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## Synthesis and Characterization of Poly(dimethyl siloxane)–Poly[alkyl (meth)acrylic acid] Block Copolymers

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**ABSTRACT:** Block copolymers containing dimethyl siloxane and carboxylic acid sequences were synthesized by group transfer polymerization (GTP) of various methacrylates and acrylates using silyl ketene acetal terminated poly(dimethylsiloxane) (PDMS) as initiator, followed by hydrolysis of the ester sequences to the free acid. The block copolymers were obtained with controlled molecular weight and narrow molecular weight distribution. The *tert*-butyl methacrylate (tBMA) and trimethyl silyl methacrylate (TMSMA) polymerized more slowly than corresponding acrylates. *tert*-Butyl and trimethyl silyl ester groups in the poly(meth)acrylate block could be quantitatively hydrolyzed. Most copolymers were contaminated by unincorporated homo-PDMS, which was efficiently removed by hexane or supercritical CO<sub>2</sub> extraction. The solubility and thermal properties (DSC, TGA) were investigated for the hydrolyzed amphiphilic polymers.

### Introduction

Copolymers containing poly(dimethylsiloxane) (PDMS) have received considerable attention due to their unique properties, such as very low glass transition temperature, low surface energy, low solubility parameter, and physiological inertness.<sup>1</sup> Some of their specialty applications are in the fields of biomaterials<sup>2</sup> and surfactants.<sup>3</sup>

Though a variety of synthetic routes have been used to prepare PDMS containing copolymers, less work has been done preparing block copolymers of dimethyl siloxane and  $\alpha,\beta$ -unsaturated esters.<sup>4</sup> This is mainly attributed to the limited copolymerizabilities of both monomers in anionic polymerization.<sup>5</sup> Recently, PDMS-*b*-PMMA copolymers were prepared via a transformation synthesis in which an anionic ring opening polymerization is converted to GTP.<sup>6</sup> Although the content of PDMS incorporated in the block copolymer was low due to the loss of initiator efficiency, this approach opens up a new method for PDMS based block copolymers.

In this article, we report the synthesis of well-defined PDMS–poly[alkyl (meth)acrylate] block copolymers with

comparatively high conversion and the selective hydrolysis of the ester alkyl group to yield a novel PDMS–poly[(meth)acrylic acid] block copolymer.

