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TECHNICAL REPORT ARCEL TR-78073

POLYMERIZATION OF THE WEED AT LOW PRESSURE
RESONANCE (NMR) SPECTROSCOPY
AND HIGH MOLECULAR WEIGHT DETERMINATION

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Double precision Fourier transform 13C nuclear magnetic resonance (NMR) spectroscopy was used to determine the microstructure of Acryloid K125-EA and high molecular weight poly(isobutyl methacrylate), PIBM. The PIBM was found to exhibit Bernoullian behavior and to have a predominately syndiotactic structure with only isolated meso additions. The triad distribution showed that only 5% of the monomer units occur in runs of three like configurations or longer. The Acryloid K125-EA was found to consist of 82 mole % methyl methacrylate, 12 mole % (Continued on reverse side)		

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20. ABSTRACT (Contd)

Ethyl acrylate and 6 mole % butyl acrylate. Like the PIBM, this polymer was also found to have a predominately syndiotactic structure with more racemic additions than meso additions.

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PREFACE

The work described in this report was authorized under Task 1T161101A91A, In-House Laboratory Independent Research. The work was started in January 1979 and completed in September 1979. The experimental data are contained in notebook 9941.

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POLYMER CHARACTERIZATION BY ^{13}C NUCLEAR MAGNETIC
RESONANCE (NMR) SPECTROSCOPY: ACRYLOID K125-EA
AND HIGH MOLECULAR WEIGHT PIBM

I. INTRODUCTION.

For more than a decade, nuclear magnetic resonance (NMR) spectroscopy has been making significant contributions to the study of both synthetic and biopolymers. The most significant contribution NMR has made in the area of synthetic polymers is their characterization in terms of microstructure and the various forms of isomerism that can occur. Since the chemical, physical and mechanical properties of synthetic polymers strongly depend upon the stereochemistry of the repeating units in the polymer chain, characterization of polymers at the molecular level is very important. Proton (^1H) NMR has been used extensively to study polymers and has provided a considerable amount of data concerning their structure-physical properties relationships.¹⁻³ With the recent advent of Fourier transform NMR spectrometers, however, characterization of synthetic polymers using ^{13}C NMR spectroscopy has moved to the forefront. Carbon-13 NMR has several advantages over ^1H NMR: (1) chemical shift differences between nuclei of the same structural unit but in different stereochemical environments are larger; (2) complex patterns due to spin-spin coupling can be eliminated by broadband decoupling of the protons; and (3) high resolution ^{13}C spectra can be obtained from highly viscous solutions and, in some cases, even from solids since the line broadening caused by dipolar spin-spin relaxation associated with slow molecular motion is much less severe for ^{13}C than for protons. Consequently, ^{13}C NMR is proving to be an excellent tool for determining the stereoregularity of various polymers, the amount of branching within the polymer and the sequence distribution in copolymers.

Both the Acryloid K125-EA and the high molecular weight poly(isobutyl methacrylate), PIBM, that were investigated have been used in various studies.^{4,5} Since the properties of polymers are strongly dependent on the stereochemistry of the repeating units, studies to determine the microstructure of these two polymers are important for several reasons: (1) to fully understand the nature of the polymer being used; (2) to be able to compare different batches of the same polymer to insure that they are the same chemically; and (3) to aid in the development of new and/or special polymers for thickening purposes. This ^{13}C NMR investigation marks the first time work has been done to characterize these polymers at the molecular level; this report describes the results of this investigation.

II. BACKGROUND.

While the polymer chemist would, ideally, like to discern the monomer sequence or sequence distribution for each chain in a particular polymer sample, characterization of polymers by NMR spectroscopy actually involves determining average structures. For a copolymer, the simplest average structural information that can be determined by ^{13}C NMR is the ratio of monomer A to monomer B, and for homopolymers that can exist in one or more different configurations (i.e., polybutadienes), the simplest information is the percent monomer as structural entity 1, 2, etc. These findings, however, give no indication of the monomer sequences nor of the distribution of structures which are so important in determining the physical properties of the polymer. But, since ^{13}C NMR is sensitive to the subtle structural features

within the polymer chain, sequencing information such as the different combinations of adjacent structural units (AA:AB:BB) can be determined. Because the concentrations of unlike connecting units (AB) can be measured independently of the concentrations of like connecting units (AA and BB), ^{13}C NMR spectroscopy can give information that will eventually lead to complete sequence distributions for the polymer. However, it must be remembered that NMR data reflects the average structure of the polymer; it does not reflect the possible differences in structural distribution that may occur either within or between the polymer chains.

A. Tacticity (Sequence Distribution).

A vinyl homopolymer, such as poly(methyl methacrylate) or poly(isobutyl methacrylate), can be considered as a copolymer of successive units of either the same (like) or opposite (unlike) handedness. There are two different systems of nomenclature that may be used to describe the sequence of like and unlike units along the polymer chain: (1) the system introduced by Price⁶ which uses a 0 and 1 nomenclature to depict individual monomer unit configurations, and (2) the system developed by Bovey⁷ which refers to adjacent monomer pairs with the same relative configurations as meso (*m*) dyads and those with opposite configurations as racemic (*r*) dyads.

