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A study of mixtures of poly(ethylene oxide) with polystyrene or poly(styrene-co-acrylic acid) by inverse gas chromatography and viscosimetry

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SUMMARY:

Systems of poly(ethylene oxide)/polystyrene and of poly(ethylene oxide)/poly(styrene-co-acrylic acid) of different ratios were studied by inverse gas chromatography using benzene and n-decane as molecule probes and by viscosimetry in tetrahydrofuran. The transition temperatures as shown in the retention diagrams and the interaction parameters as determined by inverse gas chromatography and by viscosimetry showed that whereas poly(ethylene oxide) is incompatible with polystyrene , the introduction of amounts of acrylic acid groups into polystyrene chains by free radical copolymerization led to compatible systems of the acidic copolymer with the poly(ethylene oxide).

INTRODUCTION:

Inverse gas chromatography (IGC) technique has been used not only to determine glass transition temperature or melting temperature of polymers, but also to measure the interactions between a polymer and molecule probe and polymer-polymer systems (1-8). This technique has been recently extensively used to study the compatibility of polymer blends (9-16).

Applying the Flory-Huggins theory, the interaction parameter X_{1i} between a polymer (i) and molecule probe (1) is given by :

$$X_{1i} = \mathrm{Ln}\,\frac{273.R.v_i}{Vg^\circ.P_1^\circ.V_1} - (1 - \frac{V_1}{M_1.v_i})\Phi_i - \frac{P_1^\circ}{R.T}(B_{11} - V_1) \qquad (1)$$

where V_1, M_1, P_1° and B_{11} are the probe molar volume, molecular weight, vapor pressure and second virial coefficient; R, the gas constant, T, the column temperature (°K), Φ_i and v_i are respectively the volume fraction and the specific volume of the polymer(i).

Vg°(ml/g), the specific retention volume of the solute is measured from:

$$Vg^\circ = t_N.F.J/W \qquad (2)$$

where t_N is the net retention time, F a gas carrier flow rate at 0°c, J is the James-Martin correction factor and W is the polymer or polymer mixture loading weight.

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Apparent polymer(2)-polymer(3) interaction parameter X_{23}^{app} was calculated from:

$$X_{23}^{app} = \frac{1}{\Phi_2 . \Phi_3} \left[Ln \frac{Vg_m^\circ}{W_2 . v_2 + W_3 . v_3} - \Phi_2 \, Ln \frac{Vg_2^\circ}{v_2} - \Phi_3 \, Ln \frac{Vg_3^\circ}{v_3} \right] \quad (3)$$

In the present study, transition temperatures, polymer-molecule probe and apparent polymer-polymer interaction parameters for the poly(ethylene oxide)/ polystyrene and poly(ethylene oxide)/ poly(styrene-co-acrylic acid) were first determined by inverse gas chromatography.
In addition, we have also determined the viscosimetric interaction parameters using the Krigbaum and Wall approximate method (17).

EXPERIMENTAL:

Materials: Poly(ethylene oxide) (PEO) 20,000 supplied by Merck was used as received. Polystyrene (PS) and poly(styrene-co-acrylic acid) containing 20 mole% of acrylic acid (PSAA) random copolymer were prepared under the same conditions by free radical polymerization at 60°C using the azo-bis isobutyronitrile (AIBN) as the initiator. Chromosorb W AWDMCS 60/80 mesh was obtained from Johns Mainville.

I.G.C. measurements: Gas chromatograms were recorded on HP 5730A gas chromatograph equipped with a dual flame ionisation detector. Helium was used as gas carrier and methane as non interacting marker. Small amount (0,1 µl) of benzene or n-decane as the molecule probes was injected manually using a Hamilton syringe.
The characteristics of the columns prepared in the usual way are shown in table 1.

Table 1: Stationary phases and column parameters.

Polymer	Weight of support (g)	Weight of polymer (g)	lenght of column (m)
PEO	1,4847	0,1647	1,5
PS	1,4954	0,1495	1,5
PSAA	1,5826	0,1593	1,5
PEO/PS 1:1	1,4006	0,1556	1,5
PEO/PSAA 1:1	1,5360	0,1537	1,5
PEO/PSAA 1:4	1,4499	0,1447	1,5
PEO/PSAA 3:1	1,5888	0,1595	1,5

Viscosimetric measurements: Solution viscosity measurements were all carried out with an Ubbelhod automatic viscosimeter type Fica at 25°C using tetrahydrofuran (THF) as solvant.

RESULTS AND DISCUSSION:

The retention diagrams Ln Vg° versus 1/T in figure 1 using benzene as the molecule probe shows that indeed PS is incompatible with PEO as evidenced from the observed glass transition temperature of PS at around 368°K and the melt transition temperature of PEO at around 333°K. Similar results were observed with the n-decane as the molecule probe. These results are in good agreement with those reported by T. SUZUKI et al.(11).

