

# Influence of n-alkyl ester groups on efficiency of crosslinking for methacrylate monomers copolymerized with EGDMA: Experiments and Monte Carlo simulations of reaction kinetics and sol–gel structure

Amit K. Tripathi <sup>a</sup>, Macaul L. Neenan <sup>b</sup>, Donald C. Sundberg <sup>a</sup>, John G. Tsavalas <sup>a, b, \*</sup>

<sup>a</sup> Nanostructured Polymers Research Center, Materials Science Program, University of New Hampshire, Durham, NH 03824, United States

<sup>b</sup> Department of Chemistry, University of New Hampshire, Durham, NH 03824, United States

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## ABSTRACT

We present the results of applying a computationally efficient Monte Carlo (MC) method to simulate the reaction kinetics and molecular architecture development during free-radical, bulk copolymerizations of a homologous series of methacrylate monomers with ethylene glycol dimethacrylate. The overall objective of the work was to determine the extent to which the ester side chains of the methacrylate monomers hinder chain-end radical propagation reactions through the pendent vinyl groups of the crosslinking monomer. We have determined that this steric hindrance is quite significant and increases with ester side chain length. This is expressed by a reduced reactivity parameter,  $\Psi_{C,X}$ , that is different for each monomer–crosslinker pair. With this single kinetic parameter adjustment, the MC model was able to effectively predict the reaction kinetics, gel points, and sol–gel fractions throughout the entire reactions, including, to a limited extent, the solvent swelling ratio of the gel for two different levels of crosslinker.

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## 1. Introduction

In free-radical polymerization reactions, divinyl monomers like ethylene glycol dimethacrylate (EGDMA) and divinyl benzene (DVB) are frequently used as functional comonomers to produce infinite network gels of macroscopic dimensions [1]. The cross-linked polymers produced from these copolymerization reactions are used in a variety of elastomeric applications and other areas such as fiber optics coatings, photolithography, dental restorative materials, contact lenses, and other biomaterials [2]. Various polymer properties like viscosity, swelling with a solvent, and elasticity are dependent on the crosslinking density of the gel polymer and the gel fraction.

Free-radical polymerization reactions involving long chain-long chain interactions are highly chain-length dependent, such as in the well-known ‘Trommsdorff gel effect’ for diffusion controlled

free-radical terminations [3–5]. For the copolymerization reactions with a crosslinker monomer like EGDMA, the impact of diffusion is even greater due to involvement of radicals which are part of high molecular weight species. Also the crosslinking reactions themselves involve propagation through pendent vinyl groups which would be part of polymer chains, further emphasizing the role of diffusion. Complete information on the crosslinking reaction cannot be obtained without the inclusion of diffusion controlled reactions. Various deterministic simulation approaches like differential equations and numerical fractionation have been utilized over the last two decades to simulate the free-radical copolymerization with such divinyl monomers [6–11]. However, the diffusional element in the polymerization reaction in those cases has largely been ignored. Sparingly few, such as those who employ the method of moments [12], have properly addressed the incorporation of this important element into the overall mechanism.

Another approach for simulating the copolymerization reaction with a crosslinker monomer is the Monte Carlo method [13,14] where information regarding every reactive species in the simulation volume is easily accessible. By utilizing this approach, the

\* Corresponding author. Department of Chemistry, University of New Hampshire, Durham, NH 03824, United States.

E-mail address: [John.Tsavalas@unh.edu](mailto:John.Tsavalas@unh.edu) (J.G. Tsavalas).

reaction rates including chain-length dependent terms for each possible reaction can be easily calculated making this simulation method well suited to simulating free-radical polymerization. Hamzehlou et al. [15] nicely applied MC methods to simulate DVB copolymerization reactions with styrene, yet their simulations only considered chemical kinetics and did not include the impact of diffusion. Previously we presented a complete Monte Carlo simulation of the copolymerization of EGDMA with methyl methacrylate (MMA) with the inclusion of diffusion controlled termination and crosslinking reactions for copolymerization in the pre- and post-gel regime [16]. The simulation results were validated with available experimental data including reaction kinetics and various polymer properties like the gel point, the sol–gel content at various conversions, the crosslinking density and the swelling ratio in a particular solvent. It was shown that an accurate kinetics and molecular structure can be estimated from simulation by incorporating an appropriate factor signifying the reduction of reactivity of the pendent vinyl group from EGDMA. While this factor represents the reduced reactivity of the pendent group due to rotational and conformational restrictions (not translational which is accounted for by translational diffusion terms), these restrictions might not be completely independent of the surrounding environment along the polymer backbone.

