Djamal Eddine Kherroub*, Mohammed Belbachir and Saad Lamouri

A new approach for the polymerization of tetraphenyltetramethylcyclotetrasiloxane by an environmentally friendly catalyst called Maghnite-H⁺

<https://doi.org/10.1515/gps-2017-0033>

Received March 3, 2017; accepted June 2, 2017; previously published online August 18, 2017

Abstract: This work is devoted to the study of the cationic ring opening polymerization of tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$), using a solid green catalyst prepared by the activation of a natural clay by sulfuric acid (Maghnite-H⁺). This treatment leads to the spacing of the montmorillonite sheets due to the substitution of the existing interlayer cations by the protons of the acid. This consequence is clearly shown on the X-ray diffraction (XRD) spectrum. The polymerization reaction proceeded in bulk and under mild conditions. Various tests were carried out by changing the temperature, the time and the catalyst mass content in order to increase, at the same time, the yield of the reaction and the average molecular mass of the polyphenylmethylsiloxane (PPMS) obtained. The structure of the PPMS obtained was identified by infrared (IR), ¹H nuclear magnetic resonance (NMR) and ¹³C NMR analyses over different periods of time. The thermal behavior was investigated by differential scanning calorimetry (DSC) analysis. At the end, in order to show the role played by the Maghnite-H⁺ during the various reaction stages, a reaction mechanism was proposed.

Keywords: cation polymerization; green catalyst; Maghnite-H⁺; montmorillonite.

1 Introduction

Heterogeneous catalysis is one of the major challenges of green chemistry, and is among its 12 major principles. Heterogeneous catalysts accelerate the rate of reaction by lowering the energy barrier, in other words the energy threshold necessary to allow the reaction to occur [1]. The catalyst saves energy and reduces reaction time. The catalyst thus allows a better use of the atoms of the starting molecules, all of which are found in the final product and not in secondary products which have to be separated, recycled or destroyed. The goal of green chemistry is to design chemical products and processes that reduce or eliminate the use and synthesis of hazardous substances [2]. The aim is to understand and improve existing catalysts and catalytic processes, notably by making them more selective, but also to discover new ones that simultaneously respond to new technological, economic and environmental challenges [1]. Heterogeneous polymerization catalyzed by transition metal complexes or chemically modified clays occupies an increasingly important place. Known since the 1950s with the discovery of systems based on chrome or titanium, this catalysis has never ceased to evolve to lead to more productive processes, be more selective and enrich new products. The heterogeneous polymerization strategy is highly efficient and versatile, and produces polymers with low polydispersity [3].

This study deals with cationic polymerization and examines the catalytic activity of a montmorillonite clay called “Maghnite-H⁺” via the cyclic polymerization of tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) in order to obtain phenylmethylsiloxane polymers (Scheme 1). The structure and composition of the catalyst have been reported in previous work [4, 5]. Elemental analysis of Maghnite-H⁺, obtained using X-ray fluorescence spectroscopy, shows that there is an excellent correlation between acid treatment and Maghnite-H⁺ catalytic activity.

The acid treatment of raw Maghnite reduces the octahedral content (Al_2O_3) which causes an increase in the proportion of silica. It was found that the best value for the conversion of the monomer was obtained with raw Maghnite treated by 0.23 M of sulfuric acid solution, in which there is a complete saturation of the montmorillonite with protons without destroying the catalyst structure

*Corresponding author: Djamal Eddine Kherroub, Laboratory of Polymer Chemistry, Department of Chemistry, Faculty of Exact and Applied Sciences, University of Oran 1 Ahmed Ben Bella, BP 1524 El'Menouer, Oran 31000, Algeria, e-mail: djamaledine.kherroub@yahoo.com; and University Centre of Relizane Ahmed Zabana, Institute of Sciences and Technology, BP 48000, Oran, Algeria

Mohammed Belbachir: Laboratory of Polymer Chemistry, Department of Chemistry, Faculty of Exact and Applied Sciences, University of Oran 1 Ahmed Ben Bella, BP 1524 El'Menouer, Oran 31000, Algeria

Saad Lamouri: Laboratory of Macromolecular Chemistry, Polytechnic Military School (EMP), Bordj El Bahri, 16111 Algiers, Algeria

Scheme 1: The structure of (A) tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) and (B) polyphenylmethylsiloxane.

