Predicting the Modulus of End-linked Networks from Formation Conditions

R.F.T. Stepto, J.I. Cail, D.J.R. Taylor*

Polymer Science and Technology Group, Manchester Materials Science Centre, UMIST and University of Manchester, Grosvenor Street, Manchester, M1 7HS, UK

Summary: The application of a Monte-Carlo (MC) algorithm to account fully for loop formation in $RA_2 + R'B_3$ and $RA_2 + R'B_4$ polymerizations is described. The resulting interpretation of experimental elastic moduli of HDI-based polyurethane networks prepared at different dilutions shows it is essential to account for elastic losses in loop structures of all sizes. An important parameter, x, is introduced, namely the average fractional loss of elasticity per larger loop structure relative to the loss per smallest loop structure. Values of x vary between 0.50 and 0.60. Subsequent application of the MC calculations to the formation and resulting structures of MDI-based polyurethane networks and poly(dimethyl siloxane) networks again predicts significant reductions in modulus due to loop structures. However, comparison with experimental modulus data shows that the reductions in modulus due to loops are outweighed by increases due to chain interactions and to topological entanglements.

Keywords: end-linked networks; intramolecular reaction; MDI-based polyurethane networks; Monte-Carlo (MC) algorithm; polymerization

Introduction

Relationships between concentrations of chains and junction points that assume perfect network structures are often used when interpreting elastic properties of end-linked networks.[1] The assumption is rarely true and deviations from perfect network structures may be due to chain topological entanglements and interactions,[2-4] to side reactions, incomplete reaction in end-linking polymerizations (giving loose ends)[5,6] and, more fundamentally and generally, inelastic chain or loop formation due to the intramolecular reaction of pairs of groups.[4,7] Hence, to understand and predict elastomeric properties, it is necessary to be able to model, statistically, the molecular growth leading to network formation. Further, by considering polymerizations at various dilutions of reactive groups, it is possible to evaluate the effects of loop formation resulting from intramolecular reaction.

 DOI: 10.1002/masy.200351027

Intramolecular Reaction

A useful measure of the propensity for intramolecular reaction in an RA_{fa} + $R'B_{fb}$ polymerization at a given ratio of reactants is λ_{a0} , where

$$\lambda_{a0} = P_{ab} / c_{a0}. \quad (1)$$

c_{a0} is the initial concentration of A-groups, characterizing the concentration of groups for intermolecular reaction, and P_{ab} characterizes intramolecular reaction.[7]

$$P_{ab} = (3/2\pi < r^2 >)^{3/2} / N_{Av}. \quad (2)$$

It is the mutual concentration of A- and B-groups at the ends of the shortest sub-chain, of root-mean-square end-to-end distance $<r^2>^{1/2}$, that can react intramolecularly, assuming that the end-to-end distance distribution can be represented by a Gaussian function. λ_{a0} captures the combined effects of reactant structures and reactive-group concentrations on intramolecular reaction.

Monte-Carlo Polymerization Algorithm

Detailed characterization of the connectivity, or topology of networks by experimental means is impossible. In order to investigate the effects of network topology on elastomeric properties one must use numerical simulations of the network-forming polymerizations. In such simulations, it is important to account correctly for the formation of loop structures of various sizes resulting from intramolecular reaction. To this end, a Monte-Carlo (MC) nonlinear polymerization algorithm has been developed[8-10] for self-polymerizations (RA_f), and two-monomer polymerizations of the general type RA_{fa} + $R'B_{fb}$. All the molecular connections are recorded as a function of extent of reaction of A- or B-groups, along with the calculated sol and gel fractions, and average degrees of polymerization. Ring-size distributions are found to be very broad.

Correlation of Model Network Topologies and Measured Network Moduli[8-10]

For a trifunctional network, each smallest loop structure renders three chains inelastic, but larger loops are subject only to partial losses in elasticity. These considerations lead to the expressions for the modulus, relative to that of the perfect network structure,

$$G^o / G = M_c / M_c^o = 1/(1-6p_{re,1} - x \cdot 6p_{re,i>1}) = 1/((1-x)(1-6p_{re,1})), \qquad (3)$$

where G^o is the modulus of the (unswollen) perfect network, G is that of the actual network, M_c is the average molar mass of elastically active chains connecting pairs of junction points in the actual network and M_c^o is that in the perfect network. $p_{re,1}$ is the extent of reaction (at complete reaction) leading to smallest loops, $p_{re,i>1}$ is the extent of reaction leading to larger loops, and $p_{re,1} + p_{re,i>1} = 1/6$.[11] x is the average fractional loss of elasticity for chains in loop structures larger than the smallest. A similar expression exists for tetrafunctional network structures. They lose only 2 elastic chains per smallest loop and

$$G^o / G = M_c / M_c^o = 1/(1-4p_{re,1} - x \cdot 4p_{re,i>1}) = 1/((1-x)(1-4p_{re,1})), \qquad (4)$$

with $p_{re,1} + p_{re,i>1} = 1/4$.

