

The Carbon-13 NMR Study of Polymer Structure and Dynamics

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Abstract - It has been long known that ^1H and ^{19}F NMR can provide significant structural and motional information for synthetic polymers. More recently, FT instrumentation has permitted natural abundance ^{13}C NMR spectroscopy, giving great sensitivity to tacticity, comonomer sequence, regiospecificity, branching, and other structural features. ^{19}F NMR also shows high sensitivity, particularly to tacticity and regiospecificity. High resolution ^{13}C spectroscopy in the solid state, achieved using proton dipolar decoupling, magic angle spinning, and ^1H - ^{13}C cross-polarization, is also of great interest with respect to both chain structure and dynamics.

Examples of tacticity studies by NMR include ^{13}C spectroscopy of polypropylene (and the prediction of spectral fine structure using the " γ -effect" model), poly(vinyl chloride), poly(vinyl bromide), and (by ^{19}F NMR) poly(fluoromethylene), $(\text{CFH})_n$. The detailed branch structures of polyethylene and poly(vinyl chloride) are discussed, together with their interpretation in terms of polymerization mechanisms. The solid state ^{13}C NMR spectroscopy of Hytrel polyester thermoplastic elastomers is described and discussed with regard to domain structure and chain motion. The chain mobilities in these segmented copolymers appear to range over several orders of magnitude.

INTRODUCTION

It has been known for over 20 years that proton (1-3) and ^{19}F (4) NMR spectroscopy can supply important information concerning polymer structure, particularly stereochemical configuration (2-4) and copolymer sequences (2), as well as dynamic information concerning polymers in solution (2). More recently, carbon-13 NMR has assumed increasing importance as the development of Fourier transform instrumentation with spectrum accumulation has permitted the practical observation of carbon-13 in natural abundance. Carbon spectroscopy has now developed into a method of fairly high sensitivity and can detect and measure very minor but significant features of polymer structure such as end-groups, branches, and head-to-head monomer sequences. It has now largely displaced proton spectroscopy because of the much greater range of carbon chemical shifts and the consequent greater sensitivity to details of structure.

High resolution carbon-13 spectroscopy in the solid state, achieved using high power proton decoupling, proton-carbon-13 cross-polarization, and magic angle spinning has also generated much interest and excitement (Reference 5 is a useful review by two pioneers of this field).

Fluorine-19 NMR is also highly sensitive to details of microstructure, including head-to-head: head-to-tail isomerism and tacticity, and is very valuable where applicable.

I shall briefly illustrate these applications of NMR by illustrations drawn from the work of our laboratory.

THE DEPENDENCE OF ^{13}C AND ^{19}F SHIFTS ON STEREOCHEMICAL CONFIGURATION AND ITS CONFORMATIONAL DEPENDENCE

In the observation of configurational sequences, pentads can usually be resolved by ^{13}C NMR, particularly at superconducting frequencies, and the discrimination of heptad sequences is not uncommon. An example is shown in Fig. 1, which exhibits the methyl spectrum (observed by Mr. F. C. Schilling) of an atactic polypropylene observed in three solvents at varying temperatures (6). The spectrum shows little solvent dependence but a fairly marked temperature dependence.

Dr. Tonelli in our laboratory has shown that the configurational fine structure in this spectrum, and the spectra of the α - and β - carbons of the main chain, can be very accurately predicted by a simple " γ -effect" model (7-10) which postulates that when two carbon atoms separated by three bonds are in a *gauche* conformation, they shield each other by -5.2 ppm compared to their resonance frequencies in the *trans* conformation. The CH_3 chemical shift is then determined by the *gauche* content of the main chain bonds flanking the α -carbon to which the CH_3 group is attached. This is illustrated in Fig. 2. It should be noted that when the main chain bonds are *trans*, the methyl carbons experience *gauche* interactions, but that when the main chain bonds are *gauche* they experience no *gauche* interactions (*gauche* is very sparsely populated). The chirality of neighboring α -carbons, even when removed by as many as seven intervening bonds, influences the CH_3 resonance position by affecting this local *gauche* content, which can be accurately calculated using the rotational isomeric state model for polypropylene developed by Suter and Flory (11). There is thus no need to invoke any mysterious long range influences in the polymer molecule.

