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Application of Inverse Gas Chromatography in the Study of PMMA Tacticity and It's Blending with Cholesteryl Esters

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Inverse gas chromatography (IGC) has been applied to obtain the interaction parameter between poly(methyl methacrylate (PMMA) and liquid crystalline cholesteryl n-nonanoate (CHON). The PMMA/CHON interaction parameter (χ_{23}) of blended systems comprising atactic PMMA (at-PMMA)/CHON, syndiotactic PMMA (st-PMMA)/CHON, and isotactic PMMA (it-PMMA)/CHON was calculated from the specific retention volume (V_g^0) obtained using toluene as a probe. The value of the interaction parameter, χ_{23} indicates that χ_{23} is dependent on composition, temperature, and PMMA tacticity. In the at-PMMA/CHON=1/1(weight ratio) and it-PMMA/CHON = 1/1 blend, all values of χ_{23} were positive. However, the values of χ_{23} of the st-PMMA/CHON = 1/1 blend at temperature above 150℃, and it-PMMA/CHON=2/1 and 1/2 blends at temperature above 100℃ were negative.
Keywords: liquid crystal, inverse gas chromatography, PMMA, tacticity, interaction parameter

1. INTRODUCTION

Liquid crystalline dispersions in polymers were discovered in the early 1980's and were considered an interesting phenomenon with respect to applications such as electro-optical modulators (i.e., displays). These materials had many characteristics which made them attractive for practical development and scientific research. We studied the thermodynamics of blends of amorphous and semicrystalline polymers using inverse gas chromatography (IGC). These studies confirmed that IGC is a powerful method for obtaining information on the thermodynamics of polymer blends[1,2,3,4]. Recently, our research by means of IGC has led to study the interaction parameter between atactic poly(methyl methacrylate) (at-PMMA) and liquid crystalline cholesteryl n-nonanoate (CHON) (40% at-PMMA and 60% CHON blend)[5,6]. In this study, IGC method was applied to observe the influence of the tacticity of PMMA and composition on the interaction parameter of PMMA and CHON blends.

In the IGC methods as above, the specific retention volumes (V_g^0) were calculated from the retention volumes of the PMMA(2)/CHON(3) mixture stationary phases-probe(1) systems. The retention diagrams (RD) which were plotted as $\ln V_g^0$ versus reciprocal column temperature, corresponded to the thermodynamic behaviors of PMMA and CHON mixtures. The interaction parameters (χ_{23}) are calculated from the V_g^0.

The general behavior is that, with non-solvent or poor solvents, the interaction parameters have relatively high values, whereas, the polar probes or mutual miscibility give much lower values. In this study, the tacticity of PMMA, composition, and temperature dependence of the interaction parameters for the PMMA/CHON blend is discussed.

2. EXPERIMENTS

2.1 Materials

Poly(methyl methacrylate) (PMMA), cholesteryl n-nonanoate (CHON), and probes (solvents) were commercially obtained and used without further purification. These materials are shown in Table Ⅰ and Table Ⅱ. Chromosorb WAW DMCS (60-80 mesh) was used as a support for PMMA/CHON blends.

Table Ⅰ Materials

Materials	Abbr.	*M*w	T_g/℃	Tacticity/%
atactic Poly(methyl methacrylate)	at-PMMA	3.5×10^5	120	-
syndiotactic Poly(methyl methacrylate)	st-PMMA	5.0×10^4	108	85
isotactic Poly(methyl methacrylate)	it-PMMA	3.0×10^5	45	95
Cholesteryl n-nonanoate	CHON	526.9	-	-

Table Ⅱ Probes (Solvents) used in this work

Probes (Solvents)	Abbr.	M g mol^{-1}	bp K
Toluene	TOL	92.1	383.8
Heptane	HEP	100.2	371.6
Octane	OCT	114.2	398.8

2.2 Column preparation

A calculated CHON and PMMA were completely dissolved in 2-butanone in a sealed glass tube under a nitrogen atmosphere, and a known amount of Chromosorb WAW DMCS (60 – 80 mesh) was immersed in the solution. The 2-butanone was allowed to evaporate at 40°C by gentle and continuous stirring of the solution followed by drying at ambient temperature under reduced pressure. A weighed amount of the PMMA/CHON mixture loaded on Chromosorb was tightly packed into a 2m (length) x 3 mm (inner diameter) stainless steel column that was plugged at each end using silanized glass wool. To provide even packing, the column was constantly vibrated during filling. The columns were conditioned for 48 h at ambient temperature under a constant helium stream.

