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Grating Diffraction of Blends Involving NLO Random Copolymers

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ABSTRACT: Dielectrophoresis can be employed to create a grating-like microstructure in phase-separated polymer blends. Typically, this process produces a morphology of pearl chain-like and/or elongated column-like entities spaced rather regularly throughout a matrix. In addition, these microstructures are generally waving and not uniform in terms of column size, shape, and spacing; i.e., they lack periodicity. Our recent work shows that it is possible to obtain an improved quality of elongated column-like entities in field-modified blend films. In this study, a nonlinear optically active (NLO) random copolymer, with hyperpolarizable chromophores as side groups, is mixed with a linear optical (LO) polymer. Important blend parameters, such as blend composition, polymer concentration, molecular weights of dispersed phase and matrix phase, and electric field strength, are carefully controlled to optimize the periodicity of the field-modified microstructure. The resulting unique morphology is capable of creating a grating diffraction pattern from light at 632.8 nm.

Introduction

It is well known that films made from immiscible polymer blends are typically opaque or hazy in appearance. Their value for optical-related devices is low since the loss of light passing through them caused by scattering (turbidity) is considerably high. However, highly transparent films of immiscible blends can still be made under conditions where the ratio of the refractive indexes of polymers involved in the blend is very close to 1.[1,2] An alternative way of obtaining reasonable degrees of transparency is by controlling the size of dispersed particles such that they are either much larger or much smaller than the wavelength of incident light.[2] Making a film that is thin enough so that light encounters only one of the phases present in the blend can also help in minimizing the degree of turbidity.[2] Hence, highly transparent but immiscible blend films can be produced by careful choice of preparation conditions.

We employ here a further means of controlling the phase-separated morphology; it is commonly called dielectrophoresis. In general, dielectrophoresis is defined as the alignment involving translational and rotational motions of neutral matter due to polarization effects in a nonuniform electric field.[3] One area of general application involving dielectrophoresis is electrorheological fluids, such as those made from colloidal dispersions of silica gel in mineral oils.[4] Other applications of dielectrophoretic forces are in liquid/powder pumps,[5] electrofiltration,[6] surface coolers,[7] electrostatic printing,[8] and water treatments involving removal of bacteria and algae.[9] Adaptation of dielectrophoresis to the polymer phase separation processes was pioneered by Moriya et al.[10] Instead of typical microstructures of spinodal decomposition (SD) or nucleation and growth (NG) mechanisms, they observed the pearl chain-like morphology developed in a blend of poly(styrene) (PS) and poly(ethylene oxide) (PEO). Venugopal et al.[11,12] did further investigations and observed column-like and pearl chain-like entities resulting from PEO/PS and poly(methyl methacrylate) (PMMA)/PS blend systems. However, none of the obtained morphologies seems to be appropriate for optical-related applications due to their waviness, inhomogeneity in terms of size and shape, and lack of periodicity. A simple illustration of pearl chain-like and column-like microstructures is given in Figure 1.

In this paper, we will show that it is possible to form an improved quality dielectrophoretically modified blend film by controlling important blend parameters, such as blend composition, polymer concentration, molecular weights of dispersed phase and suspending medium (matrix), and field strength. The fact that the blend morphology can be modified by changing blend parameters such as field strength and molecular weight of dispersed phase has been shown by Venugopal et al.[11] In this study, we vary all of the blend parameters mentioned earlier to search for the optimal conditions for creating a good-quality field-modified blend film. It will be shown later that the obtained microstructure can produce a grating diffraction pattern when it is exposed to a laser beam.

Experimental Section

Sample Preparation. Poly{*N*-MNA acrylamide-*co*-4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene-*co*-acrylic acid} (PM*x*D*y*) was synthesized from poly(acryloyl chloride), 2-methyl-4-nitroaniline (MNA), and disperse red 1 (DR1) using 1,4-dioxane as the solvent. The mole percentages of MNA and DR1 in PM*x*D*y* are represented by 10*x* and 10*y*, respectively. The chemical structure of PMxDy is illustrated in Chart 1. The degree of polymerization of poly(acryloyl chloride) is estimated to be about 110 using intrinsic viscosity method. The side chain NLO copolymer, PM*x*D*y*, was further purified by reprecipitation from pyridine solution with methanol. The purification was repeated to make sure no unreacted chromophores or other impurities remained in our copolymer. The copolymer structure was verified by using Fourier transform infrared (FT-IR) spectroscopy. The attachment of dyes (DR1 and MNA) to the vinyl polymer backbone is indicated by the presence of peaks of amide and ester groups in FT-IR spectra. The IR spectrum of PM*x*D*y* was illustrated in our previous paper.[13] Its chromophore contents were verified by elemental analysis, done by Oneida Research Services, Inc. (Whitesboro, NY). The estimated chromophore content obtained from the elemental analysis is in good agreement with that obtained from the ^{1}H NMR spectrum. The ^{1}H NMR spectrum of PM*x*D*y*, which was recorded in deuterated dimethyl sulfoxide

