Synthesis of Reactive Acrylic Copolymers using RAFT Mini-Emulsion Polymerization Technique

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Abstract: Acrylic copolymers carrying reactive functional groups have great attention since they are used in many fields such as composites, coatings, membranes, catalysis, biology, optoelectronics, pharmaceuticals, etc. Many efforts are being done for synthesis of these polymers with controlled molecular weight and architectures. Present study deals with the synthesis of functional acrylic copolymers carrying alkoxysilane and epoxy reactive groups via RAFT mini emulsion polymerization. For this purpose three copolymers were synthesized composed of (1) poly(butyl acrylate-co-methylmethacrylate-co-vinyl trietoxysilane) [p(MMA-co-BA-co-VTES)], (2) poly(butyl acrylate-co-methylmethacrylate-co-3-trimetoxysilylpropyl methacrylate) [p(MMA-co-BA-co-TMSPMA)], (3) poly(butyl acrylate-co-methylmethacrylate-co- glycidyl methacrylate) [p(MMA-co-BA-co-GMA)] using 2-cyano 2-propyldodecyldithiocarbonate as RAFT agent. The results showed that the conversion ratios were high and the average molecular weights of copolymers were close to the theoretical values. On the other hand, PDI values were found to be higher than conventional RAFT polymers. The particle sizes of the latexes were small with very homogenous distributions and good stability. FTIR, H-NMR, DSC and TGA results verified the success of copolymer syntheses.

Key-Words: Functional acrylic copolymers, RAFT, Mini-emulsion, alkoxysilane, epoxy

1 Introduction

Silicone containing organic polymers have considerable attention in the last decade due to their potential applications in many fields such as composites, coatings, membranes, catalysis, biology, optoelectronics, etc. The inorganic silicone constituents are also known to increase the thermal and oxidative stability, resistance to weathering, chemical and biological resistance, etc. Vinyl monomers carrying silane functionality in the monomer unit gives possibility to prepare organic-inorganic copolymers that are capable of participating directly in the sol–gel-type network formation process in the presence of an appropriate acidic or basic catalyst [1] to form an oxide framework and link together the organic and inorganic components. However, it may be a challenge sometimes to prepare copolymers containing vinyl silane monomers (i.e. Vinyltriethoxysilane, VTES) with high conversions and controlled molecular weights due to their low reactivity. On the other hand, RAFT mini emulsion polymerization as a controlled radical polymerization (CRP) technique may be used to overcome this problem with higher conversions and controlled molecular weights.

As it is known RAFT polymerization (Reversible Addition Fragmentation Chain Transfer) mechanism has advantages among the CRPs (NMP and ATRP) since it is applicable to a wide range of monomers, having no metal contamination or other catalysts. Among the monomers; styrene and its derivatives, acrylates, acrylamide, methacrylates, methacrylamide, butadiene, vinyl acetate and several vinyl monomers such as vinyl pyrrolidone have been successfully polymerized via RAFT technique with controlled molecular weights. In RAFT polymerization, the control is provided by a series of complex reactions and formation of intermediary products [2,3]. The most important component of RAFT polymerization is the chain transfer agent (CTA). The thio-carbonyl-thio compounds are usually used as chain transfer agents and commonly constitute the family of dithioesters, dithiocarbamates, trithiocarbonates and xanthates. The choice of right CTA for each monomer to be synthesized by RAFT is crucial. The use of improper CTA may cause problems in the control of reaction, retardation, long reaction times or complete inhibition of the reaction [4-6]. The RAFT agents are usually chosen depending on the nature of Z and R groups in their structures [7]. It is also important to pay attention to some factors such as the concentration and choice of initiators. The RAFT polymerization is usually performed by the conventional radical initiators, most preferably thermal initiators such as azo-based initiators (AIBN, ACVA) or persulfates (i.e. K2S2O8). On the other hand it may be advantageous to use an initiator which has the same function with the -R group of CTA [8]. Therefore, with a careful selection of the components and reaction parameters a good control on the polymerization can be achieved.

Although mini-emulsion polymerizations use the systematic of conventional emulsion polymerization they show small differences in terms of particle stabilization and reaction mechanism. Mini-emulsions can be described as colloidal dispersions of small (50-500 nm) oil in water particles that are stabilized using a surfactant and a co-stabilizer. They are commonly subjected to an efficient homogenization process using high-pressure homogenizers or ultrasound treatment. In this way, a dispersion with narrow and small particle size distribution is usually obtained. As co-stabilizer, highly water insoluble substances are used (i.e. hexadecane, HD) to avoid diffusional degradation (Ostwald ripening) [9].

