



Research Article

Thermodynamic studies on tert-amine modified polystyrene based polymer/solvent systems by inverse gas chromatography method

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ABSTRACT

In the present work, vinyl benzyl chloride (VBC) was polymerized by using free radical polymerization. The obtained PVBC was reacted with dibutyl amine to obtain tertiary amine modified polystyrene based polymer (PVBC-Dibutyl amine). The inverse gas chromatography (IGC) method was used to examine the thermodynamic properties of the polymer. Firstly, the retention diagrams of some polar and non-polar solvents on PVBC-Dibutyl amine were obtained over a temperature range from 135 to 160° C. Then, the thermodynamic parameters, including Flory–Huggins interaction parameter, weight fraction activity coefficient, partial molar heat of sorption, and partial molar heat of mixing were determined via interactions between the polymer and selected solvents at infinite dilution. The results reveal that the alkanes are poor solvents for the polymer whereas n-butyl acetate, i-butyl acetate, ethyl acetate, n-propylbenzene, i-propylbenzene, and ethylbenzene are moderately solvents in the studied temperature range.

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INTRODUCTION

In industrial and laboratory applications, to predict optimum conditions for many processes and products design knowledge of thermodynamics of polymer solutions/their blends is required. In particular, interaction parameters such as Flory–Huggins, χ_{12}^{∞} , and the weight fraction activity

coefficients, Ω_1^{∞} , are a useful tool for predicting sufficient miscibility or solubility between a solvent and a polymer/polymer-polymer blends [1–4].

Inverse gas chromatography (IGC) [5] is a commonly used method to analyze and measure the physicochemical properties of the polymers and polymer/polymer blends

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over more than 40 years. By IGC, it is possible to obtain some valuable interaction parameters such as χ_{12}^∞ , Ω_1^∞ , equation-of state interaction parameters, χ_{12}^* , effective exchange energy parameter, χ_{eff} and thermodynamic characteristics such as the partial molar heat of mixing at infinite dilution of the solvent, $\Delta\bar{H}_1^\infty$, molar heat of vaporization of solvent, $\Delta\bar{H}_v$, and the partial molar heat of sorption of the solvent, $\Delta\bar{H}_1^s$, based on polymer-solvent interactions for polymeric systems [6–13]. The term “inverse” indicates that the stationary phase of the chromatographic column is an unknown polymeric material examined and its properties are determined based on the retention behavior of carefully selected test solvents (probes). The method is powerful, reliable, and is also economical as it requires a limited amount of the solvent and polymer sample [4,14].

4-chloromethyl styrene or VBC is known as one of the important functional monomers because it has an active benzylic chloride suitable for nucleophilic substituents [15]. Besides, the nucleophilic substitution can be carried out after VBC has been polymerized to obtain poly (vinyl benzyl chloride) (PVBC). The styrene (or polystyrene) based polymers obtained in this way have various applications such as functional polymers [16], optical materials [17–18], polyelectrolytes [19–21], and biomaterials [22–24].

Synthesis of the dibutylamine modified styrene based monomer and its polymer were described in the literature [25]. In this study, after the synthesis of PVBC by free radical polymerization method, it was reacted with dibutyl amine to obtain PVBC-Dibutyl amine. The thermodynamic properties of PVBC-Dibutyl amine were investigated by the IGC method in a wide temperature range.

INVERSE GAS CHROMATOGRAPHY THEORY

The method of IGC is based on the measurement of the retention times of solvents injected into the column that contains the polymeric material under study as a stationary phase. In the method, there is a relationship between polymer-solvent interactions and the specific retention volumes, V_g^0 , expressed by the following equation [5,13]:

$$V_g^0 = \frac{Q \cdot (t_R - t_A) \cdot J \cdot 273.2}{T_r \cdot w} \quad (1)$$

where Q is the 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 James-Martin gas compressibility correction factor term is given by $J = [3(p_i/p_0)^2 - 1]/[2(p_i/p_0)^3 - 1]$ where p_i is the pressure at the column inlet and p_0 is the pressure at the column outlet and w is the weight of the polymer in the IGC column.

