Macromolecules 1986, *19*, 2383–2390

X-ray data are ambiguous, in terms of some molecular conformation and intermolecular packing features.

Acknowledgment. We acknowledge the financial assistance of NSERC (Canada) in the form of an operating grant (C.A.F.) and a Graduate Scholarship (R.P.V.). We also acknowledge the technical assistance of C. Pasztor of the University of Guelph and Dr. T. L. Bluhm of the Xerox Research Centre of Canada in obtaining the X-ray diffraction data.

Registry No. PPL (homopolymer), 24969-13-9; PPL (SRU), 24937-51-7.

References and Notes

(1) Thiebaut, R.; Fischer, N.; Etienne, Y.; Coste, J. *Ind. Plast. Mod.* **1962**, *14*, 1.

(2) Grenier, D.; Prud'homme, R. E.; Leborgne, A.; Spasky, N. J. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1781.

(3) Allegrezza, A. E.; Lenz, R.; Cornibert, J.; Marchessault, R. H. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2617.

(4) Cornibert, J.; Marchessault, R. H. *Macromolecules* **1975**, *8*, 296.

(5) Cornibert, J.; Marchessault, R. H. *J. Mol. Biol.* **1972**, *71*, 735.

(6) Carazzolo, G. *Chim. Ind. (Milan)* **1964**, *46*, 525.

(7) Perego, G.; Melis, A.; Cesari, M. *Makromol. Chem.* **1972**, *157*, 269.

(8) Knoblock, F. W.; Statton, W. O. U.S. Patent 3 299 171, 1967.

(9) Prud'homme, R. E.; Marchessault, R. H. Macromolecules **1974**, *7*, 541.

(10) Yogoachi, M.; Chatani, Y.; Tadokoro, H.; Tan, H. *Polym. J.* **1974**, *6*, 248.

(11) Prud'homme, R. E.; Marchessault, R. H. *Makromol. Chem.* **1974**, *175*, 2705.

(12) Meille, S. V.; Konishi, T.; Geil, P. H. *Polymer* **1984**, *25*, 773.

(13) (a) Schaefer, J.; Stejskal, E. O. *Top. Carbon-13 NMR Spectrosc.* **1979**, *3*. (b) Lyerla, I. R. *Contemp. Top. Polym. Sci.* **1979**, *3*, 143. (c) Wasylishen, R. E.; Fyfe, C. A. *Annu. Rev. Nucl. Magn. Reson.* **1982**, *12*, 1. (d) Fyfe, C. A. *Solid State NMR for Chemists*; CFC Press: Guelph, Ontario, Canada, 1984.

(14) (a) Dudley, R. L.; Fyfe, C. A.; Stephenson, P. J.; Deslandes, Y.; Hamer, G. K.; Marchessault, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 2469. (b) Horii, R.; Hirai, A.; Kitamaru, R. *Polym. Bull. (Berlin)* **1982**, *8*, 163. (c) Fyfe, C. A.; Dudley, R. L.; Stephenson, P. J.; Deslandes, Y.; Hamer, G. K.; Marchessault, R. H. *J. Macromol. Sci., Rev. Macromol. Chem. Phys. C* **1983**, *23*, 187.

(15) (a) Marchessault, R. H.; Taylor, M. G.; Fyfe, C. A.; Veregin, R. P. *Carbohydr. Res.* **1985**, *144*, C1. (b) Veregin, R. P.; Fyfe, C. A.; Marchessault, R. H.; Taylor, M. G. *Macromolecules* **1986**, *19*, 1030.

(16) (a) Bunn, A.; Cudby, M. E. A.; Harris, R. K.; Packer, K. J.; Say, B. J. *J. Chem. Soc. Chem. Commun.* 1981, 15. (b) Bunn, A.; Cudby, M. E. A.; Harris, R. K.; Packer, K. J.; Say, B. J. *Polymer* **1982**, *23*, 694.

(17) Oosterhof, H. A. *Polymer* **1974**, *15*, 49.

(18) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125.

(19) Fyfe, C. A.; Stephenson, P. J.; Taylor, M. G.; Bluhm, T. L.; Deslandes, Y.; Marchessault, R. H. *Macromolecules* **1984**, *17*, 501.

(20) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12*, 762.

(21) Alemany, L. B.; Grant, D. M.; Pugmire, R. J.; Alger, T. D.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 2133.

(22) Tadokoro, H. *Structure of Crystalline Polymers*; Wiley-Interscience: New York, 1979.

Methods for Determining the Molecular Weight and Solution Properties of Polyurethane Block Copolymers

Day-chyuan Lee, Thomas A. Speckhard,[†] Andrew D. Sorensen, and Stuart L. Cooper*

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706.

Received March 21, 1986

ABSTRACT: Molecular weight measurements of polyurethane block copolymers have been made with a GPC–multidetector method and compared to values obtained by the conventional polystyrene standard method and a broad molecular weight distribution calibration standard technique. The multidetector method proposed in this paper produces more accurate molecular weight values and thus its use should allow for better understanding of molecular weight effects on the structure–property relationships of polyurethane block copolymers. The multidetector technique can also be used to obtain Mark–Houwink constants and the distribution of average segmental composition with molecular weight. Mark–Houwink parameters obtained with the multidetector method appear to be more accurate than values calculated with an approach based on broad molecular weight distribution calibration standards and suggest that for a series of polyether polyurethanes in THF, the solvent power decreases with increasing hard-segment content. A comparison of the molecular weight values obtained with the various methods indicates that the relative $\bar{M}_w$ values normally reported based on a polystyrene calibration can be considered as an upper bound on the absolute $\bar{M}_w$ value.

Introduction

Linear polyurethane block copolymers are normally a condensation product of three monomers: an oligomeric diol, typically a dihydroxy-terminated polyether or polyester with a number-average molecular weight of 500–3000; a diisocyanate that is generally aromatic; and a low molecular weight aliphatic diol chain extender.[1] The final polymer structure is represented as being of the $(AB)_n$ type, where A and B represent so-called hard and soft segments. The precise definitions of the hard and soft segments vary in the literature; in this investigation the soft segment is defined as that portion of the polymer chain originating from the polyether or polyester oligomeric diol while the hard segments are either single reacted diisocyanate units or reaction products of the diisocyanate and chain-extender monomers. A typical structure of a polyurethane block copolymer is shown in Figure 1. The terms hard and soft segments arise from the fact that at room or service temperature the soft segments are normally in a rubbery or viscous state while the hard segments are crystalline or glassy. In the solid state the hard and soft segments tend to phase separate to produce hard- and

---

* To whom correspondence should be addressed.

[†] Current address: 3M Research Center, St. Paul, MN 55144.

