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Krisna Lumbanraja\*, Kadarijah\*.

ABSTRACT

TACTICITY DETERMINATION OF METHYL METHACRYLATE POLYMER PREPARED BY RADIATION USING NUCLEAR MAGNETIC RESONANCE METHOD. In this paper, the configuration of various forms of polymethyl methacrylate were determined from the interpretation of a proton Nuclear Magnetic Resonance spectra taken at 90 MHz. Measurements in chloroform-d solution were done on room temperature. Presented are the chemical shifts value assignments, the percent of tacticity calculations and the consistency of Bernoulli model determinations.

ABSTRAK

PENENTUAN TAKTISITAS POLIMER RADIASI METIL METAKRILAT DENGAN METODE RESONANSI MAKNETIK INTI. Dalam makalah ini ditentukan konfigurasi berbagai macam polimetil metakrilat melalui interpretasi spektrum Resonansi Maknetik Inti proton pada 90 MHz. Pengukuran dilakukan dalam kloroform-d pada suhu ruang. Disajikan pula penyusunan nilai pergeseran kimia, perhitungan persentase taktisitas serta penentuan konsistensi terhadap model Bernoulli.

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## INTRODUCTION

One of the most important uses of high resolution NMR in the field of polymers is the study of polymer structure: observation and measurement of isomerism in polymer chains. This emphasis comes in large from the power of NMR to reveal the symmetry properties of organic molecules.

Of the various forms of isomerism possible in polymer chains, the relative stereochemical configuration of pseudo-asymmetric centers, as founded in vinyl polymers, is of particularly great significance. It is now well known that the physical and mechanical properties of vinyl polymers are critically dependent upon their stereochemical configuration

Experimentally data obtained, especially the sequence distribution, can be used to determine whether a particular polymerization follows Bernoulli statistic propagation behavior or not. The Bernoulli model describes the polymerization in which the chain end determines polymer stereochemistry. This corresponds to the generally accepted mechanism for polymerization which yields atactic or syndiotactic polymers. Some other is controlling polymer stereochemistry if propagation doesn't follow the Bernoulli model.

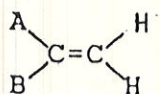
Polymethyl methacrylate, one of the vinyl class, has proved particularly amenable to NMR study. The method which had been employed should have a broader applicability. In this paper, the configuration of various forms of PMMA will be determined using the procedure described by Bovey and Tiers [1]. Quantitatively it was also calculated the percent of tacticity of the Bernoullian statistical propagation model.

## BASIC THEORY

Structural isomerism is encountered when polymers have the same overall chemical composition, but atoms or groups of atoms are bonded in different ways. Isomeric polymers can also be obtained from a single monomer if there is more than one polymerization route.



In the polymerization of a vinyl monomer of the type shown,



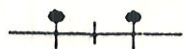
one of the principal growing polymer chain of the polymerization is the relative handedness of successive monomer units. The simplest extreme types of which are known to be syndiotactic, isotactic and atactic (Figure 1). These three kinds of placements are isomeric each other.

The above vinyl monomer comes from the alkene which one of the carbon atoms of the double bond is disubstituted with A and B substituents. Isomerism is observed in polymerization of alkenes of the least mono substituted. Every other carbon atom in the polymer after the polymerization becomes a chiral center.

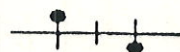
The regularity in the spatial arrangement or the configuration of successive pseudochiral centers determines the overall order or *tactic* structure of the polymer chain.

For disubstituted ethylenes, the presence and type of tacticity depends on the position of substitution and the identity of the substituents. In the polymerization of an  $\alpha, \alpha'$ -disubstituted ethylene, stereoisomerism occurs exactly analogously to the case of a monosubstituted ethylene. Polymethyl methacrylate is one of the class of  $\alpha, \alpha'$ -disubstituted polymers where  $\alpha = \text{CH}_3$  and  $\alpha' = \text{CO}_2 \text{CH}_3$ .

