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Journal:	<i>ACS Applied Energy Materials</i>
Manuscript ID	Draft
Manuscript Type:	Letter
Date Submitted by the Author:	n/a
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Exploring new functionalities for the development of high thermal stability Polypropylene-based dielectrics

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ABSTRACT: The motivation of this study was to explore the viability of a new strategy, aimed at substantially improving both thermal and dielectric performance of polypropylene (PP), especially under oxidative conditions, by preparing in one-single step a self-crosslinkable functionalized PP. For that purpose, an α -olefin bearing the N-alkylpyrrole moiety was copolymerized with propylene, by using metallocene catalysis, and the obtained materials thoroughly characterized. Thermal treatment at processing temperatures of the obtained copolymers proved that, radical chemistry associated to this function provides, *per se*, efficient PP crosslinking. The copolymers show high dielectric performance and retain a flexible behavior, thus breaking new ground in the one-single step preparation of high thermal stability PP-based dielectrics.

The most important challenge in state of the art's BOPP (bioriented polypropylene films) capacitors is to increase the energy density stored under the action of electrical fields, by increasing both the dielectric constant of the insulating material, which is 2.2 in PP films^{1,2}, and the magnitude of the electrical field applied. While the former requires to enhance the ability of the dielectric to separate or polarize electronic charges, the later demands higher thermal and mechanical stabilities, in order to hold usual voltage inputs for BOPP films, which reach about $V = 5 \text{ kV}$ ($E = 500 \text{ MV} \cdot \text{m}^{-1}$)^{3,4}.

One promising route to accomplish the first goal is the insertion of polar groups, either by modifying reactive functionalities, previously anchored, under mild conditions, or by copolymerization of propylene with α -olefins bearing the intended group³. Nevertheless, the pursuit of functionalized polyolefins⁵⁻¹⁸ involves difficulties not only from the synthetic point of view, but also from the point of view of the dimensional stability of modified PP materials. In fact, insertion of comonomers may bring about a significant material softening¹⁹⁻²¹ that would render the dielectric useless. Notwithstanding this picture, the work of Chung *et al.* has clearly shown that low level insertion of polar groups, via metallocene copolymerization, effectively raises the permittivity of PP, without a significant change of the dielectric loss²²⁻²⁵. Furthermore, some of them cause specific interactions or further crosslinking and, thus, provide mechanical and thermal endurance, when the dielectric is submitted to high voltage inputs²⁴⁻²⁷.

Metallocene-based methodology has been proved to be successful and deserves to be developed by searching for other functions, able to directly afford higher permittivity values, as well as enhanced dimensional and thermal stabilities, simply by processing, i.e. without any intermediate copolymer post-modification. Among

functionalities with such potential, we thought about the N-alkyl-pyrrole moiety because of its enhanced propensity to yield benzyl-like radicals through α -hydrogen abstraction, in the presence of peroxides, and to eventually yield intermolecular addition²⁸. Such peculiarity would make it suitable, not only to trap radical activity in initial degradation stages of a thermoplastic polyolefin, but also to prevent mechanical damage by promoting selective chain crosslinking. Furthermore, such thermally promoted radical chemistry would allow reactive processing of PP, in order to get net crosslinking without scission and oxidation, as well as tailored reticulation degrees.

In the light of this, we specifically used 1-(undec-10-ene-1-yl)-1H-pyrrole (UDPy) as a comonomer in polymerization reactions. The long spacer between the olefin and the pyrrole ring assured a minor deactivating influence of the latter, on the coordination ability of the C=C bond with the metallocene active site. Therefore, this comonomer was thought suitable to explore the thermal and dielectric performance of a pyrrol-bearing PP, as a proof of concept of new PP-based films for capacitors.

We first tried the copolymerization of propylene and UDPy by using *rac*-1,1'-dimethylsilylbis(1-indenyl)zirconium dichloride/MMAO at a low T_{pol} , 10 °C, in order to lessen usual molecular weight reduction, associated to metallocene copolymerization²⁹. The activity of the copolymerization was slower than the propylene homopolymerization (samples PP₁₀ and PP₁₀ in table 1) but, contrary to expectations, the copolymer behaved as it were high molecular weight. In fact, PP₁₀ was sparingly soluble in TCE-*d*₂ at 80 °C and the NMR analysis had to be carried out at 100 °C. Both ¹H-NMR (Figure 1) and ¹³C-NMR (Figure S1) spectra of PP₁₀ corresponded to a copolymer containing 1.6 mol% of pyrrole moieties. Assignment of peaks was made from NMR data of UDPy (Figure S2) and those reported for long-chain branched PP^{30,31}. The ¹H-

