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Introduction of a Luminophore into Generic Polymers via Mechanoradical Coupling with a Prefluorescent Reagent

Koji Kubota,*[a,b] Naoki Toyoshima,[a] Daiyo Miura,[a] Julong Jiang,[b,c] Satoshi Maeda,[b,c] Mingoo Jin,*[a,b] and Hajime Ito*[a,b]

[a] Prof. Dr. K. Kubota, N. Toyoshima, D. Miura, Prof. Dr. M. Jin, Prof. Dr. H. Ito
Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
E-mail: kbt@eng.hokudai.ac.jp, Mingoo@icredd.hokudai.ac.jp, hajito@eng.hokudai.ac.jp

[b] Prof. Dr. K. Kubota, Prof. Dr. J. Jiang, Prof. Dr. S. Maeda, Prof. Dr. M. Jin, Prof. Dr. H. Ito
Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

[c] Prof. Dr. J. Jiang, Prof. Dr. S. Maeda
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

Abstract: Herein, we report a novel strategy for introducing a luminophore into generic polymers facilitated by mechanical stimulation. In this study, polymeric mechanoradicals were formed *in situ* under ball-milling conditions to undergo radical–radical coupling with a prefluorescent nitroxide-based reagent in order to incorporate a luminophore into the polymer main chains via a covalent bond. This method allowed the direct and conceptually simple preparation of luminescent polymeric materials from a wide range of generic polymers such as polystyrene, polymethyl methacrylate, and polyethylene. These results indicate that the present mechanoradical coupling strategy may help to transform existing commodity polymers into more valuable functional materials.

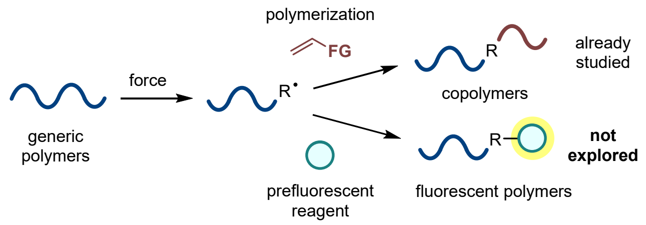
Introduction

It is well established that mechanically stimulating (e.g., grinding or crushing) polymers causes main-chain scission and generates free radicals, which are known as mechanoradicals.[1] In the 1930s, Staudinger first observed the decrease in molecular weight of polystyrene (PS) upon ball milling,[2] and Melville later discovered that polymer-chain scission was responsible for degradation.[3] In the 1960s, Sohma used electron spin resonance (ESR) spectroscopy to provide direct experimental evidence for the generation of mechanoradicals via the cleavage of polymer chains.[4] Since these pioneering studies, the generation of mechanoradicals has been focused upon as a key process of polymer degradation, and significant progress has been made in parallel in force-mediated polymerization involving mechanoradical species (Figure 1a).[5] This “constructive” approach has demonstrated that mechanoradicals are capable of acting as initiators for radical polymerizations in the presence of a monomer (Figure 1a).[5] This method can be used for the preparation of block copolymers via growth from the cleaved macroradicals, and has great potential for applications of mechanoresponsive polymeric materials.[5-7] Despite this recent progress, the preparation of functional polymers via mechanoradical transformations has scarcely been reported.[8] In fact, introduction of a luminophore into generic polymers via mechanoradical coupling has not yet been explored (Figure 1a). Such a new approach would potentially allow the direct preparation of functional polymers from chemically stable generic polymers without sophisticated chemical synthesis.