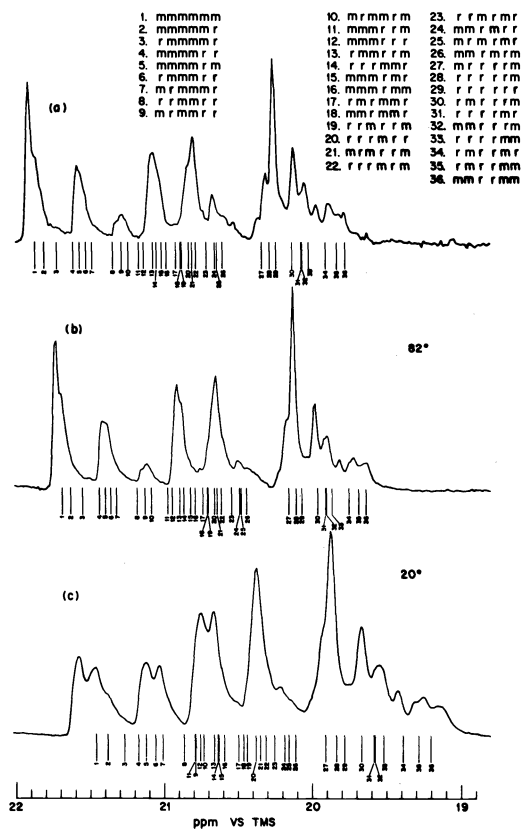


Fig. 1. 90 MHz Carbon-13 spectra of atactic polypropylene; (a) observed in heptane at 67°; (b) in 1,2,4-trichlorobenzene- d_8 at 82° (c) in 1,2,4-trichlorobenzene- d_8 at 20°. Calculated "stick" spectra (of arbitrarily equal line intensity) are shown below each spectrum.

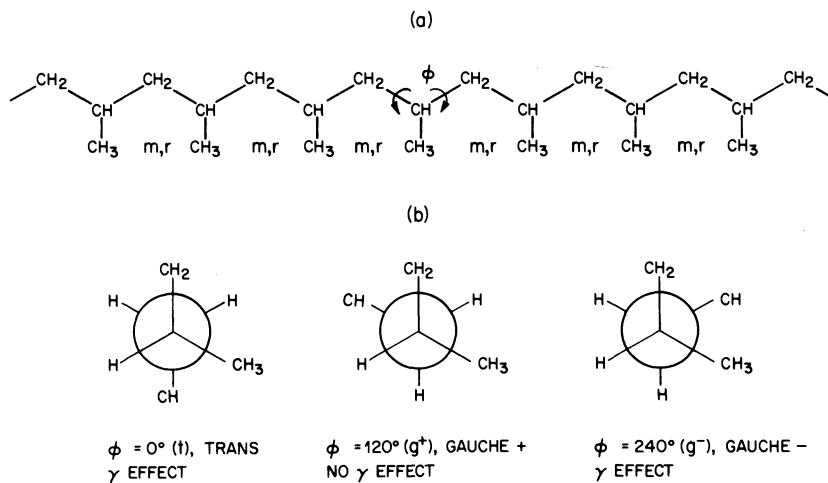


Fig. 2. Heptad configurational sequences in a polypropylene chain. The central CH_3 carbon experiences *trans*, *gauche*+, and *gauche*- interactions (below) with neighboring α -carbons about the bonds indicated by the arrows.

Carbon-13 NMR is effective in determining the stereochemistry of poly(vinyl chloride) (8, 12-14) and poly(vinyl bromide)(14) and their dependence on polymerization temperature and the presence of aldehydes, two much disputed questions. In Fig. 3 (14) are shown the 22.6 MHz ^{13}C spectra of poly(vinyl chloride) (a) and poly(vinyl bromide)

