New Copolymers with Heterocyclic Pendant Groups Obtained from PVC Using Microwave-Assisted Process

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ABSTRACT: We report the synthesis of new copolymers from poly(vinyl chloride) (PVC) with 1,2,4-triazol-5-yl-sulfanyl pendant groups (PVCT) by nucleophilic substitution using microwave energetic sources. By comparing the synthesis of PVCT between microwave and thermal conditions, it was found that the use of microwave-assisted process led to higher conversion levels than that of the thermal synthesis. Moreover, significant decrease in reaction times was obtained for the microwave assisted synthesis, which avoided secondary reactions. Conversion yields were calculated from elemental analysis and the molecular weighs were analyzed by means of SEC. The molecular structures of the new copolymers were confirmed by FTIR, ^{13}C NMR and ^{1}H NMR spectroscopies. The morphology of the new copolymers was analyzed by SEM. Thermal properties were studied by TGA and DSC techniques. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 951–956, 2011

Key words: microwave-assisted; chemical modification; PVC; 1,2,4-triazol-5-yl-sulfanyl pendant groups

INTRODUCTION

The PVC is now one of the world's main polymers and a large amount of PVC is produced worldwide for its superior mechanical and physical properties. Its applications are well known in construction, as water pipes, for packaging purposes, and in the medical area.[1,2] Many works on the improvement of PVC's properties have been carried out by adding plasticizers, heat stabilizers, lubricants, fillers, and other polymers, etc.[3] PVC was chosen because the nucleophilic substitution of chlorine atoms allows a highly controlled introduction of grafted groups when appropriate reaction conditions are employed,[4,5] in several cases the chemical modifications of PVC can be generally achieved by nucleophilic substitution reaction of chloride atoms with aromatic thiol compounds.[4,6]

Conversely, the polymers containing heterocyclic moieties have a great interest due to their intriguing topologic architecture and vast application in many fields.[7] Previously, we have described the synthesis of copolymers with heterocyclic pendant groups, by chemical modification, for its use as a gravel-pack carrier fluid,[8] completion fluid or fracturing fluid.[9,10] The properties of these new materials are significantly different from their precursors. With regard to safety, this methodology avoids the use of monomers that are, in most cases, very toxic.

Among the many heterocycles, the *N*-heterocyclic groups are well-known for their ability to coordinate metals,[11–14] for example tetrazole and triazole species are used as bridging ligands in coordination chemistry.[15,16] In search of new materials capable of capturing heavy metals, in previous article we reported the modification of an industrial polymer fiber capable to remove copper from an aqueous solution.[16]

A number of synthetic strategies are known for the preparation of new materials, but several disadvantages associated with long reaction times, use of hazardous solvents, moderate yields and secondary reactions avoid them to be fully exploited.[4,17–19] The development of eco-friendly synthetic methods, such as microwave radiation, allows the synthesis of new materials overcoming the drawbacks mentioned above.[20] Taking into account that the copolymers containing heterocyclic pendant groups, obtained from chemical modification of a commercial polymer, present great interest due to their possible application on the metal remove, we report the first synthesis of novel copolymers from PVC with 1,2,4-triazol-5-yl-sulfanyl

TABLE I
Experimental Reaction Conditions and Microanalysis Results for the New Copolymers

	PVC:3TTA	T (°C)	t (min.)	N (%)	S (%)	C (%)	N/C	S/C	Conv. Degree
PVCT-T3[a]	1 : 1	60	1800	4.44	3.42	40.91	0.11	0.08	13.42
PVCT-T4[a]	1 : 1	60	2880	7.68	5.73	41.22	0.19	0.14	23.22
PVCT-MW2[b]	1 : 1	40	30	2.54	1.90	39.55	0.06	0.05	7.68
PVCT-MW4[b]	1 : 1	60	30	2.54	1.95	39.58	0.06	0.05	7.68
PVCT-MW5[b]	1 : 2	60	30	5.92	4.57	40.16	0.15	0.11	17.90
PVCT-MW6[b]	1 : 2	60	60	6.01	4.51	39.65	1.33	0.11	18.17
PVCT-MW7[b]	1 : 2	60	120	8.38	6.45	42.59	0.20	0.15	25.34
PVCT-MW8[b]	1 : 4	60	30	8.03	6.16	44.05	0.18	0.14	24.28
PVCT-MW9[b]	1 : 5	60	30	7.83	5.98	40.48	0.19	0.15	23.68
PVCT-MW10[b]	1 : 2	80	30	15.29	11.73	42.65	0.36	0.28	46.23
PVCT-MW11[b]	1 : 2	80	60		5.90	39.00	0.20	0.15	23.13

