Poly(Methyl methacrylate)/Palladium Nanocomposites: Synthesis and Characterization of the Morphological, Thermomechanical, and Thermal Properties

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Received March 11, 2003. Revised Manuscript Received October 2, 2003

PMMA/Pd nanocomposites were prepared by means of free radical polymerization of methyl methacrylate using AIBN initiator in the presence of palladium acetate at 50 °C (48 h), and subsequent thermal conversion of palladium acetate into palladium metal at 120 °C (1 h). Morphological, thermomechanical, and thermal properties of PMMA/Pd nanocomposites were studied as a function of Pd content which was varied between 0.0001 and 0.01 vol%. According to transmission electron microscopy analyses of thin sections, the average Pd nanoparticle size increased slightly from 1.9 to 2.5 nm with increasing Pd content. Size exclusion chromatography revealed that MMA polymerization was not affected by the presence of Pd acetate. The elastic modulus and glass transition temperature, as determined by dynamic mechanical analysis, decreased from 3.4 GPa and 130 °C for neat PMMA to 2.85 GPa and 122 °C for PMMA/Pd containing 0.01 vol% Pd. Thermogravimetric analysis showed that the presence of small amounts of Pd (0.0005−0.005 vol%) significantly improved thermal stabilities, as evidenced by a degradation initiation retarded by 75 °C and a gain of 32 °C at the maximum decomposition rate.

Introduction

Numerous studies have been performed on the preparation of new organic/inorganic hybrid materials and nanocomposites.[1] The term “nanocomposite” is commonly used for filled polymers containing dispersed nanofillers with average particle sizes smaller than 100 nm.[2] In contrast to conventional filled polymers, the number of filler particles increases drastically when the filler particle size is reduced at the same filler volume fraction. As a consequence, most of the polymer is associated with nanofiller interfaces. Converting bulk polymer into interfacial polymer represents a very attractive route to diversified polymers with new property profiles. A prominent example of nanocomposite technology is represented by the production of polymer nanocomposites based upon organophilic layered silicates. Such nanocomposites exhibit a unique combination of improved thermal stability with high dimensional stability, stiffness, strength, toughness, low thermal expansion, gas barrier properties, and fire retardancy.[3−8] For several years, nanocomposites containing metal and metal oxide nanoparticles have been prepared as new materials with unusual mechanical,[9] magnetic,[10] catalytic,[11,12] optical,[13−15] or electrical[16] properties. Four processes have been used to produce metallic nanoparticles−polymer nanocomposites: (I) thermolabile metallic precursors are added to a polymer solution and the metallic nanoparticles are formed by means of thermolysis following solvent evaporation;[17] (II) the metal precursor is added during polymerization with subsequent thermal reduction upon heating at elevated temperatures;[18,19] (III) polymerization of a

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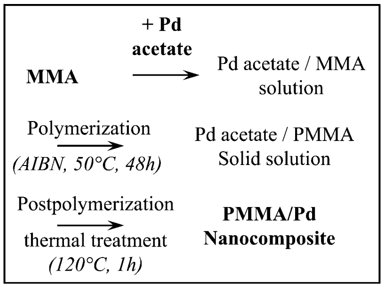

Figure 1. PMMA/Pd nanocomposite synthesis.

colloid of metallic nanoparticles in a monomer is obtained by co-deposition of metallic atoms with the monomer at −196 °C;[20] thermal properties (under nitrogen flow) of polyacrylic and poly(methacrylic acid) doped with metal clusters prepared from this process have been studied;[21] and (IV) a polymer matrix is impregnated with a solvent[22] or a supercritical fluid[23] containing a metal precursor which is reduced by a reduction agent (H_2) or by thermolysis.

Among polymeric materials, poly(methyl methacrylate) (PMMA) is well-known as a polymeric glass and engineering plastic with a wide range of applications from aircraft glazing to lightweight construction. Nakao and al. reported for the first time that the elastic modulus of PMMA was increased by 100% when 0.005 vol% of palladium (as palladium nanoparticles) was incorporated in PMMA/Pd nanocomposites.[9,24] The matrix reinforcement was attributed to the existence of an interfacial binding region which increased the effective filler volume fraction.[25]

The objective of this paper is to gain better insight into the properties of this material, in particular the correlations between morphology and thermal, optical, and thermomechanical properties. The PMMA/Pd nanocomposites are prepared via free radical MMA bulk polymerization combined with in-situ Pd nanoparticle formation resulting from the postpolymerization thermal reduction of palladium acetate.

