UC Santa Barbara

UC Santa Barbara Previously Published Works

Title

Optical characterization and confocal fluorescence imaging of mechanochromic acrylate polymers

Permalink

<https://escholarship.org/uc/item/9v16q8vc>

Journal

Journal of Applied Physics, 117(4)

ISSN

0021-8979

Authors

Van Horn, M
Smith, P
Mason, BP
et al.

Publication Date

2015

DOI

10.1063/1.4906326

Peer reviewed

Optical characterization and confocal fluorescence imaging of mechanochromic acrylate polymers

M. van Horn, P. Smith, B. P. Mason, J. R. Hemmer, J. Read de Alaniz, J. P. Hooper, and S. Osswald

Citation: *Journal of Applied Physics* **117**, 043103 (2015); doi: 10.1063/1.4906326

View online: <http://dx.doi.org/10.1063/1.4906326>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/117/4?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Neutron, fluorescence, and optical imaging: An in situ combination of complementary techniques](#)

Rev. Sci. Instrum. **86**, 093706 (2015); 10.1063/1.4931427

[A method for intermediate strain rate compression testing and study of compressive failure mechanism of Mg-Al-Zn alloy](#)

J. Appl. Phys. **109**, 103512 (2011); 10.1063/1.3590155

[A sensitive and versatile laser scanning confocal optical microscope for single-molecule fluorescence at 77 K](#)

Rev. Sci. Instrum. **81**, 113705 (2010); 10.1063/1.3499260

[Characterization of power induced heating and damage in fiber optic probes for near-field scanning optical microscopy](#)

Rev. Sci. Instrum. **78**, 053712 (2007); 10.1063/1.2740133

[Influence of the photodepoling parameters on quasiphase-matched second-harmonic generation and optical parametric fluorescence in polymer channel waveguides](#)

J. Appl. Phys. **96**, 7112 (2004); 10.1063/1.1809770

Instruments for Advanced Science

Contact Hiden Analytical for further details:
www.HidenAnalytical.com
info@hiden.co.uk

CLICK TO VIEW our product catalogue

<p>Gas Analysis</p> <ul style="list-style-type: none"> › dynamic measurement of reaction gas streams › catalysis and thermal analysis › molecular beam studies › dissolved species probes › fermentation, environmental and ecological studies	<p>Surface Science</p> <ul style="list-style-type: none"> › UHV TPD › SIMS › end point detection in ion beam etch › elemental imaging - surface mapping	<p>Plasma Diagnostics</p> <ul style="list-style-type: none"> › plasma source characterization › etch and deposition process reaction › kinetic studies › analysis of neutral and radical species	<p>Vacuum Analysis</p> <ul style="list-style-type: none"> › partial pressure measurement and control of process gases › reactive sputter process control › vacuum diagnostics › vacuum coating process monitoring
--	--	--	--

Optical characterization and confocal fluorescence imaging of mechanochromic acrylate polymers

M. van Horn,¹ P. Smith,¹ B. P. Mason,² J. R. Hemmer,³ J. Read de Alaniz,³ J. P. Hooper,¹ and S. Osswald^{1,a)}

¹*Department of Physics, Naval Postgraduate School, 1 University Circle, Monterey, California 93943, USA*

²*Research Department, Naval Surface Warfare Center, Indian Head Division, 3767 Strauss Ave., Indian Head, Maryland 20640, USA*

³*Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, USA*

(Received 15 October 2014; accepted 1 January 2015; published online 23 January 2015)

