Corona-poling of 4-BPMA/PMMA guest-host polymeric thin films

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Guest–host blends with dipolar chromophore, namely N-(4-benzoylphenyl)-2-methylacrylamide (4-BPMA) as guest and polymethylmethacrylate (PMMA) as host have been prepared and characterized by thermal and spectroscopic techniques. The prepared guest-host systems were found to be thermally stable with decomposition temperature within the range 309-327°C as determined by TGA. Thin films of these guest-host blends prepared by vacuum deposition techniques were corona-poled for the alignment of dipolar chromophores. Band gaps of guest-host blend thin film were found in the range 3.38-3.43 eV, indicating their insulating behaviour. The effect of poling voltage and poling temperature on poling efficiency was studied by UV/Vis spectroscopy. The temporal stability of aligned dipoles has also been investigated by studying the UV/Vis absorption spectra of polymeric thin films at different time-intervals.

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Keywords: Dipolar chromophore, Guest-host blend, Thin films, Optical study, Orientational stability

1. Introduction

Organic poled polymers [1-6] with dipolar chromophores have been attracting large interest in the field of nonlinear optics owing to their potential applications in photonics devices such as optical data storage, optical fibers for use in communications, second harmonic generator, optical switches, etc. The major advantages of such systems are their ultra fast optical response time, high laser damage threshold, high mechanical strength, excellent thermal stability and flexibility of chemical structure modification [7,8]. Design planning for achieving poled polymeric matrix includes synthesis and incorporation of dipolar chromophore in suitable polymeric system to maintain stable dipole alignment. These dipolar chromophores, imbedded in polymeric-matrix, are aligned by means of high DC electric field resulting into significant polar orientation and thus makes suitable for device applications. However, the primary impediment is that the chromophores tend to relax back to their random orientation and thereby decreasing the polar order. To probe the orientational stability of aligned dipoles, it is the basic requirement to study the various factors affecting poling efficiency as well as decay of polar order with time.

In the present study, we have reported the preparation and characterization of guest-host polymeric systems with varying concentrations (2-10 % by weight) of dipolar chromophore, N-(4-benzoylphenyl)-2-methylacrylamide (4-BPMA) as guest in the polymethylmethacrylate (PMMA) as host. The vacuum-deposited thin films of guest-host-matrices were poled using corona poling technique under different poling conditions to study the effect of poling voltage and poling temperature on poling efficiency. Since the molecular dipoles have a tendency to relax with time, the variation of polar order with time was studied to investigate the orientational stability of aligned dipoles.

2. Experimental

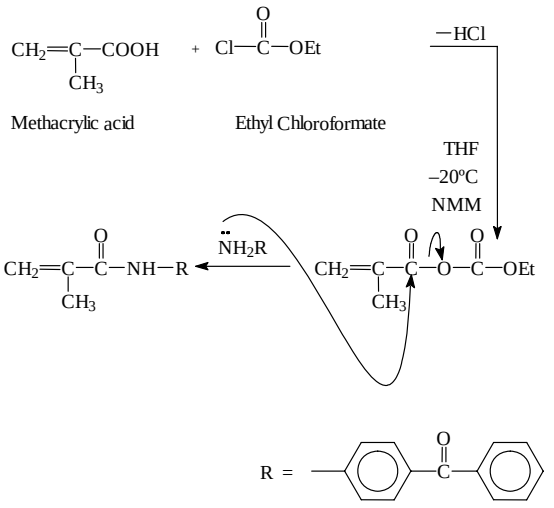
The synthesis of the dipolar chromophore, N-(4-benzoylphenyl)-2-methylacrylamide has been described in our earlier paper [9]. Guest-host polymeric systems of dipolar chromophore 4-BPMA (guest) and PMMA (host) were prepared by dissolving different concentrations of guest and host in dichloromethane separately and then mixing to get homogenous solution. The solvent was evaporated at room temperature and then the resulting guest-host systems were dried on water bath for about 10 hrs. The amount of guest was taken 2, 4, 6, 8 and 10 % by weight of PMMA as host to yield 2 -10 % guest-host systems.

I.R. spectra were recorded on BUCK SCIENTIFIC M 500 spectrometer. ^{1}H NMR spectra were recorded on BRUKER DRX 300 MHz NMR spectrometer with TMS (tetramethylsilane) as the internal reference. Thermogravimetric (TG) studies were carried out by Perkin Elmer (Pyris Diamond) thermal analyzer at the heating rate of 10°C/min under nitrogen gas atmosphere. Thin films (thickness of the order of ~ 100 nm) of the guest-host systems, with different concentrations of guest were grown on the cleaned quartz glass slides by vacuum deposition technique at a vacuum of 10^{-6} mm/Hg with the help of high vacuum coating system (NIRVAT EU-300). The vacuum deposited thin films of different guest-host systems were poled under different poling conditions using optimized high potential multi-point corona poling technique to create directional polarization of the

chromophores. The optical UV/visible spectra of these thin films were recorded with the help of Shimadzu UV-2500 PC spectrophotometer attached to integrated sphere assembly (ISR-240 A).

