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Preparation of biodegradable poly[(dimethyldichlorosilane)-*alt*-(fumaric acid/sebacic acid)]-*co*-PEG block copolymer

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Abstract

A low molecular weight linear unsaturated precursor, poly[(dimethyldichlorosilane)-*alt*-(fumaric acid/sebacic acid)], PDFS with active dimethylchlorosilyl terminal groups, has been synthesized by polycondensation of fumaric acid and sebacic acid with the aid of dimethyldichlorosilane as coupling agent. PDFS has been used to prepare poly[(dimethyldichlorosilane)-*alt*-(fumaric acid/sebacic acid)]-*co*-PEG, P(DFS-*co*-EG) block copolymer. Each of the compounds, PDFS or P(DFS-*co*-EG), has been cross-linked with a vinyl monomer like methyl methacrylate or styrene. Products thus obtained have been investigated in terms of molecular weight, composition, structure, and thermal properties. Hydrolytic degradation of P(DFS-*co*-EG) block copolymer in aqueous media (pH 7.3, 37 °C) in a 28-day period is also investigated. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Biodegradable; Polyethylene glycol; Poly[(dimethyldichlorosilane)-*alt*-(fumaric acid/sebacic acid)]-*co*-PEG

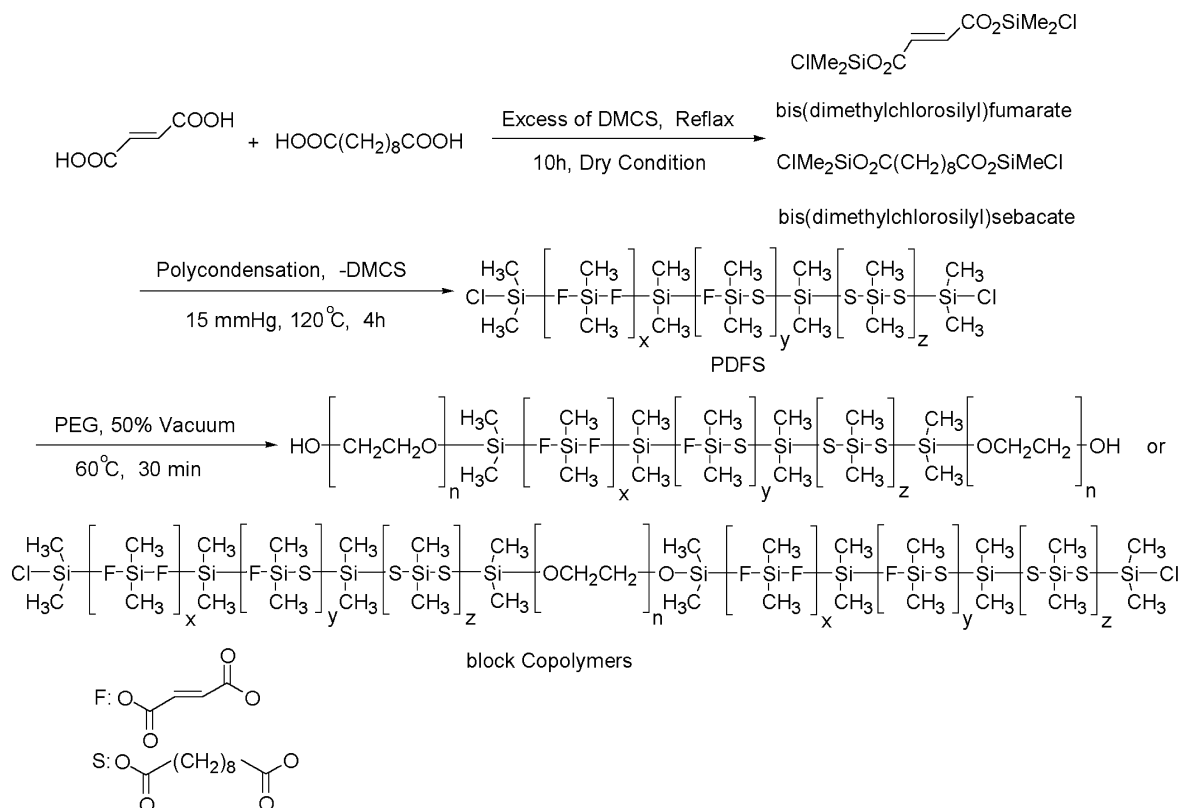
1. Introduction

Silicon polymers are being extensively used as stable biomaterials, plastics, rubbers, paints, fibers, ceramics, detergents, etc. [1]. Hydrolytic polycondensation of dimethyldichlorosilane (DMCS) in the presence of excess water leads to the formation of polydimethylsiloxanes (PDMS) and cyclic siloxanes. Most commercial applications of silicon polymers make use of proper combinations of their inherent physical and/or chemical properties that are absent in other polymers. The unique properties of PDMS can be further extended by attaching organofunctional groups to some of the silicon atoms in the polymer chain [2]. Polydimethylsilazanes and cyclic silazanes have been synthesized by polycondensation of DMCS with NH₃ (gas). Polysilazane precursors have been used in pyrolytic preparation of heat resistant ceramics [3,4]. Polyalkoxylation of DMCS by diols such as 1,4-butanediol, 1,8-octanediol, ethylene glycol, propylene glycol, hydroquinone, bisphenol A, poly(ethylene glycol), poly(propylene glycol) and diethylene glycol has been investigated. Poly(silyl ether)s with C–O–Si structure in the main chain of the silicon polymers

