

STUDIES ON THE ^{13}C -NMR SPECTRA OF ALTERNATING COPOLYMERS OF CONJUGATED DIENES WITH METHYL ACRYLATE*

ZHANG Xitian (张喜田) and HAN Xiaozu (韩孝族)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun)

ABSTRACT

The ^{13}C -NMR spectra of alternating copolymers of conjugated dienes, butadiene (BD), isoprene (IP) and chloroprene (CP), with methyl acrylate (MA) were studied. It is proved that they are all alternating copolymers. The BD units in Poly (BD-alt-MA) are joined to MA mainly in the form of *trans* 1,4-structure. The contents of *trans* 1,4-, *cis* 1,4- and 1,2-structure are 88, 7 and 5%, respectively. The IP and CP units in Poly(IP-alt-MA) and Poly(CP-alt-MA) exist essentially as *trans* 1,4-configuration and connect with MA units in "head to head" arrangement predominantly, while CP-CP units present in Poly(CP-alt-MA) in a small quantity.

INTRODUCTION

Alternating copolymers of butadiene (BD), isoprene (IP) or chloroprene (CP) with methyl acrylate (MA) have been synthesized in the presence of $\text{Al}_2\text{Et}_3\text{Cl}_3$, photoinitiated by the system $\text{Mn}_2(\text{CO})_{10}-\text{CCl}_4$ ^[1-3]. The alternating structures of these polymers have been studied by ^1H -NMR spectra, however, the microstructures and the configuration of the monomer units in these copolymers have not appeared in literature yet. This paper presents some results obtained by our investigation on these problems by ^{13}C -NMR.

EXPERIMENTAL

Alternating copolymers were obtained by previous methods^[1-3] and purified by precipitation from toluene solution with methanol.

^{13}C -NMR spectra were recorded on a JEOL FX-100 FT NMR spectrometer, using 10% (W/V) solution of CDCl_3 and tetramethylsilane (TMS) as internal reference. The diameter of sample tube was 5 mm.

RESULTS AND DISCUSSION

Alternating copolymer of BD and MA (PBM)

Fig. 1 shows the proton decoupling ^{13}C -NMR spectrum of PBM, in which only eight resonance peaks are strong. According to the previous results^[1], the following alternating structure (I) was taken into account first:

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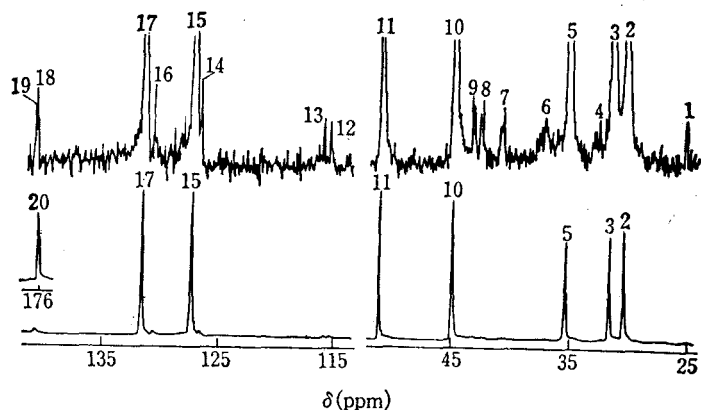
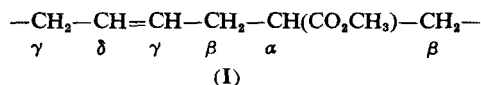


Fig. 1 Proton noise decoupling ^{13}C -NMR spectrum of PBM at room temperature
Width of spectrum: 5 KHz, width of pulse: 45° ($5\mu\text{s}$), repeat time of pulse: 0.92 s,
number of transient: 35 thousands, point of data: 8 K



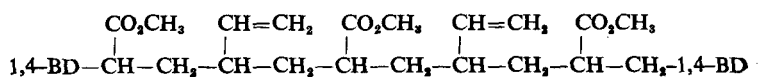
The presence of structure I in PBM will be confirmed, if chemical shifts of I is in agreement with experimental values. I could be regarded as alternating copolymer of BD and ethylene (PBE) with substituting group CO_2CH_3 . The chemical shifts of PBE^[4] and the corresponding substituent parameters of CO_2CH_3 , which could be calculated from the chemical shifts of compounds $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{CO}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ ^[5,6] to be 15.6, 2.8, -1.9 and 0.4 ppm for α , β , γ and δ carbons, respectively. Regarding this substituent parameters as those of I, the chemical shifts of I were obtained as follows:

	$\{\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{CO}_2\text{CH}_3)-\text{CH}_2\}$							
<i>trans</i> 1,4- $\delta_{\text{cal.}}$	31.0	131.1	128.8	35.7	45.0	—	—	32.2
$\delta_{\text{obs.}}$	30.27	131.69	127.49	35.24	45.08	175.94	51.32	31.48
No. of peak	2	17	15	5	10	20	11	3
<i>cis</i> 1,4- $\delta_{\text{cal.}}$	25.1	130.6	128.4	30.3	45.0	—	—	32.2
$\delta_{\text{obs.}}$	25.03	130.81	126.81	30.27	45.08	175.94	51.32	31.48
No. of peak	1	16	14	2	10	20	11	3

(I)

The chemical shifts of carbons in carbonyl group and methoxy group were determined by off resonance decoupling NMR spectra. From the above results, we have determined that PBM is an alternating copolymer consisted of repeat units like I, in which BD units exist in the form of *trans* 1,4-configuration predominantly.

Some weaker peaks present in Fig. 1, that means $-\text{CH}=\text{CH}_2$ structure (No. 12, 13, 18, and 19 peaks) must exist. The results obtained by the same way are as follows:



When **III** and **IV** are regarded as substituted **I** by methyl group, chemical shifts of which may be calculated by adding the observed chemical shifts of **I** and the substituent parameters

of methyl group. The latter was established from chemical shifts of model compounds^[7] $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$ (*cis* and *trans*) and $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (*cis* and *trans*). The values of those parameters are listed below:

	δ'	γ'	β'	α	β	γ
	CH_3	$-\text{CH}_2-$	$\text{CH} =$	$\text{C}(\text{CH}_3)-$	CH_2-	CH_3
<i>trans</i>	0.54	-4.66	-6.06	5.03	6.57	-1.26
<i>cis</i>	0.37	0.46	-4.75	5.27	4.24	-1.45

Substituting H for CH_3 in **III** and **IV**, the following structures are obtained.



Attention must be paid to the order of chemical shifts between these two structures, because the latter is formed by rearrangement of the former.

From the calculated results, we have determined that IP units connect with MA units in the form of "head to head" (**III**) or "head to tail" (**IV**) with *trans* 1,4-structure, but only "head to head" (**III**) with *cis* 1,4-structure.

	$\text{[CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CO}_2\text{CH}_3)-\text{CH}_2\text{]}$								
<i>trans</i> 1,4- $\delta_{\text{cal.}}$	25.61	125.63	132.52	—	42.81	43.82	—	—	32.02
$\delta_{\text{obs.}}$	25.85	125.76	133.00	15.67	442.81	43.81	176.23	51.25	32.02
No. of peak	4	17	20	1	11	12	22	14	8
<i>cis</i> 1,4- $\delta_{\text{cal.}}$	25.49	126.06	132.08	—	34.51	43.63	—	—	31.85
$\delta_{\text{obs.}}$	25.85	126.76	131.78	23.27	34.08	43.81	176.23	51.25	31.75
No. of peak	4	18	19	3	9	12	22	14	7

(III)

"head to head"

	$\text{[CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CO}_2\text{CH}_3)-\text{CH}_2\text{]}$								
<i>trans</i> 1,4- $\delta_{\text{cal.}}$	30.58	121.43	136.72	—	36.84	30.22	45.62	—	—
$\delta_{\text{obs.}}$	30.75	121.69	136.46	15.89	37.48	30.31	45.32	176.23	51.36
No. of peak	6	16	21	2	10	5	13	22	15

(IV)

"head to tail"

The chemical shifts of CH_3 and CO_2CH_3 were assigned with model compounds. From the peak height of $=\text{CH}$, the ratio of the above three structures, *trans* 1,4-"head to head", *cis* 1,4-"head to head" and *trans* 1,4-"head to tail", was evaluated to be 82:9:9. So we have proved that PIM is an alternating copolymer of IP and MA, connected one to the other in the form of "head to head" and IP units being *trans* 1,4-configuration mainly.

