Specific Refractive Index Increments of Segmented Polyurethanes

J. DOSTÁL,[1] L. ŠIMEK,[1] V. KAŠPÁRKOVÁ,[1] M. BOHDANECKÝ[2]

[1] Faculty of Technology, Technical University, 762 72 Zlín, Czech Republic

[2] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague, Czech Republic

ABSTRACT: Specific refractive index increments ν of polyester-based segmented polyurethanes in N,N-dimethyl formamide have been determined, and the quotient $d\nu/df_d$ has been evaluated (where f_d is the weight fraction of hard-segment units). The results are in good agreement with the values calculated from group contributions to the molar refraction, using the Vogel or the Gladstone–Dale equations. The values calculated with the Lorenz–Lorentz equation are too low. A potential explanation of this fact is proposed. The same methods have been applied to reported ν values for polyether-based polyurethanes. An explanation is proposed for differences in $d\nu/df_d$ for polyester- and polyether-based polyurethanes. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1917–1923, 1998

Key words: specific refractive index increment; segmented polyurethanes; effect of composition

INTRODUCTION

Accurate values of the specific refractive index increment, $\nu \equiv dn/dc$, of polymer solutions are indispensable for the determination of the weight-average molecular weight, $\bar{M}_w$ by light scattering or the estimation of the molecular weight distribution by size exclusion chromatography (SEC). With copolymers, the ν values depend on the refractivity and content of components. This dependence becomes complicated with copolymers comprising three or more components largely differing in refractivity.

Segmented polyurethanes (PUR) are prepared by the reaction of the following three components[1]: an oligomeric dihydroxy-terminated polyester or polyether (usually aliphatic), a di-isocyanate (typically, an aromatic one), and a low-molecular-weight aliphatic diol or diamine as chain extender.

The broad span of ν values (0.039–0.18 cm³/g) reported for polyurethanes[2] has initiated the first investigation[3] of the dependence of the specific refractive index increment on the composition of polyurethanes based on poly(ethylene adipate) (PEA), 4,4′-methylene bis(phenyl isocyanate) (MDI), and butanediol (BD). Later on, Lee et al.[4] investigated polyurethanes prepared from MDI, BD, and poly(tetramethylene oxide) (PTMO). A linear dependence of ν on the weight fraction f_d of MDI units at $f_d < 0.5$ has been established in both articles.

Schulz et al.[3] found very good correspondence of their experimental ν values with those calculated from group contributions to the molar refraction, using the method proposed by Goedhart and van Krevelen.[5,6] This success was promising for practice but was somewhat surprising as the correspondence was less satisfactory with other polymers,[6] with the differences between experimental and calculated values being as high as 20%.

Table I   Specific Refractive Index Increments of Poly(butylene adipate) (PBA) and Polyurethanes (PUR-B)

Sample	p^{a}	f_d	ν (cm^3/g)^b (Experimental)	ν^* (cm^3/g) Calculated with		
				Eq. (7)	Eq. (8)	Eq. (10)
PBA	—	0	0,046	0,043	0,043	0,040
PUR-B1	2,2	0,270	0,086	0,076	0,087	0,086
2	3,0	0,305	0,090	0,081	0,093	0,092
3	3,6	0,350	0,094	0,086	0,100	0,100
4	4,6	0,360	0,104	0,087	0,100	0,102
5	5,3	0,400	0,110	0,092	0,107	0,107
6	6,9	0,430	0,111	0,096	0,112	0,112
7	8,5	0,460	0,115	0,100	0,117	0,116
8	—	0,385	0,102^c	0,090	0,102	0,102

^{a} Molar ratio PBA : MDI : BD = 1 : p : (p + 1).
^{b} Solvent DMF at 25°C and λ = 546 nm.
^{c} From Kašpárková et al.[7]

In this article, specific refractive index increments are reported for solutions in N,N-dimethyl formamide of segmented polyurethanes prepared from MDI, BD, and poly(ε-caprolactone) (PCL) or poly(butylene adipate) (PBA). The range of composition has been extended by including oligomeric PCL and PBA ($f_d = 0$) and a PUR-D$_4$ sample ($f_d = 0.74$) containing only MDI and BD.[7] The results are compared with the values calculated from group contributions. The ν values reported in literature are also examined from this point of view.

