

AD-A151 515

PHASE SEPARATION IN POLYURETHANES - A DEUTERIUM NMR
STUDY(U) PRINCETON UNIV NJ DEPT OF CHEMICAL ENGINEERING
J J DUMAIS ET AL. 18 FEB 85 TR-1 N00014-84-K-0534

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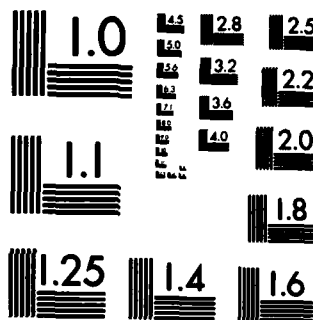
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Technical Report No. 1

Phase Separation in Polyurethanes - A

Deuterium NMR Study

by

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February 28, 1985

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1. REPORT NUMBER 1	2. GOVT ACCESSION NO. AD-A151515	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Phase Separation in Polyurethanes - A Deuterium NMR Study		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. J. Dumais, L. W. Jelinski, L. M. Leung, I. Gancarz, A. Galambos and J. T. Koberstein		8. CONTRACT OR GRANT NUMBER(s) N00014-84-K-0534
9. PERFORMING ORGANIZATION NAME AND ADDRESS Polymer Materials Program Department of Chemical Engineering Princeton University, Princeton, NJ 08544		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE February 18, 1985
		13. NUMBER OF PAGES 16
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Published in Macromolecules, 1985, 18, 116-119		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polyurethanes, Small Angle X-ray Scattering, Microphase Separation, Deuterium NMR, dsub 41		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Solid state deuterium NMR spectroscopy is used to address phase separation in specifically labeled polyurethanes. The hard segment is 4,4'-diphenylmethane diisocyanate (MDI) chain extended with [2,2,3,3-d ₄]butanediol and the soft segment is polyoxypropylene end-capped with oxyethylene. The samples contain 100, 70, 60, and 50 wt% hard segment. The results show (1) that the core of the hard segment microdomains is identical to the pure hard segment material with respect to molecular motion;		

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2) that the amount of hard segment in the interfacial regions can be quantified; 3) that the NMR and SAXS data are in good agreement concerning the fraction of interfacial hard segment; and 4), that the interfacial hard segments undergo nearly isotropic motion on a 10^{-8} s time scale, suggesting that there are few long-lived interurethane hydrogen bonding interactions in the interfacial area. Originator supplied

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Phase Separation in Polyurethanes - A Deuterium NMR Study

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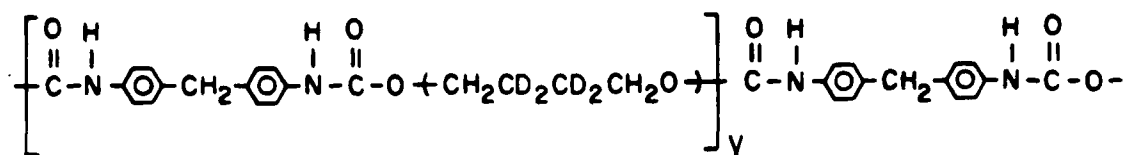
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Although numerous models have been set forth concerning the morphological microdomain structure for polyurethanes,¹ there is at present no consensus in this matter. Bonart *et al.*,²⁻⁵ on the basis of wide angle x-ray scattering (WAXS) and small angle x-ray scattering (SAXS) experiments, have proposed hard segment packing models in which the hard segments assume fully extended configurations within lamellar or sheetlike domains. This model is represented schematically in Figure 1(a). Subsequent WAXS studies by Blackwell *et al.*⁶ supported this model.

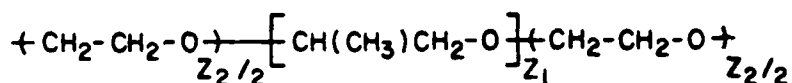
However, recent results by Van Bogart *et al.*⁷ and Koberstein and Stein⁸ are inconsistent with an extended sequence model. Using SAXS, both groups of investigators find that the hard segment chains must be present in either coiled or perhaps folded configurations. Koberstein and Stein developed a new model based on these results.⁸ In this model, the hard segment domain thickness is governed predominantly by the shortest hard segment sequence length that is insoluble in the soft segment phase. Sequences longer than this critical length adopt coiled configurations to reenter the hard segment domain and fill space efficiently. Further detailed SAXS experiments on a series of polyurethanes of varying hard segment content support this model.¹ The Koberstein-Stein model is represented schematically in Figure 1(b).