NMR analysis allowed excluding eventual oxidative coupling of pyrrole units triggered by acids^{32–34}, when the copolymer was subjected to final HCl treatment during precipitation. Both HCl concentration and temperature used were substantially below those employed by Ratcliffe

et al. to prepare polypyrrole by acid catalysis³⁴ (HCl: 0.73 mol·L⁻¹ vs 7.5 mol·L⁻¹ and T: 25 °C vs 100 °C).

Table 1. Polymerization conditions and characterization data of the materials

Sample	T _{pol} (°C)	UDPy/propene (feeding molar ratio)	[Al]/[Zr] molar ratio	UDPy (mol %)		Activity (Kg·mol ⁻¹ Zr)	Mn ^a (g·mol ⁻¹)	Tm ^b (°C)	Fc ^b (wt.%)	mmmm ^c (mol%)
				¹ H-NMR	Micro analysis					
PP ₁₀	10	0	3492	0	0	664	38200	150.8	65.6	88.0
PPy ₁₀	10	0.036	3492	1.6	1.8	51	47800	129.7	48.0	88.6
PP ₂₅	25	0	3492	0	0	737	29000	147.9	63.1	87.7
PPy ₂₅	25	0.067	3492	2.5	3.3	241	35700	121.8	39.4	92.9

a) Calculated from ¹H-NMR spectra; b) Calculated from DSC; c) Crystallinity fraction calculated from ¹³C-NM

Figure 1. ¹H-NMR spectrum of PPy₁₀ in C₂D₂Cl₂ at 100 °C.

The microanalysis of PPy₁₀ verified that the UDPy content measured by ¹H-NMR corresponded to the whole copolymer and not to a soluble fraction (table 1). Consistently, the FTIR spectrum showed the vibration modes of UDPy, except for those of the disappeared vinyl bond: (ν_{C-H}: 3077 cm⁻¹), (ν_{C=C}: 1641 cm⁻¹) and (δ_{C=C}: 909 cm⁻¹) (see table S1 and FTIR spectra in Figure S3, both in supporting information).

On account of the expected crosslinking of the copolymer at high temperatures, ¹H-NMR measurement was considered more appropriate than SEC to make an estimation of the real average polymerization degree, without taking into account chain interconnections. Thus, the relative content of chain ends evidenced a molecular weight increase of PPy₁₀, when compared with the reference PP₁₀ (table 1). Terminal groups were identified as vinylene, vinylidene and isobutylene double bonds, in the 4.5–6.0 ppm range^{35–43} (see Figure S4).

In addition to the molecular weight increase, associated to the copolymerization, it was clear that there should be another process able to account for difficulties observed during NMR work-up. A detailed analysis of the ¹H-NMR spectrum confirmed, indeed, the presence of proton traces at 3.44 ppm and 3.66 ppm, which were ascribed to methine protons arising from coupling between N-alkylpyrrole branches. Such signals are shown in Figure 2 and their assignment was made on the basis of the ¹H-NMR spectrum predicted for the expected chemical structure, according to the distinctive radical reactivity of N-alkylpyrroles²⁸ (see spectrum in Figure S5).

Figure 2. 3.0–4.0 ppm window of the ¹H-NMR spectrum of PPy₁₀.

The spectrum in Figure 2 displays one triplet and one double triplet, slightly above and below the predicted value (3.5 ppm) respectively, which correspond to the diastereotopic methine protons of the resulting two chiral carbons. The identical content of both signals strongly support the radical nature of the crosslinking mechanism.

The insoluble character of PPy₁₀ was clear after hot-pressing at 160 °C, i.e. 30 °C over T_m (see table 1), since the processed film swelled in *o*-dichlorobenzene at temperatures above 90 °C, without achieving dissolution.

The second copolymerization was carried out at 25 °C, with the aim of increasing comonomer content, shortening chain size and making easier characterization work. The obtained copolymer, PPy₂₅, was 2.5 mol% in UDPy with a significantly lower T_m (122 °C) and crystallinity (table 1). In this case, the sample was completely soluble at 80 °C and ¹H and ¹³C-NMR analysis was performed at this temperature (see spectra in Figures S6 and S7). Nevertheless and despite the freely solubility, ¹H-NMR traces of crosslinking were also apparent. Accordingly, the FTIR spectrum of PPy₂₅ exhibited both the signals of PP and those corresponding to the inserted comonomer (Figure S8).

