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Solution behavior of graft copolymers of poly(methyl methacrylate) backbone and poly(propylene oxide-b-ethylene oxide) branches: effect of structure and composition

Elizabete F. Lucas, Clara Marize F. Oliveira*

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, PO Box 68525,
21945-970 Rio de Janeiro, RJ, Brazil

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Summary

The effect of structure and composition of poly(methyl methacrylate) (PMMA) main chain and poly(propylene oxide-b-ethylene oxide) (PPO-b-PEO) graft chain on solution behavior was evaluated. Separated samples of homopolymers were also analysed to provide comparisons. The solutions were prepared by dissolving the sample in selective mixtures of tetrahydrofuran (THF) and hexane. The polymer solutions were submitted to viscometric measurements as function of the solvent composition. The ratio of ethylene oxide/propylene oxide (EO/PO) units determines the modification in molecular conformation of the (PPO-b-PEO) block copolymers as function of the solvent composition. The macromolecular structure is the most important factor on the graft copolymers behavior. The structure in which ethylene oxide is linked to the main chain provides higher interaction between graft copolymers and solvent (THF/hexane).

Introduction

Graft copolymers comprising chemically dissimilar sequences yield intramolecular phase separation and led to a number of specific application[1]. Some investigations have emphasized the surfactant behavior of graft copolymers made of poly(methyl methacrylate) (PMMA) main chain and poly(propylene oxide-b-ethylene oxide) (PPO-b-PEO) graft chain; the adsorption mechanism of graft copolymers at the water/toluene interface depends mainly on macromolecular structure[2].

Solution properties of block and graft copolymers are very much affected by interaction between chemically unlike sequences[3]. Macromolecular conformation depends on interaction between solvent and each different sequence of the copolymer that can be described, for example, as a comb or star form[4].

When a polymer dissolves in a liquid, the interaction of the two components stimulates an increase in polymer dimension over that in the unsolvated state. The increase in viscosity reflects the size and shape of the dissolved solute, even in dilute solution. One of the simplest method of examining this effect is by capillary viscometry[5].

The purpose of this work is to study the influence of structure and composition of graft copolymers made of PMMA main chain and PPO-b-PEO graft chain on solution behavior by using capillary viscometry.

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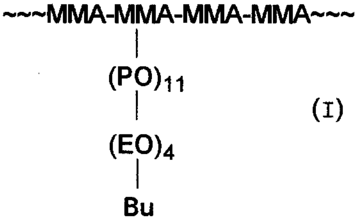
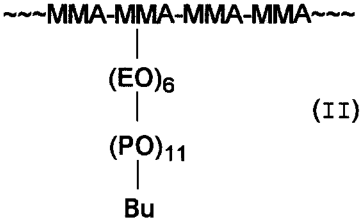
* Corresponding author

Experimental

The graft copolymers used were synthesized by macromonomer technique upon free-radical initiation[6]. The characterization dates are summarized in Table 1.

Table 1: Characterization of graft copolymers

Polymer	Graft Chain[a] (wt%)	M_n[b] x 10^{-3}	Structure	
C1	12	43.7	 $\begin{array}{c}\sim\sim\sim\text{MMA-MMA-MMA-MMA}\sim\sim\sim\\ \vert\\ (\text{PO})_{11}\\ \vert\\ (\text{EO})_4\\ \vert\\ \text{Bu}\end{array}$	(I)
C2	15	65.7		
C3	18	80.0		
C4	11	78.4	 $\begin{array}{c}\sim\sim\sim\text{MMA-MMA-MMA-MMA}\sim\sim\sim\\ \vert\\ (\text{EO})_6\\ \vert\\ (\text{PO})_{11}\\ \vert\\ \text{Bu}\end{array}$	(II)
C5	14	84.5		
C6	20	67.3		

[a] Determined by ^{1}H nuclear magnetic resonance (NMR) spectroscopy (Varian VXR-300).

[b] Determined by vapor pressure osmometry (VPO) (Wescan 232-A) in toluene at 25°C.

The poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) homopolymers and the block copolymers of ethylene oxide and propylene oxide, that make up the graft chain, were obtained from Grupo Ultra-Divisão Química (Mauá, S.P., Brazil) (Table 2).

Table 2: Characterization of ethylene oxide and propylene oxide polymers

Polymer	M_n[a]	M_w/M_n[b]	OH index	Monomer repeat units[c]	
				EO	PO
PEO	900	-	2.08	20	-
PPO	900	-	2.10	-	15
BuPPOPEO	900	1.23	1.03	6	10
BuPEOPPO	900	1.28	1.06	4	11

[a] Determined by VPO in toluene at 25°C.

[b] Determined by gel permeation chromatography in tetrahydrofuran at 25°C.

[c] Determined by ^{1}H NMR spectroscopy.

The poly(methyl methacrylate) used for comparison, were obtained from Sp^2 Scientific Polymer Products. The intrinsic viscosity, $[\eta] = 0.233$ dl/g, was determined in a Ubbelohde 0-B type viscometer in toluene, at 25°C. The viscosity average molecular weight, $M_v = 6.57 \times 10^4$, taking the $k=7.1 \times 10^{-5}$ and $a=0.73$ values from the literature[7].

The solvents used in a selective mixture for graft copolymers were chosen by testing the solubility of each homopolymer (PMMA, PEO and PPO) in several solvents; 10 mg of sample in 2 ml of solvent overnight.

The viscosity was measured at 25°C with an Ubbelohde-type viscometer in tetrahydrofuran/hexane; The compositions of the solvent mixture were 100/0, 95/5, 85/15 and 75/25. Intrinsic viscosities were determined from extrapolation of the plots of reduced viscosities, η_{sp}/c, versus concentration. All the results are collected in Figures 1-4, where they are plotted as functions of the composition of the solvent mixture.

Results and Discussion

Ethylene oxide and propylene oxide polymers

Each hompolymer that makes up the graft copolymer (PMMA, PEO and PPO) is soluble in tetrahydrofuran. On the other hand, hexane dissolves PPO and PEO being a poor solvent and does not dissolve PMMA according to the following order[8]

PPO > PEO > PMMA

Figure 1 shows intrinsic viscosity $[\eta]$ versus solvent composition for PEO and PPO. As expected $[\eta]$ of PEO decreases when hexane content increases. PEO in THF assumes a more expanded conformation due to higher interaction to this solvent when compared to the solvent mixtures which present also hexane. PPO is soluble in THF and hexane, however THF is a better solvent than hexane. The results show there is a very small variation of $[\eta]$ in the range of solvent composition investigated in this work.

Comparing $[\eta]$ values obtained from PPO and PEO solutions, it is possible to observe that both show similar conformation when dissolved in THF. Nevertheless, PPO is more expanded than PEO when dissolved in solvent mixtures.

Figure 2 shows $[\eta]$ versus solvent compositions for PEO/PPO block copolymers. For each block copolymer, $[\eta]$ values are almost the same in a different solvent composition but the $[\eta]$ values observed for $Bu(EO)_4(PO)_{11}$ are slightly higher than the ones observed for $Bu(PO)_{10}(EO)_6$ in the solvent mixtures. Such behavior is due to the slight difference in ethylene oxide (EO) and propylene oxide (PO) content in the block copolymer. The block copolymer of higher PO content presents a more expanded conformation when dissolved in a solvent mixture (higher hexane content): PPO acts as a PEO protector when hexane is present at solvent mixture and it retains the block copolymer in solution. However $Bu(PO)_{10}(EO)_6$ and $Bu(EO)_4(PO)_{11}$ are insoluble in pure hexane.

