

## Preparation of thermally labile PMMA particles by combined non-aqueous dispersion polymerization and polymer chain transfer

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We report the controlled synthesis of micrometre-sized thermally labile PMMA particles. This was achieved by a combination of dispersion polymerization and chain transfer techniques. The dispersion polymerization allows for the synthesis of spherical micrometre-size particles of PMMA, whereas the use of cobalt chain transfer agents results in vinylidene end-functionalized PMMA. Furthermore, the vinylic end-groups facilitate thermal depolymerization and this consequently limits the thermal stability. We anticipate that these PMMA particles could further serve as useful modifiers to generate porous polymers, including siloxane elastomers. © 1997 Elsevier Science Ltd. All rights reserved.

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### Introduction

Dispersion polymerization is a heterogeneous technique used to polymerize vinylic monomers in an organic diluent, in the presence of an amphipathic graft or block copolymer, to form an insoluble polymer. The graft or block copolymer, commonly called a stabilizer, lends colloidal stability to the insoluble polymer. Dispersion polymerizations are characterized by the solubility of both the monomer and the initiator in the continuous phase and the insolubility of the resulting polymer. The presence of the stabilizer allows the polymerization to proceed to a higher degree than is possible in the analogous precipitation polymerization. In addition, dispersion polymerization results in spherical particles typically ranging in size from 100 nm to 10  $\mu\text{m}$ <sup>1–5</sup>.

Catalytic chain transfer to monomer has been previously reported as a means of effectively controlling molecular weight in free radical polymerizations. The use of cobalt–porphine chain transfer catalysts (Co-CTC) in the free radical polymerization of PMMA results in oligomers with vinylic end-groups and significantly fewer head-to-head couplings than PMMA polymerized without Co-CTC<sup>6–8</sup>. This route offers an effective pathway to low molecular weight PMMA which is also more thermally labile than saturated PMMA (PMMA-H). Low molecular weight PMMA can be prepared via free-radical techniques without the need for high initiator concentrations, elevated polymerization temperatures (>120°C) or sulfur-containing chain transfer agents with their associated odour problems<sup>9</sup>.

The thermal decomposition temperature of PMMA is dependent strongly on the polymer microstructure and the resulting chain end-functionalities<sup>9–15</sup>. For example, it has been reported that vinylidene-terminated PMMA is considerably more thermally labile than saturated PMMA. More specifically, unsaturated PMMA degrades between 230 and 300°C, whereas the saturated polymer decomposes between 300 and 400°C<sup>9,13,14</sup>. Random chain scission and subsequent depolymerization is widely accepted as the

mechanism for the degradation of saturated PMMA. Facile scission of the weak C–C bond  $\beta$  to the vinyl group and efficient radical transfer to the vinyl chain-end has been proposed as the route to PMMA–CH=CH<sub>2</sub> degradation. Head-to-head chain linkages also thermally destabilize PMMA. The use of dimethylmaleic anhydride as a comonomer in free-radical-initiated PMMA synthesis results in the introduction of additional head-to-head defects beyond those formed via coupling termination. Earlier studies on the thermal degradation of oligomers containing head-to-head linkages (PMMA-HH) indicated that they were less stable than PMMA–CH=CH<sub>2</sub><sup>16</sup>. However, recent results suggest otherwise: that PMMA with head-to-head linkages (PMMA-HH) is actually more stable than PMMA–CH=CH<sub>2</sub> but less stable than saturated PMMA<sup>10</sup>. These authors observed a significant molecular weight effect, since PMMA with head-to-head defects undergoes more facile degradation than saturated PMMA only when DP < 100. At higher DP values, the thermal degradation of both were comparable, a result attributed to a large cage recombination effect of radicals produced in the viscous polymer melt.

