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Determination of dielectric properties by solubility parameter of poly(4-methyl -1-pentene)

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Specific retention volume, V_g^0 of benzene, ethyl benzene, n-propyl benzene, isopropyl benzene and chlorobenzene on poly(4-methyl-1-pentene) were obtained by inverse gas chromatography at temperature range in ^oC of 240 and 280. The Flory-Huggins polymer-solvent interaction parameters were determined. The solubility parameter of poly(4-methyl-1-pentene), δ_2 was determined as 7.64 $(cal/cm^3)^{1/2}$ at room temperature by extrapolation of the values obtained at high temperature. Then, dielectric constant and dipole moment of poly(4-methyl-1-pentene) were calculated by means of solubility parameter determined experimentally. The data found in this study are in agreement compared with the ones obtained in the literature.

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Keywords: Poly(4-methyl-1-pentene), inverse gas chromatography, Flory-Huggins interaction parameter, Solubility parameter of polymer, Dielectric constant

1. Introduction

Poly(4-methyl-1-pentene) which is a semicrystalline polyolefin has potentially a wide range of applications, owing to its excellent optical clarity combined with a high melting point, excellent dielectric properties, low bulk density, high chemical resistance, high thermal stability and high permeability to gases[1,2]. It is of practical importance as a membrane making polymer. Solubility of poly(4-methyl-1-pentene) is important because its usage as a membrane depends on their solubility behavior.

The solubility parameter, δ which is a characteristic of a polymer, is used in prediction of solubility of a polymer in a given solvent as well as some physical properties such as dielectric constant, dipole moment and refractive index. The solubility parameter of a liquid with low molecular weight is found directly from its enthalpy of vaporization and molar volume. However, for a polymer, it is usually taken to be equal to the solubility parameter of the solvent producing maximum intrinsic viscosity of its solution or maximum swelling of its network [3-5]. These procedures are time consuming. It can be also estimated by adding up the contributions of groups of repeating units. However, group contributions of some specific groups are sometimes not present in the literature. In addition, the value of solubility parameter calculated by group contribution is an approximate value. Therefore, someone needs a fast way to determine experimentally the solubility parameter of a polymer. In comparison to other techniques, inverse gas chromatography (IGC) is very fast and inexpensive to determine the solubility parameter together with polymer-solvent interaction parameter, χ of a polymer [6,7]. The interaction parameters are used in determination of the degree of interaction of a polymer with a solvent, which is needed in process and reactor design.

In this study, Flory-Huggins polymer-solvent interaction parameters and solubility parameter of poly(4-methyl-1-pentene) were determined by IGC technique. There is no any data in the literature related to the interaction parameters of poly(4-methyl-1-pentene) with any solvent. From the solubility parameters, dielectric constant and dipole moment of poly(4-methyl-1-pentene) were calculated by using some empirical relationships[8].

2. Experimental

Poly(4-methyl-1-pentene) was a product of Aldrich. Benzene (B), ethyl benzene (EB), n-propyl benzene (PB), isopropyl benzene (IPB) and chloro benzene (CB) were Merck AG. Inc. products, analytical reagent grade and used without further purification. The solvents and support

material being Chromosorb-W (AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG. Inc. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc., respectively. A Hewlett-Packard 6890 N Model, gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents. The column was stainless steel tubing with 3.2 mm o.d. and 1 m in length. The polymer was coated on the support by slowly evaporation of chloroform as stirring the Chromosorb-W in the polymer solution.

3.1. Theoretical background on IGC

The specific retention volume, V_g^0 is determined experimentally from IGC measurements as follows [9-12]

$$V_g^0 = \frac{Q(t_R - t_A)J273.2}{(T_r w)} \quad (1)$$

where Q is carrier gas flow rate measured at room temperature T_r; t_R and t_A are retention times of the solvent and air, respectively; J is pressure correction factor ; w is weight of liquid crystal in the column.

According to the Flory-Huggins theory, interaction parameters, χ_{12}^{∞} is defined in the Eq.(2)

$$\chi_{12}^{\infty} = \ln\left(\frac{273.2\,Rv_2}{p_1^0 V_g^0 V_1^0}\right) - \left(1 - \frac{V_1^0}{M_2 v_2}\right) - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \quad (2)$$

where R is the universal gas constant; p_1^0, B_{11} and V_1^0 are saturated vapor pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature T; v_2 and M_2 are specific volume and molecular weight of the polymer, respectively.

