Improved NLO Properties through a Liquid Crystal Phase Poling

Jae-Suk Lee and Young-Sun Cho
Dept. of Materials Science and Engineering, Kwangju Institute of Science and Technology,
Kwangju 506-712, Korea

Gyoujin Cho
Dept. of Chemical Engineering, Sunchon National University, Sunchon 540-742, Korea

Kyeong Taek Jung and Yong Gun Shul
Dept. of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

Cross-linkable organic NLO chromophore called DRS was chemically incorporated into silica matrices using the sol – gel process. A number of electrically poled DRS/silica matrix systems were studied to elucidate the relaxation of the oriented organic chromophore by following the decay of UV absorption as a function of time and temperatures. The value of the second harmonic coefficient d_{33} was 47 pm/V for the DRS/silica matrix films (0.4 μm thickness). From the dramatic decrease in the UV absorption after poling at 80°C, it is speculated that the DRS may act as a liquid crystalline mesogenic group and is effectively oriented in poling at the phase (nematic) transition temperature (80°C). This argument was substantiated by investigating the phase behavior of DRS itself using both DSC and a polarized optical microscope. The DRS/silica system contained the ideal matrices to retain the oriented chromophore because of optical clarity, thermal stability and effective poling at the nematic liquid crystalline phase.

Introduction

The interaction of the electromagnetic field of a high-intensity laser light with a nonlinear optical (NLO) material can generate new electromagnetic fields. As light passes through a substance, its electric field interacts with inherent charges in the material, causing the original beam to be altered in phase, frequency, amplitude, or polarization. The application of such interactions is of importance in technologies such as optical communication, optical computing, and dynamic image processing (Zyss, 1985; Boyd, 1989). These areas are now creating intense interest, not only because of the NLO properties of the materials, but also due to attempts to control other characteristics such as solubility, processability, optical clarity, absorption, and thermal stability, as these attributes will obviously determine their technological utility.

Initial developments in NLO materials gave rise to NLO devices using inorganic crystals such as quartz, $LiNbO_3$, and KH_2PO_4 (Long, 1995), followed by inorganic semiconductors such as gallium arsenide (GaAs) and indium antimonide (InSb), which displayed large optical nonlinearities (Long, 1995). Although both types of NLO materials are used in crystals, they face a "trade-off" problem between the response time and the magnitude of optical nonlinearity, and are costly and difficult to produce; furthermore, they absorb effectively in the visible region and are of poor optical quality, which eliminates many possible applications.

Organic systems have been investigated as an alternative to inorganic materials because of their low cost, fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility, high optical damage thresholds, and ability to have tailored molecular structures (Baumert et al., 1987; Dehu et al., 1993; Zyss, 1985). However, organic NLO chromophores also have some problems, such as a lack of thermal stability, and the gradual relaxation of oriented chromophores after poling. Several systems have been found to be relatively successful in solving or improving the problems, and progress has been reviewed by Burland et al. (1994). A

Correspondence concerning this article should be addressed to J.-S. Lee.

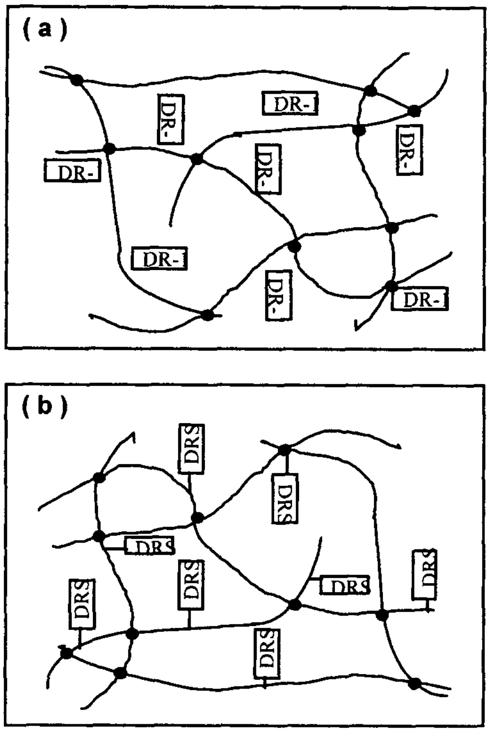

Figure 1. (a) Host guest (DR-1/Silica) and (b) new cross-linking system (DRS/Silica).

very interesting recent development in this area is the use of sol–gel chemistry to produce thermally stable matrices for the organic NLO chromophores (Nakamura et al., 1991).

