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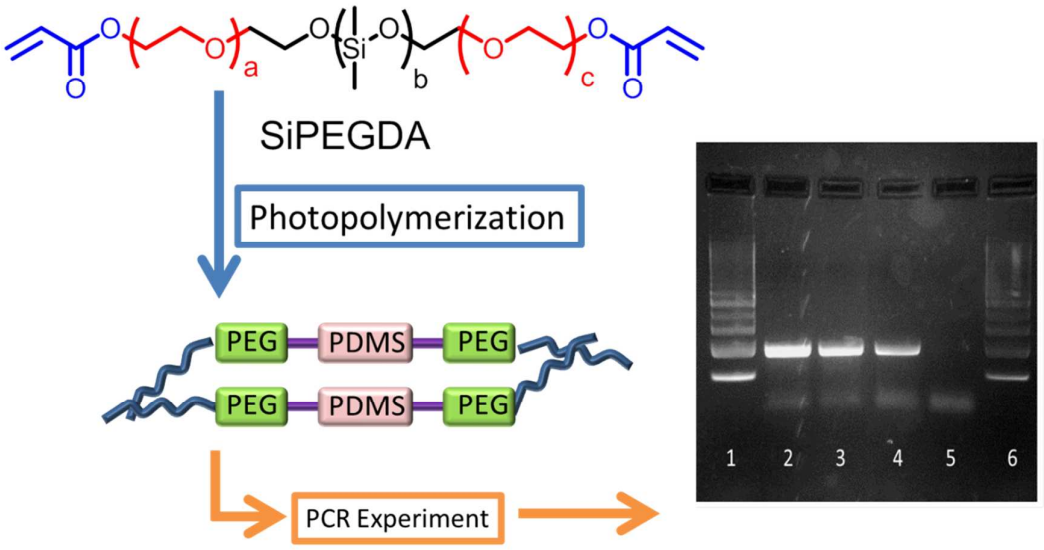
Synthesis and characterization of PCR acceptable diacrylic macromer made of a siloxane block and two polyoxyethylene blocks.



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ARTICLE TYPE

Synthesis and characterization of siloxane photopolymers used for microfluidic devices

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A linear ABA type diacrylic macromer containing an amphiphilic backbone made of a siloxane block (SiO) and two polyoxyethylene blocks (EO) was synthesized and subsequently photopolymerized and copolymerized with a polyoxyethylene diacrylate. The kinetics of the photopolymerization was monitored by rt-FTIR, confirming the reactivity of acrylic functionalities. The obtained polymers were then characterized by DMTA analyses and showed interesting biphasic morphology with two T_gs attributable to the EO domains and to the SiO domains. Swelling in different solvents was also tested: compared to siloxane acrylates, the introduction of EO enhanced the chemical resistance to most solvents, excluding water. Surface analyses showed that the incorporation of both hydrophobic siloxane groups and hydrophilic polyoxyethylene groups into the networks is a successful way of controlling their surface: due to the preferential segregation of the SiO blocks at the air interface, the wettability of the polymers with water is very low but can change depending on the environment. Compatibility toward DNA amplification reaction was successfully tested. As the possibility for fast, accurate, and cheap reproducibility of microdevices by liquid phase photopolymerization increases the polymer attractiveness, the material is a good alternative with respect to polydimethylsiloxane for the fabrication of microfluidic chips for biological analysis purposes.

1 Introduction

The tininess of chemical and biological analysis structures, such as micrototal analysis systems (μTAS) or laboratories on a chip (LOC), empowers massive enhancements in their performance both in analysis speed and throughput, in contrast among more conventional 'full-size' instrumentation.[1-3] Many functional materials were synthesized for microscale analysis systems and assured their success in these areas. Latest researches have engrossed on gauging diverse polymers for microchannel surface passivation.[5-9]

Most important task in these researches is the profitable alteration of the microchannel interior surfaces, especially in the treatment of multifaceted and complicated biological samples

Therefore, discovering an all-purpose surface-modification etiquette that proficiently lessens the broad-spectrum adsorption of proteins has appeared as one of the greatest critical stages in the progressive reduction of size of the fluidic devices and in the extension of their applications.[1-3] In the domain of μTAS the variation of the concentration range is huge and concentration can become a constrain in the use of microfluidics. Extremely concentrated samples may trigger clogging of the device due to nonspecific adsorption, while in samples were concerned molecule exists at very little concentrations the device may never allow the molecule to reach the zone envisioned for analysis.

The most well-known materials used to increase the biocompatibility of a surface is poly(ethylene glycol) (PEG), either as a surface coating or as graft material, due to its high hydrophilic and non-fouling properties.[11,12] This molecule is easily adsorbed on hydrophobic surfaces, consequently blocking nonspecific linkage of molecules. PEG chains on external layer make a hydrophilic lining like a brush that resists molecules to make linkage with the device. This characteristic depends on the size, springiness, and density of the PEG chains. Unfortunately PEG can absorb water and swelling can affect the performance of a microfluidic device.

Poly(dimethylsiloxane) (PDMS) is presently the utmost extensively and effectively used polymer in research and devices for the separation of biomolecules,[13-15] especially in microfluidics and the area wherever aqueous chemistry is involved. This material also shows the excellent transparency needed for visual inspection of chip operations for easy monitoring, for troubleshooting and for performing bright field and fluorescent detection and imaging.[16] PDMS is highly permeable to gas permeability which can lead to loss of water vapour and sample drying and unwanted influxes, but can enable gas exchange for biological cells to be cultured in microchannel. The material is also low cost for disposable LOC applications, has satisfactory elastic mechanical properties, and is biocompatible and nontoxic.

