

CHARACTERIZATION OF COPOLYMERS BY NMR SPECTROSCOPY

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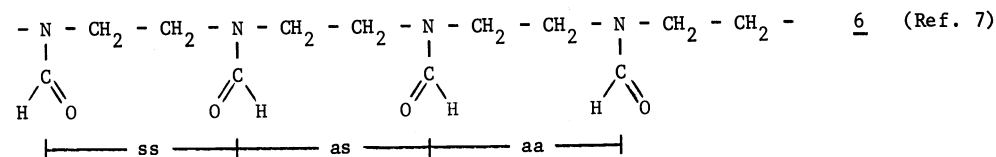
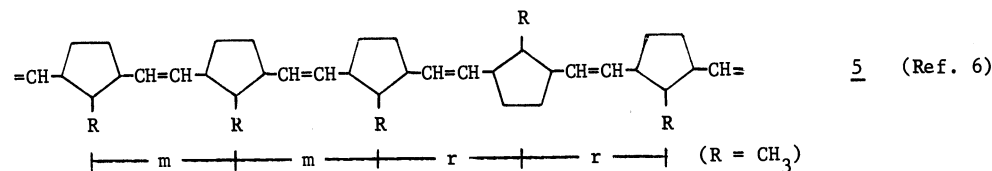
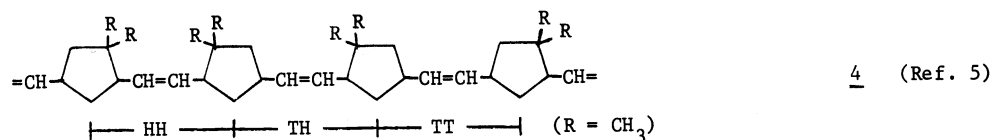
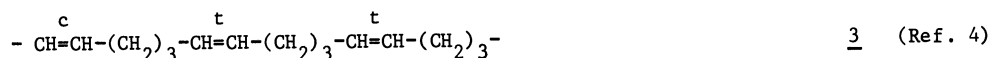
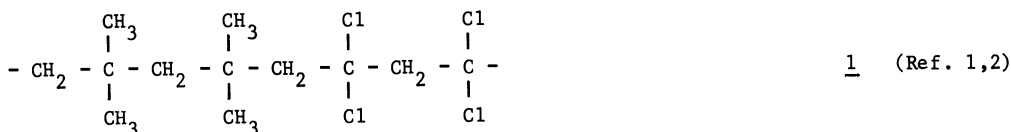
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Abstract - Some illustrative examples are given of the use of NMR to detect and determine quantitatively the various kinds of structure that can be encountered in copolymers. In this context "copolymer" has been interpreted to mean any copolymer-type structure, whether produced from a single monomer, from two monomers, from a racemic mixture of enantiomers, or by partial reaction of a homopolymer.

INTRODUCTION

Over the past 25 years it has been amply demonstrated that NMR spectroscopy is by far the most powerful tool for determining the chemical microstructure of polymers, i.e. the detailed sequence and stereochemical relationship of structural units in the polymer chain.

The effects which may be observed are of a number of kinds. Pairs of units, known as dyads, may differ in their composition as in 1, in their mode of enchainment as in 2, 3 and 4, in their configuration as in 5, or in their conformation as in 6.



In 3 the double bonds may be cis or trans; in 4 the methyl substituents may be oriented so as to give head-head (HH), head-tail (HT), or tail-tail (TT) dyads; in 5 the dyads may have a meso (m) or racemic (r) structure; and in 6 there are two possible orientations for each formyl group giving rise to syn-syn (ss), anti-syn (as) and anti-anti (aa) dyads.

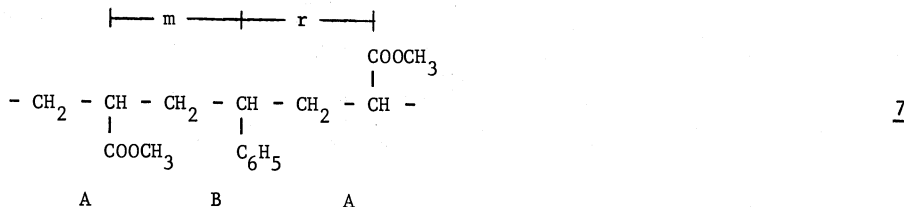
All these types of dyad give rise to distinct chemical shifts in the ^1H or ^{13}C NMR spectra. Indeed there is frequently fine structure corresponding to longer sequences of units (triads, tetrads, pentads, hexads and even heptads). A structural change at one point in a polymer molecule usually causes a detectable movement in the chemical shift of a nucleus which is four bonds away (δ effect) and often when the nucleus is separated by five or even six bonds (ϵ and ζ effects). For example, in the all-trans polymer 5, both the methyl carbon and the ring carbons attached to the double bonds are sensitive to triad structure (mm, mr, rr), corresponding to a ζ effect (Ref. 6). Again, in copolymers of 1,3,5-trioxane with 1,3-dioxolane, containing oxyethylene units E distributed amongst an excess of oxymethylene units M, all those M-centred pentads which are present in significant amount, namely MEMEM, MMEMM, EMMEM, MMMMM, MMMME and EMMME, show distinct chemical shifts in the ^{13}C NMR spectrum. For the MMM-centred pentads this means that the chemical shift is sensitive to structural changes at a distance of 5 bonds. Partial heptad sensitivity can be achieved by the addition of a lanthanide shift reagent to the sample (Ref. 8).

