

Luminescent Electrophoretic Particles via Miniemulsion Polymerization for Night-Vision Electrophoretic Displays

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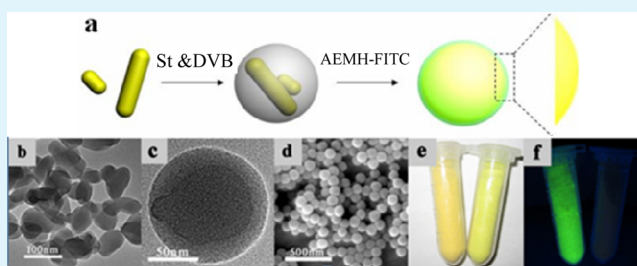
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S Supporting Information

ABSTRACT: A novel glowing electrophoretic display (EPD) is achieved by luminescent electrophoretic particles (EPs), which is potentially to improve the situation in which the existing EPDs disable in darkness. To combine both modes of reflective and emissive displays, a trilayer luminescence EP is designed and synthesized via an improved miniemulsion polymerization. The luminescence EP is composed of a pigment core, a polystyrene interlayer, and a fluorescent coating. The particle sizes are from 140 to 170 nm, and the size distribution is narrow. Their ζ potential value is -12.4 mV, which is enough to migrate in the electrophoretic fluid by the driving of an electric field. The display performance of the particles in an EPD cell has been characterized under the bias of 20 V. Both the reflectance (491 nm) and fluorescence (521 nm) intensities of the EPD cell remained in a constant range after 30 switches.

KEYWORDS: E-paper, display, night vision, electrophoretic particles, luminescence, miniemulsion polymerization



The synthesis procedure and characteristics of the LEPs

1. INTRODUCTION

An electrophoretic display (EPD) is a type of reflective display based on the motion of charged particles suspending in a low dielectric liquid under the influence of an applied electric field.^{1–7} Besides the high eye-friendliness, the near-zero-power operation⁸ endows EPD the most prominent advantage over various flat-panel displays. Since the breakthrough of micro-encapsulation of an electrophoretic dispersion in EPDs in the late 1990s,¹ the switching speed, image contrast, and display stability have steadily improved over the past few years. EPDs have reached a remarkable state of maturity, which are now widely used in consumer products like the Amazon Kindle, Sony E-Reader, advertisement board, and ID card.⁸ However, commercial EPDs stalled because of the wild popularity of the iPad. Compared with the emissive or transmissive displays such as the liquid-crystal displays used in the iPad display, EPDs suffer from a drawback of light-source dependency, which brings a large obstacle for their application at night. In order to break through the plateaus and gain further development, new technologies are required to endow e-paper with novel properties. To our best knowledge, there has been no report on the use of the luminescent electrophoretic particles (LEPs) for glowing EPDs.

It is well-known that EPDs obtain high contrast levels because of their ability to strongly reflect light, giving the displays a bold, ink-like appearance.^{9,10} Also, the reflective ability of EPDs is almost completely dependent on the backscattering properties of electrophoretic particles (EPs)

suspended in a dielectric solvent.^{11,12} EPs are the key point to realize display performance by reflection under visible light.^{13–17} Therefore, much research has focused on the modification of pigment particles to alter the scattering properties, surface charges, steric stabilization, interactions with the electrode surface, and interparticle interactions.¹⁷ The white, black, and RGB tricolor ink particles for EPDs are designed and prepared. All of the EPs possessed characteristics of narrow distribution, high surface charge density, and superior light stability. According to the display principle of EPDs, LEP is a reasonable solution to making glowing EPDs. Therefore, to make the EPD displays useful in the dark, the preparation of LEPs with good performances in both reflectance and luminescence is a feasible, simple, and brand new design.