The solubility parameter of the polymer, δ_2 is found by combining of the theories of Flory-Huggins and Hildebrand-Scathard [13,14]

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^{\infty}}{V_1^0}\right) = \left(\frac{2\delta_2\delta_1}{RT}\right) - \left(\frac{\delta_2^2}{RT}\right) \quad (3)$$

where δ_1 is solubility parameter of solvent.

3.2. Group contribution method

The relation among molar polarization, dielectric constant and dipole moment of a dielectric is given as follows[8],

$$P_{LL} = \frac{\varepsilon - 1}{\varepsilon + 2} V \quad (4)$$

or

$$P_V = \varepsilon^{1/2} M \quad (5)$$

$$R_{LL} = \left[\frac{n^2 - 1}{n^2 + 2}\right]\frac{M}{\rho} = \left[\frac{n^2 - 1}{n^2 + 2}\right] V \quad (6)$$

$$P_{LL} - R_{LL} = \frac{4}{9}\pi N_A \frac{\mu^2}{kT} \approx 20.6\mu^2 \quad \text{(at 298 K)} \quad (7)$$

where P_{LL} and P_V is the molar dielectric polarization according to Lorentz-Lorenz and Vogel respectively; ε is the dielectric constant; V is the molar volume per structural unit; M is the molar mass per structural unit; R_{LL} is the molar refraction according to Lorentz-Lorenz; n is the index of refraction; ρ is the density; N_A is the Avogadro number; μ is the dipole moment and k is the Boltzmann constant

Application of Equation (4) and (5) permits the calculation of the dielectric constant ε if the structural unit is known.

According to Darby et. al. [8], the solubility parameter of polymers is defined by the simple correlation as follows:

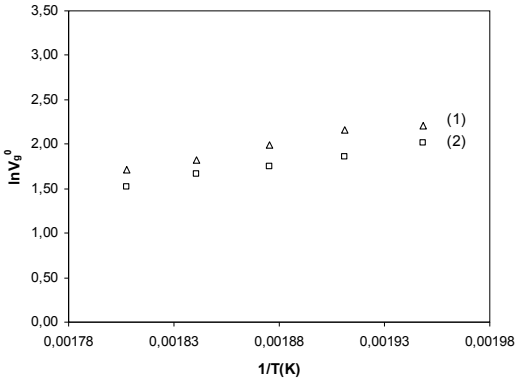
$$\delta \approx 7.0\,\varepsilon \quad (8)$$

4. Results and discussion

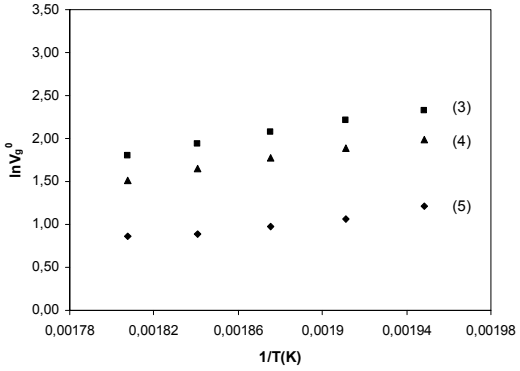
The specific retention volume, V_g^0 of the B, EB, PB, IPB and CB on the poly(4-methyl-1-pentene) were obtained from IGC measurements at temperatures in °C between 240 and 280 using Eq.1. Results were given in Fig 1.

The Flory-Huggins polymer-solvent interaction parameter, χ_{12}^{∞} was determined from Eq. 2. Results were given in Tables 1. If the parameter χ_{12}^{∞} is lower than 0.5, the solvent is good for the polymer, however, if it is higher

than 0.5, the solvent is poor for the polymer [15]. The values of parameter χ_{12}^{∞} suggest that aromatic solvents are good for poly(4-methyl-1-pentene) at temperatures in ^{o}C between 240 and 280. These data could not be compared since there are no any data of Flory-Huggins interaction parameters of poly(4-methyl-1-pentene) in the literature.



(a)



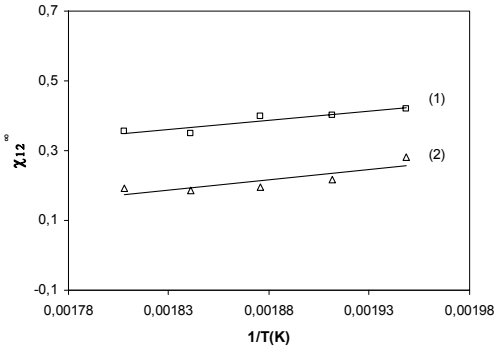
(b)

Fig. 1. The retention diagram of IPB (1) and CB (2) ***(a);*** *and PB (3), EB (4), B (5)* ***(b)*** *on poly(4-methyl-1-pentene).*

