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Design and Lipase Catalyzed Synthesis of 4-Methylcoumarin-siloxane Hybrid Copolymers

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Poly dimethylsiloxanes with amino end groups were copolymerized with diesters of 4-methylcoumarins enzymatically using a lipase (*Candida antarctica* lipase) as a biocatalyst. In a separate synthesis, 4-methylcoumarin was also incorporated into the poly siloxanes-isophthalate copolymers by functionalization of hydroxyl groups in the isophthalate moiety. The synthesis and characterization of two sets of novel copolymers are presented. The thermal and flammability properties of these polymers have also been studied using TGA and microcalorimetry, respectively.

Keywords: Chemo-enzymatic, polysiloxanes, 4-methylcoumarin, Novozyme-435, *candida antarctica* lipase B, flame retardant.

1. Introduction

Extending our strategy (1–7) to obtain new classes of polymeric materials with even wider applications, efforts were made to biocatalytically join siloxane oligomers with 4-methylcoumarin diesters **4a–b** using a lipase. The depicted naturally derived 4-methylcoumarin diesters were combined covalently with polysiloxane oligomers to explore the flame-retardant properties of these new materials. Lipases in organic synthesis have several advantages, such as superior catalytic power, high selectivity under mild conditions with regard to temperature, pressure, and pH, and give high substrate conversion efficiency, high diastereo-, regio-, and chemoselectivity. These features allow the generation of functional compounds and materials employing non-toxic natural catalysts with "green appeal". Additional advantages include catalyst recyclability and use in bulk reaction media to avoid organic solvents.

Therefore, lipase was used to incorporate 4-methylcoumarin diesters with different siloxane oligomers to give a variety of novel polymeric materials (Schemes 1 and 2). These novel polymeric materials possess a unique molecular architecture which can be explored as potential substitutes for conventional flame retardant materials owing to their exceptional thermal stability and low flammability. These features provide high flexibility and the ability to preserve physical properties over a wide range of temperature. Such polymers were challenging because of their physical and chemical differences from their organic counterparts. They allow for a unique combination of traditionally well recognized features of coumarins with polysiloxanes. The flame retardant properties of these novel materials were evaluated and found to be interesting. These polymers would not produce any toxic substances upon combustion and just produce water, carbon dioxide and cyclic siloxane analogue. The coumarin derived polymers exhibited fluorescence which allows exploration of newer applications of these materials. In this paper, we present synthesis, characterization, thermal and flammability properties of these coumarin-siloxane copolymers.

2. Experimental

2.1. *Materials*

Resorcinol, 2-methyl resorcinol, diethyl 2-acetylglutarate, ethyl bromoacetate, dimethyl 5-hydroxyisophthalate,