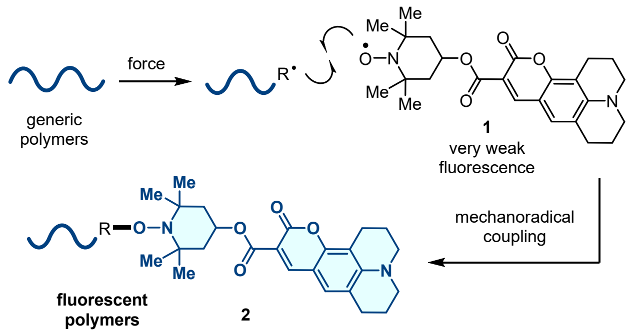
Recently, mechanically weak embedded bonds, which are known as mechanophores, have attracted considerable attention because they exhibit interesting functionalities such as mechanoresponsive luminescence.[6,7] However, the mechanophore functional groups must be introduced into the polymer main chain in advance, which limits the practical applications of these functional polymeric materials.[9]

Since 2008, our group has been investigating the mechanoresponsive luminescent properties of a series of gold(I) complexes.[10] Various mechanoresponsive gold(I) complexes that show single-crystal-to-single-crystal phase transitions,[10c,10d] multiple-colour emission,[10e] infrared (IR) emission,[10f] noncentrosymmetric-to-centrosymmetric phase transitions,[10g] and ferroelasticity[10h] have been reported. Recently, we have also become interested in applying ball-milling techniques to the development of mechanical-force-mediated organic transformations.[11-13] The borylation and C−H-bond functionalization of small organic molecules using ball milling and piezoelectric materials have been reported by our group.[13] Based on these previous studies, we realized that the application of mechanical force via ball-milling might represent a promising strategy to prepare functional materials.

a. Constructive approach via mechanoradical-mediated transformation



b. Introduction of a luminophore via mechanoradical coupling (**this work**)



- direct introduction of a luminophore via force-mediated mechanoradical coupling
- no requirement for a mechanophore or sophisticated chemical synthesis

Figure 1. A new strategy for the preparation of luminescent polymers via mechanoradical coupling with a prefluorescent reagent.

Inspired by the generation of mechanoradicals in polymers and our previous research into mechanical-force-induced luminescence and ball-milling reactions, we hypothesized that luminescent polymeric materials could be directly prepared from generic polymers without sophisticated chemical synthesis (Figure 1b). Specifically, we envisioned that a prefluorescent molecule, bearing a nitroxide radical tethered to coumarin-based luminophore **1**, could react with short-lived mechanoradicals generated by a wide range of generic polymers under ball-milling conditions to afford the corresponding luminescent materials (Figure 1b).[14] This type of prefluorescent molecules shows dramatically reduced fluorescence due to the quenching of the excited state of the luminophore via photo-induced electron or energy transfer between the luminophore and the nitroxide radical, but radical trapping by the free radical moiety restores the emission from the luminophore by removing the source of the quenching event.[14d] Thus, the changes in emission intensity can clearly indicate whether the luminophore is successfully introduced into the polymer main chain through a covalent bond. Although it is not clear whether the luminophore will be introduced at the end of the polymer main chain or within the chain, this should not affect the luminescence properties of the obtained polymers.[15] The present approach could endow a wide range of easily accessible generic polymers that do not contain mechanophores in their main chains with luminescence properties. Beyond the immediate utility of this protocol for the preparation of luminescent polymers, the present strategy is expected to inspire the development of a new design for mechanoresponsive luminescent materials and a new approach that can detect short-lived polymeric mechanoradicals visually and quantitatively in the solid-state, which is highly desirable in order to better understand the force-induced failure mechanisms of polymeric materials.

