

## High-Performance Liquid Chromatography Using Stereoregular Poly(methyl methacrylate)s as Stationary Phases

Yoshio OKAMOTO, Masanori YANAGIDA, and Koichi HATADA

*Department of Chemistry, Faculty of Engineering Science,  
Osaka University, Toyonaka, Osaka 560, Japan*

(Received April 3, 1989)

**ABSTRACT:** Poly(methyl methacrylate)s (PMMA)s with five different tacticities were prepared by radical or anionic polymerization and used as stationary phases (packing materials) for high-performance liquid chromatography (HPLC). From retention times of small molecules on these stationary phases, tacticity effect on interactions between PMMA and solutes was evaluated. Aromatic hydrocarbons were chromatographed by using polar eluents, and polar benzene derivatives by nonpolar eluents. The retention times on the syndiotactic PMMA phase were much longer than those on the isotactic PMMA phase. The infrared spectra of the PMMA and HPLC data indicated that highly isotactic PMMA changes its conformation depending on the polarity of eluents. Poly(ethyl methacrylate)s and poly(benzyl methacrylate)s with different tacticities were also used as stationary phases.

**KEY WORDS** Poly(methyl methacrylate) / High-Performance Liquid Chromatography / HPLC / Tacticity / Stationary Phase / Packing Material / Poly(ethyl methacrylate) / Poly(benzyl methacrylate) / Stereoregular Poly(methyl methacrylate) /

It is well known that the properties of polymers depend on tacticity. However, detailed studies on the tacticity dependence of polymer properties are rather limited mainly because of the difficulty in obtaining polymers with largely different tacticities. Poly(methyl methacrylate) (PMMA) and other polymethacrylates can be prepared in a wide range of tacticities. PMMA gels have been used as packing materials for gel permeation chromatography (GPC),<sup>1,2</sup> and poly(stearyl methacrylate) gel has been used as a stationary phase for high-performance liquid chromatography.<sup>3</sup> Challa and coworkers<sup>4</sup> have recently prepared a stationary phase with isotactic PMMA. However, in these studies, no data have been reported on the tacticity effect on separating properties. In this study, we prepared the stationary phases of PMMA with different tacticities by a procedure different from Challa's and investigated the influence of tac-

ticity on the adsorbing property of organic molecules in detail.

### EXPERIMENTAL

#### *Preparation of PMMA*

The isotactic (it) and syndiotactic (st) PMMA used in this study are shown in Table I. st-92-PMMA was prepared with *t*-BuLi/(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al<sup>5</sup> in toluene at -78°C; st-81-PMMA with 1,1-diphenylhexyllithium (DP-HLi)<sup>6</sup> in tetrahydrofuran (THF) at -78°C; st-62-PMMA with 2,2'-azobisisobutyronitrile (AIBN) in toluene at 60°C; it-68-PMMA with *n*-BuLi in toluene at -78°C; it-96-PMMA with *t*-BuMgBr<sup>7</sup> in toluene at -78°C.

#### *Preparation of Packing Material for HPLC*

The PMMA were adsorbed on macroporous silica gel (Macherey-Nagel, NUCLEOSIL® 1000-7, pore size 100 nm, particle size

**Table I.** PMMAs prepared by radical or anionic polymerization

PMMA	Initiator	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Tacticity/%		
				I	H	S
st-92	<i>t</i> -BuLi/Et <sub>3</sub> Al	19400	1.27	0	8	92
st-81	DPHLi <sup>a</sup>	20400	1.51	3	16	81
st-62	AIBN	23200	1.65	4	34	62
it-68	<i>n</i> -BuLi	26700	3.10	68	18	14
it-96	<i>t</i> -BuMgBr	17500	1.21	96	3	1

<sup>a</sup> 1,1-Diphenylhexyllithium.