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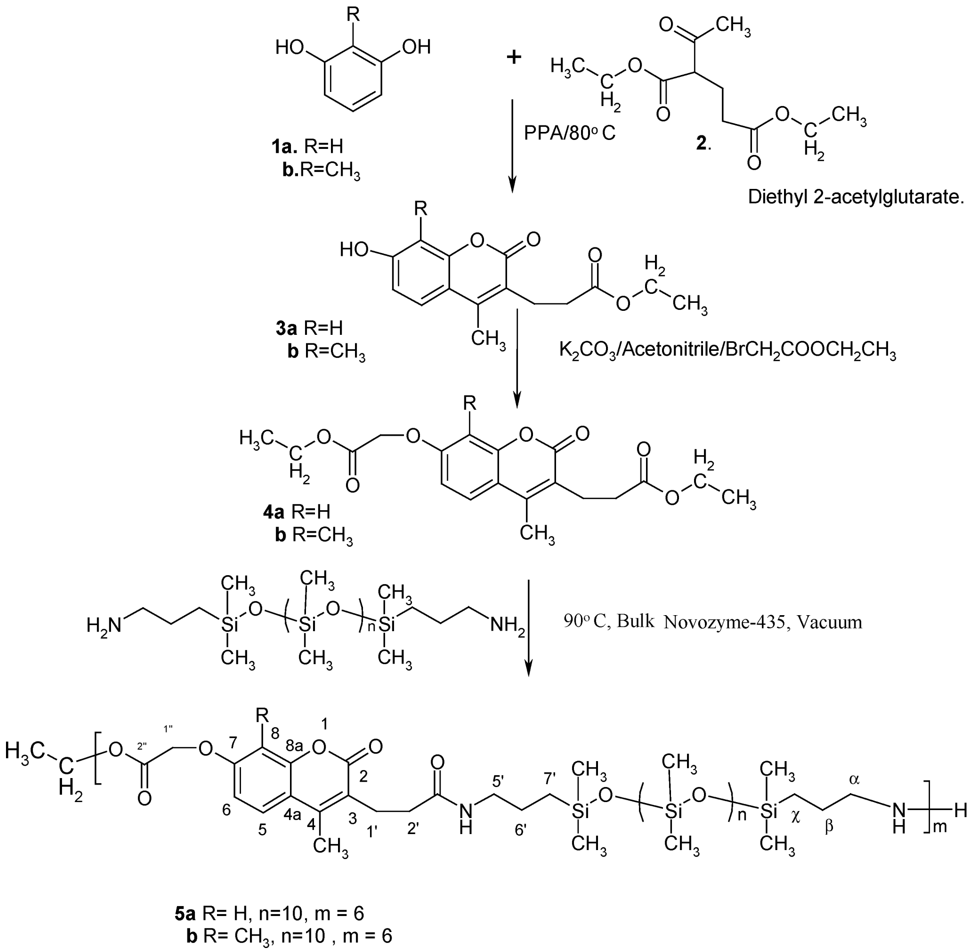


Sch. 1. Synthesis of polymers **5a–b**.

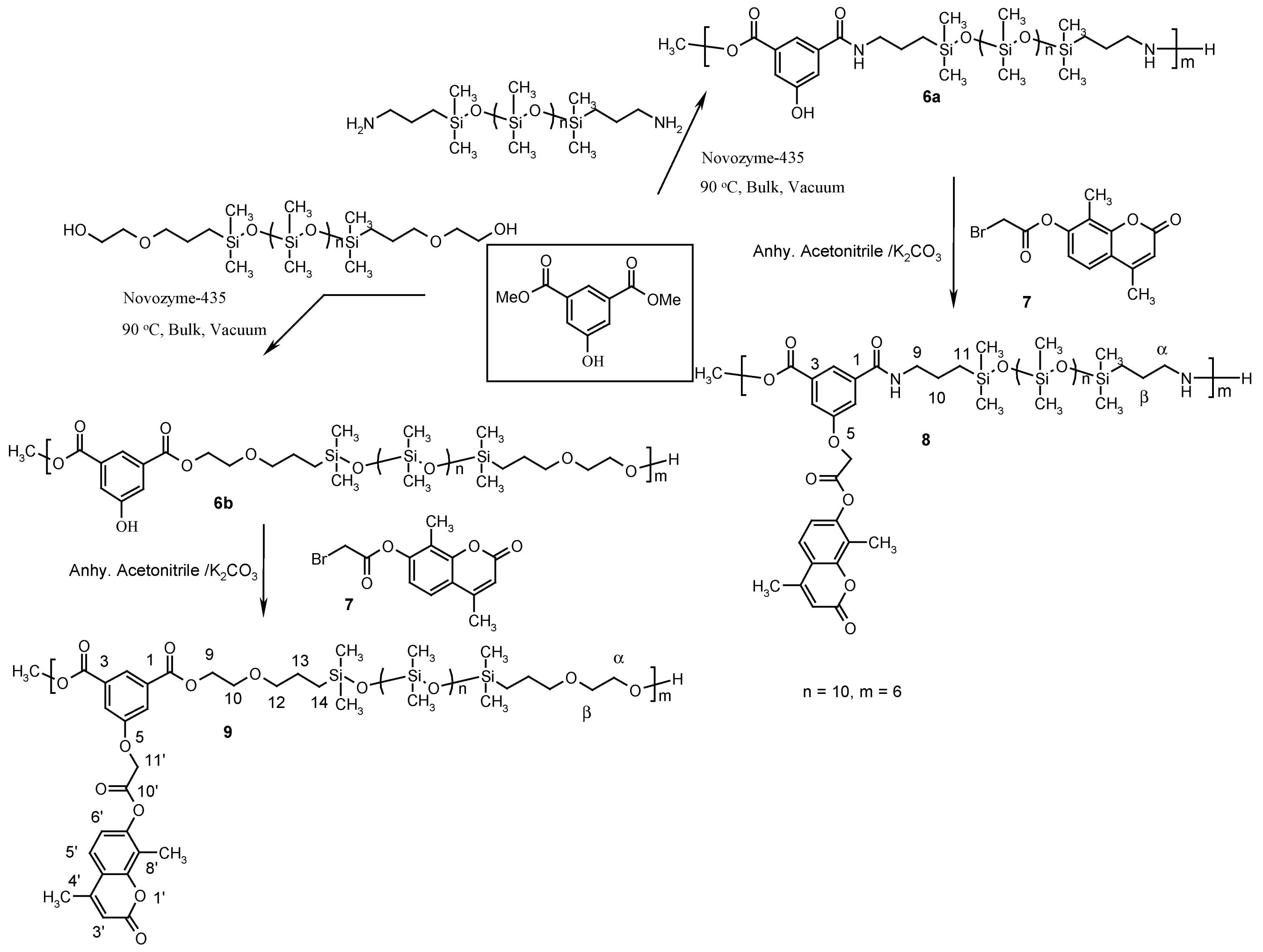
polyphosphoric acid (PPA), anhydrous potassium carbonate, and acetonitrile were purchased from Aldrich (Milwaukee, WI). Anhydrous potassium carbonate was fused overnight at 200°C before use, whereas carbinol (hydroxyl) terminated polydimethylsiloxane (Mn 1000) and aminopropyl terminated polydimethylsiloxane (Mn 900–1000) were purchased from Gelest Inc., USA. All other chemicals and solvents were of analytical grade and used without further purification. Novozyme 435, an immobilized enzyme, was a gift from the Novozymes, Inc., Denmark.

