Thermochimica Acta 495 (2009) 38–41

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Vapor pressure, kinetics and enthalpy of sublimation of bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II)

M. George Johnson, J. Selvakumar, K.S. Nagaraja*

Department of Chemistry, Loyola Institute of Frontier Energy, Loyola College, Chennai 600034, India

ARTICLE INFO

Article history:
Received 3 March 2009
Received in revised form 21 May 2009
Accepted 25 May 2009
Available online 6 June 2009

Keywords:
Volatile copper complex
Isothermal and dynamic TG
Vapor pressure
Transpiration
Sublimation kinetics

ABSTRACT

The kinetics of sublimation of bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II), [Cu(tmhd)$_2$] was studied by non-isothermal and isothermal thermogravimetric (TG) methods. The non-isothermal sublimation activation energy values determined following the procedures of Friedman, Kissinger, and Flynn–Wall methods yielded 93 ± 5, 67 ± 2, and 73 ± 4 kJ mol^{-1}, respectively and the isothermal sublimation activation energy was found to be 97 ± 3 kJ mol^{-1} over the temperature range of 375–435 K. The dynamic TG run proved the complex to be completely volatile and the equilibrium vapor pressure $(p_e)_T$ of the complex over the temperature range of 375–435 K determined by a TG-based transpiration technique, yielded a value of 96 ± 2 kJ mol^{-1} for its standard enthalpy of sublimation ($\Delta_{sub}H^\circ$).

1. Introduction

The need for high-performance interconnection materials increases as the design rules for integrated circuits shrink below 0.5 μm. Copper film has attracted much attention due to its high conductivity as well as high electromigration resistance [1]. Conventional processing has been reported to be problematic to fill features with aspect ratios even as low as 1.0 without creating internal voids [2]. As in any CVD process, the choice of precursors, together with the process parameters, determines the microstructure and related properties of copper films. The fluorinated β-diketonate and tmhd copper complexes have been developed for achieving high rate of copper deposition. The Cu(tmhd)$_2$ complex as a precursor for the CVD of copper, is chemically stable and sublimes at relatively low temperatures (~373 K) [3,4].

It is essential that the precursor has both high vapor pressure and an indefinite thermal stability under operating conditions. Based on the above requirements, the present investigation is over the thermal stability, vapor pressure, standard enthalpy of sublimation, and sublimation kinetics of Cu(tmhd)$_2$ under non-isothermal and isothermal TG methods.

2. Experimental

Synthesis: The complex was synthesised according to the literature reported [5]. Copper acetate dissolved in warm aqueous ethanol was mixed with tmhd ligand in 1:2 ratio with constant stirring. The complex formed was filtered, dried and recrystallised in chloroform.

Analysis: The FT-IR spectrum was recorded using a PerkinElmer FT-IR spectrometer (RX1, FT-IR) in the region of 4000–450 cm^{-1}. The C, H and O analyses were carried out by CARLO-ERBA-11008 CHNS-O rapid elemental analyser. The electron spray ionisation mass spectrum (ESI-MS) of the complex was recorded on a MICRO MASS QUATTRO II triple quadrupole spectrometer having a JASCO PU – 980 HPLC pump connected to it.

2.1. Non-isothermal TG

The thermogram of the complex was carried out with PerkinElmer Pyris-Diamond TG–DTA. The purge gas was high purity nitrogen dried by passing through refrigerated molecular sieves (Linde 4A) at a flow rate of 12 dm^3 h^{-1}. The thermogravimetric analysis was performed at a linear heating rate of 10 K min^{-1} over the temperature range of 320–520 K. Temperature calibration of the instrument was done using indium, tin and aluminum as reference materials. The sample weighing up to 3 mg, was loaded in an alumina crucible, placed in the sample pan and subsequently dried *in situ* at 323 K for a few minutes to remove adsorbed moisture, if any. The purpose of these runs was to observe the mass loss steps besides identifying the final temperature to attain either nil residue or constant weight.

