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Characterization of LDPE grafted with Diethylmaleate by Gamma Radiation: Application of FTIR, GPC and SSA Techniques

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Summary: The grafting of diethyl maleate onto low-density polyethylene using gamma irradiation as initiator has been evaluated. The grafting degree was estimated by FTIR and with the use of a calibration curve. The functionalized polymers were characterized by DSC, MFI, SSA and GPC. An increase in the grafting degree with the radiation dose and the concentration of the functional monomer was found. Branching seemed to be the preferential reaction induced by radiation, causing an increase in average molecular weights with the consequently reduction of melt flow index values. The molecular segregation induced by the calorimetric treatment showed that grafting occurs preferentially through secondary carbon sequences.

Keywords: diethylmaleate; gamma radiation; grafting; GPC; polyethylene; SSA

Introduction

The enhanced compatibility properties of grafted polyethylenes have increased their interest due to their potential applications, especially in the improvement of interfacial adhesion in composites and polymers blends,[1] as a consequence of the presence of polar groups able to provide interaction sites for hydrogen or covalent bonding.[2–5]

Polymer grafting has been reported by extrusion and solution methods.[3,5–6] Using these techniques, several functional monomers with unsaturated polar groups have been tested,[2–11] e.g.: maleic anhydride, maleic acid, acrylic acid, maleic and fumaric esters, diethyl maleate, etc. These studies additionally have shown that other reactions can occur while the functionalization reaction takes place, such as monomer homopolymerization, crosslinking and coupling reactions. However, some of these reactions can be prevented using diethyl maleate, because in this case insertion is the prevailing mechanism.[4–5]

As it is well known, the grafting mechanism requires a radical initiator able to promote the functional monomer insertion.[4] In this sense, the study of the effects of gamma rays in polymers[12–14] has allowed proposing grafting by gamma radiation as a promising method for the insertion of functional groups into different polymer matrices, considering its advantages such as the high radical generation rate with the additional exclusion of chemical initiator agents.[15–17]

The study of grafting by gamma irradiation could be similar to other methodologies used, where the grafting degree is related to monomer and initiator concentration, chemical nature of the substrate, with the additional consideration of the radiation conditions. However, it is well known that exposition to γ-rays can induce polymer modifications[18–19] Therefore, the selection of appropriate grafting conditions is an important task.

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In this sense, interesting results in preliminary studies have been found in our laboratory[20] when diethyl maleate (DEM) was grafted onto low-density polyethylene (LDPE) using different radiation doses and varying the monomer concentration. In this work, the grafted polymer was characterized to determine the degree of DEM incorporation and the γ-ray dose effects on its properties.

Experimental Part

A commercial low-density polyethylene (LDPE) supplied by CORAMER, C.A., with a MFI of 4.06 dg/min, determined at 190 °C and 2.16 kg according to ASTM D-1238 standard procedure, was used. Solutions were prepared at 10% wt/vol using a blend of *cis* and *trans* decahydronaphtalene (Decalin 99%), supplied by Riedel de Haën, as solvent. Ethanol and *n*-hexane were employed as washing solvents. Diethyl maleate (DEM), manufactured by Aldrich Chemical Company Inc. was used as the functional monomer.

Solutions of LDPE and 30% DEM in decalin were prepared and irradiated with γ-rays from a ^{60}Co source in air at a dose rate of 4.8 kGy/h at room temperature. The Integral doses were 50, 100, 200 kGy. The grafting degree (GD), was determined by Fourier transform infrared spectroscopy (FTIR) in a Nicolet Magna-IR 560 spectrometer, measuring the ratio of absorption band areas at 1740 cm^{-1}, corresponding to the C=O of the DEM, and at 1460 cm^{-1} ($A^{-1}_{1740cm}/A^{-1}_{1460cm}$) a band characteristic of polyethylene. Relative areas of these absorption bands are proportional to the concentration of carbonyl groups (C=O) in the polymer. The molar concentration percent (% molar) was estimated using a calibration curve reported elsewhere,[10] which relates this area ratio with the molar concentration of DEM determined experimentally by ^{13}C NMR.

Samples were characterized by FTIR using a NICOLET Magna-IR 560 equipment. Spectra were recorded from compression-molded films at 190 °C. The unsaturation bands were followed, identifying the characteristic bands present in the grafted polymers and establishing the corresponding band area ratios, using the peak at 1460 cm^{-1} as the internal standard band for LDPE.

