

Determination of Crystallinity Ratio and Some Physicochemical Properties of Poly(4-methyl-1-pentene)

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ABSTRACT: It was determined that the thermal stability of poly(4-methyl-1-pentene) (P4MP) was maintained up to 424°C in an inert atmosphere by thermogravimetric analysis. The retention diagrams of ethyl acetate, *tert*-butyl acetate, and benzene on P4MP were plotted at temperatures between 30 and 280°C by inverse gas chromatography (IGC) technique. Melting temperature of the polymer was determined as 230 and 239.5°C by IGC and differential scanning calorimetry (DSC), respectively. The percent crystallinity of P4MP was obtained from the retention diagrams at temperatures below melting point. The percent crystallinity obtained by IGC is in good agreement with the ones obtained by DSC. Then, specific retention vol-

ume, V_g^0 , weight fraction activity coefficient, Ω_1^∞ , Flory-Huggins polymer-solvent interaction parameter, χ_{12}^∞ , equation-of-state polymer-solvent interaction parameter, χ_{12}^* , and effective exchange energy parameter, X_{eff} of octane, nonane, decane, undecane, dodecane, tridecane, *n*-butyl acetate, isobutyl acetate, isoamyl acetate with P4MP, were determined between 240 and 280°C by IGC. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 901–906, 2009

Key words: inverse gas chromatography; poly(4-methyl-1-pentene); percent crystallinity; thermodynamics; differential scanning calorimetry

INTRODUCTION

Poly(4-methyl-1-pentene) (P4MP) is a semicrystalline polyolefin with a number of interesting properties. It is of practical importance as a membrane-making polymer.^{1,2} Percent crystallinity and thermodynamic interactions with solvents of P4MP are important because its usage as a membrane depends on interactions and crystallinity ratio.

Although inverse gas chromatography (IGC) has been widely used to investigate the interactions of polymeric materials with various solvents,^{3–5} it is a novel technique in determination of crystallinity ratio of polymers.^{3,6,7} The basic method for the calculation of the percent crystallinity is to compare the melting enthalpy of the studied polymeric system with the melting enthalpy of the same polymer of 100% crystallinity. We know that there is no fully crystalline polymer and the value for a polymer is taken from extrapolation (frequently performed for a low-mass molecular compound), which the chemical structure is similar to the repeating unit of the polymer. This procedure does not take into account the

crystal's polymorphism and the change of the system volume. In addition, if it is considered the problem with the baseline for differential scanning calorimetry (DSC) measurement, it seems that the procedure should not give correct values. If someone cannot find any data of melting enthalpy of a semicrystalline polymer, then its percent crystallinity cannot be determined. In some cases, different melting enthalpies are reported for 100% crystalline polymer or, sometimes, several crystalline modifications of a polymer might exist; for example, isotactic P4MP samples obtained from melt or solution exhibit five crystal modifications. However, in IGC technique, there is no need for any data other than measured specific retention volumes in order to determine the percent crystallinity of a semicrystalline polymer.

There are no any data in literature related to the thermodynamic interactions with solvents and percent crystallinity of P4MP, determined by IGC. In this study, the crystallinity ratio of P4MP was determined by using benzene, ethyl acetate, and *tert*-butyl acetate as probes by IGC and compared with the data determined by DSC to reveal the reliability of the new technique. Then, thermodynamic solubility properties of P4MP were studied by IGC. We have determined the Flory-Huggins polymer-solvent interaction parameter, χ_{12}^∞ , and the effective exchange energy parameter, X_{eff} , in the equation of state theory of P4MP with some alkanes and some esters at a temperature range of 240 and 280°C using

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IGC. The parameter X_{eff} is assumed to be independent of temperature and composition of the mixture.^{8–10} However, it has been observed that it is dependent on temperature for some polymer–solvent systems because of enthalpy and entropy contributions.¹¹ In this study, we also investigated the dependence of X_{eff} on temperature.