Mini emulsion polymerization has the characteristics of conventional emulsion polymerization such as compartmentalization effect, low viscosity, effective heat transfer, organic solvent free [10-12]. However, in mini-emulsions the particle droplets dispersed in water behave like individual reactors which provide high reaction rates. In the conventional emulsion polymerization, the main mechanism proceeds through the growing particle nuclei, and the monomers are diffused into the growing particles from the monomer reservoir droplets. For this reason, the monomer diffusion in mini-emulsion system is eliminated and the monomer droplets themselves are used as reaction sites.

Mini emulsion polymerization is usually preferred for RAFT processes instead of emulsion. This is related with the problems of low colloidal stability, slow polymerization rate and difficulties of controlling molecular weights observed in conventional RAFT emulsion systems [13]. These problems arise from the diffusion process of RAFT agent through the water phase, as required by the mechanism of emulsion polymerization. Moreover, when using a water insoluble RAFT agent the diffusion process becomes even more difficult. On the other hand, in mini-emulsion polymerization RAFT agent does not need to diffuse through the water phase due to its location in small monomer droplets where the reaction takes place. Therefore, a better control on molecular weights is usually achieved [13,14].

In literature there are many studies related with the successful use of RAFT process via mini-emulsion polymerization including different acrylic monomers [15-21]. However, there are very limited numbers of studies using functional monomers such as vinyl alkoxysilanes via RAFT mini-emulsion systems. Present study describes the RAFT co-polymerization of reactive functional monomers such as vinyl triethoxysilane, 3-trimetoxysilylpropyl methacrylate and glycidyl methacrylate in combination with butyl and methyl methacrylate via mini-emulsion polymerization technique. The control on molecular weights, reaction conditions and polymer properties were discussed in the study. The illustration of the copolymer syntheses is given in Fig. 1.

2 Material and Methods

2.1 Materials

As monomers (M) vinyl triethoxysilane (VTES, 97%), 3-trimethoxysilyl propyl methacrylate (TMSPMA, 98%) butyl acrylate (BA, 99%), methyl methacrylate (MMA, 99%), glycidyl methacrylate (GMA, 97%) were supplied from Sigma-Aldrich. As chain transfer agent (CTA) 2-cyano 2-propyldodecyldithiocarbonate (97%, Sigma-Aldrich) was used. For mini-emulsions; hexadecane (HD, Sigma-Aldrich, 99%) as co-solvent, sodium dodecyl benzene sulfonate (SDBS, Sigma-Aldrich) as anionic emulsifier, sodium bicarbonate ($NaHCO_3$, Merck, 99%) as buffer and potassium persulfate (KPS, Sigma-Aldrich, 99%) as initiator were used. The monomers of BA, MMA, GMA and VTES were distilled under reduced pressure to remove their inhibitors prior to polymerizations. All the other chemicals were used as received. Ultra-pure water was used for the preparation of emulsions.

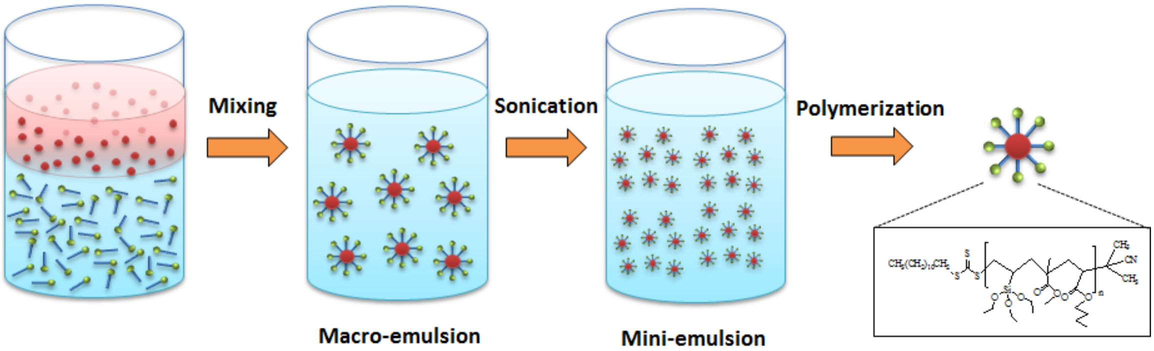

Figure 1. Representative image showing the preparation of copolymers *via* raft mini-emulsion polymerization

