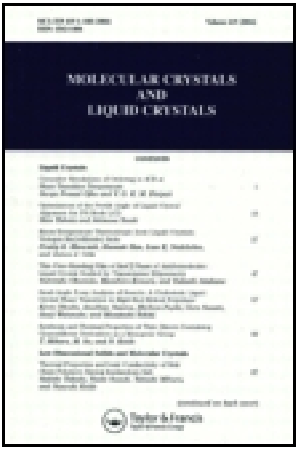

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Status and Trends in the Area of Elastomers and Rubberlike Elasticity

J. E. Mark [a]

[a] Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH, USA

To cite this article: J. E. Mark (2004): Status and Trends in the Area of Elastomers and Rubberlike Elasticity, Molecular Crystals and Liquid Crystals, 417:1, 75-86

To link to this article: http://dx.doi.org/10.1080/15421400490478821

Mol. Cryst. Liq. Cryst., Vol. 417, pp. 75/[559]–86/[570], 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490478821

STATUS AND TRENDS IN THE AREA OF ELASTOMERS AND RUBBERLIKE ELASTICITY

J. E. Mark
Department of Chemistry and the Polymer Research Center,
The University of Cincinnati, Cincinnati, OH 45221-0172, USA

General topics covered in this overview are (i) some new elastomeric polymers, (ii) unusual network structures, (iii) elastomeric composites, (iv) new characterization techniques, (v) theoretical developments, (v) unusual applications, and (vi) societal aspects.

Keywords: bimodal distributions; biosynthesis; elasticity theory; elastomers; environmental concerns; gel collapse; interfaces; mechanical properties; medical applications; model networks; polymer education; recyclability; reinforcement; rubberlike elasticity

ELASTOMERIC POLYMERS

Elastomers with very low melting points can not undergo strain-induced crystallization under normal conditions, and therefore can not benefit from reinforcing effects from the crystallites thus generated. In fact, it is well known that this reinforcement is the origin of the superb mechanical properties of crystallizable elastomers of natural rubber, *cis*-1,4-polybutadiene, and polyisobutylene [1–3]. One goal relevant to this phenomenon is to increase the melting point of an elastomer such as poly(dimethylsiloxane) (PDMS) $[-Si(CH_3)_2O-]$ by increasing the stiffness of the chains. One way of doing this is to put a *meta* or *para* phenylene group in the backbone of the repeat unit [4]. Adding more than one phenylene group in the repeat unit could be of considerable interest because of the various *meta, para* combinations that could presumably be synthesized. Cyclohexylene groups should be less stiff than phenylene groups, and either

It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR-0075198 (Polymers Program, Division of Materials Research), and by the Dow Corning Corporation.

Address correspondence to J. E. Mark, Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH 45221-0172, USA. E-mail: markje@email.uc.edu

meta- or *para*-groups could also be of interest in this approach. It is also possible, of course, to make chains stiffer through the use of bulky side groups.

Another aspect in this area involves "model networks". Elastomers of this type are made by reacting functionally-terminated chains with a multifunctional end-linking agent. Because of this very specific end-linking approach, much more information on the structures of these elastomers is known. For example, the molecular weight between cross links is simply the molecular weight of the chains being end linked, and the distribution of the network chain lengths is that of these precursor chains as well. These elastomers also have unusually good mechanical properties, perhaps because of a reduced number of dangling chains [5,6]. The same synthesis approach has been used to put known numbers of dangling chains of known lengths into intentionally-imperfect networks, to gauge the effects of these irregularities on mechanical properties.

Also of interest are fluorosiloxane elastomers. For example, placing fluorine atoms into siloxane repeat units can be useful for increasing polysiloxane solvent resistance, thermal stability, and surface-active properties [7–9]. There is also an unusual type of elastomer with permanently hydrophilic surfaces obtained by the polymerization of elastomer comonomers in the presence of an amphiphilic block copolymer [10]. This hydrophilicity could be important in applications such as elastomeric implants in the body.

Considerable interest is now focused on developing thermoplastic elastomers that are less expensive than the Kraton® styrene-butadiene-styrene triblock copolymers [11]. The leading candidates are stereochemical copolymers of polypropylene, and chemical copolymers of ethylene and comonomers such as *n*-hexene-1 [12–15].

Another interesting elastomeric material is a type of "*baro*plastic" elastomer which parallels *thermo*plastic elastomers in that a pressure increase gives the desired softening required for processing instead of the usual temperature increase [16].