Copolymers containing two or more of the structural features illustrated by 2 to 6 may have extremely complex NMR spectra, but, conversely, if these can be unravelled and the peaks assigned, a very large amount of structural information becomes available, from which deductions may be made about the mechanism of polymerization.

^1H NMR spectra were historically the first to be obtained and are still of value in certain situations, but today ^{13}C NMR spectra usually provide the most detailed information. Some applications of ^1H NMR spectra to the study of copolymers may be found in the book by Bovey (9) who gives a detailed account of the various types of configurational sequences which may occur within compositional dyads and triads. More recent accounts, dealing with ^{13}C NMR of copolymers, have been given by Koenig (10) and Ebdon (11); also see Klesper (12). Other nuclei, such as ^{15}N , ^{19}F , ^{29}Si and ^{31}P can be used in appropriate cases.

It is well known that the behaviour of many copolymerization systems, so far as composition is concerned, may be described in terms of four propagation steps and two reactivity ratios, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, where k_{12} represents the rate constant for addition of monomer M_2 to the active centre P_1 , which has previously added M_1 ; likewise for k_{11} , k_{22} and k_{21} . When $r_1 = 1/r_2$ the relative reactivity of the two monomers is the same when reacting with P_1 as it is when reacting with P_2 and the copolymerization is said to be ideal. It is then possible to describe the copolymerization in terms of a single parameter r_1 , and the probability of various compositional sequences are determined by Bernoullian statistics. If however $r_1 r_2 \neq 1$, two parameters are required to describe the system, corresponding to first-order Markov statistics. If this model does not fit the observed dyad sequence distribution a more elaborate mechanism must be postulated. For example one may postulate penultimate unit effects on the reactivity of P_1 and P_2 , or propose that the chain carriers are complexed in some way. This will require the introduction of additional parameters and permit a fit to be made with the observed compositional dyad distribution. If higher order sequences (triads, tetrads) can be measured quantitatively their relative proportions can be compared with those predicted by the two-parameter model.

Similar considerations hold for configurational sequences. These can sometimes be described in terms of Bernoullian statistics. For example if the probability of an m placement is σ_m then for an atactic polymer ($\sigma_m = \sigma_r = 0.5$), the proportions of mm, mr and rr dyads are 0.25, 0.50 and 0.25 respectively. Sometimes, however, the probability of an m placement depends on the configuration of the previous unit and then it is necessary to introduce a second parameter (first-order Markov statistics). In copolymers it is sometimes possible to determine by NMR the proportions of configurational dyads containing two types of monomer unit, e.g. methyl acrylate and styrene, 7.



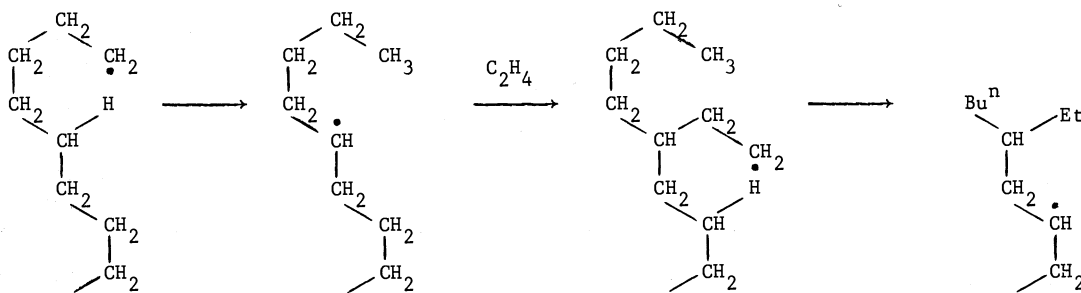
The cotacticity, σ_{mAB} , is the probability that an AB compositional dyad has an m configuration. A full discussion of statistical treatments applicable to homopolymers and copolymers may be found in the book by Randall (13) and in Ref. 9-12.

In this short account we shall consider briefly some illustrative examples of copolymer studies under four main headings: copolymer-type structures formed by the polymerization of a single monomer, copolymers made from two distinct monomers, copolymerization of enantiomers of cyclic monomers, and copolymers made by partial reactions of homopolymers.