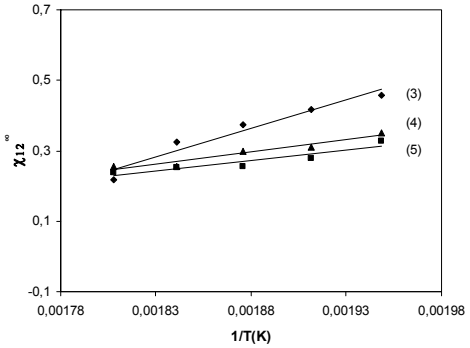
Table 1. Flory-Huggins polymer-solvent interaction parameters, χ_{12}^{∞} with poly(4-methyl-1-pentene).

t(^{o}C)	B	EB	PB	IPB	CB
240	0.46	0.35	0.33	0.28	0.42
250	0.42	0.31	0.28	0.22	0.40
260	0.37	0.30	0.26	0.19	0.40
270	0.32	0.26	0.25	0.19	0.35
280	0.22	0.26	0.24	0.19	0.36

In Fig. 2, the variation of χ_{12}^{∞} with 1/T is plotted. The extrapolated value of χ_{12}^{∞} at 25 ^{o}C is reliable since the variation is linear. The solubility parameter of poly(4-methyl-1-pentene), δ_2 was determined from the slope and intercept of the plot drawn using χ_{12}^{∞} values at 25 ^{o}C, according to Eq. 3. The plot was given in Fig. 3. The magnitudes of δ_2 was found as 7.64 $(cal/cm^3)^{1/2}$ as averaging of the values obtained from slope and intercept. It is comparable to the reported values in literature that are between 7.40 and 8.0 $(cal/cm^3)^{1/2}$ [16]. It is calculated as 7.47 $(cal/cm^3)^{1/2}$ by contribution given by Van Krevelen[8].



(a)



(b)

Fig. 2. The interaction parameters χ_{12}^{∞} of the CB(1), IPB(2) ***(a)****; B(3), EB(4), PB(5)* ***(b)****; at infinite dilution with poly(4-methyl-1-pentene) as a function of reciprocal of the absolute column temperature.*

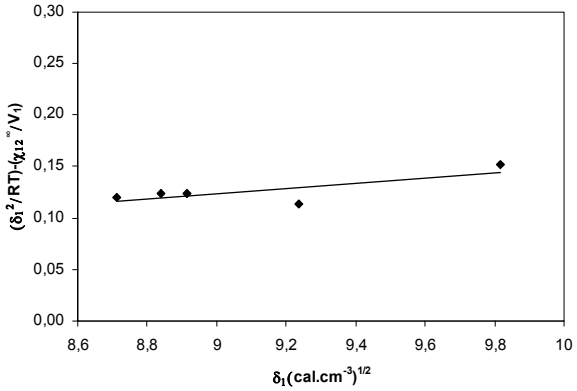


Fig. 3. Estimation of solubility parameter, δ_2 of poly(4-methyl-1-pentene) from solubility parameter of the solvents , δ_1 and Flory-Huggins interaction parameters, χ_{12}^{∞} at 25 ^{o}C.

By using the experimental value of solubility parameter of polymer, dielectric constant and dipole moment of poly(4-methyl-1-pentene) were determined as 2.23 from Eq. 8 and 0.27 Debye from Eqs. 4-7, respectively. On the other hand, dielectric constant of the polymer were calculated to be ε=. 2.38 from Eq.4 and ε=. 2.16 from Eq. 5, by group contribution. The dipole moment and refractive index of the polymer were determined as μ=0 Debye and n=1.464 by group contribution. It was seen in Table 2 that the data determined by IGC and group contribution for poly(4-methyl-1-pentene) are comparable with the literature values.

Table 2. Comparison of physical properties determined by IGC.

Physical property	IGC	Reference (15)	Group contribution
δ_2(cal/cm^3)$^{1/2}$	7.64	7.40-8.00	7.47
ε	2.23	2.16	2.38* and 2.16#
μ (Debye)	0.27	--	0
n	--	1.463	1.464

*from Eq.4
#from Eq.5

5. Conclusions

The values of the Flory Huggins interaction parameters suggest that studied aromatic solvents are good for poly(4-methyl-1-pentene) at temperatures in ^oC between 240 and 280. The solubility parameter, dielectric constant, dipole moment of poly(4-methyl-1-pentene) determined by IGC are in good agreement with the ones given in literature and estimated by other groups contributions. In conclusion, this study suggests that IGC can be expanded to determine the dielectric constant and dipole moment of a polymer.

Acknowledgements

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