---

* Corresponding author. Tel.: +91 44 28178200x374; fax: +91 44 28175566.
E-mail addresses: dr.ksnagaraja@gmail.com, mgjmgj65@yahoo.com (K.S. Nagaraja).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.05.014

2.2. *Isothermal vapor pressure measurements*

A horizontal thermal analyser was adopted as a transpiration setup for vapor pressure measurements. The block diagram of the thermal analyser, modified for its functioning in the transpiration mode is given elsewhere [6]. The details of the precise flow calibration for the carrier gas, using a capillary glass flow meter and corrections for apparent weight losses in isothermal mode, were described earlier [7,8]. The sample, finely powdered using a mortar and pestle was spread on an alumina crucible and was carefully flushed with nitrogen gas at the rate of 6 $\mathrm{dm}^3\,\mathrm{h}^{-1}$ at the ambient temperature. Vapor pressure measurements were carried out at 10 K min^{-1}. After the temperature stabilisation, subsequent changes in isothermal steps were done at a heating rate of 2 K min^{-1}.

2.3. *Sublimation kinetics*

The conventional non-isothermal thermogravimetric runs were carried out at various heating rates such as 5, 8, 10 and 12 K min^{-1}. Also, isothermally programmed thermogravimetric analysis was carried out over the temperature range of 375–435 K in nitrogen atmosphere at a flow rate of 6 $\mathrm{dm}^3\,\mathrm{h}^{-1}$. Among the several methods available for the kinetics evaluation of TG weight loss data, Arrhenius, Kissinger and Flynn–Wall methods were followed in the present paper to study the sublimation kinetics. And to study the isothermal sublimation kinetics, the activation energy was calculated from the slope of the plot of maximum mass loss rate $[\ln(\mathrm{d}\alpha/\mathrm{d}t)_\mathrm{m}]$ against the reciprocal of the several isothermal temperatures $(1/T)$.

3. Results and discussion

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) was characterised by C, H, O analysis, FT-IR, and mass spectral studies. M.Pt—463 K; CHO analysis of $\mathrm{Cu(tmhd)_2}$: C—62.05% (61.44%), H—9.18% (8.91%) and O—14.78% (14.88%); FT-IR (KBr, cm^{-1}): 2953.17 (C–H), 1551.32 (C=O), 1402.28 (C=C) and 494.86 (Cu–O); ESI-MS (at 353 K): m/z values 430 and 246 correspond to $\mathrm{Cu(tmhd)_2}^+$ and $\mathrm{Cu(tmhd)}^+$.

3.1. *Thermal properties of Cu(tmhd)$_2$*

The non-isothermal TG runs of $\mathrm{Cu(tmhd)_2}$ at different heating rates (Fig. 1) revealed that the complex was thermally stable up to 425 K. The weight loss commencing from about 375 K occurred in a single step and ended up with a total weight loss around 500 K for every heating rate. The fact that the complex showed a single step weight loss ending up with nil residue helped to identify the complex as a potential precursor for CVD of metallic copper films for technological applications [9]. As the objective of this investigation was to evaluate the equilibrium vapor pressure by a TG-based transpiration technique, a priori knowledge of the molecular weight of the complex was required. For this purpose, the $\mathrm{Cu(tmhd)_2}$ was subjected to ESI-MS analysis and its molecular mass was determined at 353 K.

3.2. *Determination of standard enthalpy of sublimation ($\Delta_{sub}H^\circ$)*

The temperature dependent equilibrium vapor pressure $(p_\mathrm{e})_\mathrm{T}$ could be calculated using the relation:

$$(p_\mathrm{e})_\mathrm{T} = \frac{WRTc}{MVc}$$

which is derived from Dalton's Law of partial pressures for a mixture of ideal gases, where W is the mass loss (mg) at various isothermal temperatures (375–435 K) caused by the flow of Vc (dm^3) of the carrier gas (measured at $Tc = 298$ K), R is the universal gas constant (8.314 $\mathrm{J\,mol^{-1}\,K^{-1}}$) and M (430 $\mathrm{g\,mol^{-1}}$) is the molecular mass of the monomeric precursor vapor species. To demonstrate the equilibrium nature of the vaporization process in this TG-based transpiration technique, a chair shaped curve was established when apparent vapor pressure (p') was plotted as a function of flow rate of the nitrogen carrier gas as mentioned earlier [7]. Attainment of equilibrium condition was also ascertained by the plot of isothermal time against mass loss for all the isothermal steps as shown in Fig. 2 and the lines passing through origin show that equal amount sublimed at equal intervals of time. The values of observed mass loss, isothermal temperatures and the calculated equilibrium vapor pressure (p_e) are listed in Table 1. The plots of $\ln(p_\mathrm{e}/\mathrm{mPa})$ and $[\ln(\mathrm{d}\alpha/\mathrm{d}t)_\mathrm{m}]$ against $1000/(T/\mathrm{K})$ are shown in Fig. 3. The temperature range considered for the measurement of p_e encompasses only the solid range of $\mathrm{Cu(tmhd)_2}$ complex. The temperature dependence of p_e could be represented by the least square expression:

$$\ln(p_\mathrm{e}/\mathrm{mPa}) = \frac{-11,562 \pm 295}{T/\mathrm{K}} + 34 \pm 1 \quad (375\text{–}435\ \mathrm{K})$$

Multiplying the slope of the expression by $-2.303R$, a value of 96 ± 2 $\mathrm{kJ\,mol^{-1}}$ was derived for the standard enthalpy of sublimation ($\Delta_\mathrm{sub}H^\circ$). The entropies of vaporization ($\Delta_\mathrm{sub}S^\circ$) for $\mathrm{Cu(tmhd)_2}$

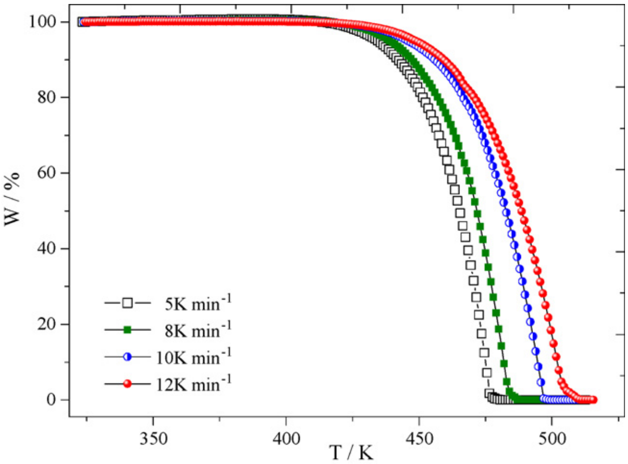

Fig. 1. Non-isothermal TG runs of $\mathrm{Cu(tmhd)_2}$ at different heating rates.

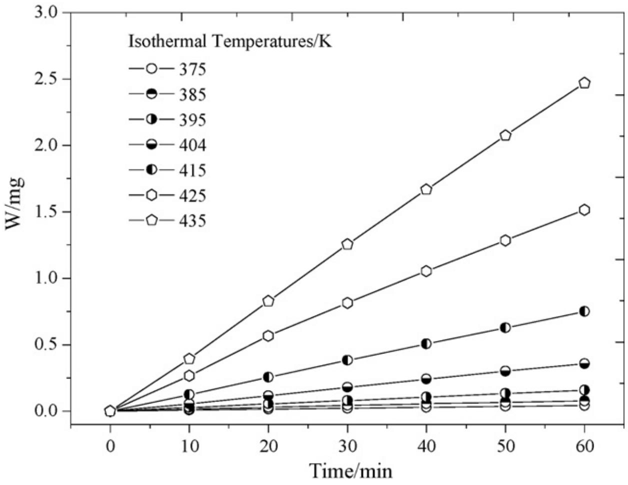

Fig. 2. Mass loss against time of 1 h isothermal holding.

Table 1
Isothermal vapor pressure and energy of activation of Cu(tmhd)$_2$.