[6]. Maghnite- H^+ can be removed at the end of the reaction by simple filtration and even reused. Numerous studies have been carried out in the laboratory of polymer chemistry at the University of Oran (Algeria) using Maghnite- H^+ as a catalyst for the polymerization of several vinyl and cyclic monomers [7, 8], and thus as an inorganic reinforcement for the synthesis of various nanocomposites [9–11].

The term “silicone” means polymers whose recurring unit is represented by $(-Si [R,R]-O-)$, where R is an organic radical, generally a methyl group (PDMS). PDMSs have unique physical and chemical properties over organic polymers. These particular properties result from the inorganic backbone Si-O-Si. Indeed, the Si-O bond energy of 460 kJ/mol is much higher than the energy of carbon-based bonds [12, 13]. This results in excellent thermal stability, high resistance to UV, oxidation and hydrolysis in the absence of acid or base [14, 15]. The phenyl group is bulky relative to the methyl group and also has a higher intermolecular force constant than this; it serves as an interesting group to replace the methyl groups linked to the silicon in order to improve its properties more and more. For example, it is well known in polymer chemistry that the crystallization temperature of a polymer can be decreased by breaking the regular structure of a homopolymer by the addition of bulky groups [16–21]. Polyphenylsiloxanes have a flexible structure and a low-softening temperature ($<200^\circ\text{C}$) which could lead to easy modeling and shaping materials and imparts a combination of properties such as good adhesion, transparency, corrosion protection and adjustable refractive index. Silicone were obtained previously in the presence of strong bases as phosphazene bases [22–25], strong acids as dodecylbenzenesulfonic acid [26], triflic acid [27], tris(pentafluorophenyl)borane [28] and trifluoromethanesulfonic acid [29], etc.

2 Materials and methods

2.1 Materials

$D_4^{\text{Ph,Me}}$ (99%) was used as purchased without further purification. Methanol was purified by vacuum distillation. All products were obtained from the aldrich chemical annex of Telemcen in Algeria. Maghnite was obtained from the Algerian company of bentonite (BENTAL), without any pretreatment.

2.2 Preparation of Maghnite- H^+

A mass of 30 g of raw Maghnite was combined with 120 ml of distilled water at room temperature; the suspension was left under stirring. After 30 min, 100 ml of a solution of sulfuric acid (0.23 M) was added and the stirring was continued for 48 h. After filtration and subsequent washing, the activated Maghnite was dried in an oven for 24 h at a temperature of 105°C . Finally, Maghnite- H^+ was crushed, sieved and stored away from air and moisture.

2.3 Polymerization procedure

Some 0.08 g of Maghnite- H^+ was heated before use under vacuum with mechanical stirring for 30 min. The polymerization was carried in bulk. The dried amount of Maghnite- H^+ was added to a flask containing 4 g (3.54 ml) of $D_4^{\text{Ph,Me}}$; the flask was immersed in an oil bath and brought to a temperature of 60°C under reflux while being stirred. After 150 min, the reaction was stopped by deactivating the Maghnite- H^+ by adding cold water to the reaction mixture. The Maghnite- H^+ was recovered by filtration, and the filtrate was precipitated in methanol (non-solvent). The insoluble product was dried at 80°C in vacuum for 3–4 h and weighed as polymer. Excess water was retrieved by evaporation at 105°C ; the amount of water necessary to stop the reaction would then be the difference between the initial amount and the recovered amount. It was assumed that the residual material was the remaining monomers and the oligomers formed during the reaction. Regarding the kinetic study, the same procedure described above was repeated by changing the temperature, time and the percentage of the catalyst.

2.4 Characterization methods

2.4.1 X-ray diffraction: The X-ray diffraction (XRD) patterns of the samples were carried out at room temperature on a Bruker D8 Advance X-ray diffractometer (40 kV, 30 mA) with a graphite monochromator, using $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at a rate of 5° min^{-1} in the range of $2\theta = 2^\circ - 80^\circ$.