0024-9297/86/2219-2383$01.50/0 © 1986 American Chemical Society

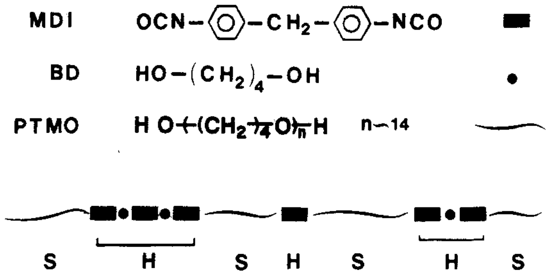

Figure 1. Schematic of polyurethane block copolymer structure.

soft-segment-rich phases; this two-phase structure gives rise to the interesting and useful properties of these materials.[2,3] The fact that polyurethane block copolymers exhibit useful properties that can be influenced in numerous ways has stimulated a large number of investigations on the structure–property relationships of these materials.[3,4]

One area that has received relatively little attention is the effect of the overall molecular weight (as opposed to segmental molecular weights) on the structure–property relationships of polyurethanes. Practically the only reported investigations explicitly designed to study the effect of overall molecular weight on the properties of polyurethanes were carried out by Schollenberger and Dinbergs.[5,6] Most structure–property investigations of polyurethanes, however, implicitly or explicitly assume no effects due to molecular weight, and molecular weight values are normally not reported. No doubt the lack of attention directed toward the effects of molecular weight on the structure–property relationships of polyurethanes is at least partially due to the difficulty of obtaining meaningful molecular weight data. Absolute molecular weight data are difficult to obtain for polyurethanes and copolymers in general because in addition to a molecular weight distribution, copolymers will normally exhibit a distribution of compositions.[7-10] In particular, for polyurethanes their generally poor solubility in common solvents, the use of three instead of two monomers in the polymerization, and the possibility of species produced by side reactions such as allophonate cross-linking are additional complicating factors. Thus, when molecular weight data are presented in the literature only relative values based on gel permeation chromatography (GPC) data and a polystyrene standard calibration curve are usually given, and it is not even clear whether these relative values are an upper or lower bound on the absolute molecular weight values. Furthermore, these relative values will most likely be markedly influenced by the choice of GPC solvent and the chemical composition of the polyurethanes, making comparisons between different samples difficult.

The major objective of this investigation was to evaluate existing methods and develop a better method for obtaining more accurate molecular weight values for a series of polyether polyurethanes with different hard-segment contents. Two approaches, one based on GPC data and the use of broad molecular weight distribution calibration standards[11-16] and one based on a GPC–multidetector method[17-19] were used. The application of the GPC–multidetector method to copolymers is not new. However, most of the researchers using refractive index (RI) detectors in combination with one of three other detectors, ultraviolet[20] (UV), infrared (IR), or light scattering (LS), have not fully utilized the universal calibration principle to calculate viscosities and estimate Mark–Houwink parameters. In this paper, we demonstrate that combining the multidetector method and the universal calibration principle information such as molecular weight distribution, composition distribution, Mark–Houwink parameters, and copolymer viscosity could be obtained in a single measurement. Broad molecular weight distribution calibration methods are reviewed breifly and compared with the GPC–multidetector and conventional polystyrene standard methods. In this investigation no attempt was made to evaluate the effects of molecular weight on structure–property relationships.

Background

Gel permeation chromatography is widely used to obtain polymer molecular weight distribution information. The usefulness of this technique is enhanced by the use of the universal calibration curve.[21-25] Under the universal calibration formalism, two polymer molecules i and j, regardless of their chemistry, eluting at the same retention volume V_i have the same hydrodynamic volume, $M_i[\eta]_i = M_j[\eta]_j$, where M_i and $[\eta]_i$ are the molecular weight and intrinsic viscosity of polymer i. For any linear polymer, if the Mark–Houwink expression ($[\eta] = KM^a$) in the mobile phase is known, then the molecular weight distribution can be calculated by comparing the measured sample GPC curve with that of a polystyrene standard (narrow molecular weight distribution) calibration. If the Mark–Houwink parameters K and a are not known, then they can be back-calculated by broad molecular weight distribution methods.[11-13] A parameter J[14-16] is defined as $J_i = M_i[\eta]_i$. It can then be shown that[14]

$$[\eta] = K^{1/(a+1)}\sum(W_i J_i^{a/(a+1)}) \tag{1}$$

and that

$$\bar{M}_n = K^{-1/(a+1)}/\sum(W_i J_i^{-1/(a+1)}) \tag{2}$$

where W_i is the weight fraction of the ith stripe of the chromatogram. An analogous expression for $\bar{M}_w$ can also be derived. If two of the three parameters $[\eta]$, $\bar{M}_n$, or $\bar{M}_w$ are known from other measurements (viscometry, osmometry, or light scattering) the equation can be solved to yield K and a along with the value of the other parameter. Once K and a are known they can be used to calculate molecular weight distributions.

Another way to obtain the molecular weight distribution of a polymer from GPC measurements is to use a light scattering spectrometer as a GPC detector.[17-19] The intensity of scattered light is expressed in terms of the Rayleigh factor. The quantity used to calculate the molecular weight in the ith stripe of a GPC chromatogram, however, is the excess Rayleigh factor:

$$\bar{R}_{\theta,i} = R_{\theta,i(\mathrm{soln})} - R_{\theta,i(\mathrm{solv})} \tag{3}$$

where $R_{\theta,i(\mathrm{soln})}$ and $R_{\theta,i(\mathrm{solv})}$ refer to Rayleigh factors of the solution and solvent, respectively, in the ith stripe of the chromatogram. At low concentrations and low scattering angles, the scattered intensity can be described by

$$HC_i/\bar{R}_{\theta,i} = 1/M_i + 2A_2C_i \tag{4}$$

where M_i is the molecular weight, A_2 (mol cm^3 g^{-2}) is the second virial coefficient, and C_i (g/cm^3) is the polymer concentration. In the range of this study C_i is on the order of 10^{-4} (g/cm^3); therefore the second term in eq 4 can be neglected. The quantity H (in units of mol cm^2 g^{-2}) is an optical constant defined by

$$H = 2\pi^2 n^2 (\mathrm{d}n/\mathrm{d}C)^2/N_A\lambda_0^4 \tag{5}$$

with n, $(\mathrm{d}n/\mathrm{d}C)$, N_A, and λ_0 being respectively the refractive index, the specific refractive index increment, Avogadro's number, and the wavelength of light in a

Table I
Refractive Index Increment in THF of the Copolymer, Soft Segment, and Hard Segment

sample	$(dn/dC)_0$	$(dn/dC)_s$	W_h[a]	$(dn/dC)_h$
PTMO-1000		0.063 ± 0.002		
MDI/BD/ PTMO-1000				
2/1/1	0.133 ± 0.002		0.37	0.25 ± 0.01
3/2/1	0.147 ± 0.002		0.48	0.24 ± 0.01
4/3/1	0.169 ± 0.002		0.56	0.24 ± 0.01
5/4/1	0.176 ± 0.002		0.62	0.24 ± 0.01
6/5/1	0.180 ± 0.002		0.66	0.24 ± 0.01

[a] Weight fraction of MDI and BD in sample based on synthesis conditions.

vacuum. The concentration in the ith stripe can be calculated from the concentration detector peak

$$C_i = mh_i/V_i(\textstyle\sum h_i) \qquad (6)$$

where m is the injected mass, V_i is the retention volume passing through the detector cell during the ith stripe, and h_i is the corresponding height of the ith stripe. The scattered intensity of the sample effluent can be continuously monitored and the data converted to molecular weight values through application of eq 4. If the molecular weight at each retention volume on the GPC chromatogram were known, one could simply perform the standard summations to calculate $\bar{M}_n$ and $\bar{M}_w$.

