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University of Science and Technology of China (USTC）

UV-Initiating Behavior of Highly Branched Polymeric Photoinitiators End-Capped With Benzophenone and Tertiary Amine Moieties

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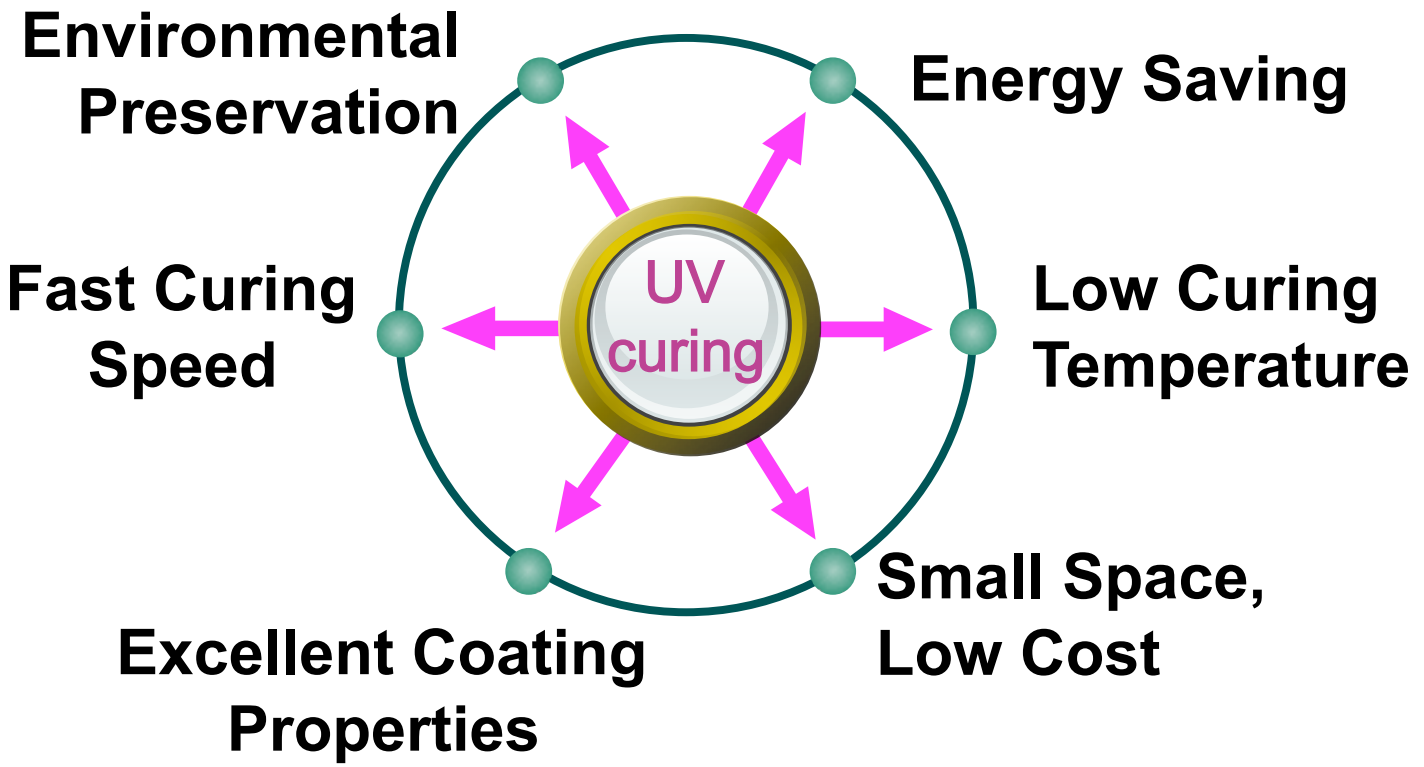
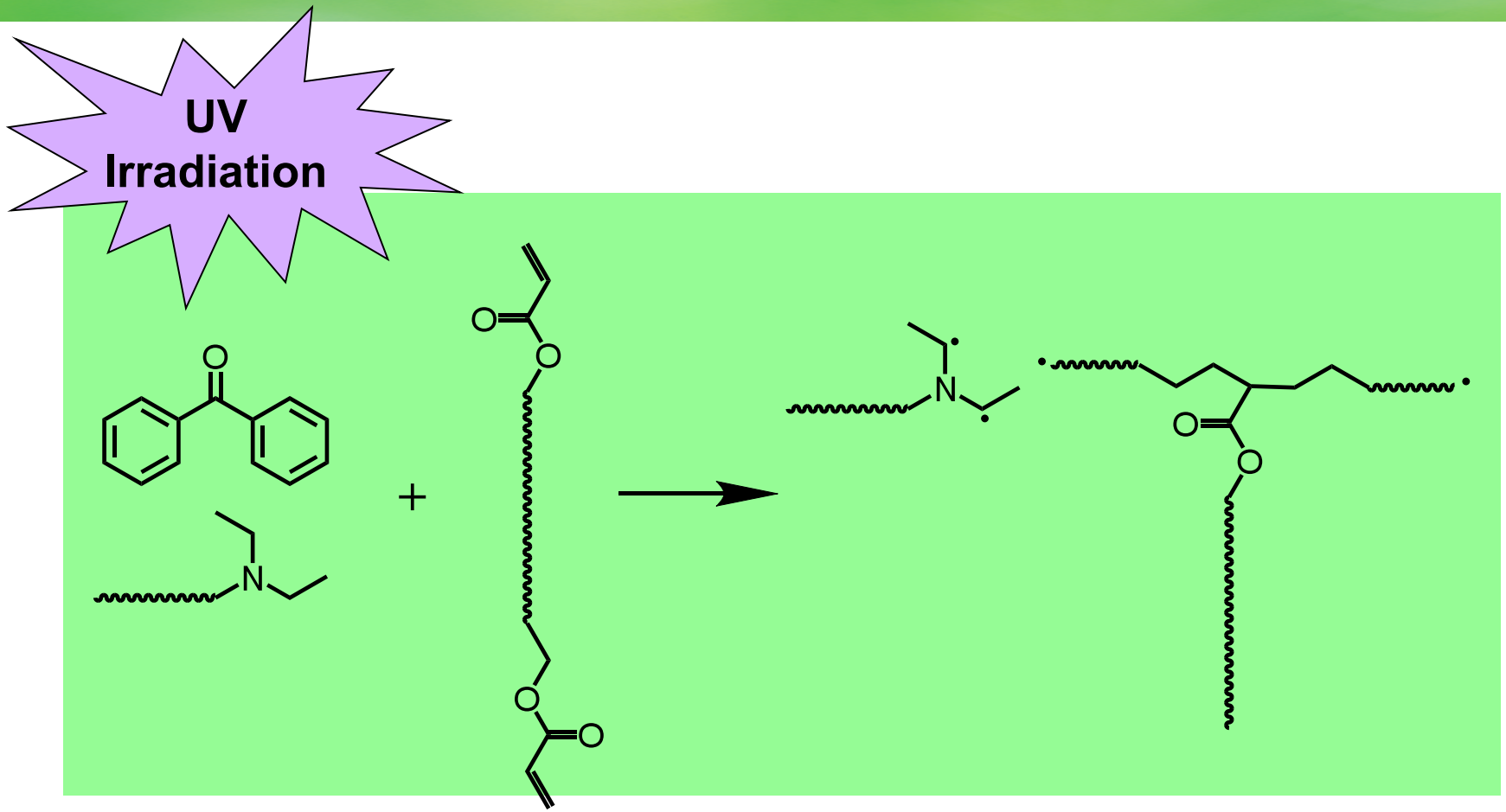
Chicago, USA 2012.05