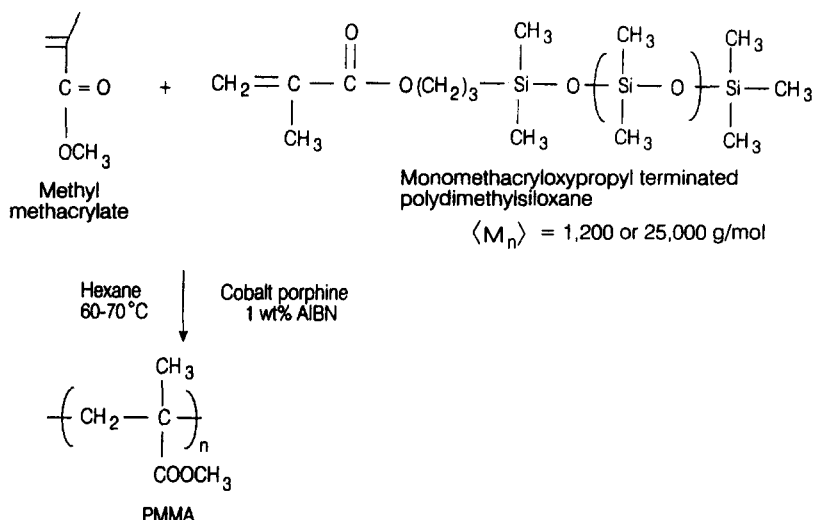
The present work describes the deliberate synthesis of PMMA particles with lower thermal stability. To achieve this result, a combination of dispersion polymerization and chain transfer techniques was employed. The PMMA particles thus generated have been used as additives for the generation of cross-linked siloxane elastomeric foams. For this application, the PMMA serves as a thermally labile organic filler which is first compounded into the cross-linkable elastomeric network. Upon subsequent thermal treatment, the organic filler is thermally decomposed to give volatile monomeric species that diffuse out through the matrix, leaving behind pores, with a size and shape of the PMMA filler particles.

### Experimental

**Materials.** Methyl methacrylate (MMA) (99%, b.p. 100°C) obtained from Aldrich was purged with

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## SYNTHESIS OF PMMA VIA DISPERSION POLYMERIZATION



Scheme 1

nitrogen, passed through an alumina column to remove any inhibitor and stored under nitrogen prior to use. Mono (methacryloxypropyl)-terminated polydimethylsiloxane (PDMS) samples ( $\langle M_n \rangle > \sim 1200$  and  $25\,000 \text{ g mol}^{-1}$ ) were obtained from Gelest, Inc. 2,3-Dimethylmaleic anhydride (DMMA) (m.p.  $93\text{--}96^\circ\text{C}$ ), 2,2'-azo-bis-isobutyronitrile (AIBN), 5,10,15,20-tetraphenyl-21H,23H-porphine cobalt(II), hexane and tetrahydrofuran (THF) were obtained from Aldrich and used as-supplied. A cobalt-porphine stock solution was prepared by dissolving  $7 \times 10^{-4} \text{ g}$  ( $10^{-6} \text{ mol}$ ) in 10 ml THF.

*Synthesis of PMMA powders (Scheme 1)*

A typical procedure for the dispersion polymerization of MMA containing 10 wt.% PDMS in hexane and Co-porphine (Co-CTC) is outlined. A 250 ml, three-neck round bottom flask was fitted with a mechanical stirrer, a condenser and a nitrogen inlet and outlet. The reactor was charged with 16 g of MMA and 2 g of the methacrylate-functionalized PDMS, and a calculated amount of the cobalt-porphine stock solution was then added. This was followed by the addition of 200 ml hexane and 0.3 g AIBN initiator. The entire system was maintained at  $70^\circ\text{C}$  under a nitrogen atmosphere. The initially homogeneous mixture became progressively more turbid with time. After 6-8 h, the dispersed PMMA particles were centrifuged, washed with hexane and dried in a vacuum oven at  $50\text{--}60^\circ\text{C}$ .

PMMA 13 was synthesized from a mixture of 16 g MMA, 2 g of  $25\,000 \text{ g mol}^{-1}$  PDMS and 0.3 g AIBN in 200 ml hexane at  $70^\circ\text{C}$ . Likewise, PMMA 29 was synthesized by polymerizing a mixture of 16 g MMA, 2 g of  $25\,000 \text{ g mol}^{-1}$  PDMS, 0.3 g AIBN and  $6.2 \times 10^{-6} \text{ mol}$  of cobalt porphine (0.0042 g of Co-CTC catalyst in 10 ml THF) in 200 ml hexane.

