



Physicochemical studies on nanosized material formed from acrylic acid and poly-di-methylsiloxane polymerization assisted by microwave

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ABSTRACT

In this study nonosized polymeric structure have been synthesized by co-polymerization between poly-di-methylsiloxane(PDMS) and acrylic acid using microwave. The average particle size achieved by this method is 4 to 5nm which is smaller than that of other method used. The particle sizes of the samples were investigated by XRD (X-ray diffraction) studies. The characterization of the synthesized microstructures was carried out with the help of UV (Ultraviolet), FT-IR (Fourier-transform-infra red), ¹H-NMR and thermogravimetric analysis (TG-DTA-DTG). The structure of the PDMS-acrylic acid graft has been confirmed by spectral data.

Keywords: Acrylic acid, PDMS, Nanomaterial, X-ray diffraction, microwave assisted co-polymerization.

INTRODUCTION

The discovery of micro fluidic devices through polymerization is one of the significant scientific developments of recent time [1-3]. The knowledge of structure and functionality of micro fluids have great importance in the design of new materials and compounds with improved properties in the field of chemistry, biology, physics, engineering, material science and medicine including nanotechnology [4-10]. In nanotechnology these micro fluids are used as steric stabilizer for magnetite nanoparticle dispersion [11]. Triblock co-polymers with controlled concentration of carboxylic acids have been prepared and utilized as stabilizer for magnetite nanoparticles. These materials have hydrophilic, hydrophobic or amphoteric tail blocks to enable dispersion in the media with different polarities and centre segment containing the carboxylic acid groups which anchor the nanomagnetite surfaces [12]. Nanomagnetic fluids may be organic solvents, oils or water in the presence of surfactants. The synthesis of nanomagnetic fluids involving functionalize polymers as stabilizers has been subject of interest to obtained a controlled assembly of nano structures having a specific structure physicochemical characteristics [13-16].

Polysiloxane is an important compound having attractive properties like good weather resistance, good thermal stability, high flexibility, low surface tension and non-toxicity. The products of polysiloxane are widely used as antifoam agents, textile finishing agent, building coating, polishes, mechanical fluids, medical additives and precursor of cosmetic [17, 18]. Poly-di-methylsiloxane has more specific properties such as physiological inertness, good blood compatibility, transparency at UV-vis wavelength, low cost etc [19, 20]. The monomers have specific importance in grafting. There are various monomers like acrylic acid [20, 21], methacrylic acid [22], acrylamide [23] etc. In general, the acrylic materials having high resistance to UV radiation and they are hardly hydrolyzed. These materials have excellent optical properties with good transparency and they have compatibility with additives and plastifires [24, 25]. There is a report on wettability patterning in microfluidic system by poly (acrylic acid) graft polymerization [26, 27].

In this work acrylic acid was grafted with poly-di-methylsiloxane (PDMS) using chemical method. In order to confirm the polymerization and to study the structure of graft, the analytical techniques, UV, XRD, ¹H-NMR, FT-IR and TG-DTA-DTG were used.

MATERIALS AND METHODS

The chemicals such as poly-di-methylsiloxane (Nice chemicals), acrylic acid (Central drug house), AIBN (Ms. Himedia chemicals) and methanol (Glaxo laboratory) were used as such without further purifications.

Synthesis of grafts obtained from acrylic acid

The grafts were prepared by co-polymerization with the help of microwave oven. The maximum bulk polymerization was carried out at power of 100 Watt with air cooling to obtain desired temperature for polymerization. The reaction mixtures were prepared with different compositions. The compositions of mixtures used in the study are given below.

- i) 1ml acrylic acid + 10mg AIBN + 5ml poly-di-methylsiloxane.
- ii) 2ml acrylic acid + 10mg AIBN + 5ml poly-di-methylsiloxane.
- iii) 3ml acrylic acid + 10mg AIBN + 5ml poly-di-methylsiloxane.

During the process of polymerization in the presence of microwave, acrylic acid acts as monomers whereas poly-di-methylsiloxane functions as a primary polymer chain. AIBN is known as 2-2 azobisisobutyronitrile, works as initiator. After putting the solution for 10 min in microwave oven the process of grafting takes place. After cooling the content, 5ml methanol was added in the graft obtained. To obtain the homogeneous composition, the contents were stirred over magnetic stirrer for 30 min. The graft co-polymers were isolated from methanol layers and desired as a final product.