In this Note we present data that further define the nature of phase separation and hard-segment phase mixing in polyurethanes. In particular, our results address the following questions: (1) What fraction of the hard segment has motional characteristics identical to the pure hard segment material? (2) How does this fraction change as a function of the weight per cent of hard component? And (3) How do the deuterium NMR data compare with the results of SAXS?

We have shown previously that solid state deuterium NMR spectroscopy⁹⁻¹² is an exceptionally powerful tool for addressing the molecular details of phase separation in segmented copolyesters.^{13,14} Deuterium NMR discriminates on the basis of molecular motion between those hard segments that are identical to the pure hard segment material and those that are "dissolved" in the soft segment phase. Here we apply solid state quadrupole echo deuterium NMR spectroscopy to the specifically labeled polyurethanes containing 100, 70, 60, and 50 weight per cent hard segment. The polymers were prepared in solution by standard techniques^{15,16} and contain hard and soft blocks represented schematically as follows:



HARD SEGMENT



SOFT SEGMENT

Because the polymers are labeled specifically at the butanediol moiety of the hard segment, the deuterium NMR spectra reflect the motional environment of this group only, and do not contain contributions from the diphenylmethane diisocyanate (MDI) or the soft segment polyol residues.

The deuterium NMR spectra¹⁹ for these four samples are shown in Figure 2. The middle column (Figure 2(d-f)) shows the spectrum obtained at 22 °C of the all-hard segment material at different vertical scales. This spectrum, although *ca.* 120 kHz in breadth, is clearly not that of a Pake doublet.²⁵ Instead, it is reminiscent of the spectra observed for similarly labeled poly(butylene terephthalate), in which *gauche-trans* conformational jumps occur at an intermediate rate on the NMR time scale.²⁰ Spin lattice relaxation experiments show that the T_1 of this component is *ca.* 20 ms. Experiments

performed with very long recycle delays indicate that more than 95% of the sample contributes signal intensity to this spectrum. Temperature-dependent experiments are underway to further define the exact details of the molecular motion of the butanediol group in this material.

The spectra shown in Figure 2(a-c) correspond to the polyurethane samples containing 70, 60, and 50 wt% hard segments, respectively. In addition to the broad, 120 kHz pattern, these spectra also show a sharp line. That the spectra shown in Figure 2(a-c) are composed of two components can be shown from inversion-recovery spectra, in which the broad and the sharp components are observed to invert at different delay times. (Detailed solid and solution state relaxation experiments are underway and will be reported later.) The broad component is attributed to those hard segments that reflect molecular motion which is identical to that of the all-hard segment material. These hard segments would constitute the core of the hard segment-rich microdomains. The sharp component indicates the occurrence of molecular motions that are nearly isotropic in nature and may be associated with hard segments residing in a more mobile environment. Such increased mobility would be expected for hard segment sequences that are short enough to dissolve in the soft segment-rich microdomains but may also be found for hard segments that reside in the diffuse boundary region between the hard and soft segment microdomains.

The difference spectra shown in Figure 2(g-i) were obtained by subtracting the spectra in Figure 2(d-f) from those in Figure 2(a-c). It is interesting to note that the linewidths of these sharp components are identical; i.e., they are not a function of the hard segment content of the polymer. The fraction of sharp component can be estimated by appropriate integration of these spectra.²⁶ These fractions are listed in Table I, and can be compared to SAXS estimates²⁷ of dissolved hard segment content.