For a multiblock copolymer containing hard and soft segments, dn/dC is a function of the composition[26,27]

$$(dn/dC)_0 = W_s(dn/dC)_s + W_h(dn/dC)_h \qquad (7)$$

where $(dn/dC)_0$ is the refractive index increment of the copolymer, $(dn/dC)_s$ is the refractive index increment of the soft segment, and $(dn/dC)_h$ is the refractive index increment of the hard segment. W_s is the weight fraction of the soft segment, and W_h is the weight fraction of the hard segment. The weight fraction of the hard segment is defined by the ratio of the hard-segment molecular weight to the overall molecular weight ($W_h = M_h/(M_s + M_h)$, where M_h and M_s are the molecular weights of the hard and soft segments, respectively). At each retention volume, due to variations in composition with molecular weight the refractive index increment $(dn/dC)_i$ is not equal to the overall refractive index increment $(dn/dC)_0$. With the help of a second detector such as a UV or IR spectrometer, which responds only to the presence of one segment type (either hard or soft), the value of $(dn/dC)_i$ for each stripe of the chromatogram can be calculated.[26] Therefore, the molecular weight of a copolymer at each stripe of the chromatogram can be evaluated. The detailed calculation is presented in Appendix I.

Experimental Section

The samples used in this investigation were five polyether polyurethanes (PU) with different molar ratios of MDI/BD/PTMO-1000 (methylenebis(4-phenyl isocyanate)/butanediol/poly(tetramethylene oxide) with $\bar{M}_n \cong 1000$) (Table I) and thus different hard-segment contents. All of these materials were synthesized by a standard two-step solution polymerization[28] except for the PU 5/4/1 sample, which was polymerized in a one-step solution reaction.[29]

Vapor Pressure Osmometry (VPO). The number-average molecular weight ($\bar{M}_n$) of the polyurethanes was determined with a Model 11.00 vapor pressure osmometer (Knauer). Measurements were made at four or more concentrations at 39 °C in THF (tetrahydrofuran) and extrapolated to zero concentration. Polystyrene standards with $\bar{M}_n$ values in the appropriate range were used for calibration.

Viscometry. The reduced viscosities of polystyrene and polyurethane in THF at four different concentrations were determined at 30 °C with an Ubbelohde dilution viscometer. Both the Huggins[30] and Kraemer[31] relations were used to extrapolate the data to zero concentration to obtain the intrinsic viscosity. A Mark–Houwink expression can be determined from the polystyrene data; the calculated K and a values calculated with $\bar{M}_n$ values provided with the polystyrene standards were 1.90×10^{-4} and 0.68, respectively.

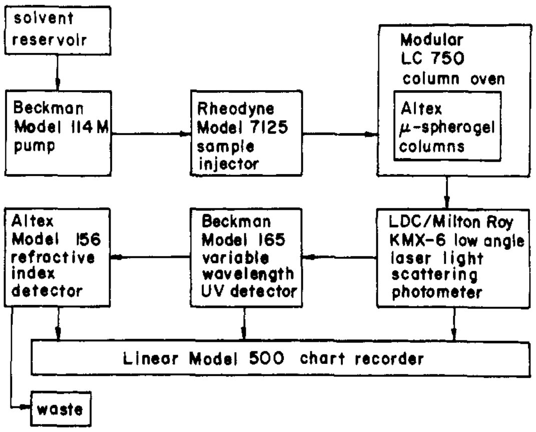

Figure 2. Schematic diagram of the GPC–multidetector system.

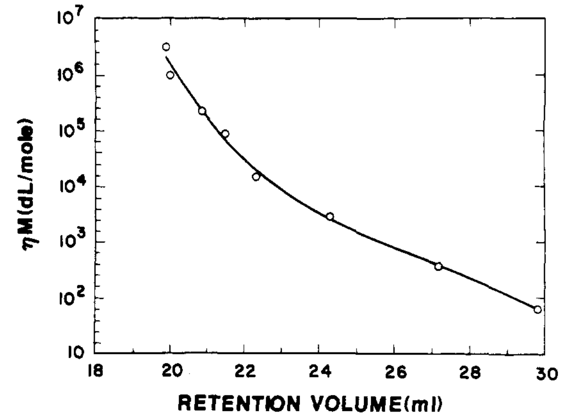

Figure 3. Polystyrene universal calibration curve: (○) data; the solid line is the curve fit through the data, eq 8.

Differential Refractometry. The refractive index increments of the PTMO-1000 oligomer and the polyurethane samples in THF at 30 °C were measured with a KMX-16 laser differential refractometer (LDC/Milton Roy). The refractive index increment of the hard segment was calculated by using eq 7. The results are summarized in Table I.

Gel Permeation Chromatography–Light Scattering Detector System. A schematic diagram of the GPC/LS system used is shown in Figure 2. It contains a Model 114M pump (Beckman), a Model 7125 sample injector (Rheodyne), a series (pore size 50, 100, 500, 10^3, and 10^4 Å) of μ-Spherogel columns (Altex), and LC 750 column oven (Modular), a KMX-6 low-angle laser light scattering photometer (LDC/Milton Roy), a Model 165 variable-wavelength UV detector (Beckman), a Model 156 refractive index detector (Altex), and a Model 500 chart recorder (Linear). The mobile phase was degassed HPLC-grade THF (Aldrich) (uninhibited) flowing at 1 mL/min. The column temperature was held constant at 30 °C. The UV detector was set at 285 nm.

Sample Preparation. All the polymers were dissolved in THF. Stock solutions of polyurethanes were prepared gravimetrically (w/w). For injection, a solution of a PU with a known concentration (w/v) was prepared by volumetric dilution of the stock solution. All solutions for injection were filtered through a 0.2-μm Fluoropore filter (Millipore Corp.) to a 200-μL sample injection loop.