Herein, a miniemulsion polymerization process has been utilized in the preparation of LEPs composed of a three-layer structure, including a pigment core, a polystyrene interlayer, and a fluorescent coating. The pigments can provide a high reflectance or hiding power under light conditions, and the fluorescent coatings cause the LEPs to have a luminous effect under black-light irradiation under dark conditions. Finally, the LEPs are successfully incorporated into an EPD cell, and a glowing e-paper display is achieved. The results obtained suggest that the EPDs are applicable both under light and dark

Received: January 9, 2013

Accepted: April 2, 2013

Published: April 2, 2013

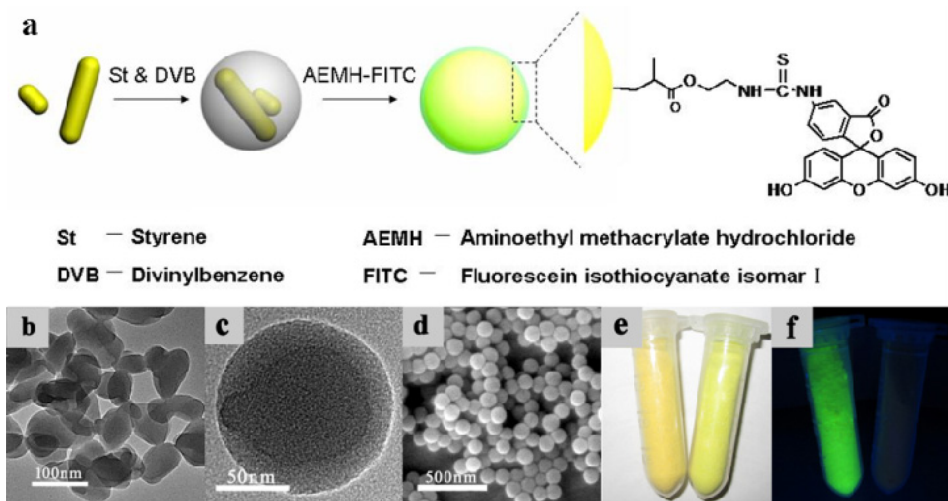


Figure 1. (a) Synthesis procedure for the LEPs, TEM images of (b) the yellow pigments and (c) LEPs, (d) SEM image of LEPs at a lower magnification, and the optical images of LEPs and general EP powders under light (e) and under black light in the dark (f).

conditions. Besides use in the display technique, the LEPs are promising tags for optical imaging and fluorescent labeling to allow for novel techniques of noninvasive diagnosis and in vivo observation of complex vital functions.

2. EXPERIMENTAL SECTION

Materials. Styrene (Aldrich) was distilled under reduced pressure before use. All other chemicals were used without further purification. Sodium dodecylbenzenesulfonate (SDBS; 98.5%), potassium peroxydisulfate (KPS; 99%), (2-aminoethyl)methacrylate hydrochloride (AEMH) (95%), and fluorescein isothiocyanate (FITC; 98%) were obtained from Aldrich Co. Yellow pigment (Heliogen Green K 0961) and a red dye (Thermoplast Red 454) were purchased from BASF Co. Poly(isobutylene succinimide) (OLOA 1200) was obtained from Chevron Co. Poly(chlorotrifluoroethylene) (Halocarbon 0.8) was obtained from Halocarbon Products Co. Hydroseal G232H was obtained from Total Co. Demineralized water was used during the experiments.

Experimental Procedures. To introduce the fluorescence performance to the ink particles, the fluorescein (FITC) was conjugated with the amino monomer (AEMH) first and then attached on the ink particle surface. A typical synthesis procedure is as follows: a mixture of 50 mg of FITC and 0.2–1 g of AEMH was solved in 60 mL of methanol, and the solution was stirred at 40 °C for 24 h to form an AEMH-FITC solution.

A mixture of pigment (0.3 g) and 10 mL of styrene was added to a three-necked flask together with 1.5 g of SDBS, 250 mL of water, and 0.4 g of KPS and ultrasonicated for 3 min to form a miniemulsion. Then the miniemulsion was stirred at 70 °C under a N₂ atmosphere. After 4 h of polymerization, the AEMH-FITC solution was pumped into the above reaction system during 1 h and polymerized at the same reaction conditions for 6 h to introduce a fluorescence ingredient into the particle surface. Particles were purified several times using distilled water and freeze-dried for 24 h.

Characterization. The morphology of the particles was observed by transmission electron microscopy (TEM; JEOL-200CX) and scanning electron microscopy (SEM; Hitachi 4300). Fourier transform infrared spectrometry (FTIR; Varian 3100 FT-IR) was employed to examine the composition of the samples. The spectral resolution is 2 cm⁻¹. Visible diffuse-reflectance spectra were recorded at room temperature on a Japan JASCO V-570. A Malvern zetasizer 2000HS was used to measure the particle ζ potentials and sizes. The photoluminescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer.

