Synthesis of polynobornene on catalyst functionalized-MWCNTs with a "grafting from" approach: The influence of the catalyst-MWCNT spacing

P. Longo*,***, C. Costabile*,***, F. Grisi*,***, N. Latorraca*, P. Ciambelli**,***, M. Sarno**,***, C. Leone**, D. Sannino**,***

* Department of Chemistry, University of Salerno, via Ponte Don Melillo, 84084 Fisciano (SA), Italy
** Department of Chemical and Food Engineering, University of Salerno,Via Ponte don Melillo, 84084 Fisciano (SA), Italy
*** NANO_MATES, Research Centre for NANOMAterials and nanoTEchnology at University of Salerno, University of Salerno, 84084 Fisciano (SA), Italy

ABSTRACT

The synthesis of polynorbornene by ring opening metathesis polymerizations (ROMP) in the presence of 2nd generation Grubbs catalyst-functionalized nanotube initiators, is reported. A full characterization of Grubbs catalyst-functionalized nanotubes was performed by FTIR (Fourier Transform Infrared Spectroscopy) and TG-DTG-MS (Thermogravimetrical Analysis coupled with Mass Spectrometer), in order to quantify the amount of catalyst grafted to the nanotube surface.

Keywords: ROMP, 2nd generation Grubbs catalyst (G2), carbon nanotubes, thermogravimetrical analysis, activity

1   INTRODUCTION

The synthesis of polymeric composite materials, containing multi-walled carbon nanotubes (MWNTs) [1], able to combine the mechanical strength and electronic conductivity of carbon nanotubes with the solubility and processability of polymers, has emerged as one of the most important and challenging topic in the framework of the nanostructured materials [2].

The main approaches to obtain homogeneously dispersed filler in the nanocomposites aim for a covalent bound between the polymer and the carbon nanotubes. In particular, as for the "grafting from" approach, catalyst functionalized nanotubes behave as polymerization initiators and polymers can be grown directly from the nanotube surface. This method prevents a full control of the polymerization reaction, but allows high amount of grafted polymer on the nanotube surface [3].

Herein, the synthesis of polynorbornene by ring opening metathesis polymerizations (ROMP) [4] in the presence of 2nd generation Grubbs catalyst-functionalized nanotube initiators is reported. Grubbs catalyst-functionalized nanotubes have been characterized by FTIR (Fourier Transform Infrared Spectroscopy) and TG-DTG-MS (Thermogravimetrical Analysis coupled with Mass Spectrometer), in order to quantify the amount of catalyst grafted to the nanotube surface. Four initiators have been prepared, differing for the length of the arm connecting the catalyst to the MWNTs.

2   EXPERIMENTAL

2.1   Materials and methods

Materials
Carbon nanotubes, have been prepared by catalytic ethylene chemical vapor deposition (CVD) [4-5] on Co/Fe modified Al$_2$O$_3$ powder, and –CCOH functionalized as reported in [5].

The –COOH-MWCNTs were successively functionalized by following the procedure reported by Adronov et al. [3], obtaining initiators **1-4**.

The synthesis of polynorbornene by ring opening metathesis polymerizations (ROMP) in the presence of 2nd generation Grubbs catalyst-functionalized nanotube, initiators **1-4** (Figure 1) has been performed. All initiators have a Grubbs catalyst linked to the nanotube through "chemical arms" differing for the alcoholic group connecting the catalyst to the –COOH functionality of the MWCNTs.

Methods
The Grubbs catalyst-functionalized nanotubes characterisation was performed by FTIR (Fourier Transform Infrared Spectroscopy) and TG-DTG-MS (Thermogravimetrical Analysis coupled with Mass Spectrometer) in order to quantify the amount of catalyst grafted to the nanotube surface. The activity of the **1-4** initiators were estimated.

