"Supramolecular Superparamagnetic Nanocomposites Based on a Magnetite-Filled Unentangled Terpyridine-Functionalized Polymer"

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Falco, Guillaume ; Griffiths, Pablo ; Coutouly, Clement ; Fustin, Charles-André ; Baeza, Guilhem P.. Supramolecular Superparamagnetic Nanocomposites Based on a Magnetite-Filled Unentangled Terpyridine-Functionalized Polymer. In: Macromolecules, Vol. 53, p. 5361-5370 (2020) <u>http://hdl.handle.net/2078.1/231251</u> -- DOI : 10.1021/acs.macromol.0c00182

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Article

¹ Supramolecular Superparamagnetic Nanocomposites Based on a ² Magnetite-Filled Unentangled Terpyridine-Functionalized Polymer

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Cite This: https://dx.doi.org/10.1021/acs.macromol.0c00182



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ABSTRACT. Bev	and their usual combination wit	h metal ions we show that ternyridine	_	T_/ ← = 0

5 (TPy)-functionalized polymers can be associated with inorganic nanoparticles to form 6 transient networks via supramolecular bonds. These interactions are first evidenced by 7 differential scanning calorimetry where a growing fraction in Fe_3O_4 nanoparticles is seen to 8 shift up and broaden significantly the glass transition of PnBA-TPy (+8 °C) whereas no 9 effect is observed in the corresponding pure PnBA matrix. The formation of an organic– 10 inorganic physical network is then revealed by rheological measurements highlighting the



11 extra friction caused by the TPy groups at longer timescales. Because they are based on unentangled polymers, such nanocomposites 12 present, in addition, the great advantage to switch rapidly from the solid to the liquid state when submitted to an oscillatory magnetic 13 field. Under this so-called induction heating, the physical network is dismantled remotely from the inside, making this class of 14 materials promising candidates for the design of responsive rubbers.

1. INTRODUCTION

15 Supramolecular polymer networks based on transient con-16 nections such as hydrogen bonding, $\pi - \pi$ stacking, ionic 17 aggregations, or metal-ligand complexes are a fascinating class 18 of materials endowed with tailorable properties.^{1–5} In the latter 19 case, terpyridine (TPy)-functionalized polymers are often 20 associated with various metallic ions to form networks 21 possessing tunable rheological properties.⁶⁻¹¹ TPy groups 22 have also been employed in combination with 2-ureido-4-23 pyrimidone to form hybrid supramolecular networks containing 24 both metal ligands and hydrogen bonds.¹² In addition, pyridine 25 (Py)-based polymers have attracted recently the interest of 26 several research groups because of their ability to form strong H-27 bonds with inorganic fillers forming "attractive nanocompo-28 sites".¹³⁻¹⁷ In particular, Holt et al.^{13,14} have shown a 29 continuous broadening of the glass transition of poly(2-vinyl-30 pyridine) (P2VP) for a growing content in colloidal silica, 31 emphasizing the strong interactions existing at the molecular 32 level between the polymer nitrogen atoms and the hydroxyl 33 groups present at the silica surface. Also, Chen et al.¹⁷ have 34 rationalized the outstanding enhancement of the rheological 35 properties through a theoretical model describing the 36 percolation of the polymer-particle network based on rubbery 37 and glassy bridges. Moreover, Baeza et al.¹⁶ have evidenced the 38 dynamical transition from the classic William-Landel-Ferry 39 (WLF) character to an Arrhenian behavior (with an activation 40 energy higher than 400 kJ mol⁻¹) when the silica content was 41 increased above 30 vol %. Although all these studies are limited 42 to the sole case of P2VP/silica nanocomposites, they suggest 43 that other functional groups, containing Py units, should interact 44 strongly with polar surfaces. Of particular interest to the present 45 study, the formation of supramolecular bonds was also reported 46 between monomeric Py and Fe oxide surfaces where the

attraction was preferentially assigned either to hydrogen 47 bonds 18 or to complexation with Fe atoms. 19,20

On top of the usual reinforcement effect provided by silica 49 nanofillers, the utilization of superparamagnetic iron oxide 50 nanoparticles (SPION) is frequently encountered in the 51 nanocomposite literature because it makes induction heating 52 possible.^{21–24} This technique consists of heating a medium 53 containing responsive nanoobjects by submitting it to an 54 oscillatory magnetic field characterized by an amplitude close to 55 10 mT and a frequency of several tens or hundreds of kHz. In 56 addition, induction heating attracts much interest in biomedical 57 engineering because it enables cancer cell elimination through 58 the injection of SPION and subsequent localized heating of +6 59 °C.^{24–26} The heating intensity depends on the following 60 parameters:

- (i) The content of nanoparticles—while it must be lower 62 than 1 wt % in biomedical applications because of toxicity 63 issues, it can be easily raised up to ca. 60 wt % (~20 vol %) 64 in polymer-based nanocomposites.
- (ii) The characteristics of the electromagnetic field—its 66 amplitude, frequency, and direction. 67
- (iii) The nature of the nanoparticles—their chemical 68 composition, size, and shape. 69

The superparamagnetic properties of nanoparticles and their 70 subsequent ability to dissipate heat originate from their 71

Received: January 24, 2020 Revised: June 5, 2020



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72 magnetic hysteresis governed by two fundamental mechanisms: 73 Néel and Brown relaxations, which are often termed as 74 responsible for the "magnetic viscosity" of SPION.^{27,28}