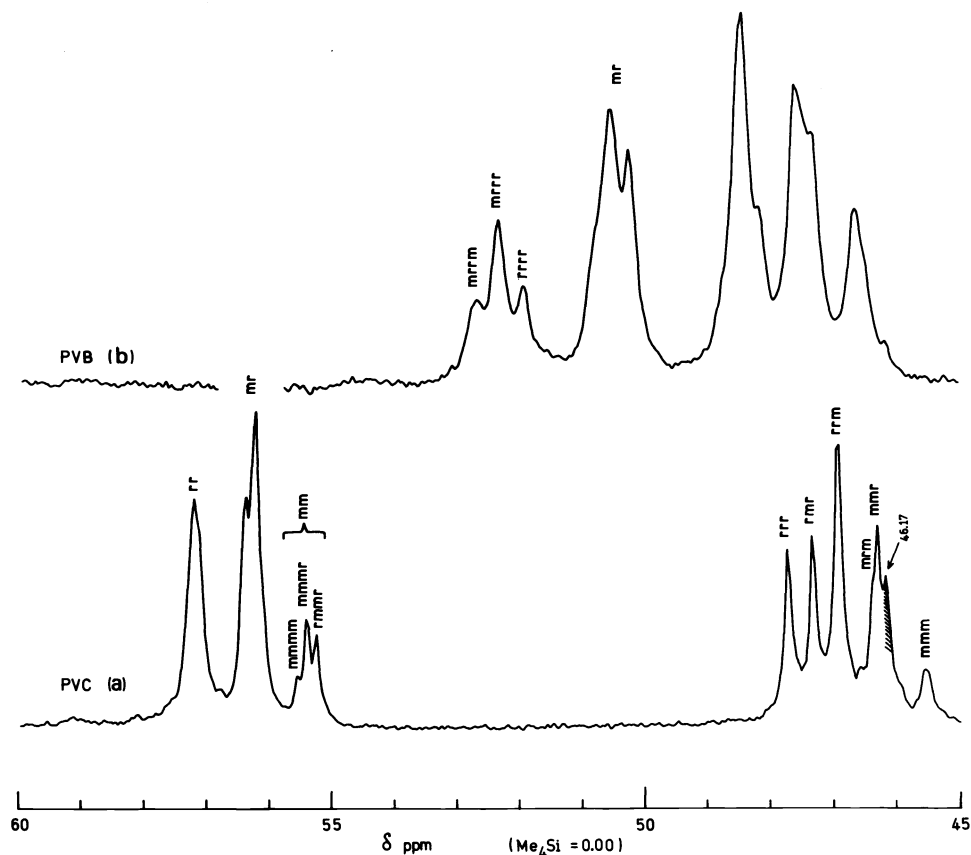


Fig. 3. 22.6 MHz Carbon-13 spectra of poly(vinyl chloride) and poly(vinyl bromide) in 1,2,4-trichlorobenzene at 100°.

(b), as reported by Dr. Cais. In spectrum (a) the α -carbon (left) and β -carbon (right) resonances are well separated and the spectrum can be interpreted in a straightforward manner. Spectrum (b) is more complex and requires observation of the *meso* and *racemic* 2,4-dibromopentane models for a satisfactory interpretation.

The temperature dependence of the stereochemical configuration can be expressed as $\Delta H_{\text{meso}}^{\ddagger} - \Delta H_{\text{racemic}}^{\ddagger}$, which has the value 260 cal.-mol $^{-1}$ for poly(vinyl chloride) and 300 cal.-mol $^{-1}$ for poly(vinyl bromide). Polymerization in *n*-butyraldehyde increases the probability of syndiotactic propagation to a perceptible degree (15). This is demonstrated in Fig. 4 (14), which shows an Arrhenius plot of the configuration of poly(vinyl chloride) and poly(vinyl bromide). The points for the aldehyde-modified polymers fall well below the plots for the others. For vinyl chloride propagation, the presence of *n*-butyraldehyde is equivalent to lowering the polymerization temperature by ca. 120°.

Carbon-13 NMR is not always the best means for measuring stereochemical configuration. For example, the proton and ^{13}C spectra are quite ineffective in resolving steric sequences in poly(fluoromethylene), $(\text{CFH})_n$, but the ^{19}F spectrum (Fig. 5) exhibits quite rich detail to the pentad level spread over the unusually large range of nearly 20 ppm (16). The computer simulation in Fig. 5 is based on Bernoullian propagation with a P_m of 0.42. Since in this system asymmetric centers are being added two at a time to the growing chain, it is not necessary that a Bernoullian model be obeyed even though this is nearly universally found for free radical propagation. However, this seems to hold within experimental error.

The *cis*- and *trans*-1,2-difluoroethylene monomers yield identical polymers. The ^{19}F chemical shifts, like those of ^{13}C , can be rationalized on the basis of a *gauche* γ -effect model (17).

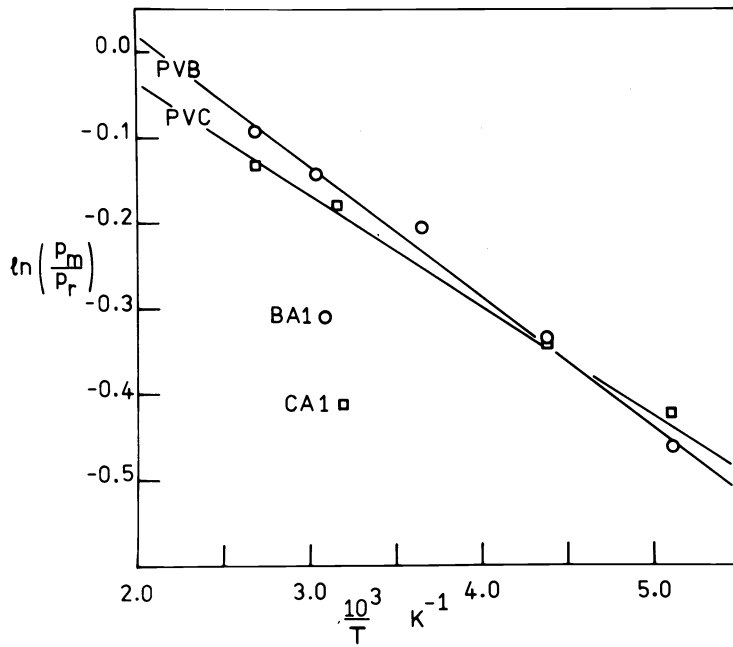


Fig. 4. Arrhenius plot of P_m/P_r [$= P_m/(1-P_m)$] for poly(vinyl chloride), O, and poly(vinyl bromide), \square . Points corresponding to polymers prepared in *n*-butyraldehyde are shown as CA1(PVC) and BA1(PVB).

