GDCh
Communication
Angewandte Chemie International Edition
www.angewandte.org
How to cite: *Angew. Chem. Int. Ed.* **2025**, *64*, e22659
doi.org/10.1002/anie.202522659

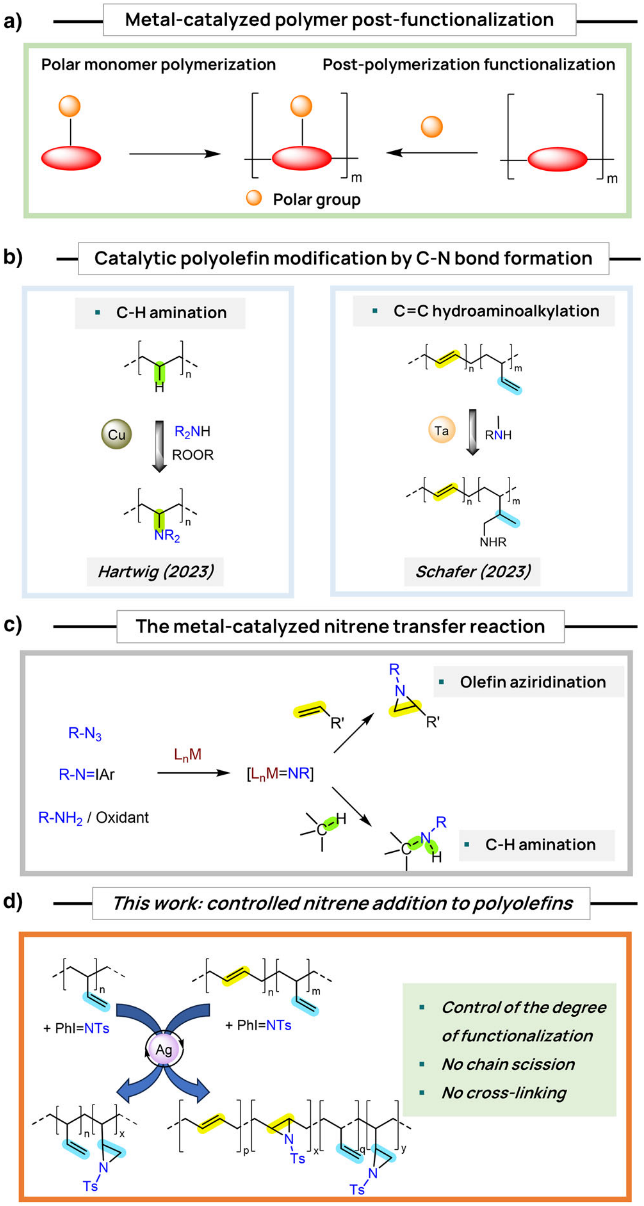
Functionalization of Polyolefins

Functionalization of Polyolefins via Catalytic Nitrene Addition

Jorge Pérez-Ruíz, Manuel R. Ramírez, Christian Rentero, Valentina Sessini, Marta E. G. Mosquera, M. Mar Díaz-Requejo,* and Pedro J. Pérez**

Dedicated to the memory of Professor Miguel Ángel Miranda

Abstract: The post-polymerization functionalization of polyolefins has emerged as a key tool for obtaining new materials with enhanced properties. With an array of approaches being already reported, the incorporation of N-containing fragments en route to the generation of amino groups in yet scarce and not disclosed for the metal-catalyzed nitrene transfer strategy. Here we introduce such tactics employing silver-based catalysts for the incorporation of nitrene NTs (Ts = *p*-toluenesulfonyl) groups to commercially available polybutadienes. The process occurs at room temperature without appreciable chain scission or cross-linking processes and enables precise control of the degree of functionalization. Thermal analyses demonstrate a correlation between such degree and the T_g values of the functionalized polymers.



Scheme 1. Polyolefin functionalization by metal-catalyzed carbon–nitrogen bond formation. a) Post-polymerization functionalization strategy. b) Polymer functionalization by catalytic C-N bond formation. c) The metal-catalyzed nitrene transfer reaction. d) This work: polyolefin catalytic functionalization by nitrene addition.