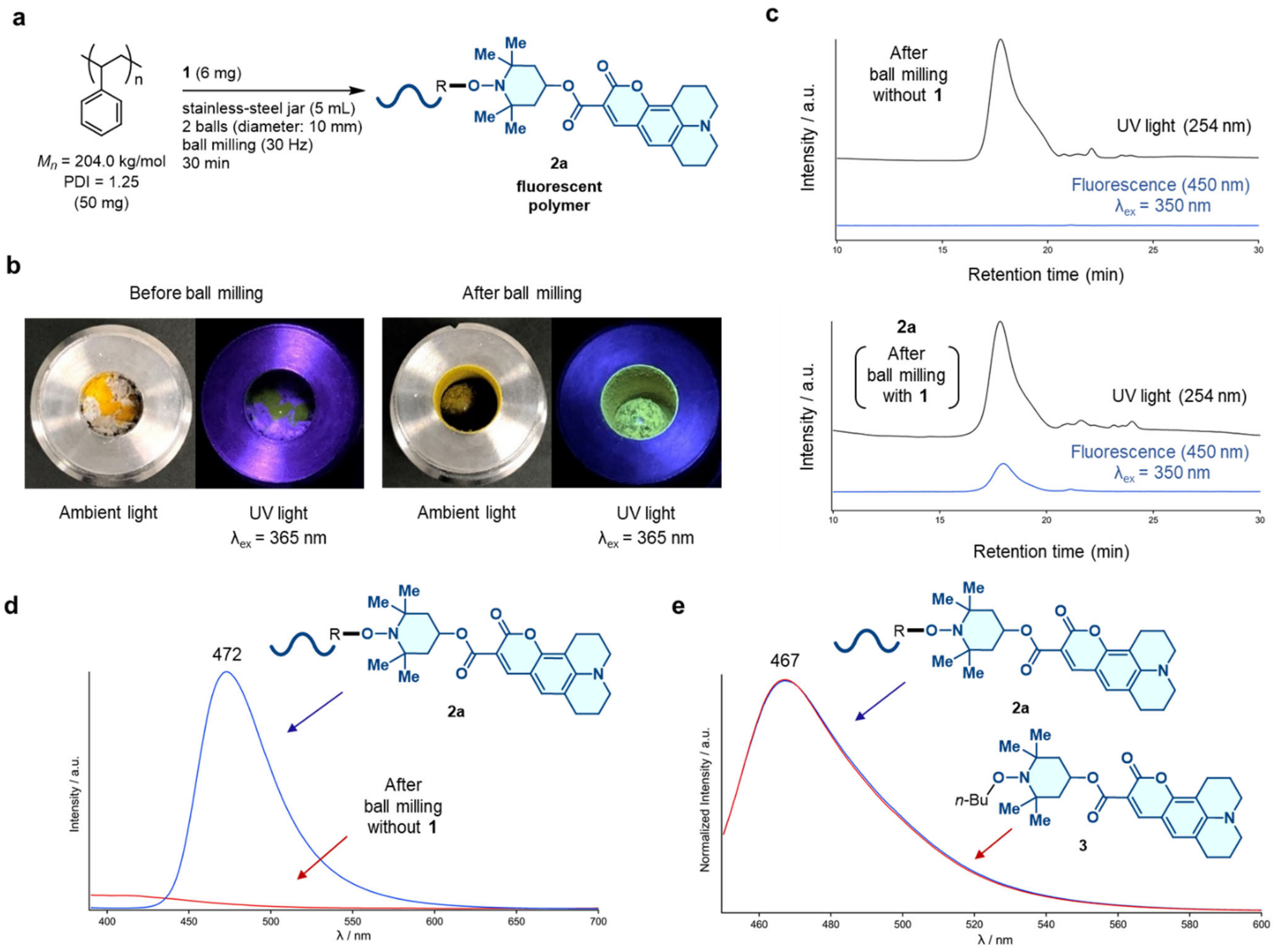


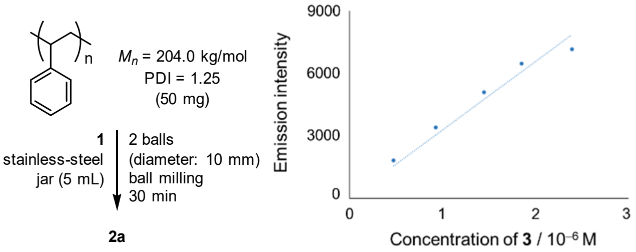
Figure 2. Preparation of luminescent polymeric materials from polystyrene (M_n = 204.0 kg/mol; PDI = 1.25) via mechanical-force-mediated radical–radical coupling with prefluorescent nitroxide radical **1** under ball-milling conditions. a) Reaction of polystyrene with **1** under ball-milling conditions. b) Photographs of a mixture of polystyrene and **1** before and after ball milling under ambient conditions and UV irradiation (λ_{ex} = 365 nm). c) GPC traces of the mixtures obtained by ball milling of polystyrene without **1** (top) and with **1** (down). d) Fluorescence spectra (λ_{ex} = 365 nm) of the ball-milled polystyrene and **2a** in the solid state. e) Fluorescence spectra (λ_{ex} = 365 nm) of **2a** and its alkylated analogue **3** in CH_2Cl_2.