The development of mechanochromic molecules has opened new pathways for the study of localized stress and failure in polymers. Their application as stress or temperature diagnostics, however, requires suitable measurement techniques capable of detecting the force- and temperature-sensitive chemical species with high spatial resolution. Confocal imaging techniques offer excellent spatial resolution but the energy input during these measurements can itself affect the activation state of the mechanochromic species. Here, we present a systematic study of the effects of laser-based imaging on the activation and fluorescence behavior of mechanochromic spiropyran (SP) integrated into poly(methyl acrylate) (PMA) and poly(methyl methacrylate) matrices using a confocal Raman microspectrometer. Localized stress and temperature activation were studied by means of high-rate compressive loading and dynamic fracture. Laser illumination of SP in PMA revealed a strong excitation wavelength- and power-dependence. Suitable correction functions were established and used to account for the observed laser effects. The presented study demonstrates that confocal imaging using conventional Raman spectrometers is a powerful characterization tool for localized stress analysis in mechanochromic polymers, offering quantifiable information on the activation state with high spatial resolution. However, laser-mechanophore interactions must be well understood and effects of laser excitation and exposure times must be taken into consideration when interpreting the obtained results.

© 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906326>]

INTRODUCTION

Mechanochromic molecules, also referred to as mechanophores, are force sensitive molecules that offer new insight into the effects of stress on bulk polymeric materials.^{1–5} These molecules can be linked to polymer chains such that mechanical strain causes structural transformations that lead to measurable changes in the optical properties (e.g., fluorescence).^{1,2,6–9} The response of mechanochromic molecules can be altered by varying the attachment points¹ and the polymeric structure they are incorporated into³ making them versatile diagnostic tools.

One of the mechanochromic molecules that is currently receiving considerable attention is spiropyran (SP). Its physical and chemical properties when integrated as a mechanophore have been widely researched, including studies on activation thresholds,³ chemical equilibrium,⁴ response to environmental factors,⁵ orientation following activation,¹⁰ and reactive behavior.¹¹ Upon activation SP undergoes a reversible transformation from its colorless spiropyran form to a highly fluorescent merocyanine (MC) and exhibits thermo-, photo-, and mechanochromic responses.^{1,12} The analysis of SP molecules embedded in a polymer matrix may thus

provide valuable information on the stress and/or temperature history of the polymer host.

The activation state of mechanochromic molecules has previously been analyzed through diffuse reflectance measurements,¹³ absorbance measurements,^{2,4} green channel intensity analysis,¹ fluorescence imaging,^{3,5,10} and confocal laser scanning microscopy.^{1,3,4} However, these optical techniques differ substantially with respect to the spatial resolution, which can range from the centimeter to the micrometer scale, and the amount of energy exchanged with the sample during measurement. For applications involving localized fracture or related damage in the polymer, it is highly desirable to have a measurement technique that can probe the SP-to-MC conversion at the micrometer scale without a significant perturbation of the molecule.

Monitoring this manner of microdamage within force sensitive polymers relies on the ability to resolve regions containing high concentrations of activated mechanochromic molecules. Consequently, imaging techniques that offer high spatial resolution, such as confocal Raman spectroscopy and confocal laser microscopy, may be well suited for these applications. While these techniques are generally considered non-destructive and easy-to-use, due to their confocal nature, the energy transferred to the sample during measurements can be extremely high. Even when integrated as a mechanophore, SP can be temperature sensitive and optical absorption by either the molecule or the polymer can cause laser heating and interfere with the activation state of the

^{a)}Author to whom correspondence should be addressed. Present Address: School of Materials Engineering, Purdue University, 701 West Stadium Avenue, West Lafayette, Indiana 47907, USA. Electronic mail: ssoswald@purdue.edu

molecule. This makes it challenging to separate thermal and mechanical activation; this distinction is particularly important during high-rate loading, where localized heating typically accompanies the rapid mechanical compression. In addition, many of the studied mechanophores are based on optical photoswitches. Photo-induced changes in these mechanophores or the polymer matrix (e.g., photobleaching and photoactivation) may also affect the optical response of the system. Therefore, understanding the effects of the characterization technique and the measurement process on the properties of the material system is critical for a successful application of mechanophores in stress and temperature diagnostics.

Here, we present a systematic study of the effect of laser excitation on the analysis of SP in poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) polymer matrices and demonstrate that great care must be taken when selecting the excitation laser and measurement condition for stress and temperature sensing.