2.4.2 Infrared spectroscopy: Infrared (IR) analysis of the polymers obtained was done using a Bruker Alpha FT-IR spectrometer equipped with an attenuated total reflection (ATR) accessory.

2.4.3 Nuclear magnetic resonance: ^1H and ^{13}C nuclear magnetic resonance (NMR) spectrums were recorded under ambient

temperature on a Bruker Avance 300 NMR spectrometer, using tetramethylsilane as the internal standard and deuterated chloroform as the solvent.

2.4.4 Differential scanning calorimetry: The different thermal characteristics such as glass transition temperature (T_g) of the synthesized polymer were measured by differential scanning calorimetry (DSC) from the corresponding thermal changes in the DSC thermogram using a Setaram 92 DSC apparatus.

2.4.5 Molecular weight measurements: Gel permeation chromatography measurements of the samples were performed using a WISP Model 712, Waters Associates chromatograph. Tetrahydrofuran was used as a solvent and the apparatus was calibrated in an initial approximation with polymethyl methacrylate of known molecular weight.

3 Results and discussion

3.1 XRD

Figure 1 shows the characterization by XRD analysis of the raw Maghnite and Maghnite treated with sulfuric acid. It is obvious that the treatment led to the removal of minerals such as calcite and mica. This is confirmed by the decline of the intensity of their peaks compared to the strong peak corresponding to montmorillonite (green area); this elimination is clearer for the quartz, as shown by the reduction of the two peaks at $2\theta = 21.93^\circ$ and 26.71° (blue areas). Moreover, the acid treatment caused a shift of the peak of montmorillonite to small values of 2θ from 8.41° to 5.73° , corresponding to an increase of the interlayer distance of

Figure 1: X-ray diffraction (XRD) patterns of the Maghnite before treatment (raw-Maghnite) and after treatment (Maghnite- H^+).

montmorillonite (d_{001}) from $10.50 \text{ \AA}$ to $15.41 \text{ \AA}$; this can be explained by the substitution of interlamellar cations of Maghnite by the acid protons which have a larger atomic diameter.

3.2 IR spectroscopy

Figure 2 provides the IR spectra of the monomer and the obtained products for 90 min, 120 min, 150 min, 180 min and 210 min at 60°C . The broad peak seen at 3425 cm^{-1} for the obtained products is attributed to the OH stretching of the Si-OH end groups in the polyphenylmethylsiloxane (PPMS) chains. The appearance of this peak is due to the linkage between the released proton of Maghnite- H^+ and the oxygen atom at the end after the $D_4^{\text{Ph,Me}}$ ring opening (Scheme 2A); the decrease in its intensity with time of the reaction is clearly noticeable, which may be explained by the increase of polymerization degree leading to a smaller number of OH chain ends. The small peak which appears at about 3072 cm^{-1} is attributed to the C-H bond of the phenyl ring. The two bands at 2953 cm^{-1} and 2928 cm^{-1} are, respectively, due to C-H asymmetric/symmetric stretching of CH_3 . The two bands seen, respectively, at 2888 cm^{-1} and 2846 cm^{-1} are assigned to the C-H asymmetric/symmetric stretching of CH_2 . The small series of bumps at 1949 cm^{-1} , 1865 cm^{-1} , 1812 cm^{-1} and 1748 cm^{-1} are caused by overtones (harmonics) of the phenyl ring vibrational modes having stretching frequencies in the fingerprint region. The bonds which occur in pairs, one at 1610 cm^{-1} and one at

Figure 2: Infrared (IR) spectra of polyphenylmethylsiloxane (PPMS) obtained by the polymerization of tetraphenyltetramethylcyclotetra-siloxane ($D_4^{\text{Ph,Me}}$) at a temperature of 60°C for different times.

Scheme 2: Polymerisation of tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) by Maghnite- H^+ ; (A) linear polymer and (B) Crosslinked polymer.