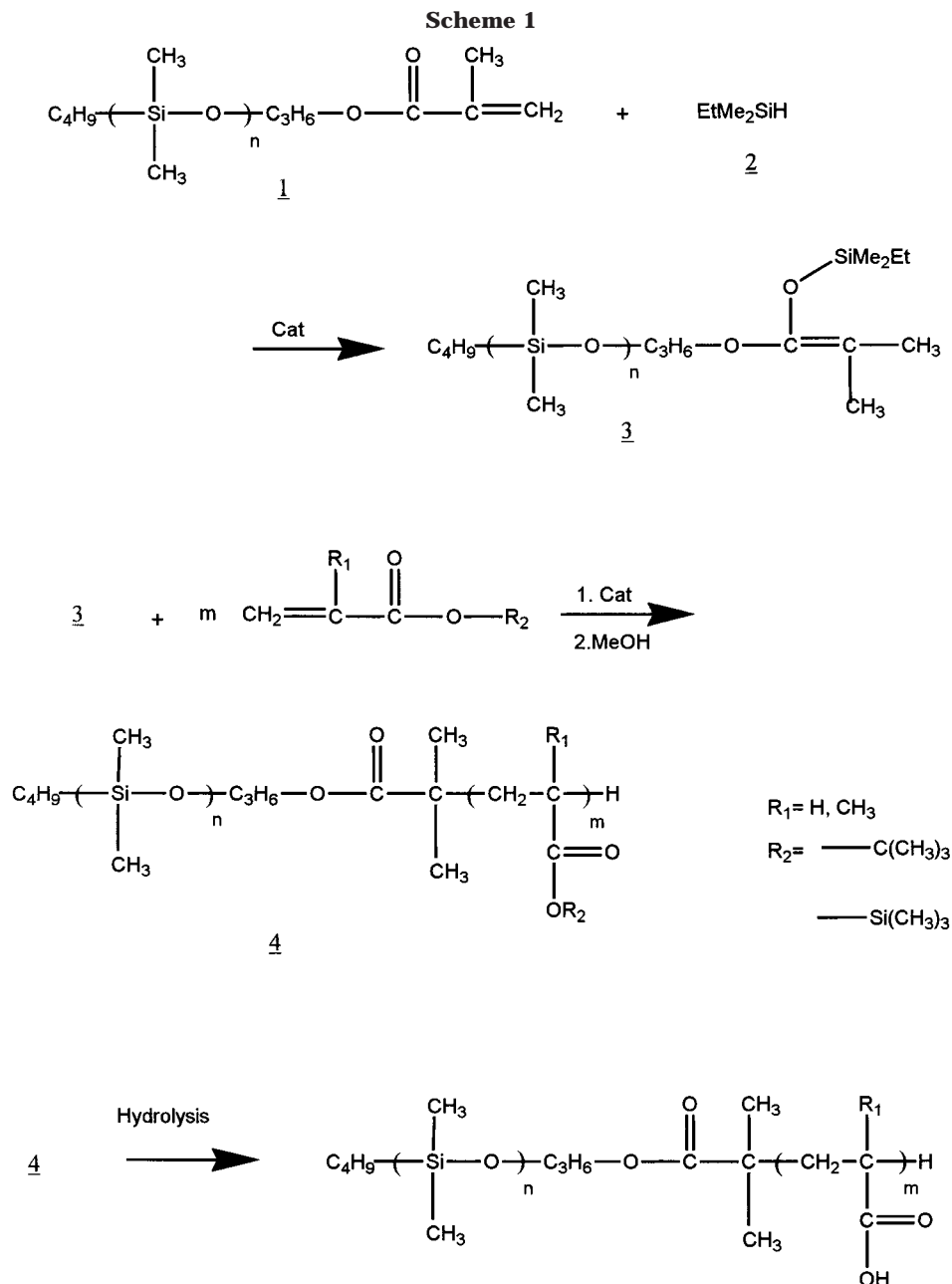
### Experimental Section

**Materials.** Tetrahydrofuran (THF) was distilled from sodium naphthalide under reduced pressure prior to use. Methyl methacrylate (MMA) (Aldrich), *tert*-butyl methacrylate (tBMA) (Polysciences), *tert*-butyl acrylate (tBA) (Polysciences), and trimethylsilyl methacrylate (TMSMA) (Aldrich) were first distilled from CaH<sub>2</sub>, followed by distillation from triethyl aluminum.<sup>7</sup>

The GTP catalyst, tetrabutylammonium bibenzoate (TBABB) was synthesized according to the procedure in the literature.<sup>8</sup> Poly(dimethyl siloxane) monomethacrylate ( $M_n = 10K$  from Aldrich;  $M_n = 5K$  from Gelest) was degassed under high vacuum for 2 days before using. Ethyl dimethylsilane (United), acrylic acid (Aldrich), *N,N*-dimethylaniline (Aldrich), Trimethylsilyl chloride ((TMS)Cl) (Aldrich) and tris(triphenylphosphine)rhodium(I) chloride (Wilkinson catalyst) (Aldrich) were used as received. Carbon dioxide (Praxair instrument grade, 99.99%, <15 ppm oxygen) was used without further purification.

**Preparation of GTP Macroinitiator.** The GTP macroinitiator, silyl ketene acetal functional PDMS was prepared by reacting poly(dimethylsiloxane) monomethacrylate with a slight molar excess of ethyl dimethylsilane for 2 h at 55 °C in

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the presence of Wilkinson catalyst (Scheme 1).<sup>6</sup> Excess ethyl dimethylsilane was thoroughly removed by stripping under vacuum.