EXPERIMENTAL

Polymers

Oligomers of ε-caprolactone (PCL) and butylene adipate (PBA), and polyurethanes PUR-B are laboratory products provided by Dr. R. Vondra (Svit, Zlín, Czech Republic). Polyurethanes PUR-B were prepared by a two-stage polymerization technique from di-hydroxyterminated poly(butylene adipate) (number-average molecular weight, $\bar{M}_n$ = 2000), 4,4'-methylene bis(phenyl isocyanate) and butanediol in solutions in N,N-dimethyl formamide (DMF) (Table I). The isolation from the reaction mixture and purification has been described.[7]

Polyurethane samples denoted as PUC (Table II) are fractions of a polymer prepared from poly(ε-caprolactone) ($\bar{M}_n$ = 2000), butanediol and 4,4'-methylene bis(phenyl isocyanate) (molar ratio p = 1 : 2.8 : 4). Fractions differing in composition were obtained by extraction fractionation.[8]

Preparation and characterization of polyurethanes PUR-D$_k$ comprising two types of units only (MDI and a low-molecular-weight diol) (Table III) has been described in a previous article.[7]

Characterization of Polymers

Polyurethanes PUR-B and PUC were characterized by the weight fraction f_d of MDI units (CO-NH-Ph-NH-CO where Ph stands for the p-phenylene group). The values for PUR-B samples were calculated from the composition of the reaction mixture; those for PUC were computed from the nitrogen content obtained by elemental analysis.[8] Oligomeric polyesters (PCL and PBA) were characterized by the viscosity-average molecular weights ($\bar{M}_n \times 10^{-3}$ = 4.2 and 12.6 for PCL and PBA, respectively) calculated from the intrinsic viscosity [η] in DMF at 25°C and by the specific refractive index increments in DMF (ν = 0.046 and 0.047 cm^3/g for PBA and PCL, respectively).

Refractive indices n_2 of solutions in N,N-dimethyl formamide (DMF) at five concentrations were measured with the Brice–Phoenix differential refractometer, and the specific refractive index increments (at 25°C and λ = 546 nm) were evaluated in standard way.

RESULTS AND DISCUSSION

Correlation of ν Values with Composition of Polyester-Based Polyurethanes

Polyurethane samples PUR-B and PUC consist of three types of structural units in various propor-

Table II   Specific Refractive Index Increments of Poly(ε-caprolactone) (PCL) and Polyurethanes (PUC)

Sample	f_d	ν (cm³/g)[a] (Experimental)	ν^* (cm³/g) Calculated with		
			Eq. (7)	Eq. (8)	Eq. (10)
PCL	0	0,047	0,050	0,055	0,040
PUC-1	0,24	0,079	0,073	0,082	0,081
2	0,26	0,081	0,075	0,086	0,084
3	0,27	0,080	0,076	0,087	0,085
4	0,27	0,083	0,076	0,087	0,085
5	0,29	0,091	0,079	0,091	0,090
6	0,31	0,095	0,081	0,093	0,093
7	0,31	0,102	0,081	0,093	0,093
8	0,37	0,104	0,089	0,105	0,102

[a] Solvent DMF at 25°C and λ = 546 nm.

tions (Table I and II). Since the contributions of polyester and diol units to the specific refractive index increment are almost equal, it is legitimate to characterize the composition by the weight fraction f_d of MDI units.

The ν values for PCL and PBA ($f_d = 0$), PUC and PUR-B ($0.24 < f_d < 0.46$), and PUR-D$_4$ ($f_d = 0.74$) are plotted against f_d in Figure 1. The dependence for $f_d \leq 0.5$ can be fitted well by the following equation:

$$\nu = \nu_0 + (d\nu/df_d)f_d \tag{1}$$

with $\nu_0 = 0.046$ cm³/g and $d\nu/df_d = 0.16$ cm³/g. No systematic differences are found between the ν values for PUC and PUR-B samples at the same composition.