HDI-Based Polyurethane Networks

Estimates of x can be made using experimentally determined values of M_c / M_c^o. This has been done for polyurethane (PU) networks based on hexamethylene diisocyanate (HDI) reacting with polyoxypropylene (POP) triols and tetrols. The results, for six series of networks prepared in bulk and at various dilutions in solvent, are shown in Figure 1. The theoretical curves have been

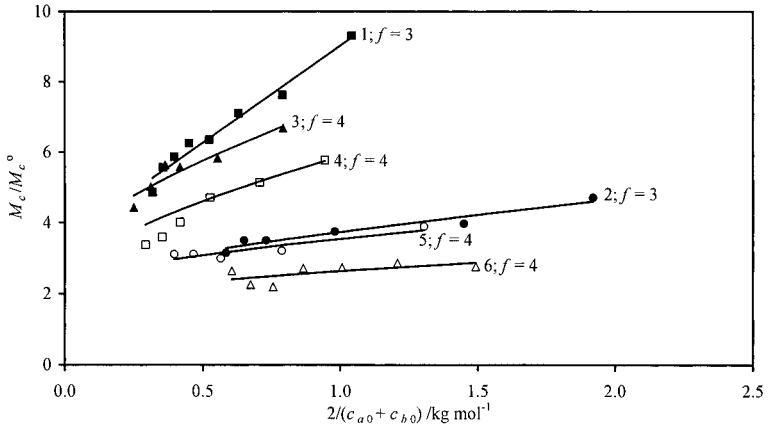

Fig. 1. Experimental and calculated values of M_c / M_c^o at complete reaction as functions of the average initial dilution of reactive groups, $2/(c_{a0}+c_{b0})$, for six series of PU networks from stoichiometric reaction mixtures. 1,2: trifunctional networks from polyoxpropylene (POP) triols of different molar masses and hexamethylene diisocyanate (HDI). 3-6: tetrafunctional networks from POP tetrols and HDI.

fitted by choosing least-squares values of the ring forming parameter, P_{ab} and x in conjunction with eqs 3 and 4. In this respect, it should be noted that, because $p_{re,1}$ and $p_{re>1}$ depend on λ_{a0}, which is directly proportional to P_{ab} (eq 1), M_c / M_c^o depends on P_{ab} as well as on x. The values of x deduced for the six reaction systems of Figure 1 are plotted in Figure 2 versus P_{ab}. Because both chain entropy and P_{ab} are related directly to $<r^2>$, it is assumed that x versus P_{ab} is a universal function for given functionalities of reactants. Thus, the plots in Figure 2 can be used in predictions of reductions in modulus for networks formed from other stoichiometric $RA_2 + R'B_3$ and $RA_2 + R'B_4$ systems.

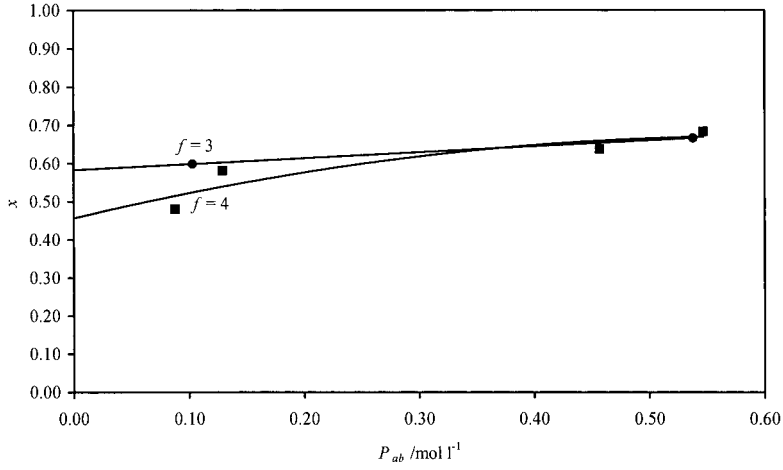

Fig. 2. x versus P_{ab}, corresponding to the theoretical curves in Figure 1.

