

## NMR Spin-Lattice Relaxation Times of Poly( $\alpha$ -substituted acrylate)s in Solution

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<sup>13</sup>C NMR spin-lattice relaxation time ( $T_1$ ) of various poly( $\alpha$ -substituted acrylate)s were measured in solution at 25MHz and in most cases at 110°C. The influence of  $\alpha$ -substituent and ester group as well as stereochemistry of the main chain on the mobility of the polymer chain was discussed based on a single correlation time assumption. As either the  $\alpha$ -substituent or the ester group in poly( $\alpha$ -alkylacrylate) becomes bulkier, <sup>13</sup>C- $T_1$ 's not only for the main chain carbons but also for those in the side groups tend to decrease. The isotactic polymers generally showed larger <sup>13</sup>C- $T_1$  than the corresponding syndiotactic ones. The difference in <sup>13</sup>C- $T_1$  between these tactic polymers decreases as the side groups become bulkier. Syndiotactic poly(diphenylmethyl methacrylate) showed larger  $T_1$  values than the isotactic one. <sup>13</sup>C- $T_1$ 's of poly( $\alpha$ -chloroacrylate)s and poly( $\alpha$ -bromoacrylate)s showed a similar tacticity dependence to those of poly( $\alpha$ -alkylacrylate)s and indicate that these polymers are less flexible than the corresponding polymethacrylates. Solvent dependency of <sup>13</sup>C- $T_1$  and <sup>1</sup>H- $T_1$  of isotactic and syndiotactic poly(methyl methacrylate)s was also studied.

KEY WORDS: Poly( $\alpha$ -substituted acrylate)/ Tacticity/ Spin-lattice Relaxation Time/ Solvent Effect/ Nuclear Overhauser Enhancement/

### INTRODUCTION

NMR relaxation parameters give valuable information on the local molecular motion of polymer chain in solution. For several vinyl polymers including polystyrene<sup>1</sup>, poly(vinyl chloride)<sup>2</sup>, poly(vinyl alcohol)<sup>2</sup> and polyacrylonitrile<sup>2</sup>, the equality of <sup>13</sup>C spin-lattice relaxation times ( $T_1$ ) was found for comparable carbons in different steric configurations. The configurational dependence of <sup>13</sup>C- $T_1$  was later reported for polypropylene<sup>3</sup> and poly(methyl methacrylate)<sup>4-7</sup>. We reported that  $T_1$ 's of protons<sup>8,9</sup> and carbons in isotactic poly(alkyl methacrylate)s were always longer than the corresponding  $T_1$ 's of syndiotactic polymers, revealing high segmental mobility of the isotactic polymers. Very recently, Research Group on NMR, Society of Polymer Science, Japan, collected <sup>1</sup>H- and <sup>13</sup>C- $T_1$ 's and <sup>13</sup>C nuclear Overhauser enhancement (NOE) data for a poly(methyl methacrylate) in CDCl<sub>3</sub> measured on a number of spectrometers, whose observing frequencies ranged from 60 to 500 MHz for <sup>1</sup>H NMR and 15 to 125 MHz for <sup>13</sup>C NMR<sup>10</sup>. The results confirmed that the protons and carbons in the sequence rich in meso dyad showed longer  $T_1$ 's than those in the corresponding sequence rich in racemo dyad.

In this paper, the relationship between the spin-lattice relaxation times and the

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stereoregularity as well as the substituents of various poly( $\alpha$ -alkylacrylate)s and poly( $\alpha$ -haloacrylate)s is described. Solvent dependency of  $^{13}\text{C}$ - $T_1$  for isotactic and syndiotactic PMMAs was also studied.

### Experimentals

Proton-decoupled  $^{13}\text{C}$  NMR spectra were taken on a JNM-FX100 Fourier transform NMR spectrometer (JEOL) operating at 25 MHz.  $^{13}\text{C}$ - $T_1$  was measured by the inversion-recovery method.  $^{13}\text{C}$ - $^1\text{H}$  nuclear Overhauser enhancement (NOE) was determined by a gated decoupling method.  $^1\text{H}$ - $T_1$  was also measured by the inversion-recovery method on a JNM-PFT-100 (JEOL) and the JNM-FX100 spectrometers at 100 MHz. The solution of polymer was degassed and sealed in an NMR sample tube under nitrogen pressure. Ten and 5 mm o.d. tubes were used for  $^{13}\text{C}$  and  $^1\text{H}$  NMR measurements, respectively. The precision of the measurement was within  $\pm 10\%$ .

## RESULTS AND DISCUSSION

### 1. *Poly( $\alpha$ -substituted acrylate)*

A simple one-correlation-time isotropic model of rotational reorientation seems capable of providing a framework for the description of the spin-lattice relaxation times of a wide variety of polymer solutions. As long as we are only trying to understand qualitatively the mobility of one particular carbon relative to other carbons, a simple first-order-correlation-time description can be both useful and revealing. Thus, it is assumed in the following discussion that a less fluxible chain has shorter spin-lattice relaxation times, and vice versa.

$^{13}\text{C}$ - $T_1$ 's of various poly( $\alpha$ -alkylacrylate)s including polymethacrylates were measured in toluene- $d_8$  at  $110^\circ\text{C}$ . The results are shown in Table I. A part of the data for poly(alkyl methacrylate)s were reported previously<sup>6,7</sup>.

In all the cases of poly(alkyl methacrylate)s, the main chain carbons ( $\text{CH}_2$  and C-4) in the isotactic polymers showed longer  $T_1$ 's than the corresponding carbons in the syndiotactic polymers. This indicates the higher mobility of the main chain of the isotactic polymethacrylates than those of the syndiotactic ones. This is also true for the mobility of the side groups in the ester function as well as  $\alpha$ -methyl group. The stereochemistry in the main chain affects not only the main chain motion but also the side group mobility.