Line 2 in Figure 1 corresponds to polyurethanes containing poly(ethylene adipate), MDI, and butanediol, investigated by Schulz et al.[3] It has been computed with eq. (1) and $\nu_0 = 0.035$ cm³/g and $d\nu/df_d = 0.168$ cm³/g, given by the
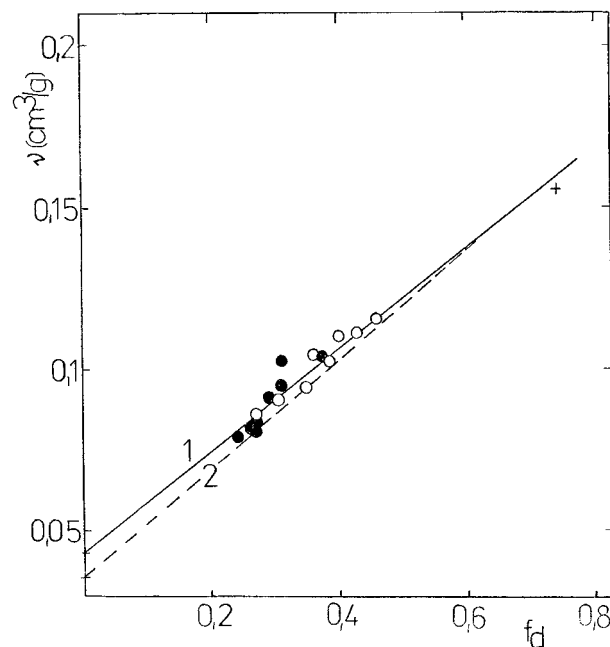
Table III   Specific Refractive Index Increments of Polyurethanes PUR-D$_k$ in DMF at 25°C (λ = 546 nm)

k	ν (cm³/g)[a] (Experimental)	ν^* (cm³/g) Calculated with		
		Eq. (7)	Eq. (8)	Eq. (10)
2	0,163	0,142	0,171	0,156
3	0,160	0,138	0,166	0,155
4	0,157	0,135	0,162	0,153
6	0,155	0,129	0,153	0,150

[a] From Kašpárková et al.[7]

authors. It can be seen that with these polymers, the ν values are lower, and the quotient $d\nu/df_d$ is higher than the corresponding values for polyurethanes based on PCL and PBA.

The quotient $d\nu/df_d$ characterizes the contribution to the increment by the hard component

Figure 1   Dependence of specific refractive index increment ν on weight fraction f_d of MDI units. Experimental data: ($\bigcirc$) PUR-B (Table I); ($\bullet$) PUC (Table II); ($+$) PUR-D$_4$ (Table III). The best-fit line [eq. (1)] is identical with the dependence calculated with eq. (8), assuming $v_2 = \bar{v}_2$; line 2 has been calculated for polyurethanes based on poly(ethylene adipate) using eq. (1) with parameters from Schulz et al.[3]

(that is, MDI). It is remarkable that the $d\nu/df_d$ values for polyester-based polyurethanes amount to only $\frac{2}{3}$ of the value, $d\nu/df_d = 0.23$ cm^3/g, derived for samples based on oligomeric poly(tetramethylene oxide),[4] although the hard component is the same (MDI). This problem will be dealt with later on.

Calculation of ν Values from Group Contributions

The methods of Goedhart and van Krevelen[5,6] of calculating the specific refractive index increments of dilute polymer solutions is based on the assumption that the molar volume V_u and the molar refraction R_u of the chain repeating unit are additive functions of composition, as follows.

$$V_u = \sum_i a_i V_i \qquad (2)$$

$$R_u = \sum_i a_i R_i \qquad (3)$$

where V_i and R_i are the contributions of groups, and a_i is the number of groups i in the repeating unit. Several equations have been proposed to relate the molar refraction to the refractive index n_2, for example,

$$R_{u,LL} = V_u(n_2^2 - 1)/(n_2^2 + 2) \qquad (4)$$

$$R_{u,GD} = V_u(n_2 - 1) \qquad (5)$$

$$R_{u,V} = n_2 M_u \qquad (6)$$

The subscripts LL, GD, and V identify the molar refraction defined by Lorenz and Lorentz,[9,10] Gladstone and Dale,[11] and Vogel,[12] respectively, and M_u is the molecular weight of the repeating unit.