Néel relaxation is intrinsically related to the nature of the r6 particles. Its characteristic time $\tau_{\rm N}$ corresponds to the time r7 during which the macrospin²⁹ of an SPION remains in a given r8 equilibrium state before switching to its antiparallel configr9 uration. While it is a spontaneous phenomenon, it engenders a 80 delay on the spin orientation when the particle is submitted to an 81 oscillatory magnetic field, causing heat dissipation. In eq 1 82 below, K is the magnetic anisotropy, close to 10 kJ m⁻³ for 83 nanospheres of Fe₃O₄,^{30,31} V is the volume of the particle, T is 84 the temperature, $k_{\rm b}$ is the Boltzmann constant, and τ_0 is the 85 extrapolation of $\tau_{\rm N}$ at an infinite temperature, close to 1 ns for 86 Fe₃O₄ SPION.^{24,30,31}

$$\tau_{\rm N} = \tau_0 \exp\!\left(\frac{KV}{k_{\rm b}T}\right) \tag{1}$$

⁸⁸ On the other hand, the Brown relaxation time $\tau_{\rm B}$ depends on ⁸⁹ the viscosity of the surrounding medium η and corresponds to ⁹⁰ the "geometrical" reversal of the particle, resulting in a ⁹¹ macrospin inversion, similarly as in the previous case. It is ⁹² commonly expressed through the rotational diffusion coefficient ⁹³ $D_{\rm r}$ calculated from the Stokes–Einstein law such as

$$\tau_{\rm B} = \frac{1}{2D_{\rm r}} = \frac{3\eta V_{\rm h}}{k_{\rm b}T} \tag{2}$$

95 in which η is the viscosity of the Newtonian fluid surrounding 96 spherical particles of volume $V_{\rm h} = \frac{4}{3}\pi r_{\rm h}^3$, with $r_{\rm h}$ being their 97 hydrodynamic radius.³² Note that the viscosity is expected to 98 match the zero shear viscosity η_0^* for polymer melts and 99 solutions.³³ The effective relaxation time τ , associated with the 100 macrospin reversal of SPION, can then be simply expressed as³⁰

$$\tau = \left(\frac{1}{\tau_{\rm N}} + \frac{1}{\tau_{\rm B}}\right)^{-1} \tag{3}$$

Our long-term idea is to combine a polymer able to form reversible bonds with SPION to produce reinforced rubbers able to switch from the solid to the liquid state in a fraction of a second when submitted to an electromagnetic stimulus. Unentangled polymers characterized by a low glass-transition temperature (T_g) and interacting favorably with Fe₃O₄ nanoparticles are thus promising candidates. We propose in the present article to deal with a TPy-functionalized short poly(nto butyl acrylate) (PnBA-TPy) reinforced with Fe₃O₄ nanoparticles. Beyond their interactions with polar surfaces, TPy functions are chosen because they will offer a great tunability of the rheological properties in the presence of additional metal the inos⁶ (not treated in the present work).

The article is organized as follows: After the description of the materials and methods in the Experimental Section2 section, we propose a dual study of the thermal and rheological properties of nanocomposites formulated either with a neat PnBA matrix or our purpose-made PnBA-TPy in the Results and Discussion3 section. We mainly focus on the rheology, which appears to be essential for both the mechanical properties of the rubber in service and its ability to generate heat. The latter aspect is finally developed in the Discussion4 section in which we compare set of the methanics of the whole set of nanocomposites and tentatively rationalize their behavior 125 based on classic SPION induction heating models. 126

2. EXPERIMENTAL SECTION

2.1. Materials. A well-defined PnBA-TPy random copolymer was 127 synthesized by copolymerizing *n*-butylacrylate (nBA) with a TPy- 128 functionalized acrylate comonomer, as shown in Figure 1. The so- 129 fl



Figure 1. Chemical structure of the two polymers used to prepare nanocomposites. (a) 7 mol % Random TPy-functionalized PnBA (PnBA-TPy) and (b) PnBA.

prepared polymer contains 7 mol % TPy-functionalized monomers 130 corresponding to ca. 10 groups per chain in average. A reference PnBA 131 was also synthesized in the same conditions. The synthesis protocol of 132 both polymers is provided in Supporting Information, Section 1. A 133 short molecular weight was desired ($M_n^- = 21 \text{ kg mol}^{-1}$ and D = 1.28) to 134 insure the fast diffusion of the chains once the physical bonds with the 135 SPION are deactivated. Note that the molecular weight between 136 entanglements of PnBA is estimated to $M_e = 17-23 \text{ kg mol}^{-1,7,34}$ 137 avoiding long reptation mechanisms. PnBA was selected for its low 138 glass-transition temperature, lack of crystallinity, and easiness of 139 modification, enabling the subsequent production of nanocomposites 140 endowed with thermoplastic elastomer-like properties. The powder of 141 Fe₃O₄ nanoparticles (14–29 nm) was purchased from Nanografi 142 (Turkey) and used as received.

