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COPOLYMERIZATION OF POLY(PROPYLENE OXIDE) METHACRYLATE MACROMONOMER WITH STYRENE

H. T. Cunha and C. M. F. Oliveira*

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, C.P. 68525, Rio de Janeiro, Brazil

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Abstract—Graft copolymers of styrene and poly(propylene oxide) were prepared by reaction between styrene and a poly(propylene oxide) methacrylate macromonomer. The graft copolymers were characterized by i.r., GPC and ^{1}H-NMR and mechanical properties were examined. The effect of zinc chloride on the copolymerization was evaluated. The results showed a decrease in the incorporation of macromonomer in the graft copolymer when zinc chloride was added to the system. This effect has been attributed to interaction among chains of poly(propylene oxide) and the zinc chloride.

INTRODUCTION

The preparation of graft copolymers by use of macromonomers has been extensively investigated. This method provides an excellent means of designing graft copolymers of controlled structure [1–4]. Poly(propylene oxide) methacrylate, poly(ethylene oxide) methacrylate and poly(propylene oxide-b-ethylene oxide) methacrylate were used to prepare graft copolymers by reaction with methyl methacrylate. These syntheses were reported previously [5, 6]. Styrene has been copolymerized with various types of macromonomers [7–10]. The reaction of styrene with the poly(ethylene oxide) methacrylate is a very useful preparative method for an amphiphilic graft copolymer [11].

The addition of transition metal chloride to the copolymerization of polar monomers containing pendant nitrile or carbonyl groups has been characterized by an increase in the incorporation of the polar monomer to the structure of the copolymer. This effect has been attributed to the formation of a complex between the polar group of the monomer and the metal halide, resulting in an increase in the reactivity of the monomer [12, 13]. However, the addition of metal halide, e.g. zinc chloride on copolymerizations with macromonomers has not been studied.

The purpose of this work is to synthesize copolymer from the reaction of styrene with poly(propylene oxide) methacrylate and to observe the effect of the zinc chloride on the incorporation of the macromonomer in the copolymer.

EXPERIMENTAL PROCEDURES

Materials

Commercial bifunctional poly(propylene oxide) (PPO) ($M_n = 940$) (Dow Chemical, Brazil) was azeotropically dried in toluene. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Styrene was purified by removal of inhibitors and then distillation under reduced pressure as usual. Zinc chloride ($ZnCl_2$) was purified by drying under vacuum and stored in a desiccator. Toluene and benzene were dried by distillation over Na. Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride [14].

Synthesis of macromonomer

Poly(propylene oxide) methacrylate was prepared by reaction of methacryloyl chloride and PPO as previously described [14] in order to obtain the same proportion of monofunctional macromonomer with respect to methacrylate. According to these previous results, the product formed in the synthesis of macromonomer contained about 56% of unreacted polyoxide homopolymers, 41% of monomethacrylate and 3% of dimethacrylate macromonomers measured by high performance liquid chromatography [14].

Synthesis of copolymers

Styrene (30 g), macromonomer (16, 19, 24, and 33 wt%), benzene (22 ml) and AIBN (0.3 mol.%) were introduced into a polymerization apparatus under N_2 flow. Polymerization took place under reflux for 48 hr. Copolymer samples of different compositions were obtained by varying the macromonomer proportion and the monomer. The reactions with zinc chloride were carried out with a constant proportion of macromonomer/monomer. The resultant viscous solution was poured into a large excess of methanol and the white precipitate was filtered and vacuum dried. The copolymer was purified by reprecipitation from toluene into methanol, filtration and vacuum dried.

Characterization of the graft copolymers

Gel permeation chromatography (GPC) was performed with a Toyo-Soda high-speed liquid chromatography HLC-803A using toluene as eluent. The retention times were calibrated against polystyrene standards. Infrared spectra were recorded using a Perkin–Elmer 1720X FTIR spectrometer and ^{1}H-NMR spectra were obtained with a Varian Gemini 200 MHz.

Mechanical properties

Films of polystyrene (PS) and graft copolymers were cast from chloroform solutions (50% w/v) onto a glass surface at room temperature and the solvent was allowed to evaporate very slowly for 24 hr. The resulting films were dried under

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*To whom all correspondence should be addressed.

