

# Effect of Electrical Field on Dipoles in Polymer Composites

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**ABSTRACT:** Orientation of two bipolar compounds embedded in polymer composites was studied. Poly(methyl methacrylate) (PMMA) dissolved in acetone was doped with a cobaltborane derivative of 1,2-dimethylimidazole and polystyrene (PS) dissolved in toluene was doped with the 3-(1,2-dimethyl imidazole)-borane. To orient the dipoles, the composites were exposed to external electrical field: PMMA composite at the temperature of glass transition ( $T_g$ ) and PS composite during evaporation of the toluene solvent. The degree of dipole orientation was estimated by the change in relative permittivity ( $\epsilon$ ) of the resulting composite film. The dependence of the  $\epsilon$  on the temperature, frequency, voltage, and dipole concentration was studied. It was found that the

dipole's distribution in the composite film was not homogeneous. At the  $T_g$ , the dipoles in PMMA became oriented by external direct electrical field and the orientation was conserved after cooling to lower temperatures. In a PS-based composite, the significant permittivity increase was observed already at low-dopant concentrations. The dipole orientation achieved during solvent evaporation was also permanent and the composite permittivity was an increasing function of the film thickness. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 40–45, 2004

**Key words:** poly(methyl methacrylate); polystyrene; composites; dipoles orientation; permittivity

## INTRODUCTION

Most polymers are typical dielectrics which can be polarized by an external electrical field. The polarization in polymers is contributed by two basic components, deformation (electronic and atomic) and orientation components.<sup>1</sup> Basic parameters characterizing a dielectric are permittivity  $\epsilon$ , electrical conductivity  $\sigma$  (S/m), dielectric loss tangent  $\text{tg}\delta$ , and dielectric strength  $E_p$  (V/m) (see ref. 2).

For some applications, the polymer polarity ought to be enhanced. This can be done in several ways, namely:

1. By using some of polar polymers such as poly(methyl methacrylate) or poly(vinyl alcohol);
2. By suitable modification of polymers, either chemical (e.g., by sulfonation of polysulfonates<sup>3</sup>) or via the same high-energy processes (e.g., ion irradiation, laser irradiation, or plasma etching<sup>4</sup>);

3. By copolymerization of different monomers (e.g., polyurethane with nitroaniline chromophores,<sup>5</sup> methyl methacrylate, and ethyl methacrylate with *N*-vinylcarbazole<sup>6</sup>);
4. By preparation of polymer–polymer composites (e.g., based on polystyrene or polypyrrole particles<sup>7</sup>), polymer–inorganic additive [e.g., poly(vinyl alcohol) doped with nanosized  $\text{CoFe}_2\text{O}_4$  particles,<sup>8</sup> poly(tetrafluoroethylene) doped with  $\text{CaF}_2$  particles,<sup>9</sup> polystyrene doped with AlN (see ref. 10), or fluorinated polymers doped with  $\text{PbTiO}_3$  particles<sup>11,12</sup>];
5. By dissolving a low-molecular bipolar compound in a polymer<sup>13</sup> (and this study).

Polymers and doped polymer films which can be polarized in an external electrical field find applications as sensors sensitive to mechanical vibrations, temperature changes,<sup>12</sup> or moisture.<sup>14</sup>

In this work, the properties of polymer composites containing boron-based bipolar molecules are studied with respect to the possibility of permanent orientation of dipoles by external electrical field. The following two experimental procedures were chosen: (1) dipole orientation in the temperature region around the glass transition temperature and subsequent cooling to room temperature; and (2) dipole orientation under external electrical field during solvent evaporation in the course of the composite film preparation.

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The degree of the dipole orientation was estimated from changes in relative permittivity.

### EXPERIMENTAL

Present experiments were performed on poly(methyl methacrylate) (PMMA) and polystyrene (PS) supplied by Goodfellow (Cambridge, UK). The glass transition temperatures of PMMA and PS, determined by DSC technique, were  $T_g = 112^\circ\text{C}$  (glass transition interval measured from  $95$  to  $126^\circ\text{C}$ ) and  $104^\circ\text{C}$ , respectively.

