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Properties of poly(methyl methacrylate-g-propylene oxide) in solution

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Summary

Graft copolymers of poly(methyl methacrylate) backbone and uniform poly(propylene oxide) branches were synthesized by the macromonomer technique and characterized by VPO, GPC and ^{1}H-NMR. Viscometric investigations of unfractionated samples were carried out at 25°C in chloroform and toluene (non-selective solvents) and in carbon tetrachloride (a selective solvent for the branches). The coefficients of the Huggins, Kraemer, Martin and Schulz-Blaschke equations were calculated. According to the values obtained for the Huggins coefficient, k_h, the best solvent for the copolymer seems to be chloroform. The positive values of the Kraemer coefficient, k_k, determined in carbon tetrachloride, suggest that the copolymer assumes a star-like conformation in this solvent.

Introduction

Copolymers present a complex behaviour in solution (1-2). A striking difference between a block and a graft copolymer of the same chemical composition and in the same solvent is that the latter shows a relatively low or no intermolecular association (3-4).

From viscometric data it is possible to show that the graft copolymer takes a segregated micellar conformation in a selective solvent for the grafted chains. Micelles are core-shell structures in which the unsolvated backbone is kept in solution by the solvated grafted chains that form a protective shell. In this case, the molecules take a star-like conformation (3-6).

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Empirical relations proposed by Huggins, Kraemer, Martin and Schulz-Blaschke (7-9) (Equations 1-4) express the viscometric behaviour of linear polymers.

$$\eta_{sp}/c = [\eta]_h + k_h[\eta]_h^2\, c \qquad \text{Equation 1}$$

$$\eta_r/c = [\eta]_k - k_k[\eta]_k^2\, c \qquad \text{Equation 2}$$

$$\ln(\eta_{sp}/c) = \ln[\eta]_m + k_m[\eta]_m c \qquad \text{Equation 3}$$

$$\eta sp/c = [\eta]_{sb} + k_{sb}[\eta]_{sb}\, \eta_{sp} \qquad \text{Equation 4}$$

The Huggins coefficient, k_h, seems to be always higher than the Schulz-Blaschke coefficient, k_{sb}. Just the opposite relation is observed when the respective intrinsic viscosities are compared. Values of k_h between 0.25 and 0.50 are attributed to a good solvation (10-15). Higher values of k_h, between 0.50 and 0.80, are expected when good solvation does not exist (12). The variations observed in the Kraemer coefficient, k_k, are interesting. Negative values are found for polymer solutions whereas positive values are observed for suspensions of spherical particles (16).

This work investigates the viscometric behaviour of poly(methyl methacrylate-g-propylene oxide) in chloroform and toluene, non-selective solvents, and in carbon tetrachloride, a selective solvent for the branches.

Experimental

Materials

Bifunctional poly(propylene oxide)(PPO) (Dow Chemical do Brasil S.A.), of $\overline{M}_n$ = 893 determined by VPO, was azeotropically dried in toluene. Methacrylate-headed poly(propylene oxide) macromonomers were prepared by reaction of poly(propylene oxide) and methacryloyl chloride, as described (17). Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Methyl methacrylate was purified by removal of inhibitors and distillation as usual. Pyridine, chloroform and carbon tetrachloride were distilled. Toluene and benzene were dried by distillation over Na.

Synthesis and purification of the graft copolymers

Methacrylate-headed poly(propylene oxide) macromonomers were prepared by reaction of poly(propylene oxide) and methacryloyl chloride (17). The reaction between the methyl methacrylate and the macromonomer was carried out in benzene under nitrogen. The initiator AIBN was added in one step at the beginning of the reaction. The mixture was refluxed at 80°C for 48 hours. Copolymer samples of different compositions were obtained by varying the macromonomer proportion and the solvent. The product was precipitated in n-heptane, filtered and dried under vacuum. The purification consisted of reprecipitation from chloroform into n-heptane, filtration and vacuum drying. Poly(methyl methacrylate) (PMMA) was synthesized with AIBN in benzene at 80°C for 8 hours and purified as the copolymers.

Characterization of the graft copolymers

Gel permeation chromatography (GPC) was performed on a Toyo Soda high-speed liquid chromatographer HLC-803A. The eluting solvent was THF. The retention times were calibrated against known monodisperse polystyrene standards. The ^{1}H-NMR spectra were recorded on a Varian XL-100 spectrometer. Number-average molecular weight analysis was performed on a Wescan 232-A vapour pressure osmometer, using toluene as solvent and benzil as primary standard. Efflux times were measured using an Ubbelohde OB viscometer in a water bath at 25 ± 0.1 °C. The viscometric measurements were carried out in chloroform, toluene and carbon tetrachloride. The initial concentration of the solutions was 1% (w/v) for the unfractionated copolymers and for poly(methyl methacrylate) and 9% (w/v) for poly(propylene oxide) due to the low molecular weights of the samples.