EPD Cell Fabrication. The display cell was composed of two parallel indium–tin oxide (ITO)-covered glass slices, and one of them

was etched with the numbers “123”. The cell (3 × 8 cm) was filled with electrophoretic inks, which were composed of dispersions of negatively charged fluorescent ink particles and red dye in a dielectric solvent (a mixture of Halocarbon 0.8 oil and Hydroseal G232H), with the presence of a surfactant T161A.

3. RESULTS AND DISCUSSION

The LEP preparation procedure includes two steps, as shown in Figure 1a: the polystyrene particles loaded with yellow organic pigments were synthesized by miniemulsion polymerization first; then the as-prepared (aminoethyl)methacrylate hydrochloride-fluorescein isothiocyanate isomer (AEMH-FITC; as shown in Figure 2) was polymerized on the preformed

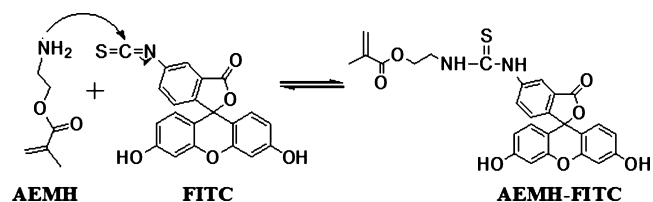


Figure 2. Reaction equation of the formation of AEMH-FITC.

polystyrene particle surfaces. According to the kinetics of radical polymerization in miniemulsions, the polymerized reaction was completely finished in 4 h (the time that the AEMH-FITC solution is pumped) with KPS as the initiator at 70 °C.^{18–20} Therefore, the postadded AEMH-FITC could polymerize onto the surfaces without particle-shape destruction. With the above-prepared procedure, the fluorescein FITC can be combined on the particles surfaces by the chemical bonds of the monomer AEMH, which is crucial for avoiding the fluorescein falling off from the particle surfaces during electrophoretic migration. The images of the yellow pigments and corresponding ink particles are presented in Figure 1b–d. As shown in Figure 1c,d, regular spherical polystyrene spheres containing pigments with narrow size distribution have been formed.

Parts e and f of Figure 1 show optical images of LEPs (on the left) and general EP powders (on the right) under light and under black-light irradiation (wavelength at 365 nm) under dark conditions. Both of them present bright-yellow under

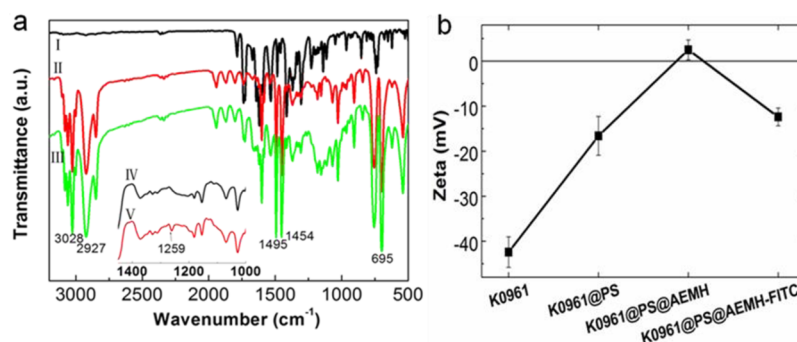


Figure 3. FTIR spectra (a) of the yellow pigment I, the polystyrene particle loaded pigment II, the LEPs III, and duplicate samples without pigment: polystyrene particles IV and polystyrene particles with fluorescent coatings V. (b) ζ potentials of different layers of LEPs.

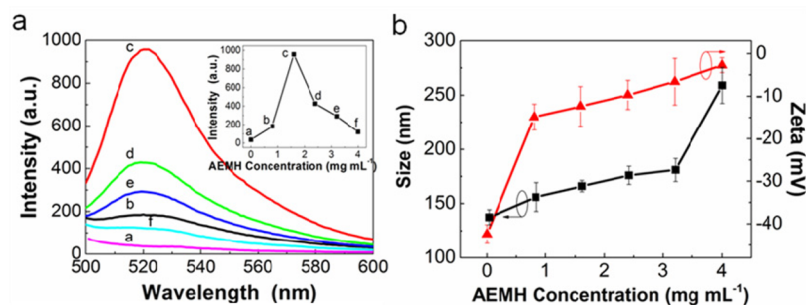


Figure 4. (a) Fluorescence spectra for different AEMH additions. Inset: fluorescence intensity (at 521 nm) versus AEMH concentration. (b) Plot of the particle size and ζ potential versus AEMH concentration.

light, while LEPs appear emerald green fluorescence under dark conditions under 365 nm black-light irradiation. In contrast, EP powder is unobservable under the same conditions.

Proof of the composite nature of the LEPs is provided by FTIR spectra. As shown in Figure 3a, the spectra of pristine pigments, polystyrene particles loaded with pigments, and the final LEPs are presented. The main component of the pigment is chinophthalone whose characteristic peaks at 1533 and 1415 cm^{-1} are assigned to the C=C bonds in the chlorobenzene ring; the peak at 1621 cm^{-1} is attributed to the C=N bonds in the quinoline ring, and the peak at 1740 cm^{-1} is assigned to the C=O bonds (spectrum I in Figure 3a). In spectra II and III, the peaks at 1454 and 1495 cm^{-1} are attributed to the stretching vibration of the C=C bonds of the phenyl ring in polystyrene and the band at 2927 cm^{-1} and the peak at 3028 cm^{-1} are characteristic peaks for the C-H bonds of the alkyl and phenyl rings, which indicates encapsulation of the pigments by polystyrene. In addition, the peak appearing at 695 cm^{-1} is assigned to the stretching vibration of the sulfonate (O=S=O), which indicates the presence of sulfonic groups on the particle surfaces. For exclusion of the disturbance of pigment (both chinophthalone and AEMH-FITC have the C-N bonds) and clear presentation of the changes of particles with a fluorescent coating, the spectra of duplicate samples without pigments are shown in the inset. The peak appearing at 1259 cm^{-1} in the spectrum is assigned to the C-N bond of AEMH-FITC, which suggests that FITC is bound to the polystyrene particles with AEMH.

The trilayer structure of the particle-forming process is also monitored through their ζ potential measurements, as shown in Figure 3b. With pristine pigments encapsulated by polystyrene, the ζ potential decreases to -24 mV from -42.4 mV because polymer surface sulfonic groups (yielded by decomposition of KPS) have replaced the original surfaces of pigments

completely. Then, the ζ potential reverses to +2.5 mV after AEMH modification, which is attributed to $-\text{NH}_3^+$ of AEMH dominating on the surfaces. Interestingly, AEMH-FITC instead of AEMH coating on the particle surfaces made them negatively charged again (-12.4 mV), which may be caused by the bonding of the S=C=N- group of FITC and the $-\text{NH}_2$ group of AEMH (as shown in Figure 2b). Although the final measurement is less than the EPs without fluorescein (-24 mV), it is still enough for particle migration under the electric field.

The amino monomer AEMH is chosen as the coupling agent for binding FITC to the polymer particle surfaces, which can affect the fluorescent performance, size distribution, and ζ potential of the as-prepared particles. The fluorescence intensity of LEPs increased with an AEMH concentration increase at a fixed FITC concentration (0.2 mg mL^{-1} based on the total dispersion medium, similarly hereinafter), as shown in Figure 4a. It presented a maximum in the AEMH concentration of 1.6 mg mL^{-1} and then decreased for the higher concentration of AEMH. The FITC bonding on the particle surface reaction is highly favored when the reaction is carried out at a higher concentration of AEMH (as shown in Figure 2), which causes more FITC bonded on the particle surfaces. On the other hand, the overplus of AEMH acts as competitors about the active sites of polymerization on the particle surfaces. As the competitive reaction becomes dominant, the fluorescence intensity of the particles begins to drop. Both the size and ζ potential of the product increase with an AEMH concentration increase, as shown in Figure 4b. It can certify the above-mentioned particle-forming mechanism. Besides, the size of particle increases sharply at a AEMH concentration of 4.0 mg mL^{-1} , which indicates aggregation of the particles caused by the abundant AEMH molecules.