have been used in producing photosensitive, heat and fire resistant materials [5–9]. Polyorganosilazoxanes have been synthesized by polycondensation of organochlorosilane in the presence of NH₃ (aqueous). Pyrolysis of polysilazoxanes has led to the production of ceramics [10]. Polyaminosilanes have been prepared by polycondensation of DMCS with diamines, such as hexamethylenediamine and aromatic diamine. Poly(silyldiamine) precursor with Si–N–C structure has been used in producing polyurethane elastomers [11,12]. DMCS has been used as a coupling agent in the condensation of copolymers with two terminal hydroxy groups such as polycarbonates consisting of bisphenol A/phosgene and epoxy resins made of bisphenol A/epichlorohydrin [13,14].

A common feature among these entire silicon polymers is their long-term stability (owing to hydrolytic resistance of Si–O–C bond) especially in biological milieu. However in some cases, where biodegradability is important, permanency turns into a disadvantage and instead biocompatibility together with biodegradability become highly desirable. Previous investigators have obtained some silicon coupling agents via condensation of DMCS with monocarboxylic acids [15]. We hereby report the synthesis of some oligomers containing mildly hydrolysable Si–O–CO bonds by polycondensation of fumaric acid (FA) and sebacic acid (SA) with DMCS and characterization of

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Scheme 1.

the products. Polycondensation of dicarboxylic acids FA and SA with DMCS have led to the production of poly[(dimethyldichlorosilane)-*alt*-(fumarate acid/sebacate acid)], PDFS. The PDFS is a linear unsaturated silicon oligomer with two active dimethylchlorosilyl terminal groups. Condensation of the precursor PDFS with PEG led to the formation of novel block copolymers. The PDFS precursor and its PEG block copolymers, P(DFS-*co*-EG), are then cross-linked in the presence of vinyl monomers like methyl methacrylate (MMA) or styrene.

2. Experimental

2.1. Materials

All compounds, and solvents used were reagent grade obtained from Merck (Darmstadt, Germany). These include fumaric acid (FA), sebacic acid (SA), dimethyldichlorosilane (DMCS), methyl methacrylate (MMA), styrene, poly(ethylene glycol), benzoyl peroxide, tetrahydrofuran (THF), chloroform, petroleum ether, diethylether, internal reference: tetramethylsilane (TMS), and deuterated solvents consist of chloroform, benzene, dimethylsulfoxide. DMSO- d_6 used was water-free (with the aid of molecular sieves).

2.2. Instrumentation

Infrared spectra were recorded on a Shimadzu-4300 FT-IR (Kyoto, Japan) spectrophotometer. Polymeric samples were in the form of either a solid film or a liquid spread onto NaCl plates. Polymeric powder samples were pressed into KBr pellets.