2.2. *Characterization*

Gel permeation chromatography (GPC) was used to determine the molecular weight and molecular weight distribution, Mw/Mn of polymers using THF as solvent and polystyrene as a standard. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Instrument Inc. DPX 500 spectrometer at 500 and 125 MHz, respectively using TMS as the internal standard. Infrared spectra were recorded from neat samples using Nicolet 4700 Fourier transform infrared (FT-IR) spectrometer. UV-visible spectra were recorded on an Agilent 8453 spectrophotometer.

2.3. *Thermal properties*

Thermal decomposition was studied in air using a TA Instruments 2050 thermogravimetric analyzer (TGA). Flammability was measured using a pyrolysis-combustion flow calorimeter (PCFC, FAA microcalorimeter) (4). In this apparatus, a sample of 2–5 mg is pyrolyzed at 1°C/s from approximately 100 to a maximum of 900°C. A metered flow of N_2 sweeps the pyrolysis gases into a mixing volume with O_2 such that the N_2/O_2 mixture would have approximately the composition of atmospheric air. The mixture is oxidized at 900°C to completion in a flow-tube reactor, H_2O and CO_2 products are removed, and the O_2 depletion is measured continuously as a function of time. The heat release rate is calculated from the consumption rate of O_2. The total heat release and the heat-release capacity reported is the average of three measurements of each sample. The heat release capacity (J/g-K) reported is the ratio of peak heat release rate (W/g) to the heating rate (°C/s).



Sch. 2. Synthesis of polymers **8** and **9**.