COPOLYMERS MADE FROM SINGLE MONOMERS

Polyethene

It is well known that polyethene made by the high pressure process contains a small proportion of short-chain branches. It is therefore a type of copolymer, the branches being responsible for its lower density and lower crystallinity compared with linear polyethene made by the Ziegler-Natta process. These branches were first detected by the infrared absorption originating from the methyl groups at the end of the branches. ^{13}C NMR spectroscopy allows a much closer investigation of the length and frequency of the branches. Ethene can be copolymerized with various olefins by the Ziegler-Natta method to yield reference polymers with known branches (Ref. 14,15). In principle it is possible to distinguish linear branches of up to 10 carbon atoms in length. The results of such investigations show that in a typical "high-pressure" polyethene there are 1.2 ethyl groups/1000 CH_2 , 5.2 n-butyl groups/1000 CH_2 , 1.5 n-amyl groups/1000 CH_2 and 0.9 longer branches/1000 CH_2 . However the degree and distribution of branches varies from one polymer to another (Ref. 16). It is thought that the dominant n-butyl branches are produced by an intramolecular hydrogen-transfer reaction (the Roedel back-biting mechanism) involving the favoured 6-membered cyclic transition state. The ethyl groups are probably the result of a further back-biting reaction after the addition of a single ethylene molecule.



Further details can be found in Ref. 10.

Poly(vinyl chloride) (Ref. 17,18,19)

Poly(vinyl chloride) contains various labile structural irregularities which can initiate dehydrochlorination on heating. These anomalous structures have only recently been identified by ^{13}C NMR. Reduction of the polymer with Bu_3SnH so as to replace some or all of the chlorine atoms by hydrogen, and comparison of the ^{13}C NMR spectra of these polymers with those of model compounds has allowed the identification of the following side groups in poly(vinyl chloride): $-\text{CHClCH}_3$, $-\text{CHClCH}_2\text{CHClCH}_3$, $-\text{CHClCH}_2\text{CHClCH}_2\text{Cl}$, $-\text{CH}_2\text{CHClCH}_2\text{CH}_2\text{Cl}$, etc. A typical polymer is found to contain about 1 C_4 , 0.6 C_2 and 2.8 C_1 branches per 1000 carbon atoms. Mechanisms for the formation of the various structural defects have been put forward.

Poly(vinyl fluoride) (Ref. 20)

Commercial poly(vinyl fluoride) is regioirregular, i.e. it contains a small proportion (about 10%) of inverted monomer units. It may thus be regarded as a copolymer in which the monomer may add either its head (CHF) or more generally its tail (CH_2) to the growing ends. A perfect head-tail poly(vinyl fluoride) may be obtained indirectly by polymerization of $\text{CH}_2=\text{CFCl}$ or $\text{CHF}=\text{CHCl}$ followed by radical-catalysed dechlorination of the polymer using Bu_3SnH . This has allowed the first correct analysis of the ^{19}F NMR spectrum of the commercial polymer as shown in Fig. 1. The configurational sequence distribution is Bernoullian ($\sigma_m = 0.46$) with complete resolution of the four mr -centred pentads. The regio-sequence distribution, however, obeys first-order Markov statistics, in which the two reactivity ratios, corresponding to the two pairs of propagation reactions, are 0.76 and 0.033.

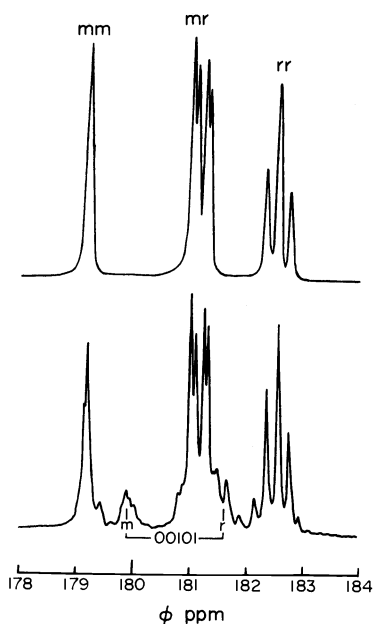


Fig. 1. ^{19}F NMR spectra of regioregular PVF (top) and commercial PVF (bottom). OOIOI denotes the structure $-\text{CH}_2\text{CH}_2\text{CHFCH}_2\text{CHF}-$. "Normal" addition is represented by $-\text{O}1 + \text{O}1 \rightarrow -\text{O}1(\text{TH})$. Reproduced with permission from Ref. 20.

COPOLYMERS MADE FROM TWO MONOMERS

The number of such copolymers which have been investigated by NMR is very large indeed and here we can do no more than select a few examples.

Ethyl acrylate (EA)/butyl methacrylate (BMA) copolymers (Ref. 21)

This system provides a simple example of the use of ^{13}C NMR to determine the composition of a copolymer, which would be difficult to achieve by other methods. The most convenient peaks to use are those due to the OCH_2 carbons in the side chains, at 60.52 ppm (EA units) and 64.73 ppm (BMA units). The relaxation times T_1 for these two carbons are 0.2 and 0.1 s respectively, so that a pulse repetition time of 1 s does not result in any significant distortion of the relative intensities. The nuclear Overhauser enhancements (NOE) are also very similar, so that, in this case, there is no need to remove the Overhauser effect by gated decoupling.