^1H NMR and ^{13}C NMR spectra were obtained on a Bruker AC80 (Germany) spectrophotometer using deuterated solvents and tetramethylsilane (TMS) as an internal reference. Molecular weight and molecular weight distribution of polymers were determined by gel permeation chromatography (GPC) of the polymer solutions in tetrahydrofuran, using a Waters chromatograph 150C model equipped with Styragel columns, flow rate 1 ml/min at 30 °C, and polystyrenes of low polydispersity as standards. Differential scanning calorimetry (DSC) thermograms were obtained on a Perkin Elmer DSC4 at a constant heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were obtained on a V5.1A DuPont 2000 (Du Pont, Delaware, USA) at a constant heating rate of 10 °C/min.

2.3. Precursor synthesis

Dimethylchlorosilylation of dicarboxylic acids FA and SA was carried out by slowly adding an excess of DMCS to an equimolar mixture of FA and SA in dry condition, while

Table 1
Reaction conditions, composition and molecular weights of precursor PDFS and block copolymers prepared by reacting precursor PDFS with PEG

Precursor PDFS and block copolymers	Amounts of PDFS (g)	Amounts of PEG 2000 (g)	Reaction time temperature and vacuum	\bar{M}_n	\bar{M}_w	Yield (%)
Precursor PDFS	–	–	4 h, 120 °C, 15 mm Hg	1931	2749	93
Copolymer 1	2	1	30 min, 60 °C, 350 mm Hg	2441	6577	79
Copolymer 2	1	2	30 min, 60 °C, 350 mm Hg	2990	7728	87
Copolymer 3 ^a	1	3	30 min, 60 °C, 350 mm Hg	–	–	84

^a Insoluble in THF.

stirring under reflux for 10 h. The HCl evolved was captured in aqueous NaOH. In the subsequent step, polycondensation of bis(dimethylchlorosilyl)fumarate and bis(dimethylchlorosilyl)sebacate was carried out at 120 °C, 15 mm Hg for 4 h, to obtain PDFS as the desired precursor, i.e. a linear unsaturated polycarboxysilane as a transparent viscous liquid. DMCS that is cleaved off during the polymerization was continually removed by condensation (Scheme 1).

2.4. Copolymer synthesis

Block copolymers of poly[(dimethyldichlorosilane)-*alt*-(fumaric acid/sebacic acid)]-*co*-PEG, P(DFS-*co*-EG) were prepared under mild conditions by adding PEG 2000 to the PDFS precursor at 60 °C under about 50% vacuum for 30 min. Amounts of PEG and PDFS have been indicated in Table 1. The HCl released during the condensation of PDFS precursor with PEG was captured in aqueous NaOH. The reaction leading to the formation of the unsaturated block copolymers is described in Scheme 1. The resulting copolymers were purified by pouring their chloroform solutions into petroleum ether (non-solvent). Precipitates were washed with dry ether and dried under vacuum at 40 °C for 4 h.

2.5. Cross-linking reaction

Cross-linking of the linear unsaturated PDFS precursor with vinyl monomers such as MMA or styrene led to the formation of a variety of products that are either flexible/rigid plastics or viscous oils. The procedure is as follows: known amounts of the PDFS precursor were mixed with different proportions of styrene or MMA, using benzoyl peroxide as an initiator and heated for 1 h at 100 °C to obtain the final product. Cross-linking reactions reached completion, when the mole fraction of the vinyl monomer was nearly equal to the mole fraction of the double bonds of the fumarate present in the chain of the PDFS precursor. Cross-linking reaction of the block copolymer P(DFS-*co*-EG) by MMA or styrene yielded elastomeric products apparently due to the presence of the PEG block in the copolymer. A thin film of PDFS cross-linked with styrene was placed in benzene for 48 h at 25 °C. The weight of thin film did not change after it was dried

under vacuum at 40 °C for 8 h, indicating the absence of any styrene homopolymer in the sample. Since the cross-linked samples were insoluble, no attempts were made in their further characterization (their melting points were above 290 °C and would degrade upon further heating).

