Macromolecules 1990, 23, 4553-4556

Determination of Molecular Weight of Nonlinear Polymers by NMR Spectroscopy: Application on a Polymer of 2,2-Bis(4-cyanatophenyl)propane

Treliant Fang

AT&T Bell Laboratories, Engineering Research Center, P.O. Box 900,
Princeton, New Jersey 08540

Received January 10, 1990; Revised Manuscript Received April 12, 1990

ABSTRACT: A general method for determining molecular weight of nonlinear polymers is developed based on the backbone to end group ratio measured by ^{13}C NMR spectroscopy. The number-average molecular weight (M_n) of the poly(cyanate ester) resin prepared from polycyclotrimerization of 2,2-bis(4-cyanatophenyl)-propane including the unreacted monomer is represented by the formula $M_n = 834((R' + R + 2)/(3R' - R + 2))$ where R is the backbone to end group ratio and R' is the monomer to end group ratio. Mathematical derivation of this equation is discussed.

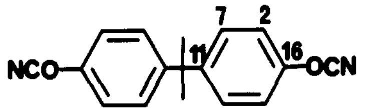
Introduction

Despite its powerful application to the qualitative structural characterization of polymers, NMR spectroscopy is seldom used to determine molecular weight of polymers because GPC and other readily available method provide both M_n and M_w, whereas previously only M_n of linear polymers were obtainable by NMR techniques. Linear polymers have been subjects of NMR end-group analysis,[1] and their molecular weights were calculated by a simple backbone to end group ratio relationship. To find a reliable method for determining the molecular weight of nonlinear polymers, we have developed a general NMR method for determining number-average molecular weights of polymers produced from polymerization of difunctional monomers. One such example is the cyanate ester polymer prepared from polycyclotrimerization of 2,2-bis(4-cyanatophenyl)propane (1).[2] This new method extends the classical NMR end-group counting technique beyond its previous dimension: as long as a polymer exhibits structural regularity as well as resolved backbone and end-group in the NMR spectrum, it is possible to derive a formula to calculate its molecular weight based on the NMR data, even in the presence of a large amount of monomer. This method can be applied to polymers that give erratic molecular weight results by GPC[3] and vapor pressure osmometry.[4]

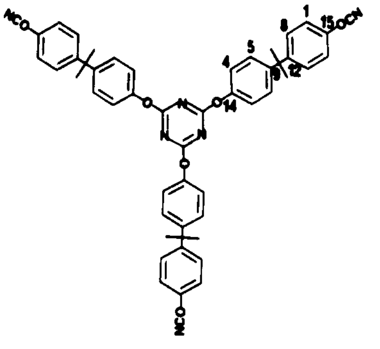
Experimental Section

General Procedures. 2,2-Bis(4-cyanatophenyl)propane (1; Figure 1) was supplied by Hi-Tek Polymers (Louisville, KY). Bisphenol A and *N*,*N*-dimethylbenzylamine (DMBA) were supplied by Aldrich. The polymerization of 1 was performed either in a sealed tube immersed in an oil bath at 120 °C or in the NMR probehead at temperatures above the melting point (79 °C) of 1, in a concentric NMR tube (Wilmad WGS-8BL) with DMSO-d_6 as locking solvent. Catalysts used were 0.5% of Bisphenol A and 50-100 ppm of DMBA in different experiments. Detailed polymerization conditions can be found in the literature.[5] Spectra were obtained on a Brüker AC-250 spectrometer, operating at 250 MHz for proton and 62.9 MHz for carbon, with an Aspect 3000 computer and a QNP four-nuclei probe operating at either room temperature (for samples dissolved in chloroform-*d*) or reaction temperatures (for in situ polymerization monitoring of molten 1). Chemical shifts were referenced to the $CDCl_3$ triplet centered at 77.00 ppm for ^{13}C NMR and the 7.26 ppm residual $CHCl_3$ peak for ^1H NMR.

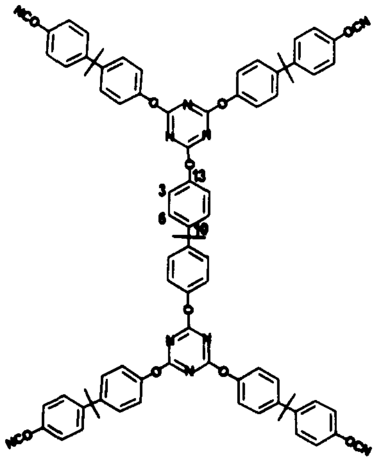
2D C-H COSY Measurements. The 2D C-H COSY experiments were performed at 298 K by using quadrature detection with the carrier frequency set in the center of the spectrum. A total of 256 scans were accumulated over 128 t_1 increments with a relaxation delay of 3 s. The initial matrix size was 10 000 Hz



1



2



3

Figure 1. Structures of 2,2-bis(4-cyanatophenyl)propane (1) and trimer and pentamer of 1. The numbers on the structures indicate the peak positions in the ^{13}C NMR spectrum.