THEORETICAL BACKGROUND

The specific retention volume, V_g^0 , is determined experimentally from IGC measurements as follows^{12–16}:

$$V_g^0 = Q(t_R - t_A)J 273.2/(T_r w) \quad (1)$$

where Q is carrier gas flow rate measured at the room temperature T_r , and t_R and t_A are retention times of the solute probe and air, respectively. J is pressure drop correction factor which equals to $[3(p_i/p_o)^2 - 1]/[2(p_i/p_o)^3 - 1]$, where p_i and p_o are column inlet and outlet pressures, respectively, and w is weight of polymer in the column.

The percentage of crystallinity of a polymer is calculated as follows³:

$$\text{Percent crystallinity} = 100(1 - V_g^0/V_g^{0'}) \quad (2)$$

where V_g^0 and $V_g^{0'}$ are measured and extrapolated values of the retention volumes at a given temperature, respectively.

The weight fraction activity coefficient of each solvent, Ω_1^∞ , is defined by the following equation:

$$\ln \Omega_1^\infty = \ln(273.2R/V_g^0 p_1^0 M_1) - p_1^0(B_{11} - V_1^0)/RT \quad (3)$$

where R is the universal gas constant; and p_1^0 , M_1 , B_{11} , and V_1^0 are saturated vapor pressure, molecular weight, gaseous state second virial coefficient, and molar volume of the solvent at temperature T , respectively.

According to Flory-Huggins and equation-of-state theory, interaction parameters, χ , are defined in the eqs. (4) and (5), respectively:

$$\chi_{12}^\infty = \ln(273.2 R v_2/p_1^0 V_g^0 V_1^0) - 1 - p_1^0(B_{11} - V_1^0)/RT \quad (4)$$

$$\chi_{12}^* = \ln(273.2 R v_2^*/p_1^0 V_g^0 V_1^*) - 1 - p_1^0(B_{11} - V_1^0)/RT \quad (5)$$

where v_2 and v_2^* are specific volume and hard core volume of polymer, respectively.

In the equation of state theory, v_r , T_r , and p_r , which are reduced volume, temperature, and pressure of the system, respectively, are ratios of the actual v , T , and P to the corresponding characteristic

parameters, V^* , T^* , and p^* , which can be evaluated from the thermal expansion and pressure coefficients as follows:

$$v_r^{1/3} = (V/V^*)^{1/3} = [(\alpha T/3)/(1 + \alpha T)] + 1 \quad (6)$$

$$T_r = T/T^* = (v_r^{1/3} - 1)/v_r^{4/3} \quad (7)$$

$$p_r^* = \gamma T v_r^2 \quad (8)$$

where α is thermal expansion coefficient defined as:

$$\alpha = (1/V)(\partial V/\partial T)_{p=0} \quad (9)$$

and γ is thermal pressure coefficient defined as:

$$\gamma(\partial p/\partial T)_v \quad (10)$$

The effective exchange energy parameter in the equation-of-state theory, X_{eff} , is defined as follows:

$$RT\chi_{12}^* = p_1^* V_1^* \{3T_{1r} \ln[(v_{1r}^{1/3} - 1)/(v_{2r}^{1/3} - 1) + v_{1r}^{-1} - v_{2r}^{-1} + X_{\text{eff}} V_1^* v_{2r}^{-1}]\} \quad (11)$$

EXPERIMENTAL

Octane (O), nonane (N), decane (D), undecane (UD), dodecane (DO), tridecane (TD), ethyl acetate (EA), *n*-butyl acetate (*n*BA), isobutyl acetate (IBA), *tert*-butyl acetate (*t*BA), isoamyl acetate (IAA), and benzene (B) were from Merck AG. P4MP was a product of Aldrich. Support material Chromosorb-W (AW-DMCS-treated, 80/100 mesh) was obtained from Merck AG. Silane-treated glass wool used to plug the ends of the column was obtained from Alltech Associates.