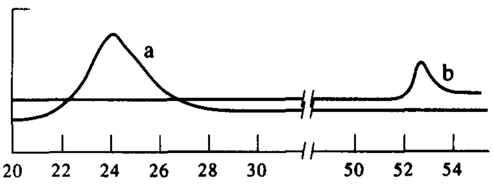

Fig. 1. GPC curves of the polymers. (a) Graft copolymer (M_n = 16,190, PPO content = 25 wt%); (b) macromonomer.

vacuum for 4 days. Stress–strain measurements were conducted on film strips of PS and graft copolymers by an Instron tester (crosshead speed, 0.1 cm/min) at 25 ± 1°C. Averages for five specimens are reported.

RESULTS AND DISCUSSION

The purity of the resulting graft copolymers was confirmed by GPC analysis indicating no peaks due to the free macromonomer. GPC characterization of the graft copolymer showed the absence of the macromonomer in the region which corresponds to the elution volume of 53 ml (Fig. 1). The molecular weights (M_n) of copolymers were in the range 10,000–25,000 with (M_w/M_n) between 1.5 and 2.0.

The formation of graft copolymer was confirmed from the i.r. spectrum (Fig. 2). The spectrum of PS [Fig. 2(a)] showed bands at 3030 cm^{-1} (aromatic C—H stretching), at 2950 cm^{-1} (symmetrical stretching band —CH_2—), among 1950 and 1800 cm^{-1} (overtone or combination bands of the monosubstituted aromatic), at 1600 cm^{-1} (C—C stretching within the ring) and at 760 and 700 cm^{-1} (out-of-plane C—H bending vibrations of the monosubstituted aromatic). The spectrum of PPO [Fig. 2(b)] showed bands at 3480 cm^{-1} (stretching band —OH) and at 1100 cm^{-1} (asymmetrical C—O—C stretching). The spectrum of the graft copolymer [Fig. 2(c)] contained bands due to PS and PPO and the band at 1730 cm^{-1} due to carbonyl absorption of the methacrylate group.

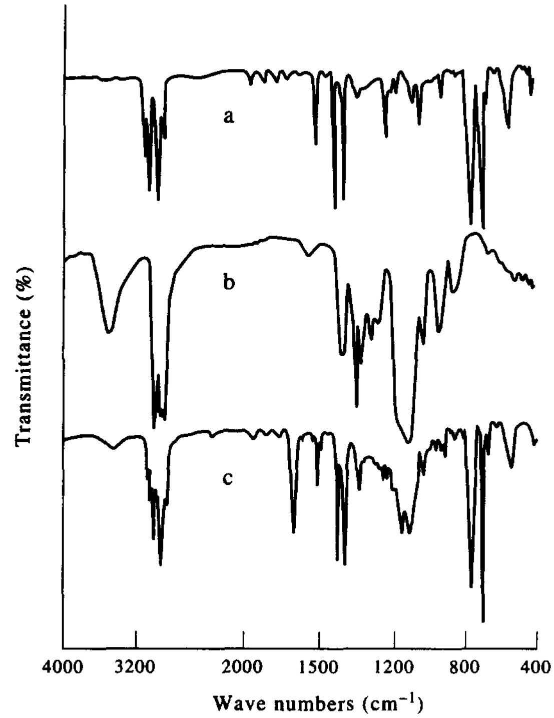

Fig. 2. Infrared spectra of polymers. (a) PS; (b) PPO; (c) graft copolymer (M_n = 24,260, PPO content = 34 wt%).

Quantitative determination of graft copolymer composition can be performed using the ^{1}H-NMR spectrum as described previously [15]. Figure 3 shows a typical spectrum of graft copolymer. The relation between the absorption peaks at 6.5 and 7.0 ppm (taken together) originating from the aromatic protons of the styrene units and the absorption at 3.5 ppm due the methylene and methine groups of the