0024-9297/90/2223-4553$02.50/0

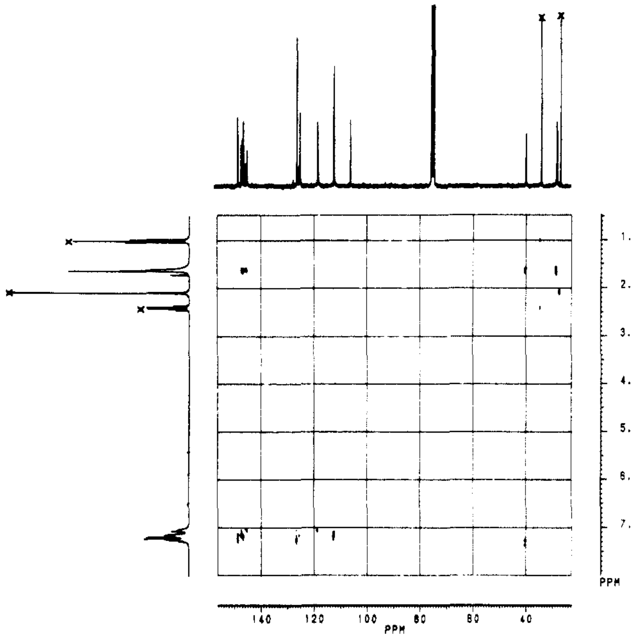


Figure 2. COLOC spectrum of a poly(cyanate ester) polymer in chloroform-*d*. The respective 1D spectra were plotted along the two axes. The ×'s were signals from methyl ethyl ketone solvent. Aromatic quaternary carbons, which showed cross peaks with methyl protons, were assigned peaks 9–12. The quaternary aliphatic carbon–aromatic proton cross peaks also appeared in the lower right. See text for detailed acquisition conditions.

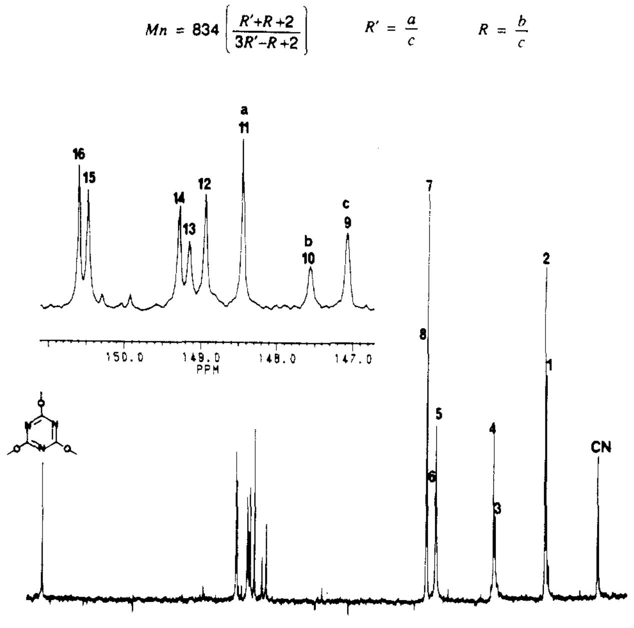


Figure 3. ^{13}C NMR spectrum of a typical poly(cyanate ester) resin recorded under inverse-gated decoupling conditions. Only the low-field signals are shown. The inset shows an expansion of the quaternary carbon region. See text for detailed acquisition conditions.

(2K) and 2000 Hz (128 w) in the F_2 and the F_1, respectively. A sinebell function without phase shift was applied in both dimensions prior to Fourier transformation. The delay times Δ_1 and Δ_2 were set at 4 and 2 ms, respectively. The digital resolutions after zero-filling in the F_1 were 9.77 Hz/point in the F_2 and 7.1 Hz/point in the F_1.

COLOC Experiments. The long-range C–H COSY (or COLOC)[6] experiments were run by using delay times of $\Delta_2 = 45$ ms and $\Delta_3 = 22$ ms. The remaining parameters were similar to those used in the C–H COSY experiments.

^{13}C Spin–Lattice Relaxation Time (T_1) Measurements. A 25% w/w solution of the polymer in deuterochloroform was measured by using standard inversion–recovery pulse sequence under proton decoupling. T_1's were calculated by Brüker standard software.