3. Results and discussion

3.1. Molecular characterization

Silicon readily expands its valence shell, a property that allows the organosilicon compounds to undergo nucleophilic substitution more easily than their carbon analogues, even with weak nucleophiles (like the hydroxyl oxygen in carboxylic acids) under mild conditions. Thus, we have used dimethyldichlorosilane as a coupling agent for FA and SA dicarboxylic acids to produce the PDFS precursor. The PDFS is an active linear unsaturated oligomer with two dimethylchlorosilyl end groups that readily react with diols under mild conditions to produce polymers of higher molecular weights. Table 1 shows the monomer composition, reaction conditions, and the average molecular weights of PDFS precursor and the P(DFS-*co*-EG) copolymers obtained. The PDFS is a transparent viscous liquid that is insoluble in water, but their block copolymers with PEG emulsify therein. As expected the solubility of the copolymers in water rises with the increase in the weight percent of the PEG in copolymers.

Fig. 1 shows the ¹H NMR spectra of the PDFS (in deuterated benzene), where four types of CH₃ protons belonging to the coupling agent (DMCS) can be seen. The methyl groups of dimethylchlorosilyl in the PDFS precursor chain appear as a small peak at $\delta = 0.55$ ppm, while the other three CH₃ protons that belong to the central dimethylsilyl unit appear at (a) $\delta = 0.86$ ppm, when it is located between two fumarate units, (b) $\delta = 0.82$ ppm, when it is between a fumarate and a sebacate unit, and (c) $\delta = 0.76$ ppm, when it is between two sebacate units. The area under peak belonging to central dimethylsilyl units shows that about 50% of the coupling agent (DMCS) connect the fumarate and sebacate units, about 30% join two sebacate units and about 20% join two fumarate units. The

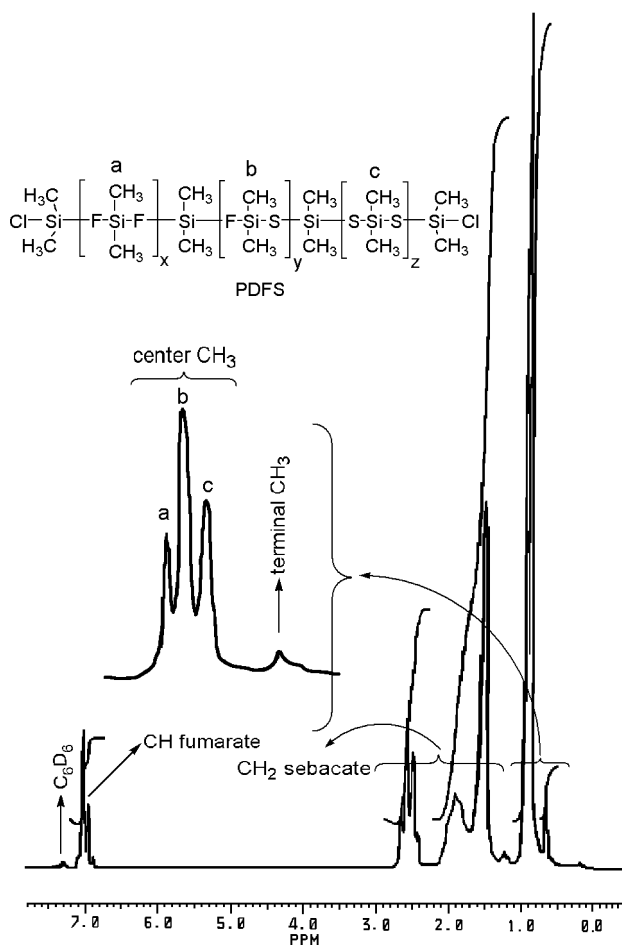


Fig. 1. ^1H NMR spectra of PDFS in C_6D_6 .

CH_2 protons of sebacate appear at 1.4–2.5 ppm and that of the CH protons of fumarate appear at 6.9–7.1 ppm.

Fig. 2 shows the ^{13}C NMR spectra of the PDFS precursor where four types of carbons for the coupling agent, DMCS, is observed. Sebacate carbons appear at 25, 26, 36 ppm and those of fumarate at 132–136 ppm. The carbonyl groups of fumarate and sebacate are seen at 164 and 173 ppm, respectively. ^1H NMR spectra of copolymer 2, Fig. 3, was obtained in water-free deuterated dimethylsulfoxide. The

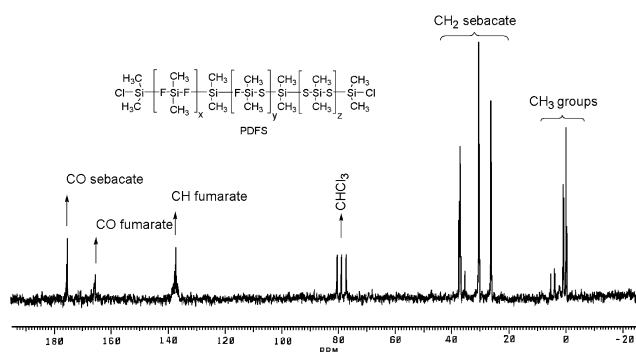


Fig. 2. ^{13}C NMR spectra of PDFS in CDCl_3 .

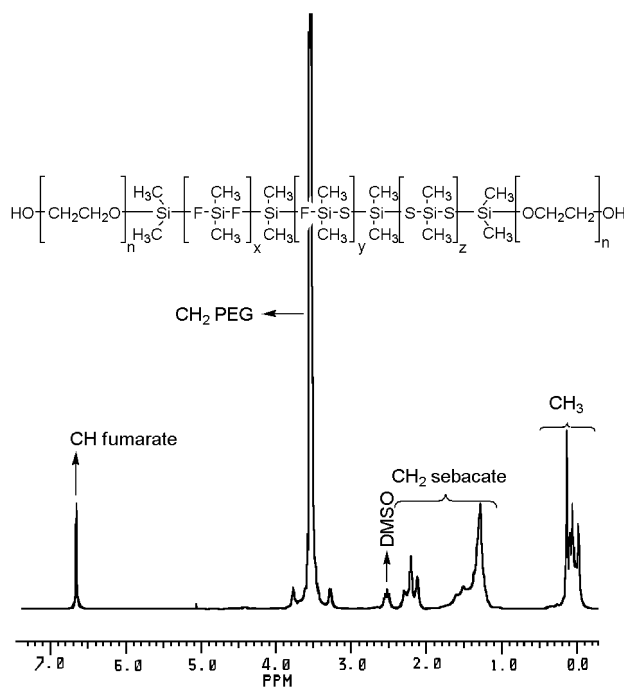


Fig. 3. ^1H NMR spectra of copolymer 2 in deuterated dimethylsulfoxide.

sharp peak at $\delta = 3.6$ ppm corresponds to CH_2 protons belonging to PEG that is reconfirmed by the peak at $\delta = 68$ ppm in the ^{13}C NMR spectra of the copolymer. Fig. 4 shows the ^{13}C NMR spectra of copolymer 2. The area under peak corresponding to the PEG protons is about fourfold that of the CH_2 protons of sebacate in copolymer 2.

The FT-IR spectra of the PDFS and the copolymer 1 are seen in Fig. 5, where in (a) a broad between 3200 and 2600 cm^{-1} includes the regions belonging to the fumarate double bond (3000–3200 cm^{-1}) and the aliphatic CH_2 stretching bond (3000–2800 and 2600 cm^{-1}). A strong relatively broad peak at 1707 cm^{-1} corresponds to the carbonyl groups belonging to sebacate and fumarate units, and the peak at 1265 cm^{-1} belonging to the silylene groups, whereas in (b) a broad stretching band at 1109 cm^{-1} corresponds to the C–O groups of the PEG block in copolymer 2 is seen, and the peaks at 1275, 1030 and 1090 cm^{-1} correspond to dimethylsiloxane groups joining the diacyls to the PEG in the copolymer [16].

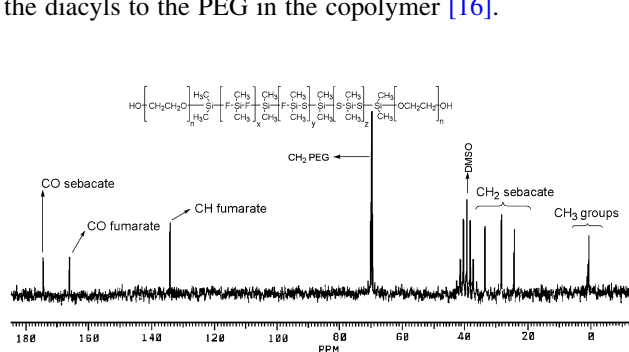


Fig. 4. ^{13}C NMR spectra of copolymer 2 in deuterated dimethylsulfoxide.