Flory-Huggins and equation-of-state interaction parameters, χ_{12}^∞ and χ_{12}^* can be calculated following Equations (2) and (3), respectively [26–27]:

$$\chi_{12}^\infty = \ln \left(\frac{273.2Rv_2}{V_g^0 P_1^0 V_1^0} \right) - 1 - \frac{P_1^0 (B_{11} - V_1^0)}{RT} \quad (2)$$

$$\chi_{12}^* = \ln \left(\frac{273.2Rv_2^*}{V_g^0 P_1^0 V_1^*} \right) - 1 - P_1^0 (B_{11} - V_1^0) / RT \quad (3)$$

where R is the universal gas constant; P_1^0 is saturated vapor pressure and the values of P_1^0 were calculated from the Antoine equation ($\log P_1^0 = A - (B/(t + C))$) where t is temperature and A , B and C are component-specific constants [28–29]; V_1^0 is the molar volume of the probe at temperature T ; v_2 and v_2^* are specific volume and specific hardcore volume of the polymer in the IGC column, respectively. V_1^* is the molar hardcore volume of the probe. B_{11} is the gaseous state second virial coefficient and the values of B_{11} were calculated ($B_{11} = (0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n - 1)(T_c/T)^{3/2})/V_c$) where n is the number of carbon atoms in solvents (for permanent gases, $n = 1$ and the last term becomes zero), T_c is the critical temperature of the solvents and V_c is the critical molar volume of the solvents [30–31].

The effective exchange energy parameter, X_{eff} in the equation of state theory is equal to Equation (4) [32]:

$$RT \chi_{12}^* = p_1^* V_1^* \left\{ 3T_{1r} \ln \left[\frac{v_{1r}^{1/3} - 1}{v_{2r}^{1/3} - 1} \right] + v_{1r}^{-1} - v_{2r}^{-1} + \frac{X_{eff}}{P_1^* v_{2r}} \right\} \quad (4)$$

where p_1^* is characteristic pressure; v_{1r} and v_{2r} are reduced volume of the probe and polymer, respectively; T_{1r} is the reduced temperature of the probe.

The partial molar heat of sorption, $\Delta\bar{H}_1^s$, of the probe sorbed by the solute is defined as Equation (5) [33]:

$$\Delta\bar{H}_1^s = -R \frac{\partial(\ln V_g^0)}{\partial(1/T)} \quad (5)$$

The partial molar heat of mixing, $\Delta\bar{H}_1^\infty$, can be determined using Equation (6);

$$\Delta\bar{H}_1^\infty = R \frac{\partial(\ln \Omega_1^\infty)}{\partial(1/T)} \quad (6)$$

where Ω_1^∞ is the weight fraction activity coefficient of the probe at infinite dilution, and is given as follows [34]:

$$\ln \Omega_1^\infty = \ln \left(\frac{273.2R}{V_g^0 P_1^0 M_1} \right) - \frac{P_1^0 (B_{11} - V_1^0)}{RT} \quad (7)$$

where, M_1 is the molecular weight of the probe.

The molar heat of vaporization of the probe, $\Delta\bar{H}_v$, is related to $\Delta\bar{H}_1^s$ and $\Delta\bar{H}_1^\infty$ as in Equation (8);

$$\Delta\bar{H}_v = \Delta\bar{H}_1^\infty - \Delta\bar{H}_1^s \quad (8)$$

MATERIALS AND METHODS

All chemicals in used the IGC experiments (n-nonane (N), n-decane (D), n-undecane (UN), n-dodecane (DD), n-tridecane (TD), n-butyl acetate (nBA), i-butyl acetate (iBA), ethyl acetate (EA), n-propylbenzene (nPB), i-propylbenzene (iPB), ethylbenzene (EB), dimethyl sulphoxide (DMSO)) and other chemicals used in the polymer synthesis were analytical grade and received from Merck AG Inc., Germany. The support material Chromosorb-W (AW-DMCS-treated, 80/100 mesh) were also obtained by Merck AG Inc. Germany. Silane-treated glass wool which was used to plug the ends of the chromatographic column was supplied from Alltech Associates Inc., USA.

