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STUDIES ON RELAXATION BEHAVIOR OF CORONA POLED
AROMATIC DIPOLAR MOLECULES IN A POLYMER MATRIX

Dr. Sukant Tripathy

University of Lowell

One, University Avenue
Lowell, MA 01854

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B. K. Mandal, Y. M. Chen, R.J. JENG, T. Takahashi, J.C. Huang, J. Kumar, S. Tripathy

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Thin Film Processing of NLO Materials: I

STUDIES ON RELAXATION BEHAVIOR OF CORONA POLED AROMATIC DIPOLAR MOLECULES IN A POLYMER MATRIX

BRAJA K. MANDAL[a], Y. M. CHEN[b], R. J. JENG[a], TORU TAKAHASHI[a],[†]
J. C. HUANG[c], JAYANT KUMAR[b] and SUKANT TRIPATHY[*][a]

Departments of Chemistry[a], Physics[b] and Plastics Engineering[c], University of Lowell, One University Avenue, MA 01854, USA

Abstract- A number of corona poled guest-host systems have been investigated to understand the nature of interaction between the guest and the host molecules, their compatibility and relaxation behavior. This has been carried out by studying the relaxation response of the nonlinear optical effects. Styrene acrylonitrile copolymer was found to be the ideal matrix studied, since the polymer itself relaxes slowly subsequent to poling and it accommodates a wide range of nonlinear optical molecules differing in molecular structure and polarity. Retention of the second-harmonic intensity has been emphasized as a measure of the relaxation and decay of the order parameters with time. Absorption characteristics of the poled and the unpoled film are also described.

[†] Visiting Sekisui Chemical Co, Fellow.

INTRODUCTION

Certain π-conjugated organic compounds substituted with electron donor and acceptor groups in appropriate positions exhibit strong second order nonlinear optical(NLO) properties. Asymmetric intramolecular charge transfer between the two groups creates complex excitation of electrons under appropriate electromagnetic fields leading to NLO effects. In the past decade a large number of such compounds have been identified or synthesized, and processed into different molecular organizations. In noncentrosymmetric organizations several of these systems have been characterized by large second order NLO coefficients, ultra fast response times, performance over a broad wavelength range and high laser damage threshold[1-6].

For NLO processes, such as second-harmonic generation(SHG) or the linear electro-optic effect, a material must be noncentrosymmetric, preferably in a crystalline organization. Prototypical inorganic second order materials such as KDP(potassium dihydrogen phosphate) may not possess the largest nonlinear coefficients but can be easily grown as large noncentrosymmetric single crystals with relatively few defects. They can also be cut and polished along preferred crystallographic planes, an essential requirement for optical application, using conventional techniques.

Organic and polymeric NLO materials, despite having large second order parameters, require convenient fabrication techniques for potential applications, since bulk crystals of these materials are not easy to grow or to handle. In recent years, various approaches have been explored to overcome the processing problems and develop unique approaches to processing of organic NLO materials taking advantage of their structural flexibility. This includes confined growth of large molecular and polymeric thin films[7-10], mono- or multilayered thin films by Langmuir-Blodgett (LB) technique[11-13], and processing of liquid crystals or liquid crystal polymers taking advantage of the cooperative order[14-16].

Amorphous polymers are extensively used as bulk and micro optical components because of their ease of processing and desirable optical characteristics such as excellent transparency and low scattering losses[17]. Materials combining the advantages of organic NLO molecules and the superior processing characteristics of the amorphous polymers, have been reported[18-21]. Thin film materials of this combination can be obtained by a number of techniques, for example: i) by casting (viz. spinning, dipping or other coating techniques) a solution of NLO molecule and amorphous polymer (guest-host systems[22]) in a common solvent, ii) by diffusing the NLO molecules into a precast polymeric thin films using SAID(solvent assisted in-diffusion[23]) technique, and iii) by making the NLO

molecules an intrinsic part of the polymer matrix by grafting it on as a side chain or part of the main chain followed by the deposition of thin films using LB technique.[12,24-26]

Unlike the LB technique, where the nonlinear moieties are highly oriented, a guest-host system comprises randomly oriented NLO molecules in the polymer matrix. Necessary polar alignment is induced by the application of external electric field in a method defined as poling. Effective poling requires the temperature of the matrix to be close to the glass transition temperature, T_g, as the electric field is applied and subsequent cooling down of the sample and freezing-in of the noncentrosymmetric order below T_g.

A number of NLO molecules, for example, MNA(2-methyl-4-nitroaniline) and DR-1(disperse red-1) in PS(polystyrene) or PMMA(polymethyl methacrylate) matrices have been studied extensively[18-21]. The results indicate that the second order parameters of the matrix are not consistent due to the relaxation of the guest and host molecules when the external poling field is off. More recently, a fairly stable polymer matrix composed of chemically cross-linked NLO molecules has been reported[27].

In the present study two approaches have been adopted to improve the stability of the matrix and to understand the molecular interactions of the guest and host molecules as a function of their molecular and electronic structure and molecular organization. First

involves investigation cf the effect of structural variation of the active molecules on the final NLO properties. Secondly, copolymer hosts have been chosen to enhance the interaction between the guest and host molecules by controlling the distribution of available free volume resulting from different polar and nonpolar components. Further, by selecting the copolymer having appropriate proportion of the polar and nonpolar components compatibility with the active molecules can be optimized.

