Comparison between Polymerization Techniques for synthesis of Energetic Thermoplastic Elastomers

Khalifa Al-Kaabi and Albert Van Reenen

Department for Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

khalifa1@eim.ae

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Lower cost solutions for 21st Century IM/EM Requirements

Outlines of presentation

- Introduction
  - Insensitive munitions (IM)
  - GAP binder
- Polymerization methods
  - **Redox polymerization techniques**
  - **Nitroxide-mediated process**
  - **Dithiocarbamate inferiter**
  - **Energetic thermoplastic polyurethane**
- Conclusions
- Acknowledgments

Insensitive munitions (IM)

- High vulnerability of ammunitions and development of insensitive munitions (IM).

- Requirements for Insensitive munitions criteria
  - high performance, low sensitivity, environmental acceptance, and reasonable costs.

- Applied of polymeric materials (inert/energetic) in low sensitivity munitions (binders/plasticizers).

M. B. G. Frankel, L.R.; Flanagan, J.E. , *Propulsion and Power*, **8**, 560 (1992)

Redox polymerization techniques

- Cerium (IV) ions used in synthesis PMMA-b-PGA copolymers based on using redox polymerization.
- Thermal analysis shows compatibility of two different segments from DSC thermal analysis
- Tensile mechanical test shows considerable decrease in tensile stress and increase in elongation values with the increase of PGA content in the block copolymer

Arslan H., Eroglu M., Hazer B., European Polymer Journal, 2001. vol. 37, p. 581-585.

Nitroxide-mediated process

- Preparation and characterization of PS-b-PGA and PVAc-b-PGA block copolymers.
- Thermal analysis showed that PGA is forming miscible and compatible block with PS and PVAc.

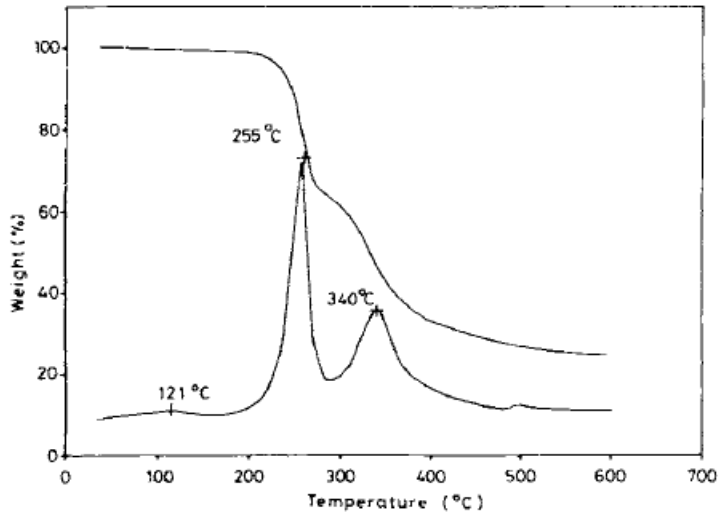


Figure 6 TGA curves of PVAc-*b*-PGA block copolymer (run no. 5 in Table II).