Tacticity dependency of side chain mobility is well demonstrated for the case of poly(*n*-butyl methacrylate)s. The  $T_1$  value for the main chain methylene carbons in the isotactic polymer is larger than in the syndiotactic one by a factor of 1.57.

NMR Spin-Lattice Relaxation Times of Poly( $\alpha$ -substituted acrylate)s

 Table I.  $^{13}\text{C}$ - $T_1$  (sec) of Poly( $\alpha$ -substituted acrylate)s in Toluene- $d_8$  at  $110^\circ\text{C}$ 

$\alpha$ -Substituent	Ester group	Tacticity (%)			CH <sub>2</sub>	C-4	C=O	$\alpha$ -Subst.		Ester group			
		I	H	S				CH <sub>2</sub>	CH <sub>3</sub>	CH	CH <sub>2</sub>	CH <sub>3</sub>	
CH <sub>3</sub> <sup>a</sup>	CH <sub>3</sub>	it	96	4	0	0.28	2.96	7.85	—	0.49	—	—	1.78
CH <sub>3</sub> <sup>a</sup>	CH <sub>3</sub>	st	2	4	91	0.10	1.63	3.03	—	0.22	—	—	1.13
CH <sub>3</sub> <sup>a</sup>	C <sub>2</sub> H <sub>5</sub>	it	94	4	2	0.19	2.38	3.50	—	0.42	—	0.82	4.84
CH <sub>3</sub> <sup>a</sup>	C <sub>2</sub> H <sub>5</sub>	st	12	17	71	0.086	1.34	2.95	—	0.22	—	0.53	2.60
CH <sub>3</sub> <sup>a</sup>	i-C <sub>3</sub> H <sub>7</sub>	it	91	5	4	0.13	2.36	2.88	—	0.35	0.64	—	1.38
CH <sub>3</sub> <sup>a</sup>	i-C <sub>3</sub> H <sub>7</sub>	st	6	28	66	0.077	1.01	2.33	—	0.18	0.36	—	0.87
CH <sub>3</sub> <sup>a</sup>	t-C <sub>4</sub> H <sub>9</sub>	it	98	1	1	0.074	1.07	2.60	—	0.24	—	—	0.93
CH <sub>3</sub> <sup>a</sup>	t-C <sub>4</sub> H <sub>9</sub>	st	18	42	40	0.036	0.67	1.84	—	0.13	—	—	0.73
CH <sub>3</sub> <sup>a</sup>	n-C <sub>4</sub> H <sub>9</sub>	it	95	3	2	0.13	1.87	4.96	—	0.33	—	0.43 <sup>b</sup>	5.83
CH <sub>3</sub> <sup>a</sup>	n-C <sub>4</sub> H <sub>9</sub>	st	3	34	63	0.084	1.00	3.14	—	0.21	—	0.30 <sup>b</sup>	4.78
C <sub>2</sub> H <sub>5</sub> <sup>c</sup>	CH <sub>3</sub>	it	44	14	42	0.098	1.40	4.32	0.12	0.62	—	—	1.07
		st	44	14	42	0.083	1.18	3.70	0.086	—	—	—	—
C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	it	56	23	21	0.092	1.31	2.91	0.084 <sup>d</sup>	0.91	—	—	0.80
CH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	at	23	49	28	0.056	0.79	1.91 (H)	0.044	—	—	—	0.40
								1.70 (S)					
CH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	at	25	47	28	0.063	0.069	1.80 (I)	0.049	—	—	0.13	0.69
								1.53 (S)					

<sup>a</sup> The data taken from the literature<sup>7</sup>.

<sup>b</sup>  $T_1$  value of  $\alpha$ -methylene carbon of n-butyl group.

<sup>c</sup> The measurement was done on the mixture of the isotactic and syndiotactic polymers formed in the polymerization in toluene with n-C<sub>4</sub>H<sub>9</sub>Li at  $-78^\circ\text{C}$ .

<sup>d,e</sup>  $T_1$  values of  $\alpha$ - and  $\beta$ -methylene carbons in  $\alpha$ -n-propyl group, respectively.

$$\text{CH}_3-\overset{\text{I}}{\underset{\text{CH}_2}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{(\alpha)}{\text{CH}_2}-\overset{(\beta)}{\text{CH}_2}-\overset{(\gamma)}{\text{CH}_2}-\overset{(\delta)}{\text{CH}_3}$$

isotactic	0.33	0.13	4.96	0.43	1.51	3.70	5.80
syndiotactic	0.21	0.08	3.14	0.30	1.05	3.50	4.08
i/s	1.53	1.57	1.58	1.44	1.44	1.06	1.21

$T_1$  values for the side chain methylenes in either the isotactic or the syndiotactic polymer increase as  $\alpha < \beta < \gamma$ . The ratio  $i/s$  of the  $T_1$  values of each methylene carbon was less than that for the main chain methylene carbon and decreases as  $\alpha = \beta > \gamma$ . Thus, the stereochemistry in the main chain affects the mobility of  $\alpha$ - and  $\beta$ -methylene carbons in the ester side chain but did not affect the  $\gamma$ -methylene mobility.  $\alpha$ -Methyl and carbonyl carbons, which are directly attached to the main chain, showed a similar extent of tacticity dependency of  $^{13}\text{C}$ - $T_1$  as the main chain carbons.