Results and Discussion

All ball-milling experiments were carried out in a Retch MM400 mixer mill (5-mL stainless-steel milling jar using two 10-mm-diameter stainless-steel balls, Figure S1). To demonstrate the feasibility of this approach, we ground polystyrene (M_n = 204.0 kg/mol; PDI = 1.25) in the presence of the prefluorescent nitroxide radical **1**, which was previously used for the fluorescence mapping of photogenerated radicals in thin polymer films,[16] by ball milling at 30 Hz for 30 min. As shown in Figures 2a and 2b, blue fluorescence was observed under UV irradiation (λ_{ex} = 365 nm) after ball milling, while no fluorescence was observed when polystyrene was milled in the absence of **1**. To determine whether the blue emission was derived from the luminophore-containing polystyrene **2a**, gel permeation chromatography (GPC) and fluorescence measurements were conducted (Figure 2c–2e). The crude mixture of **2a** was purified by reprecipitation from CH_2Cl_2/MeOH followed by recycling preparative high-performance liquid chromatography (HPLC) to remove unreacted free radicals of **1**. The fluorescence spectra in the GPC analysis of the polystyrene that was obtained by ball milling without **1** showed no fluorescence peaks under UV light (λ_{ex} = 350 nm) (Figure 2c). In contrast, the fluorescence spectra in the GPC analysis of **2a** clearly revealed that the luminophore had been introduced throughout the polymer chains (Figure 2c). The absence of solid-state fluorescence from the polystyrene obtained by ball milling without **1** was also confirmed, while **2a** showed blue fluorescence with a maximum emission-intensity wavelength ($\lambda_{em,max}$) of 472 nm under UV irradiation in the solid state (Figure 2d).[17] These results suggest that the prefluorescent nitroxide radical **1** reacted with mechanoradicals generated *in situ* to form strongly fluorescent **2a**, in agreement with our working hypothesis (Figure 1b). Next, we compared the fluorescence spectra of **2a** and its alkylated analogue **3** in CH_2Cl_2 solution. For that purpose, **3** was prepared by the reaction of **1** with *n*-butyl trifluoroborate in the presence of Ag_2O (for details, see the Supporting Information).[18] We found that the fluorescence spectra of **2a** and **3** were very similar ($\lambda_{em,max}$ = 467 nm in CH_2Cl_2), indicating that the carbon-centred mechanoradicals generated in polystyrene reacted with **1** to form the mechanoradical coupling product **2a** (Figure S2–S4). Comparison of the fluorescence properties between **1**, **2a** and **3** indicates the turn-on feature of the luminophore **1** in response to the trapping of the mechanoradicals (Figures S2–S4 and Table S1). In fact, the emission quantum yield of **3** measured at 438 nm in CH_2Cl_2 solution was much higher than that of **1** (Table S1). The fluorescence spectrum of **2a** in the solid state was slightly red-shifted compared to its fluorescence spectra in CH_2Cl_2.[19] Furthermore, the ^1H NMR analysis of **2a** showed signals derived from both the coumarin-based luminophore and polystyrene, further supporting the formation of **2a** (Figure S5–S8).