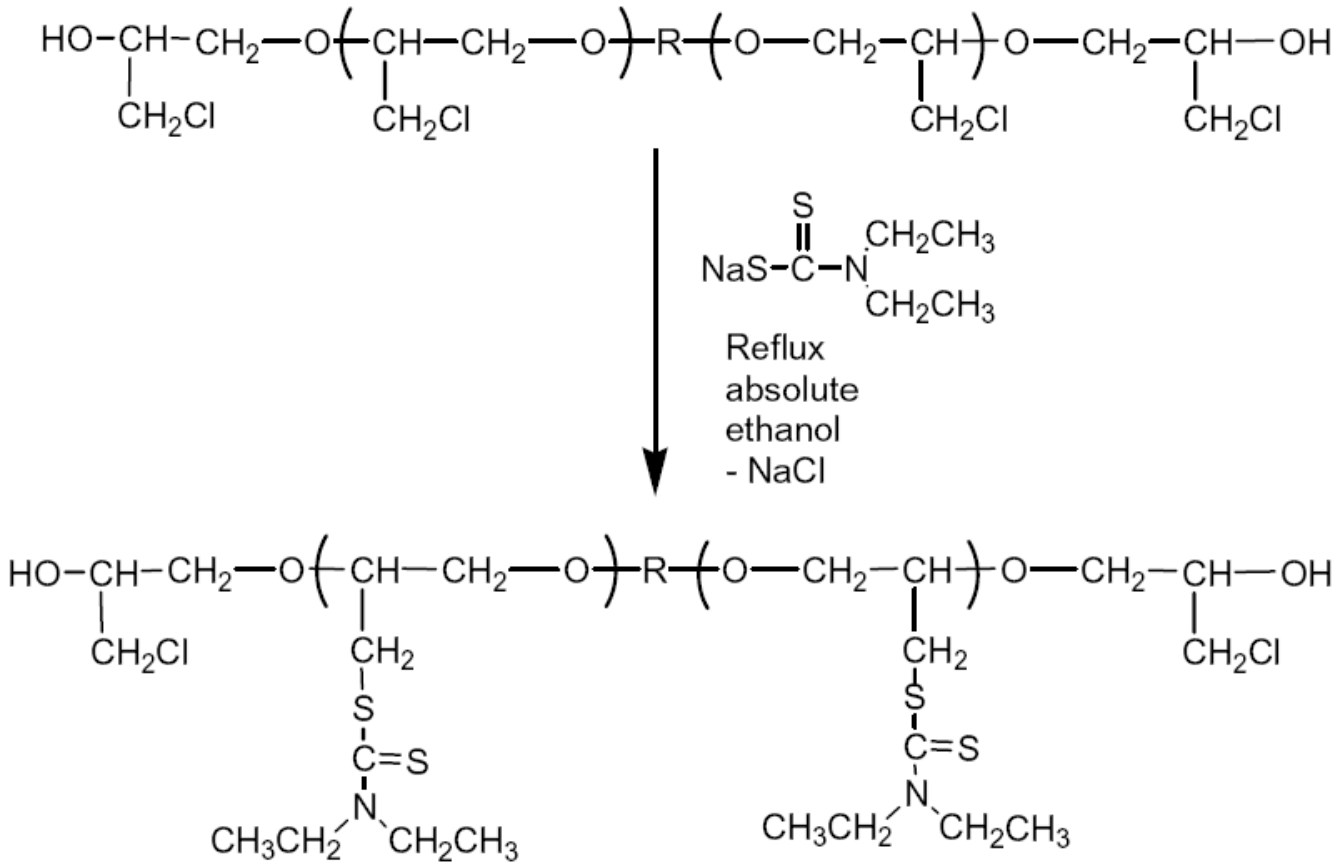
Eroglu M., Hazer B., Guven O., Baysal B., Journal of Applied polymer science, 1996. Vol. 60.