**Characterization.**  $^1\text{H}$  NMR analysis was performed on a Bruker AC 250 MHz NMR spectrometer in  $\text{CDCl}_3$ . Dynamic and isothermal thermogravimetric analyses (t.g.a.) were carried out on a DuPont TGA 1090 instrument. Scanning electron microscopy (SEM) was carried out on a Philips 420T electron microscope.

*Results and discussion*

In dispersion polymerizations, an initially homogeneous solution is transformed into an opaque suspension by homogeneous nucleation of particles from the reaction medium. The molecular weight of the growing polymer chain and its intrinsic insolubility in the solvent medium are two critical parameters that influence the formation of the dispersion. The stabilizer primarily controls the stability of the dispersion. The reaction medium is selected on the basis of its non-solvent properties for the growing polymer and the solubility of both the stabilizer and the monomer.

For free radical reactions employing cobalt chain transfer agents (Co-CTC), the concentration of the chain transfer agent is critical. Very low concentrations result in inefficient molecular weight control, whereas high concentrations limit the formation of higher molecular weights. It has been shown<sup>7</sup> that, after interaction with the growing polymer radical, the regeneration of the Co-Por catalyst occurs very rapidly and the concentration of the intermediate species is less than 1% of the initial Co-Por CTC concentration.

Our efforts have focused on the combination of dispersion polymerization techniques and cobalt chain transfer catalysis to synthesize spherical PMMA particles which are thermally labile. Such a procedure is complicated by the very kinetics of the two processes. Dispersion polymerizations proceed rapidly, whereas chain transfer occurs relatively slowly. To form a dispersion, the polymer chains must be of high enough molecular weight so as to phase separate from the solution. Thus, the chain transfer process must allow the formation of a polymer dispersion while introducing a high concentration of vinyl substituted end-groups to produce the desired thermal instability.

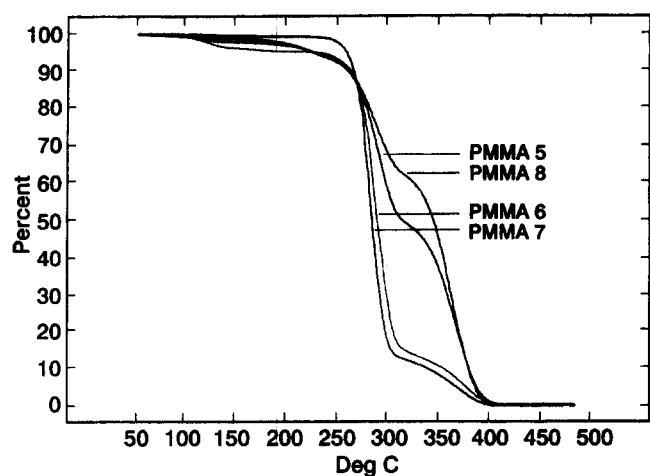
Initial experiments involved the co-polymerization of the MMA with the  $1200 \text{ g mol}^{-1}$  PDMS macromer as a steric stabilizer (Table 1). Four different PMMA samples were synthesized, either with or without Co-CTC or DMMA. The maximum amount of Co-porphine that allowed the formation of a dispersion was independently determined to be  $5 \times 10^{-7} \text{ mol}$  under these reaction conditions. The molecular weights shown in Table 1 confirm that the use of Co-CTC results in a significant decrease in molecular weight. The PMMA samples (PMMA 6 and PMMA 7),

**Table 1** Characterization of PMMA

	DMMA (wt.%)	PDMS ( $M_n$ ) = 1200 g mol <sup>-1</sup> <sup>a</sup> (wt.%)	Cobalt porphine <sup>a</sup> (mol)	$\langle M_n \rangle_{GPC}$ <sup>b</sup>	$\langle M_w \rangle_{GPC}$ <sup>b</sup>
PMMA 5	—	10	—	60 000	160 000
PMMA 8	10	10	—	157 000	272 000
PMMA 6	10	10	$3.5 \times 10^{-7}$	13 000	38 000
PMMA 7	—	10	$3.5 \times 10^{-7}$	20 000	44 000

<sup>a</sup> As charged in the reaction flask per 16 g MMA, 0.3 g AIBN and 200 ml hexane.

<sup>b</sup> Polystyrene standards.