Clear inorganic and modified inorganic/organic glasses can often be prepared *in situ* by low-temperature polymerization of appropriate monomers in the sol–gel process (Klein, 1988; Brinker and Sherrer, 1970). The procedure of this technique is shown in Figure 1a and 1b for a silicone containing glass. A number of organic NLO chromophores have been incorporated into a variety of inorganic glasses by the sol–gel technique. These materials can be classified either as network modifiers (Figure 1a) or reactive network makers (Figure 1b), depending on the functionality.

However, since the glasses are produced by subsequent densification, problems of volume contraction, brittlement, and shrinkage are often encountered when thin films are generated on substrates (Haruvy and Webber, 1991). Furthermore, due to unfavorable interactions between organic NLO chromophores and inorganic matrices, light scattering (originating from phase separation) often presents additional problems. In an efforts to minimize these problems, a wide variety of solvents and additives, including surfactants, has been used. Recently, a relatively simple procedure for the preparation of crack-free, optically clear films containing a variety of organic chromophores without additives or surfactants has been reported (Haruvy and Webber, 1991).

Here, we report experimental results from investigations of the stability of an organic-oriented chromophore called DRS in a pure glass matrix (prepared from tetraethoxy orthosilicate) with less brittlement and light scattering. In addition, there has been speculation about the origin of the observed large, second-order optical parameters for these films, and the liquid crystalline behaviors of DRS was investigated in connection with this questioning.

Experimental Studies

Materials and instruments

The starting materials, 4-[ethyl(2-hydroxyethyl)amino]-4′-nitroazobenzene, and tetraethoxy orthosilicate (TEOS), were purchased from Aldrich Chemicals and were used without further purification. The compound DRS was simply prepared from 4-[ethyl(2-hydroxyethyl)amino]-4′-nitroazo-benzene, disperse red 1 following the procedure described in our earlier works (Lee et al., 1996; Shul et al., 1996). FT-NMR (Jeol, JNM-LA 300 MHz) and differential thermal analysis (Shimazu 50A) were used to characterize the resulting DRS. The phase transitions of DRS were monitored using a differential scanning calorimeter (DSC) (Thermal Analyst 2100, TA Instruments) and a polarized optical microscope (Mettler FP90). The microscope glass slides as substrates were purchased from Fisher Scientific premium and used after they were ultrasonically cleaned in a detergent solution, washed with deionized water, and then washed with isopropanol, and dried at 50°C in a dust-free oven and stored in a desiccator. Reagent-grade HCl and absolute ethanol were obtained from Fisher Scientific. Double-distilled deionized water was used in all the experiments reported in this work. The relaxation behavior of the chromophores was studied by the decay of the UV-visible light in a spectrophotometer (Varian Cary 1E).

The second harmonic generation (SHG) of the poled DRS/silica samples were measured with 1064 nm laser radiation. A polarized Nd:YAG laser with a 15-ns pulse width and a 20-Hz repetition rate was used as the light source. The calculation of the second harmonic (SH) coefficient d_{33} followed the method previously reported by Jerphagnon and Kurtz (1970).

Films preparation using the DRS/silica system

The initial solution for the formation of glass matrices was prepared using the molar ratio of TEOS (1): EtOH (10): hexyleneglycol (0.1): HCl (0.05): H_2O (2), after which DRS (10 wt. % of TEOS) dissolved in DMF was slowly added to the precursor solution while stirring. After stirring for one more hour, the mixed solution had a viscosity of 3–5 cp, suitable for spin-coating onto the glass substrate. Then, a spin-coater (Kyowa Riken, K-359SD-1) was used at 2,000 rpm for 180 s to fabricate DRS/silica films on a glass substrate. The thickness of the films prepared under these conditions was commonly 0.4 μm and even. The poling was carried out directly using the corona discharge method. Details of the corona poling setup were reported earlier by Mortazavi et al. (1989). The poling was started at 80°C. The strength of the effective electric field used for poling was estimated to be 10 kV according to the literature (Mortazavi et al., 1989). Then, with the electric field on, the thin films were heated to a temperature at which the cross-linking of the material is fast.

