Macromolecular Rapid Communications

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RESEARCH ARTICLE OPEN ACCESS

Metal-Free Multicomponent Upcycling of Polybutadiene to Sulfonamide-Functionalized Materials

Janna Jeschke[1] | Jan Hobich[2] | Hatice Mutlu[1,3,4]

[1]Institut De Science des Matériaux de Mulhouse (IS2M), UMR 7361, Université De Haute Alsace (UHA), 15 rue Jean Starcky, Mulhouse, France | [2]Soft Matter Synthesis Laboratory, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, Germany | [3]Department of Chemistry, Technical Polymer Chemistry, Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau (RPTU), Erwin-Schrödinger-Straße, Gebäude 52–54, Kaiserslautern, Germany | [4]Leibniz-Institut Für Verbundwerkstoffe GmbH, Erwin-Schrödinger-Straße 58 Gebäude 58 / Raum 523, Kaiserslautern, Germany

Correspondence: Hatice Mutlu (hatice.mutlu@uha.fr)

Received: 4 April 2025 | **Revised:** 14 July 2025 | **Accepted:** 15 July 2025

Funding: French National Research Agency with the reference “ANR-22-CPJ1-0077-01”.

Keywords: liquid polybutadiene | multi-component reaction | non-conventional luminescence | sulfonamide | upcycling

ABSTRACT

We report a catalyst-free, one-pot method for the upcycling of liquid polybutadiene that enables simultaneous backbone editing and introduction of sulfonamide and bromine functionalities under mild conditions. This sustainable alternative to metal-catalyzed approaches, such as selenium-based methods, offers access to functional polymers with tunable thermal and interfacial properties. The introduced bromine groups enable further orthogonal modifications, exemplified by efficient azidation. Remarkably, the resulting materials display previously unreported non-conventional luminescence behavior, expanding the functional scope of upcycled commodity polymers and opening pathways toward applications in sensing, coatings, and bioimaging.

1 | Introduction

Plastics are indispensable due to their durability and affordability, yet their environmental persistence presents a major challenge. Current recycling strategies, often energy-intensive or leading to downcycling, highlight the need for innovative upcycling approaches [1]. More precisely, the average plastic production is currently increasing drastically (the global annual plastic production of 400 million metric tons in 2022 is predicted to double until 2050) [1–3]. Still, more than 50% of plastic waste is continuously discarded into landfills, following the principle of a linear economy (based on a take-make-use-waste paradigm) [4]. Accordingly, at a global recycling rate of 20%, the existing strategies to mitigate the harmful accumulation of plastics in the environment remain alarmingly insufficient [4]. Notably, approaches, such as mechanical recycling, lead to products of lower value (downcycling) or are potentially energy-intensive, e.g., chemical recycling and pyrolysis [5]. Consequently, constructing a plastic economy in a circular fashion would imply, in addition to avoiding and reducing unnecessary plastic waste, a plethora of feasible selective chemical transformations to convert discarded plastics into value-added materials (chemical upcycling) [5]. In line with this concept, the strategy of **P**ost-**P**olymerization **M**odification (**PPM**) is commonly used for the chemical upcycling of commodity polymers [6, 7] and does not require the design of new monomers for de- and re-polymerization [5]. A recent perspective by Dou et al. [5b] comprehensively discusses current strategies in polydiene

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Dedicated to Professor Michael A.R. Meier on the occasion of his 50th birthday.

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https://doi.org/10.1002/marc.202500311

