

Molecular Structure of Chain-Extended Polymeric Diols

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Synopsis

The molecular structures of a series of chain-extended polycaprolactone diols were studied by nuclear magnetic resonance (NMR) and conventional wet chemical techniques. Hydroxyl end group and per cent nitrogen values were obtained by phthalation and automated micro-Dumas techniques, respectively. The value of the NMR technique is demonstrated in providing information regarding the total structure of the polymer. Molecular weight and per cent nitrogen values obtained by this procedure for most samples agree better than 10% with results obtained by the chemical methods.

INTRODUCTION

Polymeric diols in the 2000-3000 molecular weight range can be prepared by chain-extending lower molecular weight diols with diacyl chlorides, diisocyanates, or diepoxides. The final polymeric diol has a variable molecular structure (the average structure is defined by the stoichiometry in the chain-coupling reaction) and a broad molecular weight distribution. If the extended polymer is to be used further in a polymerization reaction, e.g., in the preparation of polyurethanes, at least the average structure of the polymeric diol should be accurately known. Nuclear magnetic resonance (NMR) spectroscopy presents an excellent means for determining the molecular structure of chain-extended diols. Although the determination of molecular structure and molecular weight of polymers by NMR is not frequently reported,^{1,2} the technique offers advantages when applicable over cryoscopic, chemical, and physical methods in that more information is obtained.

EXPERIMENTAL

The NMR spectra were obtained on a Varian A-60 spectrometer using 5-mm o.d., thin-wall sample tubes. Signal areas were obtained from an average of 8-12 integrals using the standard A-60 integrator. Deuteriochloroform was used as the NMR solvent and was obtained from Columbia Organic Chemicals. The sample concentration varied from 10% to 20%.

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The chemical hydroxyl number results presented here were obtained by a phthalation procedure similar to that described by Elving and Warshowsky.³ The phthalic anhydride reagent solution is prepared by dissolving 70 g of reagent-grade phthalic anhydride in 500 ml of freshly distilled reagent-grade pyridine. (*Note:* Siggia⁴ has reported that reagent-grade pyridine may be used as purchased.) This solution should be allowed to stand overnight before using. During this time a slightly yellowish color will appear. Alternatively, the solution may be heated under hot tap water for about 1 hr. For the final titration 0.5*N* solution of potassium hydroxide in water and a 0.1% solution of phenolphthalein in pyridine are required.

For analysis the sample is weighed into a heat-resistant pressure bottle containing 25 ml of the phthalic anhydride reagent. (The sample weight can be determined by the expression $10/X$, where the X is the approximate hydroxyl content in mEq/g.) Two flasks containing only reagent are carried along as duplicate blank determinations. The bottles are then capped and covered with a protective cover such as canvas or cheese cloth to prevent injury to the operator in the event of explosion. (If the bottle caps are cork-lined, a piece of polyethylene or Teflon should be placed over the mouth before capping.) The bottles are then heated for 30 min in a boiling water bath. At the end of the reaction period the bottles are cooled to room temperature, uncapped, and 2 ml of the phenolphthalein solution is added to each. Titration is then carried out with 0.5*N* potassium hydroxide until the appearance of a pinkish color permanent for 15 sec.

The hydroxyl content of the sample is calculated as follows:

$$\text{OH content (mEq/g)} = \frac{(\text{blank titer} - \text{sample titer}) (\text{N of KOH})}{\text{sample weight in grams}}$$

Assuming each molecule contains two hydroxyl end groups, the M_n is calculated as follows:

$$M_n = \frac{2000}{\text{OH in mEq/g}}$$

Since many of these samples contain acidic impurities, an error will occur if a correction is not made. A sample of the diol should thus be titrated with the base in pyridine to a phenolphthalein endpoint. The acid content, thus calculated in mEq/g, should be added to the hydroxyl content as determined above prior to calculating M_n .

The micro-Dumas nitrogen results were obtained with a Coleman nitrogen analyzer. The temperature for combustion was set at 900°C and the time was 2 min longer than that recommended by the manufacturer.

