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## UNPERTURBED CHARACTERISTICS OF ATACTIC POLYPROPYLENE: SOME NEW THETA SOLVENTS BASED ON ALIPHATIC KETONES

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Key Words: Atactic Polypropylene, Solution Properties, Unperturbed Dimensions

### ABSTRACT

Solution properties of atactic polypropylene were studied in thermodynamically good solvents (toluene, n-butyl chloride and decalin) and in theta solvents (ethyl-n-butyl ketone, methyl-n-hexyl ketone, 1-nonanol and 2-ethylhexanol). Mark-Houwink-Sakurada relations within the temperature range between 15°C and 60°C, unperturbed dimensions  $K_\theta = 1.62 \times 10^{-3}$  at  $T_\theta = 19.7^\circ\text{C}$  in methyl-n-hexyl ketone (the  $K_\theta$  and  $T_\theta$  values for ethyl-n-butyl ketone are the same) and the temperature coefficient of unperturbed dimensions  $d \ln r_0^2/dT = -2.44 \times 10^{-3} \text{K}^{-1}$  were established.

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## INTRODUCTION

Polypropylene (PP) is one of the major thermoplastics produced in large quantities. Propylene molecules are polymerized with Ziegler-Natta catalysts and during the commercial production of PP, isotactic structure is prevailing. Atactic polypropylene (aPP) is the by-product in amounts of 3-5% of the total polypropylene production. Atactic polypropylene prepared in this way has the amorphous, stereoirregular structure.

The models of atactic polypropylenes: head-to-tail polypropylene (HTPP) and head-to-head (HHPP) polypropylene have been prepared recently by hydrogenation of 1,4-poly(2-methyl-1,3-pentadiene) [1, 2] and of 1,4-poly(2,3-dimethylbutadiene) [3, 4] and their conformational characteristics in the unperturbed state were determined.

The thermodynamic and solution properties of industrial aPP were studied by a number of authors. The heats of mixing of aPP were measured at 25°C in n-alkanes and aromatic hydrocarbons. The determined interaction parameters increase with the increasing chain length of n-alkanes and decrease with the introduction of aliphatic groups into benzene molecule [5]. The sorption of some low-molecular compounds by aPP was studied by Kolesnikova *et al.* [6]. The vapor pressures of aPP solutions and the swelling of crosslinked aPP within the range of aliphatic ketones [7-9] were studied, and in the presence of polymer order (crystallinity), the deviations of the determined interaction parameters from the theory were observed. The unperturbed chain dimensions,  $K_{\theta}$ , and their respective temperature coefficients for commercial aPP [10-13] were determined in  $\theta$  conditions and in their oligomers via intrinsic viscosity-temperature measurements.

The main industrial applications of atactic polypropylene are concentrated in the manufacturing of adhesives, hydro-insulating coatings, sealing compositions and building materials [14]. The application possibilities of aPP further increase by its chemical modification: grafting efficiency of this polymer was studied by Pavlinec *et al.* [15], the preparation of samples containing carboxyl groups was described by Schulz and Hartmann [16]. The polypropylene modification by oxidation in melt for preparing polypropylene emulsions was studied by Yaykin *et al.* [17] and its grafting with vinyl acetate and vinyl chloride and the application of the obtained graft copolymers was analyzed by Schellenberg and Hamann [18].

In this study, the characterization of technical aPP by dilute solution measurements was carried out in good and in some new theta solvents based on

aliphatic ketones. The unperturbed chain characteristics of this aPP were evaluated and the results were compared with the data obtained from model polypropylenes prepared by the hydrogenation of anionically prepared polydienes.

## EXPERIMENTAL

### Materials

Atactic polypropylene was the product of Slovnaft Bratislava (Slovakia) as a soluble part of the isotactic polypropylene production which is supposed to contain up to 25 wt% of stereoblocs. This was confirmed by successive extraction with different n-alkanes at their boiling points from a commercial product [10]. Before use, the polymer was dissolved in diethyl ether, the insoluble part (stereoblocs) was separated and removed by centrifugation. The soluble portion was then precipitated with acetone, redissolved in benzene, precipitated with excess methanol, dried in vacuum and stored in a desiccator under nitrogen atmosphere. According to NMR results of Miyamoto and Inagaki [19] the ether-soluble portion consists largely of very short tactic sequences due to the nearly random distribution of tactic placements along the chain – an atactic polypropylene without stereoblocs.

The solvents used were purified by ordinary methods before use and their purity was checked by refractive index or by gas chromatography.

