Multifunctional Covalent and Ionic Coupling Agents of Maleic Anhydride Modified Polyethylene

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ABSTRACT: Amine and alcohol functional dendritic polymers were used as covalent coupling agents for maleic anhydride grafted polyethylene and their efficiency compared with metallic salt and zinc acetate, acting as an ionic coupling agent. The crosslinking reactions in the molten state were carried out at 150°C in an internal mixer and the resulting modified polyethylenes were characterized by dynamic mechanical analysis and Small angle X-ray Scattering. These agents led to efficient coupling and crosslinking. The covalent coupling reactions were conducted in a heterogeneous multiphase system: The kinetics of crosslinking depends on the nature of the coupling agent: at 150°C, the reactions were completed within 5 min. with the amine hyperbranched polymer and 20 min. with the alcohol functionalized dendritic polymer. The zinc acetate forms ionic interactions with the grafted polyethylene in less than 1 min. Ionic interactions are thermo mechanically reversible; they correspond to electronic density fluctuations evidenced by SAXS. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2605–2610, 2007

Key words: polyethylene (PE); dendrimers; crosslinking; viscoelastic properties; X-ray

INTRODUCTION

Polypropylene (PP) and polyethylene (PE) recycling as compatibilized polymer blends in still a difficult route because of the difficulties in controlling the interfacial tension and cohesion. In our precedent articles,[1,2] maleic anhydride modified PE (PEgMA) reaction through the graft succinic anhydride or acid groups with a dioxazoline or a diamine coupling-agent were reported. Due to the relative low functionality of the used reactants (PEgMA and coupling agents), the crosslinked part of the issued material was relatively low (lower than 35 wt %). In this study, multifunctional coupling-agents were chosen to increase the crosslinking efficiency: the effect of increasing the mean functionality of the used reactants upon the coupling reaction, the structure of the obtained polymers and also the compatibilization mechanism of PP and PE was analyzed.

Moreover, multifunctional coupling agents leading to reversible or nonreversible reactions were chosen to address the migration effect of the compatibilization agent on the reorganization of the blend interface and on the resulting microstructure of the blends.

In this study, amine functional dendritic polymers were chosen as coupling agents leading to ''non reversible'' crosslinking reaction whereas alcohol functionalized dendritic polymers and zinc acetate were chosen as covalent and ionic coupling agents for reversible molecular association reactions.

Dendritic polymers synthesis and structure are relatively well-established.[3,4] Their influence on the interface in polymer has been also evidenced.[5] Moreover, the complex ionic structure formed by adding a metallic salt into a polymer having polar sites may confer comparable properties to the material.[6–9]

Typical properties of ionomers are due to their composition and structure. They are generally composed of a hydro carbonated matrix with a low dielectric constant and ionic groups that can interact leading to organized phases dispersed in a matrix.

These ionic groups present different levels of organization:

i. *Ionic pairs:* They are composed of cations and anions associations, in which the charge equilibrium is respected. The ionic pairs can also contain non ionic segments and their structure depends on the cation.[10–13]

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ii. *Multiplets:* They are composed of several ion pairs. The number of ion pairs depends on their nature and do not generally exceed eight. Multiplets can also contain covalent entities. They are often considered as spherical.[14]

iii. *Clusters:* They are composed of associated multiplets.

Multiplets presence in ionomers and their structure are often characterized using diffraction techniques.[15–17]

For polymer blends, the compatibilization through reversible linkage at the interface may be of special interest because such molecular associations can be broken at high temperature or by shear.[18] Thus, the systems can be easily transformed by the conventional processes, like extrusion or injection molding. For attending the main goal of this work, compatibilization of blends of polymers, it was shown that the interfacial coupling by ionic interactions is an interesting solution since the interactions are stable after cooling.

EXPERIMENTAL

Materials

The maleic anhydride grafted PE bears the trade name of PEgMA XA255 and was supplied by Solvay. The molecular mass are M_n = 19,600 g mol^{-1}, M_w = 93,100 g mol^{-1}, the grafting degree: 0.18 maleic anhydride wt %, resulting in a PE grafted chains fraction close to 36%.