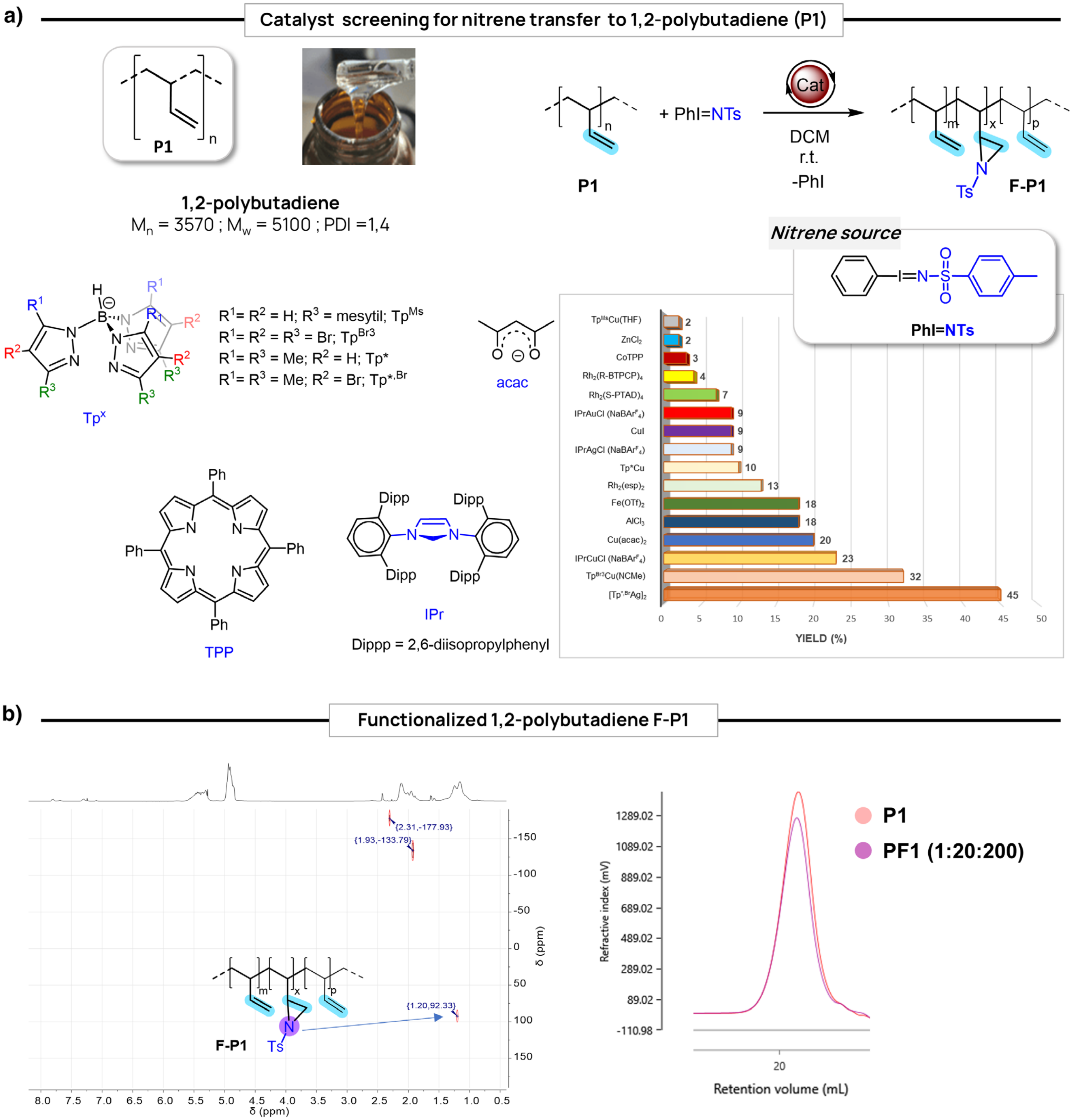
Polymers are essential components of many common items in our lives: clothing, packaging, electronics, medical devices, or the food industry, among others, use macromolecular compounds.[1] They are usually made from a monomer, which is then polymerized into the desired product (Scheme 1a), very often using a metal-based catalyst to control the polymerization process.[2] In this manner, the polymer has the properties required for its final use. In some cases, the

---

[*] J. Pérez-Ruíz, Dr. M. R. Ramírez, Prof. Dr. M. M. Díaz-Requejo, Prof. Dr. P. J. Pérez
Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, Huelva 21007, Spain
E-mail: mmdiaz@dqcm.uhu.es
perez@dqcm.uhu.es

C. Rentero, Dr. V. Sessini, Prof. Dr. M. E. G. Mosquera
Department of Organic and Inorganic Chemistry. Institute of Chemical Research "Andrés M. del Río" (IQAR), Universidad de Alcalá, Alcalá de Henares 28805, Madrid, Spain
E-mail: martaeg.mosquera@uah.es

Additional supporting information can be found online in the Supporting Information section



Scheme 2. Functionalization of 1,2-polybutadiene by catalytic nitrene addition. a) Catalyst screening. b) ^{15}N NMR and GPC traces of the functionalized polymer samples.

desired polymer contains polar groups,[3] and this strategy of monomer polymerization may fail due to the deactivation of the catalyst with the polar monomer. An alternative strategy consists in adding the polar group to an already prepared polymer (Scheme 1a); this functionalization a posteriori[4] has been successfully applied in many cases, either in a stoichiometric or catalytic manner.[5–9] These examples are always a catalytic translation from the "single molecule" world to a macromolecule: hydroformylation, hydroxylation, cyclopropanation, borylation, hydroacylation, carboxylation, or epoxidation of polyolefins have been achieved upon using catalytic systems previously described for discrete substrates.