The appearance of these peaks in the spectra of various copolymers prepared by radical initiation is shown in Fig. 2. The copolymerization is close to ideal, with $r_1 = 1/r_2 = 0.47$.

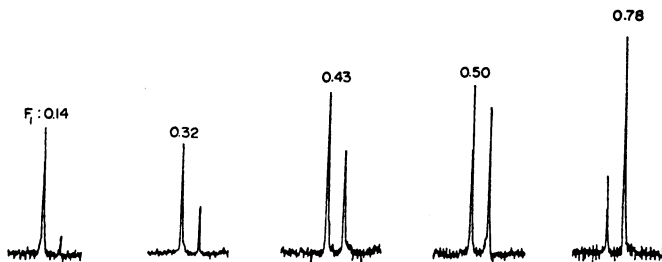


Fig. 2. The OCH_2 peaks in the ^{13}C NMR spectra of copolymers of ethyl acrylate (M_1) and butyl methacrylate (M_2). F_1 = mol fraction of M_1 units. Left-hand peak 64.73 ppm (M_2 units); right-hand peak 60.52 ppm (M_1 units). Reproduced with permission from Ref. 21.

Cyclopentene (M_1)/norbornene (M_2) copolymers (Ref. 22)

Ring-opened copolymers of cyclopentene and norbornene are readily prepared by initiation with $\text{WCl}_6/\text{Ph}_4\text{Sn}$ (1/2) in chlorobenzene solution. The chain carrier is thought to be a

metal carbene. The olefinic region of the ^{13}C NMR spectrum is shown in Fig. 3. The peaks

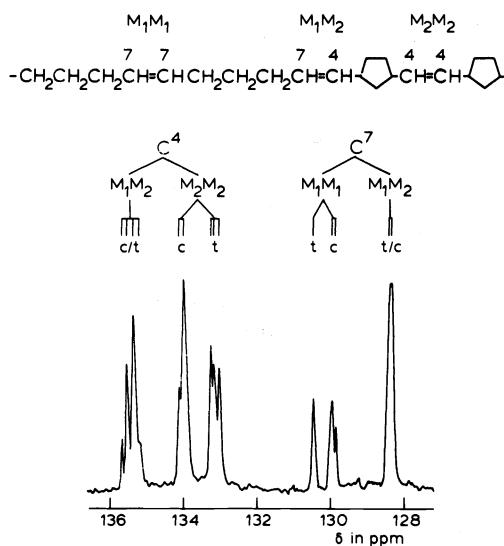


Fig. 3. Olefinic region in the ^{13}C NMR spectrum of a ring-opened copolymer of cyclopentene and norbornene, containing 33% 1-pentenylene units ($F_1 = 0.33$). Reproduced with permission from Ref. 22.

labelled M_1M_1 and M_2M_2 correspond to those seen in the spectra of the respective homopolymers. Two further sets of signals are seen, due to the two types of olefinic carbons in M_1M_2 dyads. The intensities of these are equal, as they should be if there is no distortion by differential T_1 or NOE effects. The fine structure is due to the fact that the double bonds may be cis or trans. The upfield movements of about 2 ppm for $\text{C}^4(M_1M_2 \rightarrow M_2M_2)$ and $\text{C}^7(M_1M_1 \rightarrow M_1M_2)$ correspond to γ -substitution effects in each case.

The dyad distribution, derived from the spectra of copolymers of different composition, made at 20°C and at relatively low conversion, is shown in Fig. 4. It may be seen that there is a close fit to a Bernoullian distribution. The system behaves ideally at 20°C , with $r_1 = 1/r_2 = 0.44$, but at -18°C the dyad distribution is decidedly blocky with $r_1 = 0.7$ and $r_2 = 5.8$. At the same time the cis double bond content in each type of dyad rises. These results have been interpreted in terms of two distinct types of propagating species: those in which the last-formed double bond has decoordinated from the metal site at which it was formed, and those in which this double bond has not yet left the metal site. The participation of the latter also accounts for the blocky cis/trans double bond distribution (Ref. 33).

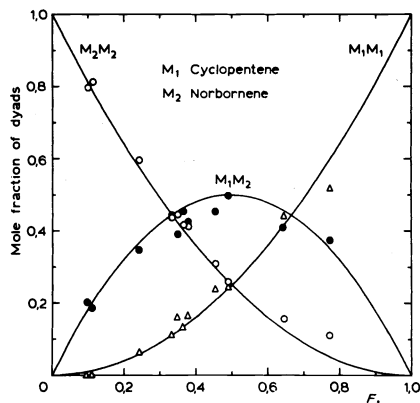
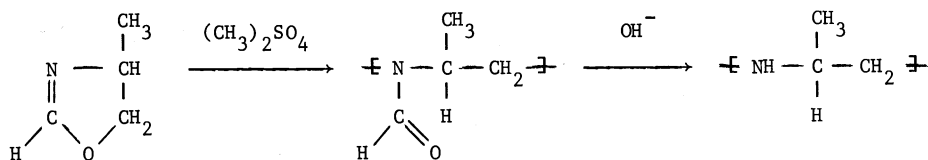


Fig. 4. Distribution of compositional dyads in copolymers of cyclopentene (M_1) and norbornene (M_2) made at 20°C with $\text{WCl}_6/\text{Ph}_4\text{Sn}$ catalyst system. The curves are those calculated for a Bernoullian distribution. F_1 = proportion of M_1 units in the copolymer. Reproduced with permission from Ref. 22.