Application of UV-Curing

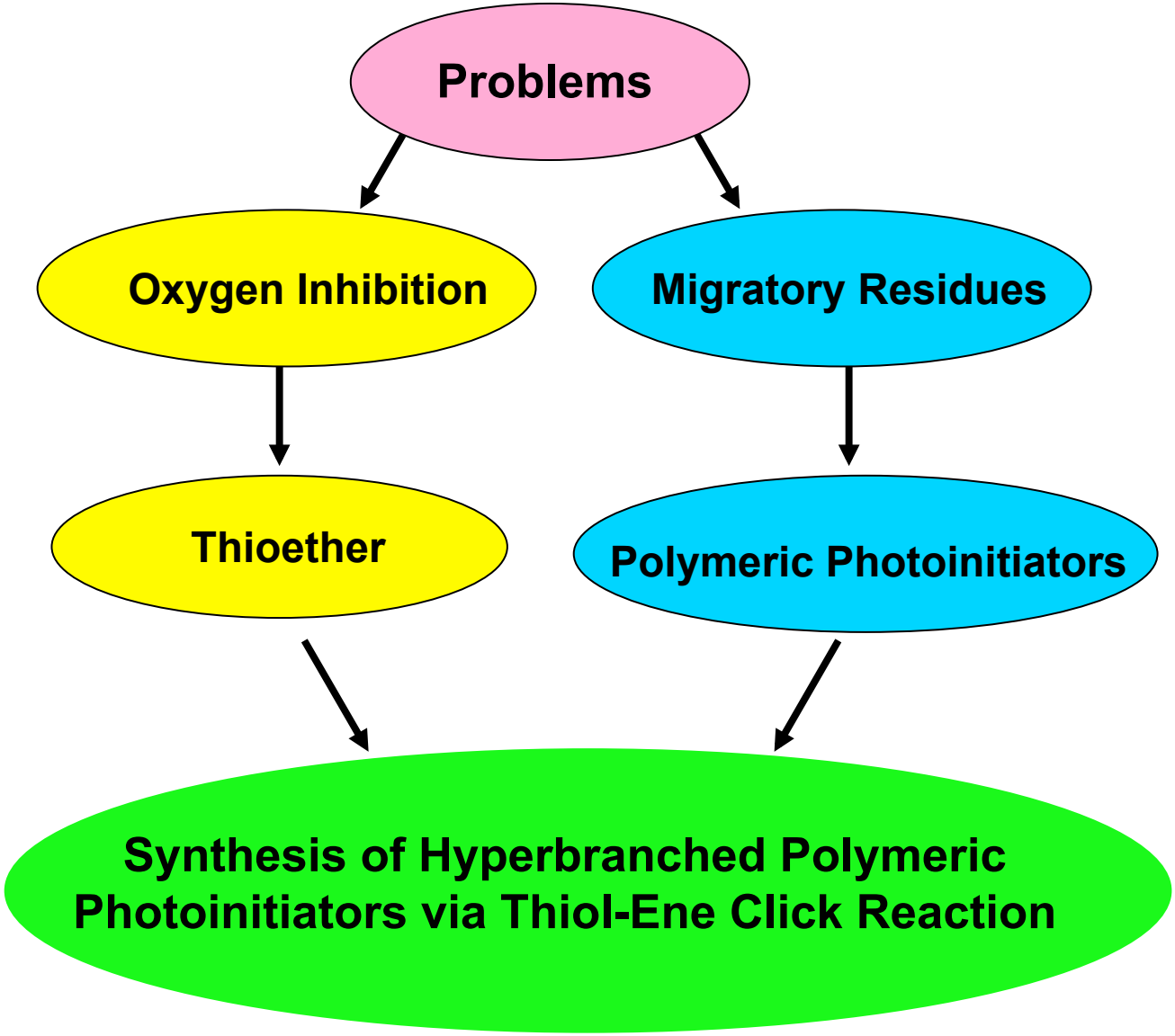


Problems



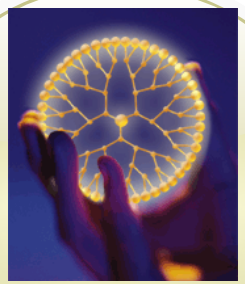
Oxygen Inhibition & Migratory Residues

Resolutions



Hyperbranched Polymeric Photoinitiators

Low Viscosity



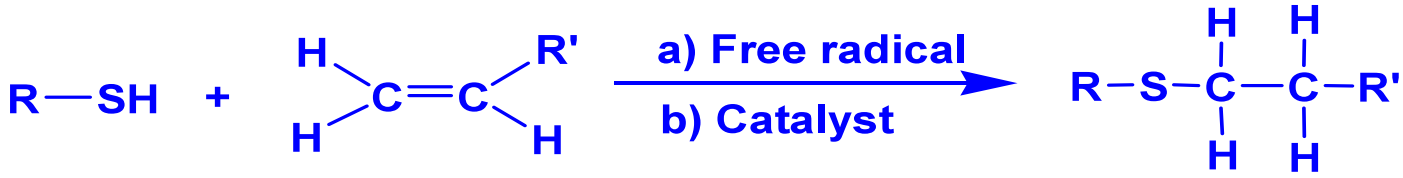
Hyperbranched Polymeric Photoinitiators

More end crosslink points
Improved thermal stability

x2

Low Use Level

Thiol-ene Click Reaction



Scheme 1. General thiol–ene coupling by a) free-radical and b) Michael addition reactions. In both idealized reactions, a single thiol reacts with a single ene to yield the product.

C. N. Bowman and C. E. HoyleAngew, Chem. Int. Ed. 2010, 49, 1540 – 1573

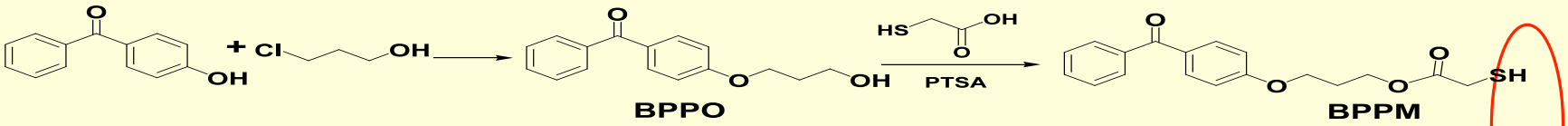
Contents

- The Syntheis and Properties of Hyperbranched Polymeric Photoinitiator Bearing BP Moiety Based on Hyperbranched Poly(ester-amine) —BP-HPEAs

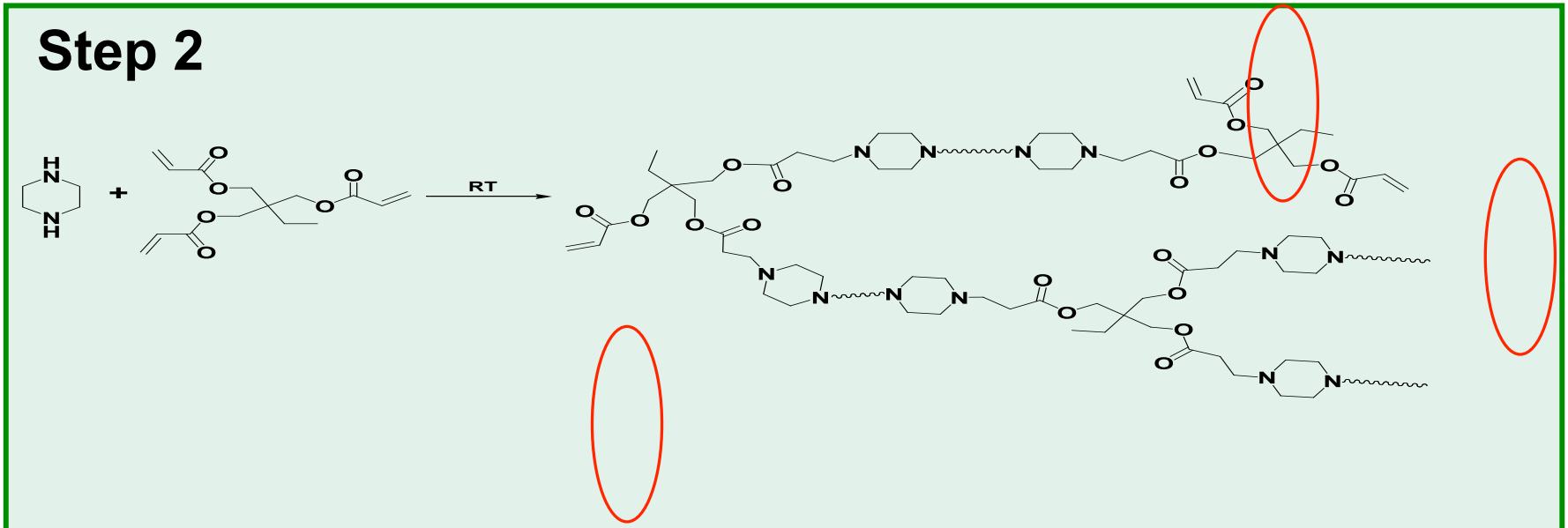
- The Syntheis and Properties of Hyperbranched Polymeric Photoinitiator end-capped with benzophenone and tertiary amine moieties—B/A-HPIs

