hydrogels containing polysaccharidic ECM components, glycosaminoglycans (GAGs) are particularly promising due to the effective binding, protection and sustained release of numerous growth factors [5]. The latter effect can be largely attributed to the sulfation pattern of the GAGs and is therefore largely determined by electrostatic interactions. In order to analyze the charge and structure of biohybrid hydrogels consisting of covalently linked star-shaped poly(ethylene glycol) (starPEG) and heparin [3], we developed and applied a mean-field approach for the numerical evaluation of surface conductivity data [6]. The comparison of the experimental data with simulation results (Fig. 1) revealed the concentration and pK values of the ionizable groups in the gel, i.e., 53 mmol/L and $pK = 0.8$ for the sulfate groups and 10 mmol/L and $pK = 4$ for the carboxyl groups [6]. As an important prerequisite for the analysis of the gel composition and its cross-linking degree, heparin of known molecular weight and number of sulfate and carboxyl groups per molecule was used for the formation of the hydrogel films [6]. As the sulfate groups are not involved in the gel formation [3], their concentration can be converted into the heparin concentration within the hydrogel. This calculation is straightforward and revealed a heparin concentration of 11.4 $\mu\text{g}/\mu\text{L}$ for the hydrogel film, which is comparable with values determined for similar (bulk) starPEG-heparin gels [3]. The obtained heparin concentration was further used to analyze the cross-linking

degree of the gels. In excellent agreement with the theoretical value expected from the gel composition we determined an average number of 12.3 carboxyl groups per heparin molecule (vs. 12 carboxyl groups expected for the molar ratio $\gamma = 3$). Since other analytical methods to determine the actual cross-linking degree via labeling of unreacted groups are prone to non-quantitative turnover or non-specific side effects (e.g. electrostatic interactions with gel components) the developed approach is clearly advantageous. The introduced method [6] can be further applied to quantify variations of the intrinsic sulfation pattern of the GAG components in the gel (e.g. used to tune its interactions with signal molecules) and to investigate biomolecular interactions between the GAGs and soluble effectors. Altogether, the introduced method allows us to interpret the characteristics of GAG-based hydrogels for regenerative and sensoric applications with unprecedented precision. Ongoing work is dedicated to explore a series of PEG-based hydrogels and differently sulfated GAGs and to correlate the results with the molecular transport and binding/release of selected growth factors. Together, these studies will provide fundamental information for the rational design of multi-biofunctional polymer matrices.



Keywords
biohybrid hydrogels
interfacial charge
formation
electrokinetics
soft interfaces

Fig. 1:
Surface conductivity and Donnan potential (inset) of a starPEG-heparin hydrogel film in 0.1 mM KCl solution of varied pH. The film was prepared at a molecular ratio starPEG to heparin of 3 (in case of a quantitative reaction of the starPEG a conversion of 12 of the 24 carboxyl groups of the heparin would occur). The experimental surface conductivity data (red circles) were reproduced by the theory (red solid line). The red dashed line shows the surface conductivity caused by counter ions compensating the charge of the sulfate groups in the gel. The blue and black dashed lines illustrate the contribution of the K^+ ions (blue) and H_3O^+ ions (black) to the overall surface conductivity. For further details see Ref. [6].

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Keywords
polymer networks
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mean-field model
segmental order
parameter
NMR

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Segmental order and thermodynamics of swollen polymer networks

Jens-Uwe Sommer

The swelling behavior of polymer networks and gels is still not fully understood. The well known Flory-Rehner (FR) model relies on simplified assumptions both about the free energy of the polymer-solvent system (equation of state) as well as on the elasticity. Equilibrium swelling in good solvents leads to several discrepancies between the predictions of this model and measurements. As a consequence it has been argued that the theta-point of a polymer gel is shifted with respect to that of an uncrosslinked solution in order to fit the experimental data to the FR-model. These arguments are commonly based on measurements of volume degree of swelling, Q , which has to be related with the a priori unknown density of elastically active network chains. We have investigated the segmental order parameter of polymer gels (experimentally accessed by solid-state NMR methods measuring the residual dipole-dipole coupling) under various solvent conditions reaching from poor to good solvents. We were able to explicitly solve the FR-model for the NMR equilibrium order parameter, \bar{s} , as a function of the equilibrium degree of swelling, \bar{Q} , taking into account the full equation of state. This relates two directly accessible experimental parameters and thus allows an independent test of the model. Taking into account ideal chain statistics we obtain [1]