MDI-Based Polyurethane Networks

Figure 3 shows the results in Figure 1 together with those for series of PU networks based on diphenylmethane diisocyanate (MDI) reacting with the same POP triol (LHT240) as used in the HDI-based PU networks of system 1. A value of $M_c / M_c^o = 1$ would signify a perfect network behaving affinely (expected at the small deformations used in the determinations of G). It can be seen that the networks containing the stiffer MDI-based chains experimentally show markedly less defects than those containing HDI-based chains. However, the increases in M_c / M_c^o with dilution shows that loop defects are present in both types of system.

Analysis, according to Ahmed-Rolfes-Stepto (ARS) theory,[14] of the extents of reaction at gelation[12] of the polymerizations used to prepare the networks of system 7 enables effective

values of λ_{a0} to be found. From these and eq 1 one finds that P_{ab} = 0.175 mol l^{-1} characterizes system 7. This value is used to determine x (from Figure 2) and values of $p_{re,1}$ are found from λ_{a0} and the MC polymerization algorithm. Use of eqs 3 and 4 then allows calculation of the values of M_c / M_c^o for the MDI-based networks, resulting in the line denoted "MDI fitted" in Figure 3.

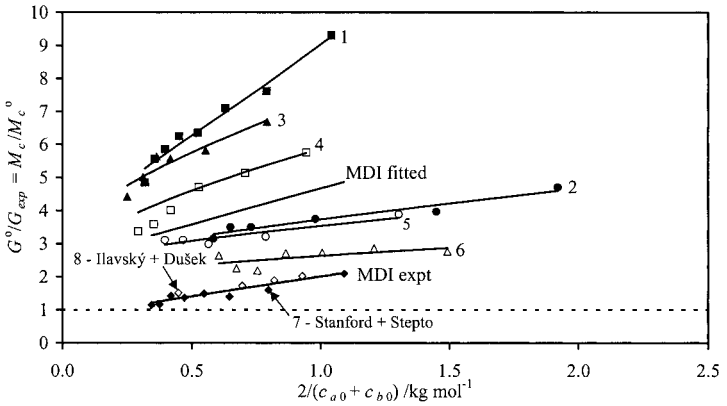

Fig. 3. Experimental and calculated values of M_c / M_c^o at complete reaction as functions of initial dilution for the HDI-based networks 1-6 of Figure 1 and MDI-based networks formed using the same POP triol as used in system 1. MDI expt; experimental values derived from 7. Stanford and Stepto[12] and 8. Ilavsky and Dusek.[13] MDI fitted; calculated values derived using the appropriate values of P_{ab} and x (see text).

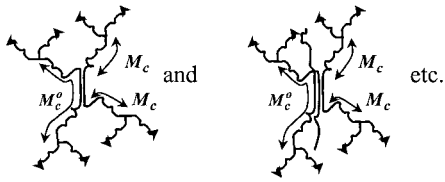

Fig. 4. Illustrating the reduction of M_c to M_c^o through incipient segmentation.

It can be seen that the experimental values of M_c / M_c^o for the MDI-based networks are much lower than those expected. Indeed, the ratio of the ordinates of the "MDI fitted" and "MDI expt" lines, $(M_c / M_c^o)_{fitted} / (M_{c,expt} / M_c^o) = 2.61$, is the factor by which chain interactions (incipient segmentation) based on the MDI units increases the moduli above those expected for networks of realistic (as distinct from tree-like) connectivity.

The factor of 2.61 can be further interpreted,[4] as illustrated in Figure 4. The segmented sections (based around the MDI unit and its associated urethane groups) have a molar mass of 284 g mol^{-1}. Thus, taking an average value of M_c^o of 755 g mol^{-1} for systems 7 and 8, the two elastic chains formed from one chain of molar mass M_c^o have a molar mass of (755 - 284)/2 = 235 g mol^{-1} or $M_c^o/3.2$. Thus, if a fraction q of the chains of molar mass M_c^o interact, with each interaction creating two chains of molar mass $M_c^o/3.2$, the relative decrease in effective molar mass between junction points

$$\frac{M_c}{M_c^o} = \frac{(1-q)+(2q/3.2)}{(1-q)+2q} = \frac{1-0.375q}{1+q} \approx \frac{M_{c,expt}}{M_{c,fitted}} = \frac{1}{2.61} \qquad (5)$$

The penultimate approximate equality indicates that the same reduction factor of 3.2 may be applied as a first approximation to the actual MDI-based networks, giving q = 0.81. In other words, on average, about 80% of the elastic chains in the actual networks are interacting with other chains at one of their MDI units to create two, shorter elastic chains.