**Figure 1** Dynamic thermogravimetric spectra at 10°C min<sup>-1</sup> in air of PMMA samples from Table 1

synthesized in the presence of cobalt-porphine CTC were of significantly lower molecular weight compared with PMMA synthesized in its absence (PMMA 5 and PMMA 8). The dynamic t.g.a. spectra of these four PMMA samples are shown in Figure 1. As expected, the PMMA samples with the lower molecular weights (PMMA 6 and PMMA 7) were significantly less stable.

On the other hand, the use of DMMA as a co-monomer did not contribute significantly towards decreasing the thermal stability of the PMMA. We had expected that its incorporation would introduce head-head defects into the polymer, thus leading to enhanced thermal instability. The reason for the unexpected stability of the DMMA-containing polymers may be twofold. One plausible explanation is cage recombination of the radicals<sup>10</sup> which causes the thermal stability of PMMA with head-head defects to be similar to that of saturated PMMA. Secondly, as DMMA and MMA tend to form alternating copolymers, a compositional heterogeneity will result whereby only a fraction of the chains will carry DMMA (as it constitutes only 10% of the total composition). A more reasonable explanation is that cleavage of the DMMA produces a bond biradial unable to diffuse away and promoting recombination.

A major problem in these initial experiments was that all four PMMA samples prepared using the 1200 g mol<sup>-1</sup> PDMS as a steric stabilizer did not form stable dispersions in hexane. The individual particles tended to aggregate (Figure 2), and it was not possible to isolate a dispersion with stabilized individual particles.

Experiments using the 25 000 g mol<sup>-1</sup> PDMS macromer were significantly more encouraging. Shown in Figure 3 are the dynamic t.g.a. spectra of two different PMMA samples



**Figure 2** Representative SEM micrograph of PMMA 7

prepared with the 25000 g mol<sup>-1</sup> PDMS stabilizer either with (PMMA 29) or without (PMMA 13) the Co-CTC chain transfer agent. The use of the chain transfer agent once again resulted in PMMA (PMMA 29) with a significantly lower thermal stability. The reported mechanism of cobalt-porphine chain transfer catalysis<sup>8</sup> suggests the formation of a high concentration of vinylidene end-groups. These undergo depolymerization at a much lower temperature than saturated PMMA, thus accounting for the trends shown in Figure 3. It should be noted, however, that the concentration of cobalt-porphine catalyst in the mixture is very critical. When  $7.7 \times 10^{-6}$  mol (0.0052 g) of cobalt-porphine was employed, the chain transfer was so effective that the low molecular weight PMMA that formed remained soluble in hexane and, consequently, did not form a dispersion even after 12 h at 70°C. On the other hand, when  $4.8 \times 10^{-6}$  mol (0.0032 g) of cobalt-porphine was employed, the dispersion formed within 15 min, but the thermal stability of the resulting polymer was comparable with that of PMMA 13, suggesting that chain transfer was ineffective! Unlike the

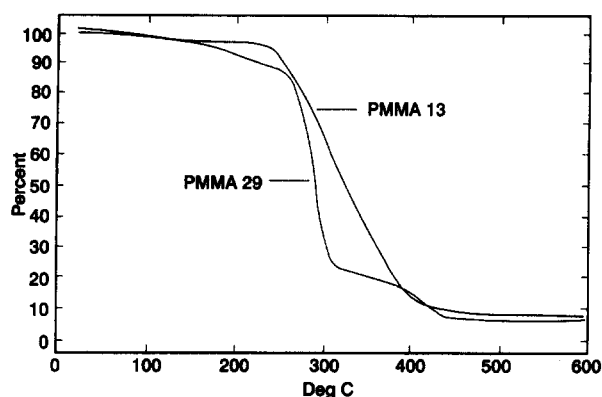


Figure 3 Dynamic thermogravimetric spectra at  $10^{\circ}\text{C min}^{-1}$  in air of PMMA 13 and PMMA 29