Results and discussion

The synthesis and characterization of poly(methyl methacrylate-g-propylene oxide) in which the copolymerization was carried out by adding the initiator in three steps has been reported (18). In this work, the synthesis was carried out in one step addition which led to high conversions and products with low molecular weight. Table 1 presents the reaction conditions and the characterization of the samples.

Graft copolymer compositions were calculated from peak intensities of ^{1}H-NMR spectra, taking into account the molecular weight of the grafted chains (17-18).

Different intrinsic viscosity values are found by the use of Huggins, Kraemer, Martin and Schulz-Blaschke equations (12,14, 15). In this work, the values for the intrinsic viscosities obtained from these four equations are almost the same for each sample analysed. These values are shown in Table 2.

Figure 1 shows the plots of η_{sp}/c x c and ln η_r/c x c for the copolymer MD-04 in chloroform, toluene and carbon tetra-

Table 1: Characterization of poly(methyl methacrylate-g-propylene oxide) samples, poly(methyl methacrylate) (PMMA) and poly(propylene oxide) (PPO).

Polymer	$\bar{M}_n$ [b]	$\bar{M}_w/\bar{M}_n$ [c]	% PPO [d]
MD-01	8900	3.6	33
MD-02	12158	2.7	29
MD-03	14652	2.9	18
MD-04	29455	3.3	18
MD-05	20263	3.8	21
MD-06	22321	-	11
PMMA[a]	14357	2.4	-
PPO	893	1.2	-

Experimental conditions: temperature: 80°C; solvent: benzene; initiator: AIBN; time of reaction: 48 h; [a] time of reaction: 8 h. [b] Determined by VPO. [c] Determined by GPC. [d] Determined by ^{1}H-NMR.

chloride. The linearity of the Huggins, Kraemer, Martin and Schulz-Blaschke relations was observed only above 1% (w/v) for the copolymers and PMMA, and 9% (w/v) for PPO.

It can be observed from Table 2 that the intrinsic viscosity values for the graft copolymers are higher than those obtained for the backbone homopolymer. The copolymer in chloroform and in toluene is more extended than poly(methyl methacrylate) because of the repulsive forces between the different repeated units that lead to a intramolecular phase separation. Similar observations were also made for other copolymers (1,3,5-6,19-20).

Table 3 represents the Huggins, Kraemer, Martin and Schulz-Blaschke coefficients obtained.

The copolymers analysed do not show a correlation or constant variation with the intrinsic viscosities, the coefficients, the compositions and the molecular weights. This absence of correlation was also reported in literature (15).

According to intrinsic viscosity values, chloroform seems to be the best solvent for the copolymers analysed, where the molecules are more extended. The small values found in carbon tetrachloride indicate that this is the poorest solvent, where the copolymer is more contracted. These facts are confirmed by the values found for the Huggins coefficient in these solvents. In chloroform and toluene, the k_h values are in the range characteristic of a good solvent and the values found in carbon tetrachloride vary in the range for poor solvents. Intrinsic viscosity data for all the copolymers analysed in carbon tetrachloride are very close. It may be due to the fact that the copolymers, inde

Table 2: Values of intrinsic viscosity for the graft copolymers, PMMA and PPO in chloroform, toluene and carbon tetrachloride.

Polymer	$CHCl_3$ $[\eta]$ (dl/g)	Toluene $[\eta]$ (dl/g)	CCl_4 $[\eta]$ (dl/g)
MD-01	0.49	0.28	0.16
MD-02	0.30	0.20	0.19
MD-03	0.34	0.25	0.17
MD-04	0.54	0.32	0.19
MD-05	0.55	0.30	0.20
MD-06	0.44	0.29	–^{a}
PMMA	0.27	0.16	–^{a}
PPO	0.05	0.03	0.04

^{a} Insoluble. Temperature: 25 ± 0.1°C.

Table 3: Huggins (k_h), Kraemer (k_k), Martin (k_m) and Schulz-Blaschke (k_{sb}) coefficients for the copolymers and PMMA in chloroform, toluene and carbon tetrachloride.