Similarly to PPy₁₀, it was also observed through ¹H-NMR analysis, that the molecular weight was higher than that one of its reference PP, PP₂₅ (table 1). The detected end-cap olefins are shown in Figure S9.

As for the stereoregularity of copolymers, the ¹³C-NMR analysis of methyl signals (19.0-22.5 ppm)⁴⁴ revealed that the isotacticity degree of propylene sequences remained virtually the same of the reference PP, for PPy₁₀, and clearly increased in the case of PPy₂₅ (see contents of isotactic pentads in table 1).

The aforementioned possibility of chain crosslinking during heating arises from the labile character of the α -methylene C-H bonds of N-alkylpyrrole units, which are expected to undergone homolytic scission under the action of heat, oxygen or pre-existing PP hydroperoxides. Thereby, relatively stable benzyl-like radicals are generated and eventually combined with each other, as it has been described in the literature²⁸ and is shown in scheme 1. This process occurs at high temperatures, likely together with the also described radical addition of the above-mentioned radical on another pyrrole ring, and lay behind the pursued stabilization effect of the N-alkylpyrrole function. Such process has been identified, in the course of NMR characterization, and is expected to go further under processing conditions but, fortunately, it seemed not to be decisive to prevent the dissolution of the copolymers at 80 °C or at 100 °C.

Scheme 1. Generation and combination of radicals

TGA analysis of PPy copolymers in air corroborated a significant stabilization effect by the insertion of N-alkylpyrrole units. Figure 3 displays that the initiation temperatures of weight loss (T_i) increased 54 °C and 90 °C for PPy₁₀ and PPy₂₅, respectively. This fact supports the hypothesis about the role of radical chemistry associated

with these groups, namely production of benzyl-like pyrrolyl radicals and further chain interconnection. It is worth remarking that pyrrole moieties not only shift upwards the weight loss starting temperature (T_i), but they act as antioxidant, suppressing the characteristic initial oxygen uptake before weight loss in PP (see expansion in Figure 3).

Figure 3. TGA curves at 10 °C·min⁻¹ for the studied samples in air. Initiation temperatures of weight loss, T_i, are indicated in each case (a colour code is inserted into the graph).

The ability of the N-alkylpyrrole modified PP to undergone crosslinking at processing temperatures by itself, has major implications on the final performance of a PP-based dielectric. Indeed, it addresses the problem of obtaining net reticulated PP, since usual crosslinking processes of this polyolefin do not take place without scissions and oxidation⁴⁵, leading to defective materials with low electrical breakdown strengths. Additionally, it enables ready access to crosslinked PP-based dielectrics simply by taking advantage of processing, without any previous polymer post-modification step.

A qualitative verification of the crosslinking was carried out in copolymer PPy₂₅, by replicating dynamic TGA conditions to further check both solubility and chemical modifications. A sufficient amount of this specimen was heated at 10 °C·min⁻¹, up to 250 °C in both air and N₂ flow. At this temperature, the materials obtained (XPPy₂₅-air and XPPy₂₅-N₂) should be insoluble and FTIR analysis should evidence chemical alterations associated with. Both treatments showed indeed that no weight loss took place and that insoluble materials were obtained in hot *o*-dichlorobenzene, from 90 °C upwards. Furthermore, and surprisingly, the materials did not show any evidence of melting since, although shrunk, the film aspect was preserved and they could still be reprocessed into thin films for FTIR analysis.

FTIR spectra of XPPy₂₅-air and XPPy₂₅-N₂ evidenced little changes concerning the content of C=O and C=C groups, when compared with the virgin copolymer film (see Figure S10). Only traces of chain scission were hardly noticeable by means of a shoulder at 887 cm⁻¹, which corresponds to chain-end vinylidene groups.

As for the thermal stability under N_2 , the T_i value was also significantly improved in both copolymers, 30 °C for PPy₁₀ and 26 °C for PPy₂₅ (see Figure S11). In this case, the effect may be related to the specific evolution of N-alkylpyrroles under pyrolysis conditions. In this respect, some ancient works reported that these pyrroles are very stable compounds, which isomerize in the 460–570 °C interval to the 2- and 3-alkyl substituted isomers^{46–48}. A similar process in a PP matrix might involve radical chain exchange between N-pendant pyrroles and, eventually, lead to a more stable crosslinked material.