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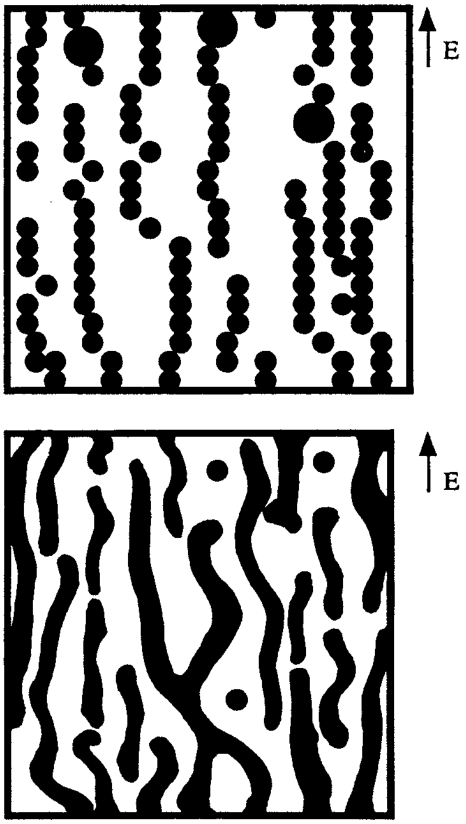
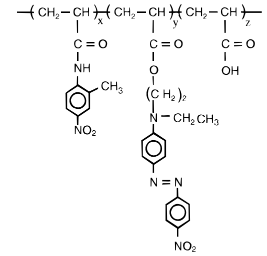


Figure 1. Simple illustrations of pearl chain-like (top) and parallel, column-like morphologies (bottom).

Chart 1



(δ = 2.49 and 3.4 ppm) with a 300-MHz Gemini-300 NMR spectrometer, is illustrated in Figure 2. The chromophore content was estimated by comparing the integrated areas of peaks that are related to MNA (δ = 2.8 ppm), DR1 (δ = 1.0 ppm), and acrylic acid (δ = 12.4 ppm), respectively.

In this study, PM1D8 (80% DR1, 7% MNA, 13% acrylic acid) was mixed with atactic poly(methyl methacrylate) (PMMA), as received from Fisher Chemical Co. and Aldrich Chemical Co., in pyridine. The number average degrees of polymerization of the two different PMMAs (N_{PMMA}) used in this study are 150 and 4000. Their polydispersity indexes are 2.27 and 1.78, respectively. To make sure that PMMA and PM1D8 have been dissolved completely, the blend solution was allowed to stand in a sealed container for 1 day. The blend solution was further filtered by using a disposable syringe filter with pore size of 5 μm in order to remove undissolved impurities that may be present. Prior to each solution casting, the blend solution must be shaken thoroughly to obtain a homogeneous mixture. PM1D8 was chosen as one of the components of the blend system, since it has a high content of nonlinear optically active chromophores (DR1), which contribute to a high second harmonic d coefficent (d_{33}). From the previous NLO study[13] on this copolymer, it was found that its d_{33} value is about 60 pm/V and its glass transition temperature (T_g) is about 115 °C. The refractive index of PM1D8, measured using an Abbe refractometer, is found to be about 1.55 for a given wavelength of 589 nm. Its dielectric constant, which was calculated from the measured capacitance using impedance spectroscopy, is found to be about 4.0. The other component of the blend, PMMA, was chosen owing to its good optical clarity and availability in different molecular weights. Also, its refractive index (~1.49)[14] measured at a wavelength of 589 nm is close to that of PM1D8, and its dielectric constant (~3.1)[15] is different from that of PM1D8.

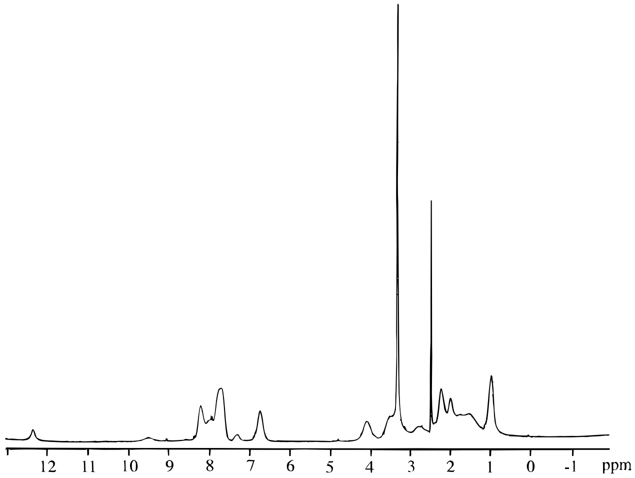


Figure 2. NMR spectra of PMxDy.

Field Modification of Blend Morphology. The purified blend solutions of PM1D8/PMMA were solution-cast on precleaned glass microscope slides. These glass slides were cleaned with chromic acid, rinsed with distilled water, and allowed to air-dry. Two parallel gold electrodes, each having dimensions of 4 cm × 0.5 cm × 0.1 μm, were then formed on top of the microscope slide. The lateral separation distance between the two parallel (positve and negative) electrodes is 2.00 ± 0.02 mm. The parallel gold electrodes were formed by the following process. The precleaned microscope slide was masked selectively using Scotch tape (3M Co.). A thin film of gold was then deposited on top of the masked and precleaned microscope slide by either the vacuum evaporation or sputtering techniques. After the deposition, the tape was carefully removed from the microscope slide. Next, copper wires were attached to the two gold electrodes using silver paste. The wires were then connected to positive and negative channels of dc power supply. The power supply can provide high dc voltage up to 6.0 kV and has a maximum current output of 0.55 mA. However, the current across our blend film is actually less than 200 nA due to its very high resistance.

In this study, parameters such as polymer concentration, blend composition, molecular weights of blend components, and field strength are varied in order to study the effects of those parameters on the resulting phase-separated microstructure. Those parameters are then carefully controlled to obtain a field-modified blend morphology with optimized quality. The experimental conditions used in the study are given in Table 1. The optical microscopy observations of the resulting microstructure are recorded photographically on Polaroid films.