The SAXS estimates are determined by assuming that all hard segment sequences of length equal to or less than a critical length, N_c , are dissolved in the soft segment phase. The critical segment length is determined from the experimental value of the hard segment domain thickness T_{HS} (see Table I). For the samples examined this length is equivalent to a hard segment containing approximately three MDI and two butanediol residues (i.e. $N_c \approx 3$). The weight fraction of butanediol residues that are dissolved in the soft segment phase, ω_D , is then given by

$$\omega_D = \frac{\sum_{i=1}^{N_c} f_i (i-1)}{\bar{N}_n - 1}$$

where f_i is the number fraction of sequences containing $(i-1)$ butanediol residues calculated from Peebles' distribution function³¹, and $\bar{N}_n$ is the number average of MDI residues per hard segment sequence. The values of ω_D calculated in this fashion (Table I) are much smaller than the weight fraction of isotropic component estimated from the NMR measurements.

The weight fraction of butanediol residues residing in the interfacial gradient, ω_I , may also be determined from the SAXS results. If E is the width of a linear diffuse boundary gradient between microdomains,^{1,27} it is easily shown that $\omega_I = (E/T_{HS})(1-\omega_D)$. Values for this quantity as well as for the weight percent of total dissolved and interfacial hard segment are presented in Table I. The total weight fractions of dissolved and interfacial hard segment estimated by the SAXS analyses are in good agreement with the NMR weight percents of isotropic component except for the sample containing 50 wt% hard segments, for which the NMR value is much higher. This discrepancy may arise from differences in the synthesis and molding procedures adopted for the NMR and SAXS samples.^{15,27} SAXS experiments on the labeled NMR samples are currently in progress. It

is apparent that hard segments residing in both the soft segment phase and within the interfacial gradient contribute to the sharp component observed in the NMR spectra. The NMR results provide support to the validity of the Kobayashi - Stejskal model.

The solid state deuterium NMR results show that this interfacial area has very nearly isotropic motion on a 10^7 s^{-1} timescale. Such rapid, nearly isotropic motions are observed in flexible polymers such *cis*-polybutadiene and poly(dimethyl siloxanes). The rapid, nearly isotropic motions observed for these butanediol residues suggest that there are few long-lived interurethane hydrogen bonding interactions in this interfacial area.

It is appropriate to compare the quadrupole echo deuterium NMR results reported here with other NMR results.³²⁻³⁸ Although they have not been performed on identical polyurethanes, the overall conclusions are relevant to the system at hand.

Using broadline proton NMR, Assink^{32,33} finds two components. One decays rapidly and is attributed to the MDI hard segments, whereas the other decays more slowly and is assigned to the polyester soft segments. With proton spin diffusion as an experimental probe, Assink and Wilkes^{34,35} evaluated phase mixing in a series of MDI-polyester polyurethanes. Their data require the presence of both short and long range degrees of mixing. The short range mixing is attributed to distances involving several molecular diameters, whereas the long range mixing is attributed to chain entanglement effects. Their results point to a fair fraction of interfacial material.

The deuterium NMR experiments reported in this work substantiate and expand on the results of Assink and Wilkes. Because only the hard segment is labeled in the present case, all ambiguities concerning the source of the signal (i.e., hard or soft segments) are removed. Furthermore, deuterium NMR spectra are dominated by quadrupolar relaxation, and spin diffusion is not a factor in interpreting the data. Most importantly, the material

comprising the interfacial area can now be directly examined and quantified by NMR measurements.

The results reported in this Communication show that the solid state deuterium NMR experiment holds much promise for providing rich and detailed information concerning microphase separation in polyurethanes and other phase-separated polymers. Multiple experiments along the lines described here are in progress and will be described at a later date.

ACKNOWLEDGEMENTS

The part of this work performed at Princeton was supported in part by the Office of Naval Research.