Poly(methyl  $\alpha$ -ethylacrylate) formed in the polymerization in toluene at  $-78^\circ\text{C}$  with n-C<sub>4</sub>H<sub>9</sub>Li was a mixture of isotactic and syndiotactic polymers<sup>11</sup>.  $^{13}\text{C}$ - $T_1$ 's for the isotactic and syndiotactic polymers could be determined separately for the tacticity sensitive peaks observed in the spectrum of this mixture. The main chain methylene,

quaternary, carbonyl and  $\alpha$ -methylene carbons in the isotactic chains showed longer  $T_1$ 's than the corresponding carbons in the syndiotactic chains, showing higher flexibility of the isotactic polymer, though the differences between  $T_1$ 's for both tactic polymers are small as compared to the cases of polymethacrylates.

$T_1$  values for main chain methylene and quaternary carbons in poly(methyl  $\alpha$ -ethylacrylate)s were smaller than those for the corresponding carbons in poly(ethyl methacrylate) as well as poly(methyl methacrylate). This indicates that the replacement of methyl group by ethyl at the  $\alpha$ -position causes greater decrease in the main chain mobility than the replacement in the ester group.

An isotactic poly(methyl  $\alpha$ -propylacrylate), atactic poly(methyl  $\alpha$ -phenoxyethylacrylate)<sup>12)</sup> and atactic poly(ethyl  $\alpha$ -phenoxyethylacrylate)<sup>12)</sup> also showed smaller  $T_1$  values for main chain carbons than the corresponding polymethacrylates. Then the main chain mobility of poly( $\alpha$ -substituted acrylate) decreases with increasing bulkiness of the  $\alpha$ -substituent. While  $T_1$ 's for the main chain carbons of poly(methyl methacrylate) and poly(ethyl methacrylate) are apparently different, the  $T_1$ 's for the methyl and ethyl esters of poly( $\alpha$ -phenoxyethylacrylate) are not evidently different, probably due to the predominant effect of the bulky  $\alpha$ -substituent on the chain mobility.

$T_1$ 's for  $\alpha$ -methylene and ester methyl carbons in poly(methyl  $\alpha$ -substituted acrylate) also decreased with increasing bulkiness of the  $\alpha$ -substituents as follows;

$\alpha$ -Substituent	$T_1$ (sec)	
	$\alpha$ -CH <sub>2</sub>	OCH <sub>3</sub>
C <sub>2</sub> H <sub>5</sub>	0.12	1.07
n-C <sub>3</sub> H <sub>7</sub>	0.084	0.80
CH <sub>2</sub> O-C <sub>6</sub> H <sub>5</sub>	0.044	0.40

Even though the methoxyl groups have much greater freedom of motion as seen from the longer  $T_1$ 's, their mobility is greatly affected by the decreased main chain mobility owing to the existence of the bulky  $\alpha$ -substituents.

## 2. Poly( $\alpha$ -haloacrylate)

<sup>13</sup>C- $T_1$ 's for the polymers of methyl, ethyl and isopropyl  $\alpha$ -chloroacrylates were measured in nitrobenzene-d<sub>5</sub> and in toluene-d<sub>8</sub> at 110°C. The results are shown in Table II. Preparation and tacticity determination of the polymers were reported previously<sup>13,14)</sup>.  $T_1$  determination was performed on the highest peak in each carbon resonance. The  $T_1$ 's of all the carbon signals except for those of ester groups are tacticity sensitive. For the methyl ester, isotactic polymer could not be obtained and the  $T_1$  values for the heterotactic and syndiotactic rich samples were determined. The poly(methyl  $\alpha$ -chloroacrylate)s were less soluble in toluene, and thus the  $T_1$  was measured in nitrobenzene-d<sub>5</sub>.

NMR Spin-Lattice Relaxation Times of Poly( $\alpha$ -substituted acrylate)s

 Table II.  $^{13}\text{C}$ - $T_1$  (sec) of Poly( $\alpha$ -chloroacrylate)s in Nitrobenzene- $d_5$  and in Toluene- $d_8$  at  $110^\circ\text{C}$ 

Ester group	Tacticity (%)			Solvent	$\text{CH}_2$	C-4	C=O	Ester group		
	I	H	S					CH	$\text{CH}_2$	$\text{CH}_3$
$\text{CH}_3$	16	47	37	Nitrobenzene	—	2.37	4.76	—	—	0.84
	7	33	60	Nitrobenzene	0.078	1.37	3.62	—	—	0.50
$\text{C}_2\text{H}_5$	64	13	23	Nitrobenzene	0.071	1.94	—	—	0.33	1.79
	16	30	54	Nitrobenzene	0.067	1.22	3.59	—	0.26	1.96
$\text{isoC}_3\text{H}_7$	53	29	18	Nitrobenzene	0.050	1.15	2.75	0.33	—	0.64
	8	18	74	Nitrobenzene	0.048	1.12	2.00	0.28	—	0.70
$\text{C}_2\text{H}_5$	64	13	23	Toluene	0.120	2.02	6.73	—	0.49	2.53
	16	30	54	Toluene	0.081	1.63	4.06	—	0.46	2.09
$\text{isoC}_3\text{H}_7$	53	29	18	Toluene	0.060	1.43	3.14	0.35	—	0.89
	8	18	74	Toluene	0.063	1.28	3.32	0.36	—	0.75

For the methyl and ethyl  $\alpha$ -chloroacrylate polymers, larger  $T_1$ 's were observed in the isotactic or heterotactic polymer than in the syndiotactic polymer as in the case of the poly( $\alpha$ -substituted acrylate)s. As the ester group becomes bulkier, the  $T_1$  values themselves as well as the difference in  $T_1$  values between the isotactic and syndiotactic polymers decreased. The isotactic and syndiotactic poly(isopropyl  $\alpha$ -chloroacrylate)s showed almost the same  $T_1$  values.

To compare the effect of  $\alpha$ -chloro and  $\alpha$ -methyl substituents on the  $T_1$  values,  $T_1$  data for polymethacrylates and poly( $\alpha$ -chloroacrylate)s with a similar tacticity were collected in Table III. Unfortunately, the isotacticities of the poly( $\alpha$ -chloroacrylate)s are much lower than those of the polymethacrylates used in this study and the tacticity difference might not be negligible. Thus, the case of syndiotactic polymers will be first discussed.