Graft copolymers

It was not done any comparison between $[\eta]$ values of two different graft copolymers since that such copolymers have different average molecular weight. The discussion is restricted to the comparison of $[\eta]$ values of the graft copolymers

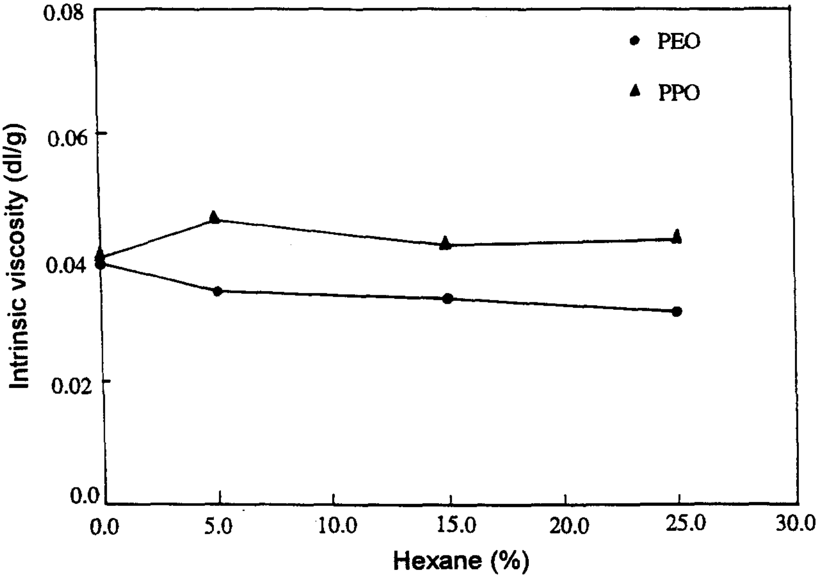


Figure 1: Intrinsic viscosity as a function of solvent composition (THF/hexane) for poly(ethylene oxide) and poly(propylene oxide), at 25 C.

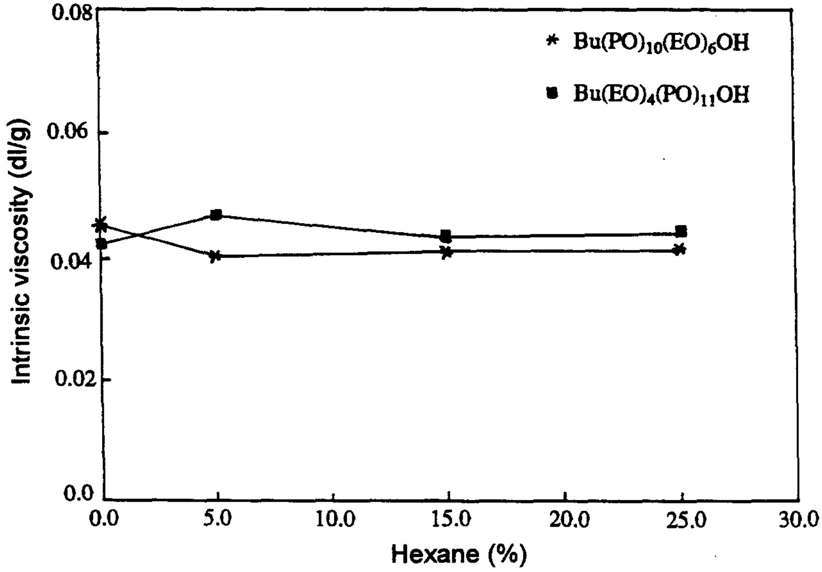


Figure 2: Intrinsic viscosity as a function of solvent composition (THF/hexane) for polyoxides, $Bu(EO)_4(PO)_{11}OH$ and $Bu(PO)_{10}(EO)_6OH$, at 25 C.

in different solvent mixtures. It is also compared the [η] variation (as function of the solvent composition) for distinct graft copolymers.

Figures 3 and 4 show the influence of the graft copolymer structure on solution behavior through the intrinsic viscosity variation as function of solvent composition. Graft copolymers are soluble in THF and insoluble in hexane. Intrinsic viscosities decrease to higher hexane content in mixture. It is possible to observe a cosolvency phenomenon at 95/5 solvent composition, for PMMA, C1, C2, C4 and C5. It means the influence of graft chain on intrinsic viscosity behavior (or cosolvency phenomenon) of graft copolymers just begins when reach ~20 wt% of graft chain.