To describe the sequence distribution of isotactic and syndiotactic placements in the polymerization of a monosubstituted alkene, the diad and triad tacticity are defined. Diad tacticity defined as the fractions of adjacent repeating units which are isotactic or syndiotactic to one another. The isotactic and syndiotactic diads can be depicted as



isotactic



syndiotactic



where the horizontal line represents a segment of the polymer chain,  $\bullet$  represents the configuration at the chiral or pseudo-chiral center in each repeating unit, and  $|$  represents the two hydrogen at the carbon in between adjacent (pseudo) chiral centers. The fractions of isotactic and syndiotactic diads are referred to as  $(m)$  and  $(r)$ , respectively. Triad tacticity describes isotactic, syndiotactic, and heterotactic triads, whose fractions are designated as  $(mm)$ ,  $(rr)$ , and  $(mr)$ , as  $i$ ,  $s$ , and  $h$  respectively.



isotactic



syndiotactic



heterotactic

The diad and triad fractions must each total unity by definition, that is,

$$(m) + (r) = 1 \quad (1)$$

$$(mm) + (rr) + (mr) = 1 \quad (2)$$

and the two are related by

$$(m) = (mm) + 1/2 (mr) \quad (4)$$

$$(r) = (rr) + 1/2 (mr) \quad (5)$$

Bernoullion statistical propagation model is frequently used for analyzing the polymer sequence distributions. The Bernoullion model assumes that only the chain end unit in the propagating chain is important in determining polymer stereochemistry.

For any given polymer, if Bernoullion, the  $mm$ ,  $mr$  and  $rr$  sequence frequencies, as estimated from the relative areas of the appropriate peaks, in practice, follows this relation [2]

$$\frac{1}{2} < \frac{4 (mm) (rr)}{(mr)^2} < 2 \quad (5)$$

If this is not the case, then the polymer's configuration



sequence deviates from Bernoullion.

### EKSPERIMENTAL

Polymethyl methacrylate grafted Natural rubber was prepared as follows: natural rubber of 40% total solid was added with MMA monomer of 100 phr and  $\text{CCl}_4$ , as the chain transfer agent, of 0, 1, 3, 5 phr. After mixing for 1 hour, they were radiated with dose of 5 kGy. Homopolymer was extracted from the dried samples. Finally, the samples were ozonized to break the rubber backbone and leave the PMMA grafted chains.

Beside those samples there are two other kinds of PMMA. One is made by radiation of an MMA emulsion with dose of 1.8 kGy and the other is commercial PMMA.

The high-resolution proton NMR spectra were taken on Jeol 90 MHz spectrometer. The spectra were run on room temperature with 5% of the polymers in 99,8% deuterated chloroform with 1% tetramethylsilane (TMS) as reference.

### RESULTS AND DISCUSSION

Figure 2 shows typical spectra of six methyl methacrylate polymers. The ester methyl group appear in the vicinity of 3.6 ppm in all spectra, and are not affected by the nearest neighboring monomer units. The methylene resonance in (a), (b), (e), and (f) spectra are approximately the expected singlet, although somewhat broaden. If the degree of polymerization is high the end effects can be neglected, then for a purely syndiotactic chain  $\text{H}_\alpha$  and  $\text{H}_\alpha'$  can be considered strictly equivalent. Thus these four spectra are dominantly syndiotactic.

There are three  $\alpha$ -methyl peaks in all the six spectra in the vicinity of 0.85ppm, 1.03ppm, and 1.25ppm. The spectrum of  $\alpha$ -substituents does not in itself provide an absolute indication of configuration. It must be correlated with the  $\beta$ -methylene resonance or some other absolute measurement. If this is done, the  $\alpha$ -substituent spectrum may give more detailed configurational information than the  $\beta$ -methy-



lene spectrum. The chemical shifts of the  $\alpha$ -methyl of methyl methacrylate polymer in  $\text{CDCl}_3$  is markedly dependent on configuration. When such discrimination is possible one can observe these three species of  $\alpha$ -methyl on the central monomer units of isotactic, syndiotactic and heterotactic triads of monomer units. The identification of the above three  $\alpha$ -methyl chemical shift values is  $i$  for 1.25ppm,  $h$  for 1.03 ppm, and  $s$  for 0.85ppm.

