

# Synthesis of Cu and CuO nanoclusters within microphase-separated diblock copolymers<sup>†</sup>

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A general methodology has been established for the synthesis of 40–120 Å Cu nanoclusters within the morphologies of [MTD]<sub>400</sub>[NORCOOH]<sub>50</sub> and [MTD]<sub>400</sub>[NORCOONa]<sub>50</sub> diblock copolymer films. In this technique the films are soaked in aqueous copper(II) acetate solutions prior to reduction of the sequestered Cu<sup>2+</sup> ions. A loading of 4.2 wt% Cu in the overall polymer–Cu composite was achieved in the case of [MTD]<sub>400</sub>[NORCOONa]<sub>50</sub>, during a single loading and reduction sequence. Upon exposure of the films to air, the polymer-imbedded Cu nanoclusters oxidize to form CuO. The transparent polymer–CuO composite films exhibit a broad absorption in the near-infrared region and may have potential applications as near-infrared filters.

Metal nanoclusters (1 to 10 nm) are interesting because of their unusual optical, electronic and catalytic properties, which often differ from those of bulk metals.<sup>1,2</sup> Quantum size effects can occur in metal nanoclusters due to their incompletely developed band structure.<sup>1,3</sup> Nonlinear optical phenomena may accompany this band gap modification, with potential uses in telecommunications and computing.<sup>4,5</sup> Polymer–metal cluster composites have potential applications as ‘smart’ materials, where the electrical conductivity of the composite varies with temperature or applied stress. Polymer–metal cluster composites have been synthesized by deposition of metal vapor into liquid monomer followed by polymerization,<sup>6</sup> by sequestration of metal salts within block copolymer micelles followed by reduction<sup>7–9</sup> and by incorporation of metal salts into polymer films from supercritical CO<sub>2</sub>, followed by reduction.<sup>10</sup> Oxidation of certain types of polymer-imbedded metal clusters leads to the formation of polymer–metal oxide cluster composites, which may be useful as infrared filters for automobile windshields or display screens used in the vicinity of night vision devices.

Previously, we reported a general methodology for the synthesis of transition metal nanoclusters (Ag, Au, Cu, Ni, Pb, Pd and Pt) stabilized within microphase-separated diblock copolymers.<sup>11</sup> In our strategy, metal ions or complexes are coordinated to carboxylic acid groups within the water-soluble polyNORCOOH domains of a [MTD]<sub>400</sub>[NORCOOH]<sub>50</sub> block copolymer (structures appear in Fig. 1, where MTD = methyltetracyclododecene and NORCOOH = 2-norbornene-5,6-dicarboxylic acid) by immersion of the polymer in aqueous metal salt solutions. The metal ions and complexes are subsequently reduced by heating the metal-loaded polymer under hydrogen or by immersion in an aqueous sodium borohydride solution. For several transition metals, the resulting nanoclusters are uniformly sized and homogeneously dispersed within the polyNORCOOH domains.

We discovered, using inductively coupled plasma atomic emission spectroscopy (ICP-AES), that metal ion transport occurs primarily through the interconnected cylindrical network of polyNORCOOH rather than through the

polyMTD matrix.<sup>12</sup> We found, using IR spectroscopy, that hydrogen reduction of the metal-loaded films re-protonates metal-bound carboxylate ions, allowing participation in further metal binding. Furthermore, as shown in Fig. 2, conversion of the carboxylic acid group, in aqueous NaOH, to the sodium carboxylate form results in large increases in both the rate and extent of transition metal and rare earth ion uptake.<sup>13</sup> This improvement in loading is due largely to the acetate ion's much lower stability constant with Na<sup>+</sup>,  $K_1 \approx 0.7 \text{ l mol}^{-1}$ ,<sup>14</sup> than with H<sup>+</sup>,  $K_1 \approx 6.3 \times 10^4 \text{ l mol}^{-1}$ ,<sup>15</sup> which allows transition metal and rare earth ions,  $K_1 \approx 3\text{--}1600 \text{ l mol}^{-1}$ ,<sup>14,15</sup> to exchange more easily with the weakly bound Na<sup>+</sup> ions than with the much more strongly bound H<sup>+</sup> ions.

We now report briefly on the loading of copper ions into our block copolymer films, reduction of these ions to form copper clusters and subsequent oxidation of Cu nanoclusters within our films to form transparent polymer–CuO composites.