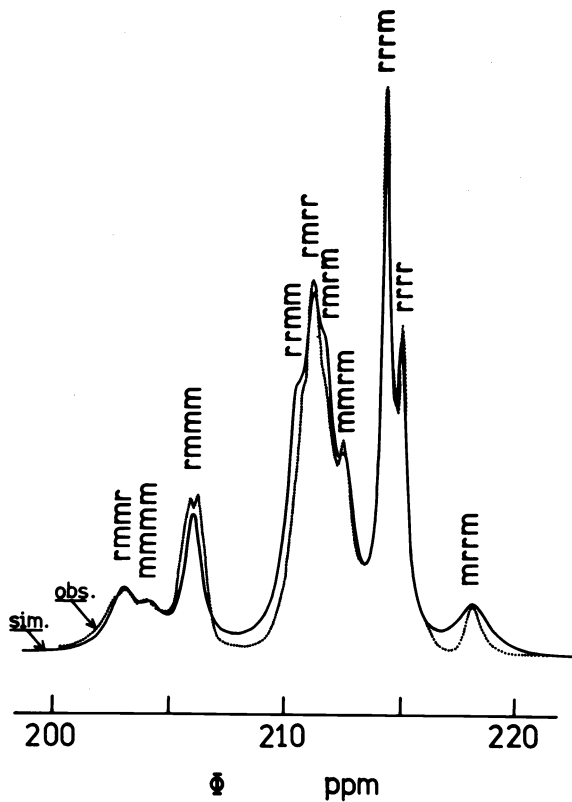


Fig. 5. Observed (.....) and computer simulated (—) 84.67 MHz ^{19}F spectra of polyfluoromethylene. The experimental spectrum was observed in acetone solution. In the simulated spectrum a P_m of 0.42 was assumed.

BRANCHING IN POLYETHYLENE AND POLY(VINYL CHLORIDE)

It is now well established (18) that branching can be observed in detail in polyethylenes by ^{13}C NMR and, under proper conditions, can be quantitatively measured. In Fig. 6 is shown the 50 MHz carbon-13 spectrum of a typical high pressure polyethylene (19), observed by Mr. F. C. Schilling. The observed composition is shown in Table 1.

Table 1. Branch Composition of High Pressure Polyethylene; $\bar{M}_n = 18,400$; $\bar{M}_w = 129,000$.

Branch type	Branches per 1000 CH_2 groups
ethyl	2.5
<i>n</i> -propyl	0.0
<i>n</i> -butyl	10.9
<i>n</i> -amyl	3.7
"long" ($\geq \text{C}_6$)	4.5
Total	21.6

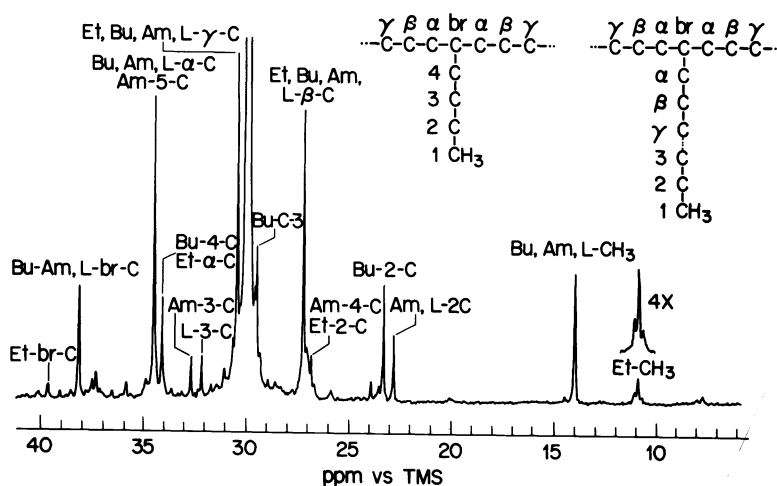


Fig. 6. 50 MHz Carbon-13 spectrum of high pressure polyethylene, observed in 1,2,4-trichlorobenzene at 110° (F. C. Schilling).

The dominant butyl and amyl branches are presumed to be formed by intramolecular chain transfer or "backbiting." The origin of ethyl branches is not certain. There are clearly spectral complications not observed in ethylene-butene-1 copolymers (20,21). The resonance at 39.5 ppm for the branch carbons of isolated ethyl branches is much smaller than the corresponding methyl intensity near 11 ppm. There are a dozen or so small unassigned resonances in the 37-39 ppm branch carbon region, and the ethyl branch methyl carbon resonance is clearly composed of a number of overlapping peaks. The Roedel (22) mechanism for short branch formation has been extended by Willbourn (23) to account for the formation of ethyl branches and could at least partially account for the complexity of their NMR spectrum, although not so intended. These reactions are summarized in Fig. 7. The presence of isolated ethyl branches, the content of which is evidently variable but not zero, is not accounted for by these mechanisms but may simply result from backbiting via a four-membered cyclic transition state. The absence of propyl branches, however, is entirely puzzling.