 Table III. Comparison of  $^{13}\text{C}$ - $T_1$  (sec) of Polymethacrylate and Poly( $\alpha$ -chloroacrylate) in Toluene- $d_8$  at  $110^\circ\text{C}$ 

	$\alpha$ -Substituent	Ester group	$\text{CH}_2$	C-4	C=O	Ester group		
						CH	$\text{CH}_2$	$\text{CH}_3$
Syndiotactic	$\text{CH}_3^{\text{a,b}}$	$\text{CH}_3$	0.081	1.26	2.95	—	—	1.15
	$\text{Cl}^{\text{b}}$	$\text{CH}_3$	0.078	1.37	3.62	—	—	0.50
	$\text{CH}_3$	$\text{C}_2\text{H}_5$	0.086	1.34	2.95	—	0.53	2.60
	$\text{Cl}$	$\text{C}_2\text{H}_5$	0.081	1.63	4.06	—	0.46	2.09
	$\text{CH}_3$	$\text{isoC}_3\text{H}_7$	0.077	1.01	2.33	0.36	—	0.87
	$\text{Cl}$	$\text{isoC}_3\text{H}_7$	0.063	1.28	3.32	0.36	—	0.75
Isotactic	$\text{CH}_3$	$\text{C}_2\text{H}_5$	0.19	2.38	3.50	—	0.82	4.84
	$\text{Cl}$	$\text{C}_2\text{H}_5$	0.12	2.02	6.73	—	0.49	2.53
	$\text{CH}_3$	$\text{isoC}_3\text{H}_7$	0.13	2.36	2.88	0.64	—	1.38
	$\text{Cl}$	$\text{isoC}_3\text{H}_7$	0.060	1.43	3.14	0.35	—	0.89

<sup>a</sup> I:H:S=6:36:58.

<sup>b</sup> Measured in nitrobenzene- $d_5$  at  $110^\circ\text{C}$ .

Main chain methylene and ester carbons in the syndiotactic poly( $\alpha$ -chloroacrylate)s showed a little shorter  $T_1$ 's than the corresponding carbons in the syndiotactic polymethacrylates. On the other hand,  $T_1$ 's for the quaternary and the carbonyl carbons of the poly( $\alpha$ -chloroacrylate)s were larger than those of the corresponding carbons in the polymethacrylates. The larger  $T_1$  values for these unprotonated carbons in poly( $\alpha$ -chloroacrylate)s may be explained as follows; magnetic relaxation of the quaternary and carbonyl carbons in polymethacrylates can occur through a dipole-dipole interaction with their neighboring protons in methylene and  $\alpha$ -methyl groups. Thus the replacement of  $\alpha$ -methyl group with chlorine atom cuts off one of the relaxation paths, leading to the larger  $T_1$ 's, while the relaxation of carbons having directly attached hydrogen could be hardly affected by the replacement because the relaxation through the directly bonded hydrogen is predominant in these cases. Therefore, the larger  $T_1$ 's for the methylene carbons in the polymethacrylates indicate the higher flexibility as compared with the poly( $\alpha$ -chloroacrylate), but the smaller  $T_1$ 's for the quaternary carbon does not mean lower flexibility.

In the case of the isotactic polymers,  $T_1$ 's not only for the main chain methylene carbons but also for the quaternary carbons in the polymethacrylates are longer than those in the corresponding poly( $\alpha$ -chloroacrylate)s. This may indicate that the flexibility of the isotactic polymethacrylates is much higher than that of the corresponding poly( $\alpha$ -chloroacrylate)s, partly due to the higher isotacticities of the former polymers, so that even the quaternary carbons in the poly( $\alpha$ -chloroacrylate)s showed smaller  $T_1$  values than those in the polymethacrylates. In general, the replacement of  $\alpha$ -methyl group in polymethacrylate by chlorine atom tends to decrease the segmental mobility of the chain. In a steric sense, chlorine may be comparable with methyl group. Thus, the decreased mobility might be due to the dipolar interaction of C-Cl bonds which restricts the chain conformation.

$^{13}\text{C}$ - $T_1$  and NOE of poly( $\alpha$ -bromoacrylate)s<sup>15)</sup> were measured in nitrobenzene- $d_5$  at 27°C and are shown in Table IV together with those for syndiotactic poly(methyl  $\alpha$ -chloroacrylate). The measurement at higher temperature was not possible because of lactone ring formation in the poly( $\alpha$ -bromoacrylate) chain during the measurement.

Table IV.  $^{13}\text{C}$ - $T_1$  (sec) and NOE of Poly( $\alpha$ -bromoacrylate)s and Poly(methyl  $\alpha$ -chloroacrylate) in Nitrobenzene- $d_5$  at 27°C

$\alpha$ -Substituent	Ester group	Tacticity	CH <sub>2</sub>	C-4	C=O	Ester group			
						$\alpha$ -CH <sub>2</sub>	$\beta$ -CH <sub>2</sub>	CH <sub>3</sub>	
Br	CH <sub>3</sub>	Isotactic	$T_1$	—	0.81	1.84	—	—	0.44
			NOE	—	1.3	1.5	—	—	1.2
		Syndiotactic	$T_1$	—	0.68	2.06	—	—	0.42
			NOE	—	1.2	1.5	—	—	1.3
Br	n-C <sub>3</sub> H <sub>7</sub>	Isotactic	$T_1$	0.06	—	(2.3)	0.13	0.41	1.35
			NOE	—	0.64	1.72	0.10	0.25	1.35
		Syndiotactic	$T_1$	—	1.6	1.4	1.8	2.2	2.2
			NOE	—	0.90	2.85	—	—	0.63
Cl	CH <sub>3</sub>	$T_1$	—	0.90	2.85	—	—	0.63	
		NOE	—	1.3	1.3	—	—	1.3	

$^{13}\text{C}$ - $T_1$  was always generally longer in the isotactic polymers than in syndiotactic one, although the difference in the  $T_1$ 's between the isotactic and syndiotactic polymers is rather small.