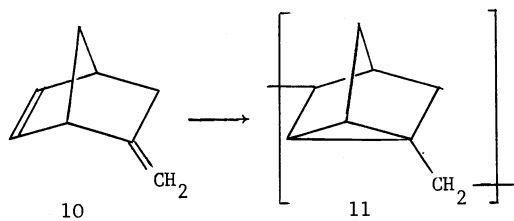
r dyads in these and other polysulfides have been achieved through the synthesis of predominantly isotactic polymers, either by polymerization of a single antipode using any anionic catalyst, e.g. $\text{Et}_2\text{Zn}/\text{H}_2\text{O}$, or by polymerization of racemic monomer with particular catalysts, e.g. cadmium tartrate, where partial (Ref. 28) or complete enantioselection occurs (Ref. 29).

Another example of random copolymerization of enantiomers is provided by the cationic polymerization of (R,S)-4-methyloxazoline (Ref. 30).



The resulting polymer may be hydrolysed to polyiminopropene whose ^{13}C NMR spectrum in acidified D_2O shows two equal lines for CH, two equal lines for CH_3 and three lines (1:2:1) for CH_2 . The spectrum of the isotactic polymer, made from optically active monomer, shows single lines for each carbon and enables assignments to be made for the atactic polymer. The triad sensitivity of CH_2 corresponds to an effect at a distance of four bonds from the more remote chiral centre.

Random copolymerization of enantiomers also occurs in the cationic cyclopolymerization of (R,S)-5-methylenebicyclo[2.2.1]hept-2-ene 10 (Ref. 31).



The ^{13}C NMR spectrum of this polymer is shown in Fig. 6.

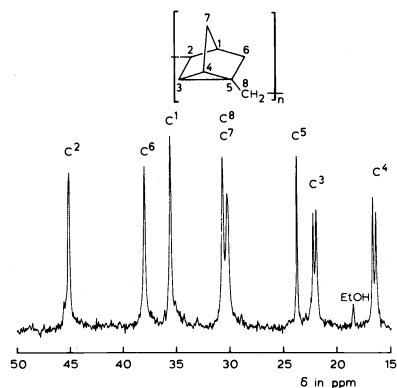


Fig. 6. ^{13}C NMR spectrum of 11. m/r splittings: C^2 0.08; C^3 0.30; C^4 0.30 ppm. Reproduced with permission from Ref. 31.

The C^2 , C^3 and C^4 signals are each split into two equal lines. It is likely that one mode of linkage is preferred between C^2 and the adjacent C^8 , so that the pairs of lines are to be attributed to m and r dyads in which successive tricyclic units may be derived either from the same or from opposite enantiomers.

Enantioselection and enantioelection

In the cases of random copolymerization of enantiomers just discussed there is no steric control at the growing chain end. There are, however, other cases where the chirality at or

near the growing chain end can influence the choice of enantiomer. When this chirality derives from that originally present in the monomer there are inevitably equal numbers of R-selective and S-selective reaction sites. The two enantiomers are then removed at equal rates but, because of the selectivity, a bias towards isotacticity or syndiotacticity may occur. One then speaks of "enantioselectivity". For example, in the polymerization of (R,S)-methylthiirane with $\text{Et}_2\text{Zn}/\text{H}_2\text{O}$ there is a strong bias towards isotacticity ($\sigma_m = 0.79$). The product is essentially a block copolymer of the two enantiomers with a structure represented by $\text{-RRRRSSSSRRRRSSSS-}$. With other catalysts such as cadmium allyl thiolate at 0°C (Ref. 32) or cadmium tartrate (Ref. 29) the bias is more or less complete and the polymer then consists essentially of a racemic mixture of poly R and poly S, which can be separated to some extent on a column of an optically active polymer (Ref. 33).

Other examples of enantioselectivity occur in the polymerizations of the N-thiocarboxy-anhydrides of D,L-leucine and D,L-valine, initiated by amines or by potassium tert-butyrate. The tacticity of the resulting poly(D,L-leucine)s and poly(D,L-valine)s may be determined from the carbonyl region in the ^{13}C NMR spectra. Formation of isotactic sequences is favoured, although the enantioselectivity is not very high, the average length of isotactic blocks never exceeding six repeat units (Ref. 34). In the polymerization of the D,L-N-carboxyanhydrides of these two amino acids, the L-L/L-D ratio in the polymers can vary from 4 to 0.2 depending on the mechanism (Ref. 35). The deviations from Bernoullian statistics are only slight so that there is no need to invoke helical secondary structure of the growing polymer chains to account for the stereospecificity.

