BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1403—1408 (1967)

Studies of Phenyl Ether Derivatives. III. Friedel-Crafts Type Condensation Reactions of Some Phenyl Ether Derivatives

Akio OSHIMA

Kanegafuchi Chemical Industry, Ltd., Yoshida-cho, Hyogo-ku, Kobe

(Received July 13, 1965)

By treating the p, p'-disubstituted diphenyl ether with stannic chloride or sulfuric acid in some solvents, two sorts of substances were obtained. One was a compound, $(ArCH_2C_6H_5)_2O$ (I), produced by the condensation of two molecules of the aromatic solvent and a molecule of the phenyl ether, the other was a self-condensation product (II) of the phenyl ether itself. Which product is obtained is dependent not upon the substituent in phenyl ether, but upon the sort of solvent. On the basis of the analytical data, molecular-weight measurements, UV- and IR-spectral analyses, and the results of pyrolyzing gas chromatography, the author has deduced the structures A and B for I and II respectively. He has inferred about the mechanism for these phenomena as follows: in each case the reaction can be regarded as a sort of Friedel-Crafts reaction. When the reactivity of the solvent molecule is high enough to bring about normal condensation, the compound (I) is produced. On the other hand, inter- and/or intra-molecular condensations take place between the phenyl ether molecules to yield the compound (II) when the reactivity of the solvent is rather low.

It is well known that benzyl-type compounds, *e. g.*, benzyl chloride,[1] benzyl methyl ether,[2] and benzyl alcohol,[3] give compounds represented by the general formula $C_6H_5CH_2Ar$ ($Ar=C_6H_5$, $CH_3C_6H_4$) when they are heated with benzene or toluene in the presence of a usual Lewis acid, such as metallic halide. The present author has attempted an analogous reaction using phenyl ether derivatives, *i. e.*, *p*-chloromethyl-phenyl ether, *p*-methoxymethyl-phenyl ether, *p*-acetoxymethyl-phenyl ether, or *p*-hydroxymethyl-phenyl ether, and has found that they also react in the same way to give products with the general formula $(ArCH_2C_6H_4)_2O$, when they are heated with stannic chloride in toluene or xylene. On the other hand, much unexpected resinous matter was obtained when the reaction was carried out in benzene, bromobenzene, nitrobenzene, or *n*-hexane.

Evidently the reactions proceed quite differently, depending upon the solvent used. Therefore, the author decided to investigate the reaction products more precisely in order to find some relationships between the reaction products and the solvents.

In the present paper the structure of the resinous matter, as well as the reaction mechanism, will be discussed on the basis of the results of its molecular-weight measurements, its ultraviolet and infrared spectra, and its pyrolysis.

Experimental

Materials. *p*-Chloromethyl-, *p*-methoxymethyl-, *p*-acetoxymethyl-, and *p*-hydroxymethyl-phenyl ethers were prepared as has been described in Parts I[4] and II[5]. All the compounds but the last one are easily soluble in organic solvents.

Reaction. Into a toluene (15 g) solution of *p*-chloromethyl-phenyl ether (0.01 mol), 3.6 g of a 70% stannic chloride solution in toluene was added, drop by drop, over a 2—3-min period at 70°C with stirring. After stirring for 60 min more at this temperature, the mixture was cooled quickly to room temperature. After the catalyst had been washed away with 10% hydrochloric acid and then water, the solvent was distilled off under reduced pressure at a temperature below 30°C (No. 1). The other phenyl ether derivatives were treated analogously, except for *p*-hydroxymethyl-phenyl ether, which was dissolved in 300 g of hot toluene, into which 7.3 g of 70% sulfuric acid was they dropped at 70°C (No. 4).

The reaction in *n*-hexane was carried out in an atmosphere of a dry nitrogen flow at 60 m*l*/min; into an *n*-hexane (30 g) solution of *p*-chloromethyl-phenyl ether (0.01 mol), 2.0 g of a 70% stannic chloride solution in *n*-hexane were added over a period of a few minutes at 60°C; then the mixture was stirred for 60 min at this temperature. The hydrogen chloride gas produced during the reaction was absorbed into a

---

[1] J. U. Neb, *Ann.*, **298**, 254 (1897); H. Meyer and K. Bernhauer, *Monatsh.*, **53/54**, 743 (1929).