The bipolar dopant, (1) MIMIDIOX, {8-[3-(1,2-dimethylimidazolium)ethoxy-ethoxy]-3-cobalt-bis(1,2-dicarbolyde)}<sup>0</sup> resulted quantitatively upon ring cleavage of the 8-dioxane-cobalt-bis(dicarbolyde) (see ref. 15) by a slight excess of 1,2-dimethyl-imidazole in dichloromethane (2 min at  $40^\circ\text{C}$ ); heavy orange oil from dichloromethane under hexane, solidifying to a brittle orange glass under hexane;  $R_f = 0.52$  (TLC on SILUFOL SiO<sub>2</sub>-layer, acetonitrile/chloroform 1 : 2 v/v as eluant),  $m/z = 510$  (heated inlet, electron impact ionization), compatible with B<sub>18</sub>C<sub>13</sub>H<sub>37</sub>N<sub>2</sub>O<sub>2</sub>Co.

<sup>1</sup>H-NMR (in deuteroacetone): C—H carborane 4.23 ppm (s, 2H); 4.17 ppm (s, 2H); spacer <sup>1</sup>H signals: 3.61 ppm (m, 4H, 2 —O—CH<sub>2</sub> groups), 3.41 ppm (m, 2H, —O—CH<sub>2</sub> group), 1.35 ppm (m, 2H, —CH<sub>2</sub> a group); imidazolium moiety: 6.87 ppm (s, 1H), 6.63 ppm (s, 1H), 3.58 ppm (s, CH<sub>3</sub>—), 2.52 ppm (s, CH<sub>3</sub>—). <sup>11</sup>B-NMR (just the most significant B<sub>(8)</sub> and B<sub>(8')</sub> signals are shown here; the eight remaining signals are omitted for clarity): 23.56 ppm (s, 1B) and 4.95 ppm (d, 1B).

The bipolar dopant, (2) DIMIBOR, 3-(1,2-dimethyl imidazole)-borane resulted in ~95% yield upon heating triethylamineborane with an equivalent of 1,2-dimethylimidazole to  $80^\circ\text{C}$  for 2 h at 130 Pa (ligand displacement approach).

Colorless prisms, m.p.  $115^\circ\text{C}$ ,  $R_f = 0.18$  (chloroform),  $m/z = 110$  (corresponding to BC<sub>5</sub>H<sub>11</sub>N<sub>2</sub>). <sup>1</sup>H-NMR (in deuteroacetone): 6.94 ppm (s, 1H), 6.75 ppm (s, 1H), 3.60 ppm (s, CH<sub>3</sub>—), 2.44 ppm (s, CH<sub>3</sub>—), 2.08 ppm (m, BH<sub>3</sub>); <sup>11</sup>B-NMR: -21.22 ppm (q, 1B).

Both polymers were doped from a solution. PMMA dissolved in acetone was doped to 0–30% concentrations with MIMIDIOX. PS dissolved in toluene was doped to 0–10% concentrations with DIMIBOR.

For the present experiments, 800- to 1000-nm-thick films of pristine and doped PMMA were prepared by common spinning onto a glass substrate. It is supposed that for such film thickness interfacial effects are reduced. The PS films, 1000- to 2000-nm-thick, were prepared on polished brass (circular samples 48 mm in diameter) by spontaneous evaporation of the parent solution. The film thickness was measured by a profilometer. For capacitance measurement, the PMMA film was provided with seven gold contacts on the back and front side. PS films on brass backing were provided with 79 gold contacts on the front side (the brass backing serves as opposite contact). The 80-nm-thick contacts, 2-mm<sup>2</sup> active area, were prepared by

vacuum evaporation. The contacting procedure showed a 60–70% yield and short-circuiting appeared scarcely. It could, therefore, be assumed that the films prepared by this procedure were continuous. The relative permittivity  $\epsilon$  of the films was determined (error  $\pm 10\%$ ) from capacitance measurements by using a standard LCRG (L=inductivity, R=resistivity, C=capacitance, G=conductivity) capacitance meter working at 100-Hz frequency and 1-V voltage.