EXPERIMENTAL

Mechanophore-bearing PMAs were generated by single electron transfer living radical polymerization (SET-LRP)¹⁴ adapted from a procedure reported by Moore and coworkers.² With SET-LRP, controlled polymerization is accomplished in a living fashion off halide groups on the spiropyran derivative. In the case of fully functionalized (FF) SP-PMA, methyl acrylate polymer is grown off either side of the spiropyran derivative (which features two halide groups for polymerization), resulting in a single spiropyran in the middle of each PMA chain. In the case of mono-functionalized (MF) SP-PMA, methyl acrylate polymer is grown off only one side of the SP (which bears only a single halide group), resulting in a single SP on only one end of each polymer chain. Because polymerization is controlled, generally narrow polydispersities of about 1.3 are achieved. Molecular weights were 106 kDa versus 127 kDa for the FF SP-PMA and MF SP-PMA, respectively. See supplementary material¹⁵ for details on the synthesis procedures. Mechanophore-crosslinked PMMAs were generated using mono- and dimethacrylate-bearing spiropyran derivatives previously reported in the literature,^{1,16} using standard free radical polymerization techniques. Thermal activation of MF SP-PMA samples was achieved by heating samples in a box furnace at 50 °C. MF SP-PMA samples were deactivated by exposure to white light from a fluorescent lamp. Samples were considered to be in their deactivated state after 24-h exposure to white light.

Localized stress and temperature activation were performed by loading samples at high strain-rates using a compression split Hopkinson pressure bar. 20 mm diameter, 8 ft long maraging steel bars were used, with a 12 in. striker bar of the same material and a copper pulse shaper to smooth the loading pulse. No momentum trap was used during these impacts, and thus samples experienced multiple high-rate compressive loadings roughly 100 μ s in duration as the waves reflected in the bar system. The samples fractured during this process and were recovered via a small collection apparatus around the impact point. All tests were performed

with minimal light conditions in order to capture only the SP to MC conversion that arose due to localized stress and temperature during the loading. Schematics and further details on the SP/polymer samples and the high-rate mechanical testing can be found in Ref. 16.

Raman spectroscopy and fluorescence mapping were conducted using a confocal inVia Raman Microspectrometer (Renishaw, UK) equipped with 514 nm Ar ion, 633 nm HeNe, and 785 nm solid state excitation lasers and 1200 (633 and 785 nm) and 1800 lines/mm (514 nm) diffraction gratings. Spectral data were recorded with 20 $\times$ /0.4, 50 $\times$ /0.75, and 100 $\times$ /0.85 microscope objectives (Leica N Plan), and power levels at the sample were measured with a Newport 1928-C optical power meter. Renishaw's Wire software was used for background corrections and data analysis. Fluorescence mapping was conducted with Wire's StreamLine function where emission spectra were collected between 590 nm and 680 nm using 1 accumulation with a 1 s collection time. All samples were mapped on silicon substrates.

Optical absorbance was measured with an Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer. Data were collected from 450 to 800 nm using 1-nm intervals and a scan rate of 600 nm/min. Neither source nor detector changeover was required in the selected wavelength range.

RESULTS AND DISCUSSION

In this study, we investigated two types of SP-PMA: MF and FF. The samples differ in the attachment mechanism between PMA chains and SP molecules. In the case of MF SP-PMA, polymer and mechanochromic molecules are connected at a single point, rendering the sample sensitive to UV light and heat, but not to mechanical stress. FF SP-PMA has acrylate polymer grown off two points on the molecule, allowing for force transfer between PMA and SP across the active bond. As a consequence, FF SP-PMA is UV light, heat, and force sensitive. Details on the chemical structure and properties of MF and FF SP-PMA were reported elsewhere.¹

Figure 1 shows the Raman spectra and corresponding optical photographs of a MF SP-PMA sample recorded at room temperature after thermal activation in a box furnace for 10, 20, and 35 min at 50 °C. Raman spectra are dominated by the PMA matrix due to the very low concentrations of SP present. Although small spectral changes resulting from the SP are observed near 1340 and 1580 cm^{-1} (red arrows in Fig. 1), the changes are too small to allow for reliable Raman-based stress or temperature diagnostics. A more prominent change was the higher background signal, likely resulting from an increase in the fluorescence caused by the activation. Upon activation, the sample color changes to a dark purple as the SP-to-MC conversion leads to a new fluorescent emission at approximately 625 nm.¹⁶