2.1.1. Sample preparation. All composites (9, 18, 24 vol $\% \pm 0.5$ vol 144 %) were prepared by solvent casting in acetone. Solutions of polymer 145 (10 vol %, PnBA-TPy or PnBA) and 5 vol % suspensions of Fe₃O₄ were 146 separately prepared and subsequently mixed via mechanical stirring in 147 appropriate quantity to formulate each sample. The so-obtained 148 mixtures were then dried at room temperature overnight insuring an 149 intimate mixing of the two components and further homogenized 150 mechanically through gentle hot-pressing at 80 °C to avoid any critical 151 particle sedimentation issues. The so-obtained 600 μ m -1 mm-thick 152 films were finally used for DSC, rheology, and induction heating 153 experiments. 154

2.2. Methods. *2.2.1. X-ray Diffraction (XRD).* XRD measurements 155 were performed at room temperature on a D8 advance apparatus 156 (Bruker, USA) using Cu-K_{α 1} radiation. The diffraction pattern of our 157 Fe₃O₄ powder was recorded in the 2 θ range of 15–90°. 158

2.2.2. Fourier Transform Infrared Spectroscopy (FTIR). The FTIR 159 spectra of our powder were recorded on a Nicolet iS50 spectropho- 160 tometer (Thermo Fisher Scientific, USA). An attenuated total 161 reflectance (ATR) mode was used with a diamond crystal. Thirty- 162 two scans were accumulated with a resolution of 4 cm^{-1} and an interval 163 of 2 cm^{-1} . 164

2.2.3. Scanning Electron Microscopy (SEM). The dispersion of 165 nanoparticles in PnBA-TPy and PnBA was studied in samples loaded 166 with 9 vol % Fe_3O_4 through scanning electron microscopy- 167 backscattered electron (SEM-BSE) by using a VEGA3 apparatus 168 (TESCAN, USA). The acceleration tension of the electrons was set to 169 20 kV, and the beam intensity "BI" was fixed at 11. Because of their 170 extreme sensitivity to the electron beam, samples were remolded via hot 171

172 pressing performed at 50 $^{\circ}$ C to obtain 1.5 mm-thick films and 173 subsequently metallized with platinum.

2.2.4. Differential Scanning Calorimetry (DSC). DSC measurements were carried out on a Perkin-Elmer DSC 8000 apparatus under a 176 20 mL min⁻¹ nitrogen flow. Temperature and enthalpy calibrations 177 were performed by using indium and zinc standards. Samples of about 178 10 mg were cooled down to -80 °C for 5 min before heating at 10 °C 179 min⁻¹ up to room temperature. This cycle was then repeated once, 180 resulting in the measurements presented in Figure 3 (second heating 181 ramp).

2.2.5. Rheology. Frequency sweeps (100 to 0.1 rad s^{-1}) were 182 183 performed in the linear regime. The strain amplitude was adjusted 184 according to the sample and the temperature from 0.1% (composite 185 loaded at 24 vol %, below -10 °C) up to 5% (neat polymers above 20 186 °C). The measurements were recorded every 5 or 10 °C on an ARES-187 G2 rheometer (TA, USA) equipped with 10 mm parallel plates and a 188 gap of 0.8 mm (\pm 0.1 mm). These data were successfully reproduced 189 with an ARES-G1 equipped with 8 mm plate-plate geometry. 190 Compliance issues at low temperatures were corrected based on the 191 work by Laukkanen.³⁵ PnBA-TPy-based samples were measured from -30 up to 30 °C. Their PnBA counterparts, which have a lower T_{o} , were 192 193 measured from -50 up to 30 °C. Corresponding master curves were 194 built by using the time-temperature superposition (TTS) principle 195 with a reference temperature T_{ref} = 0 °C. Apart from usual horizontal 196 shifts $(a_{\rm T})$, slight vertical shifts $(b_{\rm T})$ were used to enhance the quality of 197 the neat polymer master curves. Their values were systematically 198 ranging from 0.94-1.1, representing thermal expansion. Vertical shifts 199 ranging from 0.94-1.5 were also used in nanocomposites in which TTS was not necessarily expected to work because of the presence of several 200 dynamical contributions ("multiclocks" system). Although we do not 201 202 have strong evidence for it, the global decrease in $b_{\rm T}$ with increasing 203 temperature is assigned to the progressive deactivation of physical interfacial bonds (see Figure 4 below). Note that no direct correlation 204 205 between $b_{\rm T}$ and the material's expansion coefficient (α) was forced in 206 this work because of (i) the temperature range, implying nonconstant α due to its proximity to $T_{\rm g}$ and/or (ii) the biphasic nature of the 207 208 materials. We refer the readers to Supporting Information, Section 2 for more details about rheometry and data treatment. Measurements 209 210 performed above 10 °C were mostly excluded from the master curves 211 because of their poor overlap with the rest of the data (except for PnBA-212 TPy + 9 vol % Fe_3O_4). This kind of "selective" master curves were also 213 reported by Cui et al.³⁶ in systems containing more than one dynamical 214 contribution when broader master curves were impossible to form.

2.2.6. Induction Heating. Induction heating of nanocomposites was 215 216 performed with a master controller v3+ apparatus (CEIA, Italy) 217 connected to a pancake-shaped (flat spiral) inductor made of two concentric turns. A 0.1 mm-thick Teflon composite tape covered the 218 219 inductor to protect it from material flowing. The frequency of the 220 magnetic field applied was fixed to 855 kHz and its amplitude to ca. 10 mT corresponding to an intensity of 19 A in the inductor. The magnetic 221 solicitation consisted of pulses representing 10% of the total time to 222 avoid excessive heating kinetics being hardly measurable. Disk-shaped 2.2.3 samples (3 mm in diameter and 0.5 mm-thick) were heated and their 224 225 temperature variations were recorded contemporaneously with a PI 450 226 infrared camera (Optris, Germany) equipped with a 13° lens 227 characterized with an optical resolution of 382×288 pixels and a 228 measurement rate of 27 Hz. A schematic representation of the whole 229 dispositive is displayed in Figure 2.

