The Cleavage of Organosiloxanes with Dimethyl Carbonate: A Mild Approach to Graft-To-Surface Modification

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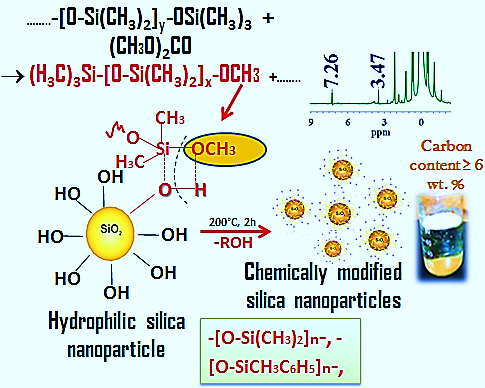
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**Viscosity measurements S1.** Depolymerization was performed with the use of 99.8 % ethanol solution. The polymer solution efflux time was measured with the use of a stopwatch by means of VPG–1 viscometer with the internal capillary diameter of 2.10 mm. Kinematic viscosity of the solution (*η*, m2/s) was calculated using the formula:

*η* = , (1)

where k – the viscometer constant that equaled 0.825 mm2/sec2, g − free-fall acceleration corresponding to 9.807 m/sec2 and τ − efflux time time, sec.

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| **Figure S2.** Apparatus for synthesis of high disperse materials with high content of the grafted organic groups:  1 – glass reactor, 2,7 – heating mantle, 3 – stirrer, 4 – glass stopper, 5 – glass laboratory thermometer, 6 – container mixing modifying reagent, 8 – batcher, 9 – injection system, 10 – inert gas cylinder, 11 – inert gas valve. |

**Equation** **S3**. The modification degree (*Θ*) of the silica surface was estimated from the ratio of the optical density of a band of free silanols at 3742 cm-1 of modified and unmodified silicas:

, (2)

where *Do* and *D* are the optical density of the mentioned band of the unmodified and modified silicas, respectively.

**Equation** **S4**. The apparent bonding density of the attached layers was calculated using the formula *3*:

*ρ =* (3)

where *MW* is the molecular weight of the methylphenylsiloxy group (131 g/mol), % *C* is the carbon weight percentage of the modified silica, and *S*(BET) is the surface area of the original silica (m2/g), *nc* is a number of carbon atoms in the grafted group. Equation 3 gives the number of [-Si(CH3C6H5)O-] repeat units per 1 nm2 of the surface (*ρ*).

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| **Figure S5.** 90 MHz 1H NMR spectrum of neat PDMS–100; the inset shows the methyl group shifts of parent PDMS–100. |

**Equation S6.** Typically we conducted End-Group Analysis using formula of total siloxane repeats (*Rt*) (*1*) and formula of number of monomers per chain (*N*) (*2*). Total siloxane repeats (*Rt*) was calculated using the formula:

(1)

Number of monomers per chain (*N*) was calculated using the formula:

*N*=, (2)

where *Ne*– number of end groups which was calculated using 1H NMR integration data, *NE*= (*N*methoxy + *N*ethoxy).

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| **Figure S7.** 90 MHz 1H NMR spectrum of depolymerizied PMPS; the inset shows the alkoxy groups shifts of depolymerized PMPS at 200 °C. |

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| **Figure S8.** 13C CP/MAS NMR spectra of silica modified with neat PMPS and their mixture with DMC (1.8 mmol) at 200 °C for 2 h; the inset shows shifts of the grafted organic groups for both samples. |

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| ***a*** | ***b*** |
| **Figure S9.** Contact angle of SiO2 nanoparticles, modified with mixture of PMPS/DMC at 200 °C for 2 h (*a*) and photograph showing hydrophobic properties of SiO2/PMPS+DMC (*b*, *1*) and unreacted SiO2 nanoparticles (*b*, *2*). | |