The NLO molecule MBNA[4,4'-methylene bis(3-nitroaniline)] which is roughly twice the size of the prototypical MNA and contains two electronically isolated electroactive components analogous to MNA was selected as an active component along with MNA. M_2[4-(4-hydroxy 2-methylphenyliminomethyl) nitrobenzene] synthesized for the first time in our laboratory and already extensively studied DR-1 were selected as the second molecule pair for investigation. DR-1 and M_2 are both expected to be in trans-configuration and are of similar size and polarity. The principal difference is the presence of an azo and azomethine bridging group in the two compounds respectively.

PMMA and PS have been traditionally used as the host matrices due to their ease of processing and good linear optical properties. PMMA matrix is significantly polar compared to PS. Consequently, the compatibility of the polar active molecules is expected to be more in PMMA than in PS. On the other hand the

relaxation subsequent to poling of the PS matrix is much better than PMMA because of structural rigidity. One severe disadvantage is that the PS matrix accommodates only low concentration of the active molecules.

INSERT Figure 1

In view of this a random copolymer matrix, SAN(styrene acrylonitrile copolymer), has been chosen for the present work along with PMMA and PS. The compatibility with the active molecules and the relaxation of the matrix have been taken care of by using a SAN matrix containing 32-33 weight percent acrylonitrile. The structures of the NLO molecules and the polymer systems used for this study are shown in Figure 1. Relaxation behavior of the poled guest-host matrices with respect to the size of the NLO molecules and the free volume in the polymer systems has been studied. UV-VIS absorption characteristics of the poled and unpoled films are also described.

EXPERIMENTAL PROCEDURES

Materials

MNA (Aldrich) and MBNA (Aldrich) were recrystallized from aqueous methanol. DR-1 (Aldrich) was purified by dissolving in acetone followed by evaporation of the filtrate. The synthesis of

azomethine derivative, M_2, has been described in another communication[28]. M_2 was recrystallized from methanol before use. PMMA (M_w: 55000, Cyro Industries), SAN (32-33 wt % acrylonitrile content; M_w: 95000, Monsanto) and PS (M_w: 280000, Aldrich) were used as received.

Processing

Conventional spinning technique used in microfabrication was employed for coating thin films of the different guest-host systems on glass substrates. 2g of the host polymer was dissolved in 10ml of N,N-dimethylformamide(DMF). The polymer solution was intimately mixed with 0.1g of NLO material using an ultrasonic mixer at 35°C. The resulting solution was used to spin-coat a microscopic glass plate (2.5cm X 7.5cm) at 1000 to 2500 rpm for 45 seconds. The sample was then baked at 60°C for 4 hour under vacuum to remove residual solvent.

Poling

Corona poling technique was used to align the dipolar molecules[19,20]. A schematic of the experimental set-up is given in Figure 2. Poling was done at 95°C for SAN and 85°C for PMMA and PS based films. The applied voltage on the corona wire was

maintained at 5.5 kV while the corona current of approximately 3μA was established. Electric field was kept on during both the heating and the cooling cycles which were maintained for three minutes and one minute respectively. Effective poled area, approximately 1.5cm wide and 2.5cm long, was more transparent compared to the unpoled region as expected subsequent to poling.

INSERT Figure 2

NLO Measurements

The relaxation behavior of various guest-host combinations was studied by the loss of second-harmonic(SH) intensity as a function of time after poling. Measurements were made on a Q-switched Nd-YAG laser (Quantel 660A) in which a polarized beam of 1064 nm wavelength was passed through the sample as shown in Figure 3. The fundamental wave was blocked using $CuSO_4$ solution and a 532 nm interference filter was used to allow the 2nd harmonic to pass. The SH signal was detected by a photomultiplier tube(PMT), then amplified and averaged in a boxcar integrator (Stanford Research SR-250).

INSERT Figure 3

UV-VIS   Spectroscopy

The absorption spectra of the NLO molecules in an organic solvent and in polymer matrices were recorded in a Perkin-Elmer (Model 559) UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

Compatibility

The active molecules are homogeneously spread in an amorphous matrix and usually to a higher concentration.   The size and the solubility of the NLO molecules in the   solid   polymer solution are very important for obtaining a film with good optical quality. Unwanted crystallization and phase segregation of the NLO molecules lead to losses as a result of optical scattering from the resultant two phase film. What is desired is the largest possible concentration and optical orientation of the active molecules without introducing any optical losses in the material transparent region.

A general guideline can be drawn concerning the compatibility of the guest-host systems from the solubility parameter(δ) obtained by the group computation method[29]. The δ values of PMMA, PS and our sample of SAN are obtained as 18.0, 15.8 and 18.6 respectively.

It was not possible to calculate the δ value of DR-1 precisely since no reliable parameter exists for $-NO_2$ and $-N=N-$ groups. However, rough approximation yields the δ value of 27.5, 24.4, 26.1 and 23.9 corresponding to MNA, MBNA, M_2 and DR-1 respectively. This clearly indicates that these polar NLO molecules can not be homogeneously distributed to a high concentration in the PS matrix. In fact, crystallization or blooming of the NLO molecules was observed even at low concentration of the NLO molecules in the PS matrix. On the other hand, homogeneous thin film of PMMA or SAN was obtained with the NLO molecules having concentration upto 30 weight percent.

