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Complexation of poly(methyl methacrylate-g-propylene oxide) and alkali-metal ions

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Summary

Copolymers of poly(methyl methacrylate-g-propylene oxide) with grafted branches having different molecular weights were complexed with K^+, Na^+ and Ca^{2+}. The efficiency of the graft copolymers in binding cations was evaluated from salt distribution equilibria in water-methylene chloride. Among the used cations, K^+ was more easily complexed than Na^+ and Ca^{2+}.

Introduction

The interest in polymer complexes formed by polyethers and metals has increased due to their application in high density batteries as solid electrolytes. Poly(propylene oxide) has been used more extensively than other polyethers because it is amorphous and the complicating effects of crystallinity are avoided (1-3).

Complexing in solution can be detected in different ways, such as spectral changes, altered solubilities and electrochemically (4,5).

This paper investigates the efficiency of complexation between poly(methyl methacrylate-g-propylene oxide) and Na, K and Ca picrates by the extraction technique using immiscible solvents (5,6).

Experimental

Materials

Bifunctional poly(propylene oxide)(PPO)(Curtume Carioca S.A.) of $\overline{M}_n$ = 1040, 1990 and 3010 determined by VPO, was azeotropically dried in toluene. Methacrylate-headed poly-

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(propylene oxide) macromonomers were prepared by reaction of poly(propylene oxide) and methacryloyl chloride, as described (7). Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Methyl methacrylate was purified by removal of inhibitors and distillation as usual. Pyridine and chloroform were distilled. Toluene and benzene were dried by distillation over Na. Methylene chloride, calcium chloride, potassium and sodium hydroxide were used as received.

Synthesis and purification of graft copolymers

Graft copolymers of poly(methyl methacrylate) and poly(propylene oxide) were prepared by reaction of methacrylate-headed poly(propylene oxide) macromonomers and methyl methacrylate. The macromonomers were prepared in solution, by reaction of poly(propylene oxide) and methacryloyl chloride (7). Copolymer samples were obtained of different compositions by varying the macromonomer proportion. The copolymers were purified by reprecipitation from toluene into n-hexane, filtered and vacuum dried.

Characterization of graft copolymers

The graft copolymers were characterized by VPO and ^{1}H-NMR. Number-average molecular weight analysis was performed on a Wescan 232 A vapour pressure osmometer, using toluene as solvent and benzil as primary standard. ^{1}H-NMR spectra were recorded on a Brucker (200 MHz) apparatus.

Evaluation of the complexation efficiency

Metal picrates were prepared by using aqueous solutions of NaOH, KOH and $CaCl_2$ (0,1 M) and adding to these solutions aqueous picrate solution ($6{,}5 \times 10^{-5}$ M) (4). Organic solutions were prepared by dissolving different quantities of polymer in methylene chloride. Five ml of aqueous solution and 5 ml of organic solution were added in a test tube. The test tube was closed and two immiscible phases formed. The test tube was placed in the Vortex mixer for at least 3 min, found to be sufficient for extraction. After that, the amount of the ion extracted was determined. The aqueous phase was measured on a Cary 17 Spectrophotometer at 355 nm. The amount of the picrate passed to the organic phase was determined by the difference between picrate concentration in the initial solution and final picrate concentration in the aqueous phase.

Results and discussion

The purpose of this investigation is to evaluate the complexation efficiency of graft copolymers in solution. The synthesis conditions and characterization of the graft copolymers are presented in Table 1.

Table 1: Radical copolymerization of poly(propylene oxide)(PPO) macromonomers (M_1) with methyl methacrylate (M_2)

Run	Feed	Graft copolymers					
	PPO-M_1 g	Yield wt%	M_n[a]	M_s[b]	X[c]	ng[d]	PPO content[e] wt%
1	8.2	80	31513	7743	67	4	14
2	11.0	83	60611	5643	46	11	19
3	16.4	60	17856	3543	25	5	29
4	16.4	73	55909	7394	54	8	27
5	21.9	74	59281	7094	51	8	28
6	32.8	69	49507	5894	39	8	34
7	33.7	80	58427	9314	63	6	32
8	44.9	58	77207	7914	49	10	38
9	67.4	66	61813	6114	31	10	49