[a] Experiments performed with thermal source.
[b] Experiments developed with microwave radiation.

as pendant groups (PVCT) by nucleophilic substitution. Microwave-assisted process was used to optimize the conditions to obtain a high conversion degree, as well as we perform the traditional thermal procedure to discuss the differences between both techniques. Chemical constitution was elucidated by means of elemental analysis and the molecular structures were confirmed by FTIR and NMR spectroscopies, meanwhile the molecular weight was performed by size exclusion chromatography (SEC).

EXPERIMENTAL

General methods

Commercial polymerized PVC with molecular weight (MW) of 80,000 g/mol, 3-thiol-1,2,4-triazol (3TTA), metallic sodium (Na°), sodium hydride (NaH), absolute ethanol (EtOH), cyclohexanone, tetrahydrifurane (HPLC grade), and deuterium solvents were obtained from commercial suppliers (Aldrich Co). Cyclohexanone was doubly distilled, whereas the other compounds used in the synthesis were of commercial high purity grade, and used without further purification. The corresponding sodium salts were obtained by reaction with stoichiometric amounts of sodium ethoxide, in THF. The solution was evaporated with a vacuum pump until constant weight.

Microwave-assisted synthesis

As mentioned in previous section, a salt of 3TTA was prepared. PVC modification was carried out in the CEM Discover Microwave (300 W, power max ON), with constant agitation. PVC (100 mg) and the 3TTA salt (in several molar ratios) were dissolved in 5 mL of cyclohexanone and added to the microwave tube test, at different temperatures and/or reaction times.

All reactions were stopped by precipitating the mixture in cold methanol/water (2/1 volume ratio). The modified polymers were purified using THF/methanol as a solvent-precipitant system.

Thermal synthesis

PVC modification was carried out in a 250-mL flask equipped with a magnetic stirrer. PVC (500 mg, 8 mmol) and the 3TTA salt (1 : 1M ratio) were dissolved in 50 mL of cyclohexanone and added to the flask. The reaction started at 60°C under mechanical stirring in a N_2 atmosphere. Samples were taken at different reaction times (See Table I) to study the reaction progress. Samples were stopped by precipitating the mixture in cold methanol/water (2/1 volume ratio). The modified polymers were purified using THF/methanol as a solvent-cosolvent system. The different reaction conditions (including thermal and microwave-assisted) are shown in Table I.

General measurements

Elemental analysis were carried out in a Carlo Erba EA 1108.

The molecular weight distribution and the average molecular weights of the soluble degradation residue were determined by SEC with a LKB-2249 instrument at 25°C. Two series of μ-Styragel columns, ranging in pore size 105, 104, 103, 102 E for the modified asphalt and 500, 500, 100 Å for the base asphalt, were used with THF as an eluent. The sample concentration was 15–20 mg mL^{-1} and the flow rate was 0.5 mL min^{-1}. A UV detector Shimadzu SPD 10A was used at 254 nm, and it was coupled with refractive index detector. The calibration was performed with narrow polystyrene standard samples (Polyscience).

Fourier Infrared transmission (FTIR) spectra of the samples were performed on a Nicolet FT-IR Instrument 510P. For this purpose, KBr and solid polymer pellets were prepared.

Nuclear magnetic resonance (NMR) spectra were obtained on a Brucker AC 200 MHz or Brucker 500 MHz spectrometer, using DMSO-d$_6$ and THF-d$_8$ as solvent.
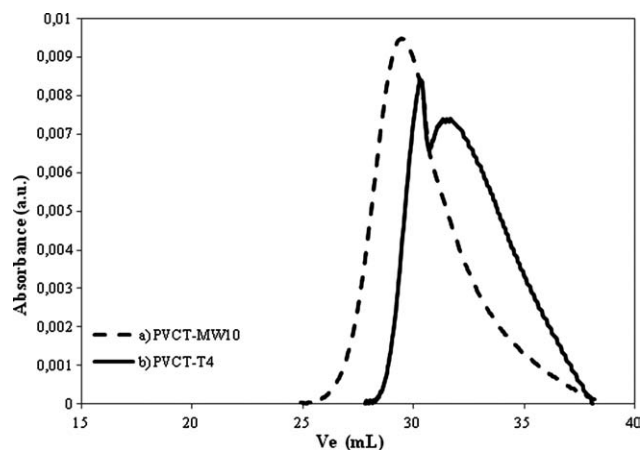
Figure 1 The elution profiles of: (a) PVCT-MW10 and (b) PVCT-T4.