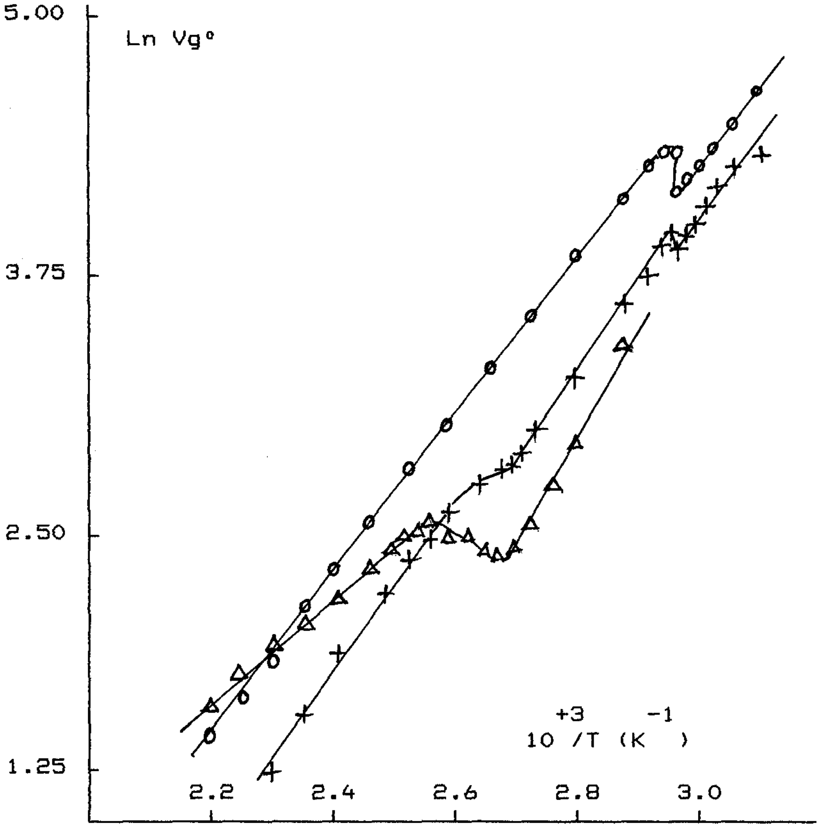

Figure 1: Retention diagrams of PS (Δ), PEO (o) and PS/PEO 1:1 (+) using benzene as molecule probe.

As shown in figure 2 the linear retention diagram observed with 1:1 ratio PSAA/PEO blend within the temperature range (318-473°K) is an evidence of the compatibility of this blend. The expected glass transition temperature of this compatible blend is below this range. The same results were observed with the n-decane as the molecule probe.

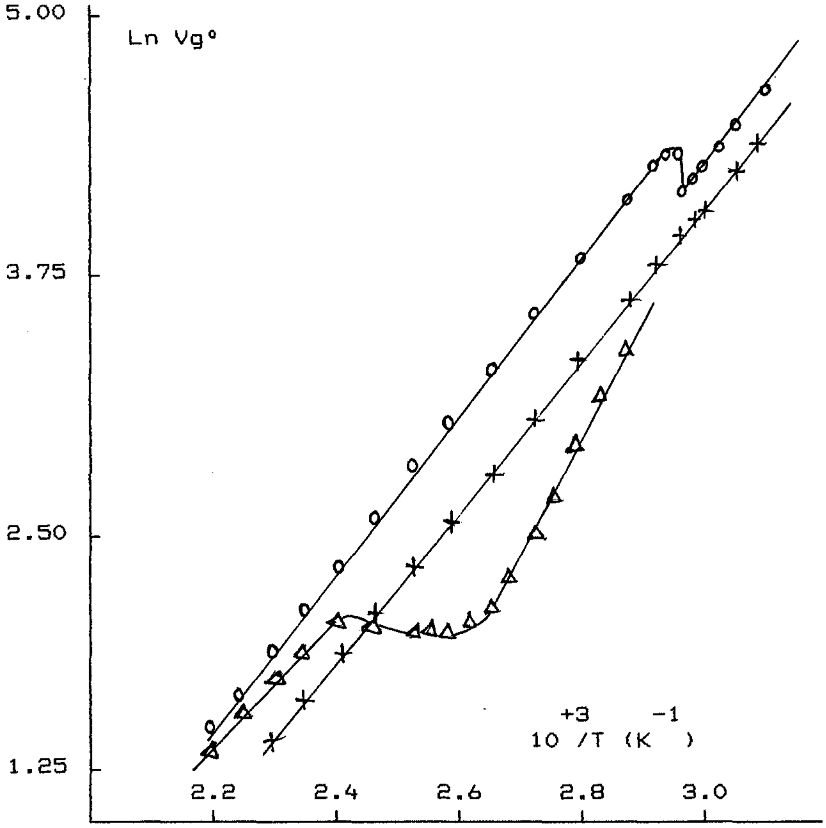

Figure 2: Retention diagrams of PSAA (△), PEO (○) and PSAA/PEO 1:1 (+) using benzene as molecule probe.