2.4. *Polymer synthesis*

The coumarin diesters **4a–b** and aminopropyl terminated polydimethylsiloxane (Mn 900–1000) were placed in a round-bottom flask and stirred to get a homogeneous mixture followed by the addition of enzyme (Novozyme 435, 10% by weight *wrt* monomers). The resultant reaction mixture was stirred at 90°C under vacuum (100 millitorr) for 48 h, after which the reaction was quenched by adding chloroform and filtering off the enzyme under vacuum. The filtrate was concentrated to get the polymers **5a–b**. The synthesis and spectroscopic characterization of compounds **3a–b** and **4a–b** and, polymers **6a–b** have already been reported (3, 6).

2.5. *Polymer 5a*

Synthesis of polymer (**5a**) was achieved via mixing the coumarin diester (**4a**, 5.00 g, 13.81 mmol), aminopropyl terminated polydimethylsiloxane (Mn 900–1000, 13.81g, 13.81 mmol), and Novozyme-435 (1.88 g) following the general procedure.

^{1}H-NMR (δ_H CDCl$_3$, 500 MHz): 0.08–0.20 (brs, methyl protons of dimethyl siloxane main chain), 0.55 (t, 4H, $CH_2 \times 2$, *H*-7′& *H*-γ main chain), 1.13 (t, 3H, OCH_2CH_3, end group), 1.50 (m, 4H, $CH_2 \times 2$, *H*-6′ & *H*-β), 1.55 (brs, 2H, NH_2, end group D_2O exchangable), 2.47 (s, 3H, CH_3 at C-4 carbon of coumarin), 2.70 (t, 2H, *H*-α end group), 2.98 (t, 2H, CH_2, *H*-1′), 3.21 (t, 2H, *H*-2′), 3.36 (t, 4H, $CH_2 \times 2$, *H*-5′ and *H*-α), 4.12 (q, 2H, OCH_2CH_3 end group), 4.58 (s, 2H, *H*-1″), 6.58 (brs, 1H, amidic N*H*, D_2O exchangable), 6.79 (brs, 1H, *H*-6), 6.91 (s, 1H, *H*-8), 7.58 (brs, 1H, *H*-5).

^{13}C-NMR (δc, CDCl$_3$, 125 MHz); 0.50–1.41(carbons of dimethyl siloxane main chain), 14.5 (OCH_2CH_3, end group), 15.4 (CH_2), 15.6 (CH_2), 23.6 (CH_2), 23.9 (CH_2), 32.9 (CH_3), 42.9 ($CONHCH_2$), 60.9 (OCH_2 end group), 67.9 (*C*−1″), 102.8 (*C*H), 112.2 (*C*H), 115.7 (q), 123.1 (q), 126.6 (*C*H), 147.8 (q), 154.0 (q), 160.8 (q), 163.8 (q), 166.8 (*C*ONH), 172.4 (>*C*=O).

IR νmax: 3294, 2961, 1709, 1662, 1617, 1549, 1387, 1256, 1162, 1010, 787, 701, 598, 521 cm^{-1}

UV λ_{max}(MeOH): 320, 268 nm.

M$_n$(GPC) 7980 Da, PD = 1.6, isolated yield 76%

2.6. *Polymer 5b*

The synthesis of polymer (**5b**) was achieved via reaction between the coumarin diester (**4b**, 5.00 g, 13.29 mmol), aminopropyl terminated polydimethylsiloxane (Mn 900–1000, 13.29 g, 13.29 mmol), and Novozyme-435 (1.82 g) following the general procedure.

^{1}H-NMR (δ_HCDCl$_3$, 500 MHz): 0.09–0.20 (brs, methyl protons of dimethyl siloxane main chain,), 0.55 (t, 4H, (CH_2×2, H-7′ & H-γ main chain), 1.13 (t, 3H, OCH$_2$CH_3, end group), 1.50 (m, 4H, CH$_2$ × 2, H-6′ and H-β), 1.56 (brs, 2H, NH_2, end group D$_2$O exchangable), 2.38 (s, 3H, CH_3 at C-8 carbon of coumarin), 2.45 (s, 3H, CH_3 at C-4 carbon of coumarin), 2.66 (t, 2H, H-α end group), 2.98 (t, 2H, CH$_2$, H-1′), 3.21 (t, 2H, H-2′), 3.37 (t, 4H, CH$_2$×2, H-5′ & H-α), 4.13 (q, 2H, OCH_2CH$_3$ end group), 4.58 (s, 2H, H-1″), 6.58 (brs, 1H, amidic NH, D$_2$O exchangable), 6.80 (brs, 1H, H-6), 7.58 (brs, 1H, H-5).