As mentioned before, surface fouling caused by proteins or analytes sorption is a serious issue in microfluidics. The main reason of this phenomenon is the strong hydrophobicity material

such as PDMS which is used in the microfluidics. Therefore, PDMS-based microfluidic devices need surface processing. [16]

Polymers like PDMS are used to fabricate microfluidic devices by several technologies (hot embossing, thermoforming, injection moulding, casting, soft lithography).[1,3] They are based on replication processes and need a master structure. It is more advantageous to use direct methods which most frequently involve the reaction of a prepolymer or a polymer with light. The reaction can be a polymerization reaction (photolithography, stereo lithography) building a solid structure out of a liquid resin, or a degradation reaction ablating the material with a laser beam.[17] Photolithography is considered to be the only fine patterning technology with both precision and mass productivity.

Therefore promising materials for microfluidics could be siloxane photocurable prepolymer which could assure the performances of PDMS and be suitable for a direct fabrication process as photolithography. In particular acrylic end groups are known to guarantee efficient photoreactivity. In order to face the issue of biofouling and avoiding surface treatment, we though interesting the designing of reactive oligomers containing both PDMS-like structures and PEG-like structures.

In this paper, we report photopolymers based on a siloxane block (SiO) and two polyoxyethylene blocks (EO) ended by acrylic groups. The synthesis and characterization of the oligomers are described. Their photopolymerization reaction and the main thermal, mechanical and surface properties of the UV-cured coatings obtained are reported, together with compatibility towards DNA amplification reactions.

2 Experimental

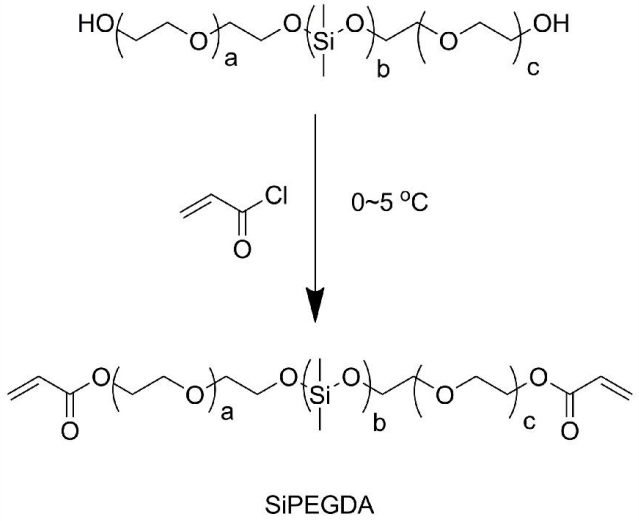
2.1 Material

Acryloyl chloride was purchased from TCI. Triethylamine (TEA), tetrahydrofuran (THF) were purchased from Sinopharm Group Chemical Reagent Co. Ltd. (Beijing, China). The hydroxy terminated polyether-silicone copolymer (XIAMETER® OFX-3667) was given by Dow Corning Co. Ltd. as a gift. 2-Hydroxy-2-methylpropiophenone (Darocur® 1173) was obtained from BASF. Poly(ethylene glycol) diacrylate (PEGDA, average M=700) was purchased from Sigma Aldrich. For the biological testing, agarose, ethidium bromide and TAE buffer (40 mM Tris-Acetate 1 mM EDTA pH 8.3) and a Low DNA Mass Ladder (Invitrogen™) were purchased from Life Technologies (Carlsbad, CA, USA). TEA and THF were dried and purified according to common laboratory methods. [18] All other reagents were used as received without further purification.

2.2 Synthesis

The synthesis route of the diacrylic macromere (SiPEGDA) is showed in Scheme 1.

Mixture of hydroxyl terminated polyether-silicone copolymer (XIAMETER® OFX-3667, M=2200 g/mol, 22 g, 10 mmol), TEA (2.02g, 20 mmol) and THF (80 mL) were stirred together for 10 min in a three-necked flask equipped with stirrer, thermometer, and dropping funnel. Acryloyl chloride (1.81g, 20 mmol) dissolved in THF (20 mL) was added drop by drop over 20 min in the ice bath. Then the mixture was removed from the ice bath



SiPEGDA

Scheme 1. The synthesis route of SiPEGDA.

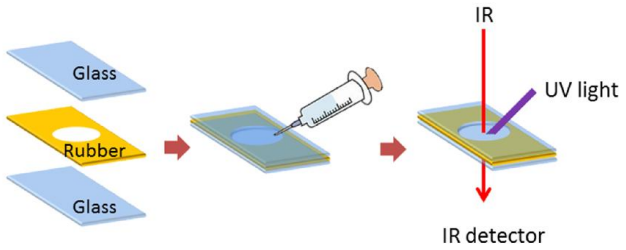
and stirred at room temperature for 2 h. After that, the mixture was cooled to 5 °C and filtered. The filter cake was washed by cooled THF. The filtrates were combined and the solvent was evaporated under vacuum. Yield of reaction was 87% (20g).
^{1}H NMR (400 MHz, $CDC1_3$, δ in ppm): 3.63 (O-$(CH_2)_2$-O), 4.02 (CH_2 of allyl group), 5.17–5.30 (CH_2 of allyl group), 5.87–5.96 (CH of allyl group).

2.3 Photopolymerization kinetics

It is well known that the free radical photopolymerization is limited by the presence of molecular oxygen which reacts with the growing radical chains to effectively quench the active centres and inhibit the polymerization. For polymerizations carried out in air, oxygen inhibition results in decreased polymerization rates, reduced polymer chain lengths, and the presence of a "tacky" surface. In the modern industrial, methods such as purging the reaction environment with inert nitrogen will avoid oxygen inhibition of free radical polymerizations, but it is difficult to use the same way in the precision instrument in the university.