[2] A. M. Perova, *J. Gen. Chem. U.S.S.R.*, 24 (1954); *Chem. Abstr.*, **49**, 6150h (1955).

[3] R. C. Houston and T. E. Friedemann., *J. Am. Chem. Soc.*, **38**, 2527 (1916); H. Meyer, *J. Prakt. Chem.*, (2) **82**, 539 (1910); L. J. Khastanor, *J. Gen. Chem. U.S.S.R.*, **2**, 515 (1932); *Chem. Abstr.*, **27**, 975 (1933).

[4] A. Oshima, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 2113 (1963).

[5] A. Oshima, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1173 (1965).

0.1 N sodium hydroxide solution (No. 13). The conditions and results are summarized in Tables 2 and 3.

Purification of the Product. In some cases (Nos. 7, 8, and 9) in which the lower polymers were the principal products, the polymers could be further purified by extracting the unreacted material with a mixture of *n*-hexane - ether (9 : 1) at 10°C, while in other cases (Nos. 10, 11, 12, and 13) in which higher polymers were the principal products, this method was invalid. The products obtained in *m*-xylene (Nos. 5 and 6) were recrystallized from benzene-ether.

Mean Molecular Weight. Measured by the depression of the freezing point in purified benzene.

Pyrolyzing Gas Chromatography. The polymer obtained from *p*-chloromethyl-phenyl ether in *n*-hexane (No. 13) was pyrolyzed, and the decomposition products were analyzed by gas chromatography.[*1] The conditions and the results are shown in Table 1 and Fig. 1.

TABLE 1. PYROLYZING GAS CHROMATOGRAPHY OF THE CONDENSATION PRODUCTS (No. 17)

Temp. of pyrolyzing room	800°C			
Sample weight	0.005 g			
Column structure	i.d.×length	4 m/m×3 m		
Stationary phase	7,8-Benzoquinoline on Shimalite 60—80 mesh (25:75)			
Carrier gas	He			
Flow rate of He	20 m*l*/min (1.0 kg/cm²)			
Temp. of column bath	80°C			
Detector	Thermal conductivity cell			
Detector bath temp.	200°C			
Peak area	Benzene	Toluene	*m*-Xylene	*o*-Xylene
(%)	$48._4$	$49._1$	1.9_5	0.5_5
Pyrolyzed residue	carbon, 0.0024 g			

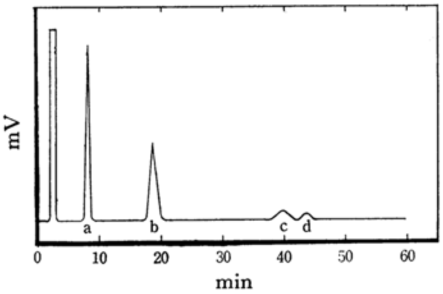


Fig. 1. Pyrolyzing gas chromatogram of the reaction product obtained from *p*-chloromethyl-phenyl ether in *n*-hexane.
a benzene, b toluene, c *m*-xylene, d *o*-xylene

Results and Discussion

The Reaction in Toluene and Xylene. From the results shown in Table 2, it may be concluded that, by the reactions in toluene, the same product (A_1), which can be represented by the formula $C_{28}H_{26}O$, was obtained from each of the phenyl ether derivatives used, *i. e.*, *p*-chloromethyl-, *p*-methoxymethyl-, *p*-acetoxymethyl-, and *p*-hydroxymethyl-phenyl ether; their infrared spectra, analytical data, and molecular weight agree with each other. The reactions in *m*-xylene, *p*-chloromethyl-, and *p*-methoxymethyl-phenyl ethers also all give the same compound (A_2), all with the formula $C_{30}H_{30}O$. In this case the identity of the compounds is further verified by the mixed-melting-point measurement. When the infrared spectrum of A_1 (Fig. 2) or A_2 (Fig. 3)

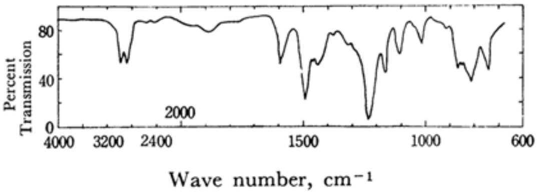


Fig. 2. Infrared spectrum of the reaction product obtained from *p*-chloromethyl-, *p*-methoxymethyl- or *p*-acetoxymethyl-phenyl ether in toluene.

