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# Dynamic Phosphorescent Probe for Facile and Reversible Stress Sensing

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**Dynamic phosphorescent copper complex incorporated into the main chain of polyurethanes produces a facile and reversible response to tensile stress. In contrast to common deformation sensors, the applied stress does not lead to bond scission, or alters the phosphor structure. The suppression of dynamics responsible for the nonradiative relaxation is found to be the major pathway governing stress response. As a result, the response of dynamic phosphor described in this work is stress specific. Compared to initial unloaded state, a nearly twofold increase of photoluminescence intensity occurs in response to a 5–35 MPa stress applied to pristine metalated polymers or their blends with various polyurethanes. Finally, the dynamic sensor proves useful for mapping stress distribution patterns and tracking dynamic phenomena in polyurethanes using simple optical imaging techniques.**

Modern materials are designed to withstand various hazards in common everyday operation as failure to do so can often inflict severe losses in material performance. Aside from environmental resistance, the ability to sustain mechanical stress is a crucial feature of a robust material. The latter is particularly important for polymers, as they are often exposed to stress of alternating duration and magnitude. Quantifying the stress in polymers provides an invaluable aid in monitoring and preventing their failure. In recent years, several remarkable strategies have been applied to detect stress in polymers. One of them relies on selective mechanochemical reactions in probe molecules incorporated into the polymer main chains.<sup>[1]</sup> Sijbesma and co-workers developed a family of materials that emit light in response to the developing fracture.<sup>[2,3]</sup> The sensing mechanism in these materials relies on a selective bond scission of a main chain-incorporated 1,2-dioxetane molecules. This strategy proved versatile as it could be translated to network polymers.<sup>[4]</sup> Another prominent example utilizes the isomerization of spiro-pyran molecular probes that leads to a rapid change of material color in response to deformation.<sup>[5–8]</sup> These elegant techniques provide rapid and clear visual response to failure development in polymers; however, their mode of action is intrinsically

irreversible as the reassembly of the fractured or isomerized probe molecules, with very few exceptions, does not occur immediately after the stress is removed.<sup>[9,10]</sup>

In addition to bond scission probes, a broad class of deformation sensitive photoluminescent (PL) materials have been designed. Among their advantages are the noninvasive nature of PL probes and experimental simplicity of the sensor response detection. Such probes are commonly introduced as fillers or additives to the fabricated polymer or polymer composite and they rely on the change of the intermolecular arrangement of photoluminescent probes.<sup>[11]</sup> Prominent examples reported by Crenshaw and Weder and