Covalent coupling agents

The amine coupling agents were a bifunctional aromatic amine, (4,4′-methylene) bis (2,6-diethylaniline) (MDEA), an aliphatic amine, amino polyoxypropylenes (T403) having an average functionality of 2.8 and a second generation dendritic polymer (ADP) with an average functionality f = 12. All amines were purchased from Aldrich.

Alcohol functionalized Dendritic polymers (HDP) of second generation (number of alcohol functions per molecule f = 16) and fourth generations (f = 64) Boltron® were supplied by PERSTORP.

Ionic coupling agents

The ionic coupling agents, sodium hydrogenocarbonate and zinc acetate, were delivered from Aldrich.

All the coupling agents were used as received. For covalent coupling agents, the stoichiometric ratio x was defined as the number of functions in the coupling agent (amine or alcohol groups) per anhydride function in PEgMA.

For ionic coupling agents, the stoichiometric ratio x was defined as the number of cations Zn^{2+} or Na^+ per carboxylate ions in PEgMA, assuming that all the anhydride functions were hydrated.

Reactive blending

The reactivity study of the coupling agents on PE grafted maleic anhydride was made in an internal mixer (Haake Polylab with a 600 mixing chamber). The total reactant mass was 50 g. The conditions of mixing used are as follows: speed of the rotors = 50 rpm, set temperature = 150°C.

Insertion of an ionic coupling agent in PEgMA in an internal mixer is difficult because the metal salt must dissociates and release the ion pairs before the reaction with the ionic polymer. Only the released cation can then interact with either the carboxylic acid functions present in the medium or directly with the maleic anhydride functions. Several experimental parameters influence the reaction or interaction rate.

i. The dissociation of metal salt into anion and cation.

ii. The hydration rate of the maleic anhydride functions grafted on PE.

iii. The ability of the cation to interact with the carboxylic acid functions.

The following procedure was applied for sample preparation:

The PEgMA was inserted first in the mixing chamber. Then, the PEgMA was hydrated by the addition of 2 mL of water in the mixer at 5 min mixing, after stabilization of the torque, the metal salt was added.

Characterization techniques

The rheological data were collected with a Rheometrics RDA2 mechanical spectrometer. The geometry was established by parallel plates with 40 mm diameter. The analysis temperature was 170°C.

The thermal characterization was carried out on a Perkin–Elmer DSC 7 apparatus. The samples were maintained 5 min at 150°C and then cooled down at 10°C/min to define a reference state with the same thermal history for all the materials. The crystallization temperature is measured during this cooling step. Then heating scan was performed at 10°C/min to obtain the melting temperature and melting enthalpy. The degree of crystallinity was calculated by dividing the experimental melting enthalpy by the melting enthalpy of totally crystalline PE that is 293 J/g.

The insoluble fraction of the modified PEgMA was determined after Kumagawa extraction with boiling xylene.
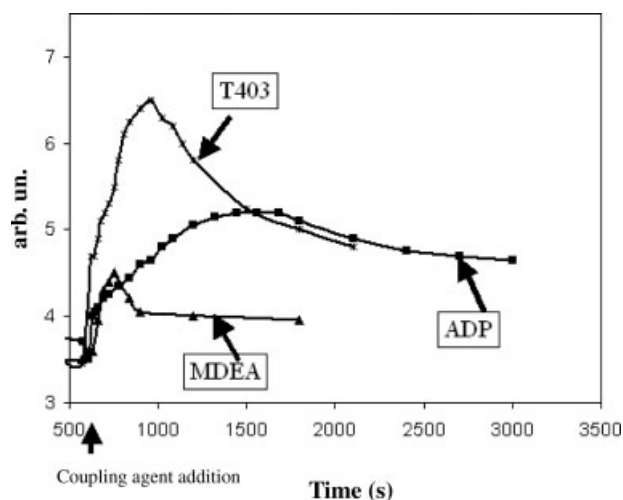
Figure 1 Comparison of the evolution of the torque (arbitrary units) of the internal mixer during mixing of different amine/PEgMA systems, showing the reactivity of amine functional coupling agents on PEgMA at 150°C with a stoichiometric ratio $x = 2$.

Small Angle X-ray scattering was performed on a device consisting in a rotating anode (Rugaku) generator, Franck nickel-coated mirrors and a linear detector (INEL LPS 50).