1492 cm^{-1} , are due to the $\text{C}=\text{C}$ ring stretching absorptions. The signal at 1281 cm^{-1} is assigned to the CH_3 symmetric deformation of $\text{Si}-\text{CH}_3$. Peaks appearing at 1016 cm^{-1} , 1090 cm^{-1} and 486 cm^{-1} are, respectively, attributed to the stretching vibrations and deformation vibrations of the linear $\text{Si}-\text{O}-\text{Si}$ structures. The signal at 825 cm^{-1} is due to the $\text{Si}-\text{C}$ stretching vibrations. The two bands at 743 cm^{-1} and 690 cm^{-1} are assigned to the stretching vibrations of $\text{C}-\text{H}$ in the phenyl ring. The IR spectrum of the obtained PPMS using Maghnite- H^+ as a catalyst revealed no differences from those obtained by other researchers [30, 31].

3.3 Proton NMR

In order to identify more precisely the structure of the polymer obtained by the polymerization of $D_4^{\text{Ph,Me}}$ using the Maghnite- H^+ as catalyst, the product was analyzed before and after reaction by NMR analysis by comparing the two spectra; that of the monomer and that of polymer obtained at 60°C for 150 min. The results are shown in Figure 3A and B, which show the different chemical shifts.

In both spectra, the dominant peak observed at about 1.20 ppm is attributed to the methyl groups. It is more intense in the spectrum of the polymer meaning the large number of methyl groups in the polymeric chain. The neighboring peaks at 6.83 ppm, 6.97 ppm and 7.13 ppm are assigned to the protons of the phenyl ring. The small peak appearing at 4.80 ppm is assigned to the OH groups at the ends of polymer chains during the reaction. Similar results were obtained by Fei et al. [32].

3.4 Carbon NMR (^{13}C NMR)

It was therefore necessary to analyze the products obtained by ^{13}C NMR to provide a complement to the previous study. The results are shown in Figure 4A–C showing the ^{13}C NMR spectra of the monomer, and the polymer obtained after 150 min and 180 min, respectively. The peak located at approximately 0.27 ppm for the monomer and 0.78 ppm for the polymers corresponds to the carbon of CH_3 . The peaks at 137.78 ppm, 130.44 ppm, 128.85 ppm and 125.20 ppm for the monomer, and at

Figure 3: ^1H nuclear magnetic resonance (NMR) spectra of (A) tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) and (B) polymer obtained at a temperature of 60°C for 150 min.

Figure 4: ^{13}C nuclear magnetic resonance (NMR) spectra of (A) tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$), (B) polymer obtained after 150 min and (C) polymer obtained after 180 min at a temperature of 60°C .

Figure 5: Differential scanning calorimetry (DSC) thermogram of polyphenylmethylsiloxane (PPMS) obtained after 150 min.

137.81 ppm, 129.92 ppm, 127.30 ppm and 124.13 ppm for the two polymers are assigned to the phenyl ring carbons, as shown in Figure 4. Moreover, there is a creation of a down peak at 33.85 ppm on the distortionless enhancement of polarization transfer using a 45° decoupler pulse spectrum of the polymer obtained after 180 min, that is attributed to the carbon of CH_2 , indicating the formation of ethylene bridges between linear polymer chains (Scheme 2B). These results show that beyond 180 min of reaction time, the polymer chains can be crosslinked to form organopolysiloxane elastomers.

3.5 DSC

DSC was used as a thermal analysis, to identify and confirm at the same time the structure and the purity of the obtained product. Figure 5 shows the DSC thermogram of the polymer obtained after 150 min of reaction time. The thermogram shows a small thermal deformation at about -41.35°C , which corresponds to the glass temperature of the polymer ($T_g = -41.35^\circ\text{C}$); this T_g value is comparable to that of linear PPMS. The results obtained by DSC largely support the results obtained by IR and NMR for the linear structure of the polymer obtained after 150 min; they also simulate, to a large extent, the results obtained in previous research [33, 34].