"Enantioselectivity" describes the situation in which one enantiomer is preferentially polymerized, giving an optically active polymer, while the residual monomer has an ever-increasing optical purity with respect to the other enantiomer. In order to achieve enantioselection it is necessary to use a catalyst system containing a chiral ligand or a chiral additive or solvent, which somehow generates a reaction site which continually favours one of the enantiomers, so yielding a predominantly isotactic polymer.

Enantioselection has been demonstrated with the following cyclic monomers:

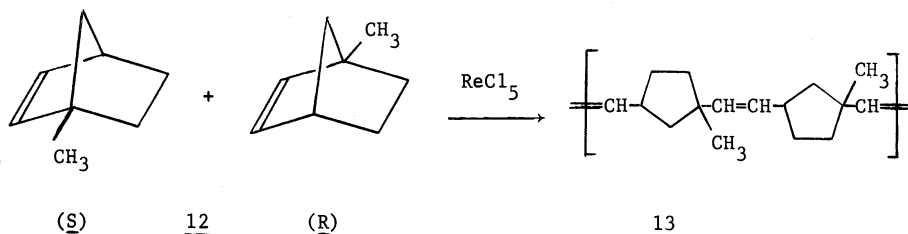
(R,S)-methyloxirane (Ref. 36), (R,S)-methylthiirane and other thiiranes (Ref. 37), and (R,S)- α -methyl- α -n-propyl- β -propiolactone (Ref. 38). $\text{Et}_2\text{Zn}/\text{R}^*\text{OH}$ is an effective catalyst system in all cases, where R^*OH represents a chiral alcohol. The most spectacular result has been achieved with (S)-1,1'-bi-2-naphthol as cocatalyst in the polymerization of (R,S)-methylthiirane, the electivity ratio reaching a value as high as 20. In the lactone polymer the ^{13}C NMR spectrum does not have any lines that are sensitive to tacticity.

Mention should also be made of the very high degrees of enantioselection that can be attained in the anionic polymerization of methacrylates at -78°C , e.g. (R,S)- α -methylbenzyl methacrylate, where the chiral centre is situated in the ester side chain. Sparteine (Ref. 39, 40,41), alcohols (Ref. 40) and 2,2'-diamino-6,6'-dimethylbiphenyl (Ref. 42) have all been used as chiral additives. After removal of the chiral side chains in the polymer and conversion to the methyl ester it is found that there is a correlation between the electivity ratio and the tacticity induced in the main chain (Ref. 40).

In the polymerizations of both (R,S)-methyloxirane (Ref. 36) and (R,S)-4-methylhex-1-ene (Ref. 43) with heterogeneous chiral catalyst systems it is found that there are two types of catalytic site present, one enantioselective yielding crystalline, optically active polymer, the other indiscriminating and yielding an amorphous, optically inactive fraction.

Alternating copolymerization of enantiomers

This is a special case of enantioselection. We have already mentioned that there is some tendency towards alternation in the polymerization of D,L-NCAs of certain amino acids under some conditions. What is believed to be the first example of perfect alternating copolymerization of enantiomers was reported recently (Ref. 44). This occurs in the ring-opening polymerization of (R,S)-1-methylbicyclo[2.2.1]hept-2-ene, 12, using ReCl_5 as catalyst. This gives an all-cis, all-head-tail, syndiotactic polymer 13.



The ^{13}C NMR spectrum of this polymer is shown in Fig. 7. It consists of two sharp olefinic

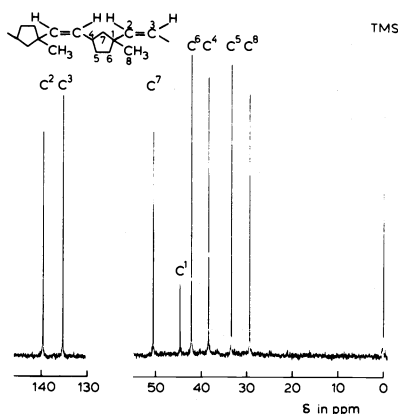
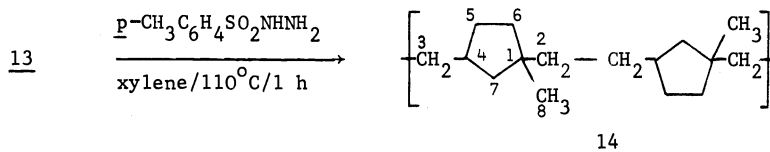


Fig. 7. ^{13}C NMR spectrum of the all-cis, head-tail, syndiotactic polymer of 1-methylbicyclo[2.2.1]hept-2-ene.

lines and six sharp upfield lines, with no trace of fine structure. This shows that the polymer must have a very regular structure. The positions of the lines are such as to indicate an all-cis, head-tail structure. The ^1H NMR spectrum has an olefinic doublet and triplet as expected for such a structure.