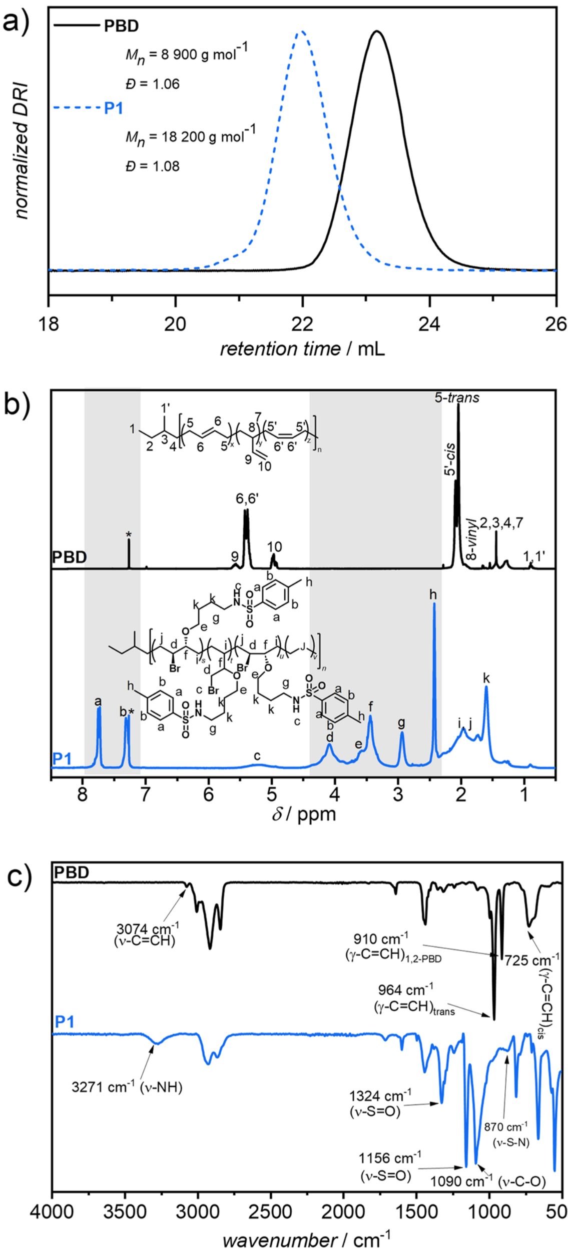

FIGURE 1 | (a) Elution traces of pristine liquid PBD (black, $M_{n,\,SEC}$ = 8 900 g mol^{-1}, Đ = 1.06) and obtained polymer, **P1** (blue, Table 1, entry 2, $M_{n,\,SEC}$ = 18 200 g mol^{-1}, Đ = 1.08), determined in THF at 35°C vs. linear PS standards. Structural characterization of **P1** after **BEGS**: (b) ^{1}H NMR (CDCl$_3$, 300 MHz) spectra of **P1** (blue) and **PBD** (black), (c) ATR-IR spectra of **P1** (blue) and **PBD** (black).

recycling and upcycling, reinforcing the relevance and timeliness of new metal-free approaches. Indeed, despite reports about the functionalisation of commodity polymers such as polyolefins [8], polystyrene [9], or polylactides [10], examples of the chemical upcycling of polybutadiene (**PBD**) and polyisoprene (main constituents in post-consumer tyres) are still scarce [11]. Previously, **PPM**s of **PBD** have been reported to enable the installation of acid functionalities [12], cyclopropane groups [13], diverse nucleophiles [14], or trifluoromethyl groups along with azide functionalities [15]. In particular, the functionalization of **PBD** to yield amine-functionalized [16] or sulfonamide decorated [11] polymers could be relevant to upcycle **PBD** into a pH-responsive [17] functional material or render it applicable for electrochemical utilization [18]. Additionally, small molecule sulfonamide derivatives (e.g., bioisosteres of amides) are also under investigation for biomedical applications due to their antibacterial properties [19]. However, still, there is a lack of metal-free approaches that do not require other potentially toxic catalysts and allow for the transformation of **PBD** into a sulfonamide decorated polymer under ambient reaction conditions. Besides, to the best of our knowledge, there has been no report about a one-pot metal-free installation of sulfonamides onto **PBD** (separated by an alkyl spacer from the backbone) along with the installation of other functionalities, e.g., bromine. Accordingly, expanding our previously reported strategy [20], based on a metal-free electrophilic cascade reaction [21], herein we propose a new methodology for the upcycling of commercially available liquid 1,4/1,2-**PBD** via **PPM** proceeding in one step (under mild reaction conditions), enabling the **b**ackbone **e**diting (reduction of double bonds to yield a polyolefin-like structure) and concomitant **g**rafting of multiple pendant functionalities (diverse **s**ulfonamides and bromine) (**BEGS**). Indeed, the choice of sulfonamide nucleophiles is particularly strategic and introduces a key element of novelty. As previously mentioned, beyond their well-known roles in tuning polymer polarity and enabling biomedical functionalities [19], aromatic sulfonamides offer post-synthetic flexibility unmatched by previously used nucleophiles such as carboxylic acids [20]. On the one hand, deprotection of the sulfonamide after polymerization could yield amine-functionalized polyolefin analogs, which can be further derivatized via orthogonal **PPM**. On the other hand, deprotection following an aza-Michael addition generates a secondary amine moiety, serving as an additional reactive site for functional diversification. These dual deprotection routes could vastly expand the chemical utility of the resulting polymers and set our approach apart from prior methods in both design logic and functional scope.

