

Optical Properties of Block Copolymers Containing Pendant Carbazole Groups and *In Situ* Synthesized CdS Nanoclusters

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Received 6 June 2002; accepted 14 June 2002

ABSTRACT: Ultraviolet–visible absorption spectra and photoluminescence spectra were used to demonstrate efficient charge-carrier migration in a novel bulk heterogeneous block copolymer system. One moiety of the block copolymer was functionalized with charge-transporting carbazole groups, whereas the other block formed domains suitable for the *in situ* synthesis of CdS nanoclusters. The excitation of the cluster-free copolymers with 350-nm-wavelength radiation led to a strong emission peak at 450 nm that was associated with the carbazole groups. When CdS clusters

were present in nearby but spatially distinct domains, the carbazole emission was completely quenched and replaced by a very broad emission in the visible range (near 560 nm). The implications of these observations are discussed in the context of the energy-transfer mechanism and possible device applications. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 177–182, 2003

Key words: block copolymers; nanocomposites; charge transfer

INTRODUCTION

Previous work in our research group has demonstrated the feasibility of growing ZnS, PbS, and CdS nanoclusters in microphase-separated block copolymers.^{1–3} CdS clusters are of special interest for optoelectronic applications because the bandgap of the bulk material is in the visible region of the spectrum (~2.42 eV or 512 nm).⁴ CdS nanoclusters were synthesized by Yue and Cohen³ inside spherical microdomains in MTD₈₀₀NORCOOH₃₀ diblocks (where MTD is methyltetracyclododecene and NORCOOH is norbornene-2,3-dicarboxylic acid). The polymer film itself was electrically insulating because the major block [poly(MTD)] was a nonconductive hydrocarbon.

The goals of this project were to extend Yue and Cohen's³ earlier results in several different ways. We introduced a novel charge-transporting repeat unit in place of the insulating MTD and examined its influence on the optical properties of the organic–inorganic nanocomposites. In addition, the cluster-confining NORCOOH block was replaced in this work with a

repeat unit containing pendant alcohol groups so that we could examine the role of polymer-cluster surface interactions⁵ on the *in situ* synthesized cluster size.

Photoluminescence and ultraviolet–visible (UV–vis) absorption spectra presented later in this article indicate that charge-carrier migration occurs efficiently in the heterogeneous block copolymer domain structure, leading to the quenching of polymer emissions and favorable energy transfer to the clusters. The CdS clusters synthesized within such block copolymer microdomains are probably too polydisperse and defect-laden to capitalize on this interesting charge-transfer mechanism for device applications. Possible alternatives are discussed.

EXPERIMENTAL

Materials

All of the polymerizations were carried out under an inert atmosphere in a nitrogen-filled drybox. Chemicals were used as received unless otherwise noted. Trimethylchlorosilane and 5-norbornene-2-methanol (OH) were purchased from Aldrich. Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride, a ring-opening metathesis polymerization (ROMP) initiator, and dimethylcadmium were purchased from Strem. Hydrogen sulfide (chemically pure) was obtained from Matheson. All solvents were commercial re-

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Contract grant sponsor: National Science Foundation (through the MRSEC Program); contract grant number: DMR 94-00334.