In this study, an alternative approach on UV curing without oxygen inhibition is proposed. As shown in Scheme 2, it was an easy method to overcome the oxygen inhibition of free radical polymerizations in the lab and will dramatically reduce costs in the university while providing enhanced flexibility in the photopolymerization design process. The mixtures were injected into a mould like a sandwich which was made from two glass slides and a rubber spacer with 15 ± 1mm diameter and 2 ± 0.1mm thicknesses, irradiated by a UV spot light source (EFOS Lite, 100 W miniature arc lamp with 320–500 nm filter and 5 mm crystal optical fibre, Canada) at room temperature. The light intensity was determined by a UV-light Radiometer (UV Power Puck® II, EIT, US).

The kinetics of photopolymerization was studied by a FTIR spectrometer (Nicolet 5700) with a real-time accessory. The real-time IR (RT-IR) spectrometer equipped with a MCT/A KBr detector-beam splitter combination was used to monitor the



Scheme 2. Monitoring of photopolymerization processes with RT-IR.

process of the reaction, which was operated in the absorbance mode and working in the rapid mode with an average 3 scans s^{-1} collection rate (4 cm^{-1}). The double bond conversions (DC), directly related to the decrease of the area of acrylate double bond absorption peak around 6162 cm^{-1}[19], was calculated from eqn. 1.

$$DC\% = \left[1 - \frac{(A_{6162})_t}{(A_{6162})_0}\right] \times 100\% \qquad \text{(eqn. 1)}$$

where $(A_{6162})_0$ and $(A_{6162})_t$ are the area of the absorption peak at 6162 cm^{-1} of the sample before and after photopolymerization at time ***t***, respectively.

2.4 UV curing procedure

The samples (Table 1) were cured under N_2 atmosphere for 90 s with a high pressure mercury arc lamp, and the light intensity was determined by a UV-light Radiometer (UV Power Puck® II, EIT, US). The light intensity was as follow: UVA= 67.48 mW/cm^2, UVB= 47.40 mW/cm^2, UVC= 7.2 mW/cm^2 and UVV= 43.64 mW/cm^2.

Table 1The formulations used in this study

	SiPEGDA	PEGDA	1173
Sample 1	100	0	1
Sample 2	50	50	1
Sample 3	0	100	1

Gel fraction measurements were gauging sample weight loss in chloroform for 24 hours, according to ASTM D2765-84. The gel content was calculated using the following eqn (3):

$$Gel\% = 100 - \frac{w_s - w_d}{w_d} \times 100 \qquad \text{(eqn.2)}$$

Where, w_s is weight of the sample being tested, w_d is weight of dried gel.

2.5 Thermal stability

The thermal gravimetric analysis of polymer was performed using a Mettler Toledo TGA/SDTA 851 apparatus. Scans were carried out in air or dry nitrogen atmosphere. About 10 mg of sample was heated from ambient to 800 °C at a heating rate of 10 °C min^{-1}.

2.6 DMTA analysis

Dynamic mechanical analysis of polymer films was obtained with a Triton Technology T101422D TTDMA instrument at a frequency of 1 Hz in tensile configuration: the scan was carried out from -150 to 200 °C with a heating rate of 3 °C min^{-1}.

2.7 Contact angle

Wettability was assessed by static contact angle (CA) measurements with water (γ=72.1 mNm^{-1}) by means of a First Ten Angstroms 1000C instrument, equipped with a video camera and image analyser, at room temperature with the sessile drop technique. On every examined surface, at least five angles were measured.

2.8 Swelling test

Solvent resistance of the cross linked polymer was evaluated by swelling tests (wt%). Polymer samples were immersed in a variety of solvents, and samples were weighed after different exposure times to determine the swelling progress. Swelling percentage was calculated by using eqn (3):

$$\text{Swelling}\% = \frac{w_t - w_0}{w_0} \times 100\% \qquad \text{(eqn. 3)}$$

Where w_t is the weight of the material after soaking in solvent for time ***t*** (measured immediately after removing the sample from the solvent), and w_0 is the original weight of the material.

2.9 PCR compatibility

To test the material PCR compatibility small pieces of crosslinked polymers were introduced in the PCR batch. Polymers were weighed in a PCR tube and submerged with the PCR mix to a final volume of 50 µL. PCR mix contained 2 mM $MgCl_2$, 0.2 mM dNTPs, 0.5 µM of each primer forward and reverse (C282Yfor: TGGCAAGGGTAAACAGATCC, C282Yrev: TACCTCCTCAGGCACTCCTC), 30 ng purified genomic DNA (Wizard Genomic DNA Purification Kit, Promega Corporation; DNA quantified by Nanodrop ND-1000 spectrophotometer, Nanodrop Technologies) in Tris-HCl 10 mM, KCl 50 mM, pH 8.3 and 1 U of Taq DNA polymerase (FastStart Taq DNA Polymerase, Roche). The amplified region was part of the hemochromatosis gene (HFE). The thermal protocol was: 5 min at 95 °C for the initial denaturation step, 30 s at 95 °C, 30 s at 62 °C and 30 s at 72 °C (these three steps were repeated for 35 cycles) and finally 7 min at 72 °C. At the end of thermal cycle the entire reaction volume was mixed with loading buffer (6X Blue Orange gel loading buffer, Promega) and loaded on agarose gel to check for the presence of the correct PCR product. Electrophoresis was performed in the TAE buffer by using 2 % agarose gel containing ethidium bromide (0.125 µg mL^{-1}) in a standard apparatus (BioRad). The intensity of the band was measured in a Gel-Logic 1500 detection system (Eastman Kodak Company).

3 Results and Discussion

3.1 Synthesis

SiPEGDA was prepared according to a general synthetic route which was shown in Scheme 1.