Dipole orientation under external electrical field in PMMA composite was studied at elevated temperatures in the  $T_g$  region. For PS-based composites, the measurements were accomplished at room temperature during solvent evaporation. The permittivity temperature dependence for PMMA composite in the 20–120°C interval was measured in a thermostat. The temperature was increased at a speed of  $1^\circ\text{C}/\text{min}$  and, after reaching the temperature maximum, the thermostat was switched off and the sample was left to cool down spontaneously. In such a regimen, the room temperature was achieved after 2 h. The orientation of the bipolar dopant took place under an external voltage of 0, 1, 5, and 10 V, respectively.

In the case of PS composites, the parent solution on brass backing was left to evaporate spontaneously in an electrical field between conductive backing and a grid electrode placed at a distance of 4 mm above the backing. The voltage between the backing and the electrode was either 0 or 2.5 kV. The initial amount of the solution was chosen to obtain the final film thickness of 1000–1500 nm.

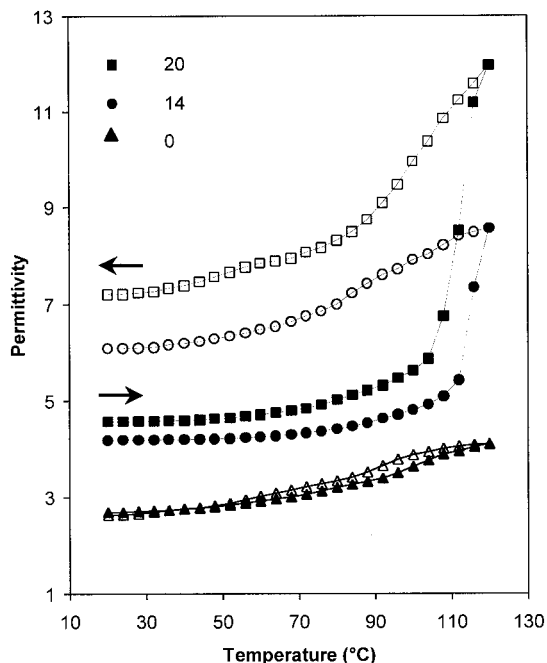
Up to now we have not been able to prepare, in a reproducible way, PMMA-based composites by spontaneous evaporation of solvent and PS-based composites by spinning.

The distribution of the boron-containing dopant throughout the film was controlled by using neutron depth profiling (NDP) technique based on the <sup>10</sup>B(n,  $\alpha$ )<sup>7</sup>Li nuclear reaction.<sup>16</sup> The boron concentration profile was measured only on PMMA composites; the depth profiling on PS composites was impossible to establish because of unfavorable signal to background ratio.

It may be expected that the permanent dipole orientation could manifest itself by a residual voltage difference between the electrodes. It was measured by using a Keithley 182 voltmeter as well as by compensation technique with Keithley 486 picoammeter; however, no significant voltage difference was observed.

### RESULTS AND DISCUSSION

The bipolar dopants for this study were carefully selected from scores of theoretical options. In principle, they can be viewed as special cases of betaines [i.e., compounds with (+)- and (-)-charged end groups



**Figure 1** Temperature dependence of the permittivity of PMMA and PMMA doped with MIMIDIOX to the concentrations in the percentages indicated (voltage, 1 V; filled symbols correspond to the sample heating; open symbols correspond to the sample cooling). The capacitance measurement was performed at 1-V voltage and  $10^2$ -Hz frequency.

mutually connected by an intervening spacer]. However, to make such betaine compatible with a variety of polymers, the charge carriers ought to be bulky groups capable of dissipating the respective charge over a more or less large surface. As anionic end groups of choice, the deltahedral boron clusters were suggested; for the cationic groups, the  $N_{(3)}$ -derivatives of the 1,2-dimethylimidazolium ion were selected as appropriate. As a prototype model of a dopant with a long spacer, MIMIDIOX was chosen. An enormous dipole moment of  $\sim 20$  D was estimated for this species in a fully stretched state.<sup>15</sup> Unfortunately, MIMIDIOX is fairly compatible only with polymers containing at least slightly polar groups (e.g., PMMA but not PS). As an example of a bipolar compound with a very short spacer, DIMIBOR was selected. This species is well soluble in a variety of organic solvents and is compatible with PS.