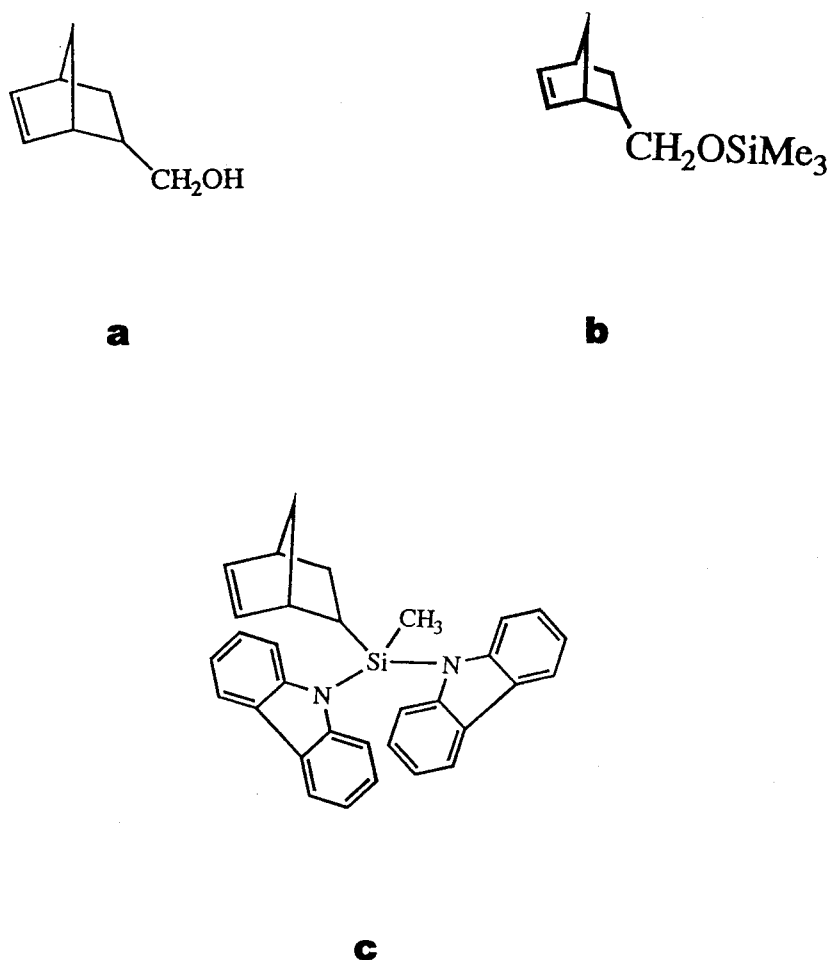


Figure 1 ROMP monomers used in this study: (a) OH, (b) OTMS, and (c) CAR.

agents or anhydrous-grade products and were used without further degassing or drying.

Characterization

¹H-NMR spectra were recorded on a Bruker 250-MHz NMR spectrometer. Gel permeation chromatography (GPC) was carried out on a series of Waters Styragel HR4 columns equipped with a differential refractometer, with polystyrene as calibration standards and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min. Solutions were diluted to a concentration of 4 mg/mL and syringe-filtered through a 0.5- μ m Millipore filter disk before injection. Transmission electron microscopy (TEM) was performed on a JEOL 200CX instrument operating at 200 kV. Ultrathin sections (~50 nm thick) for the TEM studies were prepared by the microtoming of bulk specimens on an LKB ultramicrotome. UV-vis absorption spectra and photoluminescence emission spectra were recorded on a Cary 5E spectrophotometer and a SPEX Fluorolog spectrophotometer, respectively.

Monomer and polymer synthesis

The synthesis of the charge-transporting norbornene carbazole monomer (CAR) was described in detail previously.^{6,7} The cluster-binding alcohol monomer OH was converted into its tetramethylsilane (TMS)-protected form (OTMS) by the reaction of OH with a mixture of trimethylchlorosilane and pyridine in diethyl ether, according to a previously published procedure.⁸ Figure 1 shows the relevant monomer structures. For the diblock to be made, the protected alcohol monomer (72 mg, 0.36 mmol, 200 initiator equiv) was added neat to the ruthenium ROMP-initiated and still living CAR homopolymer (**1**) reaction mixture,⁶ stirred for 1 h, and then terminated with 10 μ L of ethyl vinyl ether. The color of the solution changed from pink to yellow when the second monomer, OTMS, was added. Attempts to use the unprotected form, OH, of the alcohol monomer directly did not result in a successful addition of the second block. The polymer was precipitated in methanol and dried overnight in a vacuum oven at room temperature. The protected diblock copolymer CAR₂₀₀OTMS₂₀₀ (**2**) was obtained