Branching in poly(vinyl chloride) can be determined by carbon-13 NMR, but so far not on the polymer itself, the spectrum of which is very much complicated by configurational sequences, as we have seen. It is advantageous to abolish these complexities by reductively dehalogenating the polymer with lithium aluminum hydride (24-26) or preferably with the more convenient and effective reagent tri-*n*-butyltin hydride (27). The resulting hydrocarbon is then examined in the same manner as polyethylene. In Fig. 8a is shown the 25 MHz spectrum of reduced poly(vinyl chloride) prepared at 100° ; for the reduced polymer $\bar{M}_n = 5600$ and $\bar{M}_w = 11900$. The principal short branch (2-3 per 1000 main chain carbons) is CH_3 , with a smaller frequency of ethyl, butyl, and long branches. By reduction with (*n*-butyl) $_3\text{SnD}$ each Cl atom is replaced by D instead of H. The positions of the chlorine atoms in the original structure can be established because each D splits the resonance of the directly bonded carbon into a 1:1:1 triplet ($J_{\text{CD}} = 19.0$ Hz). There is also a shielding effect of about 0.5 ppm. (Very small resonances essentially disappear, another useful clue.) These features can be observed in the spectrum shown in Fig. 8b, which represents the same poly(vinyl chloride) as in (a). The bottom (low gain) spectrum shows the singlet resonance of the main chain CH_2 carbons and the triplet of the CHD carbons. The upper spectrum at higher gain reveals that the methyl branches are CH_2Cl groups in the original polymer. By observations on a polymer from vinyl chloride- α -D it has been established (28) that the methylene carbon of the chloromethyl branch arises from the β -carbon of the monomer and that the mechanism suggested by Rigo *et al.* (29) is correct (see below).

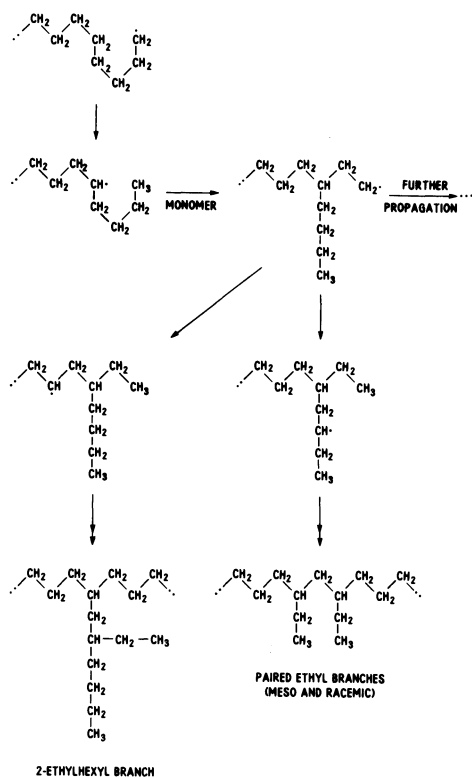


Fig. 7. Branch formation in high pressure polyethylene.

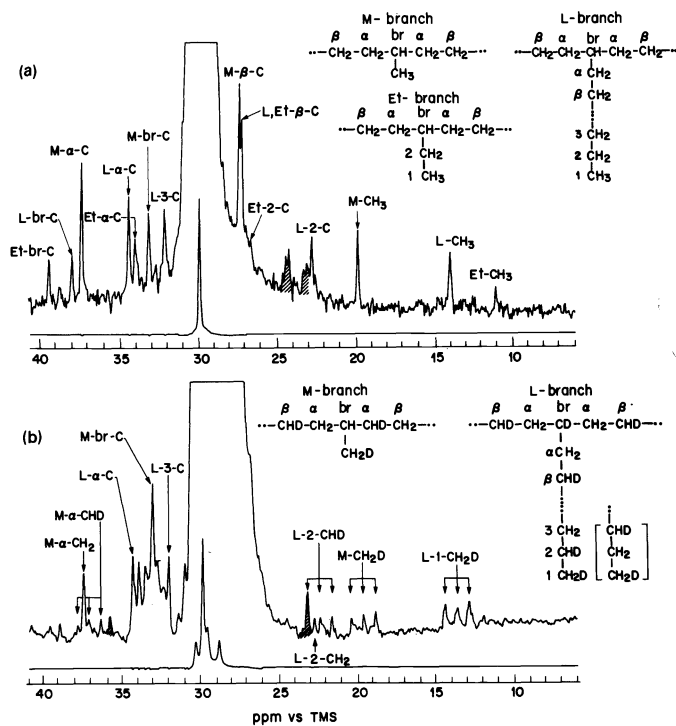


Fig. 8. 25 MHz Carbon-13 spectra of poly(vinyl chloride) reduced with (a) Bu_3SnH and (b) Bu_3SnD ; observed in 1,2,4-trichlorobenzene solution at 110° (F. C. Schilling).