^{13}C-NMR (δc, CDCl$_3$, 125 MHz); 0.50–1.40 (carbons of dimethyl siloxane main chain), 8.84 (CH$_3$), 14.5 (OCH$_2$$CH_3$, end group), 15.4 ($CH_2$), 15.7 ($CH_2$), 23.6 ($CH_2$), 23.9 ($CH_2$), 33.0 ($CH_3$), 42.9 (CONH$CH_2$), 60.8 (O$CH_2$ end group), 68.4 (C-1″), 108.0 (CH), 114.2 (q), 115.8 (q), 123.5 (q), 127.0 (CH), 147.9 (q), 151.7 (q), 157.4 (q), 162.2 (q), 167.8 (CONH), 172.3 (>C=O).

IR ν_{max}: 3294, 2961, 1703, 1661, 1604, 1555, 1440, 1356, 1256, 1010, 787, 700, 598, 529 cm^{-1}

UV λ_{max}(MeOH): 320, 268 nm.

M$_n$(GPC) 8064 Da, PD = 1.6, Isolated yield 76%

2.7. *General Procedure for Coupling of 4-Methylcoumarins*

Equimolar quantities of **6a–b** were dissolved in anhydrous acetonitrile and anhydrous potassium carbonate was added under nitrogen, followed by the addition of 4-methylcoumarin bromo acetyl ester **7** dissolved in anhydrous acetonitrile. The reaction mixture was refluxed and the progress of the reaction was monitored by TLC. After completion of the reaction, potassium carbonate was removed by filtration, and the solvent was removed under vacuum to get the polymers **8–9**.

2.8. *Polymer 8*

Polymer **8** was achieved via refluxing 4-methylcoumarin bromo acetyl ester (**7**, 0373 g, 1.2 mmol), anhydrous potassium carbonate (0.50 g, 3.65 mmol) and polymer **6a** (1.45 g, 1.21 mmol) at 80°C under nitrogen.

^{1}H-NMR (δ_HCDCl$_3$, 500 MHz): 0.10–0.20 (brs, methyl protons of dimethyl siloxane main chain), 0.61 (t, 4H, CH$_2$x2, H-11 & H-γ main chain), 1.40 (m, 4H, CH$_2$×2, H-10 and H-β), 1.65 (brs, 2H, NH_2, end group D$_2$O exchangable), 2.28 (s, 3H, CH_3 at C-8 carbon of coumarin), 2.47 (s, 3H, CH_3 at C-4 carbon of coumarin), 2.70 (t, 2H, H-α end group), 3.36 (t, 4H, CH$_2$×2, H-9 and H-α), 3.91 (s, 3H, OCH_3 end group), 4.68 (s, 2H, H-11′), 6.09 (s, 1H, H-3′), 6.60 (brs, 1H, amidic NH, H-8, D$_2$O exchangable), 7.19 (brs, 1H, H-6′), 7.58 (brs, 1H, H-5′), 7.70 (brs, 2H, H-4 and 6), 7.94 (brs, 1H, H-2).

^{13}C-NMR (δc, CDCl$_3$, 125MHz); 0.50–1.40 (carbons of dimethyl siloxane main chain), 8.54 (CH$_3$), 15.4 (CH$_2$), 19.07 (CH$_3$), 26.2 (CH$_2$), 42.9 (CONHCH$_2$), 51.7 (OCH$_3$ end group), 68.3 (OCH$_2$CO, C-11′), 108.9 (CH), 114.2 (CH), 115.8 (q), 118.51 (CH), 120.47 (CH), 122.7 (CH), 123.5 (q), 127.0 (CH), 132.3 (q), 136.3 (q), 147.9 (q), 151.7 (q), 157.0 (q), 157.4 (q), 162.2 (q), 166.2 (CONH), 166.2 (COOCH$_3$end group),172.3 (>C=O, C-10′).