Results and Discussion

Thermal stability of DRS

Prepared DRS was characterized and confirmed by ^{1}H-NMR (Shul et al., 1996). To find an optimum poling temperature, the thermal stability of DRS was investigated using differential thermal analysis (DTA). From the DTA results, thermal decomposition temperature of DRS was found to be 320°C, which is higher than that of DR-1 (290°C). Therefore, the poling and curing temperature of the whole system were set below 320°C. To fabricate the best second-order NLO films, both curing and poling proceeded simultaneously. Although the DRS/silica matrix spin-coated/cured films were very thin (0.4 μm), there was no microscopic phase separation. The cross-linking reaction between the organic chromophore (DRS) and TEOS was expected based on our earlier article (Shul et al., 1993) and that of Kim et al. (1993).

Order Parameter of DRS in silica matrices

To investigate the relaxation behavior of various chromophores and matrices after poling, the absorption behaviors of each sample was examined as a function of time. The absorption spectra were taken at regular intervals over 200 h for the poled/cured samples kept at 25, 80, 100, and 140°C, respectively. The temporal retention of DRS/silica matrices was excellent at all the temperatures studied (Figure 2). Since the stability of the orientational order of the molecule determines the potential of the materials for practical NLO applications, these system show great promise for this purpose. Indeed, in those systems the NLO chromophores (DRS) are "locked in" a noncentrosymmetric arrangement after poling and curing in the cross-linked matrices. The retention of the chromophore orientation is considerably improved compared to our previous results using the sol–gel method to form matrices in guest–host systems, as was shown in Figure 1a (Lee et al., 1996). This effect is due to the cross-linking reaction between DRS and silica matrices; similar results have been reported by other groups as well (Jeng et al., 1992).

Since all films were prepared from the same initial solution, the expected decay of UV absorption with respect to time should be similar at the investigated temperatures (e.g., 25, 80, 100 and 140°C). However, immediately after poling/curing at 80°C, a dramatic decrease in absorption was observed (Figure 3). This observation was unexpected: in both our previous article (Shul et al., 1996) and those of other groups, the amount of absorption decreased by poling was approximately 30% due to the alignment of DR-1 in the polymer or silica matrices. However, the absorption differences of the DRS/silica matrices before and after poling at 80°C was about 70%. At the same time, the order parameter of the DRS/silica matrices calculated from the UV absorption difference (Burland et al., 1994) was 0.7. The experiments were repeated several times under the same condition, and the results were reproducible. There are two possible reasons for the large decrease in the UV absorption for the films poled at 80°C; (1) some of the NLO chromophores might have been lost due to sublimation; (2) the chromophores actually align more effectively at 80°C than at other temperatures. If the decrease is due to the first reason, the UV absorption decay would increase as the poling/curing temperatures increase. However, as it was shown in Figure 2, the UV adsorption decay is almost the same at all other temperatures investigated. Therefore, we speculate that the organic chromophore in DRS exhibits a liquid crystalline phase at the specific temperature (80°C) and the poling electric field would induce more effectively oriented arrays of NLO chromophores at this temperature. Actually, electric-field-induced dipolar alignment of the mesogenic NLO-active azochromophore in a side chain liquid crystalline polysiloxane was reported by Abe et al. (1995).

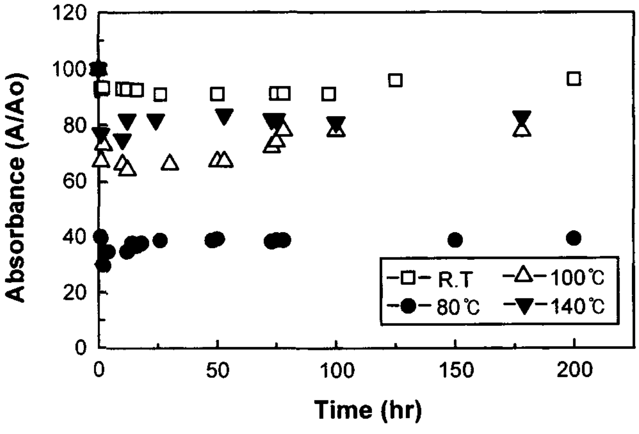

Figure 2. UV absorption changes before and after poling, and relaxation behaviors of DRS/silica matrix film at various temperatures as a function of time.