A Hewlett-Packard 6890 N 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. At first, retention time of air, t_A , was determined by injecting a large amount air with a 5- μ L Hamilton syringe. Then, retention time of the solvent, t_R , was determined by injecting trace amount solvent into the column with a 1- μ L Hamilton syringe. Solvent (0.1 μ L) was taken into the syringe and flushed into the air. The residual solvent was diluted five times by taking 1 μ L of air into the syringe. At least three consecutive injections were made for each solvent at each column temperature. The retention times were precise and reproducible to ± 0.001 min. The flow rate of the carrier gas was kept below 6 $\text{cm}^3 \text{min}^{-1}$. Before the experiments, it was determined experimentally that the retention volume does not depend on the flow rate of the carrier gas below 6 $\text{cm}^3 \text{min}^{-1}$. In determination of

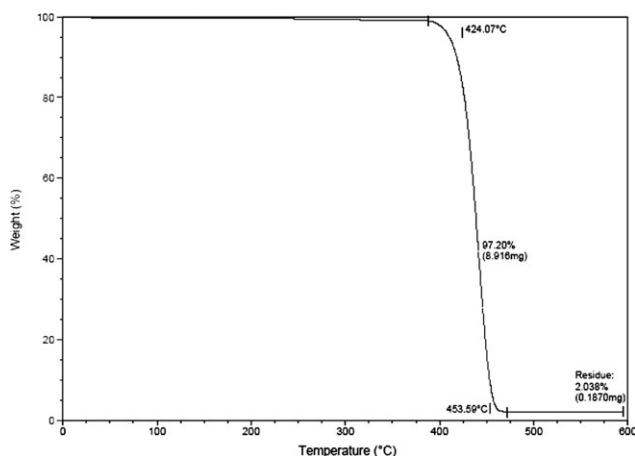


Figure 1 Thermogravimetric analysis trace of P4MP.

pressure drop correction factor, J , p_i was measured by a manometer in the column inlet in the injection section and p_o was accepted as equal to ambient pressure. The polymer was coated on the support by slow evaporation of chloroform while stirring the Chromosorb-W in the polymer solution. The loading of the coated polymer on the support was determined as 10.28% by calcination. The coated support material was filled into the empty column. The column mounted on the chromatograph was conditioned in He atmosphere at 290°C at 24 h.

The thermograms of DSC and thermogravimetric analyses (TGA) of P4MP were recorded on a SDT Q600, with a heating and cooling rate of 10 K min⁻¹ in nitrogen atmosphere.

RESULTS AND DISCUSSION

It can be seen from TGA thermogram in Figure 1 that P4MP demonstrated relative thermal stability at temperatures between 30 and 280°C. The initial decomposition temperature of the polymer is 424°C.

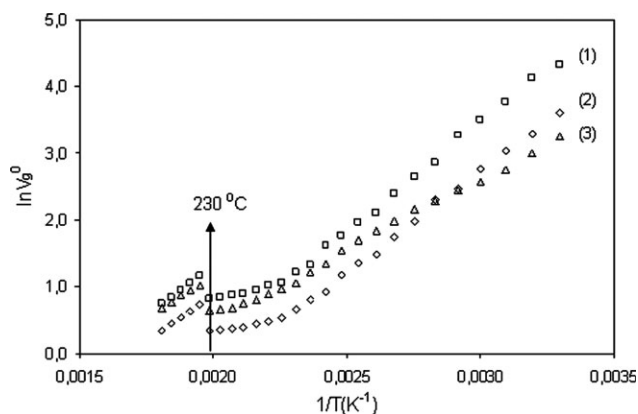


Figure 2 The retention diagram of B (1), EA (2), and *t*BA (3) on P4MP.

