Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Radical Polymerization in the Presence of Peroxide Monomer: An Approach to Branched Vinyl Polymers

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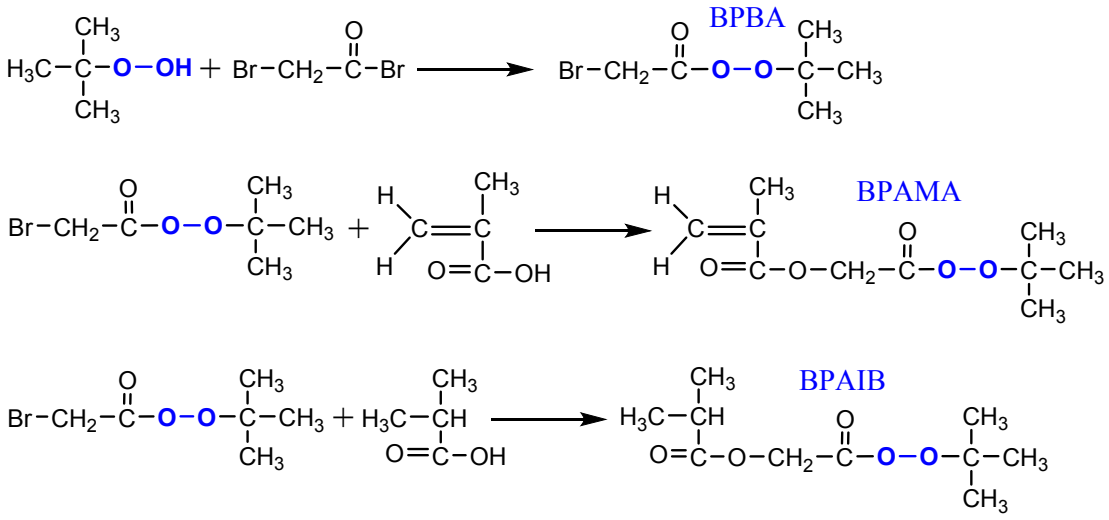


Scheme S1. Preparation of the peroxide monomer BPAMA and the model peroxide BPAIB.

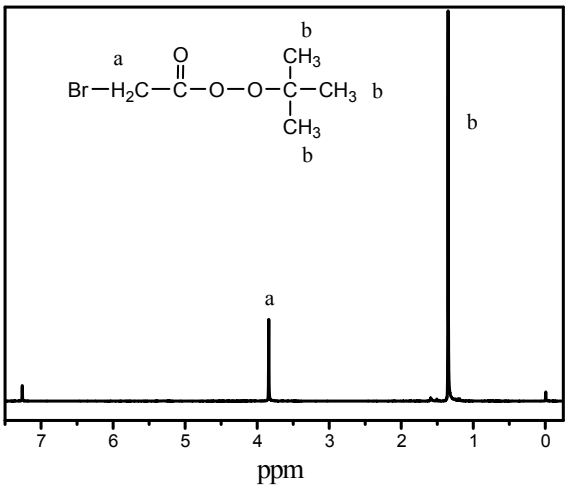


Figure S1. ^{1}H-NMR spectrum of the intermediate BPBA.

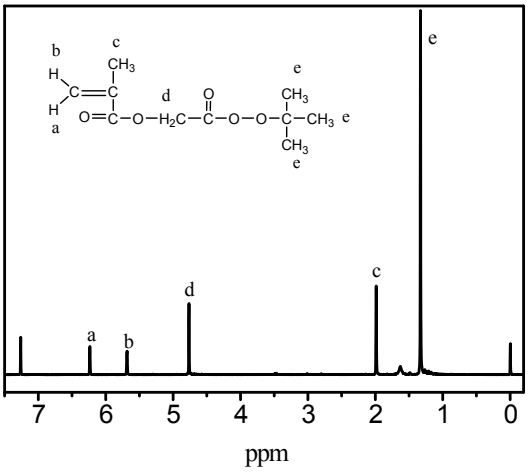


Figure S2. ^{1}H-NMR spectrum of the peroxide monomer BPAMA.

