Thermodynamic Interactions of a Copolyester of Bisphenol A with Terephthalic Acid and Isophthalic Acid with Some Solvents

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ABSTRACT: The retention diagrams of *n*-octane, *n*-nonane, *n*-decane, *n*-butyl acetate, isobutyl acetate, and isoamyl acetate on the polyarylate Ardel D-100, a copolyester of bisphenol A with terephthalic acid and isophthalic acid, were plotted at temperatures between 120 and 260°C by an inverse gas chromatography technique. The glass-transition temperature of the copolymer was determined to be 190°C from the discontinuity of these diagrams. The retention diagrams of benzene, ethyl benzene, *n*-propyl benzene, isopropyl benzene, and chlorobenzene were also plotted between 200 and 260°C. The specific retention volume, weight fraction activity coefficient, Flory–Huggins polymer–solvent interaction parameter, hard-core polymer–solvent interaction parameter, and effective exchange energy parameter were determined for the studied solvents. The parameters suggest that the studied aromatic hydrocarbons and aliphatic esters are moderately good solvents and chlorobenzene is a very good solvent for this copolyester, but the *n*-alkanes are very poor solvents. The solubility parameter of this copolymer was determined to be 11.6 $(cal/cm^3)^{1/2}$ at room temperature by extrapolation of the values of the solubility parameters from the studied temperatures to 25°C. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2365–2368, 2005

Key words: chromatography; glass transition; thermodynamics

INTRODUCTION

Ardel D-100, the trademark for an amorphous aromatic polyester of bisphenol A with terephthalic acid and isophthalic acid (50/50), offers outstanding performance, that is, retention of gloss, transparency, and lower haze, when it is exposed to ultraviolet lighting and accelerated aging tests (Scheme 1). It also has high mechanical strength up to 174°C, which is the heat distortion temperature.[1–3] However, there are not enough data about the solvent resistance in the literature. In this study, the retention diagrams of some solvents on the copolymer were obtained by inverse gas chromatography (IGC), which is a fast, reliable, and economical technique.[4–6] Then, the thermodynamic interaction parameters of the copolymer with the studied solvents were determined.

THEORETICAL BACKGROUND

The specific retention volume (V_g^0) is determined experimentally from IGC measurements as follows:[4–11]

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

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

The weight fraction activity coefficient of solvents at infinite dilution (Ω_1^∞) is defined by the following equation:

$$\ln \Omega_1^\infty = \ln(273.2R/V_g^0 p_1^0 M_1) - p_1^0(B_{11} - V_1^0)/RT \quad (2)$$

where R is the universal gas constant and p_1^0, M_1, B_{11}, and V_1^0 are the saturated vapor pressure, molecular weight, gaseous-state second virial coefficient, and molar volume of the solvent at temperature T, respectively.[12]
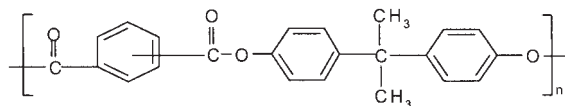
According to the Flory–Huggins and equation-of-state theories,[13] the Flory–Huggins polymer–solvent interaction parameter (χ_{12}^∞) and hard-core polymer–solvent interaction parameter (χ_{12}^*) are defined in eqs. (3) and (4), respectively:

$$\chi_{12}^\infty = \ln(273.2Rv_2/p_1^0 V_g^0 V_1^0) - 1 - p_1^0(B_{11} - V_1^0)/RT \quad (3)$$

where v_2 is the specific volume of the polymer,

Scheme 1 Chemical structure of the repeating unit of Ardel D-100.

$$\chi_{12}* = \ln(273.2Rv_2*/p_1^0V_g^0V_1*) - 1 - p_1^0(B_{11} - V_1^0)/RT \tag{4}$$

where v_2* is the specific hard-core volume of the polymer, and V_1* is the molar hard-core volume of the solvent.

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

$$RTc_{12}*/p_1*V_1* = \{3T_{1r}Ln[(v_{1r}^{1/3} - 1)/(v_{2r}^{1/3} - 1)]$$
$$+ v_{1r}^{-1} - v_{2r}^{-1}\} + X_{eff}/V_1*v_{2r} \tag{5}$$

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

The solubility parameter of the polymer (δ_2) is found by the combination of the Flory–Huggins and Hildebrand–Scathard theories:[4,5]

$$[(\delta_1^2/RT) - (\chi_{12}^\infty/V_1^0)] = (2\delta_2/RT)\delta - \delta_2^2/RT \tag{6}$$

where δ_1 is the solubility parameter of the solvent.