Quantitative ^{13}C Measurements. A 25% w/w solution of the polymer in deuterochloroform containing 0.5% of chromium acetylacetonate was subject to carbon acquisition using 90° pulses and inverse-gated proton decoupling (decoupler was on when acquiring the FID and was off during the delay) with a delay time of 5 s. A minimum of 32K memory size with a line broadening of 2 Hz afforded an integral reproducibility of at least 95% after 300 scans.

Results and Discussion

^{13}C Peak Assignment. Figure 3 shows a typical inverse-gated decoupling ^{13}C spectrum of a poly(cyanate ester) polymer prepared by the amine-catalyzed polycyclization of the monomer 1. All signals, including the eight resolved quaternary carbons in the chemical shift range from 147 to 151 ppm, were completely assigned by using C–H COSY and COLOC 2D NMR techniques. Figure 2 clearly shows those quaternary aromatic carbons exhibiting cross peaks with methyl protons are consistent with the assignment of peaks 9–12, in addition to the quaternary aliphatic carbon–aromatic proton cross peaks located in the lower right. The three diagnostic peaks in the higher field of the quaternary aromatic carbon region were used to perform the calculation, and their area integrals were assigned as *a*–*c* for the peaks at 148.43, 147.52, and 147.06 ppm, respectively. The ratios of *b*/*c* (backbone to end group ratio)[7] and *a*/*c* (monomer to end group ratio) are represented by R and R' throughout the text. The "backbone groups" are those groups located between two cyclized rings, while the "end groups" are those groups attached to only one cyclized ring.

Derivation of the Molecular Weight Formula. The number-average molecular weight of the combined oligomeric and polymeric fraction (M_o) in the poly(cyanate ester) resin is represented by eq 1, and the number-average molecular weight of the whole poly(cyanate ester) resin (M_n) including the unreacted monomer is represented by eq 2.

$$M_o = 834\left(\frac{2+R}{2-R}\right) \tag{1}$$

$$M_n = 834\left(\frac{R'+R+2}{3R'-R+2}\right) \tag{2}$$

Elucidation of these two equations is as follows. In the oligomeric fraction of the poly(cyanate ester) resin, only odd-numbered triazine rings are possible in the oligomer series, starting with trimer **2** and pentamer **3** of 2,2-bis(4-cyanatophenyl)propane (Figure 1). Careful inspection of both the structures of oligomers and their ^{13}C NMR spectrum shows that the four aromatic quaternary backbone carbons possess a nearly 2-fold symmetry, thus revealing two singlets (peaks 10 and 13) with equal areas regardless of their chain lengths for oligomer series higher than trimer.[8] The four aromatic quaternary carbon end groups do not have this symmetry and therefore appear as four singlets (peaks 9, 12, 14, and 15). The ratio between *b* and *c* can be counted from trimer to polymer to be

$$b/c = 0/3, 2/4, 4/5, 6/6, ..., 2(i-1)/(i+2)$$

where *i* represents the number of triazine rings in the oligomers (or polymer). To account for all possible distribution of oligomers, we use the explicit expression

$$c = \sum_{i=1}^{i=\infty} (i+2) N_i K_c \qquad (3)$$

where N_i is the number of oligomers containing i triazine rings and K_c is the area proportionality constant of the quaternary carbon atoms. Similar treatment affords the equation for b

$$b = \sum_{i=1}^{i=\infty} 2(i-1) N_i K_c \qquad (4)$$

and the ratio (R or b/c) becomes

$$R = \frac{b}{c} = \frac{\sum_{i=1}^{i=\infty} 2(i-1) N_i}{\sum_{i=1}^{i=\infty} (i+2) N_i} \qquad (5)$$

and therefore the ratio of $(2+R)/(2-R)$ gives

$$\frac{2+R}{2-R} = \frac{1}{3} \frac{\sum_{i=1}^{i=\infty} (2i+1) N_i}{\sum_{i=1}^{i=\infty} N_i} \qquad (6)$$