Orientation

As expected optically responsive molecules are randomly oriented in the polymer matrix although a small amount of residual anisotropy is sometimes seen as the asymmetric molecules are spin coated on the substrate. Poling of such molecules is essential since the second order parameters are directly proportional to the orientational order of the optically responsive molecules in the matrix. Poling is usually done by the application of a high electric field using different electrode configurations, viz. parallel plate poling[18], integrated electrode poling[30], and corona poling[19-21]. During the corona poling process electric charge is sprayed on the polymer film. This charge induces an image charge on the ground plate which is oppositely charged. A large electric field thus results across the

polymer film due to this surface charge which interacts with the guest molecules and induces orientational order in the matrix[31]. The discharge parameters, namely, the corona voltage (V_c) and the corona current (i_c), for such electrode configuration are given by[32]

$$V_c = (C_1 x + C_2 x^{1/2}) \ln(h/a) \qquad \text{(i)}$$

$$i_c = (V - V_c) \, V m_\mu C_3 / P \qquad \text{(ii)}$$

where the empirical constants, C_1 and C_2, consistent with x which is equal to Pa/T, while the constant C_3 largely depends on the geometry of the film. Usually, the applied voltage (V), the height between the wire and the planar electrode (h), the diameter of the wire (a) and the air pressure (P) are fixed parameters. The ion mobility (m_μ) is dependent on the ambient temperature (T). Hence, a large corona discharge current can be achieved (cf. eq. i and ii) by lowering the corona voltage V_c which varies inversely with temperature T.

SH Properties

When the external electric field which induces the orientational order in the active molecule is removed there is onset of relaxation. The stability of the orientational order of the molecule determines the potential of the system as a second order material. In a guest-

host system the NLO molecules are "locked in" the noncentrosymmetric arrangement in the polymer matrix by "freezing" the matrix below T_g. The relaxation rate of orientational order and hence second order nonlinearity in this system largely depends on the polymer parameters, viz. mobility, polarity and interchain free volume[33-35], and the size and the polarity of the NLO molecule itself.

INSERT Figure 4

The retention of SH intensity of the small molecule such as MNA was found to be very poor in the PMMA matrix while the larger rodlike molecule DR-1, shows excellent retention of SH intensity in the same matrix (Figures 4a and 4b). This is due to the fact that the PMMA matrix is flexible enough and has enough free volume to allow the rotational movement of MNA, but the larger rodlike molecule DR-1 in the ordered orientation finds a more confining environment for rotational relaxation. MBNA, where the two phenyl rings are connected by a methylene group, was found to relax faster than DR-1 and even MNA in the PMMA matrix. While this is a surprising result for a reasonably large molecule MBNA, it is easily explained by the facile intramolecular conformational change through the flexible methylene group[36]. Rapid decrease in the dipole moment of the individual MBNA molecule in the poled direction can occur through

intramolecular rearrangements without overall rotation of the molecule. Rotation of a few degrees about the bond linking the methylene unit to the phenyl rings can drastically change the net dipole moment in the poled direction.

Both MNA and DR-1 retain the highest level of SH intensity when SAN is the host polymer. As will be described later this is explained in part by the retained polarization of the host itself. Further, the poled host and guest molecules form a significantly more stable local order. The mixed polar- nonpolar nature of the SAN polymer and the orientation of the cyano groups with respect to the active molecules must play an active role in this stabilization process. The nature of the spatial distribution of the excluded volume and its dynamics in relation to the type of guest molecule must be considered. Yet a more precise role that the various factors related to the polymer structure play has to be quantitatively defined to explain the better stability of the MNA-PS system compared with MNA-PMMA. The same general arguments may be used with greater confidence for the DR1-PMMA and DR1-PS systems where as expected the poled DR1-PMMA system is more stable over the long term compared with DR1-PS system (Figure 4b).

INSERT Figure 5

Although the glassy polymers are amorphous and lack in long-range three dimensional order an even order nonlinear optical susceptibility can be imparted to these polymer matrices, by inducing orientational order through electric field induced poling. Figure 5 describes the relaxation behavior of PMMA and SAN. SAN is found to relax slowly compared to the other host polymer systems and retains a higher degree of order over long time scales. Observation of strongest SH signal from all active compound in SAN compared to the other hosts is explained in terms of this retained order in the host and its orientational influence on the guest molecules.

The SH intensity of the NLO molecules was found in the following order: DR-1 > MNA > M_2 > MBNA for all host systems for films poled in the same manner.   This is an expected result as the active compounds are in a decreasing order of $\mu\beta$, where μ is the molecular dipole moment and β is the second order hyperpolarizability.   Very weak intensity displayed by MBNA is further due to the rapid decay of the component of molecular dipole and transition dipole moments in the poled direction due to intramolecular rearrangement subsequent to poling.   There was delay of a few minutes before the SH signal of the poled film could be observed.   All NLO molecules in SAN matrix displayed the strongest SH signal and much weaker intensity in PS.

INSERT Figure 6

The decay curves for the SH signal for the guest host systems over long time scales clearly indicate two distinct decay rates. Measurements were carried out over 24 hrs and relatively flat portions of the curves over very long time scales are not shown in Figures 4 to 6. The following equation can be used to describe the decay of SH intensity

$$I = A\ e^{-\lambda_1 t}\ +\ B\ e^{-\lambda_2 t}$$
(iii)

where the constants, A and B, are dependent of the concentration of the NLO molecules, the thickness of the film and the poling field. Time constants, λ_1 and λ_2, represent two mechanisms of relaxation. The approach to estimate λ_1 and λ_2 is to assume that the more rapidly decaying first term has decayed after sufficient time. The second term alone is applied to the data after 12 hour and constant B and λ_2 are calculated by simply fitting intensity(I) against time(t). After B and λ_2 are obtained, the contribution from second term is subtracted from the experimental value of I and the remainder are fitted to another first order decay term to obtain A and λ_1.

