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OF BUTYL METHACRYLATE WITH IMPREGNATED ZnO NANOPARTICLES

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P50 GUANIDINE CONTAINING POLYACRYLAMIDE HYDROGEL

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P51 GAS SEPARATION PROPERTIES OF 6FDA-BASED COPOLYIMIDES WITH PHOSPHOROUS-CONTAINING PENDANT UNITS

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P52 CORRELATION BETWEEN GAS PERMEABILITY IN HOMO- AND CO-POLYIMIDES BASED ON HEXAFLUOROISOPROPYLIDENE AND ALICYCLIC DIANHYDRIDES AND THEIR FRACTIONAL FREE VOLUME

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P53 POLYSACCHARIDE COMPOSITES FOR FUEL CELL APPLICATION

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P54 EFFECT OF NANOCLAY MODIFICATION ON STRUCTURE AND THERMAL PROPERTIES OF NANOCOMPOSITES BASED ON CYANATE ESTER RESINS

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P55 PHOSPHORUS- AND SILICON- CONTAINING POLYMERS - SYNTHESIS AND CHARACTERIZATION

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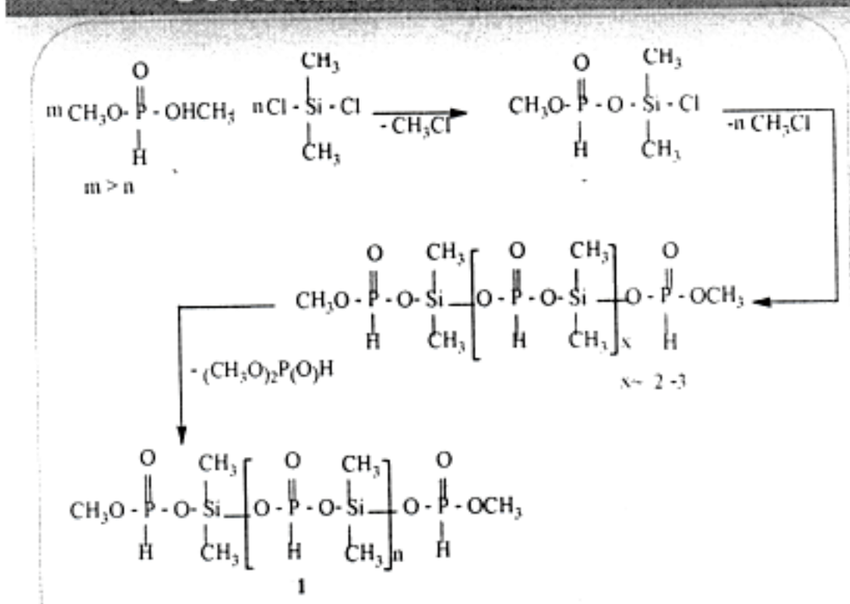
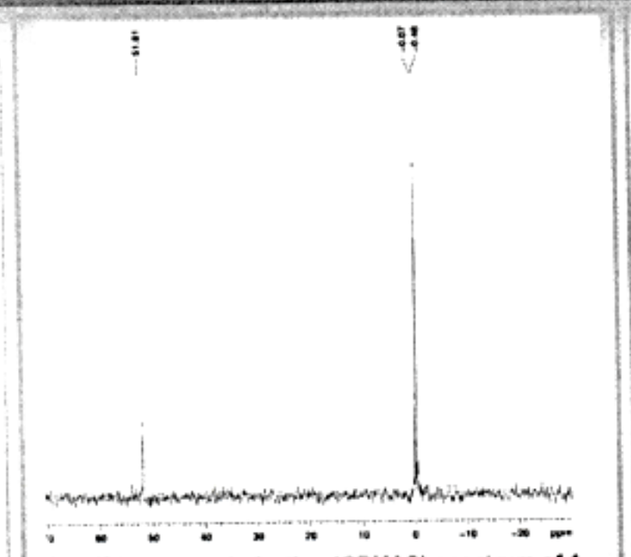
One of the most promising approaches to the development of new materials that combine the advantages of organic polymers with those of inorganic solids is to devise products that have a backbone of inorganic atoms to which are attached organic or organometallic side groups [1-3]. Such polymers are known as "inorganic-organic polymers", often abbreviated to "inorganic polymers". The inorganic backbone can provide heat-, fire-, or radiation- resistance. The side groups control properties such as solubility or resistance to solvents, liquid crystallinity or nonlinear optical behavior, hydrophobicity, hydrophilicity, adhesion, and biological compatibility [4]. Inorganic polymers find application in: catalysis; solid electrolytes; pharmacy (drug delivery); medicine (regenerative therapeutic materials); fuel cells; polymer modification (flame retardants; thermostabilizers; adhesives).

