# 283b Dynamics of Poly(Ethylene Glycol) Networks and Their Relation to Gas Transport Properties

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The relaxation characteristics of rubbery crosslinked networks based on poly(ethylene glycol) diacrylates have been investigated using dynamic mechanical and dielectric methods. A series of networks were prepared by UV polymerization of poly(ethylene glycol diacrylate) [PEGDA] with systematic variations in monomer molecular weight and reaction mixture composition. Crosslink density in the final films was controlled by two separate methods: (i) the introduction of varying amounts of water in the reaction mixture, and (ii) the copolymerization of PEGDA with either poly(ethylene glycol) monomethyl ether acrylate [PEGMEA] or poly(ethylene glycol) acrylate [PEGA]. The copolymerization strategy results in the introduction of fixed-length pendant groups into the network structure as well as a progressive reduction in overall crosslink density with increasing co-monomer content. By careful selection of the acrylate and diacrylate molecular weights, the overall chemical composition of the copolymers could be held constant at approximately 80 wt% ethylene oxide content.

The relationships between network structure, dynamic relaxation characteristics, and gas transport properties were investigated for both the water-modified and copolymer networks. Dynamic mechanical studies indicated a systematic variation in rubbery modulus for the various films that could be related to the molecular weight between crosslinks according to classical network theories. Time-temperature superposition methods were used to establish modulus-frequency master curves across the glass transition, and the data could be satisfactorily described using the “stretched exponential” Kohlrausch-Williams-Watts (KWW) relaxation function. Complementary broadband dielectric relaxation spectroscopy measurements provided detailed insight as to the molecular origin and characteristics of the various sub-glass relaxations operative in these materials.

In the case of the water-modified PEGDA networks, the measured glass transition temperature was independent of the network formulation. However, the introduction of increasing amounts of water in the reaction mixture led to a systematic decrease in overall crosslink density, as manifested in both rubbery modulus and independent swelling measurements. Also, the glass-rubber relaxation was observed to narrow with increasing distance between crosslinks for this family of samples. For the two copolymer series, the incorporation of acrylate co-monomer led to reductions in crosslink density that were consistent with the results for the PEGDA/H2O series (i.e. comparable variation in distance between crosslinks as a function of decreasing PEGDA content in the reaction mixture). The PEGDA/PEGMEA and PEGDA/PEGA series also displayed a systematic decrease in measured glass transition temperature with co-monomer content owing to the introduction of pendant groups in the network, and their corresponding influence on local free volume. This effect (i.e. the extent of Tg reduction) was stronger in the PEGDA/PEGMEA series as compared to the PEGDA/PEGA specimens.

The influence of network structure on transport properties was assessed by measuring CO2 pure gas permeability as a function of pressure at 35°C and extrapolating to infinite dilution. There was a clear distinction in the gas transport behavior observed for the two classes of networks. For the PEGDA/H2O series, the dependence of permeability on network structure was relatively modest, suggesting that crosslink density does not play a particularly important role in gas transport for these networks. However, for the copolymer series, and the PEGDA/PEGMEA series in particular, the gas transport characteristics were found to vary strongly with network structure. This indicates that the inclusion of the co-monomer pendant groups may be the determining factor. The presence of the pendant chain ends can increase polymer fractional free volume, decrease polymer glass transition temperature, and increase polymer permeability to gases. The results suggest that gas transport in these rubbery networks may be more sensitive to variations in glass transition temperature (i.e. free volume) than to overall crosslink density.