A_0 = before poling; A = after poling.

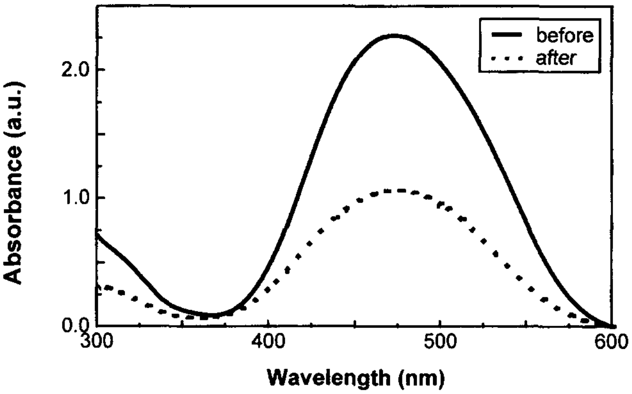

Figure 3. UV absorption changes before and after poling at 80°C.

DSC analysis of DRS

In order to examine the validity of the argument presented earlier, we used a differential scanning calorimeter (DSC) and a polarized optical microscope to observe the phase-transition behavior of the pendant mesogenic group (DRS) in the cross-linked silica matrices. For this purpose, DSC scans of DRS and DR-1 at 10°C/min were performed for comparison. Each sample was prepared by drying a small amount of the solution in the DSC sample pan. Figure 4 shows typical DSC scan of both DR-1 and DRS. The results indicate that DRS showed two peaks, one due to melting, the other to liquid crystal phase (nematic) transition. The crystal phase-transition temperature was exactly 80°C in the cooling cycle, while in the heating cycle the temperature was 100°C. The reason for the discrepancy of the crystal phase transition is probably due to supercooling, which is often observed for liquid crys-

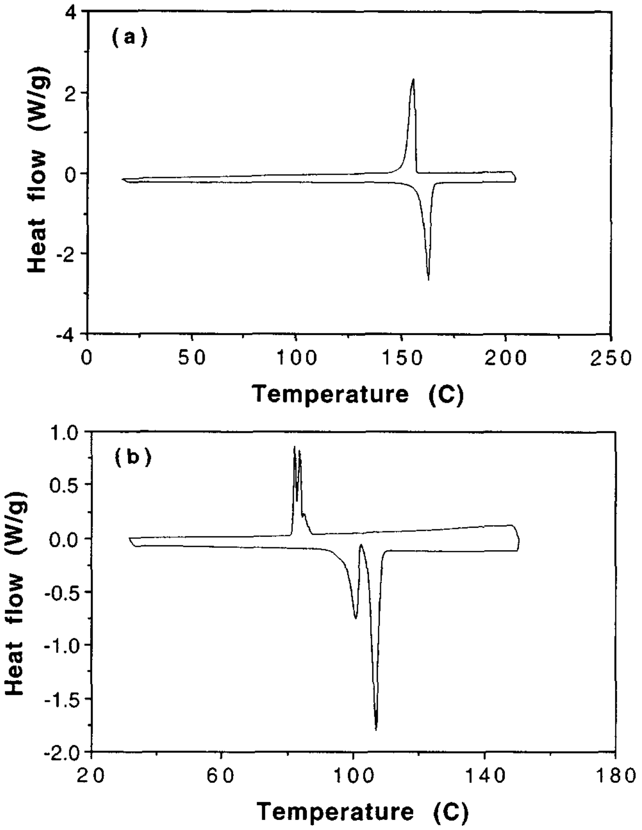

Figure 4. (a) Differential scanning calorimeter analysis of DR-1 and (b) DRS.

talline compounds. The phase transitions monitored by the optical microscope are consistent with the results obtained from DSC (Figure 5). While DSC the data of DRS obviously showed a characteristic nematic phase transition, those of DR-1 showed only a single peak due to melting at 162°C. No liquid crystalline phase was observed for DR-1 under the polarized optical microscope. Therefore, both DSC and the optical microscope results substantiate the speculation that the formation of nematic phase for DRS in the reactive silica matrix is a major factor in the large optical order parameter observed for films poled at 80°C. In other words, by poling at the phase-transition temperature of DRS (nematic phase), a large difference on the UV absorption could be obtained due to the effective alignment of the chromophores (Stupp et al., 1992). Further investigation is under way in our group to apply the observed results in an NLO device.