It is known that polymerization of other norbornene derivatives by ReCl_5 gives all-cis syndiotactic polymers (Ref. 5), but this does not constitute proof that polymer 13 is also syndiotactic. Proof was obtained by comparison of the ^{13}C NMR spectrum of the hydrogenated polymer 14 with those of known isotactic and atactic polymers. These can be produced by the polymerization of (+)- and (\pm)-12 respectively with OsCl_3 as catalyst to yield predominantly trans, head-tail polymers, which can then be hydrogenated as for 13.



The chemical shift of C^6 in the hydrogenated polymers turns out to be sensitive to the ring dyad structure (39.12 ppm m, 39.07 ppm r), the effect being transmitted through six bonds.

The syndiotacticity in the all-cis polymers made by ring-opening polymerization of norbornene derivatives is predictable assuming that the reaction is propagated by chiral metal carbenes which do not racemize between propagation steps (Ref. 5). Addition of monomer so as to form a cis double bond results in the formation of a metal carbene in which the chirality about the metal atom is opposite to that in the reactant metal carbene. The fact that the polymer has an all head-tail structure may be attributed to very strong steric hindrance to the formation of head-head cis double bond structures from monomer 12, which contains a quaternary carbon adjacent to the double bond. The consequence of this is that one chiral form of the metal carbene can react only with one enantiomer of the monomer while the mirror-image form of the metal carbene, produced in the reaction to form a cis double bond, can react only with the other enantiomer. Furthermore, the atacticity of the polymer of (\pm)-12 using OsCl_3 as catalyst indicates either that the metal carbene racemizes between each propagation step, or has an achiral structure.

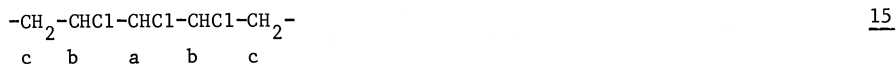
COPOLYMERS OBTAINED BY REACTIONS OF HOMOPOLYMERS

Some examples of such copolymers, most of which have been studied by NMR, are listed in Table 1. The partial hydrolysis of poly(methyl methacrylate) can yield random, blocky or alternating copolymers depending on the conditions, as shown by 220 MHz ^1H NMR (Ref. 45). The reverse partial esterification, whether done with diazomethane, diazotoluene or diazodiphenylmethane, gives essentially a random copolymer (Ref. 46).

TABLE 1. Some copolymers produced by secondary reactions of homopolymers

Initial homopolymer	Reactant	New units formed	Reference
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COOCH}_3 \end{array}$	KOH	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COOH} \end{array}$	45
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COOH} \end{array}$	$\text{CR}^1\text{R}^2\text{N}_2$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COOCHR}^1\text{R}^2 \end{array}$	46
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}$	$\text{Cl}_2/h\nu$	$\begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH}-\text{CH}-\text{CH}_2- \\ \quad \quad \\ \text{Cl} \quad \text{Cl} \quad \text{Cl} \end{array}$ and $-\text{CH}_2-\text{CCl}_2-$	47
$-\text{CH}_2\text{CH}=\text{CHCH}_2-$	$\underline{m}\text{-ClC}_6\text{H}_4\overset{\text{O}}{\parallel}\text{COOH}$	$-\text{CH}_2\overset{\text{O}}{\diagup}\text{CH}-\text{CHCH}_2-$	48
$-\text{CH}_2\text{CH}=\text{CHCH}_2-$	$\text{WCl}_6/\text{EtAlCl}_2(1/20)$	$-\text{CH}=\text{CHCH}_2\text{CH}_2-$	49
$-\text{CH}_2\text{CH}=\text{CHCH}_2-$	H_2/Pd	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	50,51
$-\text{CH}_2\text{CH}=\text{CHCH}_2-$	$\underline{p}\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHNH}_2$	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	51,52
$-\text{CH}_2\text{CH}=\text{CHCH}_2-$	$\text{CCl}_2(\text{NaOH}/\text{CHCl}_3)$	$-\text{CH}_2\overset{\text{CCl}_2}{\diagup}\text{CH}-\text{CHCH}_2-$	53
$-\text{CH}_2\text{CH}_2\text{NH}-$	CS_2	$-\text{CH}_2\text{CH}_2\overset{\text{N}}{\underset{\text{CS}_2\text{H}}{ }}-$	54

Lightly photochlorinated poly(vinyl chloride) gives initially three new groups of peaks in the ^{13}C NMR spectrum: (a) 66-70 ppm, (b) 58-60 ppm, and (c) 43-45 ppm. On the basis of the known substituent effects for chlorine the three regions can be assigned to carbons in structure 15.



Peak multiplicity seen for each carbon type arises from configurational isomerism in the chlorinated sequence 15. A new peak also appears at 89.5 ppm due to CCl_2 in isolated units ($-\text{CH}_2-\text{CCl}_2-\text{CH}_2-$) (Ref. 47).