7  $\mu$ m) which had been treated with chlorotri-methylsilane in benzene. PMMA (0.75 g) was dissolved in chloroform (10 ml) and 5 ml of the solution was added to the silica gel (3.0 g). After evaporation of the chloroform, the remaining PMMA solution was mixed again with the silica gel and the solvent was evaporated. Elemental analyses of five packing materials and the weight percentage of PMMA in the packing materials are shown in Table II. Each packing material was dispersed in a liquid paraffin-hexane (1:1) mixture and packed in a stainless steel tube (25.0 cm  $\times$  0.46 (i.d.) cm) at 400 kg cm<sup>-2</sup> using hexane as eluent. Chromatographic analysis was performed on a JASCO TRIROTAR-II chromatograph equipped with a UV (JASCO UVIDEC-100-III) detector at 25°C. A hexane-2-propanol (98:2) mixture and a methanol-water (75:25) mixture were used as eluents at a flow rate of 0.5 ml min<sup>-1</sup>. The dead time (*t*<sub>0</sub>) of the column was estimated at 6.2 min with 1,3,5-tri-*tert*-butylbenzene for a hexane-2-propanol mixture, and at 5.8 min with methanol for methanol-water eluent system.

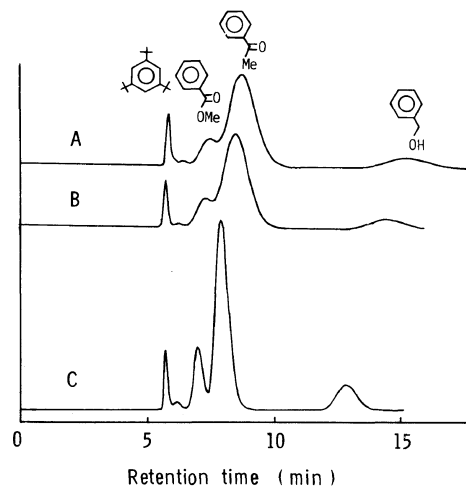
## RESULTS AND DISCUSSION

Figure 1 shows the chromatograms of separation of polar benzene derivatives, methyl benzoate, acetophenone and benzyl alcohol, on it-96-PMMA phase using a hexane-2-

**Table II.** Elemental analyses of packing materials

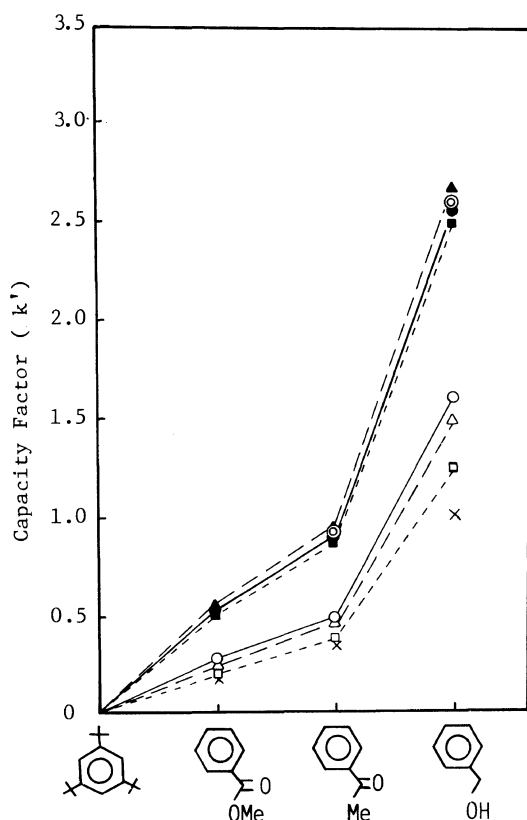
PMMA	C %	H %	PMMA
			(PMMA + Silica) (wt/wt) <sup>a</sup>
st-92	12.24	1.60	0.204
st-81	11.86	1.55	0.198
st-62	12.35	1.57	0.206
it-68	12.09	1.61	0.202
it-96	12.26	1.55	0.211

<sup>a</sup> Calculated from carbon content.