The low values of NOE for poly( $\alpha$ -bromoacrylate)s and poly(methyl  $\alpha$ -chloroacrylate) are presumably an indication of the lower mobility of these polymer chains. The  $T_1$  of syndiotactic poly(methyl  $\alpha$ -bromoacrylate) is slightly shorter than the corresponding  $T_1$  of poly(methyl  $\alpha$ -chloroacrylate), indicating that the replacement of chlorine by bromine at the  $\alpha$ -position decreases the freedom of the segmental mobility. Because dipole moment of C-Br bond is not larger than that of C-Cl bond, steric bulkiness of bromine may be an important factor for this tendency.

### 3. Polymethacrylate having aromatic ring in their ester group.

$^{13}\text{C}$ - and  $^1\text{H}$ - $T_1$ 's for polymers of benzyl,  $\alpha$ -methylbenzyl and diphenylmethyl methacrylates were measured in toluene- $d_8$  at  $110^\circ\text{C}$ . The results are shown in Table V. The bulkier the ester group (benzyl <  $\alpha$ -methylbenzyl < diphenylmethyl), the smaller the  $^{13}\text{C}$ - and  $^1\text{H}$ - $T_1$ 's. In the former two cases, the isotactic polymers generally showed longer  $T_1$ 's than the syndiotactic ones as in the cases of the poly(alkyl methacrylate)s. However, most of carbons and protons in the isotactic poly(diphenylmethyl methacrylate) showed shorter  $T_1$ 's than the corresponding ones in the syndiotactic polymer. Temperature dependence of the  $^{13}\text{C}$ - $T_1$  for the methylene and  $\alpha$ -methyl carbons are shown in Figure 1. While  $^{13}\text{C}$ - $T_1$ 's for the  $\alpha$ -methyl carbon stayed left side to their minimum,  $^{13}\text{C}$ - $T_1$ 's for the methylene carbon seem near to its minimum. However, the methylene  $T_1$  values for both the isotactic and syndiotactic polymers observed at  $110^\circ\text{C}$  seem to lie left side to the  $T_1$  minimum and would be inversely proportional to the correlation time, even though the plot for the isotactic polymer is very flat in the temperature range from  $60$  to  $110^\circ\text{C}$ . Thus, larger  $T_1$  values at  $110^\circ\text{C}$  for the syndiotactic poly(diphenylmethyl methacrylate) indicate higher mobility of the

Table V.  $^{13}\text{C}$ - and  $^1\text{H}$ - $T_1$  (sec) of Polymethacrylate Having Phenyl Group in Their Ester Function

Ester group	Tacticity (%)			Carbon							Proton				
				Ester group				Ester group			Ester group				
	I	H	S	CH <sub>2</sub>	C-4	$\alpha$ -CH <sub>3</sub>	C=O	CH	CH <sub>2</sub>	C-1 <sup>b</sup>	CH <sub>2</sub>	$\alpha$ -CH <sub>3</sub>	CH	CH <sub>2</sub>	CH <sub>3</sub>
CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	81	15	4	0.076	1.31	0.20	3.20	—	0.21	6.3	0.11	0.17	—	0.35	—
	6	31	63	0.065	0.68	0.12	1.99	—	0.19	—	0.088	0.13	—	0.37	—
CH-C <sub>6</sub> H <sub>5</sub>	76	13	11	0.053	0.80	—	1.83	0.21	—	2.81	0.11	0.13	0.73	—	0.31
CH <sub>3</sub>	4	20	76	0.045	0.85	0.13	1.42	0.18	—	2.50	0.077	0.12	0.61	—	0.32
CH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> <sup>c</sup>	99	1	0	0.032	0.54	0.096	1.56	0.092	—	1.85	0.076	0.11	0.47	—	—
				(1.45) <sup>d</sup>	(1.60) <sup>d</sup>	(2.26) <sup>d</sup>	(1.21) <sup>d</sup>	(1.49) <sup>d</sup>	(1.45) <sup>d</sup>						
	2	11	87	0.035	0.63	0.11	1.42	0.13	—	1.77	0.087	0.13	0.56	—	—
				(1.84) <sup>d</sup>	(1.86) <sup>d</sup>	(2.16) <sup>d</sup>	(1.62) <sup>d</sup>	(2.17) <sup>d</sup>		(1.70) <sup>d</sup>					

<sup>a</sup> Measured in toluene- $d_8$  at  $110^\circ\text{C}$ .

<sup>b</sup> C-1 carbon of phenyl groups.

<sup>c</sup>  $^1\text{H}$ - $T_1$  was measured in nitrobenzene- $d_5$  at  $140^\circ\text{C}$ .

<sup>d</sup> NOE value.