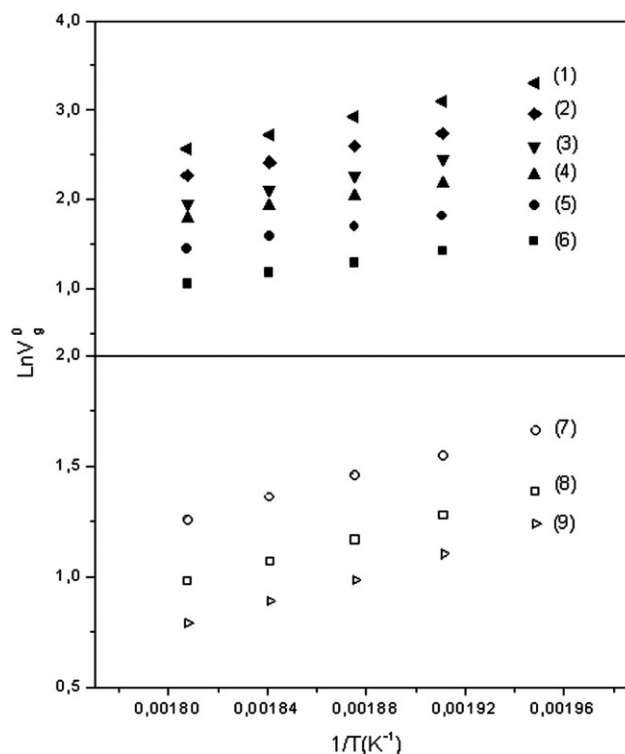


Figure 3 The retention diagram of TD (1), DD (2), UD (3), D (4), N (5), O (6), IAA (7), *n*BA (8), and IBA (9) on P4MP.

The specific retention volumes, V_g^0 , of the aliphatic esters and alkanes were obtained experimentally from IGC measurements using eq. (1). Graphical results were given in Figure 2 for B, EA, and *t*BA between 30 and 280°C, as well as in Figure 3 for O, N, D, UD, DD, TD, *n*BA, IBA, and IAA between 240 and 280°C. Melting point, T_m , of P4MP was found to be 230°C from the first-order transitions in Figure 2. Determination of crystallinity of a polymeric stationary phase is based on the different solubility of the solvent in the crystalline and amorphous regions. By assuming that the crystalline regions do not participate in the retention of the solvent molecules in the range below T_m , it is possible to estimate the degree of crystallinity of the polymer. The polymer is fully amorphous at temperatures higher than T_m , whereas it is partially crystalline at temperatures lower than

TABLE I
Percent Crystallinities of P4MP Determined by IGC

T (°C)	% Crystallinity		
	EA	B	<i>t</i> BA
30	53.6	58.9	59.1
40	55.6	53.7	59.5
50	54.8	56.1	60.5
60	55.3	56.4	58.8

EA, ethyl acetate; B, benzene; *t*BA, *tert*-butyl acetate.

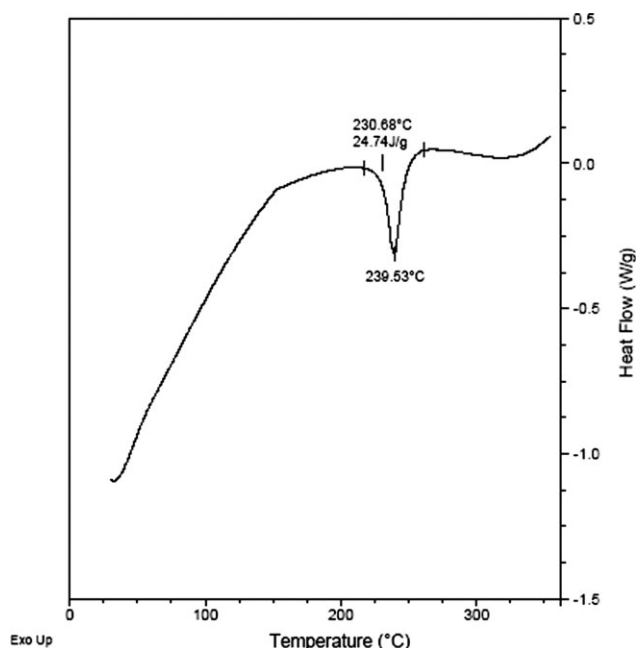


Figure 4 DSC scan of P4MP.