IGC measurements were performed on Agilent Technologies 6890N, USA, model gas chromatography with a thermal conductivity detector. A column made of stainless steel (3.2 mm × 1 m) was obtained from Alltech Associates, Inc., USA. Chromosorb W was added to the solution of the polymer prepared in DMSO to coat the support material with PVBC-Dibutyl amine. Then DMSO was removed from the solution by slow evaporation technique. The prepared material was loaded into the chromatographic column and conditioned under an atmosphere of helium (He) for 24 h at 373.2. 1 μL of Hamilton syringe, Romania, was used to inject solvents into the column. Three successive injections of solvent were performed at each column temperature examined. The flow rate of the carrier gas was experimentally determined to be 3–4 cm³.min⁻¹, this value was kept constant during the IGC measurements.

Synthesis of poly (vinyl benzyl chloride) (PVBC) and PVBC-dibutyl amine

PVBC was synthesized as described in our previous study [35]. 1 g of PVBC was dissolved in 15 mL of THF.

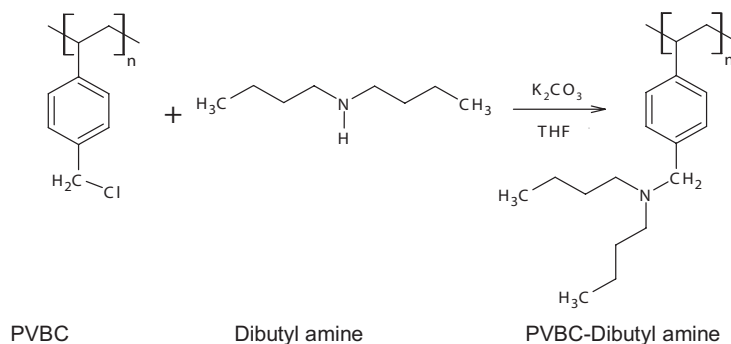
Then, a solution containing 1.20 mL (6.55 mmol) of dibutyl amine in 5 mL of THF was slowly added to this solution at 0°C. The prepared mixture was stirred at room temperature for 18 h, then at 60°C for 3 h. The reaction mixture was poured into 50 mL of hexane and the polymer precipitated. The PVBC-Dibutyl amine obtained was filtered, washed sequentially with hexane and ether. The polymer was dried at room temperature by keeping it under vacuum for 24 h. The product was obtained as 1.51 g. (Scheme 1)

The characterization of polymers was carried out by FTIR spectroscopy. In Figure 1, PVBC showed a characteristic C-Cl stretching at about 669 cm⁻¹. Furthermore, asymmetric stretching of methyl and methylene groups were observed at 2918 cm⁻¹, respectively. After modification of PVBC, C-Cl stretching vibration band was disappeared. Also, the peaks between 1379.64 cm⁻¹ and 1257.35 cm⁻¹ indicate C-N stretching frequencies of amine group.

RESULTS AND DISCUSSION

To examine the thermodynamic interactions of PVBC-Dibutyl amine and selected solvents, N, D, UN, DD, and TD as non-polar solvents and nBA, iBA, EA, nPB, iPB, and EB, as polar solvents were passed through the IGC column in the temperature range from 135 to 160°C. Using the obtained IGC data and Equation (1), the specific retention volumes, V_g^0 , of the solvents on the polymer were calculated in the temperature range studied. The retention diagrams obtained by plotting $\ln V_g^0$ values against $1/T$ are presented in Figures 2 and 3. The linearity seen in the retention diagrams reflects that the polymer does not show any phase transition in the temperature range examined, that is, the thermodynamic equilibrium has been achieved. As shown in Figures 2 and 3, it was observed that the values of $\ln V_g^0$ for all probes decreased with increasing temperature. The polymer-solvent interaction parameters, χ_{12}^∞ and χ_{12}^* were determined using Equation (2) and Equation (3), respectively and presented in Table 1 and 2.