INSERT Table I

Calculated values of λ_1 and λ_2 are listed in Table 1. The results indicate that both the first order parameters in the SAN matrix for all the active compounds studied is smaller than for the other

matrices. This establishes SAN as the best choice as a host material for all the active compounds studied in terms of the level of loading, stability of the poled film and the second harmonic intensity achieved. Long term decay constant, λ_2, is more or less same for all molecules in all the polymer matrices considered except for MNA in PMMA matrix where the decay continues to be fast.

Figure 6 summarizes the relaxation behavior of all the NLO molecules selected for the present investigation in the SAN host. SAN was found to be the best host for all the active compounds studied. Interestingly, prototypical compounds DR1 and MNA were *found to produce the most stable poled guest-host complexes with* SAN. Lower stability of MBNA has already been explained in terms of the fast decay of net dipole moment of MBNA through intramolecular rearrangement. The SH intensity from a poled film of M_2 in SAN is comparable to that of DR1-SAN guest host system prepared in the same manner. The two active compounds are also structurally very similar. Yet, the decay of SH intensity is significantly faster for the M_2-SAN poled complex compared to the DR-1 SAN system. Clearly the poled DR1 SAN complex is much more stable compared to the poled M_2-SAN complex. This is further evidenced in the absorption characteristics of these complexes as described in the following section.

Absorption   Characteristics

Optical dichroism and characteristic shifts in the spectral features of the poled guest-host systems have been described by Mortazavi et al[20].   All NLO molecules showed a red shift of 15 to 30 nm in λ_{max} in the polymer solid solution compared with their solution in a polar solvent Dichloromethane (Table 2).   This indicates a significant polymer-NLO molecule   interaction   (dipolar   and induced dipolar types) in the matrix. This points to the inadequacy of theoretical models that have been developed to describe the second order NLO properties of guest host system based upon non-interacting dipole models. The absorption maximum of the polymer film *is further shifted upon poling to longer wavelength which,* however, reduces slowly to the wavelength for the unpoled film due to the relaxation of the polymer matrix and the NLO molecules with time.

INSERT   Table   II

INSERT   Figure   7

Largest shift of 34nm in λ_{max} is observed for the poled complex of DR1-SAN compared with its solution in dichloromethane. A shift of 21nm for the poled complex of M_2-SAN indicates a much weaker complex. This partially explains the better stability of the poled DR1 SAN complex compared with the M_2-SAN complex.   Decrease in

absorption at λ_{max} can be a rough measure of the loss in SH intensity since both λ_{max} and SH intensity decay proportionally with time. Figures 7a and b describe the poling induced spectral shifts of poled films of DR-1 and MNA in SAN and PMMA. The results further indicate that the MNA relaxes faster in PMMA matrix than in SAN matrix, and the relaxation of DR-1 is fairly slow in both the matrices.

CONCLUSIONS

These investigations have established SAN as the best host material studied so far from the standpoint of high solubility of the active compound, strongest SH signal obtained for each dye system and the short and long term stability of the poled guest-host system. PS on the other hand is the poorest host material due to its incompatibility with the polar active compounds. Not only that a high level of loading can not be achieved, the poled complexes themselves are not stable. A notable exception to this is the case of MNA in PS. The poled complex has been found to be more stable than MNA in PMMA.

As expected molecules with the largest $\mu\beta$ lead to poled complexes with the strongest SH intensities. However, the role of the host polymer is equally important. Strongest SH signals were obtained when the guest-host interactions were the strongest. The mobility, polarity and the free volume of the polymer matrix, and the size, ground state dipole moment and the second order hyperpolarizability of the NLO molecules play an important role in designing novel guest-host systems. It is anticipated that the nonlinear interactions may be further optimized by suitable control of the comonomer ratio and distribution in the copolymer. This also provides a convenient handle on the tailoring of the index of refraction of the complex.

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Table 1. Time constants of the poled polymer films

Polymer	λ_1 (h^{-1})				λ_2 (h^{-1})			
	MNA	MBNA	DR-1	M_2	MNA	MBNA	DR-1	M_2
SAN	0.522	1.250	0.519	1.020	0.0034	0.0062	0.0031	0.0057
PMMA	0.766	0.800	0.656	---	0.0170	0.0069	0.0066	---
PS	0.723	0.921	0.721	---	0.0066	0.0031	0.0033	---

Table 2.   UV-VIS absorption of NLO molecules

Compounds	λ_{max} (nm)			
	Dichloromethane	PMMA[a]	SAN[a]	PS[a]
MNA	355.8	368.4 (372.2)	368.8 (372.5)	366.4 ---
DR-1	477.5	490.8 (497.5)	503.2 (511.2)	473.6 ---
MBNA	365.0	367.5 (379.0)	370.5 (377.8)	364.3 (370.1)
M_2	385.5	--- ---	401.8 (406.2)	--- ---

[a]

Values in the parentheses correspond to poled films measured immediately after poling.

