

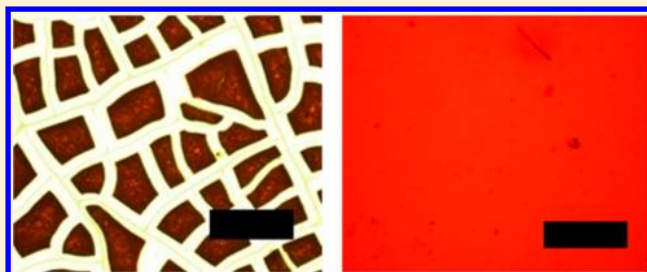
# Reducing Strain and Fracture of Electrophoretically Deposited CdSe Nanocrystal Films. II. Postdeposition Infusion of Monomers

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## S Supporting Information

**ABSTRACT:** Thick electrophoretically deposited (EPD) films of ligand-capped colloidal nanocrystals (NCs) typically crack when removed from the deposition solvent due to the loss of residual solvent. We report the suppression of fracture in several micrometers thick EPD films of CdSe NCs by treating the wet, as-deposited films with solutions of polymer precursor monomers, followed by UV-initiated polymerization. The monomers diffuse into voids and, for several monomers, dissolve the NCs to form a uniform dispersion in the film.



## 1. INTRODUCTION

In our companion paper,<sup>1</sup> we showed how fracture can be avoided in thick electrophoretically deposited (EPD) films of cadmium selenide (CdSe) colloidal nanocrystals (NCs) by infusing a solution of trioctylphosphine oxide (TOPO) capping ligands into the EPD film before solvent drying. Previous work had shown that these untreated films deposit on both electrodes and with high spatial selectivity on patterned conductive electrodes and are highly luminescing,<sup>2</sup> but fracture<sup>2–4</sup> after removal from the deposition solvent for films thicker than ~600–800 nm; this makes them unsuitable for several applications requiring nanoscale functionalization of macroscopic surfaces. This fracture occurs as a result of the stresses and strain that develop in the film, which still adheres to the substrate. Cracking also occurs and needs to be addressed in forming uniform, dense ceramic films by the EPD of stabilized nanoparticles without ligands.<sup>5</sup> In the companion paper,<sup>1</sup> fracture was suppressed in EPD NC films by the decrease in film strain and elastic modulus that accompanied the infusion of TOPO and subsequent capping of vacant binding sites on the NC cores, which had been occupied primarily by short-chain phosphonic acids and by TOPO before NC washing. In this study, we show that fracture can also be suppressed by a very different route through the infusion of small polymeric precursor molecules (i.e., monomers), followed by UV polymerization. These monomers are not known to cap the NC core and presumably initially diffuse into the voids between the NC cores. For monomers that cause relatively little film swelling, the packing density of NCs remains high. In several cases, the film becomes much thicker as a result of this treatment, which, along with other evidence, suggests that strain is relieved by the NCs dissolving into a polymer film network.

The equilibrium NC separation in the EPD film decreases as a result of the evaporation of the residual deposition solvent in

the already-formed EPD film.<sup>3,4</sup> However, the NC separation is fixed when the film adheres during drying, so in-plane tensile strain increases and, for large enough strains, fracture can occur.<sup>2–4</sup> The NC washing treatment needed for successful EPD of CdSe NCs removes a fraction of the capping ligands,<sup>6,7</sup> which leads to substantial contraction of the NC ligand shells during drying and corresponding increases in the tensile strain in the dried film and the likelihood of fracture. Fracture is suppressed after monomer infusion into the wet EPD film and UV-initiated polymerization. Because the polymer cannot evaporate and mass losses are reduced, film strain is reduced. The toughness of the NC–polymer composite may also potentially help in the ability of the film to tolerate strains that are created by the evaporation of any residual solvent.