2.2 Synthesis of copolymers using RAFT mini-emulsion technique

The experimental details of the copolymer syntheses carried out using the mini-emulsion technique are given in Table 1. In a typical mini emulsion polymerization, 4.27 mL (40 mmol) of MMA, 2.24 mL (15 mmol) of BA, 4.4 mL (21 mmol) of VTES monomer, 0.271 g (0.76 mmol) of CTA and 0.04 g of hexadecane were mixed. 0.5 g of SDBS and 0.04 g of $NaHCO_3$ were dissolved with 34 mL of water in an erlenmayer flask to obtain the pre-emulsion. The monomer mixture was then added to the pre-emulsion mixture and mixed at high speed for 30 min to obtain an oil/water emulsion. This mixture was then subjected to ultrasound (70W and 80% amplitude) in an ice bath for 15 min to obtain mini-emulsion. The resulting emulsion was added to a three neck glass reactor equipped with a condenser and nitrogen inlet. The reactor was then bubbled with nitrogen gas for 45 min to remove the dissolved oxygen from the system. Subsequently, system was immersed in a pre-heated oil bath at 80 °C, and the reaction was initiated by injecting KPS solution. At the end of the 5 h reaction time, the copolymer emulsion was obtained by cooling to room temperature. For the characterizations 5 mL latex sample was freeze-dried, washed with cold methanol and n-hexane and dried in vacuum oven for 48h at 45 °C. The conversion ratio was calculated gravimetrically from the purified samples.

2.3 Characterizations

2.3.1 Gel Permeation Chromatography (GPC) Analysis

The average molecular weights and polydispersity indexes of the obtained (co)polymers were determined by Malvern Gel Permeation Chromatography (GPC) using THF solvent with a flow rate of 1 mL/min using poly(methyl methacrylate) standards. Before the measurement, the copolymers with 2 mg/mL concentration were dissolved in THF and shaken for at least 6 hours to obtain a complete dissolution. Then, the samples were filtered through 0.45 μm injector filters and measured for the determination of number average molecular weights (M_n), weight average molecular weight (M_w), molecular weight distribution and polydispersity index (PDI).

Table 1. The experimental details of copolymer syntheses

Reaction components and parameters	**Trials**		
	C1	**C2**	**C3**
MMA (mmol)	40	30	40
BA (mmol)	15	23.4	23.4
VTES (mmol)	21	-	-
GMA (mmol)	-	28.1	-
TMSPMA (mmol)	-	-	12.0
CTA (mmol)	0.76	0.815	0.754
HD (wt.%)*	5.0	5.0	5.0
SDBS (wt.%)*	5.0	5.0	5.0
$NaHCO_3$(wt.%)*	0.5	0.5	0.5
KPS (mmol)	0.19	0.20	0.18
[M]/[CTA]/[I]	100/1/0.25	100/1/0.25	100/1/0.25
Temp. (°C)	80	80	80
Duration (h)	5	5	5
Conversion (%)	83	99	94
$M_{n,th}$ (Da)	10452	12490	12793
$M_{n,GPC}$ (Da)	10022	10659	5417
PDI	2.7	1.9	1.5

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The structural analysis of polymers was performed by using Perkin Elmer Spectrum-100 model FT-IR+ATR spectrometer. The IR spectra of samples in solid form were obtained after 5 scans between 4500 - 600 cm^{-1} using 2 cm^{-1} discriminating power.

2.3.3 H-NMR Analysis

The structure analysis of selected samples was also determined by using Liquid MERCURY plus-AS 400 model NMR spectrometer with 400 MHz operating frequency. Polymer samples were analyzed at 10-15 mg/mL concentrations by dissolving in DMSO-d_6 solvent

2.3.4 Thermal Analyses

The thermal behavior of polymers was determined by using Shimadzu-DSC 60 Plus instrument. The samples weighted between 5-6 mg were transferred to hermetic aluminum pans and sealed. Heat flows were recorded between -80 and 300 °C with heating rate of 10 °C/min under nitrogen atmosphere. The heat-induced degradation behaviors of the samples were investigated by using TA instruments TGA-SDT Q600 device by heating from the room temperature to 700°C under N_2 atmosphere with a heating rate of 10°C/min

2.3.6 Particle Size Analysis

Particle size and zeta potential of the latexes were measured by Malvern Zeta Sizer Nano ZS particle size analyzer. For the analysis copolymer latex samples were prepared by diluting x5000 times with ultrapure water.