**Figure 1.** Separation of methyl benzoate, acetophenone, and benzyl alcohol on it-96-PMMA. A, original packing material; B, packing material treated with EtOH; C, packing material treated with MeOH-H<sub>2</sub>O (75:25). Eluent, hexane-2-propanol (98:2).

propanol mixture as eluent. Retention times of the benzene derivatives depended greatly on the conditions of the pretreatment of the columns. The retainment of the compounds on the PMMA columns is ascribed to the PMMA on silica gel and not to the silica gel used here, because the compounds were scarcely retained on the silica gel phase without PMMA. The packing material which had not contacted a polar solvent exhibited the broad peaks shown in Figure 1(A). After ethanol was passed through the column, the peaks became slightly sharper [Figure 1(B)], and after treatment with a mixture of methanol-water (75:25), the

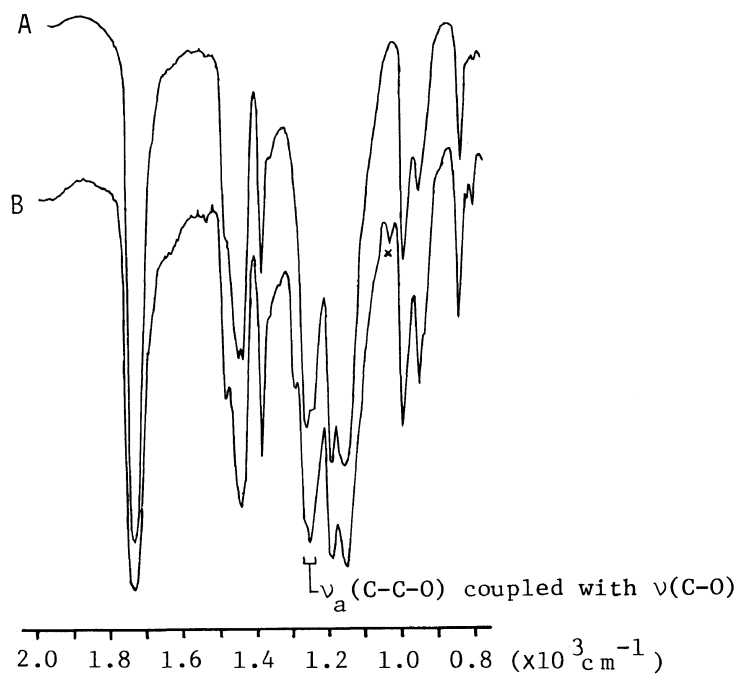


**Figure 2.** Capacity factors ( $k'$ ) of methyl benzoate, acetophenone, and benzyl alcohol on st-92-PMMA and it-96-PMMA. st-92-PMMA: ●, original packing material; ▲, packing material treated with EtOH; ■, packing material treated with MeOH-H<sub>2</sub>O (75:25); ⊙, final value. it-96-PMMA: ○, original packing material; △, packing material treated with EtOH; □, packing material treated with MeOH-H<sub>2</sub>O (75:25); ×, final value. Eluent, hexane-2-propanol (98:2).

