Reactivity Ratio Determination of Newly Synthesized Copolymers from Glycidyl Methacrylate and Tetrahydrofurfuryl Acrylate
(Penentuan Nisbah Kereaktifan Kopolimer Baru yang Disintesis daripada Glisidil Metakrilat dan Tetrahidrofurfuril Akrilat)

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ABSTRACT
Copolymers from different feed compositions of glycidyl methacrylate (GMA) and tetrahydrofurfuryl acrylate (THFA) were synthesized using free radical polymerization in toluene solution at 70±1°C using benzoyl peroxide (BPO) as initiator. The polymers were characterized by $^1$H NMR, $^{13}$C NMR and DEPT spectroscopic techniques. The copolymer compositions were determined using $^1$H NMR analysis. Reactivity ratios for GMA and THFA were determined by the Kelen-Tudos, Tidwell-Mortimer and error-in-variables model methods. The results showed that all these copolymerizations were strictly linear systems describable by the Mayo-Lewis equation based on the terminal model and that accurate reactivity ratio data can be obtained.

Keywords: Copolymerization; glycidyl methacrylate; reactivity ratios; tetrahydrofurfuryl acrylate

INTRODUCTION
Acrylic copolymers have achieved prime importance in various avenues of industrial application (Adhikari & Majumdar 2004; Arica et al. 2004; Bayramoglu et al. 2003; Hall et al. 1996; Malmsten & Larsson 2000; Nino et al. 2004; Pérez et al. 2006; Yang et al. 1999). GMA, which is of interest to us, is used to provide epoxy functionalization to our acrylate resin. However, due to the similarity in the constituent units of copolymers containing acrylate and methacrylate monomers, it is difficult to determine their compositions by normal analytical techniques (Bakhshi et al. 2009; Grassie et al. 1965). UV and IR spectroscopic methods are not very helpful and other methods such as gas-liquid chromatography, radiometric and isotopic analysis are time consuming. The determination of copolymer composition by NMR techniques would then be a better option since this technique has many advantages not only for the calculation of composition and sequence distribution of copolymers but also for the estimation of tacticity (Espinosa et al. 2001; Ghi et al. 1999; Schaefer 1969).

The precise determination of monomer reactivity ratios (MRR) would serve as a useful tool towards the accurate estimation of copolymer composition, understanding their properties and utility for tailoring copolymers with desired physicomechanical properties. Typically, reactivity ratios are estimated using the instantaneous copolymer composition equation, based on low conversion yield copolymer composition data, otherwise known as the Mayo-Lewis model. It has been suggested that, for a given pair of monomers 1 and 2 (in this case corresponding to GMA and THFA, respectively), the instantaneous copolymer composition is a function of instantaneous feed only (Mayo & Lewis 1944). The estimation method used to determine the reactivity ratios from the Mayo-Lewis model however varies from linear least squares techniques (LLS) to non-linear (NLLS). In this paper, both methods are compared and considered for any potential improvement gained in MRR estimation. The present paper reports the synthesis, NMR spectroscopic characterization and determination of reactivity ratios $r_1$ and $r_2$ for copolymers of glycidyl methacrylate (GMA) with tetrahydrofurfuryl acrylate (THFA), respectively.

EXPERIMENTAL DETAILS
GMA (Merck) and THFA (Aldrich) were purified by distillation under reduced pressure. BPO (Merck) was recrystallized from ethanol and dried under vacuum at
CONCLUSION

A series of copolymers of poly(GMA-co-THFA) were prepared using BPO as initiator in toluene at 70±1°C. 1H- and 13C-NMR spectroscopies reveal the presence of both monomeric constituents in the copolymer. The copolymer compositions were determined by the 1H-NMR method. The MRR were obtained by the KT, TM and EVM methods. Of the three, the EVM method provides the most accurate MRR estimates because it has the smallest ICR area (which leads to a higher confidence in the point estimates). The values of $r_1$ and $r_2$ are less than unity indicating that the system gives rise to an azetropic polymerization and a strong tendency to alternation.

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REFERENCES


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