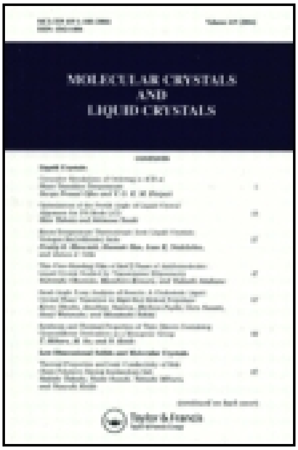

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Chromophore Rich Nanodomains in Bulk and Ultra Thin Film Polymer Blends

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Version of record first published: 24 Sep 2006.

To cite this article: Andrew H. Marcus , Terry Morkved , Heinrich Jaeger , Stuart A. Rice , Deborah M. Hussey , Nathan A. Diachun & M. D. Fayer (1996): Chromophore Rich Nanodomains in Bulk and Ultra Thin Film Polymer Blends, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 283:1, 31-35

To link to this article: http://dx.doi.org/10.1080/10587259608037860

Mol. Cryst. Liq. Cryst., 1996, Vol. 283, pp. 31–35
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Abstract The morphology of chromophore rich nanometer scale domains in binary homopolymer blends is studied, both in bulk systems and in ultra thin films. For each situation, a different experimental technique is applied. Electronic excitation transport (EET) studies are used to characterize the formation of amorphous nanodomains in the bulk, while transmission electron micrsocsopy (TEM) is used to observe nanocrystaline domains in ultra thin films.

INTRODUCTION

The details of molecular structure in polymeric solids is a topic of tremendous importance. Knowledge of structure at the molecular level is a necessary step toward a comprehensive statistical mechanical description of polymer bulk properties. Such an understanding can be employed to predict the physical properties of new materials, and to design materials with specific characteristics.

In the case of binary homopolymer blends, little is known about molecular structure during the initial stages of phase separation. The phase separation studied in this work is a nonequilibrium transformation from an unstable homogeneous phase to a stable two phase system. In the homogeneous phase, the blend's components are fully mixed on submolecular distance scales, while the phase separated blend contains segregated domains of macroscopic dimension. Molecular segregation, however, can occur on distance scales much smaller than the minimum domain size associated with macroscopic phase separation. Macroscopic domains are large enough to observe directly by light microscopy or light scattering methods ($R_d \sim$ 1,000 to 10,000Å), while nanodomains are too small to study by conventional techniques ($R_d \sim$ 10 to 100Å). A nanodomain is a region where as few as two or three polymer coils of one component have aggregated. The details of nanodomain structure and formation are not well understood. Nevertheless, it has been shown that nanodomains exist in solid blends which appear macroscopically homogeneous.[1,2]

Here we report observations of nanodomain formation in two chromophore containing polymer blend systems. In one case, nanodomains are studied in a bulk material using electronic excitation transport (EET) while in the other case, nanodomains are observed in ultra-thin films using transmission electron microscopy (TEM).

For the EET bulk studies, the experimental system is a copolymer, 6.5% atactic poly(methyl methacrylate-*co*-2-vinylnaphthalene) [P(MMA-2VN)] in atactic poly(vinylacetate) (PVAc). The naphthalene substituents serve as chromophores in the EET experiments. The mixtures are prepared such that initially the P(MMA-2VN) chains are randomly distributed in the PVAc matrix. The nanodomains are formed while low concentration mixtures of the P(MMA-2VN) in PVAc are held at constant temperature in the melt state ($T > T_g$), above the temperature at which phase separation occurs. In the melt the chains diffuse, and P(MMA-2VN) chains aggregate until the temperature is quenched below T_g. The structures of the resulting domains are examined with time resolved fluorescence depolarization measurements, and the data are analyzed using an analytical theory to model EET among interacting polymer chains.[3,4] Following this procedure, it is possible to characterize the aggregation process in terms of domain composition and size. The results of the analysis show that the nanodomains correspond to aggregates with a characteristic size equal to the radius of gyration of the copolymer, R_g. The number of P(MMA-2VN) chains in aggregates prepared under different conditions is determined.

Complimentary ultra thin film TEM studies are carried out on a similar, yet different, homopolymer blend system: 5% fluorescein tagged atactic poly(methylmethacrylate) in atactic poly(styrene) (PS). In these studies, the homopolymer mixtures are spin cast onto amorphous silicon nitride TEM membranes and held at a temperature above T_g for a fixed time. The results indicate the formation of quasi-crystaline chromophore rich domains of size approximately equal to the radius of gyration of the tagged PMMA molecules (100Å). These nanometer scale crystalites form inside the interior of microphase separated domains whose major component is the tagged PMMA. The morphological features of these films are complex and extremely sensitive to the sample preparation conditions.