The Syntheis of BP-HPEAs

Step 1

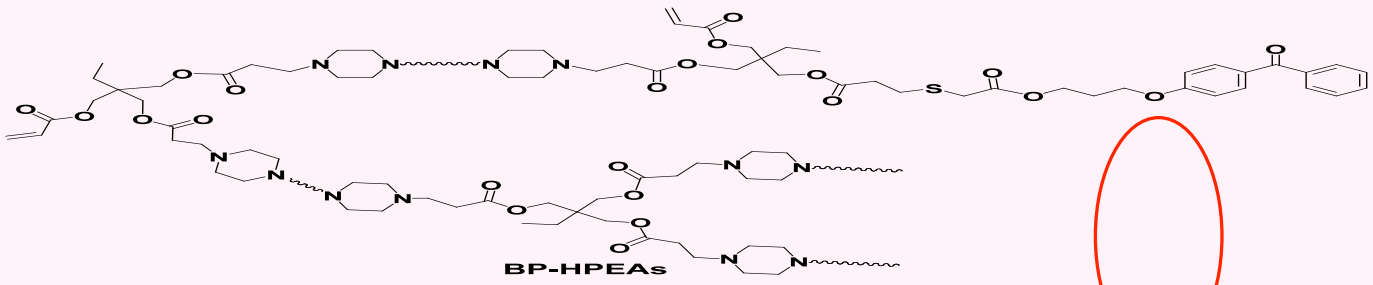


Step 2



The Syntheis of BP-HPEAs

Step 3



The Characterization of BP-HPEAs

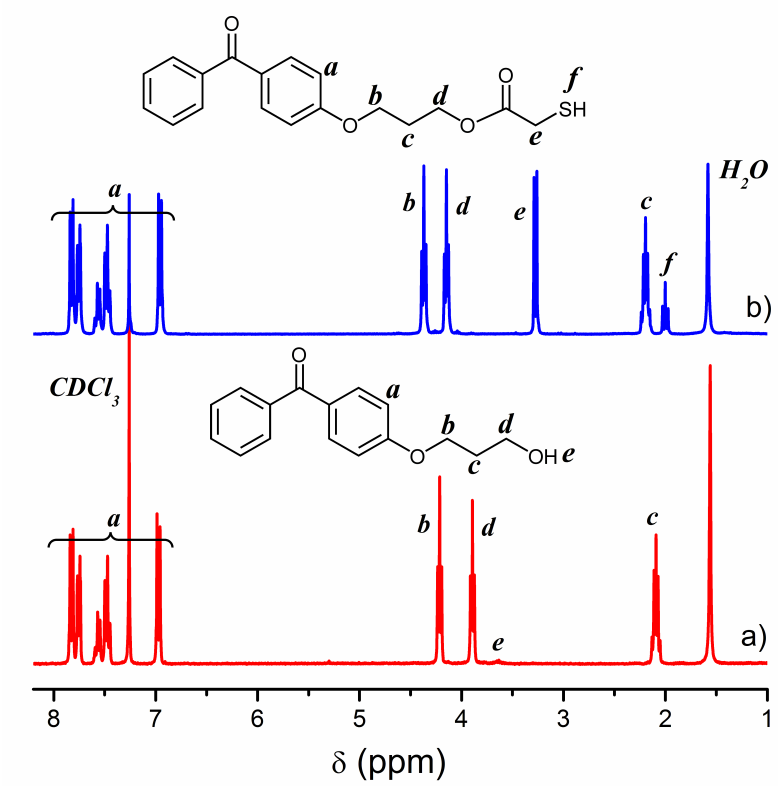


Figure 1. ^{1}H NMR spectra recorded for (a) BPPO, and (b) BPPM in $CDCl_3$

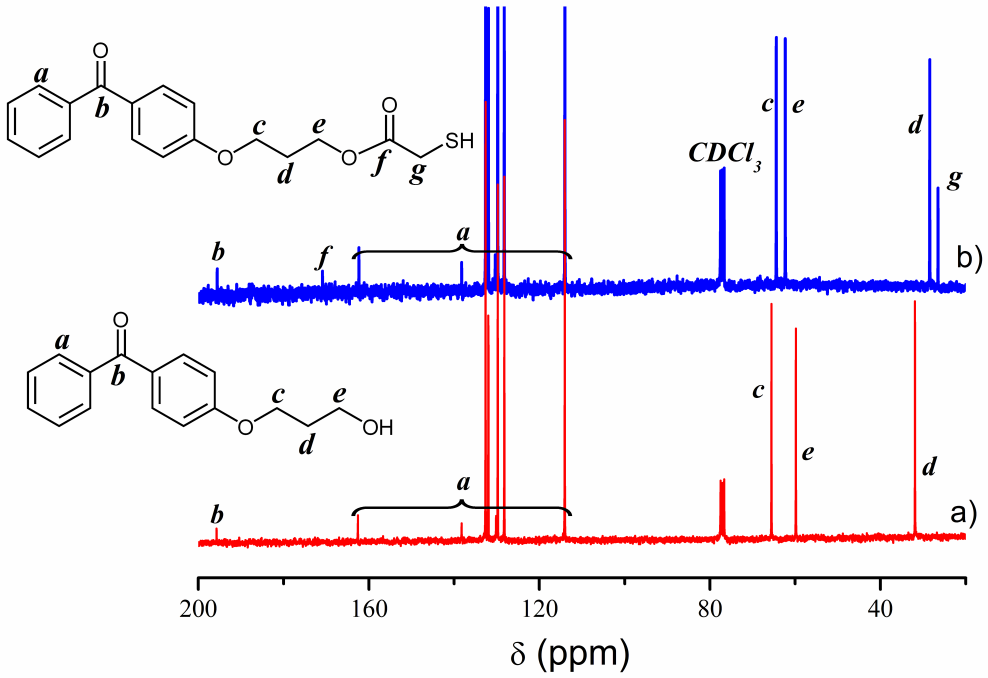


Figure 2. ^{13}C NMR spectra recorded for (a) BPPO, and (b) BPPM in $CDCl_3$

The Characterization of BP-HPEAs

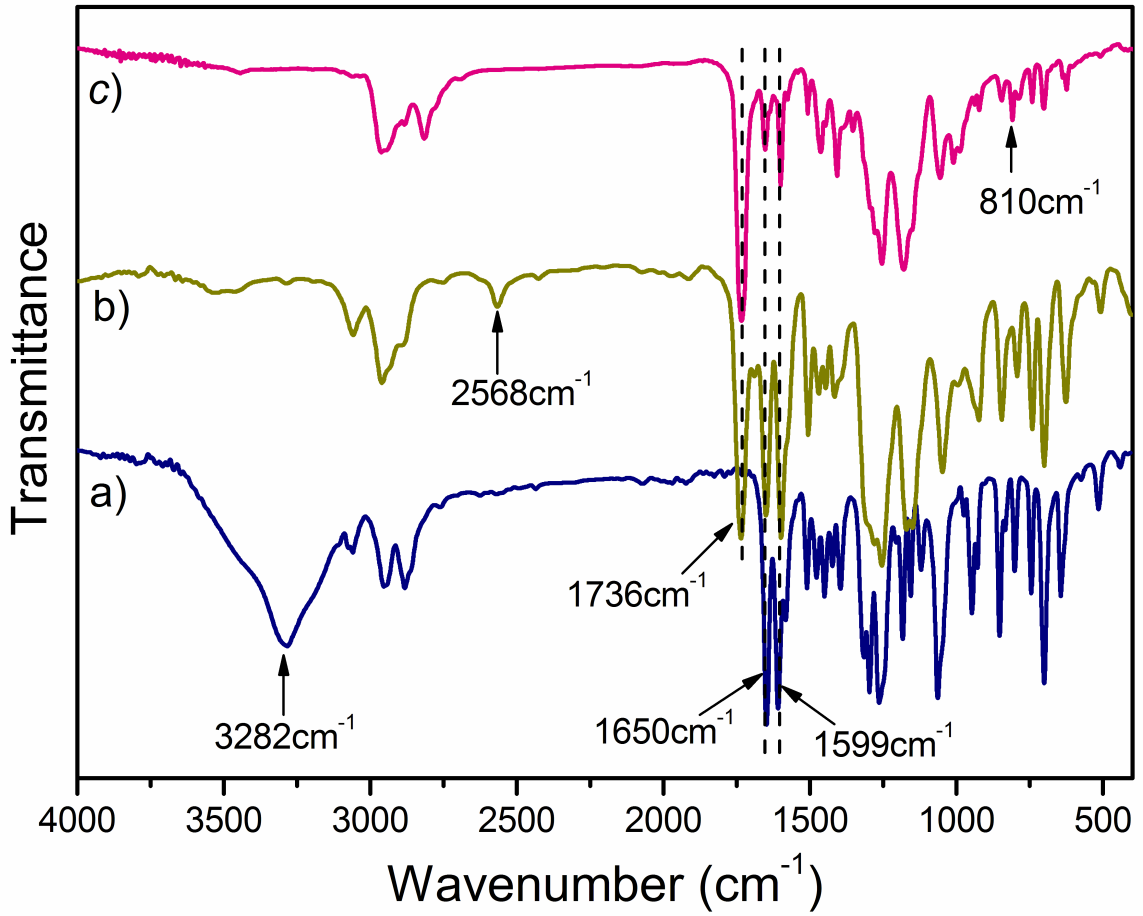