Laser Diffraction of Field-Controlled Blend Morphology. A standard optical diffraction setup is used to produce an optical transform of the structure in the modified film. The field-modified immiscible blend morphologies are exposed to a He−Ne laser for the study of their 2-D optical diffraction patterns. The power of the laser beam used is 3 mW. The wavelength of the laser beam is 632.8 nm. The sample holder is located within 3 cm from the laser source. The sample holder can be rotated from 0° to 360° about an axis collinear with the laser beam, and its height can be adjusted so that the laser beam will hit the desired spot in the modified film. The diffracted laser light is projected on a screen of white cardboard, located within 60−70 cm from the sample holder. The observed patterns on the screen are then recorded on Polaroid films.

Results and Discussion

Dielectrophoresis. The pearl chain-like or column-like microstructure created in the presence of electric

Table 1. Experimental Conditions for Field Modification of PM1D8/PMMA/Pyridine Blend

1. To Study the Effect of Field Strength	
(a) PM1D8/PMMA ratio	1:7
N_{PMMA}	4000
solution concn	2%
dc voltage	0.5, 0.8, and 2.0 kV
electrodes gap	2 mm
(b) PM1D8/PMMA ratio	7:1
N_{PMMA}	4000
solution concn	2%
dc voltage	0.7, 1.0, and 2.0 kV
electrodes gap	2 mm
2. To Study the Effect of Molecular Weight Variations of PMMA	
PM1D8/PMMA ratio	1:7
N_{PMMA}	150 and 4000
solution concn	2%
dc voltage	2.0 kV
electrodes gap	2 mm
3. To Study the Effect of Blend Composition	
PM1D8/PMMA ratio	1:7, 3:7, and 7:1 (w/w)
N_{PMMA}	4000
solution concn	2%
dc voltage	2.0 kV
electrodes gap	2 mm
4. To Study the Effect of Polymer Concentration	
PM1D8/PMMA ratio	1:7
N_{PMMA}	4000
polymer concn	2%, 10%, and 15%
dc voltage	2.0 kV
electrodes gap	2 mm

field can be understood from dielectrophoresis theory, such as has been presented in great detail by Pohl.[16] The chaining or bunching of dispersed spherical domains is basically a manifestation of mutual dielectrophoresis resulting from dielectric mismatch between the dispersed phase and the matrix. In general, the dielectrophoretic force that is responsible in the chaining or bunching process can be described by the following equation:[16]

$$F_{\mathrm{d}} = \frac{3}{2} S \epsilon_1 \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right) \nabla |E_{\mathrm{e}}|^2 \qquad (1)$$

where $\epsilon_1 = \epsilon_0 K_1$ and $\epsilon_2 = \epsilon_0 K_2$ are the absolute permittivities of dispersed phase and matrix, respectively, ϵ_0 is the permittivity of free space, K is the dielectric constant, S is the volume of the object, and $\nabla|E_{\mathrm{e}}|^2$ is the geometric gradient of the square of the field intensity. It is clear that the dielectric mismatch cannot be zero in order to have dielectrophoresis. This dielectric mismatch allows the dispersed phases to distort the externally applied field by the dispersed phases. The more irregular the shape of the dispersed particles, the more pronounced is the distortion.[16] Each particle is then experiencing a nonuniform field when it is near another one. Under the influence of inhomogeneous field, each neutral particle acquires a polarization that has the effect of putting a positive charge on the side nearer to the negative electrode and a negative one on the side closer to the positive electrode. These particles will then correspondingly exhibit mutual attractions to each other, and they are also tend to move toward the region of higher field. Those particles will then string together in such a way that columns or pearl chains aligned parallel to the field direction are formed. The formation of strings and columns can also result from either the elastic tensile deformation of large clusters of polarized particles by electric field or the continuous process of combination of clusters, both column-like and droplet-like ones, to form longer columns or pearl chains.

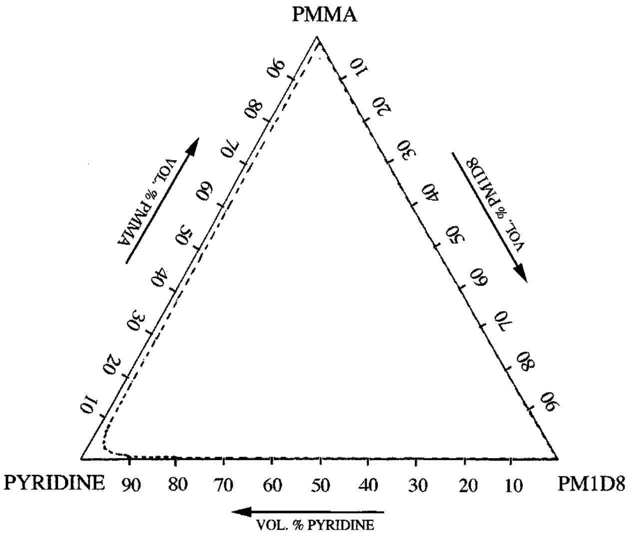


Figure 3. Phase field for the ternary system PM1D8/PMMA/pyridine. $\chi_{12} = 0.314$; $\chi_{13} = 0.0054$; $\chi_{23} = 0.43$, where subscripts 1, 2, and 3 represent pyridine, PM1D8, and PMMA, respectively. - - - represent the predicted spinodal line.