Equations relating the specific refractive index increment to the refractive indices of solvent n_1 and polymer n_2 and corresponding to eqs. (4) and (5), are, respectively,[2]
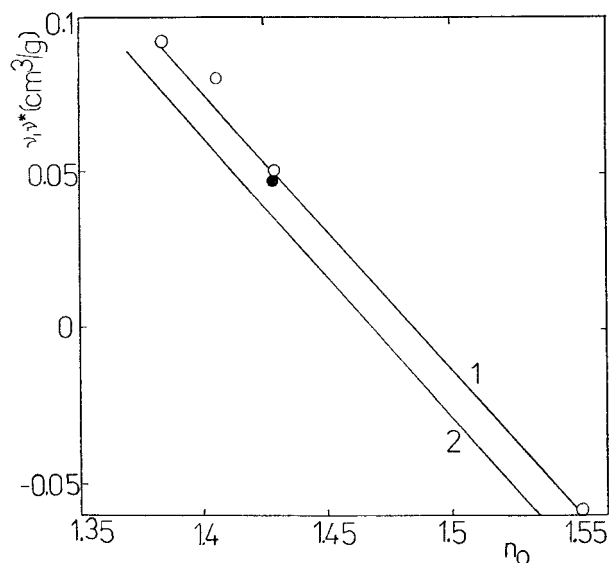
$$\nu_{LL} = \bar{v}_2[(n_2^2 - 1)/(n_2^2 + 2) - (n_1^2 - 1)/(n_1^2 + 2)](n_1^2 + 2)^2/6n_1 \qquad (7)$$

$$\nu_{GD} = \mathbf{v}_2(n_2 - 1) - \bar{v}_2(n_1 - 1) \qquad (8)$$

where v_2 is the specific volume of polymer in solid state

$$\mathbf{v}_2 = V_u/M_u \qquad (9)$$

and $\bar{v}_2$ is the partial specific volume in solution. The equation proposed by Goedhart and van

Figure 2 Specific refractive index increment ν of poly(ε-caprolactone) at 25°C plotted against the refractive index of solvent n_0. Experimental data: (○) from Knecht and Elias[14]; (●) from this article. Line 1 was calculated with eqs. (7) and (8) (ν-values); line 2 was calculated with eq. (10) (ν*-values).

Krevelen[5,6] to calculate the specific refractive index increments from group contributions $R_{V,i}$ is

$$\nu_V = \mathbf{v}_2(R_{u,V}/M_u - n_0) \qquad (10)$$

The group contributions V_i and R_i used in the present work are taken from literature.[3,6,13] The results of calculations are listed in Tables I to III. In most cases, the partial specific volume $\bar{v}_2$ has been approximated by the specific volume v_2 of polymer in solid state. The specific refractive indices thus obtained are distinguished by asterisks (ν*) from those (ν) where the partial specific volume has been used.

