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Kinetic modeling of the copolymerization of acrylic acid and trimethylolpropane triacrylate over pre and post-gelation periods

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ABSTRACT

A kinetic model based on method of moments, balance of species and sequences and numerical fractionation was developed for acrylic acid – TMPTA copolymerization. Solution copolymerizations of acrylic acid with trimethylolpropane triacrylate (TMPTA), initiated by sodium persulfate, were carried out at 55 °C. The model was compared with a different approach from literature and validated with experimental data from present work. It was a found an acrylic acid propagation rate coefficient at 6000 L mol^{-1} s^{-1} for the studied conditions. The simulations were successfully performed with a maximum number of generations in the range 3–5. The model was able to provide fair predictions for the studied experiments and additional information about the dead polymer chains formed, such as gel fraction, molecular weight distribution and concentration of cyclic chains.

1. Introduction

Smart hydrogels represent a class of polymeric materials which have affinity with water and respond to one or more stimuli. The physico-chemical properties of a hydrogel are responsible for its sensibility to variables such as pH and temperature. Due to their resemblance to living tissues, hydrogels have been studied towards their application in human health. The ability of molecules of different sizes to diffuse into (drug loading) and out of (drug release) hydrogels allows dry or swollen polymeric networks to be used as drug delivery systems for many routes of administration [1]. For example, hydrogels for oral drug delivery are made pH sensitive to respond against the pH change in the gastrointestinal tract and can provide non-invasive delivery system to some intravenous drugs such as insulin [2,3]. Smart hydrogels made of acrylic acid contain carboxylic acid groups, which has the useful characteristic of being pH responsive, on the other hand, its production process is complex and not fully understood. An important feature of acrylic acid polymerization in aqueous solution is that the propagation rate coefficient is strongly affected by the reaction medium. Kabanov et al. [4] found a specific non-linear dependence of the overall rate of polymerization on the pH and attributed this behavior to the formation of ion pairs by ionized terminal units of growing chains and cations present. Cutié et al. [5] studied the kinetic modeling of acrylic acid polymerization in reaction media with different neutralization degrees. They found a maximum in activation energy for the polymerization reaction at a 100% neutralized medium and suggested that a change of mechanism might be taking place

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Symbology

D_i	pendant double bond of type '*i*'
I	initiator
k_d	rate coefficient of initiator decomposition
k_{fr}	rate coefficient of chain transfer to polymer
k_h	rate coefficient of hydrogen abstraction
k_I	pseudo-kinetic constant of monomer initiation
k_{ID}	pseudo-kinetic rate coefficient of PDBs initiation
k_{Ij}	rate coefficient of initiation of specie or polymer group '*j*'
k_P	pseudo-kinetic rate coefficient of monomer propagation
k_{PD}	pseudo-kinetic rate coefficient of PDBs propagation
k_{pij}	rate coefficient of propagation of monomer '*j*' with radical '*i*'
k_t	rate coefficient of termination by combination
L_r	sequence of '*r*' monomeric units connecting a radical center to a D_4
M_i	monomer of type '*i*'
N_{Di}	number of moles of pendant double bonds of type '*i*'
N_I	number of moles of initiator
N_{Mi}	number of moles of type '*i*' monomer
N_{Ri}	number of moles of radicals of type '*i*'
Q_i	Moment of order '*i*' for all dead polymers
R_o	primary radical
$R_{r,i}$	polymer radical of length '*r*' and type '*i*'
S	inert specie
T_r	sequence of '*r*' monomeric units connecting a radical center to a D_3
U	monomeric unit
V	reaction volume
Y_i	moment of order '*i*' for all radicals
Z	inhibitor
ρ_M	density of the monomer
ρ_U	density of the monomeric unit

at this point. Lacik et al. [6] studied the pulsed laser polymerization of non-ionized acrylic acid and observed that a maximum in the rate coefficient of propagation (k_p) occurs at small acrylic acid concentrations, around 3 wt%. The addition of a multivinyl monomer to the reaction mixture is made in order to produce gel. Kinetic studies of acrylic acid copolymerization with trimethylolpropane triacrylate (TMPTA) are reported in literature [7,8]. Gonçalves et al. [9] have also studied this system and developed a model based on population balance in terms of generation function to represent the process. Recent modeling techniques such as balance of sequences [10,11] allows one to obtain more information about the microstructure of the polymer networks, such as the number of cyclic chains contained in the final product. It is also possible to estimate the molecular weight distribution (MWD) through the use of the numerical fractionation technique [12] in crosslinking copolymerizations. The present work aims to describe an approach for the copolymerization of acrylic acid/ TMPTA based on the method of moments, numerical fractionation and balance of sequences. Experimental data were obtained in laboratory in order to validate de model.

2. Experimental

2.1. Materials

Acrylic Acid of 99% purity, Trimethylolpropane Triacrylate (TMPTA) with 600 ppm monomethyl ether hydroquinone as inhibitor, sodium persulfate (NPS) of 98% purity were purchased from Sigma–Aldrich and used as received. The inhibitors were not removed from the reagents because water strongly absorbs oxygen, which also acts as an inhibitor in the reaction. Even after purge with N_2, considerable induction periods were observed, hence, it was decided to consider the inhibition mechanism in the kinetic approach.

2.2. Feed conditions

Aqueous solution polymerizations were carried out in 10 mL glass tubes at 55 °C. The TMPTA amounts used in the experiments are listed in Table 1.

Y_C is the molar fraction of crosslinker (TMPTA) in the mixture Acrylic acid + TMPTA. The initial molar ratio initiator/carbon–carbon double bonds (Y_I) was set at 0.0008. In the present work, sodium persulfate was used as initiator and the ratio