The interpretation of PMMA numbered (a), (b), (e), and (f) as the predominantly syndiotactic is relevant to the highest part of the  $s$  configuration of the  $\alpha$ -methyl spectra. The  $\alpha$ -methyl of two other PMMA spectra, (c) and (d), also shows the highest peak in  $s$  configuration. Therefore the PMMA numbered (c) and (d) can be stated as the predominantly syndiotactic configuration.

Table 1 shows the analysis of spectra in terms of the proportion of  $i$ ,  $h$ , and  $s$  units. This results were used to calculate the relation (5) for determining the consistency of Bernoullian behavior. The polymerization of commercially PMMA shows non Bernoullian statistical propagation, while the radiated emulsion of MMA shows the consistency to Bernoullian statistic. This result is in agreement with the finding of Bovey et.al [1].

PMMA grafted polymerization follows the Bernoullian statistical propagation for the high phr of  $\text{CCl}_4$ , in this case that is 3 and 5 phr.

### CONCLUSION

The tacticity of polymer numbered (a) to (f) are predominantly syndiotactic (Figure 3). Polymerizations of radiation MMA emulsion and PMMA grafted 3 and 5 phr  $\text{CCl}_4$  are in agreement with Bernoullian statistic propagation. Polymerizations of commercially PMMA and PMMA grafted 0 and 1 phr  $\text{CCl}_4$  do not follow the Bernoullian statistic propagation.

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(a)



(b)



(c)

Figure 1: Tacticity of the relative handedness of a vinyl monomer  $\begin{matrix} A \\ \diagdown \\ C \\ \diagup \\ B \end{matrix} = C \begin{matrix} H \\ \diagup \\ C \\ \diagdown \\ H \end{matrix}$ . (a) syndiotactic, (b) isotactic, (c) atactic.



TABLE 1  
Structure of Polymers of Methyl Methacrylate

Polymer	Polymerization condition	P X 100			Statistical Propagation
		i	h	s	
(a)	Commercially obtained	0.10	0.22	0.68	—
(b)	MMA emulsion was irradiated by $\gamma$ Co-60	0.07	0.3	0.63	Bernoullian
(c)	PMMA grafted NR, ozonisation	0.1	0.31	0.59	—
(d)	PMMA grafted NR, 1 phr $\text{CCl}_4$ , ozonisation	0.14	0.36	0.50	—
(e)	PMMA grafted NR, 3 phr $\text{CCl}_4$ , ozonisation	0.09	0.36	0.55	Bernoullian
(f)	PMMA grafted NR, 5 phr $\text{CCl}_4$ , ozonisation	0.04	0.37	0.59	Bernoullian

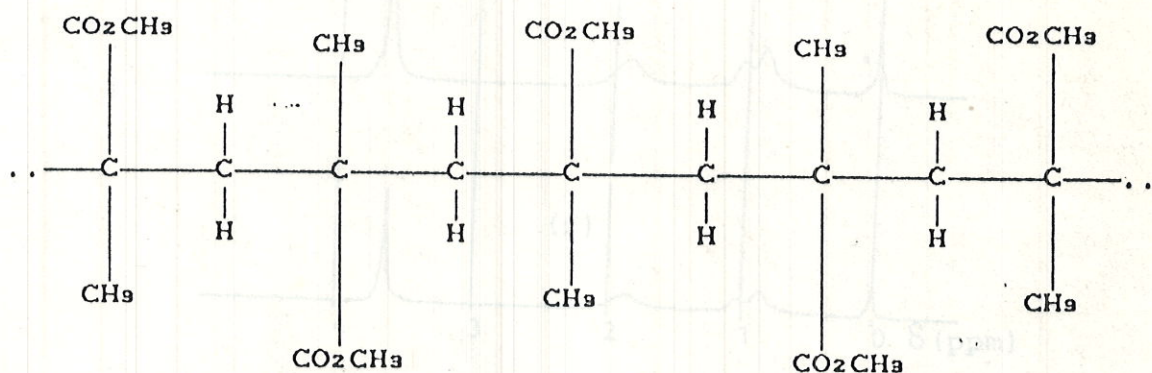


Figure 3: PMMA syndiotactic