Absorbance measurements were conducted to identify the most suitable wavelength for stimulating fluorescence in MF SP-PMA with Raman spectrometer setup. The sample was deactivated with white light and subsequently thermally activated for 30 min at 50 °C. The absorbance spectra of the activated and deactivated MF SP-PMA are shown in

FIG. 1. Raman spectra of MF SP-PMA measured at different states of activation, in comparison to pure PMA. Data were collected using 785-nm laser excitation at room temperature, after heat-treatment for 10, 20, and 35 min at 50°C. The photographs on the left side illustrate the color changes of sample upon activation.

Fig. 2(a) along with that of pure PMA. The presence of activated SP molecules causes a notable broad increase in absorption between 500 and 650 nm. Therefore, a 514-nm Ar ion laser was selected to excite the sample and stimulate fluorescence. The emission spectra recorded with the Raman spectrometer are displayed in Fig. 2(b). The activated MF SP-PMA sample exhibits a strong emission peak around 625 nm, suggesting that conventional Raman spectrometers may be used for probing the activation state of mechanochromic molecules, such as SP.

To evaluate the feasibility of Raman spectrometer-based fluorescence imaging, we recorded the emission spectra of FF SP-PMA and FF SP-PMMA samples using a confocal inVia Raman Microspectrometer (Renishaw) with 514-nm laser excitation. The FF SP-PMA sample was

mechanically activated by scratching (Fig. 3(a)), while the FF SP-PMMA sample was mechanically activated by compression in a Hopkinson bar leading to dynamic fracture (Figs. 3(b) and 3(c)). Our previous studies on these materials have suggested that much of the observed activation in the FF SP-PMMA sample is thermal in origin and is due to local dissipation around dynamic fracture surfaces.¹⁶ The false color maps shown in Figure 3 display the spatial distribution of the collected fluorescence intensity (absolute intensity in counts at 625 nm). The FF SP-PMA and MF SP-PMA were also tested in the Hopkinson bar and showed activation under severe loading, with activation again predominately on fracture surfaces. Further details on the mechanical activation during high-rate compression are given in Ref. 16. These images demonstrate the capabilities and versatility of this technique for measuring stress and temperature distributions in polymers with submicrometer resolution.

During the course of the mapping studies, it was discovered that despite being at the lowest power level capable of producing a useful signal ($<0.25 \text{ kW/cm}^2$), the measurements themselves had a noticeable effect on the activation state of the samples. A similar observation was reported by Richert and Bassler, who studied the thermal kinetics of isolated SP molecules using conventional spectrophotometers, though the authors did not characterize or quantify the effect.¹⁷

Therefore, we further investigated the effect of laser exposure on mechanochromic polymer samples. Figure 4(a) shows the decrease in fluorescence intensity of the MF SP-PMMA during a series of five 1-s emission measurements. All five images are based on the same false color scale and were recorded from the same sample spot. The obtained results clearly demonstrate that upon laser illumination, the fluorescence of the sample gradually diminishes. While the information on the spatial distribution of the activation is

FIG. 2. (a) Absorbance spectra of activated and deactivated MF SP-PMA, in comparison to pure PMA. The activation of SP causes an additional absorption peak between 500 and 650 nm. (b) Fluorescence spectra of activated MF SP-PMA and pure PMA, recorded using an inVia Raman Microspectrometer with 514-nm laser excitation (0.23 kW/cm^2 at the sample). Spectra were normalized and offset for illustration purposes.