Infrared spectroscopy has been used to characterize the functionalized MWNTs. The infrared spectra were obtained at room temperature by using a Nexus Thermo Nicolet FTIR (32 scans collected). Powdered materials (100 mg, 0.5 wt% of CNT in KBr) were pelleted (pressure 2 . 104 kg cm22) in self-supporting disks of 0.1–0.2 mm.

Simultaneous TG-DTG-MS analysis, on G2 and initiators **1-4,** was performed at 10K/mn heating rate under flowing air, with a Thermogravimetric Analyser (SDTQ

600 TA Instruments), online connected to a quadrupole mass detector (Quadstar 422, Pfeiffer Vacuum).
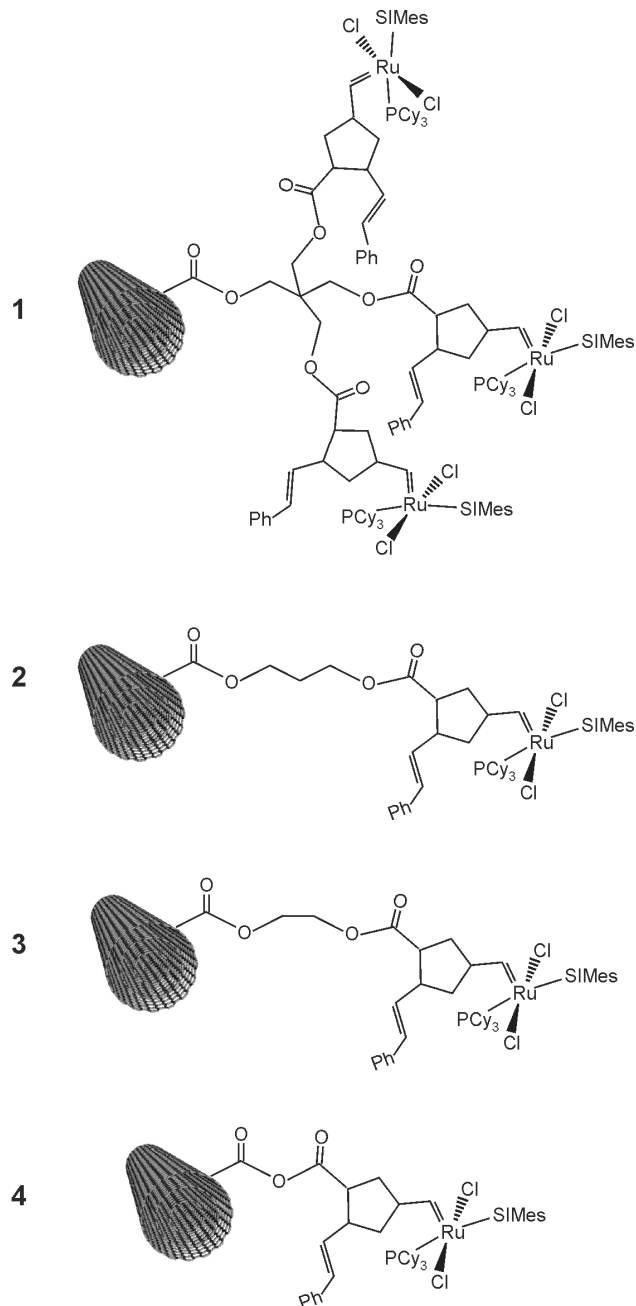