3.6 Effect of temperature

In an effort to understand and control more the polymerization reaction of $D_4^{\text{Ph,Me}}$ catalyzed by Maghnite- H^+ , we

Table 1: Effect of reaction temperature on tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) polymerization.^a

Temperature (°C)	Conversion of monomer (wt%)	M_n	M_w/M_n
30	37	3547	1.08
40	59	12,100	1.08
50	71	21,321	1.08
60	85	36,625	1.13
70	87	32,201	1.29
80	89	26,870	1.42
90	89	16,308	1.63

^aMaghnite- H^+ /tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$)

weight ratio = 2%. Reaction time: 150 min.

M_n , Number average molecular mass; M_w/M_n , polydispersity index.

examined the effect of the temperature of the medium on the reaction that takes place there. Table 1 gives measured values of the monomer conversion and number of average molecular mass of the polymers obtained in a temperature range of 30 – 90°C . The increase in temperature leads to a significant increase in conversion reaching 85% at 60°C ; beyond this temperature, this increase becomes negligible until the conversion stabilizes at its maximum at about 89%. By contrast, the variation in average molecular mass shows two different behaviors; a gradual increase from 30°C to 60°C , followed by a reduction after just exceeding its highest value at about 60°C . We assume that this is the ceiling temperature; the decrease in average molecular mass can be explained by the fragmentation of the chains and suggests the thermal decomposition of PPMS after the breaking of Si-O bonds when approaching the boiling point. The thermal degradation phenomenon reflects a wide divergence between the molecular mass values, resulting in the increase of the polydispersity index, which is found in Table 1.

3.7 Effect of Maghnite- H^+ /monomer weight ratio

In order to study the catalytic action of Maghnite- H^+ as a heterogeneous catalyst in the polymerization reaction of $D_4^{\text{Ph,Me}}$, we performed the reaction with a catalyst content ranging from 0.5% to 4% by weight, so that for each catalyst content, the reaction time varied from 30 min to 210 min. The results of the influence of the Maghnite- H^+ content on the monomer conversion and on the number average molecular mass are shown in Figures 6 and 7, respectively. In all tests, the reaction was carried out in

Figure 6: Effect of Maghnite- H^+ /tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) weight ratio on the conversion of monomer.

Figure 7: Effect of Maghnite- H^+ /tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) weight ratio on the average molecular mass.

bulk and at a temperature of 60°C . It is clearly noticeable that for all the different Maghnite- H^+ contents, the reaction time had an effect proportionally positive on the monomer conversion before 180 min. After this duration, the effect of reaction time became negative (Figure 6). The reduction in the monomer conversion for large periods may be explained by the occurrence of depolymerization phenomenon of polymer chains caused by the active sites of the Maghnite- H^+ still remaining in the reaction medium. This result indicates that Maghnite- H^+ can play the opposite role after sufficiently large periods of time. Similar results were previously obtained by several authors [7, 8]. By contrast, the average molecular mass

increased with increasing reaction time; the maximum value for the different Maghnite- H^+ contents was about 150 min, then it stabilized almost up to 180 min, so that it began to decrease. The reduction over time of the peak corresponding to OH groups, which exist only at the end of the polymer chains of PPMS synthesized by Maghnite- H^+ , shown by the IR analysis (Figure 2), indicates that the chains became longer, resulting in large molecular mass. The temporary stabilization between 150 min and 180 min of the average molecular mass, and at the same time the increase in the monomer conversion, were due to the crosslinking phenomenon, leading to branched structures, because of the formation of ethylene bridges between the linear chains; this explanation is clearly supported by what was obtained by ^{13}C NMR analysis (Figure 4C). The decrease in the average molecular mass after 180 min can be explained by backbiting degradation in the growing polymer chains, which generates oligomers

Table 2: Kinetic evolution of tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) polymerization^a initiated by Maghnite- H^+ .

Time (h)	Conversion of monomer (wt%)	M_n	M_w/M_n
30	16	11,248	1.05
60	35	15,552	1.06
90	58	23,547	1.08
120	71	31,725	1.11
150	85	36,625	1.13
180	87	35,017	1.33
210	82	24,158	1.51

^aMaghnite- H^+ /tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) weight ratio = 2%. Reaction temperature: 60°C .

