MATHEMATICAL MODELING AND PARAMETER ESTIMATION FOR 1,6-HEXANEDIOL DIACRYLATE PHOTOPOLYMERIZATION WITH BIFUNCTIONAL INITIATOR

KAVEH ABDI

A dynamic model is proposed for photopolymerization of 1,6-hexanediol diacrylate (HDDA) using bifunctional initiator bis-acylphosphine oxide (BAPO). The proposed model accounts for branching, backbiting and cyclization reactions, and for diffusion-dependent reaction rates during photopolymerization. The proposed model contains 40 adjustable kinetic and free-volume parameters. Experimental data available for parameter estimation are vinyl group conversions obtained using a variety of light intensities and exposure times, and monomer conversions for three experiments. Systematic parameter ranking and estimation is used to evaluate the influence of phenomena included in the model on the quality of the fit. Estimation and ranking results indicate that branching, backbiting, and cyclization reactions have important influences on conversion. Reactions involving two large molecules and propagation reactions become diffusion-dependent. Incorporating diffusion-dependent initiator efficiency results in improved model predictions.

FREE-RADICAL POLYMERIZATION KINETICS OF 2-(DIMETHYLAMINO)ETHYL METHACRYLATE STIMULI-RESPONSIVE POLYMERS

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The homopolymer and copolymers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) are triggered by external stimuli (e.g., pH, temperature, ionic strength and carbon dioxide (CO_2)). There are numerous applications of these polymers such as coatings, drug delivery, gene delivery, tissue engineering and polymeric surfactants. The development of the polymers have been widely investigated for stimuli-responsiveness; however, the reaction mechanisms and kinetics have not been fully explored for process and product development. In this work, the solution free radical polymerization of DMAEMA is investigated in organic, organic-aqueous and aqueous solvents.

The propagation rate coefficient, k_p, of DMAEMA is probed by the pulsed laser polymerization – size exclusion chromatography (PLP-SEC) technique. Bulk and solution homopolymerizations are conducted in 1-butanol (BuOH), ethanol (EtOH) and EtOH/H_2O mixture. When 50 wt% DMAEMA was present in BuOH, the k_p decreased slightly from the bulk values (7%). A similar trend was observed in EtOH, where a further decrease occurred in the polar solvent (12%).

However, a 75/25 wt% EtOH/H_2O mixture had a k_p value very close to the bulk k_p. In addition, the k_p values of DMAEMA/EtOH mixtures varied little with monomer concentration. The propagation kinetics of DMAEMA showed little sensitivity to solvent choice. The Mark-Houwink parameters of poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) were established in THF and 1 mmol·L^{-1} DMF solution.

The synthesis of the homopolymer and copolymers, which are conducted by conventional free-radical and reversible-deactivation radical polymerizations, are complicated by monomer ionizability and propensity to undergo hydrolysis when the monomer is dissolved in aqueous or aqueous-alcohol solutions. Therefore, a better understanding of DMAEMA radical polymerization kinetics is needed to facilitate efficient polymer synthesis and aid product development efforts. The aqueous polymerization kinetics of DMAEMA is explored with an in-situ nuclear magnetic resonance (NMR) spectroscopy technique. The pH and temperatures are varied and rate of monomer hydrolysis is measured without the occurrence of polymerization. One of the hydrolysis products, methacrylic acid (MAA), contains a reactive double bond, which leads to poly(MAA-co-DMAEMA) copolymer formation rather than PDMAEMA homopolymer at pH 10.1. The polymerization of fully ionized monomer (pH 1) proceeds to approximately full conversion under the same reaction conditions. The co- and terpolymerization kinetics of protonated DMAEMA, unprotonated DMAEMA and deprotonated MAA must be quantified and PREDICI® has been used to develop a mechanistic model of the partially-ionized copolymerization system.

NON-AQUEOUS GRAPHENE BASED SUPERCAPACITORS

MATTHEW HAWRYLOW

In this study, graphene hydrogels formed through the reduction of a graphene oxide (GO) dispersion in water are used as electrodes in a supercapacitor. Graphene has a theoretical surface area of 2600 m^2/g and using graphene gels formed of reduced graphene oxide a high surface area of 1300m^2/g was achieved to give high energy storage. Combining these electrodes with a non-aqueous electrolyte with a wide electrochemical window even higher energy storage can be achieved. 1, 3- ethyl methylimidazolium Tetrafluoroborate is used as the ionic liquid in this study for its combination of high ionic conductivity of 16 mS/cm and wide electrochemical window of 3.6V.