The average molecular weights and molecular weight distribution were measured by gel permeation chromatography (WATERS Alliance GPCV 2000) at 135 °C with 1,2,4-trichlorobenzene as mobile phase, stabilized with 0.25 g/l of butylated hydroxytoluene (BHT). The results were analyzed using a universal calibration curve based on polystyrene standards.

The distribution of melting points induced by the self-nucleation annealing technique (SSA) developed by Muller et al.[21] was recorded in a Mettler Toledo DSC 821. Once the thermal history was erased, the sample was heated at 10 °C/min up to the selected self-seeding and annealing temperature (T_s), where it was isothermally kept for 5 min and then cooled down to 25 °C. Then, the sample was heated again to a new self-seeding and annealing temperature, which was 5 °C lower than the previous T_s and held again for 5 min before cooling to 25 °C at 10 °C/min. This thermal treatment was repeated, being each T_s 5 °C lower than the previous one, until the minimum temperature selected was reached. Finally, the sample was heated at 10 °C/min up to 170 °C and its thermogram recorded.

Results and Discussion

Figure 1 evidences the feasibility of using gamma radiation as initiator in the functionalization reaction of LDPE with DEM. The GD, known as the molar concentration of the functional monomer inserted into the polymer chains, was found to be dependant on the radiation dose, increasing as higher doses were used. The functionalized polymers in this study achieved a maximum grafting degree of 0.34 molar % at 200 kGy. That means that the polymer needs higher radiation energies in order to produce

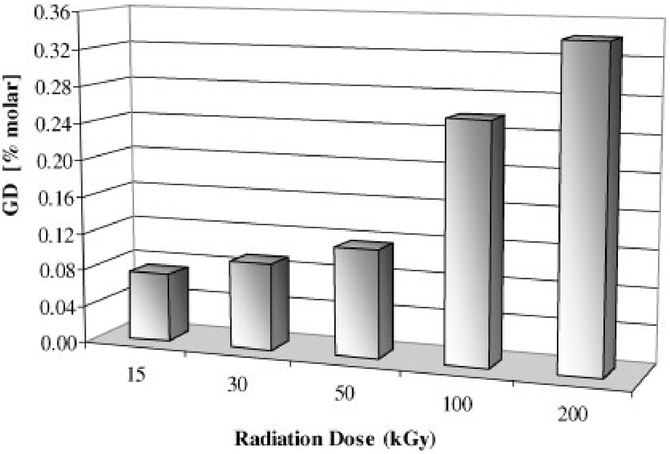

Figure 1.
Grafting degree of LDPE at different radiation doses, using 30% DEM in the solution.

enough number of radicals that can induce the functional monomer insertion.

FTIR spectra not only allowed identifying the DEM insertion, but also to identify[22] and quantify[6] the vinyl unsaturations, through the absorption bands analysis in the region 1000–800 cm^{-1}(Figure 2). The observed bands were assigned to out of plane C–H vibrations, associated to pendant vinyl groups ($R_2C{=}CH_2$) at 887 cm^{-1} and transvinylene groups (RCH=CHR) at 967 cm^{-1}. The presence of these bands depends on the radiation dose, because the transvinylene group is evident only when high radiation doses are employed. This group has been related[22] to the generation of long chain branching and additional unsaturations, due to the coupling reactions between radicals that take place, simultaneously, with the grafting reaction

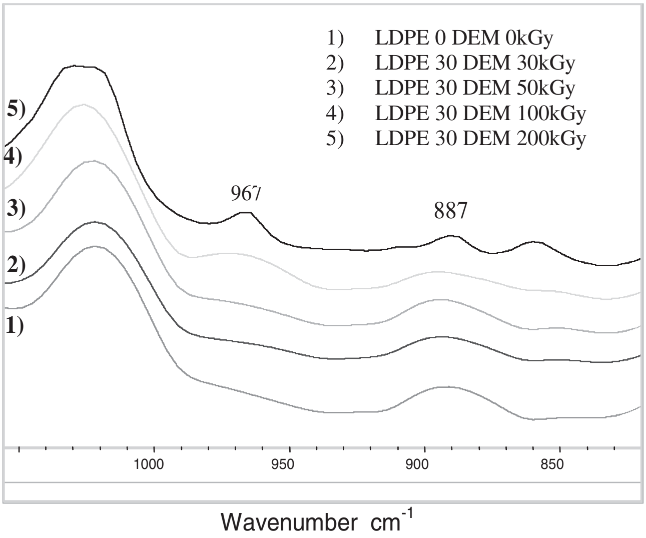

Figure 2.
FTIR of grafted LDPE at different radiation doses, using 30% DEM in the solution; detail of the 800–1000 cm^{-1} region.

