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A contribution to the fractionation of polystyrene – poly-(alpha-methylstyrene) mixture using the methyl ethyl ketone – benzene/methanol system

Bluma Guenther Soares and Ailton de Souza Gomes

Instituto de Química, Universidade Federal do Rio de Janeiro Ilha do Fundão, CT, Bl.A, S.616, Rio de Janeiro, Brasil

Summary

The fractionation of polystyrene, poly(alpha-methylstyrene) and physical mixture of these homopolymers in methyl ethyl ketone - benzene/methanol system was investigated. The solubility of poly(alpha-methylstyrene) increases with the decreasing of molecular weight and becomes similar to polystyrene at $\overline{M}_w$ 29,000. Polystyrene and poly(alpha-methylstyrene) which precipitate simultaneously have different molecular weight and can be further separated by another method.

Introduction

In our studies concerning the cationic copolymerization of styrene (Sty) and alpha-methylstyrene (AMS) in liquid sulfur dioxide, we have been interested in proving the block copolymerization tendency of these reactions (1). In order to do that we have submitted several samples to fractionation by successive precipitation. The selective fractionation of a polymer mixture can be made according to the molecular weight or to the chemical composition depending on the solvent - precipitant system employed (2). In our case, there was the possibility of having the presence of the copolymer and the homopolymers in the sample. So, we had to use a system separable by chemical composition. Separation is not easy because of the similarity of polystyrene(PSty) and poly(alpha-methylstyrene)(PAMS) and similarity in their solubilities. In a previous report by M. Baer, a mixture of methyl ethyl ketone(MEK) - benzene (6:1 volume ratio) as solvent and methanol (0.01% $CaCl_2$) as precipitant was used to fractionate block copolymers of Sty and AMS made by anionic technique (3). In these systems, PAMS is precipitated first because it is less soluble than the block copolymer and the PSty.

In this paper we would like to report our results concerning the fractional precipitation of PSty-PAMS mixtures obtained by cationic polymerization, using the MEK - benzene/

methanol system.

Experimental

PSty, $\overline{M}_w$: 65,000 was obtained by cationic polymerization in liquid sulfur dioxide initiated by m-chloroperbenzoic acid, as previously reported (4). PAMS, $\overline{M}_w$: 11,000 and 16,000 were obtained in similar way. Toluene, MEK, benzene and methanol were purified by distillation.

The fractionation was carried out with an initial 1%(p/v) solution of polymer. Methanol was slowly added under strong stirring, until the onset of turbidity. The turbid solution was warmed until this turbidity just disappeared, then the system was stored overnight at room temperature and the supernatant clear fraction was decanted (5).

The composition of the fraction was determined by ultraviolet spectroscopy (6) on a Varian Cary 17 spectrophotometer. The molecular weight was determined by a CG-480C GPC equipped with three Waters ultrastyragel (10^3,10^4,10^5 A) columns and a SHODEX column (10^4 A).

Results and Discussion

The PSty-PAMS copolymers were first fractionated using toluene as solvent and methanol as precipitant (1). The efficiency of this system was tested by fractionating a physical mixture of the corresponding homopolymers. The results are shown in Table 1; evidently mixtures of the homopolymers exist in all fractions. This system is not able to identify the presence of block copolymers or physical mixture of homopolymers because of the similarity in the solubilities of PSty and PAMS. Separation has ocurred by molecular weight instead of chemical composition.

We have then tested the MEK-benzene/methanol system used by M.Baer (3). The samples employed in this report were synthesized by cationic technique, with molecular weights lower than those reported in literature (3). Thus we have fractionated mixtures of PSty ($\overline{M}_w$:65,000) and PAMS ($\overline{M}_w$:16,000) and the results are presented in Tables 2 and 3, respectively. The precipitant volume/solvent volume ratio at the beginning of precipitation is 0.09 in the case of PAMS and 0.2 in the case of PSty, indicating that PAMS is less soluble. The fractionation curves are compared with those obtained by M.Baer (3), in Fig. 1. It can be noted that the molecular weight of PSty does not influence significantly the initial precipitation of the polymers. Both PSty ($\overline{M}_v$:250,000) and PSty ($\overline{M}_w$:65,000) begin to precipitate at a precip./solv. ratio near 0.2. The deviation observed in curve D (Fig. 1) may be due to the polydispersity of the sample

TABLE 1. Fractionation of PSty($\overline{M}_w$:65,000) - PAMS($\overline{M}_w$:11,000) mixture; (solvent: toluene; precipitant: methanol)

fraction	cum.weight of fraction (%)	precip./ solv.	$\overline{M}_w$ x 10^{-3}	Sty mol. frac.in mix. (%)
1	10.0	0.30	220.0	95
2	55.5	0.44	53.0	75
3	71.5	0.55	20.6	45
4	80.5	0.68	14.5	40
5	85.0	0.83	9.0	40
6	91.0	0.97	6.7	12
7	93.5	1.43	4.5	25
8	96.0	1.78	4.2	20

($\overline{M}_w/\overline{M}_n$: 2.1). The solubility of PAMS is quite dependent on the molecular weight. PAMS($\overline{M}_v$:160,000) (3) is practically insoluble in this system and begins to precipitate as soon as the methanol is added, whili PAMS($\overline{M}_w$:16,000) remains in solution until the precip./solv. ratio reaches 0.09. Once again we observe the deviation because of the relatively broad polydispersity ($\overline{M}_w/\overline{M}_n$: 2.4).