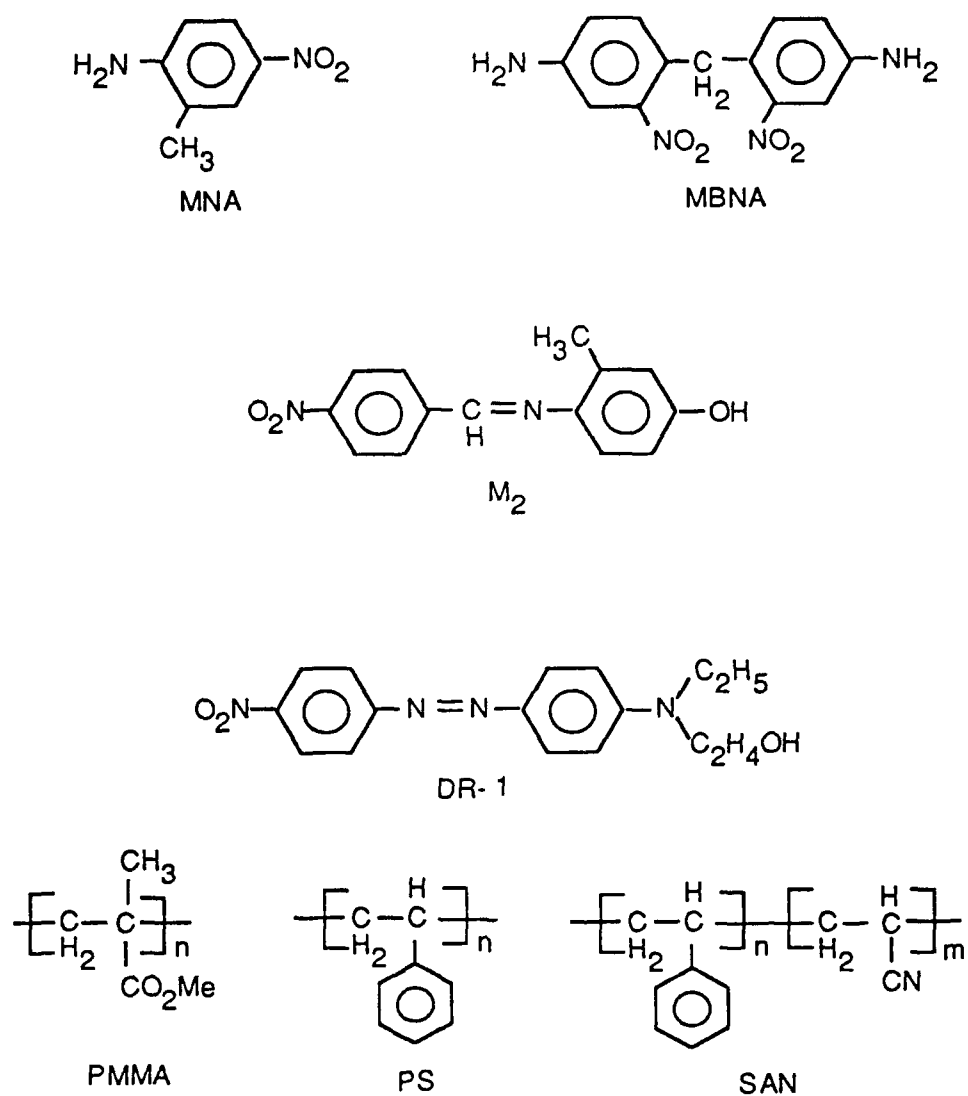# Legend to the Figures

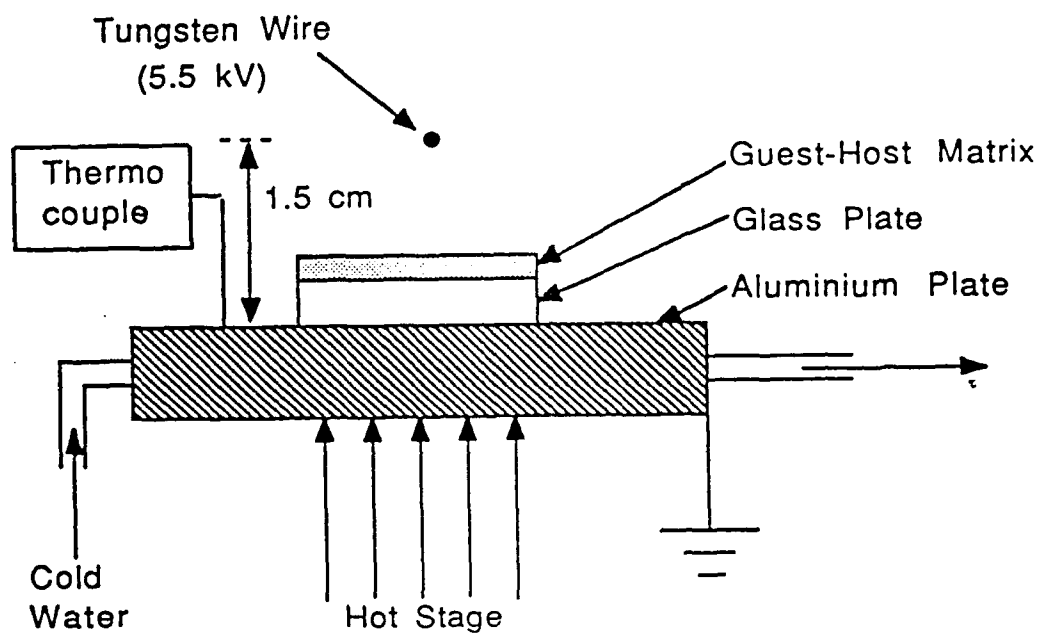Fig. 1.   Structures of selected guest and host molecules.