Predicted Ternary Phase Diagram. To have insight into the phase separation mechanisms involved here, a simulation of the spinodal line and its critical point for the ternary system (PM1D8/PMMA/pyridine) was constructed, as shown in Figure 3. The degrees of polymerization of PM1D8 and PMMA applied in the simulation are assumed to be 100 and 4000, respectively. For simplification, the simulation was based on the Flory–Huggins expression of free energy of mixing under an assumption that both polymers involved in the blend are monodisperse.[17,18] The interaction constant between two components in the ternary system was calculated by applying Hildebrand solubility parameters, which can be estimated by using the connectivity indexes of Bicerano.[19] In the diagram, we see that the two-phase spinodal region is predicted to be very large. In this case, a miscible ternary system exists only when the solvent content is high (>94 wt %). However, our experiments indicate that a completely miscible ternary system can still be achieved even when the solvent content is possibly no larger than 85 wt %. This deviation may be due to the fact that both PM1D8 and PMMA are actually polydisperse. This deviation will not be our concern, since most of our experiments involve solvent content of about 98 wt %.

Effect of Field Strength on Strings Formation. The effect of field strength on the field-modified immiscible blend microstructure was studied. The experimental conditions for this study are given in Table 1, and the resulting microstructures are shown in Figure 4. It is seen in the figures that there was an increase in the string length as we increased the field strength for both PM1D8/PMMA 1:7 and 7:1 blends. This result has been observed by Venugopal et al.[11,12] for a ternary blend system (polymer/polymer/solvent) and by Bezruk et al.[20] for a binary blend system (polymer/solvent). This is reasonable since the higher the field strength, the more dispersed droplets are joined together over a period of time. The increase in yield of collected droplets (Y) with increasing electric field has been shown in the equation derived by Pohl and Crane[21] for dielectrophoresis in real dielectrics:

$$Y \propto \frac{CV}{d} \left[\frac{2t\epsilon_1(\epsilon_2 - \epsilon_1)}{\eta(\epsilon_2 + 2\epsilon_1)} \right]^{1/2} \qquad (2)$$

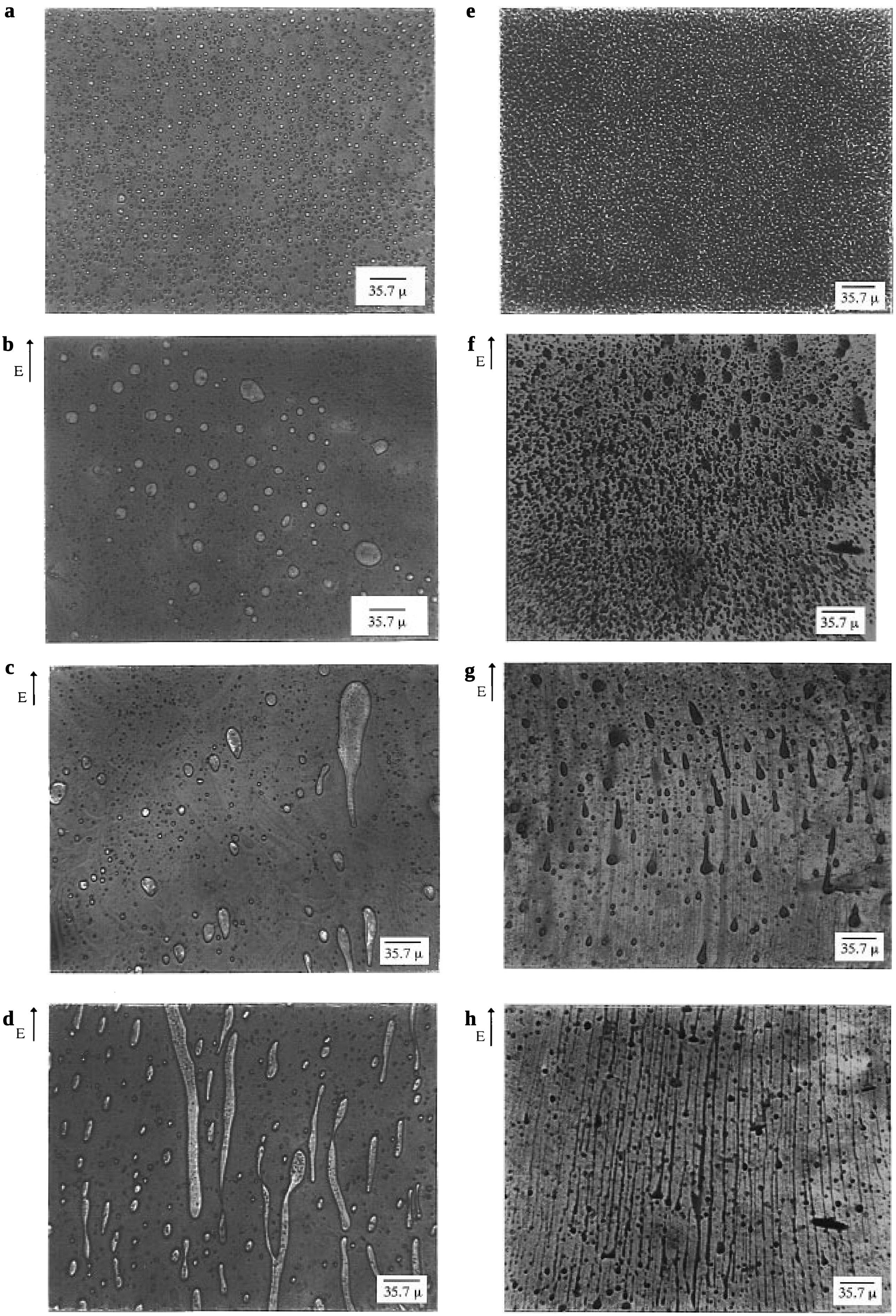


Figure 4. Optical micrographs of the PM1D8/PMMA blend films with $N_{\mathrm{PMMA}} = 4000$ and 2% concentration. (a) 7:1 blend film cast with the field off; (b−d) 7:1 blend film cast under dc field of 3.5, 5.0, and 10.0 kV/cm, respectively. (e) 1:7 blend film cast with the field off; (f−h) 1:7 blend film cast under dc field of 2.5, 4.0, and 10.0 kV/cm, respectively.