(Figure 3). Theses bands were more pronounced at 200 kGy, evidencing that the branching reaction can occur additionally as a consequence of radiation effects.

Table 1 shows that the pendant vinyl groups are consumed during the grafting reaction, while the amount of *trans*-vinyl groups corresponding to long-branch formation increases, which is a consequence of coupling allylic radicals.[6] Additionally, the content of pendant vinyl groups increase with the radiation dose at doses higher than 50 kGy, which could be a consequence of other secondary reactions like branch scission, as Figure 4 shows. Branch scissions take place at lower proportions. Thus, their effect on the molecular-weight distribution curve is negligible. Additionally, the interconnection of the long branches could lead to crosslinking of the polymeric chains.

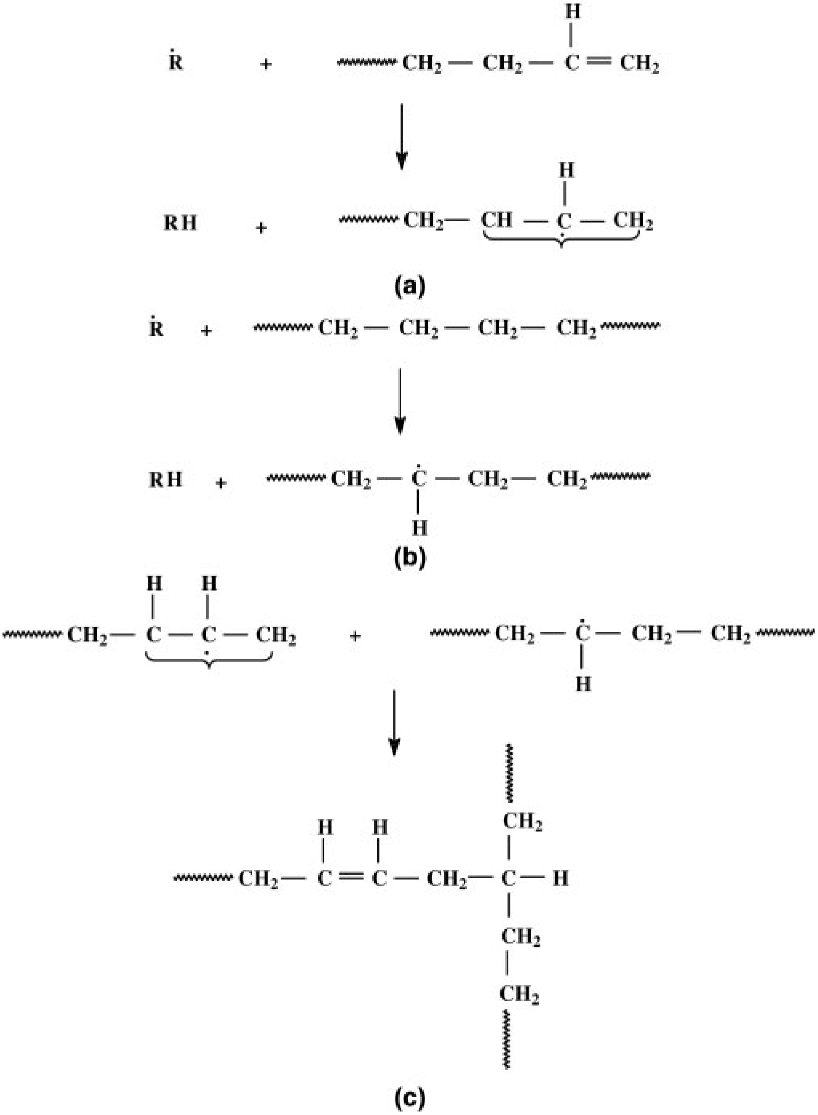

Figure 3.