The distribution of meso and racemic configurations, or alternately, the sequence of 0 and 1 monomer units falls under the general heading of polymer tacticity. An excellent technique for determining the tacticity of vinyl homopolymers is ^{13}C NMR spectroscopy since the chemical shifts of the various resonances of the vinyl homopolymers are usually sensitive to structural features many bonds away. For example, if a resonance exhibits triad (3 monomer units) sensitivity, separate peaks would be observed for the *mm* (isotactic) sequence, the *mr* (heterotactic) sequence and the *rr* (syndiotactic) sequence, figure 1. It is not unusual, though, to see ^{13}C NMR resonances with tetrad (4 monomer units), pentad (5 monomer units) and even hexad (6 monomer units) sensitivity. An added advantage is the fact that the areas under these peaks are directly proportional to the concentrations of the various sequences since the Nuclear Overhauser Effect (NOE) is cancelled out due to the restricted molecular motion of the polymer.⁸ Using model compounds, then, one can identify which sequences produce which resonances, and from the ratio of the concentrations, the monomer distribution for the homopolymer can be discerned.

The sequencing distribution in vinyl copolymers is the same as that described above for vinyl homopolymers except that 0 and 1 now represent the monomers A and B. But, for copolymers, the situation becomes much more complex since these two monomer units also can add meso and racemic. Thus, for a triad sequence, there would be the possibility of 6 unique resonances for a copolymer made up of monomer units A and B compared with 3 unique resonances for the triad sequence of a vinyl homopolymer.

B. Number-Average Sequence Lengths.

The monomer distribution for a vinyl copolymer or homopolymer can be expressed in terms of a quantity called the number-average sequence length.⁹ Number-average sequence lengths may be expressed in terms of runs of like additions or, for vinyl homopolymers, in terms

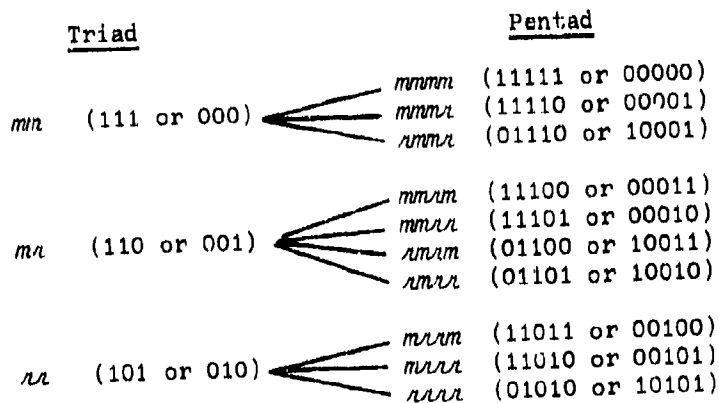
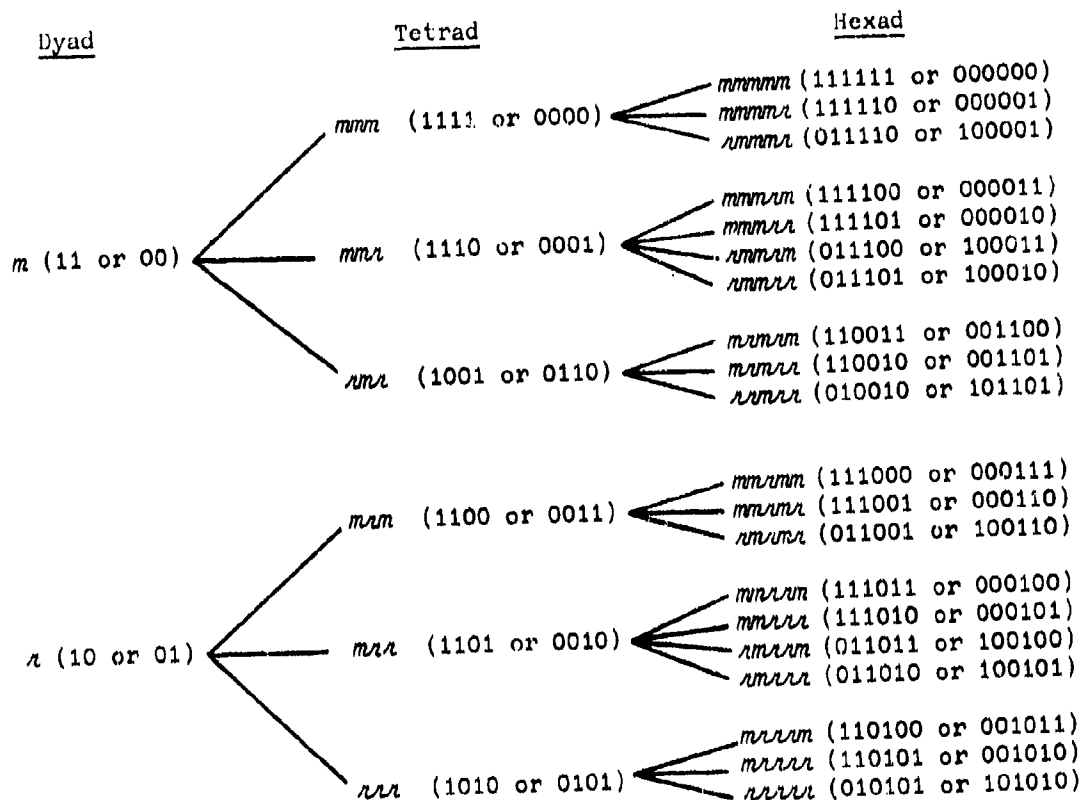