3 Results and Discussion

In the synthesis of copolymers via RAFT mini-emulsion polymerization butyl acrylate (BA), methyl methacrylate (MMA) were used as common acrylic monomers which were combined with reactive monomers of vinyltriethoxysilane (VTES), glycidyl methacrylate (GMA) and 3-trimethoxysilyl propyl methacrylate (TMSPMA), respectively. A hydrophobic RAFT agent 2-cyano 2-propyldodecylthiocarbonate- having a long alkyl chain at R group was chosen as chain transfer agent to facilitate its location in monomer droplets. The molar ratios of [M] / [CTA] / [I] in the reactions were selected as 100/1/0.25, respectively for all experiments. Hexadecane (HD) as co-solvent and sodium dodecyl benzene sulfonate as anionic emulsifier, were used in the stabilization of mini-emulsions with a ratio of 5% (w/w). The solid content of all emulsions was adjusted to be 25%.

During the preparation of the mini-emulsions it was observed that the yellow color of the emulsions due to the RAFT agent were turned into yellowish white color subsequent to the ultrasound treatment, indicating that the CTA molecules were efficiently transferred into the monomer droplets. The emulsion polymers obtained after the reaction showed no phase separation, no sedimentation or coagulum.

3.1 GPC analysis of the copolymers

GPC analysis was performed to determine the molecular weight of the obtained copolymers. The molecular weight distributions, average number molecular weights and PDI values are given at Fig. 2. From the analysis, the number average molecular weight (M_n) of P(*MMA-co-BA-co-VTES*) (C1) was found to be 10.022 Da, close to the theoretical M_n value (10.452 Da). However, the polydispersity was high as 2.7 indicating a relatively wide molecular weight distribution. When the molecular weight distribution curve of the copolymer C2 was examined, the M_n value was found to be 10.659 Da with PDI value of 1.9, which was close to the theoretical value. The M_n value of the copolymer C3 was calculated as 5.417 Da lower than the theoretical value with a lower PDI of 1.5. It was also observed that the distribution curve of C3 was partially overlapped with the peak of HD possibly remained in the sample. It's accepted that the obtained PDI values are generally higher in emulsion polymerizations than the solvent-based reactions using RAFT technique. Moreover, it is also known that emulsion polymerizations usually result in high molecular weights. Therefore, the low average molecular weights obtained from the copolymers indicated that there was a control over the reactions. The high PDI values could be due to the lower compatibility of the reactive monomers with the RAFT agent. To understand better this phenomenon further investigation is needed using different types of CTAs.

3.2 Particle size and zeta potential of the copolymer mini-emulsions

Particle size analysis (zetasize) and zeta potential measurements were performed on the copolymer latexes. The average zeta-size diameters, PDI and zeta potential values are given at Table 2 and particle distribution curves at Fig. 3. The results showed that all mini-emulsions had a very homogeneous particle size distribution and high stability. The average particle diameters of the minemulsions varied between 94-139 nm and the PDI values were found to be low being between 0.062-0.177. The zeta potential values of the latexes were within the range of -38.4 to -45.6 mV, indicating that the emulsions had good electrostatic stability. The results showed that the mini-emulsion system designed for the syntheses were efficient, the particles are small in size and electrostatically stable.

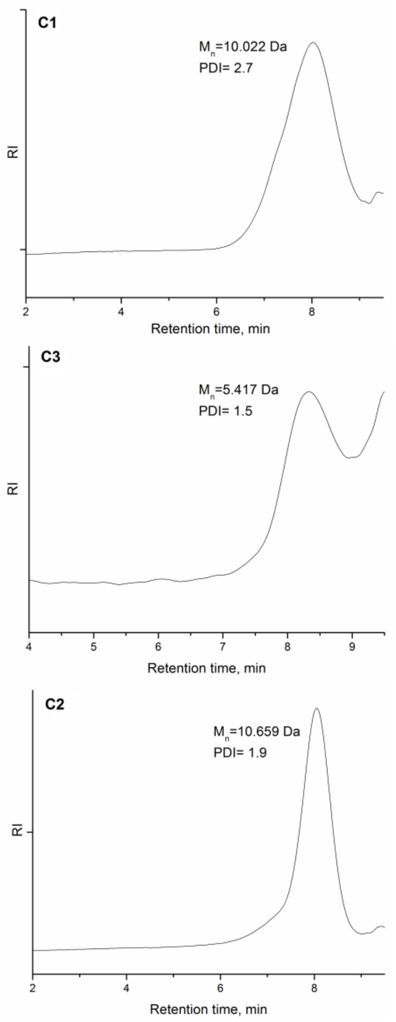

Figure 2. GPC curves of the synthesized copolymers via RAFT miniemulsion polymerization.