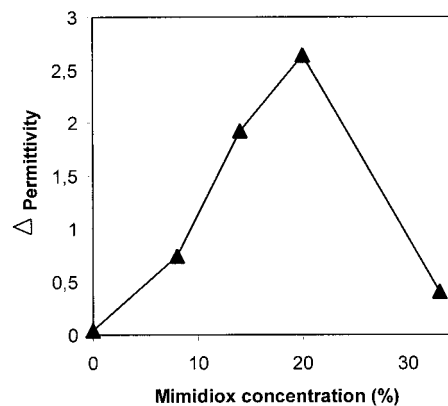
#### PMMA composites prepared by spinning

In our former publication,<sup>13</sup> we have shown that for PMMA dipole doped films prepared by spinning, the  $\epsilon$  increased with increasing dopant concentration. It was further shown that an external electrical field affects the dipole orientation with the effect depending on the temperature. In what follows, the dopant

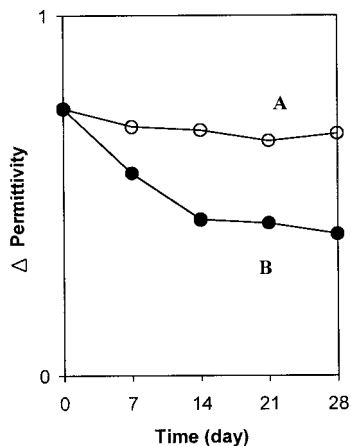
concentration, temperature, and voltage needed for creation of composite films with maximum increase of  $\epsilon$  are searched for. In Figure 1, the temperature dependence of the relative permittivity  $\epsilon$  for PMMA and PMMA doped to 14 and 20% of MIMIDIOX is shown. The curves for other concentrations are omitted for the sake of transparency. The samples were first heated from room temperature to glass transition temperature ( $T_g$ ) and then cooled under an external field of 1 V. It is seen that even for pristine PMMA that the  $\epsilon$  is an increasing function of the temperature with the most pronounced increase occurring around  $T_g$ . After cooling to room temperature, the  $\epsilon$  decreases to its initial value. This behavior also gives evidence that the contacts remain unchanged during temperature cycling. The present value of the  $\epsilon$  for pristine PMMA agrees well with earlier data [e.g.,  $\epsilon_{\text{PMMA}} = 2.6\text{--}3.7$  (see ref. <sup>2</sup>)]. After cooling, the PMMA compared exhibit higher  $\epsilon$  compared to the initial one.

In the next experiment, PMMA doped with 20% of mimidiox was, after heating, kept at 120°C for about 1 h and then it was left to cool spontaneously. During the whole procedure, the sample was exposed to 1-V voltage. After the procedure, we have observed the same dependence as for the sample annealed at 120°C for a shorter time (Fig. 1). It may therefore be concluded that the chosen rate of the PMMA composite heating is sufficient for the dipole orientation.

The dependence of the  $\epsilon$  on the dopant concentration in the PMMA composite is shown in Figure 2. It is seen that for the composites with 14–33% dopant concentration it is possible to achieve a significant  $\epsilon$  increase by initial heating to  $T_g$  and subsequent cooling of the samples under external electrical field. This observation can be explained in the following way. At  $T_g$ , when the polymer segments are partially movable, the embedded molecular dipoles are oriented by ex-



**Figure 2** The dependence of permittivity increase  $\Delta\epsilon$  of doped PMMA films on the concentration of MIMIDIOX. The measurement was performed after film heating and cooling with a voltage of 1 V. The capacitance measurement was performed at 1-V voltage and  $10^2$ -Hz frequency.