IR ν_{max}: 3204, 2960, 1703, 1661, 1600, 1572, 1434, 1361, 1305, 1257, 1012, 858, 791, 759, 705, 598, 563, 529 cm^{-1}

UV λ_{max}(MeOH): 320 nm

2.9. *Polymer 9*

Polymer **9** was achieved via refluxing 4-methylcoumarin bromo acetyl ester (**7**, 0.373 g 1.20 mmol), anhydrous potassium carbonate (0.50 g, 3.65 mmol) and polymer **6b** (1.45 g, 1.20 mmol) at 80°C under nitrogen.

^{1}H-NMR (δ_HCDCl$_3$, 500 MHz): 0.10–0.21 (brs, methyl protons of dimethyl siloxane main chain), 0.60 (t, 4H, CH$_2$×2, H-14), 1.60 (m, 4H, CH$_2$×2, H-13), 2.33 (s, 3H, CH$_3$ at C-8′ carbon of coumarin), 2.45 (s, 3H, CH_3 at C-4′ carbon of coumarin), 3.45 (t, 2H, H-α end group), 3.54 (t, 4H, CH$_2$×2, H-12), 3.82 (t, 4H, CH$_2$×2, H-10), 3.91 (s, 3H, OCH_3 end group), 4.54 (t, 4H, CH$_2$×2, H-9), 4.68 (s, 2H, H-11′), 6.12 (s, 1H, H-3′), 7.19 (brs, 1H, H-6′), 7.48 (brs, 1H, H-5′), 7.71 (brs, 2H, H-4 and 6), 8.04 (brs, 1H, H-2).

Table 1. Flammability properties of the polymers **5a–b** and **8–9** from PCFC measurements

Polymer	Heat Release Capacity(J/g K)	Total Heat Release (KJ/g)	Char Yield (%)
5a	220	21	5.7
5b	242	23	4.1
8	242	16	9.4
9	264	17	7.1

Table 2. Decomposition temperatures (°C) of the polymers **5a–b** and **8–9** from TGA in air

Polymer	Decomposition Temp at 10 wt% loss (°C)	Decomposition Temp at 50 wt% loss (°C)
5a	318	410
5b	360	425
8	387	405
9	305	402

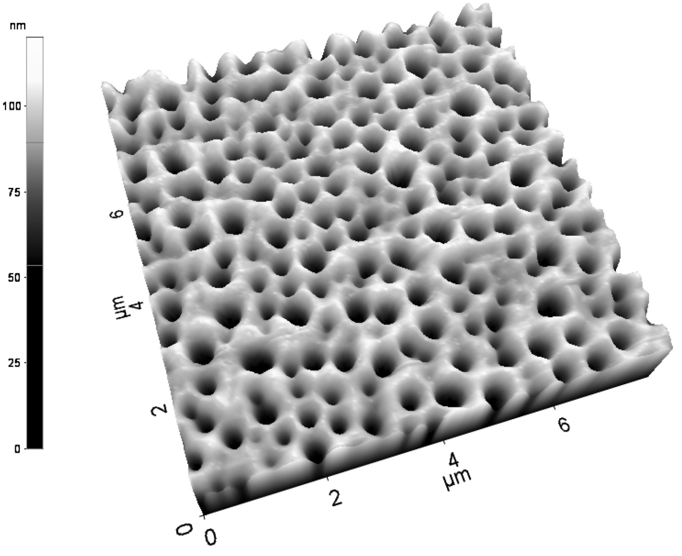


Fig. 1. 3-D topographical AFM image of spin coated polymer **5b** film.