2 | Results and Discussion

First, as an illustrative example, we employed our **BEGS** methodology (cf. Scheme 1c), utilizing commercial liquid polybutadiene (**PBD**, $M_{n,\,SEC}$ = 8900 g mol^{-1}, Đ = 1.06; 23% vinyl and 77% trans-1,4 + cis-1,4 olefin C=C bonds) along with 1.0 eq. *para*-toluenesulfonamide (refer to Supporting Information for experimental details), thus yielding polymer **P1** (cf. Table 1, entry 2).

^{1}H and ^{13}C nuclear magnetic resonance (NMR) measurements confirm backbone editing and successful grafting of sulfonamide and bromine moieties, forming polyvinylether-/polyvinylbromide-like architectures (cf. Figure 1b and Figure S1, respectively). As shown in Figure 1b, a quantitative conversion of the olefinic double bonds was achieved (cf. Figure 1b depicting the disappearance of magnetic resonances, attributed to the vinylic protons 6,6',9, and 10 of **PBD** between 5.75 and 4.75 ppm). In line with the quantitative C=C double bond conversion, new magnetic resonances a and b (characteristic of the aromatic protons arising from the sulfonamide) appear between 7.79 and 7.23 ppm (cf. Figure 1b). Further, in contrast to pristine liquid **PBD**, the new magnetic resonances between 4.55 and 3.15 ppm indicate the presence of protons c and e, arising from the post-functionalized backbone (cf. Figure 1b).

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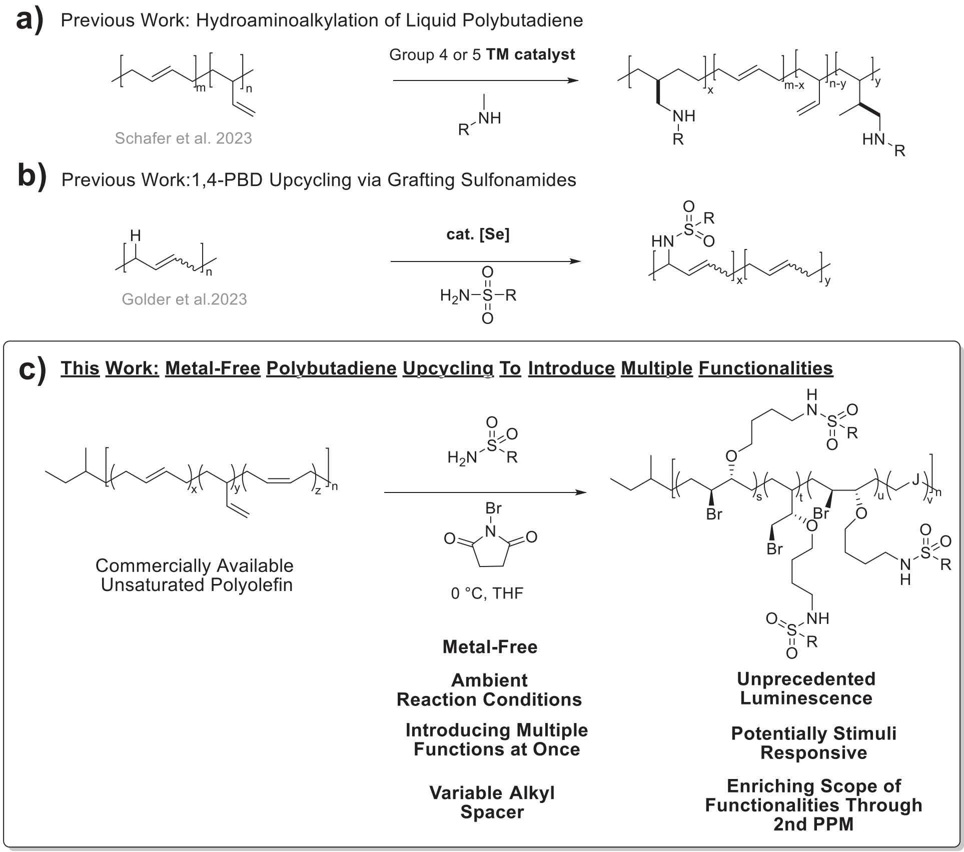

SCHEME 1 | (a) Hydroamionalkylation of liquid PBD catalyzed by transition metal catalysts [16], (b) Selenium-catalyzed 1,4-polybutadiene upcycling via grafting sulfonamides [11], (c) Reaction scheme reflecting how the one-pot MCR toolbox is expanded toward nitrogen nucleophiles for unsaturated polyolefin upcycling as described in the current report, (**R** = -*p*-MePh(**P1**), -Me(**P2**), -*p*-NO$_2$Ar(**P3**)).