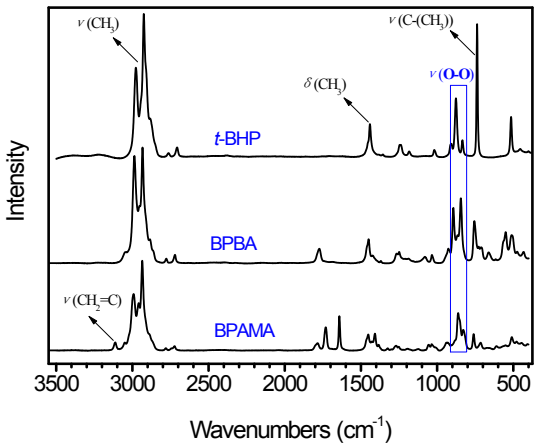


Figure S3. Raman spectra of *t*-PBH, the intermediate BPBA, and the peroxide monomer BPAMA.

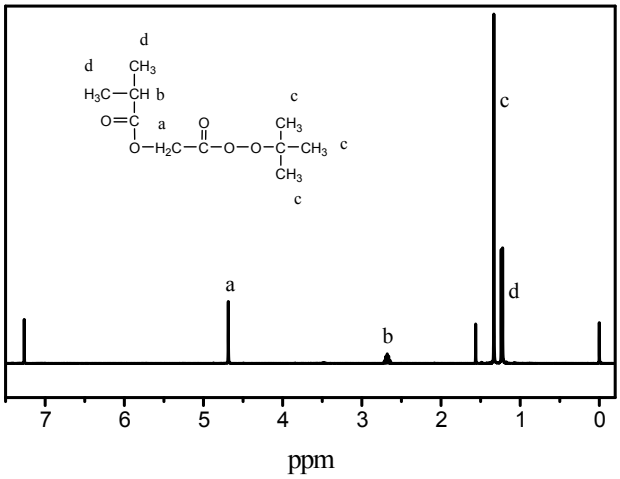


Figure S4. ^{1}H-NMR spectrum of the model peroxide BPAIB.

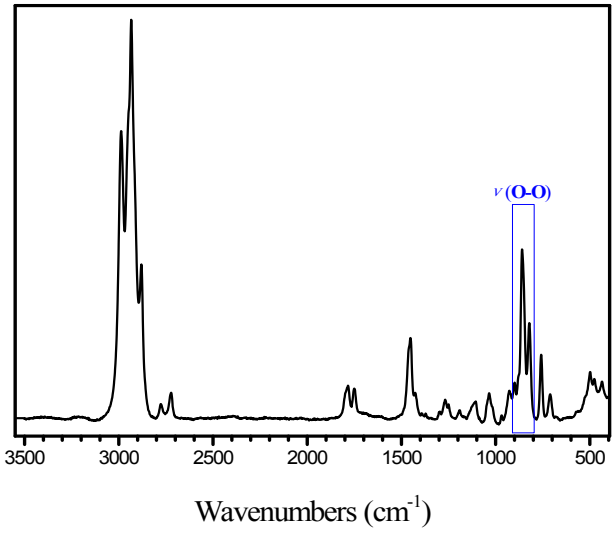


Figure S5. Raman spectrum of the model peroxide BPAIB.

