

Carbon-13 NMR in Polymer Science



Edited by
J. E. McGrath

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Carbon-13 NMR in Polymer Science

Wallace M. Pasika, EDITOR


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FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable since symposia may embrace both types of presentation.

PREFACE

Carbon-13 NMR is opening up new vistas in polymer chemistry. Analytical information on polymeric systems, information regarding their structural, dynamic, and polymerization characteristics, can be provided by C-13 NMR. In many instances C-13 NMR complements already familiar characterization techniques or allows characterization to be carried out more readily. In other instances, only C-13 NMR can provide answers.

While organizing the symposium upon which this volume is based, the Macromolecular Science Division of the Chemical Institute of Canada attempted to include papers representing a wide range of applications for using Carbon-13 NMR to characterize polymers and to have both synthetic and biomacromolecular systems considered.

Many contributed to the success of the symposium. The executive and members of the Macromolecular Science Division thank the following firms for fiscal support: Polysar Limited; Abitibi Paper Company; Reichhold Limited; Xerox Research Centre of Canada Limited; Varian Associates of Canada; Glidden Company; Domtar Limited; DuPont of Canada; Shell Canada; Gulf Oil Canada; and the Dunlop Research Centre. A special vote of thanks is extended to the speakers at the symposium and to the authors for their excellent presentations and for their cooperation in "putting it together." J. Comstock of the American Chemical Society showed understanding and patience in bringing this volume to print.

Laurentian University
Sudbury, Ontario
Canada
March 26, 1979

WALLACE M. PASIKA

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The Study of the Structure and Chain Dynamics of Polysulfones by Carbon-13 NMR

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Sulfur dioxide does not homopolymerize but does participate in a rather wide variety of free radical copolymerizations with unsaturated monomers. The resulting polysulfones have been known for quite a long time. Solonina (1,2) obtained a white solid from the reaction of SO_2 with allyl ethers in 1898, but such products were not recognized as copolymers until the work of Marvel and Staudinger in the 1930's.

The class of vinyl monomers which will copolymerize with SO_2 is not clearly distinguishable in terms of fundamental structural characteristics from the class of those that will not. All terminal olefins, beginning with ethylene and continuing on up to the higher olefins, copolymerize and, with the exception of ethylene, give copolymers of strictly 1:1 alternating structure, since neither the chains ending in SO_2 nor those ending in olefin can add their own monomer; i.e. both reactivity ratios r_1 and r_2 are zero. Others include cyclopentene, cyclohexene, cycloheptene and some open-chain olefins with internal double bonds, provided the substituents at the double bond are not all larger than methyl.

Monomers which can add to their own radicals are capable of copolymerizing with SO_2 to give products of variable composition. These include styrene and ring-substituted styrenes (but not α -methylstyrene), vinyl acetate, vinyl bromide, vinyl chloride, and vinyl fluoride, acrylamide (but not N-substituted acrylamides) and allyl esters. Methyl methacrylate, acrylic acid, acrylates, and acrylonitrile do not copolymerize and in fact can be homopolymerized in SO_2 as solvent. Dienes such as butadiene and 2-chlorobutadiene do copolymerize, and we will be concerned with the latter compound in this discussion.

An important feature of olefin- SO_2 polymerizations is their relatively low ceiling temperatures: the reverse reaction becomes evident at quite low temperatures. In fact, it is while studying such copolymers that Dainton and Ivin in 1948 (3) first clearly recognized the existence of ceiling temperatures in vinyl polymers. The reversibility of the propagation has important effects on the composition of the chains, which, as we shall see, exhibits a very

strong dependence on temperature even at constant monomer feed ratio. This dependence invariably takes the form of tending to exclude SO_2 as the temperature is increased. This reversibility accounts also for some other unusual features of the chain structure, including deviation from first-order Markov statistics and, in the case of chloroprene, a seemingly anomalous and rather interesting tendency to form a more regular chain structure as the polymerization temperature is increased.

The use of nmr, --carbon-13 nmr in particular--, has given a much deeper insight into the structure of SO_2 copolymers than was possible by the older, traditional method of analytically determining monomer ratios in the polymer as a function of the monomer feed. In fact, it can be safely said that the use of nmr has completely revolutionized the study of copolymers. (The impact of nmr on copolymer studies is studiously ignored in all polymer textbooks, which tend to reflect the status of the field twenty years ago.)