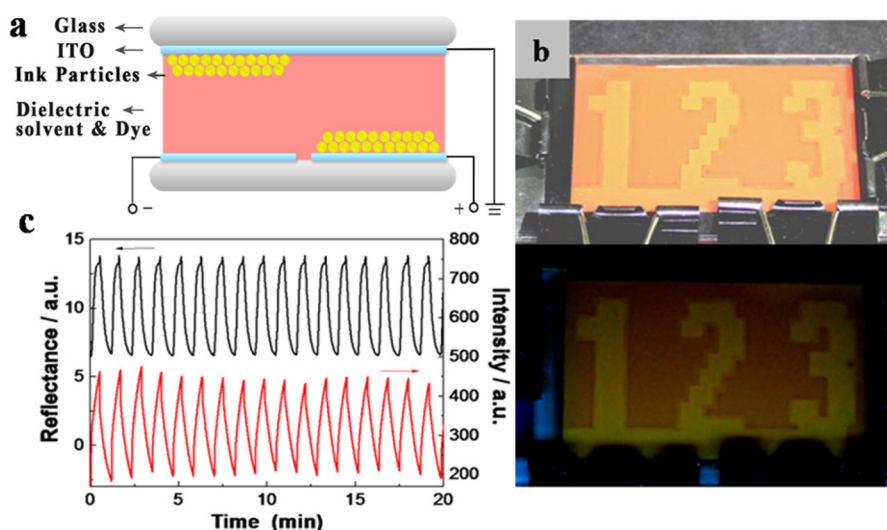


Figure 5. Schematic representation of the display mechanism and a photograph of the chromatic EPD cell: (a) a schematic representation of the cross-sectional structure of the display cell with a bias voltage of 20 V; (b) EPD cell under light (the above) and under UV in the dark (the below); (c) corresponding switching measurement. Reflectance versus switching time (above) and fluorescence intensity versus switching time (below).

Finally, the display cell has been fabricated with an electric ink composed of a dielectric solvent, a dispersant, as-prepared LEPs, and red dye as the background. A schematic representation of the cross-sectional structure of the display cell is shown in Figure 5a. The LEPs are negatively charged. If now the front electrode is positive relative to the rear electrode, the LEPs will be attracted to the front electrode, so that a layer of LEPs particles will coat the front electrode and the medium will appear the characteristic color of LEPs to the observer. Conversely, if the front electrode is negative relative to the rear electrode, the LEPs will be attracted to the rear electrode, so that the medium will appear the characteristic colors of the background to the observer. The optical image in Figure 5b shows the display device with drawing “123” in bright and dark environments separately.

In the device, the LEPs move to the front, showing bright yellow under sufficient light (above image) and being luminous under 365 nm black-light irradiation under dark conditions (below image). The display switches by periodically reversing the bias of 20 V at the electrodes, which is characterized by changes of the reflectance and fluorescence intensity. The characteristic peak locations of the reflectance (491 nm) and fluorescence intensity (521 nm) are chosen as the monitored parameter for this switching measurement. The direction of the applied field is changed every 35 s. With continuous switching for 20 min (34 switches), both the reflectance and fluorescence intensity have kept in a constant range, as shown in Figure 5c.

4. CONCLUSION

In conclusion, we have first designed and prepared a new glowing e-paper by the fluorescent EPs with pigment cores. The particle sizes range from 140 to 170 nm and the size distribution is narrow. Their ζ potential value is -12.4 mV. These particles are composed of three layers including pigment cores, polystyrene interlayers, and fluorescent coatings. The pigment cores provided the particles with hiding power, and the fluorescent coatings, which are attached to the surfaces of the particles with chemical bonds, make the particles luminous under 365 nm black-light irradiation under dark conditions. Finally, a glowing EPD display cell has been fabricated with an

electric ink composed of a dielectric solvent, a dispersant, as-prepared LEPs, and red dye as the background. By switching the bias voltage of 20 V, a color switch of the cell is achieved. Both the reflectance (491 nm) and fluorescence intensity (521 nm) of the EPD cell have kept in a constant range after 30 switches. Hence, the particles are promising in the application of EPDs with both reflective and emissive display principles. The displays developed using this approach comprise promising candidates for next-generation glowing e-papers.