REFERENCES AND NOTES

1. For a review of current work in this area, see Leung, L. M.; Koberstein, J. T. *J. Polym. Chem., Polym. Phys. Ed.* **1985**, 0000.
2. Bonart, R.; Morbitzer, L.; Hentze, G. *J. Macromol. Sci. Phys.* **1969**, B3, 337.
3. Bonart, R.; Morbitzer, L.; Muller, E. H. *J. Macromol. Sci. Phys.* **1974**, B9, 447.
4. Bonart, R.; Muller, E. H. *J. Macromol. Sci. Phys.* **1974**, B10, 177.
5. Bonart, R.; Muller, E. H. *J. Macromol. Sci. Phys.* **1974**, B10, 345.
6. Blackwell, J.; Lee, C. D. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, 21, 2169, and references cited.
7. Van Bogart, J. W. C.; Gibson, P. E.; Cooper, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, 21, 65.
8. Koberstein, J. T.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, 21, 1439.
9. Jelinski, L. W. in "High Resolution NMR of Synthetic Polymers in Bulk," (Komoroski, R. A., ed.), Verlag Chemie, p. 000, 1985.
10. Spiess, H. W. *Colloid and Polym. Sci.* **1984**, 261, 193.
11. Spiess, H. W. *J. Mol. Struct.* **1983**, 111, 119.
12. Spiess, H. W. in "Advances in Polymer Science," (Kausch, H. H.; Zachmann, H. G., eds.), Springer-Verlag: Berlin, 1984.
13. Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *ACS Symp. Ser.* **1984**, 247, 55.
14. Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *Org. Coat. Appl. Polym. Sci. Proc.* **1983**, 248, 102.

15. The polyurethanes used in this study were synthesized in THF solution under a dry argon atmosphere following established literature procedures (see for example reference 16). The hard segment is 4,4'-diphenylmethane diisocyanate (MDI) (Eastman Kodak) chain extended with [2,2,3,3- d_4] butane diol (Merck Isotopes). The soft segment is polyoxypropylene end-capped with 30.4 wt% oxyethylene (Union Carbide NIAX polyol, $M_n = 2000$, functionality = 1.94). NMR samples were cut from 2 mm thick disks that were molded under vacuum for *ca.* 5 min at 180-190°C and 4000 psi and slow-cooled under pressure. Transurethanefication, known to be rapid above 170°C,^{17,18} should lead to a most probable distribution of sequence lengths.
16. Lyman, D. J. *J. Polym. Sci.* **1960**, *45*, 49.
17. Camberlin, Y.; Pascault, J. P.; Letoffe, M.; Claudy, P. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 383.
18. Chang, A. L.; Briber, R. M.; Thomas, E. L.; Zdrahala, R. J.; Critchfield, F. E. *Polymer* **1982**, *23*, 1060.
19. Solid state deuterium NMR spectra were obtained on *ca.* 100 mg samples at 55.26 MHz for ^2H using a home-built spectrometer.²⁰ The quadrupole echo²¹⁻²³ and the inversion-recovery quadrupole echo pulse sequence²⁴ were used to observe the spectra. Detection was performed in quadrature using 2K points per channel and a 100 ns/point (10 MHz) digitization rate. The 90° pulse width was 3.3 μs and the echo delay was 30 μs .
20. Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *Macromolecules* **1983**, *16*, 492.
21. Davis, J. H.; Jeffrey, K. R.; Bloom, M.; Valic, M. I.; Higgs, T. P. *Chem. Phys. Lett.* **1976**, *42*, 390.

22. Blinc, R.; Rutar, V.; Seliger, J.; Slak, J.; Srnolej, V. *Chem. Phys. Lett.* **1977**, *48*, 576.
23. Hentschel, R.; Spiess, H. W. *J. Magn. Reson.* **1979**, *35*, 157.
24. Cholli, A. L.; Dumais, J. J.; Engel, A. K.; Jeliaski, L. W. *Macromolecules* **1984**, *17*, 0000.
25. Pake, G. E. *J. Chem. Phys.* **1948**, *16*, 327.
26. These spectra have not been corrected for T_2 losses. Because polymers are generally characterized by a distribution of motional frequencies, this assumption is expected to have a small effect on the reported integrals.³⁹
27. SAXS measurements of lamellar thickness and diffuse phase boundary thickness were carried out by analyses described in previous communications.^{1,8} For the present study, bulk polymerized samples prepared from unlabeled butanediol²⁸ were employed in the SAXS studies. The samples were molded under vacuum at 180°C and 4000 psi and slow cooled under pressure. The urethane exchange reaction is rapid at this temperature^{17,18} and should correct for any non-random sequence length distribution which may have resulted during polymerization.^{29,30}
28. Zdrahala, R. J.; Critchfield, F. E.; Gerkin, R. M.; Hager, S. L. *J. Elast. and Plastic* **1980**, *12*, 184.
29. Chen, C. H. Y.; Briber, R. M.; Thomas, E. L.; Xu, M.; MacKnight, W. J. *Polymer* **1983**, *24*, 1333.
30. Xu, M.; MacKnight, W. J.; Chen, C. H. Y.; Thomas, E. L. *Polymer* **1983**, *24*, 1327.
31. Peebles, L. H., Jr. *Macromolecules* **1976**, *9*, 58.