Results and Discussion

A universal calibration curve for our instrument was constructed from GPC data and intrinsic viscosities of commercially available polystyrene standards. The univ-

Table II
Molecular Weight Values Calculated by Using the Polystyrene Calibration

sample	$[\eta]_{\mathrm{exptl}}$, dL/g	$\bar{M}_n^{\mathrm{exptl}} \times 10^{-4}$	calcd values $\bar{M}_w \times 10^{-4}$	 $\bar{M}_n \times 10^{-4}$	calcd adjusted values $\bar{M}_w \times 10^{-4}$	 $\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	peak values $\bar{M}_w \times 10^{-4}$
2/1/1	0.455 ± 0.009	1.7 ± 0.2	6.3 ± 0.1	2.0 ± 0.1	4.7 ± 0.3	1.5 ± 0.1	3.1 ± 0.5	6.4 ± 0.1
3/2/1	0.360 ± 0.007	1.5 ± 0.2	4.9 ± 0.1	1.88 ± 0.09	3.8 ± 0.2	1.5 ± 0.1	2.5 ± 0.4	5.2 ± 0.1
4/3/1	0.370 ± 0.007	1.4 ± 0.1	4.7 ± 0.1	1.64 ± 0.08	3.4 ± 0.2	1.2 ± 0.1	2.8 ± 0.4	4.9 ± 0.1
5/4/1	0.369 ± 0.007	1.2 ± 0.1	4.3 ± 0.1	1.54 ± 0.08	3.0 ± 0.2	1.1 ± 0.1	2.7 ± 0.4	4.3 ± 0.1
6/5/1	0.387 [illegible] 0.008	1.4 ± 0.1	7.1 ± 0.1	1.34 ± 0.07	6.5 ± 0.4	1.2 ± 0.1	5.4 ± 0.8	7.5 ± 0.1

Table III
Molecular Weight and Mark-Houwink Parameters Calculated by Using the Broad Molecular Weight Distribution Standard Iterative Technique

sample	$[\eta]_{\mathrm{exptl}}$, dL/g	$\bar{M}_n^{\mathrm{exptl}} \times 10^{-4}$	$K \times 10^4$	a	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$[\eta]$, dL/g
2/1/1	0.455 ± 0.009	1.7 ± 0.2	1.9	0.74	3.9 ± 0.5	1.7 ± 0.2	2.3 ± 0.5	0.455 ± 0.009
3/2/1	0.360 ± 0.007	1.5 ± 0.2	9.1	0.58	3.8 ± 0.5	1.5 ± 0.2	2.5 ± 0.6	0.360 ± 0.007
4/3/1	0.370 ± 0.007	1.4 ± 0.1	4.3	0.67	3.0 ± 0.4	1.4 ± 0.1	2.1 ± 0.5	0.370 ± 0.007
5/4/1	0.369 ± 0.007	1.2 ± 0.1	3.9	0.68	2.6 ± 0.3	1.2 ± 0.1	2.2 ± 0.5	0.369 ± 0.007
6/5/1	0.387 ± 0.008	1.4 ± 0.1	2.9	0.66	9 ± 1	1.4 ± 0.1	6 ± 1	0.387 ± 0.008

ersal calibration curve is shown in Figure 3 and can be expressed analytically by the following calibration equation:

$$\log([\eta]M) = -1.02 + 6.52V - 0.67V^2 + 0.024V^3 - 0.29 \times 10^{-3}V^4 \quad (8)$$

A similar expression can be derived for a normal polystyrene standard calibration curve ($\log M = 0.91 + 3.99V - 0.41V^2 + 0.014V^3 - 0.17 \times 10^{-3}V^4$) and an intrinsic viscosity calibration curve ($\log \eta = -2.12 + 2.55V - 0.26V^2 + 0.95 \times 10^{-2}V^3 - 0.11 \times 10^{-3}V^4$). In both cases it is apparent that the correct polystyrene standard molecular weight value to use in constructing the calibration curve is $\bar{M}_n$.[13] This is important for copolymers because due to their composition distribution there is still even at infinite resolution a distribution of molecular weights in any given fraction coming off the GPC.

Table II contains molecular weight values determined by using the normal polystyrene standard calibration along with experimentally determined intrinsic viscosity ($[\eta]$) and $\bar{M}_n$ (from VPO) values for the five PU samples. In all cases the calculated $\bar{M}_n$ values (PS equivalents) are higher than the experimentally determined values. On the basis of the universal calibration principle this trend can be taken as an indication that the intrinsic viscosity in THF at 30 °C for a polystyrene fraction of a certain molecular weight is lower than the intrinsic viscosity of the polyurethane fraction with the same molecular weight. A simple method to partially account for the effect on molecular weight values of the difference in viscosities is to multiply the calculated molecular weight value by the ratio of the polystyrene intrinsic viscosity to the PU intrinsic viscosity.[32] The PU $[\eta]$ value needs to be determined experimentally while the appropriate PS $[\eta]$ value can be calculated by using known Mark–Houwink parameters and M from the normal polystyrene calibration curve or from an intrinsic viscosity vs. retention volume calibration curve.[11] These "adjusted" values are also reported in Table II for both $\bar{M}_w$ and $\bar{M}_n$ and in all cases the values are reduced, indicating that $[\eta]_{\mathrm{PS}}$ is always less than $[\eta]_{\mathrm{PU}}$. Note that the adjusted $\bar{M}_n$ values are in reasonably good agreement with the $\bar{M}_n$ values determined from the VPO data, especially considering the rather large experimental errors associated with VPO data and the questionable validity of the standard method used to calibrate the VPO.[10,33] It is interesting to note that the "adjustment factors", which range from about 0.6 to 0.9, are considerably higher than a value of 0.23 calculated in a similar manner for polyester polyurethanes.[32] It should also be noted that the "adjustment procedure" is probably more valid for $\bar{M}_n$ values.[13]

Another common and very simple method for estimating molecular weight values is to take the peak retention volume of the sample and calculate the PS equivalent value based on a normal polystyrene standard calibration curve. Both $\bar{M}_n$ and $\bar{M}_w$ values can be calculated in this manner by using PS calibration curves based on PS $\bar{M}_n$ and $\bar{M}_w$ values, respectively. However, since for most broad molecular weight distribution materials $\bar{M}_w$ is much closer to the peak molecular weight than $\bar{M}_n$, the technique is normally only used to calculate $\bar{M}_w$ values. $\bar{M}_w$ values calculated from the peak of the curve as described above are included in Table II for comparison. Note that these values are generally higher than the PS equivalent values based on the entire GPC curve. These "PS equivalent peak" molecular weights could also be "adjusted" in the same manner noted above.

A better and more sophisticated method for accounting for the difference in the intrinsic viscosities of the PS standards and the PU samples is as noted previously to employ a broad molecular weight distribution standard approach.[11-16] This technique requires normal GPC data and two of the following three additional data values, either η, $\bar{M}_n$, or $\bar{M}_w$ for the whole sample determined separately. Since $\bar{M}_w$ and $[\eta]$ are normally highly correlated, it is usually not practical to generate reasonble results with these two parameters. The variation that produces the best results is to use two samples with different viscosities of the same polymer type.[16] This approach is less satisfactory for polyurethanes since one cannot be sure if the difference in viscosities is due to differences in molecular weight distributions as the calculation assumes no differences in the composition distributions. Using a broad molecular weight distribution as described previously with $\bar{M}_n$ and $[\eta]$ values, we were able to determine the molecular weight values and Mark–Houwink constants for the series of polyurethane samples as shown in Table III. Note that the calculated $\bar{M}_n$ and $[\eta]$ values agree exactly with the experimental data because these are the values that are matched in order to determine K and a.