Fig. 2.   Experimental set-up for corona discharge poling.
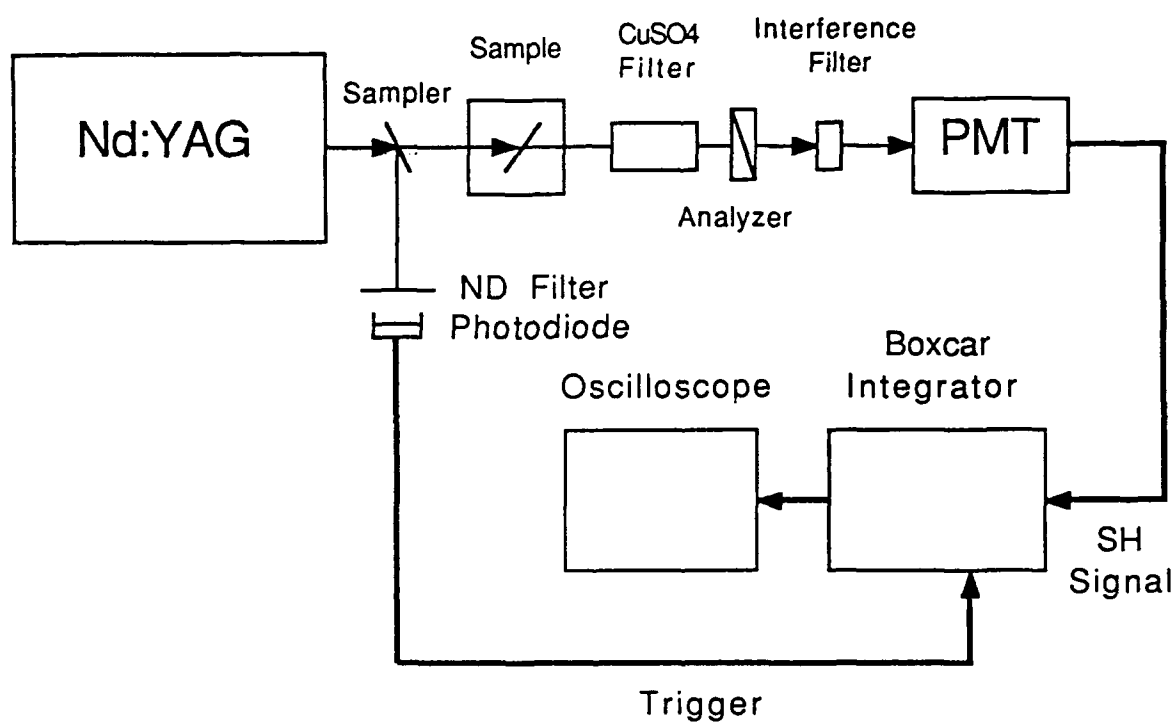
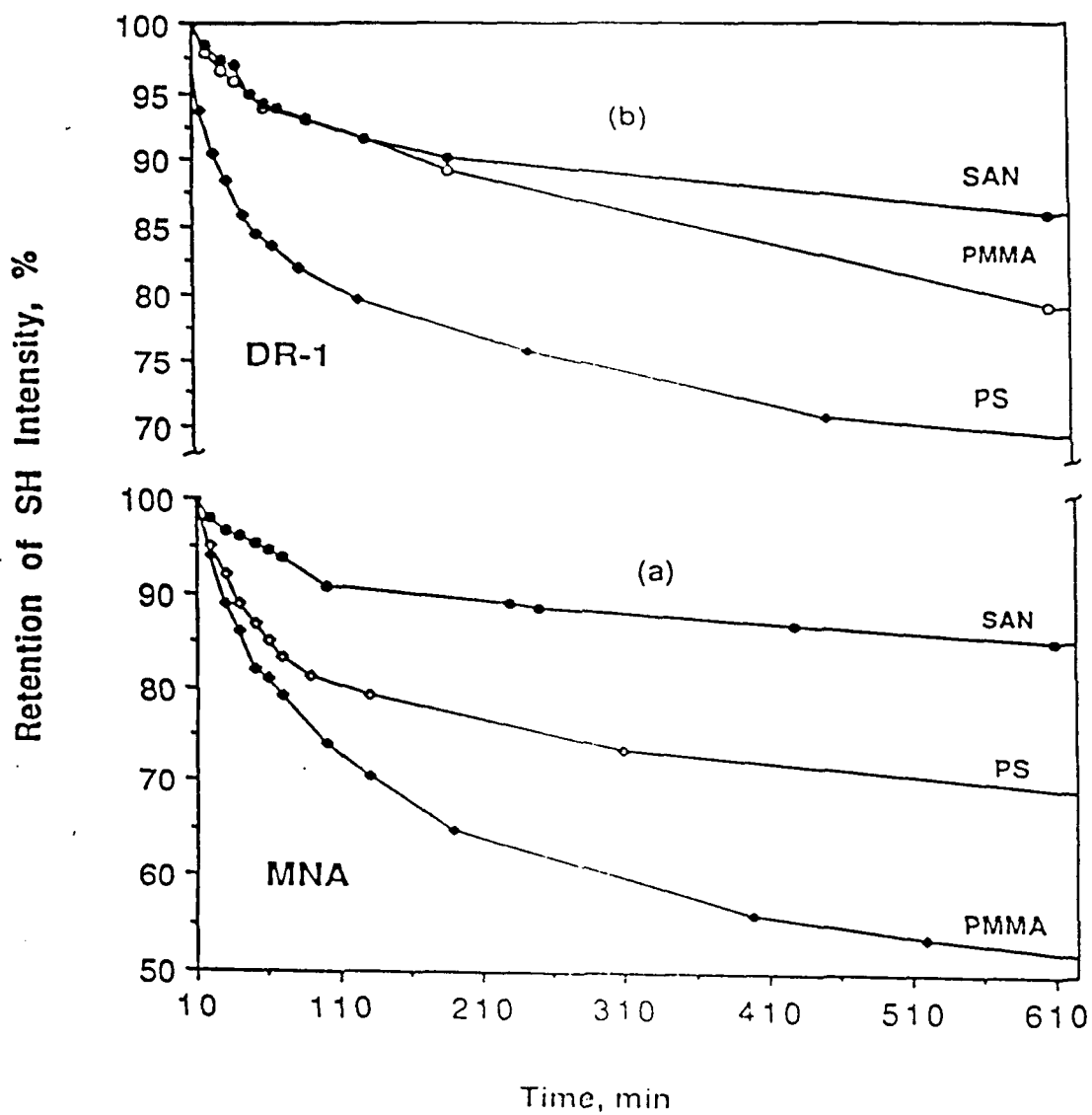Fig. 3.   Experimental set-up for SHG and intensity measurement.