In dilute polymer solutions, $\chi_{12} < 0.5$ values indicate strong intermolecular interactions between polymer chains and solvent molecules, while values of $\chi_{12} > 0.5$ indicate



Scheme 1 Preparation of PVBC-Dibutyl amine.

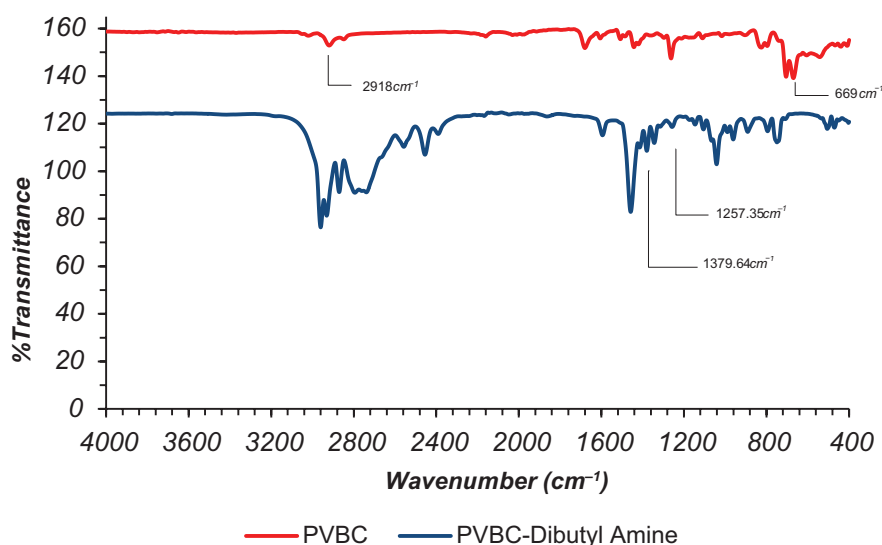


Figure 1. FTIR spectra of PVBC and PVBC-Dibutyl amine.

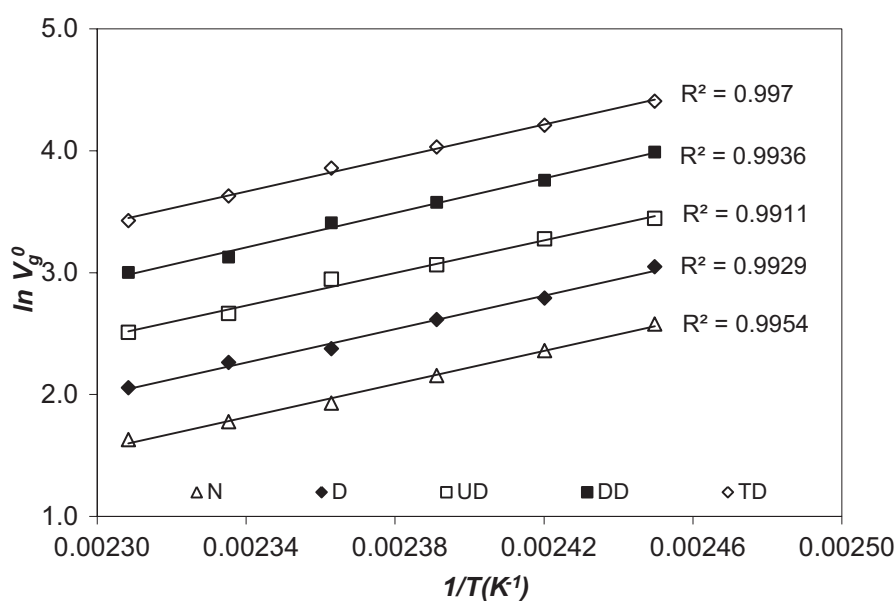


Figure 2. Retention diagram of the non-polar solvents on PVBC-Dibutyl amine.

weak interactions. According to Table 1 and Table 2, it is seen that alkanes are poor solvents for the polymer at temperatures examined. It can be said that nBA, iBA, nPB, iPB, EB, and EA are moderately solvents for the polymer, respectively. In general, it has been determined that the solubility of the polymer in nBA, iBA, and EA is endothermic, while its solubility in N, D, UD, DD, TD, nPB and iPB is exothermic. The effective exchange energy parameter, X_{eff} , was calculated from Equation (4) and the results obtained are given in Table 3.