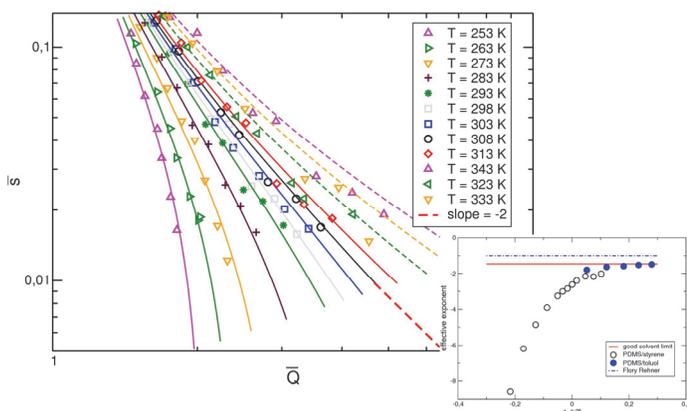
$$\bar{s} = \frac{3}{5} A_0 \bar{Q}^{-1} \left\{ \frac{1}{2} v^{-2} \ln(1 - \bar{Q}^{-1}) \bar{Q}^2 \right\} \quad (1)$$

where A_0 denotes a numerical constant and $v = (1 - \theta/T)$ is the effective excluded volume interaction (second virial coefficient). The function ${}^2 \ln(1-x)$ denotes all higher than second order terms in the full expansion of the logarithm-function with respect to x . It is worth noting that Eq. (1) takes into account all higher virial coefficients of the Flory-Huggins equation of state for the polymer solution, thus going beyond the commonly used approximations. The limiting case of the theta-point ($v=0$) by ignoring all higher order contributions leads to

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$\bar{s} \sim \bar{Q}^{-2}$, which is only valid for the case of high degrees of swelling. This, on the other hand, is usually not reached in uncharged polymer networks under theta-conditions.

In Fig. 1 we display the results of NMR measurements of the segmental order parameter, s , for PDMS networks in styrene solution. Using the theta-point of the uncrosslinked solution (308 K) we obtain excellent fits to all data close to and below the theta-point. At higher temperatures, in the good solvent limit, the theory overestimated the order parameter. This can be explained by the contribution of the excluded volume to the statistics of the segmental order parameter itself. In the lower right of Fig. 1 we display the effective exponent, a , of the order parameter using the approximate equation $\bar{s} \sim \bar{Q}^{-a}$ comprising data for two different solvents (styrene and toluene). It is clearly shown that in the limit of good solvent the value of $a = 3/2$ (instead of $a = 1$) is reached, which concurs by the aforementioned effect of excluded volume on the order parameter statistics [2].



Our combined theoretical and experimental studies indicate that crosslinking does not change the theta-point in polymer gels. On the other hand, at rather low degrees of swelling under theta-conditions many-body interactions (higher order virial coefficients) contribute essentially to the swelling and only the solution of the FR-model taking into account the full equation of state can explain the experimental findings. In the limit of good solvents, where the FR-model has been applied mostly in the literature, deviations of from the predictions of the FR-model in combination with the Gaussian chain statistics are observed.

In this case the excluded volume effect reduces the order parameter at a given deformation of the network chains which leads to an over-estimation for the NMR results. Our results indicate that polymer gels display a smooth crossover from good to poor solvent behavior where the theta-point is "hidden" by the rather low degree of swelling related to small characteristic length scales of freely fluctuating chain sequences (Fig. 2). This explains some of the dispute in literature about the value of the theta-point in polymer networks. Our results also show that the FR-model works very well for the case of low solvent qualities.