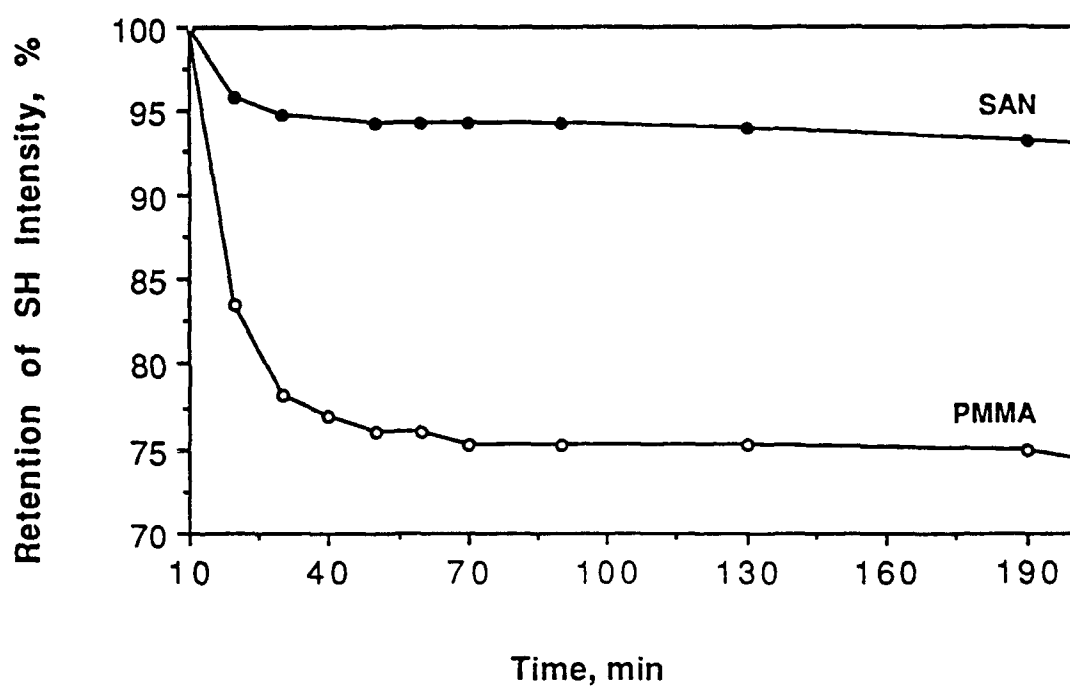Fig. 4.   Retention of SH properties of various guest-host systems with time.

Fig. 5.   Retention of SH intensity of poled polymer films with time.

Fig. 6.   Retention of SH intensity of SAN based films with time.

Fig. 7.   Absorption characteristics of the poled polymer films.

Legend to the Tables

Table 1. Time constants of the poled polymer films

Table 2. UV-VIS absorption of NLO molecules

Fig. 1. Structures of selected guest and host molecules.

Figure 2   Experimental set-up for corona discharge poling

Fig. 3.   Experimental set-up for SHG and intensity measurement.

Figure 4 Retention of SH properties of various guest-host systems with time

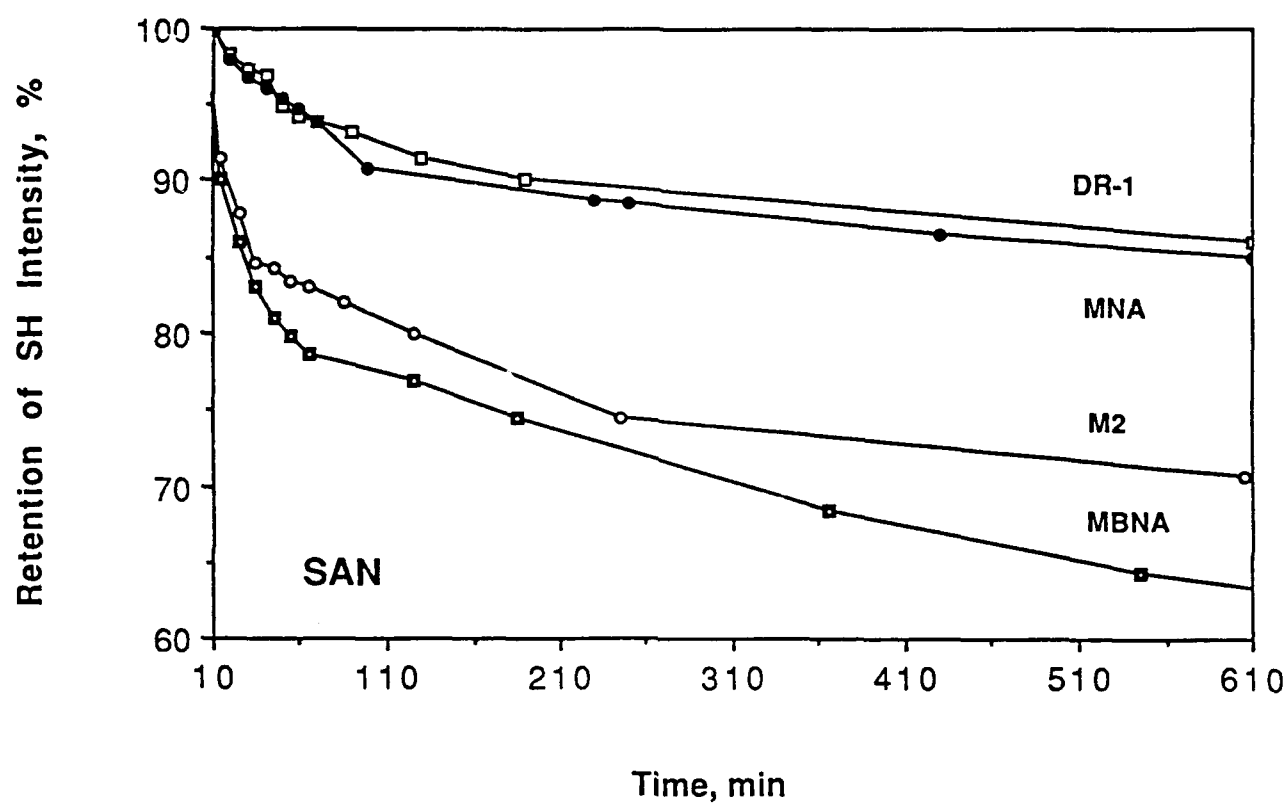Fig. 5.   Retention of SH intensity of poled polymer films with time.