FIG. 3. Optical microscope images (upper row) and corresponding fluorescent maps (lower row) of different mechanochromic polymers. (a) Low-magnification map of FF SP-PMMA after mechanical activation by scratching and low-(b) and high-magnification (c) maps of FF SP-PMMA after activation in a Hopkinson bar, recorded using 514-nm excitation. The false color images represent the absolute intensity (counts) measured at the fluorescent emission peak of 625 nm. Low- and high-magnification maps were recorded with $5\times$ and $100\times$ objectives, respectively.

largely maintained during the initial cycles and can be visualized by adjusting the color scale (Figure 4(b)), the exposure lowers the overall intensity of the signal, which eventually will fall below the detection limit of the recording instrument.

We next consider whether this process is the expected photo-induced reversion of MC to SP, or if photobleaching of the chromophore also plays a role. To exclude photobleaching or other irreversible damage to the SP or the PMMA matrix as potential cause for the observed changes,

FIG. 4. (a) False color images from sequential fluorescent measurements of MF SP-PMMA on a high-rate fracture surface following Hopkinson bar impact. The maps were recorded using 514-nm laser excitation ($<0.23 \text{ kW/cm}^2$ at sample) and $20\times$ objective and are subject to the same color scale. (b) Comparison of fluorescent maps after the 1st and 5th scan. The color scale of each map is normalized to the respective 5%–95% intensity range. (c) Changes in fluorescent intensity during continued activation/measurement/deactivation cycling.

we subjected the same sample area to three activation/measurement/deactivation cycles (Figure 4(c)). The deactivation caused by the measurement due to laser exposure was found to be reversible, suggesting that the observed changes in fluorescence intensity can be solely ascribed to photo-induced deactivation. Variations of 2%–5% were observed between the subsequent activation/deactivation cycles, giving a gauge of the error in our intensity measurements.

To further quantify the effect, we subjected a thermally activated MF SP-PMMA sample to a series of 1-s laser exposures at various wavelengths and power levels (Figure 5(a)). Following each exposure, the fluorescence was measured using 514-nm laser excitation (0.23 kW/cm²) and a 1-s collection time. Emission spectra were recorded from the same sample area in the wavelength range 590–680 nm, and the absolute intensity (in counts) at 620 nm was used to quantify the fluorescence.

The data presented in Figure 5(a) displays the combined effects of laser illumination (514, 633, and 785 nm) and laser exposure during emission measurements (514 nm). The level of deactivation was found to depend on both illumination wavelength and laser power. In general, the deactivation increased with increasing laser power, whereas the effect was more pronounced for shorter wavelength. To fully understand this dependence, it is necessary to separate the effects of laser illumination and contributions from the emission measurements themselves. Therefore, a series of sequential emission measurements (at 514 nm) were taken to quantify the measurement effect without additional laser exposure (bottom graph in Fig. 5(a)). The decrease in emission intensity due to deactivation during measurements can be approximated by an exponential decay of the form

$$I_m = A + B \exp(R \cdot t_m), \quad (1)$$

where I is the fluorescent intensity, R is the rate coefficient, t is the exposure time, and A and B are experimentally determined constants. Assuming that the deactivation caused by

all laser wavelengths and power levels exhibits the same exponential behavior, and that there are no additional processes affecting the state of activation of the samples during the short time of measurement, the combined effects of laser illumination (index “l”) and emission measurement (index “m”) can be expressed as

$$I_{comb} = I_m + I_l - 1, \quad (2)$$

where I_{comb} is the recorded intensity, and I_l and I_m are the contributions due to laser exposure and emission measurement, respectively. Because I_{comb} and I_m were measured directly, I_l of 633 and 785 nm-laser excitation can be derived from the experimental data using Eq. (2). In the case of 514-nm excitation, I_l and I_m are the same. In our experiments, laser exposures and emission measurement were applied in pairs with the same exposure time ($t_m = t_l = 1$ s).

Figure 5(b) shows the corrected data (I_l) for the three different excitation wavelengths (514, 633, and 785 nm) at various power levels. To better illustrate the effect of laser power for the different wavelengths, we plotted I_l after 5-s exposure to different power densities (Fig. 5(c)). It can be seen that exposure to 785-nm excitation showed very little effect on the fluorescence intensity and the power-dependence is relatively small. This is expected as the absorbance measurement (Fig. 2(a)) showed very little interaction between the 785-nm wavelength and the activated SP molecules. In contrast, both 633 and 514-nm laser exposure are strongly dependent on the power level. Particularly in the case of 514-nm excitation, the fluorescence intensity drops significantly, even at very low power levels.