Characterization

UV-vis spectra were recorded over spectrophotometer model Genesis 10 Thermospectronic USA. ¹H-NMR data were recorded from CDRI (Lucknow). For graft polymers CDCl₃ was used as a solvent. X-ray diffraction pattern were measured by using a RINT/DMAX 2200 H/Pc (Rigaku, Japan) diffractometer at room temperature and 20 mA. The XRD peaks were recorded at 2θ. The size of the particle was calculated with the help of Scherrer equation. Fourier transform infrared (FT-IR) spectra were recorded on Galaxy 300 Mattson FT-IR spectro photometer using KBr pellet. TG-DTA-DTG with differential pattern has been taken with the help of EXSTAR TG/DTA 6300 thermal analyzer in N₂ @ 10⁰C/min. The temperature range up to 700⁰C has been utilized for recording the data. The different sample weights were used with reference weight alumina powder 10.500mg.

RESULTS AND DISCUSSION

UV Analysis

In this study we have recorded four spectra including one acrylic acid and three co-polymers. In case of acrylic acid the maximum absorbance 1.77 was obtained at 217 nm. For the graft prepared from 1ml of acrylic acid absorbance is 1.73 at 212 nm, for 2ml acrylic acid graft absorbance is 1.37 at 211nm and for 3ml graft absorbance is 1.45 at 209nm was obtained.

It is clear that absorption maxima shifts takes place towards shorter wavelength when acrylic acid undergoes copolymerization with poly-di-methylsiloxane. In the present case the blue shift can be explained due to the attachment of double bonds where an electrons are available C=O and partial hydrogen bonding is also possible. The hypochromic change was observed in the case of grafts having higher concentration of acrylic acid indicates the more association/polymerization in comparison to the pure constituent. Conjugation of carboxylic or alkoxide carbonyl with a double bond, results in high intensity π-π* absorption near to 230 nm. In our case the acrylic acid has absorbance at 217 nm which justify that on polymerization the hypochromic shifts takes place as there is reduction in conjugation. The observed spectral data is in good agreement with the fact that the polymerization between poly-di-methylsiloxane and acrylic acid results in the formation of grafts.

XRD Analysis

XRD measurement were carried out in the scattering angular range (2θ) 5-60. The average size of the particle was calculated from diffraction line width based on the Scherrer relation

$d = 0.9\lambda/\beta \cos\theta$, where λ is the wavelength of the X-ray and β is the half maximum line width. The obtained data for different parameters and particle size for 1ml, 2ml and 3ml grafts is given in Table 1. The average size of the

particles as calculated from the XRD line width as mentioned above is nearly between 4 to 5nm for all grafts synthesized. This study confirms the formation of nanosized particles in grafting. A representative graph of XRD for 2 ml acrylic acid is given in Figure 1.