Characterization of these components was done with particular focus on the physical characterization of the graphene hydrogels. These gels can be used as flexible electrodes for use in flexible devices, so more in-depth characterization of their material properties is needed. In addition, the full supercapacitor device was tested under various strains to determine the effect of compression on device performance. The compression of these devices has a significant impact on the internal resistance of the device and thus the performance, particularly, the capacitance. Higher compression resulted in better capacitance at high current density while lower compression gave better performance at lower current densities. Devices with capacitances reaching 160 F/g were constructed at a compression 67% and current density of 1A/g. Further research is being conducted into modifying the electrolyte used by the addition polymer to improve the physical properties of the gel electrode and the performance under strain.

CORONAVIRUS PLEOMORPHISM

MONA KANSO

The coronavirus is always idealized as a spherical capsid with radially protruding spikes. However, histologically, in the tissues of infected patients, capsids in cross section are elliptical, and only sometimes spherical [**B.W. Neuman**, *J Virol*, **80**, 7918 (2006)]. This capsid ellipticity implies that coronaviruses are oblate or prolate or both. We call this diversity of shapes, *pleomorphism*. Recently, the rotational diffusivity of the spherical coronavirus in suspension was calculated, from first principles, using general rigid bead-rod theory [**M.A. Kanso**, *Phys Fluids*, **32**, 113101 (2020)]. We did so by beading the spherical capsid, and then also by replacing each of its bulbous spikes with a single bead. In this paper, we use energy minimization for the spreading of the spikes, charged identically, over the oblate or prolate capsids. We use general rigid bead-rod theory to explore the role of such coronavirus cross-sectional ellipticity on its rotational diffusivity, the transport property around which its cell attachment revolves. We learn that coronavirus ellipticity drastically decreases its rotational diffusivity, be it oblate or prolate.

NOISE SENSITIVITY REDUCTION IN LOW-POWER MULTI HIGH GAIN OBSERVERS USING LOW-PASS FILTERS

MOEIN MOUSAVI

Low-power multi high gain observers (LP MHGO) are proven to be effective in reducing the peaking of state estimation of nonlinear systems to an arbitrarily small magnitude. Moreover, they reduce the sensitivity of estimates to measurement noise. They also relax the numerical implementation problem of high gain observers by using gains powered up to the order of 2 instead of n. In this work, we aim to further improve the noise sensitivity of these observers by employing low-pass filters in the observer dynamics. The main results establish the convergence of the estimation error to zero with an arbitrarily small decay rate in the absence of noise, as well as an input to state stability feature when the noise is present. We also demonstrate in the linear case that the proposed observer improves the upper bound on the estimates. Simulation results compare the performance of the proposed observer with similar works and show the effectiveness of the proposed method.

SIMPLIFYING THE MODIFICATION OF CELLULOSE NANOCRYSTALS BY POLYMER ADSORPTION

AMANDA RIGG

Cellulose nanocrystals (CNCs) are attractive reinforcing agents for polymer nanocomposites, due their excellent mechanical properties, natural abundance, and sustainable value proposition. Applications are limited, as the hydrophilicity of the CNC surface prevents effective dispersion in hydrophobic polymer matrices. Grafting hydrophobic polymers to the CNC surface has facilitated the formation of CNC-reinforced polymer nanocomposites, while introducing complexity and cost. This work aims to simplify the modification of CNCs by substituting polymer grafting in favour of non-covalent techniques. We demonstrate that cationic copolymers can electrostatically adsorb to anionic CNCs and form stable CNC dispersions in non-polar solvents. These results demonstrate that non-covalent modifications have the potential to improve the economic feasibility of CNC-reinforced polymer nanocomposites.

USING GAIN CONDITIONING TO ADDRESS COLLINEARITY IN LINEAR MODEL PREDICTIVE CONTROL

STEPHEN SANBORN

Linear model predictive control is used in a wide variety of process industries. Model predictive controllers rely on optimizers to calculate adjustments in manipulated variables to ensure that operating constraints are obeyed and that controlled variables are maintained near their setpoints. There is significant industrial interest in preventing erratic behaviour of model predictive controllers caused by imperfect models with ill-conditioned gain matrices. Currently, control practitioners use time-consuming processes based on the relative gain array or singular-value thresholding to condition their gain matrices to prevent degraded controller performance.

In the proposed new approach, we extend a widely-used parameter ranking algorithm to identify manipulated variables with highly correlated influence. A linear optimization algorithm is then used to find optimal gain adjustments to condition the gain matrix. To test the effectiveness of the proposed algorithm, we investigate 3 case studies based on a fluid catalytic cracker.