32. Assink, R. A. *Macromolecules* 1978, 11, 1233.
33. Assink, R. A. *J. Polym. Sci., Polym. Phys. Ed.* 1977, 15, 59.
34. Assink, R. A.; Wilkes, G. L. *Polym. Eng. and Sci.* 1977, 17, 606.
35. Assink, R. A.; Wilkes, G. L. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* 1977, 18(1), 307.
36. Lagasse, R. R. *J. Appl. Polym. Sci.* 1977, 21, 2489.
37. Froix, M. F.; Pochan, J. M. *J. Polym. Sci., Polym. Phys. Ed.* 1976, 14, 1047.
38. Goldwasser, D. J. *J. Polym. Sci., Polym. Phys. Ed.* 1979, 17, 1465.
39. Spies, H. W.; Sillescu, H. J. Magn. Reson. 1981, 42, 381.

TABLE I
BUTANEDIOL HARD SEGMENT COMPONENT

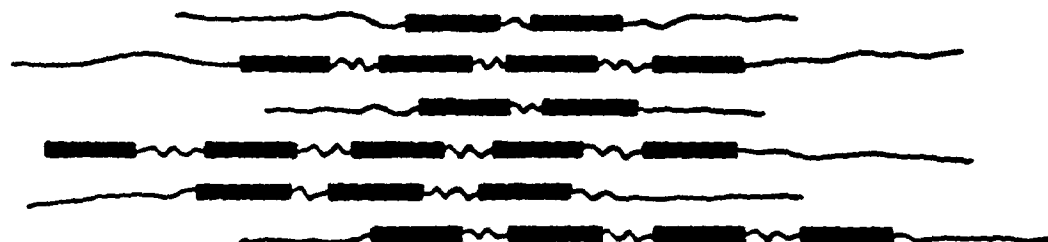
Overall Wt% Hard Segment	Hard Domain Thickness T_{HS} (nm)	Interphase Width E (nm)	Percent Dissolved Butanediol ($\omega_D \times 100\%$)	Percent of Butanediol in Interfacial Hard Segment ($\omega_I \times 100\%$)	Percent Dissolved and Interfacial Butanediol	Percent Sharp Butanediol Component by NMR ^a
70	7.7	1.1	2.1	13.5	15.6	14
60	7.3	1.1	4.0	14.4	18.4	20
50	6.1	1.1	7.8	15.9	23.7	50

FIGURE CAPTIONS

Figure 1: Schematic representation of (a) the extended hard segment configuration model, and (b) the Koberstein–Stein model.⁸ The bars represent the MDI units.

Figure 2: Solid state quadrupole echo deuterium NMR spectra of hard segment labeled polyurethanes obtained at 22°C and 55.26 MHz. Spectrum (a) 70, (b) 60, and (c) 50 wt% hard segment. Spectra (d-f) are of the all-hard segment material reported at different vertical gains. Spectra (g-i) were obtained by subtracting an appropriate amount of the symmetrized spectra in the center column from those in the left column. All spectra were obtained with a 2s recycle delay.