RESULTS AND DISCUSSION

Polymers which are prepared by chain-extending lower molecular weight systems are characterized by a broad molecular weight distribution and a variable molecular structure. If one can assume that the reaction medium

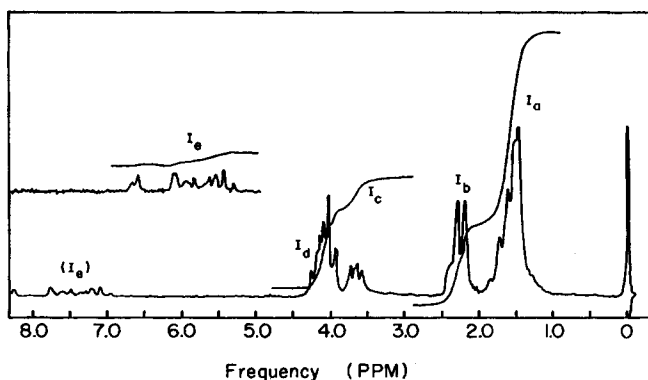


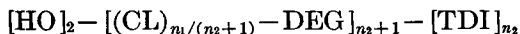
Fig. 1. NMR Spectrum of a chain-extended polycaprolactone diol.

is homogeneous and there is perfect mixing, the average structure of a chain-extended polymer can be predicted from the stoichiometry of the reactants and the relative reactivities of functional groups.⁵ In practice, ideal conditions are difficult to maintain; secondly, the reaction conditions of a commercial product are generally not revealed. Thus, chain-extended polymeric systems, whether prepared in the laboratory or obtained commercially, must be accurately characterized prior to synthetic use.

The polymeric diol of interest in this study was a tolylene diisocyanate chain-extended polycaprolactone. The polycaprolactone substrate was prepared by diethylene glycol-initiated addition polymerization of caprolactone. The NMR spectrum with integrated peak areas of the chain-extended polycaprolactone diol is shown in Figure 1. The integrals are designated I_a to I_e and are listed below with frequency limits in ppm and contributing molecular structures:

I_a	1.0–2.0 ppm	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-$
I_b	2.0–2.7 ppm	$-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-, \phi-\text{CH}_3$
I_c	3.3–3.8 ppm	$-\text{CH}_2-\text{OH}, \text{CH}_2-\text{O}-$
I_d	4.5–3.8 ppm	$-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-$
I_e	8.5–6.8 ppm	aromatic and urethane NH hydrogens

The ratio of integrals I_c/I_d will depend on the substrate molecular weight, the glycol initiator (DEG), and final diol molecular weight. The tolylene diisocyanate extender (TDI) was an 80–20 mixture of the 2,4- and 2,6-isomers. An empirical structure of the chain-extended polycaprolactone diol is given below:



In the structure, n_1 represents the number of caprolactone (CL) units and n_2 the number of TDI units per average polymer molecule. The NMR integrals I_a to I_e can be defined algebraically in terms of numbers of repeat units n_1 and n_2 as follows:

$$I_a = 6n_1k \quad (1)$$

$$I_b = 2n_1k + 3n_2k \quad (2)$$

$$I_c = 4n_2k + 8k \quad (3)$$

$$I_d = 2n_1k + 4n_2k \quad (4)$$

$$I_e = 5n_2k \quad (5)$$

where k is the NMR proportionality constant. (According to the above definitions of n_1 and n_2 , k is the average area per proton.) After solving for n_1 and n_2 , the polymer molecular weight is given by

$$M_n = 114n_1 + 174n_2 + 106(n_2 + 1) \quad (6)$$

where 114, 174, and 106 are the molecular weights of caprolactone, tolylene diisocyanate, and diethylene glycol, respectively.

Since the molecular weight by NMR was based on the average structure, considerably more information is available. The number-average molecular weight of the substrate can be calculated from eq. (7) below:

$$(M_n)_{\text{diol}} = (n_2 + 1) (M_n)_{\text{substrate}} + 174n_2. \quad (7)$$

The wt-% nitrogen is given by

$$\text{wt-\% nitrogen} = \frac{28.02n_2(100)}{(M_n)_{\text{diol}}} \quad (8)$$

The NMR results for the diol number-average molecular weight and wt-% nitrogen are given in Table I, with values obtained independently by chemical analysis and the micro-Dumas technique, respectively. The series of diols, A to H, represent different chain extension runs. The agreement

TABLE I
Polycaprolactone (Chain Coupled) Number-Average Molecular
Weights as Determined by NMR and Chemical Analysis.
Elemental Per Cent Nitrogen by NMR and Micro-Dumas Methods