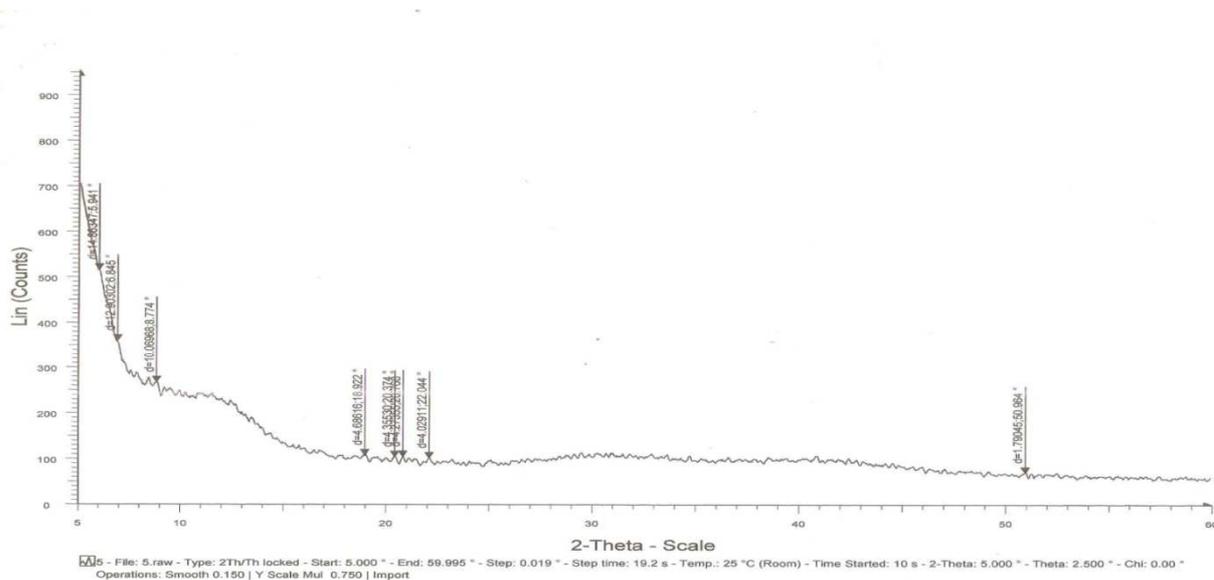


Fig.1 XRD of graft of 2ml acrylic acid with PDMS

Table-1 XRD of graft of acrylic acid with PDMS

*XRD of graft of 1 ml acrylic acid with PDMS

** XRD of graft of 2 ml acrylic acid with PDMS

*** XRD of graft of 3 ml acrylic acid with PDMS

S. No.	2θ	d	Full width half maximum(β)	Particle size(nm)
1.*	5.996*	14.72747*	1.4497*	5.48*
2.	21.944	4.04727	1.4497	5.58
3.	36.601	2.45318	1.4497	5.76
4.**	6.101**	14.47549**	1.6003**	4.97**
5.	20.695	4.28861	1.6003	5.05
6.	36.415	2.46531	1.6003	5.23
7	49.548	1.83823	1.6003	5.47
8.***	6.135***	14.39504***	1.6379***	4.88***
9.	20.974	4.23220	1.6379	4.95
10.	36.584	2.45431	1.6379	5.13

Table-2 ¹H-NMR spectra of acrylic acid and grafts

Presence of proton	Type of proton	δ value(ppm)			
		Acrylic acid	1ml Acrylic acid graft	2ml Acrylic acid graft	3ml Acrylic acid graft
CH ₂	Methylene (α-CH ₂)	----	1.253	1.230	1.254
CH ₂	Methylene (β-CH ₂)	----	1.681	1.67	1.62
CH ₃	Methyl α-O-Si	----	3.65	3.610	3.7
CH ₃	Methyl β-O-Si	----	1.107	1.004	1.1
H	cis w.r.t. (-C=O)	6.189-6.075	----	----	----
H	trans w.r.t. (-C=O)	6.534-6.382	----	----	----
H	gem w.r.t. (-C=O)	5.992-5.845	----	----	----

¹H-NMR Analysis

Before polymerization the ¹H-NMR spectra of monomer acrylic acid was recorded. After polymerization with different compositions of acrylic acid 1ml, 2ml and 3ml have been recorded. A comparative value of chemical shifts for the grafts synthesized as summarized from the ¹H-NMR spectra given in Table 2. The acrylic acid spectrum shows three quadruplets centered at 6.63, 6.18 and 6.0 ppm corresponding to this cis, germinal and trans protons respectively as also reported in literature [25]. The signals of the spectra for sample containing low concentration of monomers show a field of chemical shift with a little line broadening relative to the polymer synthesized from the high concentration of 2 ml and 3ml acrylic acid. The presence of signals at between 3.65 to 3.4 ppm confirms the polymerization between PDMS and acrylic acid because of methyl groups which are present in the vicinity of silicon atom and signals present quadruplets are missing.

FT-IR Analysis

The acrylic acid exhibits infrared bands in the region 536-3656 cm⁻¹. FT-IR spectra of monomer acrylic acid and for different compositions of acrylic acid 1ml, 2ml and 3ml have been recorded. The IR spectra obtained from three grafts were utilized in the characterization of grafts and composition of the reaction between the reagents. These bands arise due to the presence of O-H stretching in the compound. The position of IR band at 3656 cm⁻¹ has been assigned to O-H stretching in several reports [28]. The position of the C-O stretching phenolic or ether differs from the carbonyl stretching. The stretching 1726.7cm⁻¹ indicates the carbonyl stretching. The participation of C-O-H bond appears at 1062.1 cm⁻¹. The band appears between 1062-1726.7 cm⁻¹ shows the presence of C=C stretching in the acrylic acid. On the basis of IR bands, the presence of band in the far infrared region at 536 cm⁻¹ also confirm that the stretching vibration arises due to the presence of COOH. The specific O-H present in out-of-plane exhibits IR band at 929 cm⁻¹.

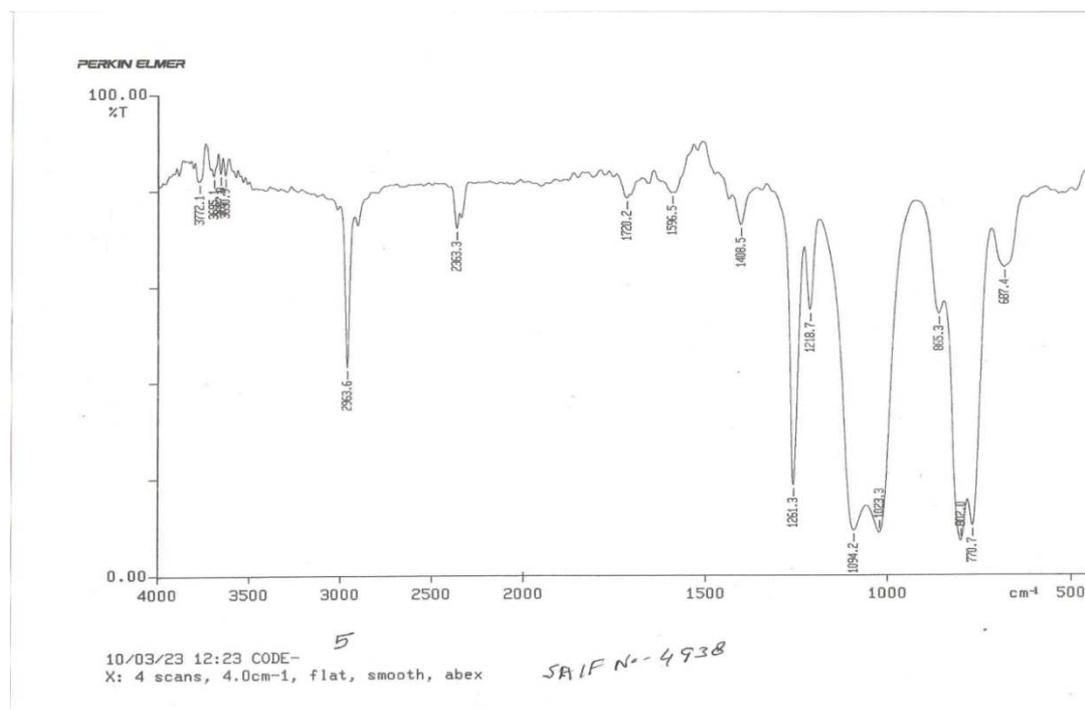


Fig.2 FT-IR spectra of graft of 2ml acrylic acid with PDMS

In the study we have used different quantity of acrylic acid in order to obtain the graft with different structures. From Table 3, it is clear that the presence of OH stretching remains same after polymerization in all the grafts which may be due to the terminal O-H bond of silicon oil as obtained whose frequency can be compared from the band obtained at 3698 cm⁻¹ in the IR spectra of pure silicon oil. The complete absence of vibrational band in case of 2ml acrylic acid, confirm the formation of graft whereas in case of 1ml and 3ml acrylic acid, it shifts by 26 cm⁻¹ from acrylic acid also supports the results obtained in case of 2ml acrylic acid it is important to mention here that the IR spectra of pure silicon oil has no any bands at these positions. The presence of vibrational band at 1594 cm⁻¹, 1596 cm⁻¹, 1591 cm⁻¹ in case of grafts indicates the Si-C stretching vibration of Si-C bond. The signals of Si-C stretching overlap with strong C-CH_x vibrational signals [29]. These results clearly indicates that the acrylic acid form the chemical bond to the surface via a covalent Si-C bond resulting from the reaction at the hydrogen terminated silicon surface and alkene group of acrylic acid. A comparison between the peak intensity of the Si-C and C-C signals

supports the conclusion drawn but it is not possible to exclude the effect of oligomerization of some monomers. The representative spectra for 2ml acrylic acid graft have been given in Figure 2.