Controlled/living Free radical polymerization

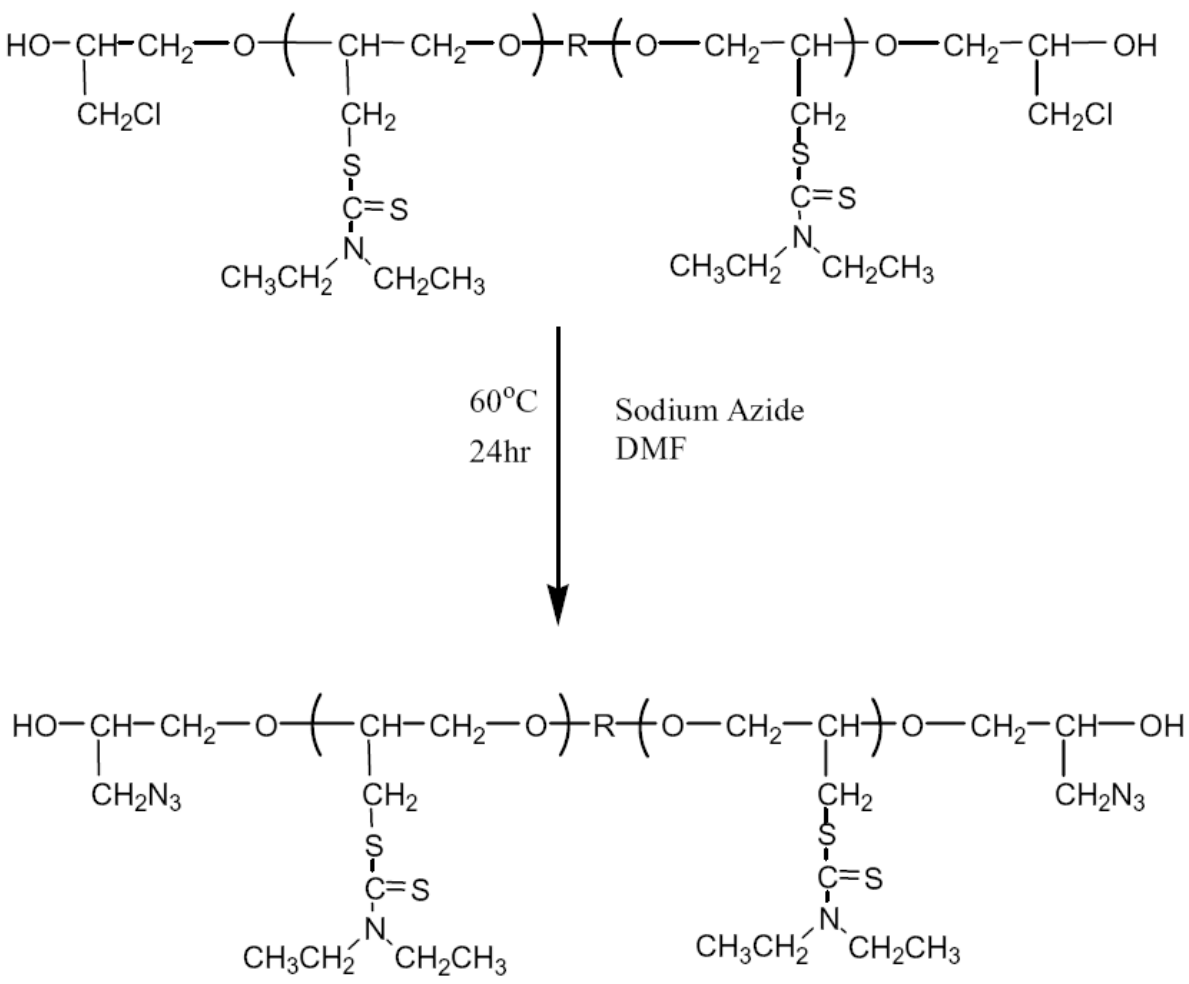
- Characteristics of Living/Controlled radical polymerization.
- Requirements for living/controlled free radical polymerization.
- Living/controlled radical polymerization methods
  - **Dithiocarbamate iniferters**
  - Atom transfer radical polymerization (ATRP)
  - Reversible addition-fragmentation transfer (RAFT)

-Anton Sebenik, *Progress Polymer Science*, 23, 875 (1998).

-Greeme Moad, Ezio Rizzardo, and San H. Thang, *Aust. Journal Chemistry*, 58, 379 (2005).



Scheme 6.7 The reaction of hydroxyl terminated poly(epichlorohydrin) with sodium diethyl dithiocarbamate to produce *N,N*-diethyl dithiocarbamate-poly(epichlorohydrin) (R is 1, 4-butanediol).



Scheme 6.8 Proposed reaction mechanism for the synthesis of *N,N*-diethyl dithiocarbamate-glycidyl azide polymer photoinitiators by the reaction of *N,N*-diethyl dithiocarbamate-poly(epichlorohydrin) photoinitiators with sodium azide in DMF (R is 1, 4-butanediol).

