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Thermoset Magnetic Materials Based on Poly(ionic liquid)s Block Copolymers

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ABSTRACT: A new methodology for the preparation of nanostructured magnetic thermoset materials without any kind of metal oxide or metal magnetic nanoparticles has been proposed. The present study focuses on the nanostructuration of thermoset materials based on poly(ionic liquid)s block copolymer and the subsequent production of magnetic nanostructured thermoset. Judicious selection of block copolymer, such as P2VP-*b*-PMMA, soluble in epoxy and its subsequent quaternization leads to a phase modification of the system, from totally soluble to a nanostructured system. Different degree of quaternization of the pyridine groups showed the range of quaternization values which allowed the nanostructuration of the thermoset. Magnetic material was obtained by anion exchange of the quaternized poly(ionic liquid) block copolymer without using any kind of metal oxide or metal magnetic nanoparticles. The different materials obtained by quaternization of the block copolymers, the anion exchange of the polymeric ionic liquid and thermoset materials were characterized by ^{1}H nuclear magnetic resonance (^{1}H NMR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), high resolution transmission electron microscopy (HR-TEM) and magnetic properties were measured by a superconducting quantum interference device (SQUID).
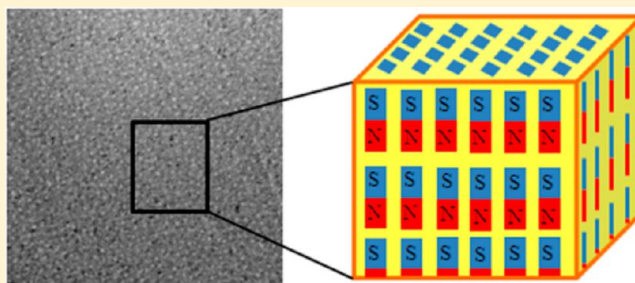
INTRODUCTION

Conventional plastics form a wide variety of durable and lightweight materials that are easy and inexpensive to process, but they often lack properties such as electrical conductivity, mechanical strength, heat resistance, magnetism or high dielectric constants.[1] For this reason, in the past few years, research in the field of advanced materials with novel properties has targeted combining materials with different properties. The term "nanocomposites" relates to composite materials whose characteristic length scale of the reinforcing agent is in the nanometer range. When different materials are combined to form a heterogeneous structure, the properties of the resulting nanocomposites depend closely on the properties of the constituent materials, i.e., the length scale, as well as the chemical and morphological details of the dispersion. In the field of nanocomposites, recent studies have shown that magnetic polymer nanocomposites prepared with magnetic nanoparticles are one promising material[2] with high-valued potential applications in high density magnetic recording, magnetic sensors, magnetic carriers, color imaging, biomedical, magnetic storage, and electronics.[3−6] So far, most of the works reported on magnetic nanocomposites have been based on metal oxide or metal magnetic nanoparticles in various polymers, such as vinyl−ester resin, polyurethane, parylene, poly(methyl methacrylate), epoxy resin, and block copolymers.[7−13]

In the current work, we describe a novel route to obtain nanostructured magnetic thermoset materials without using any kind of metal oxide or metal magnetic nanoparticles but simply introducing magnetic poly(ionic liquid) block copolymer. The resulting material exhibits well-defined ferromagnetic interactions, remanence and coercivity at room temperature.

Ionic liquids (ILs) are organic salts with low melting point. Like salts, ionic liquids are composed of cations and anions responsible for the material properties.[14] Moreover, the ILs properties can be tuned by simple anion exchange.[15] Ionic liquids have been combined with polymer networks which offer great value practical applications like specialty polymer additives and for the development of functional polymers.[16−19] However, ionic liquids present one main disadvantage by

exuding easily from the polymer network. To tackle this problem poly(ionic liquid)s (PILs) it may be used. PILs are described as a new class of polymeric materials with unique properties combining those of ILs (ionic conductivity, thermal stability, tunable solution properties and chemical stability) and specific properties of polymers. Although several studies have been devoted to magnetic ILs,[20−22] the synthesis, characterization and application of paramagnetic PILs are still at their infancy. For example, Tang et al. investigated the properties and application of PILs as optically transparent microwave absorbing materials[23] since PILs contain anion−cation pairs. Therefore, PILs have a relatively high density of strong dipoles, which makes them promising candidates for microwave absorption. That is the reason why the development of a magnetic structural material, such as magnetic epoxy, should be of great interest as a microwave absorption material and could open new fields of application to structural materials.

In order to develop the nanostructured epoxy material, in the present work we report (i) the anionic synthesis of poly(2-vinylpyridine)-b-poly(methyl methacrylate), (ii) the production of a microphase separated thermoset system which consists of an epoxy resin containing a diblock copolymer, like poly(2-vinylpyridine)-b-poly(methyl methacrylate) [where the two blocks are selected in order to be completely miscible with the epoxy], (iii) the influence of the degree of quaternization of the poly(2-vinylpyridine) block on the morphology of the final nanostructured thermoset materials and (iv) the development of a novel magnetic nanostructured thermoset material based on a magnetic PILs block copolymer obtained by anion exchange.

■ EXPERIMENTAL PART

Materials. Calcium hydride (CaH$_2$ purity 95%, Acros), 1,1 diphenylethylene (DPE) (purity 97%), n-butyllithium (1.6 M in hexanes), butyllithium (sec-BuLi) (1.4 M in cyclohexane), 1,1-diphenylethylene (98%, Acros), methyl methacrylate (99%, MMA), triethylaluminum (TEA) (25% in toluene), 2-vinylpyridine (95%, 2-VP, Aldrich), bromoethane, diethyl ether, and iron(III) bromide (FeBr$_3$) were purchased from SigmaAldrich. Tetrahydrofuran (THF) (99.99%), hexane (99.7%), and methanol (99.9%), were purchased from Fisher Scientific, Riedel de Haen, and Fluka, respectively. The epoxy system was composed by an epoxy resin (Araldite LY556), an anhydride hardener (Aradur 917) and an imidazole accelerator (DY 070) that were supplied separately.