Table 2. Average zeta-size diameter, PDI and zeta potential values of the mini-emulsions

Copolymer	Average size diameter (nm)	Polydispersity (PDI)	Zeta potential (mV)
C1	96	0.122	-38.4
C2	139	0.062	-43.4
C3	94	0.177	-45.6

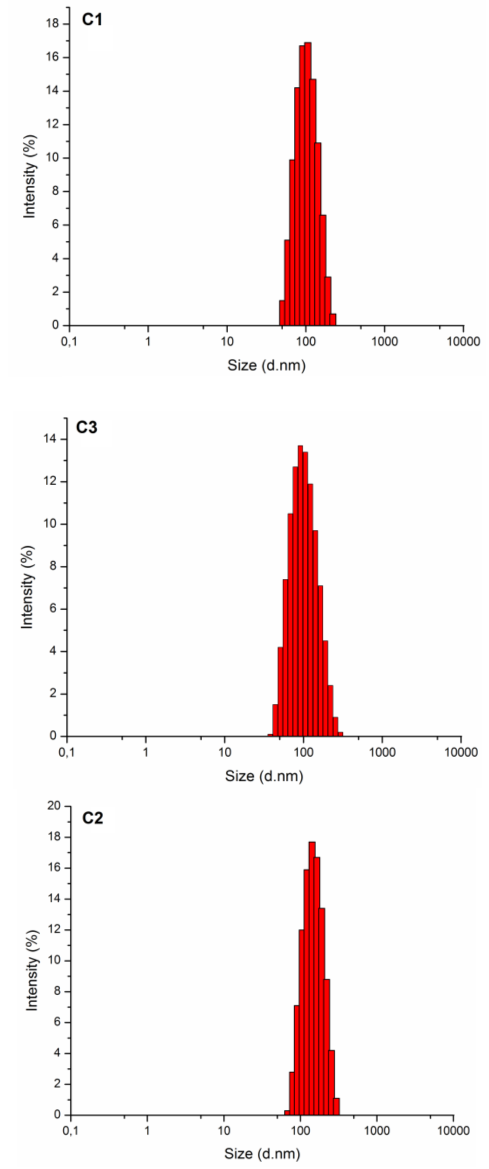

Figure 3. Particle size distribution of the copolymer latexes

3.3 FTIR spectra of the copolymers

The IR spectra of the monomers used in the reactions with the assignation of their characteristics absorption bands are shown in Fig. 4, and the spectra of copolymers are given in Fig. 5. From the spectra of monomers; -CH stretching of -CH_2 and -CH_3 was observed between 2800-3000 cm^{-1}, C═O stretching vibration in the range of 1714-1724 cm^{-1}, the vibration of -C═C- vinyl carbons between 1600-1641 cm^{-1}, and ester group vibrations were observed at 1150-1180 cm^{-1}. The characteristic absorption peaks of reactive groups were observed at 1073 cm^{-1} for Si-O-C groups of VTES, 907 cm^{-1} for epoxy ring of GMA and Si-O-C vibration of TMSPMA monomer at 1078 cm^{-1}.