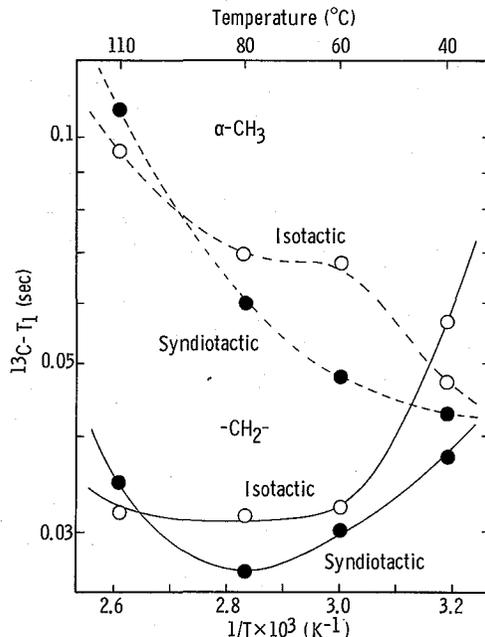


Figure 1. Temperature dependence of  $^{13}\text{C}-T_1$  for methylene and  $\alpha$ -methyl carbons in isotactic and syndiotactic poly(diphenylmethyl methacrylate)s in toluene- $d_8$ . (O; isotactic, ●; syndiotactic)

polymer than the isotactic polymer. NOE values at  $110^\circ\text{C}$  were higher for the syndiotactic polymer than isotactic one, also supporting the above results. It has been believed that isotactic polymer chain tends to take helical structure. If this is the case for poly(diphenylmethyl methacrylate), more restricted mobility of the isotactic chains would be ascribed to interactions among the phenyl groups in the neighboring ester functions, which make the helical conformation rigid.

As described previously, most of  $T_1$  values for poly(benzyl methacrylate) were larger for the isotactic polymer than for the syndiotactic one. However, the  $^1\text{H}$ - and  $^{13}\text{C}-T_1$ 's for benzyl methylene groups in both the polymers were very close to each other in contrast to the cases of ester groups in poly(alkyl methacrylate)s. Figure 2 shows  $^1\text{H}-T_1$  data for isotactic and syndiotactic poly(MMA-co-benzyl methacrylate)s with various compositions, which were prepared with  $n\text{-C}_4\text{H}_9\text{Li}$  in toluene (for isotactic copolymers) and in THF (for syndiotactic copolymers) and were found random in their monomer sequence distribution<sup>16</sup>. All the  $T_1$  values became larger as the content of MMA units increased.  $^1\text{H}-T_1$ 's for the benzyl methylene protons in the isotactic and syndiotactic copolymers were always very close to each other, while the other protons showed larger  $T_1$ 's for the isotactic copolymers regardless of the composition. The results indicate that the relaxation of the benzyl methylene protons is mainly determined by the internal mobility of the ester group, such as rotation around  $\text{CH}_2\text{-Ph}$  bond.

Triphenylmethyl methacrylate(TrMA) gives only isotactic polymers under various polymerization conditions, because the bulky triphenylmethyl group prevents the syn-

NMR Spin-Lattice Relaxation Times of Poly( $\alpha$ -substituted acrylate)s

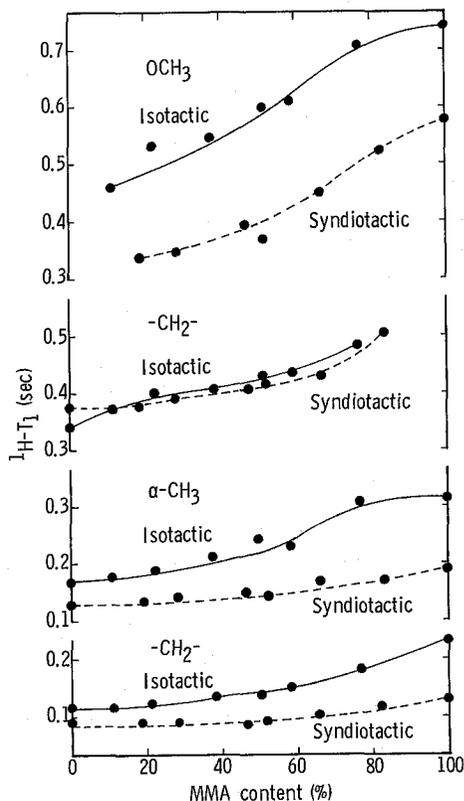


Figure 2.  $^1\text{H-T}_1$  of isotactic and syndiotactic poly(methyl methacrylate-co-benzyl methacrylate)s in toluene- $d_8$  at  $110^\circ\text{C}$ .  
 (—●—; isotactic, ---●---; syndiotactic)

diotactic placement of the incoming monomer to the growing chain end, favors isotactic propagation as a result, and forces the polymer chain to take a helical structure<sup>17</sup>. The helical structure was found to be stable enough to give optically active polymer whose optical activity arises only from the helicity of the chain, when the polymer was prepared with chiral anionic initiators<sup>18-21</sup>. Anionic copolymerization of TrMA with a small amount of (S)- $\alpha$ -methylbenzyl methacrylate gave optically active copolymers containing the one-handed helical sequence of TrMA<sup>22</sup>.

To examine the flexibility of poly(TrMA) chain, NMR measurements were performed on the homopolymer of TrMA and two copolymers of TrMA with (S)- $\alpha$ -methylbenzyl methacrylate in toluene- $d_8$ , which were prepared in THF with  $n\text{-C}_4\text{H}_9\text{Li}$  at  $-78^\circ\text{C}$ <sup>22</sup>. The polymers were less soluble at higher temperature and NMR measurements were made at  $27^\circ\text{C}$ . The results are shown in Table VI. Because of the broadness of peaks due to the rigidity of the chain,  $T_1$  and NOE data were obtained for only a limited number of sharp signals. NOE values for the main chain quaternary carbon are near to unity and smaller than that in PMMA at  $24^\circ\text{C}$ (1.95)<sup>10</sup>, indicating lower mobility of the chain. Average TrMA sequence length of the copolymer A(80% TrMA content) is shorter than those of the homopolymer and the copolymer B(95%

Table VI.  $^{13}\text{C}$ - $T_1$  and NOE of Triphenylmethyl Methacrylate Units in the Homopolymer and Copolymers with (S)- $\alpha$ -Methylbenzyl Methacrylate in Toluene- $d_8$  at 27°C and at 25MHz

Polymer	TrMA content	C-4		C=O		C-1 <sup>a</sup>		OC(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	
		$T_1$	NOE	$T_1$	NOE	$T_1$	NOE	$T_1$	NOE
Homopolymer	1.00	0.82	1.2	1.42	1.3	1.67	1.2	2.53	1.4
Copolymer A	0.80	0.98	1.5	1.60	1.2	2.14	1.7	3.88	1.5
Copolymer B	0.95	—	—	—	—	1.6	—	—	—

<sup>a</sup> C-1 carbon in the phenyl group.