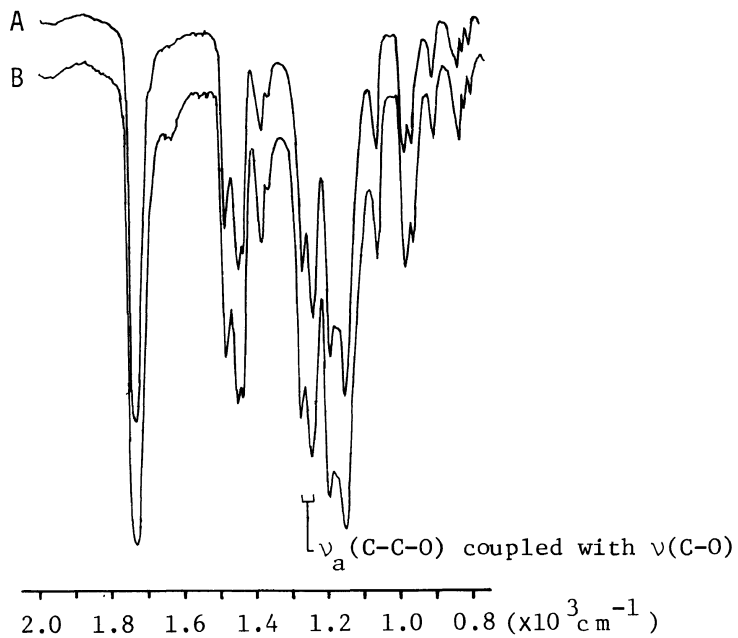
peaks became even sharper with shorter retention times. The separation on st-92-PMMA phase was also performed in the same way. The capacity factors,  $k' = [(retention\ time - t_0) / t_0]$  for the aromatic compounds after treatment of it-96-PMMA and st-92-PMMA with polar solvents are shown in Figure 2. The capacity factors for the analyses on st-92-PMMA were almost constant regardless of pretreatment of the column. These results suggest that only it-96-PMMA may change its conformation by treatment with polar solvents. This confor-

mational change was confirmed by infrared spectroscopy. Three samples, it-96-PMMA, st-92-PMMA and it-68-PMMA, dissolved in CHCl<sub>3</sub> were cast on NaCl plates to form films. Figure 3 shows the infrared spectra of it-96-PMMA film. Figure 3(A) is the spectrum of film cast from a CHCl<sub>3</sub> solution, and Figure 3(B) is the spectrum of the film after immersed in methanol. The difference between the two spectra appeared at 1200–1300 cm<sup>-1</sup>. In both spectra, the absorption of  $\nu_a(C-C-O)$  coupled with  $\nu(C-O)$ <sup>8</sup> appears at 1260 cm<sup>-1</sup> and at 1240 cm<sup>-1</sup>. In the spectrum A the former absorption is stronger than the latter. However, in the spectrum B, the latter absorption is observed at 1252 cm<sup>-1</sup> as a more intense peak. This shows that a structural transformation of it-96-PMMA occurred by treatment with methanol. Figures 4 and 5 show the infrared spectra of st-92-PMMA and it-68-PMMA, respectively. These spectra indicate that both st-92-PMMA and it-68-PMMA did not change their structures by treatment with methanol. Therefore, only the conformation of highly isotactic PMMA was influenced by treatment with the polar solvent. The change in chromatograms shown in Figure 1 seems due to this conformational change.

Nonpolar aromatic hydrocarbons, benzene, toluene, xylene, naphthalene, and anthracene, were chromatographed on the five columns by using a methanol-water (75:25) mixture as an eluent (Figure 6), and polar benzene derivatives, methyl benzoate, acetophenone and benzyl alcohol, by using a hexane-2-propanol (98:2) mixture (Figure 7). In most cases, the retention times on the st-PMMA phase were much longer than those on the it-PMMA phase in the both eluent systems. These results indicate that st-PMMA possesses greater hydrophobicity in the polar eluent system and greater polarity in the nonpolar eluent system than it-PMMA. Similar retention times were observed for the three syndiotactic PMMAs, whereas the two isotactic PMMAs exhibited



**Figure 3.** Infrared spectra of films of it-96-PMMA. A, cast from  $\text{CHCl}_3$  solution; B, after being immersed in  $\text{CH}_3\text{OH}$ .  $\times$ , absorption due to  $\text{CH}_3\text{OH}$ .



**Figure 4.** Infrared spectra of films of st-92-PMMA. A, cast from  $\text{CHCl}_3$  solution; B, after being immersed in  $\text{CH}_3\text{OH}$ .