where C is the concentration of dispersed particles, V is the applied voltage, t is the elapsed time, η is the viscosity of the suspending medium, and d is the electrode gap. However, there is a limit to the field strength that can be applied. If the field strength is too low, no long columns can be formed, as shown in Figure 4b,c,f, and g. But, if the increase in field strength is too high, then the strings/columns will start to break up, as predicted by Garton and Krasucki.[22] Also, the electric field cannot be too intense, since dielectric breakdown can also occur.

Effect of Molecular Weight of Dispersed Phases. The higher the molecular weight of the dispersed phases involved in the blend, the higher the field strength needed to form oriented long columns. As shown in Figure 4d and h, under the same field strength of 10 kV/cm, we observed more columns of PM1D8-rich droplets formed in the PM1D8/PMMA 1:7 blend than those of PMMA-rich droplets formed in the PM1D8/PMMA 7:1 blend for the same area of observation. The columns formed in PM1D8/PMMA 7:1 are shorter but fatter than those formed in PM1D8/PMMA 1:7. The observed phenomena suggest that long columns are more readily formed in the PM1D8/PMMA 1:7, which have lower molecular weights of dispersed droplets. This may be because those dispersed phases with higher molecular weight have higher viscosity. In other word, they are more resistant to the process of column formation, and thus they need longer times in the effort of forming longer columns. For our blend system, the working time (the time that allows dispersed domains to move around before they stop completely since the viscosity is already too high) is short (~3 min). Given the limitation by the working time, the PM1D8/PMMA 7:1 blend needs higher field strength in order to form longer columns. However, if the molecular weights of dispersed phases are too low in the presence of high field strength, chains of dispersed droplets (pearl chain) will be formed, as has been observed by Moriya et al.[10] in PEO/PS 1:99 under a field strength of 78 kV/cm and Venugopal et al.[11] in PEO/PS 1:9 under a field strength of 10.5 kV/cm.

Effect of Molecular Weight of Suspending Medium. To study the effect of the molecular weight of the suspending medium on field-modified blend morphology, two samples of PMMA with different degrees of polymerization ($N_{\mathrm{PMMA}} = 150$ and 4000) in PM1D8/PMMA 1:7 blends were used. It was shown in Figure 4h that long columns of PM1D8-rich droplets are formed in the PM1D8/PMMA 1:7 blend with $N_{\mathrm{PMMA}} = 4000$. However, as shown in Figure 5, short columns and chains of PM1D8-rich droplets are formed in the blend with $N_{\mathrm{PMMA}} = 150$ under the same field strength of 10 kV/cm and solution concentration of 2%. These chains of droplets may result from those already formed columns that are broken again. These results suggest that the higher the molecular weight of the suspending medium in the blend, the higher the stability of the already formed columns against Rayleigh instability. The Rayleigh instability is basically the breakup phenomenon of liquid cylinders in a liquid matrix. The Rayleigh instability phenomenon has been observed by Venugopal et al.[12] with their PMMA/PS blend systems. Based on the theoretical study done by Tomotika,[23] the breakup rate of columns is directly proportional to the interfacial tension and inversely proportional to the viscosity of the liquid matrix. Higher viscosity of the liquid matrix will compensate for the increase in breakup rate resulting from an increase in interfacial tension during solvent evaporation. Such an elevated viscosity can result from a higher molecular weight of the solute polymer in this matrix phase. Please note that the viscosity of both phases also increases as more and more solvent evaporates. In the case of the blend with $N_{\mathrm{PMMA}} = 4000$, we observed much less broken columns, which contributes to the formation of long columns during the solvent evaporation. Moreover, we did not observe any breakup phenomenon after the field was turned off, which may be due to reasonably high viscosity of the liquid matrix that helps suppress the kinetics of the Rayleigh instability such that it is slower than the time scale of the experiment (working time).

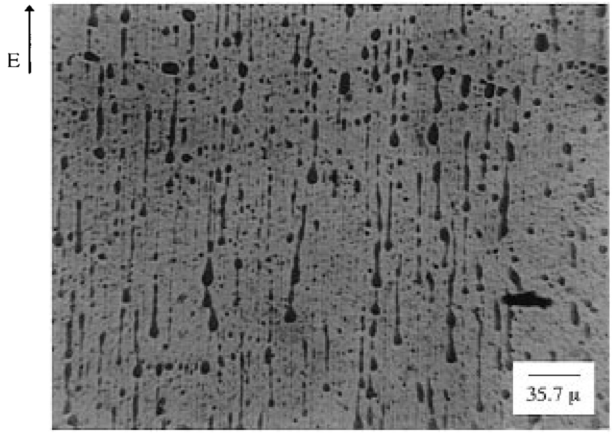


Figure 5. Optical micrographs of the PM1D8/PMMA 1:7 blend film cast under dc field of 10.0 kV/cm (2% polymer concentration; $N_{\mathrm{PMMA}} = 150$).

