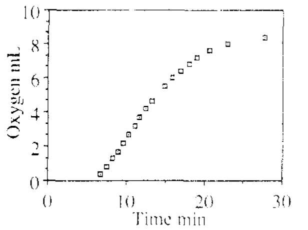

Figure 1. Dioxygen consumption with time during autoxidation of 1-decanethiol catalyzed by LC-1 (experiment 3). One mole of dioxygen per 4 mol of thiol corresponds to 8.6 mL.

analysis. Slightly more than 1 mol of O_2 per 4 mol of 1-decanethiol was consumed, which corresponds with the stoichiometry of eq 1.

$$4CH_3(CH_2)_9SH + O_2 \rightarrow 2[CH_3(CH_2)_9S]_2 + 2H_2O \quad (1)$$

After an induction period the volume of dioxygen consumed was linear with time to about 65% conversion of 1-decanethiol, as shown in Figure 1, which indicates a zero-order rate dependence on 1-decanethiol. The relative zero-order rate constants in Table I show that the latex catalyst LC-1 is 11 times more active than either soluble CoPcTs or cobalt-free latex L-1 (experiments 1–3). Increased oxidation rates with increasing pH in the range 7.0–9.0 (experiments 3–5) indicate that the thiolate ion is the likely reactive species, as found with other polymer-bound CoPcTs catalysts.[1,2] The increase of rate constants with increasing amounts of latex (at constant loading of CoPcTs in the latex, experiments 3, 6, and 7) and with decreasing amounts of initial thiol (at constant weight and loading of LC-1, experiments 3, 8, and 9) may be attributed to absorption of thiol and thiolate ion into the latexes. Higher initial thiol concentration (experiment 9) showed a decrease in the rate of consumption of dioxygen at >65% conversion. This may be due to accumulation of the didecyl disulfide as well as 1-decanethiol in the polymer. We have not determined yet the kinetic order in dioxygen, but in one experiment (10, Table I) the rate of oxidation was 0.30 times as fast under air as it was under oxygen (experiment 3) at atmospheric pressure. A solution of surfactant 1 and $CoPcTsNa_4$ at the same concentrations as in experiment 3 was 0.5 times as active as the latex catalyst. However, the latex preparations contained less than 5% of the initial surfactant in free form (according to conductometric analysis), so the contribution of micellar catalysis to the rates in Table I is negligible. Under the conditions of experiment 3 (except for 0.016-mmol of CoPcTs) magnetic stirring, shaking, and sonication of reaction mixtures gave 79%, 86%, and 90% conversion of thiol, respectively, in 40 min. Increased conversion with more vigorous agitation of reaction mixtures suggests a partial mass transfer limitation to the reaction rates.

Colloidal catalyst LC-3 was more active and catalyst LC-2 was less active than LC-1. The higher activity of the colloidal catalysts than of $CoPcTsNa_4$ suggests that many other autoxidations of organic compounds, such as alkyl aromatic hydrocarbons[11] and phenols,[12] in water may be strongly catalyzed by transition-metal catalysts bound to polymer latexes. We are continuing study of the kinetics of the 1-decanethiol oxidations to gain a better understanding of the mechanisms and to prepare more active catalysts.

Acknowledgment. We thank the U.S. Army Research Office for support of this research and H. Turk for providing the cobalt phthalocyaninetetra(sodium sulfonate).

Registry No. $HS(CH_2)_9CH_3$, 143-10-2; $(H_3C(CH_2)_9S)_2$, 10496-18-1.

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Orientation and Second Harmonic Generation in Doped Polystyrene and Poly(methyl methacrylate) Films

Doped polymeric films have the potential to become important in many industrial uses requiring nonlinear optical materials with wide-ranging physical and chemical properties.[2-3] Many of these uses involve materials capable of second harmonic generation (SHG), conversion of light of frequency ν to light of frequency 2ν. Materials combining the advantages of efficient SHG dopants with glassy polymers can have good optical and physical properties. Orienting these dopants in the polymeric matrix not only gives material capable of highly efficient SHG but will also allow the use of SHG as a probe of dopant orientation and polymer relaxation phenomena. The long-term stability of these oriented materials, along with their physical and mechanical properties, will ultimately determine their practical commercial value. In the present study, glassy polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) doped with optically characterized second harmonic generating dyes[4-6] were examined for their nonlinear optical properties as determined by sample treatment and physical aging.