In the present study a new type of inorganic polymer with a structure [-O-P(O)(H)-O-Si$(CH_3)_2$-] has been obtained. ^1H, $^{13}C\{H\}$, $^{31}P\{H\}$, and ^{31}P NMR spectroscopy in solution and under magic angle spinning conditions (MAS) have been applied to prove the structure of the polymer. The presence of P-H group makes this polymer highly reactive.

SYNTHETIC STEPS AND CHARACTERIZATION OF THE PHOSPHORUS- AND SILICON- CONTAINING POLYMERS

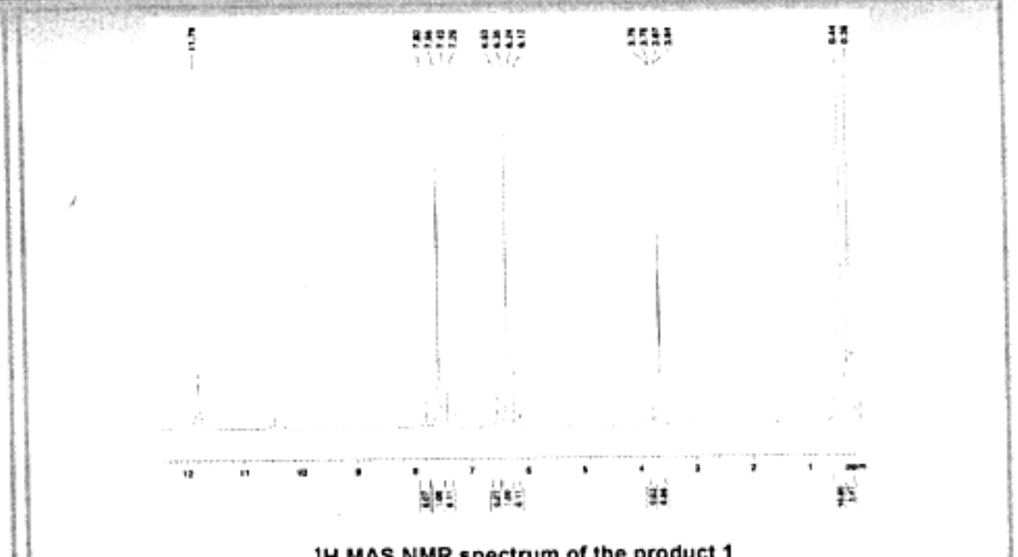


Scheme 1. Reaction pathways of the interaction of dimethyl H-phosphonate (DMPH) with dichlorodimethylsilane (DCDMSi).



$^1H \rightarrow ^{13}C$ cross-polarization (CPMAS) spectrum of 1

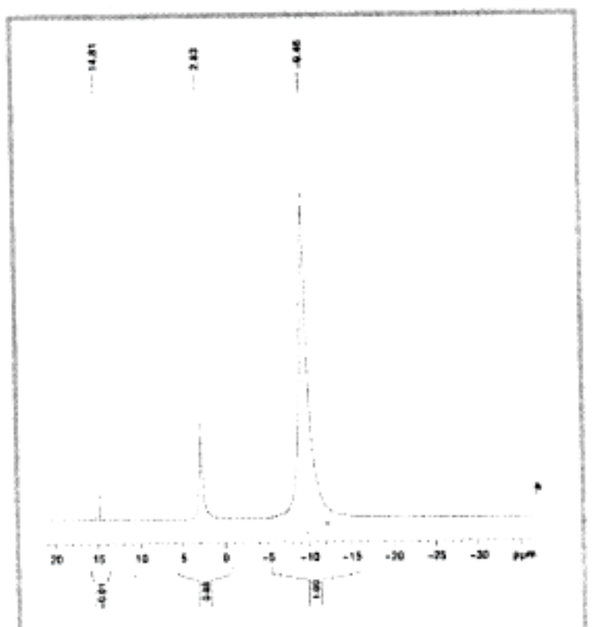
In $^{13}C\{H\}$NMR spectrum there are signals at -0.07 ppm and -0.48 ppm for S-CH_3 carbon atoms in end group and in the repeating units, respectively; at 51.81 ppm for P-OCH_3 carbon atom.