Synthesis of P2VP-b-PMMA. The synthesis of poly(2-vinyl-pyridine)-b-poly(methyl methacrylate) (poly(**0**)) was carried out according to the protocol: The solvent for the polymerization was tetrahydrofuran purified via freezing - degassing cycles in the presence of calcium hydride, distillation from sodium/potassium alloy (Na/K), and finally stored under high vacuum in diphenylhexyllithium (DPHLi), which was prepared through the reaction of 1,1-diphenyl-ethylene and n-butyllithium. The initiator used was sec-BuLi and was diluted in hexane to a more convenient concentration (0.2 M) in a custom-made Pyrex glass apparatus through scientific glassblowing. 1,1-diphenylethylene was purified by reaction with n-BuLi, distilled under vacuum, diluted with hexane and stored in a custom-made Pyrex glass apparatus through scientific glassblowing into precalibrated ampules. A Pyrex glass ampule was calibrated at ambient conditions with distilled water according to a well-established procedure thoroughly described in the literature.[24] In all cases the amount of solvent used for dilution was adjusted according to the concentration required to achieve the desired molecular weight of each block.

2-Vinylpyridine was purified twice with calcium hydride to remove water traces, distilled over at least two sodium mirrors in order to be completely dried and finally distilled from triethylaluminum for final purification under stirring for 20 minutes. 2VP was finally distilled in

an evacuated calibrated glass ampule, stored at −27 °C and was freshly distilled prior to use and was continuously kept frozen.

The second monomer, methyl methacrylate, was purified as well through freeze-drying via CaH$_2$, TEA and then distilled in a custom-made Pyrex precalibrated ampule through scientific glassblowing. During the anionic polymerization procedure, 2VP as well as MMA were kept frozen at −196 °C (liquid nitrogen temperature) prior to their use. The living chains were terminated with methanol, which was purified after freeze-drying cycles and finally distilled into Pyrex glass precalibrated ampules through calcium hydride.

The polymerization was carried out according to the literature and methods usually adopted for anionic polymerization and a brief description is given below.[25−27]

The diblock copolymer of the poly(**0**) type was synthesized through sequential anionic polymerization and high vacuum techniques.[28] A specific Pyrex glass apparatus was built up via scientific glassblowing. After the purification of the Pyrex custom-made glass apparatus with DPHLi through continuous rinsing of THF until no red color appears throughout the main reactor, the appropriate amount of 2VP (0.030 mol or 3.15 g) was distilled in the reactor followed by the addition of the initiator (0.141 mmol). An intense red color appeared due to the living ends of P2VP$^{(-)}$Li$^{(+)}$ and the mixture was left to react for approximately 1 h. All procedures were performed at −78 °C, using a 2-propanol/liquid nitrogen bath. Then, 1,1-DPE (0.155 mmol, ratio 1:1.1, excess of DPE when compared with the initial sec-BuLi concentration) was added in order to avoid the competitive reaction of the carbonyl bond from the MMA monomeric units leading eventually to side products.[28] Following the addition of the protective agent, the second monomer (MMA, 0.070 mol or 7 g) was added via distillation and almost immediately the dark red color disappeared due to the fast initiation and propagation of the MMA quantity through the macroinitiator [P2VP$^{(-)}$Li$^{(+)}$]. The mixture was left to react for approximately 1 h again at −78 °C. The synthesis procedure was accomplished in approximately 200 mL of THF as solvent. Finally, a small quantity of methanol was added for the termination of the living ends. The diblock copolymer was precipitated into a large excess of hexanes, then dried from the solvents and stored under vacuum in sealed ampules. The synthesis procedure of the diblock copolymers is shown in Figure 1.

Synthesis of the Ionic Liquid Block Copolymer. [P2VP-r-poly(1-ethyl-2-vinylpyridinium bromide)]-b-Poly(methyl methacrylate) block copolymer were prepared (poly(**1**), poly(**2**), and poly(**3**)) following a similar procedure to the one described in the literature.[29] Under vigorous stirring, 40 mL of bromoethane was added to 0.4 g of poly(**0**) in a round-bottom flask. The mixture was refluxed for 168 h. At specific time intervals, aliquots were taken from the flask using syringes. The resulting white-yellow solid was allowed to cool down at room temperature, and then washed several times with diethyl ether. The product was isolated and dried with a vacuum oven at 50 °C.

Synthesis of Paramagnetic Ionic Liquid Block Copolymer. [P2VP-r-poly(1-ethyl-2-vinylpyridinium Fe$_3$Br$_{10}^-$)]-b-Poly(methyl methacrylate) (poly(**4**)) was prepared following a similar procedure to the one described in the literature.[30] For the synthesis of paramagnetic ionic liquid block copolymer, three equivalents (with respect to monomer units) of FeBr$_3$ were dissolved in methanol and added dropwise under stirring to poly(**1**), previously dissolved in methanol. After addition of the iron halogenide, the final solution was stirred for 24 h. Finally, poly(**4**) was obtained by removing the solvents using a rotary evaporator followed by freeze-drying up to a constant weight. Reactions for the synthesis of poly(ionic liquid)s and magnetic poly(ionic liquid) are given in Figure 2.