Figure 4 shows higher [η] values for C6, even though its number average molecular weight is lower; it means a more expanded conformation for the higher graft chain content. The same behavior is not observed for the structure I (Figure 3). It suggests that structure II (which presents PPO at the end of the graft chain) assumes a more expanded conformation in solution than structure I (PEO at the end of the graft chain), although the structure I presents higher PPO (more soluble in hexane) content than the structure II. The same structure dependency has been observed for miscibility studies in solid state[9].

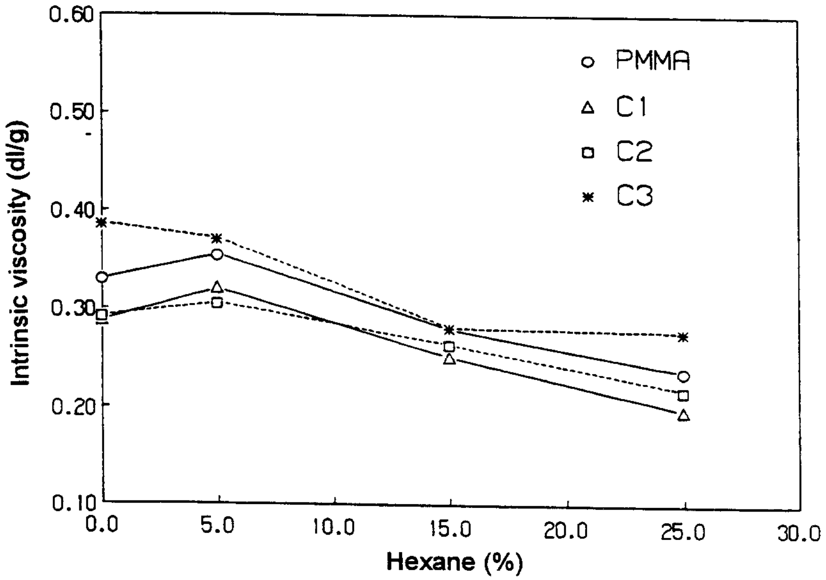


Figure 3: Intrinsic viscosity as a function of solvent composition (THF/hexane) for PMMA homopolymer and structure I copolymers, at 25 C.

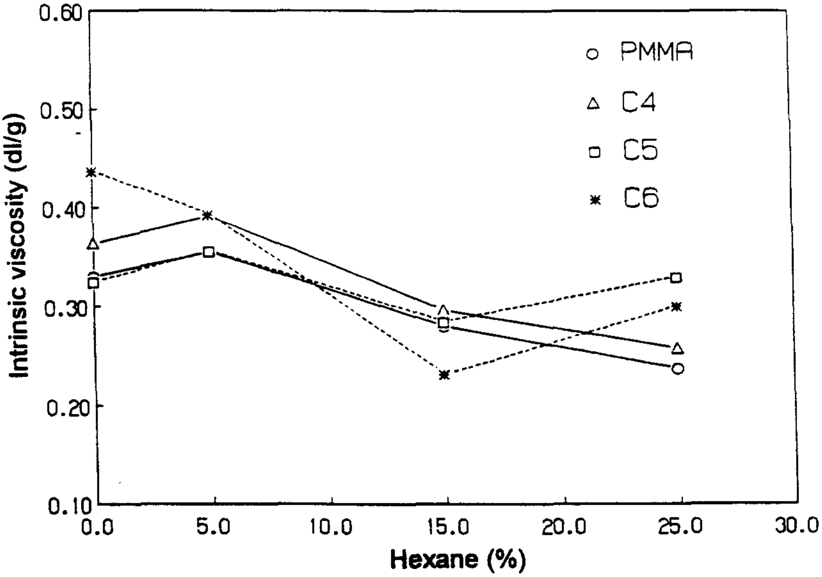


Figure 4: Intrinsic viscosity as a function of solvent composition (THF/hexane) for PMMA homopolymer and structure I copolymers, at 25 C.

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