Initiation and Termination Group Identification in Polymers by ¹³C N.M.R. Spectroscopy

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Abstract

A ¹³C n.m.r. inversion/recovery method is described for the identification of initiation and termination groups in low molecular weight polymers.

The initiation and termination (end) groups can have a significant effect on the properties of a polymer. This is particularly so if the groups are reactive and can be involved in polymer degradation. However, the identification and estimation of the end groups is difficult because of their low overall concentration.

Recently we have used ¹³C n.m.r. spectroscopy to analyse the structures of the cyclopolymers obtained from the cyanoisopropyl radical induced polymerization of diallylamines.[1] The major peaks in the proton-decoupled ¹³C n.m.r. spectrum of the cyclopolymer (1) from diallyl(N-methyl)amine (Fig. 1a) can be assigned,[2] as indicated, to the *cis*- and *trans*-polypyrrolidine units in the polymer backbone but minor peaks remain unassigned and these could originate from the end groups.

(1)
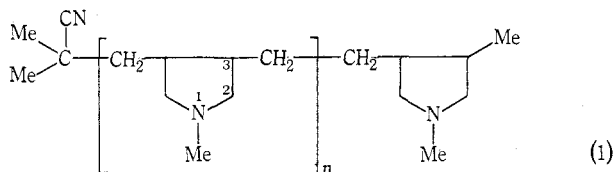
We have now used an inversion/recovery technique, similar to that employed in the determination of longitudinal relaxation times (T_1),[3] to assign signals to those carbons of the initiation and termination groups. Because of the restriction of motion along a polymer chain the T_1 values of the backbone carbons of a cyclopolymer such as (1) are expected to be quite short. By contrast, the T_1 values of the carbons of the end groups of the polymer chains will be much longer because of their greater mobility. By choosing a time, τ, in an inversion/recovery, $\pi-\tau-\pi/2$, sequence such that the backbone carbons have recovered their magnetism in the positive z' axis these signals will appear upright whereas the signals from the carbons with the longer T_1 values, i.e. those of the initiation and termination groups, will retain magnetism in the negative z' axis and afford inverted signals.

[1] Hawthorne, D. G., Johns, S. R., Solomon, D. H., and Willing, R. I., *Aust. J. Chem.*, 1976, **29**, 1955.
[2] Johns, S. R., Willing, R. I., Middleton, S., and Ong, A. K., *J. Macromol. Sci., Chem.*, 1976, **105**, 875.
[3] Vold, R. L., Waugh, J. S., Klein, M. P., and Phelps, D. E., *J. Chem. Phys.*, 1969, **48**, 3831.

A comparison of the spectra of the cyanoisopropyl radical induced copolymer (1) from diallyl(N-methyl)amine (mol. wt c. 2000, i.e. 20 units) after τ 20 s and τ 0·2 s (Figs 1a and 1b respectively) shows a number of inverted signals in Fig. 1b that can be assigned to carbon atoms of the initiation and termination groups. Specifically, the signal at 31·7 ppm can be assigned to the methyl groups of the initiating cyano-isopropyl radical as the methyl signal in t-butyl cyanide resonates at 28·4 ppm. The
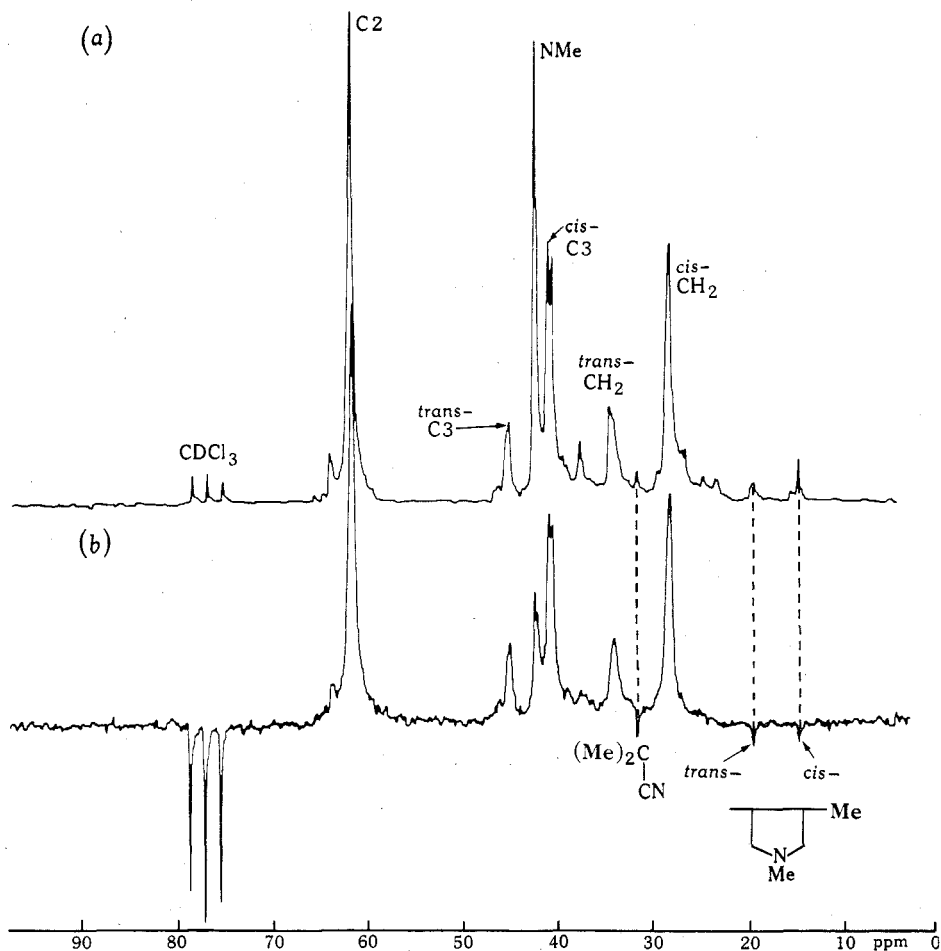

Fig. 1. Proton-decoupled ^{13}C n.m.r. spectra of the cyclopolymer (1) from the cyanoisopropyl radical induced polymerization of diallyl(N-methyl)amine after a π–τ–$\pi/2$ sequence: (a) τ 20 s; (b) τ 0·2 s. Spectra were measured at 20 MHz on a Varian CFT-20 spectrometer on 20% w/v solutions in CDCl$_3$ over a spectral width of 2000 Hz for 4096 data points and 2000 transients.

signals at 14·6 ppm and at 19·3 ppm can be assigned to the *cis*- and *trans*-methyl groups respectively of terminating methylpyrrolidine residues as the respective methyl signals in 1,3,4-*cis*-trimethyl- and 1,3,4-*trans*-trimethyl-pyrrolidine resonate at 14·4 and 18·8 ppm.[4] The presence of C-methyl groups on the terminating pyrrolidine indicates that termination occurs by an abstraction of hydrogen, probably from the solvent.[1]

[4] Hawthorne, D. G., Johns, S. R., and Willing, R. I., *Aust. J. Chem.*, 1976, **29**, 315.

We therefore propose that the described ^{13}C n.m.r. inversion/recovery method is an excellent technique for the determination of initiation and termination groups in polymers of low molecular weight in which the ^{13}C chemical shifts of the end groups are different to those of the main chain repeating units.