



Stereoselective propagation in free radical polymerization of acrylamides: A DFT study



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ABSTRACT

In this study stereospecific free radical polymerization of *N,N*-alkylamides [*N,N*-dimethylacrylamide (DMAAm), *N*-methyl-*N*-phenylacrylamide (MphAAm) and *N,N*-diphenylacrylamide (DPAAm)] is investigated with density functional theory (DFT) calculations. Model propagation reactions at dimeric stage are used to elucidate the effect of substituent bulkiness, temperature and solvent polarity on stereospecific addition modes. In calculations all the monomers favor gauche conformation in their pro-meso and pro-racemo additions in general. The DFT calculations have reproduced the stereospecificity seen in these monomers. The implicit solvent calculations performed with IEFPCM have further refined the quantitative agreement. The calculations of DMAAm in solvents of different polarity (toluene, THF, chloroform and 2-propanol) have successfully reproduced the experimental trend both qualitatively and quantitatively. Tartrate molecules as stereospecificity inducer in DMAAm are considered and the experimentally observed change in stereospecificity from iso to syn in their presence have been elucidated by modeling the possible orientations of transition states in the propagation step. The favorable stereospecific addition modes are explained via interplay between the steric effects and the hydrogen bonding interactions.

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1. Introduction

Free radical polymerization (FRP) is one of the most important and widely used techniques to obtain polymers due to its applicability to wide range of monomers, relative cheapness and the easiness of the process. Tacticity control in free radical polymerization is an important topic since it affects the properties of end-products such as the mechanical strength, the melting and glass transition temperatures or solubility. However, most of the polymers produced by free-radical polymerization lack tacticity and are mostly atactic polymers. The structure of the propagating polymer chains makes it hard to control the stereospecific addition mode of the polymerization reaction because the sp^2 planar propagating radical species do not efficiently control the addition mode as compared to ionic or coordination polymerizations. Experimental works reveal that in order to control the stereospecificity of free radical polymerization, reaction conditions such as temperature, solvent, monomer/initiator ratio or stereospecificity additives should be regulated since they all affect the tacticity of the polymer.

Quantum mechanical calculations have been employed in polymer area as well as in other applications of chemistry. Especially, many studies have helped in understanding the steps of reactions

by concentrating on kinetics as well as thermodynamics of FRP reactions [1–12]. Calculations also give chance to investigate the steric and electronic effects of substituents, solvent, temperature and stereospecific additives on the energy barriers of the different stages of the reactions individually. Quantum chemical calculations is also an advantageous way to study the tacticity phenomenon comprehensively because it enables to explore all of the possible addition modes of the monomer to the propagating radical together, which is the origin of stereoselective propagation in these polymeric systems. The difference between the activation barriers for the addition to the diastereotopic faces of the radical with the propagating chains determines the selectivity of the propagation reaction. In the literature, there are many studies that successfully use quantum mechanical procedures to investigate stereoselectivity in the propagation step of free radical polymerization of various polymers [13–16]. These studies have accounted on the modes of addition that control tacticity and the effects of substituents on them. In one of those studies [13], the tacticities of methylacrylate (MA) and methyl methacrylate (MMA) have also been modeled with density functional theory using B3LYP/6-31+G(d) basis set for calculating the reaction barriers for the iso and syn additions. The reported results have shown qualitative agreement with the experimental finding that both of the monomers favor syndiotactic addition over the isotactic one. Another study [14] on the solvent effect of methyl methacrylate in its stereospecific polymerization have revealed that using methanol and $(CF_3)_3COH$ as a solvent

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has yielded syndiotactic rich polymer due to the hydrogen bond formation between the carbonyl oxygen of the monomer and alcohol's hydrogen in the transition structures. Stabilizing effect of the $(CF_3)_3COH$ on the transition structures has been attributed to the relatively higher steric effect of the solvent molecules and stronger hydrogen bond formation as compared to methanol as solvent. In another study, the tacticity of *N*-isopropylacrylamide (NIPAAm) was modeled to understand the solvent effect [15].

Experimental studies revealed that free radical polymerization of *N,N*-dimethylacrylamide (DMAAm) gives isotactic rich polymer in various reaction conditions. For example Hirano et al. obtained isotactic rich polymer in toluene at low temperatures [17]. They found that at $-80^\circ C$ poly(DMAAm) has m/r ratio of 73/27. However, it was found that syndiotactic rich polymer is favored in the case of *N*-methyl-*N*-phenylacrylamide (MphAAm) [18] and *N,N*-diphenylacrylamide (DPAAm) [18,19] in similar experimental conditions.

In this study, we focus on the tacticity of a series of *N,N*-alkylacrylamide monomers in their free radical polymerization reactions. We have investigated all the possible addition modes of various acrylamides in their propagation step of free radical polymerization to account on their stereospecificity with quantum chemical tools. For this purpose, three different substituted acrylamides, *N,N*-dimethylacrylamide (DMAAm), *N*-methyl-*N*-phenylacrylamide (MphAAm) and *N,N*-diphenylacrylamide (DPAAm) have been studied (Fig. 1). The effects of substituent, solvent and temperature on the stereospecific addition modes in free radical polymerization of these aforementioned acrylamides have been elucidated. Experiments on the free radical polymerization of DMAAm by Hirano et al. have shown a change from isotactic to syndiotactic products when tartrate molecules are present in the reaction medium. In order to induce stereospecificity in free radical polymerization, Lewis acids and bases have been utilized many times [20–22]. Various phosphoric acid esters have been tested on NIPAAm and hydrogen bonding interaction between monomer–phosphate complexes were found to induce stereospecificity [22]. Another study also investigated the stereospecific polymerization of *N*-vinylacetamide by using Lewis acids and alcohol compounds in which they found the importance of hydrogen bonding formation between additives and monomers such that the tartrates, a diol, induced isotacticity in toluene at low temperatures [23]. The effect of 3,5-dimethylpyridine *N*-oxide as an isotacticity inducer in various solvents in FRP of *N*-methylacrylamide has been tested and shown [24]. In all these and unreferenced examples, the main procedure is to add ingredients that form H-bondings with monomer and/or polymeric fragments to induce synthesis of stereospecific polymers.

In this study we aim to model the propagation steps of free radical polymerization of a series of acrylamide monomers (Fig. 1) to elucidate the reasons of stereospecificity in their different addition modes.

2. Methodology

In this study, all calculations were performed with density functional theory by using Gaussian 09 program package [25]. Studying polymerization reactions require a reasonable method that is both cost effective and reliable because of the large size of the polymer systems that need a model to mimic the real system [26]. DFT is widely used in a huge number of computational studies involving similar systems, involving radical addition reactions; propagations, homopolymerizations, β -scission and chain transfer in free radical reactions [10,27–35].

B3LYP method with 6-31+G(d,p) basis set was chosen for geometry optimizations of monomers, radicals and transition state structures in the gas phase. Even though this methodology is less

accurate in prediction of electronic energies, it is generally accepted that B3LYP methods provide excellent low cost performance especially in geometries. Non-systematic errors in DFT have also been reported in the literature [3,36]. However, these studies are concerned with predicting absolute rate constants, which are very sensitive to prediction of accurate activation energies and pre-exponential factors. Since we are not dealing with absolute rate constants in this study but rather interested in comparing the relative energy barriers of the two modes of addition in propagation reaction of a monomer with it radical (one gives rise to a meso and the other to racemo addition), B3LYP functional set which is known to yield satisfactory results especially for the geometries was used [9,10,13,34]. In the literature, energetics were recalculated by single point calculations with some other functionals such as M06X, BMK and MPW by making use of B3LYP geometries, based on the general agreement that B3LYP methods provide satisfactory low-cost performance for structure optimizations [10,13,32,37–39]. In this study, a series of benchmark calculations are performed with BMK [40], MPWB1K [41], M05-2X [42], M06-2X [43] and MP2 at 6-311+G(3df,2p) level of theory at the B3LYP/6-31+G(d,p) geometries. Those functionals are chosen since BMK is reported to have good performance in kinetics of radical reactions in general [11,31,44,45], MPWB1K in describing H-bondings and accurate thermochemical results [11,41,46], M06-2X [47] in thermochemistry and M05-2X [42,48] in describing radical species.

IRC calculations were also carried out to ensure that the correct transition state structures were found on the potential energy surface of propagation reactions. All possible conformers of the species have been searched carefully to ensure that the global minimum structures have been obtained and the B3LYP vibrational frequencies were used to characterize species as minima or transition states.

To include the solvent effect on the stereospecific addition mode of the propagating radical to the monomer, implicit solvation methodology is used without re-optimization of the gas phase geometries. For this purpose, the integral equation formalism model (IEF-PCM) which is one of the continuum solvation methods that include polar environment effects is utilized. In this method solvent is characterized by its dielectric constant ϵ and treated as a continuum medium around the solvated species [49]. This model is a self-consistent reaction field method which treats the solvent as a continuum of uniform dielectric constant by creating the solute cavity as a set of overlapping spheres. IEF-PCM methodology has been used to model the solvent effect on free radical polymerization of systems including various acrylates [10,14,47].

In order to understand the temperature and solvent effects on the addition modes, the Boltzmann distribution is used to obtain the relative population of transition state structures for pro-meso and pro-racemo additions as in literature [50]. In cases where there are multiple transition states within almost 2 kcal/mol relative energy, these are included in the distribution calculations as well. The results from these calculations are used to compare the with the experimental meso (m) and racemo (r) dyads ratio, including the level of theory calculations. In the solvent and temperature effect calculations only the most stable transition state has been used.

In the discussion that follows, all the energies in the gas phase are free energies at $25^\circ C$ and in solvent electronic energies unless otherwise stated. The zero of the reaction coordinate will be considered as the point of reactants at infinite separation and the radical addition barriers will be calculated accordingly.

3. Results and discussion

In free radical polymerization, the propagating radical attacks the monomer, breaks the C=C double bond of the monomer which

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