The effective exchange energy parameter, X_{eff} , which quantifies the change in contact energy when a polymer segment in the surroundings of another polymer segment, is replaced by a solvent molecule. In Table 3, it is seen that the χ_{eff} values are generally higher in alkanes with poor solubility, and the X_{eff} values are lower in solvents with better solubility than alkanes. It has been determined that it is in good agreement with χ_{12}^{∞} and χ_{12}^* values obtained. Ω_1^{∞} values of the polymer at infinite dilution were calculated using Equation (7). The Ω_1^{∞} values obtained are given in Table 4.

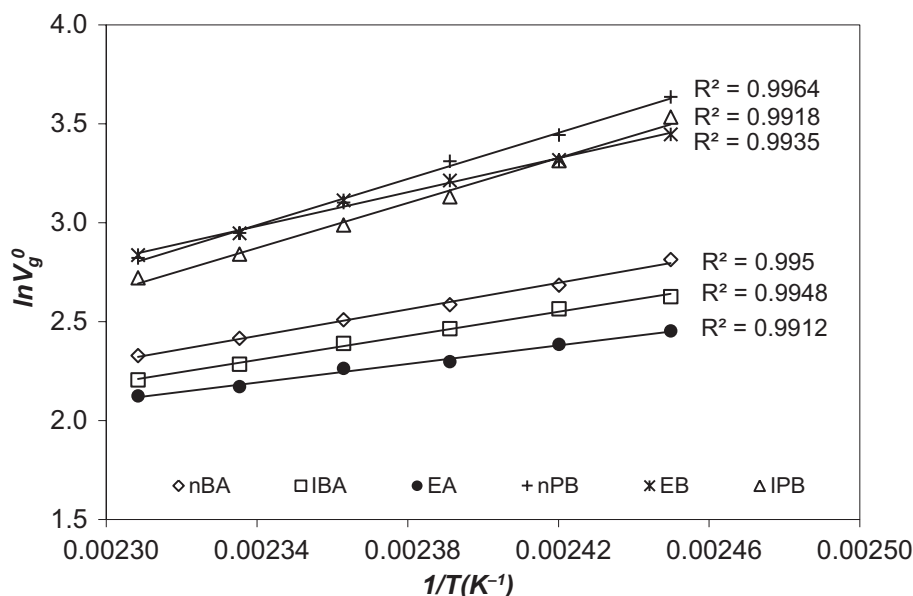


Figure 3. Retention diagram of the polar solvents on PVBC-Dibutyl amine.

Table 1. Flory–Huggins polymer–solvent interaction parameters, χ_{12}^{∞} , of PVBC-Dibutyl amine with selected probes at temperatures studied

T(°C)	135	140	145	150	155	160
N	2.68	2.77	2.85	2.95	2.98	3.01
D	2.87	2.98	3.02	3.12	3.10	3.18
UD	3.13	3.14	3.20	3.17	3.30	3.32
DD	3.25	3.30	3.32	3.32	3.44	3.42
TD	3.50	3.50	3.50	3.49	3.55	3.58
nBA	1.82	1.83	1.80	1.76	1.74	1.72
iBA	1.76	1.70	1.69	1.65	1.65	1.62
EA	1.04	1.01	1.00	0.94	0.93	0.89
nPB	1.87	1.93	1.93	2.01	2.04	2.04
iPB	1.74	1.83	1.88	1.90	1.93	1.93
EB	1.49	1.49	1.48	1.46	1.51	1.51