Acryloyl chloride is most commonly employed in organic synthesis for the introduction of acrylic moieties into other compounds and it is also used extensively in the preparation of acrylate monomers and polymers. Reactions with alcohols will result in the formation of esters and reactions with amines will generate amides. In this study, the acrylic moiety was attached

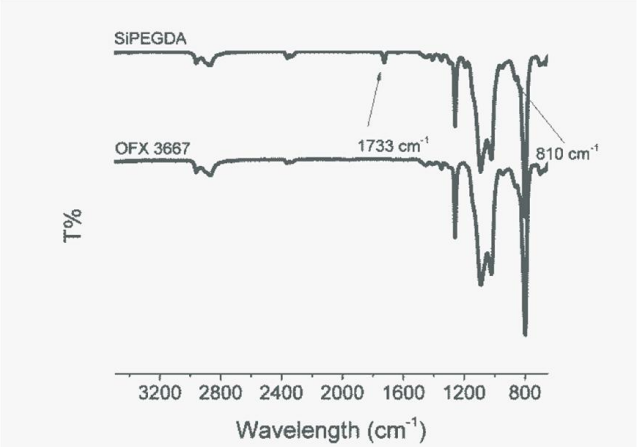


Figure 1. The FTIR of the raw material and the SiPEGDA

directly to the precursor, the polyether-silicone copolymer (XIAMETER® OFX-3667). The esterification of its hydroxyl functionalities present as end groups was done with the acryloyl chloride in the presence of TEA, which was used as a hydrogen chloride acceptor in the reaction. As the byproduct triethylamine hydrochloride was insoluble in the THF and was easy to be separated [20], the resulting reaction mixture was filtered off and the residue was washed with cooled THF. The organic phase was combined and the solvent was then removed under vacuum to give a faint yellow liquid with the viscosity of 315 cPs. Due to the high activity reaction between acryloyl chloride and hydroxyl, the product could be considered as diacrylate macromere. By analysing the copolymer precursor (OFX 3667) and the obtained acrylic product via FTIR (Figure 1), one can notice that a new peak of carbon-carbon double bond appeared at 810 cm^{-1} while the carbonyl group was generated at 1733 cm^{-1} .

3.2 Photopolymerization kinetics

The SiPEGDA monomer prepared is intended for photolithographic processes suitable for the fabrication of microfluidics. Therefore we checked the reactivity of the monomer upon irradiation. We wanted also to compare it with PEGDA. Besides characterizing the pure polymer SiPEGDA and PEGDA, we also prepared a blend of them (50/50 wt/wt).

The kinetics of photopolymerization of the SiPEGDA and of the blend SiPEGDA/PEGDA, which was used to optimize the photocuring conditions, was measured by real time FTIR on a thin polymeric film (about 2mm). The double bond conversion (DC) was calculated by the decrease of the area of acrylate double bond absorption in the near IR area.

As a comparison the plots of DC versus irradiation time for PEGDA is also shown in Figure 2. It is clear that SiPEGDA could be effectively photo induced by the photoinitiator Darocur® 1173, however its reactivity is much lower than that of PEGDA which has lower viscosity (183 cPs@25°C) and higher density of double bonds. SiPEGDA shows a long induction time (t_{ind}) and a limited reaction rate (R_p). Main data of photopolymerization kinetics are reported in Table 1.

As the curing proceeds and the viscosity of the systems increases, the resulting gel-effect set a limit to the rate of photopolymerization.[21] However the maximum conversion around 100% was obtained which was usually a feature required

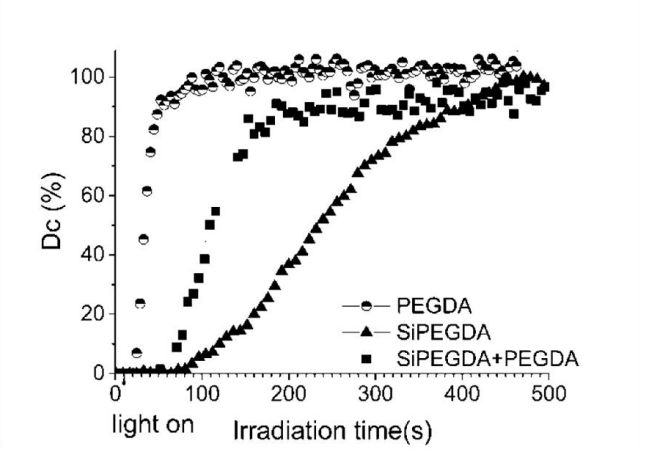


Figure 2 Double-bond conversion of different monomers (1173%=1wt%; light intensity= 1 mW/cm^2)

Table 1. The kinetics data of photopolymerization

Formulation PEGDA/SiPEGDA/1173	t_{ind} (s) [1]	R_p^{max} (s^{-1}) [2]	t_{max} (s) [3]	DC_f (%) [4]
100/0/1	8.3	6.2	29.5	99.6
50/50/1	51.2	2.6	82.2	99.3
0/100/1	83.5	1.5	173.1	98.9

[1] t_{ind} was the inhibition time at the beginning of the photopolymerization.

[2] The maximum rate of photopolymerization.

[3] The time at which R_p^{max} appeared.

[4] DC_f represents the final double bond conversion.

for most applications. The macromer was also copolymerized with PEGDA: the copolymerization is successful, resulting in an increase of reaction rate and obtaining of full conversion. The SiPEGDA polymer and the SiPEGDA/PEGDA copolymer obtained are transparent, could be easily handled and have a high crosslinking degrees because the gel percentage of SiPEGDA is 91% while that of the copolymer is 95%.