Some novel elastomers have network chain-length distributions that are bimodal [17], and are obtained by end linking a mixture of very short chains with the much longer chains that are typical of elastomers. The resulting bimodal elastomers have unusually good ultimate mechanical properties, including toughness [18]. This is illustrated by the modulus reciprocal elongation isotherms shown in Figure 1.

Forming networks by cross linking in solution or in a state of deformation has a number of advantages, including the synthesis of elastomers exhibiting less stress relaxation, and stress-strain relationships that are closer to those expected from the simplest molecular theories [5,19,20]. Recent studies on networks cross linked in solution have focused on their unusually

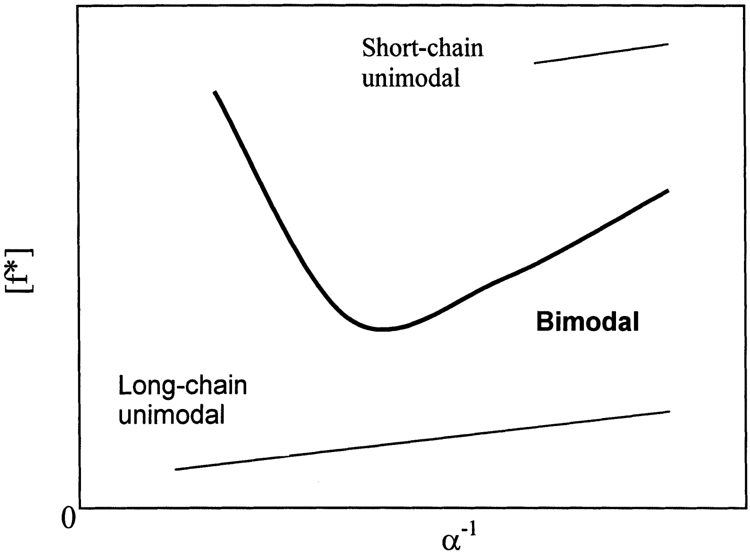

FIGURE 1 Typical Mooney Rivlin plots of modulus against reciprocal elongation for two unimodal networks having either all short chains or all long chains, and a bimodal network having some of both.

high extensibilities [21], and changes in their extents of strain-induced crystallization [22,23].

A relatively new area involves "gel collapse". Gels, which are networks swollen with a diluent, can be brought to the point where only small changes in a variable such as temperature, pH, ionic strength, etc. can bring about an abrupt shrinkage [24–27]. The collapse is illustrated schematically in Figure 2. The shrinkage occurs rapidly enough in fibers and films to be of interest with regard to producing switches, actuators, artificial muscle, and drug-delivery systems.

Some protein bioelastomers are relevant here, for example the elastin occurring in mammals, the resilin in insects, and the abductin in shellfish. Investigations of their properties can be used to obtain insights into cross linking and elastic behavior in general, and is useful in what has been termed "biomimicry" or "bio-inspired design" [4,28–31]. Spider silks have also been under intense investigation [32–37]. There are a number of types of silks spun by a typical spider, with mechanical properties designed for a range of structural purposes. Several of these materials are elastomeric, with one in particular being designed to be unusually "lossy" to better irreversibly absorb impact energies from flying insects [6]. Most relevant in the present context is the possible use of some of Nature's design principles in the preparation of synthetic elastomers with improved properties.

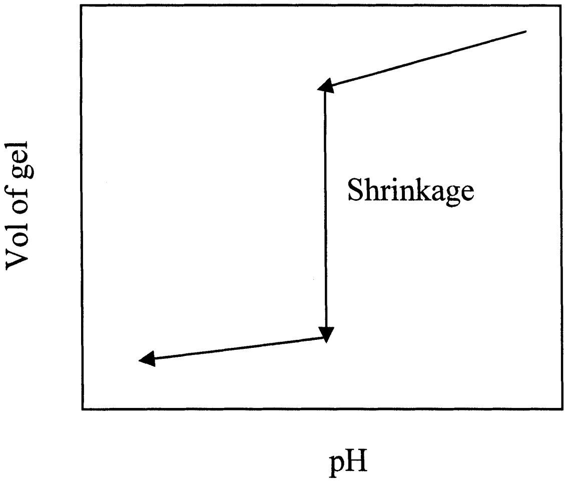

FIGURE 2 A gel exuding solvent ("syneresis") upon change in pH, with the shrinkage representing gel collapse.

