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APPLICATION NOTE # 0707101

Determination of Intrinsic Viscosity of Functionalized Polypropylene

The intrinsic viscosity (IV) of a functionalized polypropylene sample was determined from flow measurements obtained using a Polyvisc instrument in the CANNON Instrument Company (CIC) applications lab. The sample preparation was performed with the CANNON Solution Preparation System. Data regarding the solution preparation are included in the appendix along with literature data used to determine the density of Decalin at 135ºC (page 4). The calibration results are given in Table I. It was apparent from the negligible dependence of KV/t on t^{-3} that a kinetic energy correction was not necessary for the applied flow conditions. The tube constant determined from the calibration data was used to check the kinematic viscosity of Decalin at 135ºC. The calculations of the intrinsic viscosities (Table II) were made according to the Fikenstscher-Mark equation with the given Huggins coefficient of 0.38. The results were compared to other single point calculations that are based on the approaches of Billmeyer and of Solomom-Ciuta. Additional comparison was made with results obtained from the conventional extrapolation to zero concentration. All the single-point approaches yielded similar intrinsic viscosity values but the extrapolation approach revealed data that supports an anomaly in dilute polymer solution behavior that has been noted in other studies.[1,2] Specifically, the concentration dependencies of the reduced and inherent viscosities may not be monotonic in the region of very high dilution. The Huggins plot contains a minimum reduced viscosity at a finite concentration and the Kraemer plot has an increase in slope at the same concentration (Figure III). This finding suggests a possibility of over-estimating the intrinsic viscosity when using a single-point determination if the measurement is made below the characteristic concentration.

<u>Method Details for the Analysis of Polypropylene Samples from Anderson Dev.</u>

Viscometer:	Ubbelohde, 0.3-30, both bulbs
Temperature:	135ºC, 15 minute initial equilibration time
Solvent:	Decalin (0.3% BHT)
Dissolution:	135ºC+/-5ºC for 60-90 minutes with continuous stirring
Concentration:	0.11% (g/mL) at ambient
Measurement:	Blank and samples were measured five times.
Calculation:	Fikenstscher-Mark, Billmeyer, Solomon-Ciuta, extrapolated conc.
Wash solvent:	Decalin, two passes
Rinse solvent:	none

The calibration data listed in Table I are plotted in Figures I and II. The data indicates that a kinetic energy correction is not required and the determined tube constant (y-intercept in Figure II) was 0.009244 mm^2/sec^2. The kinematic viscosity values for the viscosity standards were calculated using CANNON's VISDISK software.

[1] Determination of Molecular Weight, A. R. Cooper, Ed., John Wiley & Sons, 1989, p. 184-185
[2] Techniques of Polymer Characterization, P. W. Allen, Ed., Academic Press, 1959, p. 198

Table I – Calibration of Viscometer with Kinematic Viscosity Standards

viscosity standard	kinematic viscosity	drop times					<t>	RSD
		t1	t2	t3	t4	t5		
S6	1.1765 cSt	125.98	125.66	125.64	125.64	125.65	125.648	0.0076%
S20	2.1792 cSt	238.80	238.38	238.37	238.37	238.38	238.375	0.0024%
N35	2.9970 cSt	324.55	323.92	323.92	323.91	323.93	323.920	0.0025%
S60	3.9083 cSt	424.54	423.91	423.94	423.96	423.98	423.948	0.0070%

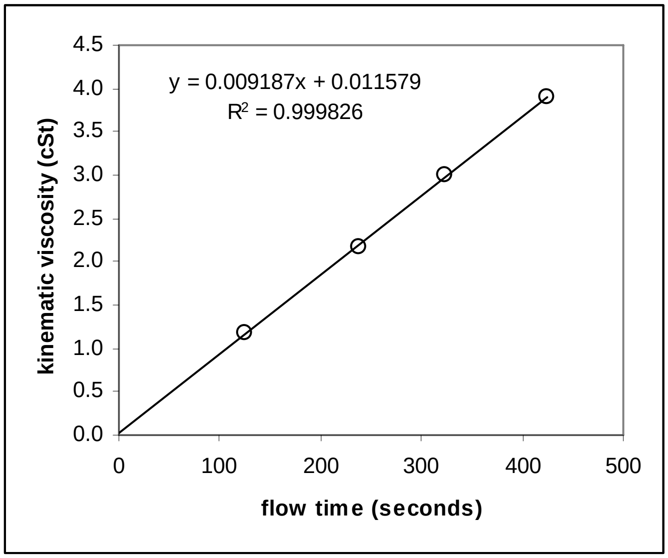

Figure I – Relation Between Flow Times and Kinematic Viscosity for CANNON Viscosity Standards in Polyvisc at 135ºC.