Styrene- SO_2 Copolymers. I would now like to discuss two systems which illustrate the power of C-13 nmr in structural studies. The first is the styrene- SO_2 system. As already indicated, this is of the type in which the chain composition varies with monomer feed ratio and also with temperature at a constant feed ratio (and probably with pressure as well.) The deviation of the system from simple, first-order Markov statistics, --i.e. the Lewis-Mayo copolymerization equation--, was first noted by Barb in 1952 (4) who proposed that the mechanism involved complex formation between the monomers. This proposal was reiterated about a decade later by Matsuda and his coworkers (5,6). Such charge transfer complexes do in fact exist, with the olefin acting as the donor, but we shall see that it is not necessary to invoke complex formation to explain the observed kinetics. It is also unnecessary to invoke penultimate effects in the reaction of the propagating radicals.

The traditional compositional and kinetic measurements cannot distinguish effectively between the various models proposed to account for deviations from the simple copolymerization model. To do this requires monomer sequence data, and for this nmr is the method par excellence. But in order to make use of the potentially rich information provided by nmr, one must be able to make assignments of the resonances in spectra which are often quite complex. This is usually done by (1) isotopic labelling; (2) observing carbon multiplicity in the absence of decoupling; (3) relaxation measurements; (4) logical deduction from the spectra of a series of copolymers of varied composition; and (5) invoking chemical shift rules. In order to interpret the spectra of SO_2 copolymers, we must recognize certain features of the monomer sequences, the principal one of which is that they have a sense of direction. To avoid confusion, we must remember that for any particular sequence we are always looking at the central vinyl monomer unit in the β -to- α direction from left to right. A

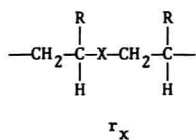
second, minor point is that since SO_2 units are not chiral, compositional triads are actually configurational dyads and compositional tetrads are configurational triads. These points are illustrated in Figures 1 and 2, where the chain sequences are represented as planar zigzags (viewed edge on). Figure 1 shows compositional triads involving the unit X, which in our case is SO_2 . As configurational dyads they may be racemic or meso of two types, depending on whether the chiral centers straddle an X unit or not. Also, we must note that XMM is not the same as MMX. In Fig. 2 the same representation is extended to compositional tetrads, i.e. configurational triads.

An important first step in interpreting the C-13 spectra is to distinguish α -carbons from β -carbons, i.e. methine from methylene. Observation of multiplicity when the proton decoupler is off is one way, but this is not always easy if the lines are broadened by chemical shift multiplicity. Measurement of T_1 has been used for this purpose since the β -carbon with two bonded protons relaxes about twice as fast as the α -carbon with only one. A very positive way is by deuterium labelling. In Fig. 3 is shown the main-chain 25 MHz carbon spectrum of two styrene- SO_2 copolymers containing 58 mol% styrene, or a ratio of styrene to SO_2 of 1.38 (7). In the bottom one, $\beta, \beta\text{-d}_2$ -styrene has been used, and all the β -carbon resonances are distinguishable from the α -carbon resonances since the presence of deuterium has eliminated their nuclear Overhauser effect; because of this and the deuterium J coupling (~ 20 Hz), they are markedly smaller and broader than the α -carbon resonances.

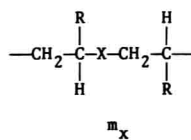
The assignments of resonances to particular monomer sequences are based primarily on their relative intensities as a function of overall composition. We define R as the overall ratio of styrene to SO_2 in the polymer. In Fig. 4 are shown the complete 25 MHz C-13 spectra, including at the left the aromatic carbons, for four copolymers of varied R (7). The spectrum of atactic polystyrene is also shown. The number of resonances shows that compositional triads are being distinguished: SMS, SMM, MMS, and MMM. Here, M stands for styrene and S for SO_2 . As the ratio R increases, MMM sequences become evident and can be assigned on the basis of the polystyrene spectrum. In the latter, the β -carbon is highly sensitive to configuration whereas the α -carbon is entirely insensitive, appearing as a narrow spike.

In Table 1 are shown the chemical shifts of the resonances in polystyrene sulfones. They are based on relative resonance intensities as a function of monomer ratio and on a consistent set of rules. We observe that the least shielded α - and β -carbons are those bonded directly to sulfone sulfur atoms. One can recognize very clearly a sulfone oxygen shielding effect when the carbon concerned is in the γ -position with relation to the oxygens. It appears to be analogous to the well known carbon γ -effect. Comparing α -MMS with α -SMS we see that for α -carbons it causes a shielding of about 5 ppm. Comparing β -SMM with β -SMS, we see a

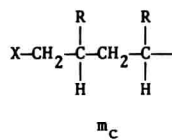
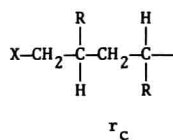
TRIADS:



MXM



XMM



MMX

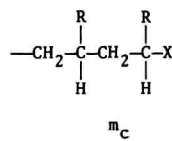
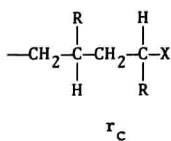
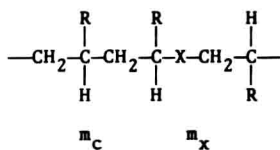