## Experimental

### Materials

MTD monomer, donated by B.F. Goodrich, was vacuum distilled, degassed and stored over sodium prior to use. NORCOOTMS (2-norbornene-5,6-dicarboxylic acid bis-trimethylsilyl ester)<sup>16</sup> and Mo(CHCMe<sub>2</sub>Ph)(NAr)(OBu)<sub>2</sub>

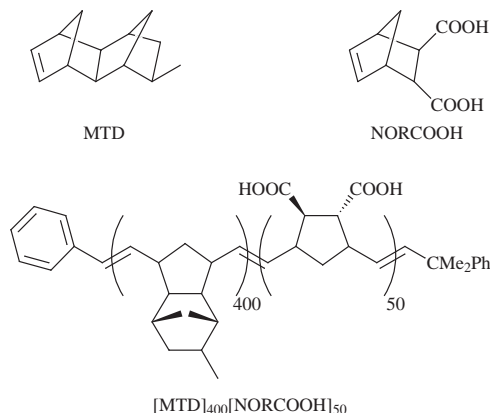


Fig. 1 Chemical structures of monomers and block copolymer

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<sup>†</sup> Non-SI units employed: atm  $\approx$  101 kPa.

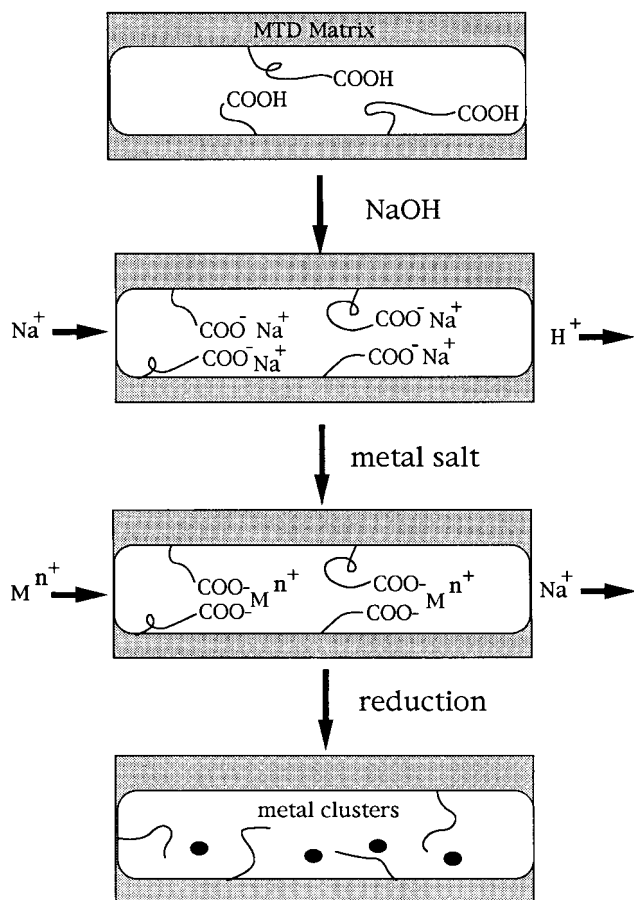


Fig. 2 Metal cluster synthesis scheme

(Ar = 2,6- $\text{C}_6\text{H}_3\text{Pr}_2^i$ )<sup>17,18</sup> were prepared according to literature procedures. Anhydrous toluene from Aldrich was stored over sodium prior to use. Copper(II) acetate (99%), from Strem, was used without further purification. All copper(II) acetate solutions were prepared using de-ionized water.

### Polymer synthesis

[MTD]<sub>400</sub>[NORCOOH]<sub>50</sub> diblock copolymer was synthesized as previously reported,<sup>11</sup> using a ring-opening metathesis polymerization in anhydrous toluene with a  $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})(\text{O}i\text{Bu})_2$  (Ar = 2,6- $\text{C}_6\text{H}_3\text{Pr}_2^i$ ) initiator.

Polymer films (10  $\mu\text{m}$  thick) were static cast from a 0.5 wt% solution in tetrahydrofuran (THF). Transmission electron microscopy (TEM) observation of microtomed (400  $\text{\AA}$  thick),  $\text{Cu}^{2+}$  stained sections of film revealed a non-equilibrium interconnected cylindrical morphology, consisting of poly-NORCOOH cylinders within a polyMTD matrix. Carboxylic acid groups within the films were converted to the sodium carboxylate form ([MTD]<sub>400</sub>[NORCOONa]<sub>50</sub>) by soaking in a 0.015 M aqueous NaOH solution (48 h, 25  $^\circ\text{C}$ ).