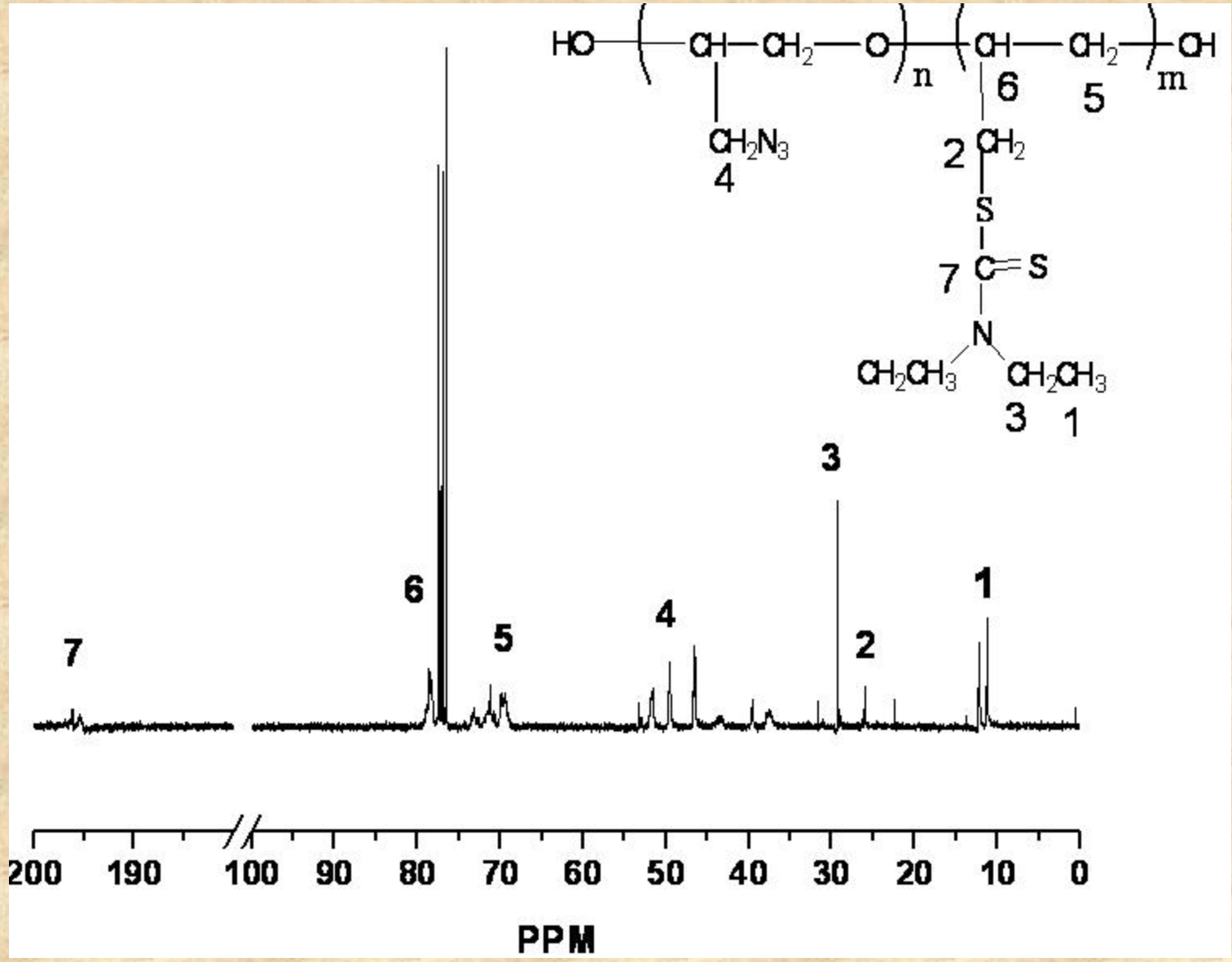


Figure.1. ^{13}C NMR($CDCl_3$) spectrum of GAP Macro-initiators.

Alkaabi K. and Albert van Reenen, 38th International ICT-Conference, Karlsruhe, Germany, 26-29 June, 2007.