TrMA content). The copolymer A showed larger  $T_1$  and NOE values than the latter two polymers. This indicates that the longer TrMA sequence in the copolymer B or homopolymer takes more rigid helical structure than the shorter TrMA sequence in the copolymer A. Signal intensities of the copolymer B were lower than those for the copolymer A by factors of 3 to 24 depending on the type of carbon, also indicating higher rigidity of the longer TrMA sequence in the copolymer B. These are consistent with the observation that the copolymer A changed its optical rotation upon heating due to racemization of the helix, while the copolymer B did not<sup>22</sup>).

#### 4. Solvent effect on $T_1$ of isotactic and syndiotactic PMMAs.

Solvent dependence of  $^{13}\text{C}$ - $T_1$  for PMMA was reported for chloroform, benzene and acetonitrile solutions<sup>23,24</sup>. More recently Levy and Wang reported  $^{13}\text{C}$ - $T_1$  data for poly(butyl methacrylate) in concentrated solution using a wide variety of solvents, and discussed relationship between the side-chain mobility and solvent solubility parameters<sup>25</sup>. We reported previously  $^{13}\text{C}$ - $T_1$  data for the isotactic and syndiotactic PMMAs in five solvents<sup>7</sup>. The data were rearranged as in Figure 3, where  $1/nT_1$  ( $n$  is the number of attached protons to the carbon of interest) for methylene and  $\alpha$ -methyl carbons are plotted against solubility parameter  $\delta$  of the solvent used. NOE values for these carbons in the PMMAs in toluene- $d_8$  were close to the theoretical maximum of 2.998 except for the NOE for the methylene carbon in the syndiotactic PMMA at 60°C (2.29)<sup>7</sup>. Therefore, if we assume isotropic reorientation and single correlation time model, most of  $1/nT_1$  data are proportional to correlation time. Both methylene and  $\alpha$ -methyl carbons in isotactic PMMA showed maximum  $1/nT_1$  in nitrobenzene- $d_5$  at 60°C and 110°C. Apparent activation energy obtained from Arrhenius plot of  $1/nT_1$  for the methylene group were 6.2 (nitrobenzene), 5.7 (N, N-dimethylformamide) and 4.7 kcal/mol (toluene). These indicate that the chain mobility of the isotactic PMMA is most restricted in nitrobenzene. Reported values of  $\delta$  for conventional PMMA scatter from 9.08 to 12.84 (cal/cm<sup>3</sup>)<sup>1/2</sup>, and most of them are between 9.1 and 9.5<sup>26</sup>. The smaller the difference in  $\delta$  between polymer and solvent, the stronger the interaction between them. Therefore, the difference in  $\delta$  seems to predict the stronger interaction of PMMA with chloroform rather than with nitrobenzene, if the interaction more strongly restricts the chain mobility. This contradiction is owing either to other

NMR Spin-Lattice Relaxation Times of Poly( $\alpha$ -substituted acrylate)s

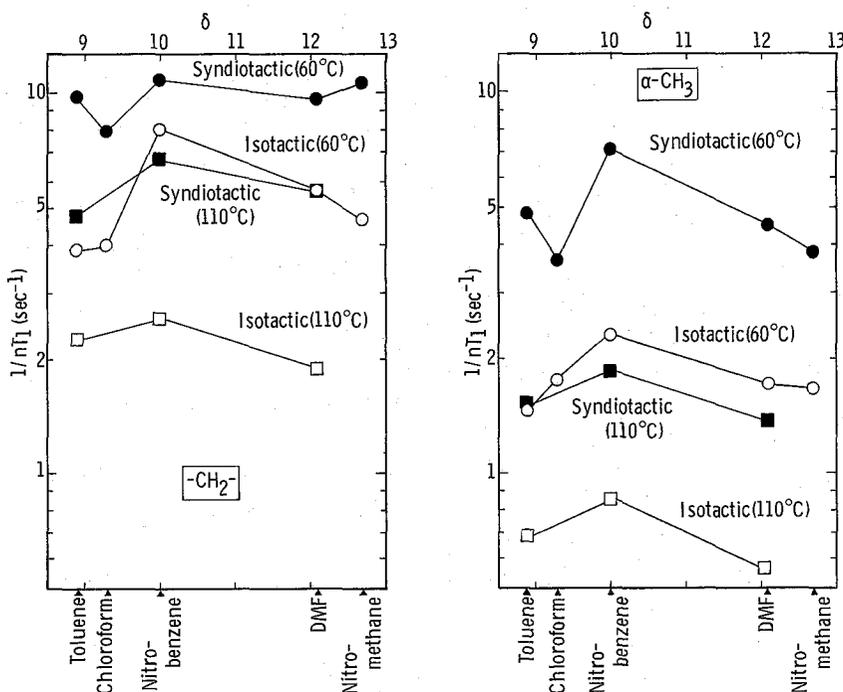


Figure 3.  $1/nT_1$  for methylene and  $\alpha$ -methyl carbons in isotactic and syndiotactic PMMAs in various solvents at 60 and 110°C.

specific interaction of nitrobenzene to PMMA or to different  $\delta$  value for the isotactic PMMA from that for conventional PMMA.