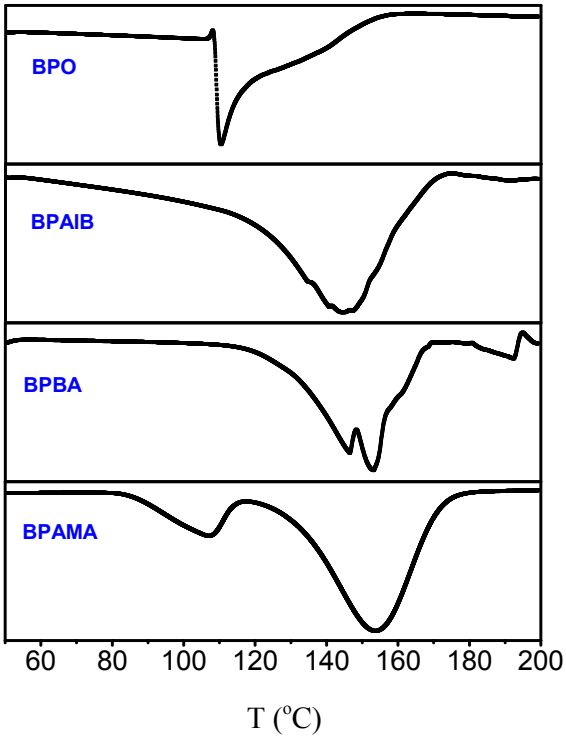
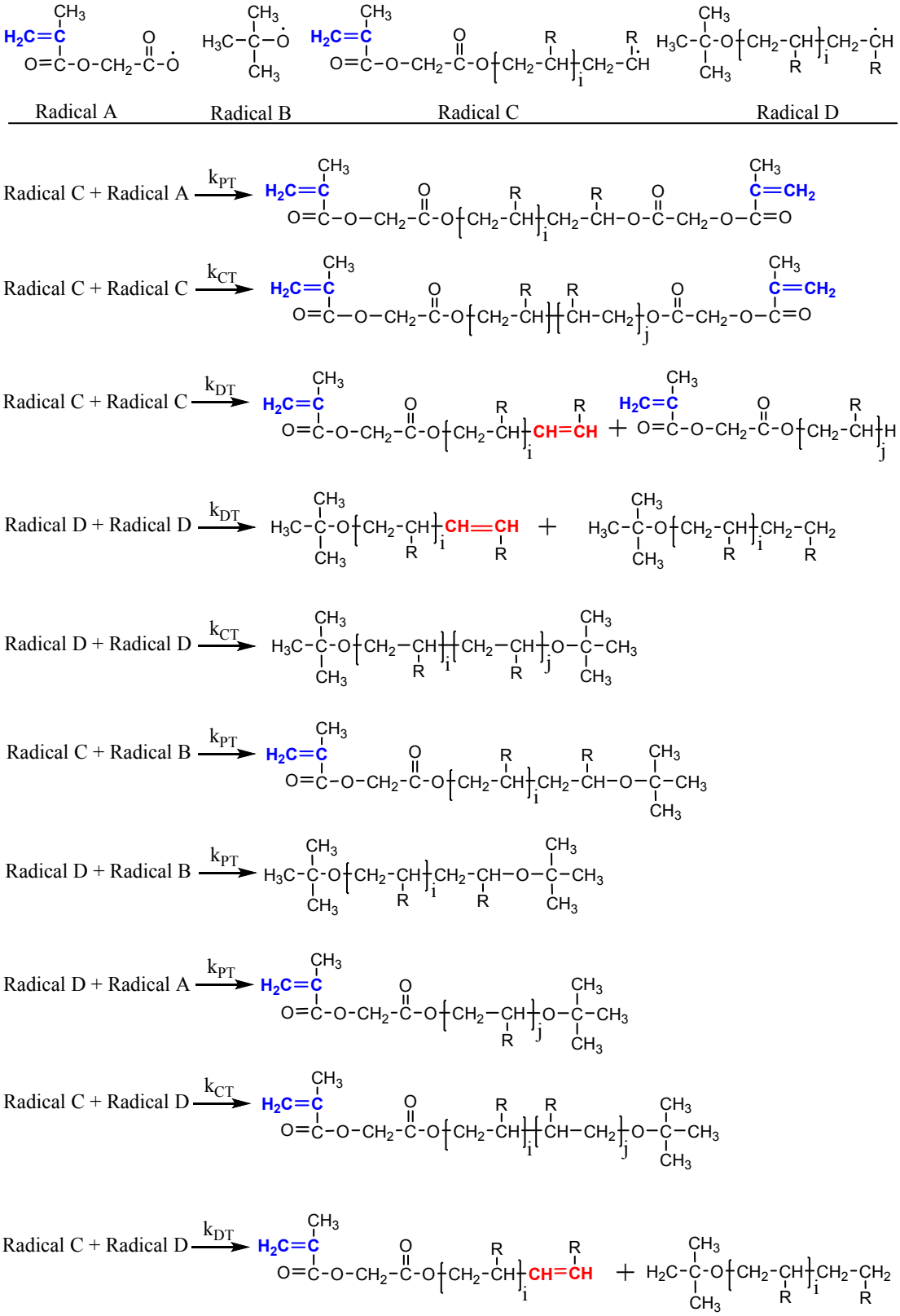


Figure S6. DSC curves for the peroxides (heating at 10 °C/min in N_2).



