

## Communications to the Editor

### Thermochromic Composite Prepared via a Propagating Polymerization Front

Istvan P. Nagy,<sup>†,‡</sup> Laszlo Sike,<sup>‡</sup> and John A. Pojman<sup>\*,†</sup>

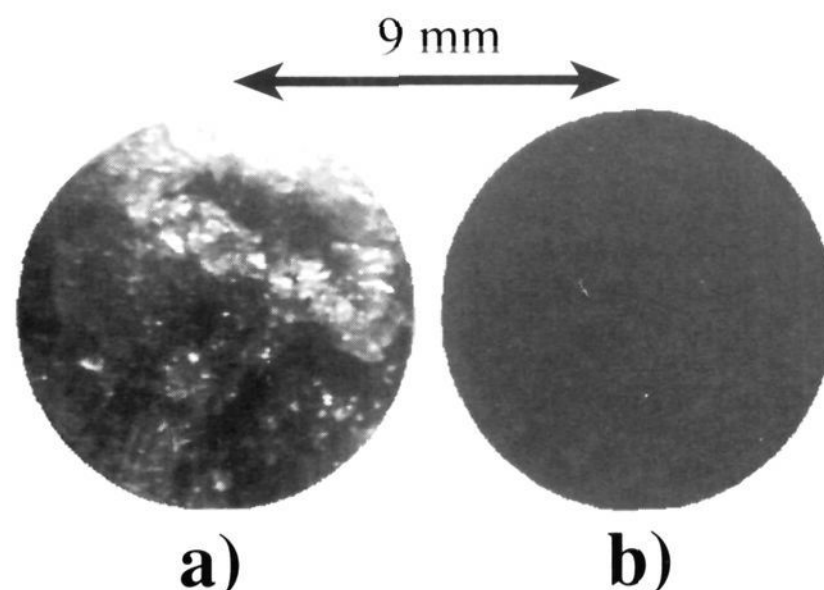
Department of Chemistry and Biochemistry  
University of Southern Mississippi  
Hattiesburg, Mississippi 39406-5043  
Department of Physical Chemistry  
Kossuth Lajos University  
Debrecen, Hungary H-4010

Received November 17, 1994

Thermochromic materials change their visible absorption spectrum as a function of temperature. The most common examples are cholesteric liquid crystals, which have been used in a wide range of applications, including medical thermography and temperature measurements.<sup>1–8</sup> Another type of thermochromic material, based on the temperature dependence of complexation equilibria of transition metals, can be prepared. We previously developed a video-based method of remote temperature measurement using cobalt chloride and alcohols.<sup>9,10</sup>

Our previous method used solutions that had to be contained in capillary tubes. We report here the synthesis of a machinable thermochromic composite whose color change occurs over a wide and high temperature range (80–140 °C) with excellent resolution (0.5 °C). This composite is also the first material uniquely prepared via a propagating polymerization front.

Workers in the former USSR have studied propagating fronts in vinyl polymerizations since 1972.<sup>11–21</sup> Pojman et al. have



**Figure 1.** Cross sections of products synthesized (a) by homogeneous polymerization performed at 60 °C and (b) by frontal polymerization in a 9.0 mm (i.d.) tube. Initial composition: 54.5 w/w % acrylamide, 26.7 w/w % TGDMA, 16.3 w/w % glycerol, 1.4 w/w % cobalt(II) chloride, 1.1 w/w % AIBN.

studied traveling fronts with a variety of neat monomers at ambient pressure using liquid and solid monomers.<sup>22–27</sup>

Polymerization of triethylene glycol dimethacrylate (TGDMA), with AIBN initiator, in the presence of glycerin and cobalt to produce a thermochromic material occurs very slowly. The presence of acrylamide increases the rate of reaction. However, if this reaction is carried out in a batch reactor, phase separation occurs because the polymerization occurs too slowly for the cross-linking to “freeze in” the nonequilibrium phase distribution. From work with acrylamide fronts, we know that in the reaction zone the monomer is converted to polymer in 3 s.<sup>25</sup> Fronts with TGDMA were first studied by Chechilo and Enikolopyan<sup>12</sup> and recently by Pojman et al.<sup>26</sup> We have combined the acrylamide polymerization front with cobalt, glycerin, and TGDMA to produce a thermochromic composite.