2.3 Instrumentation and procedure

IGC measurements were carried out on a Shimadzu GC-8A gas chromatograph equipped with a TCD detector. A very small probe was introduced manually. The pressures at the inlet and outlet of the column were measured using the pressure gauge. Dry purified helium was used as the carrier gas. The carrier gas flow rates were measured within error limits, manually using a soap bubble flowmeter at room temperature. The injection of probe vapor with air as a marker was performed using a microsyringe (full scale 1μl). This was carried out by taking $< 0.1\mu l$. The chromatograms were recorded using a Shimadzu C-R6A Chromatopac. Usually the retention volume is obtained using the experimental maximum peak to define the retention time. Most of the probes were characterized by symmetrical elution peaks, and generally exhibited by little sample size at low injection volumes, at low carrier gas flow rates and moderate column loading.

2.4 Calculation

$$t_N = t_R - t_M \quad (1)$$

t_N: net retention time, t_R: probe retention time,

t_M: marker retention time

$$V_N = t_N \cdot F \cdot J \quad (2)$$

$$J = (3((P_i/P_o)^2 - 1))/(2((P_i/P_o)^3 - 1)) \quad (3)$$

V_N : net retention volume

F: volume flow rate of the carrier gas measured at room temperature (T_r), P_i: inlet pressure, P_o: outlet pressure.

Usually, the retention volume is obtained using the experimental peak maximum to define the retention time. The specific retention volume (V_g^0) is calculated using

$$V_g^0 = (V_N \cdot 273.15 \cdot (P_o - P_w))/(w \cdot P_o \cdot T_r) \quad (4)$$

P_w: vapor pressure of water at T_r

w : mass of the stationary phase

The stationary phase/probe interaction parameter (χ_{12}) is

$$\chi_{12} = \ln((273.15 \cdot R \cdot v_2)/(V_g^0 \cdot V_1 \cdot P_1^0)) + V_1/(M_2 \cdot v_2) - P_1^0(B_{11} - V_1)/(R \cdot T) \quad (5)$$

R: gas constant, V_1: molar volume of the probe, B_{11}: second virial coefficient of the probe in the gaseous state, v_2: polymer specific volume.

Considering a ternary system of two components, 3 (PMMA) and 2 (CHON), and 1 (probe), the Flory-Huggins free energy parameter ($\chi_{1(2,3)}$) in single liquid approximation is given by

$$\chi_{1(2,3)} = \varphi_2\chi_{12} + \varphi_3\chi_{13} - \varphi_2\varphi_3\chi_{23} \quad (6)$$

χ_{12}, χ_{13}, and $\chi_{1(23)}$ represent the free energy parameters of the binary systems probe 1/polymer 2 (or 3), and quasi-binary system probe 1/blend 2,3. Consequently, χ_{23} describes the CHON 2/polymer 3 interaction energy.

So the interaction of the GHON2/polymer 3, interaction parameter is

$$\chi_{23} = (\varphi_2\chi_{12} + \varphi_3\chi_{13} - \chi_{1(23)})/\varphi_2\varphi_3 \quad (7)$$

where, φ_2 and φ_3 refer to the volume fractions of the stationary phases.

3. RESULTS AND DISCUSSION

3.1 Retention diagrams

In Figure 1 , specific retention volumes (V_g^0) for toluene in cholesteryl n-nonanoate (CHON) are plotted against the reciprocal column temperature. There are sharp changes in the $\ln V_g^0$ for toluene when GHON styationary phases were used. Same behaviors were found for HEP and OCT.

