P-V-T Properties of Polyimides and Model Imide Compounds

Summary of Research

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Introduction

Aromatic polyimides are used as matrix resins in advanced composites, as high strength films, and as high-temperature adhesives, owing in part to their unusual thermal and chemical stability. The polyimides' desirable qualities of very high softening temperatures and negligibly small solubilities in and low permeabilities by most solvents have limited the kinds of fundamental studies that can be performed on these systems. Consequently, relationships between the molecular structure of polyimides and their bulk properties are not as well understood as might be expected given their widespread applications. In particular, the intermolecular forces in polyimides that play a critical role determining their densities, solubilities, viscosities, moduli, glass transitions, *etc.* are less well characterized for polyimides than for other widely used polymeric materials.

The purpose of the present study is to obtain experimental data for establishing parameters that characterize the intermolecular forces in polyimides. We report here our studies on tractable low molecular-weight imides that contain the same structural features that are present in polyimide materials. We have measured equation-of-state properties and dipole moments for a variety of such systems in the liquid state. Both pure compounds and binary mixtures have been studied.

Experiments

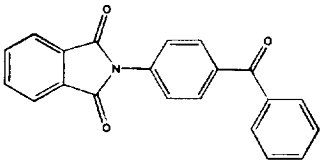
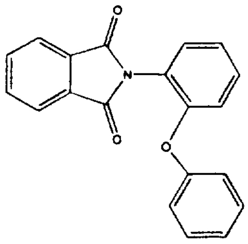
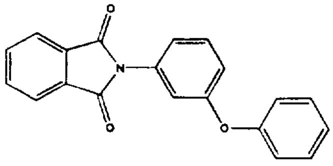
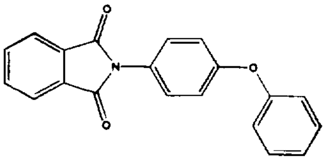
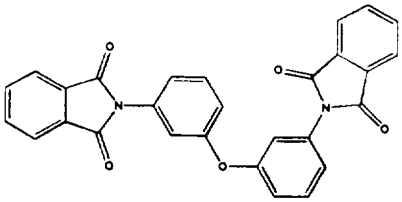
Materials

The imides used in this study are listed in Table I. They were synthesized by reacting aromatic amines with phthalic anhydride. An example of a synthesis is described next.

N-(4-phenoxyphenyl) phthalimide (designated in this report as the *p*-imide ether) was synthesized by reacting 12.55 grams (67.8 mmoles) of 4-phenoxyanaline (Aldrich Chemical Co.) with 10.11 grams (68.3 mmoles) of phthalic anhydride (Aldrich Chemical Co.). The reactants were dissolved in 108 mL of glacial acetic acid. After mixing for 3 hr at ambient temperature, the system was heated to reflux temperatures for 3 hr. The solution was then poured into 1 L of water and allowed to sit overnight. The crystals of imide that formed were collected in a Büchner funnel and then washed with three 10-mL portions of hot ethanol. Finally the imide was recrystallized from *p*-xylene and sublimed.

N-(4-benzoylphenyl) phthalimide was obtained as a gift from Dr. Jeffrey Hinkley of the NASA Langley Research Center.

Table I. Melting points, dipole moments, and structures.

p-imide ketone, 182-3 °C, 4.8D 	*o*-imide ether, 149-51 °C, 2.1D 
m-imide ether, 167-9°C, 2.8D 	*p*-imide ether, 161-2°C*, 3.0D 
m,m-diimide ether, 199-200°C, 3.3D 	

*Lit., 160-1 °C [G. Pagani, A. Baruffini, P. Borgna, and G. Caccialanza, *Farmaco, Ed. Science*, **23** 448 (1968).]