Cis-1,4-polybutadiene gives a ^{13}C NMR spectrum with only two peaks, one in the olefinic region (~ 130 ppm) and one upfield (~ 28 ppm). After moderate epoxidation, the resulting copolymer has the spectrum shown in Fig. 8 (Ref. 48). Two new olefinic peaks appear, α and β , as well as two new CH_2 peaks γ and δ ; also a peak A at 56.5 ppm due to the oxirane ring carbons. The effect of the epoxidation is thus felt up to a distance of four bonds. The assignments of the peaks labelled α and β may be made on the basis of the effect of lanthanide shift reagents, the effect being greater for the carbon closer to the oxygen. Similar results have been obtained with trans-1,4-polybutadiene and with the analogous cis- and trans-1,4-polyisoprenes (Ref. 48).

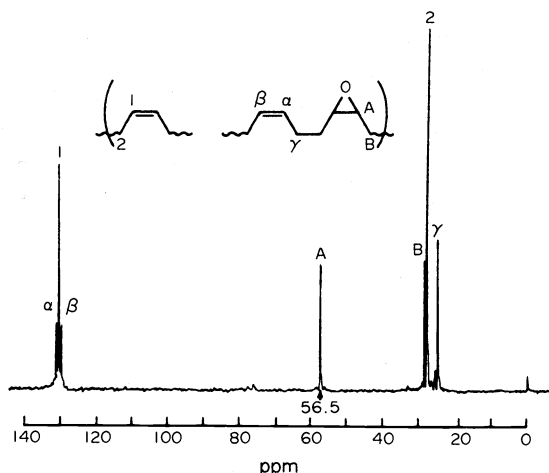


Fig. 8. ^{13}C NMR spectrum of partially epoxidized cis-1,4-polybutadiene. Reproduced with permission from Ref. 48.

In the ring-opening polymerization of cycloocta-1,5-diene with $\text{WCl}_6/\text{EtAlCl}_2$ as catalyst the initial product is cis/trans-1,4-polybutadiene. However if too much EtAlCl_2 is used the double bonds migrate by a secondary cationic reaction, giving rise to a copolymer-type structure containing units of the type $\text{CH}(\text{CH}_2)_n\text{CH}=\text{}$ ($n = 1, 2, 3$), which may be readily distinguished by ^{13}C NMR; see Fig. 9. Similarly with cyclopentene as starting material a copolymer with units having $n = 2, 3, 4$ is formed (Ref. 49). The unit with $n = 4$ cannot be obtained by direct polymerization of cyclohexene because the absence of ring strain makes the reaction thermodynamically impossible.

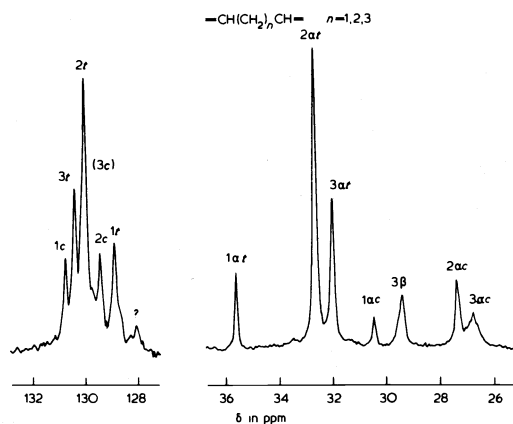


Fig. 9. ^{13}C NMR spectrum of ring-opened polymer of cycloocta-1,5-diene which has undergone a double bond shift reaction. The numbers above the peaks refer to the number n of CH_2 units in the unit $\text{CH}(\text{CH}_2)_n\text{CH}=\text{}$; c and t refer to cis and trans, α , β are positions with respect to the double bond. Reproduced with permission from Ref. 49.

The partial hydrogenation of 1,4-polybutadiene may be carried out either heterogeneously (Ref. 50,51) using H_2/Pd , or homogeneously (Ref. 51,52) using $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHNH}_2$ in xylene at 130°C . The distribution of double bonds in the product may be found by carrying out a total metathetic degradation with cis-oct-4-ene ($\text{WCl}_6/\text{Me}_4\text{Sn}$ catalyst) followed by GLC analysis of the degradation products. The homogeneous hydrogenation is found to occur at random along the chains, but with the heterogeneous reaction there appears to be simultaneous occurrence of random and blockwise processes leading to a non-negligible amount of quasi-polyethene.

In the reaction of CCl_2 with cis- and trans-1,4-polybutadienes the two partially reacted products are stereochemically distinct and the CCl_2 signal in the ^{13}C NMR spectrum is sensitive to compositional triad structure (cis: ABA 65.6, BBA 65.3, BBB 65.0; trans: ABA 66.9, BBA 66.6, BBB 66.2 ppm). The compositional distributions are in reasonable agreement with those expected from Bernoullian statistics when the reaction is carried out with aqueous NaOH , but are somewhat blocky when solid NaOH has been used (Ref. 53).

CONCLUSIONS

NMR spectra can be used to obtain a great deal of information about copolymer structure, especially concerning compositional, structural, and configurational sequences; also to discover whether the reactions of homopolymers occur at random or in a blockwise manner.

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