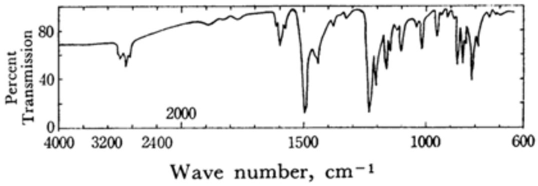
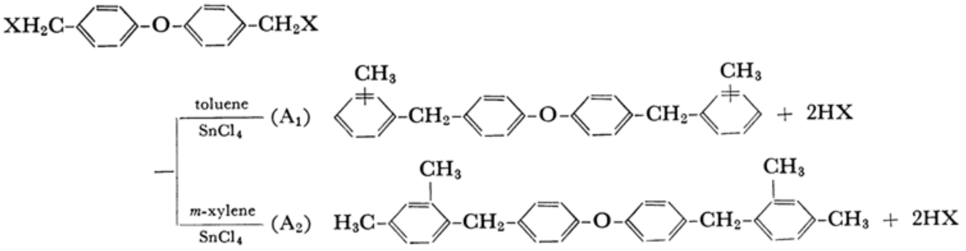


Fig. 3. Infrared spectrum of the reaction product obtained from *p*-chloromethyl- or *p*-methoxymethyl-phenyl ether in *m*-xylene (KBr-disk).

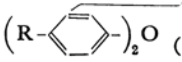


(X: Cl, OCH_3, OAc, OH)

(A)

[*1] Shimadzu GC-1B

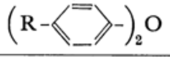
TABLE 2. THE REACTION OF p,p'-DISUBSTITUTED DIPHENYL ETHERS IN SOLVENTS IN THE PRESENCE OF THE CATALYST

No.	Diphenyl ethers			Solvent			Catalyst			Reaction		Yield g	Found mol wt	Mp, °C	Found	
		mol (10⁻³)	g	Sort	mol (10⁻³)	g	Sort	mol (10⁻³)	g	Temp. °C	Time min				C %	H %
1	R=CH_2Cl	10	2.6	Toluene	174	16	$SnCl_4$	10	2.6	70	60	3.4	403	Liquid	88.74	6.89a)
2	R=CH_2OCH_3	10	2.6	Toluene	225	21	$SnCl_4$	10	2.6	70	60	3.5	414	Liquid	88.51	7.01a)
3	R=CH_2OOCH_3	10	2.8	Toluene	174	16	$SnCl_4$	10	2.6	70	60	2.8	403	Liquid	88.86	7.19a)
4	R=CH_2OH	10	2.3	Toluene	32600	300	70% H_2SO_4	52	7.3	70	60	3.5	425	Liquid		
5	R=CH_2Cl	10	2.6	m-Xylene	174	18	$SnCl_4$	10	2.6	70	60	3.8	411	100	88.31	7.76b)
6	R=CH_2OCH_3	10	2.6	m-Xylene	174	18	$SnCl_4$	10	2.6	70	60	3.7	407	100	88.32	7.71b)

a) Calcd for $C_{28}H_{26}O$: C, 88.38; H, 7.44; mol wt, 380.5

b) Calcd for $C_{30}H_{30}O$: C, 88.62; H, 7.44; mol wt, 406.6

TABLE 3. THE REACTION OF p,p'-DISUBSTITUTED DIPHENYL ETHERS IN SOLVENTS IN THE PRESENCE OF THE CATALYST

No.	Diphenyl ethers			Solvent			Catalyst			Reaction		Yield g	Found mol wt	Mp, °C	Found Cl %
		mol (10⁻³)	g	Sort	mol (10⁻³)	g	Sort	mol (10⁻³)	g	Temp. °C	Time min				
7	R=CH_2Cl	10	2.6	Benzene	450	32	$SnCl_4$	2.5	0.65	45	15	2.3a)	315	40—50	
8	R=CH_2Cl	10	2.6	Benzene	450	32	$SnCl_4$	5	1.3	45	30	2.3a)	362	30—40	
9	R=CH_2Cl	10	2.6	Benzene	450	32	$SnCl_4$	10	2.6	45	60	2.0a)	1497	soften ~100	
10	R=CH_2Cl	10	2.6	Benzene	225	16	$SnCl_4$	10	2.6	70	30	2.0	—c)	>300	0.1_3
11	R=CH_2Cl	10	2.6	Benzene	225	16	$SnCl_4$	10	2.6	80	10	2.1	—c)	>300	0.1_0
12	R=CH_2Cl	10	2·6	Nitrobenzene	450	55	$SnCl_4$	5	1.3	45	60	1.8	—c)		
13	R=CH_2Cl	10	2.6	n-Hexane	186	16	$SnCl_4$	11	1.3	60	60	1.9b)	—c)	>300	0.1_0
14	R=CH_2OCH_3	10	2.6	Benzene	225	16	$SnCl_4$	10	2.6	55	60	1.8	1657	>40	
15	R=CH_2OCH_3	10	2.6	Benzene	225	16	$SnCl_4$	20	5.2	70	60	2.0	—c)		
16	R=CH_2OCH_3	10	2.6	Bromobenzene	102	16	$SnCl_4$	5	1.3	60	60	1.9	1864	65—70	
17	R=CH_2OCH_3	10	2.6	n-Hexane	186	16	$SnCl_4$	5	1.3	60	60	1.5	—c)	>300	
18	R=CH_2OOCH_3	10	2.8	Benzene	225	16	$SnCl_4$	10	2.6	55	60	2.1	2001	95—102	
19	R=CH_2OH	10	2.3	Benzene	25700	200	70% H_2SO_4	52	7.3	70	60	1.7	—c)	>300	

a) Raw yield

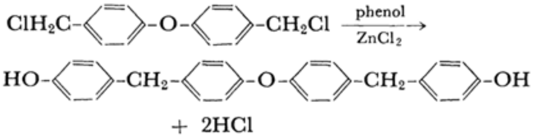
b) HCl gas produced during the reaction was 0.725 g, corresponding to 99% of the total chlorine in the starting material.

c) The molecular weight could not be determinated because of the insolubility of the material in benzene.

is compared with that of any starting material, it will be noticed that, in the former, two new absorption bands due to the methyl group, appear at 2960 cm^{-1} and at 740 cm^{-1} (due to the 1, 2-disubstituted benzene nucleus (for A_1)) or at 1205 cm^{-1} (due to the 1, 2, 4-trisubstituted benzene nucleus (for A_2)), but neither at 1100 cm^{-1} (due to the methoxy- group), at 1700 cm^{-1} (due to the carbonyl- group), nor at 3420 cm^{-1} (due to the hydroxyl-group).

These facts may be explained by assuming that one molecule of the phenyl ether derivatives condenses with two molecules of toluene or *m*-xylene to produce A_1 or A_2, the functional groups being eliminated.

The product A_1 may be a mixture of *o*- and *p*-methyl isomers, because the IR spectrum shows the presence of a 1, 2- (but no 1, 3-) disubstituted benzene nucleus. Murao *et al.*[6] have reported an analogous reaction between *p*-chloromethyl-phenyl ether and phenol in carbon disulfide in the presence of zinc chloride:



The Reaction in Benzene, Nitrobenzene, Bromobenzene or *n*-Hexane. Contrary to the cases described above, the results shown in Table 3 seem to indicate that the reactions in these cases are principally self-condensation; they proceed quite similarly, regardless of the solvent used, and the products always contain chlorine, though the molecular weight varies with the conditions.

Ultraviolet Spectrum. The ultraviolet spectrum of the polymer (No. 8 was used as a sample) shows no unsaturated bonds of the stilbene type; this agrees with the fact that it consumes neither bromine nor potassium permanganate.

Infrared Spectrum. No difference can be found among the infrared spectra of any of the polymers obtained from *p*-chloromethyl-phenyl ether (Fig. 4), but they all differ from that of *p*-chloromethyl-phenyl ether, the starting material, in some respects: (1) the absorption band at 2925 cm^{-1} due to methylene is strengthened, and those at 2850 cm^{-1} and 1450 cm^{-1} due to methylene, though weak, and the one at 1435 cm^{-1} due to the $-CH_2-$ adjacent to the benzene nucleus are newly observed; (2) the absorption band at 1205 cm^{-1} due to the 1, 2, 4-trisubstituted benzene nucleus, which is especially strong in No. 10, is observed; (3) the absorption bands at 725 cm^{-1} and 695 cm^{-1} due to the monosubstituted benzene nucleus are observed. The infrared spectra of the polymers obtained from *p*-chloromethyl-phenyl ether by heating it in nitrobenzene and *n*-hexane are shown in Figs. 5 and 6. They resemble that of the polymer mentioned above in most respects, though they lack the absorption bands due to the monosubstituted benzene nucleus.