Protocol for Blending. The protocol to prepare the thermoset samples of block copolymer and epoxy system was already described and was typical:[31] all block copolymers were dissolved in THF in all cases (except poly(**4**), which was dissolved in dichloromethane), Araldite LY556 was added to the block copolymer (all samples contain 30 wt % of the diblock copolymer). Then, the solvent was partially evaporated at room temperature. Aradur 917 and DY 070 were added and blended with the concentrated mixture. A small amount of this mixture was introduced and degassed in a mold at room temperature
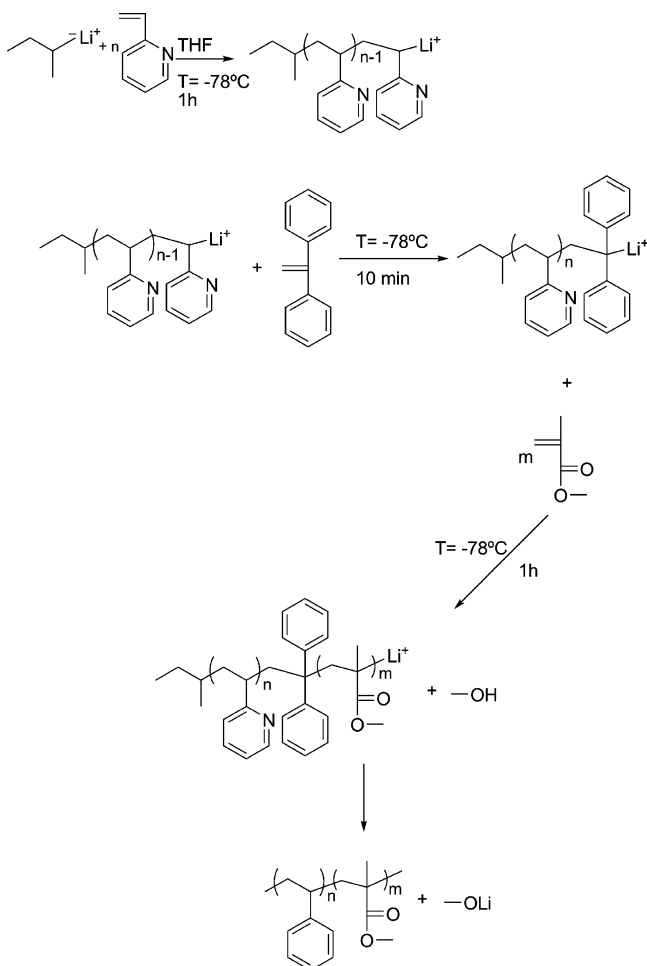
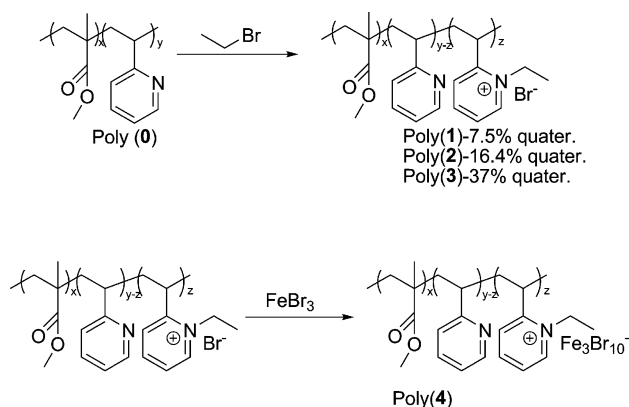**Figure 1.** Synthesis procedure of the poly(**0**) diblock copolymer through anionic polymerization.

Figure 2. Synthesis reactions of the poly(ionic liquid)s and magnetic poly(ionic liquid).

and heated up to 80 °C for 2 h. Finally, the sample was postcured at 100 °C for 2 h.

Techniques. ^{1}H NMR experiments were performed on a Bruker AVANCE III spectrometer at 500 MHz. Measurements were performed at room temperature in deuterated chloroform (CDCl₃) and DMSO-d_6.

Transmission electron microscopy (TEM) was performed using a ZEISS Libra120 TEM with an acceleration voltage of 120 kV. Samples for TEM were prepared by ultramicrotomy, using an Ultramicrotome Reichert Ultracut S (Leica) to obtain thin slices (ca. 70 nm thick).

Diamond knives for cryo-temperatures (Diatome) were used for both the trimming (model cryotrim 45) and cutting process (model cryo 35°). The slices were placed on copper grids (400 mesh Cu, Agar), and stained for 8−13 h with iodine.

Thermal analysis was performed by differential scanning calorimetry (DSC) using a DSC instrument from Perkin-Elmer (Pyris Diamond DSC) in a temperature range from 50 to 220 °C, under nitrogen. The glass transition temperature (T_g) was obtained as the onset point of the heat flow step recorded at a scan rate of 40 °C min⁻¹ in case of thermoset materials and 20 °C min⁻¹ for the block copolymers.

Thermal gravimetry analysis (TGA) measurements were carried out with a TA-Instrument Q500 TGA using a temperature range of 30−800 °C at a heating rate of 10 °C min⁻¹ under nitrogen.

Fourrier-transform infrared (FTIR) spectra were recorded at room temperature using a Nicolet Avatar 360 spectrophotometer. All samples were cast directly onto KBr pellets. A 4 cm⁻¹ resolution in a wavenumber range from 4000 to 600 cm⁻¹ was used.

The synthesized copolymers were characterized by high temperature size exclusion chromatography (HT-SEC) to confirm the molecular weight distributions and the corresponding number-average molecular weight (M_n) values. Additionally, membrane osmometry (MO) technique was carried out to confirm the results obtained by HT-SEC. Moreover, proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and infrared spectroscopy (IR) were used to calculate the weight fraction of each block and to certify the chemical structure of the final diblock copolymers, respectively. The equipment used for the characterization was a HT-GPC from Polymer Laboratories (PL-GPC-120) equipped with one precolumn for organic solutions, three PLgel 5 μm MIXED-C columns and a refractive index (RI) detector. The solvent used was THF containing 0.5% pyridine at 35 °C with a flow rate of 1 mL/min. Size exclusion chromatography (SEC) was calibrated with eight PS standards (M_p: 4300 g/mol to 3 000 000 g/mol) and PS standard were regularly tested to ensure the accuracy of the SEC instrument. The number-average molecular weights (M_n) (higher than 15 000 g/mol) of the precursors and the final products were measured with a membrane osmometer (MO) Gonotec-Osmomat 090 at 35 °C. Toluene, distilled over CaH₂, was used as the measuring solvent.

For the magnetic characterization a "superconducting quantum interference device" (SQUID) from Quantum Design Magnetic Property Measurement System (MPMS) 5T was used. Isothermal hysteresis cycles were measured at 300 K with an applied magnetic field ranging between −50 000 and +50 000 Oe.

■ RESULTS

Production of the magnetic thermoset involved several steps. First, a copolymer poly(**0**) was synthesized by anionic polymerization as described in the Experimental Section. After purification, the resulting poly(**0**) block copolymer had a number-average molecular weight roughly equal to 71 000 g/mol. The molecular characteristics are summarized in Table 1 as determined with the aforementioned instrumentation. It is important to mention that the final diblock copolymer can be considered a model material, according to molecular characterization results since it exhibits molecular and compositional homogeneity.

Figure 3 shows the ^{1}H NMR spectrum obtained for poly(**0**) in CDCl₃. The weight fraction of P2VP was estimated to be 30%. This value was determined by taking into account the relative peak integration values at $\delta \approx 8.3$ ppm corresponding to the proton (N−CH−) of P2VP compare to the signal at $\delta \approx 3.6$ ppm was attributed to the methyl group of PMMA .

Poly(**1**), poly(**2**), and poly(**3**) were prepared following a similar procedure to the one described in the literature.[29] In order to calculate the extent of quaternization of poly(**0**), the initial diblock and the intermediate PILs were characterized by ^{1}H NMR in DMSO-d_6 (Figure 4a). The decrease of the signals

Table 1. Molecular Characterization Results for the Initial P2VP Segments and the Final Diblock Copolymer Poly(0) As Calculated from HT-SEC and ^{1}H NMR Spectroscopy

	$\bar{M}_n^{P2VP}$ (g/mol)^{a,b}	PDI^a P2VP	$\bar{M}_n^{PMMA}$ (g/mol)^c	$\bar{M}_n^{total}$ (g/mol)^b	$\bar{M}_w^{total}$ (g/mol)^a	PDI^a	% wt P2VP^d
poly(0)	22 000	1.08	49 000	71 000	80 200	1.13	30

^{a}Calculated from size exclusion chromatography (HT-SEC). ^{b}Calculated from membrane osmometry (MO). ^{c}Calculated from the equation

$$\bar{M}_n^{total} = \bar{M}_n^{P2VP} + \bar{M}_n^{PMMA}$$

^{d}Calculated from ^{1}H NMR spectroscopy (^{1}H NMR).
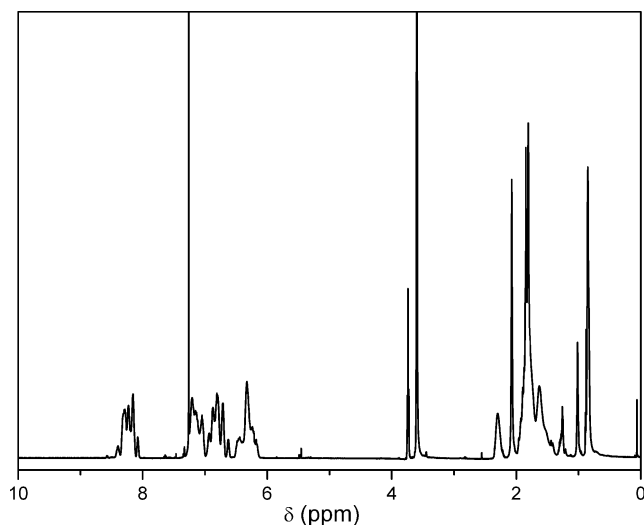
Figure 3. ^{1}H NMR spectra in CDCl$_3$ of poly(0).

characteristic of the pyridine protons ($\delta \approx 8.27-6.10$ ppm) as well as the appearance of the (N$^+$−CH) peak ($\delta \approx 8.85$ ppm) of the pyridine group after quaternization confirmed the successful quaternization of the nitrogen from the P2VP chains. Furthermore, the doublet observed at $\delta = 8.3$ ppm corresponding to the proton (N−CH−) of P2VP at short reaction time (or low conversion) became a singlet at longer reaction time (or higher conversion). Ruiz de Luzuriaga et al.[32] reported similar behavior during the quaternization of poly(4-vinylpyridine) which was attributed to the mobility reduction of monomeric units after quaternization. ^{1}H NMR was used to monitor the kinetics of quaternization of poly(0). The degree of quaternization P2VP increased linearly until 90 h reaching a plateau at 37%. The steric hindrance induced by the neighboring 2-vinylpyridine units could explain the low conversion obtained for the quaternization reaction.

The influence of the quaternization degree of 2-vinylpyridine in the nanostructuration of the thermoset materials was carried out using three PILs with different degrees of quaternization (poly(1) = 7.5, poly(2) = 16.4 and poly(3) = 37). Poly(1), poly(2), and poly(3) were characterized by DSC and TGA prior to blending with epoxy resin.

Figure 5 shows TGA curves of poly(0), poly(1), poly(2), and poly(3). It can be seen that poly(0) only shows one weight loss that starts at 275 °C. This weight loss is attributed to backbone degradation. However, in the case of poly(1), poly(2), and poly(3), quaternized block copolymers, two weight losses were observed. The first one, in the range 175−250 °C which could corresponds to the loss of the bromide anion as alkyl bromide after dealkylation of pyridinium salt.[33] Likewise, these block copolymers show the same weight loss that starts at 275 °C as poly(0). From the first weight drop quaternization degree
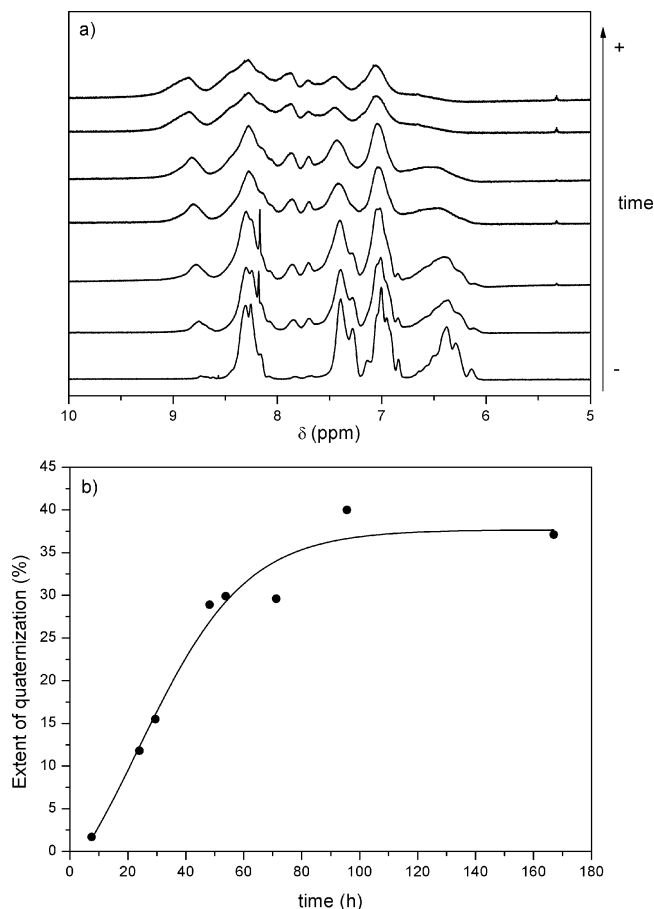
Figure 4. (a) ^{1}H NMR spectra in DMSO-d_6 spectra for quaternization degree and (b) extent of quaternization versus time of reaction of neat poly(0).

could be estimated. As expected, the weight decreased in the range of 175−250 °C increased as the quaternization degree increased. Degree of quaternization determined by TGA confirmed the value obtained by ^{1}H NMR. Nevertheless, it is worth pointing out that the values determined by ^{1}H NMR are more accurate.