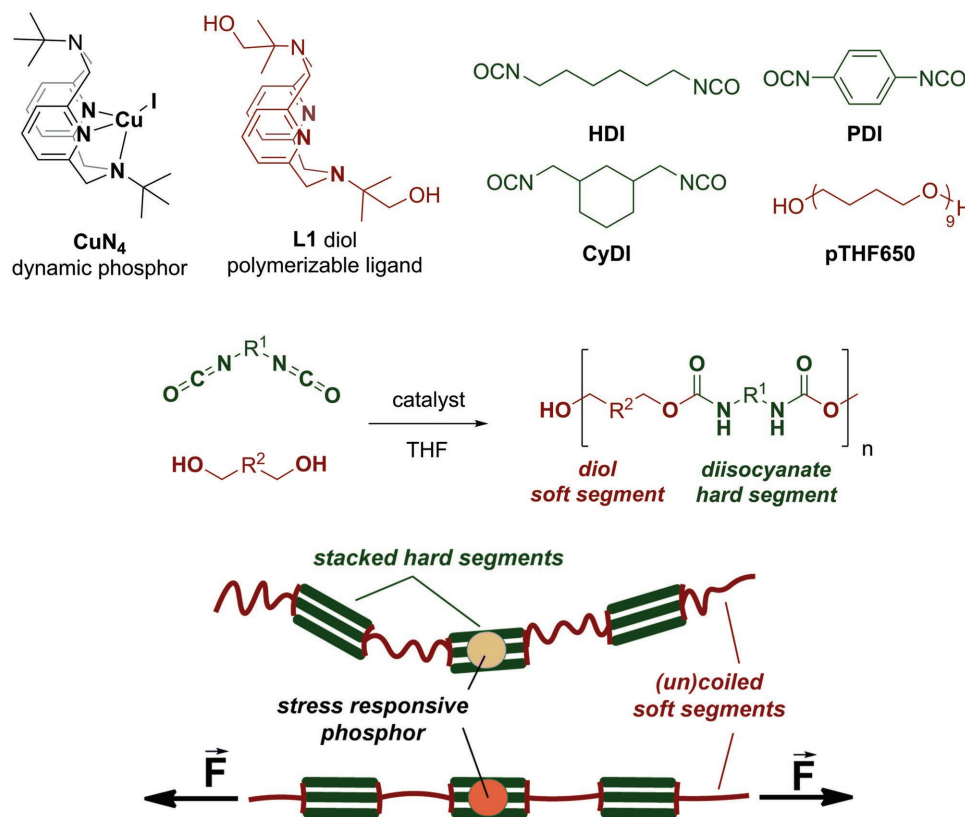
Pucci et al. were among the first reports that described a readily detectable color change of polymer films in response to deformation in blended and main chain modified polymers.<sup>[12,13]</sup> The response in these materials was generated due to the change of the phosphor arrangement that exhibits different emission color in monomeric and aggregated states. The relative contribution of monomer and excimer to the overall emission was found to be directly linked to sample deformation and mirrored the stress–strain curve. A separate class of deformation sensitive PL sensors employed nanocrystalline probes including ZnO<sup>[14]</sup> and CdSe–CdS<sup>[15–17]</sup> nanocrystals, core–shell quantum dots,<sup>[18]</sup> and doped alumina nanocomposites.<sup>[19]</sup> The common feature of the majority of PL-based sensors is their reliance on the structural rearrangements of the PL probe to detect deformation that is typically proportional to stress. This suggests that the state-of-the-art materials respond primarily to mechanical deformation, rather than mechanical force itself. Since such behavior puts limitations on sensor reliability and reversibility, designing a stress sensor that does not require chemical bond cleavage or other significant structural changes would give rise to a conceptually novel class of materials which respond intrinsically to stress and produce a rapid and fully reversible response. In a broader context, the development of mechanophores with new operational principles could provide valuable insight into the mechanisms of translation of macroscopic phenomena into a response generated on the molecular scale.<sup>[20,21]</sup> This is particularly important when seeking to design new nanoscale materials controlled by macroscopic action.<sup>[22]</sup>

The starting point of our investigation was marked by the recent development of a family of Cu(I) phosphorescent complexes that have showed a remarkable sensitivity of the PL properties to the local environment.<sup>[23]</sup> Namely, the subtle variations

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**Figure 1.** Structures of the building blocks and properties of materials used in this work.

of the substituent bulk in the macrocyclic cyclophane-inspired ligand resulted in dramatic changes of the quantum yield in the solid state. Accordingly, increasing the steric bulk restricted the solution dynamics of the complex, making the phosphor less fluxional. As a result, the suppression of dynamics in our best performing phosphor ( $\text{CuN}_4$ , **Figure 1**) allowed for the observation of solution state emission, while the more fluxional analogues of  $\text{CuN}_4$  were nonemissive. We hypothesized that the dynamics of  $\text{CuN}_4$  could be altered when this phosphor is incorporated into the polymer and subjected to mechanical force. In this way, we sought to exploit the emission intensity as the direct measure of the stress in tested material.

In this work, we describe the detailed study of dynamic PL probes for reporting stress in polyurethanes. As we demonstrate below, a conceptually new stress sensing mechanism that relies on modulating the phosphor dynamics was found to produce a readily detectable increase of the emission quantum yield in response to mechanical force. Unlike previous examples, this mechanism does not rely on bond breaking/formation processes. As a consequence, we have obtained fast-acting and fully reversible sensors capable of reporting local stress and describing dynamic stress relaxation phenomena on a sub-second timescale. In contrast to previously reported examples, the new sensor did not exhibit any structural change during operation and relied solely on photophysical phenomena. To the best of our knowledge, such a combination of properties has not been reported previously.