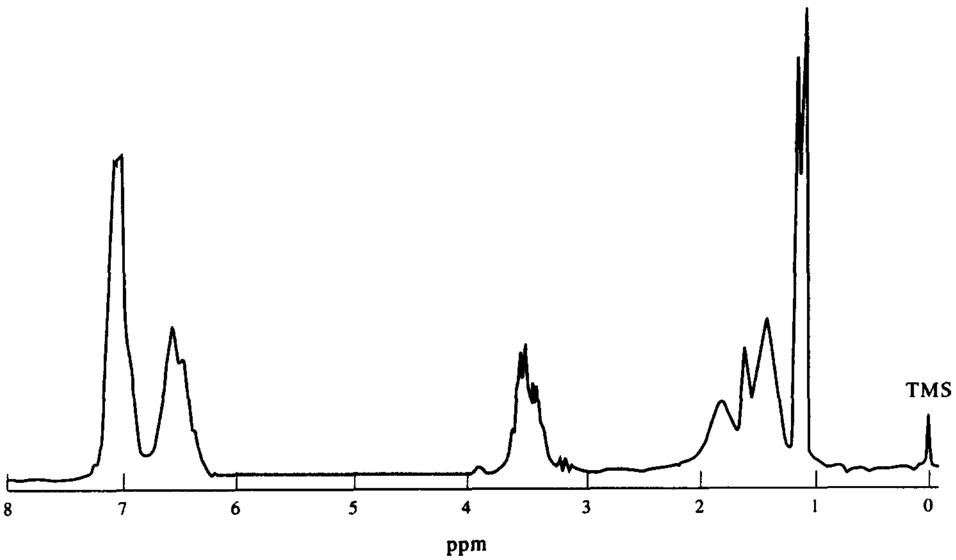

Fig. 3. ^{1}H-NMR spectrum of graft copolymer (M_n = 24,260, PPO content = 34 wt%).

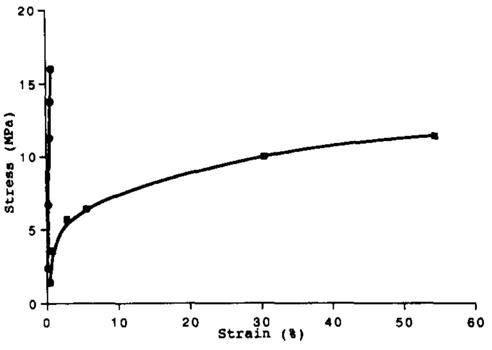

Fig. 4. Stress–strain curves. (●) PS; (■) graft copolymer (M_n = 24,260, PPO content = 34 wt%).

Table 1. Radical copolymerization of poly(propylene oxide) methacrylate (M_1) with styrene (M_2) in presence of $ZnCl_2$

Run	$ZnCl_2$ (g)	Yield* (wt%)	PPO† (wt%)
1	—	33	24
2	1.0	39	22
3	2.0	40	~0
4	3.0	43	~0
5	4.0	42	~0
PS	—	46	—

Experimental conditions: macromonomer (M_1), 14 wt%; styrene (M_2), 15 g; benzene, 10 ml; temperature, 80°C; time of reaction, 24 hr.
*Average for two reactions.
†Determined by ^{1}H-NMR.

poly(propylene oxide) grafts, is employed to determine the composition. It follows that:

$$\frac{I_{6.5-7}}{I_{3.5}} = \frac{5m}{3nx}$$

where I is the area related to absorptions, m is the number of styrene units per chain, x is the average number of grafts per chain, and n is the number of oxypropylene units per graft. Knowing the value of n (from the molecular weight of the PPO) and fixing $x = 1$, the value of m can be calculated easily. Values of the PPO in the graft copolymers were 21, 25, 29 and 34 wt%, respectively. The results have showed that the more macromonomer in the feed the higher the PPO content in the copolymer.

Films of the graft copolymers were relatively opaque on visual observation and brittle, except when the sum of grafted chains reached 34%. For this sample the mechanical properties were examined by tensile analysis of the polymer film and compared with the mechanical properties of polystyrene synthesized under the same experimental conditions. Figure 4 shows the stress–strain curves of polystyrene and graft copolymer. It can be noted in Fig. 4 a larger rupture elongation of the graft copolymer in relation to polystyrene. This indicates an effect of flexible grafted chains on the rigid polystyrene matrix (plasticizing effect); however, this effect has only been observed with a PPO content of 34 wt%.

The reaction conditions and results of the copolymerizations in the presence of zinc chloride are presented in Table 1. These results indicate that increasing the quantity of $ZnCl_2$ in the feed generate an increase in the yield and decrease the incorporation of the macromonomer to copolymer. In some cases only polystyrene has been obtained. The effect of the increase in the macromonomer reactivity that would be expected as a result of complexation between the polar groups of the methacrylate and the metal halide was not observed. This behaviour is believed to result from the formation of chelate rings by coordination of two adjacent oxygens in the grafted chain (PPO) with a $ZnCl_2$ molecule. This would decrease the flexibility of the polymer chain. Wetton *et al.* [16] observed an increase on the glass transition temperature (Tg) of PPO with an increase of the $ZnCl_2$ concentration. In the case of the macromonomer the decrease of flexibility of the polymer chain would cause an increase in the segmental density around the propagation radicals which would make access of the methacrylate group of the macromonomer difficult.

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