Figure 1. Progression from Dyad to Tetrad to Hexad Sequences and from Triad to Pentad Sequences in Vinyl Polymers

of runs of meso (*m*) and racemic (*r*) additions. The number-average sequence length of like additions ($\bar{n}$) for an average polymer chain is calculated from the following general equation:¹⁰

$$\bar{n} = \frac{\sum_{l=0}^{l=n} l N_l (0)_l}{\sum_{l=0}^{l=n} N_l (0)_l}$$

where

n = the length of the run of like additions

N = number of runs for each n

For a vinyl homopolymer, the above equation may be expressed in terms of the meso-racemic nomenclature and reduces to $\bar{n} = 1/(r)$ where r = concentration of racemic dyad sequences.¹⁰ Thus, $\bar{n}$, the number-average sequence length of like additions, can be obtained from any monomer distribution 2 units or longer. As can be seen from the equation, an ideally random polymer, where $m = r = 1/2$, has $\bar{n} = 2.0$, and a completely syndiotactic polymer ($r = 1$) has $\bar{n} = 1.0$. A sequence length greater than 2 denotes a polymer with more meso additions than racemic additions.

Number-average sequence lengths for a vinyl homopolymer may also be expressed in terms of meso and racemic additions rather than in terms of like configurations. Characterization of polymer tacticity through the meso-racemic copolymer model, however, requires a higher chemical shift sensitivity since a knowledge of the monomer distribution over at least 3 units is needed. The number-average sequence lengths of meso and racemic additions are calculated from the following equations derived for triad sensitivity:¹⁰

$$\bar{n}_m = \frac{(mm) + \frac{1}{2}(mr)}{\frac{1}{2}(mr)}$$

$$\bar{n}_r = \frac{(rr) + \frac{1}{2}(mr)}{\frac{1}{2}(mr)}$$

As was the case for number-average sequence lengths of like configurations, ideally random polymers give $\bar{n}_m = \bar{n}_r = 2.0$.

C. Statistical Analysis of Polymer Tacticity.

Bovey¹¹ and Price⁶ pioneered the development of the statistical analyses of polymers. The most frequently used statistical models are Bernoullian and first-order Markov. The Bernoullian model describes a random distribution of monomer units where the probability of a monomer addition is independent of the outcome of any previous addition. All first- (and higher) order Markovian models describe those polymers in which the probability of addition is dependent upon previous events: a first-order Markov model depends on the outcome

of a single preceding event; a second-order Markov model depends upon the outcome of two preceding events; etc. Statistical analysis of polymers is important since it allows for the assignment of specific NMR chemical shifts to particular polymer sequences when model compounds are of no help or when they give ambiguous results.

III. EXPERIMENTATION.

A. Materials.

The sample of Acryloid K125-EA, (Lot No. 3-6326, Code No. 6-4077), was manufactured by Rohm and Haas. A terpolymer, it is reported to consist of methyl methacrylate, ethyl acrylate and butyl acrylate and to have an average molecular weight of approximately 2 million as determined by gel permeation chromatography.*

The sample of high molecular weight PIBM, poly(isobutyl methacrylate), SW 63-0082, was also manufactured by Rohm and Haas and has an average molecular weight of 5.5 to 9.5 million as determined by viscosity and light-scattering techniques, respectively.*

The Acryloid K125-EA, the PIBM, the deuterated benzene, C_6D_6 , (Norell Chem. Co., Inc.), the chloroform, $CHCl_3$ (Allied Chemical, Reagent grade), and the deuterated chloroform, $CDCl_3$ (Norell Chem. Co., Inc.), were all used as received.

The pyridine (Eastman, Karl Fischer Reagent grade) was dried over sodium hydroxide pellets before use.

B. Instrumentation.

The carbon-13 NMR spectra were obtained using a Varian FT-80A multinuclear Fourier-transform NMR spectrometer operating at 20.0 MHz with broadband proton heteronuclear decoupling. The spectra were accumulated using double precision software (D² ACCUM)** and the following spectral parameters: sweep width, 4000 Hz; pulse width, 8 μ sec (33°); acquisition time, 1.023 sec; and pulse delay, 2.5 sec. The probe temperature was maintained at 35°C, and $CDCl_3$ was used for the internal lock signal. Relative peak areas were determined by electronic integration, by cutting and weighing, and through curve resolving using the spin simulation program SIMEQ.** Chemical shift values are reported relative to tetramethylsilane (TMS) using the solvent peak as the internal standard.

C. Sample Preparation.

A 10% (wt/vol) solution of each polymer was prepared by adding 10 ml of the appropriate solvent to 1 gram of polymer contained in a small, glass bottle. The mixture was stirred using a glass stirring rod until all the polymer appeared "wet." The bottle containing the polymer and solvent was placed on a tumbler and tumbled at ambient temperature for at least

* Personal communication, E. C. Penski, Physical Organic Section.

** Software courtesy of Steven L. Patt, Varian Associates.

24 hours in order to obtain a homogeneous solution. The thick polymer solution was then transferred to a 10-mm od pyrex NMR tube using a 3-ml syringe and a 13-gage needle. The tube was capped, and the top was wrapped with Parafilm. Spectra were recorded as described above.