Figure 1 Scheme of the 4 initiators (**1-4**) prepared

2.2 Results and discussion

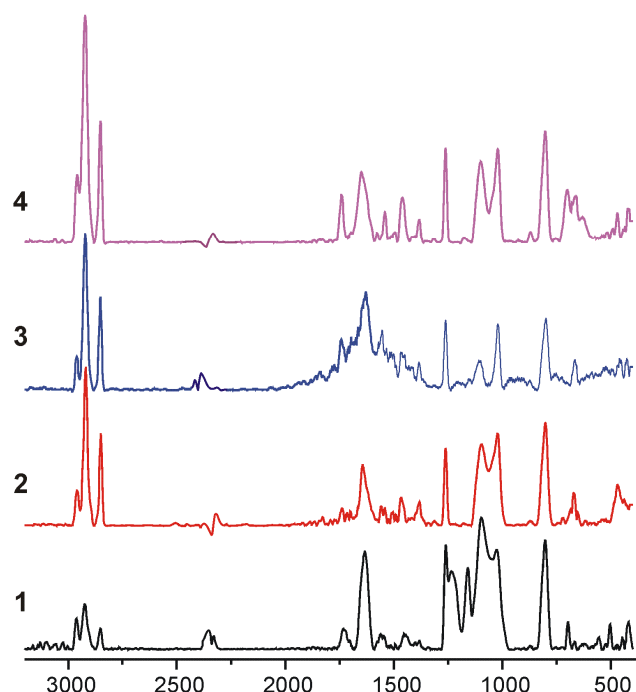FTIR spectra of initiators **1**-**4** are reported in Figure 2.

Figure 2: FTIR spectra of initiators **1**-**4**.

Despite the crowd of signals of FTIR spectra of all initiators, it is possible to identify some of the most characteristic signals. The spectra (Figure 2) present the C-H bond stretching at around 2960 cm^{-1}, due to methyl groups on MWCNTs and/or to –CH$_2$- groups in cyclopentane. The signals at 2125 and 2850 cm^{-1} can be attributed to the asymmetric and symmetric stretching of -CH$_2$- in cyclohexyl groups of the ruthenium coordinated PC$_{y3}$ ligands. Signals at around 1740 cm^{-1} are associated to the C=O stretching of the ester groups. CH$_2$ scissoring absorptions are observed at 1482 cm^{-1}, likely related to the aromatic ring, and at 1463 cm^{-1}, due to cyclohexyl groups. In the range 1270-900 cm^{-1} CH$_2$ rocking and wagging vibrations, mainly attributed to cyclic alkane absorption, are present for all the samples. Finally, the strong peaks at 1635 and 802, and that at 697 cm^{-1}, likely due to the abundance of aromatic groups, could be attributed, respectively, to C=C stretching of phenyl groups and to the C-H and C-C out of plane bending of the aromatic ring of the NHC ligand.

In figure 3 the TG profile of G2 was shown. We can distinguish three distinct steps of weight loss in the ranges 144-220°C, 220-375°C, 375-495°C. Moreover, figure 1c shows the ion currents of the main mass fragments (in the range 30-110 m/z). Taking into account the molecular formula of G2, the 6 most intense mass fragments (m/z = 39, 51, 65, 77, 78, 105) due to the trimethylphenyl groups release, those (m/z = 39, 41, 51, 55, 67, 77, 78, 79, 80, 81) attributed to the decomposition of tricyclohexhylphosphine, and the mass fragments (m/z = 39, 51, 61, 62, 63, 65, 89, 90, 91) coming from benzylidene can be recognized.

Together with the main fragments of HCl (35 and 36 m/z) the most intense fragment (m/z = 30) from the decomposition of imidazolidinylidene, and that from CO_2 (m/z = 44) are observed.