Alternating copolymer of CP and MA (PCM)

The ^{13}C -NMR spectrum of PCM is quite similar to that of PIM (Fig. 3), since the substi-

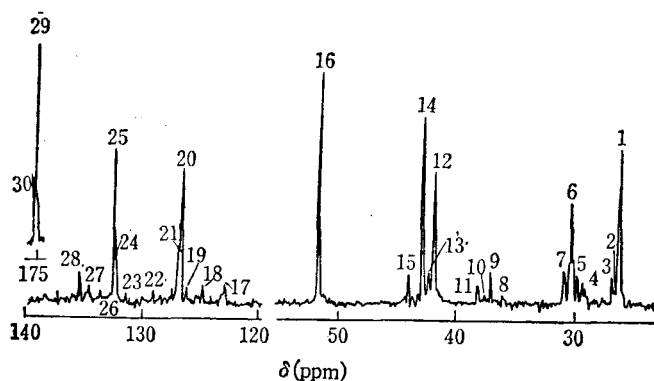


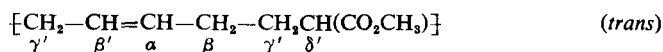
Fig. 3 Proton noise decoupling ^{13}C -NMR spectrum of PCM at room temperature
Width of spectrum: 5 KHz, width of pulse: 28° ($5\mu\text{s}$), repeat time of pulse: 1.5 s,
number of transient: 30 thousands, point of data: 8 K

tuent parameters of Cl and CH_3 are similar. The chemical shifts of eight strong peaks in Fig. 3 and those in Fig. 2 are in the same positions, so that the following structure was given.

	γ'	β'	α	β	$\gamma(\delta')$	CO_2	CH_3	$\delta'(\delta)$
$\{\text{CH}_2 - \text{CH} = \text{CCl} - \text{CH}_2 - \text{CH}(\text{CO}_2\text{CH}_3) - \text{CH}_2\}$								
<i>trans</i> 1,4- δ_{obs}	26.14	126.64	132.36	41.79	42.86	175.11	51.65	30.14
No. of peak	1	20	25	12	14	30	16	6
substituent para-	-4.13	-5.05	4.87	6.55	-2.22			-1.36
meters of Cl					(V)			
					"head to head"			

The assignment of resonance peaks of V is in agreement with off resonance decoupling ^{13}C -NMR spectrum. It is proved that CP units in PCM exist as *trans* 1,4-structure and connect with MA in the form of "head to head". The substituent parameters of Cl obtained from V and I are listed under the corresponding carbons of V.

It is difficult to determine if there is "head to tail" structure similar to IV, because there are more weak peaks in the spectrum of PCM, needing more accurate calculation. Structure I may be rewritten as

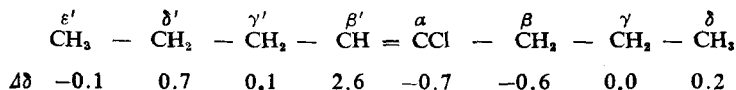


Its chemical shifts plus corresponding substituent parameters of Cl are equal to the calculated chemical shifts of VI, so that PCM can exist as the form of structure VI.

	γ'	β'	α	β	γ'	δ'	CO_2	CH_3
$\{\text{CH}_2 - \text{CH} = \text{CCl} - \text{CH}_2 - \text{CH}_2 - \text{CH}(\text{CO}_2\text{CH}_3)\}$								
<i>trans</i> 1,4- δ_{cal}	31.11	122.44	136.56	36.82	29.26	43.72	—	—
δ_{obs}	30.80	122.91	135.39	37.04	29.12	43.96	175.00	51.66
No. of peak	7	17	28	9	4	15	29	16
					(VI)			
					"head to tail"			

The influence of Cl on the chemical shifts of carbonyl group in VI is smaller than that in V, so that peak No. 29 in Fig. 3 was assigned for the peak of carbonyl group of VI.

The following method can be used to determine *cis* 1,4-configuration of CP units and "head to head" connection with MA. The differences of chemical shifts of *cis*- and *trans*-structures will be calculated from model compounds $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CClCH}_2\text{CH}_2\text{CH}_3$ (*cis* and *trans*), $\Delta\delta = \delta_{\text{cis}} - \delta_{\text{trans}}$.



By adding the $\Delta\delta$ values and corresponding chemical shifts of V, the calculated chemical shifts of VII were obtained.

	[CH ₂ - CH = CCl - CH ₂ - CH (CO ₂ CH ₃) - CH ₂]							
<i>cis</i> 1,4- δ_{cal}	26.2	129.2	131.7	35.8	42.8	—	—	31.0
δ_{obs}	26.14	129.05	131.49	35.93	42.86	175.11	51.66	29.68
No. of peak	1	22	23	8	14	30	16	5

(VII)

"head to head"

The other weak peaks in Fig. 3 arised from structures other than alternating ones are not being assigned in this paper. However, we can see from Fig. 3 that there are CP-CP units but not MA-MA units in PCM. No alternating structures in PBM and in PIM were observed. The difficulty of forming alternating copolymer of CP and MA is consistent with previous results^[3,9].

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