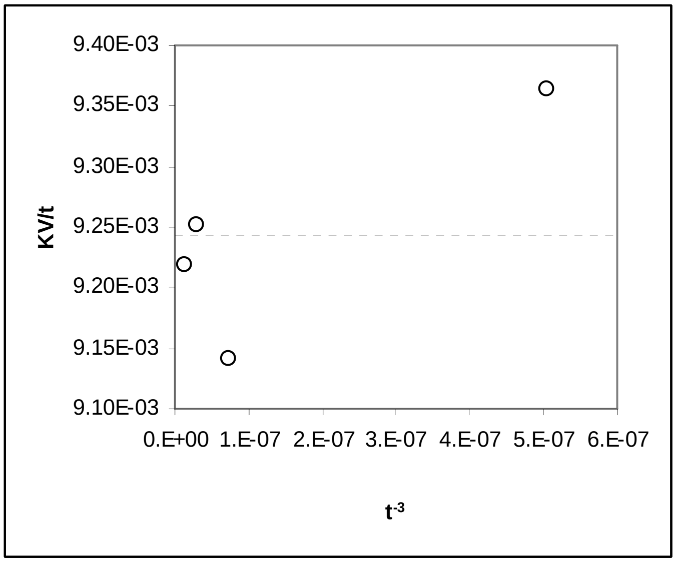

Figure II – Calibration Data for Capillary Viscometer as Analyzed by the Viscpro Software.

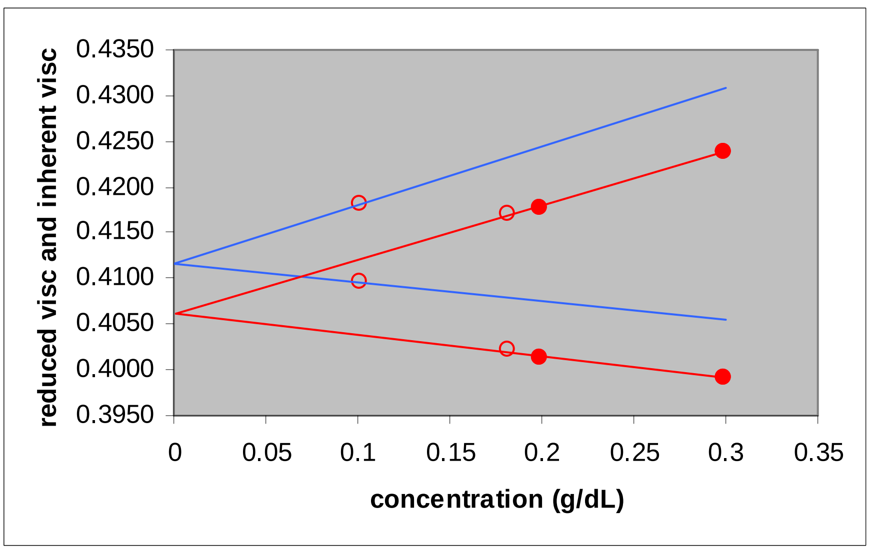

Figure III – IV determined by Fikenstscher-Mark approach (intercept of blue lines) and IV determined by extrapolation of higher concentrations (red lines).

The graphical portrayal in Figure III illustrates the basis behind the Fikenstscher-Mark calculation and how it compares with the extrapolation approach. Using the viscosity results for the lowest concentration of 0.1010 g/dL and the given Huggins value of 0.38, the Huggins and Kraemer lines were constructed in Figure III (shown in blue). The two highest concentrations (shown as solid red) were used to construct a set of empirical Huggins and Kraemer lines. The current data suggests a trend that has been described in references 1 and 2, listed in the footnote of page 1. Moreover, reference 1 mentions results published on isotactic polypropylene in Decalin by K. Kamide, Chem. High Polym., 21, 152 (1964).

Table II – Flow Times and Viscosity Results of Decalin Blank and Samples 15520, 15528, 15531.

solvent	t1	t2	t3	t4	t5	<t>	RSD	% diff.
Decalin	74.97	74.97	75.09	75.00	74.96	74.998	0.071%	-0.015%
Decalin	75.04	75.05	75.05	75.12	75.08	75.068	0.044%	0.078%
Decalin	74.99	74.95	74.95	74.94	74.98	74.962	0.029%	-0.063%
					average =	75.009	0.077%	
						0.693		
						0.710		
						-2.30%		

Huggins =	0.38
Kraemer =	-0.12

sample	t1	t2	t3	t4	t5	<t>	RSD	relvisc	spvisc	redvisc	inhvisc	Fik.-Mark	Billmeyer	S-C
A-1	78.24	78.16	78.11	78.11	78.26	78.176	0.091%	1.042	0.042	0.418	0.410	0.412	0.412	0.412
A-2	80.79	80.64	80.63	80.69	80.64	80.678	0.083%	1.076	0.076	0.417	0.402	0.411	0.406	0.407
A-3	81.14	81.19	81.27	81.20	81.36	81.232	0.105%	1.083	0.083	0.418	0.401	0.411	0.406	0.407
A-4	84.49	84.53	84.49	*85.67*	84.50	84.503	0.022%	1.127	0.127	0.424	0.399	0.417	0.405	0.407