Cooperation :

W. Chassé, K. Saalwächter, Martin-Luther-Universität Halle-Wittenberg, Institut für Physik

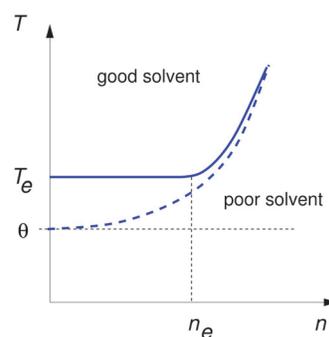


Fig. 2 (right):

Sketch of the phase diagram of polymer gels. Here, n , denotes the crosslink density. The ideal theta-point (horizontal dashed line) is reached for very low concentrations (very high degrees of swelling) only, which corresponds to very low crosslink densities, n . For finite crosslink densities the good solvent limit is reached at higher temperatures only as indicated by the dashed line. In real polymer networks entanglements limit the swelling behavior for low crosslink densities and thus prevent swelling to very low densities (solid line). As a consequence in real polymer gels the asymptotic theta-behavior can not be observed, and the behavior of the gel at the theta-point is still controlled by many body interactions of the monomers.

Fig. 1 (left):
(upper left) Equilibrium segmental order parameter obtained by NMR vs. equilibrium degree of swelling (symbols) for various temperatures for PDMS networks in styrene. The theta-point of the solution is located at 308 K and the measurements covered temperatures from poor up to good solvents. The lines display the fits to Eq.(1) using $A_0=0.9$, $B=2.4$ and $\theta=308$ K. The dashed lined indicates the slope for the ideal theta-point.
(lower right) Effective exponents in two solvents as a function of the reduced temperature. The dashed-dotted line indicates the expectation for the FR-model in the good solvent limit and the solid line is the exponent taking into account corrections to the order parameter by excluded volume effects [2].

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Keywords
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cyclic polymers
polymer conformations

The effect of topology on the conformations of cyclic polymers

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The effect of entanglements between molecules is a long standing problem of polymer physics that is still not completely understood until today. Seminal works of Edwards and de Gennes revealed in past decades that entanglements lead to a different scaling of the diffusion of long linear polymers in concentrated solutions and melts [1] or indicated the qualitative nature of the entanglement contribution to the modulus of polymer networks [2]. It was further conjectured and later observed that entanglements may lead to a collapse of the conformations of cyclic polymers when diffusing into polymer networks or inside melts of other cyclic polymers [3]. Recently, we were able to contribute to this discussion [4] by simulating two sets of solutions of cyclic polymers of different degree of polymerization N as a function of the polymer volume fractions ϕ , whereby both series of simulations differed only concerning one important point: The first set of simulations contained non-concatenated impenetrable rings, but the rings of the second set were allowed to freely penetrate each other. By comparing both sets of simulations, we were able to quantify the effect of entanglements on the conformations of the molecules directly, and we could identify the nature of the topological interactions between cyclic polymers. The first key observation was that the average number of overlapping rings penetrating a given ring, f_p , is proportional $\phi^{0.77} N$ for semi-dilute solutions of interpenetrating rings. This behavior was related via $\phi^{0.77} N \sim \phi R^2$ to the area that is spanned by the ring. It was further shown that only a fraction of all overlapping rings is concatenated for the parameters of our study. Since the number of concatenations $\sim N$ grows quicker than the total number of overlapping rings $\sim N^{1/2}$, it was concluded that there must exist a cross-over degree of polymerization N^* above which any pair of overlapping and interpenetrating rings must be concatenated. This behavior concurs with our second key observation: we found that the number fraction

of rings containing no concatenation decreases exponentially also as function of ϕR^2 . This leads again to a cross-over molecular weight N_{00} at a given ϕ below which essentially all rings are non-concatenated. The exponentially decaying fraction of non-concatenated rings above the cross-over led to new term in the free energy of rings in melts that allowed us to explain the previously observed compression of rings in melts.

In total, we suggest four different regimes for the conformations of rings in mono-disperse melts. For small rings below the onset of concatenation, $N < N_{00}$, ring conformations are rather ideal with $R \sim bN^{1/2}$. Concatenated rings below the onset of strong compression at cross-over degree of polymerization N_c , are expected to show $R \sim bN^{2/5}$ due to the balance of non-concatenation with a two body type repulsion of the monomers inside the ring. Larger degrees of polymerization $N > N_c$ become increasingly compressed, such that non-concatenation is balanced by three body interactions leading to ring conformations $R \sim bN^{3/8}$. This scaling of ring conformations continues until N^* . Then, the non-concatenation contribution to free energy is expected to be proportional to the overlap number, which implies a weaker compression of the rings and a scaling of largest rings $R \sim bN^{4/9}$. Computer simulation data [5] is close to our predictions for the scaling exponents for the first three regimes, while the fourth regime could not be reached yet. Our results have large impact on the understanding of, for instance, the packing of cyclic DNA inside cells or the cell nucleus.

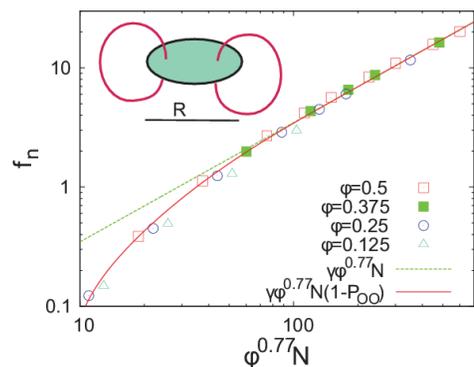


Fig. 1: Average number of penetrations per cyclic polymer as function of polymer volume fraction and degree of polymerization. The red line is taking into account the cut-off for concatenation at smallest N .

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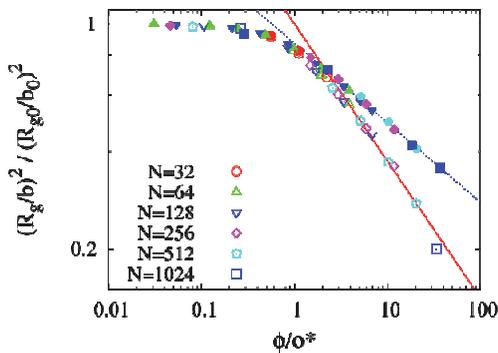


Fig. 2:
A comparison of the size of freely interpenetrating rings (full symbols) and non-concatenated rings (hollow symbols) as a function of concentration relative to the overlap concentration ϕ^* of the rings. Non-concatenated rings are compressed as compared to the test group of the interpenetrating rings. The size of interpenetrating rings is reduced at high volume fractions due to the screening of excluded volume at the absence of entanglements. The red line indicates the scaling prediction for the first collapsed regime of entangled rings before the onset of strong compression.

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LA 2735/2-1

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Ionic liquid as a multifunctional additive in elastomer compounds

Kalaivani Subramaniam, Amit Das,
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Ionic liquids (ILs) are organic salts with low melting point ($<100\text{ }^\circ\text{C}$), low vapour pressure and high thermal stability. ILs are exploited in carbon nanotubes filled elastomers as dispersing agent, coupling agent, thermal stability promoters and as anti-oxidants. The multifunctional nature of ILs is explored in polychloroprene rubber (CR). Owing to the polar nature of CR the ILs find a sort of compatibility with it and at the same time the cationic part of the ILs is interacting with the π -clouds of CNTs enabling the enhanced dispersion state of CNTs. The elastomeric composites were prepared in two steps: (1) CNTs were modified using an imidazolium based IL and (2) incorporation of modified CNTs (m-CNTs) into chloroprene rubber (CR) along with other curatives in a two roll mill [1].

As dispersing and coupling agents

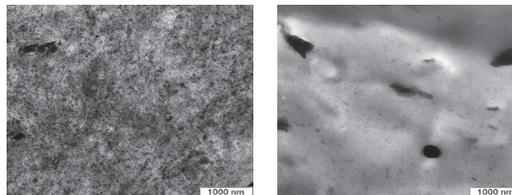


Fig. 1:
TEM images [left] CR + unmodified CNTs (u-CNTs) [right] CR + m-CNTs

A poor distribution and dispersion of u-CNTs with big agglomerates and a fine dispersion of m-CNTs with random small agglomerates are observed in CR composites. After modifying CNTs with ILs, disentanglements of CNT bundles takes place and the disentangled tubes are maintained in dispersed state in the composites as IL couples CR and CNTs [1, 2].

As thermal stability promoters

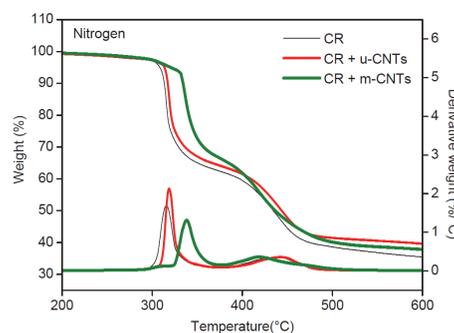


Fig. 2:
Thermal degradation of CR composites

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Keywords
 azobenzene elastomers
 light-induced
 deformation
 orientation approach
 statistical physics

CR/m-CNT composites are more thermally stable due to the improved dispersion of m-CNTs and to the interfacial interactions of CR with CNTs [3].

As anti-oxidants

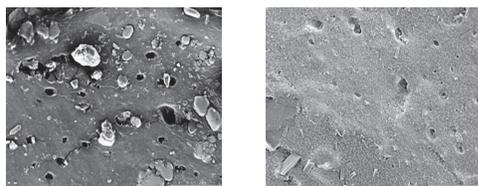


Fig. 3:
 SEM images of samples aged at 125°C for 168 hours [left] CR + u-CNTs [right] CR + m-CNTs

Less cracks and holes in aged CR/m-CNT composites indicate reduced surface oxidation thereby leading to an enhanced retention of mechanical properties [4].

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Theory of light-induced deformation of azobenzene elastomers

Vladimir P. Toshchevikov, Marina Saphiannikova, Gert Heinrich

Azobenzene elastomers containing photo-sensitive azo-moieties in their structure are smart materials which are able to transform light energy into mechanical stress. Since the light stimulus can be controlled rapidly, precisely and remotely, azobenzene elastomers have a fascinating potential for micro- and nano-technologies serving as artificial muscles, sensors, microrobots, micropumps and actuators.

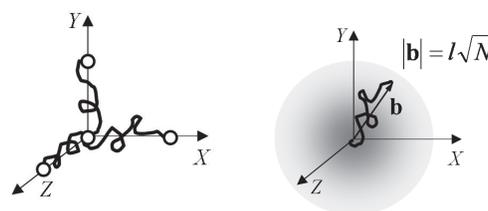


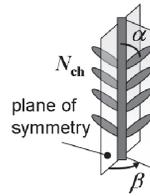
Fig. 1:
 A cell of a regular cubic network model with three network strands aligned along the axes of a rectangular frame of references

Fig. 2:
 A spherical network model with random orientation of network strands. End-to-end vector \mathbf{b} describes the orientation of a network strand.

We have proposed a statistical theory of the light-induced deformation of isotropic azobenzene elastomers using a regular cubic network model [1], see Fig. 1, as well as more realistic network models with random distribution of the end-to-end vectors of network strands [2], see Fig. 2. Each network strand consists of N rod-like Kuhn segments of the length l bearing N_{ch} azobenzene chromophores in side chains, see Figs. 2 and 3. To describe the conformational statistics of network strands we use both the Gaussian approximation and the freely-joint-rods chain model which takes into account the finite extensibility of network strands. Effects of polydispersity are also taken into consideration.

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Interaction of azobenzene chromophores with linearly polarized light is described by an effective orientation potential for the chromophores. The strength of the orientation potential V_o is proportional to the intensity of the light. The reorientation of chromophores with respect to the light polarization \mathbf{E} leads to appearance of the light-induced mechanical stress that causes uniaxial deformation of isotropic azobenzene elastomers. The elongation ratio λ as a function of V_o is calculated for azobenzene elastomers with different orientation distributions of chromophores inside the network strands and for different network structures, see Fig. 4. We have shown that both monodisperse and polydisperse azobenzene elastomers can display three types of photomechanical behavior: (i) photo-expansion along \mathbf{E} , (ii) photo-contraction along \mathbf{E} and (iii) non-monotonic light-induced deformation (expansion at weak light intensities and contraction at high light intensities). The sign of deformation of azobenzene elastomers is determined by the orientation distribution of chromophores with respect to the main chains, see Fig. 2. Azobenzene elastomers with preferable orientation of chromophores parallel (α close to 0°)/perpendicular (α close to 90°) to the main chains demonstrate photo-contraction/expansion, respectively, see Fig. 4. An important result of our study is that an azobenzene elastomer demonstrates the same photo-mechanical behavior (expansion/contraction) as its low-molecular-weight analogue, i.e. the system of oligomers, whose chemical structure is the same as the Kuhn segments of the elastomer. It has been found that the sign of deformation of azobenzene elastomers is independent both of the degree of cross-linking and of the polydispersity of network strands. However, the degree of cross-linking and polydispersity of network strands influence the magnitude of the light-induced deformation. Higher degree of cross-linking causes lower light-induced deformation. Further, we have shown that a simple regular cubic network describes very well photo-mechanical properties of azobenzene elastomers, especially of those exhibiting a light-induced contraction, see Fig. 4.



Theoretical findings are found to be in a good agreement with recent experimental data [3]. By this, we conclude that the regular cubic network model should provide a very good approximation for further studies of azobenzene elastomers under any field of the quadrupole symmetry, including molecular fields appearing in the LC-azobenzene elastomers. Theoretical studies of LC-azobenzene elastomers are currently in progress [4].

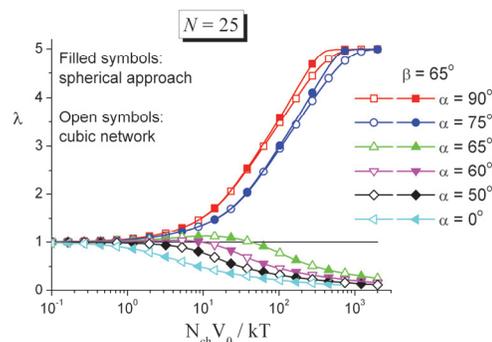


Fig. 3: Orientation distribution of azobenzene chromophores inside a Kuhn segment. It is described by the polar angle α between the rigid main chain and the long axis of a chromophore and by the azimuthal angle β for the rotation from the molecule plane of symmetry. Each Kuhn segment contains N_{ch} chromophores in side chains.

Fig. 4: Comparison of the elongation ratios λ as functions of the light-induced field strength V_o calculated in the framework of the regular cubic network model and of the spherical network model with random orientation of network strands

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D. Neher, Potsdam Universität

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Keywords

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tire
structure-property
relations
synchrotron wide-angle
X-ray scattering

Transient phenomena in strain-induced crystallization in natural rubber

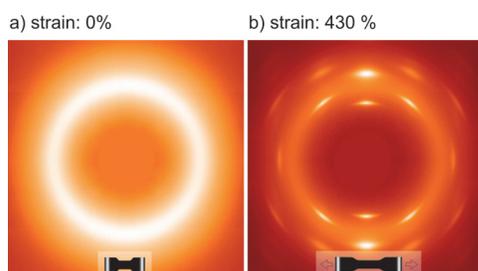
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Tailoring the properties of polymers by tuning crystallinity and orientation is common practice. Natural rubber has the astonishing ability to crystallize under strain. In regions of high strain and stress, the crystallites locally reinforce the material, while in the remainder of the rubber part the excellent elastic properties of the amorphous rubber are preserved. These properties still make natural rubber the material of choice for high-demanding applications like truck tires. Since the rubber is subjected to dynamic loads, it is critical to understand the time dependence of crystallization. By applying a steplike strain, we followed the crystallization over time in WAXD (wide-angle X-ray diffraction) with an unprecedented time resolution of 7 ms and derived a new kinetic law. Direct observation of crystallization during cyclic dynamic loading at 1 Hz gave insight into the structural processes under realistic loading conditions.

It has recently been pointed out that natural rubber is a unique material “where one pulls [...] a little bit and it snaps, but pull twice as hard and it holds together”[1]. Strain-induced crystallization is the reason behind these outstanding mechanical properties [2]. Especially tear fatigue is significantly enhanced due to the reinforcing ability of highly oriented crystallites, that form around the crack tip and reduce crack growth. While the dynamic mechanical properties are routinely measured, the establishment of structure property relations is hampered by the difficulty to characterize the structure under dynamic loading conditions.

Fig. 1:

WAXD patterns of a) unstretched and b) stretched natural rubber (under quasistatic conditions). The degree of crystallinity was extracted from the intensity of the crystalline peaks on the equator.



The classic method to quantify crystallinity is WAXD (Fig. 1), the time resolution of which is limited by photon flux and detector readout times. Owing to the brilliance of the MiNaXS beamline at DESY (Deutsches Elektronen Synchrotron), these limitations could be overcome [3, 4].

To elucidate the fundamentals of the kinetics of strain-induced crystallization, the natural rubber sample was subjected to a steplike strain, stretching it to several hundred percent within less than 10 ms. WAXD patterns were acquired with a frame rate of 140 frames per second. Already 10 ms after the strain step, a significant amount of crystallinity was detected (Fig. 2).

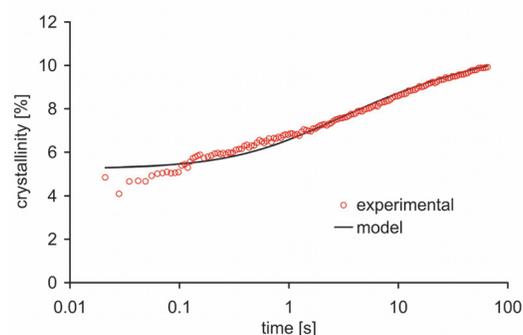


Fig. 2:

Evolution of crystallinity over time after the application of a steplike strain from 0 % strain to 410 % strain at $t = 0$ s.

So far, most studies reported longer incubation times [5]. During the following seconds, a distinct evolution of the crystallinity was observed, suggesting that the mechanism is different from thermal crystallization. This is due to the different morphologies, mobilities and driving forces in thermal crystallization and strain-induced crystallization of a cross-linked elastomer. A new physically motivated kinetic law was developed to describe the crystallinity depending on strain and time. The tensile impact tests clearly showed that the typical time scales of deformation in real rubber parts are too short to let the structure reach equilibrium. This was directly proven in a second kind of test. Cyclic dynamic tensile tests with a frequency of 1 Hz are routinely performed to study the fatigue properties of rubber. Using a selfmade tensile testing machine we carried out these experiments in situ. The crystallinity was recorded with a time

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resolution of 20 ms to resolve each deformation cycle individually as well as to follow the evolution over several cycles. We showed that the crystallinity under dynamic conditions was significantly suppressed as compared to the quasistatic level (Fig. 3). Under fully relaxing conditions (minimum cyclic strain = 0), the maximum crystallinity is suppressed by more than one half. Under non-relaxing conditions, the crystallinity is much higher, but still below the quasistatic level.

These findings can give the structural explanation to the long known observation that in strain-crystallizing elastomers, under relaxing conditions cracks grow faster despite the smaller work of deformation.

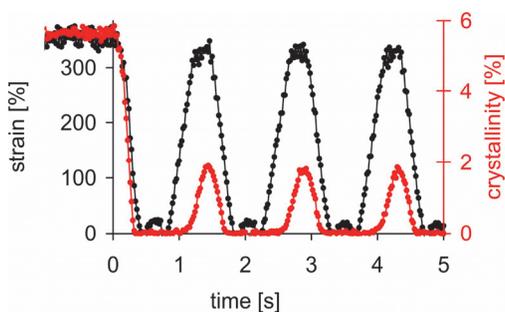


Fig. 3:
Under dynamic loading with ca. 1 Hz ($t > 0$ s), the maximum crystallinity is considerably suppressed as compared to quasistatic conditions ($t < 0$ s), despite the same maximum strain level.

This contribution is an abridged version of the article "Self-reinforcement of rubber: Crystallization under dynamic strain" originally published in the DESY Photon Science Report 2012. [4]

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