Poly(dimethyl siloxane) Networks

We now consider networks formed from linear poly(dimethyl siloxane) (PDMS) chains of various molar masses using a trifunctional and a tetrafunctional endlinker. The systems chosen first have been used previously for a gel-point investigation.[15] From the known molar masses, endlinker functionality and chain statistics of a pair of reactants, P_{ab} can be calculated. Distinct from PU-forming polymerizations,[16] calculated gel points on the basis of ARS theory and values of P_{ab} given by chain conformational statistics are, for PDMS-forming polymerizations, consistent with experimental gel points. The appropriate value of x can be found from Figure 2, and values of $p_{re,1}$ as functions of λ_{a0} can be found from the MC polymerization algorithm. Hence, curves of $G^o/G = M_c/M_c^o$ versus λ_{a0} can be constructed using eqs 3 and 4, as shown in Figure 5.

The predicted reductions in modulus are large and must be accounted for when interpreting measured moduli. Significantly, the trifunctional and tetrafunctional systems give distinct curves and, amongst the tetrafunctional systems, there is little sensitivity to reactant molar masses or P_{ab}, showing that x does not vary much over the systems chosen.

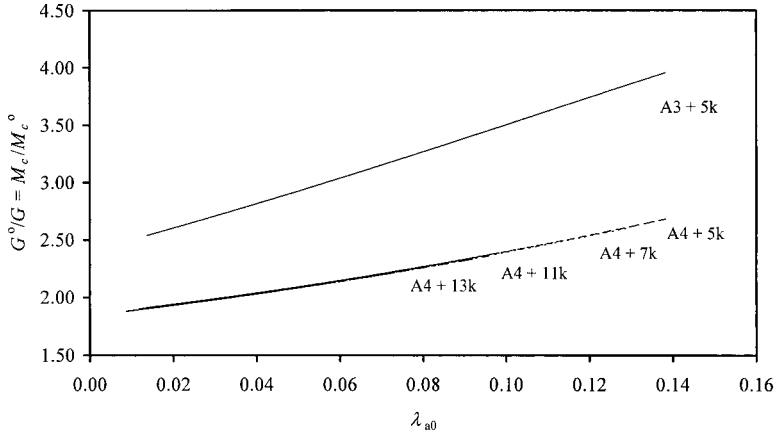

Fig. 5. Predicted reductions in modulus as a function of ring-forming parameter λ_{a0}. Networks prepared from linear PDMS fractions 5k, 7k, 11k, 13k (of nominal molar masses 5000 g mol^{-1}, 7000 g mol^{-1}, 11000 g mol^{-1} and 13000 g mol^{-1}) reacting with a trifunctional endlinker (A3) and a tetrafunctional endlinker (A4). Details of the reactants are given in reference 15.

The present calculations can be used to reconcile the measurements of Llorente and Mark[17] for the moduli of stoichiometric PDMS networks prepared at different volume fractions of diluent (D) with the occurrence of entanglements in PDMS melts as characterized, for example, by Fetters *et al.*[18] Through eq 1 and knowledge of c_{a0}, the axis in λ_{a0} may be transformed to one in dilution (c_{a0}^{-1}), for reactions diluted with solvent. For linear reactant RA_2 reacting with end-linker $R'B_f$ the equation is

$$\lambda_{a0} = \left(\frac{M_{A2}}{2} + \frac{M_{Bf}}{f} \right) \frac{P_{ab}}{\rho} \cdot \frac{1}{1-D} \qquad (6)$$

where ρ is the assumed uniform density of the reactants. The experimental results of Llorente and Mark[17] in Figures 6(a) and 6(b) show essentially constant values of M_c / M_c^o over a range of dilutions. As can be seen in Figure 7, the plots in Figure 5 also transform into nearly horizontal plots when D is used as abscissa. However, because of entanglements, the experimental values of M_c / M_c^o of 0.903 for $f = 3$ and 0.705 for $f = 4$ from Figure 6 are less than the predicted values that account only for loops.

