NMR ANALYSIS OF THE KEL-F
Co-POLYMER SYSTEM

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DEVELOPMENT DIVISION

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ABSTRACT

Dimethylacetamide solutions of several members of the Kel-F polymer system were analyzed by F^{19} NMR spectrometry. Although relatively acceptable spectral data are obtained, the mandatory methods of analysis for this type of system, such as reliable peak integration data and data time averaging, are not possible with the limited lock mode sweep range of the Varian HA-100 (1500 Hz). The possibility of electronic modification of the unit for the purpose of increasing the lock mode sweep range to cover the F^{19} spectral range is being studied.

DISCUSSION

Proton spectral analysis of the Kel-F co-polymer system has previously undergone a cursory appraisal(1). Due to the high viscosity of polymer solutions and the relatively narrow range of chemical shifts generated by a considerable number of resonance peaks, very little structural information and essentially no proportional make-up implications based on integration data were obtained. Because of the inherently wide range of chemical shifts which exist in F^{19} spectral behavior (~ 400 ppm relative to 12 to 15 ppm for protons), an initial investigation of the possible application of F^{19} spectral data for the purpose of Kel-F system characterization was undertaken.

Samples of the Kel-F system for F^{19} analysis were prepared by dissolving the samples in dimethylacetamide. Solution was effected by placing the Kel-F/dimethylacetamide mixtures in Teflon septum vials and placing on a Kahn mechanical shaker for 2 hours. Kel-F systems studied included 800, 3700, and 5500.

Although the Varian HA-100 is easily converted from 100 to 94.1 megahertz for F^{19} operation, the unit is restricted to a maximum sweep width of 1500 Hz when using internal lock operation, and dictates running the Kel-F samples in HR mode (no internal lock). The resulting sweep produces a spectral trace with fairly strong resonance peaks and somewhat good peak resolution, considering the viscosity of the sample and the nature of the solute. Resonance peak separation for each of the Kel-F materials is in the general range of 15 to 25 ppm. In the non-lock mode, the actual shift upfield from CCl_3F (the generally accepted internal F^{19} reference) can be experimentally determined by use of the audio side band technique of Tiers(2), but was not felt to be of paramount interest at this time. The matter of peak resolution and the ability to obtain meaningful peak integration data are of a more immediate concern.

Fig. 1 presents an HR sweep spectra of the center band portion of the F^{19} signal from the dimethylacetamide solution of Kel-F 800. Although, as previously noted, the resonance intensities are quite acceptable, and resolution (peak separation) is substantially improved over the H^1 spectra of these materials, several problems with this method of spectral recording

(1) G. L. Clink, *NMR Analysis of the Kel-F Co-Polymer System*, MHSMP-76-30L (April - June 1976).

(2) G. V. D. Tiers, *J. Phys. Chem.*, 1151, 62 (1958)

are apparent. There is good indication that the extreme upfield and downfield peaks of the spectrum are actually a spectral "overlap" of the absorption mode of the center band and the dispersion mode of the side bands, due to the frequency modulation of the former. The sizeable peak separation of the extreme center band signals (~ 23 ppm) and the modulation frequency of the HA-100 would, not surprisingly, generate upper-lower and lower-upper side band overlapping of the extremes of the center band signals. Separation of the sum and difference frequencies (side bands) from the center band signals by decreasing of the linear sweep range was not sufficiently effective.

Use of an internal lock mode in this system is not possible with only a 1500 Hz sweep range. Internal lock materials, such as fluorotrichloromethane (CCl_3F), occur approximately 100 ppm downfield from the Kel-F resonance range. Even if a material is found to serve as an internal lock, whose resonance occurs within the immediate upfield or downfield range of the Kel-F resonance, the chemical shift range of the material places it outside the spectral sweep range, and would accordingly rule out any possibility of reliable peak integration data. In the non-lock mode, as used to record the spectra in Fig. 1, rf phasing effects make reliability of integration values questionable. Integration values obtained for the 6 prominent peak areas are presented in Fig. 1.

The inability to effect an internal lock mode of operation also eliminates the considerable improvement in peak sharpness and resolution, through sample dilution (with its decrease in viscosity) and subsequent time averaging of the data.

COMMENTS

Although a somewhat limited and basically qualitative characterization of the Kel-F system could be made when analyzing concentrated solutions of the materials ($> 20\%$) in the HR (non-lock) mode, the practical application of F^{19} NMR to Kel-F containing systems (HE admixtures) is not possible under these restrictive operating conditions. The relatively low concentration of F^{19} polymer material which would result from solvent initiated analysis of a Kel-F admixture would necessitate time averaging or Fourier transform analysis of the data, neither of which can be effected without employing internal lock operation, such as is available on the Varian XL-100.

The possibility of electronic modification of the existing Varian HA-100, such that an increased lock mode sweep range could be developed which would allow the efficient analysis of F^{19} containing systems, is now being studied. If fluorine containing materials are to be effectively analyzed for molecular and/or polymer structure make-up, this dictates the use of magnetic resonance methods with an internal lock system capable of frequency sweep ranges covering the F^{19} spectral range.

Fig. 1. HA-100 HR Spectrum of Kel-F 800