Differential scanning calorimetry (DSC) measurements were performed on a TA Q seriesTM Q20-1041 and the program to run the samples was Advantage for Q Series Version 2.8.0.392, Thermal Advantage Release 4.8.3, Copyright(c) 2001 - 2007, TA Instruments - Waters LLC. The program analysis was carried on a TA Instrument Analysis 2000 for Windows 2000/XP, Version 4,4 A Build 4.4.05, Copyright (c) 1998 - 2006, TA Instruments - Waters LLC. We used 1.5-2.5 mg of sample weights in aluminum pans. The equipment was calibrated with indium standard. The samples were heated from 20 to 150°C at a heating rate of 5°C/min, under N_2 atmosphere.

Thermogravimetry (TGA) was carried out on a TGA-51 Shimadzu thermogravimetric analyzer. The nitrogen flux rate was 40 mL/min and the temperature range was from 25 to 500°C at a heating rate of 5°C/min with sample weights of 4.0-6.0 mg.

Field emission scanning electron microscopy

The new copolymers were studied by means of measurements FEGSEM Zeiss LEO 982 GEMINI.

RESULTS AND DISCUSSION

Chemical characterization

The results of elemental analysis, calculated N/C and S/C ratios and conversion yields for the PVCT copolymers are also listed in Table I. In this table we omitted the elemental analyses of PVCT-MW1, PVCT-MW3 PVCT-T1, and PVCT-T2, because the conversion degrees were very low or practically zero.

Herrero et al.[21] described that the nucleophilic substitution on PVC competes with the degradation process at long reaction times, so we performed the chemical modification in thermal condition up to 48 h of heating. Conversely, different microwave-assisted

conditions were studied; we observed that longer reaction times did not imply larger conversion yields.

Temperature is another parameter to take into account, since at higher temperatures there is a competition between the nucleophilic substitution with the elimination reaction.[22] We performed the experiment at different temperature and we observed that temperature values higher than 80°C did not lead to higher conversion degrees.

The molar ratio between PVC and the 3TTA salt were also analyzed, and found that ratio larger than 1 : 2 (PVC:3TTA salt) did not improve the substitution reaction, this fact could be explained taking into account the steric hindrance produced by the presence of heterocyclic moieties. We concluded that the highest degree conversions were obtained with microwave irradiation for 30 min, at 80°C with a 1 : 2M ratio (PVCT-MW10) while thermal energy the best conditions were: 2880 min, at 60°C with 1 : 1M relationship (PVCT-T4).

Because of the incorporation of S-triazolyl pendant groups to the polymer structure, an increase in nitrogen and sulfur contents (percentages) occurs. Thus, the N/C and S/C ratios become larger with the increase of conversion. This increase suggests that the higher the number of bulky heterocyclic pendant groups on the polymer backbone, the larger the separation between chains, thus allowing a more effective reactant attack. We observed a similar situation in the modification of PAM.[9]

Size exclusion chromatography

To analyze the molecular weights distribution in the samples of highest level of conversion (PVCT-MW10 and PVCT-T4) we performed the gel permeation chromatography of them. The elution profiles of PVCT-MW10 [Fig. 1(a)] showed a normal pattern, according with only one mechanism reaction involved. Conversely, the PVCT-T4 chromatogram displayed a bimodal pattern [Fig. 1(b)], suggesting that probably two mechanisms were carried out simultaneously, elimination and substitution. The elimination process can be justified due to the large time reaction involved

TABLE II
Data Obtained from SEC for PVC and Copolymers PVCT-T4, and PCVT-MW10

Sample	Elution volume (mL)	M_w	M_n	Polidispersity
PVC	27.81	56,991	33,500	1.7
PVCT-MW10	31.51	35,600	9,400	3.8
PVCT-T4	30.35	28,900		
	31.51	15,900		
	Average distribution	15,800	5,700	2.8
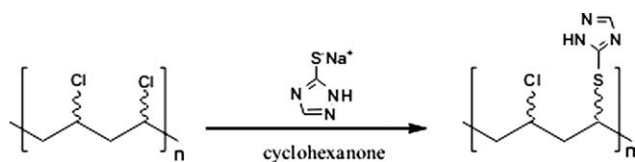
Scheme 1 Nucleophilic substitution of PVC with 3TTA salt.

in the synthesis of PVCT-T4. In Table II we show the experimental data of SEC results.