The general recipe for the thermochromic composite is as follows: 2–6 mL of TGDMA, 4–8 g of acrylamide, 2–6 mL of thermochromic solution consisting of 5–35 m/v %  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in glycerol, and 0.2–3.0 m/m % azobisisobutyronitrile initiator (AIBN) to the overall mixture. Acrylamide was ground in a rock tumbler with glass beads until a uniform powdered mixture was obtained (about 8 h), and then AIBN was mixed in with a mortar and pestle. Solid  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was dissolved in warm glycerin. After cooling, acrylamide was added to the glycerin solution and the mixture was homogenized with a mortar and pestle. The TGDMA was added to the mixture, which was homogenized again. The viscous mixture was packed into 9

<sup>†</sup> University of Southern Mississippi.

<sup>‡</sup> Kossuth Lajos University.

(1) Ennulat, R. D.; Ferguson, J. L. Thermal Radiography Utilizing Liquid Crystals. In *Liquid Crystals 3*; Brown, G. H., Labes, M. M., Eds.; Gordon and Breach: London, 1972; pp 141–156.

(2) Zharkova, G. M.; Khachatryan, V. M.; Vostokov, L. A.; Alekseev, N. M. Study of Liquid Thermoinicators. In *Advances in Liquid Crystal Research and Applications*; Bata, L., Ed.; Pergamon: Oxford, 1981; pp 1221–1239.

(3) Cherkashina, R. M.; Tishchenko, V. G.; Tolmachev, A. V. Liquid Crystalline substances for high-temperature thermoinicators. In *Advances in Liquid Crystal Research and Applications*; Bata, L., Ed.; Pergamon: Oxford, 1981; pp 1241–1256.

(4) Weigel, D.; Herold, W. The effect of layer instabilities on liquid crystalline thermography. In *Advances in Liquid Crystal Research and Applications*; Bata, L., Ed.; Pergamon: Oxford, 1981; pp 1247–1254.

(5) Herold, W.; Wiegell, D. Problems of the photographic documentation of liquid crystalline thermographs. In *Advances in Liquid Crystal Research and Applications*; Bata, L., Ed.; Pergamon: Oxford, 1981; pp 1255–1259.

(6) Brown, G. H.; Wolken, J. J. *Liquid Crystals and Biological Structures*; Academic Publishers: New York, 1979.

(7) Milbrath, J. R.; Shaffer, K. A.; Moskowitz, M.; Fox, S. H.; Bassett, L. W.; Gold, R. H. Evaluation of ELC plate thermography. In *Advances in Liquid Crystal Research and Applications*; Bata, L., Ed.; Pergamon: Oxford, 1981; pp 1261–1281.

(8) Meier, G.; Grabmaier, J. G.; Sackmann, E. *Applications of Liquid Crystals*; Springer-Verlag: Berlin, 1975.

(9) Nagy, I. P.; Pojman, J. A. *Chem. Phys. Lett.* **1992**, *200*, 147–152.

(10) Nagy, I. P.; Pojman, J. A. *J. Phys. Chem.* **1993**, *97*, 3443–3449.

(11) Chechilo, N. M.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1976**, *230*, 840–843.

(12) Chechilo, N. M.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1974**, *214*, 174–176.

(13) Khanukaev, B. B.; Kozhushner, M. A.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1974**, *214*, 84–87.

(14) Chechilo, N. M.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1975**, *221*, 392–394.

(15) Enikolopyan, N. S.; Kozhushner, M. A.; Khanukaev, B. B. *Dokl. Phys. Chem.* **1974**, *217*, 676–678.

(16) Davtyan, S. P.; Surkov, N. F.; Rozenberg, B. A.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1977**, *232*, 64–67.