The selected monomers should have good miscibility with the NC ligands (phosphonic acids and TOPO) to infiltrate the film completely. The monomer should not be volatile and should be easily polymerized using free-radical UV-polymerization to avoid the complications associated with high-temperature thermal free-radical polymerization. The polymerized film should have sufficiently high molecular weight (MW) to increase mechanical strength. To target these goals, we used the monomers methylmethacrylate (MMA), styrene, divinylbenzene (DVB), butanedioldimethacrylate (BDMA), hexanedioldimethacrylate (HDMA), and dodecanedioldimethacrylate (DDMA) to treat the still-wet EPD films. This provides an opportunity to study monomers that do not cross-link and those that do, including a series of acrylates with different chain lengths.

**Special Issue:** Electrophoretic Deposition

**Received:** June 7, 2012

**Revised:** August 27, 2012

**Published:** September 6, 2012

## 2. EXPERIMENTAL METHODS

The synthesis of CdSe NCs is described in the Supporting Information, using materials obtained from Sigma-Aldrich and used without purification. The average NC diameter was 3.5 nm in most runs (and 4.0 nm in the runs with mixtures of monomers), as determined by UV–vis absorption spectroscopy<sup>8</sup> and confirmed using transmission electron microscopy.

CdSe NCs were typically subjected to six cycles of centrifugal precipitation (washing) and dissolution using methanol and hexane, respectively. The final CdSe NC solution (in hexane) was used to deposit the EPD film on prescored gold-coated (~10 nm chromium/50 nm gold) silicon electrodes by applying 800 V across the electrodes, separated by 2 cm, for 10 min. EPD films formed on both electrodes with approximately the same thickness.<sup>2</sup> The dried, fractured untreated film was ~1.5–3.8  $\mu\text{m}$  thick, which is thicker than the threshold fracture thickness.

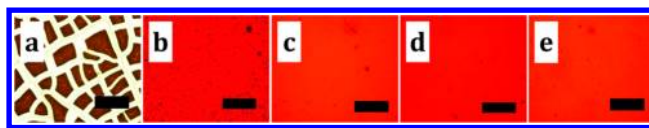
Following deposition, the films from one or both electrodes were quickly moved to baths of hexane. In most runs, the electrode was split along predefined score lines. One portion of the electrode was removed from this bath and allowed to dry in air under ambient conditions and called the untreated film. The other portions were moved to separate baths of the given monomer (MMA, styrene, DVB, BDMA, HDMA, or DDMA) with 3 wt % Irgacure 819 UV-initiator already dissolved in the monomer. (See the Supporting Information for a detailed description of monomer preparation.) These films were allowed to soak in their monomer bath for 12 h and after removal were spun for 6000 rpm for 1 min to remove excess monomer. Each film was subjected to UV radiation from a high-pressure mercury lamp for 10 min under a  $\text{N}_2$  atmosphere. Polymerized samples were placed in the dark under vacuum for 24 h to remove any unpolymerized monomer.

Film thicknesses were measured with a Dektak mechanical profilometer.<sup>9</sup> The elastic moduli of the films were measured using an Agilent G200 nanoindenter equipped with a standard diamond Berkovich tip that was oscillated at 40 Hz and driven to a depth of 1000 nm in the continuous stiffness measurement (CSM) mode, with a tip advancement of 0.2 nm per cycle (8 nm/s). Elastic moduli<sup>10,11</sup> were averaged from 200 to 250 nm into the films and were determined assuming a film Poisson ratio  $\nu = 0.18$ ; the obtained moduli were insensitive to the choice of  $\nu$  used for data analysis. (See the companion paper.<sup>1</sup>) The viscous response is described by the out-of-phase component, the loss modulus. This is presented for the films, as is usual, by the phase angles,<sup>10,11</sup>  $\tan^{-1}(\text{loss modulus/elastic modulus})$ , which were determined at 800 nm depth. Photoluminescence was measured using 514.5 nm excitation from a Melles Griot cw argon-ion laser.

See the Supporting Information in this and the companion paper<sup>1</sup> for more details about synthesis, other aspects of EPD film preparation, and measurement methods.