Specific Refractive Index Increments of Polyesters

Knecht and Elias[14] have measured the specific refractive index increments of PCL at temperatures from 20 to 70°C. Since the quotients $d\nu/dT$ are low (approximately 2.5×10^{-4} cm^3 g^{-1} deg^{-1}), the results for 25 and 35°C can be combined. The dependence of ν versus n_0 (Fig. 2) based on the data for THF, diethyl carbonate, dioxan, and o-dichlorobenzene from Knecht and Elias,[14] is completed by the value for DMF at 25°C (Table II). As the partial specific volume of PCL has been estimated ($\bar{v}_2 = 0.893$ cm^3/g in benzene at 30°C[15]), eqs. (7) and (8) are used without approx-
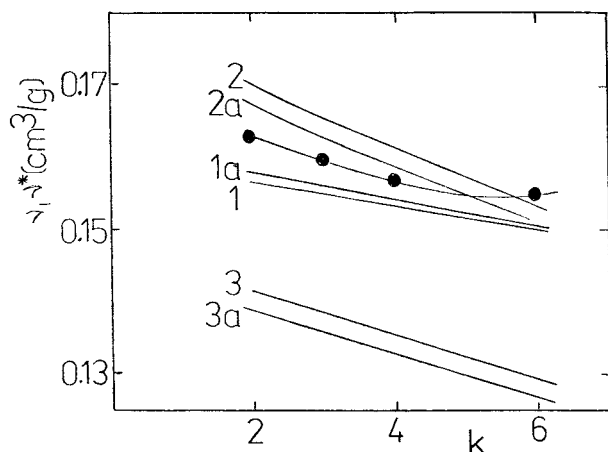
Figure 3 Specific refractive index increment for PUR-D_k samples plotted against number k of methylene groups in diol units. Experimental data: (●) (ν-values).[7] Curves (ν^*-values) were calculated using eq. (10) (curves 1, 1a), eq. (8) (curves 2, 2a), and eq. (7) (curves 3, 3a). Curves 1, 2, and 3 have been obtained with group increments V_i from Neumann and Becker[13]; curves 1a, 2a, and 3a have been obtained with V_i from van Krevelen.[6]

imating $\bar{\mathbf{v}}_2$ by v_2, only assuming that the solvent effect on $\bar{\mathbf{v}}_2$ may be neglected.

Line 1 in Figure 2 shows that identical dependences of ν of PCL on the solvent refractive index n_1 are obtained by means of eqs. (7) and (8). They fit the experimental data very well. On the contrary, the $\nu_{\mathbf{v}}^*$ values computed with eq. (10) are lower by 0.012 cm³/g, that is, by 20 and 100% at $n_1 = 1.4$ and 1.5, respectively. As shown by the results for other polymers listed by van Krevelen,[6] differences of this magnitude between the experimental values and those calculated with eq. (10) are not exceptional. No explanation is at hand, however.

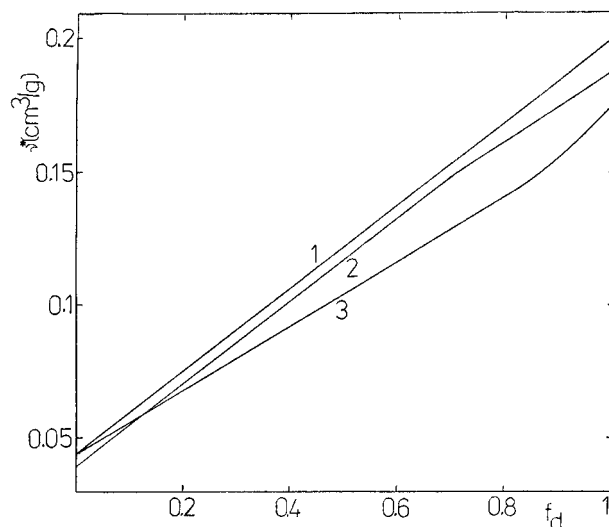## Specific Refractive Index Increment of Polyester-Based Polyurethanes

The results of calculations for MDI units cannot be checked against the experimental data. Nevertheless, they are useful for the discussion of polyurethanes. While the ν_{GD}^* and $\nu_{\mathbf{v}}^*$ values are very similar (0.195 and 0.187 cm³/g), those of ν_{LL}^* are lower by 0.015 to 0.02 cm³/g.

Figure 3 presents the dependence of ν values on the number k of methylene groups in the diol unit of PUR-D_k samples. Since the partial specific volumes of these polymers are not known, only the ν^* values can be computed. Experimental values are between ν_{GD}^* and $\nu_{\mathbf{v}}^*$ and would be fitted

well by the arithmetic means $(1/2) \cdot (\nu_{GD}^* + \nu_{\mathbf{v}}^*)$. The differences $(\nu_{\mathrm{exp}} - \nu_{\mathbf{v}}^*)$ and $(\nu_{\mathrm{exp}} - \nu_{GD}^*)$ are of approximately the same magnitude as with polyesters (Table III). As the ν values for PUR-D_k samples are three times those for polyesters, this difference would be less important in practice. It is remarkable that, similar to the situation with MDI units but unlike that with polyesters, the ν_{LL}^* values are lower systematically by 0.015 to 0.03 cm³/g.