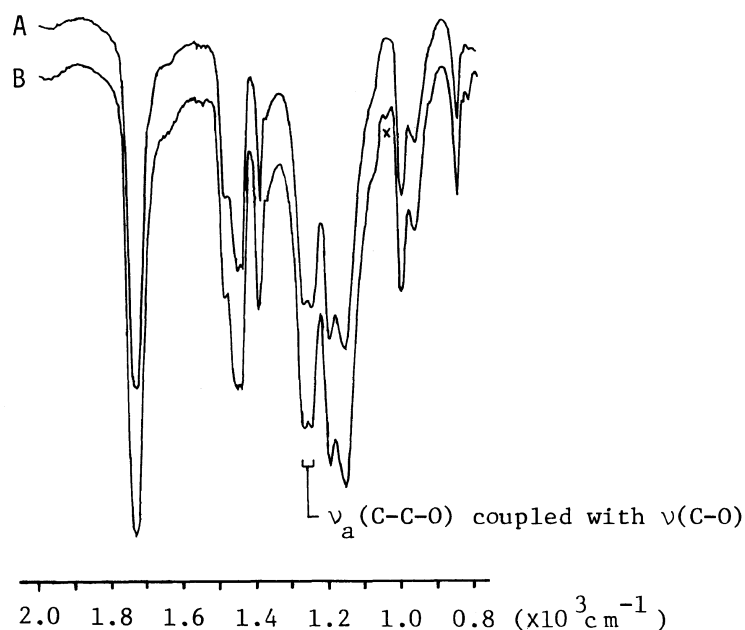


Figure 5. Infrared spectra of films of it-68-PMMA. A, cast from  $\text{CHCl}_3$  solution; B, after being immersed in  $\text{CH}_3\text{OH}$ .  $\times$ , absorption due to  $\text{CH}_3\text{OH}$ .

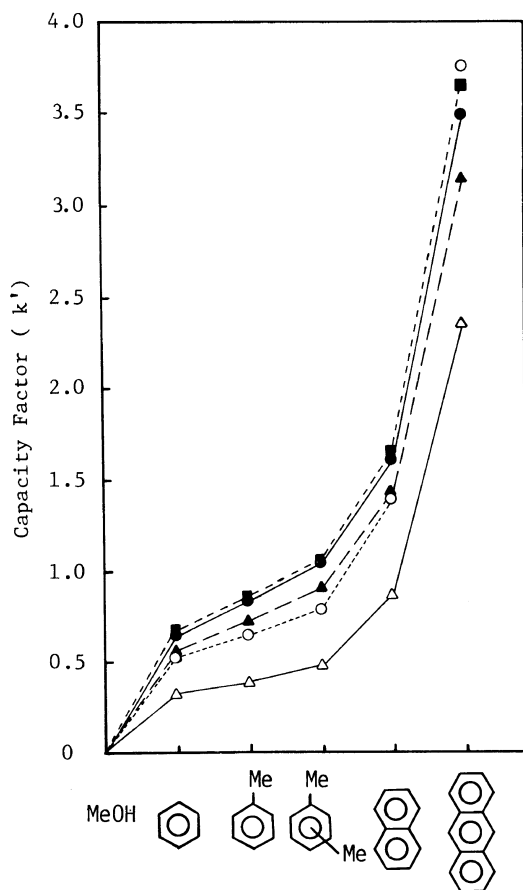
Table III. PEMAs and PBzMAs prepared by anionic polymerization

Polymer	Initiator	Solvent	Temp °C	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Tacticity/%			Ref
						I	H	S	
it-PEMA	<i>t</i> -BuMgBr	Toluene	-78	20100	4.93	97	3	0	7
st-PEMA	<i>t</i> -BuLi/ $\text{Et}_3\text{Al}$	Toluene	-78	21100	1.06 <sup>a</sup>	0	9	91	5
it-PBzMA	<i>c</i> -HexMgBr	Toluene	-78	14400	1.95	95	4	1	—
st-PBzMA	<i>c</i> -HexMgBr	THF	-78	6000	1.43	3	21	76	—

<sup>a</sup> Methanol insoluble part.