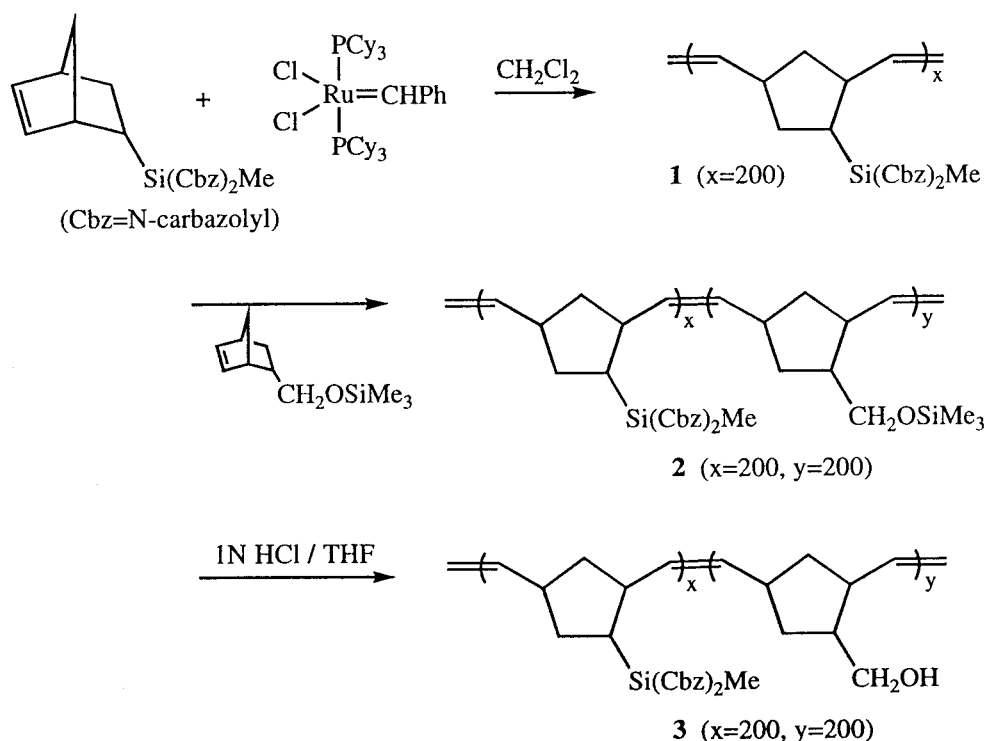


Figure 2 Protection-deprotection scheme for the synthesis of diblock copolymers 2 and 3.

as a fluffy white solid in a 100% yield. The deprotection of 2 was performed by 0.95 mL of THF and 0.05 mL of 1.0N aqueous hydrochloric acid being added to 30 mg of the polymer and by the mixture being allowed to stand at room temperature for 2 h, by which time nearly complete dissolution had been achieved. The polymer was then precipitated in methanol; diblock copolymer $\text{CAR}_{200}\text{OH}_{200}$ (3) was obtained as a flaky, white solid in a 100% yield. Figure 2 summarizes the copolymer synthesis; more details appear in refs. 6 and 7.

Film casting

Bulk films of 2 and 3 were prepared by the dissolution of approximately 45 mg of the desired polymer in 1 mL of THF and the transference of the solution to a 1.5-cm² casting dish made from Teflon-coated aluminum foil. The solvent was allowed to evaporate slowly overnight. The resulting films were transparent, colorless, and approximately 0.1 mm thick, and they were easily peeled off the supporting substrates.

In situ synthesis of CdS clusters

The vacuum-dried bulk diblock copolymer films were taken inside the drybox, sealed inside a 9-oz jar that contained a small, uncapped vial of CdMe_2 (ca. 4 mL), and allowed to soak in the organometallic vapors overnight. The appearance of the films was un-

changed after this treatment. The films were then removed from the jar and pumped down in the drybox antechamber for 30 min for the removal of any excess CdMe_2 , returned to the drybox, and sealed inside a 50-mL, round-bottom glass flask equipped with a glass stopcock. The flask was then removed from the glove box and attached to a Schlenk line, where it could be manipulated, evacuated, and backfilled with H_2S gas from a lecture bottle. After overnight exposure to H_2S , the films were removed from the flask, and any excess H_2S was allowed to dissipate inside the fume hood. At this point, the polymer films were still transparent but distinctly yellow in color, and this was consistent with the expected formation of CdS nanoclusters. In a separate control experiment, polymer films that were not loaded with cadmium remained colorless when treated with H_2S .

RESULTS AND DISCUSSION

The polymerization of the charge-transporting, carbazole-functionalized norbornene monomer proceeded smoothly with the ruthenium initiator. Attempts to prepare block copolymers by the subsequent addition of unprotected norbornene-2-methanol or unprotected norbornene-2-carboxylic acid were unsuccessful (i.e., GPC traces of the polymer did not show any increase in molecular weight after the second monomer was added), apparently because of catalyst deactivation. This result was not expected because the ruthenium-

TABLE I
Molecular Weight Data for the ROMP Polymers
and Block Copolymers of Figure 2

| Polymer ^a | M_n (observed) ^b | M_w/M_n | M_w/M_n^c |
|----------------------|----------------------------------|-----------|-------------|
| 1 | 57,000 | 1.26 | 1.05, 1.09 |
| 2 | 134,000 | 1.22 | 1.13, 1.07 |
| 3 | 104,000 | 1.46 | 1.08, 1.25 |

M_n = number-average molecular weight; M_w = weight average molecular weight.