EXPERIMENTAL METHODS

The EET experiments on bulk blends of P(MMA-2VN) in PVAc (PVAc $M_W = 80{,}000$) and the sample preparation conditions are described in detail in ref. 4. Similarly, a detailed account of the procedures used in the thin film studies of P(MMA-F) in PS (PS $M_W = 50{,}000$) will be published in the near future.[5] Only a brief overview is given here. Table I lists the physical characteristics of the copolymers used in both the bulk and the thin film studies. The value of the radius of gyration, $\langle R_g^2\rangle^{1/2}$, of the P(MMA-2VN) has been experimentally determined,[4] while that for P(MMA-F) is an approximation based on the assumption that the statistical segment length is similar to that found for P(MMA-2VN) in PVAc.

TABLE I Physical characteristics of chromophore containing copolymers

host	M_W	M_W / M_n	%chrom	$\langle N_{chrom}$ / coil$\rangle$	$\langle R_g^2\rangle^{1/2}$
bulk PVAc	25,300	1.55	6.5	16	34Å
thin film PS	15,000	2.1	5	7	~26Å

For the bulk measurements, mixtures of P(MMA-2VN) in PVAc dissolved in benzene (15% polymer in solvent) were freeze dryed by immersion in liquid nitrogen, followed by sublimation of the frozen benzene under vacuum. Optical quality samples were obtained by compression molding the freeze dryed material above the glass transition temperature of the blends ($T_g \cong 55°C$). The sample temperature was held between 82-87°C in an evacuated (~1 torr) stainless steel die cell for a fixed annealing time, after which the die was pressed to 0.5 metric tons and the sample immediately cooled. All samples were made with an appropriate width to insure an optical density below 0.2 at the peak absorption wavelength (320 nm). The samples were found to be optically clear (incapable of scattering visible light) and free of birefringence.

For the thin film measurements, mixtures of P(MMA-F) in PS dissolved in toluene (1% polymer in solvent) were spin cast onto amorphous silicon nitride substrates with 50Å thick membrane windows. Spin speeds were typically set to 9,000 rpm and the resulting sample film thicknesses (~100Å) were measured by elipsometry. The samples were placed in an evacuated glass tube (~1 torr) and the temperature held between 150-155°C for a fixed annealing time. The samples were allowed to cool gradually. The phase separated samples appeared homogeneous and free of macroscopic features when examined using an optical phase contrast microscope.

RESULTS

For the bulk studies, two series of solid solutions were prepared: series A and series B. In series A, the annealing time was held constant (t = 20 min) while the initial concentration of the copolymer was varied ($0.05\% \leq c_0 \leq 10\%$). In series B, all samples contained an identically low concentration of the chromophore containing copolymer ($c_0 = 0.31\%$), but the anneling time was varied ($0 < t \leq 16$ hr). In both series, the samples were anneled at similar temperatures ($T = 85 \pm 3°C$).

In figure 1 is shown time dependent fluorescence anisotropy data and theoretical calculations for the initial concentration dependent, series A, samples. For the calculations presented here, a Poisson average number of chromophore containing coils per domain ($\nu \equiv$ nanodomain concentration) was determined to obtain the best fit to the data. The smallest initial concentration decay (curve a, $c_0 = 0.05\%$) is the slowest and represents intra-coil EET. The calculated line through this data corresponds to $\nu = 1$. The curves that lie below represent inter-coil EET for initial concentrations $c_0 = 0.15$, 0.31, 2.5, 5 and 10%. As the initial copolymer concentration is increased, the rate of the observed EET also increases. This shows that the extent of copolymer aggregation increases monotonically with increasing c_0.

The theoretical fits shown with the data correspond to $\nu = 3, 4, 8, 10$ and 13. The disagreement for the lowest concentration at short time is due to a trace fluorescent impurity in the host PVAc. The fluorescence from this impurity occurs only at very short time and is detectable for the lowest concentration samples (0.15 and 0.05%). The theoretical calculations, with one adjustable parameter, i. e., the average number of coils per aggregate, are in quantitative agreement with the data. The theory, based on a Gaussian spatial distribution of chains in the copolymer aggregate, correctly predicts both the amplitude and the functional form of the anisotropy decays.