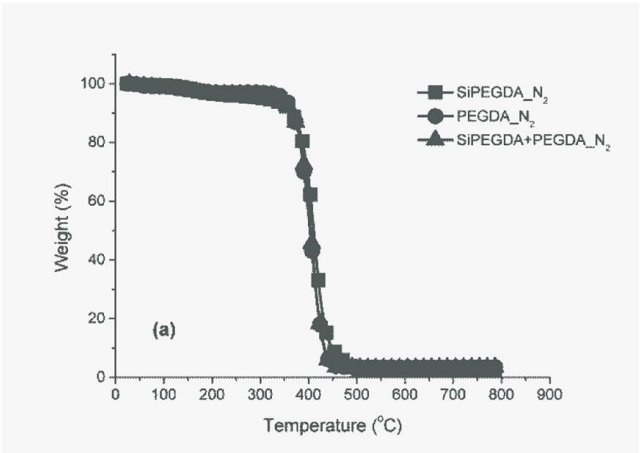
3.3 TGA

Thermo gravimetric analyses of the polymers were performed in air and N_2 to study the thermo/oxidative gravimetric behaviour of the cured films.

The TGA curve in N_2 (Figure 3) showed that SiPEGDA and its copolymer have the same thermal stability of PEGDA with an onset of degradation at T_5=308.0 °C and half weight loss at T_{50}=410.6 °C. The values are significantly lower than PDMS: (T_5=450 °C and T_{50}=560 °C [22].).This implies that introducing EO units into the molecular structure could significantly decrease the thermo stability of the macromer in N_2. That is because increasing fraction of EO units could cause the lower steric hindrance of the macromer.[23] The polyoxyethylene block degradation in N_2 produces lower molecular weight species. And the residue of SiPEGDA at 700 °C was rather low (1.26%).

It could be easily seem that all the samples lost weight in one step regardless of the composition of the sample. Both SiPEGDA and PEGDA degraded in N_2 and lost a significant weight at lower temperature. The degradation of SiPEGDA is typical for the random depolymerization mechanism.

The thermo oxidative behaviour of the SiPEGDA is obviously more complex than its thermal behaviour in nitrogen atmosphere.



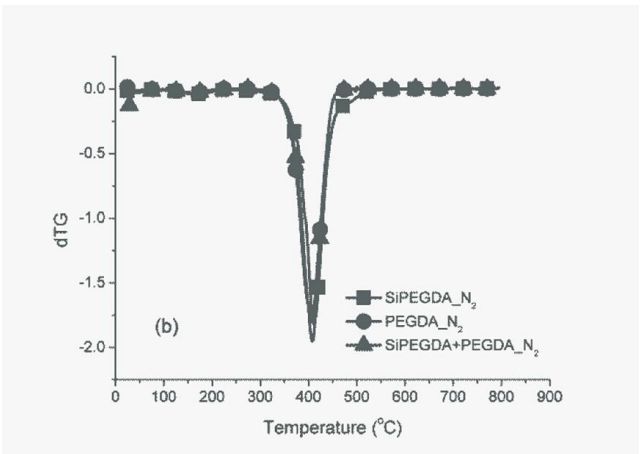
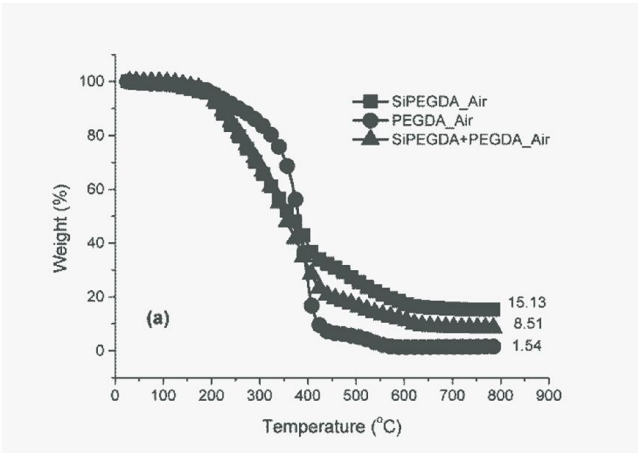


Figure 3. The TGA and dTG curve of the polymer films in N_2.



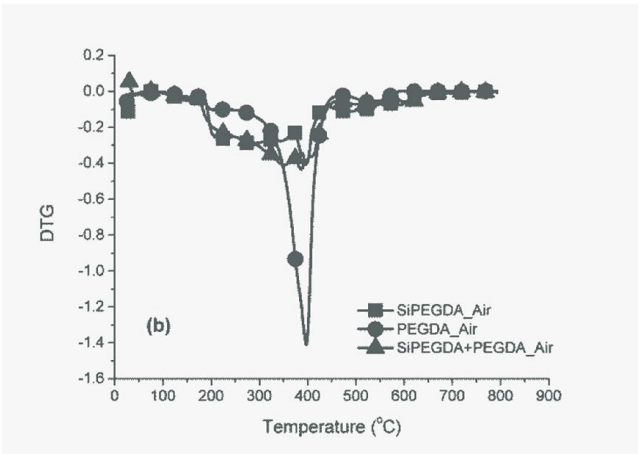


Figure 4. The TGA and dTG curve of the polymer films in air.

The TG curves obtained for the oxidative degradation of the polymers are presented in Figure 4, and their characteristic mass loss temperatures and residues in Table 2.

The TG curve of SiPEGDA is different from PEGDA. The T_{10} of PEGDA is 257.4 °C while SiPEGDA is 217.3 °C. It could be seen that introducing the siloxane blocks (SiO) in the main chain could significantly decrease the thermo stability of the polymer in the air condition. This is probably due to the higher oxygen solubility in the siloxane domains. The decrease in the thermo oxidative stability of these polymers is in agreement with the increase in the thermo oxidative residue. The dTG curves of these samples are characterized by two maxima, which can be explained by the existence of a two-stage decomposition mechanism. The most probable explanation is that the random depolymerization mechanism is accompanied by the oxidation of organic groups on the silicon atoms. [24]

As the main interest in exploring the SiPEGDA polymer is for using it as a material for devices suitable for biological reactions such as DNA amplification reaction, all the TGA results show that the SiPEGDA can easily withstand the thermal cycles performed during microfluidic biological reactions, such as.