T_m . Therefore, the extrapolation of the line above T_m to the temperature range below T_m makes it possible to estimate the retention volume that would correspond to the hypothetical amorphous state of the entire polymer at temperatures below T_m .³ By applying this on the retention diagram in the Figure 2, one can calculate the percentage of crystallinity of P4MP by using eq. (2). The percent crystallinities were determined as 53.6, 58.9, and 59.1 from injection of EA, B, and *t*BA as probes, respectively at 30°C. Results are shown in Table I.

DSC curve was given in Figure 4. T_m was defined as 239.5°C from the minimum of the DSC endothermic peak. The crystallinity ratio of the polymer was obtained according to the following definition:

$$\text{Crystallinity ratio of polymer} = \Delta H / \Delta H_c \quad (12)$$

where ΔH and ΔH_c are heats of fusion of measured sample and fully crystalline polymer, respectively.

ΔH was determined as 21.7 J g⁻¹ from the area of the DSC peak after a baseline subtraction. ΔH_c was adapted to be 61.7 J g⁻¹ for 100% crystalline polymer from the literature.¹⁷ Therefore, the crystallinity of the polymer was found 40% from the DSC in this study. The percent crystallinity varied from 36 to 63% depending on the annealing conditions in literature.¹⁸ From the DSC measurements in another study,¹⁹ percent crystallinity of a P4MP sample was found as 43% if its T_m was around 220°C; however, it was found to be ~ 62% if the T_m was about 230°C. The data found in this study are in agreement compared with the ones obtained in the literature.

The weight fraction activity coefficients of the studied solvents at infinite dilution, Ω_1^∞ , were determined from eq. (3). Results are shown in Table II for all of the studied solvents. According to Guillet,³ the solvent is good if Ω_1^∞ is lower than 5 and is poor if Ω_1^∞ is higher than 10. The values between 5 and 10 indicate moderately poor solubility. The parameter Ω_1^∞ derived from fundamental relations of physical chemistry does not include any uncertainty coming from theoretical assumptions. The values of Ω_1^∞ suggest that all studied solvents are good and almost independent on temperature at studied temperature interval.

The polymer–solvent interaction parameters, χ_{12}^∞ and χ_{12}^* , were determined from eqs. (4) and (5) and are shown in Tables III and IV, respectively. The values of $\chi_{12}^\infty > 0.5$ represent unfavorable polymer–solvent interactions, whereas the values < 0.5 indicate favorable interactions in dilute polymer solutions. The values suggest that all studied solvents are good and tend to be better with increasing temperature.

The parameters X_{eff} found by means of eqs. (5)–(11) are shown in Table V. Thermal expansion coefficient, α , and isothermal compressibility, β , of P4MP were obtained from experimental data.²⁰ The higher values of X_{eff} indicate poor solubility. The magnitudes of X_{eff} are considerably higher in the case of aliphatic esters than those of *n*-alkanes, except O. It was determined that X_{eff} increased relatively with

TABLE II
The Weight Fraction Activity Coefficients of the Solvents at Infinite Dilution, Ω_1^∞ , of P4MP with Some Alkanes and Aliphatic Esters

T (°C)	Ω_1^∞								
	O	N	D	UD	DD	TD	<i>n</i> BA	IBA	IAA
240	5.3	4.8	4.6	4.6	4.4	4.2	5.4	5.5	4.3
250	5.2	4.7	4.3	4.5	4.6	4.1	5.3	5.6	4.2
260	5.4	4.6	4.3	4.6	4.4	4.0	5.3	5.7	4.0
270	5.4	4.6	4.2	4.6	4.4	4.1	5.2	5.7	3.9
280	5.6	4.7	4.2	4.7	4.4	4.0	5.2	5.8	3.9

O, octane; N, nonane; D, decane; UD, undecane; DD, dodecane; TD, tridecane; *n*BA, *n*-butyl acetate; IBA, isobutyl acetate; IAA, isoamyl acetate.