We have selected polyurethanes (PU) as model polymers due to their ability to sustain high stress, and a modular structure

that enables chemical modification. PU are commonly prepared from diisocyanates and long chain diol building blocks (**Figure 1**). Diisocyanates form carbamate groups upon polymerization, often referred to as “hard” segments, that readily form hydrogen-bonded stacks within the PU matrix. The long chain diols or “soft” segments form coiled chains within the PU bulk.<sup>[24]</sup> To incorporate a ligand unit into the main chain of PU, we replaced a fraction of a long chain diol with a hydroxyl-terminated L1 (**Figure 1**). Employing a dibutyl tin dilaurate-catalyzed copolymerization of diol and diisocyanate building blocks, we prepared a set of polyurethane samples comprised of poly-tetrahydrofuran (pTHF) soft segments and various hard segment precursors including flexible hexamethylene diisocyanate (HDI) and more rigid 1,4-cyclohexyldiisocyanate (CyDI) and phenylene diisocyanate (PDI). The composition of samples and notations used throughout this paper is given in **Table 1**.

Incorporation of L1 diol into the PUs as well as the subsequent metalation to form corresponding Cu(I) iodide complexes in the main chain was confirmed by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectra L-PU samples after metalation is nearly identical to that of control complex  $\text{CuN}_4$ , having pseudotetrahedral geometry (see the Supporting Information). The clear yellow films (see **Figure S27** in the Supporting Information), cast from the metalated polymers L-PU1 and L-PU2 are photoluminescent. Upon excitation with 385 or 400 nm light, these films emit light at  $\approx 585$  nm with relatively low quantum yields of 1.8% (Cu-PU1) and 2.5% (Cu-PU2) that could imply that the phosphors incorporated into the polymer chains possess significant mobility.

**Table 1.** Properties and composition of polymer samples prepared for this work.

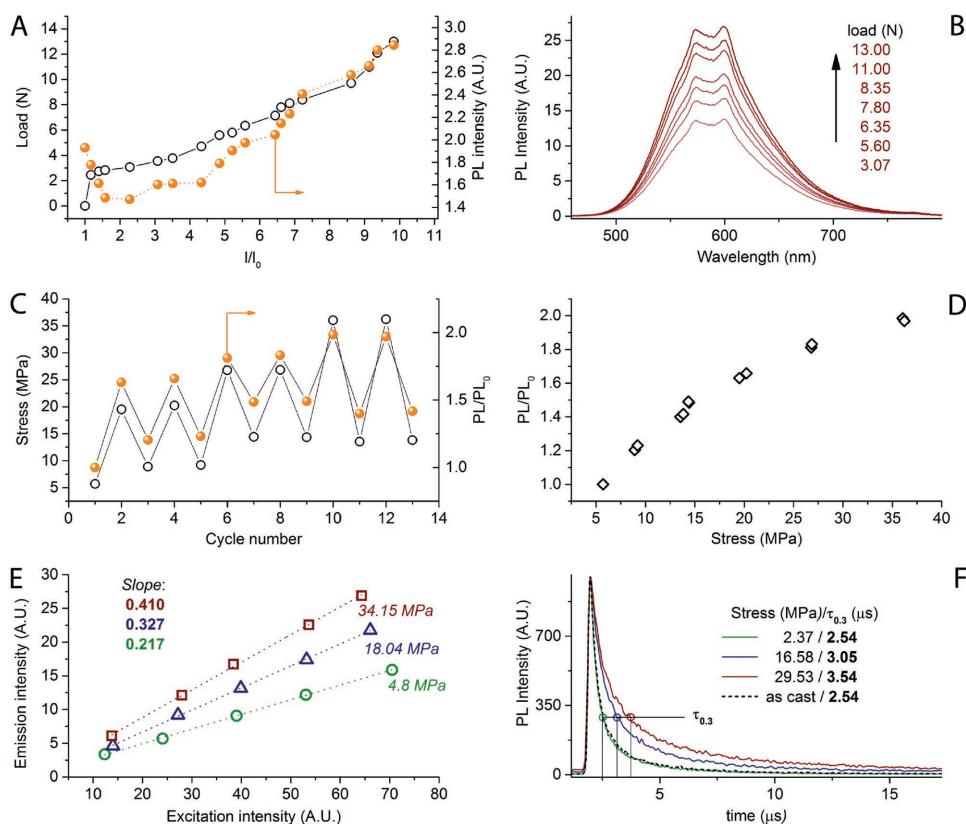
Sample <sup>a)</sup>	Isocyanate/fraction	Diol/fraction	L1 fraction	$M_w$ [kDa]/PDI
PU1	HDI/1	pTHF <sub>650</sub> /1	0	79.3/2.30
L-PU1	HDI/1	pTHF <sub>650</sub> /0.95	0.05	64.5/2.79
L-PU2	CyDI/1	pTHF <sub>650</sub> /0.95	0.05	97.8/1.85
PU3	PDI/1	pTHF <sub>650</sub> /1	0	123.6/1.81
PU4	HDI/1	pTHF <sub>1000</sub> /1	0	97.7/1.91
L-PU5	HDI/1	pTHF <sub>2900</sub> /0.8	0.2	57.7/3.10