^a See Figure 2 for identification of structures 1, 2, 3.

^b Determined by GPC with polystyrene calibration standards.

^c Individual polydispersity indices of main polymer peak and double molecular weight peak.

based initiators are known to be exceptionally tolerant^{9,10} of these functional groups. It has been reported, however, that certain polar functional groups are less well tolerated in the specific case in which they are present as 2-endo substituents on a norbornene ring.¹¹ The particular intramolecular geometry of the system in this case can encourage chelation of the functional group to the metal center, with possible adverse effects on the polymerization.¹⁰ In light of this finding, block copolymers containing the alcohol monomer had to be prepared by the polymerization of the TMS-protected form of the monomer and deprotection of the polymer afterward by acid hydrolysis (see Fig. 2 and Table I). The protecting groups on the polymer were stable indefinitely outside the drybox and were unaffected by exposure to water at neutral pH, but they could be removed easily and quantitatively by a treatment with dilute aqueous acid.

Evidence for the successful formation of the block copolymer comes in part from the microphase-separated morphologies presented later and also from GPC studies,⁶ which showed a clear increase in the molecular weight upon the addition of the protected alcohol monomer. The polymerization of the CAR monomer was essentially complete after 2 h.⁶ The addition of the OTMS protected alcohol monomer shifted the position of the polymer peak toward shorter elution times, and the location of the block copolymer peak became stable within 1 h of the addition of OTMS. The molecular weight distribution of each polymer was reasonably narrow and would have been even narrower were it not for the presence of a small high molecular weight shoulder, which occurred at exactly twice the molecular weight of the main polymer peak. A high molecular weight material of this sort has been observed previously in ruthenium-based ROMP polymerizations and may be due to some sort of slow polymer coupling reaction¹² or to a side reaction during termination.⁸

Microphase separation in static-cast films of the diblock copolymers was observed⁶ by the loading of

the films with cadmium and their examination by TEM. The heavy cadmium atoms essentially acted as selective stains for the alcohol-containing block because dimethylcadmium was readily coordinated by the oxygen atoms of the protected (OTMS) or unprotected (OH) alcohol but did not form strong dative bonds with the very weakly basic carbazole (CAR) nitrogen. Because cadmium was selectively sequestered into the OH or OTMS domains of our block copolymers, it was possible to localize the synthesis of CdS to these regions of the heterogeneous block copolymer morphologies with the block copolymer nanoreactor scheme developed by Yue and Cohen.³ Figure 3 shows a transmission electron micrograph of an ultramicrotomed section of a block copolymer exposed sequentially to CdMe₂ and H₂S. The hydrolyzed block copolymer 3, in which the OH block constituted a smaller volume fraction of the sample because of the removal of the bulky trimethylsilyl groups, displayed a spherical morphology (Fig. 3), whereas a mixed cylindrical/spherical morphology was observed^{6,7} for the protected copolymer 2. The overlapping appearance of the spheres was a result of the fact that the film thickness (~50 nm) was more than twice the diameter of the microdomains (~20 nm), so that two misaligned layers of spheres were simultaneously visible.

Evidence for CdS cluster formation came from the observed yellow color of the films and from UV-vis

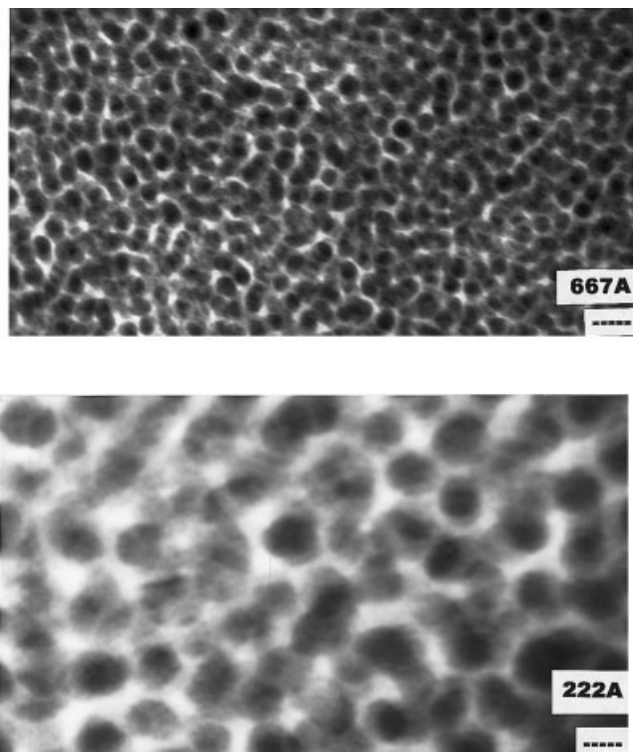


Figure 3 Transmission electron micrographs at two different magnifications for copolymer 2 after exposure to CdMe₂ and H₂S.