Sample	$(M_n)_{\text{chem.}}$	$(M_n)_{\text{NMR}}$	n_1	n_2	$(\%N)_{\text{NMR}}$	$(\%N)_{\text{micro-Dumas}}$
A	2940	2740	18.9	1.7	1.74	1.77
B	2840	3140	19.7	2.6	2.32	2.31
C	2820	2690	17.9	2.0	2.08	2.02
D	2870	2410	16.7	1.4	1.63	1.59
E	2840	3000	19.8	2.2	2.05	1.96
F	2830	2880	19.3	2.1	2.04	2.10
G	2920	3060	20.3	2.2	2.01	2.09
H	2790	2820	19.2	2.0	1.99	1.91

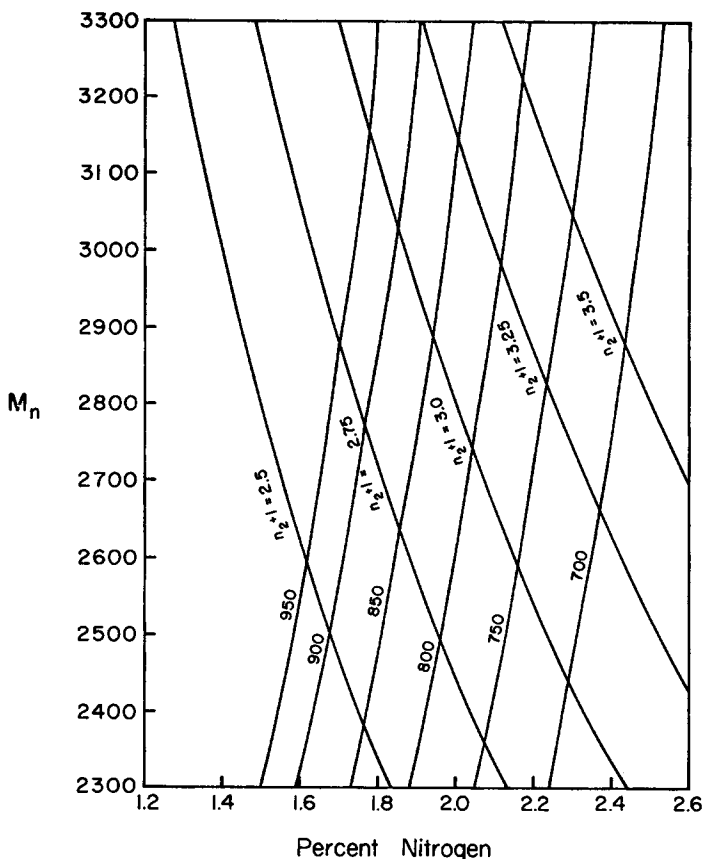


Fig. 2. Relationship of % nitrogen and molecular weight for constant substrate molecular weights and constant degrees of coupling ($n_2 + 1$) for tolylene diisocyanate-extended diols.

between molecular weights determined by NMR and chemically is better than 10%. The standard deviations for the NMR results fell within 5–10% of the reported values. Those for the chemical analyses are usually better than 5%. The closer agreement among the NMR and the micro-Dumas nitrogen values may partially result from compensating errors. The results are gratifying, however, in light of the assumptions necessarily involved in the NMR method.

The degrees of freedom that define the molecular weight of a chain-coupled polymer are the substrate molecular weight and the number of coupling units. An analysis related to the number of coupling units and the final number-average molecular weight is all that is necessary to completely characterize a chain-coupled polymer if one can be assured of the completeness of the coupling reaction and the absence of competing side reactions. In the TDI chain-extended polycaprolactone diol, knowledge of the % nitrogen and the final molecular weight completely defines the

substrate molecular weight. This fact is graphically depicted in Figure 2, a plot of molecular weight versus % nitrogen. Lines showing the relationship between M_n and % nitrogen for constant substrate molecular weights and constant degrees of coupling have been drawn. With the aid of this nomograph, it is possible to directly read the substrate molecular weight and the degree of coupling if the diol molecular weight and % nitrogen are known.

The significance of having such information over merely the diol molecular weight lies in the properties of the resultant polymer. Varying the degree of coupling may have a marked effect on the physical properties of the polymer. It is imperative, therefore, to completely characterize the diol prior to subsequent polymerizations to avoid unacceptable behavior of the final product. The suitability of the NMR method for providing such information in one analysis is evident.

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