### Applied Methods

The fractions of the original polymer with  $M_w/M_n$  approximately 4.5 were obtained by successive addition of methanol to 1% solution of aPP in toluene at 25°C; for last fractions, the system bromoform-methanol was used in order to prevent the formation of isopycnic mixture and to secure better isolation of the coacervate, which is here the upper phase. The fractions of broader distributions were refractionated in the same systems until the fractions with  $M_w/M_n$  of approximately 1.5 were obtained. All fractions were precipitated with excess of methanol and dried in vacuum to constant weight. The isolated fractions were characterized by intrinsic viscosity in toluene and n-butyl chloride, selected fractions by light scattering and membrane osmometry.

The refractive index increments were determined by a Brice-Phoenix differential refractometer at the wavelength of 546 nm (Table 1). Refractive indices

TABLE 1. Refractive Index Increments of aPP at 25°C (Wavelength 546 nm)

Solvent	Refractive Index	Refractive Index Increment ( $\text{cm}^3\text{g}^{-1}$ )
n-Butyl propionate	1.3958	0.110
n-Butyl chloride	1.3987	0.098
Cyclohexane	1.4258	0.071
Chloroform	1.4441	0.046
Trichloroethylene	1.4741	0.020
Carbon tetrachloride	1.4597	0.036
Trichloroethylene	1.4741	0.020
Toluene	1.4977	-0.003
Chlorobenzene	1.5258	-0.034
Bromobenzene	1.5617	-0.060

were measured by a Zeiss dipping refractometer. The application of Gladstone-Dale rule to the data in Table 1 gave the index of refraction of 1.493 and specific volume  $1.102 \text{ cm}^3/\text{g}$  for atactic polypropylene.

Light scattering measurements were carried out on a Brice-Phoenix light scattering photometer, Model 2000 using monochromatic light with the wavelength of 546 nm. Freshly distilled n-butyl chloride was used as a solvent. The results of the measurements were evaluated by the usual double extrapolation plot according to Zimm.

Osmotic measurements were performed with a Hewlett-Packard automatic membrane osmometer in toluene at 37°C.

The viscosity of solutions was measured in an Ubbelohde viscometer with a curved capillary having a negligible correction for kinetic energy [20]. Extrapolation to infinite dilution was carried out to obtain the intrinsic viscosity  $[\eta]$ . The sample of highest molecular weight was examined in a variable-shear viscometer and was found to exhibit Newtonian flow.

## RESULTS AND DISCUSSION

The selected fractions of atactic polypropylene were characterized by light scattering and membrane osmometry. The results are summarized in Table 2 together with the viscosity measurements in toluene and in n-butyl chloride.

TABLE 2. Characterization of the Selected Fractions of aPP in Toluene and n-butyl Chloride at 25°C

Fractions	$[\eta]_{\text{tol}}$ (dlg <sup>-1</sup> )	$k_{\text{H}}$	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	$[\eta]_{\text{bucl}}$ (dlg <sup>-1</sup> )
3	0.71	0.43	0.56	0.66	0.73
5	1.30	0.37	1.24	1.69	1.33
7	1.64	0.38	1.60	2.45	1.73
9	2.05	0.35	2.26	3.26	2.10
14	2.60	0.34	3.09	4.54	2.92

$k_{\text{H}}$  is the Huggins constant

The results obtained show that polydispersity of the fractions expressed as  $M_w/M_n$  is in the range of values acceptable for the reliable determination of the solution properties. On the basis of these data, Mark-Houwink-Sakurada equations were determined for aPP in toluene at 25°C:

$$[\eta] = 6.06 \times 10^{-4} M_w^{0.64}$$

and in n-butylchloride at 25°C:

$$[\eta] = 3.30 \times 10^{-4} M_w^{0.69}$$

These equations were used for viscometric characterization of the molecular weight for all polypropylene fractions ( $M_v$ ) used in these studies.

### Determination of Theta Conditions

The semi-empirical method suggested by Cornet and Ballegooijen [21], based upon the first cloud point titration was used for the approximate determination of theta conditions. The following theta solvents for aPP were found:

ethyl-n-butyl ketone  $T_{\theta} = 26^{\circ}\text{C}$

methyl-n-hexyl ketone  $T_{\theta} = 21^{\circ}\text{C}$

1-nonanol  $T_{\theta} = 60^{\circ}\text{C}$

2-ethylhexanol  $T_{\theta} = 55^{\circ}\text{C}$

Ketones as theta solvents and decalin (48% trans) as a good solvent were used for the following measurements. The temperature dependence of the intrinsic viscosity of fractions was measured in these solvents (Table 3). These data were used for determining the Mark-Houwink-Sakurada equations (Table 4).