Lastly, we checked the dielectric performance of the processed copolymers. The DETA analysis, performed in a wide temperature interval (–140 °C to T_m –30 °C) and for voltage frequencies in the 10^{-1} Hz to 10^5 Hz range, revealed the increase of the dielectric constant (ϵ_r) in the copolymers, with respect to PP, as it is shown in Figure 4. This change was ascribed to the polarizability of pyrrole moieties inserted but, unlike the flat responses of their corresponding PP, the ϵ_r of the copolymers was found to exhibit a frequency dependent maximum in the –30 °C to 80 °C window. It is worth remarking that the associated dielectric loss ($\tan \delta$) gain in the same temperature interval remained quite low (see Figure S12). As matter of fact, $\tan \delta$ reached 0.004 and 0.007 as a maximum in PPy₁₀ and PPy₂₅, respectively. That means lower values than those reported for functional PP samples prepared by metallocene catalysis and subsequent multistep modification²⁵. Furthermore, $\tan \delta$ becomes even lower (under 0.003) from room temperature upwards and for voltage frequencies equal or under 10^2 Hz.

Further crosslinking of the processed PPy₂₅, through thermal treatment in air up to 250 °C, restored the typical ϵ_r value of PP (Figure 4), while keeping the characteristic loss tangent behavior of the original PPy₂₅ film (Figure S12). In any case, the material retained both flexibility and high dielectric performance.

Figure 4. Dependence of the dielectric constant on temperature and voltage frequency. A color code is inserted into the Figure for samples PPy₁₀, PPy₂₅ and XPPy₂₅-air.

At this point of the work, it is worthwhile to highlight, first, that preparation of PP-based copolymers containing N-alkylpyrrole units is possible through simple metallocene

catalysis and, secondly, that the copolymers are thermoplastics with a quite sensitive microstructure to thermal treatment.

From the point of view of their prospective production and application in capacitors, the most relevant contributions are; on the one hand, that these materials are self-crosslinkable PP, just by processing without any intermediate modification step. On the other, that they are thermally stable, non-melting and flexible materials, characterized by higher dielectric constants than the PP and energy losses that meet the requirements to be used as dielectrics.

ASSOCIATED CONTENT

Supporting Information

Procedures for the synthesis of 1-(undec-10-ene-1-yl)-1*H*-pyrrole, polypropylene samples and copolymers. Processing of materials, Solubility tests and Characterization of samples (Microanalysis, NMR, FTIR, TGA, DSC and DETA) Table S1. Assignment of 1-(undec-10-ene-1-yl)-1*H*-pyrrole (UDPy) FTIR peaks; Figure S1. ¹³C-NMR spectrum of PPy₁₀; Figure S2. ¹H-NMR spectrum of 1-(undec-10-ene-1-yl)-1*H*-pyrrole; Figure S3. FTIR spectra of the UDPy comonomer, PP₁₀ and PPy₁₀; Figure S4. Olefinic window of ¹H-NMR spectra for samples PP₁₀ and PPy₁₀; Figure S5. Predicted ¹H-NMR spectrum for the crosslinking structure model; Figure S6. ¹H-NMR spectrum of PPy₂₅; Figure S7. ¹³C-NMR spectrum of PPy₂₅; Figure S8. FTIR spectra of the UDPy comonomer, PP₂₅ and PPy₂₅; Figure S9. Olefinic window of ¹H-NMR spectra for PP₂₅ and PPy₂₅; Figure S10. FTIR spectra of the samples in the C=O and C=C window; Figure S11. TGA curves at 10 °C·min⁻¹ for the studied samples in N_2 ; Figure S12. Dependence of the dielectric loss of the samples on temperature and voltage frequency.

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Notes

The authors declare no conflict of interest.

ACKNOWLEDGMENT

The financial support from project: *Polymeric Nano-dielectrics*, Proyecto Intramural Especial, PIE202060E215 (CSIC, Spain) is greatly acknowledged. A. Martín Lorenzo thanks the Universidad de Educación a Distancia (UNED) and the Consejo Superior de Investigaciones Científicas (CSIC) for the opportunity of performing her final degree project.

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