Experimental Section

Experimental Setup of PMMA/Pd Nanocomposite Synthesis. A schematic of PMMA/Pd nanocomposite synthesis is shown in Figure 1. The experimental conditions (polymerization temperature and time, initiator, initiator concentration, polymerization time, and postpolymerization temperature and time) are determined and discussed in the next section. MMA bulk polymerization was performed in a mold made of two glass plates and a silicon ring (200 mm long × 200 mm wide × 2 mm thick) which was immersed in a thermostatic water bath. Postpolymerization thermal reduction of palladium acetate was carried out in a drying oven.

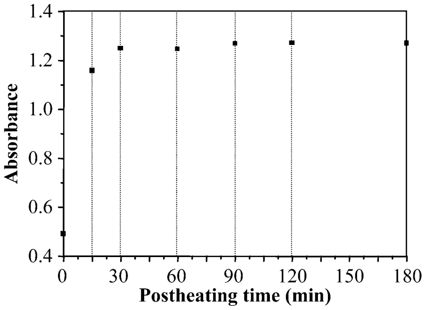

Figure 2. Absorbance at 400 nm of PMMA/Pd nanocomposite (0.005 Pd vol%) as a function of the postpolymerization thermal treatment time at 120 °C.

Chemicals. MMA (99% purity, stabilized by 0.0025% hydroquinone) was purchased from Fluka and was distilled before use. Azobisisobutyronitrile (AIBN, Fluka, 98% purity), palladium acetate (Aldrich, 98% purity), and palladium acetylacetonate (Aldrich, 99% purity) were used as received.

Characterization. The transmission electron microscopy (TEM) measurements were carried out with a LEO CEM 912 transmission electron microscope applying an acceleration voltage of 120 keV. The specimens were prepared using an ultramicrotome. Thin sections of about 50 nm were cut with a Diatome diamond knife. Absorption spectra of PMMA/Pd nanocomposites, dissolved in tetrahydrofuran (THF), were measured with a Perkin-Elmer $\lambda 2$ UV−vis spectrophotometer. The gel permeation chromatography (GPC) was performed with a tetrahydrofuran GPC equipped with a Polymer Laboratories (PL) gel 5-μ Mixed-C column with refractive index (Knauer RI K2301)/light scattering (Precision detector PD 2020) detection. The elution flow rate was 1 mL/min. Dynamic mechanical analyses (DMA) were performed by means of temperature sweeps from 20 to 140 °C in a Rheometrics dynamic mechanical analyzer RSA II equipped with dual cantilever geometry at a frequency of 1 Hz, a strain of 0.01%, and a scanning rate of 2 K/min on specimens with a dimension of 50 × 5 × 2 mm. Thermogravimetric analyses (TGA) were recorded on a Netzsch simultaneous thermoanalyzer (STA 409), controlled by a Netzsch TASC 412/2 unit, in the presence of nitrogen or air (flow of 250 mL/min), using a heating rate of 10 °C/min.

Results and Discussion

Synthesis of PMMA/Pd Nanocomposites. Polymerization of methyl methacrylate (MMA) was performed in bulk using AIBN initiator (0.2% of MMA weight) in the presence of various amounts of Pd acetate ($Pd(CH_3COO)_2$). The parameters of the polymerization process, as well as the parameters of the postpolymerization reduction step, were varied in order to achieve Pd particle formation exclusively during the thermal treatment (with a Pd volume fraction of 0.005%). At temperatures above 60 °C, MMA bulk polymerization was always accompanied by Pd particle formation, as evidenced by TEM characterization. Only when polymerization was performed for 48 h at 50 °C, the simultaneous thermal reduction was not observed. The reaction conditions for thermal reduction (during postpolymerization thermal treatment) were optimized. Pd particle formation was monitored by means of UV spectroscopy.[19,26] As is apparent from Figure 2, heating for ≥30 min at 120 °C proved to be adequate for in situ Pd particle formation. Therefore, all PMMA/Pd nanocomposite samples were prepared by postpolymerization