DSC curves of the poly(0) and the three PILs with different degree of quaternization are shown in Figure 6. The table inserted in Figure 6 shows T_g values for PMMA block and P2VP block of each block copolymer. The T_g of pure PMMA and P2VP blocks in the poly(0) copolymers were measured to be 95 and 120 °C, respectively. In the case of PILs, on one hand the disappearance of the T_g of PMMA block was observed in all cases. On the other hand, a decrease of the T_g of P2VP block was noticed with increasing the degree of quaternization. The T_g value of P2VP block of poly(1) and poly(2) was measured to be 114 and 98 °C, respectively. Surprisingly, no
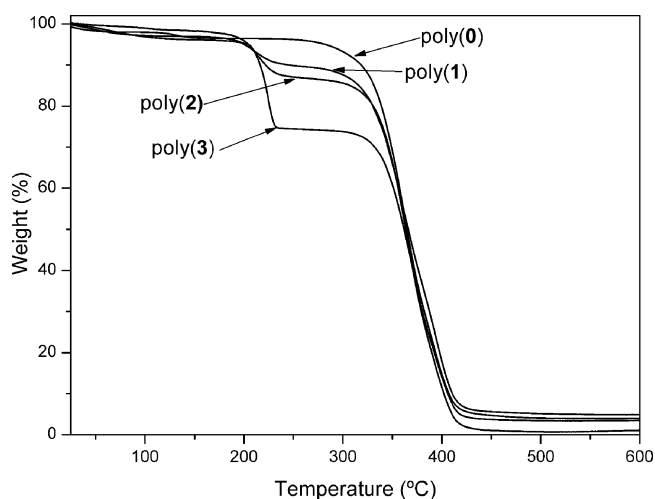
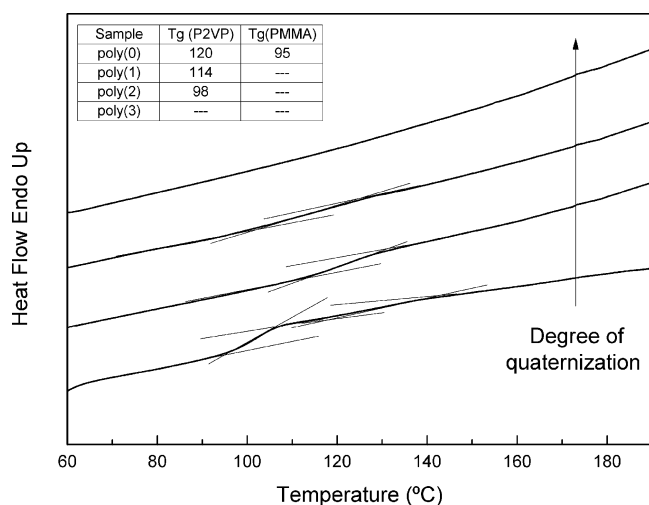**Figure 5.** TGA curves of poly(**0**), poly(**1**), poly(**2**), and poly(**3**).

Sample	Tg (P2VP)	Tg(PMMA)
poly(**0**)	120	95
poly(**1**)	114	---
poly(**2**)	98	---
poly(**3**)	---	---

Figure 6. DSC curves of poly(**0**), poly(**1**), poly(**2**), and poly(**3**).

transition could be detected for the poly(**3**). The decrease of T_g observed for the PILs is influenced by the increasing number of ethyl groups after quaternization inducing higher mobility of the polymer chains which results in a decrease of the glass transition temperature.

After characterization of poly(**0**), poly(**1**), poly(**2**), and poly(**3**), several thermoset materials were prepared at 30 wt % in epoxy resin as already reported.[31] All samples were found to be transparent indicating the absence of macroscopic phase separation, except for the sample prepared with poly(**3**) that was opaque (Figure 7).

DSC curves of the neat epoxy system and their thermoset blends are shown in Figure 8. The inserted table in Figure 8 shows T_g values for neat epoxy system and modified thermoset materials. The T_g measured for the neat epoxy system was 138
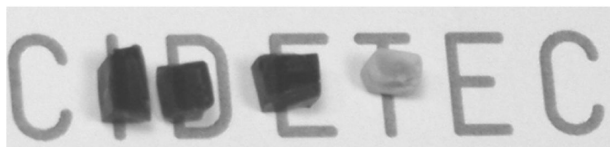

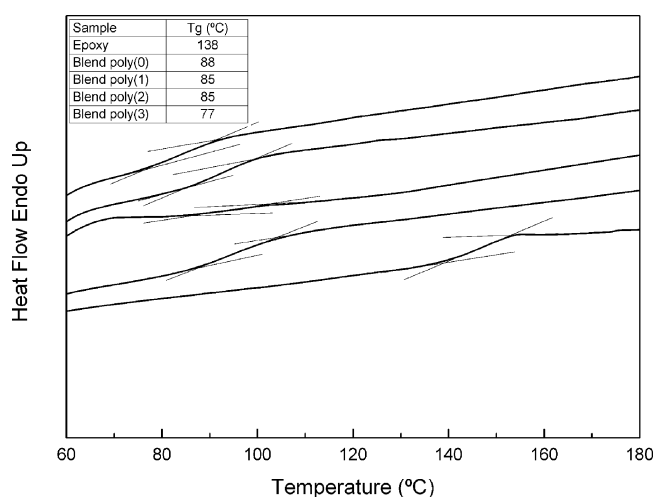**Figure 7.** From left to right sequence of photographs for the obtained thermosets with poly(**0**), poly(**1**), poly(**2**), and poly(**3**).

Sample	Tg (°C)
Epoxy	138
Blend poly(0)	88
Blend poly(1)	85
Blend poly(2)	85
Blend poly(3)	77

Figure 8. DSC curves of neat epoxy system and its blends with poly(**0**), poly(**1**), poly(**2**), and poly(**3**). Table in inset shows the corresponding glass transition temperature of neat and poly(ionic liquid) cured blends.