IV. RESULTS AND DISCUSSION.

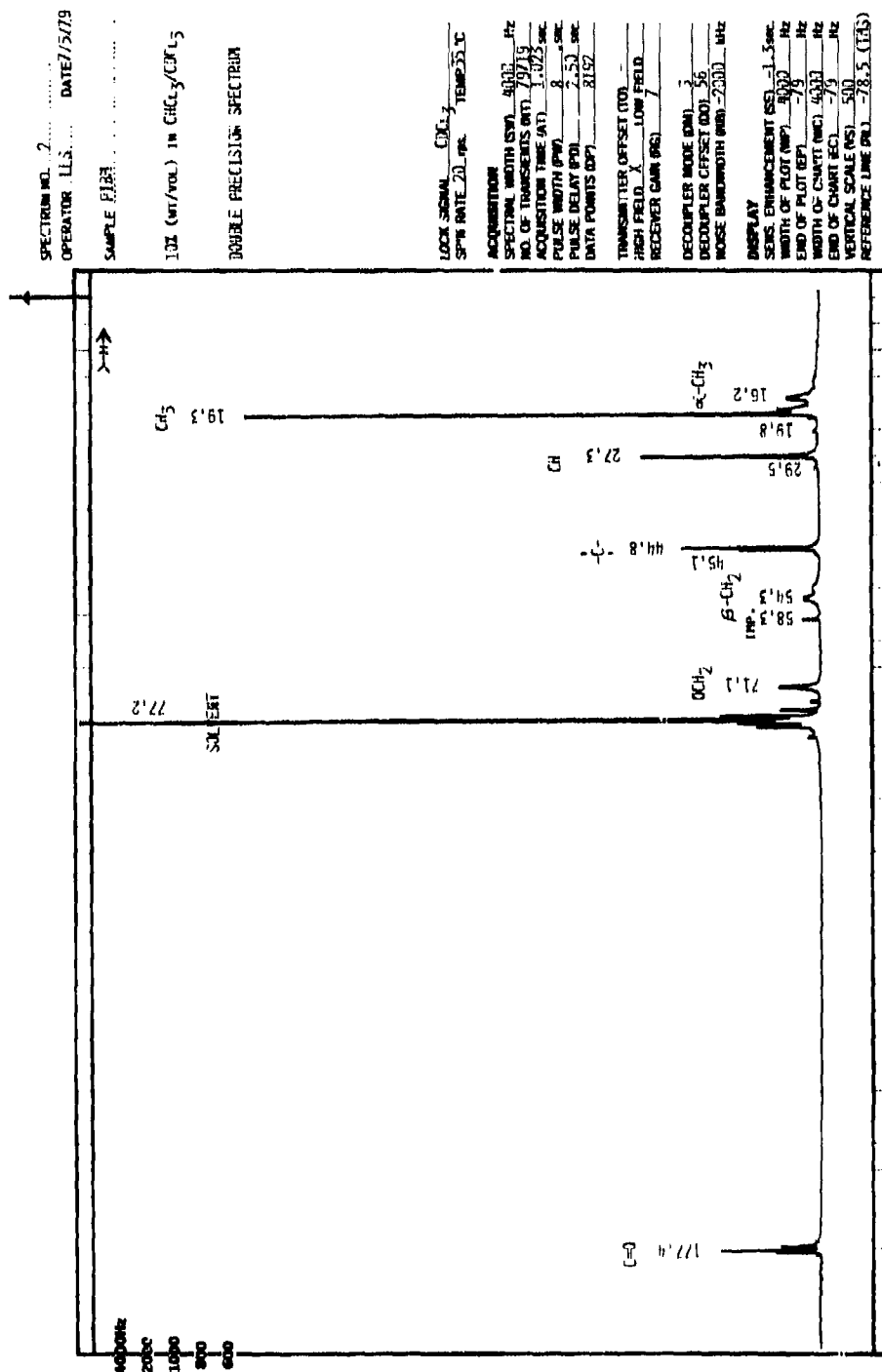
A. High Molecular Weight PIBM.

1. Identification of Carbon Types Present.

The carbon-13 NMR spectrum of the high molecular weight PIBM dissolved in $\text{CHCl}_3/\text{CDCl}_3$ is shown in figure 2. Comparison of the spectrum with various reference spectra, table 1,¹² allows the peaks to be identified:

<u>Resonances</u>	<u>δ, ppm</u>
Butyl: CH_3	19.3
CH	27.3
OCH_2	71.1
Methacrylate: CH_3	16.3, 18.4, 19.9
CH_2	54 area
C - backbone	44.8, 45.1, 45.7
C=O	175.9, 176.6, 176.8, 177.4, 177.7, 178.1

As can be seen from the spectrum, none of the butyl resonances of the PIBM shows sensitivity to the skeletal arrangement of the molecules in the polymer chain except the $-\text{OCH}_2$ resonance (δ 71.1) which is only slightly broadened and, therefore, cannot be used to obtain any sequencing information. Usually, the $\alpha\text{-CH}_3$ resonance (δ 16.3, 18.4, and 19.9) is used to determine triad ratios (syndiotactic:heterotactic:isotactic) in poly(methacrylates),¹³ but for PIBM, this region overlaps the CH_3 peak from the butyl moiety (δ 19.3) and cannot be used to evaluate tacticity. However, the tertiary carbon resonance also shows triad sensitivity (δ 44.8, 45.1 and 45.7), and the carbonyl resonance shows pentad sensitivity. Using reference spectra of various samples of poly(methyl methacrylates),^{10, 13} the carbonyl resonances for the various pentad and triad sequences in the spectrum of the PIBM were identified, figure 3. The pentad chemical shift assignments for the carbonyl carbon, from low to high field, are *mrrrm*, *rrrrm*, *rrrrr*, *mrrrm* + *mrrrm*, *rmrr* + *mmrr*, and *mrrrm* + *mrrrm* + *rmrr*.