Nonlinear optical properties

To observe the NLO properties, the SH intensity of the poled samples examined in this work was obtained with an Nd:YAG laser (Figure 6). The results show that the DRS/silica matrix system has large SH intensities. The SH coefficient is determined by measuring the SH intensity as a function of the incident angle in transmission through the film. The nonlinear optical coefficient (d_{33}) of the poled/cured DRS/silica matrices was 47 pm/V, even in very thin film (0.4 μm).

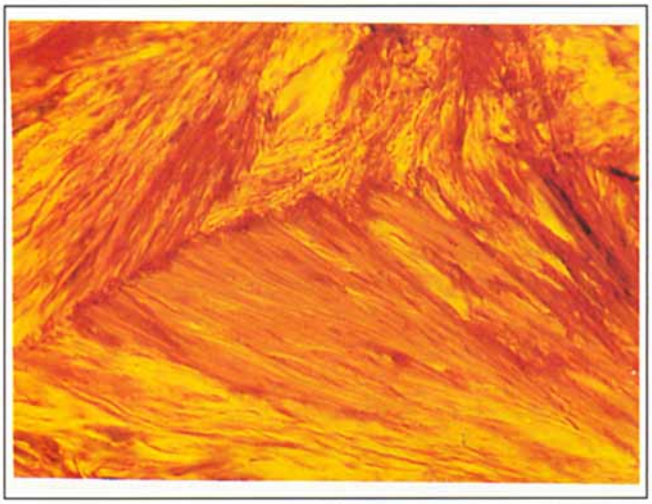

Figure 5. Polarized optical microphotograph of nematic phase of DRS at 80°C.

Conclusions

The sol-gel process was used to incorporate NLO chromophores directly into an inorganic network, and use of the DRS compound improves the retention of the oriented NLO chromophores. The most effective alignment of the chromophores can be obtained if the poling is carried out at the liquid crystal-phase transition temperature (nematic phase in this work). Therefore, it may be possible to keep the noncentrosymmetry of the liquid crystalline chromophores covalently bound in a matrix network by simply applying a magnetic field or low-voltage electric poling instead of high-voltage electric poling. Since the DRS/silica system has shown better clarity and less brittlement even in thin films, this kind of network may be a better host to lock in the oriented NLO chromophores locked in the host matrix.

Acknowledgments

The authors acknowledge helpful discussions with Prof. Bing M. Fung at the University of Oklahoma. They also thank Dr. H. Sasabe and Dr. T. Wada for SHG analysis.

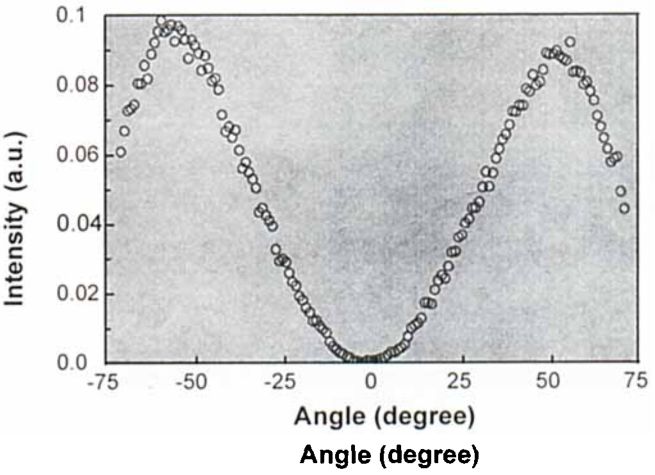

Figure 6. SH intensity change for incident angle in DRS/silica matrices poled at 80°C.

Literature Cited

Abe, J., M. Hasegawa, H. Matsushima, Y. Shirai, N. Nemoto, Y. Nagase, and N. Takamiya, "Investigation of Dipolar Alignment of Mesogenic Chromophores in Side-chain Liquid Crystalline Polysiloxane Using Electric Field Induced SHG," *Macromol.*, **28**, 2938 (1995).