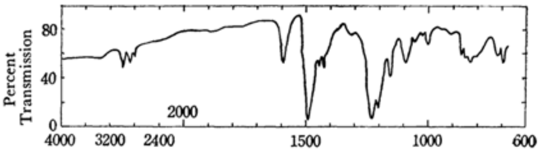


Fig. 4. Infrared spectrum of the reaction product obtained from *p*-chloromethyl- or *p*-methoxy-methyl-phenyl ether in benzene (KBr-disk).

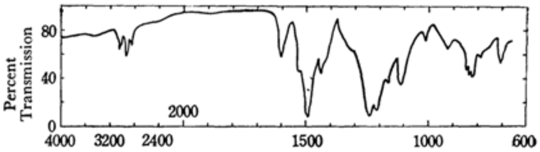


Fig. 5. Infrared spectrum of the reaction product obtained *p*-chloromethyl-phenyl ether in nitrobenzene (KBr-disk).

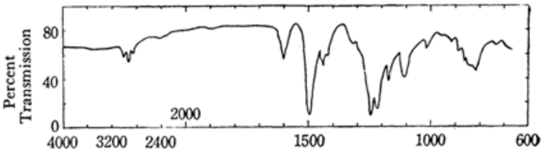
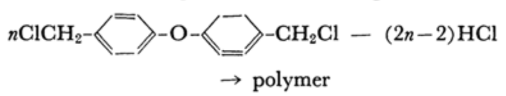


Fig. 6. Infrared spectrum of the reaction product obtained from *p*-chloromethyl- or *p*-methoxy-methyl-phenyl ether in *n*-hexane (KBr-disk).

Pyrolyzing Gas Chromatography. The pyrolysis of a high polymer (No. 13) gave benzene, toluene, *m*-xylene, and a bit of *o*-xylene as fission products.

Molecular Weight and Functional Group. As may be seen in a series of the reactions of *p*-chloro-methyl-phenyl ether in benzene in the presence of stannic chloride, the degree of polymerization could be controlled by means of the reaction conditions.

The molecular weights of the products of Nos. 7, 8, and 9, all of which are soluble in benzene, were found to be 450, 660 and 1500; these values correspond to those of the dimer, the trimer, and the heptamer respectively, provided the reaction proceeds according to the following scheme:



The products of Nos. 10 and 11 seem to be high

---

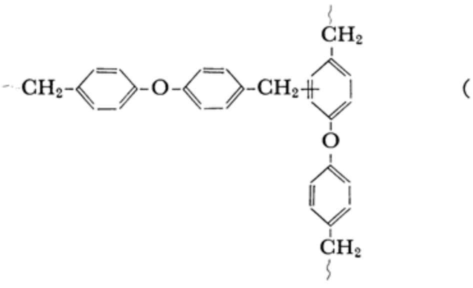
[6] Y. Murao, S. Tanimoto and R. Oda, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1538 (1963).

TABLE 4. PROPERTIES OF LOW MOLECULAR WEIGHT POLYMERS AND THE NUMBER OF CHLOROMETHYL GROUPS CALCULATED FROM THE MOLECULAR WEIGHT AND THE Cl%

No.	Reaction product after purification		$\frac{2Cl}{n\{(ClCH_2C_6H_4)_2\text{-}O\}-(2n-2)HCl}$		
	Found, mol wt	Found, Cl%	n	Calcd mol wt	Calcd Cl%
7	451	14.39	2	461	15.40
8	657	10.34	3	655	10.84
9	1510	5.12	6	1237	5.74
			7	1431	4.96
			8	1625	4.36

polymers, because they are insoluble in benzene and do not melt below 300°C. It is recognized that the greater the molecular weight, the less chlorine they contain, but even a benzene-insoluble polymer with a high molecular weight apparently contains chlorine (0.1%). When the product No. 8 was heated at 300°C, it turned, under the evolution of hydrogen chloride gas, into a dark brown, resinous matter insoluble in benzene and infusible even at 300°C. This fact indicates that the chlorine in the self-condensed product is present in a reactive form; it may be reasonalbe to assume that it exists as a chloromethyl group coming from the starting material. The calculation from the molecular weight and the chlorine content indicates that all the oligomers must have about two chloromethyls in a molecule (Table 4).