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Figure 2. Double Precision ^{13}C NMR Spectrum of P123 in $\text{CHCl}_3/\text{CDCl}_3$

Table 1. Reference Compounds¹²

Name	Structure	Solvent	δ
			ppm
Acrylic acid		Neat	C _a 131.9 C _b 127.2 C _c 170.4
Methacrylic acid		Neat	C _a 126.3 C _c 171.9 C _b 135.2 C _d 16.5
Methyl methacrylate		Dioxane	C _a 124.7 C _d 18.3 C _b 135.9 C _e 51.5 C _c 167.3
Butyl methacrylate		Dioxane	C _a 124.4 C _e 54.4 C _b 137.2 C _f 31.3 C _c 166.7 C _g 19.7 C _d 18.3 C _h 13.9
Butyl benzoate		CDCl ₃	C _a 54.7 C _e 19.3 C _b 30.8 C _d 13.7
Ethyl hexanoate		CDCl ₃	C _a 13.9 C _b 60.0
Isobutyl alcohol		CDCl ₃	C _a 18.9 C _b 30.8 C _c 69.4

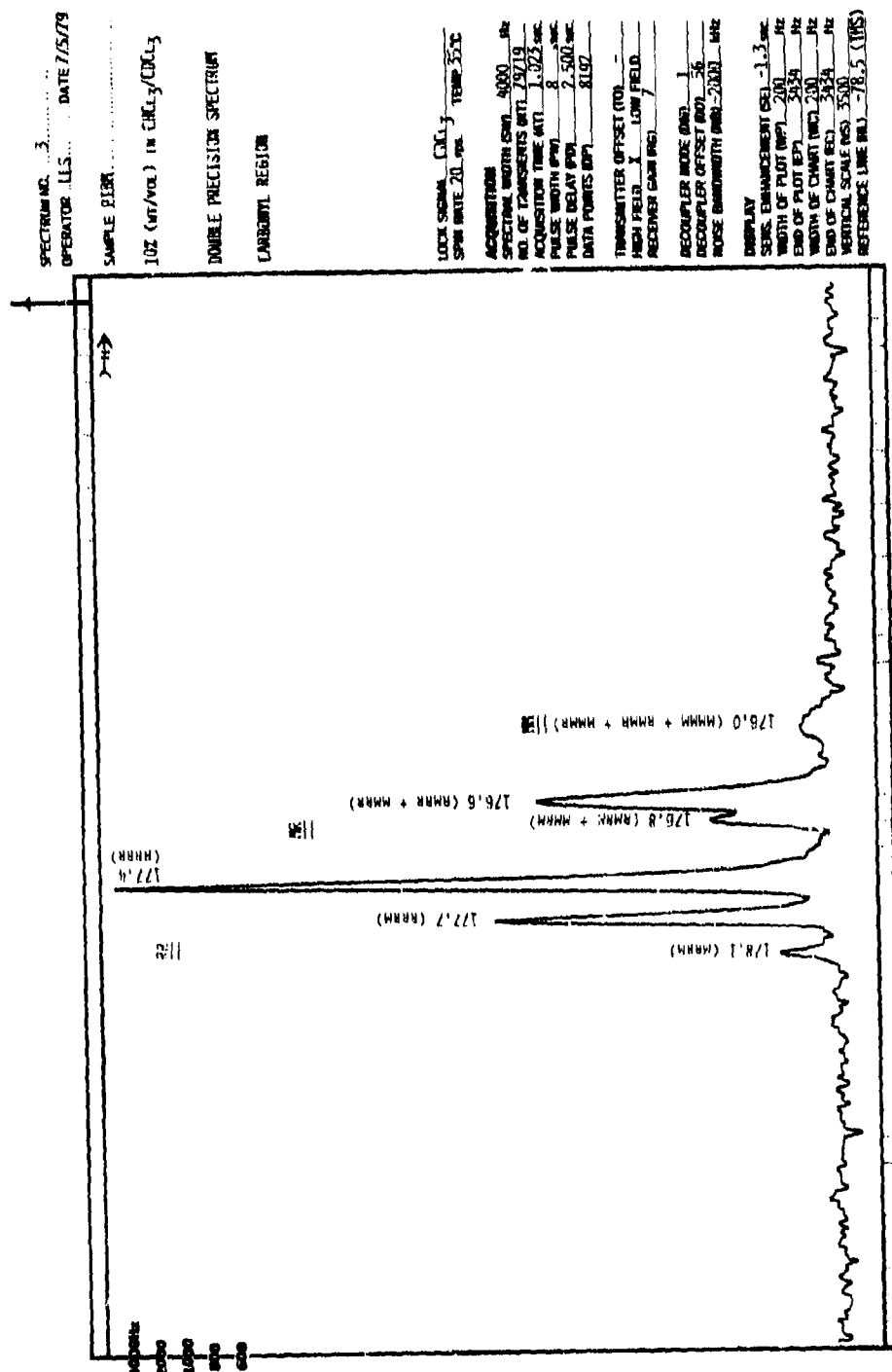
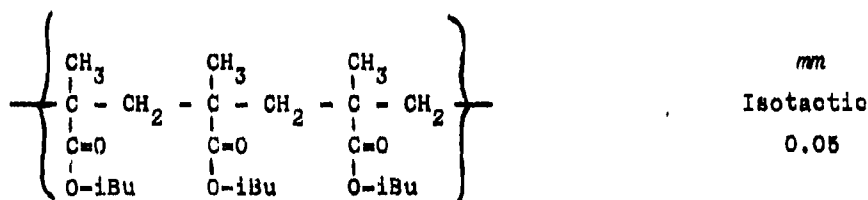
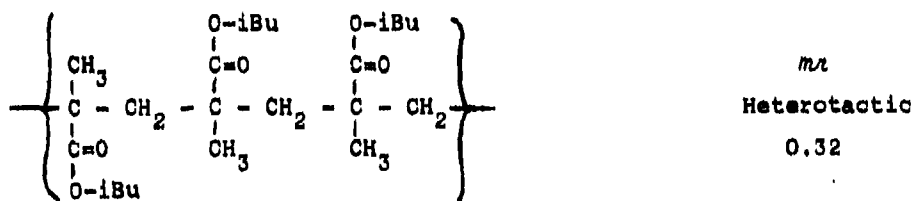
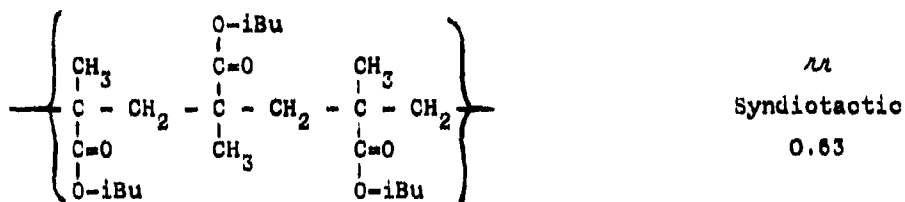


