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Route to co-acrylic modified alkyd resins via a controlled polymerization technique

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ABSTRACT

Acrylic modified alkyds were achieved from sequential polymerization of acrylic monomers in the presence of alkyd macro-RAFT agents. Macro-RAFT agents were reached by end-capping a soya-based alkyd with a carboxy-functional trithiocarbonate. The resulting material was then utilized as the RAFT chain transfer agent to affix acrylic blocks onto the alkyd backbone. Butyl acrylate, ethyl acrylate, methyl methacrylate, and ethyl methacrylate were the acrylic monomers used to achieve the acrylic blocks both individually and in combination. The resulting materials were characterized by various analytical techniques including size-exclusion chromatography (SEC), Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. Size exclusion chromatography confirms the controlled nature of this approach to acrylated-alkyds and corroborates the NMR spectra that distinctly show the presence of acrylic blocks. Side reactions with the pendant fatty acids and the formation of homopolyacrylate are also distinguished from the analytical results, however, they are suppressed. Pseudo-first-order kinetics behavior and conversion versus molecular weight plots show that the RAFT-mediated reaction afforded a more controlled free radical process for the synthesis of acrylated-alkyd materials. Use of the alkyd macro-RAFT agent provided a new path to acrylated-alkyds that affords a more controlled way to tailor specific material properties.

1. Introduction

Alkyd resins have been used as coatings binders for almost a century [1]. This special class of polyesters is derived from naturally occurring oils, including soybean, sunflower, and linseed oils, polyols, and dibasic acids [2]. The challenge with alkyds is encountered by the hydrophobicity of the materials, which requires the need of organic solvents to reach application viscosities. Over the last 50 years, researchers have developed many ways to modify alkyd resins as emission regulations have tightened. The first modification made to alkyd resins was done with styrene over half a century ago [6]. Styrenated-alkyds afford reduced viscosity systems and require less solvent, however, their end-use applications are virtually limited to primers.

Another approach to lower VOC levels of alkyd formulations has been to incorporate acid-functional monomers into the polyester backbone. This is typically accomplished by reacting a completed alkyd with maleic anhydride [3] or monoglyceride reaction with carboxylic acid groups [4]. Yet another approach to achieve modified alkyds with increased hydrophilic groups is to modify the alkyds with a mixture of acrylic monomers to create a core/shell like morphology, where the acid containing acrylic phase protects and surrounds the alkyd core. This technique has been demonstrated through miniemulsion and traditional free radical polymerization routes [5–11]. These methods of modification have all resulted in improved hydrolytic stability of the parent alkyd, however, the control of these different processes is restricted by the limitations of the individual polymerization techniques. As stricter regulations on paint formulations continue to be enforced, new paths to achieve modified alkyds with precise control over molecular structures are desirable.

In the past decade, polymer chemists have turned to controlled free radical polymerization (CFRP) processes, also commonly referred to as "living" free radical polymerization. There are three classes of CFRP techniques that are used most often, including reversible-addition fragmentation chain transfer (RAFT) polymerization, nitroxide mediated polymerization (NMP), and atom transfer radical polymerization (ATRP) [15,16]. These three processes have received the most attention because of their versatility in fabricating complex materials with controlled molecular weights, controlled block locations, and narrow molecular weight distributions [14–29]. Of these three living polymerization methods, RAFT has been reported to be the most diverse in monomer choices [12]. Effective RAFT polymerizations are accomplished in the presence of a chain-transfer agent, which introduces a functional group that actively participates in a reversible

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addition-fragmentation step [30,31]. These chain transfer agents, often referred to as RAFT agents, can be classified as trithiocarbonates, dithioesters, xanthates, and dithiocarbamates [12–15]. Use of RAFT agents are very reaction specific, thus commercial availability of these materials is limited. Synthesis of these materials can require complicated syntheses and purification steps; however, facile routes to these materials have been reported [14].

The operating mechanism for RAFT-mediated polymerizations is comparable to traditional free radical chemistry. The main difference is the chain-transfer and equilibrium steps in the RAFT process along with the basic initiation, propagation, and termination steps [13]. A general mechanism for RAFT-mediated polymerization is shown in Scheme 1. The addition of the RAFT chain transfer agent helps minimize radical–radical termination using molar ratios of CTA to initiator between 5:1 and 10:1 [13]. This in turn produces polymers with controlled molecular weights and narrow polydispersities. In addition, these RAFT chain transfer agents can be used to control block locations. When conducting RAFT polymerizations, the most important factor for successful reactions is careful selection of the proper CTA/monomer combination [12].