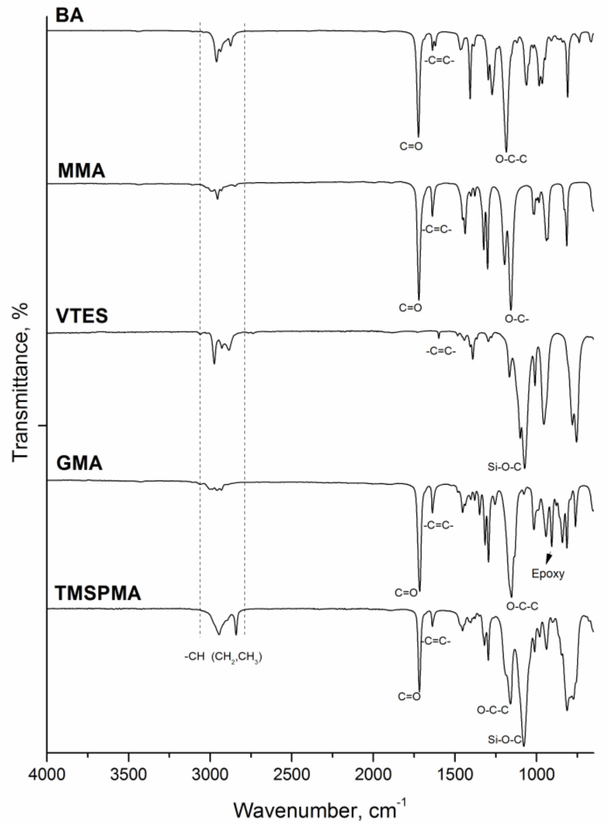

Figure 4. IR spectrum of the vinyl monomers used for copolymer synthesis

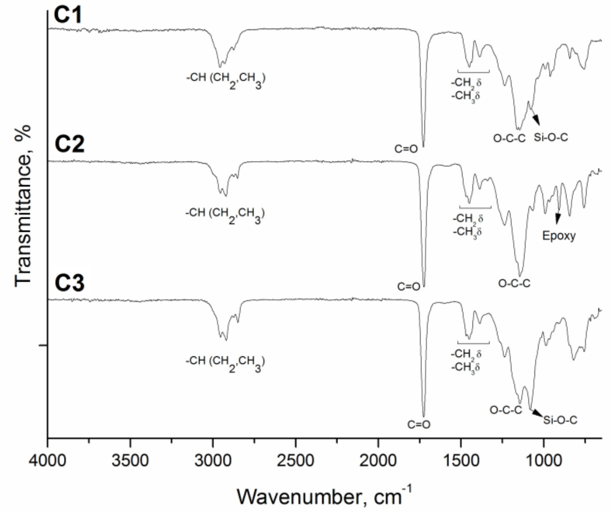

Figure 5. IR spectra of copolymers of C1: P(MMA-co-BA-co-VTES), C2: P(MMA-co-BA-co-GMA), C3: P(MMA-co-BA-co-TMSPMA)

The FTIR spectra of the copolymers are shown in Fig. 5. From the spectra the stretching vibrations of -CH groups were found to be between 2800-3000 cm^{-1}, C═O stretching between 1724-1728 cm^{-1}, -CH$_2$, -CH$_3$ and -CH deformation vibrations at 1450-1386 cm^{-1} and ester group vibrations (O-C) were observed between 1144 and 1160 cm^{-1}. The characteristic bands of reactive groups of Si-O-C vibrations of VTES segments was found at 1077 cm^{-1} for C1, the epoxy ring absorption at 907 cm^{-1} for C2 and Si-O-C absorption of TMSPMA segments at 1080 cm^{-1} for C3 copolymers. Moreover, the -C=C- absorption vibrations of the monomers between 1600 and 1641 cm^{-1} were not observed in the spectra of all copolymers. The findings showed that the copolymers were successfully synthesized.

3.4 H-NMR analysis of the copolymers

The chemical structure of the copolymers were also investigated by H-NMR analysis. Figure 6 shows the H-NMR spectra of the reactive monomers VTES, GMA and TMSPMA used in the copolymerization, and Fig. 7 shows the H-NMR spectra of the copolymers. When Fig. 6 is examined, the protons bound to vinyl carbons of VTES monomer are observed at 5.8-6.1 ppm, O-CH$_2$ protons at 3.7-3.8 ppm and CH$_3$ protons at 1.17-1.21 ppm. The characteristic proton signals of the GMA monomer were observed at 5.6 and 6.1 ppm for vinyl protons, at 4.46 and 4.0 ppm for O-CH$_2$- (b), at 3.24 ppm for CH (c), at 2.84 and 2.65 ppm for CH$_2$ (d) and for CH$_3$ at 1.94 ppm. The proton signals of the TMSPMA monomer were found at 5.45 and 6.0 ppm for vinyl protons, at 4.03 ppm for O-CH$_2$ (b), at 3.48 ppm for O-CH$_3$ (e), at 1.84 ppm for CH$_3$ (f), at 1.69 ppm for CH$_2$ protons (c) and at 0.60 ppm for Si-CH$_2$ protons (d).

