

Synthesis and Characterization Studies of Novel Reactive Polymers

Soon P.C.¹, Xu L.G.² and Ng S.C.²

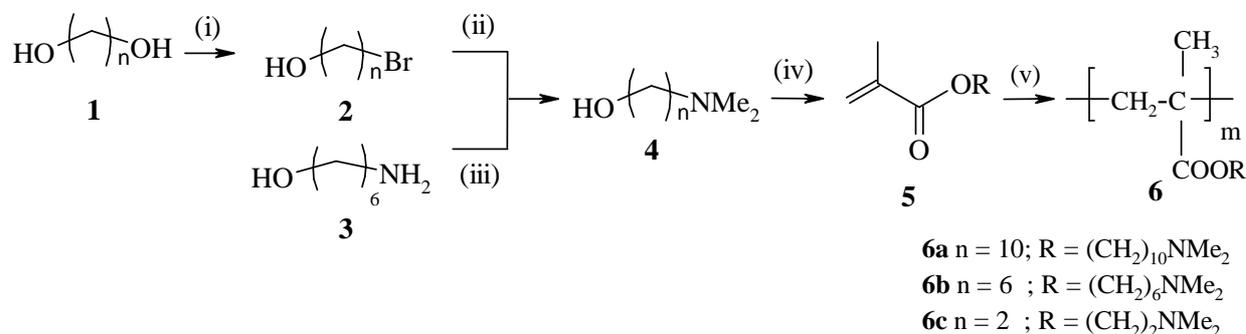
Department of Chemistry, Faculty of Science, National University of Singapore
3 Science Drive 3 Singapore 117543

ABSTRACT

In this project, novel polymers poly[n-(dimethylamino)alkyl 2-methacrylate] (n = 2, 6 and 10) with reactive pendants were synthesized and characterized by NMR, FTIR, elemental analysis (surface and bulk), SEM, TGA, MDSC and GPC.

MATERIALS AND METHODS

Synthesis of monomers and polymers



Scheme 1: Reagents and conditions - (i) HBr/Benzene; (ii) 2M HN(CH₃)₂/MeOH; (iii) HCOOH, HCHO; (iv) 2-methacryloyl chloride, pyridine, CH₂Cl₂; (v) AIBN/toluene

10-(dimethylamino)decyl 2-methacrylate 5a A suspension of 10-decanediol **1a** (200mmol) in benzene (400ml) was heated to keep benzene boiling. 48% hydrobromic solution (25ml) was added into the solution dropwise and the mixture was refluxed for 20 hours. The water generated was distilled off using the Dean Stark apparatus. Upon cooling, the mixture was washed with 6N sodium hydroxide solution (200ml), 10% hydrochloric acid (200ml), water (2 × 400ml) and brine (400ml). The organic layer was treated with anhydrous magnesium sulphate, filtered and solvent removed. Pure 10-bromodecan-1-ol **2a** (67%) was obtained after Kugelrohr distillation (Kang, 1985).

A solution of **2a** (10mmol) in 2M methanolic dimethylamine solution (20ml) was heated to 65°C for 24 hours and refluxed using water at 1°C. After methanol was removed, the remaining solution was rendered alkaline with 25% sodium hydroxide (20ml) and was extracted with chloroform. The chloroform extract was treated with anhydrous magnesium sulphate, filtered and chloroform was removed. Pure 10-(dimethylamino)decan-1-ol **4a** was obtained (70%) after column chromatography.

Anhydrous dichloromethane (50ml), pyridine (15ml) and methacryloyl chloride (100mmol) were added in order to **4a** (50mmol) at 0°C. The mixture was stirred under nitrogen for four

¹ UROPS student

² Supervisors

hours (Lowe, 1995). The workup for **5a** was similar to that for **4a** except that 10% sodium bicarbonate (70ml) was used in place of 25% sodium hydroxide. The pure monomer **5a** (63%) was obtained after column chromatography.

6-(dimethylamino)hexyl 2-methacrylate **5b** **5b** was synthesized in 60% yield via the same method as **5a**. The alternative route to prepare 6-(dimethylamino)hexan-1-ol **4b** using 6-amino-hexan-1-ol **3** is reported in Clarke et al (Clarke, 1933).

2-(dimethylamino)ethyl 2-methacrylate **5c** **5c** is commercially available. Alternatively, it could be prepared from 2-dimethylamino-ethanol **4c**.