Polymer	$CHCl_3$				Toluene				CCl_4			
	k_h	k_k	k_m	k_{sb}	k_h	k_k	k_m	k_{sb}	k_h	k_k	k_m	k_{sb}
MD-01	0.39	-0.12	0.30	0.34	0.35	-0.12	0.32	0.34	1.60	0.83	1.18	1.40
MD-02	0.36	-0.15	0.32	0.33	0.50	-0.07	0.50	0.47	0.86	0.22	0.67	0.76
MD-03	0.31	-0.18	0.25	0.29	0.65	0.10	0.54	0.63	0.81	0.20	0.63	0.67
MD-04	0.34	-0.14	0.29	0.32	0.55	-0.09	0.37	0.45	0.75	0.17	0.66	0.76
MD-05	0.35	-0.15	0.26	0.30	0.45	-0.10	0.37	0.42	0.82	0.26	0.62	0.71
MD-06	0.22	-0.22	0.18	0.19	0.44	0.29	0.39	0.41	–	–	–	–
PMMA	0.45	-0.05	0.38	0.40	0.50	0.00	0.49	0.47	–	–	–	–

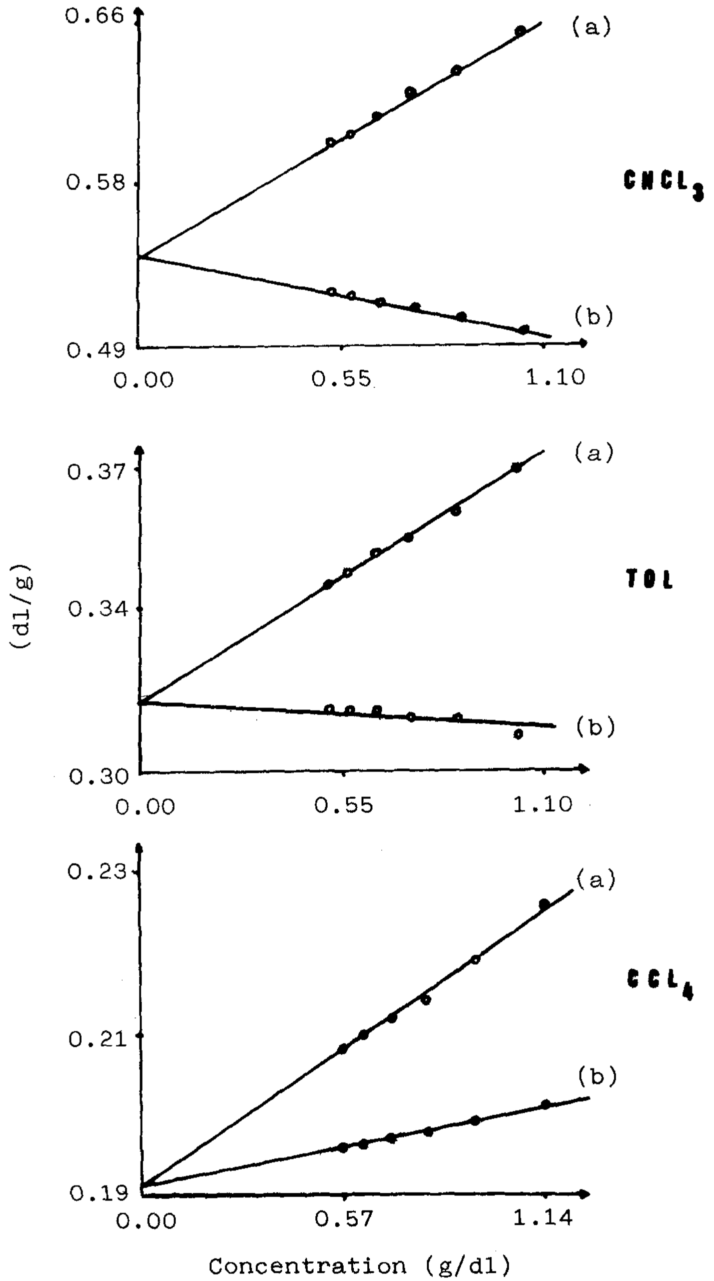

Figure 1: Viscometric behaviour of the copolymer MD-04 in chloroform ($CHCl_3$), toluene (TOL) and carbon tetrachloride (CCl_4) at 25° C. (a)- η_{sp}/c; (b)- $\ln \eta_r/c$.

pendent of the composition and molecular weight, take a similar compact conformation. The positive values of the Kraemer coefficient indicate that in carbon tetrachloride, which is a selective solvent for the branches, the copolymer exists as spherical particles, that is, they obey the ln η_r/c x c plot characteristic of a suspension (16). Table 1 shows that copolymer MD-06 has the lowest quantity of branches and it is insoluble in carbon tetrachloride. This fact may indicate that the branches are unable to protect the backbone and keep it in solution. The other copolymers are soluble in carbon tetrachloride indicating that the branches keep the contracted backbone in solution and the copolymer assumes a spherical star-like conformation.

In this work, it is suggested that for poly(methyl methacrylate-g-propylene oxide) the positive values of the Kraemer coefficient may be an evidence for the formation of segregated spherical structures in a selective solvent for the branches.

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