TABLE 1 | Overview of the conducted experiments via Multi-Component Reaction (MCR) enabling backbone editing and grafting of multiple functions, e.g., sulfonamides (**BEGS**): Ratio (s+t+u)/v, Conversion of x+y+z, Incorporation rate of sulfonamide, Isolated Yield, Macromolecular (M_n, $Đ$), thermal (T_g) and Wettability properties (Θ).

Entry	Polymer	Sulfonamide derivative	Ratio (s+t+u)/v[b]	Conversion of x+y+z[c]	Functionalization degree (sulfonamide)[d]	Isolated Yield[e] (%)	M_n[f] (g mol^{-1})	$Đ$[f]	T_g[g] (°C)	Θ[h] (°)
1	PBD	—	—	—	—	—	8900	1.06	−95	—
2	P1	1	54/46	quant.	0.54	51	18200	1.08	56	88 ± 1
3	P2	2	43/57	quant.	0.43	74	17100	1.08	21	83 ± 2
4	P3	3	52/48	quant.	0.62	88	20200	1.18	58	85 ± 1
5	P4[a]	1	—	—	—	61	19200	1.27	47	84 ± 1
6	P5[a]	3	—	—	—	50	27900	2.44	60	80 ± 1

[a] Bromine moieties substituted with azide groups due to a second **PPM** (azidation).

[b] Ratio between the repeating units (s+t+u) and v, cf. Section A.4.

[c] Conversion of the repeating units x+y+z deduced from respective ^{1}H NMR spectra.

[d] Functionalization degree (sulfonamide), cf. Section A.4.

[e] the isolated yield was calculated as detailed in Section A.4.

[f] The M_n and $Đ$ were obtained through a SEC equipped with a refractive index detector in THF as eluent at 30°C.

[g] T_g values were recorded from the second hescans of *DSC analysis (in the temperature range from −90°C to 100°C at a heating and cooling rate of 10°C/min).*

[h] Water contact angle (Θ) values as obtained by drop shape analysis, the indicated angles are an average of 10 distinct measurements on water droplets on a glass surface.