<sup>a)</sup>Synthetic details and characterization data for all samples are given in the Supporting Information.

The metalated polymer films were further subjected to tensile elongation tests. As shown in **Figure 2A**, the load versus stretch ratio curve of Cu-PU1 has three regions, typical for polyurethanes.<sup>[24]</sup> The first region corresponds to the elastic deformation of the sample associated with the proportional increase of the load that roughly corresponds to  $\approx 3$  MPa apparent stress by the end of the elastic deformation region (Figure 2A). Further elongation results in the plastic deformation of the film

concomitant with the sample necking. The load force varies marginally during this process and increases rapidly when the stable neck is formed at stretch ratio of  $\approx 4$ . At the early stages of the test, the photoluminescence intensity decreases as the sample is necked due to the decrease of the irradiated sample size. Further elongation results in the steady increase of the PL intensity that mirrors the increase in applied force. We observed a nearly twofold increase in the integral PL intensity compared to its minimal value throughout the test as the sample was drawn to the maximal stretch ratio  $l/l_0 = 10$  (Figure 2A,B). Interestingly, the shape and width of the PL emission peak throughout this test, shown in Figure 2B, remained virtually identical and the intensity increase was the sole response to applied force.

Strikingly, the increase of PL intensity was fully reversible. A complete recovery of the PL signal was observed in a series of cyclic loading tests as the sample was subjected to alternating force (Figure 2C). The corresponding changes in the PL intensity occurred immediately within seconds after loading. Moreover, we repeatedly found an identical PL intensity readings when the sample was loaded at identical stress values. The observed phenomena persisted in a stress range of 5–35 MPa (Figure 2D). In a control experiment with polymer films cast from solution containing free complex  $\text{CuN}_4$  and PU1, we



**Figure 2.** Behavior of emissive CuPU1 films under tension: A) First loading load–strain–PL intensity curves and B) selected emission spectra recorded during the same test. C) Cyclic loading at alternating stress and D) PL versus stress plot derived from the same test. E) Power dependent PL and F) PL decay curves for samples under tension. Measurements on plots (C)–(F) correspond to the second and subsequent loadings of the necked samples. Stress values for the first loading were not calculated due to ongoing necking. In all cases, except for plot (B), PL refers to integral PL intensity (450–775 nm range);  $PL_0$  corresponds to the minimal integral PL intensity consistently recorded throughout the test at 5.71 MPa; excitation at (A)–(E) 385 nm and (F) 400 nm.

found no increase of PL intensity in response to applied force similar to that applied to Cu-PU1 (up to 12.15 N, Figure S19 in the Supporting Information). This experiment clearly confirms the force-induced nature of observed phenomenon.

Since the width of the emission peak remained constant upon tension, we believe that no significant change of the phosphor structure occurred when stress was applied (Figure 2B). This suggestion is supported by the reflectance measurements of the loaded samples that exhibit no detectable change in the absorption band at  $\approx 420$  nm, corresponding to the ground state absorption to form the excited species (Figure S24 in the Supporting Information). Taken together, these data suggest that neither ground state nor the excited state of the phosphor is structurally affected by the applied mechanical force.