Figure 3. Expanded Double Precision Spectrum of the Carbonyl Region of P188 in $\text{CHCl}_3/\text{CCl}_4$

2. Tacticity.

Based on the relative areas of the carbonyl resonances, figure 3, the following ratio of triad sequences was obtained:

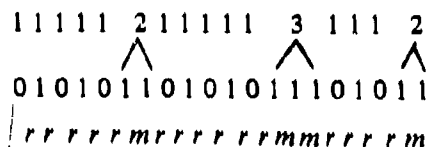


3. Number-Average Sequence Length of Like Configurations.

Using the value of the racemic dyad concentration, r , determined from the carbonyl region of the spectrum ($r = rr + \frac{1}{2}mr$), the high molecular weight PIBM investigated was found to have a number-average sequence length of like configurations ($\bar{n}$) equal to 1.3 ± 0.1 . This indicates that, during the formation of this polymer, there were more unlike (racemic) additions than like (meso) additions.

4. Number-Average Sequence Lengths of Racemic and Meso Additions.

The PIBM studied was found to have a number-average sequence length of meso additions ($\bar{n}_m$) equal to 1.3 ± 0.1 and a number-average sequence length of racemic additions ($\bar{n}_r$) equal to 5.0 ± 0.5 . Based on these results, an *average* structure for this PIBM which satisfies all the sequence length requirements is



5. Statistical Analysis.

A comparison of the observed values of the triad intensities with those calculated for a Bernoullian fit indicates that the high molecular weight PIBM exhibits Bernoullian behavior (table 2). The Bernoullian probability for a meso addition, P_m , was found to be 0.21 ± 0.01 and for a racemic addition, $1 - P_m$, 0.79 ± 0.01 .

Table 2. Monomer Distribution for PIBM Conforming to Bernoullian Behavior Based on the Carbonyl Resonance

Triad	Distribution	
	Observed	Calculated ($P_m = 0.21 \pm 0.01$)
<i>mm</i>	0.05	0.04
<i>mr + rm</i>	0.32	0.33
<i>rr</i>	0.63	0.62

B. Acryloid K125-EA.

1. Identification of Carbon Types Present.

The carbon-13 NMR spectrum of Acryloid K125-EA in pyridine-benzene-d₆ is shown in figure 4. Comparison of this spectrum with reference spectra of various butyl esters (table 1) indicates that the butyl resonances from the butyl acrylate are the peaks at δ 14.2 $\pm$ 0.1, 19.7, 30.8 and 65.2. Similarly, a comparison with reference spectra of various ethyl esters (table 1) indicates that the ethyl resonances from the ethyl acrylate are the peaks at δ 14.2 $\pm$ 0.1 and 61.0. The peaks from the methyl methacrylate are identified as follows:

<u>Resonance</u>	<u>δ, ppm</u>
α -CH ₃	17.0-22.0
β -CH ₂	54 area
C-backbone	45.2-47.0
OCH ₃	52.0

The region δ 173.8 - 178.8 exhibits at least 11 separate peaks and includes all of the carbonyl resonances from the methacrylate as well as both acrylates.