The results of calculations for segmented polyurethanes PUC and PUR-B (Fig. 4) can be summarized in the following points.

1. The plots of ν_{LL}^* and $\nu_{\mathbf{v}}^*$ versus f_d are curved at $f_d > 0.7$. The plot of ν_{GD}^* is linear in the whole range of composition.
2. Calculated dependences for PUC and PUR-B overlap almost exactly at $f_d > 0.2$ (Tables I and II). At lower contents of MDI, they differ by 0.003 cm³/g in consequence of different ν^* values for the corresponding polyesters.
3. The dependence of ν_{GD}^* versus f_d (line 1 in Fig. 4) is fitted well by eq. (1) with the parameter values estimated from experiments with PUR-B and PUC ($\nu = 0,046$ cm³/g, $d\nu/df_d = 0,16$ cm³/g). Equation (10) yields slightly lower values.
4. The calculated value of the quotient $d\nu^*/df_d$ (0.155 cm³/g) for PUC and PUR-B is in a very good agreement with the experimental one (0.16 cm³/g).

Figure 4 Calculated specific refractive index increment ν^* for PUR-B plotted against f_d. Curves 1, 2, and 3 were calculated with eqs. (8), (10), and (7), respectively. Curves for PUC overlap with those for PUR-B.
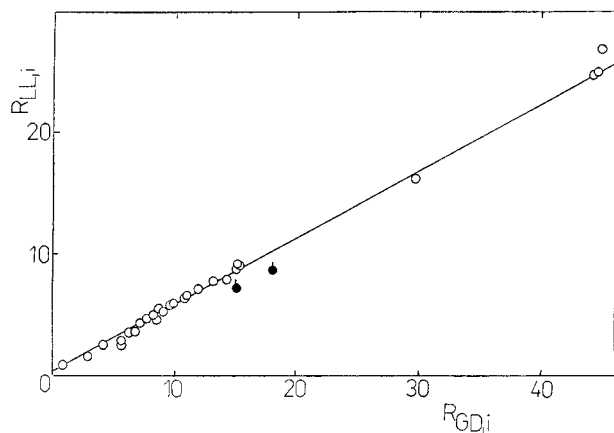
Figure 5 Correlation of group contributions $R_{LL,i}$ and $R_{GD,i}$. Data from Table II.1 in van Krevelen.[6] Values for CONH groups (●) general and (●) attached to benzene ring.

5. As follows from eqs. (8) and (10), the results of calculations are very sensitive on the value of n_0. The superposition of experimental and calculated dependences would be improved by using $n_0 = 1.425$ instead of 1.427 for DMF.

6. The ν_{LL}^* values are systematically lower by 0.01 to 0.03 cm³/g than ν_{V}^* or ν_{GD}^*. As the same difference exists with MDI and PUR-D$_k$ (Fig. 3), it is seen that eq. (7) yields too low values for polyurethanes in general. As, however, it leads to correct ν_{LL} values for polyesters, it seems that the contribution of CONH groups to the molar refraction of the repeat unit is too low. This is rather surprising because the value $R_{LL,i} = 8.5$ cm³/g used in calculations is characteristic of CONH groups attached to benzene rings and is higher than the general value ($R_{LL,i} = 7.23$ cm³/g) for these groups.[6]

To clear up this situation, we have plotted in Figure 5 $R_{LL,i}$ versus $R_{GD,i}$ for various atoms and groups.[6] The straight line fits all data points except of those for CONH groups. These are shifted below the line by approximately 2 cm³/g. We have tentatively computed ν_{LL}^* using $R_{LL,i} = 10.2$ cm³/g (instead of 8.5) and obtained $\nu_{LL}^* = 0{,}164$ and 0.156 cm³/g for PUR-D$_2$ and PUR-D$_4$, respectively. New values are in close proximity to the experimental ones as well as to those computed with eqs. (8) and (10). A similar change in ν^* is obtained with MDI, PUC, and PUR-B.

The group contributions $R_{LL,i}$ have been obtained by Goedhart by a regression analysis of data for about a thousand low-molecular-weight

organic compounds.[5,6] A similar analysis has recently been done by Groh and Zimmermann,[16] based on the density and refractive indices of 60 polymers. The results very well agree with those tabulated by van Krevelen.[6] Unfortunately, only one value, $R_{LL,i} = 8.256$ cm³/g, has been reported by these authors[16] for CONH groups without specification whether it is valid for groups linked to benzene rings. Thus, the question why the $R_{LL,i}$ values for CONH groups so strongly deviate from the correlation in Figure 5 cannot be answered.

The discussion of results for polyester-based polyurethanes shows that the ν_{GD}^* and ν_{V}^* values are accurate enough to be used, at least in the evaluation of SEC data. This result is somewhat surprising because the difference between the partial specific volume $\bar{v}_2$ and the specific volume v_2 has been neglected in calculations. Nevertheless, this neglect appears to be justified because the $\bar{v}_2$ values reported by Sato[17] for polyurethanes containing PCL (0.85–0.87 cm³/g) are almost equal to the calculated values of v_2 for $0.2 < f_d < 0.5$ (0.86–0.82 cm³/g).

ν-Values for Polyether-Based Polyurethanes

Moacanin[18] has studied methanol solutions of polyurethanes prepared from poly(propylene oxide)(PPO) and toluylene diisocyanate (TDI). Application of eq. (10) yields the following ν_{V}^* values (in cm³/g): 0.261 for TDI, 0.143 for the PPO segment, and 0.156 for polyurethanes. The last value differs from the experimental ones (0.145–0.156 cm³/g) by less than 7% only.

Žigon et al.[19] have recently measured the increments (in THF) of polyurethanes containing poly-(tetramethylene oxide)(PTMO) as soft segment, TDI, or hexamethylene diisocyanate (HDI) as hard components ($f_d \leq 0.2$), and butanediol. The ν^* value calculated with eq. (10) for PTMO (0.065 cm³/g) is in a very good agreement with those determined by experiment (0.066[19] and 0.063 ± 0.002 cm³/g[4]). The same holds for HDI units and polyurethanes in which the difference of calculated and experimental values is about 1%. There is a large discrepancy in the values for TDI (0.199 cm³/g calculated; 0.24 cm³/g reported). The latter has, however, been estimated by a long extrapolation to $f_d = 1$ of the dependence of ν versus f_d established for $0.05 \leq f_d \leq 0.2$ and therefore may be subject to a significant inaccuracy.

Solutions in THF of polyurethanes containing PTMO, MDI, and butanediol have also been studied by Lee et al.[4] Experimental values for these samples are higher than the calculated ones
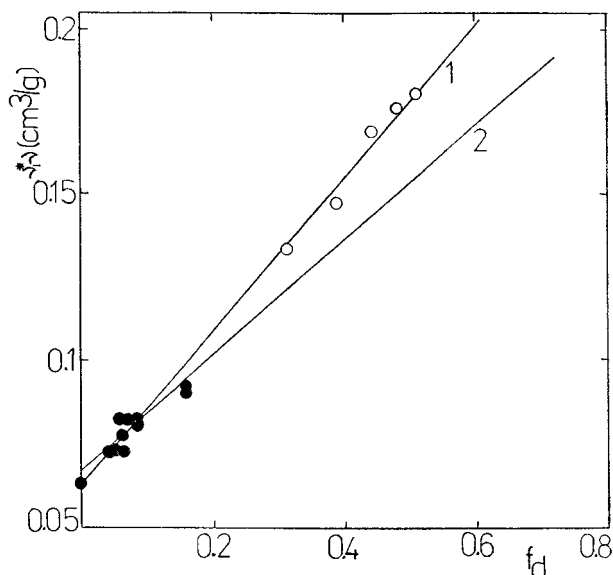
Figure 6 Specific refractive index increment of PTMO-based polyurethanes in THF. Experimental data (ν) from ($\bigcirc$) Lee et al.,[4] and ($\bullet$) Žigon et al.[19] Line 1 was best fit to experiments; line 2 was calculated with eq. (8) assuming $v_2 = \bar{\mathbf{v}}_2$ (ν^* values).