The latter observation suggests that the sensing mechanism in Cu-PU1 is different from that in the state of the art materials that employ deformation-sensitive probes. To clarify this mechanism, we investigated the emission characteristics of the phosphor in Cu-PU1 under tension. A convenient tool to study variations in photoluminescence relies on the dependence of PL intensity on the power of excitation. As shown in Figure 1E, we found a perfectly linear relationship between the latter two. The slope of this linear dependence increased by a factor of 2 as the applied stress was varied from 4.8 to 34.15 MPa. Apart from being indicative of the twofold increase in the emission quantum yield, these data suggest that at any applied stress, a single relaxation pathway governs the emission. Considering the relatively low absolute quantum yield of Cu-PU1, this pathway is likely nonradiative. As both absorption and emission characteristics of the phosphor in Cu-PU1 are unaffected by stress (Figure 2B; Figures S24 and S26 in the Supporting Information), we assumed that the stress in Cu-PU1 primarily alters the nonradiative relaxation of the phosphor.

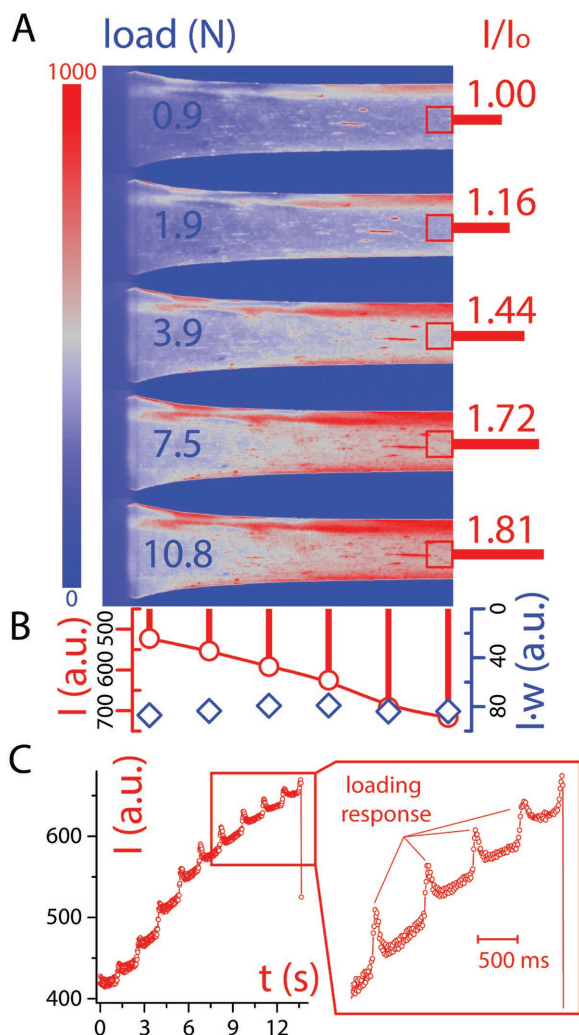
To confirm this suggestion, we have investigated the emission lifetime characteristics in Cu-PU1 films under tension. One could note that the PL quantum yield can be increased by either promoting the radiative relaxation or suppressing the nonradiative one. These pathways would have the opposite impact on the emission lifetime. The increase in radiative rate would shorten the lifetime, while the suppression of nonradiative relaxation would increase the lifetime. In agreement with our hypothesis, the apparent emission lifetime of Cu-PL1 increases by nearly a factor of 1.5 as a stress of  $\approx 29.5$  MPa is applied (Figure 2F). This clearly indicates that suppression of the nonradiative relaxation is taking place under tension. Analysis of decay rate constant distributions indicates the gradual suppression of fast relaxation processes as the mechanical stress is applied (see Figure S25 and corresponding discussion in the Supporting Information). We believe molecular dynamics to be a major source of the nonradiative relaxation. Interestingly, gradual suppression of conformational exchange in  $\text{CuN}_4$  solutions at lower temperatures that we observed previously also leads to an increase of quantum yield (Figure S23 in the Supporting Information).<sup>[20]</sup> We therefore assume that an identical mechanism is responsible for the same effect in Cu-PU1. This in turn suggests that the PL change in Cu-PU1 is exclusively characteristic of stress, since this factor directly impacts polymer dynamics.