The ability to predict the effect of illumination at different wavelength and power levels on a photo-responsive material is critical, particularly if the optical response of the material is to be quantified for diagnostic applications. For example, consider the case where the polarization of the fluorescence is characterized. The polarity of the

FIG. 5. Effect of laser excitation wavelength and power density on fluorescence intensity of activated MF SP-PMMA during mapping. Fluorescence intensity (a) as recorded (exposure and measurement effects) and (b) corrected (exposure effect only). (c) Fluorescence intensity after 5-s laser exposure as a function of laser power density.

FIG. 6. First (a) and fifth (b) fluorescence intensity maps of the same area of a MF PMMA sample. The fifth map was then corrected for laser-induced changes in the fluorescence intensity. All intensity maps are based on the same color scale.

emitted light can be used to determine the orientation of the SP molecules within an activated sample,¹⁰ which in turn provides information about the directionality of the forces that caused the activation. Polarization measurements may also be used to distinguish between thermal and force-induced activation in SP, as thermal activation is non-directional. Experimentally, measuring the spatial distribution of the polarity of the fluorescent emission requires that multiple maps of the same sample area be taken while the relative orientation of the sample to the polarization filter is varied for each map. In order to accurately quantify the activation level of the SP molecules and its spatial distribution, the effect of each measurement on the overall activation of sample must be taken into consideration. The measurement effect can be accounted for by adjusting the recorded intensity distributions. Depending on the excitation wavelength and total exposure time, all maps can be rescaled in a manner that allows a direct comparison of the individual maps. For our simplified mapping experiment, the corrected intensity, I_C , can be determined according to

$$I_C = I_R + (1 - I_m), \quad (3)$$

where I_R is the recorded fluorescence intensity, and $(1 - I_m)$ is the intensity loss due to laser exposure during the measurement itself. Figure 6 illustrates the data correction using the fluorescence maps of a MF SP-PMMA sample. All intensity maps are based on the same color scale. Five consecutive maps (1 s measurement time per spectrum) were recorded using 514 nm laser excitation. As expected, when recording the fifth map, the fluorescence intensity has dropped to approximately 70% of the initial value. Having quantified the effect of 514-nm laser excitation on the MF SP-PMMA sample in the previous measurements (Fig. 5), we corrected the collected map according to Eq. (3). The results are shown in Figure 6(c). It can be seen that the distribution of the absolute intensity is almost identical to that of the first map. Small differences likely result from the fact that the exponential function (Eq. (1)) used to describe the decay in fluorescence intensity upon laser exposure may be an oversimplification and may

not accurately describe the wavelength-dependent laser-sample interactions. However, the results demonstrate the general applicability of the approach to account for laser-induced changes in the sample during characterization. The above approach may also be used to account for the photo-aging of mechanochromic molecules, for example, during exposure to sunlight and/or temperature fluctuations in long term studies monitoring structural polymers and composites.

While the above method of determining the measurement effect on the activation state and fluorescence behavior of mechanochromic polymers can be generalized and may be applied to other mechanochromic molecules and polymer matrices, great care must be taken when selecting the experimental conditions and when interpreting the results. It was demonstrated that temperature,⁵ polymeric structure,^{3,5} and imposed forces⁴ all effect the activation thresholds and equilibrium of SP. The measurement effect for one polymeric system under certain conditions may not be applicable to other polymer matrices. For example, if the polymer matrix is strongly absorbing in the wavelength range of the excitation laser, the fluorescence measurement may lead to sample heating, which in turn could affect the activation state of the mechanochromic molecules.