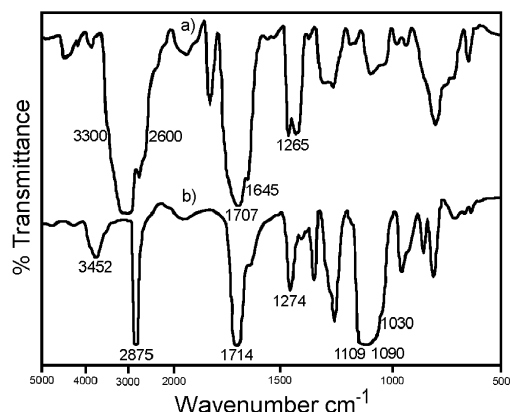


Fig. 5. FT-IR spectra of (a) PDFS precursor and (b) copolymer **1** showing the frequencies several important peaks.

3.2. Thermal analysis

Fig. 6 shows the DSC thermogram of the PDFS precursor and the copolymers **1–3** in the range 30–300 °C, while being heated at a constant heating rate of 10 °C/min. The DSC thermogram of the PDFS precursor shows an exothermic process, which starts at about 80 °C and slowly increases until 300 °C, indicating the detachment and evaporation of the terminal dimethylchlorosilyl groups from the polymer chains leading to an increase in molecular weight. Copolymers **1–3** do not exhibit this exothermic process. The DSC thermogram of the copolymer **1** shows an endothermic peak at about 50 °C corresponding to the melting point of the PEG block and a small wide exothermic peak at about 175 °C due to partial degradation of the PEG.

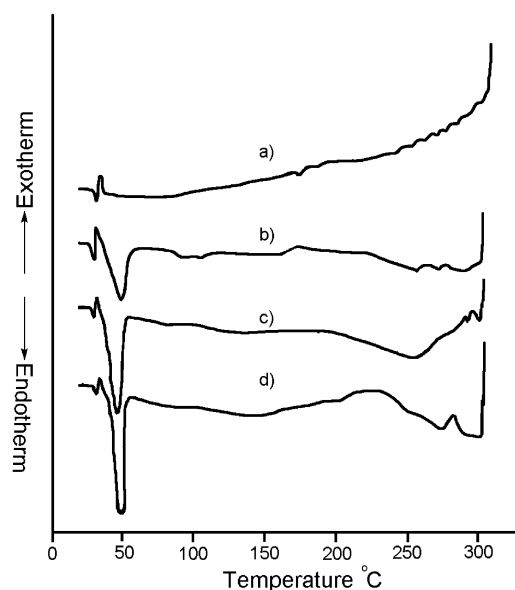


Fig. 6. DSC thermograms of (a) PDFS precursor, (b) copolymer **1**, (c) copolymer **2**, and (d) copolymer **3** in the range 30–300 °C, at a constant heating rate of 10 °C/min.

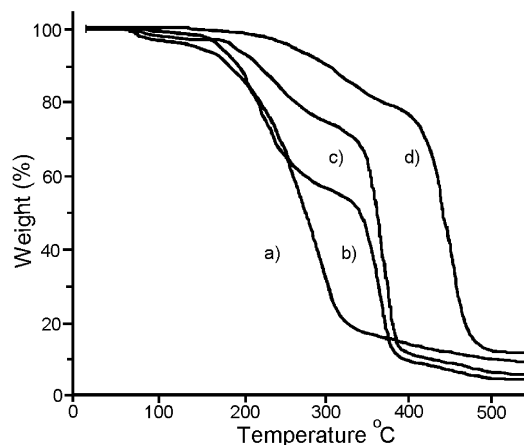


Fig. 7. TGA diagrams of (a) PDFS precursor, (b) copolymer **1**, (c) copolymer **2**, and (d) copolymer **3** in the range 25–550 °C, at a constant heating rate of 10 °C/min.

The endothermic peak for the melting point of the PEG block in copolymers **1–3** becomes sharper and more intense, as the percentage of the PEG in the copolymer increases. Copolymers **1–3** show a wide endothermic peak at about 251, 262 and 278 °C, respectively, that tends to become sharper and shifts to the right, as the weight percent of the PEG in the copolymer increases.