Except for sample 6/5/1, which has a much broader MWD than the other samples, the $\bar{M}_w$ values in Table III are considerably lower than the PS equivalent values displayed in Table II. The $\bar{M}_w$ values are also lower than the "adjusted" PS values, indicating that while the simple adjustment procedure leads to more accurate values, it does not completely account for the difference in viscosities over the whole GPC curve. Finally, it should be noted that

Table IV
Molecular Weight and Mark–Houwink Parameters Calculated by Using the GPC–Multidetector Technique

sample	$[\eta]_{\text{exptl}}$, dL/g	$\bar{M}_n^{\text{exptl}} \times 10^{-4}$	$K \times 10^4$	a	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$[\eta]$, dL/g
2/1/1	0.455 ± 0.009	1.7 ± 0.2	2.5 ± 0.7	0.72 ± 0.04	4.0 ± 0.2	1.6 ± 0.2	2.5 ± 0.4	0.45 ± 0.03
3/2/1	0.360 ± 0.007	1.5 ± 0.2	2.8 ± 0.8	0.70 ± 0.04	3.2 ± 0.2	1.6 ± 0.2	2.0 ± 0.3	0.37 ± 0.02
4/3/1	0.370 ± 0.007	1.4 ± 0.1	3.2 ± 0.9	0.69 ± 0.03	3.0 ± 0.2	1.3 ± 0.1	2.3 ± 0.4	0.37 ± 0.02
5/4/1	0.369 ± 0.007	1.2 ± 0.1	3.2 ± 0.9	0.69 ± 0.03	2.8 ± 0.1	1.3 ± 0.1	2.2 ± 0.3	0.37 ± 0.02
6/5/1	0.387 ± 0.007	1.4 ± 0.1	3.2 ± 0.9	0.66 ± 0.03	6.2 ± 0.3	1.2 ± 0.1	5.2 ± 0.8	0.38 ± 0.02

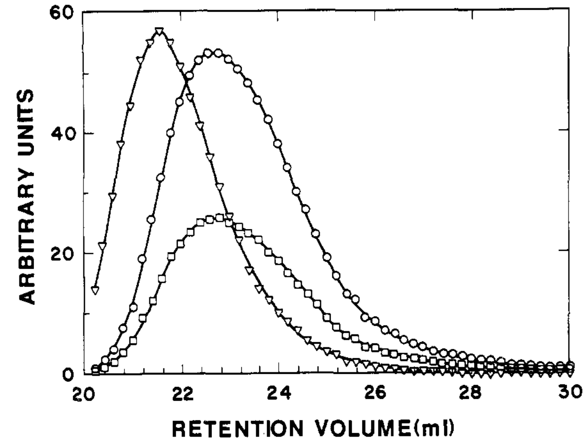

Figure 4. Chromatographic data for sample PU-2/1/1: (▽) light scattering detector; (○) UV detector; (□) RI detector.

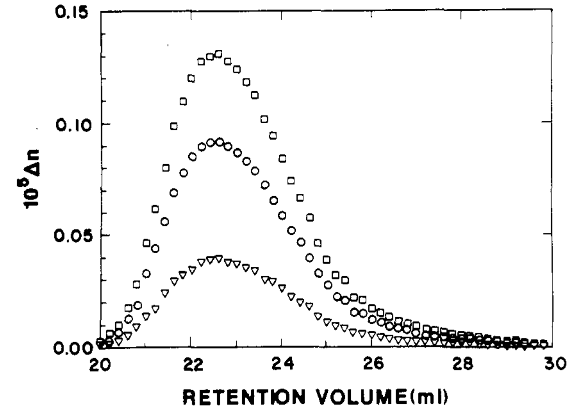

Figure 5. Refractive index difference vs. retention volume for sample PU-2/1/1: (▽) soft segment; (○) hard segment; (□) copolymer.

while the K and a values calculated with the broad MWD standard calibration method are reasonable ($0.5 < a < 0.8$),[34] there is no discernible trend with sample hard-segment content. The lack of a trend in the a values may be because the calculated a value is very sensitive to small experimental errors in $\bar{M}_n$ and $[\eta]$.[16]

The final method for determining molecular weights evaluated in this study was the GPC–multidetector method described previously. Table I displays refractive index increments for the five PU samples and the PTMO-1000 oligomer. The refractive index increment for the hard-segment portion of each PU sample was calculated by using eq 7 and the PTMO-1000 value for the soft-segment refractive index increment. The calculated values of $(\mathrm{d}n/\mathrm{d}C)_h$ (Table I) are approximately constant, as would be expected. Figure 4 displays the chromatograms from the three detectors. Note that the light scattering detector is more sensitive at high molecular weights (low retention volumes). The UV and RI detectors display similar responses, indicating that the average composition of the sample does not change appreciably with molecular weight. Figure 5 displays the refractive index increments of the hard and soft segments and the whole sample vs. retention volume for sample PU-2/1/1 (eq A2, A3, and A4) (Appendix I). Figure 6 shows the calculated molecular weight distribution for sample PU-2/1/1 (Appendix I), while Figure 7 demonstrates the fitting of eq A6 to the log M vs. retention volume data for sample PU-2/1/1 to obtain the Mark–Houwink parameters. Using the multidetector approach proposed in this paper, we can also calculate the viscosity of the polymer in each

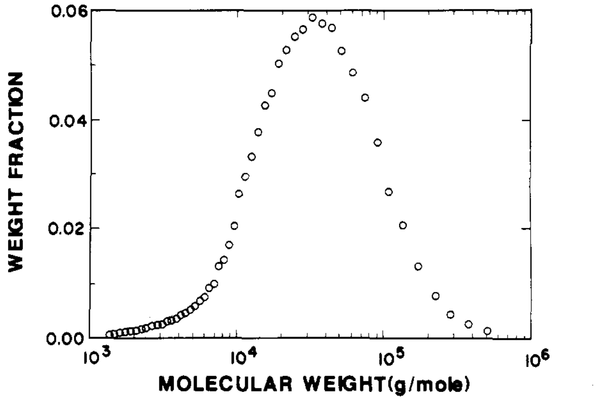

Figure 6. Molecular weight distribution for sample PU-2/1/1.

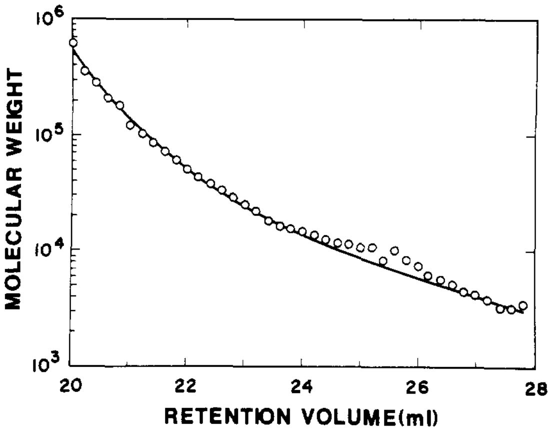

Figure 7. log M vs. retention volume for sample PU-2/1/1: (○) data; the solid line is fit through the data by using eq A6.