We prepared a calibration curve for the fluorescence intensity of the alkylated analogue **3** as a function of its concentration in dilute CH_2Cl_2 (Table 1 and Figure S9). With this calibration curve in hand, we proceeded to evaluate the amount of coumarin-based luminophore incorporated into polystyrene under various ball-milling conditions by measuring the fluorescence intensity of **2a** dissolved in CH_2Cl_2 (Table 1). In all cases, the number-average molecular weight (M_n) decreased while the molecular-weight distribution (PDI) widened, suggesting that homolytic cleavage of covalent bonds in polystyrene occurred to generate mechanoradicals (Figure S11).[19] The amount of the luminophore incorporated into the polystyrene (M_n = 204,0 kg/mol) under the applied ball-milling conditions (30 Hz, 30 min) was calculated to be 0.036 µmol/mg in the crude product (Table 1, entry 1) based on its emission intensity and the calibration curve shown in Figure 2.[20] We also calculated the amount of the luminophore incorporated into the polystyrene based on the absorbance of **2a** using a calibration curve (Figure S10) and via ^1H NMR analysis of **2a** using an internal standard (Figure S5); these analyses furnished values similar to that calculated using its fluorescence intensity (0.030 µmol and 0.050 µmol, respectively). Based on the molecular-weight changes, approximately 0.19 µmol/mg of mechanoradicals were expected to form under the applied ball-milling conditions, which in turn indicated that approximately 16−26% of the mechanoradicals reacted with the prefluorescent nitroxide radical **1**.[20] When polystyrene with a lower molecular weight (M_n = 87.6 kg/mol) was used, the amount of luminophore incorporated decreased, while the polystyrenes with different M_n values converged to the same levels of M_n and PDI after ball milling (Table 1, entries 1 and 2). This is consistent with the fact that the longer polymer chains can generate more mechanoradicals, leading to the reduction of their M_n values to the same level. Next, we investigated the correlation between the mechanical impact provided by the ball milling and the amount of luminophore incorporated (Table 1, entries 1, 3, and 4). We found that conducting the ball milling at higher ball-milling frequencies (15–30 Hz) resulted in lower M_n and greater incorporation of **1**, suggesting that stronger mechanical impact can generate more mechanoradicals. Increasing the amount of **1** also led to an increase in the fluorescence intensity of **2a** (Table 1, entry 5). We also tested the reaction between polystyrene and **1** under sonication conditions in CH_2Cl_2, but the introduction of the luminophore was unsuccessful (for details, see the Supporting Information).

Table 1. Amount of luminophore incorporated, calculated based on the fluorescence intensity of **2** under various conditions[a]



Entry	M_n of **1** [kg/mol] (PDI)	Amount of **1** (mg)	Frequency (Hz)	M_n of **2** [kg/mol] (PDI)	Amount of luminophore incorporated (µmol/mg)[b]
1	204.0 (1.25)	6.0	30	9.2 (1.71)	0.036
2	87.6 (1.29)	6.0	30	11.3 (1.98)	0.030
3	204.0 (1.25)	6.0	20	17.4 (1.81)	0.028
4	204.0 (1.25)	6.0	15	38.3 (1.81)	0.009
5	204.0 (1.25)	12.0	30	11.6 (1.65)	0.046

[a] See the Supporting Information for details of the reaction conditions (λ_{ex} = 463 nm at room temperature). [b] Calculated based on the fluorescence intensity of **2a**.