As the number-average molecular weight of the oligomers is defined by

$$M_o = \frac{\sum_{i=1}^{i=\infty} N_i M_i}{\sum_{i=1}^{i=\infty} N_i} = \frac{\sum_{i=1}^{i=\infty} 278(2i+1) N_i}{\sum_{i=1}^{i=\infty} N_i} \qquad (7)$$

because M_i = (MW of monomer)$(2i+1) = 278(2i+1)$. Substitution of eq 6 into eq 7 affords the final formula (eq 1), which represents the number-average molecular weight of the oligomeric and polymeric fraction. The derivation of the number-average molecular weight of the total poly(cyanate ester) resin, including the unreacted monomer from R and R', is similar but more elaborate. The calculation requires prior knowledge of symmetry elements of the monomer. Using 1 as an example, the area of the quaternary carbon peak 11 is represented by

$$a = 2 N_m K_c \qquad (8)$$

where N_m is the number of monomer molecules in the resin and K_c is the area proportionality constant of the quaternary carbon. Using the term $R' = a/c$, where c is defined in eq 3, resulted in the following:

$$R' = \frac{2N_m}{\sum_{i=1}^{i=\infty} (i+2) N_i} \qquad (9)$$

Since the number-average molecular weight of the resin sample including the unreacted monomer is defined by

$$M_n = 278 \frac{N_m + \sum_{i=1}^{i=\infty} (2i+1) N_i}{N_m + \sum_{i=1}^{i=\infty} N_i} \qquad (10)$$

Dividing the numerator and denominator of eq 10 with the total number of oligomer molecules in the sample gives

$$M_n = 278 \frac{\dfrac{N_m}{\sum_{i=1}^{i=\infty} N_i} + \dfrac{M_o}{278}}{\dfrac{N_m}{\sum_{i=1}^{i=\infty} N_i} + 1} \qquad (11)$$

where M_o is defined in eq 7. Using the monomer to oligomer ratio (A) expression

$$A = \frac{N_m}{\sum_{i=1}^{i=\infty} N_i} \qquad (12)$$

and defining A as a function of R' (and later R) would give

$$A = \frac{R'}{2} \frac{\sum_{i=1}^{i=\infty} (i+2) N_i}{\sum_{i=1}^{i=\infty} N_i} \qquad (13)$$

Since the following equation is always true

$$\frac{\sum_{i=1}^{i=\infty} (i+2) N_i}{\sum_{i=1}^{i=\infty} N_i} = \frac{\sum_{i=1}^{i=\infty} (2i+1) N_i}{\sum_{i=1}^{i=\infty} N_i} - \frac{\sum_{i=1}^{i=\infty} (i-1) N_i}{\sum_{i=1}^{i=\infty} N_i} \qquad (14)$$

substituting eqs 14 and 7 into eq 13 would produce

$$A = \frac{R'}{2} \left\{ \frac{M_o}{278} - \frac{\sum_{i=1}^{i=\infty} (i-1) N_i}{\sum_{i=1}^{i=\infty} N_i} \right\} \qquad (15)$$

Again using the previously defined R in eq 5 to link the term $i-1$ in eq 15 with the $i+2$ term in eq 5 gives

$$A = \frac{R'}{2} \left\{ \frac{M_o}{278} - \frac{R \sum_{i=1}^{i=\infty} (i+2) N_i}{2 \sum_{i=1}^{i=\infty} N_i} \right\} \qquad (16)$$

After rearranged eq 13 is substituted into eq 16 the equation

$$A = \frac{R'}{2} \left\{ \frac{M_o}{278} - \frac{RA}{R'} \right\} \qquad (17)$$

is obtained, and therefore A is solved as

$$A = \frac{R' M_o}{278(R+2)} \qquad (18)$$

Equation 18 leads to the numerical solution of the ratio between the number of monomers and polymers (including oligomers) in the sample. Substituting eqs 12 and 18 into eq 11 and replacing M_o with eq 1 afforded the final formula (eq 2). Similarly derived is the equation for polycyclodimerization of any difunctional monomer having a 2-fold symmetry

$$M_n = \mathrm{MW}\left(\frac{R' + R + 1}{R' + 1}\right) \qquad (19)$$

where MW, R', and R have the same definitions as previously mentioned. Similar molecular weight formulas can be derived for other structurally regular systems, e.g., "starburst dendrimers",[9] or polyisocyanurate from 4,4′-diphenylmethane diisocyanate.[10] Equations of higher polycyclomerization can also be derived, but lack of practical examples of such reactions postpones further discussion at this time.[11]