The ability of a sensor to function in various environments is crucial for its practical applicability. To demonstrate the efficiency of our stress sensing strategy, we assessed the performance of several Cu-containing polyurethane samples in blends with nonfunctionalized polyurethanes of variable composition. The composition of the polymer samples was found to directly impact the stress response properties. First, the soft Cu-PU2 polyurethane samples containing a CyDI hard segment (Figure 1) were unsuitable for the tensile elongation as they failed at very low stress levels below 1 MPa. Nevertheless, blended with the PU1, Cu-PU2/PU1 sample produced a steady response to the applied stress very similar to that of Cu-PU1 (Figure S22 in the Supporting Information). A similar response was produced by Cu-PU1/PU1 blend that was additionally demonstrated to have excellent fatigue resistance. Namely, a sample kept at 25 MPa for 10 h exhibited stress dependent PL response nearly identical to that of a fresh sample (Figure S22 in the Supporting Information). Finally, both Cu-PU1 and Cu-PU2 were stress responsive in blends with a PU3 sample that contains rigid PDI hard segments (Figure S23 in the Supporting Information). These data indicate the high potential for the application of developed materials since they remain responsive in various environments.

By varying the soft block length in PU samples, we have also managed to identify limitations of the sensors. Namely, the replacement of the of the short pTHF<sub>650</sub> segment for a four-fold longer pTHF<sub>2900</sub> yielded Cu-PU5 that produced a very weak response to stress (Figure S20 in the Supporting Information) when blended with PU1. A significantly longer soft block in Cu-PU5 compared to that of PU1 was the likely reason for this behavior since such a mismatch would severely impede the translation of mechanical force from the blank PU1 to the sensor component. Interestingly, in the opposite case where the longer soft blocks (1 vs 0.65 kDa) are incorporated into the blank PU and the phosphor is present in the shorter units, the performance was not inhibited (see data for Cu-PU1/PU4 in Figure S21 of the Supporting Information).

The large magnitude of the PL intensity change upon tension is a highly beneficial feature of stress response in CuPU1. As the twofold increase of emission intensity could readily be observed with the naked eye, we assumed that direct optical imaging can be used to study the stress response in CuPU1 instead of spectroscopic detection that is often lacking spatial resolution. Indeed, analyzing images of sample under tension, we could observe a detectable increase in the PL intensity correlated to the applied force (Figure 3A). As expected, the PL intensity increases toward the center of the sample where the film width is minimal and the true stress is nominally the highest. Importantly, the width-normalized intensity that is characteristic of applied force remained nearly constant along the sample (Figure 3B). This observation allows us to conclude that phosphor in Cu-PU1 was capable of reporting the local stress while maintaining the overall accuracy on the macroscopic scale.

Interestingly, the rapid response of Cu-PU1 to stress can also be used to track time-dependent processes in polyurethanes. A well-known example of such a process is a stress relaxation phenomenon that takes place when the polymer samples are subjected to mechanical force. Namely, the stress in polyurethanes rapidly reaches a peak value and relaxes to a lower steady



**Figure 3.** Optical imaging data for CuPU1 films under tension in pseudocolour upon excitation at 354 nm. A) Local intensity follow-up with square region of interest indicated under the bar. B) Intensity (measured across the sample elongation direction, red circles) and width-corrected intensity (blue diamonds) distribution along the sample loaded at 10.8 N. C) Time-resolved imaging illustrating the dynamic response to loading.

value within seconds after loading is suspended.<sup>[25,26]</sup> Observation of such effects usually requires a direct measurement of applied force that is often impractical. Using the response of our phosphorescent sensor in Cu-PU1, we have managed to visualize this dynamic process. Time-resolved data in Figure 3C illustrate how simultaneously with sample elongation a rapid increase of PL intensity could be observed. As expected the intensity reached its peak value during sample extension and decayed within  $\approx 150$  ms after elongation was suspended (see Figure 3; Video S1, Supporting Information). Such outstanding utility renders the use of dynamic phosphors as a promising tool to investigate the stress related phenomena in polymers.

