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Studies of Host-Guest Thin Films of Corona-Poled Betaine-Type Polar Molecules by Kelvin Probe Technique and Atomic Force Microscopy

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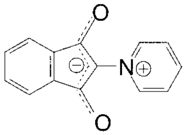
Summary: In this work betaine-type molecules were investigated. As a result of the asymmetry of charge distribution, molecules possess in the ground state a considerable permanent dipole moment. The decay of surface potential of poled polymer films is dependent at least on two relaxation processes. The influence of glass transition of PMMA on thermal dependence of the surface potential is shown. The transition temperature, where no changes of the surface potential appeared, is related to glass transition temperature of the host-guest system. The topography of the film surface was obtained by AFM.

Keywords: AFM; corona poling; host-guest systems; polar dyes; relaxation; surface potential

Introduction

Organic dye-doped materials have received considerable attention because of their large dipole moments and optical nonlinearities. Dipole electrets for photonic applications contain chromophore dipoles, which consist of acceptor and donor groups linked by a bridge of delocalized π-electron system. In this work *N*-(1,3-dioxoindan-2-yl)pyridinium betaine (IPB) molecule was investigated. As a result of the asymmetry of charge distribution, molecules possess in the ground state a considerable permanent dipole moment of 4.5 D[1,2]. In our experiments, host-guest, which have obvious advantages of synthetic simplicity, were chosen. Optically transparent poly(methyl methacrylate) (PMMA) was used as host. The high-electric field corona poling was used to generate dipole orientation of dye molecules in polymer matrices. The topography of the film surface was obtained by



IPB

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atomic force microscopy (AFM). In order to investigate the changes of the surface structure, the samples were measured as prepared, after corona poling and after thermal treatment.

Experimental

Isotactic PMMA with molecular weight 440 000 as host was used. IPB was dissolved in PMMA at a concentration of 1 wt %. The glass transition temperature, $T_g = 52 \pm 1$ °C, was obtained by differencial scanning calorimetry. Chloroform was used as solvent to deposit cast films onto gold and ITO electrodes. The thickness of the film was between 0.14 and 1.1 μm.

The high-electric field corona poling was used to generate dipole orientation of IPB molecules in polymer matrix. The corona poling of PMMA and IPB/PMMA films was performed according to Ref.[3]. A high voltage of 4 – 8 kV was applied to a tungsten wire (diameter 25 μm) at the 1 cm distance from the sample surface. During the poling procedure, which continued for 10 min, the corona current was constant, at 1 μA. The poling temperature of IPB/PMMA film was constant in the range 50 – 95 °C. The poling temperature of PMMA film was about 60 °C. The samples were corona-poled through a mask with diameter 1 cm and cooled to room temperature at applied electric field maintaining a constant current.

The changes of the molecular dipole moment of betaine molecules change the surface potential ΔU_S of the host-guest films. The measurements of the surface potential were made by the Kelvin probe technique[4]. The surface potential was measured as the difference between the surface potentials of the grounded bottom electrode and the film. Thermal dependence of the surface potential was measured between 20 and 120 °C. The heating rate was about 8.5 °C/min.

A home-made AFM in the contact mode was used in experiments. The AFM cantilever tips were from standard silicon nitride. The force constant of cantilever, measured using calibrated cantilevers, was around 0.1 and 0.16 N/m for cantilevers with two different dimensions. The typical tip radius was 30 nm.

Topography of polymer films

The topography of the film surface was obtained by AFM. The roughness of the surface was characterized by the amplitude parameter, namely the root-mean-square value S_q. Both

IPB/PMMA and PMMA films exhibited very smooth surface over range 1 × 1 μm. The evaluated roughness S_q was of ~ 0.4 nm for PMMA and ~ 0.5 nm for IPB/PMMA films (see Table 1). No influence of the substrate on the quality of films was observed.

Table 1. The root-mean-square parameter S_q of as-prepared, poled and annealed PMMA and IPB/PMMA films.

Compound	**Substrate**	**S_q (nm)**		
		unpoled	poled	annealed
PMMA	Au	0.4	12.3	0.5
IPB/PMMA	Au	0.5	8	1.8
PMMA	ITO	0.4	3.7	0.6
IPB/PMMA	ITO	0.6	3	1.0

The surface of the corona-poled polymer films drastically changed and the value of S_q increased. In the case of PMMA the structure of the film was with regularly distributed pinholes. The roughness increased several times. In the case of IPB/PMMA films, the increase was lower.[5] As shown in Ref.[6], the corona discharge promoted the rapid diffusion of polar molecules away from the polymer matrix. In our case polar IPB molecules could diffuse to the surface of the film and, due to large permanent dipole moment, the formation of dimers or crystallites of IPB molecules might appear. After annealing above the glass transition temperature, the surface of the films became smooth again.

Surface potential measurements

Surface potential U_s studies provide useful information regarding both structural and electronic properties of oriented films[7,8]. The surface potential of the film depends on both the packing density and orientation of molecules. The film is treated usually as a uniform assembly of molecular dipoles giving rise to polarization of the layer. The surface potential can be related to the dipole moment normal to the plane of the film $\mu_X = \varepsilon\varepsilon_0 A U_S$, where A is the average area occupied by the molecule[8].