In this context, the controlled incorporation of N-containing polar groups into polymers remained unknown until recently, when two pioneering examples were described (Scheme 1b). Hartwig reported[10] the use of copper-based catalysts for the amination of C—H bonds of saturated polymers via a dehydrogenative process using amines and peroxides. At the same time, Schafer described[11] the

Table 1: Functionalization of **P1** under $[Tp^{*,Br}Ag]_2$ catalysis modifying the polymer ratio.[a,b]

Entry	[Cat]:[PhI=NTs]:[**P1**]	**P1** (g)	Isolated yield **F-P1** (%)[c]	Functionaliz. (%)[d]	% NTs incorp.[e]	Mw (kDa)	Đ[f]
1	1:20:50	0.05	66	43.5	28	7.08	1.6
2	1:20:100	0.1	72	21.3	35	7.02	1.5
3	1:20:200	0.2	76	12.7	45	5.01	1.5
4	1:20:500	0.5	83	7.1	60	4.62	1.4
5	1:20:1000	1.0	89	3.8	68	3.78	1.4
6	1:20:2000	2.0	97	2.2	77	3.68	1.3
7[g]	1:20:500	2.5	85	7.0	63	4.62	1.4
8[h]	1:20:500	5.0	87	7.0	61	5.04	1.5
9	**P1**	–	–		–	5.01	1.4

[a] 0.017 mmol $[Tp^{*,Br}Ag]_2$ (2% mmol% referred to PhI=NTs), 10 mL DCM, r.t., 4–8 h. [b] Functionalization and yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. $TsNH_2$ accounted for 100% initial PhI=NTs not added to the polymer. [c] Isolated functionalized polymer relative to initial polymer (w/w). [d] NTs incorporated referred to final polymer mass (w/w). [e] NTs incorporated referred to initial PhI=NTs (w/w) [f] Determined by GPC in THF at 30 °C versus linear PS standards. [g] Scale-up reaction: mass of polymer, nitrene source, catalyst, and solvent was scaled up 5 times. [h] Mass of polymer, nitrene source, catalyst, and solvent was scaled up 10 times.

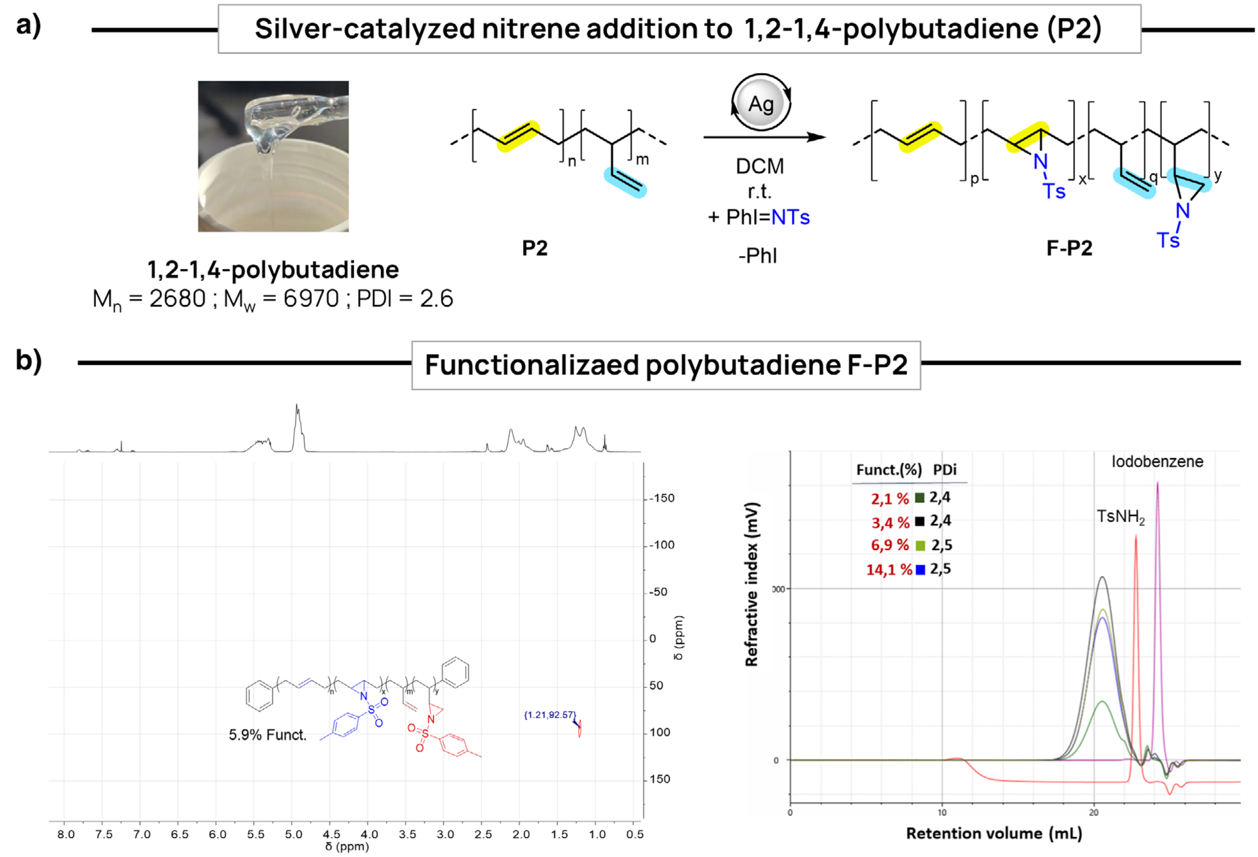
hydroaminoalkylation of polybutadienes with tantalum-based catalysts. In both cases, the catalytic system had been described for alkanes or olefins, respectively. Non-metal-based examples for the incorporation of amine functionality into polymer chains have also been reported.[12–15] Since the first report of metal-catalyzed olefin aziridination,[16] more than a thousand contributions have been published in the literature on this transformation in nearly 60 years. However, no example of its application to polyolefins has been yet disclosed. In this study, we describe the application of this strategy to such a goal, leading to the incorporation of NTs (Ts = *p*-toluenesulfonyl) units into unsaturated polymers in a process lacking chain scission or cross-linking (Scheme 1d). In addition to the synthesis and characterization of the new materials, the effect of the degree of functionalization on properties of the polymers is also described.