Careful analysis of the spectra in Fig. 8 has led to the identification of the branches and chain ends shown in Fig. 9. It is noteworthy that tertiary chlorine atoms are present at several points. Since tertiary chlorine is known to be highly labile (30) this finding strongly suggests that these structures may be a major contributor to the thermal instability of poly(vinyl chloride). One of the principal purposes of this work is to identify such weak points.

The formation of chloromethyl branches and the occurrence of 1,2,4-trichloro and 1,3-dichloro chain ends provide important information concerning the polymerization process. The reactions which have been deduced by Dr. Starnes in our laboratory are shown in Fig. 10. The occasional head-to-head addition (b) results in a primary radical which rearranges (c) by a 1,2 chlorine migration, the Rigo mechanism (29). This radical mainly propagates further, leading to chloromethyl branch formation (d-i), but may also undergo β -scission (d-ii) to give a terminal chloroallyl group and a free chlorine atom. The chlorine atom then initiates another chain (e). Some chains are terminated by transfer involving the removal of hydrogen atoms (f); if this removal occurs from another polymer chain, the new radical site will lead to the formation of a long branch.

The validity of the mechanism requires the occurrence of terminal chloroallyl groups and these have not been observed. Starnes *et al.* (31) have proposed that such groups in the presence of the tributyltin hydride will be reduced and cyclized to terminal ethylcyclopentyl groups (Fig. 9), for which evidence is found in the C-13 spectrum.

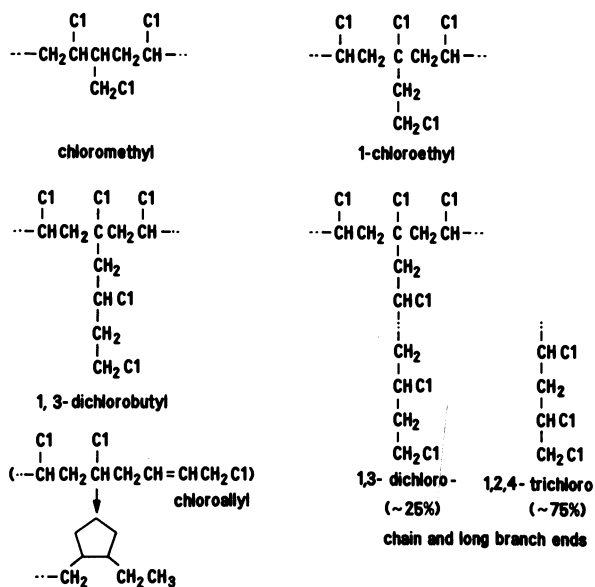


Fig. 9. Branches and chain ends in poly(vinyl chloride).

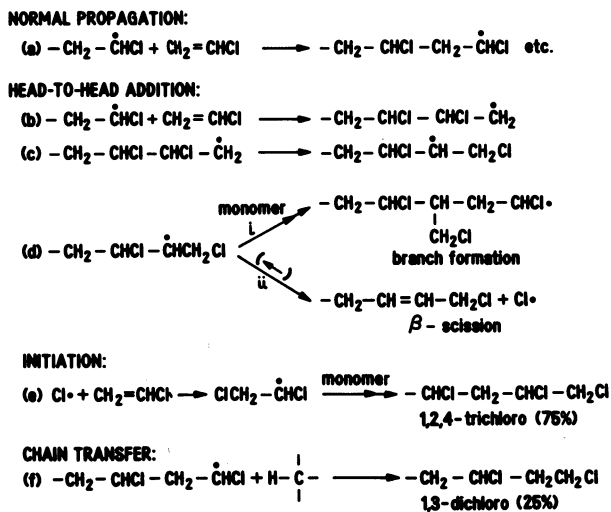
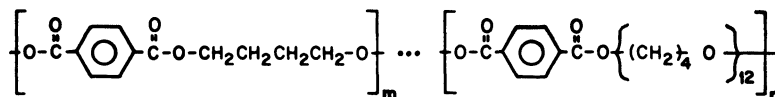


Fig. 10. Initiation, propagation, chloromethyl branch formation, and chain transfer in the polymerization of vinyl chloride.