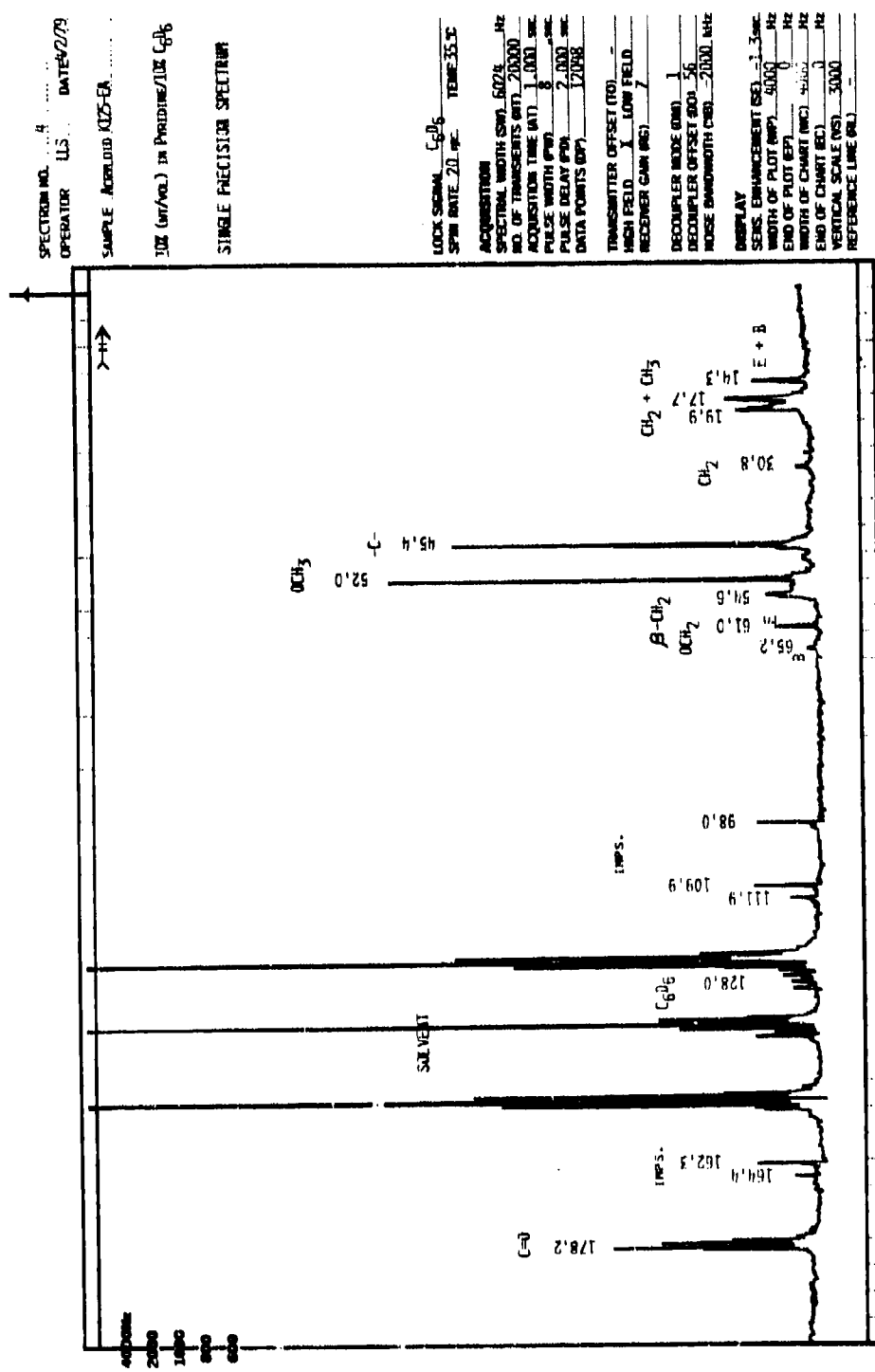


Figure 4. Single Precision ^{13}C NMR Spectrum of Acryloid K125-EA in Pyridine/ C_6D_6

2. Monomer Distribution.

Using expanded spectra and based on the areas of the OCH_2 and CH_3 regions of the acrylates and on the $\alpha\text{-CH}_3$ region of the methacrylate, the molar ratio of methyl methacrylate to ethyl and butyl acrylates was found to be 82:18 (± 3), and the molar ratio of butyl acrylate to ethyl acrylate was found to be 28:72 (± 5). The monomer distribution is, therefore:

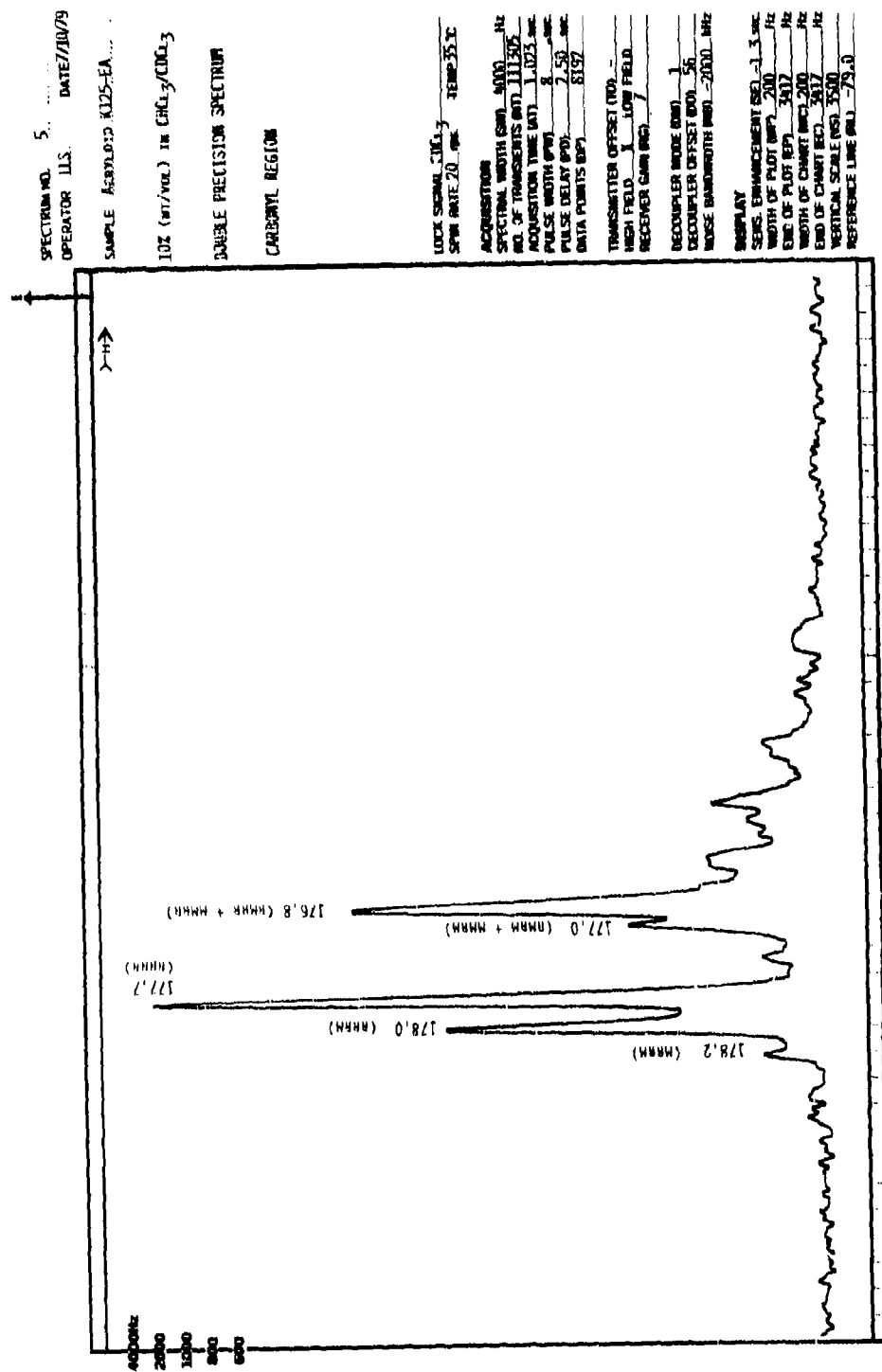
<u>Monomer</u>	<u>Found</u> Mole %
Methyl methacrylate	82
Ethyl acrylate	12
Butyl acrylate	6