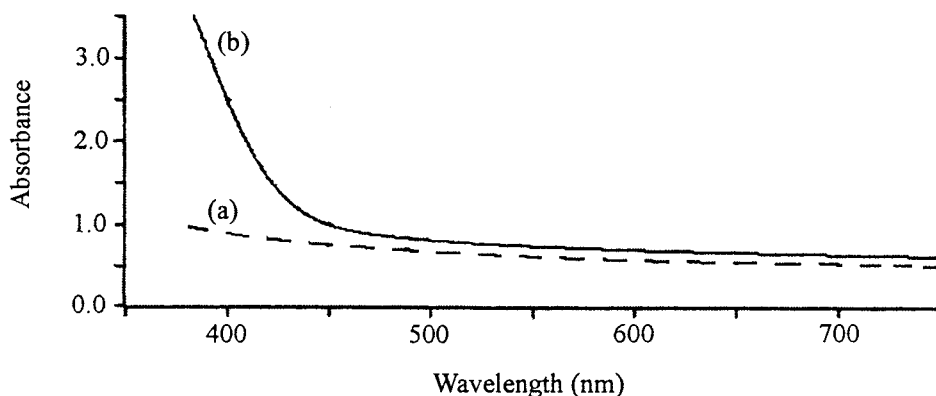


Figure 4 UV-vis absorption spectra of block copolymer 2: (a) without treatment and (b) after loading with CdMe_2 and treatment with H_2S .

and photoluminescence spectra, which are presented and discussed later. However, individual CdS clusters are not clearly discernible in the micrograph of Figure 3, although a grainy contrast is evident in certain regions of the higher magnification image. This suggests that the clusters were too small to be individually visible (<2 nm in diameter) and that multiple clusters were dispersed throughout each spherical domain. The very small cluster size is consistent with the UV-vis data that follow.

UV-vis absorption spectra for a bulk film of block copolymer 2 (both before and after treatment with CdMe_2 and H_2S) are shown in Figure 4. The equivalent absorption spectra for block copolymer 3 are nearly identical in appearance. The untreated films produced a low and relatively flat absorbance across the entire visible region of the spectrum. Films exposed to CdMe_2 and H_2S , in contrast, showed a strong

absorption edge of the type typically associated with a direct semiconductor bandgap. The onset of the absorption occurred at approximately 430 nm, highly blueshifted from the corresponding onset of absorption in bulk CdS (512 nm). This was consistent with the presence of CdS nanoclusters of extremely small size, with a larger than normal bandgap due to their less delocalized, more quantized band structure. Contrary to expectations,^{2,5} this use of alcohols in place of carboxylic acids³ as surface coordinating groups did not weaken the capping interaction enough to grow clusters of significantly larger size.

Photoluminescence spectra for bulk film copolymer 2 (both before and after treatment with CdMe_2 and H_2S) are shown in Figure 5. The corresponding spectra for block copolymer 3 (not shown) are essentially identical. The untreated films showed a strong fluorescence, attributable to the pendant carbazole groups,