1-Chloroethyl and 1,3-dichlorobutyl branches may be supposed to arise by hydrogen shifts from chlorine-bearing carbons, i.e., backbiting reactions parallel to those occurring in ethylene polymerization. When polymerization occurs in a solvent, the formation of 1,3-dichlorobutyl branches, normally scarcely observable, is markedly enhanced but ethyl branch formation is not similarly affected (32).

SOLID STATE ^{13}C NMR STUDIES OF SEGMENTED POLYMERS

Hytrel thermoplastic elastomers of duPont are segmented copolymers prepared in a range of compositions of m tetramethylene terephthalate hard units and n poly(tetramethyleneoxy) terephthalate soft units, that are assumed to be random in distribution (33). Physical chemical studies have shown that these polymers have a morphology consisting of continuous and interpenetrating crystalline and amorphous phases (34), rather than the discrete and ordered domain structure seen for other segmented copolymers (35).



Dr. Jelinski in our laboratory has studied Hytrel systems by solid state ^{13}C NMR and has shown that this technique can provide information concerning the nature of phase separation in these segmented copolymers, and concerning molecular motion in both the mobile (36) and rigid domains (37).

MOBILE DOMAINS

The carbons comprising the mobile domains in Hytrel samples containing from 0.80 to 0.96 mole fraction hard segments can be observed selectively using low power proton decoupling (scalar decoupling; $\gamma\text{H}_2/2\pi = 4$ kHz) and a standard $90^\circ - \tau$ pulse sequence. Representative spectra are shown in Fig. 11, (a)-(d). The peak centered at 29 ppm is

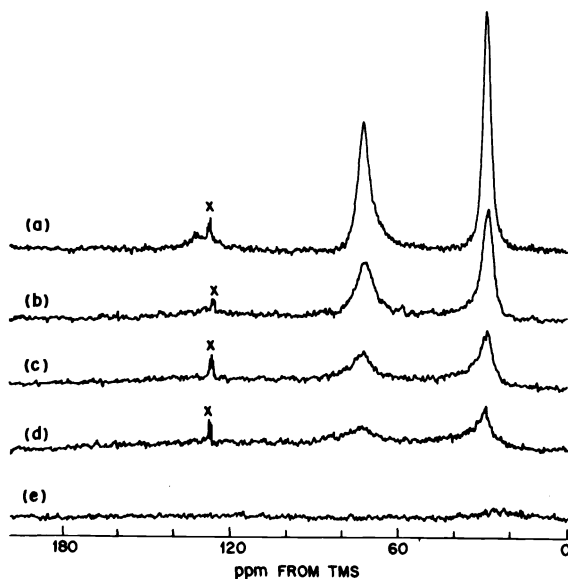


Fig. 11. Comparison of scalar decoupled ($\gamma\text{H}_2/2\pi = 4$ kHz) 50.3 MHz ^{13}C NMR spectra of Hytrel containing (a) 0.80; (b) 0.87; (c) 0.94; and (d) 0.96 mole fraction hard segments, with the spectrum of poly(butylene terephthalate) (e). All spectra were obtained at 34°C under identical conditions.

due to the $-\text{CH}_2-$ carbons flanked by methylene units on either side; the peak at 73 ppm arises from the $-\text{OCH}_2-$ carbons. Spin-counting indicates that all of the soft segment carbons and ca. 10% of the hard segment carbons contribute intensity to these scalar decoupled spectra. The additional signal intensity occurs primarily in the protonated aromatic carbon region, and apparently arises from hard segment units which are too short to crystallize. In contrast, the poly(butylene terephthalate) homopolymer has no discernible peaks under the same spectral accumulation conditions (Fig. 11 (e)). These experiments indicate that all soft segment carbons in Hytrel undergo motions which are rapid compared to the dipolar interaction (ca. 10^5 s^{-1}). However, the following experiment suggests that these motions are not isotropic. Magic angle sample spinning, in conjunction with scalar decoupling and a $90^\circ - \tau$ pulse sequence, causes an approximately four-fold reduction in the linewidths for the soft segment aliphatic carbons, indicating that the primary sources of line broadening in these spectra are residual dipole-dipole interactions and chemical shift anisotropy. With the sources of line broadening thus established, the linewidths can be interpreted in terms of phase separation and

angular range of reorientation. The linewidths for both types of soft segment aliphatic carbons are a linear function of the average hard block length of the polymer, indicating that increasing hard segment content restricts the angular range over which soft segment reorientation can take place. Further, the linear relationship between the average hard block length and the linewidth suggests that the distribution of hard and soft segments is random. The soft segment carbon linewidths are nearly independent of temperature over an approximately 80° range.

The relaxation parameters (T_1 and NOE) of the soft segment carbons can be interpreted in terms of rate of motion. The T_1 values for both types of aliphatic soft segment carbons are *ca.* 0.2 s at 50.3 MHz and 34°C. These T_1 values are independent of the hard segment content of the polymer but increase with increasing temperature and increasing magnetic field strength, indicating that the motions for these carbons are on the short correlation-time side of the T_1 curve. The NOE values for the two types of aliphatic carbons are also independent of the hard segment content of the polymer.