Scheme S2. Termination reactions for the radical polymerization in the presence of peroxide monomer.

In Scheme S2, the vinyl group from BPAMA in blue colour can participate in polymerization, the vinyl group formed from bimolecular disproportionation termination in red colour cannot participate in polymerization because of steric effect.

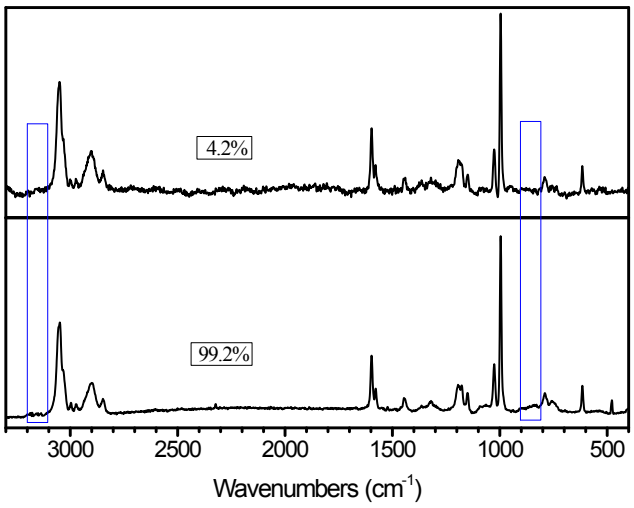
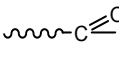


Figure S7. Raman spectra for St_{100}-$BPAIB_{5.0}$-$DDT_{0.5}$ at different monomer conversion (80 °C).

Supporting Statement for the calculation of the data illustrated in Table 1.

The areas of the signals c, d, e, f, and g in Figure 2 were represented using S_c, S_d, S_e, S_f, and S_g, respectively. N_A:N_B:N_C:N_D:N_E:N_F were used to represent the ratio of the characteristic structures shown in Scheme 2. F_{IA}, F_{PTA}: The initiation and primary termination fraction of the radical  . F_{IB}, F_{PTB}: The initiation and primary termination fraction of the radical  . F_I, F_P: The homolytically dissociating/initiating and the polymerization fraction of BPAMA

Using the TMS as the internal standard, S_c = 1.26, S_d = 20.36, S_e = 7.36, S_f = 3.78, and S_g = 2.58, respectively.

Assuming the macro-initiator has not dissociated at low conversion, e.g. no structure F shown in Scheme 2 formed, and then N_F =0.

$S_c = k*N_E$.

$S_d = k*(N_A+N_C+N_E+N_F)*2$.

$S_e = k*(N_A+N_F)*2$

$S_f = k*N_D$

$S_g = k*N_B*2$

$N_F = 0$

k: a constant relating to the number and its signal area.

From the above equations, the ratio of the characteristic structures shown in Scheme 2 at 6.5% styrene conversion was calculated, and the result is: N_A:N_B:N_C:N_D:N_E = 3.68:1.29:5.24:3.78:1.26.

N_A:N_B:N_C:N_D:N_E = 3.68:1.29:5.24:3.78:1.26.

$F_{IA} = N_A/(N_A+N_E) = 3.68/(3.68+1.26) = 74.5\%$.

F_{PTA} = 100- F_{IA}=25.5%.

$F_{IB} = N_B/(N_B+N_D) = 1.29/(1.29+3.78) = 25.4\%$.

F_{PTB} = 100- F_{IB}=74.5%.

$F_P = N_C/[\ N_C+(N_A+ N_B+N_D +N_E)/2]$=5.24/[5.24+(3.68+ 1.29+3.78 +*1.26*)/2] =51.1%.

F_I = 100- F_P=48.9%.