Here we probed this question to determine whether this reduced reactivity is exclusively derived from the nature of the crosslinking monomer, and the fact that it is now part of a polymer chain, or to what extent the structure of the adjacent monomers in the chain surrounding the divinyl monomer play a role in influencing chain end radical propagation reactions through those pendent vinyl groups. With the MMA-co-EGDMA system as a basis, where the methyl ester is somewhat removed from the vicinity of the pendent vinyl group of EGDMA, we explored a homologous series of methacrylates with a range of *n*-alkyl ester chain lengths up to hexyl methacrylate (HMA). The latter has an ester side chain of similar dimensions compared to the EGDMA pendent group.

## 2. Simulation details

The copolymerization of a vinyl monomer like methyl methacrylate (MMA) with a divinyl crosslinker monomer like EGDMA can be thought of as a ter-polymerization reaction. In such reactions,

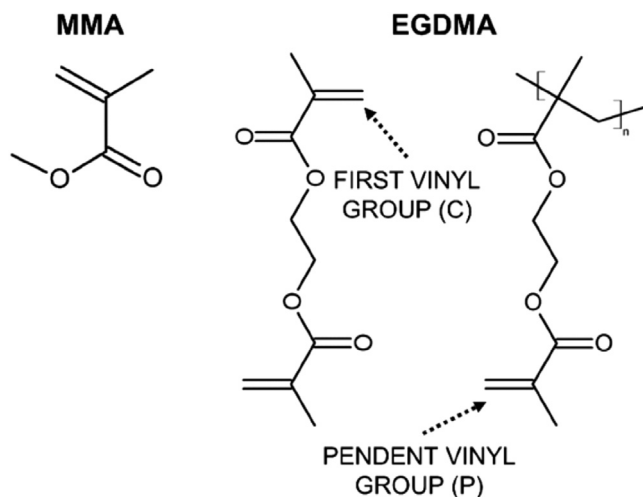


Fig. 1. Available reactive vinyl groups in copolymerization of MMA with EGDMA crosslinker.

beside the monomeric reactive vinyl groups, the radical propagation can also occur with the pendent vinyl groups of crosslinker monomers which are already incorporated into a polymer chain (Fig. 1). In these reactions, along with the propagating chain-end radicals (linear or branched), there would also be free-radicals on the polymer backbone (mid-chain radicals; different than those produced by chain-transfer to polymer, common in acrylate polymerization). Due to greater rotational and conformational restrictions, these mid-chain radicals will have very different reactivities when compared to chain-end radicals.

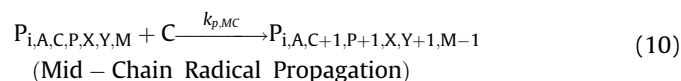
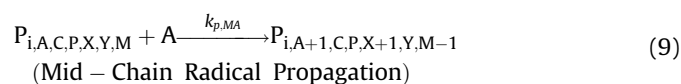
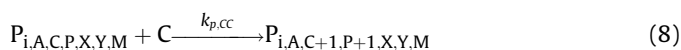
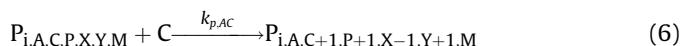
### 2.1. Kinetic scheme

A polymer chain (with or without radicals; linear or crosslinked) produced during the copolymerization reaction of a vinyl monomer with EGDMA divinyl monomer can be represented as  $P_{i,A,C,P,X,Y,M}$  where subscripts *i*, *A*, *C*, *P*, *X*, *Y* and *M* represent a polymer index, total number of noncrosslinker units (like MMA), total number of EGDMA units, available pendent groups, chain end radical from noncrosslinker, chain end radicals from EGDMA monomers and mid-chain radicals, respectively. The subscripts *i*, *A*, *C*, *P*, *X*, *Y* and *M* are non-negative integers for obvious reasons. Using this nomenclature, the kinetic scheme for copolymerization of any methacrylate monomer with the crosslinker EGDMA can be described as.

#### 2.1.1. Initiation



#### 2.1.2. Propagation



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