^1H MAS NMR spectrum of the product 1

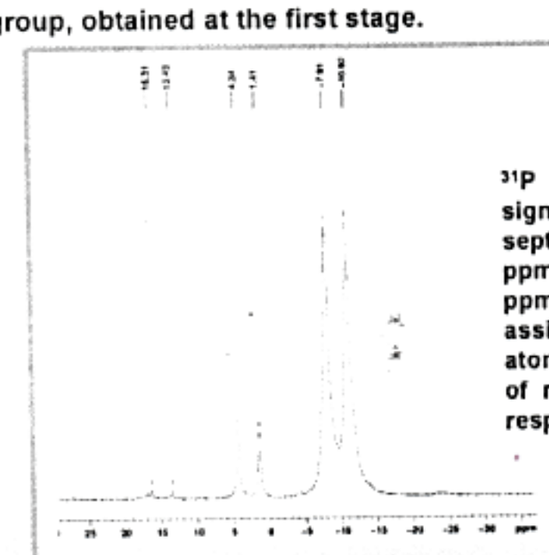
In ^1H MAS NMR spectrum there are signals at 0.44 ppm and 0.28 ppm for Si-CH_3 protons; at 3.65 ppm (d, $^3J(P,H)$=12.28 Hz) and 3.77 ppm (d, $^3J(P,H)$=12.00 Hz) for P-OCH_3 protons of the end groups of product 1 and of DMPH, respectively; at 6.70 ppm (d, $^1J(P,H)$=702.15 Hz), 6.83 ppm (d, $^1J(P,H)$=714.15 Hz) and 6.95 ppm (d, $^1J(P,H)$=726.15 Hz) for P-H protons of DMPH, of the end group and of the Repeating unit of product 1, respectively; 11.79 ppm for P-O*H* proton.

The interaction of DMPH with DCDMSi represents a dealkylation reaction with the participation of α-carbon atom of the methyl group of DMPH and chlorine atom of DCDMSi). The reaction starts with nucleophilic attack of chlorine atom at α-carbon atom of the methyl group of DMPH. We carried out the reaction in small excess of DMPH (molar ratio between DMPH and DCDMSi is 1.3:1). Under these conditions of excess of DMPH the growth of polymer chain occurs via polydisproportionaton of the oligomeric products with end phosphonate group, obtained at the first stage.



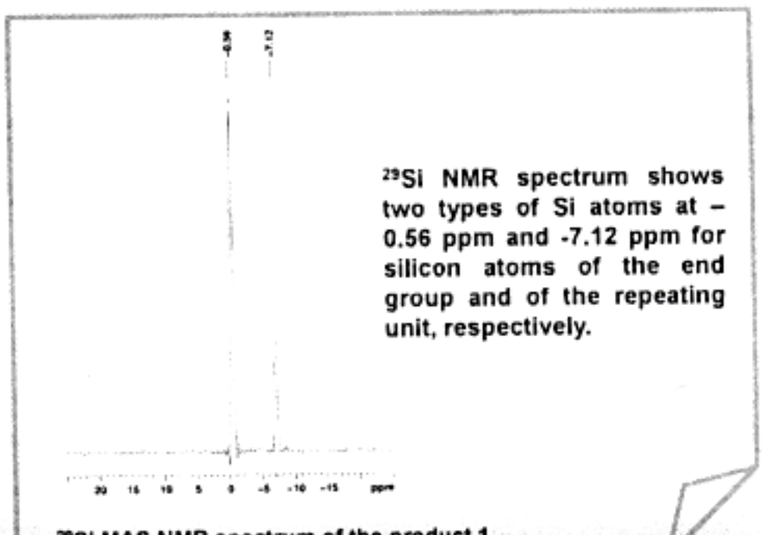
$^1H \rightarrow ^{31}P$ cross-polarization (CPMAS) spectrum of 1

$^{31}P\{H\}$ NMR spectrum of the reaction product revealed three types of phosphorus atoms at d = 14.81 ppm, 2.83 ppm, and at -9.46 ppm.