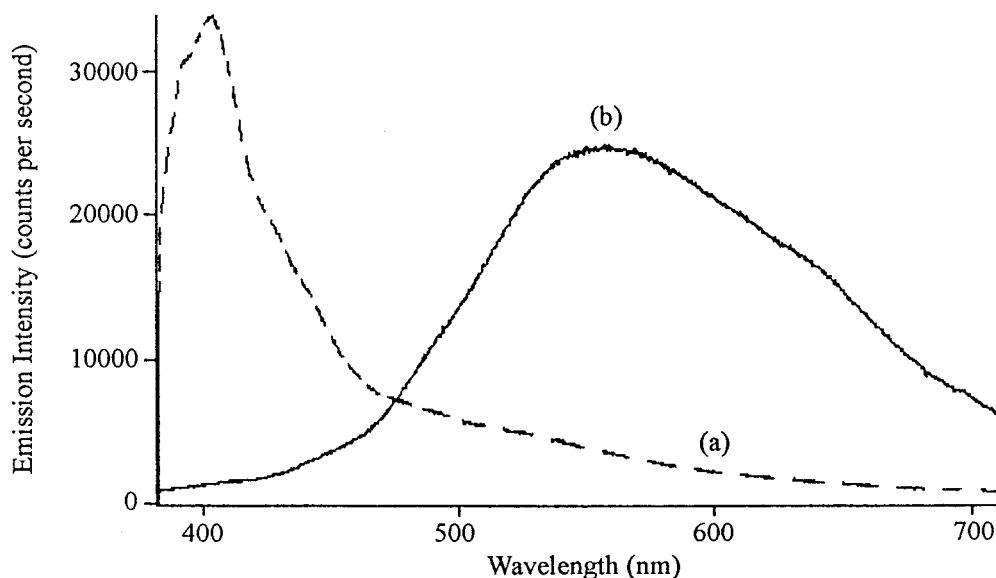


Figure 5 Photoluminescence spectra of block copolymer 2 with 350-nm excitation: (a) without treatment and (b) after loading and treatment with H_2S . The excitation wavelength was 350 nm.

in the near-UV and deep violet regions of the spectrum when excited at a wavelength of 350 nm. The peak carbazole emission occurred at approximately 405 nm. There was little emission at longer wavelengths, other than a slight tailing of the main peak. Films containing CdS nanoclusters, however, showed a strong, broad emission in the visible region of the spectrum centered at approximately 560 nm, and the carbazole emission was completely quenched. The pronounced redshifting of the CdS cluster emission peak [Fig. 5(b)] with respect to its absorption edge [Fig. 4(b)], coupled with its broadness, indicated that the emission mainly occurred from surface defects or trap states. The quenching of the carbazole emission provided strong evidence that the charge carriers that were photogenerated on the carbazole groups were efficiently migrating across the block copolymer domain boundaries to the lower energy trap states on the clusters. Recombination at the CdS clusters, rather than on the carbazole groups themselves, accounted for the redshifted emission.

The carrier migration mechanism probably involves the Förster energy transfer¹³ of bound electron-hole pairs (excitons), rather than the sequential transfer of individual charges by a hopping mechanism. The hopping mechanism operates only over relatively short (5–10-Å) distances, whereas the Förster mechanism can operate over distances of up to 50 Å.^{14,15} Because of the small and regular characteristic length scale of the heterogeneous block copolymer morphology (Fig. 3), most of the carbazole groups were indeed within 50 Å of a cluster-containing microdomain, and this enabled the efficient quenching of almost all the carbazole groups, not merely those immediately adjacent to a microdomain interface. The intensity of the cluster emission was probably enhanced by this energy transfer. We also note that the interesting energy-transfer mechanism observed here may be specific to the system under consideration because of the strong spectral overlap between the carbazole emission peak and the nanocluster absorption edge.

The broad visible emission of the *in situ* synthesized CdS clusters shown in Figure 5 may be unsuitable for optoelectronic device applications for which narrow wavelength emission bands are desired. Solution-grown nanoclusters with fewer surface traps and a narrower and more controllable size distribution might be more advantageous. The spatially selective incorporation of such externally synthesized clusters into block copolymers has been demonstrated.^{6,16} We have used this methodology to incorporate externally synthesized CdSe nanoclusters into charge-transporting block copolymers of the type discussed here. The

photovoltaic properties of the resulting block copolymer nanocomposites will be reported in a forthcoming article.

CONCLUSIONS

We have demonstrated that the efficient migration of photogenerated charge carriers occurs in the bulk heterogeneous morphology of a carbazole-functionalized block copolymer. Because of the distances involved in this migration process, the Förster energy transfer was identified as the underlying mechanism. These findings are interesting because they lead to possible efficient energy transfer from a UV-absorbing moiety in one block to optical emitters located in the domains of the second block of the copolymer. The *in situ* synthesized CdS nanoclusters employed in this study did exhibit strong emissions in the visible range (centered around 560 nm), although the broadness of their emission spectrum may limit applications. The breadth of the CdS emission spectrum was attributed to a broad cluster size distribution and to a dominance of surface defects in their optical behavior.

The authors thank M. Frongillo of the MIT Center for Materials Science and Engineering for assistance with the TEM experiments carried out in the CMSE shared experimental facilities. J.A.G. thanks the Department of Defense for a graduate fellowship.

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