Standard uncertainties u is $u(\chi_{12}^{\infty}) = 0.03$

Table 2. The equation of state polymer–solvent interaction parameter, χ_{12}^* , of PVBC-Dibutyl amine with selected probes at temperatures studied

T(°C)	135	140	145	150	155	160
N	2.52	2.60	2.67	2.76	2.79	2.82
D	2.67	2.78	2.81	2.90	2.87	2.95
UD	2.91	2.91	2.96	2.92	3.04	3.05
DD	2.99	3.04	3.04	3.04	3.16	3.12
TD	3.21	3.21	3.20	3.18	3.23	3.26
nBA	1.76	1.76	1.73	1.69	1.66	1.64
iBA	1.68	1.61	1.60	1.56	1.55	1.52
EA	1.09	1.05	1.04	0.98	0.98	0.94
nPB	1.77	1.82	1.82	1.89	1.92	1.92
iPB	1.64	1.73	1.78	1.80	1.82	1.82
EB	1.43	1.43	1.41	1.39	1.44	1.44

Standard uncertainties u is $u(\chi_{12}^*) = 0.03$

According to Guillet, $\Omega_1^{\infty} < 5$; the solvent is a “good solvent” for the polymer, $5 < \Omega_1^{\infty} < 10$; the solvent is a “moderately solvent” $\Omega_1^{\infty} > 10$ solvent is a “poor solvent”. In the Table 4, it seems that the values found for the Ω_1^{∞} parameters support the discussion given for the χ_{12}^{∞} and χ_{12}^* values.

The partial molar heat of sorption, $\Delta\bar{H}_1^s$, for solvents, the partial molar heat of mixing, $\Delta\bar{H}_1^{\infty}$, at infinite dilution, and the molar heat of vaporization of the probe, $\Delta\bar{H}_v$, are useful parameters in understanding the sorption mechanism. The values of $\Delta\bar{H}_1^s$, $\Delta\bar{H}_1^{\infty}$ and $\Delta\bar{H}_v$ were calculated from equation (5), (6) and (8), respectively and presented in Table 5. The values of $\Delta\bar{H}_1^{\infty}$ were obtained from the slopes of the plot of

$\ln\Omega_1^{\infty}$ versus $1/T$ in the studied temperature ranges using Equation (6). The value of $\Delta\bar{H}_1^{\infty}$ determines whether the solubility is exothermic (negative) or endothermic (positive) for the solvents.

According to the $\Delta\bar{H}_1^{\infty}$ values in Table 5, the solubility of the polymer in EA, nBA, and iBA is endothermic, while the solubility in N, D, UD, DD, TD, EB, nPB, and iPB is exothermic. If the boiling point of the solvents studied is close to the column temperatures studied, the $\Delta\bar{H}_v$ values found with the IGC are in agreement with the $\Delta\bar{H}_v$ values given in the literature. The $\Delta\bar{H}_v$ values obtained with the IGC experiments are generally compatible with the $\Delta\bar{H}_v$ values.

Table 3. Effective exchange energy parameters of the solvents, X_{eff} (J/cm^3), of PVBC-Dibutyl amine with selected probes at temperatures studied

T(°C)	135	140	145	150	155	160
N	57.24	60.05	62.70	66.09	67.47	68.91
D	56.60	59.85	61.11	64.23	64.06	66.61
UD	57.87	58.40	60.14	59.71	63.42	64.17
DD	55.72	57.29	57.88	58.33	61.50	61.19
TD	56.81	57.33	57.56	57.83	59.34	60.46
nBA	48.25	48.65	47.93	46.40	45.76	45.04
iBA	39.56	37.54	37.10	35.81	35.80	34.94
EA	24.96	23.28	22.84	19.59	19.92	17.82
nPB	50.02	52.23	52.49	55.72	57.06	57.53
iPB	46.46	49.95	52.19	53.17	54.44	54.86
EB	43.99	44.25	43.63	42.96	45.42	45.50

Standard uncertainties u is $u(X_{eff}) = 2$ (J/cm^3)