°C. On the other hand, the T_g for the epoxy-rich phase in modified systems with 30 wt % poly(**1**), poly(**2**), and poly(**3**) decreased with increasing degree of quaternization, ranging from 88 to 77 °C. Several factors could explain the decrease of T_g for cured blends modified with the same amount of block copolymer with different degree of quaternization such as dilution of epoxy groups and an increment of the system viscosity, leading to a decrease in the curing rate. Moreover, the solubility of PMMA block with the epoxy system could explain the decrease of T_g observed. The miscibility of PMMA in an epoxy system was evidenced by the depletion of T_g of the epoxy-rich phase as a result of its miscibility in the matrix.[34,35]

The evolution of self-assembly of the P2VP block at different degrees of quaternization is shown in Figure 9. TEM image of the poly(**0**)/epoxy cured blend (Figure 9a) did not show any nanostructure since both blocks of the copolymer are fully miscible with the epoxy. For cured blends containing poly(**1**), a thermoset material with a well-defined nanostructure was observed. The presence of round spheres corresponding to the coaxial (Figure 9b) and the parallel (Figure 9c) view to the main axis at which the cross sections were prepared, respectively. It was observed that the average diameters of P2VP-*r*-poly(1-ethyl-2-vinylpyridinium bromide) domains were approximately of 38 nm. Similar behavior was found in cured systems containing poly(**2**), where spherical nanostructures could be clearly observed (Figure 9d, coaxial view and Figure 9e, parallel to the main axis) with a diameter of the pattern approximately equal to 27 nm. It should be noted that cured blends containing poly(**3**) were opaque, thus indicating the presence of macroscopic phase separation. TEM images of poly(**3**)/epoxy cured blend (Figure 9f and 9g) showed the absence of nanodomains. Hence, TEM images indicated that the degree of quaternization of poly(2-vinylpyridine) block between 7.5% and 16.4%, allows nanostructuration of the thermoset material. P2VP-*r*-poly(1-ethyl-2-vinylpyridinium bromide) chains form spherical shape inside the epoxy cured system containing the PMMA block. It should be noted that for degrees of quaternization of 37% or more led to macrophase separation of PIL in epoxy cured blends.

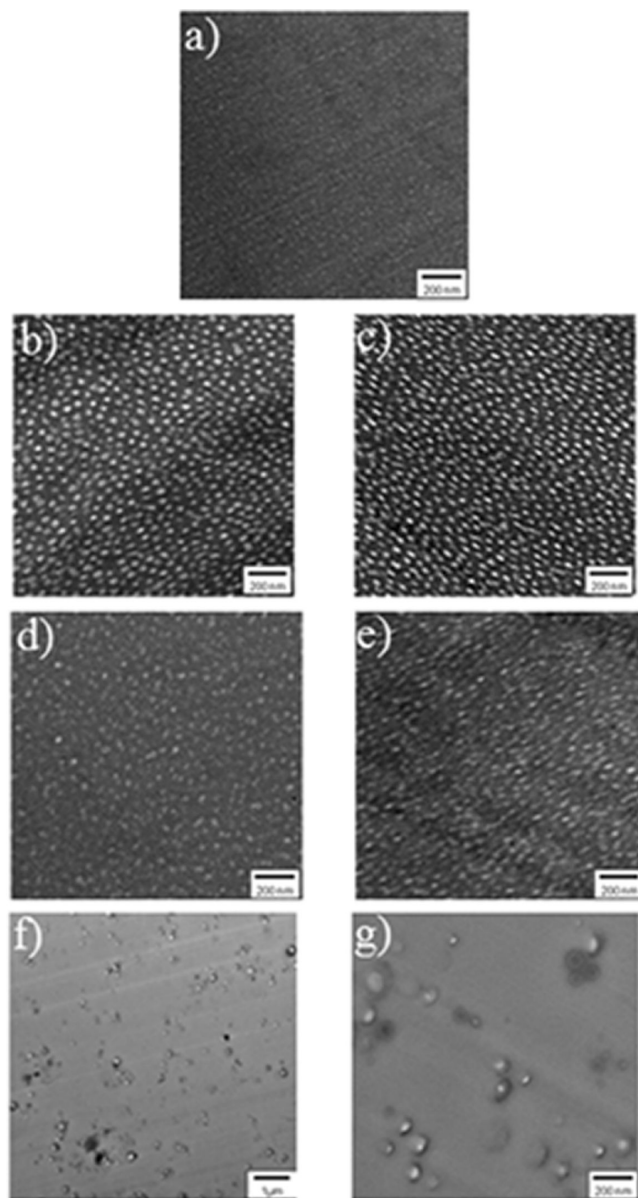Before producing thermoset with poly(**4**) FTIR characterization of poly(**0**) and poly(**4**) was carried out in order to study

Figure 9. TEM micrographs for the blends with 30 wt % poly(**0**) (a), 30 wt % poly(**1**) (b and c), 30 wt % poly(**2**) (d and e), and 30 wt % poly(**3**) (f and g). Scale bar: 200 nm except for part f where it is 1 μm.

Figure 10. FTIR spectra of poly(**0**) and poly(**4**).

Figure 11. TEM micrographs for 30 wt % poly(**4**)/epoxy cured blend (a and b) and magnetization curve of poly(**4**) and 30 wt % poly(**4**)/epoxy cured blend (c).

coordination of iron with pyridine units. Ramos et al[36] studied the complexes formation of poly(4-vinylpyridine) with different transition metals such as cobalt, nickel and iron using FTIR spectroscopy to assess the nitrogen−metal coordination bonds. They found that pyridine stretching band at 1600 cm^{-1} was displaced to higher wavenumber when coordination occurred. Figure 10 shows the infrared spectra for poly(**0**) and poly(**4**). In the presence of iron metal a new absorption band at 1623 cm^{-1} attributed to the new nitrogen−metal coordination bonds was observed. The presence of this new band indicate the coordination of the iron salt with P2VP after [Fe$_3$Br$_{10}^-$] anion exchange.