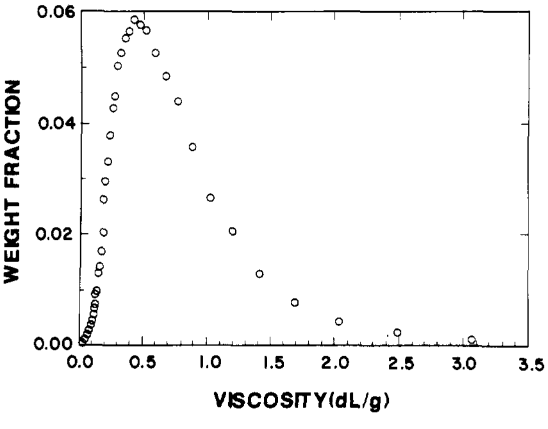

Figure 8. Viscosity distribution for sample PU-2/1/1.

Table V
Comparison between Different Techniques

	method		
	broad molecular weight distribution	GPC–multidetector	polystyrene calibration
instrument	GPC–RI detector viscosity osmometry light scattering	GPC–LS detector UV detector RI detector viscosity	GPC–RI detector viscosity
composition distribution	no	yes	no
molecular weight distribution	yes	yes	yes
Mark–Houwink constant	yes	yes	no

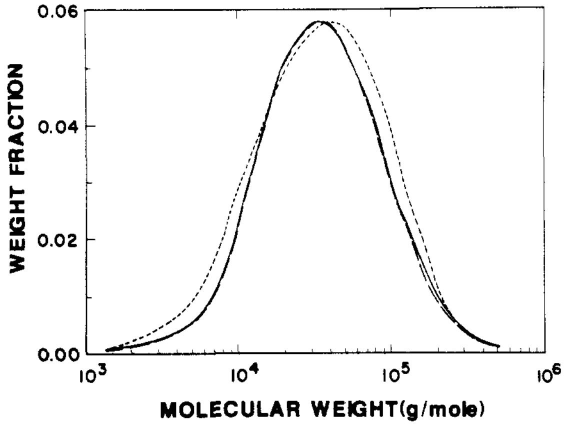

Figure 9. Comparison of different methods used in determining the molecular weight distribution: (—) GPC–light scattering detector method; (– – –) broad molecular weight distribution method; (- - -) polystyrene calibration method.

fraction as well as the overall viscosity of the polymer (eq A7 and A8 and Figure 8). Table IV displays the calculated K, a, $\bar{M}_n$, $\bar{M}_w$, and $[\eta]$ values along with the experimentally determined $\bar{M}_n$(VPO) and $[\eta]$ values for all of the PU samples. The calculated viscosities agree quite well (<2%) with the measured viscosities. The agreement between the calculated and measured $\bar{M}_n$ values is also good (<10%) considering the accuracy of the VPO data.

In comparison with the simple PS calibration method (Table II) the multidetector approach like the broad MWD standard calibration technique gives rise to lower $\bar{M}_w$ and $\bar{M}_n$ (except when the $\bar{M}_n$ values are adjusted). Thus, the relative $\bar{M}_w$ values calculated by using the PS calibration should be considered as upper bounds on the true $\bar{M}_w$ values. Comparison of molecular weight values calculated by using the multidetector (Table IV) and broad MWD (Table III) approaches shows no obvious trend in either the $\bar{M}_w$ of $\bar{M}_n$ values. Figure 9 shows molecular weight distributions for sample PU-2/1/1 calculated by the three methods; the broad MWD standard and multidetector curves are almost indistinguishable while the PS equivalent curve deviates from the other two by about 20%. The a parameters calculated with the multidetector method do decrease with increasing hard-segment content. This trend indicates that, as expected, THF is a better solvent for the soft segments than the hard segments (note that THF is a nonsolvent for the pure MDI/BD hard segment). Since the broad MWD standard approach did not give rise to a discrenible trend in a values with hard-segment content, it would appear to be less satisfactory than the multidetector method. The multidetector method is also favored because it does not rely on independently determined viscosity or molecular weight values and thus is not affected by experimental errors in those measurements. This is particularly important because of the large errors associated with $\bar{M}_n$ values determined by VPO, especially if the samples contain low molecular weight impurities. The other advantage of the multidetector method is that, as described below, it does provide some information regarding the composition distribution and can take into account the effect of a drift in average composition with molecular weight.

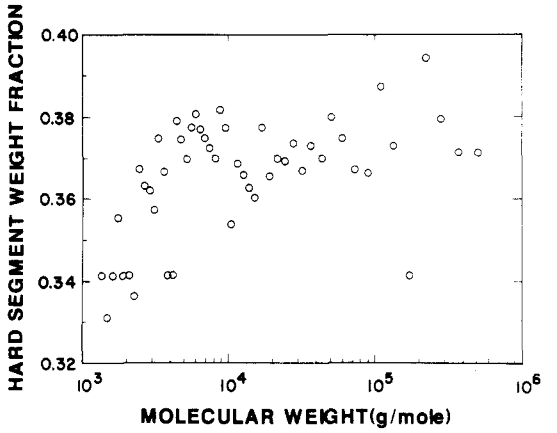

Figure 10. Hard-segment composition distribution for sample PU-2/1/1.

The average composition in terms of hard and soft segments can be determined by using the multidetector method by proper manipulation of the data from the UV and RI detectors as a function of retention volume (Appendix I). Figure 10 displays data calculated in this fashion for sample PU-2/1/1 where the retention volumes have been translated to molecular weight values. The variation in average composition is not large but is still appreciable. This variation in average composition is taken into account by the GPC–multidetector method in its calculation of molecular weight but is ignored by the broad MWD standard approach. The latter method implicitly assumes that K and a are unaffected by changes in composition. This assumption does not dramatically affect the calculated molecular weight values because these samples do not exhibit a large trend or drift of average composition with molecular weight. It is not surprising, however, that the a values calculated with the broad MWD standard approach do not show a discernible trend with sample composition. It should be noted that the K and a values calculated by the multidetector method take into account the composition distribution through the molecular weight and viscosity values used in their calculation. However, since there should be separate K and a values at each composition, the K and a values (Table IV) calculated by the multidetector method (Appendix I) are effectively averaged values over the composition range.