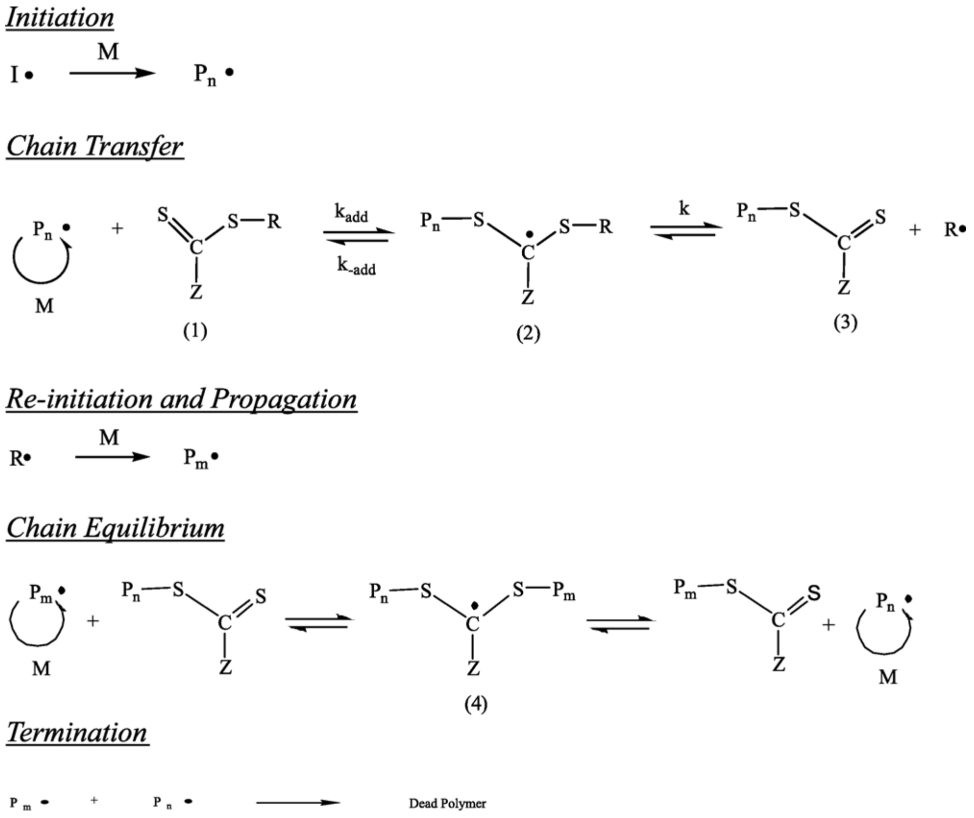
The introduction of CTAs with specific functionalities has encouraged the formation of macro-RAFT agents. A macro-RAFT agent is best described as a polymer that contains specific functional groups that are capable of participating in a living radical polymerization process [32–35]. These materials can be achieved by modifying end-functionalized polymer chains with living radical polymerization initiators, then using this novel material as a macroinitiator in the corresponding "living" polymerization process. The concept of a macroinitiator serves as a building block for the development of well controlled multi-segmented polymers [34]. The idea of these macro-RAFT agents is very attractive as materials with more well-defined microstructures are needed. The macroinitiators are being used for different purposes, such as compatibilization of two dissimilar polymeric materials [34] and a means to well-organized polymeric hybrid materials [29]. In a previous study, the synthesis of an alkyd macro-RAFT initiator achieved by esterification of a hydroxy-functional medium oil soya-based alkyd with a carboxy-functional trithiocarbonate was reported [36]. The novel macro-RAFT agent was used to polymerize different acrylic monomers in a RAFT mediated process. The resulting acrylic–alkyd materials exhibited controlled molecular weights and pseudo first-order kinetics that is commonly observed in RAFT polymerizations.

The demonstration of constructing acrylic–alkyd materials using RAFT polymerization techniques has established an original way to achieve acrylated-alkyd resins with precise control for use in coatings resins [36]. The purpose of this study was to investigate the kinetics of the raft mediated polymerization to substantiate the claim of a controlled polymerization mechanism and to show the effectiveness of the alkyd macro-RAFT agents as building blocks for multi-segmented acrylic–alkyd copolymers. The macro-RAFT agent was synthesized followed by the sequential polymerization of acrylic monomers in the presence of the macro-RAFT agent. Kinetic data is reported on the single monomer systems. Different sequences of monomers were used to demonstrate the wide range of applicability for this technique. The acrylated-alkyds were characterized by gel-permeation chromatography (GPC) and proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy.

2. Experimental

2.1. Materials

Soybean oil was obtained from Cargill. Glycerol, phthalic anhydride (PA), lithium hydroxide monohydrate, xylene, 1-dodecane



Scheme 1. Mechanism of the RAFT process.