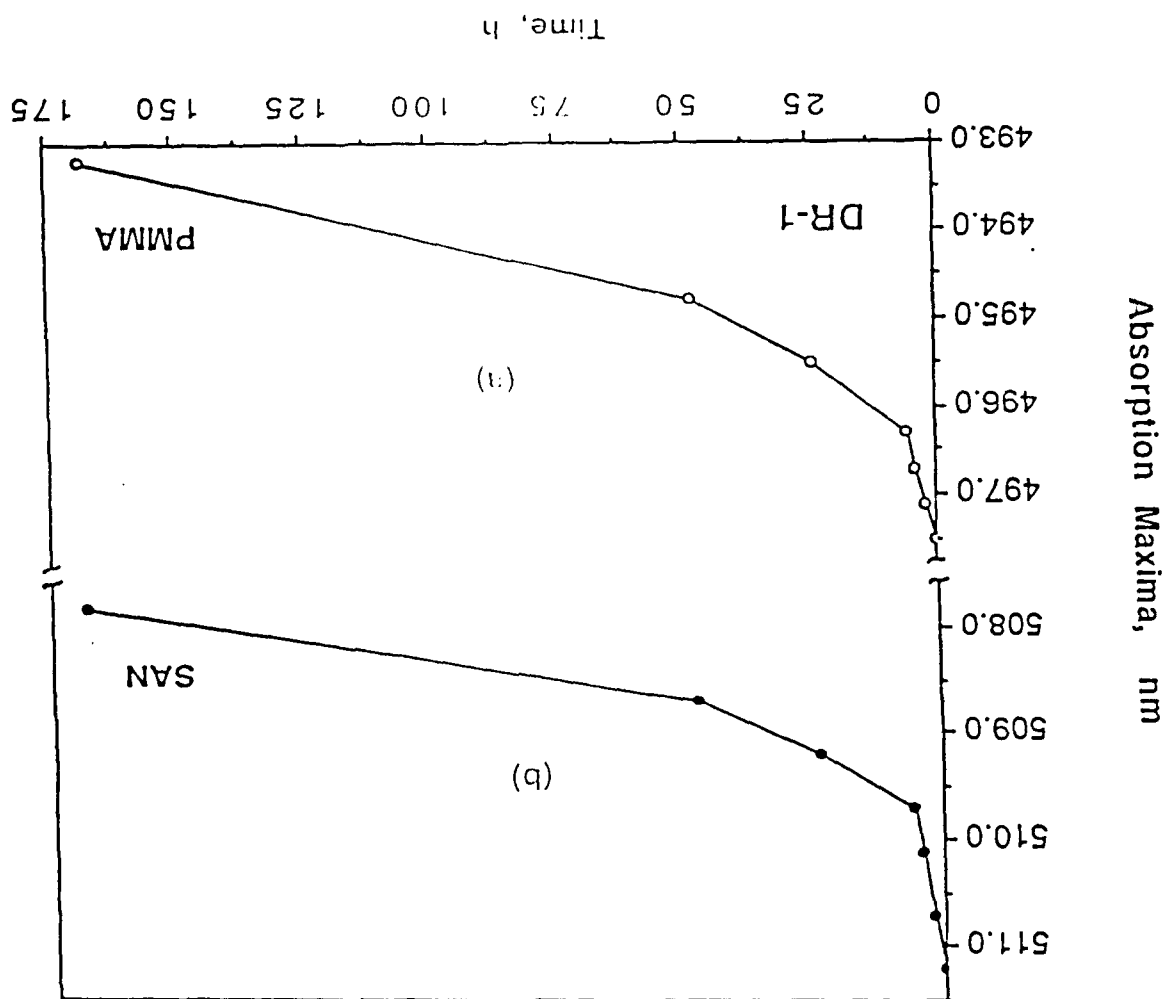Fig. 6.   Retention of SH intensity of SAN based films with time.

Figure 7 Absorption characteristics of the poled polymer films