Figure 1. Compositional triads (configurational dyads) in chains of vinyl (M) copolymers with a comonomer which places a single atom X in the main chain

TETRAADS:

MMXM



MXMM

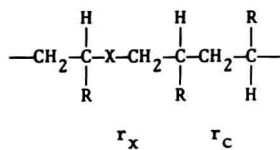
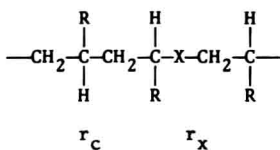
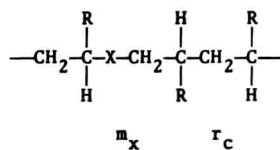
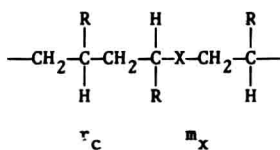
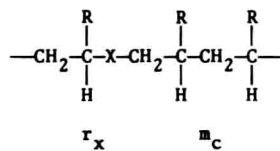
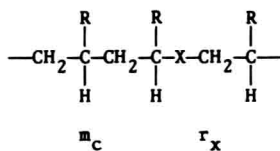
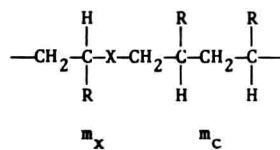


Figure 2. Compositional tetrads (configurational triads) in chains of vinyl (M) copolymers with a comonomer which places a single atom X in the main chain.

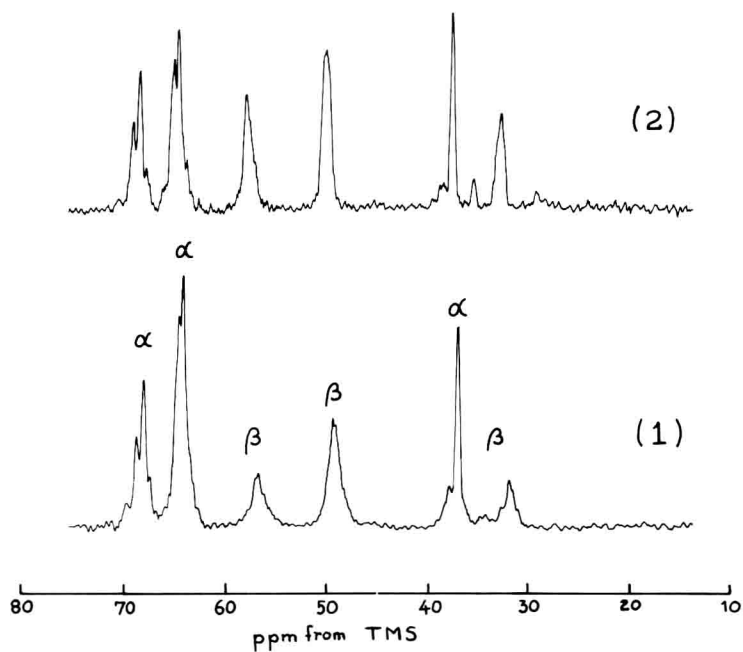


Figure 3. ^{13}C spectra (25 MHz) of the main chain of styrene- SO_2 copolymers containing 58 mol % styrene ($R = 1.38$). The bottom spectrum is of a copolymer with $\beta,\beta\text{-d}_2$ -styrene (25% solution in CDCl_3 at 55°C).