**Preparation of Trimethylsilyl Acrylate (TMSA).** This monomer was synthesized by a base-catalyzed reaction. In a 250 mL three-neck flask equipped with a nitrogen inlet were placed 14.5 g (0.2 mol) of acrylic acid and 26 g (0.24 mol) of (TMS)Cl at 0 °C. After 5 min, 38.5 g (0.32 mol) of *N,N*-dimethylaniline was added by syringe. The ice bath was then removed and the mixture was stirred at room temperature for 2 h. After the precipitate was filtered off, the mixture was fractionally distilled twice (yield 18 g, 62 %). It was normally stored over calcium hydride at -20 °C.

**Polymerization.** The group transfer polymerization was carried out under argon atmosphere in a previously flamed glass reactor. A typical example is as follows: 6.5 g ( $6.5 \times 10^{-4}$  mol) of dried macroinitiator was introduced into the reactor. Then 20 mL of THF and 6.5 mg of TBABB (2 mol % based on silyl ketene acetal functionality) were transferred into the reactor by means of a cannula. After 5 min of stirring, 3 g of tBMA was added slowly via syringe and the polymerization proceeded for 2 h under argon. The polymerization was quenched with degassed methanol (2 mL). After an additional

half hour of stirring, the THF and methanol were removed by evaporation. The polymer collected was dried at  $10^{-3}$  Torr for 24 h.

**Hydrolysis of PDMS-*b*-PtBMA. *p*-Toluenesulfonic Acid Method.**<sup>9</sup> The block copolymer was dissolved in dioxane (5 wt %) and *p*-toluenesulfonic acid was added (5 mol % relative to the PtBMA content). After being stirring for 12 h at 100 °C, the reaction mixture was concentrated by evaporating the dioxane. The hydrolyzed polymer was then precipitated into water/methanol (90/10) mixture, filtered and dried.

**NaI/(TMS)Cl Method.**<sup>10</sup> In a two-neck flask with a nitrogen inlet tube, the block copolymer was dissolved in the acetonitrile-chloroform (2:1 v/v) mixture (5 wt %). To this solution was added a 4 times molar excess (relative to the PtBMA) of sodium iodide and (TMS)Cl, in that order, and the mixture was stirred at room temperature for 3 h under N<sub>2</sub> atmosphere. The solvents and excess (TMS)Cl were removed under reduced pressure. The residue obtained was dissolved in THF (20 mL) and precipitated into 1% aqueous sodium thiosulfate/methanol (90/10) mixture, filtered, and dried.

**Hydrolysis of PDMS-*b*-PTMSMA.** About 2 g of polymer was suspended in 30 mL of 5% aqueous sodium hydroxide and the solution was stirred for 12 h at room temperature. After

Table 1. Synthesis of PDMS-*b*-Poly(meth)Acrylate

expt no.	monomer	$M_n$ of PDMS macroinitiator ( $\times 10^{-3}$ )	wt % of PDMS		GPC <sup>b</sup>		% conversion of monomer <sup>c</sup> (g)
			charged	incorp <sup>a</sup>	$M_n$ ( $\times 10^{-3}$ )	$M_w/M_n$	
1	MMA	10	72	73 (55)	27.3 (29.6)	1.28 (1.21)	94 (0.48)
2	MMA	5	55	54 (37)	13.5 (1.18)	1.26 (1.18)	100 (0.51)
3	tBMA	10	68	81	14.4	1.23	48
4	tBMA	5	50	64	9.3	1.22	60
5	TMSMA	5	66	71 (58) <sup>d</sup>	8.8 <sup>f</sup>	1.15f	78 (0.53)
6	tBA	10	62	60	29.4	1.35	95
7	TMSA	10	79	81 (69) <sup>d</sup>	14.2 <sup>f</sup>	1.20f	91 (0.43)
8	TMSA	10	63	67 (34) <sup>e</sup>	24.3 <sup>f</sup>	1.32 <sup>f</sup>	82

<sup>a</sup> Determined by <sup>1</sup>H NMR, the numbers in parentheses are for the block copolymer after hexane extraction. <sup>b</sup> Based on polystyrene standards. The numbers in parentheses are for the block copolymer after hexane extraction. <sup>c</sup> Calculated as the wt % of recovered product. <sup>d</sup> Separated from unincorporated PDMS after hydrolysis by hexane extraction. <sup>e</sup> Separated from unincorporated PDMS by fractionation with supercritical CO<sub>2</sub>. <sup>f</sup> Measured after methylation of carboxylic group of separated block copolymer. <sup>g</sup> PDMS in block copolymer/PDMS in feed (macroinitiator efficiency).

the pH of the solution was adjusted to 5 with hydrochloric acid, the hydrolyzed polymer was filtered, washed with water, and dried.