Mechanism of long-chain branching and/or crosslinking: (a) allyl hydrogen abstraction; (b) H abstraction to form a secondary radical; (c) reaction of products from (a) and (b) to form long branches.[22]

Table 1.
Absorbance area ratios of unsaturations of grafted LDPE at different radiation doses, using 30% DEM in the solution.

	Absorbance Area Ratios of Unsaturations $\times 10^3$	
	Pendants Vinyls Group 887 cm^{-1}/1460 cm^{-1}	*Trans*-Vinyl Group 967 cm^{-1}/1460 cm^{-1}
0DEM_0kGy	8.9	0.0
30DEM_30kGy	2.7	0.2
30DEM_50kGy	2.8	0.2
30DEM_200kGy	3.5	4.7
30DEM_400kGy	6.7	10.6

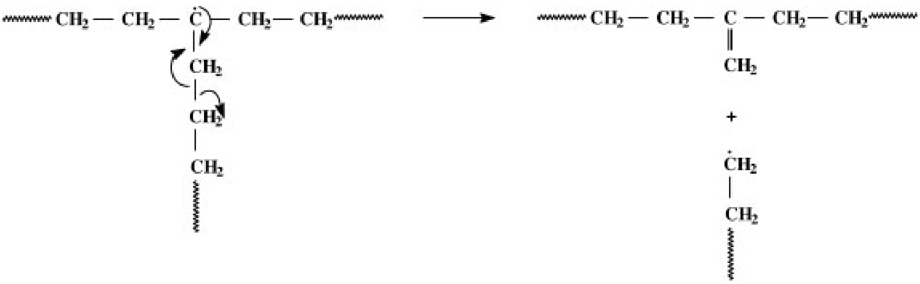

Figure 4.
Formation of pendant unsaturation in tertiary radical.[23]

Figure 5 shows the molecular weigh distribution curves of the grafted products, which show a noticeable displacement towards the fractions of higher molecular weights. An increase in the high molecular weight portion of the distribution curve with the radiation dose is clearly seen. This effect was attributed to the branching or crosslinking reactions that caused an increase in the average molecular weight compared to that of the unmodified LDPE, as shown in Table 2. The polydispersity

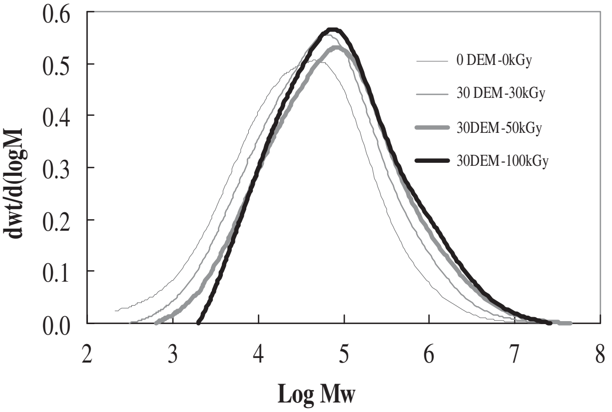

Figure 5.
Molecular-weight distribution curves of grafted LDPE at different radiation doses, using 30% DEM in the solution.

Table 2.
Average molecular weights of grafted LDPE at different radiation doses, using 30% DEM in the solution.

Radiation Dose	M_n	M_w	PDI
0DEM_0 kGy	8233	158680	19.3
30DEM_30 kGy	13099	239267	18.4
30DEM_50 kGy	20109	387837	19.3
30DEM_100 kGy	28982	410477	14.2

index (PDI) value change only at high radiation doses, where a reduction in its value was observed.

The final DSC curves, obtained after applying the SSA technique, showed the heterogeneity in the branching distribution, according to the segregation mechanism based on similar lengths of linear crystallizable sequences.[21] The final SSA thermograms showed nine fractions (Figure 6), corresponding to the segregation of the chains as a function of the branching content. As it is clearly noticed, the area under the peak with the highest melting temperature decreases significantly with the radiation dose, corresponding to the increase in grafting degree. This fact indicates that the insertion of DEM produced an interruption in the more linear sequences, showing that the grafting occurs preferentially in secondary carbons.[21,22,24–25] This fact could be corroborated comparing the results showed in Table 3, where a significant reduction in the partial area of the peak with the highest melting point in the grafted LDPE is observed, simultaneously with an increase in the melting peak areas of the fractions with higher branch contents. The maximum area reduction was observed in the LDPE grafted at 200 kGy. However, this modification could also be attributed to long-branch generation, as a consequence of radiation effects, which are as well able to interrupt the linear sequences. This fact was evidenced comparing the SSA curve of the neat irradiated LDPE, as shown in Figure 7. Additionally, no significant changes were observed in the melting temperatures of each fraction, which only depended on the chosen self-seeding temperature.

Conclusions

The characterization results evidenced the grafting of LDPE by gamma rays. LDPE needs high radiation doses in order to produce high grafting degrees. The generation of branching and unsaturations in the LDPE molecular structure depends on

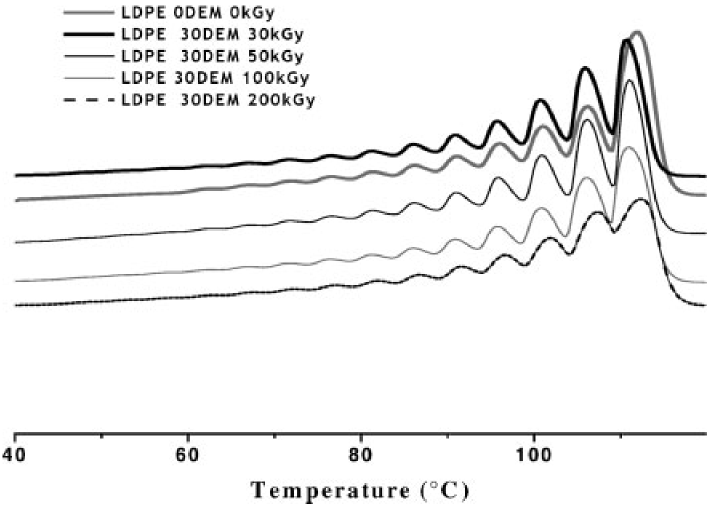

Figure 6.
SSA curves of grafted LDPE at different radiation doses, using 30% DEM in the solution.

Table 3.
Partial areas and melting peak temperatures of grafted LDPE at different radiation doses, using 30% DEM in the solution as a function of self-seeding temperature (T_s) and radiation dose.

T_s	Radiation Dose (kGy)											
	% Area						Melting Temperature (°C)					
	0	30	50	100	200	400	0	30	50	100	200	400
112	32.2	25.8	22.5	26.4	25.6	20.0	112	111	111	111	112	112
107	15.0	21.0	18.3	19.1	19.3	22.3	106	106	106	106	107	107
102	12.5	13.9	13.2	13.4	12.2	15.2	101	101	101	101	102	102
97	9.7	10.4	9.8	9.8	10.0	11.6	96	96	96	96	102	97
92	7.2	7.1	8.6	7.8	5.8	8.9	91	91	91	91	91	92
87	5.9	6.2	6.3	6.0	5.8	6.1	86	86	86	86	87	87
82	4.8	5.2	4.5	5.0	5.4	4.7	82	81	81	81	82	83
77	3.9	3.5	4.8	4.2	4.2	3.8	77	76	77	76	77	78
72	3.4	2.7	3.2	2.5	3.5	2.9	72	72	72	72	73	73

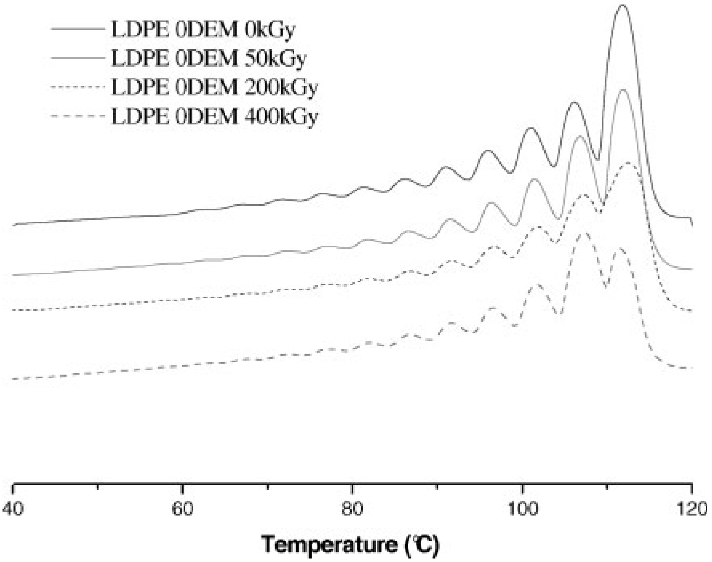

Figure 7.
SSA curves of neat LDPE irradiated at different absorbed doses.

the radiation dose and induced a significant increase in average molecular-weights. The insertion of DEM produced an interruption of the more linear sequences, which means that the functional monomer follows an insertion mechanism onto the secondary carbons.