By matching the profiles of weight losses and mass fragments of G2 we can associate the decomposition of trimethylphenyls and benzylidene to the first weight loss, and tricyclohexylphosphine to the second loss, in the same temperature range in which the mass fragments of HCl are observed. The decomposition of imidazolidinylidene fraction is associated with the presence of CO_2 mass fragments detected during the third weight loss.
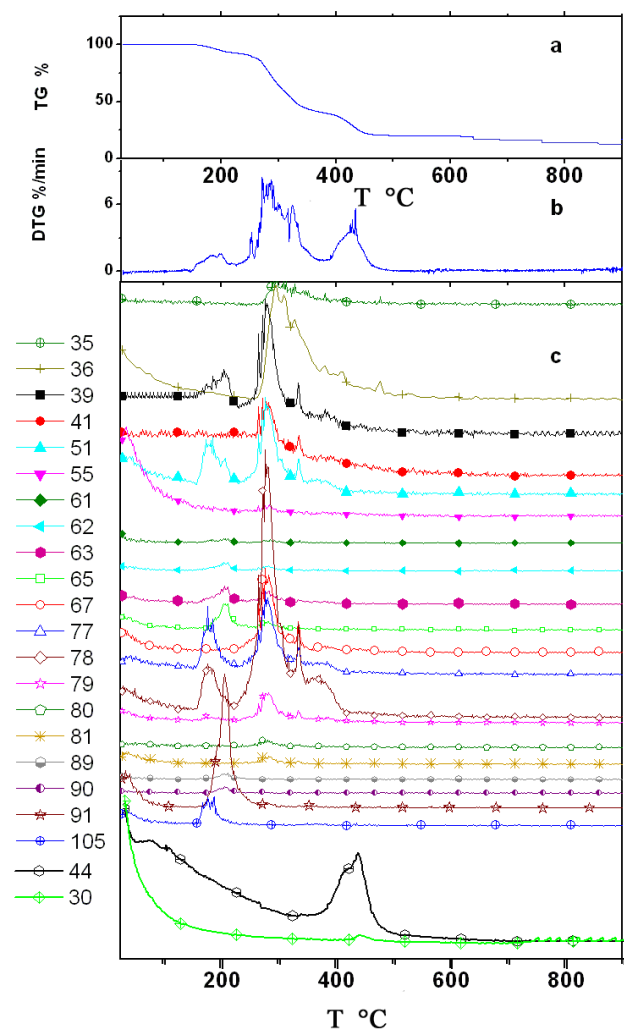
the mass detector in the same temperature range. In particular, the profile of the fragment m/z = 44, formed from the oxidation of the two composite fractions, G2 and CNT, is reported in Figure 4c. We can conclude that the nG2 weight loss at 495°C is due to G2 and the chains that bind to the nanotube G2, and that it constitutes the 28.0 wt% of nG2. From molecular weight calculations we can quantify the contribution of G2 to this first weight loss and conclude that the 23.6 wt.% of nG2 is due to G2. Reminding that in this temperature range G2 loses the 79.0 % of its weight, the total amount of G2 in nG2 is equal to 29.6 wt%. Finally, the Ru amount in G2 has been calculated according to stoichiometry (Table 1).
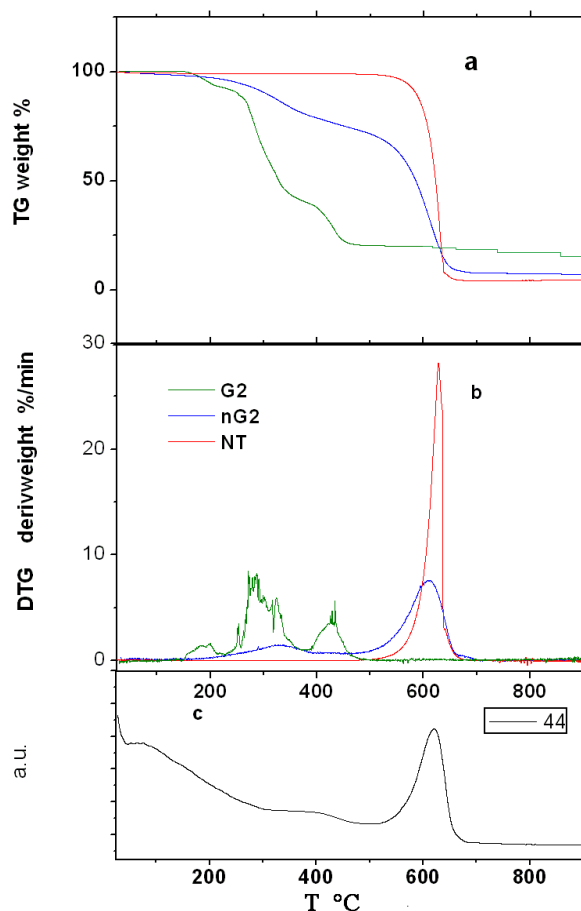