Characterization by FTIR

In Figure 2 we compare the spectrum of the precursor (PVC) with the spectra of the copolymer PVCT-MW10 and PVCT-T4. The FTIR spectrum of PVC exhibited only a few signals: one under 3000 cm^{-1} (C(sp^3)-H) and bands between 1000 and 400 cm^{-1}, whereas the FTIR spectra of the copolymers, PVCT-MW10 or PVCT-T4, showed signals corresponding to the heterocyclic moiety: a band around 3400–3150 cm^{-1} corresponding to the N—H stretching and a broad band above 3000 cm^{-1} attributable to the C(sp^2) —H stretching. The signals around 1650 cm^{-1} (C=N) and 1480 cm^{-1} (C—N) 1400 cm^{-1} were taken into account to study the chloride substitution. The signals between 1000 and 400 cm^{-1} remained in the copolymers, thus showing that chloride atoms are also present in the polymeric materials.

Nuclear Magnetic resonance spectroscopy

From ^{1}H NMR spectrum, the chemical modification can be observed due to the appearance of signals at 7.9 ppm and 8.7 ppm corresponding to C—H and 8.7 ppm (N—H) corresponding to the heterocyclic moiety. In PVC spectrum, the methylene protons appear around 2–2.5 ppm and the methines (CH-Cl protons) between 4.2 and 4.6 ppm.[23] In the PVCT-T4 and PVCT-MW10 spectra, the signals of the methylene
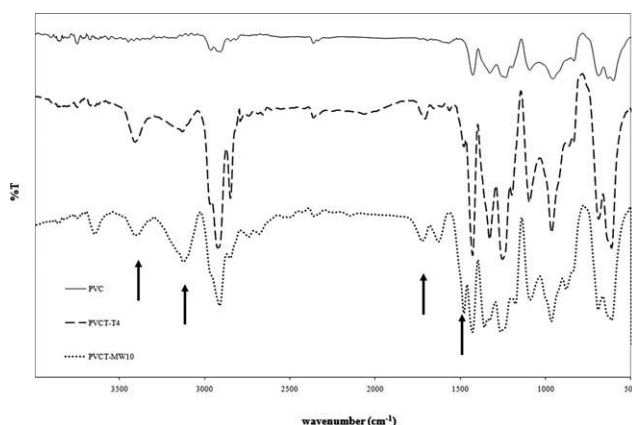

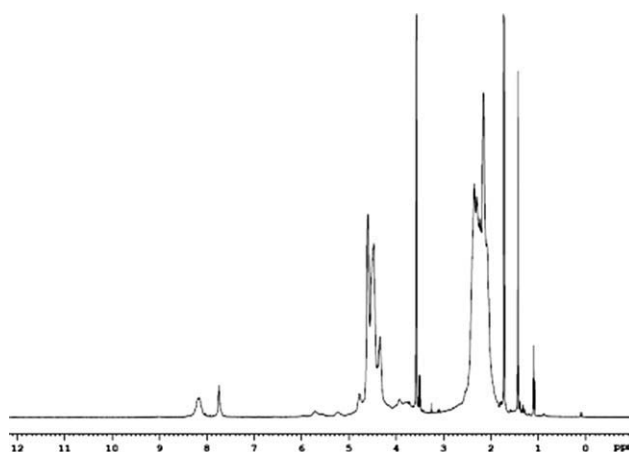**Figure 2** FT-IR spectra of PVC, PVCT-T4, and PVCT-MW10.

Figure 3 ^{1}H NMR spectrum of PVCT-T4.

and methine protons appear as broad signals at high fields: 1.8–2.9 ppm and 3.9–4.8 ppm, respectively, this fact can be explained by the effect of the sulfur atom provided by the nucleophilic substitution.

It is important to observe that in ^{1}H NMR spectrum in THF-d$_8$ of PVCT-T4, there are also two broad peaks at 5.2 and 5.7 ppm due to the presence of olefinic protons, which can came from the undesirable elimination reaction, thus confirming the data obtained by SEC (Fig. 3).