From the spectra of the copolymers in Fig. 7, characteristic proton signals of BA and MMA segments for all the copolymers were observed at the same location. O-CH$_3$ (d, d ') proton signals for MMA segments were observed at 3.51-3.52 ppm, O-CH$_2$- (e) signals of BA were observed at 3.71 and 3.91 ppm, -CH$_2$- (f) proton signals were observed at 1.51 ppm and -CH$_2$ protons next to -CH$_3$ group (g) were observed at 1.31 ppm. The characteristic protons signals of VTES segments in copolymer C1 were observed at 3.92 ppm for O-CH$_2$ (a), and at 1.17 ppm for -CH$_3$ (b). The characteristic signals of the GMA segments in C2 copolymer were observed at 4.28 and 3.92 ppm for O-CH$_2$- (a), 3.17 ppm for -CH- (b), 2.77 and 2.63 ppm for -CH$_2$- (c) protons. For TMSPMA segments in C3 copolymer; O-CH$_2$- (a) protons were found at about 3.91 ppm, O-CH$_3$ (d) at 3.46 ppm, -CH$_2$- (b) at 1.51 ppm and Si-CH$_2$- (c) at 0.60 ppm. The data obtained from the H-NMR data verified the success of copolymer syntheses.

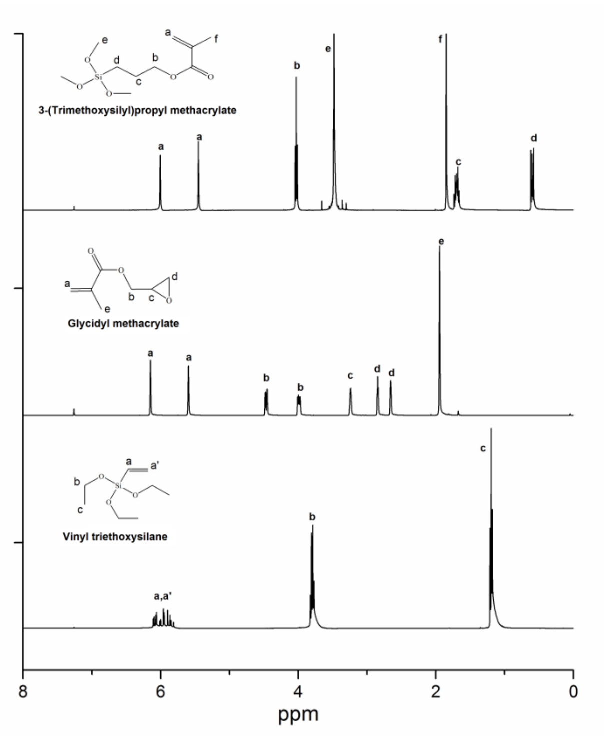

Figure 6. H-NMR spectra of the reactive monomers used in copolymer synthesis

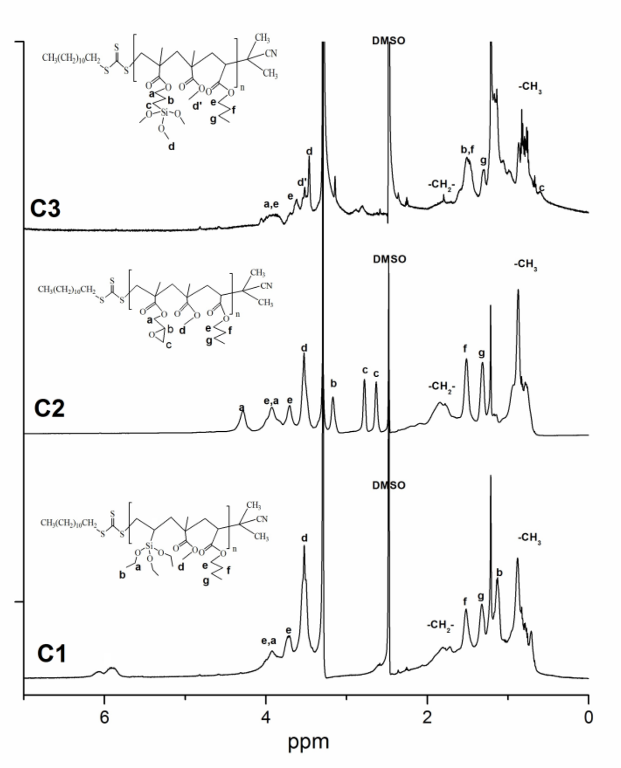

Figure 7. H-NMR spectra of the copolymers

3.5 DSC analysis of the copolymers

DSC thermograms of the copolymers are given in Fig. 8. From the thermograms it was observed that all the copolymer samples had similar behavior exhibiting a single phase transition at the selected temperature range due to the glass transition (T_g). From the calculation, the T_g values of copolymers were found to be at 34.5 °C, 37 °C and 33 °C for C1, C2 and C3, respectively, being close to the their theoretical values.