## 3. RESULTS

Cracking was suppressed across the EPD CdSe NC film in all samples that had been treated with DVB, BDMA, HDMA, and DDMA and then polymerized, as seen in the optical micrographs in Figure 1. They are stable (for at least 2 years). After soaking in MMA or styrene, there was no fracture during the early stages of drying. However, once the excess monomer overcoating the film was removed by spinning, fracture resulted over all of the MMA-treated films and over

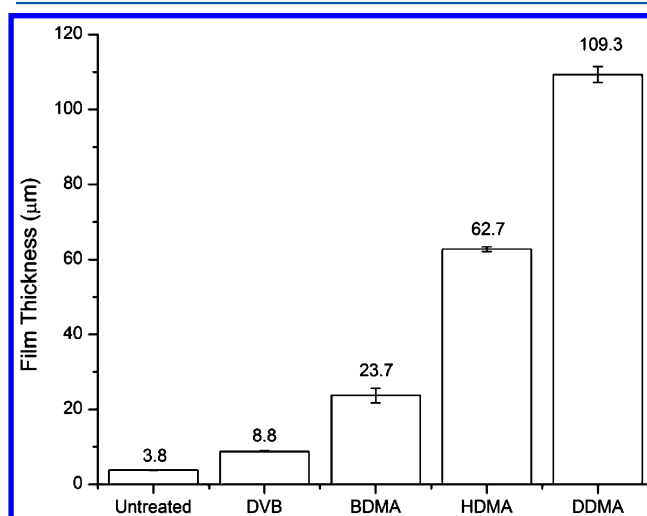


**Figure 1.** Optical micrographs of (a) 3.8  $\mu\text{m}$  thick untreated, control EPD film and EPD films treated by (b) DVB, (c) BDMA, (d) HDMA and (e) DDMA, and then polymerized (negative electrode film). The scale bar is 500  $\mu\text{m}$  wide.

much of the styrene-treated films, prior to UV polymerization, likely because of evaporation of these highly volatile monomers. Profilometry and nanoindentation measurements were made in the millimeter-dimension regions of styrene-treated films that did not crack. Films treated with styrene/DVB mixtures did not crack over the entire film.

Films were also briefly examined after monomer infusion but without polymerization. Films treated with DVB and BDMA but not polymerized eventually fracture under vacuum, likely due to monomer evaporation. HDMA and DDMA films do not crack without polymerization, even in vacuum for long times, likely because of very low monomer volatility, which is also coupled to good interactions between the monomers and NCs. Only the polymerized films are analyzed in detail below.

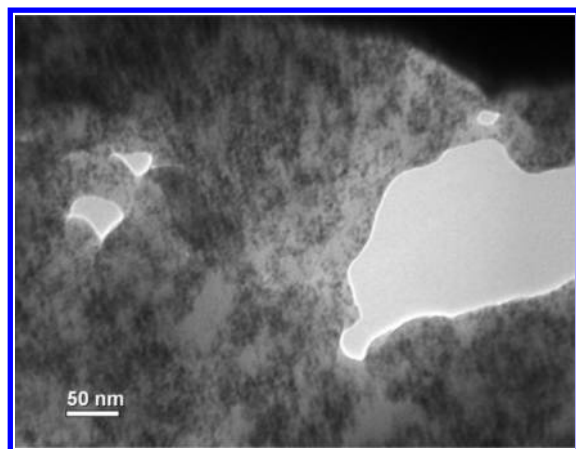
All of the treated and polymerized films are thicker than the untreated EPD films, which could be due to swelling or encapsulation by the polymeric material. DVB- and BDMA-treated films are only somewhat thicker than the untreated control, whereas the HDMA- and DDMA-treated films are much thicker than the untreated film (Figure 2).



**Figure 2.** EPD film thickness after monomer treatment and polymerization (negative electrode film).

Figure 3 shows a transmission electron micrograph (TEM) of the upper regions of the DDMA-treated film after ultramicrotoming, which shows that the NCs are dispersed in this (thickest) film. It is apparent that NCs are homogeneously dispersed in each NC/polymer composite film, with no polymer overlay that is devoid of NCs.