Figure 3. FT-IR spectra for (a) BPPO, (b) BPPM and (c) BP-HPEA-3

The Characterization of BP-HPEAs

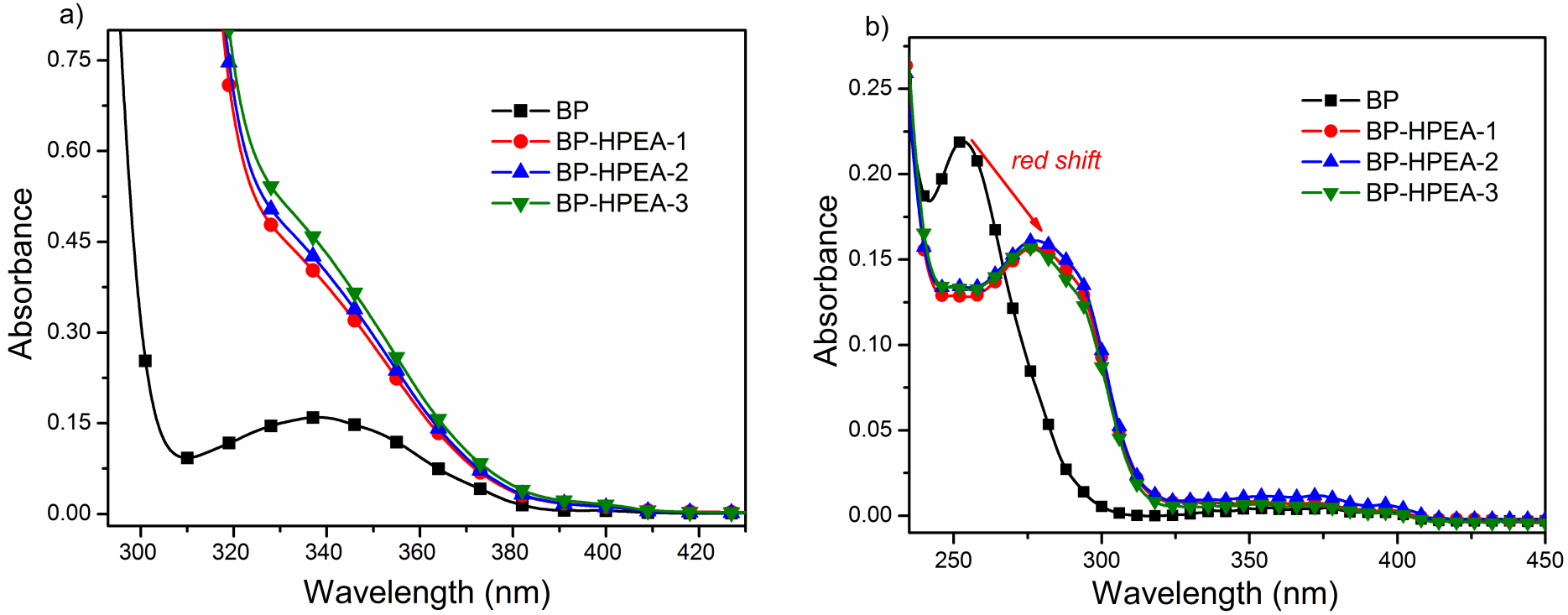


Figure 4. UV-vis absorption spectra recorded for BP and BP-HPEAs with the concentration of (a) 1.00×10^{-3} M, and (b) 1.00×10^{-5} M in CH_2Cl_2 solution at room temperature

The Photoinitiating Behavior of BP-HPEAs

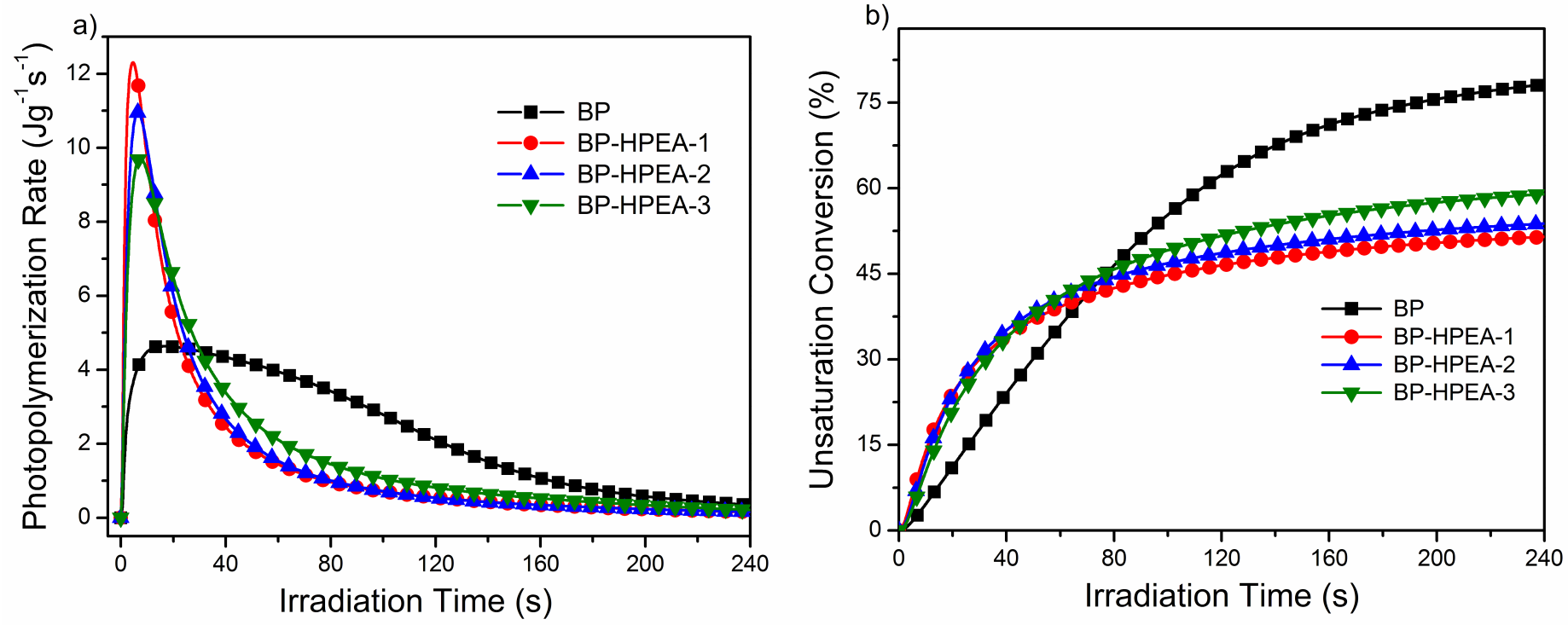


Figure 5. (a) Photo-DSC exotherms and (b) unsaturation conversion curves for the polymerization of HDDA initiated by BP and BP-HPEAs