### ICP-AES analysis of $\text{Cu}^{2+}$ uptake

$\text{Cu}^{2+}$  loading was carried out at 25  $^\circ\text{C}$  using a batch equilibrium method in which 100 mg samples of 10  $\mu\text{m}$  thick films ([MTD]<sub>400</sub>[NORCOOH]<sub>50</sub> or [MTD]<sub>400</sub>[NORCOONa]<sub>50</sub>) were submerged in 20 g aqueous solutions of 0.005 M copper(II) acetate. Agitation was maintained with magnetic stir bars. The  $\text{Cu}^{2+}$  concentration remaining in the supernatant solution was measured periodically by withdrawing small aliquots of supernatant solution. The withdrawn aliquots were diluted with de-ionized water to  $\text{Cu}^{2+}$  concentrations of <30 ppm and analyzed using ICP-AES.

The extent of  $\text{Cu}^{2+}$  uptake was calculated using  $A = W_s(C_i - C_f)/W_p$ , where  $A$  ( $\text{mg g}^{-1}$ ) is the mass of  $\text{Cu}^{2+}$  loaded per mass polyNORCOOH in the block copolymer;  $W_s$ , the mass (g) of copper(II) acetate solution;  $W_p$ , the mass (g) of polyNORCOOH in the block copolymer;  $C_i$ , the solution concentration (ppm) of  $\text{Cu}^{2+}$  prior to loading; and  $C_f$ , the solution concentration (ppm) of  $\text{Cu}^{2+}$  after loading.

$\text{Na}^+$  uptake within [MTD]<sub>400</sub>[NORCOOH]<sub>50</sub> was monitored using the same procedure. Both  $\text{Na}^+$ - and  $\text{Cu}^{2+}$ -loaded films were rinsed in de-ionized water prior to further processing.

### Reduction of $\text{Cu}^{2+}$ ions

After loading,  $\text{Cu}^{2+}$  ions within the films were reduced by heating (125  $^\circ\text{C}$ ) under hydrogen (2 atm) for 6 days.

### Characterization

Gel permeation chromatographic (GPC) analysis was carried out using a series of three Waters Ultrastrogel<sup>TM</sup> columns (10<sup>5</sup>  $\text{\AA}$ , 10<sup>4</sup>  $\text{\AA}$  and 10<sup>3</sup>  $\text{\AA}$ ) connected to a Waters Differential Refractometer R401. The mobile phase was toluene at a flow rate of 1  $\text{ml min}^{-1}$ . The GPC columns were calibrated with commercially available polystyrene standards (Polysciences).

Electron microscopy and electron diffraction studies were done using a JEOL 200 CX TEM operated at 200 kV. Ultra-thin (400  $\text{\AA}$ ) samples for TEM observation were microtomed at room temperature with glass knives using a Sorvall Ultra Microtome MT 5000. Aqueous metal ion concentrations were measured with a Perkin-Elmer Plasma 40 inductively coupled plasma atomic emission spectrophotometer. UV/VIS spectra were recorded on a Cary 5E UV-VIS-NIR spectrophotometer, in transmission mode, with a R928 photomultiplier tube detector.

The crystal structure of the metal nanoclusters was probed using wide-angle X-ray scattering (WAXS), performed with a Rigaku rotating Cu anode X-ray source ( $\lambda = 1.54$   $\text{\AA}$ ). The  $\text{Cu-K}\alpha$  line generated at 50 kV and 60 mA was filtered with a thin metal plate. The 2 $\theta$  diffraction data were collected in transmission mode with a collection time of 2 s for each 0.05 $^\circ$  step.

## Results and Discussion

GPC analysis of the first block [MTD] of the copolymer yielded a polydispersity of approximately 1.1. The block copolymer was not analyzed using GPC because poly-NORCOOH insolubility in toluene results in precipitation of the block copolymer for the particular monomer composition employed here.<sup>11–13</sup> The static cast 10  $\mu\text{m}$  thick [MTD]<sub>400</sub>[NORCOOH]<sub>50</sub> films were transparent and colorless.