3.4 DMA

DMA curves are shown in Figure 5. For SiPEGDA polymer, it could be found that the E'–T behaviour was typical of an efficiently cross-linked amorphous polymer, with a glassy region at low temperatures followed by a well-defined rubbery plateau

Table 2. The data of thermo-oxidative degradation of polymers (in air)

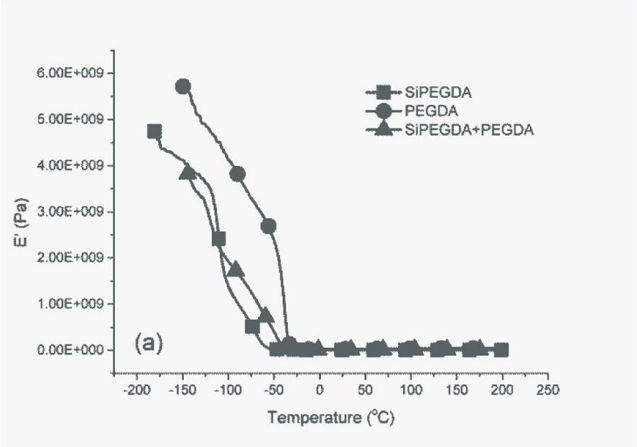
Sample	Temperature for mass loss (°C)			Residue at 800 °C (%)
PEGDA/SiPEGDA	T_5	T_{10}	T_{50}	
100/0	208.9	257.4	380.6	1.54
50/50	196.2	220.3	352.7	8.51
0/100	196.8	217.3	364.9	15.13

with a frequency independent behaviour. It could be found that two sharp decreases in modulus are evident; therefore the polymer exhibits two T_gs. As measured at f=1Hz they were at -42.6°C and -118 °C, which are attributable to the EO domains and to the SiO domains respectively.[25] The tan d curve confirm two thermal transitions. s the sharp peak in the curve, it can be inferred that the material was quite homogeneous, as also shown by the very good optical transparency of the photo cross-linked films.

3.5 Swelling tests

The sample's dimensional stability and its chemical resistance, are two important features of microfluidic structures during the device usage, which were studied by the swelling tests of the polymers.

In fact, solvents which are in direct contact with the polymer can cause swelling, discoloration of the material and contaminate the solutions inside the device. Moreover, exposed areas can also be permanently damaged by pitting or conversion to a sticky residue. The swelling results of the polymer were determined



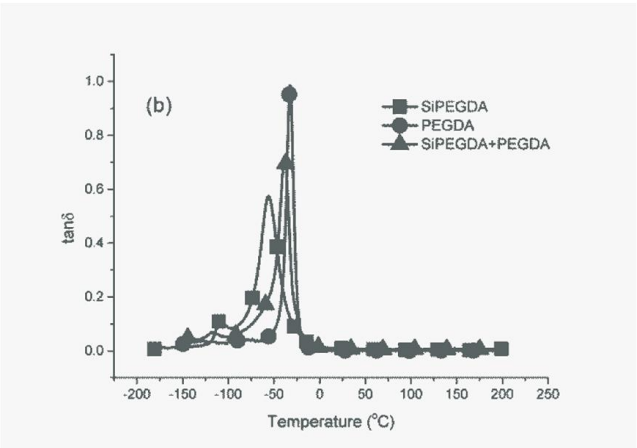


Figure 5. Storage modulus E' (a) and tanδ (b) of crosslinked polymer.

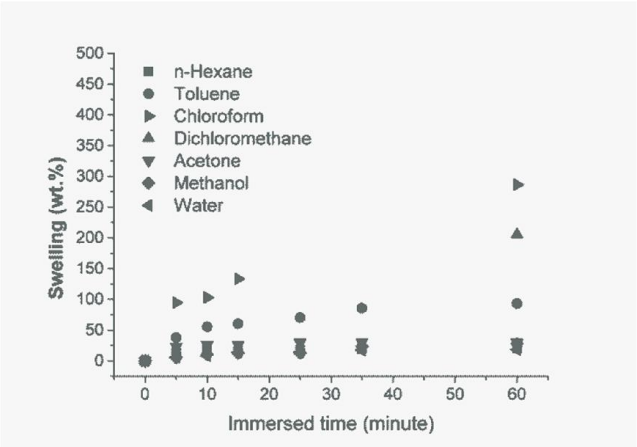


Figure 6. Swelling of SiPEGDA in different solvents.

after immersion in a variety of solvents for different periods, and the obtained data are shown in Figure 6.

Water is the most important solvent for biological applications, but it is also interesting to report data with many other solvents in the swelling test. It could be seen that the lowest swelling ratio of the SiPEGDA polymer was in water (18.2% after 1 h) Moreover, there is no trace of exposure left when water was evaporated in the immersion test, which means that SiPEGDA is suitable for the fabrication of microfluidic devices for PCR where the employed solutions are normally aqueous.

The photocured polymers show different swelling behaviours depending on the solvent used for the test, in particular the swelling get up to high values with. It is reported that the swelling of PDMS in chloroform is about 75% (immersed for 24h) while the value in hexane is ranging from 100% to 250% depending on the crosslinking degree, whereas SiPEGDA exhibited swelling of 286.3% (296.7% after 24h) and 20.5% (36.6% after 24h) in the same conditions.

The swelling values of PEGDA and the copolymer are also reported in Table 3. It could be easily seen that PEGDA has a limited swelling value in organic solvents while the copolymer has a bigger one. An interesting but expected result was obtained: the swelling value in water is increased by increasing the amount of EO units in the polymer. As EO unit is a hydrophilic group, PEGDA could absorbent more water in the polymer, which causes a higher swelling value than others. Moreover, the copolymer has a similar behaviour as the siloxane based polymer.