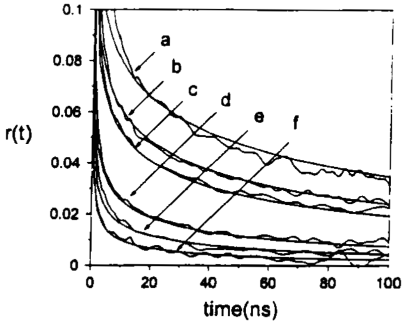


FIGURE 1 Time dependent anisotropy for series A samples.

Figure 2 shows anisotropy decays and calculations for the annealing time dependent, series B, samples. The initial concentration is identical for these samples, $c_0 = 0.31\%$. The slowest decay corresponds to longer annealing times (t_{an} = 20 min). Subsequently faster decays correspond to longer annealing times (t_{an} = 1, 4 and 16 hr). The accompanying theoretical calculations indicate that the aggregates increase in copolymer concentration (ν = 4, 6, 7 and 8) with increasing annealing time.

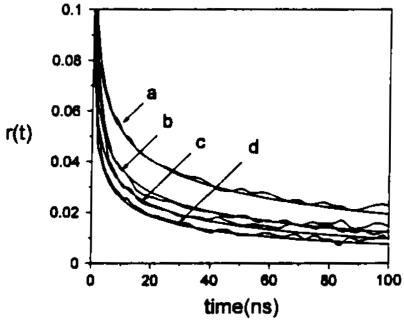
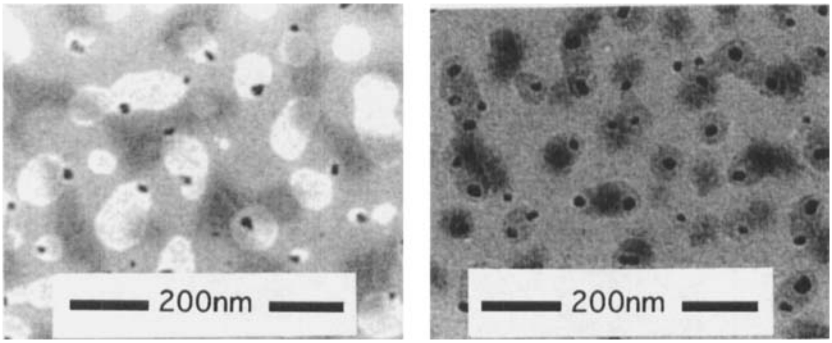


FIGURE 2 Time dependent anistropy for series B samples.

In the above analysis, the domains are assumed to maintain a constant volume, while the concentration of copolymer coils in the aggregate increases with annealing time. This situation is thought to occur during the initial stages of spinodal decomposition which is a spontaneous process that does not require thermal activation.[2] It is shown in ref. 4 that alternative mechanisms of domain growth such as thermally activated Ostwald ripening is inconsistent with the analysis. Thus according to our proposed mechanism, the nanodomains occupy a volume that has approximately the same dimension as a single chromophore containing copolymer chain. During the annealing period, those copolymer chains that approach one another within the distance $l = R_g$ form the aggregates. Each polymer chain occupies approximately 10% of the full nanodomain volume (based on the bulk density of PMMA and PVAc, identically 1.2 g cm^{-3}). Thus, for the annealing time dependent samples, the local concentration varies between 40 and 80% chromophore containing copolymer. This model has been validated further by the excellent aggrement between the results of the annealing time dependent analysis with the Smoluchowski equation used to describe the kinetics of colloid coagulation as a barrierless diffusion controlled process.[4] The c_0 dependent data is also shown to be consistent with the spinodal decomposition mechanism.

In figures 3 and 4 are shown transmission electron micrographs of a 120Å thick sample of 50% P(MMA-F) / PS that has been annealed for 4 hr. In both micrographs, two molecular layers exhibiting microscopic phase separation are distinguishable. Each layer contains PS rich (light regions) and P(MMA-F) rich (dark region) domains. The distinct layers can be seen most clearly when the dark regions in adjacent layers overlap, resulting in yet a darker shade of grey. Interestingly, the spatial correlations between like phases in adjacent layers appears to be very weak. The electron scattering contrast is believed to occur as a consequence of significant preferential beam degredation of the PMMA component of the blend.



FIGURES 3 and 4 Transmission electron micrographs of thin film samples.

The most significant features are the dark grey, circular shaped, spatially correlated objects that appear to be approximately monodisperse in size (~100Å). These nanodomains were observed to rapidly bleach during exposure to the electron beam and exhibited crystal-like character in that single domain diffraction patterns were observed when the microscope was placed in diffraction mode. We hypothesize that the thin film nanodomains are rich in fluorescein composition and that they form within the P(MMA-F) rich domains after significant microphase separation has occured. Further experiments are planned to test these assertions.

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