Figure 8: Representation of $\ln ([D_4^{\text{Ph,Me}}]_0/[D_4^{\text{Ph,Me}}]_t)$, where $D_4^{\text{Ph,Me}}$ is tetraphenyltetramethylcyclotetrasiloxane, as a function of time (Maghnite- H^+ / $D_4^{\text{Ph,Me}}$ weight ratio = 2%, $T = 60^\circ\text{C}$).

Scheme 3: Mechanism of tetraphenyltetramethylcyclotetrasiloxane ($D_4^{\text{Ph,Me}}$) polymerization catalyzed by Maghnite- H^+ .

and cyclic polysiloxanes of varying sizes, thereby increasing the polydispersity index (Table 2).

to the monomer (Figure 8). Scheme 3 shows the probable reaction mechanism.

3.8 Kinetics and mechanism of the polymerization

In order to study the chemical kinetics of the polymerization reaction of $D_4^{\text{Ph,Me}}$ catalyzed by Maghnite- H^+ , we followed the evolution of the concentration of monomer over time; we were interested just for $t \leq 180$ min, where there was not the depolymerization phenomenon. The results clearly indicate that the reaction is first-order with respect

4 Conclusion

Polymerization of $D_4^{\text{Ph,Me}}$ was carried out using an Algerian clay chemically treated as a catalyst (Maghnite- H^+). The use of Maghnite- H^+ to catalyze this polymerization reaction makes it conform to the principles of green chemistry in several points, such as handling under mild conditions, reduction of the energy barrier using a low temperature,

ease of separation of the catalyst and disposal of waste, solvents and toxic products.

The reaction was able to achieve a yield of 87%. The structure of the polymers obtained was confirmed by IR and NMR analyses. ^{13}C NMR analysis showed that the PPMS obtained can crosslink when the reaction time exceeds 150 min, giving polymer chains bridged by ethylenic groups. This effect also leads to an increase in the polydispersity index.

In order to obtain the maximum yield and molecular mass of the PPMS at the same time, the operating conditions were adjusted to $T = 60^\circ C$, $t = 150$ min and Maghnite- H^+ mass content = 2%. High temperatures can result in the degradation of the polymer, however long periods of time can cause the depolymerization phenomenon.