These results again support the conclusion that the angular range of reorientation of the soft segment carbons is inversely related to the hard segment content of the polymer, but that the rate of these motions is independent of the amount of hard segment present. These findings are consistent with a model for Hytrel structure in which there is phase separation with negligible mixing of the two phases at the domain boundaries.

RIGID DOMAINS

Various combinations of dipolar decoupling ($\gamma H_2/2\pi \approx 45$ kHz), cross polarization, and magic angle spinning (MAS) can be used to study the rigid domains in Hytrel. The proton-enhanced static powder spectrum of a Hytrel sample containing 0.96 mole fraction hard segments is shown in Fig. 12(a) and the corresponding proton-enhanced, magic angle

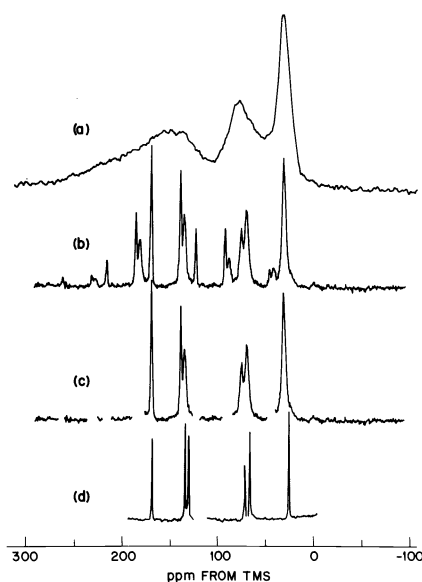


Fig. 12. 50.3 MHz ^{13}C spectra of Hytrel containing 0.96 mole fraction hard segments. (a) Proton-enhanced, dipolar decoupled static spectrum; (b) same as (a) but with magic angle spinning (MAS) at 2.3 kHz; (c) spectrum (b) with sidebands deleted; (d) solution spectrum in *m*-cresol; resonances artificially broadened and solvent peaks deleted.

spinning spectrum in Fig. 12(b). In Fig. 12(c) the sidebands have been removed. The chemical shifts in the solid state spectrum are readily assignable by comparison with the solution spectrum (Fig. 12(d)). In order of increasing shielding the resonances are assigned to the carbonyl, nonprotonated aromatic, protonated aromatic, soft segment $-\text{OCH}_2-$, hard segment $-\text{OCH}_2-$, and overlapping hard and soft segment central $-\text{CH}_2-$ carbons. The spectrum in Fig. 12(b) shows that resonances unique to the hard and soft segments can be resolved using dipolar decoupling and magic angle spinning.

The range of motions present in these polymers is illustrated by the series of dipolar decoupled, magic angle spinning spectra shown in Fig. 13. These spectra were obtained as a function of the pulse repetition rate, using a standard $90^\circ - \tau$ pulse sequence without Overhauser enhancement. At a 2 s repetition rate (Fig. 13(d)) the intensities for all of the aliphatic carbons have already attained nearly their full intensity, whereas the carbonyl and aromatic resonances require much longer pulse repetition times to reach full intensity. These results indicate that the T_1 values for the protonated aromatic and the aliphatic carbons differ by at least an order of magnitude. In addition, these results indicate that the aliphatic carbons of the hard segment units have short T_1 values, suggesting that the aliphatic carbons which reside in the rigid domains have substantial motional freedom.

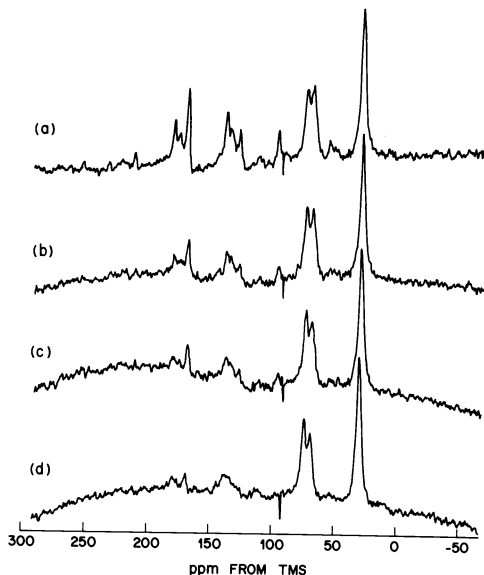


Fig. 13. Dipolar decoupled, Overhauser-suppressed 50.3 MHz ^{13}C NMR spectra of Hytrel containing 0.96 mole fraction hard segments. These spectra were obtained with MAS at 2.1 kHz using a standard $90^\circ - \tau$ pulse sequence, with pulse repetition rates (a) 30 s; (b) 6 s; (c) 4 s; (d) 2 s.

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