### ICP-AES analysis of metal ion uptake

ICP-AES measurements showed that  $\text{Na}^+$  loading into [MTD]<sub>400</sub>[NORCOOH]<sub>50</sub> reached equilibrium within 7 h, with approximately one mole of  $\text{Na}^+$  entering the film per mole of carboxylic acid.  $\text{Cu}^{2+}$  loading into [MTD]<sub>400</sub>[NORCOONa]<sub>50</sub> reached equilibrium after 24 h, at a loading level of 0.52 moles of  $\text{Cu}^{2+}$  per mole of carboxylic acid (0.36 g  $\text{Cu}^{2+}$  per g polyNORCOOH originally present, 4.2 wt% Cu in the overall polymer-Cu nanocluster composite). Corresponding amounts of  $\text{Na}^+$  were released as  $\text{Cu}^{2+}$  entered the film. Given the estimated accuracy of our measurements of  $\pm 15\%$ , this implies essentially complete exchange of carboxylic acid  $\text{H}^+$  ions for  $\text{Na}^+$  ions, and of  $\text{Na}^+$  ions for  $\text{Cu}^{2+}$  ions, respectively. After 9 days, the [MTD]<sub>400</sub>[NORCOOH]<sub>50</sub> film was removed from the 0.005 M copper(II) acetate solution with a loading of 0.14 moles of

$\text{Cu}^{2+}$  per mole of carboxylic acid (0.10 g  $\text{Cu}^{2+}$  per poly-NORCOOH originally present).

### Characterization of cluster size and composition

During reduction, the colorless 10  $\mu\text{m}$  thick  $\text{Cu}^{2+}$ -loaded  $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$  and  $[\text{MTD}]_{400}[\text{NORCOONa}]_{50}$  films became ruby in color over several days, but remained transparent.

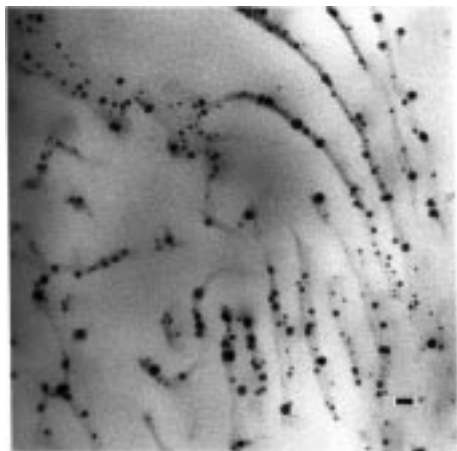
WAXS data from the  $[\text{MTD}]_{400}[\text{NORCOONa}]_{50}$  film, following  $\text{Cu}^{2+}$  loading and reduction showed a broad noisy peak at  $2\theta \approx 43^\circ$ , consistent with scattering from the  $[111]$  ( $2\theta = 43.3^\circ$ ) plane of fcc Cu crystals.<sup>19</sup> The weaker  $[200]$  ( $2\theta = 50.4^\circ$ ) and  $[220]$  ( $2\theta = 74.1^\circ$ ) peaks were not distinguishable from the background scattering. The mean Scherrer length ( $L$ ) of the Cu crystals was determined using the Scherrer equation.<sup>20</sup> We then estimated a rough mean crystal diameter ( $D$ ) of about 65 Å from<sup>21</sup>  $D = 4/3L$ . A similar WAXS pattern was observed from the  $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$  film following  $\text{Cu}^{2+}$  loading and reduction. These broad noisy crystallographic reflections from the metal clusters are rather typical results of the X-ray analyses we have performed on a wide variety of inorganic clusters in block copolymer films.<sup>11,12,22–24</sup>

Fig. 3 shows an electron micrograph of the  $[\text{MTD}]_{400}[\text{NORCOONa}]_{50}$  film following  $\text{Cu}^{2+}$  loading and reduction. It reveals copper clusters in the 40–120 Å size range, primarily confined to the carboxylic acid functionalized domains. Given the mean crystal diameter estimated from the WAXS data, most clusters appear to be single crystals. TEM revealed fewer, but similarly sized, Cu clusters within the  $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$  film.