Poly[10-(dimethylamino)decyl 2-methacrylate] **6a** A solution of **5a** (20mmol) and AIBN (0.25% mol) in anhydrous toluene (2ml) was heated to 40°C and stirred under nitrogen for two days to afford **6a**.

Poly[6-(dimethylamino)hexyl 2-methacrylate] **6b** **6b** was synthesized by the same method as **6a**.

Poly[2-(dimethylamino)ethyl 2-methacrylate] **6c** A solution of **5c** (20mmol) and AIBN (0.25% mol) in anhydrous toluene (2ml) was heated to 40°C and stirred under nitrogen for four days (Blacker, 2001) to afford **6c**.

RESULTS AND DISCUSSION

Synthesis of monomers and polymers

For **4b** and monomer **5b**, the crude product was also purified by distillation under reduced pressure to yield the colorless product (76 – 78°C/ 1mbar for **4b**; 81 – 85°C/ 0.4mbar for **5b**). The purity of all the prepared substrates was verified by ¹H NMR before proceeding to the subsequent steps.

For polymerization, we have experimented with monomers of concentration 0.5M, 10M and bulk polymerization. It was found that with less toluene used in the preparation of the polymer, the polymer formed tends to have a larger molecular weight and it becomes more insoluble in organic solvents; the optimum condition is to use 10M of monomers which then afford pale yellow polymers of reasonable molecular weights (table 2) and are soluble in THF. The polymers were analyzed using ¹H NMR, FTIR (table 1) and elemental analysis (table 2) and the results have proved the structures to be consistent with what was expected.

Table 1: FTIR absorptions for polymers **6a**, **6b** and **6c**

| Polymer | sp ³ C-H stretch | CH ₃ stretch (attached to N) | C=O stretch | sp ³ C-H bend | C-O-C stretch | C-N stretch |
|-----------|-----------------------------|---|-------------|--------------------------|---------------|-------------|
| 6a | 2929, 2856 | 2815, 2763 | 1730 | 1467, 1376 | 1270, 1041 | 1157 |
| 6b | 2940, 2862 | 2815, 2778 | 1730 | 1465, 1390 | 1267, 1064 | 1152 |
| 6c | 2973 | 2826, 2773 | 1732 | 1460, 1398 | 1271, 1063 | 1151 |

Elemental composition of surface and surface texture

For polymers **6b** and **6c**, the ratio of oxygen content was higher than expected (table 2). This was due to surface oxidation which increased the oxygen content on the surface. Under SEM, the morphology of the polymers was observed to have a creased texture (figure 1, next page).

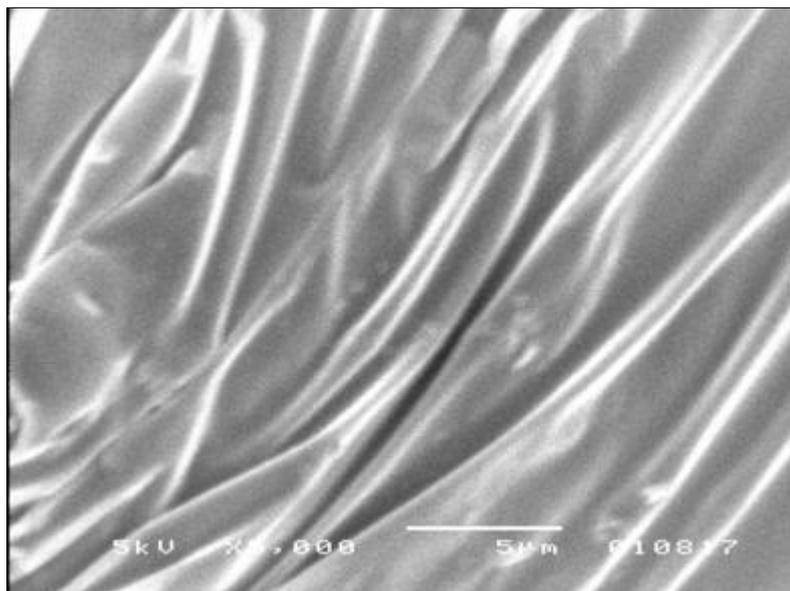


Figure 1: SEM image of poly[6-(dimethylamino)hexyl 2-methacrylate] **6b**

Table 2: Summarised experimental data for polymers **6b** and **6c**

| Polymer | Molecular weight | | Elemental analysis | | |
|-----------|------------------|----------------|--|---------------------------------------|--------------------------------------|
| | M _n | M _w | Calculated | Bulk | Surface (XPS) |
| 6b | 32 152 | 51 378 | C ₁₂ H ₂₃ O ₂ N | C _{11.6} H _{22.6} N | C _{12.7} O _{3.0} N |
| 6c | 25 613 | 34 921 | C ₈ H ₁₅ O ₂ N | C _{8.2} H _{15.9} N | C _{7.6} O _{2.2} N |