(a)



(b)

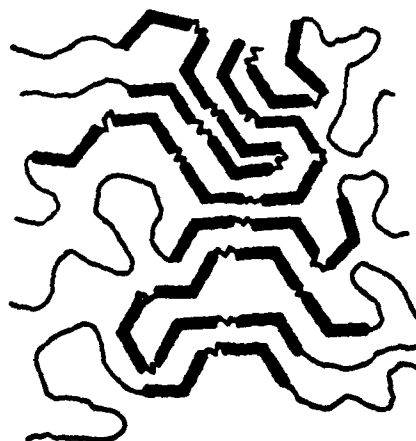


Figure 1

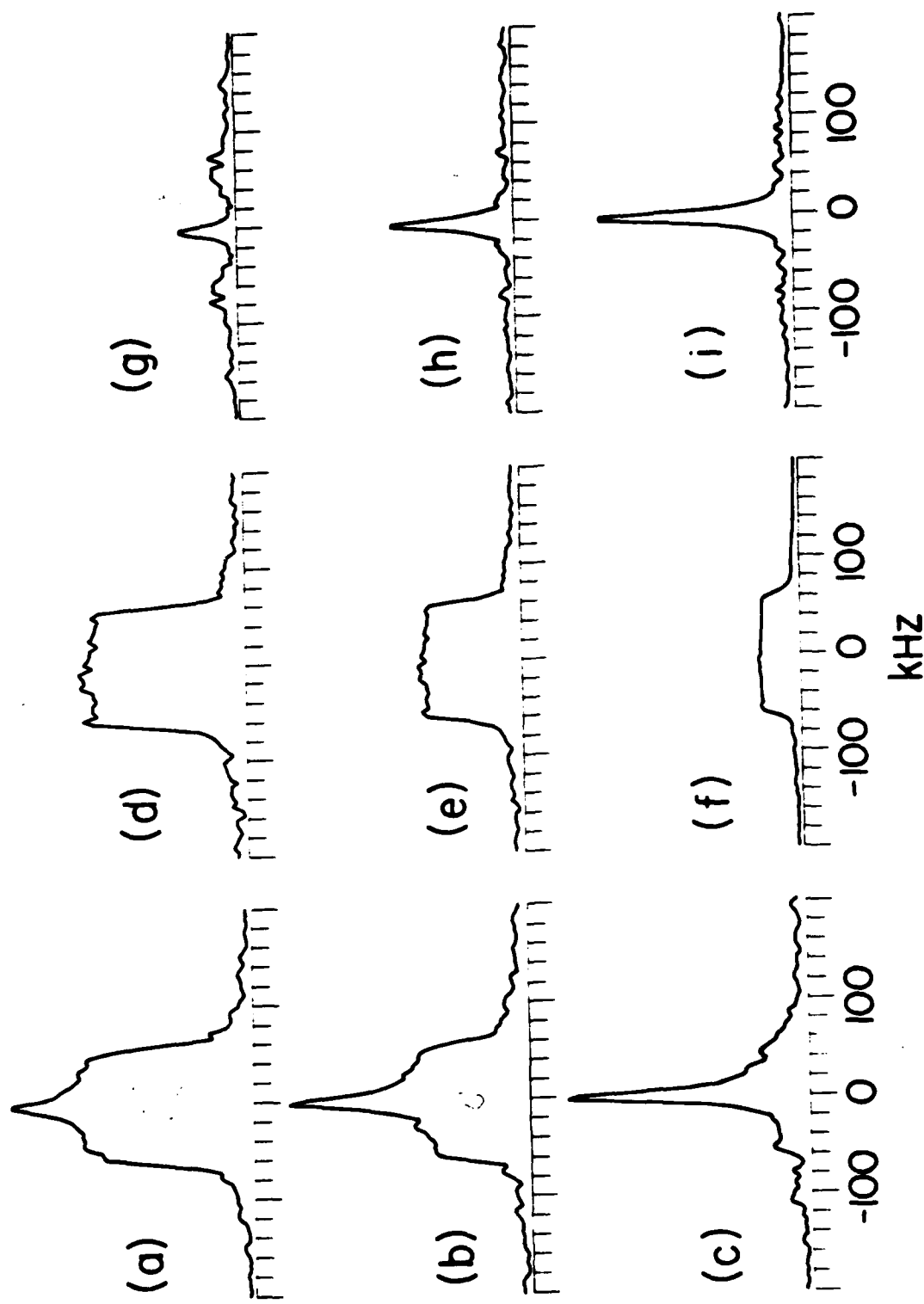


Figure 2

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