**Characterization.** Size exclusion chromatography (SEC) was carried out with a Waters GPC 510 apparatus equipped with three 5 mm cross-linked PS columns (linear mix, 500 and 100 Å, American Polymer Standards Co.) with THF as the eluent. Eight standard polystyrene samples with molecular weights between 300 and 400,000 were used to construct the calibration curve. The detector signal for all elution curves returned to the baseline, so there was no ambiguity concerning the range of integration for molecular weight analysis.

The glass transition temperature of polymers was measured by a Perkin-Elmer DSC 7. Samples were first heated to 200 °C, cooled to room temperature, and then scanned again at a rate of 20 °C/min. Thermal degradation of polymers was investigated by Perkin-Elmer TGA 7. The sample was heated to 800 °C at a rate of 20 °C/min under nitrogen.

The composition and degree of hydrolysis were determined by <sup>1</sup>H NMR using a Varian Unity Plus-300. Determination of the degree of both hydrolysis and neutralization can also be achieved by titration with 0.1 N KOH/MeOH in THF solution using phenolphthalein as an indicator. Methacrylate functionality of PDMS was determined by <sup>29</sup>Si NMR (Bruker AMX-500) in 0.04 M chromium(III) acetyl acetonate solution in CDCl<sub>3</sub>.<sup>11</sup>

IR spectra were recorded on a Nicolet Avatar 360 F-TIR.

## Results and Discussion

**Characterization of Methacryloxy-Functionalized PDMS.** The number average molecular weight ( $M_n$ ) of commercial 10K-PDMS and 5K-PDMS was measured as 11000 and 5000 by GPC using polystyrene as standard, respectively. The polydispersities were 1.18 (10K-PDMS) and 1.16 (5K-PDMS). Both PDMS macromers were confirmed to have almost quantitative functionality by comparing the integration of silicone adjacent to the methacryloxy functional fragment (7.3 ppm) with the silicone adjacent to the terminal butyl fragment (7.5 ppm) in <sup>29</sup>Si NMR.<sup>6</sup>

**Preparation of Macroinitiator.** The methacryloxy functional end group was transformed into a silyl ketene acetal (**3**) in the presence of Wilkinson catalyst (Scheme 1). Confirmation of the quantitative hydrosilylation of PDMS chain end was followed by proton NMR and FT-IR. As the hydrosilylation proceeds, a shift in the carbonyl band (1725 cm<sup>-1</sup>) is observed upon *o*-silylation of the carbonyl oxygen (1705 cm<sup>-1</sup>). A weak absorption band at 1740 cm<sup>-1</sup> also appeared, which is attributed to the hydrolysis of the silyl ketene acetal moiety. This species is estimated to be less than 5 mol % by <sup>1</sup>H NMR and may have resulted from moisture or protonic impurities in the PDMS.<sup>6</sup>