Table 4. The weight fraction activity coefficients of the solvents, Ω_1^∞ , of PVBC-Dibutyl amine with selected probes at temperatures studied

T(°C)	135	140	145	150	155	160
N	21.45	23.23	24.98	27.49	28.22	29.00
D	23.43	26.02	26.73	29.42	28.63	30.76
UD	27.59	27.59	29.00	27.88	31.69	31.92
DD	28.09	29.46	29.55	29.47	33.09	31.88
TD	32.71	32.68	32.21	31.81	33.34	34.26
nBA	9.52	9.53	9.29	8.87	8.67	8.46
iBA	9.17	8.62	8.47	8.13	8.08	7.84
EA	5.19	5.02	4.96	4.67	4.67	4.48
nPB	9.84	10.35	10.32	11.14	11.42	11.43
iPB	8.57	9.34	9.82	9.98	10.21	10.21
EB	7.26	7.26	7.11	6.96	7.32	7.29

Standard uncertainties u are as follows: $u(\Omega_1^\infty) = 0.1$

CONCLUSION

IGC method was successfully applied to determine the thermodynamic properties of PVBC-Dibutyl amine at infinite dilution using polymer-solvent interactions. For PVBC-Dibutyl amine, the thermodynamic parameters χ_{12}^∞ , χ_{12}^* , χ_{eff}^∞ , Ω_1^∞ , $\Delta\bar{H}_1^\infty$ and were calculated and evaluated together. It is understood that the results obtained are compatible with each other. It has been observed that alkanes are poor solvents for PVBC-Dibutyl amine at between 135 and 160° C temperature range. It can be said that nBA, iBA, nPB, iPB, EB, and EA are moderately solvent for the polymer. In additionally, it has been determined that nBA, iBA,

Table 5. $\Delta\bar{H}_1^\infty$ ($kcal/mol$), $\Delta\bar{H}_1^s$ ($kcal/mol$), $\Delta\bar{H}_v$ ($kcal/mol$), and molar heat of vaporization $\Delta\bar{H}_{vl}$ ($kcal/mol$) values obtained from the literature

Solvent	$\Delta\bar{H}_1^\infty$	$\Delta\bar{H}_1^s$	$\Delta\bar{H}_v$	$\Delta\bar{H}_{vl}$
N	-4.41	-13.51	9.1	8.8
D	-3.51	-13.63	10.1	9.4
UD	-2.21	-1.33	11.1	9.9
DD	-1.96	-14.01	12.1	10.4
TD	-0.55	-13.66	13.1	10.9
nBA	1.84	-6.66	8.5	8.6
iBA	2.06	-6.05	8.1	8.7
EA	2.01	-4.66	6.7	7.7
nPB	-2.26	-11.59	9.3	9.1
iPB	-2.34	-11.30	9.0	9.0
EB	-0.03	-8.55	8.5	8.5

EA show endothermic solubility, while N, D, UD, DD, TD, nPB, and iPB show exothermic solubility.

NOMENCLATURE

N	n-nonane
D	n-decane
UD	n-undecane
DD	n-dodecane
TD	n-tridecane
nBA	n-butyl acetate
iBA	i-butyl acetate
EA	ethyl acetate
nPB	n-propylbenzene
iPB	i-propylbenzene
EB	ethylbenzene
DMSO	dimethyl sulphoxide

AUTHOR CONTRIBUTION

Concept: Özlem Cankurtaran, A. Çiğdem Adıgüzel; Design: A. Çiğdem Adıgüzel, Fatih Çakar; Materials: Burak Korkmaz, B. Filiz Şenkal; Data analysis: Özlem Cankurtaran, Fatih Çakar, A. Çiğdem Adıgüzel, Burak Korkmaz, B. Filiz Şenkal; Literature research: A. Çiğdem Adıgüzel; Writing: A. Çiğdem Adıgüzel; Critical revision: Özlem Cankurtaran, Fatih Çakar, A. Çiğdem Adıgüzel, Burak Korkmaz, B. Filiz Şenkal

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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