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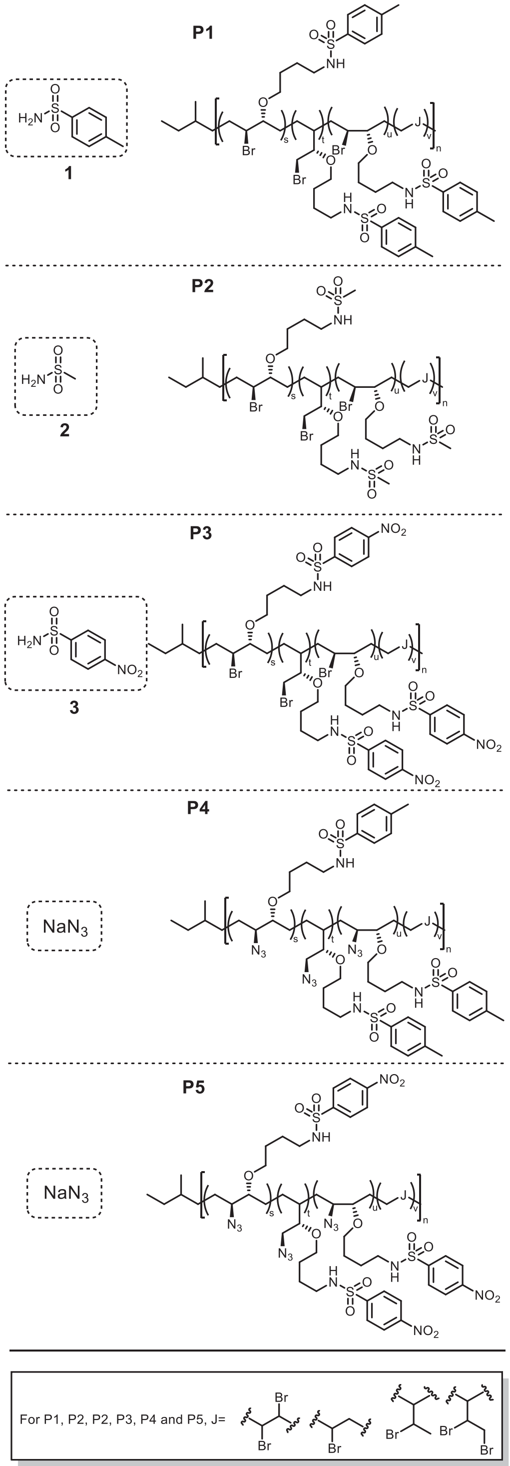
Accordingly, the magnetic resonances of protons d,e,f, and j (cf. Figure 1b) confirm the incorporation of the cyclic ether (arising from the THF) as a spacer between the backbone and the pendant sulfonamide moieties. In a complementary manner, attenuated total reflection infrared (ATR-IR) spectroscopy measurements were carried out (cf. Figure 1c), and it was observed that the characteristic C—H bending vibrations of the olefinic structure of **PBD** between 730 and 905 cm^{-1} are absent. Furthermore, the ATR-IR spectrum of **P1** displays the characteristic N—H (3271 cm^{-1}) and S═O (1324 and 1156 cm^{-1}) stretching vibrations (cf. Figure 1c), confirming the incorporation of *p*-toluenesulfonamide into **P1**. The successful introduction of the ether bond is also supported by the presence of the aliphatic C—O stretching band at 1090 cm^{-1} (cf. Figure 1c). Consequently, ^{1}H NMR, ^{13}C NMR, and ATR-IR results support the applicability of our **BEGS** methodology to edit the polymer backbone by installing bromine and sulfonamide moieties. In coherence with the previous results, the size-exclusion chromatography (SEC) trace shows a clear shift toward higher molecular weight (cf. Figure 1a) to M_n of 18 200 gmol^{-1} without any significant change in the dispersity value, *Đ* (cf. Table 1, entry 2). Thus, these results also support the incorporation of sulfonamide and bromine moieties without the occurrence of significant side reactions or degradation. To further expand our methodology and access diverse polymeric structures, we have subsequently investigated if the methodology is also compatible with aliphatic sulfonamides (methanesulfonamide) or aromatic sulfonamides bearing nitro functionalities (such as, *p*-nitrobenzenesulfonamide) (cf. Table 1, entries 3 and 4, respectively). Based on the same structural characterization techniques as for **P1** (^{1}H NMR, ^{13}C NMR, and ATR-IR, cf. Figures S2–S5 and S10 and S11, respectively) and SEC (cf. Table 1 and Figures S14 and S15), we confirmed that our approach was successfully extended to diverse sulfonamides. Notably, in addition to modifying the backbone and installing pendant bromine and sulfonamide moieties, incorporating nitro groups is particularly interesting due to their challenging introduction through conventional polymerization techniques [22, 23]. Hence, our methodology allows for the straightforward introduction of multiple (polar) functional groups with isolated yields varying from moderate to good.



SCHEME 2 | Structures of polymers **P1, P2, P3** (after metal-free backbone editing and grafting sulfonamides with different sulfonamides (**1**,**2**,**3**, respectively)), in addition to **P4** and **P5** (after second **PPM** (azidation of **P1** and **P3**, respectively)).

The discrepancy between the nearly quantitative C═C double bond conversion and the functionalization degree with sulfonamide functional group (cf. Table 1 and refer to Section A.4 for the calculation of the functionalization degree and isolated yield) could be attributed to the efficiency of the last two steps in the MCR cascade [21]. In other terms, despite the assumedly quantitative nature of the first reaction in the MCR, generating a bromonium cation intermediate, the last two steps may not occur quantitatively and, thus, explain the obtained values for the functionalization degree with the sulfonamide (cf. Table 1). Consequently, due to the high double bond conversion and the indicated values for functionalization degree with the sulfonamide, the repeating unit *J* (cf. Scheme 2) is proposed. Comparing the functionalization degree with the sulfonamide with the grafting density results of Hodges et al. [11], the values do not differ significantly in the case of sulfonamides bearing electron-withdrawing groups (EWGs) (62%, cf. Table 1 entry 4 and grafting density of 64% [11] for a system employing PCy$_3$Se (15 mol%), PhI(OAc)$_2$). Still, our methodology is particularly noteworthy as it does not require a potentially toxic catalyst. Moreover, in contrast to Hodges et al. [11], our approach requires fewer sulfonamide equivalents (2.0 double bond equivalents [11] to 1.0 equivalents, respectively). To increase the scope of the functionalities on our polymers upon **BEGS**, we applied mild azidation reaction

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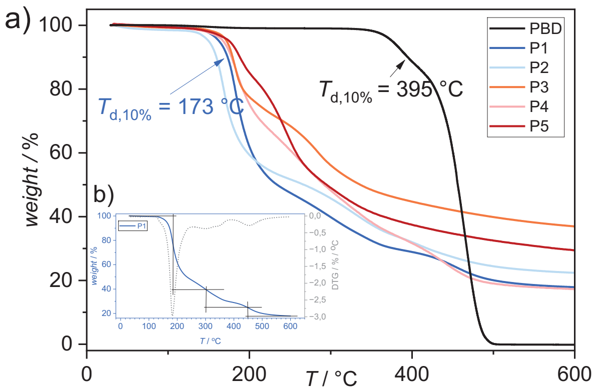

FIGURE 2 | (a) Thermogravimetric analysis (TGA) curves of respective polymers after **BEGS**, (b) Derivative Thermogravimetry (DTG) curve in %/°C, i.e., the first derivative of the TGA curve, of **P1**, revealing a multistep degradation pattern.

conditions to perform a 2nd **PPM**; i.e., the substitution of the bromine groups via azide functionalities (cf. Table 1, entries 5 and 6), and confirmed the occurrence of this reaction via ^{1}H NMR, ^{13}C NMR, ATR-IR and SEC (cf. Table 1 and Figures S6–S9 and S12 and S13 and S16 and S17). Considering, e.g., biological applications, polymers bearing pendant sulfonamides and azide groups pave the way toward subsequent **PPM** using orthogonal reactions [24]. To investigate the thermal stability of the polymers after **BEGS**, thermogravimetric analysis (TGA) was carried out (cf. Figure 2) under a nitrogen atmosphere. BEGS-functionalized polymers exhibit multi-stage decomposition, confirming backbone modification. The introduction of bromine and sulfonamide groups lowers thermal stability (e.g., $T_{d,10\%}$ from 395°C to 173°C for **P1**), which aligns with the expected decomposition behavior of functionalized polyolefins (Figure 2). In line with Hodges et al. [11], the first onset, ranging from $T_{d,10\%}$ = 159°C to $T_{d,10\%}$ = 187°C, depending on the nature of the sulfonamide or 2nd **PPM**, could be attributed to the decomposition of the sulfonamide from the pendent alkyl ether spacer along with the decomposition of pendent bromine moieties [25] from the backbone.

Second, the onset of an adjacent decomposition event is observed (cf. onset at 242°C, exemplary Figure 2 (b) for **P1**), as the alkyl ether spacer begins decomposing from the backbone. Finally, a decomposition onset is observed at 390°C for **P1** and could be characteristic for the decomposition of the backbone. This structure–property relationship is also reflected in the final char yield. As shown in Figure 2a, the residual mass at 600°C increases with the incorporation of more electron-withdrawing sulfonamide substituents. For example, polymer **P1** exhibits a residual mass of ~20%, whereas **P3**, bearing a more electron-deficient sulfonamide group, retains ~40%. On the one hand, replacing the bromine atom in **P3** with an azide group in the second **PPM** step, to result in polymer **P5,** reduces the residual mass to ~30%, as azides thermally decompose into volatile nitrogen-containing species rather than promoting char formation like bromine, which contributes to condensed-phase residue via radical trapping [26]. On the other hand, despite the absence of aromatic moieties in **P2**, which typically support char formation through thermal stabilization, a residual mass of ~22% at 600°C was still observed, likely attributable to the presence of sulfonamide and bromine functionalities that contribute to condensed-phase stability and inhibit complete volatilization. Consequently, the thermal decomposition behavior after **BEGS** can be tuned by varying the heteroatom content or the structure of the sulfonamide. In this context, bromine-containing polymers such as **P1**, **P2**, and **P3** could potentially be employed for the development of polymeric flame retardants [27].

In addition to the investigation of the thermal stability, differential scanning calorimetry (DSC) was carried out (cf. Table 1 and Figures S18 and S19). Prior to the thermal decomposition, it can be noted that pristine liquid **PBD** is amorphous (with a glass transition temperature (T_g) of −95°C [28]). However, upon introducing an aliphatic sulfonamide and bromine moieties, the glass transition temperature significantly increases to 21°C (cf. **P2**, entry 3). Moreover, this trend can be further enhanced by introducing aromatic sulfonamides and increasing the heteroatom content (cf. Table 1), leading to a T_g of 60°C (cf. Table 1, **P5**, entry 6). Consequently, our **BEGS** methodology enables tuning the thermal properties of the resulting polymers by carefully adjusting the structure of the sulfonamide or by performing a 2nd **PPM**, paving the way towards bespoke materials for new potential applications. Regarding the promising field of soft materials and flexible coatings, we hypothesized that our **BEGS** could be also used to tune the surface properties, e.g., the wettability. Hence, water contact angle (WCA) measurements were carried out for all polymers upon **BEGS** (cf. Table 1 and S20). Accordingly, the WCA of **P1** could not be significantly altered by introducing one polar group (cf. Table 1, entries 3 and 4). Compared to **P1**, the WCA significantly changed upon introducing a polar nitro group and performing a 2nd **PPM** (azide) (**P5**). The surface hydrophobicity could also be decreased from **P1** to **P5** upon introducing polar groups from 88° to 84°. Additionally, while direct WCA measurement for unfunctionalized liquid PBD was not feasible due to poor film formation, literature, and visual observation suggest a WCA of approximately 95° [29], providing a useful benchmark to assess the impact of BEGS-based modifications on surface wettability.

Complementary to WCA measurements, the luminescence behavior of **P1** was investigated. Thus, the emission spectra of **P1** were recorded at different excitation wavelengths (from 450 to 530 nm, cf. Figure 3d). Accordingly, upon increasing the excitation wavelength (from 450 to 530 nm), the emission maxima underwent a bathochromic shift (from 530 to 551 nm). In line with this, increasing the concentration of **P1** at an excitation wavelength of 510 nm (from 0.74 to 40 mg mL^{-1}) led to an increase in emission (from 146 to 960 a.u.), while the emission maxima also underwent a bathochromic shift for higher concentrations (cf. Figure 3a). Further, a mismatch between absorption and emission maxima was observed (cf. Figure 3e). Generally, these observations are in contrast to traditional organic photoluminescent materials, which display aggregation-induced quenching at high concentrations and whose emission maxima are not supposed to undergo a bathochromic shift upon increasing the concentration [30]. Due to this discrepancy, the increased emission at high concentration (from 146 to 960 a.u.) of **P1** could be rationalized by a non-conventional luminescence (**NCL**) behavior [31]. Thus, the luminescence of **P1** in solution and in solid state [32] (cf. Figure 3b) could occur without localized electronic structures, but rather due to a cluster-triggered-emission (CTE) [33] mechanism

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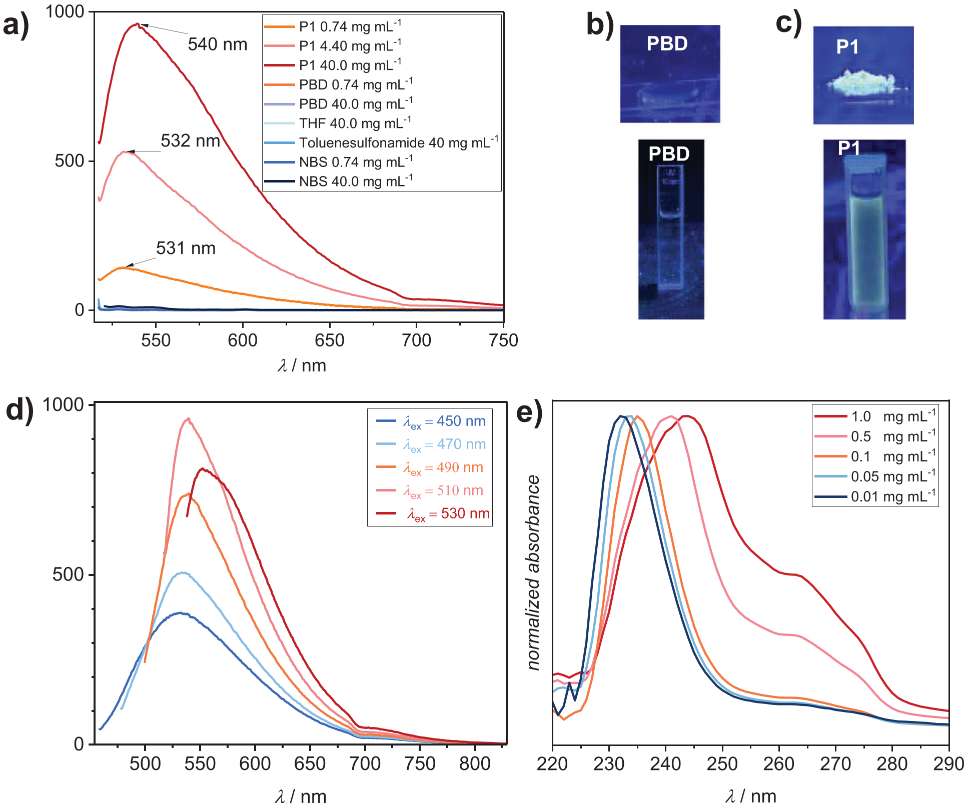