The Photoinitiating Behavior of BP-HPEAs

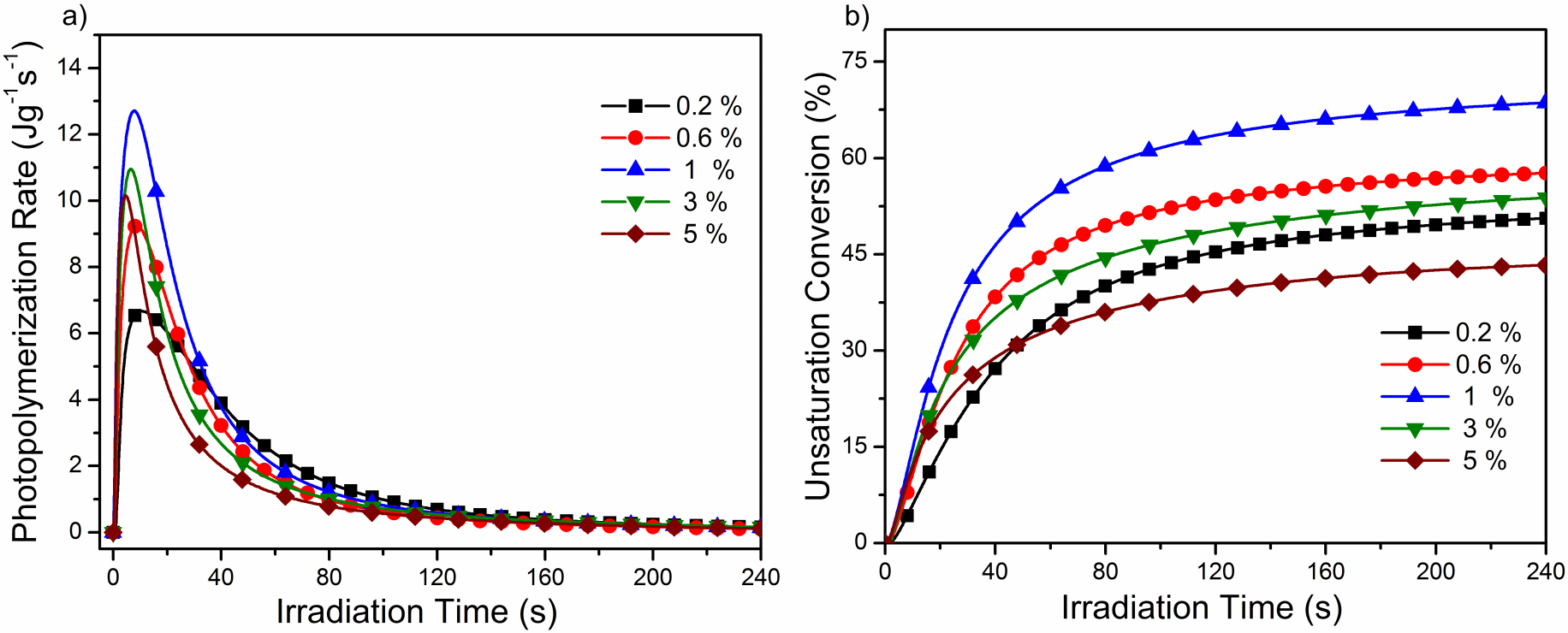


Figure 6. (a) Photo-DSC exotherms and (b) unsaturation conversion curves for the polymerization of HDDA initiated by BP-HPEA-2 in different concentration.

Compatibility of BP-HPEAs with Acrylate Oligomers

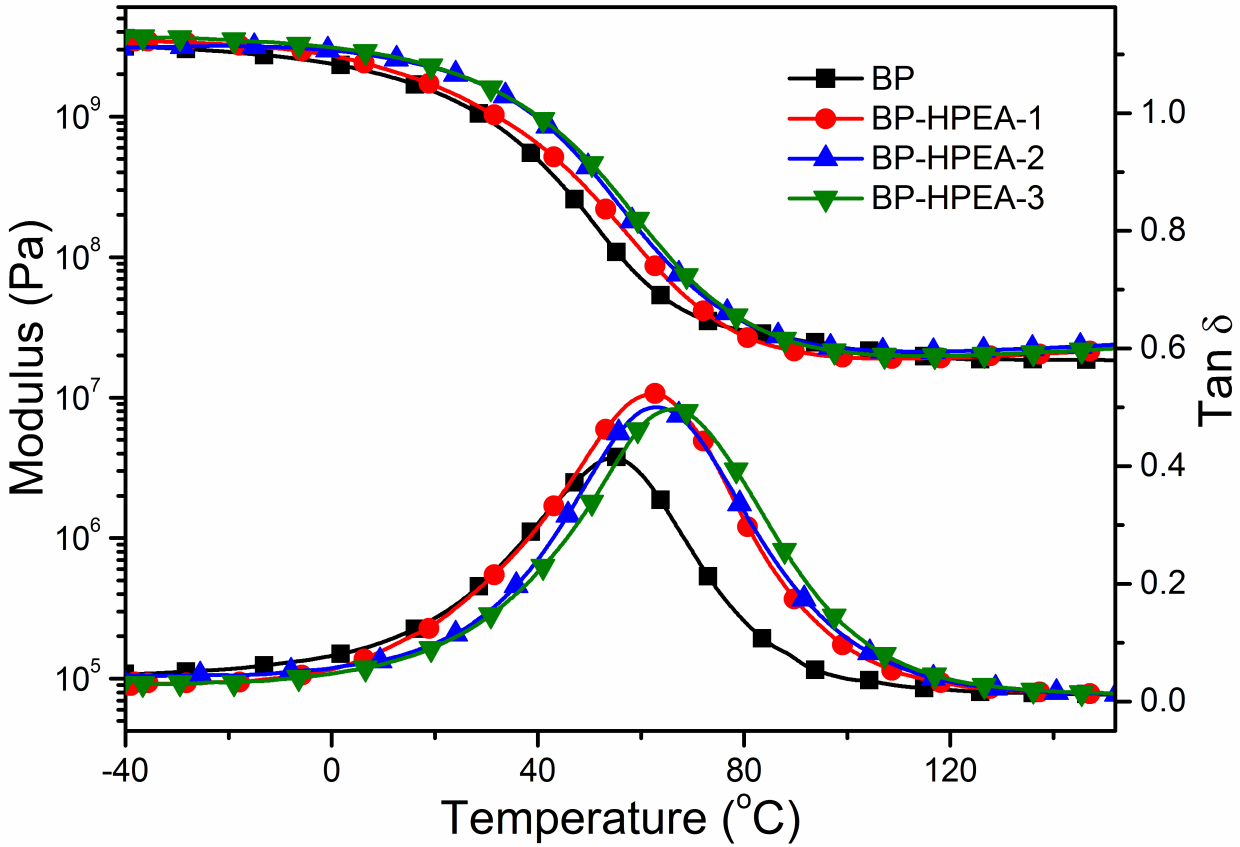
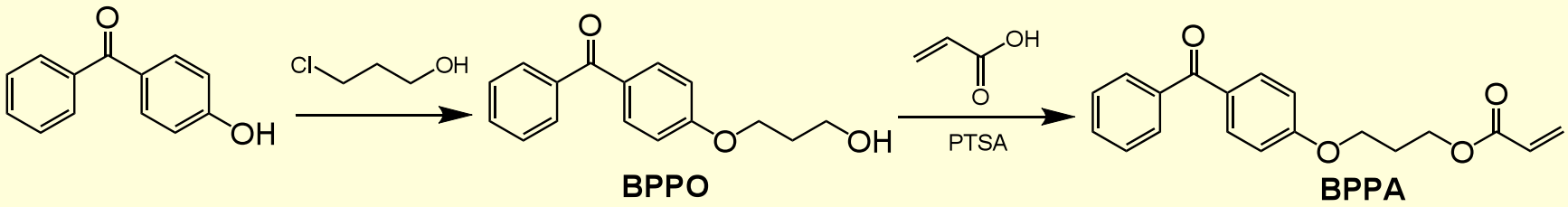