rather different adsorbing abilities. The retention of these aromatic compounds on PMMA depended on isotactic triad content rather than syndiotactic triad content. These results can be explained by differences in the structures of it-PMMA and st-PMMA.<sup>9-11</sup> It has been reported that st-PMMA chain takes a helical structure which has a sufficiently large radius as compared with the axial pitch because of steric hindrance between the bulky side groups of adjacent monomeric units,<sup>9,11</sup> and hence small molecules are included in the cavities of inner- and inter-helices. On the

other hand, it-PMMA chains take the double strand helical structure which consists of two chains.<sup>10,11</sup> Therefore, on st-PMMA phases with a polar eluent such as a methanol-water (75:25) mixture, nonpolar aromatic hydrocarbons may be strongly retained in the inside of the helical structure of the st-PMMA because the inside of the helix is hydrophobic and the outside of the helix is hydrophilic. Such an interaction seems impossible for it-PMMA since the inside of the double strand helical structure is too narrow to be retained for even small compounds. Polar benzene derivatives



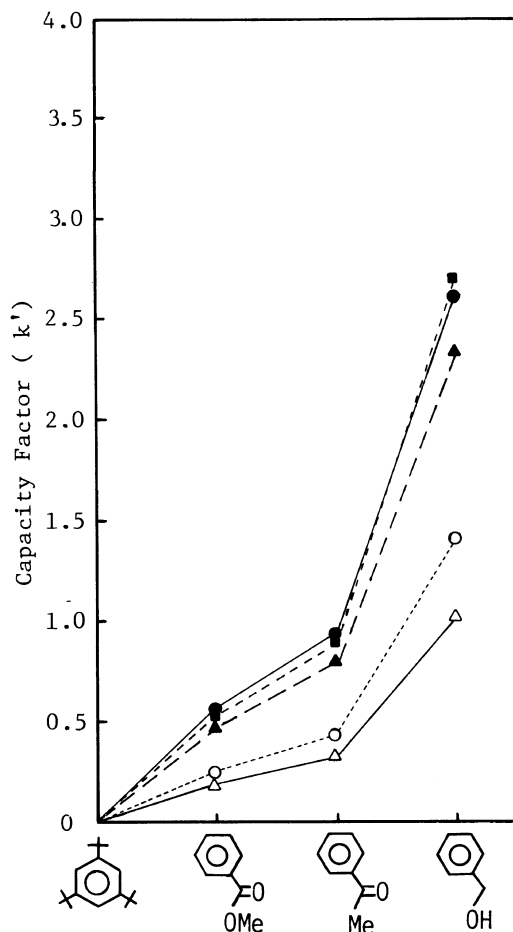
**Figure 6.** Capacity factors ( $k'$ ) in the chromatographic analyses of nonpolar aromatic compounds on PMMAs. ●, st-92; ▲, st-81; ■, st-62; ○, it-68; △, it-96. Eluent, MeOH-H<sub>2</sub>O (75:25).

**Table IV.** Elemental analyses of packing materials

Polymer	C	H	Polymer (Polymer + Silica)	(wt/wt) <sup>a</sup>
	%	%		
it-PEMA	12.53	1.71	0.199	
st-PEMA	12.75	1.74	0.202	
it-PBzMA	14.60	1.31	0.195	
st-PBzMA	14.78	1.31	0.197	

<sup>a</sup> Calculated from carbon content.

were also strongly retained on st-PMMAs when a hexane-2-propanol (98:2) mixture was used as an eluent. The polar benzene de-



**Figure 7.** Capacity factors ( $k'$ ) in the chromatographic analyses of polar aromatic compounds on PMMAs. ●, st-92; ▲, st-81; ■, st-62; ○, it-68; △, it-96. Eluent, hexane-2-propanol (98:2).

rivatives probably interact mainly with the ester groups of PMMA. In this case, they seem to be retained at the outside of the helix of st-PMMAs. However, the ester groups of it-PMMAs are used for the formation of the inner double strand helical structure. For these reasons, in both systems, st-PMMAs may retain small molecules more strongly than it-PMMAs. The content of the double strand helical structure may steeply decrease with decrease in isotactic content.