TABLE III
Flory-Huggins Polymer–Solvent Interaction Parameters, χ_{12}^{∞} , of P4MP with Some Alkenes and Aliphatic Esters

T (°C)	χ_{12}^{∞}								
	O	N	D	UD	DD	TD	nBA	IBA	IAA
240	0.24	0.21	0.22	0.26	0.25	0.27	0.51	0.42	0.36
250	0.20	0.17	0.14	0.22	0.27	0.25	0.46	0.40	0.31
260	0.18	0.13	0.11	0.22	0.21	0.21	0.42	0.36	0.24
270	0.15	0.10	0.07	0.21	0.21	0.22	0.38	0.30	0.18
280	0.12	0.09	0.05	0.21	0.18	0.19	0.31	0.22	0.14

O, octane; N, nonane; D, decane; UD, undecane; DD, dodecane; TD, tridecane; nBA, *n*-butyl acetate; IBA, isobutyl acetate; IAA, isoamyl acetate.

TABLE IV
Equation-of-State Polymer–Solvent Interaction Parameters, χ_{12}^* , of P4MP with Some Alkenes and Aliphatic Esters

T (°C)	χ_{12}^*								
	O	N	D	UD	DD	TD	nBA	IBA	IAA
240	0.61	0.53	0.51	0.52	0.49	0.48	0.88	0.82	0.68
250	0.58	0.49	0.43	0.47	0.53	0.46	0.83	0.81	0.63
260	0.59	0.46	0.41	0.48	0.45	0.43	0.80	0.79	0.57
270	0.57	0.44	0.37	0.48	0.45	0.43	0.77	0.75	0.52
280	0.57	0.45	0.36	0.47	0.42	0.40	0.73	0.72	0.49

O, octane; N, nonane; D, decane; UD, undecane; DD, dodecane; TD, tridecane; nBA, *n*-butyl acetate; IBA, isobutyl acetate; IAA, isoamyl acetate.

TABLE V
Effective Exchange Energy Parameters of the Equation-of-State Theory, X_{eff} (J cm⁻³), of P4MP with Some Alkenes and Aliphatic Esters

T (°C)	X_{eff}								
	O	N	D	UD	DD	TD	nBA	IBA	IAA
240	4.2	-0.5	-2.3	-1.8	-2.3	-2.0	16.2	13.0	5.6
250	6.7	1.2	-2.3	0.4	0.5	-0.2	19.1	17.7	7.7
260	10.3	2.5	-0.6	1.7	1.0	0.6	22.0	21.6	8.2
270	13.0	4.1	-0.1	3.5	2.5	2.5	24.4	24.6	9.1
280	16.7	6.6	1.4	5.1	3.0	2.9	26.1	28.2	10.5

O, octane; N, nonane; D, decane; UD, undecane; DD, dodecane; TD, tridecane; nBA, *n*-butyl acetate; IBA, isobutyl acetate; IAA, isoamyl acetate.

temperature. Thermodynamic interaction parameters obtained in this study could not be compared because there are no any data related to P4MP in the literature.

CONCLUSIONS

It can be seen from TGA trace that P4MP demonstrated the relatively good thermal stability in the temperature range of 240–280°C. It was seen that all studied solvents are good at temperatures studied and that solvent quality increases with temperature. The percent crystallinity of P4MP was 40% from the DSC and 57.2% as a mean value from IGC. The data

found by IGC in this study are comparable with the ones obtained in the literature. The differences between the values can be attributed to the crystal polymorphism of P4MP. Therefore, this study suggests that IGC is an easy and useful tool to determine the crystallinity ratio of a polymer.

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