The ^{13}C NMR spectra (Fig. 4) in DMSO-d$_6$ as solvent of PVCT-MW10 and PVCT-T4 are characterized by two broad peaks at 43 and 58 ppm, which can be attributed to methylene and methine carbon, respectively. The assignments were confirmed by heteronuclear bidimensional experiments. Signals that appear at 145 ppm are attributed to the C=N of the heterocyclic pendant groups.

Thermal analysis

Thermogravimetry analysis

Thermal stabilities of all samples were studied by TGA, however in Figure 5 we only show the most representative samples (PVCT-T4 and PVCT-MW10)
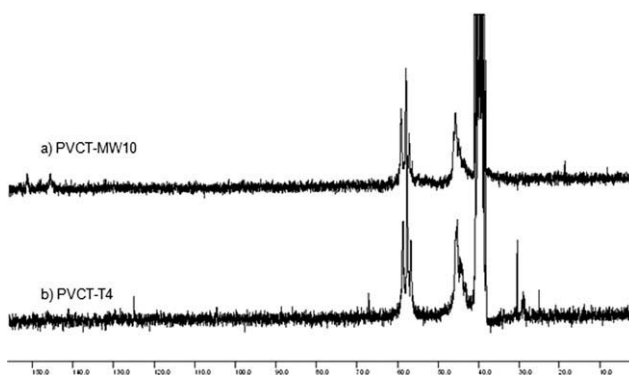

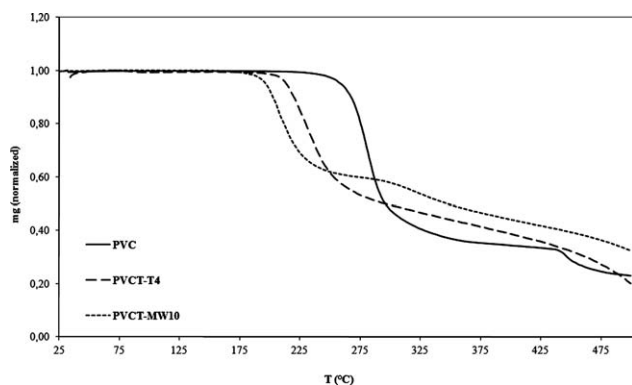**Figure 4** ^{13}C NMR spectra of (a) PVCT-MW10 and (b) PVCT-T4.

Figure 5 Thermogravimetric analyses of PVC, PVCT-T4, and PVCT-MW10.

TABLE III
T_g **Values of PVC, PVCT-MW10, and PVCT-T4**

Sample	T_g (°C)
PVC	84.3
PVCT-MW10	95.7
PVCT-T4	89.8

respect to the precursor (PVC). From these data it is concluded that the new copolymers decreased their stability as compared with PVC. For all the samples studied, the first weight loss process corresponded to the degradation of the chain sequences containing the most labile chlorine atoms.[22] At this point, we observed that in the modified polymers these weight losses decreased as compared with the loss observed for PVC, thus confirming that the chlorine atoms were successfully substituted with heterocyclic moiety. The second weight loss process corresponded to the complete degradation of the polymeric system.

Differential scanning calorimetry

In general, T_g values depends on the chain segment mobility, in our experiments, the original molecular motions of the main chain of PVC were influenced by the introduction of heterocyclic groups, which caused a different physical interaction between the chains. The T_{gs} of the new copolymers were higher than that of the precursor polymer (see Table III). This fact could be explained by the fact that in PVC only Van der Waals forces are observed, while in PVCT-MW10 interactions between chains are also produced due to the presence of 1,2,4-triazol-5-yl-

sulfanyl pendant groups. These heterocyclic substituents are capable of producing hydrogen bonds, which need more energy to be overcome.

Scanning electronic microscopy

SEM micrographs of PVC and PVCT-MW10 are shown in Figure 6(a,b). In Figure 6(a) we can observe that the surface morphology of the original PVC is generally smooth, homogeneous, and featureless. However, the SEM photograph of PVCT-MW10 [Fig. 6(b)] shows that the material is heterogeneous, with numerous micropores on the top surface (0.16–2.6 μm). Therefore, we can conclude that this drastic morphological modification is due to the substitution of chloride atoms by heterocyclic moieties, which significantly affects the shape and distribution of the polymer chains.