The nanoindentation traces leading to the data in Figure 4 are shown in Figure S1 (in the Supporting Information). The elastic moduli of DVB- and BDMA-treated films are roughly equal to that of the untreated films, whereas those of HDMA- and DDMA-treated films are much smaller than those of the untreated films (Figure 4a). Styrene-, BDMA-, HDMA-, and



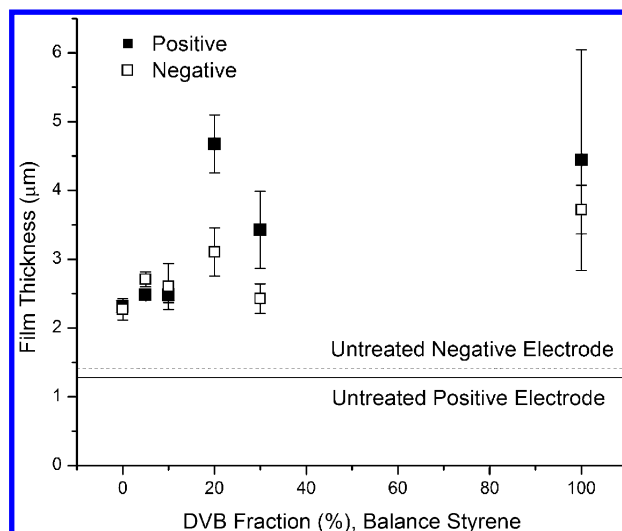
**Figure 3.** TEM of EPD film after DDMA-treatment, polymerization, and ultramicrotoming (negative electrode). Note that the sample chipped due to the ultramicrotoming.

DDMA-treated films have a larger phase angle (i.e., are more viscoelastic) than the untreated films, whereas the DVB-treated films have a phase angle comparable to that of the untreated film (Figure 4b). In each case, the elastic modulus and phase angle are nearly equal to those of films of the pure polymer.

Films treated by mixtures with varying fractions of DVB and styrene were thicker and softer (lower elastic modulus) than the untreated films and were thicker, with larger elastic modulus with more DVB, for films formed on both electrodes (Figures 5 and 6). This last result is unsurprising, given that DVB can cross-link the polymer matrix and thus increase the modulus. Styrene can yield only linear polymers with smaller elastic moduli.

Figure S3 (in the Supporting Information) shows that the film modulus of EPD films treated with styrene decreases when the initiator concentration is increased for films formed on the positive and negative electrodes. This result again reinforces the fact that the moduli are related to the MW of the chains created by polymerization; the more the initiator, presumably, the lower the MW. (We have not conducted any gel permeation chromatography or other experiments to characterize the MW; however, these are expectations derived from the long-standing knowledge of polymerization processes.)

All of the polymer-treated films have larger photoluminescence (PL) efficiency than the untreated films (Figure 7), with



**Figure 5.** Thickness of the EPD film on the positive and negative electrodes after treatment solutions of varying fractions of DVB and styrene monomers, followed by polymerization.

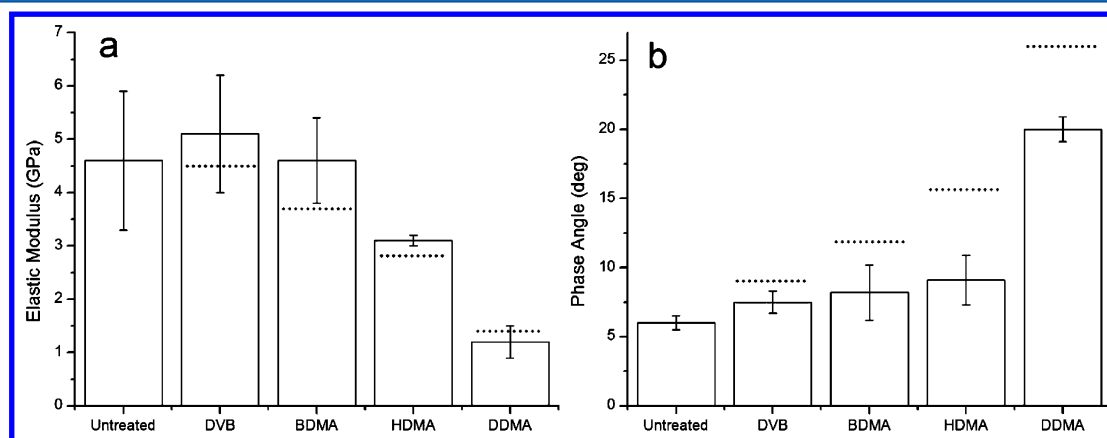
~5× increases in PL in the DVB- and polystyrene-treated films, over 10× increases in PL the BDMA- and HDMA-treated films, and even more so in the DDMA-treated films. Each shows a small red shift relative to the untreated films.