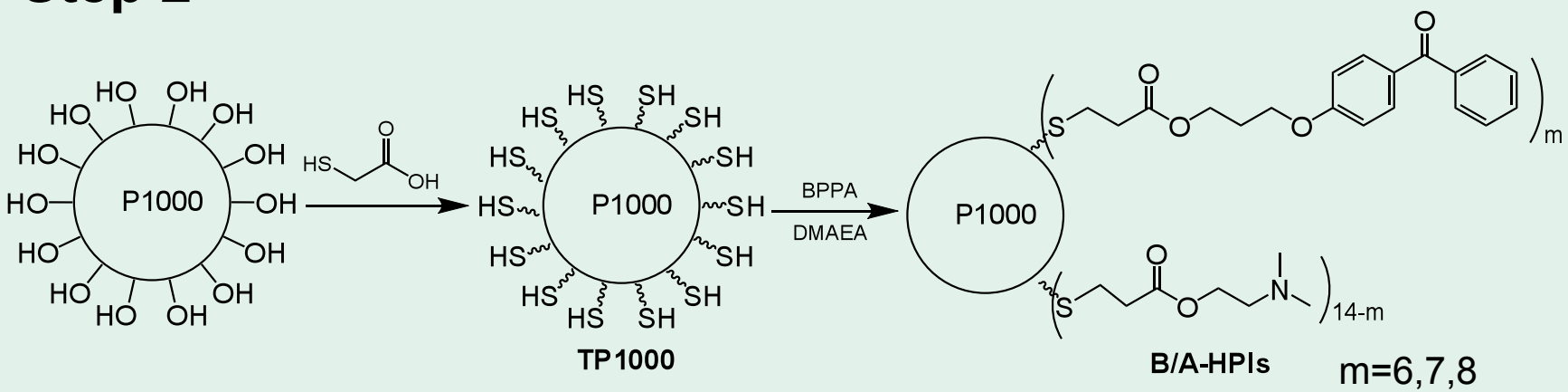
Figure 7. DMTA curves recorded for UV cured EB605 films initiated by BP and BP-HPEAs at a frequency of 10Hz and a heating rate of 10 °C/min in the range of -40~180 °C.