(curve 2 in Fig. 6) by 10 to 20%. Such discrepancy can arise[20] in calculations based on eq. (8) if the specific volume v_2 of solid polymer is substituted for the partial specific volume $\bar{\mathbf{v}}_2$ in the second term of this equation. Curve 2 would be brought to superposition with the experimental dependence (curve 1) assuming that the difference $\Delta = v_2 - \bar{\mathbf{v}}_2$ increases with increasing f_d from $\Delta = 0.03$ cm^3/g (at $f_d = 0.31$) to $\Delta = 0.06$ cm^3/g (at $f_d = 0.5$). Though the magnitude of the difference seems reasonable, the explanation is to be taken as preliminary. An experimental check is desirable.

CONCLUSIONS

1. Experimental values of the specific refractive index increment ν and the quotient $d\nu/df_d$ for polyurethanes based on poly(ε-caprolactone) or poly(butylene adipate) are practically identical. They slightly differ from those for polymers based on poly(ethylene adipate).
2. Calculations using eqs. (8) or (10) with the corresponding group contributions to the molar refraction provide ν and $d\nu/df_d$ values for polyurethanes mentioned in (1) with an accuracy satisfying the requirements of the SEC. On the contrary, the values calculated for polyurethanes based on poly(tetramethylene oxide) are too low and cannot be used in practice.
3. Equation (7) with the group contribution for CONH yields too low ν values.[6] This contribution seems to be underestimated, as suggested by the analysis of group contributions listed there.

REFERENCES

1. Z. R. Petrović and J. Fergusson, *Prog. Polym. Sci.,* **16,** 215 (1991).
2. M. B. Huglin, in *Polymer Handbook* (J. Brandrup and E. H. Immergut, Eds.), Vol. VII, 3rd ed., Wiley, New York, 1989, p. 409.
3. G. Schulz, C. Wehrstedt, and R. Gnauck, *Plaste u. Kautsch.,* **32,** 153 (1985).
4. D. Lee, T. A. Speckhard, A. D. Sorensen, and S. L. Cooper, *Macromolecules,* **19,** 2383 (1986).
5. D. J. Goedhart, *Proceedings of International GPC Seminar,* Monaco, Oct. 1969, p. 12.
6. D. W. van Krevelen, *Properties of Polymers,* Elsevier, Amsterdam, 1972.
7. V. Kašpárková, L. Šimek, and M. Bohdanecký, *Makromol. Chem. Phys.,* **197,** 3757 (1996).
8. L. Šimek and M. Bohdanecký, *J. Appl. Polym. Sci.,* **58,** 897 (1995).
9. L. V. Lorenz, *Wied. Ann. Phys.,* **11,** 70 (1880).
10. H. A. Lorentz, *Wied. Ann. Phys.,* **9,** 641 (1880).
11. J. H. Gladstone and T. P. Dale, *Trans. R. Soc. London,* **A148,** 887 (1858).
12. V. Vogel, *J. Chem. Soc.,* 1833 (1948).
13. G. Neumann and R. Becker, *Plaste u. Kautsch.,* **23,** 26 (1976).
14. M. R. Knecht and H.-G-Elias, *Makromol. Chem.,* **157,** 1 (1972).
15. J. V. Koleske and R. D. Lundberg, *J. Polym. Sci., Part A-2,* **7,** 897 (1969).
16. W. Groh and A. Zimmermann, *Macromolecules,* **24,** 6660 (1991).
17. H. Sato, *Bull. Chem. Soc. Jpn.,* **39,** 2335 (1966).
18. J. Moacanin, *J. Appl. Polym. Sci.,* **1,** 272 (1950).
19. M. Žigon, A. Mirčeva, T. Malavašić, and G. Grubišić–Gallot, *J. Liq. Chromat.,* **16,** 3813 (1993).
20. M. B. Huglin, *Light Scattering from Polymer Solutions,* Academic Press, London, 1972, p. 165.