Although the GPC–multidetector method does account for changes in average composition with molecular weight, which should allow for more accurate molecular weight values, particularly when the average composition does vary appreciably with molecular weight, the values calculated by this method are still not absolute or true values. This is because, as noted previously, at each retention volume there is a distribution of compositions and thus a distribution of molecular weights. That is, the polymer molecules passing through any of the detector cells at a given time will not necessarily have the same molecular weight due to composition differences (in addition to any resolution or band-broadening effects). This will lead to a deviation of the molecular weight calculated at each retention volume from the light scattering data analogous to the deviation in an overall $\bar{M}_w$ measured by static light scattering on a compositionally heterogeneous copolymer.[8,9,27] Furthermore, the multidetector method as used here ignores any potential hard or soft sequence length effects on the RI and UV responses.[35] Nevertheless, the good agreement between the calculated and experimentally determined $\bar{M}_n$ values (which at least theoretically are unaffected by the composition distribution) suggests that for the PU samples investigated here the multidetector method gives values that may be within experimental error of the true values. That is, the effects of compositional heterogeneity appear to be small enough that they are effectively masked by experimental errors.

One final point should be made regarding the $\bar{M}_w/\bar{M}_n$ values calculated by the various methods. Both the multidetector and broad MWD standard approaches give rise to $\bar{M}_w/\bar{M}_n$ values (except for sample 6/5/1) that are close to 2, which is approximately the ideal value for a homogeneous solution polymerization.[7] The PS equivalent method leads to $\bar{M}_w/\bar{M}_n$ values, which if assumed to be accurate would suggest that nonideal effects[36,37] such as reactivity of functional groups depending on molecular weight are occurring during the sample polymerization. This demonstrates that potential erroneous conclusions can be drawn when the simple polystyrene standard approach is used. The 6/5/1 sample has a much larger $\bar{M}_w/\bar{M}_n$ value no matter what method is used for calculation. This large $\bar{M}_w/\bar{M}_n$ value is likely a result of solubility problems during the solution polymerization which could give rise to effects similar to phase separation in a bulk polymerization.[36-38] A comparison of the methods used and the information obtained are summarized in Table V.

Summary

Several methods for determining the molecular weights of a series of polyether polyurethanes have been evaluated. Simple polystyrene calibration methods give rise to values that are generally too high and could be considered as an upper bound on the true values. These values can be adjusted by using a simple ratio of viscosities but the molecular weight values still appear to be high. The broad MWD standard approach and the GPC–multidetector method both lead to more accurate molecular weight values. The multidetector method is favored over the broad MWD standard approach because it does not depend on independently determined sample parameters and it takes into account the effect of a changing average composition with molecular weight. Thus it should give rise to more accurate molecular weight values and Mark–Houwink parameters, especially when the average composition varies appreciably with molecular weight. The Mark–Houwink parameters calculated with the multidetector approach indicate that THF is a better solvent for the polyether soft segments than for the had segments as expected. Although the multidetector method does account for changes in the average composition, the existence of a composition distribution in any given fraction coming off the GPC and possible hard and soft segment sequence length effects on the RI and UV detectors as well as on the hydrodynamic volume preclude labeling the values calculated with the multidetector approach as absolute or true values. Nevertheless these effects appear to small for the samples studied, especially in comparison to the experimental errors. The more accurate molecular weight values that can be obtained with the multidetector method should allow for a more quantitative determination of molecular weight effects on the structure–property relationships of polyurethane block copolymers.

Acknowledgment. We acknowledge partial support of this research by the National Science Foundation, Division of Materials Science, Polymer Section (Grant No. DMR 86-03839), and through a grant from the Office of Naval Research.

Appendix I. Procedure for Calculating the Composition and Molecular Weight Values Using the Multidetector Method

The UV chromatogram taken at 285 nm was divided into equivalent stripes and for each V_i value, and the corresponding composition of the hard segment was calculated by

$$C_{ih} = (h_{U,i}/\sum h_{U,i})C_{0h} \tag{A1}$$

C_{ih} is the concentration of the hard segment in the ith stripe, and $C_{0h} = W_h C_0$, where C_0 is the copolymer concentration and C_{0h} is the concentration of the overall hard segment. $h_{U,i}$ is the height of the ith stripe of the UV chromatogram. The corresponding refractive index difference of the hard segment was then calculated:

$$\mathrm{d}n_{ih} = (\mathrm{d}n/\mathrm{d}C)_h C_{ih} \tag{A2}$$

where $\mathrm{d}n_{ih}$ is the refractive index difference of the hard segment in the ith stripe and $(\mathrm{d}n/\mathrm{d}C)_h$ is determined by using eq 7 and experimentally determined values. The copolymer refractive index difference was calculated from the refractive index chromatogram as follows:

$$\mathrm{d}n_i = (h_{R,i}/\sum h_{R,i})(\mathrm{d}n/\mathrm{d}C)_0 C_0 \tag{A3}$$

where $\mathrm{d}n_i$ is the refractive index difference of the copolymer in the ith stripe, $h_{R,i}$ is the height of the ith stripe of the RI chromatogram, and C_0 is the overall copolymer concentration. The soft-segment refractive index difference was calculated indirectly from the refractometer response by

$$\mathrm{d}n_{is} = \mathrm{d}n_i - \mathrm{d}n_{ih} \tag{A4}$$

where $\mathrm{d}n_{is}$ is the refractive index difference of the soft segment in the ith stripe. The corresponding soft-segment concentration was calculated by

$$C_{is} = \mathrm{d}n_{is}/(\mathrm{d}n/\mathrm{d}C)_i \tag{A5}$$

where C_{is} is the soft-segment concentration of the ith stripe. The polymer concentration of the ith stripe (C_i) is the sum of the soft- and hard-segment concentrations in that stripe ($C_i = C_{is} + C_{ih}$). The hard-segment composition of the ith stripe (W_{ih}) is the ratio of hard-segment concentration to the overall polymer concentration in that stripe ($W_{ih} = C_{ih}/C_i$). The soft-segment composition of the ith stripe is $W_{is} = 1 - W_{ih}$. The weight fraction of the copolymer at the ith stripe (W_i) is the ratio of polymer concentration of the ith stripe to the overall polymer concentration ($W_i = C_i/C_0$). The refractive index increment of the copolymer of the ith stripe was calculated by eq 7. The molecular weight of the copolymer in the ith stripe was then calculated from data obtained from the light scattering detector by using eq 4 and 5.

Since the molecular weight at each stripe i is known, the Mark–Houwink parameters can be obtained by fitting the following equation derived by substituting the Mark–

Macromolecules 1986, *19*, 2390–2397

Houwink expression for $[\eta]$ in eq 8

$$\log M_i = ((-1.02 - \log K) + 6.52V - 0.67V^2 + 0.024V^3 - 0.29 \times 10^{-3}V^4)/(a + 1) \quad \text{(A6)}$$

and fitting the experimental M_i vs. V_i data. The weight-average and the number-average molecular weights were calculated by using the standard summations ($\bar{M}_w = \sum(M_iW_i)/\sum W_i$) and ($\bar{M}_n = \sum W_i/\sum(W_i/M_i)$). The viscosity of the ith stripe was calculated by

$$[\eta]_i = J_{i,s}/M_i \quad \text{(A7)}$$

where $J_{i,s}$ is the hydrodynamic volume determined from the polystyrene calibration. The overall viscosity of the copolymer was then calculated by

$$[\eta] = \sum W_i[\eta]_i \quad \text{(A8)}$$

and compared to the experimentally measured value.