## 4. DISCUSSION

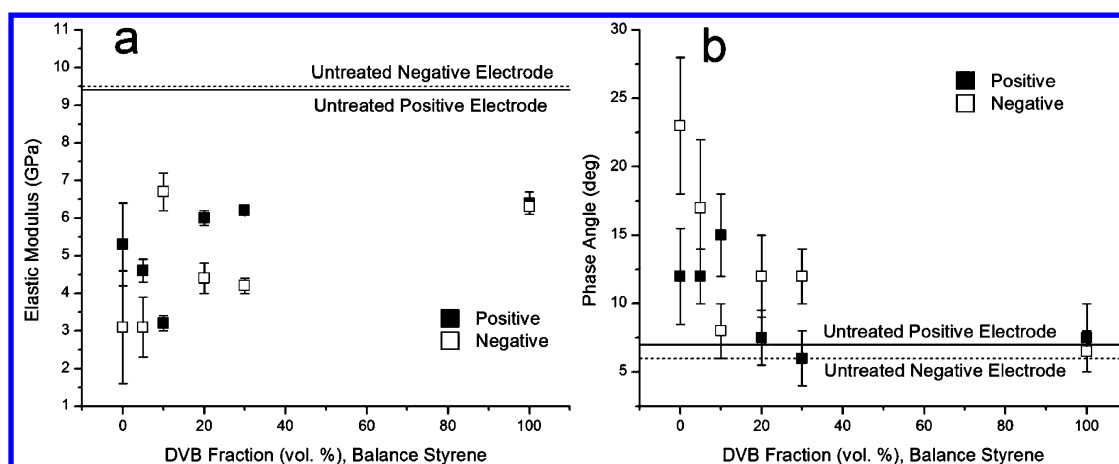
**4.1. Overview of Film Properties.** We assume that when the EPD NC film is contacted with the monomer, an equilibrium state is attained where the pure monomer is in equilibrium with a NC phase mixed with monomers. Under this assumption, the Flory–Huggins parameter  $\chi$  of the NCs in the monomer is determined using<sup>12</sup>

$$\chi = -\ln(1 - \phi)/\phi^2 - 1/\phi \quad (1)$$

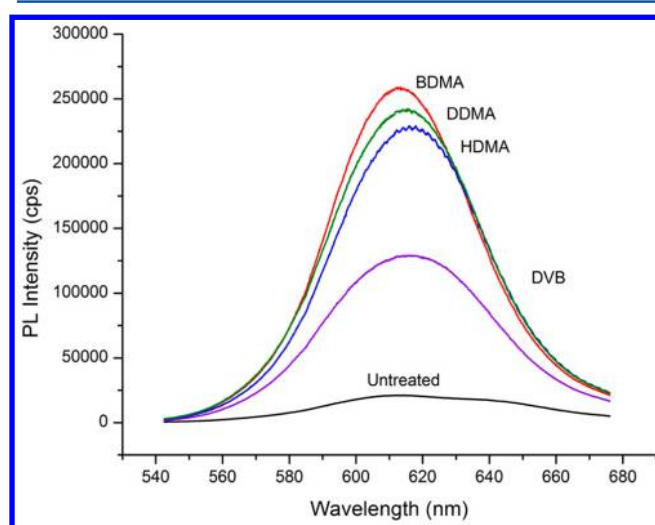
where  $\phi$  is the volume fraction or loading factor of the dried untreated EPD film in the final polymerized film (which differs from the definitions of the volume fractions  $c$  of the different components of the film in the companion paper) and where we assume that a NC corresponds to a polymer with infinite MW. The resulting  $\chi$  parameters are reported in Table 1. The values of these parameters suggest that only partial miscibility is the norm when monomers are contacted with the NC film. This



**Figure 4.** (a) Elastic modulus and (b) phase angle of EPD films after monomer treatment and polymerization along with that for the untreated film for each sample (negative electrode). Data are also shown for the pure polymer films as dashed lines.