Densities and Thermal Expansion Coefficients

Imide densities ρ were measured using a calibrated glass dilatometer. The imide was confined in the thermostated dilatometer by a known mass of mercury. On heating, mercury was expelled and weighed; on cooling, a weighed quantity of mercury was drawn into the dilatometer. The volume of the imide was obtained as the difference between the volume of the cell, corrected for the thermal expansion of the glass, and the volume of the mercury therein.[1]

Thermal Pressure Coefficients

The pressure required to fix the volume of the liquid imide as it was heated, $\gamma = (\partial P/\partial T)_V$, was measured. The experiments were performed on imide that was confined in a glass cell that was located in a thermostated pressure vessel.[2]

Dipole Moments

The permanent dipole moments of the imides in dilute *p*-xylene solutions were obtained from measurements of the change in the dielectric constant of the solutions with the molar concentration. The change in the square of the refractive index with concentration was used to correct for the induced polarization.[3,4]

Results

Densities and Thermal Expansion Coefficients

Measured densities were fitted to least-squares equations, written as either linear or quadratic functions of the celsius temperature. Examples of these results are reported in Table II along with the standard deviation of the measured densities from the least-squares line. The thermal expansion coefficients $\alpha = (1/V)(\partial V/\partial T)_P = -(\partial \ln \rho/\partial T)_P$ were determined for Table II by differentiating first or second order polynomials, obtained by the method of least-squares, for the logarithm of the density as a function of the celsius temperature.

Thermal Pressure Coefficients

The pressure required to maintain the imide at constant volume as the temperature changed was found to be linear. The slope of the pressure *versus*-temperature plot was corrected for the expansion and compressibility of the glass container and the mercury confining liquid. The results are given in Table III.

Dipole Moments

The dipole moments are reported in Table I above.

Collaborators

The following William and Mary undergraduates participated in these studies: Rachael Ward, Carolyn Clower, Raja Bakhshi, and Krish Bakhshi.

Endnotes

1. R. A. Orwoll and P. J. Flory, *J. Am. Chem. Soc.*, **89**, 6814 (1967).

2. G. Allen, G. Gee, D. Mangaraj, D. Sims, and G. J. Wilson, *Polymer*, **1**, 467 (1960).

3. E. A. Guggenheim, *Trans. Faraday Soc.*, **47**, 573 (1951).

4. C. L. Braun, W. H. Stockmeyer, R. A. Orwoll, *J. Chem. Ed.*, **47**, 287 (1970).

Table II. Densities and thermal expansion coefficients for liquid imides and their mixtures.

	Density (as function of °C): $\rho = A + Bt + Ct^2$ (g/cm^3)				Therm. Exp. Coef. (K^{-1}): $\alpha = A' + B't$			
Imide	A	$B\times10^3$	$C\times10^6$	Std. Dev. (g/cm^3)	$A'\times10^4$	$B'\times10^7$	Temp. Range (°C)	No. Data Points
p-imide ketone	1.3058	-0.7644	–	2×10^{-5}	6.59	–	184-201	19
o-imide ether	1.2702	-0.6921	-0.2838	8×10^{-5}	5.22	9.81	154-199	41
p-imide ether	1.2820	-0.7202	-0.1728	7×10^{-5}	5.45	7.65	161-200	43
m,m-diimide ether	1.3914	-0.7752	—	8×10^{-5}	6.3	—	190-208	12
o-imide ether/*p*-imide ether (49/51-wt-%)	1.2962	-0.8822	-0.2244	6×10^{-4}	6.59	10.71	133-180	16
o-imide ether/*p*-imide ether (63/37 wt-%)	1.287	-0.816	-0.014	2×10^{-4}	6.25	5.29	135-181	14
m,m-diimide ether/ *p*-imide ether (30/70 wt-%)	1.3622	-1.335	1.527	3×10^{-4}	10.54	-21.33	151-200	37
m,m-diimide ether/ *p*-imide ether (42/58 wt-%)	1.3459	-0.853	—	8×10^{-5}	7.3	—	196-200	13
m,m-diimide ether/ *p*-imide ether (55/45 wt-%)	1.3447	-0.756	-0.125	2×10^{-4}	5.50	6.39	150-204	55
m,m-diimide ether/ *p*-imide ether (70/30 wt-%)	1.3503	-0.763	—	4×10^{-5}	6.4	—	195-204	16

Table III. Thermal pressure coefficients.

Compound	Temp. (°C)	Therm. Pres. Coef., γ, (bars/K)
p-imide ketone	186.2 194.0	10.5±0.2 10.0±0.2
o-imide ether	151.3	$11._{3}\pm1$