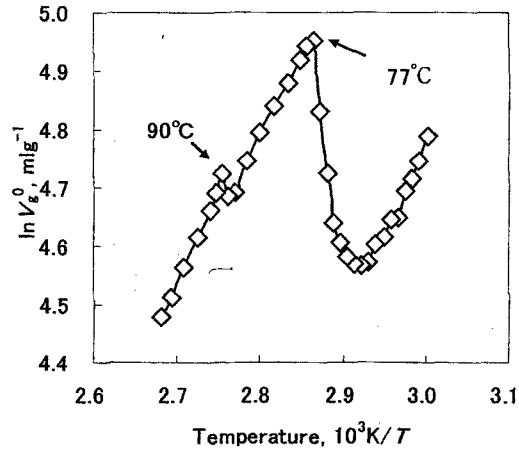
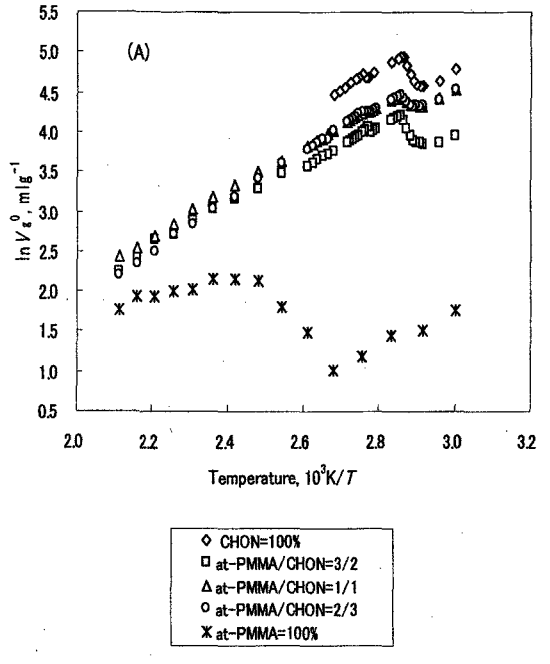
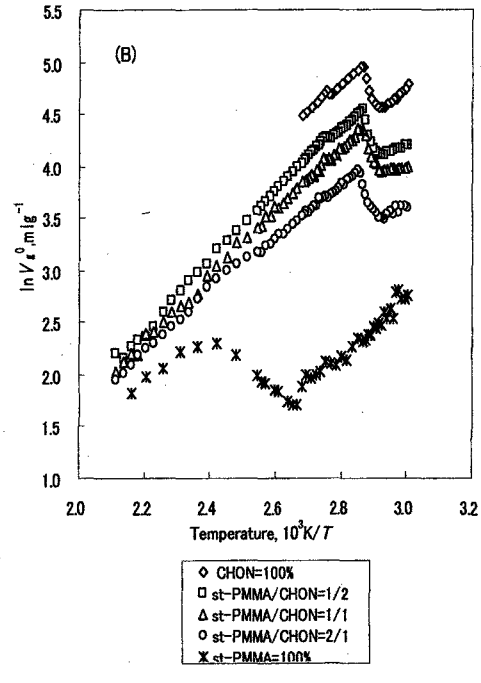


Figure 1 Retention diagram $\ln V_g^0$ versus reciprocal column temperature for toluene (TOL) in cholesteryl n-nonanoate.

When CHON is heated, CHON does not directly into the liquid state, but initially melts at 77°C to give liquid crystal, and at 90°C, a further transition occurs to a normal liquid. Chlesteryl n-nonanoate (CHON) can exist as a solid, or liquid crystal or isotropic liquid between 77 and 90°C.





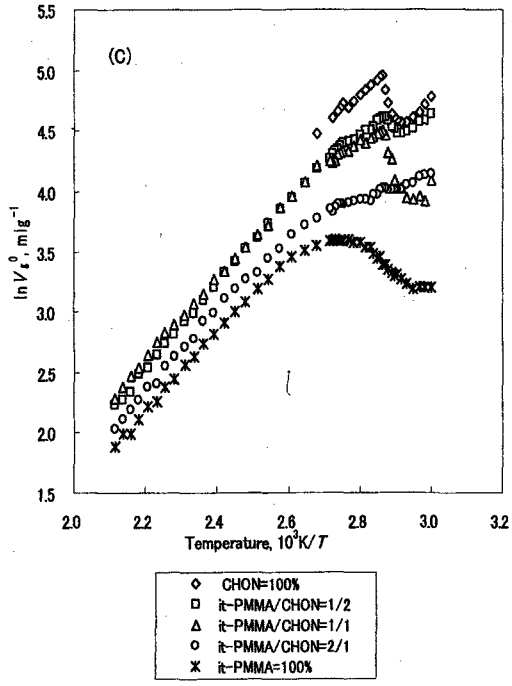


Figure 2 Natural logarithm of specific retention volume versus reciprocal column temperature of toluene in atactic (A), synsiotactic (B) and isotactic (C) PMMA and cholesteryl n-nonanoate (CHON) blends. Column temperatures increased from 60 to 200°C. Blends ratios are indicated by weights.

Figures 2 shows the specific retention volumes ($\ln V_g^0$) versus reciprocal column temperatures for at-PMMA/CHON(A), st-PMMA/CHON(B) and it-PMMA/CHON(C) blends columns, respectively, using toluene as a probe. The retention behaviors of toluene in PMMA (PMMA=100%) and CHON (CHON=100%) are shown in Figure 2. Column temperatures were increased in increments of one degree near below and above transition temperatures of CHON, and maintained at each temperature for 10 min. As the column conditioning was carried out at room temperature, the retention diagrams obtained during first heating were different from those obtained during second heating. This indicates that the conformation of the CHON in the column changed by heating to other conformations. CHON has inflection points at 77 and 90°C as shown in Figure 1. However, the inflection point at 90°C, did not observed clearly in blends systems, especially, in it-PMMA/CHON blends. As the glass transition temperature(T_g) of it-PMMA is 45°C, bulk absorption must affect the retention behaviors in the range above the T_g of it-PMMA. In the range lower than T_g of PMMA, such as at-PMMA and st-PMMA, the inflection point of CHON at 90°C is some shift. These results indicate the interaction between PMMA and CHON.