EXPERIMENTAL

Ardel D-100 was a product of Amoco Performance Products, Inc. (Alpharetta, GA) n-Octane (n-O), n-nonane (n-N), n-decane (n-D), n-butyl acetate (n-BA), isobutyl acetate (IBA), isoamyl acetate (IAA), benzene (B), ethyl benzene (EB), n-propyl benzene (n-PB), isopropyl benzene (IPB), and chlorobenzene (CB) were
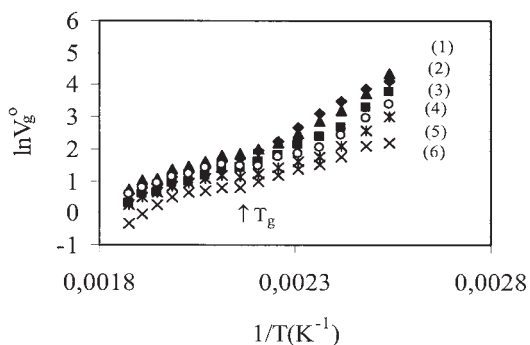
Figure 1 Retention diagram of n-alkanes and aliphatic esters on Ardel D-100: (1) IAA, (2) n-BA, (3) IBA, (4) n-D, (5) n-N, and (6) n-O.
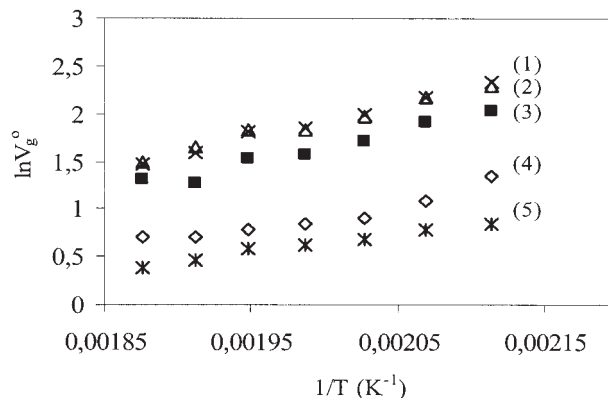
Figure 2 Retention diagram of aromatic solvents on Ardel D-100: (1) CB, (2) n-PB, (3) EB, (4) B, and (5) IPB.

analytical-reagent-grade and were used without further purification. The solvents and support material (Chromosorb-W, AW-DMCS-treated and 80/100-mesh) were supplied by Merck AG., Inc. (Darmstadt, Germany). Silane-treated glass wool, used to plug the ends of the column, was obtained from Alltech Associates, Inc. (Deerfield, IL).

A Hewlett–Packard 5890 series II gas chromatograph (Palo Alto, CA) with a thermal conductivity detector was used to measure the retention times of the solvents. Data acquisition and analysis were performed with HP-3365 software.

The column was stainless steel tubing with an outside diameter of 3.2 mm and a length of 1 m. The polymer was coated on the support by the slow evaporation of chloroform as Chromosorb-W was stirred in the polymer solution. The amount of the coated polymer on the support was determined to be 8.69% by calcination. A trace amount of the solvent was injected into the chromatograph. The column was conditioned at 230°C for 24 h.

RESULTS AND DISCUSSION

The V_g^0 values of the studied solvents were obtained experimentally from IGC measurements with eq. (1).

TABLE I
Ω_1^∞ **for Solvents with Ardel D-100**

Solvent	Ω_1^∞						
	200	210	220	230	240	250	260
n-O	20.3	18.4	17.1	16.7	19.0	22.0	26.1
n-N	19.8	18.2	17.7	16.3	17.2	17.9	19.6
n-D	20.6	18.9	18.7	17.0	17.7	17.8	18.1
n-BA	7.8	8.2	8.1	8.0	8.8	8.7	9.6
IBA	8.5	8.9	9.4	8.5	9.9	9.6	11.5
IAA	7.6	7.4	7.4	6.9	7.8	7.1	8.1
B	6.7	7.5	8.1	7.6	7.2	7.1	6.6
EB	7.3	7.0	7.3	7.2	6.5	7.3	6.2
n-PB	8.0	7.6	7.8	7.5	6.5	6.7	6.8
IPB	7.8	7.4	7.5	7.4	6.8	6.6	7.0
CB	4.6	4.6	4.7	4.6	4.2	4.5	4.6