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Table 1. Compositions and Properties of Synthesized PMMA/Pd Nanocomposites

nanocomposite	Pd content vol%	Pd content wt%	Pd size (nm)	Mn × 10^6 (g/mol)	Mw/Mn	T_g[a] (°C)	E' [b] (GPa)	T_{DTG} max[c](°C) N_2[d]	T_{DTG} max[c](°C) air[e]
1	0	0		1.15	2.2	130.1	3.40	373	335
2	0.0001	0.00097		1.30	1.9	129.8	3.35	369	355
3	0.0005	0.00483	1.88±0.29	1.10	2.1	128.8	3.30	373	367
4	0.001	0.0097	1.91±0.50	1.40	1.60	126.5	3.20	373	367
5	0.005	0.0483	2.50±0.61	1.35	2.20	125.1	3.10	373	367
6	0.01	0.097	2.31±0.70	1.15	2.00	121.7	2.85	373	360

[a] T_g is the thermomechanical glass transition temperature measured by DMA at tan δ maximum. [b] E' is the elastic modulus measured by DMA at 30 °C. [c] T_{DTG} max is the temperature at which the derivative thermogravimetry (DTG) curve reachs its maximum. DTG curves were obtained by taking the time derivative, $d(W/W_0)/dt$, of the ratio of the sample weight, W, to the initial sample weight, W_0. [d] N_2 means that the thermogravimetric analyses were performed in N_2 atmosphere. [e] Air means that the thermogravimetric analyses were performed in air atmosphere.

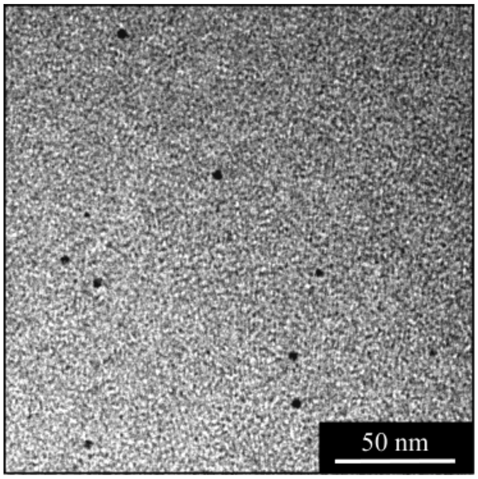

Figure 3. TEM picture of PMMA/Pd nanocomposite with 0.005 vol% Pd.

treatment of 60 min at 120 °C. The UV-spectroscopic analyses are in good agreement with TEM investigations of PMMA/Pd nanocomposites. After 30 min of thermal treatment, a PMMA/Pd nanocomposite was obtained with statistically distributed Pd nanoparticles of 2.5-nm average size (Figure 3 and Figure 4c). A thermal treatment of 60 min led to the same material morphology; no aggregation of Pd nanoparticles was observed between 30 and 60 min of postpolymerization thermal treatment.

Pd acetate is decomposed to the metallic state in the PMMA matrix at temperatures which are much lower than those necessary in bulk state (200−260 °C).[27] This could be explained by the presence of nonreacted AIBN in the PMMA matrix[19] and/or by the coordination of C=O groups (PMMA and/or nonpolymerized MMA) to Pd of Pd acetate.[28,29]

The compositions and properties of the prepared PMMA/Pd nanocomposites are listed in Table 1.

Morphology of PMMA/Pd Nanocomposites. TEM analyses of the PMMA/Pd nanocomposites were performed to study the evolution of the size of Pd nanoparticles in the PMMA matrixes as a function of the Pd volume fractions. No nanoparticle was observed for the nanocomposite 2 (Pd content of 0.0001 vol%) due to the low palladium concentration; particles were probably too small to be distinguished with a regular TEM. The histograms (Figure 4), the mean particle size, and standard deviation calculation (Table 1) were obtained from the observation of 40 Pd particles for nanocomposite 3 (Pd content of 0.0005 vol%) and 100 Pd particles for nanocomposites 4, 5, and 6 (Pd contents of 0.001, 0.005, and 0.01 vol%, respectively). The Pd nanoparticles are statistically distributed in the PMMA matrixes of the prepared nanocomposites. Globally, the Pd nanoparticle size increases slightly with the Pd volume fraction incorporated in the polymer matrix. The width of the Pd nanoparticle size distribution increases equally with the Pd volume fraction. The slight difference between the Pd particle size of the prepared nanocomposites, in particular nanocomposites 5 and 6 (Pd contents of 0.005 and 0.01 vol%, respectively), could be attributed to the effect of the polymer matrix on the Pd particle growth process.[22] In fact, when the Pd nanoparticles grow inside the polymer matrix, the elastic forces of the surrounding polymer become important and the growth of the nanoparticles is limited by the finite extension of neighboring polymer chains.