Similar results were obtained with blends of various compositions with both molecule probes. Figure 3 shows as example the retention diagram of PSAA/PEO (4:1) ratio.
The transition observed at 348°K is attributed to the glass transition temperature of the compatible blend in good agreement with the one calculated from the FOX relation (18).

At temperature above Tg of each polymer, all the measured specific retention volume Vg° were extrapolated to zero flow rate of the carrier gas. The calculated thermodynamic parameters are summarized in tables (2 and 3).

As expected positive values of the apparent polymer-polymer interaction parameters were obtained for both molecule probes with the incompatible PS/PEO blend.

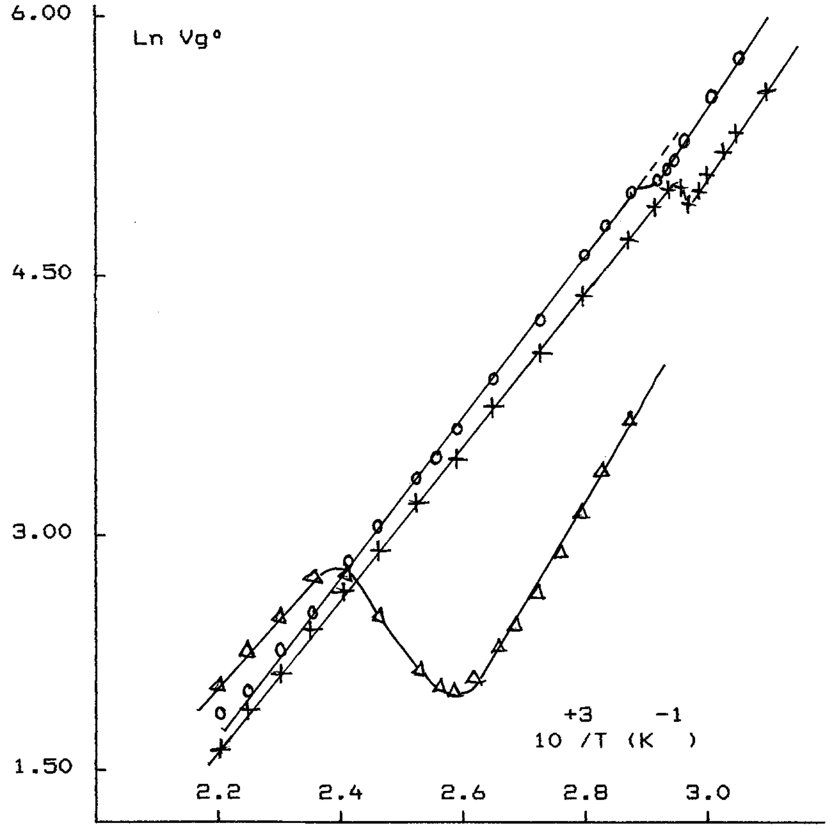

Figure 3: Retention diagrams of PSAA (Δ), PEO (+) and PSAA/PEO 4:1 (O) using n-decane as molecule probe.

Modification of polystyrene, introducing 20 mole% of acrylic acid within the chains by copolymerization made it be compatible with PEO. This is due to the specific interactions between the carboxylic groups of PSAA and the ether groups of PEO. As illustrated in table 2 and 3, the compatibility of these polymers is indeed confirmed by the negative values of X_{23}^{app}. These specific interactions between the two constituants were confirmed by Fourier Transform infra-red spectroscopy (19).

We have in addition used the approximate method of Krigbaum and Wall (17) to determine the viscosimetric interaction parameters between pairs of these polymers. According to this model, a positive difference between the experimental b_{23}(exp) and theoretical b_{23}(the) interaction parameters is evidence of compatible pair of polymers (20). Negative value is therefore expected with an incompatible pair of polymers.

Table 2 : Thermodynamic parameters for PEO, PS, PSAA, PEO/PS (1:1), PSAA/PEO of different ratios and benzene at infinite dilution.

