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Thermal and mechanical characterization of poly(vinyl chloride)-b-poly(butyl acrylate)-b-poly(vinyl chloride) obtained by single electron transfer – degenerative chain transfer living radical polymerization in water

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Abstract

This work reports the synthesis of several copolymers of poly(vinyl chloride)-b-poly(*n*-butyl acrylate)-b-Poly(vinyl chloride) prepared by single electron transfer/degenerative chain transfer mediated living radical polymerization (SET-DTLRP) in a two step process: first, a bifunctional macroinitiator of α,ω-di(iodo)poly(butyl acrylate) [α,ω-di(iodo)PBA] was synthesized by SET-DTLRP in water at 30 °C. The obtained macroinitiator was further reinitiated also by SET-DTLRP leading to the formation of the desired product. Several copolymers were synthesized in a 5L pilot reactor with different molecular weights and relative amounts of PBA and PVC. The possibility of synthesizing flexible materials made of PVC without using normal free plasticizes is extremely important for the industry. After processing the materials in a two-roll mill laboratorial equipment, the block copolymers were characterized concerning thermal and mechanical. The materials characterized in this study were prepared in a 5L pilot reactor under similar conditions to be used in industrial scale.

Keywords: Living radical polymerization; Block copolymers; Thermal properties

1. Introduction

The appearance of new polymerization strategies based on LRP brought new possibilities of preparing tailor made polymers in large scale production. The main processes reported in the literature are via metal catalyzed LRP [1,2], stable free-radical polymerization (SFRP) [3], reversible addition-fragmentation polymerization (RAFT) [4] and degenerative transfer

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[5]. These methodologies which allow to prepare tailor made polymers are often uninteresting and risky due to the fact that they typically involve conditions, which are not easily implemented on industrial large production or involve significant investments on its scaling up.

Percec and co-authors discovered a new methodology known as single-electron-transfer/degenerative-chain-transfer living radical polymerization (SET-DTLRP) that is capable of synthesis under controlled/living mechanism activated [6,7] and non-activated monomers [8–13]. This method provides the reversible activation–deactivation step required to accomplish LRP by a combination of competitive single-electron transfer (SET) and degenerative chain transfer (DT) mechanisms. Apart from the outstanding scientific achievement obtained with this technique considering the features provided by the SET-DTLRP, the possibility of being carried out in industrial scale production is foreseeable due to its moderate reaction conditions. Previous studies demonstrated the possibility of preparing flexible copolymers of PBA and PVC in small scale reactors [14,15], behaving as single materials without phase separation. This new material is a potential replacement for some flexible PVC applications, which are being subjected to strong restrictions [16] due to the migration phenomena of the typical plasticizers.

In this work an important insight has been made in the influence of the copolymer composition in the final product performance. The copolymers presented in this work were synthesized in a 5L stainless pilot reactor and were characterized by size exclusion chromatography with multiple detectors (TriSEC), dynamic mechanical thermal analysis (DMTA) and nuclear magnetic resonance (NMR).

2. Experimental section

2.1. Materials

Tetrahydrofuran HPLC-grade uninhibited, sand, alumina oxide, iodoform (99%), sodium dithionate (85%), sodium bicarbonate (99%) and BA were purchased from Sigma–Aldrich. BA was purified through a basic Al_2O_3 column. Polystyrene standards were purchased from Polymer Laboratories. Hydroxypropyl methylcellulose – Methocel F50 (MF50) was purchased from Dow Chemical Company. Partial hydrolyzed poly(vinyl alcohol) (PVA) was purchased from Syntomer. VC was purchased from ShinEtsu and used as received. The PVC suspension grade ($M_n = 91120$, $M_w/M_w = 1.9$, $K_v = 79$) used as standard for stress–strain curves was kindly given by Cires SA.

2.2. Synthesis of the α,ω-di(iodo)polyBA macroinitiator

The α,ω-di(iodo)polyBAs were synthesized in a 5L reactor by SET-DTLRP of PBA initiated with iodoform in H_2O at 30 °C according to the procedure described in the literature [17]. Macroinitiators with different molecular weight were synthesized for further reinitiation (Table 1). The DMTA of the different PBAs prepared indicate a glass transition temperature (T_g) of −43 °C.

2.3. Typical procedure to synthesize the block copolymer PVC-b-PBA-b-PVC by the SET-DTLRP of VC Initiated from α,ω-di(iodo)polyBA macroinitiator in a 5L reactor

The recipe described here is an example and was used for the following conditions: α,ω-di(iodo) PBA macroinitiator of $M_{n,\mathrm{TriSEC}} = 10895$ and $M_w/M_n = 2.1$. The target molecular weight for the block copolymer was around 110 k.

A 5L reactor was charged with 2.6 L of deionized water, 93.1 g of 3% water solution of PVA (1960 ppm w/w relative to VC), 64.4 g of 1.86% water solution MF50 (840 ppm w/w relative to VC) , 20.2 g of catalyst ($Na_2S_2O_4$ 0.116 mol), 158 g of macroinitiator (α,ω-di(iodo)PBA, 0.015 mol) and 1.77 g buffer ($NaHCO_3$, 0.021 mol). The reactor was closed and washed 5 times with nitrogen for 5 min. The vacuum was applied until −0.90 bar for 5 min. The reaction was carried out for 24 h (conversion 85%). A small sample was taken for TriSEC analysis ($M_{n,\mathrm{TriSEC}} = 97456$ and $M_w/M_n = 2.4$). The polymer was placed into a vacuum oven and dried until constant weight at room temperature.

2.4. Sample preparation for size exclusion chromatography

The procedure followed to prepare the sample for TriSEC analysis was given in a previous publication [18].

2.5. Characterization techniques

The chromatography parameters of the samples were determined using a HPSEC; Viscotek (Dual