TABLE 3. Temperature Dependence of the Intrinsic Viscosity  $[\eta]$  of aPP Fractions in Decalin and Studied  $q$  Solvents

aPP $M_v \times 10^{-5}$	$[\eta]$ decalin							
	15	20	25	30	35	40	45	50
0.27	0.45	0.43	0.47	0.44	0.41	0.38	0.37	0.36
0.77	0.99	0.94	0.92	0.89	0.88	0.91	0.88	0.83
1.16	1.41	1.35	1.49	1.41	1.39	1.33	1.28	1.32
1.23	1.59	1.54	1.64	1.64	1.64	1.52	1.49	1.47
1.58	1.82	1.75	1.82	1.82	1.72	1.70	1.70	1.70
1.81	1.89	1.85	2.04	1.92	1.85	1.96	1.89	1.85
2.21	2.44	2.33	2.44	2.38	2.33	2.27	2.22	2.33
2.31	2.63	2.38	2.56	2.44	2.38	2.38	2.38	2.38
2.50	2.78	2.63	2.70	2.78	2.63	2.63	2.56	2.50
4.08	3.45	3.51	3.57	3.70	3.57	3.33	3.33	3.33
4.86	4.00	4.00	4.17	4.00	4.00	4.00	4.00	3.85

	$[\eta]$ methyl-n-hexyl ketone							
	25	30	35	40	45	50	55	60
0.77	0.46	0.46	0.46	0.46	0.47	0.48	0.51	0.52
1.16	0.58	0.62	0.62	0.63	0.65	0.66	0.68	0.71
1.81	0.72	0.73	0.74	0.74	0.80	0.80	0.82	0.86
2.21	0.87	0.92	0.94	0.95	0.95	1.00	1.02	1.05
2.50	0.93	0.95	0.98	0.98	1.03	1.04	1.09	1.15
4.08	1.09	1.20	1.25	1.27	1.32	1.35	1.39	1.47

(continued)

The temperature dependence of the exponents  $a$ , in Mark-Houwink-Sakurada equations were used for determining  $T_0$  temperature ( $a = 0.5$ ) and the unperturbed dimensions were evaluated via the Burchard-Stockmayer-Fixman [22, 23] extrapolation procedure and  $K_0$ ,  $T_0$  values for both solvents were obtained as follows:

TABLE 3. Continued

	[ $\eta$ ] ethyl-n-butyl ketone							
0.77	0.46	0.48	0.49	0.50	0.51	0.51	0.52	0.52
1.16	0.57	0.60	0.63	0.65	0.67	0.68	0.69	0.71
1.81	0.70	0.71	0.76	0.79	0.81	0.83	0.84	0.86
2.21	0.79	0.85	0.90	0.95	0.99	1.02	1.05	1.09
2.50	0.87	0.95	1.03	1.08	1.12	1.14	1.18	1.22
4.08	1.13	1.18	1.28	1.35	1.40	1.43	1.48	1.54

ethyl-n-butyl ketone:  $K_{\theta} = 1.65 \times 10^{-3}$ ,  $T_{\theta} = 19.0^{\circ}\text{C}$   
 methyl-n-hexyl ketone:  $K_{\theta} = 1.62 \times 10^{-3}$ ,  $T_{\theta} = 19.7^{\circ}\text{C}$

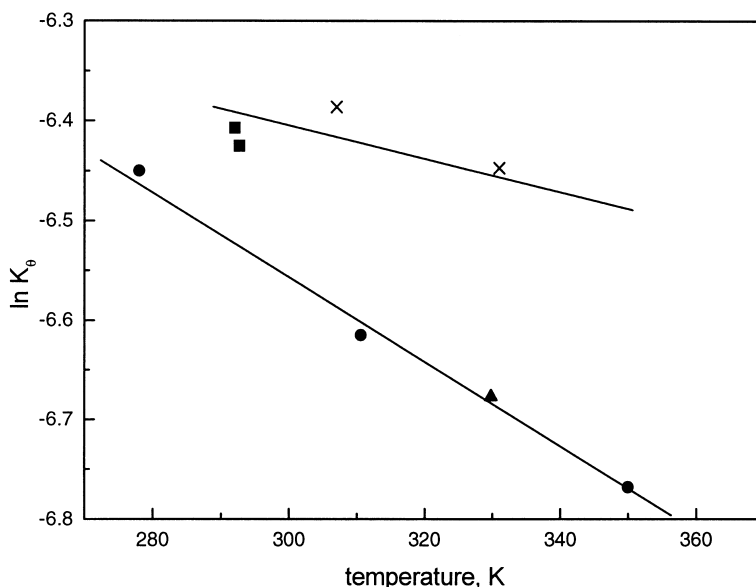
Figure 1 shows a comparison of these values with those available in the literature: our  $K_{\theta}$  values correspond with those described elsewhere [11, 12] and are higher than  $K_{\theta}$  values for model polypropylene chains.