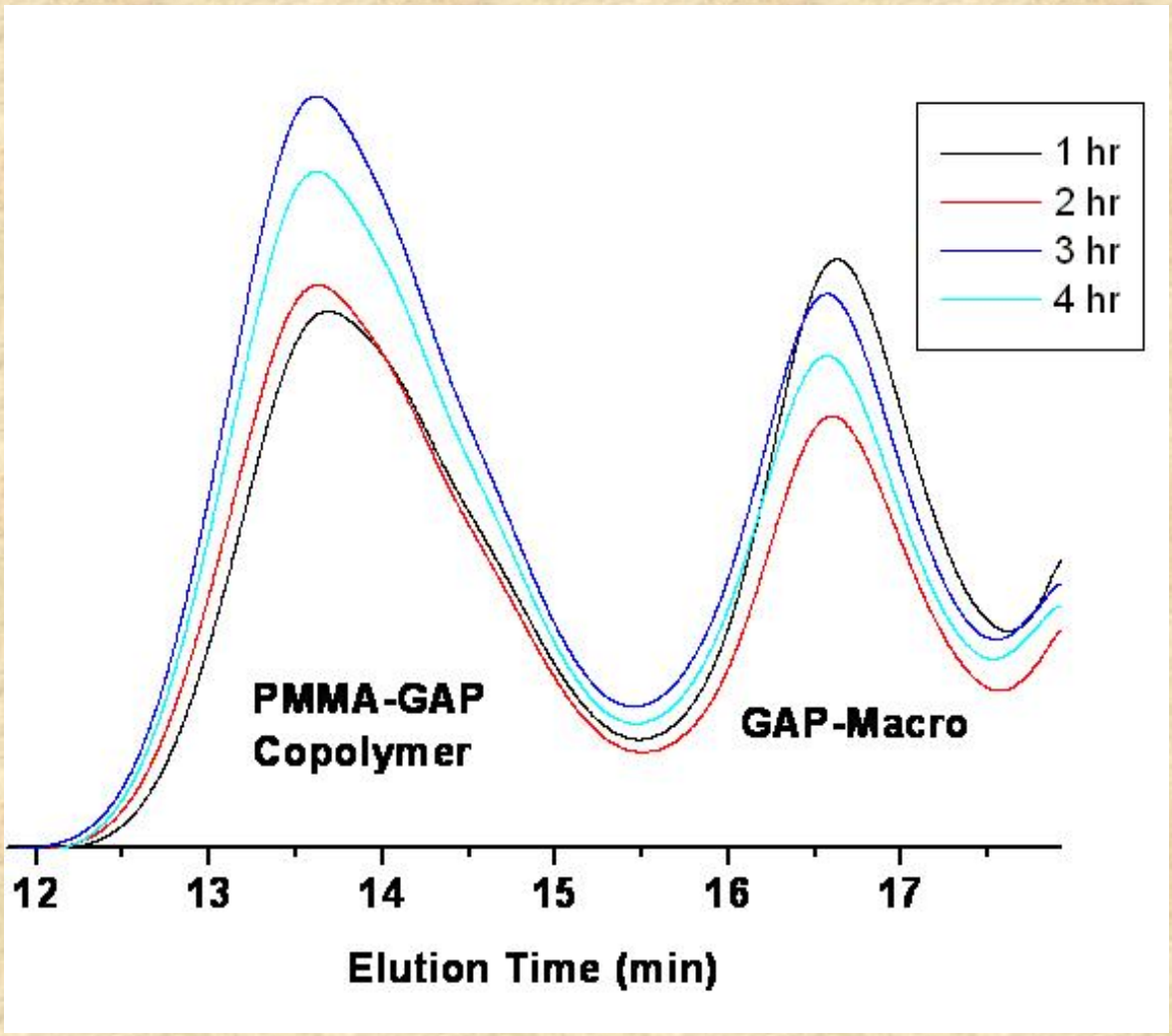


Figure 2. GPC profiles of photopolymerization of methyl methacrylate in toluene initiated by GAP-Macroinitiator.