FIGURE 3 | (a) Emission spectra of **P1** at different concentrations (red curve: 40 mg mL; rose curve: 4.40 mg mL^{-1}; orange curve: 0.74 mg mL^{-1}), **PBD** (blue curve, 40 mg mL^{-1}), ***p*-Toluenesulfonamide** (petrol curve, 40 mg mL^{-1}), **NBS** (dark blue curve, 40 mg mL^{-1}) at an excitation wavelength of 510 nm in DCM (298 K), (b) **PBD** and **P1** under irradiation with handheld UV lamp at 365 nm, (c) Solutions of **PBD** and **P1** in DCM (298 K) at 20 mg mL^{-1}, irradiated with handheld UV lamp at 365 nm, (d) Emission spectra of **P1** at various excitation wavelengths (from 450 nm (dark blue) to 530 nm (red), respectively, with an increment of 20 nm) in DCM (298 K), at a concentration of 40 mg mL^{-1}, (e) Ultraviolet–visible (UV–vis) spectra of **P1** at different concentrations (0.01 (dark blue) to 1.0 mg mL^{-1} (red)) in DCM (298 K).

based on through-space conjugation (TSC) [34] of clusters of subgroups, which strongly restricts non-radiative relaxation. The formation of clusters could also be influenced by the apolar nature of the backbone of **P1** bearing polar pendant functionalities. Even though currently, more studies to fully rationalize the **NCL** behaviour of **P1** are carried out in our laboratories; this unexpected type of emission breaks the traditional luminescence paradigm and thus, enables the use of an easily accessible system (one step **BEGS** in comparison to multi-step synthesis for conventional fluorophores bearing large π–π systems) [31]. Aside, **NCL** materials are reported to display fewer cytotoxic properties [30] than conventional fluorophores, paving the way toward the practical utilization of polymers after **BEGS** in biomedical applications.

3 | Conclusion

The herein presented work introduces a catalyst-free, one-pot strategy for liquid polybutadiene upcycling via backbone editing and functionalization. The method enables the introduction of diverse functional groups under mild conditions, paving the way for sustainable polymer design. Crucially, the successful 2nd **PPM**, transforming the bromine into azide groups, establishes a platform toward diverse orthogonal **PPM**s. Moreover, expanding the toolbox of 2nd **PPMs** [35], the scope of installable functionalities can be enriched. Depending on the nature of the sulfonamide and the potential 2nd **PPM**, introducing azide moieties, along with the surface wettability, the thermal properties were further tuned (T_g = −95°C for **PBD** compared to T_g = 60°C for **P5**). Besides, in line with the development of sustainable fluorophores [30], **P1** displays a **NCL** behavior, paving the way towards less cytotoxic materials for biomedical applications [36]. Further research on the implementation of this methodology for stimuli-responsive materials (e.g., pH responsive [17]) and energy storage applications [18] is currently carried out in our laboratories. Finally, regarding the end-of-life options of elastomers, our work could be employed in developing metal-free alternatives to advance surface modifications of vulcanized rubbers without relying on a potentially toxic catalyst [37].

Acknowledgements

H.M. acknowledges UHA for the financial support from the French National Research Agency with the reference "ANR-22-CPJ1-0077-01" (particularly for covering the PhD of J.J.) and from the CNRS for the junior professorship contract. H.M. and J.H. acknowledge the Karlsruhe Institute of Technology, the Federal Ministry of Education and Research (BMBF), and the Baden-Württemberg Ministry of Science as part of the Excellence Strategy of the German Federal and State Governments. The authors are thankful to Kuraray Europe GmbH for the kind donation

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of PBD. Bercis Pektas is acknowledged for her assistance with TGA measurements.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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