The Syntheis of B/A-HPIs

Step 1



Step 2



DMAEA：N,N-dimethylaminoethyl acrylate

The Characterization of B/A-HPIs

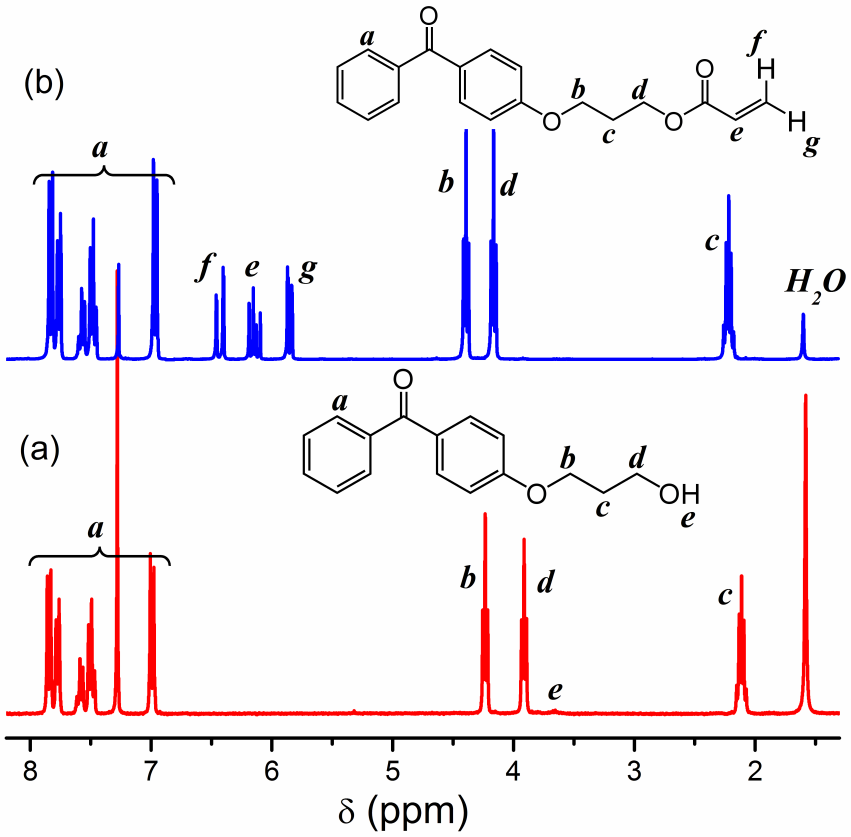


Figure 8. ^{1}H NMR spectra of (a) BPPO and (b) BPPA in $CDCl_3$

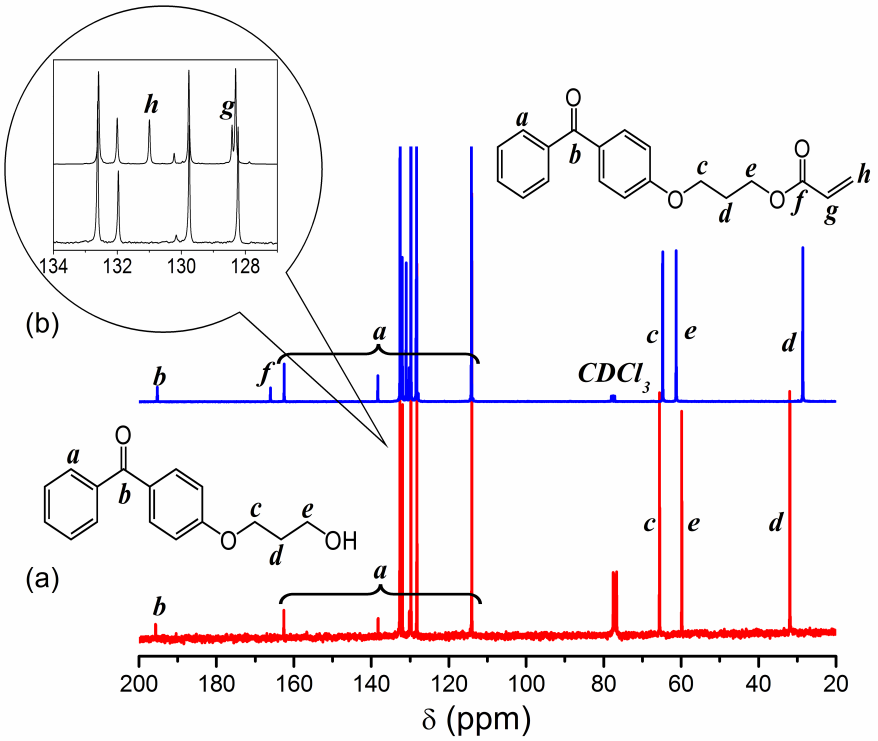


Figure 9. ^{13}C NMR spectra of (a) BPPO and (b) BPPA in $CDCl_3$

The Characterization of B/A-HPIs

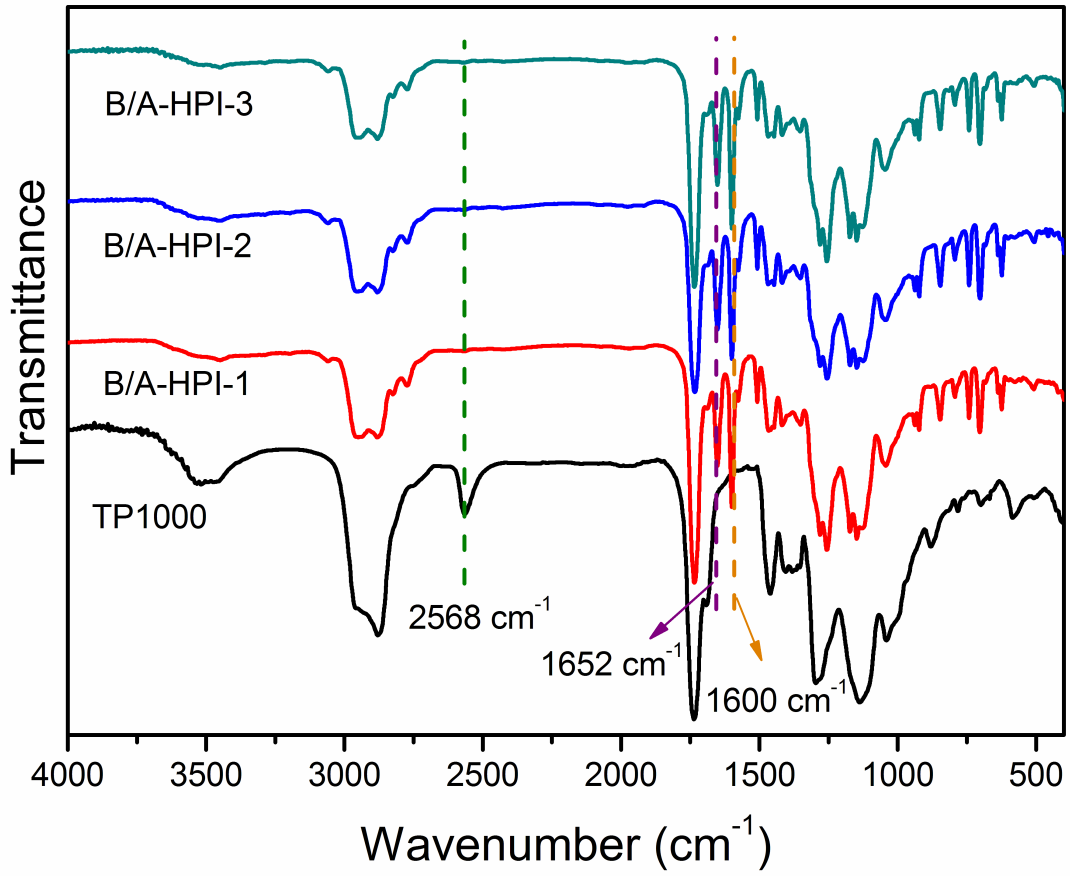


Figure 10. FT-IR spectra of TAP1000, B/A-HPI-1, B/A-HPI-2, and B/A-HPI-3.

The Characterization of B/A-HPIs

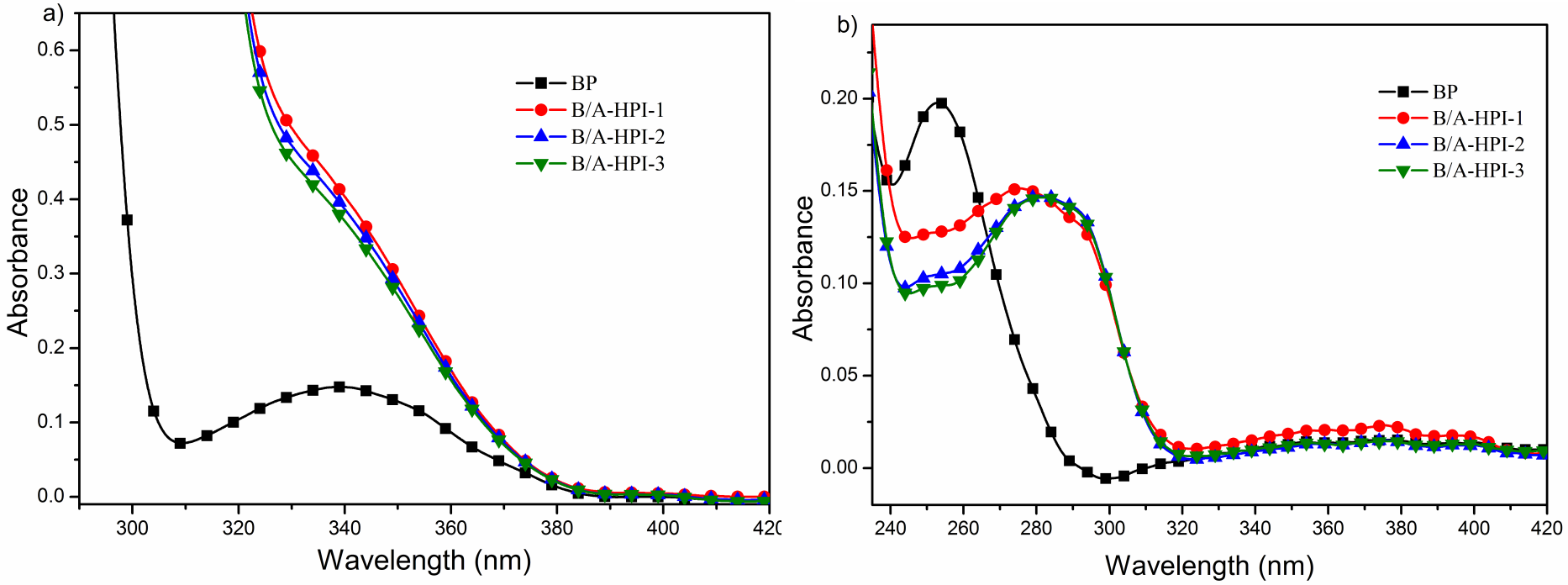


Figure 11. UV-vis absorption spectra of BP and B/A-HPIs with the concentrations of (a) 1.00×10^{-3} M and (b) 1.00×10^{-5} M in CH_2Cl_2 solution at room temperature.

The Photoinitiating Behavior of B/A-HPIs

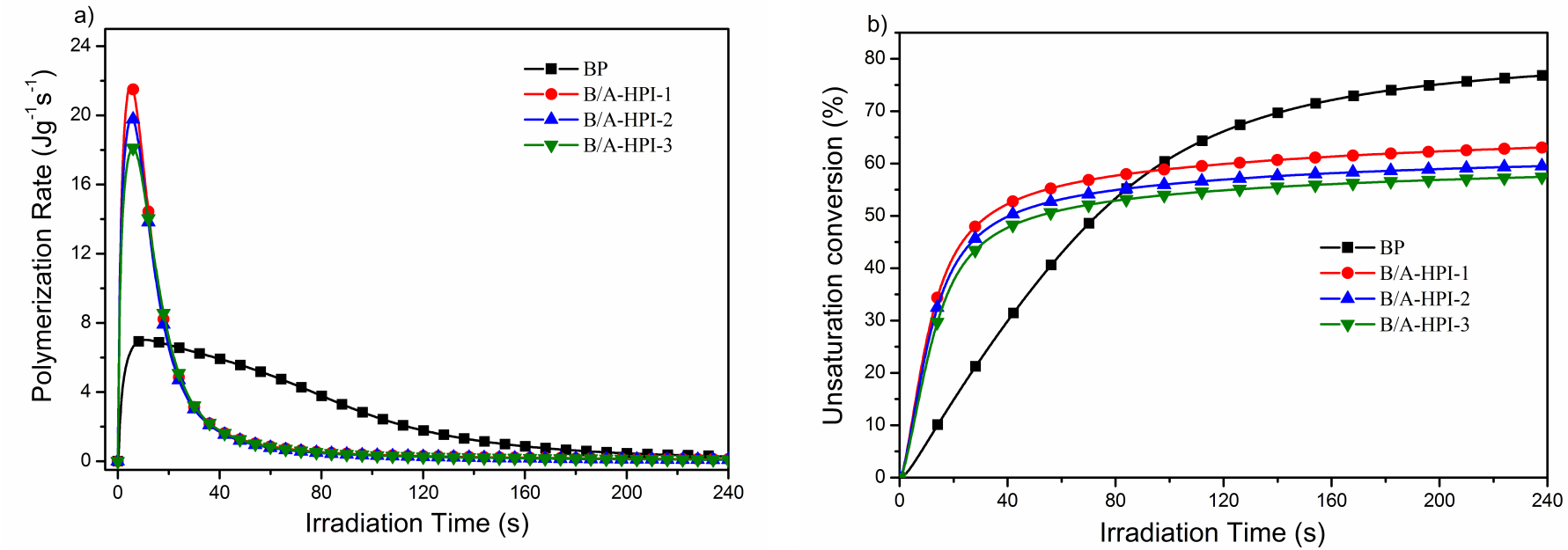


Figure 12. (a) Photopolymerization rate and (b) unsaturation conversion in the UV cured HDDA film versus irradiation time initiated by BP and B/A-HPIs