Concerning the polymer chain properties, a GPC analysis of each material was carried out to study the influence of palladium acetate on the polymerization reaction (Table 1). The molecular weights of PMMA matrixes are high and the distributions are broad, in agreement with the type of characteristics commonly obtained by free radical bulk polymerization. Furthermore, the same molecular weight distributions were approximately evaluated for the polymer matrixes of the different PMMA/Pd nanocomposites. Therefore, palladium as Pd^{II} (palladium acetate) and the palladium volume fraction have no influence on the molecular weight distributions of PMMA of the different PMMA/Pd nanocomposites.

Optical, Thermomechanical, and Thermal Properties of PMMA/Pd Nanocomposites. The color of the different nanocomposites varies between colorless PMMA at 0.0001% (Pd volume fraction) and a black material for a Pd volume fraction of 0.01%. The optical properties of nanocomposites with Pd volume fractions below 0.001% are close to those of the reference PMMA (transparent and colorless). Above this Pd content, the transparency decreases and the polymer matrixes are more and more colored when the Pd volume fraction increases. In regard to the optical properties, the nanocomposites with Pd volume fractions of 0.0001 and 0.0005% are the most interesting as transparent and colorless materials.

Inversely to the results of Nakao,[9,24] the elastic modulus (E') at 30 °C of PMMA/Pd nanocomposites

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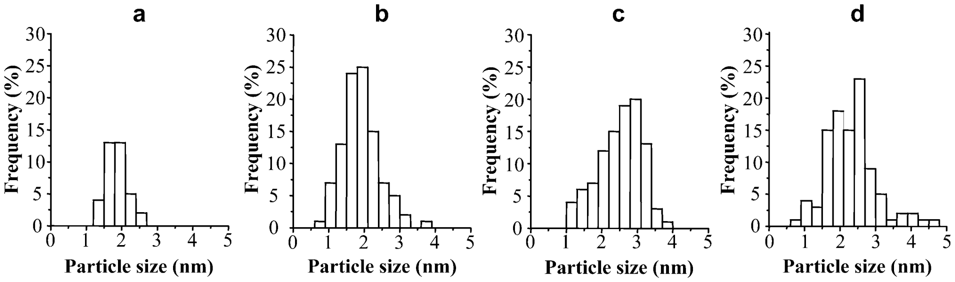

Figure 4. Evolution of Pd nanoparticle size distribution as a function of Pd content in PMMA/Pd nanocomposites. Pd contents of (a) 0.0005; (b) 0.001; (c) 0.005; and (d) 0.01 vol%.

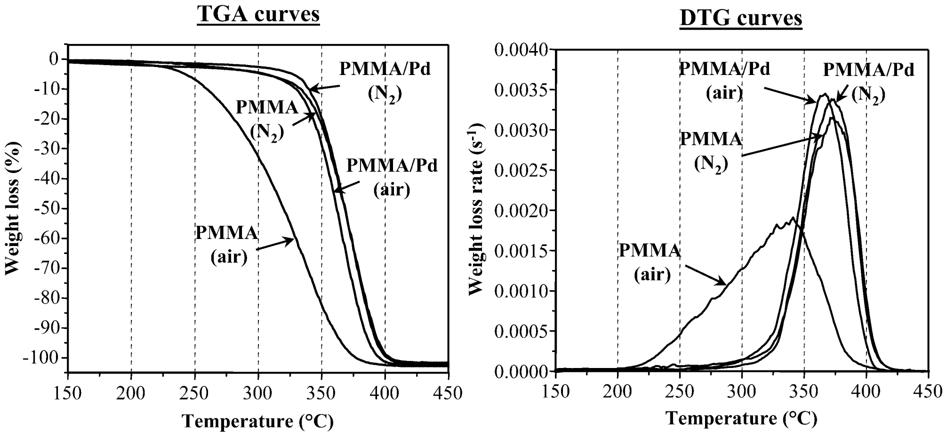

Figure 5. TGA and DTG curves of PMMA and PMMA/Pd (0.001 vol% Pd) degraded in nitrogen and in air.