The results relative to the fractionation of a physical mixture of PSty and PAMS are shown in Table 4. Until the fifth fraction only PAMS is precipitated. From the 6th fraction on,

TABLE 2. Fractionation of PSty ($\overline{M}_w$:65,000); (solvent: MEK-benzene(6:1); precipitant: methanol)

fraction	cum weight of fraction (%)	precip./ solv.	$\overline{M}_w$ x 10^{-3}
1	5.3	0.20	358.0
2	27.0	0.22	146.5
3	53.5	0.27	52.3
4	68.3	0.30	39.0
5	80.5	0.35	32.5
6	91.1	0.41	24.0
7	95.8	0.48	13.0

TABLE 3. Fractionation of PAMS ($\bar{M}_w$:16,000); (solvent: MEK-benzene(6:1); precipitant: methanol)

Fraction	cum. weight of fraction (%)	precip./ solv.	M_w x 10^{-3}
1	0.5	0.09	-
2	2.0	0.13	56.0
3	6.0	0.15	42.0
4	12.5	0.17	34.0
5	20.5	0.19	24.0
6	30.5	0.22	20.0
7	39.5	0.24	17.4
8	49.0	0.28	15.3
9	56.5	0.32	13.0
10	63.5	0.37	7.0
11	71.5	0.43	5.0
12	79.0	0.50	2.5

both homopolymers are precipitated simultaneously. The precip./solv. ratio corresponding to this fraction (0.19) is similar to that observed for the beginning of PSty precipitation (Table 2).

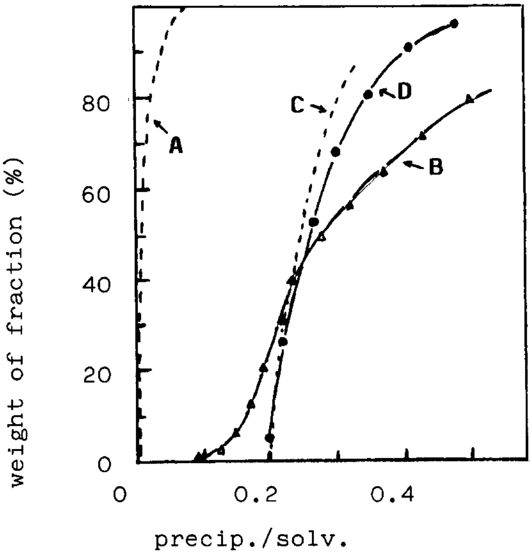

Fig.1 Fractionation curves in MEK-benzene/methanol system for PAMS ($\bar{M}_v$:160,000)(A); PAMS ($\bar{M}_w$:16,000)(B); PSty ($\bar{M}_v$:250,000)(C); PSty ($\bar{M}_w$:65,000)(D)

TABLE 4. Fractionation of PSty($\bar{M}_w$:65,000) - PAMS($\bar{M}_w$:16,000) mixture; (solvent: MEK-benzene(6:1); precipitant: methanol)

fraction	cum. weight of fraction (%)	precip./ solv.	$\bar{M}_w$ x 10^{-3}	Sty mol fraction in mixture (%)
1	0.4	0.09		0
2	3.2	0.12	58.0	0
3	8.0	0.17	35.0	0
4	12.4	0.19	380.0/29.0	70
5	28.0	0.23	101.0/18.5	85
6	45.6	0.26	58.4/15.5	85
7	58.0	0.29	39.0/ 7.5	80
8	66.8	0.37	25.5/ 6.0	80
9	74.8	0.42	18.0/ 4.5	70
10	82.8	0.49	8.0/ 2.5	55

GPC analysis presents a bimodal molecular weight distribution. For each fraction the higher and lower $\bar{M}_w$ values are comparable to the $\bar{M}_w$ values of PSty and PAMS, respectively, which precipitate at a similar precip./solv. ratio. However, for similar $\bar{M}_w$ values, the two homopolymers exhibit different solubilities.

The behavior observed in this work permits to conclude that the MEK-benzene/methanol system is better suited for the separation of high molecular weight and narrow molecular weight distribution PSty and PAMS as formed by anionic techniques. The polymers obtained by cationic mechanism have usually lower molecular weights and broader MWDs because of the possibility of transfer reactions. In this case, to achieve a satisfactory separation of PSty-PAMS mixtures it is necessary first to fractionata according to the chemical composition using the system studied and them submit the fractions to a further separation method based on the molecular weight.

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References

1. Gomes,A.S., Soares,B.G., J.Polym.Sci., Polym.Chem.Ed.,1987, 25,353-363.

2. Riess,G., Callot,P., "Fractionation of copolymers", in "Fractionation of synthetic polymers", Ch.5, ed. by L.H. Tung, Marcel Dekker, Inc., New York, 1977.

3. Baer,M., J.Polym.Sci., 1964, A-2, 417-436.

4. Soares,B.G., Gomes,A.S., J.Polym.Sci., Polym.Chem.Ed., 1987, 25, 1105-1108.

5. Vollmert,B.,"Polymer Chemistry", Springer-Verlag, New York, 1973, 389-403.

6. Soares,B.G., Gomes,A.S., Polym.Bull., 1988,20,543-548.

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