The tacticity effect on the chromatography was also examined with poly(ethyl methac-

**Table V.** Capacity factors ( $k'$ ) in the chromatographic analyses of aromatic compounds on PEMAs and PBzMA<sup>a</sup>

Compounds	it-PEMA	st-PEMA	it-PBzMA	st-PBzMA
	$k'^b$	$k'^b$	$k'^c$	$k'^c$
Methyl benzoate	0.606	0.600	0.375	0.398
Acetophenone	1.02	1.08	0.616	0.653
Benzyl alcohol	—	—	1.11	1.15
Benzene	—	—	0.106 <sup>d</sup>	0.094 <sup>d</sup>
Naphthalene	—	—	0.278 <sup>d</sup>	0.257 <sup>d</sup>
Anthracene	—	—	0.633 <sup>d</sup>	0.585 <sup>d</sup>

<sup>a</sup> Column, 25 cm × 0.46 (i.d.) cm; flow rate, 0.5 ml min<sup>-1</sup>.

<sup>b</sup> Eluent, hexane; temp, 10°C.

<sup>c</sup> Eluent, hexane-2-propanol (98:2); temp, 25°C.

<sup>d</sup> Eluent, methanol; temp, 25°C.

rylate (PEMA) and poly(benzyl methacrylate) (PBzMA) in the same way as described above. The polymethacrylates used are summarized in Table III, and the packing materials prepared therefrom are shown in Table IV. Capacity factors for the aromatic compounds on these columns are listed in Table V. Influence of tacticity on the capacity factor was very small compared with that for PMMA. Therefore, the tacticity of these polymethacrylates did not influence interactions between the polymethacrylates and the aromatic compounds. Probably, these polymethacrylates, particularly st-polymethacrylates do not take the helical structure observed for st-PMMA.

### CONCLUSIONS

The influence of tacticity of PMMA, PEMA, and PBzMA on the interaction with aromatic compounds was investigated by HPLC. Only PMMA exhibited the clear dependence of the interaction on the tacticity. This seems due to the fact that st-PMMA takes

the helical structure and it-PMMA, a double strand helical structure.

### REFERENCES

1. H. Determann, M. Kriewen, and T. Wieland, *Makromol. Chem.*, **114**, 256 (1968).
2. W. Heitz and H. Winau, *Makromol. Chem.*, **131**, 75 (1970).
3. Y. Tanaka, H. Sato, K. Miyazaki, and Y. Yamada, *J. Chromatogr.*, **407**, 197 (1987).
4. E. Schomaker, A.-J. Zwartveen, G. Challa, and M. Capca, *Polym. Commun.*, **29**, 158 (1988).
5. T. Kitayama, T. Shinozaki, E. Masuda, M. Yamamoto, and K. Hatada, *Polym. Bull.*, **20**, 505 (1988).
6. Z.-K. Cao, Y. Okamoto, and K. Hatada, *Koubunshi Ronbunshu*, **43**, 857 (1986).
7. K. Hatada, K. Ute, K. Tanaka, K. Kitayama, and Y. Okamoto, *Polym. J.*, **17**, 977 (1985); K. Hatada, K. Ute, K. Tanaka, Y. Okamoto, and T. Kitayama, *Polym. J.*, **18**, 1037 (1986).
8. H. Nagai, *J. Appl. Polym. Sci.*, **7**, 1697 (1963).
9. H. Kusuyama, N. Miyamoto, Y. Chatani, and H. Tadokoro, *Polym. Commun.*, **24**, 119 (1983).
10. H. Kusanagi, H. Tadokoro, and Y. Chatani, *Macromolecules*, **9**, 531 (1976).
11. H. Tadokoro, *Polymer*, **25**, 147 (1984).