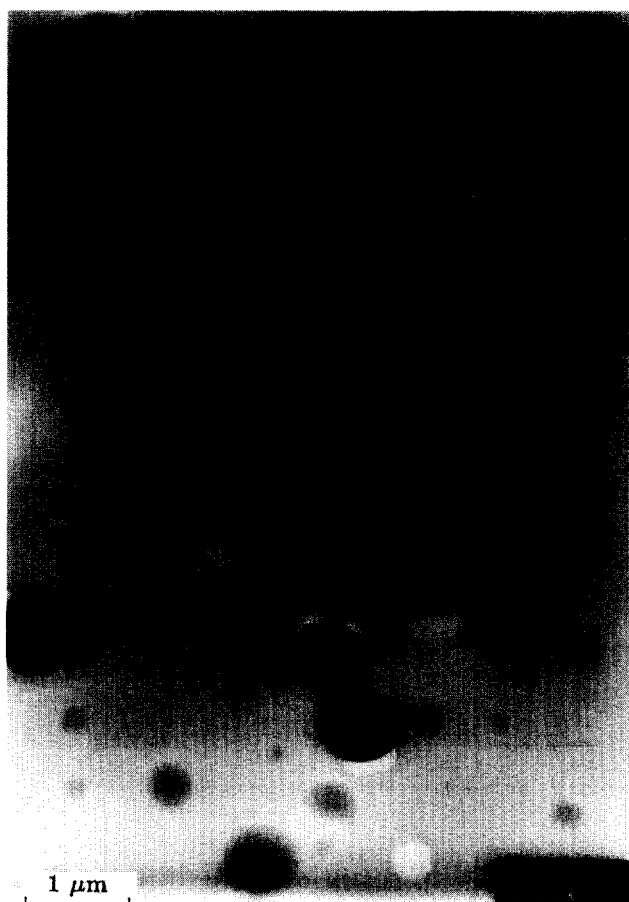


Figure 4 Representative SEM micrograph of PMMA 13

results obtained using the  $1200\text{ g mol}^{-1}$  PDMS stabilizer, the use of the  $25\,000\text{ g mol}^{-1}$  PDMS stabilizer resulted in stable dispersions (PMMA 13 and PMMA 29) of spherical PMMA particles in hexane (Figures 4 and 5). Thus, we have succeeded in synthesizing PMMA particles with lower thermal stability by a combination of dispersion polymerization and chain transfer techniques and have demonstrated the need to carefully control the amount of chain transfer agent.

#### Conclusions

Micrometre-sized thermally labile PMMA particles have

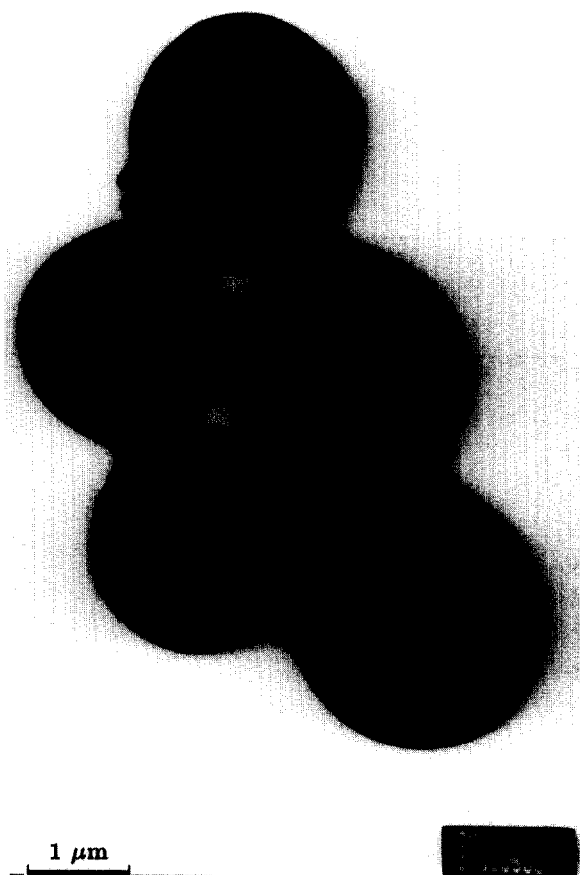


Figure 5 Representative SEM micrograph of PMMA 29

been successfully synthesized by a combination of dispersion polymerization in hexane and chain transfer employing cobalt-porphine CTC. It is presumed that the chain transfer agent led to the formation of vinylidene end-groups that contributed to thermal instability. These thermally degradable PMMA particles have been further employed as modifiers for cross-linkable siloxane rubbers in efforts to generate porous elastomeric networks.

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