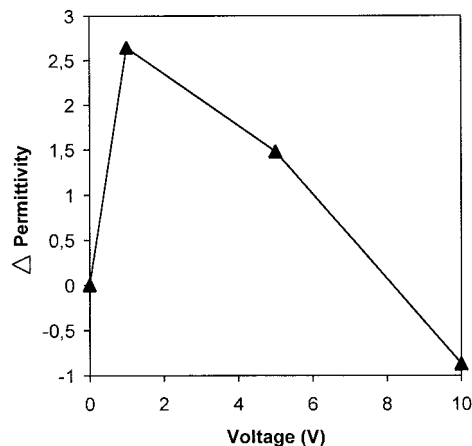


**Figure 3** The dependence of  $\Delta\epsilon$  of PMMA doped to 8% of MIMIDIOX on the time elapsed from the initial dipole orientation under the voltage of 1 V. (A) The same sample was always after 7 days oriented again (i.e., heated to  $T_g$  under external voltage and then cooled). (B) The initially oriented sample was simply measured every 7 days. Meanwhile, the sample was stored at room temperature.

ternal electrical field and the orientation remains partially conserved after cooling to room temperature. The most pronounced increase of the  $\epsilon$  was observed on the PMMA film doped to 20%.

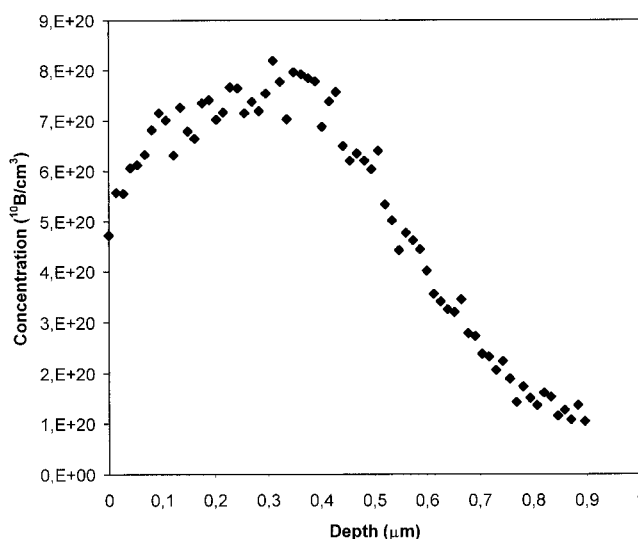
An important question is the long stability time of the composites with oriented dipoles. The  $\epsilon$  of PMMA composite doped to 8% was measured in 7-day intervals for 28 days after the first orientation; the results are shown in Figure 3. Two curves are shown corresponding to two measuring procedures. In the first one (A), the same sample was oriented again after every 7 days (i.e., heated to  $T_g$  under external voltage and then cooled). In the second case (B), the initially oriented sample was simply measured every 7 days. Meanwhile, the samples were stored at room temperature. From Figure 3, it is seen that in the case of repeated orientation (A), the  $\epsilon$  decreases slightly in the beginning, and after the first 7 days, it remains practically unchanged. In the second case (B), the  $\epsilon$  first decreases to about 30% of its initial value in the first 14 days and then remains unchanged. It may therefore be concluded that despite the initial decrease of the  $\epsilon$ , a significant part of the dipoles remains oriented permanently.

The above results were obtained for 1-V direct external voltage. In Figure 4, the dependence of the  $\epsilon$  on applied voltage is shown for the PMMA composite doped to 20% of MIMIDIOX. Decrease of the  $\epsilon$  is seen for the voltages above 1 V. The result indicates that at higher voltages a lesser portion of dipoles is oriented by the external field. A possible explanation of this rather unexpected finding may be an interaction of embedded dipoles with polar polymer environment, which may depend on the applied voltage.