TABLE II
χ_{12}^{∞} **for Solvents with Ardel D-100**

Solvent	χ_{12}^{∞}						
	200	210	220	230	240	250	260
n-O	1.23	1.11	1.02	0.97	1.07	1.19	1.34
n-N	1.25	1.15	1.11	1.01	1.04	1.06	1.12
n-D	1.32	1.23	1.21	1.09	1.11	1.10	1.10
n-BA	0.52	0.55	0.51	0.47	0.54	0.50	0.57
IBA	0.51	0.53	0.56	0.42	0.55	0.48	0.61
IAA	0.54	0.50	0.48	0.39	0.50	0.38	0.49
B	0.33	0.43	0.48	0.38	0.30	0.25	0.12
EB	0.48	0.43	0.45	0.42	0.29	0.40	0.22
n-PB	0.56	0.49	0.51	0.46	0.29	0.30	0.31
IPB	0.57	0.50	0.50	0.46	0.36	0.32	0.36
CB	0.28	0.26	0.28	0.25	0.13	0.19	0.19

TABLE IV
X_{eff} **(J/cm^3) for Solvents with Ardel D-100**

Solvent	X_{eff}						
	200	210	220	230	240	250	260
n-O	33.0	30.5	28.7	29.0	35.3	42.9	52.6
n-N	28.8	26.7	26.6	24.6	27.4	29.7	34.0
n-D	27.4	25.5	25.9	23.4	25.2	25.6	27.4
n-BA	7.3	10.5	9.8	10.3	15.9	16.9	23.6
IBA	6.3	8.5	12.0	8.8	17.4	18.3	28.7
IAA	7.6	6.2	7.1	4.5	10.6	6.9	14.1
B	9.9	19.0	25.6	22.6	21.5	22.6	20.2
EB	10.4	8.4	10.6	10.1	4.9	12.1	4.1
n-PB	11.1	8.9	10.2	8.7	2.0	3.6	4.6
IPB	11.8	9.5	10.3	9.6	5.8	5.0	8.0
CB	2.2	1.8	3.4	2.6	−3.6	1.4	2.4

The results are given in Figure 1 for *n*-alkanes and aliphatic esters between 120 and 260°C and in Figure 2 for aromatic solvents between 200 and 260°C. The glass-transition temperature (T_g) of this copolymer was determined to be 190°C from the first deviation point from linearity at lower temperatures of the plots in Figure 1.

The Ω_1^{∞} values were determined from eq. (2). The results are given in Table I for all the studied solvents. The values of Ω_1^{∞} suggest that *n*-alkanes are nonsolvents for the copolymer because of values higher than 10; however, aliphatic esters and aromatic hydrocarbons are moderately good solvents because of values between 5 and 10, whereas CB is a good solvent because of values lower than 5. The temperature dependence of the solvent quality with respect to the values of Ω_1^{∞} is different. In the case of *n*-alkanes, the solvent quality decreases, does not change, and slightly increases with temperature in *n*-O, *n*-N, and *n*-D, respectively. In aliphatic esters, the solvent quality decreases with temperature. Aromatic hydrocarbons tend to be better with temperature, except for B; however, they cannot be assumed to be good solvents in the studied temperature range.

TABLE III
χ_{12}^{*} **for Solvents with Ardel D-100**

Solvent	χ_{12}^{*}						
	200	210	220	230	240	250	260
n-O	1.52	1.43	1.35	1.32	1.45	1.59	1.77
n-N	1.52	1.43	1.40	1.32	1.37	1.40	1.49
n-D	1.56	1.48	1.47	1.37	1.41	1.40	1.43
n-BA	0.81	0.85	0.84	0.82	0.91	0.89	0.98
IBA	0.83	0.87	0.92	0.80	0.96	0.91	1.07
IAA	0.81	0.78	0.78	0.70	0.82	0.72	0.86
B	0.65	0.77	0.84	0.76	0.71	0.68	0.59
EB	0.73	0.68	0.72	0.70	0.59	0.72	0.55
n-PB	0.78	0.72	0.75	0.71	0.56	0.59	0.60
IPB	0.80	0.74	0.75	0.73	0.64	0.62	0.67
CB	0.51	0.50	0.53	0.51	0.41	0.49	0.49

χ_{12}^{∞} and χ_{12}^{*} were determined from eqs. (3) and (4). The specific volumes of the copolymer were taken from an experimental work in the literature.[14] The values of χ_{12}^{∞} and χ_{12}^{*} are given in Tables II and III. Their values suggest that *n*-alkanes are very poor solvents for the copolymer; however, aliphatic esters and aromatic hydrocarbons, except for B, are moderately good solvents, whereas B and CB are good solvents. The temperature dependence of χ_{12}^{∞} and χ_{12}^{*} confirms the discussion concerning Ω_1^{∞}.