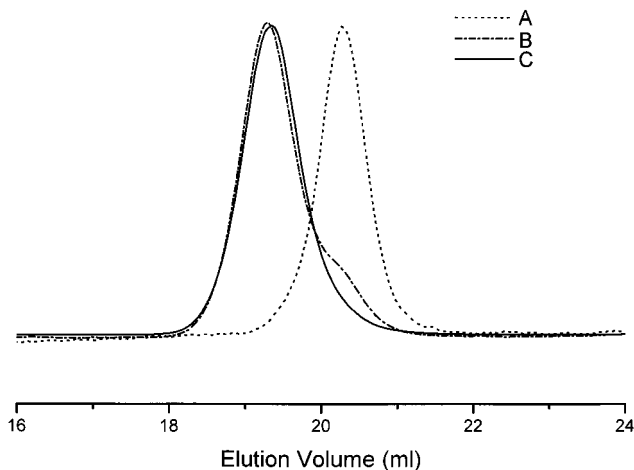


Figure 1. GPC trace of sample 1 and macroinitiator. (C) PDMS-*b*-PMMA,  $M_n = 29\,600$ ,  $M_w/M_n = 1.21$ , after extraction (see text); (B) PDMS-*b*-PMMA,  $M_n = 27\,300$ ,  $M_w/M_n = 1.28$ , before extraction; (A) 10K-PDMS macroinitiator.

**Polymerization.** The GTP proceeded successfully by introducing (meth)acrylate to the silyl ketene acetal functionalized PDMS (**3**) to give well-defined block copolymers with controlled molecular weight and narrow molecular weight distribution (Scheme 1). For PDMS-*b*-PMMA, PDMS-*b*-PtBA, and PDMS-*b*-PTMSA, the conversions of (meth)acrylate monomers to polymer were found to be almost quantitative (Table 1). Therefore, block polymers of PDMS and (meth)acrylates containing sequences of various lengths could be prepared simply by varying the ratio of monomer to macroinitiator charged in the polymerization. However, the bulky monomers of tBMA and TMSMA did not polymerize completely even after prolonged reaction time. The <sup>1</sup>H NMR of the distilled solvent after polymerization indicated a trace of unreacted monomer. The incomplete reaction may be due to early termination of the macroinitiator (see below) and the slow initiation and propagation rate of the sterically hindered ethyl dimethyl silyloxy end of PDMS macroinitiator. With acrylate monomer, the yield increased appreciably, and the molecular weight distribution was slightly broader than obtained for the corresponding methacrylates. This is consistent with higher reactivity of acrylate compared to methacrylate in GTP.<sup>12</sup> The weight percent of PDMS incorporated was less than theoretically predicted. This is probably a result of early termination of the macroinitiator by traces of moisture or protonic impurities. The unincorporated homo-PDMS was simply removed by successive hexane extraction from the PDMS-*b*-

Table 2. Hydrolysis of Block Copolymer

expt no.	block polymer	hydrolysis method	time (h)	temp (°C)	degree of hydrolysis (%) <sup>a</sup>
1	PDMS <sub>10K</sub> - <i>b</i> -PtBMA <sub>1.1K</sub>	<i>p</i> -toluene sulfonic acid	15	110	90
2	PDMS <sub>10K</sub> - <i>b</i> -PtBMA <sub>1.1K</sub>	NaI/Me <sub>3</sub> SiCl	3	25	85
3	PDMS <sub>10K</sub> - <i>b</i> -PtBA <sub>6.7K</sub>	<i>p</i> -toluene sulfonic acid	15	110	93
4	PDMS <sub>10K</sub> - <i>b</i> -PtBA <sub>6.7K</sub>	NaI/Me <sub>3</sub> SiCl	3	25	89
5	PDMS <sub>5K</sub> - <i>b</i> -PTMSMA <sub>2K</sub>	NaOH (5% aq soln)	12	25	100

<sup>a</sup> Determined by <sup>1</sup>H NMR.

PMMA copolymer (Figure 1). For other block copolymers of (meth)acrylates, however, this separation was not possible due to similar solubility behavior of both blocks. In this case, separation could be carried out effectively after hydrolysis of (meth)acrylate block to (meth)acrylic acid block. Supercritical carbon dioxide extraction of homo-PDMS from the nonhydrolyzed product was also used successfully. The polymer sample was placed in a high-pressure variable volume view cell.<sup>13</sup> CO<sub>2</sub> was bubbled through the sample via a dip tube. The upper CO<sub>2</sub> solution phase was vented into a vial in order to trap the soluble polymer. The extraction was conducted at 4000 psia and 50 °C. An ISCO computer controlled syringe pump (model 100DX) was used to maintain constant pressure during extraction. Six successive extracts were collected by the same procedure with the same amount of CO<sub>2</sub>. Because PDMS is much more soluble than the poly[(meth)acrylate] in CO<sub>2</sub>,<sup>14</sup> the first three extracts contained very little block copolymer and next three extracts were a mixture of homo-PDMS and block copolymer. After six extracts were removed, the CO<sub>2</sub> was depressurized and the residue was collected. After hydrolysis of the residue, no homo-PDMS could be removed by hexane extraction so we conclude that the residue is pure block copolymer.