Next, the applicability of the present mechanoradical coupling strategy to other generic polymeric materials was investigated (Figure 3). We found that polymethyl methacrylate (PMMA; $M_n \approx$ 120.0 kg/mol) was successfully converted into the blue-emissive polymer **2b** via mechanoradical coupling with **1** ($\lambda_{em,max}$ = 480 nm; Figure 3b). **2b** was purified by reprecipitation from CH_2Cl_2/MeOH followed by recycling preparative HPLC to remove unreacted free radicals of **1** (Figure S12). Polyethylene (PE; $M_n \approx$ 7.7 kg/mol), which is chemically stable and thus difficult to functionalize, was also converted into the corresponding blue-fluorescent polymer **2c** ($\lambda_{em,max}$ = 456 nm; Figure 3c). **2c** was purified simply by washing with CH_2Cl_2 to remove **1**, given the very low solubility of **2c** in CH_2Cl_2. We confirmed that most of the nonpolymeric fluorescent impurities in the crude mixture obtained by the ball milling of PE and **3** could be removed by washing with CH_2Cl_2 (Figure S13 and S14). This result suggests that the observed fluorescence is derived from **2c**. In the cases of polyphenylene sulfide (PPS; $M_n \approx$ 10.0 kg/mol) and polysulfone (PSF; $M_n \approx$ 22.0 kg/mol), luminescent polymers (**2d** and **2e**) with comparatively long-wavelength emissions ($\lambda_{em,max}$ = 498 nm and $\lambda_{em,max}$ = 517 nm, respectively; Figure 3d and 3e) were obtained after ball-milling with **1**, and the observed emission intensities were relatively weak (Figure 3f). **2d** is insoluble in organic solvents, and was thus purified simply by washing with CH_2Cl_2 to remove **1** as in the case of **2c**. **2e** was purified by reprecipitation from CH_2Cl_2/MeOH. The observed red-shift in their emission was probably due to the aggregation of the coumarin-based luminophore incorporated in the polymer chains.[21]

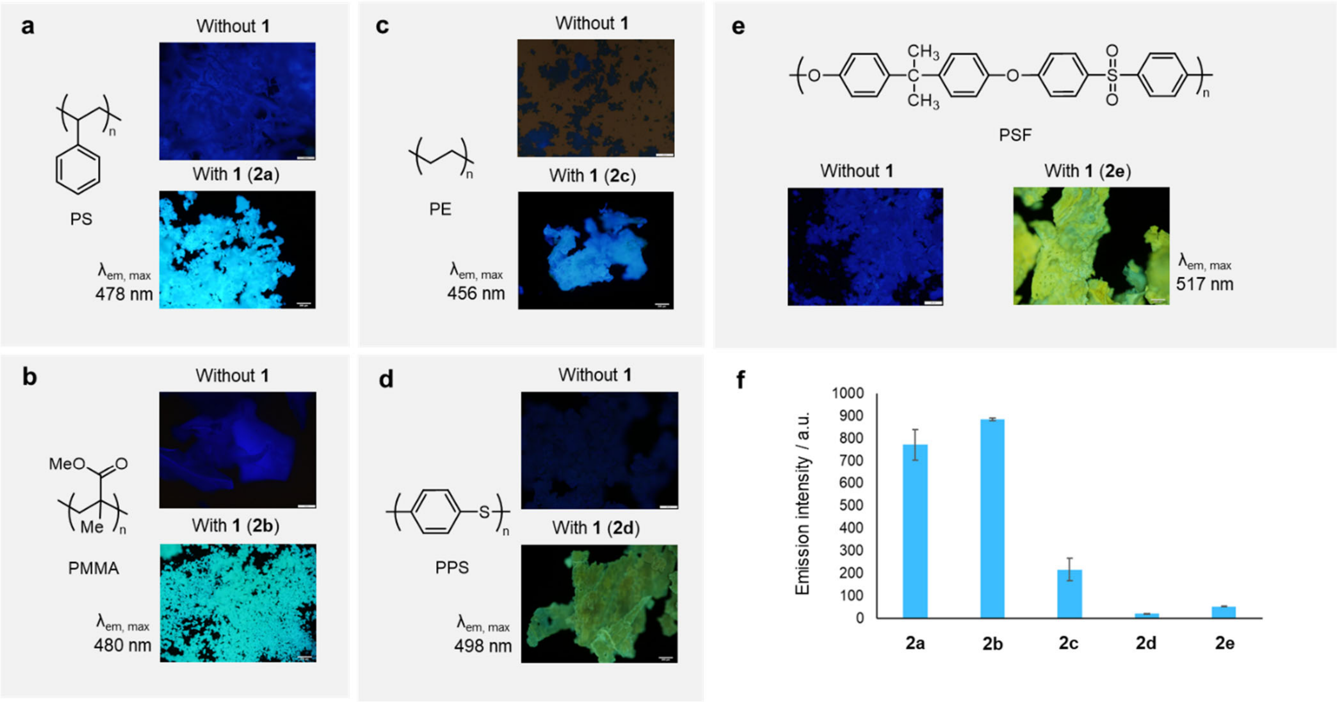


Figure 3. Preparation of luminescent polymers **2** from various generic polymers via mechanoradical coupling with **1**. All photographs were taken under UV irradiation. See the Supporting Information for detailed conditions (λ_{ex} = 365 nm).