Table 3 Swelling (wt%) of SiPEGDA after 60min immersion in different solvents at room temperature and Hildebrand solubility parameters for the selected solvents.

Solvent	$\delta(MPa)^{0.5}$	PEGDA	SiPGDA +PEGDA	SiPEGDA
n-Hexane	14.8	0	6.9	20.5
Toluene	18.2	8.3	29.3	93.2
Chloroform	18.8	179.5	238.0	286.3
Dichloromethane	19.9	169.5	180.6	205.1
Acetone	20.1	7.5	26.9	30.3
MeOH	29.2	6.3	19.3	27.9
Water	48.0	19.5	18.6	18.2

In a cross-linked polymer, the swelling of the polymer depend not only on the crosslinking density of the network in the polymer but also on the thermodynamic affinity between the network and the solvent. The crosslinking density of the film subjected to swelling tests concerning the thermodynamic affinity can be discussed in terms of the Hildebrand solubility parameters δ.[26,27] Solvents with greater differences in Hildebrand solubility parameter have less swelling effect, and the range of peak swelling occupies less than two Hildebrand units.

The Hildebrand solubility parameter for a pure liquid substance is defined as the square root of the cohesive energy density:

$$\delta = \frac{\Delta H_v - RT}{V_m} \qquad \text{(eqn.4)}$$

where $\boldsymbol{\Delta H_v}$ is the heat of vaporization and $\boldsymbol{V_m}$ the molar volume. $\boldsymbol{RT}$ is the ideal gas term. Typical units are hildebrands, i.e. 0.488 MPa $^{0.5}$.

Solvents with similar solubility parameters are miscible in most proportions; dissimilar values yield limited solubilises. The Hildebrand solubility parameter provides a numerical estimate of the degree of interaction between materials, and can be a good indication of solubility, particularly for non-polar materials such as many polymers. Materials with similar values of δ are likely to be miscible. Qualitatively the greatest degree of swelling is usually observed for solvents having a solubility parameter closest to that of the polymer. δ values can be obtained experimentally or calculated by using computational tools.

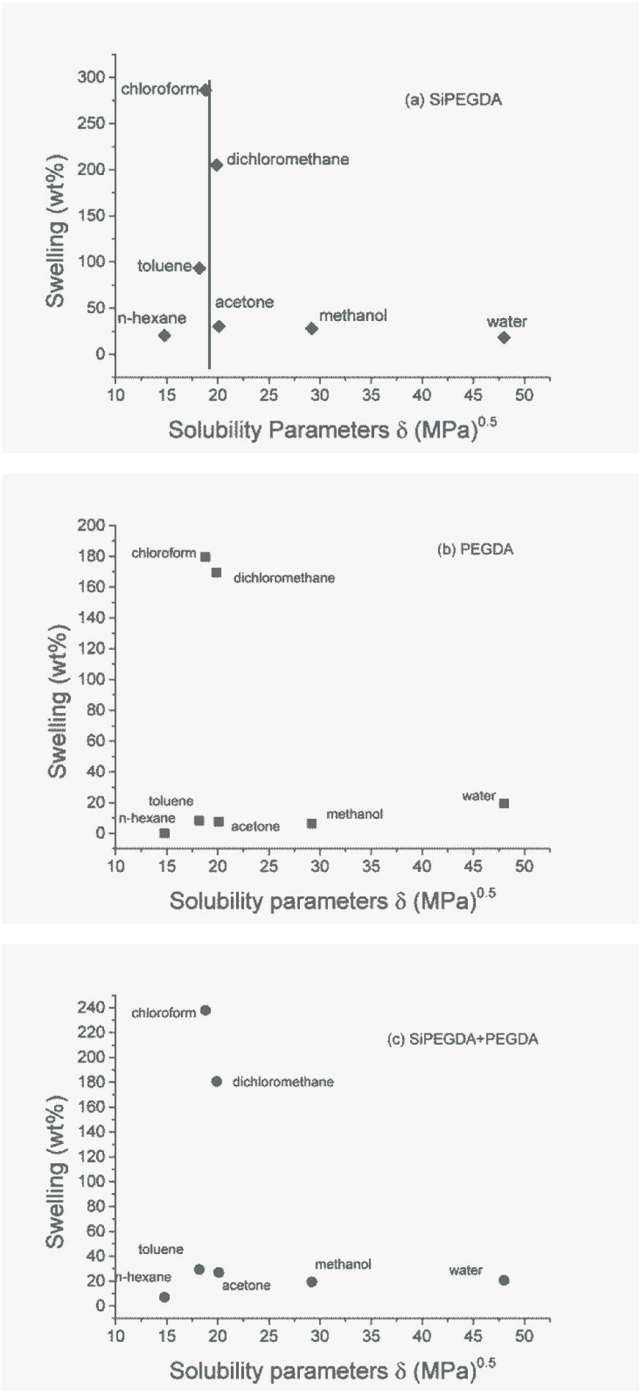


Figure 7 Correlation of swelling data and solubility parameters. (a)SiPEGDA, (b)PEGDA, (c)SiPEGDA+PEGDA

The δ values of the solvents used in the swelling test and the swelling results are reported in Table 3. Plot of the swelling percentage after 1 h of immersion versus the solvent solubility parameters is shown in Figure 7. It appears that the worst solvents, which can swell the network, are those whose δ are similar to the polymer, as predicted by the solubility theory.