ELASTOMERIC COMPOSITES

One novel way of introducing ceramic-like fillers into a polymer is by the *in-situ* hydrolysis and condensation of an organosilicate, organotitanate, organozirconate, etc. to give silica, titania, zirconia, etc. [38]. These "sol-gel" techniques have a number of advantages, including reactions that take place at low temperatures, and the possibility of obtaining good particle dispersions without the usual cumbersome problems of blending a separately prepared, agglomerated filler into a high molecular weight, high viscosity elastomer.

There is also interest in non-spherical filler particles, particularly those with ellipsoidal shapes. In one approach, reinforcing fillers are deformed from their usual approximately spherical shapes in a number of ways. For example, if the particles are a glassy polymer such as polystyrene, then deforming the matrix in which they reside above their glass transition temperature will convert them into ellipsoids. Uniaxial deformations give prolate (needle-shaped) ellipsoids, and biaxial deformations give oblate ellipsoids [39,40]. The nonsymmetrical particles are also oriented in this process, but this constraint can be removed by dissolving away the uncross-linked host polymer and then simply blending the recovered particles into an elastomeric polymer before cross linking it. These two steps are shown schematically in Figure 3. One interest here is the anisotropic reinforcements such particles provide, and there have been simulations to better understand the mechanical properties of such composites [41].

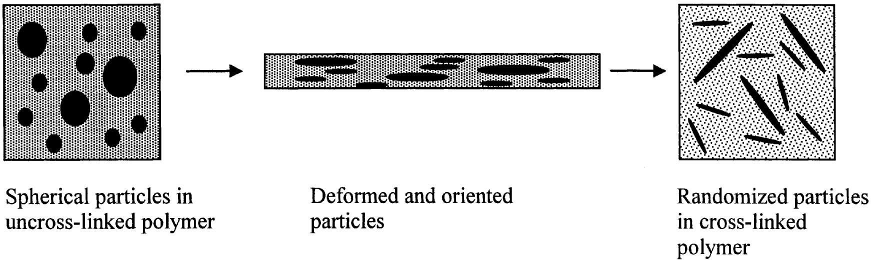

FIGURE 3 Deformation of spherical particles into prolate ellipsoids in a temporary host polymer, followed by removal of the particles and then dispersing them (with random orientations) in another, elastomeric polymer prior to its cross linking.

Exfoliating layered particles such as the clays, mica, and graphite is being used to provide very effective reinforcement of polymers at loading levels much smaller than in the case of solid particles such as carbon black and silica [42–46]. Other properties can also be substantially improved, including increased resistance to solvents, and reduced permeability and flammability.

Also of interest here are polyhedral oligomeric silsesquioxane (POSS) particles. These fillers are cage-like structures, and have been called the smallest possible silica particles. They typically contain between zero and eight organic functional groups per cage. The particles with no functional groups at all can be blended into polymers using the usual mixing or compounding processing, while those with one functional group can be attached to a polymer as side chains. Particles with two functional groups can be incorporated into polymer backbones by copolymerization, and those with more than two can be used for forming cross linked networks [47–51]. Nanotubes are also of considerable interest in this regard [52–54].

Some fillers such as zeolites are sufficiently porous to accommodate monomers, which can then be polymerized. This threads the chains through the cavities, with unusually intimate interactions between the reinforcing phase and the host elastomeric matrix [53]. Because of the constraints imposed by the cavity walls, these confined materials show no glass transition temperatures. The structures involved are illustrated in Figure 4.

The sol-gel technique used to precipitate ceramic-like fillers into an elastomer can also be used to precipitate elastomeric domains into a ceramic [5]. The main goal here is to improve the impact resistance of the resulting composite.

It is also possible to prepare composites with controlled interfaces. By choosing the appropriate chemical structures, chains that span filler

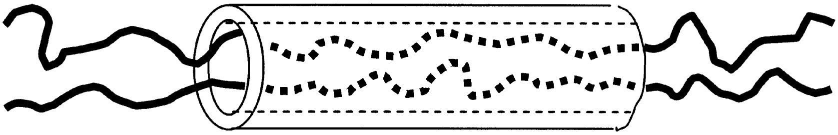

FIGURE 4 Sketch of two polymer chains threading through the cavity of a zeolite.

particles in a polymer-based composite can be designed so that they are either durable, breakable irreversibly, or breakable reversibly [55–57].

NEW CHARACTERIZATION TECHNIQUES

IR spectroscopy and birefringence [58] are being used to get new insights into the network chain orientation necessary for strain-induced crystallization [59]. Also of importance are NMR, small-angle x-ray and neutron scattering, atomic force microscopy, Brillouin scattering [60,61], and pulse propagation measurements [6,60,62]. In the last of these techniques, the delay in pulses passing through an elastomer is used to obtain information on its network structure.