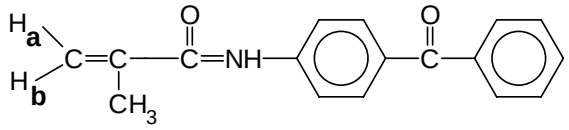
3. Results and discussion

4-BPMA as dipolar chromophore has been synthesized according to scheme-I.



Scheme 1: Synthesis of chromophore N- (4-benzoylphenyl)-2-methylacrylamide.

The structure of the chromophore was confirmed by IR, ^{1}H NMR and mass spectroscopy. The following spectral data were obtained:



Structure of 4-BPMA

IR (KBr):
3322.4 cm^{-1} (N-H str.), 1686.2 cm^{-1} (C=O str.,aryl conjugated), 1643.8 cm^{-1} (C=O str.,amide),1590.6 cm^{-1} (C=C str.),

^{1}H NMR (300M Hz, $CDCl_3$)
δ: 2.07(s, 3H,C-CH_3), 5.51(s, 1H,H-1**b**), 5,84(s, 1H,H-1**a**), 7.45-7.84(m, 9H,Ar-H), 7.91(brs, 1H,N-H),

Mass (m/z): 266 (M^++1)
The above spectral data strongly support the proposed structure of the chromophore.

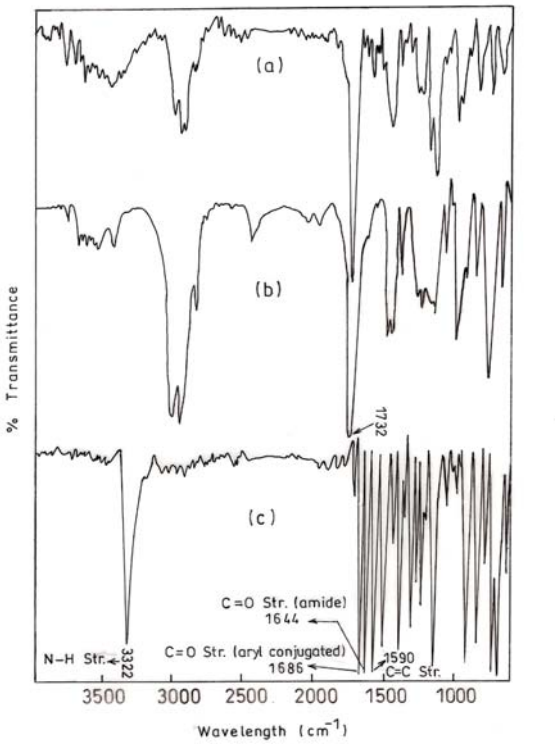


Fig. 1. IR spectra of 4 % guest-host matrix (a), PMMA (b) and guest (c).

The IR spectrum of pure host (PMMA) shows C=O absorption around 1732 cm^{-1} whereas C=O absorption frequencies of pure guest occurs around 1686 cm^{-1} (aryl conjugated) and 1644 cm^{-1} (amide) [Fig. 1]. The guest-host blends show the bands around 1632 cm^{-1} and 1664 cm^{-1} with very low intensity due to low concentration of the guest in the blend. The absorption frequency occurred around 1632 cm^{-1} might be because of carbonyl group in amide linkage. Therefore guest-host blends carbonyl frequencies in amide linkage are shifted to lower value compared to that of pure guest (1644 cm^{-1}) indicating the formation of hydrogen bonds between C=O group of host and –NH- of amide linkage in guest. However, the absorption frequency of C=O group in PMMA retained its position in guest-host blend because of low concentration of guest.

One of the most important parameters of poled polymers suitable for device applications to have long lifetime is its thermal stability. TG thermograms in concentration 2-10% of these guest-host blends from ambient temperature to 700 ºC in N_2 atmosphere were recorded. However for better clarity these thermograms (2, 6, 10% as for illustration) in the temperature range of 280-430 ºC are shown indicating their high thermal stabilities (Fig. 2).

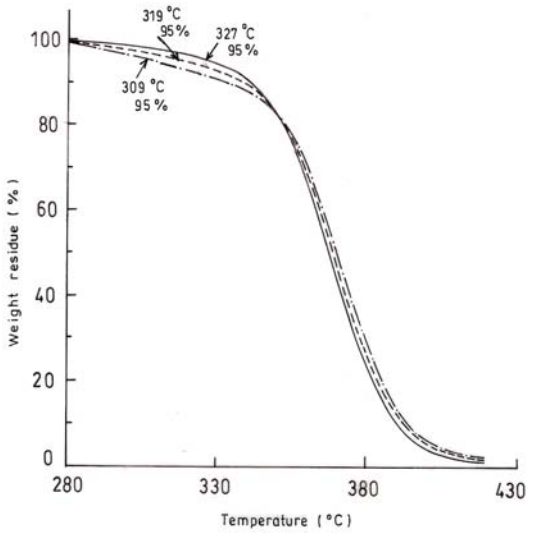


Fig. 2. TG thermograms of 2 % (———), 6 % (- - - - - -) and 10 % (— — — —) guest-host matrix.

Moreover, decomposition temperature of these guest-host blends is observed to decrease with increase in concentration of guest in PMMA, although the decrease is not so high. The decomposition temperature of 2% guest-host blend is 327 °C whereas it is 309 °C for 10%.

For these materials to be useful in practical applications, these must be transparent in visible region. Therefore, to study their transparency in the visible region, UV/Vis absorption spectra of the guest-host blends were recorded in the form of thin films. Their absorption spectra reveal that their maximum absorption occurs around 306 nm, which is out of the absorption region of the fundamental wavelength (1064 nm) as well as second-harmonic generation (SHG) wavelength (532 nm) that is generally employed in second harmonic generation experiments. Thus, in these guest-host blends, we expect to observe only nonresonant contributions to SHG.

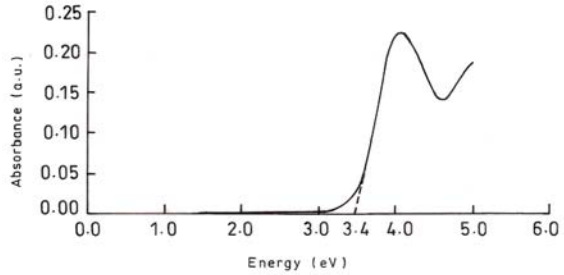


Fig. 3. Direct band gap of 4-BPMA/PMMA guest-host matrix (6%).

The optical energy band gap of the guest-host blend 4-BPMA/PMMA was determined using the relation [10]

$$\alpha = (h\nu - E_g)^{1/2} \text{ (for direct band gap)} \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the incident energy and E_g is the energy band gap.

The energy band gaps of various guest-host blends have been established around 3.38-3.43 eV, indicating their insulating behaviour. As an illustration, energy band gap for 6% guest-host matrix is shown in Fig. 3.

To understand the effect of poling, the thin films of guest-host matrices were corona poled to orient the different dipolar chromophores in proper direction. The degree of poling could be identified by several methods. Among these, the absorption change in UV/Vis spectra is common. The absorption spectrum of the polymeric system changes with electric field poling. The order parameter (ϕ), which is used to characterize poling efficiency, can be determined by the following equation

$$\phi = 1 - A_\perp / A_O \quad (2)$$

where A_O and $A_\perp$ are the absorbances of the polymer film before and after corona poling.

The effect of poling voltage on poling efficiency of guest-host-blends has been studied under varying electric field at 60 ºC for 30 min. Fig. 4 shows the UV/Vis absorption spectra of the thin films of guest-host matrix (6%) before and after poling at different voltages (only for 2 kV and 4 kV are shown), indicating decrease in absorbance after poling.

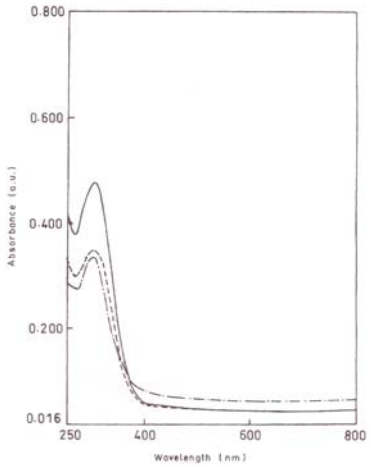


Fig. 4. UV/Vis absorption spectra of 6 % guest-host matrix, before poling (———) and after poling at (60 ℃, 30 min.) under different voltage 2 kV (- - - - - -), 4 kV (— · — · —)

This decrease in absorption can be explained on the basis that after electric poling, the dipole moments of the dipolar chromophores were aligned and hence the UV/Vis maxima of the guest-host blend shows decrease in absorption. Similarly, decrease in absorption maxima were also observed for other guest-host matrices (2%, 4%, 8%, 10%). To determine poling efficiencies, order parameters were calculated using the relation (2). Fig. 5, showing the variation of order parameter with electric field, indicates

that as the poling voltage increases from 2 kV to 5 kV, the order parameters for various guest-host polymeric thin films increases from 0.254–0.268 to 0.290-0.315.