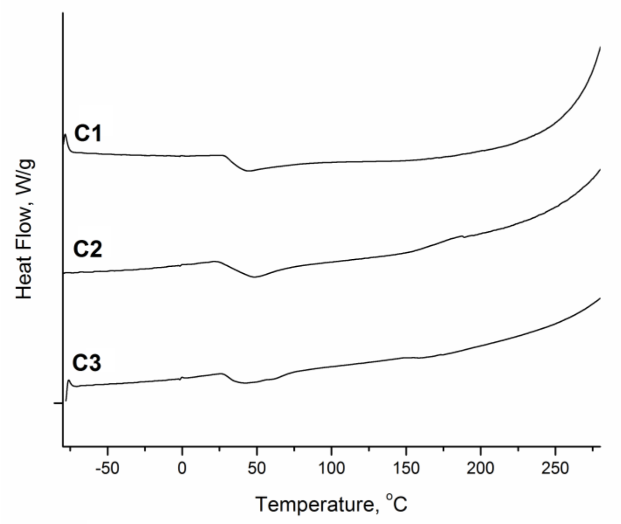

Figure 8. DSC thermograms of the copolymers

3.6 Thermogravimetric behavior of the copolymers

The thermogravimetric behaviors of the copolymers are given in Fig. 9. From the results it was observed that a small degradation took place between 120-200 °C for all copolymer samples. It’s known that thio-carbonyl-thio based RAFT agents undergo to a thermal decomposition between 90-240 °C depending on the CTA type [22,23]. Therefore, this small degradation might be due to CTA segments located at the end of copolymer chains. The main degredation process of the samples was observed between 250-500 °C. However, the copolymer C2 was found to have much lower thermal stability than the copolymers of C1 and C2, possibly due to its complete organic nature. On the other hand, the copolymers containing silane moieties showed higher thermal stability and their final masses were considerably higher. Among the silicon-containing copolymers C1 showed higher thermal stability than C3 since its silicone content was higher. The overall results showed that the thermal stability of the copolymers were affected significantly by their silicone content and degradation temperatures shifted to higher values accordingly.

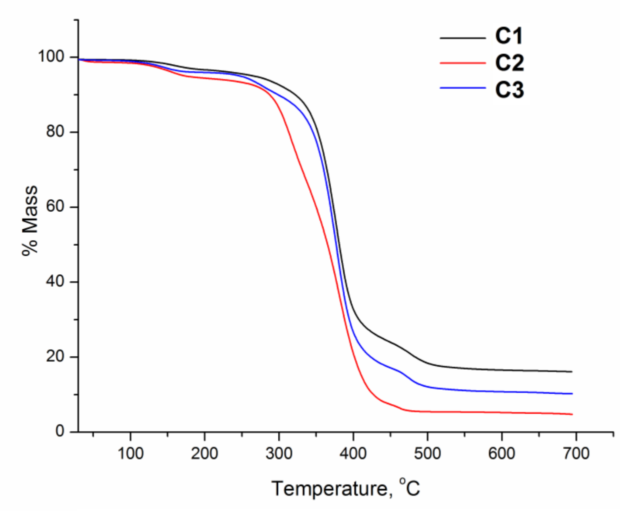

Figure 9. TGA curves of the copolymers

4 Conclusion

Functional copolymers based on P(*MMA-co-BA-co-VTES*), P(*MMA-co-BA-co-GMA*), P(*MMA-co-BA-co-TMSPMA*) were synthesized using RAFT mini-emulsion technique. For the syntheses a hydrophobic CTA; 2-cyano-2-propyl dodecyldithiocarbonate were used to facilitate its location in emulsion droplets. The results showed that the average molecular weights of the copolymers were obtained low (5.417-10.659 Da) as desired being close to the theoretical values. However, the PDI values were found to be slightly higher than conventional RAFT polymers which might be due to the insufficient compatibility of the reactive monomers with the RAFT agent. On the other hand, the obtained low molecular weights of copolymers also showed that the reaction was controlled to some extend especially for the copolymers of C2 and C3. All other results obtained from FTIR- H-NMR and DSC indicated that the copolymers were successfully synthesized containing the reactive segments on polymer backbone. TGA results also showed that the thermal stability of silicone containing copolymers (C1, C3) was higher than C2 and the increment was in proportional to the silicone content. The obtained copolymers were found to have potential use in many application fields such as chelating agents for metals in environmental applications, as protein stabilizers for medical fields or in coatings for inorganic/metal surfaces, etc.

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