The X_{eff} values in the equation-of-state theory were obtained from eq. (5), and the results are given in Table IV. The magnitudes of X_{eff} are considerably higher for *n*-alkanes than those for aliphatic esters and aromatic hydrocarbons. Therefore, the higher values of X_{eff} indicate poor solubility. The magnitudes of X_{eff} are close to each other at lower temperatures in an analogous series, but they tend to increase with temperature, especially in the most vaporizable member of the series. This can be explained as follows: the exothermic solubility exists in the vaporizable sol-
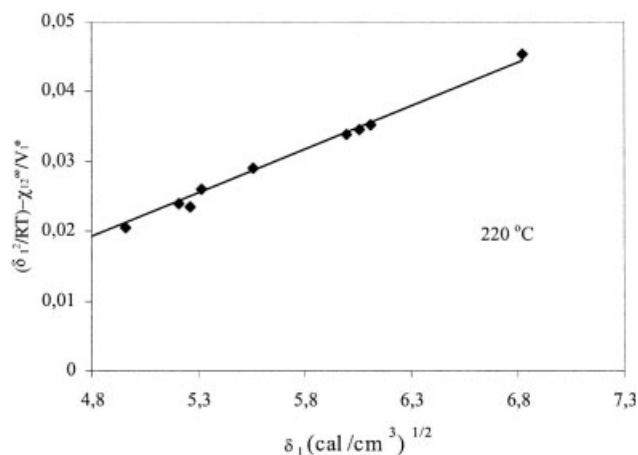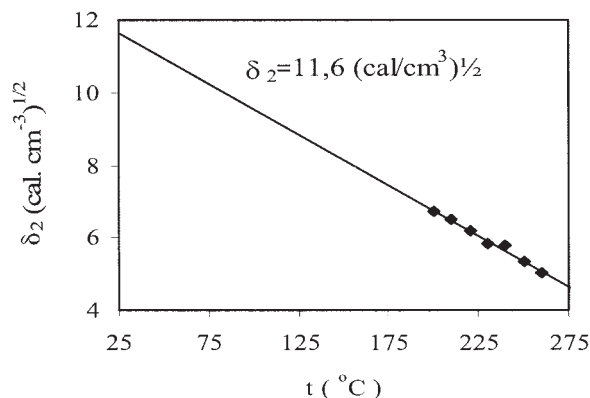

Figure 3 Estimation of δ_2 of Ardel D-100 from δ_1 and χ_{12}^{∞} at 220°C [see eq. (6)].

Figure 4 Extrapolation of δ_2 of Ardel D-100 from the studied temperatures to 25°C.

vents because the solubility of the gaseous phase in the condensed phases is always exothermic. The variation of X_{eff} with temperature is remarkable in comparison with that of other parameters determined in this study. Thus, it can be suggested that the determination of X_{eff} is better for forming an opinion about the solubility behavior of a polymer in a solvent at various temperatures.

The solubility parameter of Ardel D-100 (δ_2) was determined from the slope and intercept of plots drawn according to eq. (6). The plot at 220°C is given as an example in Figure 3. The magnitudes of δ_2 were found as averages of the values obtained from the slope and intercept at the studied temperatures. In Figure 4, δ_2 at room temperature was estimated to be approximately 11.6 $(cal/cm^3)^{1/2}$ by the extrapolation of the average values of δ_2 obtained at the studied temperatures to 25°C. It is comparable to the value of 10.8 $(cal/cm^3)^{1/2}$ calculated for δ_2 for this copolyester by the group contribution method.[15]

The results suggest that the resistivity of Ardel D-100 at the studied temperatures to petroleum products should be high because n-alkanes are nonsolvents; however, the resistivity of the copolyester to aliphatic esters and aromatic hydrocarbons, especially CB, should not be high at the studied temperatures because they are not nonsolvents.

CONCLUSIONS

This study suggests that n-alkanes are nonsolvents but aliphatic esters and aromatic hydrocarbons are moderately good solvents and CB is a good solvent for Ardel D-100 at temperatures between 200 and 260°C. Exothermic solubility has been observed in the most vaporizable solvents of each analogous series. The parameter X_{eff} more notably reflects the exothermic solubility behavior in a polymer–solvent system. T_g is 190°C, and δ_2 of the copolymer is approximately 11.6 $(cal/cm^3)^{1/2}$ at room temperature.

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