Experimental conditions: methyl methacrylate, 30 g; temp.: 80°C; solvent: benzene; initiator: AIBN (0.3 mol% to monomers); time of reaction: 48 h. [a] Determined by VPO. [b] Molecular weight of the repeat unit in the copolymer. [c] Average number of methyl methacrylate units to each grafted branch of PPO. [d] Average number of grafted branch in the copolymer (8). [a] to [e] were determined by ^{1}H-NMR spectroscopy as described in (7). Run 1-3, $\overline{M_n}$ of PPO = 1040; run 4-6, $\overline{M_n}$ of PPO = 1990; run 7-9, $\overline{M_n}$ of PPO = 3010.

Metal picrate concentration found in the organic phase after extraction was determined by the difference between picrate concentration in the initial solution [Ci] and final picrate concentration in the aqueous phase [Cf], according to Equation 1. This is called the indirect method.

$$\text{Metal picrate extracted } \% = \frac{[Ci] - [Cf]}{[Ci]} \times 100 \qquad \text{Equation 1}$$

Metal picrate concentration [Ci] and [Cf] were determined from Equation 2. The absorbance utilized in the concentration calculations is the maximum absorbance at 355 nm.

$$A = \varepsilon bc \quad \text{Equation 2}$$

where: A = absorbance at 355 nm
ε = molar absorptivity or molar extinction coefficient ($cm^{-1}\ M^{-1}$)
b = path length through the sample (cm)
c = metal picrate concentration

The molar extinction coefficient was determined by calculating the angular coefficient of the straight line obtained by plotting absorbance versus concentration of standard picrate solutions. The molar extinction coefficient was determined for each picrate solutions.

Extraction using immiscible solvents was chosen to evaluate the copolymers' complexation efficiency because these copolymers and the PPO are insoluble in water.

The efficiency of copolymer complexation was based on the content (wt%) of extracted metal picrate to organic phase by the copolymers (run 1-9, Table 1). It was verified that only PPO is effective in the formation of metal complexes while poly(methyl methacrylate)(PMMA) acts as support. The results are consistent with information in the literature (9).

Considering the values found by the extraction technique it was observed that the absolute efficiency of K^+ and Na^+ complexation by PPO is proportional to its molecular weight and that it is larger than the efficiency of copolymers. By comparing potassium and sodium picrate systems a different behavior was observed. Na^+ shows lower complexation efficiency than K^+ because the former does not form a stable cation due to its smaller size (10). The low amount of extraction of the copolymers may be due to steric hindrance caused by the methyl group of PPO and the PMMA chain.

In the case of calcium picrate content (wt%) extracted by polymers it was observed that the efficiency of complexation by homopolymer is lower than that of copolymers. The different behavior of Ca^{2+} as compared to K^+ and Na^+ may due to its divalency. The PPO attached to the main chain makes the complexation between two graft chains easy.

Figures 1,2 and 3 show the extracted metal picrate in the organic phase for each copolymer as a function of the three ions. By comparing these figures it was observed that the extent of extraction increases with the branch content of the graft.

