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Abstract

**STUDIES OF THE STRUCTURE AND ELASTICITY
OF POLYURETHANE NETWORKS**

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Techniques to generate Monte Carlo samples of polymer chains based on the rotational isomeric state (RIS) theory have been developed. The distribution functions of Monte Carlo chains for polymethylene (PM) and polydimethylsiloxane (PDMS) have been calculated. Good agreement with the previous work of Mark and Curro is found.

The polyurethane networks formed from α , ω -dihydroxy polyoxyethylene (POE) with plurifunctional isocyanate at various initial polymer volume fractions v_{2c} have been simulated. Monte Carlo samples of chains based on RIS statistics have been constructed, which yield networks comparable to those based on Gaussian statistics. A detailed study of various types of network imperfections and cycle ranks of the networks is reported. Computer simulation shows that, at a given sol fraction w_s , the Miller-Macosko theory underestimates the extent of reaction by as much as 3.2 – 8.5%. Moduli are calculated according to the phantom network model, and very good agreement with experiment is

found for networks prepared with low molecular weight polymer and with high molecular weight polymer crosslinked at high dilution.

Model urethane networks prepared from polyoxypropylene (POP) tetrols and hexamethylene diisocyanate (HDI) have been studied with the aid of the computer. Good agreement with experiment is found for gel points when the crosslinkers are treated as sticks. The simulation-theory moduli for the phantom model show good agreement with experiments for networks prepared with $M_n = 1,242$ in the bulk and at various dilutions, or with $M_n = 2,104$ in the bulk. Simulations underestimate moduli for networks prepared from $M_n = 2,104$ at various dilutions.

The third system studied is that of polyoxypropylene (POP) triol based urethane networks. Simulations show that cyclic molecules are present in substantial amounts, in the sol fraction, when the stoichiometric ratio $r_s \sim 1.0$. Simulations also show that the fractions of loops are much higher than those obtained from theory. The population of loops is dependent on both molecular weight and dilution as well as stoichiometric ratio. The proportion of dangling ends is independent of molecular weight and dilution, but depends upon r_s . It is found that, for $r_s \sim 0.8 - \sim 1.0$, the simulations underestimate moduli, but they give very good agreement either for the affine model or for the phantom model when r_s is below 0.8. Reasons for the discrepancy are given in terms of segmentation effects known to occur with the 4,4'-diphenylmethane diisocyanate used in the experimental work.