In this analysis, it was assumed that the solution and solvent densities were effectively equal. This assumption can be tested using the calculated solution and solvent densities listed in the Appendix. An additional simplification came from the negligible kinetic energy correction. This permitted the tube constant to be cancelled from the relative viscosity equation and the calculation became simply the ratio of the solution and solvent flow times. The tube constant was, however, used to obtain the kinematic viscosity of the solvent for comparison to a published value. The CRC Handbook provides a table of dynamic viscosity values that was used to extrapolate to 135ºC to find the dynamic viscosity of the *cis* and *trans* isomers. The *cis/trans* ratio obtained from Aldrich was used to calculate the dynamic viscosity for the Decalin solvent at 135ºC as .5609 cP. The density of the Decalin solvent at 135ºC was calculated to be 0.7903 g/mL as described in the appendix. The kinematic viscosity for the Decalin solvent at 135ºC was obtained by dividing the dynamic viscosity value by the solvent density. The measured kinematic viscosity was determined by multiplying the viscometer constant by the average flow time. The kinematic viscosity calculated from published data was 0.710 cSt and the measured value was 0.693 cSt, 2.3% less than the calculated value.

Appendix

Temperature Dependence of Density for Decalin

The temperature dependence of density for Decalin is given in J. Timmermans, Physico-Chemical constants of pure organic compounds, vol. 2, page 552, Elsevier Publishing Company as $\rho_T = 0.00076*T(ºC) + 0.91199$ for *cis* and $\rho_T = 0.00074*T(ºC) + 0.88489$ for *trans*. The Decalin supplier (Aldrich, 800-231-9160) specified the *cis/trans* ratio as 0.3674/0.6280. A weighted average of the respective density values gives a density for the isomer mixture as 0.7903 g/mL at 135ºC. The polymer mass and solvent mass of the prepared solutions were determined using the CANNON SPS. The solvent mass was multiplied by the calculated solvent density to determine the concentration of the polymer solution at the test temperature of 135ºC. The mass determinations for the four prepared solutions are given on the following page.

Sample Preparation using CANNON Instrument's Solution Preparation System (SPS)

A - 1

target volume	16	mL
target concentration	0.0011	g/mL solvent
solvent density at ambient	0.8742	g/mL
calc. target polymer mass	0.0176	G
initial volume fraction	0.9995	
incremental dose	0.02	mL
measured polymer mass	0.0185	G
initial dispenser volume	16.79	mL
initial balance reading	14.4870	G
calculated initial volume	16.810	mL
calculated target mass	14.7136	G
calculated dispensed vol.	16.55056	mL
calculated ambient density	0.8617	g/mL
solvent density at test temp.	0.7903	g/mL
final balance reading	14.5000	G
calc. final volume	18.3241	mL
calc. final concentration	0.1010	g/dL solvent
calc. final density	0.7913	g/mL

A - 2

target volume	16	mL
target concentration	0.0011	g/mL solvent
solvent density at ambient	0.8742	g/mL
calc. target polymer mass	0.0176	G
initial volume fraction	0.9995	
incremental dose	0.02	mL
measured polymer mass	0.0339	G
initial dispenser volume	16.91	mL
initial balance reading	14.8199	G
calculated initial volume	30.803	mL
calculated target mass	26.9617	G
calculated dispensed vol.	16.91375	mL
calculated ambient density	0.8744	g/mL
solvent density at test temp.	0.7903	g/mL
final balance reading	14.8223	G
calc. final volume	18.7124	mL
calc. final concentration	0.1812	g/dL solvent
calc. final density	0.7921	g/mL

A - 3

target volume	16	mL
target concentration	0.0022	g/mL solvent
solvent density at ambient	0.8742	g/mL
calc. target polymer mass	0.0352	G
initial volume fraction	0.9995	
incremental dose	0.04	mL
measured polymer mass	0.0372	G
initial dispenser volume	16.86	mL
initial balance reading	14.8446	G
calculated initial volume	16.901	mL
calculated target mass	14.8117	G
calculated dispensed vol.	16.93823	mL
calculated ambient density	0.8783	g/mL
solvent density at test temp.	0.7903	g/mL
final balance reading	14.8446	G
calc. final volume	18.7364	mL
calc. final concentration	0.1985	g/dL solvent
calc. final density	0.7923	g/mL

A - 4

target volume	16	mL
target concentration	0.0022	g/mL solvent
solvent density at ambient	0.8742	g/mL
calc. target polymer mass	0.0352	G
initial volume fraction	0.9995	
incremental dose	0.04	mL
measured polymer mass	0.0559	G
initial dispenser volume	16.87	mL
initial balance reading	14.8492	G
calculated initial volume	25.396	mL
calculated target mass	22.2574	G
calculated dispensed vol.	16.9221	mL
calculated ambient density	0.8769	g/mL
solvent density at test temp.	0.7903	g/mL
final balance reading	14.8492	G
calc. final volume	18.7186	mL
calc. final concentration	0.2986	g/dL solvent
calc. final density	0.7933	g/mL