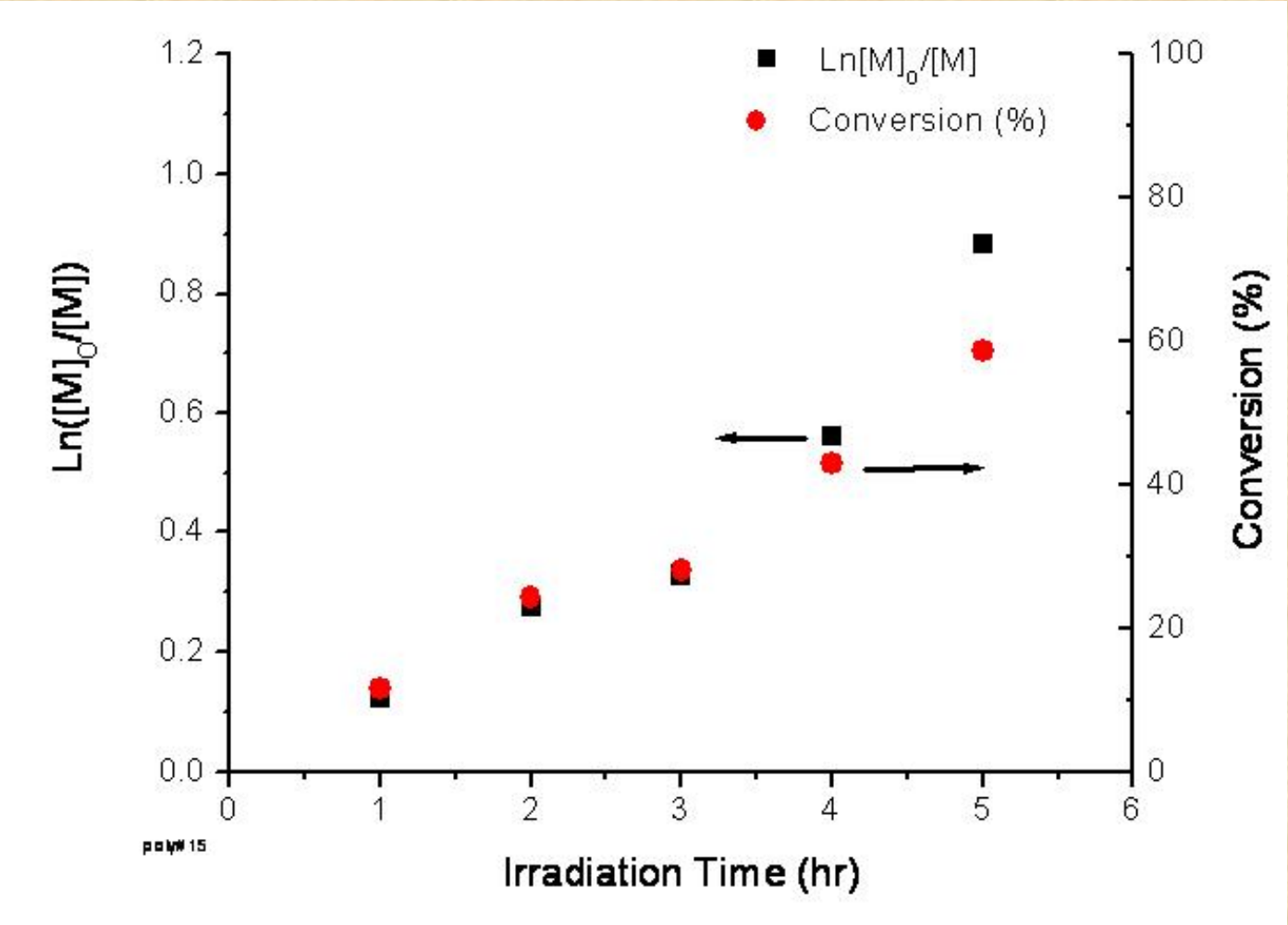


Figure 3 First-order time- conversion plots for the photopolymerization of MMA in toluene initiated by GAP-g-DDC ([GAP-g-DDC]/ [MMA] =0.014).