Isothermal vapor pressure			Isothermal max. mass loss rate	
T (K)	W (mg)	p_e (mPa)	T (K)	$(\mathrm{d}\alpha/\mathrm{d}t)_m$
375	0.04	40	375	4.43E−04
385	0.07	72	385	1.29E−03
395	0.16	151	395	2.35E−03
404	0.36	343	401	6.47E−03
415	0.75	720	415	1.30E−02
425	1.52	1456	425	2.40E−02
435	2.47	2373	435	4.20E−02
$\Delta_{sub}H^\circ$ (kJ mol^{-1}) = 96 ± 2			E_a (kJ mol^{-1}) = 103 ± 3	

as calculated from the intercept of the above linear fit expression was found to be 283 J mol^{-1} K^{-1}. The sublimation study was restricted to a maximum temperature of 445 K as against 470–510 K (obtained from TG experiment on different heating rates) to get nil residue of the precursor. This restriction originated from the fact that the value of p_e approaches the upper periphery (5 Pa at 455 K) of the applicability of the TG-based transpiration technique [10]. The $\Delta_{sub}H^\circ$ value obtained in the present investigation was found to be comparable with the literature [11–14] value of 124.6, 111.6, 105.9 and 112 kJ mol^{-1}.

3.3. Determination of activation energy, E_a

The rate constant k, for the sublimation of the complex was determined in the temperature range of 440–495 K for every 10% weight loss of the complex at different heating rates. The expression for k is given by

$$k = \frac{\mathrm{d}\alpha}{\mathrm{d}t}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the derivative of the fraction sublimed with respect to time and k is the rate constant of sublimation. By using this equation, k was calculated for every 10% weight loss. α is defined by the expression as

$$\alpha = \frac{\%w_i - \%w_t}{\%w_i - \%w_f}$$

where $\%w_t$ is the percent weight at any time t and $\%w_i$ and $\%w_f$, respectively, are the initial and final percent sample weights [15]. The Arrhenius expression is

$$\ln k = \ln A - \frac{E_a}{RT}$$

and the plot of ln k versus $1/T$ (Fig. 4) is linear. From the slope, the activation energy (E_a) for the sublimation of the complex was calculated. For the different heating rates of 5, 8, 10, and 12 K min^{-1} the activation energy values obtained are 102 ± 6.3, 99 ± 4.5, 92 ± 3.9, and 79 ± 5.4 kJ mol^{-1}, respectively.

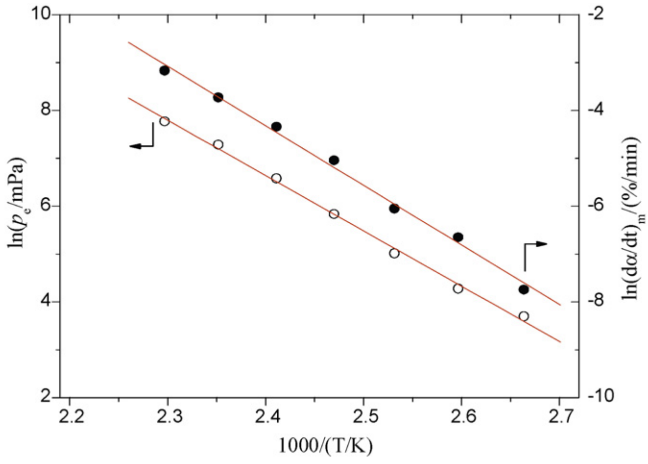

Fig. 3. Clausius–Clapeyron and Friedman isothermal plots.

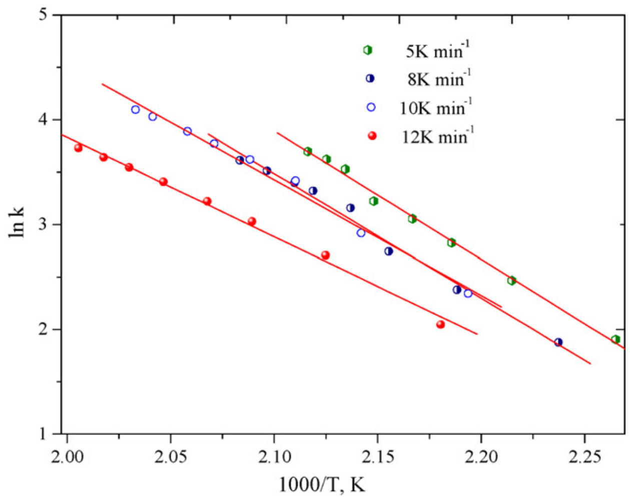

Fig. 4. Arrhenius plots of Cu(tmhd)$_2$ at various heating rates.