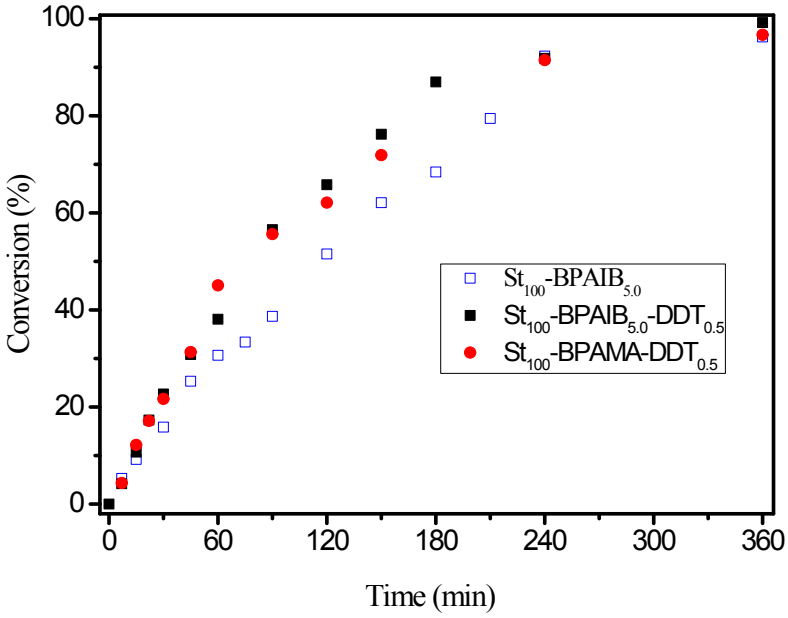


Figure S8. Comparison of the monomer conversion for St_{100}-$BPAMA_{5.0}$-$DDT_{0.5}$, St_{100}-$BPAIB_{5.0}$-$DDT_{0.5}$, and St_{100}-$BPAIB_{5.0}$ at 80 °C.

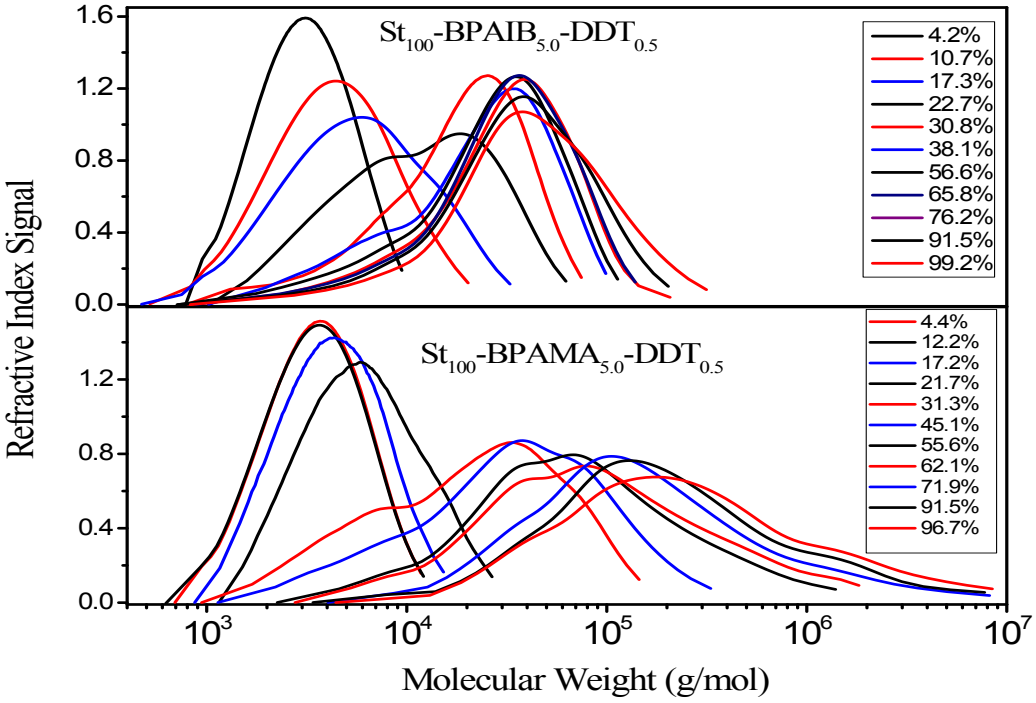


Figure S9. Molecular weight distributions for St_{100}-$BPAMA_{5.0}$-$DDT_{0.5}$ and St_{100}-$BPAIB_{5.0}$-$DDT_{0.5}$.