Generally, agreement between the  $K_{\theta}$  values (for the same temperature) is also subject to the absence of specific solvent interactions on the unperturbed

TABLE 4. Temperature Dependence of Mark-Houwink-Sakurada Constants for aPP

Temperature	Decalin (48 %) trans		Methyl-n-hexyl Ketone		Ethyl-n-butyl Ketone	
	$K \times 10^4$	a	$K \times 10^4$	a	$K \times 10^4$	a
15	4.96	0.690				
20	2.53	0.740				
25	1.58	0.780	10.30	0.543	10.69	0.538
30	1.39	0.790	7.70	0.571	9.47	0.552
35	1.19	0.800	5.50	0.560	7.06	0.607
40	0.99	0.814	5.38	0.603	5.40	0.607
45	0.86	0.825	4.46	0.619	5.06	0.615
50	0.83	0.830	4.53	0.621	4.80	0.621
55			4.61	0.623	3.96	0.639
60			4.69	0.625	3.34	0.655





**Figure 1.** Plot of  $\ln K_{\theta}$  as function of temperature for aPP (x, ref. [11, 12], ■, this work), HTPP (●, ref. [2], and HHPP (▲, ref. [3]).

chains. It is interesting to compare the  $T_{\theta}$  values in the same solvent - isoamylacetate:  $T_{\theta}$  aPP = 34°C [11],  $T_{\theta}$  HHPP = 56.8°C [3],  $T_{\theta}$  HHPP = 43°C [4]. The difference between two  $T_{\theta}$  of HHPP is probably caused by the higher concentration of non-1,3 units in polydienes prepared by Arichi *et al.* [4] and also by different distribution of configurations [3] in both samples.

### Temperature Coefficient of the Unperturbed Dimensions

The evaluation of temperature coefficient of the unperturbed chain dimensions  $d \ln \bar{r}_0^2/dT$  was made using Bohdanecky method [24], which is the modification of the method described by Flory *et al.* [25]. The temperature coefficient,  $d \ln \bar{r}_0^2/dT$ , is a chain parameter dependent upon the energy and entropy differences of various rotational isomeric states.

The value of the temperature coefficient  $d \ln \bar{r}_0^2/dT$  of aPP, determined by this method in decalin was  $-2.44 \times 10^{-3} \text{ K}^{-1}$ . A comparison of this value with those available in the literature shows a good agreement with the values of Mays and

TABLE 5. Temperature Coefficients of the Unperturbed Chain Dimensions of aPP

$(d \ln \bar{r}_0^2 / dT) \times 10^3 \text{ K}^{-1}$	Solvent	Temperature range, °C	Reference
-2.44	Decalin	15 – 55	this work
-3.00	$\theta$ solvent series	74 – 153	13
-1.70	athermal solvents	25 – 55	10
-1.40	$\theta$ solvent series	36 – 146	11,12
-2.40 <sup>a)</sup>	athermal solvents	10 – 70	2
-2.70 <sup>a)</sup>	$\theta$ solvent series	5 – 77	2

<sup>a)</sup>HTPP

Fetters [2]  $-2.4 \times 10^{-3} \text{ K}^{-1}$  in athermal solvents or  $-2.7 \times 10^{-3} \text{ K}^{-1}$  in theta solvent series (Table 5).

The average value of  $d \ln \bar{r}_0^2 / dT$  predicted from the rotational isomeric state model is for HTPP  $-0.98 \times 10^{-3} \text{ K}^{-1}$  [2]. Almost all experimental values are more than twice as large as this. Some possible reasons for these differences consist in the influence of specific solvent effects on unperturbed dimensions. Those make the evaluation of the temperature coefficient  $d \ln \bar{r}_0^2 / dT$  when not using homologous series of theta solvents less reliable.

## CONCLUSION

Fractions of industrial atactic polypropylene were characterized in thermodynamically good solvents and in some new theta solvents based on aliphatic ketones. The constants of Mark-Houwink-Sakurada equations were measured as a function of temperature and unperturbed dimensions and their temperature coefficient were determined. Both theta solvents have practical by the same  $T_\theta$  and  $K_\theta$  values and are higher than those established for model polypropylenes prepared by hydrogenation of appropriate polydienes, suggesting lower flexibility of the industrial atactic polypropylene chains.

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