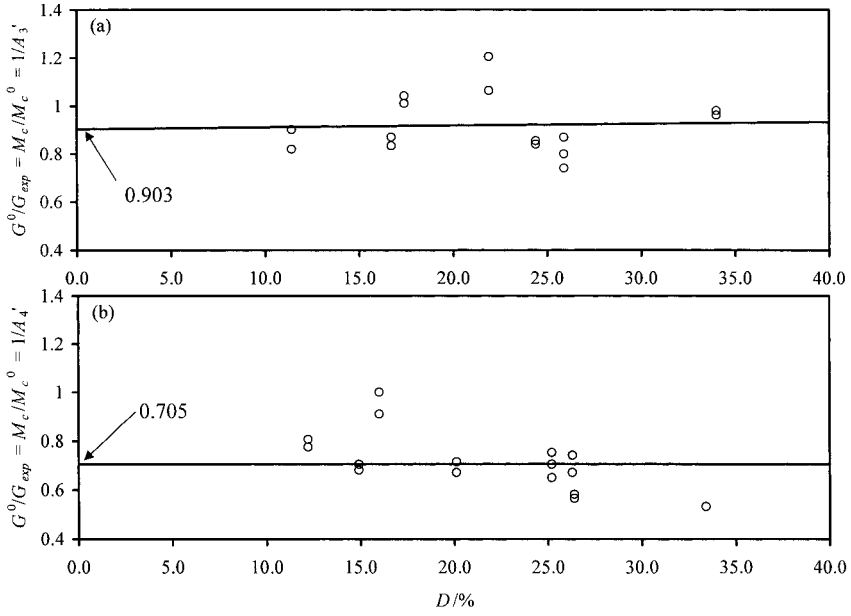

Fig. 6. $G^o/G = M_c/M_c^o = 1/A'_f$ versus dilution of preparation (D) for PDMS networks from stoichiometric polymerization using a siloxane diluent. Data of Llorente and Mark.[17] (a) RA_2 + $R'B_3$ and (b) RA_2 + $R'B_4$ polymerizations. For an explanation of the symbols A'_3 and A'_4 see reference 17.

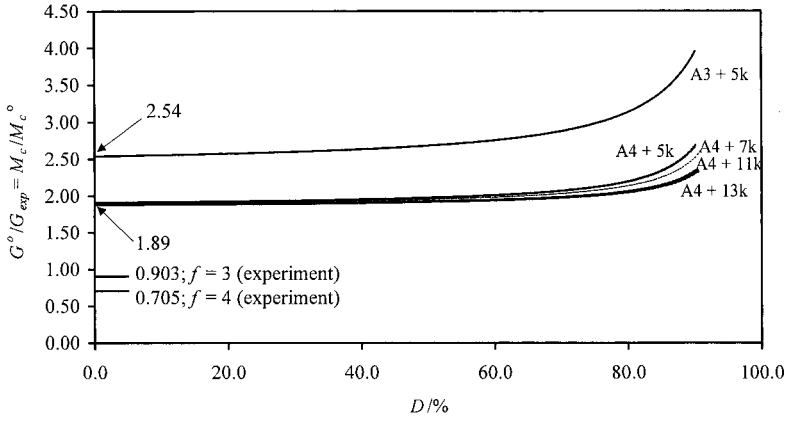

Fig. 7. Predicted (from Figure 5) and experimental modulus reductions for PDMS networks.

A reconciliation of experimental and predicted values of M_c / M_c^o is possible. M_c^o = 18500 g mol^{-1} for the systems studied. Hence, $M_{c,expt}$/g mol^{-1} = 0.903 × 18500 = 16706 for f = 3 networks and $M_{c,expt}$/g mol^{-1} = 0.705 × 18500 = 13043 for f = 4 networks. Both of these values are somewhat greater than the value of 12000 g mol^{-1} for the entanglement molar mass (M_e) in linear PDMS.[18] Accounting for loop structures, without entanglements one would expect $M_{c,chemical}$ = 2.54 × 18500 = 46990 for f = 3 networks and $M_{c,chemical}$ = 1.89 × 18500 = 34965 for f = 4 networks. Thus, $M_{c,chemical} / M_{c,expt}$ = 46990/16706 = 2.54/0.903 = 2.81 for f = 3 networks defines the factor by which $M_{c,chemical}$ is reduced due to entanglements. For f = 4 networks $M_{c,chemical} / M_{c,expt}$ = 34965/13043 = 1.89/0.705 = 2.68. As illustrated in Figure 8, one may consider that the average number of entanglements per equivalent linear chain between junctions of the actual networks is 2.81 - 1 = 1.81 for f = 3 networks and 2.68 - 1 = 1.68 for f = 4 networks.