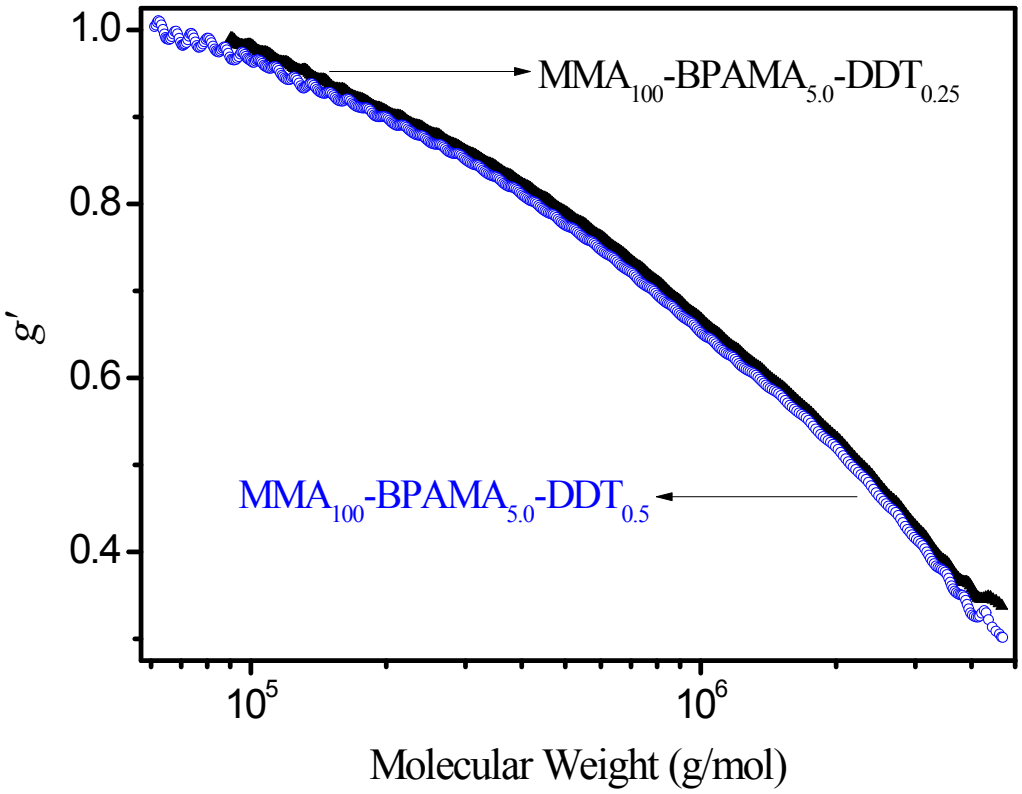


Figure S10. Variations in the Zimm branching factor *g′* with molecular weight for branched PMMA prepared at different feed ratios.