The activation energy for the non-isothermal sublimation of Cu(tmhd)$_2$ was calculated using Kissinger expression:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{n\,(1-\alpha_m)^{n-1}AR}{E_a}\right) - \left(\frac{E_a}{RT_m}\right)$$

where T_m and α_m are the absolute temperature and weight loss at the maximum weight-loss rate $(\mathrm{d}\alpha/\mathrm{d}t)_m$. This method yielded a value of 67 ± 2.0 kJ mol^{-1} from the slope of $\ln(\beta/T_m^2)$ as a function of $1/T_m$ at the maximum weight-loss rate (Fig. 5).

The activation energy was also determined by Flynn–Wall technique using the expression, $\ln\beta = \ln(AE_a/R) - \ln[F(\alpha)] - E_a/RT$. The sublimation of the complex was carried out at different heating rates (β) in this technique. The plot of the different heating rates against the temperature for every 10% weight loss at every heating rate is shown in Fig. 6. And the straight lines obtained are nearly parallel to each other showing the applicability of this method to metallorganic complexes. A mean value of 73 ± 4 kJ mol^{-1} for activation energy was found for the weight loss range of 10–80% and this value was found to be comparable with the result of Kissinger

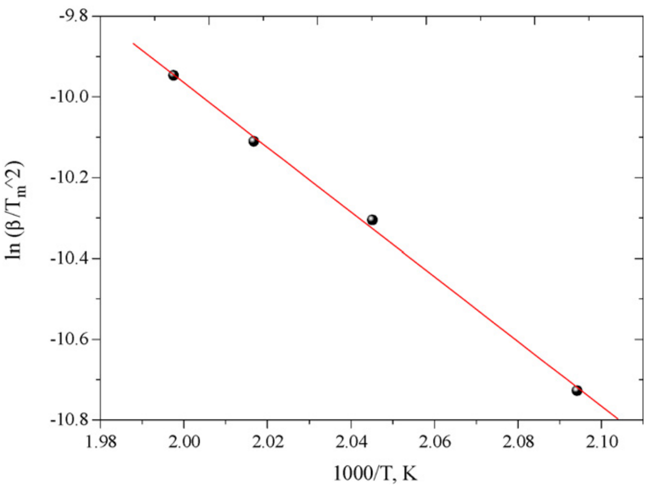

Fig. 5. Kissinger plot of ln(heating rate/T_m^2) versus $1/T$ at different heating rates.

Table 2
Various techniques of non-isothermal sublimation kinetics of Cu(tmhd)$_2$.

Arrhenius		Kissinger	Flynn–Wall	
Heating rate (β) (K min^{-1})	E_a (kJ mol^{-1})	E_a (kJ mol^{-1})	Conversion (α)	E_a (kJ mol^{-1})
5	102 ± 6	67 ± 2	10	84 ± 5
8	99 ± 4		20	79 ± 5
10	92 ± 4		30	76 ± 2
12	79 ± 5		40	72 ± 6
			50	71 ± 4
			60	70 ± 5
			70	67 ± 3
			80	66 ± 3
E_a (kJ mol^{-1})	93 ± 5	67 ± 2		73 ± 4

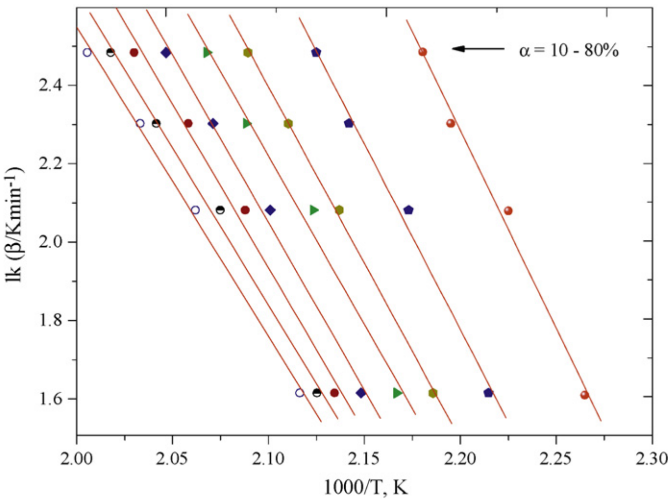

Fig. 6. Flynn–Wall plots of Cu(tmhd)$_2$ at different heating rates.

method as shown in Table 2. Both the methods do not require any previous knowledge of the reaction mechanism for the determination of activation energy [16,17].