The surface potential measurements were performed in the ambient atmosphere mainly on the day after poling. The surface potential of the host-guest film changed going from the unpoled to poled region of the film. In the case of IPB/PMMA films, the surface potential increased from some mV in the unpoled region to several volts in the poled region. The unpoled polymer is isotropic due to random distribution of polar molecules in the polymer matrix. The total dipole moment of the film is close to zero and the value of surface potential is negligible. The increase in the surface potential indicates that orientation of polar molecules is possible in the polymer. For applications, it is important that the highly poled order is maintained for a considerable time. So the efficiency and persistence of alignment and studies of relaxation rates are of considerable interest. As shown in Figure 1, a decay of the surface potential of poled PMMA and IPB/PMMA films has been observed. The decay of the surface potential is well represented by the sum of two exponential terms $U_S = A\exp[-t/\tau_1) + B\exp(-t/\tau_2)$, where τ_1 and τ_2 are the time constants of two relaxation process, a faster and slower one.

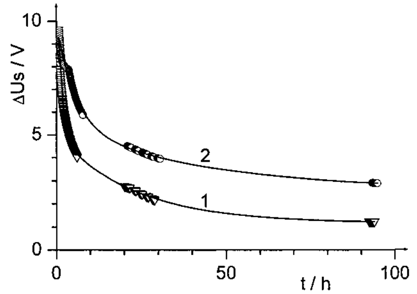

Figure 1. Decay of surface potential of corona-poled PMMA (∇) and IPB/PMMA (o) films fitted with bi-exponential functions.

The initial faster decay of the surface potential in the case of the IPB/PMMA host-guest was $\tau_1 \sim 6$ h. In the case of pure PMMA film, the decay was faster, $\tau_1 \sim 1.4$ h. According to studies of the decay of nonlinear optical properties[9], the initial faster decay of the surface potential may be related to the rotation of other polar molecules in the polymer matrix. At the same time, decay of a surface charge, which arose during corona poling, decreases both the intensity of the SHG signal and the surface potential. The slower process, with $\tau_2 = 43$ h for IPB/PMMA and $\tau_2 = 23$ h for PMMA samples, may be due to thermal relaxation of the polymer matrix. The time constants of the decay of SHG coefficient, d_{33}, was measured in poled host-guest PMMA films. In the case of Disperse Red 1 as guest molecules, the time constants are of the same order $\tau_1 \sim 0.4$ h and $\tau_2 = 10$ h[10].

Temperature dependence of the surface potential of both PMMA and IPB/PMMA poled films was measured in the range from room temperature up to 120 °C. In order to compare the temperature changes of the surface potential, the top vibrating electrode was situated on both films, where the values of surface potential is $\Delta U_S = -1$ V at room temperature. During heating the surface potential $\Delta U_S(T)$ was continuously monitored. As seen from Figure 2, curve 2, the surface potential of IPB/PMMA poled film increased on heating reaching a maximum at ~ 50 ± 5 °C. The maximum around 50 °C is observed also in the $U_S(T)$ dependence of a poled PMMA film (Figure 2, curve 1).

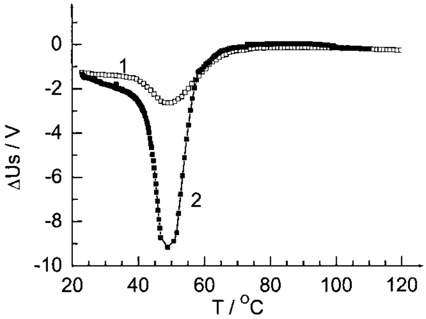

Figure 2. Thermal dependence of the changes of the surface potential of corona poled PMMA (1) and IPB/PMMA (2) films.

The maximum at ~50 °C is associated with glass transition process of the host isotactic PMMA polymer[11,12], where the reorientation of molecular dipoles may take place. In the case of the PMMA film, the changes of the surface potential are comparatively smaller than that of the IPB/PMMA film. After reaching the maximum, the value of the surface potential rapidly decreases with temperature close to zero. In the temperature range 70 – 100 °C, a broad and small peak of the changes of surface potential appeared. At higher temperatures, the signal of surface potential is small and no changes are observed. Above the glass transition temperature the orientation of molecules becomes random and the total dipole moment of the film approaches zero. Similar behavior of the $U_S(T)$ dependence of an IPB/PMMA poled film was observed. In this case, the surface potential approached zero at lower temperatures in comparison with the PMMA film. According to Ref.[12], the dipole moment of PMMA is 1.39 D and interaction with dipoles of IPB molecules may influence the thermal dependence of surface potential of the host-guest film.

As mentioned above, investigation of the glass transition temperature of host-guest films is of great importance both for corona-poling and surface potential measurements. This is especially important in the case of a new host-guest system. Generally, the glass transition temperature of polymer is obtained by differential scanning calorimetry. At the same time, several other experimental methods such as ellipsometry, x-ray reflectivity, second harmonic effect (SHG) characterize the glass transition temperature[6,13,14]. It is shown that the SHG signal delayed and disappeared completely, when the sample is heated above its glass transition temperature[6,14]. As follows from the temperature dependence of the surface potential, the drop-off surface potential signal might be characterized by the glass transition of system.

Conclusions

Corona-poled host-guest films with PMMA as host and *N*-(1,3-dioxoindan-2-yl)pyridinium betaine as guest show a considerable increase in the surface potential. The increase in surface roughness and formation of grains of the corona-poled films are shown.

An influence of glass transition of PMMA on the thermal dependence of surface potential is observed. The thermal dependence of the surface potential of poled films shows a drop-off of the surface potential at a temperature, which is related to the glass transition temperature of the host-guest system.

Acknowledgments

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