Table-3 FT-IR Spectra of acrylic acid and grafts

Acrylic Acid (AA)	Grafts			Assignment
	1ml AA	2ml AA	3ml AA	
3656.0	3629.0	3630.9	3632.3	ν COOH
1726.7	1725.1	1720.2	1721.9	ν C=O
1635.0	1661.5	-----	1661.8	C=C
-----	1019.5	1023.3	1023.3	ν Si-O-Si
-----	1594.6	1596.5	1590.7	ν Si-C
929.7	928.9	-----	-----	O-H deformation[out- of- plane]

Thermal Analysis

The thermal analysis of the grafts was carried out by TG, DTA and DTG. The decomposition of graft takes place at first stage from 200-300^oC as obtained at TG curves. In the second stage the temperature range 300-451^oC can be taken for the decomposition of the graft, where the decomposition is gradually uniform. In DTA curve exothermic nature was observed at 536^oC whereas in DTG curve two broad positions were observed at 242^oC and 543^oC. At the higher temperature the complete transformation takes place into silicon oxide whereas the temperature 242^oC corresponds to the elimination of the polymeric species and transformation into secondary stable stage. The thermal analysis data is given in Table 4 and representative graph for 2ml acrylic acid graft has been given in Figure 3.

Table-4 TG-DTA-DTG of grafts of acrylic acid with PDMS

S. No.	Grafts	TG I ₀ (% W _L) ^o /C ^a I _t (% W _L) ^o /C ^b	DTG ^o C(mg/min)	DTA [^o C(μ V)/ Δ H (mJ/mg)] ^c
1.	graft of 1 ml acrylic acid with PDMS	8.7/200 56.9/299 97.8/571	126(0.11) 247(1.02) 401(0.28) 525(0.28)	130(4.0)/15.7 249(3.1)/317 520(68.5)/ -1.64 \times 10 ³
2.	graft of 2 ml acrylic acid with PDMS	4/201 19.8/350 49.4/476	245(0.15) 485(0.42)	252(11.45)/283 252(11.45)/-1.40 \times 10 ³
3.	graft of 3 ml acrylic acid with PDMS	2.7/100 12.2/200 44.8/303 97.2/575	118(0.21) 280(0.49) 408(0.34) 540(0.22)	124(-0.03)/59.4 255(4.83)/180 540(52.2)/-1.43 \times 10 ³