The nonlinear optical properties of the guest–host polymer plus dye films are observed when highly conjugated, aromatic dyes with electron-donor and electron-acceptor substituents are oriented noncentrosymmetrically in a polymeric matrix.[4-6] The dopants have excellent nonlinear optical properties when aligned in such a way as to prevent their dipole moments from cancelling out. Our approach has been to dope PS and PMMA films with 4-(dimethylamino)-4′-nitrostilbene (DANS),[4] 2-methyl-4-nitroaniline (MNA),[6] or 4-[ethyl(2-hydroxyethyl)-amino]-4′-nitroazobenzene (disperse red-DR)[5] and align

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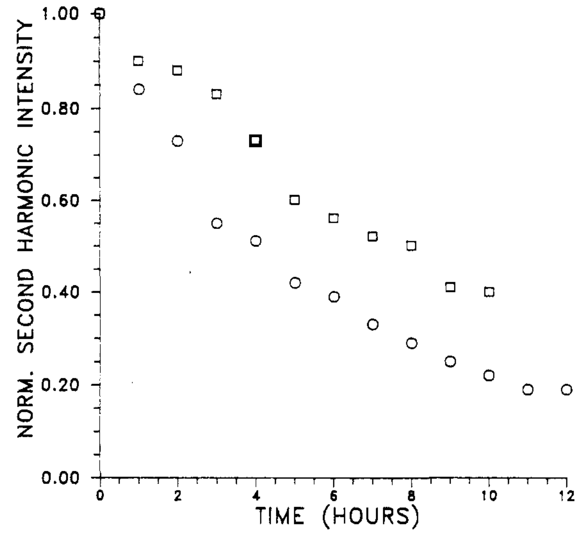

Figure 1. Short-time second harmonic intensity of PMMA (○) and PS (□) films doped with 4% DANS. Signals are normalized to initial time and referenced to a quartz standard.

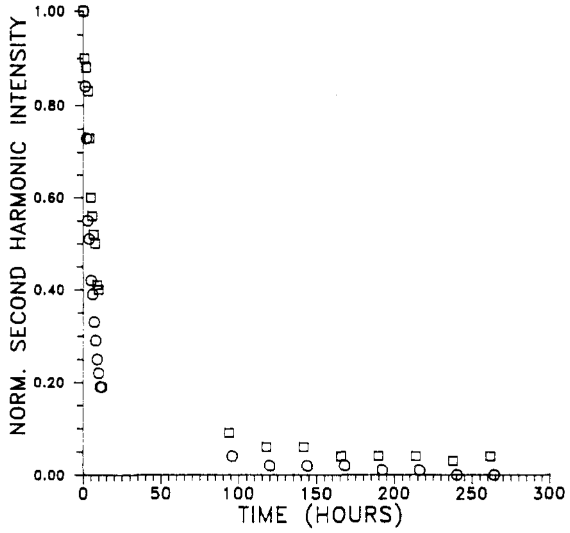

Figure 2. Long-time second harmonic intensity of PMMA (○) and PS (□) films dropped with 4% DANS. Signals are normalized to initial time and referenced to a quartz standard.

these molecules in the polymer matrix using high electric fields at elevated temperatures. Samples will be examined by using SHG as a function of aging time so that information can be obtained about the polymer physical changes demonstrated by the loss in SHG intensity as the samples relax with time, as well as to comment on the long-term stability of the dopants in materials potentially useful for SHG applications.