3. Tacticity.

As mentioned previously, the analysis of the spectrum of a copolymer can become very complicated since there are 6 unique triad configurations for a copolymer compared to 3 for a vinyl homopolymer. The Acryloid K125-EA, which is a terpolymer, has 18 unique triad combinations and 6 unique dyad combinations. Thus, for Acryloid K125-EA, even sequence descriptions in terms of dyads of monomer units is difficult especially since the concentration of one of the monomers is only about 6%.

As can be seen from the spectrum, figure 4, none of the methylene resonances from either butyl (δ 65.2, 30.8 and 19.7) or the ethyl (δ 61.0) ester moieties shows any sensitivity to the monomer sequencing in the polymer chain. In the best case, only slight peak broadening is observed. The CH_3 resonance (δ 14.2 $\pm$ 0.2), however, does show some sensitivity. But, because this region consists of 2 CH_3 resonances, one from the ethyl moiety and one from the butyl moiety, and because sensitivity to the head-to-head and head-to-tail addition of the monomer units is also expected, no concrete sequencing information can be discerned. Similarly, no sequencing information can be gained from any of the methyl methacrylate resonances since the sensitivity to the skeletal arrangement of the polymer chain (i.e. the head-to-head and head-to-tail sequences of the methyl methacrylate monomer units) appears to overshadow any sensitivity to the monomer configurational sequences.

In spite of the fact that no information about the configurational sequences in the Acryloid K125-EA could be ascertained, some knowledge of the microstructure of this terpolymer can be gleaned. An expanded spectrum of the carbonyl region of a sample of the Acryloid K125-EA dissolved in $\text{CHCl}_3/\text{CDCl}_3$ is shown in figure 5. Even though this region consists of 11 separate resonances, the major peaks, which are due to the 80% methyl methacrylate in the terpolymer, appear in the same pattern as that observed for the high molecular weight PIBM, figure 3, and for other predominately syndiotactic methyl methacrylate homopolymers.^{10, 13} Thus, chemical shift assignments, from low to high field, for the methyl methacrylate monomer units occurring in sequences of 5 units or longer may be



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Figure 5. Expanded Double Precision Spectrum of the Carbonyl Region of Acryloid K125-EA in CHCl₃/CDCl₃

identified: *mmmm*, *rrrr*, *rrrr*, *rmrm + mrrm*, and *rmrr + mrrr*. The resonances from the *mm* centered pentads are apparently small and cannot be observed over the other carbonyl peaks in the spectrum. The fact that the intensities of these resonances are so nearly like those of the PIBM investigated indicates that the Acryloid K125-EA is also a predominately syndiotactic polymer and has more racemic additions than meso additions.

V. CONCLUSION.

The high molecular weight poly(isobutyl methacrylate), PIBM, was found to exhibit Bernoullian behavior and to have a predominately syndiotactic structure with only isolated meso additions. The triad distribution showed that only 5% of the monomer units occur in runs of three like configurations or longer. The predominately syndiotactic structure of this PIBM indicates that steric interactions were encountered during the polymerization process. Thus, it appears as though this sample was prepared either by free radical polymerization¹⁴ or by using a solvent such as tetrahydrofuran during an anionic polymerization.¹⁵

The terpolymer, Acryloid K125-EA, was found to consist of 82 mole % methyl methacrylate, 12 mole % ethyl acrylate, and 6 mole % butyl acrylate. In addition, the pentad distribution indicated that this polymer has a predominately syndiotactic structure and has more racemic additions than meso additions.

LITERATURE CITED

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