decreases with the increase of Pd volume fractions from 3.40 to 2.85 GPa for Pd contents between 0 and 0.01 vol% (Table 1). The same trend is observed with the thermomechanical glass transition temperature (T_g) which decreases from 130 to 122 °C for Pd contents between 0 and 0.01 vol%. This thermomechanical behavior cannot be explained by the modification of the polymer matrix syndiotacticity rate with the Pd volume fraction increase; in fact, the PMMA matrix syndiotacticity rate remains near 61% for each sample. Furthermore, this behavior cannot be explained by the presence of oligomeric MMA species or nonpolymerized MMA because, in each nanocomposite, the lower molecular weights are superior to 10 000 g/mol and the weight fractions of nonpolymerized MMA are always lower than 0.1% as determined by NMR.

Comparative characterization of nanocomposites, synthesized in the same experimental conditions with palladium acetate and palladium acetylacetonate, shows that the plasticizing effect is only observed with nanocomposites synthesized with palladium acetate. So, this plasticizing effect of the PMMA matrix could be due to reaction products of palladium acetate thermal reduction.

In addition to the thermomechanical characterization of PMMA/Pd nanocomposites, the thermal stability of these materials was investigated for the first time by thermogravimetric analysis. The influence of Pd nanoparticles on the thermal stability of PMMA/Pd nanocomposites was studied by comparing the degradation of the reference PMMA matrix and the PMMA/Pd nanocomposite filled with a Pd content of 0.001 vol% under nitrogen and air atmospheres. The curves of thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) are shown in Figure 5 and T_{DTG} max values (temperature at which the DTG curve reaches its maximum) are provided in Table 1.

The DTG curve of the reference PMMA under nitrogen indicates a main reaction stage during the degradation from about 300 to 400 °C. Other small peaks appear at 200 °C and end at 300 °C. These results are in good agreement with those published for the thermal degradation of PMMA prepared by bulk free radical polymerization.[30] The first small peaks (200−250 °C) are not easily attributed and the peak at 300 °C could be explained by end initiation from the unsaturated double bonds at one end of polymer chains. The main reaction stage, for which the maximum weight loss rate is located at 373 °C, is caused by unzipping initiated by random scission. The degradation of PMMA in air begins at 200 °C and seems to proceed in a one-reaction stage according to the DTG curve (maximum at 335 °C). This degradation is also initiated by random scission. Comparison of the two TGA curves in air and in nitrogen shows that the oxidative random scission is significantly enhanced compared with the thermally initiated random scission ($\Delta T_{\mathrm{DTGmax}} = 32$ °C).

The TGA and DTG curves of the nanocomposite PMMA/Pd under nitrogen are nearly identical to those of the reference PMMA. Furthermore, two experiments (for PMMA and PMMA/Pd degradation under nitrogen) were performed with a ATG−FTIR apparatus to determine the main degradation product; the same FTIR spectra (spectra corresponding to the one of MMA) were obtained, indicating that MMA is the main degradation product and showing that the two materials follow the same mechanism of unzipping. The only difference

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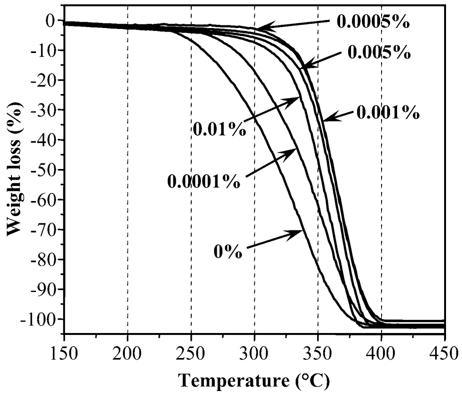

Figure 6. Influence of Pd volume fraction on PMMA/Pd thermal stability in air.

concerns the temperature at which the degradation begins; this temperature is displaced by 50 °C for the nanocomposite.

The incorporation of Pd nanoparticles in PMMA significantly increases the oxidative thermal stability of the PMMA matrix. The incorporation of a Pd content of 0.001 vol% increases the $\mathrm{DTG}_{\mathrm{max}}$ temperature by 32 °C. The TGA and DTG curves are close to those using a nitrogen flow (PMMA or PMMA/Pd) and the oxidative enhancement of random scission is not observed. This indicates that oxygen does not seem to influence the oxidative thermal degradation of PMMA in the presence of palladium. The oxygen is probably interacting with the Pd nanoparticles, which are extremely reactive. In fact, such nanoparticles develop a very large ratio of the surface to the volume, which corresponds to a large atom fraction at the nanoparticle surface. Therefore, the incorporation of Pd nanoparticles in PMMA matrix significantly improves the oxidative thermal stability of the polymer matrix.