Samples of PS (Scientific Polymer Products; M_w 430 000; M_n 119 000) and PMMA (Scientific Polymer Products; M_w 93 300; M_n 46 400) were prepared by dissolving the polymer and dye homogeneously and spin coating onto indium–tin oxide (ITO) coated glass. PS was dissolved in spectroscopic quality 1,2-dichloroethane (Aldrich) and PMMA was dissolved in spectroscopic quality chloroform (Aldrich). This paper will present preliminary results concerning samples doped with 4% DANS (higher concentrations were not adequately soluble). The film thicknesses ranged from 1 to 4 μm, as measured by using a Tencor Alpha-step 200. The films were dried at ambient conditions and then under vacuum at 85 °C for 6 h to ensure solvent removal. The optical quality of the film is extremely important. The films must be defect and pinhole free, so that the sample does not break down under the high applied electric field and the amount of scattering due to surface ripples or other defects must be small for proper measurement. Once suitable films were prepared, they were coated with a thin layer of gold to improve contact with the poling apparatus electrodes.

The samples were then placed in a sample holder so that the electrical field could be applied perpendicular to the film. The ITO substrate served as the bottom electrode, and a second piece of ITO glass served as the top electrode. The applied electric field varied from 0.3 to 0.5 MV/cm. The temperature of the film was increased slowly from room temperature to a poling temperature about 5 °C above the glass transition temperature, the electric field was applied, and the sample was maintained at this temperature for at least 20 min. This allows the dopant molecules to orient with the field when the mobility in the system is high. The temperature was then lowered to room temperature with the electric field still applied, so that the orientation of the dopants was maintained. This was performed under vacuum, again to reduce chances of sample breakdown. The SHG intensity was then measured as a function of time after poling. Measurements were made on a q-switched Nd-YAG laser with a 1.064-μm wavelength.

Figure 1 shows the normalized second harmonic intensity of PS and PMMA films doped with DANS. Second-order nonlinear coefficient d_{33} values of about 2×10^{-9} esu were found for DANS, similar to the value of 1.5×10^{-9} esu obtained by Meredith.[4] This can be compared to the d_{33} values of 0.55×10^{-9} esu for potassium dihydrogen phosphate or 7.1×10^{-9} esu for lithium niobate, current inorganic industry standards,[2] or the reported values of 1.6×10^{-9} esu for MNA[2] and 6×10^{-9} esu for disperse red.[5] It can be seen that even in as short a time period as 12 h, up to 80% of the signal in the PMMA + DANS system is lost. This is due to the rotation of molecules in areas of locally high free volume and/or mobility. It should be noted that the film thickness varied up to 0.1–0.2 μm in a 1–4-μm-thick film, giving a fairly large variation in the second harmonic signal from point to point on the film. Data were taken from the same point on the sample at each testing time. Figure 1 also shows that the loss of second harmonic intensity is greater in the PMMA sample than in the PS sample, presumably due to the greater mobility of PMMA. Over a longer period of time, as shown in Figure 2, the second harmonic intensity continues to decrease at a slower rate. In this case the polymer chains may have begun to relax, and dopant molecules that were earlier locked into alignment have greater freedom to rotate and decrease the SHG efficiency.

The complicated decay in the SHG signal over time shown in Figure 1 may signify an initial rapid rotation of the molecules in areas of high free volume in the system and a second, slower decay observed as the polymer mobility allows chains to relax, free volume to be redistributed, and more dopant molecules to rotate.[7-11] While current data are insufficient to quantitatively determine the type of decay (e.g., biexponential, triexponential, etc.), the data qualitatively agree with a rapid response followed by a slow response as described above. We are currently examining these intensities as a function of polymer physical aging, with the poling field applied to the sample during aging. It is expected that thermal history will have an effect on the secondary relaxation processes,[7] with changes in thermal history leading to different optical stabilities of these doped systems.

These results can be related to the mobility in the polymer films and free volume theory for physical aging in polymer glasses.[7-11] When secondary relaxations, associated with limited molecular mobility, are considered for PMMA and PS, it is seen that at room temperature the mobility of PMMA should be much greater due to the greater mobility of the acrylate side chain on the PMMA. Even though both polymers have glass transition temperatures at about 100 °C or slightly above, the broad secondary transition[12] for PMMA occurs between about −50 and −30 °C and for PS at about 35–50 °C. This would lead to the expectation that for a poled, unannealed sample, the mobility of the given dye would be greater in PMMA than in PS at room temperature, allowing the dye to rotate more easily in PMMA than in PS. The decrease in the orientation of the dye would cause a more rapid decrease in the SHG intensity in PMMA than in PS.