It is known that the retention behaviors of a probe depends on bulk absorption and surface adsorption. When the coated film on supports (chromosorb) is thin, surface adsorption phenomena pronounced. To minimize these effects, a series of same amount loadings (10%) on the supports were investigated in this work.

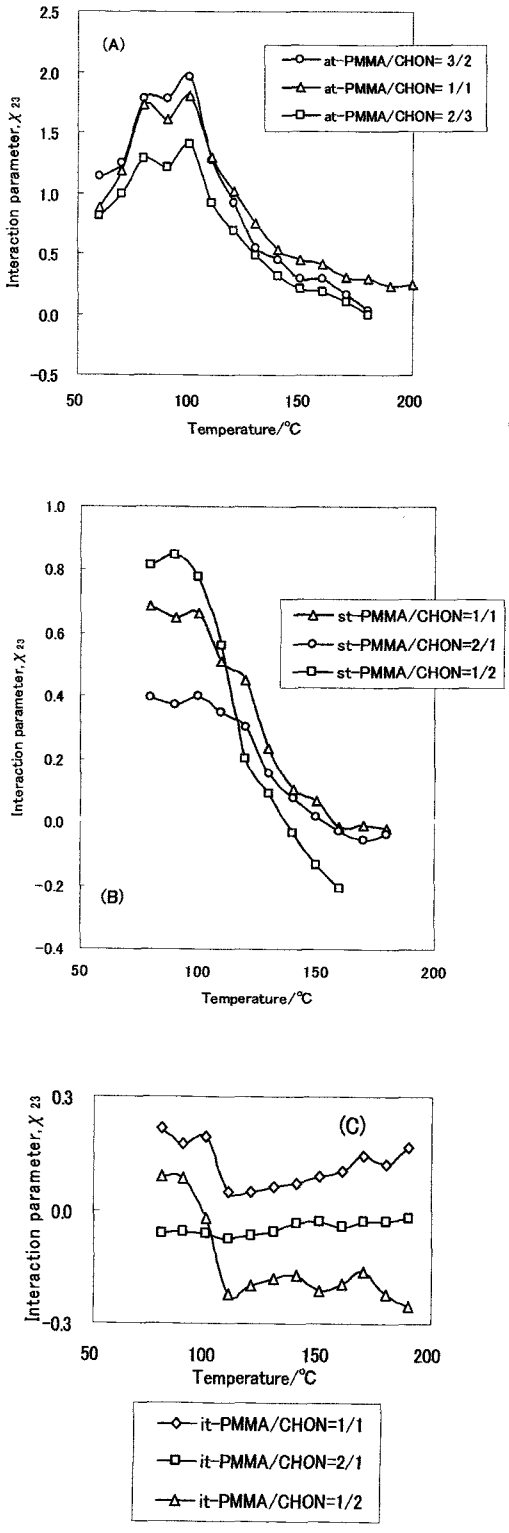


Figure 3 Dependence of interaction parameters on temperature, tacticity and composition in blends of PMMA (atactic (A), syndiotactic(B) and isotactic(C)) and cholesateryl n-nonanoate.

3.2 Interaction parameter

Figure 3 shows the interaction parameters (χ_{23}) calculated from the specific retention volume, according to equation (7). Figure 3(A) shows that the value of χ_{23} for the composition of the at-PMMA/CHON=2/3 blend at 180℃ is negative[5,6], and it-PMMA/CHON=2/1and 1/2 blend at temperature above 100 ℃ is also negative(Figure 3(C)). In the at-PMMA/CHON=1/1 (Figure 3(A) and it-PMMA/CHON=1/1 (C) blends, all values of χ_{23} are positive. χ_{23} of the st-PMMA/CHON=1/1 (Figure 3(B)) blend, are negative at temperatures above 150℃.

The values of the interaction parameter (x_{23}) of the PMMA/CHON mixture are quite dependent on compositions, temperature, and PMMA tacticity.

4. CONCLUSION

The data reported in this paper describe the interaction parameters between PMMA tacticity and liquid crystalline cholesteryl n-nonanoate (CHON) at various temperatures and compositions. The interaction parameters show the dependence on the tacticity of PMMA and the blends ratios of PMMA and CHON. The at-PMMA/CHON=1/1 and it-PMMA/CHON=1/1 blends are positive, for all the temperature regions investigated, however, the st-PMMA/CHON=1/1 blend are negative at temperatures above 150℃ and it-PMMA/CHON=2/1 and 1/2 are negative.. at temperatures above 100℃.

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