3. RESULTS AND DISCUSSION

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3.1. Characterization of the Fe₃O₄ Nanoparticles. The rcystalline structure of Fe₃O₄ nanoparticles is first characterized by XRD and their surface state is probed by FTIR. All the peaks present in the XRD diffraction pattern (Figure 3a) are assigned to Fe₃O₄ in accordance with the literature, ^{31,37–39} indicating the purity of our powder. On the other hand, the FTIR spectrum (Figure 3b) exhibits two strong Fe–O bands at 550 and 430 are assigned to stretching vibrations of tetrahedral



Figure 2. Schematic representation of the setup used for the induction heating of our nanocomposites.

(Fe_{tetra}-O) and octahedral (Fe_{octa}-O) sites, respectively.^{40,41} In 238 addition, a characteristic broad peak is observed at ca. 3300 239 cm⁻¹, standing unambiguously for hydroxyl groups covalently 240 bonded onto the particle surface.40 These -OH groups are 241 known to appear on the nanoparticles during their synthesis by 242 chemical coprecipitation in an aqueous environment.⁴² The 243 presence of both Fe atoms and -OH groups at the SPION 244 surface makes therefore the origin of the filler-polymer 245 attraction presented below uncertain. As mentioned in the 246 introduction, it is believed to come from the TPy nitrogen 247 interaction with the -OH groups at the magnetite surface (H- 248 bonding) and/or the Fe atom complexation. For the sake of 249 clarity, the two configurations are depicted schematically in 250 Figure 4. We believe that atomistic simulations, elucidating the 251 f4 configuration of the TPy group at the nanoparticle surface, could 252 help to solve this issue (see e.g., ref 43).

3.2. Impact of TPy/Fe₃O₄ Interactions on Polymer 254 Dynamics. The extra attraction between functionalized 255 polymers and magnetite nanoparticles is first suggested by 256 SEM micrographs in Figure 5. While solvent casting followed by 257 f5 mechanical homogenization insures that nanoparticles are well 258 distributed in both PnBA-TPy (a) and PnBA (b) at a 100 μ m 259 lengthscale, it seems that their local dispersion is improved when 260 the polymer is functionalized with (only) 7 mol % TPy groups, 261 being potentially of great importance for efficient induction 262 heating.⁴⁴ Note that the SEM investigation becomes difficult 263 because of the sample degradation under the electron beam in 264 spite of their careful preparation. For the sake of completeness, 265 we provide in Supporting Information, Section 3 an image 266 analysis of our SEM micrographs and additional TEM images of 267 the same nanoparticles embedded in a less sensitive semicrystal- 268 line polymer (5 vol %).

A more systematic characterization of the supramolecular 270 bond impact on polymer dynamics is presented in Figure 6 271 f6 where DSC is used to detect possible effects on the glass 272 transition.^{14,16} The two neat polymers and the corresponding 273 nanocomposites loaded with Φ =9, 18, and 24 vol % Fe₃O₄ were 274 investigated, giving rise to two important results: (i) The 275 functionalization of 7 mol % PnBA units with TPy groups shifts 276 the polymer glass transition by ca. +20 °C (from -45 to -25 277 °C). This effect is understood as an extra steric hindrance caused 278 by the bulky TPy units. In fact, smaller functional groups able to 279 form H-bonds, grafted on the same polymer, were seen to have 280 no impact on its glass transition.⁴⁵ (ii) The glass-transition 281 temperature in PnBA-TPy increased by ca. 8 °C (see Table 1) 282 t1 and significantly broadens when 9 vol % nanoparticles are added. 283 It seems however that this broadening saturates at higher filler 284 fractions, most likely because of the limited number of TPy 285



Figure 3. Fe₃O₄ powder characterization. (a) XRD measured in reflection and (b) FTIR spectroscopy (ATR mode).



Figure 4. Possible interaction pathways between the TPy nitrogen and the surface of Fe_3O_4 : (a) With -OH groups, i.e., H-bonding, or (b) through Fe complexation (example with Fe^{2+}).



Figure 5. SEM micrographs of nanocomposites containing 9 vol % Fe_3O_4 based on (a) PnBA-TPy and (b) PnBA matrixes. Brightest zones stand for SPION aggregates. The quality of the micrographs is limited by a strong degradation of the polymers under the electron beam. Complementary TEM images are provided in Supporting Information, Section 3.

286 groups in the material (about 10 TPy groups per polymer 287 chain). We believe that a gradual effect may have been observed 288 at lower contents of particles. On the contrary, the 289 corresponding nanocomposites based on neat PnBA do not 290 show any significant shift in the glass transition (although it does

Table 1. Glass Transition of PnBA-TPy- and PnBA-	Based
Samples Extracted from DSC	

	PnBA-TPy				PnBA			
vol %	neat	9	18	24	neat	9	18	24
$T_{g} (\pm 1 \ ^{\circ}C)$	-25	-18	-18	-16	-45	-44	-45	-44

broaden), remaining around -45 °C. This observation is the 291 clearest evidence of the strong attraction at the molecular level 292 existing between TPy and -OH groups or Fe atoms. It reminds 293 similar trends observed in Py-based nanocomposites, ^{14,16} which 294 indicated the presence of N…HO physical bonds. 295