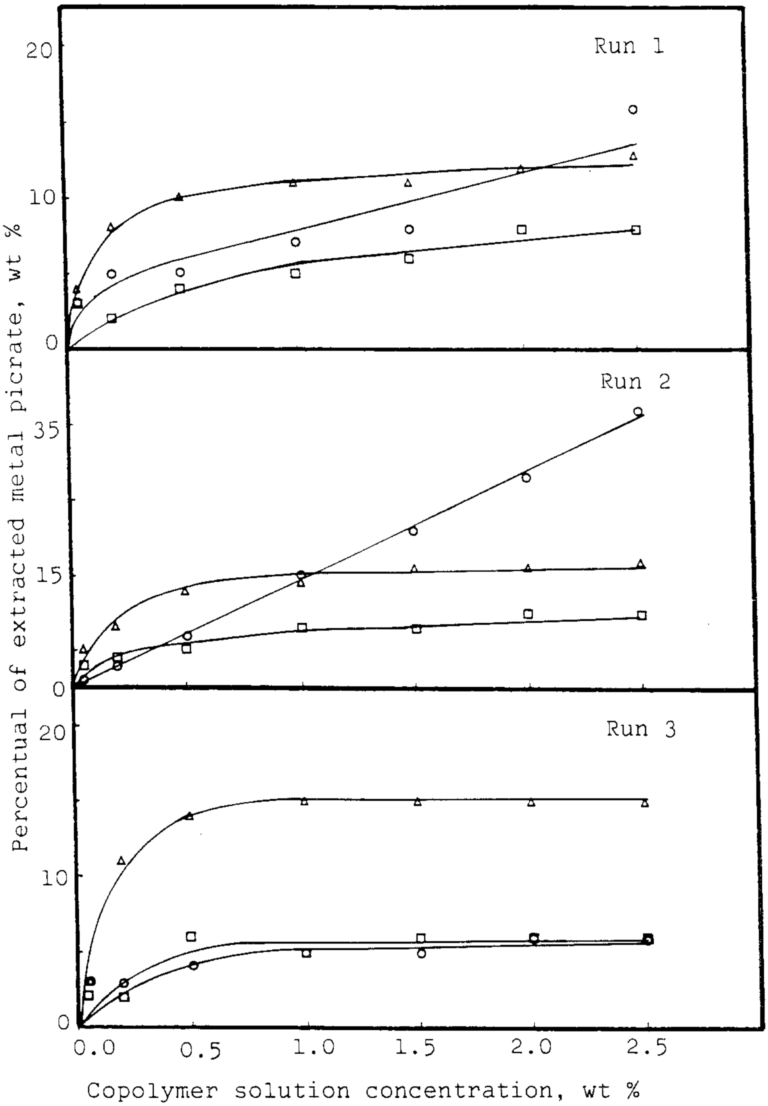

Figure 1: Percentual of extracted metal picrate to organic phase by the copolymers (runs 1,2 and 3 in Table 1) △ K^+, □ Na^+, ○ Ca^{2+}..