■ ASSOCIATED CONTENT

Supporting Information

FTIR spectra of FITC, AEMH, and AEMH-FITC, visible diffuse-reflectance spectra of the yellow pigment-based ink particles with and without fluorescent coatings, SEM image of fluorescent pigment-based ink particles, diffuse-reflectance and fluorescence spectra of both sides of the EPD cell with fluorescent pigment-based ink particles, and a representation of additive color mixing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

Dr. X. W. Meng and Dr. T. Wen contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the National Natural Science Foundation of China (Projects 81171454, 61171049, and 60907042) for financial support.

■ REFERENCES

- (1) Comiskey, B.; Albert, J. D.; Yoshizawa, H.; Jacobson, J. *Nature* 1998, 394, 253–255.

- (2) Pasteur, N.; Philips, A.; Fort, P.; Raymond, M. *Nature* **2003**, *423*, 136–137.
- (3) Meng, X. W.; Wen, T.; Sun, S.; Zheng, R.; Ren, J.; Tang, F. *Nanoscale Res. Lett.* **2010**, *5*, 1664–1668.
- (4) Peng, B.; Tang, F. Q.; Chen, D.; Ren, X. L.; Meng, X. W.; Ren, J. *J. Colloid Interface Sci.* **2009**, *329*, 62–66.
- (5) Wood, V.; Panzer, M. J.; Chen, J.; Bradley, M. S.; Halpert, J. E.; Bwendi, M. G.; Bulovic, V. *Adv. Mater.* **2009**, *21*, 1–5.
- (6) Mriaou, P.; Singer, B. *J. Appl. Phys.* **1978**, *49*, 4820.
- (7) Hayes, R. A.; Feenstra, B. J. *Nature* **2003**, *425*, 383–385.
- (8) Heikenfeld, J.; Drzaic, P.; Yeo, J. S.; Koch, T. *J. Soc. Inf. Disp.* **2011**, *2*, 129–156.
- (9) Yu, D. G.; An, J. H.; Bae, J. Y.; Jung, D. J.; Kim, S.; Ahn, S. D.; Kang, S. Y.; Suh, K. S. *Chem. Mater.* **2004**, *16*, 4693–4698.
- (10) Peng, B.; Meng, X. W.; Tang, F. Q.; Ren, X. L.; Chen, D. *J. Phys. Chem. C* **2009**, *113*, 20240–20245.
- (11) Wang, M.; Kitamura, T.; Miyagawa, N.; Nakamura, S. *J. Imaging Sci. Technol.* **2010**, *54*, 10506–10510.
- (12) Badila, M.; Hebraud, A.; Brochon, C.; Hadziioannou, G. *ACS Appl. Mater. Interfaces* **2011**, *3*, 3602–3610.
- (13) Oh, S. W.; Kim, C. W.; Cha, H. J.; Pal, U.; Kang, Y. S. *Adv. Mater.* **2009**, *21*, 4987–4991.
- (14) Yu, D. G.; An, J. H.; Bae, J. Y.; Ahn, S. D.; Kang, S. Y.; Suh, K. S. *Macromolecules* **2005**, *38*, 7485–7491.
- (15) Yu, D. G.; An, J. H.; Bae, J. Y.; Jung, D. J.; Kim, S.; Ahn, S. D.; Kang, S. Y.; Suh, K. S. *Chem. Mater.* **2004**, *16*, 4693–4698.
- (16) Wen, T.; Meng, X. W.; Li, Z. Y.; Ren, J.; Tang, F. Q. *J. Mater. Chem.* **2010**, *20*, 8112–8117.
- (17) Werts, M. P. L.; Badila, M.; Brochon, C.; Hébraud, A.; Hadziioannou, G. *Chem. Mater.* **2008**, *20*, 1292–1298.
- (18) Landfester, K. *Top. Curr. Chem.* **2003**, *227*, 75–123.
- (19) Asua, J. *Prog. Polym. Sci.* **2002**, *27*, 1283–1346.
- (20) Landfester, K.; Bechthold, N.; Tiarks, F.; Antonietti, M. *Macromolecules* **1999**, *32*, 2679–2683.