Such interactions between PnBA-TPy and magnetite nano- 296 particles are also expected to strongly impact the rheological 297 response of the composites. As mentioned above, silica particle- 298 filled P2VP not only exhibits a strong broadening of the 299 segmental relaxation but also an outstanding increase in the 300 dynamic moduli accompanied by a pronounced delay of the 301 relaxation spectrum.¹⁶ These observations are actually com- 302 parable with what we obtain here for PnBA-TPy with increasing 303 particle content, as can be seen in Figure 7a, showing reliable 304 f7 master curves built on a limited temperature range, in 305 quantitative agreement with other PnBA-based systems. 34,46,47 306 The resulting horizontal shift factors $a_{\rm T}$ are presented in Figure 8 307 f8 and fitted with the WLF equation, supporting our DSC 308 experiments. In fact, while c_1 and c_2 coefficients are found 309 similar for all the PnBA-based nanocomposites, they decrease 310 continuously with the filler content in their PnBA-TPy 311 counterparts (see Table 2). This result reminds once again the 312 t2 "steepening" of the shift factor temperature dependence 313 obtained in nanosilica-filled P2VP.¹⁶ (See also Supporting 314 Information, Section 2 for a comparison of the neat PnBA a_T 315 temperature dependence with data from ref 34 as well as vertical 316 shift factor $b_{\rm T}$). 317



Figure 6. DSC heating scans performed at $10 \,^{\circ}$ C min⁻¹ under nitrogen flow for (a) PnBA-TPy- and (b) PnBA-based nanocomposites. The heat flow is systematically normalized by the mass of polymer within the sample, and the data are shifted for clarity. Insets stand for the derivative of the normalized heat flow as a function of the temperature.

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Figure 7. Rheological master curves built at $T_{ref} = 0$ °C. Effect of the particle content on the rheology of (a) PnBA-TPy- and (b) PnBA-based nanocomposites. (Both graphs show 11 decades in abscissa).



Figure 8. Temperature dependence of the shift factor (a_T) used to build the rheology master curves of (a) PnBA-TPy- and (b) PnBA-based nanocomposites. Solid lines are WLF fits. Resulting parameters c_1 and c_2 are displayed in Table 2 below. Reference temperature is set to 0 °C.

Table 2. c_1 and c_2 Parameters at $T_{ref} = 0$ °C Obtained from WLF Fits (Figure 8)

	_	PnBA-TPy				PnBA			
vol %	neat	9	18	24	neat	9	18	24	
$c_1(-)$	9.5	10.2	8.3	6.5	5.5	5.7	5.6	5.6	
$c_2(K)$	79.8	76.1	58.3	47.7	89.6	88.5	85.8	88.1	

Back to Figure 7a, we remark that the high-frequency G'-G''319 crossover of PnBA-TPy nanocomposites shifts to a much longer 320 time when the filler content is increased, in agreement with the 321 T_g upshift observed in DSC (Figure 6a). On the contrary, we 322 show in Figure 7b that PnBA-based materials exhibit the 323 "classic" trend observed in (mostly) repulsive nanocomposites, 324 i.e., a moderate delay of the low-frequency relaxation 325 mechanisms and a limited reinforcement with no significant 326 shift of the high-frequency G'-G'' crossover. The latter trend is 327 again in line with our DSC measurements (Figure 6b).

Because of their different glass-transition temperatures, it is 328 329 then interesting to compare PnBA-TPy- and PnBA-based 330 nanocomposites containing the same fraction in particles at the same "distance" from their respective T_{g} . This is illustrated in 331 332 Figure 9 where the reference temperature for each material satisfies $T_{ref} = T_g + 45$ °C. Remarkably, while in neat matrixes 333 (Figure 9a), one can observe a similar Rouse-like behavior and 334 flow regime in both polymers because of their identical 335 molecular weights (the fit is performed with RepTate⁴⁸ on 336 PnBA data), the rheological response of nanocomposites starts 337 338 to differ from 9 vol % particles (Figure 9b-d). This is 339 particularly visible in the flow regime where PnBA-TPy 340 composites clearly display lower $G'(\omega)$ and $G''(\omega)$ exponents 341 (denoted as X' and X'') than their PnBA counterparts, 342 synonymous with an extra friction between the two phases. 343 Increasing further the Fe₃O₄ loading up to 18 and 24 vol %

impacts then the response at higher frequencies, notably the $G'-_{344}$ G'' crossover position (denoted as ω_c), and the broadening of $_{345}$ the corresponding α relaxation. 346

For clarity, we report respectively in Figure 9e,f the values of 347 $\omega_{\rm c}$ and X' and X'' as a function of Φ for the two series of $_{348}$ nanocomposites. Interestingly, ω_{c} is seen to decrease exponen- 349 tially with increasing the filler content in both pure polymers, 350 albeit a stronger dependence is observed for PnBA-TPy. This 351 result suggests therefore that, although it is clear that TPy groups 352 enhance the polymer-filler attraction, neat PnBA chains have 353 also the possibility to interact favorably with the particles, 354 probably through their side groups that contains the polar 355 acrylate function. In addition, while the flow regime exponents 356 observed in nanocomposites loaded with 9 and 18 vol % exhibit 357 similar values to the neat matrix for PnBA (i.e., $X' \approx 2$ and $X'' \approx {}_{358}$ 1), they strongly decrease when PnBA-TPy is used, indicating 359 the sluggish relaxation of the functionalized chains. At 24 vol %, 360 both exponents drop below 0.5 regardless of the host polymer, 361 suggesting the formation of an elastic network mainly controlled 362 by the filler-filler interaction, and PnBA-TPy relaxation remains 363 nevertheless slightly slower. Here, it is worth mentioning that 364 creep measurements (requiring a larger amount of sample) 365 followed by compliance inversion would have helped to further 366 broaden the master curves at lower frequencies. 367

3.3. Induction Heating of the Nanocomposites. Beyond 368 their reinforcing effect, Fe_3O_4 nanoparticles make the nano-369 composites responsive to electromagnetic fields, which is an 370 important asset for the creation of multifunctional materials. In 371 the present study, the goal is to switch from solid- to liquid-like 372 mechanical properties as quickly as possible by using induction 373 heating, which is potentially of great interest for healing or 374 sudden energy dissipation applications. The assets of such a 375 method are multiple: 376



Figure 9. Rheology master curves at $T_{ref} = T_g + 45$ °C for PnBA-TPy- and PnBA-based nanocomposites. (a) Neat matrixes (red solid lines correspond to the Rouse model computed with RepTate), (b) 9 vol %, (c) 18 vol %, and (d) 24 vol %. (e, f) Evolution of ω_c and the power law exponents in the flow regime (X', X'') as a function of the volume fraction of particles.