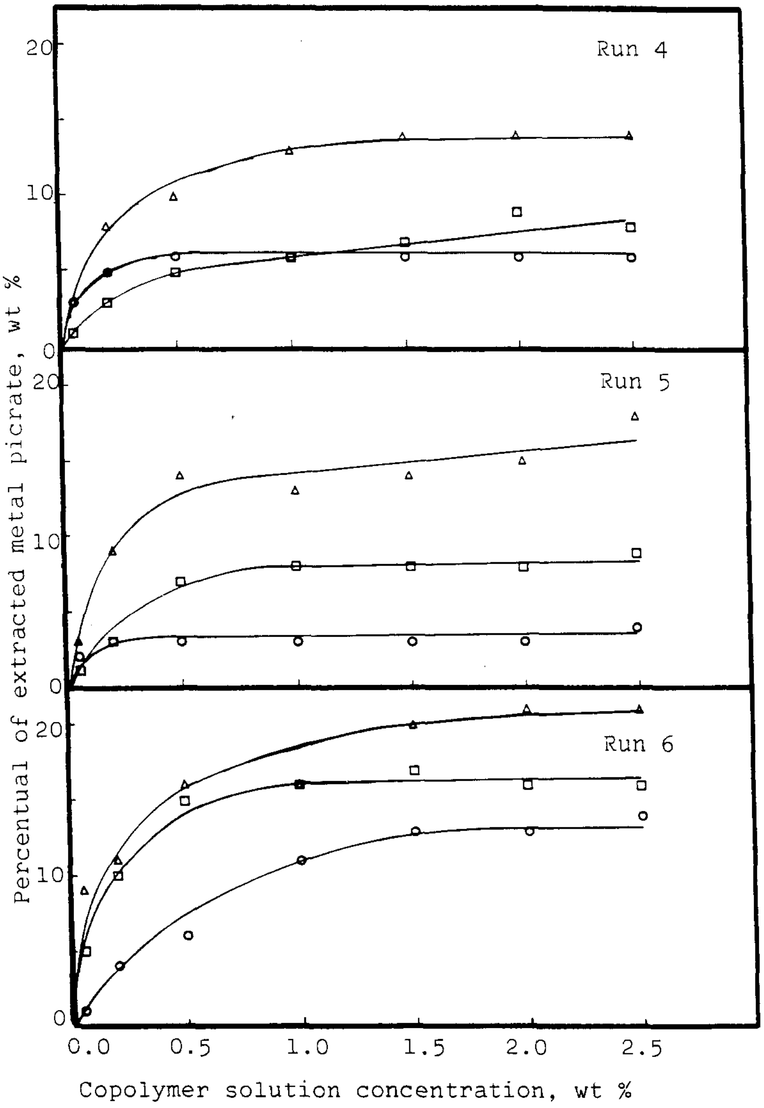

Figure 2: Percentual of extracted metal picrate to organic phase by the copolymers (runs 4, 5 and 6 in Table 1) △ K^+, □ Na^+, ○ Ca^{2+}.

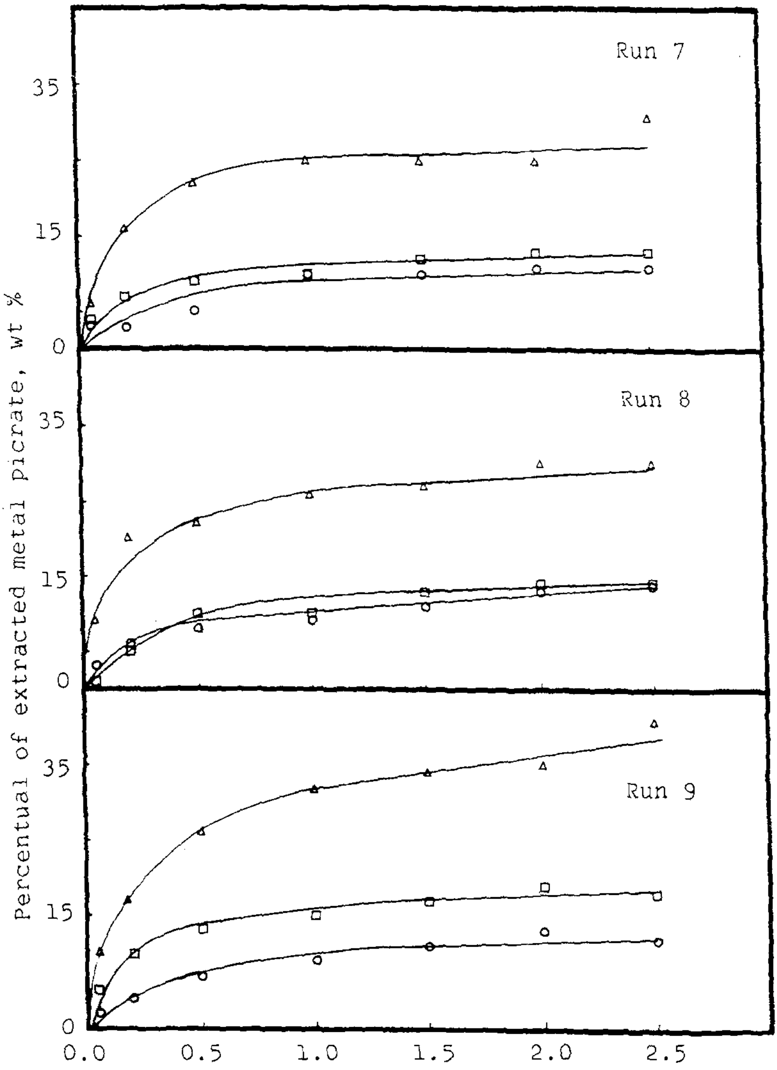

Figure 3: Percentual of extracted metal picrate to organic phase by the copolymers (runs 7,8 and 3 in Table 1) △ K^+, □ Na^+, ○ Ca^{2+}.

In most of the studied polymers the content (wt%) of the extracted metal picrate increases with the concentration of the polymer until it becomes constant. In general, the complexation efficiency is larger for K^+ than Na^+ and Ca^{2+}.

For copolymers of runs 1 and 2 (Figure 1) the content (wt%) of calcium picrate increases continuously until the studied concentration range. This may be due to the fact that the metal complexes formed with PPO branches have assumed a helical conformation at low concentrations. At higher concentrations complex formation may also take place between two grafted chains. This would be facilitated by the divalency of Ca^{2+}. In the case of K^+ and Na^+ complexes the helical form occurs preferentially.

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