**Figure 6.** (a) Elastic modulus and (b) phase modulus of the EPD film on the positive and negative electrodes after treatment solutions of varying fractions of DVB and styrene monomers, followed by polymerization.



**Figure 7.** Photoluminescence of the EPD film after monomer treatment followed by polymerization (negative electrode).

**Table 1.** Flory-Huggins Parameters  $\chi$  for the EPD Films after Monomer Diffusion and Polymerization

treatment	thickness ( $\mu\text{m}$ )	estimated EPD film loading (vol %), $\phi$	$\chi$
none	3.8	1	
DVB	8.8	0.43	0.72
BDMA	23.7	0.16	0.56
HDMA	62.7	0.06	0.52
DDMA	109.3	0.03	0.51

result arises from our underpinning assumption that there is an equilibrium between a pure monomer phase and one composed of a mixture of NC and monomer. Under these conditions,  $\chi > 0.5$ , which is indeed what is found. The differences in  $\chi$  cannot be rationalized on the basis of regular solution theory,  $\chi \propto (\delta_m - \delta_{\text{NC}})^2$  because the solubility parameter,  $\delta_m$ , is about the same for each monomer,<sup>13,14</sup> and that of the NCs,  $\delta_{\text{NC}}$ , is fixed. Our results in Table 1 show that the NCs are barely miscible in DVB and are fairly miscible in the acrylates, the more so the longer the alkane chain in the acrylate. Using single monomers, film swelling is relatively small when using DVB and is even smaller with styrene–DVB mixtures (Figure 5). Some other factor, such as specific interaction between the acrylate group

and the NC surface or the interactions of the alkane spacers in the acrylate and the alkane part of the TOPO ligand, may play a role here, but these issues cannot be resolved with the experiments that have been performed to date. We defer these issues to future work.

The inverse relationship of film elastic modulus and thickness occurs for several reasons: The elastic moduli of the polymers are smaller than those of the NCs, and they are smallest for the polymers in which the NCs are most miscible, so they are thicker and the NC loading factors are lower. The phase angle increases with film thickness because of the larger viscoelasticity of the polymers relative to the NCs, particularly for the monomers in which the NCs are most miscible.

A cross-linked polymer network, like that formed by DVB (a difunctional monomer), is expected to be more rigid than a similar polymer composed of individual chains (like that formed by styrene). Control films prepared of pure polymer confirm this, with the elastic moduli of poly-DVB and acrylate films (Figure 4a) larger than that of polystyrene ( $\sim 4.2$  GPa) and with those of the correspondingly EPD films being larger.

The cross-linking of polymers from one inter-NC interstitial region to the neighboring region may be small when there is little film swelling but is clearly important when there is much swelling and the NCs are effectively dispersed in the polymer as in Figure 3.

In addition to suppressing fracture with relatively little film swelling, styrene–DVB mixtures can be used to control the physical and chemical properties by controlling the cross-link density, which can be tuned by the DVB content, as has been seen for proton exchange membranes (PEMs).<sup>15,16</sup> Recently it has been shown that the incorporation of inorganic nanoparticles within PEMs can impart enhanced mechanical, thermal, and mass-transport properties to the composite material.

The TEM of the ultramicrotomed sample and the observed increase in PL efficiency of polymer-treated films suggest that the NCs are homogeneously distributed in an insulating film matrix. Such large increases in PL would not occur if a polymer-rich phase simply encapsulated an underlying NC-rich phase. The increase in PL efficiency suggests NC dispersion in the polymer and some passivation of the NC core surfaces; this could also explain the small PL red shifts seen in the polymer sample. The monomers are not conventionally used as ligands to cap and passivate the surfaces of CdSe cores. This increase in



PL seems to be particularly strong for the acrylates (Figure 7), which suggests strong interactions with vacant sites on the core surface. The PL red shift may suggest slight carrier delocalization at the core associated with this surface passivation.

As seen in previous studies,<sup>2</sup> similar EPD CdSe NC films form on the positive and negative electrodes. Figures 5 and 6 and Figures S3 and S4 of the Supporting Information show that they are modified in the same way by the polymer treatment.