RESULTS AND DISCUSSION

Reactivity of covalent coupling agents

Amine coupling agents

The aliphatic amine, [(amino polyoxypropylenes: (T403)] having an average functionality of 2.8 was used in reaction on melted PEgMA and is compared with a bifunctional aromatic amine, (MDEA) in Figure 1.

The torque increase successive to the amine addition would be attributed to the reaction between the amine and the maleic anhydride grafted PE. This reaction increases the molar mass by coupling of the polymer chains and thus increases the viscosity of the reaction medium leading to an increase of the internal mixer torque.

The maximum torque is higher with T403 and the torque value at the end of reaction remains always higher with T403 than with MDEA. This difference is due to the higher reactivity on the grafted anhydride and acidic functions of the aliphatic amines T403 compared with the aromatic diamine MDEA. The higher torque with T403 at longer reaction times suggests the presence of structures where a high number of PE chains are connected to the coupling agent.

By using a ADP coupling agent, more complex and original structures can be obtained. The maximum torque was obtained at longer reaction time. The torque value at the reaction end remains always higher with

ADP than with MDEA. The maximum torque is reached after a few minutes in the case of the coupling with the MDEA, whereas it needs 15 min in the case of TA403 coupling agent. This can be due to a diffusion-controlled reactive system that is likely to slow down and limit the crosslinking reaction. The advanced hyperbranched macromolecular structure that was formed presents important increase in viscosity.

HDP coupling agents

Second and fourth generation HDP coupling agents were used as coupling agents for PEgMA.

Firstly, it is necessary to notice that the addition of the Second generation HDP into the reactive medium caused an important fall in the internal mixer torque, even when the HDP mass is low in comparison to total mass (100 mg in 40 g). This is a result of the solubilization/dispersion difficulties of HDP in PEgMA: HDP first formed a separate phase at the polymer-reactor interface leading to an apparent lubrication. This effect disappeared when the HDP was dispersed in the PEgMA.

When PEgMA was hydrated prior to HDP addition, the reaction leaded to a faster increase in the internal mixer torque, and also to higher torque maximum value. (Fig. 2).

PEgMA hydration leads to succinic acid grafted PE. Anhydrides being more reactive with alcohols than carboxylic acids, this hydration mechanism cannot explain alone a higher reaction rate with alcohol functions of the dendritic polymer coupling agents.

When water is added to the reactive system (addition of 10 mL water between $t = 5$ and 10 min), it is suspected that partial hydrolysis of the some ester functions of HDP leads to smaller molecules. As a result, these molecules can be divided into two categories: multialcohols with a structure similar to initial
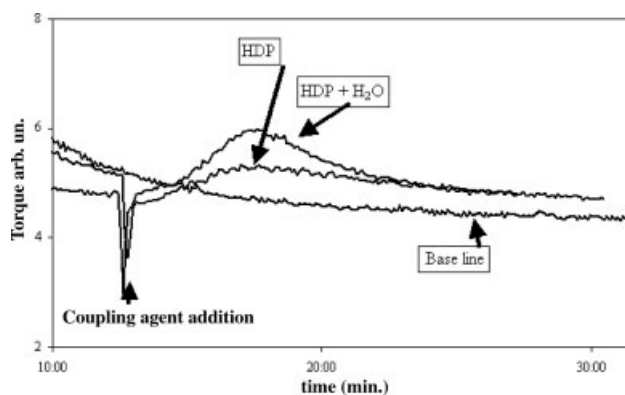

Figure 2 Comparison of the reactivity of alcohol functional dendritic polymers (generation 2) on nonhydrated and hydrated PEgMA at 150°C: stoichiometric ratio $x = 1.7$, addition of 10 mL water between 5 and 10 min. The baseline corresponds to PEgMA without coupling agent addition.
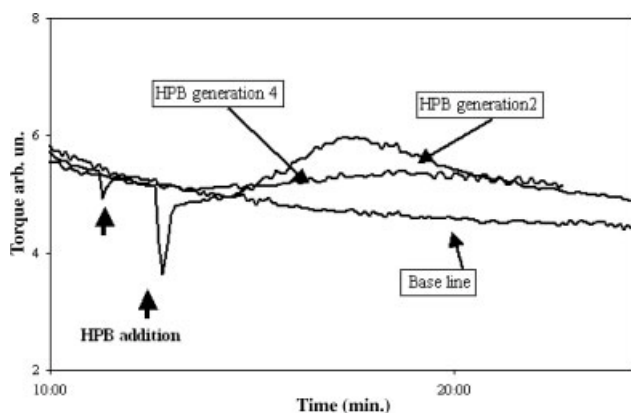
Figure 3 Comparison of the reactivity of alcohol functional dendritic polymers (generations 2 and 4) on hydrated PEgMA at 150°C: stoichiometric ratio $x = 1.7$, addition of 10 mL water between 5 and 10 min. The baseline corresponds to PEgMA without coupling agent addition.

dendritic polymer that can react directly with PEgMA and small molecules bearing an acid function and a limited number of alcohol functions. These molecules can react with PEgMA as spacers making in turn easier the reaction with all the other coupling agents present in the reactive system. This can explain the higher apparent reaction rate observed through the faster increase in the internal mixer torque, and also the higher torque maximum value, when water is added in the internal mixer.

The coupling reaction of HDP of generations 2 and 4 seems relatively slow due probably principally to the reversibility of the alcohol/anhydride reaction
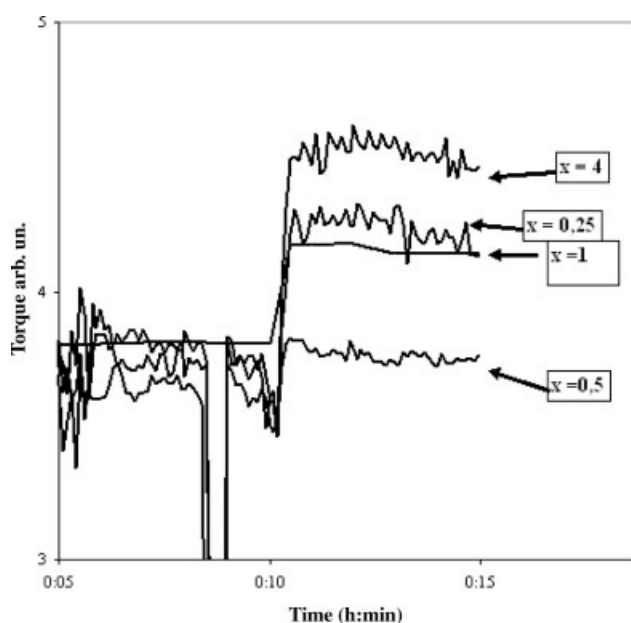
and also diffusion-controlled mechanism as displayed by Figure 3.

In addition, the second generation HDP reaction with PEgMA is faster than the equivalent reaction of the fourth generation HDP. The reactivity difference is a result of a lower solubility of the fourth generation HDP in PEgMA.

Ionic coupling agents

The torque evolution of the internal mixer during the reaction of PEgMA with ZnAc, is illustrated in Figure 4.

The torque maximum is reached in less than 1 min after the addition of the coupling agent in the mixer, indicating that the formation of the ionic interactions is relatively fast. The torque value is rather unexpected: Increasing x, the coupling increase and the torque maximum value are also expected to increase. The maximum torque for $x = 0.25$ is higher than for $x = 0.5$ and $x = 1$.

These experiments were repeated and similar evolutions were obtained.

It is difficult to give significance to the absolute value of the torque after stabilization, because the ionic interactions are reversible. However, the torque is higher than that of the baseline (without reaction). The ionic coupling between the chains is effective, even at high temperature.

Viscoelastic properties

An increase in the stoichiometric ratio between components results directly on an increase of the complex viscosity of the product obtained at the reaction end (Fig. 5). This shows that, as expected, coupling reaction becomes more important when x increases and confirms that, in this case, the absolute values of the torque are not representative of a viscosity absolute value.

Figure 4 Comparison of the reactivity of ZnAc on PEgMA at 150°C and variable stoichiometric ratios x.
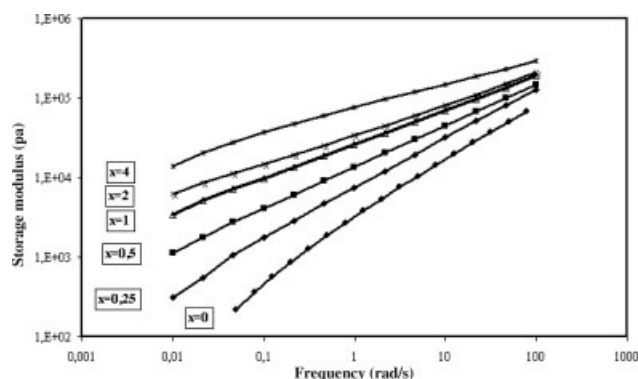

Figure 5 Effect of the stoichiometry on the viscoelastic properties of the systems obtained by reaction of ZnAc with PEgMA at 150°C. (Viscoelastic analysis carried out at 170°C).

Stoichiometric ratio	*n* value for $G' \alpha \omega^n$	*n* value for $G'' \alpha \omega^n$
0	0.763	0.648
0.25	0.648	0.571
0.5	0.525	0.498
2	0.376	0.416
4	0.351	0.317

The loss modulus and storage modulus evolution with frequency of the systems obtained by reaction of ZnAc with PEgMA with different stoichiometric ratios x, at the reaction end were fitted to a power law ($G'\alpha\omega^n$ and $G''\alpha\omega^n$) Table I.

The values of exponents n continuously decreased, when the initial stoichiometric ratio increased. This evolution gives important indications concerning interactions between the different constituents of the prepared material.

It shows that even at the temperature at which the viscoelastic measurements were conducted, i.e., 170°C, the ionic interactions between the acid or anhydride function of PEgMA and the ionic coupling agent ZnAc. remained efficient.

It also indicates that the structure of the obtained material becomes more crosslinked, when the quantity of ZnAc coupling agent increased.

Crosslinking

Seen the initial functionality of the used reactants, crosslinked products are expected to be formed on the reaction end. To verify the presence of insoluble fraction, extractions were performed in boiling xylene in a Kumagawa device. Insoluble polymer was collected even under these experimental conditions. The insoluble fractions are reported in Table II.

The insoluble fraction is thought to consist in chains in strong interaction with Zn^{2+} ions by means of ionic bonds. In this study, the rheological data indicated an apparent increase in the molar mass of PE, but the measured insoluble fraction for the AcZn modified

TABLE II
Insoluble Fraction of PEgMA After Reaction with ZnAc with PEgMA255 at 150°C

Stoichiometric ratio	Insoluble fractions wt %
0	0
0.25	3
0.5	5
2	6
4	1

PEgMA is small and its variation with the proportion of cations is not regular. For example, only 1 wt % insoluble was obtained for $x = 4$. For these reasons, it can be concluded that it is quite probable that the physical links between ZnAc and the polar functions grafted on PE are instable in boiling xylene under the used conditions.

Thermal properties of the modified PE

The degree of crystallinity was calculated by DSC as the ratio of the enthalpy of melting of the polymer, over the enthalpy of melting of a theoretical 100% crystalline polymer, ΔH_∞.

The reactions with ZnAc have a significant effect on the degree of crystallinity of the PEgMA. The degree of crystallinity decreases with increasing the proportion of ZnAc. The melting temperature decreases also significantly (see Table III).

The presence of ionic coupling between the chains and Zn ions decrease the crystallization ability of PEgMA for stoichiometric ratio above two. The decrease in melting temperature may be related to the presence of smaller crystalline lamellae, coupling bonds being rejected in the amorphous phase or acting as defects that disturb the crystalline structure.

Analysis of the ionic structure of PEgMA modified by ZnAc

The morphological study on the crosslinked system obtained by reaction of ZnAc with PEgMA was carried out by Small Angle X-ray Scattering at temperatures above the melting temperature to suppress the scattering contribution of PE crystallites, i.e., at 136°C. Ionic rich domains are known to persist at temperatures higher than complete melting temperature.[19] The scattering curves showed a well defined Guinier regime, indicating a diluted (uncorrelated) regime in all cases. The ionic Zn-rich domains present in the medium are similar to non anisometric randomly dispersed objects in the molten polymeric medium. The size of Zn-rich domains was characterized by the gyration radius R_g, according to the Guinier Law, i.e.,

TABLE III
Thermal Properties of Nonmodified PEgMA, and of the Products Obtained by Reaction of ZnAc with PEgMA255 at 150°C