The Photoinitiating Behavior of B/A-HPIs

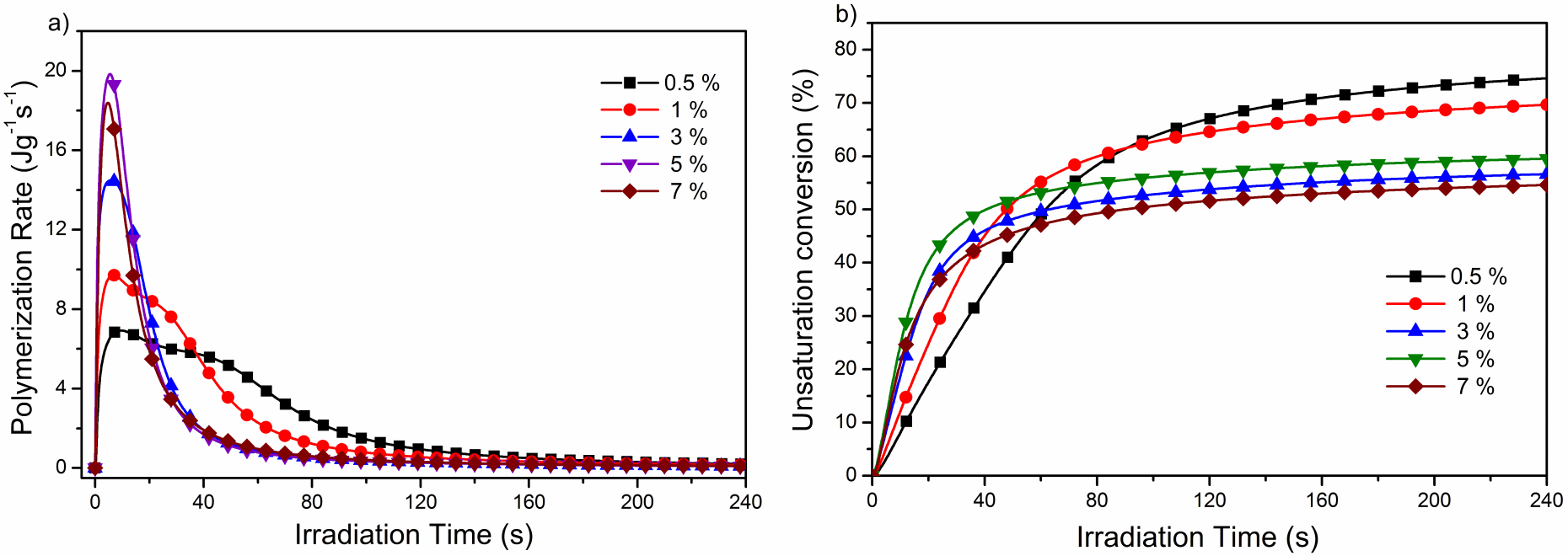


Figure 13. (a) Photopolymerization rate and (b) unsaturation conversion in the UV cured HDDA film versus irradiation time initiated by B/A-HPI-2 in different concentration.

The Photoinitiating Behavior of B/A-HPIs

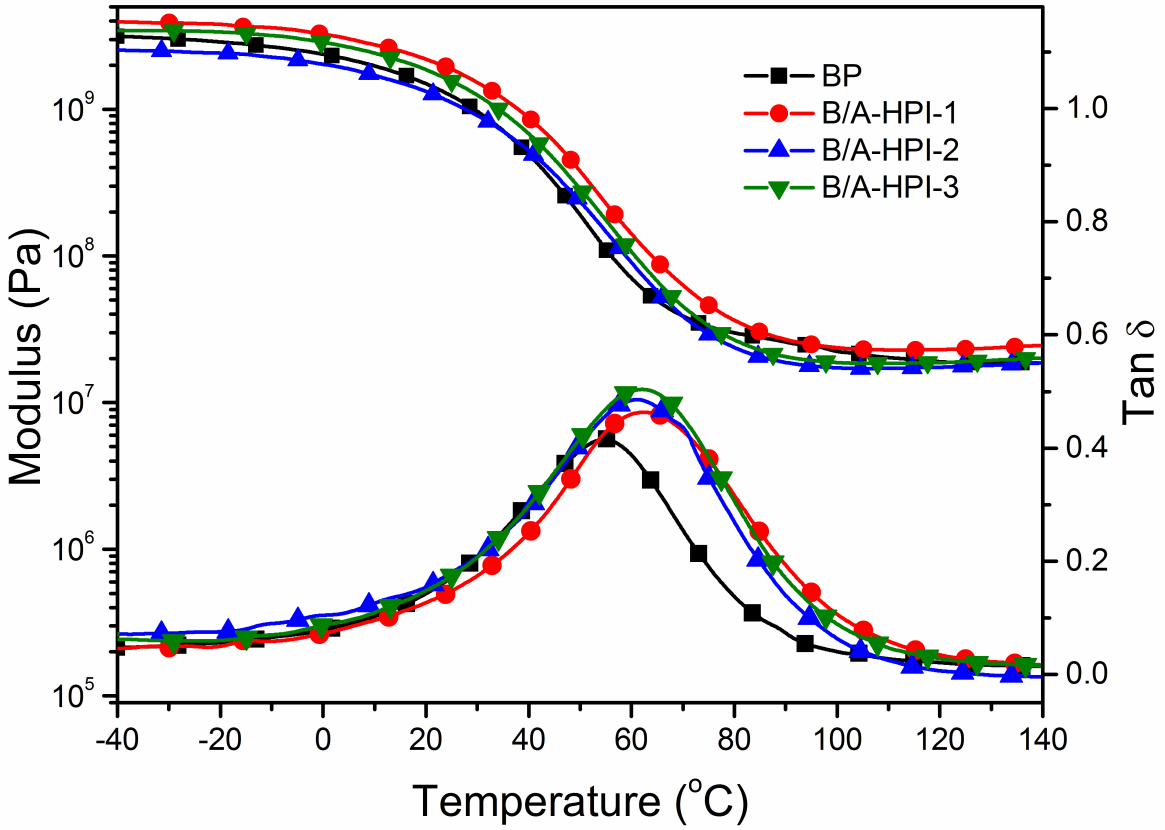


Figure 14. DMTA curves of the UV cured EB605 films initiated by BP and B/A-HPIs at a frequency of 10 Hz and a heating rate of 10 °C·min^{-1} in the range of -50~140 °C.

Summary

- Thiol-ene click reactions can be conveniently and successfully used to prepare hyperbranched polymeric photoinitiators end-capped with benzophenone (BP) and tertiary amine moieties.

- Sulfur-containing hyperbranched polymeric photoinitiators, BP-HPEAs and B/A-HPIs, have a high photoinitiating efficiency and a good compatibility with EB605.

Acknowledgement

Faculty	Graduates	Funding
Prof. Wenfang Shi	Han Xie Lihua Hu Yong Zhang	National Natural Science Foundation of China (No. 50973100)

Thank You !