The dyes used in this study increase in size in the order MNA, DANS, and DR. Using the different dyes will allow the determination of a dynamic distribution of local free volume in these systems. For a given sample at controlled conditions, the decrease in intensity of the SHG signal could be used as a map of dopant mobility versus size, giving a semiquantitative indication of the distribution of free volume in the sample. Preliminary results suggest that disperse red has greater SHG stability than DANS, which, given that DANS is smaller than disperse red, agrees with utilizing this type of approach in examining the local free volume distribution.

Physical aging of these materials should change the polymer physical characteristics in several ways, including a decrease in the specific volume and enthalpy and thus a densification of the material due to a decrease and redistribution of the available free volume.[7,8,11] Since the mobility of the system depends on the degree of primarily through changes in relaxation times.[8] Examining the decreasing SHG signal of polymers doped with these three molecules under different physical aging programs should provide a great deal of information about the free volume in the system and the redistribution of the free volume with thermal treatment. Such results may also lead to better ways to produce doped polymeric materials capable of maintaining desirable SHG properties over a long period of time. Other experiments[13,14] have shown that information about the distribution of free volume in PS and its changes during physical aging can be obtained by using probe molecules.

The degree of orientation of the dopant can be determined by SHG experiments.[5] The amount of dopant orientation will be important in determining both the efficiency of the SHG and the overall obtainable signal and the relaxation of the chains around the dopant molecules. Independent verification of the angle of dopant orientation may be obtained by using a nonlinear Raman spectroscopy or a modified FTIR-ATR dichroism technique, which will be described in a later paper.

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Registry No. PS, 9003-53-6; PMMA, 9011-14-7; DANS, 4584-57-0.

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Thermal Degradation of Saturated Poly(methyl methacrylate)

The thermal degradation of poly(methyl methacrylate) (PMMA) has been studied extensively over the last 40 years. This effort has elucidated many of the primary steps involved in PMMA thermal degradation; however, it has proven difficult to determine accurate Arrhenius parameters for the initiating reaction because of complex kinetics arising from multiple initiation steps combined with depropagation, termination, and chain transfer. We have determined the Arrhenius activation parameters for degradation of saturated PMMA. We believe this is the first accurate determination of these parameters for PMMA.

Early studies (1950s) on PMMA indicated that degradation takes place by chain-end-initiated unzipping.[1-4] It was shown that vinyl-terminated chains degrade at lower temperatures than saturated chains (both formed by the disproportionation termination step). The zip length (number of monomers lost per initiating event) was estimated to be ≈1000.[2]

Later studies suggested that PMMA degradation takes place by a combination of chain-end-initiated depolymerization and random-initiated depolymerization.[5] The rate of mass loss from polymer by a random scission initiated process is described by eq 1 and 2 for zip lengths

$$\text{zip} \gg \text{DP} \qquad \mathrm{d}[\mathrm{M}]/\mathrm{d}t = -k_s \mathrm{DP}[\mathrm{M}] \qquad (1)$$

$$\text{zip} \ll \text{DP} \qquad \mathrm{d}[\mathrm{M}]/\mathrm{d}t = -2k_s(1/\gamma)[\mathrm{M}] \qquad (2)$$

greater than the initial degree of polymerization (DP) or less than DP, respectively,[6] where k_s is the rate constant for chain scission and γ is the reciprocal of the average zip length between initiation and termination. Further restrictions on eq 1 and 2 are that eq 1 assumes a monodisperse molecular weight and eq 2 assumes that termination is either a first-order process or occurs by disproportionation.

Kinetic studies of PMMA degradation have continued to show large variations in the observed Arrhenius parameters (literature values for the activation energy of

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