Baumert, J. C., R. J. Twieg, G. C. Bjorklund, J. A. Logan, and C. W. Dirk, "Crystal Growth and Characterization of 4-(N,N-Dimethylamio)-3-Acetoamido-Nitrobenzene, a New Organic Material for Nonlinear Optics," *Appl. Phys. Lett.*, **51**, 1484 (1987).

Boyd, G.T., "Applications Requirements for Nonlinear Optical Devices and the Status of Organic Materials," *Opt. Soc. Amer. B*, **6**, 685 (1989).

Brinker, C. J., and G. W. Sherrer, *Sol–Gel Science*, Academic Press, New York (1990).

Burland, D. M., R. D. Miller, and C. A. Walsh, "Second-Order Nonlinearity in Poled-Polymer System," *Chem. Rev.*, **94**, 31 (1994).

Dehu, C., F. Meyers, and J. L. Bredas, "Donor-acceptor Diphenylacetylene: Geometric Structure, Electronic Structure, and Second-Order Nonlinear Optical Properties ," *J. Amer. Chem. Soc.*, **115**, 6198 (1993).

Haruvy, Y., and S. Webber, "Support Sol-Gel Thin Film Glasses Embodying Laser Dyes," *Chem. Mater.*, **3**, 501 (1991).

Jerphagnon, J., and S. Kurtz, "Maker Fringer: A Detail Comparison of Theory and Experiment for Isotropic and Uniaxial Crystals," *J. Appl. Phys.*, **41**, 1667 (1970).

Jeng, R. J., Y. M. Chen, A. K. Jain, J. Kumar, and S. K. Tripathy, "Second Order Optical Nonlinearity on a Modified Sol–Gel System at 100°C," *Chem. Mater.*, **4**, 972 (1992).

Kim, J. S., L. Plawsky, E. V. Wagenen, and G. M. Korenowski, "Effect of Processing Parameter and Polymerization Behavior on the Nonlinear Optical Response of Sol–Gel Materials," *Chem. Mater.*, **5**, 1118 (1993).

Klein, L., *Sol–Gel Technology for Thin Films, Fibers, Preforms, Electronics and Speciality Shapes*, Noyes, Park Ridge, NJ (1988).

Lee, J.- S., Y.- S. Cho, G. Cho, K. T. Jung, Y. G. Shul, and M. G. Choi, "UV Study on the Thermal Stability of Dispersed Red 1 Films Incorporated with Reactive Silica," *Mol. Cryst. Liq. Cryst.*, **280**, 53 (1996).

Long, N. J., "Organometallic Compounds for Nonlinear Optics—The Search for En-light-enment," *Angew. Chem. Int. Ed. Eng.*, **34**, 21 (1995).

Mortazavi, M. A., A. Knosesen, S. T. Kowel, B. G. Higgins, and A. Dienes, "Second-Harmonic Generation and Absorption Studies of Polymer-Dye Films Oriented by Corona-Onset Poling at Elevated Temperatures," *J. Opt. Soc. Amer. B*, **6**, 733 (1989).

Nakamura, M., H. Nasu, and K. Kamiya, "Preparation of Organic Dye-Doped SiO2 Gels by the Sol–Gel Process and Evaluation of their Optical Non-linearity," *Non-Cryst. Solids*, **135**, 1 (1991).

Shul, Y. G., D. J. Lee, J.-S. Lee, and T. Wada, "Incorporation of Organic Compound into Silica Matrices by a Sol–Gel Process for NLO Applications," *J. Ceram. Soc. Jpn.*, **101**, 76 (1993).

Shul, Y G., K. T. Jung, G. Cho, J.- S. Lee, T. Wada, H. Sasabe, M.-W. Jung, and M.-G. Choi, "Stable Second-Order Nonlinear Optical Properties of Sol–Gel Systems; Incorporated Disperse Red 1 into the Silica Network by Covalent Bonding," *Nonlinear Opt.*, **15**, 411 (1996).

Stupp, S. I., H. C. Lin, and D. R. Wake, "Nonlinear Optical Properties of Magnetically Aligned Solid Solutions of Nematic Polymers and Dye Molecules," *Chem. Mater.*, **4**, 947 (1992).

Zyss, J., "Second-Order Nonlinearity in Poled-Polymer Systems," *J. Mol. Electron.*, **1**, 24 (1985).

Manuscript received Oct. 28, 1996, and revision received July 1, 1997.