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Physicochemical characterization of poly(*tert*-butyl acrylate-*b*-methyl methacrylate) prepared with atom transfer radical polymerization by inverse gas chromatography

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Abstract

Poly(*tert*-butyl acrylate) (P*t*BuA) was synthesized by atom transfer radical polymerization (ATRP) using methyl-2-bromo propionate (MBP) as an initiator in bulk at 80 °C. The successive ATRP of methyl methacrylate in diphenyl ether at 80 °C using previously obtained P*t*BuA as a macroinitiator led to formation of poly(*tert*-butyl acrylate-*b*-methyl methacrylate) (poly(*t*BuA-*b*-MMA)). The synthesized macroinitiator and block copolymer have controlled molecular weight and low polydispersity ($M_w/M_n < 1.2$). The block copolymer was characterized by gel permeation chromatography (GPC) and ^{1}H NMR. The retention diagrams of poly(*t*BuA-*b*-MMA) for some aliphatic esters and aromatic hydrocarbons were obtained using inverse gas chromatography (IGC) technique. The glass transition temperatures, T_gs of poly(*t*BuA-*b*-MMA) were determined by both differential scanning calorimeter (DSC) and IGC. It was observed that the block copolymer represents three T_gs at 50, 75 and 100 °C by IGC although it represents only one T_g at 71 °C by DSC. After the column was quenched from 180 to 0 °C, the T_g at 100 °C shifted to 105 °C however others did not change. Specific retention volumes, V_g^0 and the thermodynamical polymer–solvent interaction parameters such as Flory–Huggins, χ_{12}^{∞}, equation-of-state, χ_{12}^{*} and effective exchange energy, X_{eff} were found for all studied solvents. Partial molar heat of sorption, $\Delta\bar{H}_{1,sorp}$, partial molar heat of mixing, $\Delta\bar{H}_1^{\infty}$ and molar heat of vaporization, ΔH_v, were determined. In addition, the solubility parameter of the corresponding block copolymer, δ_2 was determined as 11.0 $(cal/cm^3)^{1/2}$ at 25 °C.

Keywords: Poly(*tert*-butyl acrylate-*b*-methyl methacrylate); ATRP; Inverse gas chromatography

1. Introduction

Controlled/'living' radical polymerization includes a group of radical polymerization techniques that has attracted much attention over the past decade for providing simple and robust routes to the synthesis of well-defined, low polydispersity polymers. Among them, atom transfer radical polymerization (ATRP) is one of the most widely used living free radical polymerization technique [1–3]. This technique has been applied to prepare block copolymers with well-controlled molecular weights and well-defined structures [4]. For many applications, block copolymers are suitable materials because they allow different combinations of monomers and properties to be applied. Block copolymers of acrylates and methacrylates are synthetically interesting because of the morphological, phase, and mechanical properties of such polymers. These properties are realized partly through the combination of a high glass transition temperature (T_g) block (methacrylate) with a softer, lower T_g block (acrylate).

Inverse gas chromatography (IGC) is a gas phase technique to determine the physicochemical properties of the sample in the chromatographic column [5,6]. The principles of IGC are same as a conventional gas chromatographic (GC) experiment [7]. IGC is an extension of conventional GC in which a solid material to be investigated is immobilized within a column. Liquids of known properties are then injected into the column containing the sample. The retention times of these trace amount liquids are used in determination of their interactions

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