SUMMARY AND CONCLUSIONS

Stress- and temperature-sensitive mechanochromic molecules, such as SP, hold great promise for the study of localized stress, fracture, and microdamage in polymers. Due to their high spatial resolution, confocal imaging techniques are an attractive option for analyzing the activation state of these materials. However, as we show in this work, the high energy-input that accompanies these measurements can strongly affect the activation state of the samples and must be properly accounted for. Using the example of SP in PMA and PMMA, we have systematically studied the effect of laser illumination on the fluorescence of mechanically activated SP molecules at various laser excitation wavelengths and power densities. A confocal Raman microspectrometer was used to record sequential intensity maps of the emitted

fluorescence and to quantify the degradation resulting from the exposure to the illuminating laser light. The characterization revealed a strong wavelength- and power-dependence and showed that the laser-induced intensity decay followed an exponential power law. The obtained functions were then used to correct the recorded maps for the illumination effects, demonstrating that if the laser-sample interactions are well understood; confocal imaging techniques can offer quantifiable information on the activation state of mechanochromic material systems with extremely high spatial resolution.

ACKNOWLEDGMENTS

This work was funded by the Defense Threat Reduction Agency Basic Sciences program under Grant No. HDTRA139181 and managed by Su Peiris.

¹D. A. Davis, A. Hamilton, J. L. Yang, L. D. Cremer, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martinez, S. R. White, J. S. Moore, and N. R. Sottos, *Nature* **459**, 68 (2009).

²S. L. Potisek, D. A. Davis, N. R. Sottos, S. R. White, and J. S. Moore, *J. Am. Chem. Soc.* **129**, 13808 (2007).

³C. M. Kingsbury, P. A. May, D. A. Davis, S. R. White, J. S. Moore, and N. R. Sottos, *J. Mater. Chem.* **21**, 8381 (2011).

⁴C. K. Lee, D. A. Davis, S. R. White, J. S. Moore, N. R. Sottos, and P. V. Braun, *J. Am. Chem. Soc.* **132**, 16107 (2010).

⁵B. A. Beiermann, D. A. Davis, S. L. B. Kramer, J. S. Moore, N. R. Sottos, and S. R. White, *J. Mater. Chem.* **21**, 8443 (2011).

⁶J. M. J. Paulusse and R. P. Sijbesma, *Chem. Commun.* **2008**, 4416.

⁷A. G. Tennyson, K. M. Wiggins, and C. W. Bielawski, *J. Am. Chem. Soc.* **132**, 16631 (2010).

⁸K. M. Wiggins, T. W. Hudnall, Q. L. Shen, M. J. Kryger, J. S. Moore, and C. W. Bielawski, *J. Am. Chem. Soc.* **132**, 3256 (2010).

⁹K. M. Wiggins, J. A. Syrett, D. M. Haddleton, and C. W. Bielawski, *J. Am. Chem. Soc.* **133**, 7180 (2011).

¹⁰B. A. Beiermann, S. L. B. Kramer, J. S. Moore, S. R. White, and N. R. Sottos, *ACS Macro Lett.* **1**, 163 (2012).

¹¹M. N. Silberstein, K. M. Min, L. D. Cremer, C. M. Degen, T. J. Martinez, N. R. Aluru, S. R. White, and N. R. Sottos, *J. Appl. Phys.* **114**, 023504 (2013).

¹²V. I. Minkin, *Chem. Rev.* **104**, 2751 (2004).

¹³D. S. Tipikin, *Russ. J. Phys. Chem. A* **75**, 1720 (2001).

¹⁴V. Percec, T. Guliashvili, J. S. Ladislav, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M. J. Monteiro, and S. Sahoo, *J. Am. Chem. Soc.* **128**, 14156 (2006).

¹⁵See supplementary material at <http://dx.doi.org/10.1063/1.4906326> for detailed information on mechanophore structure and synthesis conditions.

¹⁶J. R. Hemmer, P. D. Smith, M. van Horn, S. Alnemrat, B. P. Mason, J. R. de Alaniz, S. Osswald, and J. P. Hooper, *J. Polym. Sci., Part B: Polym. Phys.* **52**, 1347 (2014).

¹⁷R. Richert and H. Bassler, *Chem. Phys. Lett.* **116**, 302 (1985).