Merits and Limitations of NMR Method. The accuracy of this new method is similar to any of the other quantitative NMR techniques (~10%).[12] Using both inverse-gated decoupling and a relaxation agent to suppress NOE is a necessary measure to ensure quantitative data acquisition. Although spin–lattice relaxation times (T_1) of ^{13}C signals are short (~2 s) for quaternary backbone carbons of the cyanate polymer, the quaternary end-group carbons have moderate T_1's (T_1(max) = 7.4 s). The monomer shows a T_1(max) of 14.4 s, which must be reduced to fractions of a second to reduce interpulse delay time. This was achieved by adding 0.5% of chromium acetylacetonate in the chloroform solution. A typical experimental time was 30 min/sample, which is comparable to that of GPC methods. Molecular weight data obtained by GPC are strongly affected by the structure of calibration standards, which are usually not the same as the polymer to be analyzed and can deviate easily from the true value by more than 100%.[3] A recent paper even pointed out the failure of the so-called "universal calibration plot" on certain radially symmetric and asymmetric macromolecules.[13] The NMR method provides an alternative so that the molecular weight of the structurally regular polymers can be independently checked. Under optimum condition, in situ molecular weight monitoring was possible for the polymerization of 1 in the NMR probe. Some conceivable limitations of this technique are as follows. The structural regularity of polymer branching is the basis from which the molecular weight equations are derived. Therefore, the structure of the polymer must be fully characterized so that the backbone and end-group signals can be identified with certainty. Equation 1 is also limited by the accuracy of the backbone to end group ratio R. As R approaches 2, the resulting polymer molecular weight will be subject to a larger error. Taking 10% as the practical error for the value of R would set a molecular weight of 16 000 as the high limit for the NMR method. Application of this method on molecular weight determination of novel two-dimensional polymers such as those produced by photopolycyclodimerization of heptacene dimer[14] will be the next target of investigation.

Acknowledgment. I thank Leila Philip and Rick So for helpful discussions and Dave Shimp for a gift of Bisphenol A dicyanate.

References and Notes

(1) Laude, D. A.; Wilkins, C. L. *Macromolecules* **1986**, *19*, 2295.

(2) (a) Storh, R.; Gerber, H. *Angew. Chem.* **1960**, *72*, 1000. (b) Grigat, E.; Putter, R. *Chem. Ber.* **1964**, *97*, 3102.

(3) Ambler, M. R.; McIntyre, D. J. *J. Polym. Sci., Part B* **1975**, *13*, 589.

(4) LaRochelle, R. W.; Cargioli, J. D.; Williams, E. A. *Macromolecules* **1976**, *9*, 85.

(5) (a) Pankratov, S. V.; Vinogradova, S. V.; Korshak, V. V. *Russ. Chem. Rev.* **1977**, *46*, 278. (b) Cozzens, R. F.; Walter, P. *J. Appl. Polym. Sci.* **1987**, *34*, 601. (c) Shimp, D. A.; Christenson, J. R.; Ising, S. J. Paper presented at the 34th International SAMPE symposium and Exhibition, May 8, 1989, Reno, NV.

(6) Kessler, H.; Griesinger, C.; Zarbock, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331.

(7) This value would have been identical with the integral ratio between peaks 3 and 4 (or peaks 6 and 5), if a base-line resolution between these two sets of backbone and end-group peaks could be achieved.

(8) The trimer does not contain a backbone group. Although strict 2-fold symmetry of backbone carbons is expected only in the pentamer, no shift of the backbone carbon signals of higher oligomers from lower oligomers was ever detected. Apparently the spectrometer is unable to resolve this small difference and exhibits as two singlets for all quaternary backbone carbons regardless of chain length.

(9) Tomalia, D. A.; Hall, M.; Hedstrand, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 1601.

(10) Jiricny, J.; Reese, C. B. *Br. Polym. J.* **1980**, *12*, 81.

(11) It can be shown that the number-average molecular weight of a polymer prepared by polycyclotetramerization of an unknown monomer would be

$$M_o = \mathrm{MW}\left(\frac{2 + R}{1 - R}\right)$$

if a 2-fold symmetry of the backbone groups exist. The number-average molecular weight of the polymer including the unreacted monomer would then be

$$M_n = \mathrm{MW}\frac{XR'^2(2 + R) + RS(R' + S)(2 + R)}{XR'^2(2 + R) + RS(R' + S)(1 - R)}$$

where X and S are the symmetry elements (i.e., $X = 2$ for 2-fold symmetry) of the backbone and the monomer, respectively.

(12) The number-average molecular weight of one commercial polycyanate resin was measured in two laboratories using similar GPC methods. The results differed by more than 40% (M_n = 408 vs 568). The NMR method gave a M_n of 590, which is close to one of the values measured by GPC using internal triazine oligomers as calibration standards. The different detector response of the monomer to that of the polymer may have contributed to the error, in addition to the calibration uncertainty.

(13) Dubin, P. L.; Principi, J. M. *Macromolecules* **1989**, *22*, 1891.

(14) Fang, T. Ph.D. Dissertation, University of California, Los Angeles, 1986; *Diss. Abstr. Int., B* **1986**, *47* (6), 2435-B.