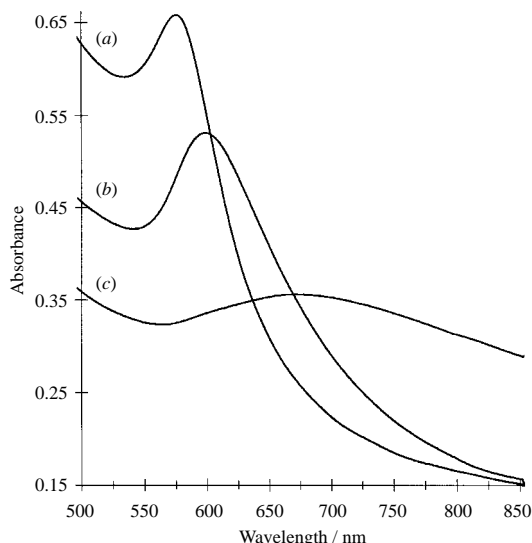
### Oxidation of Cu clusters

The ruby-colored copper-cluster-containing films become blue after 15 h in air, due to oxidation of the Cu cluster surfaces to copper oxides. After 6 days in air, only a very weak Cu WAXS scattering pattern was still observable from the  $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$  film. No WAXS scattering attributable to copper oxides was observed. Following 1 year in air, no WAXS scattering was observed from the  $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$  film. However, local area electron diffraction, from one unusually large 3000 Å particle, in this film, produced rings consistent with scattering from both fcc Cu and monoclinic CuO crystals.

In Fig. 4, curves (a) and (b) show the visible-NIR absorption spectra of the  $[\text{MTD}]_{400}[\text{NORCOONa}]_{50}$  film immediately after reduction and following 6 days in air, respectively. Curve (c) shows the visible-NIR absorption spectrum of a different sample: the loaded and reduced  $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$



**Fig. 3** Electron micrograph of  $[\text{MTD}]_{400}[\text{NORCOONa}]_{50}$  film after  $\text{Cu}^{2+}$  loading and reduction (bar = 200 Å)



**Fig. 4** Visible-NIR absorption spectra of 10  $\mu\text{m}$  thick films after  $\text{Cu}^{2+}$  loading and reduction: (a)  $[\text{MTD}]_{400}[\text{NORCOONa}]_{50}$ , no air exposure; (b)  $[\text{MTD}]_{400}[\text{NORCOONa}]_{50}$ , 6 days in air; (c)  $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$ , 1 year in air

film after 1 year in air. The absorption spectra have not been normalized. Prior to air exposure [curve (a)], the ruby-colored Cu-cluster-containing film absorbs at ca. 575 nm, a wavelength characteristic of the surface plasmon absorption of Cu nanoclusters within a glass matrix.<sup>25,26</sup> Following storage in air, the absorption of the film shifts to longer wavelengths. After 6 days in air, the film appears blue [curve (b), ca. 600 nm]. During a year in air, the  $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$  film changes from blue to pale green in color [curve (c), ca. 650 nm].

The shift in color from ruby to pale green is consistent with the oxidation of Cu nanoclusters to CuO. Glasses containing CuO are known to exhibit very broad NIR absorptions centered at wavelengths ranging from 780–800 nm, depending on the composition of the glass.<sup>27,28</sup> Although the variation of absorption with time in our copper-containing block copolymer films appears to indicate a gradual oxidation of Cu clusters to CuO, the center of the absorption peak after a year in air [curve (c), 650 nm] occurs at a lower wavelength than would be expected from pure CuO, even allowing for a variation of  $\pm 20$  nm in the absorption peak due to differences in the matrix composition. This suggests that the oxidation is not complete and the particles may contain Cu cores even after the films have been exposed to air for one year.

### Conclusions

Cu nanoclusters (40–120 Å) can be synthesized within the carboxylic acid or sodium carboxylate functionalized domains of microphase-separated 10  $\mu\text{m}$  thick  $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$  or  $[\text{MTD}]_{400}[\text{NORCOONa}]_{50}$  block copolymer films, using a technique in which the films are soaked in aqueous copper(II) acetate solutions prior to reduction under hydrogen gas. The resulting Cu nanoclusters oxidize to CuO upon storage in air, leading to the formation of transparent, green, polymer–CuO composite films. These films absorb at 650 nm rather than at 780–800 nm as observed for CuO within glasses.

$\text{Cu}^{2+}$ -loaded polymer films and CuO nanocluster composites may have potential applications<sup>29</sup> as NIR filters, for use in plastic automobile windshields or display screens used in the vicinity of night vision devices. However, for practical applications, the CuO absorption peak observed here must be shifted to higher wavelengths and the maximum absorbance of the peak must be increased relative to the absorbance in the

visible region. Such changes in the absorption spectrum will ensure a transparent film that absorbs strongly in the NIR region.