^{13}C-NMR (δc CDCl$_3$, 125 MHz); 0.50–1.40 (carbons of dimethyl siloxane main chain), 8.6 (CH_3), 15.1 (CH_2), 19.01 (CH_3), 26.2 (CH_2), 51.7 (OCH_3 end group), 62.9 (OCH_2), 63.8(OCH_2), 67.9 (OCH_2CO, C-11′), 73.6 (OCH_2), 108.6 (CH), 114.7 (CH), 116.0 (q), 118.7 (CH), 120.7 (CH), 122.7 (CH), 123.4 (q), 127.2 (CH), 132.4 (q), 136.5 (q), 147.9 (q), 151.6 (q), 157.1 (q), 157.3 (q), 162.1 (q), 166.4 (CO), 166.2 (COOCH$_3$end group),172.3 ($>C$=O, C-10′).

IR υ_{max}: 3201, 2960, 1723, 1703, 1603, 1577, 1572, 1434, 1384, 1331, 1257, 1011, 859, 788, 757, 703, 599, 543, 529 cm^{-1}

UV λ_{max}(MeOH): 314 nm

3. Results and discussion

We have designed the synthetic strategy in such a way as to combine the properties of naturally derived 4-methylcoumarins and the known flame retardant dimethylsiloxanes to get novel polymeric materials. In this approach, well known antioxidant 4-methyl coumarin diesters **4a–b** have been synthesized and used for polymerization with poly dimethylsiloxanes using lipase as a catalyst in bulk. The resulting novel polymers **5a–b** have been characterized on the basis of their proton NMR which showed a triplet at δ 3.36–3.37 (4H, CH$_2\times$2 H-5′ and H-α) due to the formation of amidic bond between 4-methylcoumarin diesters **4a–b** and polydimethylsiloxanes. Further, the presence of a broad peak at δ 6.58 (brs, 1H, amidic NH) was D$_2$O exchangable. Formation of the amidic bond was also supported by the peak at δ 166.8–167.8 due to amidic carbonyl in its ^{13}C-NMR spectrum. The obtained polymeric materials **5a–b** showed molecular weight of 7980 and 8064 Da, respectively as determined by GPC using polystyrene as a standard.

4-Methylcoumarin has also been tethered with the polymers **6a–b** to evaluate its effect on their flame retardant properties. Coupling of the bromo analogue of 4-methylcoumarin (**7**) with polymer **6a–b** was carried out with anhydrous potassium carbonate in acetonitrile. The synthesis of the bromo analogue of 4-methylcoumarin (**7**) was carried out by stirring of bromo acetic anhydride with 7-hydroxy-4-methylcoumarin in anhydrous dichloromethane.

The coupled product was characterized by NMR spectroscopy which showed a peak at δ 4.68 (s, 2H, H-11′) due to O-alkylation of phenolic hydroxyl with the 4-methylcoumarin. It was further supported by the presence of peaks at δ 68.3 (OCH_2CO, C-11′), and 67.9 (C-11′) for polymers **8** and **9**, respectively in the ^{13}C-NMR spectra.