Glass transition temperature (T_g)

The glass transition temperatures were initially determined by conventional DSC but reproducible and reliable results were difficult to obtain. Therefore modulated differential scanning calorimetry (MDSC), which is more sensitive, was used in this project instead.

Currently, only the T_g of **6c** (14.6°C) has been assigned due to certain experimental difficulties for **6a** and **6b** and time constraints. However since polymers poly[n-(dimethylamino)alkyl 2-methacrylate] can be regarded as analogs of poly(n-alkyl methacrylates), we can estimate the transition temperatures for **6a** and **6b** to be lower than **6c**: a trend of decreasing T_g with increasing length of side-chains is expected (Rogers, 1957).

Thermal stability of polymers

From figure 2 (next page), it is evident that the polymers decomposed in two major steps: degradation of side-chains followed by decomposition of polymer backbone. From the DTG curves, a multi-step profile observed for the degradation of side-chains suggests that the process is stepwise and starts with small fragments (-CH₃) before the disintegration of the entire side-chain. The onset of decomposition was the earliest for **6a** and the latest for **6c**. Thus the relative thermal stability of the polymers was observed to decrease with the increasing length in side chains.

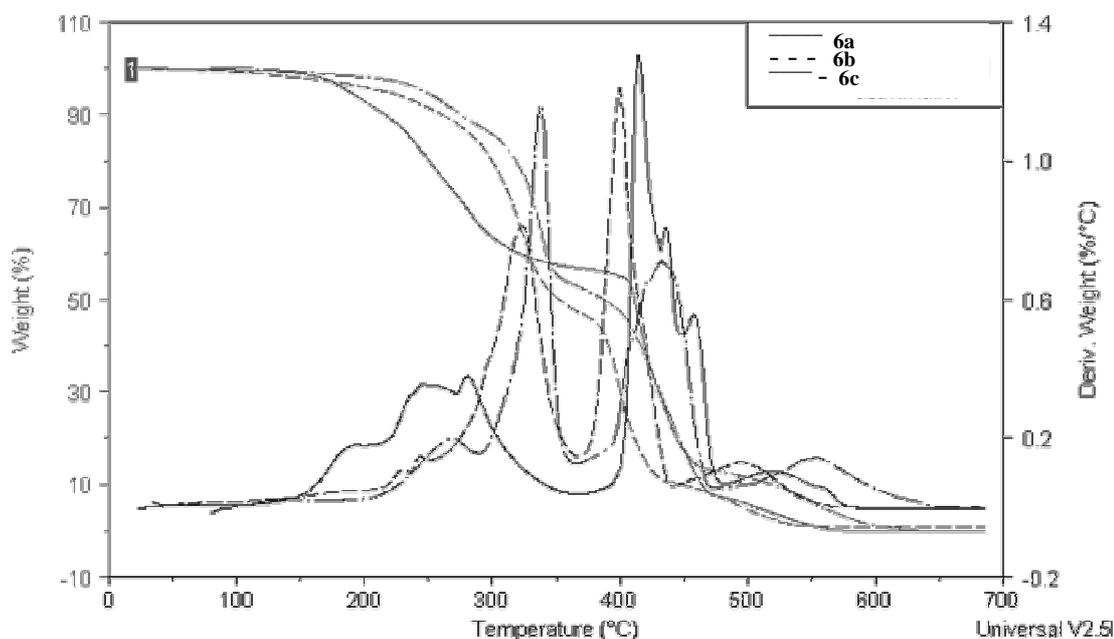


Figure 2: TG and DTG curves for **6a**, **6b** and **6c**

CONCLUSION

The polymers poly[n-(dimethylamino)alkyl 2-methacrylate] were successfully synthesized and their structures have proven to be consistent as expected through NMR, FTIR and elemental analysis. Other characterization studies are still underway.

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