NMR ANALYSIS OF THE KEL-F
CO-POLYMER SYSTEM

George L. Clink

DEVELOPMENT DIVISION

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ABSTRACT

Proton spectral analysis of the Kel-F co-polymer system does not produce spectral data which are useful from an analytical standpoint. High viscosity of the samples and lack of peak resolution give meager structural information and somewhat useless integration data. The use of F^{19} spectral techniques, which have been shown to be applicable to this type of material in the past, should be investigated.

DISCUSSION

The possibility of applying NMR spectral and integration techniques to characterize and analyze fluoropolymer containing systems is being investigated. The typically high concentration levels required for polymer proton resonances to be detectable and spectrally reproduced, without the need for time averaging techniques, and the inherent high viscosity of the resulting solutions with its broadening effect on the spectral characteristics (significant loss of peak resolution) indicate that H^1 spectral techniques are not applicable. The more obvious and generally useful F^{19} (fluorine) spectral approach is advisable. However, prior to studying the F^{19} approach, a rather cursory overlook into the H^1 spectra of the Kel-F(1) system was made.

Several members of the Kel-F system of polymers were obtained from Fred Larsen (Bendix, Kansas City) such that differential spectral comparison of the various spectra could be made. The particular Kel-F members obtained included Kel-F 3700, 5500, and 800. The co-polymers of this system are chlorotrifluoroethylene (PCTFE) and vinylidene fluoride (PVF₂). The presence of the former, because it is void of protons, causes considerable loss of structural formation when using H^1 spectral techniques, and again indicates the use of F^{19} techniques. In general terms, the Kel-F system formation proceeds along the following route:

The Kel-F members studied include the following:

<u>Member</u>	<u>x/y Ratio</u>
800	1/3
3700	7/3
5500	1/1

Kynar (polyvinylidene fluoride) was also available, but the problem of a suitable solvent eliminated its potential characterization by way of H^1 spectral techniques.

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Saturated solutions of Kel-F 800, 3700, and of 5500, were prepared by addition of an excess polymer to d^6 acetone in a Teflon septummed vial and placing on a Kahn mechanical shaker until dissolution was affected. The resultant solutions were diluted to half strength with d^6 acetone. The sample was made 5% in benzene for use as the internal lock material. The samples were run in field sweep on a Varian HA-100. The spectral results are presented in Fig. 1. The baseline spectra are at the standard 1000 hz sweep, while the spectral insets are those of the polymer resonances at an expanded 500 hz sweep. An indication of the low sensitivity of polymer protons is appreciated by the sensitivity level of the d^5 acetone peak at approximately 540 hz, only present in approximately 0.40% concentration. Fig. 2 is a spectral sequence display of the polymer proton region of the three Kel-F spectra. Although quite obvious spectral differences can be seen among the three, proton spectra provide very little peak separation (resolution) to make reliable structure correlations. In addition, the relatively high rf power levels required to obtain recordable resonance peaks create such appreciable saturation effects on the individual proton resonances as to make any integration values somewhat useless. The alternative method of using dilute solutions and applying spectral time averaging techniques produced results relatively unimproved from those obtained by routine methods.

COMMENTS

The foregoing data simply supplant the generally felt and original appraisal of the inadvisability of using H^1 spectral techniques to characterize a polymer, particularly one containing such a low proton to mass ratio.

It is strongly suggested that the application of F^{19} spectral techniques to investigate this system be studied. In addition to the advantages of lower solution concentration necessary in the F^{19} system for this group of materials (and accordingly lower viscosity), much additional spectral information is available, such as conformational data which includes the presence and extent of head to head, head to toe, and toe to toe polymer structure makeup. The ability to determine the structural consistency of future lots of Kel-F used in production activities may be quite useful.

Fig. 1. ^1H Spectra of Ke1-F System

Fig. 2. ^1H Spectral Comparison of Kel-F System