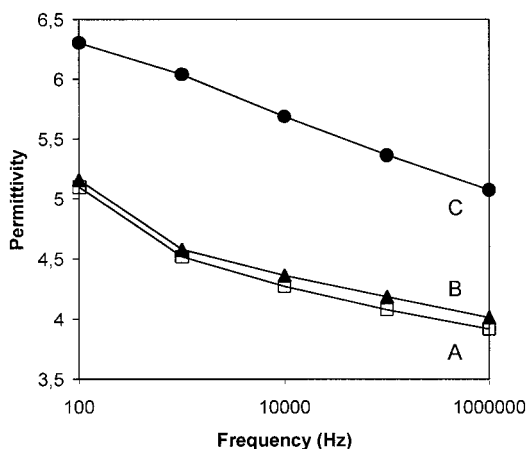


**Figure 4** Voltage dependence of the permittivity of PMMA doped with MIMIDIOX to 20% concentration.

The boron depth profile in doped composite film was determined by using NDP technique. The profile was measured nondestructively below gold contacts on pristine and oriented samples. The results are illustrated in Figure 5 on the composite doped with 20% of MIMIDIOX. It was now found that the boron containing dopant is not distributed homogeneously throughout the film. Up to a depth of about 400 nm from the film surface, the boron concentration is nearly constant and then it decreases rapidly in the direction to the glass backing. No significant differences in the measured boron depth profiles were observed between pristine and oriented samples. By comparison of the dopant profiles in PMMA composites in this work and in our previous publication,<sup>13</sup> it was found that in the boron depth profile<sup>13</sup> the description of the two curves was wrongly interchanged.



**Figure 5** Concentration depth profile of boron from the PMMA film doped with MIMIDIOX to 20% concentration. For details, see text.



**Figure 6** Frequency dependence of the permittivity of PMMA (A) and PMMA doped with 20% of MIMIDIOX (B) heated and cooled without voltage, (C) heated and cooled under the voltage of 5 V.

The frequency dependence of the  $\epsilon$  for the PMMA composite is shown in Figure 6. The dependence was measured for the pristine, undoped PMMA film (A) and for doped films which were thermally cycled without (B) and with (C) an external field. As can be expected, the relative permittivity decreases with increasing frequency because the dipoles orient with some time delay thanks to their own relaxation frequency. It is further seen that the pristine PMMA and the doped PMMA, which was not exposed to the external field during thermal cycling, exhibit the same frequency dependence of  $\epsilon$ . Analogous dependence is also observed for the doped PMMA, which was exposed to the external field, but in this case, higher  $\epsilon$  is found.

#### PS composites prepared by solvent evaporation

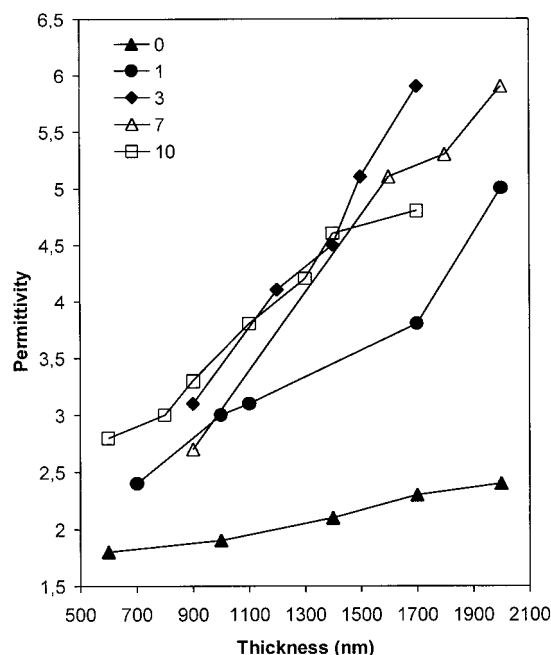
Dielectric relaxation data for several rigid molecules in PS were obtained earlier (e.g., see ref. 17, 18). Dipole doping of PS solution is more difficult compared to polar PMMA. The PS composites were prepared by doping the PS solution in toluene with up to 10% of DIMIBOR. The resulting liquid mixture was dropped onto substrate and the incorporated dipoles were oriented by an external field during the evaporation phase. The amount of the parent solution was chosen to achieve final film thickness of about 1300 nm. The films prepared in this way are not expected to be homogenous. The dependence of the  $\epsilon$  on the composite film thickness and the dopant concentration is shown in Figure 7. It is seen that the thicknesses of the prepared films vary from 600 to 2000 nm. Measured permittivity of pristine PS  $\epsilon = 1.8$ –2.4 (Fig. 7) is in reasonable agreement with the values reported elsewhere [e.g.,  $\epsilon = 2.45$  (see ref. <sup>2</sup>) or  $\epsilon = 2.4$ –3.1 (see ref.