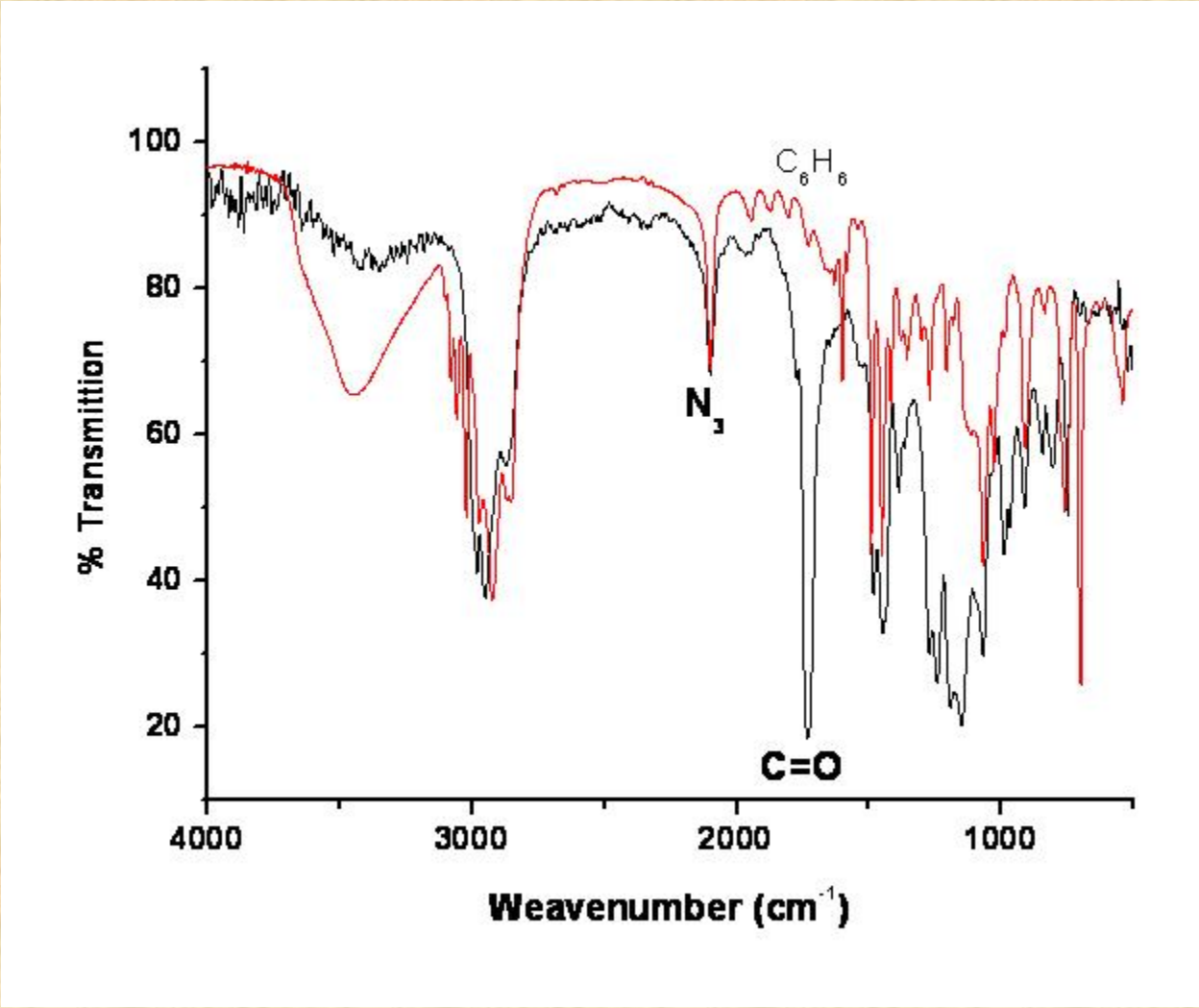


Figure 4 FT-IR spectrum of PMMA-g-GAP (black line) and PSt-g-GAP (red line) copolymer.