^{31}P MAS NMR spectrum of the product 1

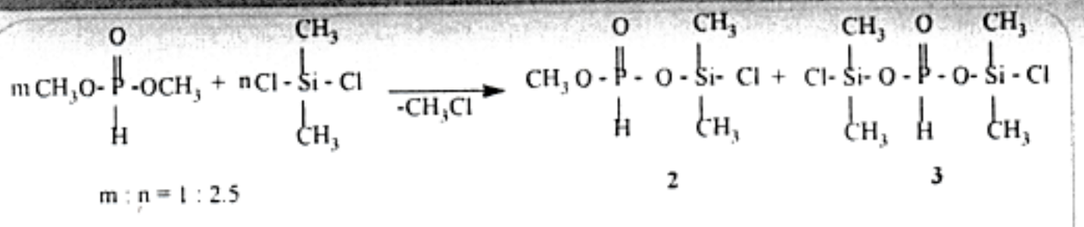
^{31}P NMR spectrum shows signals at 14.87 ppm (doublet of septets $^1J(P,H)$=699.65 Hz); 2.83 ppm (d, $^1J(P,H)$=711.80 Hz); -9.46 ppm (d, $^1J(P,H)$=731.24 Hz assigned to the phosphorus atom of DMPH, of end group and of repeating unit of product 1, respectively.



^{29}Si MAS NMR spectrum of the product 1

^{29}Si NMR spectrum shows two types of Si atoms at –0.56 ppm and -7.12 ppm for silicon atoms of the end group and of the repeating unit, respectively.

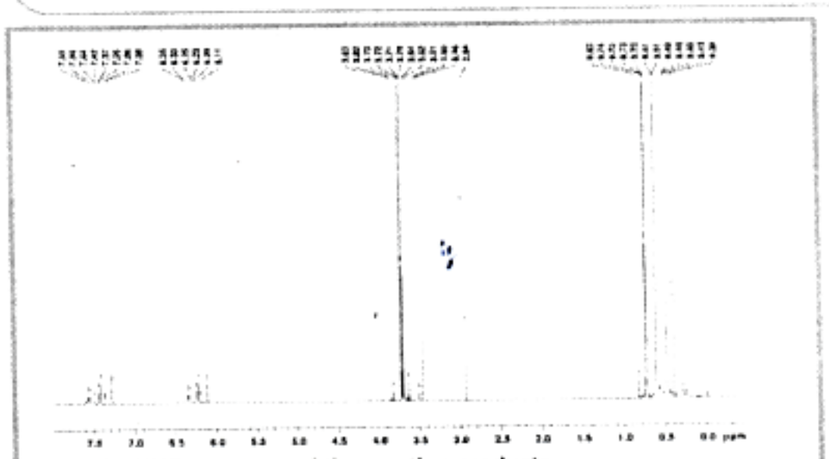
MODEL REACTION BETWEEN DIMETHYL H-PHOSPHONATE AND DICHLORODIMETHYLSILANE



* Scheme 2. Interaction of dimethyl H-phosphonate with dichlorodimethylsilane

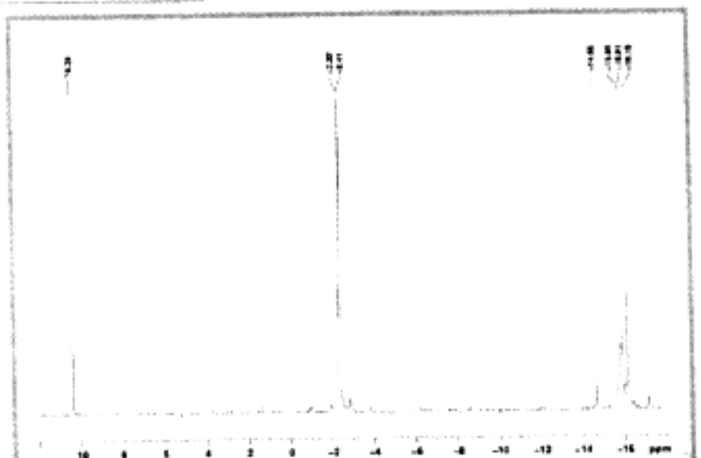
In the literature there are no any NMR (^1H and/or ^{31}P) data for the expected reaction products. In this connection we performed a model reaction between DMPH and DMPH at molar ratio 1:2.5.