Another type of characterization involves attaching probes to the two ends of a single polymer chain and then stretching it to determine its equilibrium and dynamic mechanical properties. This is generally referred to as "single molecule elasticity" [63–69]. Some rather sophisticated equipment is required, such as "optical tweezers" and sensitive force-measuring devices. Most of the effort thus far has involved biopolymers, and mechanically-induced transitions between their various conformations. Although such studies are obviously not relevant to the many unresolved issues that involve the interactions of chains within an elastomeric network, they are certainly of interest in their own right.

THEORETICAL DEVELOPMENTS

Some of the most interesting advances in rubber elasticity theory are the various approaches being developed to take better account of chain entanglements [5,70]. In the "constraint" theories, the focus is on the way the constraints are placed within the network structure, with some possibilities being illustrated in Figure 5. They correspond to (a) the "constrained junctions" theory, (b) the "constrained chain" theory, (c) the "diffused constraints" theory, and (d) an example of a possible refinement that might be suggested by future experiments.

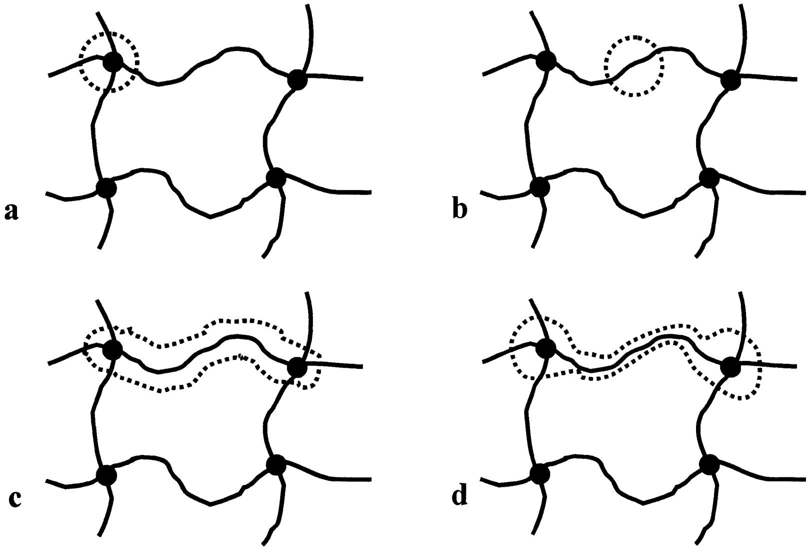

FIGURE 5 Locations of constraints in the constraint theories: (a) at the junctions themselves, (b) at the mass centers of the network chains, (c) spread uniformly along the network chains, and (d) at possibly more refined locations based on future experimental information.

UNUSUAL APPLICATIONS

Elastomeric materials can also be used to improve the mechanical properties of thermosets or thermoplastics, for example by increasing impact resistance. This is analogous to precipitating rubbery phases into a ceramic matrix, as already mentioned. One example in the present approach is to simply blend an elastomeric powder into the host polymer matrix [71,72].

Rubbery polymers have also been used in soft lithography techniques. An image is formed by the room temperature curing of a polymer, and PDMS has been particularly useful in such methods, because of its low viscosity, the ease of end linking it at room temperature, and its great flexibility [73–75].

Numerous medical applications have been developed for elastomeric materials, particularly siloxane polymers because of their relative inertness [76–78]. Prostheses, artificial organs, objects for facial reconstruction, and tubing and catheters, for example, take advantage of the inertness, stability, and pliability of the polysiloxanes. Artificial skin, contact lenses, and drug delivery systems utilize their high permeability as well. There has been considerable interest in modifying elastomeric materials to improve their suitability for biomedical applications in general [79,80].

Advances seem to be coming particularly rapidly in the area of high-tech drug-delivery systems [81,82].

It is ironic that the most striking feature of elastomeric materials, their very high extensibility, is not really exploited in major applications [1]. For example, tires, conveyor belts, seals and gaskets, stretch clothing, catheters and other biomedical devices, and arteries, veins, and various tissues in the body, etc. require only a capacity for relatively small deformations! This is reminiscent of the ability to spin synthetic fibers to almost unlimited lengths, while relatively short fibers are preferred in most applications (fabrics, carpeting, composites, etc.) [83,84].

SOCIETAL ASPECTS

Of interest here are the possible synthesis of elastomers in environmentally-friendly solvents, and the understanding and exploitation of biosynthetic techniques [85]. Another environmental goal is recyclability [86–90]. Other topics much in the news currently are the improvement of safety aspects of tires (with an emphasis on more reliable bonding to tire cords), and better barrier properties in anti-terrorism protective clothing.