Poly(**4**) was blended with the epoxy resin and cured. Afterward, this new blend was characterized by carrying out both, TEM and SQUID investigations. Figure 11 shows the TEM micrographs of 30 wt % poly(**4**)/epoxy cured blend (Figure 11a, coaxial view and Figure 11b, parallel to the main
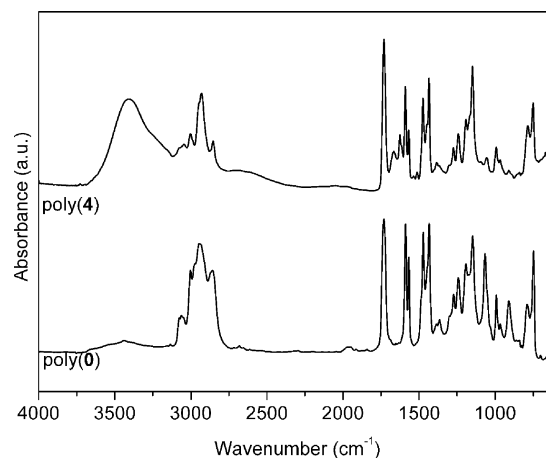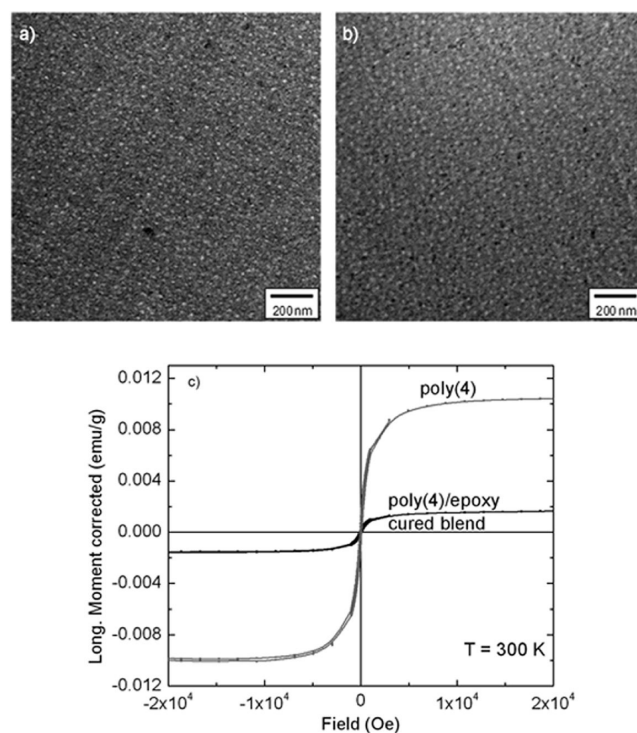
axis). TEM images revealed a well-defined spherical nanostructure of the thermoset material. The size of the spheres in this case was approximately 16 nm. It should be noted that despite having the same diblock copolymer content, the domain size was significantly different. It is well-known that, the physical and chemical properties of PILs can be modified by anion exchange without altering the main structure of the polymer.[37] As a consequence, the miscibility of PILs with organic solvents or water becomes mostly dependent on the anions. This variation of block copolymers solubility influences strongly the morphology and the orientation of nanostructures.[29]

Figure 11c shows the corrected long moment (M) vs magnetic field (H) behavior of samples poly(**4**) and 30 wt % poly(**4**)/epoxy cured blend, after careful subtraction of the diamagnetic background stemming from the organic fraction of

the polymer. For such purpose the high field data of the cyclates were fitted to a straight line with negative slope and this contribution was subsequently subtracted from the data. The resulting hysteresis cycles revealed the presence of well conformed ferromagnetic interactions exhibiting remanence and coercivity. As expected, the reference compound, poly(**4**), showed 1 order of magnitude higher saturated values of the magnetization ($M_s = 1.04 \times 10^{-2}$ emu g^{-1}) when compared to the cured blend 30 wt % poly(**4**)/epoxy ($M_s = 1.68 \times 10^{-3}$ emu g^{-1}).The same trend was observed for the remanence, $M_r = 9.40 \times 10^{-4}$ emu g^{-1} and $M_r = 1.37 \times 10^{-4}$ emu g^{-1}, for poly(**4**) and 30 wt % poly(**4**)/epoxy cured blend, respectively. These discrepancies were not observed in the coercive fields, $H_c = 72$ Oe and $H_c = 83$ Oe 30 for wt % poly(**4**) and 30 wt % poly(**4**)/epoxy respectively, pointing out toward similar levels of magnetic disorder and number of pinning centers in both samples. Differences in the saturated and remanence values of the magnetization of poly(**4**) and 30 wt % poly(**4**)/epoxy are probably due to the dilution of the magnetic entities per mass unit in the blend rather than to a real change in the basics of the ferromagnetic interactions. It is noteworthy that Döbbelin et al.[30] reported the synthesis of novel homopolymeric para-magnetic PIL. In their work, they did not observe a qualitative dependence of the magnetic behavior on the nature of the polymer (imidazolium or diallydimethylammonium-monomers, or the anion, chloride or bromine) used for building up magnetic interactions in their homopolymers. Also, the homopolymers used for their studies did not exhibit any kind of structure related to the assembly of the polymeric chains. As a result, the observed paramagnetic behavior was consistent with a single ion picture of isolated, non interacting magnetic entities (i.e., the anions lying far apart in the proximity of the linear polymer chains). In contrast, our materials, poly(**4**) and poly(**4**)/epoxy cured blend, showed a clear ferromagnetic ordering related to the material composition. Nanostructures in block copolymers are generated by the self-assembly of less miscible blocks. As inferred from the TEM micrographs, our polymeric chains undergo an ordering process that makes the P2VP-*r*-poly(1-ethyl-2-vinylpyridinium Fe$_3$Br$_{10}$$^-$) block to induce spherical nanostructuration (or assembly). This nano-structuration, in turn, allows the confinement of several magnetic anions within these spherical nanostructures, as inferred from the bright spots in Figure 11, which translates into the promotion of strong dipolar interactions between the magnetic entities and the observed ferromagnetic ordering.

In conclusion, a new methodology for the production of nanostructured magnetic thermoset materials without any kind of metal oxide or metal magnetic nanoparticles has been proposed. We have demonstrated that the degree of quaternization of the pyridine block can induce microphase separation through self-assembly of the quaternized pyridine block in the epoxy matrix. When the quaternization degree is higher than the maximum threshold, macrophase separation occurred. Furthermore, anion exchange of corresponding selected poly(ionic liquid)s block copolymer led to the formation of a new magnetic nanostructured thermoset material, which revealed the presence of well-conformed ferromagnetic interactions by exhibiting remanence and coercivity at room temperature.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Matsen, M. W.; Thompson, R. B. *Macromolecules* **2008**, *41*, 1853−1860.