The Structure of the Polymer. From the results described above, the structure of the polymer may be deduced as follows: According to the infrared spectra, the skelton of the polymer may be represented by the formula:

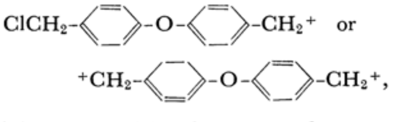


(B)

A chloromethyl group in a molecule may condense with another phenyl ether molecule at a position ortho or meta to the phenoxy group, but the result of the pyrolysis suggests the predominance of the orthocondensation, because in the fission products far more *m*-xylene is found than *o*-xylene.

The probable terminal groups of the polymer are the chloromethyl and aromatic hydrocarbon radicals coming from the solvent. However the average number of the former is calculated as about two for all the oligomers, though the number in each molecule should increase as the reaction proceeds if condensation occurs only intermolecularly. It is certain that the aromatic solvent molecules are taken into the polymer as a terminal group in some cases, because the absorption bands due to a monosubstituted benzene nucleus are apparently observed in the IR spectrum when the reaction is carried out in benzene. However such a hydrocarbon radical can never be a common one, for the polymer obtained in nitrobenzene contains no nitrogen. Moreover, this type of termination is impossible for the polymer obtainable in *n*-hexane. Hence, another sort of termination, *e. g.*, intra-molecular condensation, should be considered; this question is now being investigated.

The Mechanisms. As has been pointed out, the chemical behavior of *p*-chloromethyl-phenyl ether (and other phenyl ether derivatives) is similar to that of benzyl chloride, and their reactions with toluene or xylene in the presence of a Lewis acid can be regarded as of the Friedel-Crafts type.[7] That is, they proceed *via* the carbonium ion, *e. g.*,



which reacts with toluene or xylene at the reactive sites, producing a compound $(ArCH_2C_6H_4)_2O$. However, the reactive sites also exist in the molecule of the substituted phenyl ether itself. In fact, *p*-chloromethyl-phenyl ether gives a self-condensation product under the quantitative evolution of hydrogen chloride gas, when heated in *n*-hexane in the presence of stannic chloride. Hence, the high yield of the compound $(ArCH_2C_6H_4)_2O$ means that the reactivity of the reactive sites in phenyl ether are far inferior to those in toluene or xylene. When the reactive sites in the aromatic solvent molecule are less reactive, the reactions at the sites in *p*-chloromethyl-phenyl ether itself may become important, self-condensation taking place predominantly, probably when benzene, bromobenzene, or nitrobenzene is used as the solvent. The oligomer depicted as B would be produced as a result. The reactivity of a benzene nucleus

---

[7] C. C. Price, *Chem. Revs.*, **29**, 37 (1941); C. C. Price, "Organic Reactions," Vol III, John Wiley & Sons, Inc., New York, N. Y. (1946), pp. 1—82.

differs, of course, according to the sort of substituent and decreases in the order of benzene - bromobenzene - nitrobenzene; therefore, which the reaction with the solvent may be suppressed, while the self-condensation may be accelarated. These considerations may be supported by the facts that the polycondensation product obtained from *p*-chloromethyl-phenyl ether in benzene contains phenyl groups, and the one obtained from *p*-methoxy-methyl-phenyl ether in bromobenzene contains a trace of halogen, while that obtained from *p*-chloromethyl-phenyl ether in nitrobenzene contains no nitrogen.

The author is indebted to Professor Ryozo Goto of Kyoto University for his discussions and criticisms of this work; to Professor Hiroshi Watanabe of Konan University for his many valuable suggestions; to Mr. Tatsuo Kokan, Director of our Laboratory, for his encouragement, and to the Kanegafuchi Chemical Industry Co., Ltd., for its permission to publish this paper.