During our study, Otsuka and co-workers developed a strategy to visualize polymer mechanoradicals via a radical chain-transfer approach.[22] In their system, the mechanoradicals generated via the ball milling of polystyrene undergoes halogen-atom transfer (HAT) with diarylacetonitrile to form diarylacetonitrile radicals with yellow luminescence under UV irradiation. Although their strategy is useful for the detection of mechanoradicals, it cannot be used to prepare luminescent polymers because the luminophore is not incorporated into the polymer main chain via a covalent bond.

In conclusion, we have described the first example of the direct preparation of luminescent polymers from generic polymers that do not contain mechanophores in their main chains via mechanoradical coupling reactions. The nitroxide-based prefluorescent radical **1**, which shows very weak fluorescence under UV irradiation, undergoes radical–radical coupling with *in-situ*-formed polymeric mechanoradicals under ball-milling conditions to incorporate the coumarin-based luminophore with significantly higher emission intensity. Notably, various generic polymers, including chemically stable polyethylene (PE), were successfully converted into the corresponding luminescent materials. These results indicate that the mechanoradical coupling strategy in the solid phase may help to transform commodity polymers with various chemical structures into more valuable functional materials without requiring sophisticated chemical synthesis. In addition, the turn-on feature of the luminophore **1** would be useful for the detection of mechanoradicals generated in polymeric materials. We thus expect that the present study will also inspire the development of novel mechano-induced sensing and recording materials and a new method for the visual and quantitative detection of short-lived polymeric mechanoradicals. These related studies are currently in progress in our laboratory.[23]

Experimental Section

For the ball-milling experiments using polystyrene and **1**, polystyrene (M_n = 204.1 kg/mol; PDI = 1.25; 50 mg) and **1** (6.0 mg, 0.014 mmol) were placed in a stainless-steel milling jar (5.0 mL) with two stainless-steel balls (diameter: 10 mm) in air. The jar was closed in air and placed in a ball mill (Retsch MM 400). After 30 min of grinding at 30 Hz, the reaction mixture was transferred from the jar to a flask using CH_2Cl_2 and concentrated under reduced pressure. The crude product was then recrystallized using CH_2Cl_2 and MeOH. The mixture was further purified via gel permeation chromatography (GPC) to give emissive polymer **2a**.

Acknowledgements

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Conflict of interest

The authors declare no conflicts of interest.

Keywords: Mechanochemistry • Mechanoradical • Fluoroprobe • Polymer degradation • Ball mill

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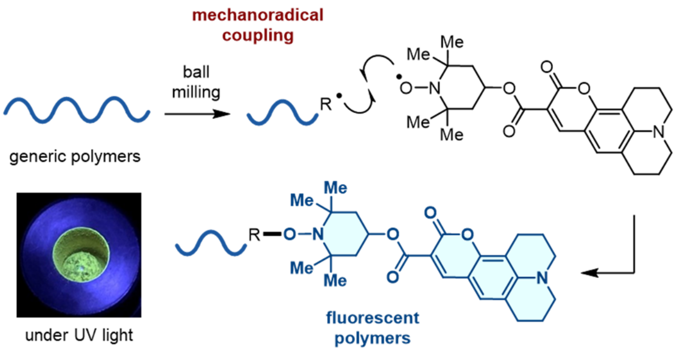

Koji Kubota, Naoki, Toyoshima, Daiyo Miura, Julong Jiang, Satoshi Maeda, Mingoo Jin*, and Hajime Ito**

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