(17) Surkov, N. F.; Davtyan, S. P.; Rozenberg, B. A.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1976**, *228*, 435–438.

(18) Babadzhanian, A. S.; Volpert, V. A.; Volpert, V. A.; Davtyan, S. P.; Megrabova, I. N. *Combust., Explos. Shock Waves* **1989**, *25*, 23–31.

(19) Volpert, V. A.; Mergabova, I. N.; Davtyan, S. P.; Begishev, V. P. *Combust., Explos. Shock Waves* **1986**, *21*, 443–447.

(20) Begishev, V. P.; Volpert, V. A.; Davtyan, S. P.; Malkin, A. Y. *Dokl. Phys. Chem.* **1985**, *279*, 1075–1077.

(21) Davtyan, S. P.; Zhirkov, P. V.; Vol'fson, S. A. *Russ. Chem. Rev.* **1984**, *53*, 150–163.

(22) Pojman, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6284–6286.

(23) Pojman, J. A.; Khan, A. M.; West, W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 1188–1189.

(24) Pojman, J. A.; Craven, R.; Khan, A.; West, W. *J. Phys. Chem.* **1992**, *96*, 7466–7472.

(25) Pojman, J. A.; Nagy, I. P.; Salter, C. *J. Am. Chem. Soc.* **1993**, *115*, 11044–11045.

(26) Pojman, J. A.; Willis, J.; Fortenberry, D.; Ilyashenko, V.; Khan, A. *J. Polym. Sci.*, in press.

(27) Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. *Physica D*, in press.

mm (i.d.) glass tubes, and fronts were initiated with a soldering iron. A region of blue solid product propagated through the pink reactant mixture. A narrow (0.2–0.5 mm) reaction zone was observed. The color of the composite returned to pink after cooling down. All reactions produced constant velocity fronts.

Batch polymerization was performed with the same composition. The reaction mixture was placed into a 10 mL thermostated glass reactor without an air gap.

Experiments were carried out to study the effect of the ratio of monomers and the initiator concentration on the rate of front propagation. The effect of the initial temperature on wave propagation was also investigated. An increase of the initiator concentration from 0.026 to 1.070 w/w % doubled the front velocity. Changing the acrylamide:TGDMA w/w % ratio from 1:1 to 5:1 also doubled the speed of propagation. Propagation rates were in the range 1.2–2.4 cm/min at 25 °C. Increasing the initial temperature of the monomer mixture from 25 to 66 °C increased the front velocity from 1.2 to 3.0 cm/min. All reaction fronts produced solid, machinable rods. Upon heating, the rods turn blue in the range 80–140 °C. The color change is reversible and can be repeated more than 100 times.

The composite was tested as a remote temperature sensor using digital image processing, as described previously.<sup>9</sup> The temperature of a heating plate was measured with 0.5 °C accuracy in the range 85–135 °C from a 1 m distance.

Batch polymerization did not produce a satisfactory product. Phase separation occurred, with the less dense glycerin rising to the top of the reactor. Smaller scale phase separation occurred in which regions of glycerin were excluded from the cross-linked regions. An inhomogeneous, rubbery material resulted. The product was not machinable but soft and breakable. The morphologies of both products are shown in Figure 1.

We conclude that this thermochromic composite can be used as a remote temperature sensor. Although we cannot exclude the possibility that this material can be prepared via a batch reaction, our experiments indicate that frontal polymerization is a superior method for preparing this novel material. Propagating polymerization fronts may be an excellent method for preparing other uniform materials from components that phase separate upon reaction.

**Acknowledgment.** This work was supported by the U.S.–Hungarian Science and Technology Joint Fund (J.F. Grant No. 247/92a), the National Scientific Research Fund of Hungary (OTKA Grant No. F-4024), the Ministry of Education of the Hungarian Government (MKM Grant No. 9/94), the National Science Foundation's Mississippi EPSCoR Program, and NASA's Microgravity Materials Science Program (NAG8-973).

JA943744J