**Hydrolysis.** Block copolymers containing carboxylic acid sequence were prepared by the hydrolysis of the esters of PtBMA, PtBA, PTMSMA, and PTMSA (Table 2). The hydrolysis of the ester of PDMS-*b*-PtBMA and PDMS-*b*-PtBA was carried out under mild conditions using a *p*-toluenesulfonic acid-catalyzed reaction. The resulting polymer was methylated by diazomethane for GPC analysis. The *tert*-butyl ester group was found to be more than 90% hydrolyzed from <sup>1</sup>H NMR. The peak of *tert*-butyl proton at 1.2 ppm disappeared, and a new methyl proton appeared at 3.5 ppm following methylation of the carboxylic acid. Under this hydrolysis condition, the molecular weight of block copolymers decreased and polydispersity increased (Figure 2), which is the result of the acid-catalyzed redistribution reaction in the PDMS block.<sup>3</sup> This chain breaking of PDMS was also observed in hydrolysis of homo-PDMS under the same reaction condition. Another mild hydrolysis method using NaI/SiMe<sub>3</sub>Cl<sup>10</sup> was employed. It was found that the PDMS block remained intact under this reaction condition with more than 80% hydrolysis of *tert*-butyl ester group. The hydrolysis of the trimethylsilyl methacrylate sequence of PDMS-*b*-PTMSMA was carried out in basic media at room temperature. Complete hydrolysis was confirmed by the absence of a Si-CH<sub>3</sub> peak in <sup>1</sup>H NMR (0.2 ppm). In the case of PDMS-*b*-PTMSA, hydrolysis was complete after exposure to the air for 1 week.

**Properties of PDMS-*b*-PAA.** The solubility behavior of typical PDMS-*b*-PAA copolymers was investigated with several solvents. The block copolymer was soluble in polar solvents such as THF, DMF, and dioxane and was insoluble in aromatic and aliphatic hydrocarbons.

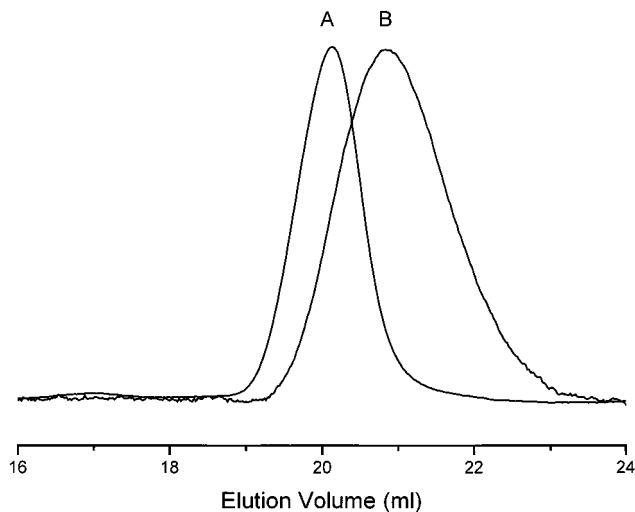


Figure 2. GPC trace of sample 3 (Table 1) and sample 1 (Table 2): (A) PDMS-*b*-PtBMA,  $M_n = 14\,400$ ,  $M_w/M_n = 1.23$ , before hydrolysis; (B) PDMS-*b*-PAA,  $M_n = 6500$ ,  $M_w/M_n = 1.62$ , after hydrolysis.