The effect of temperature on UV/Vis absorption spectra of the guest-host blends was also studied. Guest-host thin films were poled under electric field of 5 kV at different poling temperatures (30 °C, 45 °C, 60 °C and 90 °C) for 30 min.

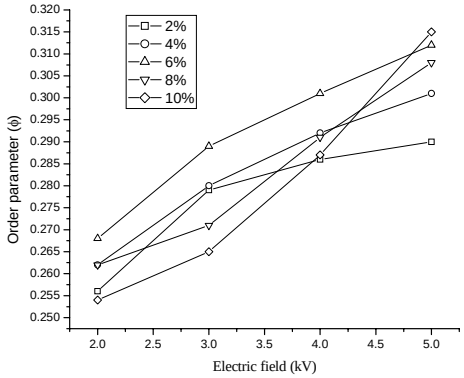


Fig. 5. Variation of order parameter of guest-host matrices with voltage under poling conditions (60 ℃, 30 min.)

As shown in fig. 6, the order parameter at 30 ºC is 0.241-0.246 that increases to 0.384-0.401 at 90 ºC indicating the poling to be more efficient at higher temperature.

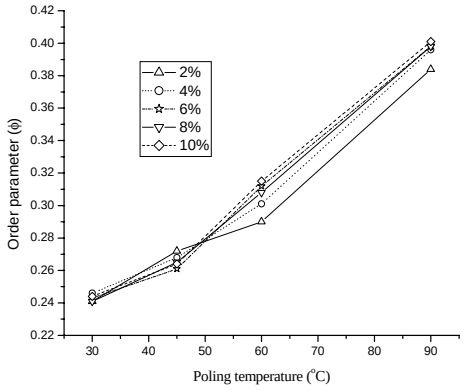


Fig. 6. Variation of order parameter of guest-host matrices with temperature under poling conditions(5 kV, 30 min.).

This can be explained on the basis that at higher temperature movements of the chromophores increases and hence their alignment can take place with more ease in the presence of applied electric field.

One of the problems to be overcome with regard to practical applications in polymeric materials is the relaxation of aligned dipoles. Therefore, we have studied the poling stability of the aligned dipoles by taking the UV/Vis absorption spectra of corona poled guest-host systems with different intervals of time. It was observed that order parameter decreased with time but the decay was more initially and negligible after some days.

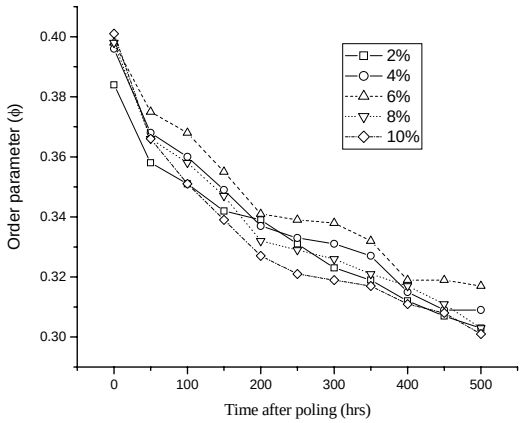


Fig. 7. Temporal stability of dipole alignment for guest-host matrices at room temperature after poling at (5 kV, 90 ℃, 30 min).

The hydrogen atom of the amino group on the chromophore N-(4-benzoylphenyl)-2-methylacrylamide forms hydrogen bonding with carbonyl group of PMMA, resulting good temporal stability of poling induced alignment. Under the poling conditions of (5 kV, 90°C, 30 min.), the order parameters for various guest-host blends were 0.384-0.401 and remained up to 0.358-0.375 (5.8-8.7% decay) after 50 hours at room temperature in air (Fig. 7). The decayed amount was only 20.4-24.9% of their original value even after 500 hours of poling.

4. Conclusions

Guest-host blends with dipolar chromophore possessing good thermal stabilities have been prepared. The prepared guest-host systems have been found to be transparent in visible region. The band gaps of the guest-host systems were in the range 3.38-3.43 eV, indicating their insulating behaviour. It was found that poling efficiency increases with poling voltage as well as poling temperature. The resulting poled polymeric thin films have been found to possess good temporal stability of aligned dipolar chromophores.

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