

LIVING RADICAL BLOCK COPOLYMERIZATION OF STYRENE AND METHACRYLATES MONOMERS WITH SPECIAL PROPERTIES

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Introduction

The growing need to obtain new materials for specific uses and with great performance demands, led to the search for new ways for obtaining the control of the physical properties and the architecture of the polymers, combining the attributes of the living systems with the economical advantages of the radical polymerization ⁽¹⁾. Several techniques were developed in order to prepare block copolymers by living free radical techniques: Inefterter, by Otsu et al in 1992 ⁽²⁾, SFRP by Georges et al in 1993 ⁽³⁾, and ATRP by Sawamoto et al ⁽⁴⁾ and Matyjaszewski in 1995 ⁽⁵⁾.

Recently, the homopolymerization and block copolymerization of a liquid crystalline acrylate, using TEMPO, was accomplished ⁽⁶⁾.

In this presentation we present the results of the living radical block copolymerization of styrene and 11-[4-(4-(2methyl)-butoxy biphenyl)-benzyloxy]-undecyl methacrylate (I) and the poly(styrene-b-ethyl methacrylate-co-{4-[4-(4-nitrophenylazo)phenyloxy]butyloxy}methacrylate) (II) obtained by SFRP and ATRP techniques.

Results and Discussion

The methacrylate monomer (I) was prepared according to the literature ⁽⁷⁾. The homopolymerization and block copolymerization by SFRP was carried out in dioxane in sealed ampoules as described in the literature ⁽⁶⁾. The homo and block polymerization by ATRP was carried out as described in the literature ⁽⁸⁾.

Both techniques showed an increase in the homopolymer conversion of the methacrylate monomer and its molecular weight versus time. In the SFRP, the conversion increased from 45%(24h) to 65%(48h), the molecular weight increased from 4000(24h) to 9100(48h), the number of active chains decrease from 0.05(24h) to 0.03(48h). The molecular mass distribution increased from 1.4 (24h) to 1.6(48h). In the ATRP, the conversion increased from 50% (24h) to 63%(48h), the molecular weight increased from 5000(24h) to 8700(48h), the number of active chains decreased from 0.05 mol (24h) to 0.036(48h). The molar mass distribution increased from 1.5(24h) to 1.6(48h). These results indicate that some termination by transfer type reaction is taking place. The block copolymerization from the macroinitiators, prepared above, with styrene at 135°C yielded about 85% conversion for both techniques and an increase in the molecular weight from 9100 to 19100(48h), with molar mass distribution of 1.6 and no decrease in the number of active chains for the SFRP. In the ATRP, it was observed an increase in the molecular weight from 8700 to 15600(48h), with molar mass distribution of 1.9 and an increase in the number of active chains, which indicates homopolymer formation during this step.

In both techniques the homopolymer and its block copolymer displayed a Sc* phase at 81°C and 93°C respectively by DSC. The macroinitiator (PS-T) was obtained by living/controlled free radical polymerization, mediated by 2,2,6,6-tetramethylpiperidinoyloxy (TEMPO^{MR}), of styrene with dibenzoyl peroxide (BPO) with molar ratio of monomer to initiator of 46 and the molar ratio of BPO/TEMPOTM of 1.2. The polymerization was proceeded in sealed ampoule under vacuum for 24 h at 130 °C. The molecular mass of PS-T was 8314 Daltons and the molecular mass distributions was 1.33. The number of chains end-capping with TEMPO was 28 % (¹³C-NMR)

The block polymerization in bulk from macroinitiator PS-T with ethyl methacrylate (EMA) and {4-[4-(4-nitrophenylazo)phenyloxy]butyloxy}methacrylate (NPAPBM) (figure 1) with molar mass ratio of PS-T/EMA of 0.5% and molar ratio of NPAPBM/PS-T of 4,1 (copolymer 1) and 6,4 (copolymer 2) on feed. The reactions were carried out in sealed ampoules under vacuum at 130 °C for 110 h. These copolymers were dissolved in chloroform (2% w/v) and casting onto glass slides, to obtain thin films of 130 at 350 nm thickness. The optical anisotropy was induced by switching on the linearly polarized Ar⁺ beam at 514 nm with intensity of 0.32 mW/mm².² The measurements were performed at room temperature. The maximum birefringence reached at 200 s was for copolymer 1 and at second stage, the writing beam is switched off and the birefringence is observed to decrease in

200 s, and the value obtained for copolymer 2 was smaller. These results indicate that the writing process in this block system was slower for copolymer with less amounts of azoaromatic units.

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