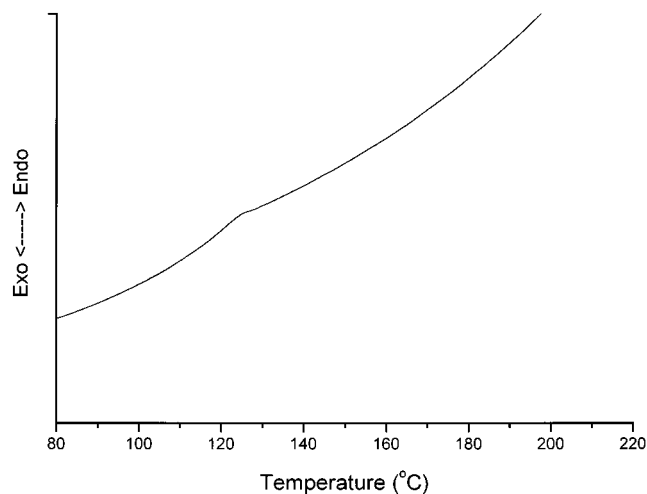
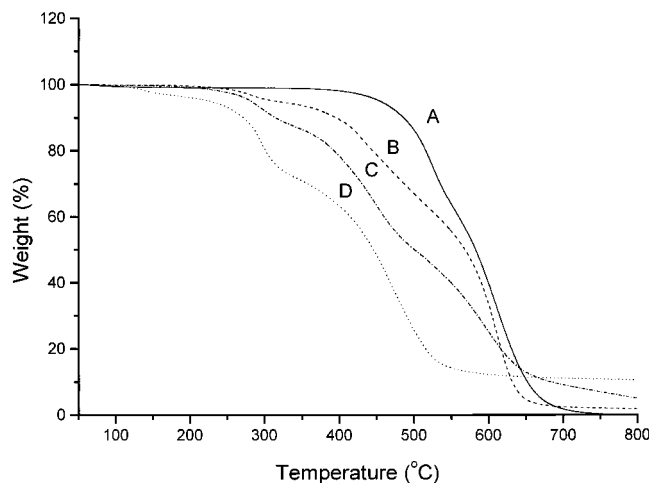


Figure 3. DSC analysis of sample 8 (Table 1) after hydrolysis: PDMS (10K)-*b*-PAA (10.2K).

When the copolymer was dissolved in methanol, which is a nonsolvent for PDMS but a good solvent for PAA, the mixture was almost clear with an iridescent bluish tinge indicative of small colloidal particles. The PDMS (10K)-*b*-PAA (10.2K) copolymer made a fairly stable dispersion in neutral water.

Figure 3 shows the DSC trace of PDMS (10K)-*b*-PAA (10.2K). The small transition at 124 °C can be attributed to the  $T_g$  of poly(acrylic acid) block.<sup>15</sup> A comparison of TGA analysis of the PDMS-*b*-PAA block copolymers with those of each homopolymer shows that the 2% and 6% weight loss at 250 °C corresponds to the dehydration of the acrylic acid block sequence with concurrent polyanhydride formation (Figure 4). The other large breaks at 360 and at 450 °C on the TGA curve result from degradation of the PAA and PDMS backbone,



**Figure 4.** TGA thermogram of polymers: (A) PDMS (10K) homopolymer; (B) PDMS (10K)-*b*-PAA (1.5K); (C) PDMS (10K)-*b*-PAA (10.2K); (D) PAA (22K) homopolymer.

respectively. The observed amount of weight loss is in good agreement with the amount calculated from the acrylic acid content in the block copolymers.

### Summary

Well-defined PDMS-poly[alkyl (meth)acrylate] block copolymers were synthesized by GTP using silyl ketene acetal terminated PDMS as initiator.

Unreacted homo-PDMS was efficiently removed from block copolymer by hexane or supercritical carbon dioxide extraction. The esters of PtBMA, PtBA, PTMSMA, and PTMSA were almost quantitatively hydrolyzed into corresponding acids to give a novel amphiphilic polymer of PDMS-*b*-PMA and PDMS-*b*-PAA. We are currently investigating the role that these block copolymers play in stabilizing dispersion polymerizations in CO<sub>2</sub>.<sup>16</sup>

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