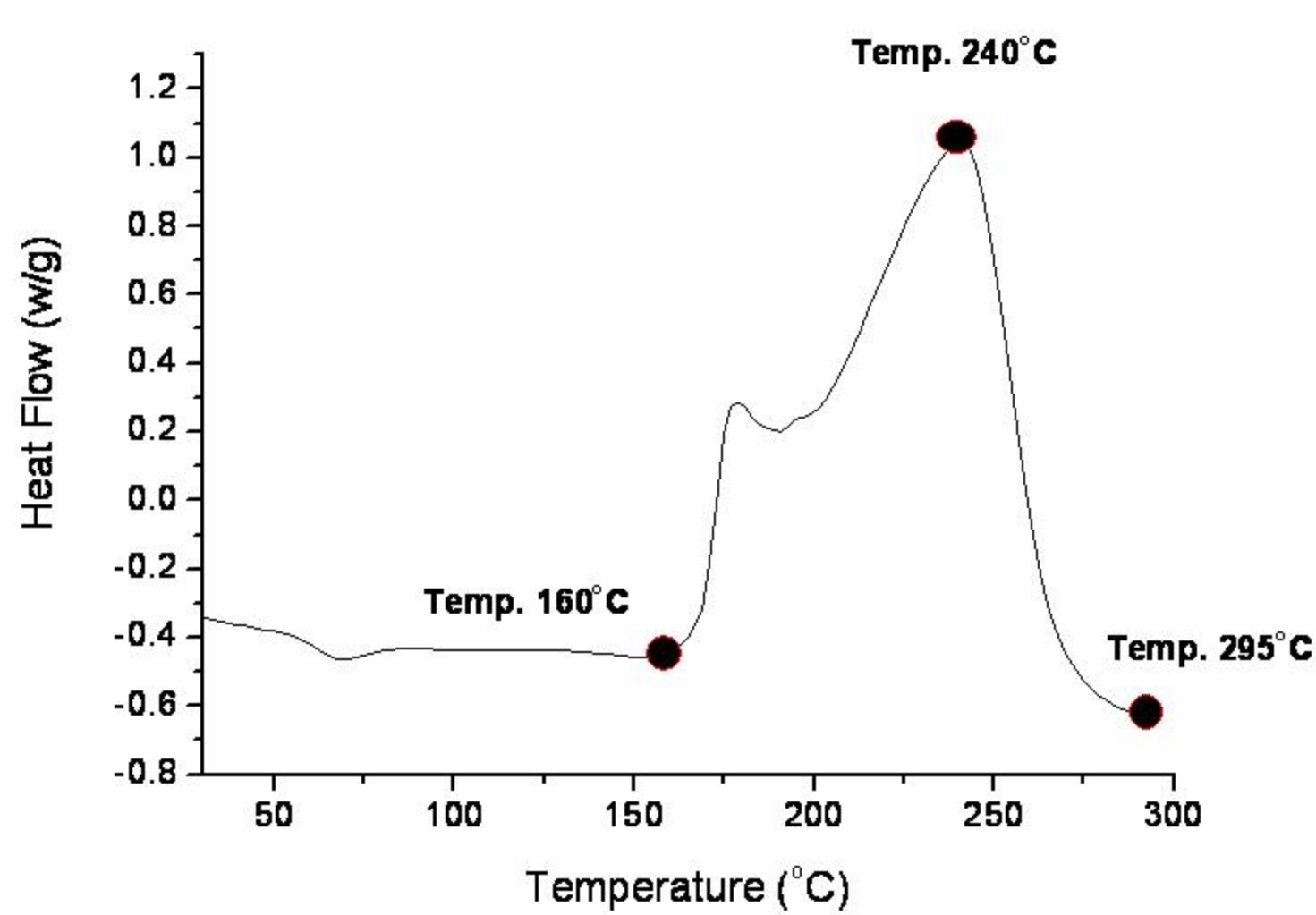
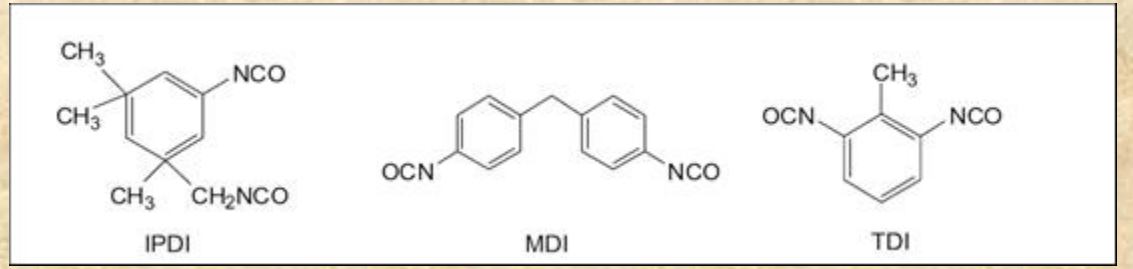


Figure 5 DSC traces of PMMA-g-GAP copolymer (1.159 mg).

Alkaabi K. and Albert van Reenen, Jornal of Applied polymer scince, 2009.

Energetic thermoplastic polyurethane

- Thermoplastic polyurethane (TPU) is an (ABA)n or AB type thermoplastic elastomer.
- The constitution of A and B in this linear block copolymer and their sequence length play an important role in the physical properties of TPEs.
- The chemical structure of hard and soft segments and their ratio form an integral part of molecular design for an optimum TPE binder.



Polymerization techniques

Manufacturing

Rest of ingredients
(stability and compatibility)

CONCLUSIONS

- Energetic thermoplastic elastomers and polymerization techniques.
- Polymerization techniques affect the final properties.
- Polymeric binder based on using economical polymerization techniques and invariable properties (physical and chemical) is the main requirements for 21st century IM.

ACKNOWLEDGEMENTS

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