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[1] D. R. Paul, C. B. Bucknall, *Polymers Blends*, Eds., John- Wiley Sons, New York Vol. *1 and 2*, **2000**.

[2] N. G. Gaylord, R. Mehta, V. Kumar, M. Tazy, *J. Appl. Polym. Sci.* **1992**, *44*, 1941–1949.

[3] N. Liu, W. Baker, K. Russell, *J. Appl. Polym. Sci.* **1990**, *41*, 2285–2300.

[4] M. Aglietto, R. Bertani, G. Ruggeri, L. Segre, *Macromolecules* **1990**, *23*, 1928–1933.

[5] M. Aglietto, R. Bertani, G. Ruggeri, F. Ciardelli, *Makromol. Chem.* **1992**, *193*, 179–186.

[6] C. Rosales, R. Perera, M. Ichazo, J. Gonzalez, H. Rojas, Y. Sanchez, A. Diaz-Barrios, *J. Appl. Polym. Sci.* **1998**, *70*, 234.

[7] A. y. Simmons, W. Baker, *J. Polym. Eng. Sci* **1989**, *29*, 16, 1117–1123.

[8] R. Greco, G. Maglio, P. Musto, *J. Appl. Polym. Sci.* **1989**, *37*, 777–788.

[9] K. y. Ganzelved, L. Janssen, *Poly. Eng. Sci.* **1992**, *32*, 7, 467–474.

[10] C. Rosales, L. Márquez, J. González, R. Perera, B. Rojas, *Poly. Eng. Sci.* **1996**, *36*, 17, 2247–2252.

[11] B. Rojas, J. Fatou, C. y. Martinez, O. Laguna, *Eur. Polym. J.* **1997**, *33*, 725–728.

[12] A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Intercience Publishers. Londres **1962**.

[13] M. Dole, *The radiation chemistry of macromolecules*, Academic Press, **1960**.

[14] A. Charlesby, Atomic Radiation and Polymers, Pergamon, 249 Press, New York **1960**.

[15] E. Bucio, G. Cedillo, G. Burillo, T. y Ogawa, *Polym. Bull.* **2001**, *46*, 115–121.

[16] B. Gupta, N. Anjum, *J. Appl. Polym. Sci.* **2001**, *82*, 2629–2635.

[17] Y. Miwa, K. Yamamoto, M. Sakaguchi, S. Shimada, *Macromolecules* **2001**, *34*, 2089–2094.

[18] S. Kumar, M. Pandya, *J. Appl. Polym. Sci.* **1997**, *64*, 823–829.

[19] H. M. Abou Zeid, Z. I. Ali y col., *J. Appl. Polym. Sci.* **2000**, *75*, 179.

[20] Y. Sánchez, C. Albano, A. Karam,, et al. *Nucl. Instr. and Meth. in Phys. Res. B.* (NIM B), **2005**, *236*, 343–347.

[21] A. J. Muller, Z. H. Hernandez, M. L. Arnal, J. J. Sánchez, *Polym Bull.* **1997**, *39*, 465.

[22] M. Lachtermacher, A. Rudín, *J. Appl. Polym. Sci.* **1995**, *58*, 2433.

[23] Z. S. Fodor, M. Iring, F. Tüdös, T. Kelen, *J Polym Sci Polym Chem Ed*, **1984**, *22*, 2530–2550.

[24] L. Márquez, I. Rivero, A. Müller, *Macromol. Chem. and Phys.* **1999**, *200*, 330–337.

[25] B. Rojas de Gascue, B. Méndez, J. L. Maonosalva, J. López, V. Ruíz Sánta Quiteria, A. J. Muller, *Polymer*, **2002**, *43*, 2151–2159.