Educational topics include curriculum development, and mobile laboratories for elastomer experiments and demonstrations.

REFERENCES

[1] Morton, M. (Ed.), (1987). *Rubber Technology*, Third ed., Van Nostrand Reinhold: New York.

[2] Mark, J. E. (Ed.), (1996). *Physical Properties of Polymers Handbook*, Springer-Verlag: New York.

[3] Mark, J. E. (Ed.), (1999). *Polymer Data Handbook*, Oxford University Press: New York.

[4] Mark J. E. & Erman, B. (1988). *Rubberlike Elasticity*, A Molecular Primer, Wiley-Interscience: New York.

[5] Erman, B. & Mark, J. E. (1997). *Structures and Properties of Rubberlike Networks*, Oxford University Press: New York.

[6] Mark, J. E. (2003). Some unusual elastomers and experiments on rubberlike elasticity. *Prog. Polym. Sci.*, *28*, 000–00.

[7] Bobear, W. J. (1973). Silicone rubber. In: *Rubber Technology*, Morton, M. (Ed.), Van Nostrand Reinhold: New York, 368–406.

[8] Kobayashi, H. & Owen, M. J. (1990). Surface tension of poly[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)methylsiloxane). *Macromolecules*, *23*, 4929–33.

[9] Patwardhan, D. V., Zimmer, H., & Mark, J. E. (1997). Synthesis of some fluorinated phenylmethylsiloxane polymers and characterization of their surface properties. *J. Inorg. Organomet. Polym.*, *7*, 93–109.

[10] Noda, I. (1991). Latex elastomer with a permanently hydrophilic surface. *Nature*, *350*, 143–44.

[11] Mark, J. E. (2003). New developments and directions in the area of elastomers and rubberlike elasticity. *Macromol. Symp.*, Kyoto issue, 000:000.

[12] Brintzinger, H. H., Fischer, D., Mulhaupt, R., Reiger, B., & Waymouth, R. M. (1995). Stereospecific olefin polymerization with chiral metallocene catalysts. *Angew. Chem. Ed. Engl.*, *34*, 1143–70.

[13] Petoff, J. L. M., Agosto, T., Lai, T. K., & Waymouth, R. M. (1998). Elastomeric polypropylenes from unbridged 2-arylindenyl zirconocenes: modeling polymerization behavior using *ansa*-metallocene analogues. *J. Am. Chem. Soc.*, *120*, 11316–22.

[14] Mansel, S., Perez, E., Benavente, R., Perena, J. M., Bello, A., Roll, W., Kirsten, R., Beck, S., & Brintzinger, H.-H. (1999). Synthesis and properties of elastomeric poly(propylene). *Macromol. Chem. Phys.*, *200*, 1292–97.

[15] Lieber, S. & Brintzinger, H.-H. (2000). Propene polymerization with catalyst mixtures containing different *ansa*-zirconocenes: Chain transfer to alkylaluminum cocatalysts and formation of stereoblock polymers. *Macromolecules*, *33*, 9192–99.

[16] Acar, M. H., Gonzales, J. A., & Mayes, A. M. (2002). Synthesis of baroplastic elastomers by atrp. preprints, *American Chemical Society Division of Polymer Chemistry, Inc.*, *43*(2), 55–56.

[17] Mark, J. E. (2003). Elastomers with multimodal distributions of network chain lengths. *Macromol. Symp.*, St. Petersburg issue, *191*, 121–30.

[18] Mark, J. E. (1999). Improved elastomers through control of network chain-length distributions. *Rubber Chem. Technol.*, *72*, 465–83.

[19] Mark, J. E. (2002). Some aspects of rubberlike elasticity useful in teaching basic concepts in physical chemistry. *J. Chem. Educ.*, *79*, 1437–43.

[20] Mark, J. E. (2003). Some recent theory, experiments, and simulations on rubberlike elasticity. *J. Phys. Chem.*, *Part B*, *107*, 903–13.

[21] Kohjiya, S., Urayama, K., & Ikeda, Y. (1997). Poly(siloxane) network of ultra-high elongation. *Kautschuk Gummi Kunstoffe*, *50*, 868–72.

[22] Premachandra, J. & Mark, J. E. (2002). Effects of dilution during cross linking on strain-induced crystallization in *cis*-1,4-polyisoprene networks. 1. Experimental results. *J. Macromol. Sci., Pure Appl. Chem.*, *39*, 287–300.