More knowledge was gained by investigating the influence of Pd volume fraction on the nanocomposite thermal stability. The TGA and DTG curves of PMMA/Pd nanocomposites filled with a Pd content of 0, 0.0001, 0.0005, 0.001, 0.005, and 0.01 vol% under nitrogen are not shown because all the curves are nearly identical to each other and to those presented in Figure 5. The maximum of the decomposition rate is reached at 373 °C (Table 1). As already explained, the only difference concerns the beginning of decomposition, which is displaced by 50 °C with a Pd content above 0.0005 vol%.

The TGA curves of PMMA/Pd nanocomposites filled with different Pd contents (0, 0.0001, 0.0005, 0.001, 0.005, and 0.01 vol%) under air are shown in Figure 6. The DTG curves are omitted for clarity; the profiles are the same as those shown in Figure 5 and the temperatures of maximum decomposition rates are mentioned in Table 1. The oxidative thermal stability of the PMMA matrix significantly increases with an increase in Pd volume fraction from 0 to 0.001%. The Pd volume fraction increase allows improved inhibition of the oxidative enhancement of random scission. The temperature of the maximum decomposition rate increases from 335 °C for neat PMMA to 367 °C for PMMA/Pd nanocomposite with a Pd content of 0.0005 vol%. For a Pd content above 0.001 vol%, the oxidative thermal stability of the PMMA matrix decreases slightly with the increase of Pd content due to increasing Pd nanoparticle size and width of Pd nanoparticle size distribution.

A Pd content of only 0.0005 vol% leads to the best improvement of the oxidative thermal stability of the PMMA matrix; the initiation of the degradation is retarded by more than 75 °C and an improvement of 32 °C is obtained at the maximum of the decomposition rate.

In regard to the optical, thermomechanical, and thermal properties, the PMMA/Pd nanocomposite filled with a Pd content of 0.0005 vol% offers the best performance; its optical (transparent and colorless) and thermomechanical properties are close to those of reference PMMA with a significantly improved thermal stability.

Conclusions

An experimental protocol has been developed to prepare PMMA/Pd nanocomposites by means of free radical polymerization of MMA in the presence of palladium acetate at 50 °C (48 h) and subsequent thermal conversion of palladium acetate into palladium metal at 120 °C (1 h); this results in in situ formation of Pd nanoparticles. PMMA/Pd nanocomposites were prepared with different Pd content varying between 0.0001 and 0.01 vol%, which corresponds to average Pd nanoparticle size between 1.9 and 2.5 nm statistically distributed in the PMMA matrix.

Morphological, optical, thermomechanical, and thermal properties of PMMA/Pd nanocomposites were studied as a function of Pd content. The color of the different nanocomposites varies between colorless PMMA and a black material as the Pd content increases from 0.0001 to 0.01 vol%. Concerning the thermomechanical properties, the elastic modulus and glass transition temperature decreased from 3.4 GPa and 130 °C for neat PMMA to 2.85 GPa and 122 °C for PMMA/Pd with a Pd content of 0.01 vol%. The incorporation of Pd nanoparticles induces a plastisizing effect on the PMMA matrix.

According to the thermogravimetric analysis, the incorporation of a small amount of Pd in the PMMA matrix considerably increases the oxidative thermal stability of the polymer matrix. The initiation of the degradation is retarded by more than 75 °C and an improvement of 32 °C is obtained at the maximum of the decomposition rate for an optimal Pd content of 0.0005 vol%; the oxidative enhancement of unzipping initiated by random scission is not observed more in the presence of Pd nanoparticles.

Acknowledgment. We thank the company ATOFINA (TOTALFINAELF) for its financial support. Dr. P. Nogues, Dr. Y. Ederle, Dr. A. Wollny (ATOFINA), and Dr. R. Kübler (Institut für Makromolekulare Chemie) are also gratefully acknowledged for their scientific contributions. We also thank Dr. R. Hanselmann (Institut für Makromolekulare Chemie) for the GPC measurements.

CM031049H