The TGA thermograms of the PDFS precursor and copolymers **1–3** were recorded at a temperature scan rate of 10 °C/min, Fig. 7. The TGA of PDFS shows that about 4% of weight loss occurs in the range 80–160 °C, due to detachment of terminal dimethylchlorosilyl groups. Most of the weight loss (78%) occurs in the range 160–360 °C. It is expected that the center dimethylsilyl units are first to detach and after that fumarate and sebacate units are, respectively, released from the polymer chain. In the range 360–550 °C, another weight loss of about 14% is observed. It is clear that the thermal stability of the block copolymers is higher than that of the PDFS precursor. Thermal stability of the copolymers **1–3** increases as the weight percent of PEG in the copolymer rises, which may be attributed to the presence of heteroatoms in the PEG blocks. In copolymer **1**, about 45% of the weight loss occurs in the range 280–320 °C and about 54% in the range 320–420 °C, whereas in the case of thermally more stable copolymer **3**, about 21% of the weight loss takes place in the range 280–320 °C and about 73% in the range 320–420 °C [17].

3.3. Hydrolytic degradation

For this purpose 1 g of copolymer **2** was stirred in 20 ml of distilled water at 37 °C for 28-day. At different time intervals, 2 ml of the medium was removed and centrifuged for 15 min at 7000 × g, and the precipitate was dried and its ¹H NMR and FT-IR spectra were obtained. Fig. 8 shows hydrolytic degradation of copolymer **2**. The ratio of the sebacate CH₂ protons to the dimethylsilyl protons in the

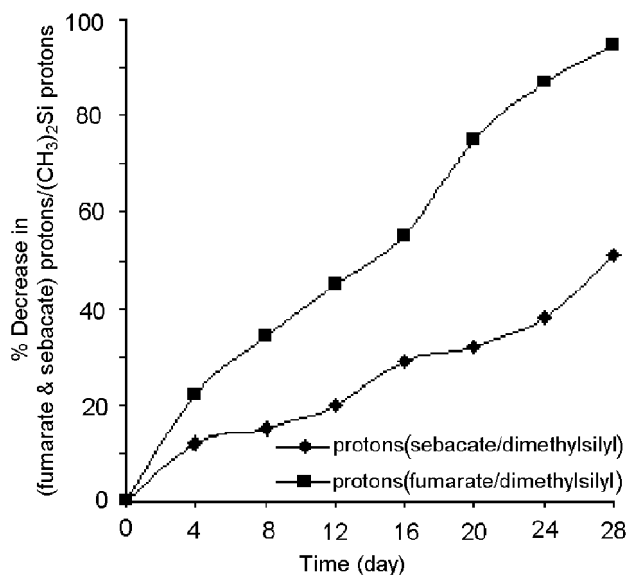


Fig. 8. Hydrolytic degradation of copolymer 2.

copolymer chain decreases about 50% after 28-day, whereas the ratio of the fumarate CH protons to dimethylsilyl protons decreases about 95%, indicating that fumarate units are detached faster than sebacate. Throughout the hydrolytic degradation of copolymer 2, the dimethylsilyl units that connect the fumarate and sebacate's units leave the copolymer chain.

4. Conclusions

The PDFS with active dimethylchlorosilyl terminal groups has been synthesized by polycondensation of fumaric and sebacic acid with the aid of dimethyldichlorosilane. PDFS and PEG have been used to prepare P(DFS-*co*-EG) block copolymer. Each of the compounds, PDFS or P(DFS-*co*-EG), has been cross-linked with a vinyl monomer like methyl methacrylate or styrene. Products thus obtained are investigated in terms of molecular weight, composition, structure and thermal properties by GPC, DSC, TGA, NMR and FT-IR spectroscopies. Hydrolytic degradation of copolymer 2 in aqueous media (pH 7.3, 37 °C) shows that the ratio of the sebacate CH₂ protons to the dimethylsilyl protons decreases about 50% after 28-day, whereas the ratio of the fumarate CH protons to the dimethylsilyl protons decreases by about 95%, indicating that fumarate units are detached faster than sebacate's.

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