- (i) Remote control: It offers the possibility of acting in a contactless manner,²² making the heating convenient to use. This may be essential for a healing treatment performed with a portative inductor.
- (ii) Localized character and selectivity: The operator does not 381 provide heat directly to the material but applies an 382 electromagnetic radiation that will stimulate only targeted 383 subdomains, able to generate, from the inside, their "own" 384 heat. This difference opens the way to localized healing of 385 coatings as well as selective "melting" in macroarchitec-386 tured materials, notably of importance in energy 387 dissipation devices. 388
- (iii) Flexibility of the heating: Since the heat generation 389 depends mainly on the electromagnetic radiation 390 characteristics and the intrinsic properties of the particles, 391 it is possible to create an optimized heater/receiver 392 coupling in contrast to resistive heating that only depends 393 on the "hot plate" characteristics. The inductor that we 394 use offers notably the possibility to tune the duration of 395 the electromagnetic pulse. 396
- (iv) Low inertia: Due to the absence of susceptor (hot plate), 397 the thermal inertia of the setup is greatly reduced. It only 398 depends on the thermal conduction of the material, 399 making the thermal cycles more efficient. This property 400 must not be neglected because the solid/liquid transition 401 in both directions must occur as fast as possible.

In Figure 10a, we show the evolution of the temperature in 403 f10 nanocomposites submitted to the oscillatory magnetic field as a 404 function of time T(t), revealing two important trends: (i) 405 Increasing the filler content is found to accelerate the heating 406 process and to increase the maximum temperature reached in 407 the permanent regime (this expected trend has a similar 408 amplitude in both PnBA and PnBA-TPy). (ii) Nanocomposites 409 loaded with a given fraction in SPION are systematically found 410 to heat faster and to a larger extent in the nonfunctionalized 411 PnBA (Figure 10b). In order to analyze in a quantitative way this 412 data, one can use the classic heat equation considering a small 413 volume of material (no spatial temperature gradient) to 414 determine the heat generated by the SPION as a function of 415 the temperature during the experiment P(T(t)), such as 416

417



Figure 10. Induction heating experiments on nanocomposites. (a) Temperature as the function of time obtained by thermal imaging. (b) Maximal temperature T_{max} reached by the nanocomposites as a function of the filler content. Lines are guides to the eye. (c) Analog dependence of SAR obtained from two fitting procedures (see Supporting Information, Section 4).

$$P(T(t)) = mC_{p} \frac{dT(t)}{dt} + hS_{1}(T(t) - T_{0}) + \lambda \frac{S_{2}}{e}(T(t) - T_{0})$$
(4)

418 where T_0 is the room temperature, *m* is the mass of the sample, 419 C_p is its specific heat capacity, S_1 is the surface of the sample in 420 contact with air (top part and edges), S_2 is the surface in contact 421 with the Teflon composite tape (bottom part), *e* is the tape 422 thickness, *h* is the convective heat transfer coefficient of air (~10 423 W m⁻² K⁻¹ at 1 atm and 40 °C),⁴⁹ and λ is the heat conduction 424 coefficient of the tape. Note that C_p values of nanocomposites 425 were calculated from theoretical values of Fe₃O₄ and PnBA at 426 room temperature (0.76 and 1.82 J g⁻¹ K⁻¹, respectively)^{38,50,51} 427 resulting in 1.48, 1.28, and 1.18 J g⁻¹ K⁻¹ for nanocomposites 428 loaded with 9, 18, and 24 vol %, respectively. For simplicity, 429 these C_p values were assumed to be constant during the 430 experiment whereas increases by +20 and + 15% are expected 431 from the literature for PnBA and nano-Fe₃O₄, respectively, when 432 passing from 300 to 470 K.^{38,50,51}

⁴³³ While good data fits T(t) can be achieved with eq 4 by letting ⁴³⁴ free P(T(t)), it seems that its variation can be eliminated by ⁴³⁵ reporting the resulting error on a different parameter, namely, λ , ⁴³⁶ that is consequently found to vary between 77 and 116 mW m⁻¹ ⁴³⁷ K⁻¹ (the theoretical value for neat Teflon is reported to be ca. ⁴³⁸ 300 mW m⁻¹ K⁻¹).⁵² We refer the reader to the whole fitting ⁴³⁹ procedure detailed in Supporting Information, Section 4. Note ⁴⁴⁰ that this choice, $P(T(t)) = P_0$, was made because of small ⁴⁴¹ variations in P(T(t)), strongly suggesting that the heat ⁴⁴² generation was mainly governed by Néel relaxation (see ⁴⁴³ below). Finally, one can determine for each nanocomposite ⁴⁴⁴ the specific absorption rate (SAR), i.e., the specific power ⁴⁴⁵ generated by the nanoparticles in different environments (in W ⁴⁴⁶ g⁻¹) as

$$SAR = \frac{P_0}{mx_{Fe_3O_4}}$$
(5) 442

where $x_{\text{Fe}_3\text{O}_4}$ is the weight fraction of magnetite in the sample. ⁴⁴⁸ Note that SAR values for Fe₃O₄ SPION (14–29 nm) reported ⁴⁴⁹ in Figure 10c (ca. 100 W g⁻¹) are well in line with results ⁴⁵⁰ obtained from similar experiments, ^{30,53} corroborating our ⁴⁵¹ hypotheses. While "global fit" SAR estimations are obtained ⁴⁵² from fitting T(t) with equation S1 between 0 and 60 s, their ⁴⁵³ "short time fit" counterparts originate from data subsets ⁴⁵⁴ satisfying $T(t) < 0.63 T_{\text{max}}$, enhancing the precision on SAR ⁴⁵⁵ values at a short time. (See details in Supporting Information, ⁴⁵⁶ Section 4).

4. DISCUSSION

While the results from our rheological analysis demonstrate 458 unambiguously the extra attraction between PnBA and Fe₃O₄ 459 when the former is functionalized with TPy units, induction 460 heating outputs, and notably the results presented in Figure 10c, 461 deserve a closer attention. In fact, in spite of the identical nature 462 and content of particles in both series of composites, SAR in 463 PnBA-TPy appears significantly lower than in PnBA up to $\Phi =$ 464 18 vol %. We also remind the reader that P(T(t)) was 465 systematically found to vary in a very limited extent. We propose 466 below to rationalize those two results by using a combination of 467 qualitative and quantitative arguments based on the classic Néel 468 and Brown models. In the present case, two opposite scenarios 469 can be considered: 470

(i) The dominating phenomenon is the Néel relaxation, i.e., 471 $\tau_{\rm N} \ll \tau_{\rm B}$, resulting in $\tau \approx \tau_{\rm N}$, meaning that the high 472 viscosity of the medium totally blocks the Brownian 473 motion. In consequence, for an identical particle 474 structure, one should observe an identical heating profile 475 in both series of samples. Since it is clearly not the case 476 (Figure 10), it suggests that the SPION are not dispersed 477

in the same way. This statement seems reasonable since 478 the extra attraction caused by the TPy units is expected to 479 enhance the dispersion of the particles in PnBA-TPy, as 480 further supported by our SEM investigation (Figure 5). 481 However, it is essential to note that reducing the 482 aggregation of particles (or agglomeration of aggregates), 483 i.e., decreasing their dipolar interactions, should accel-484 erate the Néel relaxation (lower $\tau_{\rm N}$)⁴⁴ resulting in an extra 485 heating in the PnBA-TPy series, at the opposite of our 486 experimental observations. Then, on a different aspect, 487 because $\tau_{\rm N}$ decreases exponentially with the temperature 488 (eq 1), the resulting P(T(t)) is expected to grow by a 489 (reasonable) factor $\psi \approx 2.2$ between the beginning (*T* = 490 T_0) and the end $(T = T_{max})$ of the experiment (see 491 Supporting Information, Section 5 for calculation details). 492

(ii) The dominating phenomenon is the Brown relaxation, 493 i.e., $\tau_{\rm B} \ll \tau_{\rm N}$, resulting in $\tau \approx \tau_{\rm B}$, meaning that the relatively 494 low viscosity enables the Brownian motion, occurring at a 495 shorter time than the Néel macrospin reversal. This 496 scenario is qualitatively adapted to explain the reduction 497 in SAR when PnBA-TPy is the host matrix. In fact, a 498 higher viscosity leads to a higher $\tau_{\rm B}$ and a lower SAR 499 (fewer macrospin reversal per time unit). However, this 500 hypothesis also implies a drastic reduction in $\tau_{\rm B}$ with the 501 temperature, originating not only from the intrinsic 502 inverse dependence between $\tau_{\rm B}$ and T (eq 2) but also 503 from the Arrhenian drop of the viscosity when increasing 504 the temperature. In the framework of an induction heating 505 dominated by Brownian motion, we estimate quantita-506 tively an increase in P(T(t)) by a factor close to 1000 507 during the experiment (see Supporting Information, 508 Section 5), which obviously does not match with our 509 observations, rather indicating an almost constant power 510 delivered all along the test. The latter is clearly evidenced 511 by the good fit of T(t) obtained with equation S1 (see 512 Figure S11 in Supporting Information, Section 4). 513

To summarize, it seems therefore that none of these 514 515 extrapolated scenarios can fully rationalize our experimental s16 results. On one hand, the first hypothesis ($\tau_{\rm N} \ll \tau_{\rm B}$) predicts a s17 satisfyingly small rise in P(T(t)) with the temperature whereas it 518 cannot explain, even qualitatively, the lower values of SAR found s19 for PnBA-TPy. On the other hand, the second hypothesis ($\tau_{\rm B} \ll$ s20 $\tau_{\rm N}$) can be invoked to rationalize the latter issue but predicts a 521 huge increase in P(T(t)) during a given experiment. In 522 consequence, we propose to interpret our experiments through 523 a combination of the two abovementioned scenarios as follows. First, the Néel relaxation must dominate overall the induction 524 s25 heating since the P(T(t)) values are found to evolve in a limited 526 extent regardless of the sample composition. Because the 527 temperature would not exhibit a sharp exponential profile (Figure 10a and Figure S11) in the opposite case, we can be 528 confident on this first statement. Then, lower SAR values 529 obtained in PnBA-TPy indicate that the rheological properties 530 531 must also impact the heat production. In fact, we believe that the Brown relaxation does occur but plays a minor role in the heat 532 generation because of the pronounced aggregation of particles, 533 534 limiting greatly their ability to rotate. More quantitatively, we 535 observe that 9 vol % Fe₃O₄ generates 1.5 times more heat in 536 PnBA than in PnBA-TPy. However, following a theoretical 537 approach based on the viscosity's variation would have given a 538 ratio closer to 4.4, confirming the failure of eq 2 because of the 539 nonisolated character of our SPION (see Supporting

Information, Sections 5 and 6). Finally, it is worth mentioning 540 that the SAR is seen to decrease progressively with the filler 541 content in PnBA-based nanocomposites whereas it is constant in 542 their PnBA-TPy counterparts (Figure 10c), leading ultimately to 543 a crossover at 24 vol %. Such diminution is expected with 544 increasing the filler fraction because of growing dipolar 545 interactions between the nanoparticles, particularly because of 546 their aggregation.^{30,31,44,54} On the other hand, the absence of 547 SAR diminution in PnBA-TPy nanocomposites corroborates 548 therefore the extra polymer-filler attraction resulting in a better 549 magnetite dispersion, in agreement with SEM, DSC, and 550 rheological experiments. It also supports the fact that in spite of a 551 lower aggregation, SPION embedded in the PnBA-TPy generate 552 less heat because of the higher viscosity of their local 553 environment, demonstrating that Brown relaxation cannot be 554 neglected.

Interestingly, although it is limited to a qualitative analysis in 556 the present study, one could imagine measuring the heat 557 generated by a given fraction of SPION to access the local 558 rheological properties of their surroundings. While this 559 approach reminds the magnetic particle nanorheology,^{33,55} 560 based on the Brownian rotation too, it enables, in principle, 561 measuring samples of higher viscosities, i.e., polymer melts, 562 under the restriction of a preidentification of the sole Néel 563 mechanism (achievable in the glassy state). Note that the 564 utilization of magnetically blocked particles^{32,33} is excluded in 565 our case since we need the Néel relaxation to generate heat from 566 the beginning of the experiment for applicative reasons. 567

5. CONCLUSIONS

Beyond their frequent utilization in metal-ligand supra- 568 molecular networks, we have demonstrated that TPy-function- 569 alized polymers are capable of forming attractive bonds with the 570 magnetic filler polar surface, similarly as what is observed in 571 P2VP/silica nanocomposites. This extra friction has been first 572 evidenced through DSC, where a strong upshift and a 573 broadening of the glass-transition temperature with increasing 574 the filler content were observed in PnBA-TPy whereas much 575 weaker perturbations were seen in PnBA. At a larger length scale, 576 the extra friction, most likely caused by a combination of H- 577 bonds and Fe atoms complexation, is seen to delay significantly 578 the relaxation of unentangled chains. Indeed, they pass from a 579 usual Rouse-like response to physical gels endowed with solid- 580 like properties at room temperature, opening new perspectives 581 for the design of responsive materials. In the future, we believe 582 that combining H-bonds with metal-ligand interactions could 583 lead to a new kind of double supramolecular network. These 584 materials would have the great asset to rely on a single TPy- 585 functionalized polymer from which metal ions and nanoparticles 586 would be added. In addition, the present strategy, i.e., adding a 587 small fraction of a functionalized comonomer within a base 588 polymer, offers a great chemical versatility resulting in a wide 589 range of accessible properties. Following this logic, the next step 590 will therefore consist of evaluating competing effects, i.e., 591 quantifying the TPy preference in forming metal-ligand or H- 592 bonds in ternary mixtures as well as increasing the fraction of 593 TPy groups within the chains. 594

ASSOCIATED CONTENT

Supporting Information

595 596

The Supporting Information is available free of charge at 597 https://pubs.acs.org/doi/10.1021/acs.macromol.0c00182. 598

Details on the polymer synthesis and NMR character-599 ization; details on rheometry and corresponding data 600 treatment; image analysis of SEM micrographs and 601 additional TEM micrographs obtained from a composite 602 formulated with a less sensitive polymer illustrating 603 SPION aggregation; fitting procedure of the induction 604 heating measurements; numerical applications from the 605 classic superparamagnetism theory; and magnetic char-606 acterization of the Fe₃O₄ powder (PDF) 607

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628 Notes

629 The authors declare no competing financial interest.

630 **ACKNOWLEDGMENTS**

631 G.F. and G.P.B. thank René Fulchiron and André De Almeida 632 (IMP, Univ. Claude Bernard Lyon) for their help with the 633 rheological measurements. P.G. and G.P.B. are indebted to 634 Gildas Coativy (INSA-Lyon) for his help with thermal imaging 635 and Florent Dalmas (INSA-Lyon) for TEM imaging presented 636 in the Supporting Information. All the authors are grateful to 637 Salvatore Costanzo (Univ. Naples) and Macromolecules 638 reviewers for their valuable advice on rheological data. G.P.B. 639 acknowledges the financial support of IDEX-Lyon and INSA-640 Lyon through the program ELAN-ERC as well as the Institut 641 Carnot I@L for the funding assigned to the project 642 POMMADE. This work was partially supported by funding 643 from the H2020 Programme (MARIE SKLODOWSKA-CURIE 644 ACTIONS) of the European Commission's Innovative Training 645 Networks (H2020-MSCA-ITN-2017) under DoDyNet REA 646 Grant Agreement No.765811.

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