**4.2. Stress and Strain.** After monomer infusion, the monomers fill the voids, and there is a relatively smaller increase in film thickness for the smaller monomers, and the particles effectively dissolve in the polymeric material and there is a relatively larger increase in film thickness for the larger monomers. (The companion paper<sup>1</sup> shows that there can be an ~38% increase in EPD film thickness with the relief of in-plane just by adding more ligands to cap the cores.) The infusion of monomers likely largely removes the strain that would otherwise develop in the EPD NC films as a result of solvent evaporation and adherence of the film on the substrate.

However, after UV polymerization, the volume of the composite material decreases, and the final in-plane tensile strain of these adhering films is determined by the difference in monomer and polymer densities. For pure DVB, the volume contraction is ~10% after polymerization, so the in-plane tensile strain after the isotropic contraction is ~0.03. For BDMA, the corresponding values are 3% and 0.01. In each case, the in-plane strain is much smaller than that for the untreated films and below the threshold for film fracture.

**4.3. Consideration of Fracture.** Using the Griffith's criterion for critical film thickness for fracture,<sup>17</sup> polymer treatment of EPD NC films may prevent fracture by one or more potential mechanisms:

- (1) Decreased strain: The volume of the film originally occupied by deposition solvent is now occupied by polymer, so film contraction and corresponding tensile stresses are reduced. When the NCs are miscible in the monomers, strains and stresses should vanish, that is, until polymerization. This mechanism is likely very significant in suppressing fracture.
- (2) Increased film toughness: It has been well-documented that the incorporation of nanoparticles in a polymer yields a composite material with toughness greater than that of the constituent polymeric phase.<sup>18</sup> This could be part of the reason for the suppression of fracture in the treated EPD NC films.
- (3) Increased plasticity: The infusion of monomers could be expected to increase film plasticity, so that NCs could reorganize and the film could relax prior to polymerization. Because the evaporation of monomers prior to polymerization noted in some cases led to film cracking, monomer infiltration apparently did not lessen strain film in these cases, and so this mechanism is likely not important. There could be some local relaxation, but it does not occur on a large scale. For an adhering film, a decrease in film thickness would be expected after NC relaxation over large distances, but this is not seen.
- (4) Film overcoating: The EPD film could be overcoated by a polymer film that bears a compressive stress to lessen film contraction. The TEM in Figure 3 showing NC dispersion and the polymer increase in PL (Figure 7) suggest that there is no mechanically robust overcoat,

and so this is not a primary source of crack suppression. Furthermore, such large increases in PL would not occur if a polymer-rich phase simply encapsulated an underlying NC rich phase.

## 5. CONCLUSIONS

When large strains and fracture arise after drying of EPD films formed from NC with incomplete ligands shells on the core, the mechanical state of the film can be substantially improved through the infusion of small monomers in the still wet film, followed by polymerization. Specifically, it was seen here that treating EPD CdSe NC films with several monomers, followed by UV-initiated polymerization, suppresses cracking. The packing density of NCs remains relatively high for several of the polymers (as it is for the untreated EPD NC films), in particular for those formed using DVB and styrene–DVB mixtures. However, this density is reduced when the film becomes much thicker, such as after treatment with HDMA and DDMA, for which strain is relieved by the NCs dissolving into the monomer solution. UV polymerization likely leads to some tensile strain, but this is not sufficient to cause film fracture. This monomer treatment increases film PL, apparently by passivating the NC core surfaces. Film electrical conductivity might also be controllable by the choice of the monomers that are infused; increasing charge conductivity would be important for several applications of EPD NC films, such as for solar cells<sup>19</sup> and field-effect transistors. The companion paper<sup>1</sup> shows that fracture can also be suppressed by recapping the core with ligands before film drying.

## ■ ASSOCIATED CONTENT

### Supporting Information

Further data concerning the sample preparation and properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was primarily supported by the MRSEC program of the National Science Foundation (DMR-0213574), the NSEC program of the NSF (CHE-0641523), the EFRC program of DoE (DE-SC0001085), and the New York State Office of Science, Technology, and Academic Research (NYSTAR).

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