Figure 3: TG-DTG of G2 (a, b); main mass fragments m/z of G2 (c)

In Figure 4 the air flow TG profiles of 2nd generation Grubbs catalyst, run **1** and COOH-functionalized MWNTs (NT) are reported for comparison. We can see that at 495°C the oxidation of 79.6 wt.% of G2 is completed. In the TG profile of nG2 (see, in particular, the DTG profile) we can distinguish the oxidation of G2 and that of functionalized CNTs, as confirmed by the ion currents fragments given by

Figure 4: TG-DTG of G2, run **1** and COOH-functionalized MWNT

In Table 1 were collected also the estimation of the amount of catalyst grafted to MWCNTs by TG-DTG –MS analysis for the other three initiators **run 2-4.**

All the initiators **1-4** were able to promote the ROMP of 2-norbornene, results are reported in Table 1, as well. The activities of **1-4** depend on the length of the arm connecting the catalyst to the MWCNTs. In fact, most active initiators showed to be **1** and **2**, whereas a drop of the activity is observed for catalyst **4**. These results can be rationalized by

considering the lower accessibility of the monomer to the catalyst grafted to the nanotube through a shorter arm.

Table 1. Estimation of the amount of Ru grafted to MWCNT by TG-DTG-MS and catalyst activity

Samples	$mg_{catalyst}/mg_{sample}$	mol_{Ru}/mg_{sample}	Activity*
1	0.296 ± 0.025	$3.48 * 10^{-7}$	$0.94*10^2$
2	0.309 ± 0.025	$3.64* 10^{-7}$	$0.68*10^2$
3	0.247 ± 0.025	$2.91* 10^{-7}$	$0.26*10^2$
4	0.223 ± 0.025	$2.62* 10^{-7}$	$0.65*10^1$

*Activity: $kg_{polymer}$/[monomer][catalyst]h.

3   CONCLUSION

Four 2nd generation Grubbs catalyst-functionalized nanotubes initiators have been prepared, differing for the length of the arm connecting the catalyst to the MWNTs.

The amount of catalyst grafted to the nanotube surface has been quantified by TGA on-line connected with a quadrupole-mass spectrometer. All the initiators have been able to promote the ROMP of 2-norbornene. We have found that the catalytic activity depends of the length of the arm connecting the catalyst to the MWCNTs. In fact, the most active initiators are those with longer arm, while a drop of the activity is observed for the catalyst obtained connecting G2 directly to the –COOH functionalization. These results can be rationalized by considering the lower accessibility of the monomer to the catalyst grafted to the nanotube through a shorter arm.

REFERENCES

[1] S.Iijima, Nature (London) 1991, 354, 56-58; Dai, H. Surf. Sci., 500, 218, 2002.

[2] J. N Coleman. U.Khan, Y. K. Gun'ko, Adv. Mater. 18, 689, 2006; M. Moniruzzaman,; K.Winey I., Macromolecules 39, 5194, 2006.

[3] A. Adronov, Y.Liu Macromolecules, 37, 4755, 2004.

[4] Bielawski, C.W.; Grubbs, R.H. Prog. Polym. Sci., 32, 1, 2007.

[5] P. Ciambelli, D. Sannino, M. Sarno, C. Leone, U. Lafont Diam Relat Mater 16, 1144, 2007

[6] P. Longo, C. Costabile, F. Grisi, G. Siniscalchi, P. Ciambelli, M. Sarno, C. Leone, D. Sannino Nanotech 2009 - 2009 NSTI Nanotechnology Conference and Expo, 3-7 May 2009, Houston TX ISBN: 978-1-4398-1783-4. Vol. 2 pp 531-533