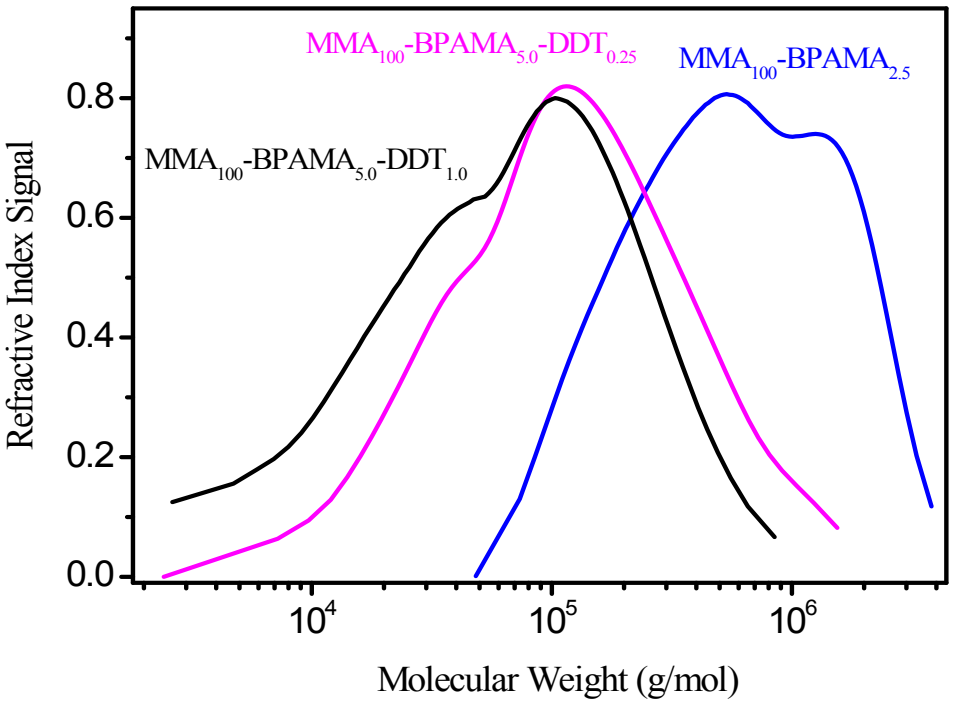


Figure S11. Comparison of the molecular weight distributions for MMA_{100}-$BPAMA_{5.0}$-$DDT_{1.0}$, MMA_{100}-$BPAMA_{5.0}$-$DDT_{0.25}$, and MMA_{100}-$BPAMA_{2.5}$.

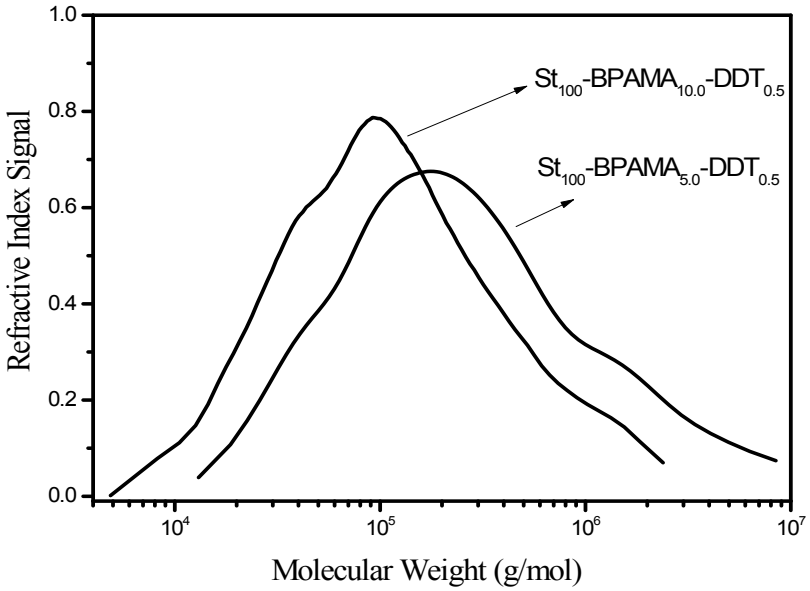


Figure S12. Comparison of the molecular weight distributions between St_{100}-$BPAMA_{5.0}$-$DDT_{0.5}$ and St_{100}-$BPAMA_{10.0}$-$DDT_{0.5}$

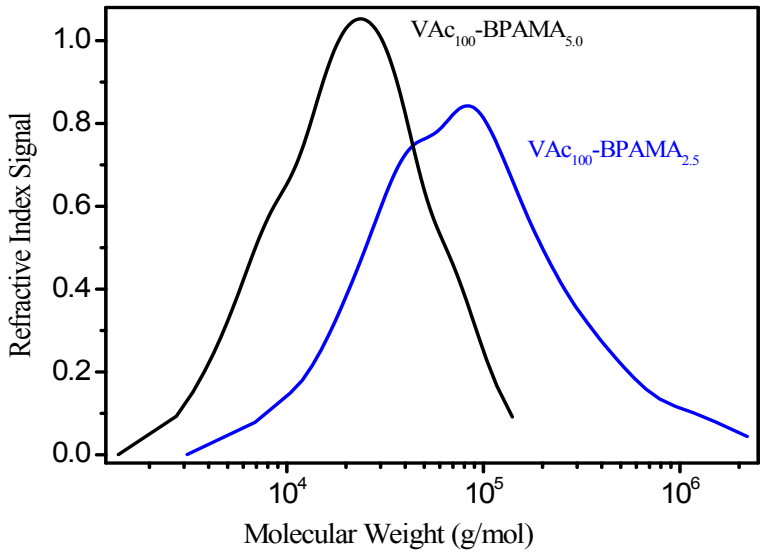


Figure S13. Comparison of the molecular weight distributions between VAc_{100}-$BPAMA_{5.0}$ and VAc_{100}-$BPAMA_{2.5}$.