In conclusion, we have developed a new type of phosphorescent sensor that produces rapid and fully reversible response to mechanical stress. Unlike its counterparts across the field, our dynamic probe does not require changes to its molecular structure or arrangement and relies fully on suppression of

nonradiative relaxation that takes place at elevated stress. Importantly, the response of the sensor can be easily monitored by direct optical imaging in addition to common spectroscopy tools. Based on a conceptually new action mechanism, our robust and fully reversible sensors have a remarkable potential for assessing stress and dynamic phenomena in soft materials in a simple and accurate way.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev.* **2009**, *109*, 5755.
- [2] Y. Chen, A. J. H. Spiering, S. Karthikeyan, G. W. M. Peters, E. W. Meijer, R. P. Sijbesma, *Nat. Chem.* **2012**, *4*, 559.
- [3] Y. Chen, R. P. Sijbesma, *Macromolecules* **2014**, *47*, 3797.
- [4] E. Ducrot, Y. Chen, M. Bulters, R. P. Sijbesma, C. Creton, *Science* **2014**, *344*, 186.
- [5] C. K. Lee, B. A. Beiermann, M. N. Silberstein, J. Wang, J. S. Moore, N. R. Sottos, P. V. Braun, *Macromolecules* **2013**, *46*, 3746.
- [6] C. K. Lee, D. A. Davis, S. R. White, J. S. Moore, N. R. Sottos, P. V. Braun, *J. Am. Chem. Soc.* **2010**, *132*, 16107.
- [7] G. O'Bryan, B. M. Wong, J. R. McElhanon, *ACS Appl. Mater. Interfaces* **2010**, *2*, 1594.
- [8] D. A. Davis, A. Hamilton, J. 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, N. R. Sottos, *Nature* **2009**, *459*, 68.
- [9] K. Imato, T. Kanehara, T. Ohishi, M. Nishihara, H. Yajima, M. Ito, A. Takahara, H. Otsuka, *ACS Macro Lett.* **2015**, *4*, 1307.
- [10] T. Kosuge, K. Imato, R. Goseki, H. Otsuka, *Macromolecules* **2016**, *49*, 5903.
- [11] A. Pucci, R. Bizzarri, G. Ruggeri, *Soft Matter* **2011**, *7*, 3689.
- [12] B. R. Crenshaw, C. Weder, *Macromolecules* **2006**, *39*, 9581.
- [13] A. Pucci, F. Di Cuia, F. Signori, G. Ruggeri, *J. Mater. Chem.* **2007**, *17*, 783.
- [14] X. Jin, M. Götz, S. Wille, Y. K. Mishra, R. Adelung, C. Zollfrank, *Adv. Mater.* **2013**, *25*, 1342.
- [15] C. L. Choi, K. J. Koski, A. C. K. Olson, A. P. Alivisatos, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 21306.
- [16] S. N. Raja, A. C. K. Olson, K. Thorkelsson, A. J. Luong, L. Hsueh, G. Chang, B. Gludovatz, L. Lin, T. Xu, R. O. Ritchie, A. P. Alivisatos, *Nano Lett.* **2013**, *13*, 3915.
- [17] S. N. Raja, D. Zherebetsky, S. Wu, P. Ercius, A. Powers, A. C. K. Olson, D. X. Du, L. Lin, S. Govindjee, L.-W. Wang, T. Xu, A. P. Alivisatos, R. O. Ritchie, *Nano Lett.* **2016**, *16*, 5060.

- [18] S. Yin, Z. Zhao, W. Luan, F. Yang, *RSC Adv.* **2016**, *6*, 18126.
- [19] A. Stevenson, A. Jones, S. Raghavan, *Nano Lett.* **2011**, *11*, 3274.
- [20] K. Ariga, T. Mori, S. Ishihara, K. Kawakami, J. P. Hill, *Chem. Mater.* **2014**, *26*, 519
- [21] K. Ariga, T. Mori, J. P. Hill, *Adv. Mater.* **2012**, *24*, 158
- [22] K. Ariga, Y. Yamauchi, T. Mori, J. P. Hill, *Adv. Mater.* **2013**, *25*, 6477
- [23] G. A. Filonenko, R. R. Fayzullin, J. R. Khusnutdinova, *J. Mater. Chem. C* **2017**, *5*, 1638.
- [24] I. Kimura, H. Ishihara, H. Ono, N. Yoshihara, S. Nomura, H. Kawai, *Macromolecules* **1974**, *7*, 355.
- [25] H. J. Qi, M. C. Boyce, *Mech. Mater.* **2005**, *37*, 817.
- [26] F. Cellini, S. Khapli, S. D. Peterson, M. Porfiri, *Appl. Phys. Lett.* **2014**, *105*, 061907.
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