References

- [1] Belbachir M, Bensaoula A. US Patent. No 6: 274,527B1, 2001.
- [2] Chen B, Zhan X, Yi L, Chen F. *Chin. J. Chem. Eng.* 2007, 15, 661–665.
- [3] Zhang C, Miao M, Cao X, An Z. *Polym. Chem.* 2012, 3, 2656–2664.
- [4] Kherroub DE, Belbachir M, Lamouri S. *Orient. J. Chem.* 2014, 30, 1647–1651.
- [5] Meghabar R, Megherbi A, Belbachir M. *Polymer* 2003, 44, 4097–4100.
- [6] Kherroub DE, Belbachir M, Lamouri S. *BCREC* 2014, 9, 74–80.
- [7] Bouchama A, Ferrahi MI, Belbachir M. *J. Mater. Environ. Sci.* 2015, 6, 977–982.
- [8] Kherroub DE, Belbachir M, Lamouri S. *Arab J. Sci. Eng.* 2015, 40, 143–150.
- [9] Kherroub DE, Belbachir M, Lamouri S, Bouhadjar L, Chikh K. *Orient. J. Chem.* 2013, 29, 1429–1436.
- [10] Kherroub DE, Belbachir M, Lamouri S. *Res. Chem. Intermed.* 2015, 41, 5217–5228.
- [11] Kherroub DE, Belbachir M, Lamouri S. *Bull. Mater. Sci.* 2015, 38, 1–7.
- [12] Kipping FS, Llyod LL. *J. Chem. Soc. Trans* 1901, 79, 449–459.
- [13] Cusa NW, Kipping FS. *J. Chem. Soc.* 1932, 2205–2209.
- [14] Rodriguez, F, Ed., *Principles of Polymer Systems*, 3rd ed., Hemisphere Publishing Corp: New York, 1989.
- [15] DeGroot JV, Norris A, Glover SO, Clapp TV. Eds., *Highly Transparent Silicone Materials*, 2nd ed., Proc. SPIE: Bellingham, 2004.
- [16] Polmanteer KE, Hunter MJ. *J. Appl. Polym. Sci.* 1959, 1, 3–10.
- [17] Gao X, Wang Q, Sun H, Tan Y, Zhang Z, Xie Z. *Phosphorus Sulfur Silicon Relat Elem* 2015, 189, 1514–1528.
- [18] Vardosanidze TSN, Andrlanov KA, Nogaideli AI, Yakushkiina SYE, Rukhadze NP. *Polym. Sci. USSR* 1969, 11, 583–588.
- [19] Kosfeld R, Heb M, Hansen D. *Polym. Bull.* 1980, 3, 603–611.
- [20] Chojnowski J, Cypryk M, Kazmierski K. *Macromolecules* 2002, 36, 9904–9911.
- [21] Sigwalt P. *Polym. J.* 1987, 19, 567–570.
- [22] Molenberg A, Möller M. *Macromol. Rapid Commun.* 1995, 16, 449–453.
- [23] Pibre G, Chaumont P, Fleury E, Cassagnau P. *Polymer* 2008, 49, 234–240.
- [24] Gee RP. *Colloids Surf. A Physicochem. Eng. Asp.* 2015, 481, 297–306.
- [25] Sun CN, Shen MM, Deng LL, Mo JQ, Zhou BW. *Chin. Chem. Lett.* 2014, 25, 621–626.
- [26] Sijiu J, Teng Q, Xiaoyu L. *Polymer* 2010, 51, 4087–4094.
- [27] Conan JT, William PW, Guoping C. *Polymer* 2003, 44, 4149–4155.
- [28] Chojnowski J, Rubinsztajn S, Fortuniak W, Kurjata J. *J. IOPM* 2007, 17, 173–187.
- [29] Wilczek L, Rubinsztajn S, Chojnowski J. *Makromol. Chem.* 1986, 187, 39–51.
- [30] Zeng J, Chen J, Lin Z, Chen W, Chen X, Wang X. *Anal. Chim. Acta* 2008, 619, 59–66.
- [31] Wang C, Huang YD, Wang B. *Int. J. Adhes. Adhes.* 2006, 26, 206–211.
- [32] Fei HF, Xie W, Wang X, Gao X, Hu T, Zhang Z, Xie Z. *RSC Adv.* 2014, 99, 56279–56287.
- [33] Clarson SJ, Semlyen JA, Dodgson K. *Polymer* 1991, 32, 2823–2827.
- [34] Alig I, Stieber F, Wartewig S. *J. Non-Cryst. Solids* 1991, 131, 801–811.

Bionotes

Djamel Eddine Kherroub

Djamel Eddine Kherroub DSc is a Researcher in the Laboratory of Polymer Chemistry, University of Oran 1, Ahmed Ben Bella, Algeria. He received his Master's degree in Applied Chemistry at the Military Polytechnic School (EMP), Algeria (2012) and his DSc in Polymer Chemistry at the University of Oran 1 (2016). Recent occupation: supervisor of Master's students of Green Chemistry and Chemical Engineering.

Mohammed Belbachir

Mohammed Belbachir is a full Senior Professor, a founding member of the Algerian Academy of Sciences and Technology (AAST) and the head of Laboratory of Polymer Chemistry, University of Oran 1, Algeria. He received his PhD at the National High School of Chemistry, Montpellier, France in 1978. He conducts research in the field of green chemistry. He was responsible for postgraduate in polymer chemistry 1990–2010 and Head Formation Master: Green Chemistry since 2011.

Saad Lamouri

Saad Lamouri is a full Senior Professor at the Teaching and Research Unit, Military Polytechnic School (EMP) in Algiers, Algeria. He was Director of Laboratory of Macromolecular Chemistry 2002–2009, and responsible for the teaching and research unit in chemistry at EMP from 2009 to 2015. He conducts research in the fields of conductive polymers and green chemistry. He was responsible for postgraduate and PhD (Doctorate) in polymer chemistry.