Effect of Blend Composition. The photographic images of field-controlled blend morphologies of different PM1D8/PMMA blend compositions (1:7, 3:7, and 7:1) and their unmodified phase-separated morphologies are shown in Figures 4 (a, d, e, and h) and 6. The experimental conditions for studying the effect of blend compositions have been described in Table 1. As shown in the figures, all blend compositions can give parallel column-like microstructures as long as the field strength applied is high enough for the formation of columns in blends with polymer concentrations within a defined range. Parts a, d, e, and h of Figure 4 indicate that the field-modified morphology of the PM1D8/PMMA 1:7 blend is different from that of PM1D8/PMMA 7:1. In the PM1D8/PMMA 7:1 blend system, columns are formed from the dispersed PMMA-rich droplets. On the other hand, columns are formed from dispersed PM1D8-rich droplets in the PM1D8/PMMA 1:7 blend. Moreover, as mentioned earlier, the columns formed in the PM1D8/PMMA 1:7 blend under the conditions illustrated in Table 1 are longer, straighter, and more uniform in quantity when compared with those formed in PM1D8/PMMA 7:1. In general, the columns formed in PM1D8/PMMA 1:7 are better in quality than those formed in PM1D8/PMMA 7:1. However, in the PM1D8/PMMA 1:7 blend system, the average spacing distance between its columns is generally much larger than the average width of each column; there is also a lack of periodicity and uniformity. This may be because the weight fraction of PM1D8 is much smaller than that of PMMA. Upon increasing the weight fraction of PM1D8, i.e., increasing the concentration of available dispersed droplets, the average width of columns will increase. Such an increase in column width with increasing droplet concentration has been predicted by Pohl and Crane,[21] as shown in eq 2. Figure 6 illustrates that the columns formed in PM1D8/PMMA 3:7 are generally wider and longer than those formed in PM1D8/PMMA

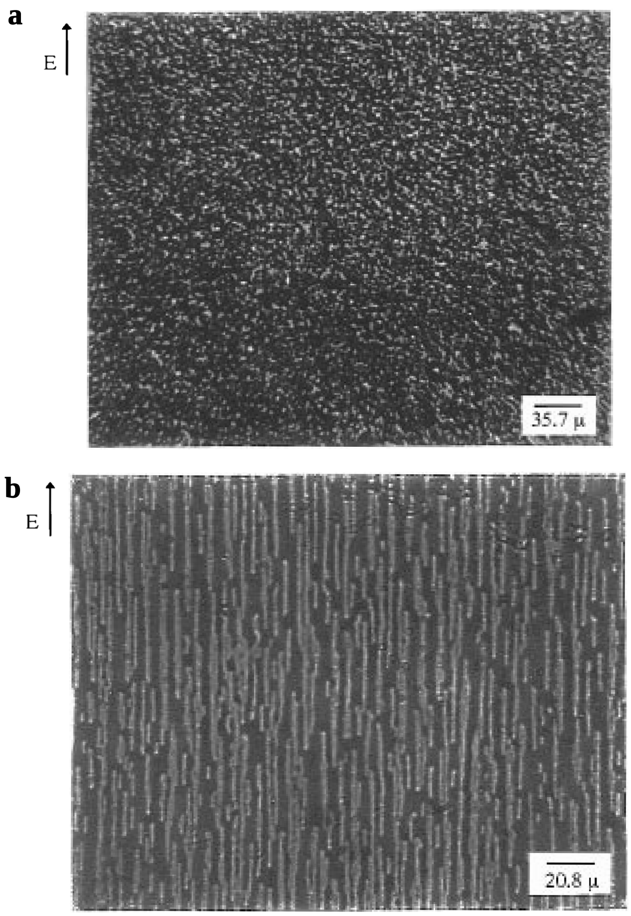


Figure 6. Optical micrographs of the PM1D8/PMMA 3:7 blend film with $N_{\mathrm{PMMA}} = 4000$ and 2% concentration, (a) cast with the field off and (b) cast under dc field of 10.0 kV/cm.

1:7. The average spacing between columns is more uniform; i.e., there is better periodicity and uniformity for columns formed in PM1D8/PMMA 3:7. The high content of PMMA can maintain the stability of the already formed columns so that those parallel, straight, long columns (gratings) can be preserved.

Effect of Polymer Concentration. To study the effect of polymer concentration in the resulting field-controlled blend microstructure, it is necessary to vary the polymer concentration while keeping the other parameters constant. The polymer concentration in these solutions should be low enough to ensure that both polymers are completely dissolved in pyridine. For this study, we tried three different polymer concentrations, *viz*. 2%, 10%, and 15%, under the experimental conditions as illustrated in Table 1.

In this study, the solvent used has a dielectric constant higher than those of both polymers. The dielectric constant of pyridine is about 12.[24] However, only chaining or fibrillation of polymer domains occurs, since both polymers dissolve completely in the solvent. No pearl chain-like or column-like microstructure appears when we are dealing with miscible binary systems such as PM1D8/pyridine and PMMA/pyridine. A clear, homogeneous film is observed, even when we apply electric field as high as 15 kV/cm. Therefore, we believe that pyridine has no effect on the resulting field-modified microstructure. However, the evaporation rate of the solvent will determine the time scale of the experiment (working time). If the working time is too short, the microstructure formed may be clusters of droplets, short columns, or wavy long columns when the field strength is also too low. This can happen because the experiment is stopped already before those clusters of droplets get the chance to form columns. Similarly for the case of short columns, the experiment is already immobilized, even before the aggregation of short columns to form longer columns takes place. For the case of wavy long columns, those short columns get the chance to aggregate, but the experiment is stopped before the formed long columns align properly in the direction of electric field. During the aggregation process, some of the short columns may not be aligned in the field direction, and some may still be capable of flexure, since they can be seen to move around in inhomogeneous fields.