Further experiments are planned in which  $[\text{MTD}]_{400}[\text{NORCOONa}]_{50}$  films will be cycled through several  $\text{Cu}^{2+}$  loading and reduction sequences, in order to increase the average cluster diameter and the overall  $\text{Cu}^{2+}$  loading, from 4.2 wt % to over 10 wt%.<sup>13</sup> We will attempt to accelerate Cu oxidation using oxygen and/or oxidizing acids as the oxidizing medium, rather than air.

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## References

- 1 A. Henglein, *Chem. Rev.*, 1989, **89**, 1861.
- 2 J. S. Bradley, E. W. Hill, S. Behal, C. Klein, B. Chaudret and A. Duteil, *Chem. Mater.*, 1992, **4**, 1234.
- 3 G. D. Stucky, *Naval Res. Rev.*, 1991, **3**, 28.
- 4 F. Hache, D. Ricard and C. Flytzanis *J. Opt. Soc. Am. B*, 1986, **3**, 1647.
- 5 G. D. Stucky and J. E. MacDougall, *Science*, 1990, **247**, 669.
- 6 K. J. Klabunde, J. Habdas and G. Cardenas-Trivino, *Chem. Mater.*, 1989, **1**, 481.
- 7 J. P. Spatz, A. Roescher and M. Möller, *Adv. Mater.*, 1996, **8**, 337.
- 8 J. P. Spatz, S. Mossmer and M. Möller *Chem. Eur. J.*, 1996, **2**, 1557.
- 9 A. B. R. Mayer and J. E. Mark, *J. Colloid Polym. Sci.*, 1997, **275**, 333; *J. Polym. Sci. B. Polym. Phys.*, 1997, **35**, 1207.
- 10 J. J. Watkins and T. J. McCarthy, *Chem. Mater.*, 1995, **7**, 1991.
- 11 R. T. Clay and R. E. Cohen, *Supramol. Sci.*, 1995, **2**, 183.
- 12 R. T. Clay and R. E. Cohen, *Supramol. Sci.*, 1997, **4**, 113.
- 13 R. T. Clay and R. E. Cohen, *Supramol. Sci.*, in press.
- 14 L. G. Sillen and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, The Chemical Society, London, 1971, p. 253.
- 15 D. D. Perrin, *Stability Constants of Metal-Ion Complexes. Part B: Organic Ligands*, Pergamon Press, New York, 1979, p. 38.
- 16 R. S. Saunders, Ph.D. Thesis, Massachusetts Institute of Technology, 1992.
- 17 R. R. Schrock, *Acc. Chem. Res.*, 1990, **24**, 158.
- 18 R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare and M. O'Regan, *J. Am. Chem. Soc.*, 1990, **112**, 3875.
- 19 H. E. Swanson and E. Tatge, *U.S. National Bureau of Standards Standard X-ray Diffraction Patterns*, NBS Circular 539, U.S. Government Printing Office, Washington DC, 1953, vol. 1.
- 20 H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures*, John Wiley & Sons, New York, 1954, p. 491.
- 21 M. G. Bawendi, A. R. Kortan, M. L. Steigerwald and L. E. Brus, *J. Chem. Phys.*, 1989, **91**, 7282.
- 22 V. Sankaran, R. E. Cohen, R. R. Schrock and R. J. Silbey, *Chem. Mater.*, 1993, **5**, 1134.
- 23 J. Yue, V. Sankaran, R. E. Cohen and R. R. Schrock, *J. Am. Chem. Soc.*, 1993, **115**, 4409.
- 24 Y. N. C. Chan, G. S. W. Craig, R. R. Schrock and R. E. Cohen, *Chem. Mater.*, 1992, **4**, 885.
- 25 J. C. Maxwell-Garnett, *Philos. Trans. R. Soc. London*, 1905, **203**, 237.
- 26 W. P. Halperin, *Rev. Mod. Phys.*, 1986, **58**, 533.
- 27 C. R. Bamford, *Phys. Chem. Glasses*, 1962, **3**, 189.
- 28 C. R. Bamford, *Colour Generation and Control in Glass*, Elsevier, New York, 1977, p. 48.
- 29 H. Katono, T. Sakagami, S. Masuhiro and T. Ogihara, *J. Appl. Polym. Sci.*, 1998, **67**, 903.

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