T (°C)		150	160	170	180
	Vg°	12,07	10,20	8,84	7,83
PEO	X_{12}	0,210	0,197	0,144	0,107
	Vg°	10,55	8,90	7,98	6,25
PS	X_{12}	0,377	0,345	0,289	0,370
	Vg°	7,10	6,13	4,97	3,99
PSAA	X_{12}	0,762	0,726	0,738	0,797
	Vg_m°	11,69	9,84	8,60	7,08
PS/PEO (1:1)	X_{23}^{app}	0,142	0,134	0,099	0,051
PSAA/PEO	Vg_m°	6,22	5,55	4,57	3,95
(1:1)	X_{23}^{app}	-1,581	-1,406	-1,470	-1,380
PSAA/PEO	Vg_m°	6,06	4,99	4,39	3,88
(4:1)	X_{23}^{app}	-1,670	-1,939	-1,490	-1,031
PSAA/PEO	Vg_m°	9,44	7,92	6,60	6,01
(1:3)	X_{23}^{app}	-0,586	-0,652	-0,770	-0,495

Table 3 : Thermodynamic parameters for PEO, PS, PSAA, PEO/PS (1:1), PSAA/PEO of different ratios and n-decane at infinite dilution.

T (°C)		150	160	170	180
	Vg°	11,20	9,93	8,73	7,16
PEO	X_{12}	2,474	2,296	2,127	2,105
	Vg°	20,20	15,88	14,80	11,20
PS	X_{12}	1,906	1,846	1,617	1,674
	Vg°	14,19	11,78	8,40	7,07
PSAA	X_{12}	2,260	2,144	2,184	2,134
	Vg_m°	16,06	12,98	11,76	9,26
PS/PEO 1:1	X_{23}^{app}	0,252	0,126	0,128	0,126
PSAA/PEO 1:1	Vg_m°	8,76	7,33	6,24	5,22
	X_{23}^{app}	-1,461	-1,402	-1,078	-1,234
PSAA/PEO 4:1	Vg_m°	12,87	10,08	7,83	5,24
	X_{23}^{app}	-0,324	-0,775	-0,490	-0,050
PSAA/PEO 1:3	Vg_m°	11,93	9,70	7,44	6,12
	X_{23}^{app}	0,017	-0,350	-0,789	-0,324

The viscosimetric interaction parameters of the PS/PEO (1:1) and PSAA/PEO (1:1) systems in THF at 25°C are summarized in table 4. The obtained results confirm once again, the compatibility of the PSAA/PEO and the incompatibility of the PS/PEO system.

Table 4: Viscosimetric interaction parameters.

System	b_{23}(exp)	b_{23}(the)	Δb_{23}
PS/PEO 1:1	0,017	0,057	-0.039
PSAA/PEO 1:1	0,474	0,084	+0,390

CONCLUSIONS:

The present study indicates from inverse gas chromatography and viscosimetry the existence of specific interactions between the carboxylic groups within the acidic copolymer (PSAA) and the ether groups of PEO. Such interactions characterized by negative values of the apparent copolymer-polymer interaction parameters and positive (Δb_{23}) differences between the experimental and the theoretical interaction parameter explain the compatibility of the PEO/PSAA blends.

REFERENCES:

1- O. Olabisi (1975), Macromolecules, 8, 316.
2- D.D. Deshpande, D. Patterson, H.S. Schreiber and C.S. Su (1974), Macromolecules, 7,530.
3- C.S. Su and D. Patterson (1977),Macromolecules,10,708.
4- M. Galin (1977), Macromolecules, 10, 1239.
5- G. Dipaola-Baranyi and J.E. Guillet (1978), Macromolecules, 11, 224.
6- T. Inui, Y. Murakami, T. Suzuki and Y. Takegami (1982), Polymer Journal, 14, 4, 261.
7- G. Dipaola-Baranyi (1980), Macromolecules, 14, 683.
8- M. Galin and M.C. Rupprecht (1979),Macromolecules,12, 506.
9- J.M. Elorza, M.J. Berridi, J.J. Iruin and C. Uriarte (1988), Makromol. Chem., 189, 1855.
10- G. Dipaola-Baranyi (1988), Polym. Mater. Sci. Eng.,58, 735.
11- T. Suzuki et al. (1981), Polymer Journal, 13, 11, 1027.
12- T. Suzuki et al. (1983), Polymer Journal, 15, 6, 415.
13- Y. Murakami (1988), Polymer Journal, 20, 7, 549.
14- M.J. Fdez Berridi et al. (1989), Polymer 30, 1493.
15- A.C. Su and J.R. Fried (1989), ACS, Symp. Ser.,391,155.
16- G. Dipaola-Baranyi (1989), ACS, Symp. Ser., 391, 109.
17- W.R. Krigbaum and F.W. Wall (1950),J. Polym. Sci.,5,505.
18- T.G. Fox (1956), Bull. Am. Phys. Soc., 1, 123.
19- D.E. Cherrak and S. Djadoun (to be submitted).
20- A. Lassoued and S. Djadoun (1985), Eur. Polym. J., 21, 7, 669.

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