There is no evidence of electrochemical polymerization of pyridine in the presence of high electric field used in our study. The pyridine that has been exposed to electric field as high as 10 kV/cm shows no change in appearance in terms of color and viscosity. No precipitation is observed. There is no change in its chemical makeup, as verified by FT-IR analysis. Also, there is no shift in its absorption maximum wavelength (λ_{max}) in its UV−visible spectrum.

From the photographically recorded blend morphologies, it is clear that, overall, the 2% blend solution has a better quality of field-modified microstructure than the higher concentration ones. Their morphologies are illustrated in Figures 4h and 7. At higher concentrations, the actual effect of the nonuniform electric field in gathering the dispersed droplets is impeded due to higher viscosity. The increase in viscosity will require longer time and higher field strength to create column-like microstructures. The reduced yield of collected droplets due to higher viscosity of the liquid matrix has been predicted by Pohl and Crane[21] as indicated in eq 2. In general, the time needed to form long, straight liquid cylinders will be longer than the working time for the case of concentrated blend solution. As mentioned earlier, clusters of droplets, short chains, or wavy long columns may be formed instead of long, straight columns if the time needed to form long, straight columns is longer than the time scale of the experiment when the field applied is not high enough. Moreover, the thicknesses of the resulting blend films for concentrated solutions are usually high. Accordingly, the thicker the film, the higher the turbidity. As shown in Figure 7, overlapping structures of wavy columns and spherical droplets are more severe in more concentrated solution. Therefore, it is important that the polymer concentration not be too high in order to obtain a good-quality field-modified blend morphology.

To obtain a good-quality column-like microstructure, it is important to know what parameters are important and to control those parameters accurately. By trying different combinations of those important parameters, we can acquire a good grating-like microstructure. As shown in Figure 6b, for the PM1D8/PMMA 3:7 blend system under the given conditions ($E_{\mathrm{a}} = 10$ kV/cm, 2% solution concentration, and $N_{\mathrm{PMMA}} = 4000$), we can obtain a delicate grating-like microstructure. The majority of grating-like microstructure is found in the region between the positive electrode and the center of the electrode gaps. That PM1D8/PMMA 3:7 blend film is characterized by parallel, straight, long column-like microstructures with good uniformity and periodicity. The average column width is similar to the average of the spacing between similar columns, which is measured to be about 6.8 μm. Also, the obtained columnar structures are stable over time. There is no evidence of microstructural changing, as observed by Venugopal et al.[12] in their PMMA/PS 2:8 blend system, after

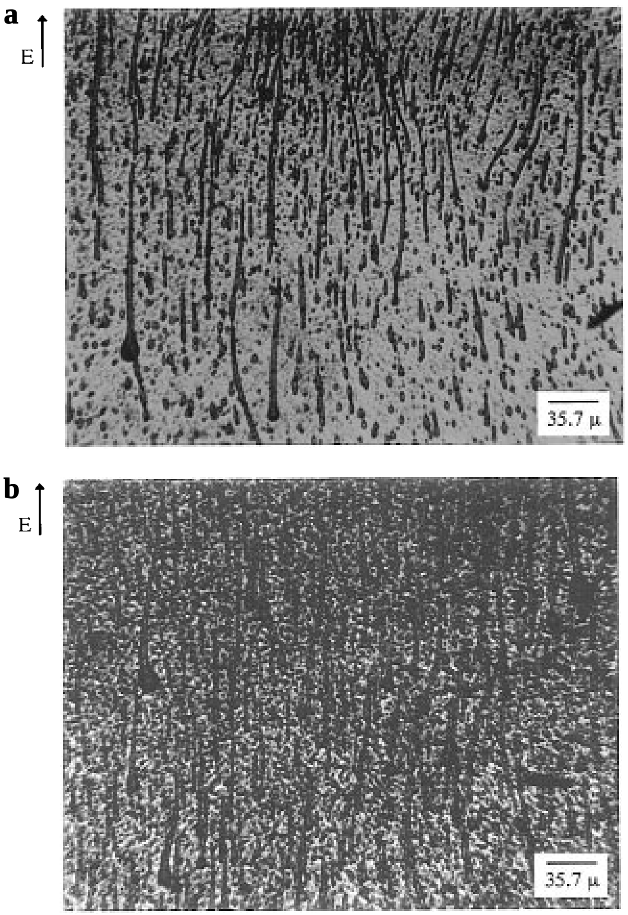


Figure 7. Optical micrographs of the PM1D8/PMMA 1:7 blend film cast under dc field of 10.0 kV/cm, with (a) $N_{\mathrm{PMMA}} =$ 4000 and 10% concentration and (b) $N_{\mathrm{PMMA}} = 4000$ and 15% concentration.

the field is off, even after 6 months. This is an indication that the breakup rate in our system is actually slower than the time needed to remove the solvent completely.

Grating Diffraction of Field-Modified Blend Film. In Figure 8, a He−Ne laser 2-D diffraction pattern obtained from the unmodified PM1D8/PMMA 3:7 blend film is compared to that obtained from the field-modified PM1D8/PMMA 3:7 blend film. Although the component polymers are completely transparent to red laser beam, their blend film can still be treated as a diffracting screen containing a large number of either rectangular apertures (obstacles) for the case of field-modified film or circular obstacles for the case of ordinary blend film. This is because the two polymers have different indices of refraction.