There are however some important deviations: for example, toluene and dichloromethane have similar difference solubility parameters compared with chloroform, but dichloromethane swells the SiPEGDA network much higher than toluene does. This observation can be explained expressing the solubility parameter by a sum of the dispersion forces, polar forces, and hydrogen-bonding forces within the materials: the Hansen's total solubility parameter is $\delta = \delta_d + \delta_p + \delta_h$ [29]. Two solvents may have the same δ value, but different ratios among the contribution values result in differences in polymer swelling. As values of δ_d, δ_p and δ_h are not readily available for our polymers, further work is needed, also taking into account the heterophasic nature of the material and the different solubility parameters of the hydrogenated groups and the siloxane segments.

3.6 Contact angle

Contact angle measurements against water and hexadecane were also carried out, the surface tension of SiPEGDA was calculated from the Owens–Wendt method and the result is listed in Table 4. Interestingly its CA value against water is higher than that of PDMS (108°)[30] which means that SiPEGDA is a hydrophobic polymer. As mentioned above, the hydrophobicity of SiPEGDA was enough for limiting swelling in water. At the same time, the result also showed that SiPEGDA was more oleophobic than PDMS, which would get the better resistance to solvent swelling. The CA value of SiPEGDA showed to be rather low as expected as the presence of SiO block and its preferential segregation at the surface. All the data showed that the incorporation of both hydrophobic siloxane groups and hydrophilic polyoxyethylene groups into the networks is a successful way of controlling their surface properties.

Table 4. Static contact angle and surface tension of SiPEGDA polymer

	Contact angle (°C)		Surface energy (mN·m^{-1})
	Water	Hexadecane	
PEGDA	51.5	38	47
SiPEGDA	126.5	43.1	18.5

3.7 PCR Experiment

Polymerase Chain Reaction (PCR) is a process that uses primers to amplify specific cloned or genomic DNA sequences with the help of a very unique enzyme. In the PCR chip design, PCR inhibition due to the LOC construction material is the most important issue. In fact, the enzyme used in PCR reaction is very sensitive, and it can be easily deactivated. A typical PCR reaction is carried out in PP cuvettes while there are still many examples of PCR-inhibiting materials commonly used in devices microfabrication, such as silicon, glass, and SU8. [31] The problem can be partially solved by covering of the inhibiting surface through self-assembly with organofunctional alkoxysilane molecules.[2] However, using a PCR compatible material in a chip designed for PCR should be the preferential choice.

In order to test the behaviour of the silicone acrylate substrates toward PCR, some preliminary in vitro DNA amplification tests were carried out in standard conditions using PP tubes containing all reagents (bases, primers, and enzyme) and in some cases a known amount of a foreign material surface.

In particular, PCR was carried out both in blank cuvettes (positive control) as well as in cuvettes containing small pieces of the SiPEGDA polymer or the SiPEGDA/PEGDA copolymer, as reported in the Experimental section. A semi-quantitative comparison among the different band intensities of the reaction in presence of the material and the positive control is reported in Figure 8. The reaction occurred also with the addition in the

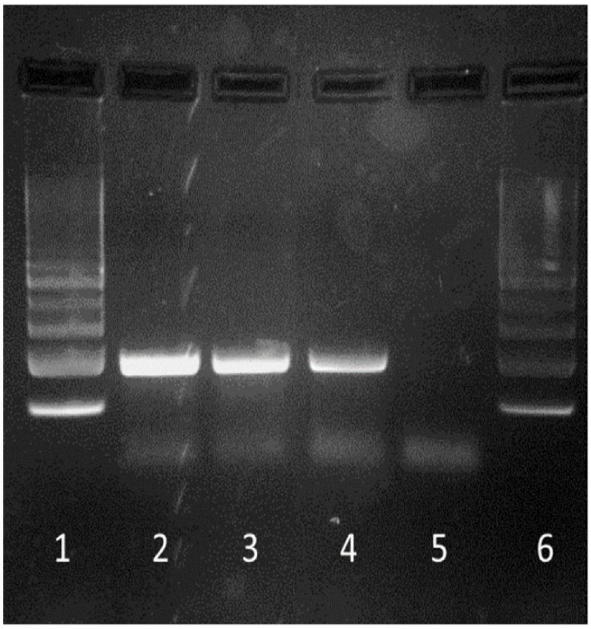


Figure 8. Gel electrophoresis analysis of PCR products: inhibition effect caused by the addition of small pieces of the crosslinked polymers. Lanes 1 and 6: DNA ladder; lane 2: addition of SiPEGDA; lane 3: addition of SiPEGDA/PEGDA (50/50); lane 4: positive control; lane 5: negative control.

cuvette of a small piece of polymer, even if the efficiency is slightly lower than the positive control. It can be concluded that both SiPEGDA and SiPEGDA/PEGDA seem biocompatible toward PCR showing no inhibition effect in the DNA amplification reaction. Moreover, no significant enzyme adsorption at the polymer surface was observed, demonstrating that the silicone material can be used without the need of surface treatments.

4 Conclusions

A linear macromer based on a siloxane block (SiO) and two polyoxyethylene blocks (EO) was synthesized and subsequently photopolymerized. The kinetics of UV-induced polymerization of the macromeres was monitored by rt-FTIR, confirming the reactivity of acrylic functionalities. The obtained polymer was then characterized by DMTA analyses and showed interesting biphasic morphology with two T_gs attributable to the EO domains and the SiO domains. Swelling in different solvents was also tested: the introduction of EO enhanced the chemical resistance to most solvents, excluding water. Surface analyses showed that the incorporation of both hydrophobic siloxane groups and hydrophilic polyoxyethylene groups into the networks is a successful way of controlling their surface: the wettability with water is very low (contact angle around 120°) and can change depending on the environment. And SiPEGDA seems biocompatible toward PCR showing no inhibition effect in the DNA amplification reaction. All these results suggest that the proposed polymer can be employed to produce PCR compatible microfluidic devices.

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