Registry No. (MDI)·(BD)·(PTMO) (copolymer), 9018-04-6.

References and Notes

(1) Saunders, J. H.; Frisch, K. C. *Polyurethane Chemistry and Technology*: *Part 1. Chemistry*; Interscience: New York, 1962.
(2) Cooper, S. L.; Tobolsky, A. V. *J. Appl. Polym. Sci.* **1966**, *10*, 1837.
(3) Estes, G. M.; Cooper, S. L.; Tobolsky, A. V. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *4*, 313.
(4) Gibson, P. E.; Vallance, M. A.; Cooper, S. L. *Developments in Block Copolymers*, Goodman, I., Ed.; Elsevier, Applied Science Publishers: London, 1982.
(5) Schollenberger, C. S.; Dinbergs, K. *J. Elastoplast.* **1973**, *5*, 222.
(6) Schollenberger, C. S.; Dinbergs, K. *J. Elastoplast.* **1979**, *11*, 58.
(7) Speckhard, T. A.; Miller, J. A.; Cooper, S. L. *Macromolecules* **1986**, *19*, 1558.
(8) Rempp, P.; Benoit, H. *Rubber Chem. Technol.* **1968**, *41*, 245.
(9) Spatorico, A. L. *J. Appl. Polym. Sci.* **1974**, *18*, 1793.
(10) Speckhard, T. A. Ph.D. Thesis, University of Wisconsin—Madison, 1985.
(11) Yau, W. W.; Jones, M. E.; Ginnard, C. R.; Bly, D. D. *ACS Symp. Ser.* **1980**, *No. 138*, 91.
(12) Janca, J. *Adv. Chromatogr.* **1981**, *19*, 37.
(13) Hamielec, A. E.; Ouano, A. C. *J. Liq. Chromatogr.* **1978**, *1*, 111.
(14) Weiss, A. R.; Cohn Ginsberg, E. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 379.
(15) Morris, M. C. *J. Chromatogr.* **1971**, *55*, 203.
(16) Dobbin, C. J. B.; Rudin, A.; Tchir, M. F. *J. Appl. Polym. Sci.* **1980**, *25*, 2985.
(17) Ouano, A. C.; Kaye, W. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1151.
(18) Ouano, A. C. *J. Chromatogr.* **1976**, *118*, 303.
(19) Jordan, R. C. *J. Liq. Chromatogr.* **1980**, *3*, 439.
(20) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; Wiley: New York, 1979.
(21) Benoit, H.; Grubisic, Z.; Rempp, P.; Decker, D.; Zilliox, J. G. *J. Chem. Phys.* **1966**, *63*, 507.
(22) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 753.
(23) Dawkins, J. V. *Br. Polym. J.* **1972**, *4*, 87.
(24) Dawkins, J. V. *Eur. Polym. J.* **1977**, *13*, 837.
(25) Samay, G.; Kubin, M.; Podesva, J. *Agnew. Makromol. Chem.* **1978**, *72*, 185.
(26) Chu, B.; Ying, Q.; Lee, D.-c.; Wu, D.-q. *Macromolecules* **1985**, *18*, 1962.
(27) Stockmayer, W. H.; Moore, L. D., Jr.; Fixman, M.; Epstein, B. N. *J. Polym. Sci.* **1955**, *16*, 517.
(28) Hwang, K. K. S.; Yang, C. Z.; Cooper, S. L. *Polym. Eng. Sci.* **1981**, *21*, 1027.
(29) Miller, J. A.; Lin, S. B.; Hwang, K. K. S.; Wu, K. S.; Gibson, P. E.; Cooper, S. L. *Macromolecules* **1985**, *18*, 32.
(30) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, *64*, 2716.
(31) Kraemer, E. O. *Ind. Eng. Chem.* **1938**, *30*, 1200.
(32) Tirrell, M.; Lee, L. J.; Macosko, C. W. *ACS Symp. Ser.* **1978**, *No. 104*, 149.
(33) Mrkvicakova, L.; Pokorny, S. *J. Appl. Polym. Sci.* **1985**, *30*, 1211.
(34) Flory, P. J. *Principles of Polymer Chemistry*, Cornell University: Ithaca, NY, 1953.
(35) Hamielec, A. *Pure Appl. Chem.* **1982**, *54*, 293.
(36) Miller, J. A.; Speckhard, T. A.; Cooper, S. L. *Macromolecules* **1986**, *19*, 1568.
(37) Miller, J. A.; Speckhard, T. A.; Homan, J. G.; Cooper, S. L. *Polymer*, submitted.
(38) Speckhard, T. A.; Homan, J. G.; Miller, J. A.; Cooper, S. L. *Polymer*, submitted.

Photophysical and Photochemical Behavior of Poly(1-vinylpyrene). Evidence for Dual Excimer Fluorescence

R. V. Todesco,[*][†] **R. A. Basheer,**[‡] **and Prashant V. Kamat**[*]

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556.

Received December 10, 1985

ABSTRACT: A high molecular weight poly(1-vinylpyrene) (PVP) has been synthesized and characterized. ^{1}H NMR spectra combined with UV spectroscopy suggested a high interaction between pyrenyl groups in the polymeric environment. The ^{13}C NMR spectrum was characteristic mainly of an atactic polymer. The singlet and triplet excited-state properties of PVP have been determined in solution at room temperature and in a matrix at 77 K. Time-dependent fluorescence measurements in THF solution at room temperature revealed the existence of two excimers with emission maxima at 485 and 530 nm. We attributed a staggered and an eclipsed conformation to the high- and low-energy excimer, respectively. In a MTHF matrix at 77 K, PVP exhibited intense structured dimer emission together with fluorescence from the high-energy excimer. Transient absorption monitored upon laser pulse (337.1 nm) excitation of PVP in THF solution indicated a very low quantum yield for the formation of triplet state ($\phi_T \leq 10^{-3}$). Upon irradiation with UV light, degradation of PVP occurred with an apparent quantum yield of 1.1×10^{-5} for random scission.

Introduction

The excited-state properties of polymers containing pendant aromatic chromophores are a topic of much current interest. Excimer-forming homopolymers[1] such as polystyrene (PS), poly(vinylnaphthalene) (PVN), and poly(N-vinylcarbazole) (PVNCz) have been intensively investigated, and the study of the excited-state behavior of suitable model compounds[2–6] (e.g., corresponding meso and racemic 2,4-diarylpentanes and 1,1′-diaryl diethyl ethers) clearly illustrates the importance of configurational and conformational aspects in the intramolecular excimer

---

[†] On leave of absence from the University Centre of Limburg, Belgium.

[‡] Present address: Polymer Department, General Motors Research Laboratories, Warren, MI 48090.

0024-9297/86/2219-2390$01.50/0 © 1986 American Chemical Society