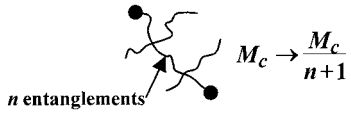

Fig. 8. Illustrating the relationship between M_c and the average number of entanglements per equivalent linear chain in PDMS networks.

Conclusions

The present paper shows the importance of accounting fully for loop formation when interpreting the absolute values of the moduli of networks. Further, it is important to study networks formed at different initial dilutions of reactive groups. Even for reactants of high molar mass, the effects of loops on elastic modulus are significant. Model networks are *never* perfect networks and the effects of loops have to be considered, alongside those of loose ends and entanglements, when interpreting modulus. For PU networks based on HDI and POP polyols, the effects of loops are dominant. For PU networks based on MDI and POP polyols, the effects of loops are present but are counteracted by increases in modulus due to chain interactions. For PDMS networks, using a linear reactant of molar mass greater than M_e, the reductions in modulus due to loops are significant, but are outweighed by those due to entanglements.

Acknowledgements

Support of the EPSRC for grant GR/L/66649 and MSI for provision of their Polymer Software is gratefully acknowledged.

[1] J.E. Mark, B. Erman, in: *Polymer Networks – Principles of Their Formation, Structure and Properties*, R.F.T. Stepto, Ed., Blackie Academic & Professional, London,1998, Chap. 7.
[2] W.W. Graessley, *Adv. Polymer Sci.* **1974**, *16*, 1.
[3] O. Kramer, in: *Elastomeric Polymer Networks*, J.E. Mark, B. Erman, Eds., Prentice Hall, Englewood Cliffs, NJ, 1992, Chap. 17.
[4] R.F.T. Stepto, B.E. Eichinger, in: *Elastomeric Polymer Networks*, J.E. Mark, B. Erman, Eds., Prentice Hall, Englewood Cliffs, New Jersey, 1992, chap. 18.
[5] M. Gottlieb, C.W. Macosko, G.S. Benjamin, K.O. Meyers, E.W. Merrill, *Macromolecules* **1981**, *14*, 1039.
[6] C.W. Macosko, J.C. Saam, *Polymer. Prepr., Div. Polymer Chem., Amer. Chem. Soc.* **1985**, *26*, 48.
[7] R.F.T. Stepto, in: *Polymer Networks – Principles of Their Formation, Structure and Properties*, R.F.T. Stepto, Ed., Blackie Academic & Professional, London, 1998, Chap. 2.
[8] R.F.T. Stepto, D.J.R. Taylor, in *Cyclic Polymers 2nd edition*, J.A. Semlyen, Ed., Kluwer Acadenic Publishers, Dordrecht, 2000, Chap.15.
[9] S. Dutton, R.F.T. Stepto, D.J.R. Taylor, *Angew. Makromol. Chem.* **1996**, *240*, 39.
[10] R.F.T. Stepto, J.I. Cail, D.J.R. Taylor, *Polimery* **2000**, *XLV*, 455.
[11] R.F.T. Stepto, *Polym. Bull. (Berlin)* **1990**, *24*, 53.
[12] J.L. Stanford, R.F.T. Stepto, in: *Elastomers and Rubber Elasticity, Amer. Chem. Soc. Symp. Series 193*. J.E. Mark, J. Lal, Eds. Amer. Chem. Soc., Washington DC 1982, Chap. 20.
[13] M. Ilavsky, K. Dusek, *Macromolecules* **1986**, *9*, 2139.
[14] H. Rolfes, R.F.T. Stepto, *Makromol. Chem., Macromol. Symp.* **1993**, *76*, 1.
[15] R.F.T. Stepto, D.J.R. Taylor, T. Partchuk, M. Gottlieb, in: *ACS Symposium Series 729, Silicones and Silicone-Modified Materials*, S.J. Clarson, J.J. Fitzgerald M.J. Owen, M.D. Smith, Eds., Amer. Chem. Soc., Washington DC 2000, Chap. 12.
[16] J.I. Cail, R.F.T. Stepto, D.J.R. Taylor, *Macromol. Symp.* **2001**, *171*, 19.
[17] M.A. Llorente, J.E. Mark, *J. Chem. Phys.* **1979**, *71*, 682.
[18] L.J. Fetters, D.J. Lohse, S.T. Milner, W.W. Graessley, *Macromolecules* **1999**, *32*, 6847.