[23] Premachandra, J., Kumudinie. C., & Mark, J. E. (2002). Effects of dilution during cross linking on strain-induced crystallization in *cis*-1,4-polyisoprene networks. 2. Comparison of experimental results with theory. *J. Macromol. Sci., Pure Appl. Chem.*, *39*, 301–20.

[24] Matsuo, E. S. & Tanaka, T. (1992). Patterns in shrinking gels. *Nature*, *358*, 482–85.

[25] Takemoto, K., Ottenbrite, R. M., & Kamachi, M. (Eds.), (1997). *Functional Monomers and Polymers*, 2nd (Ed.), Marcel Dekker: New York.

[26] Tanabe, Y. (Ed.), (1999). *Macromolecular Science and Engineering*, New Aspects, Springer: New York.

[27] Grinberg, V. Y., Dubovik, A. S., Kuznetsov, D. V., Grinberg, N. V., Grosberg, A. Y., & Tanaka, T. (2000). Studies of the thermal volume transition of poly(*n*-isopropylacrylamide) hydrogels by high-sensitivity differential scanning microcalorimetry. 2. Thermodynamic functions. *Macromolecules*, *33*, 8685–92.

[28] Hoeve, C. A. J. & Flory, P. J. (1958). The elastic properties of elastin. *J. Am. Chem. Soc.*, *80*, 6523–26.

[29] Ross, R. & Bornstein, P. (1971). *Elastin. Sci. Am.*, *224*, 44–50.

[30] Sandberg, L. B., Gray, W. R., & Franzblau, C. (Eds.), (1977). *Elastin and Elastic Tissue*, Plenum: New York.

[31] Andrady, A. L. & Mark, J. E. (1980). Thermoelasticity of swollen elastin networks at constant composition. *Biopolymers*, *19*, 849–55.

[32] Vollrath, F. (1992). Spider webs and silks. *Sci. Am.*, *266*(3), 70–76.

[33] Kaplan, D., Adams, W. W., Farmer, B., & Viney, C. (Eds.), (1994). Silk Polymers. *Materials Science and Biotechnology*, American Chemical Society: Washington, DC Vol. 544.

[34] Gosline, J. M., Nichols, C., Guerette, P., & Cheng, A. (1995). The macromolecular design of spiders' silks. In: *Biomimetics: Design and Processing of Materials Woodbury*, Sarikaya, M. & Aksay, I. A., (Eds.), American Institute of Physics Press: NY, 237–61.

[35] Simmons, A. H., Michal, C. A., & Jedlinski, L. W. (1996). Molecular orientation and two-component nature of the crystalline fraction of spider dragline silk. *Science*, *271*, 84–87.

[36] Termonia, Y. (1996). Molecular mechanism of high strength and stretch of spider dragline. *Macromol. Symp.*, *102*, 159–63.

[37] Shao, Z. & Vollrath, F. (2002). Surprising strength of silkworn silk. *Nature*, *418*, 741–41.

[38] Mark, J. E. (2003). The rubber elastic state. In: *Physical Properties of Polymers*: Third edition, Mark, J. E., Eisenberg, A., Graessley W. W., Mandelkern, L., Samulski, E. T., Koenig, J. L., & Wignall, G. D. (Eds.), Cambridge University Press: Cambridge, 000–00.

[39] Wang, S. & Mark, J. E. (1990). Generation of glassy ellipsoidal particles within an elastomer by in-situ polymerization, elongation at an elevated temperature, and finally cooling under strain. *Macromolecules*, *23*, 4288–91.

[40] Wang, S., Xu, P., & Mark, J. E. (1991). Method for generating oriented oblate ellipsoidal particles in an elastomer and characterization of the reinforcement they provide. *Macromolecules*, *24*, 6037–39.

[41] Sharaf, M. A., Kloczkowski, A., & Mark, J. E. (2002). Monte Carlo simulations on filler-induced network chain deformations and elastomer reinforcement from oriented oblate particles. *Polymer*, *43*, 643–52.

[42] Giannelis, E. P., Krishnamoorti, R., & Manias, E. (1999). Polymer-silicate nanocomposites: model systems for confined polymers and polymer brushes. *Adv. Polym. Sci.*, *138*, 107–47.

[43] Vaia, R. A. & Giannelis, E. P. (2001). Polymer nanocomposites: status and opportunities. *MRS Bull*, *26*(5), 394–401.

[44] Pinnavaia, T. J. & Beall, G. (Eds.), 2001. *Polymer-Clay Nanocomposites*, Wiley: New York.

[45] Vu, Y. T., Mark, J. E., Pham, L. H., & Engelhardt, M. (2001). Clay nanolayer reinforcement of cis-1,4-polyisoprene and epoxidized natural rubber. *J. Appl. Polym. Sci.*, *82*, 1391–403.

[46] Zhou, W., Mark, J. E., Unroe, M. R., & Arnold, F. E. (2001). Some clay nanocomposites based on a high-temperature, high-performance polymer. *J. Macromol. Sci. – Pure Appl. Chem.*, *A38*, 1–9.

[47] Lichtenhan, J. D., Schwab, J., & Reinerth, W. A. (2001). Sr.: Nanostructured chemicals. *A new era in chemical technology. Chem. Innov.*, *31*, 3–5.

[48] Laine, R. M., Choi, J., & Lee, I. (2001). Organic/inorganic nanocomposites with completely defined interfacial interactions. *Adv. Mats.*, *13*, 800–03.

[49] Loy, D. A., Baugher, C. R., Schnieder, D. A., Sanchez, A., & Gonzalez, F. (2001). Sol-gel chemistry of 3-isocyanatopropyltriethoxysilane. *Polym. Preprints*, *42*(1), 180–81.

[50] Shea, K. J. & Loy, D. A. (2001). Bridged polysilsesquioxanes: Molecular engineering of hybrid organic-inorganic materials. *MRS Bull*, *26*, 368–75.

[51] Haddad, T. S., Lee, A., & Phillips, S. H. (2001). Poly(dimethylsiloxanes) modified with inorganic polyhedra. *Polym. Preprints*, *42*(1), 88–89.

[52] Nakamura, H. & Matsui, Y. (1995). Silica gel nanotubes obtained by the sol-gel method. *J. Am. Chem. Soc.*, *117*, 2651–52.

[53] Frisch, H. L. & Mark, J. E. (1996). Nanocomposites prepared by threading polymer chains through zeolites, mesoporous silica, or silica nanotubes. *Chem. Mater.*, *8*, 1735–38.

[54] Tans, S. J., Devoret, M. H., Dai, H., Thess, A., Smalley, R. E., Geerligs, L. J., & Dekker, C. (1997). Individual single-wall carbon nanotubes as quantum wires. *Nature*, *386*, 474–77.

[55] Vu, B. T. N., Mark, J. E., & Schaefer, D. W. (2000). Surface modification of silica fillers formed in-situ for the reinforcement of polydimethylsiloxane networks. Preprints,

American Chemical Society Division of Polymeric Materials: *Science and Engineering*, *83*, 411–12.

[56] Vu, B. T. N. M. S. (2001). Thesis in Chemistry, University of Cincinnati.

[57] Schaefer, D. W., Vu, B. T. N., & Mark, J. E. (2002). The effect of interphase coupling on the structure and mechanical properties of silica-siloxane composites. *Rubber Chem. Technol.*, *75*, 795–810.

[58] Bokobza, L. & Nugay, N. (2001). Orientational effects of mica in fumed silica reinforced composites. *J. Appl. Polym. Sci.*, *81*, 215–22.

[59] Allcock, H. R., Lampe, F. W., & Mark, J. E. (2003). *Contemporary Polymer Chemistry*, Third edition. Englewood Cliffs, Prentice Hall: NJ.

[60] Sinha, M. Ph. D. (2000). Thesis in Physics, University of Cincinnati.

[61] Sinha, M., Mark, J. E., Jackson, H. E., & Walton, D. (2002). A brillouin scattering study of end-linked poly(dimethylsiloxane) networks. *J. Chem. Phys.*, *117*, 2968–74.

[62] Sinha, M., Erman, B., Mark, J. E., Ridgway, T. H., & Jackson, H. E. Pulse propagation in poly(dimethylsiloxane) networks. Macromolecules, submitted.

[63] Chu, S. (1994). Laser manipulation of atoms and particles. *Science*, *253*, 861–66.

[64] Smith, S. B., Cui, Y., & Bustamante, C. (1996). Overstretching b-DNA: The elastic response of individual double-stranded and single-stranded DNA molecules. *Science*, *271*, 795–99.

[65] Li, H., Rief, M., Oesterhelt, F., & Gaub, H. E. (1998). Single-molecule force spectroscopy on xanthan by AFM. *Adv. Mater*, *3*, 316–19.

[66] Ortiz, C. & Hadziioannou, G. (1999). Entropic elasticity of single polymer chains of poly(methacrylic acid) measured by atomic force microscopy. *Macromolecules*, *32*, 780–87.

[67] Janshoff, A., Neitzert, M., Oberdorfer, Y., & Fuchs, H. (2000). Force spectroscopy of molecular systems – single molecule spectroscopy of polymers and biomolecules. *Angew. Chem. Int. Ed.*, *39*, 3213–37.

[68] Hugel, T. & Seitz, M. (2001). The study of molecular interactions by AFM force spectroscopy. *Makromol. Rapid Commun.*, *22*, 989–1016.

[69] Onoa, B., Dumont, S., Liphardt, J., Smith, S. B., Tinoco, I. Jr., & Bustamante, C. (2003). Identifying kinetic barriers to mechanical unfolding of the t. Thermophila ribozyme. *Science*, 1892–95.

[70] Rubinstein, M. & Panyukov, S. (2002). Elasticity of polymer networks. *Macromolecules*, *35*, 6670–86.

[71] Perry, R. J. (1999). Applications for cross-linked siloxane particles. ChemTech, *29*(2), 39–44.

[72] Liles, D. T., Morita, Y., & Kobayashi, K. (2002). Silicone elastomeric powders. *Polym. News*, *27*, 406–11.

[73] Kumar, A., Abbott, N. L., Kim, E., Biebuyck, H. S., & Whitesides, G. M. (1995). Patterned self-assembled monolayers and meso-scale phenomena. *Acct. Chem. Res.*, *28*, 219–26.

[74] Whitesides, G. M. (2002). Organic materials science. *MRS Bull*, *27*(1), 56–65.

[75] Paul, K. E., Prentiss, M., & Whitesides, G. M. (2003). Patterning spherical surfaces at the two-hundred-nanometer scale using soft lithography. *Adv. Functional Mater*, *13*, 259.

[76] Warrick, E. L., Pierce, O. R., Polmanteer, K. E., & Saam, J. C. (1979). Silicone elastomer developments. *Rubber Chem. Technol.*, *52*, 437–525.

[77] Arkles, B. (1983). Look what you can make out of silicones. ChemTech, *13*, 542–55.

[78] Rochow, E. G. (1987). *Silicon and Silicones*, Berlin: Springer-Verlag.

[79] Abbasi, F., Mirzadeh, H., & Katbab, A.-A. (2001). Modification of polysiloxane polymers for biomedical applications: A review. *Polym. Int.*, *50*, 1279–87.

[80] Gao, Z., Nahrup, J. S., Mark, J. E., & Sakr, A. Poly(dimethylsiloxane) coatings for controlled drug release. I. preparation and characterization of pharmaceutically acceptable materials. *J. Appl. Polym. Sci.*, *89*, 000–00.

[81] Langer, R. (2003). Where a pill won't reach. *Sci. Am.*, *288*(4), 50–57.

[82] Fischetti, M. (2003). Potent patches. *Sci. Am.*, *288*(4), 92–93.

[83] Rodriguez, F. (1982). *Principles of Polymer Engineering*. 2nd ed., McGraw-Hill: New York.

[84] Fried, J. R. (1995). *Polymer Science and Technology*. Englewood Cliffs, Prentice Hall: NJ.

[85] Koyama, T. & Steinbuchel, A. (Eds.), (2001). *Biopolymers*, *Polyisoprenoids*, Wiley-VCH: New York, Vol. 2.

[86] Isayev, A. I., Kim, S. H., & Levin, V. Y. (1997). Superior mechanical properties of reclaimed SBR with bimodal network. *Rubber Chem. Technol.*, *70*, 194–201.

[87] Shim, S. E., Isayev, A. I., & von Meerwall, E. (2003). Molecular mobility of ultrasonically devulcanized silica-filled poly(dimethylsiloxane). *J. Polym. Sci., Polym. Phys.*, *41*, 454–65.

[88] Shim, S. E. & Isayev, A. I. (2001). Ultrasonic devulcanization of precipitated silica-filled silicone rubber. *Rubber Chem. Technol.*, *74*, 303–16.

[89] Shim, S. E., Parr, J. C., von Meerwall, E., & Isayev, A. I. (2003). Nmr relaxation and pulsed gradient nmr diffusion measurements of ultrasonically devulcanized poly(dimethylsiloxane). *J. Phys. Chem. B*, *106*, 12072–78.

[90] Shim, S. E. & Isayev, A. I. (2003). Effects of the presence of water on ultrasonic devulcanization of polydimethylsiloxane. *J. Appl. Polym. Sci.*, *88*, 2630–38.