19)]. The difference between present permittivity values and those reported in literature can be explained by well-known bulk versus size effects; therefore, the permittivity measured on thin films may differ from bulk value. The  $\epsilon$  of pristine and doped PS is an increasing function of the film thickness. This behavior may be due to a larger portion of the free volume in between polymeric chains in thinner films.<sup>20</sup> The free volume is filled with air, the presence of which reduces the total film  $\epsilon$ . The PS doping to the concentrations of 1 and 3% leads to a rapid increase of the  $\epsilon$ . Further concentration rising, however, does not result in additional  $\epsilon$  increase.

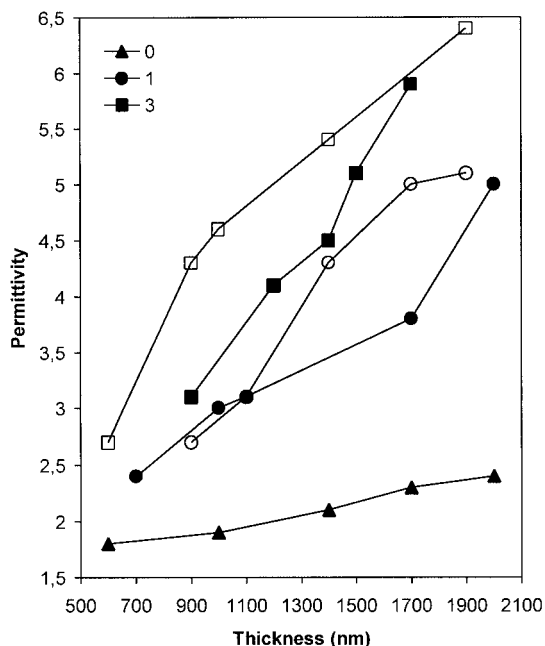
Figure 8 shows the dependence of the  $\epsilon$  on the film thickness measured on the PS composites prepared without and with external electrical field. The dopant concentrations were 0, 1, and 3% and the applied voltages were 0 and 2.5 kV. The voltage was kept well below the value leading, in the present experimental arrangement, to PS breakdown [50 kV/mm (see ref. 2)]. As expected, the application of the external electrical field did not increase the  $\epsilon$  of pristine, unpolar PS. For doped PS films, the external electrical field did increase the  $\epsilon$ . It may, therefore, be concluded that the external electrical field applied during evaporation phase oriented a significant part of the dipoles and that the orientation remained conserved after the complete solvent evaporation.

#### CONCLUSION

The present results can be summarized as follows.



**Figure 7** Dependence of the permittivity of the pristine PS and the PS composite on the thickness of the polymer films for different concentrations of DIMIBOR (in %).



**Figure 8** Dependence of the permittivity of the PS composites on the thickness for zero voltage (filled symbols) and 2.5 kV (open symbols) and various DIMIBOR concentrations (in %).

### PMMA-based composites

Application of a direct electrical field at the glass transition temperature enhances the orientation of dipoles incorporated in a PMMA. The orientation is conserved after cooling to room temperature and manifests itself in pronounced increase of  $\epsilon$  of the composite.

Most pronounced permittivity  $\epsilon$  increase was observed on PMMA composite doped to 20% MIMID-IOX and oriented under 1-V voltage bias.

The applied voltage influences the  $\epsilon$  increase of the doped composite after its heating to  $T_g$  and subsequent cooling to room temperature. The resulting  $\epsilon$ 's decrease with increasing voltage.

Long-time measurement proves that the orientation of a significant part of the dipoles in the composite film is permanent.

Dopant concentration profile, measured by the boron-sensitive NDP method, is not homogeneous and does not depend on the dipole orientation. The boron concentration decreases from the film surface to the underlying background.

### PS-based composites

For the PS composite films 600-2000 nm in thickness, prepared by spontaneous evaporation from PS or PS-doped solution in toluene, the  $\epsilon$  is an increasing function of the film thickness.

DIMIBOR doping up to 3% dopant concentration results in a pronounced increase of the relative permittivity. For higher dopant concentrations, however, the  $\epsilon$  remains constant. The relative permittivity of pristine PS is not affected by the applied electrical field.

In PS composites, doped to low concentrations, the direct electrical field applied in the course of evaporation orients the dipoles. The orientation is permanent and leads to an increase of the  $\epsilon$  of the composite.

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