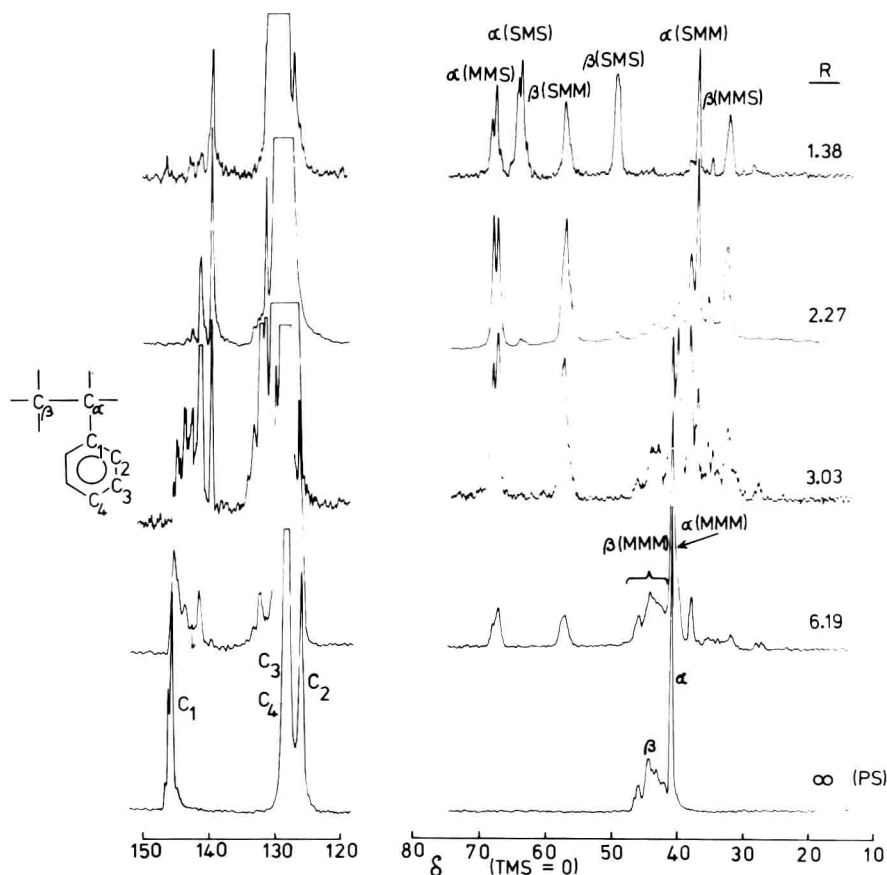
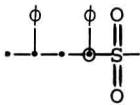
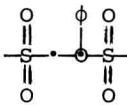
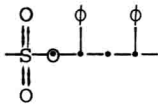
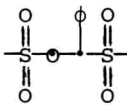
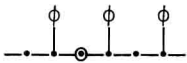
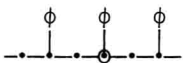
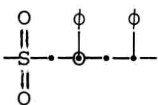
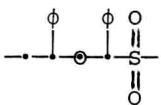


Figure 4. ¹³C spectra (25 MHz) of styrene-SO₂ copolymers of four different compositions. The aromatic carbons are on the left and the main chain carbons on the right. R values are the mole ratios of styrene to SO₂ in the copolymers. The spectrum at the bottom is that of atactic PS. (All observed as 25% solutions in CDCl₃ at 55°C except PS, which was observed as 20% solution in cyclohexane-d₁₂ at 77°C.)

shielding of about 9 ppm for β -carbons. The same is true for β -MMM vs. β -MMS. We note that α -SMM and β -MMS are actually more shielded than polystyrene itself.

Table 1

Main Chain Carbon Chemical Shifts in Styrene-SO₂ Copolymers

		<u>Shift, ppm from TMS</u>
α -MMS		68
α -SMS		63
β -SMM		57
β -SMS		48
β -MMM		44
α -MMM		40
α -SMM		38
β -MMS		33

An interesting feature of the styrene-SO₂ system, --which indeed is true of all SO₂ copolymerizations with comonomers capable of homopolymerizing-- is the existence of a ceiling temperature above which the formation of alternating units, SMS, is forbidden. The number fraction of M sequences of length n is

given by;

$$N_M(n) = \frac{p(SM^nS)}{\sum_{n=1}^{\infty} p(SM^nS)}$$

i.e. the probability of occurrence of a length of n styrene units divided by the sum of the probabilities of all styrene sequences of all lengths. Since it can be shown that:

$$\sum_{n=1}^{\infty} p(SM^nS) = p(MS),$$

and since in the present case:

$$p(MS) = p(S),$$

because all sulfone units S have M as neighbors, we have

$$N_M(n) = \frac{p(SM^nS)}{p(S)}$$

For the number fraction of SMS sequences:

$$N_M(1) = \frac{p(SMS)}{p(S)}$$

A plot of $N_M(1)$ versus polymerization temperature is shown in Fig. 5. It will be seen that at low temperature it approaches unity, which would correspond to a strictly alternating structure, and that it declines very rapidly, reaching zero at about 40° . Therefore, above 40° alternating sequences are not generated. At 40° , it turns out that a chain ending in $-SM\cdot$ will add another M and then add S , and so on, yielding a polymer with predominantly the regular structure $SMMSMMSM$ etc. As the polymerization temperature is increased further, the SO_2 units are in effect squeezed out progressively until around 100° a second ceiling temperature occurs and no appreciable amount of SO_2 is incorporated; only polystyrene is produced. There is probably a moral here with regard to those monomers which, like methyl methacrylate, acrylonitrile, and acrylate esters, merely seem to homopolymerize in SO_2 as solvent. If polymerization were conducted at a sufficiently low temperature, SO_2 probably would be incorporated.

The copolymerization scheme we favor is as follows:

