1.12 Nonlinear Optical Properties and Relaxation Processes in Main and Side Chain Polymers

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Extensive measurements on the orientational relaxation of the nonlinear optical chromophores in modified polyimide side-chain and polyamide main-chain polymers have provided a deeper understanding of the phenomenology of the underlying relaxation processes *above and below* the glass transition temperature in any kind of glassy materials. We have shown that it is possible to model these relaxations over more than 15 orders of magnitude in time modifying existing theories about the glass transition in polymers. We also indicated a link to one of the most often cited equations in the polymer relaxation literature: the Williams-Landel-Ferry (WLF) theory which describes the relaxational behavior of vitreous materials *above* their glass transition temperature in terms of two "universal" constants. We showed that relaxations *below* T_g are governed by very much the same "universality" using the appropriate nonlinear extension of the liquid state relaxation behavior through the glass transition. This leads to a scaling prediction for relaxation times in the glassy state with the scaling parameter $(T_g - T) / T$. Based on these observations predictions of the relaxation times as a function of both temperature and processing conditions (cooling rates, annealing times and temperatures, etc.) can then be made. For nonlinear optical polymers, for example, that are required not to loose more than 10 % of their initial nonlinearity within 5 years at operating temperatures of up to 80 ˚C, glass transition temperatures of 240 ˚C and more are needed; an appropriate annealing procedure could reduce these temperatures by about 20 ˚C. Nevertheless, new polymers have to be developed to fulfill these requirements for a thermally stable operation in electro-optic modulator applications.

Recently, polyamides based on DDANS were found to be promising candidates for electro-optical applications in the near infrared. The influence of doping these polymers with hole conductive agents based on DEH to increase their photoconductivity is currently investigated in terms of the nonlinear optical susceptibilities as well as the relaxation mechanisms. Doped polymers, polymer blends as well as copolymers will be compared with respect to long-term stability necessary for device processing.