We selected a representative commercial polybutadiene **P1** (Scheme 2a) derived from 1,2-butadiene polymerization reaction, with a structure in which all C=C bonds are pendant vinyl groups. In the first approach, a family of metal-based catalysts (Scheme 2a) already described for nitrene transfer reactions were tested using **P1** as the substrate and PhI=NTs as the nitrene source. A 1:20:200 mixture of [catalyst]:[PhI=NTs]:[**P1**] (0.017 mmol catalyst) was employed in all cases. A solution of the catalyst in dichloromethane at room temperature was first combined with **P1**. Once dissolved, PhI=NTs was added, and the mixture was stirred at room temperature until complete dissolution of nitrene source. NMR analysis of the reaction crudes (see Supporting Information) revealed the incorporation of nitrene units in the now functionalized polymer **F-P1**. By far, the most active catalyst were $Tp^{Br3}Cu(NCMe)$ and $[Tp^{*,Br}Ag]_2$, in agreement with their already described high efficiency in nitrene transfer to unsaturated bonds.[17,18] The former gave a 32% w/w of nitrene incorporation (NTs incorporated/initial PhI=NTs) into **F-P1**, whereas the silver catalyst induced a higher incorporation (45%). The percentage mass ratio for NTs/**F-P1** are 8.6% and 12.5% for Cu- and Ag-based catalysts, respectively. The remaining of initial PhI=NTs was converted into $TsNH_2$, as frequently observed in these transformations. Other metal-based catalysts, including some dirhodates, induced much lower conversions.

The ^{1}H NMR spectrum of **F-P1** shows characteristic resonances at 2.45, 7.35, and 7.84 ppm, corresponding to the expected signals for the tosyl groups incorporated to the polymer (see Supporting Information). ^{15}N NMR experiments were employed to unambiguously demonstrate the presence of the aziridine ring in the polymeric chains (Scheme 2b). The ^{15}N resonance for **F-P1** appears at 92.33 ppm, in the region expected for aziridine rings.[19] Reference experiments with discrete aziridines were run to assess this proposal (see Supporting Information). In addition to the **F-P1** aziridine nitrogen resonance, the reaction crude allows observing two additional resonances corresponding to the two distinct nitrogen nuclei of the pyrazolyl rings of the catalysts (Scheme 2b).

Having established the potential of the silver-based complex to catalyze the aziridination of vinyl double bonds in **P1**, an array of experiments modifying the PhI=NTs:**P1** ratio was carried out to examine the extent of NTs incorporation into the polymeric chain. Entries 1–5 in Table 1 display the results obtained when maintaining the catalyst and PhI=NTs 1:20 ratio and varying the amount of polymer in the interval 0.05–5 g. The isolated yield of **F-P1** reaches 83%–97% for experiments using 0.5–2 g, whereas those employing lower amounts of **P1** gave slightly lower yields (66%–76%) due to some mass loss during workup. The incorporation of NTs units into polymer clearly depends on the amount of initial **P1**, since we use the same 0.34 mmol of the nitrene precursor for the series shown in entries 1–6. The effectiveness of the incorporation of NTs units into the polymer referred to the initial PhI=NTs varies from 28% for the experiment with just 50 mg (entry 1) of **P1** to 77% in that with 2 g of polymer (entry 6). Since the nitrene transfer competes with the formation of $TsNH_2$, the reaction is favored when increasing the excess of **P1**.

Entries 7 and 8 correspond to scale-up experiments similar to that in entry 4, but with five- and ten-fold concentrations of catalyst, PhI=NTs and polymer. As shown in Table 1, isolated yield, functionalization, and degree of incorporation are maintained at the three scales employed. Scaling up these



Scheme 3. a) Functionalization of 1,2-1,4-polybutadiene **P2** by catalytic nitrene addition. b) ^{15}N NMR and GPC traces for **FP2** samples (TsNH$_2$ and PhI also shown for comparison).

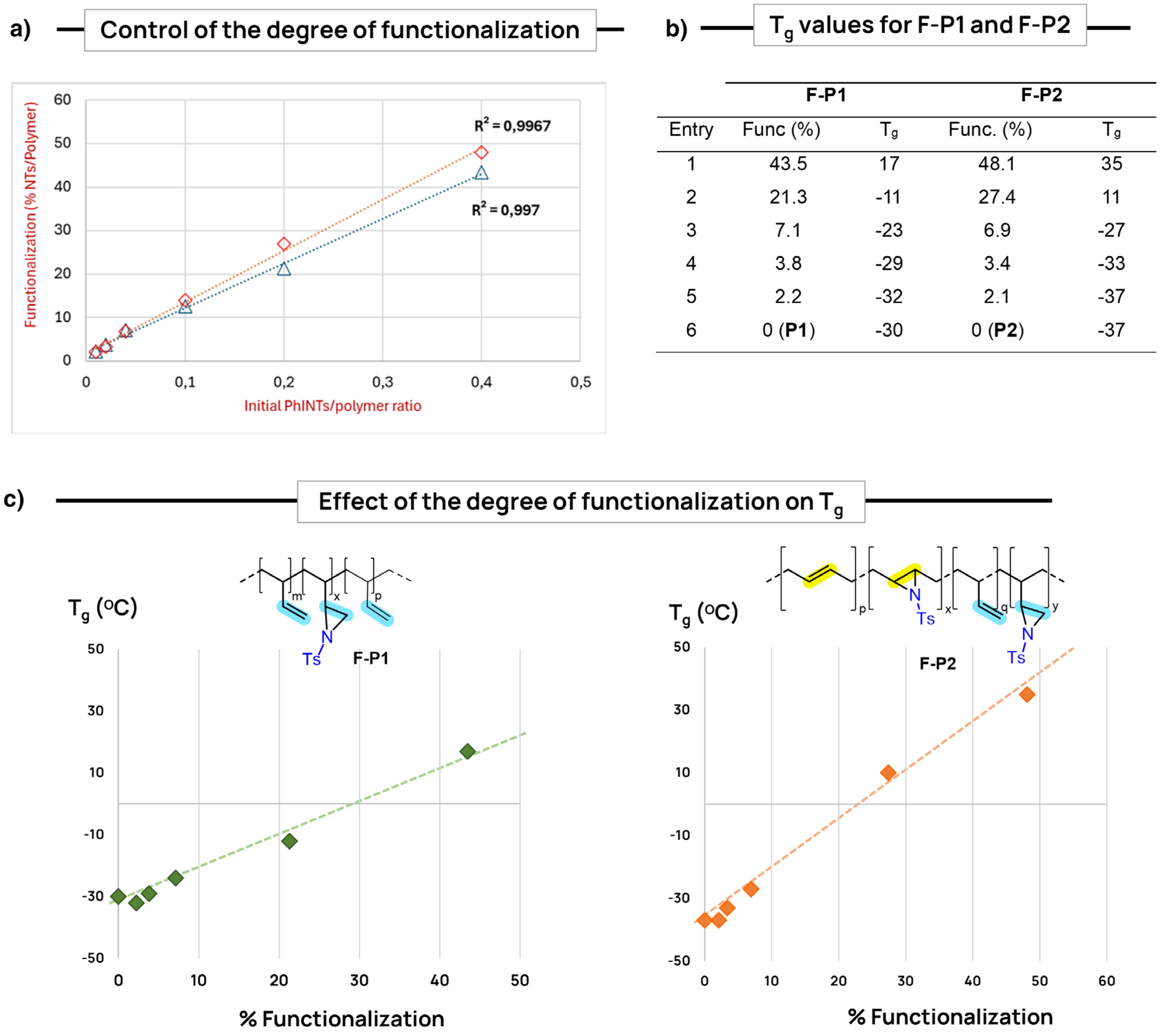
reactions is a crucial, not always simple step toward potential industrial applications.[20]

GPC experiments showed that polydispersity Đ values for both the pristine material (**P1**) and the functionalized polymers (**F-P1**) are quite similar (Scheme 2b and Table 1). Thus, the Đ value of 1.4 for **P1** compares well with those of **F-P1** of 1.3–1.6 (Table 1), regardless of the degree of functionalization, despite the latter appearing in a wide interval. This feature indicates a controlled functionalization process that preserves the polymer microstructure from chain scission or cross-linking reactions.[21]

This material **P2** contains two types of C=C bonds (Scheme 3a), pending vinyl groups and chain-contained olefinic bonds. Following a procedure similar to that employed with **P1**, and under optimized conditions (see Supporting Information), the [Tp^{*,Br}Ag]$_2$ complex was found to be the most active catalyst using a [Ag]:[PhI=NTs]:[**P2**] ratio of 1:20:200. NMR studies showed the incorporation of NTs units into the polymeric structure. ^{1}H NMR spectrum of **F-P2** contains the fingerprint resonances for the Ts groups in the aromatic region whereas ^{15}N NMR spectrum showed a resonance at 92.57 ppm (Scheme 3b), analogous to that already mentioned for **F-P1**. The existence of two potential reaction sites for the addition of the NTs group led us to evaluate the selectivity of this transformation. However, the relative intensities for the vinyl and internal double bonds did not change from **P2** to **F-P2**, indicating that both types of C=C bonds display similar reactivity toward the aziridination reaction. Albeit the internal sites could be more influenced by steric factors, it seems that the Tp^{*,Br}Ag=NTs intermediate[22] may access both sites in a similar manner. This agrees with previous work from our laboratory where these catalysts do not show significant steric effect with dienols bearing different substituents.[23]

Evaluation of the effect of the stoichiometric ratio of reactants has also been performed (Table 2), showing the same trends as those observed with **P1**. The degree of functionalization can be controlled upon modifying the PhI=NTs:**P2** ratio; we have obtained an array of polymers with NTs being incorporated within the 2%–48% interval. Moreover, the reaction is quite efficient in terms of isolation of the functionalized polymer, particularly when higher amounts (1–2 g) are employed. As mentioned for **P1**, it is very likely that the use of low polymer loadings (50–200 mg) induces some loss during workup, and this is affecting the isolated yields.

The isolated materials have been analyzed by GPC and the polydispersity values are very close to those of the starting material **P2** (Scheme 3b and Table 2). The comparison of the GPC traces for four samples with different degrees of functionalization are shown in Scheme 3b, the Đ values being maintained in the very narrow interval of 2.4–2.5, which compares well with that of initial **P2** (2.6).



	F-P1		F-P2	
Entry	Func (%)	T_g	Func. (%)	T_g
1	43.5	17	48.1	35
2	21.3	-11	27.4	11
3	7.1	-23	6.9	-27
4	3.8	-29	3.4	-33
5	2.2	-32	2.1	-37
6	0 (**P1**)	-30	0 (**P2**)	-37

Scheme 4. a) Tailoring the degree of functionalization. b–d) T_g variation with the functionalization % for **F-P1** (a) and **F-P2** (b).

Table 2: Functionalization of **P2** under $[\mathrm{Tp}^{*,\mathrm{Br}}\mathrm{Ag}]_2$ catalysis modifying the polymer ratio.[a,b]

Entry	[Cat]:[PhI=NTs]:[**P2**]	**P2** (g)	Isolated yield **F-P2** (%)[c]	Functionaliz. (%)[d]	% NTs incorp.[e]	Mw (kDa)	Đ[f]
1	1:20:50	0.05	58	48.1	21	12.93	2.6
2	1:20:100	0.1	64	27.4	29	11.04	2.8
3	1:20:200	0.2	69	14.1	32	10.10	2.5
4	1:20:500	0.5	76	6.9	37	6.73	2.5
5	1:20:1000	1.0	85	3.4	48	6.53	2.4
6	1:20:2000	2.0	92	2.1	70	6.07	2.4
7	**P2**	–				6.97	2.6

[a] 0.017 mmol $[\mathrm{Tp}^{*,\mathrm{Br}}\mathrm{Ag}]_2$ (2% mmol% referred to PhI=NTs), 10 mL DCM, r.t., 4–8 h. [b] Functionalization and yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. $\mathrm{TsNH_2}$ accounted for 100% initial PhI=NTs not added to the polymer. [c] Isolated functionalized polymer relative to initial polymer (w/w). [d] NTs incorporated referred to final polymer mass (w/w). [e] NTs incorporated referred to initial PhI=NTs. [f] Determined by GPC in THF at 30 °C versus linear PS standards.

The methodology presented in this study allows the complete control of the degree of incorporation of the NTs group into the polymer chains. Collected data in Tables 1 and 2 show that there is a correlation between such functionalization and the initial PhI=NTs:polymer ratio, for both **P1** and **P2** as starting materials. Scheme 4a plots the relationship between those two series of values, which fit quite well for both polymers. This means that with this strategy it is possible to prepare materials with the desired amounts of NTs incorporated just by adjusting that ratio.

The availability of samples of **F-P1** and **F-P2** with different degrees of functionalization led us to explore the effect of the added NTs into polymer properties. As a representative parameter, T_g was first targeted to evaluate such potential dependence. Scheme 4b displays the T_g values obtained by thermal analysis for six samples of each modified polybutadiene. A similar trend is observed for both series: as the functionalization degree increases so it does the T_g (Scheme 4c). This behavior has been previously reported for analogous polymers functionalized with N-containing groups.[11,24] T_g values for **F-P1** fall in the range −32 to + 17 °C, whereas **F-P2** samples show a wider interval from −37 to + 37 °C. This is a consequence of the existence of two different olefinic sites in **P2** which lead to aziridine rings not only in the pendant vinyl group but also in the C=C available at main polymer backbone, the latter causing chain stiffening. Besides, non-covalent interactions between the new functional groups via $\pi-\pi$ stacking or hydrogen bonding interactions involving the polar S=O from the tosyl groups can also contribute to this increase[25] as has been previously described.[11]

The effect of the aziridine functionalization on the thermal stability of both polymers was also studied. As previously reported, the thermal decomposition of polybutadiene in an oxygen-free environment proceeds through a complex sequence of reactions that initiate at temperatures lower than those associated with the polymer chain scission.[26] Comparing the thermal degradation of the pristine polymers **P1** and **P2** with the functionalized **F-P1** and **F-P2**, we can mainly conclude that the incorporation of aziridine groups has no impact in the thermal stability of the polymers, since all the materials obtained from both polymers displayed a principal T_{max} in the range of 433 °C and 456 °C.

We have developed the first catalytic system for the incorporation of nitrene units to polybutadienes as model polymers employing silver-based catalysts. This process operates at room temperature and does not induce appreciable chain scission or cross-linking. It enables a highly efficient and well-controlled functionalization of polymeric substrates bearing internal and pendant C=C bonds. Thermal analysis studies revealed a direct positive correlation between the degree of functionalization and the glass transition temperature (T_g). This methodology opens new opportunities for the development of new polymeric materials functionalized with amino groups in a selective manner, while preserving the integrity of the polymer structure.

Supporting Information

The authors have cited additional references within the Supporting Information.[27–33]

Acknowledgements

The authors thank Ministerio de Ciencia e Innovación for grant PID2020-113797RB-C21, PID2021-122708OB-C31, PID2023-146946NB-I00, Network "OASIS" RED2022-134074-T. The authors also thank Junta de Andalucía (P20-00348) and the Universidad de Huelva (P.O. Feder UHU-202016). J.P.R. thanks Programa Garantía Juvenil. V.S. would like to thank the Ministerio de Ciencia e Innovación (Spain) and the European Community (grant no.: RYC2021-033921-I) for the financial support. C.R. would like to thank the University of Alcalá for a fellowship. Funding for open access is given by Universidad de Huelva/CBUA.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Nitrene transfer • Polybutadiene amination • Polyolefin aziridination • Post-polymerization functionalization • Silver catalysis

[1] F. Lissel, J. Simmchen, "Debating the Everyday Impact of Polymer Materials". ChemistryViews, https://doi.org/10.1002/chemv.202300049.

[2] X. Zhang, M. Fevre, G. O. Jones, R. M. Waymouth, *Chem. Rev.* **2018**, *118*, 839–885. https://doi.org/10.1021/acs.chemrev.7b00329.

[3] S. Dai, S. Li, G. Xu, C. Chen, *Macromolecules* **2020**, *53*, 2539–2546. https://doi.org/10.1021/acs.macromol.0c00083.

[4] G. Menéndez Rodríguez, M. M. Díaz-Requejo, P. J. Pérez, *Macromolecules* **2021**, *54*, 4971–4985. https://doi.org/10.1021/acs.macromol.1c00374.

[5] C. M. Plummer, L. Li, Y. Chen, *Polym. Chem.* **2020**, *11*, 6862–6872. https://doi.org/10.1039/D0PY01279C.

[6] J. B. Williamson, S. E. Lewis, R. R. Johnson, I. M. Manning, F. A. Leibfarth, *Angew. Chem. Int. Ed.* **2019**, *58*, 8654–8668. https://doi.org/10.1002/anie.201810970.

[7] A. D. Mohanty, C. Bae, *Adv. Organomet. Chem.* **2015**, *64*, 1.

[8] K. A. Günay, P. Theato, H.-A. Klok, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 1–28. https://doi.org/10.1002/pola.26333.

[9] N. K. Boaen, M. A. Hillmyer, *Chem. Soc. Rev.* **2005**, *34*, 267. https://doi.org/10.1039/b311405h.

[10] N. R. Ciccia, J. X. Shi, S. Pal, M. Hua, K. G. Malollari, C. Lizandara-Pueyo, E. Risto, M. Ernst, B. A. Helms, P. B. Messersmith, J. F. Hartwig, *Science* **2023**, *381*, 1433–1440. https://doi.org/10.1126/science.adg6093.

[11] S. S. Scott, B. Kaur, C. H. M. Zheng, P. Brant, D. J. Gilmour, L. L. Schafer, *J. Am. Chem. Soc.* **2023**, *145*, 22871–22877. https://doi.org/10.1021/jacs.3c07564.

[12] S. A. Bateman, D. Y. Wu, S. S. Scott, B. Kaur, C. H. M. Zheng, P. Brant, D. J. Gilmour, L. L. Schafer, *J. App. Pol. Sci.* **2002**, *84*, 1395–1402. https://doi.org/10.1002/app.10302.

[13] M. N. Hodges, M. J. Elardo, J. Seo, A. F. Dohoda, F. E. Michael, M. R. Golder, *Angew. Chem. Int. Ed.* **2023**, *62*, e202303115. https://doi.org/10.1002/anie.202303115.

[14] S. R. Gitter, W. P. Teh, X. Yang, A. F. Doroda, F. E. Michael, A. J. Boydston, *Angew. Chem. Int. Ed.* **2023**, *62*, e202303174. https://doi.org/10.1002/anie.202303174.

[15] M. Hu, L. He, R. J. Comito, *Polym. Chem.* **2024**, *15*, 4947–4951. https://doi.org/10.1039/D4PY01021C.

[16] H. J. Dequina, C. L. Jones, J. M. Schomaker, *Chem.* **2023**, *9*, 1658–1701. https://doi.org/10.1016/j.chempr.2023.04.010.

[17] M. R. Rodríguez, M. M. Díaz-Requejo, P. J. Pérez, *Synlett* **2021**, *32*, 763.

[18] A. Caballero, M. M. Díaz-Requejo, M. R. Fructos, J. Urbano, P. J. Pérez, in *Modern Applications of Trispyrazolylborate Ligands in Coinage Metal Catalysis (Chapter 11) in Ligand Design in Metal Chemistry. Reactivity and Catalysis*, (Eds: M. Stradiotto, R. J. Lundgren), John Wiley & Sons, **2016**. https://doi.org/10.1002/9781118839621.ch11.

[19] K. Crimaldi, R. L. Lichter, *J. Org. Chem.* **1980**, *45*, 1277–1281. https://doi.org/10.1021/jo01295a022.

[20] T. Meyer, *Org. Process Res. Dev.* **2003**, *7*, 297–302. https://doi.org/10.1021/op025605p.

[21] S. Coiai, E. Passaglia, M. Aglietto, F. Ciardelli, *Macromolecules* **2004**, *37*, 8414–8423. https://doi.org/10.1021/ma0400315.

[22] L. Maestre, W. M. C. Sameera, M. M. Díaz-Requejo, F. Maseras, P. J. Pérez, *J. Am. Chem. Soc.* **2013**, *135*, 1338–1348. https://doi.org/10.1021/ja307229e.

[23] J. Llaveria, A. Beltrán, W. M. C. Sameera, A. Locati, M. M. Díaz-Requejo, M. I. Matheu, S. Castillón, F. Maseras, P. J. Pérez, *J. Am. Chem. Soc.* **2014**, *136*, 5342–5350. https://doi.org/10.1021/ja412547r.

[24] C. S. Pant, S. S. N. M. S. Mada, M. S. Banerjee, P. K. Khanna, *J. Energ. Mater.* **2016**, *34*, 440–449. https://doi.org/10.1080/07370652.2015.1119915.

[25] S. J. Bailey, S. M. Wales, A. C. Willis, P. A. Keller, *Org. Lett.* **2014**, *16*, 4344–4347. https://doi.org/10.1021/ol502164b.

[26] M. P. Luda, M. Guaita, O. Chiantore, *Makromol. Chem.* **1992**, *193*, 113–121. https://doi.org/10.1002/macp.1992.021930111.

Manuscript received: October 15, 2025
Manuscript accepted: October 20, 2025
Version of record online: November 04, 2025