In general, both films can generate Fraunhofer diffraction patterns. Fraunhofer diffraction patterns will occur if both the point source (S) and the point of observation (P) are far from the diffracting screen (D), i.e., $R > a^2/\lambda$, where R is the distance between S and D or the distance between D and P, a is the obstacle (aperture) greatest width, and λ is the wavelength of light.[25] On the other hand, if S or P or both are too near D, Fresnel diffraction will occur ($R < a^2/\lambda$). Since both the size of dispersed domains and the grating width are on the order of micrometers, a^2/λ will be very small. Thus, it is almost impossible to observe Fresnel diffraction using a He−Ne laser source.

The unmodified PM1D8/PMMA 3:7 blend film, which is characterized by a random array of inhomogeneous circular domains, will give a random distribution in the relative phases of the waves arriving at arbitrary points on the screen. The diffraction pattern of the ordinary film can be visualized as that of a diffracting screen containing a large number (N) of diffracting objects (apertures or obstacles). A mottled flux−density distribution of spots closely resembling that of an individual aperture but v times stronger will be anticipated for a diffracting screen containing v apertures (obstacles).[25] As v increases, the central spots will be the brightest, and they can obscure the rest of the pattern. Therefore, as shown in Figure 8a, a random array of nonuniform, mottled spots is observed when the unmodified blend film is used as the diffracting screen.

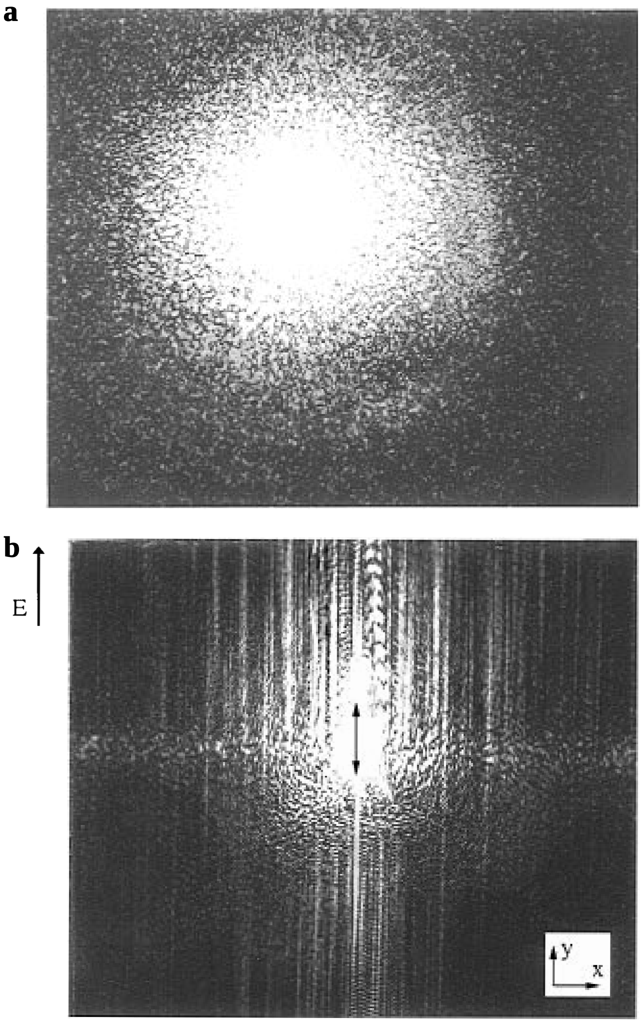


Figure 8. Optical Fraunhofer diffraction of the PM1D8/PMMA 3:7 blend film using a He−Ne laser source, (a) cast with the field off, $N_{\mathrm{PMMA}} = 4000$, and 2% polymer concentration and (b) cast under dc field of 10.0 kV/cm, $N_{\mathrm{PMMA}} = 4000$, and 2% polymer concentration.

When a He−Ne laser beam is transmitted through a transparent blend film with grating-like microstructure, the blend film can produce a Fraunhofer diffraction pattern that is similar to diffraction (multiple slit diffraction) obeying Bragg's law. The diffraction pattern on the screen will consist of images of principal diffraction maxima and subsidiary diffraction maxima. The principal maxima will be equally spaced and obey the equation $\lambda = d \sin \theta$, where d is the distance between adjacent columns (slits) and $\sin \theta$ is the distance between two adjacent principal maxima divided by the distance between the observing screen and the diffracting screen.[26] Since the average value of d was measured to be about 3.5 μm, the distance between two adjacent principal maxima was found to be about 12 cm when the wavelength of the laser beam was 632.8 nm and the distance between the observing screen and the diffracting screen was about 67 cm. The observed diffraction pattern, as shown in Figure 8b, is characterized by a principal maximum stripe, which has the brightest light intensity (arrow), and submaxima stripes, whose intensities fade away as the distance along the x axis increases. The next principal maximum was not observed in the figure, which may be due to the large separation distance between the two principal maxima and microstructural imperfections.

The obtained diffraction pattern reflects the quality of the grating-like microstructure of our modified blend film. As shown in Figure 8b, the diffraction pattern is not perfect, due to microstructural imperfections. We acknowledge that there are still some defects in our blend films, such as branches, small droplets, and a little waviness. These defects result in destructive interferences, which contribute to some missing lines. Despite these defects, a good grating diffraction pattern can still be produced with our PM1D8/PMMA 3:7 blend films. The ability to obtain a grating diffraction pattern is a strong indication that electric field is a promising tool for controlling the microstructure of an immiscible blend.

Conclusion

As shown in this study, a grating diffraction image can be produced by using an electric field-modified blend film. The obtained Fraunhofer grating diffraction pattern reflects the quality of the modified blend film. Our study indicates that it is possible to obtain an immiscible blend film with grating-like microstructure by appropriate control over experimental conditions, such as polymer concentrations, blend compositions, field strength, and molecular weights of blend components.

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