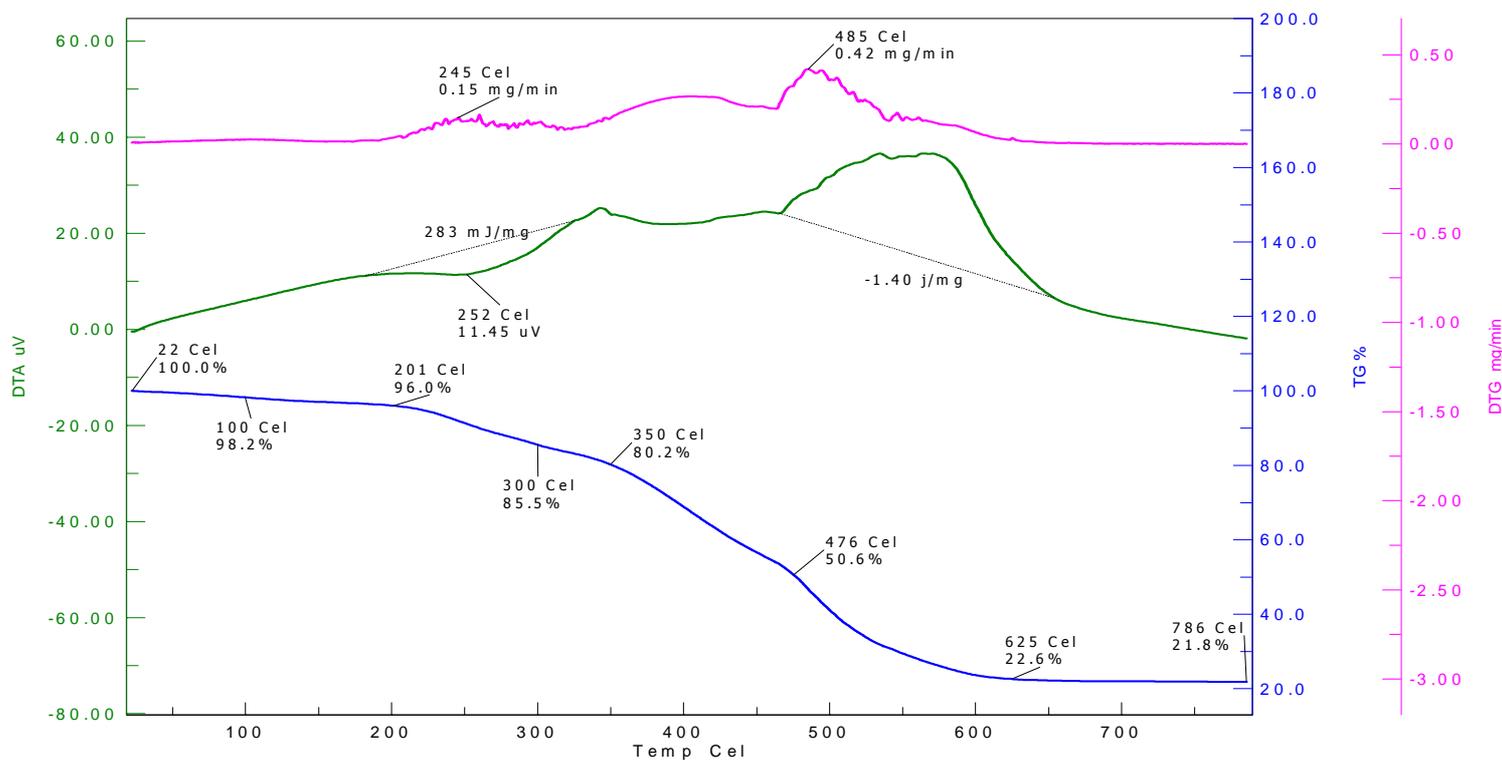


Fig.3 Thermal analysis graft of 2 ml acrylic acid with PDMS

The close agreement between the observed and calculated values of percentage mass loss indicated that the proposed formula for the acrylic acid–PDMS is correct and structure has been represented Figure 4.

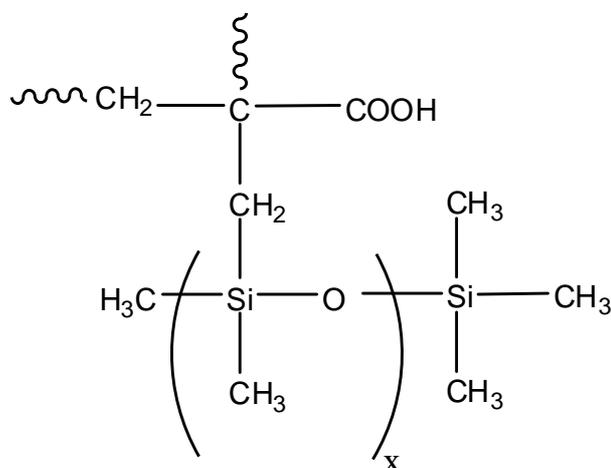


Fig.4 Structure of graft of acrylic acid with PDMS

The proposed structure was used to correlate the experimental data of NMR with the calculated results from Chemdraw 10.0. The presence of various protons are nearly verified which indicates the correctness of the polymeric structure obtained in the study.

CONCLUSION

Synthesis of polymeric assemblies having ordered functional group and controlled micro structures provides materials of scientific and technological importance. The graft prepared with poly-di-methylsiloxane in this study is useful for nanotechnology which would have fine application in the preparation of micro fluids having various applications in medicines, catalysis energy etc. The graft is also useful for non-aqueous media for the transformation of materials in the form of micro fluids. The polymeric materials have specific prospects for the preparation of various types of nanomaterials.

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