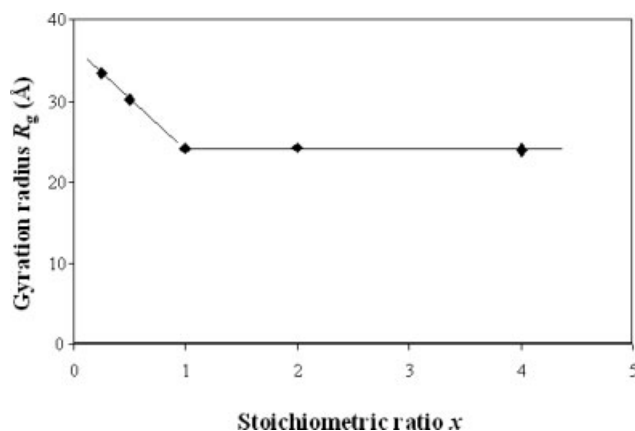|	T_m (°C)	T_c (°C)	Degree of crystallinity (%)
PEgMA255	121	117	59
PEgMA255 + ZnAc			
$x = 0.25$	120	117	60
$x = 0.5$	120	118	59
$x = 2$	118	121	53
$x = 4$	118	120	50

Figure 6 Evolution with stoichiometric ratios of the gyration radius of PEgMA/ZnAc systems obtained by reaction at 150°C.

the scattered intensity in the lower scattering angle range was modeled according to:

$$I(q) = I_0 \exp\left(-\frac{R_g^2}{3}q^2\right)$$

where q is the scattering vector ($q = 4\pi \sin\theta/\lambda$); 2θ the scattering angle.

The resulting values of the gyration radii for various stoichiometric ratios are given on Figure 6.

The particle diameter decreases until the stoichiometric ratio reaches 1, and then remains constant and equal to 25 Å for higher values of the stoichiometric ratio.

The limit of $x \geq 1$ corresponding to an excess of cations in the medium. Such a feature would be related
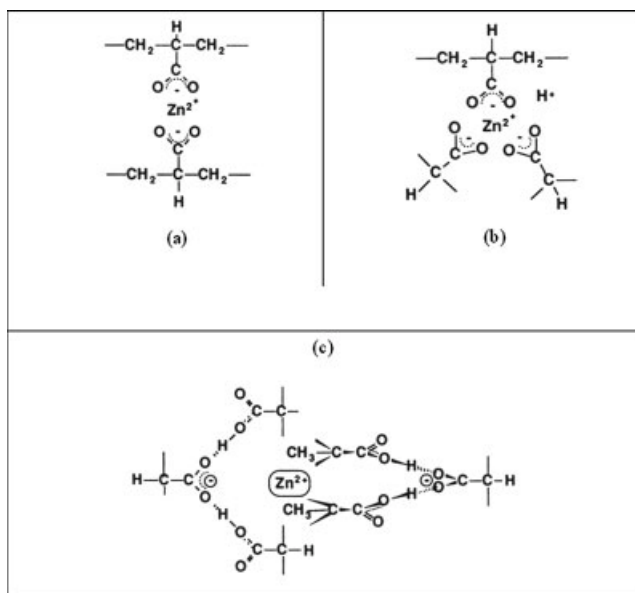
with the possible organizations of the anions around the Zn^{2+} cations.

The ion pair corresponding to neutrality are represented in Figure 7(a). The scattering heterogeneities for $x \geq 1$ are probably mainly composed of ionic pairs as in Figure 7(a), with residual multiplets [Fig. 7(b)] and clusters containing this ionic organization [Fig. 7(c)]. For x lower than one, the ionic organization should correspond mainly to the configuration presented in Figure 7(b,c) leading to larger sizes, as the multiplets and clusters can contain several polymeric ionic groups.

CONCLUSIONS

This study shows the possibility of multifunctional coupling of maleic anhydride modified polyolefins. The covalent coupling using dendritic amine and alcohol functionalyzed polymers is efficient and the reactive system is heterogeneous making the coupling relatively slow: the maximum reaction can be typically achieved within 10–20 min.

Using ZnAc, highly connected PE chains were formed through ionic interactions in less than 1 min. The reaction of the PEgMA with ZnAc is fast enough to be run in a twin-screw extruder.

Next studies will concern the use of these coupling reactions for PP and PE compatibilization.

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Figure 7 Possible ionic organizations for the products obtained by reaction of ZnAc with PEgMA255 at 150°C.