The  $T_1$ 's of methylene and  $\alpha$ -methyl carbons in the syndiotactic PMMA also showed a similar solvent dependency and the highest  $1/nT_1$  values for both the methylene and  $\alpha$ -methyl carbons were observed in nitrobenzene- $d_5$  at 60 and 110°C. Higher  $1/nT_1$  values for both carbons were observed in toluene than in chloroform at 60°C, which may be due to self-aggregation of highly syndiotactic PMMA in toluene<sup>27</sup>.

$^1\text{H}$ - $T_1$  might be sensitive to the conformation of the polymer chain as well as to the mobility. Relaxation rate ( $1/T_{\text{intra}}$ ) of methylene protons due to the partner methylene proton is expressed by the following equation<sup>28</sup>.

$$1/T_{\text{intra}} = N \frac{3}{10} \frac{\gamma_H^2 n^2}{r^6} \left( \frac{\tau}{1 + \omega_H^2 \tau^2} + \frac{4\tau}{1 + 4\omega_H^2 \tau^2} \right)$$

Here,  $\gamma_H$  is the gyromagnetic ratio of a proton,  $r$  and  $N$  are the distance between protons interacting with each other and the number of the interacting protons, respectively, and  $N=1$  in this case. If we assume the same correlation time for methylene carbon and protons,  $1/T_{\text{intra}}$  can be calculated from the correlation time estimated from  $^{13}\text{C}$ - $T_1$ .  $\tau$  was calculated from the following equation<sup>29</sup>.

$$\tau = \gamma_C^{-2} n \gamma_H^{-2} \hbar^{-2} / T_1 \sum_i r_i^{-6}$$

Observed proton relaxation rate ( $1/T_{\text{obs}}$ ) can be expressed as follows.

$$1/T_{\text{obs}} = 1/T_{\text{intra}} + 1/T_{\text{other}}$$

( $1/T_{\text{other}}$ ) represents the relaxation through the interaction with other protons than the partner methylene protons, including  $\alpha$ -methyl protons in the same monomeric unit and methylene protons in the next neighboring units. In Table VII are shown the results of the estimation.  $1/T_{\text{other}}$  may be affected by conformation difference, while  $1/T_{\text{intra}}$  directly reflects main chain mobility because H-H distance in the methylene group is fixed. The contribution of  $1/T_{\text{other}}$  (%) to  $1/T_{\text{obs}}$  changed with the solvents, indicating that solvents affect the conformation of PMMA.

Either the isotactic or syndiotactic PMMA showed the smallest  $1/T_{\text{other}}$  (%) in nitrobenzene- $d_5$  at 60°C.  $1/T_{\text{other}}$ 's of the isotactic and syndiotactic PMMAs in nitrobenzene- $d_5$  at 60°C differ most evidently. Although the meaning of these observations is not clear at present, both the  $^{13}\text{C}$ - $T_1$  data shown in Figure 3 and the above results might suggest some specific interactions of nitrobenzene and PMMA, which affect the mobility as well as the conformation of isotactic and syndiotactic PMMAs in a different way.

For elucidation of the possible interaction,  $^{13}\text{C}$ - $T_1$  of nitrobenzene was determined

Table VII. Contribution of  $1/T_{\text{intra}}$  and  $1/T_{\text{other}}$  to the Total Relaxation Rate of the Backbone Methylene Protons in PMMA in Various Solvents

Solvent <sup>a</sup>	Temp. (°C)	Isotactic RMMA			Syndiotactic PMMA		
		$1/T_{\text{obs}}$ (sec <sup>-1</sup> )	$1/T_{\text{intra}}$ (sec <sup>-1</sup> )	$1/T_{\text{other}}$ (sec <sup>-1</sup> ) (%)	$1/T_{\text{obs}}$ (sec <sup>-1</sup> )	$1/T_{\text{intra}}$ (sec <sup>-1</sup> )	$1/T_{\text{other}}$ (sec <sup>-1</sup> ) (%)
Toluene	110	4.42	2.22	2.20 (50)	9.71	5.64	4.07 (42)
Nitrobenzene	110	7.30	3.15	4.15 (57)	10.87	7.40	3.47 (32)
DMF <sup>b</sup>	110	5.15	2.34	2.82 (55)	9.90	6.32	3.58 (36)
Toluene	60	8.62	4.65	3.97 (46)	12.99	9.65	3.34 (26)
Chloroform	60	9.62	4.78	4.84 (50)	13.51	8.42	5.10 (38)
Nitrobenzene	60	12.99	8.51	4.47 (34)	11.90	10.21	1.69 (14)
DMF <sup>b</sup>	60	10.75	6.38	4.37 (41)	13.33	9.54	3.80 (28)
Nitromethane	60	9.35	5.50	3.85 (41)	13.16	10.10	3.06 (23)

<sup>a</sup> Deuterated solvents.

<sup>b</sup> N, N-Dimethylformamide.

Table VIII.  $^{13}\text{C}$ - $T_1$  (sec) of nitrobenzene in the presence and the absence of PMMA at 27°C and at 25MHz<sup>a</sup>

PMMA	Carbon			
	o-	m-	p-	C-1
None	6.99	6.85	4.65	98
Isotactic	3.93	3.82	2.84	63
Syndiotactic	4.08	4.14	2.69	63

<sup>a</sup> Nitrobenzene 1 ml, nitrobenzene- $d_5$  1 ml, PMMA 400 mg (if existed).

at 27°C in the presence and absence of the PMMA (20%). The nitrobenzene was diluted with the equivalent volume of nitrobenzene- $d_5$ . The results are shown in Table VIII.  $^{13}\text{C}$ - $T_1$  values of all the carbons decreased by the addition of PMMA. However, no appreciable difference due to the tacticity of the PMMA added was observed.

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