(2) Zhang, D.; Chung, R.; Karki, A. B.; Li, F.; Young, D. P.; Guo, Z. *J. Phys. Chem. C* **2010**, *114*, 212−219.

(3) Diaz, L.; Santos, M.; Ballesteros, C.; Marysko, M.; Pola, J. *J. Mater. Chem* **2005**, *15*, 4311−4317.

(4) Cao, H.; Huang, G.; Xuan, S.; Wu, Q.; Gu, F.; Li, C. *J. Alloys Compd.* **2008**, *448*, 272−276.

(5) Fan, N.; Ma, X.; Ju, Z.; Li, J. *J. Mater. Res. Bull.* **2008**, *43*, 1549−1554.

(6) Wei, X.-W.; Zhu, G.-X.; Xia, C.-J.; Ye, Y. *Nanotechnology* **2006**, *17*, 4307−4311.

(7) Guo, Z.; Lei, K.; Li, Y.; Ng, H. W.; Prikhodko, S.; Hahn, H. T. *Compos. Sci. Technol.* **2008**, *68*, 1513−1520.

(8) Gyergyek, S.; Huskic, M.; Makovec, D.; Drofenik, M. *Colloids Surf., A* **2008**, *317*, 49−55.

(9) Baker, C.; Ismat Shah, S.; Hasanain, S. K. *J. Magn. Magn. Mater.* **2004**, *280*, 412−418.

(10) Guo, Z.; Lin, H.; Karki, A. B.; Wei, S.; Young, D. P.; Park, S.; Willis, J.; Hahn, T. H. *Compos. Sci. Technol.* **2008**, *68*, 2551−2556.

(11) García, I.; Tercjak, A.; Rueda, L.; Mondragon, I. *Macromolecules* **2008**, *41*, 9295−9298.

(12) Garcia, I.; Tercjak, A.; Gutierrez, J.; Rueda, L.; Mondragon, I. *J. Phys. Chem. C* **2008**, *112*, 14343−14347.

(13) Garcia, I.; Ruiz de Luzuriaga, A.; Grande, H.; Jeandupeux, L.; Charmet, J.; Laux, E.; Keppner, H.; Mecerreyes, D.; Cabañero, G. *Mater. Chem. Phys.* **2010**, *124*, 780−784.

(14) Binnemans, K. *Chem. Rev* **2007**, *107*, 2592−2614.

(15) Marcilla, R.; Curri, M. L.; Cozzoli, P. D.; Martínez, M. T.; Loinaz, I.; Grande, H.; Pomposo, J. A.; Mecerreyes, D. *Small* **2006**, *2*, 507−512.

(16) Xie, Y.; Zhang, Z.; Jian, T.; He, J.; Han, B.; Wu, T.; Ding, K. *Angew. Chem. Int. Ed* **2007**, *46*, 7255−7258.

(17) Matsumoto, K.; Endo, T. I. *Macromolecules* **2008**, *41*, 6981−6986.

(18) Green, O.; Grubjesic, S.; Lee, S.; Firestone, M. A. *Polym Rev* **2009**, *49*, 339−360.

(19) Green, M. D.; Long, T. E. *Polym. Rev.* **2009**, *49*, 291−314.

(20) Hayasi, S.; Hamaguchi, H. *Chem. Lett.* **2004**, *33*, 1590−1591.

(21) Mallick, B.; Balke, B.; Felser, C.; A-V., M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7635−7638.

(22) Peppel, T.; Kockerling, M.; Geppert-Rybczynska, M.; Ralys, R. V.; Lehmann, J. K.; Verevkin, S. P.; Heintz, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 7116−7119.

(23) Mecerreyes, D. *Prog. Polym. Sci.* **2011**, *36*, 1629−1648.

(24) Uhrig, D.; W., M. J. *J. Polym. Sci. Part A: Polym. Chem* **2005**, *43*, 6179−6222.

(25) Tsitsilianis, C.; Sfika, V. *Macromol. Rapid Commun.* **2001**, *22*, 647−651.

(26) Sung, H. H.; Jin, K. K. *React. Funct. Polym.* **2009**, *69*, 493−497.

(27) Stavrouli, N. D.; Tsitsilianis, C.; Kiriy, A.; Gorodyska, G.; Stamm, M. *J. Nanostruct. Polym. Nanocomposites* **2005**, *1*, 13−21.

(28) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 3211−3234.

(29) Carrasco, P. M.; Ruiz de Luzuriaga, A.; Constantinou, M.; Georgopanos, P.; Rangou, S.; Avgeropoulos, A.; Zafeiropoulos, N. E.; Grande, H.-J.; Cabañero, G.; Mecerreyes, D.; Garcia, I. *Macromolecules* **2011**, *44*, 4936−4941.

(30) Dobbelin, M.; Jovanovski, V.; Llarena, I.; Claros Marfil, L. J.; Cabañero, G.; Rodriguez, J.; Mecerreyes, D. *Polym. Chem* **2011**, *2*, 1275−1278.

(31) Carrasco, P.; Ruiz de Luzuriaga, A.; Kirsten, M.; Constantinou, M.; Georgopanos, P.; Rangou, S.; Avgeropoulos, A.; Zafeiropoulos, N. E.; Stamm, M.; Grande, H.; Cabañero, G.; Garcia, I. *J Mater. Sci.* **2012**, *47*, 4348−4353.

(32) Ruiz de Luzuriaga, A.; Pomposo, J. A.; Grande, H.; Etxeberria, A. *Macromol. Rapid Commun.* **2009**, *30*, 932−935.

(33) Joule, J. A.; Mills, K., *Heterocyclic chemistry*, 5th ed.; Wiley-Blackwell: London, 2010.

(34) Meng, F.; Xu, Z.; Zheng, S. *Macromolecules* **2008**, *41*, 1411−1420.

(35) Blanco, M.; Lopez, M.; Kortaberria, G.; Mondragon, I. *Polym. Int.* **2010**, *59*, 523−528.

(36) Ramos, J.; Millán, A.; Palacio, F. *Polymer* **2000**, *41*, 8461−8464.

(37) Marcilla, R.; Blazquez, J. A.; Rodriguez, J.; Pomposo, J. A.; Mecerreyes, D. *J. Polym. Sci., Polym. Chem* **2004**, *41*, 208−212.