Metal-polymer interaction

A film of PVCT-MW10 was prepared dissolving the sample in THF and placing it on a watch glass and evaporating the solvent. Then, the film was added to a flask with a 3 ppm Cu (II) solution, at pH 5. The film and the solution were mixed for an hour at room temperature. After that, the film was filtered and washed several times with water. FTIR analysis was performed for the dry film of PVCT-MW10 which had been interacting with Cu (II) (PVCT-MW10 Cu (II)). The results showed (Fig. 7) that the signals corresponding to the N-H stretching (around 3400–3150 cm^{-1}) disappeared and that the signals around 1650 cm^{-1} (C=N) and 1480 cm^{-1} (C—N)
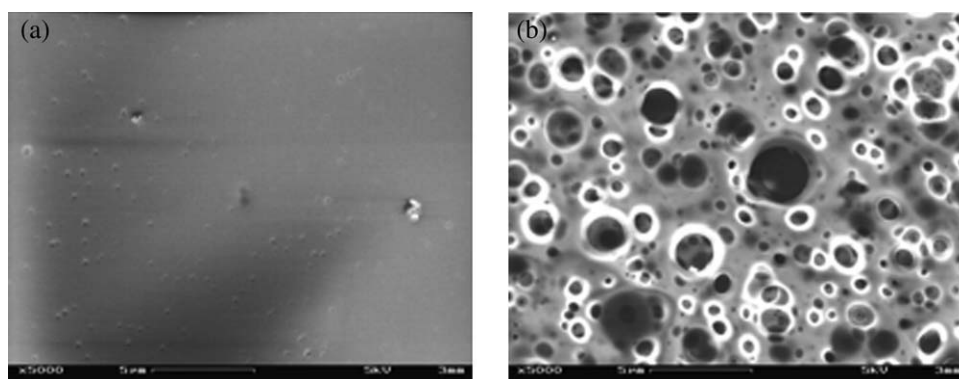

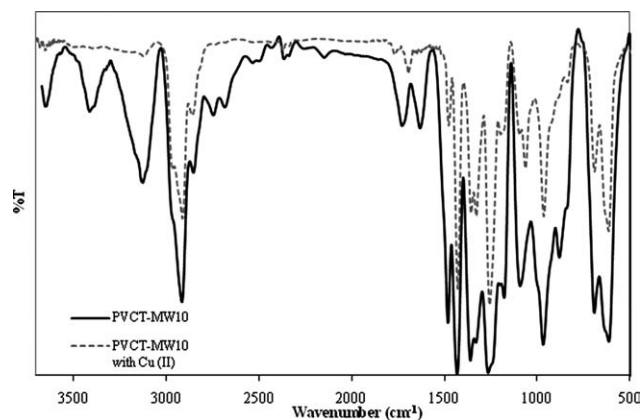**Figure 6** ESEM images of (a) PVC and (b) PVCT-MW10.

Figure 7 FTIR of PVCT-MW10, and PVCT-MW10 with Cu (II).

1400 cm^{-1} were modified and moved to higher wavelengths; so, the signals of the atoms involved were modified because of the presence of Cu (II) in the polymer structure. On the other hand, the TGA showed two steps with a different percentage of loss weight with respect to its precursor; there was a significant residue mass due to the inorganic material, which was also observed when we performed the elemental microanalysis (inorganic residue 6.76%). These facts led us to conclude that an interaction between the polymer and the metal ion had occurred.

CONCLUSIONS

The PVCT series were obtained by nucleophilic substitution of PVC with 1,2,4-triazol-5-yl-sulfanyl groups. We analyzed different conditions, PVCT-MW10 was the copolymer obtained with the highest degree conversion (46%), from the eco-friendly synthetic method for 30 min, at 80°C and at a 1 : 2M ratio minor reaction time, while with the thermal process we can obtained a sample (PVCT-T4) with only 23% of conversion degree.

It is to be mentioned that with microwave sources the nucleophilic substitution could be performed successfully with the highest conversion levels and without competition with elimination reaction.

According to thermal analysis, the PVCT series turned out to be stable up to 200°C approximately. Conversely, the PVCT copolymers showed a T_g higher than that of PVC, which can be explained by the presence of polar heterocyclic groups, capable of forming hydrogen bonds.

Preliminary results indicate that PVCT-MW10 interacts effectively with heavy metals, such as Cu (II). Further researches about this application are in progress.

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