The calculation of activation energy of isothermal sublimation process was carried out in the temperature range of 375–435 K and from the plot of ln(p_e/mPa) against 1000/T (Fig. 3). The activation energy was determined to be 103 ± 3 kJ mol^{-1} which was comparable with the enthalpy of sublimation value of 96 ± 2 kJ mol^{-1}.

4. Conclusion

The vapor pressure and sublimation enthalpies were evaluated for Cu(tmhd)$_2$ by TG-based transpiration technique. The activation energy obtained for isothermal sublimation process was found to agree with the enthalpy of isothermal sublimation. The activation energy values obtained for non-isothermal sublimation process as per the procedures of Kissinger and Flynn–Wall agree with each other.

Acknowledgements

The authors are sincerely grateful to the Department of Chemistry and Loyola Institute of Frontier Energy (LIFE), and Principal, Loyola College, Chennai-34. The Faculty Improvement Programme (FIP) grant from UGC, New Delhi and DCE, Tamil Nadu are gratefully acknowledged.

References

[1] (a) H.K. Kang, J.S.H. Cho, I. Asano, S.S. Wong, Proc. IEEE VMIC 337 (1992);
(b) S.P. Murarka, R.J. Gutmann, A.E. Kaloyeros, W.A. Lanford, Thin Solid Films 236 (1993) 257–266.
[2] H.P. Bader, M.A. Lardon, J. Vac. Sci. Technol. B4 (1986) 833–836.
[3] S. Mukhopadhyay, K. Shalini, A. Devi, S.A. Shivashankar, Bull. Mater. Sci. 25 (2002) 391–398.
[4] T. Maruyama, Y. Ikuta, J. Mater. Sci. 28 (1993) 5540–5542.
[5] G.S. Hammond, D.C. Nonhebel, C.S. Wu, Inorg. Chem. 2 (1963) 73–76.
[6] R. Pankajavalli, C. Mallika, O.M. Sreedharan, M. Premila, P. Gopalan, Thermochim. Acta 316 (1998) 101–108.
[7] P. Antony Premkumar, R. Pankajavalli, O.M. Sreedharan, V.S. Raghunathan, K.S. Nagaraja, Mater. Lett. 58 (2004) 2256–2260.
[8] P. Antony Premkumar, K.S. Nagaraja, R. Pankajavalli, C. Mallika, O.M. Sreedharan, Mater. Lett. 58 (2004) 474–477.
[9] C.J. Anthony, Chem. Vap. Depos. 4 (1998) 169–179;
C.J. Anthony, J. Mater. Chem. 12 (2002) 2576–2590.
[10] S. Arockiasamy, V.S. Raghunathan, P.A. Antony Premkumar, P. Kuppusamy, A. Dasgupta, P. Parameswaran, C. Mallika, K.S. Nagaraja, Chem. Vap. Depos. 13 (2007) 691–697.
[11] P. Tobaly, G. Lanchec, J. Chem. Thermodyn. 25 (1993) 503–510.
[12] N.E. Fedotova, A.A. Voityuk, A.A. Blitznyuk, I.K. Igumenov, Koordinatsionnaya Khimiya 14 (1988) 1493 (translated by Plenum Publishing Co., 1989).
[13] S. Yuhya, K. Kikuchi, M. Yohida, K. Sugawara, Y. Shiohara, Mol. Cryst. Liq. Cryst. 184 (1990) 231–235.
[14] M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, A.P.S.M.C. Carvalho, M.J. Akello, G. Pilcher, J. Chem. Thermodyn. 16 (1984) 1149–1155.
[15] L. Burnham, D. Dollimore, K. Alexander, Thermochim. Acta 367–368 (2001) 15–22.
[16] H. Wang, J. Yang, S. Long, X. Wang, Z. Yang, G. Li, Polym. Degrad. Stabil. 83 (2003) 229–235.
[17] L. Nunez, A. Castro, M. Villanueva, M.R. Nunez, B. Rial, J. Appl. Polym. Sci. 83 (2001) 1528–1535.