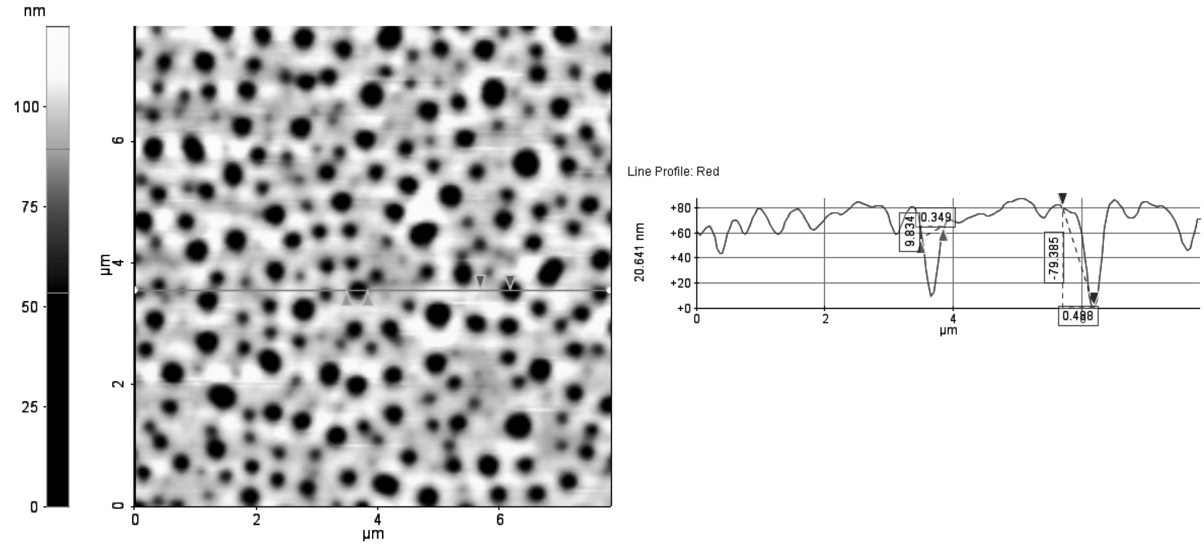


Fig. 2. AFM image of polymer **5b** showing a cross section of the film.

Flammability properties were measured by using a pyrolysis combustion flow calorimeter (PCFC). The results are shown in Table 1. The polymers with the 4-methylcoumarins in the backbone exhibited small differences in the thermal properties compared with those in which the 4-methylcoumarins were tethered to the backbone. The decomposition temperatures were also measured using thermogravimetric analyzer (TGA) and the results are shown in Table 2.

Morphology of polymer films was studied using atomic force microscopy (AFM). For this purpose, polymer films were fabricated by spin coating polymer solutions on to silicon substrates. AFM of the polymer films was carried out with a PSIA XE-100 instrument using silicon nitride tips with radii nominally less than 10 nm. A non contact mode of AFM was used to avoid any damage caused by the AFM tip to the delicate films of materials. An AFM micrograph of polymer **5b** is shown in Figures 1 and 2 as an example. It was observed that surface morphology did not change significantly with the structure of the coumarin linker in the polymers. As shown in the Figure 1, a uniform porous film was obtained, with sub-micron size pores.

4. Conclusions

In summary, four novel polysiloxanes-coumarin copolymers were synthesized and characterized. These copolymers were evaluated for their flame retardant properties which were found to be encouraging. The surface morphology of films of polymer **5a–b** were investigated using AFM and it was found that polymers **5a–b** form porous films. Applications of these polymers are currently being explored.

Acknowledgment

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References

1. Watterson, A.C., Parmar, V.S., Kumar, R., Sharma, S.K., Shakil, N.A., Tyagi, R., Sharma, A.K., Samuelson, L.A., Kumar, J., Nicolosi, R. and Shea, T. (2005) *Pure and Applied Chemistry*, 77, 201–08.
2. Tucci, Vincent B., Pandey, M.K., Tyagi, R., Parmar, V.S., Kumar, J. and Watterson, A. C. (2007) *Polymer Preprints*, 48(2), 276–277.
3. Kumar, R., Tyagi, R., Parmar, V.S., Samuelson, L.A., Kumar, J., Schoemann, A., Westmoreland, P.R. and Watterson, A.C. (2004) *Adv. Mater.,* 16, 1515–1520.
4. Mosurkal, R., Samuelson, L.A., Parmar, V.S., Kumar, J. and Watterson, A.C. (2007) *Macromolecules*, 40(22), 7742–7744.
5. Kumar, R., Shakil, N.A., Chen, Ming-H., Parmar, V.S., Samuelson, L.A., Kumar, J. and Watterson, A. C. (2002) *Journ. of Macr. Sci., Pure and Applied Chem.*, A39(10), 1137–1149.
6. Pandey, M.K., Tyagi, R., Tomar, S., Kumar, J., Parmar, V.S. and Watterson, A.C. (2007) *Journ. of Macr. Sci., Pure and Applied Chem*, 44(12), 1293–1298.
7. Kumar, R., Pandey, M.K., Tyagi, R., Parmar, V.S., Watterson, A.C. and Kumar, J. (2008) *Polymers for Biomedical Applications: ACS Symposium Series*, 977, 204–224.