The data from the ^{31}P NMR spectra revealed that the signals of the phosphorus atoms of methyldimethylchoro-silane H-phosphonate (2) and bis(dimethylchlorsilane) H-phosphonate (3) are strongly shifted upfield as compared to those of DMPH. This upfield shift can be explained with the increase of the electron density at these phosphorus atoms due to the strongly ionic character of Si- O bond.



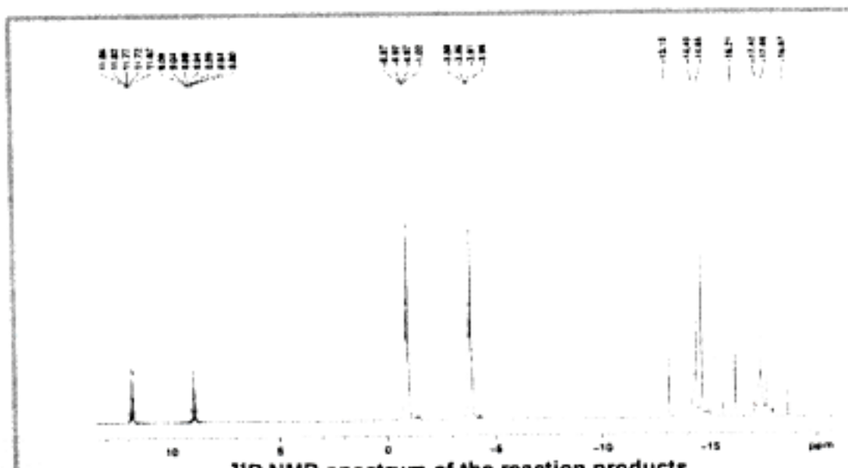
^1H NMR spectrum of the reaction products

In ^1H NMR spectrum there are signals in the region 0.38 to 0.74 ppm for Si-CH_3 protons; at 3.72 ppm (d, $^3J(P,H)$=12.45 Hz) and 3.71 ppm (d, $^3J(P,H)$=11.90 Hz) for P-OCH_3 protons; 6.69 ppm (d,$^1J(P,H)$=697.83Hz); at 6.82 ppm (d, $^1J(P,H)$=713.49 Hz) and 6.94ppm (d, $^1J(P,H)$ = 730.72 Hz) for three types of P-H protons.



$^{31}P\{H\}$ NMR spectrum of the reaction products

$^{31}P\{H\}$ NMR spectrum shows three types of phosphorus atoms at 10.36ppm, - 2.32 ppm and - 16.16ppm.



^{31}P NMR spectrum of the reaction products

In ^{31}P NMR spectrum there are signals at 10.36 ppm (doublet of septets $^1J(P,H)$=697.97 Hz, $^3J(P,H)$=11.84 Hz) for phosphorus atom of DMPH; at -2.62 ppm (doublet of quartets $^1J(P,H)$=719.47 Hz, $^3J(P,H)$=12.29 Hz) for phosphorus atom of product 2; at -16.16 ppm (d, $^1J(P,H)$ = 730.73 Hz) for phosphorus atom of product 3.

CONCLUSIONS: *The polydealkylation reaction can be used for obtaining an inorganic polymer with a structure [-O-P(O)(H)-O-Si$(CH_3)_2$-].*

1. J. E. Mark, H. R. Allcock, R. West, Inorganic Polymers, Prentice Hall, Englewood Cliffs, NJ, 1992.; 2. Peuckert M., Vaahs T., Brück M., Adv. Mater., 2 (1990) 398.; 3. Mark J. E., Allcock H. R., West R., In Inorganic Polymers, 2 end ed., Oxford Universtsity Press Inc., 2005.; 4. Allcock H. R., Wright S. Kosydar D., K. M., Macromolecules, 11 (1978) 357.

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